Selective reduction of cyclic 1,3-diesters using SmI₂ and H₂O

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General Experimental

All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. THF was distilled from sodium / benzophenone, and when used in conjunction with SmI_2 , deoxygenated by bubbling with N_2 for 15 minutes. Dichloromethane was distilled from CaH_2 , and methanol was distilled from the corresponding magnesium alkoxide and stored under argon. Water was distilled before being deoxygenated by bubbling with N_2 for 4 hours.

^1H NMR and ^{13}C NMR were recorded 300, 400 and 500 MHz spectrometers, with chemical shift values being reported in ppm relative to residual chloroform ($\delta_{\text{H}} = 7.27$ or $\delta_{\text{C}} = 77.2$) as internal standards. All coupling constants (J) are reported in Hertz (Hz).

Mass spectra were obtained using positive and negative electrospray ($\text{ES}^\pm$) or gas chromatography (GC) methodology. Infra-red spectra were recorded as evaporated films or neat using a FT/IR spectrometers.

Column chromatography was carried out using 35 – 70 μ , 60A silica gel. Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were viewed using a 254 mm ultraviolet lamp and dipped in aqueous potassium permanganate or *p*-anisaldehyde.

Preparation of Samarium Iodide (SmI₂)

Samarium Iodide was prepared by a modification of the procedure of Imamoto and Ono.¹ Samarium powder (2.00 g, 13.8 mmol, 1.2 eq) was added to an oven dried round bottomed flask, the flask sealed and flushed with N₂ for 20 min. THF (110 ml) was added and the resulting suspension bubbled with N₂ for 15 min. Finally, iodine (2.80 g, 10.8 mmol, 1 eq) was added and the flask flushed again with N₂ for 10 min. The flask was covered in aluminium foil and heated at 60 °C for 18 hours. The approximate 0.1 M solution was allowed to cool to room temperature and then used directly.

¹ Imamoto, T.; Ono, M. *Chem. Lett.* **1987**, 501.

Substrate Synthesis

Preparation of Unsaturated Cyclic 1,3-Diesters

Unsaturated Meldrum's acid derivatives **1i**, **1j**, and **I** were prepared by the Knoevenagel condensation of Meldrum's acid and the corresponding aldehyde according to Bigi's procedure.²

Preparation of Saturated Cyclic 1,3-Diesters

Unless otherwise stated, saturated cyclic diesters were prepared by either the reduction of the corresponding unsaturated system according to Smith's procedure³ (**1d**, **1e**, **1f**, **II**), or by alkylation of Meldrum's acid using a modification of Dumas' procedure⁴ (**1a**, **1b**, **1g**). 5-Benzyl-2,2-dimethyl-[1,3]dioxane-4,6-dione **1c** was prepared by the reduction of the corresponding unsaturated system which was synthesised according to Goll's procedure.⁵

² Bigi, F.; Carloni, S.; Ferrari, L.; Raimondo, M.; Mazzacani, A.; Sartori, G. *Tetrahedron Lett.* **2001**, 42, 5203.

³ Wright, A. D.; Haslego, M. L.; Smith, F. X. *Tetrahedron Lett.* **1979**, 25, 2325.

⁴ Fillion, E.; Dumas, A. M. *J. Org. Chem.* **2008**, 73, 2920.

⁵ Fillion, E.; Fishlock, D.; Wilsily, A.; Goll, J. M. *J. Org. Chem.* **2005**, 70, 1316

Preparation of 2,2-dimethyl-5-phenyl-4,6-dioxo-1,3-dioxane

2,2-dimethyl-5-phenyl-4,6-dioxo-1,3-dioxane (**1h**) was prepared according to Scheuer and Cohen's method.⁶

Preparation of Competition Substrates

Dibenzyl diethyl malonate **III** was prepared by a modification of Dumas' procedure.⁴

2-[2-(2,2-Dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-ethyl]-malonic acid diethyl ester (IV)

To a stirred suspension of NaH (260 mg, 6.47 mmol, 1.1 eq) in THF (20 mL), was added diethyl malonate dropwise. When the solution became clear, cyclopropyl Meldrum's acid (1.00 g, 5.88 mmol, 1 eq) in THF (5 mL) was added dropwise and the solution stirred at room temperature for 96 h, before heating at reflux for 1 h. After cooling, saturated ammonium chloride (30 mL) and ethyl acetate (30 mL) were added. The aqueous phase was separated, extracted with ethyl acetate (3 × 30 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 2-[2-(2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-ethyl]-malonic acid diethyl ester **IV** (528 mg, 1.60 mmol, 27%) as a colourless amorphous solid.

Preparation of Cyclisation Substrates

Cyclisation substrates **9**, **10** and **11** were synthesised by alkylation of **1f** according to a modification of Dumas' procedure.⁴

⁶ Scheuer, P. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1958**, *18*, 4933

Characterisation Data for Novel Reaction Substrates and Intermediates

Acetic acid 4-(2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-ylidenemethyl)-phenyl ester (I)

mp 126-129 °C; $\nu_{\max}$ (evap. film)/ cm^{-1} 2997, 2936, 1765 (C=O), 1727 (C=O), 1592, 1504, 1425, 1370, 1285, 1191, 1163, 1016, 932, 910, 798; ^1H NMR (400 MHz, CDCl_3) δ 1.81 (6H, s, $2 \times \text{CCH}_3$), 2.35 (3H, s, C(O)CH_3), 7.24 (2H, d, $J = 9.0$ Hz, Ar-H), 8.17 (2H, d, $J = 9.0$ Hz, Ar-H), 8.40 (1H, s, C=CH); ^{13}C (100 MHz, CDCl_3) δ 21.2 (C(O)CH_3), 27.6 ($2 \times \text{CCH}_3$), 104.6 (OCO), 114.4 (Ar- C^q), 122.0 ($2 \times \text{Ar-CH}$), 129.2 (Ar- C^q), 135.7 ($2 \times \text{Ar-CH}$), 154.7 (C^q), 156.8, (C^q), 159.8 (C=CH), 163.3 (C^q), 168.7 (OC(O)Me ; m/z (ES+) 233 (7%), 308 (($\text{M} + \text{NH}_4$), 45), 313 (($\text{M} + \text{Na}$), 100); (Found ($\text{M} + \text{Na}$), 313.0689. $\text{C}_{15}\text{H}_{14}\text{O}_6\text{Na}$ requires M , 313.0683)

Acetic acid 4-(2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-ylmethyl)-phenyl ester (II)

mp 107-109 °C; $\nu_{\max}$ (neat)/ cm^{-1} 2999, 2922, 2874, 1748 (C=O), 1508, 1395, 1383, 1370, 1345, 1307, 1199, 1067, 1017, 940, 917; ^1H (400 MHz, CDCl_3) δ 1.48 (3H, s, CCH_3), 1.67 (3H, s, CCH_3), 2.22 (3H, s, C(O)CH_3), 3.39 (2H, d, $J = 4.9$ Hz, CH_2Ph), 3.69 (1H, t, $J = 4.9$ Hz, CH), 6.93 (2H, d, $J = 8.6$ Hz, Ar-CH) and 7.29 (2H, d, $J = 8.8$ Hz, Ar-CH); ^{13}C (100 MHz, CDCl_3) δ 21.1 (C(O)CH_3), 27.1 (CCH_3), 28.5 (CCH_3), 31.2 (CH_2Ph), 48.3 (CHCH_2), 105.3 (OCO), 121.7 ($2 \times \text{Ar-CH}$), 131.0 ($2 \times \text{Ar-CH}$), 134.9 (Ar- C^q), 149.8 (Ar- C^q), 165.2 ($2 \times \text{C=O}$), 169.6 (OC(O)Me); m/z (ES-) 189 (6%), 291 ((M-H), 100), 292 (7); (Found: ($\text{M} + \text{NH}_4$), 310.1280. $\text{C}_{15}\text{H}_{20}\text{O}_6\text{N}$ requires M , 310.1285).

2-[2-(2,2-Dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-ethyl]-malonic acid dimethyl ester (IV)

$\nu_{\max}$ (neat)/ cm^{-1} 3506, 3247, 2984, 2940, 1786 (C=O), 1744 (C=O), 1449, 1394, 1384, 1369, 1341, 1299, 1204, 1155, 1096, 1053, 1027, 982, 857; ^1H (400 MHz, CDCl_3) δ 1.26 (6H, t, $J = 7.2$

Hz, 2 × OCH₂CH₃), 1.75 (3H, s, CH₃), 1.80 (3H, s, CH₃), 1.96-1.98 (1H, m, 1H from CH₂), 2.06-2.16 (3H, m, 1H from CH₂, CH₂), 3.38 (1H, t, *J* = 6.6 Hz, CH), 3.65 (1H, t, *J* = 4.7 Hz, CH), 4.13-4.23 (4H, m, 2 × OCH₂CH₃); ¹³C (100 MHz, CDCl₃) δ 13.9 (2 × CH₃), 23.6 (CH₃), 25.6 (CH₃), 26.4 (CH₂), 28.4 (CH₂), 45.9 (CH), 51.8 (CH), 61.5 (2 × CH₂), 105.0 (C^q), 165.0 (2 × CO), 168.9 (2 × CO).

5-But-3-enyl-5-isobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (9)

mp 57-59 °C; $\nu_{\max}$ (evap. film)/cm⁻¹ 2959, 1770, 1732 (2 × C=O), 1641 (C=C), 1393, 1267, 1209, 1080, 917; ¹H (400 MHz, CDCl₃) δ 0.91 (6H, d, *J* = 6.5 Hz, CH(CH₃)₂), 1.66 (1 H, m, CH(CH₃)₂), 1.75 (3H, s, CCH₃), 1.76 (3H, s, CCH₃), 1.98 (2H, d, *J* = 6.3 Hz, CH₂CH(CH₃)₂), 2.06 (4H, apparent d, *J* = 2.7 Hz, CH₂CH₂), 4.93 (1H, d, *J* = 10.6 Hz, 1H from CH=CH₂), 4.97 (1H, d, *J* = 16.8 Hz, 1H from CH=CH₂), 5.66-5.74 (1H, m, CH=CH₂); ¹³C (100 MHz, CDCl₃) δ 23.5 (CH(CH₃)₂), 25.6 (CHCH₃), 29.49 (CH₃), 29.51 (CH₂), 30.1 (CH₃), 39.4 (CH₂), 48.1 (CH₂CH(CH₃)₂), 53.01 (C^q), 105.6 (OCO), 116.2 (CH=CH₂), 136.0 (CH=CH₂), 169.1 (2 × CO); *m/z* (GC-MS) 197 (M⁺ - Bu), 167, 149, 124, 111, 99, 81, 55, 43.

5-Isobutyl-2,2-dimethyl-5-(4-phenyl-but-3-enyl)-[1,3]dioxane-4,6-dione (10)

mp 50-52 °C; $\nu_{\max}$ (evap. film)/cm⁻¹ 2958, 2360, 1772, 1741 (2 × C=O), 1391, 1268, 1201, 969; ¹H (400 MHz, CDCl₃) δ 0.90 (6H, d, *J* = 6.5 Hz, CH(CH₃)₂), 1.61-1.69 (1 H, m, CH(CH₃)₂), 1.72 (3H, s, CCH₃), 1.74 (3H, s, CCH₃), 1.98 (2H, d, *J* = 6.3 Hz, CH₂CH(CH₃)₂), 2.10-2.15 (2H, m, 1H from CH₂CH₂CH, 1H from CH₂CH₂CH), 2.17-2.23 (2H, m, 1H from CH₂CH₂CH, 1H from CH₂CH₂CH), 6.05 (1H, dt, *J* = 15.6, 6.5 Hz, CH=CH-Ph), 6.37 (1H, d, *J* = 15.6 Hz, CH=CH-Ph), 7.15-7.19 (1H, m, Ar-CH), 7.23-7.29 (4H, m, Ar-CH); ¹³C (100 MHz, CDCl₃) δ 23.5 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 28.9 (CH₂CH₂CH), 29.5 (CH₃), 30.1 (CH₃), 39.7 (CH₂CH(CH₃)₂), 53.04 (C^q), 105.7 (OCO), 126.0 (2 × Ar-CH), 127.2 (Ar-CH), 127.6 (CH=CH-

Ph), 128.5 ($2 \times \text{Ar-CH}$), 131.5 (CH=CH-Ph), 137.3 (Ar-C^q), 169.1 ($2 \times \text{CO}$) ; m/z (ES+) 251(24 %), 353 ((M + Na) 100), 354 (16), 385 (11).

5-(4,4-Diphenyl-but-3-enyl)-5-isobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione (11)

mp 134-139 °C; ν_{max} (evap. film)/ cm^{-1} 2960, 2877, 1770, 1737 (C=O), 1496, 1444, 1391, 1262, 1201, 765, 695; ^1H NMR (500 MHz, CDCl_3) δ 0.82 (6H, d, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.47 (3H, s, CCH_3), 1.55 (1H, apparent sept, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.62 (3H, s, CCH_3), 1.89 (2H, d, $J = 6.3$ Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 2.06 (4H, apparent s, $\text{CH}_2\text{CH}_2\text{CH=C}$), 5.86 (1H, br t, $J = 4.6$ Hz, CH=C), 7.03-7.29 (10H, m, Ar-CH); ^{13}C (125 MHz, CDCl_3) δ 23.5 ($\text{CH}(\text{CH}_3)_2$), 25.7 ($\text{CH}(\text{CH}_3)_2$), 26.1 (CH_2), 29.5 (CCH_3), 29.3 (CCH_3), 40.1 (CH_2), 48.24 (CH_2CH), 53.1 (C^q), 105.6 (OCO), 126.5 (CH=C), 127.2 (Ar-CH), 127.3 ($2 \times \text{Ar-CH}$), 128.2 (Ar-CH), 128.4 (Ar-CH), 129.6 (Ar-CH), 139.4 (CH=C), 142.2 (Ar-C^q), 143.5 (Ar-C^q), 169.0 ($2 \times \text{C=O}$); m/z (ES+) 429 ((M + H) 100%), 430 (20), 836 (35), 835 (18).

Experimental and Characterisation Data

General Procedure A

Reduction of cyclic 1,3-diester using $\text{SmI}_2\text{-H}_2\text{O}$.

