An Improved Suzuki–Miyaura Cross-Coupling Reaction for the Synthesis of Fluorine-Substituted 3-Biaryl-1-ferrocenyl-2-propen-1-one

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Abstract: We studied the Pd(0)-catalyzed Suzuki–Miyaura crosscoupling reaction and obtained an improved procedure with shorter reaction times and higher conversions.

We investigated two methods stepwise addition of reagents and addition of all the reagents at the same time. We found that the reaction rate of the former is faster than the latter. Methanol was shown to be the optimum solvent for the reaction, however with an alcohol as the solvent the reaction was complete in under 1.5 hours. This improved methodology was applied to the synthesis of novel fluorinesubstituted 3-biaryl-1-ferrocene-propene-1-ones, which were synthesized in good yields.

Keywords: Suzuki cross-coupling reaction, Pd(0) catalyst, alcohol solvents, ferrocene derivatives, biaryl

In the past few years, more and more interest has focused on the design of new compounds incorporating the ferrocene skeleton owing to their potential applications as NLO chromophores,¹ as liquid crystal materials,² in electrochemistry,³ in polymer chemistry,⁴ and in materials chemistry^{5,6} to name but a few. It has been well established that molecular structures with differences between ground state and excited state dipole moments and large transition moments have large second-order nonlinear optics.⁷ Molecules with π -donor–acceptor interactions such as ferrocene or its derivatives show promise in nonlinear optics,⁸ thus biaryl ferrocenyl organic compounds have been synthesized due to their extended molecular conjugation.⁹ More recently there has been much effort devoted to the introduction of a fluorine atom or trifluoromethyl group into organic molecules because these compounds exhibit particularly high physiological activities and remarkable physical properties.¹⁰

Following our previous work,⁹ due to the unsatisfactory conversion (generally below 80%) and long reaction times (general nearly 20 hours), we have further examined the role of solvents and the effect of changing the order of reagent addition to enhance the rate of the Suzuki cross-coupling reaction for the synthesis of novel fluorine-sub-stituted 3-biaryl-1-ferrocenyl-2-propen-1-one (Scheme 1).

Firstly, we investigated the influence the order of addition of reagents had on the reaction. The best results were obtained when the reaction was carried out as follows: solvent (one third of the total volume), an arylboronic acid, and sodium carbonate (10% in water) were successively added to the flask, and refluxed for five minutes; then Pd(0) catalyst, a halide, and the remaining solvent was added to the above mixture in sequence. The reaction rate was improved by adding the reagents stepwise compared with mixing all the reagents at once. For example, the reaction time of 1-ferrocenyl-3-(4'-bromo)phenyl-2-propen-1-one (4a) with 3,4,5-trifluorophenyl boronic acid (5a) in methanol was shortened from eight hours to 30 minutes (Table 1, entries 12 and 27, Scheme 2). Recently, Hassan, Smith, and Aliprantis¹¹ reported that an arylboronic acid was transformed into trihydroxyarylboronate $[ArB(OH)_3]$ before transmetallation, and it was supposed



Scheme 1

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that this anion was the reactive species rather than the neutral arylboronic acid. We hypothesize in our experiments that $ArB(OH)_2$ was fully transformed into $ArB(OH)_3^-$ before transmetallation by the method described. As transmetallation is the key step in the Suzuki cross-coupling reaction, the increase in the rate of the reaction can be attributed to the generation of the trihydroxyarylboronate (Table 1).

Secondly, the role of the solvent was investigated. It can be seen that polar solvents such as alcohols, DMF, THF, and acetone are superior to non-polar solvents such as benzene and toluene in this reaction, a trend which has been observed by others.¹⁴ It is possible that, in polar solvents, the solvent, aqueous base solution, catalyst, and substrate formed a homogeneous solution, which leads to a much-increased probability of collision and thus remarkably improved the speed of the reaction. As the solubility of the reaction components was better in methanol than in the other alcohols tested, the lower yields obtained in Table 1, entries 13, 15 and 18 may be explained by lower homogeneity of the reaction mixture. It was also observed that a faster reaction rate occurred in protic solvents rather than in polar aprotic solvents, this can be seen in particular with methanol when the reaction was complete in 30 minutes under reflux (Table 1, entry 12).

