PD Research Report for the 2014 year

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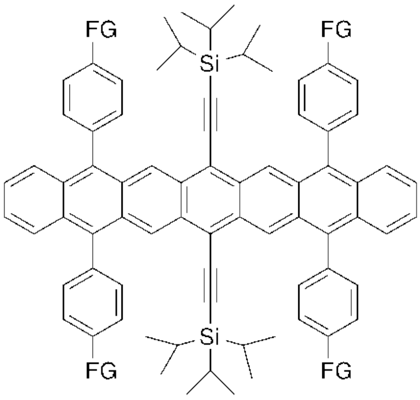
Research Theme Synthesis of functionalized heptacenes
Research Period 1st May, 2014 ～ 31st July, 2014
Research Results

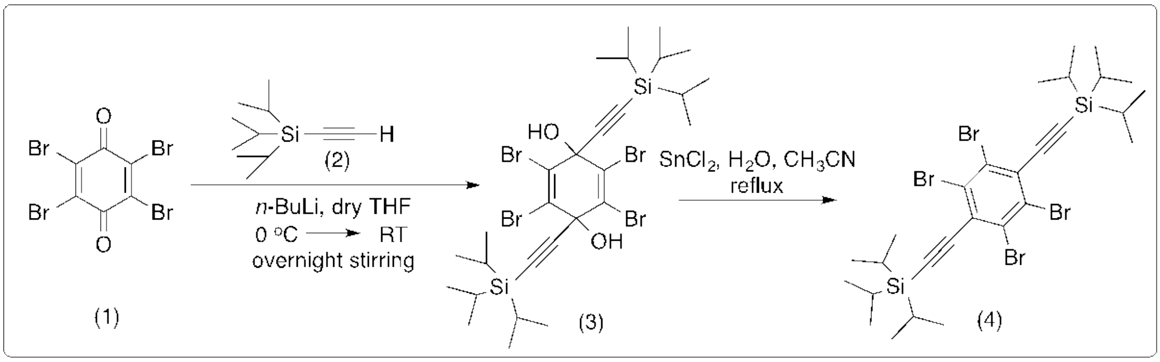
The synthesis of conjucated polyacenes has gained importance in the last few decades owing to their semiconducting nature. The strategy that we are trying to develop involves bis cycloaddition of benzyne with furan followed by successive cyclization and aromatization to give substituted heptacene molecules.

The target compound is

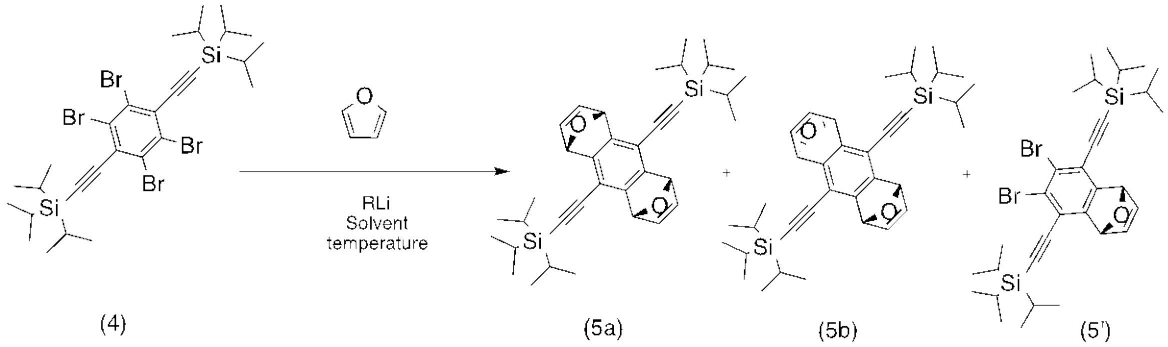


FG = functional groups

In these three months, the synthesis of the above heptacene skeleton was synthesized. At first, bromanil was converted to tetrabromo-di-(triisopropylsilylacetylene)benzene by two-stepped reaction. At first the bromoanil was reacted triisopropylsilylacetylene anion, which was subsequently aromatized to give tetrabromo-di-(triisopropylsilylacetylene)benzene. The yield of this process was 61.6%.



