

Note

Formation of benzofurans in a stoichiometric annulation reaction between stable pallada(II)cycles and hypervalent vinyl- and alkynyl(phenyl)iodonium salts

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Abstract

Stable pallada(II)cycles featuring Csp^2 -Pd and Csp^3 -Pd bonds reacted with vinyl- and alkynyl(phenyl)iodonium salts to generate two new geminal carbon-carbon bonds to the terminal carbon of the vinyl and alkynyl substituents providing benzofuran and dihydrobenzofuran heterocycles. The new annulation process was rationalized by the involvement of Pd(IV) intermediates arising via an initial oxidative addition of hypervalent iodonium electrophiles to the Pd(II) center. Reaction monitoring via low temperature 1H NMR spectroscopy was performed, and organopalladium(II) intermediates featuring a new Csp^2 - Csp^2 or Csp^2 - Csp bond were isolated and characterized, providing insights into the regiochemical course of the proposed mechanistic pathway.
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Keywords: Palladacycles; Iodonium salts; Annulation reactions; Heterocycles

1. Introduction

Palladium-catalyzed C-C bond-forming reactions involving hypervalent iodonium salts have become popular synthetic tools [1]. The traditional processes rely on catalytic cycles featuring palladium in oxidation states Pd(0) and Pd(II) [1]. However, recent developments have suggested that reactions involving Pd(IV) intermediates could give rise to synthetically attractive transformations [2]. Palladium(IV) complexes arising from palladium(II) complexes via oxidative addition of certain electrophiles have been previously detected spectroscopically, isolated, and in some cases characterized by X-ray crystallography [3]. Our most recent studies on the oxidation of stable pallada(II)cycles with allyl bromide electrophiles culminated in a successful isolation and full characterization including X-ray crystallographic data of a hexacoordinate Pd(IV) complex **II** featuring three carbon-palladium bonds

[4]. Furthermore, we have shown that the Pd(IV) complex **II** underwent a synthetically productive cascade process involving reductive elimination followed by an intramolecular Heck reaction to afford benzoxepine and benzopyran heterocycles via the formation of two new C-C bonds (Fig. 1) [4]. We envisioned that highly reactive vinyl- and alkynyl(phenyl)iodonium salts could also operate as oxidants for Pd(II) in pallada(II)cycles **I** generating a Pd(IV) intermediate **III**, which would undergo reductive elimination and subsequently the Heck reaction, giving rise to analogous annulation sequences (Fig. 2). The reports on systematic exploration of the reactivity of hypervalent iodonium electrophiles with palladium(II) complexes seeking new pathways for the carbon-carbon bond formation remain rare [5]. An impressive catalytic arylation reaction has been proposed to proceed via Pd(IV) complexes featuring two carbon-palladium bonds arising via oxidation of cyclopalladated Pd(II) complexes with aryl iodonium tetrafluoroborates [2b]. Studies in the stoichiometric mode yielded spectroscopic evidence for the formation of hexacoordinate Pd(IV) complexes with three carbon-palladium

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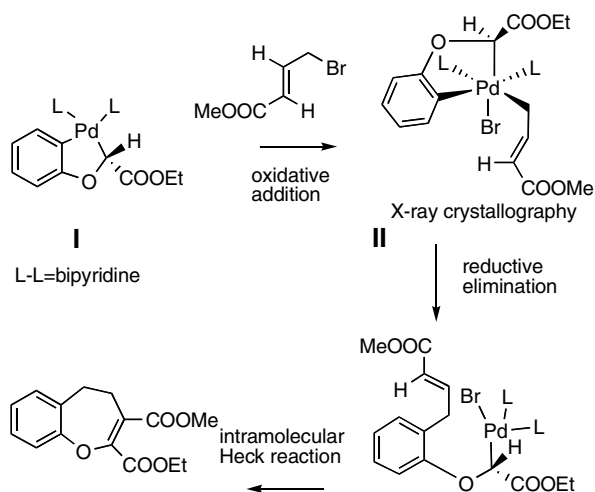


Fig. 1. Prior study reported by us (see Ref. [4]).

