RSC Advances

REVIEW

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Cite this: *RSC Adv.*, 2019, **9**, 16606

An overview on synthetic strategies for the construction of star-shaped molecules

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Strategies for the synthesis of star-shaped molecules have been in high demand in the last decades due to the importance of those compounds in various fields. The distinctly different properties of these compounds compared to their linear analogues make them versatile building blocks for the formation of mesophases of interesting mesomorphic and photophysical properties. Moreover, the applications of star-shaped molecules as building units for dendrimers as well as in supramolecular host–guest chemistry have also been recently studied. The star-shaped molecules mentioned in this review are classified according to the central core as well as the type of side arms. The properties and applications of these compounds are described in the appropriate contexts. This report summarizes the recent advances in this area.

Received 11th April 2019
Accepted 7th May 2019

DOI: 10.1039/c9ra02749a

rsc.li/rsc-advances

1. Introduction

Star-shaped molecules (SSMs) are a class of branched compounds with a general structure consisting of several (three or more) linear chains connected to a central core. Star-shaped molecules began to draw the interest of chemists and physicists in the last decades due to distinctly different properties as compared to their linear analogues. Over the years, interesting names have been given to these molecules in an attempt to describe these complex structures like tripodal, tetrapodal, octopus, hexahost or multi-armed molecules. In 1948, Schaefgen and Flory reported the synthesis of the first star-shaped polyamides.[1] In 1962, Morton *et al.* reported the synthesis of tetra-liked branched polystyrene through anionic polymerization. Due to its shape, this polymer was named for the first time as a star molecule.[2] The name star-shaped molecules (SSMs) was then given to all structures, even small molecules, in which more than two arms are attached symmetrically to a single multifunctional core. Compared to polymer materials, small molecules offer potential advantages in terms of defined molecular structure, definite molecular weight, easy purification, and good batch-to-batch reproducibility.[3–5]

Some derivatives of these compounds were synthesized as promising molecules for application in optoelectronics and electrochromic devices.[6–17] The structure of such molecules makes them versatile building blocks for the

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formation of mesophases of interesting mesomorphic and photophysical properties.[18–31] The applications of star-shaped molecules as building units for dendrimers[32,33] as well as in supramolecular host–guest chemistry have been also reported.[34,35] Moreover, the interesting biological activities of some diverse multivalent scaffolds adamantane have been recently investigated.[36] Some of these compounds were designed to study their promising photovoltaic application in organic solar cells OSCs.[37–55]

The present review casts light on the main strategies for the synthesis of star-shaped molecules especially those containing heterocyclic core and/or heterocyclic arms. The star-shaped molecules mentioned in this review are classified according to the central core as well as the type of side arms.

The properties and applications of these compounds are described in the appropriate contexts.

Mohamed R. Shaaban was born in 1971 in Cairo, Egypt. He graduated from Cairo University, Egypt in 1992 then he joined Professor Ahmad M. Farag's research group. He received his Ph.D. in 2001 at Tokyo, Institute of Technology, Japan. In 2001 he was promoted to a Lecturer of Organic Chemistry at Cairo University and continued his research work on organic synthesis as well as on palladium catalyzed C–C cross-couplings. In 2009 he was promoted to Associate Professor of Organic Chemistry, and in 2014 he was promoted to Professor of Organic Chemistry at the Faculty of Science, Cairo University.

Ismail A. Abdelhamid was born in Egypt in December 1978. He graduated from Cairo University, Egypt in 2001 then he obtained his M.Sc. and Ph.D. degrees in 2005 and 2007, respectively, at Cairo University in the field of organic synthesis. In 2017 he was appointed as a full Professor of Organic Chemistry at Cairo University. He was awarded the Alexander von Humboldt research fellowship in 2008–2011 and in 2014, 2017, and 2019 with Prof. Holger Butenschön, at Hannover University, Germany. He received several research prizes; Cairo University Incentive Award (2012), Cairo University Scientific Excellence Award (2016) and State Incentive Award (2019).

To the best of our knowledge, a number of other reviews[24,56–67] that have appeared, concerning the chemistry of star-shaped molecules, did not pay special attention to the synthesis of such systems in an organized manner with respect to central core as well as the type of side arms. The review will cover the literature in this area over the last decades. Star-shaped molecules based on triphenylamine, truxene or other polycyclicaromatic cores have been recently reviewed and will not be mentioned in this review.[56,61,66]

The reported yields of the target molecules in this review are those given in the last step reaction except when an overall yield was given.

2. Classification of star-shaped molecules

A schematic illustration of the classification of star-shaped molecules (SSMs) is depicted in Fig. 1. The cores and the side arms are the main factors in this classification. The cores are usually an atoms (C, Si, Ge and N), acyclic aliphatic (asparatic, glutamic, pentaerythritol and tris(2-aminoethyl)amine), cyclic aliphatic (cyclohexatrione and polyhedral oligomeric silsesquioxane (POSS)), aromatic (benzene, truxene, isotruxene, hexa-*peri*-hexabenzocoronene, hexakisfluorenylbenzene, oligofluorene and hexatriphenylene), heteroaromatic (1,3,5-triazine, pyrimidine, phenylquinoxaline, phenylcarbazole, oligothiophene, triindole, benzodifuran, benzodithiophene, benzotrithiophene, thieno[3,2-*b*]thiophene, dithienyl naphthothiophene, tetrathienoanthracene, naphthalimide-fused pyrazinacenes, triazatrinaphthylene, pyrrole-fused TTF and triazatruxene). It is worthy to mention that that benzene and 1,3,5-triazine are considered as the most popular aromatic and heterocyclic cores, respectively. Side arms may also contain aliphatic, aromatic or heterocyclic moieties. The incorporation of heterocyclic systems into the structure of the star-shaped molecules is highly useful for optical and electronic applications.

Ahmed H. M. Elwahy was born in 1963 in Giza, Egypt. He graduated from Cairo University, Egypt in 1984 then he obtained his M.Sc. and Ph.D. degrees in 1988 and 1991, respectively, at Cairo University in the field of organic synthesis. He was awarded the Alexander von Humboldt research fellowship in 1998–2000 and in 2003, 2005, 2009, 2010 and 2012 with Prof. Klaus Hafner, at TU Darmstadt, Germany. In 2002 he was appointed as a full Professor of Organic Chemistry at Cairo University. In 2001 he received the State-Award in Chemistry. He has published around 120 scientific papers in distinguished international journals.

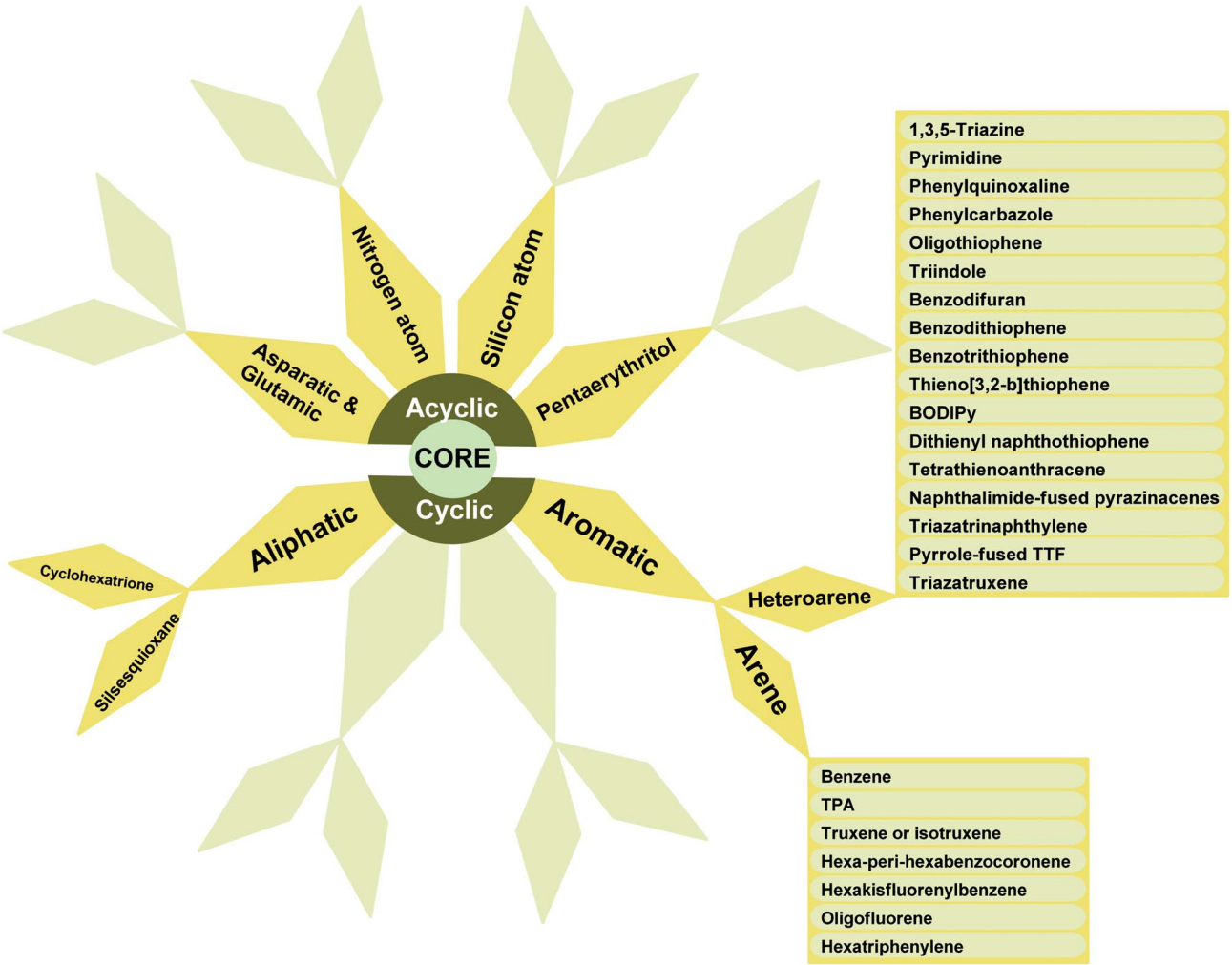
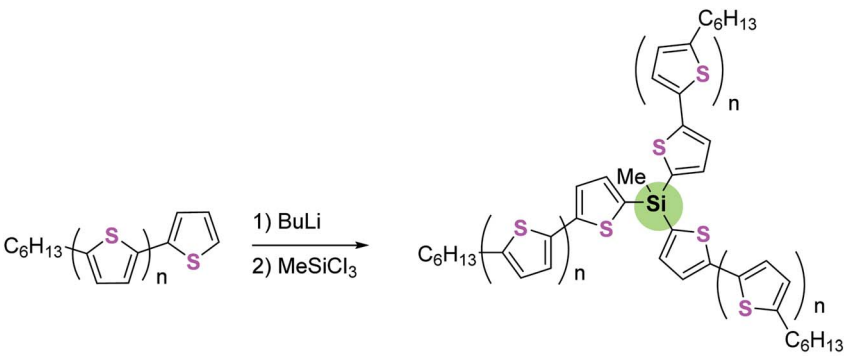


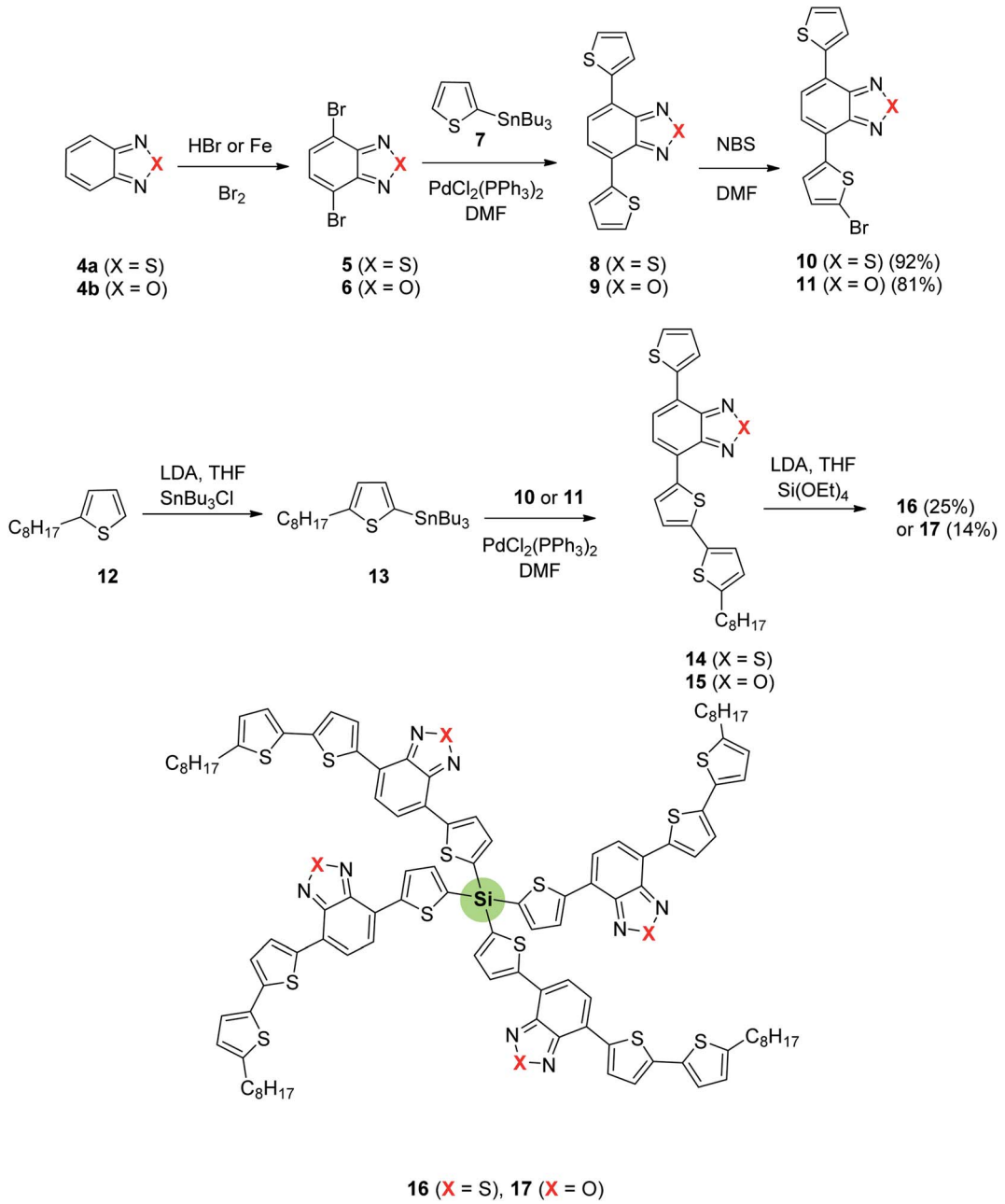
Fig. 1 Core-based classification of star-shaped molecules.

3. General synthetic approaches for star-shaped molecules

This section summarizes the synthetic approaches that have been developed for the synthesis of star-shaped molecules mentioned in this review. Generally, SSMs were synthesized from poly-functionalized building blocks which are then manipulated to generate the target compounds using mainly the following reactions:



Scheme 1 Synthesis of star-shaped oligothiophenesilanes **3**.



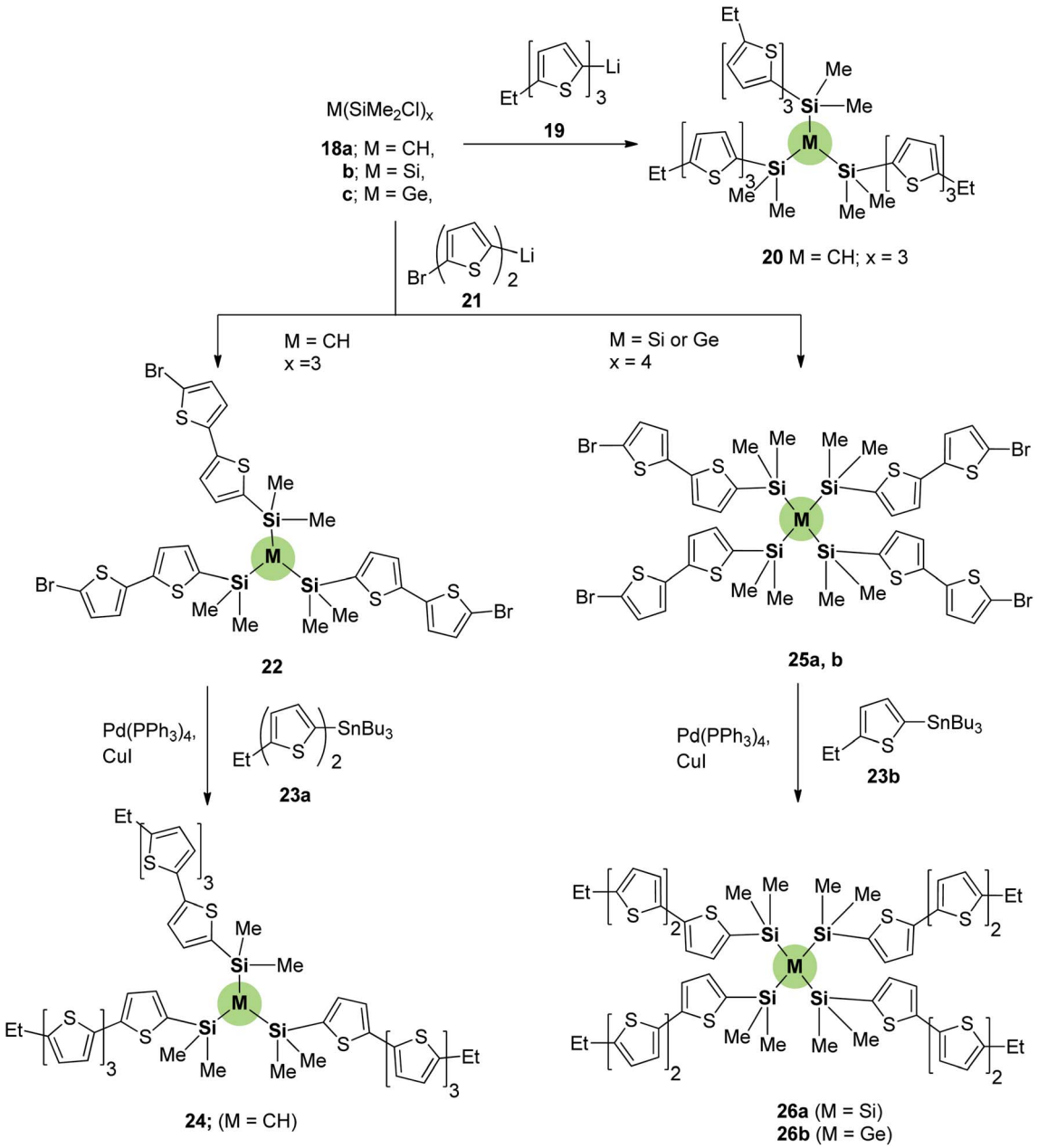
Scheme 2 Synthesis of four-armed SSMs with silicon atom-core **16** and **17**.

3.1. *O*-, *S*- and *N*-Alkylation reactions

The star shaped molecules were prepared in this case by polyalkylation of the appropriate alcohol, phenols, heterocyclic thiol, aromatic or heteraromatic amines with a variety of alkyl or aryl halides. The reactions are fast, operationally simple, and allows rapid access to a variety of poly(-heterocyclic) derivatives. Achieving selectivity in these reactions or prediction of the site of the alkylation remains a challenging point for substrates with more nucleophilic centers.

3.2. Cyclocondensation reactions

SSMs prepared using this strategy depends mainly on the formation of polychalcones and subsequent reaction with hydrazine derivatives to give the corresponding polydihydropyrazoles. Polythiazoles can also prepared by cyclocondensation of polythiosemicarbazones with the appropriate α-haloketones. Moreover, cyclization of polybenzoylhydrazides with $POCl_3$ was reported to give polyoxadiazole derivatives. Furthermore, cyclocondensation of 3-aminobut-2-enenitrile with polyaldehydes represent one of the most interesting



Scheme 3 Synthesis of silicon-cored SSMs **20**, **24**, **26a** and **26b**.

approaches which led to the formation of polydihydropyridines. Although the overall yields of these reactions are moderate, only a small library of poly(heterocycles) prepared by this strategy are available.

3.3. Cyclotrimerization reactions

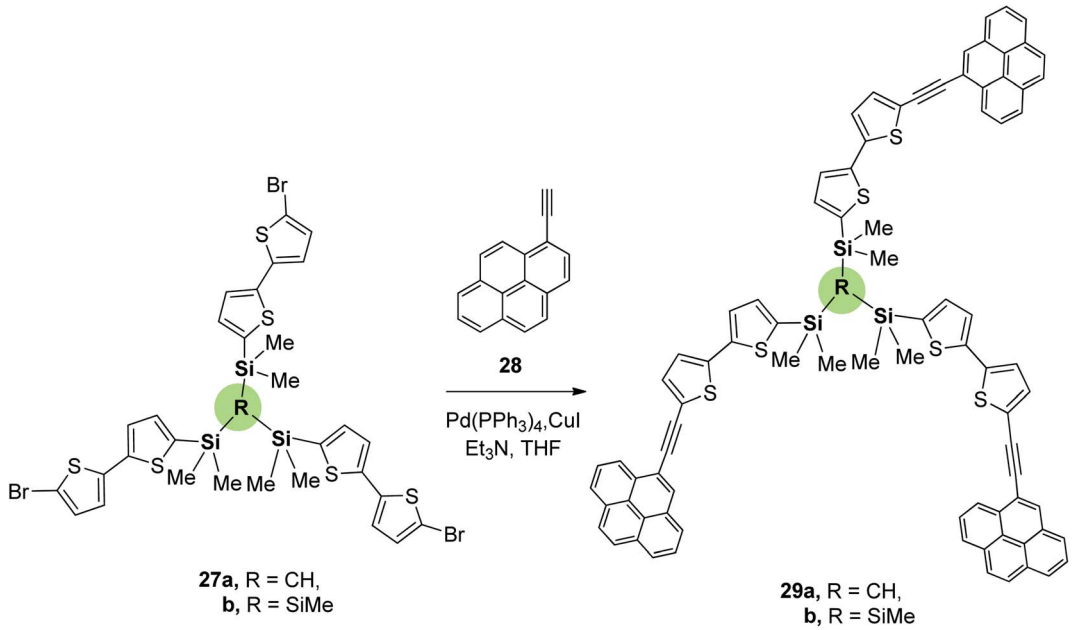
This reaction was used to prepare tris(thiophenyl)benzenes *via* cyclotrimerization of 2-acetylylthiophene derivatives upon treatment with $SiCl_4$. Tris(4-(thiophenyl)phenyl)-1,3,5-triazines can also obtained *via* cyclotrimerization of (thiophenyl)benzonitriles in the presence of CF_3SO_3H. Hexaheteroarylbenzene derivatives were prepared by cobalt-catalyzed cyclotrimerization reaction of different alkyne precursors. The scope of this reaction in this area is limited and the overall yields of the products are moderate.

3.4. 1,3-Dipolar cycloaddition reactions

This strategy was mainly used to synthesize star-shaped molecules with pyrrolidine side arms *via* the reaction of chalcones with sarcosine and paraformaldehyde.

3.5. Imidization *via* cleavage–cyclization reactions

Star-shaped molecules with cyclic imide structure were synthesized by imidization reaction of 1,3,5-triamino benzene with cyclic carboxylic anhydride in the presence of $Zn(OAc)_2$.



Scheme 4 Synthesis of silicon-cored SSMs **29a,b**.

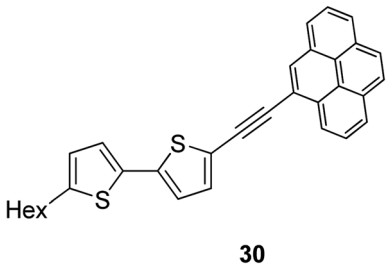


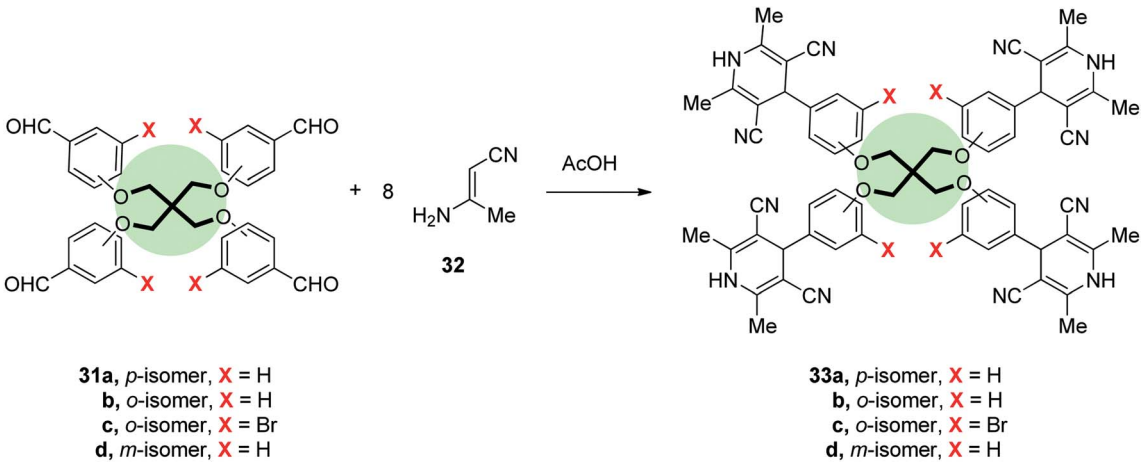
Fig. 2 Structure of linear (hexylbithiophenyl)pyrenylacetylene **30**.

3.6. Palladium-catalyzed C–C and C–N bond formation *via* Heck, Negishi, Sonogashira, Stille and Suzuki cross-coupling reactions

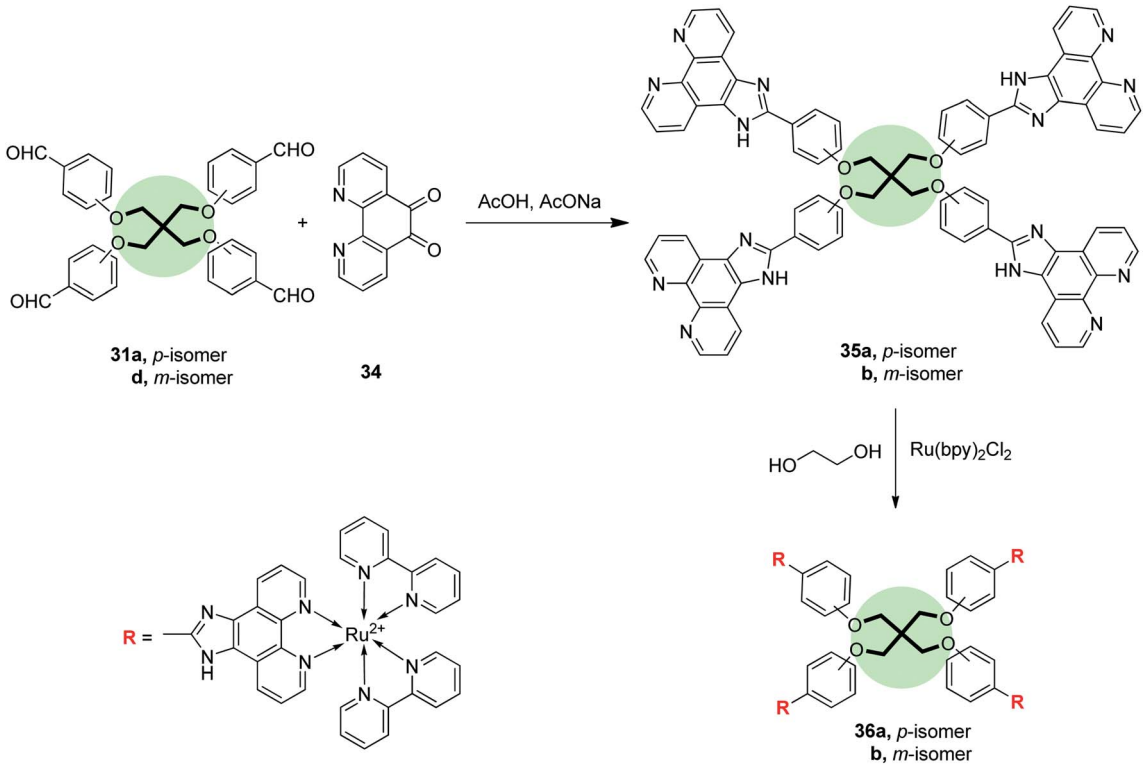
A variety of metal-catalyzed reactions, such as Suzuki, Stille, Sonogashira, Heck, and Negishi cross-coupling reactions have been employed to functionalize a range of star-shaped molecules.

3.6.1. Suzuki–Miyaura reaction. This reaction led to the formation of SSMs with biphenyl, thiophene, bithiophene, trithiophene, pyrrolo[3,4-*c*]pyrrole, quinolone carbazole or fluorine arms by cross-coupling reaction of boronic acid derivatives with the appropriate polyhalo compounds in the presence of palladium catalyst. Aryl-/alkylboronic acids or boronate esters, used in this reaction, very often suffer from a few limitations associated with their preparation, purification, and handling.

3.6.2. Sonogashira reaction. Sonogashira cross-coupling between the appropriate halo compounds with the corresponding alkyne derivatives in the presence Pd catalyst furnished star-shaped molecules with thiophene, pyrene, carbazole or fluorene side arms attached to the core *via* ethylenic linkages.



Scheme 5 Synthesis of tetrakis(2,6-dimethyl-4-phenyl-1,4-dihydropyridinyl)methanes **33a–d**.



Scheme 6 Synthesis of tetrapodal ligands **35a,b** and their ruthenium complexes **36a,b**.

3.6.3. Stille cross-coupling reactions. A Stille cross-coupling reaction between halo compounds and tributylstannyl derivatives in the presence of Pd catalyst afforded mainly thiophene-containing SSMs liked to benzothiadiazole, benzooxadiazole, pyrrolopyrrole or thiadiazolo[3,4-*c*]pyridine arms. One of the disadvantage of this reaction is the possible development of organotin by-products in reaction products.

3.6.4. Negishi cross-coupling reaction. This approach was used to prepare thiophene, thieno[3,2-*b*]thiophene, arylethynyl containing triphenylamine, fluorene, and/or carbazole-based SSMs by Pd-catalysed cross-coupling reaction of the appropriate halides with the corresponding organozinc compounds. The scope of the reactions could be significantly extended to the synthesis of a variety of SSMs using electron deficient heteroaromatic aryl bromides or chloride and acyclic zinc reagents as coupling partners.

3.6.5. Heck coupling reaction. Heck coupling reaction was utilized for the synthesis of vinylbithiophene-based SSMs *via* coupling of haloarenes with vinylbithiophene in the presence of $Pd(OAc)_2$.

3.7. van Leusen oxazoles synthesis

This reaction was used to prepare oxazole-containing star-shaped molecules by the reaction of tris-aldehydes with *p*-toluenesulfonylmethyl isocyanide (TosMIC).

The scope of this method is rather low and applied only for the synthesis of very few systems of tris((oxazolyl)thiophenyl) benzene.

3.8. Ullmann reactions

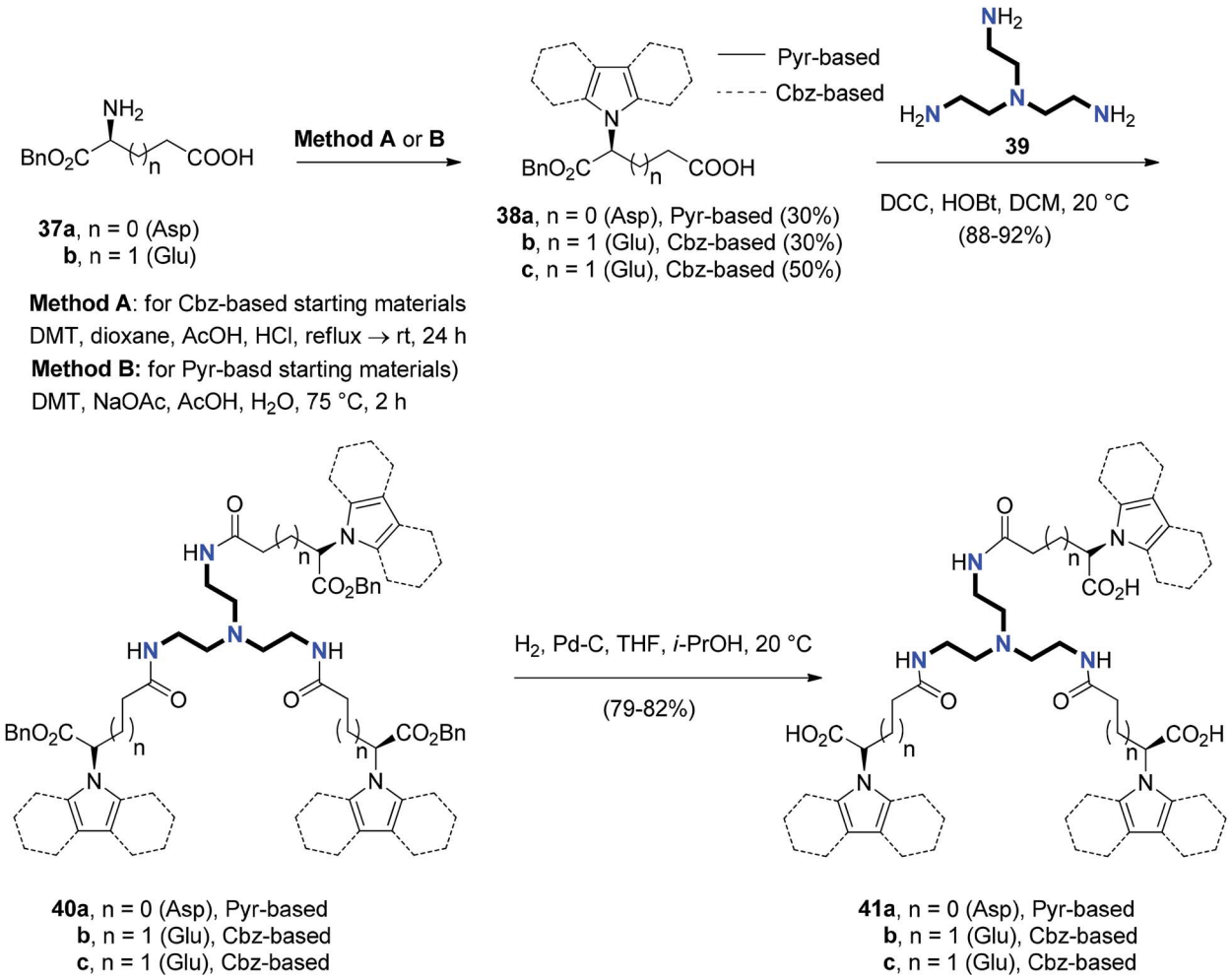
Benzimidazole-based SSMs were synthesized using this carbon–nitrogen bond-forming reaction through coupling of benzimidazole with tribromobenzene using $CuSO_4$ in the presence of a base catalyst. The applications of Ullmann reaction in this area are limited due to some limitations like harsh reaction conditions, high copper catalyst loading, poor functional group tolerance and generally the low yield of the products.

3.9. Click reaction

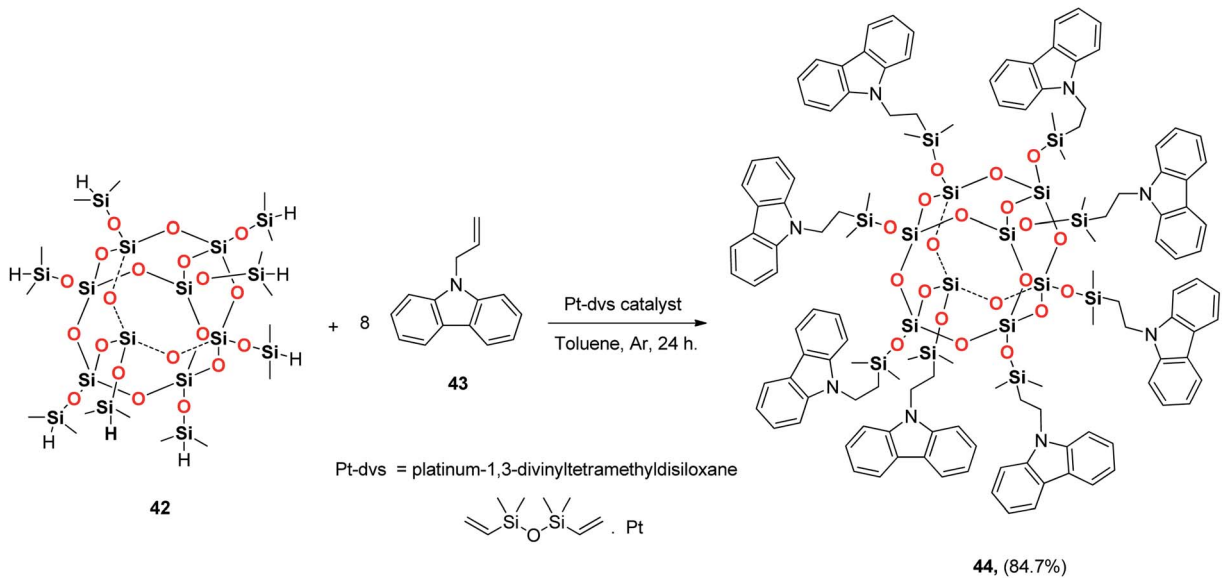
This reaction was used mainly to synthesize 1,2,3-triazole-based SSMs by the classic copper-catalyzed click reaction of the appropriate azide with the corresponding alkyne. Some important limitations of Click reaction are the stability of some azides in addition to the use of copper catalyst and the possible of alkyne homocoupling under the reaction conditions.

3.10. Diels–Alder reactions

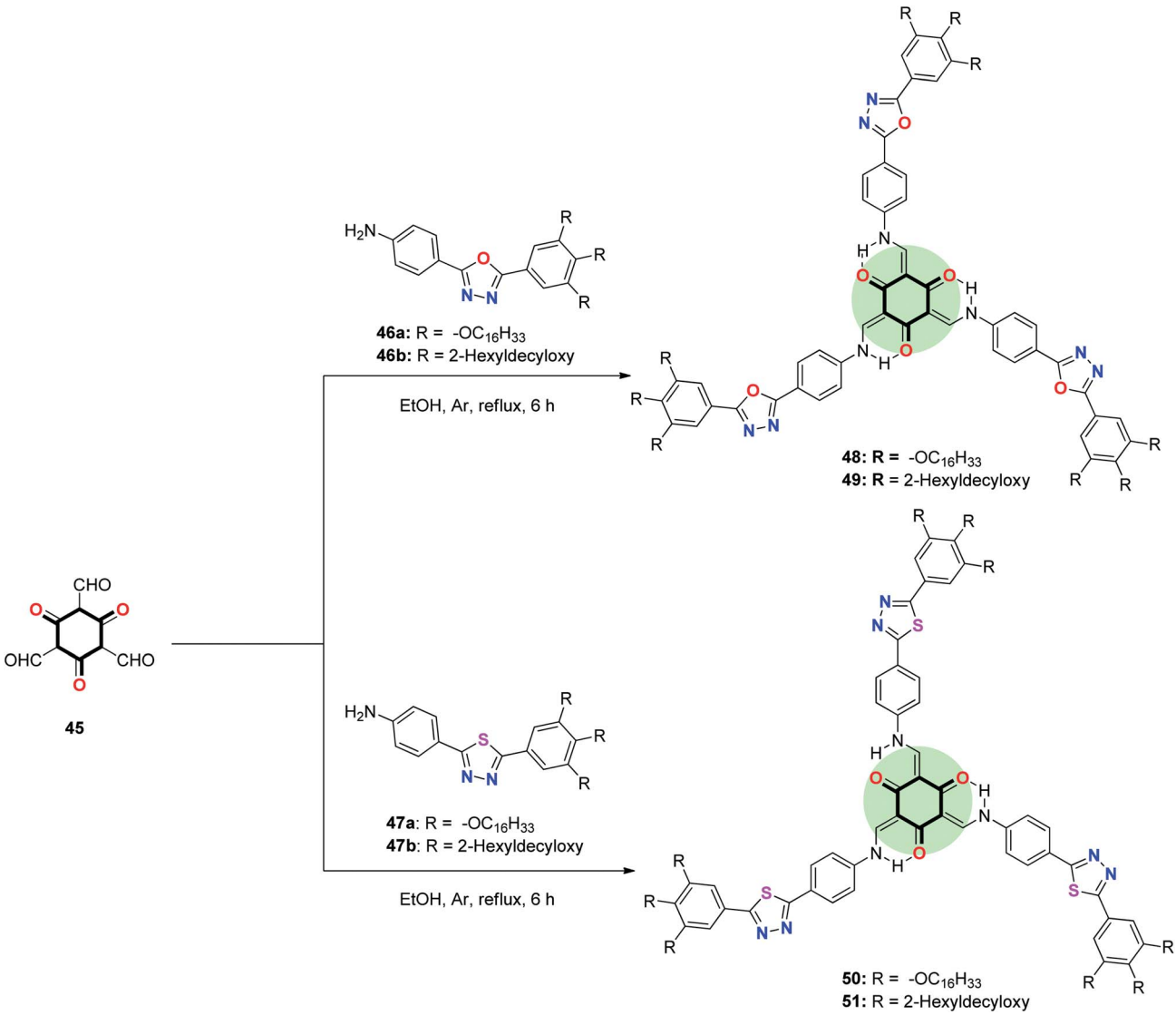
Diels–Alder reaction was used to prepare star-shaped molecules with hexakis(fluoren-2-yl)benzene by heating of cyclopentadienone with the appropriate acetylene derivatives. A significant limitation of this reaction is the poor reactivity associated with *cis*-dienes as well as prolonged reaction time.



Scheme 7 Synthesis of homochiral C3-symmetrical dendritic carboxylic acids **41a–c**.



Scheme 8 Synthesis of POSS-cored SSMs **44**.



Scheme 9 Synthesis of star-shaped tris(*N*-salicylideneanilines incorporated azoles) **48–51**.

3.11. Wittig reaction

Using this strategy tris- and tetrakis(2-(benzofuran-2-yl)vinyl) benzene as well as tris- and tetrakis[2-(benzo[*b*]thien-2-yl)vinyl] benzene were prepared by the reaction of the appropriate carbaldehyde with benzene-cored phosphonates. The reaction may be slow and give low yields in addition to the labile nature of aldehydes which can oxidize, polymerize or decompose.

4. Specific synthesis of star-shaped molecules

4.1. SSMs with acyclic cores

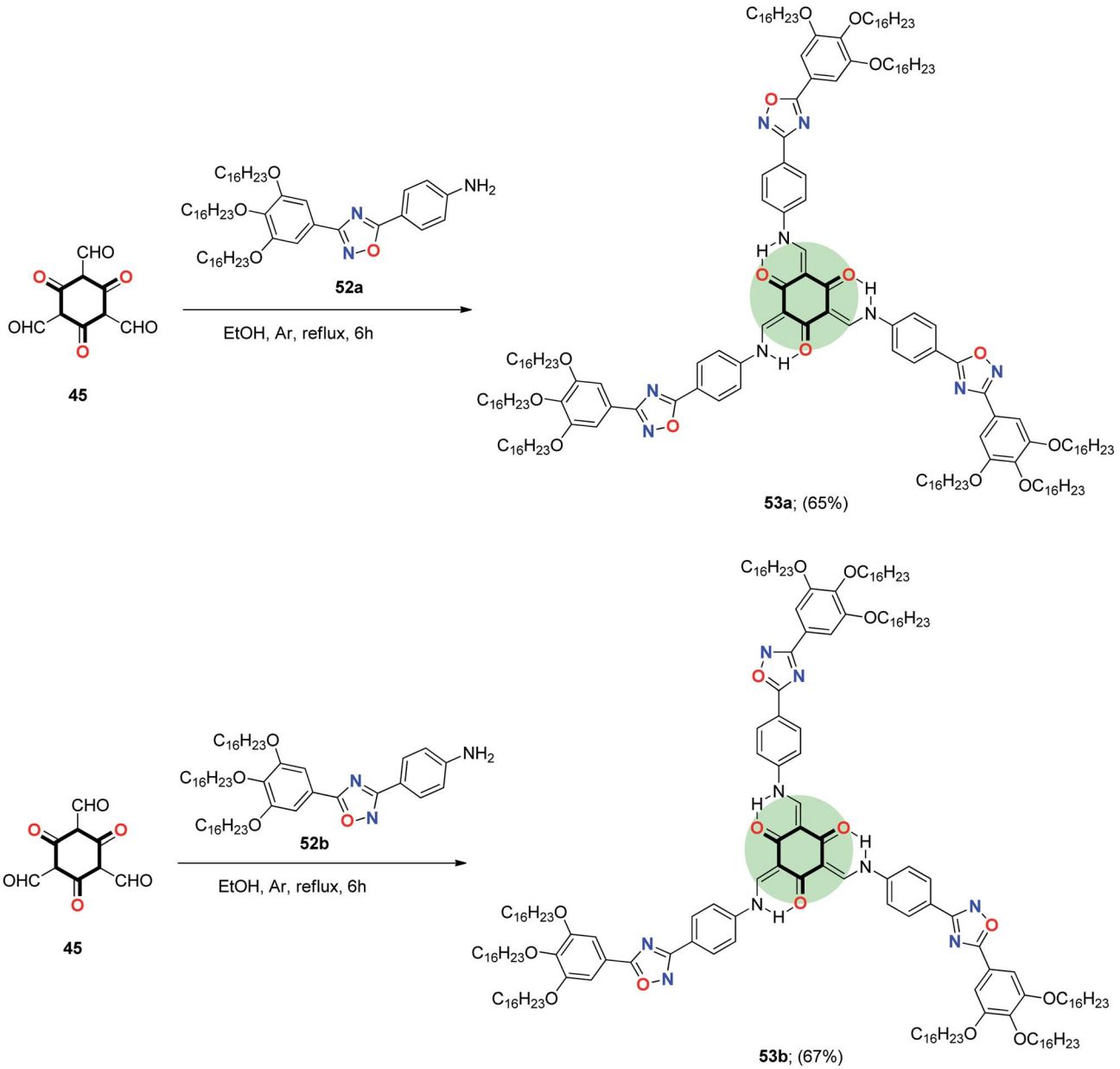
This class of star-shaped molecules comprises compounds with Si, Ge or carbon atoms as cores.

4.1.1. Silicon, germanium or carbon atom cores. Star-thiophene derivatives with one central silicon atom linked to three oligothiophene units has attracted a considerable interest since a discovery of strong fluorescence of the star-like molecules that have a regular arrangement of Si–Si bonds and bithienylene units.[68]

Luponosov *et al.*[69] synthesized star-shaped oligothiophenesilanes **3a,b** by firstly lithiation of 5-hexyl-2,2′-bithiophene **1** or 5-hexyl-2,2′:5′,2″-terthiophene **2**, respectively, followed by reaction with methyltrichlorosilane (Scheme 1). This work was extended to the synthesis of some different dentritic oligothiophenes, *via* Suzuki coupling reaction.[70–72]

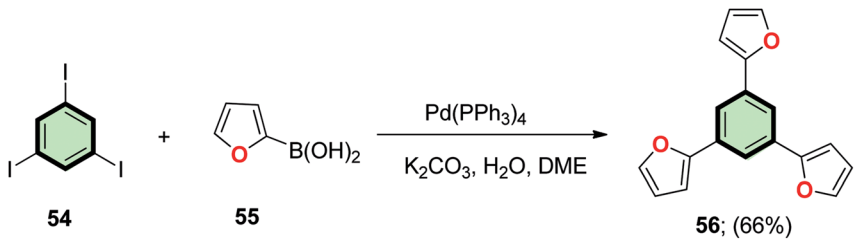
These compounds showed very effective energy transfer from the outer bithiophene to the internal terthiophenesilane units. Some of these compounds show efficient photoluminescence in the violet-blue region, the quantum yield of which is 5–15 times higher than that for the parent bithiophene or bithiophenesilanes.

The synthesis of four-armed SSMs with silicon atom-core **16** and **17** starting from benzothiadiazole or benzooxadiazole is outlined in Scheme 2. Bromination of **4a** and **4b**

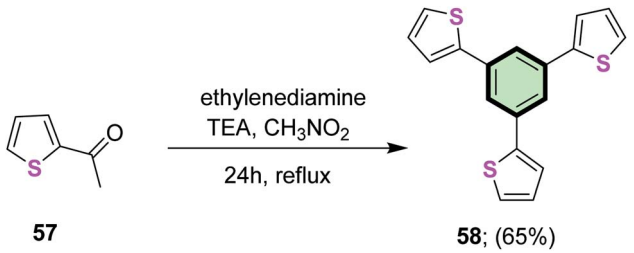


Scheme 10 Synthesis of star-shaped tris(*N*-salicylideneanilines incorporated 1,2,4-oxadiazole) **53a,b**.

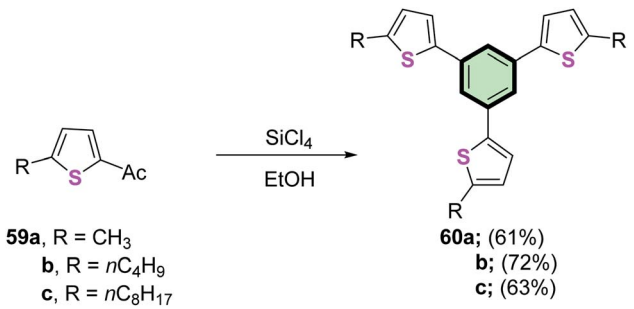
afforded the 4,7-dibromo derivatives **5** and **6**, respectively. Stille coupling of **5** or **6** with 2-tributylstannylthiophene **7** resulted in the formation of 4,7-bis(2-thienyl) derivative **8** or **9** which underwent a single bromination to yield **10** or **11**, respectively. Another Stille coupling of **10** or **11** with 2-tributylstannyl-5-octylthiophene **13** (obtained from 2-



Scheme 11 Synthesis of 1,3,5-tris(2-furyl)benzene **56**.



Scheme 12 Synthesis of 1,3,5-tri(thiophen-2-yl)benzene **58**.

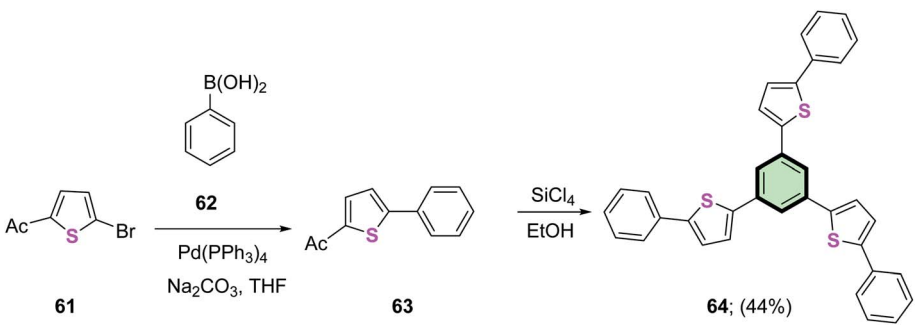


Scheme 13 Synthesis of 1,3,5-tris(5-alkylthiophen-2-yl)benzenes **60a–c**.

