SUPPORTING INFORMATION

A Cheap Metal for a “Noble” Task:
Preparative and Mechanistic Aspects of Cycloisomerization and
Cycloaddition Reactions Catalyzed by Low-Valent Iron Complexes

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**General.** All reactions were carried out under Ar in flame dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et₂O (Mg-anthracene), CH₂Cl₂ (P₄O₁₀), MeCN, Et₃N, pyridine, DMF (CaH₂), MeOH (Mg), hexane, cyclohexane, toluene, benzene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a DPX 300 or AV 400 in solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ = 77.0 ppm; residual CHCl₃ in CDCl₃: δ = 7.26 ppm; C₆D₆: δ = 128.0 ppm; residual C₆H₆ in C₆D₆: δ = 7.15 ppm). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95, Bruker APEX III FT-ICR-MS (7 T magnet). Melting points: Büchi melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Alpha, Fluka, Aldrich) were used as received unless stated otherwise.

**Iron-Catalyzed Isomerization Reaction of 1,6-Enynes**

**Representative Procedure for the Alder-Ene Reaction Catalyzed by [CpFe(COD)][Li•DME] (4).** Preparation of 3-Ethenyl-4-methylene-1,1-cyclopentanedicarboxylic acid diethyl ester. A solution of (2E)-2-butenyl-2-propynyl-propanedionic acid diethyl ester (100 mg, 0.40 mmol) in toluene (2.0 mL) was added to a solution of complex 4 (6.5 mg, 5 mol %) in toluene (17 mL) at ambient temperature and the resulting mixture was refluxed under Ar for 2-3 h. After completion of the reaction, moist tert-butyl methyl ether was added and all volatile materials were evaporated. The residue was purified by flash chromatography (SiO₂, hexane/EtOAc) to give the title compound as a colorless oil (80 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ = 5.65 (ddd, J = 8.0, 9.5, 17.6 Hz, 1H), 5.09 (m, 1H), 5.04 (br s, 1H), 4.98 (dt, J = 2.4, 2.0 Hz, 1H), 4.81 (dt, J = 2.4, 2.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.16 (m, 1H), 3.07 (d, J = 17.0 Hz, 1H), 2.93 (ddt, J = 2.3, 17.0, 2.3 Hz, 1H), 2.56 (ddd, J = 1.2, 7.8, 13.0 Hz, 1H), 2.00 (dd, J = 10.9, 13.0 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.24 ppm (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 171.5, 150.6, 139.1, 115.9, 107.9, 61.5, 61.4, 58.5, 47.7, 40.1, 14.0 ppm; IR (ATR): ν = 2983, 1728, 1289, 1248, 1175, 1161, 1067, 1023, 914, 887, 861 cm⁻¹; MS (EI): m/z (%): 252 (9), 207 (9), 178 (58), 105 (100), 29 (24); HRMS (ESI+): calcd for C₁₄H₂₀O₄+Na: 275.12549; found: 275.12538 [M⁺+Na].

**Representative Procedure for the Alder-Ene Reaction Catalyzed by [CpFe(C₂H₄)₂][Li•TMEDA] (1).** Preparation of (2R*,3S*)-3-Ethenyl-4-methylene-2-propyl-1,1-cyclopentanedicarboxylic acid diethyl ester. A solution of (2E)-(2-butenyl-1-propyl)-2-propynyl-propanedionic acid diethyl ester (50 mg, 0.17 mmol) in toluene (0.7 mL) was added to a solution of complex 1 (10.2 mg, 20 mol %) in toluene (1 mL) and the resulting mixture was

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stirred at 90-95 °C under Ar for 2 h. After completion of the reaction, moist tert-butyl methyl ether was added and all volatile materials were evaporated. The residue was purified by flash chromatography (SiO₂, hexane/EtOAc) to give the title compound as a colorless oil (24 mg, 48%; trans: cis = 20:1 (¹H NMR)); Data of the major isomer: ¹H NMR (400 MHz, CDCl₃): δ = 5.59 (ddd, J = 8.9, 10.0, 17.0 Hz, 1H), 5.08 (dd, J = 2.0, 10.0 Hz, 1H), 5.04 (dd, J = 1.8, 17.0 Hz, 1H), 4.93 (dt, J = 2.1, 2.0 Hz, 1H), 4.78 (dt, J = 2.2, 2.0 Hz, 1H), 4.20 (dq, J = 0.7, 7.1 Hz, 2H), 4.19 (dq, J = 0.8, 7.1 Hz, 2H), 3.15 (br d, J = 17.0 Hz, 1H), 2.87 (m, 1H), 2.69 (dq, J = 17.0, 2.4 Hz, 1H), 2.41 (m, 1H), 1.52 (m, 1H), 1.42-1.34 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.88 ppm (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.9, 171.1, 150.3, 140.0, 116.6, 107.5, 61.7, 61.2, 61.1, 54.8, 50.2, 41.3, 33.5, 21.3, 14.3, 14.1, 14.0 ppm; IR (ATR): v = 2961, 1726, 1247, 1178, 1095, 1045, 1015, 912, 885, 862 cm⁻¹; MS (EI): m/z (%): 294 (22), 220 (76), 147 (100), 105 (37), 91 (23), 29 (30); HRMS (ESI⁺): calculated for C₁₇H₂₆O₄: C 69.36, H 8.80; found: C 69.81, H 8.82.

The following compounds were prepared analogously:

(3E,3αR*,6αS*)-Diethyl 3-(4-methoxybenzylidene)-3,3α,6,6α-tetrahydropentalene-1,1(2H)-dicarboxylate. Colorless oil (50%); the stereochemical assignment is based on NOE experiments. ¹H NMR (400 MHz, CDCl₃): δ = 7.07 (d, J = 8.6 Hz, 2H), 6.79 (s, J = 8.6 Hz, 2H), 6.19 (s, 1H), 5.54 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 4.04 (q, J = 7.0 Hz, 2H), 3.86 (d, J = 6.8 Hz, 1H), 3.73 (s, 3H), 3.45 (m, 1H), 3.05 (d, J = 16 Hz, 1H), 2.98 (d, J = 16 Hz, 1H), 2.48 (dd, J = 17.2, 10 Hz, 1H), 2.08 (dd, J = 17.2, 6.2 Hz, 1H), 1.19 ppm (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.2, 170.0, 157.7, 140.9, 132.3, 130.4, 129.2, 129.0, 122.6, 113.2, 63.9, 61.0, 60.9, 57.2, 54.9, 44.2, 35.6, 35.2, 13.8, 13.5 ppm; IR (ATR): v = 2956, 2924, 2853, 1729, 1607, 1575, 1510, 1464, 1366, 1297, 1175, 1157, 1074, 1033, 845 cm⁻¹; MS (EI): m/z (%): 121 (36), 223 (45), 296 (100), 370 (76); HRMS (CI): calculated for C₂₂H₂₆O₅: M⁺ 393.1669; found: 393.16724 [M⁺ + Na⁺]; elemental analysis calculated (%) for C₂₂H₂₆O₅: C 71.33, H 7.07; found: C 71.50, H 6.98.

(3Z,3αR*,7αS*)-2,3,3α,6,6,6α-Hexahydro-3-(phenylmethylene)-1H-indene-1,1-dicarboxylic acid diethyl ester. Yellow oil (93%); the stereochemical assignment is based on NOE experiments. ¹H NMR (400 MHz, CDCl₃): δ = 7.31 (m, 4H), 7.18 (m, 1H), 6.22 (q, J = 2.6 Hz, 1H), 5.98 (m, 1H), 5.81 (m, 1H), 4.19 (m, 4H), 3.59 (dt, J = 18.4, 2.9 Hz, 1H), 3.44 (br s, 1H), 3.15 (br d, J = 18.4 Hz, 1H), 2.88 (m, 1H), 2.08 (m, 2H), 1.37 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.19 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 169.8, 144.3, 137.9, 128.2, 128.1, 126.9, 126.5, 126.1, 123.5, 63.2, 61.5, 61.4, 44.6, 41.9, 36.6, 24.6, 21.1, 14.1, 13.9 ppm; IR (ATR): v = 2937, 1728, 1247, 1222, 1196, 1173, 912, 729, 695 cm⁻¹; MS (EI): m/z (%): 354 (19), 309 (13), 280 (48), 207 (93), 189 (74), 173 (100), 143 (35), 115 (54), 91 (86), 29 (30); HRMS (ESI⁺): calculated for C₂₂H₂₆O₄Na⁺: 377.17285; found: 377.17233 [M⁺ + Na⁺].

(3Z,3αR*,7αR*)-2,3,3α,6,6,7α-Hexahydro-1-[(4-methylphenyl)sulfonyl]-3-phenylmethylene-1H-indole. White solid (60%); mp = 121-125 °C; ¹H NMR (400 MHz, CDCl₃): δ
= 7.74 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 7.3 Hz, 2H), 6.21 (q, J = 2.2 Hz, 1H), 5.87 (m, 1H), 5.73 (m, 1H), 4.31 (dt, J = 14.9, 1.7 Hz, 1H), 4.20 (br d, J = 14.9 Hz, 1H), 3.88 (dd, J = 3.9, 7.4, 10.4 Hz, 1H), 2.95 (br s, 1H), 2.41 (s, 3H), 2.18 (m, 1H), 2.08 (s, 1H), 1.90 (dq, J = 12.9, 4.4 Hz, 1H), 1.62 ppm (m, 1H); 13C NMR (100 MHz, CDCl3): δ = 143.4, 139.9, 136.4, 135.3, 129.8, 129.1, 128.5, 128.2, 127.3, 127.0, 124.1, 123.9, 57.5, 49.8, 44.2, 26.1, 23.3, 21.5 ppm; IR (ATR): ν = 2936, 1727, 1607, 1509, 1445, 1366, 1242, 1175, 1094, 1032, 856, 803 cm⁻¹; MS (EI): m/z (%): 365 (16), 286 (100), 274 (24), 210 (38), 182 (21), 155 (26), 115 (32), 91 (88); HRMS (ESI+): calcd for C22H23NO2S+Na: 388.13411; found: 388.13417 [M⁺+Na]; elemental analysis calcd (%) for C22H23NO2S: C 72.30, H 6.34; found: C 72.41, H 6.43.

(4E,4aS*,8aS*)-Diethyl 4-(4-methoxybenzylidene)-2,3,4,4a,8,8a-hexahydropthalphthalene-1,1(7H)-dicarboxylate and (4E,4aR*,8aS*)-diethyl 4-(4-methoxybenzylidene)-2,3,4,4a,8,8a-hexahydropthalphthalene-1,1(7H)-dicarboxylate. Colorless oil (67%, dr = 2.5:1); as the signals for both isomers are largely overlapping, an unambiguous stereochemical assignment was not possible; data of the major isomer: 1H NMR (400 MHz, CDCl3): δ = 7.06 (d, J = 8.3 Hz, 2H), 6.79 (m, 2H), 6.07 (m, 1H), 5.74 (m, 2H), 4.19 (m, 4H), 3.72 (s, 3H), 2.85 (m, 1H), 2.81 (dt, J = 13.6, 3.4 Hz, 1H), 2.70 (m, 1H), 2.40 (m, 1H), 2.2-1.35 (m, 6H), 1.21 ppm (m, 6H); 13C NMR (100 MHz, CDCl3): δ = 171.4, 171.2, 170.8, 157.0, 139.5, 131.9, 129.9, 129.0, 128.8, 127.2, 127.0, 126.8, 126.4, 124.9, 112.8, 112.5, 60.3, 60.2, 60.0, 59.5, 58.2, 58.0, 54.2, 46.0, 41.2, 39.8, 39.0, 38.8, 34.5, 27.2, 25.8, 24.5, 23.9, 23.5, 21.5, 19.5, 13.2 ppm; IR (ATR): ν = 2936, 1727, 1607, 1509, 1445, 1366, 1242, 1175, 1094, 1032, 856, 803 cm⁻¹; MS (EI): m/z (%): 121 (100), 173 (44), 251 (24), 277 (23), 398 (29); HRMS (EI): calcd for C22H23NO2S+Na: 421.19855; found: 421.19837 [M⁺+Na].

(3E,3aS*,4Z,8aS*)-Diethyl 3-benzylidene-3,3a,6,7,8,8a-hexahydroazulene-1,1(6H)-dicarboxylate. Yellow oil (63%); The stereochemistry was assigned based on NOE experiments; 1H NMR (400 MHz, CDCl3): δ = 7.27 (m, 5H), 6.27 (dd, J = 4.8, 2.4 Hz, 1H), 5.86 (m, 2H), 4.19 (m, 4H), 3.45 (d, J = 11.6 Hz, 1H), 3.31 (dd, J = 18, 2 Hz, 1H), 2.86 (dt, J = 18, 3.2 Hz, 1H), 2.32 (m, 1H), 2.2-1.3 (m, 6H), 1.19 ppm (m, 6H); 13C NMR (100 MHz, CDCl3): δ = 170.7, 168.4, 144.7, 137.9, 135.4, 132.3, 127.9, 127.40, 125.7, 121.77, 62.2, 60.8, 60.7, 49.1, 39.6, 39.1, 32.8, 29.3, 26.1, 13.8, 13.7 ppm; IR (ATR): ν = 2955, 2924, 2854, 1727, 1599, 1491, 1445, 1367, 1252, 1186, 1095, 1031, 918, 862 cm⁻¹; MS (EI): m/z (%): 29 (80), 95 (67), 151 (40), 180 (100), 221 (23), 254 (18), 294 (14), 368 (7); elemental analysis calcd (%) for C23H26O4: C 74.97, H 7.66; found: C 74.80, H 7.85.

(Z,3aS*,9aS*)-Diethyl 3,3a,7,8,9,9a-hexahydro-3-methylene-2H-yclopenta[8]annulene-1,1(6H)-dicarboxylate. Colorless oil (83%); 1H NMR (400 MHz, CDCl3): δ = 5.54 (m, 2H), 4.84 (dd, J = 4.9, 2.2 Hz, 1H), 4.78 (dd, J = 4.9, 2.4 Hz, 1H), 4.12 (m, 4H), 3.32 (br d, J = 12 Hz, 1H), 3.07 (d, J = 18 Hz, 1H), 2.63 (dd, J = 18, 2.5 Hz, 1H), 2.21 (m, 1H), 2.09 (m, 2H),
1.95 (m, 1H), 1.66 (m, 1H), 1.53-1.27 (m, 3H), 1.21 (m, 6H), 1.14 ppm (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.7, 170.4, 151.0, 132.1, 129.1, 105.0, 60.4, 60.0, 52.3, 45.1, 40.0, 28.7, 27.7, 23.8, 22.7, 13.1, 13.0 ppm; IR (ATR): $\tilde{\nu}$ = 3075, 2932, 2862, 1728, 1647, 1295, 1253, 1185, 1098, 1052, 1019, 880 cm$^{-1}$; MS (EI): m/z (%): 159 (74), 232 (100), 261 (11), 306 (14); elemental analysis calcd (%) for C$_{18}$H$_{26}$O$_4$: C 70.56, H 8.55; found: C 70.67, H 8.51.

(3E,3aS*$,4Z,9aS*$)-Diethyl 3-ethylenidene-3,3a,7,8,9,9a-hexahydro-2H-cyclopenta[8]-annulene-1,1(6H)-dicarboxylate. Colorless oil (93%); the stereochemistry was assigned based in NOE experiments. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.49 (m, 2H), 5.17 (m, 1H), 4.11 (m, 4H), 3.28 (br d, $J$ = 11.7 Hz, 1H), 2.97 (d, $J$ = 17.5 Hz, 1H), 2.47 (dd, $J$ = 17.5, 1.9 Hz, 1H), 2.18 (m, 1H), 2.07 (m, 2H), 1.96 (m, 1H), 1.63 (m, 1H), 1.55 (d, $J$ = 6.7 Hz, 3H), 1.49 (m, 1H), 1.33 (m, 2H), 1.20 (m, 6H), 1.13 ppm (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.5, 171.1, 142.4, 133.5, 129.4, 115.4, 70.0, 60.6, 52.9, 45.4, 37.6, 28.3, 27.4, 24.2, 23.3, 13.9, 13.6 ppm; IR (ATR): $\tilde{\nu}$ = 3014, 2980, 2931, 2860, 1729, 1647, 1462, 1447, 1251, 1270, 1195, 1178, 1100, 1020, 863 cm$^{-1}$; MS (EI): m/z (%): 173 (79), 217 (16), 246 (100), 320 (25); HRMS (Cl): calcd for C$_{19}$H$_{28}$O$_2$+Na: 343.1882; found: 343.1885 [M$^+$Na$^-$]; elemental analysis calcd (%) for C$_{19}$H$_{28}$O$_2$: C 71.22, H 8.81; found: C 71.29, H 8.75.

(3E,3aS*$,4Z,9aS*$)-Diethyl 3-benzylidene-3,3a,7,8,9,9a-hexahydro-2H-cyclopenta[8]-annulene-1,1(6H)-dicarboxylate. Colorless oil (95%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.23 (m, 4H), 7.08 (m, 1H), 6.15 (t, $J$ = 2.4 Hz, 1H), 5.62 (m, 2H), 4.09 (m, 4H), 3.56 (br d, $J$ = 11.6 Hz, 1H), 3.33 (d, $J$ = 17.1 Hz, 1H), 2.88 (dd, $J$ = 17.1, 2.9 Hz, 1H), 2.23 (m, 1H), 2.11 (m, 2H), 1.99 (m, 1H), 1.63 (m, 1H), 1.58-1.31 (m, 3H), 1.21 (m, 6H), 1.16 ppm (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.2, 170.8, 144.9, 137.8, 133.2, 130.0, 127.9, 127.8, 125.7, 121.9, 61.8, 60.8, 60.7, 52.0, 47.3, 39.7, 28.4, 27.3, 24.5, 23.8, 13.8, 13.7 ppm; IR (ATR): $\tilde{\nu}$ = 3056, 2980, 2933, 1727, 1600, 1447, 1367, 1252, 1190, 1158, 1098, 1036, 862, 756 cm$^{-1}$; MS (EI): m/z (%): 91 (72), 217 (90), 235 (69), 308 (100), 382 (59); elemental analysis calcd (%) for C$_{23}$H$_{30}$O$_2$: C 75.36, H 7.91; found: C 75.48, H 7.87.

