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Highly Efficient Non-palladium Catalyzed Controlled Synthesis and X-ray Analysis of Functionalized 1,2-Diaryl-, 1,2,3-Triaryl- and 1,2,3,4-Tetraarylbenzenes[#]

Atul Goel, Fateh Veer Singh , Manish Dixit, Deepti Verma , Resmi Raghunandan and Prakas R. Maulik

Abstract: A general, two-step highly efficient synthesis of 1,2-diaryl-, 1,2,3-triaryl- and 1,2,3,4-tetraarylbenzenes from simple stitching of α-oxo-ketene-*S*,*S*-acetals and active methylene compounds *via* a 'lactone intermediate' is described. This procedure offers easy access to highly functionalized arylated-benzenes containing sterically demanding groups in good to excellent yields. The novelty of the procedure lies in the fabrication of aromatic compounds with desired conformational flexibility along the molecular axis in a transition metal-free environment through easily accessible precursors. The crystal analysis of these arylated-benzene scaffolds showed that the peripheral aryl rings are arranged in propeller-like fashion with respect to the central benzene rings. Examination of the crystal packing in the structure of a 1,2,3,4-tetraarylbenzene **12c** revealed a "**N…π interaction**" between molecules related by a two-fold screw axis running in a direction. It is interesting that the repeat of the array of N…π interaction around the axis of the 1,2,3,4-tetraarylbenzene **12c** enforces the molecules in a helical pattern.

Keywords: diarylbenzene . triarylbenzene . tetraarylbenzene . lactone . non-palladium catalyzed . X-ray analysis . N…π interaction

Introduction

The demand of functionally congested biaryl compounds for both synthetic and medicinal purposes has increased dramatically during the past few decades. Besides their large diversity in complex natural products[1] and pharmaceutical agents,[2] these compounds are fascinating and challenging research objects in material[3] and polymer sciences.[4] Axially chiral biaryls are useful as versatile auxiliaries for asymmetric syntheses,[5] as chiral phases for chromatography[6] and as important substrates for chiral liquid crystalline materials.[7] Recently, numerous natural products having terphenyl architecture have been reported with interesting biological properties.[8-11] Several synthetic terphenyl derivatives have been designed as selective inhibitors for dihydroortate dehydrogenase[12] and cyclooxygenase[13] enzymes. Terphenyls containing acidic groups have recently been found to be potent insulin sensitizers.[14] Owing to their interesting optical[15] and electrical[16] properties, terphenyls find several industrial applications as liquid crystals, conducting polymers, heat storage and heat transfer agents, as textile dye carriers and as a laser dye. Recently a great deal of attention has been focused to fabricate useful teraryl- or tetraaryl-benzene building blocks with electron-withdrawing and releasing groups for preparing advanced electroluminescent materials.[17]

Limited procedures are known for the synthesis of such biaryls in which one of the aryl rings is functionalized with two or more aromatic rings in a juxtaposed manner. Palladium-catalyzed aryl-aryl cross-coupling between the electrophilic aromatic halides $Ar(X)_n$ (X being generally Br, I, and OTf; n being mainly 0, 1 or 2) and organometallic species Ar-M (M being Mg, Ni, Zn, Sn, and B) is a versatile synthetic method for the preparation of diverse arylatedbenzene.[18] Of the various coupling reactions, the Pd-catalyzed Suzuki-Miyaura couplings of a diverse array of haloarenes with arylboronic acids has dominated in this area due to the commercial availability and innocuous nature of the latter, easy workup, and tolerance of the reactions to aqueous media. Diarylbenzenes have been synthesized either by the coupling of biaryltriflate compounds with Grignard reagents in presence of a palladium catalyst in moderate to good yields,[19] or by the iterative coupling of aryl boronic acid with aromatic halides[20] separately. Despite the wide synthetic generality of these aryl-aryl cross-coupling reactions, multiple coupling on tri- or tetrahalides to prepare triaryl- or tetraarylbenzenes places constraints on the choice of reagents or catalysts and produces either low yields of desired compounds or fails completely to fulfill the demand.

Although numerous non-metal catalyzed approaches particularly, regio- and stereoselective Diels-Alder cycloadditions[21] of 2*H*-pyran-2-ones with electron-deficient and electron-rich dienophiles do exist in the literature, they require forcing thermal conditions and/or do not provide a general route for preparing di-, tri- or polyarylbenzenes. The wide-ranging applications and high demand of arylatedbenzenes and paucity of non-metal catalyzed synthetic methodologies prompted us to develop a simple, general and efficient route that could offer flexibility of substituent variations on benzene scaffold. In this article, we report a highly convenient and commercially viable synthetic route for 1,2-diaryl-, 1,2,3-triaryl- and 1,2,4-triaryl-, and 1,2,3,4-tetraarylbenzenes through simple stitching of α-oxo-ketene-*S*,*S*-acetals with active methylene molecular pieces (malononitrile 2-methoxyacetophenone or

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deoxybenzoin) in just two steps. The versatility and generality of the procedure lies in the creation of a central benzene ring with optional di-, tri- and tetraaryl moieties in a controlled fashion under organometallic reagent-free environment.

Results and Discussion

Chemistry

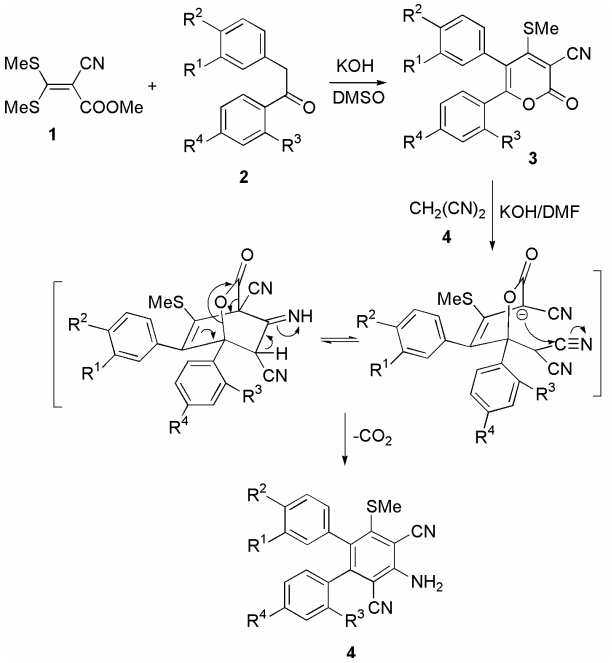
During the recent studies on the chemistry of 2*H*-pyran-2-ones, we observed[22] that 2*H*-pyran-2-ones prepared from α-oxo-ketene-*S*,*S*-acetal[23] **1** have promising structural topology as useful substrates for ring transformation reactions, flexible substitution pattern and the presence of a good leaving alkylsulfanyl group for generating molecular diversity. Our initial efforts indicated[24] that α-pyranone ring can be converted to a benzene ring under mild basic conditions. Such a new ring transformation[25] (recently termed as 'Lactone Methodology') prompted us to explore the route for preparing bent-cored oligo-pyridine[26] and oligo-phenylene[27] as useful building blocks for advanced materials. Recently, we exploited our lactone methodology to synthesize biaryls using acetyltrimethylsilane as a carbanion source.[28]

