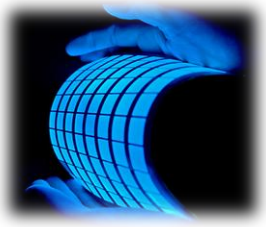
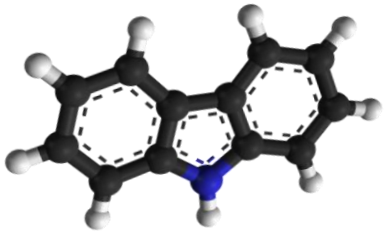
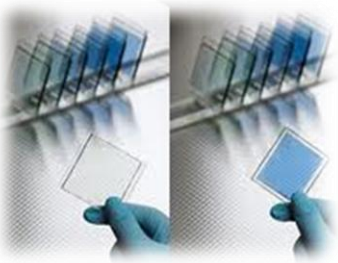
Chapter 4

SYNTHESIS OF CARBAZOLE DERIVATIVES AND THEIR APPLICATIONS

Contents

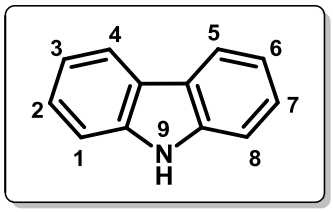






4.1 Introduction

Carbazole is a heterocyclic aromatic organic compound. It has a tricyclic structure consisting of two benzene rings fused on either side of five-membered nitrogen containing ring.[1] The structure and numbering of positions in carbazole is as shown. Carbazole unit when placed in conjugation has known to offer interesting optical and electronic properties. Carbazole has been used as a functional building block in the fabrication of many organic photoconductors, non-linear optical materials and photorefractive materials due to its strong emission, large band gap and interesting optical and electronic properties. The molecular and photo physical properties of carbazole can be tuned by structural modifications at the 2,3,6,7 and 9-H positions, which make them one of the most important classes of advanced materials being used in organic electronics. The carbazole unit is so very interesting and widely explored due to following reasons:[2] 1) 9H-carbazole is a very cheap starting material; 2) it is a fully aromatic unit providing a better chemical and environmental stability; 3) the nitrogen atom can be easily substituted with a wide variety of functional groups to help product solubility and tune the optical and electrical properties; 4) it possesses a bridged biphenyl unit resulting in materials with a lower band gap. Moreover, the carbazole unit can be substituted at the 3- and 6- positions as well as at the 2- and 7-positions to provide derivatives with different properties and potential applications.[2]



Number of carbazole derivatives have been designed and synthesized for applications in organic electronic devices such as organic light emitting diodes (OLED). They are widely used as light emitting layers in organic electronic devices due to their thermal stability and blue photo and electroluminescence due to the large band gap of the biphenyl unit.[3] Carbazole-based derivatives are known for intense luminescence and are widely used as blue, green, red and white emitters.[4] Derivatives of 3,6- or 2,7-disubstituted 9-alkylcarbazoles are widely studied as hole transporting materials for optoelectronic and electronic applications due high hole mobility in their layers, high thermal stability and good film forming properties.[5-7] Some carbazole-based materials have even been commercialized in electronic devices and processes (photocopying machines, laser printers, etc.).[8] There are many reports on the carbazole derived compounds that have been used as optical materials. Recently, Bhalla *et al* have reported a series of blue

fluorescent 3,3'-linked carbazole based conjugated molecules **1-5** with phenyl, ethynylene and ethynylphenyl spacers. They have studied their photophysical, electrochemical and thermal properties. Also they have fabricated an OLED device using compound **4** which showed bluish electroluminescence.[9]

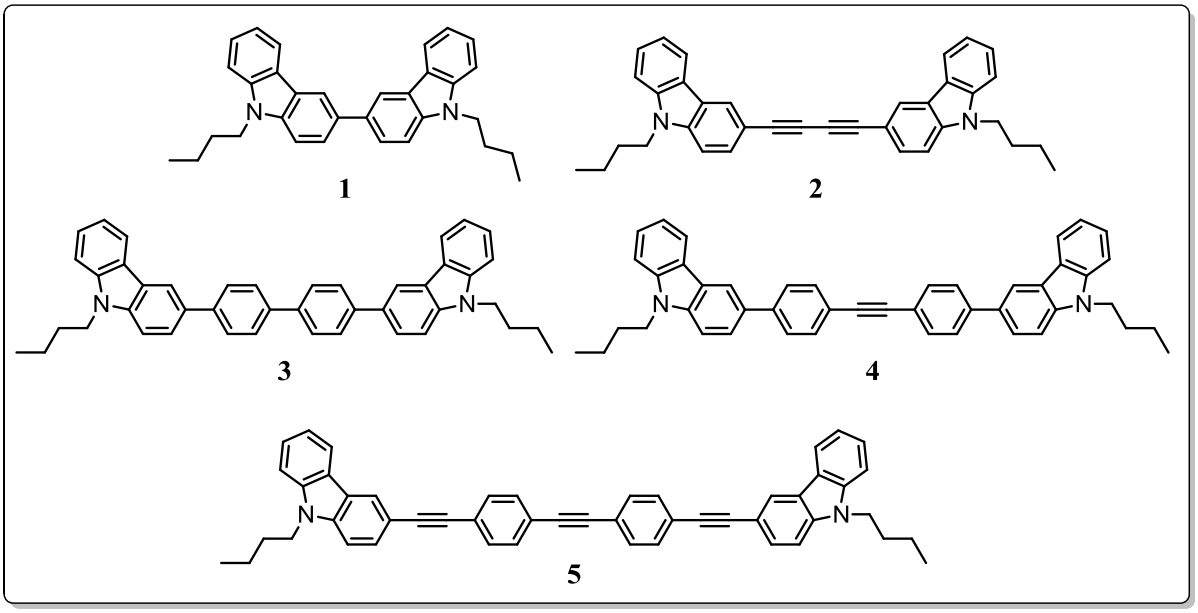
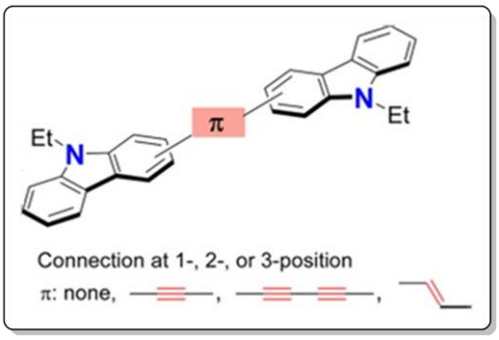


Chart 1: 3,3'-linked carbazole based conjugated molecules **1-5**

Kato *et al* have reported the synthesis of series of conjugated carbazole dimers, namely bicarbazoles where the two carbazole moieties are linked at the 1-, 2- or 3-position directly or via acetylenic or olefinic spaces. They have studied the effect of conjugation connectivity and the π-conjugated spacers on the electronic, photophysical and electrochemical properties. They have concluded that the connection at 1-position of carbazole ensures high extent of π-conjugation, while that at 3-position enhances the electron donating ability. Both acetylenic and olefinic spacers allow the extension of π-conjugation and the latter also causes the increase of the donor ability.[10]



Many N-substituted carbazole derivatives have also been reported for its distinct property and application in material chemistry. As an example Lin *et al*. have reported light-emitting carbazole derivatives as potential electroluminescent materials.[11] They have reported synthesis of stable carbazole derivatives containing peripheral diarylamines

at the 3- and 6- positions and an ethyl or aryl substituent at the 9-position of the carbazole moiety. Representative examples are as shown in **Chart 2**.

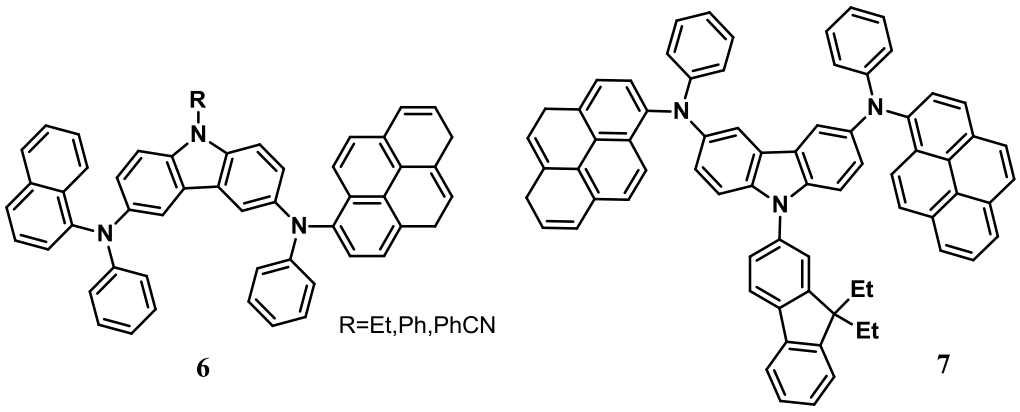


Chart 2

Another group, Jiang *et al* have reported a series of carbazole derivatives based on 9-ethyl-carbazole substituted at the 3-position with carbazole **8**, diphenylamine **9**, phenoxazine **10**, phenothiazine **11** and phenothiazine-S,S-dioxide **12** [**Chart 3**] units and a comparative study of their thermal and photoelectrical properties was done.[12] The results illustrated that the introduction of heteroatoms in to carbazole resulted in a significant change in their optoelectronic characteristics. The low LUMO, high HOMO and thermal stability of the carbazole derivatives endow them with the potential to be green, red, and even blue host materials for phosphorescent organic light-emitting diodes.

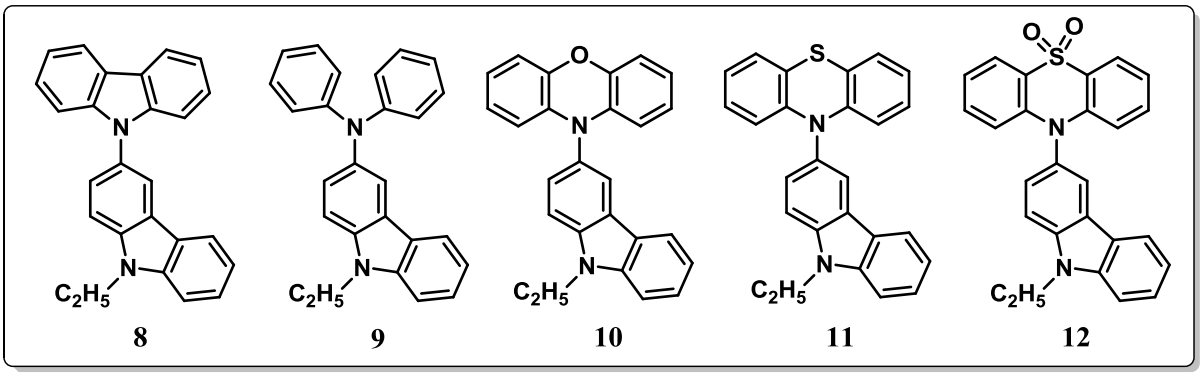


Chart 3

Apart from these materials, 3,3'-bicarbazolyl moiety is also interesting for the design and synthesis of organic semiconductors. It is a fully aromatic unit providing a high thermal, morphological, chemical and environmental stability. A wide variety of functional groups can be attached to its nitrogen atoms[13,14] as well as to 6- and 6'-positions. Materials based on 3,3'- bicarbazole units exhibit lower ionization potentials and demonstrate better hole

injection and transport properties as compared to carbazole-based materials.[15] Recently, Rasymaite *et al* have reported the synthesis of 6,6'-diaryl-9,9'-dialkyl[3,3']bicarbazoles [**13**, **14** and **15**] as electroactive materials. [**Chart 4**]

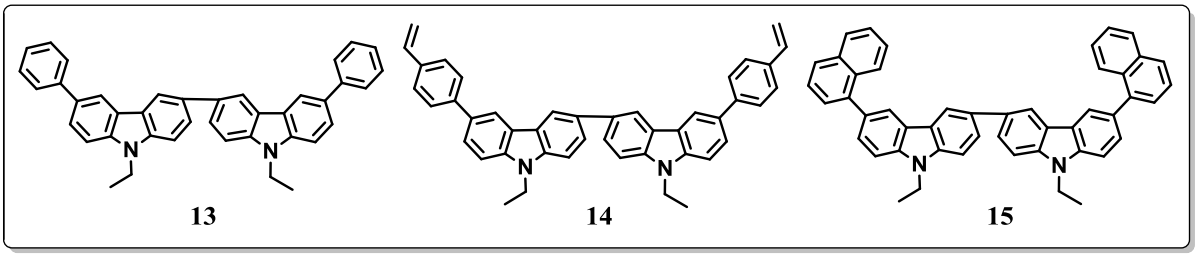


Chart 4: 6,6'-diaryl-9,9'-dialkyl[3,3']bicarbazoles [**13**, **14** and **15**]

The synthesized derivatives were studied as hole transporting materials in simple bilayer devices with Alq_3 as an emitter/electron transporting layer. The OLED with hole transporting film of 6,6'-diphenyl-9,9'-diethyl[3,3']bicarbazoles **13** exhibited the best overall performance.[16]

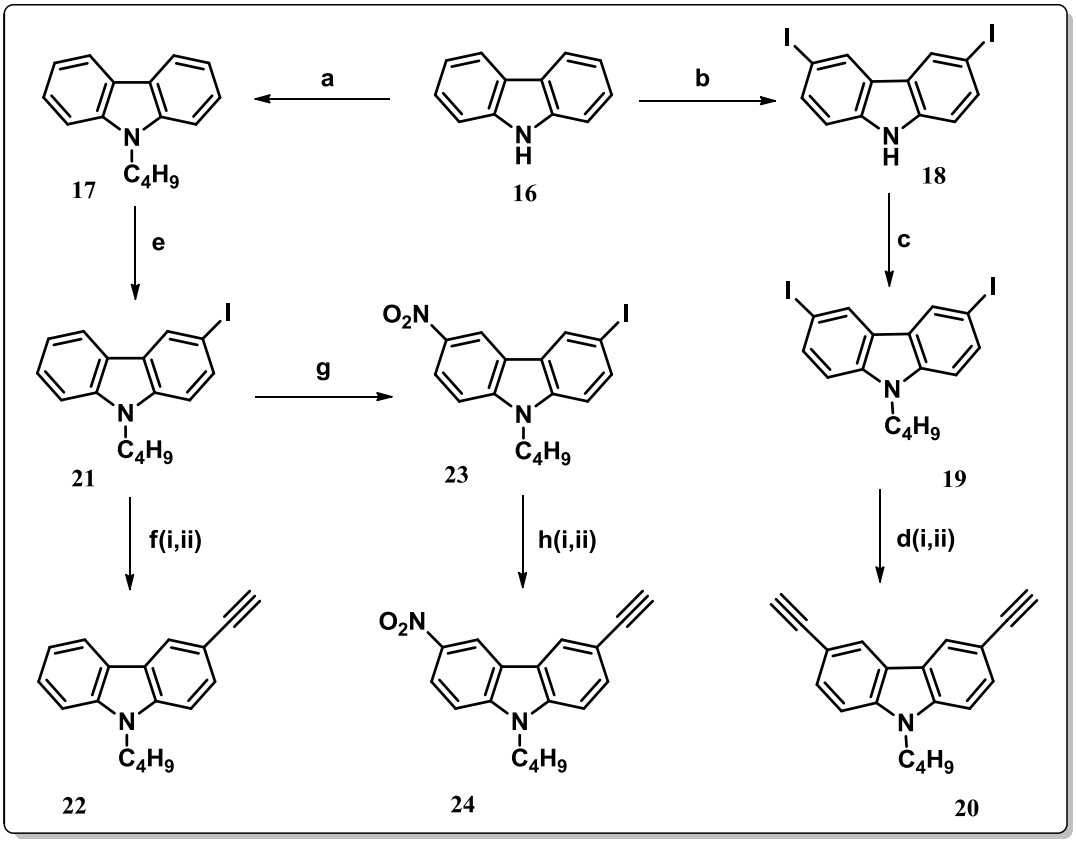
4.2 Results and Discussion

Keeping in mind the properties and importance of carbazoles in the field of material science; we have designed certain conjugated carbazole derivatives. So in this chapter we will be discussing the synthesis, characterization and study of 3,6-linked carbazole derivatives. Basically we have synthesized derivatives with alkene and alkyne spacers. Bicarbazole based molecules were also synthesized.

4.2.1 Synthesis

Firstly we synthesized different precursors for the target molecules which are presented in **Scheme 1**. As shown in the scheme the N-alkylation of commercial 9*H*-carbazole **16** was carried out with 1-bromobutane to yield N-butyl carbazole **17** in 80% yield. Carbazole **16** was also converted to 3,6-diiodo carbazole **18** by reported procedure using KI/KIO_3 in acetic acid at 80^oC. Also 3,6-diiodo carbazole **18** was alkylated using 1-bromobutane to yield 3,6-diiodo-9-butyl carbazole **19**. Likewise monoiodination of N-butyl carbazole **17** with KI/KIO_3 in aqueous MeOH in presence of HCl provided 3-iodo-9-butyl carbazole **21**, in good yield. Further compounds **19** and **21** were employed to Pd-catalysed Sonogashira reaction with TMSA to give compound **19a** and **21a** respectively which was further deprotected to remove trimethyl silane group to yield 3-ethynyl-9-butyl carbazole **20** and 3,6-diethynyl-9-butyl carbazole **22** in 62% and 92 % yield respectively. Apart from this in order to have an electron withdrawing $–NO_2$ in the carbazole system, nitration of 3-iodo-9-butyl carbazole **21** was carried out using

HNO_3/H_2SO_4 to yield 3-iodo-6-nitro-9-butyl carbazole **23** in 76% yield. Compound **23** was subjected to Pd-catalysed Sonogashira reaction with TMSA and the subsequent deprotection of trimethyl silyl group to get 3-ethynyl-6-nitro-9-butyl carbazole **24**, but in poor yield. All these precursors were used for the synthesis of different analogues of carbazole.

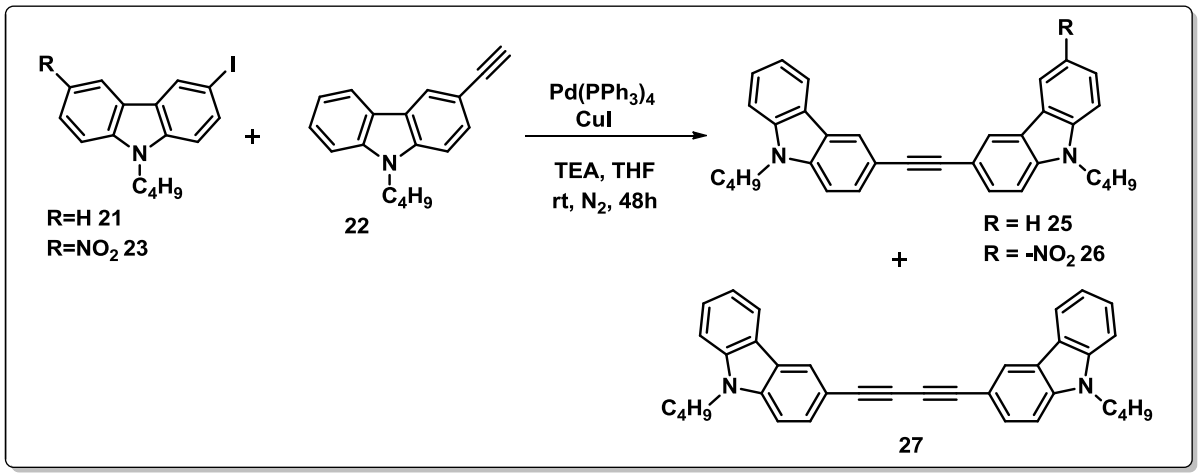


Scheme 1

Reaction conditions: (**a**) n-C_4H_9Br, KOH, Acetone, room temperature, 8h; (**b**) KI/KIO_3, AcOH, 80°C, 48h; (**c**) n-C_4H_9Br, KOH, Acetone, room temperature, 8h; (**d**) (**i**) (Trimethylsilyl)acetylene, $Pd(PPh_3)_4$, CuI, Et_3N, THF, RT, 48h; (**ii**) NaOH, EtOH, room temperature, 1h; (**e**) KI/KIO_3, HCl, MeOH-H_2O, room temperature, 3h; (**f**) (**i**) (Trimethylsilyl)acetylene, $Pd(PPh_3)_4$, CuI, Et_3N, THF, RT, 48h; (**ii**) NaOH, EtOH, room temperature, 1h; (**g**) HNO_3/H_2SO_4, AcOH, 0°C, 4h; (**h**) (**i**) (Trimethylsilyl)acetylene, $Pd(PPh_3)_4$, CuI, Et_3N, THF, RT, 48h; (**ii**) NaOH, EtOH, room temperature, 1h.

