A New Ru-Catalyzed Cascade Reaction Forming Polycyclic Cyclohexadienes from 1,6-Diynes and Alkenes

Jesús A. Varela, Silvia G. Rubín, Carlos González-Rodríguez, Luis Castedo, Carlos Saá*

Departamento de Química Orgánica y Unidad Asociada al CSIC, Facultad de Química, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

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I. General

Dry DMF (Fluka) was used as received. All other solvents and reagents were used as received, unless otherwise noted. All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring, unless otherwise indicated.

II. Preparation of starting materials and catalysts

2,2-Diprop-2-ynyl malonic acid dimethyl ester (**1a**) was prepared following published procedures.¹ Catalyst $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ was also prepared following published procedures.^{2,3}

III. General procedure for the Ru-catalyzed addition of alkenes **2** to 1,6-diynes **1** followed by $6e^- \pi$ electrocyclization.

Conditions A:

Trimethyl 6,7-dihydro-1H-indene-2,2,5(3H)-tricarboxylate (4a). To a stirred solution of $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (25 mg, 10% mol) and Et_4NCl (8 mg, 10% mol) in DMF (1.5 mL) was added the alkene **2a** (129 mg, 0.14 mL, 1.5 mmol, 3eq.) at room temperature. After stirring for 10 minutes, the diyne **1a** (104 mg, 0.5 mmol, 1 eq.) in DMF (2 mL) was added to the solution over 4 hours via syringe pump. During the slow addition of the diyne **1a** to the reaction flask the solution was heated at 80°C. Stirring was continued for 1 hour after finishing the slow addition, and the reaction was quenched with saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl ether (3 x 10 mL). The organic layers were collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. Column chromatography of the residue on silica gel using ethyl acetate/hexane (4:6) as eluents afforded 1,3-cyclohexadiene **4a** in 62% yield.

Conditions B:

Dimethyl 6-(ethoxymethyl)-4,5-dihydro-1H-indene-2,2(3H)-dicarboxylate (4f). In a 10 mL round-bottomed flask was prepared, under argon, a solution of $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (25 mg, 10% mol) and Et_4NCl (8 mg, 10% mol) in DMF (1.5 mL). After stirring for 10 minutes at room temperature the alkene **2f** (430 mg, 0.56 mL, 5 mmol, 10eq.) was added. After stirring for another 10 minutes, the diyne **1a** (104 mg, 0.5 mmol, 1 eq.) was added and the resulting solution was heated at 80°C during 2 hours. The reaction was quenched with saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl ether (3 x 10 mL). The organic layers were collected, dried over anhydrous Na_2SO_4 and evaporated under vacuum. Column chromatography of the residue on silica gel using ethyl acetate/hexane (2:8) as eluents afforded 1,3-cyclohexadiene **4f** in 90% yield.

IV. Isolation of hexatrienes **3** and ^1H -NMR experiments for the thermal $6e^- \pi$ electrocyclization of **3** to cyclohexadienes **4**

3f

(Z)-Diethyl 3-(2-(ethoxymethyl)allylidene)-4-methylenecyclopentane-1,1-dicarboxylate (3f): In a 10 mL round-bottomed flask was prepared, under argon, a solution of $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (25 mg, 10% mol) and Et_4NCl (8 mg, 10% mol) in DMF (1 mL). After stirring for 10 minutes at room temperature the alkene **2f** (430 mg, 0.56 mL, 5 mmol, 10eq.) was added to the solution, and after

another 10 minutes, the diyne **1a** (104 mg, 0.5 mmol, 1 eq.) was also added. After stirring the reaction mixture for 1.5 h at room temperature, the crude solution was charged directly to a column chromatography on silica gel and eluted using ethyl ether/hexane (7:3). After evaporating the eluent under vacuum in a rotavapor keeping the bath at room temperature, the hexatriene **3f** was isolated in a 66% yield as a colorless oil.

¹H-NMR (300 MHz, CDCl₃), δ (ppm): 5.90 (s, 1H), 5.68 (s, 1H), 5.27 (s, 1H), 5.19 (s, 1H), 5.05 (s, 1H), 3.96 (s, 2H), 3.70 (s, 6H), 3.46 (q, J = 7.0 Hz, 2H), 3.03 (s, 2H), 3.00 (s, 2H), 1.18 (t, J = 7.0 Hz, 3H). ¹³C-NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 171.5 (2 $\times$ CO), 142.6 (C), 142.3 (C), 137.2 (C), 123.4 (CH), 114.6 (CH₂), 111.3 (CH₂), 71.9 (CH₂), 65.6 (CH₂), 57.0 (C), 52.7 (2 $\times$ CH₃), 42.9 (CH₂), 42.8 (CH₂), 15.1 (CH₃).

