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$H_3PW_{12}O_{40}$-Catalysed Alkylation of Arenes and Diveratrylmethanes: Convenient Routes to Triarylmethanes and to Symmetrical and Unsymmetrical 9,10-Diaryl-2,3,6,7-tetramethoxyanthracenes

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An efficient method for the synthesis of triarylmethanes and difurylarylmethanes through solventless reactions between aldehydes and arenes in the presence of $H_3PW_{12}O_{40}$ as a reusable catalyst under thermal and microwave irradiation conditions has been developed. $H_3PW_{12}O_{40}$-catalysed one-pot consecutive Friedel–Crafts reactions between veratrole and aldehydes were also applied as a convenient protocol for the preparation of symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes. The conversion of aldehydes into their corresponding acylals in the presence of $H_3PW_{12}O_{40}$ and the one-pot reactions of diveratrylmethanes with these acylals were also used for the synthesis of symmetrical and unsymmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes.

Introduction

Triarylmethanes (TRAMs) are of great significance, due to their wide variety of applications in synthetic, medicinal and industrial chemistry and as protecting groups.[1] So far, many methods based on C–C bond formation have been reported for their synthesis. Vicarious nucleophilic substitution of hydrogen[2] and addition of arylboronic acids to aldehydes catalysed by cationic Pd^{II}/bipyridine,[3] as well as Friedel–Crafts alkylation of arenes with aldehydes catalysed variously by trifluoromethanesulfonic acid or trifluoroacetic acid,[4] $Cu(OTf)_2$,[5] sulfuric acid,[6] $InCl_3$/chloromethylsilane,[7] $[Ir(COD)Cl]_2$-$SnCl_4$,[8] $Yb(OTf)_3$,[9] $FeCl_3$[10] and $ZnBr_2/SiO_2$/AcBr[11] have been reported for the synthesis of TRAMs. These compounds are also synthesized through the alkylation of electron-rich arenes with (3-indolyl)methanamines in the presence of chiral Brønsted acids,[12a] double Friedel–Crafts reactions of indoles and 2-formylbiphenyls catalysed by chiral phosphoric acids,[12b] alkylation of α-(3-indolyl)benzylamines with *N*-methylindole catalysed by Brønsted acids,[12c] palladium-catalysed direct arylation of aryl(azaaryl)methanes with aryl halides,[13a] Suzuki–Miyaura coupling of diarylmethyl carbonates with arylboronic acids[13b] and by benzylation/[3+3] cyclocondensation in the presence of $FeCl_3$.[14]

Hashmi et al.[15] have recently shown that gold compounds can be used as efficient catalysts in synthetic organic chemistry under mild conditions. In this respect, both this group[16] and Nair et al.[17] have reported the synthesis of triheteroarylmethanes in high yields through $AuCl_3$- or $AuCl_3$/AgOTf-catalysed reactions between carbonyl compounds and electron-rich arenes.

Anthracene and its derivatives are an important class of polyaromatic hydrocarbons.[18] These compounds have been seriously assessed in nonlinear optical applications such as organic light-emitting diodes,[19] organic field-effect transistors[20] and fluorescent chemosensors.[21] Anthracenes have also been used in Diels–Alder reactions.[22] These compounds are generally prepared through Friedel–Crafts reactions,[6,11,23] aromatic cyclodehydration,[24] Haworth reactions,[25] Lewis-acid-induced Bradshare-type reactions from diveratrylmethanes,[26] Elbs reactions,[27] twofold Suzuki–Miyaura cross-coupling reactions,[28] coupling reactions between zirconacyclopentadienes and dihalonaphthalenes,[29] cyclization of diacetates with TfOH,[30] H_2SO_4-catalysed reactions between benzocrown ethers and aldehydes,[31] and addition of Grignard reagents or aryllithiums to anthraquinones followed by reduction of the resulting diols.[32]

The use of Keggin-type heteropolyacids as homogeneous or heterogeneous catalysts in organic synthesis has been developed as a result of their several advantages, such as environmental compatibility, reusability, non-corrosiveness and relative lack of disposal problems, which make them economically and environmentally attractive. Heteropolyacids, especially $H_3PW_{12}O_{40}$ (PWA), have attracted great attention, because of their high acid strengths and selectivity properties.[33] The application of these solid acid catalysts

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under solventless conditions provides even more benign processes.[34]

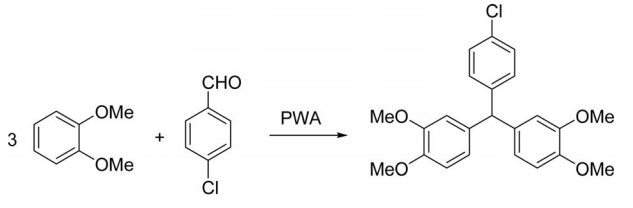
In continuation of our research into the application of heteropolyacids in useful synthetic organic transformations,[35] here we wish to disclose our results in: i) one-pot syntheses of triarylmethanes and difurylarylmethanes through PWA-catalysed reactions between arenes and aldehydes, ii) the direct preparation of symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes through reactions between veratrole and aldehydes in the presence of PWA, and iii) a convenient route to symmetrical and unsymmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes through PWA-catalysed Friedel–Crafts alkylations of diveratrylmethanes (DVMs) with acylals.

Results and Discussion

Solventless Syntheses of Triarylmethanes and Difurylarylmethanes Under Thermal and Microwave Irradiation Conditions

Initially, the reaction parameters – such as solvent, molar ratio of veratrole to aldehyde, the amount of catalyst and temperature – were optimized in the reaction between 4-chlorobenzaldehyde and veratrole (**1**) as a model under thermal conditions. The model reaction was examined in various solvents as well as under solventless conditions in the presence of PWA (Table 1, Entries 1–5). The highest yield of the corresponding DVM was obtained with 4-chlorobenzaldehyde (1 mmol), veratrole (3 mmol) and PWA (0.07 mmol) at 75 °C under solventless conditions (Table 1, Entry 5). These conditions are promising as an essential facet of "green chemistry" and are of great interest as alternatives to traditional reactions in organic solvents both from the economical and from the synthetic point of view. Increasing the amount of veratrole, the temperature or the amount of catalyst did not improve the yield (Table 1, Entries 6–8), whereas reduction of each of these parameters led to a reduction in product yield (Table 1, Entries 9–11).

Table 1. Optimization of the reaction conditions for the PWA-catalysed synthesis of DVMs.

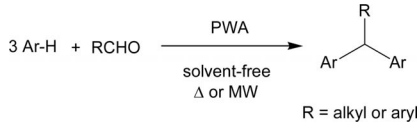


1 **2e** **3e**

Entry	PWA [mol-%]	Veratrole [mmol]	Aldehyde [mmol]	Solvent [°C]	*T*	Time [min]	Yield[a] [%]
1	7	3	1	CH_3CN	reflux	60	50
2	7	3	1	EtOH	reflux	60	12
3	7	3	1	CH_2Cl_2	reflux	60	25
4	7	3	1	$CHCl_3$	reflux	60	55
5	7	3	1	–[b]	75	25	93
6	7	3.5	1	–	75	25	93
7	7	3	1	–	90	25	93
8	9	3	1	–	75	25	93
9	7	2.5	1	–	75	25	71
10	7	3	1	–	60	25	74
11	5	3	1	–	75	25	77

[a] Isolated yield. [b] Solventless.

