Electronic Supplementary Information for

Rhodium-Catalyzed Carbene Transfer to Alkynes via 2-Furylcarbenes Generated from Enynones

María J. González, Enol López and Rubén Vicente*

Departamento de Química Orgánica e Inorgánica and Instituto Universitario de Química Organometálica “Enrique Moles”. Universidad de Oviedo. c/ Julián Clavería 8, 33007 Oviedo, Spain. Tel: +34 985103075; E-mail: vicenteruben@uniovi.es
| 1. General remarks. | S-3 |
| 2. Preliminary experiments. | S-4 |
| 3. Rhodium-catalyzed carbene transfer generated from enynones to alkynes: Procedures and characterization data of compounds 5a-r/6a-o. | S-6 |
| 4. Rhodium-catalyzed carbene transfer from alkyl substituted enynones to alkynes: Procedures and characterization data of compounds 5s-v. | S-21 |
| 5. Rhodium-catalyzed carbene cyclopropenation of alkynes using enynones as carbene source: Synthesis of cyclopropenes 4a-d. | |
| 5.1. NMR-Monitored Experiments. | S-24 |
| 5.2. Procedures and characterization data for cyclopropenes 4a-d. | S-29 |
| 6. Mechanistic rationale. | S-33 |
| References. | S-36 |
| \(^1\)H-, \(^{13}\)C-NMR spectra for new compounds. | S-37 |
1. General remarks.
All reactions were carried out under an Ar atmosphere using standard Schlenck techniques. Dichloromethane, D<sub>2</sub>-dichloromethane and 1,2-dichloroethane (DCE) were distilled from CaH<sub>2</sub> under N<sub>2</sub> atmosphere. Pentane, toluene and THF were distilled from Na using benzophenone as indicator under N<sub>2</sub> atmosphere. DMF and MeCN were dried over molecular sieves (4 Å). Solvents for column chromatography were obtained from commercial supplier and used without further purification. TLC was performed on aluminium-backed plates coated with silica gel 60 with F<sub>254</sub> indicator. Flash column chromatography was carried out on neutral Al<sub>2</sub>O<sub>3</sub> (50-200 mesh) or deactivated SiO<sub>2</sub> (200-400 mesh).[1] <sup>1</sup>H-NMR (300, 400 MHz) and <sup>13</sup>C-NMR (75 and 100 MHz) spectra were recorded at room temperature in the indicated solvent on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts (δ) are given in ppm relative to TMS (1<sup>1</sup>H, 0.0 ppm) or CDCl<sub>3</sub> (13<sup>1</sup>C, 77.0 ppm). Carbon multiplicities were assigned by DEPT experiments. High-resolution mass spectra were recorded in Agilent 6520Q-TOF and Finnigan Mat95 spectrometers. Enynones 1-2 were prepared according to literature procedures.[2-3] Alkynes 3 purchased from commercial suppliers were distilled prior to use and stored at 4 °C under inert atmosphere. Rhodium catalysts were purchased from commercial suppliers and used as received.

Figure S1. Starting materials used in this work.
2. Preliminary experiments.

Reactions with enynones 1: To a solution of the corresponding enynone 1 (0.25 mmol) and \( p \)-tolylacetylene 3a (3-6 equiv.) in DCE (0.1 M) at 25 ºC, [\( \text{Rh}_2(\text{OAc})_4 \)] (2.5 mol\%) was added. The resulting mixture was stirred in a range of temperatures varying from 0 to 80 ºC for up to 48 h (when the starting enynone was detected by TLC analysis). We did not observe the formation of cyclopropenes or compounds derived from the coupling of both reagents.

\[
\text{1a-h } + \quad \equiv \equiv \quad \text{p-Tol} \quad \xrightarrow{\text{[Rh}_2(\text{OAc})_4 \text{]} (2.5 \text{ mol\%})} \quad \text{DCE, 0-80 ºC} \quad \xrightarrow{X} \\
\text{3a}
\]

Reactions with enynones 2.

Representative procedure for screening conditions: To a solution of the enynone 2a (53 mg, 0.25 mmol) and \( p \)-tolylacetylene 3a (3-6 equiv.) in DCE (2.5 mL, 0.1 M) at 25 ºC, the corresponding rhodium catalyst (2.5 mol\%) was added. The resulting mixture was stirred at this temperature until disappearance of the starting enynone (checked by TLC). The reaction mixture was then filtered through a short pad of Celite® and dried under vacuum. The resulting residue was analyzed by \(^1\text{H-NMR (CDCl}_3\) and purified by flash column chromatography (neutral Al\(_2\)O\(_3\), hexanes:EtOAc 10:1). The ratio of products 4a/5a/6a remained essentially unchanged after a fast purification (NOTE: the long exposure to SiO\(_2\) led to appreciable changes in the ratio and decreased the yield).

The results of the screening are summarized in Table S1. The value of the yield is referred to the mixture of 4a/5a/6a. The ratio 4a:5a:6a was established by integration of representative signals in the \(^1\text{H-NMR spectra.}

S-4
## Table S1: Screening summary.

<table>
<thead>
<tr>
<th>Entry</th>
<th>equiv. 3a</th>
<th>Catalyst</th>
<th>T (ºC)/t (h)</th>
<th>Yield (%)</th>
<th>4a : 5a : 6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>26</td>
<td>6 : 1.5 : 1</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>80</td>
<td>– : 2.0 : 1</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>45</td>
<td>– : 1.3 : 1</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>0 / 4</td>
<td>41</td>
<td>7 : 2.8 : 1</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)](a)</td>
<td>-20 / 24</td>
<td>35</td>
<td>6 : 2.5 : 1</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>80</td>
<td>– : 2.0 : 1</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>[Rh(_2)(OPiv)(_4)]</td>
<td>25 / 7</td>
<td>71</td>
<td>– : 1.2 : 1</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>[Rh(_2)(OTFA)(_4)]</td>
<td>25 / 7</td>
<td>57</td>
<td>– : 3.4 : 1</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>[Rh(_2)(O(_2)CCPh(_3))(_4)]</td>
<td>25 / 7</td>
<td>42</td>
<td>– : 1 : 2.1</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>[Rh(_2)(esp)(_2)]</td>
<td>25 / 7</td>
<td>74</td>
<td>– : 1.5 : 1</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>[Rh(_2)(cap)(_4)]</td>
<td>25 / 23</td>
<td>13(^b,c)</td>
<td>1 : – : –</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>[Rh(_2)(cap)(_4)]</td>
<td>40 / 21</td>
<td>15(^b,d)</td>
<td>1 : – : –</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>[Rh(_2)(cap)(_4)]</td>
<td>70 / 15</td>
<td>24</td>
<td>– : 2.4 : 1</td>
</tr>
<tr>
<td>14(^e)</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>70</td>
<td>– : 2.0 : 1</td>
</tr>
<tr>
<td>15(^f)</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>25</td>
<td>3 : 2.0 : 1</td>
</tr>
<tr>
<td>15(^g)</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>15(^h)</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>15(^i)</td>
<td>6</td>
<td>[Rh(_2)(OAc)(_4)]</td>
<td>25 / 16</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Catalyst loading 10 mol%.  \(^a\) H-NMR yield.  \(^c\) 33% conversion of 2a.  \(^e\) 45% conversion of 2a.  \(^h\) CH\(_2\)Cl\(_2\) as solvent.  \(^f\) THF as solvent.  \(^g\) Toluene as solvent.  \(^h\) Pentane as solvent.  \(^i\) MeCN as solvent. (esp = \(a, a, a', a'\)-tetramethyl-1,3-benzene dipropionate; cap = caprolactamate).
3. Rhodium-catalyzed carbene transfer generated from enynones to alkynes: Procedures and characterization of compounds 5a-r/6a-o.

Representative procedure – Compounds 5a/6a: To a solution of the enynone 2a (50 mg, 0.24 mmol) and p-tolylacetylene 3a (165 mg, 1.42 mmol, 6.0 equiv.) in DCE (2.5 mL, 0.1 M) at 25 ºC, [Rh₂(OAc)₄] (2.6 mg, 2.5 mol%) was added. The resulting mixture was stirred for 15 h at this temperature. The reaction mixture was then filtered through a short pad of Celite® and dried under vacuum and analyzed by ¹H-NMR. The resulting residue was purified by flash column chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, Rᵣ = 0.35; hexanes:EtOAc = 5:1) to afford an inseparable mixture of 5a/6a (62 mg, 80%, 5a:6a = 2:1). Attempts to separate 5a/6a by flash chromatography were unsuccessful due to their similar Rᵣ values in different mixtures tested. Trials with low polar mixtures led to a degradation of the compounds, however, pure samples for analysis were obtained as follows. A pure sample of 5a (18 mg, pale yellow oil) for NMR/HR-MS analysis was obtained by using a Biotage® Isolera™ One apparatus (SiO₂, 50g, hexanes:EtOAc from 98:2 to 84:16 in a 20 min gradient, 12 mL/min). A pure sample of 6a (1 mg, pale yellow oil) for NMR/HR-MS analysis was obtained by flash chromatography from a mixture enriched with 6a (deactivated SiO₂, hexanes:EtOAc = 40:1).