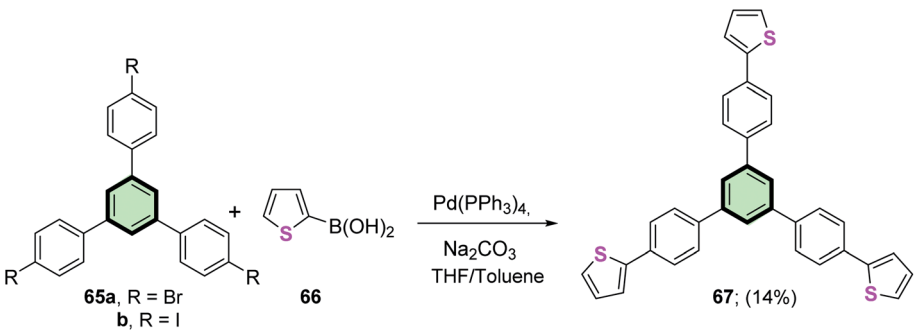
octylthiophene **12** upon treatment with tributylstannyl chloride) affords the arm **14** or **15** in 92% and 81%, respectively. Lithiation of compounds **14** and **15** followed by reaction with tetraethoxysilane led to SSMs **16** and **17** in low isolated yields of 25% and 14%, respectively, presumably due to aggregation and solubility issues. SSMs **16** and **17** were synthesized as low band gap compounds for applications in organic photovoltaic devices. Generally, benzothiazdiazole SSM **16** showed a better photovoltaic performance than benzooxadiazole SSM **17**. The energy band gaps, E_g of **16** (1.83 eV) and **17** (2.05 eV) were found to be higher than 1.5 eV (ideal organic photovoltaics). The energy gap values reflect that the electron-attracting ability of benzooxadiazole is higher than that of benzothiazdiazole moiety.[73]

Silicon-cored SSMs **20**, **24**, **26a** and **26b** were synthesized as shown in Scheme 3.[74] The three-armed thiophene-containing SSM **20** was prepared by nucleophilic substitution of tris(-chlorodimethylsilyl)methane **18a** by ethylthienyllithium **19**. SSM **24** is prepared in two steps: the first is nucleophilic substitution of **18a** with bromobithienyllithium **21** and the second is a Stille coupling with tributyl(ethyl)stannylbithiophene **23a**. Similarly, the four-armed silicon- or germanium-centered SSMs **26a** and **26b** were synthesized starting from **18b** and **18c**, respectively, by firstly reaction with **21** to give tetrabromoderivative **25** and subsequent Stille coupling reaction with **23b**. These compounds have been studied as hole-transporting materials for the sake of use as thin film transistor and TFT-active materials.

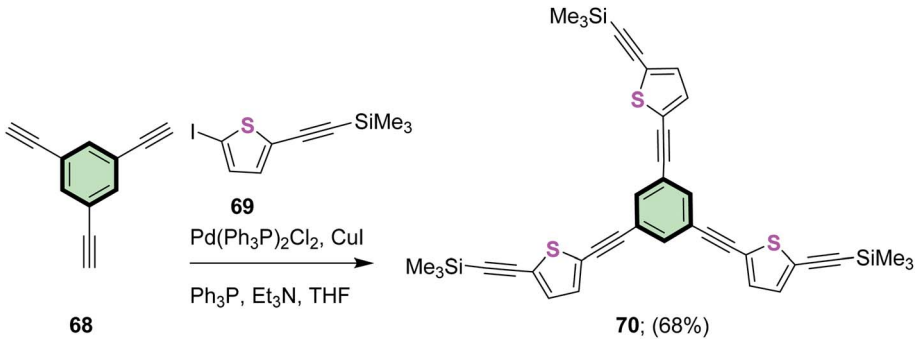
Pyrene-containing SSMs **29a,b** with high potential as photovoltaic materials were synthesized in 41 and 39%



Scheme 14 Synthesis of 1,3,5-tris(5-phenylthiophen-2-yl)benzene **64**.

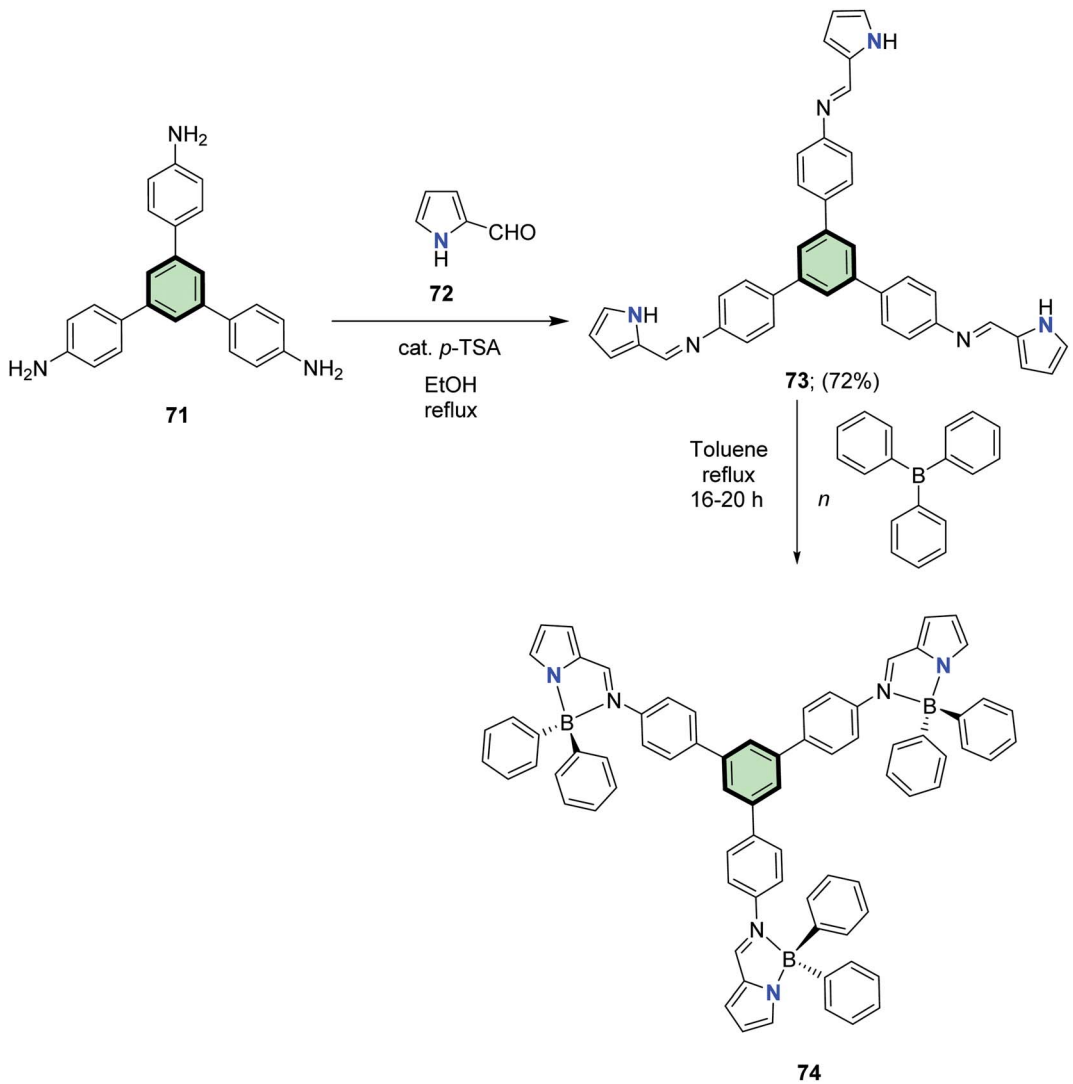


Scheme 15 Synthesis of 1,3,5-tris[4-(2′-thienyl)phenyl]benzene **67**.

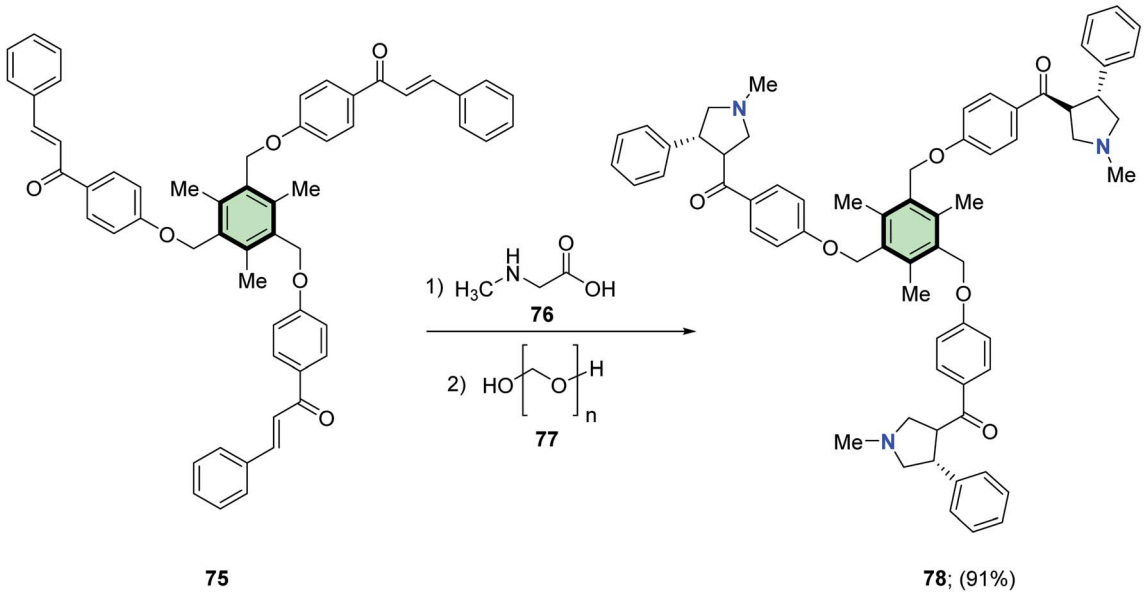


Scheme 16 Synthesis of 1,3,5-tris((5-((trimethylsilyl)ethynyl)thiophen-2-yl)ethynyl)benzene **70**.

yields by Sonogashira coupling of tris[(bromobithiophenyl) dimethylsilyl]methylsilane **27a** or tris[(bromobithiophenyl) dimethylsilyl]methane **27b**, respectively, with ethynylpyrene **28** (Scheme 4).[75] These compounds showed good solubility in common organic solvents; presumably due to the flexible organosilicon core that reduces the intermolecular π-stacking. Comparison of the UV spectra of compounds **29a** (λ_{max} = 404 nm), **29b** (λ_{max} = 407 nm) and **30** (linear



Scheme 17 Synthesis of star-shaped molecule with benzene core and pyrrole side arms **73** and its boron complex **74**.

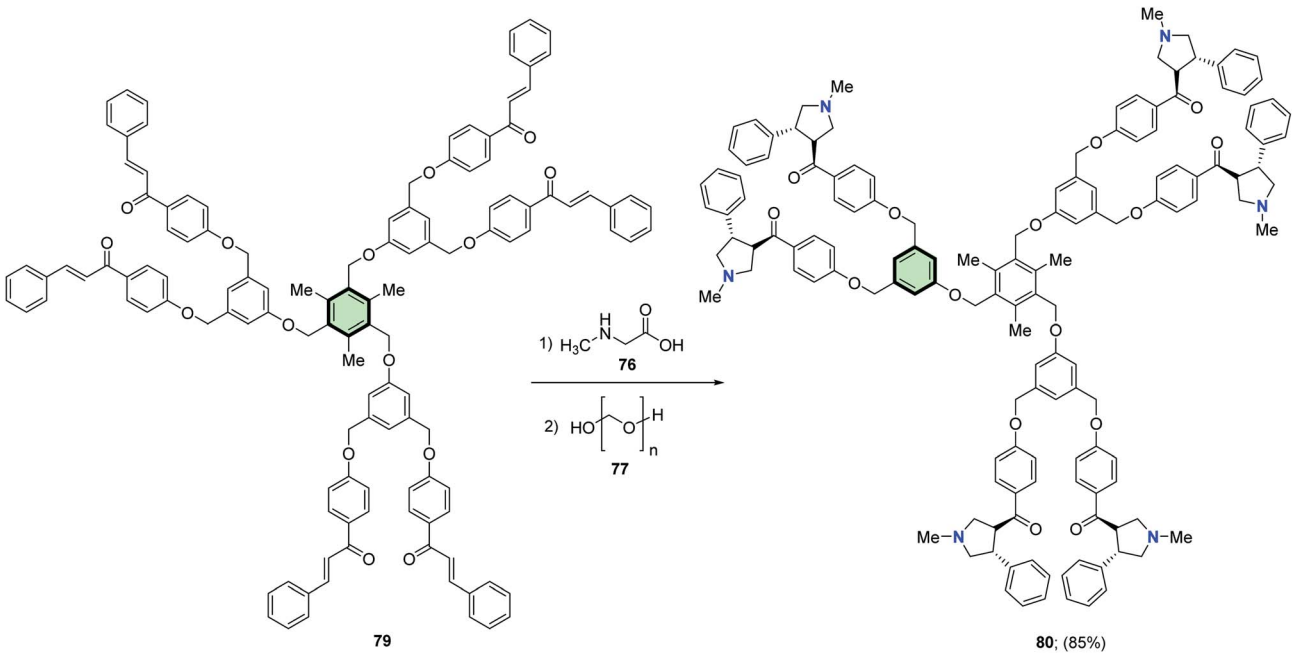


Scheme 18 Synthesis of star-shaped molecule with pyrrolidine side arms **78**.

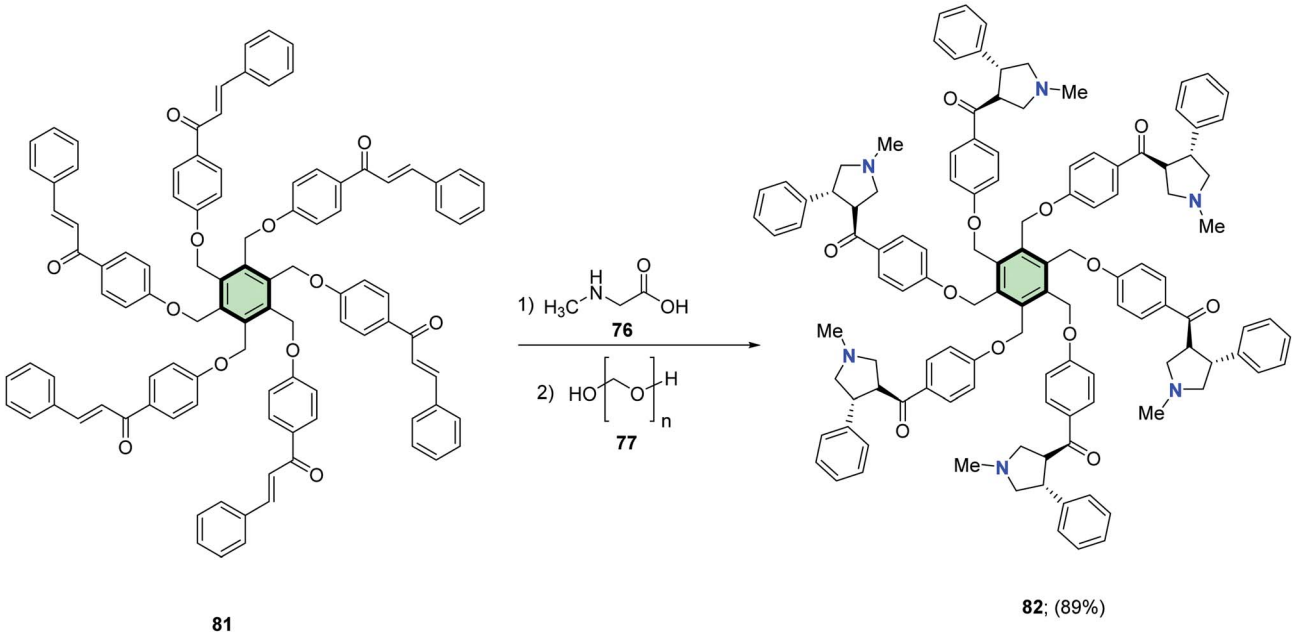
(hexylbithiophenyl)pyrenylacetylene, $\lambda_{max} = 404$ nm which is depicted in Fig. 2) showed a negligible effect of the bridging core. However, UV spectra of spin-coated films of **29a,b** showed a red shift ($\lambda_{max} = 440$ nm) apparently due to π-stacking in the solid state.

4.1.2. Pentaerythritol core. Mohamed *et al.*[76] reported the synthesis of tetrakis(2,6-dimethyl-4-phenyl-1,4-dihydropyridinyl)methanes **33a–d** by acid-catalyzed condensation of tetrakis-aldehydes **31a–d** with eight equivalents of 3-aminobut-2-enenitrile **32** in acetic acid. These tetrapodal 1,4-dihydropyridines, especially **33**, revealed high antiproliferative effect *in vitro* studies against human tumor cell lines (A549, HCT116, and MCF7) (Scheme 5).

Cheng *et al.*[77] reported the synthesis of tetrapodal ligands with imidazo[4,5-*f*][1,10]phenanthroline units **35a,b** in good yields by the reaction of 1,10-phenanthroline-5,6-dione **34**

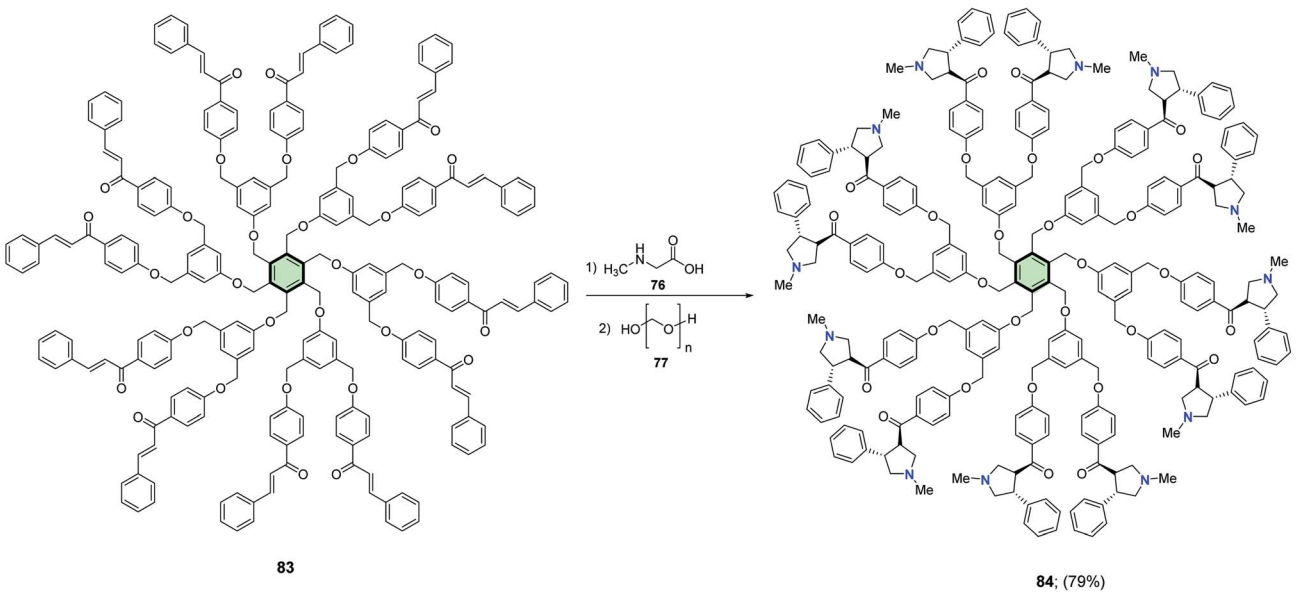


Scheme 19 Synthesis of star-shaped molecule with pyrrolidine side arms **80**.

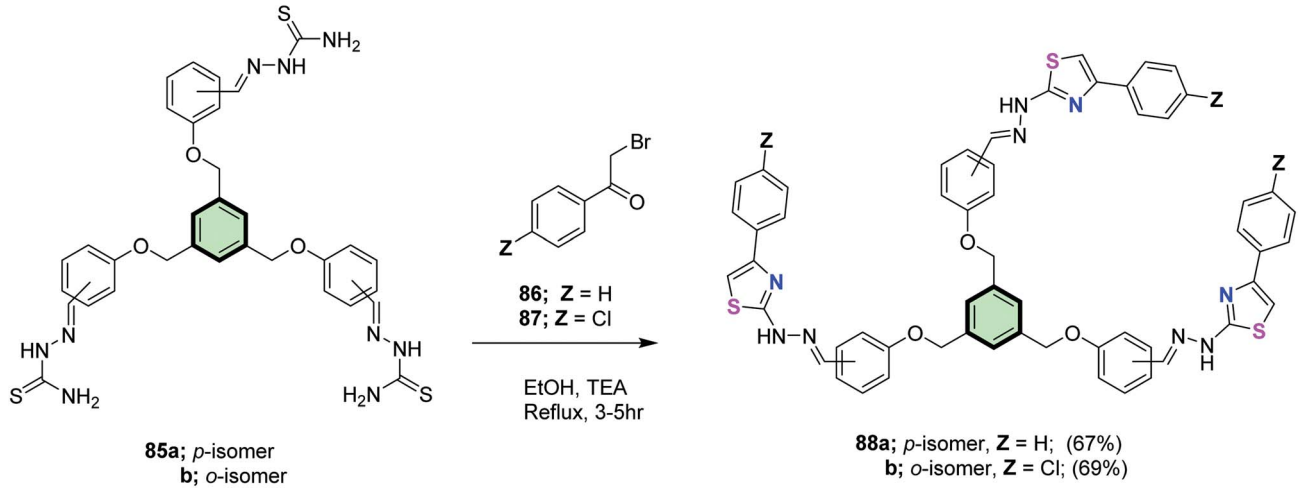


Scheme 20 Synthesis of star-shaped molecule with pyrrolidine side arms **82**.

with each of tetrakis[(4-formylphenoxy)methyl]methane **31a**, and tetrakis[(3-formylphenoxy)methyl]methane **31d**, respectively, in acetic acid at reflux. The corresponding Ru(II) complexes **36a,b** were prepared by heating **35a,b** with $Ru(bpy)_2Cl_2 \cdot 2H_2O$ in ethylene glycol solution at reflux (Scheme 6). It is worth-mentioning that these complexes are possible pH indicators because of their pH-dependent photophysical properties. For instance, the UV-vis spectra of Ru(II) complex **36a** showed three distinct bands at 458, 318, 286 nm corresponding to metal-to-ligand charge transfer, centered ligand $\pi \rightarrow \pi^*$, and bipyridyl $\pi \rightarrow \pi^*$, respectively. On the other hand, fluorescence emission spectrum of **36a** showed a characteristic peak at 592 nm for metal-to-ligand charge transfer, Ru(II) dn $\rightarrow$ dπ^*. The pH alteration 1.82 $\rightarrow$ 6.22 caused a blue shift to 598 nm with a 25% increase in the intensity while pH change 6.22 $\rightarrow$



Scheme 21 Synthesis of star-shaped molecule with pyrrolidine side arms **84**.



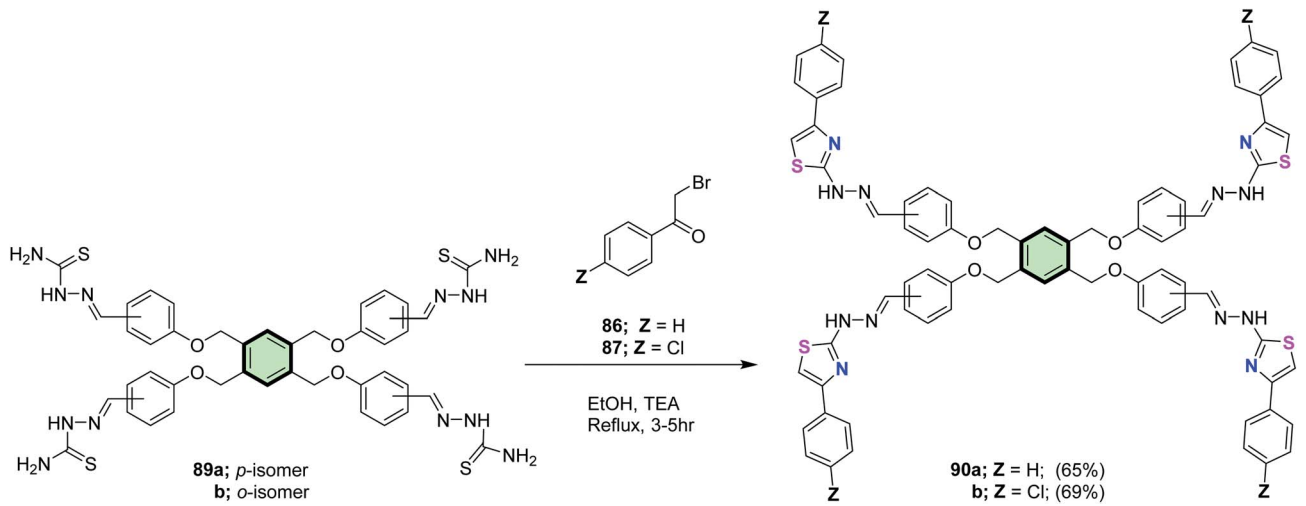
Scheme 22 Synthesis of multi-armed thiazole derivatives **88a** and **88b**.

12.04 resulted in a red-shift to 606 nm with a remarkable quenching to 78%. Thus, complex **36a** acts as off–on–off fluorescence pH switch.

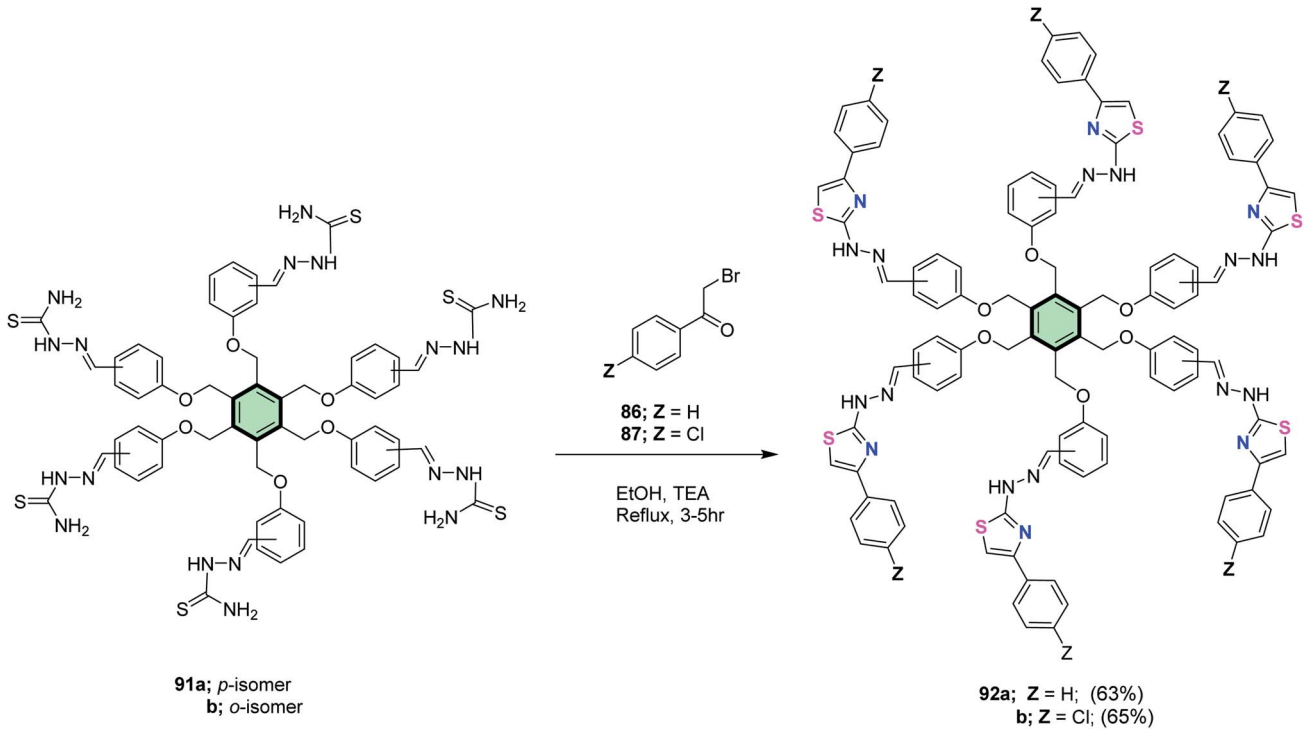
4.1.3. Tris(2-aminoethyl)amine core. Homochiral C3-symmetrical dendritic compounds **41a–c** were synthesized as shown in Scheme 7. The protected (*S*)-L-aspartic acid (Asp) **37a** and (*S*)-L-glutamic acid (Glu) **37b** underwent modified Clauson-Kaas ring closure reaction with 2,5-dimethoxytetrahydrofuran (DMT) under acidic condition to form pyrrolyl and carbazolyl derivatives **38a–c**. The amidation reactions of these compounds with tris(2-aminoethyl) amine **39** in presence of a mixture of dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBt) afforded the protected dentritic compound **40a–c**. Palladium-deprotection of the latter compound gave the dentritic carboxylic acids **41a–c**.[78] It should be noted that SSMs **41b** and **41c** with peripheral carbazole groups underwent an oxidative electropolymerization to form a stable electroactive polymer films which might find application for stereoselective recognition of biomolecules.

4.2. SSMs with alicyclic cores

4.2.1. Polyhedral oligomeric silsesquioxane core. Polyhedral oligomeric silsesquioxane, POSS-cored SSMs are examples of organic–inorganic hydrid materials which have interesting optoelectronic properties. Incorporating POSS core in place of traditional hole transport materials in organic light emitting devices (OLEDs) could improve both their brightness and efficiencies. Xu *et al.*[79] reported the synthesis of POSS-cored SSM **44** with incorporated carbazole moiety in excellent yield



Scheme 23 Synthesis of tetrakis(thiazoles) **90a** and **90b**.

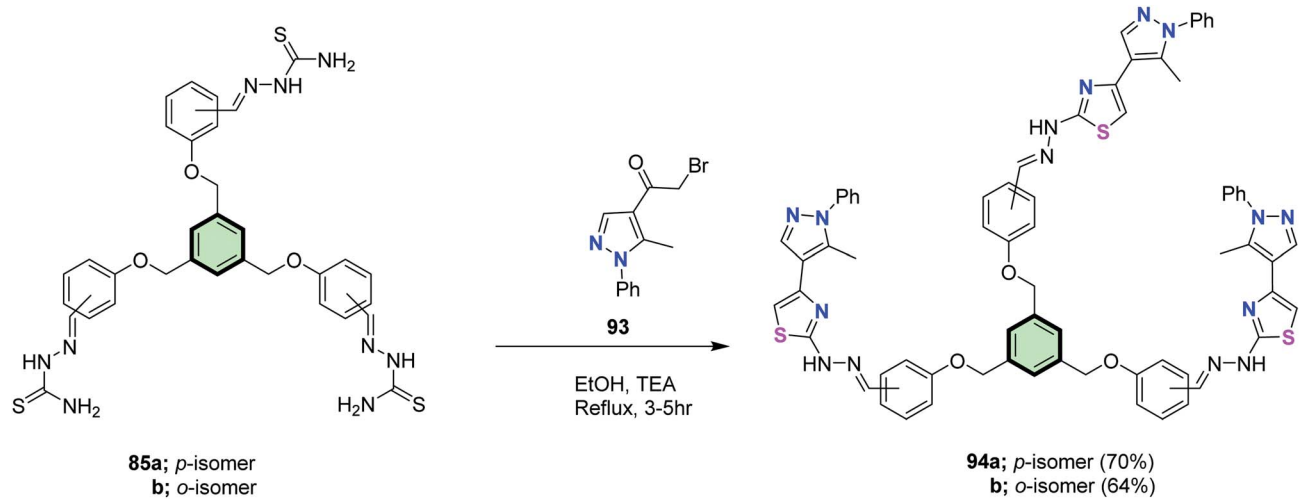


Scheme 24 Synthesis of hexakis(thiazoles) **92a** and **92b**.

(85%) *via* the hydrosilylation reaction of 9-allylcarbazole **43** by the action of POSS **42** in the presence of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt-dvs) catalyst (Scheme 8). POSS-cored SSM **44** showed thermal stability with no aggregation in either solution or solid film probably due to the short POSS spacer. The UV and photoluminescence spectra showed a blue emission in both cases.

4.2.2. Cyclohexatrione core. Pathak *et al.*[19] reported the synthesis of star-shaped tris(*N*-salicylideneanilines) (TSANs) containing 1,3,4-oxadiazole **48** and **49**, as well as 1,3,4-thiadiazole based arms **50** and **51** in 65–80% yields by the reaction of 1,3,5-triformylphloroglucinol **45** with the appropriate amine derivatives **46a,b** and **47a,b**, respectively, in EtOH at reflux (Scheme 9).

A similar approach was used to synthesize a star-shaped molecule **53a,b** with 1,3,5-cyclohexatrione as a core and 1,2,4-oxadiazole as arms in good yield by the reaction of **45** with the respective 4-(3-aryl-1,2,4-oxadiazol-5-yl)aniline **52a** and 4-(5-aryl-1,2,4-oxadiazol-3-yl)aniline **52b** in ethanol at reflux (Scheme 10).[30]



Scheme 25 Synthesis of star-shaped molecules with benzene core and (pyrazolyl)thiazole side arm **94a** and **94b**.

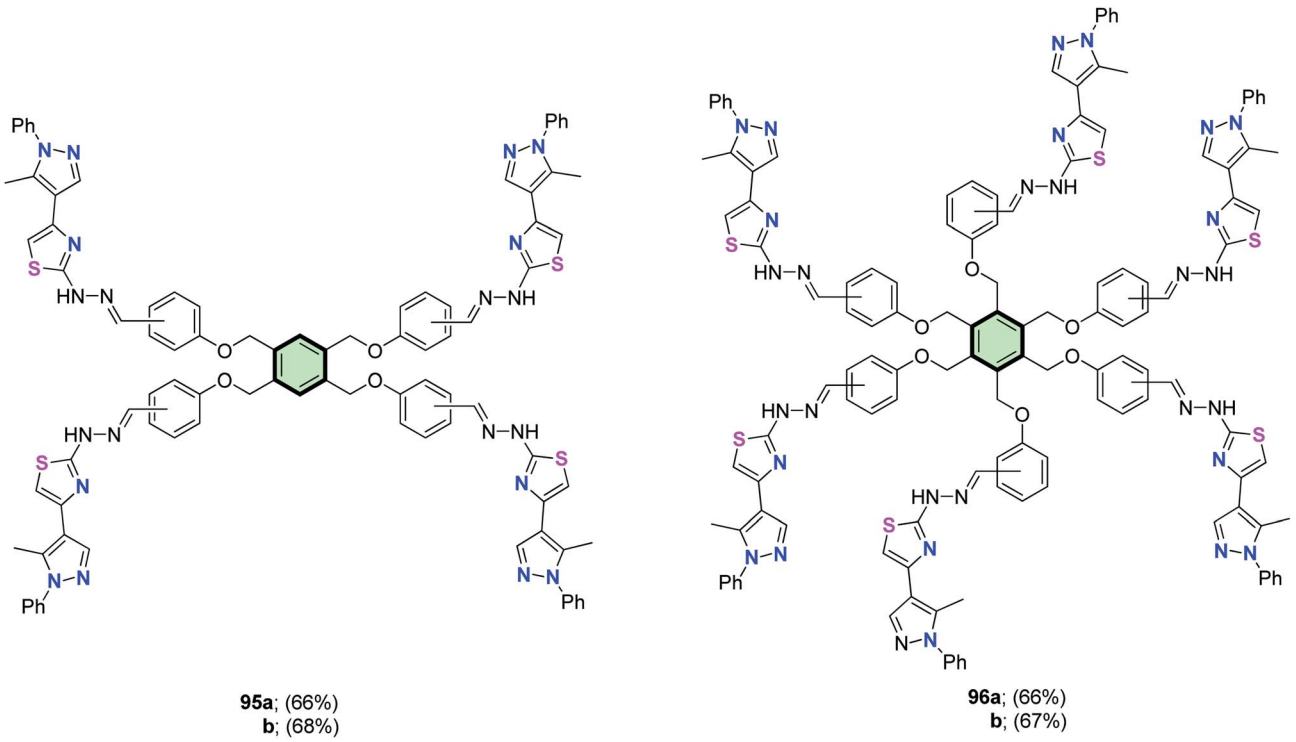
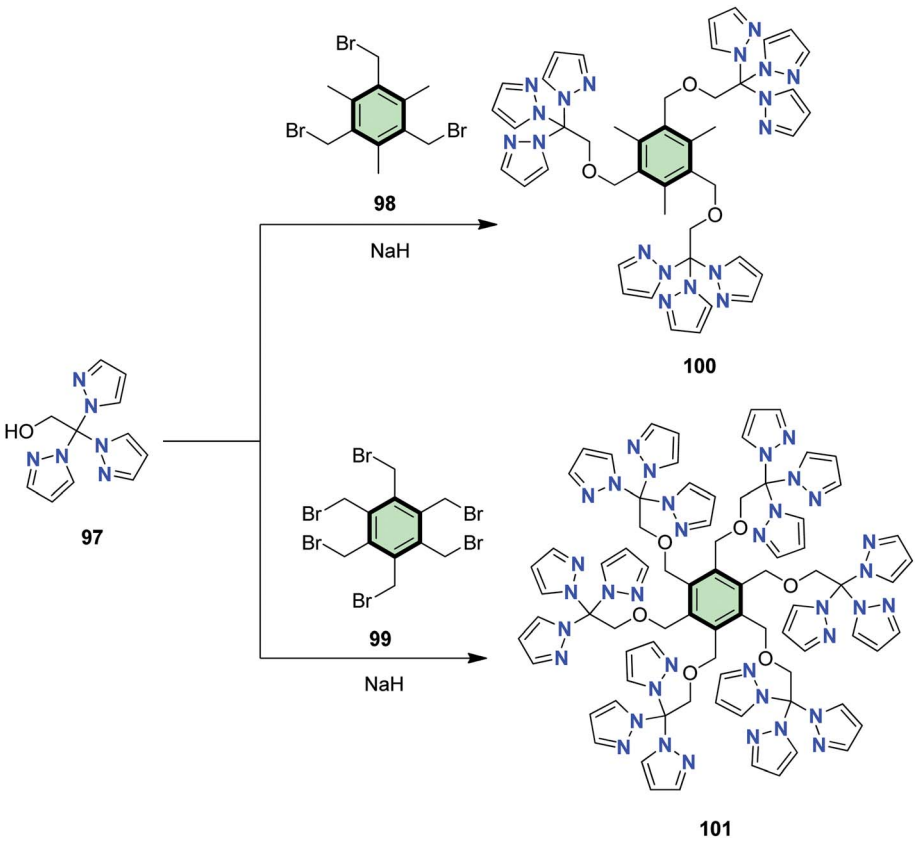
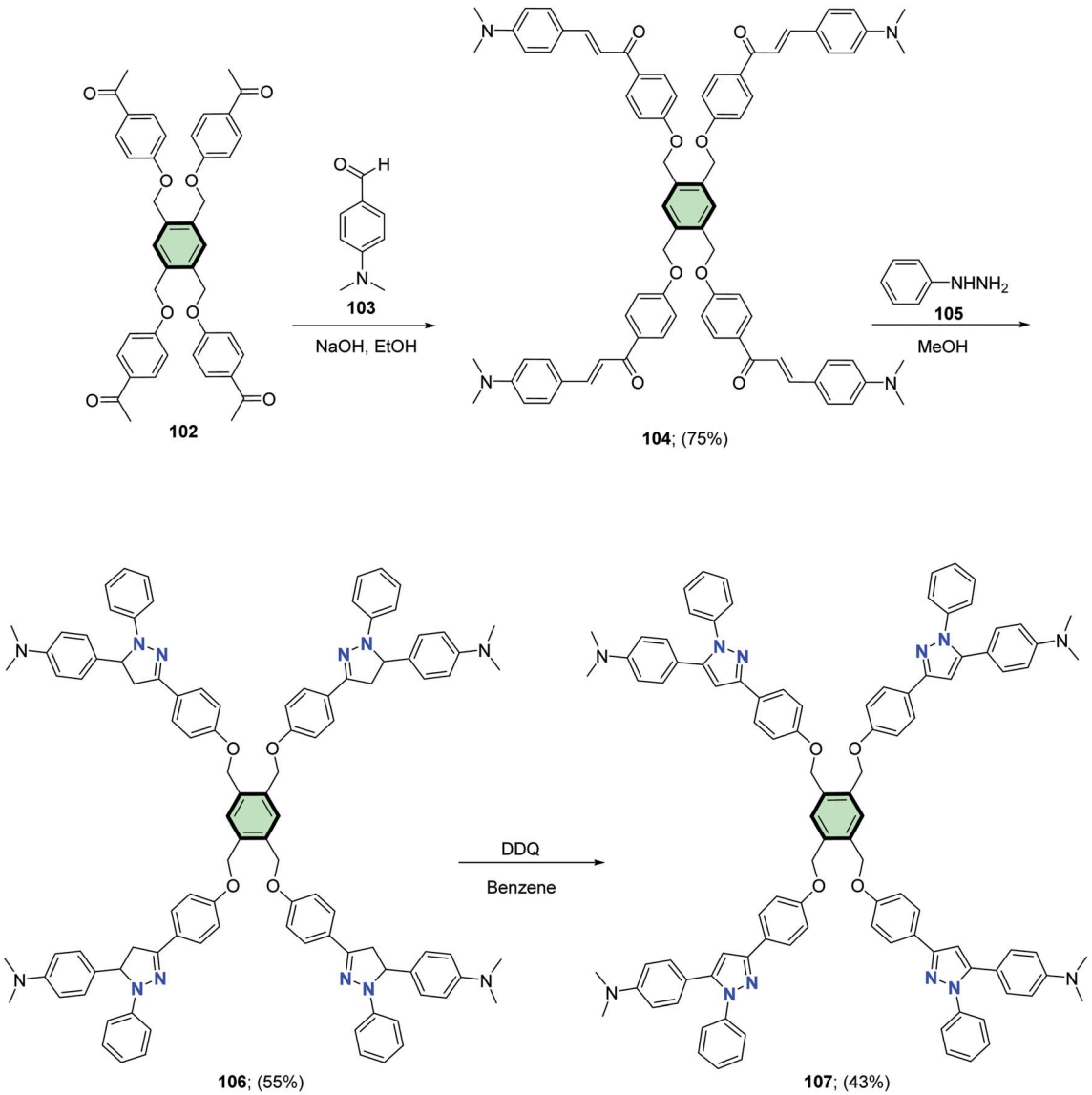


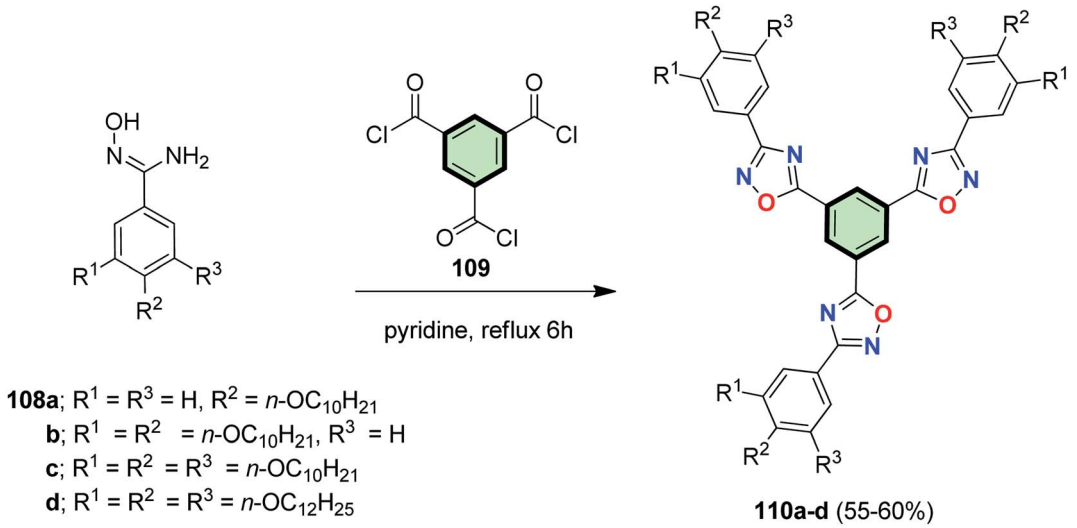
Fig. 3 Structures of tetrakis(pyrazolyl)thiazoles **95a** and **95b** and hexakis(pyrazolyl)thiazoles **96a** and **96b**.



Scheme 26 Synthesis of SSMs **100** and **101**.

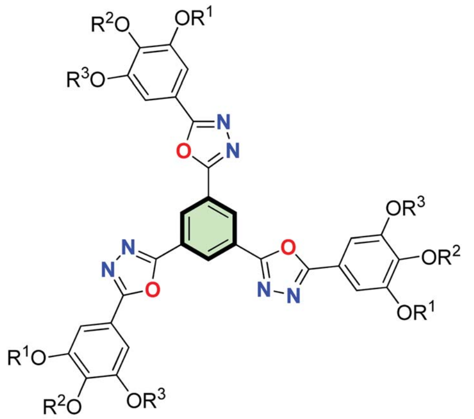


Scheme 27 Synthesis of SSMs containing four pendant pyrazole rings **107**.



108a; $R^1 = R^3 = H$, $R^2 = n\text{-}OC_{10}H_{21}$
b; $R^1 = R^2 = n\text{-}OC_{10}H_{21}$, $R^3 = H$
c; $R^1 = R^2 = R^3 = n\text{-}OC_{10}H_{21}$
d; $R^1 = R^2 = R^3 = n\text{-}OC_{12}H_{25}$

Scheme 28 Synthesis of 1,2,4-oxadiazole-based benzene-cored SSMs **110a–d**.



117-120 (31-36%)

117: $R^1 = R^3 = H$, $R^2 = n\text{-}C_{10}H_{21}$
118: $R^1 = R^2 = n\text{-}C_{10}H_{21}$, $R^3 = H$
119: $R^1 = R^2 = R^3 = n\text{-}C_{10}H_{21}$
120: $R^1 = R^2 = R^3$ = 2-Ethyl hexyl

Fig. 4 SSMs with three pendant 1,3,4-oxadiazole moieties **117–120**.

It should be mentioned that replacing oxygen in the five-membered ring (in star-shaped TSANs **48** and **49**) by a more voluminous and more basic sulfur atom (in star-shaped TSANs **50** and **51**) has a pronounced effect on bent angle and electron distribution. It caused a larger longitudinal/lateral dipole moment and attractive S⋯S interactions in the condensed state as well. Tuning the peripheral groups from straight to branched chains affected the transition temperature, self-assembly and photophysical behavior in the solid state. The 1,3,4-oxadiazole based TSANs with branched tails **49** stabilized a columnar rectangular Col_r phase at room temperature, while the straight chain analogue **48** showed a columnar hexagonal Col_h phase at a high temperature. In contrast to **48** and **49**, 1,3,4-thiadiazole TSAN with straight peripheral tail **50** showed a Col_r phase (presumably because of intermolecular attraction of 1,3,4-thiadiazole rings) while that with the bulkier branched tail **51** became a non-crystalline viscous liquid.[19] 1,2,4-Oxadiazole-based TSANs **53a,b**, on the other hand, showed lower melting, clearing points and wider mesophase range than 1,3,4-oxadiazole-based TSANs **50** and **51**. The position of trialkoxyphenyl group at the heterocycle has a prominent effect on the self-assembly properties; **53a** with a trialkoxyphenyl group at 5-position showed Col_r phase while **53b** with a trialkoxyphenyl group at 3-position exhibited Col_h phase. Both compounds **53a** and **53b** emitted green light in solution with quantum yield (0.27–0.31) and red-shifted compared to 1,3,4-oxadiazole derivatives in thin film.[30]

4.3. SSMs with aromatic or heterocyclic cores

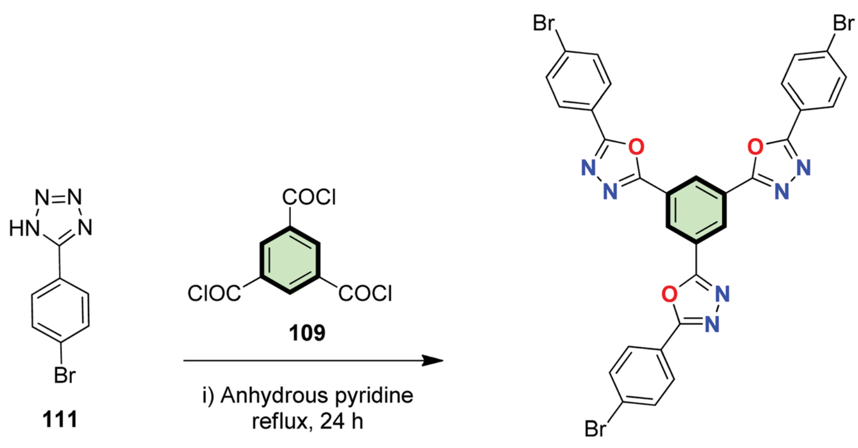
4.3.1. Benzene-cored SSMs. This class of SSMs are characterized by the presence of a central benzene core connected to different arms.

4.3.1.1. Benzene-cored SSMs with five-membered heterocyclic arms

4.3.1.1.1. Five-membered heterocyclic arms containing one heteroatom. ***4.3.1.1.1.1. Furan.*** Kotha *et al.*[80] reported the synthesis of 1,3,5-tris(2-furyl)benzene **56** in 66% yield by heating a mixture of 1,3,5-triiodobenzene **54** and furan-2-boronic acid **55** in THF/toluene mixture in the presence of $Pd(PPh_3)_4$ (Scheme 11).

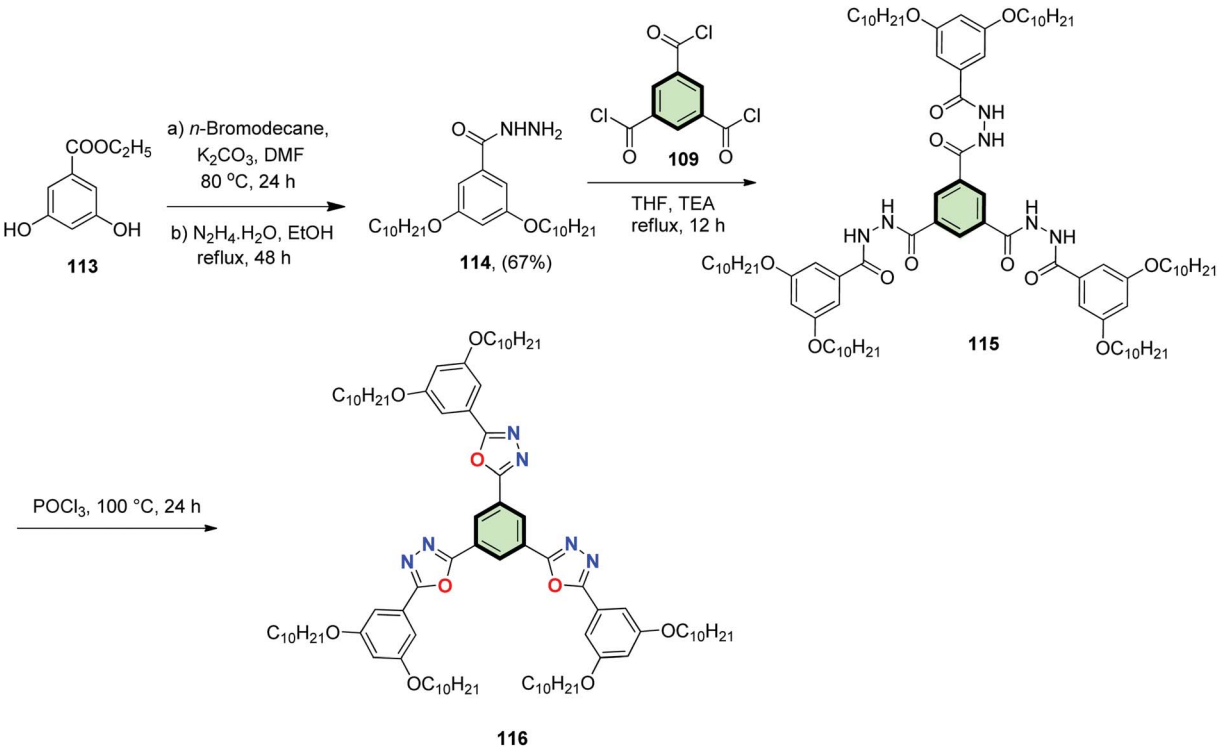
4.3.1.1.1.2. Thiophene. A star-shaped molecule 1,3,5-tri(thiophen-2-yl)benzene **58** was synthesized in 65% yield, *via* trimerization of 2-acetyl thiophene **57** in the presence of TEA (Scheme 12).[81]

2-Acetyl-5-alkylthiophenes **59a–c** underwent cyclotrimerization reaction upon treatment with $SiCl_4$ to give 1,3,5-tris(5-alkylthiophenyl)benzenes **60a–c** in 61, 72 and 63% yields, respectively (Scheme 13).[80]



112; (75%)

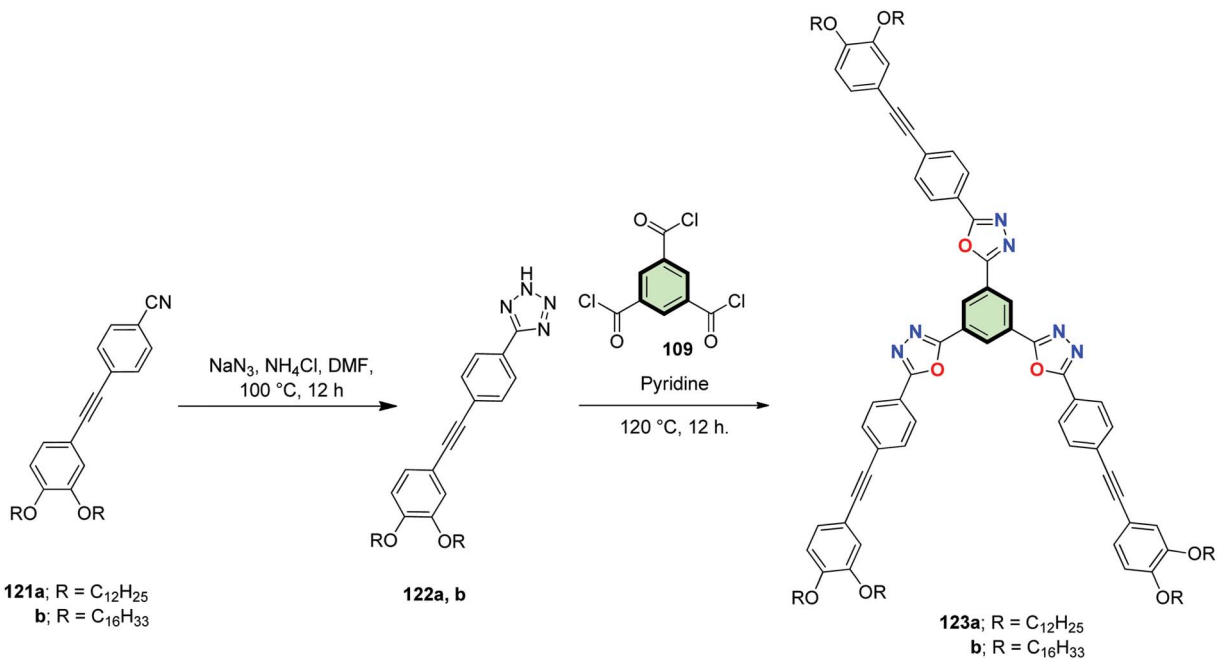
Scheme 29 Synthesis of 1,3,5-tris((4-bromophenyl)-1,3,4-oxadiazol-2-yl)benzene **112**.