(3Z,3aR*$,9aS*$)-3,3a,6,7,8,9,9a-Octahydro-1-(phenylmethyl)-3-(phenylmethylenec)-1H-cycloocta[b]pyrrole.$^1$ White solid (93%); mp = 69-71 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.35 (m, 4H), 7.28 (m, 3H), 7.14 (m, 3H), 6.16 (q, $J$ = 2.5 Hz, 1H), 5.73 (m, 2H), 4.23 (d, $J$ = 13.3 Hz, 1H), 4.00 (d, $J$ = 15.3 Hz, 1H), 3.59 (m, 1H), 3.24 (d, $J$ = 13.3 Hz, 1H), 3.20 (dt, $J$ = 15.3, 2.8 Hz, 1H), 2.50 (m, 1H), 2.26 (m, 1H), 2.16 (m, 2H), 1.82-1.55 (m, 3H), 1.42 ppm (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 138.0, 131.9, 130.8, 128.7, 128.3, 127.8, 126.9, 126.0, 120.1, 70.5, 58.6, 57.9, 50.2, 29.6, 27.9, 24.9, 21.1 ppm; IR (ATR): $\tilde{\nu}$ = 2925, 2854, 1741, 1494, 1450, 1260, 1073, 1028, 911, 804, 732, 719, 691 cm$^{-1}$; MS (EI): m/z (%): 329 (83), 286 (21), 247 (27), 91 (100); HRMS (ESI+): calcd for C$_{23}$H$_{28}$N: 330.22130; found: 330.22162 [M$^+$H$^+$.]

(3Z,3aR*$,7aS*$)-3,3a,6,7,8,9,9a-Octahydro-1-[[4-methylphenyl]sulfonyl]-3-(phenylethenylenec)-1H-cycloocta[b]pyrrole.$^1$ White solid (94%); the structure was confirmed by X-ray crystal analysis (see below). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.61 (d, $J$ = 8.2 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 2H), 7.24 (t, $J$ = 7.8 Hz, 3H), 7.12 (d, $J$ = 7.4 Hz, 2H), 6.12 (q, $J$ = 2.3 Hz,
1H), 5.74 (dt, J = 6.9, 10.2 Hz, 1H), 5.54 (dd, J = 8.0, 9.9 Hz, 1H), 4.49 (br d, J = 15.5 Hz, 1H), 4.15 (dt, J = 15.6, 2.0 Hz, 1H), 3.64 (br t, J = 8.8 Hz, 1H), 2.83 (m, 1H), 2.61 (dt, J = 2.8, 10.3 Hz, 1H), 2.39 (s, 3H), 2.37 (m, 1H), 2.16 (m, 1H), 1.80 (m, 1H), 1.68 (m, 1H), 1.28 (m, 2H), 1.08 ppm (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 143.5, 138.2, 136.5, 133.2, 132.4, 129.6, 128.5, 128.4, 128.1, 127.6, 126.9, 121.1, 66.3, 53.1, 49.7, 31.7, 27.6, 25.2, 21.5, 21.3 ppm; IR (ATR): \(\tilde{\nu} = 2924, 2854, 1448, 1345, 1160, 1091, 1030, 813, 752, 693, 662 \text{ cm}^{-1}\); MS (EI): \(m/z\) (%): 393 (14), 302 (42), 238 (100), 156 (25), 115 (20), 91 (84); HRMS (ESI\(^{+}\)) calculated for C\(_{24}\)H\(_{27}\)NO\(_2\)S+Na: 416.16528; found: 416.16547 [M\(^{+}\)+Na]; elemental analysis calculated (%) for C\(_{24}\)H\(_{27}\)NO\(_2\)S: C 73.25, H 6.92; found: C 73.08, H 7.10.

**(3E,3aS\(^{*}\),4Z,9aS\(^{*}\))-Diethyl 3-(4-bromobenzylidene)-3,3a,7,8,9,9a-hexahydro-2H-cyclopenta[8]annulene-1,1(6H)-dicarboxylate.** Yellow oil (97%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.36\) (d, \(J = 7.7\) Hz, 2H), 7.08 (d, \(J = 7.7\) Hz, 2H), 6.09 (s, 1H), 5.61 (m, 2H), 4.16 (m, 4H), 3.55 (d, \(J = 11.5\) Hz, 1H), 3.3 (d, \(J = 17.8\) Hz, 1H), 2.79 (d, \(J = 17.8\) Hz, 1H), 2.27 (m, 1H), 2.15 (m, 2H), 1.99 (m, 1H), 1.7 (m, 1H), 1.55 (m, 2H), 1.33 (m, 1H), 1.21 ppm (m, 7H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 170.5, 170.1, 145.3, 136.0, 132.1, 130.3, 128.7, 127.2, 120.1, 118.8, 61.1, 60.2, 60.1, 51.3, 46.7, 38.9, 27.7, 26.8, 23.8, 22.7, 13.1, 13.0 ppm; IR (ATR): \(\tilde{\nu} = 2977, 2929, 2859, 1724, 1588, 1488, 1367, 1249, 1187, 1096, 1073, 1008, 891, 852, 805 \text{ cm}^{-1}\); MS (EI): \(m/z\) (%): 155 (23), 232 (100), 461 (36); elemental analysis calculated (%) for C\(_{24}\)H\(_{28}\)BrO\(_4\): C 62.48, H 6.34; Br 17.32; found: C 62.56, H 6.23.

**(3E,3aS\(^{*}\),4Z,9aS\(^{*}\))-Diethyl 3-(2-cyclohexyl-2-oxoethylidene)-3,3a,7,8,9,9a-hexahydro-2H-cyclopenta[8]annulene-1,1(6H)-dicarboxylate.** Yellow oil (68%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.11\) (dd, \(J = 4.8, 2.4\) Hz, 1H), 5.61 (m, 1H), 5.48 (dd, \(J = 10.3, 7.2\) Hz, 1H), 4.19 (m, 4H), 3.65 (dd, \(J = 20.4, 2\) Hz, 1H), 3.53 (td, \(J = 10.8, 1.1\) Hz, 1H), 2.96 (dt, \(J = 20.4, 2.8\) Hz, 1H), 2.27 (m, 1H), 2.13 (m, 3H), 2.01 (m, 1H), 1.8-1.4 (m, 7H), 1.33-1.16 ppm (m, 14H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 203.1, 170.9, 170.8, 165.8, 131.4, 130.9, 118.1, 61.3, 60.8, 60.7, 51.5, 51.0, 47.7, 41.8, 29.3, 28.2, 27.2, 25.6, 25.4, 24.5, 23.1, 13.7, 13.6 ppm; IR (ATR): \(\tilde{\nu} = 2928, 2854, 1724, 1683, 1618, 1448, 1367, 1246, 1189, 1096, 1047, 861, 744 \text{ cm}^{-1}\); MS (EI): \(m/z\) (%): 83 (81), 259 (77), 343 (79), 359 (28), 371 (15), 416 (100), 432 (2); elemental analysis calculated (%) for C\(_{25}\)H\(_{30}\)O\(_3\): C 72.08, H 8.71; found: C 72.23, H 8.60.

**(3E,3aS\(^{*}\),4Z,9aS\(^{*}\))-Diethyl 3-(cyclopropylmethylene)-3,3a,7,8,9,9a-hexahydro-2H-cyclopenta[8]annulene-1,1(6H)-dicarboxylate.** Colorless oil (96%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.47\) (m, 2H), 4.54 (dd, \(J = 9.2, 2.4\) Hz, 1H), 4.15 (m, 4H), 3.29 (d, \(J = 12\) Hz, 1H), 3.14 (d, \(J = 17.6\) Hz, 1H), 2.66 (dt, \(J = 17.6, 2.8\) Hz, 1H), 2.21 (m, 1H), 2.05 (m, 2H), 1.94 (m, 1H), 1.65 (m, 1H), 1.47 (m, 2H), 1.41-1.16 (m, 9H), 0.64 (d, \(J = 8\) Hz, 2H), 0.24 ppm (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 171.8, 171.5, 140.6, 133.8, 129.8, 125.3, 61.5, 60.9, 60.8, 52.9, 45.8, 38.2, 28.7, 27.7, 24.8, 23.7, 14.1, 14.0, 11.0, 6.6 ppm; IR (ATR): \(\tilde{\nu} = 2929, 2895, 1724, 1446, 1366, 1247, 1181, 1095, 1074, 1047, 1018, 970,
904, 860, 806 cm\(^{-1}\); MS (EI): \(m/z\) (%): 91 (24), 173 (37), 199 (75), 272 (100), 346 (36); HRMS (Cl): calcd for \(C_{21}H_{30}O_4\): 369.203632; found: 309.203327 [\(M^+\)+Na]; elemental analysis calcd (%) for \(C_{21}H_{30}O_4\): C 72.80, H 8.73; found: C 72.91, H 8.66.

\((3E, 3aS^*, 4Z, 9aS^*)\)-Diethyl 3,3a,7,8,9,9a-hexahydro-3-((trimethylsilyl)methylene)-2H-cyclopenta[8]annulene-1,1(6H)-dicarboxylate. Colorless oil (70%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 5.63 (m, 2H), 5.3 (d, \(J = 1.6\) Hz, 1H), 4.21 (m, 4H), 3.51 (t, \(J = 10\) Hz, 1H), 2.4-1.9 (m, 4H), 1.83-1.51 (m, 7H), 1.22 (m, 6H), 0.04 ppm (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 172.9, 172.1, 151.9, 133.4, 131.1, 122.1, 69.4, 62.3, 62.2, 57.1, 51.9, 30.3, 28.7, 26.2, 25.5, 21.6, 15.8, 14.5, 0.1 ppm; IR (ATR): \(\tilde{\nu}\) = 2931, 1914, 1725, 1633, 1446, 1366, 1308, 1248, 1202, 1181, 1095, 1070, 1043, 963, 946, 936, 760 cm\(^{-1}\); MS (EI): \(m/z\) (%): 73 (79), 159 (26), 187 (100), 231 (29), 305 (67), 378 (75); HRMS (Cl): calcd for \(C_{21}H_{30}O_4\): 401.211663; found: 401.211861 [\(M^+\)+Na]; elemental analysis calcd (%) for \(C_{21}H_{30}O_4\): C 66.62, H 9.05; found: C 66.78, H 9.01.

\([(3E, 3aS^*, 9aS^*)-1-\text{[1,3-Dioxolane]-3-(4-methoxybenzylidene)-2,3,3a,6,7,8,9,9a-octahydro-1H-cyclopenta[a]cycloocten-1-yl}].\) White solid (96%); mp = 121.5-123 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 7.19 (d, \(J = 8.7\) Hz, 2H), 6.79 (d, \(J = 8.7\) Hz, 2H), 6.09 (d, \(J = 2.2\) Hz, 1H), 5.61 (dd, \(J = 10.4, 6.8\) Hz, 1H), 5.56 (m, 1H), 3.95 (d, \(J = 11.6\) Hz, 1H), 3.86 (dd, \(J = 11.6, 1.2\) Hz, 1H), 3.73 (s, 3H), 3.38 (m, 3H), 3.16 (dd, \(J = 17.6, 1.6\) Hz, 1H), 2.37 (d, \(J = 17.6\) Hz, 1H), 2.27 (m, 1H), 1.99 (m, 1H), 1.88 (t, \(J = 11.2\) Hz, 1H), 1.69 (m, 1H), 1.5 (m, 3H), 1.36 (s, 3H), 1.32 (s, 3H), 1.17 ppm (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 156.8, 143.0, 134.0, 130.4, 128.3, 128.2, 121.1, 112.7, 97.0, 67.9, 62.7, 54.2, 51.7, 47.3, 42.3, 40.4, 27.7, 26.6, 25.7, 23.7, 23.3, 19.1 ppm; IR (ATR): \(\tilde{\nu}\) = 2927, 2113, 1607, 1510, 1249, 1199, 1065, 1035, 834, 668 cm\(^{-1}\); MS (EI): \(m/z\) (%): 91 (8), 121 (100), 147 (31), 159 (16), 310 (4), 368 (41); HRMS (Cl): calcd for \(C_{24}H_{32}O_3\): 391.223985; found: 391.224366 [\(M^+\)+Na]; elemental analysis calcd (%) for \(C_{24}H_{32}O_3\): C 78.22, H 8.75; found: C 78.41, H 8.83.

\([(3E, 3aS^*, 9aS^*)-1-\text{[(Acetylxy)methyl]-3-(4-methoxybenzylidene)-2,3,3a,6,7,8,9,9a-octahydro-1H-cyclopenta[a]cycloocten-1-yl]methyl acetate.}\) White solid (84%); mp = 100.5-103 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 7.16 (d, \(J = 8.7\) Hz, 2H), 6.8 (d, \(J = 8.7\) Hz, 2H), 6.11 (d, \(J = 2.4\) Hz, 1H), 5.64 (dd, \(J = 10.4, 6.8\) Hz, 1H), 5.57 (m, 1H), 4.06 (m, 3H), 3.85 (d, \(J = 11.2\) Hz, 1H), 3.74 (s, 3H), 3.67 (m, 1H), 3.49 (t, \(J = 9.9\) Hz, 1H), 2.7 (dd, \(J = 17.6, 1.6\) Hz, 1H), 2.49 (dt, \(J = 17.6, 2.8\) Hz, 1H), 2.28 (m, 1H), 2.02 (s, 3H), 1.96 (s, 3H), 1.9-1.1 ppm (m, 7H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 170.6, 157.5, 143.1, 134.5, 130.8, 129.1, 128.9, 121.8, 113.4, 67.6, 66.8, 64.4, 54.8, 51.9, 48.3, 46.7, 37.6, 28.3, 25.6, 25.3, 24.3, 24.0, 20.6 ppm; IR (ATR): \(\tilde{\nu}\) = 2971, 2929, 1738, 1607, 1510, 1463, 1365, 1241, 1230, 1177, 1034, 831 cm\(^{-1}\); MS (EI): \(m/z\) (%): 43 (16), 121 (100), 171 (26), 292 (12), 412 (12); HRMS (Cl): calcd for \(C_{25}H_{32}O_5\): 435.214197; found: 435.214746 [\(M^+\)+Na]; elemental analysis calcd (%) for \(C_{25}H_{32}O_5\): C 72.79, H 7.82; found: C 72.66, H 7.84.
\[ ((3E,3aS*,9aS*)-3-(4-Methoxybenzylidene)-1-[(triisopropylsilyl)oxy]methyl]-2,3,3a,6,7,8,9,9a-octahydro-1H-cyclopenta[a]cycloocten-1-yl)methoxy][triisopropyl]-silane. \]

Colorless oil (86%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.17\) (d, \(J = 8.6\) Hz, 2H), 6.78 (d, \(J = 8.6\) Hz, 2H), 6.04 (d, \(J = 2.4\) Hz, 1H), 5.66 (dd, \(J = 10, 6.8\) Hz, 1H), 5.5 (m, 1H), 3.72 (s, 3H), 3.57 (m, 5H), 2.78 (dd, 17.4, 1.8 Hz, 1H), 2.48 (dd, \(J = 17.4, 2.8\) Hz, 1H), 2.31 (m, 1H), 1.96 (m, 2H), 1.58 (m, 4H), 1.34-1.08 (m, 3H), 0.99-0.87 ppm (m, 41H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 156.4, 145.6, 135.1, 131.1, 128.1, 127.4, 119.7, 112.5, 65.9, 63.4, 54.2, 50.7, 50.2, 48.7, 36.3, 28.0, 25.2, 23.7, 23.6, 17.1, 17.0, 16.8, 16.7, 11.7, 11.5, 11.0, 10.9 ppm; IR (ATR): \(\tilde{\nu} = 2940, 2865, 1711, 1605, 1510, 1462, 1247, 1174, 1093, 1061, 917, 881, 803, 676\) cm\(^{-1}\); elemental analysis calcd (%) for C\(_{39}\)H\(_{68}\)O\(_3\)Si\(_2\): C 73.06, H 10.69; found: C 73.11, H 10.61.

\((3Z,3aR*,9aS*)-2,3,3a,6,7,8,9,9a-octahydro-(3-phenylmethylene)-cycloocta[b]furan.\)

Yellow oil (70%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.35\) (t, \(J = 7.5\) Hz, 2H), 7.21 (t, \(J = 7.4\) Hz, 1H), 7.16 (d, \(J = 7.4\) Hz, 2H), 6.25 (dd, \(J = 2.6, 2.5\) Hz, 1H), 5.74 (m, 2H), 4.84 (d, \(J = 14.3\) Hz, 1H), 4.62 (dt, \(J = 14.4, 2.5\) Hz, 1H), 3.44 (br s, 1H), 3.28 (dt, \(J = 10.5, 3.2\) Hz, 1H), 2.42 (m, 1H), 2.20 (m, 2H), 1.79-1.48 (m, 4H), 1.31 ppm (m, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 146.1, 137.4, 132.0, 128.9, 128.5, 127.9, 126.4, 119.7, 84.4, 70.3, 49.7, 31.1, 27.2, 25.2, 20.1 ppm; IR (ATR): \(\tilde{\nu} = 2924, 2853, 1729, 1599, 1449, 1260, 1060, 1045, 1012, 951, 804, 754, 691\) cm\(^{-1}\); MS (EI): \(m/z\) (\%) 240 (52), 181 (11), 167 (23), 155 (100), 142 (39), 128 (35), 117 (46), 91 (54); HRMS (EI): calcd for C\(_{17}\)H\(_{20}\)O: 240.1519; found: 240.15142 [M\(^+\)].

