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Synthesis of Neoflavenes by a Palladium-Catalyzed Cross-Coupling Reaction of 4-Trifluoromethylsulfonyloxy-2*H*-Chromenes with Arylboronic Acids

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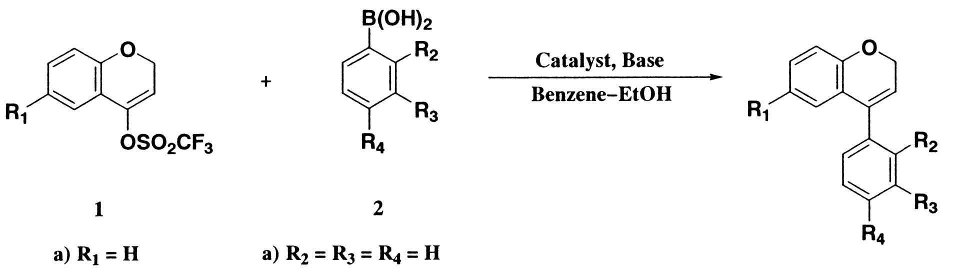
Under anhydrous conditions, 4-phenyl-2*H*-chromenes were obtained in excellent yields by a cross-coupling reaction of 4-trifluoromethylsulfonyloxy-2*H*-chromenes with arylboronic acids, except for *o*-methoxyphenylboronic acid, in the presence of K_2CO_3 and several palladium catalysts. Although copper(I) iodide, used as a co-catalyst, showed no effect on this reaction, it was confirmed to act in the case of the coupling reaction of 4-trifluoromethylsulfonyloxy-2*H*-chromene with tributylphenyltin, instead of phenylboronic acid, in the presence of $[Pd(PPh_3)_4]$.

4-Phenyl-2*H*-chromenes (**3**, neoflavenes or 4-phenyl-2*H*-1-benzopyrans), which have been known to be a group of natural products, are a series of neoflavonoids with a 4-arylchroman skeleton. They have been considered to be important precursors of 4-aryl-2*H*-chromene-2-ones (4-arylcoumarins), being the major structual type of neoflavonoids, in biosyntheses.[1] As for natural products with a neoflavene skeleton, kuhlmannene (6-hydroxy-7,8-dimethoxy-4-phenyl-2*H*-1-benzopyran) has been isolated from *Macherium nictitans* and *M. kuhlmannii*,[2] and dalbergichromene (6-hydroxy-7-methoxy-4-phenyl-2*H*-1-benzopyran) has been isolated from the stembark of *Dalbergia sissoo*[3] and *D. latifolia*.[4] Despite several reports concerning the methods used for the synthesis of neoflavenes,[5] general strategies which can efficiently provide variously substituted neoflavene systems are still in demand.

Recently, on the other hand, organic syntheses using cross-coupling reactions have been dramatically developed. These reacitons have many attractive features of general carbon-carbon bond formation. Among them, a palladium-catalyzed cross-coupling reaction of organic halides or trifluoromethanesulfonates (triflates) with a variety of organoboron compounds, which are readily accessible by the hydroboration of appropriate alkenes and alkynes or by the preparation from organolithium or Grignard reagents, have become increasingly utilized, and also noted in the field of neoflavonoid synthesis. For example, the coupling reaction of 4-trifluoromethylsulfonyloxycoumarin with sodium tetraphenylborate proceeds to give 4-phenylcoumarin in moderate yield.[6] More recently, a palladium-catalyzed aryl-vinyl coupling reaction between coumarins substituted with a 4-halogeno or a 4-trifluoromethylsulfonyloxy group and arylboronic acids was reported as a useful alternative for the synthesis of 4-arylcoumarins.[7] In this case, it is interesting to note that the coupling reactions of 4-trifluoromethylsulfonyloxycoumarins with arylboronic acids, which are generally nontoxic and thermal, air-, and moisture-stable, were carried out under modified reaction conditions involving the use of copper(I) iodide as a co-catalyst. During the course of our study on the synthesis of **3** by the cross-coupling reaction of 4-halogeno or 4-trifluoromethylsulfonyloxy-2*H*-chromenes (**1**) with arylboronic acids (**2**), the authors decided to examine the scope of the palladium-catalyzed route to **3**. However, it is difficult to introduce a halogen atom into the C_4-position of 2*H*-chromene. In contrast, **1** can be easily obtained by treating the corresponding dihydro-1-benzopyran-4-ones (4-chromanones) with trifluoromethanesulfonic anhydride. Thus, we turned our attention to the use of **1** in this coupling reaction. In the present paper, the authors discribe that 4-trifluoromethylsulfonyloxy-2*H*-chromenes underwent palladium-catalyzed cross-coupling reactions with arylboronic acids to yield the corresponding neoflavenes (Scheme 1).

