SUPPORTING INFORMATION

Cyclobutenes by Platinum-Catalyzed Cycloisomerization Reactions of Enynes

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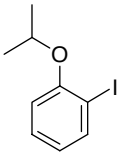
General: All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF, DMA (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Gallenkamp melting point apparatus (uncorrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 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). ***Where indicated, the signal assignments in the NMR spectra are unambiguous***; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for ^1J(C,H) = 145 Hz; HMBC (*inv4gslplrnd*) for correlations via ^nJ(C,H); HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

Starting Materials

Diethyl 2-allyl-2-(2-propynyl)malonate,[1] dimethyl 2-(2-cyclohexen-1-yl)-2-(2-propynyl)malonate,[2] 2-diethyl 2-(2-cyclohepten-1-yl)-2-(2-propynyl)malonate,[3] 4-methyl-*N*-(2-methyl-2-propenyl)-*N*-(2-propynyl)benzenesulfonamide[4] and diethyl 2-allyl-2-(3-phenyl-2-propynyl)malonate,[5] (**1a**) were prepared according to literature methods. Substrates for cycloisomerisation were then prepared via Sonogashira coupling with aryl iodides which were commercially available with the exception of 2-iodobenzofuran,[6] which was prepared according to literature, and iodo-2-isopropoxybenzene.

Iodo-2-isopropoxybenzene.



K_2CO_3 (5.47 g, 39.6 mmol) and isopropyliodide (2.00 g, 11.8 mmol) were added to a stirring solution of 2-iodophenol (1.99 g, 9.0 mmol) in DMF (18 mL) and the resulting suspension was heated to 45 °C and stirred for 12 h. The mixture was then diluted with water (200 mL) and extracted three times with Et_2O (200 mL portions). The combined organic extracts were washed three times with water (150 mL portions) before being dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford the pure iodide as a colorless oil (2.30 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 (m, 1H), 6.83 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.68 (m, 1H), 4.56 (sept, *J* = 6.4 Hz, 1H), 1.40 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.8, 139.6, 129.2, 122.5, 114.4, 88.6, 72.1, 22.1 (2C); IR (KAP): ν = 3060, 2977, 2932, 1581, 1470, 1438, 1384, 1373, 1273, 1245, 1125, 1105, 1017, 952; MS (EI): *m/z* (%): 262 (22) $[M]^+$; HR-MS (EI): *m/z:* calcd for $C_9H_{11}IO$: 261.9855, found 261.9854 $[M]^+$.

General Procedure for the Sonogashira Reaction of Enynes.

$PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%) were added to a solution of enyne (1eq.) and iodide (1.1 eq.) in triethylamine (0.1 M). The resulting mixture was stirred at 50 °C until the reaction was complete (GC/MS and TLC). On completion the mixture was allowed to cool to room temperature, MTBE or hexanes added and the mixture filtered. The solvent was removed under reduced pressure and the residue columned in MTBE/hexanes to afford the analytically

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1 Pagenkopf, B. L.; Livinghouse, T. *J. Am. Chem. Soc*. **1996**, *118*, 2285.

2 Trost, B. M.; Lautens, M. *J. Am. Chem. Soc*. **1985,** *107*, 1781.

3 Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996,** *15*, 901.

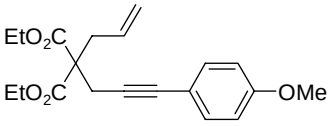
4 Kataoka, T.; Yoshimatsu, M.; Noda, Y.; Sato, T.; Shimuzu, H.; Hori, M. *J. Chem. Soc*. *Perkin Trans 1* **1993**, 121.

5 Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. M. *J. Am. Chem. Soc*., **1996**, *118*, 9450.

6 Zhang, H.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 5132.

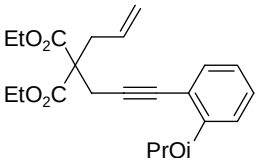
pure arylated enyne products. Colored products were further purified by bulb to bulb distillation under reduced pressure affording colorless oils.

Diethyl 2-allyl-2-[3-(4-methoxyphenyl)-2-propynyl]malonate, 1b



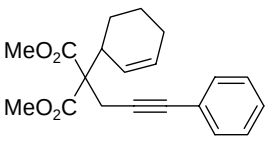
Colorless oil (0.67 g, 97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.70 (ddt, *J* = 17.1, 9.9, 7.5 Hz, 1H), 5.19 (m, 1H), 5.15 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.99 (s, 2H), 2.86 (d, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9 (2C), 159.3, 133.0 (2C), 132.0, 119.6, 115.4, 113.8 (2C), 83.3, 82.8, 61.6 (2C), 57.1, 55.3, 36.6, 23.6, 14.1 (2C); IR (KAP): ν = 3078, 2981, 2936, 2838, 1735, 1607, 1511, 1465, 1443, 1367, 1291, 1248, 1214, 1190, 1033; MS (EI): *m/z* (%): 344 (10) $[M]^+$, 299 (10), 271 (71), 197 (81), 145 (100); HR-MS (ESI+): *m/z*: calcd for $C_{20}H_{24}NaO_5$: 367.1521, found 367.1519 [*M+Na*].

