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Rh(I)-catalyzed cross-coupling reactions of alkenyl tosylates with potassium aryltrifluoroborates

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Abstract—$RhCl(PPh_3)_3$/DPPF was successfully employed as an efficient catalyst in the Suzuki–Miyaura cross-coupling reactions of potassium aryltrifluoroborates with alkenyl tosylates, affording the corresponding products in good to excellent yields.

Transition-metal catalyzed cross-coupling reactions, extensively employed in a wide range of organic chemistry, are arguably one of the most powerful methods for carbon–carbon bond formation.[1] Recently, rhodium catalyzed cross-coupling reaction captured much attention. Electron rich arylrhodium intermediate may undergo an oxidative addition of electrophilic aromatic substrate.[2] The stoichiometric activation of aryl chlorides on a phenylrhodium complex has been realized.[3] Moreover, these rhodium catalysts have been employed in the catalytic cross-coupling of arylboron reagents with acid anhydrides,[2] aryl bromides, and electron-deficient aryl chlorides,[4] as well as in the cross-coupling of arylzinc reagents with aryl iodides.[2] Not known is a system capable of handling triflates and arenesulfonates. Recently, arenesulfonates are emerging as important alternatives to aryl/vinyl triflates and halides in transition metal-catalyzed cross-coupling reactions since they are less expensive, more stable, and easier to handle than the corresponding triflates.[5,6] For example, remarkable progress of using arenesulfonates as electrophiles for Suzuki–Miyaura cross-coupling reactions have been made even though arenesulfonates are relatively unreactive compared to the corresponding halides and triflates.[5] This would be of great interest if rhodium could be utilized as an efficient catalyst for coupling reactions of arenesulfonates.

Among the cross-coupling reactions, Suzuki–Miyaura reaction is of the greatest practical importance.[7] A drawback associated with the use of boronic acids is the structural ambiguity, namely, the formation of the trimeric anhydride (boroxine).[8] An encouraging improvement is the use of trifluoroborates, which have been reported to couple with aryl halides or triflate catalyzed by palladium or nickel.[9] In view of arenesulfonates' easier preparation, increased stability, and less expensive relative to aryl triflates, as well as to broaden the application of rhodium-catalyzed cross-coupling reactions, it is of significant interest to develop general protocols to employ arenesulfonates for rhodium-catalyzed cross-coupling reactions of potassium trifluoroborates.

As part of our efforts to develop new approaches for the synthesis of some natural product-like molecules with biological activities,[10] we became interested in some privileged scaffolds, such as furan-2(5*H*)-one, coumarin, pyrone, and quinolin-2(1*H*)-one derivatives due to their extraordinary biological activities.[10,11] The structural similarity of 4-hydroxycoumarin with 4-hydroxy-2(1*H*)-quinolone, 4-hydroxy-pyrones, and 4-hydroxy-2(5*H*)-furanones led us to envisage that their 4-tosyloxy species could be employed in cross-coupling reactions as good substrates. Herein, we disclose our preliminary results, which represent the first example of rhodium catalyzed Suzuki–Miyaura couplings of alkenyl tosylates with potassium aryltrifluoroborates.

These tosylates were prepared simply from the corresponding 4-hydroxy species with *p*-toluenesulfonyl

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chloride in the presence of triethylamine (Fig. 1). Initial studies were aimed to find optimal reaction conditions for this coupling reaction. Our investigation commenced with the reaction of 4-tosyloxycoumarin **1b** and potassium phenyltrifluoroborate (Scheme 1). Under the reaction conditions shown in Scheme 1, the desired product **2c**, was obtained in a promising yield (44%). Poor results were observed when other phosphine-based ligands (dppp, P(*o*-tolyl)$_3$, P(Cy)$_3$, 2-^{t}Bu$_2$P biphenyl, 2-Cy$_2$P biphenyl) were employed. Without the addition of any ligands, only trace amount of product was detected. Toluene was proved to be the best choice after solvent screening (benzene, THF, EtOH, and H_2O, DMSO, dioxane). Among the bases investigated (KF, K_2CO_3, K_3PO_4, Cs_2CO_3, CsF, K_2HPO_4, Na_2CO_3, LiOH, NaOH, KOH), K_2HPO_4 was the most efficient (61% yield). The reaction was retarded when the temperature was decreased.

A variety of arenesulfonates and trifluoroborates have thus been examined for the Rh(I)-catalyzed cross-coupling reactions using the optimized catalyst system, and the results are summarized in Table 1. As shown in Table 1, substituted 4-tosyloxycouamrins **1b–f** showed broad generality when coupled with various potassium aryltrifluoroborates, and substrates with electron-withdrawing groups gave better results. 4-Tosyloxypyrone **1g** was also a good partner in this coupling reaction and excellent yields were obtained with various potassium aryl trifluoroborates, while reactions of 4-hydroxy-2(5*H*)-furanone **1a** and 4-tosyloxyquinolin-2(1*H*)-one **1h** afforded moderate yields (entries 1 and 2, 18 and 19).