2,2-Dibenzyl-3-hydroxy-propionic acid (**2a**)

To a stirred solution of SmI_2 (0.1 M in THF, 10.8 mL, 1.08 mmol, 7 eq) at room temperature was added distilled water (2.8 mL, 154 mmol, 1000 eq). This resulted in a colour change from deep blue/black to deep red/purple. A solution of 5,5-dibenzyl-2,2-dimethyl-[1,3]dioxan-4-one **1a** (50 mg, 0.154 mmol, 1 eq) in THF (5 mL) was added *via* cannula, and the solution left to stir until complete decolourization had occurred (~2 h). The reaction was quenched by opening to air. Aqueous saturated sodium chloride (30 mL) and tartaric acid (10 mg, 0.066 mmol) were subsequently added, and the aqueous layer extracted with ethyl acetate (3×60 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography on silica gel eluting with 50% ethyl acetate in petroleum ether (40–60 °C) gave 2,2-dibenzyl-3-hydroxy-propionic acid **2a** (39 mg, 0.140 mmol, 88%) as a white solid. mp 106–108 °C; ν_{max} (neat)/ cm^{-1} 3411 (OH), 3085, 3063, 3030, 2932, 1700 (C=O), 1495, 1454, 1223, 1191, 1057, 1017, 734; ^1H (400 MHz, CDCl_3) δ 2.78 (2H, d, $J = 13.4$ Hz, CH_2Ph), 3.15 (2H, d, $J = 13.4$ Hz, CH_2Ph), 3.47 (2H, s, CH_2OH), 7.15–7.24 (10H, m, Ar-CH); ^{13}C (100 MHz, CDCl_3) δ 40.0 ($2 \times \text{CH}_2\text{Ph}$), 53.3 (C^q), 61.5 (CH_2), 126.9 ($2 \times \text{Ar-CH}$), 128.9 ($4 \times \text{Ar-CH}$), 130.1 ($4 \times \text{Ar-CH}$), 136.3 ($2 \times \text{Ar-C}^q$), 181.3 (C=O); m/z (ES $^-$) 269 ((M-H), 100%), 270 (8); (Found: (M - H), 269.1183. $\text{C}_{17}\text{H}_{17}\text{O}_3$ requires M , 269.1183). The deuterated analogue was prepared using the same procedure. mp 110–112 °C; ν_{max} (neat)/ cm^{-1} 3413 (OH), 3029, 2927, 1703 (C=O), 1495, 1454, 1280, 1232, 1077, 1030; ^1H (400 MHz, CDCl_3) 2.79 (2H, d, $J = 13.4$ Hz, CH_2Ph), 3.16 (2H, d, $J = 13.4$ Hz, CH_2Ph) and 7.15–7.24 (10H, m, Ar-CH), CD_2OH not observed; ^{13}C (100 MHz, CDCl_3) δ 40.0 ($2 \times \text{CH}_2\text{Ph}$), 53.3 (C^q), 126.9 ($2 \times \text{Ar-CH}$), 128.6 ($4 \times \text{Ar-CH}$), 130.3 ($4 \times \text{Ar-CH}$), 136.4 ($2 \times \text{Ar-C}$), 181.4 (COOH); m/z (ES $^+$) 294 (15%), 295 ((M + Na), 100), 296 (18); (Found: (M + Na), 295.1270. $\text{C}_{17}\text{H}_{16}\text{D}_2\text{O}_3\text{Na}$ requires M , 295.1274).

1-Hydroxymethyl-cyclopentanecarboxylic acid (2b)

As for general procedure A, reaction of 8,8-dimethyl-7,9-dioxaspiro[4.5]decane-6,10-dione **1b** (82 mg, 0.414 mmol, 1 eq) in THF (5.0 mL) with SmI_2 (0.1 M in THF, 28.0 mL, 2.79 mmol, 7 eq) and distilled water (4.0 mL, 398 mmol, 961 eq), after column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 1-hydroxymethyl-cyclopentanecarboxylic acid **2b** (49 mg, 0.370 mmol, 81%) as a yellow solid. mp 97-99 °C; ν_{max} (neat)/ cm^{-1} 3356 (OH), 2957, 2940, 2868, 1692 (C=O), 1199, 1028, 1007, 951, 468; ^1H (400 MHz, CDCl_3) δ 1.65-1.70 (4H, m, $2 \times \text{CH}_2$), 1.72-1.81 (2H, m, CH_2), 1.99-2.08 (2H, m, CH_2), 3.61 (2H, s, CH_2OH), 7.10 (1H, bs, OH); ^{13}C (100 MHz, CDCl_3) δ 25.7 ($2 \times \text{CH}_2$), 33.5 ($2 \times \text{CH}_2$), 54.6 (C^q), 67.6 (CH_2OH), 183.8 (COOH); m/z (ES-) 143 ((M - H), 100%), 291 (8), 392 (22); (Found: (M - H), 295.1270. $\text{C}_7\text{H}_{11}\text{O}_3$ requires M , 143.0714).

2-Benzyl-3-hydroxy-propionic acid (2c)

As for general procedure A, reaction of 5-benzyl-2,2-dimethyl-[1,3]dioxane-4,6-dione **1c** (70 mg, 0.299 mmol, 1 eq) in THF (5.0 mL) with SmI_2 (0.1 M in THF, 21.0 mL, 2.09 mmol, 7 eq) and distilled water (5.4 mL, 299 mmol, 1000 eq), after column chromatography on silica gel, eluting with 70% ethyl acetate in petroleum ether (40-60 °C) gave 2-benzyl-3-hydroxy-propionic acid **2c** (36 mg, 0.203 mmol, 68%) as a yellow oil. ^1H (400 MHz, CDCl_3) δ 2.85-2.97 (2H, m, CH, 1H from CH_2Ph), 3.08-3.16 (1H, m, 1H from CH_2Ph), 3.75-3.85 (2H, m, CH_2OH), 5.78 (1H, bs, OH), 7.25-7.37 (5H, m, Ar-CH); ^{13}C (100 MHz, CDCl_3) δ 34.0 (CH_2Ph), 48.8 (CH), 61.9 (CH_2OH), 126.6 (Ar-CH), 128.6 ($2 \times \text{Ar-CH}$), 128.9 ($2 \times \text{Ar-CH}$), 138.2 (Ar- C^q), 179.4 (COOH). Data is in accordance with the literature⁷

⁷ Monteil T. *Synth. Commun.* **2001**, 31 (2), 211.

3-Hydroxy-2-(4-methoxy-benzyl)-propionic acid (**2d**)

As for general procedure A, reaction of 5-(4-methoxy-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione **1d** (70 mg, 0.265 mmol, 1 eq) in THF (5 mL) with SmI₂ (0.1 M in THF, 18.6 mL, 1.86 mmol, 7 eq) and distilled water (5.6 mL, 308 mmol, 1000 eq), after column chromatography on silica gel, eluting with 60% ethyl acetate in petroleum ether (40-60 °C) gave 3-hydroxy-2-(4-methoxy-benzyl)-propionic acid **2d** (40 mg, 0.210 mmol, 78%) as a white solid. mp 80-82 °C; $\nu_{\max}$ (neat)/cm⁻¹ 3402 (OH), 2933, 1713 (C=O), 1513, 1463, 1442, 1247, 1179, 1033; ¹H (400 MHz, CDCl₃) δ 2.68-2.78 (2H, m, CH, 1H from CHCH₂), 2.88-2.93 (1H, m, 1H from CHCH₂), 3.61-3.71 (2H, m, CH₂OH), 3.40 (3H, s, OCH₃), 6.75 (2H, d, *J* = 8.8 Hz, Ar-CH), 7.04 (2H, d, *J* = 8.8 Hz, Ar-CH); ¹³C (100 MHz, CDCl₃) δ 33.2 (CHCH₂), 49.1 (CH), 55.3 (CH₃), 61.9 (CH₂OH), 114.0 (2 × Ar-CH), 129.9 (2 × Ar-CH), 130.2 (Ar-C), 158.3 (Ar-C), 179.7 (COOH); *m/z* (ES⁺) 193 (8%), 228 (8), 233 ((M + Na), 100), 247 (10); (Found: (M + Na), 233.0779. C₁₁H₁₄O₄Na requires *M*, 233.0784).

2-(4-Bromo-benzyl)-3-hydroxy-propionic acid (**2e**)

As for general procedure A, reaction of 5-(4-bromo-benzyl)-2,2-dimethyl-[1,3]dioxane-4,6-dione **1e** (70 mg, 0.224 mmol, 1 eq) in THF (5.0 mL) with SmI₂ (0.1 M in THF, 15.7 mL, 1.57 mmol, 7 eq) and distilled water (4.0 mL, 223 mmol, 1000 eq), after column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 2-(4-bromo-benzyl)-3-hydroxy-propionic acid **2e** (45 mg, 0.170 mmol, 77%) as a yellow oil. $\nu_{\max}$ (neat)/cm⁻¹ 3391 (OH), 2954, 1710 (C=O), 1488, 1405, 1241, 1201, 1072, 1011; ¹H (400 MHz, CDCl₃) δ 2.71-2.79 (2H, m, CH, 1H from CHCH₂C), 2.88-2.95 (1H, m, 1H from CHCH₂C), 3.60-3.73 (2H, m, CH₂OH), 7.01 (2H, d, *J* = 8.3 Hz, Ar-CH), 7.34 (2H, d, *J* = 8.6 Hz, Ar-CH); ¹³C (100 MHz, CDCl₃) δ 33.4 (CHCH₂), 48.7 (CH), 61.9 (CH₂OH), 120.6 (Ar-C^q), 130.7 (2 × Ar-CH), 131.7 (2 × Ar-CH), 137.2 (Ar-C^q) 179.1 (COOH); *m/z* (-ES) 257 ((M - H), 98%), 259 (100), 260 (8); (Found: (M - H) 258.9797. C₁₀H₁₁⁸¹Br O₃ requires *M*, 258.9793).

2-Hydroxymethyl-2methyl-pentanoic acid (**2f**)

As for general procedure A, reaction of 5-isobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione **1f** (70 mg, 0.350 mmol, 1 eq) in THF (5.0 mL) with SmI₂ (0.1 M in THF, 24.5 mL, 2.45 mmol, 7 eq) and distilled water (6.3 mL, 350 mmol, 1000 eq), after column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 2-hydroxymethyl-2methyl-pentanoic acid **2f** (45 mg, 0.170 mmol, 77%) as a yellow oil. ¹H (400 MHz, CDCl₃) δ 0.94 (6H, apparent t, *J* = 6.2 Hz, CH(CH₃)₂), 1.37 (1H, m, CH(CH₃)₂), 1.58-1.72 (2H, m, CH₂), 2.68-2.75 (1H, m, CH₂CH(CH₂)₂), 3.77-3.79 (2H, m, CH₂OH); ¹³C (100 MHz, CDCl₃) δ 22.3 (CHCH₃), 22.5 (CHCH₃), 25.8 (CH(CH₃)₂), 37.2 (CHCH₂CH), 45.7 (CHC=O), 63.4 (CH₂OH), 180.8 (C=O). Data is in accordance with the literature.⁸

2-Benzyl-3-hydroxy-2-methyl-propionic acid (**2g**)

As for general procedure A, reaction of 5-benzyl-2,2,5-trimethyl-[1,3]dioxane-4,6-dione **1g** (70 mg, 0.282 mmol, 1 eq) in THF (5.0 mL) with SmI₂ (0.1 M in THF, 19.7 mL, 1.97 mmol, 7 eq) and distilled water (5.0 mL, 282 mmol, 1000 eq), after column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 2-benzyl-3-hydroxy-2-methyl-propionic acid **2g** (54 mg, 0.270 mmol, 98%) as a white solid. ¹H (400 MHz, CDCl₃) δ 1.17 (3H, s, CH₃), 2.92 (1H, d, *J* = 13.4 Hz, 1H from CH₂Ph), 3.02 (1H, d, *J* = 13.4 Hz, 1H from CH₂Ph), 3.61 (2H, s, CH₂OH), 7.17-7.33 (5H, m, Ar-CH); ¹³C (100 MHz, CDCl₃) δ 19.1 (CH₃), 40.5 (CH₂Ph), 48.5 (C^q), 66.6 (CH₂OH), 126.7 (Ar-CH), 128.2 (2 × Ar-CH), 130.4 (2 × Ar-CH), 136.2 (Ar-C^q), 182.3 (COOH). Data is in accordance with the literature.⁹

⁸ Park, J. D.; Dong, K. H. *J. Med. Chem.* **2002**, *45*, 911.

⁹ Lee H. S.; Kim D. H. *J. Med. Chem.* **2002**, *45*, 911.

2-Phenyl-3-hydroxy-propionic acid (**2h**)

As for general procedure A, reaction of 2,2-dimethyl-5-phenyl-4,6-dioxo-1,3-dioxane **1h** (100 mg, 0.455 mmol, 1 eq) in THF (2.0 mL) with SmI_2 (0.1 M in THF, 31.8 mL, 3.18 mmol, 7 eq) and distilled water (7.9 mL, 455 mmol, 1000 eq), after column chromatography on silica gel, eluting with 30% ethyl acetate in petroleum ether (40-60 °C) gave 2-phenyl-3-hydroxy-propionic acid **2h** (54 mg, 0.203 mmol, 72%) as a white solid. ^1H (400 MHz, CDCl_3) δ 3.76-3.83 (2H, m, CH_2), 4.80 (1H, dd, $J = 8.1$ Hz, CH), 7.21-7.30 (5H, m, Ar-CH) ^{13}C (100 MHz, MeOD) δ 55.9 (CH), 65.1 (CH_2), 128.5 (Ar-CH), 129.2 ($2 \times$ Ar-CH), 129.7 ($2 \times$ Ar-CH), 137.9 (Ar- C^q), 176.1 (COOH) Data is in accordance with the literature.

2-Hydroxymethyl-butylric acid (**2k**)

As for general procedure A, reaction of 6,6-dimethyl-5,7-dioxo-spiro[2.5]octane-4,8-dione **1k** (51 mg, 0.300 mmol, 1 eq) in THF (5.0 mL) with SmI_2 (0.1 M in THF, 31.5 mL, 3.15 mmol, 10.5 eq) and distilled water (7.9 mL, 438 mmol, 1000 eq), after column chromatography on silica gel, eluting with 40% ethyl acetate in petroleum ether (40-60 °C) and 0.5% acetic acid gave 2-hydroxymethyl-butylric acid **2k** (27 mg, 0.225 mmol, 75%) as a colourless gum. ^1H (400 MHz, CDCl_3) δ 0.98 (3H, t, $J = 7.4$ Hz, CH_3), 1.50-1.63 (1H, m, 1H from CH_2CH_3), 1.64-1.75 (1H, m, 1H from CH_2CH_3), 2.51-2.58 (1H, m, CH), 3.75-3.83 (2H, m, CH_2OH), 6.14 (1H, bs, OH); ^{13}C (100 MHz, CDCl_3) δ 11.6 (CH_3), 21.4 (CH_2), 49.0 (CH), 62.6 (CH_2OH), 180.0 (COOH). Data is in accordance with the literature.¹⁰

¹⁰ Batertz B. H.; Lollo C. P. *J. Biol. Chem.* **1979**, 254, 3468.