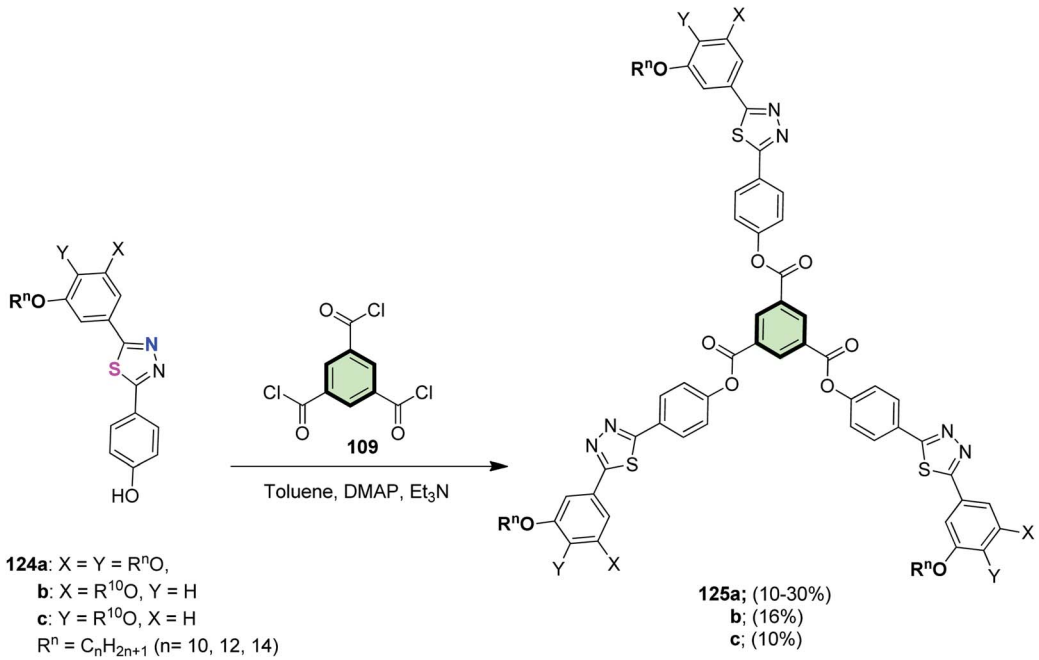
Scheme 30 Synthesis of SSMs with three pendant 1,3,4-oxadiazole moieties **116**.

1,3,5-Tris(5-phenylthiophen-2-yl)benzene **64** was synthesized in 44% yield *via* the reaction of 2-acetyl-5-phenylthiophene **63** with $SiCl_4$ in ethanol. Compound **63** was synthesized from the reaction of 2-acetyl-5-bromothiophene **61** with phenylboronic acid **62** in the presence of $Pd(PPh_3)_4$ (Scheme 14).[80]

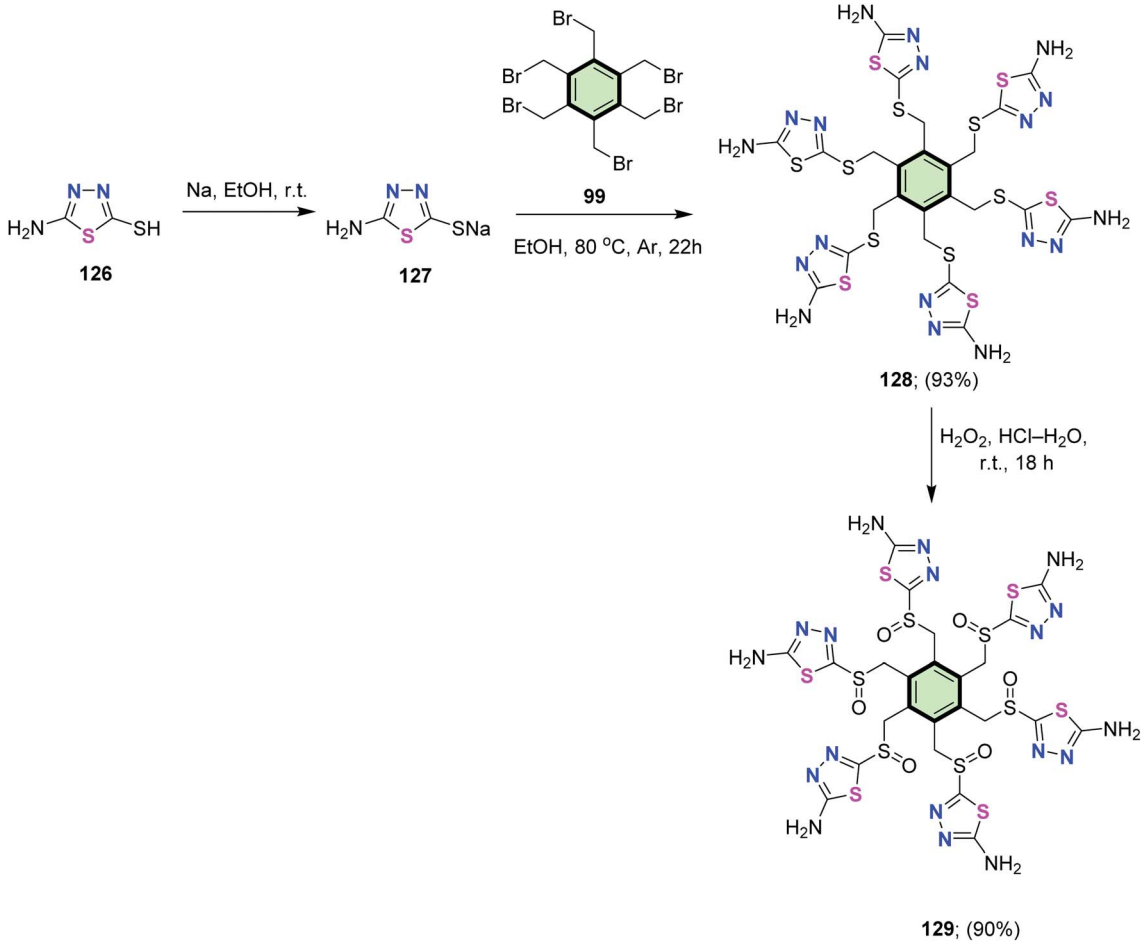
1,3,5-Tris[4-(2′-thienyl)phenyl]benzene **67** was obtained in 14% yield by the reaction of 1,3,5-tris(4-halophenyl)benzenes



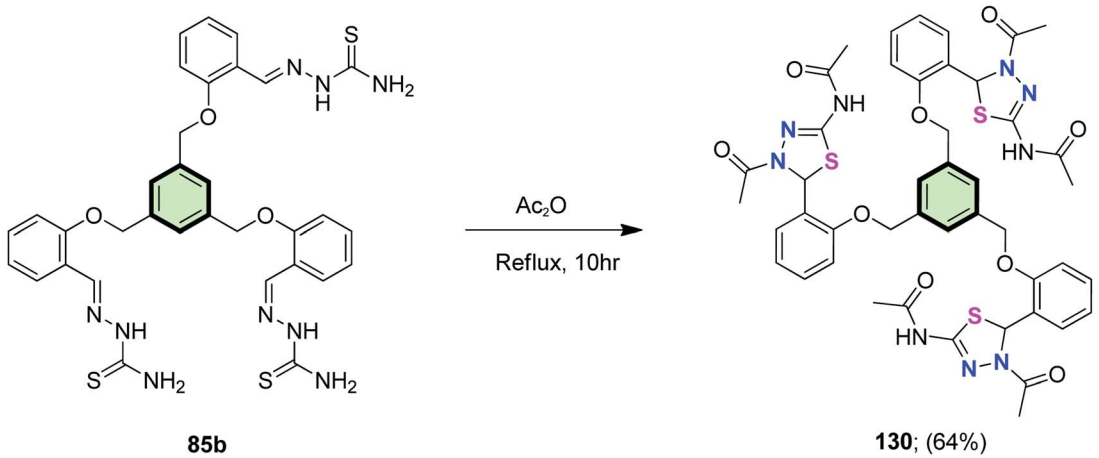
Scheme 31 Synthesis of 1,3,4-oxadiazole-based SSM **123a** and **123b**.



Scheme 32 Synthesis of SSMs with pendant 1,3,4-thiadiazole rings **125a–c**.



Scheme 33 Synthesis of hexakis(1,3,4-thiadiazol-2-amines) **128** and **129**.



Scheme 34 Synthesis of SMM with benzene core and 1,3,4-thiadiazole side arm **130**.

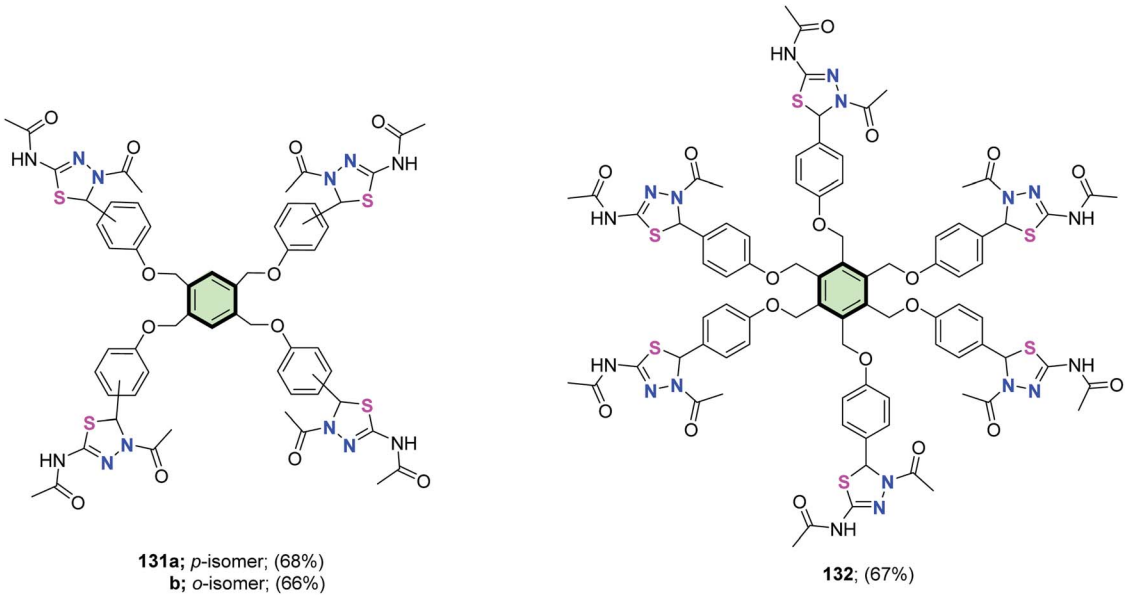
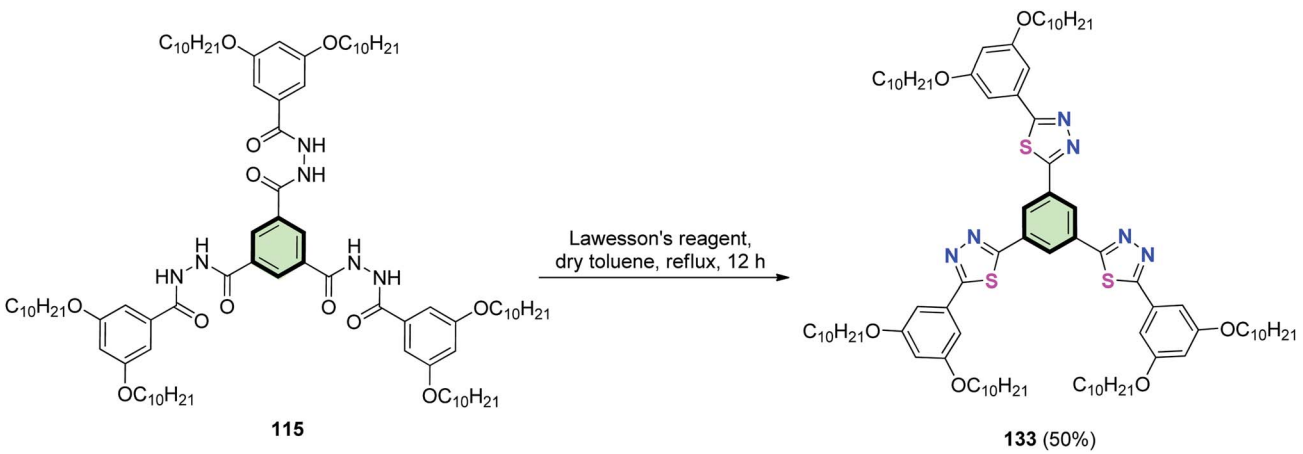
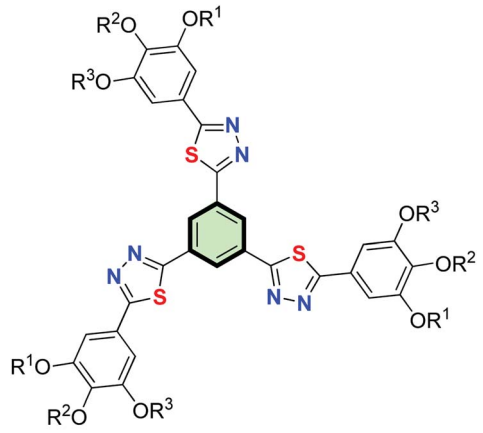


Fig. 5 Tetra- and hexakis(4,5-dihydro-1,3,4-thiadiazolyl) derivatives **131a**, **131b** and **132**.



Scheme 35 Synthesis of SSM **133** with three pendant 1,3,4-thiadiazole moieties.



134a-d (31-36%)

134a: $R^1 = R^3 = H$, $R^2 = n\text{-}C_{10}H_{21}$
134b: $R^1 = R^2 = n\text{-}C_{10}H_{21}$, $R^3 = H$
134c: $R^1 = R^2 = R^3 = n\text{-}C_{10}H_{21}$
134d: $R^1 = R^2 = R^3$ = 2-Ethyl hexyl

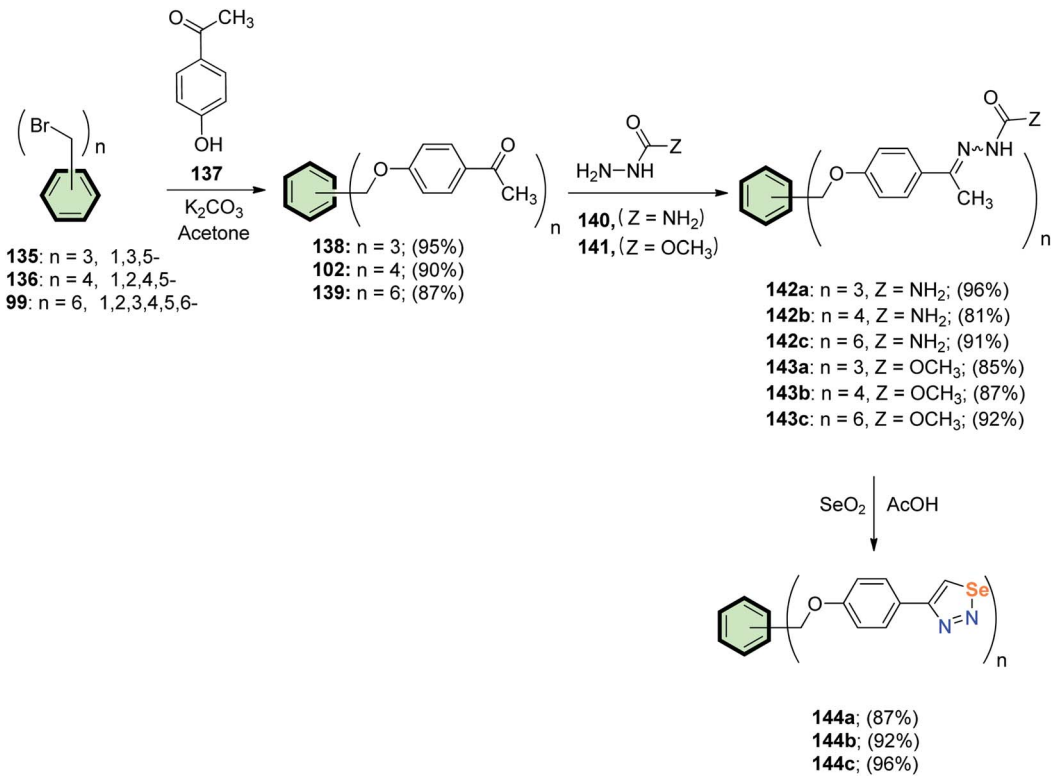
Fig. 6 SSMs **134a–d** with three pendant 1,3,4-thiadiazole moieties.

65a or **65b** with thiophene-2-boronic acid **66** in the presence of $Pd(PPh_3)_4$ in refluxing THF/toluene mixture (Scheme 15).[80]

Sonogashira coupling of ((5-iodothiophen-2-yl)ethynyl) trimethylsilane **69** and 1,3,5-triethynylbenzene **68** afforded 1,3,5-tris((5-((trimethylsilyl)ethynyl)thiophen-2-yl)ethynyl) benzene **70** in good yield (68%) (Scheme 16). Star-shaped molecule **70** showed excellent luminescent properties. The fluorescence emission spectrum of **70** indicated four peaks at 375, 390, 418 and 446 nm, respectively, and the emission maximum peak at 375 nm. The fluorescence intensities of **70** showed a dramatic change in chloroform relative to concentration; it increased (from 1235 to 6714 a.u.) with the concentration (from 5.0×10^{-4} to 5.0×10^{-6} M), while it decreased (from 5364 to 2042 a.u.) with the concentration (from 1.0×10^{-6} to 1.0×10^{-7} M). This behavior was attributed to the concentration aggregate-enhanced emission (AEE) effect[82] and aggregation-caused quenching (ACQ) effect. Increasing the polarity of solvent from toluene to acetonitrile resulted in a blue shift of the peaks.[83]

4.3.1.1.1.3. Pyrrole. Suresh *et al.*[84] reported the synthesis of star-shaped molecule with benzene core and pyrrole side arms **73** in 72% yield, through the reaction of 4′,4″,4‴-triamino-1,3,5-triphenyl-benzene **71** with three equivalents of 1*H*-pyrrole-2-carbaldehyde **72** in the presence of (*p*-TSA) in EtOH at reflux (Scheme 17). The ligand molecule **73** itself is non-emissive; however, its boron complex **74** acted as a blue emitter (510 nm) with a fluorescence quantum yield of 0.46. DFT calculations explained that in the singlet excited state, only one iminopyrrolyl group remains planar while the two others remain at their original geometries.

4.3.1.1.1.4. Pyrrolidine. Rajakumar *et al.*[85] reported the synthesis of some novel star-shaped molecules with pyrrolidine side arms **78**, **80**, **82** and **84** in high yields through 1,3-dipolar



135: n = 3, 1,3,5-
136: n = 4, 1,2,4,5-
99: n = 6, 1,2,3,4,5,6-

137, K_2CO_3, Acetone

138: n = 3; (95%)
102: n = 4; (90%)
139: n = 6; (87%)

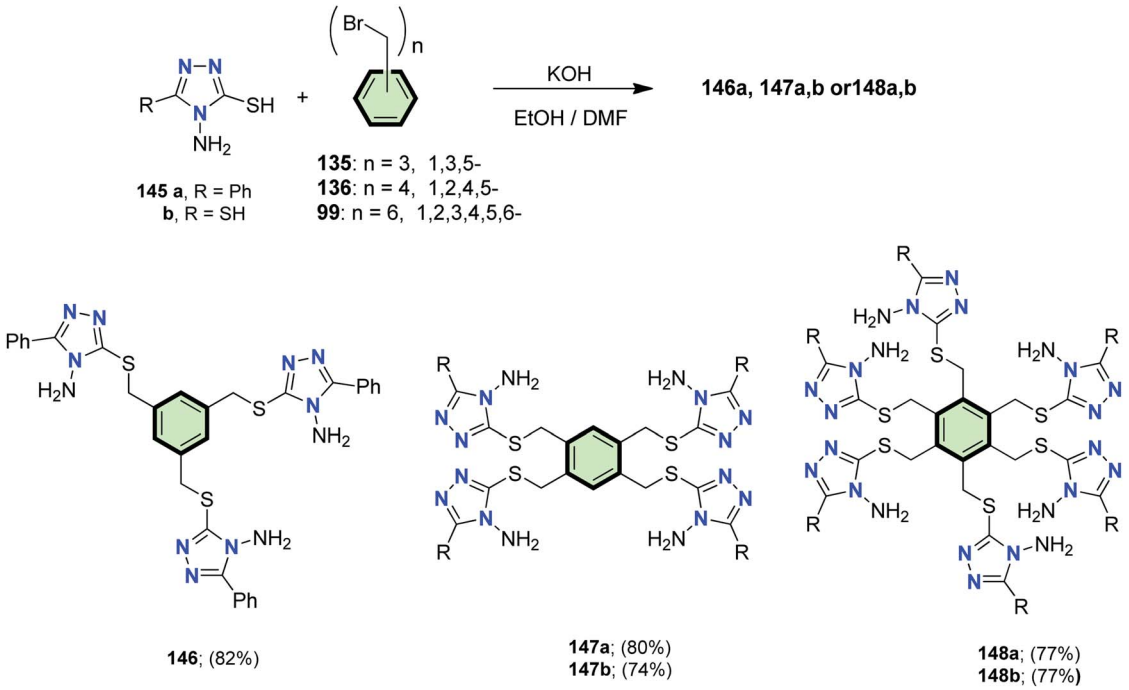
140, (Z = NH_2)
141, (Z = OCH_3)

142a: n = 3, Z = NH_2; (96%)
142b: n = 4, Z = NH_2; (81%)
142c: n = 6, Z = NH_2; (91%)
143a: n = 3, Z = OCH_3; (85%)
143b: n = 4, Z = OCH_3; (87%)
143c: n = 6, Z = OCH_3; (92%)

SeO_2 | AcOH

144a; (87%)
144b; (92%)
144c; (96%)

Scheme 36 Synthesis of SSMs **144a–c** with 1,2,3-selenadiazole side arms.



Scheme 37 Synthesis of SSMs with benzene core and 1,2,4-triazole side arms.

cycloaddition reaction of the respective chalcones **75, 79, 81** and **83** with sarcosine **76** and paraformaldehyde 77 in toluene at reflux (Schemes 18–21).

4.3.1.1.2. Five-membered heterocyclic arms containing two heteroatoms. ***4.3.1.1.2.1. Thiazole and its derivatives.*** Salem *et al.*[86] reported the synthesis of multi-armed thiazole derivatives **88a** and **88b** in 67 and 69% yields, respectively, by the reaction of tris(aldehyde thiosemicarbazones) **85a** and **85b** with each of 2-bromo-1-phenyl ethanone **86** and 2-bromo-1-(4-chlorophenyl)ethanone **87** in ethanol at reflux in the presence of TEA (Scheme 22). The same methodology was extended to the preparation of tetrakis- and hexakis(thiazoles) **90a, 90b, 92a** and **92b** in good yields from the corresponding poly(aldehyde thiosemicarbazones) **89a, 89b, 91a** and **91b** (Schemes 23 and 24).

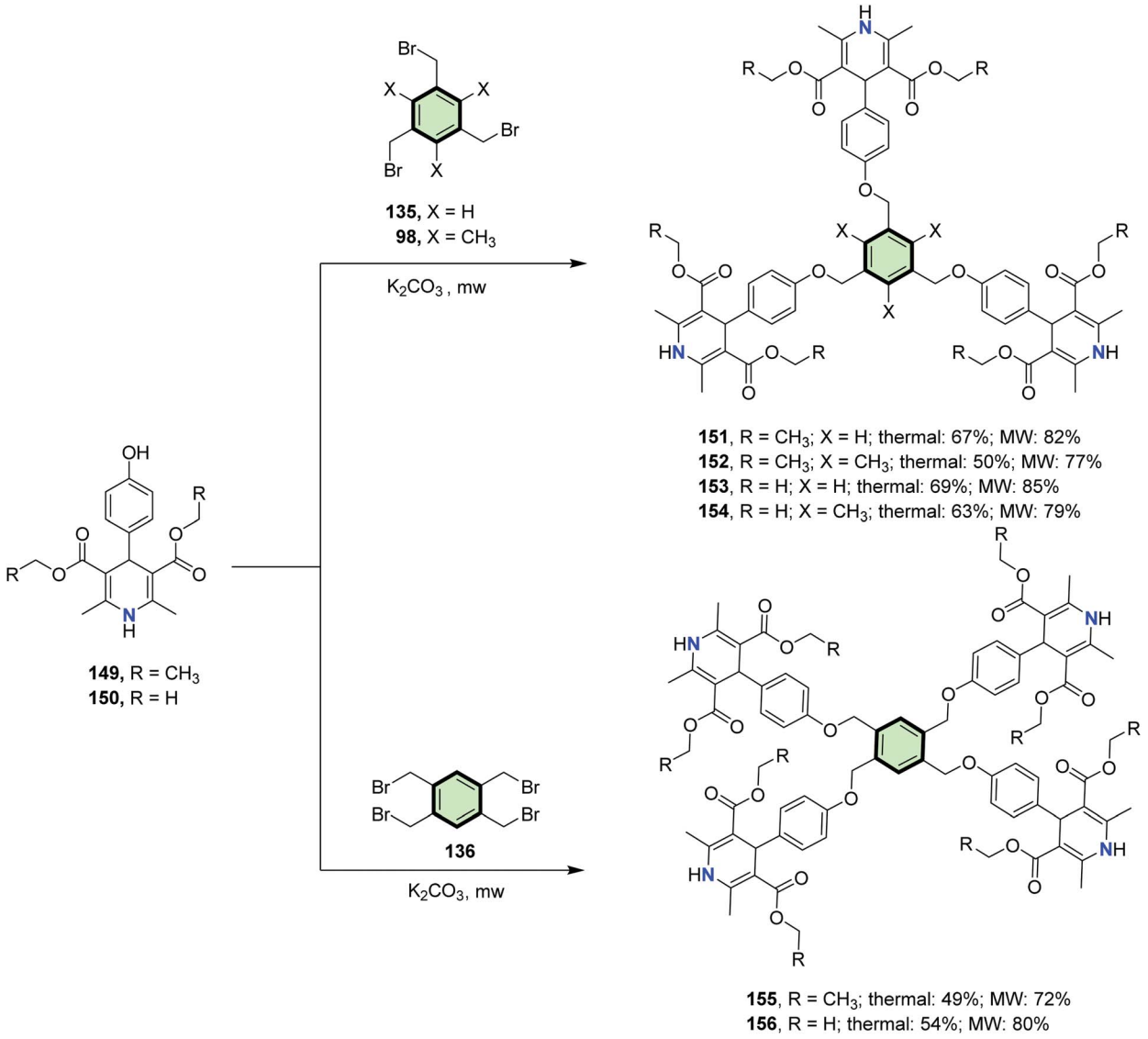
Star-shaped molecules with benzene core and (pyrazolyl) thiazole side arm **94a** and **94b** were synthesized in 70 and 64% yields, upon reaction each of tris(aldehyde thiosemicarbazones) **85a** and **85b** with 2-bromo-1-(5-methyl-1-phenyl-1*H*-pyrazol-4-yl) ethanone **93** in ethanol at reflux in the presence of TEA (Scheme 25).[86]

In analogy, tetrakis(pyrazolyl)thiazoles **95a** and **95b** and hexakis(pyrazolyl)thiazoles **96a** and **96b** were synthesized by the reaction of the appropriate poly(thiosemicarbazones) **89a,b** and **91a,b** with 4-bromoacetylpyrazole **93** under the same condition (Fig. 3).[86]

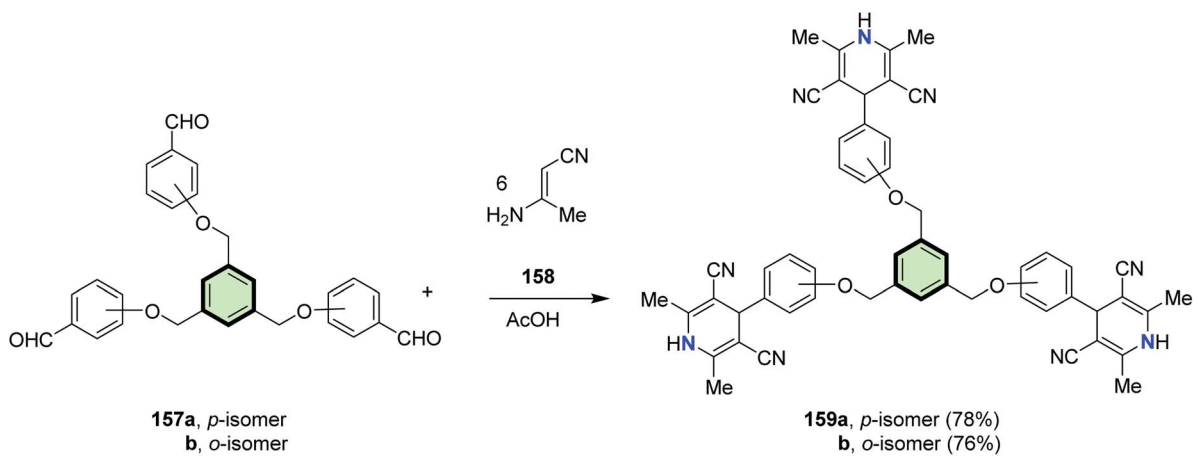
4.3.1.1.2.2. Pyrazole. Reger *et al.*[34] reported the synthesis of ligands with tris(pyrazolyl)methane units **100** and hexakis(pyrazolyl)methane units **101** in good yields by the reaction of tris-2,2,2-(1-pyrazolyl)ethanol **97** with each of 2,4,6-tris(bromomethyl)mesitylene **98** and 1,2,3,4,5,6-hexakis(bromomethyl)benzene **99**, respectively, in the presence of NaH (Scheme 26). These star-shaped ligands have been used to synthesize interesting metallacage complexes *via* symmetry-interaction approach. The ligands showed a semi-flexible coordination behavior depending on the central metal mode of bonding, *i.e.* closed metallacage of high thermal stability at 200 °C was formed in case of Ag(I) while in case of Cd(II) open cage was produced.

Al-Smadi *et al.*[87] reported the synthesis of multi-armed aromatic chalcone **104** in 75% yield through cross-aldol condensation reaction between multi-armed aromatic ketone **102** and 4-(dimethylamino)benzaldehyde **103** in basic medium. The multi-armed aromatic chalcone **104** underwent cyclization reactions upon treatment with phenyl hydrazine **105** to yield the corresponding multi-armed pyrazoline derivatives **106** in 55% yield. Aromatization of the pyrazoline rings of the latter compound with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene gave the corresponding multi-armed compound **107** in 43% yield (Scheme 27).

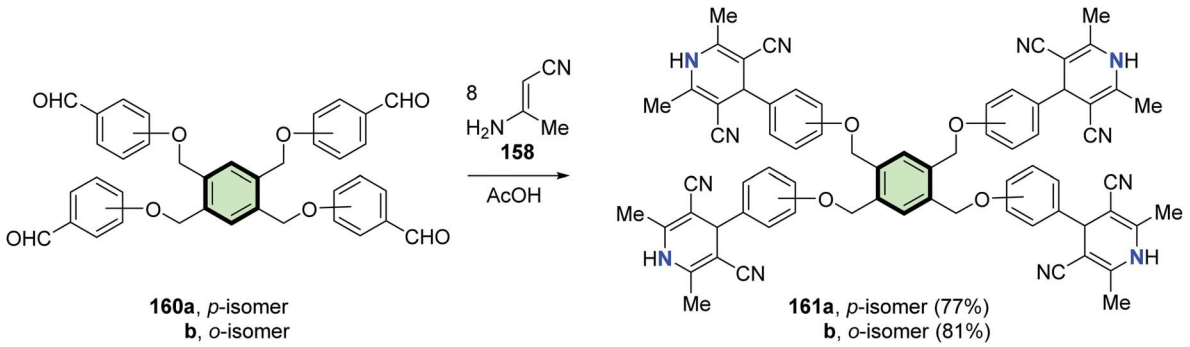
4.3.1.1.3. Five-membered heterocyclic arms containing three heteroatoms. ***4.3.1.1.3.1. 1,2,4-Oxadiazole.*** Heating benzamidoxime derivatives **108** (prepared form ethyl gallate *via* a multistep procedure) with trimesic acid chloride **109** (prepared by heating benzene-1,3,5-tricarboxylic acid **4** with thionyl chloride in DMF) in pyridine at reflux afforded 1,2,4-oxadiazole-based benzene-cored SSMs **110** in moderate yields (55–60%) (Scheme 28). The number and length of the peripheral tails altered greatly the mesophase stability and the thermal range. Single crystal XRD analysis indicated that **110a** (with



Scheme 38 Synthesis of tripodal and tetrapodal(1,4-dihydropyridines) **151–156**.



Scheme 39 Synthesis of tris(1,4-dihydropyridines) **159a** and **159b**.

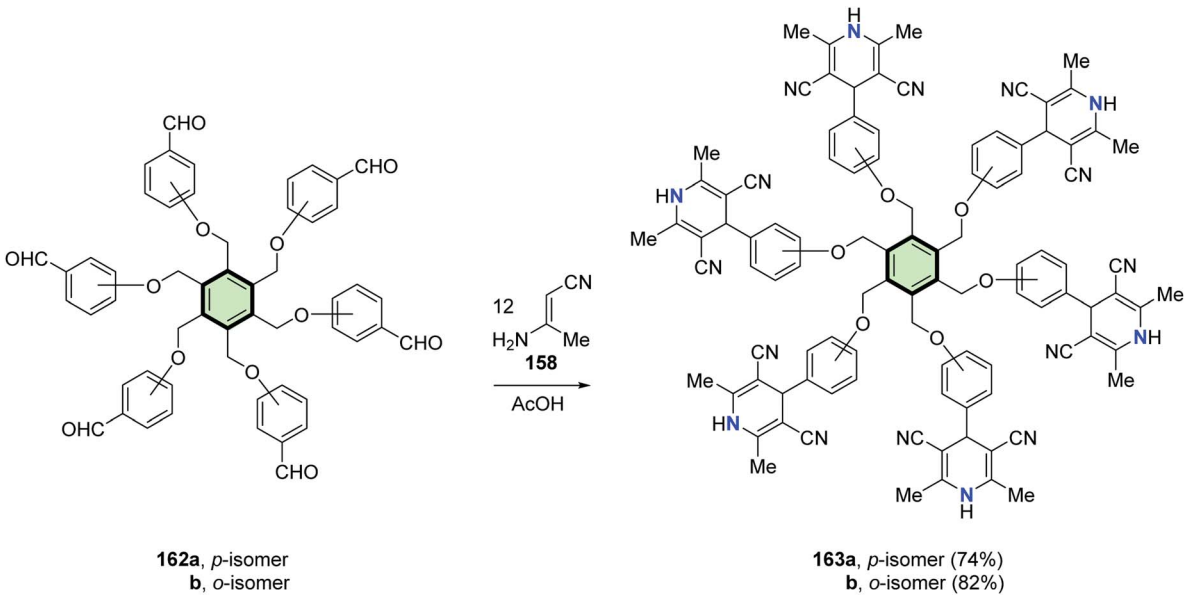


Scheme 40 Synthesis of tetrakis(1,4-dihydropyridines) **161a** and **161b**.

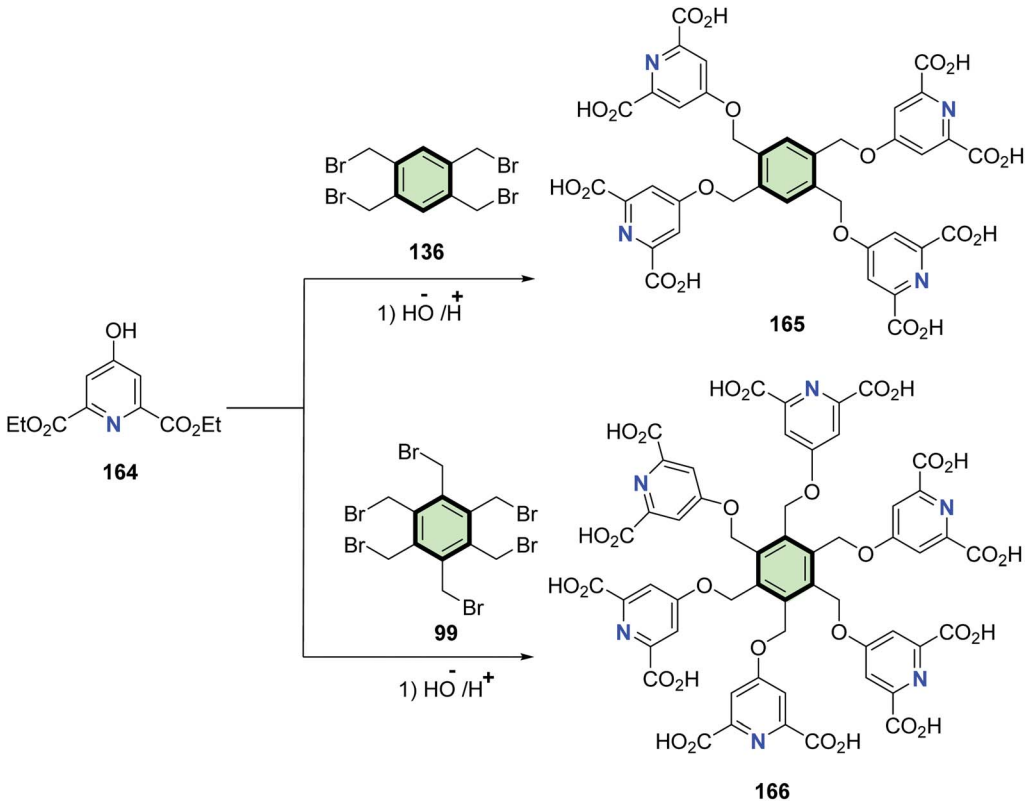
three peripheral chains) was crystalline and lamellar. The star-shaped compound has to contain at least six peripheral alkyl groups to attain a Col_h phase. The thermal range is direct proportional to the number of peripheral alkyl tails. Furthermore, increasing the length of alkyl chain led to a reduction of Col_h phase. Although all hekates **110a–d** exhibited weak fluorescence in solution, they have a strong emission in solid state and exhibited a red shift upon increasing the number of alkyl tails. The energy gap ΔE_g^{opt} values of **110a–d** are 4.21–4.23 eV which is higher than that of 1,3,4-oxadiazole analogues 117–120 (3.35–3.48 eV,[31] *cf.* Fig. 4). The emission spectra of **110a–d** displayed maxima centered at 299–314 nm which were red-shifted on increasing the number of peripheral groups. In particular, Hekate **110b** acted as a supergelator forming gel in non-polar solvent (which is so rare). At higher concentration, it formed a stable gel which could be molded. Compound **110b** exhibited aggregation-induced blue light emission twelve times higher than that of the monomer. Photophysical studies showed that **110b** forms J-aggregate in thin film while H-aggregate in gel. XRD of **110b** clarified a Col_r assembly in the xerogel state.[25]

4.3.1.1.3.2. 1,3,4-Oxadiazole. 5-(4-Bromophenyl)-1*H*-tetrazole **111** underwent cleavage–cyclization reaction upon treatment with benzene-1,3,5-tricarbonyl trichloride **109** in anhydrous pyridine to give 1,3,5-tris(5-(4-bromophenyl)-1,3,4-oxadiazol-2-yl)benzene **112** in 75% yield (Scheme 29).[88]

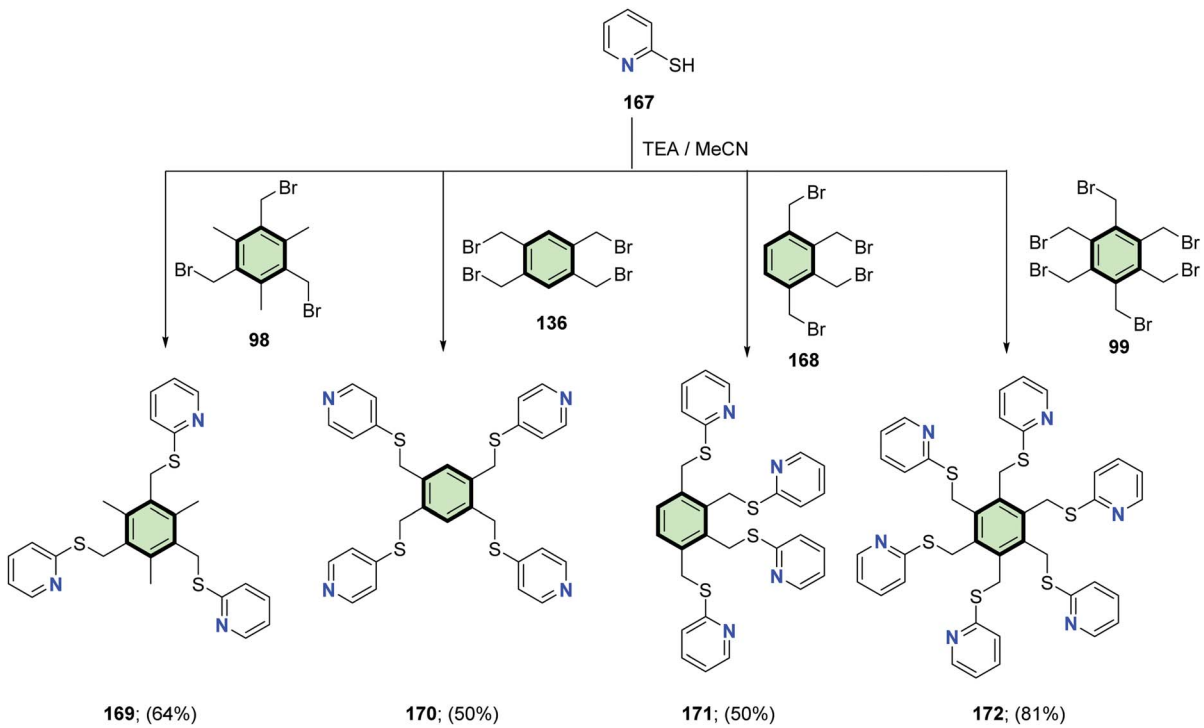
Williamson's *O*-alkylation of ethyl 3,5-dihydroxybenzoate **113** with *n*-bromodecane followed by reaction with hydrazine hydrate gave 3,5-bis(decyloxy)benzohydrazide **114** in moderate yield (67%). The acylation of **114** with benzene-1,3,5-tricarbonyl trichloride **109** in THF in the presence of triethylamine at reflux resulted in the formation of tris(aroyl)benzene-1,3,5-tricarbohydrazide **115**. Cyclization of **115** was affected by treatment with phosphorus oxychloride to form SSMs with three pendant 1,3,4-oxadiazole moieties **116** (Scheme 30). Compound **116** stabilized a Col_h phase and showed supergelation property due to π–π interactions. It also showed many fold hyperchromic increase in photoluminescence.[89]



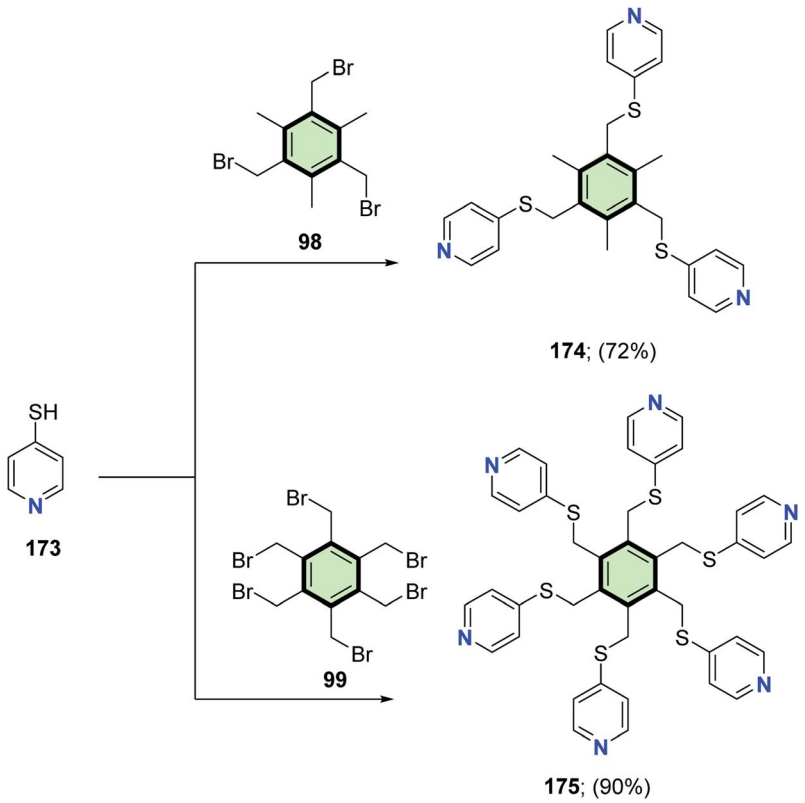
Scheme 41 Synthesis of hexakis(1,4-dihydropyridines) **163a** and **163b**.



Scheme 42 Synthesis of SMM **165** and **166** with benzene core and pyridine-2,6-dicarboxylic acid side arm.



Scheme 43 Synthesis of poly(pyridylsulfanylmethyl)arenes **169**–**172**.



Scheme 44 Synthesis of poly(pyridylsulfanylmethyl)arenes **174** and **175**.

In a similar reaction sequence, SSMs **117–120** were synthesized in 31–36% yields starting from ethyl gallate (Fig. 4).[31]

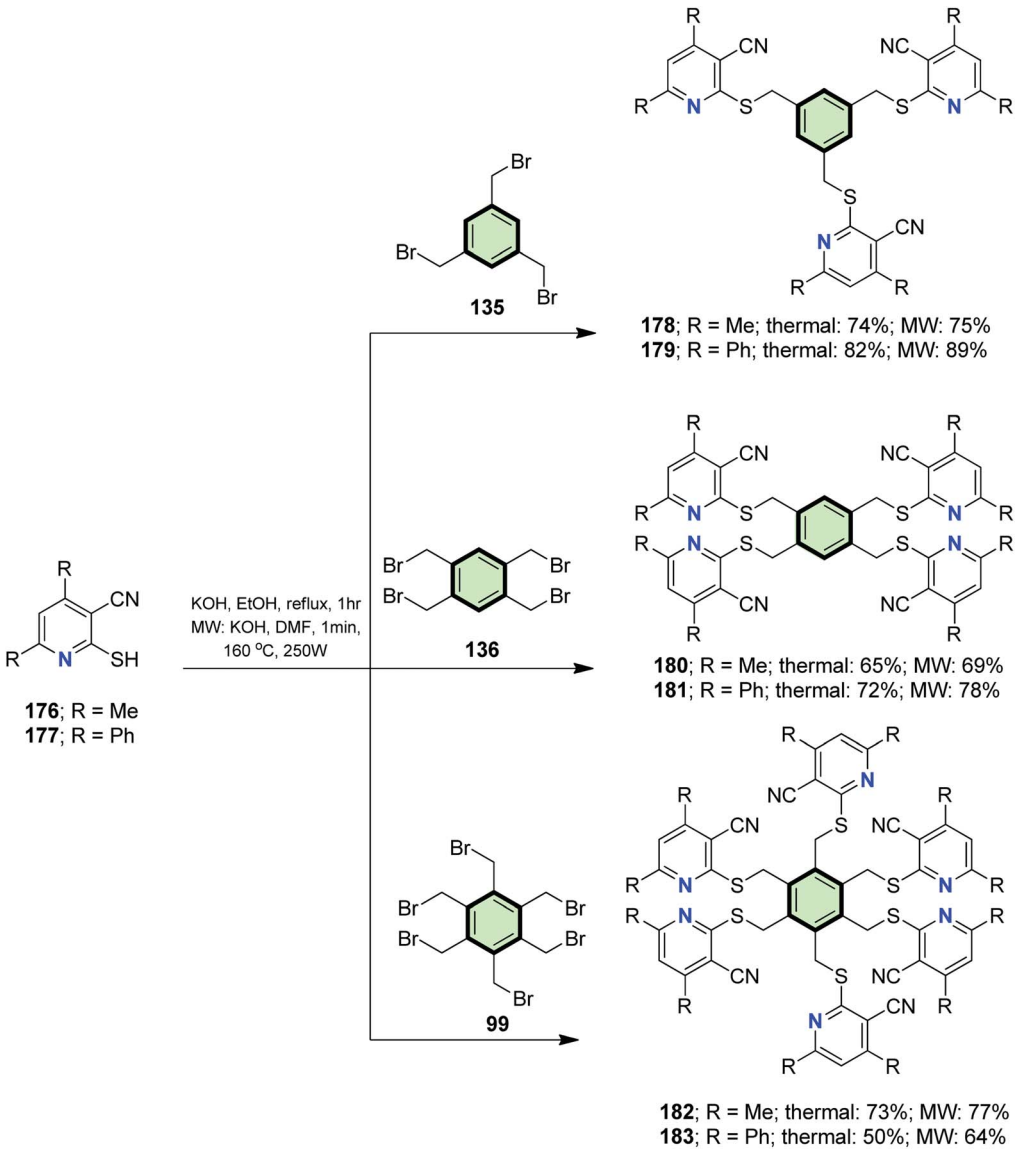
1,3,4-Oxadiazole-based SSMs **123a,b** were synthesized as outlined in Scheme 31 *via* firstly reaction of 4-((3,4-bis(alkoxy) phenyl)ethynyl)benzonitrile **121a** or **121b** with sodium azide to afford tetrazole derivatives **122a** and **122b**, respectively, in excellent yields (85–90%). Synthesis of **123a** and **123b** was then achieved *via* treating **122a** and **122b**, respectively, with trimesic acid chloride **109** by a typical Huisgen reaction mechanism. 1,3,4-Oxadiazole-SSMs **123a** and **123b** exhibited enantiotropic columnar mesophases over a wide temperature range, with the liquid crystalline phases exhibiting strong blue fluorescence. On cooling, **123a** transformed into a transparent glass at room temperature wherein the liquid crystalline texture was retained. The glassy film remained stable over a period of one year and exhibited blue luminescence with an absolute quantum yield of 26%.

