

## Palladium-Catalyzed Tandem Cyclization and Dimerization of (*Z*)-3-Iodo-3-alken-1-ones

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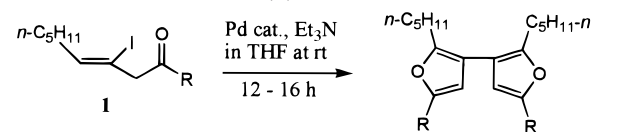
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


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Recently, we reported the synthesis of (*Z*)-3-iodo-3-alken-1-one **1** from a conjugated 2-alkyn-1-one system and its application to the synthesis of (*Z*)- $\alpha$ -alkylidene- $\gamma$ -butyrolactone.<sup>1,2</sup> In addition, we also reported the homocoupling of aryl iodide catalyzed by palladium complexes and a tertiary amine for the formation of biaryls.<sup>3</sup> To date, the palladium-catalyzed rearrangement of alkynone to form conjugated dienone and the palladium-catalyzed coupling of 3-iodo-2-butenone or 3-iodo-3-alkenone to form the corresponding substituted compounds have been extensively studied.<sup>4–10</sup> However, to the best of our knowledge, the palladium-catalyzed tandem cyclization and dimerization of a iodoenone system has not been reported in the literature. During our ongoing work on the use of palladium catalysts along with a tertiary amine, we found that a variety of highly regioselective 3,3'-bifurans can be formed in good to excellent yields through a cyclization and dimerization process of **1** by the aid of pertinent palladium complexes.

We observed that when **1** was allowed to react with 1 equiv of Et<sub>3</sub>N at room temperature in the presence of a catalytic amount of palladium complexes, e.g., Pd(PPh<sub>3</sub>)<sub>4</sub>, a dimer of **1** was formed, as detected in its <sup>13</sup>C NMR and MS spectral data analysis. The real structures of the final compounds were determined by <sup>1</sup>H NMR, DEPT, and 2D-NOESY experiments and were shown to be those of 3,3'-bifuran derivatives. A general procedure is as follows. To a solution of **1** (0.5 mmol) and 5 mol % of Pd(PPh<sub>3</sub>)<sub>4</sub> in dry THF (5 mL) was added 1 equiv of Et<sub>3</sub>N under nitrogen atmosphere at room temperature. The reaction mixture was stirred at room temperature for 12–16 h, quenched with water (20 mL), and extracted with ethyl acetate (20 mL  $\times$  2). The combined organic extracts were washed with brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The brown residue was purified by column chromatography over silica gel by using *n*-hexane as eluent to give 56–84% yields of 3,3'-bifuran derivatives as pale yellow liquids, as shown in Table 1. Using 5 mol % of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and

**Table 1.** Palladium-Catalyzed Tandem Cyclization and Dimerization of (*Z*)-3-Iodo-3-alken-1-ones **1**



Entry	Catalyst	3,3'-Bifuran R =	Iso. Yield (%)
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-H	56
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-Me	77
3 <sup>a</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-Me	35
4 <sup>b</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-Me	82
5 <sup>c</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-Me	73
6	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	-Me	74
7	Pd <sub>2</sub> (dba) <sub>3</sub>	-Me	trace <sup>d</sup>
8	Pd(OAc) <sub>2</sub>	-Me	trace <sup>d</sup>
9	Palladacycle	-Me	trace <sup>d</sup>
10	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-C <sub>5</sub> H <sub>11</sub> -n	67
11	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-Ph	74
12	Pd(PPh <sub>3</sub> ) <sub>4</sub>		79
13	Pd(PPh <sub>3</sub> ) <sub>4</sub>		84
14	Pd(PPh <sub>3</sub> ) <sub>4</sub>		20

<sup>a</sup> Used 0.5 equiv of Et<sub>3</sub>N. <sup>b</sup> Used 2 equiv of Et<sub>3</sub>N. <sup>c</sup> Used diisopropylethylamine as the base. <sup>d</sup> See text.

