The Free Internet Journal for Organic Chemistry

Paper

Archive for Organic Chemistry

Arkivoc **2018**, part v, 0-0

to be inserted by editorial office

Insights into the triple self-condensation reaction of thiophene-based methyl ketones and related compounds

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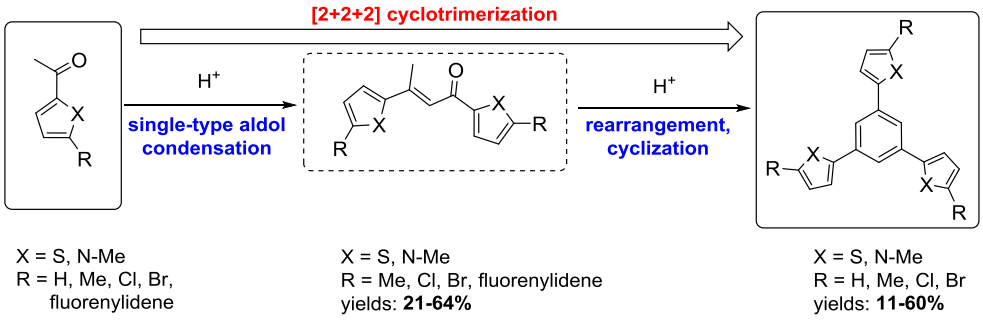
Received 02-05-2018 **Accepted** 04-14-2018 **Published on line** 06-09-2018

Abstract

The acid catalysed triple self-condensation of 1-thien-2-ylethanone (2-acetylthiophene) and five related compounds is presented. Tetrachlorosilane used as the Lewis acid produces dry hydrogen chloride which catalyzes the self-condensation process. Depending on the reaction conditions and the substitution of the carbonyl substrates, the reaction can proceed as a [2+2+2] cyclotrimerization towards C_3-symmetric 1,3,5-trisubstituted benzenes, or as the single-type aldol condensation leading to 1,3-disubstituted (*E*)-*β*-methylchalcones. This is important for the design of new aromatic/olefinic compounds beyond the model structures. Synthesis of 4′-fluoro-3,5-di-(2-thienyl)biphenyl through a mixed-type aldol reaction using erbium triflate is discussed. Mechanistic rationale is provided.



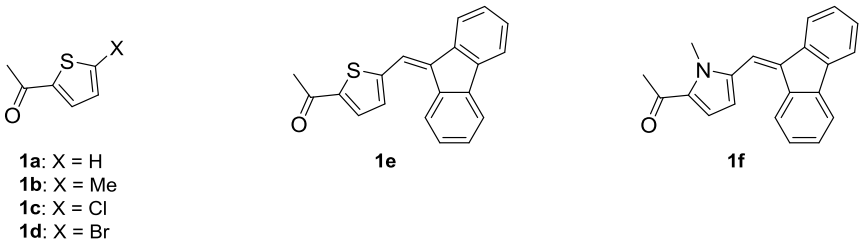
Keywords: [2+2+2] Cyclotrimerization, aldol condensation, 1,3,5-trisubstituted benzene, *β*-methylchalcone

Introduction

Star-shaped molecules based on 1,3,5-triarylbenzenes have long been recognized as a family of amorphous glasses stable above room temperature.[1,2] The bioisosteric replacement of benzene by thiophene has extended the family of C_3-symmetric compounds[3,4] and their applications in electroluminescent (EL) devices,[5] liquid crystalline materials[6] and as fluorescent probes.[7] In contrast to polymers used in similar applications, amorphous molecular materials are pure materials with well-defined molecular structures and definite molecular weights without any distribution. Consequently, 1,3,5-tri(het)arylbenzenes serve as versatile platforms in the design of organic light emitting diodes (OLEDs),[8,9] dendrimers,[10] polycyclic aromatic hydrocarbons (PAH),[11] bulky ligands[12] and truxenes (derivatives of 10,15-dihydro-5*H*-diindeno[1,2-*a*; 1',2'-*c*]fluorene).[13] The classical one-directional convergent synthetic approach, originally developed by Clapps and Morton,[14] is that most frequently reported in the literature.

The [2+2+2] cyclotrimerization of acetophenones and related compounds is expected to have outstanding potential because of its high atom economy and broad reaction scope.[15] The triple self-condensation of starting acetophenones (AP) and hetaryl methyl ketones (HetAP) takes place mostly in ethanol using Brønsted or Lewis acids such as common $SiCl_4$,[16-20] $TiCl_4$,[21,22] *p*-TsOH[23] and variations on more complex structures.[23-28] Although these processes provide regioselective approaches to polysubstituted aromatic compounds, as has been presented in a large number of studies,[16-32] there are some limitations including low yields, long reaction times, harsh reaction conditions, use of expensive metal catalysts, tedious work-up, and formation of side products.

It is generally known that [2+2+2] cyclotrimerization involving bulky substrates is not a trivial task. The presence of a bulky substituent in the structure of the starting ketone can change the reactivity in favour of formation of appropriate (*E*)-*β*-methylchalcones (dypnones), derivatives of (*E*)-1,3-diphenyl-2-buten-1-one.[33] This is because the triple self-condensation of acetophenones (AP) or hetaryl methyl ketones (HetAP), respectively, under mild reaction conditions (ambient temperature, efficient catalysis) occurs as a stepwise process, as was independently highlighted by Wu *et al*.[34] and Wagh and Akamanchi.[35] The acid catalyzed single-type aldol condensation of two equivalents of starting carbonyl compounds AP or HetAP towards the formation of (*E*)-*β*-methylchalcones (BMC) occurs first, followed by subsequent enolizazion and rearrangement of BMC into final 1,3,5-triarylbenzenes (TAB) or 1,3,5-trihetarylbenzenes (THetAB). The bulky substitution as well as the electron-withdrawing substituents in the structure of acetophenones inhibit the second aldol reaction affording only the corresponding (*E*)-*β*-methylchalcones.[34] There are two possibilities of cyclization, *i.e*. two equivalents of (*E*)-*β*-methylchalcone reacts to create C_3-symmetric benzenes (Scheme 1, A)[34] or a molecule of the key intermediate dypnone undergo condensation with another molecule of the carbonyl substrate (Scheme 1, B).[35]

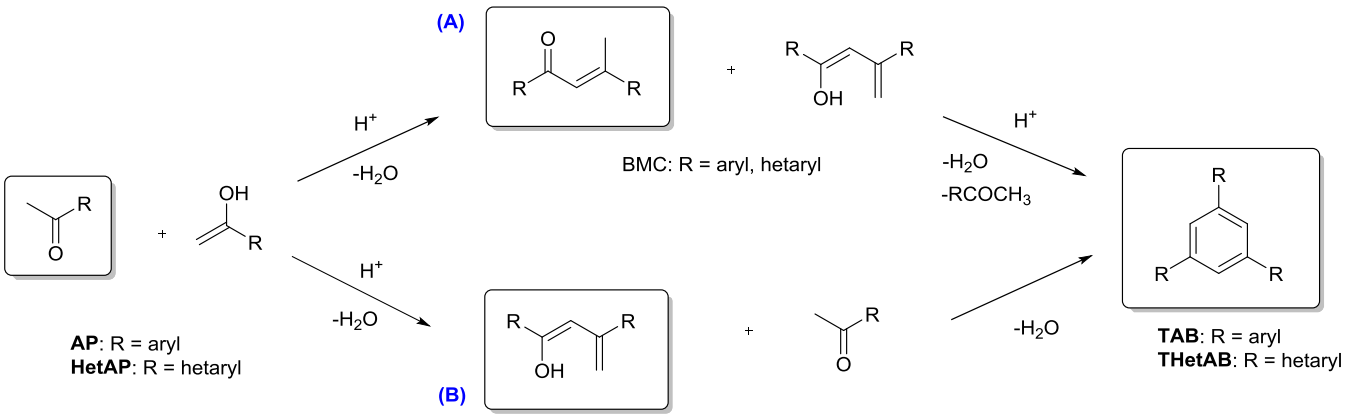


1a: X = H
1b: X = Me
1c: X = Cl
1d: X = Br

1e **1f**

Figure 1. Structures of the starting carbonyl substrates under investigation.