In summary, we have described an effective rhodium catalyst system for the Suzuki–Miyaura cross-coupling of alkenyl tosylates with potassium aryltrifluoroborates. Some natural product-like compounds, such as 4-substituted furan-2(5*H*)-ones, coumarins, pyrones, and quinolin-2(1*H*)-ones, have been synthesized efficiently and could be directly used for biological assays. This protocol not only represents the first example of rhodium-catalyzed Suzuki–Miyaura couplings of alkenyl tosylates with potassium aryl trifluoroborates, but also demonstrates the versatility of rhodium catalysts and broadens the prospect of their applications in organic synthesis.

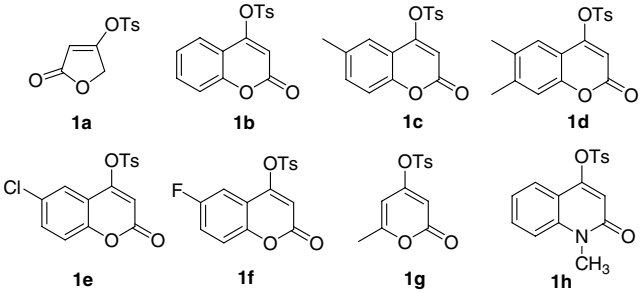
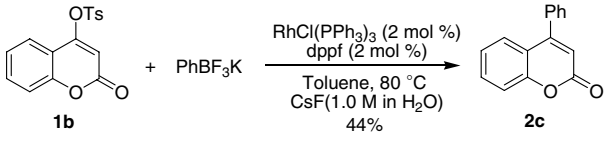
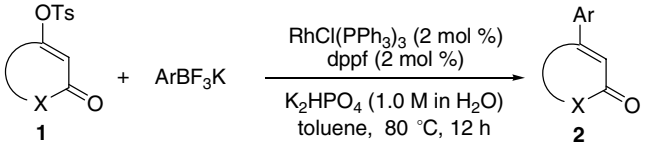


Figure 1.



Scheme 1.

Table 1. Rh(I)-catalyzed coupling reaction of tosylate **1** with potassium aryltrifluoroborates[a,12]



Entry	Tosylate	$ArBF_3K$	Product	Yield[b] (%)
1	**1a**	4-Me$C_6H_4BF_3K$	**2a**	66
2	**1a**	4-F$C_6H_4BF_3K$	**2b**	64
3	**1b**	PhBF_3K	**2c**	61
4	**1b**	4-Me$C_6H_4BF_3K$	**2d**	75
5	**1b**	4-F$C_6H_4BF_3K$	**2e**	71
6	**1c**	4-Me$C_6H_4BF_3K$	**2f**	67
7	**1c**	4-F$C_6H_4BF_3K$	**2g**	75
8	**1d**	4-Me$C_6H_4BF_3K$	**2h**	54
9	**1d**	4-F$C_6H_4BF_3K$	**2i**	63
10	**1e**	4-Me$C_6H_4BF_3K$	**2j**	69
11	**1e**	4-F$C_6H_4BF_3K$	**2k**	84
12	**1f**	PhBF_3K	**2l**	62
13	**1f**	4-Me$C_6H_4BF_3K$	**2m**	92
14	**1f**	4-F$C_6H_4BF_3K$	**2n**	94
15	**1g**	PhBF_3K	**2o**	89
16	**1g**	4-Me$C_6H_4BF_3K$	**2p**	99
17	**1g**	4-F$C_6H_4BF_3K$	**2q**	89
18	**1h**	4-Me$C_6H_4BF_3K$	**2r**	42
19	**1h**	4-F$C_6H_4BF_3K$	**2s**	46

[a] Reaction conditions: substrate (0.25 mmol), $RhCl(PPh_3)_3$ (2 mol %), dppf (2 mol %), K_2HPO_4 (1 mL, 1 M in water), toluene (2 mL), 80 °C, 12 h.
[b] Isolated yield.

