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Keywords
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Synthesis of benzo[c]chromen-6-ones via novel cyclic aryl-Pd(II)-ester enolate intermediates

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Abstract: The examination of the palladium catalysed arylation reactions of mono-iodo derivatives of the phenyl and benzyl esters of benzoic acid, phenylacetic acid and dehydrocinnamic acid has resulted in the formation of benzo[c]chromen-6-ones, unexpected cinnamate and succinate products and diphenyl dimers. Many of these products can be rationalized as arising from novel cyclic ArPd(II)-enolate intermediates, formed by intramolecular C-H activation by ArPd(II).

As part of a project concerned with the synthesis of lactones of the type C we have explored the palladium catalysed arylation reactions of mono-iodo di-aryl esters A and B as shown in Scheme 1. The formation of benzo[c]chromen-6-ones C (m = n = 0) have been readily achieved from palladium catalysed cyclization of the corresponding mono-iodophenyl benzoate derivative using this strategy.1,2 In the successful cases reported the iodo-substituent is normally attached to the more electron deficient benzoate ring as in the case of A (m = n = 0). The formation of larger lactone rings have not been reported, however the palladium catalysed arylation reaction has been used to form 7-membered carbocyclic and azepine rings.2c,3 We report here our results from the examination of the palladium catalysed arylation reactions of mono-iodo derivatives of the phenyl and benzyl esters of benzoic acid, phenylacetic acid and dehydrocinnamic acid.
Treatment of the iodo-substituted phenyl benzoate derivatives 1a-c with 26 mol % (Ph₃P)₂PdCl₂ in the presence of anhydrous sodium acetate (3 molar equiv.) in DMA with heating in a sealed tube at 125 °C for 3 h gave the benzo[c]chromen-6-ones 2a-c in good yields (Scheme 2). In the case of 1c, a small amount (8%) of the regioisomer 3 was also formed.
When the 2-iodophenyl phenyl acetates 4a-c were treated under identical conditions to 1a-c only products arising from hydrolysis of the ester group of 4a-c were obtained, even though the NaOAc and DMA had been carefully dried.

Treatment of the phenyl dihydrocinnamate 5 under these conditions resulted in formation of its cinnamate ester derivative 6 in 59% yield (Scheme 4). A possible mechanism is shown in Scheme 5.
This mechanism involves oxidative addition of the aryl iodide to Pd(0), to give the Pd(II)-intermediate D from which base (NaOAc) assisted cyclometallation occurs, via C-H functionalization, to give the palladacycle E. Intermediate E can undergo selective protonation to give the Pd(II)-enolate species F which upon β-elimination would give the cinnamate 6 and Pd(II)H. The latter species upon reaction with acetate ion would generate Pd(0) and acetic acid. The functionalization of sp³C-H and sp²C-H bonds by Pd(II), as in the case of the conversion of intermediate D to E, have been well documented⁴ and palladium(IV) species have been suggested as intermediates in some of these reactions.⁴ᵇ,⁴ᶠ,⁴ᵏ,⁴,p,⁴,q Indeed oxidative addition of intermediate D could provide the palladium(IV) intermediate G which upon reductive elimination would result in intermediate F and thus product 6 (Scheme 5).

Scheme 4
The palladium catalysed reactions of the 2-iodobenzyl 3,4-dimethoxyphenyl acetates 7a,b gave a mixture of two products which consisted of the benzo[c]chromen-6-ones 8a and 8b, respectively and the biphenyls 9a and 9b, respectively (Scheme 6). These compounds were readily separated by column chromatography. The 3,4-dimethoxybenzyl 2-iodophenyl acetates 10a,b gave different products. Iodide 10a gave a separable mixture of the succinate 11 (as a 1.8 : 1 mixture of diastereomers) and the biphenyl 12, while 10b gave the benzo[c]chromen-6-one 8b (Scheme 7). These unexpected products can be rationalized as arising through similar palladium intermediates to those suggested in Scheme 5.

In Scheme 8, the Pd(II)-palladacycle intermediate I is formed from 7a,b in an analogous fashion to E in Scheme 5. Reductive elimination of I would provide the benzo[c]chromen-6-ones 8a or 8b. Alternatively, dimerization of intermediate H would give the diphenyls 9a or 9b.

In Scheme 9, the Ar-Pd(II)I intermediate J could undergo deprotonation by NaOAc, perhaps assisted by coordination between the Pd(II) and the ester carbonyl, to give the Pd(II)-palladacycle K which could undergo selective protonation by HOAc to give the O-Pd(II)-enolate L. The latter would be
expected to be in equilibrium with the C-Pd(II)-enolate $M^\ddagger$ which could give rise to the same cyclic Pd(II)-enolate intermediate $I$ suggested in Scheme 8 and then product $8b$ via reductive elimination. Alternatively, dimerization of intermediate $M$ could provide the succinate $11$. The proposed Pd(II)-palladacycle $K$ is similar to that proposed as an intermediate in the Pd-catalysed intramolecular coupling ortho-bromophenylmethyl ketones to give benzofurans under basic conditions. However no benzofuran products could be isolated from our reactions. We assume that because our reactions generate an equivalent of HOAc, from the transformation of intermediate $J$ to $K$, that protonation of $K$ to give $L$ is more rapid than benzofuran formation.

In conclusion, the examination of the palladium catalysed arylation reactions of mono-iodo derivatives of the phenyl and benzyl esters of benzoic acid, phenylacetic acid and dehydrocinnamic acid has resulted in the formation of benzo[c]chromen-6-ones $2a$-$c$ and $8a,b$, the unexpected cinnamate $6$ and the succinate $11$ and diphenyl dimers ($9a,b$ and $12$). Many of these products can be rationalized as arising from novel cyclic ArPd(II)-enolate intermediates ($E$ and $I$). While the formation of ArPd(II)-enolate intermediates is well documented, these are normally generated from the intermolecular reaction of an in situ generated or preformed enolate anion, using a stronger base than NaOAc as in this study, and a ArPd(II)X species and not by intramolecular C-H activation by ArPd(II) as we have suggested in this paper.

