Synthesis of C_3-Symmetric Nano-Sized Polyaromatic Compounds by Trimerization and Suzuki−Miyaura Cross-Coupling Reactions

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Various C_3-symmetric molecules were prepared by trimerization of acetyl aromatic compounds and subsequently coupled with various boronic acids under Pd^0 catalysis conditions to generate oligoaryl/-heteroaryl C_3-symmetric molecules. Several furan- and thiophene-containing star-shaped molecules were prepared by the use of Suzuki–Miyaura cross-coupling as a key step. Structural and conformational details were explored by semi-empirical molecular orbital theory using the AM1 method.

Introduction

Symmetrical starting materials are useful building blocks for designing complex target molecules, and synthetic chemists might reap enormous rewards by paying attention to symmetry in this regard.[1] Structural symmetry in the target molecule can easily be exploited to reduce the length of synthetic sequences. The classical, one-directional convergent synthetic approach is most frequently found in the literature, but an alternative strategy based on two-directional syntheses involving sequential or simultaneous homologation is a powerful tool for the efficient construction of a large number of natural products. While symmetrical substances are readily constructed from intermediates of high symmetry, the synthesis of unsymmetrical molecules may also be achieved by employing symmetrical precursors and vice versa.[2] Symmetrical molecules can also be used as central cores for the design of dendrimeric frameworks with increased diversity, and higher levels of structural order in the globular morphology of dendrimers are indeed an attractive feature.[3] Interestingly, several applications of dendrimers in the forms of chemical sensors, optical switches, etc., are believed to be dependent on higher order as well as on the possibility of controllable conformations. In this regard, conformational control has often been a challenge in most commonly reported dendrimers, primarily because of the presence of groups such as methylene linkages.[4] Here we have employed the restricted rotation around biphenyl units as a tool with which to achieve better control over the conformational mobility.[5]

Before elaboration on the synthesis of C_3-symmetric molecules, it is best to discuss some applications of C_3-symmetrical compounds in diverse areas of chemistry. Miller and co-workers reported the synthesis of mono-dispersed 1,3,5-phenylene-based hydrocarbon dendrimers **1** (Figure 1) with molecular diameters of 15−31 Å and up to 46 benzene rings.[6] The luminescent star-shaped molecule 1,3,5-tris[*p*-(2,2′-bipyridylamino)phenyl]benzene (**2**) was synthesized in order to study fluorescent properties by coordination with zinc chloride.[7] In another investigation, compound **3** was prepared in order to study its electron-transfer properties in complexation with ruthenium and osmium metals.[8] Some of the 2,4,6-trisubstituted-1,3,5-triazine derivatives behave as liquid crystalline materials and find useful applications in coordination chemistry and crystal engineering.[9,10] Symmetric tetrathiafulvalene system **4** has been prepared in order to examine the interactions of tetrathiafulvalene radical cations and was used as a neutral donor in measurement of the electrolytic conductivity of charge-transfer complexes.[11] Shirota and co-workers reported the synthesis of 1,3,5-tris[5-(dimesitylboryl)thiophen-2-yl]benzene (**5**), useful in designing organic electroluminescent devices,[12] Tour and co-workers have synthesized symmetrical conjugated oligo(phenylene ethynylene)s used for various three-dimensional molecular wires and devices,[13] and the symmetrical 1,3,5-triphenylbenzene core has also been used in syntheses of dendritic chromophores[14] and hyperbranched conjugated molecules.[15] Since the applications of C_3-symmetric compounds are increasing at an accelerating rate in several areas of chemical sciences, there is a great need to develop simplified methods for their synthesis.

In view of the applications of C_3-symmetric molecules described above, we sought a general and simple methodology for the synthesis of various C_3-symmetric aromatics through the employment of readily available starting materials. Our strategy relies on the use of acid-catalyzed trimer-

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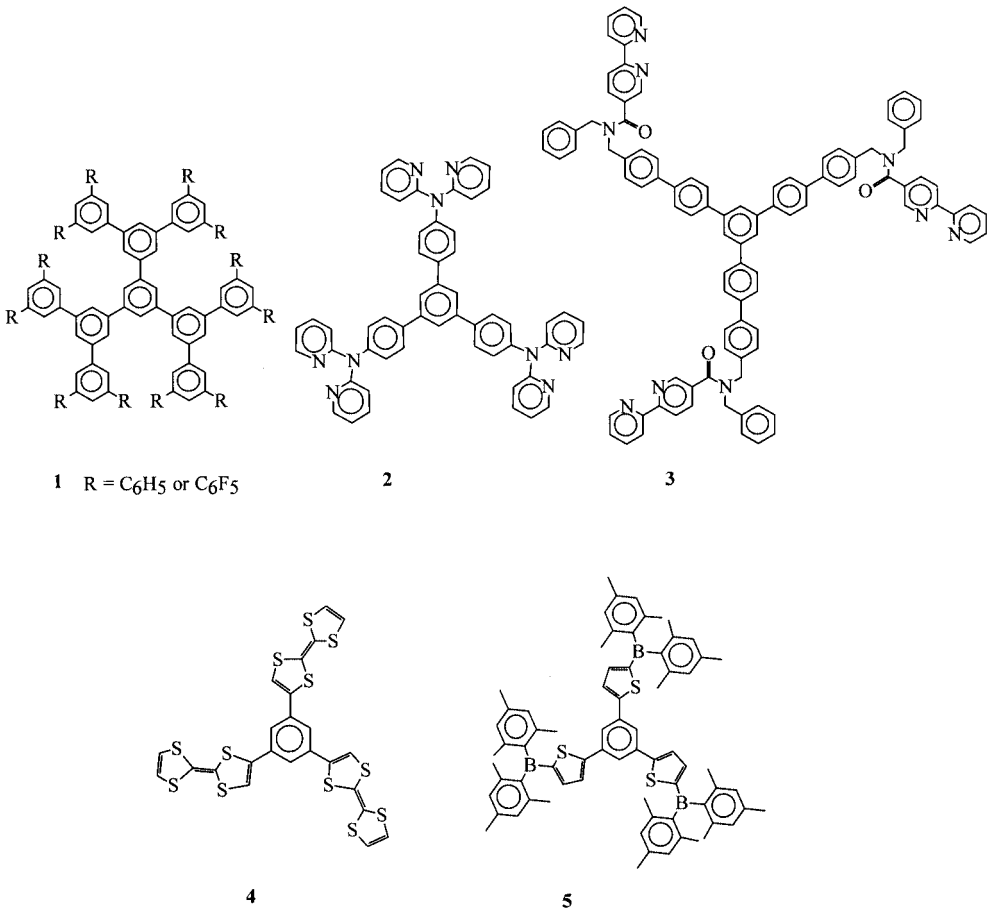


Figure 1. Various recently reported useful C_3-symmetric molecules

ization and Suzuki−Miyaura (SM) cross-coupling reactions[16] as key steps (Figure 2).

