Supporting Information

Gold(I)-Catalyzed Synthesis of Indenes and Cyclopentadienes: Access to (±)-Laurokamurene B and the Skeletons of the Cycloaurenones and Dysiherbols

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1. General Considerations

All gold-catalyzed reactions were performed using HPLC-grade solvents, without a protective inert atmosphere. Unless otherwise stated, the rest of the reactions reported herein were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolv™ Solvent Purification System (SPS, Innovative Technologies, Inc., MA). Yields refer to chromatographically and spectroscopically pure (1H NMR) homogeneous material, unless otherwise stated. Thin layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234) using short-wave UV light as visualizing agent and phosphomolybdic acid, KMnO4 or acidic vanillin followed by heat as developing agents. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 µm) as the stationary phase manually, or using a CombiFlash®Rf instrument with normal phase disposable columns of different sizes (Teledyne Isco). Preparative TLC was performed on 20 cm x 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech or 1.0 mm thick, catalogue number P02013 Analtech). NMR spectra were recorded at 23 ºC on a Bruker Avance 300, 400 Ultrasound or Bruker Avance 500 Ultrasound apparatus. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane, using the residual undeuterated solvent (CHCl3 at 7.28 ppm 1H NMR, 77.00 ppm 13C NMR) or tetramethylsilane as reference. Coupling constants are reported in hertz (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet, br = broad. Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI and APCI) or on a Autoflex Bruker Daltonics (MALDI and LDI). Melting points were determined using a MP70 Melting Point System (Mettler Toledo). Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Tropylium tetrafluoroborate was purchased from Fluorochem.

Handling of Gold(I) Catalysts

All gold complexes were synthesized according to our previously reported procedures1 or purchased from Sigma Aldrich, such as (acetonitrile)[(2-biphenyl)di-tert-butyl-phosphine]gold(I) hexafluoroantimonate (A) and (Acetonitrile)[2-di-tert-butyl(2’,4’,6’-triiso-propylbiphenyl)phosphine]gold(I) hexafluoroantimonate (B). The bottles were not stored under inert atmosphere.

1 (a) C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado, A. M. Echavarren, Angew. Chem. Int. Ed. 2005, 44, 6146-6148; (b) S. López, E. Herrero-Gómez, P. Pérez-Galán, C. Nieto-Oberhuber, A. M. Echavarren, Angew. Chem. Int. Ed. 2006, 45, 6029-6032; (c) C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, J. Org. Chem. 2008, 73, 7721-7730.
2. Preparation of 7-Aryl Cycloheptatrienes

7-Aryl-1,3,5-cycloheptatrienes (1) were prepared according to our previously reported literature procedures. Characterization data can be found below for all the new substrates.[2]

\[
\text{Br} 
\xrightarrow{1) n-BuLi, THF, -78 ^\circ\text{C}} 
\xrightarrow{2) tropylium tetrafluoroborate, 23 ^\circ\text{C}, 12 \text{~h}} 
\text{R}
\]

\(n\)-BuLi (2.5 M in hexanes, 1.2 equiv) was added dropwise to a solution of the corresponding aryl bromide (1.0 equiv) in dry THF (0.4 M) at \(-78 ^\circ\text{C}\) under argon. The mixture was stirred for 30 min at \(-78 ^\circ\text{C}\), and then tropylium tetrafluoroborate (1.3 equiv) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 ^\circ\text{C}) for 12 h. The reaction was quenched by the addition of water. The aqueous phase was extracted with diethyl ether, the combined organic extracts were dried over \(\text{MgSO}_4\), and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.

7-(2-Methoxyphenyl)cyclohepta-1,3,5-triene (1c)

This compound (yellow oil, 1.5 g, yield: 76%) was prepared according to the general procedure from 1-bromo-2-methoxybenzene (1.87 g, 10 mmol), \(n\)-BuLi (2.5 M, 4.8 mL, 12 mmol) and tropylium tetrafluoroborate (2.3 g, 13 mmol).

\[^1\text{H} \text{NMR} \text{(400 MHz, CDCl}_3\) \delta 7.39-7.34 \text{~(m, 1H), 7.33-7.27 \text{~(m, 1H), 7.06-6.99 \text{~(m, 1H), 6.98-6.94 \text{~(m, 1H), 6.79-6.69 \text{~(m, 2H), 6.30-6.23 \text{~(m, 2H), 5.48-5.41 \text{~(m, 2H), 3.83 \text{~(d, J = 2.0 Hz, 3H), 3.19-3.12 \text{~(m, 1H).}}}}}}}

\[^{13}\text{C} \text{NMR} \text{(101 MHz, CDCl}_3\) \delta 157.36, 131.80, 130.78, 128.92, 127.79, 127.18, 124.14, 120.76, 110.93, 55.40, 40.49.

HRMS-APCI: calculated for \(\text{C}_{14}\text{H}_{15}\text{O}[\text{M+H}]^+: 199.1117; \text{found: 199.1114.}

Unless otherwise noted, all of the 7-aryl cycloheptatrienes were described already: (a) C. R. Solorio- Alvarado, Y. Wang, A. M. Echavarren, J. Am. Chem. Soc. 2011, 133, 11952- 11955; (b) Y. Wang, P. R. McGonigal, B. Herlé, M. Besora, A. M. Echavarren, J. Am. Chem. Soc. 2014, 136, 801-809; (c) Y. Wang, M. E. Muratore, Z. Rong, A. M. Echavarren, Angew. Chem. Int. Ed. 2014, 53, 14022-14026.
7-(2,5-Dimethoxyphenyl)cyclohepta-1,3,5-triene (1f)

This compound (yellow oil, 2.0 g, yield: 88%) was prepared according to the general procedure from 2-bromo-1,4-dimethoxybenzene (2.2 g, 10 mmol), n-BuLi (2.5 M, 4.8 mL, 12 mmol) and tropylium tetrafluoroborate (2.3 g, 13 mmol).

^1H NMR (400 MHz, CDCl₃) δ 6.96 (d, J = 3.0 Hz, 1H), 6.89 (d, J = 8.9 Hz, 1H), 6.82 (dd, J = 8.9, 3.0 Hz, 1H), 6.74 (dd, J = 3.7, 2.7 Hz, 2H), 6.28-6.24 (m, 2H), 5.52-5.34 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 3.15-3.12 (m, 1H).

^13C NMR (101 MHz, CDCl₃) δ 153.73, 151.63, 133.09, 130.79, 126.94, 124.27, 115.26, 112.10, 111.83, 56.15, 55.73, 40.42.

HRMS-APCI: calculated for C₁₅H₁₆O₂ [M+H]^+: 229.1223; found: 229.1219.

7-(4-(tert-Butyl)phenyl)cyclohepta-1,3,5-triene (1j)

This compound (colorless oil, 1.8 g, yield: 80%) was prepared according to the general procedure from 1-bromo-4-(tert-butyl)benzene (2.1 g, 10 mmol), n-BuLi (2.5 M, 4.8 mL, 12 mmol) and tropylium tetrafluoroborate (2.3 g, 13 mmol).

^1H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 0.8 Hz, 2H), 6.77-6.73 (m, 2H), 6.29-6.23 (m, 2H), 5.48-5.39 (m, 2H), 2.72-2.66 (m, 1H), 1.35 (s, 9H).

^13C NMR (101 MHz, CDCl₃) δ 149.43, 140.83, 130.90, 127.19, 126.40, 125.57, 124.28, 44.83, 34.45, 31.41.

HRMS-APCI: calculated for C₁₇H₂₁ [M+H]^+: 225.1638; found: 225.1635.

3. Preparation of 7-Styryl Cycloheptatrienes

(E)-7-Styrylcyclohepta-1,3,5-triene (2a) and (E)-7-(4-Methylstyryl)cyclohepta-1,3,5-triene (2b) were prepared by reaction of the corresponding potassium organotrifluoroborate with tropylium tetrafluoroborate according to published literature procedures and characterization data matched the previously reported ones (for a representative procedure check 2b). (E)-7-(4-(trifluoromethyl)styryl)cyclohepta-1,3,5-
triene (2c), (E)-7-(4-methoxystyril)cyclohepta-1,3,5-triene (2d) and (E)-7-(4-Bromostyril)cyclohepta-1,3,5-triene (2e) were prepared by olefination of the corresponding aldehyde with a Julia-Kocienski reagent according to published literature procedures and characterization data matched the previously reported ones.

We have previously reported the synthesis of the styryl-cycloheptatrienes shown below.\(^3\)

\[
\begin{align*}
\text{(E)-7-(2-Fluorostyril)cyclohepta-1,3,5-triene (2f)} & \quad \text{and (E)-2-(2-(cyclohepta-2,4,6-trien-1-yl)vinyl)-naphthalene (2g)}
\end{align*}
\]

This compound (68 mg, 84%, 17:1 E/Z ratio) was obtained as a colorless oil from 2-fluorobenzaldehyde (95 mg, 0.763 mmol, 2.0 equiv) and 5-((cyclohepta-2,4,6-trien-1-yl)met-hyl)sulfonyl)-1-phenyl-1H-tetrazole (120 mg, 0.382 mmol, 1.0 equiv).

\(^1\)H NMR (400 MHz, CDCl$_3$) \(\delta \) 7.53 (td, \(J = 7.7, 1.7 \text{ Hz, 1H} \)), 7.27-7.21 (m, 1H), 7.15 (td, \(J = 7.6, 1.3 \text{ Hz, 1H} \)), 7.08 (ddd, \(J = 10.8, 8.1, 1.3 \text{ Hz, 1H} \)), 6.78-6.73 (m, 3H), 6.68-6.61 (m, 1H), 6.32-6.28 (m, 2H), 5.40 (dd, \(J = 10.0, 5.8 \text{ Hz, 2H} \)), 2.54 (q, \(J = 6.2 \text{ Hz, 1H} \)) ppm.

\(^{13}\)C NMR (101 MHz, CDCl$_3$) \(\delta \) 160.2 (d, \(J_{C,F} = 248 \text{ Hz} \)), 133.5 (d, \(J_{C,F} = 4.6 \text{ Hz} \)), 131.1, 128.5 (d, \(J_{C,F} = 8.3 \text{ Hz} \)), 127.2 (d, \(J_{C,F} = 3.8 \text{ Hz} \)), 124.7, 124.1, 124.0, 123.0 (d, \(J_{C,F} = 3.7 \text{ Hz} \)), 115.8, 115.6, 42.4 ppm.

\(^{19}\)F NMR (376 MHz, CDCl$_3$) \(\delta \) -118.39 ppm.

HRMS (APCI Positive): calculated for C$_{15}$H$_{14}$F [M+H]$^+$: 213.1074; found: 213.1072.

\((E)-2-(2-(\text{Cyclohepta-2,4,6-trien-1-yl)vinyl})\text{naphthalene (2g)}\)

\[^3\] For 7-styryl-1,3,5-cycloheptatrienes using the Julia-Kocienski olefination and from potassium styryl trifluoroborates: B. Herlé, P. M. Holstein, A. M. Echavarren, ACS Catal. 2017, 7, 3668-3675.
This compound (62 mg, 80%, >20:1 E/Z ratio) was obtained as a white solid from 2-naphthaldehyde (99 mg, 0.636 mmol, 2.0 equiv) and 5-((cyclohepta-2,4,6-trien-1-ylmethyl)sulfonyl)-1-phenyl-1H-tetrazole (100 mg, 0.318 mmol, 1.0 equiv).

\[ ^1H \text{NMR} \quad (500 \text{ MHz, CDCl}_3) \delta \quad \text{7.85-7.82 (m, 3H), 7.76 (br, 1H), 7.67 (dd, } J = 8.7, 1.7 \text{ Hz, 1H), 7.48 ( quintuplet of doublets, } J = 7.6, 1.6 \text{ Hz, 2H), 6.78-6.72 (m, 3H), 6.71-6.66 (m, 1H), 6.32-6.28 (m, 2H), 5.43 (dd, } J = 9.2, 5.8 \text{ Hz, 2H), 2.55 (q, } J = 6.0 \text{ Hz, 1H) ppm.} \]

\[ ^{13}C \text{NMR} \quad (126 \text{ MHz, CDCl}_3) \delta \quad \text{134.8, 133.6, 132.8, 131.4, 131.1, 130.6, 128.1, 127.9, 127.6, 126.2, 125.9, 125.7, 124.6, 124.3, 123.5, 77.2, 42.2 \text{ ppm.} \]

HRMS (APCI Positive): calculated for C_{19}H_{17}[M+H]^+: 245.1325; found: 245.1323.

M.p.: 69-71 ºC.

\( (E)-7-(4\text{-Methylstyrly})\text{cyclohepta-1,3,5-triene (2b) } \)

A 100 mL round-bottomed flask with a magnetic stirring bar was charged with potassium \( (E)\)-stryryltrifluoroborate (2.0 g, 8.93 mmol, 1.0 equiv) and it was dissolved in 35 mL of DMF. The solution was cooled down to 0 ºC and then tropylium tetrafluoroborate (1.67 g, 9.37 mmol, 1.05 equiv) was added in one portion. The resulting yellow mixture was allowed to warm slowly to room temperature and further stirred for 5 h, then it was quenched by the addition of water and Et\(_2\)O and the aqueous phase was extracted three times with Et\(_2\)O. Combined organic fractions were washed with water three times, once with brine, and dried over anhydrous MgSO\(_4\). After removal of the solvent, the product was purified by flash column chromatography in SiO\(_2\) (eluents cyclohexane or pentane) to give \( (E)-7-(4\text{-methylstyrly})\text{cyclohepta-1,3,5-triene (1.76 g, 8.45 mmol, 95 % yield) as a pale yellow oil that solidifies upon cooling in the fridge.} \)

\[ ^1H \text{NMR} \quad (500 \text{ MHz, CDCl}_3) \delta \quad \text{7.33-7.26 (m, 2H), 7.16-7.12 (m, 2H), 6.71 (br, 2 H), 6.54-6.46 (m, 2H), 6.34 (d, } J = 7.6 \text{ Hz, 2H), 5.35 (quint, } J = 4.7 \text{ Hz, 2H), 2.43 (quint, } J = 4.7 \text{ Hz, 1H), 2.36 (s, 3H) ppm.} \]

\[ ^{13}C \text{NMR} \quad (126 \text{ MHz, CDCl}_3) \delta \quad \text{137.0, 134.6, 131.0, 130.4, 130.0, 129.2, 126.1, 124.6, 124.5, 42.1, 21.2 \text{ ppm.} \]
HRMS (APCI Positive): calculated for C_{16}H_{17} [M+H]^+: 209.1325; found: 209.1323.