**Scheme 6**
Scheme 7
Scheme 8 (palladium ligands not shown)

7a,b \[\xrightarrow{\text{Pd(0)}}\] \(\text{H}\) \[\xrightarrow{-\text{HI}}\] \(\text{I}\)

\(8a,b + \text{Pd(0)}\)

Scheme 9 (palladium ligands not shown)

10a,b \[\xrightarrow{\text{Pd(0)}}\] \(\text{J}\) \[\xrightarrow{-\text{HOAc}}\] \(\text{K}\)

\(\text{HOAc}\) \[\xrightarrow{\text{Pd(II)}}\] \(\text{L}\) \[\xrightarrow{\text{Pd(II)}}\] \(\text{M}\) \[\xrightarrow{\text{R = OMe}}\] \(\text{I}\) \[\xrightarrow{-\text{HX}}\] \(8b\)

dimerization \(R = \text{H}\)
EXPERIMENTAL

All NMR spectra were measured in CDCl$_3$ solution at 300 MHz ($^1$H NMR) or 75 MHz ($^{13}$C NMR) unless otherwise indicated. NMR assignments are based on COSY, DEPT, and HSQC experiments and sometimes HMBC and NOESY experiments. DCM refers to CH$_2$Cl$_2$ and PS refers to petroleum spirit (b.p. 40-60 °C)

General Methods for Ester Formation

3,4-Dimethoxyphenyl 2-iodo-4,5-dimethoxybenzoate 1a

A solution of 2-iodo-4,5-dimethoxybenzoic acid (613 mg, 1.99 mmol), 3,4-dimethoxyphenol (368 mg, 2.39 mmol), DCC (493 mg, 2.39 mmol), DMAP (73 mg, 0.59 mmol) in DCM (20 mL) was stirred at rt for 18 h under N$_2$, diluted with DCM (20 mL), filtered and the filtrate washed with water (20 mL) and saturated NaHCO$_3$ solution (20 mL). The organic phase was dried (MgSO$_4$), filtered, evaporated and the residue chromatographed, using EtOAc:PS (1:1) as the mobile phase, to yield the title compound as a white solid (671 mg, 76 %). M.p. 146-148 °C. $^1$H NMR: δ 7.64 (s, 1H, Ar-H-6), 7.45 (s, 1H, Ar-H-3), 6.89 (d, 1H, J = 8.0 Hz, Ar-H-5’), 6.79 (d, 1H, J = 2.2 Hz, Ar-H-2’), 6.78 (dd, 1H, J = 8.0, 2.2 Hz, Ar-H-6’), 3.95 (s, 3H, OCH$_3$-4), 3.94 (s, 3H, OCH$_3$-5), 3.89 (s, 3H, OCH$_3$-4’), 3.88 (s, 3H, OCH$_3$-3’). $^{13}$C NMR: δ 164.0 (C=O), 152.2 (Ar-C-OCH$_3$-4), 149.3 (Ar-C-OCH$_3$-3’), 148.6 (Ar-C-OCH$_3$-5), 146.8 (Ar-C-OCH$_3$-4’), 144.2 (Ar-C-1’), 124.8 (Ar-C-1), 123.9 (Ar-C-H-3), 114.1 (Ar-C-H-6), 112.9 (Ar-C-H-6’), 111.1 (Ar-C-H-5’), 105.8 (Ar-C-H-2’), 85.5 (Ar-C-2), 56.2 (Ar-OCH$_3$-4), 56.1 (Ar-OCH$_3$-4’), 56.0 (Ar-OCH$_3$-5), 55.9 (Ar-OCH$_3$-3’). MS (EI+): m/z 444 (M+, 8 %), 291 (100 %), HRMS (EI+): Calcd for C$_{17}$H$_{17}$IO$_6$ = 444.0069 (M+), found 444.0053.

3,4-Dimethoxyphenyl 2-iodo-3,4,5-trimethoxybenzoate 1b

The title compound was prepared in 91 % yield (white solid, 483 mg) from 2-iodo-3,4,5-trimethoxybenzoic acid (379 mg, 1.12 mmol) and 3,4-dimethoxyphenol (207 mg, 1.34 mmol) in the presence of DCC (277 mg, 1.34 mmol), DMAP (34 mg, 0.28 mmol) and DCM (10 mL) according to the general esterification method. M.p. 98-100 °C. $^1$H NMR: δ 7.39 (s, 1H, Ar-H-6), 6.90 (dd, 1H, J = 7.3, 2.4 Hz Ar-H-6’), 6.84 (d, 1H, J = 2.4 Hz Ar-H-2’), 6.82 (d, 1H, J = 7.3 Hz Ar-H-5’), 3.95 (s, 3H, OCH$_3$-5), 3.93 (s, 3H, OCH$_3$-4), 3.91 (s, 3H, OCH$_3$-3), 3.90 (s, 3H, OCH$_3$-4’), 3.89 (s, 3H, OCH$_3$-3’). $^{13}$C NMR: δ 165.1 (C=O), 153.9 (Ar-C-OCH$_3$-3), 153.4 (Ar-C-OCH$_3$-4), 149.4 (Ar-C-OCH$_3$-4’), 147.0 (Ar-C-OCH$_3$-3’), 145.3 (Ar-C-OCH$_3$-5), 144.2 (Ar-C-1’), 129.9 (Ar-C-1), 112.8 (Ar-C-H-5’), 111.1 (Ar-C-H-6), 110.9 (Ar-C-H-6’), 105.6 (Ar-C-H-2’), 84.5 (Ar-C-2), 61.0 (OCH$_3$-5), 60.8 (OCH$_3$-3’),
56.3 (OCH₃-4), 56.1 (OCH₃-3), 55.9 (OCH₃-4'). MS: m/z (EI⁺) 474 (M⁺, 6 %), 321 (100 %) HRMS (EI⁺): Calcd for C₁₈H₁₅IO₇ = 474.0175 (M⁺), found 474.0152.

3,4-Dimethoxyphenyl 2-iodobenzoate 1c
The title compound was prepared in 93 % yield (white solid, 1.15 g) from 2-iodobenzoic acid (800 mg, 3.22 mmol) and 3,4-dimethoxyphenol (547 mg, 3.54 mmol) in the presence of DCC (732 mg, 3.54 mmol), DMAP (130 mg, 1.06 mmol) and DCM (15 mL) according to the general esterification method. M.p. 74-76 °C. ¹H NMR: δ 8.06 (d, 1H, J = 8.0 Hz, Ar-H-3), 8.02 (dd, 1H, J = 8.0, 1.5 Hz, Ar-H-6), 7.47 (t, 1H, J = 8.0 Hz, Ar-H-5), 7.21 (dt, 1H, J = 8.0, 1.5 Hz, Ar-H-4), 6.99 (d, 1H, J = 8.0 Hz, Ar-H-5'), 6.81 (dd, 1H, J = 8.0, 2.5 Hz, Ar-H-6'), 6.80 (d, 1H, J = 2.5 Hz, Ar-H-2'), 3.89 (s, 3H, OCH₃-3'), 3.88 (s, 3H, OCH₃-4'). ¹³C NMR: δ 165.0 (C=O), 149.3 (Ar-C-OCH₃-4), 147.0 (Ar-C-OCH₃-3), 144.2 (Ar-C-1'), 141.5 (Ar-C-H-3), 134.1 (Ar-C-1), 133.1 (Ar-C-H-4), 131.4 (Ar-C-H-6), 127.9 (Ar-C-H-5), 112.8 (Ar-C-H-6'), 111.1 (Ar-C-H-5'), 105.6 (Ar-C-H-2'), 94.5 (Ar-C-2), 56.1 (Ar-OCH₃-4'), 55.9 (Ar-OCH₃-3'). MS: m/z (EI⁺) 384 (M⁺, 6 %), 125 (100 %), HRMS (EI⁺): Calcd for C₁₅H₁₃IO₄ = 383.9858 (M⁺), found 383.9862.

