SUPPORTING INFORMATION

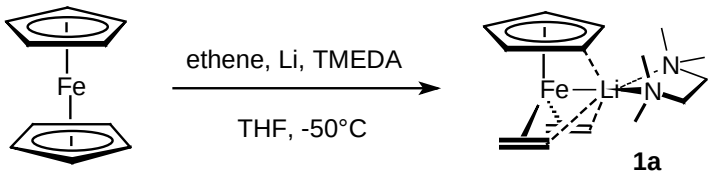
Cycloisomerization of 1,6-Enynes Catalyzed by Iron(0) Ate Complexes

Alois Fürstner*, Rubén Martin, and Keisuke Majima

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

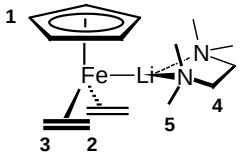
General. All reactions were carried out under Ar in flame dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N, pyridine, DMF (CaH_2), MeOH (Mg), hexane, cyclohexane, toluene, benzene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the 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 ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.24$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ 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 (Lancaster, Fluka, Aldrich) were used as received unless stated otherwise.

Preparation of [CpFe(C_2H_4)$_2$] [Li(tmeda)] (1a).[1]



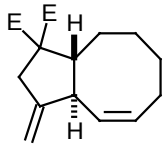
1a

A flame-dried three-necked round bottom flask equipped with a magnetic stirbar, a gas inlet, a glass stopper and a stopcock connected to the vacuum line is charged under Ar with lithium sand (2.40 g, 346 mmol) and THF (200 mL). The suspension is cooled to –50°C and vacuum is applied until gentle boiling of the solvent is observed. At that stage, the flask is back-filled with ethene gas (from a gas burette to monitor the uptake) and the evacuation/back-filling cycle is repeated three times. Ferrocene (32.1 g, 173 mmol) is then added in portions under a gentle stream of ethene and the resulting orange-brown suspension is vigorously stirred for 20 h at –50°C. During the first 2-3 h, an uptake of ethylene can be observed which slowly ceases. The resulting mixture is allowed to warm to 0°C before it is filtered under Ar through a cooled funnel (cooling jacket) at 0°C. The filtrate is evaporated under reduced pressure to ca. ½ of the original volume before freshly distilled *N,N,N',N'*-tetramethyl-ethylenediamine (TMEDA, 100 mL) is added. Storing of the resulting solution at –30°C overnight causes the precipitation of orange-red crystals which are filtered off, washed at 0°C with chilled Et_2O (200 mL in two portions) and dried at ambient temperature under vacuum (10^{-3} Torr). The resulting air-sensitive orange-red crystals of complex **1a** (23.5 g, 45%) can be handled at ambient temperature without noticeable decomposition and can be stored at –20°C for extended periods of time (> 1 year). While the signals in the ^{1}H NMR spectrum are broad, the ^{13}C NMR recorded at 193K shows characteristic sharp lines. ^{13}C NMR (100 MHz, THF-d_8, 193K, arbitrary numbering scheme as shown in the insert): δ 77.4 (C-1, d), 58.5 (C-4, t, J_{CH} = 133 Hz), 46.4 (C-5, q, J_{CH} = 132 Hz), 28.3 (C-3, t, J_{CH} = 150 Hz), 18.1 (broad, C-2, t, J_{CH} = 141 Hz).



[1] Jonas, K.; Schieferstein, L. *Angew. Chem. Int. Ed. Engl*. **1979**, *18*, 549.

Representative Procedure for the Iron-catalyzed Ene Reaction. (*Z*,3a*S,9a*S**)-Diethyl 3,3a,7,8,9,9a-hexahydro-3-methylene-2H-yclopenta[8]annulene -1,1(6H)-dicarboxylate**.

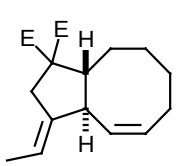


(E = COOEt)

A solution of enyne **3a** (123 mg, 0.4 mmol)[2] in toluene (2 mL) is added to a solution of complex **1a** (6 mg, 5 mol%) in toluene (2 mL) and the resulting mixture is stirred at 80-90°C under Ar for 6 h until TLC control shows complete conversion of the substrate. For work up, the solvent is evaporated and the residue is purified by flash chromatography to give the title compound **4a** as a colorless oil (102 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (2H, m), 4.84 (1H, dd, *J* = 4.9, 2.2 Hz), 4.78 (1H, dd, *J* = 4.9, 2.4 Hz), 4.12 (4H, m), 3.32 (1H, br.d, *J* = 12 Hz), 3.07 (1H, d, *J* = 18 Hz), 2.63 (1H, dd, *J* = 18, 2.5 Hz), 2.21 (1H, m), 2.09 (2H, m), 1.95 (1H, m), 1.66 (1H, m), 1.53-1.27 (3H, m), 1.21 (6H, m), 1.14 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 3075, 2932, 2862, 1728, 1647, 1295, 1253, 1185, 1098, 1052, 1019, 880. MS (EI) *m/z* (rel. intensity): 159 (74), 232 (100), 261 (11), 306 (14). HRMS (CI): *calcd for* ($C_{18}H_{26}O_4$+Na): 329.17287, *found* 329.17292. Anal. *calcd*. for $C_{18}H_{26}O_4$: C 70.56, H 8.55, *found* C 70.67, H 8.51.

The following compounds were prepared analogously:

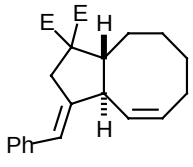
(3*E*,3a*S,4*Z*,9a*S**)-Diethyl 3-ethylidene-3,3a,7,8,9,9a-hexahydro-2H-cyclopenta[8]-annulene-1,1(6H)-dicarboxylate**. Colorless oil (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (2H, m), 5.17 (1H, m), 4.11 (4H, m), 3.28 (1H, br.d, *J* = 11.7 Hz), 2.97 (1H, d, *J* = 17.5 Hz), 2.47 (1H, dd, *J* = 17.5, 1.9 Hz), 2.18 (1H, m), 2.07 (2H, m), 1.96 (1H, m), 1.63 (1H, m), 1.55 (3H, d, *J* = 6.7 Hz), 1.49 (1H, m), 1.33 (2H, m), 1.20 (6H, m), 1.13 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 3014, 2980, 2931, 2860, 1729, 1647, 1462, 1447, 1251, 1270, 1195, 1178, 1100, 1020, 863. MS (EI) *m/z* (rel. intensity): 173 (79), 217 (16), 246 (100), 320 (25). HRMS (CI): *calcd* for ($C_{19}H_{28}O_4$+Na): 343.18828, *found* 343.18852 (M+Na). Anal. *calcd*. for $C_{19}H_{28}O_4$: C 71.22, H 8.81, *found* C 71.29, H 8.75.