3-Acetyl-2-methyl-6-phenyl-5-(p-tolyl)-4H-cyclopenta[b]furan (5a):

¹H-NMR (400 MHz, CD₂Cl₂): 7.54 (dd, J = 8.3, 1.8 Hz, 2H), 7.42-7.36 (m, 3H), 7.27 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 3.71 (s, 2H), 2.70 (s, 3H), 2.52 (s, 3H), 2.36 (s, 3H).

¹³C-NMR (100 MHz, CD₂Cl₂): 194.2 (C), 160.1 (C), 160.0 (C), 141.6 (C), 137.0 (C), 134.2 (C), 133.0 (C), 130.0 (C), 129.1 (2 x CH), 128.7 (2 x CH), 128.5 (2 x CH), 127.8 (CH), 127.7 (2 x CH), 123.8 (C), 120.7 (C), 35.6 (CH₂), 30.2 (CH₃), 20.9 (CH₃), 14.8 (CH₃).
HR-MS (EI) calc. for [C_{23}H_{20}O_2]^+ 328.1463, found 328.1467.

1-(2-Methyl-5-(2-(p-tolyl)-1H-inden-3-yl)furan-3-yl)ethanone (6a):

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): 7.64 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.37 (dd, J = 7.4, 7.0 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.64 (dt, J = 7.4, 1.1 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 3.92 (s, 2H), 2.61 (s, 3H), 2.42 (s, 3H).

$^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): 193.8 (C, 5b), 157.4 (C), 147.3 (C), 144.6 (C), 144.3 (C), 142.3 (C), 137.8 (C), 133.6 (C), 129.0 (2 x CH), 128.0 (2 x CH), 127.1 (C), 126.6 (CH), 125.2 (CH), 123.6 (CH), 122.8 (C), 120.5 (CH), 109.5 (CH), 42.3 (CH$_2$), 29.0 (CH$_3$), 21.0 (CH$_3$), 14.1 (CH$_3$).

HR-MS (EI) calc. for [C_{23}H_{20}O_2]^+ 328.1463, found 328.1467.

Compounds 5b/6b: The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and phenylacetylene (144 mg, 1.41 mmol, 6.0 equiv.). After 16 h, flash chromatography (neutral Al$_2$O$_3$, hexanes:EtOAc = 20:1, R$_f$ = 0.39; hexanes:EtOAc = 3:1) afforded an inseparable mixture of 5b/6b (65 mg, 88%, 5b:6b = 1.5:1). ($^1$H-NMR, $^{13}$C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): 7.70 (d, J = 7.5 Hz, 1H), 7.61-7.50 (m, 5b/6b), 7.49-7.20 (m, 5b/6b), 6.72 (s, 1H, 6b), 3.94 (s, 2H, 6b), 3.72 (s, 2H, 5b), 2.71 (s, 3H, 5b), 2.61 (s, 3H, 6b), 2.52 (s, 3H, 5b), 2.42 (s, 3H, 6b).

$^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): 194.1 (C, 5b), 193.7 (C, 6b), 160.1 (C, 5b), 159.9 (C, 6b), 157.4 (C, 6b), 147.2 (C, 6b), 144.4 (C), 141.4 (C), 142.4 (C), 141.4 (C), 137.1 (C, 5b), 136.7 (C, 6b), 132.8 (C), 130.6 (C), 128.7 (2 x CH, 5b), 128.6 (2 x CH, 5b), 128.4
Compounds 5c/6c: The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and 4-methoxyphenylacetylene (186 mg, 1.41 mmol, 6.0 equiv.). After 17 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, R₅ = 0.24; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5c/6c (55 mg, 68%, 5c:6c = 2.8:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CDCl₃): 7.62 (d, J = 7.7 Hz, 2H, 6c), 7.54 (d, J = 8.1 Hz, 2H, 5c), 7.50 (d, J = 7.4 Hz, 1H, 6c), 7.40-7.27 (m, 5c/6c), 6.90 (d, J = 8.9 Hz, 2H, 6c), 6.82 (d, J = 8.9 Hz, 2H, 5c), 6.70 (s, 1H, 6c), 3.88 (s, 2H, 6c), 3.86 (s, 3H, 6c), 3.82 (s, 3H, 5c), 3.65 (s, 2H, 5c), 2.71 (s, 3H, 5c), 2.64 (s, 3H, 6c), 2.52 (s, 3H, 5c), 2.44 (s, 3H, 6c).

¹³C-NMR (75 MHz, CDCl₃): 194.5 (C, 5c), 194.2 (C, 6c), 160.1 (C, 5c), 159.2 (C, 6c), 158.7 (C, 5c), 157.6 (C, 6c), 147.5 (C, 6c), 144.4 (C, 6c), 144.3 (C, 6c), 142.0 (C, 6c), 141.07 (C, 5c), 132.90 (C, 5c), 129.6 (C, 5c), 129.52 (C, 5c), 129.46 (2 x CH, 6c), 129.1 (2 x CH, 5c), 128.0 (C), 128.7 (2 x CH, 5c), 128.6 (2 x CH, 6c), 127.8 (CH, 5c), 126.7 (CH, 6c), 126.5 (C, 6c), 125.1 (CH, 6c), 123.6 (CH, 6c), 123.3 (C, 5c), 122.6 (C, 6c), 120.7 (C, 5c), 120.5 (CH, 6c), 113.9 (2 x CH, 5c), 113.8 (2 x CH, 6c), 109.4 (CH, 6c), 55.29 (CH₃, 6c), 55.24 (CH₃, 5c), 42.2 (CH₂, 6c), 35.6 (CH₂, 5c), 30.5 (CH₃, 5c), 29.2 (CH₃, 6c), 15.1 (CH₃, 5c), 14.5 (CH₃, 6c) (a C signal could not be located likely due to overlapping).

HR-MS (EI) calc. for [C₂₂H₁₉O₃]⁺ 344.1412, found 344.1418.
Compounds 5d/6d: The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and 3-methoxyphenylacetylene (186 mg, 1.41 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, Rₙ = 0.21; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5d/6d (56 mg, 69%, 5d:6d = 1.5:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CDCl₃): 7.01 (ddd, J = 7.4, 1.1, 0.9 Hz, 1H, 6d), 7.57 - 7.50 (m, 5d/6d), 7.43 - 7.22 (m, 5d/6d), 7.19 (d, J = 8.0 Hz, 1H, 5d), 7.01 (ddd, J = 7.6, 1.5, 1.0 Hz, 1H, 6d), 6.97 - 6.92 (m, 5d/6d), 6.91 - 6.85 (m, 5d/6d), 6.79 (dd, J = 8.2, 2.6, 0.9 Hz, 1H, 5d), 6.70 (s, 1H, 6d), 3.90 (s, 2H, 6d), 3.79 (s, 2H, 5d), 3.69 (s, 3H, 6d), 3.67 (s, 3H, 5d), 2.71 (s, 3H, 5d), 2.64 (s, 3H, 5d), 2.52 (s, 3H, 5d), 2.42 (s, 3H, 5d).

¹³C-NMR (75 MHz, CDCl₃): 194.4 (C, 5d), 194.15 (C, 6d), 160.5 (C, 5d), 160.0 (C, 6d), 159.5 (2 x C), 157.7 (C, 6d), 147.3 (C, 6d), 144.1 (C, 5d), 144.0 (C, 6d), 142.2 (C), 141.0 (C, 5d), 138.3 (C, 5d), 138.0 (C, 6d), 132.7 (C, 5d), 131.0 (C, 6d), 129.5 (CH, 5d), 129.3 (CH, 6d), 128.8 (2 x CH, 5d), 128.6 (2 x CH, 5d), 128.0 (CH, 5d), 126.7 (CH, 6d), 125.5 (CH, 6d), 124.0 (C, 5d), 123.7 (CH, 6d), 122.7 (C, 6d), 120.84 (CH, 6d), 120.80 (CH, 6d), 120.7 (C, 5d), 120.3 (CH, 5d), 113.7 (CH, 6d), 113.3 (CH, 6d), 113.1 (CH, 5d), 112.9 (CH, 5d), 109.7 (CH, 6d), 55.2 (CH₃, 6d), 55.0 (CH₃, 5d), 42.5 (CH₂, 6d), 35.5 (CH₂, 5d), 30.5 (CH₃, 5d), 29.2 (CH₃, 6d), 15.2 (CH₃, 5d), 14.5 (CH₃, 6d) (a C signal could not be located likely due to overlapping).

HR-MS (EI) calc. for [C₂₃H₂₅O₃]⁺ 344.1412, found 344.1419.

Compounds 5e/6e: The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and 4-fluorophenylacetylene (170 mg, 1.41 mmol, 6.0 equiv.). After 15 h, purification by flash chromatography (deactivated SiO₂, hexanes:EtOAc = 40:1) afforded 5e as pale yellow oil (30 mg, 39%) and 6e as a pale yellow oil (18 mg, 23%) (62% combined yield, 5e:6e = 1.3:1) (Rₙ = 0.36 (6e), 0.27 (5e); hexanes:EtOAc = 5:1).
3-Acetyl-6-(4-fluorophenyl)-2-methyl-5-phenyl-4H-cyclopenta[b]furan (5e):

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): 7.53 (d, $J = 7.4$ Hz, 2H), 7.42-7.33 (m, 5H), 7.01 (t, $J = 8.7$ Hz, 2H), 3.71 (s, 2H), 2.71 (s, 3H), 2.52 (s, 3H).