3,4-Dimethoxyphenyl 2-iodo-4,5-dimethoxyphenylacetate 4a
The title compound was prepared in 76 % yield (sticky white solid, 740 mg) from 2-iodo-4,5-dimethoxyphenylacetic acid (686 mg, 2.12 mmol) and 3,4-dimethoxyphenol (361 mg, 2.34 mmol) in the presence of DCC (483 mg, 2.34 mmol), DMAP (73 mg, 0.59 mmol) and DCM (10 mL) according to the esterification method. M.p. 76-78 °C. ¹H NMR: δ 7.27 (s, 1H, Ar-H-3), 6.90 (s, 1H, Ar-H-6), 6.82 (s, 1H, Ar-H-5'), 6.69 (s, 1H, Ar-H-2'), 6.68 (s, 1H, Ar-H-6'), 3.95 (s, 2H, Ar-CH₂), 3.87 (s, 3H, OCH₃-3), 3.87 (s, 3H, OCH₃-4), 3.86 (s, 3H, OCH₃-4'). ¹³C NMR: δ 169.5 (C=O), 149.4 (Ar-C-OCH₃-4), 149.3 (Ar-C-OCH₃-3'), 148.8 (Ar-C-OCH₃-3), 146.9 (Ar-C-OCH₃-4'), 144.3 (Ar-C-1'), 129.5 (Ar-C-1), 121.6 (Ar-C-H-3), 113.4 (Ar-C-H-6), 112.7 (Ar-C-H-6'), 111.1 (Ar-C-H-5'), 105.6 (Ar-C-H-2'), 88.9 (Ar-C-2), 56.1 (2 x OCH₃-3, 5), 55.9 (2 x OCH₃-4, 4'), 45.7 (Ar-CH₂). MS: m/z (EI⁺) 458 (M⁺, 3 %), 149 (100 %), HRMS (EI⁺): Calcd for C₁₈H₁₉IOn = 458.0226 (M⁺), found 458.0233.

2-Iodophenyl 3,4-dimethoxyphenylacetate 4b
The title compound was prepared in 91 % yield (clear oil, 1.65 g) from 3,4-dimethoxyphenylacetic acid (980 mg, 4.99 mmol) and 2-iodophenol (1.0 g, 4.54 mmol) in the presence of DCC (1.03 mg, 4.99
mmol), DMAP (166 mg, 1.36 mmol) and DCM (20 mL) according to esterification method. M.p. 52-54 °C. \( ^1H \) NMR: \( \delta \) 7.79 (d, 1H, \( J = 8.0 \) Hz, Ar-H-3'), 7.32 (t, 1H, \( J = 7.5 \) Hz, Ar-H-5'), 7.05 (d, 1H, \( J = 7.5 \) Hz, Ar-H-6'), 6.96 (bs, 1H, Ar-H-2), 6.96-6.93 (m, 1H, Ar-H-6), 6.94 (t, 1H, \( J = 8.0 \) Hz, Ar-H-4'), 6.85 (d, 1H, \( J = 8.0 \) Hz, Ar-H-5), 3.89 (s, 3H, OCH\(_3\)-3), 3.869 (s, 3H, OCH\(_3\)-4), 3.864 (s, 2H, Ar-CH\(_2\)). \( ^{13}C \) NMR: \( \delta \) 169.2 (C=O), 151.0 (Ar-C-OCH\(_3\)-4), 148.8 (Ar-C-OCH\(_3\)-3), 139.3 (Ar-C-H-3'), 129.2 (Ar-C-H-5'), 127.5 (Ar-C-H-4'), 125.3 (Ar-C-1), 122.8 (Ar-C-H-6'), 121.7 (Ar-C-H-6), 112.7 (Ar-C-H-2), 111.1 (Ar-C-H-5), 90.1 (Ar-C-H-2'), 55.8 (Ar-OCH\(_3\)-4), 55.7 (Ar-OCH\(_3\)-3), 40.8 (Ar-CH\(_2\)). MS: \( m/z \) (EI+) 398 (M+, 46 %), 151 (100 %), HRMS (EI+): Calcd for C\(_{16}\)H\(_{15}\)IO\(_4\) = 398.0015 (M+), found 398.0012.

3,4-Dimethoxyphenyl 2-iodophenylacetate 4c

The title compound was prepared in 92 % yield (clear oil, 1.41 g) from 2-iodophenylacetic acid (1.00 g, 3.81 mmol) and 3,4-dimethoxyphenol (647 mg, 4.19 mmol) in the presence of DCC (866 mg, 4.19 mmol), DMAP (140 mg, 1.14 mmol) and DCM (20 mL) according to esterification method. M.p. 90-92 °C. \( ^1H \) NMR: \( \delta \) 7.87 (d, 1H, \( J = 7.5 \) Hz, Ar-H-3), 7.37 (d, 1H, \( J = 7.5 \) Hz, Ar-H-6), 7.33 (t, 1H, \( J = 7.5 \) Hz, Ar-H-5), 6.98 (t, 1H, \( J = 7.5 \) Hz, Ar-H-4), 6.81 (d, 1H, \( J = 8.0 \) Hz, Ar-H-5'), 6.69 (d, 1H, \( J = 1.5 \) Hz, Ar-H-6'), 6.68 (dd, 1H, \( J = 8.0, 1.5 \) Hz, Ar-H-6'), 4.01 (s, 2H, Ar-CH\(_2\)), 3.84 (s, 3H, OCH\(_3\)-3'), 3.83 (s, 3H, OCH\(_3\)-4'). \( ^{13}C \) NMR: \( \delta \) 169.1 (C=O), 149.1 (Ar-C-OCH\(_3\)-3'), 146.7 (Ar-C-OCH\(_3\)-4'), 144.2 (Ar-C-1'), 139.4 (Ar-C-H-3), 137.2 (Ar-C-1), 130.7 (Ar-C-H-6), 129.0 (Ar-C-H-4), 128.4 (Ar-C-H-5), 112.6 (Ar-C-H-6'), 111.0 (Ar-C-H-5'), 105.5 (Ar-C-H-2'), 100.8 (Ar-C-2), 56.0 (Ar-OCH\(_3\)-3'), 55.8 (Ar-OCH\(_3\)-4'), 46.1 (Ar-CH\(_2\)). MS: \( m/z \) (EI+) 398 (M+, 5 %), 154 (100 %), HRMS (EI+): Calcd for C\(_{16}\)H\(_{15}\)IO\(_4\) = 398.0015 (M+), found 398.0002.