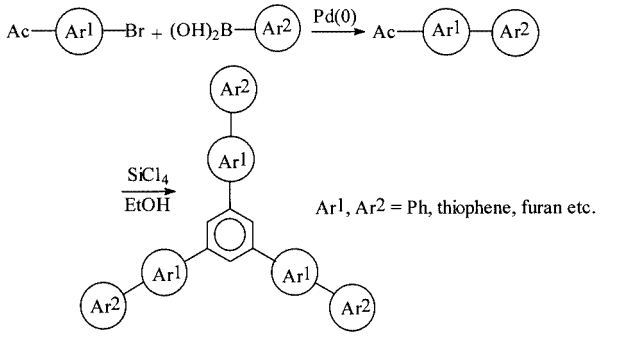
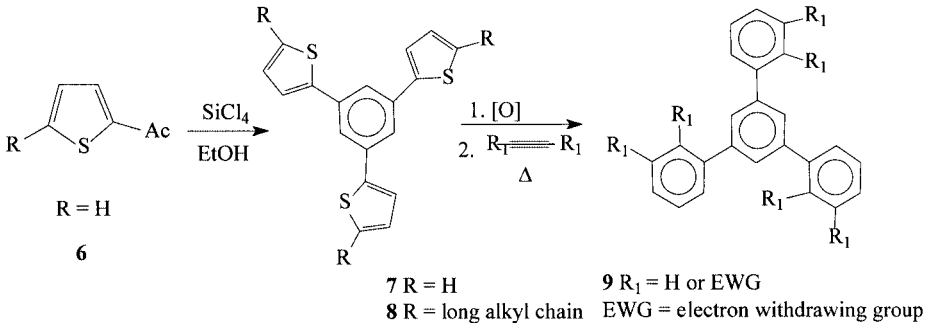


Figure 2. Our strategy for C_3-symmetric molecules by the SM cross-coupling and acid-catalyzed trimerization sequence

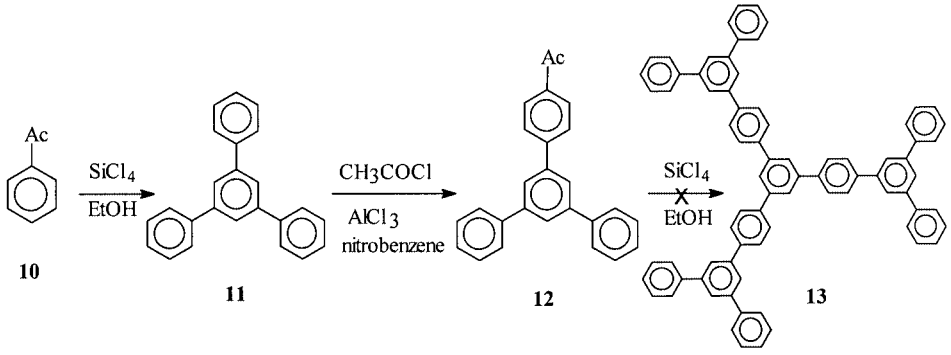
It is generally known that trimerization involving bulky substrates is not a trivial task. To address the problems associated with the sterically demanding systems, we intended to use a combination of trimerization and the SM cross-coupling reaction. Some of the C_3-symmetric building blocks prepared by this methodology can be further manipulated to provide a variety of otherwise poorly accessible C_3-symmetric derivatives such as dendrimers and fullerene fragments.[17,18] Oxidation of **7** followed by a Diels−Alder reaction with an appropriately substituted acetylenic dienophile, for example, would be expected to deliver the otherwise poorly accessible 1,3,5-triphenylbenzene derivatives (e.g., **9**, Scheme 1). Raney nickel desulfurization of the thiophene derivative **8** would provide C_3-symmetric compounds possessing long alkyl chains suitable for liquid crystalline materials. On the other hand compound **8** (R = CH_3) is also an attractive starting material for the synthesis of C_3-symmetric amino acid derivatives.

Results and Discussion

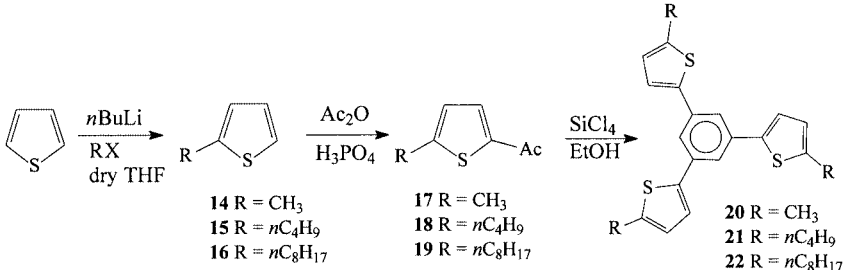
Our initial objective was to accomplish the trimerization reaction with several acetylated aromatic systems to generate C_3-symmetric oligo-aryl dendrimers. Towards this end, trimerization of acetophenone **10** by treatment with $SiCl_4$ in ethanol was attempted, and furnished the compound **11** in 86% yield.[19a] Friedel−Crafts acylation of **11** with acetyl chloride and anhydrous aluminium chloride in nitrobenzene yielded the acetylated product **12**, which on further treatment with $SiCl_4$ in ethanol failed to give the trimerized product **13** (Scheme 2). Aspects concerning the solubility of the oligomers were our major concern at each stage of the dendrimer synthesis, the solubility of the starting ketone



Scheme 1



Scheme 2



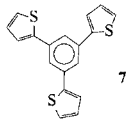
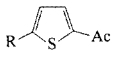
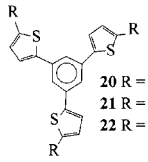
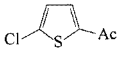
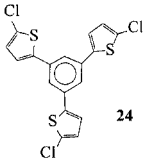
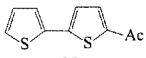
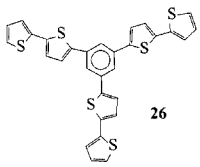
Scheme 3

being crucial for the success of the trimerization reaction. Even the acetylated derivative **12** is insoluble in ethanol at room temp. To circumvent this problem we decided to use acetylated heterocyclic molecules as a starting materials, as solubility aspects may be dealt with here thanks to the presence of the heteroatoms. In this context, $SiCl_4$-mediated trimerization of 2-acetylfuran was attempted, and it was found that a complex mixture of products was obtained.[20] In view of the facile ring-opening reactions of furan moieties under acidic conditions, this result was not surprising. Since substituted thiophenes are valuable building blocks in electronic devices and also enjoy potential applications in the flavor and pharmaceutical industries,[21,22] the trimerization of 2-acetylthiophene **6** was attempted. Treatment of **6** with $SiCl_4$ at room temp. gave compound **7** in 42% yield after column chromatography.[23] It is worth mentioning that earlier attempts to trimerize 2-acetylthiophene by treatment with Nafion-H had given no condensation product.[24a] Moreover, compounds of type **7** were also prepared by an independent strategy.[24b]

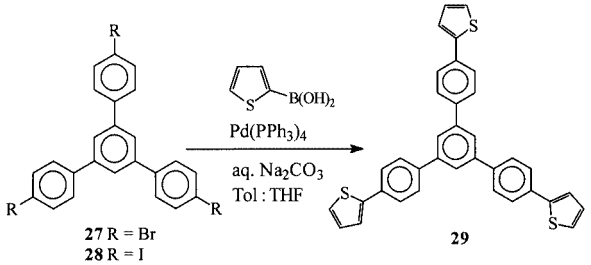
To generalize the trimerization reaction with other thiophene-related systems, various acetylated thiophene derivatives (**17**−**19**) were prepared by the alkylation[25a] and acetylation[25b] sequence (Scheme 3). Because of the volatile natures of the alkylated thiophene derivatives (**14**−**16**) they were used in subsequent reactions without additional purification. Treatment of the acetylated thiophene derivatives (**17**−**19**) with $SiCl_4$ gave the trimerized compounds (**20**−**22**). The formation of the C_3-symmetric trimerized products **20**−**22** was confirmed by ^1H and ^{13}C NMR. Similarly, 2-acetyl-5-chlorothiophene **23** and acetylated bithiophene[26,27] **25** were also treated with $SiCl_4$ in ethanol to

deliver the trimerized compounds **24** (60%) and **26** (26%) respectively. The trimerization results for various acetyl thiophene derivatives are included in Table 1.