¹H-NMR experiments for the thermal 6e⁻ π electrocyclization of **3f to cyclohexadiene **4f**:** A solution of hexatriene **3f** in CDCl₃ was placed in an NMR tube and heated to 50°C. ¹H-NMR were taken every 5 minutes observing the conversion of **3f** into **4f**. The conversion was almost quantitative after 1 hour at 50°C. Representative ¹H-NMR data of the reaction are shown below.

(3Z)-dimethyl 3-((Z)-2,3-di(methoxycarbonyl)allylidene)-4-methylenecyclopentane-1,1-dicarboxylate (3e): In a 10 mL round-bottomed flask was prepared, under argon, a solution of [Cp*Ru(CH₃CN)₃]PF₆ (25 mg, 10% mol) and Et₄NCl (8 mg, 10% mol) in DMF (1 mL). After stirring for 10 minutes at room temperature the alkene **2e** (750 mg, 0.65 mL, 5 mmol, 10eq.) was added to the solution, and after another 10 minutes, the diyne **1a** (104 mg, 0.5 mmol, 1 eq.) was also added. After stirring the reaction mixture for 1.5 h at room temperature, the crude solution was charged directly to a column chromatography on silica gel and eluted using ethyl ether/hexane (6:4). After evaporating the eluent under vacuum in a rotavapor keeping the bath at room temperature, the hexatriene **3e** was isolated in a 47% yield as a pale yellow oil.

¹H-NMR (300 MHz, CDCl₃), δ (ppm): 6.68 (q, *J* = 2.1 Hz, 1H), 6.47 (d, *J* = 2.1 Hz, 1H), 5.12 (t, *J* = 2.1 Hz, 1H), 4.97 (t, *J* = 2.1 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 6H), 3.68 (s, 3H), 3.20 (d, *J* = 2.1 Hz, 2H), 3.02 (t, *J* = 2.1 Hz, 2H). ¹³C-NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 171.3 (2xCO), 170.0 (CO), 165.7 (CO), 144.4 (C), 144.3 (C), 143.9 (C), 125.5 (CH), 117.5 (CH), 113.4 (CH₂), 57.2 (C), 52.9 (2xCH₃), 52.6 (CH₃), 51.8 (CH₃), 41.8 (CH₂), 41.4 (CH₂).

¹H-NMR experiments for the thermal 6e⁻π electrocyclization of 3e to cyclohexadiene 4e: A solution of hexatriene **3e** in CDCl₃ was placed in an NMR tube and heated to 50°C. ¹H-NMR were taken every 5 minutes observing the conversion of **3e** into **4e**. The conversion was almost quantitative after 35 min at 50°C. Representative ¹H-NMR data of the reaction are shown below.

V. Preliminary DFT calculations

Calculations were performed with the GAUSSIAN 03 package.⁴ The geometries of all complexes here reported were optimized using density functional theory (DFT) at the generalized gradient approximation using the B3LYP hybrid functional.⁵ At these preliminary studies we have used the standard LANL2DZ basis set.⁶ Harmonic frequencies were calculated at B3LYP level to characterize the stationary points. Intrinsic reaction coordinate calculations (IRC) showed that the calculated TSs connect the reagents and the products.

To determinate the reaction profile for intermediate derivatives of type **III**, we performed density functional calculations (DFT) on ruthenacycloheptadienes **III'** with $R_1=Me$, $R_2=H$ and without the five-membered cycle (Scheme 1).

Scheme 1

According to these calculations, ruthenacycle **III'** presents an agostic interaction between H1 and Ru1 as shown by the bond length between H1 and C2, and the dihedral angle H1-C2-C1-Ru1 is -9.93°. Calculations performed on **III'** led to a β -hydride elimination transition state (**TS III'-IV**) of H1 which connects intermediates **III'**-**IV** and lies 3.76 Kcal mol⁻¹ above **III'**. The following reductive elimination on intermediate **IV** led to the experimentally observed hexatriene of type **V** coordinated to the ruthenium and 29.20 Kcal mol⁻¹ more stable than **III'** (Scheme 1).