4. Procedure for the Preparation of Allenes

Allenes 5a\textsuperscript{[4a]}, 5c\textsuperscript{[4b]}, 5f\textsuperscript{[4c]} were known compounds and the obtained spectral data were in agreement with literature values. 5b, 5d, 5h were purchased from Aldrich. 5e, 5g were prepared according to the same literature procedure\textsuperscript{[4a]}

\[
\begin{align*}
\text{Ph} & \quad \text{5a} & \quad \text{5b} & \quad \text{5c} & \quad \text{5d} \\
\text{5e} & \quad \text{5f} & \quad \text{5g} & \quad \text{5h}
\end{align*}
\]

Ethynylmagnesium bromide (0.5 M in THF, 1.1 equiv) was added dropwise to a solution of the corresponding ketone (1.0 equiv) in dry THF (0.2 M) at 0 °C under argon. The mixture was stirred for 2 h at 0 °C, the disappearance of the ketone was confirmed by TLC and then methyl chloroformate (1.3 equiv) was added. The cooling bath was removed and the reaction was stirred at room temperature (23 °C) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ethyl acetate, the combined organic extracts were dried over MgSO\textsubscript{4}, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with a mixture of cyclohexane and ethyl acetate as eluent unless otherwise stated, to give the corresponding carbonate.

\[n\text{Bu}_3P\text{ (0.2 equiv)}\text{ was added dropwise to a stirred mixture of carbonate (1.0 equiv), ammonium formate (2.0 equiv) and Pd(dba)_2 (0.05 equiv) in THF (0.2 M) at 0 °C. After 12 h, the disappearance of carbonate was confirmed by TLC and the reaction mixture was filtered through a short pad of Celite. The solvent was evaporated and the residue.}\]

\textsuperscript{4} (a) J. Takaya, N. Iwasawa, J. Am. Chem. Soc. 2008, 130, 15254-15255; (b) Y. Tani, T. Fujihara, J. Terao, Y. Tsuji, J. Am. Chem. Soc. 2014, 136, 17706-17709; (c) M. Aoki, S. Izumi, M. Kaneko, K. Ukai, J. Takaya, N. Iwasawa, Org. Lett. 2007, 9, 1251-1253.
was purified by column chromatography on silica gel with pentane as eluent.

1-Ethynyl-3,3-dimethylcyclohexyl methyl carbonate

\[
\begin{align*}
\text{O} & \quad \text{1) MgBr} \quad \text{THF, 0 °C} \\
\text{1,1-Dimethyl-3-(1\lambda^5-vinylidene)cyclohexane (5e)} \\
\text{OCOOMe} & \quad \text{Pd(dba)}_2 \quad \text{HCOONH}_4 \\
\quad & \quad \text{THF, 0 - 23 °C} \\
\end{align*}
\]

This compound (colorless oil, 1.8 g, yield: 54%) was prepared according to the general procedure from cyclodecanone (2.0 g, 15.9 mmol), ethynylmagnesium bromide (0.5 M in THF, 35 ml, 17.4 mmol) and methyl chloroformate (1.9 g, 1.6 ml, 20.6 mmol).

\[^1\text{H NMR}\ (400 \text{ MHz, CDCl}_3) \delta 3.78 (s, 3\text{H}), 2.60 (s, 1\text{H}), 2.13-1.83 (m, 4\text{H}), 1.78-1.57 (m, 2\text{H}), 1.39-1.23 (m, 2\text{H}), 1.03 (s, 3\text{H}), 0.97 (s, 3\text{H}).\]

\[^{13}\text{C NMR}\ (101 \text{ MHz, CDCl}_3) \delta 153.50, 84.43, 76.66, 73.57, 54.32, 46.95, 38.34, 37.53, 31.08, 30.43, 29.00, 18.59.\]

\text{HRMS-ESI: calculated for C}_{12}\text{H}_{18}\text{NaO}_3 [\text{M+Na}^+]^+: 233.1148; \text{found: 233.1155.}\]

1,1-Dimethyl-3-(1λ^5-vinylidene)cyclohexane (5e)

\[
\begin{align*}
\text{OCOOMe} & \quad \text{Pd(dba)}_2 \quad \text{HCOONH}_4 \\
\quad & \quad \text{THF, 0 - 23 °C} \\
\end{align*}
\]

This compound (colorless oil, 800 mg, yield: 82%) was prepared according to the general procedure from 1-ethynyl-3,3-dimethylcyclohexyl methyl carbonate (2.0 g, 9.5 mmol), \(n\)-Bu\(_3\)P (385 mg, 0.46 ml, 1.9 mmol) and ammonium formate (1.2 g, 19 mmol) and Pd(dba)\(_2\) (273 mg, 0.48 mol).

\[^1\text{H NMR}\ (500 \text{ MHz, CDCl}_3) \delta 4.61-4.51 (m, 2\text{H}), 2.13-2.04 (m, 2\text{H}), 1.95-1.88 (m, 2\text{H}), 1.66-1.58 (m, 2\text{H}), 1.36-1.29 (m, 2\text{H}), 0.95 (s, 6\text{H}).\]

\[^{13}\text{C NMR}\ (101 \text{ MHz, CDCl}_3) \delta 204.47, 99.13, 72.15, 44.23, 38.94, 31.90, 30.63, 28.34, 22.76.\]

\text{HRMS-APCI: calculated for C}_{10}\text{H}_{17} [\text{M+H}]^+: 137.1325; \text{found: 137.1323.}\]

1-Ethynylcyclohexyl methyl carbonate

\[
\begin{align*}
\text{O} & \quad \text{1) MgBr} \quad \text{THF, 0 °C} \\
\text{1-Ethynylcyclohexyl methyl carbonate} \\
\text{OCOOMe} & \quad \text{THF, 0 - 23 °C} \\
\end{align*}
\]

This compound (white solid, 1.7 g, yield: 71%) was prepared according to the general procedure from cyclodecanone (1.54 g, 10 mmol), ethynylmagnesium bromide (0.5 M
in THF, 22 ml, 11 mmol) and methyl chloroformate (1.23 g, 1.0 ml, 13 mmol).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.78 (s, 3H), 2.62 (s, 1H), 2.32 (dt, $J$ = 14.6, 7.0 Hz, 2H), 2.08 (dt, $J$ = 14.9, 6.5 Hz, 2H), 1.78 – 1.45 (m, 14H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.36, 83.52, 81.01, 74.18, 54.32, 26.17, 25.53, 23.54, 20.87.

HRMS-ESI: calculated for C$_{14}$H$_{22}$NaO$_3$[M+Na]$^+$: 261.1461; found: 261.1452.

M.p.: 59-61 °C.

Vinylidene cyclodecane (5g)

This compound (brown oil, 980 mg, yield: 84%) was prepared according to the general procedure from 1-ethynylecyclodecyl methyl carbonate (1.7 g, 7.1 mmol), n-Bu$_3$P (290 mg, 0.35 ml, 1.4 mmol) and ammonium formate (900 mg, 14 mmol) and Pd(dba)$_2$ (205 mg, 0.36 mol).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.65-4.59 (m, 2H), 2.20-2.05 (m, 4H), 1.69-1.36 (m, 14H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 207.31, 101.89, 74.37, 30.69, 25.62, 24.61, 24.48, 24.38.

HRMS-APCI: calculated for C$_{12}$H$_{19}$[M-H]$^-$: 163.1481; found: 163.1477.

5. General Procedure A for the Gold(I)-Catalyzed Synthesis of Indenes

A solution of the 7-aryl-1,3,5-cycloheptatriene 1 (0.2 mmol), allene 5 (0.4 mmol, 2.0 equiv) and gold complex A (7.7 mg, 0.01 mmol, 5 mol%) in 1,2-dichloroethane (DCE, 2 mL, 0.1 M) was stirred at 120 °C in a sealed tube (in a heating block, covering the vial completely) until the starting material had been fully consumed (8 h). After that time, the reaction mixture was allowed to cool down to room temperature, the solvent was removed in vacuum and the crude residue was purified by column chromatography on silica gel. The reaction was performed under an air atmosphere with no special precautions taken to exclude water or oxygen.

Characterization Data for the Different Indenes
2,3-Dimethyl-3-phenethyl-3H-cyclopenta[a]naphthalene (6a)

The title compound (light yellow oil, 39.5 mg, yield: 66%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3] \delta 8.16 (d, J = 8.2 \text{ Hz}, 1H), 7.97 (d, J = 8.3 \text{ Hz}, 1H), 7.78 (d, J = 8.2 \text{ Hz}, 1H), 7.61-7.55 (m, 2H), 7.55-7.49 (m, 1H), 7.31 – 7.24 (m, 2H), 7.14-7.05 (m, 3H), 2.33 (td, J = 12.8, 4.6 Hz, 1H), 2.21-2.03 (m, 5H), 1.84 (td, J = 13.3, 5.1 Hz, 1H), 1.38 (s, 3H).

\[^{13}C \text{ NMR (75 MHz, CDCl}_3] \delta 153.37, 148.44, 142.73, 139.73, 133.10, 128.48, 128.25, 128.22, 127.38, 125.61, 125.42, 124.89, 124.39, 124.08, 123.14, 120.16, 54.96, 38.94, 30.34, 23.61, 13.06.

HRMS-APCI: calculated for C\text{23}H\text{23} [M+H]\(^+\): 299.1794; found: 299.1795.

1,2-Dimethyl-1-phenethyl-1H-indene (6b)

The title compound (colorless oil, 33.4 mg, yield: 67%) was synthesized according to the General Procedure A from 7-phenylcyclohepta-1,3,5-triene (34 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3] \delta 7.36-7.12 (m, 7H), 7.07-7.02 (m, 2H), 6.49 (d, J = 1.6 \text{ Hz}, 1H), 2.23-2.12 (m, 1H), 2.09-1.96 (m, 5H), 1.89-1.78 (m, 1H), 1.27 (s, 3H).

\[^{13}C \text{ NMR (101 MHz, CDCl}_3] \delta 152.62, 151.36, 143.87, 142.75, 128.20, 128.18, 126.50, 125.77, 125.55, 124.04, 121.25, 119.98, 53.92, 39.31, 30.34, 23.93, 12.69.

HRMS-APCI: calculated for C\text{19}H\text{21} [M+H]\(^+\): 249.1638; found: 249.1641.

4-Methoxy-1,2-dimethyl-1-phenethyl-1H-indene (6c)
The title compound (colorless oil, 30 mg, yield: 54%) was synthesized according to the General Procedure A from 7-(2-methoxyphenyl)cyclohepta-1,3,5-triene (40 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.22 (m, 2H), 7.21-7.13 (m, 2H), 7.08-7.04 (m, 2H), 6.99 (dt, \(J = 7.4, 0.5\) Hz, 1H), 6.81 (d, \(J = 8.0\) Hz, 1H), 6.65 (d, \(J = 1.6\) Hz, 1H), 3.93 (s, 3H), 2.20-2.11 (m, 1H), 2.08-1.97 (m, 5H), 1.90-1.81 (m, 1H), 1.27 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 153.51, 152.27, 150.95, 142.84, 131.92, 128.20, 125.39, 121.70, 114.40, 108.84, 55.39, 54.47, 39.32, 30.35, 23.99, 12.74.

HRMS-APCI: calculated for C\(_{20}\)H\(_{23}\)O\([M+H]^+\): 279.1743; found: 279.1752.

1,2-Dimethyl-1-phenethyl-4-phenoxy-1\(H\)-indene (6d)

The title compound (yellow oil, 28 mg, yield: 41%) was synthesized according to the General Procedure A from 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene (52 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.33 (m, 2H), 7.32-7.25 (m, 2H), 7.24-7.15 (m, 3H), 7.14-7.07 (m, 3H), 7.07-7.02 (m, 2H), 6.93 (dd, \(J = 7.2, 1.7\) Hz, 1H), 6.48 (d, \(J = 1.7\) Hz, 1H), 2.27-2.17 (m, 1H), 2.14-2.02 (m, 2H), 1.99 (d, \(J = 1.6\) Hz, 3H), 1.92 (td, \(J = 14.3, 4.5\) Hz, 1H), 1.33 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 158.38, 154.26, 152.37, 148.27, 142.66, 135.23, 129.64, 128.29, 128.25, 125.68, 125.55, 122.31, 121.87, 118.04, 117.42, 117.39, 54.57, 39.46, 30.37, 23.97, 12.80.

HRMS-APCI: calculated for C\(_{25}\)H\(_{25}\)O\([M+H]^+\): 341.1900; found: 341.1902.

6-Methoxy-1,2-dimethyl-1-phenethyl-1\(H\)-indene (6e)

The title compound (colorless oil, 38 mg, yield: 68%) was synthesized according to the General Procedure A from 7-(4-methoxyphenyl)cyclohepta-1,3,5-triene (40 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32-7.21 (m, 2H), 7.19-7.13 (m, 2H), 7.06 (d, $J = 7.1$ Hz, 2H), 6.92 (d, $J = 2.4$ Hz, 1H), 6.80 (dd, $J = 8.2$, 2.4 Hz, 1H), 6.42 (d, $J = 1.8$ Hz, 1H), 3.87 (s, 3H), 2.18-2.00 (m, 3H), 1.97 (d, $J = 1.6$ Hz, 3H), 1.92-1.80 (m, 1H), 1.26 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.83, 153.61, 150.69, 143.10, 137.27, 128.54, 128.43, 125.88, 125.46, 120.44, 111.42, 109.03, 55.91, 54.32, 39.79, 30.70, 24.56, 12.98.