$^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): 194.0 (C), 161.9 (C, $J = 246.5$ Hz), 160.2 (C), 159.8 (C), 140.2 (C), 133.4 (C, $J = 3.4$ Hz), 132.6 (C), 130.6 (C), 129.6 (2 x CH, $J = 7.9$ Hz), 128.7 (2 x CH), 128.0 (CH), 124.1 (C), 120.7 (C), 115.3 (2 x CH, $J = 21.5$ Hz), 35.7 (CH$_2$), 30.2 (CH$_3$), 14.8 (CH$_3$).

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): -115.63 (s).

HR-MS (EI) calc. for [C$_{22}$H$_{17}$FO$_2$]$^+$ 332.1213, found 332.1215.

1-(5-(2-(4-Fluorophenyl)-1H-inden-3-yl)-2-methylfuran-3-yl)ethanone (6e):

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): 7.69 (td, $J = 7.6$, 0.9 Hz, 1H), 7.56 (td, $J = 7.4$, 1.0 Hz, 1H), 7.45-7.38 (m, 3H), 7.32 (dt, $J = 7.4$, 1.2 Hz, 1H), 7.10 (t, $J = 8.8$ Hz, 2H), 6.74 (s, 1H), 3.92 (s, 2H), 2.61 (s, 3H), 2.43 (s, 3H).

$^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$): 193.6 (C), 162.0 (C, $J = 247.0$ Hz), 157.5 (C), 147.0 (C), 143.9 (C), 143.1 (C), 142.3 (C), 132.9 (C, $J = 3.5$ Hz), 130.0 (2 x CH, $J = 8$ Hz), 127.8 (C), 126.7 (CH), 125.4 (CH), 123.7 (CH), 122.8 (C), 120.6 (CH), 115.2 (2 x CH, $J = 21.5$ Hz), 109.7 (CH), 42.4 (CH$_2$), 29.0 (CH$_3$), 14.1 (CH$_3$).

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$): -114.66 (s).

HR-MS (EI) calc. for [C$_{22}$H$_{17}$FO$_2$]$^+$ 332.1213, found 332.1218.
Compounds 5f/6f: The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and 2-ethynylthiophene (154 mg, 1.41 mmol, 6.0 equiv.). After 13 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, Rᵣ = 0.45; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5f/6f (27 mg, 36%, 5f:6f = 1.3:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (400 MHz, CDCl₃): 7.56-7.47 (m, 5f/6f), 7.45-7.32 (m, 5f/6f), 7.30-7.24 (m, 5f/6f), 7.21-7.18 (m, 5f/6f), 7.09 (dd, J = 5.1, 1.2 Hz, 1H, 6f), 6.97 (dd, J = 3.5, 3.0 Hz, 1H, 5f), 6.77 (s, 1H, 6f), 3.90 (s, 2H, 6f), 3.68 (s, 2H, 5f), 2.67 (s, 3H, 5f), 2.66 (s, 3H, 6f), 2.50 (s, 3H, 5f), 2.46 (s, 3H, 6f).

¹³C-NMR (100 MHz, CDCl₃): 194.4 (C, 5f), 194.2 (C, 6f), 160.5 (C, 5f), 160.1 (C, 6f), 157.9 (C), 147.0 (C, 6f), 144.5 (C), 141.5 (C, 5f), 139.5 (C), 138.0 (C), 137.3 (C), 136.2 (C, 5f), 132.9 (C), 130.2 (C, 6f), 128.8 (2 x CH, 5q), 128.7 (2 x CH, 5q), 128.2 (CH), 127.2 (CH), 127.0 (C, 6d), 126.9 (CH), 126.8 (CH), 125.4 (2 x CH), 125.3 (CH), 123.63 (CH, 5f), 123.4 (CH, 6f), 123.2 (C, 5f), 122.8 (C, 6f), 121.2 (CH), 120.7 (C, 6f), 120.5 (CH), 110.0 (CH, 6f), 42.0 (CH₂, 6f), 35.4 (CH₂, 5f), 30.4 (CH₃, 5f), 29.2 (CH₃, 6f), 15.2 (CH₃, 5f), 14.5 (CH₃, 6f).

HR-MS (EI) calc. for [C₂₀H₁₆O₂S]⁺ 320.0871, found 320.0877.

Compounds 5g/6g: The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and 1-ethynylcyclohex-1-ene (150 mg, 1.41 mmol, 6.0 equiv.). After 17 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, Rᵣ = 0.55; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5g/6g (35 mg, 47%, 5g:6g =
Compounds 5h/6h: The representative procedure was followed using enynone 2b (50 mg, 0.21 mmol) and phenylacetylene (127 mg, 1.25 mmol, 6.0 equiv.). After 24 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, Rᵣ = 0.56; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5h/6h (41 mg, 58%, 5h:6h = 1:5:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CDCl₃): 7.70 (dt, J = 7.5, 0.9, 0.8 Hz, 6h), 7.58-7.52 (m, 5h/6h), 7.42-7.24 (m, 5h/6h), 6.71 (s, 1H, 6h), 3.92 (s, 2H, 6h), 3.70 (s, 2H, 5h), 3.15 (q, J = 7.5 Hz, 2H, 5h), 3.05 (q, J = 7.5 Hz, 2H, 6h), 2.87 (q, J = 7.3 Hz, 2H, 5h), 2.76 (q, J = 7.3 Hz, 2H, 6h), 1.32 (t, J = 7.5 Hz, 3H, 5h), 1.28-1.17 (m, 5h/6h).

¹³C-NMR (75 MHz, CDCl₃): 197.4 (C, 5h), 197.1 (C, 6h), 165.6 (C, 5h), 162.5 (C, 6h), 160.0 (C, 6h), 147.2 (C), 144.1 (C, 5h), 144.0 (C, 6h), 142.3 (C), 141.2 (C), 137.2 (C,
5h), 136.9 (C, 6h), 132.7 (C), 130.8 (C), 128.3 (2 x CH), 128.6 (2 x CH), 128.5 (2 x CH), 128.3 (various CH), 128.0 (various CH), 127.7 (CH), 127.0 (CH), 126.8 (CH), 125.4 (CH), 123.7 (CH), 123.6 (C, 5h), 121.1 (C, 6h), 120.7 (CH), 119.3 (C, 5h), 109.0 (CH, 6h), 42.5 (CH₂, 6h), 35.93 (CH₂, 5h), 35.86 (CH₂, 5h), 34.5 (CH₂, 6h), 22.4 (CH₂, 5h), 21.7 (CH₂, 6h), 12.6 (CH₃, 5h), 12.1 (CH₃, 6h), 7.9 (CH₃, 6h), 7.8 (CH₃, 5h) (a C signal could not be located likely due to overlapping, various aromatic CH signals are overlapped and cannot be distinguish).

HR-MS (EI) calc. for [C₂₄H₂₅O₂]⁺ 342.1620, found 342.1623.

**Compounds 5i/6i:** The representative procedure was followed using enynone 2b (50 mg, 0.21 mmol) and ρ-tolylacetylene (145 mg, 1.25 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, Rf = 0.42; hexanes:EtOAc = 10:1) afforded an inseparable mixture of 5i/6i (40 mg, 54%, 5i:6i = 2:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

**¹H-NMR** (300 MHz, CDCl₃): 7.67 (td, J = 7.5, 0.9 Hz, 1H, 6i), 7.60-7.50 (m, 5i/6i), 7.42-7.25 (m, 5i/6i), 7.19 (d, J = 7.9 Hz, 2H, 6i), 7.11 (d, J = 7.9 Hz, 2H, 5i), 6.72 (s, 1H, 6i), 3.91 (s, 2H, 6i), 3.68 (s, 2H, 5i), 3.12 (q, J = 7.5 Hz, 2H, 5i), 3.07 (q, J = 7.5 Hz, 2H, 6i), 2.87 (q, J = 7.3 Hz, 2H, 5i), 2.78 (q, J = 7.3 Hz, 2H, 6i), 2.41 (s, 3H, 6i), 2.37 (s, 3H, 5i), 1.39 (t, J = 7.5 Hz, 3H, 5i), 1.36-1.21 (m, 5i/6i).