Abstract in Hindi:

एल्फा-आक्सो-कीटीन-S-S-एसीटल और क्रियाशील मिथाइलीन यौगिकों की एक माध्यमिक लैक्टोन से सामान्य कार्यविधियों के द्वारा 1,2-डिएरिल, 1,2,3-त्रिएरिल और 1,2,3,4-चतुर्एरिल का एक सामान्य द्वि-पक्षीय अति कार्यसाधक संश्लेषण वर्णित है। यह विधि अति प्रतिस्थापित बाधित-इष्टिक समूह युक्त एरीलेटेड-बेन्जीन को अत्यधिक मात्रा में प्रदान करती है। एक संक्रमण धातु-मुक्त वातावरण में आसानी से प्राप्त अम्लमूल के द्वारा यौगिकीय अक्ष पर इष्टिक सनरूपण नम्यता के साथ ऐरोमेटिक यौगिकों के निर्माण में इस विधि की नवीनता निहित है। ऐरीलेटेड बेन्जीन यौगिकों का स्फटिक अध्ययन, परिधीय ऐरिल वलों का प्रोपेलर की आकृति में मध्य बेन्जीन वलों के परिपेक्ष्य में व्यवस्थिति प्रदर्शित करता है। एक यौगिक 12सी के स्फटिक अनुबन्धन के अध्ययन से यह स्पष्ट होता है कि यौगिकों में एक दिशीय पैटनुमा द्वि-पटल अक्षीय N...π अन्योन्य प्रभाव उपस्थित है। यह N...π पुनरावृत्ति, 1,2,3,4-चतुर्एरिल बेन्जीन 12सी के अक्ष के चारों ओर चक्राकार आकृति प्रकट करती है।

Our previous efforts were on preparing simple aromatic systems and now we have systematically prepared functionally congested 1,2-diaryl-, 1,2,3-triaryl- and 1,2,3,4-tetraarylbenzenes in just two steps, which are difficult to prepare by conventional routes. All these compounds are novel and have not been reported prior to this study.

Our aim to prepare functional group containing 1,2-diarylbenzenes was achieved by preparing a key intermediate α-cyano-ketene-*S*,*S*-acetal **1** from easily accessible precursors methyl cyanoacetate, carbon disulfide and methyl iodide through modified procedure.[29] The α-cyano-ketene-*S*,*S*-acetal **1** on Michael addition-cyclization reaction with various substituted deoxybenzoins **2a-f** under alkaline conditions furnished 5,6-diaryl-2*H*-pyran-2-ones **3a-f** in excellent yields (Scheme 1). Various functionalized deoxybenzoins were prepared by heating a mixture of functionalized phenyl acetic acid and substituted benzenes in poly phosphoric acid as described previously.[30] The 5,6-diaryllactones **3a-f** generated from α-cyano-ketene-*S*,*S*-acetal **1** possess promising structural topology as useful substrates for Michael addition reactions, dense and flexible substitution patterns and the presence of a good leaving alkylsulfanyl group for generating molecular or functional group diversity.



Entry	R^1	R^2	R^3	R^4	Yield (%)	
					3	**4**
a	H	H	H	H	91	90
b	H	H	H	OMe	88	91
c	H	F	OMe	OMe	83	94
d	H	OMe	H	OMe	90	89
e	OMe	OMe	H	OMe	87	92
f	H	F	H	OMe	86	90

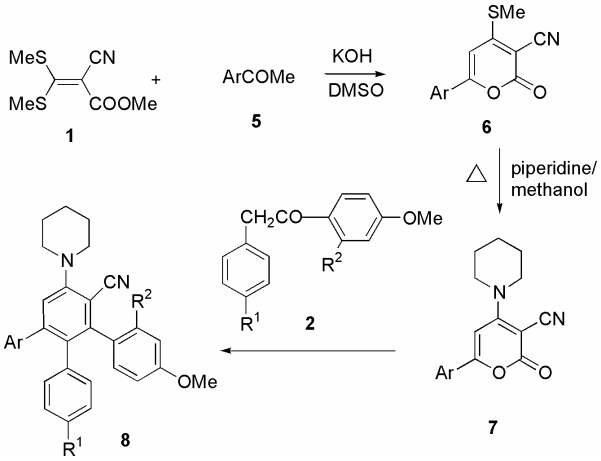
Scheme 1. Synthesis of 1,2-diarylbenzenes

Our approach to prepare 1,2-diarylbenzenes involved stirring an equimolar mixture of 2*H*-pyran-2-ones **3a-f**, malononitrile and powdered KOH in DMF for 12-15h at room temperature, which afforded functionalized 1,2-diarylbenzenes **4a-f** in 89-94% yields. It is note worthy that the functional groups such as methylsulfanyl, cyano and amino groups can be removed (desulfurization, decyanation, deamination) or modified depending upon the need of the desired diarylbenzene compounds.[31]

The plausible reaction mechanism for the formation of functionalized 1,2-diarylbenzenes **4a-f** is based on Michael-Ziegler-Thorpe-retro-Diels-Alder type reaction of **1** with active methylene compound under mild reaction conditions as depicted in Scheme 1. The reaction is initiated by the Michael addition of an anion, generated from a molecule of deoxybenzoin **2**, to the ketene-*S*,*S*-acetal **1** followed by intra-molecular cyclization to form a 2*H*-pyran-2-one intermediate **3**. The lactone **3** has three electrophilic centers; C2, C4 and C6 in which C6 is likely to be highly electrophilic due to extended conjugation, and the presence of an electron withdrawing nitrile group at position 3. The 2*H*-pyran-2-one is attacked by a malononitrile anion at C6 position, followed by Thorpe cyclization involving one of the nitrile functionalities of malononitrile and C-3

of the pyranone ring to form a bicyclic intermediate and further by decarboxylation to furnish 1,2-diarylbenzene **3** in high yield.

