

SUPPORTING INFORMATION

Title: Development of Pharmaceutical Drugs, Drug Intermediates and Ingredients by Using Direct Organo-Click Reactions

Author(s): Dhevalapally B. Ramachary,* Mamillapalli Kishor, Y. Vijayendar Reddy

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General Methods: The ^1H 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 ($\delta = 0$ ppm) for ^1H NMR spectra and relative to the central CDCl_3 resonance ($\delta = 77.0$ ppm) for ^{13}C NMR spectra. Coupling constants in ^1H NMR measurements are given in Hz. *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.* 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. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a $\text{Mo-K}\alpha$ fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$). For

thin-layer chromatography (TLC), silica gel plates Merck 60 F₂₅₄ were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H₂SO₄ (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. CH-Acids **3g-h**^[1a] and **3o**^[2b]; spiro-ketones **2h**,^[2a] and **2i**^[2b] are prepared according to literature procedures. (1-Bromomethyl-vinyl)-benzene **5f** is synthesized according to literature procedure.^[1b]

General Experimental Procedures for Organo-Click Reactions:

Amine or Amino acid-catalyzed cascade olefination-hydrogenation reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.5 mmol of the aldehyde **1** or ketone **2**, 0.5 mmol of CH-acid **3** and 0.5 mmol of Hantzsch ester **4** was added 1.0 mL of solvent, and then the catalyst amine or amino acid **6** (0.025 mmol to 0.1 mmol) was added and the reaction mixture was stirred at 25 °C for the time indicated in Tables 1-5 and 7-9. The crude reaction mixture was directly loaded on silica gel column with or without aqueous work-up and pure cascade products **10** and **12** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Proline-Cs₂CO₃ or K₂CO₃-catalyzed olefination-hydrogenation-alkylation reactions in one-pot: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.5 mmol of the aldehyde **1** or ketone **2**, 0.5 mmol of CH-acid **3** and 0.5 mmol of Hantzsch ester **4** was added 1.0 mL of solvent, and then the catalyst proline **6a** (0.1 mmol) was added and the reaction mixture was stirred at 25 °C for 1-96 h then R⁴CH₂I or R⁴CH₂Br **5** (2.5 mmol) and K₂CO₃ or Cs₂CO₃ (0.4 g) was added and stirring continued at the same temperature for 7-24 h. The crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure one-pot products **11** and **13** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Amine/acid-catalyzed hydrogenation-olefination-hydrogenation reactions in one-pot: In an ordinary glass vial equipped with a magnetic stirring bar, to morpholine **6e** (0.05 mmol, 5 mol%) and trifluoro-acetic acid

(0.05 mmol, 5 mol%) were added and stirred at 25 °C for 10 minutes then THF solvent (4.0 mL), *trans*-cinnamaldehyde **1e'** or *o*-nitrocinnamaldehyde **1f'** (1.0 mmol) and Hantzsch ester **4** (1.0 mmol) were added and stirring was continued at the same temperature for the time indicated in Scheme 5. After completion of the hydrogenation, to the crude reaction mixture were added 1.0 equiv of Meldrum's acid **3c** and 1.0 equiv of Hantzsch ester **4** and stirring was continued at the same temperature for the time indicated in Scheme 5. The crude reaction mixture was worked up with aqueous NaHCO₃ and NH₄Cl solutions and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure one-pot products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Amino acid-catalyzed olefination-hydrogenation-hydrolysis reactions in one-pot: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.5 mmol of the aldehyde **1a**, 0.5 mmol of Meldrum's acid **3c** and 0.5 mmol of Hantzsch ester **4** was added 1.0 mL of EtOH, and then the catalyst amino acid **6a** (0.1 mmol) was added and the reaction mixture was stirred at 25 °C for the time indicated in Scheme 2. To the crude reaction mixture added 0.5 mL of HCO₂H, 1.8 mL of NEt₃ and stirred at 120 °C for the 12 h. The crude reaction mixture was worked up with aqueous NaHCO₃ and NH₄Cl solutions and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure one-pot product **15ac** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

CuSO₄/Cu-Catalyzed Huisgen cycloaddition Reaction: For the synthesis of highly functionalized-triazole **17**, reactants O/H/A-cascade product **13hfd** (0.22 mmol), benzyl azide **16** (0.44 mmol), CuSO₄ (0.22 mmol, 35 mg) and Cu wire (23 mg) in ethanol (1.0 mL) was taken in an ordinary glass vial equipped with a magnetic stirring bar and stirred at 25 °C for the time indicated in Scheme 6. The crude reaction mixture was directly loaded on silica gel column without aqueous work-up and pure triazole **17** was obtained by flash column chromatography (silica gel, mixture of hexane/ethyl acetate).

Many of the cascade products **10** to **17** are commercially available or have been described previously, and their analytical data match literature values; and new compounds were characterized on the basis of IR, ^1H and ^{13}C NMR and analytical data.

5-Benzyl-1,3-dimethyl-pyrimidine-2,4,6-trione (10aa): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 90 °C. IR (neat): ν_{max} 2924, 2852, 1687, 1450, 1381, 1288, 1105, 794, 752 and 704 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.23 (3H, m), 7.03 (2H, m) [Ar-*H*]; 3.77 (1H, t, J = 4.8 Hz), 3.46 (2H, d, J = 4.8 Hz), 3.12 (6H, s, 2 x N- CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.2 (C, 2 x N-C=O), 150.9 (C, C=O), 135.1 (C), 128.8 (2 x CH), 128.6 (2 x CH), 127.8 (CH), 50.7 (CH), 37.8 (CH_2), 28.1 (2 x CH_3 , 2 x N- CH_3); LRMS: m/z 245.05 (M-H^+), calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$ 246.1004.

5-Benzyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (10ac): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 62 °C. IR (KBr): ν_{max} 2982, 2932, 1720, 1689, 1593, 1444, 1379, 1292, 1043, 852, 771 and 707 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.33-7.23 (5H, m) [Ar-*H*]; 3.77 (1H, t, J = 4.8 Hz), 3.49 (2H, d, J = 4.8 Hz), 1.73 (3H, s, CH_3), 1.49 (3H, s, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.3 (C, 2 x O-C=O), 137.2 (C), 129.7 (2 x CH), 128.6 (2 x CH), 127.2 (CH), 105.2 (C, O-C-O), 48.1 (CH), 32.1 (CH_2), 28.4 (CH_3), 27.2 (CH_3); LRMS: m/z 233.00 (M-H^+), calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4$ 234.0892.

2-Benzyl-indan-1,3-dione (10ad): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 191 °C. IR (neat): ν_{max} 2982, 1716, 1597, 1444, 1371, 1284, 1253, 1107, 1043, 771, 756 and 702 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.88 (2H, m), 7.76 (2H, m), 7.12 (5H, m) [Ar-*H*]; 3.34 (3H, s, *CH* and CH_2Ph); ^{13}C NMR (CDCl_3 , DEPT-135) δ 199.9 (2 x C, O-C=O), 142.5 (2 x C), 137.0 (C), 135.5 (2 x CH), 129.5 (2 x CH), 128.2 (2 x CH), 126.6 (CH), 123.0 (2 x CH), 55.0 (CH), 32.2 (CH_2); LRMS: m/z 235.00 (M-H^+), calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2$ 236.0837.

2-Cyano-3-phenyl-propionic acid ethyl ester (10af): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{max} 3034, 2986, 2939, 2251 ($\text{C}\equiv\text{N}$), 1745 (O-C=O), 1604, 1496, 1263, 1082, 858, 750 and 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.34-7.26 (5H, m) [Ar-*H*]; 4.23 (2H, q, J = 7.2 Hz, OCH_2CH_3), 3.71 (1H, dd, J = 8.0, 5.6 Hz), 3.30-3.16 (2H, dABq, J = 14.0, 6.0 Hz, Ph- CH_2), 1.26 (3H, t, J = 6.8 Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.4 (C, O-C=O), 135.2 (C), 129.0 (2 x CH), 128.8 (2 x CH), 127.7 (CH), 116.1 (C, $\text{C}\equiv\text{N}$), 62.8 (CH_2 , OCH_2CH_3), 39.6 (CH), 35.7 (CH_2 , Ph CH_2), 13.9 (CH_3 , OCH_2CH_3); LRMS: m/z 202.05 (M-H^+), calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ 203.0946.

2-Cyano-3-phenyl-propionic acid allyl ester (10ag): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): ν_{max} 3032, 2941, 2251 ($\text{C}\equiv\text{N}$), 1748 (O-C=O), 1649, 1605, 1497, 1455, 1271, 1190, 1082, 993, 941, 750 and 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.39-7.28 (5H, m) [Ar-*H*]; 5.92-5.84 (1H, m, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.35 (1H, d, J = 17.2 Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.30 (1H, d, J = 10.4 Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.69 (2H, d, J = 6.0 Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 3.78 (1H, dd, J = 8.4, 6.0 Hz), 3.27 (2H, dABq,

$J = 14.0, 5.6$ Hz, Ph-CH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 165.2 (C, O-C=O), 135.2 (C), 130.6 (CH), 129.0 (2 x CH), 128.9 (2 x CH), 127.8 (CH), 119.7 (CH₂), 115.9 (C, C $\equiv$ N), 67.2 (CH₂, OCH₂C=CH₂), 39.7 (CH), 35.8 (CH₂); LRMS: m/z 215.00 (M⁺), calcd for C₁₃H₁₃NO₂ 215.10; Anal. calcd for C₁₃H₁₃NO₂ (215.10): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.548; H, 6.046; N, 6.517%.

2-Cyano-3-phenyl-propionic acid prop-2-ynyl ester (10ah): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 3291, 2939, 2253 (C $\equiv$ N), 2131 (C $\equiv$ C), 1755 (O-C=O), 1604, 1496, 1373, 1267, 1082, 1030 and 1001 cm⁻¹; ¹H NMR (CDCl₃) δ 7.39-7.28 (5H, m) [Ar-H]; 4.79 (2H, s, OCH₂C $\equiv$ CH), 3.81 (1H, dd, $J = 8.4, 6.0$ Hz), 3.28 (2H, dABq, $J = 14.0, 6.0$ Hz), 2.57 (1H, t, $J = 2.4$ Hz, OCH₂C $\equiv$ CH); ¹³C NMR (CDCl₃, DEPT-135) δ 164.8 (C, O-C=O), 134.9 (C), 128.98 (2 x CH), 128.87 (2 x CH), 127.8 (CH), 115.5 (C, C $\equiv$ N), 76.2 (CH, CH₂C $\equiv$ CH), 76.1 (C, CH₂C $\equiv$ CH), 53.9 (CH₂, OCH₂C $\equiv$ CH), 39.7 (CH), 35.7 (CH₂, PhCH₂); LRMS: m/z 213.00 (M⁺), calcd for C₁₃H₁₁NO₂ 213.08; Anal. calcd for C₁₃H₁₁NO₂ (213.08): C, 73.22; H, 5.20; N, 6.57. Found: C, 73.379; H, 5.192; N, 6.452%.

2-Benzyl-malononitrile (10aj): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 88 °C. IR (KBr): $\nu_{\max}$ 3036, 2914, 2256 (C $\equiv$ N), 1495, 1454, 1074, 1030, 748 and 702 cm⁻¹; ¹H NMR (CDCl₃) δ 7.41-7.26 (5H, m) [Ar-H]; 3.91 (1H, t, $J = 6.8$ Hz, CH), 3.29 (2H, d, $J = 6.8$ Hz, PhCH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 132.9 (C), 129.3 (2 x CH), 129.1 (2 x CH), 128.8 (CH), 112.1 (2 x C, C $\equiv$ N), 36.7 (CH₂), 25.0 (CH). LRMS: m/z 155.10 (M-1), calcd for C₁₀H₈N₂ 156.0687.

2-Nitro-3-phenyl-propionic acid ethyl ester (10ak): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2926, 1749 (O-C=O), 1560, 1456, 1373, 750 and 698 cm⁻¹; ¹H NMR (CDCl₃) δ 7.34-7.20 (5H, m) [Ar-H]; 5.33 (1H, dd, $J = 9.2, 6.0$ Hz), 4.28 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 3.52 (2H, dABq, $J = 14.8, 9.6$ Hz, PhCH₂), 1.28 (3H, t, $J = 7.2$ Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 164.0 (C, O-C=O), 134.1 (C), 129.0 (2 x CH), 128.8 (2 x CH), 127.8 (CH), 89.2 (CH), 63.2 (CH₂, OCH₂CH₃), 36.2 (CH₂, PhCH₂), 13.8 (CH₃, OCH₂CH₃); LRMS: m/z 222.05 (M-H⁺), calcd for C₁₁H₁₃NO₄ 223.08.

2-Cyano-3-naphthalen-1-yl-propionic acid ethyl ester (10bf): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 3053, 2984, 2251 (C $\equiv$ N), 1744 (O-C=O), 1599, 1512, 1460, 1369, 1258, 1028, 856, 777 and 736 cm⁻¹; ¹H NMR (CDCl₃) δ 7.93 (1H, d, $J = 8.4$ Hz), 7.87 (1H, d, $J = 8.4$ Hz), 7.79 (1H, d, $J = 8.0$ Hz), 7.56-7.39 (4H, m) [Ar-H]; 4.22 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 3.89-3.80 (2H, m, ArCH₂), 3.52 (1H, dd, $J = 15.6, 10.8$ Hz, CH), 1.24 (3H, t, $J = 7.2$ Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.6 (C, O-C=O), 133.9 (C), 131.1 (C), 131.0 (C), 129.2 (CH), 128.6 (CH), 127.8 (CH), 126.6 (CH), 125.9 (CH), 125.4 (CH), 122.4 (CH), 116.1 (C, C $\equiv$ N), 62.9 (CH₂, OCH₂CH₃), 38.7 (CH), 33.0 (CH₂, ArCH₂), 13.8 (CH₃, OCH₂CH₃); LRMS: m/z 253.10 (M⁺), calcd for C₁₆H₁₅NO₂ 253.1103.

2-Cyano-3-naphthalen-2-yl-propionic acid methyl ester (10ce): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 54-56°C; IR (neat): $\nu_{\max}$ 2955, 2251 (C $\equiv$ N), 1749 (O-C=O), 1601, 1510, 1437, 1269, 1024, 897, 862, 816, 788 and 748 cm⁻¹; ¹H NMR (CDCl₃) δ 7.84 (3H, m), 7.77 (1H, s), 7.50 (2H, m), 7.39 (1H, dd, $J = 8.4, 1.72$ Hz) [Ar-H]; 3.85 (1H, dd, $J = 8.3, 5.7$ Hz), 3.81 (3H, s,

OCH₃), 3.44 (2H, dABq, $J = 13.8, 5.7$ Hz, ArCH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 166.0 (C, O-C=O), 133.4 (C), 132.8 (C), 132.7 (C), 128.8 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 126.7 (CH), 126.4 (CH), 126.2 (CH), 116.1 (C, C $\equiv$ N), 53.6 (CH₃, OCH₃), 39.5 (CH), 35.9 (CH₂, ArCH₂); LRMS: m/z 239.0 (M⁺), calcd for C₁₅H₁₃NO₂ 239.0946.

2-Cyano-3-p-tolyl-propionic acid ethyl ester (10ef): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 2986, 2930, 2251 (C $\equiv$ N), 1747 (O-C=O), 1616, 1516, 1028, 856 and 806 cm⁻¹; ¹H NMR (CDCl₃) δ 7.15 (4H, s) [Ar-H]; 4.23 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 3.70 (1H, dd, $J = 8.4, 5.6$ Hz), 3.22 (2H, dABq, $J = 13.6, 5.6$ Hz, PhCH₂), 2.36 (3H, s, PhCH₃), 1.29 (3H, t, $J = 7.2$ Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.5 (C, O-C=O), 137.4 (C), 132.2 (C), 129.5 (2 x CH), 128.8 (2 x CH), 116.2 (C, C $\equiv$ N), 62.8 (CH₂, OCH₂CH₃), 39.8 (CH), 35.3 (CH₂, PhCH₂), 21.0 (CH₃), 13.9 (CH₃, OCH₂CH₃); LRMS: m/z 215.80 (M-H⁺), calcd for C₁₃H₁₅NO₂ 217.1103.

2-Cyano-3-(2,4,6-trimethyl-phenyl)-propionic acid ethyl ester (10ff): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 70°C; IR (KBr): $\nu_{\max}$ 2988, 2916, 2247 (C $\equiv$ N), 1728 (O-C=O), 1612, 1468, 1369, 1258, 854 and 737 cm⁻¹; ¹H NMR (CDCl₃) δ 6.75 (2H, s) [Ar-H]; 4.15 (2H, q, $J = 7.0$ Hz, OCH₂CH₃), 3.52 (1H, dd, $J = 10.0, 6.0$ Hz, CH), 3.17 (2H, dABq, $J = 13.0, 6.0$ Hz, PhCH₂), 2.29 (6H, s, 2 x CH₃), 2.13 (3H, s, CH₃), 1.19 (3H, t, $J = 7.1$ Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 166.0 (C, O-C=O), 137.1 (C), 136.7 (2 x C), 129.6 (2 x CH), 129.3 (C), 116.4 (C, C $\equiv$ N), 63.0 (CH₂, OCH₂CH₃), 37.5 (CH), 29.4 (CH₂, PhCH₂), 20.9 (CH₃, PhCH₃), 19.9 (2 x CH₃, PhCH₃), 14.0 (CH₃, OCH₂CH₃); LRMS: m/z 245.20 (M⁺), calcd for C₁₅H₁₉NO₂ 245.1416; Anal. calcd for C₁₅H₁₉NO₂ (245.14): C, 73.44; H, 7.81; N, 5.71. Found: C, 73.449; H, 7.861; N, 5.735%.

2-Cyano-3-(4-isopropyl-phenyl)-propionic acid ethyl ester (10gf): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 2962, 2251 (C $\equiv$ N), 1747 (O-C=O), 1516, 1028 and 856 cm⁻¹; ¹H NMR (CDCl₃) δ 7.23 (4H, s) [Ar-H]; 4.23 (2H, q, $J = 7.1$ Hz, OCH₂CH₃), 3.72 (1H, dd, $J = 8.8, 6.0$ Hz), 3.24 (2H, dABq, $J = 13.8, 6.8$ Hz), 2.90 (1H, m, CH(CH₃)₂), 1.28 (3H, t, $J = 7.2$ Hz, OCH₂CH₃), 1.27 (6H, d, $J = 6.8$ Hz, CH(CH₃)₂); ¹³C NMR (CDCl₃, DEPT-135) δ 165.7 (C, O-C=O), 148.4 (C), 132.7 (C), 129.0 (2 x CH), 126.9 (2 x CH), 116.4 (C, C $\equiv$ N), 62.8 (CH₂, OCH₂CH₃), 39.8 (CH), 35.4 (CH₂), 33.8 (CH), 24.0 (2 x CH₃), 13.9 (CH₃, OCH₂CH₃); LRMS: m/z 246.15 (M+H⁺), calcd for C₁₅H₁₉NO₂ 245.1416.