Table 1. List of C_3-symmetric thiophene derivatives prepared by trimerization

S. No.	Substrate	Trimerized Product	$SiCl_4$(equiv)/ Time (h)	Yield %
1	 **6**	 **7**	2/6	42
2	 **17** R = CH_3 **18** R = nC_4H_9 **19** R = nC_8H_{17}	 **20** R = CH_3 **21** R = nC_4H_9 **22** R = nC_8H_{17}	6/4 6/18 6/24	61 72 63
3	 **23**	 **24**	4/12	60
4	 **25**	 **26**	15/4	26

Having generalized the trimerization reaction with various acetylated thiophene derivatives, we next turned our attention towards the preparation of mixed heterocyclic/polyaromatic C_3-symmetric derivatives by use of trimerization and the SM cross-coupling as key steps. To this end we prepared 1,3,5-tris(4-bromophenyl)benzene (**27**) and 1,3,5-tris(4-iodophenyl)benzene (**28**) from 4-bromoacetophenone and 4-iodoacetophenone, respectively, by the $SiCl_4$-mediated trimerization reaction.[19a] Next, we tried palladium-mediated SM cross-coupling of thiophene-2-boronic acid with the tribromo derivative **27**, and the coupled product **29** was obtained in 14% yield. During the preparation of **29**, we also isolated mono- and difunctional derivatives in 13% and 67% yields. Since iodo aromatics are better partners in SM cross-coupling reaction, we tried the above reaction on compound **28** and, as expected, an improved yield (60%) was obtained (Scheme 4).



Scheme 4

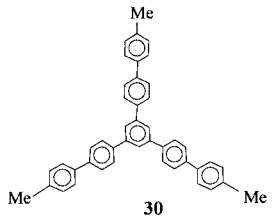
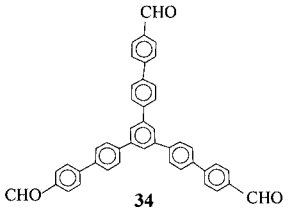
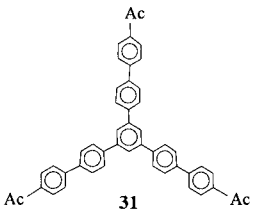
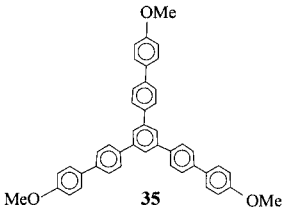
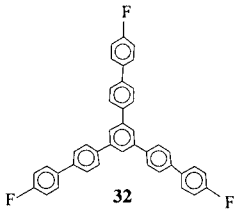
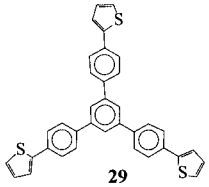
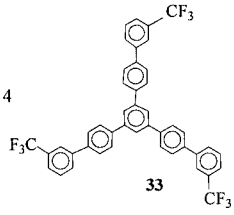
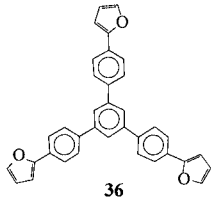
Later on, SM cross-coupling of compound **28** was attempted with other arylboronic acids [4-methylphenylboronic acid, 4-acetylphenylboronic acid, 4-fluorophenylboronic acid, 3-trifluoromethylphenylboronic acid, 4-formylphenylboronic acid, 4-methoxyphenylboronic acid and heterocyclic boronic acids (thiophene-2-boronic acid, furan-2-boronic acid)] and $(PPh_3)_4Pd$ catalyst, and the results are included in Table 2. Shirota and co-workers have recently also reported the synthesis of compound **32**.[28] Typically, 47−75% yields of the coupling products were obtained. All the coupling products were characterized by their spectroscopic data.

It is worth noting that we also considered the preparation of **29** and **37**, with thiophene units present either in the outer or in the inner core of these star-shaped molecules, by an alternative route: SM cross-coupling followed by trimerization (Scheme 5). Retrosynthetic analysis identifies **38** and **39** as possible precursors for the synthesis of **29** and **37**. Recently, Hiyama et al. prepared compound **38** by palladium-catalyzed cross-coupling of organosilicon compounds.[29a,29b] However, we have adapted Pd-catalyzed SM cross-coupling of thiopheneboronic acid and 4-bromoacetophenone to obtain **38** in 92% yield. Along similar lines, coupling of 2-acetyl-5-bromothiophene and phenylboronic acid gave compound **39** in 88% yield. The preparation of **39** through palladium-catalyzed coupling of aryl halides was also recently reported.[29c] Compounds **38** and **39** gave the trimerized compounds **29** and **37**, respectively, on treatment with $SiCl_4$. The structures of the trimerized compounds **29** and **37** have been established by ^1H and ^{13}C NMR spectroscopic data. This idea was next extended to furan derivatives; triiodobenzene[30] (**40**), prepared by known procedures, was treated with furanboronic acid under SM cross-coupling conditions to give compound **41** (66%) (Scheme 6).

Having successfully developed synthetic strategies for the C_3-symmetric polyaromatic molecules, we turned our attention to structural and conformational features of these molecules. One of the broad objectives of our study is to design molecular entities of desired shape and size. Molecular diameter in conjunction with conformational flexibility is a useful parameter with which to identify the propensities of molecules towards spherical shapes. In order to unravel the key structural features of these polyaromatics, we performed standard semi-empirical calculations by use of an AM1 Hamiltonian.[31]

Computational studies provided useful insights into the conformations of these molecules. Geometry optimizations of the compounds listed in Table 2 revealed interesting structural features. Except for furan and thiophene systems (**29** and **36**), the inter-ring torsional angles between the central trisubstituted aryl rings and the adjacent aryl rings were consistently found to be around 41 degrees. Similarly, the torsional angles between second and third rings were found to be around 40 degrees. The inter-ring torsional angles between the second aryl rings and the thiophene rings were found to be lower than all other systems by 17 degrees (Table 3).