Nevertheless, calculations performed on the ruthenacycle **III''**, conformer of **III'** but 2.98 Kcal mol⁻¹ less stable, led via the reductive elimination transition state **TSIII'-VI**, which lies 6.61 Kcal mol⁻¹ above **III''**, to the cyclohexadienes of type **VI** being 40.84 Kcal mol⁻¹ more stable (Scheme 2).

Scheme 2

All attempts to find the transition state between **VII** (Figure 1) and **III''** failed, being only able to find the transition state that led to the conformer **III'**. The attempts to connect directly **III'** with the cyclohexadiene **VI** via a transition state were unsuccessful too (reductive elimination process). Thus, according to these preliminary results, it seems that the first conformer formed is **III'**, from which two possible pathways are envisioned: Pathway A, depicted in scheme 1, affording open hexatrienes (β -hydride elimination followed by reductive elimination, experimentally observed) and pathway B, that connects intermediate **III'** with **III''** followed by the reductive elimination shown in Scheme 2. According to the results shown in Schemes 1 and 2, pathway A seems be more favorable (conformer **III'** being 2.98 Kcal mol⁻¹ more stable than **III''** and transition state for β -hydride elimination being 2.85 Kcal mol⁻¹ more stable than reductive elimination).

Figure 1

When DFT calculations were performed on the intermediates from the reactions with cyclopentene **2p**, a bicycloruthenacycle **III'''** was now available from **VII'** (Scheme 3). Conformer **III'''** has no agostic interaction between H1 and Ru1, being the dihedral angle H1-C2-C1-Ru1 of -176.35° . Therefore, it seems that the conformation of **III'''**, due to steric restrictions caused by the annulated five-membered ring, precludes the β -hydride elimination making more favorable the reductive elimination to the Ru-coordinated cyclohexadiene **VIII** (Scheme 3). Further calculations are currently being carried in order to complete all the catalytic cycle.

Scheme 3

VI. Spectral data

Trimethyl 6,7-dihydro-1H-indene-2,2,5(3H)-tricarboxylate (4a)

Pale yellow oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3), δ (ppm): 6.96 (s, 1H), 3.75 (s, 9H), 3.10 (s, 4H), 2.55 (t, $J = 9.7$ Hz, 2H), 2.27 (t, $J = 9.7$ Hz, 2H). $^{13}\text{C-NMR}$, DEPT (100 MHz, CDCl_3), δ (ppm): 172.2 ($2\times\text{CO}$), 167.8 (CO), 141.1 (C), 131.7 (CH), 130.3 (C), 126.4 (C), 58.5 (C), 52.9 ($2\times\text{CH}_3$), 51.3 (CH_3), 43.5 (CH_2), 40.8 (CH_2), 23.4 (CH_2), 22.1 (CH_2). MS, m/z (% relative intensity): 295 ($\text{M}^+ + 1$, 96), 294 (22), 293 (39), 263 (32), 235 (100). HRMS calculated for $\text{C}_{15}\text{H}_{19}\text{O}_6$: 295.1181; found: 295.1175.

Dimethyl 6-acetyl-4,5-dihydro-1H-indene-2,2(3H)-dicarboxylate (4b)

Pale yellow crystals, m.p. 83-84°C (hexane/ CH_2Cl_2). $^1\text{H-NMR}$ (250 MHz, CDCl_3), δ (ppm): 6.78 (s, 1H), 3.69 (s, 6H), 3.09-3.05 (m, 4H), 2.50-2.42 (m, 4H), 2.42 (s, 3H). $^{13}\text{C-NMR}$, DEPT (63 MHz, CDCl_3), δ (ppm): 198.0 (CO), 172.1 ($2\times\text{CO}$), 142.8 (C), 135.5 (C), 132.3 (CH), 130.3 (C), 58.4 (C), 52.9 ($2\times\text{CH}_3$), 43.4 (CH_2), 40.7 (CH_2), 25.0 (CH_3), 23.5 (CH_2), 20.7 (CH_2). MS, m/z (% relative intensity): 279 ($\text{M}^+ + 1$, 100), 278 (15), 277 (35), 219 (76). HRMS calculated for $\text{C}_{15}\text{H}_{19}\text{O}_5$: 279.1232; found: 279.1234.

