Supporting Information

Gold(I) Carbenes by Retro-Buchner Reaction: Generation
and Fate

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1. General Methods.

All reactions were carried out under Argon in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography was carried out using TLC aluminum sheets with 0.2 mm of silica gel (Merck Gf234). Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23 ºC on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra were recorded on a Waster LCT Premier Spectrometer (ESI and APCI) or on an Autoflex Broker Daltonics (MALDI and LDI). Melting points were determined using a Büchi melting point apparatus.

2. General Procedure for the Synthesis of Arylcycloheptatrienes.

Procedure A:

\[
n-\text{BuLi (1.6 M in hexanes, 0.33 mL, 0.53 mmol) was added dropwise to the solution of corresponding aryl bromide}\,^1 (0.5 \text{ mmol}) \text{ in dry THF (2 mL, 0.2 M) at } -78 \, ^\circ\text{C under argon. The mixture was stirred for 30 min at } -78 \, ^\circ\text{C, and then tropylium tetrafluoroborate or tropylium bromide}\,^2 (0.33 \text{ mmol}) \text{ was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 \, ^\circ\text{C}) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over MgSO}_4, \text{ and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.}
\]

Procedure A-2:

\[
n-\text{BuLi (1.6 M in hexanes, 0.63 mL, 1 mmol) was added dropwise to the solution of corresponding aryl bromide (0.5 mmol) in dry THF (5 mL, 0.1 M) at } -78 \, ^\circ\text{C under argon. The mixture was stirred for 30 min at } -78 \, ^\circ\text{C, and then tropylium tetrafluoroborate or tropylium bromide (1 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 \, ^\circ\text{C}) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over MgSO}_4, \text{ and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.}
\]

(1) The aryl bromides were prepared according to the literature procedures: (a) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. J. Org. Chem. 2007, 72, 9203–9207. (b) Rossi, R.; Carpita, A.; Ribecai, A.; Mannina, L. Tetrahedron. 2001, 57, 2847–2856. (c) Qi, W.-Y.; Zhu, T.-S.; Xu, M.-H. Org. Lett. 2011, 13, 3410–3413. (d) de Meijere, A.; Song, Z.-Z.; Lansky, A.; Hyudaa, S.; Raucha, K.; Noltemeyer, M.; Konig, B.; Knieriem, B. Eur. J. Org. Chem. 1998, 2289–2299.

(2) Tropylium bromide was prepared according to the reported procedure: Doering, W. E.; Knox, L. H. J. Am. Chem. Soc. 1957, 79, 352–356. Tropylium tetrafluoroborate was purchased from Alfa Aesar.
Experimental Details for the Synthesis of o-Alkenyl Cycloheptatrienes

*(E)-7-(2-Styrylphenyl)cyclohepta-1,3,5-triene (7a)*

This compound was prepared as a yellow oil in 74% yield according to the general procedure A.

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.69 (dd, J = 6.9, 2.2 Hz, 1H), 7.52 - 7.42 (m, 3H), 7.39 - 7.26 (m, 6H), 6.96 (d, J = 16.1 Hz, 1H), 6.78 (t, J = 3.2 Hz, 2H), 6.35 - 6.29 (m, 2H), 5.48 (dd, J = 9.0, 5.4 Hz, 2H), 3.12 (tt, J = 5.6, 1.6 Hz, 1H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)} \delta 141.0, 137.5, 136.4, 130.9, 130.6, 128.6, 127.9, 127.6, 126.9, 126.6, 126.5, 124.5, 42.5. \]

HRMS-APCI calculated for C\text{21}H\text{19} [M+H]^+: 271.1487; found: 271.1497

*(E)-7-(2-(4-Chlorostyryl)phenyl)cyclohepta-1,3,5-triene (7b)*

This compound was prepared as a colorless solid in 63% yield according to the general procedure A.

\[ \text{m.p. 65-67 °C} \]

\[ \text{1H NMR (500 MHz, CDCl}_3\text{)} \delta 7.66 (dd, J = 7.5, 1.7 Hz, 1H), 7.52 (dd, J = 7.5, 1.6 Hz, 1H), 7.40 - 7.30 (m, 6H), 7.26 (d, J = 16.0 Hz, 1H), 6.91 (d, J = 16.0 Hz, 1H), 6.79 (t, J = 3.2 Hz, 2H), 6.35 - 6.30 (m, 2H), 5.47 (dd, J = 9.1, 5.4 Hz, 2H), 3.09 (t, J = 5.4 Hz, 1H). \]

\[ \text{13C NMR (126 MHz, CDCl}_3\text{)} \delta 141.0, 136.0, 136.0, 133.1, 130.9, 129.2, 128.8, 128.1, 127.7, 127.6, 127.2, 126.9, 126.5, 124.5, 42.5. \]

HRMS-APCI calculated for C\text{21}H\text{18}Cl [M+H]^+: 305.1097; found: 305.1092

*(E)-7-(2-(4-Methylstyrlyl)phenyl)cyclohepta-1,3,5-triene (7c)*

This compound was prepared as a colorless solid in 76% yield according to the general procedure A.

\[ \text{m.p. 70-72 °C} \]

\[ \text{1H NMR (500 MHz, CDCl}_3\text{)} \delta 7.68 (dd, J = 7.0, 2.3 Hz, 1H), 7.51 (dd, J = 7.2, 2.0 Hz, 1H), 7.39 - 7.33 (m, 4H), 7.25 (d, J = 15.9 Hz, 1H), 7.17 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 16.1 Hz, 1H), 6.78 (t, J = 3.2 Hz, 2H), 6.33 - 6.29 (m, 2H), 5.49 (dd, J = 9.1, 5.4 Hz, 2H), 3.12 (t, J = 5.4 Hz, 1H), 2.38 (s, 3H). \]

\[ \text{13C NMR (126 MHz, CDCl}_3\text{)} \delta 140.9, 137.5, 136.6, 134.8, 130.9, 129.3, 127.7, 127.6, 126.8, 126.6, 126.5, 126.4, 125.6, 124.5, 42.5, 21.2. \]
HRMS-APCI calculated for C$_{22}$H$_{21}$ [M+H]$^+$: 285.1643; found: 285.1641

(E)-7-(2-(3-Methylstyryl)phenyl)cyclohepta-1,3,5-triene (7d)

This compound was prepared as a yellow oil in 83% yield according to the general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 (dd, $J = 7.0$, 2.2 Hz, 1H), 7.51 (dd, $J = 7.3$, 1.9 Hz, 1H), 7.39 - 7.32 (m, 2H), 7.31 - 7.24 (m, 4H), 7.09 (d, $J = 6.9$ Hz, 1H), 6.93 (d, $J = 16.1$ Hz, 1H), 6.79 (t, $J = 3.2$ Hz, 2H), 6.67 - 6.59 (m, 5H), 5.49 (dd, $J = 9.0$, 5.4 Hz, 2H), 3.12 (t, $J = 5.3$ Hz, 1H), 2.38 (s, 3H). 13C NMR (101 MHz, CDCl$_3$) δ 141.0, 138.2, 137.5, 136.5, 130.9, 130.8, 128.5, 128.4, 127.8, 127.6, 127.4, 126.9, 126.6, 126.5, 126.4, 124.5, 123.5, 42.5, 21.4.

HRMS-APCI calculated for C$_{24}$H$_{25}$ [M+H]$^+$: 313.1956; found: 313.1960

(E)-7-(2-(2,4,6-Trimethylstyryl)phenyl)cyclohepta-1,3,5-triene (7e)

This compound was prepared as a white solid in 60% yield according to the general procedure A.

m.p. 89-91 ºC

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (dd, $J = 7.1$, 2.2 Hz, 1H), 7.53 (dd, $J = 7.2$, 2.0 Hz, 1H), 7.40 - 7.36 (m, 2H), 6.98 - 6.88 (m, 3H), 6.80 - 6.70 (m, 3H), 6.27 - 6.25 (m, 2H), 5.46 (dd, $J = 9.0$, 5.4 Hz, 2H), 3.07 (dd, $J = 6.2$, 4.6 Hz, 1H), 2.30 (s, 9H). 13C NMR (101 MHz, CDCl$_3$) δ 140.9, 137.1, 136.3, 136.1, 134.2, 131.6, 130.9, 129.1, 128.6, 127.8, 127.3, 126.8, 126.4, 126.5, 124.5, 122.1, 20.9.

HRMS-APCI calculated for C$_{24}$H$_{25}$ [M+H]$^+$: 313.1956; found: 313.1960

(E)-7-(2-(3-Phenylprop-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene (7f)

This compound was prepared as a yellow oil in 49% yield according to the general procedure A.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.47 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.33 - 7.30 (m, 3H), 7.28 - 7.19 (m, 4H), 6.76 (t, $J = 3.2$ Hz, 2H), 6.59 (d, $J = 15.5$ Hz, 1H), 6.29 - 6.27 (m, 2H), 6.19 (dt, $J = 15.5$, 6.9 Hz, 1H), 5.43 (dd, $J = 9.1$, 5.4 Hz, 2H), 3.52 (dd, $J = 7.0$, 1.5 Hz, 2H), 3.04 (t, $J = 5.3$ Hz, 1H). 13C NMR (126 MHz, CDCl$_3$) δ 140.4, 140.1, 136.8, 131.4, 130.8, 129.0, 128.6, 128.4, 127.4, 127.3, 126.8, 126.7, 126.6, 126.0, 124.4, 42.2, 39.5.
HRMS-APCI calculated for C_{22}H_{21}[M+H]^+: 285.1643; found: 285.1649

7-(2-((1E,3E)-4-Phenylbuta-1,3-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7g)

This compound was prepared as a colorless solid in 82% yield according to the general procedure A from 1-bromo-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)benzene (see 7u synthesis).

m.p. 124-125 ºC

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.68 - 7.64 (m, 1H), 7.49 - 7.44 (m, 3H), 7.37 - 7.30 (m, 4H), 7.25 (t, $J = 7.3$ Hz, 1H), 6.94 (ddd, $J = 15.5, 5.9, 4.1$ Hz, 1H), 6.90 - 6.84 (m, 2H), 6.79 (dd, $J = 3.7, 2.7$ Hz, 2H), 6.68 (d, $J = 15.3$ Hz, 1H), 6.36 - 6.29 (m, 2H), 5.45 (dd, $J = 9.0, 5.3$ Hz, 2H), 3.10 (t, $J = 5.6$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.8, 137.3, 136.1, 132.8, 131.0, 130.9, 130.3, 129.5, 128.6, 127.9, 127.5, 126.8, 126.8, 126.4, 126.2, 124.5, 42.4.

HRMS-APCI calculated for C$_{23}$H$_{21}$[M+H]^+: 297.1643; found: 297.1650

(E)-7-(2-(Oct-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene (7h)

This compound was prepared as a yellow oil in 69% yield according to the general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (dd, $J = 7.2, 1.9$ Hz, 1H), 7.45 (dd, $J = 7.3, 1.8$ Hz, 1H), 7.32 - 7.24 (m, 2H), 6.76 (t, $J = 3.2$ Hz, 2H), 6.50 (d, $J = 15.5$ Hz, 1H), 6.32 - 6.26 (m, 2H), 6.03 (dt, $J = 15.5, 6.9$ Hz, 1H), 5.43 (dd, $J = 9.1, 5.5$ Hz, 2H), 3.05 (t, $J = 5.2$ Hz, 1H), 2.17 (qd, $J = 7.1, 1.5$ Hz, 2H), 1.45 - 1.25 (m, 8H), 0.90 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.2, 137.2, 133.5, 130.8, 127.5, 127.4, 127.1, 126.9, 126.7, 126.6, 124.3, 42.3, 33.2, 31.7, 29.2, 28.8, 22.6, 14.1.

HRMS-APCI calculated for C$_{21}$H$_{27}$[M+H]^+: 279.2113; found: 279.2108

(E)-7-(2-(6-Methylhepta-1,5-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7i)

This compound was prepared as a colorless oil in 78% yield according to the general procedure A.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 - 7.44 (m, 2H), 7.34 - 7.22 (m, 2H), 6.76 (t, $J = 3.2$ Hz, 2H), 6.52 (d, $J = 15.6$ Hz, 1H), 6.30 - 6.26 (m, 2H), 6.05 (dt, $J = 15.6, 6.7$ Hz, 1H), 5.43 (dd, $J = 9.1, 5.5$ Hz, 2H), 5.17 - 5.13 (m, 1H), 3.04 (t, $J = 5.6$ Hz, 1H), 2.24 - 2.17 (m, 2H), 2.13 (q, $J = 6.9$ Hz, 2H), 1.71 (s, 3H), 1.62 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.2, 137.1, 132.9, 131.9, 130.8, 127.8, 127.4, 127.2, 126.9, 126.7, 126.6, 124.3, 123.7, 42.3, 33.4, 27.8, 25.7, 17.7.
To a suspension of NaH (60% in oil, 290 mg, 7.3 mmol) in THF (20 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate 3 (2 g, 6.6 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then (±)-citronellal (1.02 g, 6.6 mmol) was added dropwise and slowly warmed to room temperature. After stirring overnight (12 h), the reaction was quenched with ice water and the aqueous phase was extracted with Et 2O. The combined organic layers were washed with brine and dried over MgSO 4. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give 1.65g (E)-1-bromo-2-(4,8-dimethylnona-1,7-dien-1-yl)benzene as colorless oil in 81% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 7.55 (dd, J = 8.0, 1.3 Hz, 1H), 7.51 (dd, J = 7.8, 1.7 Hz, 1H), 7.30 - 7.22 (m, 1H), 7.08 (ddd, J = 8.0, 1.7 Hz, 1H), 6.72 (d, J = 15.7 Hz, 1H), 6.17 (dt, J = 15.7, 7.3 Hz, 1H), 5.19 - 5.05 (m, 1H), 2.35 - 2.27 (m, 1H), 2.19 - 1.98 (m, 3H), 1.77 - 1.61 (m, 7H), 1.50 - 1.42 (m, 1H), 1.28 - 1.20 (m, 1H), 0.98 (d, J = 6.7 Hz, 3H). \]

\[ ^{13}C \text{NMR (75 MHz, CDCl}_3 \delta 137.76, 132.84, 132.80, 131.26, 129.84, 128.10, 127.35, 126.88, 124.74, 123.12, 40.48, 36.72, 32.80, 25.74, 25.61, 19.54, 17.69. \]

HRMS-APCI calculated for C17H24Br [M+H]+: 307.1056; found: 307.1050

The title compound was prepared according to general procedure A from (E)-1-bromo-2-(4,8-dimethylnona-1,7-dien-1-yl)benzene as colorless oil in 71% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 7.49 – 7.45 (m, 2H), 7.31 - 7.25 (m, 2H), 6.75 (dd, J = 3.7, 2.7 Hz, 2H), 6.50 (d, J = 15.6 Hz, 1H), 6.30 - 6.24 (m, 2H), 6.01(dt, J = 15.5, 7.3 Hz, 1H), 5.45 - 5.39 (m, 2H), 5.12 (ddt, J = 8.6, 5.7, 1.4 Hz, 1H), 3.13 - 3.00 (m, 1H), 2.24 - 2.16 (m, 1H), 2.07 - 1.95 (m, 3H), 1.71 (s, 3H), 1.64 - 1.56 (m, 4H), 1.43 - 1.34 (m, 1H), 1.20 – 1.15 (m, 1H), 0.91 (d, J = 6.7 Hz, 3H). \]

\[ ^{13}C \text{NMR (75 MHz, CDCl}_3 \delta 140.25, 137.30, 132.05, 131.12, 130.83, 128.92, 127.44, 127.21, 126.95, 126.92, 126.68, 124.83, 124.35, 42.36, 40.65, 36.65, 32.83, 25.73, 25.62, 19.52, 17.67. \]

HRMS-APCI calculated for C24H31 [M+H]+: 319.2420; found: 319.2429

7-(2-((E)-2-((1R*,2S*,3R*)-2,3-diphenylcyclopropyl)vinyl)phenyl)cyclohepta-1,3,5-triene (7k)
To a suspension of NaH (60% in oil, 99 mg, 2.47 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (759 mg, 2.47 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then trans-2,trans-3-diphenylcyclopropanecarboxaldehyde (500 mg, 2.25 mmol) in 1 mL THF was added dropwise and slowly warmed to room temperature. After stirring overnight (12 h), the reaction was quenched with ice water and the aqueous phase was extracted with Et₂O. The combined organic layers were washed with brine and dried over MgSO₄. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give 710 mg of ((E)-2-bromostyryl)cyclopropane-1,2-diyl)dibenzene as a colorless solid in 84% yield. m.p. 114-116 ºC

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3 \text{) } & \delta 7.58 (dd, J = 8.1, 1.3 \text{ Hz}, 1H), 7.56 (dd, J = 7.9, 1.7 \text{ Hz}, 1H), 7.29 (dd, J = 7.7 \text{ Hz}, 1H), 7.20 - 7.08 (m, 7H), 7.05 - 6.99 (m, 5H), 6.15 (dd, J = 15.6, 8.3 \text{ Hz}, 1H), 2.72 (d, J = 5.6 \text{ Hz}, 2H), 2.61 - 2.56 (m, 1H). \\
\text{C NMR (126 MHz, CDCl}_3 \text{) } & \delta 137.19, 137.13, 135.37, 132.98, 128.94, 128.24, 127.87, 127.58, 127.44, 126.51, 126.01, 123.11, 33.49, 30.01.
\end{align*}
\]

HRMS-APCI calculated for C₂₃H₂₀Br [M+H]⁺: 375.0743; found: 375.0740

The title compound was prepared according to general procedure A from ((E)-2-bromostyryl)cyclopropane-1,2-diyl)dibenzene as colorless oil in 84% yield.