Table 2. List of the C_3-symmetric derivatives obtained by SM cross-coupling of compound **28**

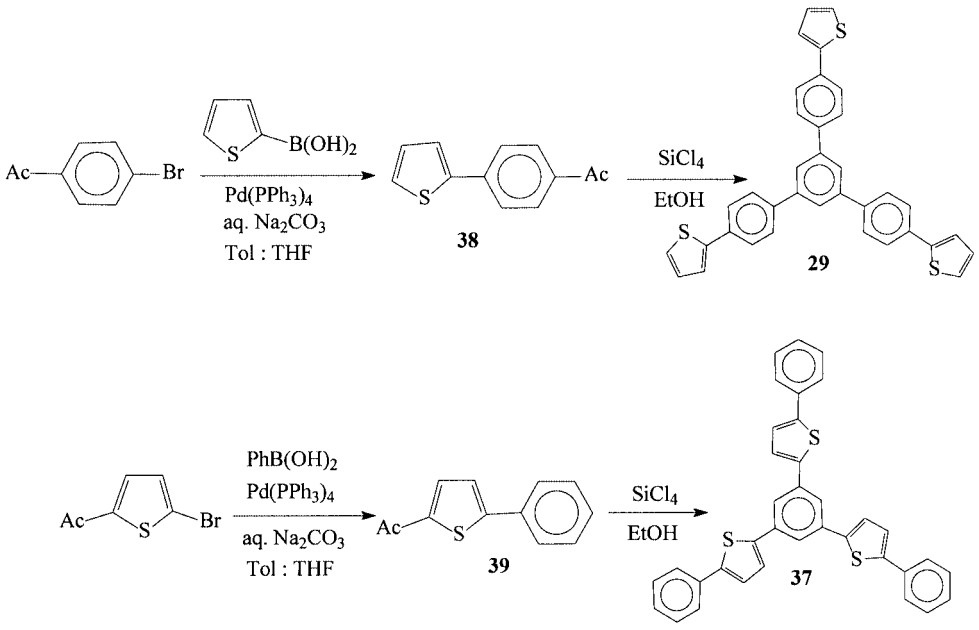
S. No.	Coupling Products	Yield (%)	S. No.	Coupling Product	Yield (%)
1	 **30**	47	5	 **34**	51
2	 **31**	52	6	 **35**	55
3	 **32**	53	7	 **29**	60
4	 **33**	75	8	 **36**	52

The higher degree of planarity between these two rings in **29** is due to the presence of weak hydrogen bonding interactions between the thiophene sulfur atoms and the hydrogen atoms of the aryl ring. The interaction distance was computed to be 0.27 nm in this case (Figure 3). Since oxygen is a better hydrogen-bond acceptor, such interactions would be expected to be stronger with the furan system, and this was indeed found to be the case in **36**, with a shorter O···H distance of 0.24 nm. More effective hydrogen bonding is found to be responsible for the reduction in the inter-ring torsional angle, resulting in a completely flat molecular geometry for **36**. This should be a useful tool in making templates while larger dendritic molecules are designed; better conformational control of the dendritic arms through the use of suitably crafted heterocycles as building blocks can be envisioned. Such strategies using heterocycles have not been widely reported in the literature. It is worth pointing out that attachment of polyaryl groups to the outer heterocyclic rings can induce angularity.

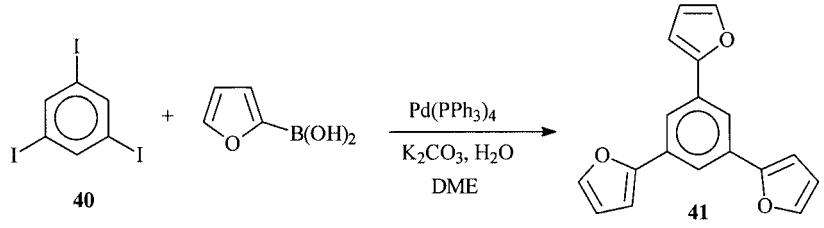
Another interesting parameter is the molecular size. We have determined important "*end-to-end*" distances as shown in Figure 3. Since the systems studied in this work have little conformational flexibility, the lengths D1 and D2 (Table 3) provide details on the dimensions of the molecule. It was found that the longest arm and largest distances were found to be for acetyl- (**31**) and formyl-substituted (**34**) systems. Furan- and thiophene-containing systems were found to have smaller distances than other polyaryls.

Conclusion

To conclude, we have shown that various acetylated thiophene derivatives undergo trimerization reactions to generate C_3-symmetric building blocks with potential for application in catalysis,[32] materials science, and organic synthesis. We have prepared star-shaped thiophenes bearing alkyl groups (e.g., **21** and **22**) which may be important in the design of liquid crystalline materials.[33] In addition, availability of mixed aryl-thienyl oligomers in which the thiophene unit is present either in the outer or in the inner core of the molecule (e.g., **29** and **37**) by this strategy may



Scheme 5



Scheme 6

Table 3. Optimized geometrical parameters for substituted C_3-symmetric compounds

Substituent[a]	D1[b] [nm]	D2 [nm]	Dihedral 1 (1,2,3,4)	Dihedral 2 (5,6,7,8)
−H	1.91	1.10	41	−40
−F	1.95	1.13	41	−40
−CHO	2.31	1.33	41	−40
$-OCH_3$	2.28	1.31	41	−40
$-CF_3$	2.20	1.21	41	−40
$-COCH_3$	2.31	1.33	41	−39
Furan	1.85	0.94	41	0
Thiophene	1.91	0.95	41	−23

[a] Except for furan and thiophene derivatives substituent refers to groups at the *para*-position of the biphenyl attached to the central aryl unit. [b] D1 represents maximum *end-to-end* total length of the molecule. D2 is the length of one arm, measured from center of aryl ring and the farthest atom. Dihedral 1 and dihedral 2 are the inter-ring dihedral angles as indicated in Figure 3.

provide easy access to novel polymers and dendrimers. We have also prepared 1,3,5-trifurylbenzene (**41**) by SM cross-coupling, this compound being difficult to prepare by acid-catalyzed trimerization of 2-acetylfuran. The structural features of the compounds synthesized here clearly indicate that biphenyl linkages in combination with heterocyclic units can be exploited to impart the desired conformational rigidity as well as distances to polyaryls. We plan to extend this approach, in concert with the SM cross-coupling reaction, towards the design of dendrimeric frameworks with increased diversity and predictable distances.

