

Electronic Supplementary Information for

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

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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 cyclopropanation 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 Schlenk techniques. Dichloromethane, D₂-dichloromethane and 1,2-dichloroethane (DCE) were distilled from CaH₂ under N₂ atmosphere. Pentane, toluene and THF were distilled from Na using benzophenone as indicator under N₂ 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 F₂₅₄ indicator. Flash column chromatography was carried out on neutral Al₂O₃ (50-200 mesh) or deactivated SiO₂ (200-400 mesh).^[1] ¹H-NMR (300, 400 MHz) and ¹³C-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 (¹H, 0.0 ppm) or CDCl₃ (¹³C, 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.

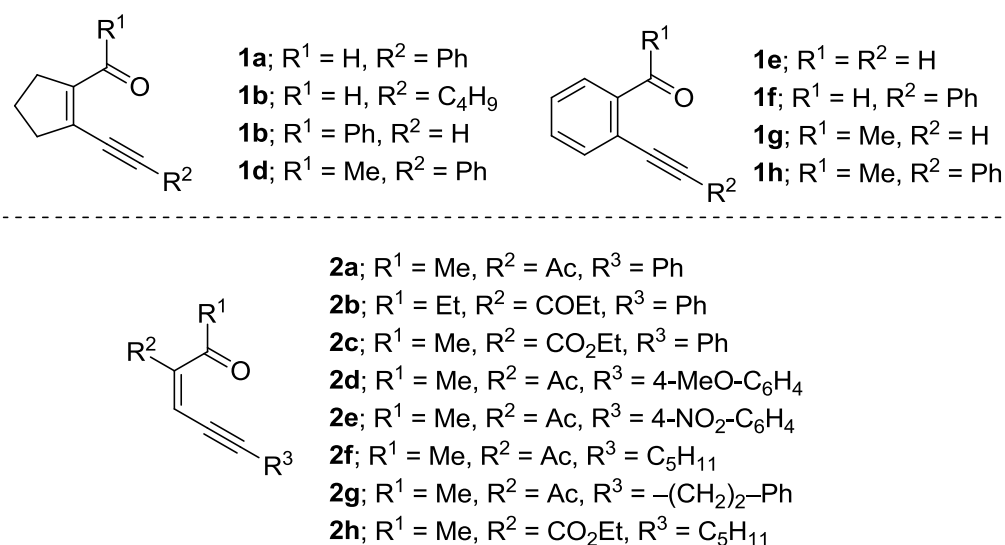
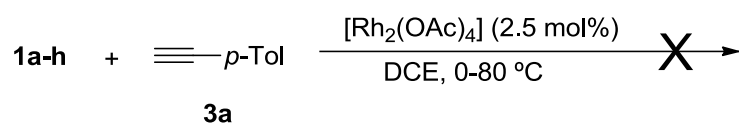


Figure S1. Starting materials used in this work.

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 °C, [Rh₂(OAc)₄] (2.5 mol%) was added. The resulting mixture was stirred in a range of temperatures varying from 0 to 80 °C 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.

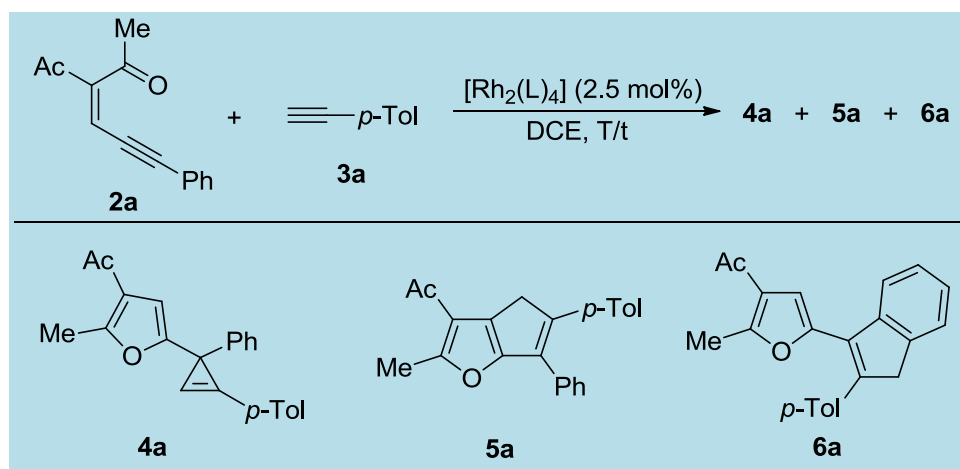


Reactions with enynones 2.

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 °C, 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 ¹H-NMR (CDCl₃) and purified by flash column chromatography (neutral Al₂O₃, hexanes:EtOAc 10:1). The ratio of products **4a/5a/6a** remained essentially unchanged after a fast purification (NOTE: the long exposure to SiO₂ 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 ¹H-NMR spectra.

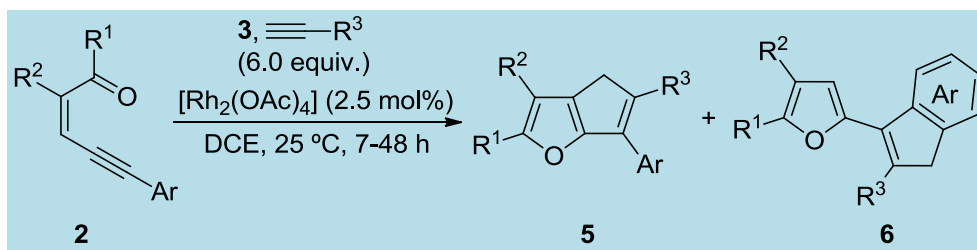
Table S1: Screening summary.



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

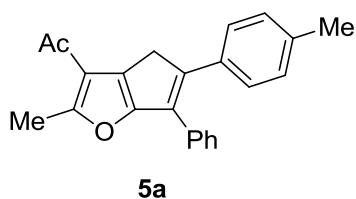
^a Catalyst loading 10 mol%. ^b ¹H-NMR yield. ^c 33% conversion of **2a**. ^d 45% conversion of **2a**. ^e CH_2Cl_2 as solvent. ^f THF as solvent. ^g Toluene as solvent. ^h Pentane as solvent. ⁱ MeCN as solvent. (esp = $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzene dipropionate; cap = caprolactamate).

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 °C, [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, R_f = 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 R_f 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).

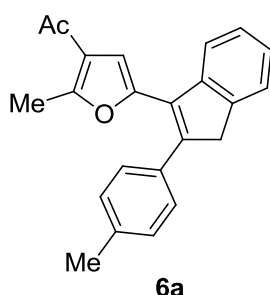


3-Acetyl-2-methyl-6-phenyl-5-(*p*-tolyl)-4*H*-cyclopenta[*b*]furan (5a**):**

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.

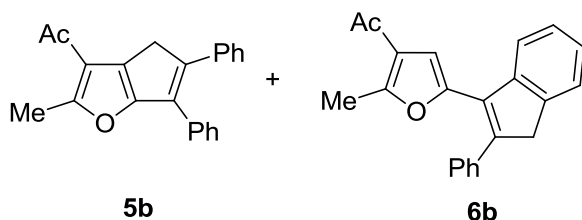


1-(2-Methyl-5-(2-(*p*-tolyl)-1*H*-inden-3-yl)furan-3-yl)ethanone (6a):

¹H-NMR (400 MHz, CD_2Cl_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), 2.40 (s, 3H).

¹³C-NMR (100 MHz, CD_2Cl_2): 193.8 (C), 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 328.1471.



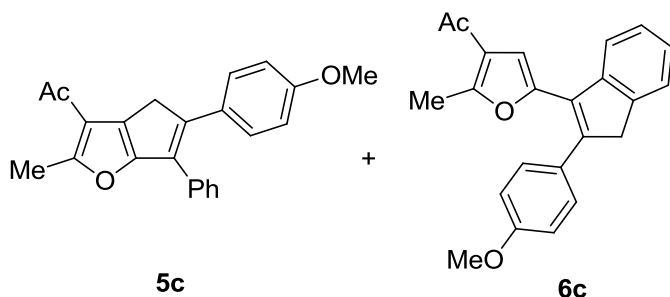
Compounds 5b/6b: The representative procedure was followed using enynone **2a** (50 mg, 0.24 mmol) and phenylacetylene (144 mg, 1.41 mmol, 6.0 equiv.). After 16 h, flash chromatography (neutral Al_2O_3 , hexanes:EtOAc = 20:1, $R_f = 0.39$; hexanes:EtOAc = 3:1) afforded an inseparable mixture of **5b/6b** (65 mg, 88%, **5b:6b** = 1.5:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (400 MHz, CD_2Cl_2): 7.70 (d, $J = 7.5$ Hz, 1H, **6b**), 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**).

¹³C-NMR (100 MHz, CD_2Cl_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), 144.1 (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

(2 x CH, **5b**), 128.24 (2 x CH, **6b**), 128.21 (2 x CH, **6b**), 127.9 (3 x CH, overlapped signal), 127.7 (CH), 127.0 (CH, **5b**), 126.6 (CH, **6b**), 125.3 (CH, **6b**), 124.2 (C, **5b**), 123.7 (CH, **6b**), 122.7 (C, **6b**), 120.7 (CH, **6b**), 109.6 (CH, **6b**), 42.4 (CH₂, **6b**), 35.6 (CH₂, **5b**), 30.3 (CH₃, **5b**), 29.0 (CH₃, **5b**), 14.8 (CH₃, **5b**), 14.1 (CH₃, **6b**) (two C signals could not be located likely due to overlapping).

HR-MS (EI) calc. for [C₂₂H₁₈O₂]⁺ 314.1307, found 314.1312.

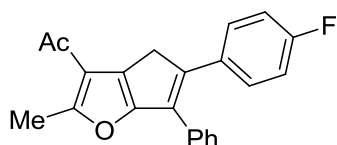


Compounds 5c/6c: The representative procedure was followed using enynone **2a** (50 mg, 0.24 mmol) and 4-methoxyphenylacetylene (186 mg, 1.41 mmol, 6.0 equiv.). After 17 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, R_f = 0.24; hexanes:EtOAc = 5:1) afforded an inseparable mixture of **5c/6c** (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, **5c**), 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 [C₂₃H₂₀O₃]⁺ 344.1412, found 344.1418.