2-Cyano-3-(2-hydroxy-phenyl)-propionic acid ethyl ester (10kf): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 3408 (O-H), 2257 (C $\equiv$ N), 1747 (O-C=O), 1597, 1506, 1041, 864 and 756 cm⁻¹; ¹H NMR (CDCl₃) δ 7.17 (1H, dt, $J = 7.6, 1.6$ Hz), 7.14 (1H, dd, $J = 8.0, 1.6$ Hz), 6.88 (1H, dt, $J = 7.2, 1.2$ Hz), 6.78 (1H, d, $J = 8.0$ Hz) [Ar-H]; 4.25 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 4.10 (1H, dd, $J = 8.4, 6.8$ Hz), 3.38 (1H, dd, $J = 13.6, 6.8$ Hz), 3.15 (1H, dd, $J = 13.6, 8.4$ Hz), 1.29 (3H, t, $J = 7.2$ Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 166.3 (C, O-C=O), 154.2 (C), 131.2 (CH), 129.1 (CH), 121.8 (CH), 120.5 (C), 116.5 (C, C $\equiv$ N), 115.4 (CH), 62.9 (CH₂, OCH₂CH₃), 37.4 (CH), 31.1 (CH₂,

PhCH₂), 14.0 (CH₃, OCH₂CH₃); LRMS: *m/z* 219.0 (M⁺), calcd for C₁₂H₁₃NO₃ 219.0895; Anal. calcd for C₁₂H₁₃NO₃ (219.09): C, 65.74; H, 5.98; N, 6.39. Found: C, 65.732; H, 5.948; N, 6.654%.

2-Cyano-3-(3-hydroxy-phenyl)-propionic acid ethyl ester (10lf): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 3443 (O-H), 2254 (C≡N), 1736 (O-C=O), 1591, 1458, 1269, 1030, 860 and 781 cm⁻¹; ¹H NMR (CDCl₃) δ 7.18 (1H, t, *J* = 8.6 Hz), 6.78 (3H, m) [Ar-*H*]; 6.67 (1H, br s, OH), 4.24 (2H, q, *J* = 7.12 Hz, OCH₂CH₃), 3.76 (1H, dd, *J* = 8.3, 5.8 Hz), 3.18 (2H, dABq, *J* = 13.8, 5.7 Hz), 1.27 (3H, t, *J* = 7.1 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.6 (C, O-C=O), 156.1 (C), 136.7 (C), 130.0 (CH), 120.9 (CH), 116.0 (C, C≡N), 115.8 (CH), 114.8 (CH), 63.0 (CH₂, OCH₂CH₃), 39.5 (CH), 35.4 (CH₂, PhCH₂), 13.8 (CH₃, OCH₂CH₃); LRMS: *m/z* 220.15 (M+H⁺), calcd for C₁₂H₁₃NO₃ 219.0895; Anal. calcd for C₁₂H₁₃NO₃ (219.09): C, 65.74; H, 5.98; N, 6.39. Found: C, 65.669; H, 6.022; N, 6.447%.

2-Cyano-3-(4-hydroxy-phenyl)-propionic acid ethyl ester (10mf): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 3408 (O-H), 2986, 2939, 2255 (C≡N), 1743 (O-C=O), 1682, 1614, 1516, 1446, 1371, 1267, 1030, 839 and 734 cm⁻¹; ¹H NMR (CDCl₃) δ 7.12 (2H, d, *J* = 8.4 Hz), 6.79 (2H, d, *J* = 8.4 Hz) [Ar-*H*]; 6.60 (1H, br s, OH), 4.24 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 3.74 (1H, dd, *J* = 8.0, 5.6 Hz), 3.10 (2H, m, PhCH₂), 1.28 (3H, t, *J* = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.9 (C, O-C=O), 155.7 (C), 130.3 (2 x CH), 126.8 (C), 116.5 (C, C≡N), 115.8 (2 x CH), 63.2 (CH₂, OCH₂CH₃), 40.1 (CH), 35.0 (CH₂, PhCH₂), 13.9 (CH₃, OCH₂CH₃); LRMS: *m/z* 219.0 (M⁺), calcd for C₁₂H₁₃NO₃ 219.0895.

2-Cyano-3-(2-nitro-phenyl)-propionic acid ethyl ester (10nf): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 64°C; IR (neat): $\nu_{\max}$ 2984, 2941, 2251 (C≡N), 1745 (O-C=O), 1610, 1578, 1348, 1026, 858, 788, 744 and 704 cm⁻¹; ¹H NMR (CDCl₃) δ 8.08 (1H, d, *J* = 8.4 Hz), 7.64 (1H, t, *J* = 7.6 Hz), 7.50 (2H, m) [Ar-*H*]; 4.26 (2H, q, *J* = 6.8 Hz, OCH₂CH₃), 4.14 (1H, dd, *J* = 9.6, 5.6 Hz), 3.68 (1H, dd, *J* = 13.6, 6.0 Hz), 3.26 (1H, dd, *J* = 13.6, 10.0 Hz), 1.30 (3H, t, *J* = 6.8 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.1 (C, O-C=O), 148.9 (C), 133.9 (CH), 133.6 (CH), 130.7 (C), 129.3 (CH), 125.5 (CH), 115.8 (C, C≡N), 63.2 (CH₂, OCH₂CH₃), 38.1 (CH), 33.4 (CH₂, PhCH₂), 13.9 (CH₃, OCH₂CH₃); LRMS: *m/z* 247.00 (M-H⁺), calcd for C₁₂H₁₂N₂O₄ 248.0797; Anal. calcd for C₁₂H₁₂N₂O₄ (248.08): C, 58.06; H, 4.87; N, 11.29. Found: C, 58.080; H, 4.905; N, 11.368%.

2-Cyano-3-(3-nitro-phenyl)-propionic acid ethyl ester (10of): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 60 °C; IR (neat): $\nu_{\max}$ 2986, 2941, 2253 (C≡N), 1745 (O-C=O), 1533, 1354, 1097, 856 and 725 cm⁻¹; ¹H NMR (CDCl₃) δ 8.20-8.17 (2H, m), 7.67 (1H, d, *J* = 7.2 Hz), 7.55 (1H, t, *J* = 8.0 Hz) [Ar-*H*]; 4.26 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 3.82 (1H, dd, *J* = 8.0, 6.0 Hz), 3.32 (2H, dABq, *J* = 14.0, 6.0 Hz), 1.29 (3H, t, *J* = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 164.9 (C, O-C=O), 148.5 (C), 137.2 (C), 135.4 (CH), 130.0 (CH), 124.1 (CH), 123.0 (CH), 115.5 (C, C≡N), 63.4 (CH₂, OCH₂CH₃), 39.0 (CH), 35.0 (CH₂, PhCH₂), 14.0 (CH₃, OCH₂CH₃); LRMS: *m/z* 247.15 (M-H⁺), calcd for

C₁₂H₁₂N₂O₄ 248.0797; Anal. calcd for C₁₂H₁₂N₂O₄ (248.08): C, 58.06; H, 4.87; N, 11.29. Found: C, 58.074; H, 4.886; N, 11.500%.

2-Cyano-3-(4-nitro-phenyl)-propionic acid ethyl ester (10pf): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 60 °C; IR (KBr): $\nu_{\max}$ 2930, 2452, 2257 (C≡N), 1952, 1603, 1520, 1446, 1348, 1107, 1014, 885, 846, 754 and 711 cm⁻¹; ¹H NMR (CDCl₃) δ 8.22 (2H, d, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 8.4 Hz) [Ar-*H*]; 4.27 (2H, q, *J* = 6.8 Hz, OCH₂CH₃), 3.88 (1H, dd, *J* = 8.0, 6.0 Hz), 3.36 (2H, dABq, *J* = 14.0, 6.0 Hz), 1.28 (3H, t, *J* = 6.4 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 164.9 (C, O-C=O), 147.6 (C), 142.6 (C), 130.2 (2 x CH), 124.0 (2 x CH), 115.6 (C, C≡N), 66.9 (CH₂, OCH₂CH₃), 38.8 (CH), 35.0 (CH₂, PhCH₂), 13.4 (CH₃, OCH₂CH₃); LRMS: *m/z* 248.0 (M⁺), calcd for C₁₂H₁₂N₂O₄ 248.0797.

2-Cyano-3-(3-cyano-phenyl)-propionic acid ethyl ester (10qf): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 52-54 °C; IR (KBr): $\nu_{\max}$ 2984, 2908, 2251 (C≡N), 2228, 1734 (O-C=O), 1030, 860, 800 and 696 cm⁻¹; ¹H NMR (CDCl₃) δ 7.59-7.54 (3H, m), 7.46 (1H, t, *J* = 7.6 Hz) [Ar-*H*]; 4.21 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 3.79 (1H, dd, *J* = 8.0, 6.0 Hz), 3.21 (2H, dABq, *J* = 14.0, 5.8 Hz), 1.25 (3H, t, *J* = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.0 (C, O-C=O), 136.9 (C), 133.8 (CH), 132.7 (CH), 131.5 (CH), 129.8 (CH), 118.4 (C), 115.7 (C, C≡N), 112.9 (C, C≡N), 63.2 (CH₂, OCH₂CH₃), 39.0 (CH), 34.8 (CH₂, PhCH₂), 13.9 (CH₃, OCH₂CH₃); LRMS: *m/z* 227.15 (M-H⁺), calcd for C₁₃H₁₂N₂O₂ 228.0899; Anal. calcd for C₁₃H₁₂N₂O₂ (228.09): C, 68.41; H, 5.30; N, 12.27. Found: C, 68.544; H, 5.323; N, 12.147%.

2-Cyano-3-[3-(2-cyano-2-methoxycarbonyl-ethyl)-phenyl]-propionic acid methyl ester (10te): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 3018, 2959, 2251 (C≡N), 1746 (O-C=O), 1611, 1439, 1269, 1022, 775 and 706 cm⁻¹; ¹H NMR (CDCl₃) δ 7.34 (1H, t, *J* = 8.0 Hz), 7.22 (3H, m) [Ar-*H*]; 3.80 (3H, s, OCH₃), 3.79 (3H, s, OCH₃), 3.77 (2H, m, CH), 3.23 (2H, dABq, *J* = 13.6, 5.2 Hz), 3.20 (2H, dABq, *J* = 13.6, 5.2 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 165.8 (2 x C, O-C=O), 135.96 (C), 135.94 (C), 129.7 (CH), 129.46 (CH), 129.44 (CH), 128.51 (CH), 128.50 (CH), 115.9 (2 x C, C≡N), 53.6 (2 x CH₃, OCH₃), 39.34 (CH), 39.28 (CH), 35.45 (CH₂, PhCH₂), 35.41 (CH₂, PhCH₂); LRMS: *m/z* 299.9 (M⁺), calcd for C₁₆H₁₆N₂O₄ 300.1110.

2-Cyano-3-furan-2-yl-propionic acid ethyl ester (10c'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2986, 2935, 2253 (C≡N), 1747 (O-C=O), 1608, 1026, 856 and 740 cm⁻¹; ¹H NMR (CDCl₃) δ 7.37 (1H, s), 6.33 (1H, s), 6.26 (1H, s) [Ar-*H*]; 4.27 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 3.84 (1H, t, *J* = 6.7 Hz), 3.32 (2H, m, PhCH₂), 1.30 (3H, t, *J* = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.0 (C, O-C=O), 148.9 (C), 142.4 (CH), 115.7 (C, C≡N), 110.5 (CH), 108.3 (CH), 62.9 (CH₂, OCH₂CH₃), 36.9 (CH), 28.4 (CH₂), 13.8 (CH₃, OCH₂CH₃); LRMS: *m/z* 192.00 (M-H⁺), calcd for C₁₀H₁₁NO₃ 193.0739.

2-Cyano-5-phenyl-pent-4-enoic acid ethyl ester (10e'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2930, 2249 (C≡N), 1743 (O-C=O), 1454, 1238 and 858 cm⁻¹; ¹H NMR (CDCl₃) δ 7.37 (2H, d, *J* = 6.8 Hz), 7.31 (2H, t, *J* = 8.0 Hz), 7.25 (1H, t, *J* = 6.8 Hz)

[Ar-H]; 6.59 (1H, d, $J = 15.6$ Hz), 6.18 (1H, dt, $J = 15.6, 7.2$ Hz), 4.28 (2H, q, $J = 6.8$ Hz, OCH_2CH_3), 3.62 (1H, t, $J = 6.4$ Hz), 2.86 (2H, t, $J = 7.2$ Hz), 1.31 (3H, t, $J = 6.8$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.5 (C, O-C=O), 136.3 (C), 135.0 (CH), 128.6 (2 x CH), 127.9 (CH), 126.4 (2 x CH), 122.4 (CH), 116.1 (C, $\text{C}\equiv\text{N}$), 62.9 (CH_2 , OCH_2CH_3), 37.9 (CH), 33.3 (CH_2), 14.0 (CH_3 , OCH_2CH_3); LCMS: m/z 228.00 (M-H^+), calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ 229.1103; Anal. calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ (229.11): C, 73.34; H, 6.59; N, 6.11. Found: C, 73.293; H, 6.547; N, 6.256%.

2-Cyano-5-(2-nitro-phenyl)-pent-4-enoic acid ethyl ester (10f'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 3069, 2928, 2872, 2251 ($\text{C}\equiv\text{N}$), 1743 (O-C=O), 1608, 1572, 1521, 968, 860 and 787 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.96 (1H, d, $J = 8.0$ Hz), 7.58 (2H, m), 7.45 (1H, m), 7.09 (1H, d, $J = 15.56$ Hz), 6.22 (1H, td, $J = 15.6, 7.2$ Hz), 4.31 (2H, q, $J = 7.12$ Hz, OCH_2CH_3), 3.69 (1H, t, $J = 7.12$ Hz), 2.92 (2H, t, $J = 6.76$ Hz), 1.33 (3H, t, $J = 7.2$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.2 (C, O-C=O), 147.6 (C), 133.3 (CH), 132.2 (C), 130.6 (CH), 129.0 (CH), 128.6 (CH), 127.9 (CH), 124.6 (CH), 115.9 (C, $\text{C}\equiv\text{N}$), 63.1 (CH_2 , OCH_2CH_3), 37.6 (CH), 33.1 (CH_2), 14.0 (CH_3 , OCH_2CH_3); LCMS: m/z 273.00 (M-H^+), calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4$ 274.10; Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4$ (274.10): C, 61.31; H, 5.14; N, 10.21. Found: C, 61.480; H, 5.138; N, 10.103%.

2-Cyano-pentanoic acid ethyl ester (10g'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2928, 2862, 2251 ($\text{C}\equiv\text{N}$), 1747 (O-C=O), 1464, 1371, 1257, 1030, 856 and 727 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.29 (2H, q, $J = 7.13$ Hz, OCH_2CH_3), 3.51 (1H, t, $J = 6.9$ Hz), 1.96 (2H, q, $J = 7.6$ Hz), 1.57 (2H, m), 1.35 (3H, t, $J = 7.1$ Hz, OCH_2CH_3), 1.01 (3H, t, $J = 7.3$ Hz, CH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.3 (C, O-C=O), 116.6 (C, $\text{C}\equiv\text{N}$), 62.7 (CH_2 , OCH_2CH_3), 37.4 (CH), 31.8 (CH_2), 20.1 (CH_2), 14.0 (CH_3), 13.3 (CH_3 , OCH_2CH_3); LRMS: m/z 156.0 ($\text{M}+\text{H}^+$), calcd for $\text{C}_8\text{H}_{13}\text{NO}_2$ 155.0946.

2-Cyano-hexanoic acid ethyl ester (10h'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2942, 2249 ($\text{C}\equiv\text{N}$), 1747 (O-C=O), 1469, 1390, 1371, 1271, 1026, 927, 858 and 760 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.26 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 3.49 (1H, t, $J = 7.0$ Hz), 1.94 (2H, q, $J = 7.2$ Hz), 1.49 (2H, m), 1.40 (2H, m), 1.32 (3H, t, $J = 6.8$ Hz, OCH_2CH_3), 0.92 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.2 (C, O-C=O), 116.6 (C, $\text{C}\equiv\text{N}$), 62.7 (CH_2 , OCH_2CH_3), 37.6 (CH), 29.6 (CH_2), 28.8 (CH_2), 21.9 (CH_2), 14.0 (CH_3), 13.6 (CH_3 , OCH_2CH_3); LRMS: m/z 169.10 (M^+), calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_2$ 169.1103.

2-Cyano-4-methyl-pentanoic acid ethyl ester (10j'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2964, 2249 ($\text{C}\equiv\text{N}$), 1747 (O-C=O), 1471, 1371, 1267 and 1024 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.11 (2H, q, $J = 7.1$ Hz, OCH_2CH_3), 3.36 (1H, dd, $J = 9.12, 5.8$ Hz, CH), 1.74-1.60 (3H, m), 1.17 (3H, t, $J = 7.16$ Hz, OCH_2CH_3), 0.84 (3H, d, $J = 6.1$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.82 (3H, d, $J = 6.1$ Hz, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.5 (C, O-C=O), 116.6 (C, $\text{C}\equiv\text{N}$), 62.7 (CH_2 , OCH_2CH_3), 38.4 (CH_2), 36.0 (CH), 26.1 (CH), 22.4 (CH_3), 21.3 (CH_3), 14.0 (CH_3 , OCH_2CH_3); GCMS: m/z 168.00 (M-H^+), calcd for $\text{C}_9\text{H}_{15}\text{NO}_2$ 169.1103.

2-Cyano-3-cyclohexyl-propionic acid ethyl ester (10m'f): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2928, 2852, 2249 (C $\equiv$ N), 1745 (O-C=O), 1624, 1450, 1249, 1190, 1026 and 854 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.26 (2H, q, J = 7.2 Hz, OCH_2CH_3), 3.55 (1H, dd, J = 9.2, 6.4 Hz, CH), 1.89-1.66 (7H, m), 1.57-1.50 (1H, m), 1.32 (3H, t, J = 7.2 Hz), 1.36-1.10 (3H, m), 1.02-0.90 (2H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.6 (C, O-C=O), 116.7 (C, C $\equiv$ N), 62.7 (CH_2 , OCH_2CH_3), 37.0 (CH_2), 35.3 (CH), 35.2 (CH), 33.0 (CH_2), 31.9 (CH_2), 26.2 (CH_2), 25.89 (CH_2), 25.77 (CH_2), 13.97 (CH_3 , OCH_2CH_3); HRMS: m/z 232.1314 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2\text{Na}$ 232.1313; Anal. calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2$ (209.1416): C, 68.87; H, 9.15; N, 6.69. Found: C, 68.781; H, 9.162; N, 6.655%.

2-Cyclohexylmethyl-malononitrile (10m'j): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2928, 2256 (C $\equiv$ N), 1450 and 1352 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.78 (1H, t, J = 7.7 Hz), 1.94 (2H, t, J = 7.3 Hz), 1.78-1.58 (6H, m), 1.36-1.14 (3H, m), 1.00 (2H, q, J = 11.8 Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 112.9 (2 x C, C $\equiv$ N), 37.8 (CH_2), 35.0 (CH), 32.1 (2 x CH_2), 26.0 (CH_2), 25.6 (2 x CH_2), 20.3 (CH); HRMS: m/z 201.1339 ($\text{M}+\text{K}^+$), calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{K}$ 201.0794; Anal. calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2$ (162.1157): C, 74.03; H, 8.70; N, 17.27. Found: C, 74.020; H, 8.731; N, 17.410%.