**¹³C-NMR** (75 MHz, CDCl₃): 197.4 (C, 5i), 197.2 (C, 6i), 165.5 (C), 162.5 (C, 6i), 160.1 (C, 5i), 147.3 (C, 6i), 144.3 (C, 5i), 142.2 (C, 6i), 141.3 (C, 5i), 137.6 (C, 6i), 136.9 (C, 5i), 134.3 (C, 5i), 133.8 (C, 6i), 132.9 (C, 5i), 130.2 (C, 6i), 129.2 (2 x CH, 5i), 129.0 (2 x CH, 6i), 128.8 (2 x CH, 5i), 128.6 (2 x CH, 6i), 128.1 (2 x CH, 6i), 127.8 (3 x CH, 5i, overlapped signal), 126.7 (CH, 6i), 125.2 (CH, 6i), 123.7 (CH, 6i), 123.3 (C, 5i), 121.1 (C, 6i), 120.6 (CH, 6i), 119.3 (C, 5i), 109.0 (CH, 6i), 42.4 (CH₂, 6i), 35.9 (CH₂, 5i), 35.8 (CH₂, 5i), 34.5 (CH₂, 6i), 22.4 (CH₂, 5i), 21.7 (CH₂, 6i), 21.3 (CH₃, 6i), 21.2 (CH₃, 5i), 12.6 (CH₃, 5i), 12.2 (CH₃, 6i), 7.9 (CH₃, 6i), 7.8 (CH₃, 5i) (two C signals could not be located likely due to overlapping).

HR-MS (EI) calc. for [C₂₅H₂₆O₂]⁺ 356.1776, found 356.1779.
Compounds 5j/6j: The representative procedure was followed using enynone 2c (50 mg, 0.21 mmol) and phenylacetylene (126 mg, 1.24 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, Rᵣ = 0.33; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5j/6j (40 mg, 56%, 5j:6j = 1.3:1). (^1H-NMR, ^13C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

^1H-NMR (300 MHz, CDCl₃): 7.70 (td, J = 7.7, 0.7 Hz, 1H, 6j), 7.57-7.54 (m, 5j/6j), 7.41-7.33 (m, 5j/6j), 6.77 (s, 6j), 4.38 (q, J = 7.1 Hz, 2H, 5j, overlapped signal), 4.35 (q, J = 7.1 Hz, 2H, 6j, overlapped signal), 3.92 (s, 2H, 6j), 3.68 (s, 2H, 5j), 2.73 (s, 3H, 5j), 2.61 (s, 3H, 6j), 1.43 (t, J = 7.1 Hz, 3H, 5j, overlapped signal), 1.40 (t, J = 7.1 Hz, 3H, 6j, overlapped signal).

^13C-NMR (75 MHz, CDCl₃): 164.4 (C, 5j), 164.1 (C, 6j), 161.0 (C, 5j), 160.1 (C), 158.4 (C), 147.3 (C), 144.2 (C), 144.1 (C), 142.3 (C), 141.5 (C), 137.4 (C), 136.7 (C), 132.9 (C), 130.6 (C), 128.8 (2 x CH), 128.6 (2 x CH), 128.4 (2 x CH), 128.3 (4 x CH), 128.0 (2 x CH), 127.8 (CH), 127.7 (CH), 126.9 (CH), 126.7 (CH), 125.3 (CH), 125.1 (C), 123.7 (CH), 120.8 (CH), 114.9 (C), 113.0 (C), 109.9 (CH, 6j), 60.22 (CH₂), 60.16 (CH₂), 42.4 (CH₂, 6j), 35.1 (CH₂, 5j), 14.6 (CH₃), 14.5 (CH₃), 14.4 (CH₃), 13.9 (CH₃) (a C signal could not be located likely due to overlapping).

HR-MS (EI) calc. for [C₂₃H₂₀O₃]⁺ 344.1412, found 344.1418.

Compounds 5k/6k: The representative procedure was followed using enynone 2c (50 mg, 0.21 mmol) and p-tolylacetylene (144 mg, 1.24 mmol, 6.0 equiv.). After 48 h, flash chromatography (neutral Al₂O₃, hexane:EtOAc = 20:1, Rᵣ = 0.58; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5k/6k (38 mg, 51%, 5k:6k = 1.5:1). (^1H-NMR, ^13C-
NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned.

$^1$H-NMR (300 MHz, CDCl$_3$): 7.65 (d, $J = 7.6$ Hz, 1H, 6k), 7.57-7.49 (m, 5k/6k), 7.41-7.22 (m, 5k/6k), 7.17 (d, $J = 8.0$ Hz, 2H, 6k), 7.09 (d, $J = 7.9$ Hz, 2H, 5k), 6.67 (s, 6k), 4.37 (q, $J = 7.2$ Hz, 2H, 5k, overlapped signal), 4.33 (q, $J = 7.2$ Hz, 2H, 6k, overlapped signal), 3.90 (s, 2H, 5k), 3.65 (s, 2H, 6k), 2.71 (s, 3H, 6k), 2.62 (s, 3H, 5k), 2.40 (s, 3H, 6k), 2.36 (s, 3H, 5k), 1.42 (t, $J = 7.2$ Hz, 2H, 5k, overlapped signal), 1.39 (t, $J = 7.2$ Hz, 2H, 6k, overlapped signal).

$^{13}$C-NMR (75 MHz, CDCl$_3$): 164.5 (C, 5k), 164.2 (C, 6k), 160.8 (C, 5k), 160.2 (C), 158.3 (C), 147.4 (C, 6k), 144.4 (C), 144.3 (C), 142.1 (C), 141.7 (C, 5k), 137.6 (C, 6k), 136.7 (C, 6k), 134.5 (C, 5k), 133.7 (C, 6k), 133.1 (C, 5k), 130.0 (C), 129.1 (2 x CH, 5k), 129.0 (2 x CH, 6k), 128.8 (2 x CH, 5k), 128.6 (2 x CH, 5k), 128.1 (2 x CH, 6k), 127.8 (2 x CH, 5k), 127.7 (CH, 5k), 127.3 (C, 6k), 126.7 (CH, 6k), 125.2 (CH, 6k), 124.7 (C, 5k), 123.6 (CH, 6k), 120.7 (CH, 6k), 114.9 (C, 6k), 112.9 (C, 5k), 109.8 (CH, 6k), 60.2 (CH$_2$, 6k), 60.1 (CH$_2$, 5k), 42.3 (CH$_2$, 6k), 35.1 (CH$_2$, 5k), 21.3 (CH$_3$, 6k), 21.2 (CH$_3$, 5k), 14.5 (CH$_3$, 5k), 14.45 (CH$_3$, 6k), 14.41 (CH$_3$, 6k), 13.9 (CH$_3$, 6k).

HR-MS (EI) calc. for [C$_{24}$H$_{22}$O$_2$]$^+$ 358.1569, found 358.1574.

**Compounds 5l/6l**: The representative procedure was followed using enynone 2d (50 mg, 0.21 mmol) and phenylacetylene (126 mg, 1.24 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al$_2$O$_3$, hexanes:EtOAc = 10:1, R$_f$ = 0.21; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5l/6l (33 mg, 46%, 5l:6l = 1:1). ($^1$H-NMR, $^{13}$C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

$^1$H-NMR (300 MHz, CDCl$_3$): 7.59 (d, $J = 8.4$ Hz, 1H, 6l), 7.49 (d, $J = 8.4$ Hz, 2H, 5l), 7.41-7.20 (m, 5l/6l), 7.12 (d, $J = 2.3$ Hz, 1H, 6l), 6.94 (dd, $J = 8.4$, 2.3 Hz, 1H, 6l, overlapped signal), 7.59 (d, $J = 8.4$ Hz, 2H, 5l, overlapped signal), 6.64 (s, 1H, 6l), 3.89 (s, 3H), 3.87 (s, 2H, 6l), 3.85 (s, 3H), 3.67 (s, 2H, 5l), 2.71 (s, 3H), 2.62 (s, 3H), 2.51 (s, 3H), 2.40 (s, 3H).

S-15
$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): 194.1 (C), 193.7 (C), 160.1 (C), 160.0 (C), 159.4 (C), 158.4 (C), 157.3 (C), 147.4 (C), 144.2 (C), 142.0 (C), 140.0 (C), 137.4 (C), 137.1 (C), 136.9 (C), 130.1 (C), 129.9 (2 x CH), 128.4 (2 x CH), 128.2 (2 x CH), 128.1 (2 x CH), 127.8 (2 x CH), 127.4 (CH), 127.2 (C), 126.8 (CH), 125.0 (C), 124.1 (C), 122.7 (C), 121.2 (CH, 6l), 120.7 (C), 113.9 (2 x CH, 5l), 112.3 (CH, 6l), 109.9 (CH, 6l), 109.4 (CH, 6l), 55.4 (CH$_3$), 55.2 (CH$_3$), 42.3 (CH$_2$, 5l), 35.5 (CH$_2$, 5l), 30.3 (CH$_3$), 29.0 (CH$_3$), 14.8 (CH$_3$), 14.1 (CH$_3$).

HR-MS (EI) calc. for [C$_{23}$H$_{20}$O$_3$]$^+$ 344.1412, found 344.1418.