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3 \text{) } & \delta 7.54 (dd, J = 7.4, 1.8 \text{ Hz}, 1H), 7.49 (dd, J = 7.4, 1.7 \text{ Hz}, 1H), 7.35 - 7.29 (m, 2H), 7.18 - 7.09 (m, 6H), 6.99 - 6.95 (m, 4H), 6.82 - 6.76 (m, 3H), 6.34 - 6.30 (m, 2H), 5.99 (dd, J = 15.5, 8.3 \text{ Hz}, 1H), 5.47 (dd, J = 9.1, 5.4 \text{ Hz}, 2H), 3.13 - 3.09 (m, 1H), 2.63 (d, J = 5.5 \text{ Hz}, 2H), 2.46 (dt, J = 8.3, 5.6 \text{ Hz}, 1H). \\
\text{C NMR (101 MHz, CDCl}_3 \text{) } & \delta 140.30, 137.39, 136.53, 134.51, 130.94, 128.95, 127.80, 127.65, 127.39, 126.88, 126.77, 126.49, 126.46, 125.90, 124.49, 42.31, 33.29, 30.11.
\end{align*}
\]

HRMS-APCI calculated for C₃₀H₂₇ [M+H]⁺: 387.2107; found: 387.2105

1,4-Bis((E)-2-cyclohepta-2,4,6-trien-1-yl)styryl]benzene (7l)

(4) Castellino, A. J.; Bruice, T. C. J. Am. Chem. Soc. 1988, 110, 7512–7519.
To a suspension of NaH (60% in oil, 217 mg, 5.42 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (1.51 g, 4.92 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of terephthalaldehyde (300 mg, 2.24 mmol) in THF (2 mL) was added dropwise and slowly warmed to room temperature. After stirring for 2 d at room temperature, (during which time a precipitate formed) the reaction was quenched with ice water and the precipitate was collected by filtering, and washed with Et2O and water, dried with vacuum. 1,4-bis((E)-2-bromostyryl)benzene was obtained as a light yellow solid. (620 mg, 63%).

m.p. 170-172 ºC

^1^H NMR (400 MHz, CDCl₃) δ 7.71 (dd, J = 7.9, 1.6 Hz, 2H), 7.62 (dd, J = 8.1, 1.2 Hz, 2H), 7.59 (s, 4H), 7.53 (d, J = 16.2 Hz, 2H), 7.35 (td, J = 7.6, 1.2 Hz, 2H), 7.15 (td, J = 7.7, 1.7 Hz, 2H), 7.08 (d, J = 16.1 Hz, 2H). ^1^C NMR (101 MHz, CDCl₃) δ 137.0, 136.8, 133.1, 130.9, 128.8, 127.5, 127.2, 126.6, 124.2.

HRMS-LDI+ calculated for C₂₂H₁₆Br₂ [M]+: 437.9619; found: 437.9621

The title compound was prepared according to general procedure A-2 from the 1,4-bis((E)-2-bromostyryl)benzene as yellow solid in 41% yield.

m.p. 161–163 ºC

^1^H NMR (500 MHz, CDCl₃) δ 7.73 - 7.66 (m, 2H), 7.54 - 7.26 (m, 12H), 6.97 (d, J = 16.0 Hz, 2H), 6.80 (t, J = 3.1 Hz, 4H), 6.32 - 6.30 (m, 4H), 5.50 (dd, J = 9.0, 5.3 Hz, 4H), 3.15 - 3.08 (m, 2H). ^1^C NMR (126 MHz, CDCl₃) δ 141.0, 136.9, 136.3, 130.9, 130.1, 127.9, 126.9, 126.8, 126.6, 126.5, 124.5, 42.6.

HRMS-LDI+ calculated for C₃₆H₂₉ [M-H]+: 461.2269; found: 461.2264

2’-(Cyclohepta-2,4,6-trien-1-yl)-2,3,4,5-tetrahydro-1,1’-biphenyl (7m)
2'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl was prepared according to a reported procedure.\(^5\)

\[
\text{[Ir(COD)Cl]}_2 \text{ (2 mol %, 20 mg) and bis(pinacolato)diboron (1.5 mmol, 381 mg) were dissolved in 1 mL neat cyclohexene. The reaction mixture was stirred at 70 °C for 24 h under argon. After cooling to room temperature the reaction mixture was diluted with a dioxane/water (6:1) mixture (4 ml), then 2-bromiodobenzene (1.5 mmol), Pd(PPh\(_3\))\(_4\) (5 mol %, 80 mg) and Ba(OH)\(_2\)·8H\(_2\)O (3.0 mmol, 946 mg) were added. Then stirring was continued for 24 h at 70 °C. The crude reaction mixture was evaporated and the residue was purified by silica gel column chromatography to give 240 mg aryl bromide as colorless oil in 67% yield.}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.25 (td, \(J = 7.4, 1.2\) Hz, 1H), 7.17 (dd, \(J = 7.6, 1.9\) Hz, 1H), 7.10 (td, \(J = 7.9, 1.8\) Hz, 1H), 5.65 (tt, \(J = 3.8, 1.8\) Hz, 1H), 2.32 – 2.28 (m, 2H), 2.22 - 2.16 (m, 2H), 1.83 - 1.76 (m, 2H), 1.75 - 1.66 (m, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.4, 139.1, 132.6, 130.0, 127.9, 127.1, 127.0, 122.5, 29.3, 25.3, 22.8, 21.9.

HRMS-EI calculated for C\(_{12}\)H\(_{13}\)Br [M\(^+\)]: 236.0201; found: 236.0204

This title compound was prepared as a colorless oil in 55% yield according to the general procedure A from 2'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (dd, \(J = 7.8, 1.4\) Hz, 1H), 7.35 (td, \(J = 7.5, 1.5\) Hz, 1H), 7.25 (td, \(J = 7.4, 1.4\) Hz, 1H), 7.14 (dd, \(J = 7.7, 1.5\) Hz, 1H), 6.73 (t, \(J = 3.2\) Hz, 2H), 6.26 - 6.22 (m, 2H), 5.49 - 5.47 (m, 1H), 5.37 (dd, \(J = 9.0, 5.4\) Hz, 2H), 2.95 (t, \(J = 5.6\) Hz, 1H), 2.10 - 2.03 (m, 4H), 1.64 - 1.51 (m, 4H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.7, 141.5, 138.0, 130.6, 128.4, 127.8, 127.1, 126.1, 126.1, 124.0, 42.0, 30.9, 25.2, 22.9, 22.0.

HRMS-EI calculated for C\(_{19}\)H\(_{20}\) [M\(^+\)]: 248.1565; found: 248.1562

\(\text{(E)}\)-1,2-Bis(2-(cyclohepta-2,4,6-trien-1-yl)phenyl)ethane (7n)

\[
\begin{align*}
\text{Br} & \quad \text{P} \quad \text{O} \quad \text{O} \\
1) \text{NaH / THF, 0 °C} & \rightarrow 23 \text{ °C} \\
2) \text{OH} & \quad \text{C} \quad \text{Br} \\
1) \text{n-BuLi, THF, -78 °C} & \\
2) \text{tropylium, 23 °C, 12 h}
\end{align*}
\]

To a suspension of NaH (60% in oil, 145 mg, 3.63 mmol) in THF (4 mL) at 0 °C was slowly added diethyl 2-bromobenzylphosphonate (1 g, 3.3 mmol). The resulting suspension was stirred for 1 h at room temperature (23 °C). The reaction mixture was cooled to 0 °C, and then a solution of 2-bromobenzaldehyde (611 mg, 3.3 mmol) in THF (2 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight, the reaction was quenched with ice water and the aqueous phase

\(\text{Br} \quad \text{P} \quad \text{O} \quad \text{O} \\
\text{Br} \quad \text{Br}
\]

\(\text{42\%}\)

\(^5\) Olsson, V. J.; Szabó, K. J. \textit{Angew. Chem. Int. Ed.} \textbf{2007}, \textit{46}, 6891–6893.
was extracted with Et₂O. The combined organic layers were washed with brine and dried over Na₂SO₄. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give 730 mg (E)-1,2-bis(2-bromophenyl)ethene as a colorless solid in 65% yield. The spectroscopic data match with those reported in the literature.

The title compound was prepared according to general procedure A-2 from (E)-1,2-bis(2-bromophenyl)ethene as white solid in 42% yield.

m.p. 135-137°C

1H NMR (300 MHz, CDCl₃) δ 7.56-7.48 (m, 4H), 7.38-7.27 (m, 4H), 7.10 (s, 2H), 6.76 (t, J = 3.1 Hz, 4H), 6.29 (d, J = 9.0 Hz, 4H), 5.45 (dd, J = 9.1, 5.5 Hz, 4H), 3.10 (t, J = 5.4 Hz, 2H). 13C NMR (75 MHz, CDCl₃) δ 141.0, 136.6, 130.9, 128.5, 127.9, 127.6, 126.9, 126.7, 126.5, 124.5, 42.4.

HRMS-MALDI: calculated for C₂₈H₂₄ [M]+: 360.1878; found: 360.1935

(E)-7-(4-Methyl-2-styrylphenyl)cyclohepta-1,3,5-triene (7p)

This compound was prepared as a white solid in 59% yield according to the general procedure A from (E)-1-bromo-4-methyl-2-styrylbenzene.
m.p. 75-76 ºC

1H NMR (400 MHz, CDCl₃) δ 7.51 (s, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.31 - 7.24 (m, 2H), 7.18 (dd, J = 7.9, 1.9 Hz, 1H), 6.96 (d, J = 16.0 Hz, 1H), 6.78 (t, J = 3.2 Hz, 2H), 6.34 - 6.28 (m, 2H), 5.47 (dd, J = 9.1, 5.5 Hz, 2H), 3.09 (t, J = 5.6 Hz, 1H), 2.43 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 138.2, 137.6, 136.3, 136.1, 130.9, 130.3, 128.7, 128.6, 127.6, 127.5, 127.1, 126.9, 126.6, 126.5, 124.4, 42.2, 21.1.

HRMS-APCI calculated for C₂₂H₂₁ [M+H]+: 285.1643; found: 285.1613

(E)-7-(4-Methyl-2-(oct-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene (7q)

(E)-1-Bromo-4-methyl-2-(oct-1-en-1-yl)benzene

To a DME/H₂O (5 ml / 2 ml) solution of 15 mg Pd(OAc)₂, 50 mg PPh₃, 424 mg K₂CO₃ and 243 mg (1.56 mmol) (E)-oct-1-en-1-ylboronic acid was added 1-bromo-2-iodo-4-methylbenzene (420 mg, 1.41 mmol) at room temperature. The mixture was then heated at 80 °C for 3 h. After cooling to room temperature, the mixture was

(6) Wyatt, P.; Hudson, A.; Charmant, J.; Orpen, A. G.; Phetmung, H. Org. Biomol. Chem. 2006, 4, 2218–2232.
(7) (E)-1-Bromo-4-methyl-2-styrylbenzene is a known compound: Watanabe, S.; Yamamoto, K.; Itagaki, Y.; Iwamura, T.; lwama, T.; Kataoka, T. Tetrahedron 2000, 56, 855–863. It can be also prepared by the Heck reaction of 1-bromo-2-iodo-4-methylbenzene with styrene.
quenched by adding saturated NH₄Cl(aq). The mixture was extracted with ethyl acetate, and the combined organic extracts were dried over MgSO₄. The solvent was removed in vacuo, and the crude residue was purified by silica gel flash column chromatography (SiO₂, c-hexane) to give (E)-1-bromo-4-methyl-2-(oct-1-en-1-yl)benzene (360 mg) colorless oil in 91% yield.

1H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 8.2 Hz, 1H), 7.32 (s, 1H), 6.89 (d, J = 8.2 Hz, 1H), 6.69 (d, J = 15.7 Hz, 1H), 6.18 (dt, J = 15.7, 7.0 Hz, 1H), 2.32 (s, 3H), 2.30 - 2.22 (m, 2H), 1.54 - 1.46 (m, 2H), 1.41 - 1.30 (m, 6H), 0.92 (t, J = 6.9 Hz, 3H).

HRMS-APCI calculated for C₁₅H₂₂Br [M+H]+: 281.0899; found: 281.0901

(E)-7-(4-Methyl-2-(oct-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene

The title compound was prepared as a colorless oil in 56% yield according to general procedure A from (E)-1-bromo-4-methyl-2-(oct-1-en-1-yl)benzene.

1H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 7.8 Hz, 1H), 7.30 (s, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.75 (dd, J = 3.6, 2.6 Hz, 2H), 6.48 (d, J = 15.6 Hz, 1H), 6.31 - 6.24 (m, 2H), 6.03 (dt, J = 15.5, 7.0 Hz, 1H), 5.50 - 5.36 (m, 2H), 3.03 - 2.97 (m, 1H), 2.38 (s, 3H), 2.16 (qd, J = 7.1, 1.5 Hz, 2H), 1.47 - 1.40 (m, 2H), 1.35 - 1.27 (m, 6H), 0.92 (d, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl₃) δ 137.38, 136.99, 136.08, 133.24, 130.79, 127.94, 127.63, 127.41, 127.37, 127.22, 124.23, 42.00, 33.20, 31.74, 29.28, 28.80, 22.65, 21.06, 14.12.

HRMS-APCI calculated for C₂₂H₂₉ [M+H]+: 293.2264; found: 293.2263

(E)-7-(4-Methoxy-2-styrylphenyl)cyclohepta-1,3,5-triene (7r)

To a suspension of NaH (60% in oil, 131 mg, 3.28 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromo-5-methoxylbenzylphosphonate (1 g, 3 mmol). The resulting suspension was stirred for an additional 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of benzaldehyde (290 mg, 2.73 mmol) in THF (1 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight (12 h), the reaction was quenched with ice water and extracted with Et₂O, dried with MgSO₄. (E)-1-bromo-4-methoxy-2-styrylbenzene was obtained as a colorless solid by silica gel column chromatography. (612 mg, 78%).
m.p. 65-67 ºC

1H NMR (500 MHz, CDCl₃) δ 7.59 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 16.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 3.0 Hz, 1H), 7.05 (d, J = 16.2 Hz, 1H), 6.75 (dd, J = 8.8, 3.0 Hz, 1H), 3.88 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 159.04, 137.85, 136.92, 133.58, 131.51, 128.75, 128.14, 127.55, 126.88, 115.08, 114.95, 114.08, 114.95, 111.81, 55.56.

HRMS-APCI calculated for C₁₅H₁₄BrO [M+H]+: 289.0223; found: 289.0218

(E)-7-(4-Methoxy-2-styrylphenyl)cyclohepta-1,3,5-triene

The title compound was prepared according to general procedure A as colorless oil in 86% yield from (E)-1-bromo-4-methoxy-2-styrylbenzene.
1H NMR (300 MHz, CDCl3) δ 7.44 - 6.92 (m, 10H), 6.77 (t, J = 3.2 Hz, 2H), 6.31 - 6.26 (m, 2H), 5.51 - 5.38 (m, 2H), 3.90 (s, 3H), 3.04 (t, J = 5.5 Hz, 1H). 13C NMR (75 MHz, CDCl3) δ 158.37, 137.50, 137.42, 133.61, 130.93, 130.69, 128.81, 128.67, 127.69, 127.03, 126.59, 126.55, 124.39, 113.56, 111.62, 55.39, 41.95.

HRMS-APCI calculated for C22H21O [M+H]+: 301.1587; found: 301.1587

(E)-7-(2-styrylphenyl)cyclohepta-1,3,5-triene-d1 (7a-d1)

The isotopically labeled (E)-1-bromo-2-styrylbenzene-d1 was synthesized as follows:

To a suspension of NaH (60% in oil, 145 mg, 3.63 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (1 g, 3.3mmol). The resulting suspension was stirred for an additional 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of benzaldehyde-α-d1 (353 mg, 3.3 mmol) in THF (2 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight (12h), the reaction was quenched with ice water and the aqueous phase was extracted with Et2O. The combined organic layers were washed with brine and dried over Na2SO4. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give 650 mg isotopically labeled (E)-1-bromo-2-styrylbenzene-d1 as colorless oil in 76% yield.

1H NMR (400 MHz, CDCl3) δ 7.70 (dd, J = 7.8, 1.7 Hz, 1H), 7.63 - 7.57 (m, 3H), 7.50 (s, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.38 - 7.30 (m, 2H), 7.15 (td, J = 7.8, 1.7 Hz, 1H), 7.08 (d, J = 16.1 Hz, 6% residual signal). 13C NMR (101 MHz, CDCl3) δ 137.1, 136.9, 133.0, 131.1 (t, JCD = 23.5 Hz), 128.7, 128.7, 128.0, 127.5, 127.3, 126.8, 126.7, 124.1.

HRMS-APCI calculated for C14H11DBr [M+H]+: 260.0185; found: 260.0189

The title compound was prepared according to general procedure A from isotopically labeled (E)-1-bromo-2-styrylbenzene-d1 as yellow oil in 82% yield.

1H NMR (400 MHz, CDCl3) δ 7.69 (dd, J = 6.9, 2.2 Hz, 1H), 7.52 - 7.42 (m, 3H), 7.39 - 7.26 (m, 6H), 6.96 (residual signal, 7%), 6.78 (t, J = 3.2 Hz, 2H), 6.35 - 6.30 (m, 2H), 5.47 (dd, J = 9.0, 5.4 Hz, 2H), 3.12 (tt, J = 5.6, 1.6 Hz, 1H). 13C NMR (126 MHz, CDCl3) δ 141.0, 137.4, 136.4, 130.9, 130.2 (t, J = 23.1 Hz), 128.6, 127.9, 127.6, 126.9, 126.6, 126.5, 126.4, 124.5. 42.5.

HRMS-APCI calculated for C21H18D [M+H]+: 272.1550; found: 272.1538

(Z)-7-(2-Styrylphenyl)cyclohepta-1,3,5-triene (cis-7a)

(8) Xue, F.; Li, X.; Wan, B. J. Org. Chem. 2011, 76, 7256–7262.