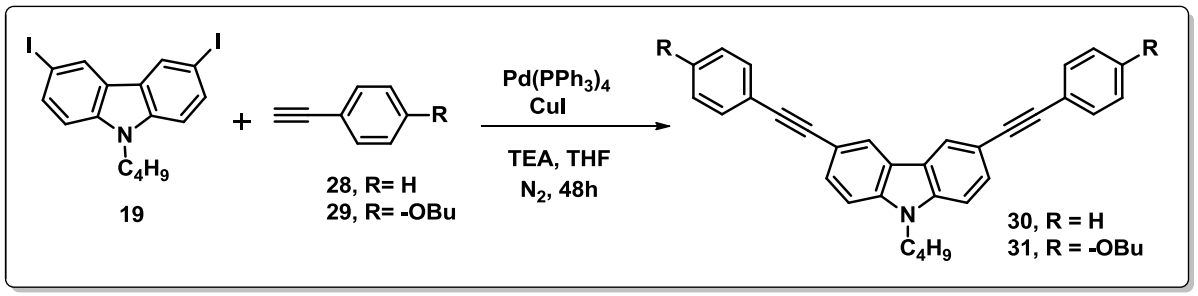
Firstly we have synthesized derivatives with ethyne spacer with varying number of carbazole units in order to increase the conjugation. So, compound **25**, i.e. 1,2-bis(9-butyl-9H-carbazol-3-yl)ethyne with two carbazole units separated by a single triple bond was synthesized by Pd-catalysed Sonogashira reaction of 3-iodo-9-butyl carbazole **21** and 3-ethynyl-9-butyl carbazole **22** as shown in **Scheme 2**. Nitro functionalized derivative **26** i.e. 9-butyl-3-((9-butyl-9H-carbazol-3-yl)ethynyl)-6-nitro-9H-carbazole was also

synthesized similarly by Sonogashira reaction of **23** and **22** in order to study the effect of electron withdrawing -NO_2 group on the system. In this reaction compound **27** was obtained as a by-product due to homocoupling of 3-ethynyl-9-butyl carbazole **22**.



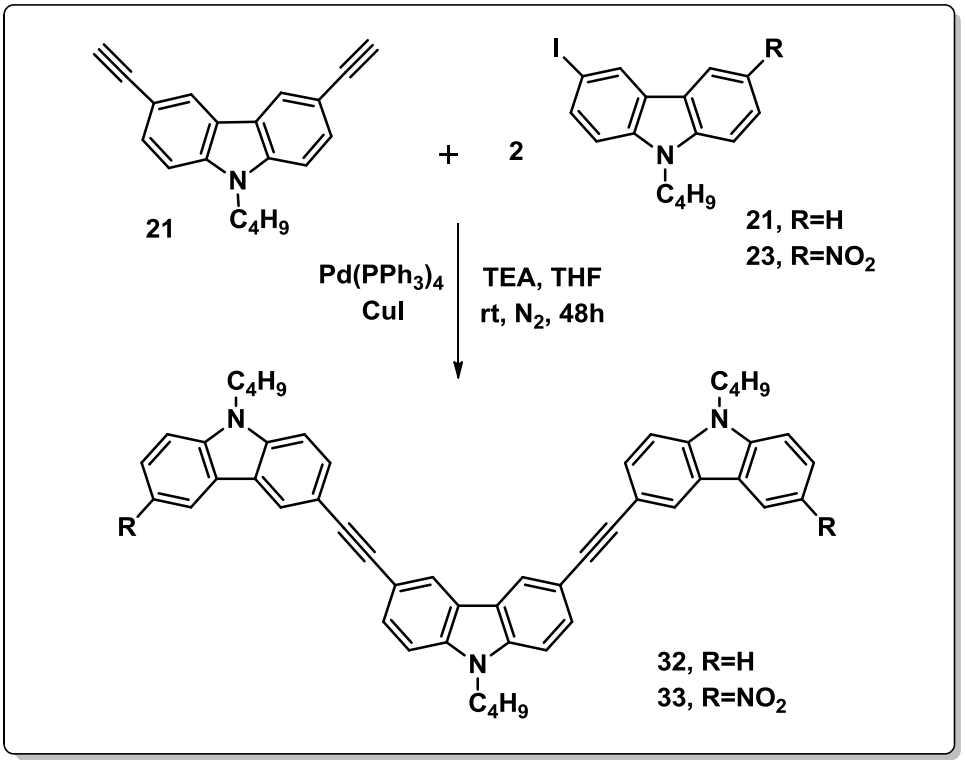
Scheme 2

Further, bis-phenyl ethynyl derivatives were synthesized with the idea to extend the conjugation. Here, 3,6-diiodo-9-butyl carbazole **19** on coupling with phenyl acetylene **28** yielded 9-butyl-3,6-bis(phenylethynyl)-9H-carbazole **30**. Also, 4-butoxy phenyl acetylene **29** was synthesized starting from 4-iodo phenol which on reaction with **19** gave 3,6-bis((4-butoxyphenyl)ethynyl)-9-butyl-9H-carbazole **31** with electron releasing butyloxy group. [**Scheme 3**]



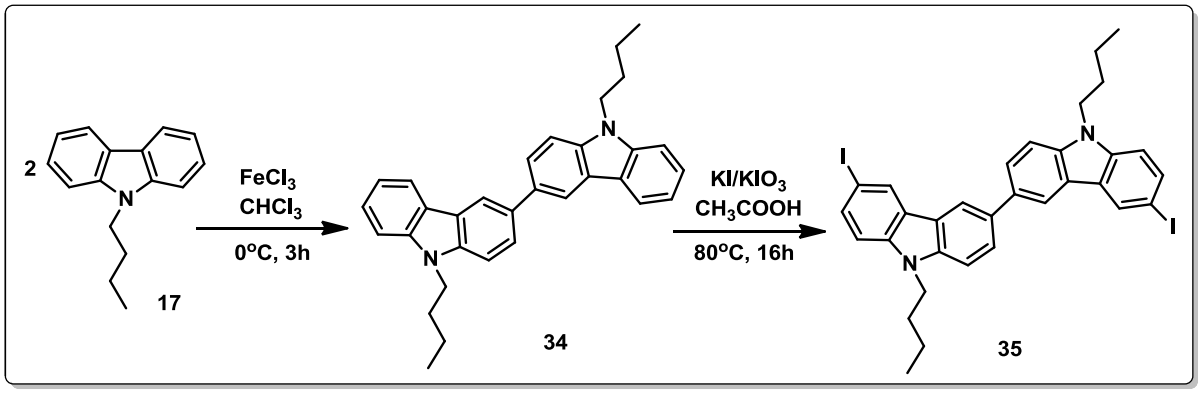
Scheme 3

Having synthesized bis-phenyl ethynyl carbazole derivatives we targeted the synthesis of compounds with three carbazole units with ethynyl spacers. Two such compounds were synthesized by coupling of 3,6-diethynyl-9-butyl carbazole **20** with 3-iodo-9-butyl carbazole **21** and 3-iodo-6-nitro-9-butyl carbazole **23** to yield compound **32** with R=H which showed blue florescence and compound **33** with R=NO_2 which showed yellow florescence. [**Scheme 4**]



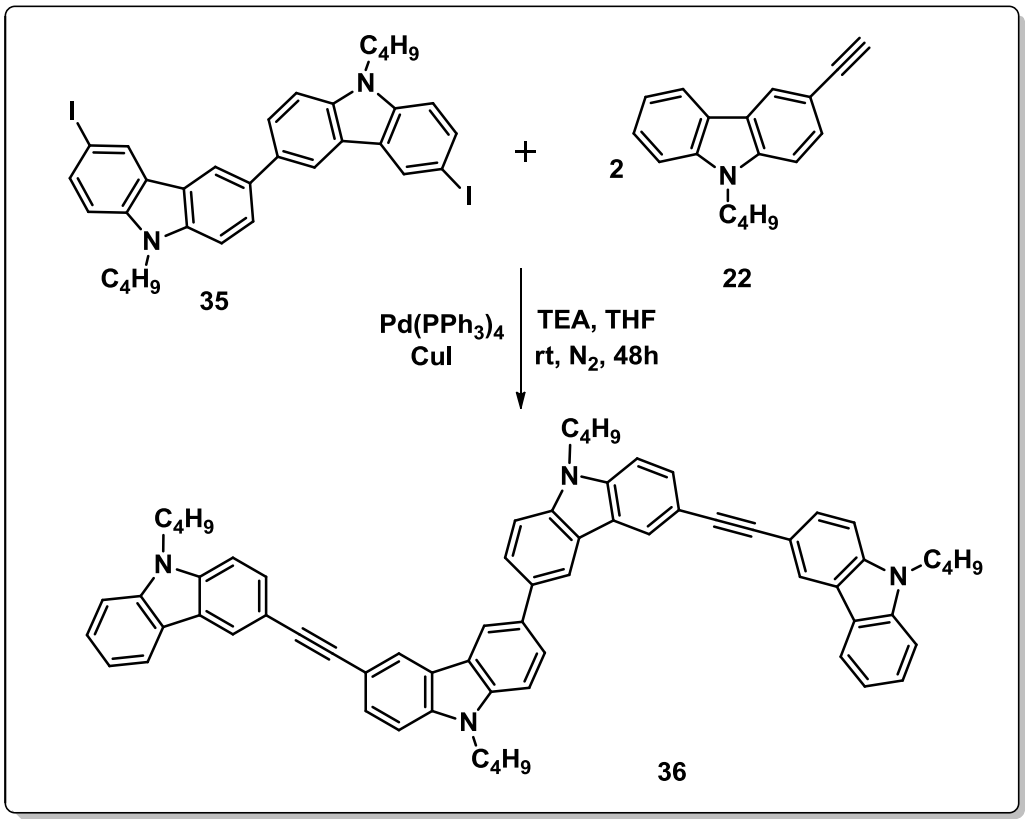
Scheme 4

Furthermore, we planned the synthesis of compounds with four carbazole units. For that we first carried out the dimerization of 9-butyl carbazole **17** using $FeCl_3$ in $CHCl_3$ to give 3,3'-bis(N-butyl carbazole) **34** which was then subjected to iodination by KI/KIO_3 to give 6,6'-diiodo-3,3'bis(N-butyl carbazole) **35**. [**Scheme 5]**



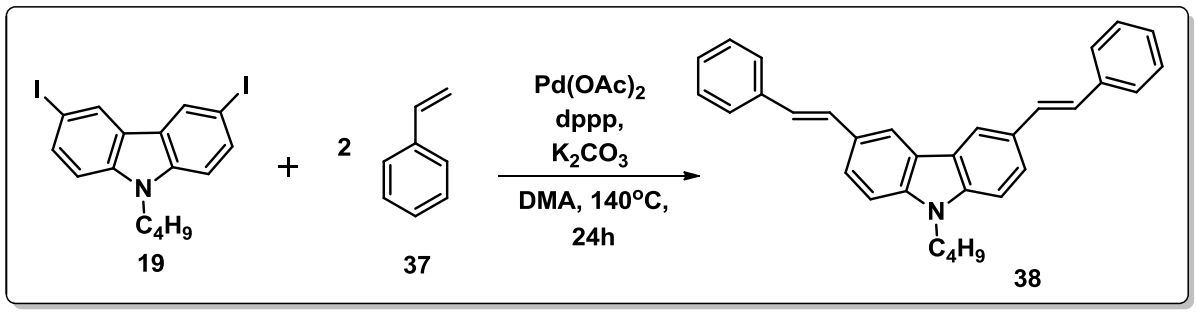
Scheme 5

Having synthesized the precursor for the compound with four carbazole units, **35** was subjected to Sonogashira reaction with two moles of 3-ethynyl-9-butyl carbazole **22**, to yield blue florescent 9,9'-dibutyl-6,6'-bis((9-butyl-9H-carbazol-3-yl)ethynyl)-9H,9'H-3,3'-bicarbazole **36 [Scheme 6**].



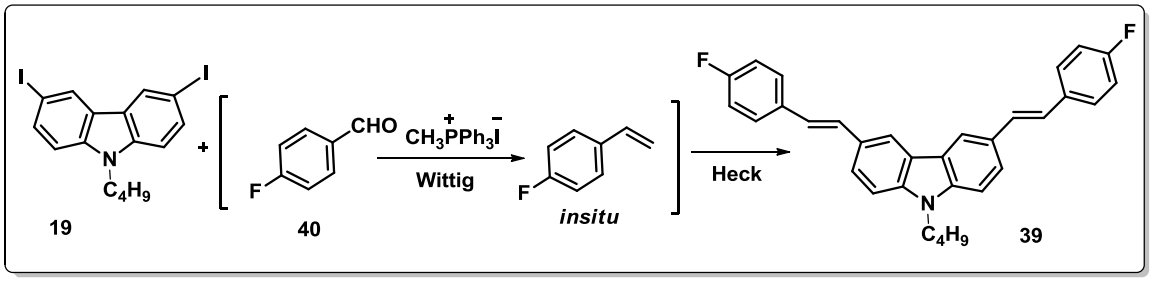
Scheme 6

Secondly, we have synthesized derivatives with ethylene spacer. Amongst them we synthesized 9-butyl-3,6-di((*E*)-styryl)-9H-carbazole **38** by carrying out Mizoroki-Heck coupling reaction of 3,6-diiodo-9-butyl carbazole **19** with two equivalent of styrene **37** [**Scheme 7**].



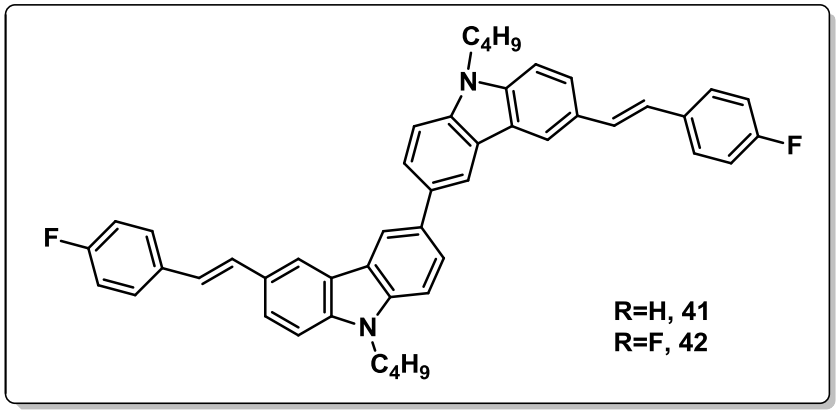
Scheme 7

In the earlier section we have described one-pot Wittig-Heck sequence for synthesis of stilbene derivatives. [17] We applied this methodology to synthesize the difloro derivative of **38** i.e. 9-butyl-3,6-bis((*E*)-4-fluorostyryl)-9H-carbazole **39** starting from 4-floro benzaldehyde **40** which will undergo Wittig reaction with methyl triphenyl phosphine iodide to form *in situ* 4-floro styrene. The 4-fluorostyrene so formed *in situ* will undergo Mizoroki-Heck reaction with 3,6-diiodo-9-butyl carbazole **19** to yield the desired product **39** [**Scheme 8**].



Scheme 8

Similar distyryl compounds were synthesized by carrying out Heck reaction of 6,6'-diiodo-3,3'bis(N-butyl carbazole) **35** and two equvivalent of styrene to give 9,9'-dibutyl-6,6'-di((*E*)-styryl)-9*H*,9'*H*-3,3'-bicarbazole **41**. Similarly 9,9'-dibutyl-6,6'-bis((*E*)-4-fluorostyryl)-9*H*,9'*H*-3,3'-bicarbazole **42** was synthesized by one-pot Wittig-Heck reaction[17] as mentioned for 9-butyl-3,6-bis((*E*)-4-fluorostyryl)-9*H*-carbazole **39** [**Scheme 9**].



Scheme 9

Thus a series of carbazole derivatives have been synthesized in good yields by adopting different synthetic approaches in this section.

4.2.2 Characterization

All the synthesized derivatives were characterized by different analytical and spectroscopic techniques. The photophysical properties of these derivatives were studied by UV-Visible absorption and fluorescence spectroscopy. All the compounds were freely soluble in most of the organic solvents. The absorption and emission of these derivatives was carried out in THF and the details are summarized in **Table 1**.

Table 1 Photophysical properties of different derivatives of carbazole

Compound	Absorption (λ_{max}) nm	Emission (λ_{max}) nm	λ_{onset}(nm)	E_g (optical gap energy) eV
25	305	393	371	3.34
27	298	410	381	3.25
30	311	396	362	3.43
31	315	401	364	3.41
32	306	483	374	3.32
33	310	424	378	3.28
36	307	419	375	3.31
38	319,353	417	408	3.04
39	320,352	407, 420	405	3.06
41	319	422	394	3.15
42	320, 353	422	404	3.06

The absorption spectra of most of the compounds showed strong absorptions in the region of 300-400 nm. The absorption band near 300 nm can be assigned to π-π* transitions of carbazole.

It was observed that absorption maxima of compound **41** with ethylene group was higher compared to compound **36** with four carbazole units separated by ethynyl spacer, probably due to the linear configuration of the sp hybridized triple bond, where substituents can rotate freely in the solution due to small energy barrier, thus leading to a more twisted structure which can obstruct the conjugation and leading to blue shift.[9] Upon excitation at their absorption maxima, all the derivatives exhibited blue emission in the range of 390 to 480 nm. A few representative absorption and emission spectra for compound **32** and **42** is presented in **Figure 1**. The optical band gap was determined by absorption edge technique.[18] So, λ_{onset} for all the compounds was determined from the absorption curve and optical band gap was determined by using the equation mentioned below:

$$E_g \text{ (optical gap energy)} = 1242/A_{onset}$$

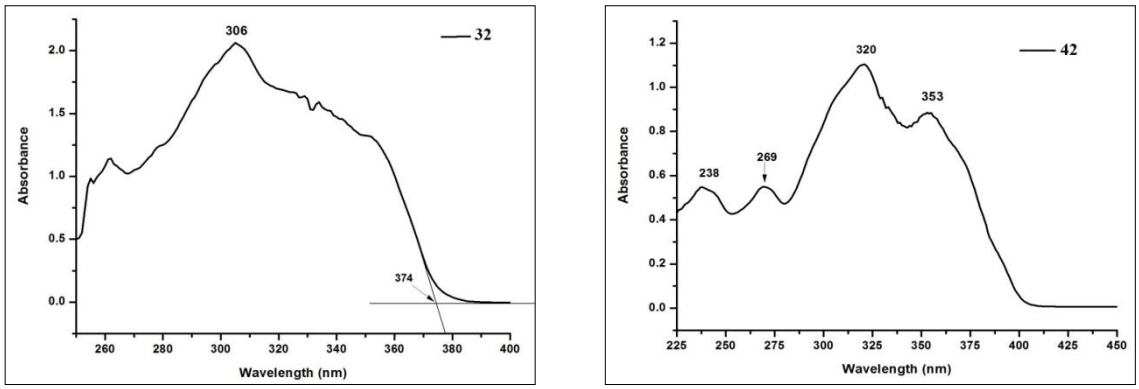


Figure 1a: UV-Visible spectrum for compound **32** and **42**

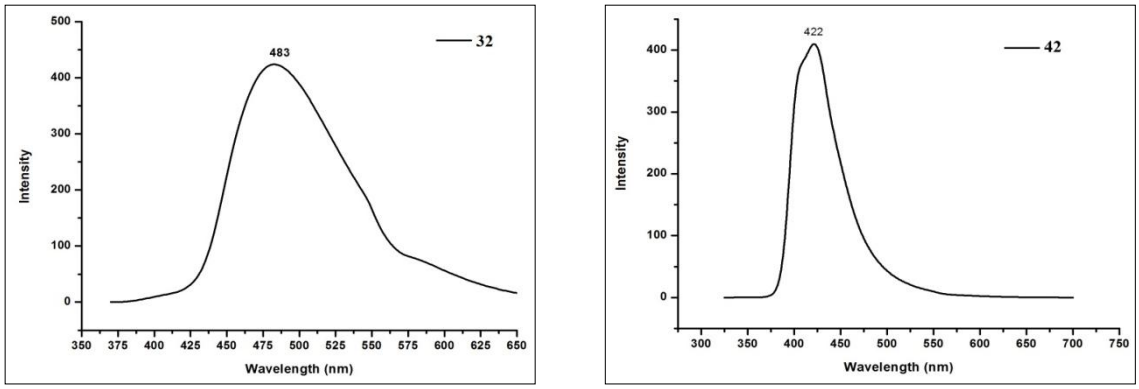


Figure 1b: Fluorescence spectrum for compound **32** and **42**

A cyclic voltammetry study was carried out for all the synthesized derivatives with alkene and alkyne spacers. The experiments were carried out in a three-electrode cell consisting of a platinum working electrode, a platinum counter electrode and Ag/AgCl as a reference electrode at the scan rate of 50mV/s. tetra-n-butyl ammonium hexafluoro phosphate(TBAFP) was used as an supporting electrolyte in DCM. Oxidation peaks for compound with alkyne spacer were very broad and without any well defined shape which may be due to the electrostatic repulsions through the alkyne spacer.[19] Representative cyclic voltammograms are presented in **Figure 2**.

