Supporting Information

Rh-Catalyzed [7+1] Cycloaddition of Buta-1,3-dienylcyclopropanes and CO for the Synthesis of Cyclooctadienones

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1. General Methods of Synthesis

Unless otherwise noted, air- and moisture-sensitive reactions were carried out in oven-dried (110 ºC) glassware capped with rubber septa under a positive pressure of dry argon from a balloon. Likewise, air- and moisture-sensitive reagents, solvents, and solutions were transferred via syringe or stainless steel cannula under a dry inert atmosphere. Stirring was achieved using oven-dried (110 ºC) Teflon-coated magnetic stir bars cooled under a stream of dry nitrogen or argon. Reaction temperatures refer to the external temperature or to the temperature of the bath in which the reaction vessel was partially immersed. Reactions were stirred using Teflon-coated magnetic stir bars. Room temperature indicates an ambient indoor temperature in the range of 10-30 ºC. Elevated temperatures were maintained using thermostat-controlled silicone oil baths. Temperatures of 0 ºC and –78 ºC refer to the bath temperatures achieved with an ice/water slurry or a dry ice/acetone mixture, respectively. Organic solutions were concentrated using a Büchi rotary evaporator with a membrane vacuum pump.

Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone prior to use. Dioxane (extra dry, water < 50 ppm, purchased from Alfa Aesar), [Rh(CO)2Cl]2 (purchased from Across) was commercially available and used as received. Analytical TLC was performed with 0.25 mm silica gel 60F plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with acidic p-anisaldehyde stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Varian Mercury Plus 300 (1H at 300 MHz, 13C at 75 MHz) or Bruker ARX400 (1H at 400 MHz, 13C at 100 MHz) nuclear magnetic resonance spectrometers. Data for 1H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, td = triplet of doublets, br = broad, m = multiplet), coupling constant (Hz), and integration. Data for 13C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl3: 77.0 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm⁻¹). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded.
on Waters micromass GCT (EI, 70 eV) and Bruker APEX IV (ESI) mass spectrometers.

Abbreviations:
THF: tetrehydrofuran
PDC: pyridinium dichromate
DIBAL-H: diisobutylaluminum hydride
DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene
TEA: triethylamine
TBSOTf: tert-butyldimethylsilyl trifluoromethanesulfonate
DCM: dichloromethane

2. General Procedure for the Synthesis of BDCPs 1a-1g, and 1i-1l

To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (12 mmol, 1.2 equiv.) and THF (40 mL). The solution was cooled to 0 °C and 4.8 mL (12 mmol, 1.2 equiv.) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 °C, ketone (10 mmol, 1.0 equiv.) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na₂SO₄, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford the buta-1,3-dienylcyclopropane.

1-(1-Cyclopropylbuta-1,3-dienyl)-4-methoxybenzene (1a)
A 2.5:1 mixture of (Z:E)-1-(1-cyclopropylbuta-1,3-dienyl)-4-methoxybenzene (820 mg, 4.1 mmol, 41 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a doublet at 6.05 ppm for the (Z)-1-(1-cyclopropylbuta-1,3-dienyl)-4-methoxybenzene and a quartet at 5.25 ppm for the (E)-olefin. The Z (1a-Z) and E (1a-E) isomers of 1a were obtained as pure compounds by flash chromatography. The determination of the Z and E isomers were deduced by analogy to the Z and E isomers of 1b.$^1$

IR (film): 3002, 2834, 1630, 1607, 1509, 1464, 1287, 1245, 1179, 1119, 1036 cm$^{-1}$. (Z)-isomer:

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.15-7.13 (d, $J = 8.4$ Hz, 2H), 6.89-6.86 (d, $J = 8.4$ Hz, 2H), 6.32-6.23 (dt, $J = 17.2$ and 10.4 Hz, 1H), 6.07-6.04 (d, $J = 10.8$ Hz, 1H), 5.16-5.11 (dd, $J = 16.8$ and 1.6 Hz, 1H), 4.90-4.87 (dd, $J = 10.4$ and 1.6 Hz, 1H), 3.81 (s, 3H), 1.64-1.56 (m, 1H), 0.74-0.69 (m, 2H), 0.54-0.50 (m, 2H). 13C-NMR (100 MHz, CDCl$_3$): $\delta$ 158.6, 144.8, 134.8, 132.1, 130.1, 125.0, 115.1, 113.3, 55.2, 18.5, 6.1. HRMS (ESI+) for C$_{14}$H$_{17}$O (M+H)$^+$: calculated: 201.1274, found: 201.1271.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.39-7.37 (d, $J = 8.8$ Hz, 2H), 7.13-7.03 (dt, $J = 16.8$ and 10.8 Hz, 1H), 6.85-6.83 (d, $J = 8.8$ Hz, 2H), 6.36-6.33 (d, $J = 10.8$ Hz, 1H), 5.27-5.23 (dd, $J = 17.2$ and 1.6 Hz, 1H), 5.18-5.14 (dd, $J = 10.4$ and 1.6 Hz, 1H), 3.80 (s, 3H), 1.82-1.75 (m, 1H), 0.91-0.86 (m, 2H), 0.41-0.37 (m, 2H). 13C-NMR (100 MHz, CDCl$_3$): $\delta$ 158.6, 141.7, 134.3, 133.9, 129.1, 128.1, 128.1, 116.9, 113.2, 55.2, 11.6, 7.2.

(1-Cyclopropylbuta-1,3-dienyl)benzene (1b)

A 2.9:1 mixture of (Z:E)-(1-cyclopropylbuta-1,3-dienyl)benzene$^1$ (1292 mg, 7.6 mmol, 76 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of
one of the olefinic protons: a doublet at 6.08 ppm for the \((Z)-(1\text{-cyclopropylbuta-1,3-diynyl})-\) benzene and a doublet at 6.39 ppm for the \((E)\)-olefin. The NMR signals of \(Z\) and \(E\) isomers were determined by the analysis of NOESY study and the previous report.\(^1\)

IR (film): 3095, 3020, 3015, 1635, 1610, 1025 cm\(^{-1}\). \((Z)\)-isomer: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.33-7.19 (m, 5H), 6.28-6.19 (dt, \(J = 16.8\) and 10.4 Hz, 1H), 6.09-6.07 (d, \(J = 10.8\) Hz, 1H), 5.17-5.12 (dd, \(J = 16.8\) and 1.6 Hz, 1H), 4.91-4.88 (dd, \(J = 10.0\) and 1.6 Hz, 1H), 1.67-1.60 (m, 1H), 0.75-0.70 (m, 2H), 0.54-0.50 (m, 2H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 145.3, 139.8, 134.5, 129.0, 127.9, 127.0, 125.3, 115.4, 18.5, 6.1. HRMS (EI\(^+\)) for C\(_{13}\)H\(_{14}\) (M\(^+\)): calculated: 170.1096, found: 170.1098.

Additional signals for the \((E)\)-isomer: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.43-7.22 (m, 5H), 7.14-7.04 (dt, \(J = 16.8\) and 10.8 Hz, 1H), 6.40-6.37 (d, \(J = 11.2\) Hz, 1H), 5.30-5.26 (dd, \(J = 16.8\) and 1.2 Hz, 1H), 5.22-5.18 (dd, \(J = 10.0\) and 1.2 Hz, 1H), 1.87-1.80 (m, 1H), 0.91-0.87 (m, 2H), 0.41-0.37 (m, 2H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.3, 141.8, 133.8, 130.3, 127.8, 127.0, 126.8, 117.6, 11.6, 7.2.

\(1-(1\text{-Cyclopropylbuta-1,3-diynyl})-4\text{-fluorobenzene (1c)}\)

A 2.9:1 mixture of \((Z):E\)-1-(1\text{-cyclopropylbuta-1,3-diynyl})-4-fluorobenzene (1524 mg, 8.1 mmol, 81\%) as a colorless liquid was obtained. The \((Z):(E)\)-ratio was determined using \(^1\)H-NMR by integration of one of the olefinic protons: a doublet at 6.08 ppm for the \((Z)\)-1-(1\text{-cyclopropylbuta-1,3-diynyl})-4-fluorobenzene and a doublet at 6.33 ppm for the \((E)\)-olefin.

IR (film): 3075, 3007, 2849, 1632, 1603, 1507, 1420, 1223, 1158, 1094, 1022 cm\(^{-1}\). \((Z)\)-isomer: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.18-6.96 (m, 4H), 6.25-6.15 (dt, \(J = 16.8\) and 10.8 Hz, 1H), 6.09-6.06 (d, \(J = 11.2\) Hz, 1H), 5.18-5.13 (dd, \(J = 16.8\) and 2.0 Hz, 1H), 4.93-4.90 (dd, \(J = 10.0\) and 2.0 Hz, 1H), 1.64-1.57 (m, 1H), 0.75-0.71 (m, 2H), 0.52-0.48 (m, 2H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.2, 160.7, 144.1, 134.2, 130.6, 130.5, 125.7, 115.8, 115.0, 114.7, 18.5, 6.1. HRMS (EI\(^+\)) for C\(_{13}\)H\(_{13}\)F (M\(^+\)): calculated: 188.1001, found: 188.1004.

Additional signals for the \((E)\)-isomer: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.41-7.36 (m, 2H),
7.11-7.02 (dt, J = 16.8 and 10.8 Hz, 1H), 7.05-6.96 (m, 2H), 6.35-6.32 (d, J = 10.8 Hz, 1H), 5.30-5.26 (dd, J = 16.8 and 2.0 Hz, 1H), 5.22-5.19 (dd, J = 10.0 and 2.0 Hz, 1H), 1.84-1.77 (m, 1H), 0.92-0.87 (m, 2H), 0.39-0.35 (m, 2H). 13C-NMR (100 MHz, CDCl₃): δ 165.0, 162.4, 141.3, 137.9, 135.7, 135.6, 133.7, 130.3, 128.6, 128.5, 117.8, 114.8, 114.6, 11.7, 7.2.

1-tert-Butyl-4-(1-cyclopropylbuta-1,3-dienyl)benzene (1d)

A 1.9:1 mixture of (Z):E-1-tert-butyl-4-(1-cyclopropylbuta-1,3-dienyl)benzene (1584 mg, 7.0 mmol, 70 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using ¹H-NMR by integration of one of the olefinic protons: a doublet at 6.04 ppm for the (Z)-1-tert-butyl-4-(1-cyclopropylbuta-1,3-dienyl)benzene and a doublet at 6.40 ppm for the (E)-olefin.

IR (film): 3084, 2963, 2903, 2870, 1670, 1631, 1510, 1462, 1420, 1394, 1363, 1269, 1202, 1116, 1100, 1022 cm⁻¹. (Z)-isomer: ¹H-NMR (400 MHz, CDCl₃): δ 7.36-7.34 (d, J = 8.4, 2H), 7.17-7.14 (d, J = 8.4 Hz, 2H), 6.35-6.26 (dt, J = 16.8 and 10.8 Hz, 1H), 6.06-6.04 (d, J = 10.8, 1H), 5.16-5.12 (dd, J = 16.8 and 1.6 Hz, 1H), 4.91-4.88 (dd, J = 10.0 and 1.6 Hz, 1H), 1.66-1.59 (m, 1H), 1.33 (s, 9H), 0.75-0.70 (m, 2H), 0.56-0.53 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 149.8, 145.2, 134.8, 128.6, 126.6, 124.9, 124.7, 115.2, 34.5, 31.4, 18.5, 6.3. HRMS (EI⁺) for C₁₇H₂₂ (M⁺): calculated: 226.1722, found: 226.1724.

Additional signals for the (E)-isomer: ¹H-NMR (400 MHz, CDCl₃): δ 7.40-7.37 (d, J = 8.8, 2H), 7.33-7.31 (d, J = 8.8, 2H), 7.14-7.05 (dt, J = 16.8 and 10.8 Hz, 1H), 6.42-6.35 (d, J = 10.8 Hz, 1H), 5.29-5.24 (dd, J = 16.8 and 2.0 Hz, 1H), 5.19-5.16 (dd, J = 10.8 and 2.0 Hz, 1H), 1.84-1.77 (m, 1H), 1.31 (s, 9H), 0.92-0.86 (m, 2H), 0.43-0.39 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 149.7, 142.0, 138.8, 136.9, 134.0, 129.8, 124.7, 117.2, 34.4, 31.3, 11.6, 7.3.

1-(1-Cyclopropyl-3-methylbuta-1,3-dienyl)-4-methoxybenzene (1e)

A 2.0:1 mixture of (Z):E-1-(1-cyclopropyl-3-methylbuta-1,3-dienyl)-4-methoxybenzene (535 mg,
2.5 mmol, 25 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a singlet at 6.10 ppm for the (Z)-1-(1-cyclopropyl-3-methylbuta-1,3-dienyl)-4-methoxybenzene and a singlet at 6.02 ppm for the (E)-olefin.