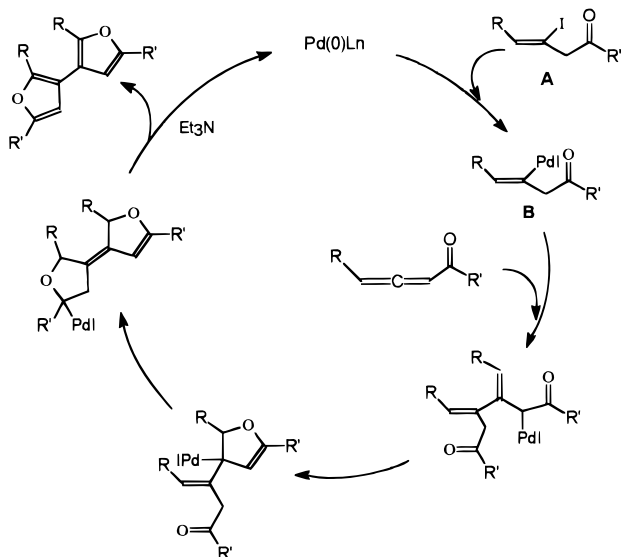
1 equiv of Et<sub>3</sub>N, we also obtained the desired bifuran in good yield (entry 6). Surprisingly, when we attempted the same reaction by using 5 mol % of Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> or Pd(OAc)<sub>2</sub>, in the presence of 1 equiv of Et<sub>3</sub>N in dry THF, we obtained only a trace amount of bifurans along with ca. 35% yield of 2,5-disubstituted furans<sup>11</sup> as detected by GC–MS and <sup>1</sup>H NMR analysis (entries 7 and 8). With the use of palladacycle catalyst<sup>12</sup> and 1 equiv of Et<sub>3</sub>N, bifurans were also obtained in very low yields; however, the corresponding 2,5-disubstituted furans were obtained in 60–85% yields (entry 9). The use of diisopropylethylamine as the base also works well with either of the catalysts, Pd(PPh<sub>3</sub>)<sub>4</sub> or PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, to produce bifurans (entry 5). Use of diisopropylamine to replace either Et<sub>3</sub>N or diisopropylethylamine resulted only in lower yields (ca. 20%) (entry 14). So far, we found that the reaction of 1 equiv of **1**, 1 equiv of Et<sub>3</sub>N, and 5 mol % of either Pd(PPh<sub>3</sub>)<sub>4</sub> or PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in THF at room temperature for 12–16 h is optimal to obtain substituted 3,3'-bifurans. The yield of bifuran dropped to 35% in the case of (*Z*)-4-iodo-4-decen-2-one when we used 0.5 equiv of Et<sub>3</sub>N in the reaction (entry 3). Although the use of 2 equiv of Et<sub>3</sub>N in the reaction could accelerate the reaction, the yield could only be improved by 5% (entry 4).

(11) For example, 2-methyl-5-pentylfuran would be obtained from (*Z*)-4-iodo-4-decen-2-one.

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**Scheme 1. Plausible Mechanism for the Tandem Dimerization and Cyclization of 3-Iodo-3-alken-1-one<sup>a</sup>**



<sup>a</sup> The allenone intermediate can be obtained from both iodoenone **A** and the oxidative addition adduct **B** by two different  $\beta$ -elimination pathways with or without the aid of  $\text{Et}_3\text{N}$ .

The control experiments showed that **1** slowly decomposed after stirring with  $\text{Pd}(\text{PPh}_3)_4$  catalyst for 24 h at room temperature in the absence of a base and no bifuran was observed. When we used 1 equiv of  $\text{Et}_3\text{N}$  alone without adding  $\text{Pd}(\text{PPh}_3)_4$  catalyst, we observed only the formation of the corresponding allenone, which is confirmed by GC-MS analysis.

It is also interesting to note that neither (*Z*)- nor (*E*)-4-iodo-3-decen-2-one undergoes similar cyclization and dimerization under the same reaction conditions to form 5-methyl-2-pentylfuran and that only starting material remained after 24 h at room temperature, as detected by their GC and crude  $^1\text{H}$  NMR spectral analysis. Thus, the use of **1** and the pertinent palladium catalyst along with 1–2 equiv of tertiary amine as the base appears to be a unique and efficient method for the formation of 2,2'-disubstituted 3,3'-bifurans. Although the reaction mechanism is not clear yet, we tentatively propose a plausible mechanism for this cyclization and dimerization as shown in Scheme 1. The oxidative addition adduct of **1** with  $\text{Pd}(0)$  could partially form the allenone in the presence of a base.<sup>4,5</sup> The oxidative addition adduct of **1** with  $\text{Pd}(0)$  will then undergo carbopalladation to the reactive allenone to form a  $\pi$ -allyl palladium complex that will then undergo oxypalladation to form a dihydrofuran ring attached to another  $\pi$ -allyl palladium system. Carbopalladation followed by base-catalyzed aromatization could give the 3,3'-bifuran product and regenerated  $\text{Pd}(0)$  catalyst. The observations that only 2,5-disubstituted furans are formed when palladium catalysts such as  $\text{Pd}_2(\text{dba})_3\text{CHCl}_3$ ,  $\text{Pd}(\text{OAc})_2$ , or palladacycle catalyst are used might be due to either a slower step in the carbopalladation of the allenone intermediate or a too-fast elimination of the oxidative addition adduct to form the reactive allenone intermediate.<sup>5</sup>