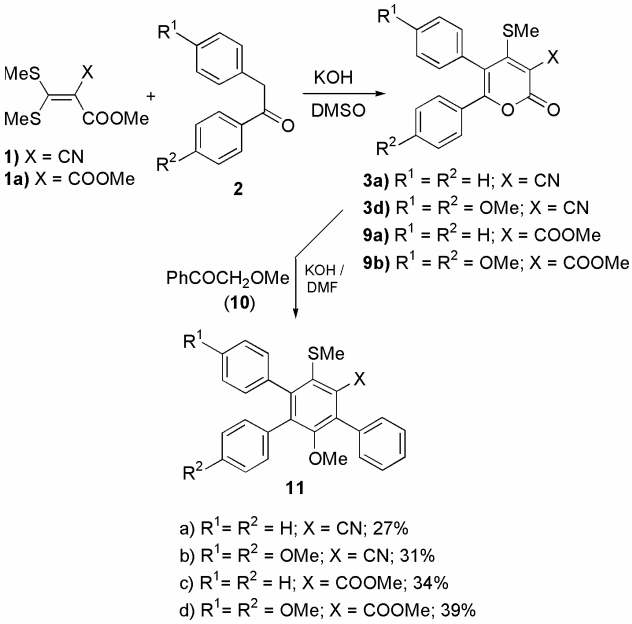
To exploit the methodology for preparing useful 1,2,3-triarylbenzene compounds, ketene dithioacetal **1** was reacted with functionalized acetophenones **5a-d**, which furnished 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles **6a-d** in high yields. In order to prepare compounds with amine functionality, a good leaving methylsulfanyl group of lactones **6a-d** was replaced with various secondary amines. We prepared 6-aryl-2-oxo-4-piperidin-1-yl-2*H*-pyran-3-carbonitriles (**7a-d**) in good yields by refluxing a mixture of **6a-d** with piperidine in methanol. These compounds **7a-d** were reacted with functionalized deoxybenzoins **2** to yield 4-cyano-5-(piperidin-1-yl)-1,2,3-triarylbenzene **8a-d** in excellent yields (Scheme 2). All the compounds were characterized by spectroscopic analyses. It is worth mentioning that the reaction proceeded smoothly even with the bulky naphthalene moiety, which furnished 1,2,3-triarylbenzene **8d** in 91% yield. This approach provides flexibility of introducing secondary amino group into the central benzene ring of 1,2,3-triarylbenzene. In addtion, the reaction can tolerate unprotected hydroxy group (R^2 = OH) particulary at sterically hindered ortho-position.



Entry	Ar	R^1	R^2	Yield (%) 8
a	4-MeC_6H_4	H	OH	94
b	thienyl	H	OH	87
c	4-FC_6H_4	OMe	H	90
d	1-naphthyl	OMe	H	91

Scheme 2. Synthesis of 1,2,3-triarylbenzenes

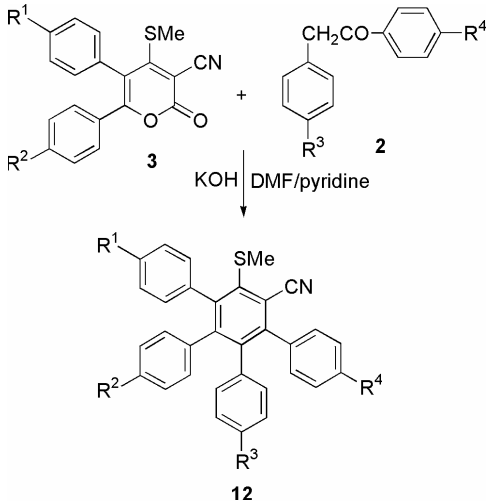
In order to explore this reaction further to prepare 1,2,4-triarylbenzenes, we carried out the reaction of 5,6-diaryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitriles **3a,d** or 5,6-diaryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carboxylic acid methyl ester **9a,b** with 2-methoxy-1-phenylethanone **10** under alkaline conditions as shown in Scheme 3. After usual workup, pure compounds were isolated as 5-cyano/methoxycarbonyl-3-methoxy-6-methylsulfanyl-1,2,4-triarylbenzenes **11a-d** in moderate yields. The course of reaction proceeded by an enolate addition of 2-methoxy-1-phenylethanone to lactone **3** or **9**, followed by intramolecular cyclization and decarboxylation to furnish 1,2,4-triarylbenzenes.



Scheme 3. Synthesis of 1,2,4-triarylbenzenes.

Finally, the synthesis of 1,2,3,4-tetraarylbenzenes were accomplished by stirring a mixture of functionalized deoxybenzoin **2** with 5,6-diaryl-2*H*-pyran-2-one **3** in the presence of KOH in dry DMF at room temperature (Scheme 4). The reaction was monitored by TLC, which showed an intense blue spot when exposed to short-wave UV radiation at 254 nm. After completion, the reaction mixture was poured into ice water and neutralized with dilute HCl. The crude product thus obtained was purified by passing through neutral alumina. The purified compound **12c** was isolated in 29% yield and characterized as 1,2-diaryl-3-(4'-methoxyphenyl)-4-(4''-methoxyphenyl)-5-cyano-6-methylsulfanylbenzene **12c** by spectroscopic analysis.

To achieve higher yields of 1,2,3,4-tetraarylbenzenes, a series of optimization studies for compound **12c** was carried out by varying reaction conditions and by changing inorganic bases such as NaH, KOH, K_2CO_3, LDA, *t*-BuOK. Only the potassium hydroxide and *t*-BuOK in various solvents were resulted in the formation of 1,2,3,4-tetraarylbenzenes, rest of the bases was found to be unsuitable. The optimization results are summarized in Table 1.



12	R^1	R^2	R^3	R^4	Yield (%)
a	H	H	H	H	60
b	H	H	H	Cl	58
c	H	H	OMe	OMe	66
d	H	OMe	OMe	OMe	61
e	OMe	OMe	H	Cl	59
f	OMe	OMe	H	H	63
g	OMe	OMe	OMe	OMe	69

Scheme 4. Synthesis of 1,2,3,4-triarylbenzenes.

Table 1. Various reactions conditions for the synthesis of a 1,2,3,4-tetraarylbenzene **12c**

Entry	Base[a]	Solvent	Temp	Duration	Yield (%)
1	KOH	DMF	RT	5h	29
2	KOH	DMSO	RT	6h	20
3	KOH	Pyridine	reflux	40h	66[b]
4	KOH	Toluene	reflux	20h	17
5	KOH	Fluoro-benzene	reflux	40h	0
6	t-BuOK	THF	reflux	30h	19

[a]1.2 Equivalents of bases was used in all the reactions. [b]Isolated yield is reported considering the total consumption of lactone **3**.

It is interesting to note (Table 1) that the KOH-pyridine combination was found to the best condition observed (Entry 3: yield: 66%) for the preparation of a 1,2,3,4-tetraarylbenzene. Except pyridine, other solvents were resulted in a mixture of side products. In the case of pyridine, no side product was obtained and the 1,2,3,4-tetraarylbenzene was the sole product. A series of 1,2,3,4-tetraarylbenzenes **12a-g** was prepared in 58-69% yields by stirring a mixture of substituted 5,6-diaryl-2*H*-pyran-2-ones **3a,b,d** with functionalized deoxybenzoins **2** in the presence of KOH in pyridine as shown in Scheme 4. All the synthesized compounds were characterized by spectroscopic analyses. It is worth pointing out that these arylated-benzenes are prepared in just two-steps through easily accessible precursors. This methodology is highly simple and economical compare to palladium-catalyzed classical approaches used today.

X-ray Crystal Structure Analysis.