3,4-Dimethoxyphenyl 3-(2-iodo-4,5-dimethoxyphenyl)propionate 5

The title compound was prepared in 81 % yield (cream solid, 669 mg) from 3-(2-iodo-4,5-dimethoxyphenyl)propanoic acid (566 mg, 1.68 mmol) and 3,4-dimethoxyphenol (286 mg, 1.85 mmol) in the presence of DCC (866 mg, 4.19 mmol), DMAP (140 mg, 1.14 mmol) and DCM (20 mL) according to esterification method. M.p. 100-102 °C. \( ^1H \) NMR: \( \delta \) 7.22 (s, 1H, Ar-H-3), 6.83 (s, 1H, Ar-H-6), 6.81 (d, 1H, \( J = 8.7 \) Hz Ar-H-5'), 6.58 (dd, 1H, \( J = 8.7, 2.5 \) Hz Ar-H-6'), 6.55 (d, 1H, \( J = 2.5 \) Hz Ar-H-2'), 3.83 (s, 3H, OCH\(_3\)), 3.84 (s, 3H, OCH\(_3\)), 3.83 (s, 3H, OCH\(_3\)), 3.82 (s, 3H, OCH\(_3\)), 3.09 (t, 2H, \( J = 7.3 \), Ar-CH\(_2\)), 2.83 (t, 2H, \( J = 7.3 \), Ar-CH\(_2\)-CH\(_2\)). \( ^{13}C \) NMR: \( \delta \) 171.3 (C=O), 149.3 (2 x Ar-C-OCH\(_3\)-4, 4'), 148.1 (Ar-C-OCH\(_3\)-5), 146.7 (Ar-C-OCH\(_3\)-3'), 144.1 (Ar-C-1'), 135.0 (Ar-C-1), 111.0 (Ar-C-H-5').
121.7 (Ar-C-H-3), 112.7 (Ar-C-H-6), 112.6 (Ar-C-H-6'), 111.0 (Ar-C-H-5'), 105.5 (Ar-C-H-2'), 87.7 (Ar-C-2), 56.1 (2 x Ar-OCH3-3'), 55.8 (2 x Ar-OCH3-4, 4'), 35.4 (Ar-CH2), 34.6 (Ar-CH2-CH2).

MS: m/z (EI+) 472 (M+, 19%), 154 (100%), HRMS (EI+): Calcd for C19H21IO6 = 472.0383 (M+), found 472.0373.

2-Iodobenzyl (3,4-dimethoxyphenyl)acetate 7a

The title compound was prepared in 81% yield (clear oil, 1.42 g) from 3,4-dimethoxyphenylacetic acid (922 mg, 4.70 mmol) and 2-iodobenzyl alcohol (1.00 g, 4.27 mmol) in the presence of DCC (969 mg, 4.70 mmol), DMAP (156 mg, 1.28 mmol) and DCM (20 mL) according to the general esterification method. M.p. 52-54 °C. 1H NMR: δ 7.82 (d, 1H, J = 7.5 Hz, Ar-H-3'), 7.30 (t, 1H, J = 7.5 Hz, Ar-H-5'), 7.28 (d, 1H, J = 7.5 Hz, Ar-H-6'), 6.99 (dt, 1H, J = 7.5, 2.0 Hz, Ar-H-4'), 6.84 (d, 1H, J = 8.5 Hz, Ar-H-6), 6.83 (bs, 1H, Ar-H-2), 6.80 (d, 1H, J = 8.5 Hz, Ar-H-5), 5.13 (s, 2H, Ar-CH2-O), 3.85 (s, 3H, OCH3-4), 3.84 (s, 3H, OCH3-3), 3.63 (s, 2H, Ar-CH2-CO). 13C NMR: δ 171.1 (C=O), 148.8 (Ar-C-OCH3-3), 148.0 (Ar-C-OCH3-4), 139.3 (Ar-C-H-3'), 138.1 (Ar-C-1'), 129.7 (Ar-C-H-4'), 129.3 (Ar-C-H-6'), 128.1 (Ar-C-H-5'), 126.0 (Ar-C-1), 121.4 (Ar-C-H-6), 112.3 (Ar-C-H-2), 111.1 (Ar-C-H-5), 98.1 (Ar-C-2'), 70.1 (Ar-CH2-O), 55.78 (Ar-OCH3-4), 55.73 (Ar-OCH3-3), 40.4 (Ar-CH2-CO). MS: m/z (EI+) 412 (M+, 62%), 151 (100%), HRMS (EI+): Calcd for C17H17IO4 = 412.0171 (M+), found 412.0151.

2-Iodo-4,5-dimethoxybenzyl 3,4-dimethoxyphenylacetate 7b

The title compound was prepared in 70% yield (92% brsm, orange solid, 720 mg) from 3,4-dimethoxyphenylacetic acid (474 mg, 2.41 mmol) and 2-iodo-4,5-dimethoxybenzyl alcohol (645 mg, 2.19 mmol) in the presence of DCC (498 mg, 2.41 mmol), DMAP (80 mg, 0.69 mmol) and DCM (10 mL) according to the general esterification method. M.p. 88-90 °C. 1H NMR: δ 7.23 (s, 1H, Ar-H-3'), 6.84 (d, 1H, J = 7.0 Hz, Ar-H-5), 6.83 – 6.81 (m, 1H, Ar-H-6), 6.81 (d, 1H, J = 2.4 Hz, Ar-H-2), 6.79 (s, 1H, Ar-H-6'), 5.09 (s, 2H, Ar-CH2-O), 3.86 (s, 6H, OCH3-4', 5'), 3.85 (s, 3H, OCH3-3), 3.76 (s, 3H, OCH3-4), 3.62 (s, 1H, Ar-CH2-CO). 13C NMR: δ 171.3 (C=O), 149.3 (Ar-C-OCH3-4), 149.2 (Ar-C-OCH3-3), 148.8 (Ar-C-OCH3-5'), 148.1 (Ar-C-OCH3-3), 130.6 (Ar-C-1'), 126.2 (Ar-C-1), 121.6 (Ar-C-H-3'), 121.4 (Ar-C-H-5), 114.6 (Ar-C-H-6'), 112.4 (Ar-C-H-6), 111.1 (Ar-C-H-2), 86.9 (Ar-C-2'), 70.2 (Ar-CH2-O), 56.1 (Ar-OCH3-3), 55.85 (2 x Ar-OCH3-4, 4'), 55.83 (Ar-OCH3-5'), 40.8 (Ar-CH2-CO). MS: m/z
(EI+) 472 (M⁺, 13 %), 151 (100 %), HRMS (EI⁺): Calced for C₁₉H₂₁IO₆ = 472.0383 (M⁺), found 472.0388.

