Synthesis of Bicarbazole-based luminescent Discotic Liquid Crystals

Pravin Kumar

A dissertation submitted for the partial fulfilment of
BS-MS dual degree in Science

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Certificate of Examination

This is to certify that the dissertation titled **"Synthesis of Bicarbazole-based luminescent Discotic Liquid Crystals"** submitted by **Mr. Pravin Kumar** (Reg. No. MS16144) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Subhabrata Maiti Dr. Raj Kumar Roy Dr. Santanu Kumar Pal
(Supervisor)

Dated: April 25, 2021

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Santanu Kumar Pal at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Pravin Kumar

(Candidate)

Dated: April 25, 2021

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Santanu Kumar Pal

(Supervisor)

Acknowledgement

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Pravin Kumar

List of Figures

Notation

LC	Liquid Crystal
DLC	Discotic Liquid Crystal
POM	Polarized Optical Microscopy
DSC	Differential Scanning Calorimetry
XRD	X-ray Diffraction
NMR	Nuclear Magnetic Resonance
Col	Columnar
OLED	Organic Light-Emitting Diode
OFET	Organic Field-Effect Transistor
OSC	Organic Solar Cell
Col_h	Hexagonal columnar phase
Col_{hd}	Hexagonal disordered columnar phase
Col_{ho}	Hexagonal ordered columnar phase
Col_l	Lamellar columnar phase
Col_{ob}	Oblique columnar phase
Col_p	Plastic columnar phase
Colr	Rectangular columnar phase
Coltet	Tetragonal columnar phase
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
N_d	Disordered nematic

Contents

Abstract

The columnar mesophase of discotic liquid crystals (DLCs) has potentially derived and self-organizing property. The self-organized columns of DLCs are thought to be a quasi-one-dimensional molecular wire, with efficient energy and charge migration, and also used as a functional material for device applications such as photovoltaic solar cells, organic light-emitting diodes (OLEDs), one-dimensional conductors, photoconductors, organic field-effect transistors (OFETs), and gas sensors, etc. So, here we synthesized bicarbazole based luminescent discotic liquid crystal. The idea behind using bicarbazole as a central rigid core and alkyne as a side mesogenic unit is to develop a donor-acceptor system. There are several benefits to using carbazole as starting material like-it is a low-cost starting material, luminescent in nature, and exhibits unique photoelectrical properties.

The initial part of the dissertation discusses the concise introduction and classification of discotic liquid crystals. Further, the synthesis and result part has been discussed.

1 Introduction

1.1 Discotic Liquid Crystal

Liquid crystals (LCs) are one-of-a-kind of soft materials that are considered the fourth state of matter. Liquid crystals have properties that are halfway between crystalline solids and traditional liquids, i.e., properties that are direction-dependent from crystalline solids and liquid-like effects from isotropic liquids. The self-assembly of these materials into different structures is the result of many forms of interactions, like dipolar, charge transfer, quadrupolar interactions, pi-pi interactions, Vander Waals and hydrogen bonding, etc.

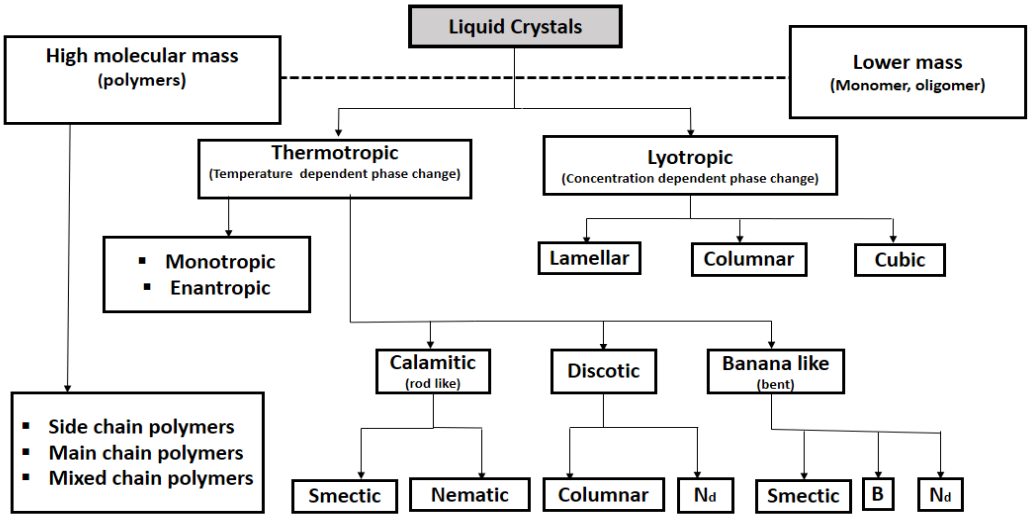


Figure 1.1 Classification of LCs

Adopted from, Kumar S.; *Chemistry of discotic liquid crystals: from monomers to polymers*, CRC Press; Boca Raton Group FL, ***2011***

The liquid crystalline materials, based on the method by which mesophase is achieved: are divided into two categories, lyotropic and thermotropic. In thermotropic liquid crystalline materials, the mesophase is achieved by heating or cooling the compound

or a mixture of compounds. Based on the shape of mesogenic units, thermotropic LCs are divided into three types: (a) rod-like LCs (calamitic LCs), (b) disc-like LCs (discotic LCs), and (c) bent-core LCs (banana LCs). [1]

Chandrasekhar et al. discovered discotic liquid crystals in 1977 when they published the mesomorphic properties of benzene-hexa-*n*-alkanoates. Generally, these materials consist of a disc-shaped central rigid aromatic core decorated by flexible alkyl chains. Here, the rigid part provides a crystalline behaviour, while the flexible part is responsible for the liquid-like behaviour of the mesophase. These discs are stacked on top of each other to form a one-dimensional column and self-assembled into nematic, columnar, or lamellar phases due to strong pi-pi interactions among central rigid cores. [1]

The discotic nematic mesophase of the lowest order, in which molecules exhibit orientational order and no comprehensive positional order. The discotic columnar phase is a highly ordered mesophase; this molecule possesses both positional and orientational orders. Both the mesophases, i.e., nematic and columnar phases, are extremely important from the device application perspective. The core-core separation in columnar structure is about 0.35 nm due to strong intracolumnar interactions. The intercolumnar distance is usually 2-6 nm and is determined by the length of lateral alkyl chains. These one-dimensional columns in DLCs are considered molecular wires, where energy and charge migrate systematically. Due to their self-organized nature, DLCs used as a functional material for device applications like photovoltaic solar cells, organic light-emitting diodes (OLEDs), one-dimensional conductors, photoconductors, organic field-effect transistors (OFETs), and gas sensors, etc. [1, 2]

1.2 Structure of Discotic mesophase

These molecules self-construct into different lattices depending upon the orientation of molecules, degree of order, and lattice symmetry of the columnar packing, etc. Based on their organization, they are classified as columnar hexagonal, rectangular, oblique, lamellar, plastic, tetragonal, and helical phases. The identification of phases can be performed by different techniques, i.e., differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). [1, 2]