2-(4-Acetoxy-benzyl)-3-hydroxy-propionic acid

As for general procedure A, reaction of acetic acid 4-(2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-ylmethyl)-phenyl ester **II** (67 mg, 0.229 mmol, 1 eq) in THF (5.0 mL) with SmI_2 (0.1 M in THF, 16.0 mL, 1.60 mmol, 7 eq) and distilled water (4.1 mL, 228 mmol, 1000 eq), after column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 2-(4-acetoxy-benzyl)-3-hydroxy-propionic acid (38 mg, 0.156 mmol, 67%) as a yellow oil. ν_{max} (neat)/ cm^{-1} 3451 (OH), 2925, 1732 (C=O), 1509, 1371, 1221, 1196, 1018, 915, 853; ^1H (400 MHz, CDCl_3) δ 2.21 (3H, s, CH_3), 2.73–2.81 (2H, m, CH, 1H from CHCH_2Ar), 2.91–2.98 (1H, m, 1H from CHCH_2Ar), 3.60–3.71 (2H, m, CH_2OH), 6.93 (2H, d, $J = 7.6$ Hz, Ar-CH), 7.14 (2H, d, $J = 8.1$ Hz, Ar-CH); ^{13}C (100 MHz, CDCl_3) δ 14.1 (CH_3), 33.3 (CH_2), 48.8 (CH), 61.9 (CH_2), 121.6 ($2 \times$ Ar-CH), 130.0 ($2 \times$ Ar-CH), 136.1 (Ar- C^q), 149.3 (Ar- C^q), 169.9 ($\text{C}(\text{O})\text{CH}_3$), 178.9 (COOH); m/z (ES-) 121 (6%), 165 (42), 166 (10), 195 (10), 207 (82), 208 (20), 237 ((M-H), 100), 238 (6), 265 (10), 311 (18), 325 (16), 339 (14); (Found: (M - H), 237.0768. $\text{C}_{12}\text{H}_{13}\text{O}_5$ requires M , 237.0763).

5-Carboxy-2-ethoxycarbonyl-6-hydroxy-hexanoic acid ethyl ester

As for general procedure A, reaction of 2-[2-(2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-ethyl]-malonic acid diethyl ester **V** (83 mg, 0.251 mmol, 1 eq) in THF (5.0 mL) with SmI_2 (0.1 M in THF, 17.6 mL, 1.76 mmol, 7 eq) and distilled water (4.5 mL, 251 mmol, 1000 eq), after column chromatography on silica gel, eluting with 50% ethyl acetate in petroleum ether (40-60 °C) gave 5-carboxy-2-ethoxycarbonyl-6-hydroxy-hexanoic acid ethyl ester (54 mg, 0.200 mmol, 78%) as a yellow oil. ν_{max} (neat)/ cm^{-1} 3464 (OH), 2941, 1729 (C=O), 1447, 1371, 1183, 1155, 1028; ^1H (400 MHz, CDCl_3) δ 1.20 (6H, t, $J = 7.2$ Hz, $2 \times \text{CH}_3$), 1.50 (1H, m, 1H from $\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$), 1.64 (1H, m, 1H from $\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$), 1.89 (2H, apparent q, $J = 7.8$ Hz, $\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$), 2.54 (1H, apparent quintet, $J = 6.3$ Hz, CHCH_2OH), 3.28 (1H, t, $J = 7.4$ Hz, $\text{CHC}(\text{O})\text{Et}$), 3.62 (1H, bs, 1H from CHCH_2OH), 3.72 (1H, d, $J = 5.8$ Hz, 1H from CH_2OH), 4.09-4.17 (4H, m, 2H from $\text{CHCH}_2\text{CH}_2\text{CH}$, 2H from $\text{CHCH}_2\text{CH}_2\text{CH}$), 5.43 (1H, bs, COOH); ^{13}C (100 MHz, CDCl_3) 14.0 ($2 \times \text{CH}_3$), 25.7 (CH_2), 26.2 (CH_2), 47.1 (CHCH_2OH), 51.7

(CH(COOEt)₂), 61.7 (2 × CH₂CH₃), 62.6 (CH₂OH), 169.4 (2 × COOEt), 178.5 (COOH); *m/z* (ES⁺) 233 (18%), 277 (18), 294 (6), 299 ((M + Na), 100), 300 (75), 301 (6), 315 (5); (Found: (M + Na), 299.1105. C₁₂H₂₀O₇Na requires *M*, 299.1101).

General Procedure B

Reduction of α,β-unsaturated cyclic 1,3-diester using SmI₂-H₂O.

2-Hydroxymethyl-2methyl-pentanoic acid (2f)

To a stirred solution of SmI₂ (0.1 M in THF, 45.3 mL, 4.53 mmol, 9 eq) at room temperature was added distilled water (11.3 mL, 630 mmol, 1250 eq). This resulted in a colour change from deep blue/black to deep red/purple. A solution of 5-isobutylidene-2,2-dimethyl-[1,3]dioxan-4-one **1i** (100 mg, 0.500 mmol, 1 eq) in THF (2 mL) was added *via* cannula, and the solution left to stir until complete decolourization had occurred (~7 h). The reaction was quenched by opening to air. Aqueous saturated sodium chloride (30 mL) and tartaric acid (10 mg, 0.066 mmol) were subsequently added, and the aqueous layer extracted with ethyl acetate (3 × 60 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Purification by column chromatography on silica gel, eluting with 5% isopropanol in petroleum ether (40-60 °C) and 1% acetic acid, gave 2-hydroxymethyl-4-methyl-pentanoic acid **2f** (63 mg, 0.440 mmol, 87%) as a yellow oil. See earlier for characterisation data.

3-Hydroxy-2-(4-methoxy-benzyl)-propionic acid (2d)

As for general procedure B, reaction of 5-(4-methoxy-benzylidene)-2,2-dimethyl-[1,3]dioxane-4,6-dione **1j** (131 mg, 0.500 mmol, 1 eq) in THF (2 mL) with SmI₂ (0.1 M in THF, 45 mL, 4.50 mmol, 9 eq) and distilled water (11.3 mL, 626 mmol, 1250 eq), after column chromatography on silica gel, eluting with 5% isopropanol in petroleum ether (40-60 °C) and 1% acetic acid, gave 3-hydroxy-2-(4-methoxy-benzyl)-propionic acid **2d** (71 mg, 0.345 mmol, 69%) as a white solid. See earlier for characterisation data.

General procedure C

Cyclisations of cyclic 1,3-diesters using $\text{SmI}_2\text{--H}_2\text{O}$.

***Rac*-(1*S*, 2*R*, 3*R*)-2-Hydroxy-1-isobutyl-3-methyl-cyclopentane carboxylic acid (**12**)**

To a stirred solution of 5-but-3-enyl-5-isobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione **9** (50 mg, 0.197 mmol, 1 eq) in THF (0.5 mL) and distilled water (4.26 mL, 236 mmol, 1200 eq), was added SmI_2 (0.1 M in THF, 15.8 mL, 1.58 mmol, 8 eq) dropwise over 1 h. The resultant deep red/purple mixture was left to stir until complete decolourisation had occurred (~ 30 minutes). The reaction was quenched by opening to the air. Aqueous saturated sodium chloride (15 mL) and tartaric acid (10 mg, 0.066 mmol) were subsequently added, and the aqueous layer extracted with ethyl acetate (3 $\times$ 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography on silica gel eluting with 20% ethyl acetate in petroleum ether (40-60 °C) gave 2-hydroxy-1-isobutyl-3-methyl-cyclopentane carboxylic acid as a mixture of four diastereoisomers (36 mg, 0.180 mmol, 92%) and traces of 2-hydroxymethyl-2-isobutyl-hex-5-enoic acid (6% by ^1H NMR). The mixture of diastereoisomers was chromatographed to afford the major diastereoisomer *rac*-(1*S*, 2*R*, 3*R*)-2-hydroxy-1-isobutyl-3-methyl-cyclopentane carboxylic acid **12**, as a white solid; mp 137 °C; ν_{max} (evap. film)/ cm^{-1} 3434 (OH), 2954, 2924, 1701 (C=O), 1465, 1224, 973; ^1H (400 MHz, CDCl_3) δ 0.91 (3H, d, J = 6.3 Hz, CHCH_3), 0.92 (3H, d, J = 6.3 Hz, CHCH_3), 1.03 (3H, d, J = 6.8 Hz, CH_3), 1.39 (1H, tdd, J = 12.6, 10.8, 5.3 Hz, 1H from CHCH_2CH_2), 1.60-1.70 (3H, m, CHCH_3 , 1H from CHCH_2CH_2 , 1H from $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.82-1.91 (2H, m, 1H from CHCH_2CH_2 , 1H from $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 2.00-2.09 (1H, m, CHCH_2CH_2), 2.35 (1H, ddd, J = 13.7, 9.1, 5.2 Hz, 1H from CHCH_2CH_2), 4.15 (1H, d, J = 3.8 Hz, CHOH); ^{13}C (100 MHz, CDCl_3) δ 14.1 (CH_3), 23.5 (CHCH_3), 23.9 (CHCH_3), 25.9 (CHCH_3), 29.2 (CHCH_2CH_2), 31.6 (CHCH_2CH_2), 37.4 (CHCH_2CH_2), 42.6 (CH_2CHCH_3), 59.5 (C^q), 80.2 (CHOH), 182.5 (COOH); m/z (ES-) 199 (($\text{M} - \text{H}$) 100%), 235 (30), 245 (15), 313 (15), 399 (80) and 527 (23); (Found: ($\text{M} - \text{H}$), 199.1334. $\text{C}_{11}\text{H}_{19}\text{O}_3$ requires M , 199.1333). The relative stereochemistry of the major diastereoisomer was confirmed by X-ray crystallography (see page S42).

***Rac*-(1*S*, 2*R*, 3*R*)-3-Benzyl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid (**13**)**

As for general procedure C, reaction of 5-isobutyl-2,2-dimethyl-5-(4-phenyl-but-3-enyl)-[1,3]dioxane-4,6-dione **10** (50 mg, 0.158 mmol, 1eq) with SmI₂ (0.1 M, 12.6 mL, 1.26 mmol, 8 eq) and water (3.42 mL, 189 mmol, 1200 eq) after purification by column chromatography on silica gel, eluting with 30% ethyl acetate in petroleum ether (40-60 °C) gave 3-benzyl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid as a mixture of four diastereoisomers (41 mg, 0.150 mmol, 94%). The mixture of diastereoisomers was purified by chromatography to afford the major diastereoisomer **13** as a colourless oil; ν_{max} (evap. film)/cm⁻¹ 3388 (OH), 2955, 2360, 1691 (C=O), 1495, 1453, 1240, 1074, 748, 699; ¹H (400 MHz, CDCl₃) δ 0.87 (3H, d, J = 6.6 Hz, CH₃), 0.95 (3H, d, J = 6.6 Hz, CH₃), 1.29-1.33 (1H, m, 1H from CH₂), 1.41 (1H, dd, J = 14.12, 5.3 Hz, 1H from CH₂), 1.66-1.73 (3H, m, CHCH₃, 1H from CH₂, 1H from CH₂), 1.88 (1H, dd, J = 14.0, 7.7 Hz, 1H from CH₂), 2.12-2.21 (2H, m, 1H from CHCH₂Ph, 1H from CH₂), 2.50 (1H, dd, J = 13.4, 9.3 Hz, 1H from CH₂Ph), 3.02 (1H, dd, J = 13.4, 4.9 Hz, 1H from CH₂Ph), 3.83 (1H, d, J = 8.8 Hz, CHOH), 7.19-7.22 (3H, m, Ar-CH), 7.28-7.31 (2H, m, Ar-CH); ¹³C (100 MHz, CDCl₃) δ 22.9 (CH₃), 24.5 (CH₃), 24.9 (CHCH₃), 26.0 (CH₂), 28.7 (CH₂), 39.7 (CH₂), 39.8 (CH₂), 45.9 (CHCH₂Ph), 54.8 (C^q), 82.6 (CHOH), 125.9 (Ar-CH), 128.3 (2 × Ar-CH), 128.9 (2 × Ar-CH), 140.7 (Ar-C^q), 183.1 (COOH); m/z (ES⁺) 299 ((M + Na) 100%), 300 (12) and 331 (20); (Found: (M + Na), 299.1627 C₁₇H₂₄O₃Na requires M , 299.1623).

2-Benzyl-5-isobutyl-cyclopentanone

When the same reaction was carried out with less SmI₂-H₂O, 2-benzyl-5-isobutyl-cyclopentanone was isolated as a (1.3:1) mixture of diastereoisomers as a clear oil (50 %). The major diastereoisomer was isolated as a white solid by column chromatography on silica gel

eluting with 5% ethyl acetate in petroleum ether (40-60 °C). The relative stereochemistry of the major diastereoisomer was not determined. (*major diastereoisomer*), mp 34-36 °C; $\nu_{\max}$ (evap. film)/ cm^{-1} 2952, 2925, 2868, 1724 (C=O), 1452, 734, 696; ^1H (400 MHz, CDCl_3) δ 0.88 (3H, d, J = 6.3 Hz, CH_3), 0.92 (3H, d, J = 6.3 Hz, CH_3), 1.18 (1H, dd, J = 10.1, 8.6 Hz, 1H from $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.32 (1H, qd, J = 11.6, 5.8 Hz, 1H from $\text{BnCHCH}_2\text{CH}_2$), 1.45 (1H, qd, J = 12.1, 5.8 Hz, 1H from BnCHCH_2), 1.63-1.72 (2H, m, $\text{CH}(\text{CH}_3)_2$, 1H from $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 2.00-2.09 (2H, m, 1H from BnCHCH_2 , 1H $\text{CHCH}_2\text{CH}(\text{CH}_3)_2$), 2.13-2.20 (1H, m, 1H from $\text{BnCHCH}_2\text{CH}_2$), 2.30-2.39 (1H, m, CHBn), 2.58 (1H, dd, J = 13.8, 9.3 Hz, 1H from CH_2Ph), 3.18 (1H, dd, J = 13.8, 4.2 Hz, 1H from CH_2Ph), 7.16-7.30 (5H, m, Ar-CH); ^{13}C (100 MHz, CDCl_3) δ 21.5 (CH_3), 23.5 (CH_3), 26.1 ($\text{CH}(\text{CH}_3)_2$), 27.4 (BnCHCH_2), 28.1 ($\text{BnCHCH}_2\text{CH}_2$), 35.9 (PhCH_2), 39.6 (CH_2CHCH_3), 48.1 ($\text{CHCH}_2\text{CHCH}_3$), 51.2 (CHBn), 126.1 (Ar-CH), 128.4 ($2 \times$ Ar-CH), 128.9 ($2 \times$ Ar-CH), 140.1 (Ar- C^q), 221.8 (C=O); m/z (ES+) 253 (($\text{M} + \text{Na}$) 100%), 285 (20) and 483 (18); (Found: ($\text{M} + \text{Na}$), 253.1577. $\text{C}_{16}\text{H}_{22}\text{ONa}$ requires M , 253.1568).