In order to study the conformational arrangments of peripheral rings of the polyarylbenzenes, which has been a matter of several studies,[18c,e,32] a compound from the series of 1,2-diaryl-, and 1,2,3,4-tetraarylbenzene was crystallized for X-ray structural studies. Diffraction-quality crystals of compounds **4e** and **12c** were obtained by slow evaporation at room temperature. The conformations of compounds **4e** and **12c** together with arbitrary numbering are shown as ORTEP diagrams in Fig. 1, which indicates propeller like conformation for peripheral aryl rings with respect to a central benzene ring. The selected torsion angles and mean-plane angles between the central benzene ring and peripheral aryl rings of the compounds **4e** and **12c** are shown in Table 2.

The structural analysis[33] of compound **4e** revealed that the average mean plane angle for the twist of the phenyl rings from the plane of the central benzene was 59.34°. The crystal packing of **4e** showed a soft C-H…π interaction involving atom C21-H21B and the centroid of the central benzene ring of another molecule (Symmetry code: x, -1+y, z) with parameters [H21B…Cg (ring C): 2.88 Å, C21…Cg (ring C): 3.836(4) Å, C21-H21B…Cg (ring C): 170°]. The X-ray structure further revealed the presence of a network of strong intermolecular H-bonding N1-H1B…O2 with hydrogen bonding parameters [N1-H1B...O2 (x, y, -1+z), H1B…O2: 2.39 Å, N1…O2: 3.020 (3) Å, and N1-H1B-O2: 131°] and C21-H21C….N3 with H-bonding parameters [C21-H21C…N3 (1-x, -y 1-z), H 21C…N3: 2.57 Å, C21…N3: 3.495 (6) Å, C21-H21C-N3: 161°].

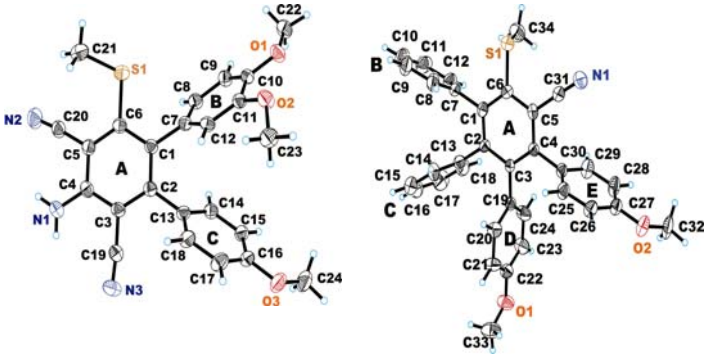


Figure 1. ORTEP diagrams of 1,2-diarylbenzene (**4e**) and 1,2,3,4-tetraarylbenzene (**12c**) with arbitrary numbering. Thermal ellipsoids are drawn at the 50% probability level. The central ring is marked as A-ring and the peripheral rings are marked consecutively as B, C, D, and E-rings.

Table 2: Selected Torsion and Twist angles for the compounds **4e** and **12c**

Comp	Atoms	Torsion angles	Mean plane angle (twist angle)	
4e	C6-C1-C7-C8	-59.5 (4)	Ring A - Ring B	57.3 (1)
	C1-C2-C13-C14	-59.6 (4)	Ring A - Ring C	61.3 (1)
12c	C6-C1-C7-C8	-80.8 (6)	Ring A - Ring B	79.6 (2)
	C1-C2-C13-C14	-79.7 (7)	Ring A - Ring C	79.7 (1)
	C2-C3-C19-C20	-74.9 (6)	Ring A - Ring D	78.9 (2)
	C3-C4-C25-C26	-83.2 (7)	Ring A - Ring E	80.4 (1)

Similarly the X-ray structure analysis[33] of compound **12c** showed that the dihedral angles between peripheral and the central benzene ring ranges from 75° to 83°. The average mean plane angle of the phenyl rings (rings B, C, D, E) from the plane of the central benzene was found to be 79.7°, which showed that the peripheral rings are arranged nearly orthogonal to the central benzene ring, which was found to be ~15° higher compare to hexaarylbenzene. As a consequence, the four π-frameworks are arranged in propeller-like fashion. The crystal packing of **12c** showed C-H...π interaction involving atom C17-H17 and the centroid of another benzene molecule (symmetry code: 1/2-x, 1-y, -1/2+z) with parameters [H17...Cg (ring B): 2.99 Å, C17…Cg (ring B): 3.602(6) Å, C17-H17…Cg (ring B): 125°]. It is highly interesting to note that the crystal structure analysis of compound **12c** showed "N…π interaction" (face lone pair-π interaction) as shown in Figure 2.

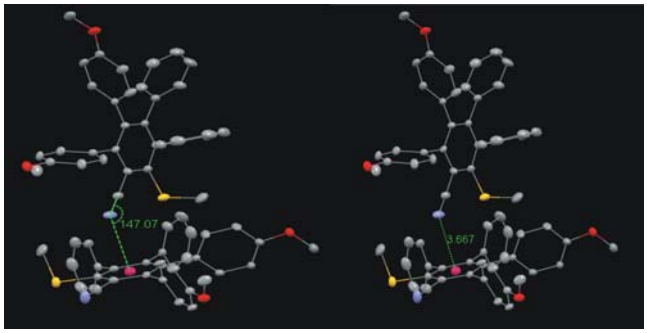


Figure 2. The crystal packing ellipsoid diagram of **12c** showing "N…π" interaction with neighbouring molecule. The *sp*-hybidized nitrogen of a cyano group (N1) is interacting directly with the face of the central benzene ring of another molecule with

C-N…benzene centroid distance of 3.668 Å with parameters [C31-N1…Cg (ring A): 3.6675 Å, CN1-Cg (ring A): 147°] and with symmetry code: [-1/2+x, 1/2-y, 2-z]. Atoms are colored as carbon-off-white; oxygen-red, nitrogen-blue and sulfur-yellow.

There are several reports on C-H…π,[34] N-H…π,[35] S…π[36] and O…π(lone pair-π)[37] interactions, but little attention has been focused on describing N…π interactions.[38] A critical Cambridge Structural Database (CSD) search (ConQuest 1.8) on such N…π interactions (Fig. 3) revealed that in most of the cases, the nonbonded distances were greater than the van der Waals summation of N and π-contact (3.3 Å). In approximately 150 hits, the observed range for N…π interactions was found to be 2.9 to 4.1 Å with no selectivity in directionality and most of the interactions were angled close to 125°. The crystal packing of **12c** (Fig. 4) revealed that lone pair of *sp*-hybridized nitrogen of a cyano group is interacting with the face of the central benzene ring at a distance of 3.667 Å with an angle of 147° showing N...π interaction between molecules related by a two-fold screw axis running in a direction.