\((E,3aS*,11aS*)-Diethyl 3,3a,7,8,9,10,11,11a-octahydro-3-methylene-2H-cyclopenta[10]-annulene-1,1(6H)-dicarboxylate.\)

Colorless oil (76%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 5.6\) (ddd, \(J = 10.8, 9.6, 5.2\) Hz, 1H), 5.21 (m, 1H), 4.89 (d, \(J = 2.4\) Hz, 1H), 4.82 (dd, \(J = 2.4, 0.9\) Hz, 1H), 4.17 (m, 4H), 3.11-3.02 (m, 2H), 2.76 (dd, \(J = 17.5, 2.4\) Hz, 1H), 2.18 (m, 3H), 1.99 (m, 1H), 1.7-1.4 (m, 7H), 1.23 ppm (m, 8H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 171.9, 171.6, 150.4, 133.07, 132.6, 107.0, 61.5, 61.1, 61.0, 54.6, 49.4, 40.5, 30.9, 27.9, 27.0, 26.5, 25.7, 22.6, 14.1, 14.0 ppm; IR (ATR): \(\tilde{\nu} = 3037, 2925, 1725, 1457, 1366, 1244, 1177, 1095, 1048, 984, 881\) cm\(^{-1}\); MS (EI): \(m/z\) (\%) 91 (39), 145 (14), 164 (13), 187 (78), 260 (100), 289 (16), 334 (26); HRMS (CI): calcd for C\(_{20}\)H\(_{30}\)O\(_4\)+Na: 357.203629; found: 357.203873 [M\(^+\)+Na]; elemental analysis calcd (%) for C\(_{20}\)H\(_{30}\)O\(_4\): C 71.82, H 9.04; found: C 71.96, H 9.17.

\((E,3aR*,11aS*)-2,3,3a,6,7,8,9,9,10,11,11a-Decahydro-1-[(4-methylphenyl)sulfonyl]-3-(phenylmethylene)-1H-cyclodecab[b]pyrrole.\)

White solid (86%); mp = 164-166 ºC; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.58\) (d, \(J = 8.2\) Hz, 2H), 7.34 (m, 2H), 7.22 (m, 1H), 6.07 (q, \(J = 2.2\) Hz, 1H), 5.74 (br s, 1H), 5.09 (br s, 1H), 4.43 (dt, \(J = 15.5, 1.8\) Hz, 1H), 4.13 (br d, \(J = 15.5\) Hz, 1H), 3.30 (br t, \(J = 8.6\) Hz, 1H), 2.80 (br s, 1H), 2.62 (br t, \(J = 12.8\) Hz, 1H), 2.39 (s, 3H), 2.25 (m, 1H), 2.16 (m, 1H), 1.86 (m, 1H), 1.72-1.46 (m, 6H), 1.34 ppm (m, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 143.4, 137.6, 137.4, 136.4, 133.0, 129.6, 128.4, 128.1, 127.7, 126.9, 122.4, 64.4, 52.7, 32.9, 31.5, 29.7, 26.7, 24.1, 23.7,
23.6, 21.5 ppm; IR (ATR): \( \tilde{\nu} = 2962, 2923, 2855, 1596, 1450, 1329, 1154, 1090, 1040, 1013, 990, 815, 751, 706, 693, 659 \text{ cm}^{-1}; \) MS (EI): \( m/z \) (%): 421 (9), 311 (15), 266 (100), 155 (15), 91 (33); HRMS (ESI+): calcd for C_{29}H_{31}NO_{5}S^{+}: 444.19736; found: 444.19677 [M^+\Na]; elemental analysis calcd (%) for C_{29}H_{31}NO_{5}S: C 74.07, H 7.41; found: C 73.72, H 7.58.

**5(3E,3aR\*,11aS\*)-2,3,3a,7,8,9,10,11,11a-decahydro-(3-phenylmethylene)-cyclodeca[b]furan.** White solid (55%); mp = 82-83 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.34 \) (t, \( J = 7.6 \text{ Hz}, 2\)H), 7.21 (t, \( J = 7.4 \text{ Hz}, 1\)H), 7.15 (d, \( J = 7.3 \text{ Hz}, 2\)H), 6.21 (q, \( J = 2.5 \text{ Hz}, 1\)H), 5.78 (ddd, \( J = 4.3, 10.5, 15.5 \text{ Hz}, 1\)H), 5.30 (m, 1H), 4.84 (dt, \( J = 14.3, 1.7 \text{ Hz}, 1\)H), 4.58 (dt, \( J = 14.4, 2.5 \text{ Hz}, 1\)H), 3.51 (br t, \( J = 9.3 \text{ Hz}, 1\)H), 3.15 (br t, \( J = 9.3 \text{ Hz}, 1\)H), 2.32 (dd, \( J = 4.1, 12.6 \text{ Hz}, 1\)H), 2.13 (m, 1H), 2.07 (dt, \( J = 10.6, 3.1 \text{ Hz}, 1\)H), 1.84 (m, 1H), 1.46 (m, 1H), 1.21 ppm (m, 3H); \(^13C\) NMR (100 MHz, CDCl\(_3\)): \( \delta = 145.1, 137.2, 136.9, 128.5, 127.9, 127.6, 126.5, 121.2, 83.9, 70.0, 57.3, 32.7, 32.3, 27.6, 25.4, 23.3 ppm; IR (ATR): \( \tilde{\nu} = 2923, 2857, 1447, 1048, 1024, 996, 961, 915, 758, 712, 691 \text{ cm}^{-1}; \) MS (EI): \( m/z \) (%): 268 (34), 169 (19), 155 (100), 141 (14), 128 (14), 115 (15), 91 (17); HRMS (EI): calcd for C_{19}H_{20}O: 268.18273; found: 268.18271 [M^+].

**5(3E,3aS\*,4E,11aS\*)-Diethyl 3-(4-(ethoxycarbonyl)-benzylidene)-3,3a,7,8,9,10,11,11a-octa-hydro-2H-cyclopenta[10]annulene-1,1(6H)-dicarboxylate.** Yellow oil (89%); \(^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.91 \) (d, \( J = 8.3 \text{ Hz}, 2\)H), 7.19 (d, \( J = 8.3 \text{ Hz}, 2\)H), 6.17 (d, \( J = 2.4 \text{ Hz}, 1\)H), 5.62 (ddd, \( J = 11.2, 9.2, 5.2 \text{ Hz}, 1\)H), 5.25 (br s, 1H), 4.29 (q, \( J = 7.1 \text{ Hz}, 2\)H), 4.17 (m, 4H), 3.34 (d, \( J = 18.4 \text{ Hz}, 1\)H), 3.21 (t, \( J = 10 \text{ Hz}, 1\)H), 2.91 (dt, \( J = 18.4, 2.8 \text{ Hz}, 1\)H), 2.2-1.91 (m, 4H), 1.7-1.33 (m, 4H), 1.32 (t, \( J = 7.1 \text{ Hz}, 3\)H), 1.28-1.11 (m, 7H), 0.77 ppm (m, 4H); \(^13C\) NMR (100 MHz, CDCl\(_3\)): \( \delta = 171.9, 171.7, 166.8, 146.9, 142.8, 134.2, 132.3, 129.9, 128.6, 128.3, 122.8, 62.4, 61.7, 61.6, 61.1, 52.5, 40.1, 31.5, 29.4, 28.1, 26.9, 26.4, 25.6, 22.9, 14.7, 14.5, 14.4 ppm; IR (ATR): \( \tilde{\nu} = 2978, 2928, 2859, 1714, 1606, 1566, 1444, 1366, 1271, 1180, 1154, 1101, 1018, 984, 877, 860 \text{ cm}^{-1}; \) MS (EI): \( m/z \) (%): 171 (19), 245 (100), 335 (52), 408 (93), 437 (22), 482 (44); HRMS (CI): calcd for C_{29}H_{30}O_{6}Na+: 505.25606; found: 505.25638 [M^+Na]; elemental analysis calcd (%) for C_{29}H_{30}O_{6}Na: C 72.17, H 7.94; found: C 72.30, H 7.88.

**5(3E,3aS\*,4E,11aS\*)-Diethyl 3-(2-(1H-pyrrol-1-yl)benzylidene)-3,3a,7,8,9,10,11,11a-octa-hydro-2H-cyclopenta[10]annulene-1,1(6H)-dicarboxylate.** Yellow oil (83%); \(^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.35 \) (m, 1H), 7.24 (m, 3H), 6.75 (t, \( J = 2 \text{ Hz}, 2\)H), 6.2 (t, \( J = 2 \text{ Hz}, 2\)H), 5.91 (d, \( J = 2.4 \text{ Hz}, 1\)H), 5.51 (m, 1H), 5.13 (m, 1H), 4.17 (m, 4H), 3.14 (m, 2H), 2.68 (d, \( J = 18, 2.2 \text{ Hz}, 1\)H), 2.13 (m, 4H), 1.41 (m, 6H), 1.21 ppm (m, 9H); \(^13C\) NMR (100 MHz, CDCl\(_3\)): \( \delta = 172.1, 171.8, 145.4, 139.7, 133.4, 129.9, 129.2, 127.6, 127.3, 126.9, 125.9, 122.7, 120.0, 109.3, 61.9, 61.6, 61.4, 52.5, 40.1, 39.3, 28.2, 26.8, 26.5, 26.1, 25.9, 25.4, 14.5, 14.4 ppm; IR (ATR): \( \tilde{\nu} = 2924, 2858, 1723, 1599, 1496, 1455, 1367, 1327, 1257, 1204, 1186, 1094, 1069, 1044, 1015, 984, 724 \text{ cm}^{-1}; \) MS (EI): \( m/z \) (%): 154 (26),
(3E,3aS*,4E,13aS*)-Diethyl 3-benzylidene-3,3a,7,9,10,11,12,13,13a-decahydro-2H-cyclo-penta[12]annulene-1,1(6H)-dicarboxylate. Colorless oil (81%); 1H NMR (400 MHz, CDCl3): δ = 5.36 (dd, J = 16.6, 10, 3.6 Hz, 1H), 5.27 (dd, J = 16.6, 8.8, 1.6 Hz, 1H), 4.89 (d, J = 2.3 Hz, 1H), 4.77 (dd, J = 2.3, 0.8 Hz, 1H), 4.19 (m, 4H), 3.09 (dd, J = 16.8, 0.8 Hz, 1H), 2.94 (td, J = 9.8, 2.4 Hz, 1H), 2.72 (dq, J = 16.8, 2.4 Hz, 1H), 2.31 (m, 2H), 2.01 (m, 1H), 1.87 (m, 1H), 1.6-1.1 ppm (m, 19H); 13C NMR (100 MHz, CDCl3): 70.3, 149.9, 131.9, 131.4, 128.3, 128.2, 127.5, 127.0, 122.8, 62.7, 54.9, 51.4, 35.4, 33.5, 26.9, 26.0, 25.6, 24.0, 23.5, 23.4, 21.5 ppm; IR (ATR): v = 3042, 2929, 2859, 1726, 1446, 1367, 1245, 1096, 859, 799 cm⁻¹; MS (EI): m/z (%): 159 (44), 173 (24), 215 (44), 288 (100), 362 (36); HRMS (CI): calcd for C30H37NO4+Na: 498.26148; found: 498.26096 [M+Na]; elemental analysis calcd (%) for C30H37NO4: C 75.76, H 7.84; N 2.94 found: C 75.88, H 7.90.

(3E,3aR*,13aS*)-2,3,3a,6,7,8,9,10,11,12,13,13a-Dodecahydro-(3-phenylmethylene)-cyclo-dodeca[b]furan. White solid (86%); mp = 73-76 °C; 1H NMR (400 MHz, CDCl3): δ = 7.33 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 7.4 Hz, 2H), 6.20 (q, J = 2.5 Hz, 1H), 5.56 (ddd, J = 4.3, 10.4, 15.2 Hz, 1H), 5.34 (ddd, J = 1.3, 9.1, 15.2 Hz, 1H), 4.81 (br d, J = 14.2 Hz, 1H), 4.58 (dt, J = 14.2, 2.5 Hz, 1H), 3.70 (dt, J = 4.2, 9.1 Hz, 1H), 3.08 (br t, J = 9.1 Hz, 1H), 1.98 (m, 2H), 1.63 (m, 3H), 1.51-1.16 ppm (m, 10H); 13C NMR (100 MHz, CDCl3): δ = 145.8, 137.4, 133.3, 130.9, 128.4, 127.9, 126.5, 121.7, 82.2, 70.0, 55.7, 33.3, 32.8, 26.4, 25.8, 24.7, 23.7, 23.6 ppm; IR (ATR): v = 2922, 2854, 1597, 1493, 1447, 1346, 1245, 1096, 859, 799 cm⁻¹; MS (EI): m/z (%): 296 (33), 268 (5), 169 (19), 155 (100), 91 (21); HRMS (EI): calcd for C21H28O: 296.21430; found: 296.21402 [M⁺].

(3aR*,13aS*)-2,3,3a,6,7,8,9,10,11,12,13,13a-Dodecahydro-(4-methylphenyl)sulfonyl]-3-(phenylmethylene)-1H-cyclo-dodeca[b]pyrrole. White solid (98%); mp = 138-140 °C; 1H NMR (400 MHz, CDCl3): δ = 7.50 (d, J = 8.3 Hz, 2H), 7.34 (m, 2H), 7.26 (m, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 5.96 (q, J = 2.0 Hz, 1H), 5.45 (ddd, J = 3.9, 10.8, 15.1 Hz, 1H), 4.75 (ddd, J = 1.4, 9.1, 15.1 Hz, 1H), 4.35 (dt, J = 15.6, 1.7 Hz, 1H), 4.25 (dt, J = 15.6, 1.9 Hz, 1H), 3.31 (ddd, J = 3.9, 7.4, 10.4 Hz, 1H), 3.19 (m, 1H), 2.39 (s, 3H), 2.31 (m, 2H), 1.88 (m, 1H), 1.72 (m, 2H), 1.53 (m, 1H), 1.34 (m, 6H), 1.13 (m, 3H), 0.86 ppm (m, 1H); 13C NMR (100 MHz, CDCl3): δ = 143.2, 139.7, 136.6, 134.3, 134.2, 130.2, 129.4, 128.3, 128.2, 127.5, 127.0, 122.8, 62.7, 54.9, 51.4, 35.4, 33.5, 26.9, 26.0, 25.6, 24.0, 23.5, 23.4, 21.5 ppm; IR (ATR): v = 2925, 2854, 1597, 1493, 1447, 1346, 1160, 1090, 1030, 1016, 975, 815, 692, 660 cm⁻¹; MS (EI): m/z (%): 449 (23), 294 (100), 155 (17), 91 (44); HRMS (ESI+): calcd for C28H33NO2S+Na: 472.22741; found: 472.22807 [M⁺+Na]; elemental analysis calcd (%) for C28H33NO2S: C 74.79, H 7.85; found: C 74.72, H 7.81.
(3E,3aS*,4E,13aS*)-Diethyl 3-(4-methoxybenzylidene)-3,3a,7,8,9,10,11,12,13,13a-decahydro-2H-cyclopenta[12]annulene-1,1(6H)-dicarboxylate. Colorless oil (96%); the stereostructure was assigned based on NOE experiments. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.26 (d, $J$ = 8.7 Hz, 2H), 6.84 (d, $J$ = 8.7 Hz, 2H), 6.11 (d, $J$ = 2.4 Hz, 1H), 5.44 (ddd, $J$ = 15.2, 10.4, 3.6 Hz, 1H), 5.32 (ddd, $J$ = 15.2, 8.8, 1.2 Hz, 1H), 4.17 (m, 4H), 3.79 (s, 3H), 3.34 (dd, $J$ = 17.2, 1.3 Hz, 1H), 3.13 (td, $J$ = 10.8, 1.3 Hz, 1H), 2.96 (dt, $J$ = 17.2, 2.8 Hz, 1H), 2.32 (m, 1H), 2.21 (m, 1H), 2.07 (m, 1H), 1.91 (m, 1H), 1.61-1.17 ppm (m, 19H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.9, 171.3, 157.9, 141.7, 133.2, 133.0, 130.9, 129.5, 122.3, 113.7, 62.3, 61.2, 61.1, 56.0, 52.2, 49.8, 39.4, 31.4, 29.5, 25.8, 25.4, 25.5, 25.1, 24.1, 24.0, 14.1, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 2933, 2871, 1725, 1607, 1510, 1444, 1366, 1248, 1177, 1034, 822 cm$^{-1}$; MS (EI): m/z (%): 121 (100), 135 (17), 273 (38), 347 (26), 394 (61), 468 (60); HRMS (CI): calcd for C$_{29}$H$_{40}$O$_5$ + Na: 491.27680; found: 491.27707 [M$^+$+Na]; elemental analysis calcd (%) for C$_{29}$H$_{40}$O$_5$: C 74.33, H 8.60; found: C 74.47, H 8.51.

(3E,3aS*,4E,13aS*)-Diethyl 3-(2-chlorobenzylidene)-3,3a,7,8,9,10,11,12,13,13a-decahydro-2H-cyclopenta[12]annulene-1,1(6H)-dicarboxylate. Colorless oil (94%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.26 (d, $J$ = 8.7 Hz, 2H), 6.84 (d, $J$ = 8.7 Hz, 2H), 6.11 (d, $J$ = 2.4 Hz, 1H), 5.44 (ddd, $J$ = 15.2, 10.4, 3.6 Hz, 1H), 5.32 (ddd, $J$ = 15.2, 8.8, 1.2 Hz, 1H), 4.17 (m, 4H), 3.79 (s, 3H), 3.34 (dd, $J$ = 17.2, 1.3 Hz, 1H), 3.13 (td, $J$ = 10.8, 1.3 Hz, 1H), 2.96 (dt, $J$ = 17.2, 2.8 Hz, 1H), 2.32 (m, 1H), 2.21 (m, 1H), 2.07 (m, 1H), 1.91 (m, 1H), 1.61-1.17 ppm (m, 19H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.7, 171.1, 146.1, 136.3, 133.5, 133.3, 132.7, 129.7, 129.4, 126.3, 120.0, 62.1, 61.3, 61.1, 55.4, 49.5, 38.8, 31.6, 29.6, 25.7, 25.6, 25.0, 24.9, 24.3, 24.1, 14.1, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 2978, 2933, 2867, 1724, 1443, 1366, 1244, 1094, 1035, 863, 835, 790, 753 cm$^{-1}$; elemental analysis calcd (%) for C$_{28}$H$_{37}$ClO$_4$: C 71.09, H 7.88; found: C 71.14, H 7.79.

