Palladium-Catalyzed Oxidative Coupling of 2-Alkylfurans with Olefins through C−H Activation: Synthesis of Difurylalkanes

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The course of the palladium-catalyzed coupling of 2-alkylfurans with olefins through C−H activation is influenced by the nature of the solvent. At room temperature, with acetic acid as solvent and benzoquinone as oxidant, the usual Heck product, 2-cinnamyl-5-methylfuran, is obtained in low yield. The use of a AcOH/CH_3CN mixture as solvent induced the formation of difurylalkanes in fair to high yields. Allylarenes and styrenes led to the formation of β,β-difurylalkanes as major compounds, while acrylates afforded selectively β,β-difuryl esters. Mechanism studies have shown that these transformations do not occur through the processes usually involved in the formation of diarylalkanes. According to ESI-MS studies and labeling experiments, two consecutive C−H activations of 2-alkylfurans by Pd(II) are followed by an insertion of the alkene, a migration of a furan ring involving β-elimination/insertion steps, and finally a reductive elimination reaction.

Introduction

The direct functionalization of a C−H bond is of high interest, and there is a growing demand for the development of catalytic procedures under mild and operationally simple conditions.[1] In this context, the intermolecular oxidative coupling of arenes with olefins has great potential. Fujiwara et al. have opened a route using palladium salts as catalysts and cupric acetate or silver acetate together with oxygen or air as reoxidants.[2] Arenes were used in excess, and the reactions were essentially performed at reflux of ArH/AcOH mixtures. The development of this reaction has focused on the use of milder conditions and oxygen as reoxidant.[3] Recently, the heterogenization of the catalyst has been performed using polymers or zeolites.[4] An alternative process, using a catalytic amount of benzoquinone as reoxidant and its electrochemical recycling, has been described.[5] The C−H functionalization of acid-sensitive arenes has been reported.[4b,6] Among these arenes, furans have received less attention,[3a] probably because of their high sensitivity to protic conditions. The use of olefins bearing an electron-withdrawing group,[7] such as acrylate, is generally required for their oxidative cross-coupling with furans and other arenes. In the course of the study on the oxidative Heck coupling of furans with less activated alkenes, we have observed a surprising effect of the solvent on the course of the reaction. Indeed, difurylalkanes can be obtained. Such compounds have led to various applications in organic synthesis,[8] such as the cascade opening/recyclization reactions of ortho-substituted phenyldifurylmethanes leading to heterocyclic compounds,[9] the synthesis of benzo[*b*]furan,[10] and the asymmetric synthesis of polycyclic polypropanoates through a double Diels−Alder addition.[11] Difurylalkanes are also important intermediates in the synthesis of various heterocyclic

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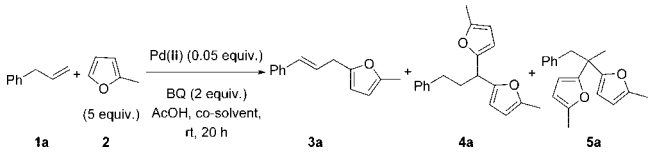
Table 1. Effect of the Cosolvent on the Coupling of 1a with 2[a]



entry	Pd(II)	cosolvent	conv., %[b]	**3a**:**4a**:**5a**, %[c]	yield, %[d]
1	$Pd(OAc)_2$		10	100:0:0	5
2	$Pd(OAc)_2$	CH_3CN	100	0:50:50	71
3	$Pd(OCOCF_3)_2$	CH_3CN	100	0:15:85	94
4	$Pd(OCOCF_3)_2$	$(CH_3)_2CO$	100	44:25:31	

[a] Conditions: **1a** (1.0 mmol), **2** (5.0 mmol), Pd(II) (0.05 mmol), BQ (2.0 mmol), AcOH (0.5 mL), cosolvent (3 mL), room temperature, 20 h. [b] Conversion of **1a**. [c] Ratio determined by ^{1}H NMR on isolated products. [d] Isolated yield.

macromolecules.[12] Herein, we describe our results and suggest a mechanism pathway based on labeling experiments and ESI-MS analysis.

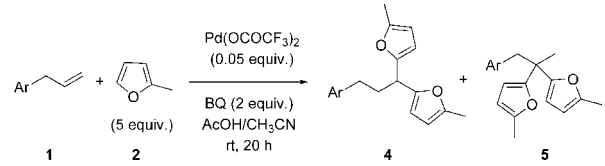
Results and Discussion

Synthesis of Difurylalkanes. Preliminary experiments were carried out using allylbenzene (**1a**), an excess of 2-methylfuran (**2**), $Pd(OAc)_2$ as the catalyst, benzoquinone (BQ) as the oxidant, and AcOH as the solvent. Conversion was low (10%), and a Heck-type product, 2-cinnamyl-5-methylfuran (**3a**), was isolated in 5% yield (Table 1, entry 1). Since precipitation of palladium(0) was observed, we have explored the use of coordinating cosolvents. To our surprise, a AcOH/CH_3CN mixture changed the course of the reaction. Indeed, bis-addition of **2** to **1a** occurred to afford a mixture of **4a** and **5a** (entry 2). Other palladium catalysts were then tested. $Pd(OCOCF_3)_2$ increased the yield to 94% and improved the selectivity in favor of the most substituted compound, **5a** (entry 3), while chlorinated palladium salts such as $PdCl_2$ and $PdCl_2(MeCN)_2$ afforded only 1-((*E*)-prop-1-enyl)benzene (**1b**; 72 and 75% conversion, respectively). The use of $Pd(OCOCF_3)_2$ with a less coordinating cosolvent, such as acetone, led to a mixture of **3a**, **4a**, and **5a** (entry 4). The coupling of **1a** with **2** in AcOH/CH_3CN, in the absence of benzoquinone or on reducing the amount of **2** to 1.0 equiv, led to mixtures of **1b**, **4a**, and **5a** (54:32:14 and 55:28:17, respectively).

To our knowledge, such a double addition of a furan to a C=C bond has not been reported before. Indeed, the oxidative coupling of furans and acrylates has only led to the formation of oxidative Heck products.[3a] The coupling of benzene with olefins afforded the expected Heck products, and when the reaction time was prolonged, double coupling products were observed.[3f,g] The formation of β,β-diaryl ketones and β,β-diaryl aldehydes has been reported,[13] but these reactions were performed using aryl iodides and under reductive conditions.[14]

The reactivity of other allylarenes has been explored under the experimental conditions of entry 3 of Table 1 (namely, afterward, standard conditions). A mixture of **4** and **5** was obtained from **1c**−**e**, **5** being the major product from **1c**,**d**, while **1e** led mainly to **4e**(Table 2). Careful analysis of GC/MS and ^{1}H NMR spectra shows the absence of isomers substituted at the benzylic position.

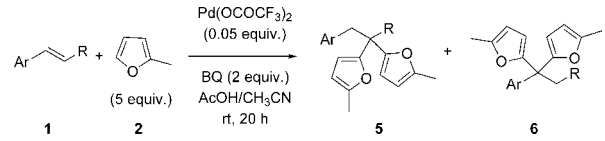
Table 2. Coupling of Allylarenes with 2[a]



entry	**1**, Ar	**4**:**5**, %[b]	yield, %[c]
1	**1c**, *p*-$MeOC_6H_4$	**4c**:**5c**, 40:60	52
2	**1d**, *p*,*m*-$(MeO)_2C_6H_3$	**4d**:**5d**, 40:60	62
3	**1e**, C_6F_5	**4e**:**5e**, 75:25	76

[a] Conditions: **1** (1.0 mmol), **2** (5.0 mmol), $Pd(OCOCF_3)_2$ (0.05 mmol), BQ (2.0 mmol), AcOH (0.5 mL), CH_3CN (3 mL), room temperature, 20 h, 100% conversion. [b] Ratio determined by ^{1}H NMR on isolated products. [c] Isolated yield.

Table 3. Coupling of Styrenes with 2[a]



entry	**1**, Ar, R	**5**:**6**, %[b]	Yield, %[c]
1	**1f**, Ph, H	**5f**:**6f**, 85:15	60
2	**1g**, *p*-MeC_6H_4, H	**5g**:**6g**, 75:25	50
3	**1h**, *p*-ClC_6H_4, H	**5h**:**6h**, 83:17	62
4	**1i**, *m*-ClC_6H_4, H	**5i**:**6i**, 89:11	62
5[d]	**1j**, 2-naphthyl, H	**5j**:**6j**, 84:16	30
6	**1k**, *p*-BrC_6H_4, H	**5k**:**6k**, 87:13	60
7	**1b**, Ph, Me	**5a**:**6a**, 100:0	70
8	**1l**, Ph, Et	**5l**:**6l**, 100:0	65
9	**1m**, *p*-$MeOC_6H_4$, Me	**5c**:**6c**, 85:15	74
10	**1n**, *o*-$MeOC_6H_4$, Me	**5n**:**6n**, 83:17	75
11	**1o**, *o*-$BnOC_6H_4$, Me	**5o**:**6o**, 80:20	41

[a] Conditions: **1** (1.0 mmol), **2** (5.0 mmol), $Pd(OCOCF_3)_2$ (0.05 mmol), BQ (2.0 mmol), AcOH (0.5 mL), CH_3CN (3 mL), room temperature, 20 h, 100% conversion. [b] Ratio determined by ^{1}H NMR on isolated products. Traces of **3** were sometimes detected by GC/MS analysis. [c] Isolated yield. [d] Reaction performed at 50 °C.