4b (E = COOEt)

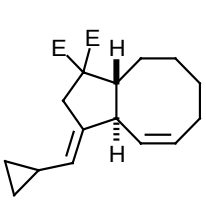
[2] Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc*. **2001**, *123*, 11863.

(3*E*,3a*S,4*Z*,9a*S**)-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, $CDCl_3$) δ 7.23 (4H, m), 7.08 (1H, m), 6.15 (1H, t, *J* = 2.4 Hz), 5.62 (2H, m), 4.09 (4H, m), 3.56 (1H, br.d, *J* = 11.6 Hz), 3.33 (1H, d, *J* = 17.1 Hz), 2.88 (1H, dd, *J* = 17.1, 2.9 Hz), 2.23 (1H, m), 2.11 (2H, m), 1.99 (1H, m), 1.63 (1H, m), 1.58-1.31 (3H, m), 1.21 (6H, m), 1.16 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 3056, 2980, 2933, 1727, 1600, 1447, 1367, 1252, 1190, 1158, 1098, 1036, 862, 756. MS (EI) *m/z* (rel. intensity): 91 (72), 217 (90), 235 (69), 308 (100), 382 (59). Anal. *calcd.* for $C_{24}H_{30}O_4$: C 75.36, H 7.91, *found* C 75.48, H 7.87.



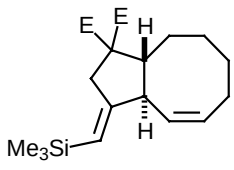
4c (E = COOEt)

(3*E*,3a*S,4*Z*,9a*S**)-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, $CDCl_3$) δ 5.47 (2H, m), 4.54 (1H, dd, *J* = 9.2, 2.4 Hz), 4.15 (4H, m), 3.29 (1H, d, *J* = 12 Hz), 3.14 (1H, d, *J* = 17.6 Hz), 2.66 (1H, dt, *J* = 17.6, 2.8 Hz), 2.21 (1H, m), 2.05 (2H, m), 1.94 (1H, m), 1.65 (1H, m), 1.47 (2H, m), 1.41-1.16 (9H, m), 0.64 (2H, d, *J* = 8 Hz), 0.24 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2929, 2895, 1724, 1446, 1366, 1247, 1181, 1095, 1074, 1047, 1018, 970, 904, 860, 806. MS (EI) *m/z* (rel. intensity): 91 (24), 173 (37), 199 (75), 272 (100), 346 (36). HRMS (CI): *calcd* for ($C_{21}H_{30}O_4$+Na): 369.20363, *found* 369.20332 (M+Na). Anal. *calcd*. for $C_{21}H_{30}O_4$: C 72.80, H 8.73, *found* C 72.91, H 8.66.



4d (E = COOEt)

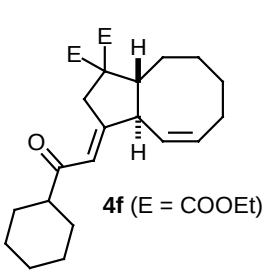
(3*E*,3a*S,4*Z*,9a*S**)-Diethyl 3,3a,7,8,9,9a-hexahydro-3-((trimethylsilyl)methylene)-2H-cyclopenta[8]annulene-1,1(6H)-dicarboxylate**. The compound was prepared according to the representative procedure outlined above using 15 mol% of catalyst **1a** and 48h reaction time. Colorless oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (2H, m), 5.3 (1H, d, *J* = 1.6 Hz), 4.21 (4H, m), 3.51 (1H, t, *J* = 10 Hz), 2.4-1.9 (4H, m), 1.83-1.51 (7H, m), 1.22 (6H, m), 0.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2931, 1914, 1725, 1633, 1446, 1366, 1308, 1248, 1202, 1181, 1095, 1070, 1043, 963, 846, 760. MS (EI) *m/z* (rel. intensity): 73 (79), 159 (26), 187 (100), 231 (29), 305 (67), 378 (75). HRMS (CI):



4e (E = COOEt)

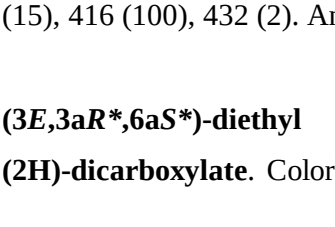
calcd for ($C_{21}H_{34}O_4Si$+Na): 401.21166, *found* 401.21186 (M+Na). Anal. *calcd*. for $C_{21}H_{34}O_4Si$: C 66.62, H 9.05, Si 7.42, *found* C 66.78, H 9.01.

(3*E*,3a*S,4*Z*,9a*S**)-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, $CDCl_3$) δ 6.11 (1H, dd, *J* = 4.8, 2.4 Hz), 5.61 (1H, m), 5.48 (1H, dd, *J* = 10.3, 7.2 Hz), 4.19 (m, 4H), 3.65 (1H, dd, *J* = 20.4, 2 Hz), 3.53 (1H, td, *J* = 10.8, 1.1 Hz), 2.96 (1H, dt, *J* = 20.4, 2.8 Hz), 2.27 (1H, m), 2.13 (3H, m), 2.01 (1H, m), 1.8-1.4 (7H, m), 1.33-1.16 (14H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2928, 2854, 1724, 1683, 1618, 1448, 1367, 1246, 1189, 1096, 1047, 861, 744. MS (EI) *m/z* (rel. intensity): 83 (81), 259 (77), 343 (79), 359 (28), 371 (15), 416 (100), 432 (2). Anal. *calcd.* for $C_{25}H_{36}O_5$: C 72.08, H 8.71, *found* C 72.23, H 8.60.