The formation of (*E*)-*β*-methylchalcones/dypnones during the process of cyclotrimerization is indeed underrated. Besides which, dypnone-involved organic synthesis is important further *i.e*. in a mixed-type aldol condensation towards unsymmetrically branched 1,3,5-trisubstituted benzenes,[36] in the reduction towards diols[37] or in the synthesis of allycyclic azides.[38] In this regard, we have studied the process of the triple self-condensation of hetaryl methyl ketones in the construction of either C_3-symmetric 1,3,5-trihetaryl benzenes or 1,3-bishetaryl (*E*)-*β*-methylchalcones/dypnones, or the mixture of the two possible compounds. Thien-2-yl-ethanone **1a** and its C5 methyl- and halogen-substituted derivatives **1b-d** were selected for our investigations under the different experimental conditions (Figure 1), either affecting the triple self-condensation by tetrachlorosilane ($SiCl_4$, 2-4 equiv.) combined with a solvent change (ethanol, ethanol/toluene mixture, 2-ethoxyethanol) or by use of trifluoromethanesulfonic acid as a Brønsted acid catalyst (TFSA-CF_3SO_3H, 2 mol %) in toluene. In fact, $SiCl_4$ and related weak Lewis acids in anhydrous alcohols produce controlled amount of dry hydrogen chloride (g) acting as the acid catalyst in aldol-type condensations.[39,40] Our study was extended employing 1-[5-(fluoren-9-ylidenemethyl)thien-2-yl]ethanone (**1e**) and 1-[5-(fluoren-9-ylidenemethyl)-1-methyl-1*H*-pyrrol-2-yl]ethanone (**1f**) with a bulky fluorenylidenemethyl substituent at the C5 position of the thiophene and pyrrole rings (Figure 1), to examine the effect of the substitution on the reaction. The synthesis of 1,3,5-unsymmetrically substituted benzene is presented according to a mixed-type aldol condensation of the appropriate (*E*)-*β*-methylchalcone and *p*-fluoroacetophenone.



Scheme 1. [2+2+2] Cyclotrimerization reaction of acetophenones and related compounds. Two possible routes to C_3-symmetric benzene formation are highlighted.[34,35]

Results and Discussion

Effects of solvent, temperature and reaction time

The [2+2+2] cyclotrimerization of starting ketones **1a**-**d** was carried out at room temperature (25 °C). The same approach with ketones **1e** and **1f** was conducted at 100 °C. Generally, a relatively low temperature of the triple self-condensation towards 1,3,5-triarylbenzenes has to be maintained to form thermodynamically stable enol-silyl ether reactive intermediates of the excited state followed by *in situ* formation of gaseous HCl.[17,36,41] Although in the triple self-condensation process promoted by $SiCl_4$ as the weak Lewis acid, ethanol proves to be the most universal solvent (Method A),[18,19,36,39] the solubility of some hetaryl methyl ketones **1a**-**f** in ethanol might be insufficient. Since the enhanced solubility of substrates together with the activity of tetrachlorosilane was crucial, we performed the [2+2+2] cyclotrimerization with the starting substrates **1a**-**d** in

a mixture of ethanol/toluene (Method B)[16,20] as well as by using 2-ethoxyethanol instead of ethanol (Method C). Use of a double and threefold excess of $SiCl_4$/EtOH (Method A and B) leads directly to 1,3,5-triarylbenzenes **3a**-**d**,[3] while use of excess of catalyst (4 equiv.) in 2-ethoxyethanol (Method C) gave good yields of *β*-methylchalcones **2b**-**d**.[17,36] Since, fluorenylidene-substituted hetaryl methyl ketones **1e** and **1f** were insoluble in the solvents used according to Methods A-C, we turned to Method D, performing the reaction with trifluoromethane sulfonic acid (TFSA, 2 mol %) in toluene. The optimal reaction time during which the formation of unidentifiable polymers was suppressed was 14 h with $SiCl_4$ (Methods A-C) and 30 h with CF_3SO_3H (Method D). The results on reaction conditions for **1a**-**f** are summarized in Table 1.

Table 1. The reaction conditions of [2+2+2] cyclotrimerization of thiophene-based methyl ketones **1a**-**e** and pyrrolyl substrate **1f**

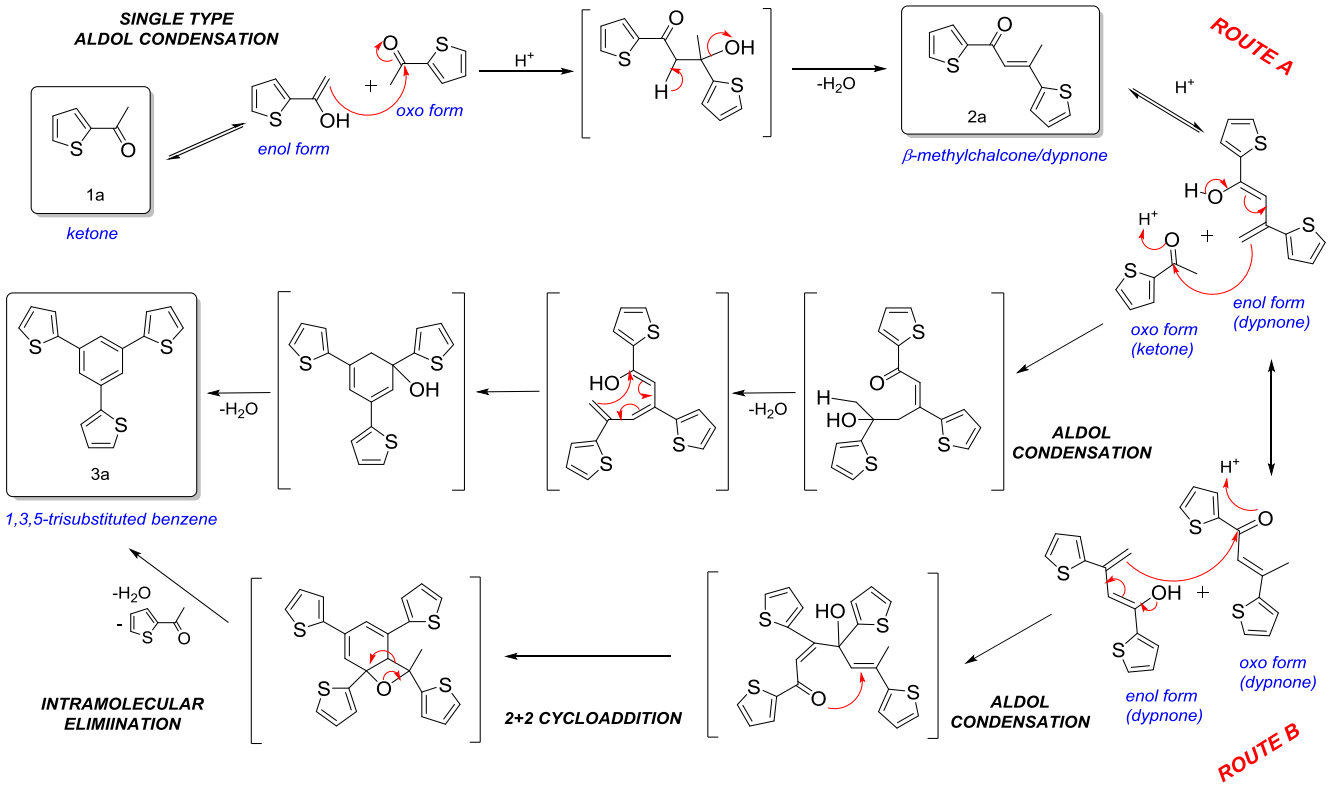
Method	Reaction conditions	Solvent	Substrat	Product / Process
Method A ref.[18,19,36,39]	$SiCl_4$ (0.078 mol, 2 equiv.), 14 h, 25 °C	EtOH	**1a**	**3a** / TSC[a]
			1b	**3b** / TSC[a]
			1c	**3c** / TSC[a]
Method B ref.[16,20]	$SiCl_4$ (0.117 mol, 3 equiv.), 14 h, 25 °C	EtOH/PhMe (50:50)	**1a**	**2a** / aldol condensation[b]
			1d	**3d** / TSC[a]
Method C	$SiCl_4$ (0.156 mol, 4 equiv.), 14 h, 25 °C	2-Ethoxyethanol	**1a**	**3a** / TSC[a]
			1b	**2b** / aldol condensation[b]
			1c	
			1d	**2c** / aldol condensation[b]
				2d / aldol condensation[b]
Method D	CF_3SO_3H (0.1 mmol, 2 mol %) 30 h, 100 °C	PhMe	**1e**	**2e** / aldol condensation[b]
			1f	**2f** / aldol condensation[b]