Experimental Section

General Remarks: Analytical TLC was performed on (10 × 5 cm) glass plate coated with silica gel G or GF 254 (containing 13% $CaSO_4$ as a binder). Viewing of the spot on the TLC plate was achieved by exposure either to I_2 vapor or to UV light. Flash chromatography was performed on silica gel (100−200 mesh) and the columns were usually eluted with EtOAc and petroleum ether (bp, 60−80 °C) mixtures. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectroscopic data were recorded on Varian VXR 300 spectrometers with TMS as internal standard and $CDCl_3$ as solvent. The coupling constants (*J*) are given in Hertz (Hz). Mass spectral measurements were carried out on a GCD 1800 Hewlett−Packard GC-MS spectrometer. Micromasses were calculated on a Q-TOF micromass machine. UV spectroscopic data were obtained (in $CHCl_3$) on Shimadzu UV-2100 or UV-260 instruments. FT-IR spectra were recorded as KBr pellets unless otherwise mentioned. Anhydrous Et_2O and THF were obtained by distillation over sodium/benzophenone ketyl. Anhydrous $MgSO_4$ was used as drying agent after workup in all the reactions. Tetrachlorosilane, absolute ethanol, and *n*-butyllithium were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA), Farco Chemi-

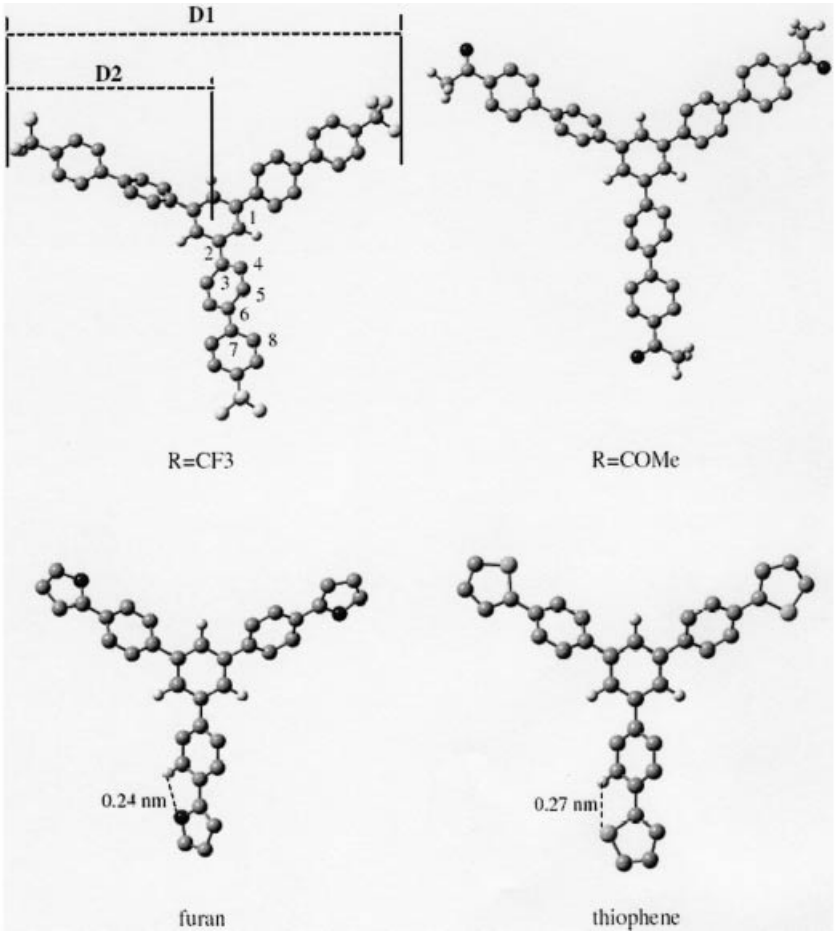


Figure 3. AM1-optimized geometries of C_3-symmetric polyaromatic compounds (distances given in nm)

cal Supplies (China), and Lancaster Chemical Co. (U.K.), respectively. Acetic anhydride was prepared from acetyl chloride and sodium acetate by the literature procedure.[34] $Pd(PPh_3)_4$ was prepared by the reported procedure.[35] Dimethyl sulfoxide (Spectrochem), 1-bromobutane (Fluka), 1-bromooctane, 2-acetyl-5-chlorothiophene (Lancaster), 4-iodoacetophenone (Lancaster chemicals), and 4-bromoacetophenone (SRL) were used as received. Thiophene-2-boronic acid, furan-2-boronic acid, phenylboronic acid, and 4-methylphenylboronic acid were prepared by literature procedures.[36] 4-Methoxyphenylboronic acid, 4-acetylphenylboronic acid, and 4-formylphenylboronic acid were purchased from Aldrich and used as received. (4-Fluorophenyl)boronic acid and 3-(trifluoromethyl)phenylboronic acid were obtained from Optima Chemical Group, LLC, USA.

Initial conformational sampling was performed by molecular mechanics methods with the MM2 force field, with a fairly large set of starting geometries. Low-energy structures were then subjected to full geometry optimizations by semi-empirical method through the use of an AM1 Hamiltonian as implemented in the Gaussian 98 suite of quantum chemical programs.[37] All the stationary points were characterized as true minima on their respective potential energy surfaces by corresponding Hessian indices.

General Procedure for Alkylation of Thiophene:[25a] A solution of *n*BuLi (0.3 mol) in Et_2O was added dropwise at 0 °C to a solution of thiophene (0.3 mol) in dry Et_2O. The reaction mixture was then stirred at room temp. for 1 h and cooled to −15 to −20 °C, and the electrophile (0.3 mol) in dry Et_2O was then added. The resultant reaction mixture was then heated at reflux for 18 h, cooled to room temp., and poured into crushed ice. The Et_2O layer was separated, washed with H_2O, dried, and fractionated to give alkylated thiophene derivatives.

General Procedure for Acetylation of 2-Alkylthiophene Derivatives:[25b] 2-Alkylthiophene (2.5 mmol) in acetic anhydride (0.2 mL, 2.2 mmol) was treated with a few drops of H_3PO_4 at 70−75 °C for 3 h. The reaction mixture was then cooled to room temp. and poured into H_2O. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was washed with $NaHCO_3$ solution, H_2O, and brine, dried, and concentrated. The crude product was loaded onto a silica gel column. Elution of the column with EtOAc/hexane gave the acetylated product.

General Procedure for Trimerization of Acetylated Derivatives:[23] $SiCl_4$ (2−18 equiv.) was added dropwise with stirring at 0 °C to a solution of acetylated derivative (0.04 mol) in absolute EtOH (40 mL) and the reaction mixture was stirred at ambient temperature. At the conclusion of the reaction (TLC monitoring), the dark reaction mixture was poured into ice-cold H_2O and extracted with CH_2Cl_2. The combined organic fraction was washed with H_2O and dried. Evaporation of the solvent and purification of the crude product by column chromatography (silica gel) with hexane as an eluent furnished the trimerized product.

1,3,5-Tris(2-thienyl)benzene (7): 2-Acetylthiophene (**6**, 5 g, 0.04 mol) in absolute EtOH (40 mL) was treated with $SiCl_4$ (9 mL, 0.08 mol) as described in the above general procedure for 6 h to deliver **7** as a white solid (1.8 g, 42%), m.p. 155−156 °C (ref.[24] m.p. 156−158 °C). R_f = 0.2 (petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.12 (dd, *J* = 3.6, 5.0 Hz, 3 H), 7.33 (dd, *J* = 1.1, 5.0 Hz, 3 H), 7.41 (dd, *J* = 1.1, 3.6 Hz, 3 H), 7.73 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 122.7, 123.9, 125.4, 128.1, 135.7, 143.5. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 296 (50359). MS: *m*/*z* = 324 [M^+].

