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Towards a facile synthesis of triarylethanones: palladium-catalyzed arylation of ketone enolates under homogeneous and heterogeneous conditions

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Abstract—The palladium-catalyzed regioselective α-monoarylation of deoxybenzoins and α,α-diarylation of acetophenones provides general, efficient access to 1,2,2-triarylethanones. After a comprehensive search for suitable experimental conditions to optimize such transformations, both reactions are alternatively conducted by means of either commercially available polymer-anchored catalysts or a very simple homogeneous catalytic system, thus avoiding the use of complex ligands. In addition, the synthesis of deoxybenzoins employing polymer-supported fibrous palladium catalysts is reported for the first time, and the excellent catalyst recycling properties suggest applicability to industrial purposes.

1. Introduction

Among the plethora of new methodologies provided by palladium based catalysts, the direct insertion of an aryl moiety next to a carbonyl group must be outlined, since such protocol has solved a long-standing problem in synthetic organic chemistry.[1] Indeed, palladium-catalyzed α-arylation of such soft, non-organometallic nucleophiles as ketone enolates with aryl halides avoids the need of preliminary transformation steps or the use of stoichiometric amounts of tin, lead or bismuth reagents.[2,3]

However, depending on the substrate, complex ligand systems are sometimes required, and several competitive processes have been described, i.e., *ortho*-arylation and uncontrolled mono/multiple arylations.[4]

Otherwise, despite its crucial role in synthetic organic chemistry, arylation of ketone enolates, as well as other modern palladium-catalyzed C–C bond-forming reactions have not been transferred to an industrial scale, bar a few examples.[5] One of the problems that the extension of such reactions to the large-scale synthesis of bulk chemicals must bear is related to the fact that working with homogeneously catalyzed systems involves costly removal of relatively expensive palladium catalyst residues. Hence the research work on developing heterogeneous catalytic systems made in the last years, essentially in order to reduce the cost and technical problems associated with removal of the catalyst and also to increase its lifetime.[5,6]

The heterogenization of homogeneous catalysts using a suitable modification of ligands by anchoring of *P*- or *N*-containing groups onto a polymer support has received much attention among the catalyst-product separation strategies developed so far, and elegant applications of such polymer-anchored palladium catalysts to Heck, Suzuki and Sonogashira coupling reactions have been described, showing in some cases high overall turning-numbers by efficient catalyst recycle.[7] Nevertheless, the catalyst preparation often involves high cost/specialized techniques, and the leaching of the catalyst due to its relative instability under reaction conditions is also a matter of concern in a world immersed in a race towards waste effluent minimization.[7a,b,e–g,8]

Following our search for reliable synthetic protocols leading to phenanthrofused heterocycles,[9] we planned the construction of the appealing pentacyclic systems **1** and **2** from a joint key precursor, 1,2,2-triarylethanones **3**, interesting by themselves not only for their close resemblance to tamoxifen, the most widely used adjuvant drug therapy for the treatment of estrogen receptor-positive breast cancer,[10] but also because they have been reported as useful drugs for the treatment of metabolic disorders.[11]

In this paper we wish to present our advances towards the

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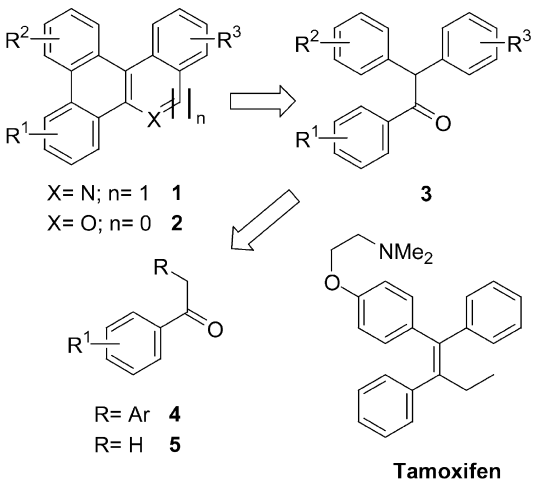
mono/multiple arylations of alkyl aryl ketones **4** and **5** by means of both homogeneous and polymer-anchored palladium catalysts, as well as a novel heterogeneously conducted monoarylation of acetophenones featuring an efficient catalyst-recycling.



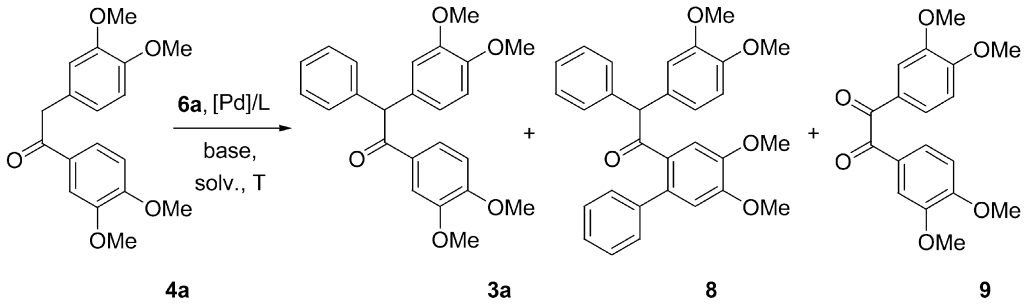
2. Results and discussion

2.1. Selective α-monoarylation of deoxybenzoins

Taking into account that the final steps of our scheduled approach to phenanthroderivatives **1** and **2** would probably require mono- or polyalkoxylated substrates, we initially envisaged that a selective α-monoarylation methodology amenable to both electron rich deoxybenzoins **4**,[12] and aryl halides **6** would constitute a convenient entry to intermediates **3**. Accordingly, an array of experimental conditions were assayed on 1,2-bis(3,4-dimethoxyphenyl)ethanone **4a** and bromobenzene **6a** in order to obtain the corresponding triarylethanone **3a**.

Despite previous reports,[1c,13] no target phenylated ketone **3a** was obtained in the absence of ligand or by using bulky bidentate phosphine ligands such us BINAP or DPPF. Another catalyst ($PdCl_2$) already used by Miura et al. to perform the arylation of 1,2-diphenylethanone[14] exhibited a high dependence on the electronic nature of the ketone precursor, as only poor results were obtained when applied to model substrate **4a**, even using iodobenzene **7** as the

Table 1. Selected α-arylation assays performed by homogenous palladium catalysts



Entry	Reaction conditions	Product (%)[a]
1	2 mol% Pd_2dba_3, NaO^{t}Bu, THF, 80 °C, 6 h[b]	**4a** (92)
2	2 mol% $Pd(OAc)_2$, KO^{t}Bu, toluene, 90 °C, 3 h[b]	**4a** (90)
3	5 mol% $Pd(OAc)_2$, K_2CO_3, toluene, 90 °C, 23 h[b]	**4a** (93)
4	2 mol% $Pd_2(dba)_3$, 5 mol% BINAP, KO^{t}Bu, THF, 70 °C, 6 h[b]	**4a** (98)
5	5 mol% $Pd_2(dba)_3$, 5 mol% DPPF, KO^{t}Bu, THF, 70 °C, 6 h[b]	**4a** (97)
6	5 mol% $PdCl_2$, K_2CO_3, DMF, 100 °C, 6 h[c]	—[d]
7	5 mol% $PdCl_2$, Cs_2CO_3, DMF, 100 °C, 6 h[c,e]	**4a** (68) **3a** (20)
8	5 mol% $PdCl_2$, 20 mol% PPh_3, K_2CO_3, DMF, 130 °C, 6 h[c]	**4a** (50) **3a** (24)
9	5 mol% $PdCl_2$, 20 mol% PPh_3, K_2CO_3, DMF, 100 °C, 6 h[c,e]	—[d]
10	2 mol% $Pd(OAc)_2$, 5 mol% PPh_3, K_2CO_3, *o*-xylene, 170 °C, 22 h[b]	**3a** (58) **8** (31) **9** (6)
11	5 mol% $Pd(OAc)_2$, 5 mol% PPh_3, Cs_2CO_3, *o*-xylene, 170 °C, 12 h[b]	**3a** (23) **8** (32) **9** (25)
12	2 mol% $Pd(OAc)_2$, 5 mol% PPh_3, Cs_2CO_3, DMF, 170 °C, 0.7 h[b]	**3a** (56) **8** (38)
13	2 mol% $Pd(OAc)_2$, 8 mol% PPh_3, K_2CO_3, *o*-xylene, 150 °C, 9 h[f]	**3a** (86)
14	2 mol% $Pd(OAc)_2$, 8 mol% PPh_3, Cs_2CO_3, DMF, 150 °C, 0.5 h[f]	**3a** (89)
15	5 mol% $Pd(OAc)_2$, 6.25 mol% PEt_3, Cs_2CO_3 DMF, 150 °C, 6 h[b]	**4a** (41) **3a** (32) **8** (29)
16	5 mol% $Pd(OAc)_2$, 6.25 mol% P^{n}Bu$_3$, NaO^{t}Bu, THF, 80 °C, 6 h[b]	**4a** (96)
17	5 mol% $Pd(OAc)_2$, 20 mol% P^{t}Bu$_3$, Cs_2CO_3 DMF, 150 °C, 7 h[b]	**4a** (56)-[d]
18	5 mol% $Pd(OAc)_2$, 6.25 mol% P^{t}Bu$_3$, NaO^{t}Bu, THF, 80 °C, 6 h[b]	**4a** (74) **3a** (12)-[d]
19	5 mol% $Pd(OAc)_2$, 20 mol% P(*o*-tolyl)$_3$, Cs_2CO_3, DMF, 150 °C, 1 h[b]	**4a** (67) **3a** (16)
20	5 mol% $Pd(OAc)_2$, 20 mol% P(*o*-tolyl)$_3$, NaO^{t}Bu, THF, 80 °C, 6 h[b]	**4a** (91)

[a] GC-MS yields of detected products measured on the basis of the starting amount of diarylketone **4a**. Propiophenone was used as the internal standard.
[b] 1.3 equiv. of **6a** and 2.5 equiv. of base were used.
[c] 1.2 equiv. of **6a** and 1.2 equiv. of base were used.
[d] Complex mixtures of products were obtained.
[e] 1.2 equiv. of iodobenzene **7** were used instead of **6a**.
[f] 1 equiv. of **6a** and 2.5 equiv. of base were used.

arylating agent. An increase of the yield of target **3a** was achieved by means of the catalytic system $Pd(OAc)_2/PPh_3$ but in this case significant amounts of *ortho*-arylated product **8** were also isolated whatever the solvent employed. This interesting[15] but inconvenient side reaction was predictable, as a similar behaviour had already been reported by the latter authors when using $Pd(OAc)_2$, leading to uncontrolled multiple arylation processes.[4d–f] Little amounts of α-diketone **9** were also isolated in some cases when no degassed solvents were used.[16] However, a careful optimization of the reaction conditions (temperature, reaction time and relative amounts of catalyst and bromobenzene **6a**) avoided both *ortho*-arylation and oxidation reactions, thus providing triarylethanone **3a** in good yields (Table 1, entries 13 and 14). After choosing DMF solvent for shorter reaction time, a range of triarylethanones **3a–n** were synthesized combining, under such conditions, different deoxybenzoins **4** and aryl bromides **6**.