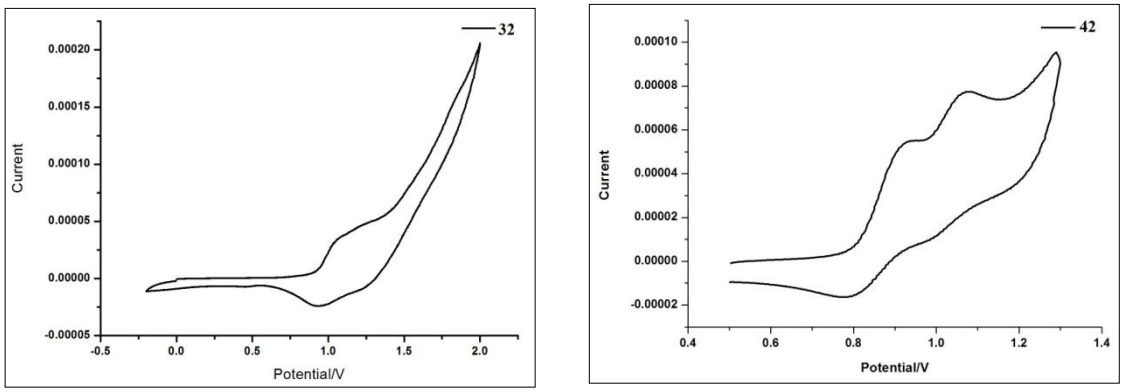
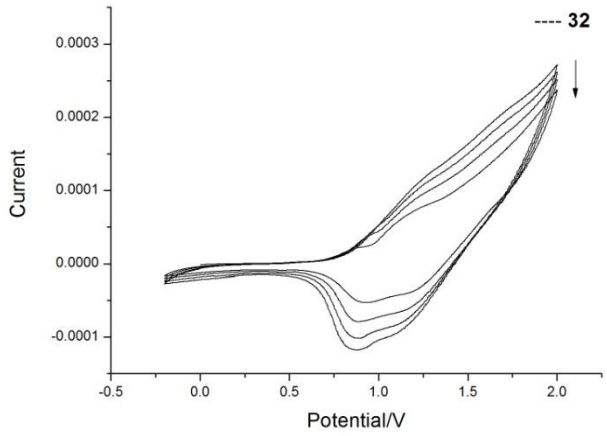


Figure 2: Cyclic voltammogram for compound **32** and **42**

It was observed that compounds with alkene spaces showed reversible behaviour in cyclic voltammetry. As an example, 9,9'-dibutyl-6,6'-di((*E*)-styryl)-9H,9'H-3,3'-bicarbazole **41** showed two oxidization peaks at 1.14V and 1.59V and the corresponding reduction peaks at 0.73V and 1.27V respectively depicting a reversible behaviour. Also, it was observed that a thin metallic green layer was deposited on the working electrode during the scan of compound **25**, **30**, **31**, **32**, **33** and **36** (i.e. compounds having 3-ethynyl carbazole unit) and the solution turned blue. The formation of this thin non-conducting layer might be responsible for slight decrease in the current on the subsequent CV scans.



On the basis of the onset oxidation potential we estimated the HOMO energy levels for all the derivatives using the equation.[18]

$$E_{HOMO} = -[E_{ox}^{onset} + 4.44]eV$$

The HOMO values were found to be in the range of 5.29 to 5.56eV. The optical band gap was previously determined by the absorption edge technique, so LUMO energy level for all the carbazole derivatives was calculated by subtracting the optical band gap from the HOMO energy. Electrochemical properties of all the derivatives have been summarized in **Table-2**.

Table 2: Electrochemical properties of carbazole derivatives

Compound	E_{ox}^{onset}/V	HOMO(eV)	LUMO(eV)	Band gap(eV) E_g
25	0.958	-5.398	-2.058	3.34
26	1.163	-5.603	-2.353	3.25
30	ND	ND	ND	3.43
31	1.121	-5.561	-2.151	3.41
32	1.022	-5.462	-2.142	3.32
33	1.079	-5.519	-2.239	3.28
34	ND	ND	ND	3.34
35	0.994	-5.434	-2.094	3.29
36	ND	ND	ND	3.31
38	0.966	-5.406	-2.366	3.04
39	0.949	-5.389	-2.319	3.07
41	0.995	-5.435	-2.285	3.15
42	0.850	-5.290	-2.220	3.07

HOMO-LUMO values were found to be in the range of 5.29-5.56 and 2.09-2.36eV respectively which are suitable for compounds to be used as HTM in electroluminescent devices.

4.3 Conclusion

Different carbazole derivatives with alkene and alkyne spacers were synthesized and characterized by ^{1}H-NMR and HRMS analysis. Photophysical properties for all derivatives were studied by UV-Visible and fluorescent spectroscopy and all compounds were found to be highly fluorescent in dilute solution. Energy band gap was calculated by Absorption edge technique and the values lies between 3.04 to 3.43eV. Cyclic voltammetric studies showed that the HOMO-LUMO values were in the range of 5.29-5.56 and 2.09-2.36eV respectively which are suitable for compounds to be used as 'hole-transporting materials' in electroluminescent devices.

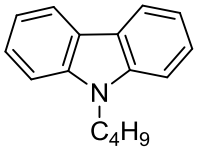
4.4 Experimental Section

All reactions were carried out in oven-dried glassware with magnetic stirring. Purification of reaction products was carried out by column chromatography using silica gel (60-120 mesh). Thin layer chromatography was performed on TLC Silica Gel 60 F_{254} (Merck). The spots were visualized under UV light or with iodine vapour. ^{1}H-NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer (400 MHz) and were run in $CDCl_3$ unless otherwise stated. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument; IR spectra were recorded on Perkin-Elmer FTIR RXI spectrometer as KBr pallets. UV-Visible absorption of all the compounds was measured as a solution in THF at room temperature on Perkin-Elmer Lambda 35 spectrometer and fluorescence was measured on Jasco FP-6300 spectro fluorometer. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

Solvents were dried and purified by distillation under reduced pressure and stored on molecular sieves. All chemicals were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc., and used without further purification.

Synthetic procedures and characterization

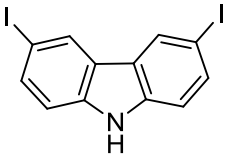
9-butyl carbazole (17)



In a round bottom flask carbazole (5 g, 0.0299 mol) was added into the solution of KOH (10.48 g, 0.186 mol) in 50 mL acetone at the conditions of stirring and room temperature. After 1 h, a solution of 1-bromobutane (6.14 g, 0.044 mol) in acetone was added to the reaction mixture and then maintained for 8 h. The final reaction mixture was concentrated under vacuum and then poured into 400 mL water. The product was extracted with ethyl acetate (50 x 3 mL). Ethyl acetate layer was washed with water twice, dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as a eluent to afford 9-butyl carbazole **17** as white solid (5.513 g, 82.6 %). Melting point: 54 ^{o}C (Lit.[20] 55-57 ^{o}C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, J=7.8 Hz, 2 H), 7.44(m, 4 H), 7.22(m, 2 H), 4.3(t, J=7.2 Hz, 2 H), 1.80–1.90 (m, 2 H), 1.34–1.46 (m, 2 H), 0.94 (t, J=7.4 Hz, 3 H).

3, 6-diiodo carbazole (18)

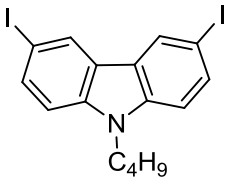


In a round bottom flask solution of carbazole (5 g, 0.0299 mol), KI (6.45 g, 0.0388 mol), KIO_3 (6.399 g, 0.0299 mol), glacial acetic acid

(45 mL) and deionized water (15 mL) was added. The reaction mixture was stirred at 80 ^{o}C for 40 h. After cooling to room temperature the reaction mixture was filtered and washed with deionized water and saturated Na_2CO_3 solution and methanol to afford a light brown solid (11.89 g, 95%). The crude product was used for the next reaction without any purification. Melting point: 210 ^{o}C (Lit.[21]211-212 ^{o}C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, *J*=7.8 Hz, 2H), 7.66 (d, *J*=7.8 Hz, 2H), 8.10 (s, 1H), 8.30 (s, 1H).

9-butyl-3,6-diiodo-9*H*-carbazole (19)



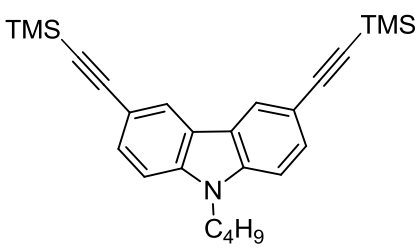
A round bottom flask was charged with 3,6-diiodo carbazole (5 g, 0.0119 mol), powdered KOH (1.004 g, 0.01789 mol) and acetone (40 mL). Reaction mixture was stirred at room temperature for 1h and then 1-bromo butane (1.96 g, 0.0143 mol) was added slowly and the reaction mixture was refluxed for 3 hours. After cooling to room temperature the mixture was concentrated under vacuum and poured to water. The product was extracted using ethyl acetate (50 x 3 mL). Ethyl acetate layer was washed with water twice, dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 9-butyl-3,6-diiodo-9H-carbazole (**19**) as white solid (4.649 g, 82%). Melting point: 110-113 ^{o}C (Lit.[20]112-113 ^{o}C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (s, 2H), 7.72 (d, *J*=8.6 Hz, 2H), 7.19 (d, *J*=8.6 Hz, 2H), 4.24 (t, *J* =7.2 Hz, 2H), 1.81 (m, 2H), 1.36-1.34 (m, 2H), 0.93 (t, *J*=7.2 Hz, 3H).

MS (EI) (m/z): 475 (41, M^{+}), 473 (59), 431 (100), 304 (66).

IR (KBr): υ 3048, 2951, 2927, 2863, 1623, 1593, 1484, 1455, 1378, 1347, 1327, 1260, 1238, 1211, 1148, 873, 747cm.$^{-1}$

9-butyl-3,6-bis((trimethylsilyl)ethynyl)-9*H*-carbazole (19a)



To a flask containing $Pd(PPh_3)_4$ (0.0243 g, 0.021 mmol), CuI (0.00801 g, 0.042 mmol) and 9-butyl-3,6-diiodo-9H-carbazole (1g, 2.10mmol) were added (trimethylsilyl)acetylene (0.826g, 8.41mmol) in triethylamine (6 mL) and tetrahydrofuran (6 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filterate was concentrated and

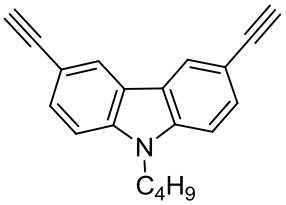
subjected to column chromatography on silica gel using petroleum ether as eluent to afford 9-butyl-3,6-bis((trimethylsilyl)ethynyl)-9H-carbazole **19a** as yellow oil (0.816 g, 93.4%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, *J*=1.2Hz, 2H), 7.59 (dd, *J*=8.4Hz, *J*=1.6Hz, 2H), 7.32 (d, *J*=8.4Hz, 2H), 4.27 (t, *J*=7.2Hz, 2H), 1.87-1.80 (m, 2H), 1.42-1.33 (m, 2H), 0.95 (t, *J*=7.2Hz, 3H).

MS (EI) (m/z): 415 (100), 400 (26), 371 (33).

IR (KBr): υ 3049, 2959, 2152, 1627, 1598, 1482, 1457, 1381, 1352, 1286, 1249, 1207, 1150, 859, 759cm.$^{-1}$

9-butyl-3,6-diethynyl-9H-carbazole (20)



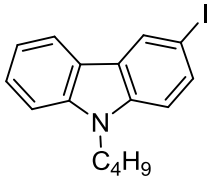
To the stirred solution of 9-butyl-3,6-bis((trimethylsilyl)ethynyl)-9H-carbazole **5i** (1 g, 2.40 mmol) in ethanol, aqueous NaOH solution (0.2M, 5 mL) was added. The reaction mixture was stirred at room temperature under N_2 for 1h and then diluted with water and dichloromethane. The phases were separated and the aqueous layer was washed with dichloromethane and the combined organic phases were washed with saturated brine. The organic phase was dried over sodium sulphate and the solvent was removed. The residual material was purified by column chromatography on silica gel using petroleum ether as eluent to give 9-butyl-3,6-diethynyl-9H-carbazole **20** (0.562 g, 86.2 %) as light yellow solid. Melting point: 98-100 ^{o}C(Lit.[20]100-101 ^{o}C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, *J* = 1.2Hz, 2H), 7.62 (dd, *J* = 8.4Hz, *J* = 1.6Hz, 2H), 7.36 (d, *J* = 8.4Hz, 2H), 4.29 (t, *J* = 7.2Hz, 2H), 1.89-1.81 (m, 2H), 1.45-1.33 (m, 2H), 0.96 (t, *J* = 7.2, 3H).

MS (EI) (m/z): 271 (93, M^+), 228 (100).

IR (KBr): υ 3057, 2957, 2926, 2855, 2152, 1626, 1601, 1482, 1380, 1352, 1286, 1249, 1205, 1150, 852, 759 cm.$^{-1}$

9-butyl-3-iodo-9H-carbazole (21)



In a round bottom flask KIO_3 (0.632 g, 2.95 mmol) and KI (0.981 g, 5.91 mmol) was dissolved in 20 mL water. To this stirred mixture, solution of 9-butyl carbazole (2 g, 8.96 mmol) in methanol was added slowly. After the solution became clear concentrated HCl (1.1 mL) was added dropwise and the reaction mixture was stirred rigorously. After addition of

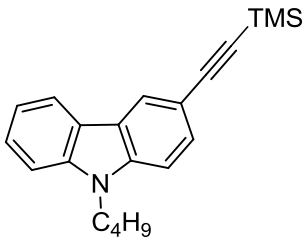
HCl oily mass was separated in the reaction mixture which was separated using separating funnel. It was washed with water and dissolved in ethyl acetate. The organic phase was washed with sodium thiosulphate and dried over sodium sulphate. Solvent was removed under vacuum and the crude product was purified through column chromatography on silica gel using petroleum ether as solvent. Pure product was isolated as pale yellow oil (2.331 g, 74.52%). Melting point: 45 ^{o}C (Lit.[20]44-46^{o}C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, *J* = 1.2, 1H), 8.05 (d, *J* = 7.6Hz, 1H), 7.72 (dd, *J*=8.4Hz, *J*=1.6Hz, 1H), 7.53-7.49 (m, 1H), 7.42 (d, *J* = 8Hz, 1H), 7.29-7.25(m, 1H), 7.21 (d, *J*=8Hz, 1H), 4.27 (t, *J*=7.2Hz, 2H), 1.88-1.81 (m, 2H), 1.42-1.37 (m, 2H), 0.97 (t, *J*=7.2Hz, 3H).

MS (EI) (m/z): 349 (25, M^+), 348 (48), 304 (37), 222 (32), 180 (100).

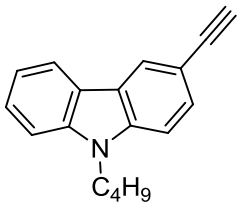
IR (KBr): υ 3048, 2956, 2924, 2856, 1619, 1588, 1473, 1458, 1345, 1331, 1273, 1213, 797, 747, 722 cm.$^{-1}$

9-butyl-3-((trimethylsilyl)ethynyl)-9H-carbazole (21a)



To a flask containing $Pd(PPh_3)_4$ (0.066 g, 0.057 mmol), CuI (0.0218 g, 0.114 mmol) and 9-butyl-3-iodo-9H-carbazole (2 g, 5.730 mmol) were added (trimethylsilyl)acetylene (0.844 g, 8.59 mmol) in triethylamine (10 mL) and tetrahydrofuran (10 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filterate was concentrated and subjected to column chromatography on silica gel using petroleum ether as eluent to afford 9-butyl-3-((trimethylsilyl)ethynyl)-9H-carbazole **21a** as yellow oil (1.133 g, 62%).

9-butyl-3-ethynyl-9H-carbazole (22)



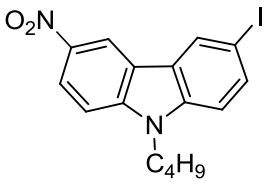
To the stirred solution of 9-butyl-3-((trimethylsilyl)ethynyl)-9H-carbazole **21a** (1 g, 3.13 mmol) in ethanol, aqueous NaOH solution (0.2 M, 2.5 mL) was added. The reaction mixture was stirred at room temperature under N_2 for 1 h and then diluted with water and dichloromethane. The phases were separated and the aqueous layer was washed with dichloromethane and the combined organic phases were washed with saturated brine. The organic phase was dried over sodium sulphate and the solvent was removed. The residual material was purified by column chromatography on silica gel

using petroleum ether as eluent to give 9-butyl-3,6-diethynyl-9H-carbazole **22** (0.550 g, 71.15 %) as yellow oil. Melting point: 45 ^{o}C(Lit.[22] 46.8-48.3 ^{o}C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (s, 1H), 8.09 (d, J= 7.6 Hz, 1H), 7.61 (d, *J*= 8.4 Hz, 1H), 7.51 (t, *J*=8.4 Hz, 1H), 7.42 (d, *J*= 8.0 Hz, 1H), 7.35 (d, *J*= 8.4 Hz, 1H), 7.28 (t, *J*= 8.4 Hz, 1H), 4.30 (t, *J*=7.2 Hz, 2H), 3.09 (s, 1H), 1.88–1.81 (m, 2H), 1.42–1.37 (m, 2H), 0.97 (t, 3H, 7.2 Hz).

MS (EI) (m/z): 247 (91, M^+), 204 (100).

9-butyl-3-iodo-6-nitro-9H-carbazole (23)

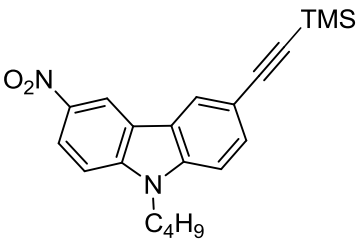


In a round bottom flask 9-butyl-3-iodo-9H-carbazole **21** (2 g) was dissolved in acetic acid. The reaction temperature was maintained at 0 ^{o}C. To this solution a mixture of HNO_3 and H_2SO_4 (3:1) (2 mL) was slowly added. Bright yellow solid was separated from the reaction. The product was extracted in ethyl acetate and organic layer was dried on sodium sulphate. Organic layer was concentrated under vacuum and the crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (5%) as eluent to afford 9-butyl-3-iodo-6-nitro-9H-carbazole **23** (1.469 g, 65.3%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.97 (d, *J*=2.4Hz, 1H), 8.48 (d, *J*=1.6Hz, 1H), 8.41 (dd, *J*=9.2 Hz, *J*=2.4 Hz, 1H), 7.82 (dd, *J*=8.8 Hz, *J*=1.6 Hz, 1H), 7.43 (d, *J*=9.2 Hz, 1H), 7.28 (d, *J*=8.8 Hz, 2H), 4.34 (t, *J*=7.2Hz, 2H), 1.91–1.83 (m, 2H), 1.44–1.35 (m, 2H), 0.97 (t, 3H, 7.2 Hz).