Results and Discussion

Cross-Coupling Reactions of 1a with 2a. According to a procedure of Boland and his co-worker,[7] **1a** (1 mmol) was treated with **2a** (3 molar amounts) in the presence of tetrakis(triphenylphosphine)palladium(0) $[Pd(PPh_3)_4]$ (0.04 molar amounts), copper(I) iodide (1.1 molar amounts), and sodium carbonate (7 molar amolunts) in benzene-ethanol at the reflux temperature, followed by a treatment with hydrogen peroxide. Under anhydrous conditions, **3a** was obtained in a good yield (86%). In order to compare other bases with sodium carbonate, the use of potassium carbonate and potassium phosphate was attemped in this reaction. Although **3a** was produced in high yields (86–91%) in every case, potassium carbonate provided the best result in this reaction (91%). While both palladium (0 or II) catalysts and bases are essential for progress in this reaction, it has generally been proposed that the common mechanism[8] of the cross-coupling reaction between organometallic reagents and electrophiles in the presence of a transition metal complex involves sequential oxidative addition, transmetallation, and reductive elimination. The difficulty of utilizing organoboron compounds for such a



1

a) $R_1 = H$
b) $R_1 = Me$
c) $R_1 = F$

2

a) $R_2 = R_3 = R_4 = H$
b) $R_2 = OMe, R_3 = R_4 = H$
c) $R_2 = R_4 = H, R_2 = OMe$
d) $R_2 = R_4 = H, R_2 = Me$
e) $R_2 = R_3 = H, R_4 = OMe$
f) $R_2 = R_3 = H, R_4 = OMe$
g) $R_2 = R_3 = H, R_4 = F$

3

a) $R_1 = R_2 = R_3 = R_4 = H$
b) $R_1 = Me, R_2 = R_3 = R_4 = H$
c) $R_1 = F, R_2 = R_3 = R_4 = H$
d) $R_1 = R_3 = R_4 = H, R_2 = OMe$
e) $R_1 = R_2 = R_4 = H, R_2 = OMe$
f) $R_1 = R_2 = R_4 = H, R_2 = Me$
g) $R_1 = R_2 = R_3 = H, R_4 = OMe$
h) $R_1 = R_2 = R_3 = H, R_4 = Me$
i) $R_1 = R_2 = R_3 = H, R_4 = F$

Scheme 1.

cross-coupling reaction is attributable to the very slow rate of transmetallation because of the low nucleophilicity of an organic group on a boron atom. Miyaura et al.[9] have already reported that the addition of a base greatly facilitates the cross-coupling of organoboron reagents with electrophiles by acceleration of the transmetallation step. Relatively strong bases, such as aqueous sodium hydroxide and sodium ethoxide, are used in ethanol for the reaction of vinylic boronates with organohalides, while it appears that anhydrous potassium carbonate suspended in benzene-ethanol is sufficient to accelerate the coupling of **1** with **2**. Although the detailed mechanism of the present reaction is still not clear, the reaction should be considered to occur in a similar manner to that proposed in the above-cited literature.