3,4-Dimethoxybenzyl (2-iodophenyl)acetate 10a
The title compound was prepared in 91 % yield (clear oil, 1.42 g) from 2-iodophenylacetic acid 261 (1.0 g, 3.82 mmol) and 3,4-dimethoxybenzyl alcohol 231 (706 mg, 4.19 mmol) in the presence of DCC (866 mg, 4.19 mmol), DMAP (140 mg, 1.14 mmol) and DCM (20 mL) according to esterification method. \(^1\)H NMR: \(\delta\) 7.83 (d, 1H, \(J = 8.0\) Hz, Ar-H-3), 7.29 (d, 1H, \(J = 8.0\) Hz, Ar-H-6), 7.28 (t, 1H, \(J = 8.0\) Hz, Ar-H-5), 6.94 (t, 1H, \(J = 8.0\) Hz, Ar-H-4), 6.90 (d, 1H, \(J = 8.0\) Hz, Ar-H-6’), 6.85 (bs, 1H, Ar-H-2’), 6.81 (d, 1H, \(J = 8.0\) Hz, Ar-H-5’), 5.10 (s, 2H, Ar-CH₂-O), 3.86 (s, 3H, OCH₃-3’), 3.84 (s, 3H, OCH₃-4’), 3.82 (s, 2H, Ar-CH₂-CO). \(^1\)C NMR: \(\delta\) 170.2 (C=O), 148.9 (Ar-C-OCH₃-4’), 148.8 (Ar-C-OCH₃-3’), 139.3 (Ar-C-H-3), 137.6 (Ar-C-1), 130.5 (Ar-C-H-5), 128.7 (Ar-C-H-4), 128.3 (Ar-C-H-6), 128.1 (Ar-C-1’), 121.0 (Ar-C-H-6’), 111.5 (Ar-C-H-2’), 110.8 (Ar-C-H-5’), 100.9 (Ar-C-2), 66.7 (Ar-CH₂-O), 55.79 (Ar-OCH₃-4’), 55.78 (Ar-OCH₃-3’), 46.2 (Ar-CH₂-CO). MS: \(m/z\) (EI⁺) 412 (M⁺, 48 %), 151 (100 %), HRMS (EI⁺): Calced for C₁₇H₁₇IO₄ = 412.0171, found 412.0158.

3,4-Dimethoxybenzyl 2-iodo-4,5-dimethoxyphenylacetate 10b
The title compound was prepared in 77 % yield (white solid, 452 mg) from 2-iodo-3,4-dimethoxyphenylacetic acid 254 (400 mg, 1.24 mmol) and 3,4-dimethoxybenzyl alcohol 231 (229 mg, 1.36 mmol) in the presence of DCC (282 mg, 1.36 mmol), DMAP (45 mg, 0.37 mmol) and DCM (10 mL) according to esterification method. M.p. 96-98 °C. \(^1\)H NMR: \(\delta\) 7.23 (s, 1H, Ar-H-3), 6.91 (dd, 1H, \(J = 8.0, 2.0\) Hz, Ar-H-6’), 6.88 (d, 1H, \(J = 2.0\) Hz, Ar-H-2’), 6.83 (d, 1H, \(J = 8.0\) Hz, Ar-H-5’), 6.78 (s, 1H, Ar-H-6), 5.11 (s, 2H, Ar-CH₂-O), 3.87 (s, 3H, OCH₃-3’), 3.86 (s, 3H, OCH₃-4’), 3.84 (s, 3H, OCH₃-5'), 3.81 (s, 3H, OCH₃-4), 3.76 (s, 2H, Ar-CH₂-CO). \(^1\)C NMR: \(\delta\) 170.6 (C=O), 149.0 (Ar-C-OCH₃-4), 148.9 (2 x Ar-C-OCH₃-4’, 5’), 148.6 (Ar-C-OCH₃-5), 129.9 (Ar-C-1), 128.2 (Ar-C-1’), 121.5 (Ar-C-H-3), 121.1 (Ar-C-H-6’), 113.2 (Ar-C-H-6), 111.6 (Ar-C-H-5’), 110.8 (Ar-C-H-2’), 88.8 (Ar-C-2), 66.7 (Ar-CH₂-O), 56.1 (Ar-OCH₃-5’), 55.87 (2 x Ar-OCH₃-4’, 4’), 55.86 (Ar-OCH₃-3’), 45.7 (Ar-CH₂-CO). MS: \(m/z\) (EI⁺) 472 (M⁺, 9 %), 151 (100 %) HRMS (ES⁺): Calced for C₁₉H₂₂IO₆ = 473.0461 (M+H⁺), found 473.0443.
**General Method For Palladium-Mediated Arylation**

**2,3,8,9-Tetramethoxy-6H-benzo[c]chromen-6-one 2a**

Compound 1a (100 mg, 0.22 mmol), (Ph₃P)₂PdCl₂ (41 mg, 0.058 mmol), anhydrous NaOAc (55 mg, 0.67 mmol) and DMA (25 mL) were combined in an ACE® pressure tube. The solution was degassed for 20 min with Ar, the vessel sealed and heated at 120 °C for 3 h. The tube was cooled to RT and the solid residue removed by filtration. The filtrate was diluted with 20 mL of 10 % HCl solution and extracted with EtOAc (2 x 20 mL). The combined extracts were washed with H₂O (4 x 20 mL), dried (MgSO₄), filtered, evaporated and the title compound was isolated as a white film (57.2 mg, 80 %) by flash silica gel chromatography using DCM:PS:EtOAc (2:2:1) as the eluent. M.p. 217-219 °C

**1H NMR:** δ 7.69 (s, 1H, Ar-H-7), 7.24 (s, 1H, Ar-H-10), 7.22 (s, 1H, Ar-H-1), 6.83 (s, 1H, Ar-H-4), 4.11 (s, 3H, OCH₃-8), 4.02 (s, 3H, OCH₃-2), 3.99 (s, 3H, OCH₃-9), 3.94 (s, 3H, OCH₃-3). **13C NMR:** δ 161.4 (C=O), 155.1 (Ar-C=OCH₃-8), 150.9 (Ar-C=OCH₃-3), 149.3 (Ar-C=OCH₃-9), 146.3 (Ar-C=4a), 146.0 (Ar-C=OCH₃-2), 130.3 (Ar-C=7a), 113.3 (Ar-C=10a), 110.5 (Ar-C=H-7), 110.0 (Ar-C=1a), 103.8 (Ar-C=H-10), 102.0 (Ar-C=H-1), 100.8 (Ar-C=H-4), 56.6 (Ar-OCH₃-2), 56.3 (Ar-OCH₃-8), 56.2 (Ar-OCH₃-9), 56.1 (Ar-OCH₃-3). **MS:** m/z (EI⁺) 316 (M⁺, 100 %) HRMS (CI⁺): Calcd for C₁₇H₁₇O₆ = 317.1025 (M+H⁺), found 317.1026 (M⁺).