IR (film): 3001, 2918, 2835, 1608, 1509, 1455, 1434, 1329, 1286, 1245, 1174, 1036 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.05-7.03 (d, $J = 8.8$ Hz, 2H), 6.83-6.81 (d, $J = 8.8$ Hz, 2H), 6.10 (s, 1H), 4.77 (s, 1H), 4.74 (s, 1H), 3.80 (s, 3H), 1.64-1.57 (m, 1H), 1.36 (s, 3H), 0.65-0.61 (m, 2H), 0.43-0.39 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 158.5, 142.6, 142.4, 130.2, 128.9, 127.4, 116.0, 113.0, 55.1, 22.4, 20.1, 5.1. HRMS (ESI+) for C$_{15}$H$_{19}$O (M+H)$^+$: calculated: 215.1430, found: 215.1430.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.26-7.24 (d, $J = 8.8$ Hz, 2H), 6.83-6.81 (d, $J = 8.8$ Hz, 1H), 6.02 (s, 1H), 5.13 (s, 1H), 5.08 (s, 1H), 3.80 (s, 3H), 2.00 (s, 3H), 1.97-1.91 (m, 1H), 0.82-0.77 (m, 2H), 0.39-0.35 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 158.4, 141.9, 141.8, 135.0, 132.0, 130.7, 115.4, 113.1, 55.2, 23.8, 13.3, 8.0.

2-(1-Cyclopropylbuta-1,3-dienyl)thiophene (If)

A 4.0:1 mixture of (Z:E)-2-(1-cyclopropylbuta-1,3-dienyl)thiophene (1250 mg, 7.1 mmol, 71 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a doublet at 6.11 ppm for the (Z)-2-(1-cyclopropylbuta-1,3-dienyl)thiophene and a doublet at 6.55 ppm for the (E)-olefin.

IR (film): 3081, 3007, 1618, 1432, 1381, 1304, 1237, 1098, 1022 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.29-7.27 (dd, $J = 4.8$ and 1.2 Hz, 1H), 7.06-7.04 (dd, $J = 3.6$ and 1.2 Hz, 1H), 7.03-7.01 (dd, $J = 4.8$ and 3.6 Hz, 1H), 6.78-6.68 (dt, $J = 16.8$ and 10.8 Hz, 1H), 6.13-6.10 (d, $J = 10.8$ Hz, 1H), 5.29-5.24 (dd, $J = 16.8$ and 1.6 Hz, 1H), 5.07-5.05 (dd, $J = 10.4$ and 1.6 Hz, 1H), 1.74-1.68 (m, 1H), 0.81-0.76 (m, 2H), 0.65-0.62 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 142.1, 136.5, 134.2, 126.8, 126.7, 126.6, 125.1, 117.3, 19.3, 6.5. HRMS (ESI+) for C$_{11}$H$_{13}$S (M+H)$^+$: calculated: 177.0733, found: 177.0730.
Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.24-7.23 (d, $J = 2.8$ Hz, 1H), 7.15-7.14 (d, $J = 5.2$ Hz, 1H), 7.10-7.04 (dt, $J = 17.2$ and 10.4 Hz, 1H), 6.98-6.96 (dd, $J = 5.2$ and 2.8 Hz, 1H), 6.57-6.54 (d, $J = 10.4$ Hz, 1H), 5.31-5.26 (dd, $J = 17.2$ and 1.2 Hz, 1H), 5.21-5.18 (dd, $J = 10.4$ and 1.2 Hz, 1H), 0.98-0.92 (m, 2H), 0.90-0.83 (m, 1H), 0.62-0.58 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 146.7, 135.3, 133.6, 128.8, 127.3, 124.3, 124.0, 117.9, 12.0, 7.3.

2-(1-Cyclopropylbuta-1,3-dienyl)naphthalene (1g)

A 2.2:1 mixture of (Z:E) 2-(1-cyclopropylbuta-1,3-dienyl)naphthalene (1125 mg, 5.1 mmol, 51 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a doublet at 6.21 ppm for the (Z)-2-(1-cyclopropylbuta-1,3-dienyl)naphthalene and a doublet at 6.58 ppm for the (E)-olefin.

IR (film): 3056, 3006, 1629, 1599, 1502, 1416, 1130, 1051, 1021 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.88-7.83 (m, 3H), 7.69 (s, 1H), 7.53-7.46 (m, 2H), 7.41-7.39 (dd, $J = 8.4$ and 1.6, 1H), 6.37-6.27 (dt, $J = 16.8$ and 10.8 Hz, 1H), 6.22-6.20 (d, $J = 10.8$ Hz, 1H), 5.25-5.20 (dd, $J = 16.8$ and 2.0 Hz, 1H), 4.96-4.93 (dd, $J = 10.0$ and 2.0 Hz, 1H), 1.79-1.72 (m, 1H), 0.83-0.78 (m, 2H), 0.68-0.60 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 145.2, 137.3, 134.6, 133.9, 132.5, 130.9, 127.9, 127.6, 127.5, 127.4, 126.0, 125.8, 125.7, 115.6, 18.6, 6.3. HRMS (EI$^+$) for C$_{17}$H$_{16}$ (M)$^+$: calculated: 220.1252, found: 220.1254.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (s, 1H), 7.88-7.79 (m, 3H), 7.64-7.61 (dd, $J = 8.4$ and 1.6 Hz, 1H), 7.53-7.45 (m, 2H), 7.24-7.14 (dt, $J = 16.8$ and 10.8 Hz, 1H), 6.60-6.57 (d, $J = 10.8$ Hz, 1H), 5.40-5.35 (dd, $J = 16.8$ and 1.6 Hz, 1H), 5.30-5.27 (dd, $J = 10.8$ and 1.6 Hz, 1H), 1.98-1.93 (m, 1H), 1.01-0.97 (m, 2H), 0.50-0.45 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 142.2, 139.3, 134.6, 133.9, 133.3, 133.1, 128.1, 127.7, 127.5, 127.2, 126.0, 125.6, 125.4, 117.9, 11.7, 7.4.

Buta-1,3-diene-1,1-diylidicycpropane (II)
Buta-1,3-diene-1,1-diylidicyclop propane\(^2\) (400 mg, 3.0 mmol, 30 %) as a colorless liquid was obtained.

IR (film): 3083, 3009, 1633, 1421, 1288, 1049, 1020 cm\(^{-1}\). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.88-6.78 (dt, \(J = 16.8\) and 10.3 Hz, 1H), 5.78-5.75 (d, \(J = 10.8\) Hz, 1H), 5.13-5.08 (dd, \(J = 16.8\) and 2.0 Hz, 1H), 5.01-4.98 (dd, \(J = 10.1\) and 2.0 Hz, 1H), 1.88-1.81 (m, 1H), 1.03-0.98 (m, 1H), 0.80-0.75 (m, 2H), 0.75-0.70 (m, 2H), 0.60-0.55 (m, 2H), 0.44-0.40 (m, 2H). \(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 143.8, 133.1, 123.5, 114.9, 13.1, 5.6, 5.3. HRMS (EI\(^+\)) for C\(_{10}\)H\(_{14}\) (M\(^+\)): calculated: 134.1096, found: 134.1098.

Penta-2,4-dien-2-ylcyclopropane (1j)

A 0.3:1 mixture of (Z):E)-penta-2,4-dien-2-ylcyclopropane\(^3\) (280 mg, 2.6 mmol, 26 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using \(^1\)H-NMR by integration of the methyl protons: a singlet at 1.49 ppm for the (Z)-penta-2,4-dien-2-ylcyclopropane and a singlet at 1.62 ppm for the (E)-olefin.

IR (film): 2955, 2921, 1644, 1460, 1015 cm\(^{-1}\). (E)-isomer: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.63-6.53 (dt, \(J = 16.8\) and 10.8 Hz, 1H), 5.93-5.90 (d, \(J = 10.8\) Hz, 1H), 5.10-5.05 (dd, \(J = 16.8\) and 2.0 Hz, 1H), 4.96-4.93 (dd, \(J = 10.8\) and 2.0 Hz, 1H), 1.62 (s, 3H), 1.47-1.40 (m, 1H), 0.64-0.58 (m, 2H), 0.55-0.51 (m, 2H). \(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.0, 133.2, 123.9, 114.1, 19.1, 14.0, 4.9. HRMS (EI\(^+\)) for C\(_8\)H\(_{12}\) (M\(^+\)): calculated: 108.0939, found: 108.0941.

Additional signals for the (Z)-isomer: \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.86-6.76 (dt, \(J = 16.8\) and 10.8 Hz, 1H), 5.95-5.93 (d, \(J = 10.8\) Hz, 1H), 5.12-5.07 (dd, \(J = 16.8\) and 2.0 Hz, 1H), 5.00-4.97 (dd, \(J = 10.8\) and 2.0 Hz, 1H), 1.90-1.85 (m, 1H), 1.49 (s, 3H), 0.73-0.58 (m, 4H). \(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.1, 132.8, 126.8, 114.4, 19.0, 12.9, 4.7.

(1-(Buta-1,3-dienyl)cyclopropyl)benzene (1k)
A 3.0:1 mixture of (Z:E)-(1-(buta-1,3-dienyl)cyclopropyl)benzene (1160 mg, 6.8 mmol, 68 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a doublet of the triplets at 6.59 ppm for the (Z)-(1-(buta-1,3-dienyl)-cyclopropyl)benzene and a doublet of the triplets at 6.29 ppm for the (E)-olefin.

IR (film): 2928, 2861, 1600, 1500, 1089, 1005 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.32-7.12 (m, 5H), 6.66-6.53 (dt, $J = 16.8$ and 11.1 Hz, 1H), 6.13-6.06 (t, $J = 11.1$ Hz, 1H), 5.72-5.68 (d, $J = 10.5$ Hz, 1H), 5.18-5.11 (dd, $J = 16.8$ and 1.6 Hz, 1H), 5.06-5.01 (dd, $J = 10.2$ and 1.6 Hz, 1H), 1.10-1.00 (m, 4H). $^{13}$C-NMR (75 MHz, CDCl$_3$): δ 144.9, 135.0, 133.3, 132.0, 128.3, 126.7, 125.6, 118.0, 23.9, 17.5. HRMS (EI$^+$) for C$_{13}$H$_{14}$ (M)$^+$: calculated: 170.1096, found: 170.1098.

Additional signals for the (E)-isomer: $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.32-7.12 (m, 5H), 6.36-6.21 (dt, $J = 16.8$ and 8.4 Hz, 1H), 5.62-5.55 (m, 2H), 5.62-5.59 (d, $J = 8.4$ Hz, 1H), 4.98-4.92 (dd, $J = 16.8$ and 1.8 Hz, 1H), 4.90-4.86 (dd, $J = 10.0$ and 1.6 Hz, 1H), 1.14-1.08 (m, 2H), 0.98-0.78 (m, 2H). $^{13}$C-NMR (75 MHz, CDCl$_3$): δ 142.3, 136.8, 129.9, 128.8, 128.2, 126.5, 114.5, 114.6, 22.7, 15.3

1-(1-(Buta-1,3-dienyl)cyclopropyl)-4-methoxybenzene (II)

A 5.4:1 mixture of (Z:E)-1-(1-(buta-1,3-dienyl)cyclopropyl)-4-methoxybenzene (1480 mg, 7.4 mmol, 74 %) as a colorless liquid was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of the methyl protons: a singlet at 3.77 ppm for the (Z)-1-(1-(buta-1,3-dienyl)-cyclopropyl)-4-methoxybenzene and a singlet at 3.80 ppm for the (E)-olefin.

IR (film): 3089, 2962, 1684, 1513, 1246, 1183, 1038, 1006 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.18-7.16 (d, $J = 8.4$ Hz, 2H), 6.82-6.80 (d, $J = 8.4$ Hz, 2H), 6.62-6.52 (dt, $J = 16.8$ and 11.1 Hz, 1H), 6.13-6.06 (t, $J = 11.1$ Hz, 1H), 5.72-5.68 (d, $J = 10.5$ Hz, 1H), 5.18-5.11 (dd, $J = 16.8$ and 1.6 Hz, 1H), 5.06-5.01 (dd, $J = 10.2$ and 1.6 Hz, 1H), 1.10-1.00 (m, 4H). $^{13}$C-NMR (75 MHz, CDCl$_3$): δ 144.9, 135.0, 133.3, 132.0, 128.3, 126.7, 125.6, 118.0, 23.9, 17.5. HRMS (EI$^+$) for C$_{13}$H$_{14}$O (M)$^+$: calculated: 176.1141, found: 176.1145.
10.8 Hz, 1H), 6.07-6.01 (t, J = 10.8 Hz, 1H), 5.65-5.62 (d, J = 10.4 Hz, 1H), 5.15-5.11 (d, J = 16.8 Hz, 1H), 5.04-5.01 (d, J = 10.0 Hz, 1H), 3.77 (s, 3H), 1.10 (br s, 2H), 1.01 (br s, 2H). 13C-NMR (100 MHz, CDCl3): δ 157.6, 136.8, 135.6, 133.2, 131.2, 128.1, 117.5, 113.6, 65.7, 23.6, 15.1. HRMS (ESI+) for C14H17O (M+H)+: calculated: 201.1274, found: 201.1273.