The length of the alkyl substituent was observed to have a significant effect on the absorption and fluorescence properties of the gels, which was attributable to the role of the alkyl substituents in controlling the nature of the molecular packing within the self-assembled fibers of the gels. The optical properties of these derivatives in gel state were found to be alkyl chain dependent. The gel derived from **123a** exhibited blue emission whereas **123b** exhibited bluish-green emission in decane.

The extent of aggregation was found to be higher in **123b** which is evident from their large red shift observed in absorption and emission spectra compared to the other derivative. These observations clearly demonstrate that perturbation of molecular structure has remarkable influence on their bulk macroscopic properties.[85]

4.3.1.1.3.3. 1,3,4-Thiadiazole. A series of star-shaped molecules based on benzene as the central core and three pendant 2-phenyl-5-(di-, and/or tri-*n*-alkoxyphenyl)-1,3,4-thiadiazole arms **125a–c** were synthesized by the reaction of 1,3,5-benzenetricarbonyl trichloride **109** with the corresponding phenolic-1,3,4-thiadiazole precursors **124a–c**, respectively, in the presence of dimethylaminopyridine (DMAP) and triethylamine in dry toluene (Scheme 32).[18] The position and number of alkoxy substituents was found to affect the photophysical and liquid crystalline properties of SSMs **125**. Of the synthesized SSMs, **125a** and **125b** showed enantiotopic liquid crystalline properties adopting hexagonal columnar phase on cooling the isotropic liquid to room temperature. These mesogens were luminescent at room temperature either in solid or in film. The cyclic voltammetry data of **125b** indicated that it can act as hole-blockers.

Yang *et al.*[90] reported that heating hexakis(bromomethyl) benzene **99** with the sodium salt of 2-amino-5-sulfanyl-1,3,4-thiadiazole **127** (obtained upon treatment of **126** with sodium ethoxide) in ethanol at reflux gave hexakis(1,3,4-thiadiazol-2-amine) **128** bonded to benzene core *via* methylenesulfinyl



Scheme 45 Synthesis of SMM with benzene core and nicotinonitrile side arm **178–183**.

(CH_2–S) linkages in 93% yield. The latter compound underwent oxidation upon treatment with hydrogen peroxide to give hexakis(methylenesulfinyl)hexakis(1,3,4-thiadiazol-2-amine) **129** in 90% yield (Scheme 33). Three arms of compound **129** could successfully encapsulate one or two copper(II) ions.

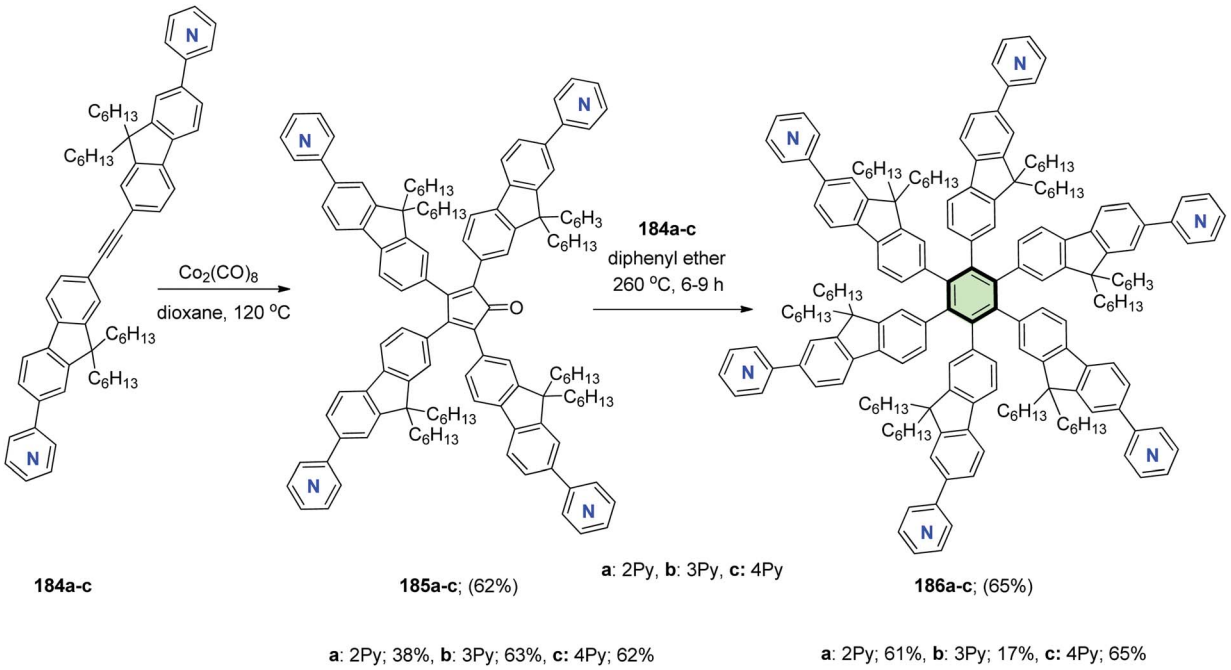
A star-shaped molecule with benzene core and 1,3,4-thiadiazole side arm **130** was synthesized in 64% yield by refluxing tris(aldehyde thiosemicarbazone) **85b** in acetic anhydride (Scheme 34).[86]

Similarly, tetrakis(4,5-dihydro-1,3,4-thiadiazolyl) derivatives **131a** and **131b** as well as hexakis(4,5-dihydro-1,3,4-thiadiazolyl) **132** have been synthesized in good yields from the corresponding tetra- and hexa(aldehyde thiosemicarbazone) (Fig. 5).[86]

Heating of tris(aroyl)benzene-1,3,5-tricarbohydrazide **115** with Lawesson's reagent in dry toluene furnished SSM 133 with three pendant 1,3,4-thiadiazole moieties (Scheme 35).[89]

In a similar reaction sequence, SSMs **134a–d** were synthesized in 30–49% yields starting from ethyl gallate (Fig. 6).[31]

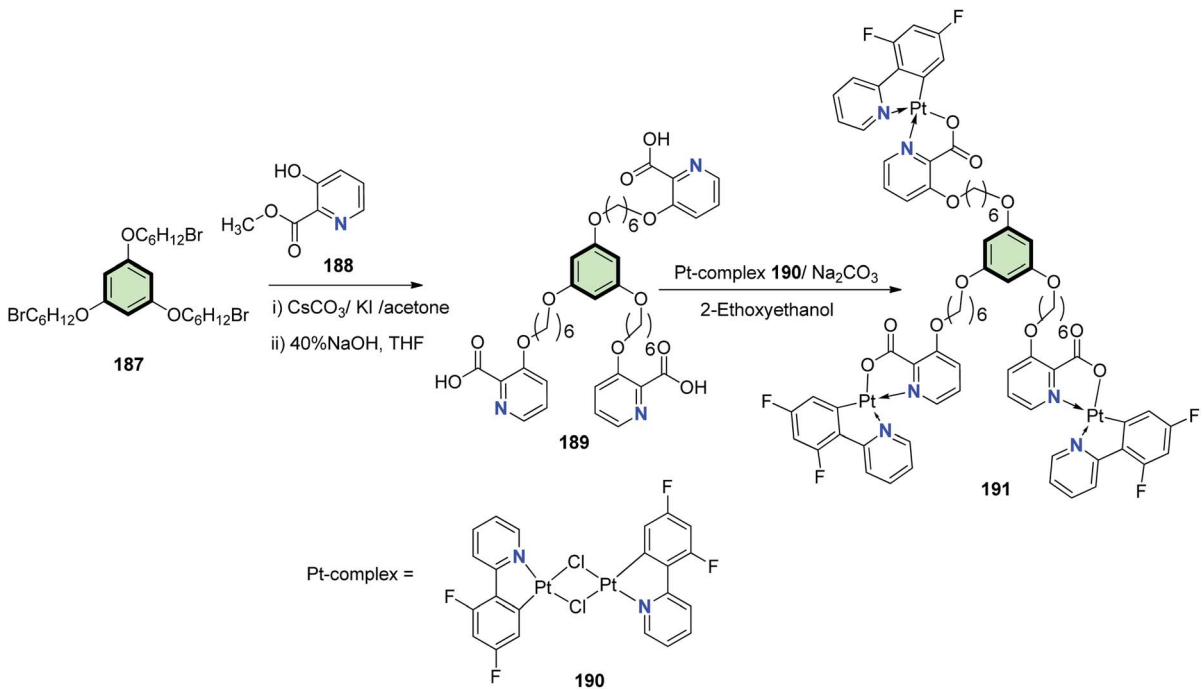
4.3.1.1.3.4. 1,2,3-Selenadiazole. Al-Smadi and Ratrout[91] reported a multi-step procedure for the synthesis of multi-armed benzene derivatives **144a–c** containing two, three, four and six 1,2,3-selenadiazole side arms as outlined in Scheme 36. The poly ketones **138**, **102** and **139** were prepared by reacting bromomethyl benzene derivatives **135**, **136** and **99**, respectively, with 4-hydroxyacetophenone **137** in acetone in the presence of K_2CO_3. Condensation of **138**, **102** and **139** with semicarbazide **140** or methyl hydrazine carboxylate **141** afforded the corresponding semicarbazones **142a–c** or the ethoxycarbonyl



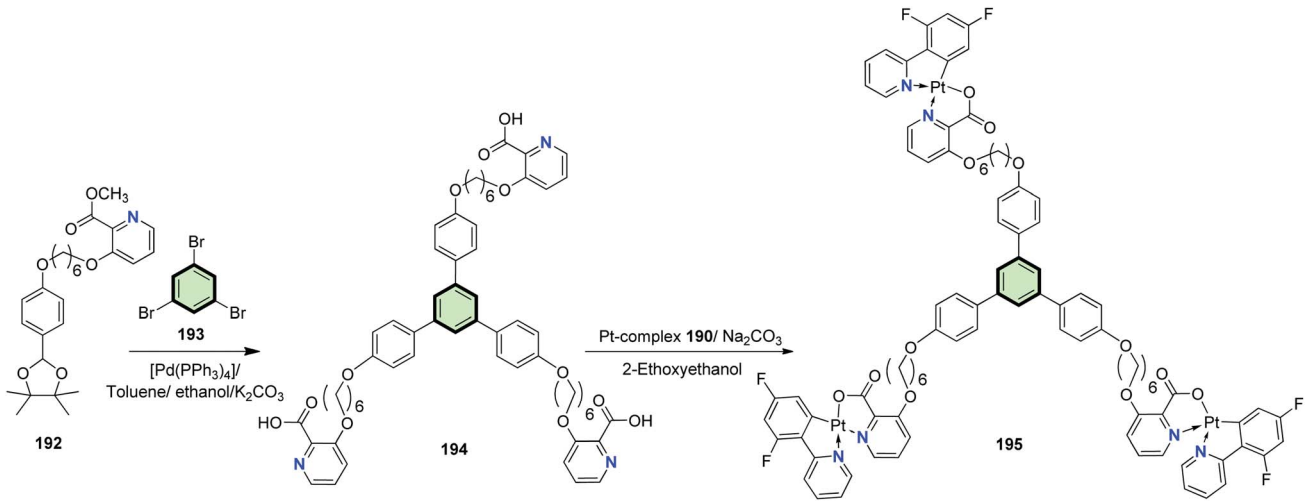
Scheme 46 Synthesis of hexakis(9,9-dihexyl-7-(pyridin-4-yl)-9*H*-fluoren-2-yl)benzene **186a–c**.

hydrazones **143a–c**, respectively. Subsequent treatment of the latter compounds with selenium dioxide in acetic acid gave compounds **144a–c** in good yields (Scheme 36).

4.3.1.1.3.5. 1,2,4-Triazole. Elwahy *et al.*[92] reported the synthesis of 1,3,5-tris(4-amino-5-phenyl-4*H*-3-sulfanylmethyl) benzene **146** in 82% yield by the reaction of tris(bromomethyl) benzene **135** with 4-amino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **145a** in refluxing EtOH/DMF mixture containing KOH. Under similar conditions, tetrakis- and hexakis(4-amino-5-phenyl-4*H*-3-sulfanyl methyl)benzenes **147a,b** and **148a,b** were prepared in 74–80% yields, respectively, upon treatment of the



Scheme 47 Synthesis of cyclometalated platinum(II) complexes **191**.



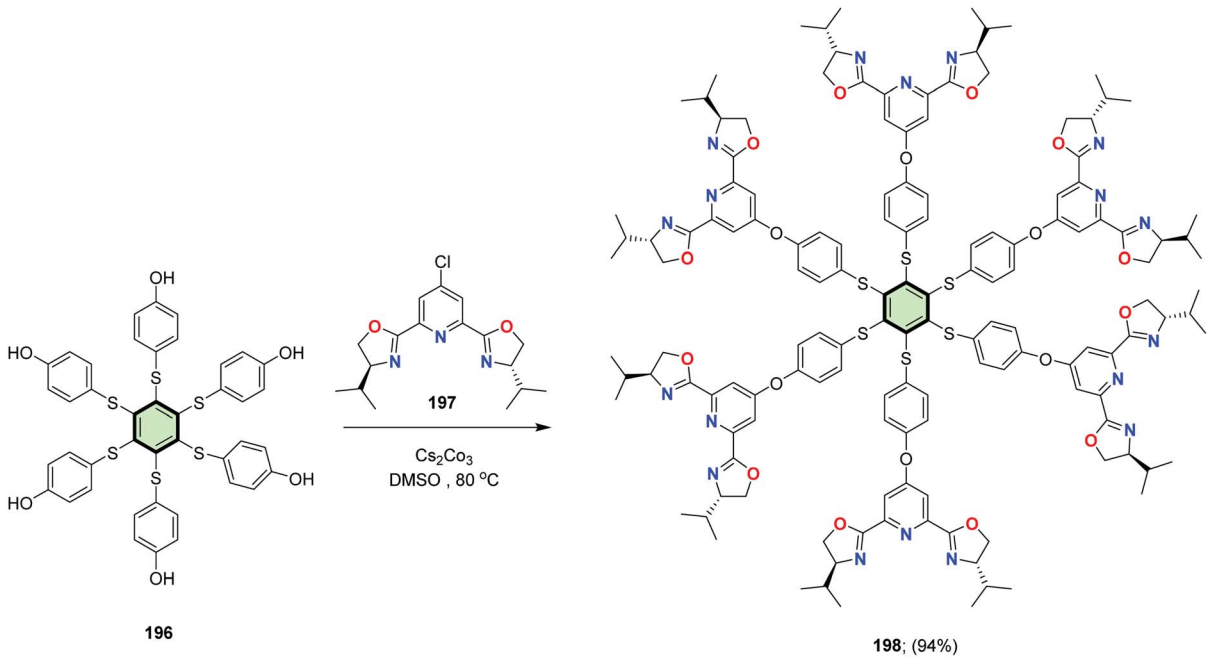
Scheme 48 Synthesis of cyclometalated platinum(II) complexes **195**.

aminotriazoles **145a,b** with the corresponding tetrakis(-bromomethyl)benzene **136** and hexakis (bromomethyl) benzene **99** in refluxing EtOH/DMF mixture containing KOH (Scheme 37).

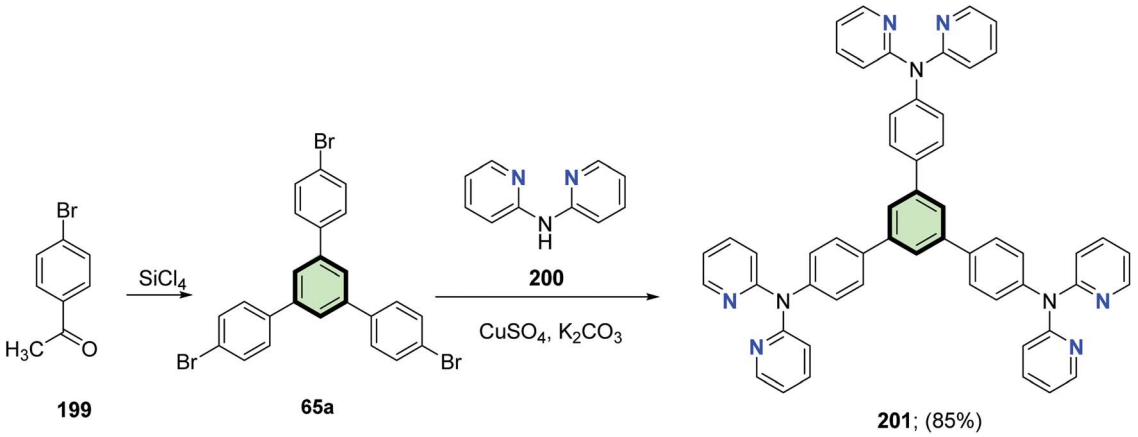
4.3.1.2. Benzene-cored SSMs with six-membered heterocyclic arms

4.3.1.2.1. Six-membered heterocyclic arms containing one heteroatom. ***4.3.1.2.1.1. 1,4-Dihydropyridine.*** Rajesh *et al.*[93] reported the synthesis of tripodal and tetrapodal 1,4-dihydropyridines (DHP) **151–156** by the reaction of monofunctional 1,4-DHP **149** and **150** with the appropriate tri-bromomethylbenzenes **135** and **98** or tetra-bromomethyl benzene **136**, respectively, in the presence of K_2CO_3 as a base. The reactions were performed under conventional heating (49–69% yields) as well as under microwave irradiation (72–85% yields) (Scheme 38).

Abdelhamid *et al.*[94] reported the synthesis of poly(2,6-dimethyl-4-phenyl-1,4-dihydropyridinyl)arenes **159a**, **159b**, **161a**, **161b**, **163a** and **163b** in good yields through reaction of tris-, tetrakis-, and hexakis(formylphenoxy methyl)benzenes **157a**, **157b**, **160a**, **160b**, **162a** and **162b**, respectively, with 3-aminobut-2-enenitrile **158** in acetic acid at reflux (Schemes 39–41).



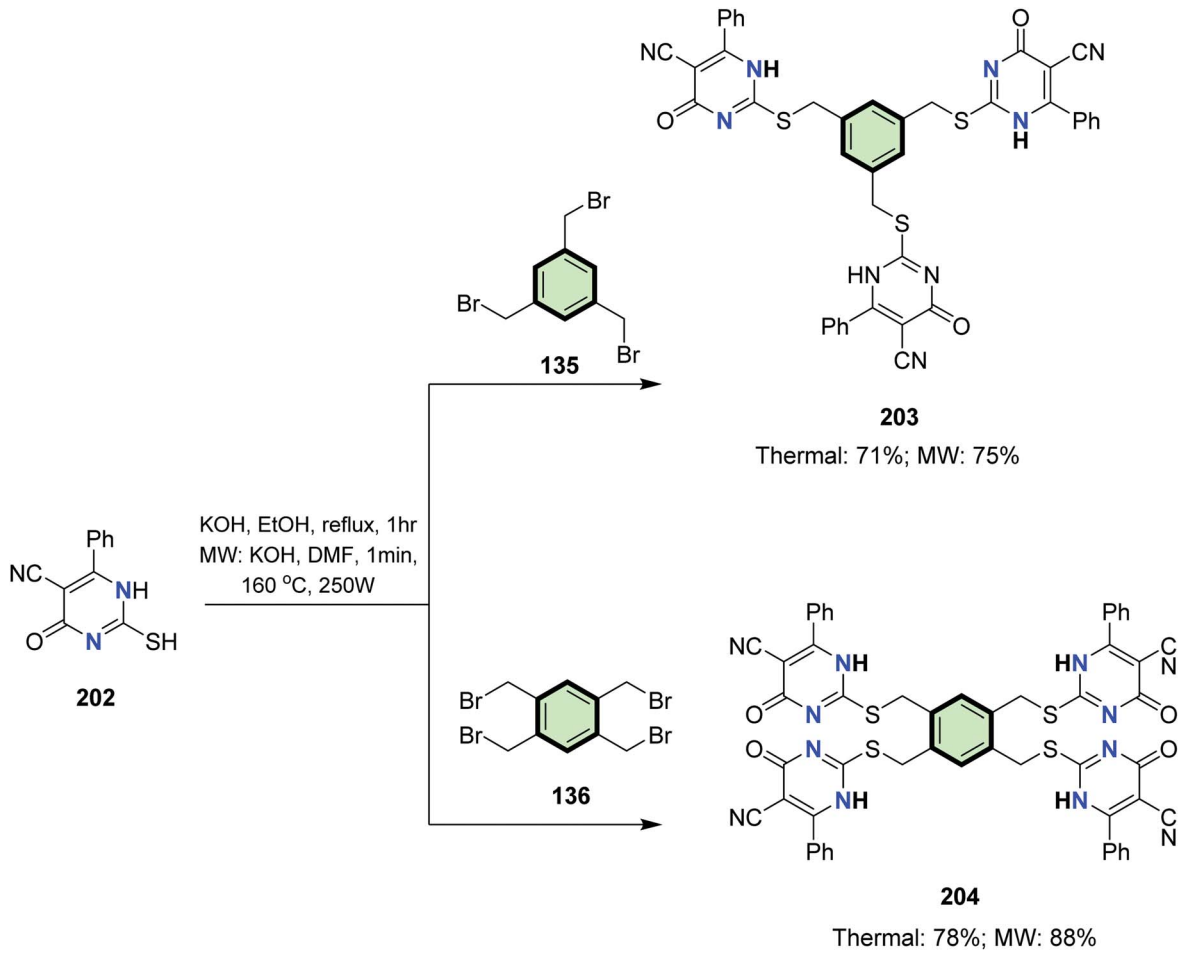
Scheme 49 Synthesis of SSMs with (phenylthio)benzene core and 2,6-bis(4,5-dihydrooxazol-2-yl)pyridine side arms **198**.



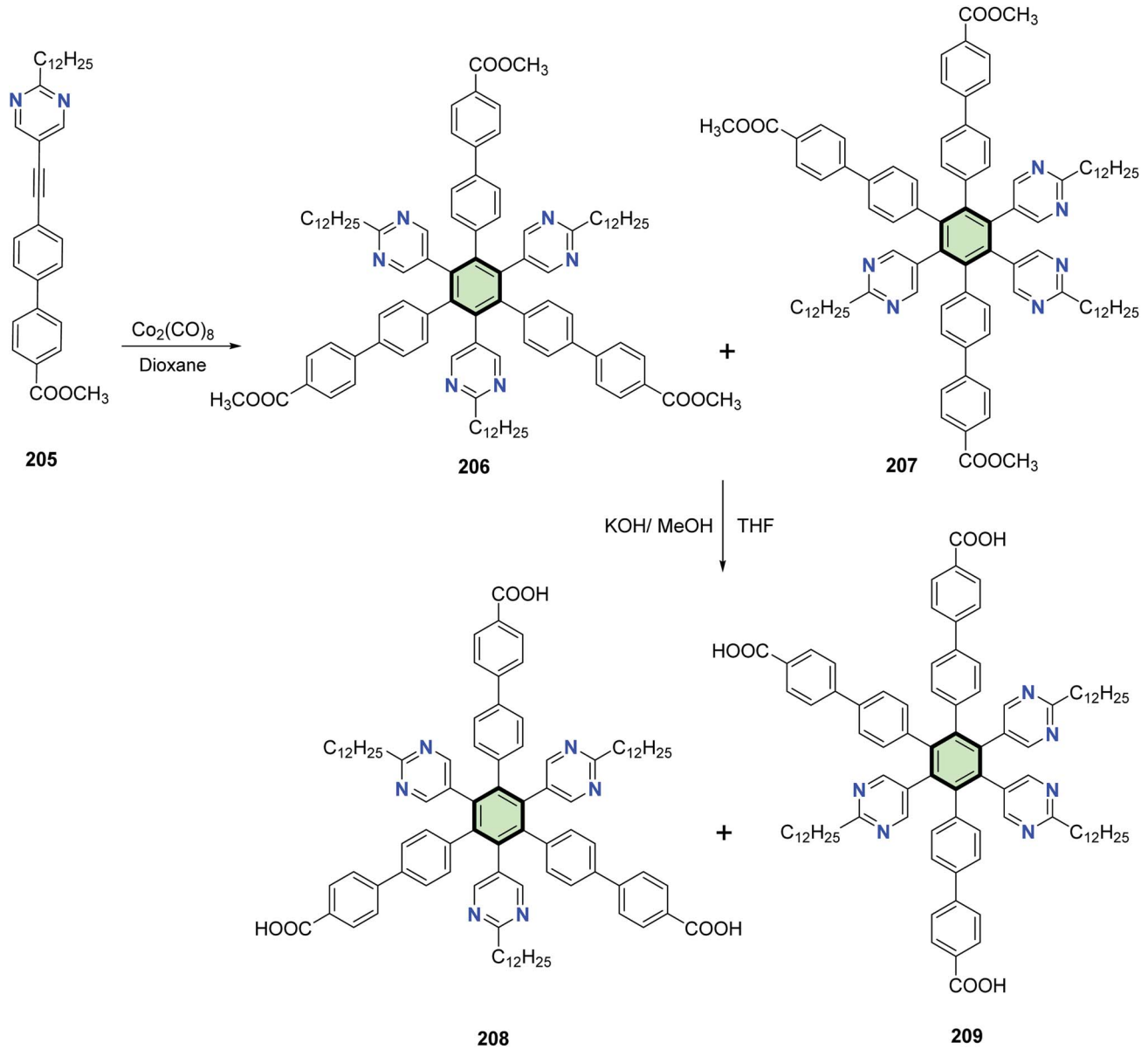
Scheme 50 Synthesis of 1,3,5-tris(*p*-(2,2′-dipyridylamino)phenyl)benzene **201**.

4.3.1.2.1.2. ***Pyridine and its derivatives.*** Yin and Tan[95] reported the synthesis of multifunctional pyridine-2,6-dicarboxylic acid derivatives **165** and **166** by coupling of diethyl 4-hydroxypyridine-2,6-dicarboxylate **164** with tetrakis(bromomethyl)benzene **136** and hexakis(-bromomethyl)benzene **99**, respectively, in basic medium (Scheme 42).

McMorran and Steel[96] reported the synthesis of a series of poly(pyridylsulfanylmethyl)arenes **169–172**, **174** and **175** in



Scheme 51 Synthesis of tris- and tetrakispyrimidine derivatives **203** and **204**.

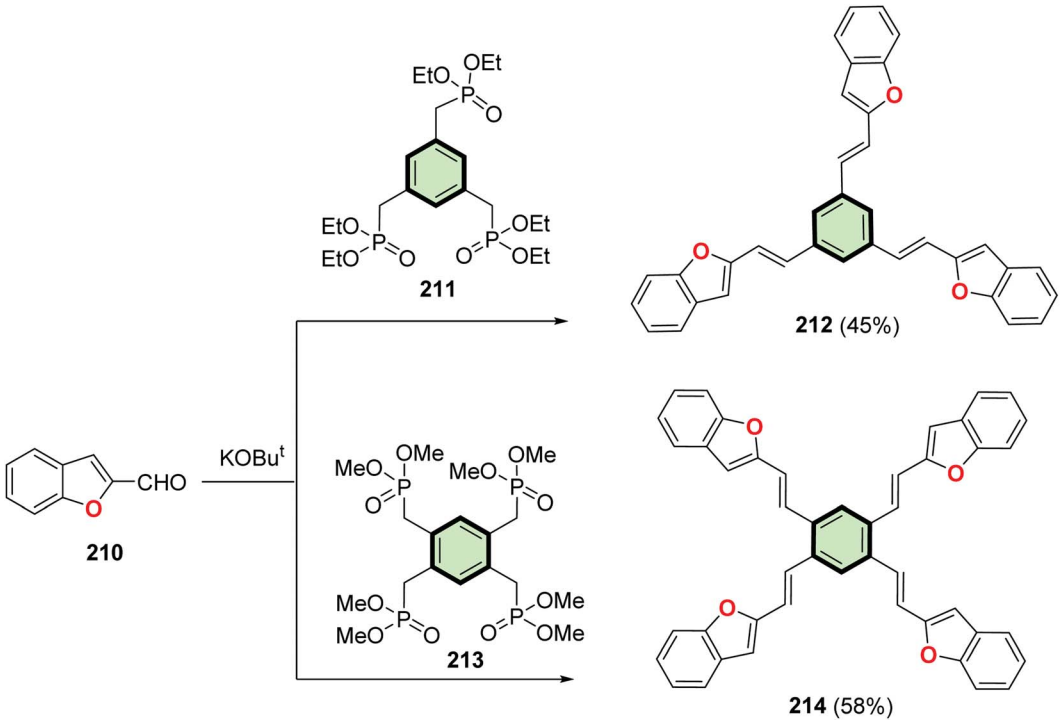


Scheme 52 Synthesis of hexaheteroaryl benzene derivatives **206–209** containing three pyrimidylbenzene side arms.

good yields from the reaction of either 2- or 4-mercaptopyridine **167** and **173** with the corresponding poly(bromomethyl)arene **98**, **136**, **168** and **99** in the presence of triethylamine (Schemes 43 and 44).

Reaction of 2-mercaptonicotinonitriles **176** and **177** with poly(bromomethyl) benzenes **135**, **136** and **99** in ethanolic KOH under conventional heating as well as under microwave irradiation, afforded the corresponding polypyridines **178–183** in good yields (Scheme 45).[97]

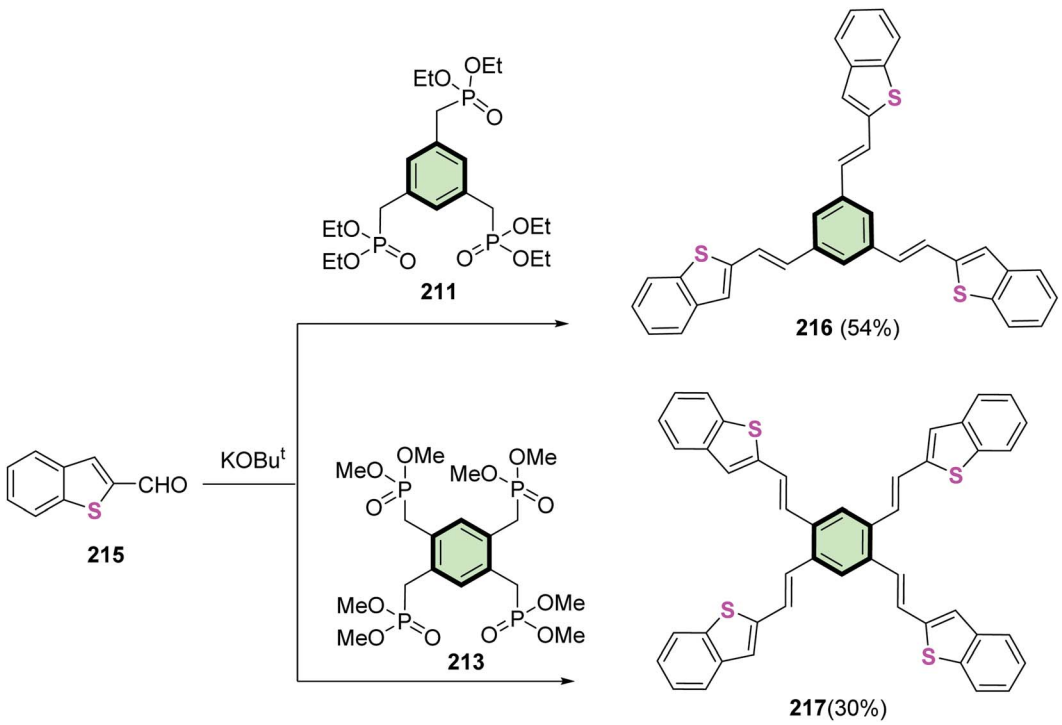
Yin *et al.*[98] reported the synthesis of star-shaped macromolecules **186a–c** with hexakis(fluoren-2-yl)benzene as the core and pyridine as the periphery. The synthetic strategy includes octacarbonyldicobalt-catalyzed cycloaddition reaction for different alkyne precursors **184a–c**. The coordination interaction between the pyridine ring of alkyne precursor and the cobalt catalyst may result in very low yield of the cyclotrimerization product. However, with the increase of the catalyst loading, the yields of the intermediates cyclopentadienone **185a–c** are more likely to generate *via* cycloaddition reactions presumably due to the electron-deficient property of the alkyne precursors. The desired cyclotrimerization products can be obtained by the Diels–Alder reactions of cyclopentadienone **185a–c** with acetylene **184a–c** in good yield (Scheme 46). Under the initial catalyst loading 10%, the desired cyclotrimerization product **186a** was exceptionally obtained from the precursor of **184a** with a good yield of 61%. These compounds exhibit good thermal stability and favorable electron affinity. By using these compounds as electron-transporting materials, all-solution-processed phosphorescent organic light-emitting devices (OLEDs) show good performance with a maximum current



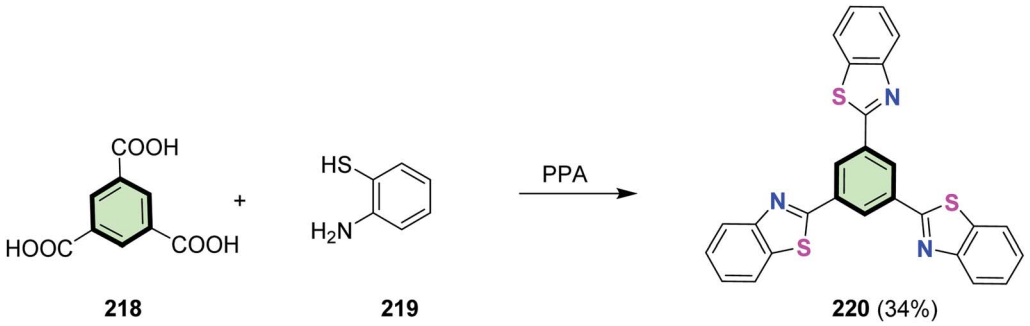
Scheme 53 Synthesis of tris- and tetrakis(2-(benzofuran-2-yl)vinyl)benzene **212** and **214**.

efficiency of 5.6 cd A^{-1} and maximum external quantum efficiency of 4.68%.

The synthesis of cyclometalated platinum(II) complexes **191** and **195** for the application as single emitters in polymeric white emitting diodes (WPLED) is described in Schemes 47 and 48. The starting SSMs containing picolinic acid residues **189** and **194** were prepared by either of the following procedures: (a) tris(bromohexyl)phloroglucinol **187** reacts with methyl 3-

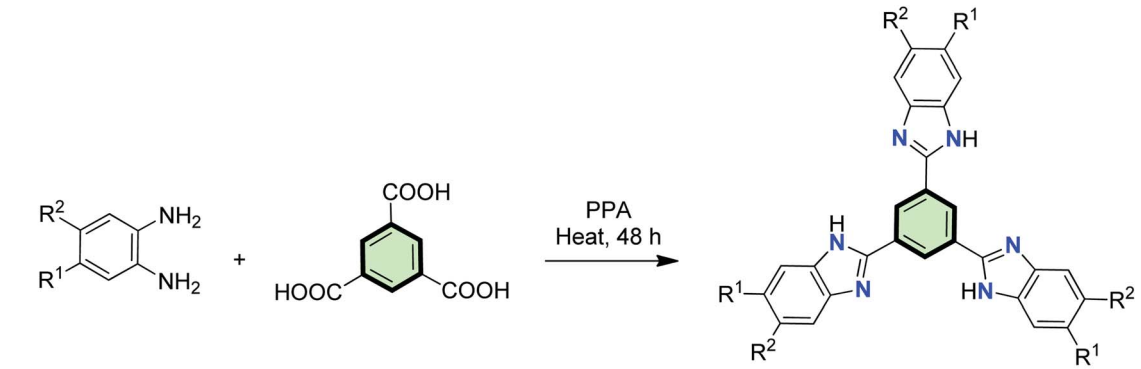


Scheme 54 Synthesis of tris and tetra[2-(benzo[*b*]thien-2-yl)vinyl]benzene **216** and **217**.



218 **219** **220** (34%)

Scheme 55 Synthesis of tris(benzo[*d*]thiazol-2-yl)benzene **220**.



221a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = CH_3$
c; $R^1 = R^2 = CH_3$

218

222a; (86%)
b; (78%)
c; (77%)

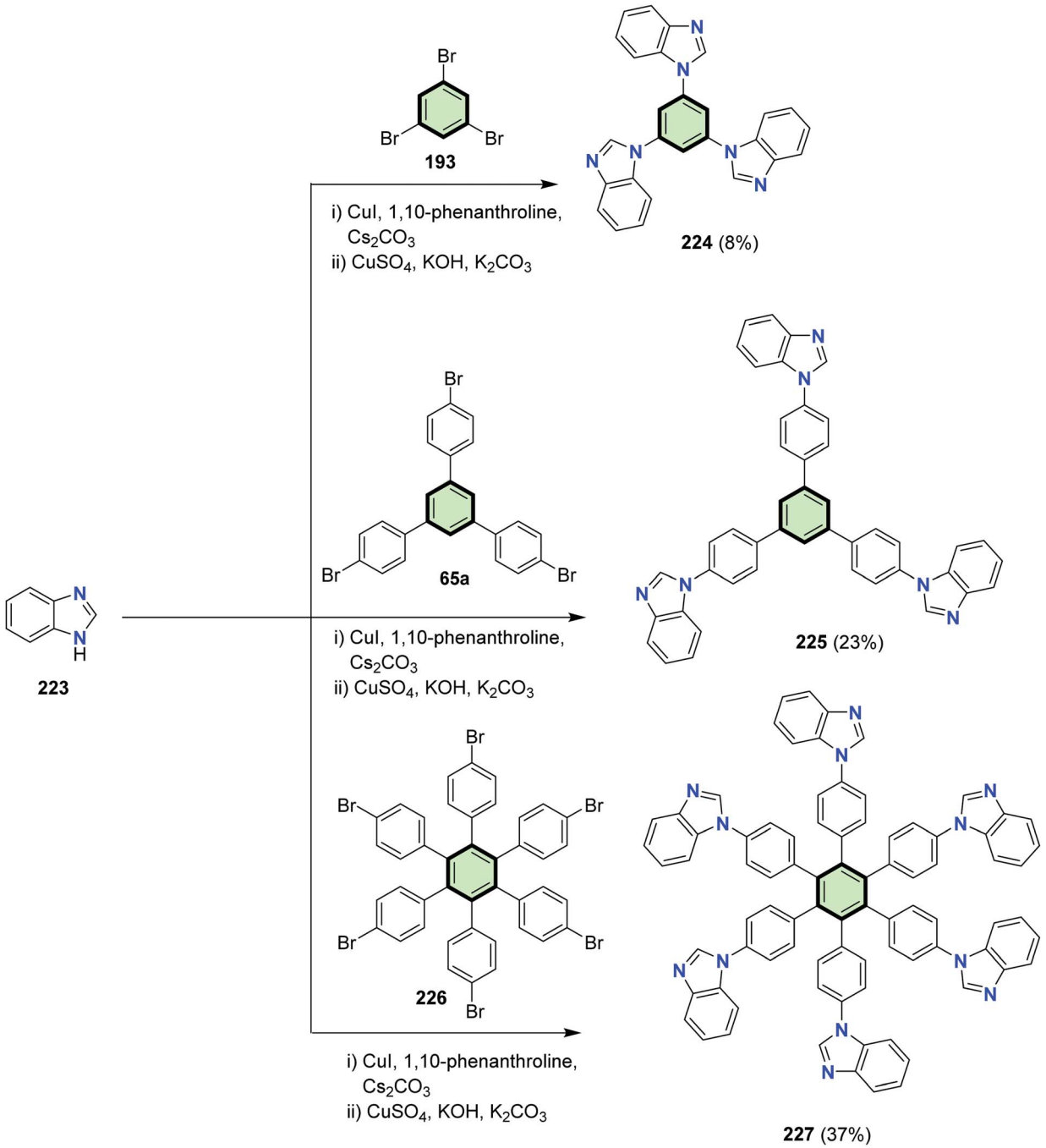
Scheme 56 Synthesis of SSMs with benzene core and benzimidazole side arms **222a–c**.

hydroxypicolinate **188** in the presence of cesium carbonate as a base followed by basic hydrolysis by sodium hydroxide in THF to yield **189**, or (b) the Suzuki coupling reaction of boronic acid bearing methyl picolinate residue **192** with 1,3,5-tribromobenzene **193** followed by basic hydrolysis to give **194**. The cyclometalated complexes **191** and **195** was then synthesized by the reaction of SSMs **189** with dimer **194** in 2-ethoxyethanol in the presence of sodium carbonate as a base.[99]

The UV/Vis absorption data of **191** showed an intense high-lying absorption band (around 240 nm) for ligand-centered π–π* electron transition and two moderate low-lying absorption peaks (about 324 nm and 352 nm) for spin-allowed and spin-forbidden metal-to-ligand charge transfer transitions. Considering **195**, a fourth intense absorption band at 266 nm owing to the effect of the 1,3,5-(4-oxytriphenyl)benzene core. Thus, modifying the aryl core has small effect on the electron transition. The photoluminescence spectra of **191** and **195** showed a clear similarity. Increasing the concentration led to gradual red-shifted emissions. In thin film, significant difference in photoluminescence: two intense high-lying bands (425–485 nm) and a moderately intense, low-lying band (600 nm) are exhibited by **191**. Complex **195** showed a much weaker low-lying emission. In general, the Pt(II) complexes **195** displayed lower aggregation with a controllable excimer emission.

Aubert *et al.*[100] described the synthesis of star shaped compound with (phenylthio)benzene core **198** in 94% overall yield, *via* coupling of (4*S*,4′*S*)-2,2′-(4-chloropyridine-2,6-diyl)bis(4-isopropyl-4,5-dihydrooxazole) **197** with hexakis(4-hydroxyphenylthio)benzene **196** in the presence of Cs_2CO_3 as a base (Scheme 49). Star compound **198** acted as a catalyst for Rh-catalyzed hydrosilylation of acetophenone.

4.3.1.2.1.3. Dipyridylamine. Pang *et al.*[101] reported the synthesis of 1,3,5-tris(*p*-(2,2′-dipyridylamino)phenyl) benzene **201** in 85% yield, by the reaction of 1,3,5-tris-(*p*-bromo phenyl)benzene **65a** [obtained from trimerization of 1-(4-bromophenyl)ethanone **199** with $SiCl_4$] with 2,2′-dipyridylamine **200** in the presence of K_2CO_3 and $CuSO_4$ (Scheme 50). Zinc(II) complex of **201** was synthesized and its application as fluorescent sensor for detection of benzene vapors was investigated.

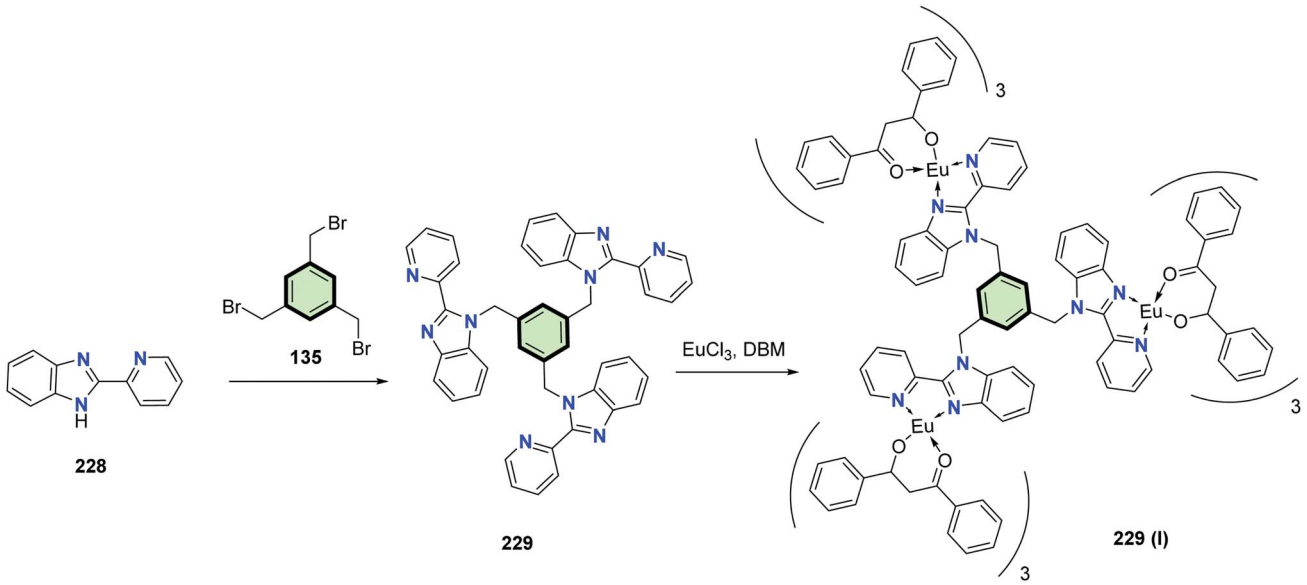


Scheme 57 Synthesis of SSMs with benzene core and benzimidazole side arms **224**, **225** and **227**.

4.3.1.2.2. Six-membered heterocyclic arms containing two heteroatoms. ***4.3.1.2.2.1. Pyrimidine.*** Tris- and tetrakispyrimidine derivatives **203** and **204** were synthesized in good yields *via* alkylation of 2-mercapto-4-oxo-6-phenyl-1,4-dihydropyrimidine-5-carbonitrile **202** with **135** and **136**, respectively (Scheme 51).[97]

Xiang *et al.*[102] reported the synthesis of electron-deficient hexaheteroarylbenzene derivatives containing three pyrimidine rings **208** and **209** through multi-step reactions including the cobalt-catalyzed cyclotrimerization reaction of methyl 4′-((2-dodecylpyrimidin-5-yl)ethynyl)-[1,1′-biphenyl]-4-carboxylate **205** to yield isomeric carboxylated hexaheteroarylbenzene derivatives **206** and **207** which were then hydrolyzed to the corresponding acids **208** and **209**, respectively, upon treatment with methanolic KOH (Scheme 52).

4.3.1.3. Benzene-cored SSMs with benzofused arms



Scheme 58 Synthesis of (1,3,5-tris((2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-1-yl)methyl)benzene) **229** and its Eu^{3+}-complex **229 (I)**.

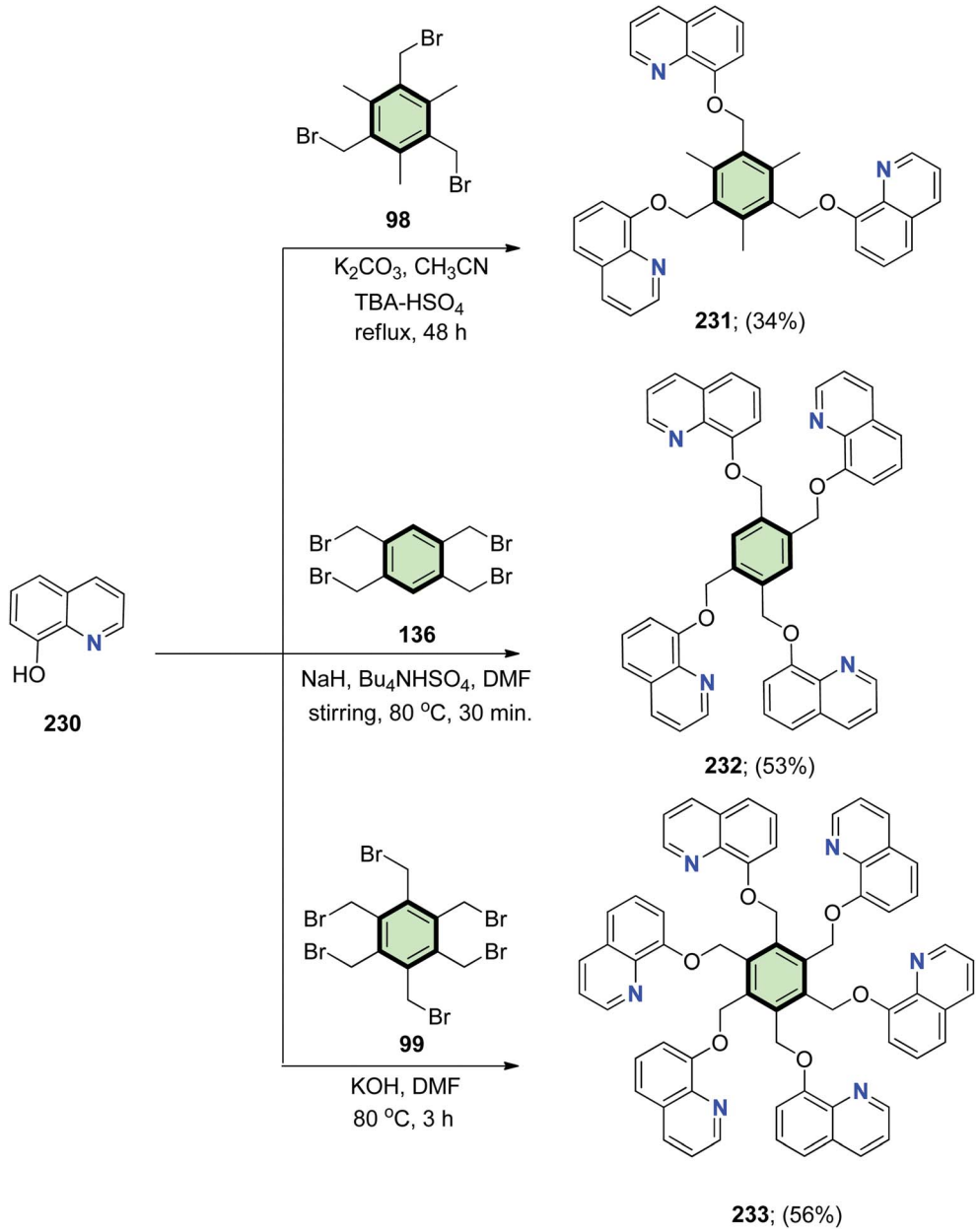
4.3.1.3.1. Benzofused five-membered heterocyclic ring arms. ***4.3.1.3.1.1. Benzo[b]furan.*** The Wittig reaction of benzo[*b*]furan-2-carbaldehyde **210** with benzene-cored tris- and tetrakis(phosphonate) **211** or **213** afforded the corresponding tris- and tetrakis(2-(benzofuran-2-yl)vinyl)benzene **212** and **214** in moderate yields of (Scheme 53). Compound **212** is sensitive to the crystallization condition involving two phases (α, β) in solution and one phase in thin film. (β-phase) Molecule of **212** pack into a three-dimensional cofacial herringbone structure (H-aggregate). It has moderate emission efficiency with quantum yield of 34% (solution), 16% (α-phase) and 22% (β-phase). On the other hand, compound **214** decomposed before melting. It adopts an inter-inserted two-dimensional hexagonal packing structure and can be considered as 2D-semiconductor. It has quantum yield of 53% (solution) and 16% (solid). Compound **212** exhibited hole-mobility and its amorphous film performance is similar to its crystalline film, which should simplify device fabrication.[103]

4.3.1.3.1.2. Benzo[b]thiophene. Reaction of benzo[*b*]thiophene-2-carbaldehyde **215** with 1,3,5-tris(diethoxy phosphorylmethyl)benzene **211** and 1,2,4,5-tetra(dimethoxyphosphoryl methyl)benzene **213** in THF in the presence of *t*-BuOK afforded the corresponding 1,3,5-tris[2-(benzo[*b*]thien-2-yl)vinyl]benzene **216** and 1,2,4,5-tetra[2-(benzo[*b*]thien-2-yl)vinyl]benzene **217**, respectively, in good yields (Scheme 54).[104] Similar to SSMs with benzo[*b*]furan arms **212** and **214**, compound **216** showed 3D-cofacial herringbone structure. Absorption and emission spectra of **216** showed a more efficient hypsochromic shift than **217**, due to discontinued π-conjugation of *meta*-substitution.