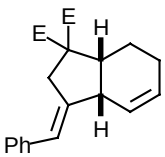


4f (E = COOEt)

(3*E*,3a*R,6a*S**)-diethyl 3-(4-methoxybenzylidene)-3,3a,6,6a-tetrahydropentalene-1,1-(2H)-dicarboxylate**. Colorless oil (50%). The compound consists of a single diastereomer which was shown by NOE experiments to have a *cis*-fused ring junction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (2H, d, *J* = 8.6 Hz), 6.79 (2H, s, *J* = 8.6 Hz), 6.19 (1H, s), 5.54 (2H, m), 4.16 (2H, q, *J* = 7.1 Hz), 4.04 (2H, q, *J* = 7.0 Hz), 3.86 (1H, d, *J* = 6.8 Hz), 3.73 (3H, s), 3.45 (1H, m), 3.05 (1H, d, *J* = 16 Hz), 2.98 (1H, d, *J* = 16 Hz), 2.48 (1H, dd, *J* = 17.2, 10 Hz), 2.08 (1H, dd, *J* = 17.2, 6.2 Hz), 1.19 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) 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. IR: 2956, 2924, 2853, 1729, 1607, 1575, 1510, 1464, 1366, 1297, 1249, 1175, 1157, 1074, 1033, 845. MS (EI) *m/z* (rel. intensity): 121 (36), 223 (45), 296 (100), 370 (76). HRMS (CI): *calcd* for ($C_{22}H_{26}O_5$+Na): 393.16691 *found* 393.16724 (M+Na). Anal. *calcd*. for $C_{22}H_{26}O_5$: C 71.33, H 7.07, *found* C 71.50, H 6.98.



5 (E = COOEt)

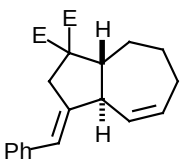


6 (E = COOMe)

(3*E*,3a*R,7a*S**)-Dimethyl 3-benzylidene-3,3a,7,7a-tetrahydro-2H-indene-1,1(6H)-dicarboxylate**. White solid (86%). The compound consists of a single diastereomer which was shown by extensive NOE experiments to have a *cis*-fused ring junction, cf. below. mp 91-93 ºC. ^{1}H NMR (400 MHz,

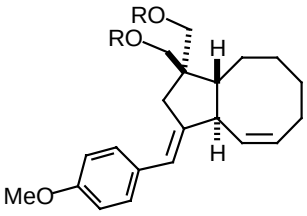
$CDCl_3$) δ 7.21 (5H, m), 6.15 (1H, s), 5.9 (1H, brs), 5.72 (1H, m), 3.68 (3H, s), 3.62 (3H, s), 3.53 (1H, m), 3.36 (1H, brs), 3.11 (1H, d, *J* = 20 Hz), 2.81 (1H, dd, *J* = 9.2, 6.4 Hz), 2.01 (2H, brs), 1.27 (1H, brs), 1.1 (1H, brs). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 170.2, 144.1, 137.9, 128.2, 128.1, 126.9, 126.4, 126.2, 123.7, 63.2, 52.7, 52.5, 44.5, 42.2, 36.6, 24.6, 21.2. IR: 2981, 2951, 2876, 1733, 1532, 1434, 1251, 1247, 1200, 1166, 1065, 921, 822, 695. MS (EI) *m/z* (rel. intensity): 91 (58), 115 (54), 145 (100), 175 (71), 207 (59), 266 (37), 326 (27). Anal. *calcd*. for $C_{20}H_{22}O_4$: C 73.60, H 6.79, *found* C 73.69, H 6.68.

(3*E*,3a*R,4*Z*,8a*S**)-Diethyl 3-benzylidene-3,3a,6,7,8,8a-hexahydroazulene-1,1(2H)-dicarboxylate**. Yellow oil (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (5H, m), 6.27 (1H, dd, *J* = 4.8, 2.4 Hz), 5.86 (2H, m), 4.19 (4H, m), 3.45 (1H, d, *J* = 11.6 Hz), 3.31 (1H, dd, *J* = 18, 2 Hz), 2.86 (1H, dt, *J* = 18, 3.2 Hz), 2.32 (1H, m), 2.2-1.3 (6H, m), 1.19 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) 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. IR: 2955, 2924, 2854, 1727, 1599, 1491, 1445, 1367, 1252, 1186, 1095, 1031, 918, 862. MS (EI) *m/z* (rel. intensity): 29 (80), 95 (67), 151 (40), 180 (100), 221 (23), 254 (18), 294 (14), 368 (7). Anal. *calcd*. for $C_{23}H_{28}O_4$: C 74.97, H 7.66, *found* C 74.80, H 7.85.



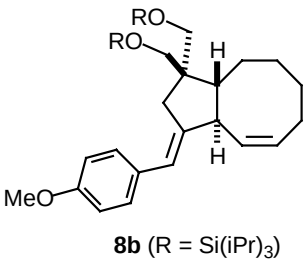
7 (E = COOEt)

[(3*E*,3a*R,9a*S**)-1-[(acetyloxy)methyl]-3-(4-methoxybenzylidene)-2,3,3a,6,7,8,9,9a-octahydro-1*H*-cyclopenta[*a*]cycloocten-1-yl]methyl acetate.** White solid (84%), mp 100−103 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (2H, d, *J* = 8.7 Hz), 6.8 (2H, d, *J* = 8.7 Hz), 6.11 (1H, d, *J* = 2.4 Hz), 5.64 (1H, dd, *J* = 10.4, 6.8 Hz), 5.57 (1H, m), 4.06 (3H, m), 3.85 (1H, d, *J* = 11.2 Hz), 3.74 (3H, s), 3.67 (1H, m), 3.49 (1H, t, *J* = 9.9 Hz), 2.7 (1H, dd, *J* = 17.6, 1.6 Hz), 2.49 (1H, dt, 17.6, 2.8 Hz), 2.28 (1H, m), 2.02 (3H, s), 1.96 (3H, s), 1.9-1.1 (7H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2971, 2929, 1738, 1607, 1510, 1463, 1365, 1241, 1230, 1177, 1034, 831. MS (EI) *m/z* (rel. intensity): 43 (16), 121 (100), 171 (26), 292 (12), 412 (12). HRMS (CI): *calcd* for ($C_{25}H_{32}O_5$+Na): 435.21420, *found* 435.21475 (M+Na). Anal. *calcd*. for $C_{25}H_{32}O_5$: C 72.79, H 7.82, *found* C 72.66, H 7.84.