***Rac*-(1*S*, 2*R*, 3*R*)-3-Benzhydryl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid (**14**)**

As general procedure C, reaction of 5-(4,4-diphenyl-but-3-enyl)-5-isobutyl-2,2-dimethyl-[1,3]dioxane-4,6-dione **11** (50 mg, 0.120 mmol, 1 eq) with SmI_2 (0.1 M, 9.6 mL, 0.960 mmol, 8 eq) and water (2.7 mL, 150 mmol, 1200 eq) after purification by column chromatography on silica gel, eluting with a 30% ethyl acetate in petroleum ether (40-60 °C) gave 3-benzhydryl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid **14** (28 mg, 0.080 mmol, 66%) as a colourless oil. The product was obtained as a mixture of four diastereoisomers. The diastereoisomers were not separable by column chromatography.

General procedure D

Esterification and oxidation of cyclisation products.

***Rac*-(1*S*, 3*R*)-1-isobutyl-3-methyl-2-oxo-cyclopentanecarboxylic acid methyl ester (15)**

To a stirred solution of the four diastereoisomers of 2-hydroxy-1-isobutyl-3-methyl-cyclopentane carboxylic acid (36 mg, 0.180 mmol, 1 eq) in a 4:1 mixture of toluene (0.75 mL) and methanol (0.18 mL), was added TMSCHN₂ (2 M in hexane, 0.19 mL, 0.390 mmol, 2.2 eq) dropwise and the reaction stirred for 1 hour at room temperature. The reaction mixture was concentrated *in vacuo*. The crude material was dissolved in dry dichloromethane (2.0 mL), Dess-Martin periodinane (101 mg, 0.240 mmol, 1.5 eq) was added and the reaction stirred at room temperature for 1 h before concentrating *in vacuo*. Purification by column chromatography on silica gel, eluting with 10% ethyl acetate in petroleum ether gave ketoester **15** (28 mg, 2:1 diastereomeric ratio, 0.13 mmol, 74% over two steps) as a colourless oil; (*major diastereoisomer*) $\nu_{\max}$ (evap. film)/cm⁻¹ 2957, 2870, 1751 (C=O), 1724 (C=O), 1456, 1273, 1213, 1150, 988, 895; ¹H (400 MHz, CDCl₃) δ 0.84 (3H, d, J = 6.8 Hz, CHCH₃), 0.89 (3H, d, J = 6.8 Hz, CHCH₃), 1.12 (3H, d, J = 7.1 Hz, CH₃), 1.42 (1H, dd, J = 14.1, 6.6 Hz, 1H from CH₂CH(CH₃)₂), 1.46-1.51 (1H, m, 1H from CH₂), 1.60-1.74 (1H, m, CH(CH₃)₂), 1.95 (1H, dd, J = 14.1, 6.8 Hz, 1H from CH₂CH(CH₃)₂), 1.96-2.02 (1H, m, 1H from CH₂), 2.16-2.25 (1H, m, 1H from CH₂), 2.30-2.40 (1H, m, CHCO), 2.53 (1H, ddd, J = 13.4, 9.3, 7.1 Hz, CH₂), 3.69 (3H, s, OCH₃); ¹³C (100 MHz, CDCl₃) δ 15.2 (CH₃), 22.8 (CHCH₃), 23.8 (CHCH₃), 25.2 (CH(CH₃)₂), 27.6 (CH₂), 29.6 (CH₂), 41.8 (CH₂), 43.2 (CHCH₃), 52.4 (OCH₃), 60.2 (C^q), 171.8 (COOCH₃), 215.7 (CO); m/z (ES⁺) 235 ((M + Na) 92%), 251 (20), 267 (28), 447 (100) and 448 (25); (Found: (M + Na), 235.1312. C₁₂H₂₀O₃Na requires M , 235.1310).

***Rac*-(1*S*, 3*R*)-3-Benzyl-1-isobutyl-2-oxo-cyclopentanecarboxylic acid methyl ester (**16**)**

As for general procedure D, reaction of the four diastereoisomers of 3-benzyl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid (44 mg, 0.160 mmol, 1 eq) and TMSCHN₂ (2 M in hexane, 0.17 mL, 0.350 mmol, 2.2 eq) gave the corresponding esters, which were subsequently oxidised with Dess-Martin periodinane (101 mg, 0.240 mmol, 1.5 eq). Purification by column chromatography on silica gel, eluting with 5% ethyl acetate in petroleum ether (40 – 60 °C) gave ketoester **16** (35 mg, 2.6:1 diastereomeric ratio, 0.120 mmol, 75% over two steps) as a colourless oil. The mixture of diastereoisomers was again chromatographed to afford the major diastereoisomer as a colourless oil; ν_{max} (evap. film)/cm⁻¹ 2953, 2872, 1749 (C=O), 1724 (C=O), 1495, 1453, 1217, 1162, 699; ¹H (400 MHz, CDCl₃) δ 0.85 (3H, d, J = 6.8 Hz, CH₃), 0.88 (3H, d, J = 6.6 Hz, CH₃), 1.42 (1H, dd, J = 14.1, 6.6 Hz, CHCH₂CH₂), 1.60-1.76 (3H, m, CHCH₃, 1H from CH₂CH(CH₃)₂, 1H from CHCH₂CH₂), 1.96-2.07 (1H, m, 1H from CH₂CH(CH₃)₂), 2.14 (1H, dd, J = 14.1, 6.6 Hz, 1H from CHCH₂CH₂), 2.45-2.53 (1H, m, CHCH₂Ph), 2.57-2.63 (2H, m, 1H from CHCH₂CH₂, 1H from PhCH₂), 3.14 (1H, dd, J = 13.6, 4.0 Hz, 1H from PhCH₂), 3.62 (3H, s, OCH₃), 7.13-7.15 (2H, m, Ar-CH), 7.18-7.22 (1H, m, Ar-CH), 7.25-7.29 (2H, m, Ar-CH); ¹³C (100 MHz, CDCl₃) δ 23.0 (CH₃), 23.6 (CH₃), 25.5 (CH(CH₃)₂), 26.4 (CH₂CH(CH₃)₂), 30.9 (CHCH₂CH₂), 36.3 (PhCH₂), 43.9 (CHCH₂CH₂), 50.8 (CHCH₂Ph), 52.4 (OCH₃), 61.5 (C^q), 126.2 (Ar-CH), 128.3 (2 × Ar-CH), 129.0 (2 × Ar-CH), 139.4 (Ar-C^q), 170.7 (COOCH₃), 214.7 (CO); m/z (ES +) 311 ((M + Na) 100%), 312 (20), 343 (13) and 389 (50); (Found: (M + Na), 311.1616. C₁₈H₂₄O₃Na requires M , 311.1623).

***Rac*-(1*S*, 3*R*)-3-Benzhydryl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid (**17**)**

As general procedure D, reaction of the four diastereoisomers of 3-benzhydryl-2-hydroxy-1-isobutyl-cyclopentanecarboxylic acid (20 mg, 0.057 mmol, 1 eq) and TMSCHN₂ (2 M in hexane, 62 μ L, 0.125 mmol, 2.2 eq) gave the corresponding crude esters, which were subsequently oxidised with Dess-Martin periodinane (37 mg, 0.090 mmol, 1.5 eq). Purification by column chromatography on silica gel eluting with 5% ethyl acetate in petroleum ether (40-60 °C) gave 3-benzhydryl-1-isobutyl-2-oxo-cyclopentanecarboxylic acid methyl ester **17** (19 mg, 5:1 diastereomeric ratio, 0.050 mmol, 64% over two steps) as a colourless oil. (*major diastereoisomer*) ν_{max} (evap. film)/cm⁻¹ 2956, 2870, 1747 (C=O), 1721 (C=O), 1595, 1495, 1451, 1220, 1160, 704; ¹H NMR (400 MHz, CDCl₃) δ 0.65 (6H, apparent t, J = 6.0 Hz, CH(CH₃)₂), 0.77 (1H, dd, J = 18.8, 6.5 Hz, 1H from CH₂CH(CH₃)₂), 1.33-1.40 (1H, m, CHCH₃), 1.39-1.48 (1H, m, CH₂), 1.58-1.72 (2H, dd, m, 1H from CH₂CH(CH₃)₂, 1H from CH₂) 2.16-2.25 (1H, m, 1H from CH₂), 2.34-2.41 (1H, m, 1H from CH₂), 3.12 (1H, apparent dt, J = 9.0, 4.5 Hz, CHC=O), 3.62 (3H, s, CH₃O), 4.61 (1H, d, J = 4.5, CHPh), 6.98-7.26 (10H, m, Ar-H); ¹³C (100 MHz, CDCl₃) δ 22.5 (CHCH₃), 23.2 (CH₂CHCH₃), 23.8 (CHCH₃), 25.0 (CHCH₃), 29.6 (CH₂), 40.4 (CH₂) 50.3 (CHPh), 52.2 (CHCHPh), 52.5 (CH₃O), 60.4 (C^q), 126.4 (Ar-CH), 126.7 (Ar-CH), 128.2 (2 $\times$ Ar-CH), 128.3 (2 $\times$ Ar-CH), 128.4 (2 $\times$ Ar-CH), 129.5 (2 $\times$ Ar-CH), 142.0 (Ar-C^q), 143.0 (Ar-C^q), 171.7 (COOCH₃), 213.3 (C=O). m/z (ES⁺) 425 (28%), 424 ((M + CH₃CONH₂) 100), 387 ((M + Na), 40); (Found: (M + Na) 287.1936. C₂₄H₂₈O₃Na requires M , 387.1936).

^1H and ^{13}C NMR spectra of new compounds

400 MHz (CDCl_3)

I

100 MHz (CDCl_3)

400 MHz (CDCl₃)

II

100 MHz (CDCl₃)

400 MHz (CDCl₃)

100 MHz (CDCl₃)

400 MHz (CDCl₃)

9

100 MHz (CDCl₃)

400 MHz (CDCl₃)

100 MHz (CDCl₃)

500 MHz (CDCl₃)

125 MHz (CDCl₃)

400 MHz (CDCl₃)

100 MHz (CDCl₃)

400 MHz (CDCl₃)

2a-D, D

100 MHz (CDCl₃)

400 MHz (CDCl₃)

2b

100 MHz (CDCl₃)

400 MHz (CDCl₃)

2d

100 MHz (CDCl₃)

400 MHz (CDCl₃)

2e

100 MHz (CDCl₃)

400 MHz (CDCl₃)

100 MHz (CDCl₃)

400 MHz (CDCl₃)

100 MHz (CDCl₃)

400 MHz (CDCl₃)

12

Mixture of four diastereoisomers

Major diastereoisomer

100 MHz (CDCl₃)

400 MHz (CDCl₃)

13

Mixture of four diastereoisomers

Major diastereoisomer

100 MHz (CDCl₃)

400 MHz (CDCl₃)

100 MHz (CDCl₃)

400 MHz (CDCl₃)

14

Mixture of four diastereoisomers

400 MHz (CDCl₃)

2:1 mixture of diastereoisomers

100 MHz (CDCl₃)

400 MHz (CDCl₃)

16

100 MHz (CDCl₃)

400 MHz (CDCl₃)

17

5:1 mixture of diastereoisomers

100 MHz (CDCl₃)

Representative Spectrum from a Competition Experiment

400 MHz (CDCl₃)

Crude NMR of mixture experiment

Recovered starting material

Isolated product

X-ray structure of a cyclisation product 12

CCDC 721800

Theoretical Calculations

As previous benchmark studies had established that the B3LYP/6-31+G* level of theory is a reliable method for the study of electron-transfer chemistry involving esters [1], we chose this method in this study.

DFT MO Calculations DFT calculations were carried out using the Gaussian 03 program [2] using standard computational methods and basis sets.

References

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Table S1 Calculated reaction energies (in kJmol⁻¹) and reaction energies with zero-point vibrational energy (ZPE) correlations for the reduction of Meldrum's acids **s1** to their anion radicals **s2** (DE₁) and for the reduction of hemiacetal radicals **s3** to their anions **s4** (DE₂).

R ¹	R ²	ΔE ₁	ΔE ₁ + ZPE	ΔE ₂	ΔE ₂ + ZPE
H	H	47.5	36.5	-60.8	-66.6
Me	H	47.9	36.9	-61.7	-68.8
Me	Me	43.5	31.9	-56.1	-62.9

Table S2 Calculated reaction energies (in kJmol⁻¹) and reaction energies with zero-point vibrational energy (ZPE) correlations for the reduction of dimethyl malonates **s5** to their anion radicals **s6** (DE₁) and for the reduction of hemiacetal radicals **s7** to their anions **s8** (DE₂).

R ¹	R ²	ΔE ₁	ΔE ₁ + ZPE	ΔE ₂	ΔE ₂ + ZPE
H	H	109.0	97.1	2.2	-7.8
Me	H	114.3	101.4	4.6	-5.8
Me	Me	102.3	90.7	-10.3	-18.7

BB1K/6-31+G* Gaussian Archive entries for the optimised structures of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid), 2,2,5-trimethyl-1,3-dioxane-4,6-dione (methyl Meldrum's acid), 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione (dimethyl Meldrum's acid), dimethyl malonate, dimethyl methylmalonate and dimethyl dimethylmalonate, their anion radicals, and hemiacetal radicals and anions of the Meldrum's acids and the malonates.