4.3.1.3.1.3. Benzo[d]thiazole. The polyphosphoric acid PPA-catalyzed cyclocondensation of trimesic acid (benzene-1,3,5-tricarboxylic acid) **218** with 2-aminothiophenol **219** affords tris(benzo[*d*]thiazol-2-yl)benzene **220** in low yield (34%) (Scheme 55). Compound **220** is an efficient iron(III) fluorescent probe with fast response of 50 s. The dynamic quenching mechanism was proven by time-correlated single photon counting (TCSPC) experiment. The probe **220** can be used to detect rapidly iron(III) ions in aqueous solutions at pH range (3–12). It can be efficiently employed for detection of iron(III) ions in real water.[105]

4.3.1.3.1.4. Benzo[b]imidazole. Star-shaped molecules with benzene core and benzimidazole side arms **222a–c** were synthesized in 86, 78 and 77% yields, by the simple condensation of *o*-phenylenediamine derivatives **221a–c** with trimesic acid **218** in the presence of polyphosphoric acid as a catalyst (Scheme 56). Compounds **221a–c** could be successfully utilized as chemosensors for fluoride ions with good selectivity, high sensitivity, and fast response. The effect of addition of fluoride ion to the chemosensors **222a–c** led to a distinct color change from blue to light cyan in either solution or solid state (with TLC or solution-coated strips) under UV irradiation. Compounds **222a–c** were efficiently applied to the detection of fluoride ion from inorganic origin and commercial toothpaste samples.[106]

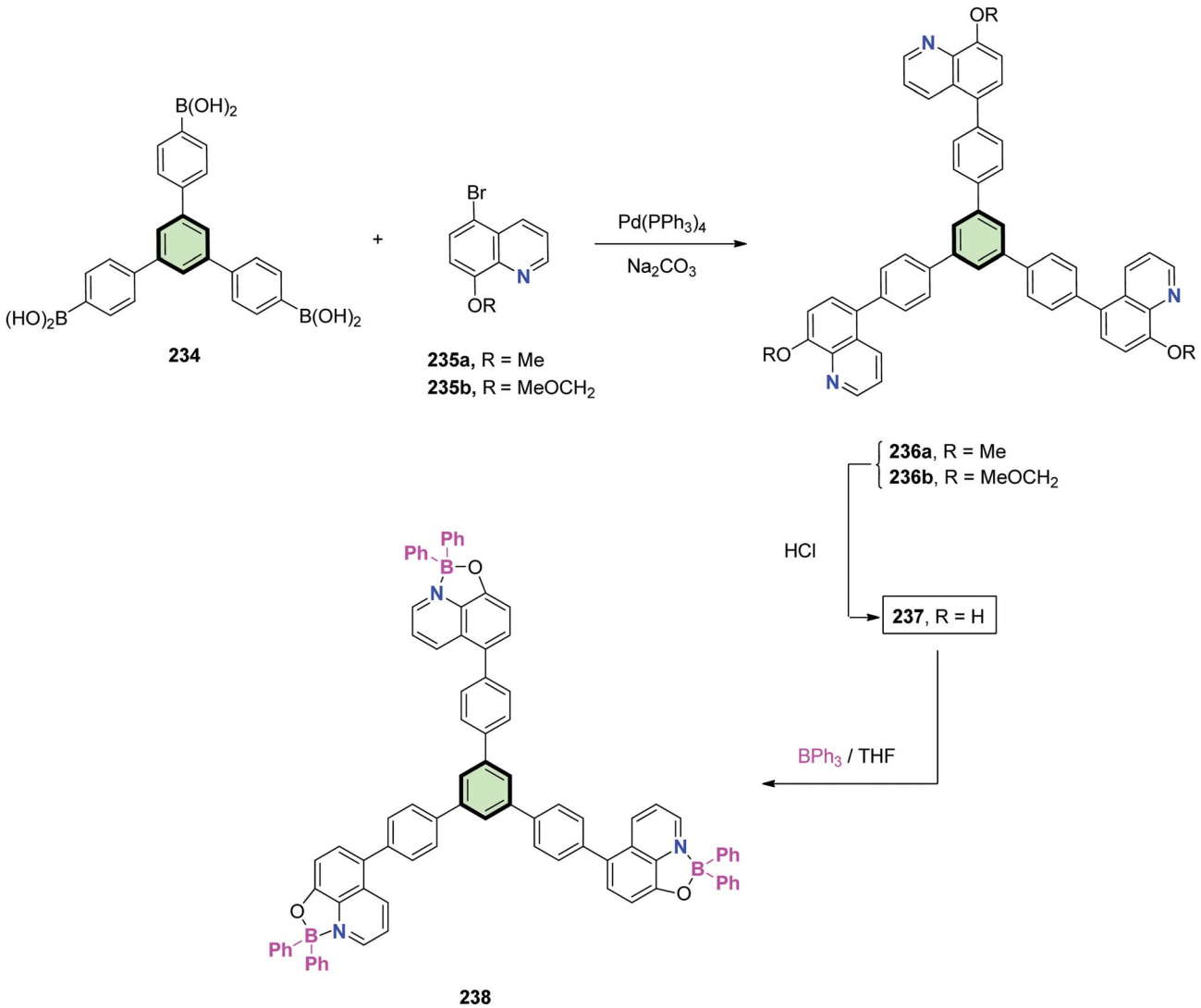
Different benzimidazole-based SSMs **224**, **225** and **227** were synthesized *via* a modified Ullmann aromatic C–N coupling of benzimidazole **223** with tribromobenzene **193**, 1,3,5-tris(4-bromophenyl)benzene **65a**, and hexakis(4-bromophenyl) benzene **226**, respectively (Scheme 57). These SSMs **224**, **225** and **227** showed all deep LUMO and HOMO–LUMO energy gap of 3.45–3.95 eV. They are fluorescent ion the UV regions and possess highly stable thermal and morphological features. They have an obvious fluorescent response to silver(I) and zinc(II) ions in solution.[107]



Scheme 59 Synthesis of SSMs with benzene core and quinoline side arms **231–233**.

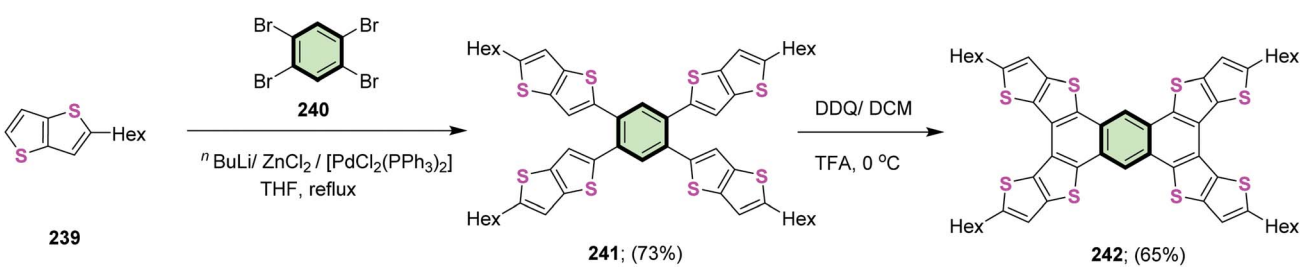
The reaction of 1,3,5-tris(bromomethyl)benzene **135** with 2-pyridylbenzimidazole **228** in DMF in the presence of sodium hydroxide at reflux afforded hexadentate ligand (1,3,5-tris((2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-1-yl)methyl)benzene) **229** in good yield (62%). Heating **229** with europium chloride/dibenzoylmethane (DBM) in ethanol at reflux in the presence of sodium hydroxide yielded the Eu^{3+}-complex **229 (I)** (Scheme 58). Europium(III) complex **229 (I)** was found to be promising red emitter in view of its structural and photophysical properties. It showed high photoluminescence yield (0.64) with a short lifetime of excited state (120 μs). It is thermally stable to high temperature (315 °C). The HOMO–LUMO energy gap (2.5 eV) of **229 (I)** is suitable for organic functional devices. Electroluminescence and photovoltaic devices of **229 (I)** led to a white emission (maximum luminance of 168 cd m^{-2}) and a maximum power conversion efficiency of 1.05%, respectively.[108]

4.3.1.3.2. Benzofused six-membered heterocyclic ring arms. ***4.3.1.3.2.1. Quinoline.*** Reaction of 8-hydroxyquinoline **230** with the appropriate bromomethyl benzenes **98, 136** and **99** afforded tris-, tetrakis-, and hexakis(8-quinolinoxymethyl) benzene derivatives **231, 232** and **233**, respectively, in good yields (Scheme 59). SSM **231** exhibited selective fluorescence quenching with copper(II) and could be used for estimation of copper(II) (1–6 ppm) even in the presence of nickel(II),

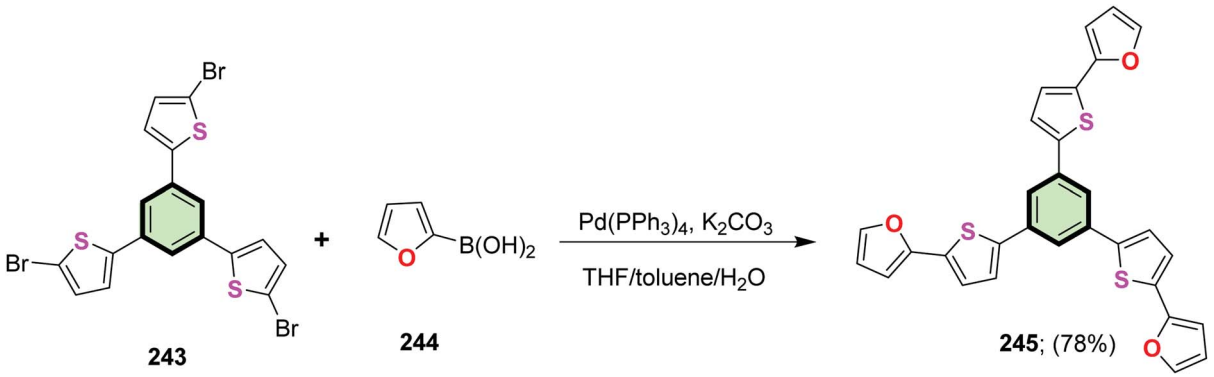


Scheme 60 Synthesis of 5,5′-(5′-(4-(8-hydroxyquinolin-5-yl)phenyl)-[1,1′:3′,1″-terphenyl]-4,4″-diyl)bis(quinolin-8-ol) **237** and its boron complex **238** 5,5′-(5′-(4-(8-hydroxyquinolin-5-yl)phenyl)-[1,1′:3′,1″-terphenyl]-4,4″-diyl)bis(quinolin-8-ol).

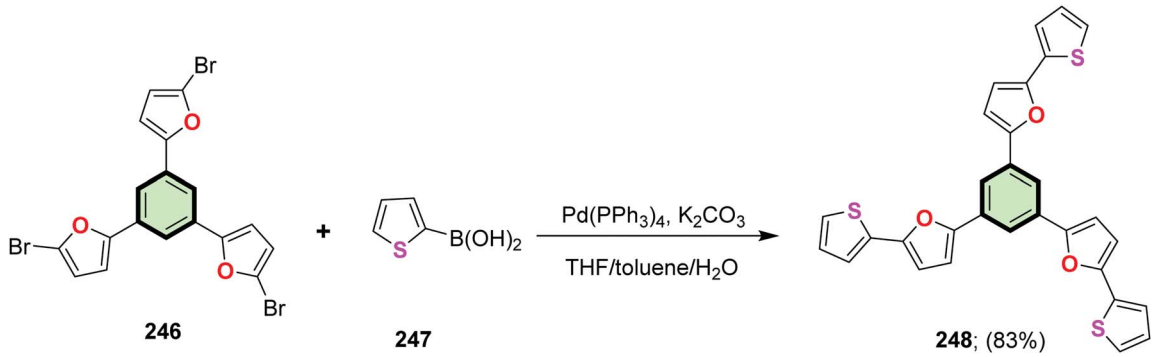
cadmium(II), zinc(II) (1000 ppm), or silver(II) (100 ppm). Different coordination modes of **232** (with silver(I) and copper(I)) and **233** (with cobalt(II) and palladium(II)) were studied. SSMs **231** and **232** displayed different fluorescence perturbation with change in the concentration of silver(I). Compound **231** showed a simultaneous fluorescence quenching with addition of silver(I). Compound **232**, on the other hand, introduced "ON–OFF–ON switching" involving two fluorescence perturbations



Scheme 61 Synthesis of tetra(5-hexyl)thieno([3,2-*b*]thieno)anthracene **242**.



Scheme 62 Synthesis of 1,3,5-tris(5-(furan-2-yl)thiophen-2-yl)benzene **245**.

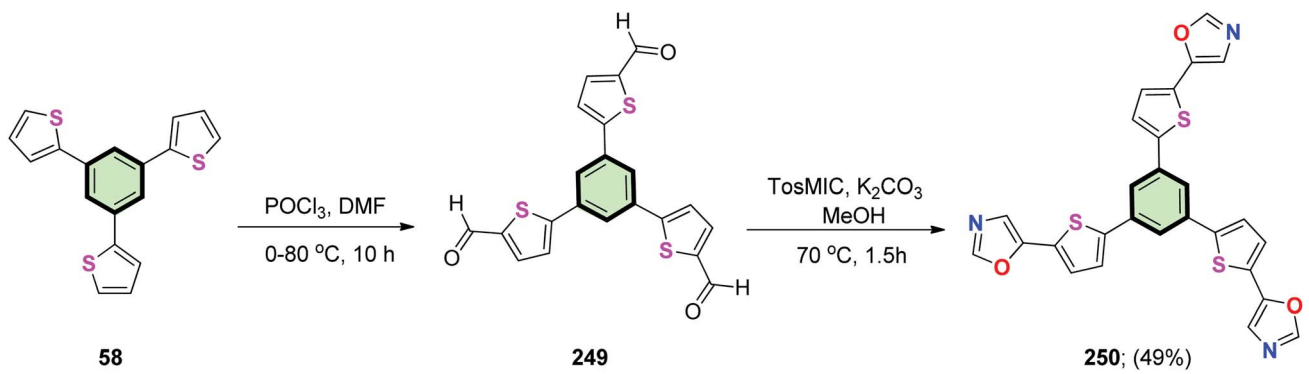


Scheme 63 Synthesis of 1,3,5-tris(5-(thiophen-2-yl)furan-2-yl)benzene **248**.

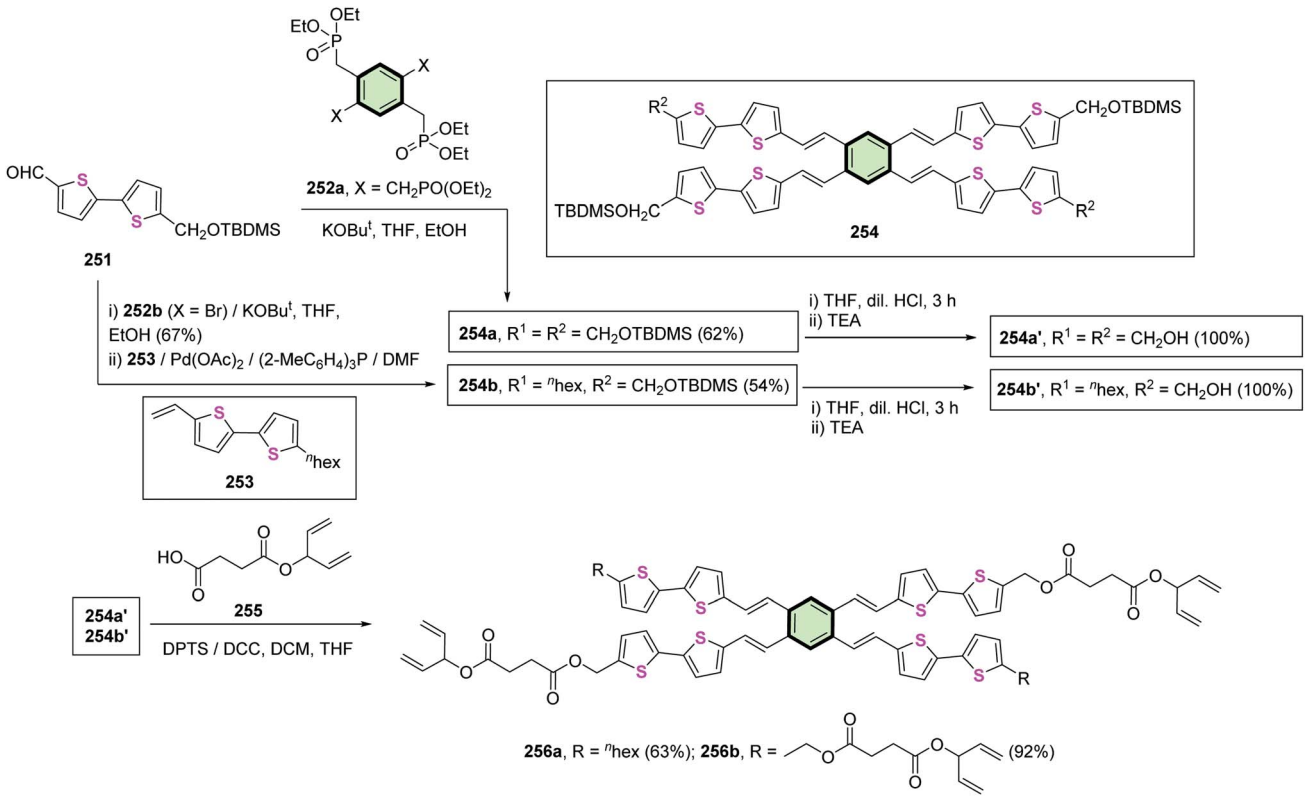
with incremental increase of silver(I) concentration: the first fluorescence quenching (with <1.0 equiv. of Ag^+, at $\lambda_{max} = 395$ nm) and the second is fluorescence enhancement (at $\lambda_{max} =$ 500 nm, with >3 equiv. of Ag^+).[109–111]

Cui and Wang[112] reported the synthesis of star-shaped conjugated molecules **236a** and **236b** in good yields using Suzuki–Miyaura coupling reaction of boronic acid derivatives **234** with 5-bromo-8-methoxyquinoline **235a** and 5-bromo-8-methoxy-2-methylquinoline **235b**, respectively, in the presence of Na_2CO_3 and $Pd(PPh_3)_4$ (Scheme 60). The starburst compounds **236a,b** were found to act as blue emitters with excellent thermal stabilities (~300 °C) and layered arrangements in solid state. Treatment of SSMs **236a,b** with HCl gave the 8-hydroxyquinoline derivative **237**. Chelation of the latter compound with triphenylborane in THF at reflux afforded the boron complex **238** which exhibited green emissions.

4.3.1.4. Miscellaneous arms



Scheme 64 Synthesis of 1,3,5-tris(5-(oxazol-5-yl)thiophen-2-yl)benzene **250**.



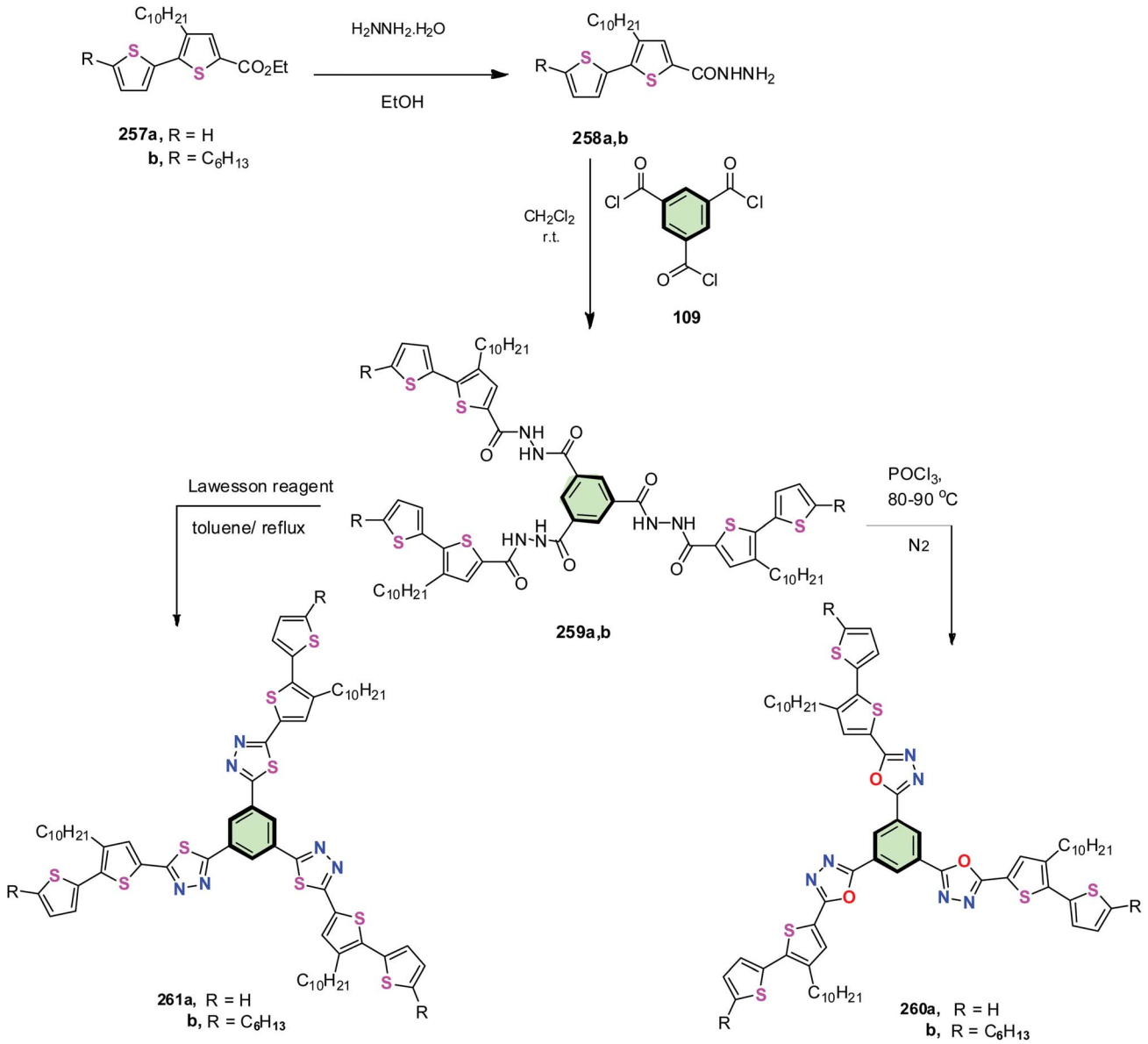
Scheme 65 Synthesis of bithiophene SSMs side arms **254** and **256**.

4.3.1.4.1. Thieno[3,2-b]thiophene. Magnan *et al.*[113] reported the synthesis of star-shaped compounds **241** in 73% yields by four-fold Negishi coupling between 1,2,4,5-tetrabromobenzene **240** with 2-hexylthieno[3,2-*b*]thiophene **239** in the presence of ^{n}BuLi and anhydrous $ZnCl_2$. Subsequent oxidative cyclodehydrogenation of the latter compound in chlorobenzene using anhydrous ferric chloride gave tetra(5-hexyl)thieno([3,2-*b*]thieno)anthracene **242** in 65% yield (Scheme 61). It was found that cyclization of **241** to **242** led a red shift of the absorption due to decrease of HOMO–LUMO energy gap affected by an efficient π-conjugation.

4.3.1.4.2. 2-(Thiophen-2-yl)furan. 1,3,5-Tris(5-(furan-2-yl) thiophen-2-yl)benzene **245** was synthesized in 78% yield by the reaction of 1,3,5-tris(5-bromothiophen-2-yl) benzene **243** with 2-furanyl boronic acid **244** in the presence of $Pd(PPh_3)_4$. Similarly, 1,3,5-tris(5-(thiophen-2-yl)furan-2-yl) benzene **248** was synthesized in 83% yield by the reaction of 1,3,5-tris(5-bromofuran-2-yl)benzene **246** with 2-thiophenylboronic acid **247** (Schemes 62 and 63).[81] SSM **248** (containing peripheral thiophene moieties) was found to be better fluorophore than **245** (containing peripheral furan) as evident from the fluorescence quantum yield values of 0.15 and 0.06, respectively.

4.3.1.4.3. 2-(Thiophen-2-yl)oxazole. Kotha *et al.*[81] reported the synthesis of a star-shaped molecule with benzene core and (thiophen-2-yl)oxazole as arms **250** by firstly treatment of 1,3,5-tri(thiophen-2-yl)benzene **58** with $POCl_3$ in DMF to give 5,5′,5″-(benzene-1,3,5-triyl)tris(thiophene-2-carbaldehyde) **249**. The latter compound underwent van Leusen reaction upon treatment with toluene sulfonylmethyl isocyanide (TosMIC)/K_2CO_3 in methanol under reflux to afford 1,3,5-tris(5-(oxazol-5-yl) thiophen-2-yl)benzene **250** in 49% yield (Scheme 64).

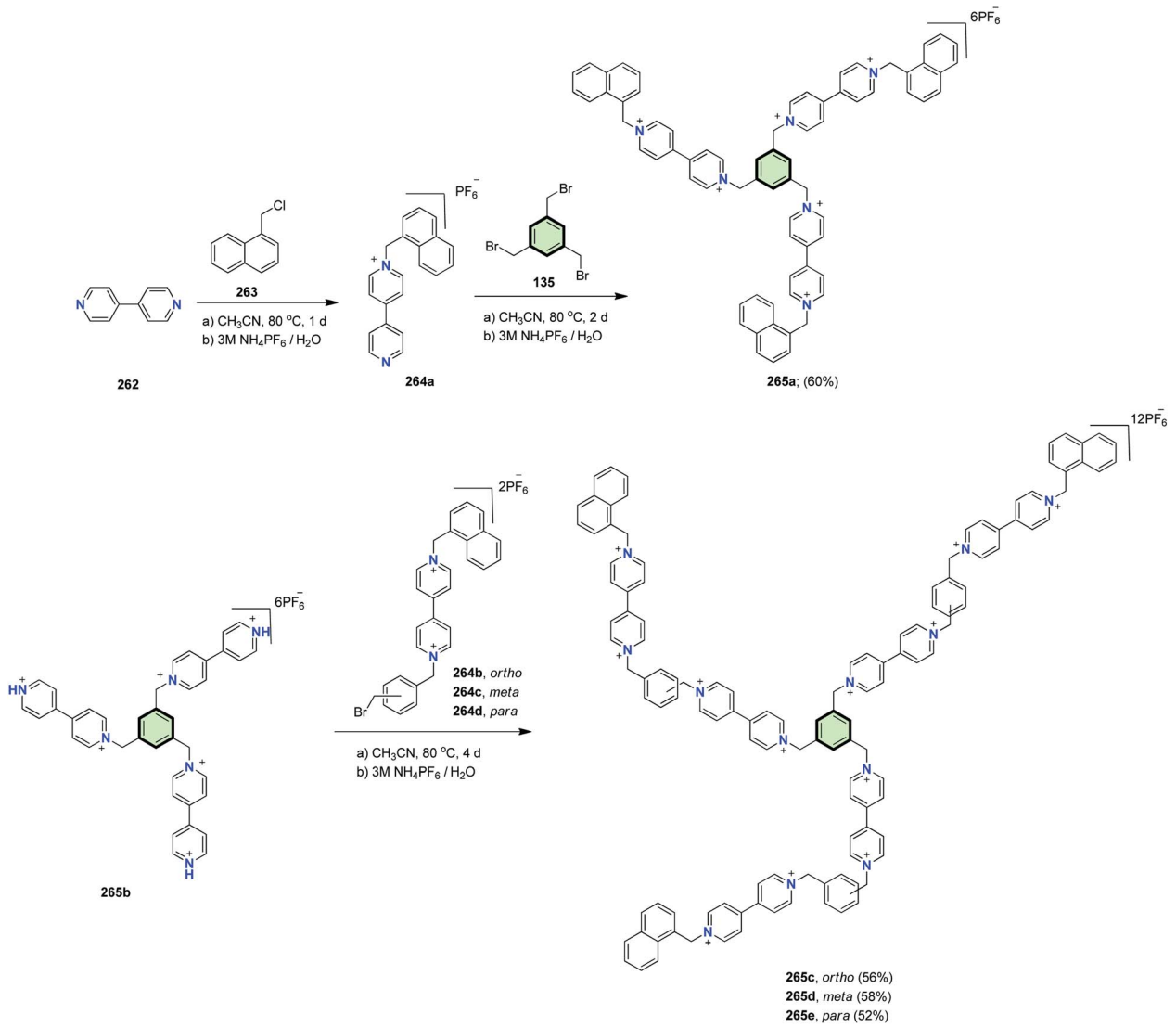
4.3.1.4.4. 2,2′-Bithiophene and 2-([2,2′-bithiophen]-5-yl)-1,3,4-oxa(thia)diazole. The synthesis of SSMs **256a,b** is represented in Scheme 65. Star-shaped tetrapod **256a** was synthesized *via* the Horner–Emmons coupling of 5′-(((*tert*-butyldimethylsilyl)oxy) methyl)-[2,2′-bithiophene]-5-carbaldehyde **251** and octaethyl (benzene-1,2,4,5-tetrayltetrakis(methylene)) tetrakis(phosphonate) **252a**. Deprotection of TBDMS proceeded to form **254a′** in a quantitative yield, followed by esterification with 4-oxo-4-(penta-1,4-dien-3-yloxy)butanoic acid **255** furnished SSMs **256a** with four pentadiene tails in good yield (63%). Other SSM **256b** (with two pentadiene tails) was synthesized similarly but with a slight modification. It employed the Horner–Emmons coupling of **251** with tetraethyl (2,5-dibromo-1,4-phenylenebis(methylene))bis(phosphonate) **252b** followed by Heck coupling of the resulting dibromo product with 5-hexyl-5′-vinyl-2,2′-bithiophene **253** to yield **254b** in moderate yield (54%). Deprotection of **254b** to **254b′** followed by reaction of **254b** with **255** afforded SSM **256b** in excellent yield (92%). The SSMs **256a** and **256b** acted as photopatternable organic semiconductors due to their ability to photopolymerize enabled by



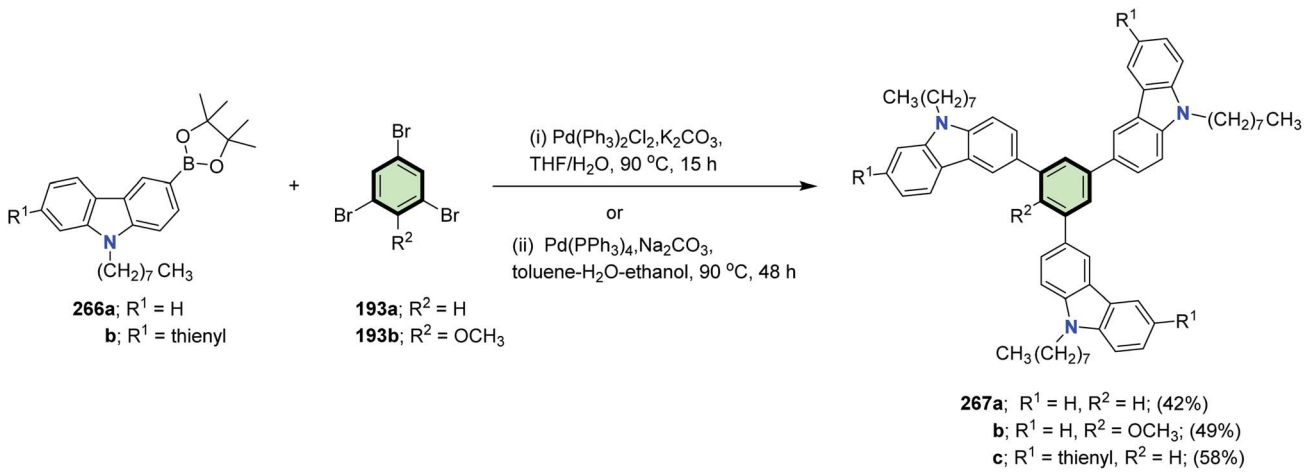
Scheme 66 Synthesis of SSMs containing either oxadiazole or thiadiazole side arms **260** and **261**.

the reactive pentadiene tails. The transistor devices based on **256a** and **256b** exhibited a field-effect mobility of 1.3 (±0.2) × 10^{-3} to 3.7 (±0.5) × 10^{-3} cm^2 V^{-1} s^{-1}, $I_{on/off}$ value (>10^3), and a small threshold voltage (−16 V). The field-effect mobility of SSM **256b** persisted even after being cross-linked during photopolymerization. This was explained on the basis of the strong intermolecular interaction of conjugated structure which may freeze the molecular axis under push–pull force during the cross-linking and is accompanied by a highly lamella-ordered in two directions.[114]

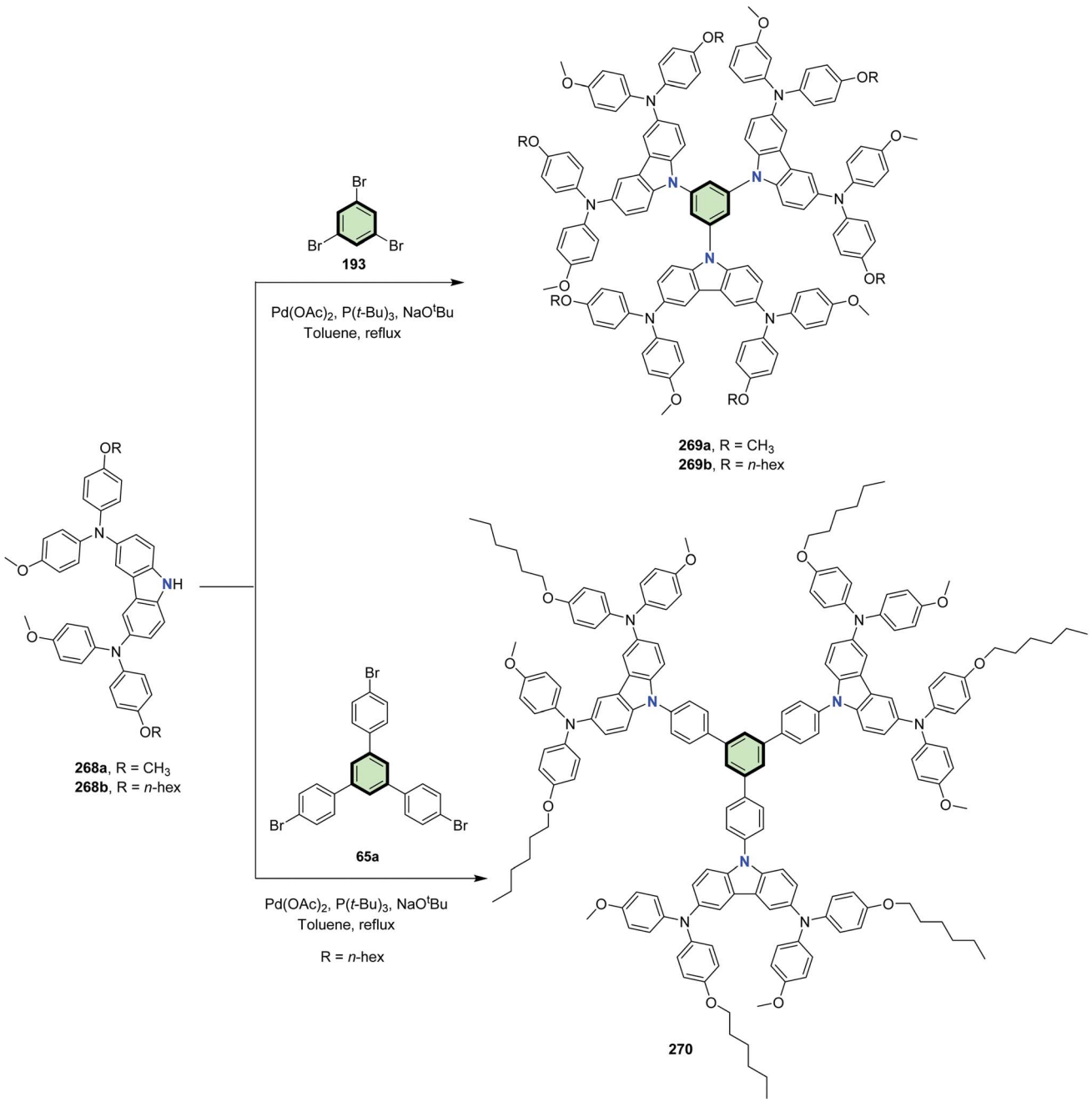
Kotwica *et al.*[115] reported the synthesis of star-shaped molecules containing either oxadiazole or thiadiazole side arms each connected by bithiophene moiety **260a**, **260b**, **261a** and **261b**. Thus, the esters **257a** and **257b** were converted into the corresponding hydrazide derivatives **258a** and **258b**, respectively, by heating with hydrazine hydrate. Treatment of **258a** and **258b** with benzene-1,3,5-tricarbonyl trichloride **109** gave alkyl-substituted *N*′1,*N*′3,*N*′5-tris[(3-decyl-2,2′-bithien-5-yl)carbonyl] benzene-1,3,5-tricarbohydrazides **259a** and **259b**, respectively. The latter compounds were converted into the oxadiazole bithiophene series **260a** and **260b** upon treatment with phosphorus oxychloride. On the other hand, treatment of **259a** and **259b** with Lawesson's reagent led to the formation of the corresponding thiadiazole bithiophene series **261a** and **261b**, respectively, in good yields (Scheme 66). The HOMO–LUMO energy gap of oxadiazole SSMs **260a,b** were found to be just below 3 eV and higher than that of thiadiazole SSMs **261a,b** by 0.2 eV. Substitutions were shown to affect further reduction of energy gap. SSMs **260** and **261** displayed an excellent electroluminescence in guest/host LEDs. Unsubstituted SSMs **260** and



Scheme 67 Synthesis of SSMs containing 4,4′-bipyridyl naphthalene side arms **265**.



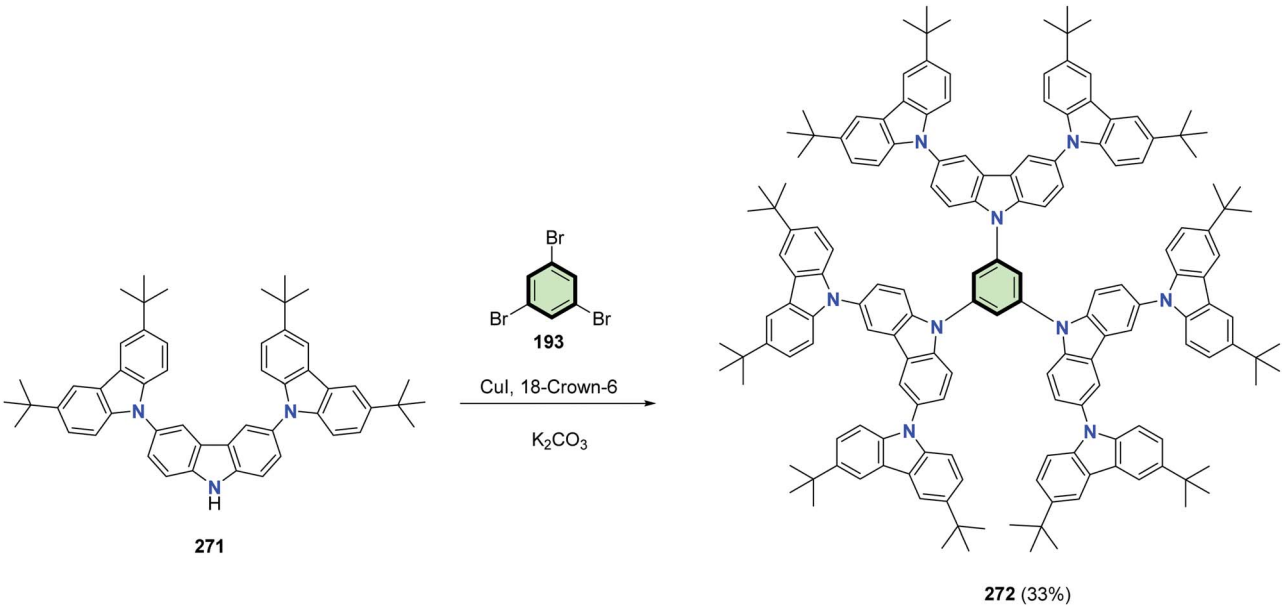
Scheme 68 Synthesis of SSMs **267a–c** with 1,3,5-tris(9-octyl-9*H*-carbazol-3-yl)benzene side arms.



Scheme 69 Synthesis of SSMs **269a,b** and **270**.

261 (R = H) were electropolymerizable. The macromolecules based on SSMs **260** and **261** retained a reversible electrochromism on the oxidation and reduction modes.

4.3.1.4.5. 4,4′-Bipyridine. Madasamy *et al.*[116] reported the synthesis of viologen (4,4′-bipyridinium) star shaped molecule with benzene core and naphthalene tails **265a** in 60% yields upon reaction of 1,3,5-tris(bromomethyl)benzene **135** with the key intermediate **264a**. The latter compound was obtained from alkylation of 4,4′-bipyridine **262** with 1-chloromethylnaphthalene **263** (Scheme 67). In addition, several dendritic viologin molecules **265c–e** were synthesized *via* a similar strategy incorporating the dealkylated star-shaped derivative **265b** and bromoxylyl viologins **264b–d**. Cyclic voltammetry showed that among the different viologen SSMs **265a–e**, only **265c** (*ortho*) exhibited the most positive reduction potential due to both intermolecular and intramolecular charge transfer. The absorption spectra of **265c** as well indicated absorption of radical monocation and pimer while **265a,e** (*meta* and *para*) revealed absorption for radical monocation only. This suggested that the intramolecular charge transfer is evident only in

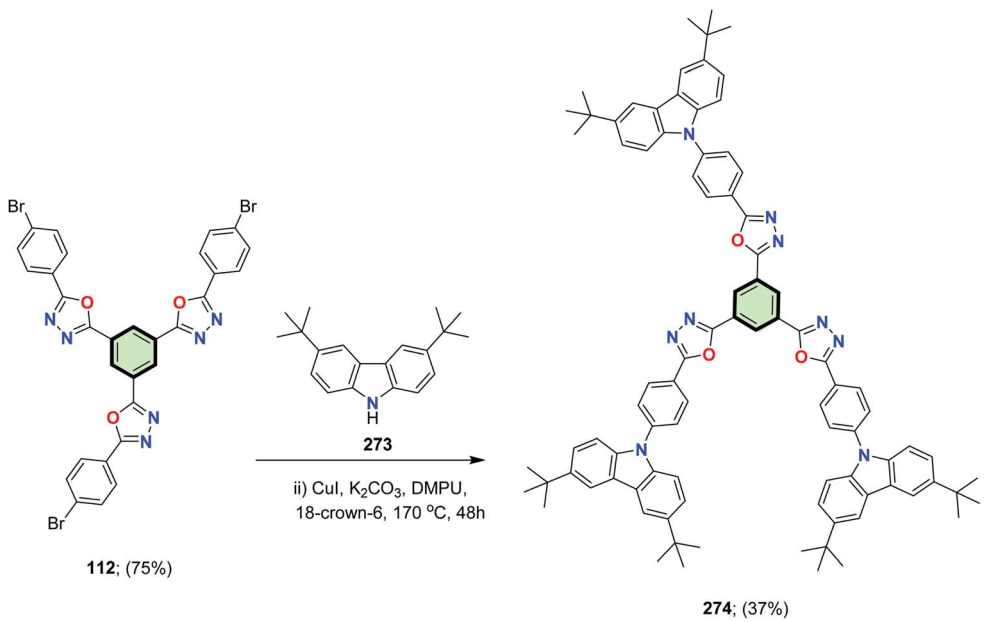


Scheme 70 Synthesis of dendritic tercarbazole-based SSM **272**.

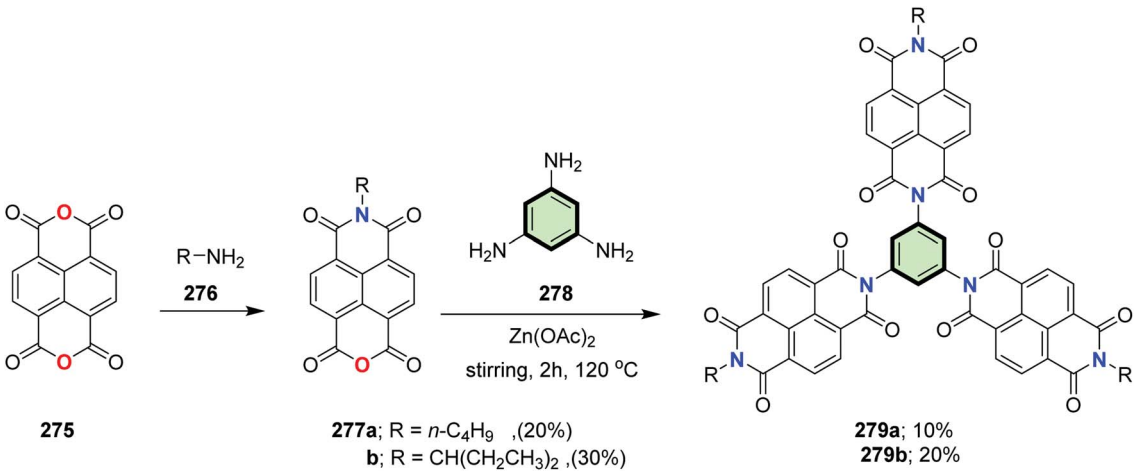
the *ortho* derivative **265c**. It should be mentioned that the viologen SSMs could form (1 : 1) inclusion complexes with β-cyclodextrin. In these complexes, β-cyclodextrin capped the hydrophobic part of **265c–e** as detected from NMR measurements. This capping was solvent-dependent. In polar aprotic solvents, no capping was observed as the solvent molecules were capped more efficiently to β-cyclodextrin. In aqueous media, a partial capping of naphthalene tails of **265c–e** to β-cyclodextrin was noticed.

Madasamy *et al.*[116] reported the synthesis of viologen (4,4′-bipyridinium) star shaped molecule with benzene core and naphthalene tails **265** in 60% yield upon reaction of 1,3,5-tris(-bromomethyl)benzene **135** with the key intermediate **264**. The latter compound was obtained from alkylation of 4,4′-bipyridine **262** with 1-chloro methylnaphthalene **263** (Scheme 67).

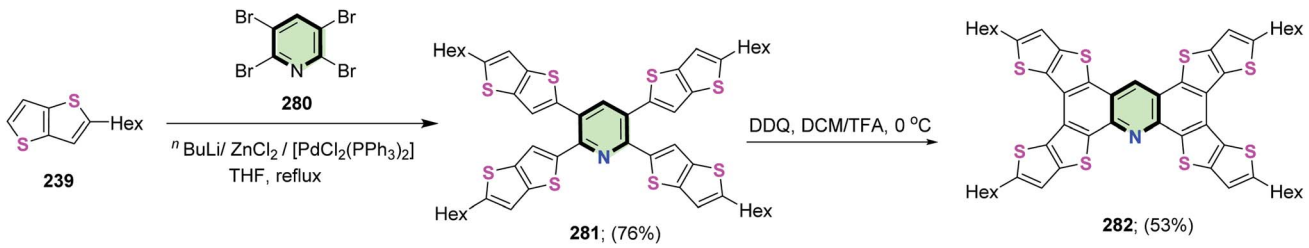
4.3.1.4.6. Carbazole and its derivatives. Brzeczek *et al.*[117] reported the synthesis of star-shaped molecules 1,3,5-tris(9-octyl-



Scheme 71 Synthesis of 1,3,5-tris(5-(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzene **274**.



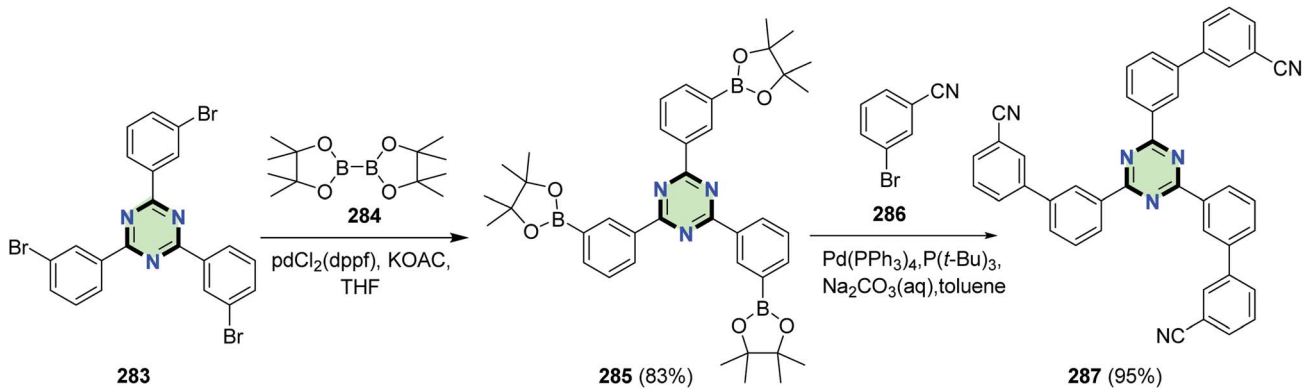
Scheme 72 Synthesis of SSMs with benzene core and three naphthalene diimide side arms **279**.



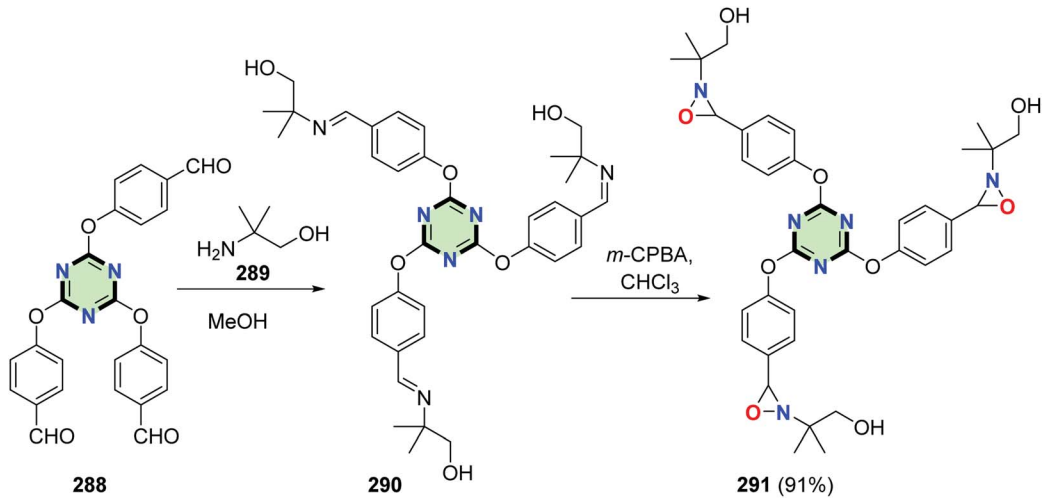
Scheme 73 Synthesis of star-shaped compound with pyrimidine core **281** and tetra(5-hexylthieno[3,2-*b*]thieno)acridine **282**.

9*H*-carbazol-3-yl)benzene **267a**, 2-methoxy-1,3,5-tris(9-octyl-9*H*-carbazol-3-yl)benzene **267b** and 1,3,5-tris(9-octyl-6-(thiophen-2-yl)-9*H*-carbazol-3-yl)benzene **267c** in 42, 49 and 58% yields, respectively, *via* Suzuki–Miyaura coupling reaction between the appropriate carbazolyl boronic acid pinacol esters **266a** and **266b** with the corresponding 1,3,5-tribromobenzene derivatives **193a** and **193b** (Scheme 68). The star-shaped compounds **267a–c** were shown to be promising p-types semiconducting materials for application in OLEDs and OFETs in view of their HOMO energies (−5.5 to −5.3 eV), energy gaps (E_g 3.20 to 3.38 eV), and IP values (5.5 eV). Presence of thiophene ring caused a red shift of both the UV and fluorescence spectra due to extra conjugation.