According to the moderate to good yields obtained in most cases, we can conclude that the presented methodology constitutes a convenient access to 1,2,2-triarylethanones, even rivaling the elegant Heck-type triarylation approach recently reported by Nilsson et al.[17] Indeed, apart from the mild conditions employed,[18] neither complex ligand systems[4a–c,19] nor excess of the coupling partners are required, unlike previous reports where up to 2.3 excess of one of them is needed and reaction yields are measured with regard of the starting amount of the haloarene.[4d,13a,e,14,20]

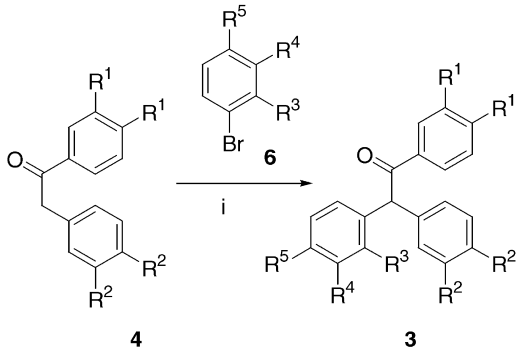
2.2. A search for structure/reactivity relationship. Theoretical and practice-based insights

It is clear from the data shown in Table 2 that our method provides a simple approach to triarylethanones **3**. However, in order to increase our knowledge about the dependence of the already optimized procedure on the electronic nature and steric volume of the coupling partners **4** and **6**, a series of computational calculations (Tables 3–5) was performed, mainly focussed on the relative stability of intermediates **10–12** shown in Scheme 1, a mechanistic depict made in concordance with the generally assumed reaction-steps.[1c,21]

With regard to enolate intermediate **11**, the calculation performed by the semiempirical protocol AM1 revealed, besides the already known higher stability of resonance form **11a**, that i) the presence of methoxy substituents stabilizes, with a cumulative effect, both resonance forms **11a–b** and ii) a complete delocalization of the negative charge across the system in **11a**, as can be deduced from the almost equivalent formation heat values found in entries 2 and 6, or 3 and 7.

PM3 semiempiririca method was used to evaluate the relative stability of palladium(II) intermediate **10**, showing in this case that substituted aryl groups, and in particular the methoxylated ones, stabilize more efficiently complex **10** than simple phenyl group. Finally, the calculated (PM3) energy levels for intermediates formed by ligand substitution **12a–c** evidence the higher stability of *O*-bound palladium complex **12b**,[22] along with the already manifested cumulative stabilizing effect of methoxy substituents.

Table 2. Palladium-catalyzed α-arylation of deoxybenzoins **4**



i: $Pd(OAc)_2/PPh_3$, Cs_2CO_3, DMF, 150°C, 0.5-1h

Entry	R^1	R^2	R^3	R^4	R^5	**3** (%)[a]
1	OMe	OMe	H	H	H	**3a** (85)
2	OMe	OMe	H	OMe	H	**3b** (51)
3	OMe	OMe	H	H	OMe	**3c** (46)
4	OMe	OMe	H	OMe	OMe	**3d** (47)
5	OMe	OMe	H	OCH_2O		**3e** (55)
6	OMe	OMe	OMe	OMe	OMe	**3f** (12)
7	OMe	OMe	H	H	NO_2	**3g** (44)
8	OMe	H	H	H	H	**3h** (74)
9	H	H	H	H	H	**3i** (80)
10	H	H	H	OMe	H	**3j** (73)
11	H	H	H	H	OMeH	**3k** (71)
12	H	H	H	OMe	OMeH	**3l** (57)
13	H	H	H	OCH_2O		**3m** (70)
14	H	H	H	H	NO_2	**3n** (54)

[a] Isolated yield.

Table 3. Calculated heats of formation of ketone enolates **11**

Entry	Ar^1	Ar^2	$E_{\mathbf{11a}}$[a]	$E_{\mathbf{11b}}$[a]
1	Ph	Ph	−10.13	6.55
2	Ph	2-$MeOC_6H_4$	−47.39	−23.23
3	Ph	3-$MeOC_6H_4$	−49.77	−32.97
4	Ph	4-$MeOC_6H_4$	−48.94	−32.39
5	Ph	3,4-$(MeO)_2C_6H_3$	−86.57	−68.03
6	2-$MeOC_6H_4$	Ph	−46.70	−4.19
7	3-$MeOC_6H_4$	Ph	−49.01	−8.23
8	4-$MeOC_6H_4$	Ph	−48.94	−7.38
9	3,4-$(MeO)_2C_6H_3$	Ph	−84.83	−42.01
10	3,4-$(MeO)_2C_6H_3$	3,4-$(MeO)_2C_6H_3$	−160.44	−149.96

[a] Heat of formation expressed in kcal/mol.

Table 4. Calculated heats of formation of oxidative addition intermediates **10**

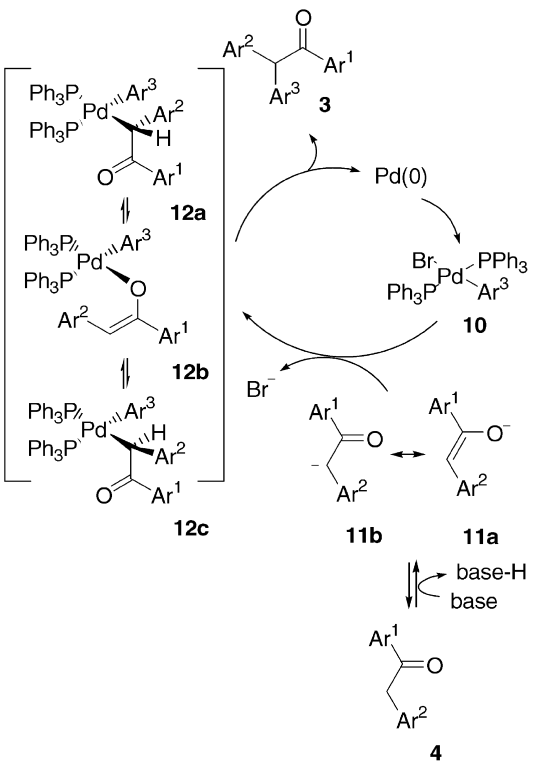
Entry	Ar^3	$E_{\mathbf{10}}$[a]
1	Ph	72.79
2	3-$MeOC_6H_4$	33.89
3	4-$MeOC_6H_4$	35.14
4	3,4-$(MeO)_2C_6H_3$	0.10
5	4-NO_2 C_6H_4	60.24
6	2,3,4-$(MeO)_3C_6H_2$	−37.65

[a] Heat of formation expressed in kcal/mol.

Table 5. Calculated heats of formation of ketone enolates **12**

Entry	Ar^1	Ar^2	Ar^3	E_{12a}[a]	E_{12b}[a]	E_{12c}[a]
1	Ph	Ph	Ph	129.26	126.75	133.03
2	Ph	3,4-$(MeO)_2C_6H_3$	Ph	55.20	53.96	56.92
3	Ph	Ph	3,4-$(MeO)_2C_6H_3$	55.1	53.34	55.48
4	3,4-$(MeO)_2C_6H_3$	Ph	Ph	57.73	52.71	58.36
5	3,4-$(MeO)_2C_6H_3$	3,4-$(MeO)_2C_6H_3$	2,3,4-$(MeO)_2C_6H_2$	−13.05	−19.08	−12.81
6	3,4-$(MeO)_2C_6H_3$	3,4-$(MeO)_2C_6H_3$	Ph	−14.43	−19.45	−15.69
7	3,4-$(MeO)_2C_6H_3$	3,4-$(MeO)_2C_6H_3$	3,4-$(MeO)_2C_6H_3$	−89.13	−93.50	−89.10

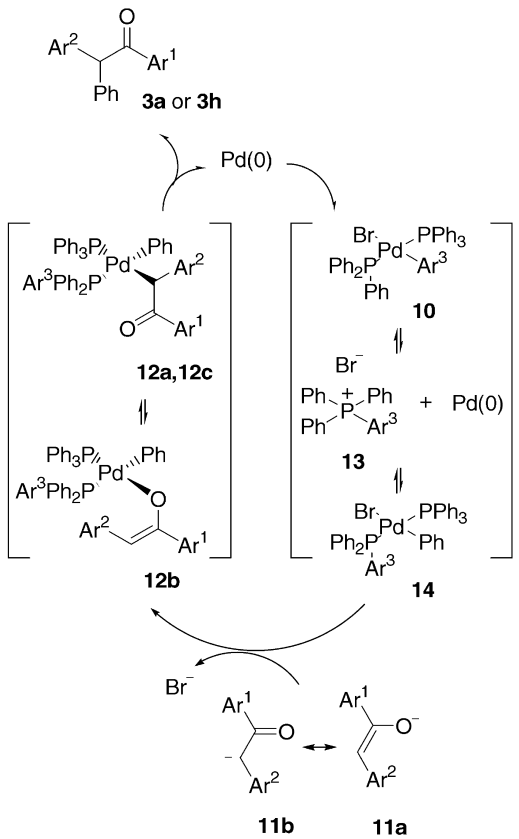
[a] Heat of formation expressed in Kcal/mol.



Scheme 1.

Turning back to experimental results, we can observe a decrease in reaction yields the higher the number of alkoxy groups is attached to both coupling reagents, especially to ketone **4**. If the calculated increasing stability of the corresponding polymethoxylated intermediates **10**–**12** is considered, such stability can be tentatively associated with a relative lack of reactivity towards formation of palladium enolate or reductive elimination key steps,[23] thus allowing competition with undesirable side-reactions. An additional factor to be considered is steric hindrance at the ligand exchange or at reductive elimination step from *C*-bound palladium enolate,[24] probably crucial to explain the low yield obtained for heptamethoxylated ketone **3f** (Table 2, entry 6).