5e

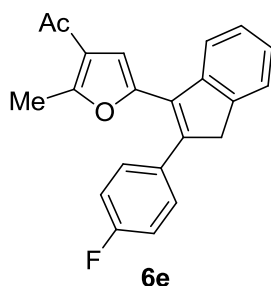
3-Acetyl-6-(4-fluorophenyl)-2-methyl-5-phenyl-4H-cyclopenta[b]furan (5e):

¹H-NMR (400 MHz, CD₂Cl₂): 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).

¹³C-NMR (100 MHz, CD₂Cl₂): 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), 128.7 (2 x CH), 128.0 (CH), 124.1 (C), 120.7 (C), 115.3 (2 x CH, *J* = 21.5 Hz), 35.7 (CH₂), 30.2 (CH₃), 14.8 (CH₃).

¹⁹F-NMR (282 MHz, CD₂Cl₂): -115.63 (s).

HR-MS (EI) calc. for [C₂₂H₁₇FO₂]⁺ 332.1213, found 332.1215.



6e

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

¹H-NMR (400 MHz, CD₂Cl₂): 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).

¹³C-NMR (100 MHz, CD₂Cl₂): 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 (CH₂), 29.0 (CH₃), 14.1 (CH₃).

¹⁹F-NMR (282 MHz, CD₂Cl₂): -114.66 (s).

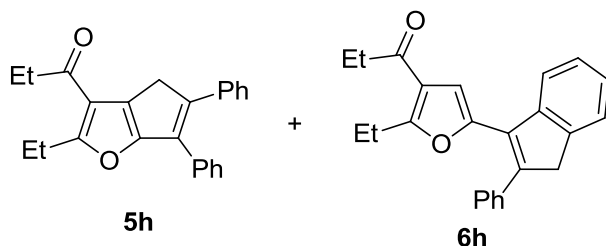
HR-MS (EI) calc. for [C₂₂H₁₇FO₂]⁺ 332.1213, found 332.1218.

1.6:1). ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.60-7.55 (m, 2H, **5g**), 7.47 (d, $J = 7.6$ Hz, 1H, **6g**), 7.45-7.38 (m, **5g/6g**), 7.34-7.28 (m, **5g/6g**), 7.21 (dt, $J = 7.4, 1.2$ Hz, 1H, **6g**), 6.74 (s, **6g**), 6.03-5.98 (m, 1H, **6g**), 5.92-5.88 (m, 1H, **5g**), 3.67 (s, 2H, **6g**), 3.45 (s, 2H, **5g**), 2.69 (s, 3H, **6g**), 2.67 (s, 3H, **5g**), 2.49 (s, 3H, **6g**), 2.48 (s, 3H, **5g**), 2.22-2.19 (m, 2H, **6g**), 2.18-2.11 (m, **5g/6g**), 2.10-2.03 (m, **5g/6g**), 1.69-1.67 (m, 4H, **6g**), 1.64-1.61 (m, 4H, **5g**).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 194.7 (C, **5g**), 194.3 (C, **6g**), 160.2 (C, **6g**), 159.9 (C, **5g**), 157.4 (C), 148.1 (C, **5g**), 147.6 (C, **6g**), 144.8 (2 x C), 141.5 (C), 134.8 (C, **5g**), 134.5 (C), 133.6 (C), 128.8 (C), 128.6 (2 x CH, **5g**), 128.4 (CH), 128.3 (2 x CH, **5g**), 127.5 (CH, **5g**), 126.9 (CH, **5g**), 126.5 (CH, **6g**), 125.8 (C, **6g**), 124.9 (CH, **6g**), 123.4 (CH, **6g**), 122.6 (C, **6g**), 122.2 (C, **5g**), 120.6 (C), 120.1 (CH, **6g**), 109.3 (CH, **6g**), 41.5 (CH_2 , **6g**), 35.2 (CH_2 , **5g**), 30.4 (CH_3 , **5g**), 29.2 (CH_3 , **6g**), 28.3 (CH_2 , **5g**), 27.5 (CH_2 , **6g**), 25.9 (CH_2 , **6g**), 25.8 (CH_2 , **5g**), 23.0 (CH_2 , **6g**), 22.95 (CH_2 , **5g**), 22.06 (2 x CH_2 , **5g/6g**), 15.1 (CH_3 , **5g**), 14.5 (CH_3 , **6g**).

HR-MS (EI) calc. for $[\text{C}_{22}\text{H}_{22}\text{O}_2]^+$ 318.1620, found 318.1624.



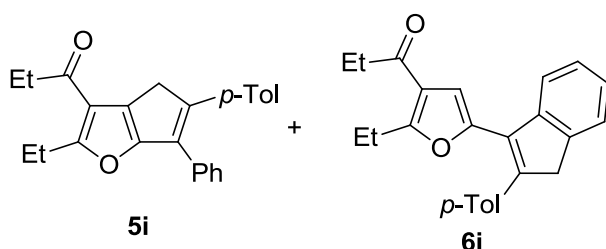
Compounds 5h/6h: The representative procedure was followed using enynone **2b** (50 mg, 0.21 mmol) and phenylacetylene (127 mg, 1.25 mmol, 6.0 equiv.). After 24 h, flash chromatography (neutral Al_2O_3 , hexanes:EtOAc = 20:1, $R_f = 0.56$; hexanes:EtOAc = 5:1) afforded an inseparable mixture of **5h/6h** (41 mg, 58%, **5h:6h** = 1.5:1). ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): 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**).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 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 [C₂₄H₂₂O₂]⁺ 342.1620, found 342.1623.

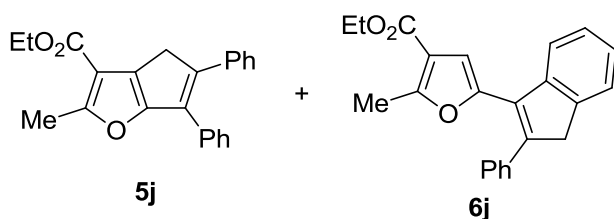


Compounds 5i/6i: The representative procedure was followed using enynone **2b** (50 mg, 0.21 mmol) and *p*-tolylacetylene (145 mg, 1.25 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, R_f = 0.42; hexanes:EtOAc = 10:1) afforded an inseparable mixture of **5i/6i** (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, **5i**), 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 [C₂₅H₂₄O₂]⁺ 356.1776, found 356.1779.

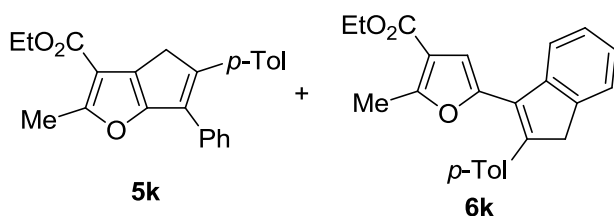


Compounds 5j/6j: The representative procedure was followed using enynone **2c** (50 mg, 0.21 mmol) and phenylacetylene (126 mg, 1.24 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 20:1, R_f = 0.33; hexanes:EtOAc = 5:1) afforded an inseparable mixture of **5j/6j** (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**), 7.41-7.23 (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.



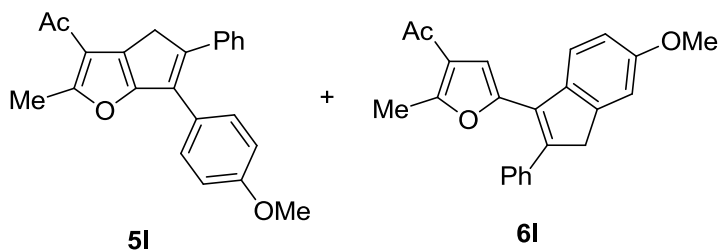
Compounds 5k/6k: The representative procedure was followed using enynone **2c** (50 mg, 0.21 mmol) and *p*-tolylacetylene (144 mg, 1.24 mmol, 6.0 equiv.). After 48 h, flash chromatography (neutral Al₂O₃, hexane:EtOAc = 20:1, R_f = 0.58; hexanes:EtOAc = 5:1) afforded an inseparable mixture of **5k/6k** (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).

¹H-NMR (300 MHz, CDCl₃): 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, **6k**), 3.65 (s, 2H, **5k**), 2.71 (s, 3H, **5k**), 2.62 (s, 3H, **6k**), 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).

¹³C-NMR (75 MHz, CDCl₃): 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 (CH₂, **6k**), 60.1 (CH₂, **5k**), 42.3 (CH₂, **6k**), 35.1 (CH₂, **5k**), 21.3 (CH₃, **6k**), 21.2 (CH₃, **5k**), 14.5 (CH₃, **5k**), 14.45 (CH₃, **5k**), 14.41 (CH₃, **6k**), 13.9 (CH₃, **6k**).

HR-MS (EI) calc. for [C₂₄H₂₂O₃]⁺ 358.1569, found 358.1574.

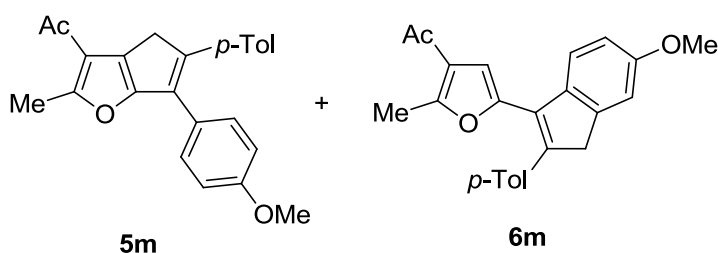


Compounds 5I/6I: The representative procedure was followed using enynone **2d** (50 mg, 0.21 mmol) and phenylacetylene (126 mg, 1.24 mmol, 6.0 equiv.). After 15 h, flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, R_f = 0.21; hexanes:EtOAc = 5:1) afforded an inseparable mixture of **5I/6I** (33 mg, 46%, **5I:6I** = 1:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CDCl₃): 7.59 (d, *J* = 8.4 Hz, 1H, **6I**), 7.49 (d, *J* = 8.4 Hz, 2H, **5I**), 7.41-7.20 (m, **5I/6I**), 7.12 (d, *J* = 2.3 Hz, 1H, **6I**), 6.94 (dd, *J* = 8.4, 2.3 Hz, 1H, **6I**, overlapped signal), 7.59 (d, *J* = 8.4 Hz, 2H, **5I**, overlapped signal), 6.64 (s, 1H, **6I**), 3.89 (s, 3H), 3.87 (s, 2H, **6I**), 3.85 (s, 3H), 3.67 (s, 2H, **5I**), 2.71 (s, 3H), 2.62 (s, 3H), 2.51 (s, 3H), 2.40 (s, 3H).