Star-shaped molecules **269a,b** and **270** were synthesized in good yields, *via* C–N palladium catalyzed coupling of 1,3,5-tribromobenzene **193** or 4,4″-dibromo-5′-(4-bromophenyl)-1,1′:3′,1″-terphenyl **65a** with *N*3,*N*6-bis(4-(alkyloxy)phenyl)-*N*3,*N*6-bis(4-methoxyphenyl)-9*H*-carbazole-3,6-

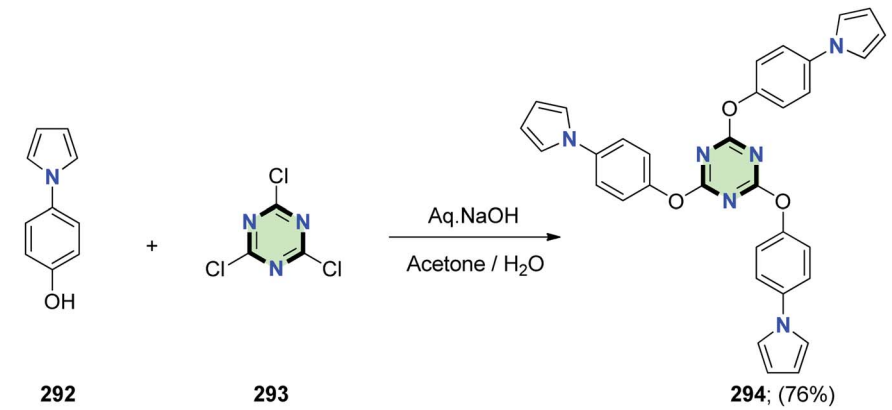


Scheme 74 Synthesis of SSM containing 1,3,5-triazine core and biphenyl arms **287**.

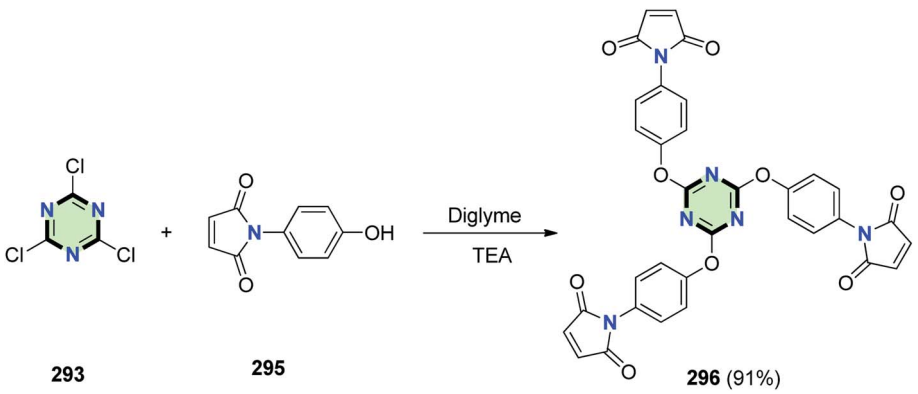


Scheme 75 Synthesis of a star-shaped molecule with triazine core and oxaziridine side arm **291**.

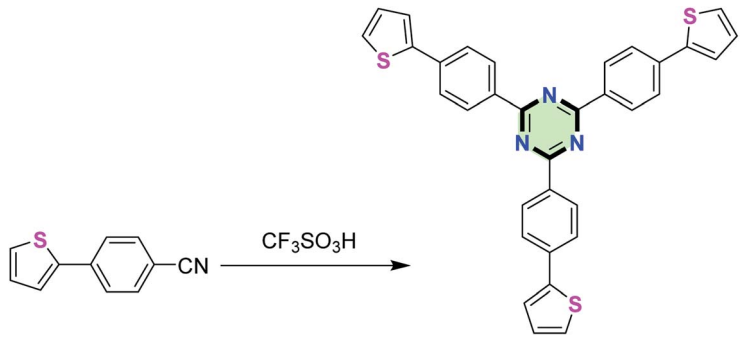
diamine **268a,b** in toluene at reflux in the presence of $Pd(OAc)_2$ (Scheme 69).[40] Among the synthesized starburst molecules, **269a** possessed the best hole-transporting properties. Mesoporous perovskite solar cells incorporating **269a** showed excellent power conversion efficiency PCE 18.87% which even higher than that of the common photovoltaic devices based on spiro-OMeTAD as a hole-transporting material with PCE 17.71%.



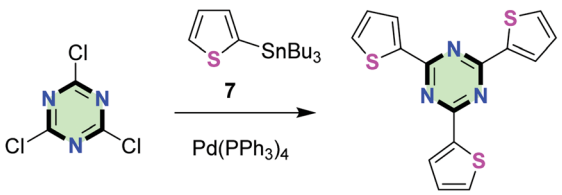
Scheme 76 Synthesis of 2,4,6-tris(4-(1*H*-pyrrol-1-yl)phenoxy)-1,3,5-triazine **294**.



Scheme 77 Synthesis of triazine-cored compound **296**.

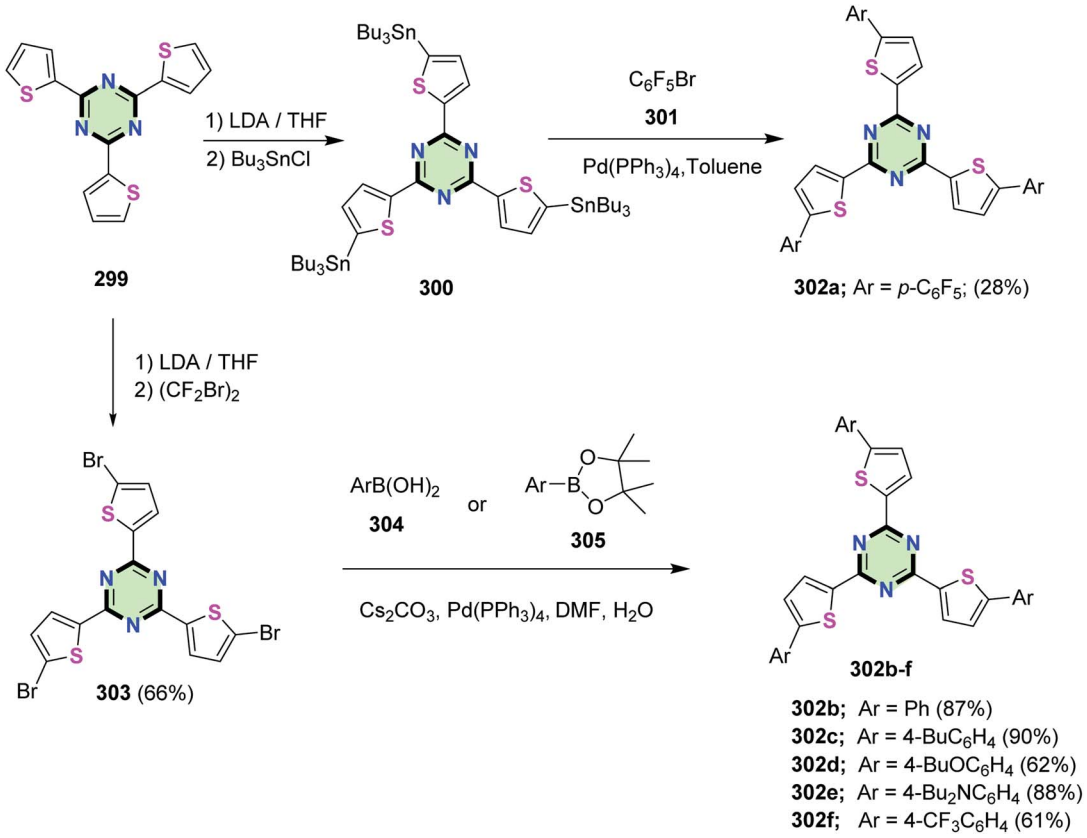


Scheme 78 Synthesis of 2,4,6-tris(4-(thiophen-2-yl)phenyl)-1,3,5-triazine **298**.

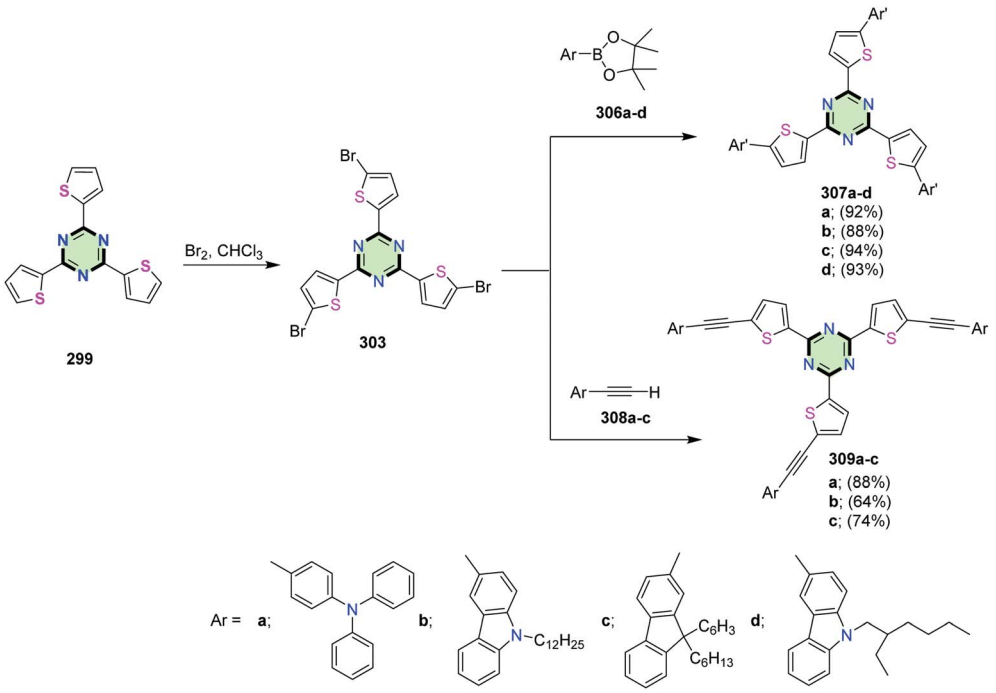


Scheme 79 Synthesis of 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine **299**.

The aromatic C–N coupling of 1,3,5-tribromobenzene **193** with 3,3″,6,6″-tetra-*tert*-butyl-9′H-9,3′:6′,9″-tercarbazole **271** in 18-crown-6 ether in the presence of copper(I) iodide and potassium carbonate resulted in the formation of dendritic tercarbazole-based SSM **272** in acceptable yield (33%) (Scheme 70). The non-planar twisted starburst configuration of **272** resulted in excellent thermal stability and morphological stabilities. It retain the triplet state energy high at 2.86 eV (compared to 1,3,5-tri(*N*-carbazolyl)benzene (TCB), 3.01 eV) showing the inefficient conjugation of the additional carbazole

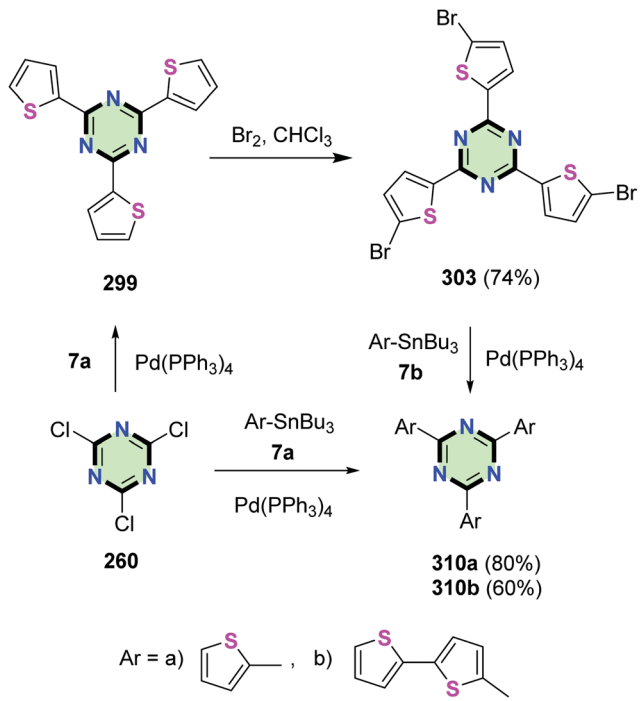


Scheme 80 Synthesis of 2,4,6-tri(5-aryl-thiophen-2-yl)-1,3,5-triazines **302a–f**.



Scheme 81 Synthesis of SSMs with 1,3,5-triazine core and thiophene side arms **307** and **309**.

moieties due to lack of planarity. The application of **272** as a dendritic host material in solution-processed phosphorescent blue OLEDs was investigated and found to be far better than TCB.[118]

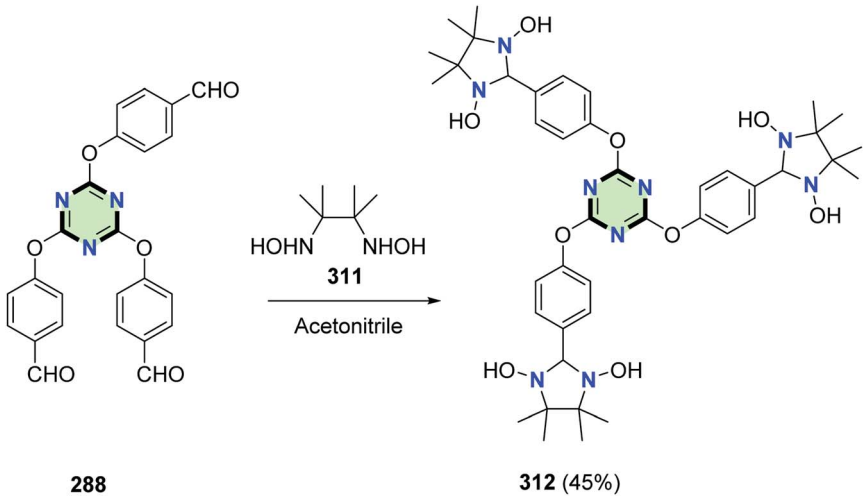


Scheme 82 Synthesis of star-shaped 1,3,5-triazines **310a,b** with thiophene or bithiophene end groups.

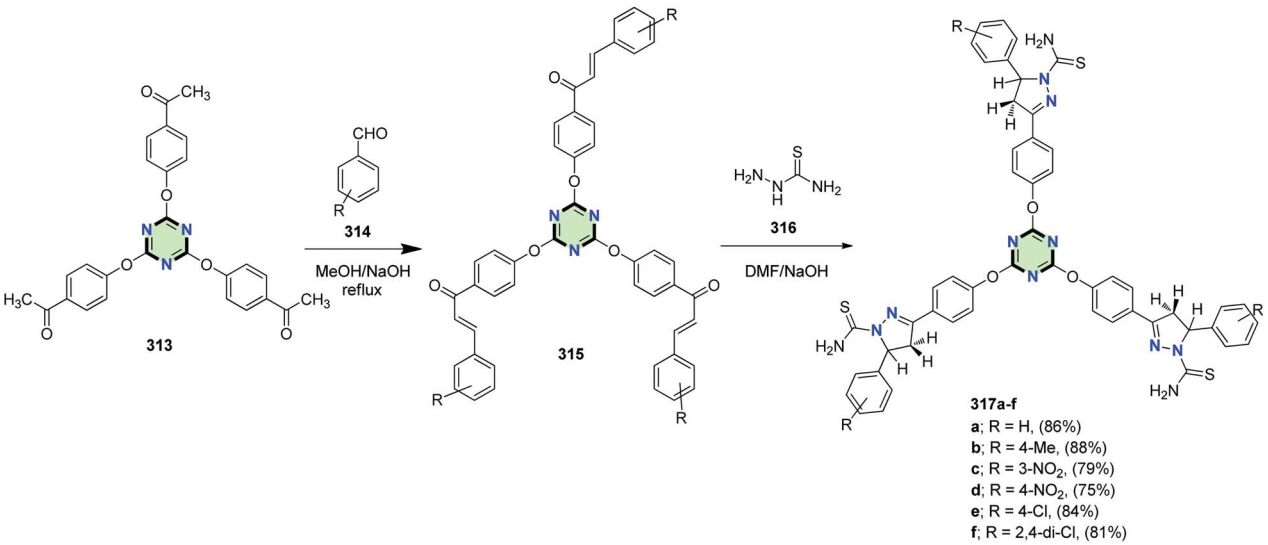
He *et al.*[88] reported the synthesis of 1,3,5-tris(5-(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzene **274** in 37% yield, upon reaction of 1,3,5-tris(5-(4-bromophenyl)-1,3,4-oxadiazol-2-yl)benzene **112** with 3,6-di-*tert*-butyl-9*H*-carbazole **273** in the presence of CuI and K_2CO_3 (Scheme 71). The donor–π–acceptor (D–π–A) structured SSM **274** emitted a blue color at 424 nm with an excellent quantum efficiency $\Phi_f = 93\%$ in dilute toluene and $\Phi_f = 72\%$ in thin film. The photoluminescence spectrum of **274** persisted even at elevated temperature 150 °C for 220 hours in air which permits an ease of applicability. Non-doped electroluminescent blue-emitting device based on **274** displayed a turn-on voltage of 3.7 V because of its bipolar structure. Excellent current efficiency (CE) and external quantum efficiency (EQE) were 4.22 cd A^{-1} and 3.37%, respectively.

4.3.1.4.7. Naphthalene diimide. Two star-shaped molecules with benzene core and three naphthalene diimide side arms **279a** and **279b** were synthesized by imidization reaction of 1,3,5-triamino benzene **278** with naphthalene derivatives **277a** and **277b**. The latter compounds were obtained by treatment of 1,4,5,8-naphthalenetetracarboxylic dianhydride **275** with amine derivatives **276** in the presence of $Zn(OAc)_2$ (Scheme 72).[119] These star-shaped compounds **279a** and **279b** showed a bathochromic shift in the film state compared to solution which reflects the aggregation in the solid state. Also, these compounds were characterized by low-lying LUMO levels at −3.83 and −3.87 eV, respectively, which indicates the applicability of these compounds as n-type semi-conductors.

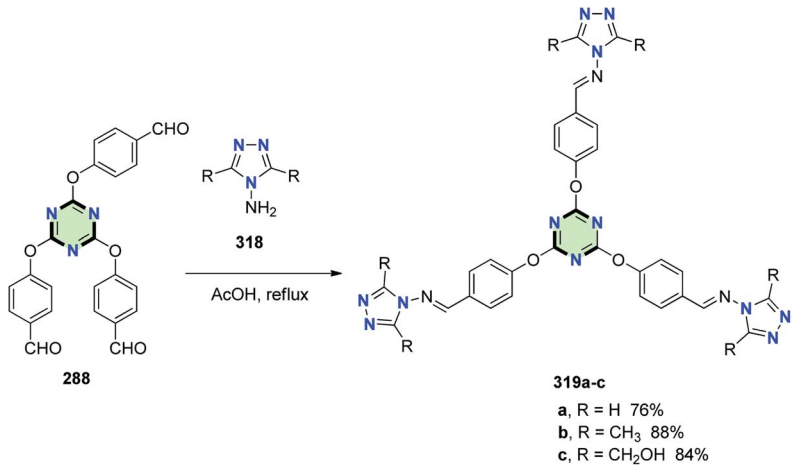
4.3.2. Pyridine-cored SSMs. Magnan *et al.*[113] reported the synthesis of star-shaped compound with pyrimidine core **281** in



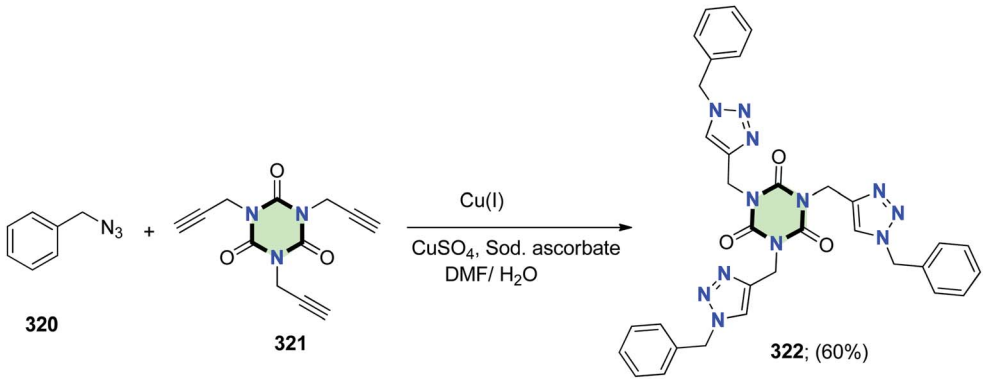
Scheme 83 Synthesis of star-shaped molecule with triazine core and imidazolidine side arms **312**.



Scheme 84 Synthesis of tris-pyrazoline **317a–f**.

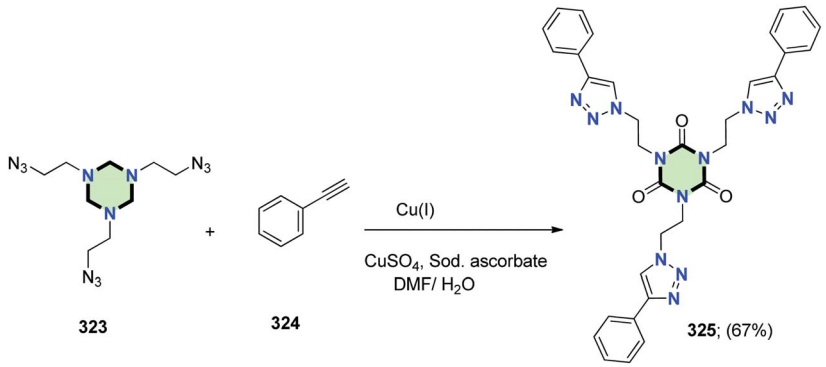


Scheme 85 Synthesis of star-shaped Schiff bases **319a–c**.



320 321 322; (60%)

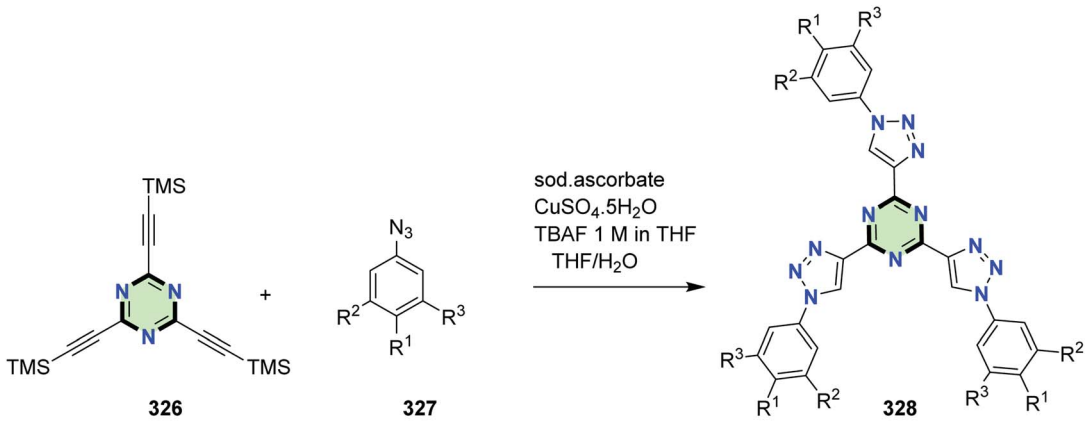
Scheme 86 Synthesis of tris(triazole) derivative **322**.



323 324 325; (67%)

Scheme 87 Synthesis of tris(triazole) derivative **325**.

76% yield by four-fold Negishi coupling between 2,3,5,6-tetrabromopyridine **280** with 2-hexylthieno[3,2-*b*]thiophene **239** in the presence of ^{n}BuLi and anhydrous $ZnCl_2$. Subsequent oxidative cyclodehydrogenation of the latter compound in chlorobenzene using anhydrous ferric chloride gave tetra(5-hexylthieno[3,2-*b*]thieno)acridine **282** in 53% yield (Scheme 73). Changing the benzene core in compound **242** (*cf.* Scheme 61) with the electron-deficient pyridine ring in **282** resulted in a red shift from 468 to



326 327 328

a; $R^1 = OC_{10}H_{21}$, $R^2 = R^3 = H$ (45%)
b; $R^1 = R^2 = OC_{10}H_{21}$, $R^3 = H$ (51%)
c; $R^1 = R^2 = R^3 = OC_{10}H_{21}$ (48%)

Scheme 88 Synthesis of SSMs with triazine core and phenyltriazole side arms **328**.

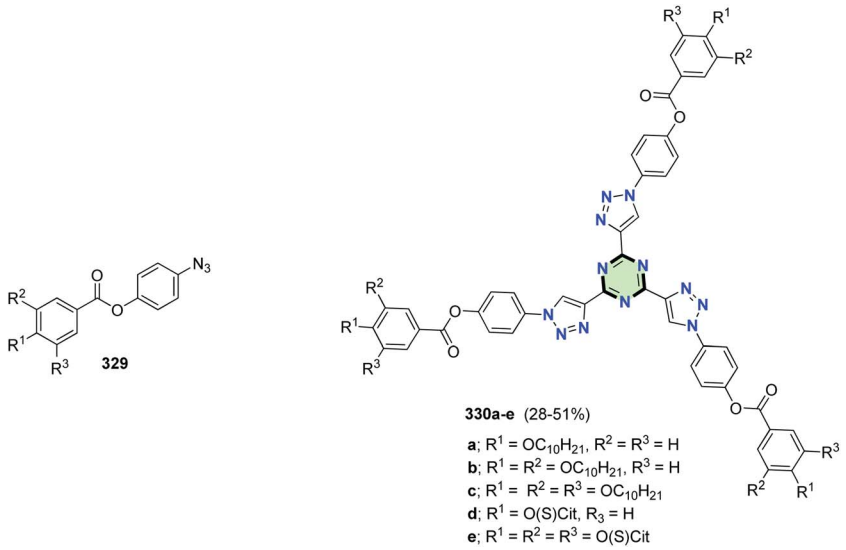


Fig. 7 Structures of 4-azidophenyl benzoate **329** and SSMs **330a–e**.

494 nm, respectively. This may be attributed to the presence of the electronegative nitrogen atom which lowers the energy of the LUMO of **282** and thus, decreases the energy gap.

4.3.3. *s*-Triazine-cored SSMs with different arms

4.3.3.1. Biphenyl. SSM containing 1,3,5-triazine core and biphenyl arms **287** was synthesized in an excellent yield (95%) *via* Suzuki cross-coupling of 2,4,6-tris(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine **285** with 3-bromobenzonitrile **286** in the presence of $Pd(PPh_3)_4$ catalyst and P(*t*-Bu)$_3$ as co-catalyst. Compound **285** was obtained in 83% yield by the reaction of 1,3,5-tris(bromophenyl)triazine **283** with octamethyl-2,2′-bi(1,3,2-dioxaborolane) **284** in the presence of Pd catalyst (Scheme 74).[120]

4.3.3.2. Oxaziridine. Peng *et al.*[121] reported the synthesis of a star-shaped molecule with triazine core and oxaziridine side arm **291** in 91% yield by reaction of 2,4,6-tris(*p*-formylphenoxy)-1,3,5-triazine **288** with 2-amino-2-methyl-1-propanol **289** to give tris(imine) **290** followed by oxidation using *m*-CPBA in chloroform (Scheme 75).

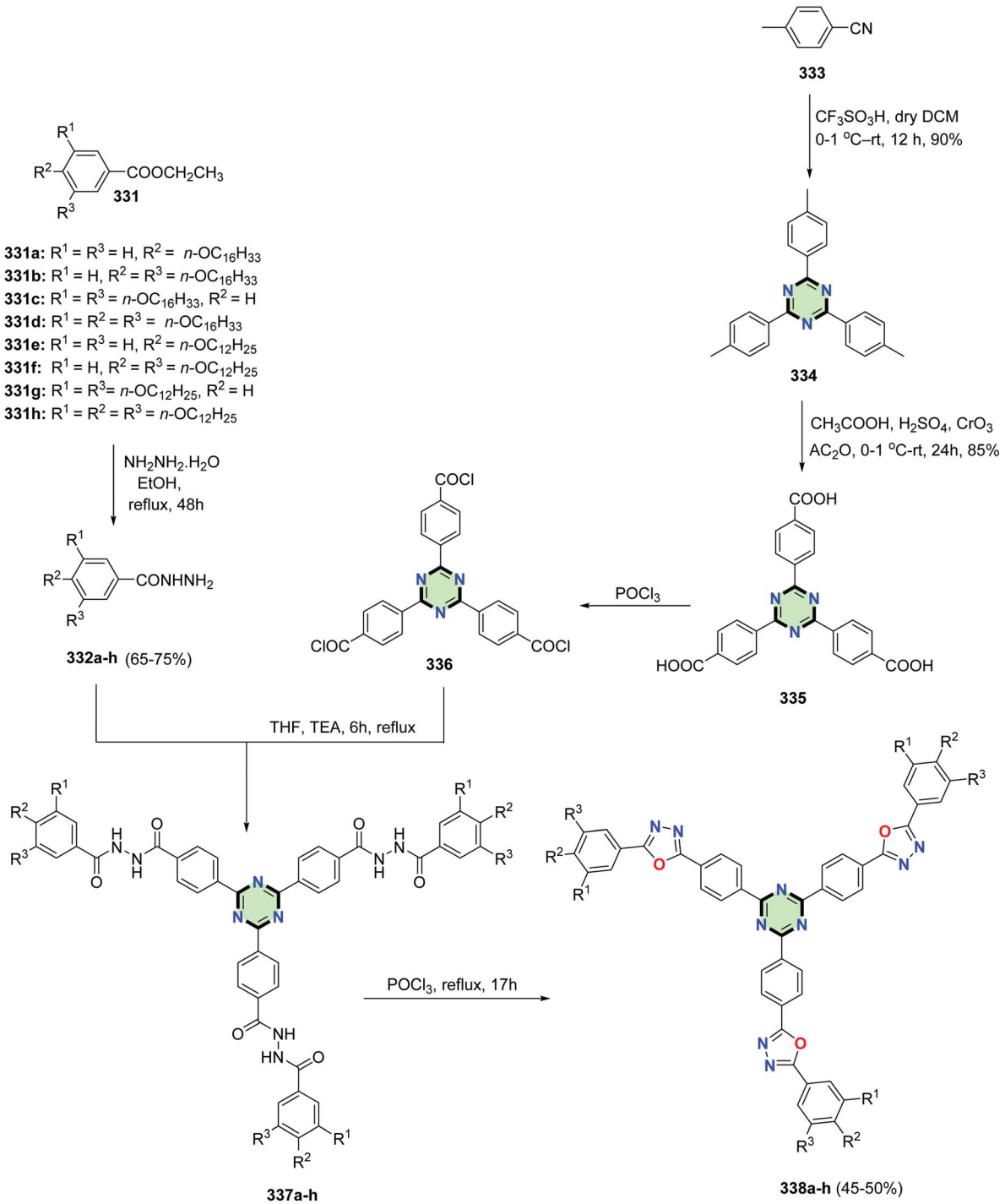
4.3.3.3. Pyrrole. 2,4,6-Tris(4-(1*H*-pyrrol-1-yl)phenoxy)-1,3,5-triazine **294** was synthesized in 76% yield upon treatment of 4-(1*H*-pyrrol-1-yl)phenol **292** with 2,4,6-trichloro-1,3,5-triazine **293** under basic condition (Scheme 76). Electropolymerization of the star-shaped molecule **294** was then conducted and the resulting polymer was studied spectroelectrochemically. Three bands were shown at 346, 508 and 665 for π–π* transition, polaron and bipolaron formation, respectively. The switching ability of this polymer was examined by means of chronoabsorptometry and the optical contrast was 20% with a switching time of 1.1 s. A dual complementary-colored electrochromic device was designed for both of the latter polymer and poly(3,4-ethylenedioxythiophene) (PEDOT) in a sandwich configuration. It switched between dark blue and red colors within 2.2 s and with an optical contrast of 25%.[122]

Triazine-cored compound **296** was synthesized in 91% yield through reaction of cyanuric chloride **293** with 1-(4-hydroxyphenyl)-1*H*-pyrrole-2,5-dione **295** in the presence of TEA (Scheme 77).

4.3.3.4. Thiophene and bithiophene. Li *et al.*[15] reported the synthesis of 2,4,6-tris(4-(thiophen-2-yl)phenyl)-1,3,5-triazine **298** in 15% yield through cyclotrimerization of 4-(thiophen-2-yl)benzonitrile **297** in the presence of CF_3SO_3H (Scheme 78). Electropolymerization of **298** resulted in the formation of a polymer of insignificant electrochromic properties. However, the copolymerization of this polymer with (a polymer of low ionization potential) PEDOT improved greatly the electrochromic properties.

2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine **299** was synthesized in 80% yield by the reaction of 2-tributylstannylthiophene **7** with cyanuric chloride **293** in the presence of $Pd(PPh_3)_4$ (Scheme 79).[6,123]

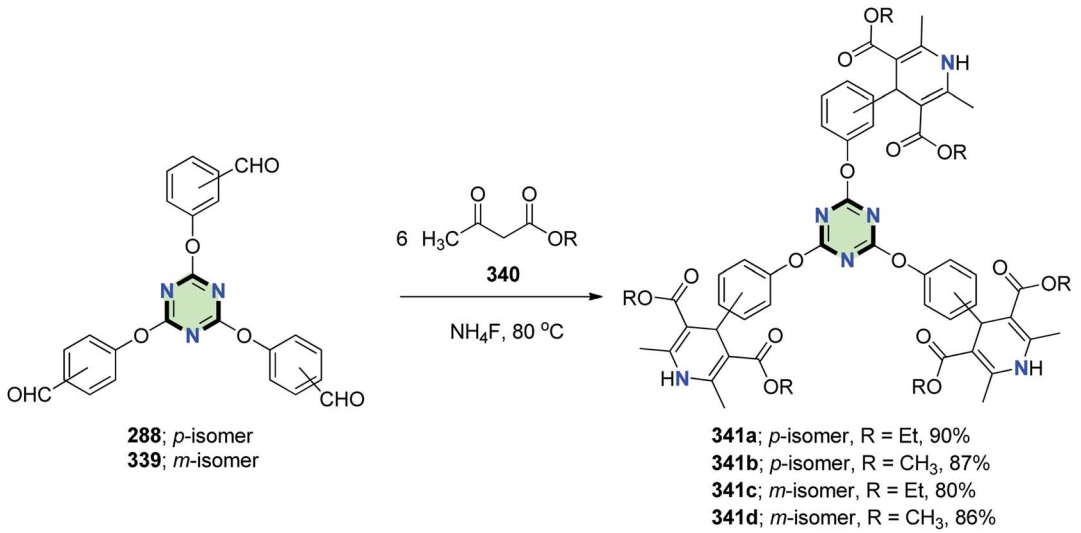
A selective lithiation of **299** and subsequent stannylation gave 2,4,6-tris(5-tributylstannyl-2-thienyl)-1,3,5-triazine **300**. The latter compound underwent Stille coupling reaction with pentafluorophenylbromide **301** in the presence of $Pd(PPh_3)_4$ to give 2,4,6-tris(5-pentafluorophenyl-2-thienyl)-1,3,5-triazine **302a** in 28% yield. On the other hand, 2,4,6-tri(5-aryl-thiophen-2-yl)-1,3,5-triazines **302b–f** were synthesized *via* Suzuki–Miyaura cross-coupling reactions of 2,4,6-tri(5-bromo-2-thienyl)-1,3,5-triazine **303** with arylboronic acids **304** or tetramethyl-2-aryl-1,3,2-dioxaborolane **305** in the presence of cesium carbonate and Pd catalyst (Scheme 80).[6] The effect of tuning the electronic nature of aryl groups connected to thiophene peripheral of SSMs **302** was found to be consistent with the electron-accepting or electron-attracting capabilities of these molecules as deduced from their UV absorption and fluorescence emission spectra. Moreover, compound **302e** having Bu_2N– group showed both absorption and emission solvatochromism (due to internal charge transfer), as well as colorimetric and luminescence proton-sensing properties in view of the visually observed changes in the color of the solution and emission related to the two-step protonation of the Bu_2N– groups and the nitrogen



Scheme 89 Synthesis of SSMs with a central triazine core appended with three 1,3,4-oxadiazole arms **338a–h**.

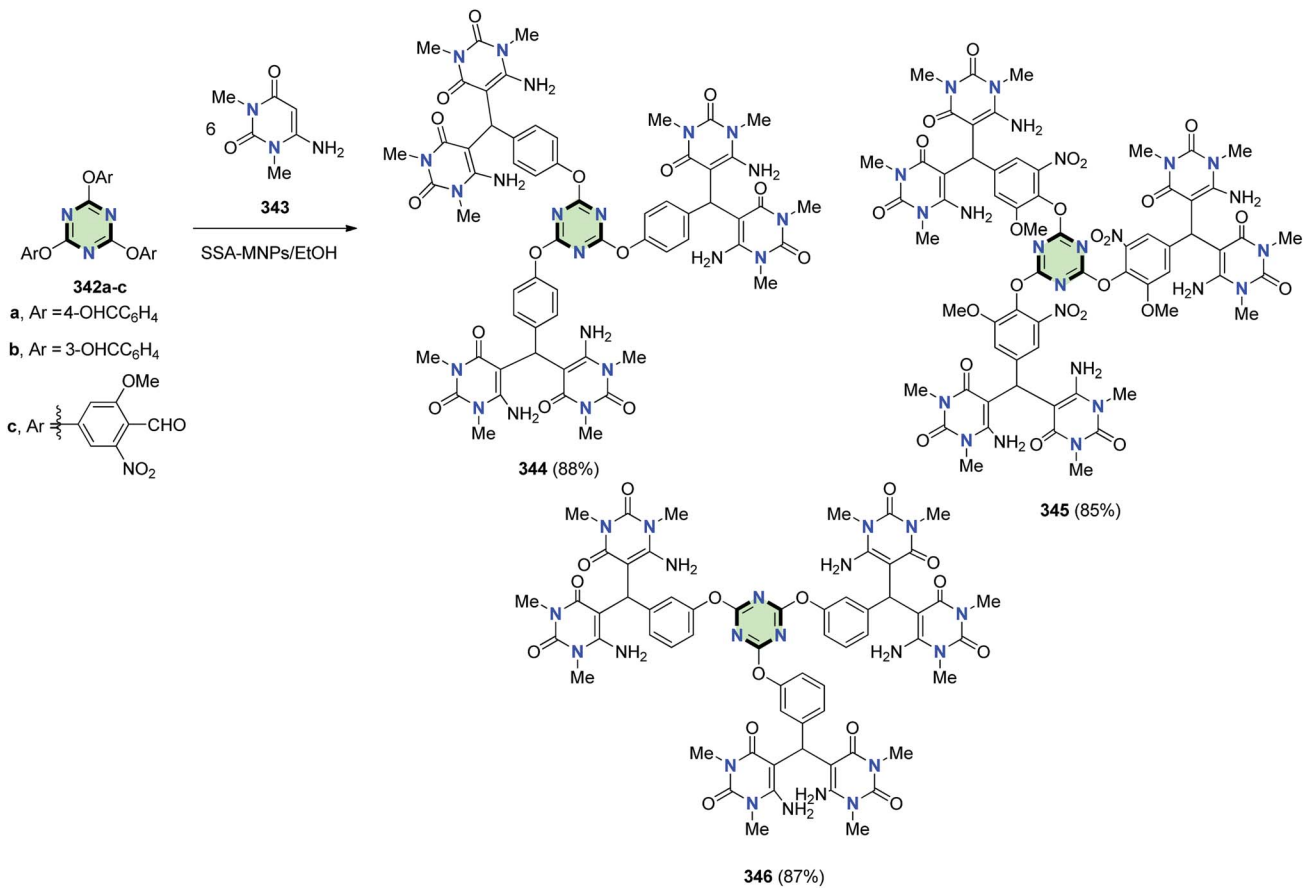
atoms on the 1,3,5-triazine moiety. This makes compound **302e** to be a promising polarity or pH sensors.

A series of SSMs with 1,3,5-triazine core and thiophene attached directly or *via* ethylenic linkages to triphenylamine, carbazole or fluorene moieties as side arms **307** and **309** could be synthesized starting from the 2,4,6-tri(5-bromo-2-thienyl)-1,3,5-triazine **303** through Suzuki–Miyaura and Sonogashira cross-coupling reactions involving arylboronates **306a–d** or ethynylarenes **308a–c**, respectively, in moderate-to-excellent yields (64–93%). Compound **303** was obtained by bromination of tris-2,4,6-thienyl-1,3,5-triazine **299** in the presence of bromine in chloroform at reflux (Scheme 81). The UV-vis spectra of compounds **307** and **309** showed that the absorption maximum was affected not only by the electron-donating

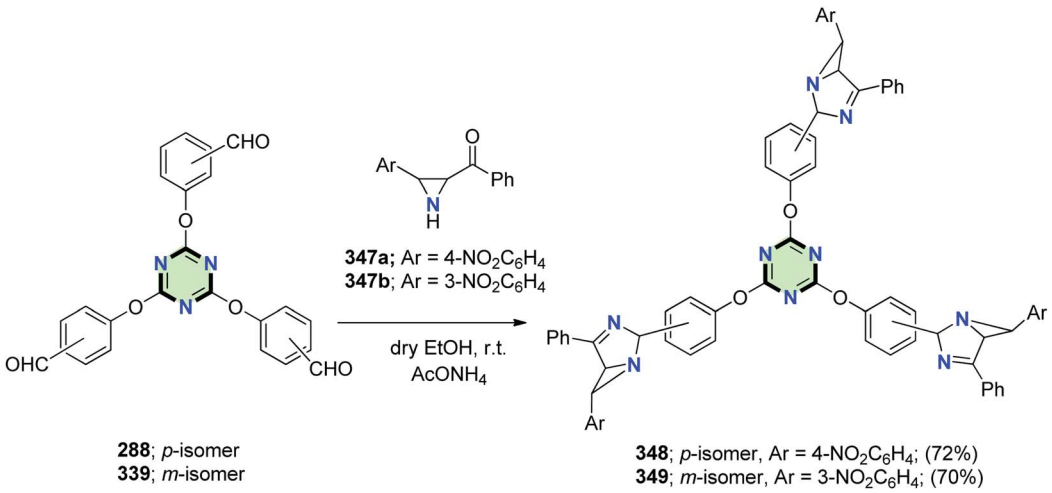


Scheme 90 Synthesis of tripodal 1,4-dihydropyridines **341a–d**.

strength of the peripheral group or introduction of an ethynyl spacer, but on the position of the same electron-donating substituent as well (as in case of **307b** and **307d**). The electrochemical data of these compounds displayed a reversible or a quasi-reversible redox behavior due to their donor–acceptor properties. In addition, these compounds indicated large two-photon absorption cross-sections at 720–880 nm, greatly



Scheme 91 Synthesis of tri[bis(6-aminopyrimidinyl)methanes] **344–346**.



Scheme 92 Synthesis of SSMs with 1,3-diazabicyclo[3.1.0]hex-3-enes side arms **348** and **349**.

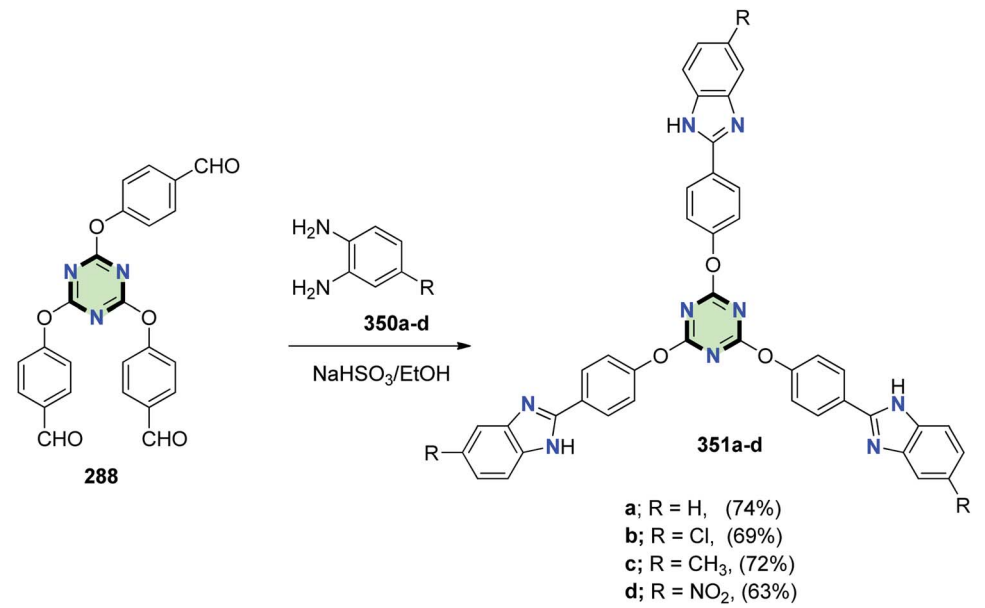
affected by the intramolecular charge transfer and the extent of π-conjugation.[124]

Leriche *et al.*[123] reported the synthesis of star-shaped 1,3,5-triazine molecules **310a,b** with thiophene or bithiophene tails in 80 and 60% yields, respectively, by the reaction of cyanuryl chloride **260** with tributylstannylarenes **7a** or by the reaction of 2,4,6-tris(5-bromothiophen-2-yl)-1,3,5-triazine **303** with 2-tributylstannylthiophene **7b** in the presence of $Pd(PPh_3)_4$ (Scheme 82). It was shown that enlargement of thiophene tail resulted in a bathochromic shift in their UV-vis absorption spectra and a reduction in their oxidation potential as shown from their cyclic voltammograms.

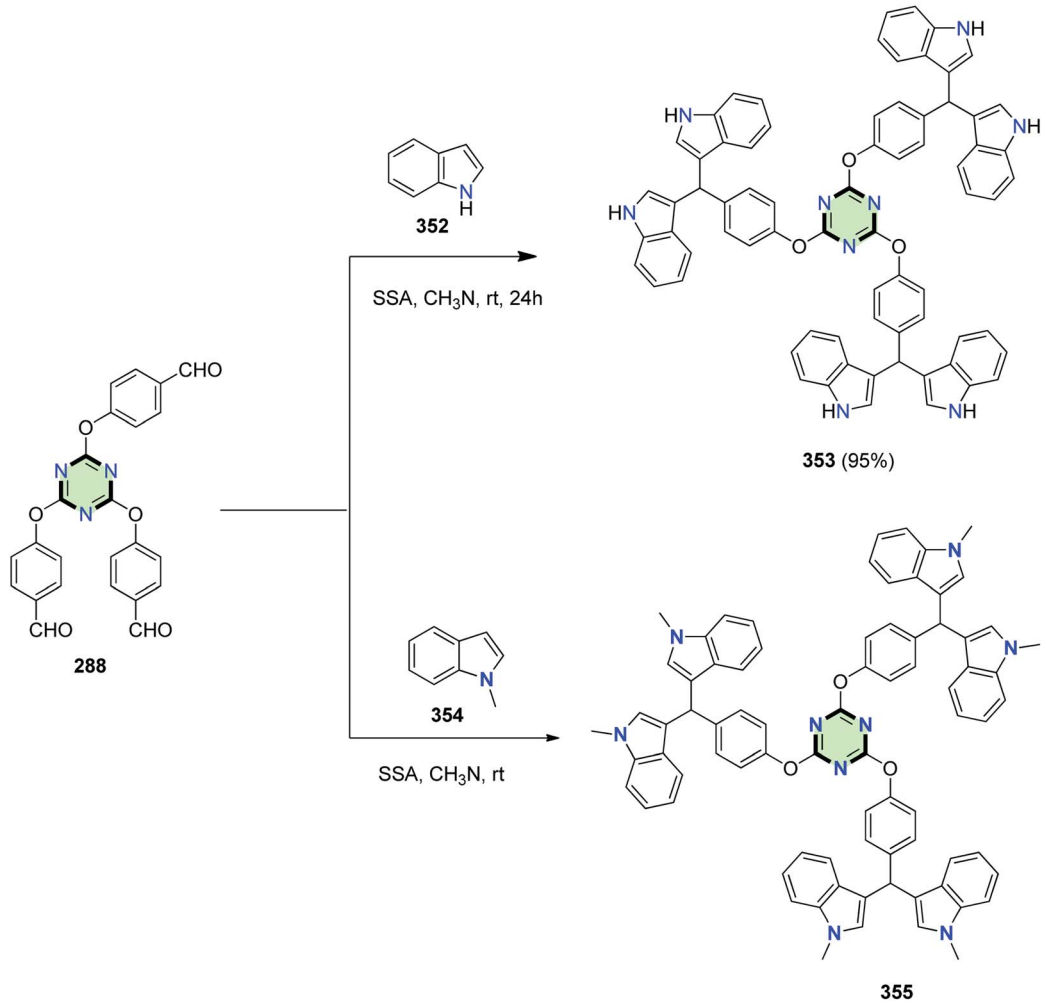
4.3.3.5. Imidazolidine. Condensation of trisaldehyde **288** with 2,3-dihydroxyamino-2,3-dimethylbutane **311** in acetonitrile afforded a star-shaped molecule with triazine core and 4,4,5,5-tetramethyl-2-phenylimidazolidine-1,3-diol side arms **312** in 45% yield (Scheme 83).

4.3.3.6. 4,5-Dihydro-1H-pyrazole. A series of tris-pyrazoline **317a–f** were synthesized in good yields by tris-cyclization of tris-chalcones **315** with thiosemicarbazide **316** under basic conditions in DMF. The chalcones **315** were prepared by condensation of tris-acetophenone **313** with the appropriate aldehydes **314** in MeOH in the presence of NaOH (Scheme 84).[125]

4.3.3.7. 1,2,4-Triazole. Star-shaped Schiff bases **319a–c** with triazine core and 1,2,4-triazole side arms were synthesized in good yields through condensation of 2,4,6-tris(*p*-formylphenoxy)-1,3,5-triazine **288** with the appropriate amino-triazole **318** in glacial acetic acid at reflux (Scheme 85).[126]

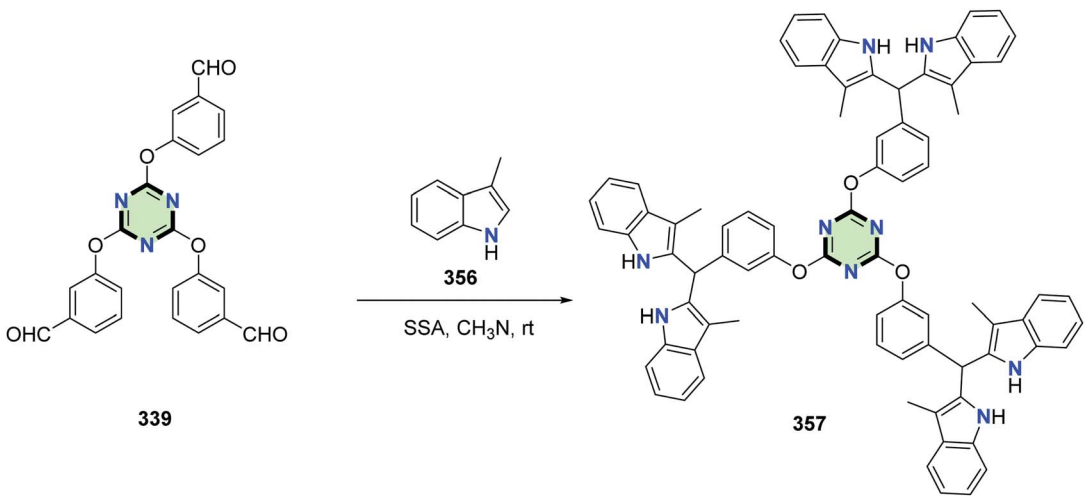


Scheme 93 Synthesis of tripodal-benzimidazole derivatives **351a–d**.

