Palladium-Catalyzed Selective Carbonylation of Vinyl Triflates in the Presence of 2-Iodophenols: A New Route to 3-Spiro-Fused Benzofuran-2(3*H*)-ones

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A convenient synthesis of 3-spiro-fused benzofuran-2(3*H*)-ones via palladium-catalyzed chemoselective carbonylation of vinyl triflates in the presence of *o*-iodophenols, followed by regioselective intramolecular Heck reaction, is described.

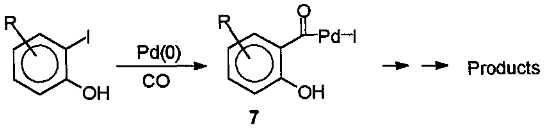
The benzofuran-2-one nucleus is present in some compounds of pharmacological interest showing hypocholesterolamic and radiation-protective activity,[1] as well as in naturally occurring products such as marginalin.[2]

Recently, synthetic procedures leading to 3-arylidenebenzofuran-2(3*H*)-ones[2,3] and 3,3-diarylbenzofuran-2(3*H*)-ones[4] have been reported.

As part of our current studies on the development of new palladium-catalyzed routes to heterocyclic systems,[5] we thought that an easy approach to α,β-unsaturated *o*-iodophenyl esters **3** could represent a practical route to functionalized 3-spiro-fused benzofuran-2(3*H*)-ones **4** via intramolecular Heck reaction[6] (see Scheme 2).

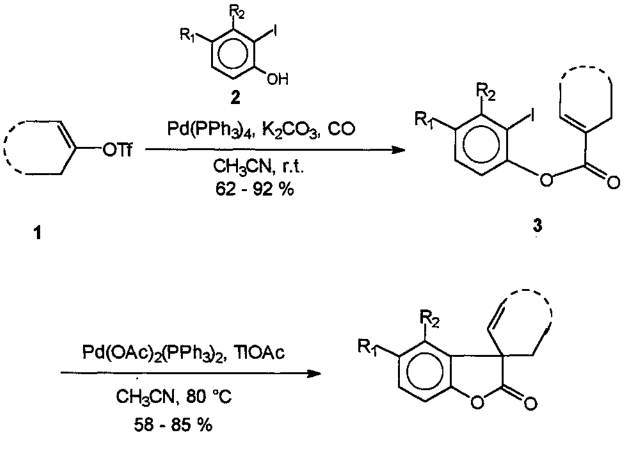
We therefore focused our attention on the preparation of compounds **3** starting from readily available vinyl triflates **1** and 2-iodophenols **2**.

Palladium-catalyzed carbonylation of aryl, vinyl or benzyl halides,[7] and aryl or vinyl triflates[8] in the presence of suitable nucleophiles represents a well-documented procedure for the synthesis of a variety of aromatic and α,β-unsaturated esters, amides, α-ketoamides, α-keto esters and acids, anhydrides, acids, acid fluorides, lactones, lactams, aldehydes and imides. The reaction involves oxidative addition of halides or triflates to a palladium(0) species, followed by CO coordination and insertion. Nucleophilic attack on the resulting acylpalladium(II) intermediate affords the product and regenerates the palladium(0) catalyst.[9] Moreover, carbonylation of 2-iodophenol derivatives has been reported to produce flavones and aurones[10] through the formation of aroyl palladium iodide intermediate **7** (Scheme 1).



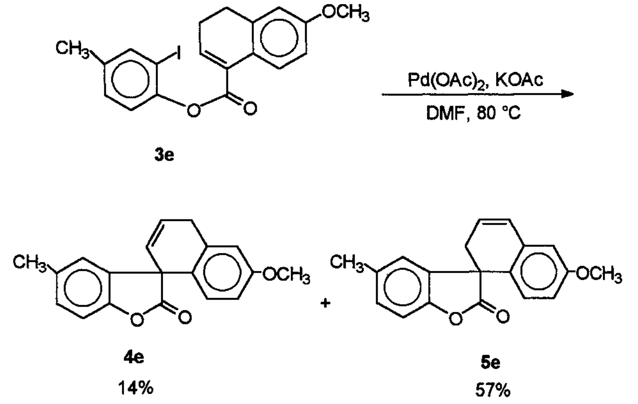
Scheme 1

We now wish to report that the palladium-catalyzed carbonylation of a mixture of 2-iodophenols **2** and vinyl triflates **1** in anhydrous MeCN at room temperature under an atmosphere of CO, in the presence of a catalytic amount of $Pd(PPh_3)_4$ and potassium carbonate as base, affords *o*-iodophenyl α,β-unsaturated esters **3** in high yield (see Scheme 2 and Table 1). It is worth noting that, under our reaction conditions, the oxidative insertion of the palladium catalyst takes place chemoselectively into the vinyl-OTf bond; the order of reactivity we observed (C=C–OTf> ArI)[11] allows an effective synthesis of compounds **3**.