Additional signals for the (E)-isomer: 1H-NMR (400 MHz, CDCl3): δ 7.24-7.22 (d, J = 8.8 Hz, 2H), 6.86-6.84 (d, J = 8.4 Hz, 2H), 6.33-6.24 (dt, J = 16.8 and 10.0 Hz, 1H), 5.62-5.55 (dd, J = 15.2 and 10.0 Hz, 1H), 5.55-5.51 (d, J = 15.2 Hz, 1H), 4.96-4.92 (d, J = 16.8 Hz, 1H), 4.88-4.86 (d, J = 10.0 Hz, 1H), 3.80 (s, 3H), 1.06 (br s, 2H), 0.96 (br s, 2H). 13C-NMR (100 MHz, CDCl3): δ 158.1, 142.7, 136.8, 135.0, 130.9, 128.6, 114.2, 113.5, 55.1, 27.4, 16.8.

3. Synthesis of Cyclopropyl(naphthalen-2-yl)methanone (S-2)

Cyclopropyl(naphthalen-2-yl)methanone (S-2)

Cyclopropyl(naphthalen-2-yl)methanol (S-1)

Cyclopropanecarbaldehyde (0.70 g, 10.0 mmol, in 80 mL THF) was cooled to 0 °C. Naphthalen-2-ylmagnesium bromide (12.0 mmol, in 80 mL THF, prepared by the literature method) was added slowly to the above cyclopropanecarbaldehyde solution. The solution was then stirred under 0 °C for 30 minutes before it was poured into the mixture of 50 g ice and 50 mL water. After extracted with Et₂O, washed with water, and brine, dried over MgSO₄, and concentrated in vacuo, the crude mixture was purified by flash column chromatography to afford 1.07 g (54% S-1 as a light yellow liquid.

IR (film): 3372, 2917, 1602, 1508, 1363, 1270, 1028 cm⁻¹.

1H-NMR (400 MHz, CDCl3): δ 7.84-7.82 (m, 4H), 7.57-7.55 (d, J = 9.6 Hz, 1H), 7.49-7.44 (m, 2H), 4.16-4.14 (d, J = 8.4 Hz, 1H), 2.17 (br s, 1H), 1.33-1.23 (m, 1H), 0.70-0.63 (m, 1H),
0.60-0.48 (m, 2H), 0.45-0.39 (m, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 141.2, 133.3, 133.0, 128.1, 128.0, 127.6, 126.0, 125.7, 124.5, 124.4, 78.6, 19.2, 3.7, 2.9.

HRMS (ESI+) for C$_{14}$H$_{14}$NaO (M+Na)$^+$: calculated: 221.0937, found: 221.0935.

Cyclopropyl(naphthalen-2-yl)methanone (S-2)$^5$

\[
\begin{align*}
&\text{Cyclopropyl(naphthalen-2-yl)methanol (S-1)} (0.99 \text{ g, 5.0 mmol}) \text{ was dissolved in 100 mL} \\
&\text{anhydrous CH$_2$Cl$_2$ and cooled to 0 °C. Then PDC (3.70 g, 10.0 mmol) was added in batches and} \\
&\text{the resulting solution was stirred for 10 h at room temperature. The product mixture was filtered} \\
&\text{through a short silica gel column. Then the filtrate was concentrated to afford 0.98 g (70%) S-2 as} \\
&\text{a white solid (melting point: 117-118 °C).} \\
&\text{IR (film): 3082, 3021, 2927, 1660, 1392, 1278, 1220, 1125, 1040 cm}^{-1}.
\end{align*}
\]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.57 (s, 1H), 8.08-8.05 (dd, $J = 8.4$ and 1.6 Hz, 1H), 7.99-7.97 (d, $J = 8.0$ Hz, 1H), 7.92-7.88 (t, $J = 8.4$ Hz, 2H), 7.62-7.54 (m, 2H), 2.88-2.82 (m, 1H), 1.33-1.29 (m, 2H), 1.13-1.08 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 200.4, 135.5, 135.4, 132.6, 129.5, 128.3, 128.2, 127.8, 126.7, 124.0, 17.2, 11.7.

HRMS (ESI+) for C$_{14}$H$_{13}$O (M+H)$^+$: calculated: 197.0961, found: 197.0960.

4. Synthesis of (2-Cyclopropylpenta-2,4-dienyl)benzene (1h)

\[
\begin{align*}
&\text{Ethyl-3-cyclopropyl-4-phenylbut-2-enoate (S-3)} \\
&\text{(S-3)} \\
&\text{(S-4)} \\
&\text{(S-5)} \\
&\text{(1h)}
\end{align*}
\]
To a flask containing NaH (0.48 g, 20.0 mmol) and 80 mL THF at 0 °C was added triethyl phosphonoacetate (4.48 g, 20.0 mmol). After stirring at room temperature for 30 min, 1-cyclopropyl-2-phenylethanone (3.2 g, 20.0 mmol, prepared by literature method) was added dropwise and the reaction was allowed to stir for 32 hours. After quenching with brine, extracting with Et₂O, and drying over MgSO₄, concentration of the organic phase in vacuo gave a crude oil that was further purified by flash chromatography to afford 3.22 g (70%) S-3 as a colorless oil.

A 0.9:1 mixture of (Z:E)-Ethyl-3-cyclopropyl-4-phenylbut-2-enoate was obtained. The (Z):(E)-ratio was determined using ¹H-NMR by integration of the olefinic proton: a singlet at 5.55 ppm for the (Z)-Ethyl-3-cyclopropyl-4-phenylbut-2-enoate and a singlet at 5.61 ppm for the (E)-olefin. IR (film): 2982, 1709, 1637, 1239, 1153, 1037 cm⁻¹.

(Z)-isomer: ¹H-NMR (400 MHz, CDCl₃): δ 7.31-7.11 (m, 5H), 5.55 (s, 1H), 4.17-4.10 (q, J = 7.2 Hz, 2H), 3.25-3.16 (m, 1H), 3.08 (s, 2H), 1.27-1.23 (t, J = 7.2 Hz, 3H), 0.90-0.80 (m, 2H), 0.73-0.69 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 167.1, 162.3, 138.0, 128.9, 128.5, 126.4, 118.4, 59.5, 37.6, 13.7, 7.0. HRMS (ESI+) for C₁₅H₁₉O₂ (M+H)+: calculated: 231.1380, found: 231.1376.

Additional signals for the (E)-isomer: ¹H-NMR (400 MHz, CDCl₃): δ 7.31-7.11 (m, 5H), 5.61 (s, 1H), 4.19-4.12 (q, J = 7.2 Hz, 2H), 4.08 (s, 2H), 1.46-1.37 (m, 1H), 1.29-1.24 (t, J = 7.2 Hz, 3H), 0.78-0.74 (m, 2H), 0.60-0.54 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 166.7, 163.1, 139.0, 128.7, 128.3, 126.0, 112.7, 59.6, 37.4, 18.1, 14.2, 8.4.

3-Cyclopropyl-4-phenylbut-2-en-1-ol (S-4)

To a Schlenk flask charged with ethyl 3-cyclopropyl-4-phenylbut-2-enoate (S-3) (2.99 g, 13 mmol) in THF at 0 °C was added DIBAL-H (29 mL, 1 M in toluene, 29 mmol) dropwise. The reaction was warmed to room temperature overnight and was quenched with ethylacetate and aqueous potassium tartrate tetrahydrate. Stirring was continued until the solution was clear. Extracted with Et₂O, washed with brine, dried over MgSO₄, evaporation and purification by flash column chromatography to provide 2.20 g (90%) S-4 as a clear, colorless oil.
A 0.67:1 mixture of (Z:E)-3-cyclopropyl-4-phenylbut-2-en-1-ol was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the methylene protons: a singlet at 3.34 ppm for the (Z)-3-cyclopropyl-4-phenylbut-2-en-1-ol and a singlet at 3.13 ppm for the (E)-olefin.

IR (film): 3354, 3083, 3025, 2923, 1657, 1602, 1494, 1452, 1029 cm$^{-1}$.

(Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.29-7.24 (m, 2H), 7.20-7.16 (m, 3H), 5.53-5.50 (t, $J =$ 7.2 Hz, 1H), 4.23-4.21 (d, $J =$ 7.2 Hz, 2H), 3.43 (s, 2H), 1.57-1.50 (m, 1H), 1.52 (br s, 1H), 0.58-0.54 (m, 2H), 0.43-0.39 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 142.9, 139.8, 128.4, 127.8, 122.6, 59.3, 36.4, 17.0, 5.8. HRMS (ESI+) for C$_{13}$H$_{16}$NaO (M+Na)$^+$: calculated: 211.1093, found: 211.1094.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.29-7.24 (m, 2H), 7.20-7.16 (m, 3H), 5.42-5.38 (td, $J =$ 6.8 and 0.8 Hz, 1H), 4.35-4.33 (d, $J =$ 6.8 Hz, 2H), 3.13 (s, 2H), 1.52 (br s, 1H), 1.33-1.26 (m, 1H), 0.67-0.62 (m, 2H), 0.52-0.48 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 142.0, 139.7, 128.9, 128.4, 128.2, 126.0, 59.2, 40.2, 12.1, 5.1.

3-Cyclopropyl-4-phenylbut-2-enal (S-5)

3-Cyclopropyl-4-phenylbut-2-en-1-ol (S-4) (2.10 g, 11.2 mmol) was dissolved in 100 mL anhydrous CH$_2$Cl$_2$ and cooled to 0 °C. Then PDC (6.3 g, 16.8 mmol) was added in batches and the resulting solution was stirred for 1 hour at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to get 1.12 g (54%) S-5 as a light yellow liquid.

A 0.5:1 mixture of (Z:E)-3-cyclopropyl-4-phenylbut-2-enal was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the methylene protons: a singlet at 3.23 ppm for the (Z)-3-cyclopropyl-4-phenylbut-2-enal and a singlet at 3.94 ppm for the (E)-olefin.

IR (film): 2989, 2901, 1668, 1613, 1491, 1449, 1261, 1159, 1030 cm$^{-1}$.

(Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 10.25-10.23 (d, $J =$ 8.0 Hz, 1H), 7.34-7.21 (m, 3H), 7.13-7.12 (d, $J =$ 7.2 Hz, 2H), 5.77-5.75 (d, $J =$ 8.0 Hz, 1H), 3.23 (s, 2H), 2.46-2.39 (m, 1H), 0.99-0.93 (m, 2H), 0.92-0.85 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 191.0, 166.0, 137.2, 130.0, 129.0, 128.7, 124.1, 39.2, 13.2, 7.4. HRMS (ESI+) for C$_{13}$H$_{15}$O (M+H)$^+$: calculated: 187.1117,
found: 187.1119.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 10.05-10.03 (d, $J$ = 8.0 Hz, 1H), 7.34-7.21 (m, 5H), 5.86-5.84 (d, $J$ = 8.0 Hz, 1H), 3.94 (s, 2H), 1.50-1.43 (m, 1H), 0.92-0.85 (m, 2H), 0.72-0.68 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 190.7, 167.9, 137.7, 128.7, 128.5, 126.8, 124.1, 36.8, 18.3, 10.0.

(2-Cyclopropylpenta-2,4-dienyl)benzene (1h)

To a flask containing methyltriphenylphosphonium bromide (2.68 g, 7.5 mmol) and 80 mL THF at 0 °C was added n-butyllithium (7.5 mL, 1 M in hexane, 7.5 mmol). After stirring at 0 °C for 30 minutes, 3-cyclopropyl-4-phenylbut-2-enal (S-5) (9.30 g, 5.0 mmol, in 10 mL THF) was added dropwise and the reaction was allowed to stir for 1 hour. After quenching with brine, extracting with Et$_2$O, and drying over MgSO$_4$, concentration of the organic phase in vacuo gave a crude oil which was further purified by flash chromatography to afford 0.76 g (83%) 1h as a colorless oil.

A 0.8:1 mixture of (Z):E-(2-cyclopropylpenta-2,4-dienyl)benzene was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the methylene protons: a singlet at 3.51 ppm for the (Z)- (2-cyclopropylpenta-2,4-dienyl)benzene and a singlet at 3.17 ppm for the (E)-olefin.