HRMS-APCI: calculated for C$_{20}$H$_{23}$O [M+H]$^+$: 279.1743; found: 279.1749.

4,7-Dimethoxy-1,2-dimethyl-1-phenethyl-1H-indene (6f)

The title compound (colorless oil, 33 mg, yield: 53%) was synthesized according to the General Procedure A from 7-(2,5-dimethoxyphenyl)cyclohepta-1,3,5-triene (46 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26-7.21 (m, 2H), 7.18-7.11 (m, 1H), 7.07-7.03 (m, 2H), 6.74 (d, $J = 8.7$ Hz, 1H), 6.63 (d, $J = 8.7$ Hz, 1H), 6.58 (d, $J = 1.6$ Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.70-2.62 (m, 1H), 2.03-1.95 (m, 4H), 1.92-1.83 (m, 2H), 1.35 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.31, 150.39, 146.89, 143.22, 138.70, 133.58, 128.26, 128.08, 125.35, 121.43, 109.78, 107.26, 56.02, 55.56, 55.55, 36.36, 30.73, 21.54, 12.45.

HRMS-APCI: calculated for C$_{21}$H$_{25}$O$_2$ [M+H]$^+$: 309.1849; found: 309.1851.

6-Chloro-1,2-dimethyl-1-phenethyl-1H-indene (6g)

The title compound (colorless oil, 31 mg, yield: 55%) was synthesized according to the General Procedure A from 7-(4-chlorophenyl)cyclohepta-1,3,5-triene (41 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).
**1H NMR** (400 MHz, CDCl$_3$) δ 7.29-7.21 (m, 4H), 7.18 (d, $J = 7.8$ Hz, 2H), 7.07-7.04 (m, 2H), 6.44 (d, $J = 1.6$ Hz, 1H), 2.18-2.10 (m, 1H), 2.08-1.97 (m, 5H), 1.89-1.81 (m, 1H), 1.26 (s, 3H).

**13C NMR** (126 MHz, CDCl$_3$) δ 153.25, 142.33, 142.29, 130.09, 128.74, 128.26, 126.67, 125.70, 125.09, 121.89, 120.75, 54.30, 39.08, 30.26, 23.81, 12.71.

**HRMS-APCI**: calculated for C$_{19}$H$_{20}$Cl [M+H]$^+$: 283.1248; found: 283.1248.

1,2-Dimethyl-1-phenethyl-4-phenyl-1H-indene (6h)

The title compound (colorless oil, 33.3 mg, yield: 51%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (49 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.60-7.55 (m, 2H), 7.53-7.46 (m, 2H), 7.42-7.36 (m, 1H), 7.34-7.22 (m, 5H), 7.20-7.13 (m, 1H), 7.09-7.04 (m, 2H), 6.68 (d, $J = 1.6$ Hz, 1H), 2.27-2.16 (m, 1H), 2.13-1.98 (m, 5H), 1.96-1.86 (m, 1H), 1.32 (s, 3H).

**13C NMR** (101 MHz, CDCl$_3$) δ 153.12, 152.09, 142.74, 141.41, 141.08, 134.16, 128.97, 128.38, 128.23, 127.05, 126.76, 125.60, 124.82, 124.47, 120.30, 54.12, 39.45, 30.43, 24.09, 12.82.

**HRMS-APCI**: calculated for C$_{25}$H$_{25}$ [M+H]$^+$: 325.1951; found: 325.1947.

1,2-Dimethyl-1,4-diphenethyl-1H-indene (6i)

The title compound (colorless oil, 42 mg, yield: 59%) was synthesized according to the General Procedure A from 7-(2-phenethylphenyl)cyclohepta-1,3,5-triene (54 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

**1H NMR** (400 MHz, CDCl$_3$) δ 7.35-7.03 (m, 13H), 6.53 (d, $J = 1.6$ Hz, 1H), 3.10-2.95 (m, 2H), 2.22-2.09 (m, 1H), 2.07-1.95 (m, 5H), 1.90-1.75 (m, 1H), 1.27 (s, 3H).

**13C NMR** (101 MHz, CDCl$_3$) δ 152.16, 151.49, 142.85, 142.23, 142.05, 133.07, 128.52, 128.31, 128.22, 126.79, 125.84, 125.55, 124.27, 123.68, 119.15, 54.04, 39.43, 37.70, 35.24, 30.42, 24.05, 12.79.
HRMS-APCI: calculated for C_{27}H_{29}[M+H]^+: 353.2264; found: 353.2262.

6-(tert-Butyl)-1,2-dimethyl-1-phenethyl-1H-indene (6j)

The title compound (colorless oil, 35 mg, yield: 58%) was synthesized according to the General Procedure A from 7-(4-(tert-butyl)phenyl)cyclohepta-1,3,5-triene (45 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.35 (m, 1H), 7.31-7.13 (m, 5H), 7.06-7.01 (m, 2H), 6.46 (d, $J = 1.5$ Hz, 1H), 2.20-2.11 (m, 1H), 2.11-2.01 (m, 2H), 2.00 (d, $J = 1.6$ Hz, 3H), 1.87-1.77 (m, 1H), 1.41 (s, 9H), 1.28 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.96, 151.21, 147.20, 142.97, 141.28, 128.24, 128.21, 128.18, 125.52, 125.40, 123.27, 119.21, 118.41, 77.35, 77.03, 76.71, 53.91, 39.52, 34.73, 31.80, 30.45, 24.01, 12.72.

HRMS-APCI: calculated for C$_{23}$H$_{29}$[M+H]^+: 305.2268; found: 305.2266.

2,3,3-Trimethyl-3H-cyclopenta[a]naphthalene (6k)

The title compound (colorless oil, 30 mg, yield: 72%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 3-methylbuta-1,2-diene (27 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.56-7.42 (m, 3H), 6.96 (d, $J = 1.7$ Hz, 1H), 2.11 (d, $J = 1.6$ Hz, 3H), 1.32 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.85, 150.73, 138.47, 132.98, 128.41, 127.42, 125.31, 124.76, 124.12, 124.06, 121.08, 120.18, 51.03, 23.40, 12.81.

HRMS-APCI: calculated for C$_{16}$H$_{17}$[M+H]^+: 209.1325; found: 209.1329.

3-Cyclohexyl-2,3-dimethyl-3H-cyclopenta[a]naphthalene (6l)
The title compound (colorless oil, 27 mg, yield: 49%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and buta-2,3-dien-2-ylcyclohexane (55 mg, 0.4 mmol).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, $J = 8.3$ Hz, 1H), 7.87 (d, $J = 8.3$ Hz, 1H), 7.63 (d, $J = 8.3$ Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H), 7.48 (ddd, $J = 8.2$, 6.8, 1.4 Hz, 1H), 7.43 (ddd, $J = 8.1$, 6.8, 1.3 Hz, 1H), 6.97 (d, $J = 1.7$ Hz, 1H), 2.05 (d, $J = 1.5$ Hz, 3H), 2.01-1.94 (m, 1H), 1.85-1.77 (m, 1H), 1.71 (tt, $J = 12.0$, 3.0 Hz, 1H), 1.64-1.54 (m, 2H), 1.44-1.33 (m, 2H), 1.30 (s, 3H), 1.27-1.19 (m, 1H), 1.15 (tt, $J = 13.0$, 3.6 Hz, 1H), 1.02 (tt, $J = 12.8$, 3.7 Hz, 1H), 0.48 (ddd, $J = 25.3$, 13.1, 3.7 Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 155.09, 148.40, 139.96, 132.77, 128.27, 127.17, 125.14, 124.70, 124.04, 123.34, 122.74, 121.80, 57.91, 44.14, 28.31, 27.40, 27.10, 26.95, 26.55, 20.79, 13.95.

HRMS-APCI: calculated for C$_{21}$H$_{25}$[M+H]$^+$: 277.1951; found: 277.1957.

$^2'$-Methyldispiro[cyclohexane-1,3'-cyclopenta[a]naphthalene] (6m)

The title compound (white solid, 36 mg, yield: 72%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylideneccyclohexane (43 mg, 0.4 mmol).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.09 (d, $J = 8.5$ Hz, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.91-7.85 (m, 1H), 7.63 (d, $J = 8.4$ Hz, 1H), 7.49 (ddd, $J = 8.3$, 6.8, 1.4 Hz, 1H), 7.44 (ddd, $J = 8.1$, 6.8, 1.3 Hz, 1H), 7.00 (d, $J = 1.8$ Hz, 1H), 2.18-2.06 (m, 5H), 2.05-1.97 (m, 1H), 1.90-1.77 (m, 4H), 1.58-1.46 (m, 1H), 1.35-1.28 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 156.08, 150.07, 139.24, 132.56, 128.11, 127.28, 125.14, 124.82, 124.09, 123.23, 122.81, 121.96, 54.63, 31.79, 25.64, 22.60, 13.92.

HRMS-APCI: calculated for C$_{19}$H$_{21}$[M+H]$^+$: 249.1638; found: 249.1638.

M.p.: 45-47 °C.

$^{2',3,3'}$-Trimethyldispiro[cyclohexane-1,3'-cyclopenta[a]naphthalene] (6n)
The title compound (colorless oil, 34 mg, yield: 62%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 1,1-dimethyl-3-vinylidenecyclohexane (55 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.07-7.98 (m, 2H), 7.86-7.82 (m, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.49-7.38 (m, 2H), 6.98-6.94 (m, 1H), 2.22-2.06 (m, 4H), 1.88-1.78 (m, 1H), 1.74-1.63 (m, 3H), 1.48-1.33 (m, 2H), 1.20 (s, 3H), 1.11 (dt, $J = 14.3$, 1.7 Hz, 1H), 1.04 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 156.60, 150.94, 139.50, 132.43, 127.94, 127.17, 125.11, 124.86, 124.10, 123.36, 122.75, 122.23, 55.62, 43.64, 38.91, 35.42, 30.52, 30.43, 28.73, 20.20, 14.05.

HRMS-APCI: calculated for C$_{21}$H$_{25}$[M+H]$^+$: 277.1951; found: 277.1960.

2'-Methylspiro[cycloheptane-1,3'-cyclopenta[a]naphthalene] (6o)

The title compound (colorless oil, 33 mg, yield: 63%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidenecycloheptane (49 mg, 0.4 mmol).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.47 (ddd, $J = 8.2$, 6.8, 1.4 Hz, 1H), 7.42 (ddd, $J = 8.1$, 6.8, 1.3 Hz, 1H), 6.85 (d, $J = 1.7$ Hz, 1H), 2.18 (d, $J = 1.5$ Hz, 3H), 2.03-1.90 (m, 2H), 1.89-1.64 (m, 10H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.62, 152.42, 138.34, 132.72, 128.20, 127.26, 125.22, 124.72, 124.07, 123.74, 121.29, 121.10, 57.44, 35.53, 32.32, 25.47, 14.66.

HRMS-APCI: calculated for C$_{20}$H$_{23}$[M+H]$^+$: 263.1794; found: 263.1805.

2'-Methylspiro[cyclodecane-1,3'-cyclopenta[a]naphthalene] (6p)
The title compound (colorless oil, 32 mg, yield: 52%) was synthesized according to the General Procedure A from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidendecyclodecane (66 mg, 0.4 mmol).

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 8.03 (d, J = 8.2 \text{ Hz, 1H}), 7.85 (d, J = 8.2 \text{ Hz, 1H}), 7.63-7.53 (m, 2H), 7.48-7.37 (m, 2H), 6.89 (d, J = 1.6 \text{ Hz, 1H}), 2.16 (d, J = 1.5 \text{ Hz, 3H}), 2.09-1.94 (m, 2H), 1.92-1.58 (m, 16H). \]

\[ \text{C NMR (126 MHz, CDCl}_3 \text{)} \delta 157.33, 150.34, 138.45, 132.69, 128.19, 127.27, 125.14, 124.72, 124.04, 123.26, 121.86, 121.74, 57.91, 29.35, 28.66, 28.13, 23.78, 22.94, 15.86. \]

HRMS-APCI: calculated for C\textsubscript{23}H\textsubscript{29}[M+H]^+: 305.2264; found: 305.2268.

1,1,2-Trimethyl-1H-cyclopenta[a]naphthalene (6q)

The title compound (white solid, 17 mg, yield: 41%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 3-methylbuta-1,2-diene (27 mg, 0.4 mmol).

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 8.15 (d, J = 8.6 \text{ Hz, 1H}), 7.94 (d, J = 8.2 \text{ Hz, 1H}), 7.79 (d, J = 8.2 \text{ Hz, 1H}), 7.57-7.51 (m, 2H), 7.42 (ddd, J = 8.1, 6.8, 1.2 \text{ Hz, 1H}), 6.52 (d, J = 1.6 \text{ Hz, 1H}), 2.11 (d, J = 1.6 \text{ Hz, 3H}), 1.49 (s, 6H). \]

\[ \text{C NMR (101 MHz, CDCl}_3 \text{)} \delta 157.02, 146.88, 140.21, 131.93, 129.58, 128.97, 127.63, 125.58, 123.96, 123.44, 122.81, 120.18, 51.80, 23.51, 12.40. \]

HRMS-APCI: calculated for C\textsubscript{16}H\textsubscript{17}[M+H]^+: 209.1325; found: 209.1333.

M.p.: 73-75 °C.

1,2-Dimethyl-1-phenethyl-1H-cyclopenta[a]naphthalene (6r)
The title compound (colorless oil, 41 mg, yield: 69%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 8.18 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.61-7.54 (m, 2H), 7.50-7.44 (m, 1H), 7.22 (tq, J = 7.1, 1.2 Hz, 2H), 7.17-7.11 (m, 1H), 6.98 (d, J = 7.0 Hz, 2H), 6.67 (s, 1H), 2.69 (td, J = 13.1, 5.2 Hz, 1H), 2.28-2.18 (m, 1H), 2.14 (s, 3H), 1.95 (td, J = 13.1, 4.5 Hz, 1H), 1.69 (td, J = 13.1, 4.8 Hz, 1H), 1.52 (s, 3H).