Scheme 2

Regioselective 5-*exo-trig* cyclization of esters **3** has been successfully accomplished[12] in MeCN at 80 °C in the presence of $Pd(OAc)_2(PPh_3)_2$ (5%) and 1.2 equiv of TlOAc[13] (see Scheme 2 and Table 1). The use of 1.2 equiv of Ag_2CO_3[14] gave moderate results; product **4a** was isolated in only 46% yield after reacting **3a** for 23 h under the usual reaction conditions but using silver carbonate instead of thallium acetate. The importance of an HI scavenger is demonstrated by the cyclization of **3e** in DMF at 80 °C (6 h) without TlOAc, in the presence of KOAc (1.2 equiv) and $Pd(OAc)_2$ (5%), resulting in the formation of an 80:20 mixture of the alkenes **4e** and **5e** (71% yield).[15]



Scheme 3

Table 1. Preparation of 2-Iodophenyl Esters **3** and Benzofuranones **4**

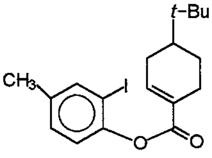
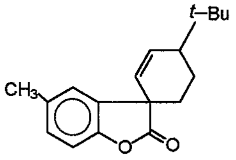
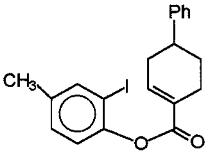
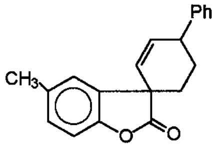
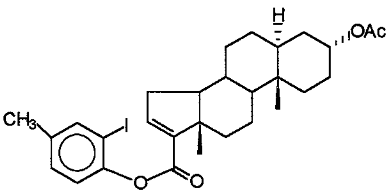
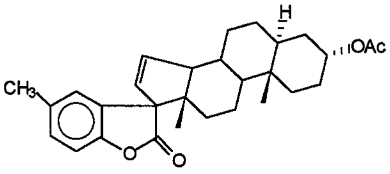
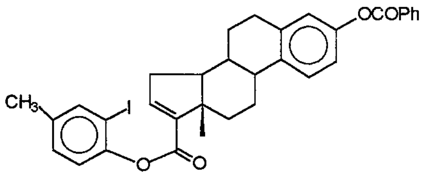
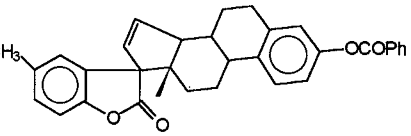
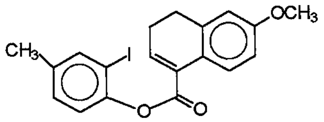
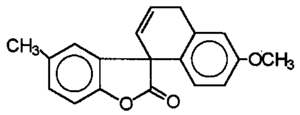
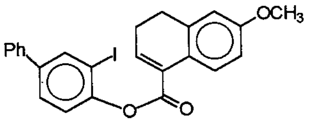
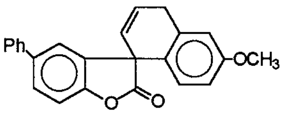
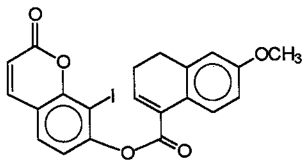
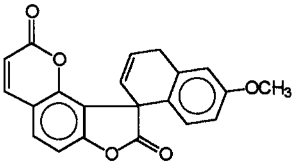
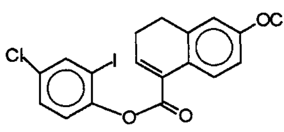
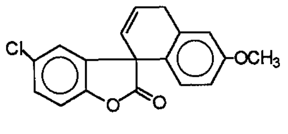
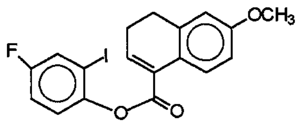
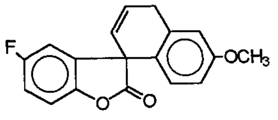
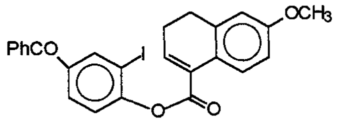
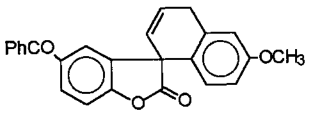
Product **3**	Yield[a] (%)	Product **4**	Time[b] (h)	Yield[c] (%)
 **3a**	74	 **4a**	2.5	85
 **3b**	71	 **4b**	5.5	75
 **3c**	79	 **4c**	2	77
 **3d**	72	 **4d**	9	70
 **3e**	88	 **4e**	1.5	66
 **3f**	75	 **4f**	6	73
 **3g**	65	 **4g**	24	59

