Supporting Information

Rhodium (III)-catalyzed dearomatizing (3+2) annulation of 2-alkenylphenols and alkynes

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1. GENERAL EXPERIMENTAL PROCEDURES

Reactions were conducted in dry solvents under Argon atmosphere unless otherwise stated. Dry solvents were acquired in Aldrich and used without further purification. Dried acetonitrile was also from Aldrich and dried with a solvent system (MBraun, SPS 800 manual), [RhCp*Cl₂]₂ (99%) [12354-85-7] was purchased in Aldrich, and [Ru(p-cymene)Cl₂]₂ was purchased in TCI [52562-29-0] (>95%). All other chemicals were purchased in Aldrich and used without further purification.

The abbreviation “rt” refers to reactions carried out at a temperature between 21-25 °C. Reaction mixtures were stirred using Teflon-coated magnetic stir bars. High reaction temperatures were maintained using Thermowatch-controlled heating blocks. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and / or by treating the plates with p-anisaldehyde or cerium nitrate solutions, followed by heating. Flash chromatography was carried out on silica gel. Dryings were performed with anhydrous Na₂SO₄.

Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by high vacuum.

All Rhodium-catalyzed reactions were carried out without particular precautions to extrude moisture or oxygen.

1H NMR (300MHz) spectra were recorded at room temperature on a Varian 300MHz spectrometer in CDCl₃ [using CHCl₃ (for 1H, δ = 7.26) as internal standard]. 13C NMR (75 MHz) spectra on a Varian spectrometer in CDCl₃ [using CDCl₃ (for 13C, δ = 77.160) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet . Carbon types and structure assignments were determined from DEPT-NMR and two dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestReNova© NMR data processing software (www.mestrelab.com). Mass spectra were acquired using electronic impact (EI), chemical ionization (CI) and electrospray (ESI) and were recorded at the CACTUS facility of the University of Santiago de Compostela.

Alkenylphenols 1d 2-(1-(4-(trifluoromethyl)phenyl)vinyl)phenol and 1e 2-(1-(4-methoxyphenyl)vinyl)phenol were prepared according to the procedure reported by Sasano, K. et al in J. Am. Chem. Soc., 2013, 135, 10954-10957. All the data recorded for the synthetic product matched the reported data.

Alkynes 2b (1,2-bis(4-methoxyphenyl)ethyne) and 2c (1,2-bis(4-(trifluoromethyl)phenyl)ethyne) were prepared according to a procedure reported in Tsuchimoto, T. et al in Tetrahedron 2005, 61, 9878-9885. Alkyne 2g was prepared according to a procedure reported by Wender PA et. al. Angew. Chem. Int. Ed. 2004, 43, 3076-3079. All the other alkynes were purchased from Aldrich.

All Alkenylphenols substrates were kept under Argon at -60 °C and used freshly within 2-3 days after made.
2. EXPERIMENTAL DATA

GENERAL PROCEDURE (A) for the synthesis of 2-alkenylphenols (1a, 1b, 1c, 1c-d2, 1f, 1h, 1i, 1j, 1m, 1n), exemplified for 1a

To a solution of sodium hydride (0.588 g, 14.7 mmol) in THF (15 mL) under Ar atmosphere was added methyltriphenylphosphoniumbromide (2.62 g, 7.35 mmol) at 0 °C. The reaction mixture was stirred for 1 h at that temperature. Then 1-(2-hydroxyphenyl)ethanone (0.500 g, 3.67 mmol) was added at 0 °C and the reaction was stirred for 3 days at room temperature and quenched with saturated NH4Cl aqueous solution. The solvent was removed in vacuo and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification by flash chromatography on silica gel (hexanes:diethylether; 8:2) gave 2-(prop-1-en-2-yl)phenol (1a) (0.44 g, 91%), yellow liquid.

1H NMR (300 MHz, CDCl3) δ 7.25 – 7.15 (m, 2H), 7.01 – 6.87 (m, 2H), 5.76 (s, 1H), 5.47 – 5.40 (m, 1H), 5.21 – 5.15 (m, 1H), 2.15 (dd, J = 1.6, 0.9 Hz, 3H).

13C NMR (75 MHz, CDCl3) δ 152.0 (C), 142.2 (C), 129.0 (C), 128.7 (CH), 127.9 (CH), 120.3 (CH), 115.9 (CH2), 115.7 (CH), 24.3 (CH3). LRMS (CI) (m/z, I): 135(100). HRMS calculated for C9H11O 135.0810, found 135.0810.

2-(but-1-en-2-yl)phenol (1b): 68%, pale yellow liquid. 1H NMR (300 MHz, CDCl3) δ 7.25 – 7.07 (m, 2H), 7.02 – 6.86 (m, 2H), 5.70 (dd, J = 1.9, 1.1 Hz, 1H), 5.41 (dd, J = 1.6, 0.8 Hz, 1H), 5.16 (dd, J = 1.8, 0.9 Hz, 1H) 2.45 (q, J = 7.4 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H).

13C NMR (75 MHz, CDCl3) δ 152.3 (C), 148.1 (C), 128.6 (CH), 128.0 (CH), 120.2 (CH), 115.5 (CH), 114.1 (CH2), 30.8 (CH2), 12.6 (CH3). LRMS (Cl) (m/z, I): 149 (100), 133 (59), 107 (83). HRMS calculated for C10H13O 149.0966, found 149.0965.

2-(1-phenylvinyl)phenol (1c): 91% yield, yellow liquid. 1H NMR (300 MHz, CDCl3) δ (ppm): 7.45 – 7.33 (m, 5H), 7.28 (dd, J = 6.2, 4.4 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.98 (ddd, J = 8.6, 5.8, 2.1 Hz, 2H), 5.91 (d, J = 1.2 Hz, 1H), 5.46 (d, J = 1.2 Hz, 1H), 5.24 (d, J = 1.2 Hz, 1H). 13C NMR (75 MHz, CDCl3) δ 153.2 (C), 145.4 (C), 139.5 (C), 130.6 (CH), 129.6 (CH), 128.8 (CH), 127.7 (C), 127.2 (CH), 120.6 (CH), 116.9 (CH3), 116 (CH). LRMS (Cl) (m/z, I): 197 (98), 195 (92), 181 (96), 103 (100). HRMS calculated for C14H12O 195.0810 found, 195.0809.