[a] TSC = triple self condensation of three equivalents of the starting substrates ([2+2+2] cyclotrimerization), according to results presented later in this research work; [b] Aldol condensation – single-type of aldol condensation between two molecules of the starting ketones, according to results presented later in this research work; [a, b] According to the mechanism discussed below.

Mechanism

To the best of our knowledge, two possible mechanisms of acid catalysed [2+2+2] cyclotrimerization of aryl- and hetaryl methyl ketones have been reported recently.[36,37] In both approaches, the crucial intermediate, (*E*)-*β*-methylchalcone/dypnone, was initially formed *via* the single-type aldol condensation of two equivalents of acetophenones and related compounds activated by the acid catalyst (Scheme 2).[34-36] Since (*E*)-*β*-methylchalcones/dypnones were stable compounds, in several cases they were isolated as the final products and the subsequent formation of 1,3,5-trisubstituted benzenes was not observed. The reactivity of (*E*)-*β*-methylchalcone/dypnone was crucial in the subsequent cyclization and aromatization reaction sequence, which may occur in the reaction with another amount of the starting carbonyl compound in the single-type aldol condensation (*route A*)[34] subsequently followed by intramolecular rearrangement supporting the ring closure (Scheme 2). In the second approach (*route B*)[35] the single-type aldol condensation occurs first between

two equivalents of the (*E*)-β-methylchalcone/dypnone, continuing as intramolecular [2+2] cycloaddition and subsequent retro [2+2] cycloaddition leading to 1,3,5-trisubstituted benzenes (Scheme 2). The bulky substituent may inhibit either the aldol condensation with another equivalent of the starting ketone (*route A*)[34] or the aldol addition with another equivalent of the dypnone (*route B*).[35] The dypnone's ability to precipitate from the reaction mixture as well as the solubility of the carbonyl substrate influences the process of [2+2+2] cyclotrimerization to a large extent. Again, the use of $SiCl_4$ generates -$OSiCl_3$ protected hydroxyl compounds, allowing to stop the addition at the aldol step.[17]



Scheme 2. Proposed mechanism of a triple self-condensation reaction sequence of 1-thien-2-ylethanone (**1a**).[34,35] The H^+ cation originates from dry HCl (g) which is generated *in situ* from $SiCl_4$ through the the excited state enolsilyl reactive intermediates.[17,34,41]

Self condensation *vs*. [2+2+2] cyclotrimerization of starting carbonyl compounds 1a-f

With optimized reaction conditions and insight on the mechanism, the scope of the reaction towards the formation either C_3-symmetric 1,3,5-trisubstituted benzenes *via* [2+2+2] cyclotrimerization, or (*E*)-β-methylchalcones/dypnones by the single-type aldol condensation was investigated (Table 2).

The reaction of 1-thien-2-yl-ethanone (**1a**), 1-(5-methylthien-2-yl)ethanone (**1b**) and 1-(5-chlorothien-2-yl)ethanone (**1c**) performed under the standard conditions (Method A**,** $SiCl_4$/EtOH) affording the 1,3,5-trisubstituted benzenes: 1,3,5-tris(thien-2-yl)benzene (**3a**), 1,3,5-tris(5-methylthien-2-yl)benzene (**3b**) and 1,3,5-tris-(5-chlorothien-2-yl)benzene (**3c**), respectively, in yields not exceeding 60%. The [2+2+2] cyclotrimerization of bromo-substituted derivative **1d** by Method B ($SiCl_4$, EtOH/PhMe) produced C_3-symmetric 1,3,5-trisubstituted benzene **3d** in a moderate 28% yield, probably as a result of the side polymerization reactions characteristic for bromo-derivatives of thiophenes. By alternating the solvent with 2-ethoxyethanol (Method C) for **1a**-**1d** only the reaction with **1a** proceeded as [2+2+2] cyclotrimerization leading

to 1,3,5-tris(thien-2-yl)benzene (**3a**, 35%), while in the case of its methyl-, chloro- and bromo-substituted derivatives **1c-1d** (*E*)-*β*-methylchalcones/dypnones **2b** (33%), **2c** (64%) and **2d** (31%) were isolated as a consequence of the single-type aldol condensation. 1,3-Dithienyl-substituted (*E*)-*β*-methylchalcone **2a** was finally isolated in the yield of 45% performing the reaction in EtOH/PhMe (50:50) mixture (Method B).

As expected, from the reactions carried out with the 1-(5-fluoren-9-ylidenemethyl)thien-2-yl)ethanone (**1e**) and the 1-(5-fluoren-9-ylidenemethyl-1-methyl-1*H*-pyrrol-2-yl)ethanone (**1f**), bearing the bulky fluorenylidene residues, in PhMe/TFSA (Method D) (*E*)-*β*-methylchalcones/dypnones **2e**,**f** were isolated in yield of 33% in both cases (Table 2). Concerning the substitution, the reaction with **1e**,**f** was completed as single-type aldol condensation without the formation of any C_3-symmetric benzenes.