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12. *General procedure for Suzuki–Miyaura coupling of alkenyl tosylates with potassium aryl trifuoroborates*: A mixture of alkenyl tosylate **1** (0.25 mmol), potassium aryltrifluoroborate (1.5 equiv), $RhCl(PPh_3)_3$ (2 mol %), and DPPF (2 mol %) was added into a reaction tube under nitrogen atmosphere. Then toluene (2.0 mL) and aqueous K_2HPO_4 (1.0 mL, 1.0 M solution) were added subsequently. The reaction mixture was stirred for 12 h at 80 °C. After the reaction was completed and monitored by TLC, the organic phase was separated and purified directly by flash chromatography column (silica gel) to afford the corresponding product **2**. (All products are known compounds. The data of products were identical with the literature reports.) 4-*p*-Tolylfuran-2(5*H*)-one **2a**:[5l] 66% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.42 (s, 3H), 5.21 (s, 2H), 6.33 (s, 1H), 7.27 (d, $J = 8.24$ Hz, 2H), 7.40 (d, $J = 7.80$ Hz, 2H). 4-(4-Fluorophenyl)furan-2(5*H*)-one **2b**:[5i] 64% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.21 (s, 2H), 6.34 (s, 1H), 7.18–7.20 (m, 2H), 7.51–7.53 (m, 2H). 4-Phenyl-2*H*-chromen-2-one **2c**:[13] 61% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.39 (s, 1H), 7.25–7.54 (m, 9H). ^{13}C NMR (125.7 MHz): δ (ppm) 161.0, 155.9, 154.5, 135.5, 132.2, 129.9, 129.1, 128.7, 127.3, 124.4, 119.3, 117.6, 115.5. MS $[C_{15}H_{10}O_2]$, *m*/*z* (M^++1): calcd 223, found 223. 4-*p*-Tolyl-2*H*-chromen-2-one **2d**:[13] 75% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.46 (s, 3H), 6.36 (s, 1H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.32–7.37 (m, 4H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.53–7.53 (m, 2H). ^{13}C NMR (125.7 MHz): δ (ppm) 161.1, 156.0, 154.5, 140.2, 132.6, 132.1, 129.8, 128.7, 127.3, 124.3, 119.4, 117.6, 115.2, 21.6. MS $[C_{16}H_{12}O_2]$, *m*/*z* (M^++1): calcd 237, found 237. 4-(4-Fluorophenyl)-2*H*-chromen-2-one **2e**:[13] 71% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.36 (s, 1H), 7.23–7.59 (m, 8H). ^{13}C NMR (125.7 MHz): δ (ppm) 160.8, 154.8, 154.4, 146.7, 132.3, 130.7, 130.6, 127.0, 124.5, 119.1, 117.7, 116.4, 116.3, 115.6. MS $[C_{15}H_9FO_2]$, *m*/*z* (M^++1): calcd 241, found 241.6-Methyl-4-*p*-tolyl-2*H*-chromen-2-one **2f**:[14] 67% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.34 (s, 3H), 2.47 (s, 3H), 6.34 (s, 1H), 7.30 (d, $J = 8$ Hz, 2H), 7.35 (m, 5H). 4-(4-Fluorophenyl)-6-methyl-2*H*-chromen-2-one **2g**:[10d] 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.35 (s, 3H), 6.33 (s, 1H), 7.21–7.44 (m, 7H). IR (KBr, cm^{-1}): 3047, 2921, 1742, 1720, 1566, 1225, 839. MS $[C_{16}H_{11}FO_2]$, *m*/*z* (M^+): calcd 254, found 254. HRMS: Anal. Calcd for $C_{16}H_{11}FO_2$, 254.07431. Found 254.07436. 6,7-Dimethyl-4-*p*-tolyl-2*H*-chromen-2-one **2h**:[10d] 54% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.23 (s, 3H), 2.35 (s, 3H), 2.46 (s, 3H), 6.27 (s, 1H), 7.17 (s, 1H), 7.23 (s, 1H), 7.34 (t, $J = 9$ Hz, 4H). ^{13}C NMR (125.7 MHz): δ (ppm) 161.4, 155.7, 152.7, 141.9, 139.7, 132.9, 132.8, 129.5, 128.4, 127.0, 117.9, 116.8, 113.9, 21.4,