Reactions between various aldehydes and veratrole in the presence of PWA under the optimized conditions were examined (Scheme 1) and the results are summarized in Table 2. The electronic properties of the substituents on the aromatic aldehydes have a significant influence on the reaction times and yields. Benzaldehyde and aldehydes bearing electron-withdrawing groups, such as nitro, chloro, cyano, formyl and 3-methoxy,[36] and also methyl as a weakly electron-donating group, afforded the corresponding products in high yields (Table 2, Entries 1–12 and 17). In contrast, aldehydes containing strongly electron-donating groups, such as 4-methoxy and 4-hydroxy groups, failed to produce the products (Table 2, Entries 18, 19). This is attributed to the reduced electrophilicity of the aldehyde group as a result of the electron-rich nature of the phenyl ring to which the aldehyde is attached. It is noteworthy that aldehydes containing both electron-donating and electron-withdrawing groups also remained unreacted in the reaction mixture (Table 2, Entries 20, 21). These results show that electron-donating substituents have more pronounced effects than electron-withdrawing ones.

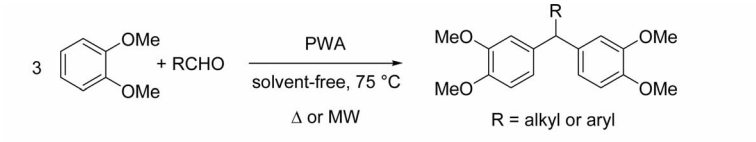


Scheme 1. PWA-catalysed syntheses of triarylmethanes.

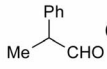
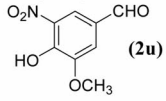
The reactivities of 2-naphthaldehyde (**2m**) and polycyclic aldehydes such as anthracene-9-carbaldehyde and phenanthrene-9-carbaldehyde were also examined. 2-Naphthaldehyde afforded the corresponding DVM **3m** in 84% yield (Table 2, Entry 13), whereas anthracene-9-carbaldehyde and phenanthrene-9-carbaldehyde failed to give the desired products and were recovered unchanged, possibly because of steric effects. To the best of our knowledge, the synthesis of fluorinated diveratrylmethanes has not been reported previously. We succeeded in preparing several fluorinated triarylmethanes (Table 2, Entries 8–10). Aliphatic aldehydes were also converted into their corresponding diveratrylmethane derivatives at room temperature in excellent yields (Table 2, Entries 14–16).

It is important to note that excellent chemoselectivity was observed in the reaction between terephthalaldehyde (**2l**) and veratrole (**1**) under thermal conditions. With a 1:2.5 molar ratio of **2l** to **1**, only one formyl moiety reacted selectively and the aldehyde **3l** was isolated in 81% yield, whereas with a 1:7 molar ratio of terephthalaldehyde to veratrole, both formyl groups reacted and the tetrakis(veratryl) adduct **4** was obtained in 78% yield (Scheme 2). Reactions between anisole derivatives and various aldehydes under the same conditions were also investigated and the correspond-

Table 2. PWA-catalysed syntheses of DVMs under thermal and microwave irradiation conditions.



1 **2** **3**

Entry	RCHO	Product	Thermal[a] (MW[b])		M.p. [°C]
			Time [min]	Yield[c] [%]	
1	PhCHO (**2a**)	**3a**	40 (2.5)	72 (86)	122-124
2	4-MeC_6H_4CHO (**2b**)	**3b**	40 (3.5)	71 (84)	129.5-131
3	3-$NO_2C_6H_4CHO$ (**2c**)	**3c**	35 (2.5)	93 (95)	154-155.5
4	2-ClC_6H_4CHO (**2d**)	**3d**	30 (3)	92 (92)	136-137
5	4-ClC_6H_4CHO (**2e**)	**3e**	25 (3)	93 (94)	155-157
6	2,4-$(Cl)_2C_6HCHO$ (**2f**)	**3f**	30 (3)	74 (90)	151-152
7	4-BrC_6H_4CHO (**2g**)	**3g**	30 (3)	85 (93)	159-161
8	3-FC_6H_4CHO (**2h**)	**3h**	40 (3.5)	90 (91)	113-115
9	4-FC_6H_4CHO (**2i**)	**3i**	40 (3.5)	87 (89)	124-125
10	2-Cl-6-FC_6H_3CHO (**2j**)	**3j**	35 (3)	93 (94)	99-101
11	4-NCC_6H_4CHO (**2k**)	**3k**	40 (3)	89 (94)	115-116
12	4-$OHCC_6H_4CHO$ (**2l**)	**3ld**	25 (2.5)	81 (88)	128-129
13	2-naphthaldehyde (**2m**)	**3m**	40 (3)	84 (91)	133-135
14	CH_3CHO (**2n**)	**3n**	15[e] (–)	88 (–)	72-73
15	$CH_3(CH_2)_2CHO$ (**2o**)	**3o**	15[e] (–)	90 (–)	oil
16	 (**2p**)	**3p**	15[e] (2.5)	93 (93)	oil
17	3-$MeOC_6H_4CHO$ (**2q**)	**3q**	45 (3.5)	83 (89)	120-122
18	4-$MeOC_6H_4CHO$ (**2r**)	**3r**	120 (10)	trace (trace)	–
19	4-HOC_6H_4CHO (**2s**)	**3s**	120 (10)	trace (trace)	–
20	3,4-$(MeO)_2C_6H_3CHO$ (**2t**)	**3t**	120 (10)	trace (trace)	–
21	 (**2u**)	**3u**	120 (10)	trace (trace)	–

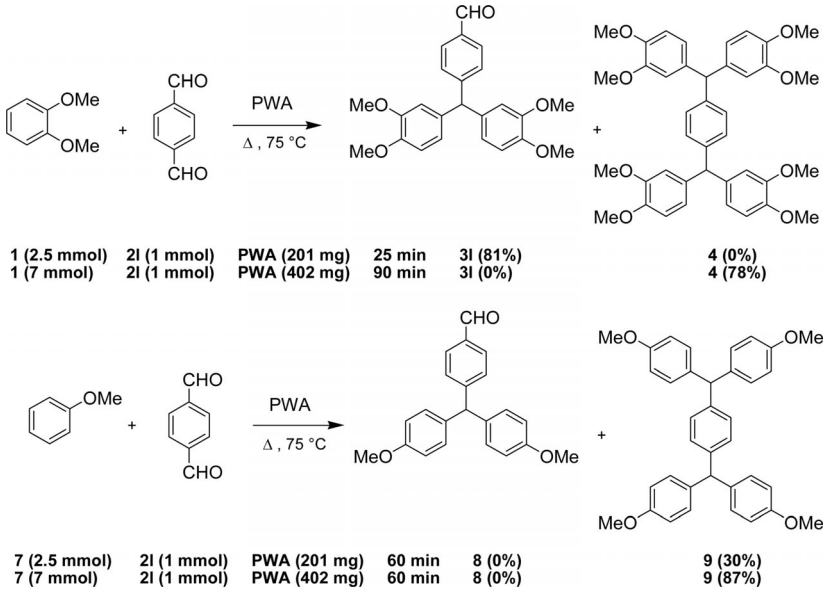
[a] Reaction conditions: veratrole (3 mmol), aldehyde (1 mmol), PWA (7 mol-%), 75 °C. [b] Reaction conditions: veratrole (3 mmol), aldehyde (1 mmol), PWA (4 mol-%), applied power: 150 W, 75 °C. [c] Isolated yield. [d] Veratrole (**1**, 2.5 mmol), terephthalaldehyde (**2l**, 1 mmol). [e] At room temperature.

ing TRAMs were obtained in excellent yields (Table 3). The reaction between anisole and terephthalaldehyde failed to produce the corresponding triarylmethane **8**, and only the tetrakis(anisyl) adduct **9** was obtained, in 87% yield under thermal conditions (Scheme 2).

The efficiency of this method for the synthesis of difurylarylmethanes was also explored. As can be seen in Table 4, the difurylarylmethanes were obtained in excellent yields on treatment of 2,5-dimethylfuran (**10**) with aldehydes.