Table 1. (continued)

Product 3	Yield[a] (%)	Product 4	Time[b] (h)	Yield[c] (%)
 **3h**	62	 **4h**	23	58[d]
 **3i**	78	 **4i**	23	75
 **3j**	72	 **4j**	4	75

[a] Yield of pure isolated **3** based on triflate.

[b] Reaction time for cyclization.

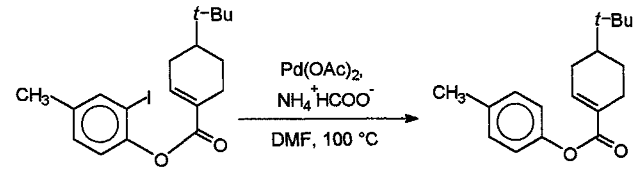
[c] Yield of pure isolated **4**.

[d] 10 mol% of Pd(OAc)$_2$(PPh$_3$)$_2$ was used.

According to the previously reported results concerning the stereoselective construction of quaternary[17] and tertiary[18] carbon centers by intramolecular Heck reaction, the cyclization of esters **3c** and **3d** occurred with high stereoinduction to form single diastereomers **4c** and **4d**.[16] On the contrary, in the cyclization of **3a** and **3b** the products **4a** and **4b** were obtained, respectively, as a 1.7:1 and 1.8:1 unseparated mixture of diastereomers, as judged by NMR analysis.

Attempts to synthesize **4e** through a one-pot procedure, starting from 6-methoxy-3,4-dihydro-1-naphthyl triflate (**1a**) and 2-iodo-4-methylphenol (**2a**), were unsuccessful.[19]

We were also unable to obtain a palladium-catalyzed tandem cyclization–hydride ion capture process;[20] reacting the substrate **3a** in DMF (100 °C, 3 h) with ammonium formate (3 equiv) and Pd(OAc)$_2$ led to **6a** in 70% yield (Scheme 4).[21] In this case the reaction outcome showed that hydride exchange of the initial arylpalladium intermediate was the favoured process.



3a **6a** 70%

Scheme 4

In conclusion, the reaction between vinyl triflates and 2-iodophenols in the presence of carbon monoxide and palladium catalyst is of significant synthetic value, since it can be used for the preparation of 2-iodophenyl α,β-unsaturated esters that represent useful intermediates for the synthesis of benzofuran-2(3*H*)-ones. Because of the ready availability of vinyl triflates from ketones[22] and 2-iodophenols from phenols,[23] the present approach provides a straightforward and convenient route to these heterocyclic compounds.

The vinyl triflates[22] and the substituted 2-iodophenols[23] were prepared as previously reported. Anhydr. MeCN and other solvents and chemicals were commercially available and were used without further purification. The products were purified by flash chromatography on silica gel (Merck, 0.040–0.063 mm). Melting points are uncorrected and were measured in capillary tubes on a Buchi apparatus. IR spectra were recorded with a Perkin-Elmer 683 spectrometer. ^{1}H NMR (200 MHz) and ^{13}C (50.3 MHz) spectra were recorded with a Bruker AC 200 spectrometer using TMS as internal standard. Electron impact mass spectra (70 EV) were recorded with an Incos XL/Finnigan/Mat instrument.