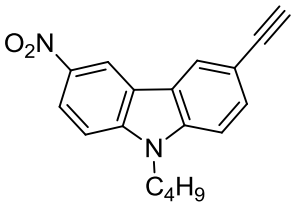
MS (EI) (m/z): 394 (100, M^+), 350 (58).

9-butyl-3-nitro-6-((trimethylsilyl)ethynyl)-9H-carbazole (23a)



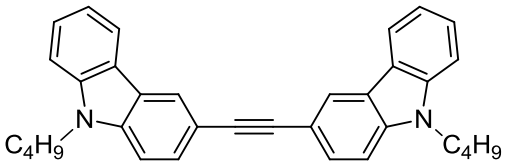
To a flask containing $Pd(PPh_3)_4$ (0.029 g, 0.025 mmol), CuI (0.0096 g, 0.0508 mmol) and 9-butyl-3-iodo-6-nitro-9H-carbazole **23** (1g, 2.53mmol) were added (trimethylsilyl)acetylene (0.299g, 3.04mmol) in triethylamine (6mL) and tetrahydrofuran (6 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filterate was concentrated and subjected to column chromatography on silica gel using ethyl acetate and petroleum ether (15%) as eluent to afford 9-butyl-3-nitro-6-((trimethylsilyl)ethynyl)-9H-carbazole **23a** as yellow oil (0.371 g, 40.25%).

9-butyl-3-ethynyl-6-nitro-9*H*-carbazole (24)



To the stirred solution of 9-butyl-3-nitro-6-((trimethylsilyl)ethynyl)-9H-carbazole **23a** (0.25 g, 0.68 mmol) in ethanol, aqueous NaOH solution (0.2 M, 1 mL) was added. The reaction mixture was stirred at room temperature under N_2 for 1 h and then diluted with water and dichloromethane. The phases were separated and the aqueous layer was washed with dichloromethane and the combined organic phases were washed with saturated brine. The organic phase was dried over sodium sulphate and the solvent was removed. The residual material was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (20%) as eluent to give 9-butyl-3-ethynyl-6-nitro-9H-carbazole **24** (0.096 g, 48%) as yellow oil.

1,2-bis(9-butyl-9*H*-carbazol-3-yl)ethyne (25)



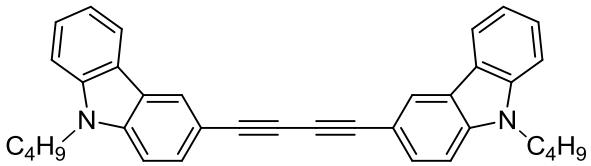
To a flask containing $Pd(PPh_3)_4$ (0.011 g, 0.010 mmol), CuI (0.0038 g, 0.020 mmol) and 9-butyl-3-iodo-9H-carbazole **21** (0.350 g, 1.002 mmol) were added 9-butyl-3-ethynyl-9H-carbazole **22** (0.297 g, 1.203 mmol) in triethylamine (6 mL) and tetrahydrofuran (6 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filterate was concentrated and poured into water. The product was extracted in ethyl acetate (3 x 25 mL). The organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (2 %) as eluent to afford 1,2-bis(9-butyl-9*H*-carbazol-3-yl)ethyne (**25**) (0.214 g, 45.62%) as white solid. Homocoupled product 1,4-bis(9-butyl-9*H*-carbazol-3-yl)buta-1,3-diyne (**27**) (0.137 g, 45.62 %) was eluted in 5 % ethyl acetate and petroleum ether.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.36 (s, 2H), 8.14 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8.8Hz, 2H), 7.53-7.49 (m, 2H, one doublet with J = 7.2Hz merged together), 7.45-7.40 (m, 4H), 7.33-7.23 (m, 2H), 4.34 (t, J = 7.2 Hz, 4H), 1.94-1.86 (m, 4H), 1.47-1.41 (m, 4H), 0.98 (t, J = 7.2 Hz, 6H)

HRMS (ESI^+): Calculated for $C_{34}H_{32}N_2$ $[M]^+$ 468.2565, found 468.2569

IR (KBr): υ 3050, 2923, 2868, 1625, 1595, 1468, 1346, 1263, 1209, 1149, 883, 805, 749, 609 cm^{-1}

1,4-bis(9-butyl-9*H*-carbazol-3-yl)buta-1,3-diyne (27)

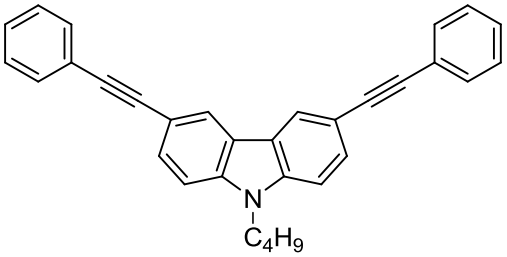


^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, *J* = 1.2 Hz, 2H), 8.11 (d, *J* = 7.6 Hz), 7.66, (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.54-7.52 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.31-7.27 (m, 2H), 4.33 (t, *J* = 7.2 Hz, 4H), 1.90-1.84 (m, 4H), 1.47-1.38 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 6H**)**

HRMS (ESI^+): Calculated for $C_{36}H_{32}N_2$ $[M]^+$ 492.2565, found 492.2567

IR (KBr): υ 3052, 2953, 2870, 2136, 1624, 1593, 1491, 1465, 1380, 1348, 1210, 1145, 882, 804, 745 $cm.^{-1}$

9-butyl-3,6-bis(phenylethynyl)-9*H*-carbazole (30)



To a flask containing $Pd(PPh_3)_4$ (0.0061 g, 0.0053 mmol), CuI (0.0019 g, 0.0105 mmol) and 9-butyl-3,6-diiodo-9H-carbazole (**19**) (0.250 g, 0.526 mmol) were added phenyl acetylene (0.161 g, 1.578 mmol) in triethylamine (4 mL) and tetrahydrofuran (4 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filterate was concentrated and poured into water. The product was extracted in ethyl acetate (3 x 25 mL). The organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 9-butyl-3,6-bis(phenylethynyl)-9*H*-carbazole (**30**) (0.192 g, 86.48%) as yellow sticky mass.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, *J* = 1.2 Hz, 2H), 7.67 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.65-7.51 (m, 4H), 7.43-7.36 (m, 8H), 4.31 (t, *J* = 7.2 Hz, 2H), 1.90-1.86 (m, 2H), 1.46-1. 39 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H)

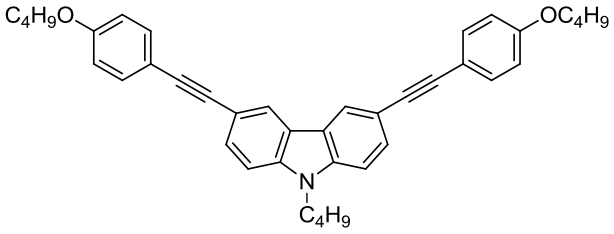
MS (EI) (m/z): 423 (47), 422 (100), 421 (41), 365 (30)

HRMS (ESI^+): Calculated for $C_{32}H_{25}N$ $[M]^+$ 423.1987, found 423.1989

3,6-bis((4-butoxyphenyl)ethynyl)-9-butyl-9*H*-carbazole (31)

To a flask containing $Pd(PPh_3)_4$ (0.017 g, 0.0147 mmol), CuI (0.0056 g, 0.0294 mmol) and 9-butyl-3,6-diiodo-9H-carbazole (**19**) (0.350 g, 0.736 mmol) were added 4-butoxy

phenyl acetylene (0.281 g, 1.62 mmol) in triethylamine (4 mL) and tetrahydrofuran (4 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 48 h and then filtered. The filterate was concentrated and poured into water. The product was extracted in ethyl acetate (3 x 25mL). The organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (5%) as eluent to afford 3,6-bis((4-butoxyphenyl)ethynyl)-9-butyl-9*H*-carbazole (**31**) (0.104 g, 25%) as white crystalline solid.



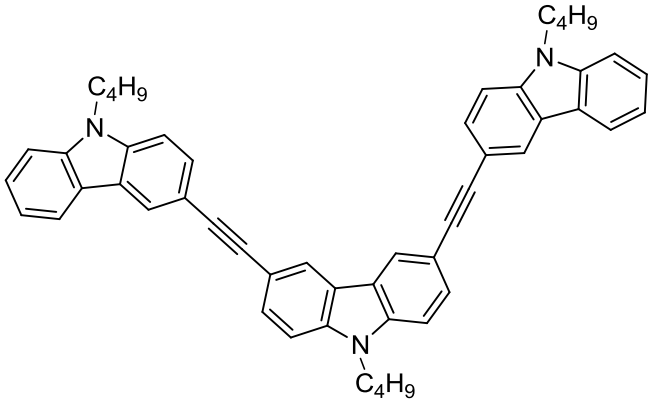
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, *J* = 1.2 Hz, 2H), 7.64 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.931 (d, *J* = 8.8 Hz, 4H), 4.31 (t, *J* = 7.2 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 4H), 1.89-1.83 (m, 2H), 1.83-1.77 (m, 4H), 1.57-1.48 (m, 4H), 1.45-1.39 (m, 2H), 1.03-0.96 (m, 9H).

MS (EI) (m/z): 567 (54), 566 (89), 565 (60), 403 (74), 401 (100), 400 (88).

HRMS (ESI^+): Calculated for $C_{40}H_{41}NO_2$ $[M+H]^+$ 568.3215, found 568.3209

3,3'-((9-butyl-9*H*-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-butyl-9*H*-carbazole) (32)

To a flask containing $Pd(PPh_3)_4$ (0.0085 g, 0.0073 mmol), CuI (0.0021 g, 0.011 mmol) and 9-butyl-3-iodo-9H-carbazole (**21**) (0.282 g, 0.810 mmol) were added 9-butyl-3,6-diethynyl-9H-carbazole (**20**) (0.100 g, 0.368 mmol) in triethylamine (4 mL) and tetrahydrofuran (4 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 24 h and then filtered. The filterate was concentrated and poured into water. The product was extracted in ethyl acetate (3 x 25mL). The organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (10%) as eluent to afford 3,3'-((9-butyl-9*H*-carbazole-



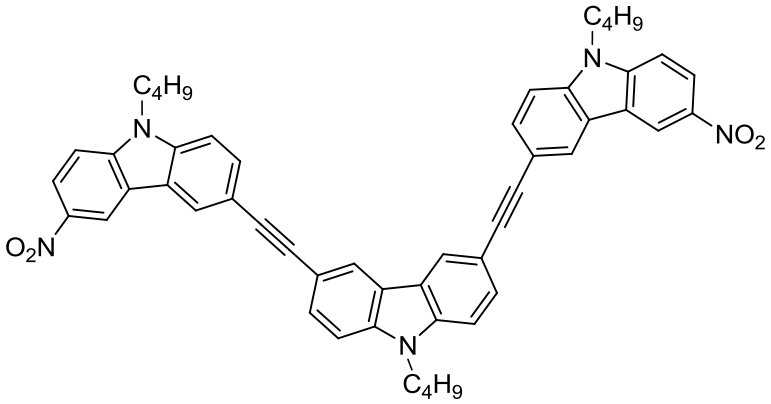
3,6-diyl)bis(ethyne-2,1-diyl))bis(9-butyl-9*H*-carbazole) (**32**) (0.175 g, 75.17%) as brown solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.37 (dd, *J* = 5.6 Hz, *J* = 0.8Hz, 4H), 8.15 (d, *J* = 7.6 Hz, 2H), 7.74-7.71 (m, 4H), 7.54-7.49 (m, 2H), 7.46-7.41 (m, 6H), 7.31-7.27 (m, 2H), 4.34 (t, *J* = 7.2Hz, 6H), 1.94-1.86 (m, 6H), 1.48-1.39 (m, 6H), 1.02-0.96 (m, 9H)

HRMS (ESI^+): Calculated for $C_{52}H_{47}N_3$ $[M+H]^+$ 714.3848, found 714.3843

IR (KBr): υ 3048, 2955, 2870, 1625, 1597, 1490, 1379, 1349, 1208, 1126, 879, 804 $cm.^{-1}$

6,6'-((9-butyl-9H-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-butyl-3-nitro-9H-carbazole) (33)



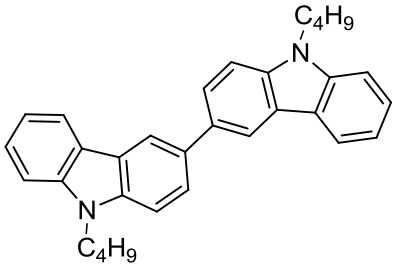
To a flask containing $Pd(PPh_3)_4$ (0.0187 g, 0.0162 mmol), CuI (0.00617 g, 0.0324 mmol) and 9-butyl-3-iodo-6-nitro-9H-carbazole (**23**) (1.40 g, 3.57 mmol) were added 9-butyl-3,6-diethynyl-9H-carbazole (**20**) (0.440 g, 1.62 mmol) in triethylamine (4 mL) and tetrahydrofuran (4 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 24 h and then filtered. The filterate was concentrated and poured into water. The product was extracted in ethyl acetate (3 x 25 mL). The organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate and petroleum ether (20%) as eluent to afford 6,6'-((9-butyl-9H-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-butyl-3-nitro-9H-carbazole) (**33**) (0.928 g, 71.42%) as yellow solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.04 (d, *J* = 2.4Hz, 2H), 8.44-8.41 (m, doublet with *J* = 2.4 Hz merged together, 4H), 8.36 (d, *J* = 1.2 Hz, 2H), 7.80 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 7.74 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.49 (d, *J* = 8.4Hz, 2H), 7.46-7.43 (m, 4H, doublets with *J* = 8.4 Hz merged togther)**,** 4.40-4.34 (m, 6H, two triplets with *J* = 7.2 Hz merged together), 1.96-1.88 (m, 6H), 1.48-1.40 (m, 6H), 1.0 (t, *J* = 7.2 Hz, 9H)

HRMS (ESI^+): Calculated for $C_{52}H_{45}N_5O_4$ $[M+H]^+$ 804.3544, found 804.3549

9,9'-dibutyl-9H,9'H-3,3'-bicarbazole (34)

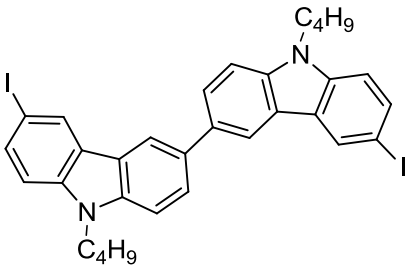
In a round bottom flask 9-butyl carbazole (**17**) (0.500 g, 2.24 mmol) was dissolve in $CHCl_3$ (10 mL). The reaction temperature was maintained at 0^oC and $FeCl_3$ (1.453 g, 8.96 mmol) was added slowly. After addition of $FeCl_3$ the reaction mixture was stirred at room temperature for further 3 h and then filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 9,9'-dibutyl-9H,9'H-3,3'-bicarbazole (**34**) (0.413 g, 83.09%) as thick colorless liquid which solidifies under vacuum. Melting point: 116-117 ^oC (Lit.[23]118 ^oC)



^{1}H-NMR ($CDCl_3$, 400 MHz) δ δ 8.44 (s, 2H), 8.22 (d, *J* = 7.6 Hz, 2H), 7.86 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.54-7.45 (m, 6H), 7.30-7.26 (m, 2H), 4.38 (t, *J* = 7.2 Hz, 4H), 1.97-1.90 (m, 4H), 1.50-1.44 (m, 4H), 1.0 (t, *J* = 7.2 Hz, 6H).

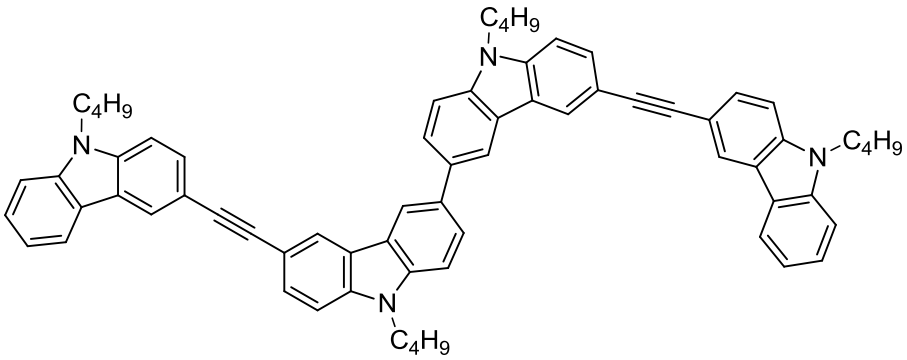
9,9'-dibutyl-6,6'-diiodo-9H,9'H-3,3'-bicarbazole (35)

9,9'-dibutyl-9H,9'H-3,3'-bicarbazole (**34**) (1.732 g, 3.89 mmol) was dissolved in acetic acid (30 mL). To this stirred solution KIO_3 (0.549 g, 2.56 mmol) and KI (0.859 g, 5.177 mmol) was added and continued to stir at 80-90 ^oC for 16 h. Reaction mixture was cooled and poured into water and neutralized using $NaHCO_3$. The product was extracted in ethyl acetate and it was washed with sodium thiosulphate. Organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified through column chromatography on silica gel using petroleum ether as eluent to afford 9,9'-dibutyl-6,6'-diiodo-9H,9'H-3,3'-bicarbazole (**35**) (1.623 g, 59.66%)



^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.51 (d, *J* = 1.6 Hz, 2H), 8.34 (d, *J* = 1.6 Hz, 2H), 7.84 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.73 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 4H), 1.93-1.86 (m, 4H), 1.48-1.38 (m, 4H), 1.00-0.98 (t, *J* = 7.2 Hz, 6 H).

9,9'-dibutyl-6,6'-bis((9-butyl-9H-carbazol-3-yl)ethynyl)-9H,9'H-3,3'-bicarbazole (36)



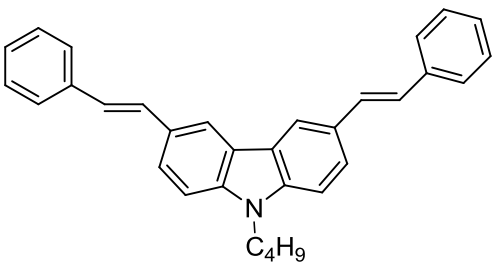
To a flask containing $Pd(PPh_3)_4$ (0.0066 g, 0.00572 mmol), CuI (0.00218 g, 0.00145 mmol) and 9,9'-dibutyl-6,6'-diiodo-9H,9'H-3,3'-bicarbazole (**35**) (0.2 g, 0.286 mmol) were added 9-butyl-3-ethynyl-9H-carbazole (**22**) (0.212 g, 0.859 mmol) in triethylamine (6 mL) and tetrahydrofuran (6 mL). The flask was then flushed with nitrogen twice. The reaction mixture was stirred at room temperature under N_2 for 24 h and then filtered. The filterate was concentrated and poured into water. The product was extracted in ethyl acetate (3 x 25 mL). The organic phase was dried over sodium sulphate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 9,9'-dibutyl-6,6'-bis((9-butyl-9H-carbazol-3-yl)ethynyl)-9H,9'H-3,3'-bicarbazole (**36**) (0.101 g, 37.82%) as brown solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.48-8.46 (two doublets, *J* = 1.2 Hz, *J* = 1.6 Hz, 2H), 8.37 (d, *J* = 1.2 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), xx-7.87 (dd, *J* = xx, *J* = 1.6 Hz, 1H), 7.75-7.71 (m, 2H), 7.56-7.40 (m, 5H), 7.27 (m, 1H), 4.39 (t, *J* = 7.2 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 2H), 1.97-1.87 (m, 4H), 1.52-1.41 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H).

HRMS (ESI^+): Calculated for $C_{68}H_{62}N_4$ $[M+H]^+$,calculated 935.50527, found 935.50537.