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 154.29, 144.49, 142.66, 141.51, 131.98, 129.68, 129.33, 128.23, 128.16, 127.87, 126.12, 125.89, 125.54, 123.63, 122.43, 120.14, 56.06, 39.37, 30.48, 24.00, 12.60.

HRMS-APCI: calculated for C\textsubscript{23}H\textsubscript{23} [M+H\textsuperscript{+}]: 299.1794; found: 299.1799.

1-Cyclohexyl-1,2-dimethyl-1H-cyclopenta[a]naphthalene (6s)

The title compound (colorless oil, 26 mg, yield: 47%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and buta-2,3-dien-2-ylcyclohexane (55 mg, 0.4 mmol).

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 8.16 (d, J = 9.1 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.52 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.40 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 6.55 (d, J = 1.7 Hz, 1H), 2.35-2.25 (m, 1H), 2.14 (d, J = 1.5 Hz, 3H), 1.91-1.83 (m, 1H), 1.67-1.44 (m, 6H), 1.37-1.24 (m, 2H), 1.14-0.78 (m, 4H).

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 155.21, 146.82, 141.33, 132.16, 129.67, 128.94, 127.61, 126.83, 125.25, 123.45, 123.22, 119.76, 59.24, 44.93, 27.85, 27.67, 26.95, 26.64, 20.46, 16.00.

HRMS-APCI: calculated for C\textsubscript{21}H\textsubscript{25} [M+H\textsuperscript{+}]: 277.1951; found: 277.1957.
2'-Methylspiro[cyclohexane-1,1'-cyclopenta[a]naphthalene] (6t)

The title compound (yellow solid, 26 mg, yield: 52%) was synthesized according to the General Procedure A from 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and vinylidene cyclohexane (44 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, $J$ = 8.6 Hz, 1H), 7.93 (d, $J$ = 8.7 Hz, 1H), 7.77 (d, $J$ = 7.8 Hz, 1H), 7.55 (ddd, $J$ = 8.5, 6.8, 1.4 Hz, 1H), 7.46 (d, $J$ = 8.2 Hz, 1H), 7.41 (ddd, $J$ = 8.1, 6.8, 1.1 Hz, 1H), 6.48 (d, $J$ = 1.6 Hz, 1H), 2.58 (ddd, $J$ = 14.5, 12.8, 6.0 Hz, 2H), 2.43 (d, $J$ = 1.6 Hz, 3H), 2.07-1.88 (m, 5H), 1.76-1.63 (m, 1H), 1.49-1.42 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 159.39, 146.80, 139.96, 132.44, 129.95, 128.01, 125.67, 125.31, 123.19, 122.90, 119.85, 54.77, 31.90, 25.37, 23.01, 19.69.

HRMS-APCI: calculated for C$_{19}$H$_{21}$[M+H]$^+$: 249.1638; found: 249.1647.

M.p.: 122-124 ºC.

1,1,2-Trimethyl-1H-cyclopenta[l]phenanthrene (6u)

The title compound (white solid, 25.5 mg, yield: 50%) was synthesized according to the General Procedure A from 9-(cyclohepta-2,4,6-trien-1-yl)phenanthrene (54 mg, 0.2 mmol) and 3-methylbuta-1,2-diene (27 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.04-8.59 (m, 2H), 8.40-8.06 (m, 2H), 7.79-7.54 (m, 4H), 7.05 (d, $J$ = 1.6 Hz, 1H), 2.20 (d, $J$ = 1.6 Hz, 3H), 1.56 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.72, 144.58, 137.06, 130.25, 129.13, 128.73, 127.52, 126.34, 126.27, 125.67, 124.62, 124.17, 123.88, 123.42, 123.16, 120.93, 52.97, 23.45, 12.65.

HRMS-APCI: calculated for C$_{20}$H$_{19}$[M+H]$^+$: 259.1481; found: 259.1486.

M.p.: 125-127 ºC.
1,2-Dimethyl-1-phenethyl-1H-cyclopenta[1]phenanthrene (6v)

The title compound (white solid, 49.3 mg, yield: 71%) was synthesized according to the General Procedure A from 9-(cyclohepta-2,4,6-trien-1-yl)phenanthrene (54 mg, 0.2 mmol) and (3-methylpenta-3,4-dien-1-yl)benzene (63 mg, 0.4 mmol).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.87 (d, $J = 8.2$ Hz, 1H), 8.85-8.80 (m, 1H), 8.28-8.22 (m, 2H), 7.75 – 7.62 (m, 4H), 7.23-7.16 (m, 3H), 7.15-7.10 (m, 1H), 6.99 – 6.93 (m, 2H), 2.74 (td, $J = 13.2$, 4.8 Hz, 1H), 2.32-2.17 (m, 4H), 1.97 (ddd, $J = 13.9$, 12.5, 4.5 Hz, 1H), 8.87 (td, $J = 12.8$, 4.9 Hz, 1H), 1.56 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.07, 142.65, 142.32, 138.53, 130.44, 129.16, 129.06, 128.26, 128.20, 127.47, 126.61, 126.45, 125.85, 125.59, 124.67, 124.44, 124.01, 123.27, 123.11, 123.01, 57.28, 39.28, 30.61, 24.01, 12.88.

HRMS-APCI: calculated for C$_{27}$H$_{25}$[M+H]$^+$: 349.1591; found: 349.1596.

M.p.: 97-99 ºC.

7-Cyclohexyl-7a-methyl-8-(naphthalen-1-yl)-7,7a,8,8a-tetrahydrocyclopropa[4,5]cyclopenta[1,2-a]naphthalene (11)

A solution of the 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol), buta-2,3-dien-2-ylcyclohexane (55 mg, 0.4 mmol) and gold complex A (7.7 mg, 5 mol%) in 1,2-dichloroethane (DCE, 2 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (16 h). After the reaction mixture had been allowed to cool to room temperature, the solvent was removed in vacuo and the crude residue was purified by preparative TLC to give 11 (11 mg, 28% yield) as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.29 (d, $J = 7.6$ Hz, 2H), 7.88-7.81 (m, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.64 (ddd, $J = 8.2$, 6.8, 1.3 Hz, 1H), 7.60-7.38 (m, 5H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.69 (dd, $J = 8.2$, 7.2 Hz, 1H), 6.20 (dt, $J = 7.3$, 1.3 Hz, 1H), 3.32 (dd, $J = 7.6$, 1.8 Hz, 1H).
Hz, 1H), 2.74 (d, J = 7.5 Hz, 1H), 2.61 (t, J = 2.1 Hz, 1H), 1.93 (s, 4H), 1.79-1.71 (m, 1H), 1.67-1.45 (m, 5H), 1.39-1.17 (m, 2H), 1.08-0.91 (m, 1H), 0.52-0.38 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.93, 139.74, 133.94, 133.43, 132.86, 132.42, 130.89, 128.69, 128.40, 128.02, 125.97, 125.80, 125.69, 125.10, 125.00, 124.84, 124.65, 124.48, 124.39, 123.51, 52.30, 40.65, 35.68, 33.69, 32.85, 32.82, 29.17, 27.61, 26.62, 26.45, 20.85.

HRMS-APCI: calculated for C$_{31}$H$_{31}$ [M+H]$^+$: 403.2420; found: 403.2417.

M.p.: 205-207 ºC.

6. General Procedure B for the Gold(I)-Catalyzed Synthesis of Cyclopentadienes

Under air, a 2.0-5.0 mL microwave vial was charged with a Teflon-coated magnetic stirring bar and an allene 5 (1.5-3.0 equiv) and it was dissolved in EtOAc (HPLC grade, 0.1 M). Then, 7-styryl-1,3,5-cycloheptatriene 2 (1.0 equiv) was added as a solid by spatula or as a liquid by glass pipette and finally gold catalyst B (5 mol%) was added. The vial was sealed with its corresponding cap and the resulting solution was stirred at 100 ºC in a heating block (covering the vial completely) for 12-16 h. The yellow-orange solution was concentrated under vacuum and the obtained residue was purified by flash column chromatography (SiO$_2$, pentane or gradients of pentane/Et$_2$O).

6.1. Characterization Data for the Different Cyclopentadienes

(4,5-Dimethyl-5-phenyleclopenta-1,3-dien-1-yl)benzene (7a)

This compound was obtained, following General Procedure B, form (E)-7-styrylcyclohepta-1,3,5-triene (50 mg, 0.257 mmol, 1.0 equiv) and (3-Methylpenta-3,4-dien-1-yl)benzene (61 mg, 0.386 mmol, 1.5 equiv) using gold catalyst B (11.6 mg, 0.013 mmol, 5 mol%) after purification by flash column (SiO$_2$, eluent: pentane) as a colorless oil (35 mg, 0.128 mmol, 50%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.56 (dt, J = 7.4, 1.4 Hz, 2H), 7.37 (tt, J = 7.5, 1.6 Hz, 2H), 7.26-7.20 (m, 3H), 7.13 (tt, J = 7.5, 1.6 Hz, 1H), 7.02 (d, J = 7.5 Hz, 2H), 6.75 (d,
\[ J = 2.2 \text{ Hz, 1H}, 2.24 \text{ (td, } J = 12.9, 4.7 \text{ Hz, 1H}), 2.12 \text{ (td, } J = 13.0, 4.7 \text{ Hz, 1H}), 2.02-1.88 \text{ (m, 2H), 1.96 (d, } J = 1.6 \text{ Hz, 3 H) ppm.}

^{13}\text{C NMR (126 MHz, CDCl}_3\text{) } \delta 153.6, 151.2, 142.8, 136.6, 128.5, 128.3, 128.2, 128.0, 126.3, 125.8, 125.6, 125.4, 57.2, 37.9, 30.3, 22.9, 12.7 \text{ ppm.}

HRMS (APCI Positive): calculated for C_{21}H_{23} [M+H]^+: 275.1794; found: 275.1788.

1-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methyl-benzene (7b)

This compound was obtained, following General Procedure B, from (E)-7-(4-methylstyril)cyclohepta-1,3,5-triene (70 mg, 0.340 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (80 mg, 0.504 mmol, 1.5 equiv) using gold catalyst B (15 mg, 0.017 mmol, 5 mol%) after purification by flash column (SiO$_2$, eluent: pentane) as a colorless oil (36 mg, 0.125 mmol, 37%).

\[ \text{EtOAc, 100 ºC} \]

\[ 12-16 \text{ h} \]

\[ \text{+} \]

\[ \text{B (5 mol%)} \]

\[ \text{Ph} \]

\[ \text{B (5 mol%)} \]

\[ \text{EtOAc, 100 ºC} \]

\[ 12-16 \text{ h} \]

\[ \text{F}_3\text{C} \]

\[ \text{Ph} \]

\[ \text{F}_3\text{C} \]

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$^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J = 8.6$ Hz, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.23 (tt, $J = 7.0$, 1.4 Hz, 2H), 7.15 (tt, $J = 7.2$, 1.4 Hz, 1H), 7.03-6.99 (m, 2H), 6.90 (d, $J = 2.4$ Hz, 1H), 6.21 (quint, $J = 1.7$ Hz, 1H), 2.28-2.20 (m, 1H), 2.08-1.94 (m, 1H), 1.99 (d, $J = 1.5$ Hz, 3H), 1.28 (s, 3H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.4, 149.5, 142.4, 130.2, 129.0, 128.4, 128.4, 128.3, 128.2, 125.7, 125.5, 125.4 (q, $J_{C-F} = 3.8$ Hz), 57.3, 37.9, 30.2, 22.9, 12.7 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.50 ppm.

HRMS (APCI Positive): calculated for C$_{22}$H$_{22}$F$_3$ [M+H]$^+$: 343.1668; found: 343.1662.

1-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methoxybenzene (7d)

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{OMe} & \quad \text{Me}
\end{align*}
\]

This compound was obtained, following General Procedure B, form (E)-7-(4-methoxystyrly)cyclohepta-1,3,5-triene (50 mg, 0.223 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (71 mg, 0.446 mmol, 2.0 equiv) using gold catalyst B (10 mg, 11 µmol, 5 mol%) after purification by flash column (SiO$_2$, eluent: pentane/Et$_2$O 99:1) as a pale yellow syrup (27 mg, 0.089 mmol, 39%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.52 (d, $J = 8.9$ Hz, 2H), 7.24 (t, $J = 7.7$ Hz, 2H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.9$ Hz, 2H), 6.93 (d, $J = 7.9$ Hz, 2H), 6.64 (d, $J = 2.2$ Hz, 1H), 6.16 (quint, $J = 1.8$ Hz, 1H), 3.87 (s, 3H), 2.21 (td, $J = 12.9$, 4.7 Hz, 1H), 2.12 (td, $J = 12.9$, 4.5 Hz, 1H), 2.00 (td, $J = 13.0$, 4.5 Hz, 1H), 1.96 (d, $J = 1.5$ Hz, 3H), 1.91 (td, $J = 12.9$, 4.5 Hz, 1H), 1.26 (s, 3H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.2, 152.5, 150.9, 142.9, 129.6, 128.4, 128.3, 126.4, 125.5, 125.4, 113.9, 77.3, 57.1, 55.3, 37.9, 30.3, 23.0, 12.6 ppm.

HRMS (APCI Positive): calculated for C$_{22}$H$_{25}$O [M+H]$^+$: 305.1900; found: 305.1904.