Dimethyl 6-formyl-4,5-dihydro-1H-indene-2,2(3H)-dicarboxylate (4c)

Pale yellow solid. $^1\text{H-NMR}$ (250 MHz, CDCl_3), δ (ppm): 9.39 (s, 1H), 6.64 (s, 1H), 3.68 (s, 6H), 3.11-3.06 (m, 4H), 2.48-2.40 (m, 2H), 2.26-2.17 (m, 2H). $^{13}\text{C-NMR}$, DEPT (63 MHz, CDCl_3), δ (ppm): 192.1 (CHO), 172.6 ($2\times\text{CO}$), 145.9 (C), 140.5 (CH), 137.4 (C), 130.6 (C), 58.5 (C), 53.4 ($2\times\text{CH}_3$), 43.8 (CH_2), 40.7 (CH_2), 23.8 (CH_2), 19.3 (CH_2). MS, m/z (% relative intensity): 265 ($\text{M}^+ + 1$, 100), 264 (10), 233 (19), 205 (72). HRMS calculated for $\text{C}_{14}\text{H}_{17}\text{O}_5$: 265.1076; found: 265.1077.

Dimethyl 5-formyl-1H-indene-2,2(3H)-dicarboxylate

White solid. $^1\text{H-NMR}$ (250 MHz, CDCl_3), δ (ppm): 9.86 (s, 1H), 7.63-7.59 (m, 2H), 7.26 (d, $J = 7.7$ Hz, 1H), 3.67 (s, 6H), 3.56 (s, 4H). $^{13}\text{C-NMR}$, DEPT (63 MHz, CDCl_3), δ (ppm): 192.0 (CHO), 171.7 ($2\times\text{CO}$), 147.3 (C), 141.1 (C), 136.0 (C), 129.7 (CH), 125.1 (CH), 124.8 (CH), 60.3 (C), 53.1 ($2\times\text{CH}_3$),

40.7 (CH₂), 40.0 (CH₂). MS, m/z (% relative intensity): 263 (M⁺+1, 100), 262 (11), 231 (46), 203 (36). HRMS calculated for C₁₄H₁₅O₅: 263.0919; found: 263.0921.

Dimethyl 6-cyano-4,5-dihydro-1H-indene-2,2(3H)-dicarboxylate (4d)

White crystals. m.p. 72-75 °C (hexane/ ethyl acetate). ¹H-NMR (500 MHz, CDCl₃), δ (ppm): 6.61 (s, 1H), 3.75 (s, 6H), 3.10 (s, 4H), 2.74 (t, *J* = 9.8 Hz, 2H), 2.31 (t, *J* = 9.8 Hz, 2H). ¹³C-NMR, DEPT (126 MHz, CDCl₃), δ (ppm): 172.0 (2×CO), 140.7 (C), 136.6 (CH), 129.5 (C), 119.7 (C), 115.7 (CN), 106.6 (C), 58.1 (C), 53.1 (2×CH₃), 43.6 (CH₂), 40.7 (CH₂), 24.4 (CH₂), 22.7 (CH₂). MS, m/z (% relative intensity): 262 (M⁺+1, 5), 41 (46), 29 (100). HRMS calculated for C₁₄H₁₆NO₄: 262.1076; found: 262.1079.

Tetramethyl 4,5-dihydro-1H-indene-2,2,5,6(3H)-tetracarboxylate (4e)

Pale yellow oil. ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 7.03 (s, 1H), 3.71 (s, 3H), 3.67 (s, 6H), 3.59 (s, 3H), 3.14-2.77 (m, 6H), 2.82-2.76 (m, 1H). ¹³C-NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 173.3 (CO), 171.9 (CO), 171.6 (CO), 166.7 (CO), 140.1 (C), 132.4 (CH), 130.0 (C), 124.4 (C), 58.4 (C), 52.8 (CH₃), 52.7 (CH₃), 52.2 (CH₃), 51.7 (CH₃), 43.0 (CH₂), 40.5 (CH₂), 38.1 (CH), 26.7 (CH₂). MS, m/z (% relative intensity): 353 (M⁺+1, 27), 351 (18), 321 (45), 319 (52), 293 (100), 261 (70). HRMS calculated for C₁₇H₂₁O₈: 353.1236; found: 353.1231.