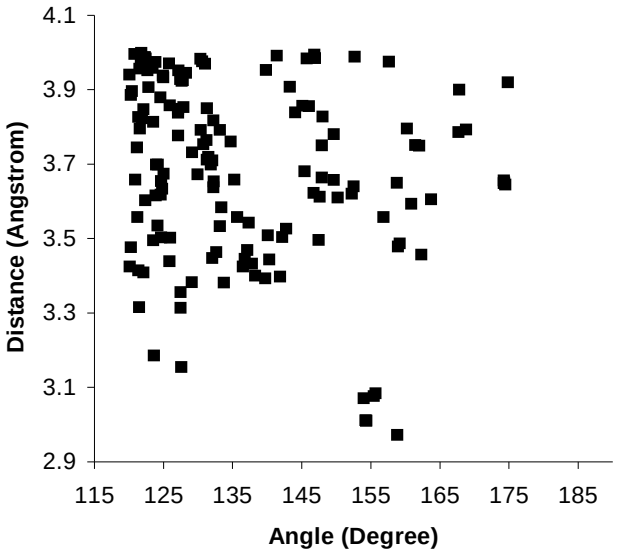


Figure 3. Scatter plot showing N…π interactions. Each black square represents a hit obtained by CSD search on N…π interactions.

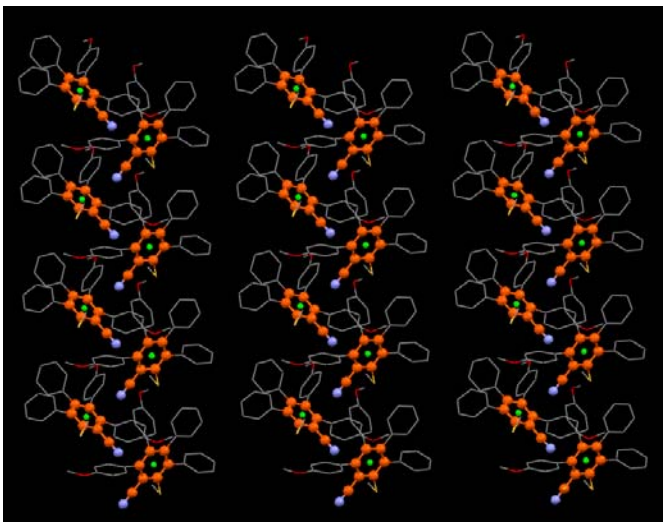


Figure 4. The crystal packing diagram of **12c** showing N...π interaction between molecules related by a two-fold screw axis running in a direction. The dihedral angle between a central benzene ring and the neighbouring central benzene ring is 70°. Central benzene rings are colored (carbon-orange, nitrogen-blue and centroid-green) for clarity. Hydrogens are omitted for clarity.

The mean plane angle between a central benzene ring and the below neighbouring central benzene ring was found to be 70°. The cyano-group containing central benzene rings are colored (carbon-orange, nitrogen-blue and centroid-green) for clarity. It is interesting that the repeat of the N…π interaction around the axis of the 1,2,3,4-tetraarylbenzene **12c** enforces the molecule in a helical-type packing as shown in Fig. 4. In the crystal lattice of **12c**, these helices are connected with each other through H…H intermolecular short contacts.

Conclusion

In summary, we have demonstrated a new synthetic approach for preparing functionally crowded 1,2-diaryl-, 1,2,3- and 1,2,4-triaryl- and 1,2,3,4-tetraarylbenzenes from ketene-*S*,*S*-acetals using readily available substrates in just two steps in good to excellent yields. This methodology have several advantages over classical metal-assisted aryl-aryl coupling reactions such as: i) highly simple reaction process; ii) flexibility of introducing electron-donor or acceptor groups even at sterically demanding *ortho*-positions, iii) does not require expensive organometallic reagent or catalyst, iv) versatile approach for generating molecular diversity, and v) high yield of aromatic compounds. X-ray structural analysis of a 1,2,3,4-tetraarylbenzene **12c** revealed a 'N…π interaction', in which lone pair of a *sp*-hybridized nitrogen atom is interacting to the face of a central benzene ring of neighbouring molecule with a distance of 3.668 Å.

Experimental Section

Mps were determined on Büchi-530 apparatus in an open capillary and are uncorrected. The reagent grade reaction solvent DMF was further purified and dried following the literature procedure. TLC was performed on precoated silica gel plastic plates and visualized by UV irradiation. IR spectra of solid samples were run as KBr pellets on a Perkin-Elmer AC-1 instrument. ^{1}H NMR spectra were recorded at 200 MHz (Bruker WM-200) in $CDCl_3$ with tetramethylsilane as internal reference. Chemical shifts and coupling constants *J* are reported in δ (ppm) and Hz respectively. Mass spectra were collected at 70 eV using Jeol JMS-300 spectrometer.

General procedure for the synthesis of 2-Cyano-3,3-bis-methylsulfanyl-acrylic acid methyl ester (1): To an ice-chilled solution of sodium hydride (10.08g a 60% oil suspension, 0.42 mol) in THF, methyl cyanoacetate (35.2 mL, 0.4 mol) was added drop wise to the cold solution for a period of 15min. After complete addition of methyl cyanoacetate, the resulting white semisolid material was vigorously stirred for another 15 min. To this solution, carbon disulfide (25.33 mL, 0.4 mol) was added drop wise while the mixture was kept below 20 °C. The reaction mixture was slowly changed from white semisolid to yellow liquid. Methyl iodide (62.55 ml, 1 mol) was added dropwise to the stirred solution over a period of 30 min. After the mixture was stirred for another 15 min. at room temp., THF was removed under reduced pressure. A small amount of crushed ice was added to consume unreacted NaH and then the residue was poured into ice-cold water with constant stirring. The white crystalline compound was filtered, washed with cold water, dried and recrystallized with ethyl acetate-hexane (1:4) as white needles. 72.54g (89.33%); mp: 52°C.

General procedure for the synthesis of 3a-f: A mixture of ethyl 2-cyano-3,3-dimethylsulfanylacrylate **1** (10 mmol), deoxybenzoin (11 mmol) and powdered KOH (12 mmol) in dry DMSO (50 mL) was stirred at room temperature for 10-14h. After completion, the reaction mixture was poured into ice water with constant stirring. The precipitate thus obtained was filtered and purified on a silica gel column using chloroform as eluent.

4-Methylsulfanyl-2-oxo-5,6-diphenyl-2*H*-pyran-3-carbonitrile (3a): White solid; mp 160-162 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.85 (s, 3H, SCH_3), 7.15-7.23 (m, 6H, ArH), 7.29-7.41 (m, 4H, ArH); IR (KBr) 1725 (CO), 2221 cm^{-1} (CN); MS (FAB) 320 (M^++1).

6-(4-Methoxy-phenyl)-4-methylsulfanyl-2-oxo-5-phenyl-2*H*-pyran-3-carbonitrile (3b): Yellow solid; mp 184-186 ^{0}C ; ^{1}H NMR (200 MHz, $CDCl_3$+CCl_4) δ 2.86 (s, 3H, SCH_3), 3.78 (s, 3H, OCH_3), 6.69 (d, J = 9.0 Hz, 2H, ArH), 7.08-7.25 (m, 7H, ArH); IR (KBr) 1713 (CO), 2220 cm^{-1} (CN); MS (FAB) 350 (M^++1).