IR (film): 3084, 3027, 1637, 1602, 1494, 1453, 1422, 1030 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.28-7.16 (m, 5H), 6.72-6.63 (dt, $J$ = 16.4 and 10.5 Hz, 1H), 5.99-5.97 (d, $J$ = 10.9 Hz, 1H), 5.20-5.16 (d, $J$ = 16.4 Hz, 1H), 5.04-5.02 (d, $J$ = 8.4 Hz, 1H), 3.51 (s, 2H), 1.36-1.29 (m, 1H), 0.60-0.55 (m, 2H), 0.45-0.42 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 142.5, 140.0, 133.1, 128.8, 128.5, 128.3, 125.9, 115.7, 36.5, 17.3, 6.1. HRMS (EI+) for C$_{14}$H$_{16}$ (M)$^+$: calculated: 184.1252, found: 184.1254.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.28-7.16 (m, 5H), 6.93-6.84 (dt, $J$ = 16.8 and 10.8 Hz, 1H), 5.89-5.86 (d, $J$ = 10.8 Hz, 1H), 5.13-5.08 (d, $J$ = 16.8 Hz, 1H), 5.06-5.04 (d, $J$ = 8.4 Hz, 1H), 3.17 (s, 2H), 1.72-1.65 (m, 1H), 0.69-0.65 (m, 2H), 0.54-0.50 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 141.6, 140.0, 133.1, 129.3, 128.2, 126.0, 124.6, 115.7, 40.5, 12.5, 5.5.
5. General Procedure for the Rhodium(I)-Catalyzed [7+1] Cycloadditions

To an oven-dried Schlenk tube with a stir bar was added 7.8 mg [Rh(CO)₂Cl]₂ (0.02 mmol, 0.1 equiv), and the flask was purged with CO gas three times. Then a solution of buta-1,3-dienylcyclopropane (0.2 mmol, 1.0 equiv) in dried dioxane was added via cannula, and the solution was bubbled with CO gas for 3 min. Then the solution stirred under balloon pressured CO (1 atm) at indicated temperature until TLC showed the reaction was complete. The solvent was removed in vacuo, and the residue purified by flash chromatography on silica gel to give the final products.

5-(4-Methoxyphenyl)cycloocta-2,4-dienone (2a)

Yellow oil.

IR (film): 2917, 2848, 1653, 1605, 1581, 1512, 1462, 1403, 1285, 1248, 1206, 1182, 1126, 1027 cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 7.49-7.47 (d, J = 8.8 Hz, 2H), 6.93-6.91 (d, J = 8.8 Hz, 2H), 6.68-6.63 (dd, J = 12.4 and 6.4 Hz, 1H), 6.56-6.54 (d, J = 6.4 Hz, 1H), 5.98-5.95 (d, J = 12.4 Hz, 1H), 3.84 (s, 3H), 2.76-2.73 (t, J = 6.4 Hz, 2H), 2.69-2.66 (t, J = 6.4 Hz, 2H), 2.23-2.16 (p, J = 6.4 Hz, 2H), 2.18-2.16 (p, J = 6.4 Hz, 2H), 2.09-2.07 (p, J = 6.4 Hz, 2H), 2.06-2.04 (p, J = 6.4 Hz, 2H), 2.03-2.01 (p, J = 6.4 Hz, 2H), 2.00-1.98 (p, J = 6.4 Hz, 2H), 1.97-1.95 (p, J = 6.4 Hz, 2H), 1.94-1.92 (p, J = 6.4 Hz, 2H), 1.91-1.89 (p, J = 6.4 Hz, 2H), 1.88-1.86 (p, J = 6.4 Hz, 2H), 1.85-1.83 (p, J = 6.4 Hz, 2H), 1.82-1.80 (p, J = 6.4 Hz, 2H), 1.79-1.77 (p, J = 6.4 Hz, 2H), 1.76-1.74 (p, J = 6.4 Hz, 2H), 1.73-1.71 (p, J = 6.4 Hz, 2H), 1.70-1.68 (p, J = 6.4 Hz, 2H), 1.67-1.65 (p, J = 6.4 Hz, 2H), 1.64-1.62 (p, J = 6.4 Hz, 2H), 1.61-1.59 (p, J = 6.4 Hz, 2H), 1.58-1.56 (p, J = 6.4 Hz, 2H), 1.55-1.53 (p, J = 6.4 Hz, 2H), 1.52-1.50 (p, J = 6.4 Hz, 2H), 1.49-1.47 (p, J = 6.4 Hz, 2H), 1.46-1.44 (p, J = 6.4 Hz, 2H), 1.43-1.41 (p, J = 6.4 Hz, 2H), 1.40-1.38 (p, J = 6.4 Hz, 2H), 1.37-1.35 (p, J = 6.4 Hz, 2H), 1.34-1.32 (p, J = 6.4 Hz, 2H), 1.31-1.29 (p, J = 6.4 Hz, 2H), 1.28-1.26 (p, J = 6.4 Hz, 2H), 1.25-1.23 (p, J = 6.4 Hz, 2H), 1.22-1.20 (p, J = 6.4 Hz, 2H), 1.19-1.17 (p, J = 6.4 Hz, 2H), 1.16-1.14 (p, J = 6.4 Hz, 2H), 1.13-1.11 (p, J = 6.4 Hz, 2H), 1.10-1.08 (p, J = 6.4 Hz, 2H), 1.07-1.05 (p, J = 6.4 Hz, 2H), 1.04-1.02 (p, J = 6.4 Hz, 2H), 1.01-0.99 (p, J = 6.4 Hz, 2H), 0.98-0.96 (p, J = 6.4 Hz, 2H), 0.95-0.93 (p, J = 6.4 Hz, 2H), 0.92-0.90 (p, J = 6.4 Hz, 2H), 0.89-0.87 (p, J = 6.4 Hz, 2H), 0.86-0.84 (p, J = 6.4 Hz, 2H), 0.83-0.81 (p, J = 6.4 Hz, 2H), 0.80-0.78 (p, J = 6.4 Hz, 2H), 0.77-0.75 (p, J = 6.4 Hz, 2H), 0.74-0.72 (p, J = 6.4 Hz, 2H), 0.71-0.69 (p, J = 6.4 Hz, 2H), 0.68-0.66 (p, J = 6.4 Hz, 2H), 0.65-0.63 (p, J = 6.4 Hz, 2H), 0.62-0.60 (p, J = 6.4 Hz, 2H), 0.59-0.57 (p, J = 6.4 Hz, 2H), 0.56-0.54 (p, J = 6.4 Hz, 2H), 0.53-0.51 (p, J = 6.4 Hz, 2H), 0.50-0.48 (p, J = 6.4 Hz, 2H), 0.47-0.45 (p, J = 6.4 Hz, 2H), 0.44-0.42 (p, J = 6.4 Hz, 2H), 0.41-0.39 (p, J = 6.4 Hz, 2H), 0.38-0.36 (p, J = 6.4 Hz, 2H), 0.35-0.33 (p, J = 6.4 Hz, 2H), 0.32-0.30 (p, J = 6.4 Hz, 2H), 0.30-0.28 (p, J = 6.4 Hz, 2H), 0.27-0.25 (p, J = 6.4 Hz, 2H), 0.24-0.22 (p, J = 6.4 Hz, 2H), 0.21-0.20 (p, J = 6.4 Hz, 2H), 0.19-0.18 (p, J = 6.4 Hz, 2H), 0.18-0.16 (p, J = 6.4 Hz, 2H), 0.16-0.14 (p, J = 6.4 Hz, 2H), 0.14-0.12 (p, J = 6.4 Hz, 2H), 0.12-0.10 (p, J = 6.4 Hz, 2H), 0.10-0.08 (p, J = 6.4 Hz, 2H), 0.08-0.06 (p, J = 6.4 Hz, 2H), 0.06-0.04 (p, J = 6.4 Hz, 2H), 0.04-0.02 (p, J = 6.4 Hz, 2H), 0.02-0.00 (p, J = 6.4 Hz, 2H).
Hz, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 205.6, 159.9, 148.4, 138.9, 133.1, 130.5, 127.4, 123.4, 114.1, 55.3, 38.7, 32.6, 29.8. HRMS (ESI+) for C$_{14}$H$_{13}$O (M+H)$^+$: calculated: 229.1223, found: 229.1222.

5-(4-Methoxyphenyl)cycloocta-3,5-dienone (3a)

\[
\begin{align*}
O & \quad \text{Yellow oil.} \\
3a & \quad \text{IR (film): 2921, 2851, 1706, 1659, 1632, 1606, 1511, 1470, 1289, 1247, 1179, 1116, 1035 cm}^{-1}.
\end{align*}
\]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.31-7.29 (d, $J = 8.4$, 2H), 6.89-6.86 (d, $J = 8.4$ Hz, 2H), 6.35-6.31 (t, $J = 7.6$ Hz, 1H), 6.24-6.21 (d, $J = 10.8$, 1H), 6.12-6.05 (dt, $J = 10.8$ and 7.6 Hz, 1H), 3.82 (s, 3H), 3.22-3.20 (d, $J = 7.6$, 2H), 2.56-2.51 (m, 2H), 2.42-2.39 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 208.7, 159.3, 138.1, 132.3, 131.4, 127.6, 127.1, 125.8, 113.8, 55.3, 44.3, 39.6, 26.0. HRMS (ESI+) for C$_{15}$H$_{17}$O$_2$ (M+H)$^+$: calculated: 229.1223, found: 229.1222.

\[
\begin{align*}
1b & \quad \text{(Z/E = 2.9)} \\
45.0 \text{ mg} & \quad \text{IR (film): 2938, 1654, 1588, 1492, 1449, 1405, 1344, 1250, 1207, 1126, 1025 cm}^{-1}.
\end{align*}
\]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.53-7.50 (m, 2H), 7.41-7.33 (m, 3H), 6.69-6.64 (dd, $J = 12.0$ and 6.4 Hz, 1H), 6.61-6.59 (d, $J = 6.4$ Hz, 1H), 6.01-5.98 (d, $J = 12.0$ Hz, 1H), 2.78-2.74 (t, $J = 6.8$ Hz, 2H), 2.71-2.67 (t, $J = 6.8$ Hz, 2H), 2.24-2.17 (p, $J = 6.8$ Hz, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 205.6, 148.8, 140.9, 138.6, 130.9, 128.7, 128.4, 126.2, 125.1, 38.6, 32.6, 30.0. HRMS (ESI+) for C$_{14}$H$_{15}$O (M+H)$^+$: calculated: 199.1117, found: 199.1115.

5-Phenylcycloocta-2,4-dienone (2b)

\[
\begin{align*}
2b & \quad \text{Yellow oil.} \\
\end{align*}
\]

IR (film): 2938, 1654, 1588, 1492, 1449, 1405, 1344, 1250, 1207, 1126, 1025 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.53-7.50 (m, 2H), 7.41-7.33 (m, 3H), 6.69-6.64 (dd, $J = 12.0$ and 6.4 Hz, 1H), 6.61-6.59 (d, $J = 6.4$ Hz, 1H), 6.01-5.98 (d, $J = 12.0$ Hz, 1H), 2.78-2.74 (t, $J = 6.8$ Hz, 2H), 2.71-2.67 (t, $J = 6.8$ Hz, 2H), 2.24-2.17 (p, $J = 6.8$ Hz, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 205.6, 148.8, 140.9, 138.6, 130.9, 128.7, 128.4, 126.2, 125.1, 38.6, 32.6, 30.0. HRMS (ESI+) for C$_{14}$H$_{15}$O (M+H)$^+$: calculated: 199.1117, found: 199.1115.
5-Phenylcycloocta-3,5-dienone (3b)

![Chemical structure of 3b](image)

Yellow oil.

IR (film): 3020, 2923, 2855, 1705, 1654, 1491, 1445, 1420, 1412, 1277, 1206, 1116 cm⁻¹.

1H-NMR (400 MHz, CDCl₃): \(\delta\) 7.39-7.29 (m, 5H), 6.44-6.40 (t, \(J = 8.0\) Hz, 1H), 6.26-6.24 (d, \(J = 10.4\) Hz, 1H), 6.14-6.07 (dt, \(J = 10.4\) and 7.6 Hz, 1H), 3.24-3.22 (d, \(J = 7.6\) Hz, 2H), 2.59-2.54 (m, 2H), 2.45-2.42 (m, 2H).

13C-NMR (100 MHz, CDCl₃): \(\delta\) 208.6, 139.7, 138.8, 131.2, 128.4, 127.6, 127.5, 127.3, 126.4, 44.3, 39.5, 26.0. HRMS (ESI⁺) for C₁₆H₁₅O (M+H⁺): calculated: 199.1117, found: 199.1115.

5-(4-Fluorophenyl)cycloocta-2,4-dienone (2c)

![Chemical structure of 2c](image)

Yellow oil.

IR (film): 2935, 1654, 1601, 1583, 1508, 1450, 1400, 1234, 1163, 1127, 1012 cm⁻¹.