IR (KBr): υ 3047, 2953, 2869,1724, 1625, 1596, 1473, 1378, 1347, 1209, 1129,873, 799, 744, 726 $cm.^{-1}$

9-butyl-3,6-di((E)-styryl)-9H-carbazole (38)

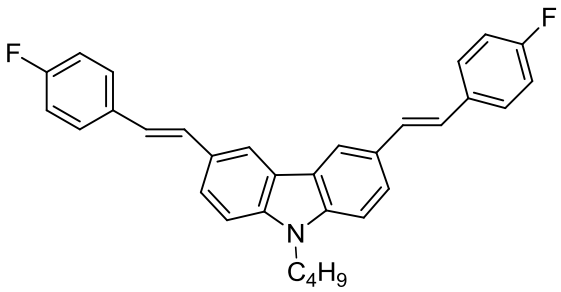


A two neck round bottom flask was charged with 9-butyl-3,6-diiodo-9H-carbazole (**19**) (0.300 g, 0.631 mmol), K_2CO_3 (0.349 g, 2.52 mmol), $Pd(OAc)_2$ (0.0014 g, 0.0063 mmol), dppp (0.0052 g, 0.0126 mmol) and N,N-dimethyl acetamide (8 mL) and stirred. The temperature was raised to 60 ^oC and styrene (0.263 g, 2.52 mmol) was added to the reaction mixture and was continued to stir at 130

^{o}C for 24 h. The reaction was cooled and poured into water and the product was extracted in ethyl acetate (25 x 3 mL). The organic phase was dried over sodium sulphate and was removed under vacuum. The crude product was purified through column chromatography on silica gel using ethyl acetate and petroleum ether (1%) as eluent to afford 9-butyl-3,6-di((E)-styryl)-9H-carbazole (**38**) (0.204 g, 75.83%) as off white solid. Melting point: 83-84^{o}C (Lit.[24] 85.2-87.6^{o}C)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.29 (d, *J* = 1.6 Hz, 2H), 7.70 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.43-7.26 (m, 10H, one doublet of olefinic proton with *J* = 16.4 Hz merged together), 7.19 (d, *J* = 16.4 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 2H), 1.91-1.88 (m, 2H), 1.46-1.40 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

9-butyl-3,6-bis((E)-4-fluorostyryl)-9H-carbazole (39)



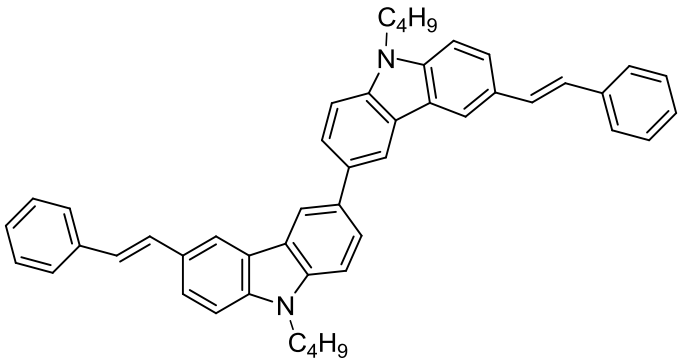
A two neck round bottom flask was charged with 9-butyl-3,6-diiodo-9H-carbazole (**19**) (0.225 g, 0.473 mmol), 4-fluoro benzaldehyde (0.141 g, 1.136 mmol), methyl triphenyl phosphine iodide (0.461 g, 1.136 mmol), K_2CO_3 (0.327 g, 2.36 mmol), $Pd(OAc)_2$ (0.001 g, 0.00473 mmol), dppp (0.0039 g, 0.00946 mmol), TBAB (0.030 g, 0.0946 mmol) and N,N-dimethyl acetamide (8 mL) and stirred. Temperature was raised to 130 ^{o}C and was continued to stir for 24 h. The reaction was cooled and poured into water and the product was extracted in ethyl acetate (25 x 3 mL). The organic phase was dried over sodium sulphate and was removed under vacuum. The crude product was purified through column chromatography on silica gel using petroleum ether as eluent to afford 9-butyl-3,6-bis((E)-4-fluorostyryl)-9H-carbazole (**39**) (0.130 g, 59.36%) as off white solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, *J* = 1.6 Hz, 2H), 7.67 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.56-7.53 (m, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 16.4 Hz, 2H), 7.14 (d, *J* = 16.4 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 4H), 4.32 (t, *J* = 7.2 Hz, 2H), 1.93-1.86 (m, 2H), 1.46-1.40 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

9,9'-dibutyl-6,6'-di((E)-styryl)-9H,9'H-3,3'-bicarbazole (41)

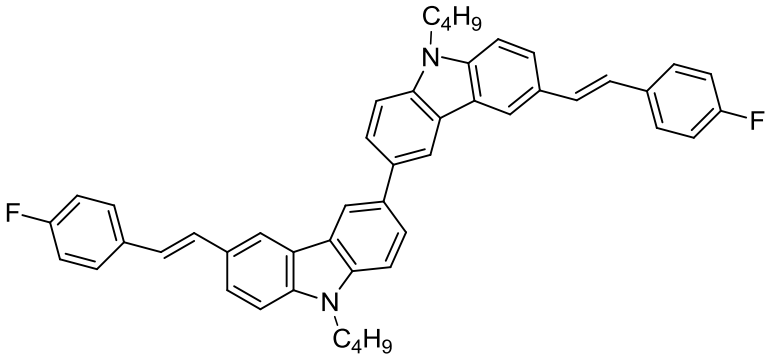
A two neck round bottom flask was charged with 9,9'-dibutyl-6,6'-diiodo-9H,9'H-3,3'-bicarbazole (**35**) (0.300 g, 0.429 mmol), K_2CO_3 (0.237 g, 1.718 mmol), $Pd(OAc)_2$ (0.00096 g, 0.0042 mmol), dppp (0.0035 g, 0.00859 mmol) and N,N-dimethyl acetamide

(8 mL) and stirred. The temperature was raised to 60 ^{o}C and styrene (0.178 g, 1.718 mmol) was added to the reaction mixture and was continued to stir at 130 ^{o}C for 24 h. The reaction was cooled and poured into water and the product was extracted in ethyl acetate (25 x 3 mL). The organic phase was dried over sodium sulphate and was removed under vacuum. The crude product was purified through column chromatography on silica gel using ethyl acetate and petroleum ether (1%) as eluent to afford 9,9'-dibutyl-6,6'-di((E)-styryl)-9H,9'H-3,3'-bicarbazole (**41**) (0.210 g, 75.55%) as pale yellow solid.



^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, *J* = 1.6 Hz, 2H), 8.36 (d, *J* = 1.2 Hz, 2H), 7.87 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H), 7.72 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.45-7.36 (m, 8H, a doublets with *J* = 8.4 Hz and a olefinic proton signal with *J* = 16.4 Hz merged together), 7.29-7.27 (m, 2H), 7.21 (d, *J* = 16 Hz, 2H), 4.36 (t, *J* = 7.2 Hz, 2H), 1.98-1.91 (m, 2H), 1.52-1.43 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).

9,9'-dibutyl-6,6'-bis((E)-4-fluorostyryl)-9H,9'H-3,3'-bicarbazole (42)



A two neck round bottom flask was charged with 9,9'-dibutyl-6,6'-diiodo-9H,9'H-3,3'-bicarbazole (**35**) (0.300 g, 0.429 mmol), 4-fluoro benzaldehyde (0.127 g, 1.030 mmol), methyl triphenyl phosphine iodide (0.418 g, 1.030 mmol), K_2CO_3 (0.296 g, 2.147 mmol), $Pd(OAc)_2$ (0.00096 g, 0.0042 mmol), dppp (0.0035 g, 0.00859 mmol), TBAB (0.027 g, 0.0859 mmol) and N,N-dimethyl acetamide (8 mL) and stirred. Temperature was raised to 130 ^{o}C and was continued to stir for 24 h. The reaction was cooled and poured into water and the product was extracted in ethyl acetate (25 x 3 mL). The organic phase was dried over sodium sulphate and was removed under vacuum. The crude product was

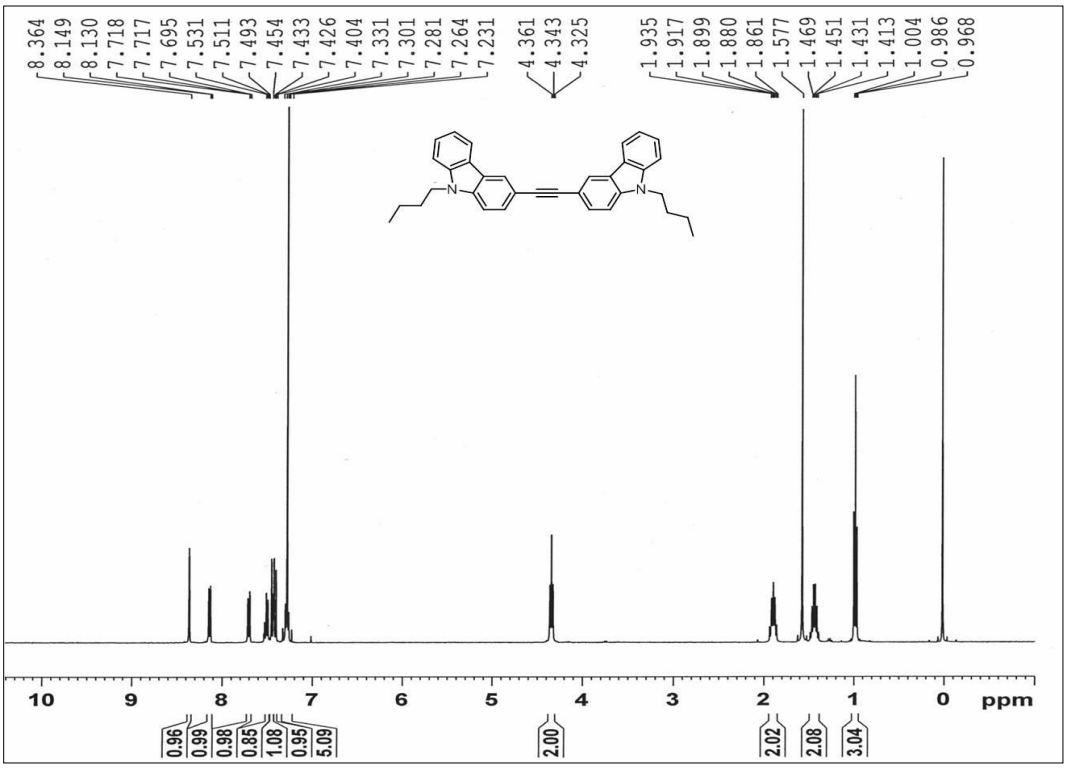
purified through column chromatography on silica gel using petroleum ether as eluent to afford 9,9'-dibutyl-6,6'-bis((*E*)-4-fluorostyryl)-9H,9'H-3,3'-bicarbazole (**42**) (0.156 g, 53.06%) as off white solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.46 (d, *J* = 1.6 Hz, 2H), 8.34 (d, *J* = 1.2 Hz, 2H), 7.72 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2H), 7.69 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.57-7.53 (m, 6H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 16 Hz, 2H), 7.16 (d, *J* = 16.4 Hz, 2H), 7.11-7.07 (m, 4H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.96-1.92 (m, 2H), 1.50-1.43 (m, 2H), 1.0 (t, *J* = 7.2 Hz, 3H).

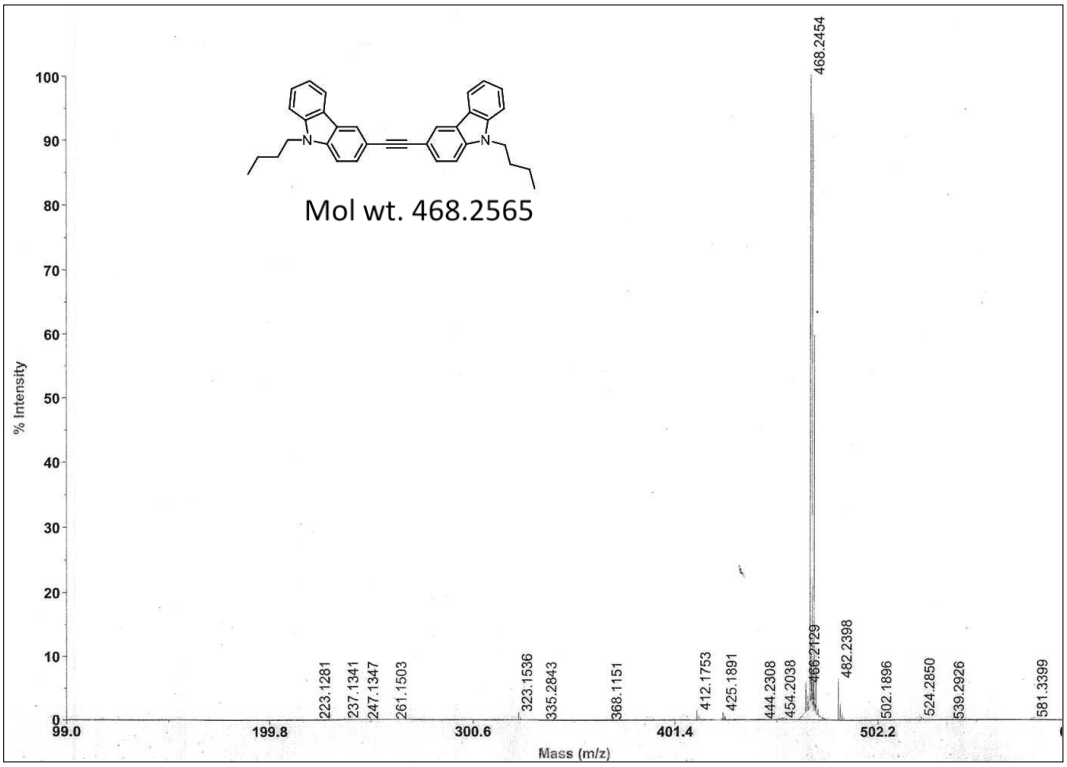
HRMS (ESI^+): Calculated for $C_{48}H_{42}F_2N_2$ $[M+H]^+$,calculated 685.33943, found 685.33889.

IR (KBr): υ 2957, 2873, 1626, 1601, 1506, 1480, 1349, 1266, 1209, 819, 796 $cm.^{-1}$

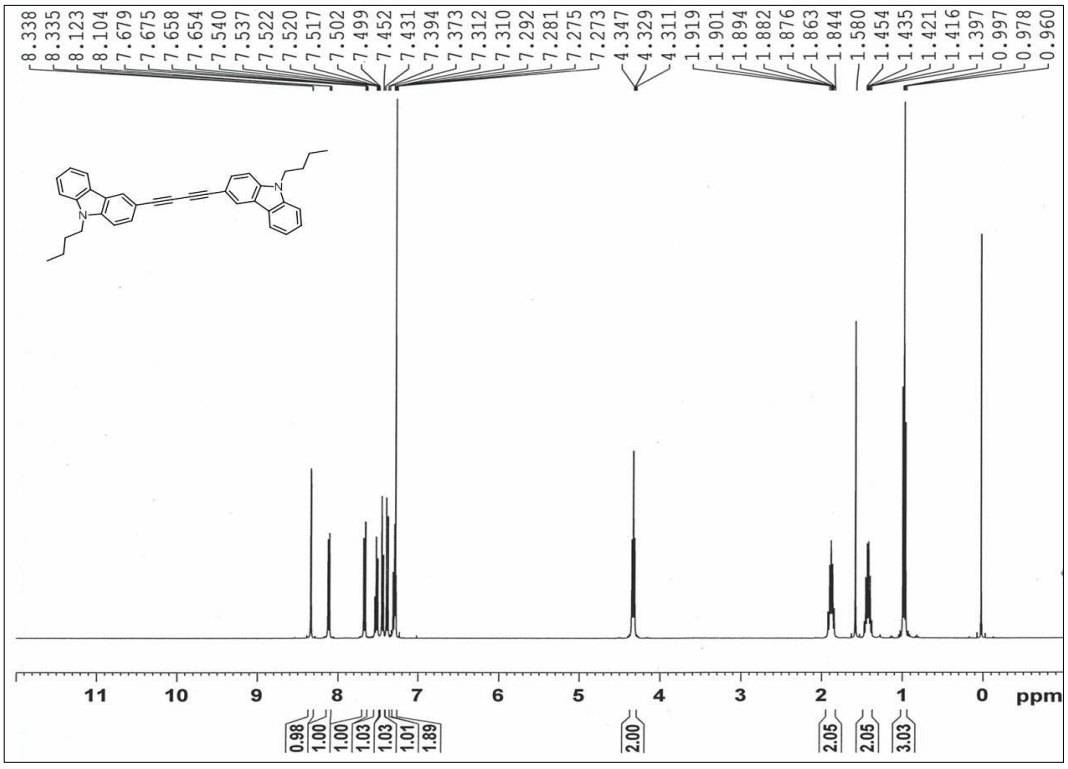
Spectral data for Carbazole derivatives



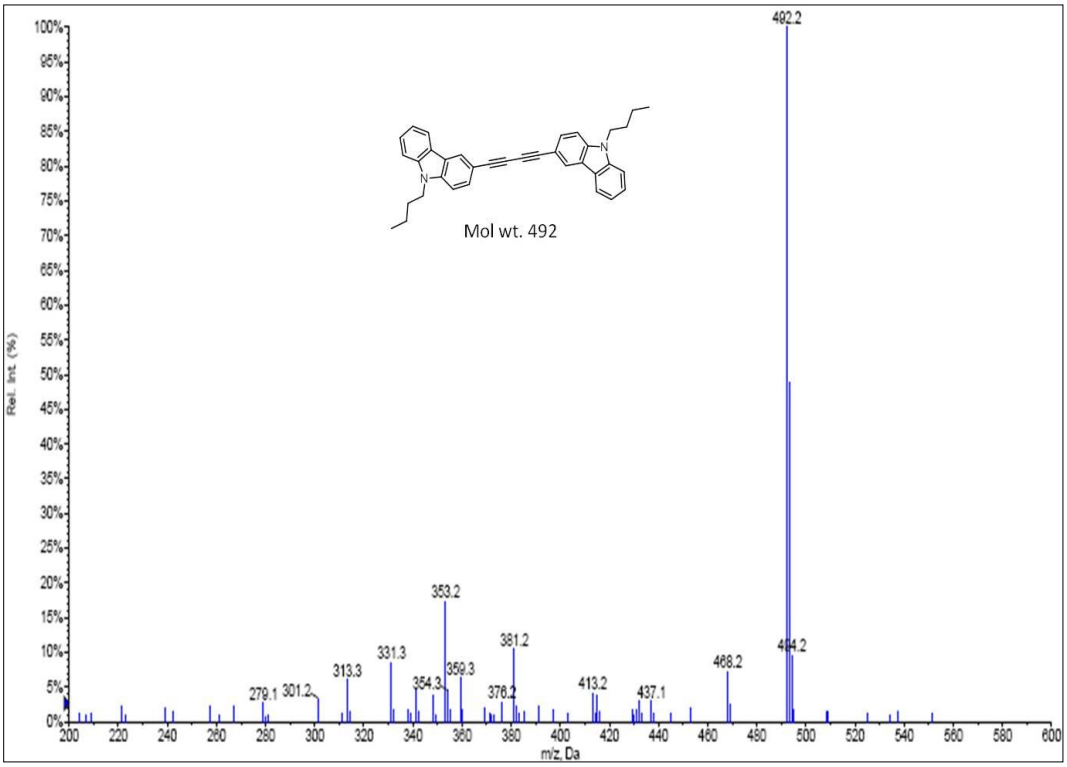
^{1}H-NMR of compound 25 ($CDCl_3$, 400 MHz)