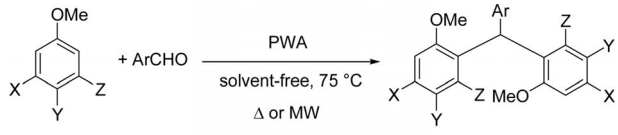
Organic reactions assisted by microwave irradiation have attracted considerable attention in recent years. The main benefits of performing the reactions under microwave irradiation are much improved reaction rates, higher yields and formation of cleaner products. A key advantage of modern scientific microwave apparatus is the ability to control reaction parameters such as temperature, pressure and reaction times very specifically.[37] Microwave irradiation had not previously been employed for the synthesis of TRAMs, and so microwave-assisted syntheses of these compounds were investigated. Optimal conditions were determined after many trials on the model reaction. The best results were obtained with a 3:1:0.04 veratrole/aldehyde/PWA molar ratio and with an applied power of 150 W at 75 °C under solventless conditions. Under these optimized conditions, a wide range of diveratrylmethanes and triarylmethanes were synthesized in excellent yields and in very short reaction times in the presence of smaller amounts of catalyst than under thermal conditions (see Tables 2, 3 and 4). When anisole and veratrole were treated with terephthalaldehyde (**2l**) under microwave irradiation conditions, different results in terms of selectivity were obtained. The reaction between anisole and terephthalaldehyde (**2l**) produced the tetrakis(anisyl) adduct **9** in 91% isolated yield (Scheme 3), whereas with veratrole only one formyl group of terephthalaldehyde contributed and the corresponding diveratrylmethane **3l** was isolated in 88% yield.

The reusability of the catalyst was also investigated, and it was observed that it could be reused at least five times under thermal or microwave irradiation conditions without any significant decrease in its activity.



Scheme 2. Investigation of selectivity in the reactions of veratrole and anisole with terephthalaldehyde under thermal conditions.

Table 3. PWA-catalysed syntheses of TRAMs under thermal and microwave irradiation conditions.

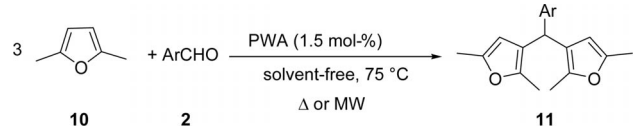


5 2 6

Entry	Compound	ArCHO	Product	Thermal[a] (MW[b]) Time [min]	Yield[c] [%]	M.p. [°C]
1	X = Z = H, Y = Me (**5a**)	4-ClC_6H_4CHO (**2e**)	**6a**	35 (4)	93 (95)	153–155
2	X = Z = H, Y = Me (**5a**)	4-MeC_6H_4CHO (**2b**)	**6b**	40 (4)	92 (93)	119–120
3	X = Z = H, Y = Me (**5a**)	4-NCC_6H_4CHO (**2k**)	**6c**	35 (4)	92 (95)	132–133
4	X = Z = H, Y = Me (**5a**)	2-naphthaldehyde (**2m**)	**6d**	40 (5)	86 (92)	138–139
5	X = Z = H, Y = Cl (**5b**)	4-$NO_2C_6H_4CHO$ (**2v**)	**6e**	50 (5)	88 (93)	168–170
6	X = Z = H, Y = Cl (**5b**)	2-ClC_6H_4CHO (**2d**)	**6f**	55 (5)	90 (94)	138–140
7	X = Z = H, Y = Cl (**5b**)	PhCHO (**2a**)	**6g**	60 (5)	78 (85)	138–139.5
8	Y = H, X = Z = OMe (**5c**)	4-BrC_6H_4CHO (**2g**)	**6h**	15 (3)	94 (95)	149–151
9	Y = H, X = Z = OMe (**5c**)	4-ClC_6H_4CHO (**2e**)	**6i**	15 (3)	93 (95)	164–165
10	Y = H, X = Z = OMe (**5c**)	2-naphthaldehyde (**2m**)	**6j**	15 (3)	92 (94)	173–174

[a] Reaction conditions: arene (3 mmol), aldehyde (1 mmol), PWA (7 mol-%), 75 °C. [b] Reaction conditions: arene (3 mmol), aldehyde (1 mmol), PWA (4 mol-%), MW irradiation (150 W), 75 °C. [c] Isolated yield.

Table 4. PWA-catalysed syntheses of difurylarylmethanes under thermal and microwave irradiation conditions.



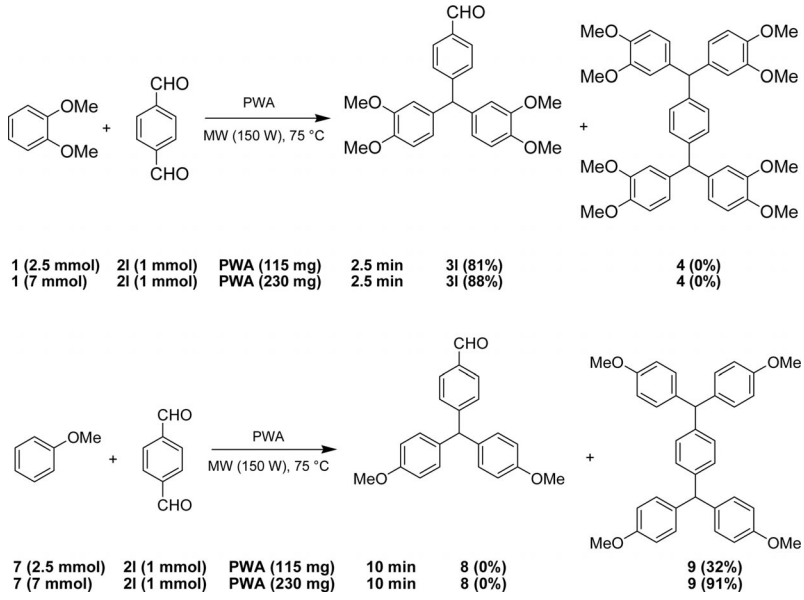
10 2 11

Entry	ArCHO	Prod.	Thermal[a] (MW[b]) Time [min]	Yield[c] [%]	M.p. [°C]
1	2,4-$(Cl)_2C_6H_3CHO$ (**2f**)	**11a**	40 (3)	90 (92)	111–113
2	4-NCC_6H_4CHO (**2k**)	**11b**	40 (3)	89 (91)	98–99
3	4-$NO_2C_6H_4CHO$ (**2r**)	**11c**	40 (3)	91 (94)	101–102

[a] Reaction conditions: 2,5-dimethylfuran (3 mmol), aldehyde (1 mmol), PWA (1.5 mol-%), 75 °C. [b] Reaction conditions: 2,5-dimethylfuran (3 mmol), aldehyde (1 mmol), PWA (1.5 mol-%), MW irradiation (150 W), 75 °C. [c] Isolated yield.

One-Pot Consecutive Preparations of Symmetrical 9,10-Diaryl-2,3,6,7-tetramethoxyanthracenes

The development of organic transformations in fewer steps increases the reaction yields and selectivity, decreases the reaction times, by-products, waste and costs, and saves on energy and resources. In the course of the last two decades a great deal of attention has therefore been paid to the design of one-pot and modern strategies in organic transformations.[38] In this context, we focused on the synthesis of symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes through Friedel–Crafts reactions between veratrole and aldehydes. Our initial investigations showed that PWA is able to catalyse these reactions. It was also found that addition of Ac_2O to the reaction mixture promotes the product formation, so a one-pot two-step strategy was postulated. In this, the first step included the diveratrylmethane synthesis



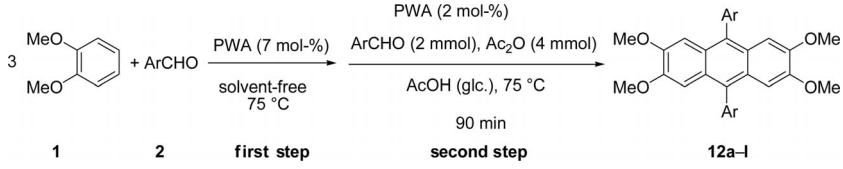
Scheme 3. Investigation of selectivity in the reactions of veratrole and anisole with terephthalaldehyde under MW irradiation conditions.

according to Table 2 and in the second step the reaction mixture was treated, without any product isolation, with an aldehyde and Ac_2O in the presence of catalytic amounts of PWA. To determine the optimal conditions for the second step, the preparation of the anthracene **12a** was chosen as a model. In the second step, the best yield was obtained with aldehyde (2 mmol), Ac_2O (4 mmol) and PWA (2 mol-%) in glacial AcOH (2 mL) at 75 °C.

