

## Synthesis of Naturally Occurring Acetylenes via an Alkylidene Carbenoid Rearrangement

Annabelle L. K. Shi Shun and Rik R. Tykwinski\*

Department of Chemistry, University of Alberta,  
Edmonton, AB, T6G 2G2 Canada

rik.tykwinski@ualberta.ca

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**Abstract:** Naturally occurring mosquito larvicidal acetylenes **1** and **2**, and analogues **3** and **4**, each containing either a 1,3-butadiynyl or a 1,3,5-hexatriynyl moiety, are synthesized via a Fritsch–Buttenberg–Wiechell rearrangement. The alkylidene carbenoid intermediate results from lithium–halogen exchange of a suitable dibromoolefin precursor, and the rearrangement is accomplished under mild conditions. Synthesis of the dibromoolefin precursors to acetylenes **1–4** is easily achieved in three steps from commercially available carboxylic acids or aldehydes, making this procedure a viable alternative to conventional methods for the synthesis of naturally occurring acetylenes.

Mosquito larvicidal agents are important in the fight to eradicate mosquito-borne diseases such as the West Nile Virus, malaria, and dengue fever.<sup>1</sup> The allure of naturally occurring toxins for this purpose is attributable to their biodegradability and the fact that they generally leave no long-lived residues.<sup>2</sup> Naturally occurring acetylenes<sup>3</sup> have been isolated from a wide variety of plant species,<sup>3</sup> cultures of higher fungi,<sup>3a–c,4</sup> and marine sponges,<sup>5</sup> and have proven to be important biologically active compounds due to their antibacterial, antimicrobial, antifungal, and pesticidal properties.<sup>2,6</sup> The natural products **1** and **2** illustrate the potency of certain acetylenes, and both are extremely phototoxic toward mosquito larvae.<sup>7</sup> Ene-triyn **1** was first isolated by Bohlmann et al. from various *Chrysanthemum* plant species.<sup>8</sup> Biologi-

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(2) (a) Towers, G. H. N.; Wat, C. K.; Lambert, J. D. H.; Arnason, J. T. Canadian Patent 1173743, 1984. (b) *Biologically Active Natural Products – Potential Use in Agriculture*; Cutler, H. G., Ed.; ACS Symp. Ser. No. 380; American Chemical Society: Washington, DC, 1988.

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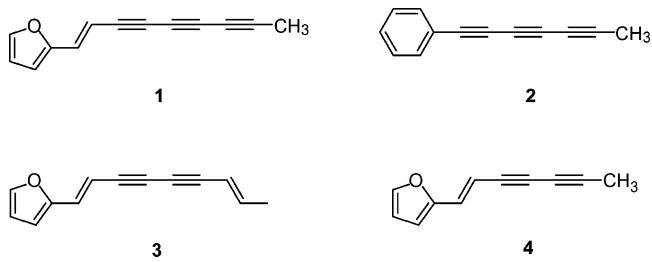


FIGURE 1.

cal studies conducted on compound **1** revealed it to be highly phototoxic toward *Aedes atropalpus* larvae and *Aedes aegypti* larvae, with LC<sub>50</sub> values of 0.100 and 0.079 ppm, respectively. Compound **1** was also phototoxic to blackfly larvae and adult nematodes.<sup>7b</sup> 1-Phenylhepta-1,3,5-triyn (**2**) has been isolated from diverse plant species, such as *Bidens pilosa* L. (Asteraceae),<sup>9</sup> and several members of the *Coreopsis* family.<sup>8b</sup> Triyne **2** has been extensively studied and displays insecticidal activity (LC<sub>50</sub> 204 ng/cm<sup>2</sup>) on first instar larvae of the fall armyworm *Spodoptera frugiperda* Smith., phototoxicity toward *Aedes aegypti* larvae, antimicrobial activity, ovicidal activity, and nematicidal activity.<sup>7b,c,10</sup> Diene-diyne **3**, atracylodin, has previously been isolated from the rhizomes of various *Atractylodes* species,<sup>11</sup> and is phototoxic and antibiotic against *Escherichia coli*, *Saccharomyces cerevisiae*, and *Candida albicans*,<sup>11c</sup> but it has not yet been tested for mosquito larvicidal activity. Ene-diyne **4**, 2-hept-1-ene-3,5-diynylfuran, is a novel synthetic compound that has been synthesized in view of its potential as a mosquito larvicidal agent due to its structural analogy to compound **1**.