(9) Gajewski, J. J.; Bocian, W.; Harris, N. J.; Olson, L.P.; Gajewski, J. P. J. Am. Chem. Soc. 1999, 121, 326–334.
This compound was prepared as a colorless oil from (Z)-1-bromo-2-styrylbenzene\(^\text{10}\) in 78% yield according to the general procedure A.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (dd, \(J = 7.8, 1.2\) Hz, 1H), 7.35 (td, \(J = 7.5, 1.8\) Hz, 1H), 7.22 - 7.13 (m, 5H), 7.12 - 7.03 (m, 2H), 6.71 (t, \(J = 3.2\) Hz, 2H), 6.61 (d, \(J = 12.1\) Hz, 1H), 6.55 (d, \(J = 12.0\) Hz, 1H), 6.25 - 6.19 (m, 2H), 5.38 (dd, \(J = 9.1, 5.5\) Hz, 2H), 3.09 - 3.05 (m, 1H). 13C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 141.7, 136.9, 136.6, 131.0, 130.7, 129.7, 129.1, 129.0, 128.0, 127.8, 127.3, 127.0, 126.5, 126.3, 124.5, 42.4.

HRMS-EI calculated for C\(_{21}\)H\(_{18}\) [M\(^+\): 270.1409; found: 270.1400

To a solution of 2-bromobenzyltriphenylphosphonium bromide (2 g, 3.9 mmol) and (E)-cinnamaldehyde (516 mg, 3.9 mmol) in 30 mL chloroform was slowly added 50% NaOH(aq) (780 mg NaOH, 19.5 mmol). The resulting mixture was stirred overnight (12 h) at room temperature (23 ºC). The layers were separated, and the aqueous phase extracted twice with DCM. The combined organic extracts were washed with water then dried over MgSO\(_4\). After concentration in vacuo, 5 mL c-hexane was added and the resulting triphenylphosphine oxide precipitate was removed by filtration. The c-hexane solution was passed through a short pad of silica gel then concentrated in vacuo to give 860 mg colorless oil (77%, Z:E = 1:1). The pure samples of Z (320mg, colorless oil) and E (280mg, light yellow solid) products were obtained by very careful silica gel chromatography using c-hexane as eluent.

**Note:** The (1\(E\),3\(E\)) sample can be also prepared from diethyl 2-bromobenzylphosphonate and (E)-cinnamaldehyde using the same procedure described for deuterated (E)-1-bromo-2-styrylbenzene synthesis shown in this SI as well. By using this HWE olefination, only the desired (1\(E\),3\(E\)) isomer was obtained, and the purification is easier.

**1-Bromo-2-((1\(E\),3\(E\))-4-phenylbuta-1,3-dien-1-yl)benzene**

m.p. 104-105 ºC

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.65 (dd, \(J = 7.9, 1.6\) Hz, 1H), 7.59 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.49 (d, \(J = 7.8\) Hz, 2H), 7.37 (t, \(J = 7.7\) Hz, 2H), 7.33 - 7.26 (m, 2H), 7.12 (ddd, \(J = 8.0, 7.3, 1.6\) Hz, 1H), 7.08 - 7.03 (m, 2H), 6.97 - 6.90 (m, 1H), 6.75 (d, \(J = 16.1\) Hz, 1H). 13C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 137.1, 136.9, 134.0, 133.1, 131.8, 131.0, 129.0, 128.7, 128.6, 127.8, 127.4, 126.5, 126.3, 123.9.

**1-Bromo-2-((1\(Z\),3\(E\))-4-phenylbuta-1,3-dien-1-yl)benzene**

\(^\text{10}\) de Meijere, A.; Zhong Song, Z.; Lansky, A.; Hyuda, S.; Rauch, K.; Noltemeyer, M.; König, B.; Knieriem, B. *Eur. J. Org. Chem.*, 1998, 2289–2299.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.47 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.41 - 7.22 (m, 6H), 7.18 (td, $J = 7.7, 1.7$ Hz, 1H), 7.12 (dd, $J = 15.6, 10.4$ Hz, 1H), 6.77 (d, $J = 15.6$ Hz, 1H), 6.63 - 6.50 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.4, 137.1, 135.4, 132.7, 131.2, 131.2, 129.7, 128.6, 128.6, 127.8, 127.0, 126.6, 124.7, 124.0.

HRMS-MALDI: calculated for C$_{16}$H$_{13}$Br [M$^+$]: 284.0195; found: 284.0166

7-(2-((1$E$,3$E$)-4-Phenylbuta-1,3-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7g)

This compound was prepared as a white solid in 82% yield according to the general procedure A from 1-bromo-2-((1$E$,3$E$)-4-phenylbuta-1,3-dien-1-yl)benzene.
m.p. 124-125 °C

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.68 - 7.64 (m, 1H), 7.49 - 7.44 (m, 3H), 7.37 - 7.30 (m, 4H), 7.25 (t, $J = 7.3$ Hz, 1H), 6.94 (ddd, $J = 15.5, 5.9, 4.1$ Hz, 1H), 6.90 - 6.84 (m, 2H), 6.79 (dd, $J = 3.7, 2.7$ Hz, 2H), 6.68 (d, $J = 15.3$ Hz, 1H), 6.36 - 6.29 (m, 2H), 5.45 (dd, $J = 9.0, 5.3$ Hz, 2H), 3.10 (t, $J = 5.6$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 140.8, 137.3, 136.1, 132.8, 131.0, 130.9, 130.3, 129.5, 128.6, 127.9, 127.5, 126.8, 126.4, 126.2, 124.5, 42.4.

HRMS-APCI calculated for C$_{23}$H$_{21}$ [M+H$^+$]: 297.1643; found: 297.1650

7-(2-((1$Z$,3$E$)-4-Phenylbuta-1,3-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7u)

This compound was prepared as a colorless oil in 49% yield according to the general procedure A from 1-bromo-2-((1$Z$,3$E$)-4-phenylbuta-1,3-dien-1-yl)benzene.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, $J = 7.8$ Hz, 1H), 7.43 - 7.21 (m, 8H), 7.07 (ddd, $J = 15.6, 10.9, 0.9$ Hz, 1H), 6.73 (dd, $J = 3.6, 2.8$ Hz, 2H), 6.67 (d, $J = 15.6$ Hz, 1H), 6.51 (d, $J = 11.3$ Hz, 1H), 6.42 (td, $J = 11.1, 0.8$ Hz, 1H), 6.31 - 6.24 (m, 2H), 5.42 (dd, $J = 8.8, 5.4$ Hz, 2H), 3.02 (ddd, $J = 5.4, 3.9, 1.5$ Hz, 1H). $^{13}$C NMR (101 MHZ, CDCl$_3$) δ 142.0, 137.3, 136.3, 134.3, 131.0, 130.8, 130.5, 129.3, 128.5, 127.9, 127.6, 127.3, 126.5, 126.3, 125.4, 124.6, 42.46.

HRMS-MALDI: calculated for C$_{23}$H$_{19}$ [M-H$^-$]: 295.1481; found: 295.1496

Experimental Details for the Synthesis of o-Aryl Cycloheptatrienes

2-(Cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17a)
2-Biphenylmagnesium bromide solution (0.5 M, 5.6 mL, 2.8 mmol) was added dropwise to a solution of tropylirium tetrafluoroborate (500 mg, 2.8 mmol) in 10 mL dry THF at 0 °C under argon. The reaction was then stirred at room temperature (23 °C) overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over MgSO₄, and the solvent was evaporated. The crude reaction mixture was purified by chromatography to give the title compound (460 mg) as a colorless solid in 67% yield.

m.p. 48-50 °C

1H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.9, 1.3 Hz, 1H), 7.45 (td, J = 7.5, 1.7 Hz, 1H), 7.37 - 7.18 (m, 7H), 6.57 (t, J = 3.2 Hz, 2H), 6.22 - 6.13 (m, 2H), 5.37 (dd, J = 9.0, 5.3 Hz, 2H), 2.88 (t, J = 5.2 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 141.9, 141.0, 130.5, 130.1, 129.2, 128.0, 127.8, 127.7, 127.6, 126.8, 126.3, 124.1, 41.9.

HRMS-APCI calculated for C₁₉H₁₇ [M+H]+: 245.1330; found: 245.1334

4'-((tert-Butyl)-2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17b)

This compound was prepared as a colorless solid in 76% yield according to the general procedure A.

m.p. 87-89 °C

1H NMR (500 MHz, CDCl₃) δ 7.66 (dd, J = 7.8, 1.1 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.38 - 7.31 (m, 4H), 7.19 (d, J = 8.4 Hz, 2H), 6.61 (t, J = 3.2 Hz, 2H), 6.25 - 6.16 (m, 2H), 5.40 (dd, J = 9.1, 5.2 Hz, 2H), 3.00 (t, J = 5.2 Hz, 1H), 1.35 (s, 9H). 13C NMR (126 MHz, CDCl₃) δ 149.6, 142.0, 141.7, 137.9, 130.5, 130.3, 128.9, 127.8, 127.8, 127.7, 126.2, 124.7, 124.1, 41.9, 34.4, 31.3.

HRMS-APCI calculated for C₂₃H₂₅ [M+H]+: 301.1956; found: 301.1957

2-(Cyclohepta-2,4,6-trien-1-yl)-1,1':4',1''-terphenyl (17c)

This compound was prepared as a white solid in 59% yield according to the general procedure A.

m.p. 86-89 °C

1H NMR (500 MHz, CDCl₃) δ 7.69 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.52 - 7.44 (m, 3H), 7.39 - 7.32 (m, 5H), 6.60 (t, J = 3.2 Hz, 2H),
6.24 – 6.21 (m, 2H), 5.43 (dd, $J = 9.0$, 5.3 Hz, 2H), 3.00 (t, $J = 5.3$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 142.0, 141.4, 140.7, 140.0, 139.5, 130.6, 130.1, 129.7, 128.7, 128.0, 127.9, 127.6, 127.2, 127.0, 126.5, 126.3, 124.2, 41.9.

HRMS-APCI calculated for C$_{25}$H$_{21}$ [M+H]$^+$: 321.1643; found: 321.1647

2-(Cyclohepta-2,4,6-trien-1-yl)-4'-methoxy-1,1'-biphenyl (17d)

This compound was prepared as a white solid in 76% yield according to the general procedure A.

m.p. 74-75 ºC

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.46 (td, $J = 7.5$, 1.8 Hz, 1H), 7.38 - 7.29 (m, 2H), 7.18 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 6.62 (dd, $J = 3.6$, 2.6 Hz, 2H), 6.20-6.22 (m, 2H), 5.40 (dd, $J = 9.0$, 5.3 Hz, 2H), 3.83 (s, 3H), 2.91 (t, $J = 5.3$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.5, 142.0, 141.5, 133.4, 130.6, 130.3, 130.2, 127.8, 127.7, 127.7, 126.2, 124.1, 113.3, 55.2, 41.9.

HRMS-APCI calculated for C$_{20}$H$_{19}$O [M+H]$^+$: 275.1436; found: 275.1442

4'-Chloro-2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17e)

This compound was prepared as a white solid in 74% yield according to the general procedure A.

m.p. 114-115 ºC

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.49 (td, $J = 7.6$, 1.5 Hz, 1H), 7.36 (td, $J = 7.5$, 1.3 Hz, 1H), 7.31 - 7.25 (m, 3H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.63 (t, $J = 3.2$ Hz, 2H), 6.24 - 6.18 (m, 2H), 5.38 (dd, $J = 9.0$, 5.3 Hz, 2H), 2.83 (tt, $J = 5.3$, 1.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.8, 140.6, 139.4, 132.9, 130.6, 130.5, 130.0, 128.3, 128.0, 127.8, 127.2, 126.4, 124.2, 41.9.

HRMS-APCI calculated for C$_{19}$H$_{16}$Cl [M+H]$^+$: 279.0941; found: 279.0942

3'-Chloro-2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17f)

This compound was prepared as a white solid in 71% yield according to the general procedure A.

m.p. 89-90 ºC
1H NMR (400 MHz, CDCl₃) δ 7.68 (dd, J = 7.8, 1.3 Hz, 1H), 7.50 (td, J = 7.5, 1.6 Hz, 1H), 7.36 (td, J = 7.5, 1.3 Hz, 1H), 7.31 - 7.24 (m, 4H), 7.12 (dt, J = 6.8, 1.7 Hz, 1H), 6.63 (t, J = 3.2 Hz, 2H), 6.24 - 6.20 (m, 2H), 5.39 (dd, J = 9.1, 5.3 Hz, 2H), 2.81 (tt, J = 5.4, 1.5 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 142.7, 141.8, 140.5, 133.7, 130.6, 129.9, 129.3, 129.0, 128.4, 127.8, 127.4, 127.1, 126.9, 126.4, 124.2, 41.9.

HRMS-APCI calculated for C₁₉H₁₆Cl [M+H]+: 279.0941; found: 279.0941

2-Bromo-2'-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17g)

A solution of 2,2'-dibromobiphenyl (1.258 g, 4 mmol) in THF (16 mL) in a dried 50 mL round-bottom flask was cooled to -78 ºC and a n-BuLi solution (2.5 M in hexanes, 1.68 mL, 4.2 mmol) was added. After stirring for 40 minutes, tropylium tetrafluoroborate (1.424 g, 8 mmol) was added and the cooling bath was removed. When the reaction reached ambient temperature (23 ºC), cyclohexane (30 mL) was added and the mixture was loaded directly onto a column of SiO₂ and purified by flash chromatography (cyclohexane as eluent), yielding the desired cycloheptatriene (958 mg, 2.9 mmol, 74%) as a colorless oil.

1H NMR (300 MHz, CDCl₃) δ 7.65 (dd, J = 7.9, 1.3 Hz, 1H), 7.48 (td, J = 7.6, 1.5 Hz, 1H), 7.34 (td, J = 7.5, 1.4 Hz, 1H), 7.24 - 7.11 (m, 4H), 6.55 - 6.45 (m, 2H), 6.22 - 6.05 (m, 2H), 5.45 (dd, J = 9.4, 5.4 Hz, 1H), 2.56 (tt, J = 5.5, 1.5 Hz, 1H). 13C NMR (75 MHz, CDCl₃) δ 183.31, 132.48, 131.27, 130.86, 130.32, 129.98, 128.89, 128.79, 127.43, 127.15, 126.94, 126.42, 126.25, 124.54, 124.30, 42.24.

HRMS-APCI calcd for C₁₉H₁₆Br (M+H)+: 323.0430; found: 323.0427.

2-(Cyclohepta-2,4,6-trien-1-yl)-2'-methyl-1,1'-biphenyl (17h)

This compound was prepared as a colorless solid in 79% yield according to the general procedure A.

m.p. 58-60 ºC

1H NMR (400 MHz, CDCl₃) δ 7.65 (dd, J = 7.9, 1.3 Hz, 1H), 7.48 (td, J = 7.6, 1.5 Hz, 1H), 7.34 (td, J = 7.5, 1.4 Hz, 1H), 7.24 - 7.11 (m, 4H), 7.05 (dd, J = 7.3, 1.4 Hz, 1H), 6.55 - 6.52 (m, 2H), 6.19 - 6.09 (m, 2H), 5.39 (dd, J = 9.4, 5.4 Hz, 1H), 5.26 (dd, J = 9.3, 5.3 Hz, 1H), 2.58 (tt, J = 5.4, 1.6 Hz, 1H), 2.03 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 142.4, 141.2, 140.5, 135.9, 130.5, 130.3, 129.6, 129.5, 129.5, 129.7, 127.3, 127.1, 127.0, 126.9, 126.1, 125.2, 124.5, 124.1, 41.9, 20.2.

HRMS-APCI calculated for C₂₀H₁₉ [M+H]+: 259.1487; found: 259.1488

1-(2-(Cyclohepta-2,4,6-trien-1-yl)phenyl)naphthalene (17i)
\( n\)-BuLi (1.6 M in hexanes, 0.23 mL, 0.37 mmol) was added dropwise to the solution of 1-(2-bromophenyl)naphthalene (100 mg, 0.23 mmol) in dry THF (1.4 mL, 0.25 M) at -78 °C under argon. The mixture was stirred for 30 min at -78 °C, and then tropylium tetrafluoroborate (75 mg, 0.42 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 °C) overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over MgSO\(_4\), and the solvent was evaporated. The crude reaction mixture was purified by preparative TLC (eluent: pentane) to yield the title compound as a colorless oil that solidified upon standing (67 mg, 64%).

\( m.p. \) 80-81 °C

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.83 (d, \( J = 8.1 \) Hz, 1H), 7.79 (d, \( J = 8.2 \) Hz, 1H), 7.72 (dd, \( J = 7.8, 1.3 \) Hz, 1H), 7.54 (dd, \( J = 7.6, 1.5 \) Hz, 1H), 7.49 (d, \( J = 8.4 \) Hz, 1H), 7.45 – 7.32 (m, 4H), 7.27 (ddd, \( J = 9.6, 7.3, 1.1 \) Hz, 2H), 6.39 (dd, \( J = 11.0, 5.6 \) Hz, 1H), 6.31 (dd, \( J = 11.0, 5.7 \) Hz, 1H), 6.08 (dd, \( J = 9.3, 5.7 \) Hz, 1H), 5.97 (dd, \( J = 9.3, 5.7 \) Hz, 1H), 5.37 (dd, \( J = 9.3, 5.4 \) Hz, 1H), 5.28 (dd, \( J = 9.3, 5.4 \) Hz, 1H), 2.54 (t, \( J = 5.4 \) Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 143.4, 140.0, 138.7, 133.5, 132.4, 131.0, 130.6, 130.3, 128.4, 128.1, 127.7, 127.6, 127.2, 127.0, 126.5, 126.2, 125.8, 125.7, 125.1, 124.5, 124.1, 42.3.