2-(1-phenylvinyl)phenol-d2 (1c-d2, 88% deuteration): 94%, pale yellow liquid. 1H NMR (300 MHz, CDCl3) δ 7.51 – 7.24 (m, 6H), 7.19 (dd, J = 4.1, 3.4 Hz, 1H), 7.07 – 6.93 (m, 2H), 5.90 (s, 0.12H), 5.46 (s, 0.12H), 5.27 (s, 1H). 13C NMR (75 MHz, CDCl3) δ 153.2(C), 145.2 (C), 139.5 (C), 130.5 (CH), 129.6 (CH), 128.8 (CH), 127.6 (C), 127.1 (CH), 120.6 (CH), 115.9 (CH) LRMS (Cl) (m/z, I): 199(100), 181 (27). HRMS calculated for C14D12O 0198.1014, found 198.1016.

This compound was synthesized using trideuterated methyltriphenylphosphoniumiodide instead of methyltriphenylphosphoniumbromide.
4-methyl-2-(prop-1-en-2-yl)phenol (1f): 80%, yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): δ 7.09 – 6.98 (m, 2H), 6.94 – 6.86 (m, 1H), 5.79 (s, 1H), 5.48 – 5.36 (m, 1H), 5.19 (dd, J = 1.9, 0.9 Hz, 1H), 2.34 (d, J = 0.5 Hz, 3H), 2.23 – 2.16 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.7 (C), 142.4 (C), 129.3 (C), 129.1 (CH), 128.8 (C), 128.3 (CH), 115.6 (CH$_2$), 115.5 (CH), 24.16 (CH$_3$), 20.5 (CH$_3$). LRMS (EI) (m/z, I): 148 (100), 133 (50), 105 (61). HRMS calculated for C$_{10}$H$_{12}$O: 148.0888 found, 148.0889.

4-bromo-2-(prop-1-en-2-yl)phenol (1h): 79% yield, red liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.29 – 7.24 (m, 2H), 6.83 (dd, J = 6.8, 2.3 Hz, 1H), 5.70 (s, 1H), 5.44 (dd, J = 1.3 Hz, 1H), 5.18 (s, 1H), 2.12 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 151.2 (C), 141.2 (C), 131.5 (CH), 131.0 (C), 130.6 (CH), 117.5 (CH), 116.9 (CH$_2$), 112.4 (C), 24.2 (CH$_3$). LRMS (EI) (m/z, I): 212 (16), 149 (64), 118 (23), 5 (100). HRMS calculated for C$_{10}$H$_{13}$Br: 211.9837 found, 211.9820.

5-fluoro-2-(prop-1-en-2-yl)phenol (1l): 36% yield, yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.09 – 6.69 – 6.58 (m, 2H), 5.91 (s, 1H), 5.41 (dd, J = 3.0, 1.5 Hz, 1H), 5.12 (dd, J = 1.7, 0.8 Hz, 1H), 2.10 (d, J = 0.9 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.7 (C, d, J = 245.5 Hz), 153.3 (C, d, J = 11.7 Hz), 141.6 (C), 128.8 (CH, d, J = 9.9 Hz), 125.0 (C, d, J = 3.1 Hz), 116.0 (CH$_2$), 107.3 (CH, d, J = 21.7 Hz), 103.1 (CH, d, J = 24.9 Hz), 24.4(CH$_3$). LRMS (EI) (m/z, I): 148 (73), 139 (38), 85 (75), 57 (100).

5-chloro-2-(prop-1-en-2-yl)phenol (1j): 73%, yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.06 (d, J = 8.2 Hz, 1H), 6.95 (d, J = 2.1 Hz, 1H), 6.90 – 6.85 (m, 1H), 5.82 (s, 1H), 5.43 – 5.40 (m, 1H), 5.15 – 5.13 (m, 1H), 2.11 – 2.08 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 152.8 (C), 141.4 (C), 133.8 (C), 128.8 (CH), 127.5 (C), 120.6 (CH), 116.4 (CH$_2$), 116.0 (CH), 24.3 (CH$_3$). LRMS (EI) (m/z, I): 168 (45), 155 (50), 104 (64), 91 (100). HRMS calculated for C$_{9}$H$_{11}$ClO: 168.0342 found, 169.0344.

2-(prop-1-en-2-yl)-5,6,7,8-tetrahydronaphthalen-1-ol (1m): 62%, yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 6.93 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 5.85 (s, 1H), 5.43 – 5.40 (m, 1H), 5.15 (s, 1H), 2.80 – 2.70 (m, 4H), 2.14 – 2.12 (m, 3H), 1.90 – 1.76 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.6 (C), 142.8 (C), 138.1 (C), 125.3 (C), 124.3 (CH), 124.1 (CH), 120.6 (C), 115.3 (CH), 29.7 (CH$_3$), 24.6 (CH$_3$), 23.5 (CH$_3$), 23 (CH$_3$), 22.9 (CH$_3$), 22.9 (CH$_3$). LRMS (EI) (m/z, I): 188 (100), 173 (90), 160 (32), 145 (67). HRMS calculated for C$_{12}$H$_{15}$O: 188.1201 found, 188.1200.

4, 5-dimethyl-2-(prop-1-en-2-yl)phenol (1n): 25% yield, white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 6.92 (d, J = 4.6 Hz, 1H), 6.76 (d, J = 4.8 Hz, 1H), 5.54 (dd, J = 4.1, 2.5 Hz, 1H), 5.37 (ddt, J = 4.8, 3.3, 1.6 Hz, 1H), 5.13 (s, 1H), 2.25 – 2.22 (m, 3H), 2.22 – 2.19 (m, 3H), 2.12 (dd, J = 3.3, 1.3 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.9 (C), 142.3 (C), 137.2 (C), 128.7 (CH), 128.1 (C), 126.1 (C), 116.8 (CH), 115.3 (CH$_2$), 77.1 (C), 24.4 (CH$_3$), 19.7 (CH$_3$), 18.9 (CH$_3$). LRMS (CI) (m/z, I): 163 (100), 162 (79), 147 (83). HRMS calculated for C$_{11}$H$_{13}$O: 163.1123 found, 163.1125.
GENERAL PROCEDURE (B) for the synthesis of 2-alkenylphenols (1g, 1k), exemplified for (1g)