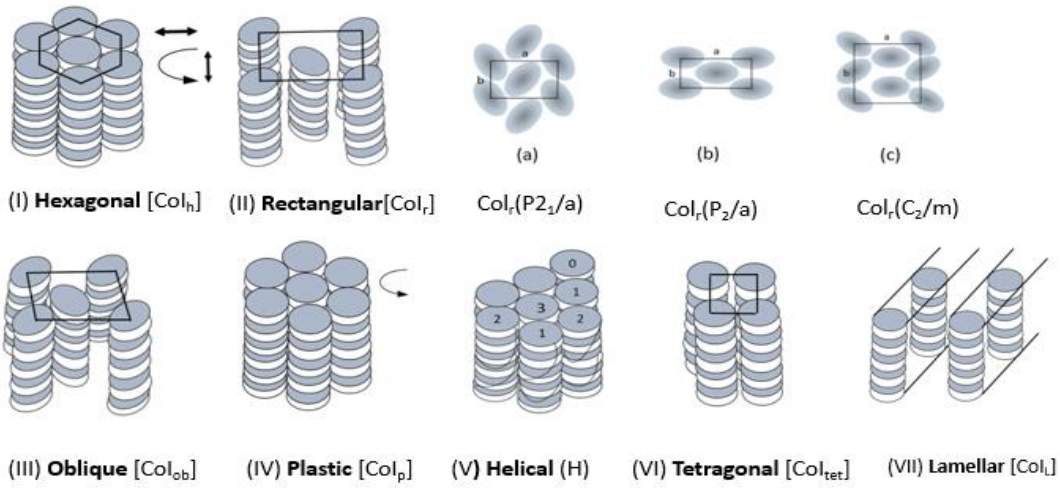


Figure 1.2 Structure of columnar mesophase

Adopted from, Kumar S.; *Chemistry of discotic liquid crystals: from monomers to polymers*, CRC Press Boca Raton Group, FL, ***2011***

1.3 Objective

The objective of our work is to synthesize bicarbazole-based luminescent discotic columnar liquid crystal for optoelectronic devices. Carbazole is a great choice for the central rigid core because of its low cost, aromaticity, easy to modify nature, and also exhibit great photoelectrical properties. Dimerization of carbazole is advantageous for thermal and morphological stability; also, the electronic and optical properties of bicarbazole derivates can be changed by chemical modification on the 9.9'-positions. These attractive features of carbazole make it excellent host material in optoelectronic devices. For the planarity of the system, an alkyne is incorporated at 9, 9'-positions of bicarbazole unit; this also helps to create a donor-acceptor system. [3, 5]

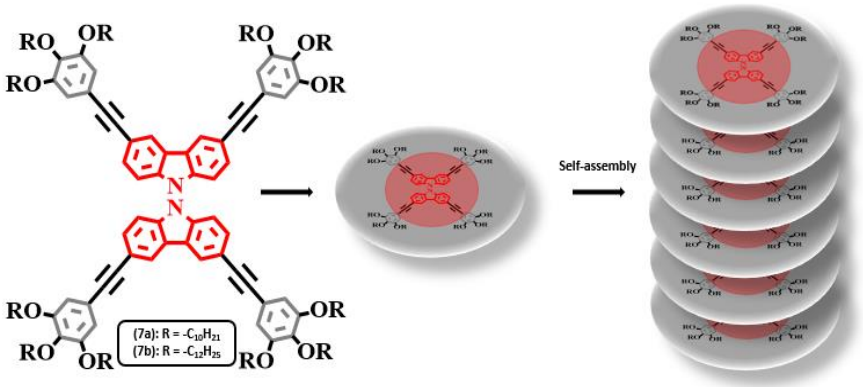
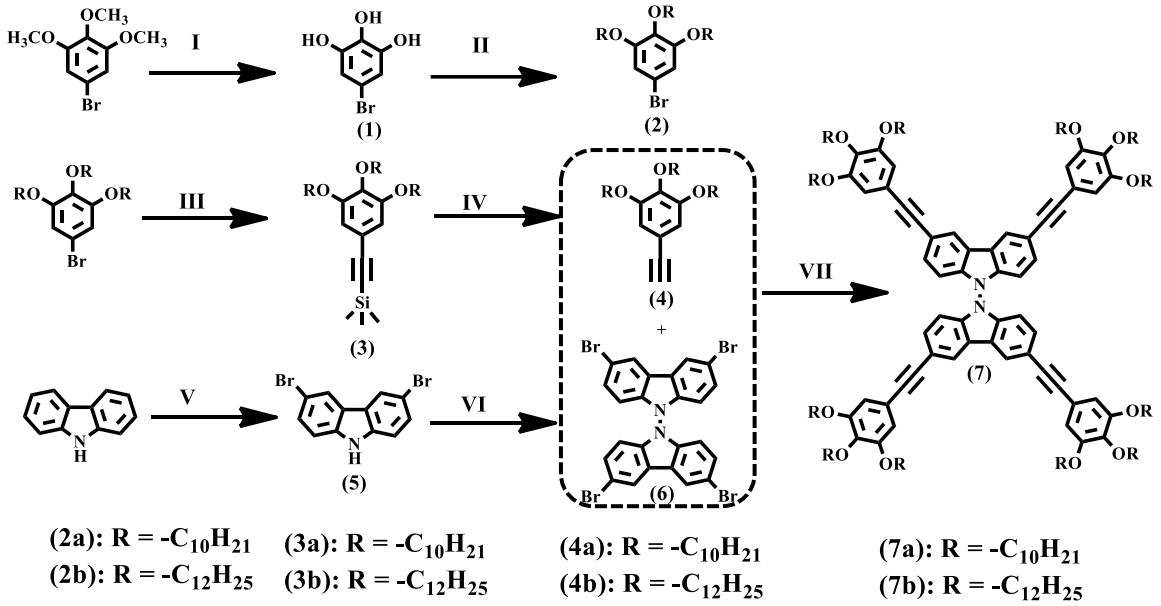


Figure 1.3 Design of bicarbazole based conjugated DLC

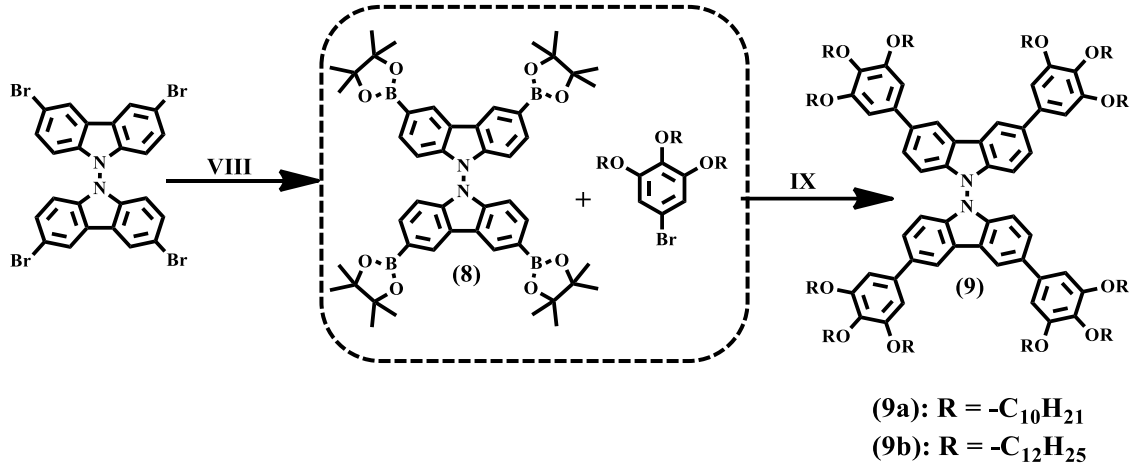
1.4 Result and Discussion

1.4.1 Synthetic scheme

Scheme 1 discusses the synthetic procedure for preparation of 3,3',6,6'-tetrakis((3,4,5-tris(dodecyloxy)phenyl)ethynyl)-9,9'-bicarbazole (7b) and (7a), in which demethylation of 5-Bromo-1,2,3-trimethoxybenzene take place with boron tribromide and further alkylation with aliphatic chain. Preparation of tetrabromobicarbazole (6) follows the bromination of carbazole in the presence of N-bromosuccinimide and further dimerizes after oxidation with KMno4. Finally sonogashira coupling between 1,2,3-tris(dodecyloxy)-5-ethynylbenzene (4b) and (4a) with 3,3',6,6'-tetrabromo-9,9'-bicarbazole gives compound (7a) and (7b). Scheme 2 discusses the synthetic procedure for preparation of 3,3',6,6'-tetrakis(3,4,5-tris(decyloxy)phenyl)-9,9'-bicarbazole (9a) and (9b), in which suzuki coupling between bicarbazole and 3,3',6,6'-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-bicarbazole take place.