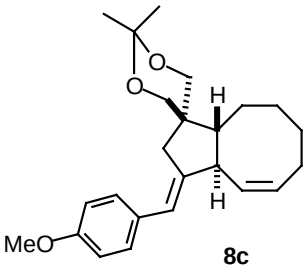
8a (R = Ac)

[((3*E*,3a*R,9a*S**)-3-(4-methoxybenzylidene)-1-{[(triisopropylsilyl)oxy]methyl}-2,3,3a,6,7,8,9,9a-octahydro-1*H*-cyclopenta[*a*]cycloocten-1-yl)methoxy]-(triisopropyl)-silane**. Colorless oil (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, d, *J* = 8.6 Hz), 6.78 (2H, d, *J* = 8.6 Hz), 6.04 (1H, d, *J* = 2.4 Hz), 5.66 (1H, dd, *J* = 10, 6.8 Hz), 5.5 (1H, m), 3.72 (3H, s), 3.57 (5H, m), 2.78 (1H, dd, 17.4, 1.8 Hz), 2.48 (1H, dd, *J* = 17.4, 2.8 Hz), 2.31 (1H, m), 1.96 (2H, m), 1.58 (4H, m), 1.34-1.08 (3H, m), 0.99-0.87 (41H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2940, 2865, 1711, 1605, 1510, 1462, 1247, 1174, 1093, 1061, 917, 881, 803, 676. Anal. *calcd.* for $C_{39}H_{68}O_3Si_2$: C 73.06, H 10.69, *found* C 73.11, H 10.61.



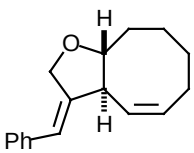
8b (R = Si(iPr)$_3$)

[(3*E*,3a*R,9a*S**)-1-[1,3-dioxolan]-3-(4-methoxybenzylidene)-2,3,3a,6,7,8,9,9a-octahydro-1*H*-cyclopenta[*a*]cycloocten-1-yl].** White solid (96%), mp 121-123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (2H, d, *J* = 8.7 Hz), 6.79 (2H, d, *J* = 8.7 Hz), 6.09 (1H, d, *J* = 2.2 Hz), 5.61 (1H, dd, *J* = 10.4, 6.8 Hz), 5.56 (1H, m), 3.95 (1H, d, *J* = 11.6 Hz), 3.86 (1H, dd, *J* = 11.6, 1.2 Hz), 3.73 (3H, s), 3.38 (3H, m), 3.16 (1H, dd, *J* = 17.6, 1.6 Hz), 2.37 (1H, d, *J* = 17.6 Hz), 2.27 (1H, m), 1.99 (1H, m), 1.88 (1H, t, *J* = 11.2 Hz), 1.69 (1H, m), 1.5 (3H, m), 1.36 (3H, s), 1.32 (3H, s), 1.17 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2927, 2113, 1607, 1510, 1249, 1199, 1065, 1035, 834, 668. MS (EI) *m/z* (rel. intensity): 91 (8), 121 (100), 147 (31), 159 (16), 310 (4), 368 (41). HRMS (CI): *calcd* for ($C_{24}H_{32}O_3$+Na): 391.22399, *found* 391.22437 (M+Na). Anal. *calcd*. for $C_{24}H_{32}O_3$: C 78.22, H 8.75, *found* C 78.41, H 8.83.



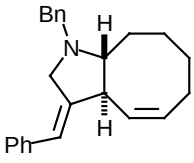
8c

3-Benzylidene-2,3,3a,6,7,8,9,9a-octahydro-cycloocta[*b*]furan. Yellow oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (2H, t, *J* = 7.5 Hz), 7.21(1H, t, *J* = 7.4 Hz), 7.16 (2H, d, *J* = 7.4 Hz), 6.25 (1H, dd, *J* = 2.6, 2.5 Hz), 5.74 (2H, m), 4.84 (1H, d, *J* = 14.3 Hz), 4.62 (1H, dt, *J*= 14.3, 2.5 Hz), 3.44 (1H, br.s), 3.28 (1H, td, *J* = 10.5, 3.2 Hz), 2.42 (1H, m), 2.20 (2H, m), 1.79-1.48 (4H, m), 1.31 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 137.4, 132.0, 128.9, 128.5, 127.9, 126.4, 119.7,



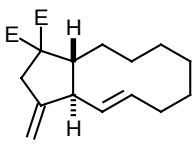
84.4, 70.3, 49.7, 31.1, 27.1, 25.2, 20.1. IR: 2924, 2853, 1729, 1599, 1449, 1260, 1060, 1045, 804, 754, 691. MS (EI) *m/z* (rel. intensity): 91 (54), 117 (46), 128 (35), 142 (39), 155 (100), 167 (23), 181 (11), 240 (52). HRMS (EI): *calcd*. for $C_{17}H_{20}O$: 240.15193, *found* 240.15142.

1-Benzyl-3-benzylidene-2,3,3a,6,7,8,9,9a-octahydro-1-*H*-cycloocta[*b*]pyrrole (9b).



Colorless oil (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (4H, m), 7.29-7.25 (3H, m), 7.16-7.12 (3H, m), 6.16 (1H, d, *J* = 2.3 Hz), 5.73 (2H, m), 4.24 (1H, d, *J* = 13.3 Hz), 4.01 (1H, d, *J* = 15.3 Hz), 3.61 (1H, br.s), 3.27 (1H, br.d, *J* = 15.2 Hz), 3.23 (1H, br.d, *J* = 17.1 Hz), 2.50 (1H, m), 2.26 (1H, m), 2.17 (2H, m), 1.83-1.59 (3H, m), 1.42 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.7, 130.9, 128.8, 128.4, 128.3, 127.8, 127.1, 126.1, 120.4, 70.6, 58.4, 57.8, 50.0, 31.9, 29.7, 29.7, 29.4, 27.9, 25.0, 22.7, 21.1, 14.1. IR: 2925, 2854, 2784, 1741, 1492, 1450, 1260, 1073, 1028, 911, 804.