The scope and limitations of the described procedure were investigated in reactions between aldehydes and veratrole. Under the optimized conditions, several symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes were successfully synthesized in good yields. As illustrated in Table 5, the preparation of 2,3,6,7-tetramethoxy-9,10-diphenylanthracene (**12a**) in 73% yield is one of the notable advantages of this protocol (Table 5, Entry 1). Halogenated aldehydes were also converted into their corresponding anthracenes with good yields and selectivities (Table 5, Entries 2–8). Another noteworthy advantage of the method was shown in the reaction between 2-naphthaldehyde (**2m**) and veratrole, in which the corresponding 2,3,6,7-tetramethoxy-9,10-dinaphthylanthracene (**12i**) was selectively prepared in 48% yield (Table 5, Entry 9). It should be noted that although aldehydes such as 4-methylbenzaldehyde (**2b**), 3-nitrobenzaldehyde (**2c**) and 4-cyanobenzaldehyde (**2k**) were highly reactive in the first step, they nevertheless failed to produce the corresponding anthracenes (Table 5, Entries 10–12).

It is noteworthy that these conditions are only suitable for syntheses of symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes. In the first step, veratrole reacts with the

Table 5. PWA-catalysed one-pot syntheses of symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes.



Entry	ArCHO	Time [min], first step	Product	Yield[a] [%]	M.p. [°C]
1	PhCHO (**2a**)	40	**12a**	73	306–308
2	2-ClC_6H_4CHO (**2d**)	30	**12b**	56	166–167.5
3	3-ClC_6H_4CHO (**2v**)	25	**12c**	61	219–220
4	4-ClC_6H_4CHO (**2e**)	25	**12d**	70	327–329
5	3-BrC_6H_4CHO (**2w**)	30	**12e**	63	249–251
6	4-BrC_6H_4CHO (**2g**)	30	**12f**	65	>330
7	3-FC_6H_4CHO (**2h**)	40	**12g**	58	211–213
8	4-FC_6H_4CHO (**2i**)	40	**12h**	65	238–239
9	2-naphthaldehyde (**2m**)	40	**12i**	48	288–290
10	4-MeC_6H_4CHO (**2b**)	40	**12j**	–	–
11	3-$NO_2C_6H_4CHO$ (**2c**)	25	**12k**	–	–
12	4-NCC_6H_4CHO (**2k**)	25	**12l**	–	–

[a] Isolated yield.

aldehyde in a 3:1 molar ratio, and some veratrole remains in the reaction mixture in addition to the produced DVM. In the second step, the added aldehyde can react with the DVM to produce the anthracene derivative. In addition, the added aldehyde also reacts with the remaining veratrole to afford the DVM, which further reacts with the aldehyde to give an anthracene derivative. If the same aldehyde is used in these two steps, only one kind of anthracene derivative is formed, and this is symmetrical. If the aldehydes used for the two steps are not the same, a mixture of anthracene derivatives is formed in low yields and the isolation and purification of the products are therefore very difficult.

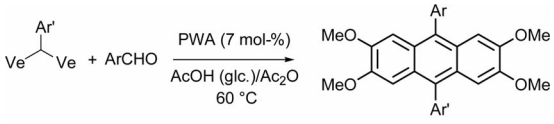
One-Pot Syntheses of Symmetrical and Unsymmetrical 9,10-Diaryl-2,3,6,7-tetramethoxyanthracenes with Diveratrylmethanes and Acylals as Key Precursors

In order to demonstrate the efficiency and applicability of this method further, syntheses of symmetrical and unsymmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes through reactions between DVMs and aldehydes in the presence of PWA were also investigated. Optimization of the reaction conditions was carried out in the reaction between the DVM **3a** and benzaldehyde (**2a**). Initial experiments showed that addition of Ac_2O to the reaction mixture improved this reaction. The best results were obtained with a DVM/aldehyde/Ac_2O molar ratio of 1:1.5:4 in the presence of PWA in glacial acetic acid at 60 °C. Under these conditions, several 9,10-diarylanthracenes were prepared as illustrated in Table 6. Drawbacks such as low yields and the need for large amounts of PWA encouraged us to find a more efficient strategy for the synthesis of target molecules via DVMs. On consideration of the role of Ac_2O in these reactions, it was postulated that aldehydes are initially converted into their corresponding acylals, which are probably more reactive than the parent aldehydes in these reactions. The acylal **13a** was therefore first prepared by treatment of benzaldehyde (**2a**) with Ac_2O. Compound **13a** (1.5 mmol) was then treated with the DVM **3a** (1 mmol) in the presence of PWA (7 mol-%) in AcOH as the solvent.

Analysis of the crude product revealed that in addition to the desired anthracene **12a**, some benzaldehyde **2a** was produced by deprotection of acylal **13a**. In order to reduce the extent of deprotection of **13a** and to increase the yield of the corresponding anthracene, this reaction was repeated in the presence of smaller amounts of PWA. It was found that 2 mol-% PWA afforded the best result.

With the knowledge of the critical role of Ac_2O, a one-pot synthetic methodology for the preparation of 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes was designed. Firstly, the acylals **13a**–**h** were prepared by treatment of the aldehydes (1.5 mmol) with Ac_2O (4 mmol) in the presence of PWA (2 mol-%) at 60 °C for 30 min under solventless conditions. The DVM of choice (1 mmol) and glacial AcOH

Table 6. Syntheses of 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes through reactions between DVMs and aldehydes.[a]



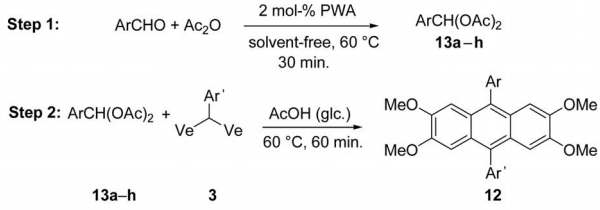
1 2 12

Ar' = Ph (**3a**), Ar' = 3-$NO_2C_6H_4$ (**3c**), Ar' = 4-ClC_6H_4 (**3e**)
Ar' = 2,4-$(Cl)_2C_6H_3$ (**3f**), Ar' = 4-FC_6H_4 (**3i**)
Ve = 3,4-dimethoxyphenyl

Entry	Ar′CH	ArCHO	Product [$(Ve)_2$]	Time [min]	Yield[b] [%]
1	**3a**	PhCHO (**2a**)	**12a**	90	59
2	**3a**	4-BrC_6H_4CHO (**2g**)	**12m**	90	37
3	**3e**	PhCHO (**2a**)	**12n**	90	58
4	**3e**	4-ClC_6H_4CHO (**2e**)	**12d**	90	46
5	**3c**	PhCHO (**2a**)	**12q**	120	NR
6	**3f**	PhCHO (**2a**)	**12r**	90	38
7	**3i**	PhCHO (**2a**)	**12o**	90	49

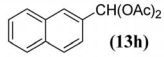
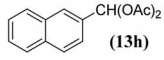
[a] Reaction conditions: DVM (1 mmol), aldehyde (1.5 mmol), Ac_2O (4 mmol), PWA (201 mg, 7 mol-%) and AcOH (glc., 2 mL) at 60 °C. [b] Isolated yield.