Table 2. Summary of triple self-condensation of heterocyclic methyl ketones **1a**-**f**

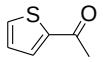
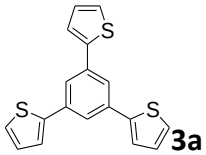
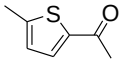
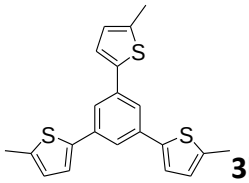
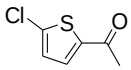
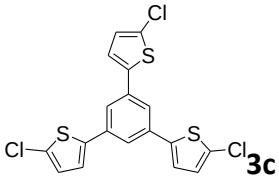
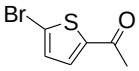
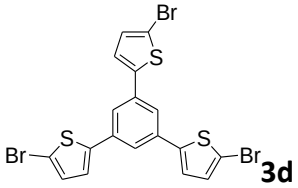
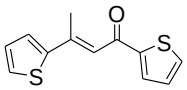
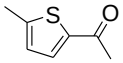
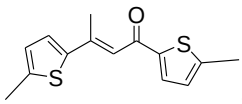
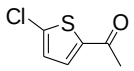
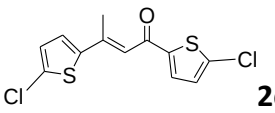
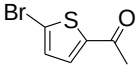
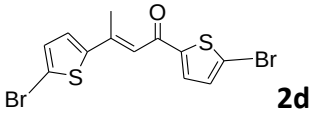
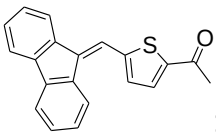
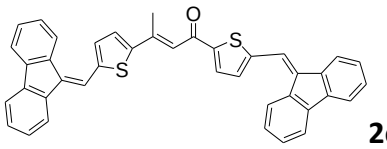
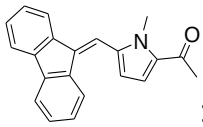
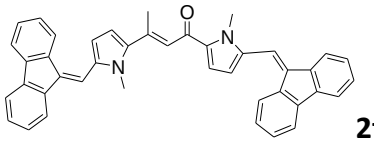
Entry	Substrate	Product	Conditions / Method / Process	Product (%)
1,2	 **1a**	 **3a**	$SiCl_4$ EtOH / 2-ethoxyethanol Method A / Method C [2+2+2] cyclotrimerization	**3a** (55%) / (35%)
3	 **1b**	 **3b**	$SiCl_4$ / EtOH Method A [2+2+2] cyclotrimerization	**3b** (58%)
4	 **1c**	 **3c**	$SiCl_4$ / EtOH Method A [2+2+2] cyclotrimerization	**3c** (58%)
5	 **1d**	 **3d**	$SiCl_4$ / EtOH/PhMe Method B [2+2+2] cyclotrimerization	**3d** (28%)
6	 **1a**	 **2a**	$SiCl_4$ / EtOH/PhMe Method B Single-type aldol condensation	**2a** (45%)
7	 **1b**	 **2b**	$SiCl_4$ / 2-ethoxyethanol Method C Single-type aldol condensation	**2b** (33%)

Table 2. Continued

Entry	Substrate	Product	Conditions / Method / Process	Product (%)
8	 **1c**	 **2c**	$SiCl_4$ / 2-ethoxyethanol Method C Single-type aldol condensation	**2c** (64%)
9	 **1d**	 **2d**	$SiCl_4$ / 2-ethoxyethanol Method C Single-type aldol condensation	**2d** (31%)
10	 **1e**	 **2e**	CF_3SO_3H / PhMe Method D Single-type aldol condensation	**2e** (33%)
11	 **1f**	 **2f**	CF_3SO_3H / PhMe Method D Single-type aldol condensation	**2f** (33%)

Effect of substitution

To examine effects of the substituent X we have compared the results of formation 1,3,5-triarylbenzene **3a**-**d** and (*E*)-*β*-methylchalcones **2a-d** from substrates **1a** (X = H), **1b** (X = Me), **1c** (X = Cl) and **1d** (X = Br) (Figure 1). Results showed that substrate **1c** possessing chlorine provided best results in both [2+2+2] cyclotrimerization approach towards 1,3,5-trisubstituted benzene **3c** as well as in a single-type aldol condensation leading to (*E*)-*β*-methylchalcone **2c** (Entries 4 and 8, Table 2). On the other hand, both types of the reaction with bromo-substituted substrate **1d** (Entries 5 and 9, Table 2) were less effective, probably due to the enhanced ability of brominated thiophenes to undergo polymerization. According to generally-accepted fact in comparison with obtained results, we can assume that electron-withdrawing effect of the halogen substituent in the *α*-position (C5) of the thiophene for substrates **1c** and **1d** (X = Cl, Br) induced the single-type aldol condensation more efficiently than the triple self-condensation process: (*E*)-*β*-methylchalcone **2c** *vs*. 1,3,5-trisubstituted benzene **3c** = 64% yield (Entry 8, Table 2) *vs*. 58% yield (Entry 4, Table 2); (*E*)-*β*-methylchalcone **2d** *vs*. 1,3,5-trisubstituted benzene **3d** = 29% yield (Entry 9, Table 2) *vs*. 31% (Entry 5, Table 2), respectively. The most significant effect of the substitution on the reaction proceeding was with subtrates **1e** and **1f** possessing fluorenylidene residue. The steric hindrance inhibited the second aldol reaction towards formation of the benzene ring once appropriate (*E*)-*β*-methylchalcones **2e** (33%, Entry 10, Table 2) and **2f** (33%, Entry 11, Table 2) are formed. The thienyl methyl ketone without substitution (**1a**, X = H) or bearing methyl substituent (**1b**, X

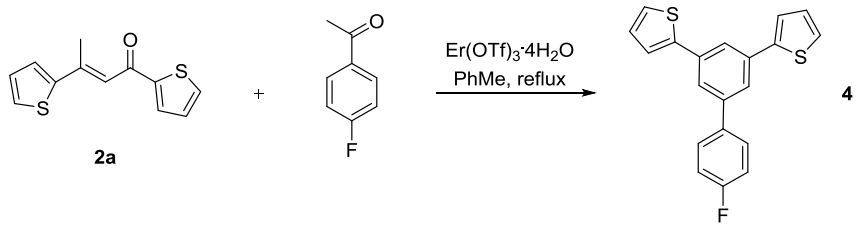
= Me) proceeded moderately in both, in [2+2+2] cyclotrimerization reaction (43% and 35% for **3a**, Entry 1 and 2; 41% for **3b**, Entry 3) and in a single-type aldol condensation (45% for **2a** Entry 6; 33% for **2b**, Entry 7, Table 2).

Taken together, we assumed that the self-condensation reactions of thiophene-based methyl ketones and related compounds were governed by several factors, such as electronic and steric effects of substituents at C5 position of the heterocyclic core together with reaction conditions (Methods A-D) applied for a particular substrate.

1,3,5-Symmetrically-substituted benzenes **3a**-**d** appear in their ^{1}H NMR spectra as singlets at 7.75–7.40 ppm due to aromatic hydrogen and in the range of 7.10–7.75 ppm as doublets or triplets of the thiophene core hydrogens. The H-*α* proton of the double bond for (*E*)-*β*-methylchalcones **2a**-**f** resonate in the range of 6.85–7.10 ppm as singlets or quartets as the result of the field interaction between olefinic hydrogen and hydrogen on C-*β* position of the thiophene together with interactions with the neighbouring methyl group. The methyl group signals appeared at 2.50 ppm

Mixed-type aldol condensation

The scope of dypnone-involved organic synthesis was expanded performing the reaction of **2a** (2.0 equiv.) with *p*-fluoroacetophenone (1.0 equiv.) as the aldol-type addition promoted by erbium triflate [$Er(OTf)_3$, 1.0 mol %].[42,43] The strong electron-withdrawing capacity of the methanesulfonate anion enhances the Lewis acid character of the catalyst and among the lanthanoid(III) triflates Er^{3+} was one of the most active cations.[44] To the best our knowledge, this is the first example of the dypnone-like aldol reaction catalysed by erbium triflate. Unsymmetricaly substituted 1,3,5-benzene **4** was isolated after heating at the boiling point of toluene (8 h, 62%, Scheme 3). In the ^{1}H NMR spectrum only aromatic hydrogen signals appear in the range of 8.00–7.10 ppm indicating the full conversion of the starting (*E*)-*β*-methylchalcone **2a**.