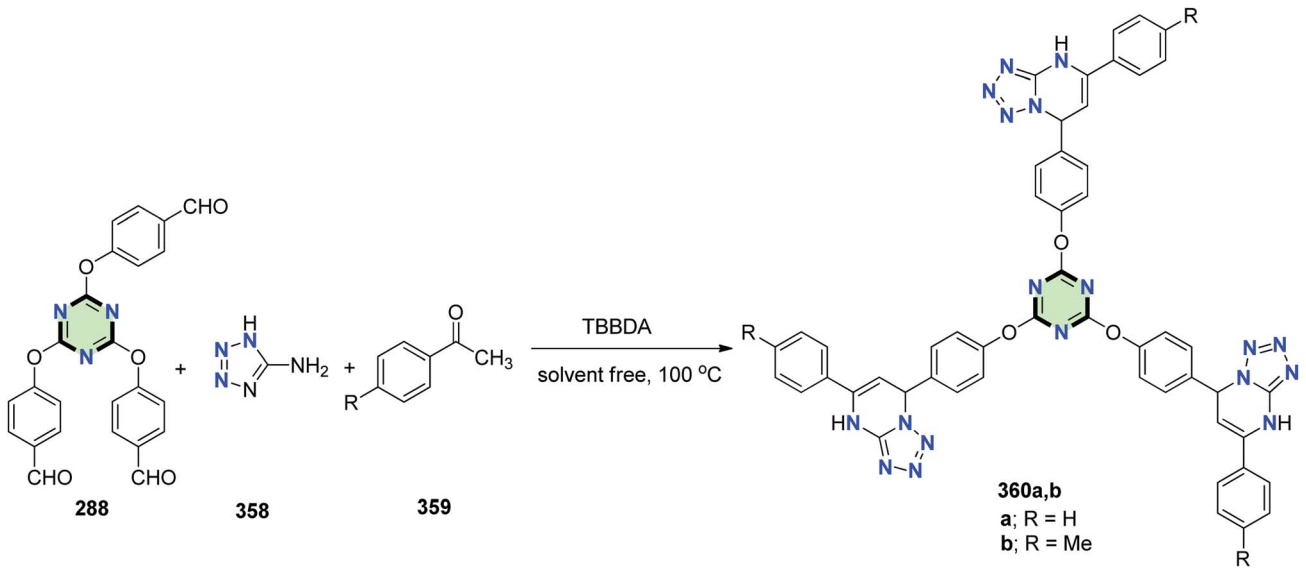


Scheme 94 Synthesis of tris(bis(indolyl)methanes) compounds **353** and **355**.

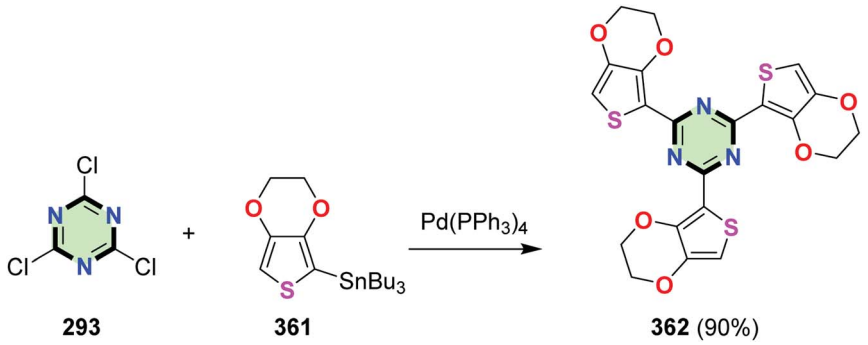
4.3.3.8. 1,2,3-Triazole. The synthesis of tripodal **322** with 1,2,3-triazole side arms were performed using a copper catalyzed Huisgen's reaction. Thus, reaction of a mixture of alkyne **321** and benzylazide **320** in DMF afforded tris[(1-benzyl-1*H*-1,2,3-triazole-4-yl)methyl]-1,3,5-triazinane-2,4,6-trione **322** in 60% yield (Scheme 86).[127]



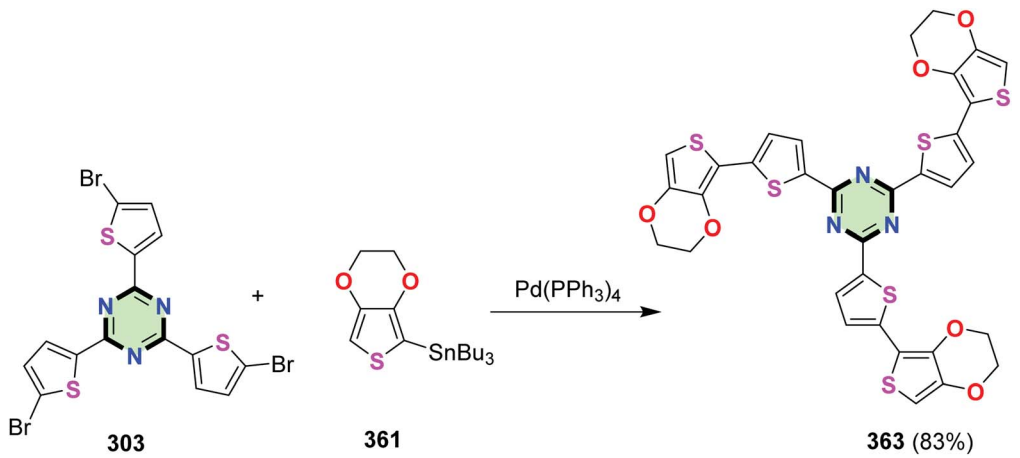
Scheme 95 Synthesis of 2,4,6-tris((bis(indol-2-yl)methyl)phenoxy)-1,3,5-triazine **357**.



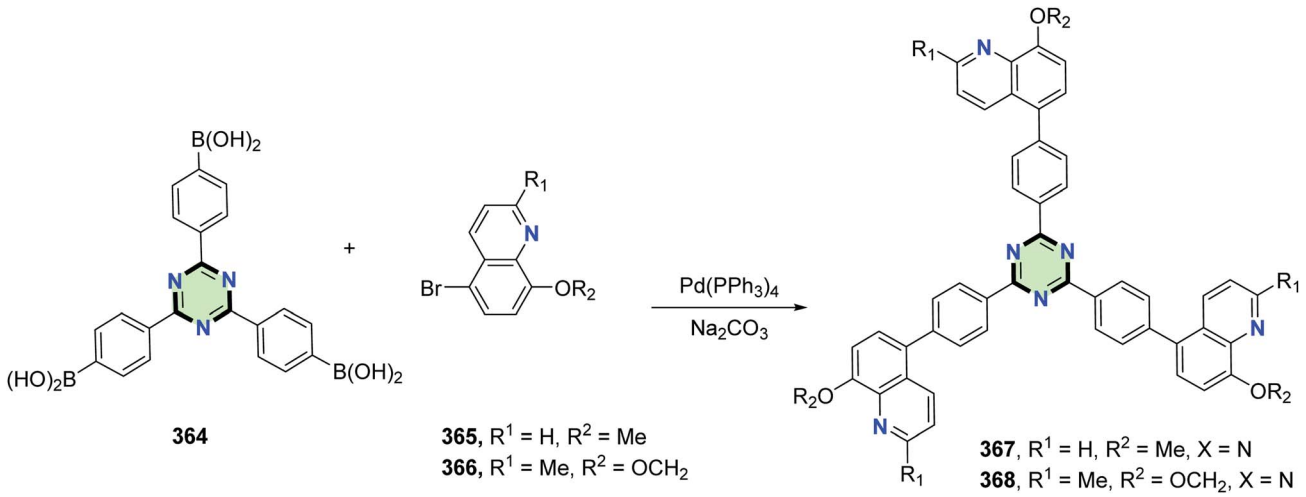
Scheme 96 Synthesis of tris-dihydrotetrazolo[1,5-*a*]pyrimidines **360a** and **360b**.



Scheme 97 Synthesis of 2,4,6-tris(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-1,3,5-triazine **362**.



Scheme 98 Synthesis of SSM with triazine core linked to thieno[3,4-*b*][1,4]dioxine.



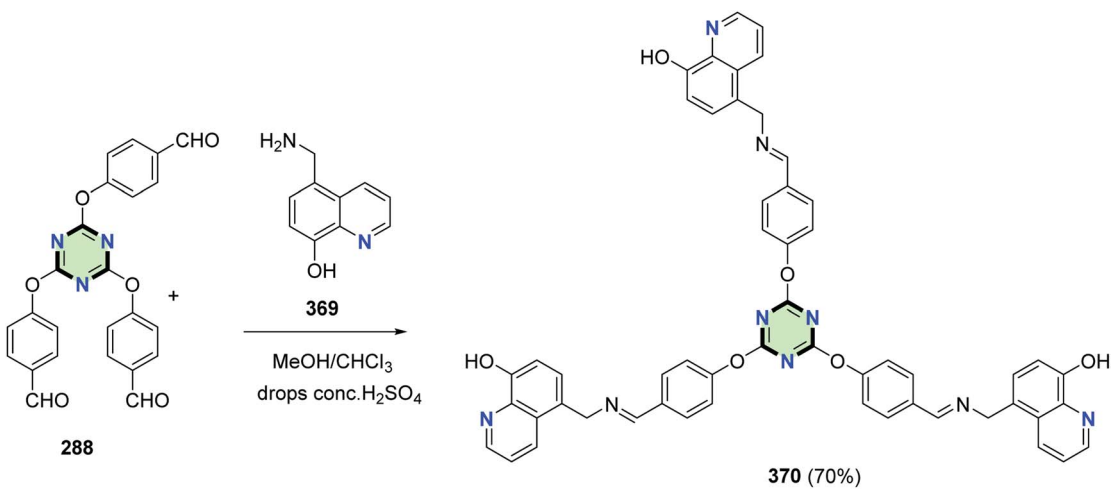
Scheme 99 Synthesis of SSMs with quinolone side arms **367** and **368**.

The same method was applied to synthesize the triazole derivative **325** in 67% yield, using the tris azide **323** and phenylacetylene **324** (Scheme 87).[127]

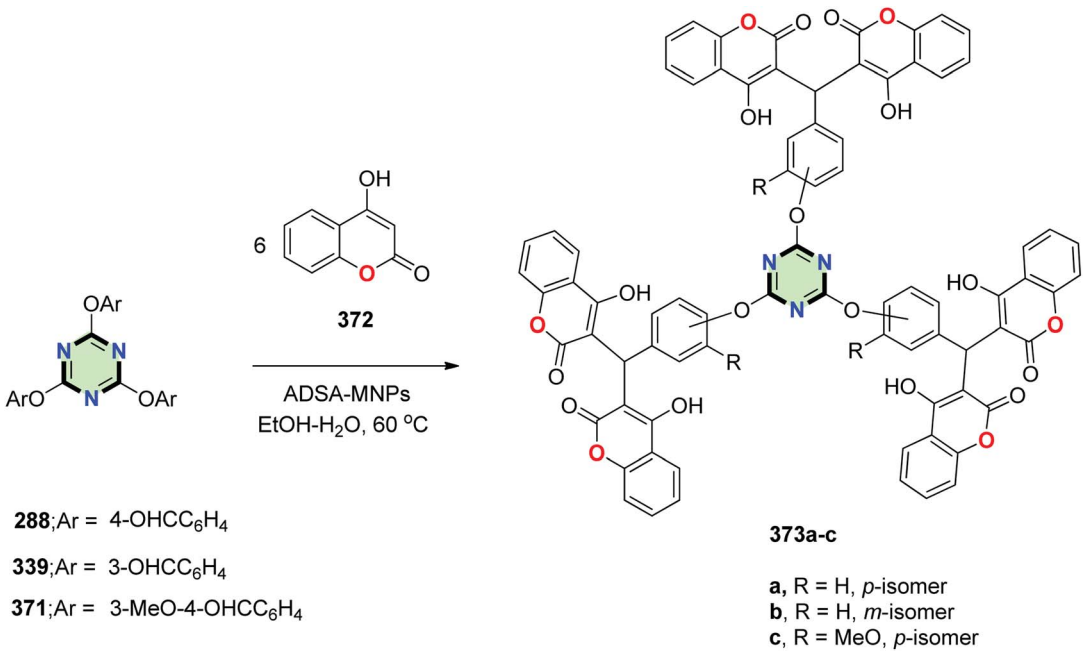
The click copper-catalyzed cycloaddition reaction of tris [(trimethylsilyl)ethynyl]-1,3,5-triazine **326** with azide derivatives **327** afforded SSMs **328** with triazine core and phenyltriazole side arms containing mono-, di-, and trialkoxy groups (Scheme 88). The star-shaped materials **328** showed ordered columnar mesophases. They displayed luminescence from the blue to green light depending on the peripheral substitution. Electrochemical behavior of these compounds was good correlated to their electron-deficient nature and their potential for electron transport.[128]

In a similar fashion, SSMs **330a–e** with triazine core and arms containing triazole moieties and aroyloxy groups could be synthesized in moderate yields (28–51%) starting from the appropriate 4-azidophenyl benzoate **329** (Fig. 7). It has been found that inclusion of long alkoxy chains in compounds **330** decreases both solvatofluorochromism and electron-accepting properties.[129]

4.3.3.9. Oxadiazole. Pradhan *et al.*[130] reported the synthesis of star-shaped molecules with a central triazine core appended with three 1,3,4-oxadiazole arms **338a–h** through multi-step reactions including, firstly the transformation of alkoxy esters **331a–h** into their respective hydrazides **332a–h** upon treatment with hydrazine hydrate in ethanol. Reaction of the hydrazides with 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tribenzoyl chloride **336** (obtained upon treatment of 4,4′,4″-(1,3,5-triazine-2,4,6-triyl) tribenzoic acid **335** with $POCl_3$) in THF in the presence of triethylamine yielded tri-*N*-benzoylbenzohydrazides **337a–h.** These compounds were heated with $POCl_3$ to give the target molecules **338a–h.** The key intermediate 4,4′,4″-(1,3,5-triazine-2,4,6-triyl) tribenzoic acid **335** was prepared in good yield from *p*-tolunitrile **333** by firstly triflic acid catalyzed trimerization to give



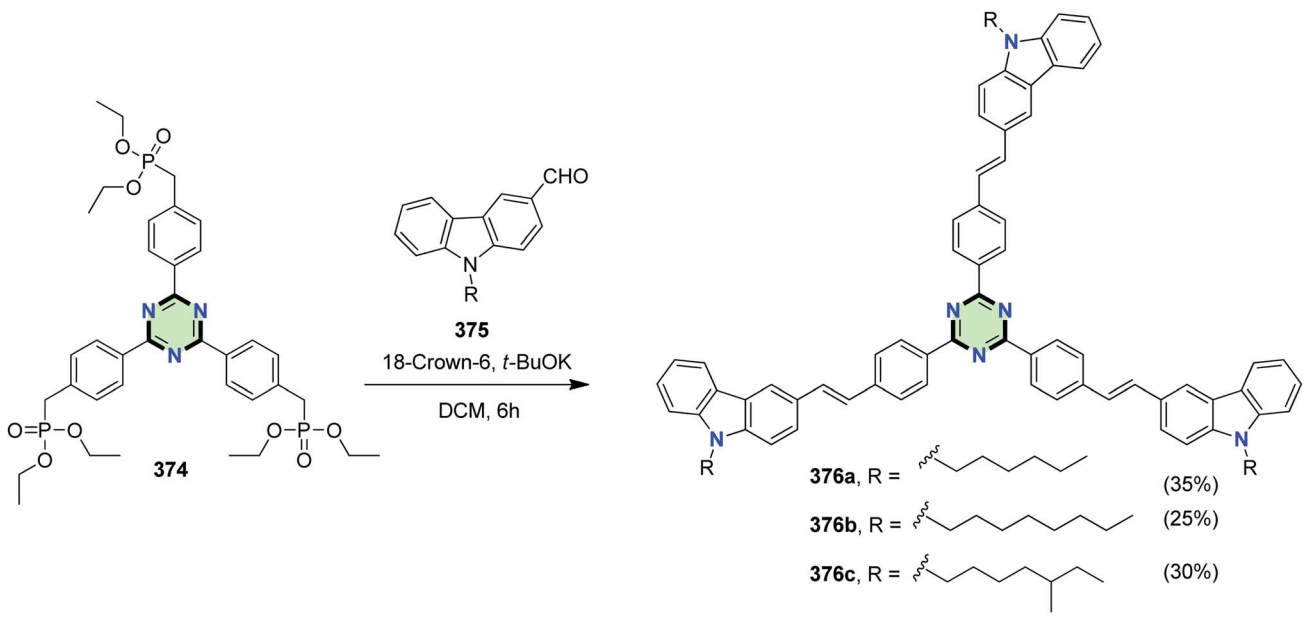
Scheme 100 Synthesis of tripodal Schiff base with triazine core and quinoline side arms **370**.



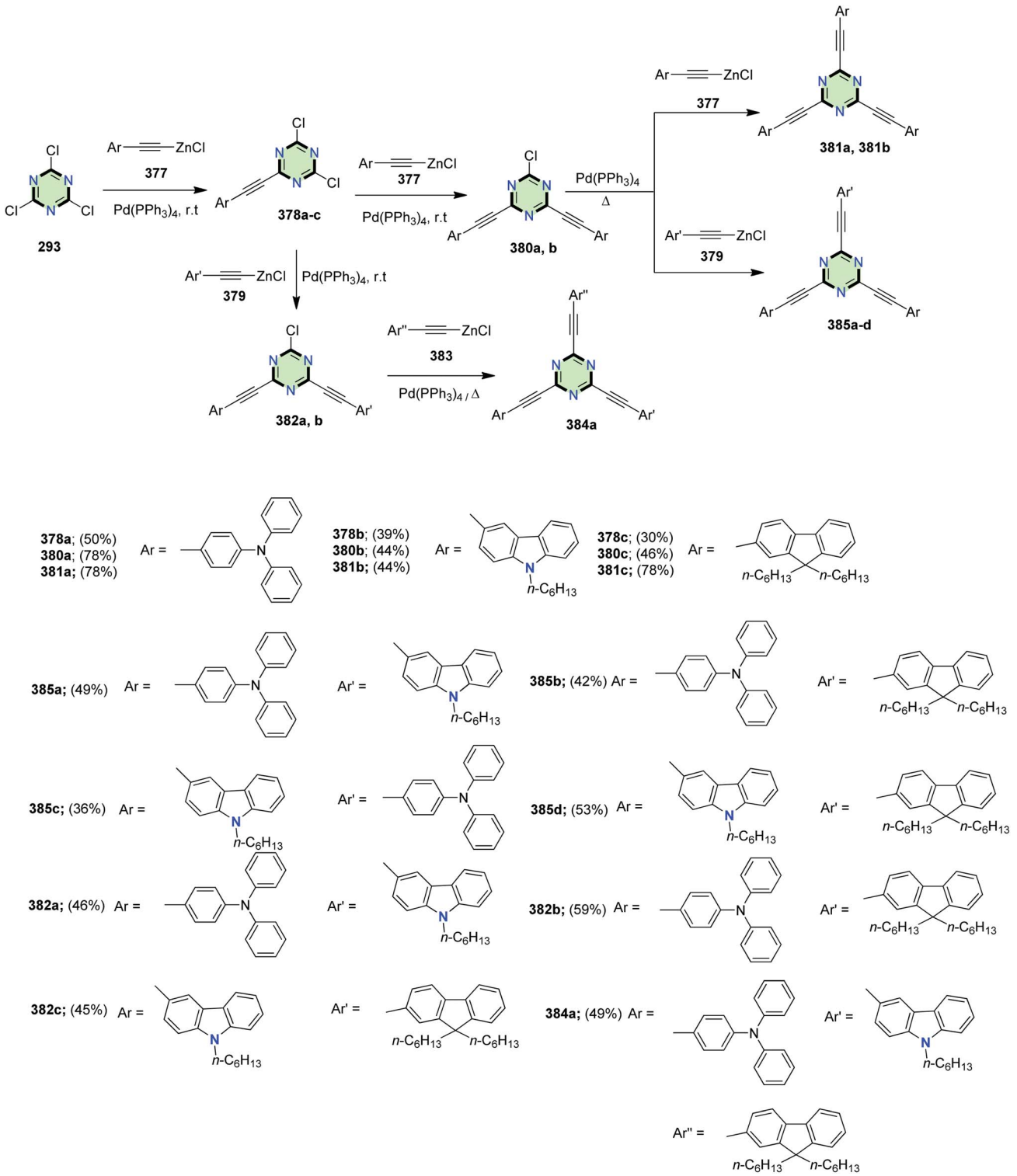
Scheme 101 Synthesis of tris[bis(4-hydroxycoumarinyl)methanes] **373a–c**.

2,4,6-tri-*p*-tolyl-1,3,5-triazine **334** and subsequent chromic oxide mediated oxidation (Scheme 89). In general, a decrease of the chain length of the alkoxy groups led to enhancement of core–core interaction and subsequently, stabilizing both Col_r and Col_h phases and improving the thermal range. The SSMs **338** fluoresced blue-green light either in solution or in the solid state according to the type of peripheral chains. The persistence of fluorescene in the solid state was attributed to the columnar assembly of the star molecules. Cyclic voltammograms of **338** implied that these molecules have lower LUMO and band gaps making them potential electron-transporting candidates for OLEDs.

4.3.3.10. 1,4-Dihydropyridine. Tripodal 1,4-dihydropyridines **341a–d** were synthesized in good yields through Hantzsch reaction of tris-aldehydes **288** and **339** with β-keto esters **340** in the presence of NH_4F (Scheme 90).[131]



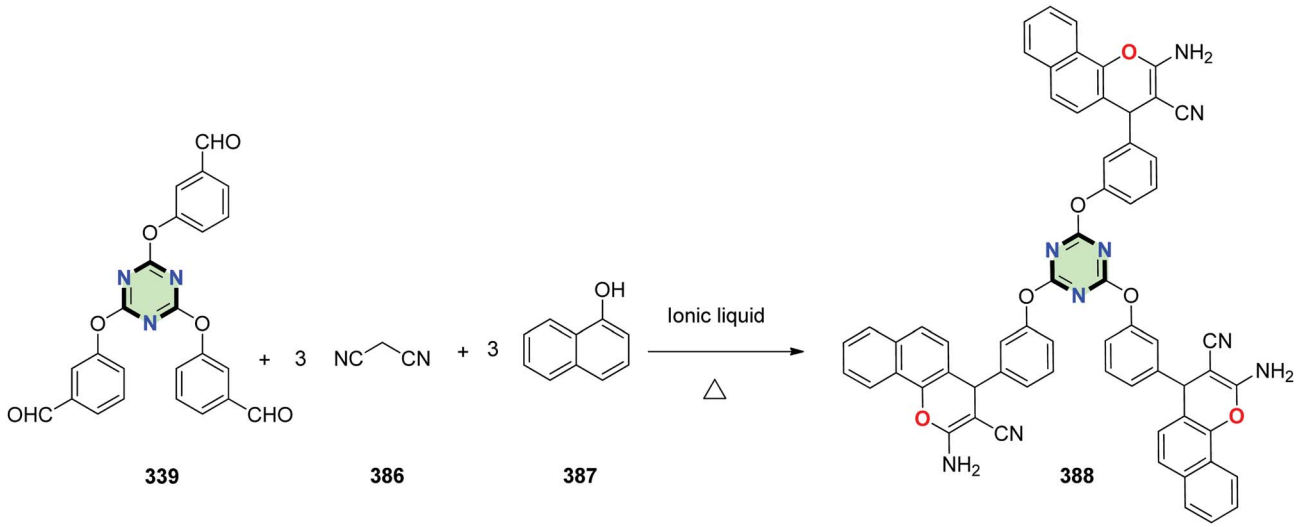
Scheme 102 Synthesis of SSMs **376a–c** with 1,3,5-triazine core linked to three carbazole units.



Scheme 103 Synthesis of symmetrical and asymmetrical 2,4,6-tris(arylethynyl)-1,3,5-triazines.

4.3.3.11. Pyrimidine. Karimi *et al.*[132] reported the synthesis of tri[bis(6-aminopyrimidinyl)methanes] **344–346** in good yields by reaction of the appropriate trisaldehydes **342a–c** with 6-amino-1,3-dimethyluracil **343** using sulfuric acid functionalized silica-coated magnetic nanoparticles (SSA-MNPs) as a catalyst (Scheme 91).

4.3.3.12. 1,3-Diazabicyclo[3.1.0]hex-3-ene. Mahmoodi *et al.*[133] reported the synthesis of star shaped molecules with 1,3-diazabicyclo[3.1.0]hex-3-enes side arms **348** and **349** in 72% and



Scheme 104 Synthesis of tris(2-amino-4*H*-chromene) **388**.

70% yields, respectively, through reaction of tris-aldehydes **288** and **339** with aziridinyl ketones **347a** and **347b**, respectively, in dry EtOH in the presence of $AcONH_4$ (Scheme 92).

4.3.3.13. Benzimidazole. A series of tripodal-benzimidazole derivatives **351a–d** were synthesized in 63–74% yields by Schiff base reaction between 2,4,6-tris(*p*-formylphenoxy)-1,3,5-triazine and *o*-phenylenediamine derivatives **350a–d** in the presence of $NaHSO_3$ (Scheme 93).[134]

2,4,6-Tris(4-(di(indol-3-yl)methyl)phenoxy)-1,3,5-triazines **353** and **355** were prepared in good yields by the Friedel–Crafts reaction of tris-aldehyde **288** with each of 1*H*-indole **352** and 1-methyl-1*H*-indole **354**, respectively, in acetonitrile in the presence of silica sulfuric acid (Scheme 94).[7,10]

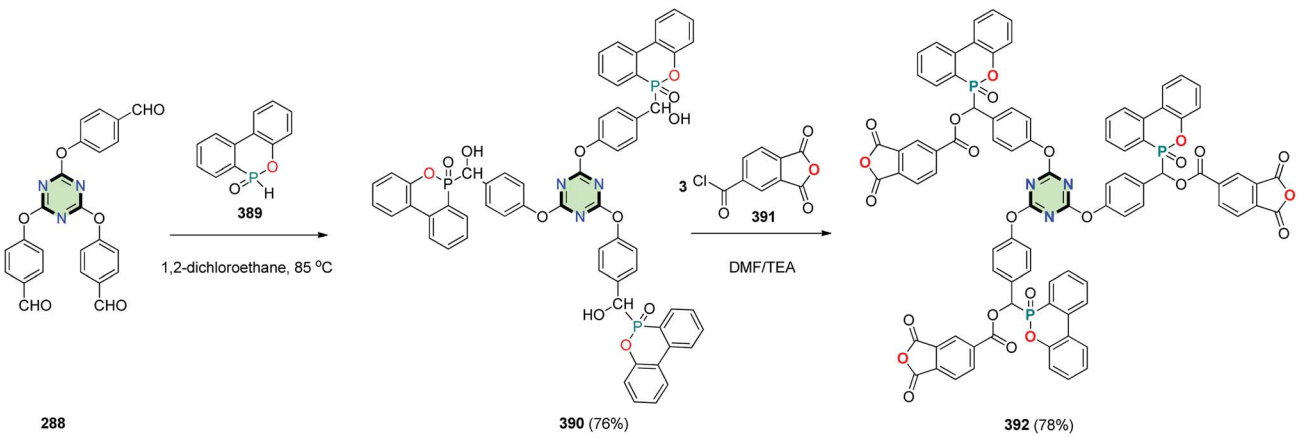
On the other hand, Shiri *et al.*[135] reported the synthesis of 2,4,6-tris(3-(bis(3-methyl-1*H*-indol-2-yl)methyl)phenoxy)-1,3,5-triazine **357** in good yields by Friedel–Crafts reaction of 3-methyl-1*H*-indole **356** with tris-aldehyde **339** catalyzed by silica sulfuric acid in acetonitrile (Scheme 95).

4.3.3.14. Dihydrotetrazolo[1,5-a]pyrimidine. Vaghei *et al.*[136] reported the synthesis of tris-dihydrotetrazolo[1,5-*a*]pyrimidines **360a** and **360b** in 85% and 92% yield, respectively, through a multi-component reaction between tris-aldehyde **288**, acetophenone derivatives **359** and 5-aminotetrazole **358** under solvent free conditions (Scheme 96).

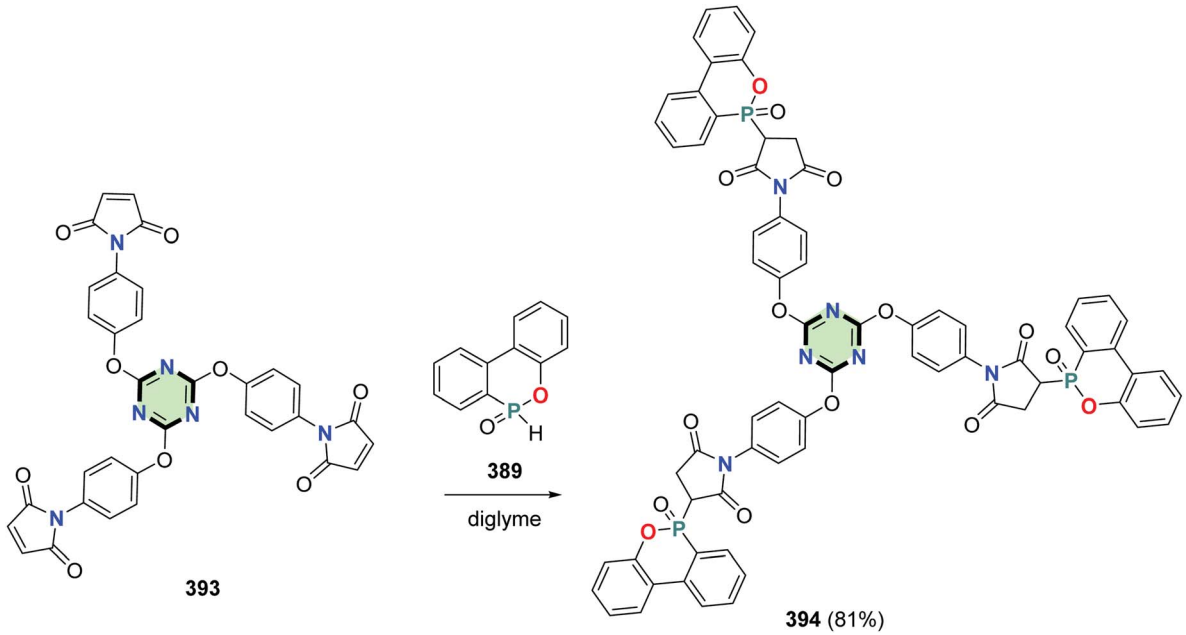
4.3.3.15. 2,3-Dihydrothieno[3,4-b][1,4]dioxine. 2,4,6-Tris(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-1,3,5-triazine **362** was synthesized in 90% yield by Stile coupling reaction between cyanuric chloride **293** and tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane **361** in the presence of $Pd(PPh_3)_4$ (Scheme 97).[123]

A star-shaped molecule with triazine core linked to thieno[3,4-*b*][1,4]dioxine *via* thiophene moiety **363** was synthesized in 83% yield by the reaction of 2,4,6-tris(5-bromothiophen-2-yl)-1,3,5-triazine **303** with tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane **361** under similar conditions (Scheme 98).[123] The effect of conjugation persisted in compounds **362** and **363.** It was shown that increasing the number of thiophene moieties led to a remarkable red shift in their UV-vis absorption spectra and a decrease in their oxidation potential as evident from cyclic voltammetry.

4.3.3.16. Quinoline. Star-shaped conjugated molecules with quinolone side arms **367** and **368** were synthesized in good



Scheme 105 Synthesis of tri(phosphaphenanthrenemethylphenoxyl)-1,3,5-triazine **390** and **392**.



Scheme 106 Synthesis of tris(3-(6-oxido-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinin-6-yl)pyrrolidine-2,5-dione) **394**.

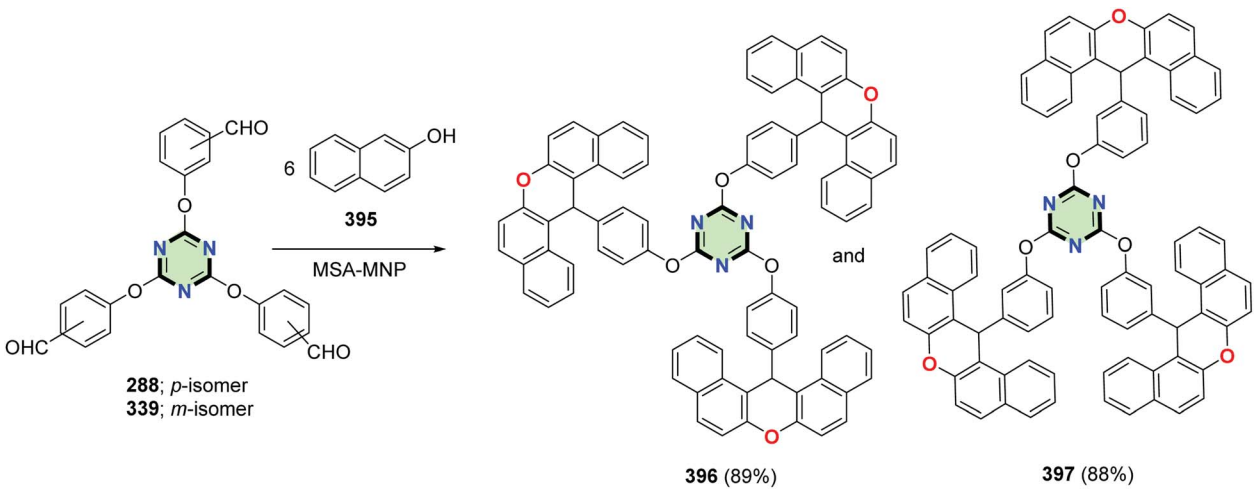
yields, using Suzuki coupling reaction of the appropriate boronic acid **364** with 5-bromo-8-methoxyquinoline **365** or 5-bromo-8-methoxy-2-methylquinoline **366** in the presence of Na_2CO_3 and $Pd(PPh_3)_4$ (Scheme 99).[112]

Karatas and Ucan reported a synthesis of a tripodal Schiff base molecule with triazine core and quinoline side arms **370** in 70% yield through reaction of 5-aminomethyl-8-hydroxylquinoline **369** with 2,4,6-tris(*p*-formylphenoxy)-1,3,5-triazine **288** in the presence of acidic catalyst (Scheme 100).[137]

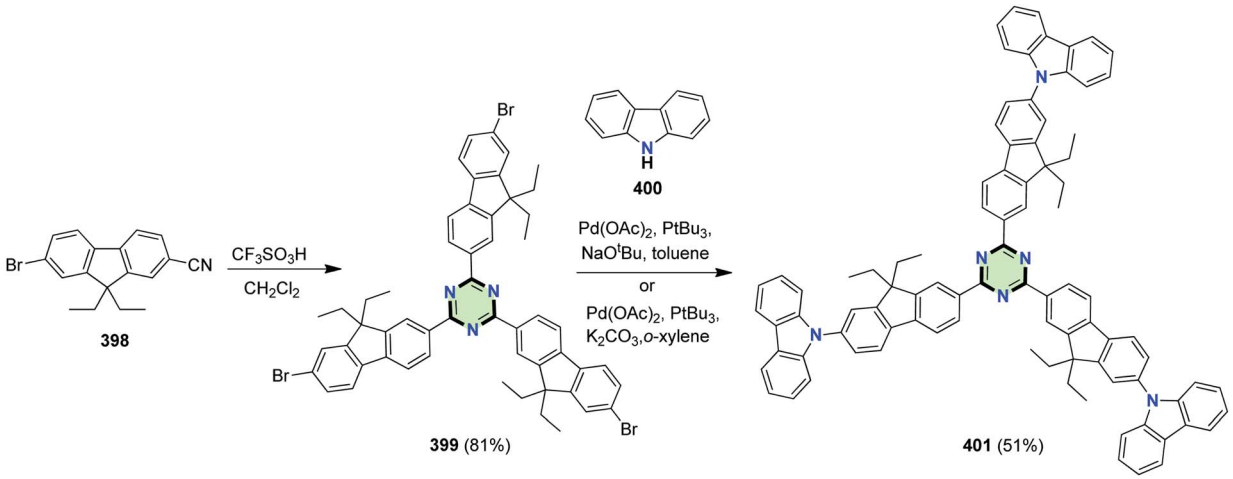
4.3.3.17. Coumarin. Tris[bis(4-hydroxycoumarinyl) methanes] **373a–c** were synthesized by condensation of 4-hydroxy-2*H*-coumarin-2-one **372** with the appropriate tris-aldehydes **288**, **339** or **371**. The reaction proceeded using alkanedisulfamic acid-functionalized silica-coated magnetic nanoparticles (ADSA-MNPs) as a catalyst (Scheme 101).[138]

4.3.3.18. Carbazole. Star-shaped molecules with 1,3,5-triazine core linked to three carbazole units *via* ethenyl linkage **376a–c** were synthesized in 35, 25 and 30% yields *via* Witting–Horner coupling reaction between the appropriate carbazole-3-carbaldehydes **375** and 2,4,6-tris[4-(diethylphosphonomethyl) phenyl]-1,3,5-triazine **374** in the presence of *t*-BuOK (Scheme 102). The star-shaped molecules showed high optical properties, efficient fluorescence, AIE properties and also provide useful information for the further design of OLEDs and solar cell materials.[139]

Symmetrical and asymmetrical star-shaped 2,4,6-tris(arylethynyl)-1,3,5-triazine **378a–c**, **380a,b**, **381a,b**, **282a,b**, **384a** and **385a–d** containing triphenylamine, fluorene, and/or carbazole moieties were synthesized in moderate yields (36–53%) *via* step-by-step Negishi reactions of 2,4,6-trichloro-1,3,5-



Scheme 107 Synthesis of tris-14*H*-dibenzo[*a*,*j*]xanthen-14-ylarenes **396** and **397**.



Scheme 108 Synthesis of SSM **401** containing triazine core and fluorine–carbazole arms.

triazine **293** with the appropriate arylethynylzinc chloride **377**, **379** or **383** in the presence of $Pd(PPh_3)_4$ (Scheme 103).[140]

4.3.3.19. 4H-Benzo[h]chromene. Tris(2-amino-4*H*-chromene) **388** has been developed using the reaction between tris(aldehyde) **339**, malononitrile **386** and α-naphthol **387** in the presence of 3,3′-(pentane-1,5-diyl)bis(1,2-dimethyl-1*H*-imidazol-3-ium)bromide. The present methodology offers several advantages such as solvent-free conditions, excellent yields, simple procedure, mild conditions and reuse of the recovered ionic liquid (Scheme 104).[141]

4.3.3.20. 6H-Dibenzo[c,e][1,2]oxaphosphinine 6-oxide. Tri(phosphaphenanthrenehydroxylmethylphenoxyl)-1,3,5-triazine **390** was synthesized in 76% yield by the reaction of 2,4,6-tris(*p*-formylphenoxy)-1,3,5-triazine **288** with 6*H* dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide **389**.[142,143] Reaction of **390** with 4-chloroformylphthalic anhydride **391** in DMF in the presence of TEA afforded SSM with triazine core and (6-oxido-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinin-6-yl)methyl 1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate side arm **392** in 78% yield (Scheme 105).[6]

Tris(3-(6-oxido-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinin-6-yl) pyrrolidine-2,5-dione) linked to 1,3,5-triazine core **394** was prepared in 81% yield by the reaction of tris(1*H*-pyrrole-2,5-dione) **393** with 6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine-6-oxide **389** in diglyme (Scheme 106).[144]

4.3.3.21. 14H-Dibenzo[a,j]xanthen. Tris-14*H*-dibenzo[*a*,*j*] xanthen-14-ylarenes **396** and **397** were synthesized in 89% and 88% yields, respectively, by reacting 2-naphthol **395** with tris-aldehydes **288** and **339**, respectively, under solvent free conditions using magnetite–sulfuric acid ($Fe_3O_4 \cdot SO_3H$) nanoparticles as a catalyst (Scheme 107).[145]

4.3.3.22. Miscellaneous arms

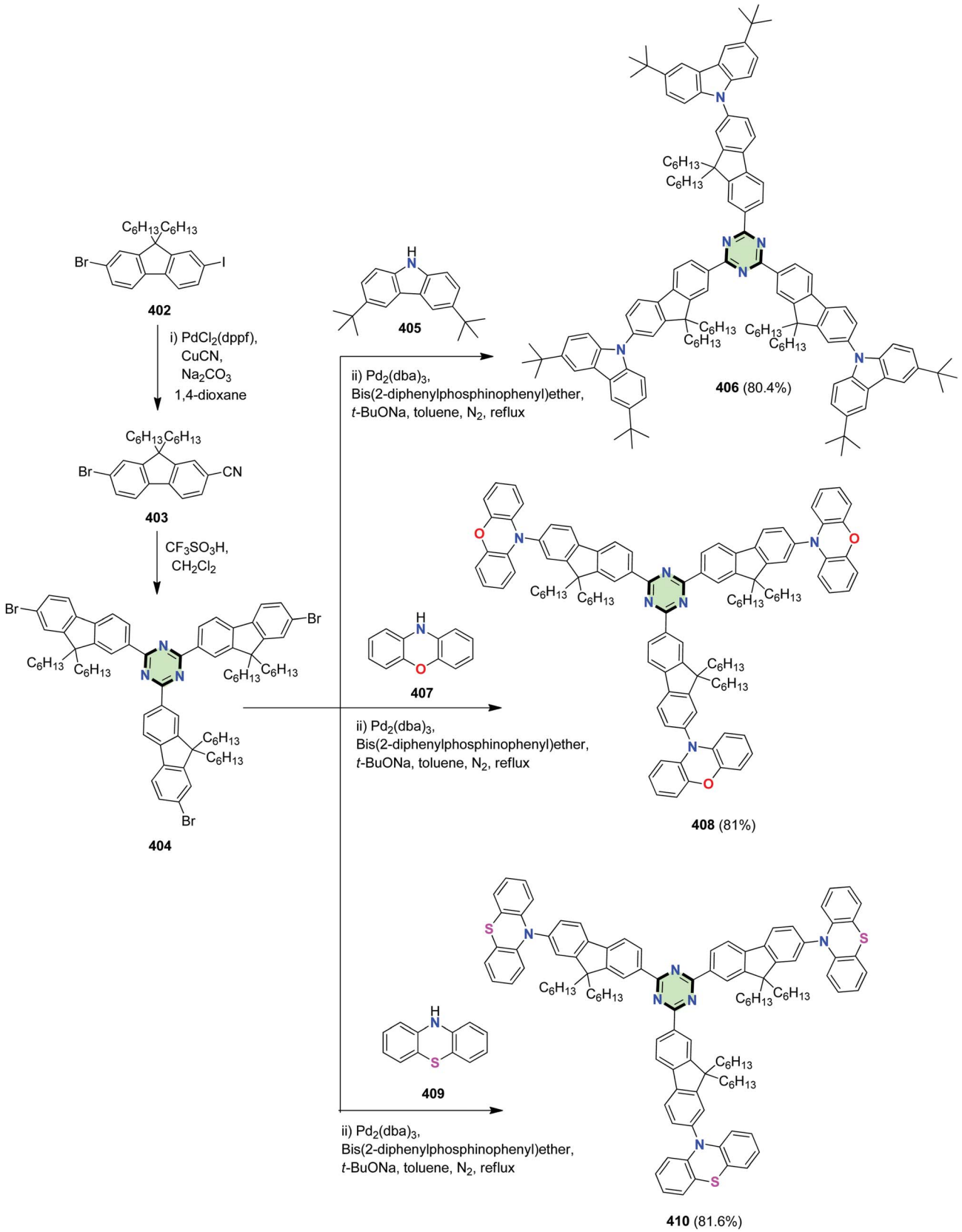
4.3.3.22.1. Fluorene linked to carbazole, phenoxazine or phenothiazine. Omer *et al.*[146] reported the synthesis of C3-symmetrical SSM **401** in a two-step procedure. The reaction starts with trifluoromethanesulfonic acid-catalyzed trimerization of 7-bromo-9,9-diethylfluorene-2-carbonitrile **398** to form triazine derivative **399** in 81% yield, followed by C–N cross-coupling reaction with 9*H*-carbazole **400** to give **401** in 51% yield (Scheme 108). Compound **401** with electron-accepting triazine core bridged by fluorene linked to electron-donating carbazolyl groups showed a high fluorescent activity. The carbazole moiety undergoes dimerization during the electrochemical oxidation producing a polymer film on the electrode surface which exhibits electrochromic behavior.[146]

By analogy, a series of 1,3,5-triazine derivatives peripherally decorated with fluorene ring linked to carbazole **406**, phenoxazine **408** or phenothiazine **410** moieties were designed and synthesized by Liu *et al.*[147]

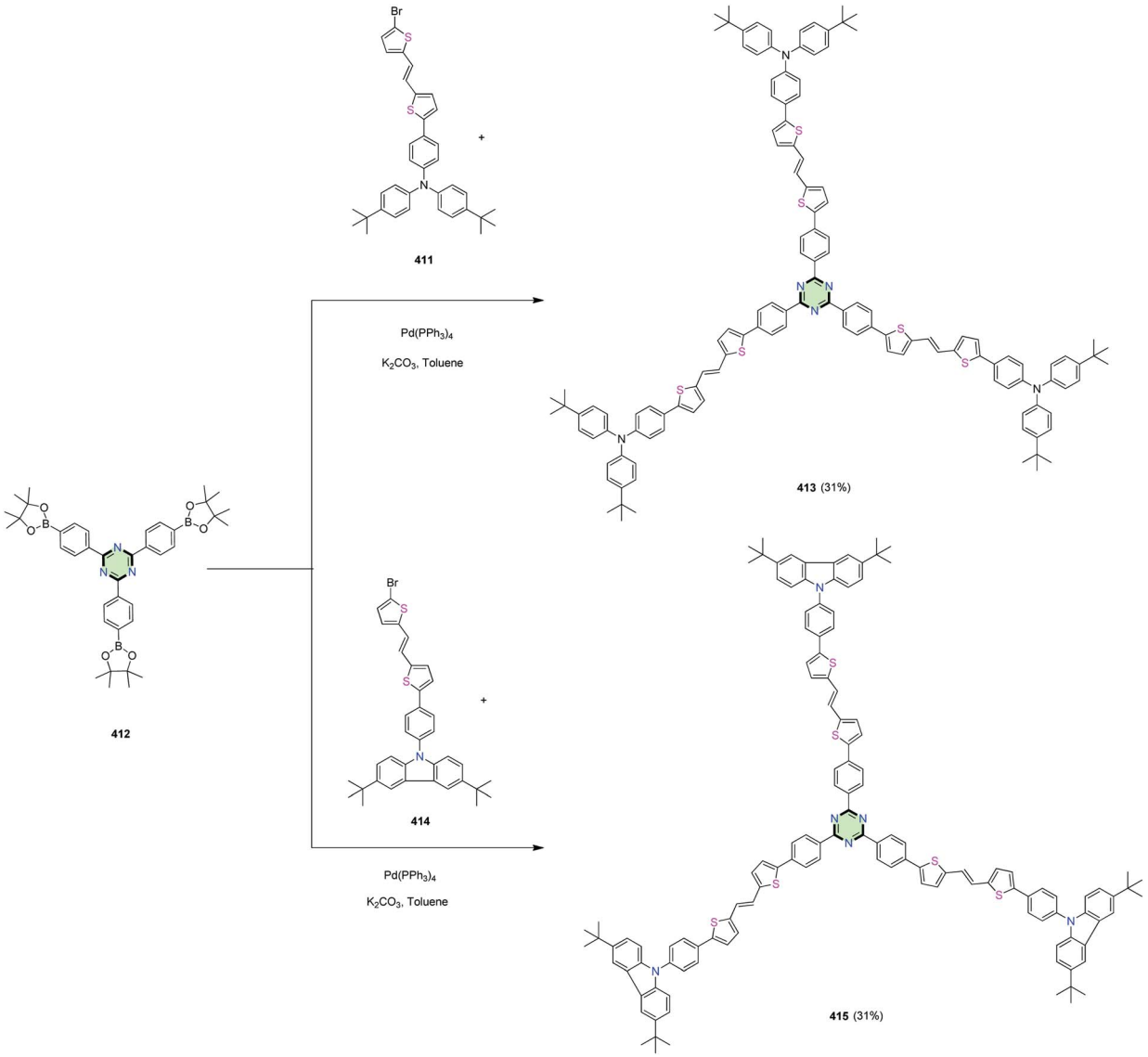
The reactions proceeded *via* initial cyanation of 2-bromo-9,9-dihexyl-7-iodo-9*H*-fluorene **402** upon treatment with CuCN in the presence of Pd catalyst to give 7-bromo-9,9-dihexyl-9*H*-fluorene-2-carbonitrile **403**. Trifluoromethanesulfonic acid-catalyzed trimerization of **403** led to the formation of triazine derivative **404**. Subsequent C–N cross-coupling reaction with the appropriate N-heterocyclic compounds **405**, **407** and **409** yielding SSMs **406**, **408** and **410**, respectively, in good yields (Scheme 109).

The carbazolyl–, phenoxazinyl– and phenothiazinyl–groups were selected as electron-donating substituents, which would not only extend the π-conjugation, but also build the donor–π–acceptor (D–π–A) architectures in the target molecules. Fluorenyl units are commonly used as building blocks in two-photon absorption (TPA) molecules, on which alkyl chains were introduced to reduce the intermolecular aggregation and consequently improve the solubility. In addition, termination by the N-heterocyclic aromatic chromophores, which can rotate around the triazine–fluorene core, may causes aggregation-induced emission (AIE) feature based on the mechanism of restriction of intramolecular rotation (RIR). These compounds exhibit intense fluorescence, AIE and TPA features.

4.3.3.22.2. Di(thiophen-2-yl)ethene linked to triphenylamine or carbazole. 1,3,5-Triazine centered star-shaped molecules with thienylvinylene arms **413** and **415** connected to structurally similar triphenylamine or carbazole end group were



Scheme 109 Synthesis of SSMs with 1,3,5-triazine core with fluorene ring linked to carbazole **406**, phenoxazine **408** and phenothiazine **410**.



Scheme 110 Synthesis of SSMs with thienylvinylene arms connected to triphenylamine **413** or carbazole **415**.

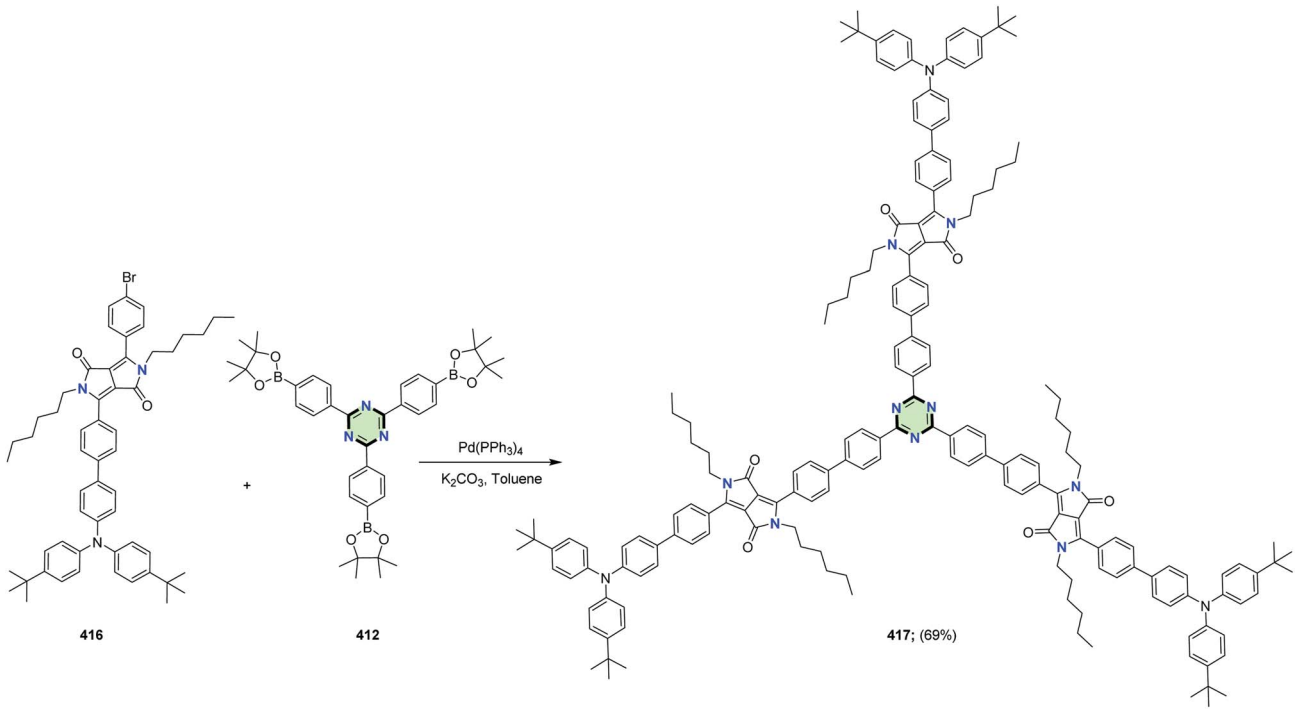
synthesized by Huang *et al.*[148] *via* Suzuki coupling reaction of 2,4,6-tris-boronic acid ester **412** with the appropriate bromo compounds **411** and **414**, respectively, in the presence of $Pd(PPh_3)_4$ (Scheme 110).[148]

4.3.3.22.3. Diketopyrrolo[3,4-c]pyrrole linked to triphenylamine, thiophene and/or carbazole. Shiau *et al.*[149] reported the synthesis of a series of star-shaped molecules with triazine-core **417**, **419** and **421** in 69, 70 and 68% yields, as a donor materials for organic solar cells, through Suzuki coupling reaction of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine **412** with the appropriate bromo derivatives **416**, **418** and **420**, respectively, in the presence of $Pd(PPh_3)_4$ in refluxing toluene (Schemes 111–113).

