Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information-I

Rapid Two-step Synthesis of Drug-like Polycyclic Substances by Sequential Multi-catalysis Cascade Reactions

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or in I_2 vapours and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received.

General Experimental Procedures for the Multi-catalysis Reactions:

Amino acid-/Self-/K_2CO_3-Catalyzed Cascade Three-component Reductive Alkylation (TCRA)/C-Allylation (C-A) Reactions: **Method-A:** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the 2-ethynyl-benzaldehyde **1a** and 0.3 mmol of CH-acid **2** was added 1.2 mL of solvent, and then the catalyst L-proline (0.06 mmol, 20 mol-%, 6.9 mg) was added and the reaction mixture was stirred at 25 °C for 3 to 16 h, then o-phenylenediamine (0.3 mmol) and benzaldehyde (0.3 mmol) was added and stirred for the 3 to 16 h. To the crude

reaction mixture was added 5 equivalents of allyl bromide (1.5 mmol, 180 mg) and 8 equivalents of K_2CO_3 (2.4 mmol, 331 mg) and the reaction mixture was stirred at 25 °C for 0.25 to 12 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure TCRA/*C*-A products **6** were obtained by column chromatography (silica gel, mixture of hexane/ ethylacetate).

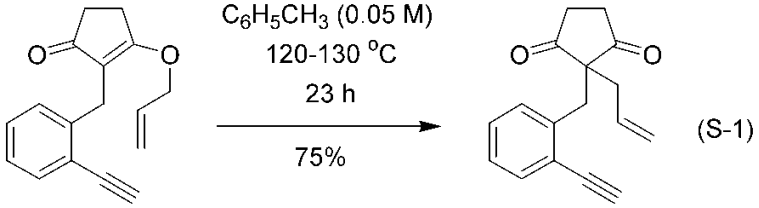
Amino acid-/Self-/K_2CO_3-Catalyzed Cascade Three-component Reductive Alkylation (TCRA)/C-Allylation (C-A) Reactions: **Method-B:** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the 2-ethynyl-benzaldehyde **1a**, 0.3 mmol of CH-acid **2** and 0.3 mmol of Hantzsch ester **3a** was added 1.2 mL of solvent, and then the catalyst L-proline (0.06 mmol, 20 mol-%, 6.9 mg) was added and the reaction mixture was stirred at 25 °C for the 0.75 to 24 h. To the crude reaction mixture was added 5 equivalents of allyl bromide (1.5 mmol, 180 mg) and 8 equivalents of K_2CO_3 (2.4 mmol, 331 mg) and the reaction mixture was stirred at 25 °C for 0.25 to 1 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure TCRA/*C*-A products **6** were obtained by column chromatography (silica gel, mixture of hexane/ ethylacetate).

Amino acid-/Self-/Self-/Self-/Self-/K_2CO_3-Catalyzed Cascade TCRA/A/K/E/C-A Reactions in One-Pot: **Method-C:** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the 2-ethynyl-benzaldehyde **1a**, 0.3 mmol of Meldrum's acid **2h** and 0.3 mmol of Hantzsch ester **3a** was added 1.2 mL of solvent (R-OH), and then the catalyst L-proline (0.06 mmol, 20 mol-%, 6.9 mg) was added and the reaction mixture was stirred at 25 °C for the 1 h. To the crude reaction mixture added 15 equivalents of an ethereal solution of diazomethane and the reaction mixture was stirred at room temperature for the time indicated in Table 3. After evaporation of the solvent and excess diazomethane completely in fume hood, DMSO (1.2 mL) was added to the crude reaction mixture followed by 5 equivalents of allyl bromide (1.5 mmol, 180 mg) and 6 equivalents of K_2CO_3 (1.8 mmol, 248 mg) and the reaction mixture was stirred at 25 °C for 12 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure TCRA/A/K/E/*C*-A products **7** were obtained by column chromatography (silica gel, mixture of hexane/ ethylacetate).

Experimental Procedure for the High-yielding Synthesis of Functionalized Carbocycles 8 and 9 via Enyne-RCM Reactions: A 10 mL oven-dried round bottom flask equipped with a stir bar was charged with enyne **6** or **7** (0.1 mmol), CH_2Cl_2 (2 ml, 0.05 M) and first generation Grubb's catalyst (4.11 mg, 0.005 mmol, 5 mol-%). The reaction mixture was stirred under N_2 at 40-45 °C for 4 to 24 h. Solvent CH_2Cl_2 were distilled off at ambient pressure and the enyne-RCM products **8** and **9** were purified by column chromatography (silica gel, mixture of hexane/ethyl acetate).

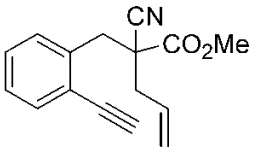
Experimental Procedure for the Cascade Synthesis of Functionalized Carbocycles 11 and 12 via Enyne-RCM/Diels-Alder Reactions: A 10 mL oven-dried round bottom flask equipped with a stir bar was charged with enyne **6** or **7** (0.1 mmol), CH_2Cl_2 (2 ml, 0.05 M) and first generation Grubb's catalyst (4.11 mg, 0.005 mmol, 5 mol-%). The reaction mixture was stirred under N_2 at 40-45 °C for 4 to 24 h. Solvent CH_2Cl_2 were distilled off at

ambient pressure and to the crude reaction mixture, *N*-phenylmaleimide **10a** (207.8 mg, 0.12 mmol, 1.2 equiv.) or diethyl acetylenedicarboxylate **10b** (0.12 mmol, 1.2 equiv) and anhydrous toluene (2 mL) were added and heated at 110-120 °C under N_2 in a sealed glass tube for 13 to 21 h. The toluene was removed and the residue was purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to gave **11** and **12** respectively (see Table 4).



13al **6al** (S-1)

2-Cyano-2-(2-ethynyl-benzyl)-pent-4-enoic acid ethyl ester (6aa): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3271, 2985, 1740 (O-C=O), 1480, 1444, 1369, 1330, 1291, 1226, 1144, 1103, 1048, 997, 932, 860, 763, 660 and 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.52 (1H, d, *J* = 7.6 Hz), 7.40 (1H, d, *J* = 7.6 Hz), 7.33 (1H, br t, *J* = 7.6 Hz), 7.26 (1H, br t, *J* = 7.6 Hz) [Ar-*H*]; 5.87-5.81 (1H, m, CH_2CH=CH_2), 5.29-5.23 (2H, m, CH_2CH=CH_2), 4.21 (2H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.50 (1H, d, *J* = 14.0 Hz), 3.39 (1H, d, *J* = 14.0 Hz), 3.31 (1H, s, Ar-C≡C-*H*), 2.84 (1H, dd, *J* = 14.0, 7.6 Hz, CH_2CH=CH_2), 2.55 (1H, dd, *J* = 14.0, 7.2 Hz, CH_2CH=CH_2), 1.22 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ: 168.0 (C, O-*C*=O), 136.6 (C), 133.3 (CH), 130.8 (CH), 129.9 (CH), 129.0 (CH), 127.7 (CH), 123.2 (C), 120.9 (CH_2, CH_2CH=CH_2), 118.4 (C, *C*N), 82.0 (CH, Ar-C≡*C*-H), 81.9 (C, Ar-*C*≡C-H), 62.9 (CH_2, $CO_2CH_2CH_3$), 50.6 (C), 40.8 (CH_2), 39.6 (CH_2, CH_2CH=CH_2), 13.9 (CH_3, $CO_2CH_2CH_3$).; LRMS m/z 268.15 (M + 1), calcd for $C_{17}H_{17}NO_2$ 267.1259; Anal. calcd. for $C_{17}H_{17}NO_2$ (267.1259): C, 76.38; H, 6.41; N, 5.24, found C, 76.21; H, 6.44; N, 5.35%.

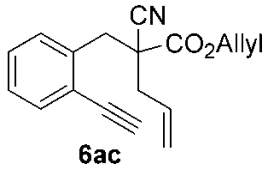


6aa

2-Cyano-2-(2-ethynyl-benzyl)-pent-4-enoic acid methyl ester (6ab): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3272, 2956, 1745 (O-C=O), 1644, 1481, 1440, 1332, 1276, 1236, 1143, 1106, 1050, 993, 931, 763, 665, 656 and 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.52 (1H, d, *J* = 7.2 Hz), 7.38-7.25 (3H, m) [Ar-*H*]; 5.88-5.77 (1H, m, CH_2CH=CH_2), 5.29-5.23 (2H, m, CH_2CH=CH_2), 3.75 (3H, s, CO_2CH_3), 3.50 (1H, d, *J* = 13.6

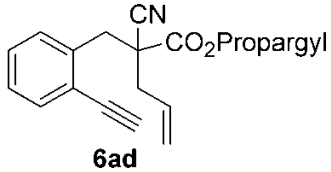
6ab

Hz), 3.39 (1H, d, *J* = 14.0 Hz), 3.31 (1H, s, Ar-C≡C-*H*), 2.83 (1H, dd, *J* = 14.0, 7.6 Hz, C*H*$_2$CH=CH$_2$), 2.55 (1H, dd, *J* = 14.0, 7.2 Hz, C*H*$_2$CH=CH$_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ: 168.5 (C, O-*C*=O), 136.4 (C), 133.2 (CH), 130.7 (CH), 129.9 (CH), 129.0 (CH), 127.7 (CH), 123.1 (C), 121.0 (CH_2, CH_2CH=*C*H_2), 118.2 (C, *C*N), 81.9 (CH, Ar-C≡*C*-H), 81.8 (C, Ar-*C*≡C-H), 53.3 (CH_3, CO_2CH_3), 50.6 (C), 40.7 (CH_2), 39.6 (CH_2, *C*H_2CH=CH_2).; LRMS m/z 254.10 (M^+ + 1), calcd for $C_{16}H_{15}NO_2$ 253.1103; Anal. calcd. for $C_{16}H_{15}NO_2$ (253.1103): C, 75.87; H, 5.97; N, 5.53, found C, 75.81; H, 6.03; N, 5.61%.



6ac

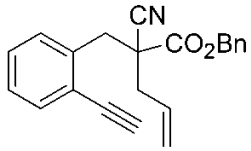
2-Cyano-2-(2-ethynyl-benzyl)-pent-4-enoic acid allyl ester (6ac): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3285, 1744 (O-C=O), 1645, 1483, 1444, 1365 1272, 1215, 1143, 1107, 994, 933, 763, 660 and 603 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.52 (1H, dd, *J* = 8.0, 1.2 Hz), 7.40 (1H, br d, *J* = 7.6 Hz), 7.33 (1H, dt, *J* = 8.0, 1.6 Hz), 7.26 (1H, dt, *J* = 8.0, 1.6 Hz) [Ar-*H*]; 5.89-5.78 (2H, m, CH_2C*H*=CH_2, CO_2CH_2C*H*=CH_2), 5.33-5.22 (4H, m, CH_2CH=C*H*$_2$, CO_2CH_2CH=C*H*$_2$), 4.64 (2H, d, *J* = 6.0 Hz, CO_2C*H*$_2$CH=CH_2), 3.52 (1H, d, *J* = 13.6 Hz), 3.41 (1H, d, *J* = 14.0 Hz), 3.31 (1H, s, Ar-C≡C-*H*), 2.85 (1H, dd, *J* = 14.0, 7.6 Hz, C*H*$_2$CH=CH_2), 2.56 (1H, dd, *J* = 14.0, 7.2 Hz, C*H*$_2$CH=CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ: 167.8 (C, O-*C*=O), 136.5 (C), 133.3 (CH), 130.74 (CH), 130.67 (CH), 130.0 (CH), 129.1 (CH), 127.8 (CH), 123.2 (C), 121.1 (CH_2, CH_2CH=*C*H_2), 119.4 (CH_2, CO_2CH_2CH=*C*H_2), 118.2 (C, *C*N), 82.0 (CH, Ar-C≡*C*-H), 81.9 (C, Ar-*C*≡C-H), 67.1 (CH_2, CO_2*C*H_2CH=CH_2), 50.7 (C), 40.8 (CH_2), 39.7 (CH_2, *C*H_2CH=CH_2).; LRMS m/z 280.0 (M^+ + 1), calcd for $C_{18}H_{17}NO_2$ 279.1259; Anal. calcd. for $C_{18}H_{17}NO_2$ (279.1259): C, 77.40; H, 6.13; N, 5.01, found C, 77.51; H, 6.10; N, 5.08%.