The reaction of styrenes with **2** under standard conditions also afforded difuryl compounds (Table 3). A mixture of **5** and **6** has usually been isolated, with **5** as the major compound. β-Substituted styrenes **1b**,**l** afforded selectively **5a**,**l** (entries 7 and 8), but the substitution of the aryl ring by a methoxy or a benzyloxy group decreased the selectivity (entries 9−11).

Acrylates **1p**,**q** reacted with **2** under standard conditions, affording β,β-difuryl esters **5p**,**q** in 71% and 57% yields, respectively (eq 1). Coupling of 2-ethylfuran with **1a**,**f** led to **4r/5r** (25/75) and **5s/6s** (90/10) in 60% and 51% yields, respectively (eqs 2 and 3).

We have attempted to use unactivated alkenes such as 1-decene and 7-tetradecene. Full conversion of the alkenes was observed, but GC/MS analysis has shown the presence of complex mixtures of difurylalkanes.

These above transformations seem to be specific to 2-alkylfurans, since no reaction of **1a** with 3-methylfuran and 2,5-

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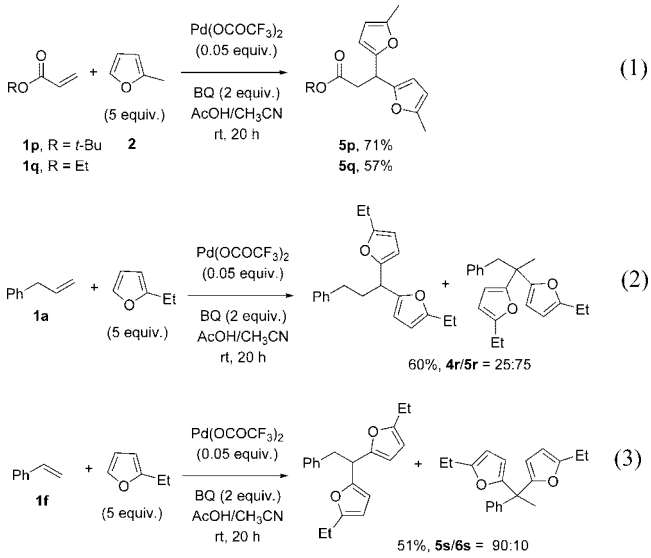
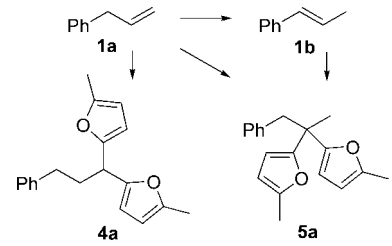


dimethylfuran occurred, while the use of furan led to a mixture of products containing only traces of the expected difurylalkane derivatives. The reaction of **1a** with 1,3-dimethoxybenzene gave small amounts of the Heck product, while with pyrrole and N-protected pyrrole (benzyl and tosyl as protecting group), no dipyrrolylalkanes or Heck products were isolated.

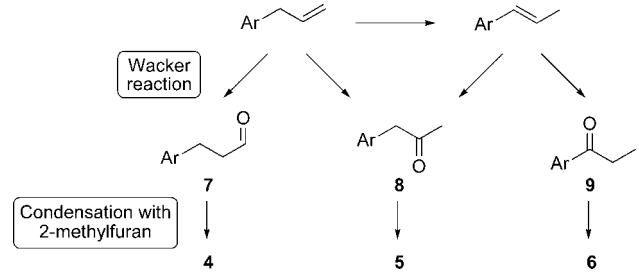
Mechanistic Studies. According to the results gathered in Table 1, the regioselectivity depends on the nature of the catalyst (Table 1, entries 2 and 3). We suspected that the differences induced by $Pd(OAc)_2$ and $Pd(OCOCF_3)_2$ could be connected to the faster isomerization of **1a** into **1b** with $Pd(OCOCF_3)_2$.[15] As shown in Scheme 1, **1a** could lead to **4a** and **5a**, while **1b** would exclusively afford **5a**. This encouraged us to study the isomerization of **1a** in an $AcOH/CH_3CN$ mixture (1/6), at room temperature, using the two Pd(II) salts above (0.05 equiv) and BQ (2 equiv). After 30 min, **1b** was produced in 32% and 50% yields with $Pd(OAc)_2$ and $Pd(OCOCF_3)_2$, respectively. The faster isomerization mediated by $Pd(OCOCF_3)_2$ agrees with the above hypothesis. However, substituted allylarenes **1c**,**e**, which provided **5c** and **4e**, respectively, as the major compounds (Table 2, entries 1 and 3), have shown slower or no isomerization under similar $Pd(OCOCF_3)_2$ catalysis (0% and 10% conversion, respectively, after 30 min). This suggests that the electronic properties of the alkene also have an impact on the regioselectivity of the coupling reaction.

Since difurylalkanes are usually obtained by the acid-catalyzed condensation of carbonyls with furans,[8,16] we have hypothesized that a palladium-catalyzed Wacker reaction could occur in the first step, due to the presence of residual water in the solvents; Pd(II) or acetic acid would then act, in the second step, as Lewis or Brønsted acid catalysts. The Wacker reaction of allylarene could lead to aldehyde **7** and ketone **8** (Scheme 2). The Pd(II)-catalyzed oxidation of alkenes usually follows the Markovnikov rule and leads to ketones. The formation of aldehydes is generally restricted to substrates containing a

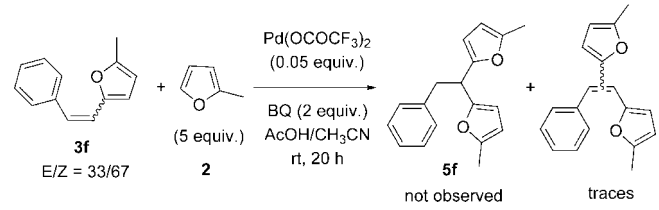
Scheme 1



Scheme 2



Scheme 3



second coordinating center.[17] Therefore, **7** and consequently **4** should be obtained as the minor compound under our conditions. This was observed from **1a**,**c**,**d**, but **1e** afforded **4e** as the main compound. We have observed that **1a** is isomerized during the course of the reaction into **1b**. A Wacker reaction from **1b** would produce ketones **8a** and **9a**[18] and consequently products **5a** and **6a**, but **6a** was not obtained from **1b**.

The Wacker hypothesis was fully discarded, since **5a** was not produced from the reaction of benzyl methyl ketone (**8a**) with **2** under the standard conditions.

Another hypothesis, the usual oxidative Heck coupling (for an example, **3f** would be obtained from **1f**), followed by a hydroarylation, was also discarded. Indeed, the reaction of **3f**[19] with **2** under our standard conditions did not produce **5f**, only traces of bis(5-methyl-2-furyl)styrene derived from a vinylic arylation was detected by GC/MS (Scheme 3).

Fujiwara et al. have proposed that the oxidative Heck reaction involves the Pd(II) activation of the arene, leading to a σ-aryl−Pd(II) complex that reacts with the olefin.[2] We have envisaged that the first C−H activation of **2** leads to the solvated species **A** and that a second C−H activation (Scheme 4, pathway a) could compete with the insertion of the olefin (pathway b).

2-Methylfuran (**2**) is more nucleophilic than alkenes **1**.[20] Consequently, the exchange from **A** between the ligated solvent and a C=C bond will be more effective by path a than by path b. A low-coordinating solvent system would decrease the

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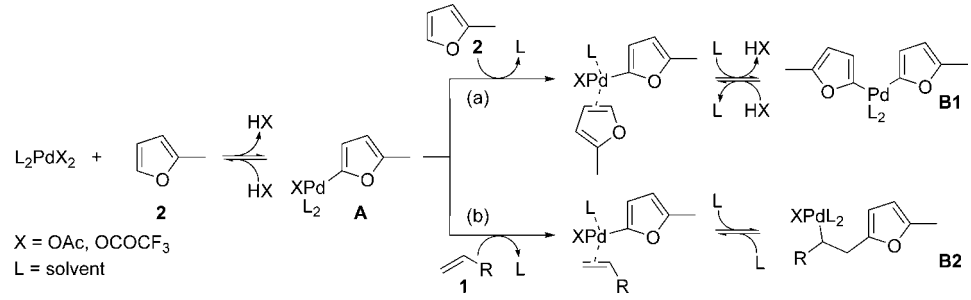
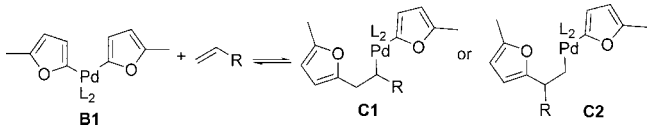
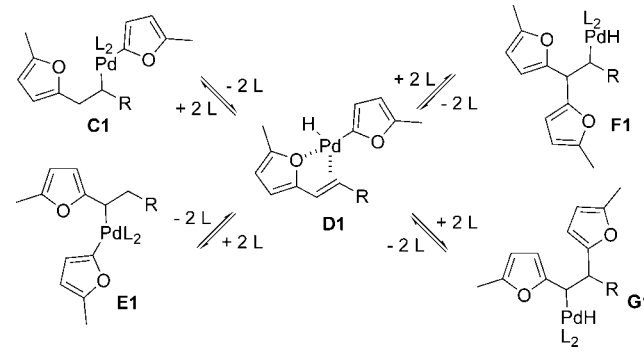
Scheme 4



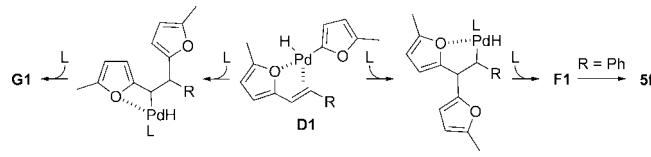
Scheme 5



Scheme 6

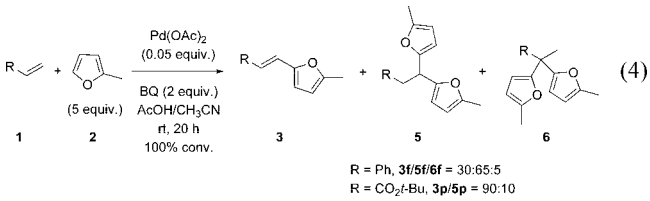


Scheme 7



differentiation between both pathways. We have indeed observed that **1a**, in acetonitrile, led exclusively to the formation of the difuryl products **4a** and **5a**, while in acetone **3a** is obtained as well (Table 1, entries 3 and 4).