2,2-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid, s1, $R^1 = R^2 = H$)

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1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C6H8O4\HIROSHI\01-Nov-2008\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\Meldrum acid BB1K\0,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,0\H,12,r18,8,a18,7,d18,0\H,12,r19,8,a19,7,d19,0\H,12,r20,8,a20,7,d20,0\H,12,r21,8,a21,7,d21,0\H,12,r22,8,a22,7,d22,0\H,12,r23,8,a23,7,d23,0\H,12,r24,8,a24,7,d24,0\H,12,r25,8,a25,7,d25,0\H,12,r26,8,a26,7,d26,0\H,12,r27,8,a27,7,d27,0\H,12,r28,8,a28,7,d28,0\H,12,r29,8,a29,7,d29,0\H,12,r30,8,a30,7,d30,0\H,12,r31,8,a31,7,d31,0\H,12,r32,8,a32,7,d32,0\H,12,r33,8,a33,7,d33,0\H,12,r34,8,a34,7,d34,0\H,12,r35,8,a35,7,d35,0\H,12,r36,8,a36,7,d36,0\H,12,r37,8,a37,7,d37,0\H,12,r38,8,a38,7,d38,0\H,12,r39,8,a39,7,d39,0\H,12,r40,8,a40,7,d40,0\H,12,r41,8,a41,7,d41,0\H,12,r42,8,a42,7,d42,0\H,12,r43,8,a43,7,d43,0\H,12,r44,8,a44,7,d44,0\H,12,r45,8,a45,7,d45,0\H,12,r46,8,a46,7,d46,0\H,12,r47,8,a47,7,d47,0\H,12,r48,8,a48,7,d48,0\H,12,r49,8,a49,7,d49,0\H,12,r50,8,a50,7,d50,0\H,12,r51,8,a51,7,d51,0\H,12,r52,8,a52,7,d52,0\H,12,r53,8,a53,7,d53,0\H,12,r54,8,a54,7,d54,0\H,12,r55,8,a55,7,d55,0\H,12,r56,8,a56,7,d56,0\H,12,r57,8,a57,7,d57,0\H,12,r58,8,a58,7,d58,0\H,12,r59,8,a59,7,d59,0\H,12,r60,8,a60,7,d60,0\H,12,r61,8,a61,7,d61,0\H,12,r62,8,a62,7,d62,0\H,12,r63,8,a63,7,d63,0\H,12,r64,8,a64,7,d64,0\H,12,r65,8,a65,7,d65,0\H,12,r66,8,a66,7,d66,0\H,12,r67,8,a67,7,d67,0\H,12,r68,8,a68,7,d68,0\H,12,r69,8,a69,7,d69,0\H,12,r70,8,a70,7,d70,0\H,12,r71,8,a71,7,d71,0\H,12,r72,8,a72,7,d72,0\H,12,r73,8,a73,7,d73,0\H,12,r74,8,a74,7,d74,0\H,12,r75,8,a75,7,d75,0\H,12,r76,8,a76,7,d76,0\H,12,r77,8,a77,7,d77,0\H,12,r78,8,a78,7,d78,0\H,12,r79,8,a79,7,d79,0\H,12,r80,8,a80,7,d80,0\H,12,r81,8,a81,7,d81,0\H,12,r82,8,a82,7,d82,0\H,12,r83,8,a83,7,d83,0\H,12,r84,8,a84,7,d84,0\H,12,r85,8,a85,7,d85,0\H,12,r86,8,a86,7,d86,0\H,12,r87,8,a87,7,d87,0\H,12,r88,8,a88,7,d88,0\H,12,r89,8,a89,7,d89,0\H,12,r90,8,a90,7,d90,0\H,12,r91,8,a91,7,d91,0\H,12,r92,8,a92,7,d92,0\H,12,r93,8,a93,7,d93,0\H,12,r94,8,a94,7,d94,0\H,12,r95,8,a95,7,d95,0\H,12,r96,8,a96,7,d96,0\H,12,r97,8,a97,7,d97,0\H,12,r98,8,a98,7,d98,0\H,12,r99,8,a99,7,d99,0\H,12,r100,8,a100,7,d100,0\H,12,r101,8,a101,7,d101,0\H,12,r102,8,a102,7,d102,0\H,12,r103,8,a103,7,d103,0\H,12,r104,8,a104,7,d104,0\H,12,r105,8,a105,7,d105,0\H,12,r106,8,a106,7,d106,0\H,12,r107,8,a107,7,d107,0\H,12,r108,8,a108,7,d108,0\H,12,r109,8,a109,7,d109,0\H,12,r110,8,a110,7,d110,0\H,12,r111,8,a111,7,d111,0\H,12,r112,8,a112,7,d112,0\H,12,r113,8,a113,7,d113,0\H,12,r114,8,a114,7,d114,0\H,12,r115,8,a115,7,d115,0\H,12,r116,8,a116,7,d116,0\H,12,r117,8,a117,7,d117,0\H,12,r118,8,a118,7,d118,0\H,12,r119,8,a119,7,d119,0\H,12,r120,8,a120,7,d120,0\H,12,r121,8,a121,7,d121,0\H,12,r122,8,a122,7,d122,0\H,12,r123,8,a123,7,d123,0\H,12,r124,8,a124,7,d124,0\H,12,r125,8,a125,7,d125,0\H,12,r126,8,a126,7,d126,0\H,12,r127,8,a127,7,d127,0\H,12,r128,8,a128,7,d128,0\H,12,r129,8,a129,7,d129,0\H,12,r130,8,a130,7,d130,0\H,12,r131,8,a131,7,d131,0\H,12,r132,8,a132,7,d132,0\H,12,r133,8,a133,7,d133,0\H,12,r134,8,a134,7,d134,0\H,12,r135,8,a135,7,d135,0\H,12,r136,8,a136,7,d136,0\H,12,r137,8,a137,7,d137,0\H,12,r138,8,a138,7,d138,0\H,12,r139,8,a139,7,d139,0\H,12,r140,8,a140,7,d140,0\H,12,r141,8,a141,7,d141,0\H,12,r142,8,a142,7,d142,0\H,12,r143,8,a143,7,d143,0\H,12,r144,8,a144,7,d144,0\H,12,r145,8,a145,7,d145,0\H,12,r146,8,a146,7,d146,0\H,12,r147,8,a147,7,d147,0\H,12,r148,8,a148,7,d148,0\H,12,r149,8,a149,7,d149,0\H,12,r150,8,a150,7,d150,0\H,12,r151,8,a151,7,d151,0\H,12,r152,8,a152,7,d152,0\H,12,r153,8,a153,7,d153,0\H,12,r154,8,a154,7,d154,0\H,12,r155,8,a155,7,d155,0\H,12,r156,8,a156,7,d156,0\H,12,r157,8,a157,7,d157,0\H,12,r158,8,a158,7,d158,0\H,12,r159,8,a159,7,d159,0\H,12,r160,8,a160,7,d160,0\H,12,r161,8,a161,7,d161,0\H,12,r162,8,a162,7,d162,0\H,12,r163,8,a163,7,d163,0\H,12,r164,8,a164,7,d164,0\H,12,r165,8,a165,7,d165,0\H,12,r166,8,a166,7,d166,0\H,12,r167,8,a167,7,d167,0\H,12,r168,8,a168,7,d168,0\H,12,r169,8,a169,7,d169,0\H,12,r170,8,a170,7,d170,0\H,12,r171,8,a171,7,d171,0\H,12,r172,8,a172,7,d172,0\H,12,r173,8,a173,7,d173,0\H,12,r174,8,a174,7,d174,0\H,12,r175,8,a175,7,d175,0\H,12,r176,8,a176,7,d176,0\H,12,r177,8,a177,7,d177,0\H,12,r178,8,a178,7,d178,0\H,12,r179,8,a179,7,d179,0\H,12,r180,8,a180,7,d180,0\H,12,r181,8,a181,7,d181,0\H,12,r182,8,a182,7,d182,0\H,12,r183,8,a183,7,d183,0\H,12,r184,8,a184,7,d184,0\H,12,r185,8,a185,7,d185,0\H,12,r186,8,a186,7,d186,0\H,12,r187,8,a187,7,d187,0\H,12,r188,8,a188,7,d188,0\H,12,r189,8,a189,7,d189,0\H,12,r190,8,a190,7,d190,0\H,12,r191,8,a191,7,d191,0\H,12,r192,8,a192,7,d192,0\H,12,r193,8,a193,7,d193,0\H,12,r194,8,a194,7,d194,0\H,12,r195,8,a195,7,d195,0\H,12,r196,8,a196,7,d196,0\H,12,r197,8,a197,7,d197,0\H,12,r198,8,a198,7,d198,0\H,12,r199,8,a199,7,d199,0\H,12,r200,8,a200,7,d200,0\H,12,r201,8,a201,7,d201,0\H,12,r202,8,a202,7,d202,0\H,12,r203,8,a203,7,d203,0\H,12,r204,8,a204,7,d204,0\H,12,r205,8,a205,7,d205,0\H,12,r206,8,a206,7,d206,0\H,12,r207,8,a207,7,d207,0\H,12,r208,8,a208,7,d208,0\H,12,r209,8,a209,7,d209,0\H,12,r210,8,a210,7,d210,0\H,12,r211,8,a211,7,d211,0\H,12,r212,8,a212,7,d212,0\H,12,r213,8,a213,7,d213,0\H,12,r214,8,a214,7,d214,0\H,12,r215,8,a215,7,d215,0\H,12,r216,8,a216,7,d216,0\H,12,r217,8,a217,7,d217,0\H,12,r218,8,a218,7,d218,0\H,12,r219,8,a219,7,d219,0\H,12,r220,8,a220,7,d220,0\H,12,r221,8,a221,7,d221,0\H,12,r222,8,a222,7,d222,0\H,12,r223,8,a223,7,d223,0\H,12,r224,8,a224,7,d224,0\H,12,r225,8,a225,7,d225,0\H,12,r226,8,a226,7,d226,0\H,12,r227,8,a227,7,d227,0\H,12,r228,8,a228,7,d228,0\H,12,r229,8,a229,7,d229,0\H,12,r230,8,a230,7,d230,0\H,12,r231,8,a231,7,d231,0\H,12,r232,8,a232,7,d232,0\H,12,r233,8,a233,7,d233,0\H,12,r234,8,a234,7,d234,0\H,12,r235,8,a235,7,d235,0\H,12,r236,8,a236,7,d236,0\H,12,r237,8,a237,7,d237,0\H,12,r238,8,a238,7,d238,0\H,12,r239,8,a239,7,d239,0\H,12,r240,8,a240,7,d240,0\H,12,r241,8,a241,7,d241,0\H,12,r242,8,a242,7,d242,0\H,12,r243,8,a243,7,d243,0\H,12,r244,8,a244,7,d244,0\H,12,r245,8,a245,7,d245,0\H,12,r246,8,a246,7,d246,0\H,12,r247,8,a247,7,d247,0\H,12,r248,8,a248,7,d248,0\H,12,r249,8,a249,7,d249,0\H,12,r250,8,a250,7,d250,0\H,12,r251,8,a251,7,d251,0\H,12,r252,8,a252,7,d252,0\H,12,r253,8,a253,7,d253,0\H,12,r254,8,a254,7,d254,0\H,12,r255,8,a255,7,d255,0\H,12,r256,8,a256,7,d256,0\H,12,r257,8,a257,7,d257,0\H,12,r258,8,a258,7,d258,0\H,12,r259,8,a259,7,d259,0\H,12,r260,8,a260,7,d260,0\H,12,r261,8,a261,7,d261,0\H,12,r262,8,a262,7,d262,0\H,12,r263,8,a263,7,d263,0\H,12,r264,8,a264,7,d264,0\H,12,r265,8,a265,7,d265,0\H,12,r266,8,a266,7,d266,0\H,12,r267,8,a267,7,d267,0\H,12,r268,8,a268,7,d268,0\H,12,r269,8,a269,7,d269,0\H,12,r270,8,a270,7,d270,0\H,12,r271,8,a271,7,d271,0\H,12,r272,8,a272,7,d272,0\H,12,r273,8,a273,7,d273,0\H,12,r274,8,a274,7,d274,0\H,12,r275,8,a275,7,d275,0\H,12,r276,8,a276,7,d276,0\H,12,r277,8,a277,7,d277,0\H,12,r278,8,a278,7,d278,0\H,12,r279,8,a279,7,d279,0\H,12,r280,8,a280,7,d280,0\H,12,r281,8,a281,7,d281,0\H,12,r282,8,a282,7,d282,0\H,12,r283,8,a283,7,d283,0\H,12,r284,8,a284,7,d284,0\H,12,r285,8,a285,7,d285,0\H,12,r286,8,a286,7,d286,0\H,12,r287,8,a287,7,d287,0\H,12,r288,8,a288,7,d288,0\H,12,r289,8,a289,7,d289,0\H,12,r290,8,a290,7,d290,0\H,12,r291,8,a291,7,d291,0\H,12,r292,8,a292,7,d292,0\H,12,r293,8,a293,7,d293,0\H,12,r294,8,a294,7,d294,0\H,12,r295,8,a295,7,d295,0\H,12,r296,8,a296,7,d296,0\H,12,r297,8,a297,7,d297,0\H,12,r298,8,a298,7,d298,0\H,12,r299,8,a299,7,d299,0\H,12,r300,8,a300,7,d300,0\H,12,r301,8,a301,7,d301,0\H,12,r302,8,a302,7,d302,0\H,12,r303,8,a303,7,d303,0\H,12,r304,8,a304,7,d304,0\H,12,r305,8,a305,7,d305,0\H,12,r306,8,a306,7,d306,0\H,12,r307,8,a307,7,d307,0\H,12,r308,8,a308,7,d308,0\H,12,r309,8,a309,7,d309,0\H,12,r310,8,a310,7,d310,0\H,12,r311,8,a311,7,d311,0\H,12,r312,8,a312,7,d312,0\H,12,r313,8,a313,7,d313,0\H,12,r314,8,a314,7,d314,0\H,12,r315,8,a315,7,d315,0\H,12,r316,8,a316,7,d316,0\H,12,r317,8,a317,7,d317,0\H,12,r318,8,a318,7,d318,0\H,12,r319,8,a319,7,d319,0\H,12,r320,8,a320,7,d320,0\H,12,r321,8,a321,7,d321,0\H,12,r322,8,a322,7,d322,0\H,12,r323,8,a323,7,d323,0\H,12,r324,8,a324,7,d324,0\H,12,r325,8,a325,7,d325,0\H,12,r326,8,a326,7,d326,0\H,12,r327,8,a327,7,d327,0\H,12,r328,8,a328,7,d328,0\H,12,r329,8,a329,7,d329,0\H,12,r330,8,a330,7,d330,0\H,12,r331,8,a331,7,d331,0\H,12,r332,8,a332,7,d332,0\H,12,r333,8,a333,7,d333,0\H,12,r334,8,a334,7,d334,0\H,12,r335,8,a335,7,d335,0\H,12,r336,8,a336,7,d336,0\H,12,r337,8,a337,7,d337,0\H,12,r338,8,a338,7,d338,0\H,12,r339,8,a339,7,d339,0\H,12,r340,8,a340,7,d340,0\H,12,r341,8,a341,7,d341,0\H,12,r342,8,a342,7,d342,0\H,12,r343,8,a343,7,d343,0\H,12,r344,8,a344,7,d344,0\H,12,r345,8,a345,7,d345,0\H,12,r346,8,a346,7,d346,0\H,12,r347,8,a347,7,d347,0\H,12,r348,8,a348,7,d348,0\H,12,r349,8,a349,7,d349,0\H,12,r350,8,a350,7,d350,0\H,12,r351,8,a351,7,d351,0\H,12,r352,8,a352,7,d352,0\H,12,r353,8,a353,7,d353,0\H,12,r354,8,a354,7,d354,0\H,12,r355,8,a355,7,d355,0\H,12,r356,8,a356,7,d356,0\H,12,r357,8,a357,7,d357,0\H,12,r358,8,a358,7,d358,0\H,12,r359,8,a359,7,d359,0\H,12,r360,8,a360,7,d360,0\H,12,r361,8,a361,7,d361,0\H,12,r362,8,a362,7,d362,0\H,12,r363,8,a363,7,d363,0\H,12,r364,8,a364,7,d364,0\H,12,r365,8,a365,7,d365,0\H,12,r366,8,a366,7,d366,0\H,12,r367,8,a367,7,d367,0\H,12,r368,8,a368,7,d368,0\H,12,r369,8,a369,7,d369,0\H,12,r370,8,a370,7,d370,0\H,12,r371,8,a371,7,d371,0\H,12,r372,8,a372,7,d372,0\H,12,r373,8,a373,7,d373,0\H,12,r374,8,a374,7,d374,0\H,12,r375,8,a375,7,d375,0\H,12,r376,8,a376,7,d376,0\H,12,r377,8,a377,7,d377,0\H,12,r378,8,a378,7,d378,0\H,12,r379,8,a379,7,d379,0\H,12,r380,8,a380,7,d380,0\H,12,r381,8,a381,7,d381,0\H,12,r382,8,a382,7,d382,0\H,12,r383,8,a383,7,d383,0\H,12,r384,8,a384,7,d384,0\H,12,r385,8,a385,7,d385,0\H,12,r386,8,a386,7,d386,0\H,12,r387,8,a387,7,d387,0\H,12,r388,8,a388,7,d388,0\H,12,r389,8,a389,7,d389,0\H,12,r390,8,a390,7,d390,0\H,12,r391,8,a391,7,d391,0\H,12,r392,8,a392,7,d392,0\H,12,r393,8,a393,7,d393,0\H,12,r394,8,a394,7,d394,0\H,12,r395,8,a395,7,d395,0\H,12,r396,8,a396,7,d396,0\H,12,r397,8,a397,7,d397,0\H,12,r398,8,a398,7,d398,0\H,12,r399,8,a399,7,d399,0\H,12,r400,8,a400,7,d400,0\H,12,r401,8,a401,7,d401,0\H,12,r402,8,a402,7,d402,0\H,12,r403,8,a403,7,d403,0\H,12,r404,8,a404,7,d404,0\H,12,r405,8,a405,7,d405,0\H,12,r406,8,a406,7,d406,0\H,12,r407,8,a407,7,d407,0\H,12,r408,8,a408,7,d408,0\H,12,r409,8,a409,7,d409,0\H,12,r410,8,a410,7,d410,0\H,12,r411,8,a411,7,d411,0\H,12,r412,8,a412,7,d412,0\H,12,r413,8,a413,7,d413,0\H,12,r414,8,a414,7,d414,0\H,12,r415,8,a415,7,d415,0\H,12,r416,8,a416,7,d416,0\H,12,r417,8,a417,7,d417,0\H,12,r418,8,a418,7,d418,0\H,12,r419,8,a419,7,d419,0\H,12,r420,8,a420,7,d420,0\H,12,r421,8,a421,7,d421,0\H,12,r422,8,a422,7,d422,0\H,12,r423,8,a423,7,d423,0\H,12,r424,8,a424,7,d424,0\H,12,r425,8,a425,7,d425,0\H,12,r426,8,a426,7,d426,0\H,12,r427,8,a427,7,d427,0\H,12,r428,8,a428,7,d428,0\H,12,r429,8,a429,7,d429,0\H,12,r430,8,a430,7,d430,0\H,12,r431,8,a431,7,d431,0\H,12,r432,8,a432,7,d432,0\H,12,r433,8,a433,7,d433,0\H,12,r434,8,a434,7,d434,0\H,12,r435,8,a435,7,d435,0\H,12,r436,8,a436,7,d436,0\H,12,r437,8,a437,7,d437,0\H,12,r438,8,a438,7,d438,0\H,12,r439,8,a439,7,d439,0\H,12,r440,8,a440,7,d440,0\H,12,r441,8,a441,7,d441,0\H,12,r442,8,a442,7,d442,0\H,12,r443,8,a443,7,d443,0\H,12,r444,8,a444,7,d444,0\H,12,r445,8,a445,7,d445,0\H,12,r446,8,a446,7,d446,0\H,12,r447,8,a447,7,d447,0\H,12,r448,8,a448,7,d448,0\H,12,r449,8,a449,7,d449,0\H,12,r450,8,a450,7,d450,0\H,12,r451,8,a451,7,d451,0\H,12,r452,8,a452,7,d452,0\H,12,r453,8,a453,7,d453,0\H,12,r454,8,a454,7,d454,0\H,12,r455,8,a455,7,d455,0\H,12,r456,8,a456,7,d456,0\H,12,r457,8,a457,7,d457,0\H,12,r458,8,a458,7,d458,0\H,12,r459,8,a459,7,d459,0\H,12,r460,8,a460,7,d460,0\H,12,r461,8,a461,7,d461,0\H,12,r462,8,a462,7,d462,0\H,12,r463,8,a463,7,d463,0\H,12,r464,8,a464,7,d464,0\H,12,r465,8,a465,7,d465,0\H,12,r466,8,a466,7,d466,0\H,12,r467,8,a467,7,d467,0\H,12,r468,8,a468,7,d468,0\H,12,r469,8,a469,7,d469,0\H,12,r470,8,a470,7,d470,0\H,12,r471,8,a471,7,d471,0\H,12,r472,8,a472,7,d472,0\H,12,r473,8,a473,7,d473,0\H,12,r474,8,a474,7,d474,0\H,12,r475,8,a475,7,d475,0\H,12,r476,8,a476,7,d476,0\H,12,r477,8,a477,7,d477,0\H,12,r478,8,a478,7,d478,0\H,12,r479,8,a479,7,d479,0\H,12,r480,8,a480,7,d480,0\H,12,r481,8,a481,7,d481,0\H,12,r482,8,a482,7,d482,0\H,12,r483,8,a483,7,d483,0\H,12,r484,8,a484,7,d484,0\H,12,r485,8,a485,7,d485,0\H,12,r486,8,a486,7,d486,0\H,12,r487,8,a487,7,d487,0\H,12,r488,8,a488,7,d488,0\H,12,r489,8,a489,7,d489,0\H,12,r490,8,a490,7,d490,0\H,12,r491,8,a491,7,d491,0\H,12,r492,8,a492,7,d492,0\H,12,r493,8,a493,7,d493,0\H,12,r494,8,a494,7,d494,0\H,12,r495,8,a495,7,d495,0\H,12,r496,8,a496,7,d496,0\H,12,r497,8,a497,7,d497,0\H,12,r498,8,a498,7,d498,0\H,12,r499,8,a499,7,d499,0\H,12,r500,8,a500,7,d500,0\H,12,r501,8,a501,7,d501,0\H,12,r502,8,a502,7,d502,0\H,12,r503,8,a503,7,d503,0\H,12,r504,8,a504,7,d504,0\H,12,r505,8,a505,7,d505,0\H,12,r506,8,a506,7,d506,0\H,12,r507,8,a507,7,d507,0\H,12,r508,8,a508,7,d508,0\H,12,r509,8,a509,7,d509,0\H,12,r510,8,a510,7,d510,0\H,12,r511,8,a511,7,d511,0\H,12,r512,8,a512,7,d512,0\H,12,r513,8,a513,7,d513,0\H,12,r514,8,a514,7,d514,0\H,12,r515,8,a515,7,d515,0\H,12,r516,8,a516,7,d516,0\H,12,r517,8,a517,7,d517,0\H,12,r518,8,a518,7,d518,0\H,12,r519,8,a519,7,d519,0\H,12,r520,8,a520,7,d520,0\H,12,r521,8,a521,7,d521,0\H,12,r522,8,a522,7,d522,0\H,12,r523,8,a523,7,d523,0\H,12,r524,8,a524,7,d524,0\H,12,r525,8,a525,7,d525,0\H,12,r526,8,a526,7,d526,0\H,12,r527,8,a527,7,d527,0\H,12,r528,8,a528,7,d528,0\H,12,r529,8,a529,7,d529,0\H,12,r530,8,a530,7,d530,0\H,12,r531,8,a531,7,d531,0\H,12,r532,8,a532,7,d532,0\H,12,r533,8,a533,7,d533,0\H,12,r534,8,a534,7,d534,0\H,12,r535,8,a535,7,d535,0\H,12,r536,8,a536,7,d536,0\H,12
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A=0.750006\RMSD=3.220e-09\RMSF=3.634e-05\Dipole=-0.5411284,0.5157499,-0.8539353\PG=C01 [X(C6H9O4)]\@