Dimethyl 6-(ethoxymethyl)-4,5-dihydro-1H-indene-2,2(3H)-dicarboxylate (4f)

Pale yellow oil. ¹H-NMR (250 MHz, CDCl₃), δ (ppm): 5.76 (s, 1H), 3.86 (s, 2H), 3.67 (s, 6H), 3.40 (q, *J* = 7.0 Hz, 2H), 2.96 (s, 4H), 2.16 (s, 4H), 1.14 (t, *J* = 7.0 Hz, 3H). ¹³C-NMR, DEPT (63 MHz, CDCl₃), δ (ppm): 172.4 (2×CO), 135.3 (C), 131.9 (C), 129.9 (C), 119.2 (CH), 73.7 (CH₂), 65.3 (CH₂), 58.5 (C), 52.8 (2×CH₃), 43.2 (CH₂), 41.4 (CH₂), 24.8 (CH₂), 23.2 (CH₂), 15.2 (CH₃). MS, m/z (% relative intensity): 295 (M⁺+1, 31), 294 (44), 293 (39), 249 (97), 247 (29), 236 (16), 235 (100), 189 (61). HRMS calculated for C₁₆H₂₃O₅: 295.1546; found: 295.1545.

Dimethyl 4,5-dihydro-6-(phenoxymethyl)-1H-indene-2,2(3H)-dicarboxylate (4g)

Pale yellow oil. ^1H -NMR (250 MHz, CDCl_3), δ (ppm): 7.31-7.19 (m, 2H), 6.97-6.84 (m, 3H), 5.95 (s, 1H), 4.48 (s, 2H), 3.74 (s, 6H), 3.04 (s, 4H), 2.37-2.24 (m, 4H). ^{13}C -NMR, DEPT (63 MHz, CDCl_3), δ (ppm): 172.6 ($2\times\text{CO}$), 158.7 (C), 133.4 (C), 132.4 (C), 129.3 ($2\times\text{CH}$), 120.7 (CH), 119.8 (CH), 114.7 ($2\times\text{CH}$), 71.0 (CH_2), 58.4 (C), 52.8 ($2\times\text{CH}_3$), 43.2 (CH_2), 41.3 (CH_2), 24.6 (CH_2), 23.1 (CH_2). MS, m/z (% relative intensity): 343 ($\text{M}^+ + 1$, 53), 342 (39), 341 (55), 311 (32), 284 (36), 283 (90), 281 (39), 251 (38), 250 (60), 249 (100), 248 (41), 247 (77), 217 (31), 191 (65), 190 (52), 189 (90), 131 (31), 94 (61), 93 (31). HRMS calculated for $\text{C}_{20}\text{H}_{23}\text{O}_5$: 343.1545; found: 343.1538.

Dimethyl 6-(trimethylsilyloxymethyl)-2,3,4,5-tetrahydro-1H-2,2-indenedicarboxylate (4h)

Pale yellow oil. ^1H -NMR (250 MHz, CDCl_3), δ (ppm): 5.72 (s, 1H), 3.98 (s, 2H), 3.63 (s, 6H), 2.92 (s, 4H), 2.10 (s, 4H), 0.03 (s, 9H). ^{13}C -NMR, DEPT (63 MHz, CDCl_3), δ (ppm): 172.7 ($2\times\text{CO}$), 137.6 (C), 131.1 (C), 130.0 (C), 116.9 (CH), 65.6 (CH_2), 58.5 (C), 52.8 ($2\times\text{CH}_3$), 43.2 (CH_2), 41.4 (CH_2), 24.6 (CH_2), 23.2 (CH_2), -0.42 ($3\times\text{CH}_3$). MS, m/z (% relative intensity): 323 ($\text{M}^+ - 15$, 13), 279 (16), 249 (44), 247 (10), 217 (58), 190 (14), 189 (100), 91 (18), 75 (28), 73 (22).

Dimethyl 4,5-dihydro-6-(hydroxymethyl)-1H-indene-2,2(3H)-dicarboxylate (4i)

Pale yellow oil. ^1H -NMR (300 MHz, CDCl_3), δ (ppm): 5.83 (s, 1H), 4.09-4.08 (m, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 3.02 (s, 4H), 2.24-2.20 (m, 4H), 2.03 (s, 1H). ^{13}C -NMR, DEPT (75 MHz, CDCl_3), δ (ppm): 172.7 ($2\times\text{CO}$), 137.5 (C), 131.8 (C), 129.9 (C), 117.5 (CH), 66.1 (CH_2), 58.6 (C), 52.9 ($2\times\text{CH}_3$), 43.1 (CH_2), 41.3 (CH_2), 24.6 (CH_2), 23.3 (CH_2). MS, m/z (% relative intensity): 267 ($\text{M}^+ + 1$, 2), 249 (46), 217 (72), 191 (23), 189 (100).