HRMS-MALDI: calculated for C\(_{23}\)H\(_{17}\) [M-H]\(^+\): 293.1330; found: 293.1361

2-(Cyclohepta-2,4,6-trien-1-yl)-1,1'-binaphthalene (17).

Following a literature procedure, a solution of 2,2'-dibromo-1,1'-binaphtyl (412 mg, 1 mmol) in THF (10 mL) in a dried 25 mL round-bottom flask was cooled to -78 °C and a \( n\)-BuLi solution (2.5 M in hexanes, 0.4 mL, 1 mmol) was added. After stirring for 1 hour, methanol (5 mL) was added and 10 minutes later the reaction was allowed to warm to room temperature (23 °C). The solution was concentrated on a rotary evaporator and then purified by flash chromatography (cyclohexane) to yield 2-bromo-1,1'-binaphtyl (312 mg, 0.94 mmol, 94%) as a colorless solid. The spectroscopic data matched with those reported in the literature.\(^{11}\)

A 10 mL round-bottom flask with a solution of 2-bromo-1,1'-binaphtyl (288 mg, 0.87 mmol) in THF (3.5 mL) was cooled to -78 °C and \( n\)-BuLi solution (2.5 M in hexanes, 0.381 mL, 1.1 equiv.) was added. After stirring for 40 minutes, tropylium tetrafluoroborate (308 mg, 1.73 mmol, 2 equiv.) was added and the solution was

\(^{11}\) Nagaki, A.; Takabayashi, N.; Tomida, Y. and Yoshida, J. Org. Lett. 2008, 10, 3937–3940.
allowed to warm to room temperature. The reaction was quenched with water, extracted with diethyl ether and washed with two portions of water and brine. After drying and concentrating, the mixture was purified by flash chromatography (cyclohexane) to yield the target compound (186 mg, 0.54 mmol, 62%) as a viscous pale-yellow oil.

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \delta 8.06 (d, J = 8.6 \text{ Hz, 1H}), 7.93 (d, J = 8.2 \text{ Hz, 1H}), 7.86 (t, J = 7.9 \text{ Hz, 3H}), 7.53 - 7.38 (m, 3H), 7.31 (d, J = 6.9 \text{ Hz, 1H}), 7.26 - 7.19 (m, 3H), 7.08 (d, J = 8.5 \text{ Hz, 1H}), 6.40 (d, J = 16.3 \text{ Hz, 1H}), 6.30 (d, J = 16.3 \text{ Hz, 1H}), 6.10 (dd, J = 9.3, 5.5 \text{ Hz, 1H}), 5.96 (dd, J = 9.2, 5.5 \text{ Hz, 1H}), 5.38 (d, J = 28.5 \text{ Hz, 2H}), 2.58 (t, J = 5.1 \text{ Hz, 1H}). ^{13}C \text{ NMR (75 MHz, CDCl}_3 \delta 140.51, 136.29, 133.46, 133.35, 133.04, 132.34, 130.67, 130.33, 128.89, 128.15, 128.09, 127.93, 127.88, 127.16, 127.00, 126.46, 126.29, 126.00, 125.87, 125.55, 125.52, 125.36, 124.58, 124.27, 42.94. \]

HRMS-APCI calcd for C$_{27}$H$_{21}$Br ([M+H]$^+$): 345.1638; found: 345.1646.

2,2''-Di(cyclohepta-2,4,6-trien-1-yl)-1,1':4',1''-terphenyl (17k)

The title compound was prepared according to general procedure A-2 from the known compound 2,2''-dibromo-1,1':4',1''-terphenyl$^{12}$ as a colorless solid in 54% yield.

m.p. 182-184 ºC

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.67 (d, J = 8.0 \text{ Hz, 2H}), 7.47 (ddd, J = 7.8, 7.0, 1.8 Hz, 2H), 7.39 - 7.31 (m, 4H), 7.19 (s, 4H), 6.61 (dd, J = 3.8, 2.7 Hz, 4H), 6.23 - 6.18 (m, 4H), 5.39 (ddd, J = 9.5, 5.3, 0.8 Hz, 4H), 2.94 (ddd, J = 5.4, 3.8, 1.5 Hz, 2H). ^{13}C \text{ NMR (126 MHz, CDCl}_3 \delta 141.8, 141.5, 139.4, 130.6, 130.2, 128.8, 127.9, 127.8, 127.5, 126.3, 124.1, 41.8. \]

HRMS-APCI calculated for C$_{32}$H$_{27}$ [M+H]$^+$: 411.2113; found: 411.2113

2,6-Di(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17l)

\[ n\text{-BuLi (1.6 M in hexanes, 2.2 mL, 3.53 mmol) was added dropwise to the solution of 550 mg (1.76 mmol) 2,6-dibromo-1,1'-biphenyl$^{13}$ in 20 mL THF at -78 ºC under \]

(12) Velian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. J. Am. Chem. Soc. 2010, 132, 6296–6297.

(13) Machuy, M. M.; Würtele, C.; Schreiner, P. R. Synthesis 2012, 44, 1405–1409.
argon. After addition, the mixture was warmed to room temperature (23 °C) slowly and allowed to stir for 1 h. After cooling down to -78 °C again, tropylium tetrafluoroborate (628 mg, 3.53 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over MgSO₄, and the solvent was evaporated. The crude reaction mixture was purified by chromatography to yield 320 mg of the title compound as a colorless crystalline solid (54%). m.p. 137-138 °C

$^1$H NMR (500 MHz, CDCl₃) δ 7.62 - 7.55 (m, 3H), 7.18 – 7.16 (m, 3H), 7.02 - 6.97 (m, 2H), 6.49 (dd, $J = 3.8, 2.7$ Hz, 4H), 6.14 - 6.11 (m, 4H), 5.35 (dd, $J = 8.7, 5.4$ Hz, 4H), 2.52 (tt, $J = 5.4, 1.5$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 142.7, 141.5, 138.4, 130.3, 129.4, 128.4, 127.5, 127.3, 126.6, 125.3, 123.9, 42.6.

HRMS-MALDI: calculated for C₂₆H₂₂ [M]+: 334.1722; found: 334.1711

7-(2-Phenoxyphenyl)cyclohepta-1,3,5-triene (22a)

$n$-BuLi (1.6 M in hexanes, 15 mL, 24 mmol) was added dropwise to the solution of diphenyl ether (3.4 g, 20 mmol) and tetramethylethylenediamine (2.79 g, 3.58 mL, 24 mmol) in 50 mL THF at 0 °C. After stirring at room temperature (23 °C) for 5 h, tropylium tetrafluoroborate (3.56 g, 20 mmol) was added, and stirred at room temperature overnight. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, 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 with cyclohexane as eluent to give 2.7 g colorless oil in 52% yield.

$^1$H NMR (500 MHz, CDCl₃) δ 7.50 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.34 - 7.24 (m, 3H), 7.19 (td, $J = 7.5, 1.3$ Hz, 1H), 7.10 - 7.05 (m, 1H), 6.97 - 6.93 (m, 3H), 6.68 (dd, $J = 3.6, 2.7$ Hz, 2H), 6.22 - 6.25 (m, 2H), 5.46 (dd, $J = 8.8, 5.6$ Hz, 2H), 3.18 (tt, $J = 5.6, 1.4$ Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 157.69, 154.74, 134.84, 130.78, 129.61, 129.34, 127.88, 126.28, 124.45, 123.94, 122.78, 119.52, 118.30, 40.18.

HRMS-MALDI: calculated for C₁₉H₁₅O [M-H]⁻: 259.1117; found: 259.1111

7-(2-(Benzyloxy)phenyl)cyclohepta-1,3,5-triene (22b)

$n$-BuLi (2.0 M in hexanes, 5.5 mL, 11 mmol) was added dropwise to the solution of 1-(benzyloxy)-2-iodobenzene ¹⁴ (3.1 g, 10 mmol) in 40 mL THF at -78 °C. After stirring for 0.5 h, tropylium tetrafluoroborate (2.0 g, 11 mmol) was added, and stirred

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(14) 1-(Benzyloxy)-2-iodobenzene was prepared according to the reported procedure: Cakir, S. P.; Stokes, S.; Sygula, A.; Mead, K. T. J. Org. Chem. **2009**, 74, 7529–7532.
at room temperature overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over MgSO\(_4\), and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel to give 1.7 g colorless oil in 62% yield.

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.43 - 7.25 (m, 7H), 7.06 - 6.99 (m, 2H), 6.75 (dd, J = 3.7, 2.6 Hz, 2H), 6.27 (dddd, J = 8.9, 3.9, 2.6, 1.4 Hz, 2H), 5.52 (dd, J = 8.7, 5.6 Hz, 2H), 5.14 (s, 2H), 3.31 - 3.21 (m, 1H). \]

\[ ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 156.44, 137.32, 132.17, 130.79, 128.87, 128.44, 127.76, 127.57, 127.02, 126.75, 124.21, 121.13, 112.62, 70.04, 40.62. \]

HRMS-APCI calculated for C\(_{20}\)H\(_{19}\)O [M+H]+: 275.1430; found: 275.1428

3. General Procedure B for the Gold-Catalyzed Formation of Indenes and Fluorenes.

A solution of the o-arylcycloheptatriene substrate (0.1 mmol) and gold complex (5 mol %) in 1,2-dichloroethane (DCE, 1 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (2-3 h). The reaction was performed under an air atmosphere with no special precautions taken to exclude water. 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.

Experimental Details on the Synthesis of Indenes.

2-Phenyl-1\(H\)-indene (8a)

This compound was prepared as a colorless solid in 74% yield from 7a according to the general procedure B.

The spectroscopic data match with those reported in the literature.\(^{15}\)

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.68 (d, J = 7.1 Hz, 2H), 7.52 (d, J = 7.4 Hz, 1H), 7.46 - 7.40 (m, 3H), 7.34 - 7.26 (m, 3H), 7.23 (td, J = 7.4, 1.2 Hz, 1H), 3.83 (s, 2H). \]

\[ ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta 146.4, 145.3, 143.1, 136.0, 128.7, 127.5, 126.6, 126.5, 125.6, 124.7, 123.6, 121.0, 39.0. \]

2-(4-Chlorophenyl)-1\(H\)-indene (8b)

This compound was prepared as a colorless solid in 65% yield from 7b according to the general procedure B.

\(^{15}\) Deng, R.; Sun, L.; Li, Z. Org. Lett. 2007, 9, 5207–5210.
The spectroscopic data match with those reported in the literature.\textsuperscript{16}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.58 (d, \(J = 8.6\) Hz, 2H), 7.50 (d, \(J = 7.2\) Hz, 1H), 7.43 (d, \(J = 7.6\) Hz, 1H), 7.37 (d, \(J = 8.5\) Hz, 2H), 7.31 (td, \(J = 7.5, 1.1\) Hz, 1H), 7.26 - 7.18 (m, 2H), 3.79 (s, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 145.1, 145.0, 143.0, 134.5, 133.1, 128.8, 127.1, 126.8, 126.7, 125.0, 123.7, 121.1, 38.9.

\textbf{2-(p-Tolyl)-1H-indene (8c)}

This compound was prepared as a colorless solid in 74\% yield from 7c according to the general procedure B.

The spectroscopic data match with those reported in the literature.\textsuperscript{17}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.57 (d, \(J = 8.1\) Hz, 2H), 7.50 (d, \(J = 7.3\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.32 (dd, \(J = 7.6, 1.1\) Hz, 1H), 7.25 - 7.18 (m, 4H), 3.81 (s, 2H), 2.41 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 146.5, 145.5, 143.0, 137.4, 133.2, 129.3, 126.5, 125.6, 125.5, 124.5, 123.6, 120.8, 39.0, 21.2.

\textbf{2-(m-Tolyl)-1H-indene (8d)}

This compound was prepared as a colorless solid in 78\% yield from 7d according to the general procedure B.

The spectroscopic data match with those reported in the literature.\textsuperscript{16}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.53 - 7.47 (m, 3H), 7.44 (d, \(J = 7.1\) Hz, 1H), 7.32 (t, \(J = 7.5\) Hz, 2H), 7.26 (s, 1H), 7.22 (td, \(J = 7.4, 1.2\) Hz, 1H), 7.14 (d, \(J = 7.2\) Hz, 1H), 3.83 (s, 2H), 2.44 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 146.6, 145.4, 143.0, 138.2, 135.9, 128.6, 128.3, 126.6, 126.4, 124.6, 123.6, 122.8, 120.9, 39.0, 21.5.

\textbf{2-Mesityl-1H-indene (8e)}

This compound was prepared as a colorless solid in 83\% yield from 7e according to the general procedure B.

The spectroscopic data match with those reported in the literature.\textsuperscript{18}

\begin{thebibliography}{99}
\bibitem{16} Greifenstein, L. G.; Lambert, J. B.; Nienhuis, R. J.; Fried, H. E.; Pagani, G. A. J. \textit{Org. Chem.} \textbf{1981}, \textit{46}, 5125–5132.
\bibitem{17} Jayamani, M.; Pant, N.; Ananthan, S.; Narayanan, K.; Pillai, C. N. \textit{Tetrahedron} \textbf{1986}, \textit{42}, 4325–4332.
\bibitem{18} Lebedev, A. Y.; Izmer, V. V.; Asachenko, A. F.; Tzarev, A. A.; Uborsky, D. V.; Homutova, Y. A.; Shperber, E. R.; Canich, J. A. M.; Voskoboynikov, A. Z. \textit{Organometallics} \textbf{2009}, \textit{28}, 1800–1816.
\end{thebibliography}
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 7.3$ Hz, 1H), 7.46 (d, $J = 7.3$ Hz, 1H), 7.35 (td, $J = 7.4$, 1.0 Hz, 1H), 7.25 (td, $J = 7.5$, 1.2 Hz, 1H), 6.98 (s, 2H), 6.69 (s, 1H), 3.60 (s, 2H), 2.37 (s, 3H), 2.22 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.6, 145.4, 143.5, 136.7, 136.2, 134.7, 130.2, 128.0, 126.4, 124.2, 123.5, 120.7, 42.1, 21.0, 20.5.

2-Benzyl-1H-indene (8f)

This compound was prepared as a colorless solid in 78% yield from 7f according to the general procedure B.

The spectroscopic data match with those reported in the literature.$^{19}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 - 7.22 (m, 8H), 7.13 (td, $J = 7.4$, 1.3 Hz, 1H), 6.55 (s, 1H), 3.85 (s, 2H), 3.32 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.2, 145.3, 143.4, 140.0, 128.8, 128.4, 127.8, 126.2, 123.8, 123.4, 120.2, 40.8, 37.9.

(E)-2-Styryl-1H-indene (8g)

This compound was prepared as a colorless solid in 42% yield from 7g according to the general procedure B.

The spectroscopic data match with those reported in the literature.$^{20}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 7.2$ Hz, 2H), 7.46 (d, $J = 7.4$ Hz, 1H), 7.40 - 7.35 (m, 3H), 7.31 - 7.19 (m, 4H), 6.88 (s, 1H), 6.81 (d, $J = 16.2$ Hz, 1H), 3.70 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.3, 145.1, 142.8, 137.3, 131.3, 129.4, 128.7, 127.5, 126.3, 125.0, 124.9, 123.6, 120.9, 37.4.

2-Hexyl-1H-indene (8h)

This compound was prepared as a colorless solid in 89% yield from 7h according to the general procedure B.

The spectroscopic data match with those reported in the literature.$^{21}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J = 7.3$ Hz, 1H), 7.31 - 7.22 (m, 2H), 7.13 (td, $J = 7.3$, 1.3 Hz, 1H), 6.53 (s, 1H), 3.34 (s, 2H), 2.51 (t, $J = 7.6$ Hz, 2H), 1.71 - 1.59 (m, 2H), 1.43 - 1.29 (m, 6H), 0.92 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.0, 145.7, 143.1, 126.2, 126.0, 123.4, 123.3, 119.8, 41.0, 31.7, 31.2, 29.1, 29.0, 22.6, 14.1.

2-(4-Methylpent-3-en-1-yl)-1H-indene (8i)

(19) Martinez, A.; Fernandez, M.; Estevez, J. C.; Estevez, R. J.; Castedo, L. Tetrahedron 2005, 61, 485–492.

(20) Deng, R.; Sun, L.; Li, Z. Org. Lett. 2007, 9, 5207–5210.

(21) Lee, D.-H.; Kwon, K.-H.; Yi, C. S. Science 2011, 333, 1613–1616.
This compound was prepared as a colorless oil in 69% yield from 7i according to the general procedure B.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, $J = 7.3$ Hz, 1H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.13 (td, $J = 7.3$, 1.3 Hz, 1H), 6.55 (s, 1H), 5.21 (t, $J = 7.0$ Hz, 1H), 3.34 (d, $J = 1.3$ Hz, 2H), 2.58 - 2.51 (m, 2H), 2.33 (q, $J = 7.4$ Hz, 2H), 1.73 (d, $J = 1.3$ Hz, 3H), 1.66 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 150.6, 145.7, 145.1, 132.0, 126.2, 126.2, 123.9, 123.5, 123.3, 119.8, 41.1, 31.4, 27.6, 25.7, 17.7.