Scheme 3. Mixed-type aldol reaction of **2a** forming an unsymmetrically branched 1,3,5-benzene **4** catalysed by erbium triflate.

Conclusions

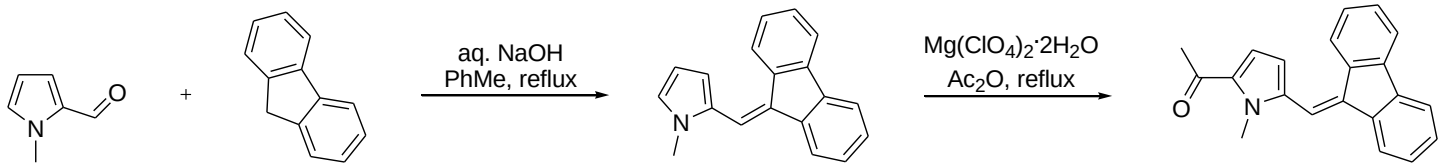
In this study we have complemented and compared the known aspects of the [2+2+2] cyclotrimerization reactions of acetophenones and related compounds with our current results. The course of the self-condensation process is indeed challenging providing the possibility of formation of different type of compounds: the C_3-symmetric aromatic derivatives or the unsaturated (*E*)-*β*-methylchalcones (dypnones). We have highlighted, that by varying the substitution of carbonyl substrates in combination with different reaction conditions the reaction can be directed either in a triple [2+2+2] cyclotrimerization manner towards 1,3,5-tris(thien-2-yl)benzenes **3a**-**d** (Table 2, Entries 1-5), or in accordance with a single-type aldol condensation producing 1,3-disubstituted (*E*)-*β*-methylchalcones **2a**-**f** (Table 2, Entries 6-11). The ability to access new

compounds **2b**-**f** through the general and simple protocols (Method B) or by their slight variations (Method C – use of ethyleneglycole monoethylether as solvent, Method D – use of trifluoromethane sulfonic acid as acid catalyst) is also described. The outlook of the synthetic application of (*E*)-*β*-methylchalcones yielding unsymmetrical 1,3,5-triarylbenzene derivatives is presented on the example of synthesis of (*E*)-3-(2,2'-dithienyl)-5-(fluorenyl)benzene (**4**). Both types of designed structures are important in a broad range of applications; 1,3,5-trisubstituted benzenes in the synthesis of star-shaped molecules acting as the π-conjugated units in opto-electronic materials and 1,3-disubstituted (*E*)-*β*-methylchalcones as intermediades in organic synthesis.

Experimental Section

General. All commercially available chemicals were used as received without further purification. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) on plates precoated with silica gel (Merck 60 F_{254}) and visualized using a UV hand lamp operating at 254/365 nm wavelengths. Melting points were recorded on a Kofler block and are uncorrected. The infrared spectra were taken on Agilent Cary 630 FTIR spectrometer with diamond ATR. Elemental analyses (EA) were performed on a Flash EA 2000 CHNS/O-OEA analyser. ESI-MS spectrum of compound **4** containing fluorine in the structure was recorded on Mass Quattro LC. NMR spectra (^{1}H at 300 and ^{13}C at 75 MHz) were obtained on the Varian VXR-300 spectrometer and products were reported relative to tetrametylsilane (TMS, 0.00 ppm) or $CDCl_3$ (7.24 ppm) or DMSO-d_6 (2.49 ppm) for ^{1}H NMR data, $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.7 ppm) for ^{13}C NMR data. Spectral data are presented as follows: chemical shifts in part per million (ppm), coupling constants *J* (Hz) and splitting patterns as s = singlet, d = doublet, t = triplet, q = quadruplet, dd = doublet of doublets, m = multiplet. Absorption spectra of the solutions in chloroform ($CHCl_3$), or dichloromethane (CH_2Cl_2) with concentration 1.10^{-5} mol·dm^{-3} measured on a UV 1650PC spectrometer (Shimadzu, Japan).

Thien-2-ylethanone (**1a**) and its C5 methyl-, chloro-, bromo- and fluorenylidene-substituted derivatives **1b-e** were synthesized following the published procedures.[45-47] 1-{5-[(9*H*-Fluorene-9-ylidene)methyl]-1-methyl-1*H*-pyrrol-2-yl}ethanone (**1f**) was synthesized in two steps according to Scheme 4 following the acetylation procedure published by us previously.[48]



1f' **1f**

Scheme 4. Synthesis of fluorenylidene-substituted 2-acetyl-1*H*-methylpyrrole substrate **1f.**

1-{5-[(9*H*-Fluorene-9-ylidene)methyl]-1-methyl-1*H*-pyrrol-2-yl}ethanone (**1f**). To a solution of 1-methyl-1*H*-pyrrole-2-carbaldehyde (0.06 mol, 6.5 g) and fluorene (0.06 mol, 10.0 g) in toluene (40 mL) sodium hydroxide (1.4 mol, 56.0 g) in water (84 mL) was added. To the toluene/water mixture the phase transfer catalyst *n*-butyltetraammonium bromide (*n*-Bu_4NBr, 0.01 mol, 3.5 g) was added and the mixture was left to stir at room

temperature (25 °C) overnight (6-8 h). After the reaction was completed the mixture was extracted with toluene (3 × 20 mL). Combined organic layers were washed with 0.1 M HCl (20 mL), then with water (2 × 20 mL) and finally with saturated solution of NaCl (20 mL). The organic layer was dried (Na_2SO_4) and solvent evaporated under reduced pressure. Crude product was purified by flash column chromatography (eluent: *n*-hexanes/EtOAc, 90:10) to give the intermediate: 2-[(9*H*-fluorene-9-ylidene)-methyl]-1-methyl-1*H*-pyrrole (**1f'**) as a yellow oil. Yield 73% (11.3 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.71 (s, 3H, N-C$\underline{H_3}$); 6.36 - 6.32 (m, 1H, pyrrole); 6.80 – 6.76(m, 2H, pyrrole); 7.24 – 7.22 (m, 1H, pyrrole); 7.37 – 7.32 (m, 4H, fluorenyl); 7.76 – 7.72 (m, 3H, fluorenyl); 8.23 (d, *J* = 7.8 Hz, 1H, fluorenyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 34.4, 108.5, 112.8, 115.8, 119.5, 119.6, 119.7, 123.7, 124.4, 126.7, 126.8, 127.6, 128.2, 129.0, 134.4, 136.6, 138.6, 139.7, 140.6. Anal. Calc. for $C_{19}H_5N$ (257.33 g·mol^{-1}): C, 88.68; H, 5.88; N, 5.44. Found: C, 88.70; H, 6.04; N, 5.22%. λ_{max} ($CHCl_3$) = 250, 258, 391 nm.