Dimethyl 4,5-dihydro-5-(hydroxymethyl)-1H-indene-2,2(3H)-dicarboxylate (4i')

Pale yellow oil. $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm): 5.51 (s, 1H), 5.46 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.54-3.50 (m, 2H), 2.93-2.90 (m, 4H), 2.03 (s, 1H), 1.85-1.66 (m, 3H). $^{13}\text{C-NMR}$, DEPT (75 MHz, CDCl_3), δ (ppm): 171.7 ($2\times\text{CO}$), 126.0 (C), 123.0 (C), 117.6 (CH), 116.7 (CH), 66.0 (CH_2), 58.5 (C), 52.9 ($2\times\text{CH}_3$), 38.8 (CH_2), 38.4 (CH_2), 36.2 (CH), 26.0 (CH_2). MS, m/z (% relative intensity): 267 (M^++1 , 2), 249 (33), 217 (46), 207 (37), 189 (100), 57 (59).

Dimethyl 4,5-dihydro-6-pentyl-1H-indene-2,2(3H)-dicarboxylate (4j)

Pale yellow oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3), δ (ppm): 5.58 (s, 1H), 3.73 (s, 6H), 3.01 (s, 4H), 2.17 (s, 4H), 2.04 (t, $J=7.5$ Hz, 2H), 1.46-1.38 (m, 2H), 1.32-1.26 (m, 4H), 0.89 (t, $J=7.1$ Hz, 3H). $^{13}\text{C-NMR}$, DEPT (100 MHz, CDCl_3), δ (ppm): 172.8 ($2\times\text{CO}$), 139.7 (C), 130.7 (C), 129.2 (C), 116.6 (CH), 58.5 (C), 52.7 ($2\times\text{CH}_3$), 43.2 (CH_2), 41.6 (CH_2), 37.1 (CH_2), 31.7 (CH_2), 27.6 (CH_2), 27.4 (CH_2), 23.6 (CH_2), 22.5 (CH_2), 14.1 (CH_3). MS, m/z (% relative intensity): 307 (M^++1 , 12), 306 (21), 305 (20), 247 (32). HRMS calculated for $\text{C}_{18}\text{H}_{27}\text{O}_4$: 307.1909; found: 307.1901.

Dimethyl 4,5-dihydro-6-(trimethylsilyl)-1H-indene-2,2(3H)-dicarboxylate (4k)

Colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3), δ (ppm): 6.10 (s, 1H), 3.72 (s, 6H), 3.05-3.03 (m, 4H), 2.28 (t, $J=9.5$ Hz, 2H), 2.08 (t, $J=9.6$ Hz, 2H), 0.06 (s, 9H). $^{13}\text{C-NMR}$, DEPT (100 MHz, CDCl_3), δ (ppm): 172.7 ($2\times\text{CO}$), 138.5 (C), 134.1 (C), 130.3 (C), 129.9 (CH), 58.2 (C), 52.7 ($2\times\text{CH}_3$), 43.5 (CH_2), 41.4 (CH_2), 25.3 (CH_2), 23.1 (CH_2), -2.20 ($3\times\text{CH}_3$). MS, m/z (% relative intensity): 309 (M^++1 , 100), 308 (90), 307 (68), 293 (45), 291 (27), 275 (23), 249 (83), 248 (20), 247 (36), 203 (26), 177 (22), 175 (36), 113 (20), 73 (26). HRMS calculated for $\text{C}_{16}\text{H}_{25}\text{O}_4\text{Si}$: 309.1522; found: 309.1518.

Dimethyl 3,3a,5,6,7,8a-hexahydro-1H-cyclopenta[f]isobenzofuran-6,6-dicarboxylate (5l)

Yellowish solid, m.p. 67-68 $^{\circ}\text{C}$ (hexane/ CH_2Cl_2) [lit.⁴ 51-52 $^{\circ}\text{C}$ (CHCl_3)]. $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm): 5.36 (s, 2H), 4.09-4.04 (m, 2H), 3.66 (s, 3H), 3.65 (s, 3H), 3.45-3.40 (m, 2H), 2.97-2.81 (m, 6H). $^{13}\text{C-NMR}$, DEPT (75 MHz, CDCl_3), δ (ppm): 171.6 ($2\times\text{CO}$), 134.8 ($2\times\text{C}$), 117.3 ($2\times\text{CH}$), 75.1 ($2\times\text{CH}_2$), 58.6 (C), 52.6 ($2\times\text{CH}_3$), 38.7 ($2\times\text{CH}_2$), 38.6 ($2\times\text{CH}$). MS, m/z (% relative intensity): 279 (M^++1 , 65), 278 (25), 261 (38), 247 (28), 229 (16), 220 (21), 219 (100), 201 (38), 129 (16). HRMS calculated for $\text{C}_{15}\text{H}_{19}\text{O}_5$: 279.1232; found: 279.1239.