1,3,5-Tris[5-(2-methylthienyl)benzene (20): 2-Acetyl-5-methylthiophene (**17**, 135 mg, 0.96 mmol) in absolute EtOH (2.5 mL) was treated with $SiCl_4$ (0.6 mL, 5.24 mmol) as described in the above general procedure for 4 h to furnish **20** as a white solid (71 mg, 61%), m.p. 137−139 °C. R_f = 0.6 (2% EtOAc/petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.52 (s, 9 H), 6.74−6.76 (m, 3 H), 7.17 (d, *J* = 3.5 Hz, 3 H), 7.57 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 15.5, 121.4, 123.5 126.2, 135.7, 140.0, 141.3. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 305 (71465). $C_{21}H_{18}S_3$ (366): calcd. C 68.85, H 4.92; found C 68.81, H 4.90.

1,3,5-Tris[5-(2-butylthienyl)]benzene (21): 2-Acetyl-5-butylthiophene (**18**, 70 mg, 0.38 mmol) in absolute EtOH (1 mL) was treated with $SiCl_4$ (0.2 mL, 1.92 mmol) as described in the above general procedure for 18 h to produce **21** as a white solid (45 mg, 72%), m.p. 40−42 °C. R_f = 0.6 (3% EtOAc/petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.98 (t, *J* = 7.3 Hz, 9 H), 1.43 (sept, *J* = 7.3 Hz, 6 H), 1.65 (pent, *J* = 7.6 Hz, 6 H), 2.86 (t, *J* = 7.6 Hz, 6 H), 6.79 (d, *J* = 3.7 Hz, 3 H), 7.22 (d, *J* = 3.3 Hz, 3 H), 7.62 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 13.9, 22.2, 30.0, 33.8, 121.4, 123.2, 125.1, 135.8, 141.0, 146.1. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 306 (32472). EI-HRMS ($C_{30}H_{36}S_3$): calcd. 492.1979; found 492.1966.

1,3,5-Tris[5-(2-octylthienyl)]benzene (22): 2-Acetyl-5-octylthiophene (**19**, 120 mg, 0.588 mmol) in absolute EtOH (1.5 mL) was treated with $SiCl_4$ (0.35 mL, 2.9 mmol) as described in the above general procedure for 24 h to give **22** (70 mg, 63%), m.p. 38−39 °C. R_f = 0.8 (1% EtOAc/petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.88 (t, *J* = 6.9 Hz, 9 H), 1.28−1.38 (m, 30 H), 1.71 (pent, *J* = 7.3 Hz, 6 H), 2.83 (t, *J* = 7.6 Hz, 6 H), 6.77 (d, *J* = 3.6 Hz, 3 H), 7.20 (d, *J* = 3.3 Hz, 3 H), 7.59 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 14.2, 22.7, 29.2, 29.3, 29.4, 30.3, 31.7, 31.9, 121.4, 123.2, 125.0, 135.8, 141.0, 146.2. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 306 (48543). EI-HRMS ($C_{42}H_{60}S_3$): calcd. 660.3857; found 660.3889.

1,3,5-Tris[5-(2-chlorothienyl)]benzene (24): 2-Acetyl-5-chlorothiophene (**23**, 300 mg, 1.87 mmol) in absolute EtOH (6 mL) was treated with $SiCl_4$ (0.9 mL, 7.85 mmol) as described in the above general procedure for 12 h to give **24** as a white solid (159 mg, 60%), m.p. 177−179 °C. R_f = 0.9 (petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 6.94 (d, *J* = 4.0 Hz, 3 H), 7.15 (d, *J* = 3.7 Hz, 3 H), 7.50 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 122.0, 123.3, 127.3, 130.2, 135.2, 141.4. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 304 (52595). $C_{18}H_9Cl_3S_3$ (427): calcd. C 50.53, H 2.12; found C 49.99, H 2.07.

1,3,5-Tris[5-(2,2′-bithienyl)]benzene (26): 5-Acetyl-2,2′-bithiophene (**25**, 80 mg, 0.38 mmol) in absolute EtOH (2.5 mL) was treated with $SiCl_4$ (0.65 mL, 5.67 mmol) under reflux conditions as described in the above general procedure for 4 h to produce **26** as a light yellow solid (19 mg, 26%), m.p. 180 °C. R_f = 0.2 (petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.06 (dd, *J* = 3.7, 4.9 Hz, 3 H), 7.20 (d, *J* = 3.8 Hz, 3 H), 7.24−7.27 (m, 6 H), 7.35 (d, *J* = 3.8 Hz, 3 H), 7.7 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 121.8, 123.9, 124.6 (3 C), 128.0, 135.4, 137.2, 137.4, 141.9. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 357 (82108). $C_{30}H_{18}S_6$ (570): calcd. C 63.16, H 3.16; found C 63.10, H 3.11.

1,3,5-Tris[4-(2-thienyl)phenyl]benzene (29): 4-(2-Thienyl)acetophenone (**38**, 65 mg, 0.322 mmol) in absolute EtOH (3 mL) was treated with $SiCl_4$ (0.5 mL, 4.36 mmol) as described in the above general procedure for 24 h to furnish **29** as a white solid (23 mg, 44%), m.p. 224−225 °C. R_f = 0.7 (2% EtOAc/petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.12 (dd, *J* = 3.3, 4.9 Hz, 3 H), 7.32 (dd, *J* = 1.1, 4.9 Hz, 3 H), 7.39 (dd, *J* = 1.1, 3.7 Hz, 3 H), 7.74 (s, 12 H), 7.83 (s, 3 H). UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 315 (91175). $C_{36}H_{24}S_3$ (552): calcd. C 78.26, H 4.35; found C 78.22, H 4.37.

1,3,5-Tris[5-(2-phenylthienyl)]benzene (37): 2-Acetyl-5-phenylthiophene (**39**, 58 mg, 0.287 mmol) in absolute EtOH (3 mL) was treated with $SiCl_4$ (0.6 mL, 5.23 mmol) as described in the above general procedure for 24 h to deliver **37** as a light yellow solid (23 mg, 44%), m.p. 244−245 °C. R_f = 0.5 (5% EtOAc/petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.29−7.44 (m, 15 H), 7.67−7.70 (m, 6 H), 7.79 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 121.9, 124.0, 124.7, 125.6, 127.6, 128.9, 134.1, 135.6, 142.5, 144.2. UV ($CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$) = 339 (72795). $C_{36}H_{24}S_3$ (552): calcd. C 78.26, H 4.35; found C 78.32, H 4.33.

1,3,5-Tris(4-bromophenyl)benzene (27):[19a] 4-Bromoacetophenone (500 mg, 2.51 mmol) in absolute EtOH (2.5 mL) was treated with $SiCl_4$ (890 mg, 5 mmol) as described in the above general procedure for 4 h to produce **27** (351 mg, 77%) as a white solid m.p.: 263 °C (ref.[19a] m.p. 264 °C). R_f = 0.5 (petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.53 (td, *J* = 2.2, 8.4 Hz, 6 H), 7.61 (td, *J* = 2.2, 8.7 Hz, 6 H), 7.69 (s, 3 H).