In conclusion, we have described an efficient and highly regioselective palladium-catalyzed tandem cyclization and dimerization of **1** in the presence of a tertiary amine

as a base. Further studies in the scope and limitations of the reaction are currently under investigation.

### Experimental Section

Precoated silica gel 60F-254 on aluminum plates made by EM chemical company was used for thin-layer chromatography. Purification by column chromatography was carried out with EM silica gel 60 (70–230 mesh ASTM). High-pressure liquid chromatography (HPLC) separation was performed at a flow rate of 0.7 mL/min by the use of two Chemco-Pak 10  $\times$  250 columns packed with Chemcosorb 5-ODS-H. GLC analyses were performed by a 3.2 cm  $\times$  3.1 m column packed with SE-30 (5% on Chromosorb W). The purity of each compound was judged to be  $\geq 95\%$  by GLC and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral analyses. THF was distilled from sodium/benzophenone ketyl immediately prior to use. The regiochemistry of 3,3'-bifurans was confirmed by their 2D NOESY spectral analysis.

**Non-2-ynal:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.87 (t,  $J = 7$  Hz, 3 H), 1.25–1.65 (m, 8 H), 2.38 (t,  $J = 7$  Hz, 2 H), 9.15 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.84, 19.02, 22.34, 27.44, 28.39, 31.08, 81.65, 99.28, 177.08 ppm; IR (neat) 2934 (s), 2862 (s), 2238 (s), 1685 (s), 1277 (m), 1204 (m), 906 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  137 ( $\text{M}^+$  - H), 123, 109, 108, 95, 94.

**(Z)-3-Iodonon-3-enal:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.25–1.50 (m, 6 H), 2.16 (q,  $J = 7$  Hz, 2 H), 3.70 (s, 2 H), 5.74 (t,  $J = 7$  Hz, 1 H), 9.67 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.96, 22.48, 27.78, 31.34, 36.65, 57.77, 93.23, 141.49, 198.76 ppm; IR (neat) 2961 (s), 2932 (s), 2862 (s), 1723 (s), 1107 (m), 907 (m), 719 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  266 ( $\text{M}^+$ ), 196, 168, 139, 121, 95; HRMS calcd for  $\text{C}_9\text{H}_{15}\text{IO}$  266.0168, found 266.0169.

**2,2'-Dipentyl-3,3'-bifuran:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.86 (m, 6 H), 1.26–1.30 (m, 8 H), 1.57–1.65 (m, 4 H), 2.60 (t,  $J = 7$  Hz, 4 H), 6.30 (s, 2 H), 7.32 (s, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.96, 22.39, 26.67, 28.01, 31.47, 111.84, 112.43, 140.17, 152.40 ppm; IR (neat) 2958 (s), 2922 (s), 2858 (m), 1569 (w), 1510 (m), 1460 (m), 1374 (w), 1220 (w), 1157 (w), 1138 (w), 1039 (w), 921 (w), 889 (w), 840 (w), 726 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  274 ( $\text{M}^+$ ), 217, 161; HRMS calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_2$  274.1933, found 274.1934. Anal. Calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_2$ : C, 78.79; H, 9.55. Found: C, 78.99; H, 9.78.

**Dec-3-yn-2-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.25–1.50 (m, 6 H), 1.52–1.65 (m, 2 H), 2.30 (s, 3 H), 2.35 (t,  $J = 7$  Hz, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.84, 18.77, 22.33, 27.53, 28.39, 31.08, 32.59, 81.28, 93.99, 184.69 ppm; IR (neat) 2934 (s), 2861 (s), 2212 (s), 1667 (s), 1456 (m), 1357 (m), 1203 (m), 726 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  152 ( $\text{M}^+$ ), 137, 123, 109, 95; HRMS calcd for  $\text{C}_{10}\text{H}_{16}\text{O}$  152.1201, found 152.1202.