Diethyl 2-allyl-2-[3-(2-isopropoxyphenyl)-2-propynyl]malonate, 4



Colorless oil (0.67 g, 84%), R_f = 0.30 (10% MTBE/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.20 (ddd, *J* =8.4, 7.4, 1.7 Hz, 1H), 6.84 (m, 2H), 5.72 (ddt, *J* = 17.0, 10.0, 7.5 Hz, 1H), 5.25 (m, 1H), 5.14 (m, 1H), 4.56 (sept, *J* = 6.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 4H), 3.06 (s, 2H), 2.94 (d, *J* = 7.5 Hz, 2H), 1.36 (d, *J* = 6.1 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9 (2C), 158.8, 133.7, 132.2, 129.0, 120.3, 119.6, 114.3, 114.3, 88.0, 80.2, 71.2, 61.5 (2C), 57.1, 36.5, 23.8, 22.1 (2C), 14.1 (2C); IR (neat): ν = 3077, 2980, 2935, 1736, 1594, 1489, 1446, 1385, 1368, 1288, 1262, 1216, 1189, 1123; MS (EI): *m/z* (%): 372 (11) $[M]^+$, 357 (28), 329 (17), 299 (83), 283 (22), 257 (52), 243 (29), 227 (29), 211 (49), 183 (100); HR-MS: *m/z* (EI): calcd for $C_{22}H_{28}O_5$: 372.1937, found 372.1940 $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{28}O_5$: C 70.94, H 7.58; found: C 70.85, H 7.54.

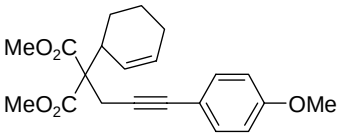
Dimethyl 2-(2-cyclohexen-1-yl)-2-(3-phenyl-2-propynyl)malonate, 6a



Colorless oil (682 mg, 95%); R_f = 0.38 (hexane/ethyl acetate, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (m, 2H), 7.26 (m, 3H), 5.77 (s, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 3.21 (m, 1H), 3.10 (AB, *J* = 17.3 Hz, 1H), 3.02 (AB, *J* = 17.3 Hz, 1H), 1.97 (m, 2H), 1.89 (m, 1H), 1.81 (m, 1H), 1.57 (m, 1H), 1.44 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5, 170.3, 131.6 (2C), 129.1, 128.2, 127.9 (2C), 127.6, 123.4, 85.2, 83.4, 60.9, 52.5, 52.4, 39.1, 24.9, 24.4, 23.3, 22.3; IR (KAP): ν = 3034, 2998, 2950, 2861, 2839, 1734, 1650, 1598, 1572, 1491, 1435, 1271, 1224, 1201, 1074, 758, 726, 692 cm^{-1}; MS (EI): *m/z* (%): 326 (27) $[M^+]$, 294 (16), 266 (100), 235 (19), 213 (44), 207 (97), 179 (43), 165 (19), 145 (21), 129 (10), 115 (65), 91 (33),

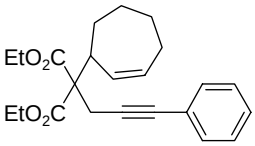
81 (32), 59 (10), 41 (8); HR-MS (EI): *m/z:* calcd for $C_{20}H_{22}O_4$: 326.1518, found 326.1522 $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{22}O_4$: C 73.60, H 6.79; found: C 73.56, H 6.85.

Dimethyl 2-(2-cyclohexen-1-yl)-2-[3-(4-methoxyphenyl)-2-propynyl]malonate, 6b



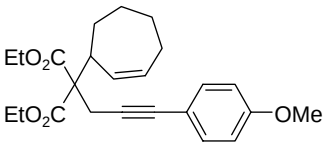
Colorless oil (0.52 g, 79%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (dt, *J* = 8.9, 2.1 Hz, 2H), 6.80 (dt, *J* = 8.9, 2.1 Hz, 2H), 5.77 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.20 (m, 1H), 3.08 (AB, d, *J* = 17.3 Hz, 1H), 3.00 (AB, d, *J* = 17.3 Hz, 1H), 1.97 (m, 2H), 1.85 (m, 2H), 1.58 (m, 1H), 1.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 170.3, 159.3, 132.9 (2C), 129.0, 127.6, 115.5, 113.8 (2C), 83.4, 83.1, 60.8, 55.2, 52.5, 52.3, 39.0, 24.9, 24.3, 23.3, 22.3; IR (neat): ν = 3036, 3000, 1950, 1838, 1733, 1607, 1510, 1435, 1290, 1247, 1224, 1200, 1181, 1032; MS (EI): *m/z* (%): 356 (100) $[M]^+$, HR-MS (ESI+): *m/z*: calcd for $C_{21}H_{24}NaO_5$: 379.1521, found 379.1517 [*M+Na*].

Diethyl 2-(2-cyclohepten-1-yl)-2-(3-phenyl-2-propynyl)malonate, 8a



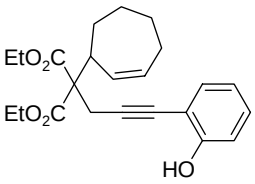
Colorless oil (194 mg, 96%); R_f = 0.40 (hexane/ethyl acetate, 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.36 (m, 2H), 7.27 (m, 3H), 5.83 (m, 2H), 4.23 (m, 4H), 3.29 (m, 1H), 3.07 (s, 2H), 2.24 (m, 2H), 2.01 (m, 2H), 1.71 (m, 2H), 1.30 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.1, 170.0, 133.0, 131.9, 131.5 (2C), 128.2 (2C), 127.8, 123.6, 85.5, 83.2, 61.5, 61.4, 60.7, 43.0, 31.6, 29.8, 28.0, 26.1, 24.1, 14.2, 14.1; IR (KAP): ν = 3078, 3022, 2980, 2925, 2851, 1730, 1648, 1598, 1571, 1491, 1443, 1273, 1221, 1192, 1098, 1046, 757, 692 cm^{-1}; MS (EI): *m/z* (%): 368 (15) $[M]^+$, 322 (8), 294 (44), 265 (16), 249 (12), 227 (24), 221 (100); HR-MS (ESI+): *m/z:* calcd for $C_{23}H_{28}NaO_4$: 391.1885, found 391.1886 [*M+Na*]; elemental analysis calcd (%) for $C_{23}H_{28}O_4$: C 74.97, H 7.66; found: C 74.88, H 7.49.

