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# SYNTHESIS OF SUBSTITUTED DIARYLMETHYLIDENEFLUORENES

**O.Venkata Subba Raju*, Y.V.Ramireddy**
Department of Chemistry, S. V. University, Tirupathi - 571 502, Andhra Pradesh, India.
Email: subbarajusvu@gmail.com

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**Abstract:** A convenient synthesis of substituted diarylmethylidenefluorene derivatives using Suzuku reaction.

**Keywords:** Diarylmethylidenefluorene, Suzukireaction, arylboronic acid.

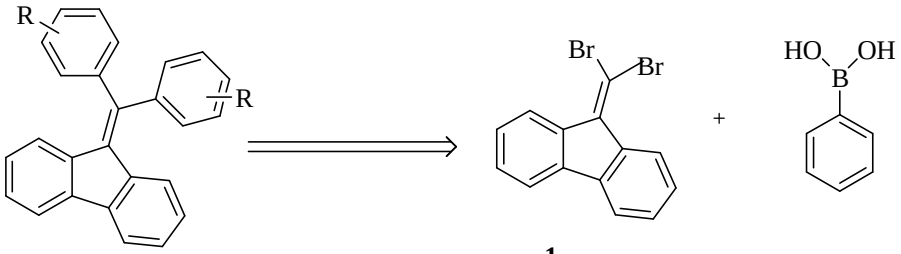
## Introduction:

There is a great current interest in the chemistry of fluorenes and its polymers as electroluminescent compositions,[1] and the alkylidene fluorine liquid crystalline semiconducting polymers[2] as organic field effect transistor devices. Diarylmethylidenefluorenes in general and the dications[3] or radical anions[4] derived from them in particular are subject of extensive physical studies related to antiaromaticity or electron spin distribution-conformation evaluated by means of either *magnetic* criteria focusing on the consequences of the existence of a ring current or ESR and ENDOR spectra. While there appears to be a great deal of discussion about the derived transient intermediates by theoretical and experimental calculations, however a little has been focused on the synthesis of these diarylmethylidenefluorene derivatives.

Substituted diarylmethylidenefluorene derivatives are in general synthesized by addition of fluorenylidene anions to benzophenone and subsequent dehydration[4,5] and very recently using Peterson olefination.[3] There are few reports where addition of diazofluorene to a thioketone,[6] Wittig olefination,[7] [2+2] addition of fluorenylidene stannene[8] to a benzophenone and subsequent [2+2] decomposition. In many of these approaches use of strong bases to generate the requisite benzylic anion and strong acids to dehydrate the intermediate alcohol limits the variation of the substituents on aromatic rings. Especially lack of a protocol compatible with base sensitive groups. Here in we

wish to report a facile synthesis of diarylmethylidenefluorenes by means of Suzuki coupling of dibromomethylidenefluorene (**2**) with arylboronic acids (**3**) (Scheme-1).

***Scheme-1***




**3** **1** **2**

**Result and Discussions**

**Synthesis of substituted Diarylmethylidenefluorenes (1a-i)**

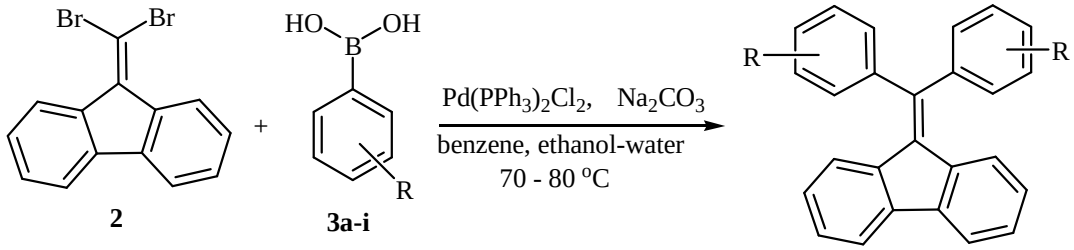
The Suzuki reaction consisting a palladium-mediated cross coupling of organoboronic acids with alkenyl or aryl halides provided a great potential tool in synthetic organic chemistry. [9] The Suzuki reaction of 1,1-dibromo-1-alkenes with alkenyl- or arylboronic acids is known and well used in the synthesis of tri- and tetrasubstituted olefins and also for the stereoselective formation of *(Z)*-1-aryl- or *(Z)*-alkenyl-1-bromo-1-alkenes.[10] Because a variety of organoboronic acid derivatives are now readily available we were inter interested to examine the feasibility of a double Suzuki reaction with the known dibromomethylidenefluorene (**2**)[11] to synthesize symmetric diarylmethylidenefluorene derivative.

