Chinese Chemical Letters Vol. 16, No. 1, pp 35-37, 2005
http://www.imm.ac.cn/journal/ccl.html

Palladium Catalyzed Synthesis of Fluorine-containing 3-Biaryl-1-ferrocenyl-2-propene-1-one

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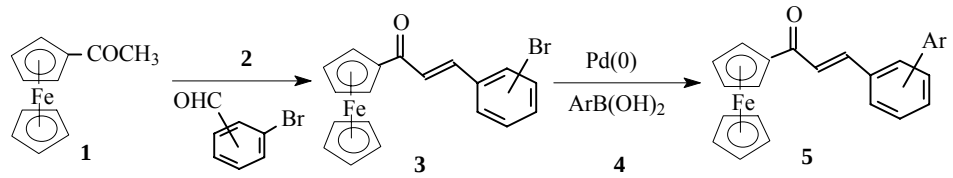
Abstract: The novel organometallic compounds, 3-[4'(or 2')-(4"-fluorophenyl)] phenyl-1-ferrocenyl-2-propen-1-ones **5** were synthesized for nonlinear optical chromophores by Pd (0) catalyzed Suzuki cross-coupling reaction. Their structures were established with elemental analysis, MS, IR and ^{1}H NMR spectroscopies.

Keywords: NLO materials, palladium catalyst, cross-coupling reaction, biaryl, ferrocene.

In the last two decades, molecular-based second-order nonlinear optical (NLO) chromophores[1, 2] have attracted much interest because of their potential applications in emerging opto-electronic technologies. These efforts have mainly focused on organic systems. More recently, organometallic molecules have been investigated as well. In comparison to common organic molecules, they offer a large variety of novel structures[3, 4]. The possibility of high environmental stability, and diversity of turnable electronic behaviors by virtue of the coordinated metal center of which might bring about NLO materials with unique characteristics such as magnetic and electrochemical properties.

In this communication, as continuing to our previous research work[5] the novel structure of containing fluorine atom of organometallic compounds, 3-biaryl-1-ferrocenyl-2-propen-1-ones, were synthesized by Suzuki cross-coupling reaction. The catalytic

Scheme 1



Ar = 4′-(4″-fluorophenyl) **5a**; 4′-(3″-formylphenyl) **5b**; 4′-(4″-methylphenyl) **5c**; 4′-(1″-naphthylphenyl) **5d**; 4′-phenyl **5e**; 2′-(4″-fluorophenyl) **5f**; 2′-(3″-formylphenyl) **5g**

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cross-coupling reaction of β-[2-(or 4-)bromphenyl]acrylferrocene **3** with arylboronic acid **4** to prepare fluorine-containing compounds **5**, permits the extension of molecular conjugation. Compounds **3** were transformed in (*E*)-3-[4'(or2')-(4"-fluoro)phenyl] phenyl-1-ferrocenyl-2-propen-1-one **5** by Suzuki cross-coupling reaction with 4-fluorophenylboronic acid **4** in the presence of Pd(0) in aqueous sodium carbonate solution. The new compounds were purified by column chromatography with petroleum ether/diethyl ether =4:1 to 30:1 (in volume) as eluents. The yield is good. The reactions are shown in **Scheme 1**.

Experimental

The analysis apparatus and the procedures of preparing of all the compounds were according the method of our previous work[5]. Compounds **5** was purified by column chromatography with petroleum ether/diethyl ether=4:1 to 30:1 (in volume) as eluents and the solvents were removed in a vacuum to afford pure products **5** as shown in **Scheme 2**.

5a: $C_{25}H_{19}FFeO$, Found (%): C 73.02, H 4.56; Calcd.(%): C 73.19, H 4.67; Rf = 0.24 (ethyl acetate/petroleum ether = 1:4); mp.: 167-169℃; Yield: 67.3%; ^{1}HNMR: 7.89(s, br, 1H, H-3), 7.71(s, br, 2H, H-2′,6′), 7.62-7.55(m, br, 4H, H-2″,3″,5″,6″), 7.16(d, 2H, J= 8.44Hz, H-3′,5′), 7.16 (d, 1H, J=16.90Hz, H-2), 5.02 (s, br, 2H, H-2‴,5‴), 4.71 (s, br, 2H, H-3‴,4‴), 4.33 (s, br, 5H, H-6‴); IR(KBr, cm^{-1}): 3086, 1650, 1590, 1455, 1375, 1242, 1080, 983, 822, 501, 483.