The mixture of 2-[(9*H*-fluorene-9-ylidene)methyl]-1-methyl-1*H*-pyrrole (**1f'**, 0.039 mol, 10.0 g) in acetic acid anhydride (acting as the solvent and as the acylating agent in the same time,[43] 0.039 mol, 4.0 mL) with magnesium perchlorate dihydrate [$Mg(ClO_4)_2 \cdot 2H_2O$, 0.01 equiv., 0.39 mmol, 42 mg] was left to stir at 80 °C for 6 h. After the reaction was completed (TLC monitoring) the mixture was poured to ice (30 mL) and then extracted with diethylether (3 × 30 mL). The solvent was evaporated under reduced pressure and crude product was purified by flash column chromatography (eluent: toluene) to give 1-{5-[(9*H*-fluorene-9-ylidene)methyl]-1-methyl-1*H*-pyrrol-2-yl}ethanone (**1f**) as pale yellow solid. Yield 45% (5.3 g), mp 150-152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.50 (s, 3H, COC$\underline{H_3}$), 3.95 (s, 3H, NC$\underline{H_3}$), 6.56 (d, $J_{4,3}$ 4.2 Hz, 1H, H-4$_{pyrrole}$), 7.06 (d, $J_{3,4}$ 4.2 Hz, 1H, H-3$_{pyrrole}$), 7.13 (t, *J* 7.6 Hz, 1H, fluorene), 7.24 (s, 1H, H-$\alpha_{fluorenylidene}$), 7.40 – 7.27 (m, 3H, fluorene), 7.68 (d, *J* 7.8 Hz, 2H, fluorene), 7.74 (d, *J* 7.8 Hz, 2H, fluorene). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 27.5, 34.2, 111.3, 114.0, 118.4, 119.5, 119.7, 119.8, 120.4, 124.2, 127.0, 127.1, 128.8, 129.2, 131.7, 136.0, 137.1, 138.7, 139.3, 139.6, 189.6. Anal. Calc. for $C_{21}H_{17}N$ (299.37 g·mol^{-1}): C, 84.25; H, 5.72; N, 4.68. Found: C, 84.35; H, 5.66; N, 4.74%. λ_{max} ($CHCl_3$) 249, 261, 381 nm.

General procedures of the self-condensation reactions

METHOD A. To a solution of starting hetaryl methyl ketone **1a**-**d** (1.0 equiv.) in absolute ethanol (30 mL) tetrachlorosilane ($SiCl_4$, 2.0 equiv.) was added slowly *via* the syringe under the inert argon atmosphere at 0 °C. The reaction mixture was left to stir overnight (14 h) at room temperature (25 °C). The dark reaction mixture was poured into ice water (100 mL) and stirred for 10 minutes. The aqueous phase was then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

METHOD B. To a solution of starting hetaryl methyl ketone **1a**-**d** (1.0 equiv.) in absolute ethanol/anhydrous toluene mixture (50:50) tetrachlorosilane ($SiCl_4$, 3.0 equiv.) was added slowly *via* the syringe under the inert argon atmosphere at 0 °C. The reaction mixture was left to stir overnight (14 h) at room temperature (25 °C). The dark reaction mixture was poured into ice water (100 mL) and stirred for 10 minutes. The aqueous phase was then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

METHOD C. To a solution of starting hetaryl methyl ketone **1a-d** (1.0 equiv.) in anhydrous 2-ethoxyethanol (30 mL) tetrachlorosilane ($SiCl_4$, 4.0 equiv.) was added slowly *via* the syringe under the inert argon atmosphere at room temperature. The reaction mixture was left to stir overnight (14 h) at room temperature (25 °C). The dark reaction mixture was poured into ice water (100 mL) and stirred for 10 minutes. The aqueous phase was

then extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

METHOD D. To a solution of starting hetaryl methyl ketone **1e** and **1f** (1.0 equiv.) in anhydrous toluene trifluoromethane sulfonic acid (TFSA, 2.0 mol%) was added slowly *via* the syringe under the inert argon atmosphere at room temperature (25 °C). The reaction mixture was left to stir for 30 h at 100 °C. Dark reaction mixture was poured to an ice water (100 mL) and stirred for 10 minutes. Water phase was then extracted with CH_2Cl_2 (3 × 50 mL). Collected organic layers were washed with water (2 × 30 mL), saturated solution of NaCl (2 × 20 mL) and then dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

1,3,5-Tris-(thien-2-yl)benzene (3a). Yellow solid, after purification on flash flow column chromatography (eluent: *n*-hexanes). Yield 55% (6.9 g) starting from 2-acetylthiophene **1a** (0.039 mol, 4.9 g; $SiCl_4$: 0.078 mol, 13.25 g, 9.0 mL, Method A, *Entry 1*, Table 2). Yield 35% (4.4 g), starting from 2-acetylthiophene (**1a**: 0.039 mol, 4.9 g; $SiCl_4$: 0.156 mol, 26.5 g, 18.0 mL, Method C, *Entry 2*, Table 2). Mp 152–156 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.11 (dd, *J* 3.6 Hz, *J* 5.1 Hz, 3H, 3 × H-4'$_{thiophene}$), 7.34 (dd, *J* 1.1 Hz, *J* 6.5 Hz, 3H, 3 × H-3'$_{thiophene}$), 7.40 (dd, *J* 1.1 Hz, *J* 6.5 Hz, 3H, 3 × H-5'$_{thiophene}$), 7.74 (s, 3H, Ar-H$_{benzene}$: H-2, H-4, H-6). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 122.7, 123.9, 125.4, 128.1, 135.7, 143.5. Anal. Calc. for $C_{18}H_{12}S_3$ (324.48 g·mol^{-1}): C, 66.63; H, 3.73; S, 29.65. Found: C, 66.50; H, 3.48; S, 29.74%. λ_{max}($CHCl_3$) 296 nm. The ^{13}C NMR and UV-Vis spectra are in accordance with Kotha *et al*. 1999.[3]

1,3,5-Tris-(5-methylthien-2-yl)benzene (3b). Colorless solid, after purification on flash flow column chromatography (eluent: CH_2Cl_2). Yield 58% (8.3 g) starting from 1-(5-methylthien-2-yl)ethanone (5-methyl-2-acetylthiophene) (**1b**: 0.039 mol, 5.5 g; $SiCl_4$: 0.078 mol, 13.25 g, 9.0 mL, Method A, *Entry 3*, Table 2). Mp 136–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.52 (s, 9H, 3 × CH_3), 6.75 (dd, *J* 3.4 Hz, *J* 6.8 Hz, 3H, 3 × H-3'$_{thiophene}$), 6.77 (d, *J* 6.8 Hz, 3H, 3 × H-4'$_{thiophene}$), 7.57 (s, 3H, ArH$_{benzene}$: H-2, H-4, H-6). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 15.5, 121.7, 123.6, 126.2, 135.7, 140.1, 141.3. Anal. Calc. for $C_{21}H_{18}S_3$ (366.56 g·mol^{-1}): C, 68.81; H, 4.95; S, 26.24. Found: C, 69.12; H, 4.80; S, 26.36%. λ_{max}($CHCl_3$) 305 nm. The ^{13}C NMR and UV-Vis spectra in accordance with Kotha *et al*. 1999.[3]