As the metalation of arenes is faster with $Pd(OCOCF_3)_2$ than with $Pd(OAc)_2$,[21] the former will induce more efficiently the two successive C−H activations (path a). Pathway b would be preferred with $Pd(OAc)_2$ and with activated alkenes that cause easier insertion reactions. This led us to examine $Pd(OAc)_2$ as catalyst with styrene (**1f**) and *tert*-butyl acrylate (**1p**) (eq 4). The results have shown that the formation of **3** (pathway b) followed the tendency of **1** to perform an insertion step.[22] This is in agreement with the previous $Pd(OAc)_2$-catalyzed reaction of allylbenzene that, in $AcOH/CH_3CN$, did not produce the oxidative Heck compound (Table 1, entry 2).[22b] Pathways a and b are therefore in competition, and the nature of both solvent and catalyst has a strong influence on the course of the reaction.



(4)

The next question focused on the regioselectivity of the furan addition to the same carbon atom. Intermediate **B1** (Scheme 4) would lead to the formation of Pd(0) and 5,5′-dimethyl-2,2′-bifuran by reductive elimination or to intermediates **C1/C2** by insertion of the alkene (Scheme 5). 5,5′-Dimethyl-2,2′-bifuran was not observed under our standard conditions (Tables 1–3), even in the absence of an alkene, but ESI-MS analysis has shown the presence of clusters associated with the protonated species $[\mathbf{B1}\text{-}2L + H]^+$, $[\mathbf{B1}\text{-}L + H]^+$, and $[\mathbf{B1} + H]^+$ (L = CH_3CN) (vide infra). This result suggests that elimination reactions are prevented under our conditions and consolidates the **C1/C2** hypothesis.

As the reductive elimination step does not occur from **B1**, we have suspected a similar behavior for **C**. We have envisaged a β-elimination leading to **D1** (Scheme 6).[23] After such a transformation, PdH is usually coordinated to the C=C bond,[24] the decomplexation leading here to the Heck product **3**. Although this process should be facilitated by coordinating solvents, the results have shown that **3** is not produced under standard conditions (Table 1). When PdH is not quickly scavenged by a base, its readdition to either extremity of the double bond may occur.[24] Consequently, **D1** could evolve to **C1** or **E1** (Scheme 6). Another possibility is the insertion of the C=C bond into the Pd−furanyl bond that yields **F1** or **G1**. This insertion is unusual but affords palladium−hydride species that are more susceptible in evolving to products via elimination or protonolysis.[25]

From **D1**, the ligation of the palladium atom by the oxygen atom of the furan ring would stabilize a five-membered palladacycle intermediate more than a four-membered species (Scheme 7). In the case of styrene (**1f**), **F1** would lead to **5f**: i.e., the main isolated product (Table 3, entry 1). A similar mechanism from **C2** would give the minor compound **6f**. Acrylates would only produce intermediates **C1**.

The regiodiscrimination of the overall process should occur during the insertion step of the alkene into **B1** (Scheme 5) and

(21) It has been proposed that metalation of an aromatic C−H bond occurs more quickly with the highly electrophilic $Pd(OCOCF_3)_2$ than with $Pd(OAc)_2$.[3c]

(22) Acrylates are known to undergo a faster insertion process than styrenes; see: (a) Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896–6901. The efficiency of the Heck reaction of vinyl bromides with alkenes, in the presence of tetraphosphine/Pd catalyst, follow the order *n*-butyl acrylates > styrene (**1f**) > allylbenzene (**1a**); see: (b) Berthiol, F.; Doucet, H.; Santelli, M. *Synlett* **2003**, 841–844.

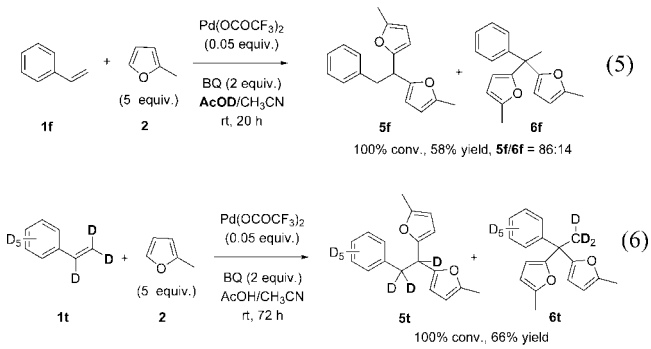
(23) β-Hydride elimination is one of the major decomposition pathways for metal alkyl complexes: Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994.

(24) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009–3066.

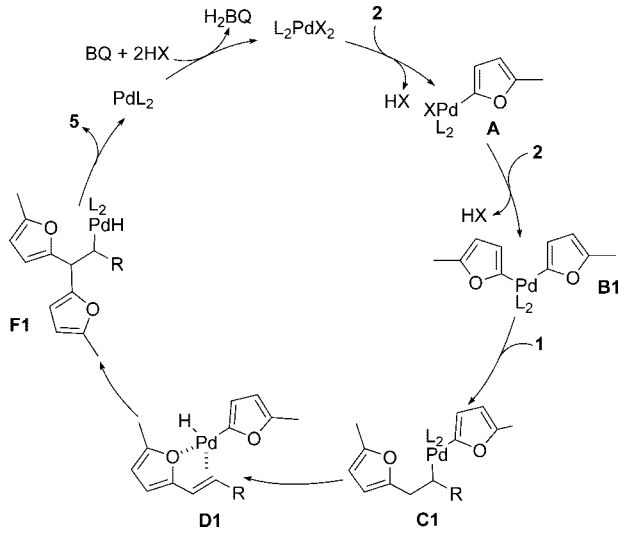
(25) Reductive eliminations occur faster with metal hydrides than with metal alkyls.[23].

would follow the tendency observed in the classical Heck reactions: acrylates and monosubstituted alkenes react rather at the terminal than the internal position.[24]

Labeling experiments were then performed. The absence of deuterium in the ethane chain of the products obtained from the coupling of **1f** with **2** in AcOD (eq 5) shows that there is no formation of products via protonolysis of **F1**. The reaction of styrene-d_8 (**1t**) with **2** led to the formation of deuteriated adducts **5t** and **6t** (eq 6). The presence of three deuteriums on the ethane moiety implies the effective deuterium shift during the course of the reaction. These results led us to propose the catalytic cycle shown in Scheme 8 for the formation of **5**.



Scheme 8



This mechanism was confirmed using mass spectroscopy techniques. Indeed, ESI-MS and the tandem version ESI-MS (/MS) are well adapted to the observation of short-lived molecular ions issued from metallocatalyzed reactions.[26] The identification of the detected species is aided by comparison between the observed and calculated isotope distribution patterns. Because palladium displays six isotopes, the ions containing this atom should be mass-detected as clusters of isotopomeric ions centered on the most abundant isotope: i.e., 106. Proposed species were characterized by high-resolution mass spectroscopy (HRMS). ESI-MS(/MS) fragmentation via collision-induced dissociation (CID) was performed on all clusters but was not significant for low-intensity signals.

The ESI(+)-MS spectrum obtained from the crude reaction of styrene (**1f**) with **2** (Table 3, entry 1) after 15 min, showed various clusters corresponding to the characteristic isotopic distribution pattern of monocharged cationic palladium complexes (Figure 1).

