



Synthesis of 2, 7-bis (9-hexyl-9H-carbazol-3-yl)-9H-fluoren-9-one

A highly conjugated dye was prepared using careful organic synthetic methods. The prepared dye was purified by using various techniques. The dye can be used in dye sensitized solar cell.

POOJA SHARMA

Introduction :

An organic dye comprising carbazole unit has been synthesized. The unit has been coupled with another unit by Suzuki coupling to obtain extended conjugated system. The product obtained is purified by using various chromatographic techniques. The product can be used as dye in DSSC because of photochemical properties.

Experimental Method :

Scheme 1 : Synthesis of 3-bromo-9H-carbazole :

Carbazole (1, 0.50 g, 2.99 mmol) was dissolved in dry DMF (5 mL) in a 50 mL round-bottom flask. The solution was cooled in an ice bath, and a solution of NBS (0.59 g, 3.29 mmol) in DMF (5 mL) was added drop wise under inert atmosphere. After the addition, the mixture was allowed to warm to RT and was then stirred overnight. The reaction mixture was then poured into water (100 mL) and the resulting white precipitate was filtered. The white powder was dissolved in DCM, washed with water to remove water soluble impurities, dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude white solid was recrystallized from ethanol to yield white crystals (0.48 g, 65%).

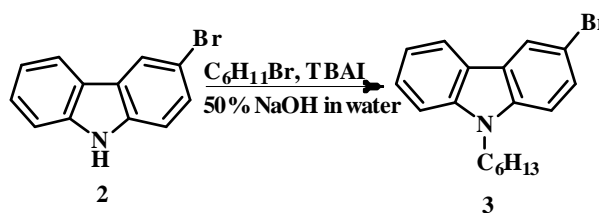


Scheme 2 : Synthesis of 3-bromo-9-hexyl-9H-carbazole:

A solution of 3-bromocarbazole (2, 0.40 g, 1.63 mmol), 1-bromohexane (0.61 g, 31.30 mmol) and TBAI

(0.30 g, 0.080 mmol) in an aqueous NaOH solution (5.0 g with 10 mL HO) was added and the reaction mixture was heated to 70 C and stirred

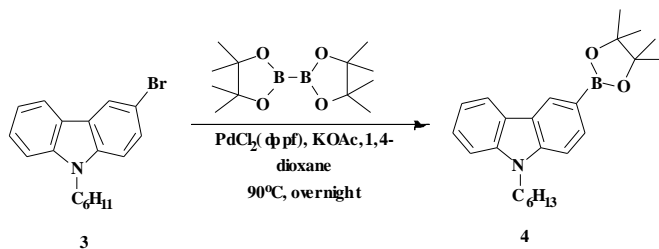
For 10h. The reaction mixture was added to a separating funnel and the water layer removed and washed with toluene (70 mL). The combined toluene layers were combined and washed with water (140 mL). It was then dried (MgSO₄) filtered and concentrated under reduced pressure. The crude brown oil was purified using a short chromatography column (silica gel) eluting with hexane to yield colorless oil (9.80 g, 96.7%).



Scheme 3 : Boronation of 3-bromo-9-hexyl-9H-Carbazole :

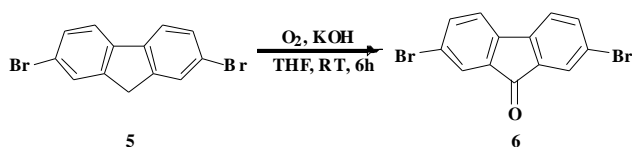
2-Bromo-9-hexyl-9H-carbazole (3, 500mg, 1.52 mmol), Bis (pinacolato) diborane (503.9 mg, 1.984 mmol), PdCl₂ (dppf) (49 mg, 0.067 mmol), KOAc (685.6 mg, 1.8 mmol) was added to round bottom flask and sparged with argon. Then 1, 4-dioxane (15 mL) was added to the mixture. The reaction mixture was stirred at 90°C for 16h. After completion of reaction, the reaction product was extracted with dichloromethane, dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. Compound was purified by column chromatography (Ethyl Acetate: Hexane, 1:9).

Assistant Professor (Department of Chemistry), Govt. College, Mahendergarh (Haryana)



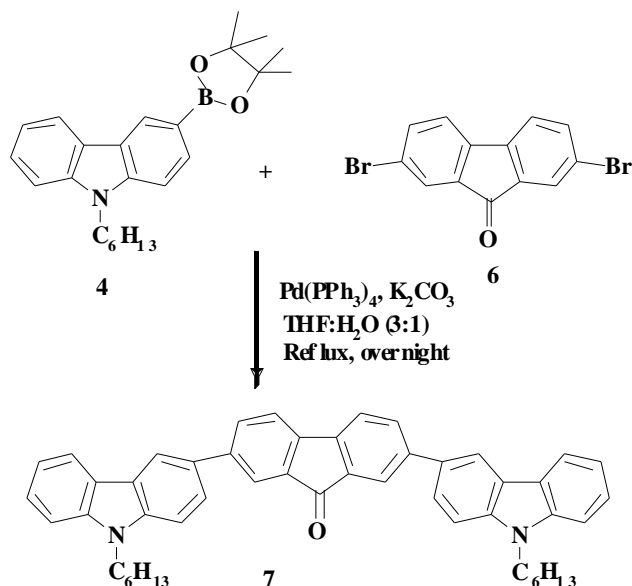
Scheme 4 : Synthesis of 2,7 Dibromo-9H-fluorene :

2, 7-dibromofluorene (800 mg 2.36 mmol) dissolved in THF (10 mL) and transfer to round bottom flask. To it, 140 mg of KOH was added. The mixture was allowed to stir overnight in presence of oxygen at room temperature. Yellow colored mixture was obtained. The solvent was evaporated and mixture was washed with water. The final product was obtained as yellow colored precipitate



Scheme 5 : Synthesis of 2, 7-bis (9-hexyl-9H-carbazol-3-yl)-9H-fluoren-9-one :

Boronic ester (4,130 mg 0.345 mmol), 2,7-dibromofluorene (58 mg, 0.167 mmol), $\text{Pd}(\text{PPh}_3)_4$ (9.92 mg, 0.0086 mmol) and K_2CO_3 was added to a round bottom flask containing 3:1 THF/water mixture. The reaction mixture was allowed to heat for 45 minutes. Then the product was extracted with ethyl acetate followed by column chromatography.



2,7-bis(9-hexyl-9H-carbazol-3-yl)-9H-fluoren-9-one

Conclusion :

A highly conjugated dye was prepared using careful organic synthetic methods. The prepared dye was purified by using various techniques. The dye can be used in dye sensitized solar cell.

References :

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