To a solution of methyltriphenylphosphoniumbromide (2.10 g, 6.02 mmol) in THF (25 mL) was added dropwise a butyllithium solution in THF (2.6 mL, 6.02 mmol) at -78 °C. The resulting mixture was stirred 15 minutes and allowed to reach rt. After cooling the mixture again to -78 °C, 1-(2-hydroxy-4-methoxyphenyl)ethanone (0.5 g, 3.01 mmol) was added and the reaction was stirred for 4 hours at room temperature and quenched with saturated NH₄Cl aqueous solution. The solvent was removed in vacuo and the resulting mixture was extracted with diethyl ether. The combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Solvent evaporation followed by flash column chromatography purification on silica gel (hexanes:diethylether; 8:3) yielded 4-methoxy-2-(prop-1-en-2-yl)phenol (1g) (0.16 g, 32%), yellow liquid.

$$^1$$H NMR (300 MHz, CDCl₃) δ (ppm): 7.07 (d, J = 7.9 Hz, 1H), 6.58 – 6.48 (m, 2H), 5.94 (s, 1H), 5.35 (dt, J = 3.2, 1.5 Hz, 1H), 5.11 (dd, J = 1.8, 0.9 Hz, 1H), 3.79 (d, J = 3.4 Hz, 3H), 2.11 – 2.10 (m, 3H).

$$^{13}$$C NMR (75 MHz, CDCl₃) δ: 160.0 (C), 153.2 (C), 142.1 (C), 128.5 (CH), 121.5 (C), 114.9 (CH₂), 106.4 (CH), 101.1 (CH), 55.3 (CH₃), 24.5 (CH₃).

LRMS (EI) (m/z, I): 164 (100), 149 (23), 137 (10). HRMS calculated for C₁₀H₁₂O₂: 165.0916 found, 165.0916.

5-methoxy-2-(prop-1-en-2-yl)phenol (1k): 42 %, yellow liquid. $$^1$$H NMR (300 MHz, CDCl₃) δ (ppm): 7.06 (d, J = 8.3 Hz, 1H), 6.52 – 6.44 (m, 2H), 5.91 (s, 1H), 5.37 – 5.32 (m, 1H), 5.13 – 5.07 (m, 1H), 3.78 (s, 3H), 2.10 (dd, J = 1.4, 0.9 Hz, 3H).

$$^{13}$$C NMR (75 MHz, CDCl₃) δ: 160.1 (C), 153.2 (C), 142.1 (C), 128.5 (CH), 121.5 (C), 114.9 (CH₂), 106.5 (CH), 101.1 (CH), 55.4 (CH₃), 24.6 (CH₃).

LRMS (CI) (m/z, I): 164 (100), 152 (85), 149 (72), 108 (64). HRMS calculated for C₁₀H₁₂O₂: 164.1 found, 164.1.
Rh-catalyzed annulations (protocol A)

\[
\text{HO} \begin{array}{c} \text{Ph} \\ \text{Ph} \\ \text{Me} \\ \text{Ph} \\ \text{Ph} \\ \text{Me} \\ \text{Ph} \\ \text{Ph} \\ \text{Ph} \\ \text{Ph} \\ \text{Ph} \end{array} \quad + \quad \begin{array}{c} \text{R}_3 \\ \text{R}_4 \end{array} \quad \xrightarrow{2.5 \text{ mol}\% [\text{Cp*RhCl}_2]} \quad 0.5 \text{ equiv Cu(OAc)}_2 \cdot \text{H}_2\text{O} \quad \text{air, CH}_3\text{CN, 40 °C, 1-16h} \quad \text{O} \\ \text{R}_1 \\ \text{R}_2 \end{array}
\]

To a solution of \([\text{Cp*RhCl}_2]_2\) (5.2 mg, 2.5 mol%) and \(\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}\) (33 mg, 0.5 equiv, 0.165 mmol) in \(\text{CH}_3\text{CN}\) (2 mL) under air atmosphere was added the alkyne 2 (0.333 mmol) followed by the addition of corresponding \(\text{orto-vinylphenols}\) 1 (0.50 mmol, 1.5 equiv). The reaction was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 40 °C, stirred until full conversion as followed by TLC and then cooled to room temperature. The solvents were removed \textit{in vacuo} and the remaining residue was purified by flash column chromatography on silica gel to afford the corresponding spirocycles 4. In some cases we also isolated small proportions of products 3 and 5.

Yields are indicated in the main manuscript.

4\text{-methyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4aa)}: brown solid. \(\textsuperscript{1}H\) \text{NMR} (500 MHz, \text{CDCl}_3) \(\delta\) 7.39 – 7.33 (m, 2H), 7.32 – 7.23 (m, 3H), 7.22 – 7.17 (m, 1H), 7.16 – 7.11 (m, 3H), 7.10 – 7.04 (m, 2H), 6.63 – 6.59 (m, 1H), 6.55 – 6.49 (m, 1H), 6.29 (dd, \(J = 9.9, 0.5\) Hz, 1H), 6.11 – 6.07 (m, 1H), 1.89 – 1.74 (m, 3H). \(\textsuperscript{13}C\) \text{NMR} (126 MHz, \text{CDCl}_3) \(\delta\) 197.3 (C), 145.6 (C), 143.3 (CH), 141.9 (CH), 141.2 (C), 135.9 (C), 135.7 (C), 135.6 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.6 (CH), 127.0 (CH), 122.8 (CH), 77.2 (C), 13.1 (CH\_3). \text{LRMS (CI)} (m/z, I): 311 (29), 137 (100). \text{HRMS} calculated for C\_23H\_19O\_3 311.1436, found 311.1438.

The structure of this compound was further confirmed by XR-analyis. CCDC 995495 contains the crystallographic data of 4aa, which can be obtained via www.ccdc.cam.ac.uk/data_request/cif.