On the other hand, to confirm the effect of co-catalytic copper(I) iodide in this reaction, the couplings were also carried out in the absence of a co-catalyst (91%). Furthermore, by employing dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) [$PdCl_2$(dppf)], instead of [$Pd(PPh_3)_4$], the reactions were also examined in a similar manner to the forgoing case. Although, in the case of using [$PdCl_2$(dppf)], **3a** was obtained in 88% yield without the addtion of CuI, the use of a co-catalyst lowered the yield (71%) of **3a**. It is apparent that copper(I) iodide has scarcely a co-catalytic effect on this reaction. From the viewpoint of the reaction mechanism, it is known that the presence of a free ligand plays a key inhibitor role to limit the efficiency of the Suzuki arylation.[10] It was therefore suggested by Boland et al.[7] that the effect of copper(I) iodide could be explained by its influence as a scavenger of a dissociated free phosphine ligand. Concerning the Stille coupling,[11] the presence of a free ligand was shown to inhibit the transmetallation step;[12] this effect was suppressed by a copper(I) co-catalyst.[13,14] These results prompted us to perform a Stille aryl coupling of **1a** with arylstannan. According to a method of Gómez–Bengoa et al.,[13] the reactins of **1a** with tributylphenyltin, instead of phenylboronic acid, were carried out in the presence of [$Pd(PPh_3)_4$] and lithium chloride in 1,4-dioxane in both the presence and absence of a co-catalyst. In the case using CuI, **3a** was obtained in 40% yield, whereas the desired product was not given in the non-co-catalyzed case. From these facts, it may be considered that, in the present coupling of **1a** with **2a**, the copper(I) iodide plays no role as a scavenger of a free ligand, and it may be concluded that the co-catalytic effect is observed in the coupling of **1a** with organostannans, whereas that in the case using phenylboronic acid is not observed. Accordingly, the authors decided to carry out additional experiments without copper(I) iodide.

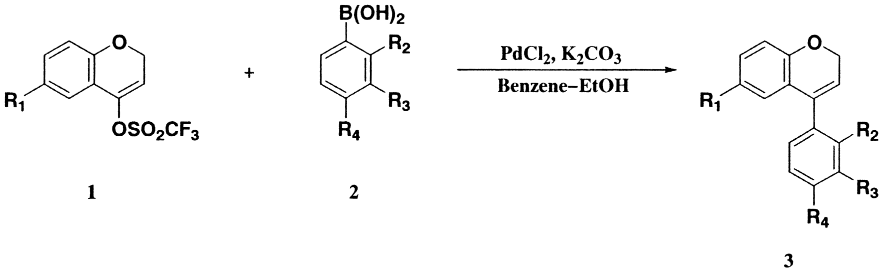
Reactions Using Other Palladium Catalysts. In order to compare various catalysts, cross-coupling reactions were carried out in the presence of several palladium catalysts, as well as [$Pd(PPh_3)_4$]; the results are summarized in Table 1. Among them, bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] and

Table 1. Cross-Coupling Reactions of 4-Trifluoromethylsulfonyloxy-2*H*-Chromene (**1a**) with Phenylboronic Acid (**2a**) in the Presence of Several Transition Metal Catalysts[a)]

Run	Catalyst[b)]	Yield of **3a**[c)]
		%
1	[$Pd(PPh_3)_4$] (0.04)	91
2	[$PdCl_2$(dppf)[d)]] (0.04)	88
3	$PdCl_2$ (0.04)	92
4	$Pd(OAc)_2$ (0.04)	27
5	[$Pd(dba)_2$[e)]] (0.04)	93
6	$RhCl_3 \cdot 3H_2O$ (0.04)	46
7	[$Ni(acac)_2$[f)]] (0.04)	49
8	[$Fe(acac)_3$] (0.04)	31

a) All the reactions were carried out under a nitrogen atmosphere at the reflux temperature in the presence of K_2CO_3 (7 mmol), using 1 mmol of **1a** and 3 mmol of **2a**.
b) Figures in parenthese indicate the added amount in a mmol-unit.
c) Isolated yields based on **1a**.
d) dppf: 1,1′-bis(diphenylphosphino)ferrocene.
e) dba: dibenzylideneacetone.
f) acac: acetylacetonate.