2-Benzo[1,3]dioxol-5-ylmethyl-malononitrile (10ij): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 78-80 $^{\circ}\text{C}$; IR (KBr): $\nu_{\max}$ 2934, 2251 (C $\equiv$ N), 1608, 1446, 1039, 864 and 794 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.83 (3H, m) [Ar-H]; 6.00 (2H, s, OCH_2O), 3.91 (1H, t, J = 6.8 Hz, CH), 3.21 (2H, d, J = 6.8 Hz, ArCH_2); ^{13}C NMR (CDCl_3 , DEPT-135) δ 148.3 (C), 148.1 (C), 126.5 (C), 122.8 (CH), 113.2 (2 x C, C $\equiv$ N), 109.3 (CH), 108.9 (CH), 101.5 (CH_2 , OCH_2O), 36.4 (CH_2), 25.2 (CH); LRMS: m/z 199.00 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$ 200.0586.

2-(4-Nitro-benzyl)-malononitrile (10pj): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 136-138 $^{\circ}\text{C}$; IR (KBr): $\nu_{\max}$ 3051, 2930, 2256 (C $\equiv$ N), 1602, 1520, 1446, 1346, 1292, 885 and 754 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.31 (2H, d, J = 8.5 Hz), 7.56 (2H, d, J = 8.5 Hz), 4.05 (1H, t, J = 6.6 Hz), 3.43 (2H, d, J = 6.6 Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 148.4 (C), 139.6 (C), 130.4 (2 x CH), 124.5 (2 x CH), 111.4 (2 x C, C $\equiv$ N), 36.1 (CH_2), 24.4 (CH); LRMS: m/z 200.00 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{10}\text{H}_7\text{N}_3\text{O}_2$ 201.0538.

2-(4-Chloro-benzyl)-malononitrile (10yj): Purified by column chromatography using EtOAc/hexane and isolated as solid. Mp 60 $^{\circ}\text{C}$; IR (KBr): $\nu_{\max}$ 2926, 2256 (C $\equiv$ N), 1599, 1494, 1412, 1257, 848 and 711 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.41 (2H, d, J = 8.0 Hz), 7.29 (2H, d, J = 8.0 Hz), 3.95 (1H, t, J = 6.8 Hz), 3.28 (2H, d, J = 6.8 Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 134.9 (C), 131.2 (C), 130.6 (2 x CH), 129.6 (2 x CH), 111.9 (2 x C, C $\equiv$ N), 35.9 (CH_2), 24.8 (CH); LRMS: m/z 189.00 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{10}\text{H}_7\text{ClN}_2$ 190.0298.

5-Anthracen-9-ylmethyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (10dc): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 140 $^{\circ}\text{C}$. IR (KBr): $\nu_{\max}$ 2924, 2876, 1736, 1311, 1203, 1068, 1033, 958, 908, 883, 796 and 729 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.45 (3H, d, J = 8.4 Hz), 8.03 (2H, d, J = 8.4 Hz), 7.57 (2H, br dt, J = 8.0, 1.2 Hz), 7.48 (2H, br dt, J = 8.0, 1.2 Hz) [Ar-H]; 4.50 (2H, d, J = 5.2 Hz), 3.97 (1H, t, J = 5.2 Hz), 1.77 (3H, s, CH_3), 1.64 (3H, s, CH_3); ^{13}C NMR (CDCl_3 ,

DEPT-135) δ 165.2 (2 x C, O-C=O), 131.5 (2 x C), 130.5 (C), 129.9 (2 x C), 129.4 (2 x CH), 127.5 (CH), 126.3 (2 x CH), 125.0 (2 x CH), 124.3 (2 x CH), 104.9 (C, O-C-O), 49.2 (CH), 28.8 (CH₂), 26.3 (CH₃), 23.9 (CH₃); LCMS: m/z 333.15 (M-H⁺), calcd for C₂₁H₁₈O₄ 334.1205.

2,2-Dimethyl-5-(4-methyl-benzyl)-[1,3]dioxane-4,6-dione (10ec): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 98 °C. IR (KBr): $\nu_{\max}$ 3427, 2926, 1788, 1732, 1597, 1518, 1442, 1277, 1203, 1114, 1060, 1024, 941, 912, 794 and 713 cm⁻¹; ¹H NMR (CDCl₃) δ 7.20 (2H, d, J = 8.0 Hz), 7.09 (2H, d, J = 8.0 Hz) [Ar- H]; 3.73 (1H, t, J = 4.8 Hz), 3.45 (2H, d, J = 4.8 Hz), 2.31 (3H, s, ArCH₃), 1.73 (3H, s, CH₃), 1.50 (3H, s, CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.3 (2 x C, O-C=O), 136.8 (C), 134.1 (C), 129.6 (2 x CH), 129.3 (2 x CH), 105.2 (C, O-C-O), 48.3 (CH), 31.8 (CH₂), 28.5 (CH₃), 27.3 (CH₃), 21.0 (CH₃); LRMS: m/z 247.05 (M-H⁺), calcd for C₁₄H₁₆O₄ 248.1049.

5-(4-Methoxy-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (10hc): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (KBr): $\nu_{\max}$ 2930, 1745, 1701, 1610, 1510, 1458, 1032, 945, and 833 cm⁻¹; ¹H NMR (CDCl₃) δ 7.24 (2H, d, J = 8.8 Hz), 6.82 (2H, d, J = 8.8 Hz) [Ar- H]; 3.77 (3H, s, OCH₃), 3.72 (1H, t, J = 4.8 Hz), 3.44 (2H, d, J = 5.2 Hz), 1.72 (3H, s, CH₃), 1.48 (3H, s, CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.4 (2 x C, O-C=O), 158.8 (C), 131.0 (2 x CH), 129.0 (C), 113.8 (2 x CH), 105.2 (C, O-C-O), 55.2 (C, OCH₃), 48.3 (CH), 31.5 (CH₂), 28.4 (CH₃), 27.4 (CH₃); LRMS: m/z 263.00 (M-H⁺), calcd for C₁₄H₁₆O₅ 264.0998.

5-Benzo[1,3]dioxol-5-ylmethyl-pyrimidine-2,4,6-trione (10ib): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 210 °C. IR (KBr): $\nu_{\max}$ 3223, 3096, 1714 (HN-C=O), 1504, 1440, 1356, 1248, 1039, 802 and 623 cm⁻¹; ¹H NMR (DMSO-D₆) δ 11.2 (2H, br s, 2 x NH), 6.78 (1H, d, J = 7.6 Hz), 6.67-6.56 (2H, m) [Ar- H]; 5.95 (2H, s, OCH₂O), 4.00-3.80 (1H, br s, CH), 3.16 (2H, br s, ArCH₂); ¹³C NMR (DMSO-D₆, DEPT-135) δ 170.4 (2 x C, N-C=O), 151.0 (C, (HN)₂C=O), 147.4 (C, O-C-O), 146.2 (C, O-C-O), 131.2 (C), 122.3 (CH), 109.6 (CH), 108.5 (CH), 101.2 (CH₂, OCH₂O), 49.9 (CH₂, PhCH₂), 40.1 (CH); LRMS: m/z 261.00 (M-H⁺), calcd for C₁₂H₁₀N₂O₅ 262.0590; Anal. calcd for C₁₂H₁₀N₂O₅ (262.06): C, 54.97; H, 3.84; N, 10.68. Found: C, 55.019; H, 3.844; N, 10.573%.

2-(2-Hydroxy-benzyl)-malonic acid monomethyl ester (10km): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 3421, 2981, 1737, 1723 (O-C=O, CO₂Et), 1710 (O-C=O, CO₂H), 1495, 1259, 1234, 1153, 1101 and 755 cm⁻¹; ¹H NMR (CDCl₃) δ 7.51 (2H, bs, CO₂H, O- H), 7.10 (2H, m), 6.84-6.78 (2H, m) [Ar- H]; 3.89 (1H, t, J = 7.2 Hz, CH), 3.70 (3H, s, OCH₃), 3.21 (2H, d, J = 7.6 Hz, ArCH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 173.8 (C, CO₂Me), 170.4 (C, CO₂H), 154.1 (C), 131.0 (CH), 128.5 (CH), 123.8 (C), 120.8 (CH), 116.4 (CH), 53.0 (CH₃, OCH₃), 52.0 (CH), 29.5 (CH₂).; To a magnetically stirred ice-cold solution of malonic acid monomethyl ester **10km** (0.100 g) in ether (3 ml) was added an ice-cold ethereal diazomethane solution (excess, prepared from 1.5 gm of *N*-nitroso-*N*-methylurea and 15 ml of 60% aqueous KOH solution and 10 ml of ether) and stirred for 0.5 h at the same temperature. Careful evaporation of the excess diazomethane and solvent followed by purification of the residue over a silica gel column using ethyl acetate-hexane (1:20 to 1:5) as eluent furnished the malonic acid dimethyl ester (95%) as oil. **2-(2-Hydroxy-benzyl)-malonic acid dimethyl ester:** Purified by column

chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 3431 (O-H), 2954, 2924, 1737, 1725, 1712, 1459, 1439, 1351, 1234, 1154 and 755 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.13-7.08 (2H, m), 6.84 (2H, br t, $J = 8.0$ Hz) [Ar-*H*]; 6.69 (1H, bs, OH), 3.83 (1H, dt, $J = 7.2, 2.0$ Hz), 3.723 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 3.19 (2H, dd, $J = 7.2, 2.0$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 170.2 (2 x C, CO_2Me), 154.2 (C), 131.0 (CH), 128.5 (CH), 124.1 (C), 120.8 (CH), 116.8 (CH), 52.8 (2 x CH_3 , OCH_3), 52.5 (CH), 29.3 (CH_2); LRMS: m/z 237.00 (M-H^+), calcd for $\text{C}_{12}\text{H}_{14}\text{O}_5$ 238.0841.

2-(2-Hydroxy-benzyl)-malonic acid monoethyl ester (10kn): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 3433, 2981, 1737, 1722 (O-C=O, CO_2Et), 1710 (O-C=O, CO_2H), 1459, 1371, 1234, 1101 and 755 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36 (2H, bs, CO_2H , O-*H*), 7.10 (2H, t, $J = 8.0$ Hz), 6.85-6.80 (2H, m) [Ar-*H*]; 4.21-4.13 (2H, m, OCH_2CH_3), 3.87 (1H, t, $J = 8.0$ Hz, CH), 3.09 (2H, d, $J = 8.0$ Hz, ArCH_2), 1.21 (3H, t, $J = 8.0$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 174.1 (C, CO_2H), 170.1 (C, CO_2Et), 154.2 (C), 131.1 (CH), 128.5 (CH), 123.9 (C), 120.8 (CH), 116.5 (CH), 62.2 (CH_2 , OCH_2CH_3), 52.3 (CH), 29.5 (CH_2), 13.8 (CH_3 , OCH_2CH_3); LRMS: m/z 239.00 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{12}\text{H}_{14}\text{O}_5$ 238.0841; Anal. calcd for $\text{C}_{12}\text{H}_{14}\text{O}_5$ (238.08): C, 60.50; H, 5.92. Found: C, 60.503; H, 5.913 %.

2-Oxo-chroman-3-carboxylic acid (14kc): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 120 °C. IR (neat): $\nu_{\max}$ 3627 (CO_2H), 2966, 1778, 1775, 1690, 1218 and 1157 cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 6.43 (2H, m), 6.20 (2H, m) [Ar-*H*]; 3.32 (1H, br s, CH), 3.07 (2H, br s, CH_2); ^{13}C NMR ($\text{DMSO-}d_6$, DEPT-135) δ 169.6 (C, O-C=O), 165.5 (C, O-C=O), 151.5 (C), 129.1 (CH), 128.7 (CH), 125.0 (CH), 122.0 (C), 116.6 (CH), 46.3 (CH), 27.0 (CH_2); Anal. calcd for $\text{C}_{10}\text{H}_8\text{O}_4$ (192.04): C, 62.50; H, 4.20. Found: C, 62.553; H, 4.224 %.

2-Oxo-chroman-3-carboxylic acid methyl ester (14kca): To a magnetically stirred ice-cold solution of acid **14kc** (0.134 g) in ether (3 ml) was added an ice-cold ethereal diazomethane solution (excess, prepared from 1.5 gm of *N*-nitroso-*N*-methylurea and 15 ml of 60% aqueous KOH solution and 10 ml of ether) and stirred for 0.5 h at the same temperature. Careful evaporation of the excess diazomethane and solvent followed by purification of the residue over a silica gel column using ethyl acetate-hexane (1:20 to 1:5) as eluent furnished the ester **14kca** (95%) as white solid. MP 88 °C. IR (neat): $\nu_{\max}$ 2974, 1765, 1737, 1731, 1458, 1440, 1353, 1253, 1241, 1220, 1181, 1146, 778 and 760 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.27 (1H, t, $J = 7.6$ Hz), 7.22 (1H, d, $J = 7.2$ Hz), 7.12 (1H, t, $J = 7.6$ Hz), 7.06 (1H, d, $J = 8.4$ Hz) [Ar-*H*]; 3.77 (1H, dd, $J = 8.8, 6.0$ Hz), 3.76 (3H, s, OCH_3), 3.42 (1H, dd, $J = 16.0, 9.2$ Hz), 3.18 (1H, dd, $J = 16.0, 6.0$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135) δ 167.9 (C, O-C=O), 164.6 (C, O-C=O), 151.5 (C), 128.6 (CH), 128.2 (CH), 124.8 (CH), 120.6 (C), 116.7 (CH), 52.9 (CH_3 , OCH_3), 46.1 (CH), 27.1 (CH_2); LRMS: m/z 205.00 (M-H^+), calcd for $\text{C}_{11}\text{H}_{10}\text{O}_4$ 206.0579; Anal. calcd for $\text{C}_{11}\text{H}_{10}\text{O}_4$ (206.06): C, 64.07; H, 4.89. Found: C, 64.038; H, 4.916 %.

2-Amino-4H-chromene-3-carbonitrile (14kj): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 126 °C. IR (neat): $\nu_{\max}$ 3447 (NH_2), 3332 (NH_2), 2191, 1664, 1659, 1608, 1581, 1492, 1457, 1410, 1266, 1229, 1184 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.23-7.15 (1H, m), 7.15-7.04 (2H,

m), 6.92 (1H, d, $J = 8.0$ Hz) [Ar- H]; 4.65 (2H, br s, NH_2), 3.52 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 160.1 (C), 149.3 (C), 128.6 (CH), 127.9 (CH), 124.7 (CH), 120.4 (C), 118.9 (C), 116.3 (CH), 53.4 (C), 23.8 (CH_2); Anal. calcd for $C_{10}H_8N_2O$ (172.06): C, 69.76; H, 4.68; N, 16.27. Found: C, 69.749; H, 4.680; N, 16.480 %.

5-(3-Hydroxy-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (10lc): Purified by column chromatography using EtOAc/hexane and isolated as white solid. MP 116 °C. IR (neat): ν_{max} 3369, 1777, 1736 (O-C=O), 1730, 1601, 1460, 1399, 1354, 1320, 1227, 1199, 1084, 1066, 959, 877 and 782 cm^{-1} ; 1H NMR (DMSO- D_6) δ 8.4 (1H, br s, OH), 6.13 (1H, m), 5.73 (3H, m) [Ar- H]; 3.82 (1H, s, CH), 2.30 (2H, d, $J = 4.0$ Hz), 0.88 (3H, s, CH_3), 0.67 (3H, s, CH_3); ^{13}C NMR (DMSO- D_6 , DEPT-135) δ 166.2 (2 x C, O-C=O), 157.6 (C), 139.7 (C), 129.5 (CH), 120.1 (CH), 116.5 (CH), 113.8 (CH), 105.4 (C, O-C-O), 47.1 (CH), 31.6 (CH_2), 28.3 (CH_3), 26.7 (CH_3); LRMS: m/z 249.00 ($M-H^+$), calcd for $C_{13}H_{14}O_5$ 250.0841; Anal. calcd for $C_{13}H_{14}O_5$ (250.08): C, 62.39; H, 5.64. Found: C, 62.476; H, 5.666 %.

5-(4-Hydroxy-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (10mc): Purified by column chromatography using EtOAc/hexane and isolated as white solid. MP 118 °C. IR (neat): ν_{max} 3347, 1780, 1727 (O-C=O), 1493, 1357, 1306, 1205, 1176, 1073 and 734 cm^{-1} ; 1H NMR (DMSO- D_6) δ 8.32 (1H, br s, OH), 6.12 (2H, d, $J = 7.92$ Hz), 5.73 (2H, d, $J = 7.96$ Hz) [Ar- H]; 3.76 (1H, br s, CH), 2.28 (2H, br s), 0.86 (3H, s, CH_3), 0.63 (3H, s, CH_3); ^{13}C NMR (DMSO- D_6 , DEPT-135) δ 166.2 (2 x C, O-C=O), 156.4 (C), 130.8 (2 x CH), 128.3 (C), 115.4 (2 x CH), 105.3 (C, O-C-O), 47.8 (CH), 31.0 (CH_2), 28.3 (CH_3), 26.8 (CH_3); LRMS: m/z 249.00 ($M-H^+$), calcd for $C_{13}H_{14}O_5$ 250.0841; Anal. calcd for $C_{13}H_{14}O_5$ (250.08): C, 62.39; H, 5.64. Found: C, 62.345; H, 5.655 %.

5-(2-Methoxy-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (10n'c): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 118 °C. IR (KBr): ν_{max} 2928, 2874, 1784, 1749 (O-C=O), 1602, 1496, 1388, 1068, 1016, 949 and 763 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.34 (1H, br d, $J = 7.6$ Hz), 7.23 (1H, br t, $J = 8.0$ Hz), 6.92 (1H, br t, $J = 7.2$ Hz), 6.85 (1H, br d, $J = 8.4$ Hz) [Ar- H]; 4.02 (1H, t, $J = 6.0$ Hz), 3.82 (3H, s, OCH_3), 3.39 (2H, d, $J = 5.6$ Hz), 1.76 (3H, s, CH_3), 1.72 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 165.3 (2 x C, O-C=O), 157.1 (C), 131.8 (CH), 128.3 (CH), 125.7 (C), 120.6 (CH), 110.2 (CH), 104.8 (C, O-C-O), 55.2 (CH_3 , OCH_3), 46.1 (CH), 28.6 (CH_3), 28.0 (CH_2), 26.5 (CH_3); LRMS: m/z 263.00 ($M-H^+$), calcd for $C_{14}H_{16}O_5$ 264.0998; Anal. calcd for $C_{14}H_{16}O_5$ (264.0998): C, 63.63; H, 6.10. Found: C, 63.586; H, 6.136 %.