2,2-Dimethyl-4-hydroxy-1,3-dioxane-5-one-4-ide anion (s4, $R^1 = R^2 = H$)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C6H9O4(1-)\HIROSHI\03-Nov-2008\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\Meldrum anion BB1K\1,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,0\H,12,r18,8,a18,7,d18,0\H,6,r19,5,a19,1,d19,0\2=1.49855999\r3=1.21059462\3=123.99998139\r4=1.33316592\4=118.29930322\d4=-181.65508265\r5=1.50802692\5=111.39006449\d5=29.99925267\r6=1.42074793\6=104.69186922\d6=194.86692917\r7=1.50551716\7=98.95523679\d7=-59.61733338\r8=1.35195999\8=111.32953003\d8=75.97438895\r9=1.10668352\r10=1.08742464\9=106.62851233\10=107.18938962\d9=-91.34175089\d10=153.54907635\r11=1.51327743\r12=1.52001416\11=108.43756041\12=114.07931832\d11=-169.48062761\d12=65.27860526\r13=1.08762247\r14=1.08883301\r15=1.08923526\r16=1.09059589\r17=1.08580519\r18=1.08951849\13=109.32709427\14=109.34197476\15=110.65211103\16=108.99316567\17=108.23748571\18=110.62908778\d13=56.19984036\d14=-62.86793547\d15=176.64996523\d16=65.18032113\d17=-53.12698726\d18=185.30655971\r19=0.95364378\19=105.45891131\d19=-154.83319241\Version=x86-Linux-G03RevB.05\HF=-534.7003375\RMSD=7.162e-09\RMSF=1.166e-04\Dipole=-1.6095319,-0.1389385,0.525308\PG=C01 [X(C6H9O4)]\@

2,2,5-Trimethyl-1,3-dioxane-4,6-dione (methyl Meldrum's acid, s1, $R^1 = Me$, $R^2 = H$)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C7H10O4\HIROSHI\05-Nov-2008\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\methyl-Meldrum BB1K\0,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,0\H,12,r18,8,a18,7,d18,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\2=1.50899148\r3=1.19264037\3=123.80903197\r4=1.34012184\4=120.14135377\d4=-179.59102076\r5=1.50883421\5=111.57108597\d5=33.15815139\r6=1.19265347\6=123.80130222\d6=146.36819623\r7=1.34052581\7=116.07703855\d7=-33.1463447\r8=1.41649573\8=120.98314291\d8=-4.02101302\r9=1.09456463\r10=1.51404696\9=105.81336427\10=112.14670261\d9=-81.48107095\d10=160.00581465\r11=1.5043259\r12=1.51236939\11=105.84680498\12=110.79663594\d11=155.62342466\d12=-82.37002293\r13=1.08652293\r14=1.08616936\r15=1.0865375\r16=1.08664636\r17=1.08685179\r18=1.08682393\13=109.7737515\14=109.49528384\15=109.78144622\16=112.50985159\17=109.33438717\18=109.36952065\d13=60.80312398\d14=-59.02356643\d15=181.14785334\d16=61.56906805\d17=-58.72188809\d18=181.94671312\r22=1.08537866\r23=1.08676614\r24=1.08534624\22=109.83917738\23=110.59620758\24=109.9304966\d22=55.86330921\d23=-63.60181755\d24=176.87952248\Version=x86-Linux-G03RevB.05\HF=-573.4445842\RMSD=5.629e-09\RMSF=4.122e-05\Dipole=-0.9327471,-1.124487,0.1051289\PG=C01 [X(C7H10O4)]\@

2,2,5-Trimethyl-1,3-dioxane-4,6-dione anion radical (s2, $R^1 = Me$, $R^2 = H$)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C7H10O4(1-,2)\HIROSHI\05-Nov-2008\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\methyl-Meldrum anion radical BB1K\1,2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,0\H,12,r18,8,a18,7,d18,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\2=1.50629755\r3=1.20837452\3=123.56317455\r4=1.33488589\4=118.11637293\d4=-182.75179932\r5=1.51246779\5=112.15667258\d5=26.44909485\r6=1.25152047\6=120.60868574\d6=177.65165491\r7=1.47559757\7=104.54972619\d7=-50.97352953\r8=1.35876818\8=113.27325214\d8=68.24804347\r9=1.10794283\r10=1.51367435\9=104.79206853\10=111.30592865\d9=-90.15491107\d10=153.02096309\r11=1.51180205\r12=1.51928467\11=108.31472073\12=113.11017012\d11=-169.05166656\d12=66.37200833\r13=1.08740272\r14=1.08827275\r15=1.08893837\r16=1.08926902\r17=1.08726595\r18=1.08919517\13=109.27801429\14=109.31761987\15=110.66257788\16=109.14371812\17=109.01687453\18=110.71295819\d13=56.79834396\d14=-62.23130646\d15=177.18616574\d16=62.61756687\d17=-55.73439965\d18=183.18255023\r22=1.08788882\r23=1.09035351\r24=1.08755433\22=111.46863265\23=110.28492145\24=108.43575639\d22=56.57348297\d23=-63.94088418\d24=178.0659436\Version=x86-Linux-G03RevB.05\HF=-573.4263439\S2=0.754626\S2-1=0\S2A=0.750012\RMSD=8.660e-09\RMSF=8.130e-05\Dipole=-0.7772178,-0.2128979,1.7043298\PG=C01 [X(C7H10O4)]\@

2,2,5-Trimethyl-4-hydroxy-1,3-dioxane-5-one-4-yl radical (s3, $R^1 = Me$, $R^2 = H$)