**2,3,8,9,10-Pentamethoxy-6H-benzo[c]chromen-6-one 2b**

The title compound was prepared in 85 % yield (white solid, 63 mg) from 1b (100 mg, 0.21 mmol), in the presence of (Ph₃P)₂PdCl₂ (39 mg, 0.055 mmol), NaOAc (52 mg, 0.63 mmol) and DMA (25 mL) according to the general arylation method described above. M.p. 148-150 °C

**1H NMR:** δ 8.39 (s, 1H, Ar-H-7), 7.72 (s, 1H, Ar-H-1), 6.86 (s, 1H, Ar-H-4), 4.05 (s, 3H, OCH₃-8), 4.00 (s, 3H, OCH₃-9), 3.99 (s, 3H, OCH₃-10), 3.98 (s, 3H, OCH₃-3), 3.94 (s, 3H, OCH₃-2). **13C NMR:** δ 161.3 (C=O), 152.8 (Ar-C=OCH₃-10), 150.1 (Ar-C=OCH₃-9), 149.9 (Ar-C=OCH₃-2), 148.9 (Ar-C=OCH₃-3), 145.7 (Ar-C=OCH₃-8), 145.4 (Ar-C=4a), 123.1 (Ar-C=7a), 116.2 (Ar-C=10a), 109.4 (Ar-C=1a), 108.1 (Ar-C=H-7), 107.9 (Ar-C=H-1), 100.3 (Ar-C=H-4), 61.1 (Ar-OCH₃-8), 60.6 (Ar-OCH₃-3), 56.2 (Ar-OCH₃-9), 56.1 (Ar-OCH₃-10), 56.0 (Ar-OCH₃-2). **MS:** m/z (CI⁺) 347 (M+H⁺, 100 %) HRMS (Cl⁺): Calcd for C₁₈H₁₉O₇ = 347.1131 (M+H⁺), found 347.1132.
2,3-Dimethoxy-6\textit{H}-benzo[c]chromen-6-one 2c and 1,2-Dimethoxy-6\textit{H}-benzo[c]chromen-6-one 3

Compound 2c was prepared in 71 % yield (white solid, 47.3 mg) from 1c (100 mg, 0.26 mmol), in the presence of (Ph\textsubscript{3}P\textsubscript{2}PdCl\textsubscript{2} (39 mg, 0.067 mmol), NaOAc (64 mg, 0.78 mmol) and DMA (25 mL) according to the general arylation method described above. Regioisomer 3 was also isolated from the reaction as a white solid (9.2 mg, 8 %). NMR data was consistent with the literature for 2c and 3.\textsuperscript{8}

3,4-Dimethoxyphenyl (2\textit{E})-3-(3,4-dimethoxyphenyl)acrylate 6

The title compound was prepared in 59 % yield (yellow film, 43 mg) from 5 (100 mg, 0.20 mmol), in the presence of (Ph\textsubscript{3}P\textsubscript{2}PdCl\textsubscript{2} (37 mg, 0.053 mmol), NaOAc (51 mg, 0.61 mmol) and DMA (25 mL) according to the general arylation method described above. While this is a known compound NMR data was not reported.\textsuperscript{9} \textsuperscript{1}H NMR: δ 7.80 (d, 1H, J = 15.9 Hz, Ar-CH=CH), 7.16 (dd, 1H, J = 8.1, 1.5 Hz, Ar-\textsubscript{H}-6), 7.10 (d, 1H, J = 1.5 Hz, Ar-\textsubscript{H}-2), 6.89 (d, 1H, J = 8.1 Hz, Ar-\textsubscript{H}-5), 6.86 (d, 1H, J = 9.3 Hz, Ar-\textsubscript{H}-5'), 6.72 (d, 1H, J = 2.7 Hz, Ar-\textsubscript{H}-2'), 6.71 (dd, 1H, J = 9.3, 2.7 Hz, Ar-\textsubscript{H}-6'), 6.48 (d, 1H, J = 15.9 Hz, Ar-CH=CH), 3.92 (s, 6H, 2 x OCH\textsubscript{3}-3, 4), 3.88 (s, 3H, OCH\textsubscript{3}-3'), 3.86 (s, 3H, OCH\textsubscript{3}-4').

\textsuperscript{13}C NMR: δ 166.0 (C=O), 151.4 (Ar-\textsubscript{C}-OCH\textsubscript{3}-3), 149.3 (Ar-\textsubscript{C}-OCH\textsubscript{3}-4), 149.2 (Ar-\textsubscript{C}-OCH\textsubscript{3}-4'), 146.7 (Ar-\textsubscript{C}-OCH\textsubscript{3}-3'), 146.4 (Ar-CH=CH), 144.4 (Ar-\textsubscript{C}-1'), 127.1 (Ar-\textsubscript{C}-CH=CH), 122.9 (Ar-\textsubscript{C}-H-6), 114.7 (Ar-CH=CH), 112.9 (Ar-\textsubscript{C}-H-6'), 111.1 (Ar-\textsubscript{C}-H-5), 111.0 (Ar-\textsubscript{C}-H-5'), 109.7 (Ar-\textsubscript{C}-H-2), 105.8 (Ar-\textsubscript{C}-H-2'), 56.1 (Ar-OCH\textsubscript{3}), 55.96 (Ar-OCH\textsubscript{3}), 55.94 (Ar-OCH\textsubscript{3}), 55.8 (Ar-OCH\textsubscript{3}). MS: m/z (EI\textsuperscript{+}) 344 (M\textsuperscript{+}, 13 %), 191 (100 %) HRMS (EI\textsuperscript{+}): Calcd for C\textsubscript{19}H\textsubscript{20}O\textsubscript{6} = 344.1260 (M\textsuperscript{+}), found 344.1256.