3a,5,7,8a-Tetrahydro-1H,3H-furo[3,4-f]isobenzofuran (5I')

Yellowish solid, m.p. 116-118 °C (hexane/ ethyl acetate). ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 5.36 (s, 2H), 4.41-4.29 (m, 4H), 4.14-4.09 (m, 2H), 3.50-3.45 (m, 2H), 2.99 (s, 2H). ¹³C-NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 135.0 (2×C), 114.0 (2×CH), 75.1 (2×CH₂), 70.3 (2×CH₂), 39.0 (2×CH). MS, m/z (% relative intensity): 165 (M⁺+1, 29), 163 (38), 147 (60), 135 (64), 133 (28), 119 (100). HRMS calculated for C₁₀H₁₃O₂: 165.0915; found: 165.0910.

3,3a,5,6,7,8a-Hexahydro-1H-cyclopenta[f]isobenzofuran (5I'')

Pale yellow oil. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 5.34-5.33 (m, 2H), 4.12-4.08 (m, 2H), 3.52-3.48 (m, 2H), 2.95-2.94 (m, 2H), 2.36-2.22 (m, 4H), 1.72-1.60 (m, 2H). ¹³C-NMR, DEPT (100 MHz, CDCl₃), δ (ppm): 138.7 (2×C), 115.7 (2×CH), 75.4 (2×CH₂), 38.9 (2×CH), 31.2 (2×CH₂), 24.7 (CH₂). MS, m/z (% relative intensity): 163 (M⁺+1, 33), 161 (100), 159 (29), 149 (25), 147 (53), 133 (53), 131 (25).

Dimethyl 5,6,7,7a-tetrahydro-5-oxo s-indacene-2,2(1H,3H,4aH)-dicarboxylate (5m)*

Pale yellow oil. ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 5.60 (s, 1H), 5.43 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.05-2.89 (m, 6H), 2.26-2.04 (m, 3H), 1.84-1.74 (m, 1H). ¹³C-NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 219.8 (CO), 171.5 (CO), 171.4 (CO), 136.2 (C), 135.3 (C), 119.9 (CH), 112.4 (CH), 58.5 (C), 52.8 (2×CH₃), 48.8 (CH), 38.6 (2×CH₂), 36.4 (CH), 36.2 (CH₂), 29.2 (CH₂). MS, m/z (% relative intensity): 291 (M⁺+1, 16), 290 (14), 289 (35), 231 (100). HRMS calculated for C₁₆H₁₉O₅: 291.1232; found: 291.1233.

*Note: reaction performed using acetone as solvent.

Dimethyl 5,6-dihydro-7-oxo s-indacene-2,2(1H,3H,5H)-dicarboxylate

White crystals, m.p. 90-93°C (hexane/ ethyl acetate). ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 7.53 (s, 1H), 7.27 (s, 1H), 3.73 (s, 6H), 3.59 (s, 2H), 3.57 (s, 2H), 3.05 (t, *J* = 5.8 Hz, 2H), 2.65 (t, *J* = 5.8 Hz, 2H). ¹³C-NMR, DEPT (75 MHz, CDCl₃), δ (ppm): 206.4 (CO), 171.8 (2×CO), 155.0 (C), 148.3 (C), 139.7 (C), 136.6 (C), 122.3 (CH), 119.2 (CH), 60.6 (C), 53.0 (2×CH₃), 40.4 (CH₂), 39.6 (CH₂), 36.6 (CH₂), 25.5 (CH₂). MS, m/z (% relative intensity): 289 (M⁺+1, 100), 288 (7), 257 (19), 229 (21). HRMS calculated for C₁₆H₁₇O₅: 289.1076; found: 289.1073.