Our initial attempts to optimize the reaction conditions were carried out with simple phenylboronic acid (**3a**). After a careful examination of various reaction conditions, such as reaction temperature, reaction time, base, solvent, and amount of phenylboronic acid, we concluded that the best result for the intended double-Suzuki reaction were achieved by using a suspension of benzene-ethanol-water as a solvent, $Na_2CO_3$ as a base, conducting

the reaction at 70-80 °C and addition of catalyst $Pd(PPh_3)_2Cl_2$ (7.5 mol%) and phenylboronic acid (1.5 eq) twice to the reaction mixture in 10 h interval.

Thus, the reaction of **2** with differently substituted aryl boronic acids **3b-3i** following the above conditions led to previously known and a couple of unknown diarylmethylidenefluorene derivatives **1b-1i**. In general, the reactions with electron deficient boronic acids are facile and the yields are good. For those boronic acids with an electron-donating group, the reactions are sluggish and resulted in low yields. The physical data of all the known compounds are in agreement with those of the reported data. All the new compounds are characterized by their spectral and analytical data and a single crystal *X*-ray structure for compound **1h**.[12]

***Scheme-2***




**2** **3a-i** **1a-i**

**3a** R =H
**3b** R = *p*-Me
**3c** R = *p*-Cl
**3d** R = *p*-$NMe_2$
**3e** R = m-OMe
**3f** R = *m*-$NO_2$
**3g** R = *m,p*-diOMe
**3h** R = *p*-$COCH_3$
**3i** R = *m*-$COCH_3$

**1a** R =H
**1b** R = *p*-Me
**1c** R = *p*-Cl
**1d** R = *p*-$NMe_2$
**1e** R = *m*-OMe
**1f** R = *m*-$NO_2$
**1g** R = *m,p*-diOMe
**1h** R = *p*-$COCH_3$
**1i** R = *m*-$COCH_3$

## Experimental

**General**: - Melting points were determined in a sulfuric acid-bath and are uncorrected. IR spectra were recorded in KBr on a Shimadzu 435 spectrometer, $^1$H NMR spectra on a Varian Gemini 200 MHz spectrometer with TMS as an internal standard and mass spectra on a Perkin Elmer Hitachi RDO-62 and MS-30 instrument.

**General procedure for the synthesis of of *9-(*Diphenylmethylene)-*9H*-fluorene (1a-i)**

Under argon atmosphere, a solution of dibromide **(2)** (200 mg, 0.6 mmol) in benzene (15 ml) was treated with solid $Na_2CO_3$ (157 mg, 1.5 mmol), $PdC1_2PPh_3$ (40 mg, 0.06 mmol) and boronic acid **3a** (108 mg, 0.9 mmol)

and the contents were degassed for 5 minutes. To this, ethanol (0.5 ml) and water (0.5 ml) were added and the reaction mixture was heated at 80 °C for 10 h in dark condition. The reaction mixture was cooled, catalyst (40 mg, 0.06 mmol) and boronic acid **3a** (108 mg, 0.9 mmol) were introduced and the heating at 80 °C was continued for additional 10 h. The reaction mixture was concentrated under reduced pressure and diluted with EtOAc (30 ml) and washed with water. The organic layer was separated, dried ($Na_2SO_4$), concentrated and purified by silica gel column chromatography (10% ethyl acetate in pet ether) gave **1a** (120 mg, 61%) as yellow color solid.

Mp. 215 ºC

Mol. Formula: $C_{26}H_{18}$

$^1$H NMR ($CDC1_3$, 200 MHz): δ 6.62 (d, J= 7.96 Hz, 2H), 6.92 (dt, J= 1.1, 7.96 Hz,

2H), 7.20-7.28 (m, 211), 7.35-7.44 (m, 10H), 7.69 (d, J=7.46 Hz, 2H) ppm.

$^{13}$C NMR CDC13, 50 MHz): 128.7 (d), 129.6 (d), 134.1 (s),(s), 145.4 (s) ppm. 138.6 (s),

ESI-MS (m/z) 353.61 $[M+Na]^+$.

Elemental Analysis: Calcd. C, 94.51; H, 5.49. Found: C, 94.21; H, 5.29.