4-(3,4-Dimethoxyphenyl)-1,4-dihydro-3\textit{H}-isochromen-3-one 8a and 2,2'-((dimethylenebiphenyl-2,2'-diyl) [di(3,4-dimethoxyphenyl)] diacetate 9a

Compounds 8a (white film, 20 mg, 29 %) and 9a (white film, 31 mg, 30%) were prepared from 7a (100 mg, 0.24 mmol), in the presence of (Ph\textsubscript{3}P\textsubscript{2}PdCl\textsubscript{2} (44 mg, 0.063 mmol), NaOAc (60 mg, 0.73 mmol) and DMA (25 mL) according to the general arylation method described above.

8a: \textsuperscript{1}H NMR: δ 7.38 (d, 1H, J = 8.4 Hz, Ar-\textsubscript{H}-5), 7.37 (t, 1H, J = 8.4 Hz, Ar-\textsubscript{H}-7), 7.29 (d, 1H, J = 8.4 Hz, Ar-\textsubscript{H}-8), 7.15 (t, 1H, J = 8.4 Hz, Ar-\textsubscript{H}-6), 6.81 (d, 1H, J = 2.1 Ar-\textsubscript{H}-2'), 6.78 (d, 1H, J = 8.2 Hz, Ar-\textsubscript{H}-5'), 6.53 (dd, 1H, J = 8.2, 2.1 Hz, Ar-\textsubscript{H}-6'), 5.23 (ABq, 2H, J = 16.5 Hz, Ar-CH\textsubscript{2}-O), 4.95 (Ar-CH=CO), 3.85 (s, 3H, OCH\textsubscript{3}-4'), 3.82 (s, 3H, OCH\textsubscript{3}-3'). \textsuperscript{13}C NMR: δ 171.6 (C=O), 149.6 (Ar-\textsubscript{C}-OCH\textsubscript{3}-3'), 149.0 (Ar-\textsubscript{C}-OCH\textsubscript{3}-4'), 134.4 (Ar-\textsubscript{C}-5a), 132.2 (Ar-\textsubscript{C}-8a), 129.2 (Ar-\textsubscript{C}-H-5), 128.2 (Ar-\textsubscript{C}-H-6), 128.0 (Ar-\textsubscript{C}-H-7), 126.7 (Ar-\textsubscript{C}-1'), 125.0 (Ar-\textsubscript{C}-H-8), 120.5 (Ar-\textsubscript{C}-H-6'), 111.7 (Ar-\textsubscript{C}-H-2'), 111.3
(Ar-C-H-5’), 69.7 (Ar-C-H-5’), 69.7 (Ar-C-H-2-O), 56.1 (2 x Ar-OC-H3-3, 4), 51.5 (Ar-CH-CO). MS: m/z (EI+) 284 (M+, 73%), 209 (100%), HRMS (EI+): Calcd for C17H16O4 = 284.1048 (M+), found 284.1057.

9a: 1H NMR: δ 7.37 (dd, 2H, J = 7.5, 1.5 Hz, Ar-H-3’), 7.33 (dt, 2H, J = 7.5, 1.0 Hz, Ar-H-6’), 6.78 (d, 2H, J = 9.0 Hz, Ar-H-5), 6.74 (dd, 2H, J = 9.0, 1.5 Hz, Ar-H-6), 6.73 (bs, 2H, Ar-H-2), 4.83 (ABq, 4H, J = 12.5, Hz Ar-CH2-O), 3.85 (s, 6H, OCH3-4), 3.81 (s, 6H, OCH3-3), 3.48 (s, 4H, Ar-CH2-CO). 13C NMR: δ 171.2 (C=O), 148.8 (Ar-C-OCH3-3), 148.1 (Ar-C-OCH3-4), 139.6 (Ar-C-H-3’), 133.7 (Ar-C-1’), 129.9 (Ar-C-2’), 128.9 (Ar-C-H-3’), 127.9 (2 x Ar-C-H-4’, 5’), 126.2 (Ar-C-1), 121.4 (Ar-C-H-6), 112.3 (Ar-C-H-2), 111.1 (Ar-C-H-5), 64.5 (Ar-CH2-O), 55.8 (Ar-OCH3-4), 55.7 (Ar-OCH3-3), 40.7 (Ar-CH2-CO).

MS: m/z (EI+) 570 (M+, 47%), 151 (100%), HRMS (EI+): Calcd for C34H34O8 = 570.2254 (M+), found 570.2271.

4-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-1,4-dihydro-3H-isochromen-3-one 8b and 2,2’-[dimethylene(4,4’,5,5’-tetramethoxybiphenyl-2,2’-diyl](di(3,4-dimethoxyphenyl))diacetate 9b

Compounds 8b (yellow film, 21 mg, 29 %) and 9b (orange film, 39 mg, 46%) were prepared from 7b (115 mg, 0.24 mmol), in the presence of (Ph3P)2PdCl2 (44 mg, 0.063 mmol), NaOAc (60 mg, 0.73 mmol) and DMA (25 mL) according to the general arylation method described above. 1H NMR: δ 6.84 (s, 2H, Ar-H-6’), 6.78 (d, 2H, J = 9.0 Hz, Ar-H-5), 6.76 (d, 2H, J = 9.0 Hz, Ar-H-6), 6.75 (bs, 2H, Ar-H-2), 6.69 (s, 2H, Ar-H-3’), 4.81 (ABq, 4H, J = 12.0 Hz, Ar-CH2-O), 3.85 (s, 6H, OCH3-5’), 3.84 (s, 6H, OCH3-4’), 3.81 (s, 6H, OCH3-3), 3.80 (s, 6H OCH3-4), 3.51 (s, 4H Ar-CH2-CO). 13C NMR: δ 171.3 (C=O), 148.9 (Ar-C-OCH3-4’), 148.4 (2 x Ar-C-OCH3-3, 4), 148.3 (Ar-C-OCH3-3’), 132.3 (Ar-C-1’), 126.3 (Ar-C-2’), 126.2 (Ar-C-1), 121.3 (Ar-C-H-6), 113.1 (Ar-C-H-3), 112.3 (Ar-C-H-2), 111.9 (Ar-C-H-6), 111.1 (Ar-C-H-5), 64.4 (Ar-CH2-O), 56.0 (Ar-OCH3-3), 55.9 (Ar-OCH3-4), 55.8 (Ar-OCH3-4’), 55.7 (Ar-OCH3-3’), 40.8 (Ar-CH2-CO). MS: m/z (EI+) 690 (M+, 11%), 368 (100%), HRMS (EI+): Calcd for C39H42O12 = 690.2676 (M+), found 690.2679.