6ad

2-Cyano-2-(2-ethynyl-benzyl)-pent-4-enoic acid prop-2-ynyl ester (6ad): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3291, 1751 (O-C=O), 1645, 1483, 1442, 1370, 1272, 1204, 1140, 1106, 1045, 996, 930, 764, 678 and 649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.53 (1H, d, *J* = 7.4 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.34 (1H, br t, *J* = 7.6 Hz), 7.28 (1H, br t, *J* = 8.0 Hz) [Ar-*H*]; 5.90-5.79 (1H, m, CH_2C*H*=CH_2), 5.30-5.25 (2H, m, CH_2CH=C*H*$_2$), 4.75 (2H, d, *J* = 2.2 Hz, CO_2C*H*$_2$C≡C-H), 3.53 (1H, d, *J* = 13.9 Hz), 3.42 (1H, d, *J* = 13.9 Hz), 3.32 (1H, s, Ar-C≡C-*H*), 2.88 (1H, dd, *J* = 13.8,

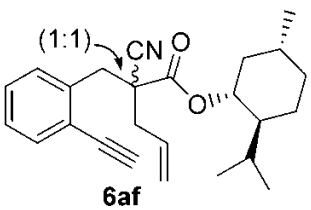
7.3 Hz, C*H*$_2$CH=CH$_2$), 2.58 (1H, dd, *J* = 13.8, 7.2 Hz, C*H*$_2$CH=CH$_2$), 2.51 (1H, t, *J* = 2.4 Hz, CO$_2$CH$_2$C≡C-*H*); ^{13}C NMR (CDCl$_3$, DEPT-135) δ: 167.4 (C, O-*C*=O), 136.2 (C), 133.3 (CH), 130.4 (CH), 130.0 (CH), 129.1 (CH), 127.8 (CH), 123.2 (C), 121.4 (CH$_2$, CH$_2$CH=*C*H$_2$), 117.8 (C, *C*N), 82.0 (CH, Ar-C≡*C*-H), 81.8 (C, Ar-*C*≡C-H), 76.3 (C, CO$_2$CH$_2$*C*≡C-H), 76.0 (CH, CH$_2$C≡*C*-H), 53.9 (CH$_2$, CO$_2$*C*H$_2$C≡C-H), 50.7 (C), 40.7 (CH$_2$), 39.5 (CH$_2$, *C*H$_2$CH=CH$_2$).; LRMS m/z 278.10 (M$^+$ + 1), calcd for C$_{18}$H$_{15}$NO$_2$ 277.1103; Anal. calcd. for C$_{18}$H$_{15}$NO$_2$ (277.1103): C, 77.96; H, 5.45; N, 5.05, found C, 77.85; H, 5.41; N, 5.12%.



6ae

2-Cyano-2-(2-ethynyl-benzyl)-pent-4-enoic acid benzyl ester (6ae): Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν$_{max}$ 3288, 3069, 3032, 1744 (O-C=O), 1644, 1484, 1446, 1376, 1328, 1212, 1143, 1106, 1048, 993, 931, 759, 697, 637 and 612 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 7.50-7.47 (1H, m), 7.34-7.20 (8H, m) [Ar-*H*]; 5.84-5.74 (1H, m, CH$_2$C*H*=CH$_2$), 5.22-5.17 (4H, m, CH$_2$CH=C*H*$_2$, CO$_2$C*H*$_2$Ph), 3.50 (1H, d, *J* = 13.8 Hz), 3.39 (1H, d, *J* = 13.8 Hz), 3.27 (1H, s, Ar-C≡C-*H*), 2.83 (1H, dd, *J* = 13.8, 7.3 Hz, C*H*$_2$CH=CH$_2$), 2.55 (1H, dd, *J* = 13.8, 7.1 Hz, C*H*$_2$CH=CH$_2$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ: 167.9 (C, O-*C*=O), 136.4 (C), 134.5 (C), 133.2 (CH), 130.5 (CH), 129.8 (CH), 129.0 (CH), 128.54 (2 x CH), 128.52 (CH), 128.3 (2 x CH), 127.7 (CH), 123.1 (C), 121.1 (CH$_2$, CH$_2$CH=*C*H$_2$), 118.1 (C, *C*N), 82.0 (CH, Ar-C≡*C*-H), 81.8 (C, Ar-*C*≡C-H), 68.2 (CH$_2$, CO$_2$*C*H$_2$Ph), 50.7 (C), 40.8 (CH$_2$), 39.6 (CH$_2$, *C*H$_2$CH=CH$_2$).; LRMS m/z 330.00 (M$^+$ + 1), calcd for C$_{22}$H$_{19}$NO$_2$ 329.1416; Anal. calcd. for C$_{22}$H$_{19}$NO$_2$ (329.1416): C, 80.22; H, 5.81; N, 4.25, found C, 80.15; H, 5.86; N, 4.33%.

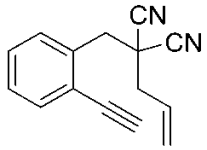
2-Cyano-2-(2-ethynyl-benzyl)-pent-4-enoic acid 2-isopropyl-5-methyl-cyclohexyl ester (6af): Purified by column chromatography using EtOAc/hexane and isolated as a gummy liquid;



6af

[α]^{25}D = –51.1 (*c* 0.1, CHCl$_3$); IR (neat) ν$_{max}$ 3296, 2957, 2871, 1735 (O-C=O), 1645, 1448, 1369, 1277, 1237, 1184, 1146, 1103, 1040, 989, 951, 763, 676 and 630 cm^{-1}; ^{1}H NMR (CDCl$_3$, 1:1 mixture of two diastereomers) δ 7.52 (2H, d, *J* = 7.6 Hz), 7.46 (2H, t, *J* = 7.6 Hz), 7.34-7.23 (4H, m) [Ar-*H*]; 5.87-5.76 (2H, m, 2 x CH$_2$C*H*=CH$_2$), 5.27-5.20 (4H, m, 2 x CH$_2$CH=C*H*$_2$), 4.73-4.66 (2H, m), 3.51-3.38 (4H, m), 3.32 (2H, s, 2 x Ar-C≡C-*H*), 2.87-2.79 (2H, m), 2.58-2.48 (2H, m), 1.94-1.82 (2H, m), 1.67-1.56 (6H, m), 1.45-1.39 (4H, m), 1.04-0.94 (4H, m), 0.90-0.79 (8H, m), 0.68 (3H, d, *J* = 7.2 Hz), 0.65 (3H, d, *J* = 7.2 Hz); ^{13}C NMR (CDCl$_3$,

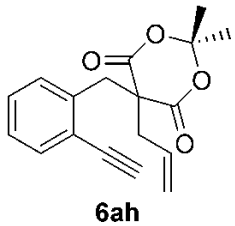
DEPT-135, 1:1 mixture of two diastereomers) δ 167.7 (C, O-*C*=O), 167.6 (C, O-*C*=O), 136.7 (C), 136.6 (C), 133.3 (CH), 133.2 (CH), 130.7 (CH), 130.5 (CH), 129.8 (CH), 129.6 (CH), 128.94 (CH), 128.92 (CH), 127.6 (CH), 127.5 (CH), 123.3 (C), 123.2 (C), 120.9 (2 x CH_2, 2 x $CH_2CH=CH_2$), 118.42 (C, *C*N), 118.37 (C, *C*N), 82.04 (CH, Ar-C≡*C*-H), 81.97 (CH, Ar-C≡*C*-H), 81.94 (C, Ar-*C*≡C-H), 81.89 (C, Ar-*C*≡C-H), 77.6 (CH), 77.4 (CH), 50.7 (C), 50.6 (C), 46.4 (CH), 46.3 (CH), 41.6 (CH_2), 40.8 (CH_2), 40.4 (CH_2), 40.1 (CH_2), 39.7 (CH_2), 39.2 (CH_2), 33.9 (2 x CH_2), 31.31 (CH), 31.27 (CH), 25.7 (2 x CH), 23.0 (CH_2), 22.9 (CH_2), 21.87 (CH_3), 21.83 (CH_3), 20.68 (CH_3), 20.66 (CH_3), 15.98 (CH_3), 15.73 (CH_3).; LRMS m/z 378.20 (M^+ + 1), calcd for $C_{25}H_{31}NO_2$ 377.2355; Anal. calcd. for $C_{25}H_{31}NO_2$ (377.2355): C, 79.54; H, 8.28; N, 3.71, found C, 79.45; H, 8.31; N, 3.77%.



6ag

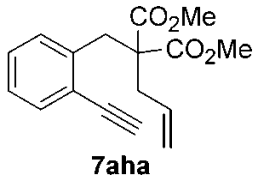
2-Allyl-2-(2-ethynyl-benzyl)-malononitrile (6ag): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3292, 3272, 1484, 1445, 1286, 1098, 998, 940, 766, 697, 666 and 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.59 (1H, d, *J* = 7.6 Hz), 7.53 (1H, d, *J* = 7.6 Hz), 7.42 (1H, t, *J* = 7.6 Hz), 7.35 (1H, t, *J* = 7.6 Hz) [Ar-*H*]; 6.00-5.90 (1H, m, $CH_2CH=CH_2$), 5.45-5.40 (2H, m, $CH_2CH=CH_2$), 3.53 (2H, s, Ar-CH_2), 3.38 (1H, s, Ar-C≡C-*H*), 2.75 (2H, d, *J* = 7.2 Hz, $CH_2CH=CH_2$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ: 134.2 (C), 133.5 (CH), 130.2 (CH), 129.4 (CH), 128.7 (CH), 128.6 (CH), 123.4 (C), 123.2 (CH_2, $CH_2CH=CH_2$), 114.8 (2 x C, 2 x *C*≡N), 82.8 (CH, Ar-C≡*C*-H), 81.6 (C, Ar-*C*≡C-H), 41.2 (CH_2), 39.9 (CH_2, $CH_2CH=CH_2$), 38.8 (C).; LRMS m/z 221.10 (M^+ + 1), calcd for $C_{15}H_{12}N_2$ 220.1000; Anal. calcd. for $C_{15}H_{12}N_2$ (220.1000): C, 81.79; H, 5.49; N, 12.72, found C, 81.72; H, 5.53; N, 12.85%.