3a\text{-methyl-1,2-diphenylazulen-4(3aH)-one (5aa)}: yellow oil.\(\textsuperscript{1}H\) \text{NMR} (500 MHz, \text{CDCl}_3) \(\delta\) 7.27 – 7.20 (m, 4H), 7.16 – 7.09 (m, 3H), 7.05 – 6.99 (m, 4H), 6.72 (d, \(J = 11.2\) Hz, 1H), 6.62 (dd, \(J = 12.3, 8.3\) Hz, 1H), 6.07 (dd, \(J = 11.1, 8.3\) Hz, 1H), 5.70 (d, \(J = 12.3\) Hz, 1H), 1.32 (s, 3H). \(\textsuperscript{13}C\) \text{NMR} (126 MHz, \text{CDCl}_3) \(\delta\) 199.7 (C), 150.3 (C), 145.4 (C), 144.0 (CH), 140.9 (C), 137.1 (CH), 134.9 (C), 134.4 (C), 132.0 (CH), 130.5 (CH), 128.4 (CH), 128.8 (CH), 128.0 (CH), 127.5 (CH), 123.1 (CH), 122.7 (CH), 67.7 (C), 24.6 (CH\_3). \text{LRMS (EI)} (m/z, I): 310 (100), 295 (10), 282 (53), 267 (71) \text{HRMS} calculated for C\_23H\_18O\_3 310.1358, found 310.1359.
1,2-bis(4-methoxyphenyl)-4-methylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ab): brown solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.32 – 7.23 (m, 2H), 7.19 – 7.12 (m, 1H), 7.04 – 6.94 (m, 2H), 6.83 – 6.75 (m, 2H), 6.70 – 6.61 (m, 2H), 6.55 (d, $J$ = 1.5 Hz, 1H), 6.47 (dd, $J$ = 9.2, 6.0 Hz, 1H), 6.24 (d, $J$ = 9.8 Hz, 1H), 6.08 – 6.01 (m, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 1.78 (d, $J$ = 1.4 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.3 (C), 158.9 (C), 158.3 (C), 144.5 (C), 143.8 (C), 143.4 (CH), 142.3 (CH), 139.5 (C), 135.6 (CH), 129.7 (CH), 129.4 (CH), 128.5 (CH), 128.3 (C), 122.5 (CH), 113.7 (CH), 113.7 (CH), 77.1 (C), 55.2 (CH$_2$), 55.1 (CH$_3$), 13.0 (CH$_3$). LRMS (CI) ($m/z$, $I$): 371 (100).

HRMS calculated for C$_{35}$H$_{35}$O$_3$ 371.1647, found 371.1647.

4-methyl-1,2-bis(4-trifluoromethyl)phenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ac): brown solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.13 – 7.07 (m, 2H), 6.60 – 6.51 (m, 2H), 6.29 (d, $J$ = 9.9 Hz, 1H), 6.08 – 6.01 (m, 1H), 1.83 (d, $J$ = 1.6 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.4 (C), 147.6 (C), 146.1 (C), 143.5 (CH), 141.2 (C), 140.7 (CH), 139.0 (C), 138.7 (C), 134.9 (CH), 130.0 (C, $q$, $J$ = 31.9 Hz), 128.9 (CH), 128.8 (CH), 128.4 (CH), 125.7 (CH, $q$, $J$ = 3.7 Hz), 125.5 (CH, $q$, $J$ = 3.7 Hz), 124.1 (q, $J$ = 272.0 Hz), 123.5 (CH), 13.1 (CH$_3$). LRMS (CI) ($m/z$, $I$): 447 (99), 427 (100). HRMS calculated for C$_{32}$H$_{25}$F$_5$O$_4$ 447.1194, found 447.1194.

1,2-diethyl-4-methylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ad): yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.20 – 7.11 (m, 1H), 6.41 (dd, $J$ = 9.1, 5.9 Hz, 1H), 6.24 – 6.14 (m, 2H), 5.73 (dd, $J$ = 9.1, 1.1 Hz, 1H), 2.26 (q, $J$ = 7.6 Hz, 2H), 2.05 (q, $J$ = 7.6 Hz, 2H), 1.64 (d, $J$ = 1.3 Hz, 3H), 1.06 (t, $J$ = 7.6 Hz, 3H), 0.88 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 198.8 (C), 146.4 (C), 143.3 (CH), 143.2 (C), 142.7 (CH), 141.9 (C), 134.1 (CH), 128.3 (CH), 122.1 (CH), 76.1 (C), 20.6 (CH$_3$), 20.0 (CH$_2$), 14.7 (CH$_3$), 13.9 (CH$_3$), 13.2 (CH$_2$). LRMS (CI) ($m/z$, $I$): 215 (100), 199 (17), 185 (98). HRMS calculated for C$_{24}$H$_{24}$O$_2$ 215.1436, found 215.1439.

1,2-bis(((tert-butyl(dimethyl)silyl)oxy)methyl)-4-methylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ae): yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.14 – 7.05 (m, 1H), 6.38 (dd, $J$ = 9.2, 5.9 Hz, 1H), 6.27 (d, $J$ = 1.6 Hz, 1H), 6.17 (d, $J$ = 9.8 Hz, 1H), 5.84 – 5.74 (m, 1H), 4.46 (q, $J$ = 13.5 Hz, 2H), 4.25 (q, $J$ = 13.2 Hz, 2H), 1.67 (d, $J$ = 1.3 Hz, 3H), 0.90 (s, 9H), 0.81 (s, 9H), 0.07 (d, $J$ = 3.3 Hz, 6H), -0.05 (d, $J$ = 4.1 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.3 (C), 145.0 (C), 144.8 (C), 142.6 (CH), 141.6 (CH), 141.2 (C), 132.5 (CH), 128.4 (CH), 121.8 (CH), 74.9 (C), 59.0 (CH$_2$), 58.2 (CH$_2$), 26.04 (CH$_3$), 26.00 (CH$_3$), 21.85 (C), 13.0 (CH$_2$), -5.1 (CH$_3$), -5.49 (CH$_3$), -5.53 (CH$_3$). LRMS (CI) ($m/z$, $I$): 446 (7), 389 (13), 314 (19), 301 (63). HRMS calculated for C$_{37}$H$_{43}$SiO$_4$ 446.2673, found 446.2673.

2-ethyl-4-methyl-1-phenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4af): yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.27 – 7.07 (m, 6H), 6.48 – 6.34 (m, 2H), 6.22 (d, $J$ = 9.8 Hz, 1H), 5.99 – 5.91 (m, 1H), 2.49 (q, $J$ = 7.5 Hz, 2H), 1.74 (d, $J$ = 1.4 Hz, 3H), 1.18 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.9 (C), 148.8 (C), 145.2 (C), 143.3 (CH), 142.6 (CH), 140.0 (C), 135.7 (CH), 134.9 (CH), 128.5 (CH), 128.2 (CH), 128.0 (CH), 126.6 (CH), 122.4 (CH), 76.5 (C), 21.7 (CH$_3$), 13.8 (CH$_3$), 12.9 (CH$_3$). LRMS (EI) ($m/z$, $I$): 262 (100), 247(67), 233 (27), 219 (28), 205 (58). HRMS calculated for C$_{38}$H$_{36}$O$_2$ 262.1358, found 262.1358.
Assignment of the regiochemistry

The major regioisomer was assigned based on the HMBC, HSQC, COSY experiments, as well as by the observation of nOe between the ethyl chain and the C3 hydrogen of the spiro unit.