¹³C-NMR (75 MHz, CD₂Cl₂): 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 (CH₃), 55.2 (CH₃), 42.3 (CH₂, **5l**), 35.5 (CH₂, **5l**), 30.3 (CH₃), 29.0 (CH₃), 14.8 (CH₃), 14.1 (CH₃).

HR-MS (EI) calc. for [C₂₃H₂₀O₃]⁺ 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 (Al₂O₃, hexanes:EtOAc = 10:1, R_f = 0.26; hexanes:EtOAc = 5:1) afforded an inseparable mixture of **5m/6m** (37 mg, 50%, **5m:6m** = 2.7:1). (¹H-NMR, ¹³C-NMR spectra and HR-MS were recorded from the mixture; only unambiguous NMR signals were assigned).

¹H-NMR (300 MHz, CDCl₃): 7.56 (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**).

¹³C-NMR (75 MHz, CDCl₃): 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 (CH₃, **6m**), 55.2 (CH₃, **5m**), 42.3 (CH₂, **6m**), 35.5 (CH₂, **5m**), 30.5 (CH₃, **5m**), 29.2 (CH₃, **6m**), 21.3 (CH₃, **6m**), 21.2 (CH₃, **5m**), 15.1 (CH₃, **5m**), 14.5 (CH₃, **6m**) (a C signal could not be located likely due to overlapping).

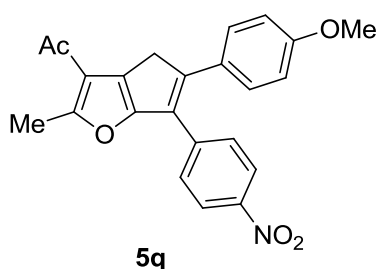
HR-MS (EI) calc. for [C₂₄H₂₂O₃]⁺ 358.1569, found 358.1572.

phenylacetylene (119 mg, 1.17 mmol, 6.0 equiv.). After 18 h, purification by flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, R_f = 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.



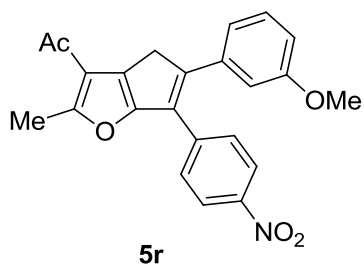
3-Acetyl-5-(4-methoxyphenyl)-2-methyl-6-(4-nitrophenyl)-4H-cyclopenta[b]furan

(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, R_f = 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

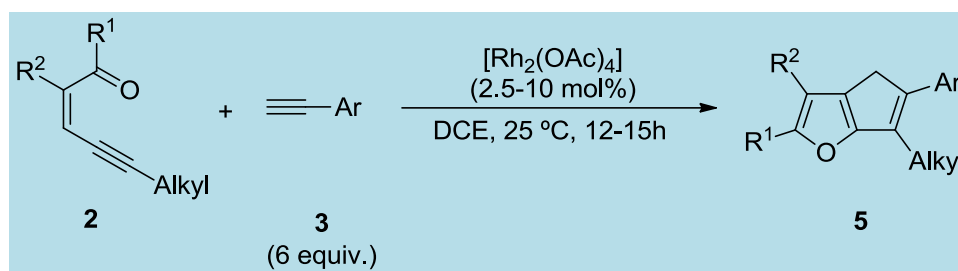
(5r): The representative procedure was followed using enynone **2e** (50 mg, 0.19 mmol) and 3-methoxyphenylacetylene (154 mg, 1.16 mmol, 6.0 equiv.). After 15 h, purification by flash chromatography (neutral Al₂O₃, hexanes:EtOAc = 10:1, R_f = 0.50; hexanes:EtOAc = 3:1) afforded **5r** (27 mg, 35%) as 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).

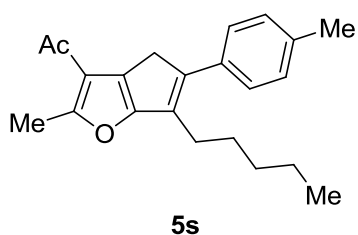
¹³C-NMR (75 MHz, CDCl₃): 194.1 (C), 160.9 (C), 159.8 (C), 158.7 (C), 147.0 (C), 144.7 (C), 139.3 (C), 137.5 (C), 129.9 (CH), 129.5 (2 x CH), 128.9 (C), 124.6 (C), 123.9 (2 x CH), 120.8 (C), 120.5 (CH), 113.8 (CH), 113.2 (CH), 55.2 (CH₃), 36.3 (CH₂), 30.5 (CH₃), 15.2 (CH₃).

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, $[\text{Rh}_2(\text{OAc})_4]$ (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 SiO_2 , hexanes:EtOAc = 100:1, R_f = 0.21; hexanes:EtOAc = 5:1) to afford **5s** (31 mg, 40%) as a yellow oil.

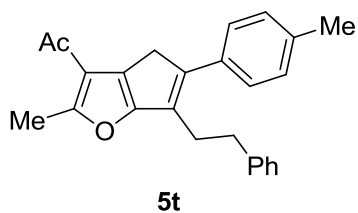


3-Acetyl-2-methyl-6-pentyl-5-(*p*-tolyl)-4H-cyclopenta[*b*]furan (5s):

¹H-NMR (300 MHz, CD_2Cl_2): 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), 1.79-1.68 (m, 2H), 1.42-1.31 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H).

¹³C-NMR (75 MHz, CD_2Cl_2): 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 (CH_2), 31.9 (CH_2), 30.4 (CH_3), 28.3 (CH_2), 26.0 (CH_2), 22.5 (CH_2), 21.2 (CH_3), 15.1 (CH_3), 14.0 (CH_3).

HR-MS (EI) calc. for $[\text{C}_{22}\text{H}_{26}\text{O}_2]^+$ 322.1933, found 322.1940.

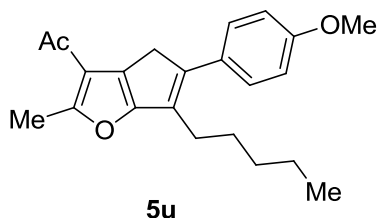


3-Acetyl-2-methyl-6-phenethyl-5-(*p*-tolyl)-4*H*-cyclopenta[*b*]furan (5t): The representative procedure was followed using enynone **2g** (50 mg, 0.21 mmol), *p*-tolylacetylene (145 mg, 1.25 mmol, 6.0 equiv.) and [Rh₂(OAc)₄] (2.5 mg, 2.5 mol%). After 12 h, purification by flash column chromatography (deactivated SiO₂, hexanes:EtOAc = 40:1, R_f = 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).

¹H-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).

¹³C-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).

HR-MS (EI) calc. for [C₂₅H₂₄O₂]⁺ 356.1776, found 356.1780.



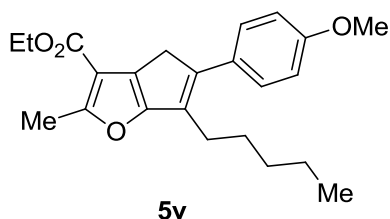
3-Acetyl-2-methyl-5-(4-methoxyphenyl)-6-pentyl-4*H*-cyclopenta[*b*]furan (5u): The representative procedure was followed using enynone **2f** (50 mg, 0.24 mmol), 4-methoxyphenylacetylene (192 mg, 1.45 mmol, 6.0 equiv.) and [Rh₂(OAc)₄] (2.5 mg, 2.5 mol%). After 13 h, purification by flash column chromatography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

¹H-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).

¹³C-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 (EI) 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, R_f = 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).

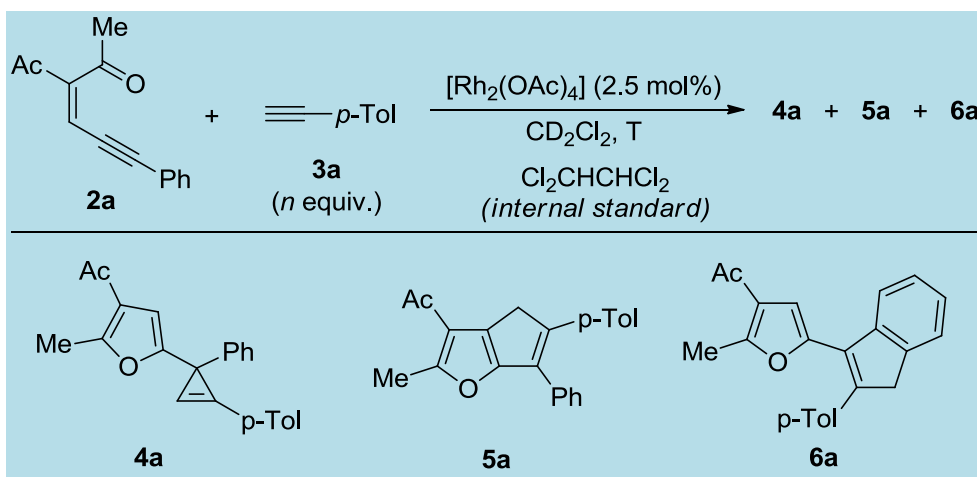
HR-MS (EI) calc. for [C₂₃H₂₈O₃]⁺ 368.1988, found 368.1994.

5. Rhodium-catalyzed carbene cyclopropenation of alkynes using enynes 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 $^1\text{H-NMR}$ analysis.

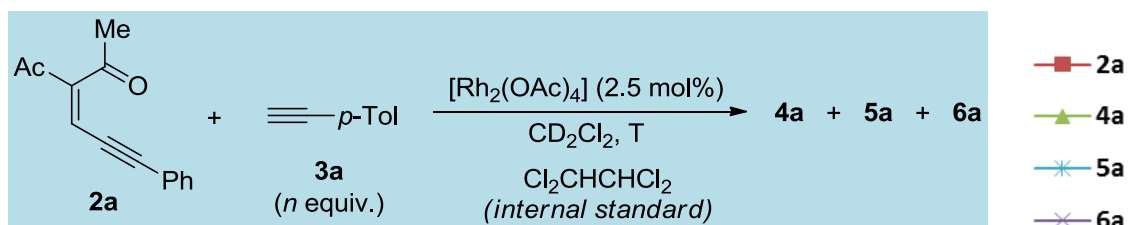
5.1. NMR-Monitored Experiments.