**Compounds 5m/6m:** The representative procedure was followed using enynone 2d (50 mg, 0.21 mmol) and $p$-tolylacetylene (144 mg, 1.24 mmol, 6.0 equiv.). After 48 h, flash chromatography (Al$_2$O$_3$, hexanes:EtOAc = 10:1, $R_t = 0.26$; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5m/6m (37 mg, 50%, 5m:6m = 2.7:1). ($^1$H-NMR, $^{13}$C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

$^1$H-NMR (300 MHz, CDCl$_3$): 7.56 (d, $J = 8.4$ Hz, 1H, 6m), 7.49 (d, $J = 8.9$ Hz, 2H, 5m), 7.31-7.25 (m, 5m/6m), 7.17 (d, $J = 8.0$ Hz, 1H, 6m), 7.12-7.07 (m, 5m/6m), 6.94-6.89 (m, 5m/6m), 6.66 (s, 1H, 6m), 3.88 (s, 2H, 6m), 3.85 (s, 3H, 5m/6m, overlapped signals), 3.65 (s, 2H, 5m), 2.71 (s, 3H, 5m), 2.63 (s, 3H, 6m), 2.51 (s, 3H, 5m), 2.42 (s, 3H, 6m), 2.39 (s, 3H, 6m), 2.36 (s, 3H, 5m).

$^{13}$C-NMR (75 MHz, CDCl$_3$): 194.6 (C, 5m), 194.2 (C, 6m), 160.3 (C), 160.2 (C, 5m), 159.2 (C, 5m), 158.2 (C, 6m), 157.5 (C, 6m), 147.7 (C, 6m), 144.0 (C, 6m), 142.1 (C, 6m), 140.0 (C, 5m), 137.4 (C), 136.7 (C, 5m), 134.4 (C, 5m), 133.8 (C, 6m), 129.9 (2 x CH, 5m), 129.7 (C, 5m), 129.2 (2 x CH, 5m), 129.0 (2 x CH, 6m), 128.0 (2 x CH, 6m), 127.7 (2 x CH, 5m), 126.7 (C, 6m), 125.2 (C, 5m), 123.5 (C, 5m), 122.7 (C, 6m), 121.2 (CH, 6m), 120.7 (C, 5m), 114.0 (2 x CH, 5m), 112.3 (CH, 6m), 110.0 (CH, 6m), 109.2 (CH, 6m), 55.6 (CH$_3$, 6m), 55.2 (CH$_3$, 5m), 42.3 (CH$_2$, 6m), 35.5 (CH$_2$, 5m), 30.5 (CH$_3$, 5m), 29.2 (CH$_3$, 6m), 21.3 (CH$_3$, 6m), 21.2 (CH$_3$, 5m), 15.1 (CH$_3$, 5m), 14.5 (CH$_3$, 6m) (a C signal could not be located likely due to overlapping).

HR-MS (EI) calc. for [C$_{24}$H$_{22}$O$_3$]$^+$ 358.1569, found 358.1572.
Compounds 5n/6n: The representative procedure was followed using enynone 2d (50 mg, 0.21 mmol) and 4-methoxyphenylacetylene (163 mg, 1.24 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 5:1, Rᵣ = 0.27; hexanes:EtOAc = 3:1) afforded an inseparable mixture of 5n/6n (44 mg, 57%, 5n:6n = 3.3:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CD₂Cl₂): 7.53 (d, J = 8.5 Hz, 1H, 6n), 7.48 (d, J = 8.9 Hz, 2H, 5n), 7.37-7.28 (m, 5n/6n), 7.12 (d, J = 2.1 Hz, 1H, 6n), 6.96-6.88 (m, 5n/6n), 6.85 (d, J = 8.9 Hz, 1H, 6n), 6.67 (s, 1H, 6n), 3.87 (s, 3H, 6n), 3.85 (s, 3H - 5n + 2H - 6n + 3H - 6n, overlapped signals), 3.82 (s, 3H, 5n), 3.65 (s, 2H, 5n), 2.69 (s, 3H, 5n), 2.62 (s, 3H, 6n), 2.50 (s, 3H, 5n), 2.43 (s, 3H, 6n).

¹³C-NMR (75 MHz, CD₂Cl₂): 194.2 (C, 5n), 193.8 (C, 6n), 160.2 (C, 5n), 159.7 (C, 5n), 159.3 (C, 5n), 159.1 (C, 6n), 158.7 (C, 5n), 158.2 (C, 6n), 157.2 (C, 6n), 147.6 (C, 6n), 143.9 (C, 6n), 141.9 (C, 6n), 139.9 (2 x C, 5n), 137.4 (C, 6n), 129.9 (2 x CH, 5n), 129.3 (2 x CH, 6n), 129.1 (C, 6n), 129.0 (2 x CH, 5n), 128.9 (C, 5n), 126.0 (C, 6n), 125.3 (C, 5n), 123.3 (C, 5n), 122.7 (C, 6n), 120.8 (CH, 6n), 120.7 (C, 5n), 113.9 (2 x CH, 5n), 113.8 (2 x CH, 5n), 113.6 (2 x CH, 6n), 112.1 (CH, 6n), 109.9 (CH, 6n), 109.3 (CH, 6n), 55.4 (CH₃, 6n, the second methoxy group is overlapped), 55.2 (CH₃, 5n), 55.2 (CH₃, 5n), 42.1 (CH₂, 6n), 35.5 (CH₂, 5n), 30.2 (CH₃, 5n), 29.0 (CH₃, 6n), 14.7 (CH₃, 5n), 14.1 (CH₃, 6n).

HR-MS (EI) calc. for [C₂₄H₂₂O₄⁺] 374.1518, found 374.1522.
Compounds 5o/6o: The representative procedure was followed using enynone 2d (50 mg, 0.21 mmol) and 4-fluorophenylacetylene (148 mg, 1.25 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, Rᵣ = 0.15; hexanes:EtOAc = 5:1) afforded an inseparable mixture of 5o/6o (38 mg, 51%, 5o:6o = 1.5:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CDCl₃): 7.57 (d, J = 8.5 Hz, 1H, 6o), 7.46 (d, J = 8.8 Hz, 2H, 5o), 7.39-7.28 (m, 5o/6o), 7.13-6.89 (m, 5o/6o), 6.65 (s, 1H, 6o), 3.88 (s, 3H, 6o), 3.85 (s, 3H, 5o), 3.83 (s, 2H, 6o), 3.63 (s, 2H, 5o), 2.71 (s, 3H, 5o), 2.61 (s, 3H, 6o), 2.51 (s, 3H, 5o), 2.37 (s, 3H, 6o).

¹³C-NMR (75 MHz, CDCl₃): 194.4 (C, 5o), 194.1 (C, 6o), 163.1 (C, J = 247.6 Hz, 6o), 162.8 (C, J = 247.1 Hz, 5o), 160.4 (C, 6o), 160.1 (C, 6o), 159.4 (C, 6o), 158.4 (C, 6o), 157.6 (C, 6o), 147.4 (C), 143.9 (C, 5o), 140.7 (C), 138.6 (C, 5o), 137.0 (C), 133.5 (C, J = 3.1 Hz, 5o), 132.9 (C, J = 2.9 Hz, 6o), 130.3 (C), 130.0 (2 x CH, 5o), 129.8 (2 x CH, J = 7.9 Hz, 6o), 129.5 (2 x CH, J = 7.8 Hz, 5o), 127.3 (C, 6o), 124.7 (C), 123.8 (C, 5o), 122.7 (C, 6o), 121.3 (CH, 6o), 120.7 (C, 6o), 115.5 (2 x CH, J = 21.4 Hz, 5o), 115.3 (2 x CH, J = 21.4 Hz, 6o), 114.1 (2 x CH, 5o), 112.4 (CH, 6o), 110.1 (CH, 6o), 109.4 (CH, 6o), 55.6 (CH₃, 6o), 55.3 (CH₃, 5o), 42.4 (CH₂, 6o), 35.6 (CH₂, 5o), 30.4 (CH₃, 5o), 29.2 (CH₃, 6o), 15.1 (CH₃, 5o), 14.4 (CH₃, 6o).

¹⁹F-NMR (282 MHz, CDCl₃): -115.1 (s, 6o), -115.9 (s, 5o).

HR-MS (EI) calc. for [C₂₃H₁₉F₃O₃]⁺ 362.1318, found 362.1326.

3-Acetyl-2-methyl-6-(4-nitrophenyl)-5-phenyl-4H-cyclopenta[b]furan (5p): The representative procedure was followed using enynone 2e (50 mg, 0.19 mmol) and
phenylacetylene (119 mg, 1.17 mmol, 6.0 equiv.). After 18 h, purification by flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, Rᵣ = 0.40; hexanes:EtOAc = 3:1) afforded 5p (17 mg, 25%) as a yellow oil.

**¹H-NMR** (300 MHz, CDCl₃): 8.21 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.33 (bs, 5H), 3.76 (s, 2H), 2.74 (s, 3H), 2.53 (s, 3H).

**¹³C-NMR** (75 MHz, CDCl₃): 194.1 (C), 160.8 (C), 158.7 (C), 147.0 (C), 145.0 (C), 139.4 (C), 136.2 (C), 129.5 (2 x CH), 128.8 (2 x CH), 128.7 (C), 128.1 (2 x CH), 128.0 (CH), 124.6 (C), 123.9 (2 x CH), 120.8 (C), 36.3 (CH₂), 30.4 (CH₃), 15.2 (CH₃).