HRMS-EI calculated for C$_{15}$H$_{18}$ [M]+: 198.1409; found: 198.1405

2-(2,6-Dimethylhept-5-en-1-yl)-1H-indene (8j)

A 1 mL DCE solution of substrate 7j (32 mg, 0.1 mmol) and gold catalyst E (4 mg, 5 mol %) was heated at 120 °C overnight. After cooling to room temperature, the solvent was removed in vacuo. The residue was purified with preparative TLC to give 8j as a colorless oil (19.2 mg, 80%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.1$ Hz, 1H), 7.13 (td, $J = 7.3$, 1.3 Hz, 1H), 6.54 (d, $J = 1.1$ Hz, 1H), 5.19 - 5.09 (m, 1H), 3.34 (d, $J = 22.9$ Hz, 1H), 3.32 (d, $J = 22.7$ Hz, 1H), 2.52 (ddd, $J = 14.2$, 6.1, 1.4 Hz, 1H), 2.33 (ddd, $J = 14.0$, 8.0, 1.2 Hz, 1H), 2.15 - 1.98 (m, 2H), 1.82 - 1.76 (m, 1H), 1.73 (s, 3H), 1.65 (s, 3H), 1.48 - 1.43 (m, 1H), 1.28 - 1.19 (m, 1H), 0.96 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.75, 145.72, 143.28, 142.16, 131.27, 127.51, 126.21, 124.72, 123.50, 123.30, 119.83, 41.25, 39.06, 37.04, 32.67, 25.74, 25.64, 19.79, 17.69.

HRMS-APCI calculated for C$_{18}$H$_{25}$ [M+H]$^+$: 241.1951; found: 241.1953

2-((1R*,2S*,3R*)-2,3-diphenylcyclopropyl)-1H-indene (8k)

This compound was prepared according to the general procedure B. The 1 mL DCE solution of substrate 7k (39 mg, 0.1 mmol) and gold catalyst A (3.7 mg, 5 mol %) was heated at 120 °C for 2 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was purified with preparative TLC to give 8k as a colorless solid (19.2 mg, 62%).

m.p. 129-131 °C

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 7.1$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 1H), 7.21 - 7.11 (m, 7H), 7.05 - 7.01 (m, 4H), 6.75 (s, 1H), 3.48 (s, 2H), 2.85 - 2.75 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.25, 145.72, 143.19, 132.75, 127.51, 126.21, 124.72, 123.50, 123.30, 119.83, 41.25, 39.06, 37.04, 32.67, 25.74, 25.64, 19.79, 17.69.
137.48, 128.92, 127.89, 126.50, 126.01, 125.56, 123.82, 123.52, 119.99, 39.79, 34.27, 27.76.

HRMS-APCI calculated for C_{24}H_{21} [M+H]^+: 309.1638; found: 309.1637

1,4-Di(1H-inden-2-yl)benzene (8l)

This compound was prepared from 7l according to the general procedure B. A highly insoluble yellow solid was collected by filtration after cooling down to r.t. (in 41% yield). No further purification was necessary.

$^{1}$H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d$_2$; 398 K) δ 7.60 (s, 4H), 7.44 (d, $J = 7.3$ Hz, 2H), 7.37 (d, $J = 7.5$ Hz, 2H), 7.24 (t, $J = 7.4$ Hz, 2H), 7.19 (s, 2H), 7.15 (t, $J = 7.3$ Hz, 2H), 3.78 (s, 4H). $^{13}$C NMR (126 MHz, 1,1,2,2-tetrachloroethane-d$_2$; 398 K) δ $^{13}$C NMR (126 MHz, 1,1,2,2-tetrachloroethane-d$_2$) δ 145.7, 144.8, 142.6, 134.9, 126.2, 126.1, 125.4, 124.3, 123.0, 120.4, 38.6. HRMS-MALDI calculated for C$_{24}$H$_{18}$ [M]^+: 306.1403; found 306.1402

2,3,4,4a-Tetrahydro-1H-fluorene (8m)

This compound was prepared as a colorless oil in 73% yield from 7m according to the general procedure B.

$^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.38 (d, $J = 7.3$ Hz, 1H), 7.31 (d, $J = 7.4$ Hz, 1H), 7.24 (td, $J = 7.5$, 1.1 Hz, 1H), 7.13 (td, $J = 7.5$, 1.3 Hz, 1H), 6.40 (s, 1H), 3.08 (dd, $J = 12.5$, 6.1 Hz, 1H), 2.82 - 2.76 (m, 1H), 2.59 - 2.54 (m, 1H), 2.42 - 2.34 (m, 1H), 2.07 - 2.00 (m, 1H), 1.92 - 1.88 (m, 1H), 1.65 - 1.58 (m, 1H), 1.29 - 1.21 (m, 1H), 0.94 (qd, $J = 12.8$, 3.5 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 153.6, 147.7, 144.8, 126.3, 123.4, 122.3, 121.7, 120.0, 50.0, 32.4, 29.2, 28.0, 25.4.

HRMS-APCI calculated for C$_{13}$H$_{15}$ [M+H]^+: 171.1174; found: 171.1169

4b,5-Dihydroindeno[2,1-a]indene (8n)

This compound was prepared from 7n according to the general procedure B as a colorless solid in 31% yield.

m.p. 103-105 ºC

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.57 (dd, $J = 7.5$, 0.6 Hz, 1H), 7.48 (d, $J = 7.4$ Hz, 1H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 7.3$ Hz, 1H), 7.31 - 7.26 (m, 2H), 7.23 - 7.16 (m, 2H), 6.75 (d, $J = 2.5$ Hz, 1H), 4.45 (td, $J = 8.5$, 2.6 Hz, 1H), 3.45 (dd, $J = 14.8$, 8.6 Hz, 1H), 2.70 (dd, $J = 14.7$, 8.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.8, 151.1, 149.2, 145.2, 136.9, 127.3, 127.0, 126.9, 125.7, 124.1, 123.5, 121.8, 121.7, 119.1, 58.5, 33.1.

HRMS-MALDI: calculated for C$_{16}$H$_{12}$ [M]^+: 204.0939; found: 204.0957
5-Methyl-2-phenyl-1H-indene (8p') and 6-methyl-2-phenyl-1H-indene (8p)

This mixture of compounds was prepared as a colorless solid in 81% yield (1:1 mixture) from 7p according to the general procedure B. m.p. 180-181 ºC

Some proton signals arising of the two isomers could be differentiated (labeled as isomer a and isomer b); however, these could not be assigned definitively to 8p or 8p.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.69 - 7.66 (m, 2H), 7.45 - 7.23 (m, 6H), 7.16 - 7.13 (d, $J = 7.9$ Hz, 1H, isomer a), 7.06 (dd, $J = 7.7$, 1.5 Hz, 1H, isomer b), 3.80 (s, 2H), 2.46 (s, 3H, isomer a), 2.45 (s, 3H, isomer b). $^{13}$C NMR (126 MHz, CDCl$_3$, mixture of signals) δ 146.6, 145.6, 145.3, 143.5, 142.7, 140.2, 136.2, 136.1, 134.5, 128.6, 127.4, 127.3, 127.3, 126.5, 126.4, 125.6, 125.5, 123.3, 121.7, 120.6, 38.8, 38.6, 21.5, 21.5.

HRMS-APCI calculated for C$_{16}$H$_{15}$ [M+H]$^+$: 207.1174; found: 207.1173

2-Hexyl-5-methyl-1H-indene (8q') and 2-hexyl-6-methyl-1H-indene (8q)

This mixture of compounds was prepared as a colorless oil in 84% yield (1:1 mixture) from 7q according to the general procedure B.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, $J = 7.7$ Hz, 1H), 7.23 (s, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.12 (s, 1H), 7.05 (d, $J = 7.7$ Hz, 1H), 6.95 (d, $J = 7.7$ Hz, 1H), 6.48 (m, 2H), 3.29 (s, 4H), 2.53 - 2.47 (m, 4H), 2.40 (s, 6H), 1.68 - 1.58 (m, 4H), 1.39 - 1.29 (m, 12H), 0.94 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.33, 149.93, 146.02, 143.47, 143.09, 140.16, 135.73, 133.00, 126.83, 125.96, 125.79, 124.38, 124.23, 123.04, 120.61, 119.43, 40.84, 40.64, 31.77, 31.31, 31.25, 29.15, 29.05, 22.65, 21.46, 21.39, 14.12.

HRMS-APCI calculated for C$_{16}$H$_{23}$ [M+H]$^+$: 215.1794; found: 215.1801

5-Methoxyl-2-phenyl-1H-indene (8r') and 6-methoxyl-2-phenyl-1H-indene (8r)

This mixture of compounds was prepared as a colorless solid in 81% yield (2:1 mixture, 8r' as the major product) from 7r according to the general procedure B. The
ratio of products was determined by integration of peaks in the $^1$H NMR spectrum. HMBC was used to elucidate which were the major and minor products.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 - 7.61 (m, major2H+minor2H), 7.44 - 7.31 (m, major4H+minor4H), 7.20 (s, major1H+minor1H), 7.10 (d, $J = 0.7$ Hz, minor1H), 6.99 (d, $J = 2.4$ Hz, major1H), 6.87 (dd, $J = 8.2, 2.4$ Hz, minor1H), 6.78 (dd, $J = 8.1, 2.4$ Hz, major1H), 3.87 (s, major3H+minor3H), 3.79 (s, minor2H), 3.77 (s, major2H). $^{13}$C NMR (101 MHz, CDCl$_3$, mixed signals) $\delta$ 159.08, 158.01, 147.85, 146.70, 145.09, 144.25, 138.54, 136.21, 136.00, 135.34, 128.68, 128.65, 127.57, 127.09, 126.46, 126.06, 125.63, 125.32, 124.06, 121.29, 112.19, 110.82, 110.38, 106.50, 55.58, 55.51, 39.07, 38.26.

HRMS-APCI calculated for C$_{16}$H$_{15}$O [M+H]$^+$: 223.1117; found: 223.1116

HMBC cross peak of 8r ($\delta$(H) 3.79, $\delta$(C) 110.25)

This compound was prepared as a colorless solid in 73% yield from 7a-$d_1$ according to the general procedure B.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 7.2$ Hz, 2H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.46 - 7.40 (m, 3H), 7.33 - 7.29 (m, 2H), 7.27 (d, $J = 1.4$ Hz, 1H), 7.22 (td, $J = 7.4, 1.1$ Hz, 1H), 3.81 (s, 1H and 7% residual signal). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 146.4, 145.4, 143.1, 136.0, 128.6, 127.5, 126.6, 126.5, 125.6, 124.7, 123.6, 120.9, 38.7 (t, $J_{CD} = 19.7$ Hz).

HRMS-APCI calculated for C$_{15}$H$_{12}$D [M+H]$^+$: 194.1080; found: 194.1081

9H-Cyclohepta[a]naphthalene (12)
This compound was prepared as a colorless oil in 28% yield from cis-7a according to the general procedure B.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.24 (d, J = 8.6 \text{ Hz, } 1\text{H}), 7.88 (dd, J = 7.9, 1.5 \text{ Hz, } 1\text{H}), 7.76 (d, J = 8.6 \text{ Hz, } 1\text{H}), 7.61 - 7.51 (m, 2\text{H}), 7.48 (d, J = 8.6 \text{ Hz, } 1\text{H}), 7.24 (d, J = 10.0 \text{ Hz, } 1\text{H}), 6.82 (d, J = 10.0 \text{ Hz, } 1\text{H}), 6.05 (ddt, J = 9.9, 8.6, 6.9 \text{ Hz, } 2\text{H}), 2.41 (t, J = 6.9 \text{ Hz, } 2\text{H}). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 134.8, 133.6, 132.2, 131.7, 130.3, 128.8, 128.3, 128.2, 126.9, 126.5, 126.2, 125.7, 125.2, 124.8, 26.5.\)

HRMS-EI calculated for C\(_{15}\)H\(_{12}\) [M]+: 192.0939; found: 192.0939

(1R*,1aS*,1bS*,2S*,2aS*,6bS*)-1,2-diphenyl-1,1a,1b,2a,6b-hexahydrodicyclopropa[\(a,c\)]naphthalene (15)

The 1 mL DCE solution of 7u (45 mg, 0.15 mmol) and gold catalyst A (5.5 mg, 5 mol %) was heated at 120 °C for 5 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was passed through a short column of silica, and naphthalene (colorless solid, 4.6 mg, 24%) was separated from the crude residue. The remaining mixture was purified carefully with preparative TLC to give 15 as a colorless solid (5.9 mg, 12%).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.39 - 7.10 (m, 12\text{H}), 7.00 (td, J = 7.5, 1.4 \text{ Hz, } 1\text{H}), 6.90 (dd, J = 7.6, 1.4 \text{ Hz, } 1\text{H}), 2.59 (dd, J = 9.4, 8.2 \text{ Hz, } 1\text{H}), 2.38 - 2.32 (m, 2\text{H}), 2.11 (t, J = 4.6 \text{ Hz, } 1\text{H}), 2.01 (dd, J = 8.5, 4.7 \text{ Hz, } 1\text{H}), 1.66 (dd, J = 8.6, 4.3 \text{ Hz, } 1\text{H}). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 142.2, 136.6, 135.8, 131.3, 130.9, 130.1, 128.5, 128.3, 127.6, 125.7, 125.6, 125.4, 125.3, 35.7, 29.7, 29.0, 25.4, 20.8, 20.2.

HRMS-APCI calculated for C\(_{24}\)H\(_{21}\) [M+H]+: 309.1643; found: 309.1649

(1R*,1aS*,6aR*)-1,6a-diphenyl-1,1a,6,6a-tetrahydrocyclopropa[j]indene (5a) and (5a')

The 1 mL DCE solution of (E)-7-(2-styrylphenyl)cyclohepta-1,3,5-triene 7a (27 mg, 0.1 mmol) and gold complex (3.7 mg, 5 mol %) was heated at 120 °C for 2 h. After cooling to room temperature, 7-phenylcyclohepta-1,3,5-triene 1a\(^{22}\) (34 mg, 0.2 mmol) was added, and the mixture was heated to 120 °C overnight (12 h). The reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the resulting residue was purified by preparative TLC to give 19 mg of the title mixture (67%, 4:1) as a colorless solid.

m.p. 84.5-87.8 °C

(22) This compound was reported in: Solorio-Alvarado, C. R.; Wang, Y.; Echavarren, A. M. J. Am. Chem. Soc. 2011, 133, 11952-11955.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 - 6.83 (m, aromatic 14H major + 14H minor), 3.68 (d, $J$ = 16.9 Hz, 1H minor), 3.49 (d, $J$ = 17.0 Hz, 1H minor), 3.42 (d, $J$ = 17.3 Hz, 1H major), 3.34 (dd, $J$ = 8.4, 1.6 Hz, 1H major), 3.26 (dd, $J$ = 3.6, 1.5 Hz, 1H minor), 3.16 (d, $J$ = 17.3 Hz, 1H major), 2.88 (d, $J$ = 8.3 Hz, 1H major), 2.11 (d, $J$ = 3.5 Hz, 1H minor). $^{13}$C NMR (101 MHz, CDCl$_3$, major + minor) δ 146.3, 145.1, 142.6, 141.8, 139.8, 138.7, 135.4, 130.7, 129.8, 128.6, 128.1, 127.6, 127.2, 126.3, 126.1, 125.8, 125.6, 125.3, 125.2, 124.2, 124.1, 123.3, 45.3, 41.7, 41.5, 38.5, 38.4, 37.7, 37.2, 35.9.

The relative configuration was confirmed by NOE.

HRMS-APCI: calculated for C$_{22}$H$_{19}$ [M+H]$^+$: 283.1481; found: 283.1498

**Experimental Details on the Synthesis of Fluorenes**

**9H-Fluorene (18a)**

This compound was prepared as a colorless solid in 64% yield from 17a according to the general procedure B.

The spectroscopic data match with those reported in the literature.$^{23}$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J$ = 7.4 Hz, 2H), 7.58 (d, $J$ = 7.4 Hz, 2H), 7.41 (td, $J$ = 7.5, 1.1 Hz, 2H), 7.33 (td, $J$ = 7.4, 1.2 Hz, 2H), 3.94 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.2, 141.7, 126.7, 126.6, 125.0, 119.8, 36.9.

**2-(tert-Butyl)-9H-fluorene (18b)**

This compound was prepared as a colorless solid in 87% yield from 17b according to the general procedure B.

The spectroscopic data match with those reported in the literature.$^{24}$

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.69 (d, $J$ = 7.5 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.53 (s, 1H), 7.47 (d, $J$ = 7.3 Hz, 1H), 7.37 (d, $J$ = 7.9 Hz, 1H), 7.29 (t, $J$ = 7.3 Hz, 1H), 7.20 (t, $J$ = 7.3 Hz, 1H), 3.83 (s, 2H), 1.33 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.9, 143.2, 143.0, 141.6, 139.0, 126.5, 126.1, 124.8, 123.8, 121.8, 119.5, 119.2, 36.9, 34.7, 31.5.

**2-Phenyl-9H-fluorene (18c)**

This compound was prepared as a colorless solid in 56% yield from 17c according to the general procedure B using catalyst E.

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(23) Clive, D. L. J.; Sunasee, R. *Org. Lett.* 2007, 9, 2677–2680.
(24) Fukuihe, K. *J. Am. Chem. Soc.* 2006, 128, 1434-1435.
The spectroscopic data match with those reported in the literature.\textsuperscript{25}

\begin{itemize}
\item $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.90 - 7.80 (m, 3H), 7.73 - 7.64 (m, 3H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.9$ Hz, 2H), 7.45 - 7.32 (m, 3H), 4.00 (s, 2H).
\item $^{13}$C NMR (101 MHz, CDCl\textsubscript{3}) $\delta$ 143.8, 143.4, 141.5, 141.4, 140.9, 139.8, 128.7, 127.1, 127.1, 126.8, 126.7, 126.0, 125.0, 123.8, 120.1, 119.9, 37.0.
\end{itemize}

2-Methoxy-9H-fluorene (18d)

\[ \text{O} \]

This compound was prepared as a colorless solid in 52% yield from 17d according to the general procedure B using catalyst E.