Table 7. One-pot two-step syntheses of symmetrical and unsymmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes through reactions between DVMs and acylals in the presence of PWA.[a]



13a–h 3 12

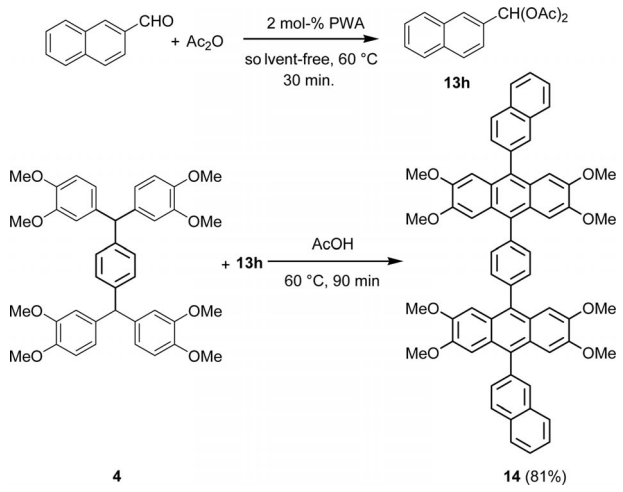
Ve = 3,4-dimethoxyphenyl
Ar' = Ph (**3a**), Ar' = 4-MeC_6H_4 (**3b**), Ar' = 3-$NO_2C_6H_4$ (**3c**), Ar' = 2-ClC_6H_4 (**3d**), Ar' = 4-ClC_6H_4 (**3e**),Ar' = 2,4-$(Cl)_2C_6H_3$ (**3f**), Ar' = 4-BrC_6H_4 (**3g**), Ar' = 3-FC_6H_4 (**3h**), Ar' = 4-FC_6H_4 (**3i**), Ar' = 2-naphthyl (**3m**), Ar' = 3-BrC_6H_4 (**3v**)

Entry	$ArCH(OAc)_2$	Ar'$CH(Ve)_2$	Product	Yield[b] [%]	M.p. [°C]
1	$PhCH(OAc)_2$ (**13a**)	**3a**	**12a**	71	306-308
2	$PhCH(OAc)_2$ (**13a**)	**3g**	**12m**	55	271-273
3	4-$BrC_6H_4CH(OAc)_2$ (**13b**)	**3a**	**12m**	47	271-272
4	$PhCH(OAc)_2$ (**13a**)	**3e**	**12n**	70	242-243
5	$PhCH(OAc)_2$ (**13a**)	**3i**	**12o**	66	228-230
6	$PhCH(OAc)_2$ (**13a**)	**3m**	**12p**	67	219-221
7	$PhCH(OAc)_2$ (**13a**)	**3c**	**12q**	n.r.	-
8	$PhCH(OAc)_2$ (**13a**)	**3f**	**12r**	51	215-216.5
9	4-$ClC_6H_4CH(OAc)_2$ (**13c**)	**3m**	**12s**	45	246-248
10	4-$ClC_6H_4CH(OAc)_2$ (**13c**)	**3e**	**12d**	71	327-329
11	2-$ClC_6H_4CH(OAc)_2$ (**13d**)	**3d**	**12b**	61	166-167.5
12	3-$BrC_6H_4CH(OAc)_2$ (**13e**)	**3d**	**12t**	44	203-205
13	3-$BrC_6H_4CH(OAc)_2$ (**13e**)	**3v**	**12e**	69	249-251
14	4-$FC_6H_4CH(OAc)_2$ (**13f**)	**3m**	**12u**	65	197-199
15	3-$FC_6H_4CH(OAc)_2$ (**13g**)	**3h**	**12g**	55	211-213
16	 (**13h**)	**3e**	**12s**	67	246-248
17	 (**13h**)	**3m**	**12i**	51	288-290

[a] First-step reaction conditions: aldehyde (1.5 mmol), Ac_2O (4 mmol), PWA (2 mol-%), 60 °C, 30 min. Second-step reaction conditions: DVM (1 mmol), AcOH (glc., 2 mL), 60 °C, 60 min. [b] Isolated yield.

(2 mL) were added and the resulting mixture was stirred at 60 °C for a further 1 h. As can be seen in Table 7, various symmetrical and unsymmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes were successfully synthesized under these conditions. The condensation reactions between acylals and DVMs containing halogenated aryl, phenyl and naphthyl groups afforded the corresponding anthracenes for the first time and in good yields.

Comparison of the results shown in Tables 6 and 7 shows that the syntheses of anthracene derivatives via the acylal intermediates are superior in terms of yield and amounts of the catalyst.



Scheme 4. Synthesis of the adduct **14** through the one-pot consecutive reaction between the DVM **4** and the acylal **13h**.

The applicability of this protocol was also confirmed when the tetrakis(veratryl) adduct **4** reacted with 2-[bis-(acetoxy)methyl]naphthaline **13h** through both diveratrylmethane moieties to afford the adduct **14** in 81% yield (Scheme 4).

A plausible mechanism for the formation of the 9,10-diarylanthracenes is proposed in Scheme 5. The acylal **A** is first produced through the reaction between the aldehyde and Ac_2O in the presence of PWA. The produced acylal undergoes two successive Friedel–Crafts reactions with the DVM **B** in the presence of the catalyst to give the intermediates **C** and **D**. The intermediate **D** is then converted into **E**. Finally, aromatization of **E** under air in the presence of catalyst affords the corresponding 9,10-diarylanthracene **F** as

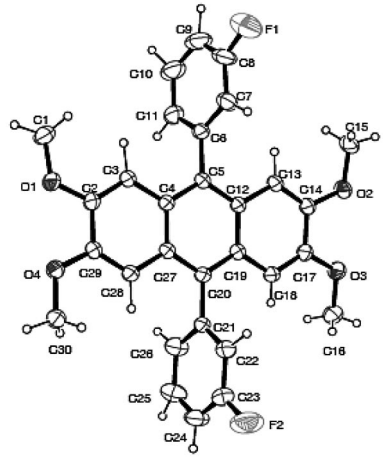
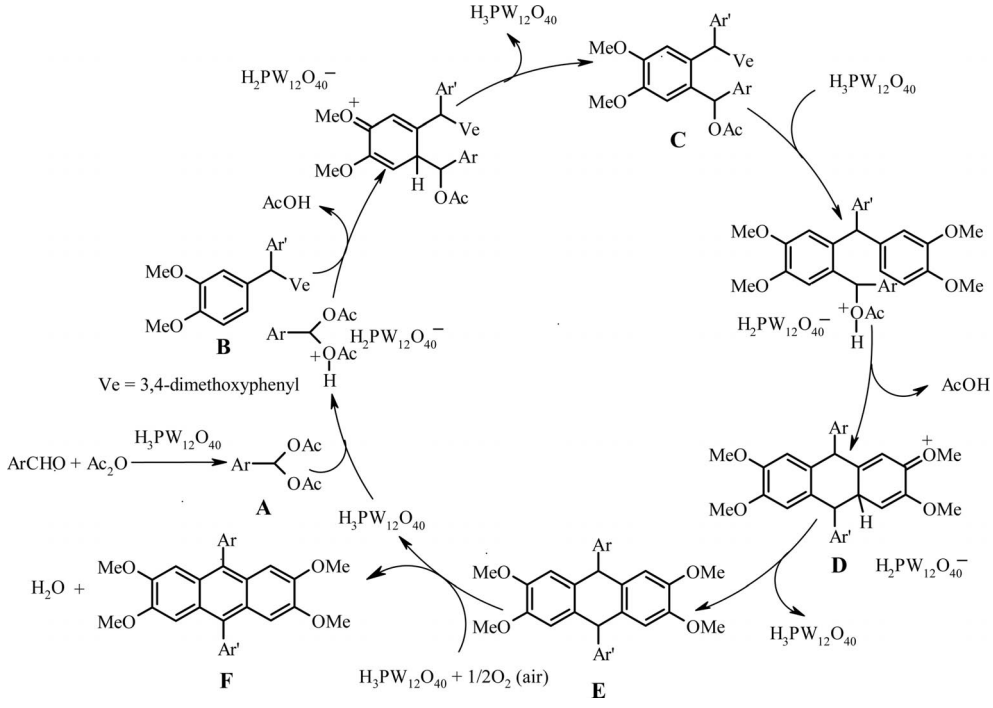


Figure 1. Crystal structure of **12g**.