Scheme 1: **(I)** BBr_3, DCM, -78 ^oC. **(II)** RBr, K_2CO_3, KI, DMF, 110 ^oC, 72h. **(III)** $Pd(PPh_3)_2Cl_2$, PPh_3 Et_3N, CuI, TMSA, 70 ^oC, 48h. **(IV)** K_2CO_3, Methanol, THF R.T. **(V)** NBS, DCM, DMF, R.T, 12h. **(VI)** $KMnO_4$, Acetone, 50 ^oC, 8h **(VII)** $Pd(PPh_3)_4$, CuI, DMF, Et_3N, 110 ^oC, 72h.



Scheme 2: **(VIII)** $PdCl_2$(dppf), 1,4-Dioxane, KOAc, Bis(pinacolato)diboron, 80 ^oC, 72h. **(IX)** $Pd(PPh_3)_4$, CuI, 1,4-Dioxane, H_2O, K_2CO_3, 100 ^oC, 48h.

1.5 Experimental procedure

1.5.1 Synthesis of 5-bromobenzene-1,2,3-triol

In a 100 ml single-neck RBF, 5-Bromo-1,2,3-trimethoxybenzene (4 g, 16.187 mmol) and dry dichloromethane (30 ml) were added and stirred at -78 ℃ for several minutes, then BBr_3 (5.4 ml) was added slowly by using a needle. The RBF was kept to stir overnight at R.T. A sufficient amount of ice and water were used to quench the reaction. Extraction of the reaction mixture was done with ethyl acetate. The ethyl acetate layer was collected by passing through anhydrous Na_2SO_4 and evaporated in *vacuo*. The solid compound was recrystallized with hexane/ethyl acetate and dried using a high vacuum pump to get a white-brown solid (3.8 g, yield = 95 %). [4]

1.5.2 Synthesis of (2a) 5-bromo-1,2,3-tris(decyloxy)benzene, and (2b) 5-bromo-1,2,3-tris(dodecyloxy)benzene

(2a) In a 100 ml double-neck RBF, dry N, N-dimethylformamide (40 ml) was added using a needle and purged with N_2 gas for 15 minutes. After that, compound (1) (1 g, 4.878 mmol), K_2CO_3 (5.83 g, 39.024 mmol), and 1-bromodecane (6.43 ml, 29.267 mmol) were added, followed by a little potassium iodide (KI). The RBF was kept to stir at 80 ℃ for two days. After cooling the reaction mixture up to R.T., it was extracted with diethyl ether. The diethylether layer was passed through anhydrous Na_2SO_4, collected, and evaporated in *vacuo*. Purification of the solid mixture was done by column chromatography using silica

gel and hexane: ethyl acetate (100: 1, v/v) used for eluting the column to get white solid compound (0.92 g, yield = 92 %). [4]

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.67 (s, 2H), 3.96-3.91 (m, 6H), 1.82-1.72 (m, 6H), 1.49-1.47 (m, 6H), 1.32-1.23 (m, 36H), 1.3-1.0 (t, 9H, J = 8 Hz).

(2b) Compound (2b) was synthesized using the same process as for compound (2a) (0.90g, yield = 90 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.67 (s, 2H), 3.96-3.941 (m, 6H), 1.82-1.72 (m, 6H), 1.49-1.45 (m, 6H), 1.32-1.23 (m, 48H), 1.3-1.0 (t, 9H, J = 8 Hz).

1.5.3 Synthesis of (3a) trimethyl((3,4,5tris(decyloxy)phenyl)ethynyl)silane, and (3b) trimethyl((3,4,5tris(dodecyloxy)phenyl)ethynyl)silane

(3a) An empty 100 ml double-neck RBF was purged with N_2 atmosphere for 15 minutes, then dry trimethylamine (50 ml) was added and again purged for 20 minutes. After that, palladium catalyst bis(triphenylphosphine)palladium(ll)dichloride (47.02 mg, 0.067 mmol), triphenylphosphine (35.22 mg, 0.134 mmol) and Copper (1) iodide (CuI) (25.52 mg, 0.134 mmol) were added and further purged for another 15 minutes. At last compound (2a) (1.4 g, 2.237 mmol) and trimethylsilylacetylene (0.618ml, 4.474 mmol) were added. The RBF was kept to stir at 65 ℃ for two days. The ongoing reaction was cooled down to R.T., then HCl (15 ml, 12.5 N) and water (20 ml) were added to quench it and extracted with DCM. The DCM layer was passed through anhydrous Na_2SO_4, collected, and evaporated in rota-vapor. Purification of the solid mixture was done by alumina-packed column chromatography and hexane: ethyl acetate (100:1, v/v) used for eluting to get a white-brown compound (1.5 g). The next reaction was set up directly with this compound, without performing NMR**.** [6]

(3b) Compound (3b) was prepared by following the earlier method used for compound (3a)**.**

1.5.4 Synthesis of (4a) 1,2,3-tris(decyloxy)-5-ethynylbenzene, and (4b) 1,2,3-tris (dodecyloxy)-5-ethynylbenzene

(4a) In RBF containing trimethyl((3,4,5-tris(decyloxy)phenyl)ethynyl)silane (1.5 g, 2.405 mmol), methanol (15 ml) and tetrahydrofuran (45 ml) were added respectively. After that,

K_2CO_3 (831.29 mg, 6.014 mmol) was added and kept to stir at 65 ℃ overnight. After cooling down the reaction mixture up to R.T., it was evaporated in *vacuo.* Purification of the solid mixture was done by column chromatography packed with neutral alumina and hexane: ethyl acetate (100: 1, v/v) used for eluting the column to get white solid compound (1.2 g, yield = 86.67%). [6]

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.71 (s, 2H), 3.98-3.95 (t, 6H, *J* = 4 Hz), 3.01 (s, 1H), 1.82-1.79 (m, 6H), 1.47-1.45 (m, 6H), 1.32-1.28 (m, 36H), 0.91-0.89 (t, 9H, *J* = 4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 152.95, 139.50, 116.40, 110.64, 84.04, 75.76, 73.53, 69.12, 31.97, 31.95, 29.78, 29.76, 29.72, 29.68, 29.66, 29.40, 29.31, 26.08, 22.72, 14.14.

(4b) Compound (4b) was prepared by following the earlier method used for compound (4a), (1.2 g, yield = 85.71%).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.71(s, 2H), 3.98-3.95 (m, 6H, *J* = 4Hz), 3.01 (s, 1H), 1.82-1.79 (m, 6H), 1.47-1.45 (m, 6H), 1.32-1.28 (m, 48H), 0.91-0.89 (t, 9H, *J* = 4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): (δ in ppm) 152.95, 139.50, 116.40, 110.64, 84.04, 75.76, 73.53, 69.12, 31.95, 29.98, 29.76, 29.72, 29.69, 29.66, 29.43, 29.40, 29.31, 26.08, 22.72, 14.14.