Diethyl 2-(2-cyclohepten-1-yl)-2-[3-(4-methoxyphenyl)-2-propynyl]malonate, 8b



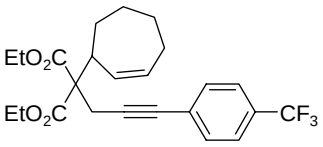
Colorless oil (0.17 g, 92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (m, 2H), 6.72 (m, 2H), 5.74 (m, 2H), 4.14 (m, 4H), 3.70 (s, 3H), 3.21 (m, 1H), 2.97 (s, 2H), 2.09 (m, 2H), 1.96 (m, 1H), 1.86 (m, 1H), 1.62 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.23 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.0 (2C), 159.2, 133.0 (2C), 132.8, 131.6, 115.8, 113.8 (2C), 83.8, 82.9, 61.3, 61.3, 60.7, 55.2, 43.0, 31.5, 29.8, 27.9, 26.1, 24.0, 14.1, 14.0; IR (neat): ν = 2930, 1725, 1606, 1509, 1444, 1244, 1181, 1030, 831; MS (EI): *m/z* (%): 398 (48) $[M]^+$, 324 (65), 251 (100); HR-MS (ESI+): *m/z*: calcd for $C_{24}H_{30}NaO_5$: 421.1991, found 421.1989 [*M+Na*].

Diethyl 2-(2-cyclohepten-1-yl)-2-[3-(2-hydroxyphenyl)-2-propynyl]malonate, 8c



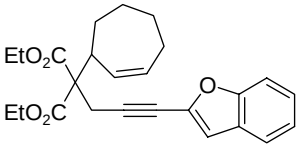
Light brown oil (0.21 g, 90%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (m, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.81 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 6.60 (s, 1H), 5.87 (m, 1H), 5.70 (dd, *J* = 11.0, 4.8 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.24 (m, 1H), 3.09 (A part of AB, *J* = 17.5 Hz, 1H), 3.03 (B part of AB, *J* = 17.5 Hz, 1H), 2.15 (m, 2H), 2.03 (m, 1H), 1.81 (m, 1H), 1.67 (m, 2H), 1.34 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 170.2, 157.9, 132.7, 132.3, 130.9, 129.9, 119.7, 114.8, 109.5, 92.3, 78.2, 61.8, 61.7, 61.1, 43.2, 31.6, 30.1, 27.9, 26.0, 25.0, 14.1, 14.0; IR (neat): ν = 3453, 2925, 1717, 1486, 1236, 1184, 1043, 1032; MS (EI): *m/z* (%): 384 (19) $[M]^+$, 310 (28), 237 (100); HR-MS (ESI+): *m/z*: calcd for $C_{23}H_{28}NaO_5$: 407.1834, found 407.1829 [*M+Na*].

Diethyl 2-(2-cyclohepten-1-yl)-2-{3-[4-(trifluoromethyl)phenyl]-2-propynyl}malonate, 8d



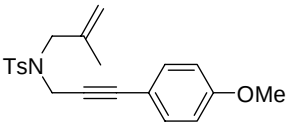
Colorless oil (0.44 g, 98%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 5.85 (m, 1H), 5.77 (dd, *J* = 11.1, 4.7 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 10.4, 3.7 Hz, 1H), 3.08 (s, 2H), 2.17 (m, 2H), 2.05 (m, 1H), 1.91 (m, 1H), 1.70 (m, 2H), 1.30 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 169.8, 132.7, 132.0, 131.7 (2C), 129.6 (q, *J* = 33 Hz), 127.3, 125.1 (q, *J* = 4 Hz, 2C), 124.0 (q, *J* = 272 Hz), 88.5, 82.0, 61.5 (2C), 60.7, 43.2, 31.5, 29.9, 28.0, 26.1, 24.0, 14.1 (2C); IR (kap): ν = 2982, 2928, 2852, 1732, 1616, 1446, 1404, 1325, 1372, 1331, 1186, 1167, 1128, 1105, 1068, 1047, 1018; MS (EI): *m/z* (%): 436 (7) $[M]^+$, 417 (8), 390 (11), 362 (68), 289 (100); HR-MS (ESI+): *m/z*: calcd for $C_{24}H_{27}F_3NaO_4$: 459.1759, found 459.1758 [*M+Na*].

Diethyl 2-[3-(1-benzofuran-2-yl)-2-propynyl]-2-(2-cyclohepten-1-yl)malonate, 8e



Colorless oil (0.27 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.7, 1.3 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.7, 1.0 Hz, 1H), 6.82 (s, 1H), 5.87 (m, 1H), 5.76 (dd, *J* = 11.3, 4.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 1H), 3.27 (m, 1H), 3.15 (s, 2H), 2.18 (m, 2H), 2.05 (m, 1H), 1.91 (m, 1H), 1.71 (m, 2H), 1.34 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8, 169.7, 154.6, 138.9, 132.5, 132.3, 127.7, 125.2, 123.1, 121.0, 111.1, 110.8, 92.3, 73.8, 61.6 (2C), 60.7, 43.3, 31.4, 29.9, 27.9, 26.0, 24.2, 13.1 (2C); IR (neat): ν = 2980, 2927, 2851, 1731, 1568, 1450, 1306, 1255, 1222, 1194, 1097, 1046; MS (EI): *m/z* (%): 408 (70) $[M]^+$, 334 (69), 261 (100); HR-MS (ESI+): *m/z*: calcd for $C_{25}H_{28}NaO_5$: 431.1834, found 431.1831 [*M+Na*]; elemental analysis calcd (%) for $C_{25}H_{28}O_5$: C 73.51, H 6.91; found: C 73.39, H 6.83.