1-Bromo-4-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-benzene (7e)

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{Br} & \quad \text{Me}
\end{align*}
\]

This compound was obtained, following General Procedure B, form (E)-7-(4-bromostyrly)cyclohepta-1,3,5-triene (60 mg, 0.220 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (70 mg, 0.439 mmol, 2.0 equiv) using gold catalyst.
B (9.9 mg, 11 µmol, 5 mol%) after purification by flash column (SiO$_2$, eluent: pentane) as a white syrup (39 mg, 0.110 mmol, 50%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (dt, $J = 8.7$, 2.2 Hz, 2H), 7.44 (dt, $J = 8.6$, 2.2 Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 2H), 7.16 (tt, $J = 7.2$, 2.1 Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 2H), 6.78 (d, $J = 2.3$), 6.18 (quint, $J = 1.8$ Hz, 1H), 2.19 (td, $J = 12.4$, 4.8 Hz, 1H), 2.08-1.90 (m, 3H), 1.97 (d, $J = 1.5$ Hz, 3H), 1.26 (s, 3H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.3, 149.9, 142.6, 135.4, 131.6, 128.6, 128.3, 128.2, 127.2, 125.7, 125.5, 120.0, 57.2, 37.9, 30.2, 22.9, 12.7 ppm.

HRMS (APCI Positive): calculated for C$_{21}$H$_{22}$Br [M+H]$^+$: 353.0899; found: 353.0895.

1-(4,5-Dimethyl-5-phenethylcyclopen-ta-1,3-dien-1-yl)-2-fluoro-benzene (7f)

This compound was obtained, following General Procedure B, form (E)-7-(2-fluorostyryl)cyclohepta-1,3,5-triene (40 mg, 0.188 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (60 mg, 0.377 mmol, 2.0 equiv) using gold catalyst B (8.5 mg, 9.4 µmol, 5 mol%) after filtering through silica gel and further purification by preparative TLC (1000 micron SiO$_2$, eluent: pentane) as a colorless viscous oil (28 mg, 0.096 mmol, 48%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (td, $J = 7.9$, 1.9 Hz, 1H), 7.26-7.21 (m, 3H), 7.18-7.12 (m, 3H), 7.08-7.04 (m, 2H), 6.79 (t, $J = 2.2$ Hz 1H), 6.20 (quint, $J = 1.7$ Hz, 1H), 2.25-2.17 (m, 1H), 2.12-2.03 (m, 2H), 1.97 (d, $J = 1.6$ Hz, 3H), 1.90-1.84 (m, 1H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.4 (d, $J_{C-F} = 248.1$ Hz), 153.4, 144.6, 142.8, 132.7 (d, $J_{C-F} = 9.7$ Hz), 128.6 (d, $J_{C-F} = 3.8$ Hz), 128.2, 128.2, 127.6 (d, $J_{C-F} = 8.7$ Hz), 125.7, 125.6, 123.7 (d, $J_{C-F} = 4.8$ Hz), 116.2, 116.0, 58.3, 37.5, 30.1, 22.6, 12.8 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.30 ppm.

HRMS (APCI Positive): calculated for C$_{21}$H$_{22}$F [M+H]$^+$: 293.1700; found: 293.1701.

(4,5,5-Trimethylcyclopenta-1,3-dien-1-yl)benzene (7g)

This compound was obtained, following General Procedure B, form (E)-7-styrlycyclohepta-1,3,5-triene (0.26 g, 1.34 mmol, 1.0 equiv) and 3-methylbuta-1,2-diene
(0.27 g, 4.01 mmol, 3.0 equiv) using gold catalyst B (60 mg, 0.05 mmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a colorless low boiling point oil (121 mg, 0.66 mmol, 49%).

**¹H NMR** (500 MHz, CDCl₃) δ 7.51 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.19 (t, J = 7.9 Hz, 1H), 6.63 (d, J = 2.3 Hz, 1H), 6.02 (quint, J = 1.4 Hz, 1H), 1.92 (d, J = 1.4 Hz, 3H), 1.22 (s, 3H) ppm.

**¹³C NMR** (126 MHz, CDCl₃) δ 156.3, 153.6, 136.5, 128.3, 126.1, 126.1, 126.0, 123.3, 53.1, 22.5, 12.5 ppm.

**HRMS** (APCI Positive): calculated for C₁₅H₁₉ [M+H]^+: 185.1325; found: 185.1321.

**1-Methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (7h)**

This compound was obtained, following General Procedure B, from (E)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (0.21 g, 1.01 mmol, 1.0 equiv) and 3-methylbuta-1,2-diene (0.21 g, 3.02 mmol, 3.0 equiv) using gold catalyst B (45 mg, 0.05 mmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a colorless low boiling point oil (95 mg, 0.48 mmol, 43-48%).

**¹H NMR** (400 MHz, CDCl₃) δ 7.45 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 2.1 Hz, 1H), 6.04 (quint, J = 1.5 Hz, 1H), 2.38 (s, 3H), 1.95 (d, J = 1.4 Hz, 3H), 1.25 (d, J = 0.6 Hz, 6H) ppm.

**¹³C NMR** (101 MHz, CDCl₃) δ 155.8, 153.6, 135.8, 133.6, 129.0, 125.9, 125.3, 123.3, 53.0, 22.5, 21.1, 12.5 ppm.

**HRMS** (APCI Positive): calculated for C₁₅H₁₉ [M+H]^+: 199.1481; found: 199.1482.

**1-Methyl-4-(p-tolyl)spiro[4.5]deca-1,3-diene (7i)**

This compound was obtained, following General Procedure B, from (E)-7-(4-methylstyryl)-cyclohepta-1,3,5-triene (67 mg, 0.32 mmol, 1.0 equiv) and vinylidencyclohexane (77 mg, 0.643 mmol, 2.0 equiv) using gold catalyst B (14 mg, 0.016 mmol, 5 mol%) after purification by flash column (SiO₂, eluent: pentane) as a colorless oil (28 mg, 0.117 mmol, 37%).
1H NMR (500 MHz, CDCl3) δ 7.29 (t, J = 4.1 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 6.28 (d, J = 2.2 Hz, 1H), 6.00 (quint, J = 1.7 Hz, 1H), 2.38 (s, 3H), 2.16 (d, J = 1.6 Hz, 3H), 1.91-1.85 (m, 2H), 1.80-1.72 (m, 2H), 1.67-1.59 (m, 3H), 1.50-1.42 (m, 3H) ppm.

13C NMR (126 MHz, CDCl3) δ 155.9, 155.4, 135.8, 135.7, 128.5, 128.1, 126.6, 124.7, 56.9, 30.5, 25.4, 22.4, 21.1, 17.3 ppm.

HRMS (APCI Positive): calculated for C18H23 [M+H]+: 239.1794; found: 239.1788.

2-(4,5,5-Trimethylcyclopenta-1,3-dien-1-yl)naphthalene (7j)

This compound was obtained, following General Procedure B, form (E)-2-(2-(cyclohepta-2,4,6-trien-1-yl)vinyl)naphthalene (65 mg, 0.266 mmol, 1.0 equiv) and 3-methylbuta-1,2-diene (54 mg, 0.798 mmol, 3.0 equiv) using gold catalyst B (12 mg, 13 µmol, 5 mol%) after purification by flash column (SiO2, eluent: pentane) as a pale yellow solid (35 mg, 0.149 mmol, 56%).

1H NMR (400 MHz, CDCl3) δ 7.95 – 7.89 (m, 1H), 7.89 – 7.70 (m, 4H), 7.46 (dqd, J = 9.4, 6.9, 1.5 Hz, 2H), 6.84 (dd, J = 27.7, 2.3 Hz, 1H), 6.17 – 6.08 (m, 1H), 2.01 (d, J = 1.6 Hz, 3H), 1.36 (s, 6H).

13C NMR (101 MHz, CDCl3) δ 157.0, 153.3, 133.6, 133.5, 132.0, 128.1, 127.7, 127.5, 126.9, 126.0, 125.3, 125.2, 123.5, 123.4, 53.2, 22.8, 12.5.

HRMS (APCI Positive): calculated for C18H19 [M+H]+: 235.1481; found: 235.1485.

M.p.: 58-62 ºC.

2-(4,5-Dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)naphthalene (7k)

This compound was obtained, following General Procedure B, form (E)-2-(2-(cyclohepta-2,4,6-trien-1-yl)vinyl)naphthalene (30 mg, 0.123 mmol, 1.0 equiv) and (3-methylpenta-3,4-dien-1-yl)benzene (29 mg, 0.184 mmol, 1.5 equiv) using gold catalyst B (5.5 mg, 6.1 µmol, 5 mol%) after filtering through silica gel and further purification by preparative TLC (1000 micron SiO2, eluent: pentane) as a pale yellow syrup (22 mg, 0.068 mmol, 55%).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (br, 1H), 7.86-7.76 (m, 4H), 7.47 (quint, $J = 7.3$ Hz, 2H), 7.20 (t, $J = 7.3$ Hz, 2H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.04-7.00 (m, 2H), 6.93 (d, $J = 2.3$ Hz, 1H), 6.24 (quint, $J = 1.7$ Hz), 2.43-2.36 (m, 1H), 2.19-2.10 (m, 1H), 2.06-1.95 (m, 2H), 2.01 (d, $J = 1.5$ Hz, 3H), 1.37 (s, 3H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.3, 150.8, 142.8, 133.8, 133.7, 132.2, 128.8, 128.3, 128.3, 128.2, 128.0, 127.5, 126.1, 125.6, 125.6, 125.5, 125.1, 123.1, 57.3, 38.4, 30.4, 23.3, 12.8 ppm.

HRMS (APCI Positive): calculated for C$_{25}$H$_{25}$ [M+H]$^+$: 325.1951; found: 325.1949.

6.2. Kinetic and Mechanistic Studies

The synthesis of cyclopentadiene 7a was followed by GC-FID using diphenylmethane as internal standard.
For the NMR analysis, the reaction was stopped after 25 min and immediate flash column chromatography in SiO\(_2\) with pentane afforded the mixture of the product and the two diastereomeric intermediates.
7. Diels-Alder Reaction of Highly Substituted Cyclopentadienes with Maleic Anhydride

![Diels-Alder Reaction](image)

To a solution of (4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene 7g (58 mg, 0.315 mmol, 1.0 equiv) in 1.5 mL of anhydrous toluene (0.2 M) open to air was added maleic anhydride (40 mg, 0.409 mmol, 1.3 equiv) and the resulting yellow mixture was stirred at 100 ºC for 4 h. The obtained colorless suspension was cooled to room temperature and the solvent was removed under reduced pressure. Purification by flash column chromatography on SiO₂ (eluent pentane/Et₂O from 8:2 to 7:3) afforded endo-4,8,8-trimethyl-7-phenyl-3a,7a-tetrahydro-4,7-methano-isobenzofuran-1,3-dione 12 (80 mg, 90%) as a white solid. Slow evaporation overnight of a solution of 12 in heptane/DCM afforded crystals suitable for X-ray analysis.

1H NMR (500 MHz, CDCl₃) δ 7.47-7.42 (m, 2H), 7.38 (dd, J = 8.2, 2.2 Hz, 3H), 6.39 (d, J = 5.8 Hz, 1H), 6.20 (d, J = 5.8 Hz, 1H), 4.30 (d, J = 7.8 Hz, 1H), 3.49 (d, J = 7.8 Hz, 1H), 1.45 (s, 3H), 0.78 (s, 3H), 0.72 (s, 3H). ppm.

13C NMR (126 MHz, CDCl₃) δ 171.5, 170.6, 139.3, 136.8, 135.0, 128.5, 127.7, 127.7, 68.9, 67.9, 60.8, 52.5, 49.1, 17.42, 17.36, 12.8. ppm.

HRMS (ESI Positive): calculated for C₁₈H₁₈NaO₃ [M+Na+CH₃OH]⁺: 337.1410; found: 337.1413.

M.p.: 185-187 ºC.

8. Total Synthesis of Laurokamurene B (10)

The synthesis of (±)-laurokamurene B was achieved in one step directly from cyclopentadiene 7h, (1-methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene, see above for preparation).

![Total Synthesis](image)

To a stirred solution of 1-methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (50 mg, 0.252 mmol, 1.0 equiv) in 1.5 mL of anhydrous toluene (0.17 M) under Ar atmosphere, was added Wilkinson’s Catalyst, [Rh(PPh₃)₃Cl] (23 mg, 0.025 mmol, 10 molar percent) and 3 atm of hydrogen (1 atm balloon) at 25 ºC for 3 h.

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5 Endo configuration confirmed by NOESY NMR experiments and single crystal X-ray diffraction. Exo diastereoisomer was not detected.
mol%, prepared following a reported procedure\textsuperscript{6}). The Ar atmosphere was exchanged for an H\textsubscript{2} atmosphere though 3 vacuum/H\textsubscript{2} cycles using a H\textsubscript{2} balloon which was finally left attached to the flask. The reaction mixture was allowed to stir at room temperature for 3 h. The reaction was followed using both TLC and GC/MS (the later allowed the separation of the starting cyclopentadiene, the desired product and the double hydrogenation byproduct) and it was found that longer reaction times were detrimental to the desired product yield, as the second olefin gets also hydrogenated. After that time, the reaction was filtered through silica gel, and then purified by slow flash column in SiO\textsubscript{2} (eluent pentane, careful evaporation of pentane under 150-200 mbar at 20 \degree C was performed, since the product is relatively volatile) to afford (±)-laurokamurene B (43 mg, 0.220 mmol, 86\%).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.23 (d, \(J = 8.0\) Hz, 2H), 7.12 (d, \(J = 8.0\) Hz, 2H), 5.71 (br, 1H), 2.45-2.40 (m, 1H), 2.35 (s, 3H), 2.07-1.99 (m, 2H), 1.11 (s, 3H), 1.02 (d, \(J = 6.7\) Hz, 3H), 1.00 (s, 3H) ppm.

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 152.8, 136.2, 135.5, 128.6, 127.5, 126.2, 47.7, 45.8, 37.9, 26.3, 21.1, 20.7, 14.1 ppm.

HRMS (APCI Positive): calculated for C\textsubscript{15}H\textsubscript{21} [M+H]\textsuperscript{+}: 201.1638; found: 201.1636.