1.5.5 Synthesis of 3, 6-dibromo-9H-carbazole (5)

In a single-neck 100 ml RBF, carbazole (1 g, 5.98 mmol) and dichloromethane (50 ml) were added to make a suspension. In another beaker N-bromosuccinimide (2.218g, 11.96 mmol) and N, N-Dimethylformamide (10 ml) were added to make a solution and slowly added to the suspension. The RBF was kept to stir overnight at RT. It was extracted with DCM. The DCM layer was passed through anhydrous Na_2SO_4, collected, and evaporated in *vacuo*. It was rinsed with DCM and dried using a high vacuum pump to get a white solid compound (0.75g, yield = 75%). [5]

^{1}H NMR (400MHz, DMSO, δ in ppm): 11.61 (NH, 1H), 8.43 (s, 2H), 7.54-7.55 (dd, 2H, *J* = 4 Hz), 7.49-7.46 (d, 2H, *J* = 12).

^{13}C NMR (100 MHz, DMSO, δ in ppm): 139.29, 129.19, 123.81, 123.76, 113.66, 111.45.

1.5.6 Synthesis of 3,3',6,6'-tetrabromo-9,9'-bicarbazole (6)

In a 100 ml single-neck RBF, acetone (50 ml) and compound **(5)** (1 g, 3.076 mmol) was added and heated up to 50 ℃, then $KMnO_4$ (2.04 g, 9.230 mmol) was added. The RBF was kept to stir at 50 ℃ for overnight. After cooling down the RBF to RT, it was extracted with DCM. The DCM layer was passed through anhydrous Na_2SO_4, collected and evaporated in *vacuo*. It was rinsed with DCM and dried using a high vacuum pump to get a white solid compound (0.6 g, yield = 60%). [5]

^{1}H NMR (400MHz, DMSO, δ in ppm): 8.68-8.67 (d, 4H, J = 4 Hz), 7.53-7.50 (dd, 4H, J = 4 Hz), 6.86-6.84 (d, 4H, J = 8 Hz).

^{13}C NMR (100 MHz, DMSO, δ in ppm): 139.23, 129.19, 123.81, 123.76, 113.66, 111.45.

1.5.7 Synthesis of (7a) 3,3',6,6'-tetrakis((3,4,5-tris(decyloxy)phenyl)ethynyl)-9,9'-bicarbazole, and (7b) 3,3',6,6'-tetrakis((3,4,5-tris(dodecyloxy)phenyl)ethynyl)-9,9'-bicarbazole

(7a) In an oven-dried 100 ml double-neck RBF, dry DMF (15 ml) and diisopropylamine (30 ml) was added and purged out vigorously with nitrogen gas for about 30 minutes. Compound 3,3',6,6'-tetrabromo-9,9'-bicarbazole (150 mg, 0.231 mmol) was added and again purged for 5 minutes. After that, $Pd(PPh_3)_4$ (21.37 mg, 0.019mmol) and CuI (4.39 mg, 0.0231 mmol) were introduced consecutively. Then the RBF was kept to stir further for 10 minutes under N_2 atmosphere. Finally, compound (4a) **(**1.056 g, 1.851 mmol) was introduced and kept to stir at 110 ℃ for 72 hours. A solution of HCl (15 ml) and distilled water (20 ml) were added to quench the ongoing reaction. It was extracted with diethyl ether. The diethyl ether layer was passed through anhydrous Na_2SO_4, collected, and concentrated in rota-vapor. Purification of the solid mixture was done by column chromatography packed with neutral alumina and hexane: ethyl acetate (100: 1, v/v) used for eluting the column to get a yellow color compound. The achieved compound was impure. [6]

(7b) Compound (7b) was prepared by following the earlier method used for compound (7a), (264 mg, yield = 35 %). [6]

^{1}H NMR (400MHz, $CDCl_3$, δ in ppm): 8.38-8.31(d, 4H), 7.58-7.56 (d, 4H), 6.93-6.88 (d, 4H), 6.81 (s, 8H), 4.05-3.99 (m, 24H), 1.85-1.83 (m, 30H), 1.53-1.49 (m, 30H), 1.38-1.32 (m, 180H), 0.92-0.88 (t, 36H, J = 8 Hz).

1.5.8 Synthesis of 3,3',6,6'-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)- 9,9'-bicarbazole (8)

In a 50 ml schlenk RBF, 3,3',6,6'-tetrabromo-9,9'-bicarbazole (300 mg, 0.46 mmol) and bis(pinacolate)diborane (950 mg , 3.703 mmol) were added and put on high vacuum for 20 minutes. After that, catalyst $Pd(dppf)Cl_2$ (53.56 mg, 0.073 mmol) and potassium acetate (550mg, 5.544 mmol) were added and again put on high vacuum for 20 minutes then 1,4-dry dioxane (15 ml) was added. The RBF was kept to stir at 110 ℃ for two days. After cooling down the ongoing reaction to R.T., it was extracted with diethylether. The ether layer was passed through anhydrous Na_2SO_4, collected and evaporated in *vacuo*. This compound was rinsed with DCM and dried using a high vacuum pump to get a light yellow compound. The final reaction is set up directly with this compound. [4]

1.5.9 Synthesis of (9a) 3,3',6,6'-tetrakis(3,4,5-tris(decyloxy)phenyl)-9,9'-bicarbazole, and (9b) 3,3',6,6'-tetrakis(3,4,5-tris(dodecyloxy)phenyl)-9,9'-bicarbazole

(9a) In an oven-dry 100 ml single-neck RBF, compound **(8)** (164 mg, 0.196 mmol), (2a) (976 mg, 1.568 mmol), $Pd(PPh_3)_4$ (41 mg, 0.0352 mmol) and K_2CO_3 (216 mg, 1.568 mmol) were added under argon atmosphere. In another 50 ml schlenk RBF, water (6 ml) and dioxane (30 ml) were introduced and degassed using liquid nitrogen and hot water three times; then, it was introduced to the mixture. The RBF was kept to stir at 100 ℃ for 48 hours. After cooling down the ongoing reaction to RT, it was extracted with diethylether and the solvent evaporated in *vacuo*. Purification was done by column chromatography packed with neutral alumina and hexane: ethyl acetate (100: 1, v/v) for eluting the column. The achieved product was impure. [4]

(9b) Compound (9b) was prepared by following the earlier method used for compound (9a).

1.6 Characterization

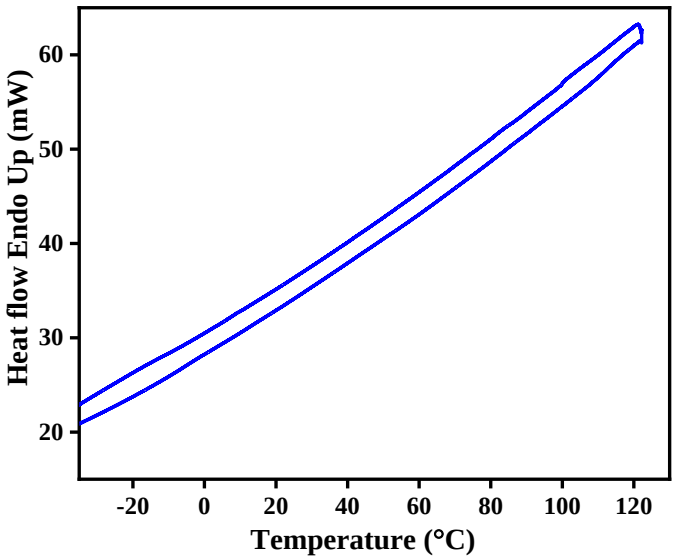


Figure 1.4 DSC thermograph of compound **(7b)**

2 Conclusions and Future work

2.1 Conclusions

Compound 3,3',6,6'-tetrakis((3,4,5-tris(dodecyloxy)phenyl)ethynyl)-9,9'-bicarbazole (7b) has been successfully synthesized, purity is confirmed by NMR. After characterization by polarized optical microscope (POM), it has been confirmed that it is liquid in nature, which is also confirmed by DSC. Compound 3,3',6,6'tetrakis((3,4,5tris(decyloxy)phenyl)ethynyl)- 9,9'-bicarbazole (7b) still in the purification process. We couldn't succeed in synthesising the compound 3,3',6,6'-tetrakis(3,4,5-tris(decyloxy)phenyl)-9,9'-bicarbazole (9a) and 3,3',6,6'-tetrakis(3,4,5-tris(decyloxy)phenyl)-9,9'-bicarbazole (9b).