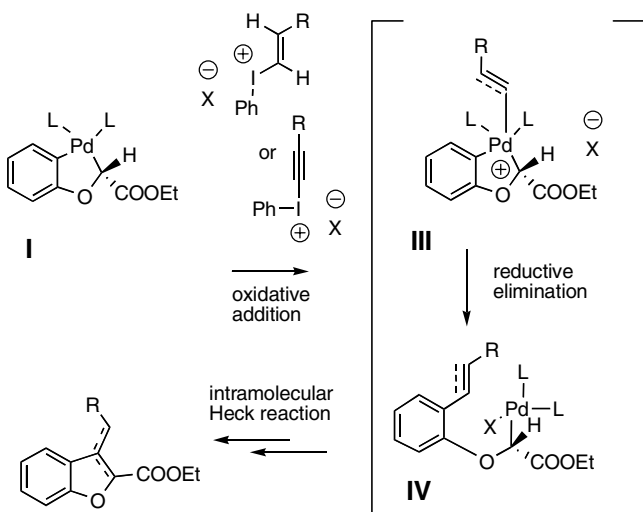


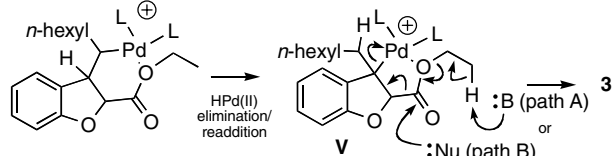
Fig. 2. Proposed annulation with iodine (III) salts.

bonds from the oxidation of pallada(II)cycles with aryl and alkynyl iodonium salts [5]. However, no synthetically productive carbon–carbon bond forming processes of these complexes have been described. Herein we report a study on the outcome of stoichiometric reactions between stable pallada(II)cycles featuring a Csp²–Pd bond and a Csp³–Pd bond with vinyl- and alkynyl(phenyl)iodonium salts. As anticipated according to our prior work [4] and literature reports [2,5], the treatment of palladacycles **I** with vinyl- or alkynyl(phenyl)iodonium salts afforded benzofuran or dihydrobenzofuran derivatives, realizing the formation of two new carbon–carbon bonds. Under controlled conditions, organopalladium(II) intermediates **IV** featuring a new Csp²–Csp² or Csp²–Csp bond were isolated and characterized, providing insights into the regiochemical course of the reductive elimination step of the proposed mechanistic pathway. Reaction monitoring via low temperature ¹H

NMR afforded spectroscopic evidence consistent with the involvement of the proposed Pd(IV) intermediate. Results reported herein provide a stoichiometric proof of concept for the application of vinyl- and alkynyl hypervalent iodonium salts in potentially synthetically useful cascade carbon–carbon bond-forming processes.

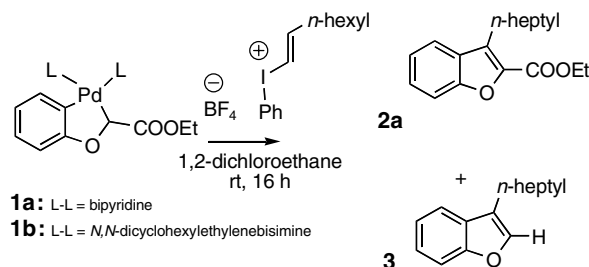
2. Results and discussion

Stable palladacycles **1a–b** (Table 1) featuring either bipyridine or *N,N'*-dicyclohexylethylenediamine ligands were prepared from the corresponding *o*-iodophenoxy acetates by established methods.[6] The treatment of palladacycle **1a** with 1-octenyl(phenyl)iodonium tetrafluoroborate at room temperature afforded benzofurans **2a** (48%) and **3** (9%) (entry 1, Table 1). Thus, the anticipated formation of two new C–C bonds to the carbon C1 of the 1-octenyl substituent indeed occurred, and was accompanied by aromatization via double-bond migration, as well as an unexpected decarboxylation leading to the benzofuran **3**. β -Hydride elimination followed by readdition of the H–Pd(II) complex [7], and a base- (path A) or nucleophile-induced (path B) fragmentation causing a formal elimination of the ester group activated by association with the cationic Pd(II) center in intermediate **V**, could account for the



decarboxylation [8]. We observed that careful solvent purification (treatment with basic alumina and CaH₂) was an important factor in limiting the extent of the decarboxylation. Notably, the sterically demanding bisimine ligand in palladacycle **1b** completely foiled the decarboxylation providing benzofuran **2a** as a single product in 74% yield (entry 2, Table 1). We reason that the process reported in

Table 1
Annulations with an unactivated vinyl iodine(III) salt



Entry	Substrate	Product (% yield)
1	1a	2a (48) ^a 3 (9) ^a
2	1b	2a (74) ^b Not formed

^a The solvent was dried over basic alumina and distilled from CaH₂.