Table S2. Laurokamurene B Spectra Comparison

| Position | \textsuperscript{1}H NMR (\(\delta\)) Natural Sample (400 MHz, CDCl\textsubscript{3}) | \textsuperscript{1}H NMR (\(\delta\)) Synthetic Sample (500 MHz, CDCl\textsubscript{3}) | \textsuperscript{13}C NMR (\(\delta\)) Natural Sample (400 MHz, CDCl\textsubscript{3}) | \textsuperscript{13}C NMR (\(\delta\)) Synthetic Sample (500 MHz, CDCl\textsubscript{3}) |
|----------|------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1        | -                                               | -                               | 152.8 (C)                      | 152.83 (C)                     |
| 2        | -                                               | -                               | 47.7 (C)                       | 47.73 (C)                      |
| 3        | 2.01 (m)                                        | 2.03 (m)                        | 45.8 (CH)                      | 45.80 (CH)                     |
| 4        | 2.01 (m)                                        | 2.03 (m)                        | 37.8 (CH\textsubscript{2})     | 37.86 (CH\textsubscript{2})    |
|          | 2.41 (ddd, 11.5, 9.7, 2.9)                      | 2.43 (m)                        | -                              | -                              |
| 5        | 5.69 (br)                                       | 5.71 (br)                       | 126.1 (CH)                     | 126.15 (CH)                    |
| 6        | -                                               | -                               | 135.5 (C)                      | 135.48 (C)                     |

\textsuperscript{6} J. A. Osborn, G. Wilkinson, \textit{Inorg. Syn.} 1967, 10, 67.
9. Procedures for the Synthesis of the Tetracyclic Carbon Skeleton of Cycloaurenones

3-(2-Oxocyclohexyl)propanenitrile (SI1)

![Reaction scheme]

The title compound was synthesized according to a literature procedure. To a stirred mixture of cyclohexanone (35g, 37 mL, 0.36 mol) and acrylonitrile (28 g, 35 mL, 0.54 mol) was added cyclohexylamine (3.5 g, 4.1 mL, 36 mmol) and acetic acid (214 mg, 0.2 mL, 3.6 mmol). The reaction mixture was heated at 120 ºC for 3 h. The resulting liquid was purified by column chromatography on silica gel (elucent cyclohexane/ethyl acetate 90/10) to result in a colorless oil (46.5 g, 86% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.56-2.27 (m, 5H), 2.18-2.01 (m, 3H), 1.94-1.85 (m, 1H), 1.79-1.60 (m, 2H), 1.56-1.46 (m, 1H), 1.45-1.32 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 211.75, 119.72, 48.87, 42.25, 34.30, 28.00, 25.61, 25.18, 15.26.

HRMS-ESI: calculated for C$_9$H$_{13}$NNaO [M+Na]$^+$: 174.0895; found: 174.0889.

2-(2-Cyanoethyl)-1-ethynylcyclohexyl methyl carbonate (SI2)

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7 S.-C. Mao, Y.-W. Guo, *J. Nat. Prod.* 2006, 69, 1209-1211.
8 D. H. Woodmansee, M.-A. Muller, M. Neuburger, A. Pfaltz, *Chem. Sci.* 2010, 1, 72-78.
Ethynylmagnesium bromide (32 mL, 15.9 mol, 0.5 M in THF) was added dropwise to a solution of 3-(2-oxocyclohexyl)propanenitrile SI1 (2 g, 13.2 mmol) in dry THF (30 mL) at 0 °C under argon. The mixture was stirred for 2 h at 0 °C, the disappearance of ketone was confirmed by TLC and then methyl chloroformate (1.6 g, 1.3 mL, 17.2 mmol) was added. The cooling bath was removed and the reaction was stirred at room temperature (23 °C) for 12 h. The reaction was quenched by the addition of water. The aqueous phase was extracted with ethyl acetate, the combined organic extracts were dried over MgSO₄, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 90:10) to give carbonate SI2 (2.65 g, 85% yield, d.r. = 1:1) as a colorless oil.

**^1H NMR** (400 MHz, CDCl₃) δ 3.77 (d, J = 4.2 Hz, 6H), 2.92-2.78 (m, 2H), 2.70 (s, 1H), 2.66 (s, 1H), 2.55-2.14 (m, 6H), 1.85-1.18 (m, 18H).

**^13C NMR** (101 MHz, CDCl₃) δ 153.26, 153.13, 119.73, 119.55, 82.69, 81.45, 79.54, 78.14, 77.62, 74.97, 54.50, 54.42, 45.20, 45.15, 35.95, 34.73, 28.59, 26.83, 26.24, 25.63, 24.73, 24.24, 23.10, 20.57, 15.53, 15.35.

**HRMS-ESI**: calculated for C₁₃H₁₇NNaO₃ [M+Na⁺]: 258.1101; found: 258.1099.

**3-(2-(1-Vinylidene)cyclohexyl)propanenitrile (SI3)**

n-Bu₃P (340 mg, 0.4 ml, 1.7 mmol) was added dropwise to a stirred mixture of carbonate SI2 (2.0 g, 8.5 mmol), ammonium formate (1.1 g, 17 mmol) and Pd(dba)₂ (244 mg, 0.4 mmol) in THF (50 mL) at 0 °C under argon. After 12 h, the disappearance of carbonate 7 was confirmed by TLC and the reaction mixture was filtered through a short pad of Celite. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 50:1) to give allene SI3 (1.1 g, 80% yield) as a colorless oil.

**^1H NMR** (400 MHz, CDCl₃) δ 4.75-4.68 (m, 2H), 2.46-2.39 (m, 2H), 2.35-2.27 (m, 1H), 2.09-1.72 (m, 6H), 1.69-1.58 (m, 1H), 1.48-1.35 (m, 2H), 1.25-1.12 (m, 1H).

**^13C NMR** (101 MHz, CDCl₃) δ 202.42, 120.05, 104.25, 75.83, 38.32, 33.45, 31.34, 29.29, 27.20, 25.43, 15.17.

S33
HRMS-ESI: calculated for $C_{11}H_{15}NNa\ [M+Na]^+$: 184.1102; found: 184.1099.

4-(Vinylidene)cyclohexyl)butan-2-one (SI4)

MeLi (30 mL, 48 mmol, 1.6 M in Et$_2$O) was added dropwise to a stirred solution of SI3 (2.2 g, 13.6 mmol) in Et$_2$O (90 mL) at -78 ºC under argon. The mixture was allowed to warm to 0 ºC during 4 h. Thereafter, a saturated solution of NH$_4$Cl (20 mL) was added dropwise while stirring at 0 ºC. The aqueous phase was extracted with Et$_2$O, the combined organic extracts were dried over MgSO$_4$. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 50:1) to give ketone SI4 (1.9 g, 78% yield) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.64 (t, $J = 3.3$ Hz, 2H), 2.58-2.39 (m, 2H), 2.31-2.22 (m, 1H), 2.13 (s, 3H), 2.01-1.68 (m, 6H), 1.61-1.51 (m, 1H), 1.48-1.28 (m, 2H), 1.23-1.12 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 206.40, 199.94, 102.10, 72.03, 38.86, 35.99, 30.72, 28.36, 26.97, 24.53, 24.41, 22.42.

HRMS-ESI: calculated for $C_{12}H_{18}N\ [M+N]^+$: 201.1250; found: 201.1254.

4-(Vinylidene)cyclohexyl)butan-2-ol (SI5)

Cerium(III) chloride heptahydrate (12.5 g, 33.7 mmol) was added to a solution of SI4 (1.5 g, 8.4 mmol) in MeOH (100 mL) at 0 ºC. The mixture was stirred 10 min and then NaBH$_4$ (350 mg, 9.3 mmol) was added. After 1 h, the disappearance of ketone was confirmed by TLC and MeOH was removed. To the residue was added water and it was extracted with ethyl acetate, the combined organic extracts were dried over MgSO$_4$. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 10:1) to give alcohol SI5 (1.2 g, 79% yield, d.r. = 1:1) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.63-4.62 (m, 2H), 3.81-3.73 (m, 1H), 2.34-2.21 (m, 1H), 2.04-1.10 (m, 16H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 203.06, 203.03, 105.68, 105.57, 74.79, 74.76, 68.46, 68.38, 39.40, 39.26, 37.19, 37.10, 33.66, 33.64, 31.50, 31.44, 29.68, 29.50, 27.43, 25.56, 25.51, 23.50, 23.46.

HRMS-APCI: calculated for C$_{12}$H$_{21}$O [M+H]$^+$: 181.1587; found: 181.1582.

4-(Vinylidene)cyclohexyl)butan-2-yl benzoate (5i)

To a solution of SI5 (1.0 g, 5.6 mmol) in CH$_2$Cl$_2$ (60 mL) was added pyridine (1.3 mL, 16.6 mmol) at 0 °C. The mixture was kept at 0 °C for 10 min and then benzoyl chloride (1.0 mL, 8.3 mmol) was added dropwise. After stirring for 24 h at 23 °C and SI5 was no longer detected by TLC, water (50 ml) was added. The residue was extracted with CH$_2$Cl$_2$, the combined organic extracts were dried over MgSO$_4$. The solvent was evaporated, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound 5i (1.3 g, 83% yield, d.r. = 1:1) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16-8.02 (m, 2H), 7.62-7.53 (m, 1H), 7.51-7.41 (m, 2H), 5.26-5.04 (m, 1H), 4.71-4.54 (m, 2H), 2.29 (dd, $J$ = 13.4, 4.6 Hz, 1H), 2.08-1.52 (m, 8H), 1.51-1.26 (m, 6H), 1.25-1.08 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 202.91, 166.22, 132.64, 130.98, 129.51, 128.24, 105.45, 105.42, 74.93, 72.08, 71.90, 39.35, 39.16, 33.93, 33.81, 33.77, 33.72, 31.50, 31.48, 29.33, 29.20, 27.42, 25.57, 25.55, 20.06.

HRMS-ESI: calculated for C$_{19}$H$_{24}$NaO$_2$ [M+Na]$^+$: 307.1669; found: 307.1672.

Procedure for synthesis of compounds 14a and 14b.
Step i:

A solution of the 7-(2,5-dimethoxyphenyl)cyclohepta-1,3,5-triene 1f (913 mg, 4 mmol), 4-(2-(1λ5-vinylidene)cyclohexyl)butan-2-yl benzoate 5i (284 mg, 1 mmol) and gold complex F, [IPrAu(PhCN)]SbF₆, (46 mg, 0.05 mmol) in 1,2-dichloroethane (DCE, 20 mL) was heated at 120 ºC in a sealed tube under nitrogen. After 8 h, the reaction mixture was allowed to cool to room temperature, the solvent was removed in vacuum and the crude residue was passed through a short pad of silica to provide crude product 13 with all (4) isomers together, which was used directly for the next step.

Note: The procedure was developed after the following optimization.

**Table S1. Optimization of the key (3 + 2) cycloaddition.**

| Entry | Catalyst (5 mol%) | Yield (%)<sup>a</sup> |
|-------|-------------------|------------------------|
| 1<sup>b</sup> | A                 | 15                     |
| 2<sup>c</sup> | A                 | 21                     |
| 3<sup>c,d</sup> | A                 | 25                     |
| 4<sup>c,d</sup> | F                 | 41(59)<sup>e</sup>     |
| 5<sup>f</sup> | F                 | 39(55)<sup>e</sup>     |

<sup>a</sup> Yields determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as internal standard.<br><sup>b</sup> Reaction at 120 ºC (0.1 M in 1,2-dichloroethane), 2 equiv of 5i, catalyst A (5 mol%), 12 h.<br><sup>c</sup> 2 equiv of 1f.<br><sup>d</sup> Reaction under Argon.<br><sup>e</sup> Yield based on recovered starting material.<br><sup>f</sup> 1 mmol scale.

Step ii:

To a solution of crude 13 in MeOH/THF (4:1, 40:10 mL) was added K₂CO₃ (276 mg, 2 mmol). The reaction mixture stirred for 18 h at 50 ºC and was quenched by saturated aqueous solution of NH₄Cl. The residue was extracted with ethyl acetate and the combined organic extracts were dried over MgSO₄. The solvent was evaporated to provide the crude deprotected alcohol 13′, which was used directly for the next step.

Step iii:

To a solution of crude product 13′ in CH₂Cl₂ (50 mL) was added DMP (466 mg, 1.1 mmol) at 0 ºC. The reaction mixture stirred for 2 h and was quenched with saturated aqueous Na₂S₂O₃ (10 mL) at 0 ºC. The layers were separated and aqueous layer was extracted with CH₂Cl₂ (3×25 mL), the combined organic extracts were dried over
MgSO$_4$. The solvent was evaporated, the residue was purified by preparative TLC (pentane/ethyl ether 10:1) to give alcohol **14a** (60 mg, 18% for 3 steps) as colorless oil and **14b** (60 mg, 18% for 3 steps) as a colorless oil as well.

4-((1$R^*$,2$S^*$)-4',7'-Dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (**14a**)  

$^1$H NMR (500 MHz, CDCl$_3$) δ 6.68 (d, $J = 8.7$ Hz, 1H), 6.57 (d, $J = 8.7$ Hz, 1H), 6.52-6.47 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.67-2.53 (m, 2H), 2.29-2.19 (m, 4H), 2.07 (ddd, $J = 16.0, 8.7, 7.3$ Hz, 1H), 1.95-1.66 (m, 7H), 1.56-1.44 (m, 2H), 1.36-1.27 (m, 1H), 1.21-1.10 (m, 1H), 1.05-0.96 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 209.76, 153.09, 149.64, 146.47, 140.49, 133.08, 123.86, 109.67, 107.67, 59.27, 55.91, 55.30, 42.43, 37.31, 31.26, 29.08, 27.70, 25.90, 25.78, 22.53, 20.56.

HRMS-ESI: calculated for C$_{21}$H$_{28}$NaO$_3$ [M+Na]$^+$: 351.1931; found: 351.1936.