2,2-Dimethyl-5-(2-nitro-benzyl)-[1,3]dioxane-4,6-dione (10nc): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): ν_{max} 3501, 2922, 1780, 1741, 1641, 1525, 1448, 1358, 1197, 1062, 945, 912, 860, 808, 785 and 734 cm^{-1} ; 1H NMR ($CDCl_3$) δ 8.01 (1H, d, $J = 8.4$ Hz), 7.77 (1H, d, $J = 7.6$ Hz), 7.60 (1H, t, $J = 7.2$ Hz), 7.44 (1H, t, $J = 8.0$ Hz) [Ar- H]; 4.20 (1H, t, $J = 5.6$ Hz), 3.65 (2H, d, $J = 5.6$ Hz), 1.82 (3H, s, CH_3), 1.78 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 164.6 (2 x C, O-C=O), 149.3 (C), 134.8 (CH), 133.3 (CH), 133.0 (C), 128.4 (CH), 125.0 (CH), 105.3 (C, O-C-O), 47.7 (CH), 29.3 (CH_2), 28.7 (CH_3), 26.1 (CH_3); LRMS: m/z 278.00 ($M-H^+$), calcd for $C_{13}H_{13}NO_6$ 279.0743.

2,2-Dimethyl-5-(3-nitro-benzyl)-[1,3]dioxane-4,6-dione (10oc): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 129 °C. IR (KBr): $\nu_{\max}$ 2926, 1778, 1736, 1531, 1350, 1315, 1277, 1197, 1066, 1022, 952, 922, 873, 815 and 740 cm^{-1} ; ^1H NMR ($\text{DMSO-}D_6$) δ 8.22 (1H, br s), 8.08 (1H, d, $J = 7.6$ Hz), 7.77 (1H, br s), 7.58 (1H, t, $J = 8.0$ Hz) [Ar-*H*]; 4.89 (1H, br s, *CH*), 3.43 (2H, br s, Ar*CH*₂), 1.84 (3H, s, *CH*₃), 1.65 (3H, s, *CH*₃); ^{13}C NMR ($\text{DMSO-}D_6$, DEPT-135) δ 165.3 (2 x C, O-C=O), 147.5 (C), 140.7 (C), 136.3 (CH), 129.3 (CH), 123.9 (CH), 121.2 (CH), 105.0 (C, O-C-O), 46.7 (CH), 30.6 (*CH*₂), 27.8 (*CH*₃), 25.8 (*CH*₃); LRMS: m/z 278.25 (M-H^+), calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_6$ 279.0743.

2,2-Dimethyl-5-(4-nitro-benzyl)-[1,3]dioxane-4,6-dione (10pc): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 120 °C. IR (KBr): $\nu_{\max}$ 3427, 2926, 1778, 1732, 1664, 1346, 1064, 943, 858, 802 and 758 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.15 (2H, d, $J = 8.8$ Hz), 7.54 (2H, d, $J = 7.2$ Hz) [Ar-*H*]; 3.84 (1H, t, $J = 4.8$ Hz), 3.58 (2H, d, $J = 4.8$ Hz), 1.80 (3H, s, *CH*₃), 1.69 (3H, s, *CH*₃); ^{13}C NMR (CDCl_3 , DEPT-135) δ 164.6 (2 x C, O-C=O), 147.1 (C), 144.7 (C), 130.8 (2 x CH), 123.6 (2 x CH), 105.4 (C, O-C-O), 47.6 (CH), 31.4 (*CH*₂), 28.3 (*CH*₃), 26.9 (*CH*₃); LRMS: m/z 278.20 (M-H^+), calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_6$ 279.0743.

4-(2,2-Dimethyl-4,6-dioxo-[1,3]dioxan-5-ylmethyl)-benzonitrile (10rc): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): $\nu_{\max}$ 2926, 2854, 2226 ($\text{C}\equiv\text{N}$), 1778, 1734, 1340, 1066 and 941 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.59 (2H, d, $J = 8.4$ Hz), 7.47 (2H, d, $J = 8.4$ Hz) [Ar-*H*]; 3.78 (1H, t, $J = 4.4$ Hz), 3.53 (2H, d, $J = 4.4$ Hz), 1.78 (3H, s, *CH*₃), 1.65 (3H, s, *CH*₃); ^{13}C NMR (CDCl_3 , DEPT-135) δ 164.7 (2 x C, O-C=O), 142.6 (C), 132.3 (2 x CH), 130.7 (2 x CH), 118.6 (C, $\text{C}\equiv\text{N}$), 111.2 (C), 105.4 (C, O-C-O), 47.7 (CH), 31.7 (*CH*₂), 28.4 (*CH*₃), 26.9 (*CH*₃); LRMS: m/z 258.05 (M-H^+), calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4$ 259.0845.

5-(4-Chloro-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (10yc): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 120 °C. IR (KBr): $\nu_{\max}$ 2926, 1734, 1494, 1381, 1288, 1109, 1059, 1012, 951, 910, 825, 792 and 707 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.26 (4H, m) [Ar-*H*]; 3.74 (1H, t, $J = 4.8$ Hz, *CH*), 3.46 (2H, d, $J = 4.8$ Hz, Ar*CH*₂), 1.75 (3H, s, *CH*₃), 1.58 (3H, s, *CH*₃); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.0 (2 x C, O-C=O), 135.5 (C), 133.1 (C), 131.3 (2 x CH), 128.7 (2 x CH), 105.2 (C, O-C-O), 48.0 (CH), 31.3 (*CH*₂), 28.4 (*CH*₃), 27.2 (*CH*₃); LRMS: m/z 267.00 (M-H^+), calcd for $\text{C}_{13}\text{H}_{13}\text{ClO}_4$ 268.0502.

5-(4-Bromo-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione (10b'c): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 128 °C. IR (KBr): $\nu_{\max}$ 2928, 1741, 1660, 1491, 1383, 1060, 1006, 937, 910 and 781 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.41 (2H, d, $J = 8.4$ Hz), 7.22 (2H, d, $J = 8.4$ Hz) [Ar-*H*]; 3.74 (1H, t, $J = 4.8$ Hz), 3.44 (2H, d, $J = 4.8$ Hz), 1.75 (3H, s, *CH*₃), 1.59 (3H, s, *CH*₃); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.0 (2 x C, O-C=O), 136.1 (C), 131.6 (4 x CH), 121.2 (C), 105.2 (C, O-C-O), 47.9 (CH), 31.3 (*CH*₂), 28.4 (*CH*₃), 27.1 (*CH*₃); LRMS: m/z 312.10 (M^+), 314.10 (M^++2), calcd for $\text{C}_{13}\text{H}_{13}\text{BrO}_4$ 311.9997.

5-Furan-2-ylmethyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (10c'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): $\nu_{\max}$ 2922, 1790, 1749, 1313, 1008, 945 and 738 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.30 (1H, d, $J = 1.20$ Hz), 6.29 (1H, dd, $J = 3.2, 2.0$ Hz), 6.18 (1H, d, $J = 2.8$ Hz) [Ar- H]; 3.83 (1H, t, $J = 3.6$ Hz), 3.52 (2H, d, $J = 3.6$ Hz), 1.79 (3H, s, CH_3), 1.68 (3H, s, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 164.8 (2 x C, O-C=O), 150.5 (C), 141.6 (CH), 110.6 (CH), 107.8 (CH), 105.2 (C, O-C-O), 45.5 (CH), 29.7 (CH_2), 28.4 (CH_3), 27.1 (CH_3); LRMS: m/z 223.00 (M-H^+), calcd for $\text{C}_{11}\text{H}_{12}\text{O}_5$ 224.0685.

2,2-Dimethyl-5-thiophen-2-ylmethyl-[1,3]dioxane-4,6-dione (10d'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): $\nu_{\max}$ 3001, 2926, 1784, 1747, 1342, 1296, 1203, 1072, 1012, 939 and 704 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.16 (1H, dd, $J = 4.0, 1.20$ Hz), 6.98 (1H, d, $J = 2.4$ Hz), 6.92 (1H, dd, $J = 4.8, 3.2$ Hz) [Ar- H]; 3.77 (1H, t, $J = 4.4$ Hz), 3.70 (2H, d, $J = 4.4$ Hz), 1.76 (3H, s, CH_3), 1.59 (3H, s, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 164.9 (2 x C, O-C=O), 138.1 (C), 127.9 (CH), 126.9 (CH), 125.1 (CH), 105.3 (C, O-C-O), 48.2 (CH), 28.4 (CH_2), 27.2 (CH_3), 26.4 (CH_3); LRMS: m/z 239.00 (M-H^+), calcd for $\text{C}_{11}\text{H}_{12}\text{O}_4\text{S}$ 240.0456.

2,2-Dimethyl-5-(3-phenyl-allyl)-[1,3]dioxane-4,6-dione (10e'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 90 $^{\circ}\text{C}$. IR (KBr): $\nu_{\max}$ 2924, 1743, 1315, 1205, 1068, 945, 787 and 738 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36-7.20 (5H, m) [Ar- H]; 6.60 (1H, d, $J = 16.0$ Hz, olefinic- H), 6.25 (1H, td, $J = 16.0, 7.6$ Hz, olefinic- H), 3.66 (1H, t, $J = 4.8$ Hz), 3.03 (2H, ddd, $J = 7.2, 5.2, 1.2$ Hz), 1.79 (3H, s, CH_3), 1.74 (3H, s, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 164.9 (2 x C, O-C=O), 136.7 (C), 134.7 (CH), 128.4 (2 x CH), 127.6 (CH), 126.3 (2 x CH), 123.9 (CH), 105.1 (C, O-C-O), 46.6 (CH), 29.6 (CH_2), 28.4 (CH_3), 26.9 (CH_3); LRMS: m/z 259.20 (M-H^+), calcd for $\text{C}_{15}\text{H}_{16}\text{O}_4$ 260.1049.

2,2-Dimethyl-5-[3-(2-nitro-phenyl)-allyl]-[1,3]dioxane-4,6-dione (10f'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 108 $^{\circ}\text{C}$. IR (KBr): $\nu_{\max}$ 2951, 2878, 1780, 1734, 1608, 1520, 1340, 1207, 829, 788 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.92 (1H, d, $J = 8.4$ Hz), 7.57-7.54 (2H, m), 7.40-7.36 (1H, m) [Ar- H]; 7.06 (1H, d, $J = 16.0$ Hz, olefinic- H), 6.31 (1H, td, $J = 16.0, 7.2$ Hz, olefinic- H), 3.71 (1H, t, $J = 5.2$ Hz), 3.07 (2H, br t, $J = 6.8$ Hz, PhCH=CHCH_2), 1.83 (3H, s, CH_3), 1.78 (3H, s, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 164.7 (2 x C, O-C=O), 147.8 (C), 133.0 (CH), 132.6 (C), 129.9 (CH), 129.6 (CH), 128.8 (CH), 128.1 (CH), 124.5 (CH), 105.2 (C, O-C-O), 46.6 (CH), 29.4 (CH_2), 28.5 (CH_3), 26.8 (CH_3); LRMS: m/z 304.00 (M-H^+), calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_6$ 305.0899; Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_6$ (305.09): C, 59.01; H, 4.95; N, 4.59. Found: C, 59.018; H, 4.938; N, 4.437%.

5-Isobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (10j'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (KBr): $\nu_{\max}$ 2957, 1745, 1641, and 1211 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.44 (1H, t, $J = 5.2$ Hz), 1.99 (2H, m), 1.80 (3H, s, CH_3), 1.76 (3H, s, CH_3), 0.95 (6H, d, $J = 6.0$ Hz, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.0 (2 x C, O-C=O), 104.8 (C, O-C-O), 44.2 (CH), 35.4 (CH_2), 28.6 (CH), 26.9 (CH_3), 25.9 (CH_3), 22.1 (2 x CH_3); LRMS: m/z 199.10 (M-H^+), calcd for $\text{C}_{10}\text{H}_{16}\text{O}_4$ 200.1049.

2,2-Dimethyl-5-(3-methyl-butyl)-[1,3]dioxane-4,6-dione (10k'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (Neat): $\nu_{\max}$ cm^{-1} ; ^1H NMR (CDCl_3) δ 3.51 (1H, t, $J = 5.2$ Hz, CH), 2.11 (2H, m), 1.79 (3H, s, CH_3), 1.76 (3H, s, CH_3), 1.60 (1H, m), 1.35 (2H, m), 0.91 (6H, d, $J = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.6 (2 x C, O-C=O), 104.7 (C, O-C-O), 46.2 (CH), 35.3, 28.4, 28.1, 26.9, 24.6, 22.2 (2 x CH_3); LRMS: m/z 213.10 (M-H^+), calcd for $\text{C}_{11}\text{H}_{18}\text{O}_4$ 214.1205.

2,2-Dimethyl-5-(3-phenyl-propyl)-[1,3]dioxane-4,6-dione (10l'e): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): $\nu_{\max}$ 3364, 2926, 1784, 1750 and 1452 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.28-7.17 (5H, m), 3.47 (1H, t, $J = 4.8$ Hz), 2.69 (2H, t, $J = 7.6$ Hz), 2.17 (2H, m), 1.82 (2H, m), 1.74 (6H, s, 2 x CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.4 (2 x C, O-C=O), 141.5 (C), 128.39 (2 x CH), 128.36 (2 x CH), 125.9 (CH), 104.8 (C, O-C-O), 46.1 (CH), 35.8 (CH_2), 28.4 (CH_2), 28.1 (CH_2), 26.8 (CH_3), 26.3 (CH_3); LRMS: m/z 261.15 (M-H^+), calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$ 262.1205.

5-Cyclohexylmethyl-1,3-dimethyl-pyrimidine-2,4,6-trione (10m'a): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 80 °C. IR (KBr): $\nu_{\max}$ 3433, 2924, 2851, 1695, 1454, 1379, 1284 and 910 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.50 (1H, t, $J = 6.4$ Hz), 3.30 (6H, s, 2 x N- CH_3), 1.94 (2H, t, $J = 6.8$ Hz), 1.72-1.63 (5H, m), 1.56-1.41 (1H, m), 1.26-1.18 (3H, m), 0.95-0.91 (2H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.9 (2 x C, N-C=O), 151.7 (C, $\text{N}(\text{CH}_3)_2\text{C=O}$), 47.1 (CH), 38.9 (CH_2), 34.8 (CH), 32.8 (2 x CH_2), 28.5 (2 x CH_3 , N- CH_3), 26.2 (CH_2), 25.9 (2 x CH_2); HRMS: m/z 253.1543 (M+H^+), calcd for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_3\text{H}$ 253.1552; Anal. calcd for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_3$ (253.16): C, 61.88; H, 7.99; N, 11.10. Found: C, 61.783; H, 8.036; N, 11.243%.

5-Cyclohexylmethyl-pyrimidine-2,4,6-trione (10m'b): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 230 °C. IR (KBr): $\nu_{\max}$ 3219, 3099, 2924, 2849, 1741, 1685, 1444, 1369, 1344, 1213, 1051, 987 and 839 cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 11.12 (2H, br s, 2 x N-H), 3.49 (1H, s, CH), 1.76 (2H, m), 1.58 (5H, m), 1.40 (1H, br s), 1.10 (3H, m), 0.82 (2H, m); ^{13}C NMR ($\text{DMSO-}d_6$, DEPT-135) δ 171.2 (2 x C, HN-C=O), 151.4 (C, $(\text{NH})_2\text{C=O}$), 46.3 (CH), 35.6 (CH_2), 35.2 (CH), 32.9 (2 x CH_2), 26.4 (CH_2), 26.1 (2 x CH_2); HRMS: m/z 247.1065 (M+Na^+), calcd for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$ 247.1059; Anal. calcd for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3$ (246.11): C, 58.91; H, 7.19; N, 12.49. Found: C, 58.954; H, 7.150; N, 12.427%.

5-Cyclohexylmethyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (10m'c): Purified by column chromatography using EtOAc/hexane and isolated as white solid. MP 98 °C. IR (KBr): $\nu_{\max}$ 2999, 1745, 1647, 1446, 1336, 1315, 1296, 1205, 1060, 1006 and 945 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.51 (1H, t, $J = 5.6$ Hz), 2.02 (2H, t, $J = 6.40$ Hz), 1.82 (3H, s, CH_3), 1.79 (3H, s, CH_3), 1.75-1.60 (6H, m), 1.29-1.16 (3H, m), 1.02-0.94 (2H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.1 (2 x C, O-C=O), 104.8 (C, O-C-O), 43.6 (CH), 35.2 (CH), 33.9 (CH_2), 32.9 (2 x CH_2), 28.6 (CH_3), 26.9 (CH_3), 26.3 (CH_2), 26.0 (2 x CH_2); HRMS: m/z 241.1440 (M+H^+), calcd for $\text{C}_{13}\text{H}_{20}\text{O}_4\text{H}$ 241.1440; Anal. calcd for $\text{C}_{13}\text{H}_{20}\text{O}_4$ (240.14): C, 64.98; H, 8.39. Found: C, 65.059; H, 8.336%.

2-(2-Allyloxy-benzyl)-2-cyano-pent-4-enoic acid ethyl ester (11kfc): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): $\nu_{\max}$ 3080, 2982, 2930, 2245 ($\text{C}\equiv\text{N}$),

1741 (O-C=O), 1645, 1602, 1494, 1454, 1246, 1120, 1020, 929, 860 and 756 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.24 (1H, t, $J = 8.0$ Hz), 7.23 (1H, d, $J = 8.0$ Hz), 6.91 (1H, t, $J = 7.6$ Hz), 6.87 (1H, d, $J = 8.4$ Hz) [Ar-H]; 6.13-6.03 (1H, m, olefinic-H), 5.83 (1H, m, olefinic-H), 5.43 (1H, d, $J = 17.2$ Hz), 5.30-5.21 (3H, m, olefinic-H), 4.55 (2H, d, $J = 4.60$ Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.21-4.15 (2H, m, OCH_2CH_3), 3.35 (1H, d, $J = 13.5$ Hz), 3.18 (1H, d, $J = 13.59$ Hz), 2.78 (1H, dd, $J = 13.76, 7.39$ Hz), 2.53 (1H, dd, $J = 13.72, 7.01$ Hz), 1.22 (3H, t, $J = 7.05$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.4 (C, O-C=O), 156.9 (C), 133.3 (CH), 131.5 (CH), 131.2 (CH), 129.2 (CH), 123.0 (C), 120.7 (CH_2), 120.6 (CH), 118.6 (C, $\text{C}\equiv\text{N}$), 117.3 (CH_2), 111.8 (CH), 69.0 (CH_2 , $\text{OCH}_2\text{CH}=\text{CH}_2$), 62.6 (CH_2 , OCH_2CH_3), 50.5 (C), 41.0 (CH_2), 35.9 (CH_2), 14.0 (CH_3 , OCH_2CH_3); HRMS m/z 322.1419 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3\text{Na}$ 322.1419.