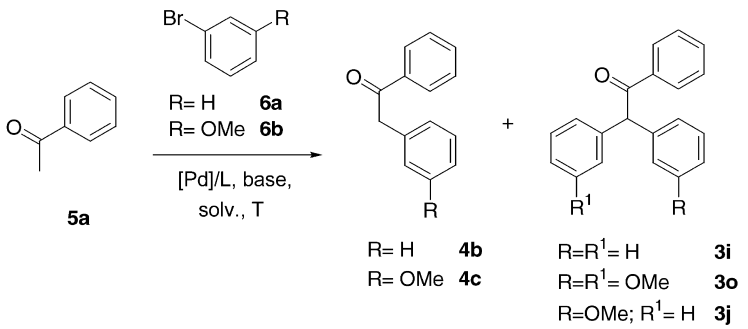
Regarding concomitant side-processes, if *ortho*-arylation had been effectively avoided, which one remained? A more detailed examination of the crude mixtures from the reaction leading to ketone **3d** revealed the presence of phenylated product **3a** (20%). Although to a lower extent (10–15%), undesired phenyl derivatives **3a** and **3h** were also isolated from every reaction mixture leading to ketones **3b**–**g** and **3j**–**n**, respectively. Such behaviour, provoked by a palladium-mediated P–C bond cleavage in phosphanes, is already known in other organic reactions where the catalytic system comprises palladium and phosphine ligands,[25] but unreported so far in arylation of ketone enolates. In order to illustrate the latter process in our arylation, a tentative mechanistic proposal is shown in Scheme 2, including phosphonium bromide **13**, which has been suggested by some authors as a necessary intermediate in this kind of reactions.[26]



Scheme 2.

Taking into account that phenyl migration from phosphine ligands occurs most likely when electron rich arenes or aryl halides are employed,[25a,j,26] it is not surprising in our case the observed exchange with methoxylated haloarenes **6**. Unfortunately, all attempts to avoid phenyl migration by using other phosphines (see entries 15–20 in Table 1) provided negligible results.

Table 6. Selected α,α-diarylation assays performed by homogeneous palladium catalysts



Entry	Reaction conditions	Product (%)[a]
1	**6a**, 5 mol% Pd_2dba_3, NaO^{t}Bu, THF, 80 °C, 6 h[b,c]	**5a** (99)
2	**6a**, 3 mol% $PdCl_2$, 12 mol% PPh_3, K_2CO_3, DMF, 130 °C, 1.5 h[b,c]	**3i** (11) **5a** (79)
3	**7**, 3 mol% $PdCl_2$, Cs_2CO_3, DMF, 100 °C, 6 h[d,e]	**3i** (49) **5a** (31)
4	**6a**, 5 mol% $Pd(OCOCF_3)_2$, 20 mol% PPh_3, Cs_2CO_3, DMF, 150 °C, 1.5 h[b,e]	**3i** (82) **5a** (4) **4b** (4)
5	**6a**, 0.5 mol% $Pd(PPh_3)_4$, Cs_2CO_3, DMF, 150 °C, 3 h[b,e]	**3i** (18) **5a** (65) **4b** (1)
6	**6a**, 1 mol% $Pd(PPh_3)_4$, Cs_2CO_3, *o*-xylene, 150 °C, 5 h[b,e]	**3i** (71) **5a** (1) **4b** (2)
7	**6a**, 1 mol% $Pd(OAc)_2$, 5 mol% PPh_3, Cs_2CO_3, DMF, 150 °C, 2 h[b,e]	**3i** (68) **5a** (12) **4b** (1)
8	**6a**, 5 mol% $Pd(OAc)_2$, 20 mol% PPh_3, Cs_2CO_3, DMF, 150 °C, 1 h[b,e]	**3i** (94) **5a** (2) **4b** (2)
9	**6a**, 5 mol% $Pd(OAc)_2$, 6.3 mol% PEt_3, Cs_2CO_3, DMF, 150 °C, 6 h[b,c]	**3i** (27) **5a** (35)
10	**6a**, 5 mol% $Pd(OAc)_2$, 20 mol% P(*o*-tolyl)$_3$, Cs_2CO_3, DMF, 153 °C, 1 h[b,c]	**3i** (8) **5a** (51) **4b** (22)
11	**6a**, 5 mol% $Pd(OAc)_2$, 6.3 mol% P(*o*-tolyl)$_3$, NaO^{t}Bu, THF, 80 °C, 6 h[b,c]	**5a** (4) **4b** (80)
12	**6b**, 5 mol% $Pd(OCOCF_3)_2$, 20 mol% PPh_3, Cs_2CO_3, DMF, 150 °C, 1.5 h[b,e]	**3o** (54) **5a** (8) **4c** (11) **3j** (9)
13	**6b**, 1 mol% $Pd(PPh_3)_4$, Cs_2CO_3, *o*-xylene, 150 °C, 5 h[b,e]	**3o** (25) **5a** (59) **3j** (11)
14	**6b**, 5 mol% $Pd(OAc)_2$, 20 mol% PPh_3, Cs_2CO_3, DMF, 153 °C, 1.5 h[b,e]	**3o** (72) **5a** (2) **4c** (4) **3j** (8)
15	**6b**, 5 mol% $Pd(OAc)_2$, 20 mol% P^{t}Bu$_3$, NaO^{t}Bu, THF, 80 °C, 6 h[b,c]	**3o** (5) **5a** (70)

[a] GC-MS yields of detected products measured on the basis of the starting amount of acetophenone **5a**. Propiophenone was used as the internal standard.
[b] 3.4 equiv. of bromoarene **6** were used.
[c] 2.5 equiv. of base were used.
[d] 2.2 equiv. of iodobenzene **7** were used instead of **6a**.
[e] 3.0 equiv. of base were used.

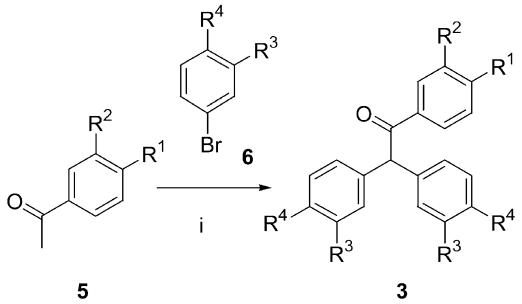
2.3. α,α-Diarylation of acetophenones

To the best of our knowledge, although diverse examples of palladium-catalyzed multiple arylation of carbonyl compounds have been reported in the last years,[4d–e,13a,c–e,14,27] no examples of a general, regioselective methodology for the α,α-diarylation of ketones have been presented so far.[28] Interestingly, in our case, such transformation would constitute a direct access to target triarylethanones **3** from commercially available acetophenones **5**, thus eluding a preliminary preparation of deoxybenzoins **4**.

With this aim in mind, and taking into account the above disclosed results on the monoarylation of deoxybenzoins **4**, acetophenone **5a** was submitted to an array of experimental conditions employing bromobenzene **6a** and 3-bromoanisole **6b** as arylating agents (Table 6). In spite of the good results provided by $Pd(OCOCF_3)_2/PPh_3$, $Pd(PPh_3)_4$ and $Pd(OAc)_2/PPh_3$ when using **6a**, diarylation of methoxylated derivative **6b** required the use of the latter catalytic system, in a slightly different but reasonably similar conditions to the already optimized protocol for the monoarylation of deoxybenzoins (compare Table 6, entries 8 and 14 with Table 1, entry 14).

In order to test the generality of the reported procedure, a series of commercially available acetophenones **5** and bromoarenes **6** were coupled under the latter conditions, and save for the relatively low yield of nitro derivative **3q**,

Table 7. Palladium-catalyzed α,α-diarylation of acetophenones **5**



i: $Pd(OAc)_2/PPh_3$, Cs_2CO_3, DMF, 153°C, 1-7h

Entry	R^1	R^2	R^3	R^4	**3** (%)[a]
1	OMe	OMe	H	H	**3h** (62)
2	OMe	OMe	OMe	H	**3p** (57)
3	OMe	OMe	OMe	OMe	**3d** (47)
4	OMe	OMe	H	NO_2	**3q** (35)
5	OMe	OMe	H	F	**3r** (52)
6	H	H	H	H	**3i** (91)
7	H	H	OMe	H	**3o** (71)
8	H	H	OMe	OMe	**3s** (61)
9	H	H	H	F	**3t** (63)
10	Me	H	H	H	**3u** (87)
11	Me	H	OMe	H	**3v** (69)
12	Me	H	OMe	OMe	**3w** (60)
13	Me	H	H	F	**3x** (68)

[a] Isolated yields.

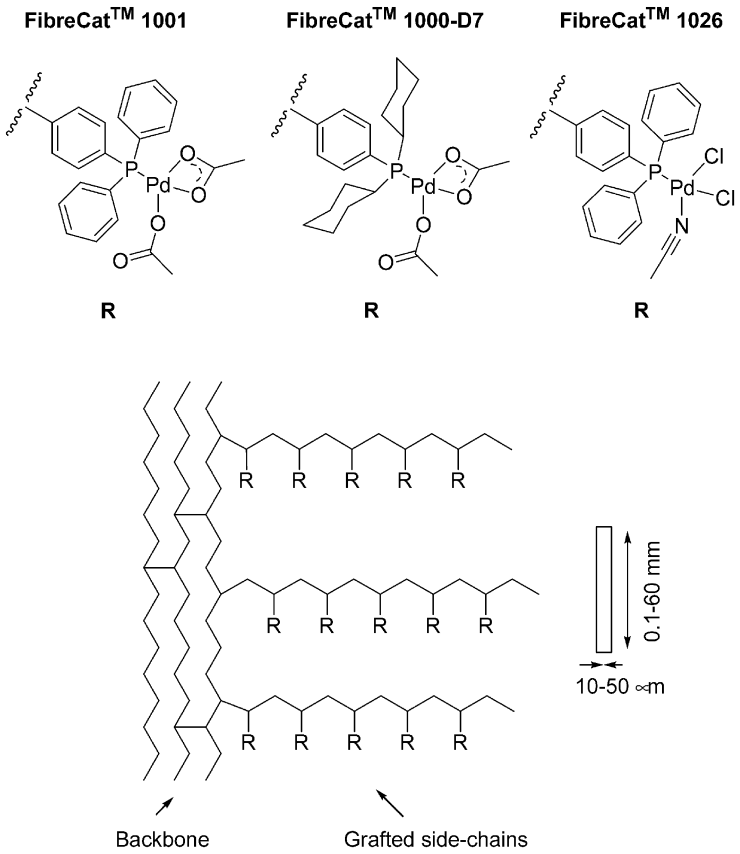


Figure 1. Example of FibreCat™ structure and different catalytic centers in FibreCat™ 1000 series.

the good results shown in Table 7 confirm that a reliable entry to triarylethanones **3** had been achieved by means of a simple, convenient protocol.

The trend of nitro group to be reduced in the presence of Pd/PPh_3 catalytic systems is already known,[25h] and certainly, according to the NMR signals corresponding to free amino groups detected in the crude mixture, it is one of the reasons of the low yield for ketone **3q**. Although $AsPh_3$ has been employed for the palladium-catalyzed arsination of *p*-nitrophenyl triflate without observing any reducing process,[25i] in our hands reduction to amino group was again observed along with an even lower yield for **3q** (7%) when replacing PPh_3 by $AsPh_3$.