1,3,5-Tris-(5-chlorothien-2-yl)benzene (3c). Colorless solid, after purification on flash flow column chromatography (eluent: PhMe). Yield 58% (9.7 g) starting from 1-(5-chlorothien-2-yl)ethanone (5-chloro-2-acetylthiophene) (**1c**: 0.039 mol, 6.2 g; $SiCl_4$: 0.078 mol, 13.25 g, 9.0 mL, Method A, *Entry 4*, Table 2). Mp 172–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.07 (d, *J* 6.4 Hz, 3H, 3 × H-4'$_{thiophene}$), 7.14 (d, *J* 6.4 Hz, 3H, 3 × H-3'$_{thiophene}$), 7.54 (s, 3H, ArH$_{benzene}$: H-2, H-4, H-6). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 121.9, 123.2, 127.2, 130.1, 135.2, 141.4. Anal. Calc. for $C_{18}H_9Cl_3S_3$ (427.82 g·mol^{-1}): C, 50.53; H, 2.12; S, 22.49. Found: C, 50.62; H, 2.10; S, 22.64%. λ_{max}($CHCl_3$) 304 nm. The ^{13}C NMR and UV-Vis spectra in accordance with Kotha *et al*. 1999.[3]

1,3,5-Tris-(5-bromothien-2-yl)benzene (3d). Colorless solid, after purification on flash flow column chromatography (eluent: PhMe). Yield 28% (6.1 g) starting from 1-(5-bromothien-2-yl)ethanone (5-bromo-2-acetylthiophene) (**1d**: 0.039 mol, 8.0 g; $SiCl_4$: 0.117 mol, 20.0 g, 13.5 mL, Method B, *Entry 5*, Table 2). Mp 112–114 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.07 (d, *J* 6.8 Hz, 3H, 3 × H-3'$_{thiophene}$), 7.14 (d, *J* 6.8 Hz, 3H, 3 × H-4'$_{thiophene}$), 7.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 112.4, 122.1, 124.5, 131.1, 135.6, 144.5. Anal. Calc. for $C_{18}H_9Br_3S_3$ (561.17 g·mol^{-1}): C, 38.53; H, 1.62; S, 17.14. Found: C, 38.64; H, 1.80; S, 17.40%. λ_{max}($CHCl_3$) 264 nm. The analytical data are in accordance with Cao *et al*.[49]

(*E*)-1,3-Bis-(thien-2-yl)but-2-en-1-one (2a). Pale green-yellow oil, after purification on flash flow column chromatography (eluent: CH_2Cl_2/*i*-hexane, 50:50). Yield 45% (4.1 g) starting from 2-acetylthiophene (**1a**: 0.039 mol, 4.9 g; $SiCl_4$: 0.117 mol, 20.0 g, 13.5 mL, Method B, *Entry 6*, Table 2). Bp 160–164 °C/4.8 mm Hg; mp 70–74

°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.50 (d, *J* 0.4 Hz, 3H, CH_3), 6.12 (s, 1H, H-$\alpha_{olefinic}$), 7.14 (dd, *J* 1.2 Hz, *J* 6.4 Hz, 1H, H-4'$_{thiophene}$), 7.22 (dd, *J* 1.6 Hz, *J* 6.8 Hz, 1H, H-4''$_{thiophene}$), 7.62 (d, *J* 6.4 Hz, 1H, H-3'$_{thiophene}$), 7.65 (d, *J* 6.4 Hz, 1H, H-5'$_{thiophene}$), 7.70 (dd, *J* 1.6 Hz, *J* 6.8 Hz, 1H, H-5″$_{thiophene}$), 7.84 (d, *J* 6.8 Hz, 1H, H-3″$_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 20.4, 117.0, 125.5, 127.2, 128.8, 129.5, 134.8, 135.2, 136.0, 136.2, 144.0, 151.3, 182.1. Anal. Calc. for $C_{12}H_{10}OS_2$ (234.34 g·mol^{-1}): C, 61.50; H, 4.30; S, 27.37. Found: C, 61.72; H, 4.55; S, 27.25%. λ_{max}(CH_2Cl_2) 268, 366 nm.

(*E*)-1,3-Bis-(5-methylthien-2-yl)but-2-en-1-one (2b). Pale yellow oil, after purification on flash flow column chromatography (eluent: CH_2Cl_2/*i*-hexane, 50:50). Yield 33% (3.4 g) starting from 1-(5-methylthien-2-yl)ethanone (5-methyl-2-acetylthiophene) (**1b**: 0.039 mol, 5.4 g; $SiCl_4$: 0.117 mol, 20.0 g, 13.5 mL, Method B, *Entry 7*, Table 2). Bp 132–136°C / 4.8 mm Hg; mp 62–64 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.53 (s, 6H, 2 × C$\underline{H}_3$), 2.64 (s, 3H, C$\underline{H}_3$), 6.23 (s, 1H, H-$\alpha_{olefinic}$), 6.75 (d, *J* 6.5 Hz, 1H, H-3'$_{thiophene}$), 7.07 (d, *J* 6.5 Hz, 1H, H-4'$_{thiophene}$), 7.17 (d, *J* 6.8 Hz, 1H, H-4″$_{thiophene}$), 7.20 (d, *J* 6.8 Hz, 1H, H-3″$_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 15.9, 16.0, 17.5, 121.3, 126.6, 127.8, 128.7, 129.8, 133.6, 142.6, 145.3, 147.7, 148.9, 182.6. Anal. Calc. for $C_{14}H_{14}OS_2$ (265.05 g·mol^{-1}): C, 64.08; H, 5.38; S, 24.44. Found: C, 64.20; H, 5.55; S, 24.75%. λ_{max}(CH_2Cl_2) 255, 306, 363 nm.

(*E*)-1,3-Bis-(5-chlorothien-2-yl)but-2-en-1-one (2c). Pale yellowish oil, after purification on flash flow column chromatography (eluent: PhMe) or by vaccum distillation. Yield 64% (7.5 g) starting from 1-(5-chlorothien-2-yl)ethanone (5-chloro-2-acetylthiophene) (**1c**: 0.039 mol, 6.2 g; $SiCl_4$: 0.156 mol, 26.5 g, 18.0 mL, Method C, *Entry 8*, Table 2). Bp 82–86 °C / 4.8 mm Hg; mp 89–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.60 (d, *J* 1.2 Hz, 3H, C$\underline{H}_3$), 6.91 (d, *J* 4.2 Hz, 1H, H-$\alpha_{olefinic}$), 6.94 (q, *J* 1.2 Hz, *J* 6.90 Hz, 1H, H-4″$_{thiophene}$), 6.96 (d, *J* 6.2 Hz, 1H, H-4'$_{thiophene}$), 7.19 (d, *J* 6.2 Hz, 1H, H-3'$_{thiophene}$), 7.50 (d, *J* 6.9 Hz, 1H, H-3″$_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 17.4, 116.6, 127.3, 127.5, 130.1, 132.5, 139.1, 144.0, 145.8, 147.8, 181.6. Anal. Calc. for $C_{12}H_8Cl_2OS_2$ (303.23 g·mol^{-1}): C, 47.53; H, 2.66; S, 21.15. Found: C, 47.19; H, 2.74; S, 21.34%. λ_{max}(CH_2Cl_2) 272, 361 nm. The boiling and the melting point are in accordance with Farrar and Levine.[50]