**HR-MS** (EI) calc. for [C₂₂H₁₇NO₄]⁺ 359.1158, found 359.1160.

3-Acetyl-5-(4-methoxyphenyl)-2-methyl-6-(4-nitrophenyl)-4H-cyclopenta[b]furan (5q): The representative procedure was followed using enynone 2e (50 mg, 0.19 mmol) and 4-methoxyphenylacetylene (156 mg, 1.17 mmol, 6.0 equiv.). After 15 h, purification by flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, Rᵣ = 0.47; hexanes:EtOAc = 3:1) afforded 5q (38 mg, 50%) as a yellow oil.

**¹H-NMR** (300 MHz, CDCl₃): 8.19 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 3.69 (s, 2H), 2.71 (s, 3H), 2.50 (s, 3H).

**¹³C-NMR** (75 MHz, CDCl₃): 194.2 (C), 160.5 (C), 159.4 (C), 158.9 (C), 146.8 (C), 144.9 (C), 139.7 (C), 129.4 (2 x CH), 129.3 (2 x CH), 128.7 (C), 127.5 (C), 123.9 (2 x CH), 120.8 (C), 114.3 (2 x CH), 55.3 (CH₃), 36.3 (CH₂), 30.4 (CH₃), 15.2 (CH₃) (a C signal is overlapped).

**HR-MS** (EI) calc. for [C₂₃H₁₉NO₅]⁺ 389.1263, found 389.1266.
3-Acetyl-5-(3-Methoxyphenyl)-2-methyl-6-(4-nitrophenyl)-4H-cyclopenta[b]furan (5r): The representative procedure was followed using enynone 2e (50 mg, 0.19 mmol) and 3-methoxyphenylacetylene (154 mg, 1.16 mmol, 6.0 equiv.). After 15 h, purification by flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, Rᵣ = 0.50; hexanes:EtOAc = 3:1) afforded 5r (27 mg, 35%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃): 8.21 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 9.0 Hz, 2H), 7.28-7.21 (m, 1H), 6.91-6.85 (m, 2H), 6.84 (bs, 1H), 3.75 (s, 3H), 3.73 (s, 2H), 2.73 (s, 3H), 2.52 (s, 3H).

¹³C-NMR (75 MHz, CDCl₃): 194.1 (C), 160.9 (C), 159.8 (C), 158.7 (C), 147.0 (C), 144.7 (C), 139.3 (C), 137.5 (C), 129.9 (CH), 129.5 (2 x CH), 128.9 (C), 124.6 (C), 123.9 (2 x CH), 120.8 (C), 120.5 (CH), 113.8 (CH), 113.2 (CH), 55.2 (CH₃), 36.3 (CH₂), 30.5 (CH₃), 15.2 (CH₃).

HR-MS (EI) calc. for [C₂₃H₁₉NO₅]⁺ 389.1263, found 389.1265.
4. Rhodium-catalyzed carbene transfer from alkyl substituted enynones to alkynes: Procedures and characterization data of compounds 5s-v.

Representative procedure (5s): To a solution of the enynone 2f (50 mg, 0.24 mmol) and p-tolylacetylene 3a (168 mg, 1.45 mmol, 6.0 equiv.) in DCE (2.5 mL, 0.1 M) at 25 °C, [Rh₂(OAc)₄] (10 mg, 10 mol%) was added. The resulting mixture was stirred for 15 h at this temperature. The reaction mixture was then filtered through a short pad of Celite® and dried under vacuum. The resulting residue was purified by flash column chromatography (deactivated SiO₂, hexanes:EtOAc = 100:1, Rf = 0.21; hexanes:EtOAc = 5:1) to afford 5s (31 mg, 40%) as a yellow oil.

3-Acetyl-2-methyl-6-pentyl-5-(p-tolyl)-4H-cyclopenta[b]furan (5s):

**¹H-NMR** (300 MHz, CD₂Cl₂): 7.28 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 3.50 (s, 2H), 2.69 (s, 3H), 2.66 (dd, J = 7.8, 7.8 Hz, 2H), 2.47 (s, 3H), 2.38 (s, 3H), 1.79-.168 (m, 2H), 1.42-1.31 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H).

**¹³C-NMR** (75 MHz, CD₂Cl₂): 194.7 (C), 161.7 (C), 159.9 (C), 140.3 (C), 136.3 (C), 134.6 (C), 131.5 (C), 129.2 (2 x CH), 127.5 (2 x CH), 123.2 (C), 120.5 (C), 34.7 (CH₂), 31.9 (CH₂), 30.4 (CH₃), 28.3 (CH₂), 26.0 (CH₂), 22.5 (CH₂), 21.2 (CH₃), 15.1 (CH₃), 14.0 (CH₃).

**HR-MS** (EI) calc. for [C₂₂H₂₆O₂]⁺ 322.1933, found 322.1940.
3-Acetyl-2-methyl-6-phenethyl-5-(p-tolyl)-4H-cyclopenta[b]furan (5t): The representative procedure was followed using enynone 2g (50 mg, 0.21 mmol), p-tolylacetylene (145 mg, 1.25 mmol, 6.0 equiv.) and [Rh2(OAc)4] (2.5 mg, 2.5 mol%). After 12 h, purification by flash column chromatography (deactivated SiO2, hexanes:EtOAc = 40:1, Rf = 0.37; hexanes:EtOAc = 5:1) afforded 5t (38 mg, 52%) as a yellow oil. (An unidentified by-product was detected along with 5t, but its structure was not established due to the impossibility to obtain a pure sample).

\[^1\text{H-NMR}\] (400 MHz, CD2Cl2): 7.33-7.25 (m, 3H), 7.24-7.16 (m, 6H), 3.51 (s, 2H), 3.11-3.04 (m, 2H), 3.03-2.96 (m, 2H), 2.69 (s, 3H), 2.48 (s, 3H), 2.38 (s, 3H).

\[^{13}\text{C-NMR}\] (100 MHz, CDCl3): 194.7 (C), 161.4 (C), 160.1 (C), 141.5 (C), 141.1 (C), 136.4 (C), 134.4 (C), 130.3 (C), 129.2 (2 x CH), 128.42 (2 x CH), 128.38 (2 x CH), 127.5 (2 x CH), 126.1 (CH), 123.3 (C), 120.6 (C), 34.8 (CH2), 34.7 (CH2), 30.4 (CH3), 28.1 (CH2), 21.2 (CH3), 15.1 (CH3).


3-Acetyl-2-methyl-5-(4-methoxyphenyl)-6-pentyl-4H-cyclopenta[b]furan (5u): The representative procedure was followed using enynone 2f (50 mg, 0.24 mmol), 4-methoxyphenylacetylene (192 mg, 1.45 mmol, 6.0 equiv.) and [Rh2(OAc)4] (2.5 mg, 2.5 mol%). After 13 h, purification by flash column chromatography (neutral Al2O3, hexanes:EtOAc = 10:1, Rf = 0.39; hexanes:EtOAc = 5:1) afforded 5u (34 mg, 41%) as a yellow oil.

\[^1\text{H-NMR}\] (300 MHz, CDCl3): 7.31 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 3.47 (s, 2H), 2.68 (s, 3H), 2.63 (dd, J = 8.8, 7.8 Hz, 2H), 2.46 (s, 3H), 1.76-1.69 (m, 2H), 1.40-1.28 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H).

\[^{13}\text{C-NMR}\] (75 MHz, CDCl3): 194.7 (C), 161.7 (C), 159.8 (C), 158.3 (C), 140.0 (C), 130.8 (C), 130.2 (C), 128.7 (2 x CH), 122.8 (C), 120.5 (C), 114.0 (2 x CH), 55.3 (CH3), 34.7
(CH₂), 31.9 (CH₂), 30.4 (CH₃), 28.3 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 15.1 (CH₃), 14.0 (CH₃).

HR-MS (El) calc. for [C₂₂H₂₆O₃]+ 338.1882, found 338.1888.

3-Ethoxycarbonyl-2-methyl-5-(4-methoxyphenyl)-6-pentyl-4H-cyclopenta[b]furan (5v): The representative procedure was followed using enynone 2h (50 mg, 0.21 mmol), 4-methoxyphenylacetylene (168 mg, 1.27 mmol, 6.0 equiv.) and [Rh₂(OAc)₄] (2.5 mg, 2.5 mol%). After 12 h, purification by flash column chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, Rₚ = 0.15; hexanes:EtOAc = 5:1) afforded 5v (28 mg, 36%) as a yellow oil. (An unidentified by-product was detected, but its structure was not established due to the impossibility to obtain a pure sample).

¹H-NMR (300 MHz, CD₂Cl₂): 7.35 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.46 (s, 2H), 2.68 (s, 3H, overlapped signal), 2.65 (dd, J = 7.9, 7.9 Hz, 2H, overlapped signal), 1.79-1.71 (m, 2H), 1.42-1.33 (m, 7H, overlapped signals), 0.92 (t, J = 8.0 Hz, 3H).

¹³C-NMR (75 MHz, CDCl₃): 164.6 (C), 161.8 (C), 160.3 (C), 158.2 (C), 140.3 (C), 130.6 (C), 130.5 (C), 128.7 (2 x CH), 123.8 (C), 113.9 (2 x CH), 112.7 (C), 60.0 (CH₂), 55.3 (CH₃), 34.2 (CH₂), 31.9 (CH₂), 28.4 (CH₂), 26.0 (CH₂), 22.5 (CH₂), 14.5 (CH₃), 14.4 (CH₃), 14.0 (CH₃).