The second factor that presumably decreased the yield of ketone **3q** and the rest of triarylethanones generated from other bromoarenes than bromobenzene **6a** was again phenyl-aryl exchange between bromoarenes **6** and PPh_3 ligand. Indeed, variable amounts of monophenylated ketones like **3j** (5–17%) were detected from the corresponding reaction mixtures,[29] and the similarity of such products generated from 'phenyl migration' to target ketones interfered with the purification works, thus even reducing the so-isolated yields.

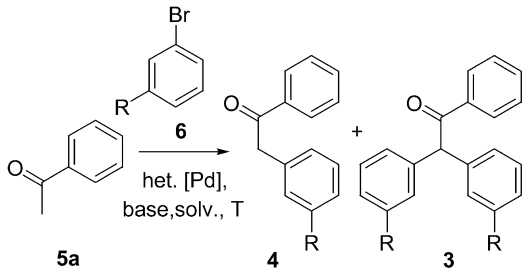
2.4. α,α-Diarylation conducted by heterogeneous catalysis

A preliminary literature search for heterogeneous palladium catalysis applied to arylation of ketones or even to arylation of other carbonyl compounds revealed an only report on arylation of a diactivated methylene derivative, diethyl malonate, by means of a Pd-loaded zeolite catalyst.[30]

Considering the difference between substrates, and more interested in polymer-supported catalysts, we sought for a convenient polymer-anchored catalyst to perform diarylation of acetophenones **5**, finally choosing commercially available FibreCat™ 1001, FibreCat™ 1000-D7 and FibreCat™ 1026 to carry out a series of preliminary assays. Our election was made considering not only the fibrous nature of the latter catalysts (Fig. 1), a feature that involves several advantages in terms of ease of handling, good mechanical properties and high functional group accessibility but also the excellent results displayed in other palladium-catalyzed coupling processes like Suzuki or Heck reactions.[31] In order to extend our comparative search to other heterogeneous systems, Pd/C catalyst[32] was also assayed and the results compared to those obtained from polymer-supported catalysts.

As summarized in Table 8, although all the heterogenized catalysts assayed provided target diphenylated product **3i**, only by using FibreCat™ 1026 the latter ketone **3i** was obtained with good yield (entry 10), and this procedure resulted also applicable to diarylation with methoxylated bromoarene **6b** (entry 13). Obviously palladium catalyzed processes cannot be compared when so different conditions as homogeneous and heterogeneous catalysis have been employed, but it is somehow surprising that the polymer-anchored catalyst FibreCat™ 1001, with a higher similarity

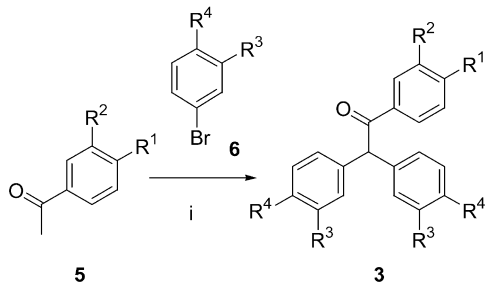
Table 8. Selected α,α-diarylation assays performed by heterogeneous catalysis



Entry	Reaction conditions	Product (%)[a]
1	**6a**, 5% Pd/C, Na_2CO_3, MeOH, 80 °C, 6 h[b]	**5a** (98)
2	**6a**, 5% Pd/C, NaOH, NH_4HCO_2, 100 °C, H_20, 2 h[b]	**5a** (94)
3	**6a**, 5% Pd/C, Na_2CO_3, DMF, 150 °C, 1.5 h[b]	**3i** (2) **5a** (89) **4b** (3)
4	**6a**, 1% FC 1001, K_2CO_3, toluene, 130 °C, 10 h[c]	**3i** (4) **5a** (71) **4b** (13)
5	**6a**, 5% FC 1001, K_2CO_3, toluene, 130 °C, 10 h[c]	**3i** (8) **5a** (40) **4b** (43)
6	**6a**, 1% FC 1000-D7, K_2CO_3, toluene, 130 °C, 10 h[c]	**3i** (45) **5a** (32) **4b** (16)
7	**6a**, 2% FC 1000-D7, K_2CO_3, *o*-xilene, 153 °C, 6 h[c]	**3i** (15) **5a** (32) **4b** (42)
8	**6a**, 2% FC 1000-D7, Cs_2CO_3, DMF, 153 °C, 1 h[c]	**5a** (87) **4b** (3)
9	**6a**, 2% FC 1026, Cs_2CO_3, DMF, 153 °C, 3 h[c]	**3i** (17) **5a** (41)
10	**6a**, 5% FC 1026, Cs_2CO_3, DMF, 153 °C, 1 h[c]	**3i** (93) **5a** (2) **4b** (2)
11	**6b**, 5% FC 1001, K_2CO_3, toluene, 130 °C, 10 h[c]	**3o** (6) **5a** (47) **4c** (32)
12	**6b**, 1% FC 1000-D7, K_2CO_3, toluene, 130 °C, 10 h[c]	**3o** (32) **5a** (37) **4c** (17)
13	**6b**, 5% FC 1026, Cs_2CO_3, DMF, 153 °C, 1 h[c]	**3o** (85) **4c** (2) **3j** (1)

[a] GC-MS yields measured on the basis of the starting amount of ketone **2a**. Propiophenone was used as the internal standard.
[b] 3.3 equiv. of aryl bromide **6**, a 5% Pd/C mixture and 3 equiv. of base were used.
[c] 3.3 equiv. of aryl bromide **6**, 3 equiv. of base and the indicated FibreCat™ catalyst (FC) were used. The disclosed proportion of FC (%) refers to the relative amount of Pd metal from the FC catalyst. The average content of Pd in the employed FC samples is 3%.

Table 9. Polymer-anchored palladium-catalyzed α,α-diarylation of acetophenones **5**



i: FibreCat™ 1026, Cs_2CO_3, DMF, 153°C, 0.8-1h

Entry	R^1	R^2	R^3	R^4	**3** (%)[a]
1	OMe	OMe	H	H	**3h** (90)
2	OMe	OMe	OMe	H	**3p** (82)
3	OMe	OMe	OMe	OMe	**3d** (64)
4	OMe	OMe	H	NO_2	**3q** (20)
5	OMe	OMe	H	F	**3r** (70)
6	H	H	H	H	**3i** (89)
7	H	H	OMe	H	**3o** (79)
8	H	H	OMe	OMe	**3s** (80)
9	H	H	H	F	**3t** (73)
10	Me	H	H	H	**3u** (93)
11	Me	H	OMe	H	**3v** (75)
12	Me	H	OMe	OMe	**3w** (92)
13	Me	H	H	F	**3x** (80)

[a] Isolated yields.

to the optimized homogeneous system $Pd(OAc)_2/PPh_3$, turned out to be the least efficient to perform target diarylation. On the other hand, FibreCat™ 1026, with a closer resemblance to the non-effective homogeneous $PdCl_2/PPh_3$ system, featured excellent qualities for such task and therefore was applied to the synthesis of triaryl ethanones **3** disclosed in Table 9.[33]

A brief comparative look at Tables 7 and 9 shows an evident advantage in terms of yield when the heterogeneous system was employed. Such improvement is mainly due to the practical avoidance (<4%) of phenyl migration, which in addition facilitates purification of target ketones **3**. Moreover, catalyst separation carried out by simple filtration of the reaction mixture. However, there is a weak spot in our firstly reported diarylation under heterogeneous conditions, clearly related to the relatively high temperatures required (153 °C). The limit of the thermal stability of FibreCat™ Series has been established at *circa* 120 °C,[31] therefore it was predictable that leaching of the catalyst could happen under our harsher reaction conditions. Indeed, no catalytic activity was found for already used FibreCat™ 1026 catalyst, and such leaching behaviour would also explain the detected traces of phenyl exchange products.

2.5. α-Monoarylation of deoxybenzoins under heterogeneous conditions

Once observed the improvement made in diarylation reaction by means of polymer anchored FibreCat™ 1026, a range of experimental conditions similar to the ones shown in Table 8 were assayed in order to effect the regioselective α-monoarylation of deoxybenzoins **4** using polymer-supported catalysts.

Again FibreCat™ 1026 turn out to be the most efficient catalyst for this task, but despite an easier purification, the yields of target triarylethanones **3** prepared under such conditions were in most cases, as shown in Table 10, clearly inferior to the ones obtained from the previously mentioned homogeneous $Pd(OAc)_2/PPh_3$ catalyst (Table 7). We tentatively propose that, in comparison with acetophenone derivatives **5**, deoxybenzoins **4** could encounter a higher steric hindrance to reach the catalytic centers attached to the polymer-bone, thus preventing to some extent an effective catalysis.

In addition, the same relatively high temperature (153 °C) was required, thus damaging the catalyst and making it useless for further arylations.

It should be pointed out that, in spite of the lack of catalyst recycling shown in the polymer-supported versions of the described arylations, four different approaches to the 1,2,2-triarylethanone system **3** have been presented.

Apart from the Heck-type synthesis reported by Nilsson et al.[17] the other existing methodologies to construct such interesting framework,[10,11,34] which involve (i) $TiCl_4$/Sm-promoted reductive coupling of benzophenones and nitriles,[35] (ii) oxidative nucleophilic addition of diphenyl methyl anion to benzaldehyde,[36] (iii) pinacolinic rearrangement[37] and (iv) nucleophilic substitution with benzotriazole derived carbanions,[38] generally present serious limitations concerning tolerability of functional groups and restricted substitution patterns at the precursors.

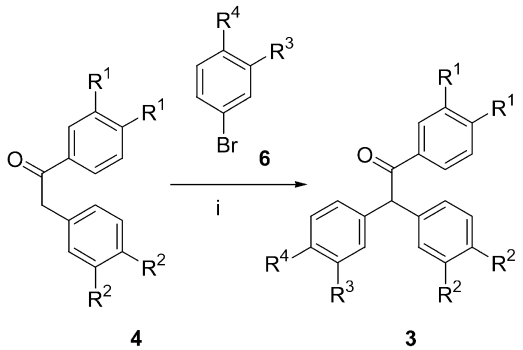
In addition, the applicability of our four procedures to mono/polymethoxylated substrates have been completely proved, thus extending the scope of palladium-catalyzed arylation of ketone enolates to electron-rich substrates. It cannot be ignored that in previous reports on this subject, neutral or electron-deficient coupling partners are normally used,[4a,c,13a,b,e] and no account on the use of methoxylated ketones has been found in the literature.