6-(2,4-Dimethoxy-phenyl)-5-(4-fluoro-phenyl)-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (3c) : Yellow solid; mp 176-177 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$+CCl_4) δ 2.85 (s, 3H, SCH_3), 3.60 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.20 (s, 1H, ArH), 6.32 (d, J = 8.4 Hz, 1H, ArH), 6.88-7.07 (m, 5H, ArH); IR (KBr) 1727 (CO), 2219 cm^{-1} (CN); MS (FAB) 398 (M^++1).

5,6-Bis-(4-methoxy-phenyl)-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (3d): Yellow solid; mp 176-177 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.83 (s, 3H, SCH_3), 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.70 (d, J = 8.8 Hz, 2H, ArH), 6.92 (d, J = 8.8 Hz, 2H, ArH), 7.08 (d, J = 8.8 Hz, 2H, ArH), 7.22 (d, J = 8.8 Hz, 2H, ArH); IR (KBr) 1718 (CO), 2217 cm^{-1} (CN); MS (FAB) 380 (M^++1).

5-(2,4-Dimethoxy-phenyl)-6-(4-methoxy-phenyl)-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (3e): Yellow solid; mp 181-182 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.84 (s, 3H, SCH_3), 3.78 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.66-6.75 (m, 4H, ArH), 6.89 (d, J = 8.2 Hz, 1H, ArH), 7.25 (d, J = 8.2 Hz, 2H, ArH); IR (KBr) 1721 (CO), 2219 cm^{-1} (CN); MS (FAB) 410 (M^++1).

5-(4-Fluoro-phenyl)-6-(4-methoxy-phenyl)-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile (3f) :Yellow solid; mp 158-160 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.86 (s, 3H, SCH_3), 3.77 (s, 3H, OCH_3), 6.66 (d, J = 9.0 Hz, 2H, ArH), 7.04-7.20 (m, 6H, ArH); IR (KBr) 1713 (CO), 2220 cm^{-1} (CN); MS (FAB) 368 (M^++1).

General procedure for the synthesis of 4a-f: A mixture of 4-methylsulfanyl-2-oxo-5,6-diphenyl-2H-pyran-3-carbonitrile 3a-f (1 mmol), malononitrile (1 mmol) and powdered KOH (1.2 mmol) in dry DMF (5 mL) was stirred at room temperature for 6-8h. At the end reaction mixture was poured into ice water with vigorous stirring and finally neutralized with dilute HCl. The solid thus obtained was filtered and purified on a neutral alumina column using chloroform-hexane (1:4) as eluent.

4'-Amino-6'-methylsulfanyl-[1,1';2',1'']terphenyl-3',5'-dicarbonitrile (4a): White solid; mp 198-200 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.27 (s, 3H, SCH_3), 5.31 (brs, 2H, NH_2), 6.93-6.96 (m, 2H, ArH), 7.00-7.04 (m, 2H, ArH), 7.15-7.22 (m, 6H, ArH); ^{13}C (200 MHz, $CDCl_3$) δ 19.67 (SCH_3), 97.92, 100.83, 115.77 (CN), 115.9 (CN), 127.85, 128.21, 128.41, 128.87, 129.57, 131.31, 135.19, 137.18, 147.73, 150.03, 152.03; IR (KBr) 2219 (CN), 3353, 3468 cm^{-1} (NH_2); MS (FAB) 342 (M^++1).

4'-Amino-4''-methoxy-6'-methylsulfanyl-[1,1';2',1'']terphenyl-3',5'-dicarbonitrile (4b): White solid; mp 240-242 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.26 (s, 3H, SCH_3), 3.74 (s, 3H, OCH_3), 5.29 (brs, 2H, NH_2), 6.71 (d, J = 8.6 Hz, 2H, ArH), 6.94 (d, J = 8.2 Hz, 4H, ArH), 7.17-7.20 (m, 3H, ArH); ^{13}C (200 MHz, $CDCl_3$) δ 19.63 (SCH_3), 55.54 (OCH_3), 98.16, 100.60, 113.87, 115.79 (CN), 116.10 (CN), 127.79, 128.26, 129.34, 131.04, 131.33, 135.49, 137.35, 149.85, 151.97, 159.95; IR (KBr) 2214 (CN), 3348, 3464 cm^{-1} (NH_2); MS (FAB) 372 (M^++1).

4'-Amino-4-fluoro-2'',4''-dimethoxy-6'-methylsulfanyl-[1,1';2',1'']terphenyl-3',5'-dicarbonitrile (4c): White solid; mp 238-240 ^{0}C ; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.28 (s, 3H, SCH_3), 3.64 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 5.22 (brs, 2H, NH_2), 6.31 (d, J = 8.0 Hz, 1H, ArH), 6.71 (d, J = 8.0 Hz, 1H, ArH), 6.84-6.90 (m, 4H, ArH), 7.17 (d, J = 8.0 Hz, 1H, ArH); IR (KBr) 2214 (CN), 3348, 3464 cm^{-1} (NH_2); MS (FAB) 420 (M^++1).

4'-Amino-4,4''-dimethoxy-6'-methylsulfanyl-[1,1';2',1'']terphenyl-3',5'-dicarbonitrile (4d): White solid; mp 220-222 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.27 (s, 3H, SCH_3), 3.76 (s, 6H, $2OCH_3$), 5.25 (brs, 2H, NH_2), 6.69-6.76 (m, 4H, ArH), 6.85 (d, J = 8.8 Hz, 2H, ArH), 6.95 (d, J = 8.8 Hz, 2H, ArH); IR (KBr) 2209 (CN), 3347, 3423 cm^{-1} (NH_2); MS (FAB) 402 (M^++1).

4'-Amino-3,4,4''-trimethoxy-6'-methylsulfanyl-[1,1';2',1'']terphenyl-3',5'-dicarbonitrile (4e) : White solid; mp 202-204 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 3H, SCH_3), 3.65 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.27 (brs, 2H, NH_2), 6.38 (s, 1H, ArH), 6.54 (d, J = 8.0 Hz, 1H, ArH), 6.69-6.76 (m, 3H, ArH), 6.92-6.96 (m, 2H, ArH); IR (KBr) 2216 (CN), 3350, 3466 cm^{-1} (NH_2); MS (FAB) 432 (M^++1).

4'-Amino-4-fluoro-4''-methoxy-6'-methylsulfanyl-[1,1';2',1'']-terphenyl-3',5'-dicarbonitrile (4f): White solid; mp 224-226 ^{0}C ; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 3H, SCH_3), 3.76 (s, 3H, OCH_3), 5.29 (brs, 2H, NH_2), 6.74 (d, J = 8.6 Hz, 2H, ArH), 6.88-6.92 (m, 6H, ArH); IR (KBr) 2219 (CN), 3349, 3470 cm^{-1} (NH_2); MS (FAB) 390 (M^++1).