1H-NMR (400 MHz, CDCl₃): \(\delta\) 7.51-7.47 (m, 2H), 7.10-7.05 (m, 2H), 6.67-6.63 (dd, \(J = 12.4\) and 6.0 Hz, 1H), 6.55-6.53 (d, \(J = 6.0\) Hz, 1H), 6.01-5.98 (d, \(J = 12.4\) Hz, 1H), 2.75-2.72 (t, \(J = 6.8\) Hz, 2H), 2.70-2.66 (t, \(J = 6.8\) Hz, 2H), 2.22-2.15 (p, \(J = 6.8\) Hz, 2H).

13C-NMR (100 MHz, CDCl₃): \(\delta\) 205.3, 164.0, 161.6, 147.7, 138.3, 137.0, 136.9, 131.0, 128.0, 127.9, 125.0, 124.9, 115.7, 115.5, 38.6, 32.3, 30.1. HRMS (ESI⁺) for C₁₄H₁₃FNaO (M+Na⁺): calculated: 239.0843, found: 239.0844.

5-(4-Fluorophenyl)cycloocta-3,5-dienone (3c)

![Chemical structure of 3c](image)

Yellow oil.
IR (film): 2918, 2849, 1706, 1507, 1423, 1342, 1223, 1159, 1116, 1013 cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 7.35-7.31 (dd, J = 8.8 and 5.2 Hz, 2H), 7.04-7.00 (t, J = 8.8 Hz, 2H), 6.37-6.33 (t, J = 8.0 Hz, 1H), 6.21-6.19 (d, J = 10.8 Hz, 1H), 6.13-6.07 (dt, J = 10.8 and 7.2 Hz, 1H), 3.23-3.21 (d, J = 7.2 Hz, 2H), 2.59-2.54 (m, 2H), 2.45-2.42 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 208.4, 163.7, 161.2, 137.7, 135.9, 135.8, 130.8, 128.1, 128.0, 127.6, 127.4, 115.3, 115.1, 44.3, 39.5, 25.9. HRMS (ESI⁺) for C₁₄H₁₃FNaO (M+Na)⁺: calculated: 239.0843, found: 239.0844.

5-(4-tert-Butylphenyl)cycloocta-2,4-dienone (2d)

黄色油状物。

IR (film): 2955, 2924, 2868, 1656, 1507, 1462, 1363, 1341, 1270, 1250, 1128, 1015 cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 7.49-7.46 (dt, J = 8.4 and 2.0 Hz, 2H), 7.43-7.39 (dt, J = 8.4 and 2.0 Hz, 2H), 6.68-6.64 (dd, J = 12.4 and 6.4 Hz, 1H), 6.62-6.60 (d, J = 6.4 Hz, 1H), 6.00-5.97 (d, J = 12.4 Hz, 1H), 2.77-2.74 (t, J = 8.4 Hz, 2H), 2.69-2.66 (t, J = 6.8 Hz, 2H), 2.24-2.17 (p, J = 6.8 Hz, 2H), 1.34 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃): δ 205.6, 151.7, 148.6, 138.8, 137.8, 130.8, 125.9, 125.6, 124.4, 38.7, 34.6, 32.6, 31.2, 29.8. HRMS (ESI⁺) for C₁₈H₂₃O (M+H)⁺: calculated: 255.1743, found: 255.1742.

5-(4-tert-Butylphenyl)cycloocta-3,5-dienone (3d)

黄色油状物。

IR (film): 2959, 2917, 2849, 1707, 1656, 1507, 1462, 1363, 1341, 1270, 1204, 1113, 1074, 1023
cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 7.39-7.30 (m, 4H), 6.44-6.39 (t, J = 7.8 Hz, 1H), 6.27-6.24 (d, J = 10.5 Hz, 1H), 6.14-6.07 (dt, J = 10.5 and 7.5 Hz, 1H), 3.22-3.20 (d, J = 7.5 Hz, 2H), 2.59-2.52 (m, 2H), 2.43-2.39 (m, 2H), 1.33 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃): δ 208.8, 150.7, 138.4, 136.7, 131.3, 127.1, 126.8, 126.1, 125.3, 44.2, 39.5, 34.5, 31.3, 25.9. HRMS (ESI+) for C₁₈H₂₃O (M+H)⁺: calculated: 255.1743, found: 255.1742.

5-(4-Methoxyphenyl)-3-methylcycloocta-2,4-dienone (2e)

Yellow oil.

IR (film): 2934, 1642, 1605, 1586, 1571, 1511, 1447, 1372, 1343, 1289, 1250, 1182, 1119, 1031 cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 7.49-7.46 (d, J = 8.8 Hz, 2H), 6.93-6.91 (d, J = 8.8 Hz, 2H), 6.43 (s, 1H), 5.98 (s, 1H), 3.84 (s, 3H), 2.75-2.71 (t, J = 6.8 Hz, 2H), 2.66 (br s, 2H), 2.11-2.08 (t, J = 6.4 Hz, 2H), 2.05 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 204.2, 159.8, 149.7, 146.2, 133.1, 129.4, 127.5, 126.5, 114.0, 55.3, 38.2, 31.3, 29.9, 26.8. HRMS (ESI+) for C₁₆H₁₉O₂ (M+H)⁺: calculated: 243.1380, found: 243.1373.

5-(4-Methoxyphenyl)-3-methylcycloocta-3,5-dienone (3e)

Yellow oil.

IR (film): 2926, 1701, 1648, 1607, 1574, 1510, 1442, 1289, 1246, 1178, 1117, 1034 cm⁻¹.

¹H-NMR (400 MHz, CDCl₃): δ 7.32-7.29 (d, J = 8.8 Hz, 2H), 6.88-6.86 (d, J = 8.8 Hz, 2H),
6.33-6.29 (t, J = 7.6 Hz, 1H), 5.94 (s, 1H), 3.82 (s, 3H), 3.22 (s, 2H), 2.53-2.48 (m, 2H), 2.39-2.36 (m, 2H), 2.00 (s, 3H). \(^\text{13}\text{C-NMR (100 MHz, CDCl}_3\)): \(\delta\) 208.8, 159.3, 140.0, 136.1, 132.7, 127.5, 126.0, 125.1, 113.7, 55.3, 48.9, 39.4, 26.4, 23.7. HRMS (ESI\(^+\)) for C\(_{16}\)H\(_{19}\)O\(_2\) (M+H\(^+\)): calculated: 243.1380, found: 243.1374.

5-(Thiophen-2-yl)cycloocta-2,4-dienone (2f)

Yellow oil.

IR (film): 2931, 1653, 1605, 1576, 1450, 1406, 1342, 1250, 1127, 1058 cm\(^{-1}\).

\(^1\text{H-NMR (400 MHz, CDCl}_3\)): \(\delta\) 7.31-7.29 (dd, J = 5.0 and 0.8 Hz, 1H), 7.22-7.21 (dd, J = 3.8 and 0.8 Hz, 1H), 7.06-7.04 (dd, J = 5.0 and 3.8 Hz, 1H), 6.71-6.69 (d, J = 6.2 Hz, 1H), 6.64-6.59 (dd, J = 12.3 and 6.2 Hz, 2H), 5.98-5.95 (d, J = 12.3 Hz, 1H), 2.80-2.77 (t, J = 6.6 Hz, 2H), 2.69-2.66 (t, J = 6.6 Hz, 2H), 2.28-2.21 (p, J = 6.6 Hz, 2H), \(^\text{13}\text{C-NMR (100 MHz, CDCl}_3\)): \(\delta\) 205.5, 144.8, 142.4, 137.8, 130.9, 128.1, 126.2, 125.1, 122.9, 38.7, 32.2, 30.0. HRMS (ESI\(^+\)) for C\(_{12}\)H\(_{13}\)OS (M+H\(^+\)): calculated: 205.0682, found: 205.0683.

5-(Thiophen-2-yl)cycloocta-3,5-dienone (3f)

Yellow oil.

IR (film): 2921, 2850, 1747, 1704, 1653, 1577, 1427, 1339, 1249, 1226, 1210, 1174, 1128, 1115, 1067, 1024 cm\(^{-1}\).

\(^1\text{H-NMR (400 MHz, CDCl}_3\)): \(\delta\) 7.20-7.18 (d, J = 5.2 Hz, 1H), 7.00-6.98 (dd, J = 5.2 and 3.6 Hz, 1H), 6.94-6.93 (d, J = 3.6 Hz, 1H), 6.48-6.44 (t, J = 7.6 Hz, 1H), 6.33-6.31 (d, J = 10.8 Hz, 1H), 6.11-6.05 (dt, J = 10.8 and 7.6 Hz, 1H), 3.23-3.21 (d, J = 7.6 Hz, 2H), 2.55-2.50 (m, 2H),
2.43-2.40 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 208.2, 143.9, 132.8, 130.0, 127.7, 127.5, 126.3, 124.4, 124.2, 44.3, 39.3, 25.6. HRMS (ESI+) for C$_{12}$H$_{13}$OS (M+H)$^+$: calculated: 205.0682, found: 205.0680.

5-(Naphthalen-2-yl)cycloocta-2,4-dienone (2g)

White solid, melting point: 91-92°C.

IR (film): 2942, 1654, 1448, 1435, 1404, 1344, 1249, 1196, 1127 cm$^{-1}$.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.94-7.93 (d, J = 1.5 Hz, 1H), 7.86-7.81 (m, 3H), 7.67-7.63 (dd, J = 8.7 and 2.1 Hz, 1H), 7.51-7.46 (m, 2H), 6.74-6.66 (m, 2H), 6.04-6.00 (d, J = 11.1 Hz, 1H), 2.89-2.84 (t, J = 6.6 Hz, 2H), 2.74-2.69 (t, J = 6.6 Hz, 2H), 2.28-2.21 (p, J = 6.6 Hz, 2H), 13C-NMR (75 MHz, CDCl$_3$): $\delta$ 205.5, 148.6, 138.5, 137.9, 133.3, 133.1, 131.0, 128.3, 127.5, 126.5, 125.5, 125.4, 123.9, 38.7, 32.5, 29.8. HRMS (ESI+) for C$_{18}$H$_{17}$O (M+H)$^+$: calculated: 249.1274, found: 249.1270.

5-(Naphthalen-2-yl)cycloocta-3,5-dienone (3g)

Yellow oil.

IR (film): 3362, 2918, 2849, 1705, 1653, 1632, 1426, 1339, 1276, 1114, 1020 cm$^{-1}$.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.73-7.80 (m, 3H), 7.74 (s, 1H), 7.60-7.57 (dd, J = 8.8 and 2.0 Hz, 1H), 7.49-7.44 (m, 2H), 6.60-6.56 (t, J = 8.0 Hz, 1H), 6.38-6.35 (d, J = 10.8 Hz, 1H), 6.21-6.14 (dt, J = 10.8 and 8.0 Hz, 1H), 3.28-3.26 (d, J = 8.0 Hz, 2H), 2.67-2.60 (m, 2H), 2.48-2.44 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 208.5, 138.6, 136.9, 133.4, 132.9, 131.2, 128.1, 128.0, 127.6,
127.5, 127.4, 126.3, 126.0, 125.6, 124.3, 44.4, 39.5, 26.1. HRMS (ESI+) for C_{18}H_{17}O (M+H)^+: calculated: 249.1274, found: 249.1273.

\[
\begin{array}{c}
\text{1h (Z/E = 0.8)} \\
67.0 \text{ mg}
\end{array}
\]

\[
\begin{array}{c}
\text{2h} \\
62.0 \text{ mg (80\%)}
\end{array}
\]

\[
\begin{array}{c}
\text{3h} \\
4.2 \text{ mg (5.4\%)}
\end{array}
\]

5-Benzylcycloocta-2,4-dienone (2h)

\[
\begin{array}{c}
\text{2h} \\
\text{Yellow oil.}
\end{array}
\]

IR (film): 2928, 1654, 1629, 1592, 1494, 1449, 1435, 1408, 1344, 1251, 1192, 1128, 1076, 1030 cm\(^{-1}\).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.34-7.20 (m, 5H), 6.49-6.44 (dd, \(J = 12.4\) and 5.6 Hz, 1H), 6.05-6.04 (d, \(J = 5.6\) Hz, 1H), 5.89-5.86 (d, \(J = 12.4\) Hz, 1H), 3.54 (s, 2H), 2.58-2.55 (t, \(J = 6.8\) Hz, 2H), 2.27-2.24 (t, \(J = 6.8\) Hz, 2H), 1.93-1.86 (p, \(J = 6.8\) Hz, 2H), 13C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 205.9, 151.1, 138.5, 138.3, 130.5, 129.2, 128.6, 126.7, 125.1, 45.1, 38.8, 31.9, 30.5. HRMS (ESI+) for C\(_{15}\)H\(_{16}\)NaO (M+Na)^+: calculated: 235.1093, found: 235.1091.