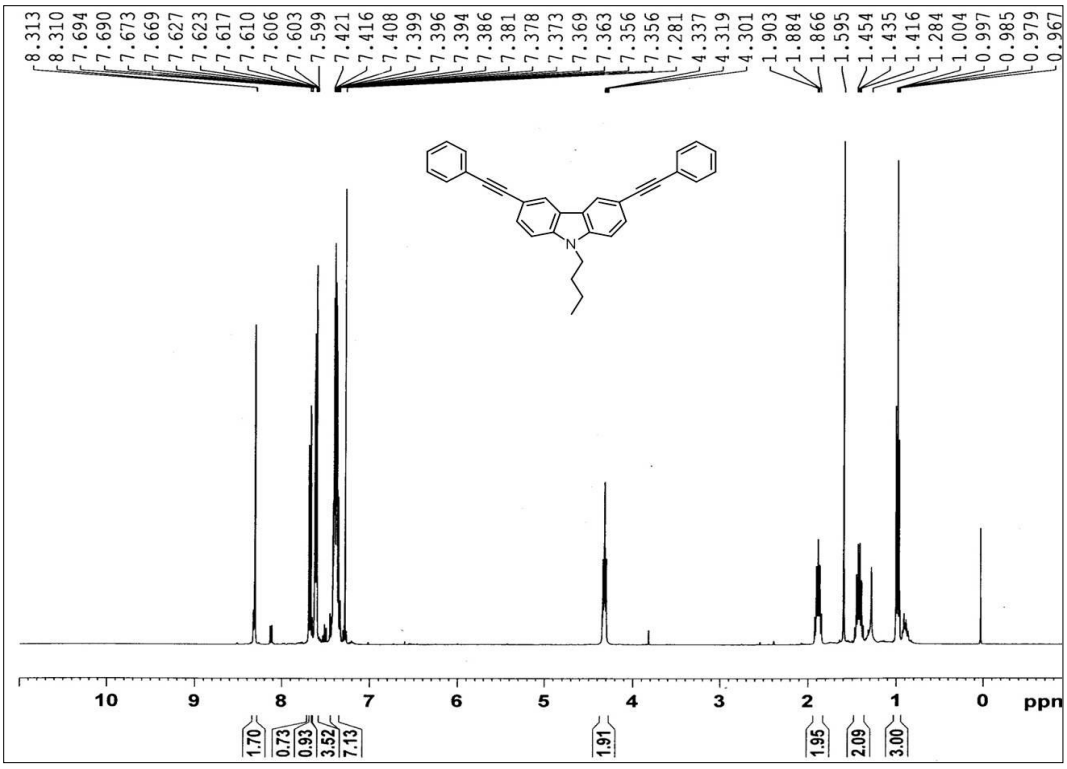
Mass spectra of compound 25



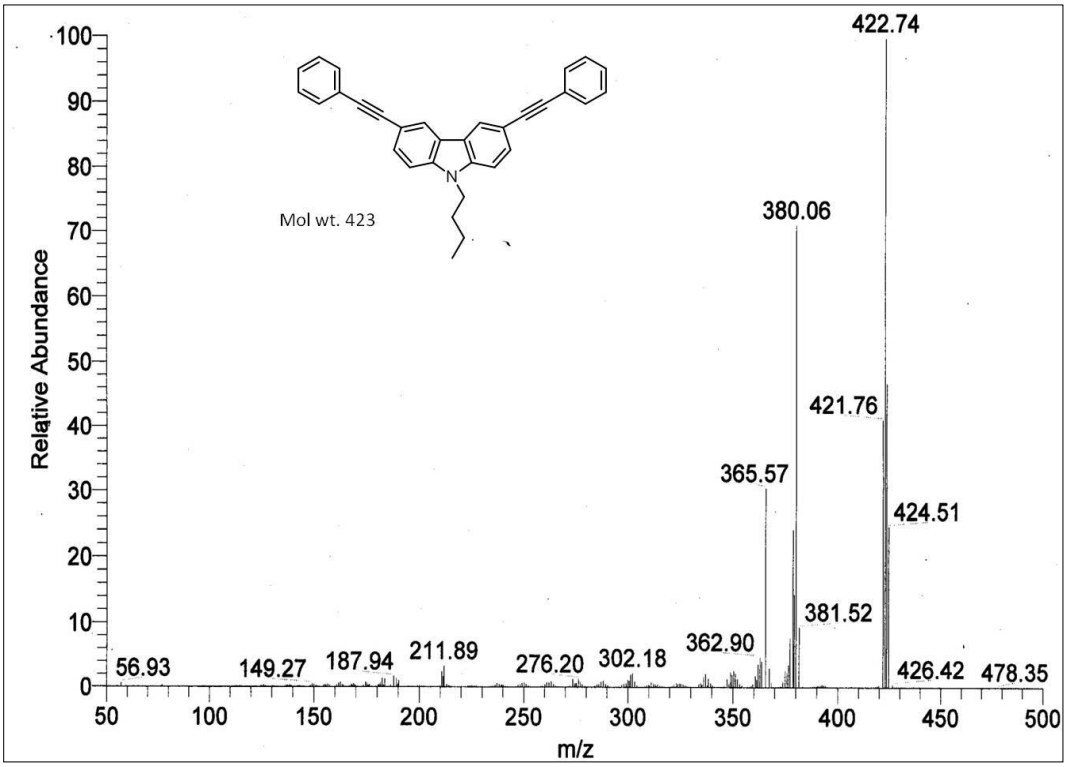
^{1}H-NMR of compound 27 ($CDCl_3$, 400 MHz)



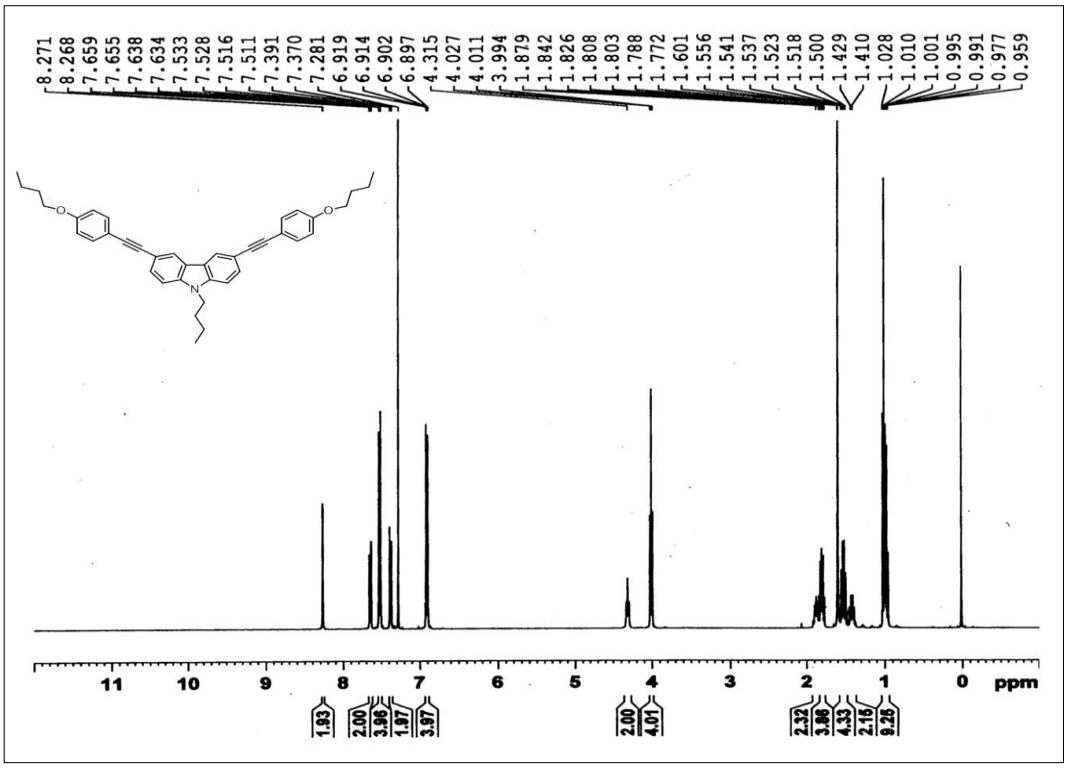
Mass spectra of compound 27



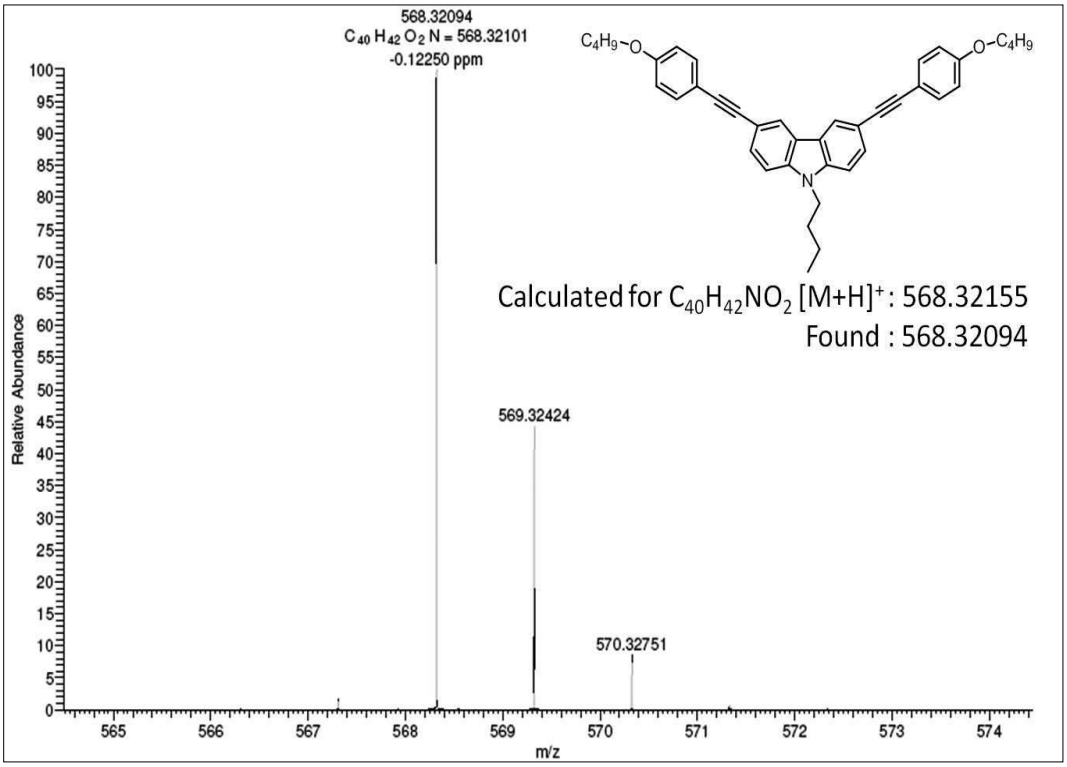
^{1}H-NMR of compound 30 ($CDCl_3$, 400 MHz)



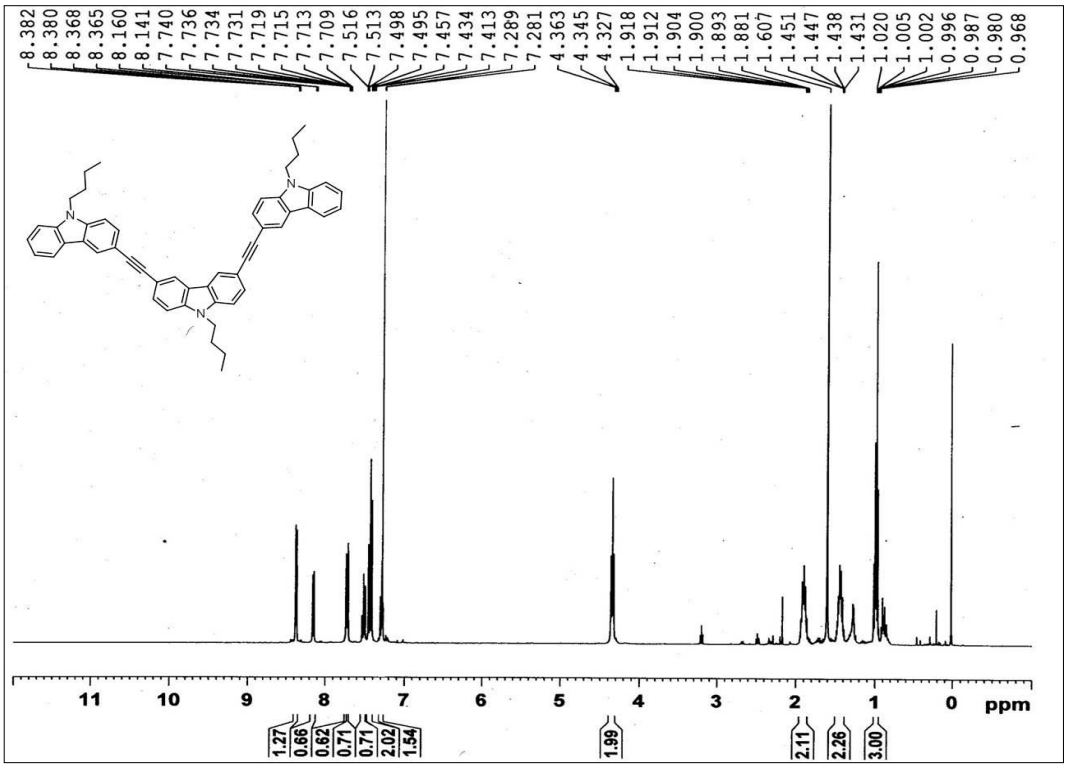
Mass spectra of compound 30



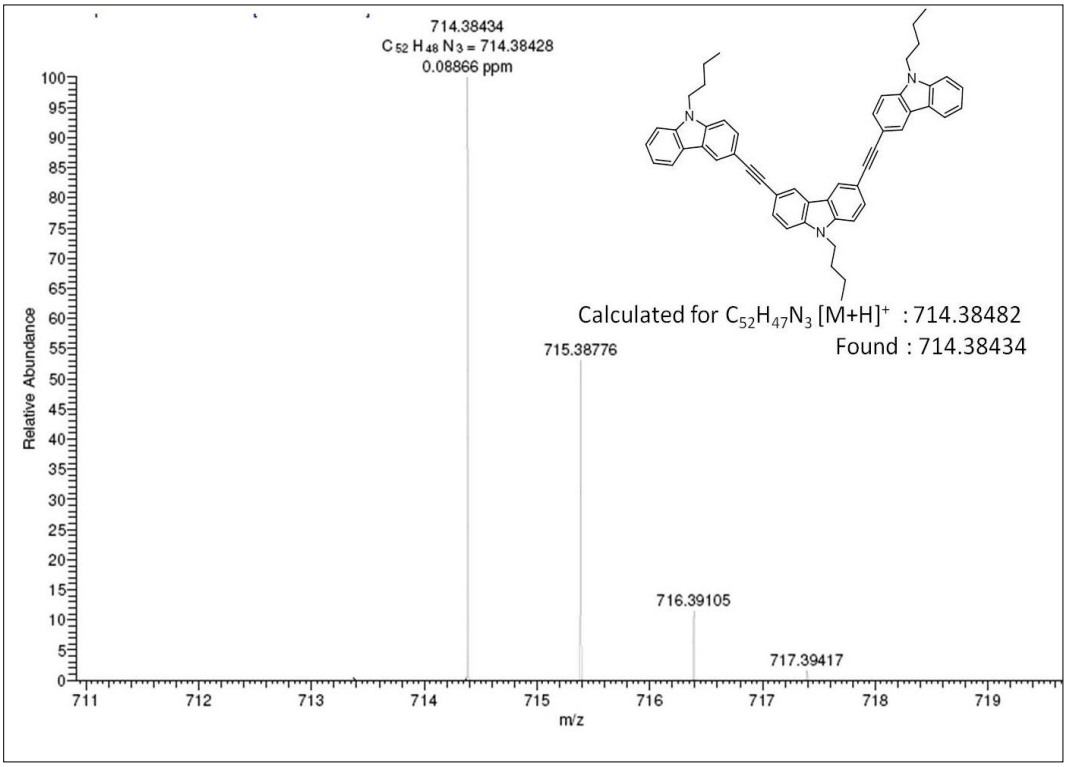
^{1}H-NMR of compound 31 ($CDCl_3$, 400 MHz)



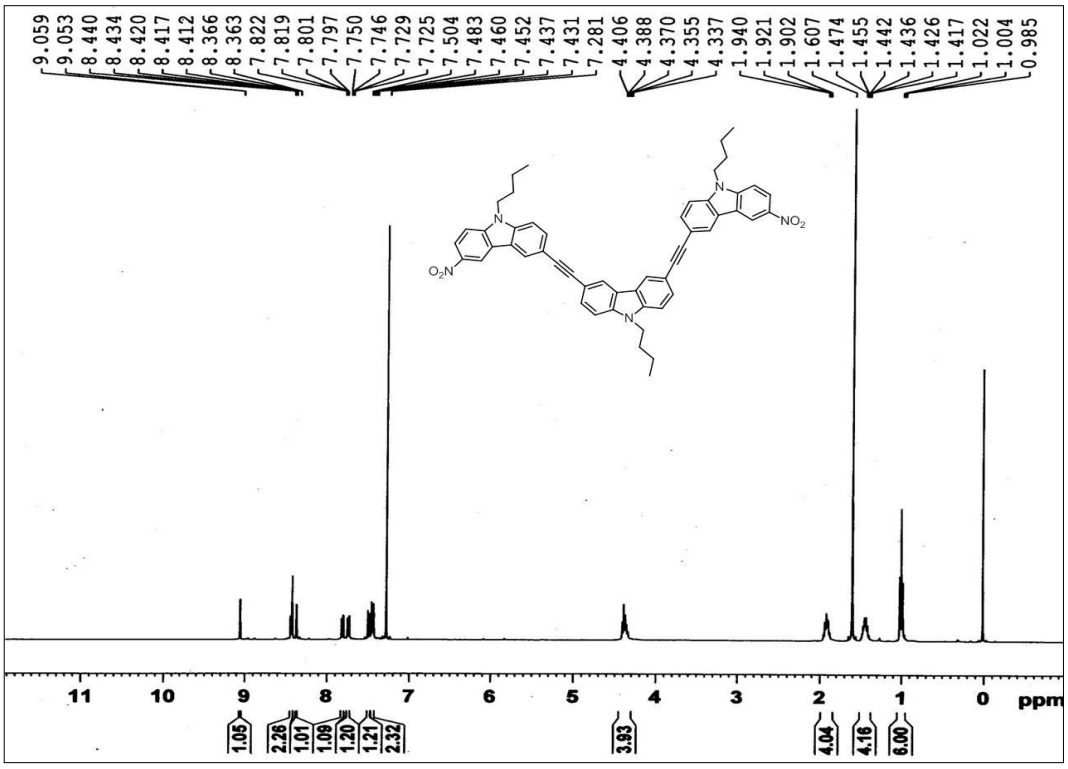
HRMS of compound 31



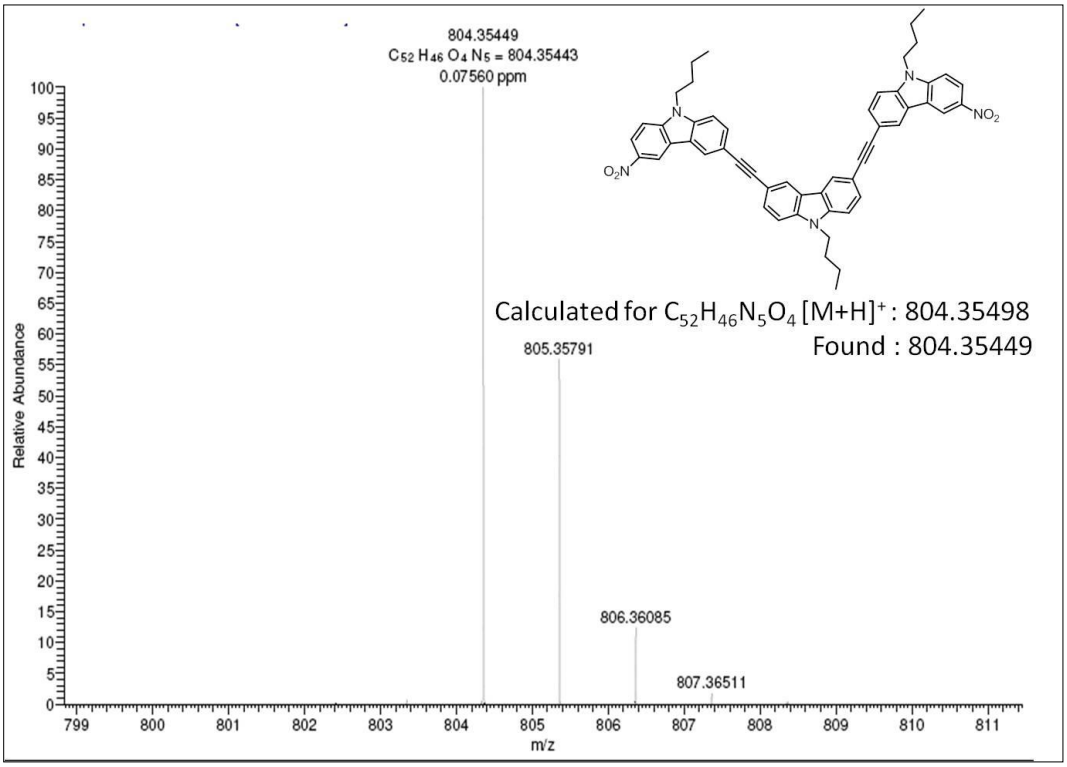
^{1}H-NMR of compound 32 ($CDCl_3$, 400 MHz)