2-cyclopropyl-4-methyl-1-phenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ag): yellow oil. $^1$H NMR $^{(300}$ MHz, CDCl$_3$) δ 7.35 – 7.23 (m, 4H), 7.22 – 7.13 (m, 2H), 6.50 – 6.43 (m, 1H), 6.27 (dd, $J = 9.8$, 0.6 Hz, 1H), 6.05 – 5.95 (m, 2H), 2.03 – 1.91 (m, 1H), 1.74 (d, $J = 1.6$ Hz, 3H), 0.99 – 0.81 (m, 3H), 0.79 – 0.63 (m, 1H). $^{13}$C NMR $^{(75}$ MHz, CDCl$_3$) δ 197.9 (C), 148.5 (C), 145.4 (C), 143.3 (CH), 142.8 (CH), 139.8 (C), 135.9 (C), 131.2 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 126.5 (CH), 122.4 (CH), 76.6 (C), 13.0 (CH$_3$), 10.5 (CH), 7.7 (CH$_2$), 7.6 (CH$_2$). LRMS (EI) $^{(m/z, I)}$: 274 (100), 259 (48), 246 (27), 231 (47), 215 (79). HRMS calculated for $\text{C}_{20}$H$_{18}$O$_2$ 274.1349, found 274.1358.

Assignment of the regiochemistry

The major regioisomer was assigned based on the HMBC, HSQC, COSY experiments, as well as by the observation of nOe between the cyclopropyl chain and the hydrogen of the C3 of the spiro unit.

2-(hydroxymethyl)-4-methyl-1-phenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ah): yellow oil. $^1$H NMR $^{(500}$ MHz, CDCl$_3$) δ 7.27 – 7.17 (m, 4H), 7.09 – 7.04 (m, 2H), 6.57 (q, $J = 1.5$ Hz, 1H), 6.50 (dd, $J = 9.2$, 5.9 Hz, 1H), 6.01 – 5.97 (m, 1H), 4.53 (dd, $J = 51.2$, 13.0 Hz, 2H), 3.00 (br s, 1H), 1.73 (d, $J = 1.5$ Hz, 3H). $^{13}$C NMR $^{(75}$ MHz, CDCl$_3$) δ 197.7 (C), 146.2 (C), 145.5 (C), 143.8 (CH), 142.2 (C), 141.9 (CH), 134.4 (C), 133.8 (CH), 128.2 (CH), 127.7 (CH), 127.0 (CH), 122.5 (CH), 76.3 (C), 58.5 (CH$_2$), 12.7 (CH$_3$). LRMS (EI) $^{(m/z, I)}$: 264 (100), 247 (30), 234 (31), 219 (27), 202 (50). HRMS calculated for $\text{C}_{22}$H$_{16}$O$_2$ 264.1150, found 264.1150.

Assignment of the regiochemistry

The major regioisomer was assigned based on the HMBC, HSQC, COSY experiments, as well as by the observation of nOe between the CH$_2$OH chain and the hydrogen of the C3.

2-ethyl-4-methyl-1-(prop-1-en-2-yl)spiro[4.5]deca-1,3,7,9-tetraen-6-one (4ai): yellow oil. $^1$H NMR $^{(300}$ MHz, CDCl$_3$) δ 7.21 – 7.11 (m, 1H), 6.47 – 6.38 (m, 1H), 6.27 – 6.21 (m, 2H), 5.89 – 5.80 (m, 1H), 4.77 (s, 1H), 4.46 (s, 1H), 2.63 – 2.38 (m, 2H), 1.86 – 1.81 (m, 3H), 1.64 (d, $J = 1.3$ Hz, 3H), 1.12 (dd, $J = 7.8$, 7.3 Hz, 3H). $^{13}$C NMR $^{(75}$ MHz, CDCl$_3$) δ 197.9 (C), 148.8 (C), 144.2 (C), 143.9 (CH), 143.0 (CH), 142.0 (C), 139.1 (C), 135.7 (C), 128.4 (CH), 121.8 (CH), 114.1 (CH), 75.6 (C), 23.4 (CH$_3$), 22.3 (CH$_2$), 14.2 (CH$_3$), 12.5 (CH$_3$). LRMS (EI) $^{(m/z, I)}$: 226 (67), 211 (65), 198 (100), 183 (72). HRMS calculated for $\text{C}_{16}$H$_{18}$O 226.1358, found 226.1356.

Assignment of the regiochemistry

The major regioisomer was assigned based on the HMBC, HSQC, COSY experiments, as well as by the observation of nOe between the PH chain and the hydrogen of the C3.
the CH₃CH₃ chain and the hydrogen of the C3.

4-ethyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ba): brown solid. ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.33 (m, 2H), 7.30 – 7.21 (m, 3H), 7.20 – 7.01 (m, 6H), 6.62 (t, J = 1.9 Hz, 1H), 6.48 (dd, J = 9.1, 6.0 Hz, 1H), 6.25 (d, J = 9.8 Hz, 1H), 6.15 – 5.98 (m, 1H), 2.21 – 2.00 (m, 2H), 1.16 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 197.4 (C), 152.1 (C), 145.4 (C), 143.3 (CH), 142.1 (CH), 140.9 (C), 135.9 (C), 135.6 (C), 133.2 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.6 (CH), 127.0 (CH), 122.7 (CH), 77.1 (C), 20.6 (CH₃), 12.1 (CH₃). LRMS (EI) (m/z, l): 324 (100), 309 (45), 296 (21), 279 (18), 267 (86). HRMS calculated for C₂₈H₂₃O₂.1514, found 324.1523.

4,9-dimethyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4fa): Red oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.31 (dt, J = 8.5, 4.4 Hz, 2H), 7.27 – 7.2 (m, 3H), 7.14 – 7.08 (m, 3H), 7.01 (dd, J = 6.3, 3.4 Hz, 3H), 6.53 (d, J = 1.6 Hz, 1H), 6.20 (d, J = 9.9 Hz, 1H), 5.73 (s, 1H), 2.03 (d, J = 1.4 Hz, 3H), 1.79 (d, J = 1.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ(ppm): 197.5 (C), 147.6 (CH), 146.3 (C), 145.1 (C), 141.5 (C), 136.0 (C), 135.8 (C), 135.4 (CH), 134.9 (CH), 130.6 (C), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.5 (CH), 126.9 (CH), 76.5 (C), 21.2 (CH₃), 13.2 (CH₃). HRMS (m/z, ESI) for C₂₉H₂₄O⁺: 325.1639.