2-Iodophenyl α,β-Unsaturated Esters 3a–j; General Procedure:
To a stirred solution of the triflate **1** (2 mmol) in anhydr. MeCN (10 mL) was added the 2-iodophenol **2** (2.4 mmol), K$_2$CO$_3$ (6 mmol) and Pd(PPh$_3$)$_4$ (0.04 mmol). The flask was purged with CO for 1–2 s, connected to a balloon of CO and stirred overnight at r.t. The reaction mixture was then poured into a separatory funnel containing 0.1 N aq HCl (150 mL) and extracted with EtOAc (3 × 150 mL). The organic layer was separated and the aqueous layer was washed twice with EtOAc. The combined organic layers were dried (Na$_2$SO$_4$) and concentrated at reduced pressure. The residue, purified by flash chromatography (hexane – EtOAc mixtures), gave esters **3a–j**.

Table 2. Characterization of 2-Iodophenyl Esters **3** and Benzofuranones **4**

Product	mp^a (°C)	EIMS^b m/z (rel. intensity)	IR ν (cm^{-1})	^{1}H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$)^c δ, J (Hz)
3a	95–98	398 (M^+, 2), 165 (100)	(KBr) 1740	7.64 (d, $J = 2.0$, 1 H), 7.34–7.30 (m, 1 H, 7.14 (dd, $J = 8.2$, 2.0, 1 H), 7.00 (d, $J = 8.2$, 1 H), 2.73–2.60 (m, 1 H), 2.30 (s, 3 H), 0.91 (s, 9 H)	165.1, 149.1, 143.2, 139.5, 137.2, 130.0, 129.5, 122.6, 90.2, 43.2, 32.1, 27.8, 27.1, 25.7, 23.5, 20.4
3b	99–102	418 (M^+, 3), 185 (100)	(KBr) 1740	7.82 (bs, 1 H), 7.40–7.05 (m, 7 H), 7.00 (d, $J = 8.2$, 1 H), 2.90–2.75 (m, 1 H), 2.27, (s, 3 H)	164.8, 149.0, 145.7, 142.0, 139.5, 137.3, 130.0, 129.4, 128.5, 126.7, 126.3, 122.5, 90.2, 39.0, 34.0, 29.3, 24.9, 20.3
3c	173–175	576 (M^+, 4), 343 (100), 283 (18)	(KBr) 1740	7.64 (d, $J = 1.7$, 1 H), 7.17–7.09 (m, 2 H), 7.00 (d, $J = 8.2$, 1 H), 5.01 (bs, 1 H), 2.30 (s, 3 H), 2.05 (s, 3 H), 1.02 (s, 3 H), 0.83 (s, 3 H)	170.6, 162.3, 148.9, 146.7, 145.9, 139.5, 137.2, 129.9, 122.6, 90.3, 69.9, 56.6, 54.6
3d	135–137	618 (M^+, 1), 385 (63), 105 (100)	(KBr) 1730	8.19 (d, $J = 7.6$, 2 H), 7.65–7.56 (m, 2 H), 7.51–7.74 (m, 2 H), 7.35–7.31 (m, 1 H), 7.17–7.11 (m, 2 H), 7.04–6.92 (m, 3 H), 2.29 (s, 3 H), 1.06 (s, 3 H)	165.3, 162.2, 148.8, 148.6, 146.5, 145.8, 139.5, 137.92, 137.91, 137.2, 133.4, 130.0, 129.9, 129.5, 128.4, 126.1, 122.6, 121.5, 118.6, 90.3, 55.7, 46.2, 44.3