2.6. α-Monoarylation of acetophenones using polymer-anchored catalysts

Taking profit of our experience in the synthesis of triarylethanones **3** from acetophenones **5** and deoxybenzoins **4** by both homogeneous and heterogeneous catalysis, and in order to complete the interconversion among the three systems **3**–**5**, we planned the heterogeneously conducted monoarylation of acetophenones **5** as a new general entry to such important intermediates as deoxybenzoins.[39]

Although different procedures for the synthesis of deoxybenzoins by palladium-catalyzed arylation of acetophenones have been reported,[40] no heterogeneous conditions have been used so far. As described above, several assays to effect α,α-diarylation of acetophenones **5**

Table 10. Polymer-anchored palladium-catalyzed α-arylation of deoxybenzoins **4**

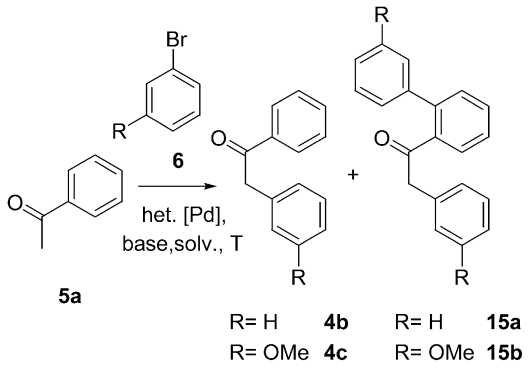


i: FibreCat™ 1026, Cs_2CO_3, DMF, 153°C, 0.8-1h

Entry	R^1	R^2	R^3	R^4	**3** (%)[a,b]
1	OMe	OMe	H	H	**3a** (40)[c]
2	OMe	OMe	OMe	H	**3b** (53)[c]
3	OMe	OMe	OMe	OMe	**3d** (53)
4	OMe	OMe	OCH_2O		**3e** (38)
5	OMe	H	H	H	**3h** (51)[c]
6	H	H	H	H	**3i** (57)[c]
7	H	H	OMe	H	**3j** (54)
8	H	H	H	OMe	**3k** (60)
9	H	H	OMe	OMe	**3l** (37)
10	H	H	OCH_2O		**3m** (45)

[a] Isolated yield.
[b] Unless indicated, 3.3 equiv. of aryl bromide **6**, 5% FibreCatTM 1026 catalyst and 3 equiv. of Cs_2CO_3 were used.
[c] 2.2 equiv. of aryl bromide **6** were used.

Table 11. Selected α-monoarylation assays performed by heterogeneous catalysis



Entry	Reaction conditions	Product (%)[a]
1	**6a**, 5% FC 1001, K_2CO_3, toluene, 100 °C, 10 h[b]	**5a** (41) **4b** (45)
2	**6a**, 2% FC 1000-D7, K_2CO_3, *o*-xylene, 100 °C, 6 h[b]	**5a** (35) **4b** (42)
3	**6b**, 5% FC 1001, K_2CO_3, toluene, 130 °C, 10 h[b]	**5a** (54) **4c** (31)
4	**6a**, 2% FC 1000-D7, Cs_2CO_3, DMF, 100 °C, 1 h[b]	**5a** (87) **4b** (1)
5	**6a**, 5% FC 1001, NaO^{t}Bu, THF, 85 °C, 6 h[b]	**4b** (52) **15a** (4)
6	**6b**, 2% FC 1001, NaO^{t}Bu, THF, 85 °C, 6 h[c]	**4c** (39) **15b** (47)
7	**6a**, 5% FC 1000-D7, NaO^{t}Bu, THF, 85 °C, 6 h[b]	**4b** (89) **15a** (1)
8	**6b**, 5% FC 1000-D7, NaO^{t}Bu, THF, 85 °C, 6 h[b]	**4c** (95)
9	**6b**, 2% FC 1000-D7, NaO^{t}Bu, THF, 85 °C, 6 h[c]	**4c** (26) **15b** (43)
10	**6a**, 2% FC 1026, NaO^{t}Bu, THF, 85 °C, 6 h[b]	**5a** (40) **4b** (31)
11	**6a**, 5% FC 1026, NaO^{t}Bu, THF, 85 °C, 6 h[b]	**5a** (1) **4b** (35)

[a] GC-MS yields measured on the basis of the starting amount of ketone **2a**. Propiophenone was used as the internal standard.
[b] 3.4 equiv. of aryl bromide **6**, 3 equiv. of base and the indicated FibreCat™ catalyst (FC) were used. The disclosed proportion of FC (%) refers to the relative amount of Pd metal from the FC catalyst. The average content of Pd in the employed FC samples is 3%.
[c] 2.4 equiv. of aryl bromide **6** were used.

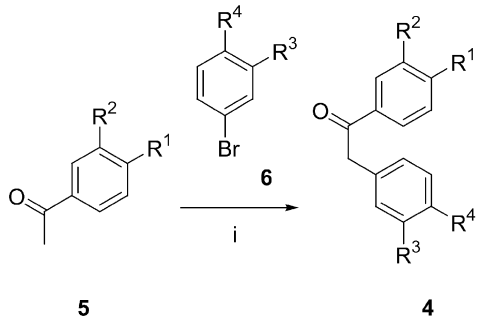
using FibreCat™ catalysts had afforded deoxybenzoins in different proportions (see for example entries 5, 7 and 11 in Table 8). Keeping in mind that the insertion of the second aryl group required relatively high temperatures, a range of milder conditions were assayed on acetophenone **5a** and aryl bromides **6a**–**b**.

Indeed, lowering the reaction temperatures to 85 °C along with suitable changes in the base/solvent system allowed us to obtain target diaryl ketones **4b** and **4c** in good yields (Table 11, entries 7 and 8), this time using FibreCat™ 1000-D7 as the most adequate catalyst. Accordingly, a series of deoxybenzoins **4** were easily prepared by the above-optimized procedure combining commercially available acetophenones **5** and aryl bromides **6** (Table 12). Apart from the good results achieved in this firstly reported synthesis of deoxybenzoins by heterogeneous catalysis, it is worth mentioning that no aryl exchange-derived product was detected. Moreover, *ortho*-arylation side-reaction leading to derivatives **15** was efficiently avoided.

With regard to catalyst recycle features, both recovery and reusability must be outlined. Recovery of the polymer-anchored catalyst was nearly quantitative (>97%) in all cases by simple filtration from the reaction mixture, and the so-recovered catalyst, after an easy treatment,[41] was reused up to 5 times without noticing any decrease in its catalytic activity, since the same yields were obtained employing equivalent amounts of the catalyst.

Finally, a comparative reflection on the use of the four protocols to access the triarylethanone framework **3**

Table 12. Polymer-anchored palladium-catalyzed α-monoarylation of acetophenones **4**



i: FibreCat™ 1000-D7, NaO^{t}Bu, THF, 85°C, 6h

Entry	R^1	R^2	R^3	R^4	**4** (%)[a,b]
1	OMe	OMe	OMe	OMe	**4a** (72)
2	OMe	OMe	H	H	**4d** (90)[c]
3	OMe	OMe	OMe	H	**4e** (88)[d]
4	OMe	OMe	H	F	**4f** (74)[c]
5	H	H	H	H	**4b** (87)
6	H	H	OMe	H	**4c** (92)
7	H	H	OMe	OMe	**4g** (91)[c]
8	H	H	H	F	**4h** (80)[c]
9	Me	H	H	H	**4i** (86)[c]
10	Me	H	OMe	H	**4j** (86)
11	Me	H	OMe	OMe	**4k** (82)[c]
12	Me	H	H	F	**4l** (74)[c]

[a] Isolated yield. The same value was obtained after five uses of the recovered catalyst.
[b] Unless indicated, 3.3 equiv. of aryl bromide **6**, %5 FibreCatTM 1000-D7 catalyst and 3 equiv. of NaO^{t}Bu were used.
[c] 2.2 equiv. of aryl bromide **6** were used.
[d] 1.5 equiv. of aryl bromide **6** were used.

presented in this paper should be made, considering as well the significance of the above described synthesis of deoxybenzoins. Although considered as alternative ways to the same end, the term complementary is more accurate, above all in the cases where the aryl group attached to C-2 position are different, as only monoarylation of deoxybenzoins **4** would provide such products.

In terms of number of steps required, α,α-diarylation of acetophenones **5** is clearly more direct. According to the slightly better yields obtained and the ease of purification, the approach based on polymer-anchored FibreCat™ 1026 would be the most convenient, although the lack of catalyst reuse cannot be obviated.

On the other hand, comparison between homogeneous and polymer-support catalysts in the α-monoarylation of deoxybenzoins features that the simple $Pd(OAc)_2/PPh_3$ system provides better results, probably due to the already mentioned hindrance of the substrate to access the catalyst site.

However, the best candidates of monoarylation (homogeneous) and diarylation (heterogeneous) approaches to triarylethanones **3** match if the highly advantageous preparation of deoxybenzoins **4** by means of recyclable FibreCat™ 1000-D7 catalyst is considered.

3. Conclusion

To sum up, the synthesis of structurally appealing 1,2,2-triarylethanones has been effected by four arylation procedures mediated by palladium catalysts. Two of them involve the α-monoarylation of deoxybenzoins performed by both homogeneous and polymer-anchored catalysts. Slight modifications in the corresponding experimental conditions provide two alternative protocols based on the regioselective α-diarylation of commercially available acetophenones conducted again in both homogeneous and hetereogeneous fashions. Altogether, the presented monoarylation and diarylation procedures comprise a general, efficient entry to the 1,2,2-triarylethanone system, featuring a high functional group tolerance, especially amenable to mono/polymethoxylated substrates. This research is elegantly complemented by the firstly reported α-monoarylation of acetophenones performed by polymer-supported catalysts, a cleaner, more efficient (in terms of chemical usage) protocol for the preparation of deoxybenzoins with obvious environmental and economic benefits regarding catalyst recovery and reuse.

4. Experimental

4.1. General methods

For general experimental details, see Ref. 12c. The semi-empirical calculations were performed[42] according to the models Austin Method 1 (AM1)[42] and Parametrization Method 3 with extensions for most transition metals (PM3)[43,44]

4.2. General procedure for the α-monoarylation of deoxybenzoins 4 under homogeneous conditions

Dry degassed DMF (20 mL) was added to an oven dried reaction flask charged with $Pd(OAc)_2$ (0.065 mmol), Cs_2CO_3 (7.75 mmol), PPh_3 (0.25 mmol), ketone **1** (3.1 mmol) and arylbromide **4** (3.1 mmol) under argon at room temperature. The resultant stirred suspension was heated to 150 °C for 0.5–1 h. After cooling, HCl (50 mL of a 1.4 M solution in water) was added and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl (5×100 mL), dried over anhydrous sodium sulfate and evaporated in vacuo to give a residue which was purified by flash chromatography on silicagel using 10–50% EtOAc/hexane as eluent.