Representative procedure for the $^1\text{H-NMR}$ -monitor reactions.

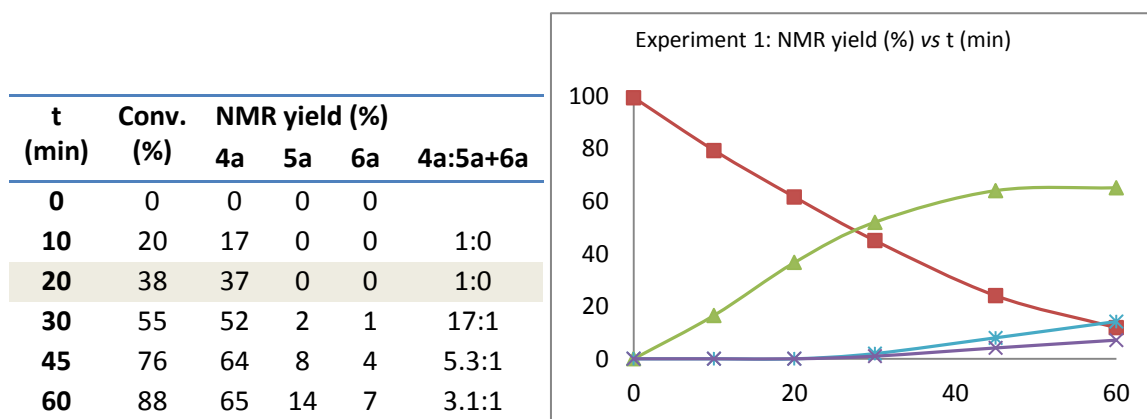


A solution of **2a** (42 mg, 0.2 mmol), **3a** (*n* equiv.) and 1,1,2,2-tetrachloroethane (37 mg, 0.2 mmol, 1.0 equiv., as internal standard) in CD_2Cl_2 (2.0 mL) (distilled over CaH_2 and stored in the dark over molecular sieves 4\AA) was prepared at the indicated temperature. From the resulting solution, $50\ \mu\text{L}$ 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 $^1\text{H-NMR}$ measurement was immediately done (the NMR apparatus was kept at the reaction temperature). Then, $[\text{Rh}_2(\text{OAc})_4]$ (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).

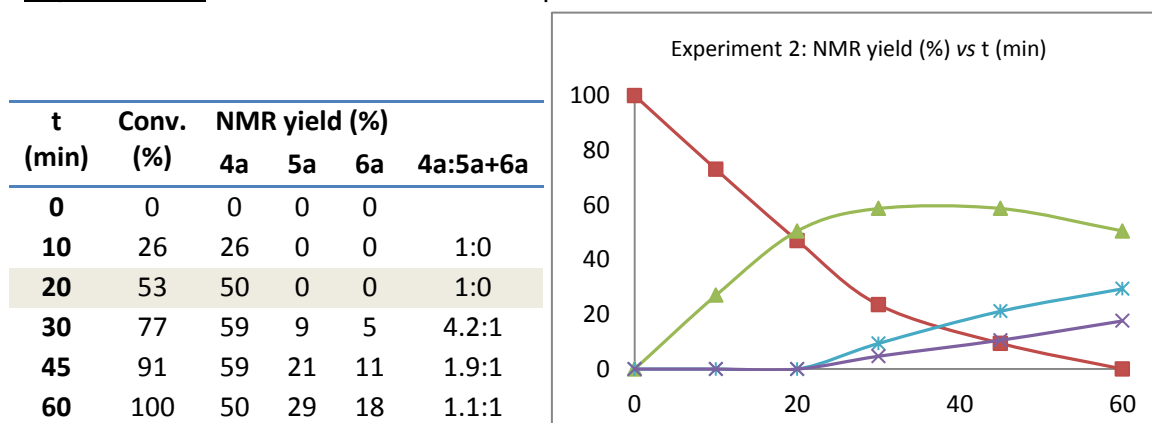
The results of the optimization experiments are summarized below. These include tables with conversions and yields calculated through integration of selected signals of the ¹H-NMR spectra and the corresponding NMR-yield vs time plots to represent the reaction profile.



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

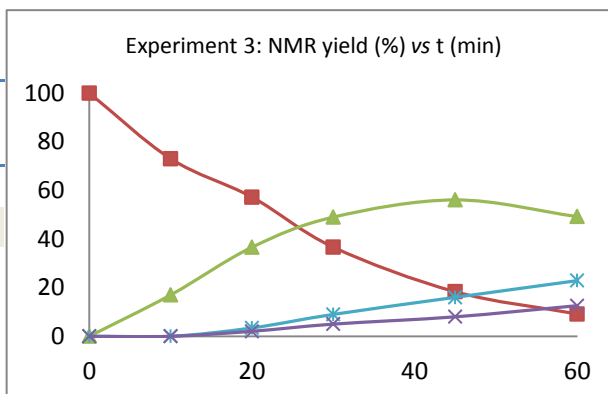


Experiment 2. Reaction Conditions: 9 equiv. of **3a** at 25 °C.



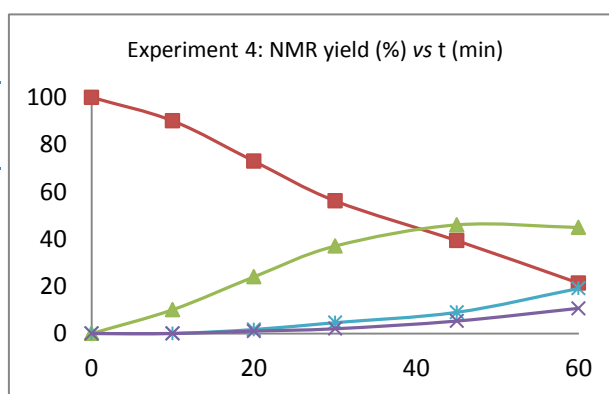
Experiment 3. Reaction Conditions: 6 equiv. of **3a** at 25 °C.

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



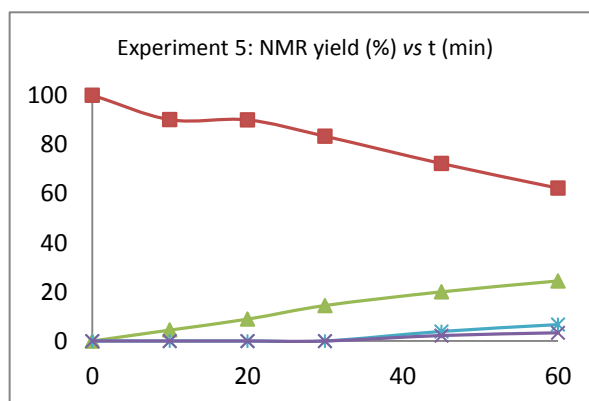
Experiment 4. Reaction Conditions: 3 equiv. of **3a** at 25 °C.

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



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

t (min)	Conv. (%)	NMR yield (%)			4a:5a+6a
		4a	5a	6a	
0	0	0	0	0	
10	5	4	0	0	1:0
20	10	9	0	0	1:0
30	17	14	0	0	1:0
45	28	20	4	2	3.3:1
60	38	24	7	3	2.4:1



Experiment 6. Reaction Conditions: 9 equiv. of **3a** at 0 °C.

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

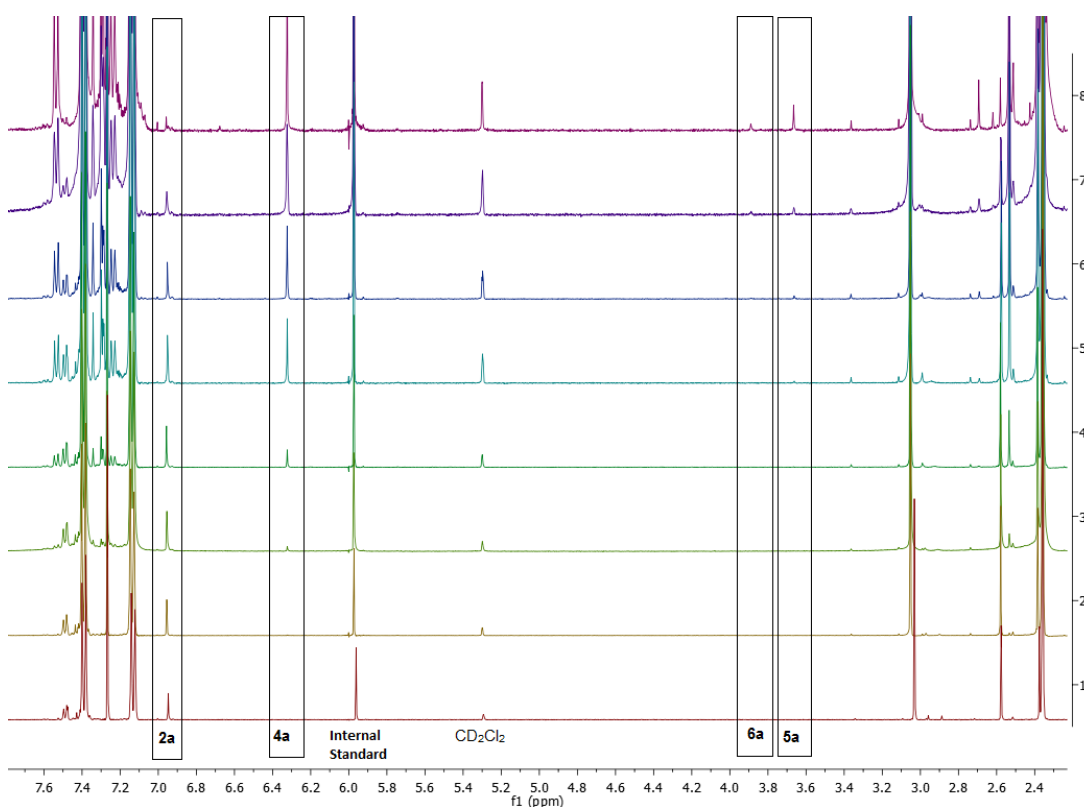
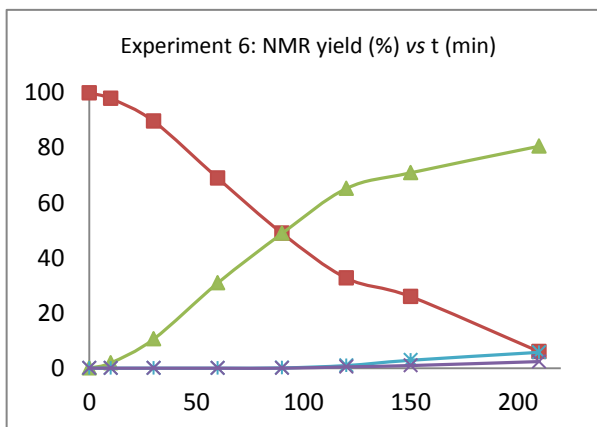