2'''-Hydroxy-4'''-methoxy-4-methyl-5'-(piperidin-1-yl)-[1,1';2',1'';3', 1''']quarter-phenyl-4'-carbonitrile (8a) : Yellow crystalline solid; mp 188-189 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.64-1.68 (m, 2H, CH_2), 1.78-1.84 (m, 4H, $2CH_2$), 2.28 (s, 3H, CH_3), 3.25-3.30 (m, 4H, $2CH_2$), 3.76 (s, 3H, OCH_3), 6.25 (dd, J = 9.2 & 2.6 Hz, 1H, ArH), 6.58 (d, J = 9.2 Hz, 1H, ArH), 6.73 (d, J = 2.6 Hz, 1H, ArH), 6.85-7.04 (m, 7H, ArH), 7.17-7.21 (m, 3H, ArH); IR (KBr) 2218 cm^{-1} (CN); MS (FAB) 475 (M^++1).

2'''-hydroxy-4'''-methoxy-4-thienyl-5'-(piperidin-1-yl)-[1,1';2',1'';3', 1''']quarter-phenyl-4'-carbonitrile (8b): Yellow crystalline solid; mp 211-212 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.61-1.64 (m, 2H, CH_2), 1.79-1.84 (m, 4H, $2CH_2$), 3.24-3.32 (m, 4H, $2CH_2$), 3.77 (s, 3H, OCH_3), 6.26 (dd, *J* = 9.2 & 2.6 Hz, 1H, ArH), 6.56-6.65 (m, 2H, ArH), 6.73 (d, *J*=2.6 Hz, 1H, ArH), 6.80-6.86 (m, 1H, ArH), 6.95-7.01 (m, 1H, ArH), 7.10-7.16 (m 2H, ArH), 7.16-7.22 (m, 2H, ArH), 7.27-7.34 (m, 2H, ArH); IR (KBr) 2218 cm^{-1} (CN); MS (FAB): *m/z* 468 (M^++1).

4-Floro-4'',4'''-dimethoxy-5'-(piperidin-1-yl)-[1,1';2',1'';3',1''']quaterphenyl-4'-carbonitrile (8c): White solid; mp 128-129 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.59-1.63 (m, 2H, CH_2), 1.79-1.84 (m, 4H, $2CH_2$), 3.20-3.27 (m, 4H, $2CH_2$), 3.68 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.49 (d, *J* = 8.8 Hz, 2H, ArH), 6.56 (d, *J* = 8.8 Hz, 2H, ArH), 6.73 (d, *J* = 8.8 Hz, 2H, ArH), 6.87-7.08 (m, 5H, ArH), 7.27-7.33 (m, 2H, ArH); IR (KBr) 2217 cm^{-1} (CN); MS (FAB): *m/z* 492 (M^++1).

4'',4'''-Dimethoxy-4-(naphthalene-1-yl)-5'-(piperidin-1-yl)-[1,1';2',1'';3', 1''']quaterphenyl-4'-carbonitrile (8d) : White solid; mp 170-171^{0}C; ^{1}H NMR(200 MHz, $CDCl_3$): δ 1.58-1.64 (m, 2H, CH_2), 1.77-1.83 (m, 4H, $2CH_2$), 3.22-3.31 (m, 4H, $2CH_2$), 3.61 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.43 (d, *J* = 8.7 Hz, 2H, ArH), 6.65 (d, *J* = 8.7 Hz, 2H, ArH) 6.74 (d, *J* = 8.7 Hz, 2H, ArH), 6.98-7.11 (m, 4H, ArH), 7.41-7.53 (m, 3H, ArH), 7.67-7.74 (m, 3H, ArH); IR (KBr) 2215 cm^{-1} (CN); MS (FAB): *m/z* 524 (M^++1).

5,6-Diphenyl-4-methylsulfanyl-2-oxo-2H-pyran-3-carboxylic acid methyl ester (9a): White solid; mp 162-164 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.25 (s, 3H, SCH_3), 3.93 (s, 3H, OCH_3), 7.10-7.35 (m, 10H, ArH); IR (KBr) 1693 (CO), 1722 cm^{-1}(CO); MS (FAB) 353 (M^++1).

5,6-Bis-(4-methoxyphenyl)-4-methylsulfanyl-2-oxo-2H-pyran-3-carboxylic acid methyl ester (9b): Yellow solid; mp 218-220 ^{0}C ; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.27 (s, 3H, SCH_3), 3.76 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 6.69 (d, J = 8.8 Hz, 2H, ArH), 6.90 (d, J = 8.8 Hz, 2H, ArH), 7.11 (d, J = 8.8 Hz, 2H, ArH), 7.20 (d, J = 8.8 Hz, 2H, ArH); IR (KBr) 1695 (CO), 1737 cm^{-1} (CO); MS (FAB) 413 (M^++1).

3'-Methoxy-6'-methylsulfanyl-[1,1';2',1'';4',1''']quaterphenyl-5'-carbonitrile (11a): White solid; mp 186-188 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.23 (s, 3H, SCH_3), 3.00 (s, 3H, OCH_3), 7.00-7.07 (m, 4H, ArH), 7.12-7.22 (m, 6H, ArH), 7.43-7.60 (m, 5H, ArH); IR (KBr) 2222 (CN) cm^{-1}; MS (FAB) 408 (M^++1).

4'-Methyl-6'-methylsulfanyl-3',4,4''-trimethoxy-[1,1';2',1'';4',1''']quaterphenyl-5'-carbonitrile (11b): White solid; mp 226-228 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.21 (s, 3H, SCH_3), 2.98 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.66-6.79 (m, 4H, ArH), 6.96 (d, J = 8.6 Hz, 4H, ArH), 7.42-7.55 (m, 5H, ArH); IR (KBr) 2221 (CN) cm^{-1}; MS (FAB) 468 (M^++1).

3'-Methoxy-6'-methylsulfanyl-[1,1';2',1'';4',1''']quaterphenyl-5'-carboxylic acid methyl ester (11c): White solid; mp 188-190 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.00 (s, 3H, SCH_3), 2.99 (s, 3H, OCH_3), 3.62 (s, 3H, $COOCH_3$), 7.05-7.16 (m, 9H, ArH), 7.36-7.49 (m, 6H, ArH); IR (KBr) 1731 (CO) cm^{-1}; MS (FAB) 440 (M^+).

4'-Methyl-6'-methylsulfanyl-3',4,4''-trimethoxy-[1,1';2',1'';4',1''']-quaterphenyl-5'-carboxylic acid methyl ester (11d): White solid; mp 196-198 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.98 (s, 3H, SCH_3), 2.98 (s, 3H, OCH_3), 3.61 (s, 3H, $COOCH_3$), 3.74 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.65-6.76 (m, 4H, ArH), 6.92-7.05 (m, 4H, ArH), 7.36-7.47 (m, 5H, ArH); IR (KBr) 1731 (CO) cm^{-1}; MS (FAB) 500 (M^+).