4.2.1. 1,2-Bis(3,4-dimethoxyphenyl)-2-phenylethanone (3a).[45] 85%. Amber oil; R_f 0.51 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.82 (3H, s), 3.84 (3H, s), 3.88 (3H, s), 3.90 (3H, s), 5.96 (1H, s), 6.81 (2H, s), 6.82 (1H, d, J=9.0 Hz), 7.23–7.29 (5H, m), 7.32 (1H, s), 7.59 (1H, d, J=1.9 Hz), 7.65 (1H, dd, J=8.3, 1.9 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.7, 55.9, 58.3, 109.8, 110.8, 110.9, 111.9, 121.1, 123.5, 126.9, 128.5, 128.8, 129.7, 131.6, 139.5, 147.9, 148.7, 148.9, 153.0, 196.9; FTIR (neat film, cm^{-1}): 1672, 1262, 1024; EIMS (*m*/*z*, %) 392 (M^+, 3), 390 (17), 227 (27), 165 (100). Anal. calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.41; H, 6.22.

4.2.2. 1,2-Bis(3,4-dimethoxyphenyl)-2-(3-methoxyphenyl)-ethanone (3b). 51%. Reddish oil; R_f 0.42 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.72 (3H, s), 3.81 (6H, s), 3.86 (3H, s), 3.87 (3H, s), 5.93 (1H, s), 6.75–6.86 (7H, m), 7.20 (1H, d, J=9.5 Hz), 7.57 (1H, s), 7.64 (1H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 54.9, 55.6, 55.8, 58.1, 109.7, 110.7, 110.9, 111.9, 114.7, 121.1, 123.4, 129.4, 129.6, 131.4, 141.0, 147.8, 148.7, 148.8, 152.9 159.5, 196.6; FTIR (neat film, cm^{-1}): 1673, 1263, 1025; EIMS (*m*/*z*, %) 422 (M^+, 3), 257 (34), 165 (100); HRMS calcd for $C_{25}H_{26}O_6$ 422.1729, found 422.1722. Anal. calcd for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 70.96; H, 6.27.

4.2.3. 1,2-Bis(3,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-ethanone (3c). 46%. Orange oil; R_f 0.49 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.73 (3H, s), 3.79 (3H, s), 3.81 (3H, s), 3.85 (3H, s), 3.86 (3H, s), 5.91 (1H, s), 6.78–6.85 (6H, m), 7.16 (2H, d, J=8.3 Hz), 7.57 (1H, s), 7.63 (1H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 54.9, 55.6, 55.8, 57.4, 109.7, 110.7, 110.9, 111.8, 113.8, 120.9, 123.4, 129.7, 129.6, 131.5, 131.9, 147.8, 148.6, 148.8, 152.9, 158.3, 197.1; FTIR (neat film, cm^{-1}): 1673, 1263, 1025; EIMS (*m*/*z*, %) 422 (M^+, 3), 257 (100), 165 (34); HRMS calcd for $C_{25}H_{26}O_6$ 422.1729, found 422.1725. Anal. calcd for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20. Found: C, 71.13; H, 6.31.

4.2.4. 1,2,2-Tris(3,4-dimethoxyphenyl)ethanone (3d). 47%. Reddish oil; R_f 0.30 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.78 (6H, s), 3.79 (6H, s), 3.84 (3H, s), 3.85 (3H, s), 5.89 (1H, s), 6.77 (6H, s), 6.79 (1H, d, J=8.3 Hz), 7.56 (1H, s), 7.63 (1H, dd, J=8.3, 1.6 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.6, 55.9, 57.8, 109.8, 110.8,

110.9, 111.8, 121.0, 123.5, 129.7, 131.8, 147.9, 148.7, 148.8, 153.0, 197.1; FTIR (neat film, cm^{-1}): 1676, 1260, 1025; EIMS (*m/z*, %) 452 (M^+, 1), 287 (100), 165 (27); HRMS calcd for $C_{26}H_{28}O_7$ 452.1835, found 452.1819. Anal. calcd for $C_{26}H_{28}O_7$: C, 69.01; H, 6.24. Found: C, 68.91; H, 6.26.

4.2.5. 1,2-Bis(3,4-dimethoxyphenyl)-2-(3,4-methylenedioxyphenyl)ethanone (3e). 55%. Orange oil; R_f 0.49 (50% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 3.82 (3H, s), 3.83 (3H, s), 3.87 (3H, s), 3.90 (3H, s), 5.86 (1H, s), 5.90 (2H, s), 6.70–6.83 (7H, m), 7.57 (1H, s), 7.62 (1H, d, *J*=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.7, 57.8, 100.9, 108.1, 109.4, 109.8, 110.8, 111.0, 111.8, 121.0, 121.9, 123.4, 129.6, 131.7, 133.3, 146.4, 147.7, 148.0, 148.8, 148.9, 153.0, 196.9; FTIR (neat film, cm^{-1}): 1673, 1263, 1025; EIMS (*m/z*, %) 436 (M^+, 3), 271 (100), 165 (59); HRMS calcd for $C_{25}H_{24}O_7$ 436.1522, found 436.1536. Anal. calcd for $C_{25}H_{24}O_7$: C, 68.80; H, 5.54. Found: C, 68.84; H, 5.47.

4.2.6. 1,2-Bis(3,4-dimethoxyphenyl)-2-(2,3,4-trimethoxyphenyl)ethanone (3f). 12%. Orange oil; R_f 0.41 (50% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 3.72 (3H, s), 3.80 (3H, s), 3.82 (3H, s), 3.85 (6H, s), 3.88 (3H, s), 3.89 (3H, s), 6.19 (1H, s), 6.55 (1H, d, *J*=8.7 Hz), 6.63 (1H, d, *J*=8.7 Hz), 6.82–6.84 (4H, m), 7.58 (1H, s), 7.69 (1H, d, *J*=7.5 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 51.9, 55.8, 55.9, 60.6, 106.6, 109. 9, 110.8, 111.0, 112.3, 121.6, 123.2, 123.7, 126.5, 129.7, 130.5, 141.8, 147.9, 148.6, 148.9, 150.6, 152.8, 197.5; FTIR (neat film, cm^{-1}): 1670, 1262, 1095; EIMS (*m/z*, %) 482 (M^+, 2), 317 (100), 165 (12), 151 (45); HRMS calcd for $C_{27}H_{30}O_8$ 482.1941, found 482.1944. Anal. calcd for $C_{27}H_{30}O_8$: C, 67.21; H, 6.27. Found: C, 67.26; H, 6.20.

4.2.7. 1,2-Bis(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)-ethanone (3g). 44%. Orange oil; R_f 0.45 (50% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 3.77 (3H, s), 3.81 (3H, s), 3.84 (3H, s), 3.87 (3H, s), 6.04 (1H, s), 6.80–6.84 (4H, m), 7.34 (2H, d, *J*=8.3 Hz), 7.51 (1H, s) 7.59 (1H, d, *J*=8.3 Hz), 8.06 (2H, d, *J*=7.5 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.8, 55.9, 57.9, 109.9, 110.7, 111.3, 111.5, 121.0, 123.4, 126.7, 129.0, 129.8, 130.0, 146.6, 147.2, 148.4, 148.9, 149.3, 153.4, 195.5; FTIR (neat film, cm^{-1}): 1653, 1507, 1344, 1261, 1022; EIMS (*m/z*, %) 165 (100); HRMS calcd for $C_{24}H_{23}NO_7$ 437.1475, found 437.1484. Anal. calcd for $C_{24}H_{23}NO_7$: C, 65.90; H, 5.30; N 3.20. Found: C, 65.95; H, 5.21; N 3.27.

4.2.8. 1-(3,4-Dimethoxyphenyl)-2,2-diphenylethanone (3h).[46] 74%. White powder: mp 142–143 °C (MeOH); R_f 0.63 (50% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 3.87 (3H, s), 3.90 (3H, s), 6.02 (1H, s), 6.82 (1H, d, *J*=8.3 Hz), 7.22–7.35 (10H, m), 7.58 (1H, s), 7.64 (1H, d, *J*=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.4, 55.6, 58.6, 109.7, 110.6, 123.3, 126.7, 128.3, 128.7, 129.4, 139.1, 148.5, 152.8, 196.4; FTIR (neat film, cm^{-1}): 1673, 1260, 1023; EIMS (*m/z*, %) 165 (100), 137 (6), 122 (2), 77 (4). Anal. calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.43; H, 6.17.

4.2.9. 1,2,2-Triphenylethanone (3i). 80%. White powder: mp 137–138 °C (MeOH)(Lit.[14] 138–138.5 °C (MeOH)).

4.2.10. 2-(3-Methoxyphenyl)-1,2-diphenylethanone (3j). 73%. Yellow oil; R_f 0.62 (30% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 3.76 (3H, s), 6.26 (1H, s), 6.92 (1H, d, *J*=8.3 Hz), 7.09 (1H, d, *J*=7.5 Hz), 7.11 (1H, s) 7.33–7.47 (9H, m), 8.21 (2H, d, *J*=7.1 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 54.5, 58.8, 111.8, 114.8, 121.1, 126.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.7, 129.3, 132.6, 136.3, 138.6, 140.1, 159.4, 197.5 (CO); FTIR (neat film, cm^{-1}): 1686, 1261, 1049; EIMS (*m/z*, %) 302 (M^+,15), 197 (57), 182 (15), 165 (20), 153 (12), 105 (100); HRMS calcd for $C_{21}H_{18}O_2$ 302.1307, found 302.1303. Anal. calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.38; H, 6.14.

4.2.11. 2-(4-Methoxyphenyl)-1,2-diphenylethanone (3k). 71%. Yellow powder: mp 128–129 °C (MeOH)(Lit.[14] 128–130 °C (MeOH))

4.2.12. 2-(3,4-Dimethoxyphenyl)-1,2-diphenylethanone (3l).[45] 57%. Yellow powder: mp 98–99 °C; R_f 0.60 (50% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 3.76 (6H, s), 6.00 (1H, s), 6.78 (2H, s), 6.82 (1H, s), 7.26–7.44 (9H, m), 7.99 (2H, d, *J*=7.1 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.6, 58.7, 111.0, 112.0, 121.2, 126.9, 128.4, 128.5, 128.7, 131.2, 132.9, 136.6, 139.1, 147.9, 148.9, 198.2; FTIR (neat film, cm^{-1}): 1684, 1263, 1027; EIMS (*m/z*, %) 332 (M^+, 7), 227 (100), 196 (11), 105 (9), 77 (10). Anal. calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.58; H, 5.97.

4.2.13. 2-(3,4-Methylendioxyphenyl)-1,2-diphenylethanone (3m). 70%. Yellow powder: mp 117–118 °C; R_f 0.60 (30% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 5.83 (2H, s), 5.94 (1H, s), 6.70 (2H, s), 6.77 (1H, s), 7.19 (1H, d, *J*=7.1 Hz), 7.23–7.28 (4H, m), 7.34 (2H, dd, *J*=7.1, 7.1 Hz) 7.43 (1H, d, *J*=7.5 Hz), 7.98 (2H, d, *J*=7.1 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 58.7, 100.9, 108.1, 109.5, 122.1, 127.0, 128.4, 128.6, 132.9, 136.5, 139.0, 146.5, 147.8, 198.0; FTIR (neat film, cm^{-1}): 1684, 1249, 1038; EIMS (*m/z*, %) 316 (M^+, 7), 211 (100), 181 (15), 152 (20), 105 (21), 77 (16); HRMS calcd for $C_{21}H_{16}O_3$ 316.1099, found 316.1097. Anal. calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.63; H, 5.17.