(3E,3aS*,4E,7E,11E,13aS*)-Diethyl 3-(4-methoxybenzylidene)-3,3a,9,10,11,12,13,13a-hexahydro-2H-cyclopenta[12]annulene-1,1(6H)-dicarboxylate. Yellow oil (79%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.31 (m, 4H), 6.36 (d, $J$ = 2.3 Hz, 1H), 5.49 (ddd, $J$ = 15.2, 10, 3.6 Hz, 1H), 5.39 (ddd, $J$ = 15.2, 8.4, 1.2 Hz, 1H), 4.19 (m, 4H), 3.23 (ddd, $J$ = 17.6, 1.6 Hz, 1H), 3.17 (dd, $J$ = 10.4, 8.8 Hz, 1H), 2.84 (dt, $J$ = 17.6, 2.4 Hz, 1H), 2.31 (m, 2H), 2.07 (m, 1H), 1.87 (m, 1H), 1.7-1.17 ppm (m, 19H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.7, 171.1, 146.1, 136.3, 133.5, 133.3, 132.7, 129.7, 129.4, 126.3, 120.0, 62.1, 61.3, 61.1, 55.4, 49.5, 38.8, 31.6, 29.6, 25.7, 25.6, 25.0, 24.9, 24.3, 24.1, 14.1, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 2978, 2933, 2867, 1724, 1443, 1366, 1244, 1094, 1035, 863, 835, 790, 753 cm$^{-1}$; elemental analysis calcd (%) for C$_{29}$H$_{40}$O$_5$: C 74.97, H 7.81; found: C 75.03, H 7.69.

(3E,3aS*,4E,7E,11E,13aS*)-Diethyl 3-(3-methylbut-2-enylidene)-2H-cyclopenta[12]annulene-1,1(6H)-dicarboxylate. Colorless oil (94%); $^1$H NMR
3-Ethenyl-4-methylene-1-[(4-methylphenyl)sulfonyl]-pyrrolidine. Colorless oil (79%): \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.71\) (d, \(J = 8.3\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 5.51 (ddd, \(J = 8.1\), 10.5, 16.7 Hz, 1H), 5.11 (m, 1H), 5.10 (m, 1H), 4.97 (q, \(J = 2.2\) Hz, 1H), 4.86 (q, \(J = 2.4\) Hz, 1H), 4.00 (dtt, \(J = 1.1, 14.1, 2.2\) Hz, 1H), 3.73 (dq, \(J = 14.1, 2.0\) Hz, 1H), 3.62 (dd, \(J = 7.9, 9.5\) Hz, 1H), 3.23 (m, 1H), 2.87 (dd, \(J = 9.0, 9.2\) Hz, 1H), 2.44 ppm (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 146.6, 143.7, 135.6, 132.9, 129.7, 127.8, 118.0, 108.2, 53.2, 51.9, 47.7, 21.5\) ppm; IR (ATR): \(\tilde{\nu} = 2925, 2853, 1597, 1344, 1159, 1093, 1049, 898, 814, 709, 660\) cm\(^{-1}\); MS (EI): \(m/z\) (%): 263 (21), 155 (17), 108 (100), 91 (59), 81 (84), 65 (23), 42 (21); HRMS (ESI\(+\)): calcd for \(C_{14}H_{12}NO_{2}S+\text{Na}^{+}\): 286.0872; found: 286.08722 \([M^{+}+\text{Na}]\).

\((4E)-3\)-Ethenyl-4-(phenylmethylene)-1,1-cyclopentanedicarboxylic acid diethyl ester. \(^{2}\) White solid (88%); mp = 65-66 °C; \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.31\) (m, 4H), 7.19 (m, 1H), 6.21 (q, \(J = 2.4\) Hz, 1H), 5.72 (ddd, \(J = 8.3, 9.5, 17.5\) Hz, 1H), 5.17 (m, 1H), 5.14 (br s, 1H), 4.20 (m, 4H), 3.38 (d, \(J = 17.7\) Hz, 1H), 3.37 (m, 1H), 3.20 (dt, \(J = 17.7, 2.7\) Hz, 1H), 2.61 (ddd, \(J = 1.4, 7.4, 12.8\) Hz, 1H), 2.01 (dd, \(J = 11.3, 12.8\) Hz, 1H), 1.25 (t, \(J = 7.1\) Hz, 3H), 1.25 ppm (t, \(J = 7.1\) Hz, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 171.6, 143.5, 139.4, 137.8, 128.3, 126.3, 123.9, 116.6, 61.6, 59.5, 49.7, 39.6, 38.7, 14.0\) ppm; IR (ATR): \(\tilde{\nu} = 2981, 1727, 1260, 1239, 1174, 1059, 916, 861, 753, 694\) cm\(^{-1}\); MS (EI): \(m/z\) (%): 328 (24), 254 (79), 181 (100), 91 (27); HRMS (ESI\(+\)): calcd for \(C_{20}H_{24}O_{4}\text{Na}^{+}\): 351.15688; found: 351.15668 \([M^{+}+\text{Na}]\).

\((2S*, 3S*)\)-Diethyl 2-methyl-4-methylene-3-vinylcyclopentane-1,1-dicarboxylate. Colorless oil (93%, \(trans: cis = 5:1\)); the stereochemistry was assigned based on NOE experiments. Data of the major isomer: \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.46\) (ddd, \(J = 15.6, 10, 8.8\) Hz, 1H), 5.07 (dd, \(J = 10, 2\) Hz, 1H), 4.98 (dd, \(J = 10, 1.6\) Hz, 1H), 4.86 (d, \(J = 2\) Hz, 1H), 4.73 (d, \(J = 2\) Hz, 1H), 4.15 (m, 4H), 3.09 (dd, \(J = 17.6, 0.8\) Hz, 1H), 2.81 (m, 1H), 2.74 (dd, \(J = 9.2, 2.4\) Hz, 1H), 2.64 (dq, \(J = 17.6, 2.4\) Hz, 1H), 2.26 (m, 1H), 1.21-1.17 (m, 5H), 0.99 ppm (d, \(J = 6.9\) Hz, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 170.8, 170.6, 149.2, 148.9, 137.7, 137.7, 135.8, 124.3, 116.9, 116.5, 107.1, 106.4, 64.8, 61.9, 60.5, 60.3, 54.3, 51.1, 44.8, 42.2, 39.5, 36.5, 13.1, 12.9, 10.4\) ppm; IR (ATR): \(\tilde{\nu} = 2981, 2934, 1726,\)

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1543, 1368, 1213, 1094, 899, 863 cm\(^{-1}\); MS (EI): \(m/z\) (%): 29 (100), 55 (34), 91 (48), 135 (72), 173 (30), 191 (26), 237 (6), 266 (2); elemental analysis calcd (%) for \(\text{C}_{15}\text{H}_{22}\text{O}_{4}\): C 67.64, H 8.33; found: C 67.71, H 8.19.

\((E,2S^*,3S^*)\)-Diethyl 4-(cyclopropylmethylene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate. Colorless oil (97%, \(\text{trans: cis} = 6.7:1\)); data of the major isomer: \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.37\) (ddd, \(J = 16.0, 10.0, 8.8 \text{ Hz}, 1\text{H})\), 5.01 (dd, \(J = 10.0, 2 \text{ Hz}, 1\text{H})\), 4.95 (dd, \(J = 16, 2 \text{ Hz}, 1\text{H})\), 4.47 (dd, \(J = 9.6, 2.4 \text{ Hz}, 1\text{H})\), 4.16 (m, 4H), 3.12 (dd, \(J = 18.8, 2 \text{ Hz}, 1\text{H})\), 2.67 (m, 2H), 2.20 (m, 1H), 1.33-1.17 (m, 7H), 0.99 (dd, \(J = 6.8 \text{ Hz}, 3\text{H})\), 0.63 (m, 2H), 0.24 ppm (m, 2H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 170.9, 170.3, 138.3, 137.8, 137.3, 126.5, 125.9, 116.7, 116.3, 60.6, 60.4, 60.3, 60.1, 54.3, 51.5, 44.7, 42.1, 36.8, 33.7, 13.2, 13.1, 12.9, 10.4, 10.1, 5.8, 5.6 ppm; IR (ATR): \(\nu = 2991, 2950, 2980, 2957, 1725, 1446, 1367, 1254, 1183, 1093, 1019, 912, 860, 804 \text{ cm}^{-1}\); MS (EI): \(m/z\) (%): 29 (100), 55 (34), 91 (48), 131 (32), 159 (100), 173 (48), 232 (57), 306 (15); HRMS (CI): calcd for \(\text{C}_{18}\text{H}_{26}\text{O}_{4}\): C 70.56, H 8.55; found: C 70.62, H 8.39.

\((E,2S^*,3R^*)\)-Diethyl 4-(4-acetylbenzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate. Colorless oil (97%, \(\text{trans: cis} = 6.7:1\)); data of the major isomer: \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.83\) (d, \(J = 7.6 \text{ Hz}, 2\text{H})\), 7.29 (d, \(J = 7.6 \text{ Hz}, 2\text{H})\), 6.13 (d, \(J = 2.5 \text{ Hz}, 1\text{H})\), 5.51 (ddd, \(J = 15.9, 9.8, 8.8 \text{ Hz}, 1\text{H})\), 5.17 (dd, \(J = 9.8, 2.2 \text{ Hz}, 1\text{H})\), 5.11 (dd, \(J = 15.5, 2.2 \text{ Hz}, 1\text{H})\), 4.15 (m, 4H), 3.41 (dd, \(J = 18, 2 \text{ Hz}, 1\text{H})\), 2.99 (dd, \(J = 11.6, 9.2 \text{ Hz}, 1\text{H})\), 2.88 (dt, \(J = 18, 2.4 \text{ Hz}, 1\text{H})\), 2.51 (s, 3H), 2.29 (m, 1H), 1.21 (m, 6H), 1.07 ppm (d, \(J = 6.8 \text{ Hz}, 3\text{H})\); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 170.1, 170.0, 146.3, 146.1, 142.2, 138.0, 136.1, 134.4, 128.1, 127.9, 122.9, 122.3, 118.7, 118.3, 61.8, 61.2, 61.1, 61.0, 56.9, 54.4, 44.5, 42.1, 39.3, 36.4, 26.1, 13.7, 13.6, 11.1 ppm; IR (ATR): \(\nu = 2983, 2948, 1727, 1683, 1602, 1363, 1265, 1189, 991, 804, 771 \text{ cm}^{-1}\); MS (EI): \(m/z\) (%): 43 (100), 193 (22), 237 (82), 310 (82), 384 (26); HRMS (CI): calcd for \(\text{C}_{23}\text{H}_{28}\text{O}_{5}\): \(\delta = 407.18309\); found: \(\delta = 407.18289\) \([M^+\text{Na}]\).
(2R*,3R*)-3-Ethenyl-4-methylene-2-(1-methylethyl)-1,1-cyclopentanedicarboxylic acid diethyl ester. Colorless oil (68%); trans: cis = 20:1 (1H NMR); data of the major isomer: 1H NMR (400 MHz, CDCl3): δ = 5.62 (ddd, J = 9.0, 10.0, 17.0 Hz, 1H), 5.07 (dd, J = 1.8, 10.0 Hz, 1H), 5.04 (dd, J = 1.7, 17.0 Hz, 1H), 4.93 (br d, J = 2.1 Hz, 1H), 4.79 (br d, J = 2.1 Hz, 1H), 4.18 (m, 4H), 3.16 (br d, J = 17.4 Hz, 1H), 3.13 (m, 1H), 2.60 (dq, J = 16.8, 2.2 Hz, 1H), 2.50 (dd, J = 2.9, 10.6 Hz, 1H), 2.13 (ddd, J = 2.9, 6.9, 13.8 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.01 (d, J = 7.1 Hz, 3H), 0.82 ppm (d, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 172.0, 171.2, 150.4, 141.2, 115.9, 107.7, 61.4, 61.3, 61.2, 55.4, 49.2, 41.4, 27.8, 23.9, 17.8, 14.0, 13.9 ppm; IR (ATR): ν = 2963, 1726, 1252, 1178, 1095, 1079, 1052, 910, 885 cm⁻¹; MS (EI): m/z (%): 294 (28), 249 (12), 220 (100), 203 (24), 177 (33), 147 (95), 105 (58), 91 (31), 29 (45); HRMS (ESI+): m/z: calcld for C₁₇H₂₀N₂O₄Na: 317.17214; found: 317.17233 [M⁺+Na⁺]

(2R*,3S*)-3-Ethenyl-4-methylene-2-phenyl-1,1-cyclopentanedicarboxylic acid diethyl ester. Colorless oil (78%); trans: cis = 9:1 (1H NMR); The stereochemistry was determined by NOESY experiments. Data of the major isomer: 1H NMR (400 MHz, CDCl3): δ = 7.30 (d, J = 7.2 Hz, 2H), 7.25 (t, J = 7.0 Hz, 2H), 7.19 (t, J = 7.1 Hz, 1H), 5.57 (ddd, J = 8.4, 10.4, 17.2 Hz, 1H), 5.03 (dd, J = 1.8, 10.2 Hz, 1H), 5.01 (dq, J = 0.8, 2.4 Hz, 1H), 4.97 (ddd, J = 0.7, 1.8, 17.2 Hz, 1H), 4.90 (dq, J = 0.7, 2.4 Hz, 1H), 4.22 (dq, J = 10.8, 7.0 Hz, 1H), 4.16 (dq, J = 10.8, 7.0 Hz, 1H), 3.88 (dq, J = 10.8, 7.2 Hz, 1H), 3.82 (d, J = 11.8 Hz, 1H), 3.62 (m, 1H), 3.54 (dq, J = 10.8, 7.2 Hz, 1H), 3.47 (ddt, J = 1.2, 17.2, 2.4 Hz, 1H), 2.78 (dq, J = 17.3, 2.0 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H), 0.80 ppm (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 171.7, 170.7, 149.5, 138.3, 137.4, 129.0, 127.8, 127.0, 118.1, 107.6, 63.4, 61.3, 61.1, 55.5, 52.8, 40.9, 14.0, 13.4 ppm; IR (ATR): ν = 2982, 2927, 1723, 1253, 1208, 1178, 1096, 1039, 916, 886, 748, 698 cm⁻¹; MS (EI): m/z (%): 328 (8), 254 (45), 208 (12), 181 (100), 165 (17), 91 (14); HRMS (ESI+): calcld for C₂₀H₂₂O₄Na: 351.15675; found: 351.15668 [M⁺+Na⁺]; elemental analysis calcld (%) for C₂₀H₂₂O₄: C 73.15, H 7.37; found: C 72.68, H 7.85.

(5S*,4E)-Diethyl 4-(4-methoxybenzylidene)-2,2-dimethyl-3-((E)-pent-1-eny)cyclopentane-1,1-dicarboxylate. Colorless oil (98%); 1H NMR (400 MHz, CDCl3): δ = 7.19 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.03 (d, J = 2.4 Hz, 1H), 5.51 (m, 1H), 5.20 (dd, J = 15.2, 8.8 Hz, 1H), 4.11 (m, 4H), 3.73 (s, 3H), 3.53 (d, J = 8.8 Hz, 1H), 3.37 (dt, J = 18.4, 2.8 Hz, 1H), 3.0 (d, J = 18.4 Hz, 1H), 2.04 (m, 2H), 1.39 (m, 2H), 1.21 (m, 9H), 0.88 (t, J = 7.4 Hz, 3H), 0.72 ppm (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 171.0, 170.1, 157.5, 140.9, 135.8, 130.7, 129.0, 127.5, 122.3, 113.8, 65.5, 60.7, 60.6, 58.8, 54.9, 46.6, 37.8, 34.5, 22.3, 21.3, 19.7, 13.7, 13.6, 13.2 ppm; IR (ATR): ν = 2986, 2960, 2954, 1726, 1608, 1510, 1464, 1366, 1246, 1176, 1095, 1073, 1035, 976, 845 cm⁻¹; MS (EI): m/z (%): 121 (100), 265 (30), 281 (74), 339 (71), 413 (38), 428 (75); HRMS (CI): calcld for C₂₆H₃₆O₅⁺Na: 451.24550; found: 451.24602 [M⁺+Na⁺]; elemental analysis calcld (%) for C₂₆H₃₆O₅: C 72.87, H 8.47; found: C 72.98, H 8.41.
3-Ethyl-4-methylene-1,1-cyclohexanedicarboxylic acid diethyl ester. Colorless oil (81%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.80$ (ddd, $J = 7.7, 10.4, 17.2$ Hz, 1H), 5.09 (br d, $J = 7.7$ Hz, 1H), 5.05 (d, $J = 15.9$ Hz, 1H), 4.73 (d, $J = 1.5$ Hz, 1H), 4.65 (d, $J = 1.5$ Hz, 1H), 4.23 (dq, $J = 3.4, 7.1$ Hz, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.83 (m, 1H), 2.42 (m, 2H), 2.36 (m, 2H), 2.17 (m, 1H), 1.76 (dt, $J = 12.7, 4.6$ Hz, 1H), 1.65 (dd, $J = 12.7, 12.7$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.21 ppm (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.7, 170.9, 148.8, 139.2, 115.6, 107.8, 61.4, 61.2, 54.8, 43.4, 37.6, 32.3, 32.0, 14.0, 13.9 ppm; IR (ATR): $\tilde{\nu} = 2981, 1728, 1235, 1194, 1159, 1141, 1086, 1022, 916, 895, 862$ cm$^{-1}$; MS (EI): $m/z$ (%): 266 (5), 193 (47), 173 (32), 119 (100), 91 (35), 29 (26); HRMS (ESI+): calcd for C$_{13}$H$_{22}$O$_2$Na: 289.14099; found: 289.14103 [$M^+\text{Na}$].