2.2 Future work

In the future, we are interested in the synthesis of different derivatives of the same compound with shorter aliphatic chains (i.e., 1-bromhexane and 1-bromoctane), further interested in explaining the Electro-optical and luminescence property.

3 Appendix

3.1 Nuclear magnetic Resonance (NMR)

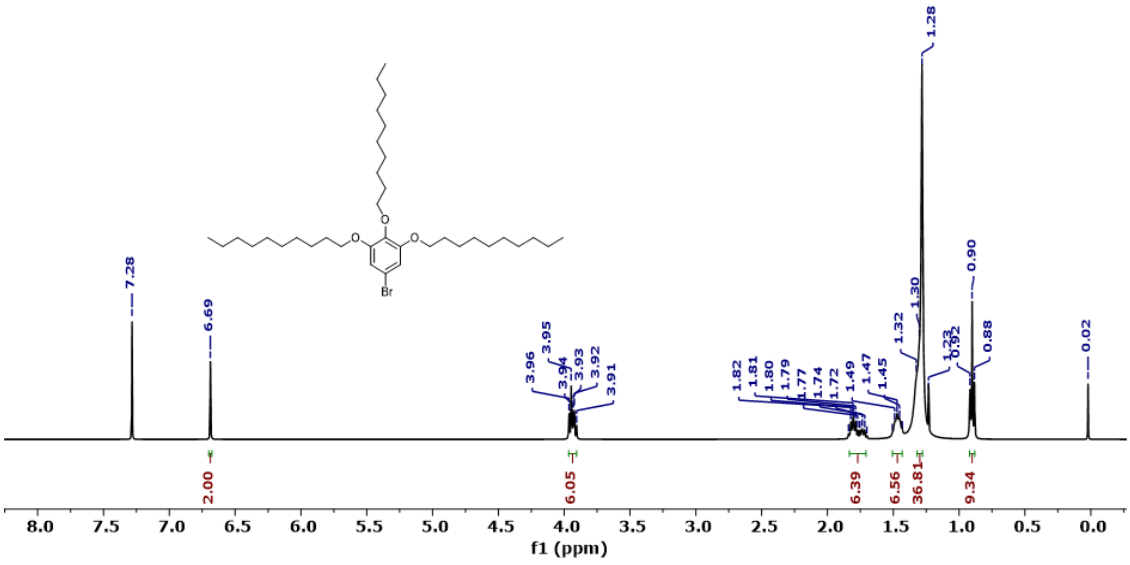


Figure 3.1 [1]H NMR spectra of 5-bromo-1,2,3-tris(decyloxy)benzene **(2a)**

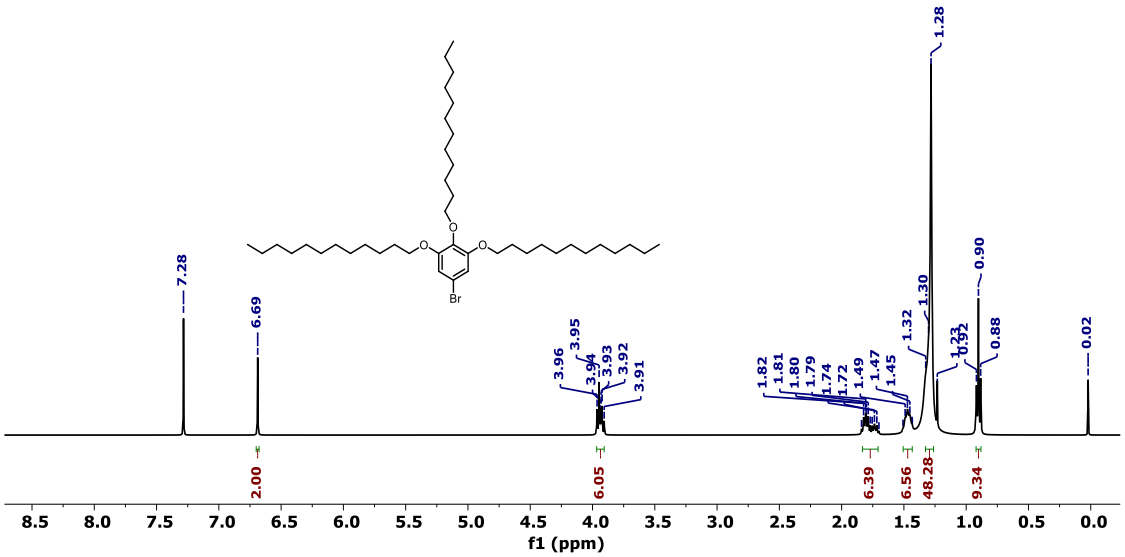


Figure 3.2 [1]H NMR spectra of 5-bromo-1,2,3-tris(dodecyloxy)benzene **(2b)**

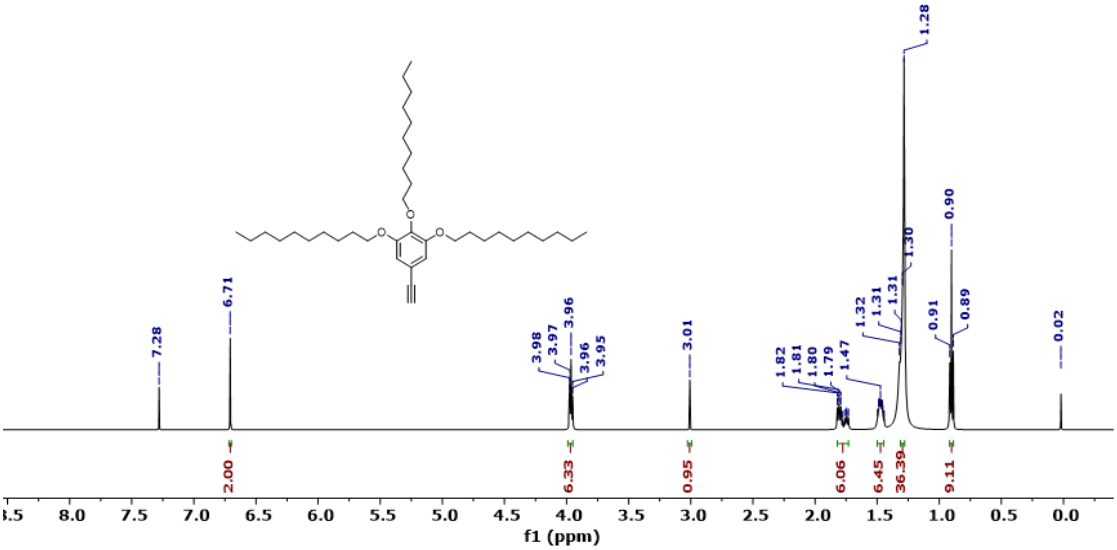


Figure 3.3 ^{1}H NMR spectra of 1,2,3-tris(decyloxy)-5-ethynylbenzene **(4a)**

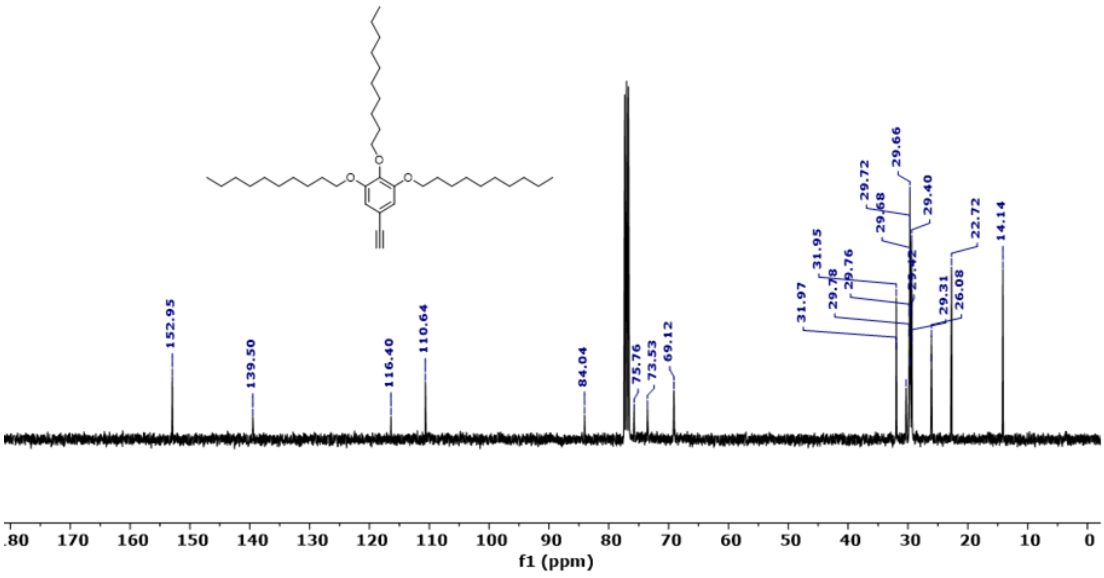


Figure 3.4 ^{13}C NMR spectra of 1,2,3-tris(decyloxy)-5-ethynylbenzene **(4a)**

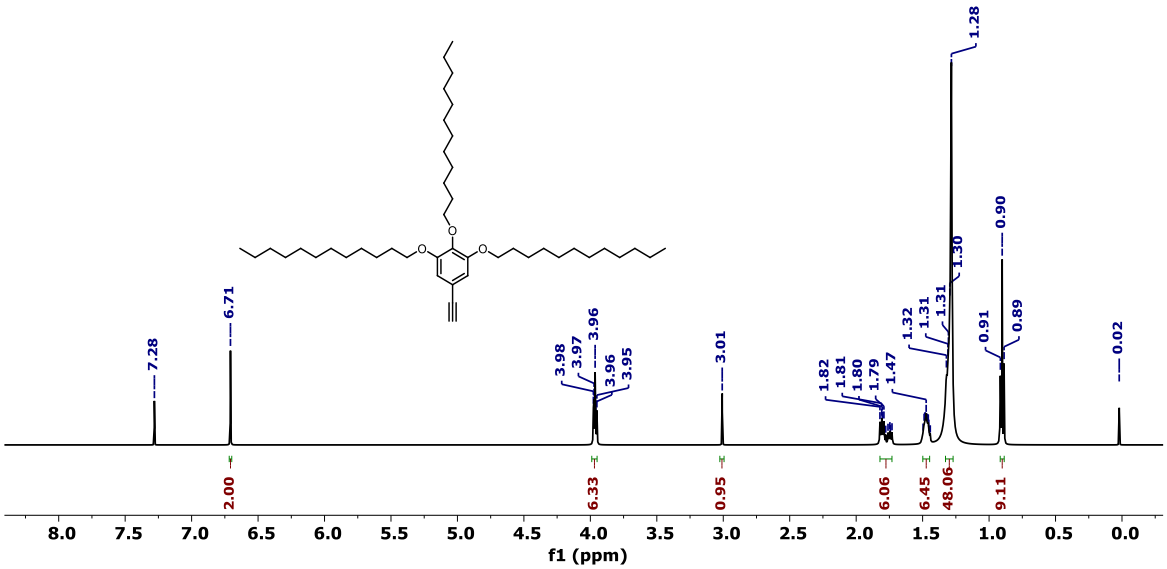