5-Allyl-5-(2-ethynyl-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (6ah): Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν_{max} 3732, 3270, 1776, 1742 (O-C=O), 1441, 1387, 1355, 1269, 1204, 1080, 1028, 950, 765 and 644 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49 (1H, d, *J* = 7.6 Hz), 7.31-7.21 (3H, m) [Ar-*H*]; 5.74-5.64 (1H, m, $CH_2CH=CH_2$), 5.25 (1H, d, *J* = 17.2 Hz, $CH_2CH=CH_2$), 5.18 (1H, d, *J* = 10.0 Hz, $CH_2CH=CH_2$), 3.59 (2H, s, ArCH_2), 3.31 (1H, s, Ar-C≡C-*H*), 2.91 (2H, d, *J* = 7.6 Hz, $CH_2CH=CH_2$), 1.57 (3H, s, CH_3), 1.06 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (2 x C, 2 x O-C=O), 136.8 (C), 133.5 (CH), 130.8 (CH), 130.6 (CH), 128.8 (CH), 127.6 (CH), 123.1 (C), 121.5 (CH_2, $CH_2CH=CH_2$), 105.6 (C, O-C-O),


6ah

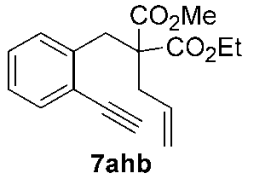
81.9 (CH, Ar-C≡*C*-H), 81.2 (C, Ar-*C*≡C-H), 56.3 (C), 42.3 (2 x CH_2), 30.2 (CH_3), 28.4 (CH_3, *C*H_3).; LRMS m/z 297.0 (M-1), calcd for $C_{18}H_{18}O_4$ 298.1205; Anal. calcd. for $C_{18}H_{18}O_4$ (298.1205): C, 72.47; H, 6.08, found C, 72.41; H, 6.12%.

2-Allyl-2-(2-ethynyl-benzyl)-malonic acid dimethyl ester (7aha): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3274, 3010, 2955, 1736 (O-C=O), 1731 (O-C=O), 1439, 1258, 1210, 1140, 1106, 1058, 760, 673, 634, 610 and 604 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47 (1H, br d, *J* = 8.0 Hz), 7.26-7.22 (1H, m), 7.19-7.14 (2H, m) [Ar-*H*]; 5.92-5.85 (1H, m, CH_2CH=CH_2), 5.11-5.07 (2H, m, CH_2CH=CH_2), 3.69 (6H, s, 2 x CO_2CH_3), 3.53 (2H, s, ArCH_2), 3.25 (1H, s, Ar-C≡C-*H*), 2.62 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.2 (2 x C, 2 x O-*C*=O), 138.7 (C), 133.23 (CH), 133.19 (CH), 129.9 (CH), 128.7 (CH), 126.9 (CH), 123.4 (C), 118.8 (CH_2, CH_2CH=*C*H_2), 82.4 (C, Ar-*C*≡C-H), 81.3 (CH, Ar-C≡*C*-H), 59.4 (C), 52.3 (2 x CH_3, 2 x CO_2CH_3), 37.5 (CH_2), 36.4 (CH_2, *C*H_2CH=CH_2).; LRMS m/z 287.00 (M^+ + 1), calcd for $C_{17}H_{18}O_4$ 286.1205; Anal. calcd. for $C_{17}H_{18}O_4$ (286.1205): C, 71.31; H, 6.34, found C, 71.25; H, 6.41%.



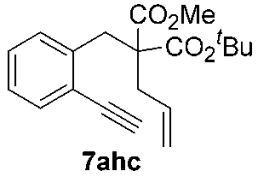
7aha

2-Allyl-2-(2-ethynyl-benzyl)-malonic acid ethyl ester methyl ester (7ahb): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3278, 2984, 1736 (O-C=O), 1731 (O-C=O), 1441, 1273, 1210, 1141, 1106, 1047, 758 and 635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48 (1H, d, *J* = 6.8 Hz), 7.28-7.18 (3H, m) [Ar-*H*]; 5.94-5.87 (1H, m, CH_2CH=CH_2), 5.13-5.08 (2H, m, CH_2CH=CH_2), 4.20-4.12 (2H, m, $CO_2CH_2CH_3$), 3.71 (3H, s, CO_2CH_3), 3.55 (2H, s, ArCH_2), 3.27 (1H, s, Ar-C≡C-*H*), 2.64 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2), 1.22 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.2 (C, O-*C*=O), 170.6 (C, O-*C*=O), 138.8 (C), 133.1 (2 x CH), 129.8 (CH), 128.6 (CH), 126.7 (CH), 123.3 (C), 118.6 (CH_2, CH_2CH=*C*H_2), 82.4 (C, Ar-*C*≡C-H), 81.2 (CH, Ar-C≡*C*-H), 61.3 (CH_2, $CO_2CH_2CH_3$), 59.2 (C), 52.2 (CH_3, CO_2CH_3), 37.4 (CH_2), 36.2 (CH_2, *C*H_2CH=CH_2), 13.9 (CH_3, $CO_2CH_2CH_3$).; LRMS m/z 301.00 (M^+ + 1), calcd for $C_{18}H_{20}O_4$ 300.1362; Anal. calcd. for $C_{18}H_{20}O_4$ (300.1362): C, 71.98; H, 6.71, found C, 71.85; H, 6.76%.



7ahb

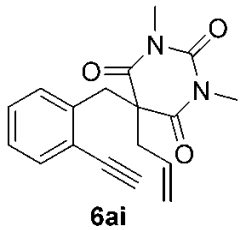
2-Allyl-2-(2-ethynyl-benzyl)-malonic acid tert-butyl ester methyl ester (7ahc): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR



7ahc

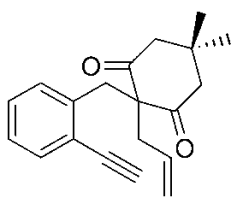
(neat) ν_{max} 3274, 2978, 1736 (O-C=O), 1731 (O-C=O), 1441, 1252, 1210, 1141, 1106, 1045, 922, 835, 763, 661 and 634 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47 (1H, d, *J* = 7.6 Hz), 7.27-7.15 (3H, m) [Ar-*H*]; 5.95-5.85 (1H, m, CH_2CH=CH_2), 5.11-5.06 (2H, m, CH_2CH=CH_2), 3.70 (3H, s, CO_2CH_3), 3.51 (2H, s, $ArCH_2$), 3.26 (1H, s, Ar-C≡C-*H*), 2.59 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2), 1.40 (9H, s, O-C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.7 (C, O-*C*=O), 169.7 (C, O-*C*=O), 139.3 (C), 133.4 (CH), 133.2 (CH), 129.8 (CH), 128.6 (CH), 126.6 (CH), 123.4 (C), 118.5 (CH_2, CH_2CH=*C*H_2), 82.6 (C, Ar-*C*≡C-H), 81.9 (C, O-*C*(CH_3)$_3$), 81.3 (CH, Ar-C≡*C*-H), 59.5 (C), 52.1 (CH_3, CO_2CH_3), 37.6 (CH_2), 36.1 (CH_2, *C*H_2CH=CH_2), 27.8 (3 x CH_3, O-C(*C*H_3)$_3$).; LRMS m/z 329.00 (M^+ + 1), calcd for $C_{20}H_{24}O_4$ 328.1675; Anal. calcd. for $C_{20}H_{24}O_4$ (328.1675): C, 73.15; H, 7.37, found C, 73.22; H, 7.33%.

5-Allyl-5-(2-ethynyl-benzyl)-1,3-dimethyl-pyrimidine-2,4,6-trione (6ai): Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν_{max} 3261, 1691, 1688, 1678, 1444, 1380, 1323, 1289, 1085, 1046, 930, 761 and 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45-7.43 (1H, dd, *J* = 6.9, 2.0 Hz,), 7.25-7.18 (2H, m), 7.01-6.99 (1H, m) [Ar-*H*]; 5.63-5.52 (1H, m, CH_2CH=CH_2), 5.16 (1H, d, *J* = 17.0 Hz, CH_2CH=CH_2), 5.06 (1H, d, *J* = 10.2 Hz, CH_2CH=CH_2), 3.46 (2H, s, $ArCH_2$), 3.27 (1H, s, Ar-C≡C-*H*), 3.12 (6H, s, 2 x NCH_3), 2.95 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.0 (2 x C, 2 x N-C=O), 150.5 (C, C=O), 136.7 (C), 133.2 (CH), 131.4 (CH), 129.4 (CH), 128.5 (CH), 127.7 (CH), 122.4 (C), 120.4 (CH_2, CH_2CH=*C*H_2), 81.7 (CH, Ar-C≡*C*-H), 81.1 (C, Ar-*C*≡C-H), 57.7 (C), 44.0 (CH_2), 40.7 (CH_2, *C*H_2CH=CH_2), 28.4 (2 x CH_3, 2 x N-*C*H_3).; LRMS m/z 311.10 (M^+ + 1), calcd for $C_{18}H_{18}N_2O_3$ 310.1317; Anal. calcd. for $C_{18}H_{18}N_2O_3$ (310.1317): C, 69.66; H, 5.85; N, 9.03, found C, 69.55; H, 5.91; N, 9.12%.



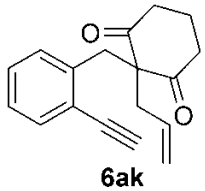
6ai

2-Allyl-2-(2-ethynyl-benzyl)-5,5-dimethyl-cyclohexane-1,3-dione (6aj): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3289, 2956, 1724 (C=O), 1692 (C=O), 1462, 1330, 1254, 1203, 928, 764 692, 663, 646 and 619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48 (1H, d, *J* = 8.0 Hz), 7.28-7.19 (2H, m), 7.03 (1H, d, *J* = 8.0 Hz) [Ar-*H*]; 5.59-5.50 (1H, m, CH_2CH=CH_2), 5.08 (1H, dd, *J* = 16.0, 2.0 Hz, CH_2CH=CH_2), 4.99 (1H, dd, *J* = 8.0, 2.0 Hz, CH_2CH=CH_2), 3.29 (1H, s, Ar-C≡C-*H*), 3.27 (2H, s, $ArCH_2$), 2.65 (2H, d, *J* = 8.0 Hz,

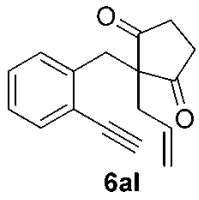


6aj

C*H*$_2$CH=CH$_2$), 2.56 (2H, d, *J* = 16.0 Hz), 2.43 (2H, d, *J* = 16.0 Hz), 0.97 (3H, s, CH$_3$), 0.85 (3H, s, CH$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 209.2 (2 x C, 2 x C=O), 137.8 (C), 133.4 (CH), 133.3 (CH), 130.7 (CH), 128.7 (CH), 127.3 (CH), 123.0 (C), 119.5 (CH$_2$, CH$_2$CH=*C*H$_2$), 82.2 (C, Ar-*C*≡C-H), 82.1 (CH, Ar-C≡*C*-H), 68.4 (C), 53.0 (2 x CH$_2$), 42.2 (CH$_2$), 36.9 (CH$_2$, *C*H$_2$CH=CH$_2$), 30.6 (CH$_3$), 30.5 (C), 27.2 (CH$_3$).; LRMS m/z 295.25 (M$^+$ + 1), calcd for C$_{20}$H$_{22}$O$_2$ 294.1620; Anal. calcd. for C$_{20}$H$_{22}$O$_2$ (294.1620): C, 81.60; H, 7.53, found C, 81.52; H, 7.58%.