**(Z)-4-Iodo-4-decen-2-one:** colorless oil;  $R_f = 0.53$  (silica gel, ethyl acetate/hexanes = 1/4),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.28–1.45 (m, 6 H), 2.14 (q with one singlet at  $\delta$  2.18,  $J = 7$  Hz, 5 H), 3.70 (s, 2 H), 5.67 (t,  $J = 7$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.93, 22.34, 27.71, 29.26, 31.18, 36.51, 59.08, 95.89, 140.75, 204.89 ppm; IR (neat) 2959 (m), 2930 (m), 1708 (s), 1630 (w), 1580 (w), 1455 (w), 1410 (w), 1353 (m), 1205 (m), 1150 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  280 ( $\text{M}^+$ ) 209, 170, 153, 135, 109, 95, 81, 71, 67, 54; HRMS calcd for  $\text{C}_{10}\text{H}_{17}\text{IO}$  280.0325, found 280.0328. Anal. Calcd for  $\text{C}_{10}\text{H}_{17}\text{IO}$ : C, 42.87; H, 6.11. Found: C, 42.92; H, 6.13.

**5,5'-Dimethyl-2,2'-dipentyl-3,3'-bifuran:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.80–0.83 (m, 6 H), 1.18–1.35 (m, 8 H), 1.50–1.67 (m, 4 H), 2.25 (s, 6 H), 2.56 (t,  $J = 8$  Hz, 4 H), 5.84 (s, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.47, 13.98, 22.43, 26.78, 28.33, 31.56, 107.67, 113.27, 149.33, 150.27 ppm; IR (neat) 2949 (m), 2913 (s), 2849 (m), 1460 (w), 1378 (w), 1220 (w), 1003 (w), 930 (w), 794 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  302 ( $\text{M}^+$ ), 245, 231, 189, 159; HRMS calcd for  $\text{C}_{20}\text{H}_{30}\text{O}_2$  302.2246, found 302.2246. Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{O}_2$ : C, 79.42; H, 10.00. Found: C, 79.75; H, 10.25.

**1-(2-Furyl)non-2-yn-1-ol:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.89 (t,  $J = 7$  Hz, 3 H), 1.28–1.42 (m, 6 H), 1.52–1.56 (m, 2 H), 2.24 (bs, 1 H), 2.26–2.29 (m, 2 H), 5.45 (bs, 1 H), 6.34–6.35 (m, 1 H), 6.43 (d,  $J = 3$  Hz, 1 H), 7.40 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.00, 18.70, 22.49, 28.37, 28.52, 31.26, 58.29, 77.38, 86.96, 107.40, 110.28, 142.80, 153.63 ppm; IR (neat) 3411 (bm), 2949 (s), 2922 (s), 2849 (s), 2224 (w), 1732 (m), 1668 (m), 1460 (m), 1369 (m), 1247 (m), 1134 (w), 1043 (w), 1007 (m), 928 (w),

735 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  206 ( $\text{M}^+$ ), 136, 135, 121, 120, 107, 95, 94; HRMS calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_2$  206.1307, found 206.1308.

**1-(2-Furyl)non-2-yn-1-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.30–1.32 (m, 4 H), 1.43–1.48 (m, 2 H), 1.60–1.67 (m, 2 H), 2.46 (t,  $J = 7$  Hz, 2 H), 6.55–6.57 (m, 1 H), 7.31 (d,  $J = 4$  Hz, 1 H), 7.64 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.92, 19.05, 22.39, 27.60, 28.49, 31.13, 78.93, 95.56, 112.40, 120.53, 147.65, 153.22, 164.97 ppm; IR (neat) 3121 (w), 2931 (s), 2859 (s), 2197 (s), 1632 (s), 1560 (m), 1455 (s), 1388 (m), 1301 (m), 1166 (m), 1120 (m), 1012 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  204 ( $\text{M}^+$ ), 203, 175, 161, 147, 134, 95, 94; HRMS calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_2$  204.1150, found 204.1151.