In an aqueous system, the reaction time was substantially increased, however, a reasonable yield was achieved with tetramethylammonium chloride as the phase-transfer catalyst (Table 1, entries 24, 25, and 26). DMSO was found to be unsuitable for the reaction (Table 1, entries 21–23); even a small amount of DMSO was found to inhibit the reaction (MeOH–DMSO, 30:1). It was supposed that the catalyst was poisoned by low-valence sulfur in DMSO.

Finally, the relationship between solvent or temperature and byproducts was investigated. At 80 $^{\circ}$ C and above byproducts started to appear and accumulated as the temperature increased. However, with DMF as the solvent, unidentified, insoluble byproducts were observed even below 78 $^{\circ}$ C.

Due to the advantages of stepwise addition, we applied it to a general Suzuki cross-coupling reaction of aryl halides and arylboronic acids and found that the reaction rate was much improved (Table 2).

Thus, taking into account cost, byproducts formed, and the reaction rate, we expanded the synthetic utility of this methodology. Six novel fluorine-substituted organometallic compounds were synthesized using the above methodology (Scheme 2, Table 3). 3-Biaryl-1-ferrocenyl-2propene-1-ones, were formed by stepwise addition of reagents in methanol. The reaction rate increased when one third of the volume of methanol, arylboronic acid, and sodium carbonate were refluxed for five minutes, and then the other reagents (catalyst, halide, and remaining methanol) were added. Byproducts were not observed when the addition was carried out in this way.

Table 1	Suzuki Cross-Coupling Reaction of 1-Ferrocenyl-3-(4'-
bromophe	enyl)- 2-propen-1-one with 3,4,5-Trifluorophenylboronic
Acid with	Pd(0) Catalyst ^a

Entry	Tempera (°C)	ture Time (h)	Solvent ^b	Conversion (%)
1	110	1.0	DMF	96
2	100	1.0	DMF	76
3	90	2.5	DMF	80
4	78	2.5	DMF	64
5	78	4.0	Benzene	48
6	78	24.0	Benzene	80
7	95	4.0	Toluene	65
8	95	16.5	Toluene	83
9	60	4.0	THF	57
10	54	4.0	Acetone	42
11	66	0.25	МеОН	96
12	66	0.50	МеОН	100
13	76	0.25	EtOH	45
14	76	1.0	EtOH	98
15	66	0.5	<i>i</i> -PrOH	25
16	66	2.5	<i>i</i> -PrOH	62
17	78	1.0	<i>i</i> -PrOH	89
18	66	0.5	PrOH	35
19	66	2.5	PrOH	75
20	90	0.25	PrOH	95
21	78	24.0	DMSO	0
22	100	24.0	DMSO	0
23	66	24.0	MeOH-DMSO (5:1)	0
24	66	24.0	H_2O –EtOAc (15:2) ^c	57
25	80	14.0	H_2O^c	35
26	80	43.5	H_2O^c	69
27 ^d	66	8.0	MeOH	80

^a 1-Ferrocenyl-3-(4'-bromophenyl)-2-propen-1-one (20 mg), 3,4,5trifluorophenyl boronic acid (11.6 mg), aq solution Na_2CO_3 (2 M, 0.2 mL), solvent (15 mL), Pd(PPh₃)₄ (3 mmol%). Stepwise addition under a N_2 atmosphere.

^b All solvents were used as received.

 c Phase-transfer catalyst (C_{4}H_{9})_{4}N^{+}Cl^{-} (70% in water; 5%) was added.

^d All materials were mixed at the same time under a N₂ atmosphere.

Entry	Time (h)	Halide	Boronic acid	Conversion (%)
1 ^b	1.5	Br	B(OH)2	98
2°	4.0	вг-	B(OH)2	90
3 ^b	0.25	Вг-	B(OH)2	95
4 ^c	1.0	Вг-	B(OH)2	92
5 ^b	1.0	Br		90
6 ^c	3.0	Br		89
7 ^b	0.25	Br		90
8 ^c	6.5	Br	——————————————————————————————————————	65
9 ^b	0.25	Br		85
10 ^c	1.0	Br		80

Table 2 Suzuki Cross-Coupling Reaction of Halides and Boronic Acida

^a Aryl bromide (20 mg), boronic acid (1.1 equiv), Na₂CO₃ (3.8 equiv), solvent (8 mL), Pd(PPh₃)₄ (3 mmol%), reflux, MeOH, under N₂ atmosphere.