2-(3-Allyloxy-benzyl)-2-cyano-pent-4-enoic acid ethyl ester (11lfc): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 3082, 2982, 2930, 2245 ($\text{C}\equiv\text{N}$), 1741 (O-C=O), 1645, 1601, 1494, 1454, 1248, 1020, 929 and 756 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.21 (1H, t, $J = 8.1$ Hz), 6.85 (3H, m) [Ar-H]; 6.07-5.99 (1H, m, olefinic-H), 5.88-5.79 (1H, m, olefinic-H), 5.43 (1H, d, $J = 17.2$ Hz, olefinic-H), 5.28-5.24 (3H, m, olefinic-H), 4.52 (2H, d, $J = 5.40$ Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.16 (2H, q, $J = 7.12$ Hz, OCH_2CH_3), 3.17 (1H, d, $J = 13.56$ Hz), 3.03 (1H, d, $J = 13.56$ Hz), 2.73 (1H, dd, $J = 13.72, 7.32$ Hz), 2.57 (1H, dd, $J = 13.72, 7.00$ Hz), 1.18 (3H, t, $J = 7.16$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.0 (C, O-C=O), 158.7 (C), 135.5 (C), 133.7, 130.6, 129.5, 122.4, 121.0 (CH), 118.6 (C, $\text{C}\equiv\text{N}$), 117.7, 116.3, 114.4, 68.8 (CH_2 , $\text{OCH}_2\text{CH}=\text{CH}_2$), 62.7 (CH_2 , OCH_2CH_3), 51.1 (C), 42.5 (CH_2), 41.4 (CH_2), 14.0 (CH_3 , OCH_2CH_3); LRMS m/z 300.10 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$ 299.1521; Anal. calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$ (299.15): C, 72.22; H, 7.07; N, 4.68. Found: C, 72.207; H, 7.044; N, 4.783%.

2-(4-Allyloxy-benzyl)-2-cyano-pent-4-enoic acid ethyl ester (11mfc): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 3082, 2984, 2930, 2245 ($\text{C}\equiv\text{N}$), 1739 (O-C=O), 1695, 1610, 1512, 1244, 1022, 929 and 837 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.18 (2H, d, $J = 8.28$ Hz), 6.85 (2H, d, $J = 8.40$ Hz) [Ar-H]; 6.04-6.00 (1H, m, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.84-5.80 (1H, m, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.39 (1H, d, $J = 17.53$ Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.28-5.23 (3H, m, olefinic-H), 4.51 (2H, d, $J = 4.72$ Hz, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.14 (2H, q, $J = 6.92$ Hz, OCH_2CH_3), 3.14 (1H, d, $J = 13.70$ Hz), 3.00 (1H, d, $J = 13.70$ Hz), 2.71 (1H, dd, $J = 13.70, 7.4$ Hz), 2.55 (1H, dd, $J = 11.90, 5.30$ Hz), 1.17 (3H, t, $J = 7.00$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.0 (C, O-C=O), 158.2 (C), 133.1 (CH), 130.9 (2 x CH), 130.5 (CH), 126.2 (C), 120.8 (CH_2), 118.6 (C, $\text{C}\equiv\text{N}$), 117.6 (CH_2), 114.7 (2 x CH), 68.7 (CH_2 , $\text{OCH}_2\text{CH}=\text{CH}_2$), 62.5 (CH_2 , OCH_2CH_3), 53.4 (C), 41.7 (CH_2), 41.1 (CH_2), 13.9 (CH_3 , OCH_2CH_3); LRMS m/z 300.10 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$ 299.1521; Anal. calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$ (299.15): C, 72.22; H, 7.07; N, 4.68. Found: C, 72.211; H, 7.049; N, 4.849%.

2-Cyano-2-(4-nitro-benzyl)-pent-4-enoic acid ethyl ester (11pfc): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 2972, 2930, 2247 ($\text{C}\equiv\text{N}$), 1743 (O-C=O), 1602, 1493 and 1444 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.20 (2H, d, $J = 8.8$ Hz), 7.47 (2H, d, $J = 8.40$ Hz) [Ar-H]; 5.88-5.82 (1H, m, olefinic-H), 5.32 (1H, br s, olefinic-H), 5.28 (1H, dd, $J = 7.2, 1.2$ Hz), 4.17 (2H, q, $J = 6.8$ Hz,

OCH₂CH₃), 3.32 (1H, d, *J* = 13.6 Hz), 3.14 (1H, d, *J* = 13.6 Hz), 2.78 (1H, dd, *J* = 13.6, 7.6 Hz), 2.62 (1H, dd, *J* = 13.60, 7.2 Hz), 1.19 (3H, t, *J* = 7.20 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 167.5 (C, O-C=O), 141.6 (C), 131.0 (2 x CH), 129.9 (CH), 123.8 (2 x CH), 121.7 (CH₂, CH=CH₂), 117.9 (C, C≡N), 63.1 (CH₂, OCH₂CH₃), 50.7 (C), 41.8 (CH₂), 41.7 (CH₂), 14.0 (CH₃, OCH₂CH₃); LRMS *m/z* 288.1 (M⁺), calcd for C₁₅H₁₆N₂O₄ 288.11; Anal. calcd for C₁₅H₁₆N₂O₄ (288.11): C, 62.49; H, 5.59; N, 9.72. Found: C, 62.588; H, 5.569; N, 9.667%.

2-Allyl-2-(2-chloro-benzyl)-malononitrile (11wj): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): *v*_{max} 2986, 2200 (C≡N), 1903, 1647, 1491, 1452, 1273 and 1016 cm⁻¹; ¹H NMR (CDCl₃) δ 7.56 (1H, m), 7.50 (1H, m), 7.35 (2H, m) [Ar-H]; 5.93 (1H, m, olefinic-H), 5.45 (2H, m, olefinic-H), 3.49 (2H, s, ArCH₂), 2.80 (2H, d, *J* = 7.2 Hz, CH₂CH=CH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 135.1 (C), 131.8 (CH), 130.23 (CH), 130.20 (CH), 130.1 (C), 128.5 (CH), 127.4 (CH), 123.4 (CH₂), 114.7 (2 x C, C≡N), 41.4 (CH₂), 38.8 (CH₂), 38.5 (C); LRMS *m/z* 230 (M⁺), calcd for C₁₃H₁₁ClN₂ 230.06; Anal. calcd for C₁₃H₁₁ClN₂ (230.06): C, 67.68; H, 4.81; N, 12.14. Found: C, 67.802; H, 4.820; N, 12.621%.

2-Allyl-2-(4-chloro-benzyl)-malononitrile (11yj): Purified by column chromatography using EtOAc/hexane and isolated as a solid. MP 72 °C IR (KBr): *v*_{max} 2989, 2924, 2847, 2249 (C≡N), 1647, 1599, 1493, 1450, 1097, 1016, 989, 939 and 841 cm⁻¹; ¹H NMR (CDCl₃) δ 7.39 (2H, d, *J* = 8.4 Hz), 7.31 (2H, d, *J* = 7.2 Hz) [Ar-H]; 5.99-5.89 (1H, m, CH=CH₂), 5.48-5.41 (2H, m, CH=CH₂), 3.17 (2H, s, ArCH₂), 2.71 (2H, d, *J* = 7.2 Hz, CH₂CH=CH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 135.0 (C), 131.5 (2 x CH), 130.3 (C), 129.2 (2 x CH), 128.3 (CH), 123.6 (CH₂, CH=CH₂), 114.6 (2 x C, C≡N), 41.9 (CH₂), 41.3 (CH₂), 39.1 (C); LRMS *m/z* 230 (M⁺), calcd for C₁₃H₁₁ClN₂ 230.06; Anal. calcd for C₁₃H₁₁ClN₂ (230.06): C, 67.68; H, 4.81; N, 12.14. Found: C, 67.633; H, 4.791; N, 12.131%.

2-Benzyl-2-cyano-pent-4-enoic acid allyl ester (11ag): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): *v*_{max} 3086, 2928, 2245 (C≡N), 1745 (O-C=O), 1645, 1496, 1452 and 1221 cm⁻¹; ¹H NMR (CDCl₃) δ 7.37-7.28 (5H) [Ar-H]; 5.93-5.74 (2H, m, 2 x CH=CH₂), 5.32-5.22 (4H, m, 2 x CH=CH₂), 4.64-4.55 (2H, m, OCH₂CH=CH₂), 3.23 (1H, d, *J* = 13.52 Hz), 3.11 (1H, d, *J* = 13.52 Hz), 2.78 (1H, dd, *J* = 13.7, 7.40 Hz, CH₂CH=CH₂), 2.61 (1H, dd, *J* = 13.7, 7.10 Hz, CH₂CH=CH₂); ¹³C NMR (CDCl₃, DEPT-135) δ 167.8 (C, O-C=O), 134.0 (C), 130.7 (CH, CH=CH₂), 130.5 (CH, CH=CH₂), 130.0 (2 x CH), 128.6 (2 x CH), 127.9 (CH), 121.2 (CH₂, CH=CH₂), 119.4 (CH₂, CH=CH₂), 118.4 (C, C≡N), 67.0 (CH₂, OCH₂CH=CH₂), 51.3 (C), 42.5 (CH₂), 41.4 (CH₂, CH₂CH=CH₂); HRMS *m/z* 278.1158 (M+Na⁺), calcd for C₁₆H₁₇NO₂Na 278.1157.

2-Benzyl-2-cyano-pent-4-ynoic acid allyl ester (11agd): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): *v*_{max} 3294, 3034, 2935, 2247 (C≡N), 1745 (O-C=O), 1649, 1604, 1201, 1086, 1053, 941 and 742 cm⁻¹; ¹H NMR (CDCl₃) δ 7.38-7.30 (5H, m) [Ar-H]; 5.87-5.78 (1H, m, CH=CH₂), 5.32 (1H, dd, *J* = 17.0, 1.0 Hz, CH=CH₂), 5.27 (1H, br d, *J* = 10.4 Hz, CH=CH₂), 4.65 (2H, m, OCH₂CH=CH₂), 3.29 (2H, s, PhCH₂), 2.76 (2H, dABq, *J* = 16.70, 2.50 Hz, CH₂C≡CH), 2.29 (1H, t, *J* =

2.44 Hz, $\text{CH}_2\text{C}\equiv\text{CH}$); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.8 (C, $\text{O}-\text{C}=\text{O}$), 133.4 (C), 130.6 (CH, $\text{CH}=\text{CH}_2$), 130.0 (2 x CH), 128.7 (2 x CH), 128.2 (CH), 119.6 (CH_2 , $\text{CH}=\text{CH}_2$), 117.8 (C, $\text{C}\equiv\text{N}$), 76.8 (C, $\text{CH}_2\text{C}\equiv\text{CH}$), 73.7 (CH, $\text{CH}_2\text{C}\equiv\text{CH}$), 67.4 (CH_2 , $\text{OCH}_2\text{CH}=\text{CH}_2$), 50.0 (C), 41.4 (CH_2), 26.5 (CH_2 , $\text{CH}_2\text{C}\equiv\text{CH}$); HRMS m/z 276.1000 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}$ 276.1000.

2-Benzyl-3-[3-(2-benzyl-2-cyano-2-ethoxycarbonyl-ethyl)-phenyl]-2-cyano-propionic acid ethyl ester (11tfe): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 3032, 2984, 2934, 2245 ($\text{C}\equiv\text{N}$), 1739 ($\text{O}-\text{C}=\text{O}$), 1606, 1496, 1454, 1369, 1228, 1099, 856, 744 and 702 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36-7.28 (14H, m) [Ar-H]; 4.04 (4H, q, $J = 7.20$ Hz, OCH_2CH_3); 3.35 (2H, br d, $J = 9.20$ Hz), 3.32 (2H, br d, $J = 9.2$ Hz), 3.14 (2H, br s), 3.10 (2H, br s), 1.02 (3H, t, $J = 7.20$ Hz, OCH_2CH_3), 1.00 (3H, t, $J = 7.2$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.0 (C, $\text{O}-\text{C}=\text{O}$), 168.0 (C, $\text{O}-\text{C}=\text{O}$), 134.6 (C), 134.5 (C), 134.1 (C), 134.0 (C), 132.03 (CH), 132.0 (CH), 130.03 (2 x CH), 130.01 (2 x CH), 129.6 (2 x CH), 128.91 (CH), 128.86 (CH), 128.59 (2 x CH), 127.93 (CH), 127.90 (CH), 118.54 (C, $\text{C}\equiv\text{N}$), 118.51 (C, $\text{C}\equiv\text{N}$), 62.71 (CH_2 , OCH_2CH_3), 62.70 (CH_2 , OCH_2CH_3), 53.0 (2 x C), 43.5 (CH_2), 43.25 (CH_2), 43.02 (2 x CH_2), 13.8 (CH_3 , OCH_2CH_3), 13.70 (CH_3 , OCH_2CH_3); LRMS m/z 508.20 (M^+), calcd for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_4$ 508.2362; Anal. calcd for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_4$ (508.24): C, 75.57; H, 6.34; N, 5.51. Found: C, 75.600; H, 6.358; N, 5.546%.

2,2-Dimethyl-5-[3-(2-nitro-phenyl)-propyl]-[1,3]dioxane-4,6-dione (10p'c): Purified by column chromatography using EtOAc/hexane and isolated as a solid. MP 112°C . IR (KBr): ν_{max} 2951, 2878, 1790, 1741, 1608, 1520, 1348, 1269, 1203, 987, 887, 788 and 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.90 (1H, br d, $J = 8.4$ Hz), 7.53 (1H, br t, $J = 7.6$ Hz), 7.38 (1H, d, $J = 8.0$ Hz), 7.35 (1H, t, $J = 7.6$ Hz) [Ar-H]; 3.59 (1H, t, $J = 4.8$ Hz), 2.95 (2H, t, $J = 8.0$ Hz), 2.22-2.17 (2H, m), 1.92-1.86 (2H, m), 1.81 (3H, s, CH_3), 1.75 (3H, s, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.3 (C, $\text{O}-\text{C}=\text{O}$), 149.3 (C), 136.4 (C), 133.0 (CH), 131.8 (CH), 127.2 (CH), 124.7 (CH), 104.9 (C, $\text{O}-\text{C}-\text{O}$), 45.9 (CH), 32.5 (CH_2), 28.4 (CH_3), 27.5 (CH_2), 26.6 (CH_3), 25.8 (CH_2); LRMS m/z 306.05 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6$ 307.1056; Anal. calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6$ (307.11): C, 58.63; H, 5.58; N, 4.56. Found: C, 58.726; H, 5.560; N, 4.617%.

2-Benzyl-2-(2-phenyl-allyl)-indan-1,3-dione (11adf): Purified by column chromatography using EtOAc/hexane and isolated as a solid. MP 58°C . IR (KBr): ν_{max} 3074, 2924, 1739, 1705, 1593, 1493, 1444, 1356, 1248, 1028 and 912 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.54-7.49 (4H, m), 7.13-6.94 (8H, m), 6.84 (2H, m) [Ar-H]; 5.05 (1H, s), 5.02 (1H, s) [$\text{C}=\text{CH}_2$]; 3.24 (2H, br s), 3.23 (2H, br s); ^{13}C NMR (CDCl_3 , DEPT-135) δ 202.8 (2 x C, $\text{C}=\text{O}$), 144.0 (C), 142.6 (2 x C), 140.1 (C), 135.3 (C), 134.8 (2 x CH), 130.0 (2 x CH), 127.9 (2 x CH), 127.7 (2 x CH), 127.4 (CH), 126.8 (2 x CH), 126.5 (CH), 122.2 (2 x CH), 118.4 (CH_2), 60.7 (C), 42.0 (CH_2), 41.1 (CH_2); HRMS m/z 375.1345 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{25}\text{H}_{20}\text{O}_2\text{Na}$ 375.1361.

2-Ethyl-2-(2-phenyl-allyl)-indan-1,3-dione (11o'df): Purified by column chromatography using EtOAc/hexane and isolated as a solid. MP 55°C . IR (KBr): ν_{max} 2966, 2930, 1741, 1701, 1593, 1454, 1361, 1251, 914, 781 and 748 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.69-7.63 (4H, m), 7.09 (1H, t, $J = 7.6$ Hz), 7.01 (2H, t, $J = 7.6$ Hz), 6.80 (2H, d, $J = 7.2$ Hz) [Ar-H]; 4.98 (1H, br s), 4.97 (1H, br s) [$\text{C}=\text{CH}_2$]; 3.08 (2H, s), 1.93 (2H,

q, $J = 7.6$ Hz, CH_2CH_3), 0.65 (3H, t, $J = 7.6$ Hz, CH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 203.8 (2 x C, C=O), 144.4 (C), 142.8 (2 x C), 140.2 (C), 135.1 (2 x CH), 127.7 (2 x CH), 127.5 (CH), 126.9 (2 x CH), 122.4 (2 x CH), 118.2 (CH_2), 59.5 (C), 41.7 (CH_2), 28.6 (CH_2), 9.1 (CH_3); HRMS m/z 313.1201 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Na}$ 313.1204.

5-Cyclohexyl-1,3-dimethyl-pyrimidine-2,4,6-trione (12aa): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 95 °C. IR (KBr): ν_{max} 2935, 2914, 1718, 1658, 1444, 1369, 1257, 1113, 987 and 763 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.33 (1H, d, $J = 3.6$ Hz, CH), 3.29 (6H, s, 2 x N- CH_3), 2.19 (1H, m, CH), 1.76 (2H, m), 1.65 (3H, m), 1.25 (4H, m), 1.10 (1H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.5 (2 x C, N-C=O), 151.9 (C, $(\text{NMe})_2\text{C}=\text{O}$), 55.5 (CH), 44.1 (CH), 29.9 (2 x CH_2), 28.3 (2 x CH_3 , N- CH_3), 26.3 (2 x CH_2), 25.5 (CH_2); LRMS: m/z 237.10 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_3$ 238.1317.

5-Cyclohexyl-pyrimidine-2,4,6-trione (12ab): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 230 °C. IR (KBr): ν_{max} 3209, 3070, 2939, 2860, 1757, 1685, 1554, 1442, 1358, 1217 and 821 cm^{-1} ; ^1H NMR (CDCl_3) δ 12.48 (2H, s, 2 x NH), 4.41 (1H, d, $J = 3.2$ Hz), 3.30 (1H, m, CH), 2.97 (2H, br d, $J = 12.0$ Hz), 2.58-2.40 (4H, m), 2.28 (1H, m), 2.85 (3H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 170.2 (2 x C, N-C=O), 151.0 (C, $(\text{NH})_2\text{C}=\text{O}$), 54.0 (CH), 41.5 (CH), 29.4 (2 x CH_2), 25.9 (2 x CH_2), 25.4 (CH_2); LRMS: m/z 209.00 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_3$ 210.1004.

5-Cyclohexyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (12ac): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): ν_{max} 2934, 2854, 1780, 1738, 1315, 1308, 1213 and 955 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.32 (1H, d, $J = 3.2$ Hz, CH), 2.44-2.30 (1H, m), 1.74 (6H, s, 2 x CH_3), 1.68-1.62 (6H, m), 1.32-1.18 (4H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.3 (2 x C, O-C=O), 104.7 (C, O-C-O), 51.4 (CH), 39.6 (CH), 29.4 (2 x CH_2), 28.2 (CH_3), 27.7 (CH_3), 26.5 (2 x CH_2), 25.6 (CH_2); LRMS: m/z 225.10 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4$ 226.1205.