The next target was to convert compound (4) to bis cycloadduct by reacting it with furan. This reaction leads to generation of three types of products. One is monocycloadduct, and other two are the diasteromers of bis-cycloaddition product – syn, syn and syn-anti. The yield of diasteromers was 61 %. The reaction was optimized under different conditions as depicted below:

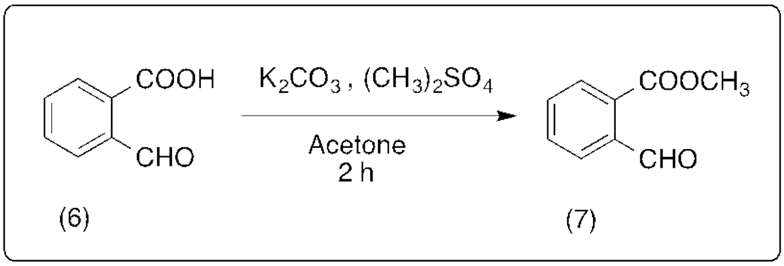


Entry	4 (in mg)	R	Solvent	temperature °C	5a (mg)	5b (mg)	5' (mg)
1	50	n-Bu	Toluene	-15 - rt	19.1 (mixture)		6.5
2	50	Ph	Toluene	-15 - rt	21.6 (mixture)		13.6
3	50	Ph	chlorobenzene	-15 - rt	18.8 (mixture)		14.5
4	50	n-Bu	Toluene	-78 - rt	7.3 (mixture)		15.5
5	500	Ph (1.2 eq.)	Toluene	-15 - rt	23.7	23.6	176

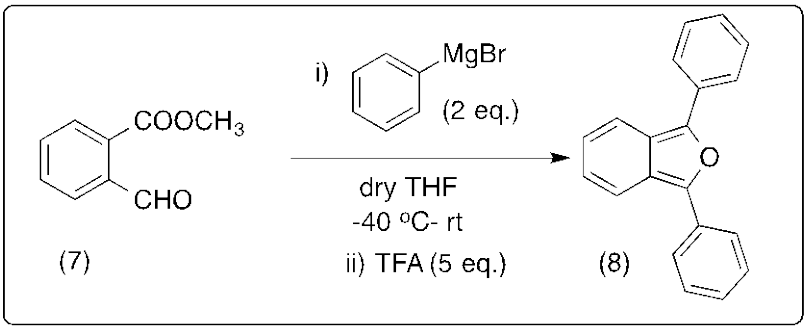
Next step was the reaction of compound 5a and 5b with isobenzofuran moieties. For this several isobenzofuran synthesis was targeted. The schemes are given below:

Preparation of 2-Formylmethylbenzoate

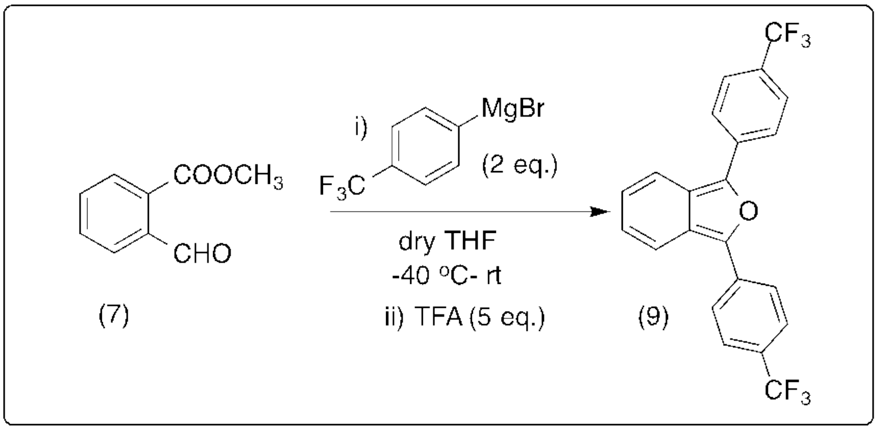
Phthalaldehydic acid (6, 5.0 g, 33.33 mmol) and potassium carbobate (6.0 g, 43.33 mmol) was taken in acetone (110 mL) under argon atmosphere. To it, dropwise dimethylsulfate was added and the reaction was stirred for 2 h at room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was finally filtered through celite bed and was concentrated in vaccuo. The pure product (7) was obtained by column chromatography in a quantitative yield using hexane and ethyl acetate (8:2) as eluent