1\1\ GINC-DUAL1FOpt\UBB95\6-31+G(d)\C7H11O4(2)\HIROSHI\04-Nov-2008\1\#BB95/6-31+G* OPT=(Z-M ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\meth yl-Meldrum radical BB1K\0,2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7, 1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\ H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17, 0\H,12,r18,8,a18,7,d18,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\H,6,r25,5,a25,1,d25 ,0\|r2=1.51380668\|r3=1.19631064\|a3=122.64152365\|r4=1.33701527\|a4=119.84851604\|d4=-184.94227183\|r5=1.49 666838\|a5=110.39609294\|d5=24.96038073\|r6=1.35014785\|a6=118.55723758\|d6=186.53992524\|r7=1.35530379\|a7 =113.52166124\|d7=-44.01403948\|r8=1.39984409\|a8=113.78315345\|d8=60.67580713\|r9=1.10111037\|r10=1.51655 068\|a9=104.16576268\|a10=111.09217114\|d9=-89.91996139\|d10=153.0435113\|r11=1.50305212\|r12=1.51171508\|a 11=106.76786833\|a12=111.34110033\|d11=-168.27577794\|d12=67.55430776\|r13=1.08642056\|r14=1.08685004\|r15 =1.08637403\|r16=1.08734928\|r17=1.08793693\|r18=1.08668338\|a13=109.67646392\|a14=109.62587592\|a15=109.8 7870624\|a16=109.65630926\|a17=110.54387484\|a18=109.81053447\|d13=57.41653202\|d14=-62.3770285\|d15=177. 4194316\|d16=-59.77678568\|d17=-59.93830467\|d18=179.98230267\|r22=1.08565635\|r23=1.08869276\|r24=1.089986 25\|a22=109.87200533\|a23=111.02135938\|a24=111.25173361\|d22=49.64966982\|d23=-69.9343619\|d24=168.89500 508\|r25=0.9598209\|a25=109.13050863\|d25=-47.21450276\|Version=x86-Linux-G03RevB.05\HF=-573.9695512\|S2 =0.752963\|S2-1=0\|S2A=0.750006\|RMSD=3.340e-09\|RMSF=4.127e-05\|Dipole=-0.4064683,0.4742803,-0.7778275 \PG=C01 [X(C7H11O4)]\|@

2,2,5-Trimethyl-4-hydroxy-1,3-dioxane-5-one-4-ide anion (s4, R¹ = Me, R² = H)

1\1\ GINC-DUAL1FOpt\RBB95\6-31+G(d)\C7H11O4(1-)\HIROSHI\04-Nov-2008\1\#BB95/6-31+G* OPT=(Z-M ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\meth yl-Meldrum anion BB1K\0,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1 ,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\H ,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,0\ H,12,r18,8,a18,7,d18,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\H,6,r25,5,a25,1,d25,0 \|r2=1.50727699\|r3=1.21010316\|a3=123.77252016\|r4=1.33392182\|a4=117.97350435\|d4=-181.92884043\|r5=1.5125 3599\|a5=109.8308519\|d5=30.34725823\|r6=1.42194177\|a6=104.79226271\|d6=194.76994316\|r7=1.49739223\|a7=10 0.01961969\|d7=-59.51103076\|r8=1.35235598\|a8=111.36569652\|d8=76.32307405\|r9=1.10832137\|r10=1.51409093\ |a9=105.08988229\|a10=110.57031723\|d9=-87.03889101\|d10=155.8927065\|r11=1.5133267\|r12=1.52027861\|a11=10 8.40437297\|a12=114.0573763\|d11=-169.40635579\|d12=65.45252564\|r13=1.08760683\|r14=1.08879973\|r15=1.089 18254\|r16=1.09056112\|r17=1.08591864\|r18=1.08948244\|a13=109.33286677\|a14=109.34682711\|a15=110.6381120 1\|a16=109.02599617\|a17=108.25680703\|a18=110.61055304\|d13=56.24599579\|d14=-62.83762054\|d15=176.69429 949\|d16=65.33071132\|d17=-53.03985291\|d18=185.45464529\|r22=1.08871561\|r23=1.09018759\|r24=1.08863358\|a 22=111.61621779\|a23=110.03891853\|a24=108.8320241\|d22=55.08955023\|d23=-65.4160042\|d24=176.20792069\|r 25=0.95336066\|a25=105.51536829\|d25=-152.13142339\|Version=x86-Linux-G03RevB.05\HF=-573.9930642\|RMS D=3.107e-09\|RMSF=1.341e-04\|Dipole=-1.2044891,-0.0611235,0.3389047\PG=C01 [X(C7H11O4)]\|@

2,2,5,5-Tetramethyl-1,3-dioxane-4,6-dione (dimethyl Meldrum's acid, s1, R¹ = R² = Me)

1\1\ GINC-DUAL1FOpt\RBB95\6-31+G(d)\C8H12O4\HIROSHI\05-Nov-2008\1\#BB95/6-31+G* OPT=(Z-MAT RIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethy l-Meldrum BB1K\0,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7, 0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\H,11,r13,8 ,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,0\H,12,r18 ,8,a18,7,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,9,r21,1,a21,2,d21,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1 ,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\|r2=1.51445014\|r3=1.19450437\|a3=121.99959959\|r4=1.34086335\|a4=119.933 47538\|d4=-174.94653398\|r5=1.51424703\|a5=114.76820962\|d5=-5.06456666\|r6=1.19442344\|a6=122.05023609\|d6 =179.84267103\|r7=1.34183634\|a7=117.85751858\|d7=4.83999789\|r8=1.41384254\|a8=119.71442671\|d8=-27.37697 603\|r9=1.5261848\|r10=1.53788996\|a9=110.20086373\|a10=106.24891493\|d9=-130.15274915\|d10=112.09812018\|r 11=1.50208493\|r12=1.51124365\|a11=106.45454968\|a12=109.56285824\|d11=163.57011164\|d12=-73.34141702\|r13 =1.08644687\|r14=1.08632418\|r15=1.08646859\|r16=1.08930837\|r17=1.08668945\|r18=1.08669869\|a13=109.764525 13\|a14=109.58527639\|a15=109.76912243\|a16=110.78110181\|a17=109.92103205\|a18=109.92921425\|d13=60.4695 8271\|d14=-59.37690619\|d15=180.77023841\|d16=61.24952998\|d17=-58.47924482\|d18=180.9732976\|r19=1.08853 804\|r20=1.08661532\|r21=1.08663265\|r22=1.08663742\|r23=1.08861278\|r24=1.08662395\|a19=112.34230713\|a20=1 09.08992283\|a21=109.1200553\|a22=108.93414776\|a23=111.7312826\|a24=108.96099498\|d19=64.15285856\|d20=- 55.96183577\|d21=184.26593415\|d22=58.63720967\|d23=-61.43232623\|d24=178.47796018\|Version=x86-Linux-G0 3RevB.05\HF=-612.7330449\|RMSD=5.531e-09\|RMSF=9.434e-05\|Dipole=-0.5532865,-0.477709,0.3576435\PG=C 01 [X(C8H12O4)]\|@


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1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C8H12O4(1-,2)\HIROSHI\05-Nov-2008\1\#BB95\6-31+G* OPT=(Z-  
MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dim  
ethyl-Meldrum anion radical BB1K\1-,2\C\1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,  
0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,  
5,d12,0\H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a1  
7,7,d17,0\H,12,r18,8,a18,7,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,9,r21,1,a21,2,d21,0\H,10,r22,1,a22,  
2,d22,0\H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\vr2=1.5124671\vr3=1.20893992\vr4=1.22.98603506\vr5=1.3339  
1031\vr6=117.95621596\vr7=-182.84842092\vr8=1.5266607\vr9=111.32029215\vr10=23.7605571\vr11=1.25409396\vr12=1  
19.61512968\vr13=179.80019122\vr14=-1.48252721\vr15=104.89394403\vr16=-49.92331667\vr17=1.35736282\vr18=112.85043  
151\vr19=69.06566254\vr20=1.53633741\vr21=1.51783548\vr22=107.23131963\vr23=109.31591334\vr24=-96.55706586\vr25  
=145.14915021\vr26=1.51222743\vr27=1.51931795\vr28=108.3641376\vr29=113.29558977\vr30=-169.35117649\vr31=6  
5.96837834\vr32=1.08751798\vr33=1.08826388\vr34=1.08896149\vr35=1.08930296\vr36=1.08712048\vr37=1.08928056\  
vr38=109.29639301\vr39=109.31329518\vr40=110.70536256\vr41=109.13060342\vr42=109.01651314\vr43=110.700185  
06\vr44=56.65687779\vr45=-62.35951037\vr46=177.03182205\vr47=62.83502936\vr48=-55.5084452\vr49=183.348844  
23\vr50=1.08924594\vr51=1.09172985\vr52=1.08943302\vr53=1.08888438\vr54=1.09000359\vr55=1.08843024\vr56=110.  
67863489\vr57=111.49058603\vr58=107.75277118\vr59=111.09487415\vr60=110.73257831\vr61=108.14498046\vr62=19  
61.62904398\vr63=-60.21408834\vr64=179.49370922\vr65=59.39543883\vr66=61.43908997\vr67=180.46976542\Ver  
sion=x86-Linux-G03RevB.05\HF=-612.7164612\S2=0.754665\S2-1=0.\S2A=0.75001\RMSE=7.588e-09\RMSE=6.  
843e-05\Dipole=-0.5340667,-0.4196054,1.4955058\PG=C01 [X(C8H12O4)]\ \@
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1\| GINCDUAL1\FOpt\UBB95\6-31+G(d)\C8H13O4(2)\HIROSHI\10-Nov-2008\1\#BB95\6-31+G* OPT=(Z-M
ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimet
hy-Meldrum radical BB1K\0,2\C\1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,
1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\
H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,
0\H,12,r18,8,a18,7,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,9,r21,1,a21,2,d21,0\H,10,r22,1,a22,2,d22,0\
H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\H,6,r25,5,a25,1,d25,0\r2=1.51881021\r3=1.19691092\A3=122.46182
631\r4=1.338151\A4=119.5279279\d4=-185.77812788\r5=1.50429233\A5=108.77503193\d5=-26.28971082\r6=1.351
33023\A6=118.63393646\d6=183.99560329\r7=1.35662306\A7=113.72054391\d7=-46.33231517\r8=1.39960605\A8
=113.39509062\d8=62.42205945\r9=1.53895225\r10=1.51967076\A9=106.12845869\A10=109.46065616\d9=-92.15
896978\d10=149.0488164\r11=1.50330959\r12=1.51169192\A11=106.83736197\A12=111.31634214\d11=-167.7111
4439\d12=68.13243593\r13=1.08649025\r14=1.0868796\r15=1.086371\r16=1.08737558\r17=1.0878791\r18=1.086
7087\A13=109.70511815\A14=109.6393181\A15=109.89523627\A16=109.67014997\A17=110.43017105\A18=109.84
143473\d13=57.4490178\d14=-62.34602902\d15=177.43816236\d16=59.9810635\d17=-59.71506647\d18=180.213
20959\r19=1.08784326\r20=1.08821851\r21=1.08855972\r22=1.08625481\r23=1.08877414\r24=1.09121393\A19=1.
11.17215708\A20=109.950977 55\A21=109.69731614\A22=109.8241917\A23=111.53832027\A24=110.73836654\d19
=60.76579301\d20=-59.97500717\d21=180.30096783\d22=52.85159865\d23=-67.12083442\d24=171.62363649\r2
5=0.95998644\A25=109.03920592\d25=-48.93894388\Version=x86-Linux-G03RevB.05\HF=-613.2604865\S2=0.7
52902\S2-1=0.\S2A=0.750006\RMSD=8.707e-09\RMSF=3.455e-05\Dipole=-0.4110773,0.3854928,-0.7890375\PG
=C01 [X(C8H13O4)]\@