2-Cyclohexyl-indan-1,3-dione (12ad): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 70 °C. IR (KBr): ν_{max} 2924, 2854, 1709, 1593, 1452, 1350, 1275, 1047, 825 and 758 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.93 (2H, d, $J = 8.8$ Hz), 7.80 (2H, d, $J = 6.0$ Hz) [Ar-H]; 2.83 (1H, d, $J = 4.0$ Hz), 2.21 (1H, m), 1.70-1.50 (5H, m), 1.42 (2H, m), 1.30-1.08 (3H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 201.3 (2 x C, C=O), 142.8 (2 x C), 135.4 (2 x CH), 122.8 (2 x CH), 58.7 (CH), 39.3 (CH), 29.7 (2 x CH_2), 26.4 (2 x CH_2), 25.7 (CH_2); LRMS: m/z 227.10 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ 228.1150.

Cyano-cyclohexyl-acetic acid methyl ester (12ae): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2930, 2856, 2249 ($\text{C}\equiv\text{N}$), 1749 (O-C=O), 1452, 1257, and 1016 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.80 (3H, s, OCH_3), 3.39 (1H, d, $J = 5.6$ Hz, CH), 2.04 (1H, m), 1.78-1.61 (6H, m), 1.30-1.15 (4H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 166.3 (C, O-C=O), 115.6 (C, $\text{C}\equiv\text{N}$), 53.2 (CH_3 , OCH_3), 44.4 (CH), 38.8 (CH), 31.0 (CH_2), 29.4 (CH_2), 25.7 (CH_2), 25.5 (CH_2), 25.4 (CH_2); LRMS: m/z 180.15 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2$ 181.1103.

Cyano-cyclohexyl-acetic acid ethyl ester (12af): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2932, 2856, 2251 ($\text{C}\equiv\text{N}$), 1745 (O-C=O), 1450, 1253,

1192 and 1028 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.25 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 3.36 (1H, d, $J = 5.6$ Hz), 2.03 (1H, m), 1.78-1.60 (6H, m), 1.30 (4H, m), 1.27 (3H, t, $J = 6.8$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.8 (C, $\text{O}-\text{C}=\text{O}$), 115.7 (C, $\text{C}\equiv\text{N}$), 62.5 (CH_2 , OCH_2CH_3), 44.5 (CH), 38.8 (CH), 31.0 (CH_2), 29.3 (CH_2), 25.8 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 14.0 (CH_3 , OCH_2CH_3); LRMS: m/z 194.15 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_2$ 195.1259.

Cyclohexyl-(toluene-4-sulfonyl)-acetonitrile (12ai): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 80 $^\circ\text{C}$. IR (KBr): ν_{max} 2924, 2854, 2249, 1595, 1448, 1323, 1170, 1149, 1086, 815 and 748 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.88 (2H, d, $J = 8.0$ Hz), 7.42 (2H, d, $J = 8.0$ Hz) [Ar-H]; 3.74 (1H, d, $J = 3.6$ Hz), 2.48 (3H, s, PhCH_3), 2.17 (1H, m), 1.82-1.60 (4H, m), 1.42-1.20 (6H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 146.3 (C), 134.2 (C), 130.2 (2 x CH), 129.1 (2 x CH), 113.2 (C, $\text{C}\equiv\text{N}$), 63.5 (CH), 36.0 (CH), 32.2 (CH_2), 29.4 (CH_2), 26.0 (CH_2), 25.32 (CH_2), 25.30 (CH_2), 21.8 (CH_3); LRMS: m/z 276.0 ($\text{M}-\text{H}^+$), calcd $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$ 277.1136; HRMS: m/z 300.1026 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{SNa}$ 300.1034.

2-Cyclohexyl-malononitrile (12aj): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2932, 2858, 2254, 1452, 1319, 1224, 1170, 1062 and 892 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.58 (1H, d, $J = 5.6$ Hz), 1.96 (3H, m), 1.85 (2H, m), 1.73 (1H, m), 1.33-1.17 (5H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 111.9 (2 x C, $\text{C}\equiv\text{N}$), 39.3 (CH), 29.9 (2 x CH_2), 29.3 (CH), 25.2 (2 x CH_2), 25.0 (CH_2); LRMS: m/z 147.05 ($\text{M}-\text{H}^+$), calcd for $\text{C}_9\text{H}_{12}\text{N}_2$ 148.1000.

3-Cyclohexyl-1,5-dioxaspiro[5.5]undecane-2,4-dione (12ao): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 134 $^\circ\text{C}$. IR (KBr): ν_{max} 2935, 2874, 1784, 1739, 1450, 1302, 1209, 995 and 933 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.35 (1H, d, $J = 2.8$ Hz), 2.39 (1H, m), 1.93 (4H, m), 1.76 (4H, m), 1.70-1.60 (7H, m), 1.49 (2H, m), 1.30-1.17 (3H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 165.3 (2 x C, $\text{O}-\text{C}=\text{O}$), 105.5 (C, $\text{O}-\text{C}-\text{O}$), 51.7 (CH), 39.6 (CH), 36.89 (CH_2), 36.7 (CH_2), 29.4 (2 x CH_2), 26.5 (2 x CH_2), 25.5 (CH_2), 24.0 (CH_2), 22.4 (CH_2), 21.7 (CH_2); LRMS: m/z 265.20 ($\text{M}-\text{H}^+$), calcd $\text{C}_{15}\text{H}_{22}\text{O}_4$ 266.1518; HRMS: m/z 267.1599 ($\text{M}+\text{H}^+$), 289.1417 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{H}$ 267.1596, $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na}$ 289.1416.

Cyano-(2-methyl-cyclohexyl)-acetic acid ethyl ester (12bf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2930, 2856, 2249, 1745 ($\text{O}-\text{C}=\text{O}$), 1448, 1369, 1253, 1192, 1028 and 854 cm^{-1} ; ^1H NMR (CDCl_3 , 3.3:1 ratio of isomers, major isomer) δ 4.28 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 3.84 (1H, d, $J = 3.6$ Hz), 1.79-1.70 (4H, m), 1.57 (1H, m), 1.32 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.30 (3H, m), 0.97 (3H, d, $J = 6.4$ Hz), 0.85 (1H, m); ^{13}C NMR (CDCl_3 , DEPT-135, 3.3:1 ratio of isomers, major isomer) δ 166.5 (C, $\text{O}-\text{C}=\text{O}$), 115.1 (C, $\text{C}\equiv\text{N}$), 62.6 (CH_2 , OCH_2CH_3), 45.1 (CH), 41.4 (CH), 35.1 (CH_2), 34.6 (CH), 28.3 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 19.7 (CH_3), 14.0 (CH_3); LRMS: m/z 208.15 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2$ 209.1416.

(-)-(1R, 3R)-2-(3-Methyl-cyclohexyl)-malononitrile (12cj): Purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_{\text{D}}^{25} = -2.403^\circ$ ($c = 0.5$ g/100 mL, CHCl_3); IR (neat): ν_{max} 2930, 2860, 2254, 1460, 1381, 1217 and 1055 cm^{-1} ; ^1H NMR (CDCl_3 , 3.0:1 ratio of isomers, major isomer) δ 3.64

(1H, d, $J = 7.6$ Hz, CH), 2.32-2.27 (1H, m), 1.98-1.85 (2H, m), 1.68-1.41 (6H, m), 1.38-1.33 (1H, m), 0.98 (3H, d, $J = 7.2$ Hz, CH₃); ¹³C NMR (CDCl₃, DEPT-135, 3.0:1 ratio of isomers, major isomer) δ 112.2 (C, C $\equiv$ N), 112.1 (C, C $\equiv$ N), 35.6 (CH), 35.0 (CH₂), 31.5 (CH), 29.2 (CH), 28.2 (CH₂), 26.9 (CH₂), 19.7 (CH₃), 19.0 (CH₂); LRMS: m/z 161.10 (M-H⁺), calcd for C₁₀H₁₄N₂ 162.1157; Anal. calcd for C₁₀H₁₄N₂ (162.12): C, 74.03; H, 8.70; N, 17.27. Found: C, 74.062; H, 8.721; N, 17.486%.

Cyano-(4-methyl-cyclohexyl)-acetic acid ethyl ester (12df): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2930, 2858, 2249, 1745 (O-C=O), 1450, 1369, 1251, 1192, 1030 and 854 cm⁻¹; ¹H NMR (CDCl₃, 3.4:1 ratio of isomers, major isomer) δ 4.22 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 3.43 (1H, d, $J = 7.6$ Hz), 2.12 (1H, m), 1.76 (1H, m), 1.67-1.37 (6H, m), 1.37 (2H, m), 1.27 (3H, t, $J = 6.8$ Hz, OCH₂CH₃), 0.91 (3H, d, $J = 6.8$ Hz, CH₃); ¹³C NMR (CDCl₃, DEPT-135, 3.4:1 ratio of isomers, major isomer) δ 165.9 (C, O-C=O), 115.9 (C, C $\equiv$ N), 62.5 (CH₂, OCH₂CH₃), 42.8 (CH), 37.8 (CH), 30.4 (CH₂), 30.3 (CH₂), 27.9 (CH), 25.8 (CH₂), 24.9 (CH₂), 18.6 (CH₃), 13.9 (CH₃, OCH₂CH₃); LRMS: m/z 208.15 (M-H⁺), calcd for C₁₂H₁₉NO₂ 209.1416.

(4-tert-Butyl-cyclohexyl)-cyano-acetic acid ethyl ester (12ef): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2945, 2868, 2247, 1747 (O-C=O), 1602, 1456, 1367, 1251, 1180, 1095, 1035 and 846 cm⁻¹; ¹H NMR (CDCl₃, 6.0:1 ratio of isomers, major isomer) δ 4.25 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 3.60 (1H, d, $J = 11.6$ Hz), 2.38 (1H, d, $J = 5.2$ Hz), 2.10 (1H, d, $J = 11.6$ Hz), 1.60 (5H, m), 1.31 (3H, t, $J = 7.2$ Hz, OCH₂CH₃), 1.06 (3H, m), 0.84 (9H, s, 3 x CH₃); ¹³C NMR (CDCl₃, DEPT-135, 6.0:1 ratio of isomers, major isomer) δ 166.2 (C, O-C=O), 116.6 (C, C $\equiv$ N), 62.5 (CH₂, OCH₂CH₃), 47.7 (CH), 38.8 (CH), 34.7 (CH), 32.5 (C), 28.8 (CH₂), 28.0 (CH₂), 27.3 (3 x CH₃, *t*-Bu), 21.5 (CH₂), 21.2 (CH₂), 14.0 (CH₃); LRMS: m/z 250.25 (M-H⁺), calcd for C₁₅H₂₅NO₂ 251.1885.

Cyano-(1,4-dioxa-spiro[4.5]dec-8-yl)-acetic acid ethyl ester (12ff): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2939, 2885, 2249, 1741 (O-C=O), 1446, 1371, 1336, 1105, 1033 and 927 cm⁻¹; ¹H NMR (CDCl₃) δ 4.29 (2H, q, $J = 7.2$ Hz, OCH₂CH₃), 3.96 (4H, s, OCH₂CH₂O), 3.40 (1H, d, $J = 6.4$ Hz), 2.10 (1H, m), 1.87-1.74 (4H, m), 1.68-1.50 (4H, m), 1.34 (3H, t, $J = 7.2$ Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.6 (C, O-C=O), 115.4 (C, C $\equiv$ N), 107.6 (C, O-C-O), 64.4 (CH₂), 64.3 (CH₂) [OCH₂CH₂O]; 62.7 (CH₂, OCH₂CH₃), 43.5 (CH), 37.5 (CH), 34.1 (CH₂), 33.9 (CH₂), 28.2 (CH₂), 26.9 (CH₂), 14.0 (CH₃, OCH₂CH₃); HRMS: m/z 254.1377 (M+H⁺), calcd for C₁₃H₁₉NO₄H 254.1392.

Cyano-[4-(cyano-ethoxycarbonyl-methyl)-cyclohexyl]-acetic acid ethyl ester (12gf): Purified by column chromatography using EtOAc/hexane and isolated as oil. ¹H NMR (CDCl₃, 10.0:1 ratio of isomers, major isomer) δ 4.27 (4H, q, $J = 7.2$ Hz, 2 x OCH₂CH₃), 3.52 (2H, d, $J = 8.4$ Hz), 2.29 (2H, m), 1.78-1.56 (8H, m), 1.32 (6H, t, $J = 7.2$ Hz, 2 x OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135, 10.0:1 ratio of isomers, major isomer) δ 165.5 (2 x C, O-C=O), 115.6 (2 x C, C $\equiv$ N), 62.9 (2 x CH₂, 2 x OCH₂CH₃), 41.2 (2 x CH), 35.9 (2 x CH), 25.9 (CH₂), 25.8 (CH₂), 25.6 (CH₂), 25.5 (CH₂), 14.0 (2 x CH₃, 2 x OCH₂CH₃); LRMS: m/z 305.00 (M-H⁺), calcd for C₁₆H₂₂N₂O₄ 306.1580; Anal. calcd for C₁₆H₂₂N₂O₄ (306.16): C, 62.73; H, 7.24; N, 9.14. Found: C, 62.739; H, 7.243; N, 9.267 %.

Cyano-[4-(cyano-methoxycarbonyl-methyl)-cyclohexyl]-acetic acid methyl ester (12ge): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (neat): $\nu_{\max}$ 2937, 2249, 1747 (O-C=O), 1456, 1259, 1020, 939, 842 and 775 cm^{-1} ; ^1H NMR (CDCl_3 , 10.0:1 ratio of isomers, major isomer) δ 3.79 (6H, s, 2 x OCH_3), 3.52 (2H, dd, $J = 8.8, 1.6$ Hz), 2.28-2.25 (2H, m), 1.77-1.48 (8H, m); ^{13}C NMR (CDCl_3 , DEPT-135, 10.0:1 ratio of isomers, major isomer) δ 166.0 (2 x C, O-C=O), 115.5 (2 x C, $\text{C}\equiv\text{N}$), 53.4 (2 x CH_3 , 2 x OCH_3), 41.0 (2 x CH), 35.9 (2 x CH), 25.84 (CH_2), 25.80 (CH_2), 25.5 (CH_2), 25.4 (CH_2); LRMS: m/z 277.05 (M-H^+), calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4$ 278.1267; Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4$ (278.12): C, 60.42; H, 6.52; N, 10.07. Found: C, 60.439; H, 6.526; N, 10.079 %.

Cyano-(3,3-dimethyl-1,5-dioxo-7,11-diphenyl-2,4-dioxo-spiro[5.5]undec-9-yl)-acetic acid ethyl ester (12hf): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 170 °C. IR (KBr): $\nu_{\max}$ 3034, 2980, 2868, 2249 ($\text{C}\equiv\text{N}$), 1734 (O-C=O), 1601, 1494, 1458, 1375, 1068, 1030, 900, 860 and 767 cm^{-1} ; ^1H NMR (CDCl_3 , 10.0:1 ratio of isomers, major isomer) δ 7.33-7.19 (10H, m, 2 x Ph-*H*); 4.23 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 4.16 (1H, d, $J = 11.6$ Hz), 3.72 (1H, dd, $J = 13.6, 3.2$ Hz), 3.67 (1H, dd, $J = 14.0, 3.2$ Hz), 3.18 (1H, dt, $J = 14.8, 4.8$ Hz), 3.10 (1H, dt, $J = 14.8, 4.8$ Hz), 2.97 (1H, m), 2.21 (1H, br d, $J = 13.6$ Hz), 1.72 (1H, br d, $J = 13.6$ Hz), 1.24 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 0.50 (6H, s, 2 x CH_3); ^{13}C NMR (CDCl_3 , DEPT-135, 10.0:1 ratio of isomers, major isomer) δ 169.3 (C, O-C=O), 165.6 (C, O-C=O), 164.8 (C, O-C=O), 138.3 (C), 138.2 (C), 129.0 (4 x CH), 128.7 (2 x CH), 128.6 (2 x CH), 128.4 (CH), 128.0 (CH), 116.0 (C, $\text{C}\equiv\text{N}$), 106.0 (C, O-C-O), 62.9 (CH_2 , OCH_2CH_3), 61.1 (C), 44.98 (CH), 44.7 (CH), 38.9 (CH), 35.2 (CH), 28.4 (CH_2), 28.2 (2 x CH_3), 27.7 (CH_2), 13.9 (CH_3 , OCH_2CH_3); LRMS: m/z 474.25 (M-H^+), calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_6$ 475.1995; HRMS: m/z 498.1908 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_6\text{Na}$ 498.1893.

Cyano-(2,4-dimethyl-1,3,5-trioxo-7,11-diphenyl-2,4-diaza-spiro[5.5]undec-9-yl)-acetic acid ethyl ester (12if): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 106 °C. IR (KBr): $\nu_{\max}$ 3030, 2928, 2245, 1741 (O-C=O), 1676, 1442, 1381, 1259, 1024, 848 and 758 cm^{-1} ; ^1H NMR (CDCl_3 , 10.0:1 ratio of isomers, major isomer) δ 7.18 (6H, m), 7.05 (4H, m) [Ar-*H*]; 4.23 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 4.25-4.18 (1H, m, CH), 3.72 (2H, m), 3.16 (2H, m), 2.98 (1H, m), 2.92 (3H, s, N- CH_3), 2.87 (3H, s, N- CH_3), 2.18 (1H, br d, $J = 14.4$ Hz), 1.69 (1H, br d, $J = 14.4$ Hz), 1.22 (3H, t, $J = 7.2$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135, 10.0:1 ratio of isomers, major isomer) δ 171.4 (C, O-C=O), 168.4 (C, O-C=O), 165.5 (C, O-C=O), 149.5 (C, O-C=O), 138.1 (C), 137.9 (C), 128.5 (4 x CH), 128.1 (CH), 128.0 (CH), 127.6 (2 x CH), 127.5 (2 x CH), 116.0 (C, $\text{C}\equiv\text{N}$), 62.7 (CH_2 , OCH_2CH_3), 61.1 (C), 45.1 (CH), 44.7 (CH), 38.8 (CH), 35.2 (CH), 28.2 (CH_2), 28.0 (CH_3 , N- CH_3), 27.5 (CH_3 , N- CH_3), 27.4 (CH_2), 13.8 (CH_3 , OCH_2CH_3); LRMS: m/z 486.20 (M-H^+), calcd for $\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_5$ 487.2107; HRMS: m/z 510.2022 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_5\text{Na}$ 510.2005.