5n**Dimethyl 5,8-dioxo-1H-cyclopenta[b]naphthalene-2,2(3H,5H,8H)-dicarboxylate (5n)**

Orangish solid. M. p. 115-117 °C (hexane/ CH_2Cl_2). ^1H -NMR (400 MHz, CDCl_3), δ (ppm): 7.92 (s, 2H), 6.93 (s, 2H), 3.77 (s, 6H), 3.70 (s, 4H). ^{13}C -NMR, DEPT (100 MHz, CDCl_3), δ (ppm): 184.9 (2 $\times$ CO), 171.2 (2 $\times$ CO), 146.6 (2 $\times$ C), 138.7 (2 $\times$ CH), 131.8 (2 $\times$ C), 122.8 (2 $\times$ CH), 60.0 (C), 53.2 (2 $\times$ CH₂), 40.8 (2 $\times$ CH₃). MS, m/z (% relative intensity): 315 (M^+ +1, 100), 283 (6), 255 (7), 85 (7), 83 (11), 57 (6). HRMS calculated for $\text{C}_{17}\text{H}_{15}\text{O}_6$: 315.0869; found: 315.0870.

5o**Dimethyl 1-oxo-3,3a,5,6,7,8a-hexahydro-1H-cyclopenta[f]isobenzofuran-6,6-dicarboxylate (5o)**

Colorless oil. ^1H -NMR (300 MHz, CDCl_3), δ (ppm): 5.48 (s, 2H), 4.48-4.42 (m, 1H), 3.95-3.89 (m, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.32 (s, 2H), 3.04-2.84 (m, 4H). ^{13}C -NMR, DEPT (75 MHz, CDCl_3), δ (ppm): 178.0 (CO), 171.2 (CO), 171.1 (CO), 137.3 (C), 137.2 (C), 115.3 (CH), 110.7 (CH), 73.6 (CH₂), 58.2 (C), 52.8 (2 $\times$ CH₃), 40.6 (CH), 38.5 (2 $\times$ CH₂), 35.4 (CH). MS, m/z (% relative intensity): 293 (M^+ +1, 45), 291(12), 261(20), 233(100). HRMS calculated for $\text{C}_{15}\text{H}_{17}\text{O}_6$: 293.1025; found: 293.1026.

5p**Dimethyl 4a,5,6,7-tetrahydro s-indacene-2,2(1H,3H,4aH)-dicarboxylate (5p)**

Pale yellow oil. ^1H -NMR (400 MHz, CDCl_3), δ (ppm): 5.37 (s, 2H), 3.68 (s, 3H), 3.67 (s, 3H), 2.87 (q, J = 16.2 Hz, 4H), 2.61 (s, 2H), 1.97-1.87 (m, 2H), 1.43-1.21 (m, 4H). ^{13}C -NMR, DEPT (100 MHz, CDCl_3), δ (ppm): 171.8 (2 $\times$ CO), 132.5 (2 $\times$ C), 121.6 (2 $\times$ CH), 59.1 (C), 53.3 (2 $\times$ CH₃), 38.8 (2 $\times$ CH₂), 37.9 (2 $\times$ CH), 35.2 (2 $\times$ CH₂), 23.2 (CH₂). MS, m/z (% relative intensity): 277 (M^+ +1, 4), 41 (100), 28 (74), 27 (84). HRMS calculated for $\text{C}_{16}\text{H}_{21}\text{O}_4$: 277.1440; found: 277.1448.

5q**Dimethyl 4a,5,6,7,8,8a-hexahydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (5q)**

Pale yellow oil. ^1H -NMR (400 MHz, CDCl_3), δ (ppm): 5.43 (s, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 2.94 (s, 4H), 2.30 (s, 2H), 1.43-1.41 (m, 4H), 1.30-1.24 (m, 4H). ^{13}C -NMR, DEPT (100 MHz, CDCl_3), δ (ppm): 171.9 (2 $\times$ CO), 135.9 (2 $\times$ C), 122.9 (2 $\times$ CH), 59.3 (C), 52.7 (CH₃), 52.6 (CH₃), 38.5 (2 $\times$ CH₂), 35.8 (2 $\times$ CH), 28.3 (2 $\times$ CH₂), 23.4 (2 $\times$ CH₂). MS, m/z (% relative intensity): 291 (M^+ +1, 4), 289 (20), 59 (18), 41 (100), 29 (86). HRMS calculated for $\text{C}_{17}\text{H}_{22}\text{O}_4$: 291.1587; found: 291.1582.

VII. References

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VIII. Spectra