3e	117–119	420 (M^+, 7), 187 (100), 159 (92)	(KBr) 1740	7.94 (d, $J = 8.4$, 1 H), 7.67 (d, $J = 1.9$, 1 H), 7.48 (t, $J = 5.0$, 1 H), 7.17 (dd, $J = 8.2$, 1.9, 1 H), 7.04 (d, $J = 8.2$, 1 H), 6.79–6.72 (m, 2 H), 3.79 (s, 3 H), 2.80 (t, $J = 7.9$, 2 H), 2.53–2.42 (m, 2 H), 2.31 (s, 3 H)	163.9, 159.0, 149.1, 140.2, 139.7, 138.0, 137.5, 130.1, 129.2, 127.4, 123.5, 122.7, 113.8, 111.1, 90.3, 55.2, 27.8, 23.7, 20.4
3f	105–107	482 (M^+, 10), 296 (6), 187 (100), 159 (70)	(KBr) 1740	8.04 (d, $J = 2.1$, 1 H), 7.97 (d, $J = 8.4$, 1 H), 7.58–7.33 (m, 7 H), 7.22 (d, $J = 8.4$, 1 H), 6.80–6.74 (m, 2 H), 3.77 (s, 3 H), 2.79 (t, $J = 7.9$, 2 H), 2.52–2.41 (m, 2 H)	163.7, 159.0, 150.6, 140.8, 140.6, 138.8, 138.0, 137.8, 129.0, 128.8, 128.1, 127.7, 127.4, 127.0, 123.32, 123.25, 113.7, 111.1, 91.0, 55.1, 27.7, 23.7
3g	142–145	474 (M^+, 12), 288 (5), 187 (100), 159 (78)	(KBr) 1750	7.90 (d, $J = 9.4$, 1 H), 7.64 (d, $J = 9.6$, 1 H), 7.59 (t, $J = 5.0$, 1 H), 7.50 (d, $J = 8.4$, 1 H), 7.16 (d, $J = 8.4$, 1 H), 6.80–6.74 (m, 2 H), 6.39 (d, $J = 9.6$, 1 H), 3.80 (s, 3 H), 2.82 (t, $J = 7.9$, 2 H), 2.58–2.47 (m, 2 H)	163.1, 159.7, 159.1, 154.7, 154.6, 142.8, 141.4, 138.0, 128.5, 127.2, 123.0, 119.5, 117.0, 116.3, 113.7, 111.2, 82.3, 55.2, 27.6, 23.7
3h	141–143	442 ($M^+ + 2$, 2), 440 (M^+, 6), 187 (100), 159 (68)	(KBr) 1740	7.91 (d, $J = 8.2$, 1 H), 7.82 (d, $J = 2.4$, 1 H), 7.50 (t, $J = 5.0$, 1 H), 7.34 (dd, $J = 8.7$, 2.4, 1 H), 7.10 (d, $J = 8.7$, 1 H), 6.79–6.74 (m, 2 H), 3.79 (s, 3 H), 2.79 (t, $J = 8.7$, 2 H), 2.53–2.42 (m, 2 H)	163.4, 159.1, 150.1, 140.8, 138.6, 138.0, 131.9, 129.4, 127.3, 123.9, 123.2, 113.8, 111.2, 91.0, 55.2, 27.7, 23.7
3i	105–107	424 (M^+, 16), 187 (100), 159 (64)	(KBr) 1740	7.92 (d, $J = 8.4$, 1 H), 7.58–7.47 (m, 2 H), 7.13–7.08 (m, 2 H), 6.80–6.74 (m, 2 H), 3.79 (s, 3 H), 2.79 (t, $J = 2.9$, 2 H), 2.53–2.43 (m, 2 H)	163.7 (d, $J = 1$ Hz), 159.7 (d, $J = 250$, C-F), 159.1, 147.7 (d, $J = 4$), 140.7, 138.0, 113.8, 111.2, 90.3 (d, $J = 8$), 55.2, 27.7, 23.7