5-Benzylcycloocta-3,5-dienone (3h)

\[
\begin{array}{c}
\text{3h} \\
\text{Yellow oil.}
\end{array}
\]

IR (film): 3023, 2923, 1706, 1494, 1453, 1430, 1334, 1278, 1113, 1075, 1029 cm\(^{-1}\).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): 7.31-7.26 (m, 2H), 7.22-7.17 (m, 3H), 5.88-5.85 (d, \(J = 10.8\) Hz, 1H), 5.80-5.70 (m, 2H), 3.40 (s, 2H), 3.08-3.06 (d, \(J = 7.2\) Hz, 2H), 2.45-2.39 (m, 4H). 13C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 209.4, 139.2, 138.1, 131.4, 128.8, 128.3, 127.2, 126.2, 125.8, 44.5, 43.8, 40.2, 25.2. HRMS (ESI+) for C\(_{15}\)H\(_{16}\)NaO (M+Na)^+: calculated: 235.1093, found: 235.1093.
5-Cyclopropylcycloocta-2,4-dienone (2i)

Yellow oil.

**IR (film):** 3012, 2941, 2863, 1654, 1589, 1449, 1410, 1344, 1251, 1206, 1127, 1019 cm⁻¹.

**¹H-NMR (400 MHz, CDCl₃):** δ 6.48-6.44 (dd, J = 12.3 and 6.0 Hz, 1H), 6.05-6.04 (d, J = 6.0 Hz, 1H), 5.87-5.84 (d, J = 12.3 Hz, 1H), 2.61-2.58 (t, J = 6.5 Hz, 2H), 2.14-2.05 (m, 4H), 1.62-1.55 (m, 1H), 0.86-0.81 (m, 2H), 0.63-0.59 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 206.0, 153.8, 138.7, 129.7, 121.6, 38.6, 33.1, 28.3, 18.6, 7.2. HRMS (ESI⁺) for C₁₁H₁₅O (M+H)⁺: calculated: 163.1117, found: 163.1115.

5-Cyclopropylcycloocta-3,5-dienone (3i)

Yellow oil.

**IR (film):** 3002, 2925, 2856, 1706, 1657, 1428, 1278, 1117, 1022 cm⁻¹.

**¹H-NMR (400 MHz, CDCl₃):** δ 5.86-5.78 (m, 3H), 3.13-3.12 (d, J = 6.0 Hz, 2H), 2.36-2.35 (d, J = 4.0 Hz, 4H), 1.50-1.44 (m, 1H), 0.63-0.59 (m, 2H), 0.47-0.43 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃): δ 209.5, 139.7, 129.7, 126.4, 123.9, 44.4, 40.2, 25.0, 16.8, 4.5. HRMS (ESI⁺) for C₁₁H₁₅O (M+H)⁺: calculated: 163.1117, found: 163.1116.
5-Methylcycloocta-2,4-dienone (2j)

Yellow oil.

IR (film): 2933, 2862, 1654, 1631, 1591, 1451, 1406, 1343, 1306, 1250, 1192, 1130, 1052, 1011 cm\(^{-1}\).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.46-6.42 (dd, J = 12.4 and 5.6 Hz, 1H), 6.06-6.05 (d, J = 5.6 Hz, 1H), 5.88-5.86 (d, J = 12.4 Hz, 1H), 2.62-2.58 (t, J = 6.8 Hz, 2H), 2.28-2.25 (t, J = 6.8 Hz, 2H), 2.14-2.07 (p, J = 6.8 Hz, 2H), 1.98 (s, 3H).

\(^13\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 206.2, 148.8, 138.6, 130.3, 124.1, 38.8, 32.1, 31.6, 24.9. HRMS (ESI\(^+\)) for C\(_9\)H\(_{12}\)NaO (M+Na\(^+\)): calculated: 159.0780, found: 159.0778.

6. General Procedure for the Synthesis of 4k and 4l

To an oven-dried Schlenk tube with a stir bar was added 7.8 mg [Rh(CO)\(_2\)Cl\(_2\)] (0.02 mmol, 0.1 equiv), and the flask was purged with CO gas three times. Then a solution of buta-1,3-dienylcyclopropane (0.2 mmol, 1.0 equiv) in dried dioxane was added via cannula, and the solution was bubbled with CO gas for 3 min. Then the solution stirred under balloon pressured CO (1 atm) at indicated temperature until TLC showed the reaction was complete. The
solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel.

\[
\begin{align*}
\text{[Rh(CO)\textsubscript{2}Cl\textsubscript{2}]} & \quad \text{Dioxane, 80 }&\text{C, 24 h} \\
1k & \quad & 4k \\
\frac{86 \text{ mg}}{} & \quad & \frac{61 \text{ mg (99\%)}}{}
\end{align*}
\]

(Z)-4-Phenyl-2-((E)-3-(1-phenylcyclopropyl)hex-4-enylidene)cyclohex-3-enone (4k)

IR (film): 3026, 2916, 2849, 1698, 1622, 1590, 1495, 1445, 1377, 1322, 1238, 1189, 1019 cm\(^{-1}\).

\(\text{^{1}H-NMR (400 MHz, CDCl\textsubscript{3})}: \delta \) 7.48-7.19 (m, 10H), 6.76 (s, 1H), 6.66-6.62 (t, J = 8.0 Hz, 1H), 5.46-5.37 (dq, J = 15.2 and 6.4 Hz, 1H), 5.26-5.20 (ddd, J = 15.2, 8.7 and 1.5 Hz, 1H), 2.91-2.88 (t, J = 6.8 Hz, 2H), 2.71-2.67 (t, J = 6.8 Hz, 2H), 2.53-2.46 (ddd, J = 15.3, 8.2 and 5.2 Hz, 1H), 2.18-2.10 (ddd, J = 15.3, 9.0 and 7.3 Hz, 1H), 1.89-1.83 (dt, J = 5.2 and 9.0 Hz, 1H), 1.68-1.66 (dd, J = 6.4 and 1.5 Hz, 3H), 0.88-0.67 (m, 4H). \(\text{^{13}C-NMR (100 MHz, CDCl\textsubscript{3})}: \delta \) 198.8, 143.1, 140.6, 137.9, 136.7, 131.7, 131.6, 131.1, 128.5, 127.8, 127.7, 126.8, 126.4, 125.2, 120.9, 51.3, 38.2, 31.0, 30.6, 26.6, 18.1, 12.7, 11.0. HRMS (ESI+) for C\(_{27}\)H\(_{28}\)NaO (M+Na\(^+\))\(^{\dagger}\): calculated: 391.2032, found: 391.2042.

\[
\begin{align*}
\text{[Rh(CO)\textsubscript{2}Cl\textsubscript{2}]} & \quad \text{Dioxane, 80 }&\text{C, 30 h} \\
1l & \quad & 4l \\
\frac{180 \text{ mg}}{} & \quad & \frac{133 \text{ mg (99\%)}}{}
\end{align*}
\]

(Z)-4-(4-Methoxyphenyl)-2-((E)-3-(1-(4-methoxyphenyl)cyclopropyl)hex-4-enylidene)cyclohex-3-enone (4l)
Yellow oil.

IR (film): 2916, 2849, 1697, 1606, 1589, 1512, 1463, 1441, 1376, 1288, 1246, 1180, 1109, 1034 cm\(^{-1}\).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.43-7.41 (d, \(J = 8.8\) Hz, 2H), 7.26-7.24 (d, \(J = 8.8\) Hz, 2H), 6.96-6.94 (d, \(J = 8.8\) Hz, 2H), 6.84-6.82 (d, \(J = 8.8\) Hz, 2H), 6.73-6.72 (d, \(J = 1.2\) Hz, 1H), 6.65-6.61 (t, \(J = 8.0\) Hz, 1H), 5.47-5.39 (dq, \(J = 15.2\) and 6.4 Hz, 1H), 5.30-5.24 (ddd, \(J = 15.2\), 8.4 and 1.6 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.92-2.89 (t, \(J = 6.8\) Hz, 2H), 2.73-2.70 (t, \(J = 6.8\) Hz, 2H), 2.54-2.47 (ddd, \(J = 15.6\), 8.4 and 5.2 Hz, 1H), 2.20-2.12 (ddd, \(J = 15.6\), 8.8 and 7.4 Hz, 1H), 1.85-1.80 (ddd, \(J = 8.8\), 8.8 and 5.2 Hz, 1H), 1.71-1.69 (dd, \(J = 6.4\) and 1.6 Hz, 3H), 0.79-0.67 (m, 4H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.0, 159.4, 158.1, 137.3, 135.8, 135.2, 133.1, 132.1, 132.0, 131.7, 126.5, 126.4, 119.4, 113.9, 113.1, 55.3, 55.2, 51.5, 38.2, 31.0, 29.8, 26.6, 18.0, 12.8, 11.2.

HRMS (ESI\(^+\)) for C\(_{29}\)H\(_{33}\)O\(_3\) (M+H\(^+\))\(^+\): calculated: 429.2424, found: 429.2416.

7. Structure Determination

The structures of \(2a\) and \(4l\) were identified by \(^1\)H NMR and \(^{13}\)C NMR of \(2a\) and \(4l\), and confirmed by the crystallographic data of hydrazone derivatives of \(2a\) and \(4l\), respectively. Then the structures of cycloadducts \(2b-2j\) were deduced by analogy to \(2a\), and the structure of \(4k\) was deduced by analogy to \(4l\).

Synthesis of the Hydrazone Derivatives of 2a

A flame-dried round-bottomed flask with a stir bar was charged with 2,4-dinitrophenylhydrazine (168 mg, 0.85 mmol, 1.5 equiv), MeOH/THF(1:1, 2mL). The suspension was heated at 50 °C, until the suspension became clear. Then the red brown solution was allowed to cool to room temperature and \(2a\) (120 mg, 0.57 mmol, 1 equiv, in 1 mL THF) and one drop of concentrated hydrochloric acid was added afterwards. The resulting solution was heated at 50 °C for 5 minutes and allowed to cool to room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography to afford 150 mg (70%) \(5a\) as a red
brown solid.

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{N} \quad \text{O} \\
\end{array}
\xrightarrow{2,4-DNP (1.0 equiv), HCl (cat.)}
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{N} \quad \text{O} \\
\end{array}
\]

\((E)-1-(2,4-\text{Dinitrophenyl})-2-((2Z,4E)-5-(4-\text{methoxyphenyl})\text{cycloocta-2,4-dienylidene})\text{hydrazine (5a)}\)

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{N} \quad \text{O} \\
\end{array}
\]

Brown solid, melting point: 207-208 ℃.

IR (film): 3056, 2957, 2927, 1731, 1590, 1512, 1335, 1265, 1180, 1134, 1088 cm\(^{-1}\).

\(^1\text{H}-\text{NMR (400 MHz, CDCl}_3\)): \(\delta\) 11.45 (s, 1H), 9.15-9.14 (d, J = 2.0 Hz, 1H), 8.35-8.32 (dd, J = 9.6 and 2.0 Hz, 1H), 8.06-8.04 (d, J = 9.6 Hz, 1H), 7.48-7.46 (d, J = 8.5 Hz, 2H), 6.92-6.90 (d, J = 8.5 Hz, 2H), 6.58-6.56 (d, J = 5.8 Hz, 1H), 6.41-6.38 (d, J = 12.3 Hz, 1H), 6.35-6.31 (dd, J = 12.3 and 5.8 Hz, 1H), 3.84 (s, 3H), 2.71 (br s, 4H), 2.20 (br s, 2H). \(^{13}\text{C}-\text{NMR (100 MHz, CDCl}_3\)): \(\delta\) 159.9, 158.8, 144.6, 143.7, 138.4, 133.4, 131.9, 130.0, 129.91, 129.88, 127.3, 124.1, 123.4, 116.7, 114.2, 55.4, 29.8, 26.7, 24.7. HRMS (ESI+) for C\(_{21}\)H\(_{21}\)N\(_4\)O\(_5\) (M+H): calculated: 409.1507, found: 409.1508.

The ORTEP Diagrams of Cycloadducts 5a (CCDC: 787186)

Synthesis of the Hydrazine Derivatives of 4l
A flame-dried round-bottomed flask with a stir bar was charged with 2,4-dinitrophenylhydrazine (35 mg, 0.18 mmol, 1.5 equiv), MeOH/THF(1:1, 2mL). The suspension was heated at 50 °C, until the suspension became clear. Then the red brown solution was allowed to cool to room temperature and 4l (50 mg, 0.12 mmol, 1 equiv, in 1 mL THF) and one drop of concentrated hydrochloric acid was added afterwards. The resulting solution was heated at 50 °C for 5 minutes and allowed to cool to room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography to afford 44 mg (62%) 5l as a red brown solid. This hydrazine 5l should be generated from the isomerization of hydrazone 5l' through simultaneous [1,3] hydrogen shift and [1,5] hydrogen shift.

(E)-1-(2,4-Dinitrophenyl)-2-(4'-methoxy-3-(3-(1-(4-methoxyphenyl)cyclopropyl)hex-4-enyl)-biphenyl-4-yl)hydrazine (5l)

Brown solid, melting point: 165-166°C.