5b: $C_{26}H_{20}FeO_2$, Found (%): C 74.20, H 4.71; Calcd.(%): C 74.29, H 4.80; Rf = 0.27 (ethyl acetate/petroleum ether = 1:4); mp.: 144-145℃; Yield: 67.8%; ^{1}HNMR: 10.11(s, 1H, CHO), 8.18-7.70(m, 9H, H-3, H-2′,3′,5′,6′, H-2″,4″,5″,6″), 7.18(d, 1H, J=13.90Hz, H-2), 4.94(s, 2H, H-2‴,5‴), 4.62(s, 2H, H-3‴,4‴), 4.24(s, 5H, H-6‴); IR(KBr, cm^{-1}): 3087, 1701, 1652, 1597, 1456, 1378, 1081, 986, 830, 796, 696, 500, 482.

5c: $C_{26}H_{22}FeO$, Found(%): C 76.55, H 5.32; Calcd.(%): C 76.85, H 5.46; Rf = 0.36 (ethyl acetate/petroleum ether = 1:8); mp.: 162-164℃; Yield: 67.8%; ^{1}HNMR: 7.88(d, 1H, J=16.20Hz, H-3), 7.71(d, 2H, J=8.50Hz, H-3′,5′), 7.65(d, 2H, J=8.04Hz, H-2′,6′), 7.54(d, 2H, J=7.95Hz, H-2″,6″), 7.28 (d, 2H, J=7.75Hz, H-3″,5″), 7.17(d, 1H, J=16.04Hz, H-2), 4.94(s, 2H, H-2‴,5‴), 4.61(s, 2H, H-3‴,4‴), 4.23(s, 5H, H-6‴), 2.41(s, 3H, CH_3); IR(KBr, cm^{-1}): 3081, 1650, 1590, 1454, 1376, 1078, 986, 812, 500, 479.

5d: $C_{29}H_{22}FeO$, Found(%): C 78.60, H 4.93; Calcd.(%): C 78.74, H 5.01; Rf = 0.32 (ethyl acetate/petroleum ether = 1:10); mp.: 148-150℃; Yield: 72.2%; ^{1}HNMR: 7.95-7.85(m, 4H, H-3, H-4″,5″,8″), 7.78(d, 2H, J=7.70Hz, H-2′,6′), 7.58(d, 2H, J=7.90Hz, H-3′,5′), 7.56-7.44(m, 4H, H-2″,3″,6″,7″), 7.22(d, 1H, J=15.64Hz, H-2), 4.95(s, 2H, H-2‴,5‴), 4.62(s, 2H, H-3‴,4‴), 4.25(s, 5H, H-6‴); IR (KBr, cm^{-1}): 3082, 1644, 1589, 1454, 1377, 1079, 985, 838, 823, 807, 779, 506, 486.