9-methoxy-4-methyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ga): Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.37 (dd, J = 1.4, 2H), 7.33 – 7.25 (m, 3H), 7.19 – 7.10 (m, 5H), 6.67 – 6.63 (m, 1H), 6.43 – 6.37 (m, 1H), 6.13 – 6.05 (m, 1H), 5.74 (d, J = 1.8 Hz, 1H), 3.83 (s, 3H), 1.90 – 1.83 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ(ppm): 195.5 (C), 173.0 (C), 145.8 (C), 145.5 (C), 142.3 (CH), 141.4 (C), 135.8 (C), 135.2 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 127.5 (CH), 127 (CH), 122.9 (CH), 102.9 (CH), 75.4 (C), 56.0 (CH₃), 13.1(CH₃). HRMS (m/z, ESI) calculated for C₂₉H₂₄O₂ [M+H]⁺: 341.1638.

8-methoxy-4-methyl-1,2-diphenylspiro[4.5] deca-1,3,7,9-tetraen-6-one (4ka): Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.39 – 7.33 (m, 2H), 7.31 – 7.23 (m, 3H), 7.17 – 7.09 (m, 5H), 6.63 (d, J = 1.6 Hz, 1H), 6.41 – 6.36 (m, 1H), 6.08 (d, J = 9.8 Hz, 1H), 5.73 (d, J = 1.8 Hz, 1H), 3.82 (s, 3H), 1.85 (d, J = 1.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ(ppm): 195.6 (C), 173.1 (C), 145.8 (C), 145.5 (C), 142.4 (CH), 141.4 (C), 135.8 (C), 135.3 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127 (CH), 123 (CH), 103 (CH), 75.4 (C), 56.0 (CH₃), 13.1 (CH₃). HRMS (m/z, ESI) calculated for C₂₉H₂₄O₂ [M+H]⁺: 341.1533 found, 341.1536.

8-fluoro-4-methyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one (4ja): Red oil. ¹H NMR (500 MHz, CDCl₃ δ(ppm): 7.38 – 7.30 (m, 2H), 7.31 – 7.22 (m, 3H), 7.19 – 7.12 (m, 3H), 7.08 – 7.02 (m, 2H), 6.65 (q, J = 1.5 Hz, 1H), 6.55 – 6.48 (m, 1H), 6.24 – 6.20 (m, 1H), 6.04 (dd, J = 12.5, 2.0 Hz, 1H), 1.84 (t, J = 2.0 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃ δ(ppm): 196.1 (C, d, J = 18.1 Hz), 175 (C, d, J = 279.2 Hz), 146.2 (C), 145.2 (CH, d, J = 13.8 Hz), 144.9 (C), 140.7 (C), 136.3 (CH), 135.4 (C), 135.3 (C), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.3 (CH), 119.7 (CH, d, J = 33.1 Hz), 109.8 (CH, d, J = 12.6 Hz), 76.5 (C), 13.1 (CH₃). HRMS (m/z, ESI) calculated for C₂₉H₁₉FO [M+H]⁺: 329.1336 found, 329.1342.
8-chloro-4-methyl-1,2-diphenylspiro[4,5]deca-1,3,7,9-tetraen-6-one (4ja): Red solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.29 (dd, $J = 5.2$, 3.3 Hz, 1H), 7.24 (dd, $J = 5.1$, 2.0 Hz, 3H), 7.11 ($t$, $J = 3.2$ Hz, 3H), 7.00 (dd, $J = 6.6$, 3.0 Hz, 3H), 6.60 (d, $J = 1.5$ Hz, 1H), 6.51 (dd, $J = 9.6$, 1.3 Hz, 1H), 6.44 (s, 1H), 6.07 (s, 1H), 1.81 (d, $J = 1.4$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 194.2 (C), 152.9 (C), 146.1 (C), 145.2 (C), 142.4 (CH), 140.9 (C), 136.2 (CH), 135.5 (C), 135.4 (C), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.3 (CH), 126.8 (CH), 126.3 (CH), 75.9 (C), 13.2 (CH$_3$). HRMS (m/z, ESI) calculated for C$_{23}$H$_{18}$ClO: 345.1047 found, 345.1041.

confirmed by XR-analysis. CCDC 995496 contains the crystallographic data of 4aj, which can be obtained via www.ccdc.cam.ac.uk/data_request/cif.

8-chloro-2-ethyl-4-methyl-1-phenylspiro[4,5]deca-1,3,7,9-tetraen-6-one (4jf): Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.30 – 7.19 (m, 3H), 7.10 – 7.06 (m, 2H), 6.49 – 6.45 (m, 1H), 6.43 – 6.40 (m, 2H), 6.01 – 5.97 (m, 1H), 2.47 (q, $J = 7.3$ Hz, 2H), 1.76 (d, $J = 1.6$ Hz, 3H), 1.18 ($t$, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 194.7 (C), 152.9 (C), 149.5 (C), 144.9 (C), 143.1 (CH), 139.9 (C), 135.5 (CH), 135.4 (C), 128.4 (CH), 128.0 (CH), 127.0 (CH), 126.7 (CH), 125.9 (CH), 75.2 (C), 21.7 (CH$_2$), 13.8 (CH$_3$), 13.1 (CH$_3$). HRMS (m/z, ESI) calculated for C$_{18}$H$_{16}$ClO: 297.1036 found, 297.1041.

Assignment of the regiochemistry. The major regioisomer was assigned based on the HMBC, HSQC, COSY experiments, as well as by the observation of nOe between the CH$_2$ to ethyl chain and the hydrogen of the C3.