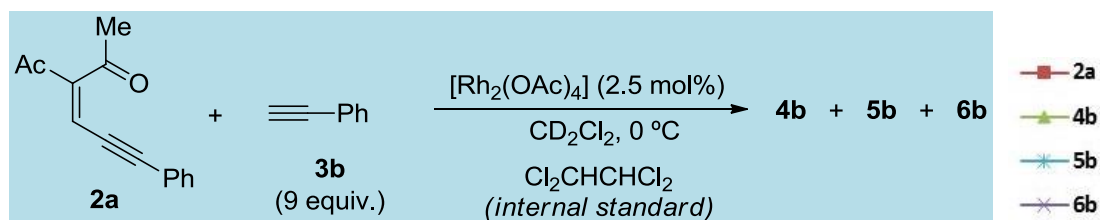
Figure S2. ¹H-NMR-spectra collected in Experiment 6.

From the analysis of the obtained ¹H-NMR spectra (Figure S2), we can conclude that the formation of compounds **5a/6a** started prior the full conversion of the starting enyne **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

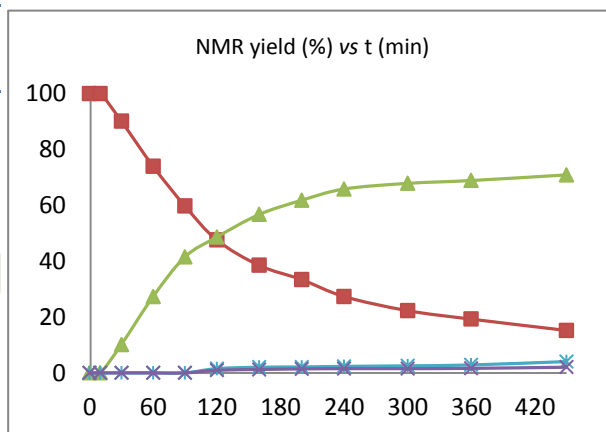
exclusive formation of cyclopropene **4a** (indicated in the tables with a coloured entry). According to the results, we considered conditions of Experiment 6 the most convenient for the preparation of the cyclopropene **4a** as they led to the highest yield and conversion in a reasonable reaction time (*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.

Experiment 7.

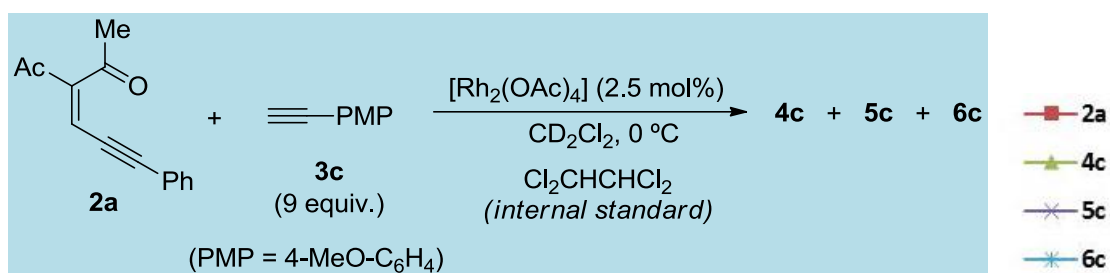


t (min)	Conv. (%)	NMR yield (%)			
		4b	5b	6b	4b:5b+6b
0	0	0	0	0	
10	0	0	0	0	
30	10	10	0	0	1:0
60	27	26	0	0	1:0
90	42	41	0	0	1:0
120	52	48	1	2	16.3:1
160	62	57	1	2	19:1
200	67	62	1	2	20.6:1
240	73	66	2	2	16.5:1
300	78	68	2	3	13.6:1
360	81	69	2	3	13.8:1
450	85	71	2	4	11.8:1
26h	100	4	35	22	1:14

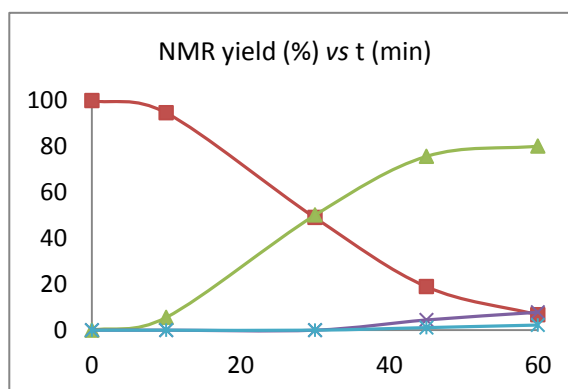


As indicated in the last entry of the Table, compounds **5b/6b** were predominantly formed after long reaction times when most of enyne **2a** was already transformed into **4b**. These results support that **5/6** arise from **4** and not directly from the starting enyne.

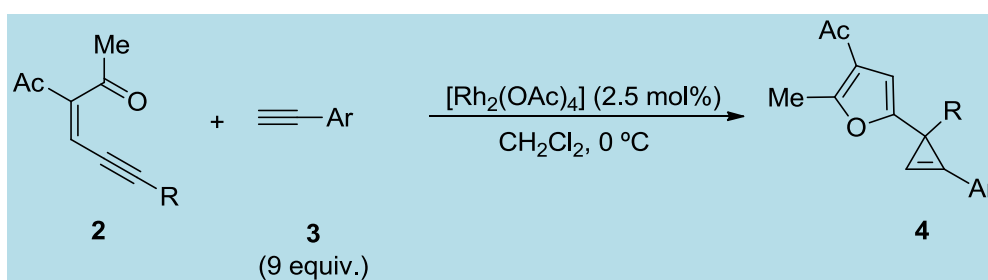
Experiment 8.



t (min)	Conv. (%)	NMR yield (%)			
		4c	5c	6c	4c:5c+6c
0	0	0	0	0	
10	6	6	0	0	1:0
30	51	50	0	0	1:0
45	81	76	4	1	10.9:1
60	93	80	8	2	8:1

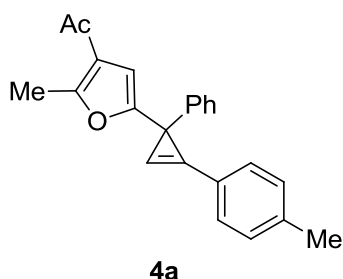


5.2. Procedures and characterization data for cyclopropenes 4a-d.



To a solution of the enyne **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 (20 μL, 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 SiO₂, hexanes:EtOAc = 40:1, R_f = 0.59; hexanes:EtOAc = 3:1) to afford **4a** (43 mg, 56%) as a yellow oil.

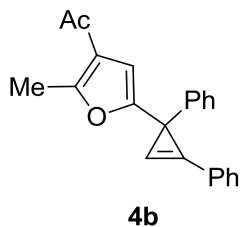


3-((4-Acetyl-5-methyl)furan-2-yl)-3-phenyl-1-(p-tolyl)cyclopropene (4a):

¹H-NMR (300 MHz, CDCl₃): 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).

¹³C-NMR (75 MHz, CDCl₃): 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 (CH₃), 28.9 (C), 22.0 (CH₃), 14.9 (CH₃).

HR-MS (EI) calc. for [C₂₃H₂₀O₂]⁺ 328.1463, found 328.1469.

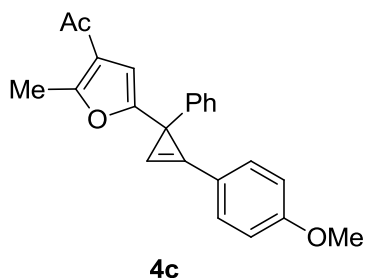


3-((4-Acetyl-5-methyl)furan-2-yl)-1,3-diphenylcyclopropene (4b): The representative procedure was followed using enynone **2a** (50 mg, 0.24 mmol) and phenylacetylene (216 mg, 2.1 mmol, 9.0 equiv.). After 120 min, purification by flash chromatography (deactivated SiO₂, hexanes:EtOAc = 40:1, R_f = 0.24; hexanes:EtOAc = 5:1) afforded **4b** (29 mg, 40%) as a pale yellow oil.

¹H-NMR (300 MHz, CD₂Cl₂): 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).

¹³C-NMR (75 MHz, CD₂Cl₂): 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 (CH₃), 28.6 (C), 14.2 (CH₃) (a signal corresponding to a quaternary C is overlapped).

HR-MS (EI) calc. for [C₂₂H₁₈O₂]⁺ 314.1307, found 314.1309.



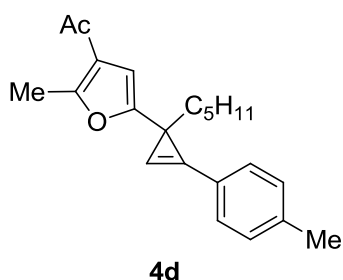
3-((4-Acetyl-5-methyl)furan-2-yl)-3-(4-methoxyphenyl)-1-phenylcyclopropene

(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, R_f = 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 (EI) calc. for [C₂₃H₂₀O₃]⁺ 344.1412, found 344.1414.