Figure 3.5 [1]HNMR spectra of 1,2,3-tris(dodecyloxy)-5-ethynylbenzene **(4b)**

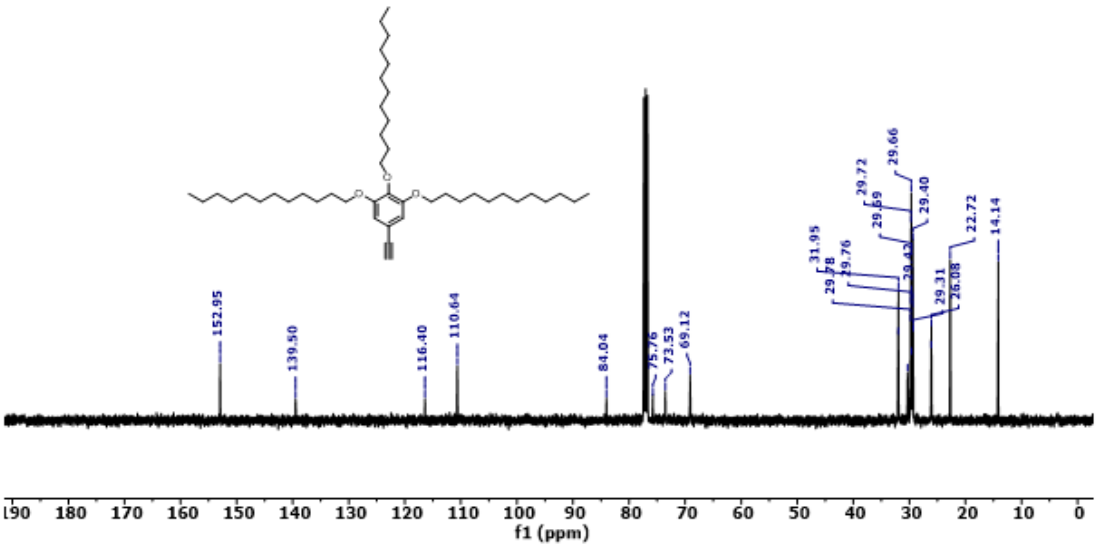


Figure 3.6 [13]C NMR spectra of 1,2,3-tris(dodecyloxy)-5-ethynylbenzene **(4b)**

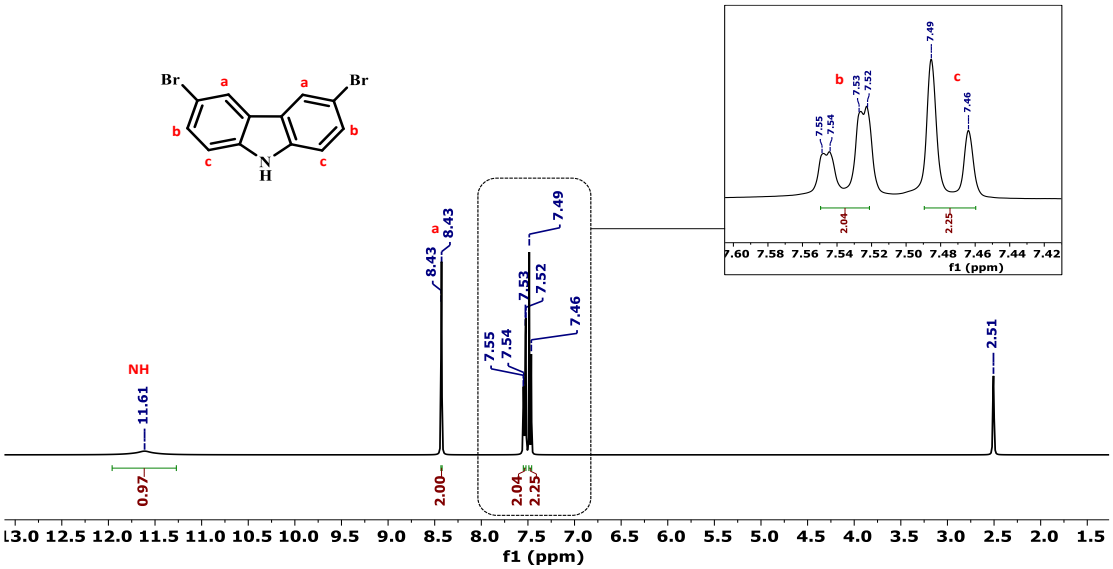


Figure 3.7 ^{1}H NMR spectra of 3,6-dibromo-9H-carbazole **(5)**

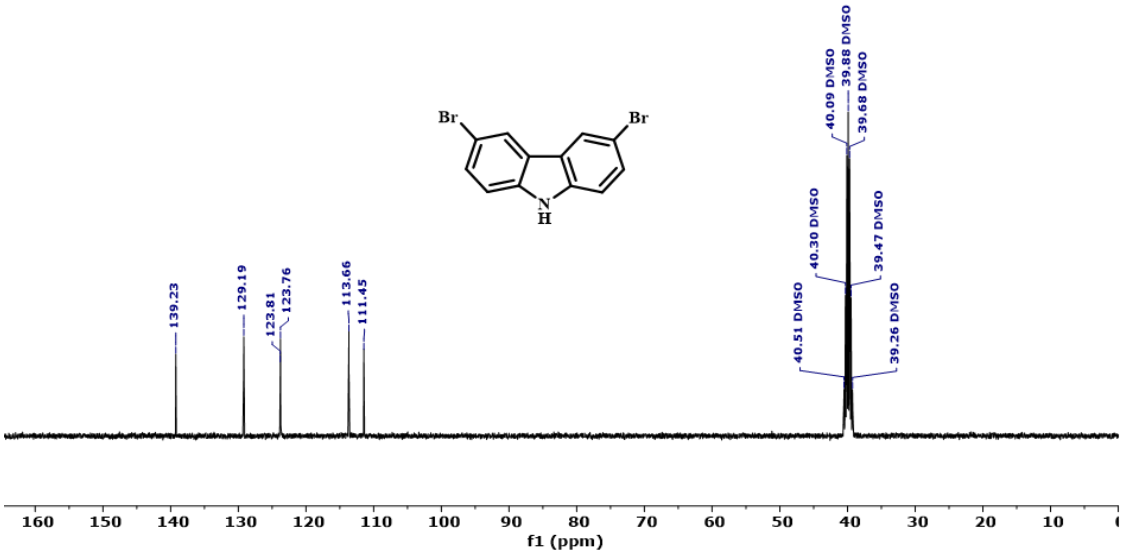


Figure 3.8 ^{13}C NMR spectra of 3,6-dibromo-9H-carbazole **(5)**

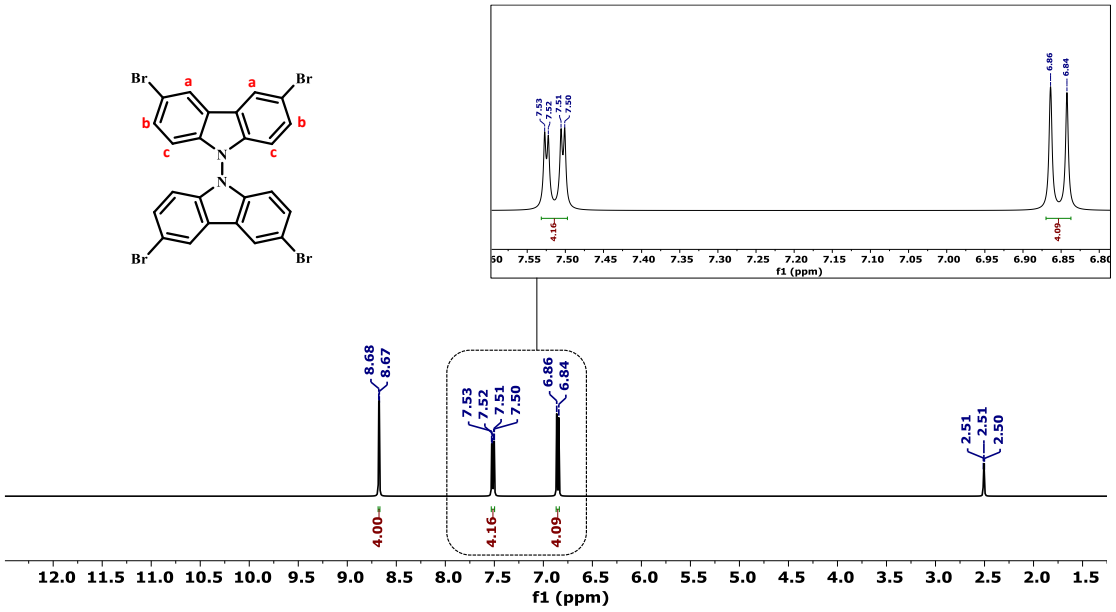


Figure 2.9 ^{1}H NMR spectra of 3,3',6,6'-tetrabromo-9,9'-bicarbazole **(6)**

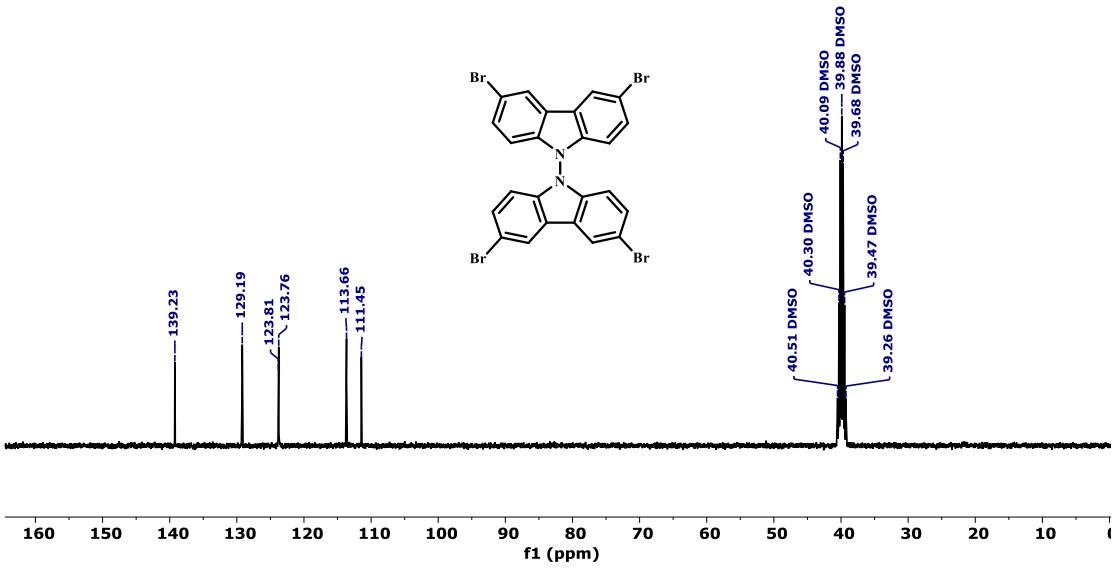


Figure 3.10 ^{13}CNMR spectra of 3,3' 6,6'-tetrabromo-9,9'-bicarbazole **(6)**

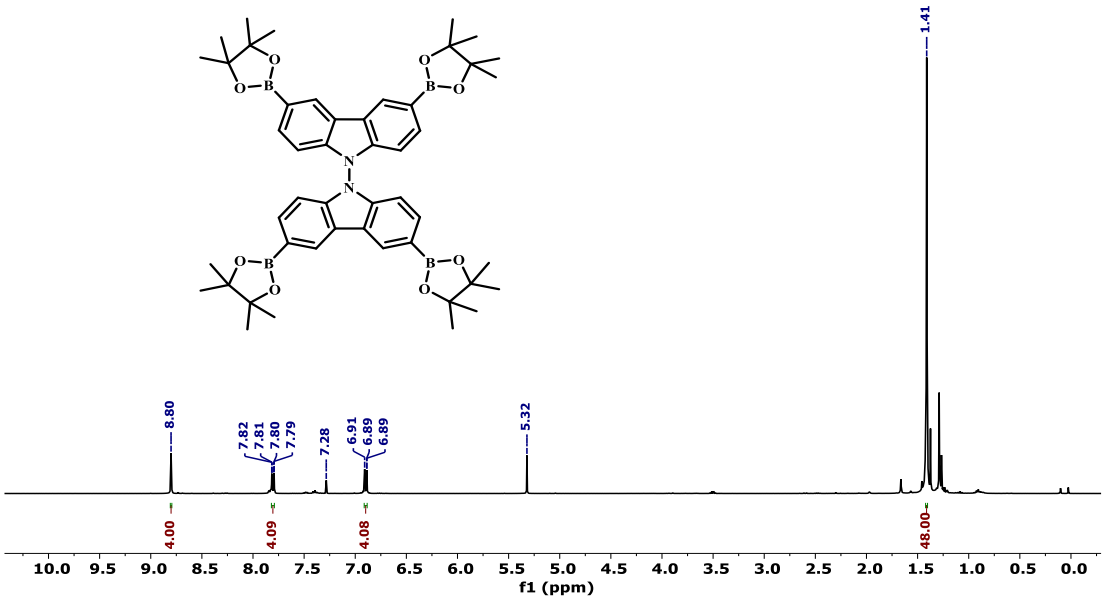


Figure 3.11 ^{1}H NMR spectra of 3,3',6,6'-tetrakis(4,4',5,5'-tetramethyl-1,2,3-dioxaborane-2-yl)-9,9'-bicarbazole **(8)**

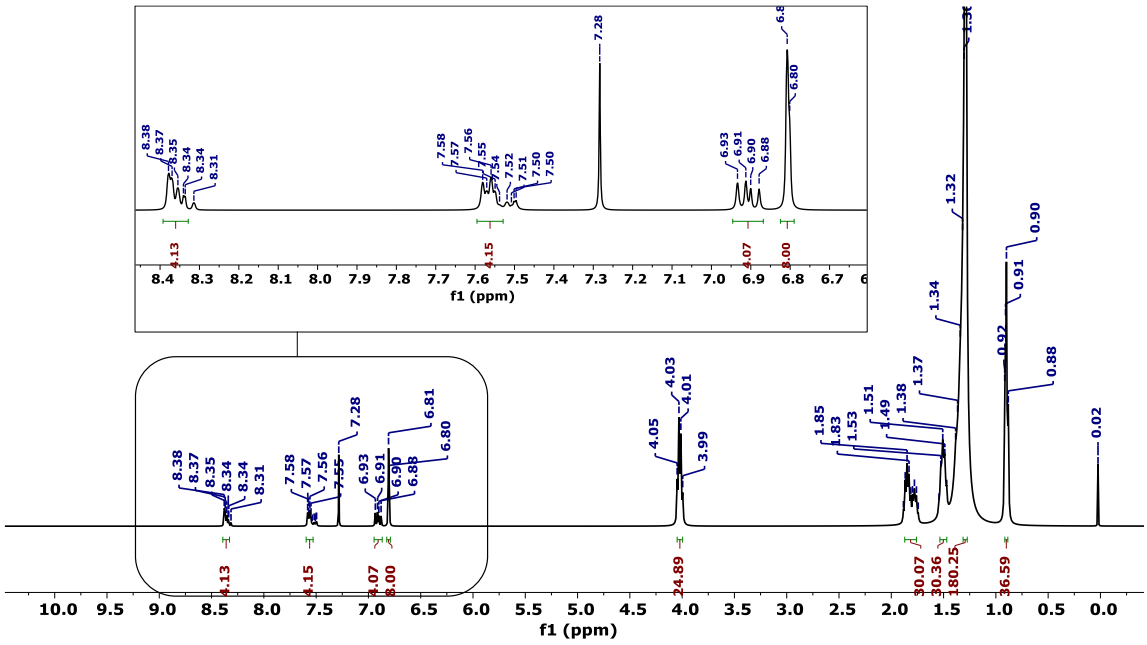