^b Stepwise addition of reagents.

^c Reagents added at the same time.



5b 5c 5a

Scheme 2

¹H and ¹³C NMR spectra were performed on a Mercury Plus 400 MHz NMR spectrometer in CDCl₃ with TMS as an internal reference. IR spectra were record on a Bruker Vector-22 spectrometer as KBr pellets. Mps were determined with a X-4 digital display binocular microscope and were uncorrected. EtOH (95%) was used.

Table 3 Pd(0)-Catalyzed Suzuki Cross-Coupling Reaction of 1-Ferrocenyl- 3-(4'/2')-bromophenyl)-2-propen-1-one with Fluorine-Substituted Arylboronic Acids^a

Entry	Bromide	Substrate	Product	Tempera- ture (°C)	Conver- sion (%) ^b
1	4 a	5a	6a	66	98
2	4a	5b	6b	66	94
3	4 a	5c	6c	66	96
4	4b	5a	6d	66	97
5	4b	5b	6e	66	93
6	4b	5c	6f	66	96

^a Halide (1 mmol), arylboronic acid (1.2 mmol), aq soln Na₂CO₃ (2 M; 3.8 mmol), MeOH (40 mL), Pd(PPh₃)₄ (3 mmol%), 1 h. Stepwise addition of reagents under a N2 atmosphere. ^b Determined by HPLC.

Acetylferrocene,¹² 3,4,5-trifluorophenylboronic acid, 3,4-difluoro phenylboronic acid, and 3,5-difluorophenylboronic acid,13a,b and $Pd(0)^{13c}$ were prepared by known procedures.

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1-Ferrocenyl-3-[2'-bromophenyl]-2-propen-1-one (4a); Typical Procedure

Acetylferrocene (**2**; 5.7 g, 25 mmol) was dissolved in EtOH (20 mL), *p*-bromobenzaldehyde (**3a**; 4.8 g, 26 mmol) in EtOH (6 mL) was added with stirring. Stirring was continued for 0.5 h until all the solid had dissolved. A solution of EtOH (20 mL), H₂O (20 mL), and NaOH (2.0 g, 50 mmol) was added dropwise under stirring at r.t. A reddish precipitate appeared after 1 h, and continued to form, eventually preventing stirring after 2 h. When the reaction was complete (TLC) the mixture was poured into H₂O (200 mL) and HCl (2 M) was added until the pH of the solution reached 7. The reaction was cooled, filtered, the solid was washed with H₂O (3 × 20 mL), and dried in vacuo. The crude product was recrystallized (CHCl₃) to give **4a** as dark claret crystals (8.1 g, 96%); mp 111–113 °C; R_f 0.36 (EtOAc–petroleum ether, 1:8).

Fluorine-Substituted 3-Biaryl-1-ferrocenyl-2-propen-1-ones 6; General Procedure

A 100-mL three-necked round-bottomed flask was charged with arylboronic acid (5; 1.2 mmol), MeOH (10 mL), and an aq solution of Na₂CO₃ (2 M; 2 mL) under a N₂ atmosphere. The mixture was heated to reflux and stirred vigorously; after 5 min halide 4 (1 mmol), Pd(PPh₃)₄ (0.03 mmol), and MeOH (30mL) were added, under a N₂ atmosphere. After the reaction was complete (TLC), the reaction mixture was cooled to r.t. and the solvents were removed in vacuo to give the crude product. The crude product was purified by column chromatography (neutral alumina; petroleum ether–EtOAc, 4:1→20:1; the first red band was the starting material and the second red band was the product). The second fraction was concentrated in vacuo to give pure **6**.

3-[4'-(3",4",5"-Trifluorophenyl)phenyl]-1-ferrocenyl-2-propen-1-one (6a)

Yield: 76% (0.340 g); red crystals; mp 182–183 °C; R_f 0.35 (petroleum ether–EtOAc, 6:1).

IR (KBr): 3080, 1651, 1537, 1506, 1455, 1252, 1076, 1039, 821, 746, 531 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.82 (d, 1 H, *J* = 15.6 Hz), 7.74 (d, 2 H, *J* = 8.0 Hz), 7.57 (d, 2 H, *J* = 8.0 Hz), 7.23 (d, 2 H, *J* = 7.2 Hz), 7.17 (d, 1 H, *J* = 15.2 Hz), 4.94 (s, 2 H), 4.63 (s, 2 H), 4.24 (s, 5 H).