^b The solvent was dried over molecular sieves.

Table 1 indeed proceeds according to the pathway outlined in Fig. 2. The reported ability of aryl- and alkynyl iodonium salts to oxidize pallada(II)cycles [5], as well as the competency of palladacycles **1** to generate Pd(IV) intermediates with allylic electrophiles [4] provide an indirect support for this proposition. Although a pathway invoking transmetallation between two Pd(II) centers has been proposed as a possible alternative to processes involving Pd(IV) intermediates, and was supported by recent computational studies [9], its operation in the stoichiometric process described herein appears unlikely since only one Pd(II) complex is present in appreciable concentration [10].

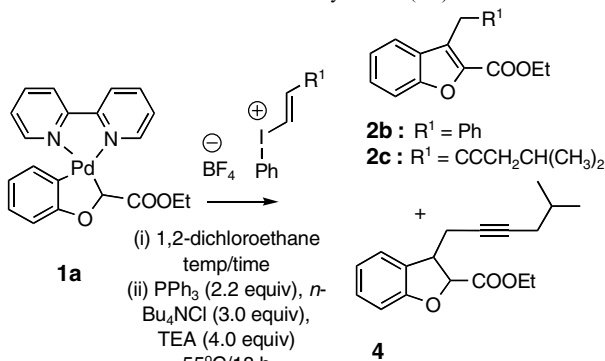
To assess the generality of the annulation protocol, functionalized vinyl(phenyl)iodonium tetrafluoroborates bearing phenyl or 4-methyl-1-pentyne-1-yl substituents R^1 (Table 2) were prepared [11] and reacted with palladacycle **1a**. Although the functionalized iodonium salts apparently oxidized the palladacycles even faster than their unfunctionalized counterparts, the anticipated heterocyclic products did not form. Aiming to facilitate the migratory insertion step (vide supra), appropriate additives were sought. Indeed, benzofuran **2b** (54% yield, entry 1, Table 2, $R^1 = \text{Ph}$) was obtained via a one pot/two-step protocol, employing elevated temperatures and PPh_3 (2.2 equiv.), TEA (4.0 equiv.) and $(n\text{-Bu})_4\text{NCl}$ (3.0 equiv.) in the second step [12]. The treatment of palladacycle **1a** with the alkyne-containing ($R^1 = 4\text{-methyl-1-pentyne-1-yl}$)vinyl(phenyl)iodonium tetrafluoroborate under these conditions afforded benzofuran **2c** (20%) along with a single diastereomer of a 2,3-dihydrobenzofuran **4** (35%) (entry 2, Table 2). Con-


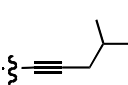
trol experiments on the reaction reported in entry 2 (Table 2) had shown that only traces, or no product formation occurred in the absence of either PPh_3 or TEA, whereas benzofuran **2c** (35%) was isolated exclusively from an experiment performed in the absence of $n\text{-Bu}_4\text{NCl}$. Conceivably, the (σ -propargyl)Pd(II) complex arising via migratory insertion is stabilized by interconversion to (σ -allenyl)Pd(II) species [13] allowing for protonolysis of the C–Pd bond to afford benzofuran **4**.

Finally, an alkynyl iodonium salt, 4-methyl-1-pentyne-1-yl(phenyl)iodonium tetrafluoroborate [11] was tested for its utility in the model annulation reaction with palladacycle **1a** (Table 3). However, a rapid consumption of the palladacycle **1a** presumably by oxidative addition was not followed by the formation of heterocyclic products. Seeking to activate the alkyne functionality towards carbometallation, Lewis acids (AlCl_3 or CuI) [14] were employed in the second stage of a one pot/two-step protocol (Table 3). Indeed, the anticipated benzofurans **2d** (76%, entry 1, Table 3) or **2d** (26%) and **5** (53%, entry 2, Table 3) were obtained using AlCl_3 and CuI additives, respectively.