_N_-[3-(4-methoxyphenyl)-2-propynyl]-4-methyl-_N_-(2-methyl-2-propenyl)benzene-sulfonamide, 12



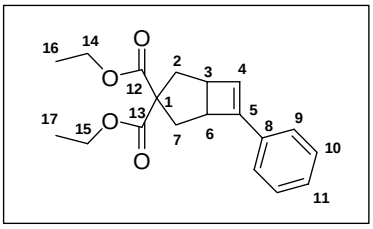
Oil (0.28 g, 93%), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.99 (dt, *J* = 8.9, 2.1 Hz, 2H), 6.76 (dd, *J* = 8.9, 2.1 Hz, 2H), 5.00 (d, *J* = 5.3 Hz, 2H), 4.24 (s, 2H), 3.79 (s, 3H), 3.79 (s, 2H), 2.35 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.6, 143.3, 139.4, 136. 2, 132.9 (2C), 129.4 (2C), 127.8 (2C), 115.4, 114.4, 113.7 (2C), 85.6, 80.2, 55.3, 52.7, 36.5, 21.4, 19.7; IR (neat): ν = 2971, 2916, 1606, 1510, 1442, 1348, 1292, 1248, 1162, 1097, 1032, 902; MS (EI): *m/z* (%): 369 (14) $[M]^+$, 354 (13), 214 (92), 145 (100); HR-MS (ESI+): *m/z*: calcd for $C_{21}H_{23}NaSO_3N$: 392.1296, found 392.1292 [*M+Na*].

Products

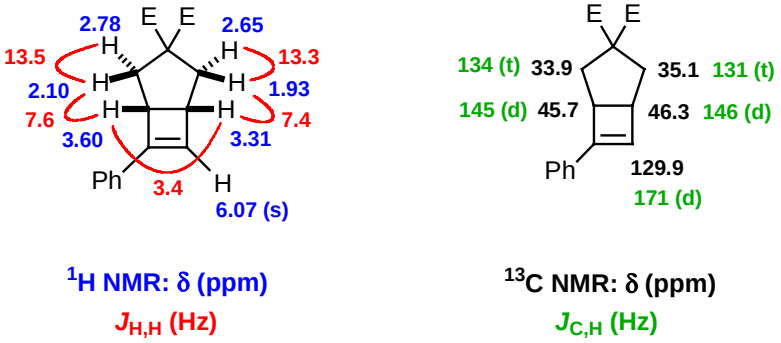
General Procedure for the $PtCl_2$-Catalyzed Cycloisomerization Reaction

$PtCl_2$ (10 mol-%) was added to a solution of the enyne in toluene (0.2 M), CO was bubbled through the solution for ca. 30 seconds and the resulting mixture was stirred at 80 °C under CO atmosphere until the reaction was complete (GC/MS and TLC). The solvent was evaporated and the residue purified by flash chromatography (hexane/ethyl acetate or pentane/diethyl ether mixture) to give the cyclobutene derivative in analytically pure form.

Diethyl 6-phenylbicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate, 2a

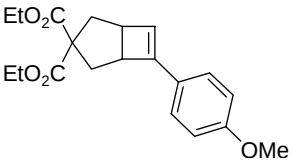


Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 3.3 Hz, 2H, H-9), 7.28 (d, *J* = 5.2 Hz, 2H, H-10), 7.21 (m, 1H, H-11), 6.07 (s, 1H, H-4), 4.12 (q, *J* = 7.0 Hz, 1H, H-14a), 4.12 (q, *J* = 7.0 Hz, 1H, H-14b), 3.87 (dq, *J* = 10.0, 7.0 Hz, 1H, H-15a), 3.60 (dd, *J* = 7.6, 3.6 Hz, 1H, H-6), 3.51 (dq, *J* = 10.0, 7.0 Hz, 1H, H-15b), 3.31 (dd, *J* = 3.4, 7.4 Hz, 1H, H-3), 2.78 (d, *J* = 13.5, 1H, H-7a), 2.65 (d, *J* = 13.3, 1H, H-2a), 2.10 (d, *J* = 13.5, 1H, H-7b), 1.93 (dd, *J* = 13.3, 7.4 Hz, 1H, H-2b), 1.19 (t, *J* = 7.3 Hz, 3H, H-16), 0.71 (t, *J* = 7.0 Hz, 3H, H-17); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3 (C-12), 171.5 (C-13), 146.6 (C-5), 133.5 (C-8), 129.9 (C-4), 128.3 (C-9), 127.7 (C-11), 124.6 (C-10), 61.6 (C-14), 61.2 (C-1), 61.0 (C-15), 45.7 (C-6), 43.6 (C-3), 35.1 (C-2), 33.9 (C-7), 14.0 (C-16), 13.2 (C-17); IR (neat): ν = 2980, 2935, 1730, 1448, 1299, 1262, 1243, 1187, 1085, 1055; MS (EI): *m/z* (%): 314 (14) $[M]^+$, 268 (18), 240 (18), 211 (26), 167 (100) ; HR-MS (ESI+): *m/z*: calcd for $C_{19}H_{22}NaO_4$: 337.1416, found 337.1415 [*M+Na*]; elemental analysis calcd (%) for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found: C 72.68, H 7.10.



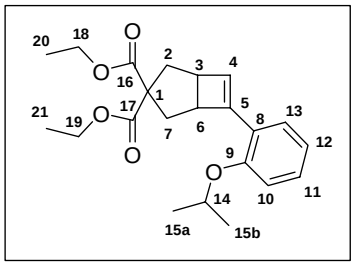
Scheme S-1. Graphical representation of the most relevant NMR data establishing the constitution of product **2a**; for a detailed discussion, see the closely related compound **5**.