5-methyl-2,3-diphenyl-5′, 6′, 7′, 8′-tetrahydro-1′H-spiro[cyclopenta[2,4]diene-1,2-naphthalene]1′-one (4ma): Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.39 – 7.34 (m, 2H), 7.28 (t, $J = 2.2$ Hz, 1H), 7.27 – 7.25 (m, 2H), 7.16 – 7.11 (m, 3H), 7.07 – 7.02 (m, 2H), 6.57 (q, $J = 1.4$ Hz, 1H), 6.28 (d, $J = 9.3$ Hz, 1H), 5.92 (d, $J = 9.3$ Hz, 1H), 2.47 – 2.33 (m, 4H), 1.81 (d, $J = 1.5$ Hz, 3H), 1.71 (dt, $J = 11.5$, 4.6 Hz, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 196.2 (C), 150.7 (C), 146.1 (C), 144.9 (C), 141.6 (C), 136.6 (CH), 136.2 (C), 135.9 (C), 134.7 (CH), 133.6 (C), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 76.0 (C), 30.8 (CH$_2$), 22.1 (CH$_3$), 22.0 (CH$_2$), 13.2 (CH$_3$). LRMS (CI) (m/z, l): 346 (69), 344 (69), 173 (100).

4,8,9-Trimethyl-1,2-diphenylspiro[4,5] deca-1,3,7,9-tetraen-6-one (4na): Yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.37 – 7.28 (m, 2H), 7.24 (ddd, $J = 6.5$, 3.7, 1.1 Hz, 3H), 7.16 – 7.07 (m, 3H), 7.07 – 7.00 (m, 2H), 6.59 – 6.51 (m, 1H), 6.15 (s, 1H), 5.76 (s, 1H), 2.13 (s, 3H), 2.03 (d, $J = 1.0$ Hz, 3H), 1.81 – 1.78 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm): 197.1 (C), 157.3 (C), 146.3 (C), 145.0 (C), 141.6 (C), 136.1 (C), 136 (CH), 135.9 (C), 134.8 (CH), 132.4 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.4 (CH), 127 (CH), 126.8 (CH), 21.7 (CH$_3$), 19.2 (CH$_3$), 13.2 (CH$_3$). LRMS (CI) (m/z, l): 339 (60), 338 (39), 275 (71), 257 (100), 246 (86), 149 (91). HRMS calculated for C$_{25}$H$_{23}$O: 339.1749 found, 339.1749.

S10
Rh-catalyzed annulation to give spirocycles 4ca, 4da, 4ea, 4ha. Protocol B

To a solution of [Cp*RhCl₂]₂ (5.2 mg, 2.5 mol%) and Cu(OAc)₂·H₂O (33 mg, 0.5 equiv, 0.165 mmol) in CH₃CN (2 mL) under air atmosphere was added the alkyne 2 (0.333 mmol) followed by the addition of corresponding orto-vinylphenols 1 (0.50 mmol, 1.5 equiv). The reaction flask was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 60 °C, stirred until completion followed by TLC and then cooled to room temperature. The solvents were removed in vacuo and the remaining residue was purified by flash column chromatography on silica gel to afford the corresponding spirocycles 4.

1,2,4-triphenylspiro[4,5]deca-1,3,7,9-tetraen-6-one (4ca): Orange solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.51 (s, 1H), 7.36 – 7.32 (m, 6H), 7.28 – 7.18 (m, 7H), 7.17 – 7.09 (m, 3H), 6.53 (dd, J = 9.2, 6.0 Hz, 1H), 6.33 (d, J = 9.9 Hz, 1H), 6.28 – 6.23 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 196.5 (C), 148.2 (C), 145.7 (C), 143.1 (CH), 142.3 (C), 141.5 (CH), 135.0 (C), 134.9 (C), 134.1 (CH), 133.6 (C), 129.4 (CH), 129.2 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.7 (CH), 127.5 (CH), 123.2 (CH), 75.5 (C). HRMS (m/z, ESI) calculated for C₂₈H₂₁O [M+H]⁺ 373.1587 found, 373.1577.

4-(4-methoxyphenyl)-1,2-diphenylspiro[4,5]deca-1,3,7,9-tetraen-6-one (4ea): Brown foam. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.30 – 7.15 (m, 11H), 7.14 – 7.06 (m, 3H), 6.89 – 6.80 (m, 2H), 6.48 (dd, J = 9.0, 6.0 Hz, 1H), 6.27 – 6.17 (m, 2H), 3.78 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 196.8 (C), 159.8 (C), 148.6 (C), 146.3 (C), 143.6 (CH), 142.1 (CH), 141.9 (C), 135.7 (C), 135.6 (C), 132.5 (CH), 129.8 (CH), 129.5 (CH), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.0 (CH), 127.4 (CH), 127.1 (C), 123.6 (CH), 114.7 (CH), 75.9 (C), 55.8 (CH₃). LRMS (CI) (m/z, I): 403 (49), 271 (50), 228 (100). HRMS calculated for C₂₉H₂₃O₂ 441.1466.

8-bromo-4-methyl-1,2-diphenylspiro[4,5]deca-1,3,7,9-tetraen-6-one (4ha): Red oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.32 – 7.22 (m, 4H), 7.17 – 7.13 (m, 4H), 7.11 (d, J = 2.7 Hz, 1H), 7.04 – 7.01 (m, 2H), 6.58 (t, J = 1.6 Hz, 1H), 6.30 (d, J = 2.6 Hz, 1H), 6.15 (d, J = 10.1 Hz, 1H), 1.86 (d, J = 1.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 194.9 (C), 146.7 (CH), 145.7 (C), 145.0 (C), 140.4 (C), 139.6 (CH), 135.7 (CH), 135.4 (C), 135.2 (C), 130.0 (CH), 129.0 (CH), 128.5 (CH), 128.0 (CH), 127.9 (CH), 127.5 (CH), 124.2 (q, J = 271.8 Hz, C) 123.6 (CH), 75.3 (C). LRMS (CI) (m/z, I): 440 (100), 421 (50), 412 (58). HRMS calculated for C₂₉H₂₀BrO 431.1408, found 431.1466.
128.5 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.3 (CH), 114.5 (C), 78.7 (C), 13.4 (CH3).

**HRMS** (m/z, ESI) calculated for C23H18BrO [M+H]+ 389.0536 found, 389.0551.

1,2-triphenylazulen-7-bromo-4(3aH)-one (Sha):\(^2\) red solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ (ppm): 7.41 – 7.35 (m, 2H), 7.30 (dd, \(J = 2.9, 2.3\) Hz, 2H), 7.27 – 7.24 (m, 3H), 7.20 (d, \(J = 0.7\) Hz, 1H), 7.15 – 7.08 (m, 4H), 7.00 – 6.94 (m, 1H), 5.68 (d, \(J = 12.9\) Hz, 1H), 1.46 (s, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ (ppm): 197.8 (C), 151.2 (C), 145.8 (C), 143.9 (CH), 140.8 (CH), 139.4 (C), 134.5 (C), 133.9 (C), 133.8 (CH), 130.4 (CH), 128.8 (CH), 128.4(CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 122.2 (CH), 117.1 (C), 67.6 (C), 24.3 (CH3). **LRMS (CI)** (m/z, I): 390 (52), 311 (68), 310 (100). calculated for C23H18BrO [M+H]+ 389.0536 found, 389.0530.