Clusters at *m/z* 186.9, 268.9, and 310.0 were attributed to the species $[\mathbf{A}\text{-2L-X}]^+$, $[\mathbf{B1}\text{-2L} + \text{H}]^+$, and $[\mathbf{B1}\text{-L} + \text{H}]^+$ (L = CH_3CN), respectively, showing that two consecutive C−H activations of **2** occurred. ESI-MS(/MS) of the cluster at *m/z* 268.9 has shown the formation of carbonyl−Pd species at *m/z* 135.1 and 163.1 (see Figure S1 in the Supporting Information). EI mass spectra of furans are usually governed by loss of formyl groups,[27] and CO has been observed during the decomposition of furan on palladium surfaces.[28] The cluster at *m/z* 163.1 could also be associated with the loss of [Pd], but this transformation should occur through a reductive elimination. ESI-MS(/MS) of the cluster at *m/z* 310.0 has shown the loss of CH_3CN under 5 eV CID, as expected by the relative weakness of the Pd−L bond (Figure S2, Supporting Information). A cluster at *m/z* 351.0 (Figure 1) was attributed to $[\mathbf{B1} + \text{H}]^+$ and confirmed by HRMS; however, the intensity of the signal was too low to perform an ESI-MS(/MS) analysis. Clusters at *m/z* 291.0 and 332.0 (Figure 1) were assigned to $[\mathbf{C1}\text{-2L-}C_5H_5O]^+$ and the acetonitrile adduct $[\mathbf{C1}\text{-L-}C_5H_5O]^+$.[29] ESI-MS(/MS) of the cluster at *m/z* 291.0 has shown the loss of $[C_5H_5O]$ and [Pd] (Figure S3, Supporting Information). Cleavage of the C−furanyl bond occurred on polyfurylarylmethanes in protic media,[8] and the loss of a "sole" Pd atom has been observed in certain cases.[26e,30] ESI-MS(/MS) of the cluster at *m/z* 332.0 has shown the loss of CH_3CN under 4 eV CID (Figure S4, Supporting Information). Clusters at *m/z* 291.0 and 332.0 (Figure 1) could correspond to the coordinated complexes $[\mathbf{1f} + \text{A-2L-X}]^+$ and $[\mathbf{1f} + \text{A-L-X}]^+$, but ESI-MS(/MS) performed under 4 and 10 eV CID did not show the loss of coordinated **1f**.

The cluster at *m/z* 371.0 (Figure 1) could be attributed to the species $[\mathbf{C1}\text{-2L-H}]^+$, $[\mathbf{D1}\text{-H}]^+$, and $[\mathbf{F1}\text{-2L-H}]^+$. The loss of a hydrogen atom is, however, easier from **D1** and **F1** than from **C1**. ESI-MS(/MS) using low CID energy did not show the loss of $[HPdC_5H_5O]$, eliminating **D1** as a possible intermediate (Figure S5, Supporting Information). Under higher energy, the loss of $[C_5H_5O]$ and $[C_3H_4]$ has been observed. The loss of $[C_3H_4]$ is unusual in substituted furans; however, the proximity of two furyl rings could promote rearrangement reactions.[31] The acetonitrile adducts $[\mathbf{F1}\text{-L-H}]^+$ and $[\mathbf{F1}\text{-H}]^+$ were observed at *m/z* 412.0 and 453.0 (Figure 1). The ESI-MS(/MS) spectra of these clusters have shown the loss of one or two CH_3CN groups under 5 eV CID (Figures S6 and S7, Supporting Information).

At least, clusters at *m/z* 211.0 and 252.0 (Figure 1) were attributed to $[\mathbf{1f} + \text{Pd} + \text{H}]^+$ and $[\mathbf{1f} + \text{Pd} + CH_3CN + \text{H}]^+$.

(26) Recent references: (a) Enquist, P.-A.; Nilsson, P.; Sjöberg, P.; Larhed, M. *J. Org. Chem.* **2006**, *71*, 8779–8786. (b) Thiery, E.; Chevrin, C.; Le Bras, J.; Harakat, D.; Muzart, J. *J. Org. Chem.* **2007**, *72*, 1859–1862. (c) Chevrin, C.; Le Bras, J.; Roglans, A.; Harakat, D.; Muzart, J. *New J. Chem.* **2007**, *31*, 121–126. (d) Markert, C.; Neuburger, M.; Kuliche, K.; Meuwly, M.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5892–5895. (e) Taccardi, N.; Paolillo, R.; Gallo, V.; Mastrorilli, P.; Nobile, C. F.; Räisänen, M.; Repo, T. *Eur. J. Inorg. Chem.* **2007**, 4645–4652. (f) Santos, L. S.; Rosso, G. B.; Pilli, R. A.; Eberlin, M. *J. Org. Chem.* **2007**, *72*, 5809–5812. (g) DaSilveira Neto, B. A.; Alves, M. B.; Lapis, A. A. M.; Nachtigall, F. M.; Eberlin, M. N.; Dupont, J.; Suarez, P. A. Z. *J. Catal.* **2007**, *249*, 154–161. (h) Masllorens, J.; González, I.; Roglans, A. *Eur. J. Org. Chem.* **2007**, 158–166. (i) Santos, L. S. *Eur. J. Org. Chem.* **2008**, 235–253. (j) Svennebring, A.; Sjöberg, P. J. R.; Larhed, M.; Nilsson, P. *Tetrahedron* **2008**, *64*, 1808–1812.

(27) Gross, J. H. *Mass Spectrometry: A Textbook*; Springer-Verlag: Berlin, Heidelberg, 2004.

(28) Caldwell, T. E.; Abdelrehim, I. M.; Land, D. P. *J. Am. Chem. Soc.* **1996**, *118*, 907–908.

(29) These clusters could also be associated with the species **E1**.

(30) Tomazela, D. M.; Gozzo, F. C.; Ebeling, G.; Livotto, P. R.; Eberlin, M. N.; Dupont, J. *Inorg. Chim. Acta* **2004**, *357*, 2349–2357.

(31) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day: San Fransisco, 1967.

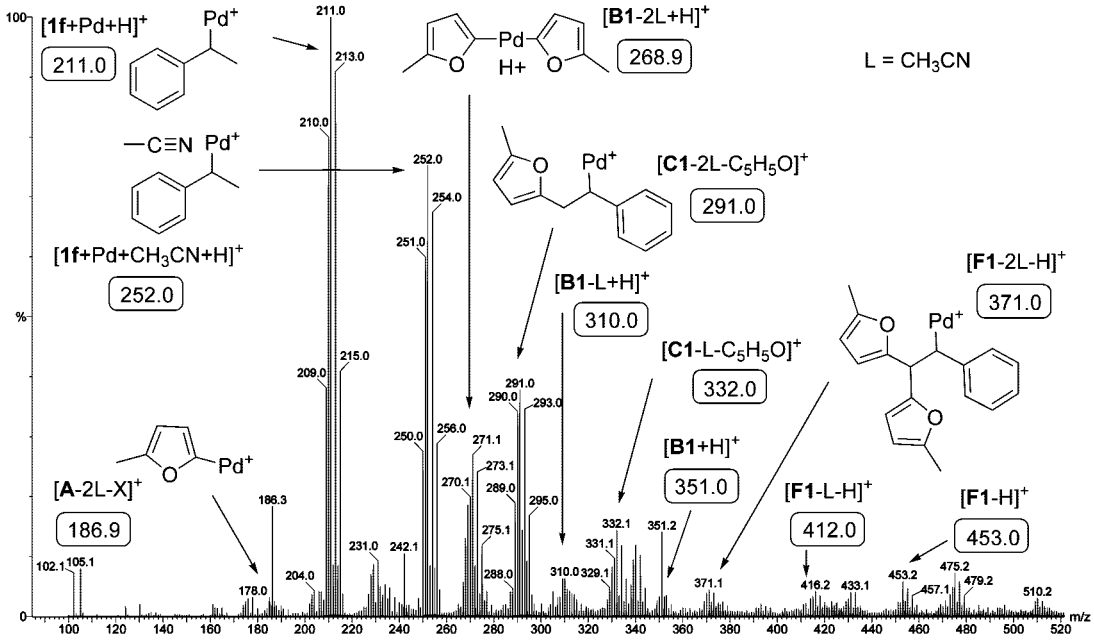
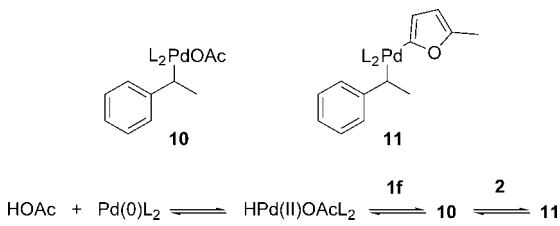


Figure 1. ESI(+)-MS of the reaction of **1f** with **2**. Conditions: **1f** (1.0 mmol), **2** (5.0 mmol), $Pd(OCOCF_3)_2$ (0.05 mmol), BQ (2.0 mmol), AcOH (0.5 mL), MeCN (3 mL), room temperature, 15 min.

Scheme 9



ESI-MS(/MS) of the species at *m/z* 211.0 has shown the loss of $[H_2]$, $[C_2H_2]$, and [Pd] (Figure S8, Supporting Information). Loss of dihydrogen has been observed in collision-induced dissociations of $PhCH_2CH_2O^-$ alkoxides,[32] and $[C_2H_2]$ loss is usually observed from phenyl ion.[27] ESI-MS(/MS) of the cluster at *m/z* 252.0 has shown the loss of CH_3CN under 5 eV CID (Figure S9, Supporting Information). These clusters could be associated with complexes **10** and **11** (Scheme 9). Compound **10** could result from the insertion of **1f** into $HPd^{II}OAcL_2$, the latter being formed from Pd^0L_2 and AcOH. The reaction of **10** with **2** would lead to **11**.

The reaction of protons with low-valent transition metals usually leads to the formation of hydridometal complexes and, in the presence of unsaturated carbon−carbon bonds, to a subsequent hydrometalation.[33] The oxidative addition of acetic acid to a palladium(0)−phosphine complex has been described in DMF as an unfavorable equilibrium, and a large excess of acid is required for the quantitative formation of the palladium hydride complex.[34] Acetonitrile could act as a ligand, and the use of acetic acid as cosolvent could promote the formation of the hydride complex $HPd^{II}OAcL_2$.