The spectroscopic data match with those reported in the literature.\textsuperscript{26}

\begin{itemize}
\item $^1$H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.73 – 7.69 (m, 2H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.26 (td, $J = 7.4$, 1.1 Hz, 1H), 7.13 (d, $J = 2.4$ Hz, 1H), 6.96 (dd, $J = 8.4$, 2.5 Hz, 1H), 3.90 (s, 5H).
\item $^{13}$C NMR (126 MHz, CDCl\textsubscript{3}) $\delta$ 159.2, 145.0, 142.6, 141.6, 134.7, 126.7, 125.5, 124.8, 120.5, 119.0, 112.9, 110.5, 55.5, 37.0.
\end{itemize}

2-Chloro-9H-fluorene (18e)

\[ \text{Cl} \]

This compound was prepared as a colorless solid in 42% yield from 17e according to the general procedure B.

The spectroscopic data match with those reported in the literature.\textsuperscript{26}

\begin{itemize}
\item $^1$H NMR (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.78 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.59 - 7.53 (m, 2H), 7.41 (td, $J = 7.5$, 1.0 Hz, 1H), 7.38 (dd, $J = 8.1$, 2.0 Hz, 1H), 7.34 (td, $J = 7.4$, 1.2 Hz, 1H), 3.92 (s, 2H).
\item $^{13}$C NMR (126 MHz, CDCl\textsubscript{3}) $\delta$ 144.8, 142.9, 140.6, 140.2, 132.3, 127.0, 126.9, 126.9, 125.3, 125.0, 120.7, 119.9, 36.8.
\end{itemize}

1-Chloro-9H-fluorene (18f) and 3-Chloro-9H-fluorene (18f\textsuperscript{′})

\[ \text{Cl} + \text{Cl} \]

1.2 : 1

These compounds were prepared as a colorless solid in 56% yield from 17f according to the general procedure B.

Their spectroscopic data match with those reported in the literature.\textsuperscript{26}

\begin{itemize}
\item $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.82 - 7.76 (m, major 1H, minor 2H), 7.70 (dd, $J = 7.3$, 1.1 Hz, major 1H), 7.63 – 7.54 (m, major 1H, minor 1H), 7.48 – 7.27 (m, major 4H, minor 4H), 3.95 (s, major 2H), 3.88 (s, minor 2H).
\item $^{13}$C NMR (101 MHz, CDCl\textsubscript{3}) $\delta$ major + minor : $^{13}$C NMR (101 MHz, CDCl\textsubscript{3}) $\delta$ 143.7, 143.5, 143.5, 142.6, 141.3,
\end{itemize}

\begin{itemize}
\item (25) Mu, B.; Li, T.; Li, J.; Wu, Y. *J. Organomet. Chem.* 2008, 693, 1243–1251.
\item (26) Hwang, S.-J.; Kim, H.-J.; Chang, S. *Org. Lett.*, 2009, 11, 4588-4591.
\end{itemize}
Gold catalyst B (13.5 mg, 0.015 mmol) and 2-bromo-2'-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl 17g (97 mg, 0.3 mmol) were mixed in a Biotage 2 – 5 mL microwave vial. The solids were dissolved in 1,2-dichloroethane (1.2 mL) before the vial was sealed and heated to 120 ºC in a Biotage initiator microwave for 8 h. Afterwards, the solution was filtered through Celite, concentrated and purified by flash chromatography (cyclohexane) to yield the desired fluorene (18.1 mg, 0.074 mmol, 25%) as a colorless solid.

\[
\delta 8.64 (d, J = 9.0 \text{ Hz}, 1H), 7.60 - 7.32 (m, 5H), 7.14 (t, J = 7.7 \text{ Hz}, 1H), 3.95 (s, 2H)
\]

\[
\delta 146.17, 143.68, 141.16, 140.01, 131.90, 127.64, 127.45, 126.61, 124.85, 123.93, 123.67, 117.05, 37.40.
\]

HRMS-APCI calculated for C\textsubscript{13}H\textsubscript{9}Br \([M]^+\): 243.9882; found: 243.9880.

4-Methyl-9\textit{H}\textsubscript{2}-fluorene (18h)

This compound was prepared as a colorless solid in 74% yield from 17h according to the general procedure B.

The spectroscopic data match with those reported in the literature.\textsuperscript{26}

\[
\delta 7.98 (d, J = 7.7 \text{ Hz}, 1H), 7.61 (d, J = 7.4 \text{ Hz}, 1H), 7.44 (td, J = 7.6, 1.1 \text{ Hz}, 2H), 7.35 (td, J = 7.4, 1.2 \text{ Hz}, 1H), 7.26 (t, J = 7.4 \text{ Hz}, 1H), 7.20 (d, J = 7.5 \text{ Hz}, 1H), 3.96 (s, 2H), 2.79 (s, 3H)
\]

\[
\delta 143.6, 143.6, 142.7, 139.8, 133.0, 128.9, 126.9, 126.4, 126.0, 124.8, 123.1, 122.4, 37.1, 21.1.
\]

7\textit{H}-benzo[c]fluorene (18i)

A solution of 1-(2-(cyclohepta-2,4,6-trien-1-yl)phenyl)naphthalene 17i (20.2 mg, 69 µmol) and gold complex A (2.6 mg, 3.4 µmol) in DCE (0.68 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (3 h). The reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the crude residue was purified by chromatography (Combiflash 4 g column, cyclohexane eluent) to give the title compound in 59% yield as a colorless solid (8.7 mg).
The spectroscopic data match with those reported in the literature.27

\[ ^1\text{H NMR (500 MHz, CDCl}_3) \delta 8.79 (d, J = 8.4 \text{ Hz}, 1\text{H}), 8.41 (d, J = 7.8 \text{ Hz}, 1\text{H}), 7.98 (d, J = 8.1 \text{ Hz}, 1\text{H}), 7.83 (d, J = 8.2 \text{ Hz}, 1\text{H}), 7.71 (d, J = 8.3 \text{ Hz}, 1\text{H}), 7.68 – 7.63 (m, 2\text{H}), 7.56 – 7.48 (m, 2\text{H}), 7.36 (td, J = 7.4, 1.0 \text{ Hz}, 1\text{H}), 4.03 (s, 2\text{H}). \]

\[ ^1\text{C NMR (126 MHz, CDCl}_3) \delta 144.3, 142.9, 142.4, 136.2, 133.5, 129.7, 129.3, 127.8, 127.0, 126.6, 125.8, 125.1, 125.0, 123.8, 123.4, 123.0, 37.9. \]

**7H-Dibenzo[c,g]fluorene (18j)**

![Chemical structure of 7H-Dibenzo[c,g]fluorene (18j)](image)

This compound was synthesized in 67% yield as a colorless solid following the general procedure B, starting from 2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-binaphthalene 17j and gold catalyst A. After cooling to room temperature, the solution was filtered through Celite, concentrated and purified by flash chromatography (cyclohexane) to yield the title compound. The spectroscopic data matched with those reported in the literature.28

\[ ^1\text{H NMR (300 MHz, CDCl}_3) \delta 8.76 (dq, J = 7.9, 0.9 \text{ Hz}, 2\text{H}), 8.00 (dd, J = 7.9, 1.7 \text{ Hz}, 2\text{H}), 7.89 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.76 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.63 - 7.50 (m, 4\text{H}), 4.14 (s, 2\text{H}). \]

\[ ^1\text{C NMR (75 MHz, CDCl}_3) \delta 143.02, 138.49, 134.02, 128.98, 128.89, 127.70, 126.82, 125.00, 124.88, 123.00, 39.02. \]

**6,12-Dihydroindeno[1,2-b]fluorene (18k/18k′)**

![Chemical structure of 6,12-Dihydroindeno[1,2-b]fluorene (18k/18k')] (image)

The 1 mL DCE solution of substrate 17k (41 mg, 0.1 mmol) and gold catalyst A (3.7 mg, 5 mol %) was heated at 120 °C for 2 h. After cooling to room temperature, the solvent was removed in vacuo. 1 mL acetone was added to dissolve some of the residue. The liquid was decanted, leaving behind a colorless solid which was dried in vacuo to give a 4:1 mixture of 18k/18k′ (13.5 mg, 53%).

The spectroscopic data match with those reported in the literature.29

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(27) Laali, K. K; Okazaki, T.; Sultana, F.; Bunge, S. D.; Banik, B. K.; Swartz, C. *Eur. J. Org. Chem.* 2008, 1740–1752.

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(29) Major isomer: (a) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cochere, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Wantz, G.; Hirsch, L. *Chem. Eur. J. 2007*, 13, 1005–
S-34

\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \delta 7.97 (s, 2H, major), 7.85 - 7.81 (m, 2H major + 4H minor), 7.60 - 7.56 (m, 2H major + 2H minor), 7.42 (td, J = 7.5, 1.2 Hz, 2H major + 2H minor), 7.32 (td, J = 7.4, 1.3 Hz, 2H major + 2H minor), 4.00 (s, 4H major), 3.98 (s, 4H minor). \]

\[ ^{13} \text{C NMR (101 MHz, CDCl}_3 \delta 143.6, 142.3, 141.8, 140.8, 126.8 \text{ (minor), 126.7, 126.5 \text{ (minor), 126.4, 125.1 \text{ (minor), 125.0, 119.9 \text{ (minor), 119.5, 118.7 \text{ (minor), 116.4, 36.7, 35.5 \text{ (minor).} \]}

(1\text{R}^*, 2\text{R}^*, 3\text{R}^*, 4\text{R}^*, 7\text{R}^*, 8\text{S}^*)-3,8\text{-di}(9\text{H}-\text{fluoren-4-yl})\text{tricyclo[5.1.0.0}^{2,4}\text{oct-5-ene (19)}

This compound (19) was prepared as a yellow oil in 35% yield from 17l according to the general procedure B.

\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \delta 8.36 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.61 - 7.56 (m, 2H), 7.50 - 7.31 (m, 7H), 7.21 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 5.76 (dd, J = 9.8, 4.5 Hz, 1H), 5.68 (dd, J = 9.8, 4.6 Hz, 1H), 3.95 (s, 2H), 3.90 (s, 2H), 2.83 (t, J = 8.5 Hz, 1H), 2.67 (t, J = 4.7 Hz, 1H), 2.54 (t, J = 8.5 Hz, 1H), 2.09 - 1.94 (m, 2H), 0.97 (dt, J = 8.6, 4.5 Hz, 1H). \]

\[ ^{13} \text{C NMR (101 MHz, CDCl}_3 \delta 143.6, 143.6, 143.5, 142.6, 142.3, 142.2, 141.9, 140.6, 136.1, 132.0, 130.6, 127.1, 126.6, 126.5, 126.3, 126.0, 125.9, 125.5, 124.9, 124.7, 124.7, 123.5, 123.2, 122.8, 122.6, 121.4, 37.1, 36.9, 35.3, 30.7, 21.9, 21.5, 20.5, 17.4. \]

HRMS-MALDI: calculated for C\text{34H26} [M]^+ : 434.2035; found: 434.2098

9\text{H}-\text{xanthene (23a)}

A solution of 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene 22a (26 mg, 0.1 mmol) and gold complex E (4 mg, 5 mol %) in toluene (1 mL) was heated at 120 °C in a sealed tube for 2 h. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified by preparative TLC (eluent: cyclohexane) to give 5.5 mg the title compound in 30% yield as a colorless solid.

The spectroscopic data match with those reported in the literature.\textsuperscript{30} 

\[ ^1 \text{H NMR (500 MHz, CDCl}_3 \delta 7.25 - 7.18 (m, 4H), 7.09 - 7.03 (m, 4H), 4.08 (s, 2H). \]

\[ ^{13} \text{C NMR (126 MHz, CDCl}_3 \delta 151.96, 128.90, 127.63, 122.94, 120.58, 116.45, 27.89. \]

((1\text{R}^*, 2\text{R}^*)-3-(2-\text{Phenoxyphenyl})\text{cyclopropane-1,2-diyl)dibenzene (24a)}

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10069. Minor isomer: (b) Thirion, D., Poriel, C., Rault-Berthelot, J.; Barrière, F.; Jeannin, O. \textit{Chem. Eur. J.} \textbf{2010}, \textit{16}, 13646–13658.

(30) Okuma, K.; Nojima, A.; Matsunaga, N.; Shioji, K. \textit{Org. Lett.} \textbf{2009}, \textit{11}, 169–171.
A solution of 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene 22a (26 mg, 0.1 mmol), (E)-1,2-diphenylethene (36 mg, 0.2 mmol) and gold complex A (3.7 mg, 5%) in DCE (0.5 mL) was heated at 120 °C in a sealed tube for 2 h. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified by preparative TLC (eluent: cyclohexane) to give 29.2 mg the title compound in 81% yield as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 - 6.96 (m, 13H), 7.05 - 6.96 (m, 3H), 6.76 - 6.66 (m, 3H), 3.02 - 2.95 (m, 2H), 2.81 (dd, $J = 8.6, 6.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.27, 156.45, 141.84, 138.23, 130.27, 129.55, 128.46, 128.39, 128.15, 127.73, 127.53, 126.59, 126.06, 125.73, 122.83, 122.81, 118.52, 118.16, 34.30, 30.27, 29.64.

HRMS-APCI: calculated for C$_{27}$H$_{23}$O [M+H]$^+$: 363.1743; found: 363.1740

((1$^R$,2$^R$)-3-(2-(benzyloxy)phenyl)cyclopropane-1,2-diyl)dibenzene (24b)

A solution of 7-(2-(benzyloxy)phenyl)cyclohepta-1,3,5-triene 22b (27 mg, 0.1 mmol), (E)-1,2-diphenylethene (36 mg, 0.2 mmol) and gold complex A (3.7 mg, 5 mol %) in DCE (0.5 mL) was heated at 120 °C in a sealed tube for 2 h. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified by preparative TLC (eluent: cyclohexane) to give 28.4 mg the title compound in 75% yield as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 - 7.26 (m, 10H), 7.20 - 7.10 (m, 5H), 7.00 (dd, $J = 7.7, 1.8$ Hz, 2H), 6.88 (td, $J = 7.5, 1.1$ Hz, 1H), 6.81 - 6.77 (m, 1H), 5.06 (d, $J = 12.2$ Hz, 1H), 4.88 (d, $J = 12.2$ Hz, 1H), 3.06 (dd, $J = 9.6, 6.4$ Hz, 1H), 2.95 (t, $J = 6.0$ Hz, 1H), 2.83 (dd, $J = 9.6, 5.7$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.01, 142.23, 138.73, 137.49, 129.95, 128.47, 128.45, 127.97, 127.58, 127.57, 127.50, 126.96, 126.71, 126.14, 126.00, 125.56, 120.26, 111.58, 69.80, 34.18, 30.56, 29.74.

HRMS-APCI: calculated for C$_{28}$H$_{25}$O [M+H]$^+$: 377.1900; found: 377.1890

2-(2-Phenoxybenzyl)-1-phenylbutane-1,3-dione (25a)
The solution of 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene 22a (0.3mmol, 78mg), 1-phenylbutane-1, 3-dione (0.15mmol, 24mg) and gold complex A (5.5mg, 5mol %) in DCE (0.5mL) was heated at 120 ºC in a sealed tube for 3h. The reaction mixture was cooled down to room temperature, after removing the solvent in vacuum, purified by chromatography directly to give 46mg yellow oil in 89% yield.

\[ \text{H NMR (300 MHz, CDCl}_3\text{) } \delta \text{ 7.94 (d, } J = 7.0 \text{ Hz, 2H), 7.55 (t, } J = 7.4 \text{ Hz, 1H), 7.46 - 7.30 (m, 5H), 7.21 - 7.09 (m, 2H), 7.07 - 6.96 (m, 3H), 6.86 (dd, } J = 8.1, 1.2 \text{ Hz, 1H), 4.99 (t, } J = 7.1 \text{ Hz, 1H), 3.45 - 3.27 (m, 2H), 2.14 (s, 3H).} \]

\[ \text{C NMR (75 MHz, CDCl}_3\text{) } \delta \text{ 203.25, 196.10, 157.18, 154.84, 136.34, 133.62, 132.02, 129.91, 129.55, 128.76, 128.74, 128.29, 123.82, 123.22, 118.89, 118.11, 62.48, 30.15, 28.94.} \]

HRMS-ESI: calculated for C_{23}H_{20}NaO_3 [M+Na]^+: 367.1305; found: 367.1314
4. NMR Spectra
S-47
1:1

S-94
MeO-Ph + MeO-Ph
81% 2:1
S-100
1.2 : 1
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1.- Computational methods.

Calculations were performed using the M06$^1$ functional together with the standard 6-31G(d) basis set to describe the H, C and P atoms.$^2$ The large core scalar relativistic pseudopotentials by Dolg et al. were used for Gold coupled to a double-zeta quality basis set.$^3$ Full geometry optimizations were performed in solution, with the Polarizable Continuum Model (IEFPCM) method,$^4$ and using Gaussian 09$^5$ defaults for dichloroethane (DCE). Some test calculations presented in the text as notes, were performed instead with the B3LYP$^6$ functional. Unless otherwise stated, all the energies presented correspond to free energies in solution. The nature of the stationary points was characterized by a vibrational analysis performed within the harmonic approximation at 298 K and 1 atm. Transition states were identified by the presence of one imaginary frequency and minima by a full set of real frequencies.

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2.- Free energy reaction profiles for the formation of IIIa-c, III’a-c and the anti-rotamers IIIaa-cc and III’aa-cc.

Free energy reaction profile for the formation of IIIa and the anti-rotamer IIIaa, energies correspond to free energies in solution, in kcal/mol. Energies in grey correspond to the transition states for the metal-migration competitive process.

Free energy reaction profile for the formation of III’a and the anti-rotamer III’aa, through the metal-migration mechanism, energies correspond to free energies in solution, in kcal/mol.
Free energy reaction profile for the formation of IIIb and the anti-rotamer IIIbb, energies correspond to free energies in solution, in kcal/mol. Energies in grey correspond to the transition states for the metal-migration competitive process.

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Free energy reaction profile for the formation of III'c and the anti-rotamer III'cc, through the metal-migration mechanism, energies correspond to free energies in solution, in kcal/mol.
3. Free energy reaction profiles for the isomerization via 1,4-H-shift.