Figure 3.12 ^{1}H NMR spectra of 3,3'6,6'-tertakis((3,4,5-tris(dodecyloxy)phenyl)ethynyl)-9,9'-bicarbazole **(7b)**

Bibliography

1. Kumar, S. *Chemistry of Discotic Liquid Crystals: From Monomers to Polymers*; CRC Press: Boca Raton, FL, **2011.**

2. Collings, P. J.; Hird, M. *Introduction to Liquid Crystals Chemistry and Physics*; CRC Press, **2017**.

3. Wex, B.; Kaafarani, B. R. Perspective on Carbazole-Based Organic Compounds as Emitters and Hosts in TADF Applications. *J. Mater. Chem. C Mater. Opt. Electron. Devices* **2017**, *5* (34), 8622–8653.

4. Yasuda, T.; Shimizu, T.; Liu, F.; Ungar, G.; Kato, T. Electro-Functional Octupolar π-Conjugated Columnar Liquid Crystals. *J. Am. Chem. Soc.* **2011**, *133* (34), 13437–13444

5. Yin, C.; Lu, J.; Xu, Y.; Yun, Y.; Wang, K.; Li, J.; Jiang, L.; Sun, J.; Scully, A. D.; Huang, F.; Zhong, J.; Wang, J.; Cheng, Y.-B.; Qin, T.; Huang, W. Low-Cost N ,N ′-Bicarbazole-Based Dopant-Free Hole-Transporting Materials for Large-Area Perovskite Solar Cells. *Adv. Energy Mater.* **2018**, *8* (21), 1800538

6. Bala, I.; De, J.; Gupta, S. P.; Singh, H.; Pandey, U. K.; Pal, S. K. High Hole Mobility in Room Temperature Discotic Liquid Crystalline Tetrathienoanthracenes. *Chem. Commun. (Camb.)* **2020**, *56* (42), 5629–5632.

7. Zhao, K.-Q.; Gao, Y.; Yu, W.-H.; Hu, P.; Wang, B.-Q.; Heinrich, B.; Donnio, B. Discogens Possessing Aryl Side Groups Synthesized by Suzuki Coupling of Triphenylene Triflates and Their Self-Organization Behavior: Discogens Possessing Aryl Side Groups Synthesized by Suzuki Coupling of Triphenylene Triflates and Their Self-Organization Behavior. *European J. Org. Chem.* **2016**, *2016* (16), 2802–2814.