The analysis of the reaction medium after 2.5 and 6 h showed similar signals, but some of them were detected in different proportions (Figures S10 and S11, Supporting Information). The main feature is the progressive disappearance of clusters at *m/z* 211.0 and 252.0, attributed to $[\mathbf{1f} + Pd + H]^+$ and $[\mathbf{1f} + CH_3CN + Pd + H]^+$, probably due to a decrease of the concentration of **1f** during the advancement of the reaction. A new cluster at *m/z* 475.0 was also observed. After 24 h, a rather simple spectrum was obtained (Figure S12, Supporting Information). The most abundant cluster was detected at *m/z* 268.9 and was attributed by HRMS and ESI-MS(/MS) to $[\mathbf{B1}\text{-}2L + H]^+$. In the absence of alkene, and since reductive elimination from **B1** was discarded, it is not surprising to observe this signal with such intensity at the end of the reaction. The solvated species $[\mathbf{B1}\text{-}L + H]^+$ ($L = CH_3CN$) was also detected at *m/z* 310.0. A small cluster was observed at *m/z* 291.0 and was attributed to $[\mathbf{C1}\text{-}2L\text{-}C_5H_5O]^+$. It should be noted that the intensity of this signal was low compared to that observed after 15 min and that other solvated species were not detected. According to HRMS and ESI-MS(/MS), clusters at *m/z* 453.0 and 475.0 are not associated with catalytic intermediates but rather with palladium complexes of **3f** (Figures S13 and S14, Supporting Information).[35]

Conclusion

A coordinating solvent, such as acetonitrile, has a strong influence on the palladium-catalyzed coupling of 2-alkylfurans with olefins. Although allylarenes and styrenes are usually reluctant to react as alkenes in oxidative Heck type reactions, both compounds afforded difurylalkanes in good to high yields. Acrylates led selectively to the formation of β,β-difuryl esters in fair yields. The proposed mechanism involves two consecutive C−H activations of the electron-rich alkylfurans, followed by the insertion of the alkene, the migration of a furan ring and a hydrogen atom, and finally, an elimination reaction producing the difurylalkanes. The use of ESI-MS spectroscopy has allowed

(32) Raftery, M. J.; Bowie, J. H.; Sheldon, J. C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 563–569.
(33) Trost, B. M. *Chem. Eur. J.* **1998**, *4*, 2405–2412.
(34) Amatore, C.; Jutand, A.; Meyer, G.; Carelli, I.; Chiarotto, I. *Eur. J. Inorg. Chem.* **2000**, 1855–1859.
(35) Traces of **3f** were sometimes detected in the coupling of **1f** with **2**, and **3f** could interact with palladium catalytic species.

us to detect clusters associated with four intermediates of the catalytic cycle.

Experimental Section

General Comments. All reagents were commercially available in high purity. Acetonitrile, acetone, and AcOH were used as received. $Pd(OCOCF_3)_2$ was prepared from $Pd(OAc)_2$ in trifluoroacetic acid.[36] Column chromatography was conducted over silica gel 63−200 μm (SDS). NMR spectroscopy was performed with a Bruker Avance DRX (250 MHz) apparatus in $CDCl_3$ and referenced to TMS. FT IR spectra were recorded on Avatar 320 FT-IR as films. Electrospray ionization mass spectrometry experiments (MS and HRMS) were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manshester, U.K.) operated in positive mode. ALPHAGAZ AR2 gas was used for CID. The electrospray potential was set to 3 kV in positive ion mode, and the extraction cone voltage was usually varied between (30−60 V, flow of injection 5 μL/min). Spectra were typically an average of 20−40 scans. Theoretical isotope patterns calculated with the Isoform program were used to aid assignment.

Catalytic Coupling of Alkenes with 2-Alkylfurans. A flask was charged with benzoquinone (2.0 mmol, 216 mg), acetonitrile (3 mL), **1** (1 mmol), **2** (5 mmol, 450 μL), $Pd(OCOCF_3)_2$ (0.05 mmol, 16.6 mg), and acetic acid (0.5 mL). The mixture was stirred at room temperature for 20 h. Saturated aqueous $NaHCO_3$ solution (25 mL) was then slowly added, and the mixture was extracted with Et_2O (3 × 10 mL). The organic phase was washed with water (30 mL) and dried over $MgSO_4$. Evaporation of the solvent and flash chromatography (SiO_2, 100% petroleum ether to 95% petroleum ether/5% EtOAc) provided products.

2-Cinnamyl-5-methylfuran (3a):[37] pale yellow oil; t_R = 8.55, *m/z* (%) 198 (98) $[M]^+$, 155 (100) $[M - C_2H_3O]^+$; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3H), 3.40 (d, J = 6.5 Hz, 2H), 5.62−5.88 (m, 2H), 5.99−6.27 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 7.02−7.32 (m, 5H).

(*E*)-*tert*-Butyl 3-(5-methylfuran-2-yl) Acrylate (3p): t_R = 7.49, *m/z* (%) 208 (14) $[M]^+$, 152(38) $[M - C_4H_8]^+$, 56 (100), $[C_4H_8]^+$; IR ν 2978, 2925, 1733, 1704, 1634, 1584, 1367, 1149 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9H), 2.26 (s, 3H), 5.98 (m, 1H), 6.10 (d, J = 15.7 Hz, 1H), 6.39 (m, 1H), 7.19 (d, J = 15.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.9 (CH_3), 26.2 ($3CH_3$), 78.1 (C), 106.6 (CH), 113.7 (CH), 114.1 (CH), 128.1 (CH), 147.7 (C), 153.0 (C), 164.7 (C═O); ESHRMS for $C_{12}H_{16}O_3Na$ *m/z* calcd 231.0999, found 231.0997.

3-Phenyl-bis(5-methyl-2-furyl)propane (4a) and Phenyl-2,2′-bis(5-methyl-2-furyl)propane (5a): clear oil, 94%; **4a/5a** 15/85; t_R(**4a**) = 10.46, *m/z* (%) 280 (12) $[M]^+$, 175 (100) $[M - C_6H_5(CH_2)_2]^+$; t_R(**5a**) = 9.86, *m/z* (%) 280 (12) $[M]^+$, 189 (100) $[M - C_6H_5CH_2]^+$; IR ν 2922, 1604, 1560, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$) (**4a**) δ 2.25 (s, 6H), 2.23−2.32 (m, 2H), 2.61 (t, J = 7.2 Hz, 2H), 3.96 (t, J = 7.3 Hz, 1H), 5.94−5.96 (m, 4H), 6.75−6.79 (m, 2H), 7.14−7.24 (m, 3H); ^{1}H NMR ($CDCl_3$) (**5a**) δ 1.40 (s, 3H), 2.30 (s, 6H), 3.31 (s, 2H), 5.83−5.86 (m, 4H), 6.75−6.79 (m, 2H), 7.14−7.24 (m, 3H); ^{13}C NMR ($CDCl_3$) (**4a**) δ 14.1 ($2CH_3$), 34.0 (CH_2), 35.0 (CH_2), 38.8 (CH), 106.3, (2CH), 106.7 (2CH), 126.3 (CH), 128.8 (2CH), 129.0 (2CH), 142.3 (C), 151.3 (2C), 153.8 (2C); ^{13}C NMR ($CDCl_3$) (**5a**) δ 14.2 ($2CH_3$), 22.7 (CH_3), 42.4 (C), 45.6 (CH_2), 106.4 (2CH), 106.8 (2CH), 126.7 (CH), 128.1 (2CH), 130.8 (2CH), 138.1 (C), 151.1 (2C), 157.4 (2C); ESHRMS for $C_{19}H_{20}O_2Na$ *m/z* calcd 303.1361, found 303.1357.

3-(*p*-Methoxyphenyl)bis(5-methyl-2-furyl)propane (4c) and *p*-Methoxyphenyl-2,2′-bis(5-methyl-2-furyl)propane (5c): pale yellow oil, 52%; **4c/5c** 40/60; t_R(**4c**) = 11.87, *m/z* (%) 310 (16) $[M]^+$, 175 (100) $[M - MeOC_6H_4(CH_2)_2]^+$; t_R(**5c**) = 11.12, *m/z* (%) 310 (2) $[M]^+$, 189 (100) $[M - MeOC_6H_4CH_2]^+$; IR ν 2934, 1611, 1583, 1560, 1512, 1248, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$): (**4c**) δ 2.15−2.24 (m, 2H), 2.19 (s, 6H), 2.50 (t, J = 7.6 Hz, 2H), 3.74 (s, 3H), 3.89 (t, J = 7.5 Hz, 1H), 5.80 (s, 4H), 6.76 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H); ^{1}H NMR ($CDCl_3$) (**5c**) δ 1.34 (s, 3H), 2.26 (s, 6H), 3.20 (s, 2H), 3.70 (s, 3H), 5.80 (s, 4H), 6.64 (s, 4H); ^{13}C NMR ($CDCl_3$) (**4c**) δ 13.7 ($2CH_3$), 32.7 (CH_2), 34.8 (CH_2), 38.3 (CH), 55.3 (CH_3), 106.1 (2CH), 106.5 (2CH), 113.9 (2CH), 129.0 (C), 129.5 (2CH), 150.8 (C), 153.8 (2C), 157.1 (2C); ^{13}C NMR ($CDCl_3$) (**5c**) δ 13.8 ($2CH_3$), 22.3 (CH_3), 42.0 (C), 44.3 (CH_2), 55.2 (CH_3), 106.0 (2CH), 106.4 (2CH), 113.1 (2CH), 129.8 (C), 131.3 (2CH), 150.6 (C), 157.1 (2C), 158.1 (2C); ESHRMS for $C_{20}H_{22}O_3Na$ *m/z* calcd 333.1467, found 333.1471.