Diethyl 6-(4-methoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate, 2b



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 1H), 3.93 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.80 (s, 3H), 3.59 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.58 (dd, *J* = 7.6, 3.6 Hz, 1H), 3.30 (dd, *J* = 3.4, 7.3 Hz, 1H), 2.78 (d, *J* = 13.4, 1H), 2.66 (d, *J* = 13.2, 1H), 2.01 (dd, *J* = 13.4, 7.6 Hz, 1H), 1.94 (dd, *J* = 13.2, 7.4 Hz, 1H), 1.21 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 171.4, 159.3, 146.2, 127.2, 126.7, 126.0 (2C), 113.7 (2C), 61.5, 61.2, 61.0, 55.3, 45.7, 43.5, 35.2, 33.9, 14.0, 13.4; IR (KAP): ν = 2981, 2937, 1841, 1777, 1729, 1601, 1513, 1464, 1445, 1367, 1255, 1180, 1097, 1031; MS (EI): *m/z* (%): 344 (67) $[M]^+$, 298 (30), 271 (33), 197 (100); HR-MS (EI): *m/z*: calcd for $C_{20}H_{24}O_5$: 344.1624, found 344.1626 $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{24}O_5$: C 69.75, H 7.02; found: C 69.67, H 6.94.

Diethyl 6-(2-isopropoxyphenyl)bicyclo[3.2.0]hept-6-ene-3,3-dicarboxylate, 5



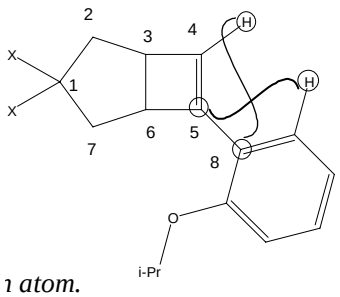
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (dd, *J* = 7.6, 1.7 Hz, 1H, H-13), 7.15 (td, *J* = 8.2, 1.7 Hz, 1H, H-11), 6.85 (t, *J* = 7.7 Hz, 1H, H-12), 6.82 (d, *J* = 8.3 Hz, 1H, H-10), 6.14 (s, 1H, H-4), 4.59 (sept, *J* = 6.2 Hz, 1H, H-14), 4.13 (q, *J* = 7.2 Hz, 2H, H-18), 3.89 (q, *J* = 7.1 Hz, 1H, H-19a), 3.65 (td, *J* = 7.0, 7.5 Hz, 1H, H-6), 3.60 (q, *J* = 7.1 Hz, 1H, H-19b), 3.33 (dd, *J* = 7.4, 3.4 Hz, 1H, H-3), 2.83 (d, *J* = 13.4 Hz, 1H, H-7a), 2.66 (d, *J* = 13.1 Hz, 1H, H-2a), 2.00 (dd, *J* = 13.4, 7.6 Hz, 1H, H-7b), 1.95 (dd, *J* = 13.6, 7.5 Hz, 1H, H-2b), 1.36 (d, *J* = 6.2 Hz, 6H, H-15ab), 1.21 (t, *J* = 7.1 Hz, 3H, H-20), 0.75 (t, *J* = 7.1 Hz, 3H, H-21); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.5 (C-16), 171.4 (C-17), 156.8 (C-9), 143.6 (C-5), 134.1 (C-4), 128.4 (C-11), 127.3 (C-13), 122.8 (C-8), 119.6 (C-12), 112.0 (C-10), 69.4 (C-14), 61.5 (C-18), 61.1 (C-1), 60.8 (C-19), 46.8 (C-6), 44.5 (C-3), 35.4 (C-2), 34.3 (C-7), 22.2 (C-15a), 22.2 (C-15b), 14.0 (C-20), 13.2 (C-21); IR (KAP): ν = 2978,

2936, 1731, 1597, 1488, 1447, 1385, 1368, 1243, 1193, 1124, 1078, 1054; MS (EI): *m/z* (%): 372 (46) $[M]^+$, 329 (29), 283 (33), 255 (80), 183 (100); HR-MS (ESI+): *m/z*: calcd for $C_{22}H_{28}NaO_5$: 395.1824, found 395.1833 [*M+Na*]; elemental analysis calcd (%) for $C_{22}H_{28}O_5$: C 70.94, H 7.58; found: C 71.05, H 7.54.

Comments on structure analysis:

1. *The COSY spectrum together with the HMQC spectrum reveals the presence of a CH_2-CH-CH-CH_2 chain (i.e., C-2,C-3,C-6,C-7). It rules out that the double bond could be between C-5 and C-6, or between C-3 and C-4, or C-3 and C-6, or C-6 and C-7.*

2. *While the presence of a CH_2-CH-CH-CH_2 chain could be reconciled with a C2-C-3 double bond (i.e., the CH_2-CH-CH-CH_2 chain is C-4,C-5,C-6,C-7), this is inconsistent with the observation of a strong cross peak in the HMBC spectrum [due to long range $J(^{13}C,^1H)$ coupling] between the olefinic carbon and H-13 in the aromatic group and a weaker one between C-8 (Ar, C-ipso) and the olefinic H.*



   It follows that the aromatic group is bonded to an olefinic carbon atom.

   The assigned structure is fully consistent with the cross peaks observed in the HMBC spectrum.

3. *If the double bond were located elsewhere in the bicycloheptene framework, either C-3 or C-6 would have no directly bonded proton. However, clearly, both C3 and C-6 are* ***methine*** *carbons.*

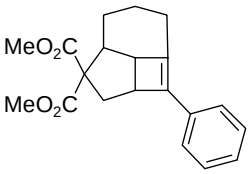
   The magnitudes of the $^1J(^{13}C,^1H)$ coupling constants remove any possible remaining doubt. While the $^{13}C,^1H$ coupling constants for C-2 and C-7 in the cyclopentane ring fall in the range of 131-134 Hz, they are, as expected, larger for the ring junction carbon atoms C-3 and C-6 (145-146 Hz).