2-(2,4-Dimethyl-1,3,5-trioxo-7,11-diphenyl-2,4-diaza-spiro[5.5]undec-9-yl)-malononitrile (12ij): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 186 °C. IR (KBr): $\nu_{\max}$ 3063, 3034, 2256, 1743 (N-C=O), 1680, 1602, 1439, 1265, 1205, 850 and 734 cm^{-1} ; ^1H NMR (CDCl_3 ,

6.0:1 ratio of isomers, major isomer) δ 7.25 (6H, m), 7.06 (4H, m) [Ar-*H*]; 4.49 (1H, d, J = 11.6 Hz), 3.61 (2H, dd, J = 14.0, 3.2 Hz), 3.28 (2H, dt, J = 14.8, 5.2 Hz), 3.03 (1H, m), 2.95 (3H, s, N-CH₃), 2.90 (3H, s, N-CH₃), 2.16 (2H, br d, J = 14.8 Hz); ¹³C NMR (CDCl₃, DEPT-135, 6.0:1 ratio of isomers, major isomer) δ 171.4 (C, N-C=O), 168.4 (C, N-C=O), 149.5 (C, (NMe)₂C=O), 137.3 (2 x C), 128.8 (4 x CH), 128.6 (2 x CH), 127.7 (4 x CH), 112.2 (2 x C, C $\equiv$ N), 61.1 (C), 44.7 (2 x CH), 36.4 (CH), 28.3 (CH₃, N-CH₃), 27.7 (CH₃, N-CH₃), 27.4 (2 x CH₂), 24.9 (CH); LRMS: m/z 439.10 (M-H⁺), calcd for C₂₆H₂₄N₄O₃ 440.1848; Anal. calcd for C₂₆H₂₄N₄O₃ (440.18): C, 70.89; H, 5.49; N, 12.72. Found: C, 71.002; H, 5.488; N, 12.457%.

5-Cyclobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (12jc): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 96 °C. IR (KBr): $\nu_{\max}$ 3506, 2999, 2947, 1792 1743, 1462, 1379, 1325, 1259, 1155 and 997 cm⁻¹; ¹H NMR (CDCl₃) δ 3.46 (1H, d, J = 8.4 Hz), 2.99 (1H, sextet, J = 8.4 Hz), 2.35-2.26 (2H, m), 2.20-2.05 (2H, m), 2.05-1.80 (2H, m), 1.79 (3H, s, CH₃), 1.74 (3H, s, CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 164.8 (2 x C, 2 x O-C=O), 104.9 (C, O-C-O), 50.9 (CH), 34.6 (CH), 28.7 (CH₃), 28.1 (2 x CH₂), 27.1 (CH₃), 19.2 (CH₂); HRMS: m/z 199.0962 (M+H⁺), calcd for C₁₀H₁₄O₄ 198.0970; Anal. calcd for C₁₀H₁₄O₄ (198.09): C, 60.59; H, 7.12. Found: C, 60.702; H, 7.117%.

Cyano-cyclobutyl-acetic acid ethyl ester (12jf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2986, 2945, 2870, 2249, 1745 (O-C=O), 1631, 1446, 1369, 1249 1024 and 914 cm⁻¹; ¹H NMR (CDCl₃) δ 4.24 (2H, q, J = 7.2 Hz, OCH₂CH₃), 3.50 (1H, d, J = 7.2 Hz), 2.93 (1H, sextet, J = 8.0 Hz), 2.22-2.10 (2H, m), 2.10-1.98 (2H, m), 1.98-1.85 (2H, m), 1.31 (3H, t, J = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.3 (C, O-C=O), 115.5 (C, C $\equiv$ N), 62.5 (CH₂, OCH₂CH₃), 43.0 (CH), 35.1 (CH), 26.4 (CH₂), 25.7 (CH₂), 17.7 (CH₂), 13.9 (CH₃, OCH₂CH₃); HRMS: m/z 190.0843 (M+Na⁺), calcd for C₉H₁₃NO₂Na 190.0844.

Cyano-cyclopentyl-acetic acid ethyl ester (12kf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2961, 2874, 2253, 1745 (O-C=O), 1618, 1452, 1369, 1269, 1201 and 1032 cm⁻¹; ¹H NMR (CDCl₃) δ 4.24 (2H, q, J = 7.2 Hz, OCH₂CH₃), 3.48 (1H, d, J = 7.2 Hz), 2.47 (1H, sextet, J = 7.6 Hz), 1.85 (2H, m), 1.70 (2H, m), 1.59 (2H, m), 1.40 (2H, m), 1.30 (3H, t, J = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 166.0 (C, O-C=O), 116.0 (C, C $\equiv$ N), 62.5 (CH₂, OCH₂CH₃), 42.5 (CH), 40.1 (CH), 30.6 (CH₂), 29.7 (CH₂), 25.0 (CH₂), 24.9 (CH₂), 13.9 (CH₃, OCH₂CH₃); LRMS: m/z 180.00 (M-H⁺), calcd for C₁₀H₁₅NO₂ 181.1103.

Cyano-cycloheptyl-acetic acid ethyl ester (12lf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2930, 2858, 2249, 1743 (O-C=O), 1593, 1462, 1369, 1251, 1028 and 854 cm⁻¹; ¹H NMR (CDCl₃) δ 4.23 (2H, q, J = 7.2 Hz, OCH₂CH₃), 3.40 (1H, d, J = 5.2 Hz), 2.21 (1H, m), 1.72 (5H, m), 1.60-1.20 (7H, m), 1.29 (3H, t, J = 7.2 Hz, OCH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.9 (C, O-C=O), 115.9 (C, C $\equiv$ N), 62.5 (CH₂, OCH₂CH₃), 45.1 (CH), 40.4 (CH), 32.9 (CH₂), 30.8 (CH₂), 27.7 (CH₂), 27.5 (CH₂), 26.1 (CH₂), 25.9 (CH₂), 13.9 (CH₃); LRMS: m/z 208.15 (M-H⁺), calcd for C₁₂H₁₉NO₂ 209.1416.

2-(1-Phenyl-ethyl)-malononitrile (12mj): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 3067, 3034, 2980, 2908, 2254 (C $\equiv$ N), 1718, 1597, 1496, 1371, 1286, 1045, 844 and 773 cm⁻¹; ¹H NMR (CDCl₃) δ 7.45-7.28 (5H, m) [Ar-*H*]; 3.88 (1H, d, *J* = 6.4 Hz), 3.48 (1H, quintet, *J* = 6.8 Hz), 1.67 (3H, d, *J* = 7.2 Hz, PhCHCH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 138.2 (C), 129.3 (2 x CH), 128.9 (CH), 127.2 (2 x CH), 111.9 (C, C $\equiv$ N), 111.7 (C, C $\equiv$ N), 41.2 (CH), 31.2 (CH), 17.7 (CH₃); LRMS: *m/z* 169.05 (M-H⁺), calcd for C₁₁H₁₀N₂ 170.0844.

2-(1-p-Tolyl-ethyl)-malononitrile (12nj): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2924, 2254 (C $\equiv$ N), 1608, 1454, 1269, 815 and 727 cm⁻¹; ¹H NMR (CDCl₃) δ 7.24 (4H, s, Ph-*H*); 3.85 (1H, d, *J* = 6.4 Hz), 3.45 (1H, m), 2.40 (3H, s, PhCH₃), 1.65 (3H, d, *J* = 7.2 Hz, PhCHCH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 138.7 (C), 135.2 (C), 129.9 (2 x CH), 127.1 (2 x CH), 112.1 (C, C $\equiv$ N), 111.8 (C, C $\equiv$ N), 40.9 (CH), 31.3 (CH), 21.1 (CH₃), 17.8 (CH₃); LRMS: *m/z* 183.00 (M-H⁺), calcd for C₁₂H₁₂N₂ 184.1000.

2-[1-(4-Nitro-phenyl)-ethyl]-malononitrile (12oj): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP 72 °C. IR (neat): $\nu_{\max}$ 2976, 2912, 2253 (C $\equiv$ N), 1606, 1520, 1352, 860 and 738 cm⁻¹; ¹H NMR (CDCl₃) δ 8.28 (2H, d, *J* = 8.4 Hz), 7.58 (2H, d, *J* = 8.4 Hz) [Ar-*H*]; 4.05 (1H, d, *J* = 6.0 Hz), 3.64-3.61 (1H, quintet, *J* = 6.7 Hz), 1.70 (3H, d, *J* = 7.0 Hz, PhCHCH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 148.1 (C), 145.2 (C), 128.7 (2 x CH), 124.4 (2 x CH), 111.5 (C, C $\equiv$ N), 111.4 (C, C $\equiv$ N), 40.7 (CH), 30.6 (CH), 17.7 (CH₃); LRMS: *m/z* 214.00 (M-H⁺), calcd for C₁₁H₉N₃O₂ 215.0695; Anal. calcd for C₁₁H₉N₃O₂ (215.07): C, 61.39; H, 4.22; N, 19.53. Found: C, 61.375; H, 4.216; N, 19.573%.

2-Cyano-3-methyl-butyrlic acid ethyl ester (12pf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2970, 2937, 2249, 1745 (O-C=O), 1462, 1253, 1097, 1028 and 854 cm⁻¹; ¹H NMR (CDCl₃) δ 4.25 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 3.38 (1H, d, *J* = 4.8 Hz), 2.40 (1H, m), 1.30 (3H, t, *J* = 7.2 Hz, OCH₂CH₃), 1.11 (3H, d, *J* = 6.8 Hz, CHCH₃), 1.08 (3H, d, *J* = 6.8 Hz, CHCH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 165.8 (C, O-C=O), 115.4 (C, C $\equiv$ N), 62.5 (CH₂, OCH₂CH₃), 42.2 (CH), 29.9 (CH), 20.6 (CH₃), 18.7 (CH₃), 13.9 (CH₃, OCH₂CH₃); LRMS: *m/z* 154.10 (M-H⁺), calcd for C₈H₁₃NO₂ 155.0946.

2-Cyano-3-ethyl-pentanoic acid ethyl ester (12qf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2970, 2879, 2249, 1745 (O-C=O), 1464, 1369, 1265 and 1028 cm⁻¹; ¹H NMR (CDCl₃) δ 4.28 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 3.60 (1H, d, *J* = 4.4 Hz), 1.99 (1H, m), 1.63-1.38 (4H, m), 1.32 (3H, t, *J* = 7.2 Hz, OCH₂CH₃), 0.96 (3H, t, *J* = 8.0 Hz, CH₂CH₃), 0.94 (3H, t, *J* = 7.6 Hz, CH₂CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 166.5 (C, O-C=O), 115.6 (C, C $\equiv$ N), 62.6 (CH₂, OCH₂CH₃), 42.5 (CH), 41.4 (CH), 24.14 (CH₂), 24.11 (CH₂), 14.0 (CH₃, OCH₂CH₃), 11.2 (CH₃, CH₂CH₃), 11.1 (CH₃, CH₂CH₃); LRMS: *m/z* 182.00 (M-H⁺), calcd for C₁₀H₁₇NO₂ 183.1259.

2-Cyano-3-ethyl-pentanoic acid methyl ester (12qe): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): $\nu_{\max}$ 2966, 2934, 2249, 1749 (O-C=O), 1462, 1385, 1018 and 927 cm⁻¹; ¹H NMR (CDCl₃) δ 3.81 (3H, s, OCH₃), 3.62 (1H, d, *J* = 4.8 Hz), 1.98 (1H, m), 1.65-1.36

(4H, m), 0.95 (3H, t, $J = 7.6$ Hz, CH_2CH_3), 0.93 (3H, t, $J = 7.6$ Hz, CH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 167.0 (C, O-C=O), 115.4 (C, $\text{C}\equiv\text{N}$), 53.2 (CH_3 , OCH₃), 42.5 (CH), 41.2 (CH), 24.1 (2 x CH_2), 11.2 (CH_3), 11.1 (CH_3); LRMS: m/z 168.00 ($\text{M}-\text{H}^+$), calcd for $\text{C}_9\text{H}_{15}\text{NO}_2$ 169.1103; HRMS: m/z 192.1002 ($\text{M}+\text{Na}^+$), calcd $\text{C}_9\text{H}_{15}\text{NO}_2\text{Na}$ 192.1000.

2-Cyano-3-methyl-pentanoic acid ethyl ester (12rf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2970, 2249 ($\text{C}\equiv\text{N}$), 1745 (O-C=O), 1614, 1460, 1255 and 1028 cm^{-1} ; ^1H NMR (CDCl_3 , 1.6:1 ratio of isomers) δ 4.26 (4H, q, $J = 7.2$ Hz, 2 x OCH_2CH_3), 3.54 (1H, d, $J = 4.4$ Hz), 3.41 (1H, d, $J = 5.2$ Hz), 2.14 (2H, m), 1.46 (4H, m), 1.30 (6H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.07 (3H, d, $J = 7.2$ Hz), 1.03 (3H, d, $J = 7.2$ Hz), 0.93 (3H, t, $J = 7.2$ Hz), 0.92 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135, 1.6:1 ratio of isomers) δ 166.1 (C, O-C=O), 165.8 (C, O-C=O), 115.7 (C, $\text{C}\equiv\text{N}$), 115.2 (C, $\text{C}\equiv\text{N}$), 62.5 (CH_2 , OCH_2CH_3), 62.4 (CH_2 , OCH_2CH_3), 44.3 (CH), 43.3 (CH), 36.1 (2 x CH), 27.6 (CH_2), 26.1 (CH_2), 17.1 (CH_3), 16.0 (CH_3), 13.9 (2 x CH_3 , OCH_2CH_3), 11.3 (CH_3), 11.1 (CH_3); LRMS: m/z 168.10 ($\text{M}-\text{H}^+$), calcd for $\text{C}_9\text{H}_{15}\text{NO}_2$ 169.1103.

2-Cyano-3,4-dimethyl-pentanoic acid ethyl ester (12sf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2968, 2249 ($\text{C}\equiv\text{N}$), 1747 (O-C=O), 1622, 1467, 1371, 1251, 1116 and 1030 cm^{-1} ; ^1H NMR (CDCl_3 , 2:1 ratio of isomers) δ 4.25 (4H, q, $J = 7.2$ Hz, 2 x OCH_2CH_3), 3.63 (1H, d, $J = 4.4$ Hz), 3.38 (1H, d, $J = 8.0$ Hz), 2.09 (1H, m), 1.96 (2H, m), 1.66 (1H, m), 1.30 (6H, t, $J = 7.2$ Hz, 2 x OCH_2CH_3), 1.04 (3H, d, $J = 6.8$ Hz), 0.96 (12H, m, 4 x CH_3 , 2 x $(\text{CH}_3)_2\text{CH}$), 0.88 (3H, d, $J = 6.8$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135, 2:1 ratio of isomers) δ 166.5 (C, O-C=O), 166.0 (C, O-C=O), 116.2 (C, $\text{C}\equiv\text{N}$), 115.5 (C, $\text{C}\equiv\text{N}$), 62.6 (CH_2 , OCH_2CH_3), 62.5 (CH_2 , OCH_2CH_3), 42.7 (CH), 42.1 (CH), 40.7 (CH), 40.2 (CH), 31.2 (CH), 29.9 (CH), 21.1 (CH_3), 20.7 (CH_3), 19.3 (CH_3), 17.0 (CH_3), 14.0 (CH_3 , OCH_2CH_3), 13.9 (CH_3 , OCH_2CH_3), 13.8 (CH_3), 13.0 (CH_3); LRMS: m/z 182.15 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_2$ 183.1259.

2-Cyano-3-methyl-hexanedioic acid diethyl ester (12tf): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2984, 2932, 2251, 1739 (O-C=O), 1462, 1371, 1097, 1028 and 856 cm^{-1} ; ^1H NMR (CDCl_3 , 1.4:1 ratio of isomers) δ 4.25 (4H, q, $J = 7.2$ Hz, 2 x OCH_2CH_3), 4.11 (4H, q, $J = 7.2$ Hz, 2 x OCH_2CH_3), 3.55 (1H, d, $J = 4.4$ Hz), 3.45 (1H, d, $J = 5.2$ Hz), 2.40-2.25 (5H, m), 1.87-1.61 (5H, m), 1.30 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.29 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.24 (6H, t, $J = 7.2$ Hz, 2 x OCH_2CH_3), 1.11 (3H, d, $J = 7.2$ Hz), 1.06 (3H, d, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , DEPT-135, 1.4:1 ratio of isomers) δ 172.5 (C, O-C=O), 172.4 (C, O-C=O), 165.6 (C, O-C=O), 165.4 (C, O-C=O), 115.3 (C, $\text{C}\equiv\text{N}$), 114.9 (C, $\text{C}\equiv\text{N}$), 62.7 (2 x CH_2 , 2 x OCH_2CH_3), 60.6 (CH_2 , OCH_2CH_3), 60.5 (CH_2 , OCH_2CH_3), 44.2 (CH), 43.6 (CH), 33.8 (CH), 33.7 (CH), 31.6 (CH_2), 31.4 (CH_2), 29.7 (CH_2), 28.1 (CH_2), 17.3 (CH_3), 15.9 (CH_3), 14.1 (2 x CH_3 , 2 x OCH_2CH_3), 13.9 (2 x CH_3 , 2 x OCH_2CH_3); LRMS: m/z 240.05 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_4$ 241.1314.

Cyano-cyclohexyl-methyl-acetic acid ethyl ester (13afa): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2934, 2858, 2239, 1741 (O-C=O), 1452, 1381, 1242,

1116 and 1018 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.25 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 1.80 (4H, m), 1.66 (2H, m), 1.52 (3H, s, CH_3), 1.33 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.31-1.13 (5H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 169.5 (C, $\text{O}-\text{C}=\text{O}$), 119.3 (C, $\text{C}\equiv\text{N}$), 62.4 (CH_2 , OCH_2CH_3), 48.99 (C), 44.2 (CH), 28.9 (CH_2), 27.2 (CH_2), 25.9 (2 x CH_2), 25.6 (CH_2), 20.7 (CH_3), 14.0 (CH_3 , OCH_2CH_3); LRMS: m/z 210.20 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2$ 209.1416; HRMS: m/z 232.1303 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2\text{Na}$ 232.1313.

2-Cyano-2-cyclohexyl-butyric acid ethyl ester (13afb): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2934, 2856, 2241, 1739 ($\text{O}-\text{C}=\text{O}$), 1452, 1232, 1157, 1124 and 1022 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.26 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 1.98-1.93 (1H, m), 1.90-1.76 (5H, m), 1.67 (1H, br d, $J = 9.6$ Hz), 1.57 (1H, br d, $J = 12.0$ Hz), 1.32 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.27-1.19 (5H, m), 1.02 (3H, t, $J = 7.6$ Hz, CH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 169.1 (C, $\text{O}-\text{C}=\text{O}$), 118.6 (C, $\text{C}\equiv\text{N}$), 62.3 (CH_2 , OCH_2CH_3), 56.3 (C), 44.0 (CH), 29.3 (CH_2), 28.3 (CH_2), 27.6 (CH_2), 26.0 (2 x CH_2), 25.7 (CH_2), 14.2 (CH_3 , OCH_2CH_3), 9.9 (CH_3 , CH_2CH_3); LRMS: m/z 224.25 ($\text{M}+\text{H}^+$), calcd $\text{C}_{13}\text{H}_{21}\text{NO}_2$ 223.1572; HRMS: m/z 246.1465 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2\text{Na}$ 246.1470.