1,3,5-Tris-(4-iodophenyl)benzene (28): 4-Iodoacetophenone (200 mg, 0.08 mmol) in absolute EtOH (3 mL) was treated with $SiCl_4$ (0.6 mL, 5.24 mmol) as described in the above general procedure for 12 h to furnish **28** as a white, crystalline solid (141 mg, 76%), m.p. 262−263 °C (ref.[38] m.p. 265 °C). R_f = 0.6 (petroleum ether). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.40 (AB part of AA′BB′ system, *J* = 8.4 Hz, 6 H), 7.68 (s, 3 H), 7.81 (A′B′ part of AA′BB′ system, *J* = 8.4 Hz, 6 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 93.7, 124.9, 129.2, 138.1, 140.3, 141.7. EI-HRMS ($C_{24}H_{15}I_3$): calcd. 684.8386; found 684.8392.

General Procedure for the Suzuki−Miyaura Cross-Coupling Reaction:[16] A mixture of aryl halide (1 equiv.), arylboronic acid (6−7 equiv.), $Pd(PPh_3)_4$ (ca. 8−10 mol %), Na_2CO_3 (6 equiv.) in H_2O, and solvent [DME or THF and toluene (1:1)] was heated at 90 °C under N_2. At the conclusion of the reaction (TLC), the mixture was diluted with H_2O and extracted with EtOAc. The combined organic layers were washed with H_2O and brine and dried ($MgSO_4$). The solvent was evaporated, and the remaining crude product was loaded onto a silica gel column. Elution of the column with EtOAc/petroleum ether gave the desired cross-coupling product.

4-(2-Thienyl)acetophenone (38): A mixture of 4-bromoacetophenone (282 mg, 1.42 mmol), thiophene-2-boronic acid (300 mg, 2.34 mmol), $Pd(PPh_3)_4$ (20 mg, 0.0173 mmol), K_2CO_3 (320 mg, 2.13 mmol) in H_2O (1 mL), and solvent DME (2 mL) was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography.

Elution of the column with 8% EtOAc/petroleum ether gave the desired cross-coupling product **38** (262 mg, 92%) as a white solid, m.p. 115−117 °C (ref.[29b] m.p. 116−117 °C). R_f = 0.7 (20% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.62 (s, 3 H), 7.13 (dd, J = 3.7, 5.1 Hz, 1 H), 7.38 (dd, J = 1.1, 5.1 Hz, 1 H), 7.44 (dd, J = 1.1, 3.7 Hz, 1 H), 7.70 (td, J = 1.8, 8.4 Hz, 2 H), 7.97 (td, J = 1.8, 8.4 Hz, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 26.5, 124.6, 125.6, 126.4, 128.3, 129.1, 135.7, 138.7, 142.9, 197.3.

5-Acetyl-2-phenylthiophene (39): A mixture of 2-acetyl-5-bromothiophene (300 mg, 1.46 mmol), phenylboronic acid (291 mg, 2.39 mmol), $Pd(PPh_3)_4$ (44 mg, 0.038 mmol), K_2CO_3 (309 mg, 8.3 mmol) in H_2O (1 mL), and solvent DME (2 mL) was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with 5% EtOAc/petroleum ether gave the desired cross-coupling product **39** (261 mg, 88%) as a white solid, m.p. 109−112 °C (ref.[29c] m.p. 115 °C). R_f = 0.3 (5% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.57 (s, 3 H), 7.33 (d, J = 3.7 Hz, 1 H), 7.37−7.46 (m, 3 H), 7.64−7.67 (m, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): δ = 26.5, 123.9, 126.2, 129.0, 129.1, 133.3, 133.4, 143.1, 152.8, 190.6.

1,3,5-Tris[4-(2′-thienyl)phenyl]benzene (29) from 27: A mixture of **27** (100 mg, 0.184 mmol), thiophene-2-boronic acid (130 mg, 1.02 mmol), $Pd(PPh_3)_4$ (20 mg, 0.0173 mmol), Na_2CO_3 (189 mg, 1.7 mmol) in H_2O (3 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **29** (14 mg, 14%) as a white solid. The physical characteristics and spectroscopic data of the compound **29** obtained by this route were the same as those of the product obtained by the trimerization reaction. R_f = 0.3 (2% EtOAc/petroleum ether).

1,3,5-Tris[4-(2′-thienyl)phenyl]benzene (29) from 28: A mixture of **28** (33 mg, 0.048 mmol), thiophene-2-boronic acid (33 mg, 0.25 mmol), $Pd(PPh_3)_4$ (20 mg, 0.0173 mmol), Na_2CO_3 (26 mg, 0.24 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of the reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **29** (16 mg, 60%) as a white solid. The physical characteristics and spectroscopic data of the compound **29** obtained by this route were the same as those of the product obtained by the trimerization reaction. R_f = 0.3 (2% EtOAc/petroleum ether).

1,3,5-Tris[4-(4′-methylphenyl)phenyl]benzene (30): A mixture of **29** (30 mg, 0.043 mmol), 4-methylphenylboronic acid (35 mg, 0.25 mmol), $Pd(PPh_3)_4$ (14.8 mg, 0.012 mmol), Na_2CO_3 (24 mg, 0.22 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **30** (12 mg, 47%) as a white, crystalline solid, m.p. 184−186 °C. R_f = 0.4 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.42 (s, 9 H), 7.29 (AB part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.57 (A′B′ part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.71 (AB part of AA′BB′ system, J = 8.4 Hz, 6 H), 7.79 (A′B′ part of AA′BB′ system, J = 8.4 Hz, 6 H), 7.87 (s, 3 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 21.3, 96.3, 124.9, 127.4, 127.7, 129.6, 136.9, 137.9, 139.9, 140.5, 142.1. UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 300 (108901). EI-HRMS ($C_{45}H_{36}$): calcd. 576.2817; found 576.2813.

1,3,5-Tris[4-(4′-acetylphenyl)phenyl]benzene (31): A mixture of **29** (30 mg, 0.043 mmol), 4-acetylphenylboronic acid (44 mg, 0.26 mmol), $Pd(PPh_3)_4$ (14.8 mg, 0.012 mmol), Na_2CO_3 (24 mg, 0.22 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of reaction (TLC) the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with 16% EtOAc/petroleum ether gave the desired cross-coupling product **31** (15 mg, 52%) as a white, crystalline solid, m.p. 196−198 °C. R_f = 0.3 (25% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.67 (s, 9 H), 7.77 (AB part of AA′BB′ system, J = 8.4 Hz, 6 H), 7.78 (A′B′ part of AA′BB′ system, J = 8.4 Hz, 6 H), 7.85 (AB part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.91 (s, 3 H), 8.08 (A′B′ part of AA′BB′ system, J = 8.0 Hz, 6 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 26.8, 125.4, 127.3, 127.9, 128.1, 131.1, 136.1, 139.3, 141.0, 142.0, 145.3, 198.1. UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 310 (335757). IR (neat, cm^{-1}): $\tilde{\nu}$ = 815.1, 1026.9, 1263.4, 1594.4, 1670.5, 2851.0, 2919.7 cm^{-1}. EI-HRMS ($C_{48}H_{36}O_3$): calcd. 660.2664; found 661.2725 [M + 1].