Scheme 5. Plausible mechanism for the synthesis of 9,10-diarylanthracenes.

a desired product and releases the catalyst for the next run. In order to confirm this point, O_2 was bubbled into the reaction mixture of benzaldehyde (**2a**) and veratrole (**1**, Table 5, Entry 1). The results showed that the reaction was accelerated several times and the reaction time was reduced from 90 min to 30 min.[39]

The structures of the products were deduced from their IR, mass, ^{1}H NMR and ^{13}C NMR spectra and their elemental analyses. The structure of the product **12g** was also confirmed unambiguously by single-crystal X-ray analysis (see the Supporting Information and Figure 1).[40]

Conclusions

In summary, we have developed an efficient and green method for the solventless synthesis of triarylmethanes and difurylarylmethanes under thermal and microwave irradiation conditions in the presence of PWA as a reusable catalyst. One-pot reactions between veratrole and aldehydes were successfully used for the synthesis of symmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes. Moreover, the one-pot consecutive protocol has been used for the synthesis of symmetrical and unsymmetrical 9,10-diaryl-2,3,6,7-tetramethoxyanthracenes in good yields from acylals and DVMs as key precursors.

Experimental Section

General Information: The chemicals used in this work were purchased from Fluka and Merck. Progress of reactions was monitored by TLC (0.25 μm pre-coated silica gel plates). Melting point were determined with a Stuart Scientific SMP2 apparatus and are uncorrected. ^{1}H and ^{13}C NMR (500 and 125 MHz) spectra were recorded with a Bruker AC 500 spectrometer. FT-IR spectra were recorded over the 400–4000 cm^{-1} range with a Nicolet-Impact 400D instrument. Elemental analysis was carried out with a LECO, CHNS-932 instrument. Mass spectra were recorded with a Platform II spectrometer from Micromass. EI mode at 70 eV. The microwave system used in these experiments includes the following items: Micro-SYNTH labstation, complete with glass door, dual magnetron system with pyramid-shaped diffuser, 1000 W delivered power, exhaust system, magnetic stirrer, "quality pressure" sensor for flammable organic solvents, ATCFO fibre optic system for automatic temperature control.

Typical Procedure for Synthesis of DVMs and TRAMs Under Thermal Conditions (Table 2, Entry 3): Veratrole (**1**, 414 mg, 3 mmol), 3-nitrobenzaldehyde (**2c**, 151 mg, 1 mmol) and PWA (7 mol-%) were mixed in a 25 mL flask and stirred at 75 °C for 35 min. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc 4:1). At the end of the reaction, the mixture was allowed to cool to room temperature. CH_2Cl_2 (2 × 5 mL) was added and the catalyst was separated by simple filtration. The solvent was evaporated and the resulting mixture was recrystallized from EtOH. The pure product **3c** was obtained as a yellow solid in 93% yield; m.p. 154–155.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05–8.08 (m, 1 H, 4-H 3-nitrophenyl), 8.00 (s, 1 H, 2-H 3-nitrophenyl), 7.44–7.46 (m, 2 H, 5,6-H 3-nitrophenyl), 6.81 (d, J = 8.25 Hz, 2 H, 5-H veratryl), 6.65 (d, J = 1.95 Hz, 2 H, 2-H veratryl), 6.57 (dd, J = 8.25, J = 1.95 Hz, 2 H, 6-H veratryl), 5.53 (s, 1 H, Ar_3CH), 3.86 (s, 6 H, OCH_3), 3.77 (s, 6 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.16, 148.44, 148.04, 146.68, 135.35, 135.17, 129.12, 124.05, 121.51, 121.39, 112.72, 111.26, 55.91, 55.59 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3084, 3003, 2947, 1589, 1516, 1463, 1342, 1028, 916, 869, 736 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 410.12 (25.86) [M + 1]$^+$, 409.11 (100) [M]$^+$, 378.06 (46.26), 287.18 (40.23), 226.13 (9.99), 152.10 (7.33), 139.08 (6.90), 77.02 (14.01). $C_{23}H_{23}NO_6$ (409.15): calcd. C 67.47, H 5.66, N 3.42; found C 67.34, H 5.64, N 3.42.

Typical Procedure for Synthesis of DVMs and TRAMs Under Microwave Irradiation Conditions: See Table 3, Entry 4; 4-methylanisole (**5a**, 366 mg, 3 mmol), 2-naphthaldehyde (**2m**, 156 mg, 1 mmol) and PWA (4 mol-%) were mixed and exposed to MW irradiation (150 W) for 5 min. The reaction temperature was monitored with an IR optical sensor. At the end of the reaction, the mixture was allowed to cool to room temperature. The workup was performed as described for the thermal method and the pure product **6d** was obtained in 92% yield; m.p. 138–139 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.86 (m, 1 H, 6-H naphthyl), 7.78 (d, J = 8.78 Hz, 1 H, 4-H naphthyl), 7.74–7.78 (m, 1 H, 7-H naphthyl), 7.47 (d, J = 3.24 Hz, 1 H, 5-H naphthyl), 7.45 (d, J = 3.26 Hz, 1 H, 8-H naphthyl), 7.44 (s, 1 H, 1-H naphthyl), 7.34 (dd, J = 7.4, J = 1.71 Hz, 1 H, 3-H naphthyl), 7.07 (dd, J = 8.22, J = 1.96 Hz, 2 H, 4-H naphthyl), 6.85 (d, J = 8.24 Hz, 2 H, 3-H anisyl), 6.38 (s, 1 H, Ar_3CH), 3.71 (s, 6 H, OCH_3), 2.24 (s, 6 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.79, 142.41, 133.90, 132.66, 132.53, 131.40, 129.68, 129.14, 128.33, 128.08, 127.94, 127.79, 127.64, 125.94, 125.51, 111.39, 56.44, 43.61, 21.24 ppm. FT-IR (KBr): $\tilde{\nu}$ = 3049, 2935, 1068, 1492, 1436, 1363, 1234, 1105, 1035, 804, 742 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 384.15 (9.55) [M + 2]$^+$, 383.14 (56.50) [M + 1]$^+$, 382.04 (97.56) [M]$^+$, 367.07 (47.97), 351.02 (81.30), 335.07 (16.67), 319.06 (18.70), 289.03 (10.87), 260.14 (33.33), 245.11 (32.11), 229.16 (19.21), 215.18 (12.30), 152.24 (29.27), 140.96 (100), 135.08 (60.98), 122.07 (47.97), 104.96 (73.98), 91.03 (20.43), 77.05 (17.99). $C_{27}H_{26}O_2$ (382.19): calcd. C 84.78, H 6.85; found C 84.31, H 6.86.