Table 2. Cross-Coupling Reactions of 4-Trifluoromethylsulfonyloxy-2*H*-Chromene (**1**) with Arylboronic Acids (**2**) in the Presence of $PdCl_2$[a)]



Entry	Substituent				Yield of **3**[b)]
	R_1	R_2	R_3	R_4	%
1	H	H	H	H	92 (**3a**)
2	F	H	H	H	98 (**3b**)
3	Me	H	H	H	89 (**3c**)
4	H	OMe	H	H	43 (**3d**)
5	H	H	OMe	H	96 (**3e**)
6	H	H	Me	H	98 (**3f**)
7	H	H	H	OMe	86 (**3g**)
8	H	H	H	Me	91 (**3h**)
9	H	H	H	F	94 (**3i**)

a) All the reactions were carried out under a nitrogen atmosphere at the reflux temperature in the presence of 0.04 mmol of $PdCl_2$ and 7 mmol of K_2CO_3, using 1 mmol of **1** and 3 mmol of **2**.

b) Isolated yields based on **1**.

palladium(II) chloride tended to give the desired product in high yields. However, only when palladium(II) acetate (Run 4 in Table 1) was used, a considerable decrease in the yield of **3a** (27%) was observed. This result may be due to some side reactions, such as a ring cleavage and a decomposition[15] of phenylboronic acid with AcO^- produced by a dissociation of $Pd(OAc)_2$ under the present reaction conditions, because many spots were observed, more than those in the case of other catalysts in a TLC analysis at the isolation process. It is noteworthy that, in the case using easily available and stable $PdCl_2$ (Run 3 in Table 1) as a catalyst for the present reaction, **3a** was given in 92% yield. Thus, the fact that the use of $PdCl_2$, which has no ligand, such as phosphines, showed an excellent result might be regarded as a second piece of evidence of the possibility that copper(I) iodide had only a small effect as a co-catalyst in this reaciton. Although several transition-metal compounds other than palladium were also examined in the reaction, all of them afforded yields of **3a** less than those obtained by the Pd-catalysts, except for $Pd(OAc)_2$ (Runs 6–8 in Table 1).

Substituent Effect. For two derivatives, which have a fluoro or a methyl group on the C_6-position of **1a** (**1b** and **1c**, respectively), the couplings were carried out under the same conditions in order to examine the generality of the present reaction. The obtained results are given in Table 2. It appears that the reaction center is insensitive to substituents introduced on the C_6-position of **1a**, since approximately the same extents of yields were obtained in both cases in spite of the presence of groups possessing the opposite electronic effects from each other.

In addition, several boronic acid derivatives were attempted in the couplings with **1a**; these results are given in Table 2. The yields of **3** seem to depend largely upon the position of the substituent on **2**. While **3** was synthesized by using phenylboronic acids with *meta* (**2c** and **2d**) or *para* (**2e**, **2f**, and **2g**) substituents in yields ranging from 86 to 98% (**3e**–**3i**, Entries 4–8 in Table 2), only using the boronic acid introduced an *ortho* methoxyl group (**2b**) gave the desired product in low yield (43%, **3d**, Entry 3 in Table 2). This may be due to the low solubility substrate in ethanol and/or an steric hindrance of the *ortho* substituent against the reaction center, though the details are still not clear.

Conclusion

While the use of copper(I) iodide as a co-catalyst showed no effect on the reaction, the cross-coupling of 4-trifluoromethylsulfonyloxyl-2*H*-chromenes with arylboronic acids in the presence of palladium catalysts provided a new and effective route to neoflavenes. Furthermore, it is worth noting in this article that the point superior to the report by Boland et al. is that these reactions proceeded smoothly without CuI by using easily available and stable $PdCl_2$ as a catalyst in the cross-coupling reaction to give the desired products in excellent yields, except for 4-(*o*-methoxyphenyl)-2*H*-chromene. Since the 4-trifluoromethylsulfonyloxy-2*H*-chromenes can be readily obtained by an exiting reaction of the corresponding 4-chromanones with trifluoromethanesulfonic anhydride in dichloromethane and pyridine, and arylboronic acids are also conventionally synthesized, it can be concluded that the present procedure is a general and straightforward method for neoflavene synthesis.