Free energy reaction profile for the isomerization via 1,4-H-shift, energies correspond to free energies in solution, in kcal/mol.
4.- Energies (hartree) and coordinates (angstrom) of the structures presented.

Ia

ΔE(DCE) -983.050536 h.
ΔG(DCE)-983.097758 h.

79   -0.578043   -0.487161   -0.266964
15   -2.807697   -0.071098    0.426246
  6   -3.671985    1.269945   -0.459703
  1   -3.661848    1.079482   -1.538777
  1   -4.712589    1.332948   -0.114565
  1   -3.175594    2.227876   -0.265828
  6   -3.918955   -1.506034    0.246863
  1   -3.536008   -2.351058    0.829897
  1   -4.926019   -1.248953    0.601414
  1   -3.972802   -1.805242   -0.805951
  6   -2.957908     0.399613    2.182017
  1   -2.397095    1.323183   2.368195
  1   -4.012815    0.561175   -2.434973
  6   -1.341091    0.561175   2.819206
  1   -1.390355   -0.153969   -0.381283
  1   -2.789375    0.381395    0.447243
  6   -3.547897    1.220670    0.876939
  1   -3.561086    1.873220   -0.003810
  1   -4.576535    1.071029    1.230484
  6   -3.958393   -1.136121   -0.729556
  1   -2.628582   -2.149292   -0.985122
  1   -2.851599   -1.183848   -2.858577
  6   -3.907640    0.789992   -1.647576
  1   -2.952246   -1.382813    1.960719
  1   -2.345165   -0.948082    2.762585
  1   -4.002549   -1.412728    2.279276
  1   -2.603527   -2.404256    1.771870
  1   1.322793   -0.014768   -1.181564
  1   1.378243   -0.998539   -2.277156
  6   2.545094   -0.269309    0.512283
  3   3.459727   -1.270197   -0.927804
  6   2.835908    0.491152    0.660991
  6   4.408416   -1.625161   -0.850801
  1   3.291650   -1.801445   -1.863475
  6   3.885529    0.987579    1.516540
  6   4.693152   -0.952902    1.143936
  1   5.157163   -2.438252   -0.363487
  6   4.077872    0.658834    2.430433
  1   5.525133   -1.496434    1.779601
  1   2.040836   1.645296    0.778062
  6   1.369307    2.122821   -0.334227
  1   0.722393    3.131330   -0.280433
  1   1.858308    2.015477   -1.310085
  1   -0.457387    2.970840   -1.852421
  1   0.688911   1.433845   -0.432124
  1   1.899420    2.139940    1.746516
  1   -0.255353    3.114508    0.680352

IIa=II’a

ΔE(DCE) -983.039943 h.
ΔG(DCE)-983.087670 h.

79   0.526829    0.201924   -0.326001
15   2.663970   -0.488230    0.345648
  6   3.579049    0.788193    1.268875
  1   3.012838    1.080635    2.160272
  1   4.559246    0.399148    1.574773
  1   3.722457    1.672980    0.638609
  6   2.664939   -1.939030    1.448866
  1   2.191509   -2.790126    0.946925
  1   3.696626   -2.204227    1.715933
  1   2.102408   -1.714123    2.612676
  1   3.775134   -0.948550   -1.220283
  1   3.910948   -0.095173    1.695669
  1   4.751198   -1.252280   -0.621078
  1   3.344195   -1.780170    1.590404
  1   -2.789574    1.450244    0.894343
  1   -3.218661    1.983879    1.741289
  1   -2.928162    0.114272    0.637250
  1   -3.681181   -0.902331    1.309867
  1   -2.182745   -0.193986   -0.574360
  1   -3.540280   -2.141777    0.740777
  1   -4.201669   -0.668976    2.237087
  1   -2.307105   -1.490048   -1.144910
  1   -3.066159   -2.420758   -0.489199
  1   -4.310803   -2.936238    1.224101

TSIa-IIa

ΔE(DCE) -983.039943 h.
ΔG(DCE)-983.087485 h.

79   -0.600288   -0.153969   -0.381283
15   -2.789375   -0.391395    0.447243
  6   -3.547897    1.220670    0.876939
  1   -3.561086    1.873220   -0.003810
\[
\begin{align*}
\text{IIIa} = \text{III}'a = \text{IIIaa} = \text{III}'aa
\end{align*}
\]

\[
\begin{align*}
\Delta \text{E(DCE)} & = -983.123010 \text{ h.} \\
\Delta G(DCE) & = -983.171280 \text{ h.}
\end{align*}
\]

\[
\begin{align*}
\text{TSIIa-IIIa} = \text{TSII}'a-\text{III}'a
\end{align*}
\]

\[
\begin{align*}
\Delta \text{E(DCE)} & = -983.071726 \text{ h.} \\
\Delta G(DCE) & = -983.119500 \text{ h.}
\end{align*}
\]

\[
\begin{align*}
\Delta \text{E(DCE)} & = -983.068742 \text{ h.} \\
\Delta G(DCE) & = -983.114542 \text{ h.}
\end{align*}
\]
\[
\begin{array}{cccc}
1 & 2.835768 & -3.256977 & 1.240580 \\
1 & 2.422661 & -1.199222 & -2.533097 \\
1 & -2.840062 & -3.256468 & -1.236691 \\
6 & -1.984731 & 1.340027 & -1.178669 \\
6 & -1.939311 & 2.254245 & 0.013411 \\
6 & -1.961519 & 1.677477 & -2.216560 \\
6 & -2.921085 & 2.777048 & -0.00447 \\
6 & -0.839996 & 3.312940 & -0.000656 \\
6 & -0.915473 & 3.950172 & 0.888853 \\
6 & -0.909640 & 3.948858 & 0.889835 \\
6 & 0.152053 & 2.835302 & -0.000465 \\
\end{array}
\]

**Δ(E(DCE))** -983.050303 h.

**ΔG(DCE)** -983.100068 h.

1

1.800367
-1.922486
0.297237

2.173482
-0.578091
-0.019018

1.541437
1.214437
-0.892893

1.168130
0.322565
-0.376258

1.541347
1.214437
-0.892893

2.173482
-0.578091
-0.019018

-0.839996
3.312940
-0.000656

6

0.152053
2.835302
-0.000465
\[ \Delta E(DCE) = -983.069878 \text{ h.} \]
\[ \Delta G(DCE) = -983.117221 \text{ h.} \]

\[ \Delta E(DCE) = -983.091201 \text{ h.} \]
\[ \Delta G(DCE) = -983.135522 \text{ h.} \]
$$\Delta E(DCE) = -983.006724 \text{ h.}$$

$$\Delta G(DCE) = -983.053887 \text{ h.}$$
\[ \Delta E(DCE) = -1097.493812 \text{ h.} \]
\[ \Delta G(DCE) = -1097.544848 \text{ h.} \]

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 1 | 0.678626 | -2.385287 | -1.118758 |   |   |
| 6 | 0.683136 | -1.355226 | -0.739137 |   |   |
| 1 | 3.772848 | 1.763393 | 0.680374 |   |   |
| 1 | -1.451442 | 2.623829 | -1.608474 |   |   |
| 1 | 0.456071 | 1.028323 | -2.119086 |   |   |
| 6 | -0.409572 | 2.944006 | -1.462076 |   |   |
| 1 | -5.407889 | 0.843528 | -0.322045 |   |   |
| 6 | -4.091866 | -0.890606 | 1.777578 |   |   |
| 1 | -5.024803 | -1.029107 | 2.666676 |   |   |
| 1 | -2.468795 | -1.869209 | 1.319536 |   |   |
| 6 | -3.175553 | 1.816907 | 1.441583 |   |   |
| 1 | -2.772485 | 2.580325 | 0.764387 |   |   |
| 1 | -4.178063 | 2.118523 | 1.767141 |   |   |
| 1 | -2.516422 | 1.747511 | 2.316089 |   |   |
| 6 | 0.681316 | -3.355226 | -0.739137 |   |   |
| 1 | 0.678626 | -2.385287 | -1.118758 |   |   |
| 1 | 1.971514 | -0.854507 | -0.621786 |   |   |
| 6 | 3.059316 | -1.793583 | -0.701385 |   |   |
| 1 | 2.288244 | 0.493530 | -0.186637 |   |   |
| 6 | 4.305399 | -1.504481 | -0.243369 |   |   |
| 1 | 2.846919 | -2.784936 | -1.108675 |   |   |
| 6 | 3.552869 | 0.758144 | 0.327917 |   |   |
| 1 | 4.555407 | -0.222918 | 0.312297 |   |   |
| 1 | 5.118517 | -2.222630 | -0.267918 |   |   |
| 1 | 3.772848 | 1.763393 | 0.680374 |   |   |
| 6 | 1.362720 | 1.602276 | -0.304748 |   |   |
| 1 | 0.483130 | 1.766291 | -1.314059 |   |   |
| 1 | -0.409572 | 2.944006 | -1.462076 |   |   |
| 1 | 0.456071 | 1.028323 | -2.119086 |   |   |
| 1 | -1.451442 | 2.623829 | -1.608474 |   |   |
| 1 | -0.141809 | 3.525137 | -2.356034 |   |   |
| 1 | 1.473567 | 2.404149 | 0.430720 |   |   |
| 1 | -0.363313 | 3.606595 | -0.589375 |   |   |
| 1 | 5.785179 | -0.034802 | 0.763425 |   |   |
| 1 | 6.146478 | 1.219879 | 1.340801 |   |   |
| 6 | 7.187066 | 1.113935 | 1.647220 |   |   |
| 1 | 6.057897 | 2.022313 | 0.599273 |   |   |
| 1 | 5.521630 | 1.435769 | 2.215170 |   |   |

**TSb-IIb**

\[ \Delta E(DCE) = -1097.523592 \text{ h.} \]
\[ \Delta G(DCE) = -1097.574930 \text{ h.} \]

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 6 | 3.494482 | 0.058683 | 0.698812 |   |   |
| 1 | 2.435291 | 0.950746 | 0.327831 |   |   |
| 6 | 1.609825 | 0.693298 | -0.842164 |   |   |
| 1 | 1.946759 | -0.401239 | 1.692545 |   |   |
| 6 | 2.979613 | -1.209051 | -1.330614 |   |   |
| 1 | 3.747207 | -1.001766 | 0.123728 |   |   |
| 6 | 4.670738 | 0.258201 | 1.598591 |   |   |
| 1 | 1.374801 | -0.590582 | 2.596621 |   |   |
| 1 | 0.575695 | 1.656019 | -0.933884 |   |   |
| 1 | -1.024296 | 0.266567 | -0.273701 |   |   |
| 15 | -2.818508 | -1.098725 | 0.365620 |   |   |
| 6 | -2.344079 | -2.778243 | 0.889259 |   |   |
| 1 | -1.670152 | -2.723063 | 1.751371 |   |   |
| 6 | -3.239904 | -3.349545 | 1.166972 |   |   |
| 1 | -1.827646 | -3.292684 | 0.071301 |   |   |
| 6 | -4.043561 | -1.353039 | -0.957921 |   |   |
| 1 | -4.866051 | -1.934046 | -0.589724 |   |   |
| 1 | -4.444817 | -0.392010 | -1.288720 |   |   |
| 1 | -3.567429 | -1.850339 | -1.812423 |   |   |
|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |
| 79 | 1.108619    | 0.352370     |
| 1 | 2.785961    | -1.240509    |

**TSIIb-IIIb**

AE(DCE) = -1097.503991 h.  
ΔG(DCE) = -1097.555021 h.

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

**IIIb**

AE(DCE) = -1097.556006 h.  
ΔG(DCE) = -1097.606620 h.

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

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**TSIIb-II'b**

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

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**TSIIb-IIb**

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

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**TSIIb-IIh**

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

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**TSIIb-IIh**

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |

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**TSIIb-IIh**

|   | E(DCE)       | G(DCE)       |
|---|--------------|--------------|
| 6 | -1097.503991 | -1097.555021 |
| 6 | -1097.506008 | -1097.606620 |
|  |  |  |  |
|---|---|---|---|
| 1 | -4.783631 | -1.575164 | -1.798431 |
| 2 | 0.873934 | 0.198482 | -0.310169 |
| 3 | -4.898666 | -3.247546 | -1.169824 |
| 4 | 2.792071 | -0.949718 | 0.407534 |
| 5 | 4.270697 | 0.107294 | 0.544050 |
| 6 | 5.135789 | -0.493211 | 0.855421 |
| 7 | 4.484960 | 0.573332 | -0.423414 |
| 8 | 2.641690 | -1.734754 | 2.045472 |
| 9 | 1.812655 | -2.451122 | 2.040963 |
| 10 | 3.572474 | -2.260089 | 2.297999 |
| 11 | 2.441827 | -0.971850 | 2.806194 |
| 12 | 3.304136 | -2.302394 | -0.701775 |
| 13 | 3.508399 | -1.904777 | -1.702188 |
| 14 | 4.210781 | -2.784395 | -0.312461 |
| 15 | 2.503774 | -3.046904 | -0.776820 |
| 16 | -1.862826 | 2.624045 | 0.634070 |
| 17 | -2.044545 | 3.445345 | 1.326168 |
| 18 | -2.423262 | 1.383632 | 0.709914 |
| 19 | -3.409568 | 0.845633 | 1.602157 |
| 20 | -1.910877 | 0.578239 | -0.388309 |
| 21 | -3.700473 | -0.391458 | 1.353204 |
| 22 | -3.759513 | 1.434046 | 2.448235 |

\[ \Delta E(DCE) -1097.508858 \text{ h.} \]

\[ \Delta G(DCE) -1097.559719 \text{ h.} \]
|     | AE(DCE) | ΔG(DCE) |     | AE(DCE) | ΔG(DCE) |
|-----|---------|---------|-----|---------|---------|
| 79  | -1.372567 | 0.145711 | -0.126878 |
| 15  | -3.660100 | -0.458185 | 0.082916 |
| 6   | -4.405925 | -0.006685 | 1.685677 |
| 1   | -4.330461 | 1.075700  | 1.838822 |
| 1   | -5.463567 | -0.301349 | 1.705690 |
| 1   | -3.875857 | -0.512487 | 2.500657 |
| 6   | -4.753790 | 0.323551  | -1.150524 |
| 1   | -4.448816 | 0.030314  | -2.169051 |
| 1   | -5.793532 | 0.010379  | -0.987097 |
| 1   | -4.688929 | 1.414185  | -1.065593 |
| 6   | -4.008163 | -2.249120 | -0.078511 |
| 1   | -3.476320 | -2.796922 | 0.702528 |
| 1   | -5.086364 | -2.424390 | 0.021138 |
| 1   | -3.670614 | -2.603336 | -1.056284 |
| 6   | -5.863056 | 0.739057  | -0.313456 |
| 6   | -0.768117 | 1.715538  | -0.775707 |
| 1   | 0.742998 | -0.035716 | 0.212243 |
| 1   | 1.654673 | -1.343155 | 0.350642 |
| 6   | 3.069079 | 0.624563  | -0.100733 |
| 6   | 2.751357 | -2.149455 | 0.376480 |
| 1   | 0.661617 | -1.757763 | 0.522964 |
| 1   | 4.173840 | -0.218914 | -0.144022 |
| 6   | 4.026670 | -1.591782 | 0.097546 |
| 6   | 2.686536 | -3.214558 | 0.585877 |
| 1   | 5.162073 | 0.212547  | -0.268621 |
| 6   | 3.303695 | 2.053262  | -0.236198 |
| 6   | 2.585998 | 3.008154  | 0.386214 |
| 6   | 2.876647 | 4.461228  | 0.297630 |
| 1   | 1.758439 | 2.716439  | 1.038232 |
| 6   | 3.067720 | 4.884155  | 1.290444 |
| 1   | 2.008577 | 5.003597  | -0.103338 |
| 1   | 3.740536 | 4.668256  | -0.344682 |
| 6   | 4.196345 | 2.351674  | -0.792834 |
| 6   | 5.033095 | -2.452546 | 0.115810 |
| 6   | 6.358822 | -2.063995 | -0.171928 |
| 6   | 6.984041 | -2.969294 | -0.139219 |
| 6   | 6.403705 | -1.544829 | -1.170696 |
| 6   | 6.693934 | -1.287318 | 0.586297 |

|     | AE(DCE) | ΔG(DCE) |     | AE(DCE) | ΔG(DCE) |
|-----|---------|---------|-----|---------|---------|
| 79  | -1.267440 | 0.087089 | -0.224920 |
| 15  | -3.467289 | -0.657597 | 0.258470 |
| 6   | -4.154660 | 0.011433  | 1.810642 |
| 1   | -4.194571 | 1.103597  | 1.756707 |
| 1   | -5.168276 | -0.378483 | 1.972935 |
| 1   | -3.519152 | -0.276328 | 2.655746 |
| 6   | -4.721012 | -0.232909 | -0.996710 |
| 1   | -4.451577 | -0.678911 | -1.960762 |
| 1   | -5.704563 | -0.610414 | -0.868391 |
| 1   | -4.755379 | 0.854867  | -1.117500 |
| 6   | -3.632725 | -2.465401 | 0.445129 |
| 1   | -2.971659 | -2.815204 | 1.253536 |
| 1   | -4.662841 | -2.732135 | 0.678977 |
| 1   | -3.328517 | -2.963582 | -0.484508 |
| 6   | 0.651613 | 0.751938  | -0.638267 |
$$\Delta E(\text{DCE}) = -1097.585622 \text{ h.}$$
$$\Delta G(\text{DCE}) = -1097.607484 \text{ h.}$$