We now report the synthesis of acetylenes **1–4**<sup>12–14</sup> via a modification of the Fritsch–Buttenberg–Wiechell rear-

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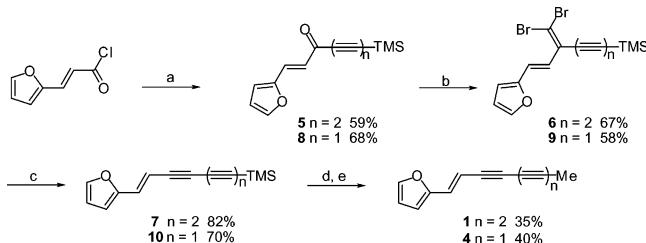
(9) (a) Wat, C.-K.; Biswas, R. K.; Graham, E. A.; Bohm, L.; Towers, G. H. N.; Waygood, E. R. *J. Nat. Prod.* **1979**, *42*, 103–111. (b) Alvarez, L.; Marquina, S.; Villarreal, M. L.; Alonso, D.; Aranda, E.; Delgado, G. *Planta Med.* **1996**, *62*, 355–357.

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(12) The ene-triyn **1** has previously been synthesized by Bohlmann et al. using a Wittig reaction, ref 8a.

(13) 1-Phenylhepta-1,3,5-triyn (**2**) has previously been synthesized by Cadiot–Chodkiewicz coupling and elimination protocols: (a) Meier, J.; Chodkiewicz, W.; Cadiot, P.; Willemart, A. *C. R. Hebd. Séances Acad. Sci.* **1957**, *245*, 1634–1636. (b) Mavrov, M. V.; Kucherov, V. F. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1966**, *833*–836. (c) Shim, S. C.; Lee, T. S. *Bull. Korean Chem. Soc.* **1986**, *7*, 357–362.

SCHEME 1<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a)  $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ ,  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ . (b)  $\text{PPh}_3$  (2 equiv),  $\text{CBr}_4$ ,  $\text{CH}_2\text{Cl}_2$ , rt. (c)  $n\text{-BuLi}$ , hexanes,  $-78$  to  $-40^\circ\text{C}$ . (d)  $\text{K}_2\text{CO}_3$ ,  $\text{MeOH/THF}$ . (e)  $n\text{-BuLi}$ ,  $\text{THF}$ ,  $-78^\circ\text{C}$ , then  $\text{MeI}$ ,  $-78^\circ\text{C}$  to rt.

rangement<sup>15</sup> recently developed by our group.<sup>16</sup> The synthesis of the dibromolefin precursors is easily achieved in three procedurally facile steps from commercially available carboxylic acids or aldehydes, rendering this route a viable alternative to previous methods for acetylenic natural product synthesis.<sup>12–14</sup>

Ene-triye **1** was synthesized as shown in Scheme 1. Friedel–Crafts acylation of 3-(2-furyl)acryloyl chloride with 1,4-bis(trimethylsilyl)-1,3-butadiyne gave ketone **5**, and dibromolefination produced compound **6**. Subjecting dibromolefin **6** to  $n\text{-BuLi}$  at  $-78^\circ\text{C}$  in hexanes gave ene-triye **7** in an excellent 82% yield. Protodesilylation of **7** with  $\text{K}_2\text{CO}_3$  afforded the corresponding terminal ene-triye, which was then converted to the lithium acetylide. Methylation with methyl iodide gave the target ene-triye **1** (11% overall yield).<sup>17</sup>

Likewise, the diyne analogue of compound **1**, 2-hept-1-ene-3,5-diynefurane (**4**), was synthesized via a similar sequence of Friedel–Crafts acylation to provide ketone **8**, dibromolefination to **9**, and rearrangement to **10**. Protodesilylation of **10**, lithiation of the corresponding terminal ene-diyne, and subsequent methylation furnished **4** in 11% overall yield.

Clearly, the weakest step in the above scheme involves methylation of the unstable terminal alkyne to afford either **1** or **4**, so a more effective synthetic pathway for targets **1** and **4** was explored (Scheme 2). Friedel–Crafts acylation with trimethylsilylpenta-1,3-diyne<sup>18</sup> gave the ketone **11** directly from 3-(2-furyl)acryloyl chloride. Dibromolefination provided **12**, and rearrangement produced the desired product, ene-triye **1**, in 84% yield. This amounted to an overall yield of 21%, a 2-fold increase relative to the previous synthetic scheme for compound **1**.