4-((1$R^*$,2$R^*$)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (**14b**)  

$^1$H NMR (500 MHz, CDCl$_3$) δ 6.72 (d, $J = 8.7$ Hz, 1H), 6.62 (d, $J = 8.7$ Hz, 1H), 6.55-6.47 (m, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.35-2.06 (m, 4H), 2.01 (s, 3H), 1.97-1.91 (m, 4H), 1.77-1.56 (m, 4H), 1.46-1.32 (m, 1H), 1.21-1.15 (m, 1H), 1.11-1.02 (m, 1H), 0.95-0.86 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 209.65, 153.48, 150.23, 147.05, 147.05, 138.34, 135.07, 121.48, 109.75, 107.45, 61.45, 55.94, 54.83, 41.71, 38.42, 34.35, 29.62, 26.84, 26.26, 25.59, 22.64, 13.65.

HRMS-APCI: calculated for C$_{21}$H$_{28}$NaO$_3$ [M+Na]$^+$: 351.1931; found: 351.1933.

(1$R^*$,2$S^*$)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (**15a**).

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**Step i:**

To a solution of the **14a** (60 mg, 0.18 mmol) in MeOH (10 mL) was added NaBH$_4$ (10.3 mg, 0.27 mmol) at 0 °C. After 30 min, the disappearance of the ketone was confirmed by TLC and MeOH was removed. To the residue was added water and it was extracted with ethyl acetate, the combined organic extracts were dried over MgSO$_4$. The solvent was evaporated to provide crude alcohol **14a´**, which was used directly for the next step.
Step ii:

To a mixture of alcohol 14a and imidazole (15 mg, 0.22 mmol) in CH$_2$Cl$_2$ (4 mL) was added Ph$_3$PBr$_2$ (92 mg, 0.22 mmol) in the glove box. The reaction was stirred for 12 h and the solvent was removed, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound 15a (45 mg, 63% yield for two steps, d.r. = 1:1) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 6.69 (dd, $J = 8.7$, 2.4 Hz, 1H), 6.58 (dd, $J = 8.7$, 4.4 Hz, 1H), 6.52-6.47 (m, 1H), 4.01-3.81 (m, 7H), 2.72-2.48 (m, 2H), 2.26 (dd, $J = 4.8$, 1.6 Hz, 3H), 1.97-1.31 (m, 13H), 1.11-0.89 (m, 1H), 0.86-0.74 (m, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 153.23, 153.20, 149.75, 149.63, 146.48, 146.43, 140.58, 140.56, 133.13, 133.10, 123.75, 123.74, 109.69, 109.64, 107.79, 107.70, 59.41, 59.36, 55.96, 55.42, 55.37, 52.08, 51.30, 39.67, 39.51, 37.36, 36.83, 31.30, 29.29, 28.93, 28.03, 27.67, 26.67, 26.03, 26.02, 25.34, 22.62, 22.57, 20.61, 20.60.

HRMS-APCI: calculated for C$_{21}$H$_{30}$BrO$_2$ [M+H]$^+$: 393.1424; found: 393.1422.

(4aS*,7R*,7aS*,12bR*)-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[$d$]fluorine (16a).

MeO
MeO
\[\begin{array}{c}
\text{Br} \\
\text{MeO} \\
\text{MeO}
\end{array}\]

15a

\[\begin{array}{c}
\text{AlBN, nBu$_3$SnH} \\
\text{Benzene, 80 ºC}
\end{array}\]

16a

d.r 4:1

To a refluxing solution of 15a (45 mg, 0.11 mmol) and AIBN (3.8 mg, 0.02 mmol) in benzene (8 mL) was added over 2 h a solution of $n$Bu$_3$SnH (0.154 ml, 0.57 mmol) in benzene (8 mL). The resulting solution was heated at reflux for 2 h, then the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound 16a (12 mg, 33% yield, d.r. = 4:1) as a yellow solid.

M.p.: 102-104 ºC

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.67-6.64 (m, 1H), 6.61 (d, $J = 8.7$ Hz, 1H), 3.78 (s, 6H), 3.16 (d, $J = 12.9$ Hz, 1H), 2.78 (d, $J = 15.8$ Hz, 1H), 2.53 (dd, $J = 15.8$, 0.9 Hz, 1H), 1.92-1.33 (m, 12H), 1.23 (s, 3H), 1.19-1.12 (m, 1H), 0.87 (d, $J = 6.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.98, 150.48, 141.47, 131.18, 110.14, 108.16, 55.84, 55.52, 55.16, 49.06, 39.94, 37.25, 35.60, 33.11, 30.86, 29.10, 26.27, 26.20, 24.12, 19.51, 18.13.
HRMS-APCI: calculated for C_{21}H_{31}O_2 [M+H]^+ 315.2319; found: 315.2317.

(4aS*,7R*,7aS*,12bR*)-7,7a-Dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[d]fluorene-9,12-dione (17a).

An ice-cold solution of cerium ammonium nitrate (87 mg, 0.16 mmol) in 1:1 MeCN/water (0.4 mL) was added slowly to a stirred and cooled (0 °C) solution of 16a (10 mg, 0.032 mmol) in 1:2:1 CH_2Cl_2/MeCN/water (0.8 mL) containing 2,6-dicarboxypyridine 1-oxide (14.6 mg, 0.08 mmol). After 40 min, the mixture was diluted with water (5 mL), and extracted with CH_2Cl_2. The combined organic extracts were dried (MgSO_4) and evaporated. The residue was purified by preparative TLC (pentane/ethyl ether 10:1) to give compound 17a (6.2 mg, 68% yield) as a yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 6.61 (d, J = 10.0 Hz, 1H), 6.57 (d, J = 10.0 Hz, 1H), 2.94 (d, J = 12.8 Hz, 1H), 2.62 (d, J = 18.0 Hz, 1H), 2.38 (d, J = 18.0 Hz, 1H), 1.82-1.75 (m, 2H), 1.71-1.56 (m, 4H), 1.50-1.34 (m, 7H), 1.21 (s, 3H), 0.88 (d, J = 6.1 Hz, 3H).

^13C NMR (126 MHz, CDCl_3) δ 187.14, 186.83, 153.77, 147.55, 138.11, 135.14, 135.14, 56.02, 48.33, 39.85, 37.81, 34.50, 31.46, 31.36, 28.60, 25.55, 25.47, 23.38, 18.76, 17.94.

HRMS-ESI: calculated for C_{19}H_{24}NaO_2 [M+H]^+ 307.1699; found: 307.1676.

10. Procedures for the Synthesis of the Tetracyclic Carbon Skeleton of Dysiherbols

(1R*,2R*)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (15b).

Step i:
To a solution of the 14b (60 mg, 0.18 mmol) in MeOH (10 mL) was added NaBH_4 (10.3 mg, 0.27 mmol) at 0 °C. After 30 min, the disappearance of ketone was confirmed by TLC and MeOH was removed. To the residue was added water and extracted with ethyl acetate, the combined organic extracts were dried over MgSO_4. The solvent was
evaporated to provide crude product 14b*, which was used directly for the next step.

Step ii:

In a glovebox, to a mixture of 14b* and imidazole (15 mg, 0.22 mmol) in CH$_2$Cl$_2$ (4 mL) was added Ph$_3$PBr$_2$ (92 mg, 0.22 mmol). The reaction stirred for 12 h and the solvent was removed, the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 20:1) to give compound 15b (43 mg, 60% yield for two steps, d.r. = 1:1) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.73 (d, $J = 8.7$ Hz, 1H), 6.63 (dd, $J = 8.7$, 2.1 Hz, 1H), 6.57-6.53 (m, 1H), 3.94-3.75 (m, 7H), 2.23-2.06 (m, 2H), 1.95 (dd, $J = 7.7$, 1.5 Hz, 3H), 1.86-1.50 (m, 10H), 1.49-1.26 (m, 1H), 1.24-1.13 (m, 1H), 0.98-0.63 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.46, 153.39, 150.29, 150.27, 147.02, 147.00, 138.54, 138.49, 135.10, 135.07, 121.46, 121.40, 109.72, 109.70, 107.56, 107.49, 61.53, 55.97, 55.95, 54.95, 54.90, 51.92, 51.85, 39.67, 39.18, 39.00, 38.34, 34.38, 34.32, 29.05, 28.92, 27.11, 26.86, 26.54, 26.37, 26.36, 26.00, 22.68, 22.66, 13.75, 13.68.

HRMS-APCI: calculated for C$_{21}$H$_{30}$BrO$_2$ [M+H]$^+$: 393.1424; found: 393.1425.

(4aR*,7aS*)-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo [d]fluorine (16b).

To a refluxing solution of 15b (43 mg, 0.11 mmol) and AIBN (3.6 mg, 0.02 mmol) in benzene (8 mL) was added over 2 h a solution of Bu$_3$SnH (0.147 mL, 0.55 mmol) in benzene (8 mL). The resulting solution was heated at reflux for 2 h, then the solvent was evaporated under vacuum. The residue was purified by column chromatography in silica gel (cyclohexane/ethyl acetate 20:1) to give compound 16b (28 mg, 81% yield, d.r. = 1:1) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.80-6.59 (m, 4H), 3.84-3.74 (m, 12H), 2.92 (d, $J = 16.5$ Hz, 1H), 2.77 (d, $J = 15.9$ Hz, 1H), 2.54-2.40 (m, 3H), 2.32 (qd, $J = 12.6$, 5.1 Hz, 1H), 1.85-1.61 (m, 3H), 1.57-1.23 (m, 22H), 1.14 (s, 3H), 1.02 (s, 3H), 0.95-0.82 (m, 1H), 0.79 (d, $J = 6.2$ Hz, 3H), 0.65 (d, $J = 7.1$ Hz, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.10, 151.06, 150.24, 149.69, 140.36, 139.73, 133.66, 132.84, 109.82, 109.62, 108.86, 108.64, 59.35, 56.86, 55.68, 55.65, 54.88, 50.46, 49.85, 38.73, 38.40, 37.31, 36.22, 35.98, 35.45, 35.29, 32.24, 31.25, 29.64, 28.96, 27.79, 26.80, 26.73, 23.65, 22.53, 22.14, 18.45, 17.98, 13.30.

HRMS-APCI: calculated for C\(_{21}\)H\(_{31}\)O\(_2\) [M+H]\(^{+}\): 315.2319; found: 315.2324.

Note: The title compound was obtained as 1:1 mixture of diastereoisomers at C7. The configuration at C7a was assumed based on simple structure modelling and geometry considerations, as the radical cyclization is expected to occur much easier from the same face of the substituent than from the opposite one.

(4a\(R^*\),7a\(S^*\))-7,7a-Dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[d]fluorene-9,12-dione (17b).

An ice-cold solution of cerium ammonium nitrate (87 mg, 0.16 mmol) in 1:1 MeCN/water (0.4 mL) was added slowly to a stirred and cooled (0 °C) solution of 16b (10 mg, 0.032 mmol) in 1:2:1 CH\(_2\)Cl\(_2\)/MeCN/water (0.8 mL) containing 2,6-dicarboxypyridine 1-oxide (14.6 mg, 0.08 mmol). After 40 min, the mixture was diluted with water (5 mL), and extracted with CH\(_2\)Cl\(_2\). The combined organic extracts were dried (MgSO\(_4\)) and evaporated. The residue was purified by preparative TLC (pentane/ethyl ether 10:1) to give compound 17b (5.5 mg, 61% yield) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.64 (s, 4H), 4.49-3.66 (m, 1H), 2.89 (d, \(J = 19.2\) Hz, 1H), 2.74-2.58 (m, 2H), 2.45-2.27 (m, 3H), 1.90-1.75 (m, 2H), 1.68-1.04 (m, 27H), 1.01 (s, 3H), 0.83 (dd, \(J = 6.7, 4.9\) Hz, 6H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 187.21, 186.93, 186.74, 156.25, 155.29, 151.42, 151.17, 138.74, 138.58, 134.34, 134.22, 61.30, 58.85, 49.67, 48.68, 38.96, 38.04, 37.80, 36.01, 35.77, 35.59, 35.43, 35.03, 31.69, 29.38, 29.31, 27.95, 27.78, 26.40, 26.17, 23.35, 23.11, 22.43, 18.33, 17.88, 12.99.

HRMS-ESI: calculated for C\(_{19}\)H\(_{24}\)NaO\(_2\) [M+H]\(^{+}\): 307.1699; found: 307.1671.
11. Crystal Data and Structure Refinement

11.1. 1,2-dimethyl-1-phenethyl-4-phenoxy-1H-indene (6d)

The single crystals of compound 6d suitable for X-ray diffraction analysis were obtained from a solution of dichloromethane. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571036 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

Identification code: XY-TMR173
Empirical formula: C25H24O
Formula weight: 340.44
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: P2(1)/c
Unit cell dimensions:
- a = 17.9170(4) Å, α = 90°
- b = 7.7642(2) Å, β = 92.617(2)°
- c = 13.8078(3) Å, γ = 90°
Volume: 1918.82(8) Å³
Z: 4
Density (calculated): 1.178 Mg/m³
Absorption coefficient: 0.070 mm⁻¹
F(000): 728
Crystal size: 0.01 x 0.01 x 0.01 mm³
Theta range for data collection: 2.860 to 30.737°
Index ranges:
- h = -24 to 25
- k = -11 to 11
- l = -19 to 19
Reflections collected: 31032
Independent reflections: 5478 [R(int) = 0.0301]
Completeness to theta = 30.737°: 91.7%
Absorption correction: Multi-scan
Max. and min. transmission: 0.999 and 0.768
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 5478 / 0 / 237
Goodness-of-fit on F²: 1.031
Final R indices [I>2sigma(I)]: R1 = 0.0470, wR2 = 0.1102
R indices (all data): R1 = 0.0581, wR2 = 0.1154
Largest diff. peak and hole: 0.394 and -0.203 e.Å⁻³

11.2. 2'-methylspiro[cyclohexane-1,1'-cyclopenta[α]naphthalene] (6t)
The single crystals of compound 6t suitable for X-ray diffraction analysis were obtained from a solution of cyclohexane/ethyl acetate. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571032 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