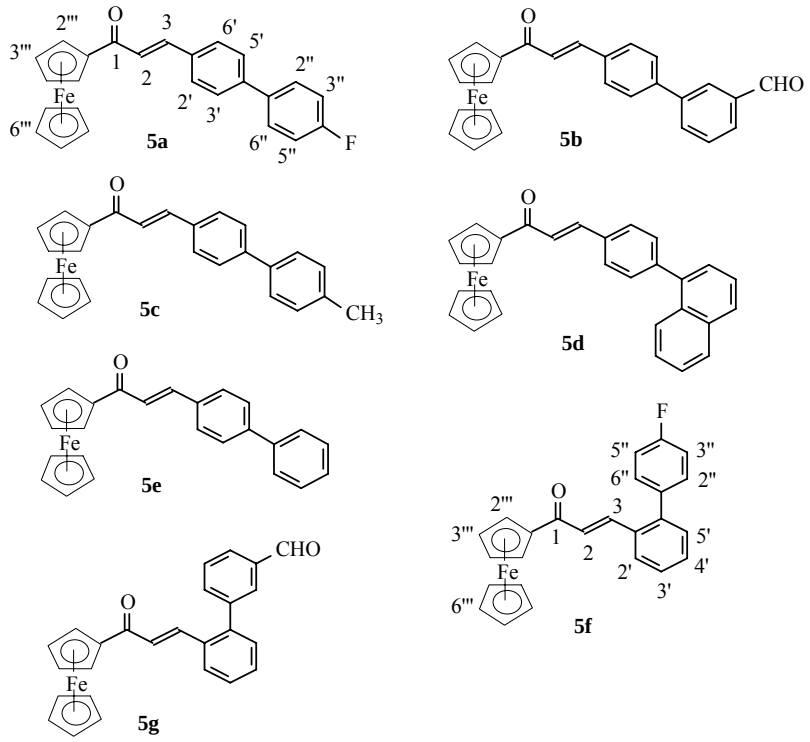
5e: $C_{25}H_{20}FeO$, Found(%): C 76.28, H 5.08; Calcd.(%): C 76.54, H 5.14; Rf = 0.16 (ethyl acetate/petroleum ether = 1:14); mp.: 170-172℃; Yield: 64.0%; ^{1}HNMR: 7.84(d, 1H, J=15.60 Hz, H-3), 7.80-7.35(m, 9H, H-2′,3′,5,′6′, H-2″,3″,4″,5″,6″), 7.17(d, 1H, J=15.25Hz, H-2), 4.94(s, 2H, H-2‴,5‴), 4.61(s, 2H, H-3‴,4‴), 4.23(s, 5H, H-6‴); IR (KBr, cm^{-1}): 3080, 1651, 1596, 1459, 1378, 1086, 984, 836, 767, 698, 500, 480.

5f: $C_{25}H_{19}FFeO$, Found (%): C 73.10, H 4.67, Calcd.(%): C 73,19, H 4.67; Rf = 0.22

(ethyl acetate/petroleum ether=1:10), Yield: 65.8%, mp.: 152-154℃; ^{1}HNMR: 7.77(d, br, 1H, J=17.25 Hz, H-3), 7.79,7.40-7.30(br, 4H, H-3′,4′,5′,6′), 7.45(br, 2H, H-3″,5″), 7.15(br, 2H, H-2″,6″), 7.02(d, br, 1H, J=13.20Hz, H-2), 4.85(s, br, 2H, H-2‴,5‴), 4.58(s, br, 2H, H-3‴,4‴), 4.20(s, br, 5H, H-6‴); IR(KBr, cm^{-1}): 3081, 1647, 1583, 1455, 1214, 1158, 1080, 1000, 836, 764, 501, 473.

5g: $C_{26}H_{20}FeO_2$, Found (%): C 74.22, H 4.81; Calcd.(%): C 74.29, H 4.80; Rf = 0.31 (ethyl acetate/petroleum ether=1:4), Yield: 67.6%, mp.: 142-144℃; ^{1}H NMR: 10.08(s, 1H, CHO), 7.93(br, 1H, H-2″), 7.90(s, 1H, H-4″), 7.85(br, 1H, H-6″), 7.78(d, 1H, J=15.60Hz, H-3), 7.63(m, 2H, H-6′,5″), 7.49(m, 2H, H-3′,4′), 7.41(br, 1H, H-5′), 7.02(d, 1H, J=15.26Hz, H-2), 4.84(s, 2H, H-2‴,5‴), 4.58(s, 2H, H-3‴,4‴), 4.19(s, 5H, H-6‴); IR(KBr, cm^{-1}): 3087, 1686, 1643, 1582, 1452, 1081, 990, 900, 817, 764, 700, 502, 479.

Scheme 2 Structures of **5**



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Received 3 December, 2003