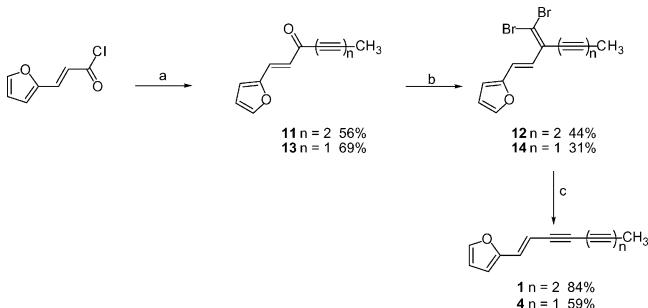
(14) Atractyldolin (**3**) has been synthesized by oxidative coupling, but no yield was reported: Yosioka, I.; Hikino, H.; Sasaki, Y. *Chem. Pharm. Bull.* **1960**, *8*, 957–959.

(15) (a) Fritsch, P. *Liebigs Ann. Chem.* **1894**, *279*, 319–323. (b) Buttenberg, W. P. *Liebigs Ann. Chem.* **1894**, *279*, 324–337. (c) Wiechell, H. *Liebigs Ann. Chem.* **1894**, *279*, 337–344.

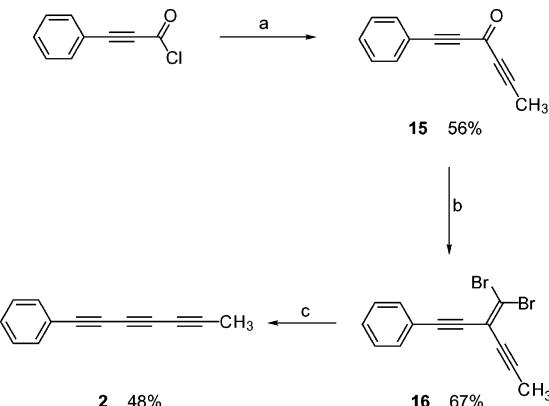
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(17) Transformation of the terminal triyne into its methylated derivative **1** required that THF be used as solvent. Use of diethyl ether was unsuccessful, consistent with that observed by Holmes and Jones in a similar methylation reaction, see: Holmes, A. B.; Jones, E. G. *Tetrahedron Lett.* **1980**, *21*, 3111–3112.

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SCHEME 2<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a)  $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{Me}$ ,  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ . (b)  $\text{PPh}_3$  (2 equiv),  $\text{CBr}_4$ ,  $\text{CH}_2\text{Cl}_2$ , rt. (c)  $n\text{-BuLi}$ , hexanes,  $-78$  to  $-40^\circ\text{C}$ .

SCHEME 3<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a)  $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ,  $\text{AlCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ . (b)  $\text{PPh}_3$  (2 equiv),  $\text{CBr}_4$ ,  $\text{CH}_2\text{Cl}_2$ , rt. (c)  $n\text{-BuLi}$ , hexanes,  $-78$  to  $-40^\circ\text{C}$ .

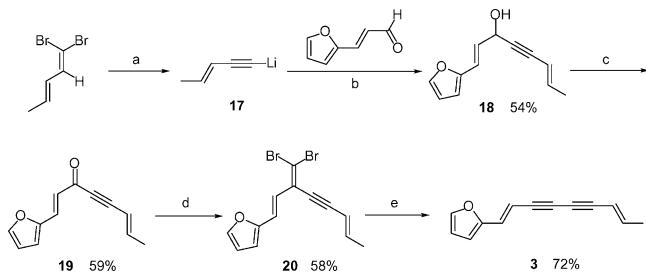
Similarly, ene-diyne **4** was synthesized via a sequence of Friedel–Crafts acylation with trimethylsilylpropane to produce ketone **13**, dibromolefination to give **14**, and carbene rearrangement of **14** to afford the desired product **4** in 59% yield. Thus, the overall yield of 13% is slightly higher than that for the previous synthetic route and consists of one less step. Somewhat surprising is the fact that dibromolefins **9** and **14** are less stable than their diyne counterparts **6** and **12**, which ultimately lowers the overall yield of **4** in both cases.