**(Z)-1-(2-Furyl)-3-iodonon-3-en-1-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.89 (t,  $J = 7$  Hz, 3 H), 1.28–1.31 (m, 4 H), 1.41–1.45 (m, 2 H), 2.16 (q,  $J = 7$  Hz, 2 H), 4.12 (s, 2 H), 5.73 (t,  $J = 7$  Hz, 1 H), 6.55–6.57 (m, 1 H), 7.26 (d,  $J = 4$  Hz, 1 H), 7.61 (s, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.97, 22.46, 27.76, 31.27, 36.57, 53.51, 94.92, 112.41, 117.97, 140.78, 146.66, 152.38, 184.87 ppm; IR (neat) 3130 (w), 2949 (s), 2922 (s), 2849 (s), 1944 (w), 1677 (s), 1559 (m), 1460 (s), 1387 (m), 1012 (m), 758 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  205 ( $\text{M}^+ - \text{I}$ ), 204, 175, 147, 146, 95; HRMS calcd for  $\text{C}_{13}\text{H}_{17}\text{O}_2$  205.1129, found 205.1130.

**5,5'-Bis(2-furyl)-2,2'-dipentyl-3,3'-bifuran:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.87 (t,  $J = 7$  Hz, 6 H), 1.29–1.33 (m, 8 H), 1.61–1.74 (m, 4 H), 2.67 (t,  $J = 7$  Hz, 4 H), 6.45–6.53 (m, 6 H), 7.41 (s, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.15, 22.56, 26.95, 28.32, 31.62, 104.67, 107.42, 111.49, 114.19, 141.66, 144.54, 146.90, 152.51 ppm; IR (neat) 3130 (w), 2949 (s), 2922 (s), 2858 (s), 1709 (w), 1646 (w), 1560 (w), 1582 (w), 1460 (s), 1215 (m), 1161 (m), 1003 (s), 948 (m), 880 (m), 794 (s), 726 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  406 ( $\text{M}^+$ ), 349, 293, 207, 146, 95; HRMS calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_4$  406.2144, found 406.2144. Anal. Calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_4$ : C, 76.82; H, 7.44. Found: C, 76.63; H, 7.67.

**1-(2-Thienyl)non-2-yn-1-ol:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.89 (t,  $J = 7$  Hz, 3 H), 1.28–1.43 (m, 6 H), 1.52–1.57 (m, 2 H), 2.25–2.32 (m, 3 H), 5.64 (d,  $J = 7$  Hz, 1 H), 6.96–6.99 (m, 1 H), 7.16 (d,  $J = 3$  Hz, 1 H), 7.29 (d,  $J = 4$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.01, 18.71, 22.51, 28.40, 28.52, 31.28, 60.42, 79.43, 87.22, 125.29, 125.78, 126.66, 145.54 ppm; IR (neat) 3538 (bm), 2958 (s), 2922 (s), 2849 (s), 2224 (w), 1623 (w), 1460 (m), 1433 (m), 1365 (w), 1324 (w), 1297 (m), 1274 (m), 1116 (m), 1034 (s), 1012 (s), 858 (m), 817 (m), 699 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  222 ( $\text{M}^+$ ), 189, 152, 151, 147, 137, 136, 134, 123, 111, 110, 97; HRMS calcd for  $\text{C}_{13}\text{H}_{18}\text{OS}$  222.1078, found 222.1079.

**1-(2-Thienyl)non-2-yn-1-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.25–1.36 (m, 4 H), 1.42–1.52 (m, 2 H), 1.60–1.68 (m, 2 H), 2.47 (t,  $J = 7$  Hz, 2 H), 7.13–7.16 (m, 1 H), 7.67 (d,  $J = 4$  Hz, 1 H), 7.88 (d,  $J = 3$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.79, 18.86, 22.26, 27.50, 28.36, 30.99, 79.11, 95.18, 128.00, 134.66 (2  $\times$  Cs), 144.82, 169.76 ppm; IR (neat) 2930 (s), 2858 (s), 2229 (s), 1626 (s), 1515 (m), 1411 (s), 1357 (m), 1279 (s), 1256 (m), 1213 (m), 1041 (m), 838 (m), 727 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  220 ( $\text{M}^+$ ), 203, 192, 187, 163, 150, 149, 121, 111; HRMS calcd for  $\text{C}_{13}\text{H}_{16}\text{OS}$  220.0922, found 220.0923.