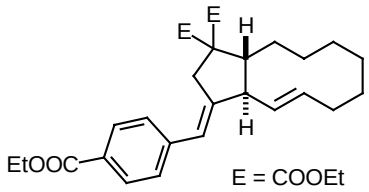
3-Benzylidene-1-(toluene-4-sulfonyl)-2,3,3a,6,7,8,9,9a-octahydro-1-*H*-cycloocta[*b*]-pyrrole (9c). White solid (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, d, *J* = 8.2 H), 7.23 (2H, d, *J* = 7.7 Hz), 7.14 (3H, m), 7.01 (2H, d, *J* = 7.4 Hz), 6.02 (1H, br.d, *J* = 2.3 Hz), 5.64 (1H, m), 5.44 (1H, dd, *J* = 9.9, 8.0 Hz), 4.38 (1H, d, *J* = 15.5 Hz), 4.05 (1H, d, *J* = 15.5 Hz), 3.53 (1H, t, *J* = 8.8 Hz), 2.73 (1H, td, *J* = 14.0, 2.0 Hz), 2.51 (1H, td, *J* = 10.3, 2.8 Hz), 2.29 (3H, s), 2.28 (1H, m), 2.07 (1H, m), 1.69 (1H, m), 1.58 (1H, m), 1.47 (3H , m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2924, 2854, 173,0 1598, 1448, 1345, 1160, 1091, 813. MS (EI) *m/z* (rel. intensity): 91 (84), 115 (20), 156 (25), 238 (100), 302 (42), 393 (14). HRMS (ESI): *calcd* for ($C_{24}H_{27}NO_2S$+Na): 416.165282, *found* (M+Na) 416.165473.



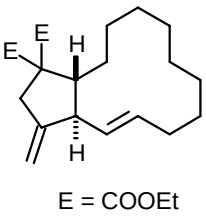
(*E*,3a*S,11a*S**)-Diethyl 3,3a,7,8,9,10,11,11a-octahydro-3-methylene-2H-cyclopenta[10]-annulene-1,1(6H)-dicarboxylate**. Colorless oil (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.6 (1H, ddd, *J* = 13.8, 9.6, 5.2 Hz), 5.21 (1H, m), 4.89 (1H, d, *J* = 2.4 Hz), 4.82 (1H, dd, *J* = 2.4, 0.9 Hz), 4.17 (4H, m), 3.11-3.02 (2H, m), 2.76 (1H, dd, *J* = 17.5, 2.4 Hz), 2.18 (3H, m), 1.99 (1H, m), 1.7-1.4 (7H, m), 1.23 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 3037, 2925, 1725, 1457, 1366, 1244, 1177, 1095, 1048, 984, 881. MS (EI) *m/z* (rel. intensity):

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): 357.20363, *found* 357.20387 (M+Na). Anal. *calcd.* for $C_{20}H_{30}O_4$: C 71.82, H 9.04, *found* C 71.96, H 9.17.

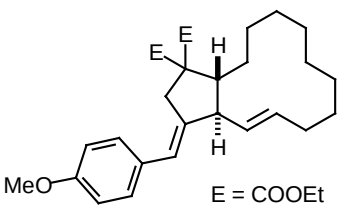
(3*E*,3a*S,4*E*,11a*S**)-Diethyl 3-(4-(ethoxycarbonyl)benzylidene)-3,3a,7,8,9,10,11,11a-octa-hydro-2H-cyclopenta[10]annulene-1,1(6H)-dicarboxylate**. Yellow oil (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (2H, d, *J* = 8.3 Hz), 7.19 (2H, 2, *J* = 8.3 Hz), 6.17 (1H, d, *J* = 2.4 Hz), 5.62 (1H, ddd, *J* = 14.2, 9.2, 5.2 Hz), 5.25 (1H, brs), 4.29 (2H, q, *J* = 7.1 Hz), 4.17 (4H, m), 3.34 (1H, d, *J* = 18.4 Hz), 3.21 (1H, t, *J* = 10 Hz), 2,91 (1H, dt, *J* = 18.4, 2.8 Hz), 2.2-1.91 (4H, m), 1.7-1.33 (4H, m), 1.32 (3H, t, *J* = 7.1 Hz), 1.28-1.1 (7H, m), 0.77 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2978, 2928, 2859, 1714, 1606, 1566, 1444, 1366, 1271, 1180, 1154, 1101, 1018, 984, 877, 860. MS (EI) *m/z* (rel. intensity): 171 (19), 245 (100), 335 (52), 408 (93), 437 (22), 482 (44). HRMS (CI): *calcd* for ($C_{29}H_{38}O_6$+Na): 505.25606, *found* 505.25638 (M+Na). Anal. *calcd*. for $C_{29}H_{38}O_6$: C 72.17, H 7.94, *found* C 72.30, H 7.88.



(3*E*,3a*S,4*E*,13a*S**)-Diethyl 3-benzylidene-3,3a,7,8,9,10,11,12,13,13a-decahydro-2H-cyclo-penta[12]annulene-1,1(6H)-dicarboxylate**. Colorless oil (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (1H, ddd, *J* = 16.6, 10, 3.6 Hz), 5.27 (1H, ddd, *J* = 16.6, 8.8, 1.6 Hz), 4.89 (1H, d, *J* = 2.3 Hz), 4.77 (1H, dd, *J* = 2.3, 0.8 Hz), 4.19 (m, 4H), 3.09 (1H, dd, *J* = 16.8, 0.8 Hz), 2.94 (1H, td, *J* = 9.8, 2.4 Hz), 2.72 (1H, dq, *J* = 16.8, 2.4 Hz), 2.31 (2H, m), 2.01 (1H, m), 1.87 (1H, m), 1.6-1.1 (19H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170. 9, 170.3, 149.9, 131.9, 131.4, 106.0, 60.7, 60.1, 60.0, 53.0, 49.0, 39.8, 30.6, 28.8, 24.7, 23.9, 23.8, 23.4, 22.9, 13.1, 13.0. IR: 3042, 2929, 2859, 1726, 1446, 1367, 1245, 1096, 1044, 859, 799. MS (EI) *m/z* (rel. intensity): 159 (44), 173 (24), 215 (44), 288 (100), 362 (36). HRMS (CI): *calcd* for ($C_{22}H_{34}O_4$+Na): 385.23493, *found* 385.23523 (M+Na). Anal. *calcd.* for $C_{22}H_{34}O_4$: C 72.89, H 9.45, *found* C 72.91, H 9.36.