4-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-1,4-dihydro-3H-isochromen-3-one 8b

The title compound was also prepared in 21 % yield (yellow film, 15 mg) from 3,4-dimethoxybenzyl (2-iodo-4,5-dimethophenyl)acetate (115 mg, 0.24 mmol), in the presence of (Ph3P)2PdCl2 (44 mg, 0.063 mmol), NaOAc (60 mg, 0.73 mmol) and DMA (25 mL) according to the general arylation method described above. 1H NMR: δ 6.84 (d, 1H, J = 2.0 Ar-H-2’), 6.77 (s, 1H, Ar-H-5), 6.78 (d, 1H, J
= 8.7 Hz, Ar-H-5'), 6.65 (s, 1H, Ar-H-8), 6.51 (dd, 1H, J = 8.7, 2.0 Hz, Ar-H-6'), 5.17 (ABq, 2H, J = 13.5 Hz, Ar-CH2-O), 4.89 (Ar-CH-CO), 3.92 (s, 3H, OCH3-6), 3.85 (s, 3H, OCH3-7), 3.84 (s, 3H, OCH3-3'), 3.83 (s, 3H, OCH3-4'). 13C NMR: δ 171.5 (C=O), 149.8 (Ar-C-OCH3-3), 149.6 (Ar-C-OCH3-4'), 149.0 (Ar-C-OCH3-4), 148.8 (Ar-C-OCH3-5'), 127.0 (Ar-C-5a), 126.2 (Ar-C-1'), 124.3 (Ar-C-8a), 120.2 (Ar-C-H-6'), 111.5 (Ar-C-H-2'), 111.3 (Ar-C-H-5'), 111.2 (Ar-C-H-8), 108.1 (Ar-C-H-5), 69.6 (Ar-CH2-O), 56.4 (Ar-OCH3), 56.3 (Ar-OCH3), 56.2 (Ar-OCH3), 56.1 (Ar-OCH3), 50.9 (Ar-CH-CO). MS: m/z (EI+) 344 (M+, 46 %), 269 (100 %), HRMS (CI+): Calcd for C19H21O6 = 345.1338 (M+H+), found 345.1327.

Di-(3,4-dimethoxybenzyl) 2,3-diphenylsuccinate 11 and di-(3,4-dimethoxybenzyl) 2,2′-biphenyl-2,2′-diylacetate 12

Compound 11 was prepared in 27 % yield (clear film, 19 mg) from 10a (100 mg, 0.24 mmol), in the presence of (Ph3P)2PdCl2 (65 mg, 0.093 mmol), NaOAc (60 mg, 0.73 mmol) and DMA (25 mL) according to the general arylation method described above, and with HPLC separation of 12 (clear film, 4 mg, 7 %) from the reaction mixture. The major and minor diastereomers could not be separated by HPLC and are reported together. The diastereomeric ratio was major: minor = 1.8:1. NMR signals for the minor diastereomer are shown in brackets.

11: 1H NMR: δ 7.47 (dd, 2H, J = 7.5, 2.1 Hz, Ar-H-4), 7.13 (t, 4H, J = 7.5 Ar-H-3,5), 7.03 (dd, 4H, Ar-H-2,6), 6.73 (d, 2H, J = 7.8 Hz, Ar-H-5'), 6.59 (dd, 2H, J = 7.8, 2.1 Hz, Ar-H-6'), 6.48 (d, 2H, J = 2.1 Hz, Ar-H-2'), 5.04 (4.76) (ABq, 4H, J = 12.3 Hz, Ar-CH2-O), 4.30 (4.43) (s, 2H, Ar-CH2-O), 3.85 (3.85) (s, 3H, OCH3-3'), 3.74 (3.69) (s, 3H, OCH3-4'). 13C NMR: δ 172.8 (171.4) (C=O), 148.9 (Ar-C-OCH3-3'), 148.8 (Ar-C-OCH3-4'), 135.5 (136.1) (Ar-C-H-2'), 128.5 (128.6) (Ar-C-H-4), 128.3 (128.2) (Ar-C-H-3,5), 128.4 (Ar-C-1), 128.0 (127.9) (Ar-C-1'), 127.4 (127.8) (Ar-C-H-2,6), 120.8 (120.5) (Ar-C-H-6'), 110.9 (111.2) (Ar-C-H-2'), 110.7 (110.9) (Ar-C-H-5'), 66.6 (Ar-CH2-O), 55.8 (Ar-OCH3), 55.7 (55.6) (Ar-OCH3), 54.8 (54.9) (Ar-CH-CO). MS: m/z (EI+) 570 (M+, 10 %), 151 (100 %), HRMS (EI+): Calcd for C34H34O8 = 570.2253 (M+H+), found 570.2231.

12: 1H NMR: δ 7.30-7.26 (m, 4H, Ar-H-5,6), 7.22-7.16 (m, 4H, Ar-H-3,4), 7.07 (d, 2H, J = 7.2 Hz, Ar-H-5), 6.78 (d, 2H, J = 1.2 Hz, Ar-H-2'), 6.72 (dd, 2H, J = 7.2, 1.2 Hz, Ar-H-6'), 4.91 (s, 4H Ar-CH3-O), 3.85 (s, 6H, OCH3-3'), 3.80 (s, 6H OCH3-4'), 3.36 (ABq, 4H, J = 16.0 Hz, Ar-CH2-CO).

13C NMR: δ 171.4 (C=O), 149.0 (Ar-C-OCH3-4'), 148.9 (Ar-C-OCH3-3'), 140.6 (Ar-C-H-3), 132.4 (Ar-C-1'), 130.2 (Ar-C-H-5), 130.1 (Ar-C-H-4), 128.5 (Ar-C-1), 127.7 (Ar-C-H-6), 126.9 (Ar-C-2'), 17
121.1 (Ar-\(\text{C-H-6}^{\prime}\)), 111.6 (Ar-\(\text{C-H-5}^{\prime}\)), 110.8 (Ar-\(\text{C-H-2}^{\prime}\)), 66.9 (Ar-\(\text{C-H2-O}\)), 55.9 (Ar-\(\text{OCH3-4}^{\prime}\)), 55.8 (Ar-\(\text{OCH3-3}^{\prime}\)), 38.7 (Ar-\(\text{C-H2-CO}\)). MS: \(m/z\) (EI\(^{+}\)) 570 (M\(^{+}\), 5 %), 151 (100 %), HRMS (EI\(^{+}\)): Calcd for \(C_{34}H_{34}O_{8}\) = 570.2253 (M\(^{+}\)), found 570.2239.

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REFERENCES


6. We thank a referee for drawing this possibility to our attention.


**GRAPHICAL ABSTRACT**
Synthesis of benzo[c]chromen-6-ones via novel cyclic aryl-Pd(II)-ester enolate intermediates

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