5. Rhodium-catalyzed carbene cyclopropenation of alkynes using enynones as carbene source: Synthesis of cyclopropenes 4a-d.

During the preliminary studies, all attempts to isolate the corresponding cyclopropene 4a were unsuccessful as compounds 5a/6a were always obtained. TLC analysis of the reaction did not provide information since all compounds were almost undistinguishable. Thus, attempts under mild reaction conditions and low conversions led to 4a with variable amounts of 5a/6a. In order to get more precise information, we decided to monitor the reaction by $^1$H-NMR analysis.

5.1. NMR-Monitored Experiments.

Representative procedure for the $^1$H-NMR-monitor reactions.

A solution of 2a (42 mg, 0.2 mmol), 3a (n equiv.) and 1,1,2,2-tetrachloroethane (37 mg, 0.2 mmol, 1.0 equiv., as internal standard) in CD$_2$Cl$_2$ (2.0 mL) (distilled over CaH$_2$ and stored in the dark over molecular sieves 4Å) was prepared at the indicated temperature. From the resulting solution, 50 µL were taken using a microsyringe under a positive pressure of N$_2$, placed in an NMR tube and diluted in CDCl$_3$ (3.0 mL) (stored at the reaction temperature) and a $^1$H-NMR measurement was immediately done (the NMR apparatus was kept at the reaction temperature). Then, [Rh$_2$(OAc)$_4$] (2.2 mg, 2.5 mol%) were added to the reaction mixture and it was stirred at the indicated temperature. Samples were taken and analyzed periodically in the same manner as described before. (NOTE: It was not possible to follow the reaction in the NMR tube since it resulted very slow. This fact could be attributed to the low solubility of the catalyst).
The results of the optimization experiments are summarized below. These include tables with conversions and yields calculated through integration of selected signals of the $^1$H-NMR spectra and the corresponding NMR-yield vs time plots to represent the reaction profile.

**Experiment 1.** Reaction Conditions: 14 equiv. of 3a at 25 ºC.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>4a:5a+6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>17</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>20</td>
<td>38</td>
<td>37</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>30</td>
<td>55</td>
<td>52</td>
<td>2</td>
<td>1</td>
<td>17:1</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>76</td>
<td>64</td>
<td>8</td>
<td>4</td>
<td>5.3:1</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>88</td>
<td>65</td>
<td>14</td>
<td>7</td>
<td>3.1:1</td>
<td></td>
</tr>
</tbody>
</table>

**Experiment 2.** Reaction Conditions: 9 equiv. of 3a at 25 ºC.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>4a:5a+6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>20</td>
<td>53</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>30</td>
<td>77</td>
<td>59</td>
<td>9</td>
<td>5</td>
<td>4.2:1</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>91</td>
<td>59</td>
<td>21</td>
<td>11</td>
<td>1.9:1</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>100</td>
<td>50</td>
<td>29</td>
<td>18</td>
<td>1.1:1</td>
<td></td>
</tr>
</tbody>
</table>
**Experiment 3.** Reaction Conditions: 6 equiv. of 3a at 25 ºC.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>4a:5a+6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0:1</td>
</tr>
<tr>
<td>10</td>
<td>17</td>
<td>17</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>20</td>
<td>43</td>
<td>37</td>
<td>3</td>
<td>2</td>
<td>7.4:1</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>63</td>
<td>49</td>
<td>9</td>
<td>5</td>
<td>3.5:1</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>82</td>
<td>56</td>
<td>16</td>
<td>8</td>
<td>2.3:1</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>91</td>
<td>49</td>
<td>23</td>
<td>13</td>
<td>1.4:1</td>
<td></td>
</tr>
</tbody>
</table>

**Experiment 4.** Reaction Conditions: 3 equiv. of 3a at 25 ºC.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>4a:5a+6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0:1</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>20</td>
<td>27</td>
<td>24</td>
<td>2</td>
<td>1</td>
<td>8:1</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>44</td>
<td>37</td>
<td>5</td>
<td>2</td>
<td>5.3:1</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>61</td>
<td>46</td>
<td>9</td>
<td>5</td>
<td>3.3:1</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>79</td>
<td>45</td>
<td>19</td>
<td>11</td>
<td>1.5:1</td>
<td></td>
</tr>
</tbody>
</table>

**Experiment 5.** Reaction Conditions: 1 equiv. of 3a at 25 ºC.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>4a:5a+6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0:1</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>30</td>
<td>17</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>45</td>
<td>28</td>
<td>20</td>
<td>4</td>
<td>2</td>
<td>3.3:1</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>38</td>
<td>24</td>
<td>7</td>
<td>3</td>
<td>2.4:1</td>
<td></td>
</tr>
</tbody>
</table>

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
**Experiment 6.** Reaction Conditions: 9 equiv. of 3a at 0 ºC.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>4a:5a+6a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>30</td>
<td>11</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>60</td>
<td>31</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>90</td>
<td>52</td>
<td>49</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td>120</td>
<td>66</td>
<td>65</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>65:1</td>
</tr>
<tr>
<td>150</td>
<td>75</td>
<td>71</td>
<td>3</td>
<td>1</td>
<td>17.8:1</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>95</td>
<td>81</td>
<td>6</td>
<td>2</td>
<td>10.1:1</td>
<td></td>
</tr>
</tbody>
</table>

From the analysis of the obtained $^1$H-NMR spectra (Figure S2), we can conclude that the formation of compounds 5a/6a started prior the full conversion of the starting enynone 2a into the desired cyclopropene 4a (at least under the studied conditions). However, at moderate values of conversion it is possible to stop the reaction with the

---

**Figure S2.** $^1$H-NMR-spectra collected in Experiment 6.
exclusive formation of cyclopropane \(4a\) (indicated in the tables with a coloured entry). According to the results, we considered conditions of Experiment 6 the most convenient for the preparation of the cyclopropane \(4a\) as they led to the highest yield and conversion in a reasonable reaction time (\textit{NOTE}: conditions of Experiment 2 might be suitable as well, however, a more accurate control of the reaction time is necessary).

The reaction conditions described in Experiment 6 were subsequently applied for the preparation of other representative cyclopropenes using phenylacetylene (\(3b\)) and 4-methoxyphenylacetylene (\(3c\)). The results are described below.

\begin{Verbatim}
\textit{Experiment 7.}
\end{Verbatim}

\begin{verbatimtable}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{t (min)} & \textbf{Conv. (\%)} & \textbf{NMR yield (\%)} & \textbf{4b} & \textbf{5b} & \textbf{6b} \\
\hline
0 & 0 & 0 & 0 & 0 & 0  \\
10 & 0 & 0 & 0 & 0 & 0  \\
30 & 10 & 10 & 0 & 0 & 1:0  \\
60 & 27 & 26 & 0 & 0 & 1:0  \\
90 & 42 & 41 & 0 & 0 & 1:0  \\
120 & 52 & 48 & 1 & 2 & 16.3:1  \\
160 & 62 & 57 & 1 & 2 & 19:1  \\
200 & 67 & 62 & 1 & 2 & 20.6:1  \\
240 & 73 & 66 & 2 & 2 & 16.5:1  \\
300 & 78 & 68 & 2 & 3 & 13.6:1  \\
360 & 81 & 69 & 2 & 3 & 13.8:1  \\
450 & 85 & 71 & 2 & 4 & 11.8:1  \\
26h & 100 & 4 & 35 & 22 & 1:14  \\
\hline
\end{tabular}
\end{verbatimtable}

As indicated in the last entry of the Table, compounds \(5b/6b\) were predominantly formed after long reaction times when most of enynone \(2a\) was already transformed into \(4b\). These results support that \(5/6\) arise from \(4\) and not directly from the starting enynone.
**Experiment 8.**

<table>
<thead>
<tr>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>NMR yield (%)</th>
<th>4c</th>
<th>5c</th>
<th>6c</th>
<th>4c:5c:6c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0:1:0</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0:0</td>
</tr>
<tr>
<td>30</td>
<td>51</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1:0:0</td>
</tr>
<tr>
<td>45</td>
<td>81</td>
<td>76</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>10.9:1</td>
</tr>
<tr>
<td>60</td>
<td>93</td>
<td>80</td>
<td>8</td>
<td>2</td>
<td>0</td>
<td>8:1:0</td>
</tr>
</tbody>
</table>

To a solution of the enynone 2a (50 mg, 0.24 mmol) and p-tolylacetylene 3a (247 mg, 2.1 mmol, 9.0 equiv.) in CH₂Cl₂ (2.5 mL, 0.1 M) at 0 °C, [Rh₂(OAc)₄] (2.6 mg, 2.5 mol%) was added. The resulting mixture was stirred for 90 min at this temperature. Then, pyridine (20μL, 0.24 mmol, 1.0 equiv.) was added to the reaction mixture to poison the catalyst (the colour changed from dark green to pale yellow upon addition) and the solvent was quickly removed under vacuum. The resulting residue was purified by flash...
column chromatography (deactivated SiO$_2$, hexanes:EtOAc = 40:1, R$_f$ = 0.59; hexanes:EtOAc = 3:1) to afford 4a (43 mg, 56%) as a yellow oil.