3-(*p*,*m*-Dimethoxyphenyl)bis(5-methyl-2-furyl)propane (4d) and *p*,*m*-Dimethoxyphenyl-2,2′-bis(5-methyl-2-furyl)propane (5d): yellow oil, 62%; **4d/5d** 40/60; t_R(**4d**) = 13.26, *m/z* (%) 340 (20) $[M]^+$, 175 (100) $[M - (MeO)_2C_6H_4(CH_2)_2]^+$; t_R(**5d**) = 12.12, *m/z* (%) 340(5) $[M]^+$, 189 (100) $[M - (MeO)_2C_6H_4CH_2]^+$; IR ν 2935, 1608, 1590, 1561, 1514, 1261, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$) (**4d**) δ 2.20−2.30 (m, 2H), 2.25 (s, 6H), 2.54 (t, J = 7.4 Hz, 2H), 3.84 (s, 3H), 3.85 (s, 3H), 3.94 (t, J = 7.4 Hz, 1H), 5.86 (s, 4H), 6.49 (d, J = 8.3 Hz, 1H), 6.67−6.80 (m, 2H); ^{1}H NMR ($CDCl_3$) (**5d**) δ 1.39 (s, 3H), 2.29 (6H), 3.24 (s, 2H), 3.66 (s, 3H), 3.81 (s, 3H), 5.86 (s, 4H), 6.49 (d, J = 8.3 Hz, 1H), 6.67−6.80 (m, 2H); ^{13}C NMR ($CDCl_3$) (**4d**) δ 13.7 ($2CH_3$), 33.2 (CH_2), 34.7 (CH_2), 38.3 (CH), 55.9 (CH_3), 56.0 (CH_3), 106.0 (2CH), 106.6 (2CH), 111.3 (CH), 112.0 (CH), 120.4 (CH), 134.5 (C), 147.2 (C), 148.8 (C), 150.8 (2C), 153.8 (2C); ^{13}C NMR ($CDCl_3$) (**5d**) 13.8 ($2CH_3$), 22.3 (CH_3), 42.0 (C), 44.8 (CH_2), 55.4 (CH_3), 55.8 (CH_3), 106.1 (2CH), 106.4 (2CH), 110.3 (CH), 112.9 (CH), 122.6 (CH), 130.2 (C), 147.4 (C), 148.0 (C), 150.5 (2C), 157.1 (2C); ESHRMS for $C_{21}H_{24}O_4Na$ *m/z* calcd 363.1572, found 363.1573.

3-(Perfluorophenyl)bis(5-methyl-2-furyl)propane (4e) and (Perfluorophenyl)-2,2′-bis(5-methyl-2-furyl)propane (5e): pale yellow oil, 76%; **4e/5e** 75/25; t_R(**4e**) = 9.81, *m/z* (%) 370 (12) $[M]^+$, 175 (100) $[M - C_6F_5(CH_2)_2]^+$; t_R(**5e**) = 9.30, *m/z* (%) 370 (2) $[M]^+$, 189 (100) $[M - C_6F_5CH_2]^+$; IR ν 2925, 1656, 1645, 1564, 1495, 1219 cm^{-1}; ^{1}H NMR ($CDCl_3$) (**4e**) δ 2.20−2.26 (m, 2H), 2.24 (s, 6H), 2.71 (t, J = 7.7 Hz, 2H), 3.99 (t, J = 7.5 Hz, 1H), 5.86 (s, 4H); ^{1}H NMR ($CDCl_3$) (**5e**) δ 1.53 (s, 3H), 2.24 (s, 6H), 3.37 (s, 2H), 5.96 (s, 4H); ^{19}F NMR ($CDCl_3$) (**4e**) δ −163.53 (td, ^3J = 20.7 Hz, ^5J = 8.6 Hz, 2F), −158.47 (t, ^3J = 20.7 Hz, 1F), −144.32 (dd, ^3J = 20.7 Hz, ^5J = 8.6 Hz, 2F); ^{19}F NMR ($CDCl_3$) (**5e**) δ −164,07 (td, ^3J = 20.7 Hz, ^5J = 8.6 Hz, 2F), −157.14 (t, ^3J = 20.7 Hz, 1F), −141.67 (dd, ^3J = 20.7 Hz, ^5J = 8.6 Hz, 2F); ^{13}C NMR ($CDCl_3$) (**4e**) δ 13.7 ($2CH_3$), 20.7 (CH_2), 32.3 (CH_2), 38.9 (CH), 106.2 (2CH), 106.9 (2CH), 114.7−147.4 (m, 5CF, C), 151.3 (2C), 152.8 (2C); ^{13}C NMR ($CDCl_3$) (**5e**) δ 13.8 ($2CH_3$), 22.5 (CH_3), 32.7 (CH_2), 41.9 (C), 106.0 (2CH), 106.6 (2CH), 114.7−147.4 (m, 5CF, C), 151.5 (2C), 155.5 (2C). Anal. Calcd for $C_{19}H_{15}F_5O_2$: C, 61.62; H, 4.05. Found: C, 61.87; H, 4.43.

2-Phenylbis(5-methyl-2-furyl)ethane (5f) and Phenylbis(5-methyl-2-furyl)ethane (6f):[38] pale yellow oil, 60%; **5f/6f** 85/15; t_R(**5f**) = 9.73, *m/z* (%) 266 (2) $[M]^+$, 175 (100) $[M - C_6H_5CH_2]^+$; t_R(**6f**) = 9.41, *m/z* (%) 266 (26) $[M]^+$, 251 (100) $[M - CH_3]^+$, 189 (30) $[M - C_6H_5]^+$; IR ν 2921, 1605, 1564, 1218 cm^{-1}; ^{1}H NMR ($CDCl_3$) (**5f**) δ 2.25 (s, 6H), 3.25 (d, J = 7.7 Hz, 2H), 4.19 (t, J = 7.7 Hz, 1H), 5.83−5.88 (m, 4H), 7.02−7.46 (m, 5H); ^{1}H NMR ($CDCl_3$) (**6f**) δ 1.97 (s, 3H), 2.25 (s, 6H), 5.83−5.88 (m, 4H), 7.02−7.46 (m, 5H); ^{13}C NMR ($CDCl_3$) (**5f**) δ 13.8 ($2CH_3$),

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39.5 (CH_2), 41.3 (CH), 106.1 (2CH), 107.0 (2CH), 126.2 (CH), 128.1 (2CH), 129.1 (2CH), 139.7 (C), 150.9 (2C) 153.1 (2C); ESHRMS for $C_{18}H_{18}O_2K$ *m/z* calcd 305.0944, found 305.0942.

2-(*p*-Tolyl)bis(5-methyl-2-furyl)ethane (5g) and (*p*-Tolyl)bis(5-methyl-2-furyl)ethane (6g): pale yellow oil, 50%; **5g/6g** 75/25; t_R(**5g**) = 10.13, *m/z* (%) 280 (28) $[M]^+$, 175 (100) $[M - CH_3C_6H_4CH_2]^+$; t_R(**6g**) = 9.85, *m/z* (%) 280 (28) $[M]^+$, 265 (100) $[M - CH_3]^+$, 189 (10) $[M - CH_3C_6H_4]^+$; IR ν 2921, 1608, 1564, 1219 cm^{-1}; ^1H NMR ($CDCl_3$) (**5g**) δ 2.23 (s, 6H), 2.25 (s, 3H), 3.22 (d, J = 7.7 Hz, 2H), 4.16 (t, J = 7.7 Hz, 1H), 5.80−5.87 (m, 4H), 6.91 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H); ^1H NMR ($CDCl_3$) (**6g**) δ 1.95 (s, 3H), 2.23 (s, 6H), 2.25 (s, 3H), 5.80−5.87 (m, 4H), 7.01−7.13 (m, 4H); ^{13}C NMR ($CDCl_3$) (**5g**) δ 13.2 ($2CH_3$), 20.6 (CH_3), 38.4 (CH_2), 40.8 (CH), 105.5 (2CH), 106.4 (2CH), 128.3 (2CH), 128.4 (2CH), 135.0 (C), 136.0 (C), 150.2 (2C), 152.6 (2C); ESHRMS for $C_{19}H_{20}O_2Na$ *m/z* calcd 303.1361, found 303.1351.

2-(*p*-Chlorophenyl)bis(5-methyl-2-furyl)ethane (5h) and (*p*-Chlorophenyl)bis(5-methyl-2-furyl)ethane (6h): pale yellow oil, 62%; **5h/6h** 83/17; t_R(**5h**) = 10.70, *m/z* (%) 300 (2) $[M]^+$, 175 (100) $[M - ClC_6H_4CH_2]^+$; t_R(**6h**) = 10.35, *m/z* (%) 300 (24) $[M]^+$, 285 (100) $[M - CH_3]^+$, 189 (14) $[M - ClC_6H_4]^+$; IR ν 2921, 1615, 1564, 1518 cm^{-1}; ^1H NMR ($CDCl_3$) δ (**5h**) 2.35 (s, 6H), 3.21 (d, J = 7.7 Hz, 2H), 4.14 (t, J = 7.7 Hz, 1H), 5.83−5.87 (m, 4H), 6.84 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H); ^1H NMR ($CDCl_3$) (**6h**) δ 1.55 (s, 3H), 2.35 (s, 6H), 5.83−5.87 (m, 4H), 6.84 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) (**5h**) δ 13.7 ($2CH_3$), 38.9 (CH_2), 41.2 (CH), 106.2 (2CH), 107.2 (2CH), 128.3 (2CH), 130.5 (2CH), 132.0 (C), 138.1 (C), 151.0 (2C), 152.7 (2C); ESHRMS for $C_{18}H_{17}O_2ClNa$ *m/z* calcd 323.0815, found 323.0822.