IR (film): 3333, 2916, 2851, 1621, 1610, 1593, 1513, 1493, 1465, 1425, 1335, 1313, 1275, 1244,
1180, 1139, 1110, 1060, 1031 cm\(^{-1}\).

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.46 (s, 1H), 9.16-9.15 (d, \(J = 2.5\) Hz, 1H), 8.26-8.23 (dd, \(J = 9.5\) and 2.5 Hz, 1H), 7.45-7.43 (d, \(J = 8.7\) Hz, 2H), 7.39-7.36 (d, \(J = 9.5\) Hz, 1H), 7.30-7.25 (m, 2H), 7.24-7.22 (d, \(J = 8.8\) Hz, 2H), 6.96-6.94 (d, \(J = 8.7\) Hz, 2H), 6.79-6.77 (d, \(J = 8.8\) Hz, 2H), 6.77-6.74 (d, \(J = 8.8\) Hz, 1H), 5.70 (s, 1H), 5.56-5.48 (dt, \(J = 15.2\) and 6.4 Hz, 1H), 5.32-5.26 (ddd, \(J = 15.2, 9.0\) and 1.2 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 2.62-2.47 (m, 2H), 1.95-1.86 (m, 1H), 1.75-1.73 (dd, \(J = 6.4\) and 1.2 Hz, 3H), 1.69-1.64 (td, \(J = 10.0\) and 3.6 Hz, 1H), 1.57-1.48 (m, 1H), 0.78-0.66 (m, 4H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.9, 158.1, 150.0, 141.9, 137.9, 135.3, 134.6, 133.1, 132.8, 131.8, 130.5, 130.1, 128.5, 127.8, 127.6, 127.0, 125.4, 123.7, 115.2, 114.2, 113.1, 112.1, 55.3, 5.1, 51.6, 32.4, 29.8, 29.5, 18.1, 12.8, 11.4. HRMS (ESI+) for C\(_{35}\)H\(_{36}\)N\(_4\)NaO\(_6\) (M+Na\(^+\)): calculated: 631.2533, found: 631.2520.

The ORTEP Diagrams of Cycloadducts 5l (CCDC: 764829)

8. Isomerization of 3a and 3c

\[
\begin{align*}
\text{Rh(CO)\(_2\)Cl\(_2\)} & \quad \text{(10 mol %)} \\
\text{Dioxane, 85 °C, 24 h} & \quad \text{[R]} \\
\text{3a} & \quad R = 4-\text{MeOC\(_2\)H\(_4\)} \quad 86\% \text{ convn, 86\% yield} \quad 2a \\
\text{3c} & \quad R = 4-\text{FC\(_2\)H\(_4\)} \quad 90\% \text{ convn, 76\% yield} \quad 2c
\end{align*}
\]
To an oven-dried Schlenk tube with a stir bar was added 7.8 mg [Rh(CO)\(_2\)Cl]\(_2\) (0.02 mmol, 0.1 equiv), and the flask was purged with Ar gas three times. Then a solution of \(3a\) or \(3c\) (0.2 mmol, 1.0 equiv) in dried dioxane was added via cannula, and the solution was bubbled with Ar gas for 3 min. The resulting solution was stirred under balloon pressured Ar (1 atm) at indicated temperature until TLC showed the reaction was complete. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel to give the final product. We also used sodium ethanolate\(^7\) or DBU\(^8\) as base to promote the isomerization of \(3a\) and \(3c\). The starting materials were untouched by DBU, but decomposed when treated with sodium ethanolate.

9. The Proposed Mechanism for the Reaction of 1k-l to 4k-l

We propose the following pathway accounting for the formation of 4k-l. The active catalyst Rh(CO)\(_2\)Cl, generated by disassociation of its precursor [Rh(CO)\(_2\)Cl]\(_2\), coordinates to buta-1,3-dienylcyclopropane 1k-l, giving the intermediate G. Ring opening of the cyclopropane ring converts G to the six-membered rhodacycle intermediate H, which undergoes CO coordination, CO insertion, and reductive elimination to give intermediate J. The process of G to J can be regarded as a formal [5+1] reaction of BDCP and CO. However, the reaction does not stop at the [5+1] process. Instead, intermediate J undergoes an allylic C-H activation\(^9\) process to generate intermediate K, which then adds its Rh-H bond to the diene part of BDCP 1k-l, giving a bisallylic Rh complex L. Finally reductive elimination from L produces 4k-l, accompanied with the regeneration of the active catalyst for the next catalytic cycle.
10. Unsuccessful Substrates for the [7+1] Reaction

In all these unsuccessful cases, only starting materials were recovered under the standard [7+1] reaction conditions.

**Synthesis of (2-(1-Phenylbuta-1,3-dienyl)cyclopropyl)benzene (1m)**

To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (2.25 mmol, 2.0 equiv) and THF (10 mL). The solution was cooled to 0 °C and 0.9 mL (2.25 mmol, 2.0 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 °C, phenyl(-2-phenylcyclopropyl)methanone\(^1\) (1.12 mmol, 1.0 equiv) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 83 mg (30%) 1m as a colorless oil.

A 4:1 mixture of (Z:E)-(2-(1-phenylbuta-1,3-dienyl)cyclopropyl)benzene was obtained. The (Z):(E)-ratio was determined using \(^1\)H-NMR by integration of one of the olefinic protons.
doublet at 6.14 ppm for the (Z)-(2-(1-phenylbuta-1,3-dienyl)cyclopropyl)benzene and a doublet at 6.46 ppm for the (E)-olefin.

IR (film): 3026, 1604, 1497, 1442, 1418, 1029 cm⁻¹. (Z)-isomer: ¹H-NMR (300 MHz, CDCl₃): δ 7.39-7.06 (m, 10H), 6.34-6.21 (dt, J = 16.8 and 10.8 Hz, 1H), 6.16-6.12 (d, J = 10.8 Hz, 1H), 5.22-5.15 (dd, J = 16.8 and 1.8 Hz, 1H), 4.96-4.92 (dd, J = 10.8 and 1.8 Hz, 1H), 2.04-1.85 (m, 2H), 1.30-1.19 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 143.8, 142.3, 139.5, 134.4, 129.0, 128.3, 128.0, 127.1, 125.8, 125.7, 125.6, 116.1, 30.8, 25.3, 15.5. HRMS (EI⁺) for C₁₉H₁₈ (M)⁺: calculated: 246.1409, found: 246.1412.

Additional signals for the (E)-isomer: ¹H-NMR (300 MHz, CDCl₃): δ 7.45-7.06 (m, 10H), 7.04-6.91 (dt, J = 16.8 and 10.8 Hz, 1H), 6.48-6.44 (d, J = 10.8 Hz, 1H), 5.34-5.27 (dd, J = 16.8 and 1.8 Hz, 1H), 5.18-5.15 (dd, J = 10.8 and 1.8 Hz, 1H), 2.14-2.09 (m, 1H), 2.04-1.85 (m, 1H), 1.43-1.32 (m, 1H), 1.14-1.05 (m, 1H). ¹³C-NMR (75 MHz, CDCl₃): δ 142.5, 141.4, 141.2, 133.8, 130.7, 128.4, 128.0, 127.0, 126.1, 125.8, 125.6, 118.3, 25.3, 24.3, 18.0.

Synthesis of (3-Cyclopropylhexa-3,5-dien-1-ynyl)benzene (1n)

To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (9.9 mmol, 1.2 equiv) and THF (40 mL). The solution was cooled to 0 °C and 4.0 mL (10.0 mmol, 1.2 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 °C, 1-cyclopropyl-3-phenylprop-2-yn-1-one¹¹ (8.3 mmol, 1.0 equiv) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na₂SO₄, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 498 mg (32%) 1n as a colorless oil.
A 2.5:1 mixture of (Z:E)-(3-cyclopropylhexa-3,5-dien-1-ynyl)benzene was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a doublet at 6.44 ppm for the (Z)-(3-cyclopropylhexa-3,5-dien-1-ynyl)benzene and a doublet at 6.54 ppm for the (E)-olefin.

IR (film): 3005, 1616, 1489, 1442, 1420, 1026 cm$^{-1}$. (Z)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.39 (m, 1H), 7.33-7.28 (m, 4H), 6.97-6.87 (dt, $J = 16.8$ and 10.8 Hz, 1H), 6.45-6.43 (d, $J = 10.8$ Hz, 1H), 5.30-5.24 (dd, $J = 16.8$ and 1.6 Hz, 1H), 5.14-5.11 (dd, $J = 10.8$ and 1.6 Hz, 1H), 1.63-1.57 (m, 1H), 0.86-0.81 (m, 2H), 0.78-0.72 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 134.9, 134.3, 131.5, 128.3, 128.2, 127.6, 123.1, 116.9, 95.9, 84.6, 16.4, 6.1. HRMS (EI+) for C$_{15}$H$_{14}$ (M$^+$): calculated: 194.1096, found: 194.1097.

Additional signals for the (E)-isomer: $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.45-7.39 (m, 5H), 6.90-6.83 (dt, $J = 16.8$ and 10.8 Hz, 1H), 6.55-6.52 (d, $J = 10.8$ Hz, 1H), 5.35-5.29 (dd, $J = 16.8$ and 1.6 Hz, 1H), 5.22-5.18 (dd, $J = 10.8$ and 1.6 Hz, 1H), 1.93-1.86 (m, 1H), 0.92-0.87 (m, 2H), 0.82-0.77 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 135.3, 132.1, 131.5, 128.2, 128.0, 126.9, 123.4, 118.6, 90.4, 88.1, 11.1, 6.5.

**Synthesis of tert-Butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane (1o)**

![Synthesis of tert-Butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane (1o)](image)

To an oven-dried round-bottomed flask with a stir bar was added 1-cyclopropylbut-3-en-1-one (220 mg, 2.0 mmol, 1.0 equiv), THF (15 mL), and TEA (1.26 mL, 9.0 mmol, 4.5 equiv). The solution was cooled to 0 ºC and TBSOTf (0.9 mL, 4.0 mmol, 2.0 equiv) was added dropwise. The solution was stirred for 4 hours at 0 ºC. Then pentane (40 mL) and TEA (5 mL) were added. The resulted solution was washed with brine (10 mL), and then dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography to afford 83 mg (37%) 1o as a colorless oil.

A 0.7:1 mixture of (Z:E)-tert-butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane was obtained. The (Z):(E)-ratio was determined using $^1$H-NMR by integration of one of the olefinic protons: a
doublet at 5.27 ppm for the (Z)-tert-butyl(1-cyclopropylbuta-1,3-dienyloxy)dimethylsilane and a
doublet at 5.66 ppm for the (E)-olefin.
IR (film): 2957, 2930, 2858, 1637, 1472, 1254, 1229 cm\(^{-1}\). (Z)-isomer: \(\text{\(^1\)}\text{H-NMR}\) (400 MHz, 
\(\text{CDCl}_3\)): \(\delta\) 7.00-6.90 (dt, \(J = 16.8\) and 10.8 Hz, 1H), 5.29-5.26 (d, \(J = 10.8\) Hz, 1H), 5.08-5.04 (dd, 
\(J = 16.8\) and 1.8 Hz, 1H), 4.92-4.89 (dd, \(J = 10.8\) and 1.8 Hz, 1H), 1.18-1.11 (m, 1H), 1.00 (s, 9H), 
0.85-0.82 (m, 4H), 0.14 (s, 6H). \(\text{\(^1\)}\text{C-NMR}\) (100 MHz, \(\text{CDCl}_3\)): \(\delta\) 155.2, 132.7, 112.2, 108.4, 26.5,
19.0, 17.0, 7.3, -3.1. HRMS (ESI+) for \(\text{C}_{13}\text{H}_{25}\text{OSi (M+H)}^+\): calculated: 225.1669, found: 
225.1669.
Additional signals for the (E)-isomer: \(\text{\(^1\)}\text{H-NMR}\) (400 MHz, \(\text{CDCl}_3\)): \(\delta\) 6.75-6.65 (dt, \(J = 16.8\) and 
10.8 Hz, 1H), 5.67-5.65 (d, \(J = 10.8\) Hz, 1H), 5.12-5.07 (dd, \(J = 16.8\) and 1.8 Hz, 1H), 4.95-4.92 
(dd, \(J = 10.8\) and 1.8 Hz, 1H), 1.73-1.66 (m, 1H), 0.87 (s, 9H), 0.47-0.39 (m, 4H), 0.09 (s, 6H).
\(\text{\(^1\)}\text{C-NMR}\) (100 MHz, \(\text{CDCl}_3\)): \(\delta\) 155.5, 133.5, 111.6, 109.6, 26.3, 18.8, 12.5, 5.5, -3.9.