At the completion of reactions with 1-*n*-octenyl(phenyl)iodonium tetrafluoroborates (Table 1), palladium was recovered as a black precipitate of Pd(0). In contrast, mixtures of poorly soluble complexes of palladium were isolated from reactions described in Tables 2 and 3. Although our efforts at isolating the proposed Pd(IV) complexes **III** were unsuccessful, palladium(II) complexes **6** and **7** presumably arising from Pd(IV) intermediates of type **III** (e.g. structure **8**) via reductive elimination were isolated in good yields (82% and 88%, respectively) and fully characterized (Scheme 1). The results indicate that reductive elimination from the presumed Pd(IV) complexes favors the formation of $\text{Csp}^2\text{-Csp}^2$ and $\text{Csp}^2\text{-Csp}$ bonds over $\text{Csp}^3\text{-Csp}^2$ and $\text{Csp}^3\text{-Csp}$ bond, respectively [15]. Aiming to provide spectroscopic evidence for the formation of the putative Pd(IV) intermediate **8**, in situ monitoring of the reaction between

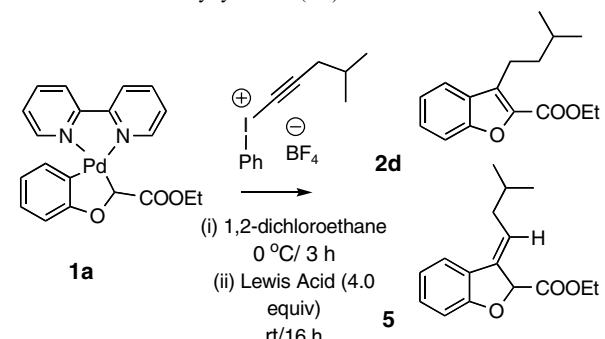
Table 2
Annulations with an functionalized vinyl iodine(III) salt



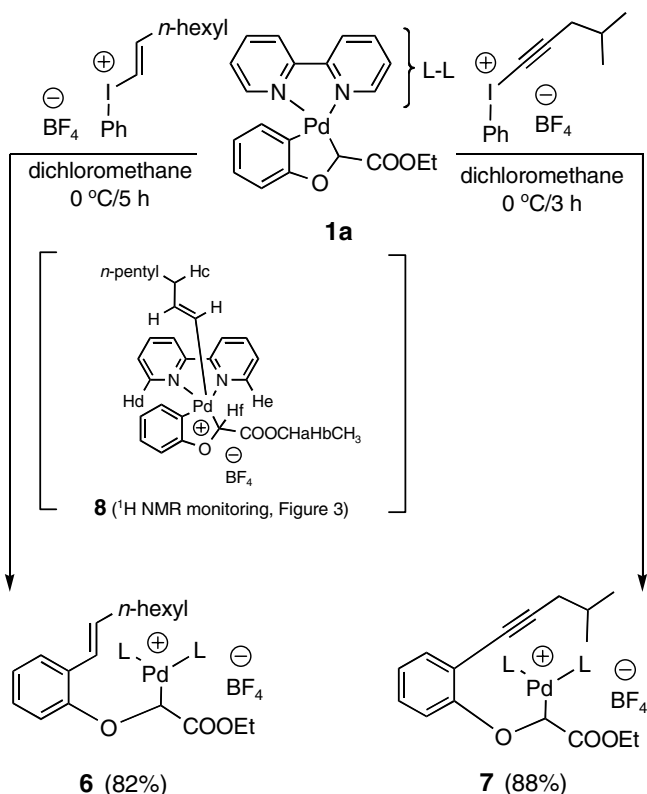
Entry	R^1	Temperature ($^{\circ}\text{C}$)/time (h)	Product (% yield)
1		25/2	2b (54)
2		25/8	2c (20) 4 (35) ^a

^a Inconclusive NOE analysis and J coupling data did not allow for an unequivocal assignment of the relative stereochemistry.