**(1b-i)** were prepared from **(2b-i)** respectively.

*9-(Di p-tolylmethylene)-9H-fluorene **(33b)***

Mp: 137 °C.

$^1$H NMR: δ 2.42 (s, 6H), 6.73 (d, J= 7.95 Hz, 2H), 6.94 (dt, J= 1. 1,A 7.9 Hz, 2H), 7.17-7.27 (m, 1OH), 7.70 (d,J= 7.32 Hz, 2H)

$^{13}$C NMR ($CDC1_3$, 50 MHz): 125.0 (d), 126.4 (d), 127.6 (d), 129.8 (d), 134.0 (s), 138.4(s), 140.4 (s), 144.0 (s), 144.8 (s), 159.8 (s) ppm

ESI-MS (m/z): 359.64 $[M + Na^{]+}$

Elemental Analysis: Calcd: C, 93.81: H, 6.19. found C, 93.11: H, 6.16.

*9-(Bis (4-chlorophenyl)methylene)-9H-fluorene **(33c)***

Mol. Formula: $C_{26}H_{16}C_{12}$

Mp. 215 °C.

$^{1}$H NMR ($CDC1_3$, 200 MHz): δ 8 6.70 (d, J= 8.8 Hz, 2H), 6.97 (dt;J= 1.2, 7.9 Hz, 2H),

7.22-7.32 (m, 6H), 7.36-7.45 (m, 4H), 7.69 (d, J = 7.3, 2H) ppm.

$^{13}$C NMR ($CDC1_3$, 50 MHz: 8 119.4 (d), 124.7 (d), 126.5 (d), 131.3 (d), 134.5 (s), 135.1 (s), 138.1(s), 142.1 (s) ppm.

ESI-MS (m/z): 422.21 [M+Na].

Elemental Analysis**:** Calcd. C, 78.20; H, 4.04; Cl, 17.76. Found: C, 78.20; H, 4.04; Cl, 17.76.

*4-((4-(Dimethylamino) phenyl) (9H-fluoren-9-ylidene) methyl)- N,N-dimethylbenzenamine* ***(33d)***

Mol. Formula: $C_{30}H_{28}CN_2$

Mp**.** 235 °C.

$^{1}$H NMR ($CDC1_3$, 200 MHz) δ 8 6.70 (d, J= 8.8 Hz, 2H), 6.97 (dt;J= 1.2, 7.9 Hz, 2H),

7.22-7.32 (m, 6H), 7.36-7.45 (m, 4H), 7.69 (d, J = 7.3, 2H) ppm.

$^{13}$C NMR ($CDC1_3$, 50 MHz8 119.4 (d), 124.7 (d), 126.5 (d), 131.3 (d), 134.5 (s), 135.1(s), 138.1

(s), 142.1 (s) ppm.

ESI-MS (m/z): 422.21 [M+Na].

Elemental Analysis: Calcd: C, 86.50; H, 4.04; N, 17.76. Found: C, 86.50, H, 4.04; N, 17.76.

*9-(Bis(3-methoxyphenyl)methylene)-9H-fluorene* ***(33e)***

Mol. Formula : $C_{28}H_{22}O_2$

Mp. 129-130 °C.

$^{1}$H NMR (CDC13, 200 MHz): δ 6 3.69 (s, 6H), 6.60 (d, J = 7.8 Hz, 2H), 6.83-6.93 (m, 8H), 7.12-7.16 (in, 2H), 7.20-7.29 (m, 2H), 7.61 (d, J =7.4 Hz, 2H) ppm.

$^{13}$C NMR CDC13, 50 MHz) 6 55.2 (q),113.8(d),114.5(d), 119.1(d), 125.0 (d), 126.4 (d), 127.6 (d), 129.8 (d), 134.0125.0 (d), 126.4 (d), 127.6 (d), 129.8 (d), 134.0

ESI-MS (in/z): 391.20 $[M+Na]^+$.

Elemental Analysis Calcd: C, 86.13; H, 5.68. Found: C, 86.03; H, 5.45.

*9-(Bis(4-nitrophenyl)methylene)-9H-fluorene* ***(33f)***

Mol. Formula: $C_{26}H_{16}N_20_4$

Mp.165-167°C.

IR ($CHC1_3$): 3072 1609, 1528, 1477, 1446, 1347, 1096, 908, 830, 784, 732 $cm^{-1}$.