20.2, 19.3. MS [$C_{18}H_{16}O_2$], m/z (M^+): calcd 264, found 264. HRMS: Anal. Calcd for $C_{18}H_{16}O_2$, 264.11503. Found 264.11556. 4-(4-Fluorophenyl)-6,7-dimethyl-2*H*-chromen-2-one **2i**:[10d] 63% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.24 (s, 3H), 2.36 (s, 3H), 6.27 (s, 1H), 7.16–7.44 (m, 6H). 4-(4-Fluorophenyl)-6,7-dimethyl-2*H*-chromen-2-one **2i**:[10d] 63% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.24 (s, 3H), 2.36 (s, 3H), 6.27 (s, 1H), 7.16–7.44 (m, 6H). 6-Chloro-4-*p*-tolyl-2*H*-chromen-2-one **2j**:[10d] 69% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.47 (s, 3H), 6.39 (s, 1H), 7.33–7.37 (m, 5H), 7.49–7.50 (m, 2H). IR (KBr, cm^{-1}): 3063, 2914, 1735, 1122, 819. MS [$C_{16}H_{11}ClO_2$], m/z (M^+): calcd 270, found 270. HRMS: Anal. Calcd for $C_{16}H_{11}ClO_2$, 270.04476. Found 270.04385. 6-Chloro-4-(4-fluorophenyl)-2*H*-chromen-2-one **2k**:[10d] 84% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.38 (s, 1H), 7.24–7.42 (m, 7H). IR (KBr, cm^{-1}): 2920, 2850, 1740, 1721, 1232, 936, 886, 823. MS [$C_{15}H_8ClFO_2$], m/z (M^+): calcd 274, found 274. HRMS: Anal. Calcd for $C_{15}H_8ClFO_2$, 274.01969. Found 274.01942. 6-Fluoro-4-phenyl-2*H*-chromen-2-one **2l**:[15] 62% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.43 (s, 1H), 7.18–7.46 (m, 4H), 7.54–7.56 (m, 4H). 6-Fluoro-4-*p*-tolyl-2*H*-chromen-2-one **2m**:[10d] 92% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.46 (s, 3H), 6.41 (s, 1H), 7.20–7.40 (m, 7H). IR (KBr, cm^{-1}): 3075, 2925, 1717, 1433, 1251, 816. MS [$C_{16}H_{11}FO_2$], m/z (M^+): calcd 254, found 254. HRMS: Anal. Calcd for $C_{16}H_{11}FO_2$, 254.07431. Found 254.07370. 6-Fluoro-4-(4-fluorophenyl)-2*H*-chromen-2-one **2n**:[10d] 94% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.41 (s, 1H), 7.12–7.16 (m, 1H), 7.23–7.28 (m, 3H), 7.38–7.46 (m, 3H). IR (KBr, cm^{-1}): 2923, 2850, 1745, 1221, 943, 840, 825. MS [$C_{15}H_8F_2O_2$], m/z (M^+): calcd 258, found 258. HRMS: Anal. Calcd for $C_{15}H_8F_2O_2$, 258.04924. Found 258.04895. 6-Methyl-4-phenyl-2*H*-pyran-2-one **2o**:[16] 89% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.33 (s, 3H), 6.31 (s, 1H), 6.36 (s, 1H), 7.47–7.57 (m, 5H). 6-Methyl-4-*p*-tolyl-2*H*-pyran-2-one **2p**:[17] 99% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.31 (s, 3H), 2.41 (s, 3H), 6.30 (s, 1H), 6.34 (s, 1H), 7.27 (d, $J = 7.80$ Hz, 2H), 7.46 (d, $J = 7.76$ Hz, 2H). 4-(4-Fluorophenyl)-6-methyl-2*H*-pyran-2-one **2q**:[10b] 89% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.33 (s, 3H), 6.27 (s, 1H), 6.31 (s, 1H), 7.15–7.19 (m, 2H), 7.55–7.59 (m, 2H). ^{13}C NMR (125.7 MHz): δ (ppm) 165.4, 163.4, 163.1, 163.0, 154.1, 132.0, 130.2, 130.1, 116.9, 116.7, 107.5, 103.4, 20.3. MS [$C_{12}H_9FO_2$], m/z (M^++Na): calcd 227, found 227. 1-Methyl-4-*p*-tolylquinolin-2(1*H*)-one **2r**:[10d] 42% yield, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.45 (s, 3H), 3.78 (s, 3H), 6.69 (s, 1H), 7.18 (t, $J = 7$ Hz, 1H), 7.29–7.33 (m, 4H), 7.44 (d, $J = 8.5$ Hz, 1H), 7.58–7.60 (m, 2H). ^{13}C NMR (125.7 MHz): δ (ppm) 162.1, 151.0, 140.4, 138.7, 134.2, 130.6, 129.3, 128.9, 127.8, 122.6, 121.9, 120.7, 114.5, 29.5, 21.3. MS [$C_{17}H_{15}NO$], m/z (M^+): calcd 249, found 249. HRMS: Anal. Calcd for $C_{17}H_{15}NO$, 249.11536. Found 249.11678. 4-(4-Fluorophenyl)-1-methylquinolin-2(1*H*)-one **2s**:[10b] 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.79 (s, 3H), 6.67 (s, 1H), 7.17–7.22 (m, 3H), 7.39–7.46 (m, 3H), 7.51 (d, $J = 8.28$ Hz, 1H), 7.58 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (125.7 MHz): δ (ppm) 164.0, 162.1, 161.1, 149.9, 140.7, 133.6, 131.8, 131.7, 127.5, 122.8, 121.5, 120.1, 116.4, 116.3, 116.0, 29.8. MS [$C_{16}H_{12}FNO$], m/z (M^+): calcd 253, found 253. HRMS: Anal. Calcd for $C_{16}H_{12}FNO$, 253.09029. Found 253.09034.

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