Table 3
Annulations with an alkynyl iodine(III) salt



Entry	Lewis acid	Product (% yield)
1	AlCl_3	2d (76)
2	CuI	2d (26) 5 (53)



Scheme 1. Isolation of palladium(II) complexes.

palladacycle **1a** and (*E*)-1-octenyl(phenyl)iodonium tetrafluoroborate in 1:1.1 molar ratio was performed utilizing low temperature ^1H NMR (400 MHz) spectroscopy [16]. Experiments conducted at $-10\text{ }^\circ\text{C}$ indicated an immediate formation of a 1:1 mixture of complex **6** with a new organopalladium intermediate distinct from the palladacycle **1a**. A complete clean conversion of the new intermediate, tentatively assigned the structure of organopalladium(IV) complex **8** (Scheme 1), into complex **6** occurred within 1 h at $-10\text{ }^\circ\text{C}$ [17]. Subsequently, the temperature for the reaction monitoring experiment was lowered to $-50\text{ }^\circ\text{C}$ (Fig. 3). Under these conditions, palladacycle **1a** (trace a, Fig. 3) was again immediately converted into an intermediate identical to the complex detected at $-10\text{ }^\circ\text{C}$, and distinct from the complex **6** (trace d, Fig. 3). The putative complex **8** proved to be stable in solution at temperatures -50 to $40\text{ }^\circ\text{C}$, and an ^1H NMR spectra of an essentially pure (contains phenyl iodide) [18] complex **8** was recorded (trace b, Fig. 3). The first signals indicating the conversion of complex **8** into the “open form” complex **6** were detected following the treatment of the reaction mixture for 10 min at $-30\text{ }^\circ\text{C}$ (trace c, Fig. 3) [16]. The proposed structure of the intermediate **8** is further supported by the assignments of the characteristic signals observed in ^1H NMR spectra of the intermediate (trace b in Fig. 3) to structure **8** in Scheme 1.

In conclusion, the mild reaction conditions permitting the initial C–C bond formation (Scheme 1) highlight the considerable potential of hypervalent iodine(III) reagents

in novel Pd-catalyzed cascade reactions. The stoichiometric model study described herein provides a conceptual guidance for future design of novel Pd-mediated annulation protocols.

3. Experimental

Unless otherwise indicated, all NMR data were collected at room temperature in CDCl_3 with internal CHCl_3 or SiMe_4 as the references (δ 7.26 ppm for ^1H and 77.00 ppm for ^{13}C in the case of CHCl_3 and 0.00 ppm for ^1H and ^{13}C in the case of TMS). IR spectra were measured as thin films on salt (NaCl) plates. Melting points are uncorrected and were taken in open capillary tubes. MS were measured under electrospray ionization (ES+) conditions and fast atom bombardment ionization (FAB) conditions. Analytical thin-layer chromatography (TLC) was carried out on commercial Merck silica gel 60 plates, 250 μm thickness, with fluorescent indicator (F-254) or stained with aqueous KMnO_4 solution. Column chromatography was performed with 32–63 μm silica gel (Sorbent).

4. Materials

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. 1,2-Dichloroethane, dichloromethane and benzene were kept over 3 Å (8–12 mesh) molecular sieves under an atmosphere of dry argon; other solvents were used as received. Unless otherwise specified, all reactions were carried out under an atmosphere of dry argon in oven-dried (at least 6 h at $140\text{ }^\circ\text{C}$) glassware. The preparation and characterization of palladacycles (**1a**, **1b**) was reported in our previous work [6]. Other materials were used as received from commercial suppliers. The vinyl- and alkynyl(phenyl) iodonium salts were prepared according to methods reported in the literature [11].

4.1. A representative procedure for the experiments reported in Table 1

Entry 2: Ethyl 3-*n*-heptyl-2-benzofurancarboxylate (**2a**). A solution of (*E*)-1-octenyl(phenyl)iodonium tetrafluoroborate (0.063 g, 0.15 mmol) in 1,2-dichloroethane (1.0 mL) was cannulated to a solution of palladacycle **1b** (0.056 g, 0.11 mmol) in 1,2-dichloroethane (2.0 mL). The orange solution was stirred for 16 h at r.t. The resulting black mixture was filtered over celite separating the Pd(0) precipitate, solvents were removed under reduced pressure, and the crude product was purified by preparative TLC over silica eluting with hexane:EtOAc (6:1) mixtures to afford benzofuran **2a** (0.023 g, 74%) as a colorless oil: R_f = 0.7 (silica gel, EtOAc/hexanes 1:6); IR (neat, cm^{-1}): 2956, 2927, 2856, 1712 (CO), 1595; ^1H NMR (CDCl_3 , 400 MHz) δ 7.58 (d, J = 6.2 Hz, 1H), 7.50 (d, J = 6.7 Hz, 1H), 7.38 (td, J = 5.8 Hz, J = 0.96 Hz, 1H), 7.21 (t, J = 6.4 Hz, 1H), 4.41 (q, J = 5.6 Hz, 2H), 3.01 (t, J = 6.2 Hz,