6ak

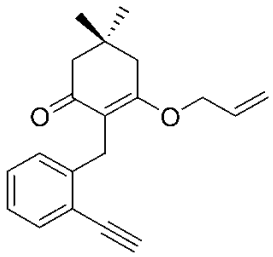
2-Allyl-2-(2-ethynyl-benzyl)-cyclohexane-1,3-dione (6ak): Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν$_{max}$ 3267, 2965, 1723 (C=O), 1692 (C=O), 1482, 1440, 1338, 1263, 1215, 1102, 1035, 1000, 927, 765, 676, 654 and 621 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.45 (1H, d, *J* = 7.6 Hz), 7.24 (1H, t, *J* = 7.6 Hz), 7.18 (1H, t, *J* = 7.6 Hz), 7.02 (1H, d, *J* = 7.6 Hz) [Ar-*H*]; 5.54-5.44 (1H, m, CH$_2$C*H*=CH$_2$), 5.02 (1H, *J* = 17.2 Hz, CH$_2$CH=C*H*$_2$), 4.99 (1H, *J* = 10.0 Hz, CH$_2$CH=C*H*$_2$), 3.31 (2H, s, ArC*H*$_2$), 3.30 (1H, s, Ar-C≡C-*H*), 2.67 (2H, d, *J* = 7.2 Hz, C*H*$_2$CH=CH$_2$), 2.49-2.34 (4H, m), 1.77-1.61 (2H, m); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 210.2 (2 x C, 2 x C=O), 138.3 (C), 133.3 (CH), 132.6 (CH), 130.2 (CH), 128.6 (CH), 126.9 (CH), 122.6 (C), 119.3 (CH$_2$, CH$_2$CH=*C*H$_2$), 81.9 (CH, Ar-C≡*C*-H), 81.8 (C, Ar-*C*≡C-H), 68.5 (C), 41.5 (CH$_2$), 40.28 (2 x CH$_2$), 40.20 (CH$_2$), 16.0 (CH$_2$).; LRMS m/z 267.10 (M + 1), calcd for C$_{18}$H$_{18}$O$_2$ 266.1307; Anal. calcd. for C$_{18}$H$_{18}$O$_2$ (266.1307): C, 81.17; H, 6.81, found C, 81.25; H, 6.77%.


6al

2-Allyl-2-(2-ethynyl-benzyl)-cyclopentane-1,3-dione (6al): Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν$_{max}$ 3256, 1720 (C=O), 1644, 1482, 1412, 1337, 1279, 1181, 1099, 1028, 992, 921, 766, 711, 683, 636 and 612 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.46 (1H, d, *J* = 7.2 Hz), 7.33-7.17 (2H, m), 7.07 (1H, d, *J* = 7.6 Hz) [Ar-*H*]; 5.59-5.48 (1H, m, CH$_2$C*H*=CH$_2$), 5.06 (1H, *J* = 17.2 Hz, CH$_2$CH=C*H*$_2$), 5.02 (1H, *J* = 10.0 Hz, CH$_2$CH=C*H*$_2$), 3.31 (1H, s, Ar-C≡C-*H*), 3.20 (2H, s, ArC*H*$_2$), 2.53 (2H, d, *J* = 7.2 Hz, C*H*$_2$CH=CH$_2$), 2.49-2.37 (4H, m); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 215.7 (2 x C, 2 x C=O), 137.6 (C), 133.4 (CH), 131.5 (CH), 130.0 (CH), 128.7 (CH), 127.2 (CH), 122.7 (C), 120.0 (CH$_2$, CH$_2$CH=*C*H$_2$), 81.9 (CH, Ar-C≡*C*-H), 81.7 (C, Ar-*C*≡C-H), 61.8 (C), 39.4 (CH$_2$), 38.8 (CH$_2$), 36.4 (2 x CH$_2$).; LRMS m/z 253.10 (M + 1), calcd

for $C_{17}H_{16}O_2$ 252.1150; Anal. calcd. for $C_{17}H_{16}O_2$ (252.1150): C, 80.93; H, 6.39, found C, 80.97; H, 6.44%.

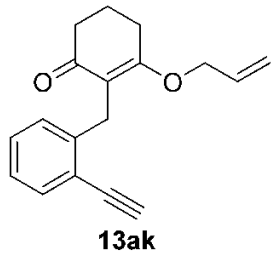
3-Allyloxy-2-(2-ethynyl-benzyl)-5,5-dimethyl-cyclohex-2-enone (13aj): Purified by column chromatography using EtOAc/ Hexane and isolated as a liquid; IR (neat) ν_{max} 3288, 2960, 2930, 1647, 1612, 1472, 1414, 1371, 1297, 1267, 1227, 1168, 1100, 1059, 928, 759, 662 and 638 cm^{-1};



13aj

^{1}H NMR ($CDCl_3$) δ 7.42 (1H, d, *J* = 7.6 Hz, Ar-H), 7.17 (1H, t, *J* = 7.6 Hz, Ar-H), 7.06 (1H, t, *J* = 7.6 Hz, Ar-H), 7.00 (1H, d, *J* = 7.6 Hz, Ar-H), 5.81-5.71 (1H, m, OCH_2CH=CH_2), 5.14-5.09 (2H, m, OCH_2CH=CH_2), 4.48 (2H, d, *J* = 4.8 Hz, OCH_2CH=CH_2), 3.88 (2H, s, $ArCH_2$), 3.26 (1H, s, Ar-C≡C-*H*), 2.43 (2H, s), 2.30 (2H, s), 1.10 (6H, s, 2 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.7 (C, C=O), 170.6 (C, C-O), 143.9 (C), 132.8 (CH), 132.4 (CH), 128.5 (CH), 127.6 (CH), 125.1 (CH), 121.6 (C), 117.4 (C), 117.2 (CH_2, OCH_2CH=*C*H_2), 82.8 (C, Ar-*C*≡C-H), 80.8 (CH, Ar-C≡*C*-H), 68.0 (CH_2, O*C*H_2CH=CH_2), 50.2 (CH_2), 39.2 (CH_2), 32.2 (C), 28.5 (2 x CH_3), 26.1 (CH_2).; LRMS m/z 295.30 (M^+ +1), calcd for $C_{20}H_{22}O_2$ 294.1620; Anal. calcd. for $C_{20}H_{22}O_2$ (294.1620): C, 81.60; H, 7.53, found C, 81.71; H, 7.49%.

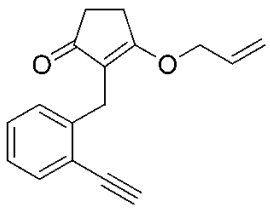
3-Allyloxy-2-(2-ethynyl-benzyl)-cyclohex-2-enone (13ak): Purified by column chromatography using EtOAc/ Hexane and isolated as a liquid; IR (neat) ν_{max} 3195, 2932, 1638, 1610, 1453, 1407, 1372, 1246, 1185, 1075, 1036, 937, 759, 726, 687, 654 and 615 cm^{-1}; ^{1}H



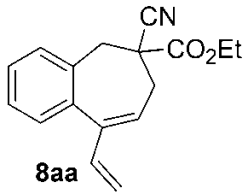
13ak

NMR ($CDCl_3$) δ 7.42 (1H, d, *J* = 7.6 Hz, Ar-H), 7.17 (1H, t, *J* = 7.6 Hz, Ar-H), 7.07 (1H, t, *J* = 7.6 Hz, Ar-H), 7.01 (1H, d, *J* = 8.0 Hz, Ar-H), 5.82- 5.72 (1H, m, OCH_2CH=CH_2), 5.16- 5.11 (2H, m, OCH_2CH=CH_2), 4.49 (2H, br d, *J* = 4.8 Hz, OCH_2CH=CH_2), 3.88 (2H, s, $ArCH_2$), 3.26 (1H, s, Ar-C≡C-*H*), 2.58 (2H, t, *J* = 6.4 Hz), 2.42 (2H, t, *J* = 7.2 Hz), 2.06-1.99 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 197.9 (C, C=O), 172.4 (C, C-O), 143.8 (C), 132.7 (CH), 132.4 (CH), 128.5 (CH), 127.5 (CH), 125.1 (CH), 121.6 (C), 118.5 (C), 117.3 (CH_2, OCH_2CH=*C*H_2), 82.8 (C, Ar-*C*≡C-H), 80.9 (CH, Ar-C≡*C*-H), 68.1 (CH_2, O*C*H_2CH=CH_2), 36.3 (CH_2), 26.1 (CH_2), 25.4 (CH_2), 20.9 (CH_2).; LRMS m/z 267.10 (M^+ +1), calcd for $C_{18}H_{18}O_2$ 266.1307; Anal. calcd. for $C_{18}H_{18}O_2$ (266.1307): C, 81.17; H, 6.81, found C, 81.10; H, 6.85%.

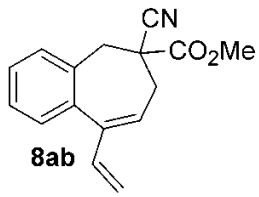
3-Allyloxy-2-(2-ethynyl-benzyl)-cyclopent-2-enone (13al): Purified by column chromatography using EtOAc/ Hexane and isolated as a liquid; IR (neat) ν_{max} 3288, 2917, 1684, 1621, 1481, 1385, 1351, 1262,1228 1101, 1045, 966, 761, 670, 644 and 622 cm^{-1}; ^1H NMR


13al

($CDCl_3$) δ 7.43 (1H, d, *J* = 7.2 Hz, Ar-H), 7.28-7.15 (2H, m, Ar-H), 7.10 (1H, t, *J* = 7.6 Hz, Ar-H), 5.91-5.82 (1H, m, OCH_2CH=CH_2), 5.25-5.20 (2H, m, OCH_2CH=CH_2), 4.61 (2H, d, *J* = 5.2 Hz, OCH_2CH=CH_2), 3.72 (2H, s, $ArCH_2$), 3.28 (1H, s, Ar-C≡C-*H*), 2.68 (2H, br t, *J* = 4.4 Hz), 2.50-2.48 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 204.2 (C, C=O), 184.7 (C), 142.0 (C), 132.5 (CH), 132.0 (CH), 128.6 (CH), 128.3 (CH), 125.6 (CH), 121.4 (C), 118.9 (C), 117.8 (CH_2, OCH_2CH=CH_2), 82.3 (C, Ar-*C*≡C-H), 81.3 (CH, Ar-C≡*C*-H), 69.6 (CH_2, OCH_2CH=CH_2), 33.4 (CH_2), 25.5 (CH_2), 24.9 (CH_2).; LRMS m/z 253.50 (M^+ + 1), calcd for $C_{17}H_{16}O_2$ 252.1150; Anal. calcd. for $C_{17}H_{16}O_2$ (252.1150): C, 80.93; H, 6.39, found C, 80.85; H, 6.44%.


8aa

6-Cyano-9-vinyl-6,7-dihydro-5*H*-benzocycloheptene-6-carboxylic acid ethyl ester (8aa): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2981, 1743 (O-C=O), 1447, 1368, 1328, 1239, 1081, 1037, 917, 855 and 771 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38-7.28 (4H, m, Ar-*H*), 6.56 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.13 (1H, t, *J* = 7.2 Hz, olefinic-*H*), 5.27-5.20 (2H, m, CH=CH_2), 4.29 (2H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.22 (1H, d, *J* = 13.6 Hz), 3.03 (1H, d, *J* = 13.2 Hz), 2.55 (1H, dd, *J* = 13.2, 7.6 Hz), 2.33 (1H, dd, *J* = 13.6, 7.2 Hz), 1.35 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.9 (C, O-*C*=O), 143.8 (C), 136.9 (CH), 136.7 (C), 134.6 (C), 130.3 (CH), 128.9 (CH), 128.0 (CH), 127.5 (CH), 124.7 (CH), 119.7 (C, *C*N), 116.9 (CH_2, CH=CH_2), 62.9 (CH_2, $CO_2CH_2CH_3$),

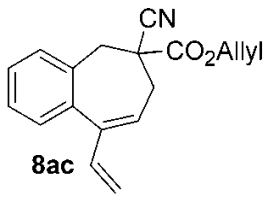

8ab

54.7 (C), 39.2 (CH_2), 32.8 (CH_2), 14.0 (CH_3, $CO_2CH_2CH_3$).; LRMS m/z 268.50 (M^+ + 1), calcd for $C_{17}H_{17}NO_2$ 267.1259; Anal. calcd. for $C_{17}H_{17}NO_2$ (267.1259): C, 76.38; H, 6.41; N, 5.24, found C, 76.25; H, 6.48; N, 5.33%.