The syntheses of the tetrakis(veratryl) adduct **4**, the tetrakis(anisyl) adduct **9** and the difurylarylmethanes **11a**–**c** were carried out, both under thermal and under microwave irradiation conditions, by the same methods as described for the synthesis of DVMs and TRAMs.

Typical Procedure for the Synthesis of Symmetrical 9,10-Diaryl-2,3,6,7-tetramethoxyanthracenes: See Table 5, Entry 6; In the first step, a mixture of veratrole (**1**, 414 mg, 3 mmol), 4-bromobenzaldehyde (185 mg, 1 mmol) and PWA (7 mol-%) was stirred at 75 °C for 30 min. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc 4:1). 4-Bromobenzaldehyde (370 mg, 2 mmol), PWA (2 mol-%), Ac_2O (4 mmol) and glacial AcOH (2 mL) were then added and the mixture was stirred at 75 °C for 90 min. The reaction mixture was allowed to cool to room temperature, CH_2Cl_2 (3 × 5 mL) was added, and PWA was separated by simple filtration. The organic layer was neutralized with saturated aqueous $NaHCO_3$ and dried with Na_2SO_4. The solvent was evaporated and the residue was purified with a short column of silica gel (eluent: *n*-hexane/EtOAc 4:1) to provide the pure anthracene **12f** in 65% yield; m.p. >330 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.2 Hz, 4 H, 2,6-H phenyl), 7.37 (d, J = 8.25 Hz, 4 H, 3,5-H phenyl), 6.76 (s, 4 H, 1,4,5,8-H anthracene), 3.76 (s, 12 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.20, 138.81, 132.79, 132.05, 131.88, 125.73, 121.73, 103.66, 55.64 ppm. FT-IR (KBr): $\tilde{\nu}$ = 2933, 2827, 1635, 1527, 1492, 1435, 1240, 1207, 1124, 1012, 974, 898, 844, 754, 582 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 610.00 (54.86) [M + 4]$^+$, 608.00 (100) [M + 2]$^+$, 606.02 (52.78) [M]$^+$. $C_{30}H_{24}Br_2O_4$ (606): calcd. C 59.23, H 3.98; found C 59.17, H 4.02.

Typical Procedure for One-Pot Syntheses of Symmetrical and Unsymmetrical 9,10-Diaryl-2,3,6,7-tetramethoxyanthracenes: See Table 7, Entry 6; A mixture of benzaldehyde (**2a**, 159 mg, 1.5 mmol), Ac_2O (408 mg, 4 mmol) and PWA (2 mol-%) was stirred at 60 °C for 30 min to afford the acylal **13a**. Afterward, the DVM **3m** (1 mmol) and glacial AcOH (2 mL) were added and the resulting mixture was stirred at 60 °C for 1 h. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc 4:1). The reaction mixture was allowed to cool to room temperature and CH_2Cl_2 (3× 5 mL) was then added. The catalyst was separated by simple filtration. The solution was neutralized with saturated aqueous $NaHCO_3$. The organic layer was separated and dried with Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc 4:1) to afford the pure anthracene **12p** in 67% yield; m.p. 219–221 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.0 Hz, 1 H, 3-H naphthyl), 8.04 (d, J = 8.05 Hz, 1 H, 4-H naphthyl), 8.00 (s, 1 H, 1-H naphthyl), 7.95 (d, J = 7.2 Hz, 1 H, 8-H naphthyl), 7.59–7.65 (m, 5 H, phenyl), 7.51–7.59 (m, 3 H, 5,6,7-H naphthyl), 6.86 (s, 4 H, 1,4,5,8-H anthracene), 3.74 (s, 6 H, OCH_3), 3.65 (s, 6 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.04, 148.92, 139.88, 137.41, 133.80, 133.33, 132.78, 131.08, 130.00, 129.46, 128.72, 128.30, 128.16, 127.95, 127.46, 126.31, 126.13, 126.06, 125.93, 104.11, 103.99, 55.58, 55.51 ppm. FT-IR (KBr): $\tilde{\nu}$ = 2922, 2850, 1527, 1490, 1431, 1382, 1236, 1205, 1132, 1111, 1041, 999, 846, 758 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 502.17 (5.36) $[M + 2]^+$, 501.16 (32.62) $[M + 1]^+$, 500.12 (67.38) $[M]^+$. $C_{34}H_{28}O_4$ (500.20): calcd. C 81.58, H 5.64; found C 81.23, H 5.66.

The adduct **14** was prepared by the same method, through condensation of the acylal **13h** and the adduct **4** in the presence of PWA. Firstly, a mixture of 2-naphthaldehyde (**2m**, 312 mg, 2 mmol), Ac_2O (612 mg, 6 mmol) and PWA (2 mol-%) was stirred at 60 °C for 30 min to give the acylal **13h**. The tetrakis(veratryl) adduct **4** (325.5 mg, 0.5 mmol) and glacial AcOH (3 mL) were then added to the reaction mixture. The resulting mixture was stirred at 60 °C for 90 min. The workup was performed as mentioned and the pure adduct **14** was obtained in 81% yield; m.p. >330 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–8.17 (m, 8 H, naphthyl), 7.86 (s, 4 H, 2,3,5,6-H terephthaloyl), 7.63–7.71 (m, 6 H, naphthyl), 7.16 (s, 4 H, 4,4′,5,5′-H anthracene), 6.96 (s, 4 H, 1,1′,8,8′-H anthracene), 3.72 (s, 12 H, OMe), 3.82 (s, 12 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.05, 149.00, 139.08, 137.28, 133.78, 133.13, 132.98, 132.82, 131.63, 130.88, 129.99, 129.38, 128.40, 128.17, 127.98, 126.38, 126.25, 125.96, 104.23, 103.94, 55.65, 54.97 ppm. FT-IR (KBr): $\tilde{\nu}$ = 2947, 2827, 1629, 1527, 1492, 1435, 1238, 1205, 1132, 1112, 1006, 997, 898, 848, 748 cm^{-1}. $C_{62}H_{50}O_8$ (922.35): calcd. C 80.67, H 5.46; found C 82.58, H 5.47.

Supporting Information (see footnote on the first page of this article): General experimental procedures and characterization data along with copies of ^{1}H and ^{13}C NMR spectra.