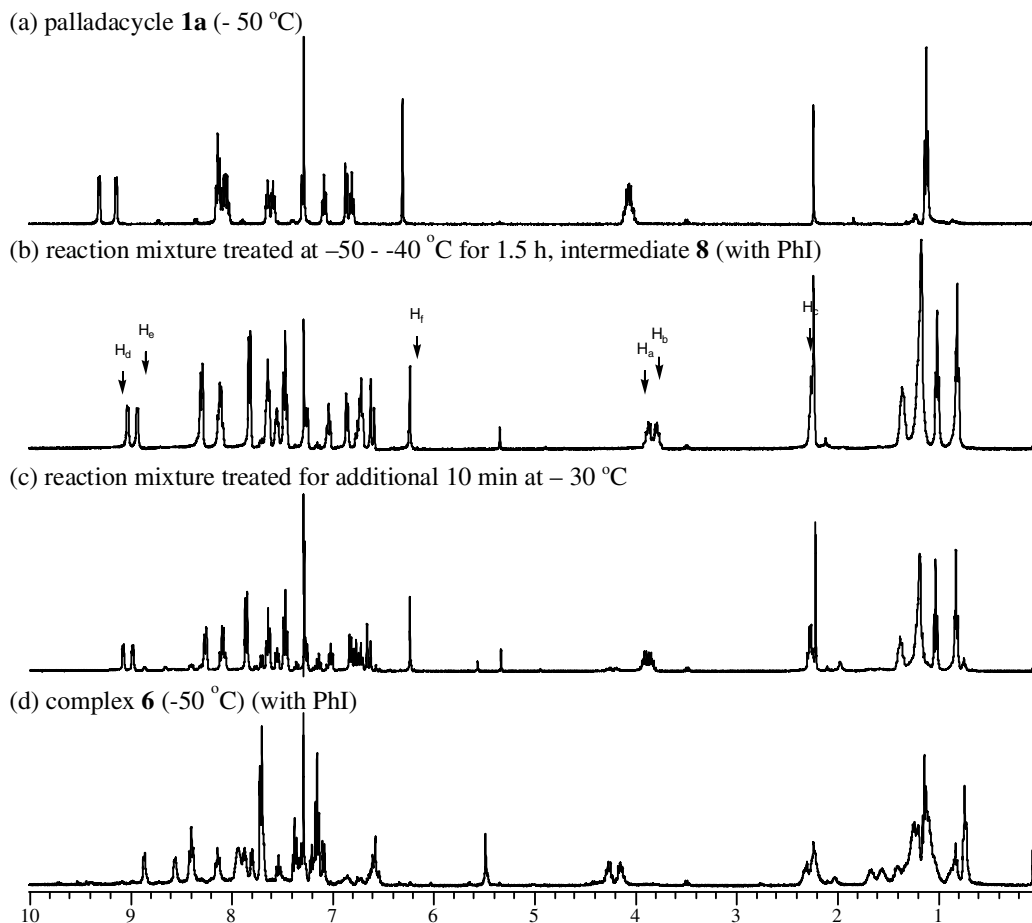


Fig. 3. Low temperature ^1H NMR (400 MHz, CDCl_3) monitoring of the reaction between palladacycle **1a** and (*E*)-1-octenyl(phenyl)iodonium tetrafluoroborate.

2H), 1.65 (p, $J = 5.9$ Hz, 2H), 1.41 (t, $J = 5.7$ Hz, 3H), 1.37–1.15 (m, 8H), 0.81 (t, $J = 5.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 159.4, 153.4, 139.6, 129.5, 127.5, 126.6, 122.0, 120.3, 111.3, 60.1, 30.9, 28.7, 28.3, 28.1, 23.2, 21.6, 13.4, 13.1; HRMS (ESI TOF) Calc. for $\text{C}_{18}\text{H}_{25}\text{O}_3$ [$\text{M} + \text{H}^+$]: 289.1804. Found: 289.1807.