4. *Analysis of the proton NMR spectra provides further convincing support for this structure assignment. The "parent" compound with H on C-5 instead of the aromatic residue has a plane of symmetry. The presence of the C-5-aryl group lifts this symmetry, but the chemical shifts of H-2' and H-7' are very similar, as are those of H-2″and H-7″, and those of H-3 and H-6.*

   Furthermore, the $^1H,^1H$ coupling constants between H-2', H-2″and H-3 are very similar to the corresponding couplings between H-7', H-7″and H-6.

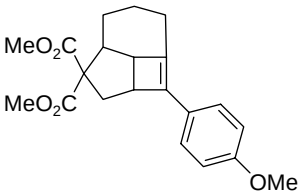
The essential features of the spectra remain unaltered by introduction of the -$(CH_2)_4$- chain spanning C-2 and C-4 as present in the following compounds:

Dimethyl 1-phenyl-1a,3a,4,5,6,6b-hexahydrocyclobuta[*cd*]indene-3,3(2*H*)-dicarboxylate dimethyl ester, 7a



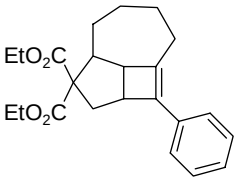
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (m, 3H), 7.23 (m, 2H), 3.73 (s, 3H), 3.57 (s, 3H), 3.37 (m, 1H), 3.20 (m, 1H), 2.83 (m, 1H), 2.62 (m, 1H), 2.49 (dd, *J* = 14.2, 4.8 Hz, 1H), 2.42 (m, 1H), 2.28 (dd, *J* = 14.2, 7.8 Hz, 1H), 1.55 (m, 3H), 1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 170.7, 142.8, 141.9, 134.8, 128.4 (2C), 127.3, 125.4 (2C), 68.8, 52.7, 52.1, 46.3, 42.6, 41.1, 34.1, 25.9, 23.6, 21.6; IR (KAP): ν = 3057, 3026, 2951, 2862, 1733, 1653, 1598, 1581, 1493, 1448, 1434, 1255, 1206, 1162, 1063, 765, 753, 737, 698 cm^{-1}; MS (EI): *m/z* (%): 326 (100) [*M*]$^{+}$, 311 (4), 295 (14), 266 (60), 235 (17), 207 (70), 179 (35), 165 (31), 145 (63), 128 (19), 115 (33), 91 (39), 77 (18), 65 (8), 59 (19), 39 (5); HR-MS (ESI+): *m/z:* calcd for $C_{20}H_{22}NaO_4$: 349.1416, found 349.1418 [*M+Na*]; elemental analysis calcd (%) for $C_{20}H_{22}O_4$: C 73.60, H 6.79; found: C 73.49, H 6.74.

Dimethyl 1-(4-methoxyphenyl)-1a,3a,4,5,6,6b-hexahydrocyclobuta[*cd*]indene-3,3(2*H*)-dicarboxylate, 7b



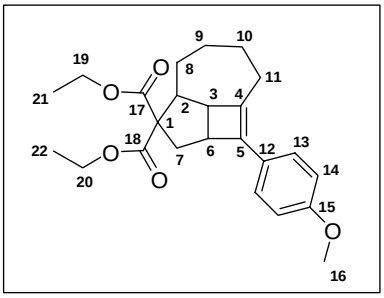
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.74 (s, 3H), 3.59 (s, 3H), 3.34 (m, 1H), 3.18 (m, 1H), 2.83 (m, 1H), 2.53 (m, 1H), 2.47 (dd, *J* = 14.1, 4.8 Hz, 1H), 2.39 (m, 1H), 2.26 (dd, *J* = 14.1, 7.7 Hz, 1H), 1.53 (m, 3H), 1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.2, 170.7, 158.5, 141.3, 139.5, 127.9, 126.6 (2C), 113.9 (2C), 68.7, 55.2, 52.6, 52.0, 46.1, 42.6, 41.1, 34.1, 25.8, 23.6, 21.5; IR (KAP): ν = 2952, 1733, 1604, 1511, 1435, 1249, 1175, 1032; MS (EI): *m/z* (%): 356 (100) [*M*]$^{+}$; HR-MS (ESI+): *m/z*: calcd for $C_{21}H_{24}NaO_5$: 379.1521, found 379.1516 [*M+Na*].

1-Phenyl-1a,2,3a,4,5,6,7,7b-octahydro-cyclobuta[*cd*]azulene-3,3-dicarboxylic acid diethyl ester, 9a



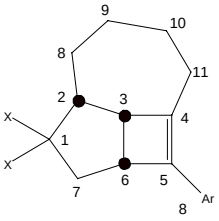
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (m, 4H), 7.19 (m, 1H), 4.15 (m, 4H), 3.52 (m, 1H), 3.24 (m, 1H), 2.83 (m, 2H), 2.38 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.29 (ddd, *J* = 13.8, 8.1, 0.9 Hz, 1H), 2.20 (m, 1H), 1.82 (m, 2H), 1.51 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 169.7, 145.4, 140.3, 135.0, 128.5 (2C), 126.7, 125.7 (2C), 71.5, 61.3, 60.9, 49.8, 42.5, 40.9, 32.2, 29.6, 28.6, 27.6, 27.5, 14.1 (2C); IR (KAP): ν = 3080, 3055, 3023, 2979, 2928, 2854, 1731, 1653, 1597, 1573, 1494, 1446, 1366, 1295, 1249, 1177, 1126, 1059, 767, 695 cm^{-1}; MS (EI): *m/z* (%): 368 (64) [*M*]$^{+}$, 322 (31), 294 (100), 249 (20), 221 (81), 194 (42), 179 (25), 173 (25), 165 (21), 141 (10), 127 (14), 115 (18), 91 (24), 77 (6), 55 (3), 41 (3); HR-MS (ESI+): *m/z:* calcd for $C_{23}H_{28}NaO_4$: 391.1885, found 391.1887 [*M+Na*]; elemental analysis calcd (%) for $C_{23}H_{28}O_4$: C 74.97, H 7.66; found: C 74.86, H 7.66.