Experimental

All of the reactions were carried out under a nitrogen atmosphere. The melting points were determined by using a Yanaco micro-melting-point apparatus and are uncorrected. The IR spectra were recorded on a JASCO-IRA-1 spectrometer by means of a KBr pellet or neat. ^{1}H NMR spectra were obtained with a JEOL JNM-EX270 Fourier Transform NMR spectrometer (270 MHz), and are reported in δ units using tetramethylsilane as an internal standard. Mass spectra were taken on a JEOL-JMS-D300. Column chromatography was performed using a Wakogel C-200 (silica gel).

Arylboronic Acids. Phenylboronic acid (**2a**),[16] *o*-, *m*-, and *p*-methoxyphenylboronic acids (**2b**, **2c**, and **2e**),[16] *m*- and *p*-tolylboronic acids (**2d** and **2f**),[16] and *p*-fluorophenylboronic acid (**2g**)[17] were prepared by known procedures.[18]

Transition Metal Catalysts. Tetrakis(triphenylphosphine)palladium(0)[19] and dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II)[20] were prepared according to reported procedures. Bis(dibenzylideneacetone)palladium(0), rhodium(III) chloride trihydrate, tris(acetylacetonato)iron(III), and bis(acetylacetonato)nickel(II) were of commercially available grades, and were used without further purification.

Materials. The benzene employed was died and stored over sodium, and ethanol was used after distillation. All 4-trifluoromethylsulfonyloxy-2*H*-chromenes (**1a**–**1c**) were prepared from 4-chromanones according to a known synthetic method[21] of triflate, and were identified by means of the IR and ^{1}H NMR spectra. The main products of the present reactions were isolated from residual solutions by silica-gel column chromatography using a mixture of benzene–hexane (1:1) as an eluent. These physical data are as follows.

4-Phenyl-2*H*-chromene (3a): IR (neat) 1230 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 4.85 (d, J = 4.0 Hz, 2H, C$_2$-H), 5.79 (t, J = 4.0 Hz, 1H, C$_3$-H), and 6.81–7.42 (m, 9H, aromatic). MS Found: *m*/*z* 208.0889. Calcd for $C_{15}H_{12}O$: M, 208.0888.

6-Fluoro-4-phenyl-2*H*-chromene (3b): IR (neat) 1240 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 4.83 (d, J = 4.0 Hz, 2H, C$_2$-H), 5.86 (t, J = 4.0 Hz, 1H, C$_3$-H), and 6.70–7.42 (m, 8H, aromatic). MS Found: *m*/*z* 226.0745. Calcd for $C_{15}H_{11}FO$: M, 226.0749.

6-Methyl-4-phenyl-2*H*-chromene (3c): IR (neat) 1230 (–O–), 1490 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 2.19 (s, 3H, -CH$_3$), 4.81 (d, J = 4.0 Hz, 2H, C$_2$-H), 5.79 (t, J = 4.0 Hz, 1H, C$_3$-H), and 6.82–7.38 (m, 8H, aromatic). MS Found: *m*/*z* 222.1033. Calcd for $C_{16}H_{14}O$: M, 222.1045.

4-(*o*-Methoxyphenyl)-2*H*-chromene (3d): IR (neat) 1230 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 3.73 (s, 3H, -OCH$_3$), 4.92 (d, J = 3.6 Hz, 2H, C$_2$-H), 5.74 (t, J = 3.6 Hz, 1H, C$_3$-H), and 6.66–7.38 (m, 8H, aromatic). MS Found: *m*/*z* 238.0992. Calcd for $C_{16}H_{14}O_2$: M, 238.0994.