6-Cyano-9-vinyl-6,7-dihydro-5*H*-benzocycloheptene-6-carboxylic acid methyl ester (8ab): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2955, 2921, 2850, 1746 (O-C=O), 1444, 1245, 1091, 1040, 924, 854, 768, 699, 673, 652 and

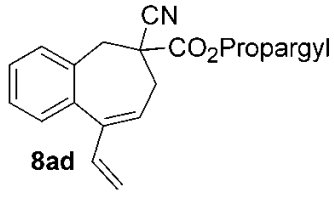
627cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38-7.30 (4H, m, Ar-*H*), 6.56 (1H, dd, *J* = 16.0, 12.0 Hz, C*H*=CH_2), 6.13 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.25 (1H, d, *J* = 16.0 Hz, CH=C*H*$_2$), 5.21 (1H, d, *J* = 12.0 Hz, CH=C*H*$_2$), 3.85 (3H, s, CO_2CH_3), 3.22 (1H, d, *J* = 12.0 Hz), 3.03 (1H, d, *J* = 13.6 Hz), 2.56 (1H, dd, *J* = 13.6, 7.6 Hz), 2.34 (1H, dd, *J* = 13.6, 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.4 (C, O-*C*=O), 143.9 (C), 136.9 (CH), 136.7 (C), 134.5 (C), 130.3 (CH), 128.9 (CH), 128.0 (CH), 127.6 (CH), 124.5 (CH), 119.5 (C, *C*N), 117.0 (CH_2, CH=*C*H$_2$), 54.5 (C), 53.6 (CH_3, CO_2CH_3), 39.2 (CH_2), 32.8 (CH_2).; LRMS m/z 253.50 (M^+), calcd for $C_{16}H_{15}NO_2$ 253.1103; Anal. calcd. for $C_{16}H_{15}NO_2$ (253.1103): C, 75.87; H, 5.97; N, 5.53, found C, 75.71; H, 6.07; N, 5.61%.

6-Cyano-9-vinyl-6,7-dihydro-5H-benzocycloheptene-6-carboxylic acid allyl ester (8ac):



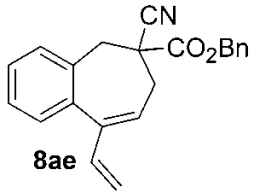
Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 1745 (O-C=O), 1448, 1226, 991, 920 and 769 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38-7.28 (4H, m, Ar-*H*), 6.56 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.13 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 6.00-5.90 (1H, m, CO_2CH_2CH=CH_2), 5.40 (1H, dd, *J* = 18.8, 1.2 Hz, CH=C*H*$_2$), 5.32 (1H, dd, *J* = 10.4, 1.2 Hz, CH=C*H*$_2$), 5.24 (1H, d, *J* = 16.0 Hz, CO_2CH_2CH=C*H*$_2$), 5.21 (1H, d, *J* = 10.0 Hz, CO_2CH_2CH=C*H*$_2$), 4.72 (2H, dd, *J* = 5.6, 1.2 Hz, CO_2CH_2CH=CH_2), 3.23 (1H, d, *J* = 13.2 Hz), 3.04 (1H, d, *J* = 13.2 Hz), 2.56 (1H, dd, *J* = 13.6, 7.2 Hz), 2.35 (1H, dd, *J* = 13.6, 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 143.9 (C), 136.9 (CH), 136.7 (C), 134.5 (C), 130.8 (CH), 130.3 (CH), 128.9 (CH), 128.0 (CH), 127.6 (CH), 124.6 (CH), 119.6 (CH_2, CH=*C*H$_2$), 119.5 (C, *C*N), 117.0 (CH_2, CO_2CH_2CH=*C*H$_2$), 67.2 (CH_2, CO_2CH_2CH=CH_2), 54.7 (C), 39.3 (CH_2), 32.8 (CH_2).; LRMS m/z 280.00 (M^+ + 1), calcd for $C_{18}H_{17}NO_2$ 279.1259; Anal. calcd. for $C_{18}H_{17}NO_2$ (279.1259): C, 77.40; H, 6.13; N, 5.01, found C, 77.31; H, 6.18; N, 5.10%.

6-Cyano-9-vinyl-6,7-dihydro-5*H*-benzocycloheptene-6-carboxylic acid prop-2-ynyl ester



(8ad): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3290, 2923, 1750 (O-C=O), 1447, 1371, 1330, 1202, 1083, 1039, 923, 870, 805, 770, 671 and 659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39-7.28 (4H, m, Ar-*H*), 6.56 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.13 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.26 (1H, d, *J* = 17.6 Hz, CH=C*H*$_2$), 5.22 (1H, d, *J* = 10.4 Hz, CH=C*H*$_2$), 4.82 (2H, dABq, *J* = 15.6, 2.4 Hz, CO_2CH_2C≡CH), 3.24 (1H, d, *J* = 13.6 Hz), 3.06 (1H, d, *J* = 13.6 Hz), 2.57 (1H, dd, *J* = 13.6, 7.2

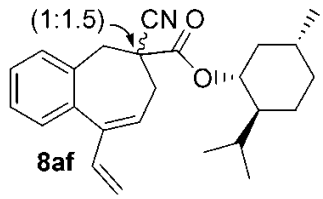
Hz, C*H*$_2$CH=C), 2.56 (1H, t, *J* = 2.4 Hz, CO$_2$CH$_2$C≡C*H*), 2.36 (1H, dd, *J* = 13.6, 7.2 Hz, C*H*$_2$CH=C); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.2 (C, O-*C*=O), 144.1 (C), 136.89 (CH), 136.75 (C), 134.2 (C), 130.4 (CH), 128.9 (CH), 128.1 (CH), 127.7 (CH), 124.3 (CH), 119.1 (C, *C*N), 117.2 (CH$_2$, CH=*C*H$_2$), 77.2 (C, CO$_2$CH$_2$C≡CH), 76.1 (CH, CO$_2$CH$_2$C≡*C*H), 54.4 (C), 54.0 (CH$_2$), 39.2 (CH$_2$), 32.7 (CH$_2$).; LRMS m/z 277.30 (M$^+$), calcd for C$_{18}$H$_{15}$NO$_2$ 277.1103; Anal. calcd. for C$_{18}$H$_{15}$NO$_2$ (277.1103): C, 77.96; H, 5.45; N, 5.05, found C, 77.85; H, 5.51; N, 5.15%.



8ae

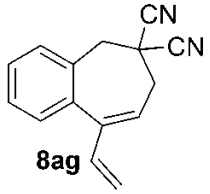
6-Cyano-9-vinyl-6,7-dihydro-5*H*-benzocycloheptene-6-carboxylic acid benzyl ester (8ae): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν$_{max}$ 3032, 1746 (O-C=O), 1448, 1214, 1079, 992, 915, 740, 697 and 644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38-7.32 (7H, m), 7.27-7.22 (2H, m) [Ar-*H*]; 6.53 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH$_2$), 6.09 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.29-5.19 (4H, m, CH=C*H*$_2$, CO$_2$C*H*$_2$Ph), 3.19 (1H, d, *J* = 13.6 Hz), 3.02 (1H, d, *J* = 13.6 Hz), 2.54 (1H, dd, *J* = 13.6, 7.6 Hz), 2.34 (1H, dd, *J* = 13.6, 7.2 Hz); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.6 (C, O-*C*=O), 143.9 (C), 136.9 (CH), 136.7 (C), 134.7 (C), 134.3 (C), 130.3 (CH), 128.9 (CH), 128.7 (2 x CH), 128.2 (2 x CH), 127.9 (2 x CH), 127.5 (CH), 124.5 (CH), 119.4 (C, *C*N), 117.0 (CH$_2$, CH=*C*H$_2$), 68.3 (CH$_2$, CO$_2$CH$_2$Ph), 54.6 (C), 39.2 (CH$_2$), 32.7 (CH$_2$).; LRMS m/z 330.55 (M$^+$ + 1), calcd for C$_{22}$H$_{19}$NO$_2$ 329.1416; Anal. calcd. for C$_{22}$H$_{19}$NO$_2$ (329.1416): C, 80.22; H, 5.81; N, 4.25, found C, 80.16; H, 5.87; N, 4.37%.

6-Cyano-9-vinyl-6,7-dihydro-5*H*-benzocycloheptene-6-carboxylic acid 2-isopropyl-5-methyl-cyclohexyl ester (8af): Purified by column chromatography using EtOAc/hexane and isolated as a gummy liquid; **[α]^{25}D = –52.1 (*c* 0.1, CHCl$_3$);** IR (neat) ν$_{max}$ 2957, 2870, 1736 (O-C=O), 1451, 1372, 1326, 1244, 1087, 1039, 987, 952, 911, 850, 769, 737 and 679 cm^{-1}; ^{1}H NMR (CDCl$_3$, 1:1.5 mixture of two diastereomers) δ 7.38-7.28 (8H, m, Ar-*H*), 6.56 (2H, dd, *J* = 17.6, 10.8 Hz, 2 x C*H*=CH$_2$), 6.12 (2H, t, *J* = 7.2 Hz, 2 x olefinic-*H*), 5.27-5.20 (4H, m, 2 x CH=C*H*$_2$), 4.76 (2H, dt, *J* = 10.8, 4.4 Hz), 3.21 (2H, t, *J* = 14.0 Hz), 3.02 (2H, dd, *J* = 13.2, 7.6 Hz), 2.59-2.50 (2H, m), 2.38-2.29 (2H, m), 2.05-1.99 (2H, m), 1.94-1.89 (2H, m), 1.75-1.70 (4H, m), 1.56-1.49 (4H, m), 1.12-1.03 (4H, m), 0.95-0.89 (8H, m), 0.79 (3H, d, *J* = 7.2 Hz), 0.76 (3H, d, *J* = 7.2 Hz) [2 x C*H*$_3$]; ^{13}C NMR (CDCl$_3$, DEPT-135, 1:1.5 mixture

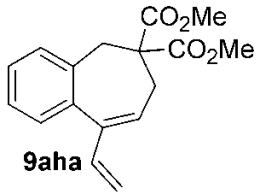


8af

of two diastereomers) δ 167.46 (C, O-*C*=O), 167.43 (C, O-*C*=O), 143.9 (C), 143.7 (C), 136.97 (2 x CH), 136.78 (C), 136.75 (C), 134.71 (C), 134.6 (C), 130.4 (CH), 130.2 (CH), 128.9 (2 x CH), 127.96 (CH), 127.93 (CH), 127.53 (CH), 127.47 (CH), 124.9 (CH), 124.6 (CH), 119.74 (C, *C*N), 119.67 (C, *C*N), 116.9 (CH_2, CH=*C*H_2), 116.8 (CH_2, CH=*C*H_2), 77.33 (2 x CH), 54.9 (C), 54.8 (C), 46.87 (CH), 46.82 (CH), 40.4 (CH_2), 40.3 (CH_2), 39.4 (CH_2), 39.1 (CH_2), 34.1 (2 x CH_2), 33.0 (CH_2), 32.7 (CH_2), 31.4 (2 x CH), 26.2 (2 x CH), 23.17 (CH_2), 23.13 (CH_2), 21.93 (CH_3), 21.90 (CH_3), 20.79 (CH_3), 20.76 (CH_3), 16.01 (2 x CH_3).; LRMS m/z 378.00 (M^+ + 1), calcd for $C_{25}H_{31}NO_2$ 377.2355; Anal. calcd. for $C_{25}H_{31}NO_2$ (377.2355): C, 79.54; H, 8.28; N, 3.71, found C, 79.65; H, 8.22; N, 3.78%.