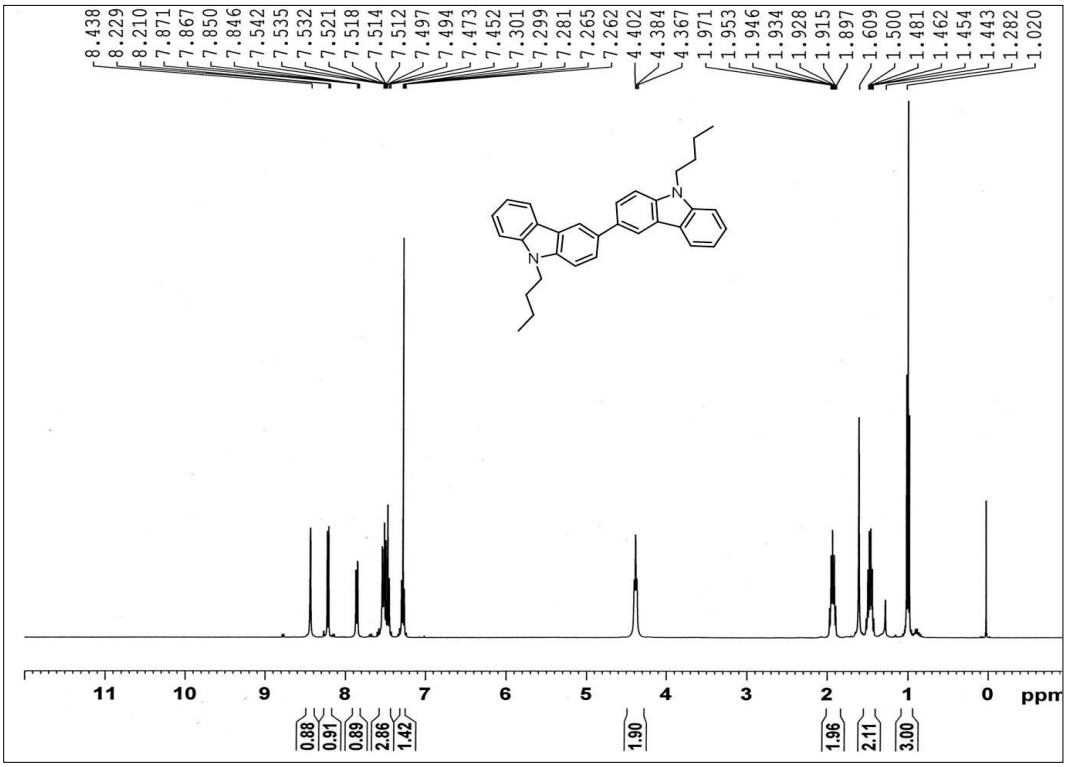
HRMS of compound 32



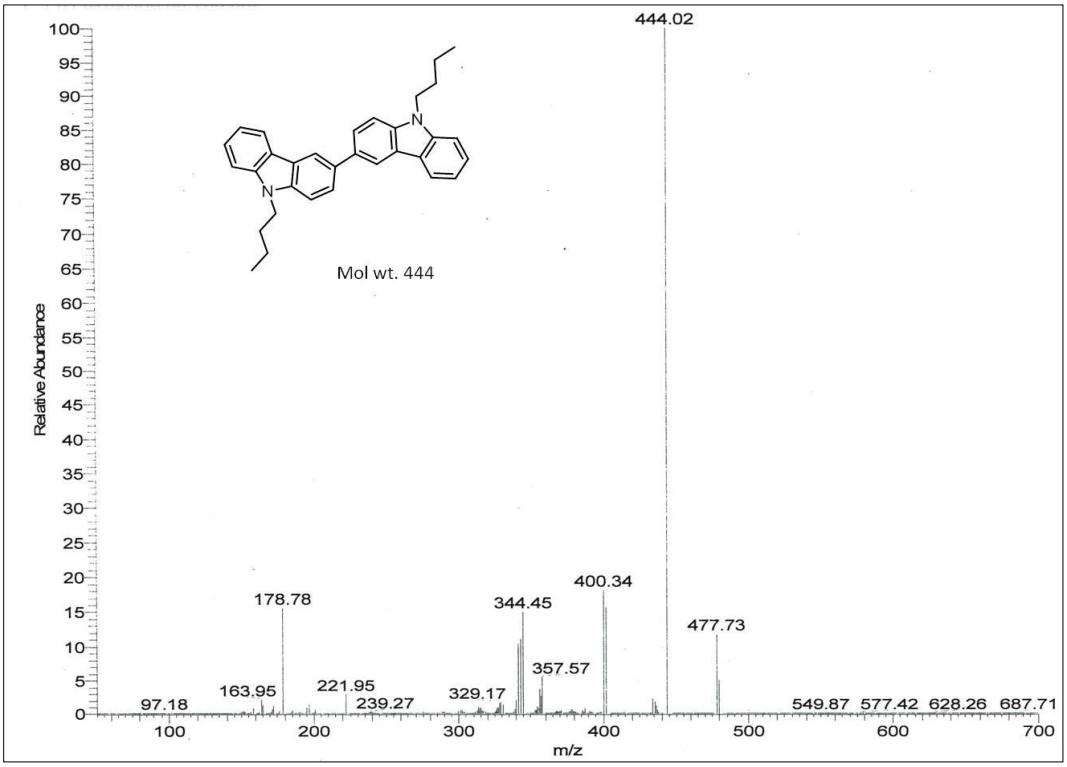
^{1}H-NMR of compound 33 ($CDCl_3$, 400 MHz)



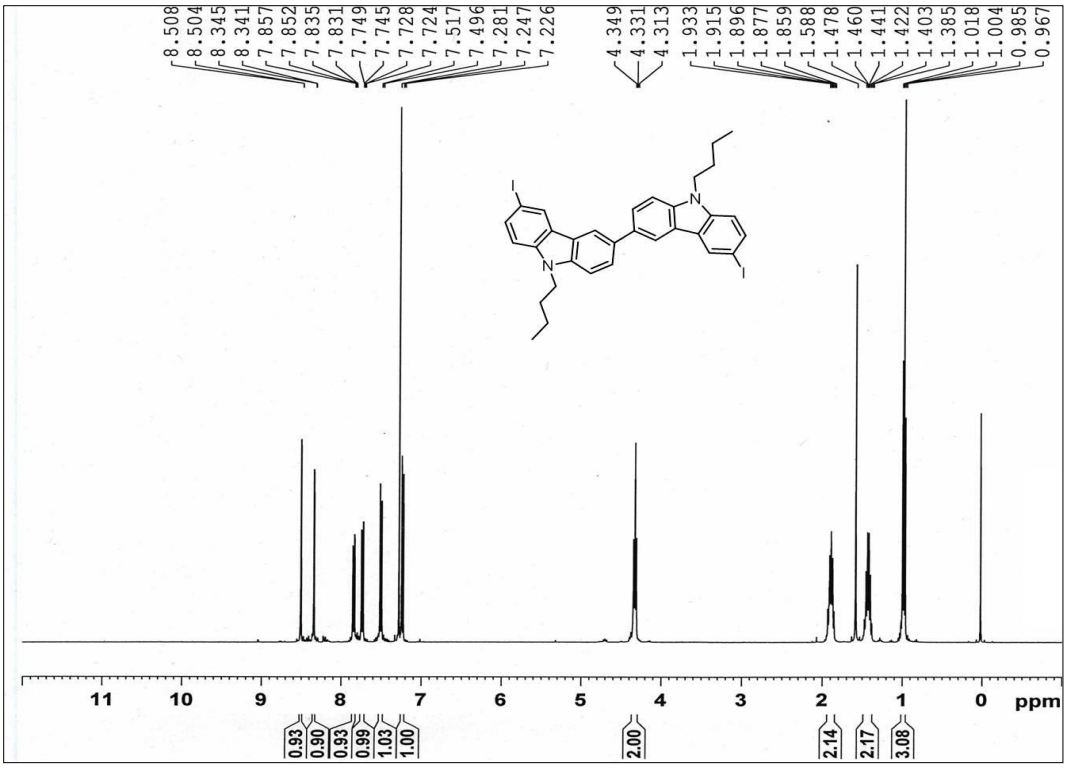
HRMS of compound 33



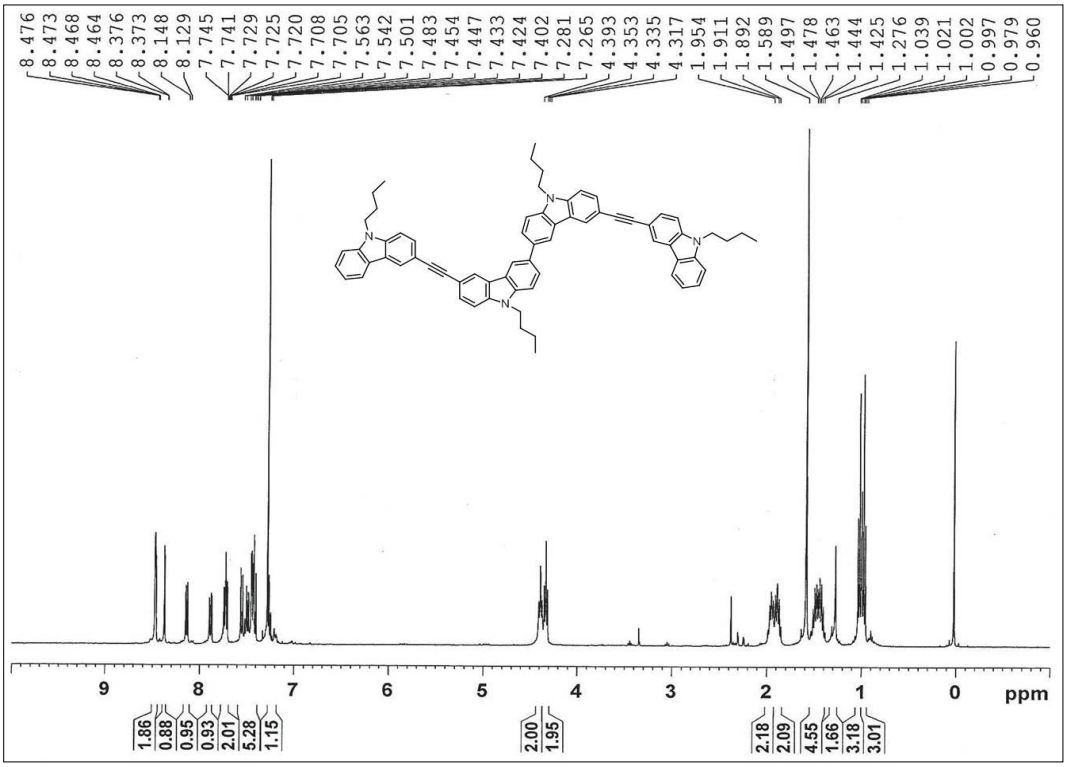
^{1}H-NMR of compound 34 ($CDCl_3$, 400 MHz)



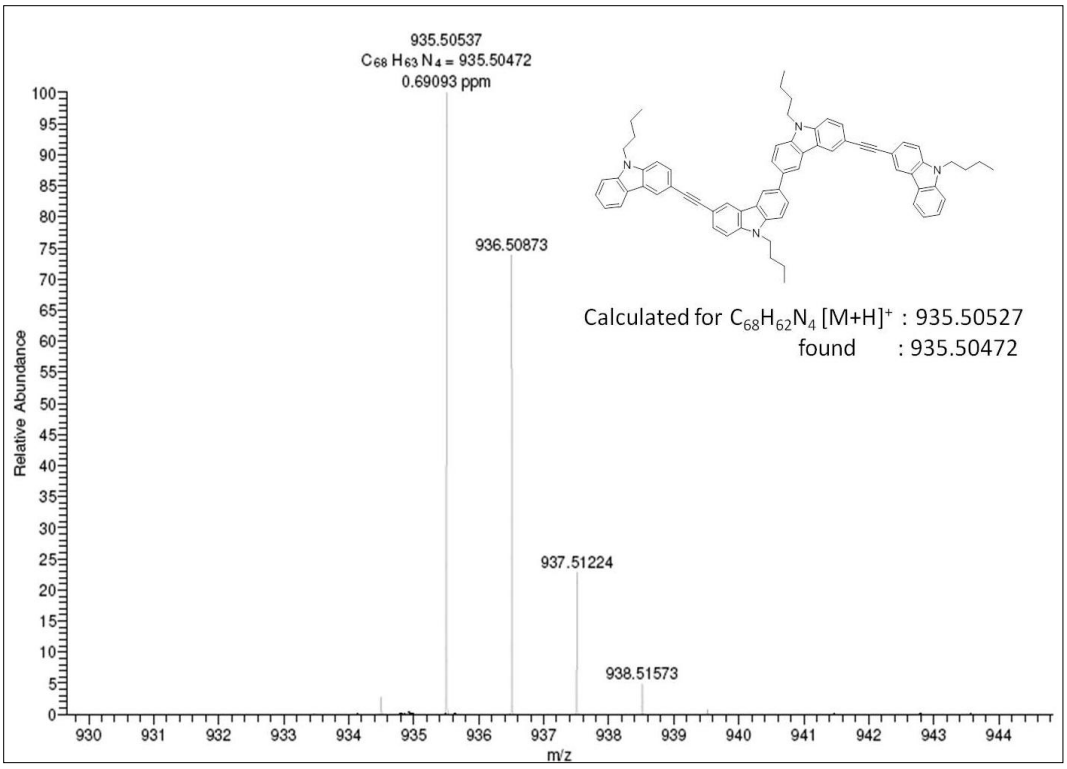
Mass spectra of compound 34



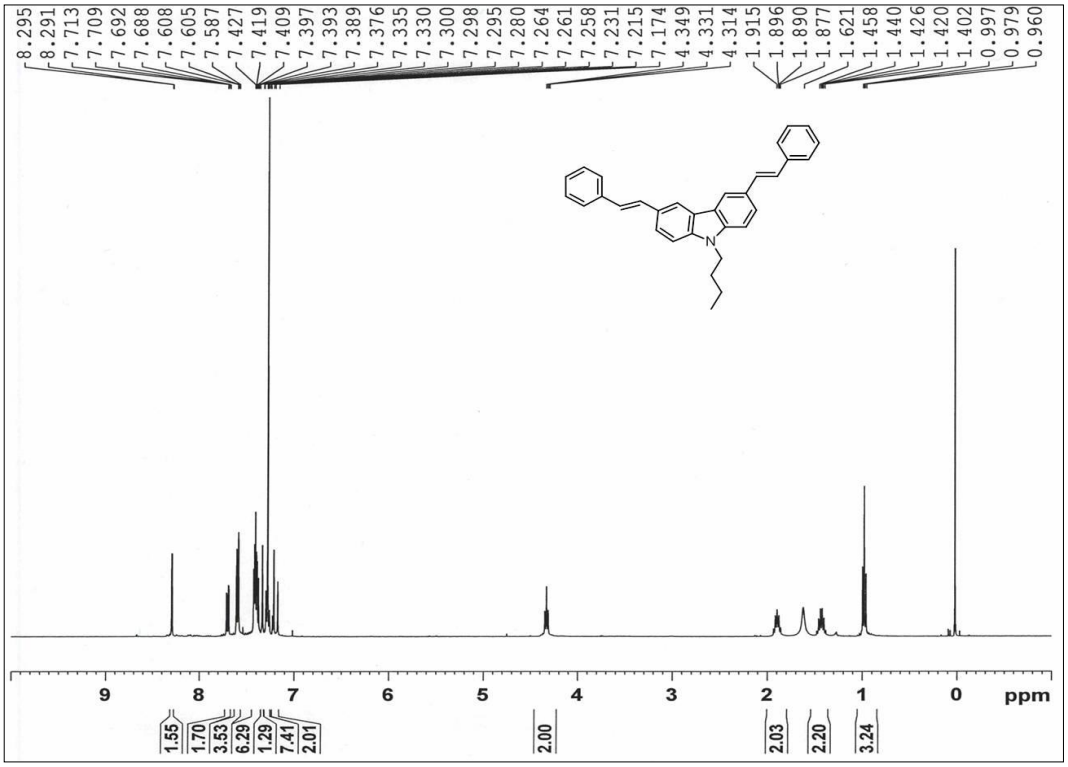
^{1}H-NMR of compound 35 ($CDCl_3$, 400 MHz)



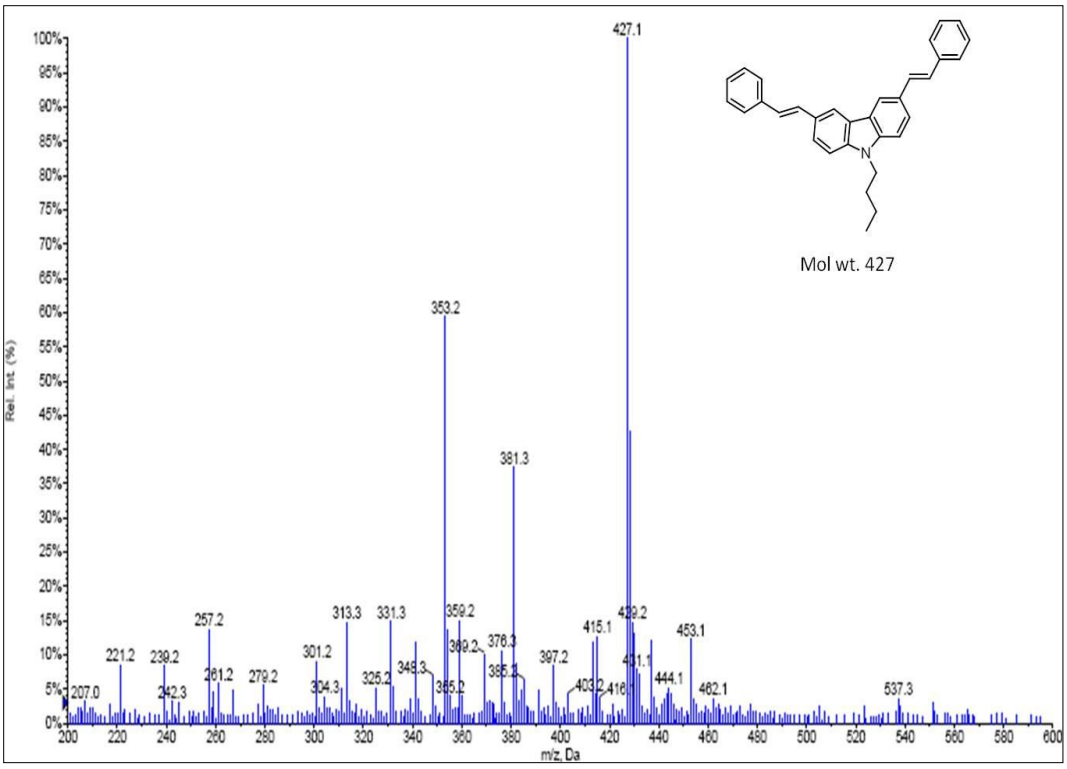
^{1}H-NMR of compound 36 ($CDCl_3$, 400 MHz)