4.2. A representative procedure for the experiments reported in Table 2

Entry 1: Ethyl 3-benzyl-2-benzofurancarboxylate (**2b**). To a solution of palladacycle **1a** (0.064 g, 0.145 mmol) in dichloroethane (2 mL) was added a solution of (*E*)-styryl(phenyl)iodonium tetrafluoroborate (0.083 g, 0.203 mmol) in dichloroethane (1 mL). The reaction mixture was stirred at rt for 2 h prior to the addition of *n*- Bu_4NCl (0.120 g, 0.435 mmol), PPh_3 (0.084 g, 0.32 mmol) and Et_3N (0.08 mL, 0.58 mmol). The resulting reddish-brown suspension was heated at 55 °C for 18 h. The reaction mixture was then cooled, filtered over celite, and the solvent was removed under reduced pressure to afford the crude product, which was purified by preparative TLC over silica, eluting with hexane:EtOAc (6:1) to afford benzopyran **2b** (0.020 g, 54%) as a colorless oil: $R_f = 0.55$ (silica

gel, EtOAc/hexanes 1:6); IR (neat, cm^{-1}): 3028, 2966, 1712 (CO), 1294, 1267; ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (d, $J = 6.7$ Hz, 1H), 7.42 (d, $J = 6.3$ Hz, 1H), 7.34 (td, $J = 4.9$ Hz, $J = 1.0$ Hz, 1H), 7.23–7.10 (m, 6H), 4.42 (s, 2H), 4.38 (q, $J = 5.6$ Hz, 2H), 1.31 (t, $J = 5.7$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 159.4, 153.5, 140.1, 137.9, 127.5 (2C), 127.4 (2C), 127.3, 127.1, 126.7, 125.3, 122.3, 120.7, 111.2, 60.3, 29.1, 13.4; HRMS (ESI TOF) Calc. for $\text{C}_{18}\text{H}_{17}\text{O}_3$ [$\text{M} + \text{H}^+$]: 281.1178. Found: 281.1184.

4.3. A representative procedure for the experiments reported in Table 3

Entry 1: Ethyl 3-isopentyl-2-benzofurancarboxylate (**2d**). To a solution of palladacycle **1a** (0.064 g, 0.145 mmol) in dichloroethane (3 mL) was added a solution of 4-methyl-1-pentyne-1-yl(phenyl)iodonium tetrafluoroborate (0.075 g, 0.203 mmol) in dichloroethane (3 mL) at 0 °C under argon. The solution immediately turned dark brown and was stirred at 0 °C for additional 3 h. Then, AlCl_3 (0.058 g, 0.435 mmol) was added, and the mixture was gradually warmed to rt and stirred for 16 h. The reaction mixture was filtered over celite, and solvent was evaporated under reduced pressure to afford the crude product, which was

purified by preparative TLC over silica eluting with hexane:EtOAc (6:1) to afford benzofuran **2d** (0.030 g, 76%) as a colorless oil: R_f = 0.60 (silica gel, EtOAc/hexanes 1:6); IR (neat, cm^{-1}): 2956, 2929, 1712 (CO), 1299, 1064, 1027; ^1H NMR (CDCl_3 , 400 MHz) δ 7.59 (d, J = 6.3 Hz, 1H), 7.48 (d, J = 6.7 Hz, 1H), 7.36 (td, J = 4.9 Hz, J = 0.96 Hz, 1H), 7.22 (td, J = 5.7 Hz, J = 0.5 Hz, 1H), 4.39 (q, J = 5.7 Hz, 2H), 3.01 (t, J = 6.5 Hz, 2H), 1.65–1.52 (m, 1H), 1.50–1.46 (m, 2H), 1.36 (t, J = 5.7 Hz, 3H), 0.92 (d, J = 5.2 Hz, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 159.4, 153.5, 139.4, 129.6, 127.4, 126.6, 122.0, 120.2, 111.3, 60.1, 37.9, 27.2, 21.4 (2C), 21.2, 13.4; HRMS (ESI TOF) Calc. for $\text{C}_{16}\text{H}_{21}\text{O}_3^+$ [$\text{M} + \text{H}^+$]: 261.1491. Found: 261.1484.