1-Phenylhepta-1,3,5-triye (**2**) was synthesized (Scheme 3) starting from a Friedel–Crafts acylation reaction of phenylpropiolyl chloride with trimethylsilylpropane, giving ketone **15** in 56% yield.<sup>19</sup> Dibromolefination yielded compound **16** (67%), and subjecting **16** to  $n\text{-BuLi}$  produced 1-phenylhepta-1,3,5-triye (**2**) in 18% overall yield.

The synthesis of atractyldolin (**3**) is outlined in Scheme 4. The lithium acetylide **17** was generated from 1,1-dibromo-1,3-pentadiene<sup>20</sup> and reacted with 2-furanacrolein to give alcohol **18** (54% yield over two steps). Oxidation of **18** to ketone **19**, followed by dibromolefination, yielded compound **20** (58%). Finally, rearrangement of dibromolefin **20** gave atractyldolin **3** in 13% overall yield.

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SCHEME 4<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) *n*-BuLi, THF,  $-78^{\circ}\text{C}$  to rt. (b) THF,  $-78^{\circ}\text{C}$  to rt. (c)  $\text{MnO}_2$ ,  $\text{CH}_2\text{Cl}_2$ , rt. (d)  $\text{PPh}_3$  (2 equiv),  $\text{CBr}_4$ ,  $\text{CH}_2\text{Cl}_2$ , rt. (e) *n*-BuLi, hexanes,  $-78$  to  $-40^{\circ}\text{C}$ .

In conclusion, the applicability of an alkylidene carbenoid rearrangement toward the synthesis of naturally occurring acetylenes and their analogues has been demonstrated by the total synthesis of acetylenes **1–4**. The usefulness of this method is emphasized by the fact that the dibromoolefin precursors of this reaction can be easily realized from commercially available carboxylic acids and aldehydes. This feature eliminates the need for unstable acetylenic precursors commonly required for other routes.

## Experimental Section

**General.** Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium/benzophenone ketyl, and hexanes were distilled from  $\text{CaH}_2$  immediately prior to use. Anhydrous  $\text{MgSO}_4$  was used as the drying agent after aqueous workup. Evaporation and concentration in vacuo was done at  $\text{H}_2\text{O}$ -aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of  $\text{N}_2$ . For mass spectral analyses, low-resolution data are provided in cases when  $\text{M}^+$  is not the base peak; otherwise, only high-resolution data are provided.

**General Procedure for Diyne/Triyne Formation.** Unless otherwise noted, the following procedure was followed. To the appropriate dibromoolefin (0.368 mmol) in dry hexanes (10 mL) at  $-78^{\circ}\text{C}$  was added dropwise over 10 min 1.1–1.2 equiv of *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol). The mixture was warmed to approximately  $-40^{\circ}\text{C}$  for 30 min, re-cooled to  $-78^{\circ}\text{C}$ , and quenched with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ .  $\text{Et}_2\text{O}$  was added ( $\sim 50$  mL), and the organic layer was separated, washed with brine, and dried over magnesium sulfate. Solvent removal in vacuo and passing the residue through a short plug of silica gel with the solvent system detailed for each product afforded the desired diyne/triyne. If necessary, additional purification could be achieved via flash column chromatography.<sup>21</sup>

**2-Non-1-en-3,5,7-triynylfuran (1).** To a solution of triyne **7** (0.132 g, 0.554 mmol) in a 1:1 mixture of methanol (5 mL) and THF (5 mL) at room temperature was added  $\text{K}_2\text{CO}_3$  (5 mg). After the reaction mixture was stirred for 1 h, saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) was added and the solution was extracted with ether (20 mL). Evaporation of the solvent in vacuo yielded a white solid that was used directly in the next step. To a solution of the deprotected triyne in THF (10 mL) at  $-78^{\circ}\text{C}$  was added *n*-BuLi (0.22 mL, 2.5 M in hexanes, 0.55 mmol). After the reaction mixture was stirred for 1 h, methyl iodide (0.70 mL, 1.6 g, 11 mmol) was added, and the reaction was warmed to