¹³C NMR (100 MHz, CDCl₃): δ = 192.74, 151.43 (dq, $C_{3'',5''}$, J = 253.4, 9.9 Hz), 139.62, 139.53 (dt, $C_{4''}$, J = 251.0, 15.2 Hz), 139.41, 136.37 (m, $C_{1''}$), 135.28, 128.91, 127.30, 123.56, 110.97 (dd, $C_{2'',6''}$, J = 16.0, 6.1 Hz), 80.50, 72.92, 70.13, 69.75.

Anal. calcd for $C_{25}H_{17}F_3$ FeO: C, 67.29; H, 3.84. Found: C, 67.20; H, 3.78.

3-[4'-(3",5"-Difluorophenyl)phenyl]-1-ferrocenyl-2-propen-1one (6b)

Yield: 88% (0.375 g); red crystals; mp 162–163 °C; R_f 0.38 (petro-leum ether–EtOAc, 6:1).

IR (KBr): 3088, 1655, 1596, 1458, 1377, 1241, 1081, 987, 829, 760, 542 $\rm cm^{-1}$

¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, 1 H, *J* = 15.6 Hz), 7.74 (d, 2 H, *J* = 7.2 Hz), 7.62 (d, 2 H, *J* = 7.6 Hz), 7.17 (d, 1 H, *J* = 14.8 Hz), 7.16–7.14 (d, 2 H, *J* = 5.6 Hz), 6.83 (t, 1 H, *J* = 7.6 Hz), 4.94 (s, 2 H), 4.62 (s, 2 H), 4.24 (s, 5 H).

¹³C NMR (100 MHz, CDCl₃): δ = 193.66, 163.67 (dd, C_{3",5"}, J = 246.5, 12.9 Hz), 143.84 (t, C_{1"}, J = 9.4 Hz), 140.60, 140.04, 135.68, 129.19, 127.78, 124.36, 110.17 (dd, C_{2",6"}, J = 18.6, 7.0 Hz), 103.30 (t, C_{4"}, J = 25.0 Hz), 81.90, 73.26, 70.45, 70.05

Anal. calcd for $C_{25}H_{18}F_2$ FeO: C, 70.11; H, 4.24. Found: C, 69.96; H, 4.15.

3-[4'-(3",4"-Difluorophenyl)phenyl]-1-ferrocenyl-2-propen-1one (6c)

Yield: 85% (0.364 g); red crystals; mp 178–179 °C; R_f 0.34 (petro-leum ether–EtOAc, 6:1).

IR (KBr): 3090, 1652, 1594, 1499, 1376, 1265, 1079, 981, 817, 771, 547 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, 1 H, *J* = 15.6 Hz), 7.73 (d, 2 H, *J* = 8.4 Hz), 7.59 (d, 2 H, *J* = 7.2 Hz), 7.46–7.40 (m, 1 H), 7.36–7.33 (m, 1 H), 7.29–7.22 (q, 1 H), 7.19 (d, 1 H, *J* = 15.2 Hz), 4.94 (s, 2 H), 4.62 (s, 2 H), 4.23 (s, 5 H).

¹³C NMR (100 MHz, CDCl₃): δ = 192.82, 150.55 (dd, $C_{3''}$ or $C_{4''}$, *J* = 246.6, 12.9 Hz), 150.17 (dd, $C_{4''}$ or $C_{3''}$, *J* = 248.0, 12.1 Hz), 140.57, 139.87, 137.31 (t, $C_{1''}$, *J* = 5.3 Hz), 134.70, 128.84, 127.36, 123.48, 122.95 (dd, $C_{6''}$, *J* = 6.5, 3.8 Hz), 117.69 (d, $C_{2''}$ or $C_{5''}$, *J* = 17.5 Hz), 115.89 (d, $C_{5''}$ or $C_{2''}$, *J* = 17.4 Hz), 81.08, 72.88, 70.12, 69.73.

Anal. calcd for $C_{25}H_{18}F_2$ FeO: C, 70.11; H, 4.24. Found: C, 70.08; H, 4.20.