Diethyl 1-(4-methoxyphenyl)-1a,2,3a,4,5,6,7,7b-octahydro-3*H*-cyclobuta[*cd*]azulene-3,3-dicarboxylate, 9b



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.8, 2H, H-13), 6.85 (d, *J* = 8.9 Hz, 2H, H-14), 4.18 (m, 2H, H-19), 4.07 (m, 2H, H-20), 3.78 (s, 3H, H-16), 3.48 (m, 1H, H-3), 3.17 (m, 1H, H-6), 2.70 (m, 1H, H-2), 2.62 (m, 1H, H-11a), 2.31 (dd, *J* = 13.8, 7.3 Hz, 1H, H-7a), 2.26 (ddd, *J* = 13.8, 8.0, 0.6 Hz, 1H, H-7b), 2.17 (m, 1H, H-11b), 1.80 (m, 2H, H-10), 1.53 (m, 2H, H-9), 1.43 (m, 2H, H-8), 1.24 (t, *J* = 7.1 Hz, 3H, H-21), 1.17 (t, *J* = 7.1 Hz, 3H, H-22); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4 (C17), 169.7 (C18), 158.5 (C15), 142.4 (C4), 139.8 (C5), 128.1 (C12), 126.9 (C13), 114.0 (C14), 71.5 (C1), 61.2 (C19), 60.9 (C20), 55.3 (C16), 49.6 (C3), 42.6 (C2), 40.8 (C6), 32.1 (C7), 29.4 (C11), 28.6 (C8), 27.6 (C10), 27.5 (C9), 14.1 (C21), 14.1 (C22); IR (KAP): ν = 2979, 2935, 1729, 1602, 1512, 1251, 1178, 1030; MS (EI): *m/z* (%): 398 (93) $[M]^+$, 353 (12), 324 (36), 251 (62), 173 (100); HR-MS (ESI+): *m/z*: calcd for $C_{24}H_{30}NaO_5$: 421.1991, found 421.1989 [*M+Na*]; elemental analysis calcd (%) for $C_{24}H_{30}O_5$: C 73.51, H 6.91; found: C 72.94, H 6.79.

Comments on structure analysis:



*It can safely be assumed that the protons on the ring junction carbons (i.e., H-3 and H-6) are **cis**.*

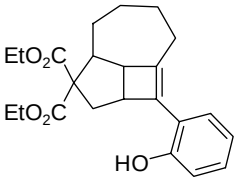
In the cyclopentane ring the magnitudes of the vicinal coupling constants between cis and trans protons are similar. Thus the relative configuration of C-2 cannot be unambiguously determined from the coupling constant ^{3}J(H-2,H-3) = 8.1 Hz) and is therefore based on NOE data.

In the 1D proton NMR spectrum, H-2 and one of the signals from the methylene chain (H-11a) are not resolved. However, in the 2D NOESY spectrum they are resolved just enough to show that there is no significant contribution to the intensity of the NOE cross peak between H-3 and H-2 from NOE between H-3 and the methylene proton H-11a .

Volume integrals of the cross peaks indicate that the cross peaks between H-2 and H-3 (relative intensity scaled to 100%) are more intensive than those between H-3 and H-6 (intensity ca. 70%). Since H-3 and H-6 must be cis, then H-2 and H-3 must also be cis.

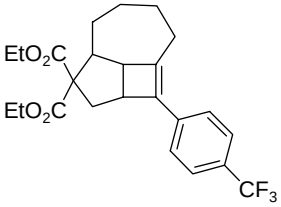
Because of the extensive signal overlap and strong second order character, the protons in the C-8—C-11 methylene chain provided no reliable NOE data that might have supported this structure assignment.

Diethyl 1-(2-hydroxyphenyl)-1a,2,3a,4,5,6,7,7b-octahydro-3*H*-cyclobuta[*cd*]azulene-3,3-dicarboxylate, 9c



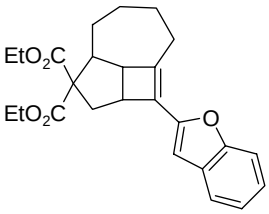
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (m, 2H), 6.87 (m, 2H), 5.67 (s, 1H), 4.26-4.04 (m, 4H), 3.49 (m, 1H), 3.36 (m, 1H), 2.80 (m, 1H), 2.56 (m, 1H), 2.49 (dd, *J* = 14.0, 5.7 Hz, 1H), 2.17 (m, 2H), 1.73 (m, 2H), 1.58 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 171.1, 152.9, 146.6, 134.4, 128.5, 127.9, 122.5, 120.4, 116.2, 69.5, 61.3, 61.2, 50.2, 43.3, 42.9, 33.4, 30.0, 29.1, 27.8, 27.0, 14.0, 14.0; IR (neat): ν = 3444, 2979, 2928, 2711, 1447, 1246, 1177, 1094, 1051, 1013; MS (EI): *m/z* (%): 384 (72) $[M]^+$, 310 (57), 237 (100); HR-MS (ESI+): *m/z*: calcd for $C_{23}H_{28}NaO_5$: 407.1834, found 407.1836 [*M+Na*].