**(Z)-3-Iodo-1-(2-thienyl)non-3-en-1-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.89 (t,  $J = 7$  Hz, 3 H), 1.28–1.32 (m, 4 H), 1.39–1.48 (m, 2 H), 2.16 (q,  $J = 7$  Hz, 1 H), 4.17 (s, 2 H), 5.73 (t,  $J = 7$  Hz, 1 H), 7.14 (t,  $J = 4$  Hz, 1 H), 7.66 (d,  $J = 4$  Hz, 1 H), 7.76 (d,  $J = 4$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.97, 22.46, 27.73, 31.29, 36.59, 54.57, 95.41, 128.13, 132.57, 134.24, 140.77, 143.63, 188.78 ppm; IR (neat) 3099 (w), 2956 (s), 2927 (s), 2835 (m), 1665 (s), 1516 (m), 1462 (w), 1414 (s), 1357 (m), 1319 (w), 1235 (m), 1220 (m), 1056 (w), 857 (w), 755 (m), 722 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  221 ( $\text{M}^+ - \text{I}$ ), 163, 150, 111; HRMS calcd for  $\text{C}_{13}\text{H}_{17}\text{OS}$  221.1000, found 221.1001.

**5,5'-Bis(2-thienyl)-2,2'-dipentyl-3,3'-bifuran:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.89–0.91 (m, 6 H), 1.31–1.34 (m, 8 H), 1.63–1.75 (m, 4 H), 2.60 (t,  $J = 7$  Hz, 4 H), 6.43 (s, 2 H), 7.01–7.04 (m, 2 H), 7.18–7.25 (m, 4 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.00, 22.38, 26.74, 28.12, 31.44, 107.16, 114.31, 121.88, 123.57, 127.57, 133.99, 147.17, 152.08 ppm; IR (neat) 3112 (w), 3067 (w), 2958 (s), 2922 (s), 2849 (m), 1641 (w), 1460 (w), 1424 (w), 1369 (w), 1261 (w), 1211 (w), 953 (m), 844 (m), 799 (m), 686 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  438 ( $\text{M}^+$ ), 381, 281, 207, 191, 111; HRMS calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_2\text{S}_2$  438.1687, found 438.1687. Anal. Calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_2\text{S}_2$ : C, 71.19; H, 6.89. Found: C, 71.35; H, 6.99.

**1-Phenylnon-2-yn-1-ol:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.89 (t,  $J = 7$  Hz, 3 H), 1.27–1.42 (m, 6 H), 1.51–1.57 (m, 2 H), 2.11 (d,  $J = 7$  Hz, 1 H), 2.27 (t,  $J = 7$  Hz, 2 H), 5.45 (bs, 1 H), 7.31–7.40 (m, 4 H), 7.54 (d,  $J = 7$  Hz, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.00, 18.80, 22.51, 28.53 (2  $\times$  Cs), 31.28, 64.85, 79.90, 87.76, 126.61, 128.18, 128.50, 141.28 ppm; IR (neat) 3418 (bs), 2930 (m), 2857 (m), 2260 (w), 1650 (m), 1492 (w), 1454 (m), 1000 (m), 700 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  216 ( $\text{M}^+$ ), 145, 131, 115, 105; HRMS calcd for  $\text{C}_{15}\text{H}_{20}\text{O}$  216.1514, found 216.1515.

**1-Phenylnon-2-yn-1-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.33–1.58 (m, 6 H), 1.60–1.75 (m, 2 H), 2.50 (t,  $J = 7$  Hz, 2 H), 7.48 (t,  $J = 7$  Hz, 2 H), 7.59 (t,  $J = 7$  Hz, 1 H), 8.15 (d,  $J = 7$  Hz, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.81, 19.04, 22.32, 27.67, 28.47, 31.07, 79.62, 96.61, 128.32, 129.35, 133.64, 136.93, 177.93 ppm; IR (neat) 2934 (s), 2862 (m), 2236 (m), 2203 (s), 1637 (s), 1598 (m), 1578 (m), 1447 (m), 1312 (m), 1263 (s), 907 (w), 691 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  214 ( $\text{M}^+$ ), 213, 199, 186, 171, 157, 145, 128, 115, 105; HRMS calcd for  $\text{C}_{15}\text{H}_{18}\text{O}$  214.1358, found 214.1359.

**(Z)-3-Iodo-1-phenylnon-3-en-1-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 3 H), 1.33–1.48 (m, 6 H), 2.16 (q,  $J = 7$  Hz, 2 H), 4.27 (s, 2 H), 5.67 (t,  $J = 7$  Hz, 1 H), 7.48 (t,  $J = 7$  Hz, 2 H), 7.58 (t,  $J = 7$  Hz, 1 H), 7.95 (d,  $J = 7$  Hz, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.97, 22.46, 27.77, 31.26, 36.62, 53.81, 95.89, 128.38, 128.62, 133.33, 136.45, 140.48, 196.14 ppm; IR (neat) 1683 (m), 1601 (s), 712 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  342 ( $\text{M}^+$ ), 281, 214, 157, 105, 104; HRMS calcd for  $\text{C}_{15}\text{H}_{19}\text{IO}$  342.0481, found 342.0481.