Acknowledgments

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[1] a) V. Nair, S. Thomas, S. C. Mathew, K. G. Abhilash, *Tetrahedron* **2006**, *62*, 6731; b) M. S. Shchepinov, V. A. Korshun, *Chem. Soc. Rev.* **2003**, *32*, 170; c) D. F. Dubury, *Chem. Rev.* **1993**, *93*, 381; d) M. K. Parai, G. Panda, V. Chaturvedi, Y. K. Manju, S. Sinha, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 289.
[2] A. Katritzky, D. Toader, *J. Org. Chem.* **1997**, *62*, 4137.
[3] S. Lin, X. Lu, *J. Org. Chem.* **2007**, *72*, 9757.
[4] S. Saito, T. Ohawada, K. Shudo, *J. Am. Chem. Soc.* **1995**, *117*, 11081.
[5] J. Esquivias, R. G. Arrayas, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 629.
[6] R. Goossens, M. Smet, W. Dehaen, *Tetrahedron Lett.* **2002**, *43*, 6605.
[7] T. Miyai, Y. Onishi, A. Baba, *Tetrahedron* **1999**, *55*, 1017.
[8] S. Poder, J. Choudhury, U. K. Roy, S. Roy, *J. Org. Chem.* **2007**, *72*, 3100.
[9] S. Genovese, F. Epifano, P. Caroline, M. Curini, *Eur. J. Org. Chem.* **2009**, *8*, 1132.
[10] Z. Li, Z. Duan, J. Kang, H. Wang, L. Yu, Y. Wu, *Tetrahedron* **2008**, *64*, 1924.
[11] M. Kodomari, M. Nagamatsu, M. Akaike, T. Aoyama, *Tetrahedron Lett.* **2008**, *49*, 2537.
[12] a) F.-L. Sun, X.-J. Zheng, Q. Gu, Q.-L. He, S.-L. You, *Eur. J. Org. Chem.* **2010**, 47; b) F.-L. Sun, M. Zeng, Q. Gu, S.-L. You, *Chem. Eur. J.* **2009**, *15*, 8709; c) Q.-L. He, F.-L. Sun, X.-J. Zheng, S.-L. You, *Synlett* **2009**, 1111.
[13] a) T. Niwa, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 2373; b) J.-Y. Yu, R. Kuwano, *Org. Lett.* **2008**, *10*, 973.
[14] R. Ahmad, A. Riahi, P. Langer, *Tetrahedron Lett.* **2009**, *50*, 1490.
[15] a) A. S. K. Hashmi, *Catal. Today* **2007**, *122*, 211; b) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896; c) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; d) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232.
[16] A. S. K. Hashmi, L. Schwarz, P. Rubenbauer, M. C. Blanco, *Adv. Synth. Catal.* **2006**, *348*, 705.
[17] V. Nair, K. G. Abhilash, N. Vidya, *Org. Lett.* **2005**, *7*, 5857.
[18] a) D. M. Cho, S. R. Parkin, M. D. Watson, *Org. Lett.* **2005**, *7*, 1067; b) L. Shuhong, X. Junfeng, M. Xuening, X. Caihong, *Tetrahedron Lett.* **2008**, *49*, 1690; c) X. Chunsog, Z. Yuhong, *Org. Lett.* **2007**, *9*, 781; d) D. J. Morrison, T. K. Trefz, W. E. Piers, R. McDonald, M. Parvez, *J. Org. Chem.* **2005**, *70*, 5309; e) I. P. Beletskaya, A. Averin, A. G. Bessmertnykh, F. Dent, R. Guilard, *Tetrahedron Lett.* **2002**, *43*, 1193; f) C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer, G. G. Malliaras, *Org. Lett.* **2005**, *7*, 3163.
[19] a) M. Pope, H. Kallman, P. Magnante, *J. Chem. Phys.* **1963**, *38*, 2042; b) P. S. Vincett, W. A. Barlow, R. A. Hann, G. G. Roberts, *Thin Solid Films* **1982**, *94*, 171; c) K. Danel, T. Hyang, J. T. Lin, Y. Tao, C. Chuen, *Chem. Mater.* **2002**, *14*, 3860; d) C. A. Landis, S. R. Parkin, J. E. Anthony, *Jpn. J. Appl. Phys.* **2005**, *44*, 3921; e) E. Gondek, I. V. Kityk, A. Danel, *Mater. Chem. Phys.* **2008**, *112*, 301; f) R. Mondal, B. K. Shah, D. C. Neckers, *J. Org. Chem.* **2006**, *71*, 4085.
[20] a) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028; b) H. Meng, F. Sun, M. B. Goldfinger, G. D. Jaycox, Z. Li, W. J. Marshall, G. S. Blackman, *J. Am. Chem. Soc.* **2005**, *127*, 2406; c) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99; d) K. Itp, T. Suzuli, Y. Sakamato, D. Kuboto, Y. Inoue, F. Sato, S. Tokito, *Angew. Chem. Int. Ed.* **2003**, *42*, 1159; e) S. Ando, J.-I. Nishida, E. Fujiwara, H. Tada, Y. Inoue, S. Tokito, Y. Yamashita, *Chem. Mater.* **2005**, *17*, 1261.
[21] a) K. Varazo, F. Xie, D. Gulledge, Q. Wang, *Tetrahedron Lett.* **2008**, *49*, 5293; b) T. Gunnlaugsson, T. C. Lee, R. Parkesh, *Tetrahedron* **2004**, *60*, 11239; c) C. S. Park, J. Y. Lee, E.-J. Kang, J.-E. Lee, S. S. Lee, *Tetrahedron Lett.* **2009**, *50*, 671.
[22] D. H. Hua, M. Tamura, X. Huang, H. A. Stephany, B. A. Helfrich, E. M. Perchellet, B. J. Sperfslage, J.-P. Perchellet, S. Jiang, D. E. Kyle, P. K. Chiang, *J. Org. Chem.* **2002**, *67*, 2907.
[23] a) L. R. Barclay, *Friedel–Crafts and Related Reactions* (Eds.: G. A. Olah), Interscience, New York, **1964**, vol. 2, chapter 22; b) S. Saito, T. Ohwada, K. Shudo, *J. Am. Chem. Soc.* **1995**, *117*, 11081.
[24] C. K. Bradsher, *Chem. Rev.* **1946**, *38*, 447.
[25] I. Arganat, Y. S. Shih, *Synthesis* **1974**, 865.

[26] a) M. Ahmed, J. Ashby, M. Ayad, O. Meth-Cohn, *J. Chem. Soc. Perkin Trans. 1* **1973**, 1099; b) T. Yamato, N. Sakaue, N. Shinoda, K. Matsuo, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1193.
[27] L. F. Fieser, *Organic Reactions* (Eds.: R. Adams), John Wiley & Sons, Inc., New York, **1942**, vol. 1, p. 129.
[28] S. Kotha, A. K. Ghosh, *Synlett* **2002**, 451.
[29] T. Takahashi, Y. Li, P. Stepnicka, M. Kitamura, Y. Liu, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **2002**, *124*, 576.
[30] G. Li, S. Zhou, G. Su, Y. Liu, P. G. Wang, *J. Org. Chem.* **2007**, *72*, 9830.
[31] R. Ostaszewski, *Tetrahedron* **1998**, *54*, 6897.
[32] a) M. Smet, J. Van Dijk, W. Dehaen, *Synlett* **1999**, 495; b) M. Smet, J. Van Dijk, W. Dehaen, *Tetrahedron* **1999**, *55*, 7859.
[33] a) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171; b) M. Misono, *Chem. Commun.* **2001**, 1141; c) D. E. Katsoulis, *Chem. Rev.* **1998**, *98*, 359; d) G.-W. Wang, Y.-B. Shen, X.-L. Wu, *Eur. J. Org. Chem.* **2008**, 4367.
[34] a) K. Tanaka, *Solvent-Free Organic Synthesis*, Wiley-VCH, Weinheim, Germany, **2003**; b) K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025.
[35] a) I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, A. Mirjafari, *Polyhedron* **2008**, *27*, 2612; b) I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, S. F. Hojati, *Polyhedron* **2008**, *27*, 750; c) I. Mohammadpoor-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, S. F. Hojati, *Catal. Commun.* **2008**, *9*, 1153.
[36] The Hammett substituent constant (σ value) for the *meta*-MeO group is +0.115, suggesting that it has an electron-withdrawing effect; see: L. P. Hammett, *J. Am. Chem. Soc.* **1937**, *59*, 96.
[37] a) L. Perreux, A. Loupy, *Tetrahedron* **2001**, *57*, 9199; b) O. C. Kappe, D. Dallinger, *Nat. Rev.* **2006**, *5*, 51; c) O. C. Kappe, *Chem. Soc. Rev.* **2008**, *37*; d) O. C. Kappe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6250; e) A. De La Hoz, A. Diaz-Oritz, A. Moreno, *Chem. Soc. Rev.* **2005**, *34*, 164; f) B. L. Hayes, *Aldrichimica Acta* **2004**, *37*, 66.
[38] a) L. F. Tietze, U. Beifuss, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131; b) L. F. Tietze, B. Gordon, M. G. Kersten, *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, Germany, **2006**; c) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115; d) N. Hall, *Science* **1994**, *266*, 32.
[39] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171.
[40] CCDC-780464 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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