2-(*m*-Chlorophenyl)bis(5-methyl-2-furyl)ethane (5i) and (*m*-Chlorophenyl)bis(5-methyl-2-furyl)ethane (6i): pale yellow oil, 62%; **5i/6i** 89/11; t_R(**5i**) = 10.57, *m/z* (%) 300 (2) $[M]^+$, 175 (100) $[M - ClC_6H_4CH_2]^+$; t_R(**6i**) = 10.18, *m/z* (%) 300 (26) $[M]^+$, 285 (100) $[M - CH_3]^+$, 189 (24) $[M - ClC_6H_4]^+$; IR ν 2921, 1598, 1564, 1218 cm^{-1}; ^1H NMR ($CDCl_3$) (**5i**) δ 2.26 (s, 6H), 3.22 (d, J = 7.8 Hz, 2H), 4.16 (t, J = 7.8 Hz, 1H), 5.83−5.89 (m, 4H), 6.84−7.28 (m, 4H); ^1H NMR ($CDCl_3$) (**6i**) δ 1.55 (s, 3H), 2.26 (s, 6H), 5.83−5.89 (m, 4H), 6.84−7.28 (m, 4H); ^{13}C NMR ($CDCl_3$) (**5i**) δ 13.8 ($2CH_3$), 39.3 (CH_2), 41.2 (CH), 106.2 (2CH), 107.3 (2CH), 126.5 (CH), 127.4 (CH), 129.4 (CH), 129.5 (CH), 133.9 (C), 141.7 (C), 151.1 (2C), 152.7 (2C); ESHRMS for $C_{18}H_{17}O_2ClNa$ *m/z* calcd 323.0815, found 323.0823.

2-(2-Naphthalenyl)bis(5-methyl-2-furyl)ethane (5j) and (2-Naphthalenyl)bis(5-methyl-2-furyl)ethane (6j): pale yellow oil, 30%; **5j/6j** 84/16; t_R(**5j**) = 13.44, *m/z* (%) 316 (4) $[M]^+$, 175 (100) $[M - C_{10}H_7CH_2]^+$; t_R(**6j**) = 12.77, *m/z* (%) 316 (32) $[M]^+$, 301 (100) $[M - CH_3]^+$, 189 (10) $[M - C_{10}H_7]^+$; IR ν 2920, 1601, 1564, 1218 cm^{-1}; ^1H NMR ($CDCl_3$) (**5j**) δ 2.19 (s, 6H), 3.35 (d, J = 7.7 Hz, 2H), 4.22 (t, J = 7.7 Hz, 1H), 5.74−5.83 (m, 4H), 7.08 (d, J = 8.4 Hz, 1H), 7.31−7.43 (m, 3H), 7.59−7.70 (m, 3H); ^1H NMR ($CDCl_3$) (**6j**) δ 1.46 (s, 3H), 2.17 (s, 6H), 5.83−5.89 (m, 4H), 7.23 (d, J = 8.4 Hz, 1H), 7.31−7.43 (m, 3H), 7.59−7.70 (m, 3H); ^{13}C NMR ($CDCl_3$) (**5j**) δ 13.8 ($2CH_3$), 39.7 (CH_2), 41.3 (CH), 106.2 (2CH), 107.1 (2CH), 125.4 (CH), 125.9 (CH), 127.6 (CH), 127.7 (CH), 127.8 (3CH), 132.3 (C), 133.6 (C), 137.3 (C), 151.0 (2C), 153.1 (2C); ESHRMS for $C_{22}H_{20}O_2Na$ *m/z* calcd 339.1361, found 339.1353.

2-(*p*-Bromophenyl)bis(5-methyl-2-furyl)ethane (5k) and (*p*-Bromophenyl)bis(5-methyl-2-furyl)ethane (6k): pale yellow oil, 60%; **5k/6k** 87/13; t_R(**5k**) = 11.36, *m/z* (%) 344 (2) to 346 (2) $[M]^+$, 175 (100) $[M - BrC_6H_4CH_2]^+$; t_R(**6k**) = 10.91, *m/z* (%) 344 (18) to 346 (18) $[M]^+$, 329 (100) to 331 (100) $[M - CH_3]^+$, 189 (10) $[M - BrC_6H_4]^+$; IR ν 2920, 1613, 1565, 1218; ^1H NMR ($CDCl_3$) (**5k**) δ 2.22 (s, 6H), 3.19 (d, J = 7.7 Hz, 2H), 4.13 (t, J = 7.7 Hz, 1H), 5.80−5.86 (m, 4H), 6.86 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H); ^1H NMR ($CDCl_3$) (**6k**) δ 1.93 (s, 3H), 2.31 (s, 6H), 5.80−5.86 (m, 4H), 6.96 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) (**5k**) δ 14.1 ($2CH_3$), 39.3 (CH_2), 41.5 (CH), 106.6 (2CH), 107.6 (2CH), 128.1 (C), 131.3 (2CH), 131.6 (2CH), 139.0 (C), 151.4 (2C), 153.0 (2C); ESHRMS for $C_{18}H_{17}O_2BrNa$ *m/z* calcd 367.0310, found 367.0302.

Phenyl-2,2′-bis(5-methyl-2-furyl)butane (5l): clear oil, 65%; t_R = 10.06, *m/z* (%) 294 (2) $[M]^+$, 203 (100) $[M - C_6H_5CH_2]^+$; IR ν 2969, 2936, 1604, 1559, 1221 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (t, J = 7.4 Hz, 3H), 1.74 (q, J = 7.4 Hz, 2H), 2.18 (s, 6H), 3.21 (s, 2H), 5.76−5.81 (m, 4H), 6.58−6.62 (m, 2H), 7.01−7.04 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 9.0 (CH_3), 13.9 ($2CH_3$), 27.7 (CH_2), 42.5 (CH_2), 46.8 (C), 105.9 (2CH), 107.8 (2CH), 126.2 (CH), 127.6 (2CH), 130.3 (2CH), 137.8 (C), 150.6 (2C), 155.6 (2C); ESHRMS for $C_{20}H_{22}O_2Na$ *m/z* calcd 317.1517, found 317.1511.

(*p*-Methoxyphenyl)-2,2′-bis(5-methyl-2-furyl)propane (5c) and (*p*-Methoxyphenyl)bis(5-methyl-2-furyl)propane (6c): pale yellow oil, 74%; **5c/6c** 85/15; t_R(**5c**) = 11.12, *m/z* (%) 310 (2) $[M]^+$, 189 (100) $[M - MeOC_6H_4CH_2]^+$; t_R(**6c**) = 10.97, *m/z* (%) 310 (2) $[M]^+$, 281 (100) $[M - CH_2CH_3]^+$; IR ν 2934, 1611, 1583, 1560, 1512, 1248, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ (**6c**) 0.89 (t, J = 7.3 Hz, 3H), 2.26 (s, 6H), 2.39 (q, J = 7.3 Hz, 2H), 3.73 (s, 3H), 5.80 (s, 4H), 6.64 (s, 4H); ESHRMS for $C_{20}H_{22}O_3Na$ *m/z* calcd 333.1467, found 333.1474.

(*o*-Methoxyphenyl)-2,2′-bis(5-methyl-2-furyl)propane (5n) and (*o*-Methoxyphenyl)bis(5-methyl-2-furyl)propane (6n): pale yellow oil, 75%; **5n/6n** 83/17; t_R(**5n**) = 10.77, *m/z* (%) 310 (2) $[M]^+$, 189 (100) $[M - MeOC_6H_4CH_2]^+$; t_R(**6n**) = 10.22, *m/z* (%) 310(6) $[M]^+$, 281(100) $[M - CH_2CH_3]^+$; IR ν 2938, 1601, 1587, 1560, 1494, 1244, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) (**5n**) δ 1.39 (s, 3H), 2.29 (s, 6H), 3.38 (s, 2H), 3.73 (s, 3H), 5.86 (s, 4H), 6.45 (d, J = 7.7 Hz, 1H), 6.70 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H); ^1H NMR ($CDCl_3$) (**6n**) δ 0.88 (t, J = 6.8 Hz, 3H), 2.25 (s, 6H), 2.56 (q, J = 6.8 Hz, 2H), 3.73 (s, 3H), 5.86 (s, 4H), 6.45 (d, J = 7.7 Hz, 1H), 6.70 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) (**5n**) δ 13.8 ($2CH_3$), 21.8 (CH_3), 37.5 (CH_2), 42.3 (C), 55.1 (CH_3), 106.0 (2CH), 106.1 (2CH), 110.0 (CH), 119.8 (CH), 126.2 (C), 127.5 (CH), 131.7 (CH), 150.6 (C), 157.5 (2C), 158.3 (2C); ESHRMS for $C_{20}H_{22}O_3Na$ *m/z* calcd 333.1467, found 333.1458.