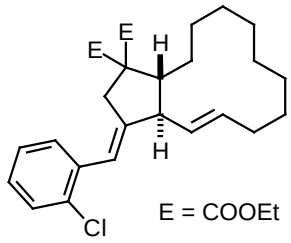


(3*E*,3a*S,4*E*,13a*S**)-Diethyl 3-(4-methoxybenzylidene)-3,3a,7,8,9,10,11,12,13,13a-decahydro-2H-cyclopenta[12]annulene-1,1(6H)-dicarboxylate**. Colorless oil (96%). ^{1}H NMR



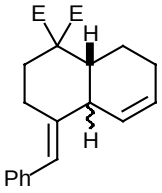
(400 MHz, $CDCl_3$) δ 7.26 (2H, d, *J* = 8.7 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 6.11 (1H, d, *J* = 2.4 Hz), 5.44 (1H, ddd, *J* = 15.2, 10.4, 3.6 Hz), 5.32 (1H, ddd, *J* = 15.2, 8.8, 1.2 Hz), 4.17 (4H, m), 3.79 (3H, s), 3.34 (1H, dd, *J* = 17.2, 1.3 Hz), 3.13 (1H, td, *J* = 10.8, 1.3 Hz), 2.96 (1H, dt, *J* = 17.2, 2.8 Hz), 2.32 (1H, m), 2.21 (1H, m), 2.07 (1H, m), 1.91 (1H, m), 1.61-1.17 (19H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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, 55.2, 49.8, 39.4, 31.4, 29.5, 25.8, 25.4, 25.3, 25.1, 24.1, 24.0, 14.1, 14.0. IR: 2933, 2871, 1725, 1607, 1510, 1444, 1366, 1248, 1177, 1034, 822. MS (EI) *m/z* (rel. intensity): 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* 491.27757 (M+Na). Anal. *calcd.* for $C_{29}H_{40}O_5$: C 74.33, H 8.60, *found* C 74.47, H 8.51.

(3*E*,3a*S,4*E*,13a*S**)-Diethyl 3-(2-chlorobenzylidene)-3,3a,7,8,9,10,11,12,13,13a-decahydro-2H-cyclopenta[12]annulene-1,1(6H)-dicarboxylate**. Yellow oil (95%). ^{1}H NMR



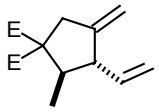
(400 MHz, $CDCl_3$) δ 7.31 (4H, m), 6.36 (1H, d, *J* = 2.3 Hz), 5.49 (1H, ddd, *J* = 15.2, 10, 3.6 Hz), 5.39 (1H, ddd, *J* = 15.2, 8.4, 1.2 Hz), 4.19 (4H, m), 3.23 (1H, dd, *J* = 17.6, 1.6 Hz), 3.17 (1H, dd, *J* = 10.4, 8.8 Hz), 2.84 (1H, dt, *J* = 17.6, 2.4 Hz), 2.31 (2H, m), 2.07 (1H, m), 1.87 (1H, m), 1.7-1.17 (19H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 171.1, 146.1, 136.3, 133.5, 133.3, 132.7, 129.7, 129.4, 127.5, 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. IR: 2978, 2933, 2867, 1724, 1443, 1366, 1244, 1094, 1035, 863, 835, 790, 753. Anal. *calcd.* for $C_{28}H_{37}ClO_4$: C 71.09, H 7.88, *found* C 71.14, H 7.79.

(4*E*,4a*S,8a*S**)-Diethyl 4-(4-methoxybenzylidene)-2,3,4,4a,8,8a-hexahydronaphthalene-1,1(7H)-dicarboxylate and (4*E*,4a*R**,8a*S**)-diethyl 4-(4-methoxybenzylidene)-2,3,4,4a,8,8a-hexahydronaphthalene-1,1(7H)-dicarboxylate**. Prepared using 15% of catalyst and 72 h as reaction time. Colorless oil (67%, *cis:trans* = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (2H, d, *J* = 8.8 Hz), 7.06 (2H, d, *J* = 8.3 Hz), 6.79 (2H, m), 6.15 (1H, s), 6.07 (1H, s), 5.74 (2H, m), 4.19 (4H, m), 3.72 (3H, s), 3.27 (3H, s), 2.85 (1H, m), 2.81 (1H, dt, *J* = 13.6, 3.4 Hz),



2.70 (1H, m), 2.48 (1H, m), 2.2-1.35 (m, 7H), 1.21 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$) 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. IR: 2936, 1727, 1607, 1509, 1445, 1366, 1242, 1175, 1094, 1032, 856, 803. MS (EI) *m/z* (rel. intensity): 121 (100), 173 (44), 251 (24), 277 (23), 398 (29). HRMS (CI): *calcd* for ($C_{24}H_{30}O_5$+Na): 421.198546, *found* 421.198371 (M+Na).

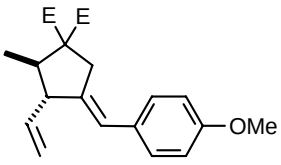
(2*S,3*S**)-Diethyl 2-methyl-4-methylene-3-vinylcyclopentane-1,1-dicarboxylate and (2*S**,3*R**)-diethyl 2-methyl-4-methylene-3-vinylcyclopentane-1,1-dicarboxylate**.



E = COOEt
major isomer

Colorless oil (93%); *trans : cis* = 5.8:1 (^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63-5.53 (1H, m), 5.46 (1H, ddd, *J* = 15.6, 10, 8.8 Hz), 5.07 (1H, dd, *J* = 10, 2 Hz), 4.98 (1H, dd, *J* = 10, 1.6 Hz), 4.86 (1H, d, *J* = 2 Hz), 4.73 (1H, d, *J* = 2 Hz), 4.15 (4H, m), 3.21 (1H, m), 3.09 (1H, dd, *J* = 17.6, 0.8 Hz), 2.81 (1H, m), 2.74 (1H, dd, *J* = 9.2, 2.4 Hz), 2.64 (1H, dq, *J* = 17.6, 2.4 Hz), 2.26 (1H, m), 1.21-1.17 (6H, m), 0.99 (3H, d, *J* = 6.9 Hz), 0.71 (3H, d, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2981, 2934, 1726, 1543, 1368, 1255, 1213, 1094, 899, 863. MS (EI) *m/z* (rel. intensity): 29 (100), 55 (34), 91 (48), 135 (72), 173 (30), 191 (26), 237 (6), 266 (2). Anal. *calcd.* for $C_{15}H_{22}O_4$: C 67.64, H 8.33, *found* C 67.71, H 8.19.