1,3,5-Tris[4-(4′-fluorophenyl)phenyl]benzene (32): A mixture of **29** (50 mg, 0.073 mmol), 4-fluorophenylboronic acid (58 mg, 0.41 mmol), $Pd(PPh_3)_4$ (25.2 mg, 0.02 mmol), Na_2CO_3 (40 mg, 0.37 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **32** (23 mg, 53%) as a white, crystalline solid, m.p. 228−230 °C (ref.[28] m.p. 236 °C). R_f = 0.4 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.14−7.11 (m, 6 H), 7.62−7.58 (m, 6 H), 7.65 (AB part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.77 (A′B′ part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.85 (s, 3 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 115.7 (J = 21.4 Hz), 115.8, 124.9, 127.4, 127.7, 128.6 (J = 8.0 Hz), 136.6, 139.5, 139.9, 141.9, 162.5 (J = 246.0 Hz), [values in parenthesis are C-F coupling constants]. UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 297 (268676). EI-HRMS ($C_{42}H_{27}F_3$): calcd. 588.2064; found 588.2072.

1,3,5-Tris[4-(3′-trifluoromethylphenyl)phenyl]benzene (33): A mixture of **29** (50 mg, 0.073 mmol), 3-trifluoromethylphenylboronic acid (84 mg, 0.41 mmol), $Pd(PPh_3)_4$ (25.2 mg, 0.02 mmol), Na_2CO_3 (40 mg, 0.37 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **33** (40 mg, 75%) as a white, crystalline solid, m.p. 222−224 °C. R_f = 0.4 (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.65−7.85 (m, 9 H), 7.71 (AB part of AA′BB′ system, J = 8.4 Hz, 6 H), 7.84 (A′B′ part of AA′BB′ system, J = 8.4 Hz, 6 H), 7.85−7.91 (m, 6 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 123.6 (J = 3.7 Hz), 124.1, 124.2 (J = 272.1 Hz), 125.2, 127.7, 127.9, 129.3, 130.3, 131.3 (J = 32.1 Hz), 139.0, 140.6, 141.4, 141.8, [values in parenthesis are C-F coupling constants]. UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$):

294 nm (103925). EI-HRMS ($C_{45}H_{27}F_9$): calcd. 738.1963; found 738.1956.

1,3,5-Tris[4-(4′-methoxyphenyl)phenyl]benzene (35): A mixture of **29** (30 mg, 0.043 mmol), 4-methoxyphenylboronic acid (40 mg, 0.263 mmol), $Pd(PPh_3)_4$ (14.8 mg, 0.012 mmol), Na_2CO_3 (24 mg, 0.22 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of the reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **35** (15 mg, 55%) as a white, crystalline solid, m.p. 182−184 °C. R_f = 0.3 (15% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 3.86 (s, 9 H), 7.00 (AB part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.60 (A′B′ part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.67 (AB part of AA′BB′ system, J = 7.3 Hz, 6 H), 7.77 (A′B′ part of AA′BB′ system, J = 7.3 Hz, 6 H), 7.86 (s, 3 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 55.3, 114.2, 124.8, 127.1, 127.6, 128.1, 133.1, 139.3, 140.0, 141.9, 159.2. UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 302 (104034). EI Mass (QTOF): 625.2323 [M + 1].

1,3,5-Tris[4-(4′-formylphenyl)phenyl]benzene (34): A mixture of **29** (50 mg, 0.073 mmol) 4-formylphenylboronic acid (66 mg, 0.43 mmol), $Pd(PPh_3)_4$ (25.2 mg, 0.02 mmol), Na_2CO_3 (40 mg, 0.37 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of the reaction (TLC), the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with 13% EtOAc/petroleum ether gave the desired cross-coupling product **34** (23 mg, 51%) as a white, crystalline solid, m.p. 174−176 °C. R_f = 0.3 (20% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.52 (AB part of AA′BB′ system, J = 8.0 Hz, 6 H), 7.87−7.80 (m, 12 H), 7.91 (s, 3 H), 8.00 (A′B′ part of AA′BB′ system, J = 8.0 Hz, 6 H), 10.08 (s, 3 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 125.2, 127.5, 127.9 (2C), 130.3, 135.3, 139.1, 141.0, 141.8, 146.4, 191.8. UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 315 (103502). IR (neat, cm^{-1}): $\tilde{\nu}$ = 803.7, 1025.7, 1170.2, 1208.0, 1600.7, 1696.2, 2857.1, 2925.7 cm^{-1}. EI Mass (QTOF): 619.1276[M + 1].

1,3,5-Tris[4-(2′-furyl)phenyl]benzene (36): A mixture of **29** (55 mg, 0.080 mmol), furan-2-boronic acid (42 mg, 0.3 mmol), $Pd(PPh_3)_4$ (27 mg, 0.02 mmol), Na_2CO_3 (40 mg, 0.37 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of the reaction (TLC) the mixture was worked up as described in the general procedure. The crude product was purified by silica gel column chromatography. Elution of the column with petroleum ether gave the desired cross-coupling product **36** (21 mg, 52%) as a white, crystalline solid, m.p. 140−142 °C. R_f = 0.4 (2% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 6.51 (dd, J = 3.4, 3.2 Hz, 3 H), 6.72 (d, J = 3.2 Hz, 3 H), 7.51(d, J = 1.3 Hz, 3 H), 7.74 (AB part of AA′BB′ system, J = 8.5 Hz, 6 H), 7.80 (A′B′ part of AA′BB′ system, J = 8.5 Hz, 6 H), 7.83 (s, 3 H). ^{13}C NMR (75.43 MHz, $CDCl_3$, ppm): δ = 105.3, 111.7, 124.2, 124.6, 127.5, 130.2, 139.8, 141.8, 142.2, 153.7. EI-HRMS ($C_{36}H_{24}O_3$): calcd. 504.1725; found 504.1728.

1,3,5-Tris(2-furyl)benzene (41): A mixture of **40** (100 mg, 0.219 mmol), furan-2-boronic acid (208 mg, 1.861 mmol), $Pd(PPh_3)_4$ (53 mg, 0.045 mmol), Na_2CO_3 (140 mg, 1.32 mmol) in H_2O (1 mL), and solvent [THF (3 mL) and toluene (3 mL)] was heated at 90 °C under N_2. At the conclusion of reaction (TLC), the mixture was worked up with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O and brine and dried with $MgSO_4$. Evaporation of the solvent and purification of the crude product by neutral alumina column chromatography with 2% EtOAc/petroleum ether mixture as an eluent gave the desired coupling product **41** (40 mg, 66%) as a white, crystalline solid, m.p. 125−128 °C(ref.[39] m.p. 125−126 °C). R_f = 0.3 (5% EtOAc/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 6.52 (dd, J = 1.8, 3.3 Hz, 3 H), 6.78 (d, J = 3.3 Hz, 3 H), 7.52 (d, J = 1.8 Hz, 3 H), 7.88 (s, 3 H). UV (in $CHCl_3$): λ_{max} [nm] (ε, $M^{-1}cm^{-1}$): 302 (38853). EI-HRMS ($C_{18}H_{12}O_3$): calcd. 276.0786; found 276.0782.

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