(*E*)-1,3-Bis-(5-bromothien-2-yl)but-2-en-1-one (2d). Pale yellow-green oil, after purification on flash flow column chromatography (eluent: PhMe) or by vacuum distillation. Yield 31% (4.7 g) starting from 1-(5-bromothien-2-yl)ethanone (5-bromo-2-acetylthiophene) (**1d**: 0.039 mol, 8.0 g; $SiCl_4$: 0.156 mol, 26.5 g, 18.0 mL, Method C, *Entry 9*, Table 2). [§]Bp 98–102°C / 4.8 mm Hg; mp 105–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.55 (d, *J* 1.3 Hz, 3H, C$\underline{H}_3$), 6.95 (q, *J* 1.3 Hz, 1H, H-$\alpha_{olefinic}$), 7.05 (d, *J* 6.2 Hz, 1H, H-4″$_{thiophene}$), 7.10 (d, *J* 6.4 Hz, 1H, H-4'$_{thiophene}$), 7.15 (d, *J* 6.4 Hz, 1H, H-3'$_{thiophene}$), 7.45 (d, *J* 6.2 Hz, 1H, H-3″$_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 15.9, 116.8, 127.1, 127.4, 130.2, 130.5, 132.2, 139.8, 140.0, 145.5, 147.9, 182.1. Anal. Calc. for $C_{12}H_8Br_2OS_2$ (389.84 g·mol^{-1}): C, 37.79; H, 2.06; S, 16.35. Found: C, 38.12; H, 2.44; S, 16.14%. λ_{max}(CH_2Cl_2) 268, 354 nm.

(*E*)-1,3-Bis-{5-[(9*H*-fluorene-9-ylidene)methyl]thiene-2-yl}-but-2-en-1-one (2e). Viscous yellow oil, after purification on flash flow column chromatography (eluent: CH_2Cl_2). Yield 33% (330 mg). Starting from 1-(5-fluoren-9-ylidenemethylthien-2-yl)ethanone (**1e**: 1.7 mmol, 500 mg; CF_3SO_3H: 0.1 mmol, 15 mg, 9.0 µL; Method D, *Entry 10*, Table 2). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 2.65 (s, 3H, CH_3), 6.85 (s, 1H, $H_{fluorenylidene}$), 6.95 (s, 1H, $H_{fluorenylidene}$), 7.05 (q, *J* 1.3 Hz, 1H, H-$\alpha_{olefinic}$), 7.30 (d, *J* 7.9 Hz, 2H, H-3'$_{thiophene}$, H-3″$_{thiophene}$), 7.83–7.72 (m, 8$H_{fluorene}$), 7.89 (d, *J* 7.7 Hz, 2H, H-4'$_{thiophene}$, H-4″$_{thiophene}$), 8.00-8.19 (m, 8$H_{fluorene}$). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 18.2, 117.6, 118.5, 118.7, 119.5, 119.9, 120.1, 120.5, 120.7, 123.9, 124.0, 126.9, 127.1, 128.5, 128.6, 128.7, 129.2, 131.2, 131.7, 131.9, 134.8, 134.9, 138.1, 138.3, 138.6, 138.9, 140.7, 140.9, 145.9, 146.7, 147.3, 181.7. Anal. Calc. for $C_{40}H_{26}OS_2$ (586.76 g·mol^{-1}): C, 81.88; H, 4.47; S, 10.93. Found: C, 82.12; H, 5.00; S, 10.87%. λ_{max}($CHCl_3$) 251, 259, 468 nm.

(*E*)-1,3-Bis-{5-[(9*H*-fluorene-9-ylidene)methyl]-1-methyl-1*H*-pyrrole-2-yl}-but-2-en-1-one (2f). Viscous yellow, after purification on flash flow column chromatography (eluent: CH_2Cl_2). Yield 33% (326 mg). Starting from 1-{5-[(9*H*-fluorene-9-ylidene)methyl]-1-methyl-1*H*-pyrrole-2-yl}ethanone (**1f**: 1.7 mmol, 510 mg; CF_3SO_3H: 0.1 mmol, 15 mg, 9.0 µL; Method D, *Entry 11*, Table 2). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 2.55 (s, 3H, CH_3), 3.46 (s, 6H, 2 × $C\underline{H}_3$), 6.45 (d, *J* 3.9 Hz, 3H, 1 × H-$\alpha_{olefinic}$, 2 × $H_{fluorenylidene}$), 6.83 (d, *J* 6.9 Hz, 2H, H-4'$_{pyrrole}$, H-4''$_{pyrrole}$), 7.21 (d, *J* 6.9 Hz, 2H, H-3'$_{pyrrole}$, H-3''$_{pyrrole}$), 7.37–7.33 (m, 8H, 8 × $H_{fluorene}$), 7.78–7.73 (m, 8H, 8 × $H_{fluorene}$). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 24.2, 32.2, 110.9, 112.8, 112.9, 116.7, 119.8, 119.9, 120.1, 126.9, 127.7, 128.3, 131.4, 132.3, 136.4, 136.5, 139.6, 140.7, 182.0. Anal. Calc. for $C_{42}H_{32}N_2O$ (580.72 g·mol^{-1}): C, 86.87; H, 5.55; N, 4.82. Found: C, 86.53; H, 5.34; N, 4.67%. λ_{max}($CHCl_3$) 252, 261, 460 nm.

1,3-Bis-(thien-2-yl)-5-(4-fluorophenyl)benzene (4). To a solution of (*E*)-1,3-bis-(2-thienyl)but-2-en-1-one (**2a**, 1.22 mmol, 290 mg) and 4'-fluoroacetophenone (1.22 mmol, 168.5 mg, 148 µL) in anhydrous toluene (5 mL) the tetrahydrate of erbium triflate [$Er(OTf)_3 \cdot 4H_2O$, 0.12 mmol, 81.0 mg] was added. The mixture was stirred at the boiling point of toluene (110 °C) for 6 h (Scheme 3). Reaction mixture was poured to a water (10 mL). Water phase was extracted with toluene (3 × 15 mL). Collected organic layers were washed with water (2 × 10 mL), saturated solution of NaCl (2 × 10 mL) and then dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (eluent: *n*-hexanes). Yield 62% (254 mg) of cream-yellow solid. Mp 208-211 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.17 (t, *J* 6.6 Hz, 2H, H-4'$_{thiophene}$, H-4''$_{thiophene}$), 7.22 (t, *J* 1.9 Hz, *J* 6.6 Hz, 2H, H-4'$_{thiophene}$, H-4''$_{thiophene}$), 7.37 (s, 2H, ArH, H-4, H-6), 7.58 (d, *J* 6.6 Hz, 2H, H-3'$_{thiophene}$, H-3''$_{thiophene}$), 7.70 (d, *J* 6.6 Hz, 2H, H-5'$_{thiophene}$, H-5''$_{thiophene}$), 7.71 (*J* 3.7 Hz, 2H, H-2'''$_{benzene}$, H-6'''$_{benzene}$), 7.92 (d, *J* 3.7 Hz, 2H, H-3'''$_{benzene}$, H-5'''$_{benzene}$), 8.21 (s, 1H, ArH, H-1$_{benzene}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 118.4, 124.6, 137.7, 145.9, 153.4, 154.7, 165.9, 175.6, 178.9, 198.7, 198.9. For $C_{20}H_{13}FS_2$ (336.45 g·mol^{-1}) (ESI) *m/z* 337.14 [M+H$^+$].

Acknowledgements

This work was financially supported by grants provided by the Ministry of Education of the Slovak Republic, Nos VEGA 1/0534/16; VEGA 2/0161/17 and VEGA 1/0871/16. Financial support of the Slovak Research and Development Agency APVV (contract no. 15-0079) is also acknowledged.

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