room temperature, quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ , and extracted with ether. After removal of the solvent under reduced pressure, the resulting product was purified by flash column chromatography ( $\text{SiO}_2$ , hexanes) to give triyne **1** (34.4 mg, 35%) as a white solid that darkens to a yellow color: mp  $63$ – $66^{\circ}\text{C}$ ;  $R_f$  0.30 (hexanes); UV-vis (THF)  $\lambda_{\text{max}}$  (ε) 272 (14 600), 274 (14 600), 287 (29 100), 325 (19 100), 340 (29 900), 365 (29 000) nm; IR ( $\text{CH}_2\text{Cl}_2$  cast) 3119, 3013, 2913, 2219, 2199, 2166, 1612, 1479, 1261  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.38 (d,  $J$  = 1.3 Hz, 1H), 6.84 (d,  $J$  = 15.9 Hz, 1H), 6.40 (m, 2H), 6.04 (dd,  $J$  = 15.9, 0.4 Hz, 1H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, APT,  $\text{CDCl}_3$ ) δ 151.7, 143.8, 132.3, 112.2, 111.7, 103.9, 78.9, 77.7, 75.1, 68.5, 65.0, 59.2, 4.7; EI HRMS  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{O}$  ( $\text{M}^+$ ) 180.0574, found 180.0574. Spectral data were consistent with those reported in ref 8a.

**2-Non-1-en-3,5,7-triynylfuran (1).** Dibromoolefin **12** (0.139 g, 0.407 mmol) was reacted with *n*-BuLi (0.20 mL, 2.5 M in hexanes, 0.49 mmol) as per the general procedure to give triyne **1** (61.9 mg, 84%) as a white solid that turns progressively yellow. Spectral data were consistent with those for the triyne **1** obtained from the previous procedure.

**1-Phenylhepta-1,3,5-triynylfuran (2).** Dibromoolefin **16** (0.131 g, 0.404 mmol) was reacted with *n*-BuLi (0.19 mL, 2.5 M in hexanes, 0.49 mmol) as per the general procedure to give triyne **2** (31.9 mg, 48%) as a white solid: mp 58  $^{\circ}\text{C}$ ;  $R_f$  0.40 (hexanes); UV-vis (THF)  $\lambda_{\text{max}}$  (ε) 241 (61 600), 252 (172 000), 276 (10 100), 292 (19 600), 311 (26 700), 333 (19 700) nm; IR ( $\text{CH}_2\text{Cl}_2$  cast) 2220, 1593, 1490, 1441  $\text{cm}^{-1}$ ; EI HRMS  $m/z$  calcd for  $\text{C}_{13}\text{H}_8$  ( $\text{M}^+$ ) 164.0626, found 164.0624. Anal. Calcd for  $\text{C}_{13}\text{H}_8$ : C, 95.09; H, 4.91. Found C, 94.69; H, 4.64. Spectral data were consistent with literature values.<sup>9b,10a,22</sup>

**Attractylodin (3).** Dibromoolefin **20** (0.145 g, 0.424 mmol) was reacted with *n*-BuLi (0.20 mL, 2.5 M in hexanes, 0.51 mmol) as per the general procedure and purified by column chromatography (pentane) to give diyne **3** (55.9 mg, 72%) as a white solid that turns progressively pale yellow: mp 50–52  $^{\circ}\text{C}$ ;  $R_f$  0.18 (hexanes); UV-vis (THF)  $\lambda_{\text{max}}$  (ε) 260 (11 500), 273 (12 600), 339 (32 700) nm; IR ( $\text{CDCl}_3$  cast) 3113, 2182, 2124, 1616, 1477, 1442  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.37 (m, 1H), 6.77 (d,  $J$  = 15.9 Hz, 1H), 6.40 (dd,  $J$  = 3.4, 1.8 Hz, 1H), 6.35 (m, 1H), 6.31 (m, 1H), 6.09 (d,  $J$  = 15.9 Hz, 1H), 5.58 (m, 1H), 1.82 (dd,  $J$  = 6.9, 1.8 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, APT,  $\text{CDCl}_3$ ) δ 151.9, 143.6, 143.5, 130.7, 112.1, 111.0, 110.0, 104.9, 81.9, 80.2, 77.2, 72.5, 18.9; EI HRMS  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{O}$  ( $\text{M}^+$ ) 182.0732, found 182.0732.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data were consistent with literature values.<sup>14,23</sup>