(2$R^*$,3$S^*$)-3-Ethyl-4-methylene-1-[(4-methylphenyl)sulfonyl]-2-methyl-pyrrolidine.

Colorless oil (65%), $trans:cis = 3:9$ ($^1$H NMR); data of major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.69$ (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 5.24 (m, 1H), 5.03 (d, $J = 4.3$ Hz, 1H), 5.00 (s, 1H), 4.93 (q, $J = 1.6$ Hz, 1H), 4.82 (d, $J = 1.9$ Hz, 1H), 4.09 (d, $J = 14.4$ Hz, 1H), 3.82 (dd, $J = 1.4, 14.4$ Hz, 1H), 3.19 (dq, $J = 6.4, 6.3$ Hz, 1H), 2.84 (m, 1H), 2.42 (s, 3H), 1.38 ppm (d, $J = 6.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 145.2, 143.5, 135.7, 129.6, 127.6, 127.2, 118.1, 108.2, 61.4, 56.6, 52.7, 21.5, 20.4$ ppm; IR (ATR): $\tilde{\nu} = 2970, 2926, 2867, 1713, 1598, 1456, 1342, 1159, 1092, 1049, 899, 815, 660$ cm$^{-1}$; MS (EI): $m/z$ (%): 277 (4), 262 (100), 155 (44), 122 (30), 106 (20), 91 (91), 79 (32), 69 (30), 41 (34); HRMS (ESI+): calcd for C$_{13}$H$_{19}$NO$_2$S$\text{+Na}$: 300.10286; found: 300.10287 [$M^+\text{Na}$].

(2$R^*$,3$S^*$)-3-Ethyl-4-methylene-1-[(4-methylphenyl)sulfonyl]-2-propyl-pyrrolidine.

Yellow oil (60%), $trans:cis = 5:1$ ($^1$H NMR); data of the major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.70$ (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.09 (ddd, $J = 7.5, 10.0, 17.0$ Hz, 1H), 4.96 (m, 1H), 4.86 (br d, $J = 17.1$ Hz, 1H), 4.84 (m, 1H), 4.78 (br d, $J = 10.0$ Hz, 1H), 3.95 (m, 2H), 3.51 (m, 1H), 2.96 (br s, 1H), 2.42 (s, 3H), 1.69 (m, 1H), 1.62 (m, 1H), 1.40 (m, 2H), 0.93 ppm (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 146.1, 143.3, 137.2, 135.0, 129.5, 127.6, 115.9, 108.9, 65.9, 53.5, 52.0, 37.5, 21.5, 18.5, 14.0$ ppm; IR (ATR): $\tilde{\nu} = 2960, 2930, 2867, 1459, 1344, 1159, 1093, 1053, 911, 814, 731, 708, 661$ cm$^{-1}$; MS (EI); $m/z$ (%): 305 (4), 262 (100), 155 (26), 106 (18), 91 (40), 79 (19); HRMS (ESI+): calcd for C$_{17}$H$_{23}$NO$_2$S$\text{Na}$: 328.13418; found: 328.13417 [$M^+\text{Na}$]; elemental analysis calcd (%) for C$_{17}$H$_{23}$NO$_2$S: C 66.85, H 7.59; found: C 67.14, H 7.65.

(2$R^*$,3$S^*$)-2-Cyclopropyl-3-ethyl-4-methylene-1-[(4-methylphenyl)sulfonyl]-pyrrolidine.

Yellow oil (60%), $trans:cis = 2:1$ ($^1$H NMR); data of the major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.71$ (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 5.19 (ddd, $J = 7.1, 10.1, 17.0$ Hz, 1H), 5.00 (q, $J = 1.7$ Hz, 1H), 4.91 (dt, $J = 17.0, 1.3$ Hz, 1H), 4.91 (dt, $J = 1.6, 2.1$ Hz, 1H), 4.79 (dt, $J = 10.1, 1.2$ Hz, 1H), 4.06 (br d, $J = 14.3$ Hz, 1H), 3.98 (br d, $J = 14.3$ Hz, 1H), 3.14 (dd, $J = 2.9, 8.1$ Hz, 1H), 3.11 (br d, $J = 7.6$ Hz, 1H), 2.41 (s, 3H), 0.93 (m, 1H), 0.60 (m, 1H), 0.48

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(2R,3S*)-3-Ethenyl-2-methyl-1-[(4-methylphenyl)sulfonyl]-4-phenylmethylene-pyrrolidine. White solid (98%, trans: cis = 4.2:1 (1H NMR)); mp = 96-98 °C; data of the major isomer: 1H NMR (400 MHz, CDCl3): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.11 (q, J = 2.2 Hz, 1H), 5.33 (ddd, J = 8.2, 9.7, 17.3 Hz, 1H), 5.09 (m, 1H), 5.08 (br d, J = 17.3 Hz, 1H), 4.40 (br d, J = 15.1 Hz, 1H), 4.09 (dt, J = 15.1, 2.2 Hz, 1H), 3.81 (s, 3H), 3.17 (ddq, J = 6.4, 6.2, 1.1 Hz, 1H), 3.00 (br t, J = 7.2 Hz, 1H), 2.39 (s, 3H), 1.40 ppm (d, J = 6.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 158.6, 143.4, 136.4, 129.8, 129.6, 129.4, 129.1, 127.6, 127.1, 127.3, 112.5, 118.2, 113.9, 60.0, 58.2, 55.3, 51.3, 21.5, 20.1 ppm; IR (ATR): ν = 2974, 1608, 1511, 1343, 1250, 1160, 1082, 1033, 912, 850, 815, 730, 708, 602 cm⁻¹; MS (EI): m/z (%): 383 (39), 228 (83), 186 (100), 145 (41), 121 (99), 91 (60), 56 (52); HRMS (ESI+): calcd for C22H23NO2S+: 406.14495; found: 406.14473 [M+Na]+; elemental analysis calcd (%) for C22H23NO2S: C 68.90, H 6.57; found: C 68.79, H 6.51.

(2R,3S*)-3-Ethenyl-2-methyl-1-[(4-methylphenyl)sulfonyl]-4-[(4-methoxyphenyl)-methylene]-pyrrolidine. Colorless oil (84%, trans: cis = 3.0:1 (1H NMR)); data of the major isomer: 1H NMR (400 MHz, CDCl3): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.11 (q, J = 2.2 Hz, 1H), 5.33 (ddd, J = 8.2, 9.7, 17.3 Hz, 1H), 5.09 (m, 1H), 5.08 (br d, J = 17.3 Hz, 1H), 4.40 (br d, J = 15.1 Hz, 1H), 4.09 (dt, J = 15.1, 2.2 Hz, 1H), 3.81 (s, 3H), 3.17 (ddq, J = 6.4, 6.2, 1.1 Hz, 1H), 3.00 (br t, J = 7.2 Hz, 1H), 2.39 (s, 3H), 1.40 ppm (d, J = 6.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 158.6, 143.4, 136.4, 129.8, 129.6, 129.4, 129.1, 127.6, 127.1, 127.3, 112.5, 118.2, 113.9, 60.0, 58.2, 55.3, 51.3, 21.5, 20.1 ppm; IR (ATR): ν = 2974, 1608, 1511, 1343, 1250, 1160, 1082, 1033, 912, 850, 815, 730, 708, 602 cm⁻¹; MS (EI): m/z (%): 383 (39), 228 (83), 186 (100), 145 (41), 121 (99), 91 (60), 56 (52); HRMS (ESI+): calcd for C22H23NO2S+: 406.14495; found: 406.14473 [M+Na]+; elemental analysis calcd (%) for C22H23NO2S: C 68.90, H 6.57; found: C 68.79, H 6.51.

(2R,3S*)-3-Ethenyl-2-methyl-1-[(4-methylphenyl)sulfonyl]-4-[(4-fluorophenyl)-methylene]-pyrrolidine. Colorless oil (90%, trans: cis = 3.0:1 (1H NMR)); data of the major isomer: 1H NMR (400 MHz, CDCl3): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.06 (m, 4H), 6.14 (q, J = 2.2 Hz, 1H), 5.32 (ddd, J = 8.2, 9.4, 17.5 Hz, 1H), 5.12 (m, 1H), 5.07 (m, 1H), 4.38 (br d, J = 14.5 Hz, 1H), 4.06 (br d, J = 15.1 Hz, 1H), 3.18 (ddq, J = 6.5, 6.5, 6.3 Hz, 1H), 3.02 (br t, J = 7.3 Hz, 1H), 2.40 (s, 3H), 1.41 ppm (d, J = 6.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 158.6 (JCF = 246 Hz), 143.5, 137.5, 136.0, 129.7 (JCF = 8.4 Hz), 129.6, 127.5, 127.1, 122.8, 118.5, 115.4 (JCF = 21 Hz), 60.0, 58.2, 51.1, 21.5, 20.1 ppm; IR (ATR): ν = 2973, 2929, 1601, 1508, 1343, 1227, 1158, 1092, 814, 662 cm⁻¹; MS (EI): m/z (%): 371 (26), 356 (30), 304 (31), 216 (72), 174 (96), 136 (41), 121 (99), 91 (60), 56 (52); HRMS (ESI+): calcd for C22H23NO2S+Na+: 426.14718; found: 426.14734 [M+Na]+; elemental analysis calcd (%) for C22H23NO2S: C 68.90, H 6.57; found: C 68.79, H 6.51.
133 (36), 109 (100), 91 (74), 56 (43); HRMS (ESI+): calcd for C$_{21}$H$_{22}$NO$_2$SF+Na: 394.12440; found: 394.12475 [M$^+$+Na]; elemental analysis calcd (%) for C$_{21}$H$_{22}$NO$_2$SF: C 67.90, H 5.97; found: C 67.82, H 5.90.

(2$R^*$,3$S^*$)-3-Ethenyl-2-methyl-4-methylene-1-(phenylmethyl)-pyrrolidine. Yellow oil (53%, trans:cis = 2.3:1 (1H NMR)); data of the major isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.33 (m, 4H), 7.26 (m, 1H), 5.59 (dd, J = 8.9, 10.2, 16.6 Hz, 1H), 5.15 (dd, J = 2.0, 5.8 Hz, 1H), 5.11 (dd, J = 2.0, 12.4 Hz, 1H), 4.87 (br d, J = 2.3 Hz, 1H), 4.77 (br d, J = 2.3 Hz, 1H), 4.13 (d, J = 12.8 Hz, 1H), 3.55 (d, J = 14.1 Hz, 1H), 3.11 (d, J = 12.8 Hz, 1H), 2.86 (dq, J = 14.1, 2.5 Hz, 1H), 2.80 (m, 1H), 2.29 (dq, J = 9.5, 5.9 Hz, 1H), 1.23 ppm (d, J = 5.9 Hz, 3H); IR (ATR): v = 2965, 2927, 2785, 1453, 1376, 1330, 1132, 1028, 991, 915, 886, 738, 697, 668 cm$^{-1}$; MS (EI): m/z (%): 213 (32), 198 (58), 132 (17), 91 (100), 79 (12), 65 (13); HRMS (ESI+): calcd for C$_{15}$H$_{20}$N: 214.15901; found: 214.15903 [M$^+$+H].

(2$R^*$,3$S^*$)-(4$Z$)-3-Ethenyl-tetrahydro-2-methyl-4-(phenylmethylene)-furan. Colorless oil (74%, trans:cis = 1.3:1 (1H NMR)); data of the major isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.34 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 3H), 7.14 (m, 3H), 6.14 (q, J = 2.4 Hz, 1H), 5.66 (ddd, J = 9.2, 10.0, 16.9 Hz, 1H), 5.24 (dd, J = 2.0, 10.0 Hz, 1H), 5.21 (dd, J = 1.8, 16.4 Hz, 1H), 4.19 (d, J = 13.3 Hz, 1H), 3.98 (d, J = 15.1 Hz, 1H), 3.30 (d, J = 13.1 Hz, 1H), 3.19 (d, J = 15.1 Hz, 1H), 3.03 (br t, J = 8.3 Hz, 1H), 2.39 (m, 1H), 1.28 ppm (d, J = 6.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 137.7, 128.9, 128.2, 126.9, 117.5, 105.7, 65.0, 58.6, 57.9, 57.1, 27.0, 16.9 ppm; IR (ATR): v = 2965, 2927, 2785, 1453, 1376, 1330, 1132, 1028, 991, 915, 886, 738, 697, 668 cm$^{-1}$; MS (EI): m/z (%): 289 (51), 274 (46), 155 (16), 115 (18), 91 (100); HRMS (ESI+): calcd for C$_{14}$H$_{16}$O: 290.19043; found: 290.19032 [M$^+$+H].

(2$R^*$,3$S^*$)-(4$Z$)-3-Ethenyl-tetrahydro-2-methyl-4-(phenylmethylene)-furan. Colorless oil (74%, trans:cis = 1.3:1 (1H NMR)); data of the major isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.34 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 6.18 (q, J = 2.5 Hz, 1H), 5.66 (ddd, J = 9.9, 10.0, 16.8 Hz, 1H), 5.28 (dd, J = 1.8, 10.2 Hz, 1H), 5.24 (ddd, J = 0.6, 1.8, 16.8 Hz, 1H), 4.84 (ddd, J = 1.4, 2.3, 14.3 Hz, 1H), 4.61 (dt, J = 14.4, 2.6 Hz, 1H), 3.66 (dq, J = 9.6, 6.0 Hz, 1H), 2.96 (m, 1H), 1.34 ppm (d, J = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 144.7, 137.2, 136.1, 128.5, 127.9, 126.6, 121.8, 118.9, 79.1, 70.1, 58.4, 18.2 ppm; IR (ATR): v = 2925, 2854, 1490, 1447, 1383, 1259, 1078, 1030, 914, 755, 691 cm$^{-1}$; MS (EI): m/z (%): 200 (16), 156 (100), 141 (41), 128 (34), 115 (49), 91 (44), 68 (26); HRMS (ESI+): calcd for C$_{14}$H$_{16}$O: 200.12033; found: 200.12011 [M$^+$].

**Deuterium Labelling Study**

**4-Chloro-2-cyclohexen-1-ol acetate.** Prepared according to the literature as a yellow oil (86%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.97\) (dd, \(J = 1.5, 3.8, 10.0\) Hz, 1H), 5.80 (dd, \(J = 2.6, 10.0\) Hz, 1H), 5.27 (m, 1H), 4.55 (m, 1H), 2.12 (m, 2H), 2.07 (s, 2H), 1.97 ppm (m, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 180.6, 131.7, 129.3, 67.7, 53.5, 29.6, 24.5, 21.2\) ppm; IR (ATR): \(\tilde{\nu} = 2960, 1731, 1371, 1231, 1191, 1031, 992, 899, 875, 766, 730\) cm\(^{-1}\); MS (EI): \(m/z\) (%): 139 (11), 96 (100), 79 (72), 43 (89); HRMS (CI): caleld for C\(_8\)H\(_{12}\)O\(_2\)Cl: 175.05274; found: 175.05258 [M\(^{+}\)+H].

**[cis-(4-Acetoxy)-2-cyclohexen-1-yl]-propanedioic acid diethyl ester.** Prepared according to the literature as a colorless oil (92%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.72\) (br d, \(J = 10.2\) Hz, 1H), 5.66 (br d, \(J = 10.2\) Hz, 1H), 5.02 (m, 1H), 4.05 (q, \(J = 7.1\) Hz, 4H), 3.15 (d, \(J = 9.0\) Hz, 1H), 2.70 (m, 1H), 1.86 (s, 3H), 1.74-1.53 (m, 3H), 1.42 (m, 1H), 1.12 (t, \(J = 7.1\) Hz, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 170.0, 167.7, 167.6, 133.3, 126.3, 71.8, 36.7, 28.9, 23.1, 18.9\) ppm; IR (ATR): \(\tilde{\nu} = 2958, 2930, 2867, 1730, 1370, 1230, 1190, 1053, 992, 875, 766, 730\) cm\(^{-1}\); MS (CI): \(m/z\) (%): 228 (9), 156 (100), 141 (34), 128 (28), 115 (39), 91 (37); HRMS (CI): caleld for C\(_{16}\)H\(_{20}\)O: 228.15170; found: 228.15141 [M\(^{+}\)].

65.9, 61.0, 55.8, 34.9, 26.7, 21.9, 20.8, 13.7 ppm; IR (ATR): $\nu = 2982, 1726, 1369, 1238, 77, 913, 729\text{ cm}^{-1}$; MS (EI): $m/z$ (%): 237 (62), 211 (28), 161 (98), 136 (81), 118 (30), 96 (100), 79 (42), 43 (51); HRMS (ESI+): calcd. for C$_{13}$H$_{22}$O$_6$Na: 321.13050; found: 321.13086 [$M^+ + \text{Na}$].

**trans-4-Deuterio-2-cyclohexen-1-yl)-propanedionic acid diethyl ester.** To a stirred solution of [cis-(4-acetoxy)-2-cyclohexen-1-yl]-propanedionic acid diethyl ester (500 mg, 1.68 mmol) and Pd(PPh)$_4$ (195 mg, 10 mol %) in CH$_3$CN (12 mL) was added NaBD$_4$ (140 mg, 3.35 mmol). After 60 h, the reaction was quenched with aq. sat. NH$_4$Cl, the aqueous layer was extracted with tert-butyl methyl ether, the combined organic phases were washed with brine, and dried over Na$_2$SO$_4$, the solvent was evaporated, and the residue was purified by flash chromatography (SiO$_2$, hexane/EtOAc) to give a 1:1 mixture of regioisomers (214 mg, 53%) as a colorless oil. This mixture was separated by preparative HPLC (YMC-Pack ODS-A, MeOH/H$_2$O) to give an analytically pure fraction of the title compound as a colorless oil (22 mg, 6%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.76$ (dt, $J = 10.2, 2.6$ Hz, 1H), 5.50 (dt, $J = 0.7, 10.2, 2.4$ Hz, 1H), 4.20 (dq, $J = 0.7, 7.1$ Hz, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.24 (d, $J = 9.4$ Hz, 1H), 2.90 (m, 1H), 1.96 (s, 1H), 1.78 (m, 1H), 1.71 (m, 1H), 1.56 (m, 1H), 1.38 (m, 1H), 1.27 ppm (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 168.5, 168.5, 129.4, 127.6, 61.2, 57.2, 35.3, 26.6, 24.6$ ($J_{CD} = 22$ Hz), 20.9, 14.1 ppm.