(*o*-Benzyloxyphenyl)-2,2′-bis(5-methyl-2-furyl)propane (5o) and (*o*-Benzyloxyphenyl)bis(5-methyl-2-furyl)propane (6o): pale yellow oil, 41%; **5o/6o** 80/20; t_R(**5o**) = 17.43, *m/z* (%) 386 (2) $[M]^+$, 189 (100) $[M - BnOC_6H_4CH_2]^+$; t_R(**6o**) = 15.36, *m/z* (%) 386 (1) $[M]^+$, 357 (39) $[M - CH_2CH_3]^+$, 171 (100) $[C_{12}H_{11}O]^+$; IR ν 2920, 1600, 1586, 1557, 1495, 1240, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) (**5o**) δ 1.44 (s, 3H), 2.26 (s, 6H), 3.48 (s, 2H), 5.02 (s, 2H), 5.86 (s, 4H), 6.42 (d, J = 7.5 Hz, 1H), 6.71 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 7.06−7.43 (m, 6H); ^1H NMR ($CDCl_3$) (**6o**) δ 0.88 (t, J = 7.3 Hz, 3H), 2.26 (s, 6H), 2.63 (q, J = 7.3 Hz, 2H), 4.85 (s, 2H), 5.86 (s, 4H), 6.42 (d, J = 7.5 Hz, 1H), 6.71 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.5 Hz, 1H), 7.06−7.43 (m, 6H); ^{13}C NMR ($CDCl_3$) (**5o**) δ 13.9 ($2CH_3$), 22.0 (CH_3), 37.4 (CH_2), 42.6 (C), 70.0 (CH_2), 106.0 (2CH), 106.3 (2CH), 111.6 (CH), 120.3 (CH), 126.8 (C) 127.0 (2CH), 127.5 (CH), 127.7 (CH), 128.6 (2CH), 130.2 (C), 131.8 (CH), 137.8 (C), 150.6 (2C), 157.5 (2C); ESHRMS for $C_{26}H_{26}O_3Na$ *m/z* calcd 409.1780, found 409.1788.

***tert*-Butyl 3,3-Bis(5-methylfuran-2-yl)propanoate (5p):** pale yellow oil, 71%; t_R = 9.10, *m/z* (%) 290 (4) $[M]^+$, 233 (66), $[M - (CH_3)_3C]^+$, 175 (100) $[M - (CH_3)_3OCOCH_2]^+$; IR ν 2978, 1732, 1615, 1563, 1222, 783 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 2.23 (s, 6H), 2.85 (d, J = 7.8 Hz, 2H), 4.48 (t, J = 7.8 Hz, 1H), 5.84 (d, J = 3.0 Hz, 2H), 5.93 (d, J = 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($2CH_3$), 28.1 ($3CH_3$), 35.7 (CH), 39.2 (CH_2), 80.6 (C), 106.1 (2CH), 106.6 (2CH), 151.1 (2C), 152.5 (2C), 170.6 (C); ESHRMS for $C_{17}H_{22}O_4Na$ *m/z* calcd 313.1416, found 313.1425.

Ethyl 3,3-Bis(5-methylfuran-2-yl)propanoate (5q): pale yellow oil, 57%; t_R = 8.72, *m/z* (%) 262 (16) $[M]^+$, 175 (100) $[M - CH_3CH_2OCOCH_2]^+$; IR ν 2982, 1738, 1613, 1564, 1219, 786 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, J = 7.3 Hz, 3H), 2.23 (s, 6H), 2.94 (d, J = 7.7 Hz, 2H), 4.11 (q, J = 7.3 Hz, 2H), 4.54 (t, J = 7.7 Hz, 1H), 5.85 (d, J = 3.0 Hz, 2H), 5.93 (d, J = 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8 ($2CH_3$), 14.2 (CH_3), 35.5 (CH), 38.0 (CH_2), 60.6 (CH_2), 106.2 (2CH), 106.7 (2CH), 151.2 (2C), 152.3 (2C), 171.4 (C); ESHRMS for $C_{15}H_{18}O_4Na$ *m/z* calcd 285.1103, found 285.1096.

3-Phenylbis(5-ethyl-2-furyl)propane (4r) and phenyl-2,2′-bis(5-ethyl-2-furyl)propane (5r): clear yellow oil, 60%; **4r/5r** 25/75; t_R(**4r**) = 11.15, *m/z* (%) 308 (8) $[M]^+$, 203 (100) $[M - C_6H_5(CH_2)_2]^+$; t_R(**5r**) = 10.49, *m/z* (%) 308 (2) $[M]^+$, 217 (100) $[M - C_6H_5CH_2]^+$; IR ν 2973, 1604, 1558, 1208 cm^{-1}; ^1H NMR ($CDCl_3$) (**4r**) δ 1.16 (t, J = 7.5 Hz, 6H), 2.20 (m, 2H), 2.51 (m, 2H), 2.58 (q, J = 7.5 Hz, 4H), 3.90 (t, J = 7.5 Hz, 1H), 5.79 (m, 4H), 6.70 (m, 2H), 7.07 (m, 3H); ^1H NMR ($CDCl_3$) (**5r**) δ 1.16 (t, J = 7.5 Hz, 6H), 1.34 (s, 3H), 2.58 (q, J = 7.5 Hz, 4H), 3.24 (s, 2H), 5.79 (m, 4H), 6.70 (m, 2H), 7.07 (m, 3H); ^{13}C NMR ($CDCl_3$) (**5r**) δ 12.6 ($2CH_3$), 21.6 (CH_3), 22.3 ($2CH_2$), 42.2 (C), 45.5 (CH_2), 104.4 (2CH), 106.2 (2CH), 126.0 (CH), 127.7 (2CH), 130.4 (2CH), 137.9 (C), 156.4 (2C), 156.9 (2C); ESHRMS for $C_{21}H_{24}O_2Na$ *m/z* calcd 331.1674, found 331.1671.

2-Phenylbis(5-ethyl-2-furyl)ethane (5s) and Phenylbis(5-ethyl-2-furyl)ethane (6s): clear oil, 51%; **5s/6s** 90/10; t_R(**5s**) = 10.38, *m/z* (%) 294 (2) $[M]^+$, 203 (100), $[M - C_6H_5CH_2]^+$; t_R(**6s**) = 9.99, *m/z* (%) 294 (20) $[M]^+$, 279 (100), $[M - CH_3]^+$; IR ν 2972, 1605, 1562, 1207 cm^{-1}; ^1H NMR ($CDCl_3$) (**5s**) δ1.12 (t, J = 7.5 Hz, 6H), 2.53 (q, J = 7.5 Hz, 4H), 3.19 (d, J = 7.5 Hz, 2H), 4.13 (t, J = 7.5 Hz, 1H), 5.78 (m, 4H), 6.95 (m, 2H), 7.12 (m, 3H); ^1H NMR ($CDCl_3$) (**6s**) δ 1.12 (t, J = 7.5 Hz, 6H), 1.91 (s, 3H), 2.53 (q, J = 7.5 Hz, 4H), 5.78 (m, 4H), 6.95 (m, 2H), 7.12 (m, 3H); ^{13}C NMR ($CDCl_3$) (**5s**) δ 12.4 ($2CH_3$), 21.6 ($2CH_2$), 39.8 (CH_2), 41.4 (CH), 104.5 (2CH), 106.8 (2CH), 126.2 (CH), 128.2 (2CH), 129.1 (2CH), 139.7 (C), 153.0 (2C), 156.6 (2C); ESHRMS for $C_{20}H_{22}O_2Na$ *m/z* calcd 317.1517, found 317.1527.

2-(Phenyl-d_5)bis(5-ethyl-2-furyl)ethane-d_3 (5t) and (Phenyl-d_5)bis(5-ethyl-2-furyl)ethane-d_3(6t): clear oil, 66%; t_R(**5t**) = 9.61, *m/z* (%) 274 (2) $[M]^+$, 176 (100) $[M - C_6D_5CD_2]^+$; t_R(**6t**) = 9.30, *m/z* (%) 274 (23) $[M]^+$, 256 (100) $[M - CD_3]^+$; IR ν 2921, 1611, 1563, 1219 cm^{-1}; ^1H NMR ($CDCl_3$) (**5t** and **6t**) δ 2.25 (s, 6H), 5.85 (m, 4H); ^{13}C NMR ($CDCl_3$) (**5t**) δ 13.7 ($2CH_3$), 38.6 (q, J = 20.4 Hz, CD_2), 40.7 (t, J = 19.3 Hz, CD), 106.1 (2CH), 106.9 (2CH), 125.5−128.8 (m, 5CD), 139.4 (C), 150.8 (2C), 153.1 (2C); ^{13}C NMR ($CDCl_3$) (**6t**) δ 13.8 ($2CH_3$), 25.1 (sept, J = 22.4 Hz, CD_3), 106.0 (2CH), 107.8 (2CH), 125.5−128.8 (m, 5CD), 145.6 (C), 151.3 (2C), 156.8 (2C); ESHRMS for $C_{18}H_{10}D_8O_2Na$ *m/z* calcd 297.1707, found 297.1706.

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Supporting Information Available: Text and figures giving details of the synthesis of **3f**, HRMS and ESI-MS(/MS) spectra of species **A**−**C**, **F**, $[\mathbf{1f} + Pd + H]^+$, $[\mathbf{1f} + Pd + CH_3CN + H]^+$, and complexes of **3f**, and ESI-MS spectra of reaction mixtures after 2.5, 6, and 24 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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