4.2.14. 2-(4-Nitrophenyl)-1,2-diphenylethanone (3n).[47] 54%. Orange oil; R_f 0.58 (30% EtOAc/hexane); ^1H NMR (250 MHz, $CDCl_3$) δ 6.21 (1H, s), 7.32–7.46 (9H, m), 7.52 (1H, d, *J*=7.1 Hz), 8.03 (2H, d, *J*=8.2 Hz), 8.14 (2H, d, *J*=8.2 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 58.9, 123.5, 127.7, 128.3, 128.6, 128.7, 128.8, 128.9, 129.2, 130.1, 130.2, 133.5, 135.9, 137.4, 146.6, 196.8; FTIR (neat film, cm^{-1}): 1684, 1518, 1346; EIMS (*m/z*, %) 362 (M^+, 3), 257 (100), 91 (54). Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N 4.41. Found: C, 75.60; H, 4.81; N 4.53.

4.3. General procedure for the α,α-diarylation of acetophenones 5 under homogeneous conditions

Dry degassed DMF (5 mL) was added to an oven-dried reaction flask charged with $Pd(OAc)_2$ (0.04 mmol), Cs_2CO_3 (2.46 mmol), PPh_3 (0.16 mmol), acetophenone **5** (0.82 mmol), and aryl bromide **6** (2.79 mmol) under argon at room temperature. The resultant stirred suspension was heated to 153 °C for 0.8–7 h. After cooling, HCl (15 mL of a 1.4 M solution in water) was added, and the aqueous layer

was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl (5×40 mL), dried over anhydrous sodium sulfate, and evaporated in vacuo to give a residue that was purified by flash chromatography on silicagel using 10–50% EtOAc/hexane as eluent. By use of this procedure the compounds **3i**, **3o**, **3s**–**t** and **3w** were prepared. However, the preparation of triarylethanones **3d**, **3h**, **3p**–**r**, **3u**–**v** and **3x** required the use of 1.80 mmol of arylbromide **6**.

1,2,2-Tris(3,4-dimethoxyphenyl)ethanone (**3d**) (47%).

1-(3,4-Dimethoxyphenyl)-2,2-diphenylethanone (**3h**) (62%).

1,2,2-Triphenylethanone (**3i**) (91%).

4.3.1. 2,2-Bis(3-methoxyphenyl)-1-phenylethanone (3o).[48] 71%. Orange powder: mp 73–75 °C (MeOH); R_f 0.66 (30% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.76 (6H, s), 6.10 (1H, s), 6.86 (2H, d, J=8.3 Hz), 6.97–6.99 (4H, m), 7.30 (2H, dd, J=8.3, 7.9 Hz), 7.39–7.51 (3H, m), 8.11 (2H, d, J=7.1 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 54.8, 59.0, 112.0, 114.9, 121.2, 128.3, 128.6, 129.4, 132.8, 136.4, 140.1, 159.5, 197.5; FTIR (neat film, cm^{-1}): 1684, 1260, 1049; EIMS (*m*/*z*, %) 322 (M^+, 13), 227 (73), 105 (100); HRMS calcd for $C_{22}H_{20}O_3$ 332.1401, found 332.1405. Anal. calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.58; H, 6.01.

4.3.2. 2,2-Bis(3-methoxyphenyl)-1-(3,4-dimethoxyphenyl)-ethanone (3p). 57%. Yellow oil; R_f 0.64 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.75 (6H, s), 3.87 (3H, s), 3.89 (3H, s), 5.96 (1H, s), 6.76–6.89 (7H, m), 7.21 (2H, d, J=7.9 Hz), 7.59 (1H, d, J=1.9 Hz), 7.65 (1H, dd, J=8.3, 1.9 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.0, 55.7, 55.8, 58.7, 109.8, 110.8, 112.1, 114.9, 121.3, 123.5, 129.4, 129.6, 140.5, 148.7, 153.0, 159.6, 196.3; FTIR (neat film, cm^{-1}): 1675, 1261, 1048; EIMS (*m*/*z*, %) 165 (100); HRMS calcd for $C_{24}H_{24}O_5$ 392.1624, found 392.1616. Anal. calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.57; H, 6.07.

4.3.3. 2,2-Bis(4-nitrophenyl)-1-(3,4-dimethoxyphenyl)-ethanone (3q). 35%. Orange oil; R_f 0.30 (20% Et_2O/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.90 (3H, s), 3.93 (3H, s), 6.21 (1H, s), 6.84 (1H, d, J=9.1 Hz), 7.44 (4H, d, J=8.7 Hz), 7.54–7.58 (2H, m), 8.21 (4H, d, J=8.7 Hz);^{13}C NMR (63 MHz, $CDCl_3$) δ 55.9, 56.1, 57.7, 110.0, 110.8, 123.8, 124.1, 128.6, 129.9, 145.2, 147.3, 149.4, 154.1, 194.0; FTIR (neat film, cm^{-1}): 1682, 1516, 1345, 1262, 1022; EIMS (*m*/*z*, %) 422 (M^+, 1), 227 (5), 207 (17), 165 (100), 137 (10), 77 (12); HRMS calcd for $C_{22}H_{18}N_2O_7$ 422.1114, found 422.1111. Anal. calcd for $C_{22}H_{18}N_2O_7$: C, 62.56; H, 4.30; N 6.63. Found: C, 62.49; H, 4.25; N 6.71.

4.3.4. 2,2-Bis(4-fluorophenyl)-1-(3,4-dimethoxyphenyl)-ethanone (3r). 52%. Yellow oil; R_f 0.47 (40% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.88 (3H, s), 3.90 (3H, s), 5.98 (1H, s), 6.82 (1H, d, J=8.7 Hz), 6.99 (4H, ddd, J=8.7, 8.3, 1.9 Hz), 7.22 (4H, ddd, J=8.7, 5.1, 2.4 Hz), 7.56 (1H, d, J=1.9 Hz) 7.61 (1H, dd, J=8.7, 1.9 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.8, 55.9, 57.0, 109.9, 110.9, 115.5, 123.6, 129.6, 130.4, 135.0, 149.0, 153.3, 161.8, 196.4; FTIR (neat film, cm^{-1}): 1678, 1265, 1026; EIMS (*m*/*z*, %) 366 (M^+, 2), 165 (100), 137 (10), 77 (10); HRMS calcd for $C_{22}H_{18}F_2O_3$ 368.1224, found 368.1227. Anal. calcd for $C_{22}H_{18}F_2O_3$: C, 71.73; H, 4.93. Found: C, 71.69; H, 4.84.

4.3.5. 2,2-Bis(3,4-dimethoxyphenyl)-1-phenylethanone 3s.[45] 61%. Orange oil; R_f 0.66 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.77 (6H, s), 3.78 (3H, s), 3.79 (3H, s), 5.92 (1H, s), 6.77 (5H, m), 7.32–7.40 (4H, m), 7.98 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.4, 55.6, 55.7, 58.0, 110.8, 111.8, 120.9, 128.3, 128.5, 131.3, 132.7, 136.5, 147.8, 148.7, 198.3; FTIR (neat film, cm^{-1}): 1684, 1265, 1026; EIMS (*m*/*z*, %) 392 (M^+, 2), 287 (100), 105 (50). Anal. calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.53; H, 6.11.

4.3.6. 2,2-Bis(4-fluorophenyl)-1-phenylethanone (3t). 63%. Yellow oil; R_f 0.32 (20% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.00 (1H, s), 7.02 (4H, ddd, J=8.7, 8.3, 1.9 Hz), 7.29 (4H, ddd, J=8.7, 5.5, 2.4 Hz), 7.39–7.45 (2H, m), 7.53 (1H, dddd, J=7.5, 7.1, 2.4, 1.6 Hz), 7.95–7.99 (2H, m); ^{13}C NMR (63 MHz, $CDCl_3$) δ 57.6, 115.7, 128.7, 128.9, 129.6, 130.5, 133.3, 134.6, 161.9, 167.9; FTIR (neat film, cm^{-1}): 1626; EIMS (*m*/*z*, %) 203 (10), 105 (100), 77 (28); HRMS calcd for $C_{20}H_{14}F_2O$ 308.1013, found 308.1010. Anal. calcd for $C_{20}H_{14}F_2O$: C, 77.91; H, 4.58. Found: C, 77.86; H, 4.64.

4.3.7. 2,2-Diphenyl-1-(4-methylphenyl)ethanone (3u). 87%. White powder: mp 99–100 °C (MeOH)(Lit.[49] 100–101 °C (MeOH)).

4.3.8. 2,2-Bis(3-methoxyphenyl)-1-(4-methylphenyl)-ethanone (3v). 69%. Yellow oil; R_f 0.39 (30% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.38 (3H, s), 3.76 (6H, s), 5.97 (1H, s), 6.80 (2H, dd, J=8.3, 2.3 Hz), 6.84 (2H, d, J=2.3 Hz), 6.88 (2H, d, J=7.9 Hz), 7.21 (2 h, d, J=8.3 Hz), 7.25 (2H, dd, J=8.3, 7.9 Hz), 7.93 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.4, 54.9, 59.0, 112.1, 114.9, 121.3, 128.9, 129.1, 129.4, 134.0, 140.3, 143.7, 159.6, 197.2; FTIR (neat film, cm^{-1}): 1682, 1260, 1050; EIMS (*m*/*z*, %) 346 (M^+, 4), 227 (6), 119 (100), 91 (7); HRMS calcd for $C_{23}H_{22}O_3$ 346.1569, found 346.1572. Anal. calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.62; H, 6.47.

4.3.9. 2,2-Bis(3,4-dimethoxyphenyl)-1-(4-methylphenyl)-ethanone (3w). 60%. Orange oil; R_f 0.64 (50% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.36 (3H, s), 3.81 (6H, s), 3.81 (6H, s), 5.91 (1H, s), 6.79 (6H, m), 7.20 (2H, d, J=8.3 Hz), 7.91 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.5, 55.7, 58.1, 110.9, 112.0, 121.1, 128.9, 129.2, 131.7, 134.2, 143.7, 147.9, 148.8, 198.1; FTIR (neat film, cm^{-1}): 1681, 1263, 1027; EIMS (*m*/*z*, %) 406 (M^+, 4), 287 (100), 207 (48), 119 (10); HRMS calcd for $C_{25}H_{26}O_5$ 406.1780, found 406.1768. Anal. calcd for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 73.93; H, 6.49.