(*E*,2*S,3*S**)-Diethyl 4-(4-methoxybenzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate and (*E*,2*S**,3*R**)-Diethyl 4-(4-methoxybenzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate**. Colorless oil (97%); *trans : cis* = 6.3:1 (^{1}H NMR). ^{1}H

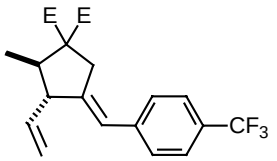


E = COOEt, *major isomer*

NMR (400 MHz, $CDCl_3$) δ 7.15 (2H, d, *J* = 8.6 Hz), 6.78 (2H, d, *J* = 8.6 Hz), 6.06 (1H, dd, *J* = 4.8, 2.4 Hz), 6.01 (1H, dd, *J* = 4.7, 2.3 Hz), 5.65 (1H, m), 5.51 (1H, ddd, *J* = 15.6, 10, 8.8 Hz), 5.1 (1H, ddd, *J* = 15.6, 10, 2 Hz), 4.19 (4H, m), 3.72 (3H, s), 3.46 (1H, m), 3.33 (1H, d, *J* = 18 Hz), 2.93 (1H, dd, *J* = 11.6, 9.6 Hz), 2.84 (1H, dt, *J* = 18, 2.8 Hz), 2.24 (1H, m), 1.19 (6H, m), 1.03 (3H, d, *J* = 6.8 Hz), 0.73 (3H, d, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.8, 169.7, 140.6, 138.8, 136.8, 130.3, 129.1, 122.9, 122.4, 118.0, 117.6, 113.4, 61.9, 61.1, 61.0, 56.6, 54.9, 54.0, 44.6, 42.2, 39.0, 36.0, 13.8, 13.6. IR: 2979, 2956, 1724, 1638, 11607, 1510, 1463, 1367, 1246, 1176, 1137, 1121,

1093, 1033, 917, 852, 821. MS (EI) *m/z* (rel. intensity): 121 (100), 147 (17), 225 (70), 298 (84), 327 (15), 372 (53). HRMS (CI): *calcd* for ($C_{22}H_{28}O_5$+Na): 395.18289, *found* 395.18329 (M+Na). Anal. *calcd.* for $C_{22}H_{28}O_5$: C 70.94, H 7.58, *found* C 70.83, H 7.63.

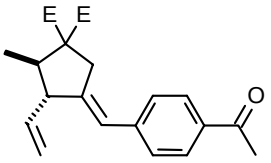
(*E*,2*S,3*R**)-Diethyl 4-(4-(trifluoromethyl)benzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate and (*E*,2*S**,3*S**)-Diethyl 4-(4-(trifluoromethyl)benzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate**. Colorless oil (96%); *trans : cis* = 4.8:1 (^{1}H NMR).



E = COOEt, *major isomer*

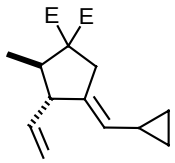
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, d, *J* = 8.2 Hz), 7.29 (2H, d, *J* = 8.2 Hz), 6.15 (1H, 2, *J* = 2.3 Hz), 6.1 (1H, d, *J* = 2.4 Hz), 5.63 (1H, m), 5.51 (1H, ddd, *J* = 16.9, 9.9, 8.9 Hz), 5.19 (1H, dd, *J* = 10.0, 1.9 Hz), 5.08 (1H, dd, *J* = 17, *J* = 1.8 Hz), 3.43 (1H, m), 3.39 (1H, m), 2.94 (1H, t, *J* = 11.6 Hz), 2.83 (1H, dt, *J* = 17.9, 2.7 Hz), 2.28 (1H, m), 1.18 (6H, m), 1.06 (3H, d, *J* = 6.9 Hz), 0.74 (3H, d, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.0, 145.2, 140.3, 137.4, 135.5, 127.4, 127.3, 126.9, 124.3, 124.2, 124.1, 121.9, 118.1, 117.7, 64.8, 61.1, 60.7, 60.6, 60.4, 60.2, 56.1, 53.6, 43.9, 41.5, 38.5, 35.6, 14.3, 13.1, 13.0, 12.9, 10.5. IR: 2981, 2945, 1725, 1616, 1415, 1367, 1323, 1257, 1162, 1121, 1066, 1016, 921, 854, 778. MS (EI) *m/z* (rel. intensity): 145 (21), 173 (48), 263 (100), 279 (28), 336 (80), 410 (24). Anal. *calcd.* for $C_{22}H_{25}F_3O_4$: C 64.38, H 6.14, *found* C 64.29, H 6.23.

(*E*,2*S,3*R**)-Diethyl 4-(4-acetylbenzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate and (*E*,2*S**,3*S**)-Diethyl 4-(4-acetylbenzylidene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate**. Colorless oil (91%); *trans : cis* = 4.1:1 (^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (2H, d, *J* = 7.6 Hz), 7.29 (2H, d, *J* = 7.6 Hz), 6.16 (1H, d, *J* = 2.4 Hz), 6.13 (1H, d, *J* = 2.5 Hz), 5.64 (1H, m), 5.51 (1H, ddd, *J* = 15.5, 9.8, 8.8), 5.17 (1H, dd, *J* = 9.8, 2.2 Hz), 5.11 (1H, dd, *J* = 15.5, 2.2 Hz), 4.15 (4H, m), 3.41 (1H, dd, *J* = 18, 1.6 Hz), 2.99 (1H, dd, *J* = 11.6, 9.2 Hz), 2.88 (1H, dt, *J* = 18, 2.4 Hz), 2.51 (3H, s), 2.29 (1H, m), 1.21 (6H, m), 1.07 (3H, d, *J* = 6.8 Hz), 0.75 (3H, d, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 171.0, 170.6, 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. IR: 2983, 2948, 1727, 1683, 1602, 1363, 1265, 1189, 991, 804, 771. MS (EI) *m/z* (rel. intensity): 43 (100), 193 (22), 237 (82), 310 (82), 384 (26). HRMS (CI): *calcd* for ($C_{23}H_{28}O_5$+Na): 407.18309, *found* 407.18289 (M+Na).