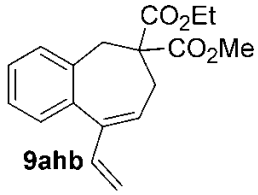


9-Vinyl-5,7-dihydro-benzocycloheptene-6,6-dicarbonitrile (8ag): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2252, 1648, 1470, 1440, 1303, 1074, 906, 776, 732, 686, 679 and 652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47-7.35 (4H, m, Ar-*H*), 6.59 (1H, dd, *J* = 17.6, 11.2 Hz, C*H*=CH_2), 6.13 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.30 (2H, m, CH=CH_2), 3.21 (2H, s, Ar-CH_2), 2.53 (2H, d, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 146.1 (C), 136.7 (C), 136.3 (CH), 132.3 (C), 130.2 (CH), 129.3 (CH), 128.7 (CH), 128.6 (CH), 121.3 (CH), 118.7 (CH_2, CH=*C*H_2), 115.7 (2 x C, 2 x *C*≡N), 40.8 (C), 40.7 (CH_2), 34.6 (CH_2).; LRMS m/z 221.00 (M^+ + 1), calcd for $C_{15}H_{12}N_2$ 220.1000; Anal. calcd. for $C_{15}H_{12}N_2$ (220.1000): C, 81.79; H, 5.49; N, 12.72, found C, 81.65; H, 5.54; N, 12.66%.

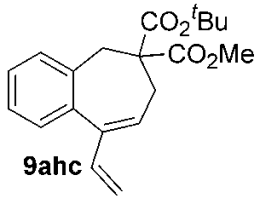


9-Vinyl-5,7-dihydro-benzocycloheptene-6,6-dicarboxylic acid dimethyl ester (9aha): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2954, 1736 (O-C=O), 1732 (O-C=O), 1440, 1274, 1217, 1074, 761 and 649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39 (1H, d, *J* = 7.2 Hz), 7.33-7.23 (3H, m) [Ar-*H*]; 6.54 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.19 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.20 (1H, d, *J* = 17.2 Hz, CH=CH_2), 5.13 (1H, d, *J* = 10.8 Hz, CH=CH_2), 3.74 (6H, s, 2 x CO_2CH_3), 3.11 (2H, s, ArCH_2), 2.40 (2H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.4 (2 x C, 2 x O-*C*=O), 142.2 (C), 137.5 (CH), 136.90 (C), 136.85 (C), 130.6 (CH), 128.5 (CH), 127.6 (CH), 127.3 (CH), 126.5 (CH), 115.6 (CH_2, CH=*C*H_2), 67.0 (C), 52.7 (2 x CH_3, 2 x CO_2CH_3), 37.4 (CH_2), 31.0 (CH_2).; LRMS m/z

287.00 (M^+ + 1), calcd for $C_{17}H_{18}O_4$ 286.1205; Anal. calcd. for $C_{17}H_{18}O_4$ (286.1205): C, 71.31; H, 6.34, found C, 71.42; H, 6.29%.

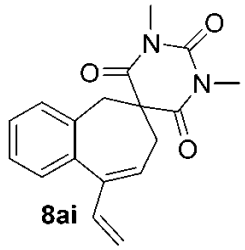


9-Vinyl-5,7-dihydro-benzocycloheptene-6,6-dicarboxylic acid ethyl ester methyl ester (9ahb): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2981, 1736 (O-C=O), 1731 (O-C=O), 1449, 1254, 1214, 1073, 911, 856, 767, 697, 668 and 633 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39 (1H, d, *J* = 7.2 Hz), 7.32-7.23 (3H, m) [Ar-*H*]; 6.52 (1H, dd, *J* = 17.6, 6.8 Hz, C*H*=CH_2), 6.17 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.20 (1H, d, *J* = 17.6 Hz, CH=C*H*$_2$), 5.13 (1H, d, *J* = 11.2 Hz, CH=C*H*$_2$), 4.20 (1H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 4.19 (1H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.74 (3H, s, CO_2CH_3), 3.11 (2H, s, $ArCH_2$), 2.40 (2H, d, *J* = 7.2 Hz), 1.26 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.6 (C, O-*C*=O), 171.0 (C, O-*C*=O), 142.2 (C), 137.5 (CH), 137.0 (2 x C), 130.6 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH), 126.5 (CH), 115.6 (CH_2, CH=*C*H_2), 67.1 (C), 61.6 (CH_2, $CO_2CH_2CH_3$), 52.7 (CH_3, CO_2CH_3), 37.4 (CH_2), 31.1 (CH_2), 14.1 (CH_3, $CO_2CH_2CH_3$).; LRMS m/z 301.00 (M^+ + 1), calcd for $C_{18}H_{20}O_4$ 300.1362; Anal. calcd. for $C_{18}H_{20}O_4$ (300.1362): C, 71.98; H, 6.71, found C, 72.10; H, 6.67%.

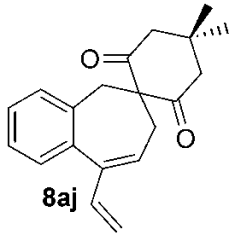


9-Vinyl-5,7-dihydro-benzocycloheptene-6,6-dicarboxylic acid tert-butyl ester methyl ester (9ahc): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2978, 1735 (O-C=O), 1730 (O-C=O), 1443, 1368, 1277, 1254, 1222, 1155, 1074, 993, 911, 850, 770, 746, 683, 633 and 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37 (1H, d, *J* = 7.2 Hz), 7.33-7.22 (3H, m) [Ar-*H*]; 6.54 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.18 (1H, t, *J* = 7.2 Hz, olefinic-*H*), 5.20 (1H, d, *J* = 17.6 Hz, CH=C*H*$_2$), 5.13 (1H, d, *J* = 10.8 Hz, CH=C*H*$_2$), 3.74 (3H, s, CO_2CH_3), 3.07 (2H, ABq, *J* = 16.0 Hz), 2.36 (2H, m), 1.45 (9H, s, 3 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.9 (C, O-*C*=O), 170.0 (C, O-*C*=O), 142.1 (C), 137.6 (CH), 137.2 (C), 137.0 (C), 130.6 (CH), 128.5 (CH), 127.9 (CH), 127.2 (CH), 126.4 (CH), 115.4 (CH_2, CH=*C*H_2), 81.9 (C), 67.8 (C), 52.4 (CH_3, CO_2CH_3), 37.4 (CH_2), 31.1 (CH_2), 27.9 (3 x CH_3).; LRMS m/z 329.00 (M^+ + 1), calcd for $C_{20}H_{24}O_4$ 328.1675; Anal. calcd. for $C_{20}H_{24}O_4$ (328.1675): C, 73.15; H, 7.37, found C, 73.25; H, 7.32%.

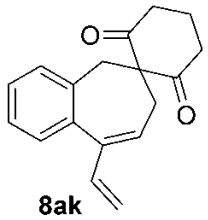
9-ethenyl-1',3'-dimethyl-5,7-dihydro-2'*H*-spiro[benzo[7]annulene-6,5'-pyrimidine]-



2',4',6'(1'*H*,3'*H*)-trione (8ai): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2928, 1686 (N-C=O), 1672, 1667, 1450, 1418, 1375, 1327, 1056, 779 and 624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 4.0 Hz), 7.28-7.24 (1H, m), 7.12 (1H, d, *J* = 7.6 Hz) [Ar-*H*]; 6.58 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.19 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.22 (1H, d, *J* = 17.2 Hz, CH=CH_2), 5.16 (1H, d, *J* = 10.8 Hz, CH=CH_2), 3.32 (6H, s, 2 x NCH_3), 3.08 (2H, s, ArCH_2), 2.45 (2H, d, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.0 (2 x C, 2 x N-*C*=O), 151.3 (C, C=O), 141.7 (C), 137.5 (CH), 136.7 (C), 134.8 (C), 131.0 (CH), 128.8 (CH), 127.44 (CH), 127.32 (CH), 127.22 (CH), 115.8 (CH_2, CH=*C*H_2), 65.5 (C), 41.0 (CH_2), 31.9 (CH_2), 28.9 (2 x CH_3, 2 x NCH_3).; LRMS m/z 311.20 (M^+ + 1), calcd for $C_{18}H_{18}N_2O_3$ 310.1317; Anal. calcd. for $C_{18}H_{18}N_2O_3$ (310.1317): C, 69.66; H,5.85; N, 9.03; found C, 69.54; H, 5.90; N, 9.15%.



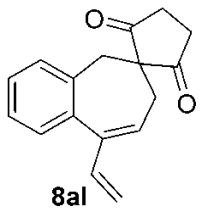
9-ethenyl-4',4'-dimethyl-5,7-dihydro-2'*H*,6'*H*-spiro[benzo[7]annulene-6,1'-cyclohexane]-2',6'-dione (8aj): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2962, 2331, 1724 (C=O), 1691 (C=O), 1446, 1393, 1369, 1320, 1260, 1186, 1144, 1081, 990, 911, 806, 758, 670, 646 and 604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28-7.25 (2H, m), 7.23-7.17 (2H, m) [Ar-*H*]; 6.52 (1H, dd, *J* = 17.6, 10.8 Hz, C*H*=CH_2), 6.19 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.16 (1H, d, *J* = 16.0 Hz, CH=CH_2), 5.11 (1H, d, *J* = 12.0 Hz, CH=CH_2), 2.99 (2H, s, ArCH_2), 2.80 (2H, d, *J* = 12.0 Hz), 2.57 (2H, d, *J* = 12.0 Hz), 2.29 (2H, d, *J* = 8.0 Hz), 1.10 (3H, s, CH_3), 0.92 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 206.9 (2 x C, 2 x C=O), 141.0 (C), 137.5 (CH), 137.0 (C), 135.9 (C), 130.2 (CH), 128.9 (CH), 128.7 (CH), 127.3 (CH), 126.8 (CH), 115.1 (CH_2, CH=*C*H_2), 80.0 (C), 51.3 (2 x CH_2), 38.5 (CH_2), 30.9 (C), 29.3 (CH_3), 28.9 (CH_2), 27.8 (CH_3).; LRMS m/z 295.00 (M^+ + 1), calcd for $C_{20}H_{22}O_2$ 294.1620; Anal. calcd. for $C_{20}H_{22}O_2$ (294.1620): C, 81.60; H,7.53; found C, 81.45; H, 7.48%.