3-[2'-(3",4",5"-Trifluorophenyl)phenyl]-1-ferrocenyl-2-propen-1-one (6d)

Yield: 82% (0.367 g); red crystals, mp 171–172 °C; R_f 0.41 (petro-leum ether–EtOAc, 6:1).

IR (KBr): 3075, 1649, 1588, 1531, 1449, 1367, 1239, 1045, 832, 767, 488 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.80 (br, 1 H), 7.71 (d, 1 H, *J* = 15.6 Hz), 7.47 (br, 2 H), 7.32 (br, 1 H), 7.03 (d, 1 H, *J* = 20.8 Hz), 7.00–6.98 (m, 2 H), 4.86 (s, 2 H), 4.60 (s, 2 H), 4.21 (s, 5 H).

¹³C NMR (100 MHz, CDCl₃): δ = 192.58, 150.92 (dd, $C_{3'',5''}$, J = 251.1, 9.9 Hz), 139.96, 139.44 (dt, $C_{4''}$, J = 250.7, 15.3Hz), 138.49, 136.15 (m, $C_{1''}$), 133.49, 130.28, 129.80, 128.64, 127.15, 125.42, 113.97 (d, $C_{2'',6''}$, J = 19.6 Hz), 80.46, 72.90, 70.07, 69.71.

Anal. calcd for $C_{25}H_{17}F_3FeO: C, 67.29; H, 3.84$. Found: C, 67.22; H, 3.77.

3-[2'-(3'',5''-Difluorophenyl)phenyl]-1-ferrocenyl-2-propen-1one (6e)

Yield: 84% (0.361 g); red crystals; mp 138–139 °C; R_f 0.44 (petro-leum ether–EtOAc, 6:1).

IR(KBr): 3075, 1648, 1587, 1449, 1376, 1240, 1081, 986, 830, 762, 548 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.80 (m, 1 H), 7.74 (d, 1 H, *J* = 15.6 Hz), 7.49–7.46 (m, 2 H), 7.36–7.33 (m, 1 H), 7.01 (d, 1 H, *J* = 15.6 Hz), 6.91–6.83 (m, 3 H), 4.85 (s, 2 H), 4.59 (s, 2 H), 4.20 (s, 5 H).

¹³C NMR (100 MHz, CDCl₃): δ = 192.90, 162.73 (dd, C_{3",5"}, J = 248.0, 12.9 Hz), 143.52 (t, C_{1"}, J = 9.3 Hz), 140.69, 138.80, 133.51, 130.26, 129.72, 128.52, 127.30, 125.87, 112.83 (dd, C_{2",6"}, J = 19.0, 6.8 Hz), 103.07 (t, C_{4"}, J = 25.0 Hz), 80.68, 72.88, 70.09, 69.72.

Anal. calcd for $C_{25}H_{18}F_2$ FeO: C, 70.11; H, 4.24. Found: C, 69.92; H, 4.12.

3-[2'-(3'',4''-Difluorophenyl)phenyl]-1-ferrocenyl-2-propen-1- one (6f)

Yield: 89% (0.380 g); red crystals; mp 134–135 °C; R_f 0.42 (petroleum ether–EtOAc, 6:1).

IR: 3095, 1649, 1586, 1450, 1312, 1261, 1080, 987, 823, 762, 548 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.80 (br, 1 H), 7.74 (d, 1 H, *J* = 16.0 Hz), 7.46 (br, 2 H), 7.35 (br, 1 H), 7.24–7.19 (m, 2 H), 7.17–7.00 (m, 1 H), 7.02 (d, 1 H, J = 15.6 Hz), 4.85 (s, 2 H), 4.59 (s, 2 H), 4.20 (s, 5 H).

¹³C NMR (100 MHz, CDCl₃): δ = 192.69, 150.01 (dm, J = 247.7 Hz), 140.91, 139.10, 138.42 (s, C_{1"}), 137.11, 133.49, 130.48, 129.72, 128.20, 127.12, 125.96 (s, C_{6"}), 118.66 (dd, C_{2"} or C_{5"}, J = 17.4, 8.7 Hz), 117.23 (d, C_{5"} or C_{2"}, J = 17.4 Hz), 80.34, 72.80, 70.04, 69.68.

Anal. calcd for $C_{25}H_{18}F_2FeO$: C, 70.11; H, 4.24. Found: C, 70.02; H, 4.13.

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