**2-Hept-1-ene-3,5-diyynylfuran (4).** To a solution of diyne **10** (0.108 g, 0.505 mmol) in a 1:1 mixture of methanol (5 mL) and THF (5 mL) at room temperature was added  $\text{K}_2\text{CO}_3$  (5 mg). After the reaction mixture was stirred for 1 h, saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) was added and the solution was then extracted with ether (20 mL). Evaporation of the solvent in vacuo yielded a white solid that was used directly in the next step. To a solution of the deprotected diyne in THF (10 mL) at  $-78^{\circ}\text{C}$  was added *n*-BuLi (0.20 mL, 2.5 M in hexanes, 0.51 mmol). After the reaction mixture was stirred for 1 h, methyl iodide (0.64 mL, 1.45 g, 10 mmol) was added, and the reaction was warmed to room temperature, quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ , and extracted with ether. After removal of the solvent under reduced pressure, the resulting product was purified by flash column chromatography ( $\text{SiO}_2$ , hexanes) to give diyne **4** (31.2 mg, 40%) as a yellow oil:  $R_f$  0.25 (hexanes); IR ( $\text{CHCl}_3$  cast) 3117, 3046, 2912, 2841, 2230, 2138, 1618, 1480, 1262  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.36 (d,  $J$  = 1.8 Hz, 1H), 6.77 (d,  $J$  = 16.0 Hz, 1H), 6.40 (dd,  $J$  = 3.4, 1.8 Hz, 1H), 6.34 (d,  $J$  = 3.4 Hz, 1H), 6.04 (d,  $J$  = 16.0 Hz, 1H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, APT,  $\text{CDCl}_3$ ) δ 151.9, 143.3, 130.7, 112.0, 110.7, 105.0, 81.3, 77.4, 73.8, 64.6, 4.7; EI HRMS  $m/z$  calcd for  $\text{C}_{11}\text{H}_8\text{O}$  ( $\text{M}^+$ ) 156.0575, found 156.0575.

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**2-Hept-1-ene-3,5-diynylfuran (4).** Dibromoolefin **14** (0.129 g, 0.409 mmol) was reacted with *n*-BuLi (0.20 mL, 2.5 M in hexanes, 0.49 mmol) as per the general procedure to give diyne **4** (37.4 mg, 59%) as a yellow oil. Spectral data were consistent with those for the diyne **4** obtained from the previous procedure.

**[8-(2-Furyl)-oct-7-en-1,3,5-triynyl]trimethylsilane (7).** Dibromoolefin **6** (60.0 mg, 0.151 mmol) was reacted with *n*-BuLi (0.07 mL, 2.5 M in hexanes, 0.18 mmol) as per the general procedure to give triyne **7** (29.5 mg, 82%) as an orange oil: *R*<sub>f</sub> 0.31 (hexanes); IR (CHCl<sub>3</sub> cast) 2959, 2160, 2074, 2070, 1612, 1479, 1251 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 1.6 Hz, 1H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.41 (m, 2H), 6.05 (d, *J* = 15.9 Hz, 1H), 0.23 (s, 9H); <sup>13</sup>C NMR (100 MHz, APT, CDCl<sub>3</sub>) δ 151.6, 144.0, 132.8, 112.3, 112.0, 103.5, 89.6, 88.1, 77.3, 76.8, 67.9, 61.8, -0.5; EI HRMS *m/z* calcd for C<sub>15</sub>H<sub>14</sub>OSi (M<sup>+</sup>) 238.0814, found 238.0814.

**[6-(2-Furyl)-hex-5-ene-1,3-diynyl]trimethylsilane (10).** Dibromoolefin **9** (0.912 g, 2.44 mmol) was reacted with *n*-BuLi (1.17 mL, 2.5 M in hexanes, 2.92 mmol) as per the general procedure to give diyne **10** (0.366 g, 70%) as a yellow oil: *R*<sub>f</sub> 0.3 (hexanes); IR (CHCl<sub>3</sub> cast) 2959, 2925, 2188, 2101, 2095, 1616,

1479, 1251 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 1.8 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.41 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.37 (d, *J* = 3.4 Hz, 1H), 6.04 (d, *J* = 16.0 Hz, 1H), 0.20 (s, 9H); <sup>13</sup>C NMR (100 MHz, APT, CDCl<sub>3</sub>) δ 151.7, 143.6, 131.6, 112.1, 111.4, 104.2, 91.7, 88.0, 77.1, 76.5, -0.4; EI HRMS *m/z* calcd for C<sub>13</sub>H<sub>14</sub>OSi (M<sup>+</sup>) 214.0814, found 214.0814.

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**Supporting Information Available:** General experimental and spectroscopic details for precursor alcohols, ketones, and dibromoolefins, and <sup>1</sup>H and <sup>13</sup>C NMR spectra for precursor alcohols, ketones, dibromoolefins, and di- and triyne products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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