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

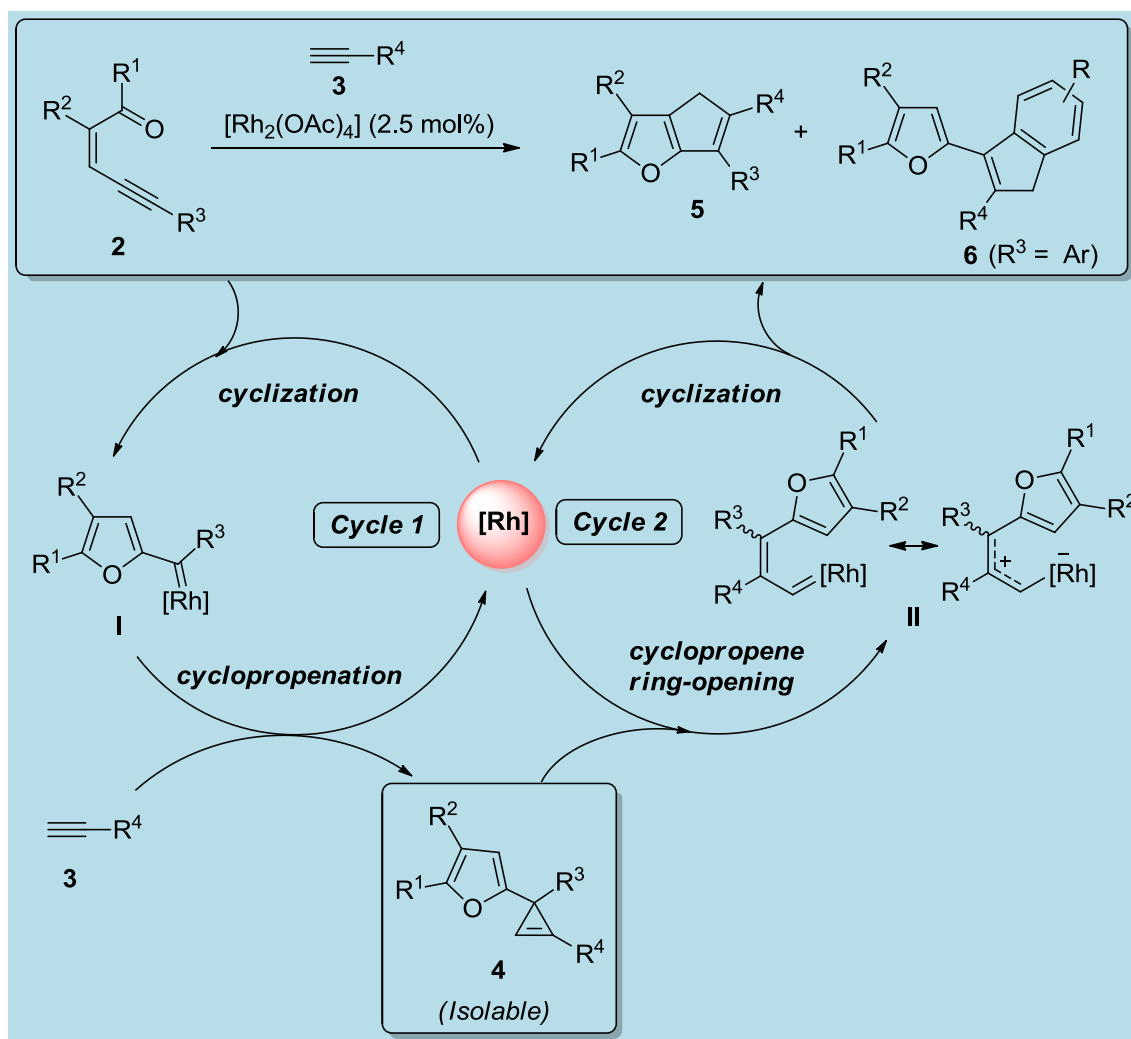
The representative procedure was followed using enynone **2f** (50 mg, 0.24 mmol) and *p*-tolylacetylene (168 mg, 1.45 mmol, 6.0 equiv.). After 12 h, purification by flash chromatography (deactivated SiO₂, hexanes:EtOAc = 40:1, R_f = 0.67; hexanes:EtOAc = 5:1) afforded **4d** (40 mg, 51%) as a pale yellow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

¹³C-NMR (75 MHz, CDCl₃): 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 (CH₂), 32.4 (CH₂), 29.5 (CH₃), 27.1 (CH₂), 25.8 (C), 23.0 (CH₂), 21.9 (CH₃), 14.9 (CH₃), 14.5 (CH₃).

HR-MS (EI) calc. for [C₂₂H₂₆O₂]⁺ 322.1933, found 322.1937.

6. Mechanistic rationale.

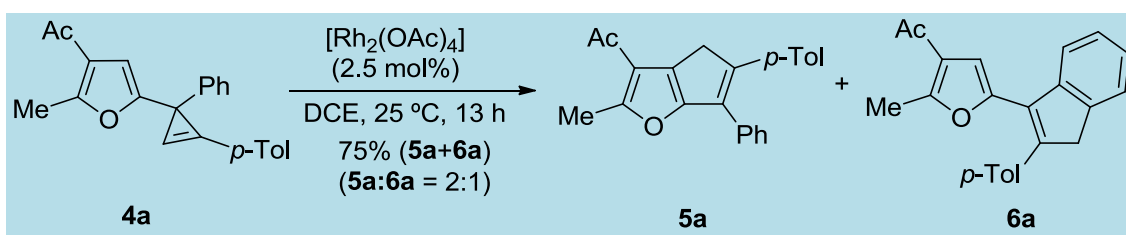


Scheme S1. Proposed mechanism.

A plausible mechanism that accounts for the observed results is depicted in Scheme S1. As discussed by Iwasawa, Ohe, Uemura and others,^[4] enone **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 cyclopropanation of alkyne **3** takes place leading to the corresponding cyclopropene **4**.^[5] 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 ($\text{S}_{\text{E}}\text{Ar}$).^[6] Remarkably, not only the electronic properties of the arenes involved in the last step (furan or R^3 -arene

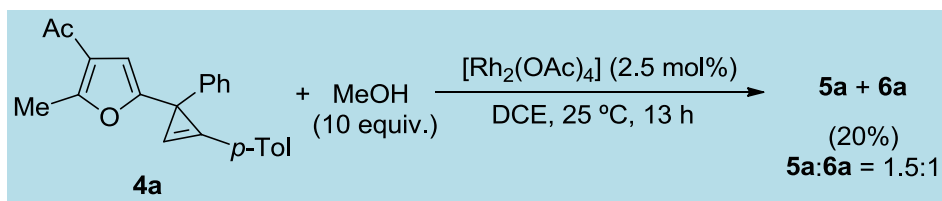
groups), but the *Z/E*-geometry in the intermediate **II** must be considered. Thus, the *Z/E*-isomeric ratio will play a significant role by approaching the arenes for the S_EAr -cyclization. The rhodium catalyst participates as a single catalyst in two mechanistically different catalytic cycles, thus, 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 evidences 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 $[Rh_2(OAc)_4]$ 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**.



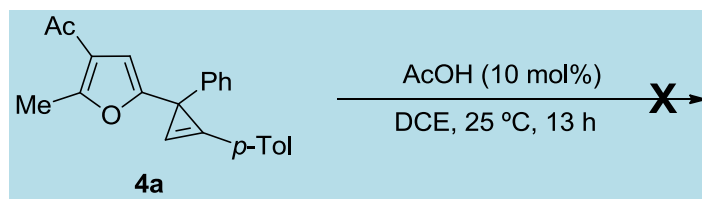
Scheme S2. Formation of compounds **5a/6a** from cyclopropene **4a**.

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 1H -NMR using 1,1,2,2-tetrachloroethane as internal standard).

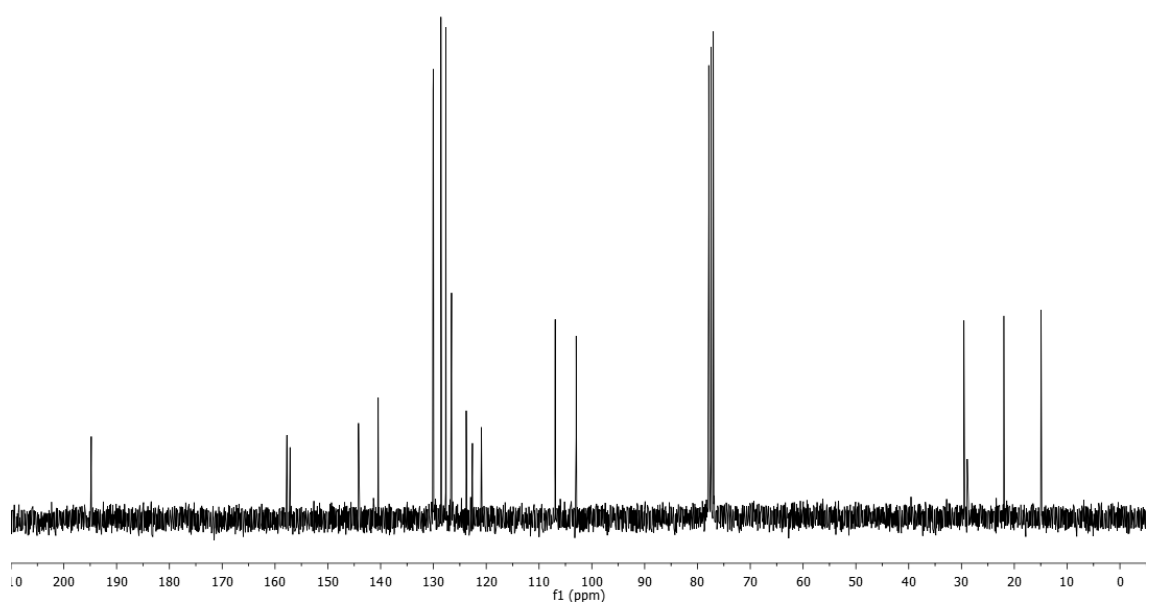
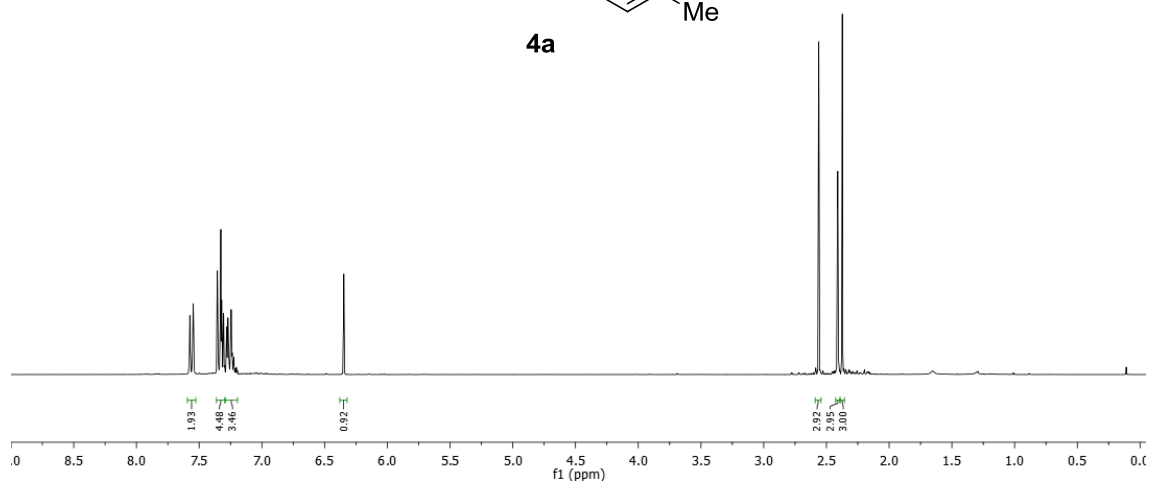
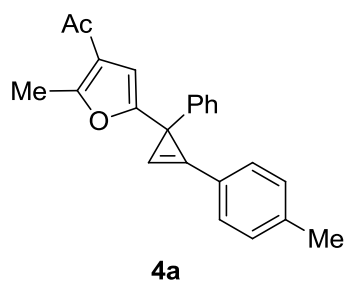
Finally, we checked the possibility that adventitious protic acids, specifically AcOH from the catalyst ligand, could promote the cyclopropene ring opening and the subsequent S_EAr cyclization. A control experiment using cyclopropene **4a**, AcOH (10 mol%) and in the absence of rhodium catalyst did not 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.