6'-Methylsulfanyl-[1,1';2',1'';3',1''';4',1''']quinquephenyl-5'-carbonitrile (12a): White solid; mp 216-218 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.34 (s, 3H, SCH_3), 6.64-6.67 (m, 5H, ArH), 6.81-6.90 (m, 6H, ArH), 7.01-7.25 (m, 9H, ArH); IR (KBr) 2224 cm^{-1} (CN); MS (FAB) 454 (M^++1).

4'''-Chloro-6'-methylsulfanyl-[1,1';2',1'';3',1''';4',1''']-quinquephenyl-5'-carbonitrile (12b): White solid; mp 248-250 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H, SCH_3), 6.62-6.80 (m, 3H, ArH), 6.83-6.93 (m, 6H, ArH), 7.00-7.09 (m, 2H, ArH), 7.12-7.35 (m, 8H, ArH); IR (KBr) 2215 cm^{-1} (CN); MS (FAB) 488 (M^++1).

4''',4''''-Dimethoxy-6'-methylsulfanyl-[1,1';2',1'';3',1''';4',1'''']-quinquephenyl-5'-carbonitrile (12c): White solid; mp 210-212 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H, SCH_3), 3.61 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.42-6.46 (m, 2H, ArH), 6.58-6.86 (m, 10H, ArH), 7.05-7.16 (m, 6H, ArH); IR (KBr) 2215 cm^{-1} (CN); MS (FAB) 514 (M^++1).

6'-Methylsulfanyl-4'',4''',4''''-trimethoxy-[1,1';2',1'';3',1''';4',1''']-quinquephenyl-5'-carbonitrile (12d): White solid; mp 162-164 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H, SCH_3), 3.61 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.40 (d, J = 8.6 Hz, 2H, ArH), 6.44 (d, J = 8.6 Hz, 2H, ArH), 6.56-6.63 (m, 4H, ArH), 6.76 (d, J = 8.6 Hz, 2H, ArH), 7.04-7.10 (m, 4H, ArH), 7.17-7.20 (m, 3H, ArH); IR (KBr) 2214 cm^{-1} (CN); MS (FAB) 544 (M^++1).

4''''-Chloro-4,4''-dimethoxy-6'-methylsulfanyl-[1,1';2',1'';3',1''';4',1''']-quinquephenyl-5'-carbonitrile (12e): White solid; mp 222-224 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H, SCH_3), 3.61 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.41 (d, J = 8.4 Hz, 2H, ArH), 6.58 (d, J = 8.4 Hz, 2H, ArH), 6.68-6.76 (m, 4H, ArH), 6.90-7.98 (m, 5H, ArH), 7.09 (d, J = 8.4 Hz, 2H, ArH), 7.20 (d, J = 8.4 Hz, 2H, ArH); IR (KBr) 2214 cm^{-1} (CN); MS (FAB) 548 (M^++1).

4,4''-Dimethoxy-6'-methylsulfanyl-[1,1';2',1'';3',1''';4',1''']-quinquephenyl-5'-carbonitrile (12f): White solid; mp 202-204 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H, SCH_3), 3.61 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.42 (d, J = 8.6 Hz, 2H, ArH), 6.62 (d, J = 8.6 Hz, 2H, ArH), 6.69-6.87 (m, 8H, ArH), 7.02-7.18 (m, 6H, ArH); IR (KBr) 2215 cm^{-1} (CN); MS (FAB) 514 (M^++1).

6'-Methylsulfanyl-4,4'',4''',4''''-tetramethoxy-[1,1';2',1'';3',1''';4',1''']-quinquephenyl-5'-carbonitrile (12g): White solid; mp 218-220 ^{0}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H, SCH_3), 3.63 (s, 6H, $2OCH_3$), 3.76 (s, 6H, $2OCH_3$), 6.39-6.45 (m, 4H, ArH), 6.56-6.62 (m, 4H, ArH), 6.70-6.78 (m, 4H, ArH), 6.95 (d, J = 8.6 Hz, 2H, ArH) 7.07 (d, J = 8.6 Hz, 2H, ArH); ^{13}C (200 MHz, $CDCl_3$) 20.16 (SCH_3), 55.32 (OCH_3), 55.48 (OCH_3), 112.88, 113.02, 113.27, 113.76, 118.11 (CN), 118.81, 130.82, 131.26, 131.63, 131.86, 132.01, 132.31,139.80, 142.42, 146.21, 146.48, 146.75, 157.87, 158.64, 159.31; IR (KBr) 2219 cm^{-1} (CN); MS (FAB) 574 (M^++1).

X-ray Structure Determination: Unit cell determination and intensity data collection (2θ= 50°) was performed on a Bruker P4 diffractometer at 293(2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F^2. Programs: XSCANS [Siemens Analytical X-ray Instrument Inc.: Madison, Wisconsin, USA 1996], SHELXTL-NT [Bruker AXS Inc.: Madison, Wisconsin, USA 1997]; PLATON, A. L. Spek, Utrecht University, Utrecht, Netherlands; 2004. MERCURY, Version 1.4. CCDC Nos. **4e:** 298046 and **12c:** 298045 contains the supplementary crystallographic data. These data can be obtained free of charge from www.ccdc.cam.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U. K; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk

Crystal data of compound 4e: Mol. Formula: $C_{24}H_{21}N_3O_3S$, M = 431.5, triclinic, space group P (–1) , a = 10.228(1) Å, b = 10.325(1) Å, c = 11.575(2) Å, α = 101.05 (1) °, β = 109.11 (10)°, γ = 102.63(1)°, V = 1080.1(2) Å^3, Z = 2, D_c = 1.327 g cm^{-3}, μ (Mo-Kα) = 0.181 mm^{-1}, F(000) = 452, yellow, rectangular block, size = 0.23 x 0.20 x 0.10 mm, 4374 reflections measured (R_{int} = 0.0266), 3717 unique, $wR_{2\ =}$ 0.1415 for all data, conventional R = 0.0487 [$(\Delta/\sigma)_{max}$ = 000)] on 2064 reflections with I>2σ(I), S = 1.021 for all data and 284 parameters.

Crystal data of compound 12c: Mol. Formula: $C_{34}H_{27}NO_2S$, M = 513.63, Orthorhombic, $P2_12_12_1$, a = 8.787 (1) Å, b = 17.177 (2) Å, c = 18.374 (2) Å, V = 2773.3 (5) Å^3, Z = 4, D_c = 1.23 g cm^{-3}, μ (Mo-Kα) = 0.148 mm^{-1}, F(000)= 1080, colourless block, crystal dimensions 0.23 x 0.23 x 0.10 mm, 3579 reflections measured (R_{int} = 0.0385), 3374 unique, wR2 = 0.1184 for all data, R = 0.0504 [$(\Delta/\sigma)_{max}$ = 000)] on 1590 reflections with I>2σ(I), S = 0.958 for all data and 346 parameters.

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