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Synthesis of 3-Biaryl-1-ferrocenyl-2-propene-1-ones

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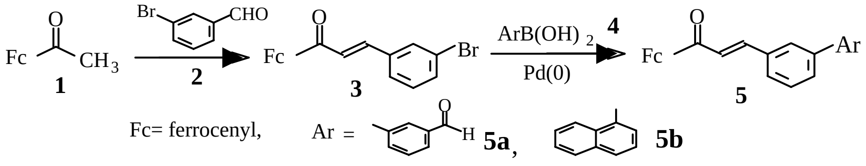
Abstract: The novel structures of organometallic compounds 3-biaryl-1-ferrocenyl-2-propene-1-ones **5** were synthesized for nonlinear optical chromophores by Suzuki cross-coupling reaction. Their structures were determined with elemental analyses, ^{1}H NMR spectra and ^{13}C NMR spectra.

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

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. 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 electro-chemical properties.

In the present communication, we report the synthesis of a novel structure of organometallic chalcone analogues, 1-ferrocenyl-3-biaryl chalcone, as electro-active materials by Suzuki cross-coupling reaction.



The catalytic cross-coupling reaction of haloarenes to prepare chalcone analogues, permit the extension of molecular conjugation. Compound **3** were transformed to E-1-biaryl-3-ferrocenyl chalcones **5** by Suzuki cross-coupling reaction with aryl boronic acid in the presence of Pd(0) in aqueous sodium carbonate solution. The new compounds were separated by column chromatography with hexane/diethyl ether =1:1 to 8:1 as

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eluant in good yield.

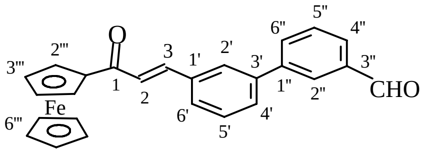
Experimental

Melting point was determined with a Thomas Hoover capillary melting point apparatus, the thermometer was uncorrected. IR spectra was recorded on a FT-170 SX spectrometer as KBr pellets. ^{1}H NMR, ^{13}C NMR were measured on a Bruker AM-400 FT-NMR spectrometer in $CDCl_3$. Elemental analysis was performed on a Carlo Erba 1106 instrument. Naphylthylboronic acid[3], 3-formyl phenylboronic acid[4] and Pd(0)[5] were prepared according to literatures.

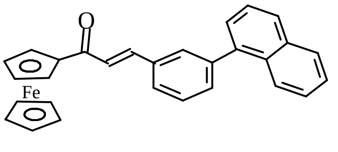
General procedure for the preparation of the title compounds

A 50 mL three-necked round-bottomed flask was charged with an aryl bromide **3** 4.2 mmol, Pd(0) [tetrakis(triphenylphosphine)palladium] 0.12 mmol (3% of the substrate in mole), benzene(20 mL) and 2 mol/L aqueous sodium carbonate solution (5 mL) under N_2 atmosphere. The mixture was stirred vigorously, aryl boronic acid **4** (4.2 mmol) was added to the mixture, subsequently. The reaction mixture was heated to reflux, stirring under N_2 atmosphere for an appropriate time. The reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, diluted with 60 mL of dichloromethane and 40 mL of water, the organic layer was separated, and washed with water and brine, dried over anhydrous magnesium sulphate. The solvents were removed under reduced pressure. The crude product was purified by column chromatography with hexane/diethyl ether=1:1 to 8:1 as eluents. The first red band was retrieved for initial chalcone, the second red-band was collected, after removing solvent in vaccum to afford pure product.

5a: Found: C 74.02%, H 4.70%, Calcd. for $C_{26}H_{20}FeO_2$: C 74.30%, H 4.80%; m.p.: 126-128°C; ^{1}H NMR($CDCl_3$, δppm): 10.14(s, 1H, CHO), 8.16(s, 1H, $H_{2''}$), 7.93(d, 2H, J=7.28Hz, $H_{4''}$, $H_{6''}$), 7.88(d, 1H, J=15.64Hz, H_3), 7.87(s, 1H, $H_{2'}$), 7.66-7.71(q, 2H, J=7.52, $H_{4'}$, $H_{6'}$), 7.68(t, 1H, J=7.32Hz, $H_{5''}$), 7.56(t, 1H, J=7.52Hz, $H_{5'}$), 7.21(d, 1H, J=15.68Hz, H_2), 4.96(s, 2H, $H_{2''',5'''}$), 4.63(s, 2H, $H_{3''',4'''}$), 4.24(s, 5H, $H_{6'''}$); ^{13}C NMR($CDCl_3$, δppm): 192.7, 192.1, 141.5, 140.5, 140.3, 136.9, 135.9, 133.0, 129.6, 129.5, 129.1, 128.8, 128.0, 127.6, 127.0, 123.6, 80.42, 72.83, 70.08, 69.75; IR(KBr pellets, cm^{-1}): 1728, 1653, 1587, 1385, 1071, 979, 822, 741, 699, 480.



5a



5b

5b: Found: C 78.36%, H 4.89%, Calcd. for $C_{29}H_{22}FeO$: C 78.74%, H 5.01%; m.p.: 165--167°C; ^{1}H NMR($CDCl_3$, δppm): 7.90(d, 1H, J=16.06Hz, H_3), 7.79(s, 1H, $H_{2'}$), 7.45-7.96(m, 10H), 7.17(d, 1H, J=16.18Hz, H_2), 4.91(s, 2H, $H_{2''',5'''}$), 4.59(s, 2H,

$H_{3''',4'''}$), 4.22(s, 5H, $H_{6'''}$); ^{13}C NMR($CDCl_3$, δppm): 192.8, 141.5, 140.6, 139.4, 135.2, 131.5-133.8, 131.8, 129.4, 128.9, 127.4, 126.9-128.4, 125.4-126.3, 123.3, 80.73, 72.77, 70.08, 69.72; IR(KBr pellets, cm^{-1}): 1654, 1589, 1030, 977, 733, 685, 492.

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