4.3.10. 2,2-Bis(4-fluorophenyl)-1-(4-methylphenyl)ethanone (3x). 68%. Yellow oil; R_f 0.43 (20% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.37 (3H, s), 3.76 (6H, s), 5.99 (1H, s), 7.02 (2H, d, J=8.7 Hz), 7.19–7.31 (8H, m), 7.89 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.5, 57.3, 115.6, 128.3, 129.0, 129.3, 130.4, 134.8, 144.2, 161.9,

197.4; FTIR (neat film, cm^{-1}): 1620; EIMS (*m/z*, %) 320 (M^+, 2), 119 (100), 91 (21); HRMS calcd for $C_{21}H_{16}F_2O$ 322.1169, found 322.1175. Anal. calcd for $C_{21}H_{16}F_2O$: C, 78.25; H, 5.00. Found: C, 78.34; H, 4.96.

4.4. General procedure for the α,α-diarylation of acetophenones 5 by means of polymer-anchored palladium catalysts

Dry degassed DMF (1 mL) was added to an oven-dried reaction flask charged with FibreCat™ 1026 (0.01 mmol of Pd), Cs_2CO_3 (0.6 mmol), ketone **2** (0.2 mmol), and aryl bromide **3** (0.68 mmol) under argon at room temperature. The resultant stirred suspension was heated to 153 °C for 0.8–1 h. After cooling, the mixture was filtered, washed with CH_2Cl_2 and the filtrate was evaporated in vacuo to give a residue that was purified by flash chromatography on silicagel using 10–50% EtOAc/hexane as eluent.

1,2,2-Tris(3,4-dimethoxyphenyl)ethanone (**3d**) (64%).

1-(3,4-Dimethoxyphenyl)-2,2-diphenylethanone (**3h**) (90%).

1,2,2-Triphenylethanone (**3i**) (89%).

2,2-Bis(3-methoxyphenyl)-1-phenylethanone (**3o**) (79%).

2,2-Bis(3-methoxyphenyl)-1-(3,4-dimethoxyphenyl)ethanone (**3p**) (82%).

2,2-Bis(4-nitrophenyl)-1-(3,4-dimethoxyphenyl)ethanone (**3q**) (20%).

2,2-Bis(4-fluorophenyl)-1-(3,4-dimethoxyphenyl)ethanone (**3r**) (70%).

2,2-Bis(3,4-dimethoxyphenyl)-1-phenylethanone **3s** (80%).

2,2-Bis(4-fluorophenyl)-1-phenylethanone (**3t**) (73%).

2,2-Diphenyl-1-(4-methylphenyl)ethanone (**3u**) (93%).

2,2-Bis(3-methoxyphenyl)-1-(4-methylphenyl)ethanone (**3v**) (75%).

2,2-Bis(3,4-dimethoxyphenyl)-1-(4-methylphenyl)ethanone (**3w**) (92%).

2,2-Bis(4-fluorophenyl)-1-(4-methylphenyl)ethanone (**3x**) (80%).

4.5. General procedure for the α-monoarylation of deoxybenzoins 4 by means of polymer-anchored palladium catalysts

Dry degassed DMF (1 mL) was added to an oven-dried reaction flask charged with FibreCat™ 1026 (0.01 mmol of Pd), Cs_2CO_3 (0.6 mmol), ketone **4** (0.2 mmol), and arylbromide **6** (0.68 mmol) under argon at room temperature. The resultant stirred suspension was heated to 153 °C for 1 h. After cooling, the mixture was filtered, washed with CH_2Cl_2 and the filtrate was evaporated in vacuo to give a residue that was purified by flash chromatography on silicagel using 10–50% EtOAc/hexane as eluent. By use of this procedure the compounds **3d–e** and **3j–m** were prepared. However, the preparation of triarylethanones **3a–b** and **3h–i** required the use of 0.44 mmol of arylbromide **6**.

1,2-Bis(3,4-dimethoxyphenyl)-2-phenylethanone (**3a**) (40%).

1,2-Bis(3,4-dimethoxyphenyl)-2-(3-methoxyphenyl)ethanone (**3b**) (53%).

1,2,2-Tris(3,4-dimethoxyphenyl)ethanone (**3d**) (53%).

1,2-Bis(3,4-dimethoxyphenyl)-2-(3,4-methylenedioxyphenyl)ethanone (**3e**) (38%).

1-(3,4-dimethoxyphenyl)-2,2-diphenylethanone (3 h) (51%).

1,2,2-Triphenylethanone (**3i**) (57%).

2-(3-Methoxyphenyl)-1,2-diphenylethanone (**3j**) (54%).

2-(4-Methoxyphenyl)-1,2-diphenylethanone (**3k**) (60%).

2-(3,4-Dimethoxyphenyl)-1,2-diphenylethanone (**3l**) (37%).

2-(3,4-Methylendioxyphenyl)-1,2-diphenylethanone (**3m**) (45%).

4.6. General procedure for the α-monoarylation of acetophenones 5 by means of polymer-anchored palladium catalysts

Dry degassed THF (1 mL) was added to an oven-dried reaction flask charged with FibreCat™ 1000-D7 (0.01 mmol of Pd), NaO^{t}Bu (0.6 mmol), ketone **5** (0.2 mmol), and arylbromide **6** (0.68 mmol) under argon at room temperature. The resultant stirred suspension was heated to 85 °C for 1 h. After cooling, the mixture was filtered, washed with CH_2Cl_2 and the filtrate was evaporated in vacuo to give a residue that was purified by flash chromatography on silicagel using 10–50% EtOAc/hexane as eluent.

After each reaction, the the filtrand was washed successively with HCl (3 mL of a 5% solution in water), Na_2CO_3 (3 mL of a 10% solution in water), H_2O (2 mL), THF (2 mL) and NaCl (5 mL of a saturated solution in CH_3CN). After drying in vacuo, the so-recycled catalyst was ready to be reused under the above described conditions. The same experiment was carried out 5 times, providing the corresponding deoxybenzoin **4** with the same yield.

By use of this procedure the compounds **4a**, **4b–c** and **4j** were prepared. However, the preparation of deoxybenzoins **4d**, **4f**, **4g–h** and **4k–l** required the use of 0.44 mmol of arylbromide **6** and the preparation of deoxybenzoin **4e** required the use of 0.24 mmol of arylbromide **6**.

4.6.1. 1,2-Bis(3,4-dimethoxyphenyl)ethanone 4a. 72%. White powder: mp 105–106 °C (MeOH)(Lit.[50] 105–107 °C ($EtOH/H_20$)).

4.6.2. 1-(3,4-Dimethoxyphenyl)-2-phenylethanone 4d.

90%. Yellow powder: mp 101–103 °C (MeOH)(Lit.[51] 105 °C (MeOH)).

4.6.3. 1-(3,4-Dimethoxyphenyl)-2-(3-methoxyphenyl)-ethanone 4e. 88%. Yellow powder: mp 58–60 °C (MeOH)(Lit.[52] 57–60 °C (MeOH)).

4.6.4. 1-(3,4-Dimethoxyphenyl)-2-(4-fluorophenyl)ethanone 4f. 74%. Yellow powder: mp 102–103 °C (MeOH) (Lit.[53] 102–104 °C (MeOH)).

4.6.5. 1,2-Diphenylethanone 4b. 87%. White powder: mp 55–56 °C (MeOH)(Lit.[54] 56 °C (MeOH)).

4.6.6. 1-Phenyl-2-(3-methoxyphenyl)ethanone 4c. 92%.[55] Yellow oil. The spectroscopic data of **4c** correspond to the literature[55] data.

4.6.7. 1-Phenyl-2-(3,4-dimethoxyphenyl)ethanone 4g. 91%. Yellow powder: mp 80–81 °C (MeOH)(Lit.[56] 87–88 °C (EtOH)).

4.6.8. 1-Phenyl-2-(4-fluorophenyl)ethanone 4h. 80%. White powder: mp 107–108 °C (MeOH)(Lit.[54] 108–110 °C (MeOH)).

4.6.9. 2-Phenyl-1-(4-methylphenyl)ethanone 4i. 86%. White powder: mp 107–108 °C (MeOH)(Lit.[56] 108–109°C (MeOH)).

4.6.10. 2-(3-Methoxyphenyl)-1-(4-methylphenyl)ethanone 4j. 86%. Yellow oil; R_f 0.55 (20% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.45 (3H, s), 3.83 (3H, s), 4.28 (2H, s), 6.82–6.93 (3H, m), 7.30 (2H, d, J=7.5 Hz), 7.97 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.6, 45.4, 55.0, 112.2, 114.9, 121.7, 128.8, 129.2, 129.5, 133.9, 136.1, 143.9, 159.6, 197.1; FTIR (neat film, cm^{-1}): 1684, 1257, 1045; EIMS (*m*/*z*, %) 240 (M^+, 10), 119 (100), 91 (25); HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1155. Anal. calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.89; H, 6.60.

4.6.11. 2-(3,4-Dimethoxyphenyl)-1-(4-methylphenyl)-ethanone 4k.[57] 82%. Orange powder: mp 92–93 °C (MeOH); R_f 0.51 (30% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.39 (3H, s), 3.84 (3H, s), 3.85 (3H, s), 4.19 (2H, s), 6.77–6.80 (3H, m), 7.24 (2H, d, J=7.9 Hz), 7.91 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.6, 44.9, 55.8, 111.1, 112.3, 121.5, 127.0, 128.7, 129.2, 133.9, 143.9, 147.8, 148.9, 197.5; FTIR (neat film, cm^{-1}): 1682, 1268, 1028; EIMS (*m*/*z*, %) 270 (M^+, 23), 151 (33), 119 (100), 91 (19). Anal. calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.61; H, 6.65.

4.6.12. 2-(4-Fluorophenyl)-1-(4-methylphenyl)ethanone 4l.[58] 74%. Orange powder: mp 103–104 °C (MeOH); R_f 0.41 (20% EtOAc/hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.41 (3H, s), 4.23 (2H, s), 7.01 (2H, dd, J=8.7, 8.3 Hz), 7.21 (2H, dd, J=8.7, 5.5 Hz), 7.26 (2H, d, J=8.3 Hz), 7.80 (2H, d, J=8.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.6, 44.3, 115.4 (d, J_{C-F}=21.5 Hz), 128.6, 129.3, 130.3 (d, J_{C-F}=3.6 Hz), 130.9 (d, J_{C-F}=9.0), 133.9, 144.1, 161.8 (d, J_{C-F}=244.1 Hz), 197.0; FTIR (neat film, cm^{-1}): 1685; EIMS (*m*/*z*, %) 119 (100), 91 (36). Anal. calcd for $C_{15}H_{13}FO$: C, 78.93; H, 5.74. Found: C, 78.99; H, 5.80.

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