4-(*m*-Methoxyphenyl)-2*H*-chromene (3e): IR (neat) 1220 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 3.82 (s, 3H, -OCH$_3$), 4.85 (d, J = 4.0 Hz, 2H, C$_2$-H), 5.80 (t, J = 4.0 Hz, 1H, C$_3$-H), 6.82–7.36 (m, 8H, aromatic). MS Found: *m*/*z* 238.1001. Calcd for $C_{16}H_{14}O_2$: M, 238.0994.

4-(*m*-Tolyl)-2*H*-chromene (3f): IR (neat) 1220 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 2.38 (s, 3H, -CH$_3$), 4.85 (d, J = 4.0 Hz, 2H, C$_2$-H), 5.78 (t, J = 4.0 Hz, 1H, C$_3$-H), 6.81–7.36 (m, 8H, aromatic). MS Found: *m*/*z* 222.1047. Calcd for $C_{16}H_{14}O$: M, 222.1045.

4-(*p*-Methoxyphenyl)-2*H*-chromene (3g): Mp 91.5–93.5 °C; IR (KBr) 1240 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 3.84 (s, 3H, -OCH$_3$), 4.83 (d, J = 4.3 Hz, 2H, C$_2$-H), 5.76 (t, J = 4.0 Hz, 1H, C$_3$-H), 6.83–7.36 (m, 8H, aromatic). MS Found: *m*/*z* 238.0988. Calcd for $C_{16}H_{14}O_2$: M, 238.0994.

4-(*p*-Tolyl)-2*H*-chromene (3h): IR (neat) 1220 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 2.39 (s, 3H, -CH$_3$), 4.84 (d, J = 4.0 Hz, 2H, C$_2$-H), 5.77 (t, J = 4.0 Hz, 1H, C$_3$-H), 6.81–7.24 (m, 8H, aromatic). MS Found: *m*/*z* 222.1044. Calcd for $C_{16}H_{14}O$: M, 222.1045.

4-(*p*-Fluorophenyl)-2*H*-chromene (3i): IR (neat) 1220 (–O–), 1480 cm^{-1}(–C=C–); ^{1}H NMR (CDCl$_3$) δ 4.84 (d, J = 3.6 Hz, 2H, C$_2$-H), 5.77 (t, J = 3.6 Hz, 1H, C$_3$-H), 6.82–7.36 (m, 8H, aromatic). MS Found: *m*/*z* 226.0752. Calcd for $C_{15}H_{11}FO$: M, 226.0749.

General Procedure. After a mixture of 4-trifluoromethylsulfonyloxy-2*H*-chromene (**1a**, 280 mg, 1 mmol), palladium(II) chloride (0.04 mmol), anhydrous potassium carbonate (7 mmol), and dry benzene (20 mL) was stirred for 30 min, a solution of the phenylboronic acid (**2a**, 3mmol) in ethanol (6 mL) was added. The reaction mixture was heated overnight at the reflux temperature and, after cooling, hydrogen peroxide (2 mL of an aqueous 30% w/v solution) was added to oxidize any unreacted boronic acid. After the mixture was diluted with chloroform and washed with water and saturated aqueous sodium hydrogencarbonate, the aqueous layer was re-extracted with chloroform. The combined organic layers were dried on anhydrous magnesium sulfate, and then concentrated to dryness under reduced pressure. The residue was chromatographed on a silica-gel column (benzene/hexanes = 1:1) to give a coupling product, 4-phenyl-2*H*-chromene (**3a**), as a pale-yellow oil.

Stille Coupling of 4-Trifluoromethylsulfonyloxy-2*H*-chromene with Tributylphenyltin. A mixture of 4-trifluoromethylsulfonyloxy-2*H*-chromene (**1a**, 280 mg, 1 mmol), tributylphenyltin (1.5 mmol), lithium chloride (2.5 mmol), copper(I) iodide (0.05 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.05 mmol) in 1,4-dioxane (15 mL) was stirred overnight at the reflux temperature. After cooling to room temperature, the mixture was diluted with chloroform. After the above-mentioned workup, the residue was chromatographed (benzene/hexanes = 1:1) to isolate the desired product, 4-phenyl-2*H*-chromene (**3a**), as a pale-yellow oil.

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