3j	oil	510 (M^+, 6), 187 (100), 159 (60)	(neat) 1740, 1670	8.31 (d, $J = 1.9$, 1 H), 7.94 (d, $J = 8.4$, 1 H), 7.83–7.75 (m, 3 H), 7.58–7.41 (m, 4 H), 7.30 (d, $J = 8.4$, 1 H), 6.79–6.73 (m, 2 H), 3.77 (s, 3 H), 2.79 (t, $J = 7.8$, 2 H), 2.53–2.43 (m, 2 H)	193.9, 163.0, 159.1, 154.5, 141.2, 150.0, 138.0, 136.8, 136.5, 132.7, 131.2, 129.9, 128.6, 128.4, 127.3, 123.1, 123.0, 113.7, 112.2, 90.7, 55.1, 27.6, 23.8
4a^d	oil	270 (M^+, 25), 214 (41), 57 (100)	(neat) 1810	7.11–6.94 (m, 3 H), 6.20–6.13 (m, 1 H), 5.50–5.38 (m, 1 H), 2.35/2.34 (two *Me*-Ar), 1.01/0.98 (two *t*-Bu)	180.0/178.1 (CO), 48.7/47.5 (quat)
4b^d	oil	290 (M^+, 38), 262 (20)	(neat) 1810	7.34–6.87 (m, 8 H), 6.10 (major diast., dd, $J = 9.8$, 2.9), 6.04 (minor diast., dd, $J = 9.8$, 2.9), 5.52 (major diast., dd, $J = 9.8$, 2.4), 5.46 (minor diast., dd, $J = 9.8$, 2.4), 2.27 (bs, 3 H)	179.1/178.4 (CO), 48.2/47.6 (quat)
4c	198–200	448 (M^+, 24), 388 (100)	(KBr) 1810, 1730	7.09–7.04 (m, 1 H), 6.97–6.94 (m, 2 H), 6.29 (d, $J = 5.9$, 1 H), 5.83 (dd, $J = 5.9$, 3.3, 1 H), 5.01 (bs, 1 H), 2.36 (s, 3 H), 2.05 (s, 3 H), 1.82 (s, 3 H), 0.84 (s, 3 H)	177.0, 170.5, 150.6, 135.9, 132.9, 132.2, 129.1, 127.1, 124.9, 110.3, 65.4 (quat), 55.1 (quat), 36.0 (quat)
4d	196–198	490 (M^+, 2), 105 (100)	(KBr) 1800, 1740	8.22–8.17 (m, 2 H), 7.65–7.46 (m, 3 H), 7.27–7.21 (m, 1 H), 7.13–6.93 (m, 5 H), 6.41 (dd, $J = 5.8$, 1.7, 1 H), 5.92 (dd, $J = 5.8$, 3.3, 1 H), 2.36 (s, 3 H), 1.25 (s, 3 H)	176.9, 165.4, 150.7, 148.9, 137.9, 137.4, 135.6, 133.5, 133.1, 132.8, 130.1, 129.6, 129.3, 128.5, 126.9, 126.1, 124.9, 121.7, 118.8, 110.5, 65.4 (quat), 55.3 (quat)
4e	oil	292 (M^+, 92), 264 (100)	(neat) 1810	7.17–7.05 (m, 2 H), 6.84 (bs, 1 H), 6.78 (d, $J = 2.2$, 1 H), 6.70–6.56 (m, 2 H), 6.34 (ddd, $J = 9.8$, 4.3, 3.1, 1 H), 5.67 (ddd, $J = 9.8$, 2.6, 1.7, 1 H), 3.83–3.48 (m, 2 H), 3.78 (s, 3 H)	177.3, 159.1, 151.1, 135.2, 134.7, 133.5, 129.7, 128.6, 128.3, 125.4, 125.3, 124.7, 113.5, 113.1, 110.3, 55.2, 52.8 (quat), 30.2, 21.1