Diethyl 1-[4-(trifluoromethyl)phenyl]-1a,2,3a,4,5,6,7,7b-octahydro-3*H*-cyclobuta[*cd*]-azulene-3,3-dicarboxylate, 9d



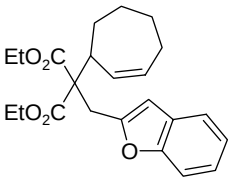
A mixture of two compounds as a colorless oil. Separation by preparative HPLC afforded the title compound; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.1, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.30-4.00 (m, 4H), 3.54 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.26 (m, 1H), 2.76 (m, 2H), 2.31 (m, 3H), 1.81 (m, 2H), 1.53 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2, 169.6, 148.9, 145.7, 136.8, 125.7 (2C), (3 carbon signals are not detected), 125.4 (q, J_{CF}=3.7 Hz, 2C), 71.1, 61.4, 61.0, 50.1, 42.4, 40.9, 32.1, 29.7, 28.5, 27.3, 27.3, 14.1, 14.0; IR (neat): ν = 2931, 1730, 1614, 1324, 1250, 1164, 1123, 1064; MS (EI): *m/z* (%): 436 (37) $[M]^+$, 417 (11), 390 (89), 362 (61), 289 (67), 262 (100); HR-MS (ESI+): *m/z*: calcd for $C_{24}H_{27}F_3NaO_4$: 459.1759, found 459.1756 [*M+Na*].

Diethyl 1-(1-benzofuran-2-yl)-1a,2,3a,4,5,6,7,7b-octahydro-3*H*-cyclobuta[*cd*]azulene-3,3-dicarboxylate, 9e



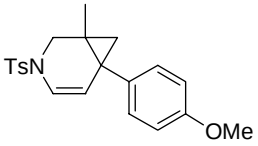
White solid, mp = 93-95 °C (Et_2O/pentane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.0, 1H), 7.38 (d, *J* = 8.0, 1H), 7.17 (m, 2H), 6.41 (s, 1H), 3.98-4.24 (m, 4H), 3.57 (dd, *J* = 8.1, 4.8 Hz, 1H), 3.23 (m, 1H), 2.90 (m, 1H), 2.74 (m, 1H), 2.41 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.24 (ddd, *J* = 13.9, 8.1, 0.6 Hz, 1H), 2.14 (m, 1H), 1.82 (m, 2H), 1.49 (m, 2H), 1.43 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 169.5, 154.9, 152.4, 148.0, 131.4, 128.7, 124.0, 122.7, 120.7, 111.0, 102.1, 71.4, 61.3, 61.0, 51.5, 42.8, 40.7, 32.2, 30.0, 29.3, 28.6, 27.3, 14.1, 14.0; IR (neat): ν = 2979, 2929, 2855, 1731, 1671, 1450, 1366, 1298, 1252, 1177, 1125, 1108, 1058, 1017; MS (EI): *m/z* (%): 408 (100) $[M]^+$; HR-MS (ESI+): *m/z*: calcd for $C_{25}H_{28}NaO_5$: 431.1834, found 431.1833 [*M+Na*].

Diethyl 2-(1-benzofuran-2-ylmethyl)-2-(2-cyclohepten-1-yl)malonate, 10



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.18 (m, 2H), 6.47 (s, 1H), 5.83 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 1H), 3.48 (A part of AB, *J* = 15.2, 1H), 3.41 (B part of AB, *J* = 15.2, 1H), 3.05 (dd, *J* = 10.2, 3.6 Hz, 1H), 2.13 (m, 2H), 2.00 (m, 1H), 1.86 (m, 1H), 1.66 (m, 2H), 1.23 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.3 (2C), 154.6, 154.1, 133.2, 131.7, 128.7, 123.5, 122.4, 120.5, 110.8, 105.5, 61.3, 61.3, 61.2, 43.1, 32.6, 31.6, 30.0, 27.9, 26.0, 14.0, 13.9; IR (neat): ν = 2980, 2925, 2852, 1725, 1453, 1249, 1214, 1191, 1164, 1041; MS (EI): *m/z* (%): 384 (7) $[M]^+$, 289 (20), 243 (100); HR-MS (ESI+): *m/z*: calcd for $C_{23}H_{28}NaO_5$: 407.1834, found 407.1831 [*M+Na*].

6-(4-methoxyphenyl)-1-methyl-3-[(4-methylphenyl)sulfonyl]-3-azabicyclo[4.1.0]hept-4-ene, 13



White solid; mp = 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3, 2H), 7.35 (m, 2H), 7.05 (m, 2H), 6.80 (m, 2H), 6.37 (d, *J* = 8.0, 1.0 Hz, 1H), 5.32 (d, *J* = 8.0 Hz, 1H), 3.92 (dd, *J* = 11.5, 0.8 Hz, 1H), 3.78 (s, 3H), 2.78 (d, *J* = 11.5 Hz, 1H), 2.45 (s, 3H), 1.14 (dd, *J* = 4.8, 0.8 Hz, 1H), 1.00 (d, *J* = 4.8 Hz, 1H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.2, 143.7, 135.2, 133.4, 130.1 (2C), 129.8 (2C), 127.1 (2C), 120.3, 117.7, 113.5 (2C), 55.2, 46.5, 32.4, 27.6, 23.7, 21.6, 18.9; IR (neat): ν = 2956, 2929, 1636, 1514, 1440, 1351, 1276, 1240, 1166, 1090, 1030, 1020, 1006, 994, 963; MS (EI): *m/z* (%): 369 (27) $[M]^+$, 338 (27), 214 (100); HR-MS (ESI+): *m/z*: calcd for $C_{21}H_{23}NaSO_3N$: 392.1296, found 392.1297 [*M+Na*].