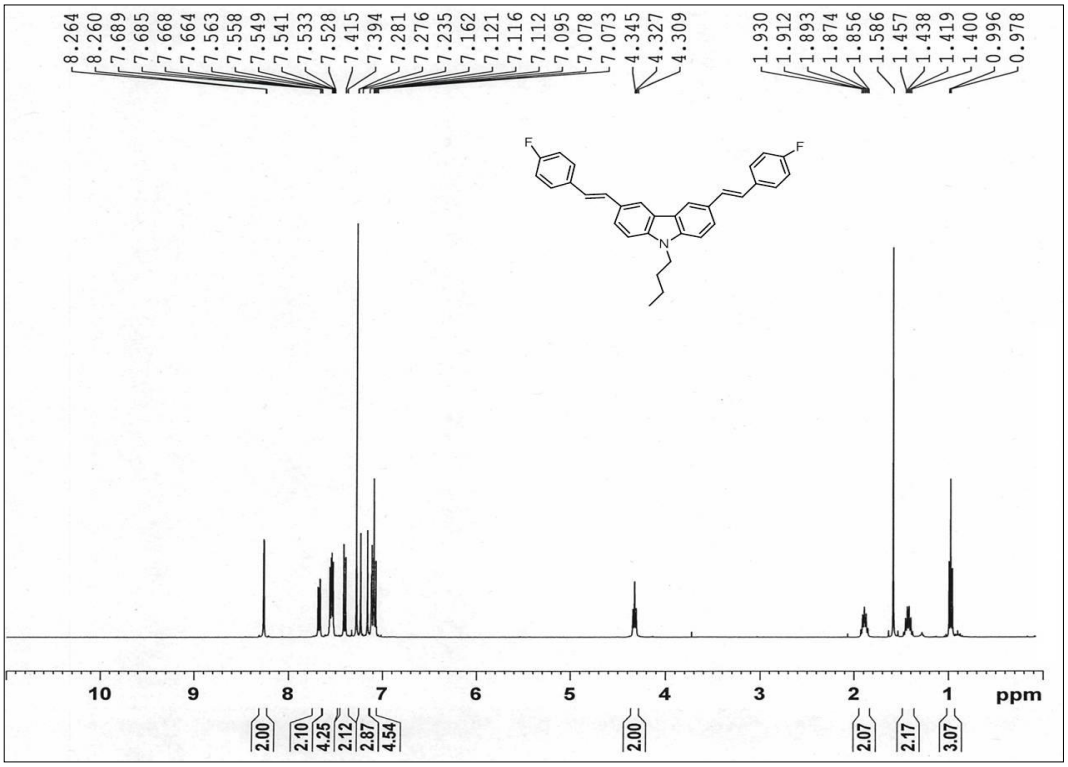
HRMS of compound 36



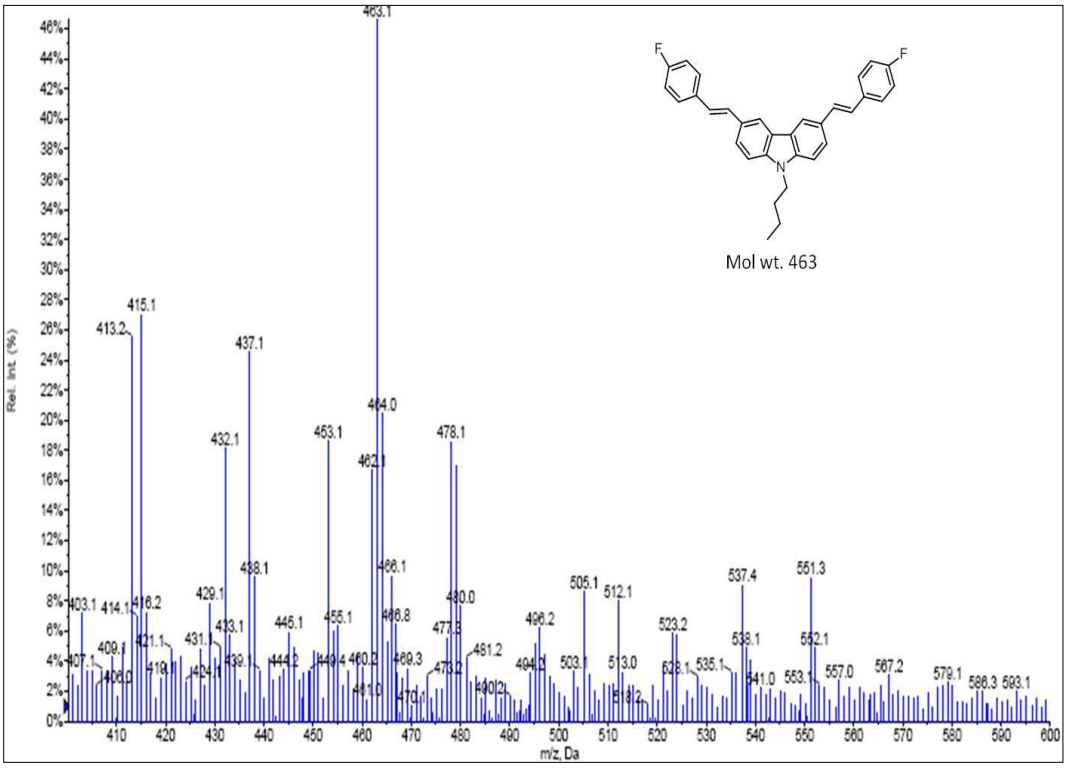
^{1}H-NMR of compound 38 ($CDCl_3$, 400 MHz)



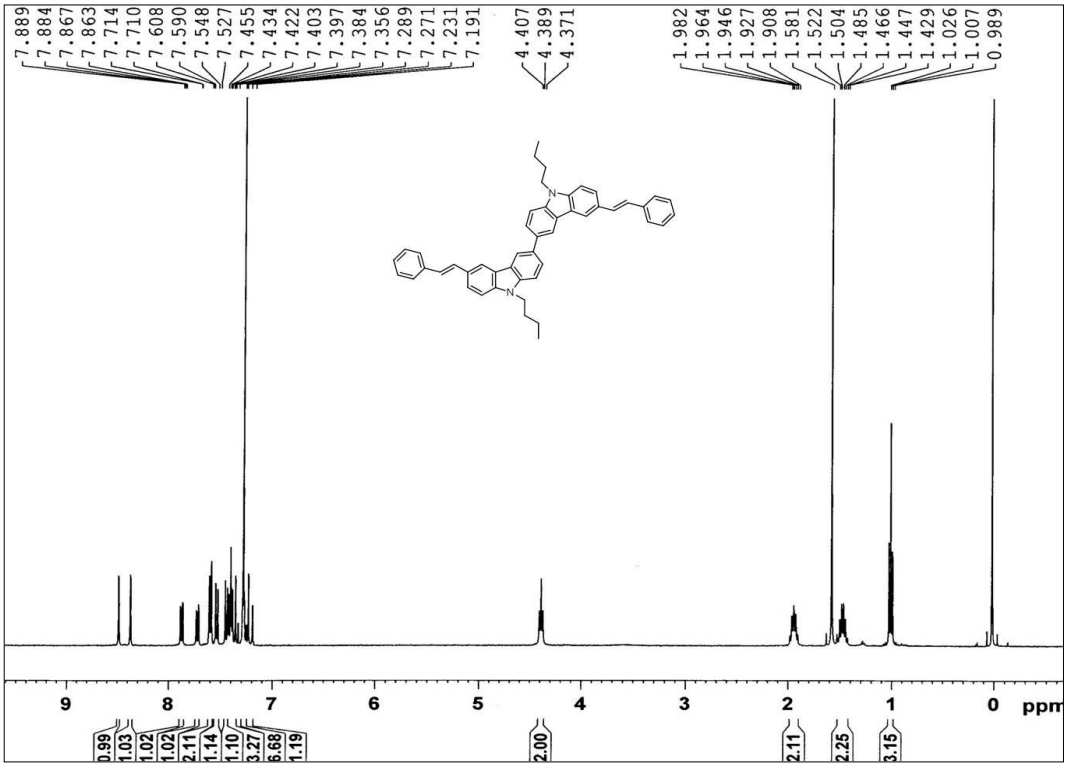
Mass spectra of compound 38



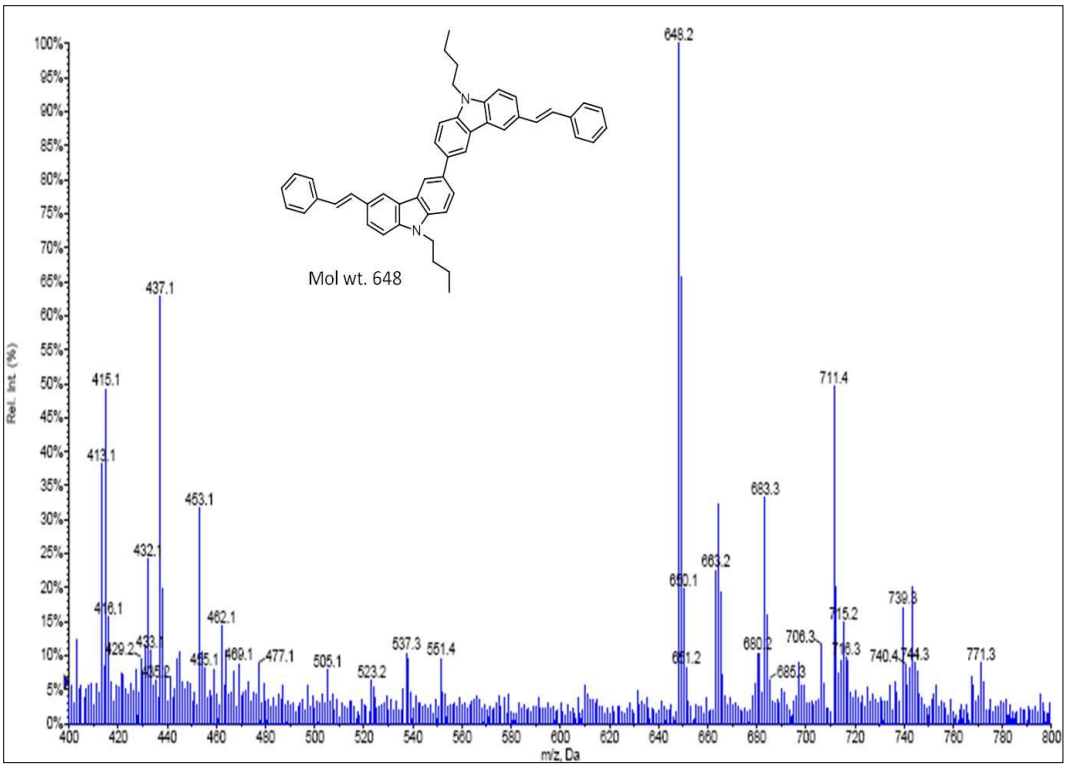
^{1}H-NMR of compound 39 ($CDCl_3$, 400 MHz)



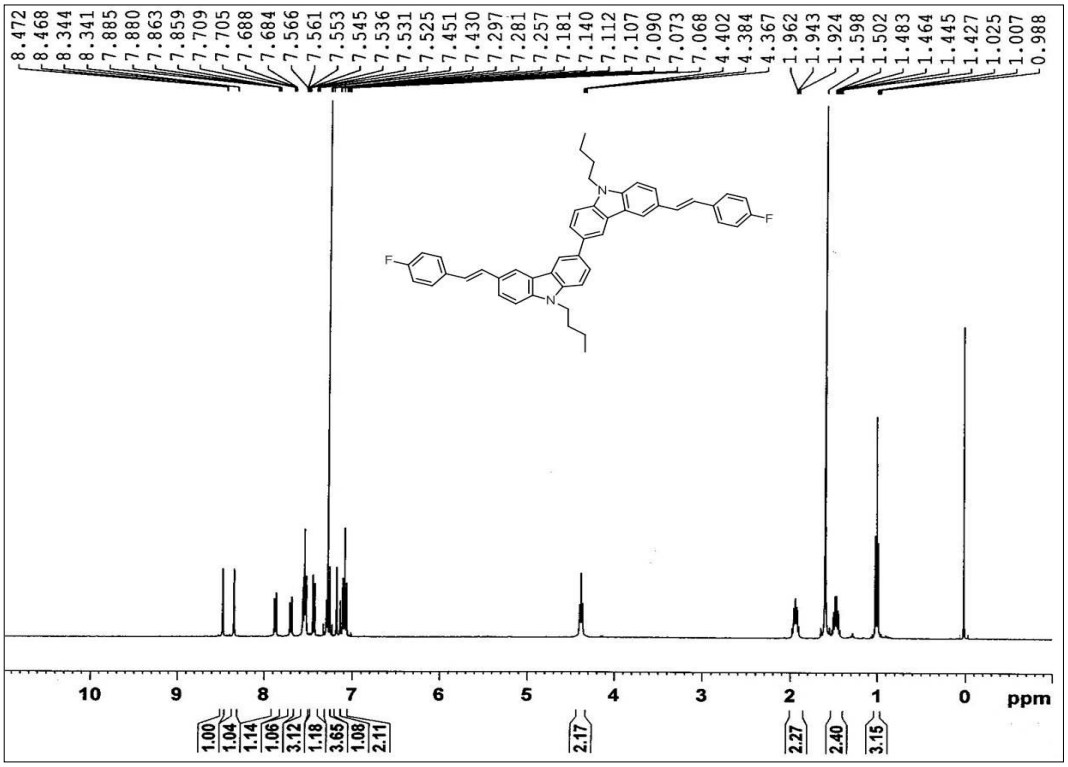
Mass spectra of compound 39



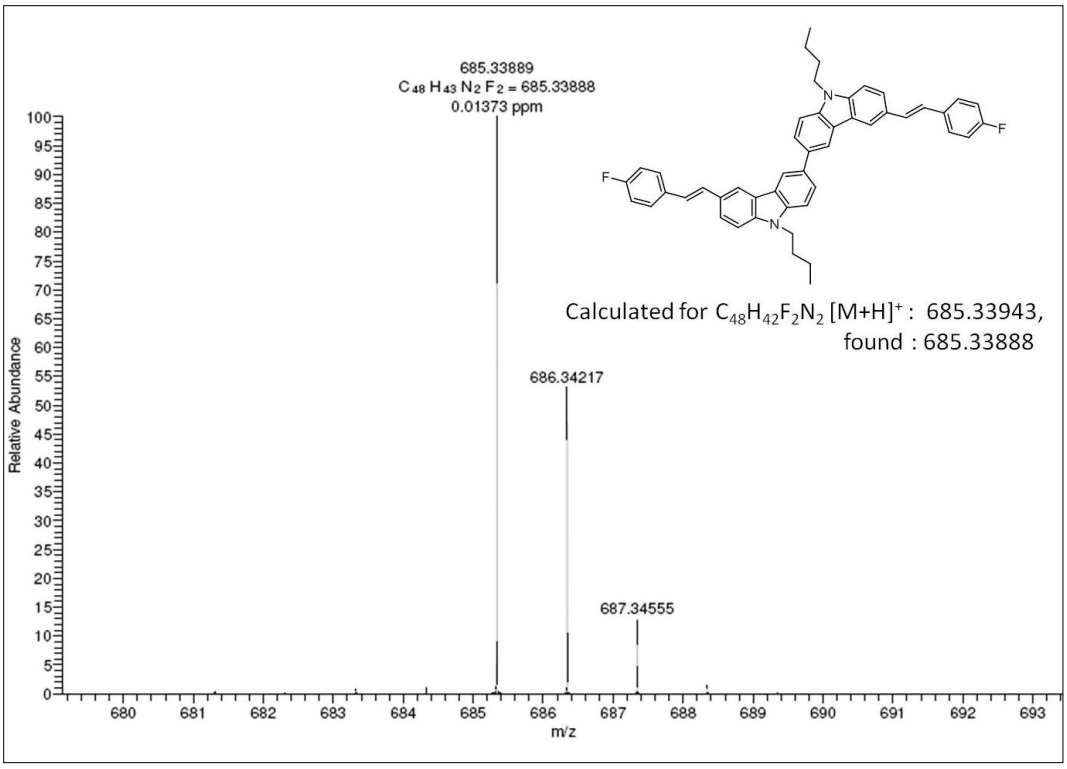
^{1}H-NMR of compound 41 ($CDCl_3$, 400 MHz)



Mass spectra of compound 41



^{1}H-NMR of compound 42 ($CDCl_3$, 400 MHz)



HRMS of compound 42

4.5 References

1. *http://en.wikipedia.org/wiki/Carbazole.*
2. Morin, J-F.; Leclerc, M.; Ades, D.; Siove, A. *Macromol. Rapid Commun*. **2005**, *26*, 761.
3. Yang, J.-X.; Tao, X.-T.; Yuan, C. X.; Yan, Y. X.; Wang, L.; Liu, Z.; Ren, Y.; Jiang, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 3278.
4. Adhikari, R. M.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem*. **2007**, *72*, 4727.
5. Lengvinaite, S.; Grazulevicius, J. V.; Grigalevicius, S.; Zhang, B.; Yang, J.; Xie, Z.; Wang, L. *Synth. Met*. **2008**, *158*, 213.
6. Grazulevicius, J.V. *Polym. Adv. Technol*. **2006**, *17*, 694.
7. Tomkeviciene, A.; Grazulevicius, J.; *Mater. Sci.-Medziagotyra* **2011**, *17*, 335.
8. Strohriegl, P.; Grazulevicius, J.V.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci*. **2003**, *28*, 1297.
9. Bhalla, V.; Singh, G.; Kumar, M.; Singh, C.; Rawat, M.; Anand, R. S. *RSC Adv*., **2013**, *3*, 147220.
10. Kato, S-I.; Noguchi, H.; Kobayashi, A.; Yoshihara, T.; Tobita, S.; Nakamura, Y. *J. Org. Chem.* **2012**, *77*, 9120.
11. Thomas, K.; Lin, J.; Tao, Y.; Ko, C. *J. Am. Chem. Soc.*, **2001**, *123*, 9404.
12. Sun, J.; H. Jiang, H.; Zhang, J.; Tao, Y.; Chen, R. *New J. Chem.*, **2013**, *37*, 977.
13. Balionyte, A.; Lideikis, E.; Grigalevicius, S.; Ostrauskaite, J.; Burbulis, E.; Jankauskas, V.; Montrimas, E.; Grazulevicius, J. *J. Photochem. Photobiol. A: Chem.* **2004**, *162*, 187.
14. Vaitkeviciene, V.; Kruzinauskiene, A.; Grigalevicius, S.; Grazulevicius, J.; Rutkaite, R.; Jankauskas, V. *Synth. Met.* **2008**, *158*, 383.
15. Stanionyte, R.; Buika, G.; Grazulevicius, J.; Grigalevicius, S. *Polym. Int*. **2008**, *57*, 1036.
16. Rasymaite, D.; Griniene, R.; Grazulevicius, J.; Liub, L.; Zhang, B.; Xie, Z.; Grigalevicius, S. *Optical Materials*, **2013**, *35*, 2072.
17. Saiyed, A. S.; Bedekar, A. V. *Tetrahedron Lett.* **2010**, *51*, 6227.
18. Moonsin, P.; Prachumrak, N.; Namuangruk, S.; Jungsuttiwong, S.; Keawin, T.; Sudyoadsuka, T.; Promarak, V. *J. Mater. Chem. C* **2014**, *2*, 5540.
19. Michinobu, T.; Osako, H.; Shigehara, K. *Macromolecules*, **2009**, *42*, 8172.

20. Zhao, T.; Liu, Z.; Song, Y.; Xu, W.; Zhang, D.; Zhu, D. *J. Org. Chem.* **2006**, *71*, 7422.
21. Bogdal, D.; Lukasiewicz, M.; Pielichowski, J. *Green Chem.***2004**, *6*, 110
22. Yang, P.; Wu, W.; Zhao, J.; Huang, D.; Yi, X. *J. Mater. Chem.*, **2012**, *22*, 20273.
23. Grigalevicius, S.; Lideikis, E.; Grazulevicius, J. V.; Gaidelis, V.; Jankauskas, V. *Environmental and Chemical Physics*, **2001**, *23*, 77.
24. Lia, L.; Wua,Y.; Zhoua, Q.; Heb, C. *J. Phys. Org. Chem*. **2012**, *25*, 362.