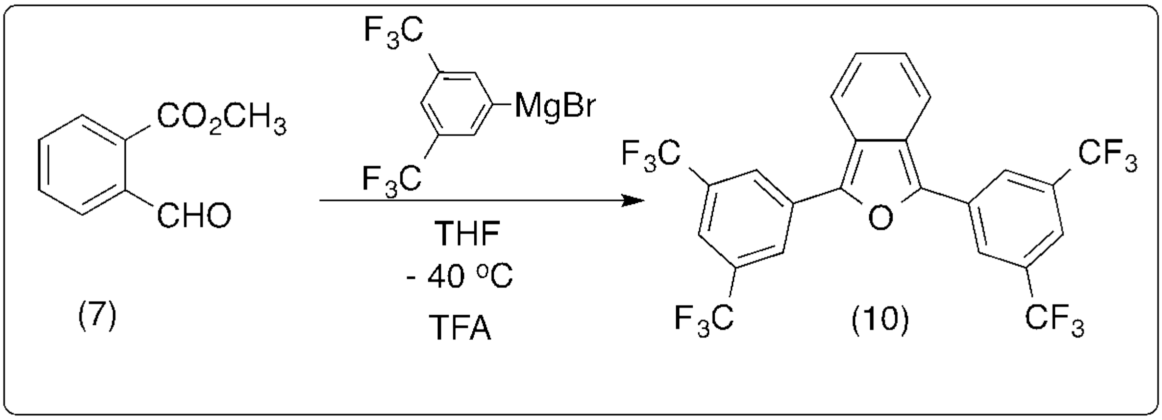
The compound (7, 3.0 g, 18.27 mmol) was dissolved in dry THF (15 mL) and was cooled to -40 °C under argon atmosphere. To this cooled solution, phenyl magnesium bromide in THF (2 eq.) was added dropwise. The reaction was allowed to stir overnight at room temperature. The reaction was cooled to 0 °C and trifluoroacetic acid (5 eq, 7 ml) was added and the solution was stirred for 30 min. The reaction was quenched by adding saturated $NaHCO_3$ solution. The compound was extracted by ethyl acetate (x3), washed with brine, dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator. The crude was subjected to column chromatography using silica gel. The desired compound eluted using hexane: dichloromethane (8:2). The isolated yield of the diphenyl isobenzofuran (8, 1.8 g).



The compound (7, 328 mg, 2.0 mmol) was dissolved in dry THF (5 mL) and was cooled to -40 °C under argon atmosphere. To this cooled solution, *p*-trifluoromethyl phenyl magnesium bromide in THF (2 eq.) was added dropwise. The reaction was allowed to stir overnight at room temperature. The reaction was cooled to 0 °C and trifluoroacetic acid (5 eq, 7 ml) was added and the solution was stirred for 30 min. The reaction was quenched by adding saturated $NaHCO_3$ solution. The compound was extracted by ethyl acetate (x3), washed with brine, dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator. The crude was subjected to column chromatography using silica gel. The desired compound eluted using hexane: dichloromethane (8:2). The isolated yield of the di-(4-trifluoromethyl phenyl) isobenzofuran (15, 25 mg).

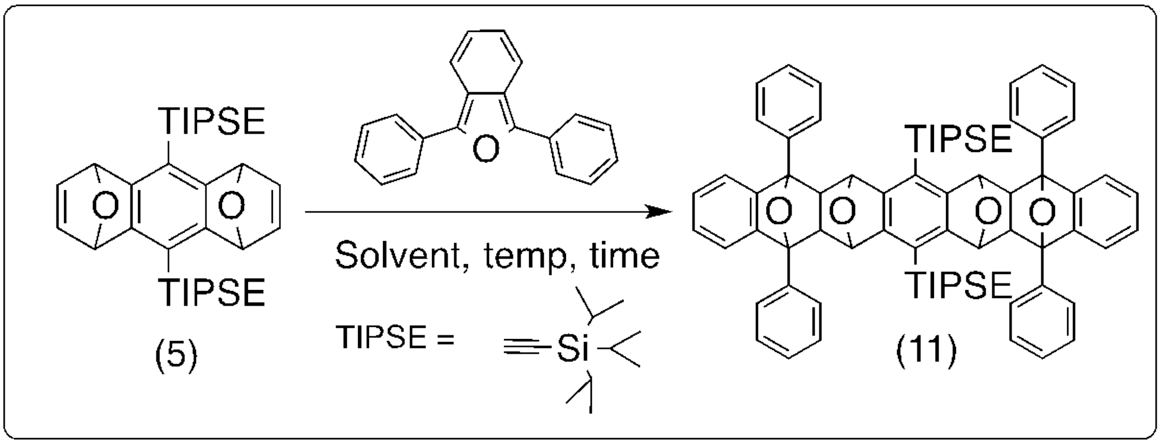


The compound (7, 1.0 g, 6.09 mmol) was dissolved in dry THF (20 mL) and was cooled to -40 ºC under argon atmosphere. To this cooled solution, 3,5-bis-trifluoromethyl phenyl magnesium bromide in THF (2.5 eq.) was added dropwise. The reaction was allowed to stir to attain room temperature. The reaction was cooled to 0 ºC and trifluoroacetic acid (5 eq, 2.32 ml) was added and the solution was stirred for 30 min. The reaction was quenched by adding saturated $NaHCO_3$ solution. The compound was extracted by ethyl acetate (x3), washed with brine, dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator. The crude was triturated using cooled hexane to give pure product. The isolated yield of the isobenzofuran (10, 3.2 g, 97 %).