**trans-4-Deutero-2-cyclohexen-1-yl)-2-propynyl-propanedionic acid diethyl ester.** To a suspension of NaH (2.5 mg, 0.1 mmol) in THF (0.3 mL) was added (trans-4-deutero-2-cyclohexen-1-yl)-propanedionic acid diethyl ester (22 mg, 0.1 mmol) at 0 °C. After stirring for 30 min at room temperature, (3-iodo-1-propynyl)-benzene $^7$ (30 mg, 0.12 mmol) was introduced and stirring continued until TLC showed complete conversion. For work up, the reaction was quenched with aq. sat. NH$_4$Cl, the aqueous phase extracted with methyl tert-butylether, the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and evaporated, and the residue was purified by flash chromatography (SiO$_2$, hexane/EtOAc) to give the title compound as a colorless oil (7 mg, 21%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.34$ (m, 2H), 7.26 (m, 3H), 5.80 (dq, $J = 10.5, 1.6$ Hz, 1H), 5.74 (br d, $J = 10.6$ Hz, 1H), 4.23 (dq, $J = 2.6, 7.1$ Hz, 2H), 4.20 (dq, $J = 1.2, 7.1$ Hz, 2H), 3.20 (m, 1H), 3.09 (d, $J = 17.3$ Hz, 1H), 3.01 (d, $J = 17.3$ Hz, 1H), 1.92 (m, 2H), 1.80 (m, 1H), 1.57 (m, 1H), 1.42 (m, 1H), 1.26 ppm (t, $J = 7.1$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 169.9, 169.8, 131.5, 128.7, 128.1, 127.9, 127.8, 123.5, 85.3, 83.2, 61.4, 61.3, 60.4, 38.8, 24.5 ($J_{CD} = 21$ Hz), 24.3, 23.2, 22.3, 14.1 ppm.

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[(4-Acetoxy)-2-cycloocten-1-yl]-propanedionionic acid diethyl ester. Prepared according to the literature as a yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.63\) (m, 1H), 5.59 (m, 1H), 5.42 (dd, \(J = 9.4, 9.4\) Hz, 1H), 4.20 (m, 4H), 3.32 (d, \(J = 8.5\) Hz, 1H), 3.20 (m, 1H), 2.03 (s, 3H), 1.94 (m, 1H), 1.65 (m, 3H), 1.49 (m, 3H), 1.29 (m, 1H), 1.26 (t, \(J = 7.1\) Hz, 3H), 1.24 ppm (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 170.0, 168.3, 168.1, 132.0, 128.7, 72.7, 61.4, 57.0, 36.8, 35.6, 33.3, 24.8, 23.2, 21.3, 14.1, 14.0\) ppm; IR (ATR): \(\tilde{\nu} = 2934, 1730, 1449, 1239, 1148, 1024\) cm\(^{-1}\); MS (EI): \(m/z\) (\%): 380 (5), 267 (16), 193 (56), 160 (100), 133 (18), 119 (32), 79 (24), 29 (30); HRMS (ESI+): calcd for C\(_{17}\)H\(_{23}\)O\(_6\)Na: 349.16193; found: 349.16216 [\(M^+\)+Na].

[(4-Hydroxy)-2-cycloocten-1-yl]-propanedionionic acid diethyl ester. NaOEt (0.2 mL, 1.0 M in EtOH) was added to a solution of [(4-acetoxy)-2-cycloocten-1-yl]-propanedionionic acid diethyl ester (1.2 g, 3.68 mmol) in EtOH (37 mL) at 0 °C and the resulting mixture were stirred at ambient temperature for 16 h. A standard extractive work up followed by flash chromatography of the crude material (SiO\(_2\), hexane/EtOAc) gave the title compound as a colorless oil (833 mg, 82%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.63\) (ddd, \(J = 0.8, 6.6, 10.8\) Hz, 1H), 5.31 (m, 1H), 4.65 (m, 1H), 4.20 (m, 4H), 3.29 (d, \(J = 9.0\) Hz, 1H), 3.13 (m, 1H), 1.91 (m, 1H), 1.64 (m, 4H), 1.43 (m, 3H), 1.27 (m, 1H), 1.27 (t, \(J = 7.1\) Hz, 3H), 1.25 ppm (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 168.4, 168.3, 136.4, 127.7, 70.0, 61.4, 61.3, 57.1, 38.9, 36.9, 33.6, 24.9, 23.4, 14.1\) ppm; IR (ATR): \(\tilde{\nu} = 3401, 2936, 1742, 1716, 1280, 1243, 1189, 1145, 1095, 1026, 856, 727\) cm\(^{-1}\); MS (EI): \(m/z\) (\%): 284 (3), 193 (21), 161 (89), 133 (32), 124 (100), 80 (22), 55 (21), 29 (29); HRMS (ESI+): calcd for C\(_{15}\)H\(_{24}\)O\(_5\)Na: 307.15160; found: 307.15139; found: 307.15160 [\(M^+\)+Na].

[(4-Trifluoroacetoxy)-2-cycloocten-1-yl]-propanedionionic acid diethyl ester. Trifluoroacetic acid anhydride (3.96 mL, 28.5 mL) was added to a solution of [(4-hydroxy)-2-cycloocten-1-yl]-propanedionionic acid diethyl ester (809 mg, 2.85 mmol) in Et\(_2\)O (28 mL) at 0 °C. After stirring at room temperature for 0.5 h, all volatile materials were evaporated to give the title product as a colorless oil which was pure enough for further use (1.32 g). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.80\) (m, 1H), 5.64 (dd, \(J = 6.7, 10.9\) Hz, 1H), 5.52 (dd, \(J = 10.6, 10.9\) Hz, 1H), 4.20 (m, 4H), 3.35 (d, \(J = 8.7\) Hz, 1H), 3.17 (m, 1H), 2.02 (m, 1H), 1.81-1.64 (m, 4H), 1.53 (m, 2H), 1.33 (m, 1H), 1.27 (t, \(J = 7.1\) Hz, 3H), 1.24 ppm (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 168.4, 168.3, 158.3, 156.8, 156.4, 130.3, 129.8, 61.7, 56.9, 37.0, 35.0, 33.2, 30.9, 24.6, 22.8, 14.0, 13.9\) ppm; IR (ATR): \(\tilde{\nu} = 2938, 1782, 1732, 1371, 1216, 1148, 1096, 1027, 776, 733\) cm\(^{-1}\); MS (EI): \(m/z\) (\%): 380 (5), 267 (16), 193 (56), 160 (100), 133 (18), 119 (32), 79 (24), 29 (30); HRMS (ESI+): calcd for C\(_{17}\)H\(_{23}\)O\(_6\)F\(_3\)Na: 403.13395; found: 403.13389 [\(M^+\)+Na].

(trans-4-Deutero-2-cycloocten-1-yl)-propanedionionic acid diethyl ester. Pd(PPh\(_4\)) (310 mg, 20 mol %) and NaBD\(_4\) (14 mg, 059 mmol) were added to a solution of [(4-trifluoroacetoxy)-2-cycloocten-1-yl]-propanedionionic acid diethyl ester (500 mg, 1.32 mmol) in CH\(_3\)CN (9 mL).
After 24, 30 and 42 h, additional NaBD$_4$ (7 mg each) was introduced. 1 h after the last addition, the reaction was quenched with aq. sat. NH$_4$Cl, the aqueous phase was extracted with tert-butyl methyl ether, the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and evaporated. Flash chromatography (SiO$_2$, hexane/EtOAc) of the crude material gave a mixture of the desired product and its regioisomer (192 mg, 54%, dr = 1:1).

A solution of this material (190 mg, 0.71 mmol) in THF (1 mL) was added to a suspension of NaH (2.5 mg, 0.1 mmol) in THF (2 mL) at 0 °C. After stirring for 30 min at room temperature, (3-iodo-1-propynyl)-benzene (222 mg, 0.92 mmol) was introduced and stirring continued for 5 h. Flash chromatography (SiO$_2$, hexane/EtOAc) of crude material gave a mixture of the desired product and its isomer (192 mg, 54%, dr = 1:1).

The Alder-ene reaction was performed according to the representative procedure outlined above affording the title compound as a colorless oil (82%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.35 (m, 2H), 7.27 (m, 3H), 5.78 (dd, $J$ = 7.5, 10.2 Hz, 1H), 5.47 (dd, $J$ = 10.2, 10.2 Hz, 1H), 4.23 (m, 4H), 3.55 (m, 1H), 3.08 (d, $J$ = 17.1 Hz, 1H), 3.02 (d, $J$ = 17.1 Hz, 1H), 2.04 (m, 1H), 1.96 (m, 1H), 1.68 (m, 3H), 1.48 (m, 2H), 1.27 (t, $J$ = 7.1 Hz, 3H), 1.27 (t, $J$ = 7.1 Hz, 3H), 1.20 ppm (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.1, 170.0, 131.5, 131.4, 128.3, 128.2, 127.7, 123.5, 85.4, 83.0, 61.2, 61.2, 59.8, 39.1 ppm; IR (ATR): $\nu$ = 2924, 2855, 1725, 1272, 1216, 1183, 1095, 1046, 1029, 756, 691 cm$^{-1}$; MS (EI): $m$/z (%): 383 (20), 337 (33), 309 (57), 236 (100), 227 (46), 115 (81), 91 (42), 29 (57); HRMS (ESI+): calcd for C$_{24}$H$_{29}$O$_4$D+: 406.20985; found: 406.20991 [M$^+$Na$^+$].

(3Z,3R*,7S*)-4-Deuterio-2,3,3a,6,7,7a-hexahydro-3-(phenylmethylene)-1H-indene-1,1-dicarboxylic acid diethyl ester. The Alder-ene reaction was performed according to the representative procedure outlined above affording the title compound as a colorless oil (82%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.31 (m, 4H), 7.18 (m, 1H), 6.22 (m, 1H), 5.98 (m, 1H), 4.20 (m, 4H), 3.60 (dt, $J$ = 4, 2.7 Hz, 1H), 3.45 (br s, 1H), 3.16 (d, $J$ = 18.4 Hz, 1H), 2.88 (m, 1H), 2.07 (m, 2H), 1.38 (m, 2H), 1.28 (t, $J$ = 7.1 Hz, 3H), 1.22 (t, $J$ = 7.1 Hz, 3H), 1.19 ppm (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.7, 169.8, 144.4, 137.9, 131.5, 128.2, 128.1 ($\nu_\text{CD} = 23$ Hz), 126.4, 126.1, 123.5, 63.3, 61.5, 61.4, 44.6, 42.0, 36.6, 24.5, 21.1, 14.1, 14.0 ppm; IR (ATR): $\nu$ = 2979, 2930, 1728, 1446, 1260, 1216, 1183, 1095, 1046, 1029, 756, 691 cm$^{-1}$; MS (EI): $m$/z (%): 355 (22), 310 (12), 281 (39), 208 (76), 190 (64), 173 (100), 144 (31), 116 (35), 91 (64), 29 (28); HRMS (ESI+): calcd for C$_{22}$H$_{25}$O$_4$D+: 406.20985; found: 406.20991 [M$^+$Na$^+$].

(3E,3aR*,9aR*)-2,3,3a,6,7,8,9,9a-Octahydro-3-phenylmethylene-1H-cyclopentacyclooctene-1,1-dicarboxylic acid diethyl ester. The Alder-ene reaction was performed according to the representative procedure outlined above affording the title compound as a colorless oil (90%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.31 (m, 4H), 7.18 (m, 1H), 5.69 (m, 2H), 4.21 (m, 4H), 3.64 (m, 1H), 3.43 (d, $J$ = 17.9 Hz, 1H), 2.94 (dd, $J$ = 17.8, 2.8 Hz, 1H), 2.35 (m, 1H), 2.19 (m, 2H), 2.08 (m, 1H), 1.74 (m, 1H), 1.58 (m, 2H), 1.45 (m, 1H), 1.28 (t, $J$ = 7.1 Hz, 3H), 1.25 (t, $J$ = 7.1 Hz, 3H), 0.88 ppm (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.6, 171.2, 145.1, 138.1, 133.5, 130.3 ($\nu_\text{CD} = 23$ Hz), 128.3, 128.1, 126.1, 122.2, 62.2, 61.2, 61.1, 52.3, 47.6, 40.0, 28.7, 27.6, 24.9, 23.7, 14.1, 14.1 ppm;
IR (ATR): $\tilde{\nu} = 2929, 2855, 1724, 1250, 1180, 1097, 1074, 1050, 910, 730, 695 \text{ cm}^{-1}$; MS (EI): $m/z$ (%): 383 (43), 309 (92), 291 (48), 236 (76), 217 (100), 92 (49); HRMS (ESI+): calcd for C$_{24}$H$_{29}$O$_{4}$D+: 406.20974; found: 406.20991 [$M^+$/Na].

**Iron-Catalyzed [4+2] Cycloadditions**

**2-(Toluene-4-sulfonyl)-2,3,3a,6-tetrahydro-1H-isoidole.** A solution of 4-methyl-N-penta-2,4-dienyl-N-prop-2-ynyl-benzenesulfonamide (64 mg, 0.25 mmol)$^8$ in toluene (500 µL) was added to a solution of complex 4 (8.2 mg, 25 µmol) in toluene (12 mL) causing a color change from yellow to orange-brown. The mixture was stirred for 90 min at 80 °C before all volatile materials were evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 8/1) to give the title compounds as a colorless solid (35 mg, 54%). The compound readily aromatizes when kept in air. mp = 110-112 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.71$ (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 5.80-5.75 (m, 1H), 5.67-5.64 (dq, $J = 9.9$, 2.0 Hz, 1H), 5.54 (m, 1H), 4.04-3.99 (m, 1H), 3.83 (dd, $J = 8.3$, 8.3 Hz, 1H), 3.72 (dt, $J = 13.2$, 1.4 Hz, 1H), 3.02-2.92 (m, 1H), 2.66 (dd, $J = 11.3$, 8.8 Hz, 1H), 2.67-2.60 (m, 2H), 2.41 ppm (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 143.4$, 134.8, 133.7, 129.6, 127.5, 126.7, 123.1, 117.1, 52.8, 50.7, 37.8, 26.6, 21.5 ppm; IR (ATR): $\tilde{\nu} = 3029, 2920, 2861, 1639, 1597, 1493, 1459, 1048, 1017, 816, 750, 705, 664, 591, 551 \text{ cm}^{-1}$; MS (EI): $m/z$ (%): 275 (11), 155 (8), 120 (91), 91 (100), 65 (9), 42 (12); HRMS (ESI+): $m/z$: calcd. for C$_{15}$H$_{17}$NO$_2$: 298.0872; found 298.0872 [$M^+$/Na]; elemental analysis calcd for C$_{15}$H$_{17}$NO$_2$: C 65.43, H 6.22, N 5.09; found C 65.37, H 6.14, N 4.96.

The following compounds were prepared analogously:

**Diethyl 1,3,3a,6-tetrahydro-2H-indene-2,2-dicarboxylate.** Colorless oil (85%); the compound readily aromatizes when kept in air. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.80-5.72$ (m, 2H), 5.50 (m, 1H), 4.23-4.14 (m, 4H), 2.97-2.88 (m, 3H), 2.67-2.61 (m, 3H), 1.81 (dd, $J = 12.1$, 12.0 Hz, 1H), 1.27-1.21 ppm (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 172.5$, 171.9, 138.7, 126.5, 125.2, 115.8, 61.5, 57.3, 40.1, 38.4, 38.2, 27.1, 14.0 ppm; IR (ATR): $\tilde{\nu} = 3432$, 3073, 3025, 2937, 2822, 1732, 1641, 1606, 1462, 1466, 1367, 1280, 1249, 1189, 1158, 1096, 1071, 1053, 1026, 861, 757 cm$^{-1}$; MS (EI): $m/z$ (%): 264 (11), 190 (45), 161 (14), 144 (11), 117 (100).

**Diethyl 7-(trimethylsilyl)-1,3,3a,6-tetrahydro-2H-indene-2,2-dicarboxylate.** Colorless oil (66%); the compound readily aromatizes when kept in air. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 5.78$ (m, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.01 (m, 2H), 2.86-2.51 (m, 4H), 1.81 (t, $J = 12.3$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.13 ppm (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 172.4$, 171.9, 147.8, 126.9, 126.0, 125.6, 61.5, 61.4, 57.9,

Diethyl 7-methyl-1,3,3a,6-tetrahydro-2H-indene-2,2-dicarboxylate. Colorless oil; the compound readily aromatizes when kept in air. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.79-5.72$ (m, 2H), 4.21 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.02-2.90 (m, 3H), 2.69-2.44 (m, 3H), 1.74 (t, $J = 12.5$ Hz, 1H), 1.66 (s, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.24 ppm (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 172.4$, 172.1, 131.2, 126.8, 125.6, 122.4, 61.5, 61.4, 57.8, 39.9, 39.6, 35.9, 32.6, 18.8, 14.0 ppm.