$^1$H NMR ($CDC1_3$, 200 MHz):δ 6.50 (d, J = 8.05 Hz, 2H), 6.94 (t, J = 7.57 Hz, 2H),

7.30 (t, J = 7.58 Hz, 211), 7.68-7.72 (d, J = 7.45 Hz, 6H), 8.18-8.36 (m, 411) ppm.

$^{13}$C NMR ($CDC1_3$, 50 MHz): δ119.81 (d), 123.57 (d), 124.53(s), 124.64 (d), 126.9 (d),

129.0 (d), 130.3 (d), 137.3 (s), 137.9 (s), 141.1 (s), 143.3 (s), 148.8 (s) ppm.

ESI-MS (m/z):443.20 $[M+Na]^+$.

Elemental Analysis:Calcd. : C, 74.28; H, 3.84; N, 6.66. Found: C, 74.14; H, 3.64; N, 6.53.

*9-(Bis (3,4-dimethoxyphenyl)methylene)-9H-fluorene* ***(33g)***

Mol. Formula : $C_{30}H_{26}O_4$

Mp. 176 °C.

$^1$H NMR (CDC13, 200 MHz): δ 6 3.88-3.89 (m, 10H), 6.69 (q, J = 7.96 Hz, 2H),

13C NMR (CDC13, 50 MHz) δ 84-7.05 (m, 12H), 7.17 (dt, J = 1.01, 7.33 Hz, 2H) ppm.

: 6 55.8 (q), 110.3 (d), 111.0 (d), 111.4 (d), 113.5 (d), 119.0 (d), 124.6 (d), 126.1 (d), 127.1 (d), 133.3 (s), 134.1 (s),

138.8 (s), 140.0 (s), 145.4 (s), 148.7 (s), 149.2 (s) ppm.

ESI-MS (m/z): 473.67 $[M+Na]^+$.

Elemental Analysis Calcd: C, 79.98; H, 5.82. Found: C, 79.98; H, 5.82.

*1, 1'-(4,4'-((9H-Fluoren-9-ylidene)methylene)bis(4,1- phenylene))diethanone* ***(33h)***

MoL Formula: $C_{30}H_{22}O_2$

Mp. 231-233 ºC.

IR:(CHC13)3019,1682,1601,1446,1403,1360,1266,1215,1075,

958, 849 $cm^{-1}$ .

$^{1}$HNMR (CDC13, 200 MHz) : δ 2.66 (s, 611), 6.62 (d,J= 7.8 Hz, 2H), 6.93 (dt,1 1. 14,7.96 Hz, 2H), 7.27 (dt, J = 1.0, 7.4 Hz, 2H, 2H), 7.49 (br dt,J= 1.6, 8.1 Hz, 411), 7.67-7.75 (m, 2H), 8.64 (br dt, J)

Elemental Analysis: Calcd. C, 86.93; H, 5.35. Found: C. 86.73; H, 5.25.

*1,1 '-(3,3'-((9H-Fluoren-9-ylidene)methylene)bis(3,1phenylene))diethanone* ***(33i)***

Mol. Formala: $C_{30}H_{22}0_2$

Mp. 230- 231 °C.

IR ($CHCl_3$): 3019, 1682, 1601, 1446, 1403, 1360, 1266, 1215, 1075, 958, 849

$^{1}$H NMR δ 2.58 (s, 6 H), 6.55 (d, J = 7.9 Hz, 211), 6.91 (dt, J =- 1.14, 7.96 Hz, 2H), 7.22-7.30 (m, 2H), 7.51-7.62 (m, 31-1), 7.70 (d, J = 7.3 Hz, 3H), 7.95-8.06 (m, 4H) ppm.

$^{13}$C NMR: δ 26.6 (q), 119.4 (d), 124.5 (d), 126.5 (d), 128.1 (d),129.3 (d), 134.3 (d), 135.59 (s), 137.6 (s), 137.9 (s), 140.6 (s), 142.2 (s), 142.7 (s), 197.4 (s) ppm.

ESI-MS (m/z) 437.84 $[M+Na]^{+}$

Elemental Analysis Calcd: C, 86.93; H, 5.35.Found: C, 86.23; H, 5.15.

**Conclusion**

A simple method for synthesis of symmetric substituted diarylmethylidenefluorenes was reported using double Suzuki reaction. Work in the direction of stepwise coupling of different boronic acids to address the synthesis of unsymmetric derivatives is in progress.

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**Corresponding Author:**

**O.Venkata Subba Raju*,**

**Email:***subbarajusvu@gmail.com*