The structure of this compound was further confirmed by XR-analysys. CCDC 995497 contains the crystallographic data of Sha, which can be obtained via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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\(^2\)This compound was isolated as minor product in the reaction of 1h and 2a following general procedure D.
MECHANISTIC EXPERIMENTS

DETERMINATION OF THE KINETIC ISOTOPIC EFFECT

To a solution of \([\text{Cp}^*\text{RhCl}_2]_2\) (4.5 mg, 2.5 mol%) and Cu(OAc)$_2$·H$_2$O (29 mg, 0.146 mmol, 0.5 equiv) and diphenylacetylene (52 mg, 0.293 mmol) in MeCN (1 mL) under air atmosphere was added a equimolar solution of 1a and 1a-$d_2$ (0.386 mmol each) in MeCN (1 mL). This solution was prepared by mixing 75 mg of 1c and 99 mg of 1c-$d_2$ (88% deuterated). The reaction mixture was heated at 40 °C. After 45 minutes the reaction was poured into Et$_2$O (10 mL), the solvents were evaporated in vacuo and the remaining residue was purified by flash column chromatography on silica gel to remove the remaining starting material. The residue was analyzed by H NMR. The KIE value (approx 2.3) was obtained by integrating the H$_3$ of the spiro 4ca and the H$_9$ of the spiro 4ca and 4ca-$d$. The conversion (approx 10%) was determined based on the starting material (2a) recovered.

EXPERIMENT IN PRESENCE OF D$_2$O (without alkyne)

To a solution of \([\text{Cp}^*\text{RhCl}_2]_2\) (5.2 mg, 2.5 mol%) and Cu(OAc)$_2$·H$_2$O (33 mg, 0.5 equiv, 0.165 mmol) in CH$_3$CN (1.7 mL) under air atmosphere was added 2-(prop-1-en-2-yl)phenol 1a (0.50 mmol, 1.5 equiv) and D$_2$O (0.3 mL). The reaction was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 40 °C, stirred for 4 h and then cooled to room temperature. The solvents were removed in vacuo and the remaining residue was purified by
flash column chromatography on silica gel to give 1a and 1a-d₆ (26 mg, 39% recovery). 30% deuteration on both olefinic protons based on ¹H-NMR.⁵

1) 1-H-NMR of starting material 1aa

   ![1a-NMRpectrum](image)

2) 1H-NMR of the starting material 1aa-recovered (30% deuteration)

   ![1aa-recovered-NMRpectrum](image)

EXPERIMENT IN PRESENCE OF D₂O (with alkyne)

To a solution of [Cp*RhCl₂]₂ (5.2 mg, 2.5 mol%) and Cu(OAc)₂·H₂O (33 mg, 0.5 equiv, 0.165 mmol) in CH₃CN (1.7 mL) under air atmosphere was added diphenylacetylene (59 mg, 1 equiv, 0.333 mmol) followed by the addition of 2-(prop-1-en-2-yl)phenol 1a (0.50 mmol, 1.5 equiv) and D₂O (0.3 mL). The reaction was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 40 °C, stirred for 4 h and then cooled to room temperature.

³No deuteration was observed in absence of the either the rhodium catalyst or copper acetate.
The solvents were removed in vacuo and the remaining residue was purified by flash column chromatography on silica gel to afford the 4-methyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one 4aa (12 mg, 11%), diphenylacetylene 2aa (49 mg, 83% recovered) and 2-(prop-1-en-2-yl)phenol 1a (44 mg, 66% recovered).

3) 1H-NMR of product 4aa recovered

4) 1H-NMR of 1a-recovered

COMPETITION EXPERIMENT between alkynes 2b and 2c

To a solution of [Cp*RhCl₂] (4.6 mg, 2.5 mol%) and Cu(OAc)₂·H₂O (30 mg, 0.150 mmol, 0.5 equiv) and alkynes 2b (143 mg, 2 equiv, 0.6 mmol) and 2c (189 mg, 2 equiv, 0.6 mmol) in MeCN (2 mL) under air
atmosphere was added 2-(prop-1-en-2-yl)phenol (1a) (40 mg, 1 equiv, 0.3 mmol). The reaction was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The reaction was heated at 40 °C and stirred at that temperature. After 2h, the resulting mixture was filtered through silica, washing with diethylether; the solvents were evaporated in vacuo and the residue was analyzed by H NMR in CDCl₃ indicating a 1:7 mixture of 4ab : 4ac and a conversion of approx 35%, based on the amount of starting materials recovered.

**STOICHEMOMETRIC EXPERIMENT**

![Diagram of reaction](attachment:image.png)

To a solution of [Cp*RhCl₂]₂ (50 mg, 0.5 equiv) in CH₃CN (1 mL) under air atmosphere was added diphenylacetylene (29 mg, 1 equiv, 0.162 mmol) followed by the addition of 2-(prop-1-en-2-yl)phenol 1a (22 mg, 1 equiv, 0.162 mmol). The reaction was sealed with a rubber septum and an air atmosphere was injected in the flask with a balloon and a needle. The solution was stirred for 45 min at 40 °C and no conversion was observed through TLC, after that, CsOAc (62 mg, 2 equiv) was added and the mixture stirred 1h. The solvents were removed in vacuo and the remaining residue was purified by flash column chromatography on silica gel to afford the 4-methyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one 4aa (43 mg, 86%).

A similar experiment was carried out using Et₃N (41 µL, 2 equiv) instead of CsOAc to afford the 4-methyl-1,2-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-one 4aa (32 mg, 64%) after 5h of reaction.

**Thermal rearrangement of 4aa or 5aa**

![Diagram of rearrangement](attachment:image.png)

A solution of 4aa (31 mg, 0.10 mmol) or 5aa (31 mg, 0.10 mmol) in CH₂CN (2 mL) was refluxed for 12h. The solvents were removed in vacuo and the product was isolated in quantitative yield without further manipulation. Analysis of the 1H-NMR shows approx. 1:1 mixture of 4aa and 5aa.
NMR SPECTRA