Iron-Catalyzed Intramolecular [5+2] Cycloadditions

Representative Procedure for the [5+2] Reaction Catalyzed by [CpFe(COD)][Li•DME] (4). Preparation of 3,3a,6,7-Tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester. A solution of [(2$E$)-(3-cyclopropyl-2-propenyl)-2-propynyl]-propanedioic acid diethyl ester (100 mg, 0.36 mmol) in toluene (2.0 mL) was added to a solution of complex 4 (6.5 mg, 5 mol%) in toluene (16 mL) and the resulting mixture was stirred at reflux temperature under Ar for 2 h. For work up, moist tert-butyl methyl ether was added and all volatile materials were evaporated. The residue was purified by flash chromatography (SiO$_2$, hexane/EtOAc) to give the title compound as a colorless oil (66 mg, 66%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.72$-5.61 (m, 2H), 5.50 (d, $J = 10.8$ Hz, 1H), 4.19 (q, $J = 7.0$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.68 (m, 1H), 3.31 (m, 2H), 2.64 (dd, $J = 8.6$, 12.7 Hz, 1H), 2.32 (m, 2H), 2.03 (m, 2H), 2.01 (dd, $J = 11.1$, 12.7 Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.24 ppm (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.6$, 171.4, 142.7, 132.2, 130.1, 122.1, 61.4, 58.6, 41.4, 41.2, 39.6, 26.3, 25.7, 14.0 ppm; IR (ATR): $\tilde{\nu} = 2981, 2936, 1728, 1286, 1244, 1186, 1158, 1095, 1069, 1026, 861$, 671 cm$^{-1}$; MS (EI): m/z (%): 278 (10), 204 (51), 131 (100), 91 (24), 29 (22); HRMS (ESI+): calcd for C$_{16}$H$_{22}$O$_4$Na: 301.14148; found: 301.14103 [M$^+$Na].

Representative Procedure for the [5+2] Reaction Catalyzed by [CpFe(C$_2$H$_4$)$_2$][Li•TMEDA] (1). Preparation of 3-Methyl-3,3a,6,7-tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester. A solution of [(2$E$)-(3-cyclopropyl-1-methyl-2-propenyl)-2-propynyl]-propanedioic acid diethyl ester (100 mg, 0.34 mmol) in toluene (1.4 mL) was added to a solution of complex 1 (5.2 mg, 5 mol%) in toluene (2.0 mL) and the resulting mixture was stirred at 90-95 °C under Ar for 2-3 h. For work-up, moist tert-butyl methyl ether was added and all the volatile materials were evaporated. The residue was purified by flash chromatography (SiO$_2$, hexane/EtOAc) to give the title compound as a colorless oil (91 mg, 91%, trans: $\text{cis} = 6.7:1$ (GC-MS)). The stereochemistry of major isomer was confirmed by NOESY data; Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.75$ (ddt, $J = 2.9$, 11.0, 5.9 Hz, 1H), 5.57 (m, 1H), 5.55 (ddd, $J = 1.8$, 2.6, 10.7 Hz, 1H).
4.20 (dq, J = 10.8, 7.2 Hz, 2H), 4.15 (dq, J = 10.8, 7.2 Hz, 2H), 3.32 (dsep, J = 11.8, 2.7 Hz, 3H), 1.14 ppm (s, 9H); 

13C NMR (100 MHz, CDCl3): δ = 171.5, 171.0, 141.7, 131.6, 130.6, 121.3, 61.1, 61.0, 60.9, 46.8, 46.2, 41.2, 26.3, 25.7, 14.7, 14.1, 14.0 ppm; IR (ATR): ν = 2979, 2935, 1726, 1241, 1183, 1094, 1072, 1046, 1021, 856, 731 cm⁻¹; MS (EI): m/z (%): 292 (16), 218 (59), 145 (100), 91 (14); HRMS (ESI⁺): calcd for C₁₇H₂₄O₄Na: 315.15685; found: 315.15668 [M⁺+Na].

The following compounds were prepared analogously:

3,3a,6,7-Tetrahydro-8-trimethyl silanyl-2,2-(1H)-azulenedicarboxylic acid diethyl ester. Colorless oil (66%); ¹H NMR (400 MHz, CDCl3): δ = 5.47 (m, 1H), 5.27 (ddt, J = 2.1, 11.3, 1.9 Hz, 1H), 5.26 (q, J = 7.1 Hz, 4H), 3.83 (m, 1H), 3.01 (d, J = 16.0 Hz, 1H), 2.96 (dt, J = 16.0, 2.1 Hz, 1H), 2.69 (ddd, J = 1.4, 8.8, 1 Hz, 1H), 2.59 (br t, J = 13.5 Hz, 1H), 2.20 (m, 1H), 2.15 (m, 1H), 1.96 (m, 1H), 1.89 (dd, J = 10.0, 12.7 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 0.13 ppm (s, 9H); 

13C NMR (100 MHz, CDCl3): δ = 171.4, 171.3, 155.6, 133.4, 130.3, 129.6, 61.4, 61.4, 59.4, 41.2, 41.1, 41.0, 29.1, 27.7, 14.0 ppm; IR (ATR): ν = 2980, 1727, 1250, 1229, 1191, 1068, 1022, 861, 762, 700 cm⁻¹; MS (EI): m/z (%): 47 (18), 203 (58), 159 (15), 131 (77), 73 (100); HRMS (ESI⁺): calcd for C₁₉H₂₄O₄Si⁺Na: 377.17240; found: 377.17233 [M⁺+Na].

3,3a,6,7-Tetrahydro-8-(4-methoxy-phenyl)-2,2-(1H)-azulenedicarboxylic acid diethyl ester. Yellow oil (75%); ¹H NMR (400 MHz, CDCl3): δ = 7.31 (m, 2H), 7.21 (m, 3H), 5.61 (m, 1H), 5.46 (ddt, J = 1.9, 11.2, 1.9 Hz, 1H), 4.15 (q, J = 7.1 Hz, 4H), 3.87 (br s, 1H), 2.98 (m, 1H), 2.97 (d, J = 16.7 Hz, 1H), 2.88 (d, J = 16.7 Hz, 1H), 2.73 (ddd, J = 1.7, 8.6, 12.7 Hz, 1H), 2.35-2.22 (m, 3H), 2.04 (dd, J = 10.2, 12.7 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H), 1.20 ppm (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl3): δ = 171.4, 143.7, 140.5, 135.2, 131.1, 129.4, 128.1, 127.6, 61.4, 61.3, 59.1, 41.6, 40.2, 40.0, 32.8, 26.8, 14.0 ppm; IR (ATR): ν = 2980, 1727, 1250, 1229, 1191, 1156, 1068, 1022, 861, 762, 700 cm⁻¹; MS (EI): m/z (%): 354 (45), 280 (73), 207 (100), 165 (15), 91 (32); HRMS (ESI⁺): calcd for C₂₂H₂₆O₅Si⁺Na: 377.17240; found: 377.17233 [M⁺+Na].

3,3a,6,7-Tetrahydro-8-(4-methoxy-phenyl)-2,2-(1H)-azulenedicarboxylic acid diethyl ester. Yellow oil (58%); ¹H NMR (400 MHz, CDCl3): δ = 7.15 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.60 (m, 1H), 5.45 (ddt, J = 1.8, 11.2, 1.7 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.85 (br s, 1H), 3.80 (s, 3H), 2.99 (m, 1H), 2.97 (d, J = 16.7 Hz, 1H), 2.88 (d, J = 16.7 Hz, 1H), 2.72 (ddd, J = 1.7, 8.6, 12.7 Hz, 1H), 2.26 (m, 3H), 2.03 (dd, J = 10.2, 12.7 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H), 1.19 ppm (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl3): δ = 171.4, 157.9, 139.9, 136.1, 134.7, 131.1, 129.4, 128.8, 113.5, 61.4, 61.3, 59.1, 55.2, 41.7, 40.1, 32.9, 26.8, 14.0 ppm; IR (ATR): ν = 2980, 1727, 1509, 1244, 1175, 1156, 1067, 1026, 828, 732 cm⁻¹; MS (EI): m/z (%): 384 (78), 310 (68), 237 (100), 121 (36); HRMS (ESI⁺): calcd for C₂₃H₂₈O₃Si⁺Na: 407.18322; found: 407.18290 [M⁺+Na].
3,3a,6,7-Tetrahydro-8-(4-fluoro-phenyl)-2,2-(1H)-azulenedicarboxylic acid diethyl ester. Yellow oil (69%); 1H NMR (400 MHz, CDCl3): δ = 7.18 (m, 2H), 6.99 (m, 2H), 5.61 (m, 1H), 5.45 (dd, J = 1.7, 11.3 Hz, 1H), 4.15 (q, J = 7.1 Hz, 4H), 3.84 (br s, 1H), 2.94 (m, 1H), 2.93 (d, J = 16.7 Hz, 1H), 2.83 (d, J = 16.7 Hz, 1H), 2.73 (ddd, J = 1.7, 8.6, 12.7 Hz, 1H), 2.25 (m, 3H), 2.04 (dd, J = 10.3, 12.7 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H), 1.20 ppm (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 171.3, 171.3, 155.0 (JCFC = 155 Hz), 140.8, 139.6, 134.2, 131.0, 129.4, 129.3 (JCFC = 10 Hz), 115.0 (JCFC = 28 Hz), 61.5, 61.4, 59.0, 41.6, 40.1, 40.0, 32.8, 26.7, 14.0 ppm; IR (ATR): ν = 2981, 1727, 1507, 1251, 1223, 1193, 1156, 1068, 1014, 832, 731 cm-1; MS (EI): m/z (%): 372 (33), 298 (67), 225 (100), 109 (35); HRMS (ESI+): calcld for C22H25O4F+Na: 395.16312; found: 395.16291 [M'+Na].

Acetic acid 2-acetoxy methyl-1,2,3,3a,6,7-hexahydro-azulen-2-yl methyl ester. Colorless oil (62%); 1H NMR (400 MHz, CDCl3): δ = 5.66-5.57 (m, 2H), 5.45 (br d, J = 11.0 Hz, 1H), 3.99 (m, 2H), 3.98 (d, J = 11.2 Hz, 1H), 3.90 (d, J = 11.2 Hz, 1H), 3.69 (br s, 1H), 2.33 (m, 2H), 2.27 (d, J = 11.0 Hz, 2H), 2.04 (s, 3H), 2.04 (s, 3H), 2.01 (m, 3H), 1.45 ppm (dd, J = 9.6, 13.0 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ = 171.0, 144.3, 133.1, 129.9, 122.6, 67.1, 65.6, 44.3, 39.9, 39.4, 38.7, 26.3, 25.7, 20.8 ppm; IR (ATR): ν = 2940, 1737, 1379, 1364, 1220, 1032 cm-1; MS (EI): m/z (%): 278 (1), 218 (11), 158 (100), 143 (71), 130 (35), 91 (33), 43 (67); HRMS (ESI+): calcld for C16H22O2Na: 301.14136; found: 301.14103 [M'+Na].

2,2-Bis-(tert-butyl-dimethyl-silanyloxy-methyl)-1,2,3,3a,6,7-hexahydro-azulene. Colorless oil (73%); 1H NMR (400 MHz, CDCl3): δ = 5.62 (m, 1H), 5.55 (m, 1H), 5.49 (br d, J = 11.0 Hz, 1H), 3.63 (br s, 1H), 3.42 (m, 4H), 2.35 (m, 2H), 2.16 (d, J = 11.4 Hz, 2H), 2.05 (m, 2H), 1.95 (dd, J = 9.5, 12.7 Hz, 1H), 1.31 (dd, J = 9.5, 12.7 Hz, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.02 ppm (s, 6H); 13C NMR (100 MHz, CDCl3): δ = 146.9, 134.4, 129.2, 121.1, 65.8, 64.2, 48.3, 39.5, 39.2, 38.9, 26.7, 25.9, 18.3, −5.5 ppm; IR (ATR): ν = 2928, 2856, 1471, 1250, 1078, 832, 814, 772, 666 cm-1; MS (EI): m/z (%): 423 (3), 365 (14), 290 (21), 233 (41), 189 (23), 171 (23), 159 (75), 147 (90), 129 (39), 89 (44), 73 (100); HRMS (ESI+): calcld for C42H42O8Si2Na: 445.29258; found: 445.29286 [M'+Na].

1,3,4,6,7,9a-Hexahydro-benzocycloheptene-2,2-dicarboxylic acid diethyl ester. Colorless oil (54%); 1H NMR (400 MHz, CDCl3): δ = 5.80 (m, 1H), 5.59 (br s, 1H), 5.36 (dd, J = 4.7, 11.4 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 2.98 (br d, J = 12.9 Hz, 1H), 2.40 (m, 2H), 2.17 (m, 4H), 2.13 (m, 2H), 1.80 (dt, J = 4.7, 12.7 Hz, 1H), 1.70 (t, J = 13.1 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.22 ppm (t, J = 7.1 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ = 171.9, 171.1, 138.8, 132.3, 130.7, 124.2, 61.4, 61.2, 55.2, 40.3, 38.9, 35.0, 32.7, 27.8, 27.7, 14.1, 14.0 ppm; IR (ATR): ν = 2933, 2850, 1728, 1445, 1299, 1229, 1204, 1163, 1095, 1072, 1042, 1022, 860 cm-1; MS (EI): m/z (%): 292 (23), 218 (59), 145 (100), 91 (30), 29 (31); HRMS (ESI+): calcld for C17H24O4Na: 315.15657; found: 315.15668 [M'+Na].

3-Methyl-1,2,3,3a,6,7-hexahydro-2-[(4-methylphenyl)sulfonyl]-cyclohepta[c]pyrrole. Colorless oil (56%, trans: cis = 5.5:1 (GC-MS)); Major isomer: 1H NMR (400 MHz, CDCl3):
δ = 7.67 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 5.74 (m, 1H), 5.50 (m, 1H), 5.33 (ddd, J = 2.0, 2.1, 10.8 Hz, 1H), 4.10 (br d, J = 14.0 Hz, 1H), 3.64 (br d, J = 13.9 Hz, 1H), 3.37 (m, 1H), 2.88 (dq, J = 9.5, 6.1 Hz, 1H), 2.42 (s, 3H), 2.33 (m, 1H), 2.20 (m, 1H), 2.01 (m, 2H), 1.49 ppm (d, J = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 143.5, 135.9, 132.0, 129.7, 128.9, 127.9, 127.2, 121.7, 62.6, 54.6, 48.9, 29.2, 25.9, 25.5, 21.5, 19.8 ppm; IR (ATR): ν = 2928, 1706, 1337, 1304, 1160, 1092, 1065, 1047, 814, 658 cm$^{-1}$; MS (EI): m/z (%): 303 (29), 288 (10), 155 (22), 148 (48), 105 (75), 91 (100), 79 (33), 65 (18); HRMS (ESI+): calcd for C$_{17}$H$_{21}$NO$_2$S+Na: 326.11846; found: 326.11852 [$M^+$/Na].

3,8-Dimethyl-3,3a,6,7-tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester.

Colorless oil (92%, trans:cis = 9.4:1 (GC-MS)); Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ = 5.69 (m, 1H), 5.49 (br d, J = 11.9 Hz, 1H), 4.17 (m, 4H), 3.23 (br d, J = 11.7 Hz, 1H), 2.96 (d, J = 16.6 Hz, 1H), 2.58 (d, J = 16.6 Hz, 1H), 2.45 (br t, J = 12.6 Hz, 1H), 2.30 (dq, J = 11.9, 6.8 Hz, 1H), 2.29 (m, 1H), 2.05 (m, 1H), 1.88 (m, 1H), 1.63 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.13 ppm (d, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 171.6, 171.0, 134.7, 131.6, 130.0, 128.3, 61.0, 60.9, 60.8, 47.1, 46.5, 39.4, 32.4, 26.0, 21.0, 14.6, 14.1, 14.0 ppm; IR (ATR): ν = 2979, 2933, 1726, 1251, 1185, 1095, 1076, 1042, 1022 cm$^{-1}$; MS (EI): m/z (%): 306 (17), 232 (51), 159 (100), 91 (10); HRMS (ESI+): calcd for C$_{18}$H$_{20}$O$_4$Na: 329.17197; found: 329.17233 [$M^+$/Na].

1-Methyl-3,5,6,8a-tetrahydro-1H-azulene-2,2,4-tricarboxylic acid triethyl ester.

Colorless oil (76%, trans:cis = 2.3:1 (GC-MS)); Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ = 5.60 (m, 1H), 5.32 (dd, J = 1.9, 11.5 Hz, 1H), 4.18 (m, 6H), 3.66 (d, J = 18.9 Hz, 1H), 3.46 (br d, J = 11.6 Hz, 1H), 2.94 (dt, J = 18.8, 2.7 Hz, 1H), 2.78 (dt, J = 14.2, 4.0 Hz, 1H), 2.62 (br t, J = 13.4 Hz, 1H), 2.34 (dq, J = 11.6, 6.8 Hz, 1H), 2.12 (m, 1H), 2.10 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.18 ppm (d, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 171.1, 170.7, 167.5, 160.2, 130.2, 127.9, 125.7, 61.5, 61.1, 61.0, 60.2, 49.0, 46.6, 42.0, 26.5, 26.2, 14.6, 14.3, 14.1, 14.0 ppm; IR (ATR): ν = 2981, 1726, 1703, 1367, 1254, 1234, 1186, 1095, 1075, 1056, 1035 cm$^{-1}$; MS (EI): m/z (%): 364 (3), 318 (100), 244 (55), 217 (32), 171 (20), 143 (43), 29 (41); HRMS (ESI+): calcd for C$_{20}$H$_{23}$O$_3$Na: 387.17763; found: 387.17781 [$M^+$/Na].

3-Methyl-8-trimethylsilyl-3,3a,6,7-tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester.

Colorless oil (99%, trans:cis = 14.6:1 (GC-MS)); Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): δ = 5.52 (m, 1H), 5.30 (ddd, J = 1.8, 2.1, 11.4 Hz, 1H), 4.18 (m, 2H), 4.14 (m, 2H), 3.38 (m, 1H), 3.01 (d, J = 16.2 Hz, 1H), 2.73 (dt, J = 16.2, 2.7 Hz, 1H), 2.57 (br t, J = 13.5 Hz, 1H), 2.24 (dq, J = 11.3, 6.8 Hz, 1H), 2.17 (m, 2H), 1.94 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H), 0.11 ppm (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 171.4, 170.5, 155.2, 132.3, 129.8, 129.1, 61.7, 61.1, 60.8, 48.6, 46.9, 41.5, 28.9, 27.8, 14.6, 14.1, 14.0, -0.4 ppm; IR (ATR): ν = 2955, 1728, 1366, 1246, 1217, 1185, 1094, 1071, 1048, 1033, 833, 732 cm$^{-1}$; MS (EI): m/z (%): 364 (40), 217 (38), 173 (36), 145 (47), 73 (100); HRMS (ESI+): calcd for C$_{20}$H$_{24}$O$_3$Si$_2$Na: 387.19678;
3-Methyl-8-phenyl-3,3a,6,7-tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester.