4.3.4. Miscellaneous heterocyclic-cored SSMs with different arms

4.3.4.1. Thieno[3,2-b]thiophene. Magnan *et al.*[113] reported the synthesis of star shaped molecules **424** and **427** in 63 and 62% yields, respectively, by fourfold Negishi coupling between tetrabromothieno[3,2-*b*]thiophene **422** with each of 2-hexylthiophene **423** and 2-hexylthieno[3,2-*b*]thiophene **426**. Subsequent oxidative cyclodehydrogenation of the latter compounds using anhydrous ferric chloride gave tetra(5-hexylthieno)benzothieno[3,2-*b*]benzothiophene **425** and tetra(5-hexylthieno[3,2-*b*]thieno)benzo thieno[3,2-*b*]benzothiophene **428** in 30 and 53% yield, respectively (Scheme 114).

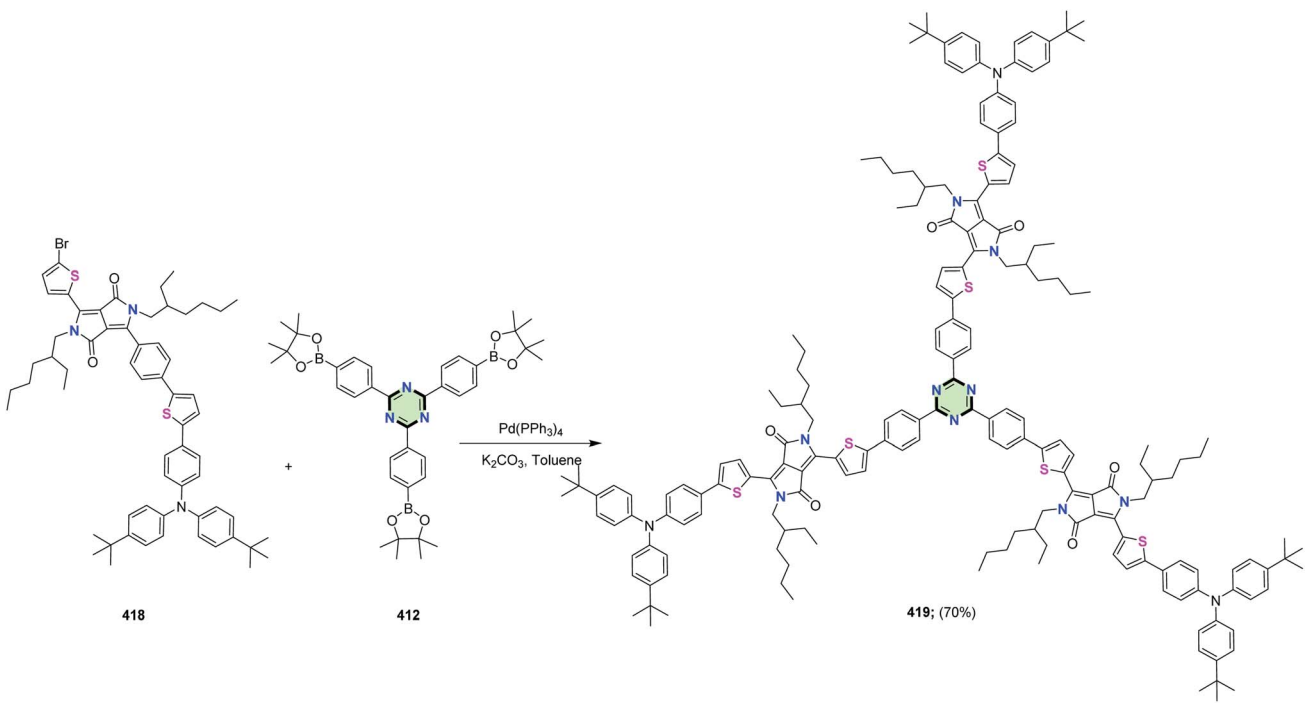
4.3.4.2. Benzo[1,2-b:4,5-b′]dithiophene. Sheng *et al.*[150] reported the synthesis of a star shaped molecule with benzo[1,2-*b*:4,5-*b*′]dithiophene core and terthiophene side arm **431** in good yield, by Stille coupling reaction between tributyl(5,5″-didodecyl-[2,2′:3′,2″-terthiophen]-5′-yl)stannane **430** with the dibromo compound **429** in the presence of $Pd(PPh_3)_4$ (Scheme 115). Compound **431** showed high thermal stability with decomposition temperature (447 °C), low-lying HOMO level



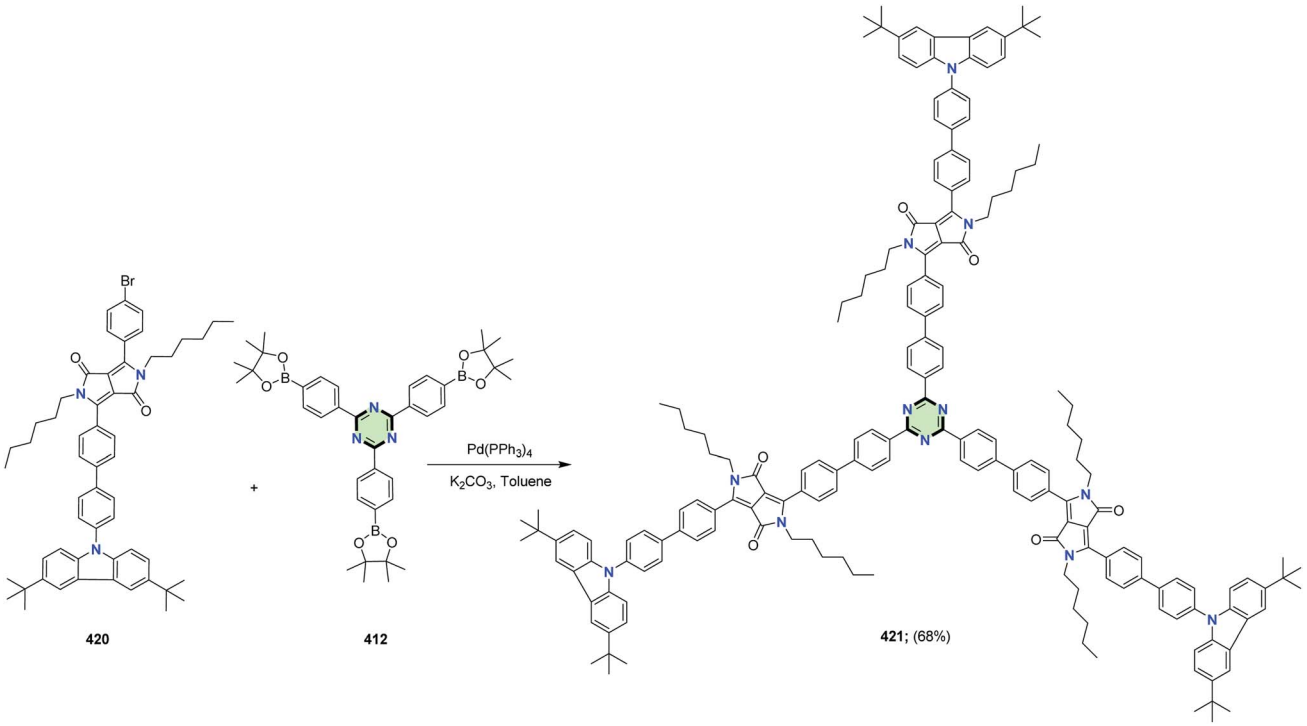
Scheme 111 Synthesis of SSM with triazine-core linked to diketopyrrolo[3,4-*c*]pyrrole and triphenylamine **417**.

(−5.52 eV), and wide UV-vis absorption between 300 and 530 nm (E_g = 2.36 eV).

4.3.4.3. Benzo[1,2-b:4,5-b′]difuran. The Suzuki cross-coupling reaction of 2,3,6-tris(4-bromophenyl)-4,8-didecyl-7-phenylbenzo[1,2-*b*:4,5-*b*′]difuran **432** with 1,3,6,2-dioxazaborocane-4,8-diones **433** afforded different SSMs with benzo[1,2-*b*:4,5-*b*′]difuran core **434a–c** in 37–99% yields (Scheme 116).[151]



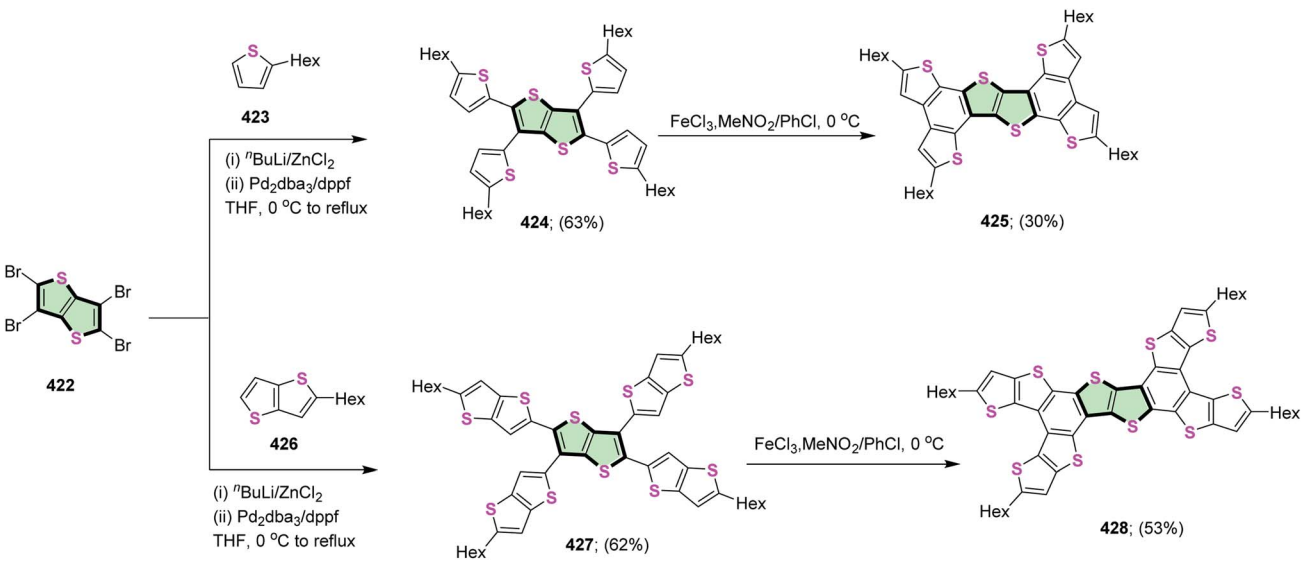
Scheme 112 Synthesis of SSM with triazine-core linked to diketopyrrolo[3,4-*c*]pyrrole and thiophene **419**.



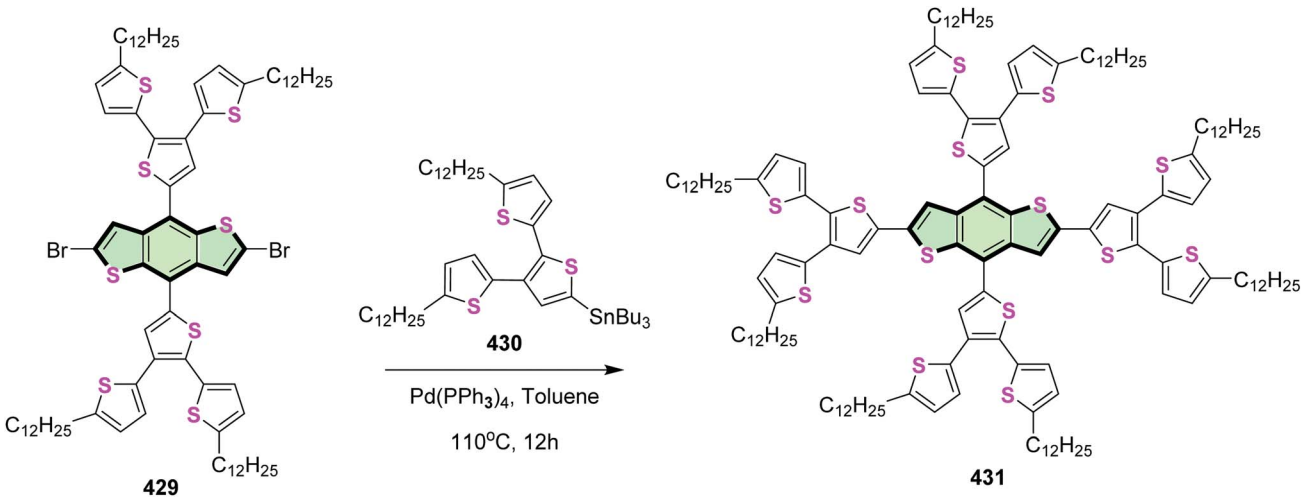
Scheme 113 Synthesis of SSM with triazine-core linked to diketopyrrolo[3,4-*c*]pyrrole and carbazole **421**.

4.3.4.4. 9H-Carbazole. Tribromo compound **436** was obtained *via* the bromination of 9-(4-bromophenyl)-9*H*-carbazole **435** with *n*-bromosuccinimide. Lithiation of **436** followed by treatment with fluorodimesitylborane yielded SSM with carbazole core **437** (Scheme 117). The latter compound showed excellent thermal stability ($T_d = 234$ °C), electrochemical stability and high Φ (0.95) as well as high triplet energy (2.83 eV).[152]

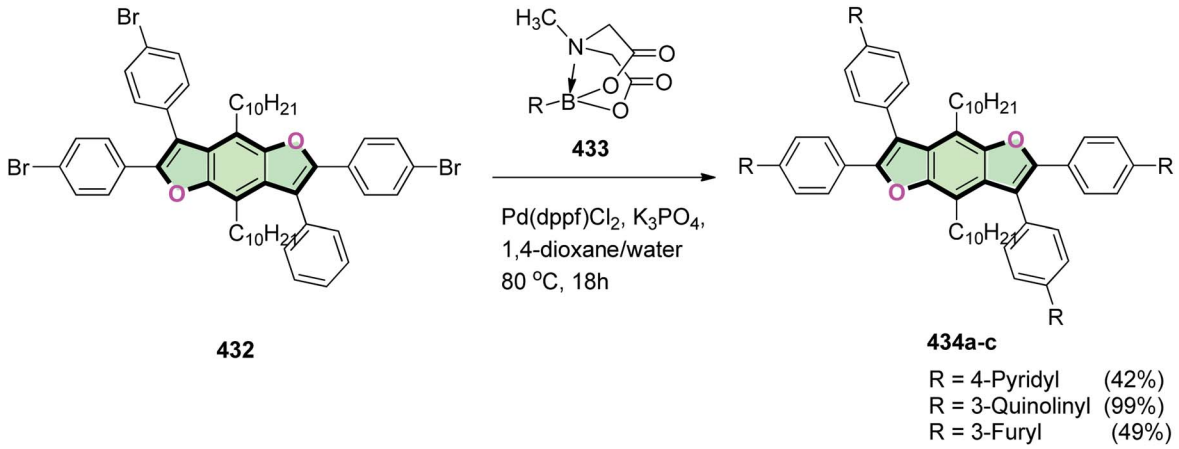
4.3.4.5. Naphthothiophene. Tan *et al.*[153] reported the synthesis of two molecules **440** and **442** having 4,9-di(thiophen-2-yl)naphtho[2,3-*b*]thiophene core and diketopyrrolopyrrole arms **440** and **442** in 62% and 73% yields, respectively. The formation of the latter compounds proceeded through Stille coupling reaction of (5,5′-(6,7-dimethoxy-2-(trimethylstannyl)naphtha[2,3-*b*]thiophene-4,9-diyl)bis(thiophene-5,2-diyl))bis(trimethylstannane) **438** with each



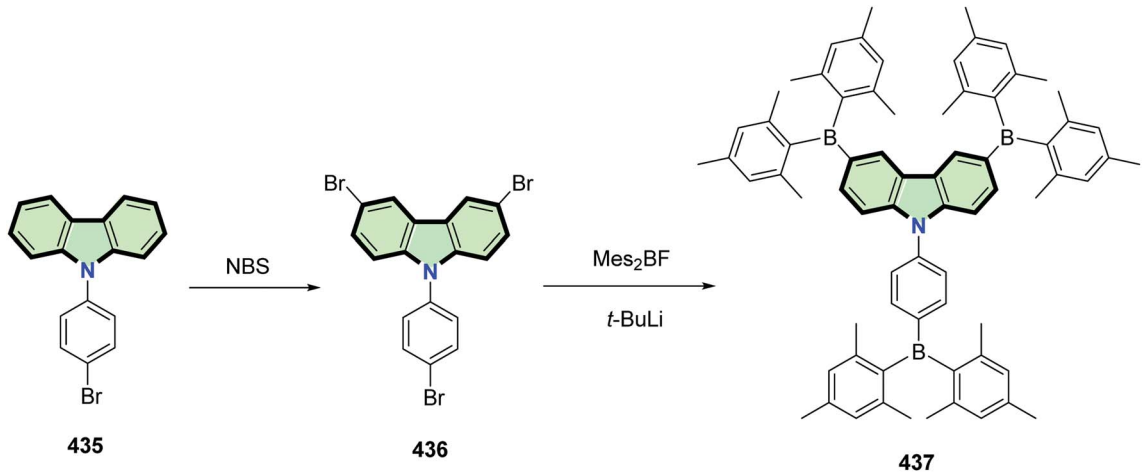
Scheme 114 Synthesis of SSMs **425** and **428** with thieno[3,2-*b*]thiophene core and their oxidized derivatives **425** and **428**.



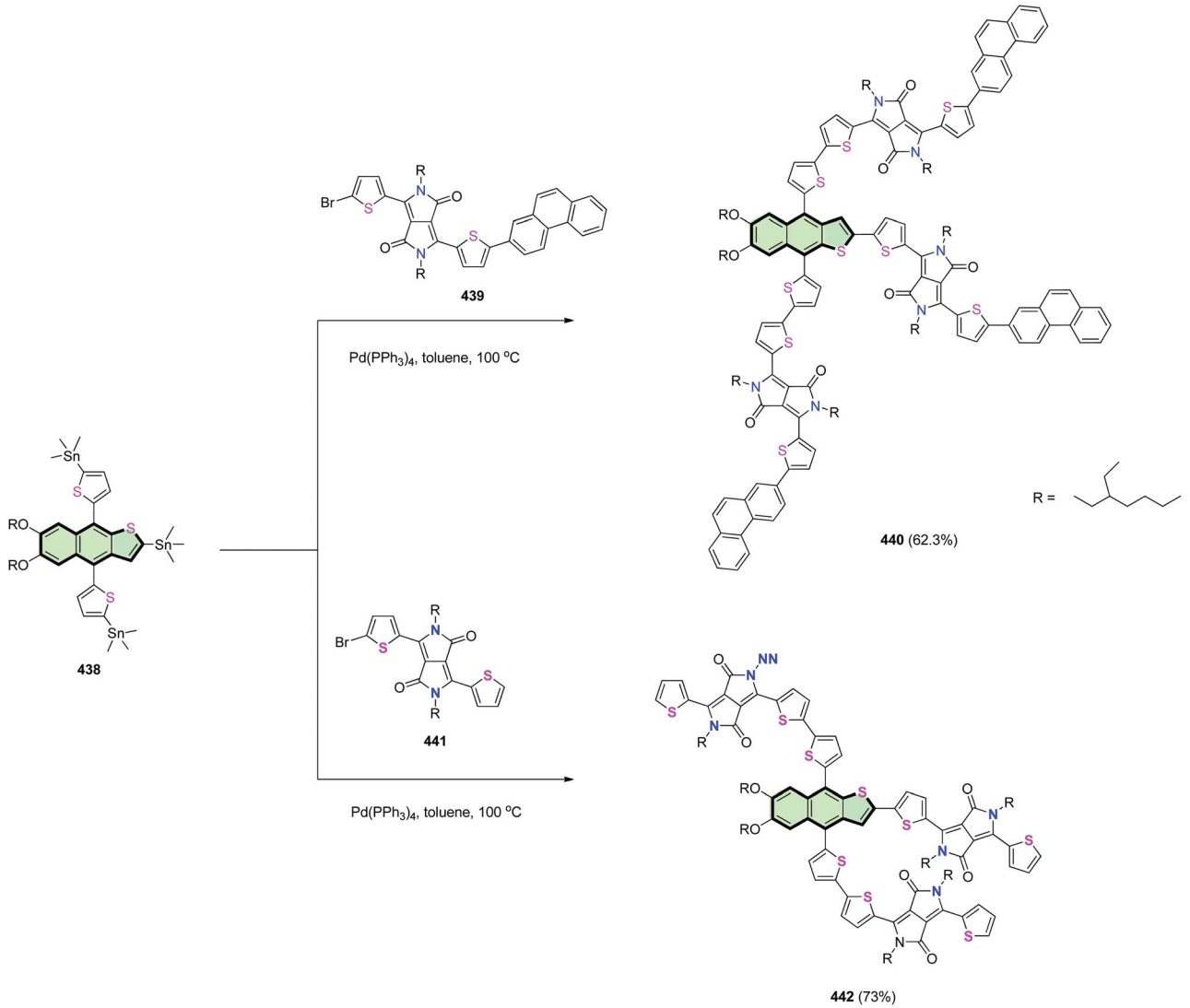
Scheme 115 Synthesis of SSMs with benzo[1,2-*b*:4,5-*b*′]dithiophene core **431**.



Scheme 116 Synthesis of SSMs with benzo[1,2-*b*:4,5-*b*′]difuran core **434a–c**.



Scheme 117 Synthesis of SSM with carbazole core **437**.



Scheme 118 Synthesis of SSMs with naphtho[2,3-*b*]thiophene core **440** and **442**.

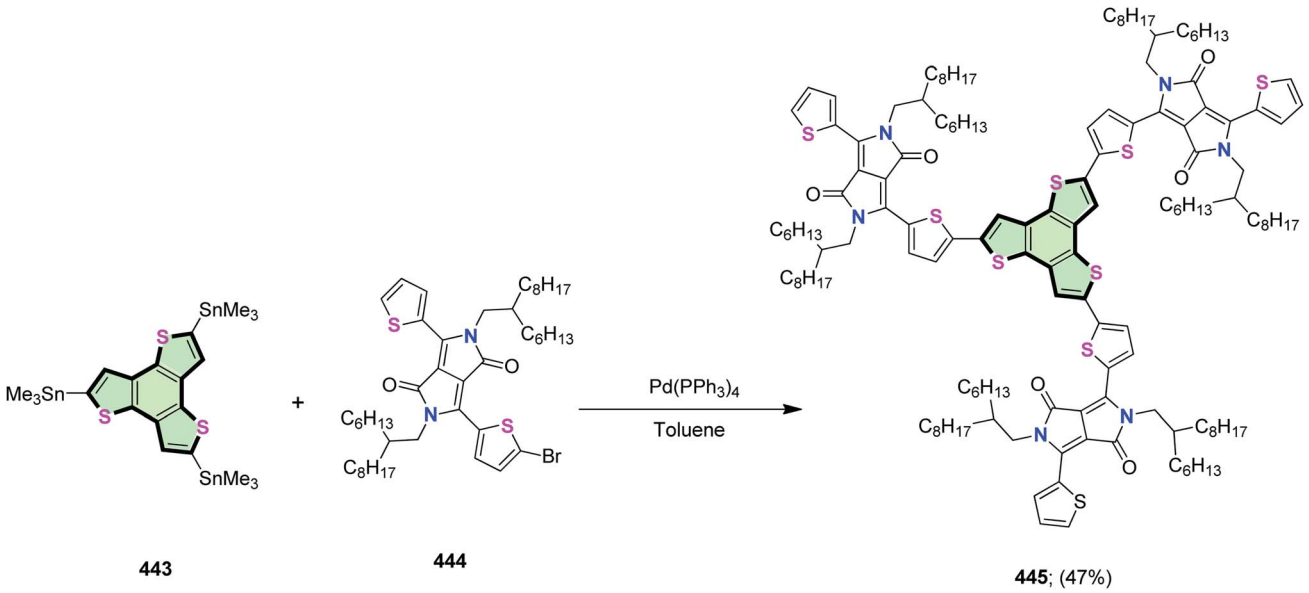
of 3-(5-bromothiophen-2-yl)-6-(5-(phenanthren-2-yl)thiophen-2-yl) pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **439** and 3-(5-bromothiophen-2-yl)-2,5-dimethyl-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **441**, respectively (Scheme 118).[153]

4.3.4.6. Benzo[1,2-b:3,4-b′:4,6-b″]trithiophene. Star-shaped molecule with benzotrithiophene core and diketopyrrolo[3,4-*c*] pyrrole unit arms **445** was synthesized in 47% yield *via* Stille coupling of 2,5,8-tris(trimethylstannyl)benzo[1,2-*b*:3,4-*b*′:5,6-*b*″] trithiophene **443** with bromo(thieophen-2-yl)pyrrolo[3,4-*c*] pyrrole derivative **444** in the presence of $Pd(PPh_3)_4$ (Scheme 119).[20,154]

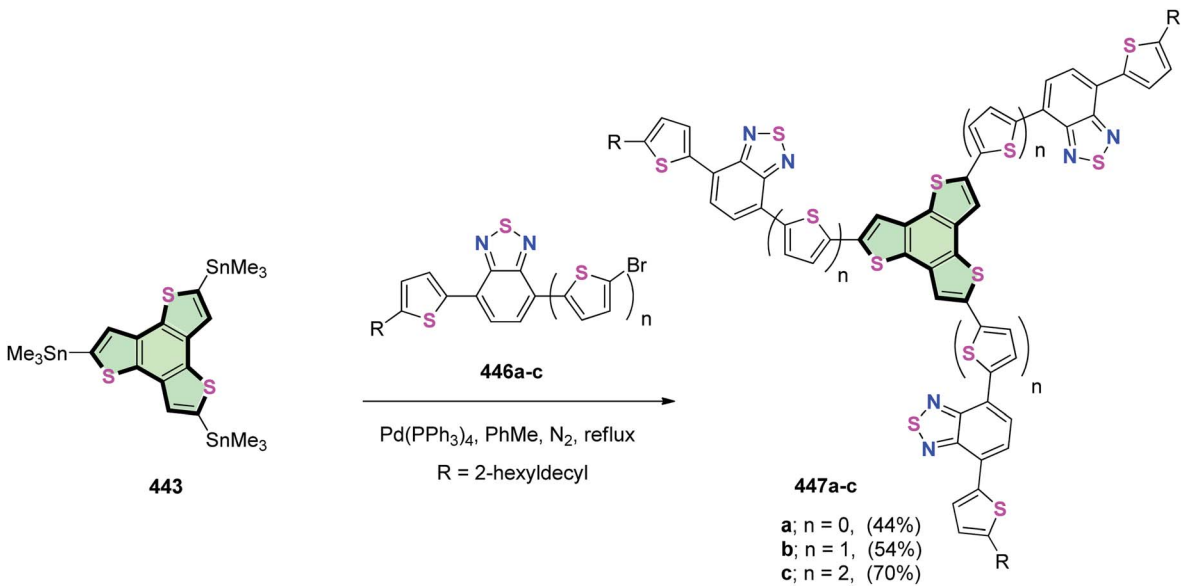
Similarly, Stille coupling of **443** with bromo derivatives **446a–c** afforded SSMs with benzotrithiophene core and (oligo)thiophene-benzo[*c*][1,2,5]thiadiazole-thiophene side arms **447a–c** in good yields (44–70%) (Scheme 120). The star-shaped molecule **447c** with enlarged π-can be delocalization used in photovoltaic applications as increasing the number of thiophene connecting units elevates the HOMO energy level of the based molecule.[155]

4.3.4.7. Benzo[9,1]quinolizino[3,4,5,6,7-defg]acridine. Paek *et al.*[156] managed to synthesize SSM **450** with benzo[9,1]quinolizino[3,4,5,6,7-*defg*]acridine core and trithiophene as a side arm *via* Suzuki coupling of the trithiophene boronic acid **448** with tribromo compound **449** in the presence of $Pd(PPh_3)_4$ (Scheme 121). Compound **450** with π-conjugated bridge undergoes photovoltaic performances in solution-processed organic solar cells OSCs.

Lim *et al.*[157] reported the synthesis of SSM **453** which contain benzo[9,1]quinolizino[3,4,5,6,7-*defg*]acridine core and 4-(silylene-2,2′-bithiophen-5-yl)-7-(2,2′,2‴-terthiophen-5-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridine as a side arm *via* Stille coupling reaction of bromo compound **451** with 4,4,8,8,12,12-hexamethyl-2,6,10-tris(trimethylstannyl)-8,12-dihydro-4*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine **452** (Scheme 122). This star-shaped molecule has optical and



Scheme 119 Synthesis of SSM with benzotrithiophene core **445**.



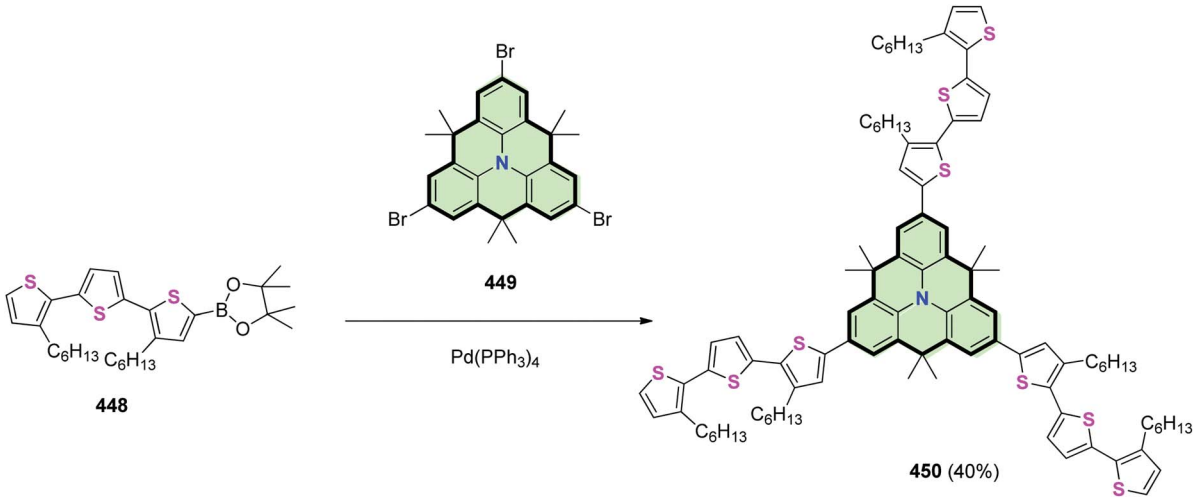
Scheme 120 Synthesis of SSMs with benzotrithiophene core **447**.

electrochemical properties and can be used as donor components in solution-processed organic solar cells.

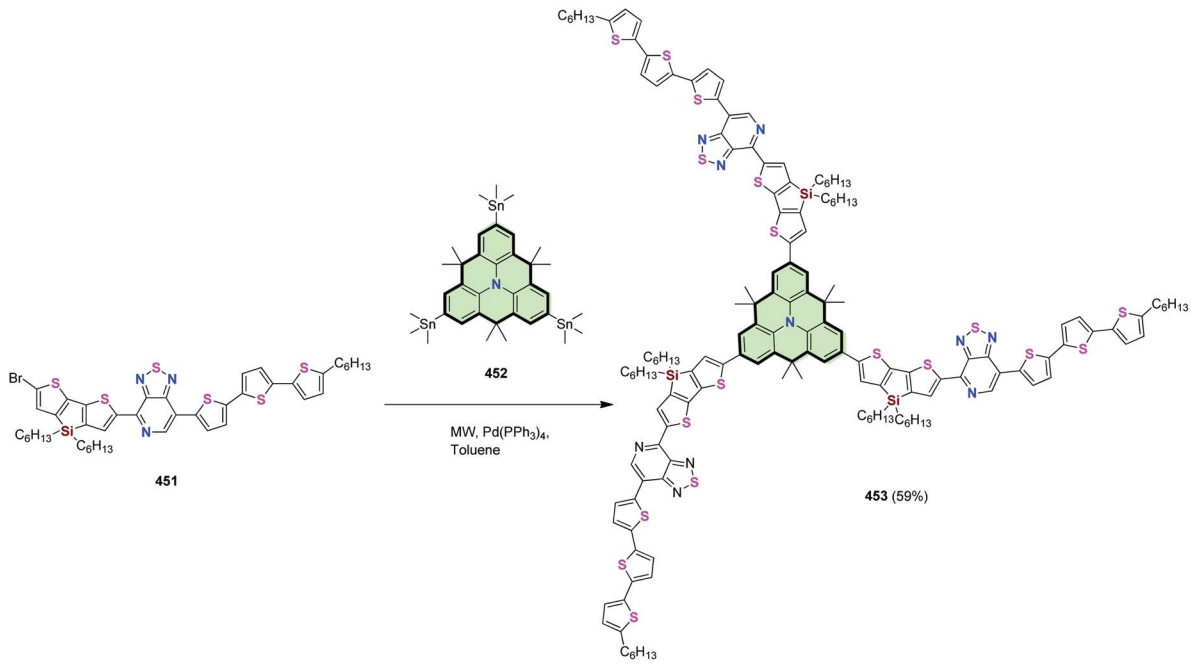
4.3.4.8. Diindolo[3,2-a:3′,2′-c]carbazole. SSMs **456** and **458** with diindolo[3,2-*a*:3′,2′-*c*]carbazole core were synthesized in 85% and 84% yields by Shao *et al.*[158] *via* the Horner–Wadsworth–Emmons reaction of the trialdehyde **454** with phosphonate esters **455** and **457**, respectively (Scheme 123).

2,2′,2″-((5,5′,5″-((5,10,15-Tridodecyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3′,2′-*c*]carbazole-3,8,13-triyl)tris(ethene-2,1-diyl))tris(thiophene-5,2-diyl))tris(ethene-2,1-diyl))tris(benzo[*d*]thiazole) **462** was synthesized in 82% yield by Shao *et al.*[158] *via* the Horner–Wadsworth–Emmons reaction of the tris(thiophene-2-carbaldehyde) **460** with diethyl (benzo[*d*]thiazol-2-ylmethyl) phosphonate **461**. The trialdehyde **460** was obtained in 93% yield by formylation of tris(-2-(thiophen-2-yl)vinyl)-10,15-dihydro-5*H*-diindolo[3,2-*a*:3′,2′-*c*]carbazole **459** upon treatement with $POCl_3$ in DMF (Scheme 124). Compound **462** showed good thermal and photo stabilities. It can be used as chromophore with significant bathochromic shift of the emission spectra together with a larger Stokes shift in polar solvents due to intramolecular charge transfer.

Lu *et al.*[159] reported the synthesis of triindole-cored star-shaped molecules **465** in 70% yield by heating a mixture of



Scheme 121 Synthesis of SSM **450** with benzo[9,1]quinolizino[3,4,5,6,7-*defg*]acridine core.

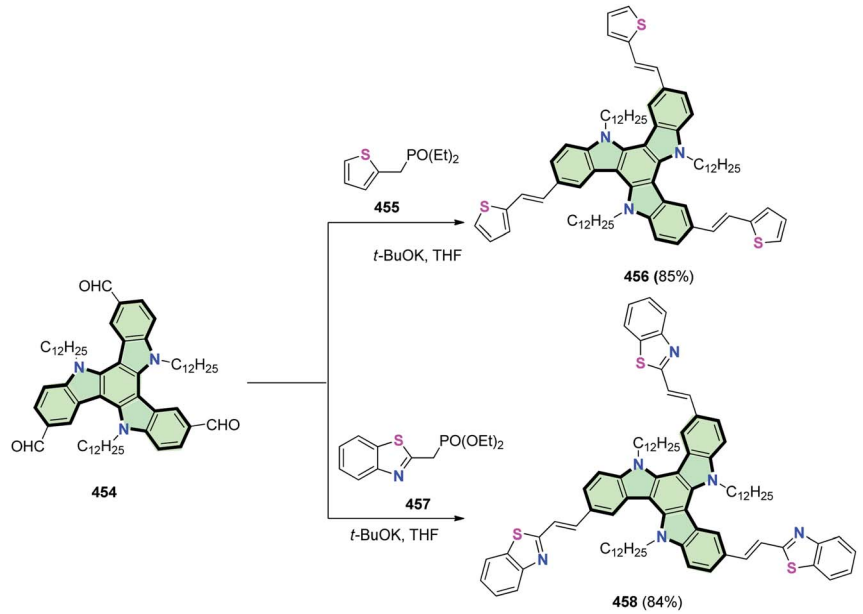


Scheme 122 Synthesis of SSM **453** with benzo[9,1]quinolizino[3,4,5,6,7-*defg*]acridine core.

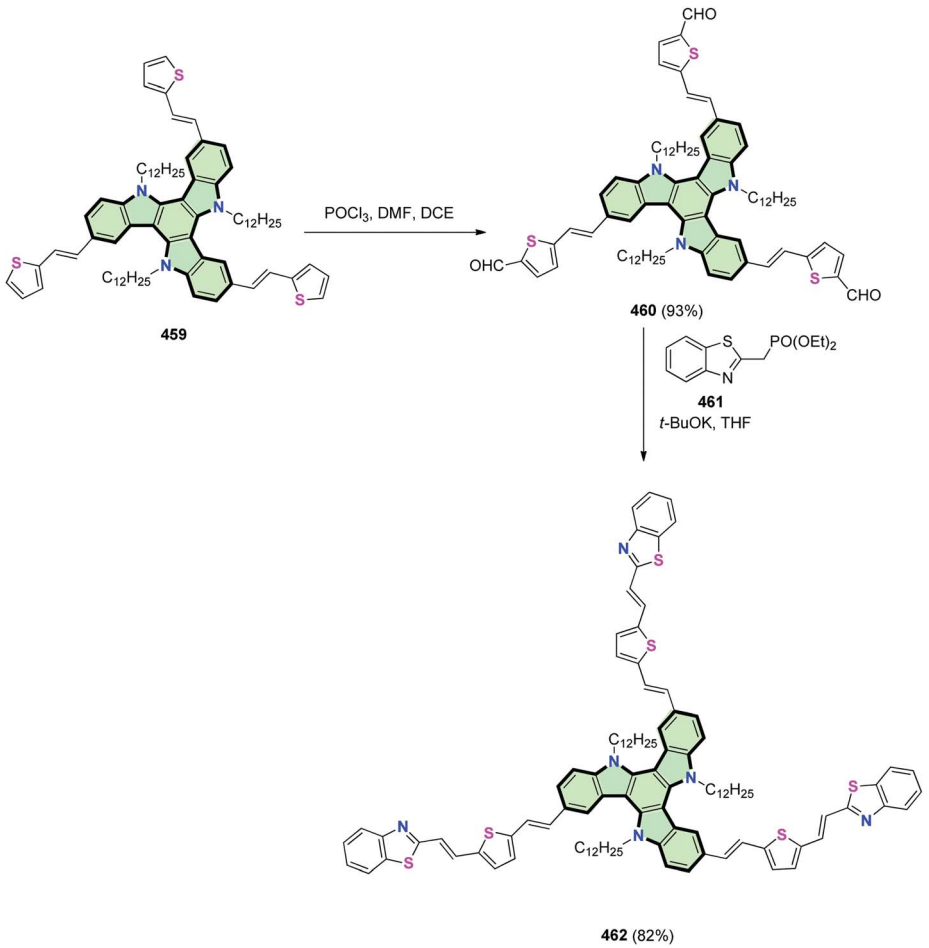
5,10,15-trihexyltriindole-2,7,12-triboronic ester **463** and 5-(5-bromothiophen-2-yl)thiophene-2-carbaldehyde **464** in the presence of K_2CO_3 and $Pd(PPh_3)$. On the other hand, heating compound **463** with 4-(5-(4-(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-7-yl)-thiophen-2-yl)-*N*,*N*-diphenylbenzenamine **466** in the presence of Bu_4NBr and $Pd(PPh_3)_4$ at reflux afforded triindole-cored star-shaped compound **467** in 75% yield. The two star-shaped molecules **465** and **467** showed good thermal stability, intensive absorption in a broad region, relatively high hole mobility and high efficiency as organic solar cells (Scheme 125).

4.3.4.9. Anthra[1,2-b:4,3-b′:5,6-b″:8,7-b‴]tetrathiophene. Komiyama *et al.*[160] reported the synthesis of a star shaped molecule **470** in 44% yield by the reaction of 2,5,9,12-tetrabromoanthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene **468** with stannyl(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole derivative **469** in dry DMF and in the presence of $Pd(PPh_3)_4$ (Scheme 126).

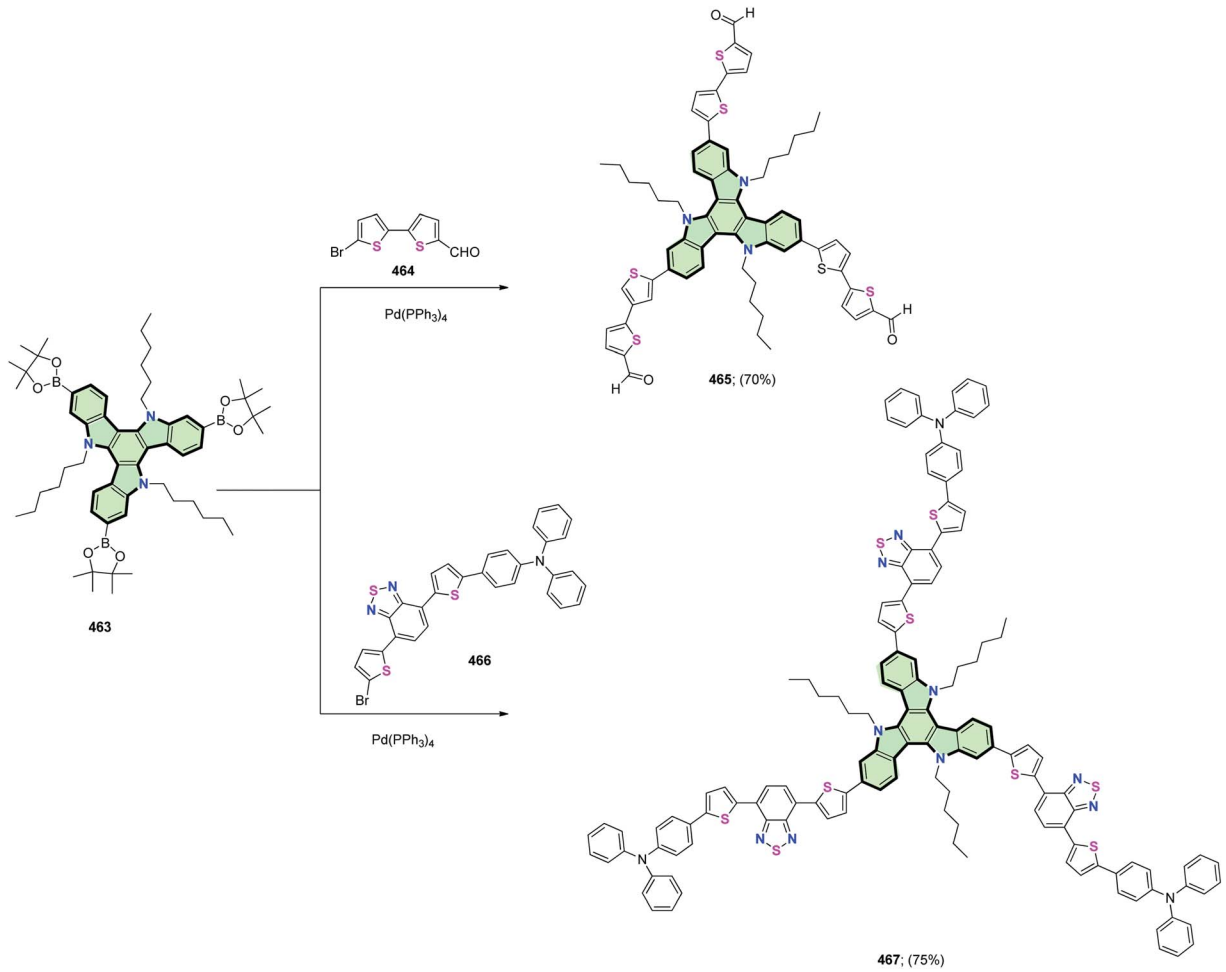
4.3.4.10. Diquinoxalino[2,3-a:2′,3′-c]phenazine. Zhao *et al.*[161] reported the synthesis of SSM **473** containing hexaazatriphenylene cored fused with perylene-3,4,9,10-tetracarboxylic acid bisimides, as conjugated n-type semi-



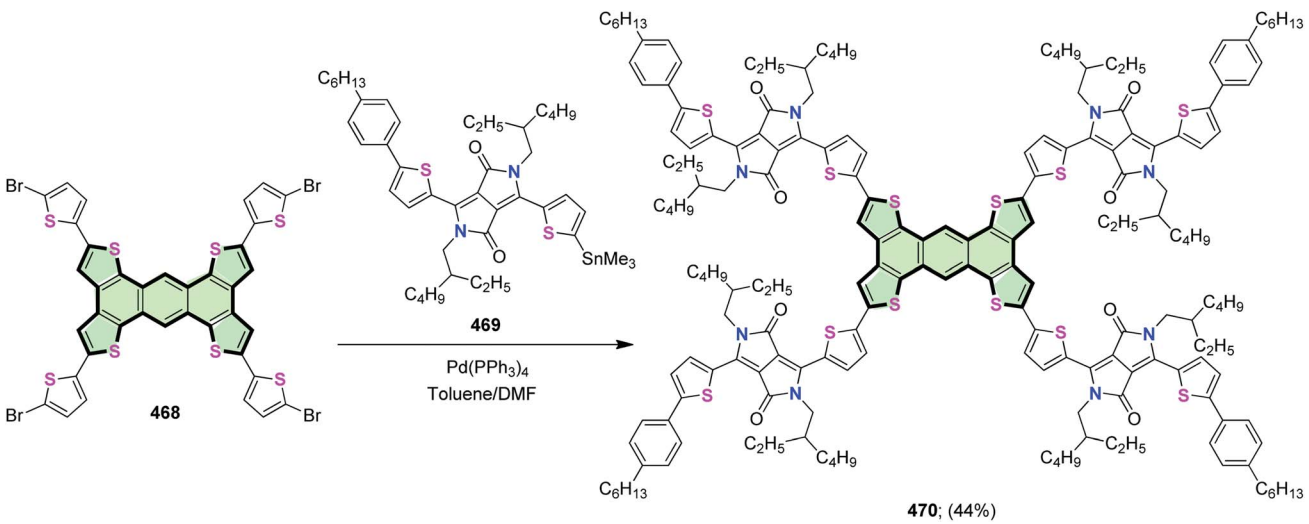
Scheme 123 Synthesis of SSMs **456** and **458** with diindolo[3,2-*a*:3′,2′-*c*]carbazole core.



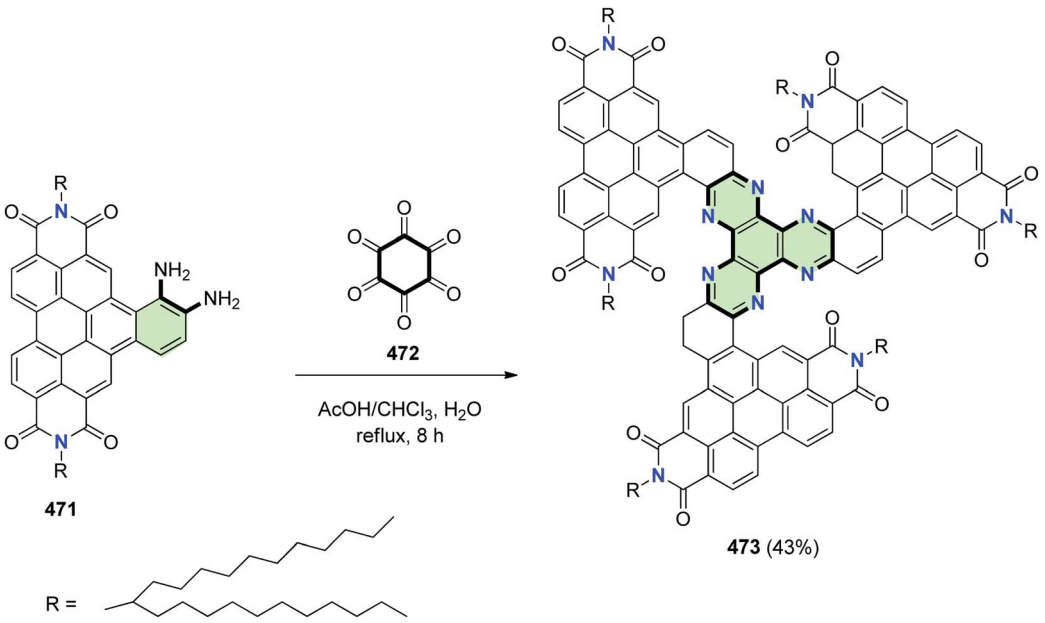
Scheme 124 Synthesis of SSM **462** with diindolo[3,2-*a*:3′,2′-*c*]carbazole core.



Scheme 125 Synthesis of triindole-cored star-shaped molecules **465** and **467**.



Scheme 126 Synthesis of SSM **470** with anthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene core.



Scheme 127 Synthesis of SSM **473** with hexaazatriphenylene core.

conductor in 43% yield by fusion of 9,10-diaminonaphtho[1,2,3,4-*ghi*]perylene **471** with cyclohexane-1,2,3,4,5,6-hexaone **472** (Scheme 127).

5. Conclusions

This review gives an overview of the new developments over the last decades in the synthesis of star-shaped molecules especially those containing heterocyclic core and/or heterocyclic arms. The physical properties of these compounds are markedly different to their linear analogues. These molecules are considered as versatile building blocks for the formation of liquid crystals, dendrimers as well supramolecular host–guest compounds. Their applications in organic solar cells OSCs and as promising candidates for organic semiconducting materials are recently studied. The star-shaped molecules mentioned in this review are arranged in an organized manner with respect to the type of the core as well as the side arms.

The methods described for the synthesis of such compounds includes a variety of synthetic methodologies, among which the *O*-, *S*- and *N*-alkylation, condensation and cyclocondensation, cyclotrimerization reactions, and palladium-catalyzed C–C and C–N bond formation *via* Heck, Negishi, Sonogashira, Stille and Suzuki cross-coupling reactions seem to be the most interesting strategies.

From a synthetic chemist's perspective, it is extremely challenges to develop new strategies to synthesize novel structures of these molecules.

We hope that this review will be useful not only for organic synthetic chemists, but also for Physicists as well as for those who are interested in the field of industrial applications.

Conflicts of interest

There are no conflicts to declare.

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