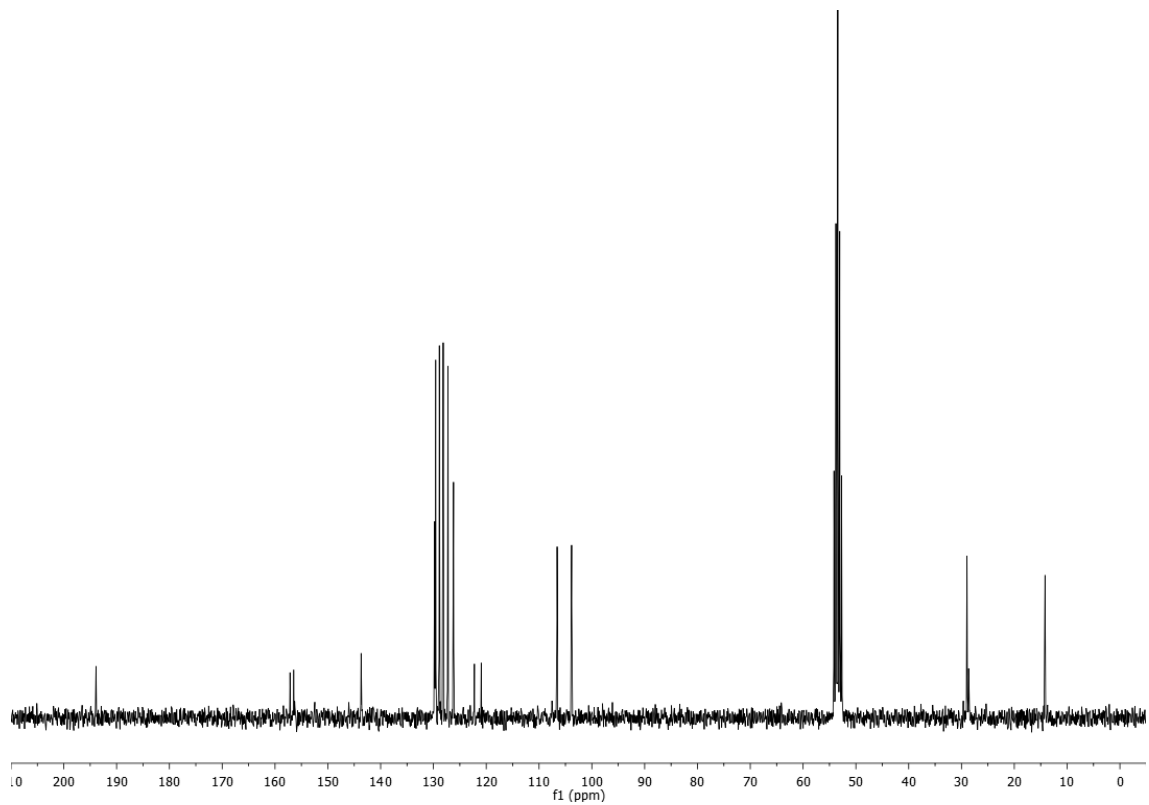
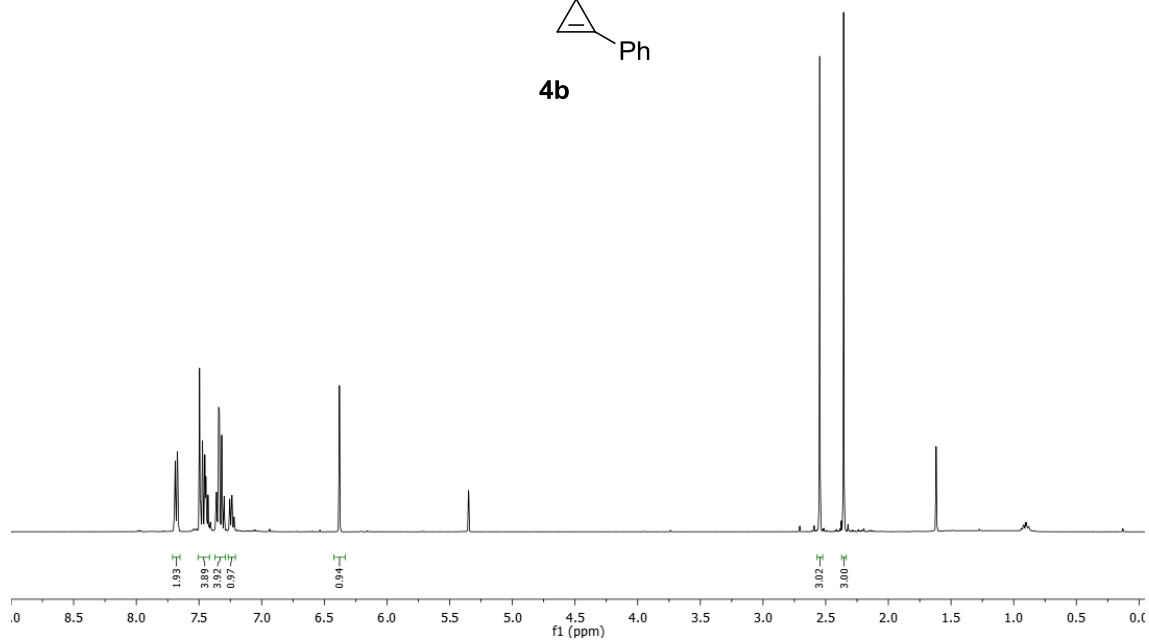
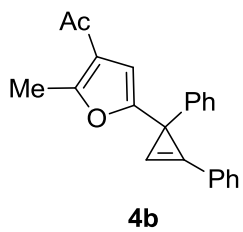