Yellow oil (98%, trans:cis = 6:2:1 (GC-MS)); Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31$ (m, 2H), 7.21 (m, 3H), 5.69 (m, 1H), 5.52 (dd, $J = 1.7$, 11.3 Hz, 1H), 4.19 (m, 2H), 4.13 (m, 2H), 3.45 (m, 1H), 2.96 (m, 1H), 2.87 (d, $J = 16.7$ Hz, 1H), 2.72 (dt, $J = 16.7$, 2.6 Hz, 1H), 2.40 (dq, $J = 11.5$, 6.8 Hz, 1H), 2.42-2.22 (m, 3H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.21 ppm (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.3, 170.6, 143.8, 139.8, 134.3, 130.0, 129.7, 128.1, 127.7, 126.1, 126.0, 61.2, 60.8, 47.3, 47.2, 40.2, 32.6, 26.8, 14.6, 14.1, 14.0 ppm; IR (ATR): $\tilde{v} = 2980, 1725, 1252, 1179, 1094, 1073, 1044, 1022, 765, 731, 700$ cm$^{-1}$; MS (EI): $m/z$ (%): 368 (34), 294 (75), 221 (100), 91 (36); HRMS (ESI+): calcd for C$_{23}$H$_{28}$O$_4$Na: 391.18758; found: 391.18798 [$M^+ + Na$].

3-Methyl-8-(4-methoxy-phenyl)-3,3a,6,7-tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester. Colorless oil (98%, trans:cis = 7:3:1 (GC-MS)); Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.14$ (m, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 5.67 (m, 1H), 5.51 (dd, $J = 1.6$, 11.3 Hz, 1H), 4.15 (m, 2H), 4.21 ppm (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.4, 170.6, 157.8, 139.3, 136.2, 133.8, 130.1, 129.7, 128.8, 113.5, 61.2, 61.0, 60.8, 55.2, 47.3, 47.1, 40.2, 32.7, 26.8, 14.6, 14.1, 14.0 ppm; IR (ATR): $\tilde{v} = 2979, 2904, 1725, 1509, 1243, 1174, 1094, 1071, 1033, 828$ cm$^{-1}$; MS (EI): $m/z$ (%): 398 (80), 324 (81), 251 (100), 121 (45); HRMS (EI): calcd for C$_{24}$H$_{30}$O$_5$: 398.20925; found: 398.20932 [$M^+ + Na$].

3-Methyl-8-(4-fluoro-phenyl)-3,3a,6,7-tetrahydro-2,2-(1H)-azulenedicarboxylic acid diethyl ester. Yellow oil (97%, trans:cis = 6:6:1 (GC-MS)); Major isomer: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.16$ (dd, $J = 5.5$, 8.8 Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 5.68 (m, 1H), 5.51 (dd, $J = 1.8$, 11.3 Hz, 1H), 4.15 (m, 4H), 3.42 (br d, $J = 11.5$ Hz, 1H), 2.93 (m, 1H), 2.82 (d, $J = 16.6$ Hz, 1H), 2.67 (dt, $J = 16.6$, 2.6 Hz, 1H), 2.39 (dq, $J = 11.5$, 6.8 Hz, 1H), 2.30-2.18 (m, 3H), 1.21 (t, $J = 7.1$ Hz, 6H), 1.19 ppm (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.3, 170.6, 161.2$ ($J_{CF} = 248$ Hz), 140.1, 133.3, 130.1, 129.7, 129.3, 129.2, 114.9 ($J_{CF} = 21$ Hz), 61.2, 61.1, 60.8, 47.3, 47.1, 40.2, 32.7, 26.7, 14.7, 14.1, 14.0 ppm; IR (ATR): $\tilde{v} = 2980, 2904, 1725, 1507, 1252, 1219, 1179, 1157, 1094, 1071, 1043, 1022, 832$ cm$^{-1}$; MS (EI): $m/z$ (%): 386 (37), 312 (79), 239 (100), 109 (29); HRMS (EI): calcd for C$_{23}$H$_{27}$O$_4$F: 386.18922; found: 386.18934 [$M^+]$; elemental analysis calcd (%) for C$_{23}$H$_{27}$O$_4$F: C 71.48, H 7.04; found: C 71.10, H 6.85.
Iron Catalyzed [2+2+2] Cycloadditions

Indacene-2,2,7,7-tetracarboxylic acid, 1,3,6,8-tetrahydro-tetraethyl ester. A solution of 1-dodec-6,11-diyne-4,4,9,9-tetracarboxylic acid tetraethyl ester (100 mg, 0.22 mmol) in toluene (1.8 mL) was added to a solution of complex 4 (7.3 mg, 10 mol%) in toluene (1 mL) and the resulting mixture was stirred at reflux temperature under Ar for 2-3 h. After completion of the reaction, moist methyl tert-butylether was added and all volatile materials were evaporated. The residue was purified by flash chromatography (SiO$_2$, hexane/EtOAc) to give the title compound (89 mg, 89%) as a white solid. mp 74-76 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.00 (s, 2H), 4.20 (q, $J$ = 7.1 Hz, 8H), 3.55 (s, 4H), 3.49 (s, 4H), 1.25 ppm (t, $J$ = 7.1 Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.7, 138.9, 135.7, 122.7, 61.7, 60.5, 40.4, 38.9, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 2982, 1727, 1244, 1182, 1154, 1095, 1065, 1045, 1012, 859 cm$^{-1}$; MS (EI): $m$/z (%): 446 (39), 372 (100), 298 (10), 227 (16), 153 (24); HRMS (ESI+): calcd for C$_{24}$H$_{30}$O$_8$: 469.18339; found: 469.1855; [M$^+$+Na].

5-[2,2-Bis(ethoxycarbonyl)-4-pentyn-1-yl]-1,3-dihydro-2,2-diethyl-ester-2H-inden-2,2-dicarboxylic acid. Prepared analogously as a colorless oil (31 mg, 62%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.08 (d, $J$ = 7.7 Hz, 1H), 6.99 (s, 1H), 6.96 (d, $J$ = 7.7 Hz, 1H), 4.19 (q, $J$ = 7.1 Hz, 8H), 3.54 (s, 4H), 3.34 (s, 2H), 2.66 (d, $J$ = 2.6 Hz, 2H), 2.13 (t, $J$ = 2.6 Hz, 1H), 1.25 (t, $J$ = 7.1 Hz, 6H), 1.25 ppm (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.6, 169.7, 140.3, 138.9, 134.3, 128.6, 125.6, 124.1, 125.6, 124.1, 79.4, 72.1, 61.7, 60.4, 58.1, 40.4, 40.2, 37.1, 22.1, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 3281, 2982, 2937, 1731, 1276, 1247, 1182, 1095, 1063, 1050, 1011, 858, 732 cm$^{-1}$; MS (EI): $m$/z (%): 472 (27), 427 (26), 399 (91), 325 (58), 274 (58), 201 (100), 129 (44); HRMS (ESI+): calcd for C$_{26}$H$_{32}$O$_8$: 495.19914; found: 495.19894 [M$^+$+Na].

6-(2,2-Bis-ethoxycarbonyl-pent-4-enyl)-1,3,4,5-tetrahydro-indene-2,2-dicarboxylic acid diethyl ester. Prepared analogously as a colorless oil (63 mg, 63%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.69 (br d, $J$ = 8.9 Hz, 2H), 5.65 (m, 1H), 5.09 (d, $J$ = 4.2 Hz, 1H), 5.05 (s, 1H), 4.16 (m, 8H), 3.11 (d, $J$ = 18.5 Hz, 1H), 2.90 (d, $J$ = 18.4 Hz, 1H), 2.80 (d, $J$ = 14.1 Hz, 1H), 2.63 (m, 5H), 2.03 (dd, $J$ = 7.2, 16.0 Hz, 1H), 1.83 (m, 2H), 1.23 ppm (t, $J$ = 7.0 Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.7, 171.6, 171.2, 171.0, 141.7, 132.7, 131.2, 131.2, 125.0, 125.6, 118.9, 116.1, 61.5, 61.2, 59.5, 57.5, 54.6, 39.6, 38.5, 37.8, 37.0, 33.6, 14.0 ppm; IR (ATR): $\tilde{\nu}$ = 2980, 2933, 1727, 1445, 1366, 1279, 1242, 1205, 1182, 1095, 1063, 1026, 860 cm$^{-1}$; MS (EI): $m$/z (%): 476 (7), 431 (8), 276 (86), 230 (43), 202 (100), 155 (30), 129 (66); HRMS (ESI+): calcd for C$_{26}$H$_{36}$O$_8$: 499.23007; found: 499.23024 [M$^+$+Na].
X-Ray Crystallographic Study

Figure S-1. The structure of 4 in the solid state comprises four crystallographically independent molecules. Anisotropic displacement parameter ellipsoids are shown at the 50% probability level, hydrogen atoms have been omitted for clarity.

The structure of 4 in the solid state (Figure 1) is composed of four crystallographically independent molecules, which show almost identical molecular conformations. Small but significant differences of the lithium and iron coordination spheres are revealed only upon closer inspection. All four independent molecules are characterized by a remarkably close contact between the iron center and the lithium atom which averages 2.493(4) Å and is significantly shorter than the Fe···Li distance in the related TMEDA complex 3 (2.530 Å). Further short contacts are observed between the lithium atom and one of the Cp ring carbon atoms (2.466(13) Å) as well as one of the two proximal olefinic sites of the COD ligand (2.33(4) Å). The distance to the other double bond is substantially longer (2.73(6) Å), a trend not observed in complex 3. While the larger variance of the latter two means might indicate a more variable and hence weaker interaction between the lithium atom and the ligands, this

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9 All errors reported in this discussion are calculated as the sample standard deviation $s_N$.

picture is changed when the sum over all the close lithium contacts in each of the four independent molecules is formed, since the sum of the six distances (including Li...O) varies only between 11.456 and 11.482 Å, the average being 11.475(11) Å.

Substantial back-bonding of electron density from the metal into the $\pi^*$ orbital of the alkenes is evident from the considerable elongation of the C=C bond from a theoretical value of 1.34 Å in free COD to an average of 1.436(10) Å. Even more subtle effects result from the competition of the lithium cation and the iron center. In all four molecules the shorter of the two C=C double bonds is associated with a longer Li...C contact (and vice versa), while the variance of the Fe-C distances does not follow this trend directly. However, the sum of all four Fe-COD bond lengths of each molecule is constant within 0.009 Å. As far as the Fe-Cp distances are concerned, there are significant differences between the five Fe-C bonds, which also remain significant after averaging the equivalent bonds in the four molecules. Interestingly, the Fe-C bonds do not show mirror symmetry with regard to the carbon atom closest to lithium but reflect the rotation of the Cp ring with regard to the COD ligand. This is in contrast to complex 3, which exhibits almost $C_s$ symmetry and where the Fe-C bonds follow a pattern with the shortest Fe-C distance for the carbon atom closest to the lithium atom, while the next pair of bonds is significantly longer and the next pair is still longer. In addition, there is a distortion of the Cp ring itself which has already been discussed by Jonas and Krüger. In complex 4 this distortion is only significant in the molecules with the iron atoms labeled Fe1 and Fe2, which are also the two molecules where the difference between the two COD double bonds is significant. The other two molecules display a more even distribution of C-C bond lengths.

The crystal structure of 4 also invites comparison with that of the [CpFe(cod)] radical.\footnote{Angermund, K.; Claus, K. H.; Goddard, R.; Krüger, C. Angew. Chem. 1985, 97, 241; Angew. Chem., Int. Ed. Engl. 1985, 24, 237.} Forma! addition of an electron to the [CpFe(cod)] moiety in 4 by the lithium results in a movement of the ligands toward the Fe atom. Thus, whereas the average Fe-C distance to the COD ligand in the radial is 2.039(5) Å, in 4 it is 2.019(11) Å. In fact, the Fe-C distances to the COD ligand in 4 can be divided into two groups, with those that are further from the Li atom significantly shorter than those that are not (2.009(3) Å vs. 2.029(7) Å). The effect of formal single electron reduction is even more noticeable in the distances of the Fe atom to the midpoints of the Cp rings: in the 4 it is 1.706(2) Å, while in the radical it is 1.790 Å. Clearly, the additional electron supplied by the Li atom in 4 results in stronger bonding of the Cp and COD ligands to the Fe atom.

Data were recorded using a Bruker-AXS KappaCCD-diffractometer with graphite-monochromated Mo-K$_\alpha$-radiation ($\lambda$ = 0.71073 Å). The crystal was mounted in a stream of cold nitrogen gas and measured at 100 K. The structures were solved by direct methods (SHELXS-97)\footnote{Sheldrick, G. M., SHELXS-97, Program for the determination of crystal structures, University of Göttingen, Germany, 1997} and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-
97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program.

**Selected X-ray Crystallographic Data for Ferrate Complex 1:** C$_{18}$H$_{29}$FeLiN$_2$, $M_r = 300.19$ g · mol$^{-1}$, orange plate, crystal size 0.25 x 0.11 x 0.10 mm, triclinic, space group $PT$, $a = 8.1030(2)$ Å, $b = 9.4613(2)$ Å, $c = 11.1671(2)$ Å, $\alpha = 94.945(1)^\circ$, $\beta = 98.755(1)^\circ$, $\gamma = 107.135(1)^\circ$, $V = 800.77(3)$ Å$^3$, $Z = 2$, $D_{calc} = 1.245$ g·cm$^{-3}$, $\mu(Mo-Ka) = 0.930$ mm$^{-1}$, gaussian absorption correction ($T_{min.} = 0.87/T_{max.} = 0.93$), 2.92 $< \theta < 37.47$, 29174 measured reflections, 8064 independent reflections, 7358 reflections with $I > 2\sigma(I)$, $R_I = 0.036$ [$I > 2\sigma(I)$], $wR_2 = 0.093$, 172 parameters, $S = 1.057$, residual electron density +0.8 / -1.0 e Å$^{-3}$.

**Selected X-ray Crystallographic Data for Ferrate Complex 4:** C$_{17}$H$_{27}$FeLiO$_2$, $M_r = 326.18$ g · mol$^{-1}$, brown-orange plate, crystal size 0.16 x 0.14 x 0.12 mm, monoclinic, space group $Cc$, $a = 18.9769(3)$ Å, $b = 24.3810(3)$ Å, $c = 15.8073(2)$ Å, $\beta = 118.19^\circ$, $V = 6446.39(15)$ Å$^3$, $Z = 16$, $D_{calc} = 1.344$ g·cm$^{-3}$, $\mu(Mo-Ka) = 0.936$ mm$^{-1}$, multi-scan absorption correction ($T_{min.} = 0.41/T_{max.} = 0.75$), 5.13 $< \theta < 36.34$, 114161 measured reflections, 30999 independent reflections, 30999 reflections with $I > 2\sigma(I)$, $R_I = 0.043$ [$I > 2\sigma(I)$], $wR_2 = 0.116$, 757 parameters, $S = 1.048$, absolute structure parameter 0.353(9), residual electron density +0.6 / -1.3 e Å$^{-3}$.

**Selected X-ray Crystallographic Data for Compound 15:** C$_{24}$H$_{27}$NO$_2$S, $M_r = 393.53$ g · mol$^{-1}$, colorless plate, crystal size 0.10 x 0.05 x 0.02 mm, monoclinic, space group $P2_1/n$, $a = 8.3738(2)$ Å, $b = 12.9293(2)$ Å, $c = 18.6530(4)$ Å, $\beta = 96.2740(10)^\circ$, $V = 2007.42(7)$ Å$^3$, $Z = 4$, $D_{calc} = 1.302$ g·cm$^{-3}$, $\mu(Mo-Ka) = 0.181$ mm$^{-1}$, multi-scan absorption correction ($T_{min.} = 0.53/T_{max.} = 0.76$), 2.91 $< \theta < 33.11$, 43093 measured reflections, 7622 independent reflections, 5599 reflections with $I > 2\sigma(I)$, $R_I = 0.046$ [$I > 2\sigma(I)$], $wR_2 = 0.151$, 247 parameters, $S = 1.113$, residual electron density +0.5 / -0.5 e Å$^{-3}$.

**Selected X-ray Crystallographic Data for Complex 38:** C$_{35}$H$_{35}$Fe, $M_r = 547.51$ g · mol$^{-1}$, brown plate, crystal size 0.38 x 0.12 x 0.07 mm, monoclinic, space group $P2_1/n$, $a = 13.7287(5)$ Å, $b = 14.0318(6)$ Å, $c = 15.9173(5)$ Å, $\beta = 113.860(2)^\circ$, $V = 2804.23(18)$ Å$^3$, $Z = 4$, $D_{calc} = 1.297$ g·cm$^{-3}$, $\mu(Mo-Ka) = 0.563$ mm$^{-1}$, gaussian absorption correction ($T_{min.} = 0.93/T_{max.} = 0.98$), 2.92 $< \theta < 33.19$, 51290 measured reflections, 10702 independent reflections, 6640 reflections with $I > 2\sigma(I)$, $R_I = 0.056$ [$I > 2\sigma(I)$], $wR_2 = 0.123$, 375 parameters, $S = 1.008$, residual electron density +0.6 / -0.7 e Å$^{-3}$.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers **CCDC 662118 - 662121**

Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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13 Sheldrick, G. M., *SHELXL*-97, Program for least-squares refinement of crystal structures, University of Göttingen, Germany, 1997