**Identification code**  
mo_XYTMR10_0m

**Empirical formula**  
C19H20

**Formula weight**  
248.35

**Temperature**  
100(2) K

**Wavelength**  
0.71073 Å

**Crystal system**  
Orthorhombic

**Space group**  
P2(1)2(1)2(1)

**Unit cell dimensions**  
an = 7.4471(5) Å  
b = 14.2495(11) Å  
c = 26.067(2) Å

**Volume**  
2766.1(4) Å³

**Z**  
8

**Density (calculated)**  
1.193 Mg/m³

**Absorption coefficient**  
0.067 mm⁻¹

**F(000)**  
1072

**Crystal size**  
0.40 x 0.40 x 0.40 mm³

**Theta range for data collection**  
1.629 to 30.466°

**Index ranges**  
-6<=h<=9, -10<=k<=20, -37<=l<=33

**Reflections collected**  
18432

**Independent reflections**  
7871[R(int) = 0.0324]

**Completeness to theta =30.466°**  
97.5%

**Absorption correction**  
Multi-scan

**Max. and min. transmission**  
0.974 and 0.749

**Refinement method**  
Full-matrix least-squares on F²

**Data / restraints / parameters**  
7871/ 441/ 467

**Goodness-of-fit on F²**  
1.049

**Final R indices [I>2sigma(I)]**  
R1 = 0.0560, wR2 = 0.1344

**R indices (all data)**  
R1 = 0.0693, wR2 = 0.1438

**Flack parameter**  
x = -4.9(10)

**Largest diff. peak and hole**  
0.309 and -0.294 e.Å⁻³

### 11.3. 1,1,2-trimethyl-1H-cyclopenta[l]phenanthrene (6u)

The single crystals of compound 6u suitable for X-ray diffraction analysis were obtained from a solution of cyclohexane/isopropanol. The crystal structure information for this compound has been deposited at...
the Cambridge Crystallographic Data Centre. CCDC 1571033 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

Identification code mo_XYTMR76
Empirical formula C20H18
Formula weight 258.34
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Orthorhombic
Space group Iba2
Unit cell dimensions a = 20.2195(6) Å, a = 90°,
b = 31.6626(10) Å, b = 90°,
c = 8.7280(2) Å, c = 90°.
Volume 5587.7(3) Å³
Z 16
Density (calculated) 1.228 Mg/m³
Absorption coefficient 0.069 mm⁻¹
F(000) 2208
Crystal size 0.30 x 0.30 x 0.20 mm³
Theta range for data collection 1.195 to 31.531°.
Index ranges -29<=h<=20, -46<=k<=45, -12<=l<=7
Reflections collected 23162
Independent reflections 7300[R(int) = 0.0281]
Completeness to theta =31.531° 96.5%
Absorption correction Multi-scan
Max. and min. transmission 0.986 and 0.758
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 7300/ 1/ 367
Goodness-of-fit on F² 1.021
Final R indices [I>2sigma(I)] R1 = 0.0391, wR2 = 0.1008
R indices (all data) R1 = 0.0446, wR2 = 0.1054
Flack parameter x =0.3(10)
Largest diff. peak and hole 0.344 and -0.225 e.Å⁻³

11.4. (7S*,7aR*,8R*,8aS*)-7-cyclohexyl-7a-methyl-8-(naphthalen-1-yl)-7,7a,8,8*-tetrahydrocyclopropa[4,5]cyclopenta[1,2-a]naphthalene (11)
The single crystals of compound 11 suitable for X-ray diffraction analysis were obtained from a solution of cyclohexane/isopropanol. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571035 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

Identification code: mo_XY_TMR15_0m
Empirical formula: C31H30
Formula weight: 402.55
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: Pca2(1)
Unit cell dimensions:
\[a = 21.3313(10)\text{Å} \quad a = 90^\circ,\]
\[b = 6.0491(2)\text{Å} \quad b = 90^\circ,\]
\[c = 34.2679(15)\text{Å} \quad g = 90^\circ.\]
Volume: 4421.8(3) Å³
Z: 8
Density (calculated): 1.209 Mg/m³
Absorption coefficient: 0.068 mm⁻¹
\(F(000)\): 1728
Crystal size: 0.45 x 0.08 x 0.04 mm³
Theta range for data collection: 2.000 to 27.501°
Index ranges: -27<=h<=27, -7<=k<=7, -44<=l<=44
Reflections collected: 72531
Independent reflections: 10136\([R(int) = 0.0381]\)
Completeness to theta =27.501°: 99.9%
Absorption correction: Empirical
Max. and min. transmission: 0.997 and 0.95
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 10136/ 1/ 561
Goodness-of-fit on F²: 1.031
Final R indices [I>2sigma(I)]: R1 = 0.0379, wR2 = 0.0907
R indices (all data): R1 = 0.0455, wR2 = 0.0950
Flack parameter: x = -2.9(10)
Largest diff. peak and hole: 0.236 and -0.235 e.Å⁻³

11.5. endo-4,8,8-trimethyl-7-phenyl-3a,4,7,7a-tetrahydro-4,7-methano-isobenzofuran-1,3-dione (12)
The single crystals of compound 12 suitable for X-ray diffraction analysis were obtained from a solution of heptane/dichloromethane. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571037 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

Identification code: mo_MM143F_0m
Empirical formula: C18 H18 O3
Formula weight: 282.32
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: P2(1)2(1)2(1)
Unit cell dimensions:
- a = 6.4200(5)Å, a = 90°.
- b = 12.0907(9)Å, b = 90°.
- c = 18.3454(14)Å, g = 90°.
Volume: 1424.01(19) Å³
Z: 4
Density (calculated): 1.317 Mg/m³
Absorption coefficient: 0.089 mm⁻¹
F(000): 600
Crystal size: 0.20 x 0.10 x 0.02 mm³
Theta range for data collection: 2.017 to 29.904°.
Index ranges:
-8<=h<=9, -10<=k<=16, -24<=l<=25
Reflections collected: 22310
Independent reflections: 93 [R(int) = 0.0436]
Completeness to theta =29.904°: 99.8%
Absorption correction: Multi-scan
Max. and min. transmission: 0.998 and 0.768
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 4093/ 0/ 193
Goodness-of-fit on F²: 1.044
Final R indices [I>2sigma(I)]: R1 = 0.0408, wR2 = 0.0931
R indices (all data): R1 = 0.0529, wR2 = 0.0995
Flack parameter: x =0.3(5)
Largest diff. peak and hole: 0.300 and -0.233 e.Å

11.6. (4aS*,7R*,7aS*,12bR*)-9,12-dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[d]fluorine (16a)
The single crystals of compound 16a suitable for X-ray diffraction analysis were obtained from a solution of CDCl₃. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1571034 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

Identification code       mo_XYTS184D_0m
Empirical formula        C21 H30 O2
Formula weight           314.45
Temperature              100(2) K
Wavelength               0.71073 Å
Crystal system           Triclinic
Space group              P-1
Unit cell dimensions     a = 9.1291(4)Å  a= 70.1811(9)°.
b = 9.5424(3)Å  b = 85.6475(11)°.
c = 11.2264(4)Å  g = 69.8209(10)°.
Volume                   862.64(6) Å³
Z                        2
Density (calculated)     1.211 Mg/m³
Absorption coefficient   0.075 mm⁻¹
F(000)                   344
Crystal size             0.30 x 0.20 x 0.20 mm³
Theta range for data collection 2.379 to 30.535°.
Index ranges            -7<=h<=13,-12<=k<=13,-16<=l<=15
Reflections collected   10347
Independent reflections 5004[R(int) = 0.0154]
Completeness to theta =30.535° 94.8%
Absorption correction   Multi-scan
Max. and min. transmission 0.985 and 0.955
Refinement method       Full-matrix least-squares on F2
Data / restraints / parameters 5004/ 0/ 212
Goodness-of-fit on F2    1.046
Final R indices [I>2sigma(I)] R1 = 0.0406, wR2 = 0.1098
R indices (all data)     R1 = 0.0468, wR2 = 0.1151
Largest diff. peak and hole 0.424 and -0.194 e.Å⁻³
11. NMR Spectra

7-(2-Methoxyphenyl)cyclohepta-1,3,5-triene (1c)
7-(2,5-Dimethoxyphenyl)cyclohepta-1,3,5-triene (1f)
7-(4-(Tert-butyl)phenyl)cyclohepta-1,3,5-triene (1j)
1-Ethynyl-3,3-dimethylcyclohexyl methyl carbonate
1,1-Dimethyl-3-(1\textcircled{5}\textsuperscript{-}vinylidene)cyclohexane (5e)
1-Ethynylecyclodecyl methyl carbonate
(1\(\lambda^5\)-Vinylidene)cyclodecane (5g)
2,3-Dimethyl-3-phenethyl-3H-cyclopenta[a]naphthalene (6a)
1,2-Dimethyl-1-phenethyl-1H-indene (6b)
4-Methoxy-1,2-dimethyl-1-phenethyl-1H-indene (6c)
1,2-Dimethyl-1-phenethyl-4-phenoxy-1H-indene (6d)
6-Methoxy-1,2-dimethyl-1-phenethyl-1H-indene (6e)
4,7-Dimethoxy-1,2-dimethyl-1-phenethyl-1H-indene (6f)
6-Chloro-1,2-dimethyl-1-phenethyl-1H-indene (6g)
1,2-Dimethyl-1-phenethyl-4-phenyl-1H-indene (6h)
1,2-Dimethyl-1,4-diphenethyl-1H-indene (6i)
6-(Tert-butyl)-1,2-dimethyl-1-phenethyl-1H-indene (6j)
2,3,3-Trimethyl-3H-cyclopenta[a]naphthalene (6k)
3-Cyclohexyl-2,3-dimethyl-3H-cyclopta[a]naphthalene (6l)
2'-Methylspiro[cyclohexane-1,3'-cyclopenta[a]naphthalene] (6m)
2',3,3-Trimethylspiro[cyclohexane-1,3'-cyclopenta[a]naphthalene] (6n)
2'-Methylspiro[cycloheptane-1,3'-cyclopenta[a]naphthalene] (60)
2'-Methylospiro[cyclodecane-1,3'-cyclopenta[a]naphthalene] (6p)
1,1,2-Trimethyl-\(1H\)-cyclopenta[\(a\)]naphthalene (6q)
1,2-Dimethyl-1-phenethyl-1H-cyclopenta[a]naphthalene (6r)
1-Cyclohexyl-1,2-dimethyl-1H-cyclopenta[a]naphthalene (6s)
2'-Methylspiro[cyclohexane-1,1'-cyclopenta[a]naphthalene] (6t)
1,1,2-Trimethyl-1H-cyclopental[lf]phenanthrene (6u)
1,2-Dimethyl-1-phenethyl-1H-cyclopenta[/]phenanthrene (6v)
7-Cyclohexyl-7a-methyl-8-(naphthalen-1-yl)-7,7a,8a-tetrahydrocyclopropa[4,5]cyclopenta[1,2-a]naphthalene (11)
(E)-7-(4-methylstyryl)cyclohepta-1,3,5-triene (2b)
(E)-7-(2-Fluorostyryl)cyclohepta-1,3,5-triene (2f)
$^{13}$C NMR Detail and $^{19}$F NMR
(E)-2-(2-(cyclohepta-2,4,6-trien-1-yl)vinyl)naphthalene (2g)
(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)benzene (7a)
1-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methylbenzene (7b)
(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (7c)
$^{13}$C NMR Detail and $^{19}$F NMR
1-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-4-methoxybenzene (7d)
1-bromo-4-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-benzene (7e)
1-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)-2-fluorobenzene (7f)
$^{13}C$ NMR Detail and $^{19}F$ NMR

![Diagram of molecular structure]

![NMR spectra]

![Diagram of molecular structure]

![NMR spectra]
(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (7g)
1-methyl-4-(4,5,5-trimethylcyclopenta-1,3-dien-1-yl)benzene (7h)
1-methyl-4-(p-tolyl)spiro[4.5]deca-1,3-diene (7i)
2-(4,5,5-trimethyl-cyclopenta-1,3-dien-1-yl)naphthalene (7j)
2-(4,5-dimethyl-5-phenethylcyclopenta-1,3-dien-1-yl)naphthalene (7k)
Endo-4,8,8-trimethyl-7-phenyl-3a,4,7,7a-tetrahydro-4,7-methano-isobenzofuran-1,3-dione (12)
Laurokamurene B (10)

-152.83
-140.00
-128.60
-126.76
-116.15
-110.47
-106.67
-103.97
-101.07
-97.73
-93.80
-87.86
-83.26
-75.62

Me

Me

Me

Me

Me

Me
2-(2-Cyanoethyl)-1-ethynylcyclohexyl methyl carbonate (SI2)
3-(2-(1λ⁵-Vinylidene)cyclohexyl)propanenitrile (SI3)
4-(2-(1,5-Vinylidene)cyclohexyl)butan-2-one (SI4)
4-(2-(1\textsuperscript{5}\textsuperscript{5}\textsuperscript{5}-Vinylidene)cyclohexyl)butan-2-ol (SI5)
4-(2-(1\textsuperscript{\textdegree}V Vinylidene)cyclohexyl)butan-2-yl benzoate (5i)
4-((1R*)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-yl benzoate (13)

4-((1R)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-yl benzoate (13')
4-((1R*,2S*)-4’,7’-Dimethoxy-2’-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (14a)
4-((1R*,2R*)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-inden]-2-yl)butan-2-one (14b)
(1R*,2S*)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (15a)
(4aS*,7R*,7aS*,12bR*)-9,12-Dimethoxy-7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzod[\textdagger]fluorine (16a)
(4aS*,7R*,7aS*,12bR*)-7,7a-Dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[d]fluorene-9,12-dione (17a) – Cycloaurenones Carbon Skeleton
(1R*,2R*)-2-(3-Bromobutyl)-4',7'-dimethoxy-2'-methylspiro[cyclohexane-1,1'-indene] (15b).
(4a\textsuperscript{R},7a\textsuperscript{S})-9,12-Dimethoxy-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo [d]fluorine (16b) – Dysiherbols Carbon Skeleton
(4aR*,7aS*)-7,7a-dimethyl-1,2,3,4,4a,5,6,7,7a,8-decahydrobenzo[d]fluorene-9,12-dione (17b).