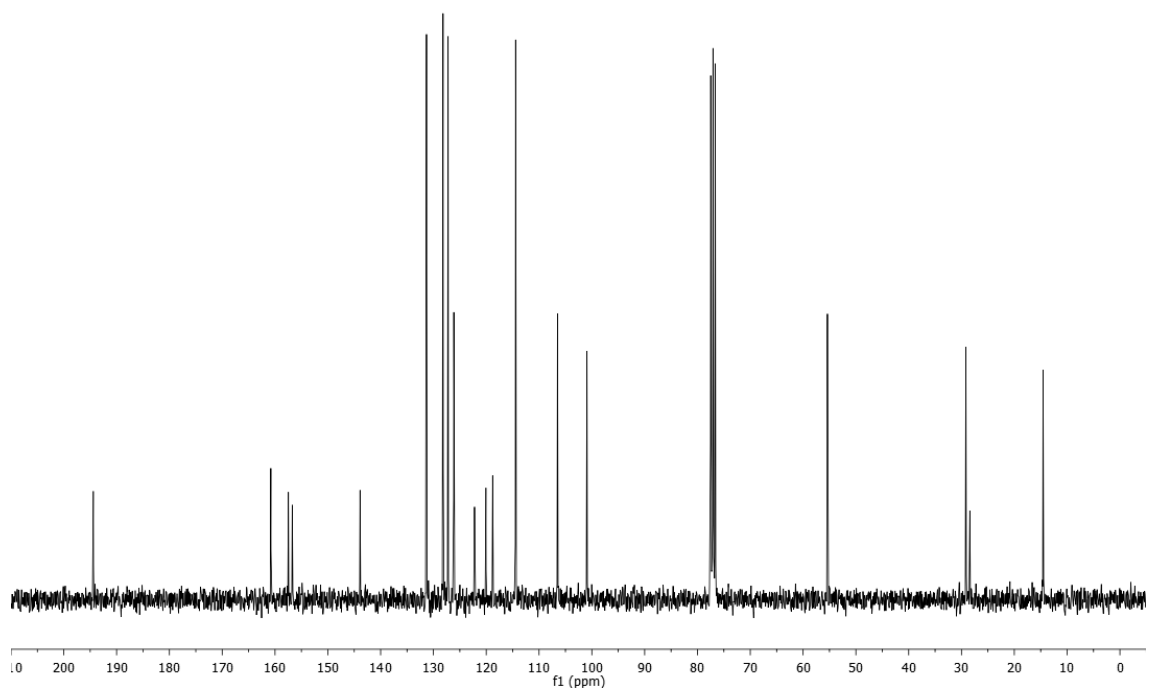
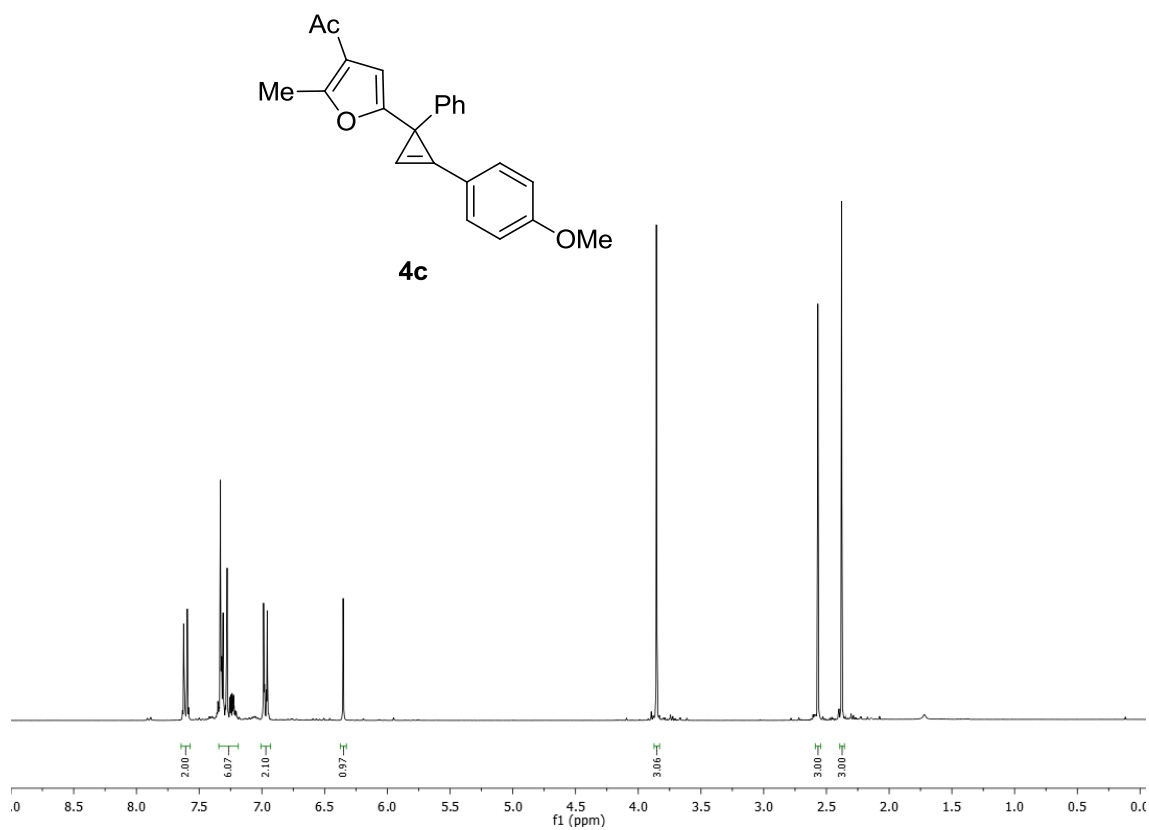
Scheme S4. Reaction of cyclopropene **4a** in the presence of AcOH.

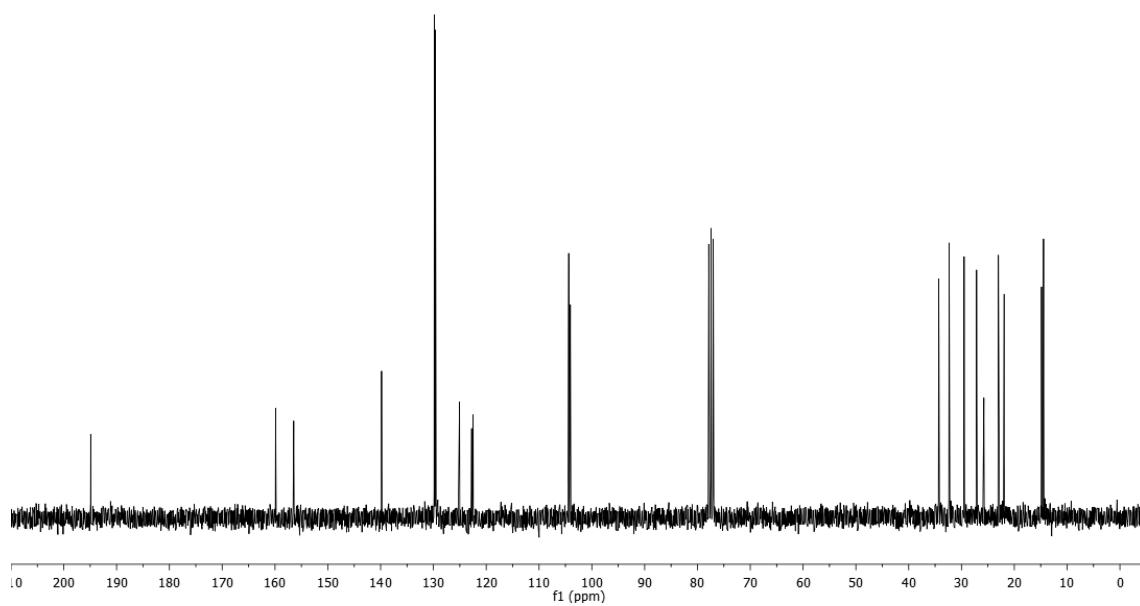
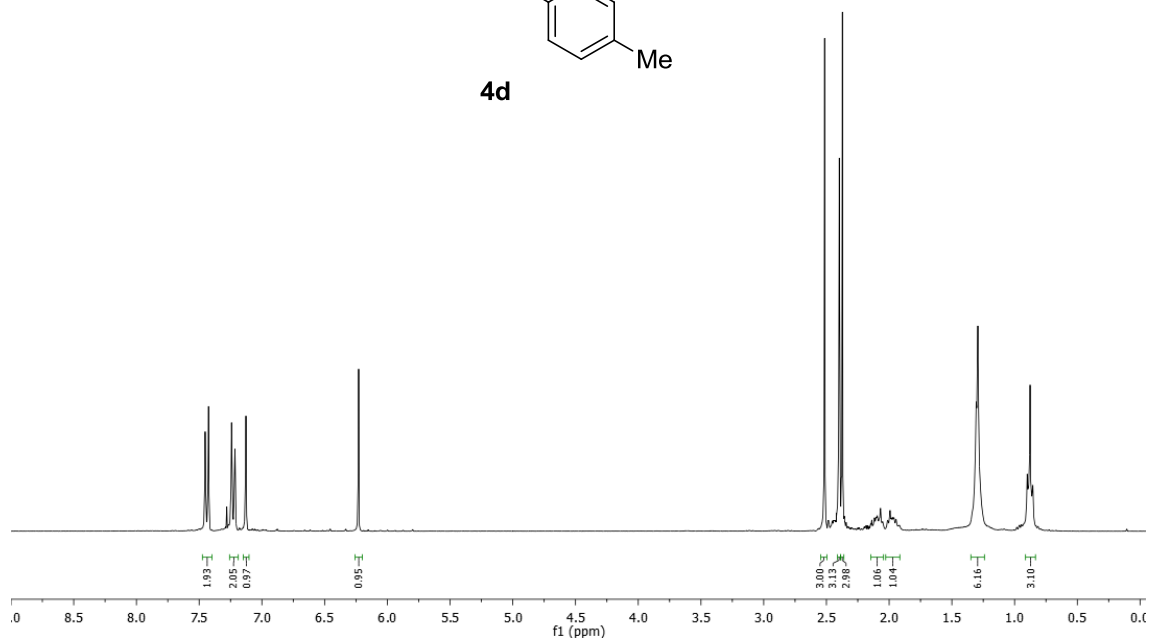
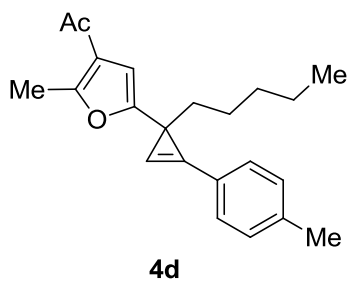
References.

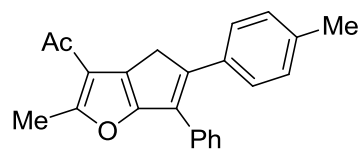
- [1] Procedure for SiO₂ deactivation: A suspension of 500 g of SiO₂ in 2 L of an aqueous K₂HPO₄ solution (4% wt.) was stirred for 3 h at 25 °C. The suspension was filtered and dried at 120 °C for 48 h.
- [2] Enynones **1** were prepared as described in: K. Miki, F. Nishino, K. Ohe and S. Uemura, *J. Am. Chem. Soc.* **2002**, *124*, 5260.
- [3] Enynones **2** were prepared as described in: (a) G. Bartoli, M. Bosco, A. Carlone, R. Dalpozzo, P. Galzerano, P. Melchiorre and L. Sambri, *Tetrahedron Lett.* **2008**, *49*, 2555; (b) J. González, J. González, C. Pérez-Calleja, L. A. López and R. Vicente, *Angew. Chem. Int. Ed.* **2013**, *52*, 5853.
- [4] (a) K. Miki, S. Uemura and K. Ohe, *Chem. Lett.* **2005**, *34*, 1068; (b) H. Kusama and N. Iwasawa, *Chem. Lett.* **2006**, *35*, 1082; (c) K. Ohe and K. Miki, *J. Synth. Org. Chem. Jpn.* **2009**, *67*, 1161.
- [5] For experimental and computation studies on rhodium-catalyzed cyclopropanations, see: (a) D. T. Nowlan III and D. A. Singleton, *J. Am. Chem. Soc.* **2005**, *127*, 6190; (b) J. A. S. Howell, *Dalton Trans.* **2007**, 3798; (c) J. F. Briones, J. Hansen, K. I. Hardcastle, J. Autschbach and H. M. L. Davies, *J. Am. Chem. Soc.* **2010**, *132*, 17211.
- [6] C. P. Park, A. Nagle, C. H. Yoon, C. Chen and K. W. Jung, *J. Org. Chem.* **2009**, *71*, 6231.











5a