9-ethenyl-5,7-dihydro-2'*H*,6'*H*-spiro[benzo[7]annulene-6,1'-cyclohexane]-2',6'-dione (8ak): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2962, 1724 (C=O), 1692 (C=O), 1443, 1311, 1278, 1187, 1136, 1109, 1032, 993, 913, 768, 733 and 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30-7.25 (2H, m), 7.23-7.19 (2H, m) [Ar-*H*]; 6.52 (1H, dd, *J* = 17.6, 10.8 Hz,

C*H*=CH_2), 6.16 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.16 (1H, d, *J* = 17.6 Hz, CH=C*H*$_2$), 5.10 (1H, d, *J* = 11.2 Hz, CH=C*H*$_2$), 3.03 (2H, s, ArC*H*$_2$), 2.88-2.80 (2H, m), 2.73-2.66 (2H, m), 2.31 (2H, d, *J* = 7.2 Hz), 2.09-1.99 (1H, m), 1.90-1.79 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 206.8 (2 x C, 2 x C=O), 141.1 (C), 137.4 (CH), 136.9 (C), 135.9 (C), 130.1 (CH), 128.7 (2 x CH), 127.3 (CH), 126.8 (CH), 115.1 (CH_2, CH=*C*H_2), 81.4 (C), 38.2 (CH_2), 37.4 (2 x CH_2), 28.8 (CH_2), 18.3 (CH_2).; LRMS m/z 267.05 (M^+ + 1), calcd for $C_{18}H_{18}O_2$ 266.1307; Anal. calcd. for $C_{18}H_{18}O_2$ (266.1307): C, 81.17; H, 6.81; found C, 81.25; H, 6.76%.

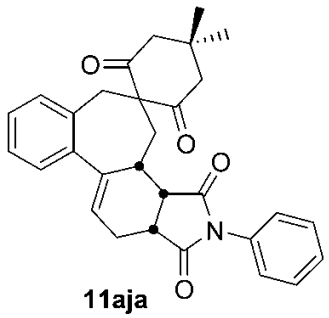
9-ethenyl-5,7-dihydro-2'*H*,5'*H*-spiro[benzo[7]annulene-6,1'-cyclopentane]-2',5'-dione (8al):



8al

Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν_{max} 2920, 1721 (C=O), 1446, 1420, 1277, 1157, 1031, 992, 912, 855, 770, 732 and 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34-7.24 (3H, m), 7.15 (1H, d, *J* = 7.2 Hz) [Ar-*H*]; 6.58 (1H, dd, *J* = 17.6, 11.2 Hz, C*H*=CH_2), 6.10 (1H, t, *J* = 7.6 Hz, olefinic-*H*), 5.22 (1H, d, *J* = 17.6 Hz, CH=C*H*$_2$), 5.16 (1H, d, *J* = 10.8 Hz, CH=C*H*$_2$), 2.92-2.80 (4H, m), 2.78 (2H, s, ArC*H*$_2$), 2.10 (2H, d, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 213.1 (2 x C, 2 x C=O), 142.2 (C), 137.5 (CH), 136.6 (C), 134.7 (C), 130.6 (CH), 128.8 (CH), 127.5 (CH), 127.0 (CH), 126.2 (CH), 115. (CH_2, CH=*C*H_2), 69.9 (C), 36.6 (CH_2), 34.4 (2 x CH_2), 29.3 (CH_2).; LRMS m/z 252.00 (M^+), calcd for $C_{17}H_{16}O_2$ 252.1150; Anal. calcd. for $C_{17}H_{16}O_2$ (252.1150): C, 80.93; H, 6.39; found C, 80.96; H, 6.34%.

4',4'-Dimethyl-2-phenylspiro[1,2,3,3a,3b,4,5,6,12,12a-decahydrobenzo[3,4]cyclohepta[e]isoindole-5,1'-cyclohexane]-1,2',3,6'-tetraone (11aja):

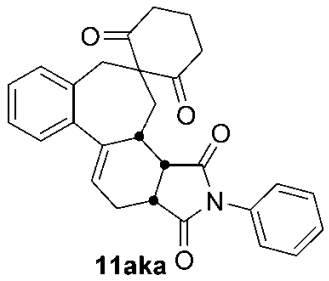


11aja

Purified by column chromatography using EtOAc/hexane and isolated as a solid; IR (neat) ν_{max} 1698 (C=O), 1494, 1439, 1378, 1318, 1244, 1196, 1174, 1073, 915, 758, 734, 691, 672 and 630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45 (2H, t, *J* = 7.6 Hz), 7.38 (1H, t, *J* = 7.6 Hz), 7.27-7.15 (5H, m), 6.98 (1H, dd, *J* = 7.2, 1.2 Hz) [Ar-*H*]; 6.04 (1H, m, olefinic-*H*), 3.34 (1H, t, *J* = 7.2 Hz), 3.24-3.16 (2H, m), 3.00-2.91 (2H, m), 2.82-2.75 (3H, m), 2.66-2.57 (2H, m), 2.48-2.33 (3H, m), 1.05 (3H, s, C*H*$_3$), 0.99 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.0 (C, C=O), 206.4 (C, C=O), 178.5 (C, N-C=O), 176.2 (C, N-C=O), 145.2 (C), 139.0 (C), 133.9 (C), 131.8 (C), 130.6 (CH), 129.0 (2 x CH), 128.5 (CH), 127.9 (CH), 127.6 (CH), 126.8 (CH), 126.2 (2 x CH), 125.0 (CH), 67.9 (C), 51.4 (CH_2), 50.9 (CH_2), 45.3 (CH), 40.8 (CH), 34.5 (CH_2), 33.7 (CH), 32.2 (CH_2), 30.8 (C), 28.9

(CH_3), 28.0 (CH_3), 25.2 (CH_2).; LRMS m/z 467.00 (M^+), calcd for $C_{30}H_{29}NO_4$ 467.2097; Anal. calcd. for $C_{30}H_{29}NO_4$ (467.2097): C, 77.06; H, 6.25; N, 3.00; found C, 77.14; H, 6.21; N, 3.10%.

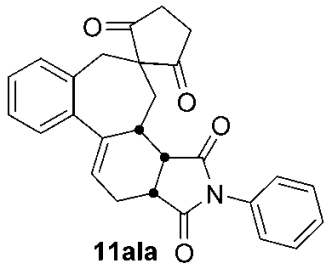
2-Phenylspiro[1,2,3,3a,3b,4,5,6,12,12a-decahydrobenzo[3,4]cyclohepta[e]isoindole-5,1'-cyclohexane]-1,2',3,6'-tetraone (11aka): Purified by column chromatography using



11aka

EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2297, 1705 (C=O), 1493, 1439, 1377, 1312, 1196, 1117, 832, 780, 690, 667, 653 and 621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48 (2H, t, *J* = 7.6 Hz), 7.36 (1H, t, *J* = 7.6 Hz), 7.30-7.18 (5H, m), 7.03 (1H, dd, *J* = 7.2, 1.6 Hz) [Ar-*H*]; 6.04 (1H, m, olefinic-*H*), 3.41-3.37 (1H, m), 3.28-3.19 (2H, m), 3.04-2.98 (2H, m), 2.93-2.70 (5H, m), 2.52-2.36 (3H, m), 2.09-1.87 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 209.0 (C, C=O), 206.4 (C, C=O), 178.5 (C, N-C=O), 176.2 (C, N-C=O), 145.2 (C), 139.0 (C), 133.9 (C), 131.8 (C), 130.7 (CH), 129.1 (2 x CH), 128.5 (CH), 127.9 (CH), 127.6 (CH), 126.9 (CH), 126.3 (2 x CH), 125.0 (CH), 69.3 (C), 45.4 (CH), 40.8 (CH), 37.7 (CH_2), 37.1 (CH_2), 34.2 (CH_2), 33.7 (CH), 32.1 (CH_2), 25.2 (CH_2), 18.3 (CH_2).; LRMS m/z 440.30 (M^+ + 1), calcd for $C_{28}H_{25}NO_4$ 439.1784; Anal. calcd. for $C_{28}H_{25}NO_4$ (439.1784): C, 76.52; H, 5.73; N, 3.19; found C, 76.44; H, 5.78; N, 3.25%.

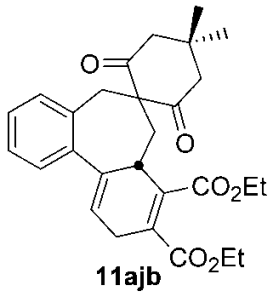
2-Phenylspiro[1,2,3,3a,3b,4,5,6,12,12a-decahydrobenzo[3,4]cyclohepta[e]isoindole-5,1'-cyclopentane]-1,2',3,5'-tetraone (11ala): Purified by column chromatography using



11ala

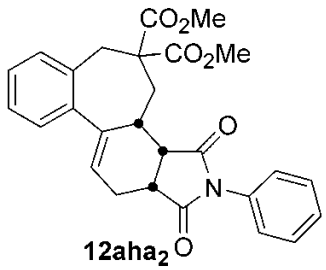
EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 3730, 1766, 1722 (C=O), 1701 (N-C=O), 1493, 1389, 1320, 1288, 1193, 1098, 1039, 828, 757, 695, 667 and 636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49-7.44 (2H, m), 7.41-7.37 (1H, m), 7.29-7.25 (2H, m), 7.20-7.17 (2H, m), 7.10-7.06 (2H, m) [Ar-*H*]; 6.12 (1H, m, olefinic-*H*), 3.43 (1H, br t, *J* = 7.6 Hz), 3.24-3.17 (2H, m), 3.07-3.01 (2H, m), 2.96-2.82 (4H, m), 2.54-2.45 (2H, m), 2.27 (1H, dd, *J* = 14.8, 12.0 Hz), 1.98 (1H, d, *J* = 14.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 215.9 (C, C=O), 212.6 (C, C=O), 178.5 (C, N-C=O), 176.1 (C, N-C=O), 145.1 (C), 139.0 (C), 132.4 (C), 131.7 (C), 130.3 (CH), 129.1 (2 x CH), 128.6 (CH), 128.15 (CH), 128.10 (CH), 127.3 (CH), 126.3 (2 x CH), 125.6 (CH), 57.6 (C), 45.2 (CH), 40.9 (CH), 34.8 (CH_2), 34.7 (CH_2), 34.2 (CH_2), 32.1 (CH), 31.0 (CH_2), 25.3 (CH_2).; LRMS m/z 426.30 (M^+ + 1), calcd for $C_{27}H_{23}NO_4$ 425.1627; Anal calcd for $C_{27}H_{23}NO_4$ (425.1627): C, 76.22; H, 5.45; N, 3.29; found C, 76.15; H, 5.49; N, 3.35%.

Diethyl 4,4-dimethyl-2,6-dioxospiro[cyclohexane-1,6'-(4a',5',6',7'-tetrahydro-2'*H*-dibenzo[a,c]cycloheptene)]-3',4'-dicarboxylate (11ajb): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2958, 1722 (C=O), 1694 (O-C=O), 1645, 1446, 1392, 1369, 1289, 1260, 1237, 1183, 1071, 1052, 1020, 732 and 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22-7.16 (3H, m), 7.13-7.09 (1H, m) [Ar-*H*]; 5.74 (1H, dd, *J* = 4.8, 2.8 Hz, olefinic-*H*), 4.30-4.22 (4H, q, *J* = 7.2 Hz, 2 x $CO_2CH_2CH_3$), 3.70-3.64 (1H, m), 3.21-3.15 (4H, m), 2.82 (1H, d, *J* = 15.2 Hz), 2.71-2.57 (4H, m), 2.00 (1H, dd, *J* = 13.6, 12.0 Hz), 1.34 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 1.29 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 1.09 (3H, s, CH_3), 0.95 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 207.9 (C, C=O), 207.3 (C, C=O), 167.7 (C, O-C=O), 167.3 (C, O-C=O), 142.5 (C), 141.1 (C), 137.6 (C), 134.7 (C), 133.4 (C), 129.7 (CH), 128.0 (CH), 127.4 (CH), 127.2 (CH), 121.4 (CH), 66.8 (C), 61.19 (CH_2, $CO_2CH_2CH_3$), 61.17 (CH_2, $CO_2CH_2CH_3$), 52.1 (CH_2), 50.5 (CH_2), 41.1 (CH_2), 39.8 (CH_2), 36.6 (CH), 30.6 (C), 29.1 (CH_3), 28.4 (CH_2), 28.1 (CH_3), 13.96 (CH_3, $CO_2CH_2CH_3$), 13.94 (CH_3, $CO_2CH_2CH_3$).; LRMS m/z 463.00 (M^+ - 1), calcd for $C_{28}H_{32}O_6$ 464.2199; Anal. calcd. for $C_{28}H_{32}O_6$ (464.2199): C, 72.39; H, 6.94; found C, 72.61; H, 6.80%.