**2,2'-Dipentyl-5,5'-Diphenyl-3,3'-bifuran:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7.0$  Hz, 6 H), 1.33–1.38 (m, 8 H), 1.70–1.75 (m, 4 H), 2.70 (t,  $J = 7.4$  Hz, 4 H), 6.59 (s, 2 H), 7.25 (t,  $J = 7$  Hz, 2 H), 7.37 (t,  $J = 7$  Hz, 4 H), 7.67 (d,  $J = 7$  Hz, 4 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.98, 22.40, 26.85, 28.15, 31.48, 107.25, 114.64, 123.36, 126.89, 128.61, 131.02, 151.49, 152.42 ppm; IR (neat) 2955 (s), 2928 (s), 1487 (m), 1440 (m), 958 (m), 932 (m), 759 (s), 691 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  426 ( $\text{M}^+$ ), 369, 313, 207, 156, 105, 77; HRMS calcd for  $\text{C}_{30}\text{H}_{34}\text{O}_2$  426.2559, found 426.2559. Anal. Calcd for  $\text{C}_{30}\text{H}_{34}\text{O}_2$ : C, 84.47; H, 8.03. Found: C, 84.67; H, 8.24.

**Tetradec-7-yn-6-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.90 (t,  $J = 7$  Hz, 6 H), 1.26–1.50 (m, 8 H), 1.51–1.70 (m, 4 H), 2.36 (t,  $J = 7$  Hz, 2 H), 2.51 (t,  $J = 7$  Hz, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.78, 13.89, 18.88, 22.32, 22.40, 23.84, 27.67, 28.47, 31.14 (2  $\times$  Cs), 45.46, 80.92, 94.16, 188.40 ppm; IR (neat) 2931 (s), 2860 (s), 2213 (s), 1674 (s), 1466 (s), 1378 (w), 1326 (w), 1238 (m), 1166 (m), 726 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  209 ( $\text{M}^+ + 1$ ), 193, 179, 137, 109.

**(Z)-8-Iodotetradec-8-en-6-one:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.87–0.91 (m, 6 H), 1.21–1.50 (m, 10 H), 1.51–1.68 (m, 2 H), 2.14 (q,  $J = 7$  Hz, 2 H), 2.46 (t,  $J = 7$  Hz, 2 H), 2.67 (s, 2 H), 5.63 (t,  $J = 7$  Hz, 1 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  13.89, 13.98, 22.42, 22.47, 23.25, 27.80, 31.31 (2 Cs), 36.56, 42.11, 58.22, 96.11, 140.54, 207.06 ppm; IR (neat) 2957 (s), 2929 (s), 2858 (s), 1720 (s), 1641 (w), 1467 (m), 1405 (m), 1378 (m), 1308 (m), 1132 (m), 1085 (m), 1030 (m), 726 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  336 ( $\text{M}^+$ ), 307, 265, 209, 99; HRMS calcd for  $\text{C}_{14}\text{H}_{25}\text{IO}$  336.0950, found 336.0951.

**2,2',5,5'-Tetrapentyl-3,3'-bifuran:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  0.84–0.92 (m, 12 H), 1.25–1.37 (m, 16 H), 1.54–1.65 (m, 8 H), 2.53–2.59 (m, 8 H), 5.87 (s, 2 H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  14.08, 22.50, 26.86, 27.79, 28.05, 28.35, 31.49, 31.59, 106.78, 113.16, 150.07, 153.95; IR (neat) 2958 (s), 2922 (s), 2849 (m), 1555 (w), 1455 (m), 1374 (w), 1215 (w), 939 (w), 794 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  414 ( $\text{M}^+$ ), 357, 343, 301, 99, 71; HRMS calcd for  $\text{C}_{28}\text{H}_{46}\text{O}_2$  414.3498, found 414.3498. Anal. Calcd for  $\text{C}_{28}\text{H}_{46}\text{O}_2$ : C, 81.10; H, 11.18. Found: C, 81.46; H, 11.36.

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