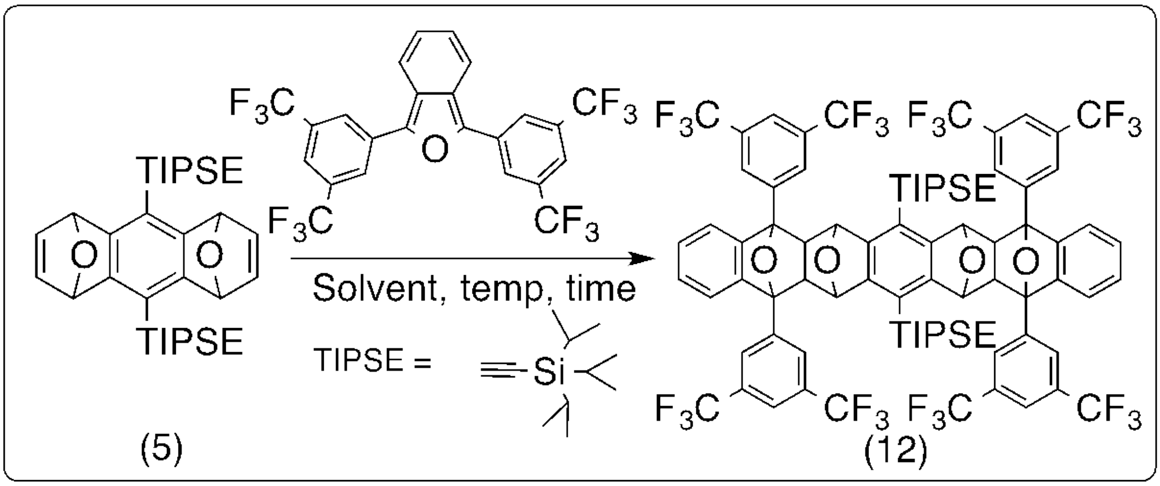
Synthesis of heptacene precursor

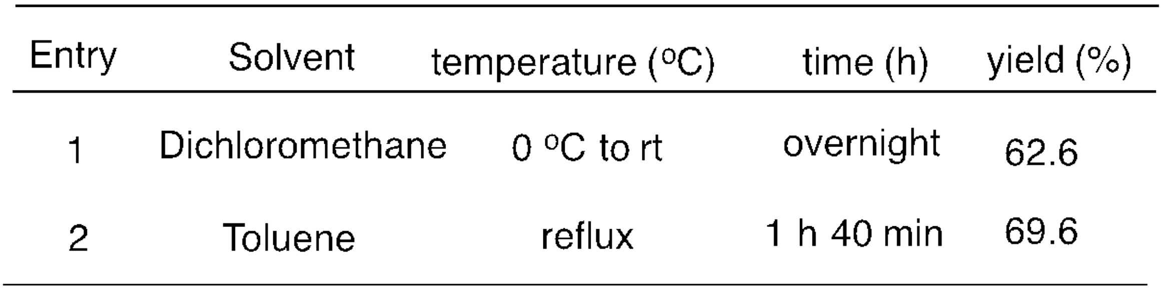
a) The compound 5 (1eq.) was taken in different solvents like toluene or super dehydrated dichloromethane (2 mL), to it isobenzofuran, 8 (2.2 eq) and was subjected to different reaction conditions as enlisted in the above table. After the reaction was complete as monitored by TLC, the solvent was removed in a rotor evaporator and the compound was purified by PTLC. The NMR confirmed the formation of diasteromers of compound 7. The isolated yields of the diasteromers are given in the table.



Entry	Solvent	temperature (°C)	time (h)	yield (%)
1	Toluene	reflux	2.5	71.8
2	Toluene	rt	2.5	68.0
3	Dichloromethane	0 °C to rt	2.5	70.0

b) The compound 5 (1eq.) was taken in different solvents like toluene or super dehydrated dichloromethane (2 mL), to it isobenzofuran, 10 (2.2 eq) and was subjected to different reaction conditions as enlisted in the above table. After the reaction was complete as monitored by TLC, the solvent was removed in a rotor evaporator and the compound was purified by PTLC. The NMR confirmed the formation of diasteromers of compound 9. The isolated yields of the diasteromers are given in the table





Entry	Solvent	temperature (°C)	time (h)	yield (%)
1	Dichloromethane	0 °C to rt	overnight	62.6
2	Toluene	reflux	1 h 40 min	69.6

The other reactions performed are shown in schemes.