![Formula 4a](image)

3-((4-Acetyl-5-methyl)furan-2-yl)-3-phenyl-1-(p-tolyl)cyclopropene (4a): 
$^1$H-NMR (300 MHz, CDCl$_3$): 7.56 (d, $J$ = 8.1 Hz, 2H), 7.36-7.29 (m, 5H), 7.28-7.22 (m, 3H), 6.35 (s, 1H), 2.56 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$): 194.8 (C), 157.8 (C), 157.2 (C), 144.2 (C), 140.5 (C), 130.1 (2 x CH), 130.0 (2 x CH), 128.6 (2 x CH), 127.7 (2 x CH), 126.6 (CH), 123.8 (C), 122.6 (C), 120.9 (C), 107.0 (CH), 103.0 (CH), 29.6 (CH$_3$), 28.9 (C), 22.0 (CH$_3$), 14.9 (CH$_3$).

HR-MS (El) calc. for [C$_{23}$H$_{20}$O$_2$]$^+$ 328.1463, found 328.1469.

![Formula 4b](image)

3-((4-Acetyl-5-methyl)furan-2-yl)-1,3-diphenylcyclopropene (4b): The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and phenylacetylene (216 mg, 2.1 mmol, 9.0 equiv.). After 120 min, purification by flash chromatography (deactivated SiO$_2$, hexanes:EtOAc = 40:1, R$_f$ = 0.24; hexanes:EtOAc = 5:1) afforded 4b (29 mg, 40%) as a pale yellow oil.

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$): 7.68 (dd, $J$ = 8.2, 1.6 Hz, 2H), 7.50-7.41 (m, 4H), 7.37-7.30 (m, 4H), 7.24 (dddd, $J$ = 6.1, 6.1, 1.7, 1.7 Hz, 1H), 6.38 (s, 1H), 2.55 (s, 3H), 2.36 (s, 3H).

$^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$): 193.9 (C), 157.2 (C), 156.5 (C), 143.7 (C), 129.8 (CH), 129.6 (2 x CH), 128.9 (2 x CH), 128.2 (2 x CH), 127.3 (2 x CH), 126.2 (CH), 122.2 (C), 121.0 (C), 106.6 (CH), 103.8 (CH), 29.0 (CH$_3$), 28.6 (C), 14.2 (CH$_3$) (a signal corresponding to a quaternary C is overlapped).

HR-MS (El) calc. for [C$_{22}$H$_{18}$O$_2$]$^+$ 314.1307, found 314.1309.
3-((4-Acetyl-5-methyl)furan-2-yl)-3-(4-methoxyphenyl)-1-phenylcyclopropene (Scheme 4, 4c): The representative procedure was followed using enynone 2a (50 mg, 0.24 mmol) and 4-methoxyphenylacetylene (280 mg, 2.1 mmol, 9.0 equiv.). After 30 min, purification by flash chromatography (deactivated SiO₂, hexanes:EtOAc = 20:1, Rᵣ = 0.24; hexanes:EtOAc = 5:1) afforded 4c (39 mg, 48%) as a pale yellow oil.

**¹H-NMR** (300 MHz, CDCl₃): 7.61 (d, J = 8.9 Hz, 2H), 7.33-7.23 (m, 6H), 6.97 (d, J = 8.9 Hz, 2H), 6.35 (s, 1H), 3.86 (s, 3H), 2.57 (s, 3H), 2.38 (s, 3H).

**¹³C-NMR** (75 MHz, CDCl₃): 194.4 (C), 160.8 (C), 157.5 (C), 156.8 (C), 143.9 (C), 131.3 (2 x CH), 128.2 (2 x CH), 127.3 (2 x CH), 126.2 (CH), 122.2 (C), 120.1 (C), 118.8 (C), 114.4 (2 x CH), 106.5 (CH), 100.9 (CH), 55.4 (CH₃), 29.3 (CH₃), 28.4 (C), 14.6 (CH₃).

**HR-MS** (El) calc. for [C₂₃H₂₅O₃]⁺ 344.1412, found 344.1414.

3-((4-Acetyl-5-methyl)furan-2-yl)-3-pentyl-1-(p-tolyl)cyclopropene (Scheme 4, 4d):

The representative procedure was followed using enynone 2f (50 mg, 0.24 mmol) and p-tolylacetylene (168 mg, 1.45 mmol, 6.0 equiv.). After 12 h, purification by flash chromatography (deactivated SiO₂, hexanes:EtOAc = 40:1, Rᵣ = 0.67; hexanes:EtOAc = 5:1) afforded 4d (40 mg, 51%) as a pale yellow oil.

**¹H-NMR** (300 MHz, CDCl₃): 7.44 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.14 (s, 1H), 6.23 (s, 1H), 2.51 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H), 2.15-2.05 (m, 1H), 2.01-1.92 (m, 1H), 1.36-1.21 (bs, 6H), 0.88 (t, J = 6.7 Hz, 3H).
\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)): 194.9 (C), 159.9 (C), 156.5 (C), 139.8 (C), 129.8 (2 x CH), 129.6 (2 x CH), 125.1 (C), 122.8 (C), 122.5 (C), 104.4 (CH), 104.1 (CH), 34.3 (CH\(_2\)), 32.4 (CH\(_2\)), 29.5 (CH\(_3\)), 27.1 (CH\(_2\)), 25.8 (C), 23.0 (CH\(_2\)), 21.9 (CH\(_3\)), 14.9 (CH\(_3\)), 14.5 (CH\(_3\)).

\textbf{HR-MS (EI)} calc. for [C\(_{22}\)H\(_{26}\)O\(_2\)]\(^+\) 322.1933, found 322.1937.

A plausible mechanism that accounts for the observed results is depicted in Scheme S1. As discussed by Iwasawa, Ohe, Uemura and others, enynone 2 serves as a source of 2-furilcarbene by means of a rhodium-catalyzed 5-exo-dig cyclization, which affords carbene intermediate I. Then, the cyclopropenation of alkyne 3 takes place leading to the corresponding cyclopropene 4. Under controlled reaction conditions cyclopropene 4 could be isolated. The released rhodium species is catalytically active to promote the cyclopropene 4 ring-opening towards intermediate II. At this stage, the structure of II is not known, yet might be represented as an intermediate of a vinyl carbenoid or an allyl cation species. Finally, the cyclization towards compounds 5/6 occurs likely through an electrophilic aromatic substitution (S_{EAr}). Remarkably, not only the electronic properties of the arenes involved in the last step (furan or R^{3}-arene
groups), but the $Z/E$-geometry in the intermediate II must be considered. Thus, the $Z/E$-isomeric ratio will play a significant role by approaching the arenes for the $S_2Ar$-cyclization. The rhodium catalyst participates as a single catalyst in two mechanistically different catalytic cycles, thus, the cascade sequence can be considered as an example of auto-tandem catalysis.

The formation of compounds 5/6 occurred from the corresponding cyclopropene 4, although it takes place before the full conversion of enynones 2 into 4, as it was suspected in the preliminary experiments and pointed out by the NMR studies. In order to gain further evidence of the origin of the transformation into 5/6, we performed an additional experiment to support this proposal (Scheme S2). Thus, isolated cyclopropene 4a was treated with $[\text{Rh}_2(\text{OAc})_4]$ under the standard reaction conditions and gave rise to the corresponding mixture of 5a/6a in similar yield and selectivity as in the transformation started from the enynone 2a.

![Scheme S2. Formation of compounds 5a/6a from cyclopropene 4a.](image)

Various experiments using MeOH as nucleophilic trapping reagent in the reaction of 4a were performed in order to obtain information about the nature of intermediate II (Scheme S3). However, products showing MeOH (10 equiv.) incorporation were not detected and very low conversion into 5a/6a (~20%) was observed. Larger amounts of MeOH inhibited the transformation.

![Scheme S3. Reaction of cyclopropene 4a in the presence of MeOH (Yield and ratio were established by $^1$H-NMR using 1,1,2,2-tetrachloroethane as internal standard).](image)
Finally, we checked the possibility that adventitious protic acids, specifically AcOH from the catalyst ligand, could promote the cyclopropene ring opening and the subsequent $\text{S}_\text{E}\text{Ar}$ cyclization. A control experiment using cyclopropene 4a, AcOH (10 mol%) and in the absence of rhodium catalyst did not give rise to compounds 5a/6a (Scheme S4). This outcome confirmed that the Rh(II) catalysts played a pivotal role in the reaction and the uncomplexed ligands have an insignificant effect on the reaction.

**Scheme S4.** Reaction of cyclopropene 4a in the presence of AcOH.
References.

[1] Procedure for SiO$_2$ deactivation: A suspension of 500 g of SiO$_2$ in 2 L of an aqueous K$_2$HPO$_4$ solution (4% wt.) was stirred for 3 h at 25 ºC. The suspension was filtered and dried at 120 ºC for 48 h.


Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013