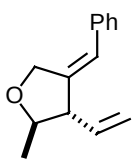
E = COOEt, *major isomer*

(*E*,2*S,3*S**)-Diethyl 4-(cyclopropylmethylene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate and (*E*,2*S**,3*R**)-Diethyl 4-(cyclopropylmethylene)-2-methyl-3-vinylcyclopentane-1,1-dicarboxylate**. Colorless oil (97%), *trans : cis* = 6.7:1 (^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (1H, m), 5.37 (1H, ddd, *J* = 16, 10, 8.8 Hz), 5.01 (1H, dd, *J* = 10, 2 Hz), 4.95 (1H, dd, *J* = 16, 2 Hz), 4.47 (1H, dd, *J* = 9.6, 2.4 Hz), 4.16 (4H, m), 3.28 (1H, m), 3.12 (1H, dd, *J* = 18.8, 2 Hz), 2.83 (1H, m), 2.67 (2H, m), 2.20 (1H, m), 1.33-1.17 (7H, m), 0.99 (3H, d, *J* = 6.8 Hz), 0.66 (3H, d, *J* = 7.2 Hz), 0.63 (2H, m), 0.24 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. IR: 2991, 2980, 2957, 1725, 1446, 1367, 1254, 1183, 1093, 1019, 912, 860, 804. MS (EI) *m/z* (rel. intensity): 91 (30), 131 (32), 159 (100), 173 (48), 232 (57), 306 (15). HRMS (CI): *calcd* for ($C_{18}H_{26}O_4$+Na): 329.17233, *found* 329.17264 (M+Na). Anal. *calcd.* for $C_{18}H_{26}O_4$: C 70.56, H 8.55, *found* C 70.62, H 8.39.



E = COOEt, *major isomer*

(*S,4*E*)-Diethyl 4-(4-methoxybenzylidene)-2,2-dimethyl-3-((*E*)-pent-1-enyl)cyclopentane-1,1-dicarboxylate**. Colorless oil (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (2H, d, *J* = 8.8 Hz), 6.79 (2H, d, *J* = 8.8 Hz), 6.03 (1H, d, *J* = 2.4 Hz), 5.51 (1H, m), 5.20 (1H, dd, *J* = 15.2, 8.8 Hz), 4.11 (4H, m), 3.73 (3H, s), 3.53 (1H, d, *J* = 8.8 Hz), 3.37 (1H, dt, *J* = 18.4, 2.8 Hz), 3.0 (1H, d, *J* = 18.4 Hz), 2.04 (2H, m), 1.39 (2H, m), 1.21 (9H, m), 0.88 (3H, t, *J* = 7.4 Hz), 0.72 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) 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. IR: 2986, 2960, 2954, 1726, 1608, 1510, 1464, 1366, 1246, 1176, 1095, 1073, 1035, 976, 845. MS (EI) *m/z* (rel. intensity): 121 (100), 265 (30), 281 (74), 339 (71), 413 (38), 428 (75). HRMS (CI): *calcd* for ($C_{26}H_{36}O_5$+Na): 451.24550, *found* 451.24620 (M+Na). Anal. *calcd.* for $C_{26}H_{36}O_5$: C 72.87, H 8.47, *found* C 72.98, H 8.41.

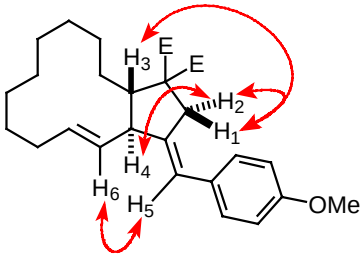


major isomer

4-Benzylidene-2-methyl-3-vinyl-tetrahydrofuran. Yellow oil (70%, *trans*: *cis* = 9.8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (2H, m), 7.21 (1H, t, *J* = 7.4 Hz), 7.15 (2H, d, *J* = 7.4 Hz), 6.18 (1H, dd, *J* = 5.1, 2.5 Hz), 5.65 (1H, ddd, *J* = 16.9, 10.1, 8.8 Hz), 5.28 (1H, dd, *J* = 10.1, 1.8 Hz), 5.24 (1H, dd, *J* = 16.9, 1.8 Hz), 4.84 (1H, br.d, *J* = 14.3 Hz), 4.61 (1H, td, *J* = 14.3, 2.5 Hz), 3.66 (1H,

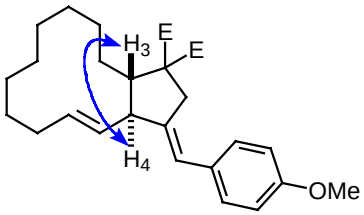
dq, J = 9.5, 6.0 Hz), 2.95 (1H, br.t, J = 9.0 Hz), 1.33 (3H, d, J = 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 137.2, 136.1, 128.5, 127.9, 126.6, 121.8, 119.0, 79.1, 70.2, 58.4, 18.3. IR: 2972, 2927, 2853, 1638, 1491, 1447, 1384, 1260, 1036, 916, 753, 692.

Assignment of the Stereochemistry of the Ring Junction – Representative Cases:



strong NOE

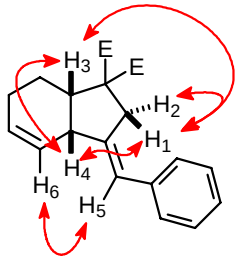
$J_{H3,H4}$ = 11.0 Hz



very feeble NOE

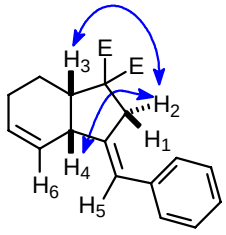
(the NOE between H_3/H_4 is < 7% of that observed between H_1/H_2)

CAVEAT: Even though the NOE between H_3 and H_4 is weak, it is observable in the NOESY spectrum. For the assignment of the stereochemistry it is therefore essential to make a *full* analysis of all NOE effects because the measurement of the NOE between the protons at the ring junction alone is potentially misleading. As indicated in the graphic, however, the other NOE's clearly show that compound **11b** is *trans*-annelated. This conclusion is consistent with the large coupling constant $^3J_{H3,H4}$ = 11.0 Hz between the pertinent protons.



strong NOE

$J_{H3,H4}$ = 8.1 Hz



very feeble NOE

< 7% of that observed between H_1/H_2

The intensity of the observed NOE's for compound **6** is significantly different and makes clear that this product must be *cis*-annelated, with the strong NOE's between H_3/H_4, H_1/H_3, and H_1/H_4 being particularly diagnostic. The notion, however, that a full analysis is necessary for an unambiguous assignment is again supported by the fact that weak effects are observed even for protons in a formal *trans* disposed. The *cis*-junction is consistent with the observed coupling constant of $^3J_{H3,H4}$ = 8.1 Hz.