Table 2. (continued)

Product	mp[a] (°C)	EIMS[b] m/z (rel. intensity)	IR ν (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$)[c] δ, J (Hz)
4f	60–63	354 (M^+, 50), 326 (100)	(KBr) 1810	7.58 (dd, J = 8.4, 1.9, 1 H), 7.51–7.45 (m, 2 H), 7.42–7.24 (m, 5 H), 6.80–6.78 (m, 1 H), 6.66–6.64 (m, 2 H), 6.37 (ddd, J = 9.8, 4.3, 3.1, 1 H), 5.73 (ddd, J = 9.8, 2.6, 1.7, 1 H), 3.85–3.50 (m, 2 H), 3.76 (s, 3 H)	177.0, 159.1, 152.7, 140.2, 138.5, 135.3, 134.2, 128.9, 128.8, 128.4, 128.1, 127.4, 126.9, 125.2, 124.6, 123.7, 113.5, 113.2, 111.0, 55.2, 52.8 (quat), 30.2
4g	174–176	346 (M^+, 46), 318 (100)	(KBr) 1820, 1750	7.63 (d, J = 9.6, 1 H), 7.48 (d, J = 8.4, 1 H), 7.16 (d, J = 8.4, 1 H), 6.80 (bs, 1 H), 6.65–6.64 (m, 2 H), 6.45 (dd, J = 9.8, 3.8, 1 H), 6.25 (d, J = 9.6, 1 H), 5.71 (dd, J = 9.8, 2.2, 1 H), 3.94–3.60 (m, 2 H), 3.76 (s, 3 H)	176.2, 159.3, 159.2, 155.2, 150.0, 143.3, 135.8, 130.5, 129.3, 127.0, 123.2, 121.4, 119.7, 116.1, 115.1, 113.7, 113.3, 107.8, 55.2, 51.7 (quat), 30.3
4h	oil	314 (M^+ + 2, 24), 312 (M^+, 72), 284 (100)	(neat) 1810	7.35–7.30 (m, 1 H), 7.14 (J = 8.4, 1 H), 7.03 (d, J = 2.2, 1 H), 6.80–6.77 (m, 1 H), 6.71–6.65 (m, 1 H), 6.56 (d, J = 8.4, 1 H), 6.37 (ddd, J = 9.8, 4.3, 3.1, 1 H), 5.66 (ddd, J = 9.8, 2.6, 1.7, 1 H), 3.84–3.49 (m, 2 H), 3.78 (s, 3 H)	176.3, 159.3, 151.6, 135.22, 135.20, 130.2, 129.4, 129.3, 128.2, 125.2, 124.5, 123.8, 113.7, 113.3, 112.1, 55.3, 52.8 (quat), 30.1
4i	134–136	296 (M^+, 88), 268 (100)	(KBr) 1810	7.20–6.99 (m, 2 H), 6.80–6.65 (m, 3 H), 6.57 (d, J = 8.6, 1 H), 6.37 (ddd, J = 9.8, 4.3, 3.1, 1 H), 5.67 (ddd, J = 9.8, 2.6, 1.7, 1 H), 3.83–3.48 (m, 2 H), 3.78 (s, 3 H)	175.1, 160.0 (d, J = 243, C-F), 159.3, 149.0, 135.2, 55.3, 55.2 (d, J = 1.8, quat), 30.2
4j	oil	382 (M^+, 64), 354 (80), 277 (100)	(neat) 1820, 1670	7.85 (dd, J = 8.4, 1.9, 1 H), 7.75–7.70 (m, 2 H), 7.60–7.40 (m, 4 H), 7.29 (d, J = 8.4, 1 H), 6.79–6.77 (m, 1 H), 6.71–6.56 (m, 2 H), 6.38 (ddd, J = 9.8, 4.3, 3.2, 1 H), 5.70 (ddd, J = 9.8, 2.4, 1.7, 1 H), 3.82–3.50 (m, 2 H), 3.76 (s, 3 H)	195.1, 176.2, 159.2, 156.2, 137.3, 135.2, 134.5, 134.1, 132.5, 132.4, 129.7, 129.5, 128.3, 128.1, 127.0, 124.5, 123.8, 113.6, 113.3, 110.5, 55.2, 52.3 (quat), 30.1
5f[d]	oil	292 (M^+, 39), 264 (100)	(neat) 1820	7.09–7.04 (m, 3 H), 6.75 (d, J = 2.6, 1 H), 6.70–6.60 (m, 3 H), 6.04 (ddd, J = 9.6, 5.1, 3.6, 1 H), 3.78 (s, 3 H), 3.02 (ddd, J = 17.3, 3.6, 1.4, 1 H), 2.67 (ddd, J = 17.3, 5.1, 2.4, 1 H), 2.26 (s, 3 H)	179.5, 159.6, 149.5, 134.15, 134.12, 132.7, 129.4, 128.6, 127.2, 125.5, 124.4, 124.3, 113.21, 113.19, 110.5, 55.3, 50.3 (quat), 34.8, 21.1
6a	101–102	272 (M^+, 4), 165 (100), 107 (29)	(KBr) 1740	7.22 (t, J = 3.1, 1 H), 7.16 (d, J = 8.5, 2 H), 6.96 (d, J = 8.5, 2 H), 2.51–2.53 (m, 1 H), 2.34 (s, 3 H), 0.91 (s, 9 H)	166.1, 148.9, 142.1, 135.1, 129.9, 121.4, 43.3, 32.2, 27.8, 27.1, 25.7, 23.6, 20.9

[a] Uncorrected, measured in capillary tubes.

[b] Satisfactory microanalyses obtained: C ± 0.32; H ± 0.39.

[c] "quat" = quaternary aliphatic carbons.

[d] Obtained as unseparated mixture of two diastereoisomers.

3-Spiro-Fused Benzofuran-2(3*H*)-ones 4a–j; General Procedure:
To a stirred solution of esters **3a–j** (0.5 mmol) in MeCN (10 mL) were added TlOAc (0.6 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.025 mmol). The reaction mixture was stirred at 80 °C under an N_2 atmosphere for the time required (see Table 1). The reaction mixture was then poured into a separating funnel containing 0.1 N aq HCl (150 mL) and extracted with EtOAc (3 × 150 mL). The organic layer was separated and the aqueous layer was washed twice with EtOAc. The combined organic layers were dried (Na_2SO_4) and concentrated at reduced pressure. The residue, purified by flash chromatography (hexane – EtOAc mixtures), gave benzofuran-2(3*H*)-ones **4a–j**.

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