**Synthesis of (Z)-1-(1-Phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane (1p)**

\[
\begin{align*}
\text{S-6 & \xrightarrow{\text{PhMgBr, THF, 0 \text{°C}-RT, 86\%}} & \text{S-7}} \\
\text{S-8 & \xrightarrow{\text{DIBAL-H, DCM, -78 \text{°C}-RT, 100\%}} & \text{S-9}} \\
\text{S-10 & \xrightarrow{\text{CH_3PPh_3, \text{BuLi, THF, 0 \text{°C}-RT, 77\%}} & \text{1p}}}
\end{align*}
\]

**Bicyclo[4.1.0]heptan-1-yl(phenyl)methanone (S-7)**

\[
\begin{align*}
\text{S-6 & \xrightarrow{\text{PhMgBr, THF, 0 \text{°C}-RT, 86\%}} & \text{S-7}}
\end{align*}
\]

\(\text{Bicyclo[4.1.0]heptane-1-carbaldehyde}\)\(^\text{13}\) (0.80 g, 6.5 mmol, in 50 mL THF) was cooled to 0 °C. 
Phenylmagnesium bromide (10.0 mmol, 1M solution in THF) was added slowly to the above 
bicyclo[4.1.0]heptane-1-carbaldehyde solution. The solution was then stirred under 0 °C for 30 
minutes before it was poured into the mixture of 50 g ice and 50 mL water. After extracted with
Et₂O, washed with water, and brine, dried over MgSO₄, and concentrated in vacuo, the crude mixture was purified by flash column chromatography to afford 1.13 g (86%) diastereoisomer S-6 as a light yellow liquid.

Diastereoisomer bicyclo[4.1.0]heptan-1-yl(phenyl)methanol (S-6) (1.13 g, 5.6 mmol) was dissolved in 60 mL anhydrous CH₂Cl₂ and cooled to 0 °C. Then PDC (2.52 g, 6.7 mmol) was added in batches and the resulting solution was stirred for 10 h at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to afford 0.95 g (85%) S-7 as a colorless oil.

IR (film): 2930, 2857, 1670, 1447, 1302, 1260 cm⁻¹.

¹H-NMR (300 MHz, CDCl₃): δ 7.81-7.77 (m, 2H), 7.52-7.40 (m, 3H), 2.28-2.19 (dt, J = 14.4 and 5.1 Hz, 1H), 1.98-1.75 (m, 3H), 1.69-1.61 (m, 1H), 1.52-1.16 (m, 5H), 0.76-0.73 (dd, J = 6.3 and 4.2 Hz, 1H). ¹³C-NMR (75 MHz, CDCl₃): δ 204.6, 137.7, 131.6, 128.2, 128.1, 29.0, 27.1, 22.8, 21.6, 20.2, 19.5, 18.9.

HRMS (ESI⁺) for C₁₄H₁₆NaO (M+Na)⁺: calculated: 223.1093, found: 223.1091.

(Ε)-Ethyl 3-(bicyclo[4.1.0]heptan-1-yl)-3-phenylacrylate (S-8)

To a flask containing NaH (0.18 g, 7.5 mmol) and 40 mL THF at 0 °C was added triethyl phosphonoacetate (1.68 g, 7.5 mmol). After stirring at room temperature for 30 min, bicyclo[4.1.0]heptan-1-yl(phenyl)methanone (S-7) (0.60 g, 3.0 mmol) was added dropwise and the reaction was allowed to stir for 32 hours. After quenching with brine, extracting with Et₂O, and drying over MgSO₄, concentration of the organic phase in vacuo gave a crude oil that was further purified by flash chromatography to afford 0.27 g (33%) S-8 as a colorless oil.

IR (film): 2929, 2856, 1721, 1613, 1446, 1260, 1154, 1038 cm⁻¹.

¹H-NMR (300 MHz, CDCl₃): δ 7.60-7.55 (m, 2H), 7.36-7.31 (m, 3H), 6.13 (s, 1H), 4.28-4.17 (m, 2H), 2.21-2.11 (m, 1H), 2.01-1.92 (m, 2H), 1.76-1.65 (m, 1H), 1.58-1.42 (m, 2H), 1.40-1.20 (m, 5H), 1.02-0.94 (m, 1H), 0.75-0.64 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 166.1, 162.8, 140.6, 128.5, 128.2, 127.1, 118.5, 59.9, 30.5, 23.2, 22.4, 21.7, 20.7, 20.0, 19.8, 14.4. HRMS (ESI⁺) for C₁₈H₃₅O₂ (M+H)⁺: calculated: 271.1693, found: 271.1689.
(E)-3-(Bicyclo[4.1.0]heptan-1-yl)-3-phenylprop-2-en-1-ol (S-9)

To a Schlenk flask charged with (E)-ethyl 3-(bicyclo[4.1.0]heptan-1-yl)-3-phenylacrylate (S-8) (190 mg, 0.7 mmol) in THF at 0 °C was added DIBAL-H (2.8 mL, 1 M in toluene, 2.8 mmol) dropwise. The reaction was warmed to room temperature overnight and was quenched with ethylacetate and aqueous potassium tartrate tetrahydrate. Stirring was continued until the solution was clear. Extracted with Et₂O, washed with brine, dried over MgSO₄, evaporation and purification by flash column chromatography to give 168 mg (100%) S-9 as a colorless oil.

IR (film): 2927, 2855, 1493, 1447, 1024 cm⁻¹.

¹H-NMR (300 MHz, CDCl₃): δ 7.49-7.45 (m, 2H), 7.32-7.20 (m, 3H), 5.96-5.92 (t, J = 6.3 Hz, 1H), 4.57-4.54 (dd, J = 6.3 and 3.6 Hz, 2H), 2.04-1.90 (m, 3H), 1.77-1.70 (m, 1H), 1.60 (br s, 1H), 1.46-1.20 (m, 4H), 0.97-0.92 (m, 1H), 0.66-0.61 (m, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 148.8, 141.3, 128.7, 128.0, 126.8, 126.4, 60.3, 31.7, 23.2, 21.8, 20.9, 20.3, 19.8, 19.1. HRMS (ESI+) for C₁₆H₂₀NaO (M+Na)+: calculated: 251.1406, found: 251.1405.

(E)-3-(Bicyclo[4.1.0]heptan-1-yl)-3-phenylacrylaldehyde (S-10)

(E)-3-(Bicyclo[4.1.0]heptan-1-yl)-3-phenylprop-2-en-1-ol (S-9) (168 mg, 0.7 mmol) was dissolved in 20 mL anhydrous CH₂Cl₂ and cooled to 0 °C. Then PDC (570 mg, 1.5 mmol) was added in batches and the resulting solution was stirred for 1 hour at room temperature. The product mixture was filtered through a short silica gel column. Then the filtrate was concentrated to get 87 mg (51%) S-10 as a light yellow liquid.

IR (film): 2931, 2855, 1664, 1590, 1447, 1136 cm⁻¹.

¹H-NMR (300 MHz, CDCl₃): δ 10.50-10.46 (d, J = 8.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.42-7.37 (m, 3H), 6.32-6.30 (d, J = 8.4 Hz, 1H), 2.11-1.98 (m, 3H), 1.86-1.79 (m, 1H), 1.55-1.43 (m, 3H), 1.37-1.13 (m, 2H), 0.89-0.87 (d, J = 7.5 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 193.1, 168.7,
138.8, 129.7, 128.5, 127.6, 127.3, 33.1, 22.5, 21.6, 21.3, 20.2, 19.8, 19.7. HRMS (ESI+) for C_{16}H_{19}O (M+H)^{+}: calculated: 227.1430, found: 227.1427.

\((E)-1-(1\text{-phenylbuta-1,3-dienyl})bicyclo[4.1.0]heptane (1p)\)

![Synthesis of 1p](image)

To an oven-dried round-bottomed flask with a stir bar was added methyltriphenylphosphonium bromide (544 mg, 1.5 mmol, 4.0 equiv) and THF (10 mL). The solution was cooled to 0 °C and 0.61 mL (1.5 mmol, 4.0 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 °C, aldehyde (S-10) (86 mg, 0.4 mmol, 1.0 equiv) in 2 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 2 hours. The reaction was then quenched with 8 mL brine and diluted with 40 mL of diethyl ether. The organic layer was separated and the aqueous layer was extracted by diethyl ether in one time. The combined organic layers were dried over Na_{2}SO_{4}, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 66 mg (77%) 1p as a colorless oil.

IR (film): 2928, 2855, 1492, 1447, 1029 cm⁻¹. \(^1\)H-NMR (400 MHz, CDCl₃): \(\delta\) 7.54-7.52 (d, J = 7.2 Hz, 2H), 7.32-7.28 (t, J = 7.2 Hz, 2H), 7.23-7.21 (d, J = 7.2 Hz, 1H), 7.12-7.03 (dt, J = 16.8 and 10.8 Hz, 1H), 6.46-6.43 (d, J = 10.8 Hz, 1H), 5.32-5.28 (dd, J = 16.8 and 1.6 Hz, 1H), 5.22-5.19 (dd, J = 10.8 and 1.6 Hz, 1H), 2.13-1.94 (m, 3H), 1.81-1.74 (m, 1H), 1.51-1.25 (m, 5H), 1.02-0.96 (m, 1H), 0.68-0.67 (d, J = 7.6 Hz, 2H). \(^{13}\)C-NMR (100 MHz, CDCl₃): \(\delta\) 148.3, 141.4, 134.4, 129.0, 128.0, 126.7, 126.3, 117.7, 31.8, 23.4, 22.0, 21.0, 20.4, 20.0, 19.4. HRMS (EI+) for C_{17}H_{20} (M)^{+}: calculated: 224.1565, found: 224.1568.

Synthesis of 7-(1-phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane (1q)
To an oven-dried round-bottomed flask with a stir bar was added allyltriphenylphosphonium bromide (3.0 mmol, 1.5 equiv) and THF (20 mL). The solution was cooled to 0 °C and 1.2 mL (3.0 mmol, 1.5 equiv) of a 2.5 M solution of n-butyllithium in hexane was added dropwise. The solution was stirred for 30 minutes at 0 °C, bicyclo[4.1.0]heptan-7-yl(phenyl)methanone14 (2.0 mmol, 1.0 equiv) in 6 mL THF was added. The reaction was allowed to warm to room temperature, stirring for 24 hours. The reaction was then quenched with 10 mL brine and diluted with 50 mL of diethyl ether. The organic layer was separated and dried over Na2SO4, filtered, then concentrated in vacuo. The crude product was purified by flash chromatography to afford 56 mg (13%) 1q as a colorless oil.

A 1.3:1 mixture of (Z:E)-7-(1-phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane was obtained. The (Z):(E)-ratio was determined using 1H-NMR by integration of one of the olefinic protons: a doublet at 5.97 ppm for the (Z)-7-(1-phenylbuta-1,3-dienyl)bicyclo[4.1.0]heptane and a doublet at 6.39 ppm for the (E)-olefin.

IR (film): 2925, 2852, 1624, 1448, 1077, 1018 cm⁻¹. (Z)-isomer: 1H-NMR (400 MHz, CDCl₃): δ 7.40-7.18 (m, 5H), 6.30-6.21 (dt, J = 16.8 and 10.8 Hz, 1H), 5.99-5.96 (d, J = 10.8 Hz, 1H), 5.13-5.09 (dd, J = 16.8 and 2.0 Hz, 1H), 4.87-4.84 (dd, J = 10.8 and 2.0 Hz, 1H), 1.99-1.78 (m, 4H), 1.50-1.48 (t, J = 3.6 Hz, 1H), 1.34-1.15 (m, 6H), 1.13-1.10 (m, 2H). 13C-NMR (100 MHz, CDCl₃): δ 146.0, 140.5, 134.7, 128.9, 127.8, 126.8, 126.8, 123.7, 114.8, 31.4, 23.3, 21.4, 19.4. HRMS (EI+) for C17H20 (M)+: calculated: 224.1565, found: 224.1568.

Additional signals for the (E)-isomer: 1H-NMR (400 MHz, CDCl₃): δ 7.40-7.18 (m, 5H), 7.01-6.91 (dt, J = 16.8 and 10.8 Hz, 1H), 6.40-6.38 (d, J = 10.8 Hz, 1H), 5.30-5.25 (dd, J = 16.8 and 1.6 Hz, 1H), 5.21-5.18 (dd, J = 10.8 and 1.6 Hz, 1H), 1.99-1.67 (m, 5H), 1.34-1.15 (m, 6H), 0.93-0.91 (m, 2H). 13C-NMR (100 MHz, CDCl₃): δ 143.0, 142.1, 134.3, 129.9, 128.1, 126.7, 126.0, 117.4, 24.6, 23.4, 21.5, 19.8.
11. References


Usually, in the $^1$H NMR spectra, $^a$H is in the upfield compared with $^a$'H, and $^b$H is also in the upfield compared with $^b$'H.


12. $^1$H and $^{13}$C Spectra for all New Compounds
1a-Z
1a-E

ppm (H)

150 100 50 0
1b
2b
2h
$3h$
5a