4.4. General procedure for the synthesis of palladium(II) complexes

{1-(Ethoxycarbonyl)-1-[2-(1-octene-1-yl)phenoxy]methyl} (N,N' -2,2'-dipyridyl)palladium tetrafluoroborate (**6**) and {1-(Ethoxycarbonyl)-1-[2-(4-methyl-1-pentyne-1-yl)phenoxy]methyl} (N,N' -2,2'-dipyridyl)palladium tetrafluoroborate (**7**) reported in Scheme 1. To a solution of palladacycle **1a** (0.050 g, 0.11 mmol) in dichloromethane (2 mL) at 0 °C was cannulated a solution of (*E*)-1-octenyl(phenyl)iodonium tetrafluoroborate (0.050 g, 0.12 mmol) or 4-methyl-1-pentyne-1-yl(phenyl)iodonium tetrafluoroborate (0.056 g, 0.15 mmol) in dichloromethane (1 mL). The yellow colored suspension was stirred at 0 °C for 3 or 5 h. The suspension was filtered over celite and the solid was washed with dichloromethane. The solvent was removed under reduced pressure to afford an orange oil, which was triturated with ether at –78 °C to afford complex **6** (0.058 g, 82%) or complex **7** (0.058 g, 88%) as orange or brown solids.

Analytical data for complex **6**: IR (neat, cm^{-1}): 3467, 2966, 1739 (CO), 1298, 1203, 1145; ^1H NMR (CDCl_3 , 400 MHz) δ 8.87 (br s, 2H), 8.52 (d, J = 8.0 Hz, 2H), 8.22 (t, J = 7.9 Hz, 2H), 7.70 (d, J = 6.1 Hz, 2H), 7.20 (t, J = 6.4 Hz, 2H), 7.16 (t, J = 6.4 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.78–6.73 (m, 1H), 6.54 (d, J = 15.0 Hz, 1H), 5.57 (s, 1H), 4.35–4.27 (m, 2H), 2.39–2.22 (m, 2H), 1.78–1.63 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H), 1.24–1.18 (m, 6H), 0.81 (t, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 171.4, 156.7 (2C), 150.0 (2C), 142.4, 141.5, 130.5, 130.4, 128.6, 127.4 (2C), 126.4, 125.4, 124.2 (2C), 120.4, 112.3, 104.2, 93.1, 61.7, 34.5, 31.4, 30.1, 29.1, 22.6, 14.1, 13.9; HRMS (FAB) Calc. for $\text{C}_{28}\text{H}_{33}\text{N}_2\text{O}_3\text{Pd}^+$ [M^+]: 551.1526. Found: 551.1541.

Analytical data for complex **7**: IR (neat, cm^{-1}): 2954, 1737 (CO), 1622, 1610; ^1H NMR (CDCl_3 , 400 MHz) δ 8.54–8.49 (m, 3H), 8.45 (d, J = 6.0 Hz, 1H), 8.30 (td, J = 7.9 Hz, J = 1.4 Hz, 1H), 8.22 (td, J = 7.9 Hz, J = 1.6 Hz, 1H), 7.75 (td, J = 5.3 Hz, J = 0.9 Hz, 1H), 7.64 (td, J = 5.7 Hz, J = 1.3 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.18 (t, J = 7.1 Hz, 1H), 7.01 (t, J = 6.8 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.50 (s, 1H), 4.84–4.78 (m, 1H), 4.73–4.64 (m, 1H), 2.71 (dd,

J = 6.8 Hz, J = 6.4 Hz, 1H), 2.30 (dd, J = 6.8 Hz, J = 6.5 Hz, 1H), 2.21–2.14 (m, 1H), 1.53 (t, J = 7.1 Hz, 3H), 1.14 (d, J = 6.5 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 182.3, 163.5, 156.7, 152.9, 152.5, 150.6, 148.9, 141.4, 141.1, 129.8, 128.9, 128.4, 127.7, 127.6, 124.5, 123.5, 123.3, 122.0, 110.8, 85.3, 68.2, 45.3, 29.5, 23.8, 22.9, 13.9. HRMS (FAB) Calc. for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_3\text{Pd}^+$ [M^+]: 521.1056. Found: 521.1079.

Acknowledgements

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Appendix A. Supplementary material

Complete description of the synthesis and characterization of all the compounds reported in the text above can be found in the online version, at [doi:10.1016/j.jorganchem.2007.11.034](https://doi.org/10.1016/j.jorganchem.2007.11.034).

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