|   |   |   |   |
|---|---|---|---|
| 79 | 0.110697 | 0.345768 | 0.119064 |
| 15 | 2.804638 | -1.226385 | -0.189952 |
| 6  | 1.733694 | -2.688138 | -1.797838 |
| 3  | 3.064692 | -3.260181 | -1.28724 |
| 4  | 6.097329 | -0.693127 | -1.358814 |
| 1  | 1.106977 | 1.345768 | 0.119064 |
| 6  | 2.804638 | -1.226385 | -0.189952 |
| 79 | 2.216748 | -2.827449 | -0.824355 |
| 6  | 1.733694 | -2.688138 | -1.797838 |
| 3  | 3.064692 | -3.260181 | -1.28724 |
| 4  | 6.097329 | -0.693127 | -1.358814 |
| 1  | 1.106977 | 1.345768 | 0.119064 |

$$\Delta E(\text{DCE}) = -1097.503492 \text{ h.}$$
$$\Delta G(\text{DCE}) = -1097.553766 \text{ h.}$$

|   |   |   |   |
|---|---|---|---|
| 79 | 0.938201 | 0.281712 | -0.259970 |
| 15 | 2.960289 | -0.760589 | 0.325603 |
| 6  | 4.305337 | -0.512464 | -0.879404 |
| 3  | 5.228087 | 0.556519 | -0.981906 |
| 5  | 1.520263 | -1.034740 | -0.541776 |
| 1  | 4.006781 | -0.904520 | -1.858049 |
| 6  | 3.663229 | -0.197502 | 1.910310 |
| 15 | 2.953856 | -0.91882 | 2.722511 |
| 6  | 4.601265 | -0.730262 | 2.115418 |
| 1  | 3.862211 | 0.879372 | 1.869220 |
| 6  | 2.842023 | -2.57107 | 0.502016 |
| 15 | 2.501738 | -3.015440 | -0.440024 |
| 6  | 3.823753 | -2.987688 | 0.764023 |
| 1  | 2.120960 | -2.82189 | 2.88068 |
| 6  | -1.942127 | 2.355294 | 1.022453 |
| 1  | -2.173672 | 3.068285 | 1.799120 |
| 6  | -2.438462 | 1.807908 | 0.949497 |
| 1  | -3.392445 | 0.401491 | 1.772979 |
| 6  | -1.882818 | 0.442252 | -0.235228 |
| 15 | -3.816941 | -0.824686 | 1.385243 |
| 6  | -3.771404 | 0.870474 | 2.690930 |
| 1  | -3.237351 | -0.819964 | -0.629613 |
| 6  | -3.321112 | -1.431278 | 0.171691 |
ΔE(DCE) -1097.506978 h.
ΔG(DCE) -1097.558189 h.
\[ \Delta G(DCE) = -1099.747897 \text{ h.} \]

\[ \Delta G(DCE) = -1099.698186 \text{ h.} \]
\[ E(DCE) -1099.708955 \text{ h.} \]
\[ G(DCE) -1099.759893 \text{ h.} \]

\[ \Delta \]
\[ E(DCE) -1099.634469 \text{ h.} \]
\[ G(DCE) -1099.686582 \text{ h.} \]

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ΔE(DCE) = -1099.626766

ΔG(DCE) = -1099.678063

89 1.189266 0.012627 -0.209453
15 3.517940 -0.216542 0.182813
6 3.957131 -1.359918 1.535487
1 3.575434 -2.363775 1.315842
1 5.046836 -1.404238 1.650030
1 3.509962 -1.014240 2.475007
6 4.457815 -0.837344 -1.251554
1 4.339374 1.737989 1.558118
1 5.434970 1.150320 0.782571
1 4.234342 0.516632 -1.560444
6 4.497729 -0.359075 -0.910012
1 5.510203 -0.444415 -0.954475
1 4.286061 -0.291652 -1.516264
6 3.845080 1.209590 1.406057
1 3.216446 1.331702 2.295173
1 4.886827 1.058043 1.718703
1 3.779442 2.120983 0.801416

ΔE(DCE) -1099.681479 h.

ΔG(DCE) = -1099.732543 h.

79 1.049271 -0.123879 -0.309115
15 3.277323 -0.223960 0.434130
6 3.623312 -1.658349 1.505438
1 3.398214 -2.586829 0.968247
1 4.680684 -1.660186 1.802223
1 2.997045 -1.613074 2.403502
6 4.497729 -0.365907 -0.913344
1 4.430666 0.516632 -1.560375
1 5.510203 -0.444415 -0.954475
1 4.286061 -0.291652 -1.516264
6 3.845080 1.209590 1.406057
1 3.216446 1.331702 2.295173
1 4.886827 1.058043 1.718703
1 3.779442 2.120983 0.801416

IIcc

TSIIcc-IIIcc

S-139
| S-140 | 6.186034 | 2.443665 | -0.153246 |
| 1.063778 | 3.153230 | 0.896196 |

**TSIce-H°ce**

| ΔG(DCE) | -1099.706059 h. |
| 79 | -0.761290 | 0.076063 | 0.097794 |
| 15 | -2.905476 | -0.737632 | -0.109707 |
| 6 | -2.969638 | -2.362187 | -0.924888 |
| 12 | -2.404981 | -3.096970 | -0.339714 |
| 1 | -0.13287 | -2.692730 | -0.101124 |
| 6 | -2.527891 | -2.292647 | -0.924951 |
| 1 | -3.763340 | -0.958488 | 1.478360 |
| 1 | -3.851073 | 0.059391 | 1.990783 |
| 1 | -4.766623 | -1.368186 | 1.302095 |
| 1 | -3.198240 | -1.647040 | 2.115719 |
| 6 | -3.990674 | 0.337013 | -0.958197 |
| 1 | -3.577317 | 0.462664 | 2.102427 |
| 1 | -4.987678 | -0.117830 | -1.166696 |
| 1 | -4.075238 | 1.321208 | -0.622790 |

**IIIce**

| ΔG(DCE) | -1099.607981 h. |
| 79 | -0.820562 | 0.039920 | -0.317320 |
| 15 | -3.012005 | -0.280175 | 0.437248 |
| 6 | -4.017781 | 1.235580 | 0.409110 |
| 1 | -4.064457 | 1.634748 | -0.609895 |
| 1 | -5.034582 | 1.007846 | 0.755609 |
| 1 | -3.573926 | 1.992171 | 1.065236 |
| 6 | -3.939776 | -1.483953 | -0.562553 |
| 1 | -3.433208 | -2.454885 | -0.544467 |
| 1 | -9.953140 | -1.597044 | -1.55389 |
| 6 | -4.003363 | -1.133084 | -1.660051 |
| 1 | -3.126596 | -0.893407 | 2.146516 |
| 6 | -2.654023 | -0.182870 | 2.833467 |
| 1 | -4.182795 | -1.013168 | 2.421461 |
| 6 | -2.618733 | -1.860218 | 2.235301 |
| 6 | -1.238646 | -0.144262 | -1.385900 |
| 6 | 0.920272 | -0.178053 | 2.428886 |
| 1 | 1.953022 | -1.233579 | -0.705800 |
| 1 | 2.135881 | -2.564322 | -1.072885 |
| 6 | 2.505564 | -0.724827 | 0.484059 |
| 1 | 2.890397 | -3.828276 | -0.233277 |
| 6 | 1.706842 | -2.954626 | -1.995190 |
| 1 | 3.242931 | -1.541834 | 1.322472 |
| 1 | 3.437231 | -2.881412 | 0.951286 |
| 1 | 3.057622 | -4.242548 | -0.502844 |
| 1 | 3.672444 | -1.163425 | 2.248361 |
| 1 | 4.027370 | -3.536955 | 1.589034 |
| 1 | 2.150886 | 0.725527 | 0.625429 |
| 1 | 3.148959 | 1.011646 | -0.630465 |
| 1 | 3.220576 | 1.718999 | 0.643414 |
| 6 | 1.186034 | 2.443665 | -1.035246 |
| 1 | 1.545905 | 0.894374 | 1.535151 |
| 1 | 2.809325 | 3.164773 | 0.755643 |
| 6 | 4.000990 | 1.476364 | 1.470190 |
| 1 | 3.896798 | 1.578324 | -0.285044 |
| 1 | 4.142867 | 3.362684 | 0.142576 |
| 1 | 0.213221 | 2.623834 | -1.528860 |
| 1 | 1.944274 | 2.647396 | -1.829586 |
| 1 | 2.781056 | 3.466742 | 1.811832 |
| 1 | 3.528920 | 3.834429 | 0.264645 |
| 1 | 1.724357 | 4.409686 | -0.154007 |
| 6 | 0.636778 | 3.153230 | 0.896196 |
\begin{align*}
\text{AE}(\text{DCE}) & - \text{-1099.645262 h.} \\
\Delta G(\text{DCE}) & - \text{-1099.695360 h.}
\end{align*}

\begin{align*}
\text{TSII'ce-III'c} & \\
\Delta E(\text{DCE}) & - \text{-1099.671281 h.} \\
\Delta G(\text{DCE}) & - \text{-1099.721874 h.}
\end{align*}
ΔE(DCE)-1097.286187 h.
ΔG(DCE)-1097.336036 h.

|    |       |       |       |
|----|-------|-------|-------|
| 79 | -0.613679 | -0.871876 | -0.113651 |
| 15 | -2.843513 | -0.175635 | 0.307666 |
|  6 | -3.596719 |  0.770800 | -1.059086 |
|  1 | -3.595188 |  0.171102 | -1.976328 |
|  1 | -4.630800 |  1.038358 | -0.804008 |
|  1 | -3.022524 |  1.688374 | -1.238664 |
|  6 | -4.023298 | -1.530722 |  0.620746 |
|  1 | -3.703841 | -2.107721 |  1.495959 |
|  1 | -5.026713 | -1.123717 |  0.803360 |
|  1 | -4.057981 | -2.200661 | -0.245751 |
|  6 | -3.018760 |  0.923333 |  1.752112 |
|  1 | -2.423237 |  1.831291 |  1.597798 |
|  6 | -4.207724 | -0.966093 | -0.518387 |

ΔE(DCE)-1097.267084 h.
ΔG(DCE)-1097.315563 h.

|    |       |       |       |
|----|-------|-------|-------|
| 79 | -0.707493 | -0.527733 | -0.385815 |
| 15 | -2.857115 | -0.375772 |  0.553555 |
\[
\begin{array}{cccc}
6 & 3.475010 & -2.773631 & 0.995627 \\
1 & 2.572141 & -3.447803 & -0.119743 \\
6 & 1.902248 & 1.210868 & -0.905224 \\
6 & 2.809443 & 3.116067 & 0.969112 \\
1 & 1.374656 & 3.500225 & -0.031367 \\
6 & 3.247444 & 1.820806 & 1.120946 \\
1 & 3.172109 & 3.879215 & 1.656988 \\
6 & 0.668617 & 2.869396 & -1.690880 \\
6 & 1.524521 & 4.534857 & -0.068281 \\
6 & 4.241479 & -0.982123 & 1.913297 \\
1 & 3.913715 & 1.555095 & 1.939919 \\
\end{array}
\]

TSV-VI

\[
\begin{array}{cccc}
6 & 6.271344 & -3.471845 & -0.910538 \\
1 & 3.172109 & 3.879215 & 1.656988 \\
1 & 0.668617 & 2.869396 & -1.690880 \\
1 & 1.524521 & 4.534857 & -0.068281 \\
6 & 4.241479 & -0.982123 & 1.913297 \\
1 & 3.913715 & 1.555095 & 1.939919 \\
\end{array}
\]

\[\Delta E(DCE) = -1097.272389 \text{ h.} \]
\[\Delta G(DCE) = -1097.322036 \text{ h.} \]

\[
\begin{array}{cccc}
79 & -0.869189 & -0.044632 & -0.419427 \\
15 & -2.974219 & -0.081559 & 0.556181 \\
6 & -3.308585 & 1.334099 & 1.650361 \\
1 & -3.255194 & 2.268373 & 1.080504 \\
1 & -4.311140 & 1.232731 & 2.086810 \\
6 & -4.342227 & -0.081181 & -0.644444 \\
1 & -4.263970 & -0.957244 & -1.297610 \\
6 & -5.300904 & -0.111617 & -0.197077 \\
6 & -3.206368 & 1.553603 & 1.586979 \\
6 & -2.510460 & -1.606157 & 2.383662 \\
6 & -4.261901 & -1.499181 & 2.033596 \\
1 & -3.186827 & -2.458668 & 0.973869 \\
6 & -1.65738 & -1.00738 & -3.325741 \\
1 & -0.793334 & -0.211703 & -2.352578 \\
1 & -1.902053 & -1.161971 & -0.640202 \\
6 & -1.860459 & -2.545005 & -0.856620 \\
6 & -2.738342 & -0.616295 & 0.361811 \\
1 & -2.628643 & -3.364242 & -0.045642 \\
6 & 1.222213 & -2.964321 & 1.633876 \\
1 & 3.511930 & -1.460293 & 1.713535 \\
6 & 3.446501 & -2.826945 & 0.967090 \\
1 & 2.599918 & -4.442837 & -0.191465 \\
6 & 4.038582 & -3.496750 & 1.588154 \\
6 & 2.649244 & 0.819737 & 0.328353 \\
6 & 3.222112 & 1.798720 & 1.151522 \\
1 & 1.770895 & 1.220036 & -0.714545 \\
6 & 2.921012 & 3.131674 & 0.930213 \\
1 & 1.456743 & 2.589669 & -0.929901 \\
6 & 2.112421 & 0.682058 & -1.788316 \\
6 & 2.045808 & 3.524227 & -0.104377 \\
6 & 3.364832 & 3.894577 & 1.566942 \\
6 & 0.783029 & 2.881625 & -1.733667 \\
6 & 1.829046 & 4.580404 & -0.251404 \\
6 & 4.156344 & -1.047083 & 1.948711 \\
6 & 3.889232 & 1.511071 & 1.962766 \\
\end{array}
\]
TSVIIid-VIII

\[ \Delta E(DCE) -1098.614032 \text{ h.} \]
\[ \Delta G(DCE) -1098.663856 \text{ h.} \]

VIII

\[ \Delta E(DCE) -1098.628265 \]
\[ \Delta G(DCE) -1098.680711 \]

ΔE(DCE) -1098.614032 h.
ΔG(DCE) - 1098.663856 h.

6     -0.562379  1.799558  1.044426
       -1.474361  0.729359  -0.662582
       -1.527610  2.124006  -0.021852
       0.625908  2.522765  1.253690
       -1.042786  3.188341  -0.935458
       0.927332  3.552655  0.415306
       0.103891  3.856028  -0.721356
       -0.904839  1.097700  1.817989
       -2.535071  2.370618  0.349452
       1.272010  2.262741  2.084561
       -1.671410  3.422790  1.789999
       1.184866  4.146729  0.591642
       0.416092  4.642872  -1.399464
       0.463466  -0.159393  -0.179785
       2.573372  -1.228533  0.119392
       3.487236  -1.516888  -1.425085
       3.639059  -0.567143  -1.943675
       4.459756  -1.969902  -1.206170
       2.915081  -2.183994  -2.073789
       3.708308  -0.236678  1.137967
       3.273406  -0.088424  1.229634
       4.674513  -0.742386  1.255660
       3.855024  0.740966  0.671297
       2.525081  -2.852380  0.934327
       1.930784  -3.547112  0.336483
       3.540878  -3.246787  1.409282
       2.065100  -2.756227  1.920555
       -1.321789  0.781511  -1.742949
       -2.480935  -0.261982  -0.242652
       -3.292700  -0.108076  0.886106
       -2.659370  -1.412060  -0.298193
       -4.246765  -1.064588  1.211682
       -3.191750  0.763416  1.526304
       -3.616088  -2.356520  -0.078876
       -2.035058  -1.547456  -1.910010
       -4.418480  -2.190468  0.419705
       -4.486570  -0.922331  2.092411
       -3.741523  -3.230824  -1.340332
       -5.161803  -2.934737  0.676346

1      -0.330776  5.241558  -0.105384
6      -0.526379  1.799558  1.044426
       -1.474361  0.729359  -0.662582
       -1.527610  2.124006  -0.021852
       0.625908  2.522765  1.253690
       -1.042786  3.188341  -0.935458
       0.927332  3.552655  0.415306
       0.103891  3.856028  -0.721356
       -0.904839  1.097700  1.817989
       -2.535071  2.370618  0.349452
       1.272010  2.262741  2.084561
       -1.671410  3.422790  1.789999
       1.184866  4.146729  0.591642
       0.416092  4.642872  -1.399464
       0.463466  -0.159393  -0.179785
       2.573372  -1.228533  0.119392
       3.487236  -1.516888  -1.425085
       3.639059  -0.567143  -1.943675
       4.459756  -1.969902  -1.206170
       2.915081  -2.183994  -2.073789
       3.708308  -0.236678  1.137967
       3.273406  -0.088424  1.229634
       4.674513  -0.742386  1.255660
       3.855024  0.740966  0.671297
       2.525081  -2.852380  0.934327
       1.930784  -3.547112  0.336483
       3.540878  -3.246787  1.409282
       2.065100  -2.756227  1.920555
       -1.321789  0.781511  -1.742949
       -2.480935  -0.261982  -0.242652
       -3.292700  -0.108076  0.886106
       -2.659370  -1.412060  -0.298193
       -4.246765  -1.064588  1.211682
       -3.191750  0.763416  1.526304
       -3.616088  -2.356520  -0.078876
       -2.035058  -1.547456  -1.910010
       -4.418480  -2.190468  0.419705
       -4.486570  -0.922331  2.092411
       -3.741523  -3.230824  -1.340332
       -5.161803  -2.934737  0.676346

S-145
benzene

\[ \Delta E(\text{DCE}) = -232.015548 \text{ h.} \]
\[ \Delta G(\text{DCE}) = -232.043028 \text{ h.} \]

IX (no benzene)

\[ \Delta E(\text{DCE}) = -866.608514 \text{ h.} \]
\[ \Delta G(\text{DCE}) = -866.653884 \text{ h.} \]