2-Cyano-2-cyclohexyl-pent-4-enoic acid ethyl ester (13afc): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 3082, 2934, 2856, 2243, 1741 ($\text{O}-\text{C}=\text{O}$), 1643, 1450, 1369, 1222, 1155, 1032, 927 and 860 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.82-5.72 (1H, m, olefinic-*H*), 5.22-5.16 (2H, m, olefinic-*H*), 4.23 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 2.64 (1H, dd, $J = 13.6$, 6.8 Hz), 2.52 (1H, dd, $J = 13.6$, 8.0 Hz), 1.90-1.70 (4H, m), 1.67 (1H, br d, $J = 10.4$ Hz), 1.57 (1H, br d, $J = 10.4$ Hz), 1.29 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.30-1.10 (5H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.5 (C, $\text{O}-\text{C}=\text{O}$), 131.0 (CH, $\text{CH}=\text{CH}_2$), 120.4 (CH_2 , $\text{CH}=\text{CH}_2$), 118.2 (C, $\text{C}\equiv\text{N}$), 62.3 (CH_2 , OCH_2CH_3), 55.2 (C), 43.7 (CH), 39.0 (CH_2), 29.1 (CH_2), 27.5 (CH_2), 25.9 (2 x CH_2), 25.6 (CH_2), 14.1 (CH_3 , OCH_2CH_3); LRMS: m/z 235.10 (M^+), calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2$ 235.1572; HRMS: m/z 258.1473 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{Na}$ 258.1470.

2-Cyano-2-cyclohexyl-pent-4-ynoic acid ethyl ester (13afd): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 3287, 2934, 2858, 2247, 2125, 1743 ($\text{O}-\text{C}=\text{O}$), 1450, 1369, 1219, 1043, 896 and 858 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.29 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 2.76 (2H, dABq, $J = 16.8$, 2.0 Hz, $\text{CH}_2\text{C}\equiv\text{CH}$), 2.16 (1H, t, $J = 2.0$ Hz, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.87-1.70 (5H, m), 1.67 (1H, br d, $J = 10.8$ Hz), 1.60 (1H, br d, $J = 10.8$ Hz), 1.30 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.29-1.16 (4H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 167.7 (C, $\text{O}-\text{C}=\text{O}$), 117.6 (C, $\text{C}\equiv\text{N}$), 77.3 (C, $\text{CH}_2\text{C}\equiv\text{CH}$), 72.7 (CH, $\text{CH}_2\text{C}\equiv\text{CH}$), 62.8 (CH_2 , OCH_2CH_3), 54.4 (C), 43.4 (CH), 28.8 (CH_2), 27.6 (CH_2), 25.8 (2 x CH_2), 25.5 (CH_2), 25.1 (CH_2), 14.0 (CH_3 , OCH_2CH_3); LRMS: m/z 233.00 (M^+), calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ 233.1416; HRMS: m/z 256.1323 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{Na}$ 256.1313.

Benzyl-cyano-cyclohexyl-acetic acid ethyl ester (13afe): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 3034, 2932, 2856, 2243, 1738 ($\text{O}-\text{C}=\text{O}$), 1604, 1496, 1369, 1265, 1089, 1035, 858 and 744 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.28 (5H, s, Ph-*H*), 4.03 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 3.21 (1H, d, $J = 13.6$ Hz), 3.03 (1H, d, $J = 12.8$ Hz), 2.05-1.96 (2H, m), 1.90 (1H, m), 1.80 (1H, m), 1.72 (1H, br d, $J = 10.4$ Hz), 1.59 (1H, br d, $J = 12.4$ Hz), 1.50-1.10 (5H, m), 1.04 (3H, t, $J = 6.8$

Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.4 (C, $\text{O}-\text{C}=\text{O}$), 134.7 (C), 129.8 (2 x CH), 128.4 (2 x CH), 127.5 (CH), 118.3 (C, $\text{C}\equiv\text{N}$), 62.2 (CH_2 , OCH_2CH_3), 57.2 (C), 44.7 (CH), 40.8 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 13.8 (CH_3 , OCH_2CH_3); LRMS: m/z 285.00 (M^+), calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2$ 285.1729; HRMS: m/z 308.1632 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2\text{Na}$ 308.1626.

2-Cyclohexyl-2-prop-2-ynyl-malononitrile (13ajd): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 3294, 2935, 2860, 2251, 1452, 1302, 1261, 1078, 985 and 738 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.93 (2H, d, $J = 2.8\text{ Hz}$, $\text{CH}_2\text{C}\equiv\text{CH}$), 2.37 (1H, t, $J = 2.8\text{ Hz}$, $\text{CH}_2\text{C}\equiv\text{CH}$), 2.01 (4H, m), 1.90 (2H, m), 1.74 (1H, br d, $J = 11.2\text{ Hz}$), 1.33-1.18 (4H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 114.1 (2 x C, $\text{C}\equiv\text{N}$), 74.9 (CH, $\text{C}\equiv\text{CH}$), 74.6 (C, $\text{C}\equiv\text{CH}$), 42.5 (CH), 42.2 (C), 28.0 (2 x CH_2), 25.9 (CH_2), 25.4 (2 x CH_2), 25.1 (CH_2); HRMS: m/z 209.1064 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Na}$ 209.1055.

2-Cyano-2-cyclopentyl-pent-4-ynoic acid ethyl ester (13kfd): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 3292, 2961, 2872, 2247, 1747 ($\text{O}-\text{C}=\text{O}$), 1456, 1369, 1224, 1097, 1049 and 858 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.32 (2H, q, $J = 7.2\text{ Hz}$, OCH_2CH_3), 2.78 (2H, dABq, $J = 14.0, 2.8\text{ Hz}$), 2.43-2.33 (1H, m), 2.18 (1H, t, $J = 2.8\text{ Hz}$, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.87 (1H, m), 1.74 (3H, m), 1.60-1.40 (4H, m), 1.35 (3H, t, $J = 7.2\text{ Hz}$, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 167.7 (C, $\text{O}-\text{C}=\text{O}$), 117.5 (C, $\text{C}\equiv\text{N}$), 77.3 (C, $\text{C}\equiv\text{CH}$), 72.6 (CH, $\text{C}\equiv\text{CH}$), 62.9 (CH_2 , OCH_2CH_3), 53.7 (C), 45.5 (CH), 28.9 (CH_2), 28.2 (CH_2), 26.7 (CH_2), 25.0 (CH_2), 24.90 (CH_2), 14.1 (CH_3 , OCH_2CH_3); LRMS: m/z 220.15 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.1259; HRMS: m/z 242.1143 (M^+), calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 242.1157.

2-Cyano-2-(3,3-dimethyl-1,5-dioxo-7,11-diphenyl-2,4-dioxo-spiro[5.5]undec-9-yl)-pent-4-ynoic acid ethyl ester (13hfd): Purified by column chromatography using EtOAc/hexane and isolated as solid. MP $175\text{ }^\circ\text{C}$. IR (KBr): ν_{max} 3296, 2939, 1734 ($\text{O}-\text{C}=\text{O}$), 1494, 1456, 1377, 1288, 1230, 1066, 896 and 765 cm^{-1} ; ^1H NMR (CDCl_3 , 10:1 ratio of isomers, major isomer) δ 7.31-7.19 (10H, m, 2 x Ph-*H*), 4.43 (2H, q, $J = 7.2\text{ Hz}$, OCH_2CH_3), 4.10 (1H, dd, $J = 14.0, 3.2\text{ Hz}$), 4.00 (1H, dd, $J = 14.0, 3.6\text{ Hz}$), 3.13 (2H, m), 2.94 (2H, d, $J = 3.0\text{ Hz}$), 2.88 (1H, m), 2.29 (1H, br d, $J = 15.6\text{ Hz}$), 2.22 (1H, t, $J = 3.0\text{ Hz}$, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.93 (1H, br d, $J = 15.6\text{ Hz}$), 1.38 (3H, t, $J = 7.2\text{ Hz}$, OCH_2CH_3), 0.5 (6H, br s, 2 x CH_3); ^{13}C NMR (CDCl_3 , DEPT-135, 10:1 ratio of isomers, major isomer) δ 168.7 (C, $\text{O}-\text{C}=\text{O}$), 168.1 (C, $\text{O}-\text{C}=\text{O}$), 165.3 (C, $\text{O}-\text{C}=\text{O}$), 138.8 (C), 138.7 (C), 129.0 (2 x CH), 128.9 (2 x CH), 128.6 (4 x CH), 128.2 (CH), 128.1 (CH), 119.0 (C, $\text{C}\equiv\text{N}$), 105.7 (C, $\text{O}-\text{C}-\text{O}$), 76.8 (C, $\text{C}\equiv\text{CH}$), 73.4 (CH, $\text{C}\equiv\text{CH}$), 63.8 (CH_2 , OCH_2CH_3), 60.6 (C), 51.3 (C), 45.1 (2 x CH), 38.5 (CH), 28.2 (2 x CH_3), 27.3 (CH_2), 27.1 (CH_2), 26.8 (CH_2), 14.0 (CH_3 , OCH_2CH_3); LRMS: m/z 512.25 ($\text{M}-\text{H}^+$), calcd for $\text{C}_{31}\text{H}_{31}\text{NO}_6$ 513.22; HRMS: m/z 536.2059 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{31}\text{H}_{31}\text{NO}_6\text{Na}$ 536.2049.

2-Cyano-2-(2,4-dimethyl-1,3,5-trioxo-7,11-diphenyl-2,4-diaza-spiro[5.5]undec-9-yl)-pent-4-ynoic acid ethyl ester (13ifd): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (KBr): ν_{max} 3287, 3063, 2934, 2858, 2245, 1739 ($\text{N}-\text{C}=\text{O}$), 1682, 1448, 1377, 1226, 1028, 850 and 756 cm^{-1} ; ^1H NMR (CDCl_3 , 10:1 ratio of isomers, major isomer) δ 7.19-7.03 (10H, m, 2 x Ph-*H*), 4.43 (2H, q, $J = 7.2\text{ Hz}$, OCH_2CH_3), 4.13 (1H, dd, $J = 14.0, 3.6\text{ Hz}$), 4.04 (1H, dd, $J = 14.0, 3.6\text{ Hz}$), 3.11 (2H, m), 2.93 (2H, d, $J = 2.4\text{ Hz}$, $\text{CH}_2\text{C}\equiv\text{CH}$), 2.91 (3H, s, $\text{N}-\text{CH}_3$), 2.85 (3H, s, $\text{N}-\text{CH}_3$), 2.91-2.85 (1H, m, *CH*), 2.24

(1H, br dd, $J = 15.2, 3.2$ Hz), 2.22 (1H, t, $J = 2.4$ Hz, $\text{CH}_2\text{C}\equiv\text{CH}$), 1.86 (1H, br dd, $J = 15.2, 3.2$ Hz), 1.36 (3H, t, $J = 7.2$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135, 10:1 ratio of isomers, major isomer) δ 171.1 (C, O-C=O), 168.8 (C, N-C=O), 168.1 (C, N-C=O), 149.7 (C, N-C=O), 138.7 (C), 138.6 (C), 128.5 (2 x CH), 128.4 (2 x CH), 128.0 (CH), 127.99 (CH), 127.6 (2 x CH), 127.5 (2 x CH), 118.99 (C, $\text{C}\equiv\text{N}$), 76.8 (C, $\text{C}\equiv\text{CH}$), 73.3 (CH, $\text{C}\equiv\text{CH}$), 63.5 (CH_2 , OCH_2CH_3), 60.8 (C), 51.4 (C), 45.5 (CH), 45.4 (CH), 38.6 (CH), 28.0 (CH_3 , N- CH_3), 27.6 (CH_3 , N- CH_3), 27.2 (CH_2), 26.99 (CH_2), 26.9 (CH_2), 13.8 (CH_3 , OCH_2CH_3); LRMS: m/z 526.30 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{31}\text{H}_{31}\text{N}_3\text{O}_5$ 525.23; HRMS: m/z 548.2144 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{31}\text{H}_{31}\text{N}_3\text{O}_5\text{Na}$ 548.2161.

2-Cyano-2-cyclohexyl-5,9-dimethyl-deca-4,8-dienoic acid ethyl ester (13afg): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2930, 2856, 1741 (O-C=O), 1450, 1375, 1224, 1097 and 862 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.18 (1H, m, olefinic- H), 5.07 (1H, br s, olefinic- H), 4.23 (2H, m, OCH_2CH_3), 2.59 (2H, dABq, $J = 14.4, 6.8$ Hz), 2.07-1.70 (10H, m), 1.68 (3H, s, CH_3), 1.63 (3H, s, CH_3), 1.60 (3H, s, CH_3), 1.30-1.20 (5H, m), 1.30 (3H, t, $J = 7.2$ Hz, OCH_2CH_3); ^{13}C NMR (CDCl_3 , DEPT-135) δ 168.9 (C, O-C=O), 140.7 (C), 131.6 (C), 123.8 (CH), 118.6 (C, $\text{C}\equiv\text{N}$), 116.7 (CH), 62.1 (CH_2 , OCH_2CH_3), 55.4 (C), 43.8 (CH), 39.8 (CH_2), 33.6 (CH_2), 29.2 (CH_2), 27.7 (CH_2), 26.5 (CH_2), 25.98 (CH_2), 25.96 (CH_2), 25.7 (CH_2), 25.6 (CH_3), 17.7 (CH_3), 16.4 (CH_3), 14.2 (CH_3 , OCH_2CH_3); LRMS: m/z 354.30 ($\text{M}+\text{Na}$), calcd for $\text{C}_{21}\text{H}_{33}\text{NO}_2\text{Na}$ 354.25; HRMS: m/z 354.2413 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{21}\text{H}_{33}\text{NO}_2\text{Na}$ 354.2409.

2-Cyano-2-cyclohexyl-5,9-dimethyl-deca-4,8-dienoic acid methyl ester (13aeg): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2928, 2856, 2241, 1745 (O-C=O), 1450, 1377, 1228, 1064 and 839 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.13 (1H, t, $J = 7.2$ Hz), 5.06 (1H, br s) [olefinic- H]; 3.75 (3H, s, OCH_3), 2.58 (2H, dABq, $J = 14.0, 6.8$ Hz), 2.01 (4H, m), 1.84 (4H, m), 1.67-1.51 (1H, m), 1.67 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.59 (3H, s, CH_3), 1.35-1.15 (6H, m); ^{13}C NMR (CDCl_3 , DEPT-135) δ 169.5 (C, O-C=O), 141.0 (C), 131.6 (C), 123.7 (CH), 118.6 (C, $\text{C}\equiv\text{N}$), 116.7 (CH), 55.4 (C), 52.8 (CH_3 , OCH_3), 43.8 (CH), 39.8 (CH_2), 33.6 (CH_2), 29.2 (CH_2), 27.6 (CH_2), 26.04 (CH_2), 25.94 (CH_2), 25.92 (CH_2), 25.7 (CH_2), 25.6 (CH_3), 17.6 (CH_3), 16.2 (CH_3); LRMS: m/z 318.30 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_2$ 317.24; HRMS: m/z 340.2254 ($\text{M}+\text{Na}^+$), calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_2\text{Na}$ 340.2252.

2-Cyano-5,9-dimethyl-2-(4-methyl-cyclohexyl)-deca-4,8-dienoic acid ethyl ester (13dfg): Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (neat): ν_{max} 2934, 2854, 2241, 1739 (O-C=O), 1668, 1448, 1379, 1300, 1222, 1097, 1049 and 862 cm^{-1} ; ^1H NMR (CDCl_3 , 3.0:1 ratio of isomers, major isomer) δ 5.14 (1H, t, $J = 7.2$ Hz), 5.04 (1H, t, $J = 6.8$ Hz) [olefinic- H]; 4.23-4.17 (2H, m), 2.54 (2H, dABq, $J = 14.0, 7.6$ Hz), 2.06-1.50 (12H, m), 1.67 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.58 (3H, s, CH_3), 1.30 (3H, t, $J = 7.6$ Hz, OCH_2CH_3), 0.97 (3H, d, $J = 7.2$ Hz, CH_3); ^{13}C NMR (CDCl_3 , DEPT-135, 3.0:1 ratio of isomers, major isomer) δ 169.0 (C, O-C=O), 140.8 (C), 131.6 (C), 123.8 (CH), 118.6 (C, $\text{C}\equiv\text{N}$), 116.8 (CH), 62.2 (CH_2 , OCH_2CH_3), 55.4 (C), 44.1 (CH), 39.8 (CH_2), 33.6 (CH_2), 31.22 (CH_2), 31.20 (CH_2), 26.5 (CH_2), 26.4 (CH_3), 25.7 (CH), 23.2 (CH_2), 21.7 (CH_2), 17.6 (CH_3), 17.0 (CH_3), 16.4 (CH_3), 14.2 (CH_3 ,

OCH₂CH₃); LRMS: m/z 368.35 (M+Na⁺), calcd for C₂₂H₃₅NO₂Na 368.27; HRMS: m/z 368.2575 (M+Na⁺), calcd for C₂₂H₃₅NO₂Na 368.2565.

(1-Benzyl-1H-[1,2,3]triazol-4-ylmethyl)-cyano-(3,3-dimethyl-1,5-dioxo-7,11-diphenyl-2,4-dioxaspiro[5.5]undec-9-yl)-acetic acid ethyl ester (17): Purified by column chromatography using EtOAc/hexane and isolated as solid. IR (neat): $\nu_{\max}$ 2935, 2243, 1732 (O-C=O), 1552, 1454, 896 and 869 cm⁻¹; ¹H NMR (CDCl₃) δ 7.53 (1H, s, olefinic-*H*), 7.40-7.20 (15H, m, 3 x Ph-*H*), 5.52 (2H, br s, N-CH₂Ph), 4.28 (2H, q, *J* = 7.2 Hz, OCH₂CH₃), 4.22 (1H, dd, *J* = 14.4, 4.0 Hz), 4.10 (1H, m), 3.49-3.39 (2H, q, *J* = 14.4 Hz), 3.20-3.06 (2H, m), 2.83 (1H, br s), 2.31 (1H, br d, *J* = 15.6 Hz), 1.98 (1H, br d, *J* = 15.6 Hz), 1.25 (3H, t, *J* = 6.8 Hz, OCH₂CH₃), 0.53 (3H, s, CH₃), 0.50 (3H, s, CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 168.7 (C, O-C=O), 168.4 (C, O-C=O), 165.2 (C, O-C=O), 141.3 (C), 138.8 (2 x C), 134.5 (C), 129.0 (2 x CH), 128.85 (2 x CH), 128.82 (2 x CH), 128.6 (3 x CH), 128.5 (2 x CH), 128.08 (CH), 128.03 (CH), 127.8 (2 x CH), 122.7 (CH), 119.7 (C, C $\equiv$ N), 105.6 (C, O-C-O), 63.4 (CH₂, OCH₂CH₃), 60.8 (C), 54.0 (CH₂), 52.6 (C), 45.1 (CH), 44.9 (CH), 38.8 (CH), 33.2 (CH₂), 28.2 (CH₃), 28.1 (CH₃), 27.2 (CH₂), 26.8 (CH₂), 13.7 (CH₃, OCH₂CH₃); HRMS: m/z 669.2704 (M+Na⁺), calcd for C₃₁H₃₈N₄O₆Na 669.2689.

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