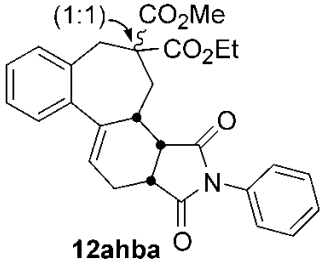
11ajb

1,3-Dioxo-2-phenyl-2,3,3a,3b,4,6,12,12a-octahydro-1*H*-2-aza-benzo[3,4]cyclohepta[1,2-e]indene-5,5-dicarboxylic acid dimethyl ester (12aha$_2$): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2929, 1730 (O-C=O), 1701 (N-C=O), 1595, 1444, 1384, 1278, 1199, 1162, 1096, 1030, 943, 850, 822, 758, 690, 656, 631 and 608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44 (2H, t, *J* = 8.0 Hz), 7.36 (1H, t, *J* = 7.2 Hz), 7.26-7.18 (5H, m), 7.04 (1H, d, *J* = 4.8 Hz) [Ar-*H*]; 6.06 (1H, t, *J* = 3.2 Hz), 3.81 (3H, s, CO_2CH_3), 3.68 (3H, s, CO_2CH_3), 3.41-3.34 (3H, m), 3.02-2.92 (3H, m), 2.69 (1H, d, *J* = 15.2 Hz), 2.40-2.37 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 178.6 (C, O-C=O), 176.2 (C, O-C=O), 172.1 (C, N-C=O), 170.9 (C, N-C=O), 145.5 (C), 139.4 (C), 133.4 (C), 131.8 (C), 130.3 (CH), 129.0 (2 x CH), 128.4 (CH), 127.97 (CH), 127.9 (CH), 126.9 (CH), 126.2 (2 x CH), 125.1 (CH), 56.6 (C), 52.8 (CH_3, CO_2CH_3), 52.6 (CH_3, CO_2CH_3), 45.3 (CH), 40.7 (CH), 36.2 (CH_2), 34.5 (CH), 32.0 (CH_2), 25.3 (CH_2).; LRMS m/z 460.00 (M^+ + 1), calcd for $C_{27}H_{25}NO_6$ 459.1682; Anal. calcd. for $C_{27}H_{25}NO_6$ (459.1682): C, 70.58; H, 5.48; N, 3.05; found C, 70.49; H, 5.52; N, 3.10%.



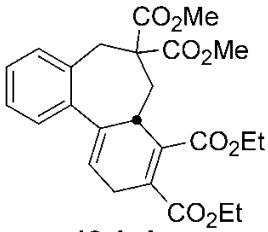
12aha$_2$

1,3-Dioxo-2-phenyl-2,3,3a,3b,4,6,12,12a-octahydro-1H-2-aza-benzo[3,4]cyclohepta[1,2-e]indene-5,5-dicarboxylic acid ethyl ester methyl ester (12ahba): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2955, 1730 (O-C=O), 1710 (N-C=O), 1597, 1494, 1451, 1383, 1275, 1202, 1164, 1094, 1032, 944, 854, 755, 691, 656, 630 and 608 cm^{-1}; ^1H NMR ($CDCl_3$, 1:1 mixture of two diastereomers) δ 7.38-6.94 (18H, m) [Ar-*H*]; 5.98-5.96 (2H, br s, 2 x olefinic-*H*), 4.22-4.01 (4H, m, 2 x $CO_2CH_2CH_3$), 3.72 (3H, s, CO_2CH_3), 3.59 (3H, s, CO_2CH_3), 3.34-3.23 (6H, m), 2.95-2.84 (6H, m), 2.60 (2H, d, *J* = 12.0 Hz), 2.34-2.24 (4H, m), 1.23 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 1.21 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, 1:1 mixture of two diastereomers) δ 178.7 (2 x C, 2 x O-C=O), 176.3 (2 x C, 2 x O-C=O), 172.4 (C, N-C=O), 171.7 (C, N-C=O), 171.0 (C, N-C=O), 170.5 (C, N-C=O), 145.6 (2 x C), 139.5 (2 x C), 133.6 (2 x C), 131.9 (2 x C), 130.47 (CH), 130.40 (CH), 129.1 (4 x CH), 128.6 (2 x CH), 128.1 (CH), 128.0 (CH), 127.9 (2 x CH), 127.0 (2 x CH), 126.4 (2 x CH), 126.3 (2 x CH), 125.1 (2 x CH), 61.8 (CH_2, $CO_2CH_2CH_3$), 61.6 (CH_2, $CO_2CH_2CH_3$), 56.7 (2 x C), 52.8 (CH_3, CO_2CH_3), 52.6 (CH_3, CO_2CH_3), 45.4 (2 x CH), 40.8 (2 x CH), 36.2 (2 x CH_2), 34.6 (2 x CH), 32.1 (2 x CH_2), 25.4 (2 x CH_2), 14.1 (CH_3, $CO_2CH_2CH_3$), 14.0 (CH_3, $CO_2CH_2CH_3$).; LRMS m/z 474.00 (M^+ + 1), calcd for $C_{28}H_{27}NO_6$ 473.1838; Anal. calcd. for $C_{28}H_{27}NO_6$ (473.1838): C, 71.02; H, 5.75; N, 2.96; found C, 71.12; H, 5.68; N, 3.07%.



12ahba

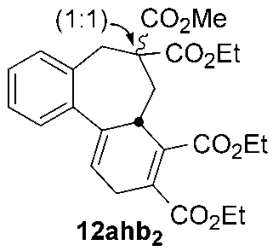
2,4a,5,7-Tetrahydro-dibenzo[a,c]cycloheptene-3,4,6,6-tetracarboxylic acid 3,4-diethyl ester 6,6-dimethyl ester (12ahab): Purified by column chromatography using EtOAc/hexane and isolated as a liquid; IR (neat) ν_{max} 2958, 1736 (O-C=O), 1730 (O-C=O), 1679, 1645, 1444, 1367, 1242, 1177, 1070, 932, 818, 757, 637 and 604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21-7.14 (3H, m), 7.11-7.08 (1H, m) [Ar-*H*]; 5.79 (1H, dd, *J* = 4.8, 2.4 Hz, olefinic-*H*), 4.34-4.24 (4H, m, 2 x $CO_2CH_2CH_3$), 3.74 (3H, s, CO_2CH_3), 3.61 (3H, s, CO_2CH_3), 3.55 (1H, m), 3.44-3.00 (4H, m), 2.88 (1H, br d, *J* = 13.2 Hz), 1.85 (1H, t, *J* = 12.8 Hz), 1.33 (6H, t, *J* = 7.2 Hz, 2 x $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 172.0 (C, O-C=O), 169.6 (C, O-C=O), 167.4 (2 x C, 2 x O-C=O), 143.0 (C), 140.5 (C), 138.6 (C), 134.4 (C), 132.0 (C), 130.7 (CH), 127.8 (CH), 127.3 (CH), 127.2 (CH), 121.5 (CH), 61.24 (CH_2, $CO_2CH_2CH_3$), 61.18 (CH_2, $CO_2CH_2CH_3$), 56.0 (C), 52.9 (CH_3, CO_2CH_3), 52.0 (CH_3, CO_2CH_3), 41.0 (CH_2), 40.0 (CH_2),



12ahab

37.2 (CH), 28.0 (CH_2), 13.9 (2 x CH_3, 2 x $CO_2CH_2CH_3$).; LRMS m/z 455.85 (M^+ - 1), calcd for $C_{25}H_{28}O_8$ 456.1784; Anal. calcd. for $C_{25}H_{28}O_8$ (456.1784): C, 65.78; H, 6.18, found C, 65.87; H, 6.13%.

2,4a,5,7-Tetrahydro-dibenzo[a,c]cycloheptene-3,4,6,6-tetracarboxylic acid 3,4,6-triethyl ester 6-methyl ester (12ahb$_2$): Purified by column chromatography using EtOAc/hexane and



12ahb$_2$

isolated as a liquid; IR (neat) ν_{max} 2983, 1736 (OC=O), 1728 (OC=O), 1644, 1445, 1368, 1241, 1180, 1099, 1069 and 758 cm^{-1}; ^{1}H NMR ($CDCl_3$, 1:1 mixture of two diastereomers) δ 7.19-7.14 (6H, m), 7.09-7.07 (2H, m) [Ar-*H*]; 5.79 (2H, m, olefinic-*H*), 4.33-4.23 (8H, m, 4 x $CO_2CH_2CH_3$), 4.20-4.17 (2H, m, $CO_2CH_2CH_3$), 4.04-4.02 (2H, m, $CO_2CH_2CH_3$), 3.73 (3H, s, CO_2CH_3), 3.59 (3H, s, CO_2CH_3), 3.58 (2H, m), 3.40-3.10 (8H, m), 2.86 (2H, m), 1.87 (2H, m), 1.32 (12H, t, *J* = 6.0 Hz, 4 x $CO_2CH_2CH_3$), 1.24 (3H, t, *J* = 6.0 Hz, $CO_2CH_2CH_3$), 1.13 (3H, t, *J* = 6.0 Hz, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, 1:1 mixture of two diastereomers) δ 172.2 (C, O-C=O), 171.6 (C, O-C=O), 169.8 (C, O-C=O), 169.2 (C, O-C=O), 167.57 (C, O-C=O), 167.51 (C, O-C=O), 167.43 (C, O-C=O), 167.36 (C, O-C=O), 143.08 (C), 143.01 (C), 140.6 (2 x C), 138.9 (C), 138.7 (C), 134.54 (C), 134.45 (C), 132.0 (C), 131.8 (C), 131.0 (CH), 130.7 (CH), 127.8 (2 x CH), 127.36 (CH), 127.26 (CH), 127.2 (2 x CH), 121.5 (2 x CH), 61.8 (CH_2, $CO_2CH_2CH_3$), 61.29 (2 x CH_2, 2 x $CO_2CH_2CH_3$), 61.24 (2 x CH_2, 2 x $CO_2CH_2CH_3$), 61.1 (CH_2, $CO_2CH_2CH_3$), 56.1 (C), 55.9 (C), 52.8 (CH_3, CO_2CH_3), 52.0 (CH_3, CO_2CH_3), 41.0 (CH_2), 40.9 (CH_2), 40.0 (2 x CH_2), 37.3 (2 x CH), 28.03 (CH_2), 27.99 (CH_2), 14.0 (6 x CH_3, 6 x $CO_2CH_2CH_3$).; LRMS m/z 469.40 (M^+ - 1), calcd for $C_{26}H_{30}O_8$ 470.1941; Anal. calcd. for $C_{26}H_{30}O_8$ (470.1941): C, 66.37; H, 6.43; found C, 66.28; H, 6.47%.