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1\| GINC-DUAL\FOpt\RBB95\6-31+G(d)\C8H13O4(1-)\HIROSHI\09-Nov-2008\1\#BB95/6-31+G* OPT=(Z-M
ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\\dimet
hy-Meldrum anion BB1K\|-1,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,
1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\C,8,r11,7,a11,5,d11,0\C,8,r12,7,a12,5,d12,0\
H,11,r13,8,a13,7,d13,0\H,11,r14,8,a14,7,d14,0\H,11,r15,8,a15,7,d15,0\H,12,r16,8,a16,7,d16,0\H,12,r17,8,a17,7,d17,
0\H,12,r18,8,a18,7,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,9,r21,1,a21,2,d21,0\H,10,r22,1,a22,2,d22,0\
H,10,r23,1,a23,2,d23,0\H,10,r24,1,a24,2,d24,0\H,6,r25,5,a25,1,d25,0\r2=1.51472132\r3=1.21020957\a3=123.31658
742\r4=1.33388622\a4=117.81349224\d4=-182.91282976\r5=1.52898485\xa5=108.05303505\d5=29.93506315\r6=1.
42505572\xa6=105.55632129\d6=193.95917981\r7=1.49682157\xa7=101.06647603\d7=-59.66041136\r8=1.352242\xa
8=110.76587482\d8=76.98385675\r9=1.53811769\r10=1.51823716\xa9=106.79656419\xa10=108.86671319\d9=-93.4
3065932\d10=149.22478201\r11=1.51347532\r12=1.52020733\xa11=108.37295171\xa12=114.13562037\d11=-169.02
104506\d12=65.79811352\r13=1.0877903\r14=1.08878665\r15=1.08915361\r16=1.09061897\r17=1.08591311\r18=
1.08948003\xa13=109.39494531\xa14=109.31647897\xa15=110.68196504\xa16=109.01937374\xa17=108.13892738\xa18
=110.59034054\d13=56.33098414\d14=-62.7495442\d15=176.76318962\d16=65.47850371\d17=-52.9108784\d18=
185.56907031\r19=1.08859748\r20=1.09201124\r21=1.08931055\r22=1.08959525\r23=1.08939812\r24=1.0900706
```

7\19=110.9150699\20=111.18295027\21=108.51188076\22=111.50144554\23=110.35245906\24=108.34978
268\19=63.08890975\20=-58.61697857\21=181.39244174\22=58.79168035\23=-62.3940837\24=179.38798
902\25=0.95273575\25=105.00285287\25=-148.91897084\Version=x86-Linux-G03RevB.05\HF=-613.2818553\
RMSD=5.697e-09\RMSF=1.024e-04\Dipole=-1.014867,-0.279609,0.1570299\PG=C01 [X(C8H13O4)]\@

Dimethyl malonate (s5, $R^1 = R^2 = H$)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C5H8O4\HIROSHI\02-Sep-2003\1\#BB95/6-31+G* OPT=(Z-MATRI
X,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl m
alonate BB1K\0,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C
,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13
,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\2=1.5007811
6\3=1.19966565\3=124.71471009\4=1.3265909\4=124.09785686\4=180.54227719\5=1.50401876\5=111.206
85834\5=-73.76896786\6=1.1991164\6=125.4027621\6=-6.54849065\7=1.32890879\7=110.68951111\7=-18
5.67973865\8=1.42001545\8=115.3689263\8=178.52156868\9=1.08813358\10=1.08693692\9=110.70451892\
a10=109.03568268\9=47.26798357\10=166.22373961\11=1.0831191\12=1.08628163\13=1.08628778\11=105
.6960274\12=110.27574934\13=110.27680272\11=180.60045999\12=-59.69729939\13=60.93909548\14=1.4
1842066\14=115.44106947\14=176.53830654\15=1.08649462\16=1.08615853\17=1.08314542\15=110.36931
56\16=110.06895281\17=105.74949404\15=60.88233116\16=-59.8404883\17=-179.36204584\Version=x86-
Linux-G03RevB.05\HF=-496.0464415\RMSD=6.700e-09\RMSF=3.295e-05\Dipole=-0.7179929,0.2782581,-0.7696
018\PG=C01 [X(C5H8O4)]\@

Dimethyl malonate anion radical (s6, $R^1 = R^2 = H$)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C5H8O4(1,-2)\HIROSHI\02-Nov-2008\1\#BB95/6-31+G* OPT=(Z-
MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dim
ethyl malonate anion radical BB1K another\1,2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,
a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r
12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r
17,4,a17,2,d17,0\2=1.48337413\3=1.20893453\3=126.53415056\4=1.34303946\4=121.09064967\4=179.2423
8618\5=1.53801961\5=110.65859185\5=-88.5445403\6=1.25955442\6=119.84950883\6=52.13492323\7=1.4
4257903\7=103.39220616\7=-173.83465428\8=1.38698229\8=112.14586936\8=185.16957478\9=1.09845288
\10=1.08542392\9=109.07366244\10=109.05791548\9=31.15681011\10=150.56433442\11=1.09134501\12=
1.09839527\13=1.0913322\11=107.4843532\12=111.1157311\13=111.73464581\11=178.7959252\12=-62.04
536238\13=58.32974601\14=1.40402823\14=115.03840534\14=-187.4508572\15=1.08950936\16=1.0878943
4\17=1.08590886\15=111.15379454\16=110.56578295\17=106.01981057\15=62.71045781\16=-57.9739156\
d17=-177.39574072\Version=x86-Linux-G03RevB.05\HF=-496.0049323\S2=0.754376\S2-1=0.\S2A=0.750011\R
MSD=6.439e-09\RMSF=3.498e-05\Dipole=-0.566235,1.07086,0.981543\PG=C01 [X(C5H8O4)]\@

1-Hydroxy-1-methoxy-2-methoxycarbonyleth-1-yl radical (s7, $R^1 = R^2 = H$)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C5H9O4(2)\HIROSHI\05-Sep-2003\1\#BB95/6-31+G* OPT=(Z-MA
TRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimeth
yl malonate radical BB1K\0,2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,
a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\
H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\
H,6,r18,5,a18,1,d18,0\2=1.49952233\3=1.19782637\3=125.51734432\4=1.34270935\4=122.41678843\4=181.
658771\5=1.49661556\5=114.45365989\5=-42.32630525\6=1.36197039\6=117.73150014\6=67.69015181\7
=1.34488914\7=111.46250269\7=-159.80223131\8=1.4109919\8=115.82051524\8=179.64547834\9=1.09850
161\10=1.0843352\9=107.48195853\10=107.63045101\9=80.1416254\10=195.83244334\11=1.08450075\12
=1.08979265\13=1.08690145\11=106.08877055\12=110.36611954\13=111.04959906\11=186.68796024\12
=-54.35358194\13=67.20264462\14=1.4213536\14=115.59321455\14=-179.30800942\15=1.08580208\16=1.0
8577963\17=1.08332363\15=110.13523765\16=110.18106259\17=105.85778008\15=60.78515203\16=-59.8
6205947\17=-179.59057216\18=0.96328768\18=107.40111617\18=-48.55127596\Version=x86-Linux-G03Rev
B.05\HF=-496.5698312\S2=0.753106\S2-1=0.\S2A=0.750007\RMSD=8.771e-09\RMSF=4.225e-05\Dipole=-0.8561
397,-0.0035092,0.3616987\PG=C01 [X(C5H9O4)]\@

1-Hydroxy-1-methoxy-2-methoxycarbonylethan-1-ide anion (s8, $R^1 = R^2 = H$)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C5H9O4(1-)\HIROSHI\10-Nov-2008\1\#BB95/6-31+G* OPT=(Z-M
ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimet
hyl malonate anion BB1K\1,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,
1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\H,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\
H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\
H,6,r18,5,a18,1,d18,0\2=1.49952233\3=1.19782637\3=125.51734432\4=1.34270935\4=122.41678843\4=181.
658771\5=1.49661556\5=114.45365989\5=-42.32630525\6=1.36197039\6=117.73150014\6=67.69015181\7
=1.34488914\7=111.46250269\7=-159.80223131\8=1.4109919\8=115.82051524\8=179.64547834\9=1.09850
161\10=1.0843352\9=107.48195853\10=107.63045101\9=80.1416254\10=195.83244334\11=1.08450075\12
=1.08979265\13=1.08690145\11=106.08877055\12=110.36611954\13=111.04959906\11=186.68796024\12
=-54.35358194\13=67.20264462\14=1.4213536\14=115.59321455\14=-179.30800942\15=1.08580208\16=1.0
8577963\17=1.08332363\15=110.13523765\16=110.18106259\17=105.85778008\15=60.78515203\16=-59.8
6205947\17=-179.59057216\18=0.96328768\18=107.40111617\18=-48.55127596\Version=x86-Linux-G03Rev
B.05\HF=-496.5698312\S2=0.753106\S2-1=0.\S2A=0.750007\RMSD=8.771e-09\RMSF=4.225e-05\Dipole=-0.8561
397,-0.0035092,0.3616987\PG=C01 [X(C5H9O4)]\@

H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,6,r18,5,a18,1,d18,0\r2=1.4859997\r3=1.21056381\A3=126.57383105\r4=1.34539882\A4=120.29865886\A4=180.34039572\r5=1.5273001\A5=111.32709003\A5=-67.14490255\r6=1.45528522\A6=105.03627746\A6=89.09722644\r7=1.43896702\A7=101.16782548\A7=-162.29095726\r8=1.38040022\A8=111.92196895\A8=170.96688076\r9=1.10319192\r10=1.08601564\A9=109.30391135\A10=106.63396621\A9=55.74002436\A10=173.88594145\r11=1.09415668\r12=1.09759594\r13=1.09633744\A11=108.1095717\A12=110.90531244\A13=111.81339606\A11=184.41531539\A12=-55.27450403\A13=65.28846169\r14=1.40335055\A14=114.97725776\A14=-183.89026392\r15=1.08954904\r16=1.08848148\r17=1.08646575\A15=111.25569121\A16=110.84950622\A17=106.02038429\A15=62.65692064\A16=-57.9447116\A17=-177.62155901\r18=0.95240617\A18=104.43639444\A18=-125.71571429\Version=x86-Linux-G03RevB.05\HF=-496.5689998\RMSD=5.497e-09\RMSF=2.960e-05\Dipole=-0.7903941,0.344451,1.3869861\PG=C01 [X(C5H9O4)]\@

Dimethyl methylmalonate (s5, R¹ = Me, R² = H)

1\1\ GINC-DUAL1\FOpt\BB95\6-31+G(d)\C6H10O4\HIROSHI\03-Sep-2003\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl methylmalonate BB1K another\0,1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\r2=1.50788379\r3=1.20055089\A3=124.67855438\r4=1.3293936\A4=123.69026439\A4=177.12551589\r5=1.5089762\A5=109.43975807\A5=-213.79035869\r6=1.19934703\A6=125.00291887\A6=122.54120218\r7=1.32805275\A7=111.08968988\A7=-58.93770937\r8=1.41854184\A8=115.48929881\A8=-181.89372263\r9=1.52076862\r10=1.08947312\A9=110.03874752\A10=107.90288476\A9=-91.30099121\A10=29.03763797\r11=1.08317588\r12=1.08629802\r13=1.08652773\A11=105.78182295\A12=110.08248076\A13=110.34597937\A11=180.24230499\A12=-60.19217775\A13=60.45734214\r14=1.41937093\A14=115.31962769\A14=176.93340706\r15=1.08619194\r16=1.08643974\r17=1.08322702\A15=110.24307832\A16=110.3511037\A17=105.73337364\A15=59.45847954\A16=-61.15867415\A17=-180.83889891\r18=1.08753032\r19=1.08678608\r20=1.08656027\A18=110.37621994\A19=110.43081623\A20=110.0295809\A18=60.09316314\A19=-60.81027449\A20=180.22977075\Version=x86-Linux-G03RevB.05\HF=-535.3381458\RMSD=4.498e-09\RMSF=3.719e-05\Dipole=-1.0209668,0.3878004,0.2866564\PG=C01 [X(C6H10O4)]\@

Dimethyl methylmalonate anion radical (s6, R¹ = Me, R² = H)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C6H10O4(1-,2)\HIROSHI\27-Aug-2003\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl methylmalonate anion radical BB1K another\1,2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\r2=1.4914047\r3=1.20948449\A3=126.10498722\r4=1.34111232\A4=120.90731673\A4=179.98424673\r5=1.54643517\A5=108.73674477\A5=-84.30066071\r6=1.26355845\A6=118.91901849\A6=71.44085318\r7=1.44948074\A7=103.46181811\A7=-155.90718593\r8=1.38574077\A8=112.00884784\A8=186.42902011\r9=1.52471854\r10=1.08725736\A9=112.87028465\A10=106.04323536\A9=38.37371763\A10=160.27830558\r11=1.091693\r12=1.09868307\r13=1.09159796\A11=107.57441735\A12=111.12508003\A13=111.74825635\A11=178.80613671\A12=-62.01752582\A13=58.27931362\r14=1.40402919\A14=115.19307956\A14=-185.84998254\r15=1.0893881\r16=1.08794412\r17=1.08588843\A15=111.1551921\A16=110.62118377\A17=106.00516325\A15=62.7646073\A16=-57.8627569\A17=-177.34101706\r18=1.09346474\r19=1.08780426\r20=1.08913529\A18=112.98295904\A19=109.01404916\A20=108.52846497\A18=54.01439803\A19=-67.5826849\A20=174.71160618\Version=x86-Linux-G03RevB.05\HF=-535.2946224\S2=0.754789\S2=0.\S2A=0.750012\RMSD=6.695e-09\RMSF=8.444e-05\Dipole=-0.4614946,1.3251252,0.9396783\PG=C01 [X(C6H10O4)]\@

1-Hydroxy-1-methoxy-2-methoxycarbonylpropan-1-yl radical (s7, R¹ = Me, R² = H)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C6H11O4(2)\HIROSHI\05-Sep-2003\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl methylmalonate OH radical BB1K\0,2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,6,r21,5,a21,1,d21,0\r2=1.5036891\r3=1.19844538\A3=125.64293611\r4=1.34425945\A4=122.25758632\A4=182.24279506\r5=1.50363891\A5=112.21556029\A5=-47.66748703\r6=1.36354172\A6=117.940773\A6=69.45599119\r7=1.34655916\A7=111.15185256\A7=-158.58293029\r8=1.41053083\A8=115.87720752\A8=179.98927288\r9=1.53310345\r10=1.08624017\A9=109.78678

384\ a10=105.85728856\ d9=77.83479135\ d10=195.83678856\ r11=1.08459846\ r12=1.08989122\ r13=1.08702428\ a11=106.13596117\ a12=110.36636373\ a13=111.05802221\ d11=186.39649192\ d12=-54.64412309\ d13=66.87377247\ r14=1.42084188\ a14=115.59751439\ d14=-178.56835762\ r15=1.08588918\ r16=1.08590129\ r17=1.08341907\ a15=110.13575137\ a16=110.21028629\ a17=105.9030928\ d15=60.59476444\ d16=-60.01032275\ d17=-179.78669778\ r18=1.08849078\ r19=1.08793142\ r20=1.08726054\ a18=110.83278068\ a19=110.87952306\ a20=109.2067517\ d18=57.44701967\ d19=-63.5777566\ d20=177.115918\ r21=0.96332116\ a21=107.31049653\ d21=-49.25014987\ \Version=x86-Linux-G03RevB.05\ HF=-535.8603909\ S2=0.753092\ S2-1=0.\ S2A=0.750007\ RMSD=3.997e-09\ RMSF=5.884e-05\ Dipole=-0.8456912,0.0982689,0.2845471\ PG=C01 [X(C6H11O4)]\ \@

1-Hydroxy-1-methoxy-2-methoxycarbonylpropan-1-ide anion (s8, R¹ = Me, R² = H)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C6H11O4(1-)\HIROSHI\05-Sep-2003\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl methylmalonate anion BB1K\1\1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\H,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,6,r21,5,a21,1,d21,0\ r2=1.49230287\ r3=1.21026297\ a3=126.64319456\ r4=1.34623949\ a4=120.30125256\ d4=180.98473983\ r5=1.53969967\ a5=108.45790093\ d5=-71.53871442\ r6=1.45810333\ a6=106.17122142\ d6=89.35138444\ r7=1.44321178\ a7=100.82995574\ d7=-16.206837392\ r8=1.37984637\ a8=111.87403412\ d8=169.31336335\ r9=1.52832706\ r10=1.08781911\ a9=112.19718599\ a10=104.71557276\ d9=56.76916636\ d10=175.84267605\ r11=1.09442025\ r12=1.09755788\ r13=1.09656882\ a11=108.18397706\ a12=110.8918442\ a13=111.81381569\ d11=184.46891925\ d12=-55.17300344\ d13=65.34738021\ r14=1.40300121\ a14=115.06251913\ d14=-183.65753232\ r15=1.08947943\ r16=1.08862564\ r17=1.08654598\ a15=111.24870275\ a16=110.81968816\ a17=106.06294639\ d15=61.7527656\ d16=-58.84024188\ d17=-178.46284733\ r18=1.094113\ r19=1.08728896\ r20=1.08904741\ a18=112.35534503\ a19=110.32795718\ a20=108.19602683\ d18=59.33381897\ d19=-62.68072626\ d20=179.39047563\ r21=0.95193877\ a21=103.89703992\ d21=-126.90947711\ \Version=x86-Linux-G03RevB.05\ HF=-535.8586319\ RMSD=2.953e-09\ RMSF=5.178e-05\ Dipole=-0.873607,0.7035819,1.1418572\ PG=C01 [X(C6H11O4)]\ \@

Dimethyl dimethylmalonate (s5, R¹ = R² = Me)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C7H12O4\HIROSHI\30-Oct-2008\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl dimethylmalonate BB1K\0\1\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,10,r21,1,a21,2,d21,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1,a23,2,d23,0\ r2=1.51560071\ r3=1.20168675\ a3=123.6451509\ r4=1.32806653\ a4=123.37256967\ d4=176.58291706\ r5=1.51736072\ a5=107.26842668\ d5=-214.33043912\ r6=1.19965951\ a6=125.08139685\ d6=124.2608468\ r7=1.32884509\ a7=111.22611669\ d7=-58.11066935\ r8=1.41801115\ a8=115.51434575\ d8=-181.14379667\ r9=1.5247916\ r10=1.52529063\ a9=107.36088753\ a10=112.8816638\ d9=-97.02268867\ d10=25.52619015\ r11=1.08329138\ r12=1.08630083\ r13=1.08660158\ a11=105.80858589\ a12=110.08996223\ a13=110.37404884\ d11=180.93974922\ d12=-59.48327844\ d13=61.1728935\ r14=1.41924146\ a14=115.27165159\ d14=176.72978373\ r15=1.08618687\ r16=1.0864221\ r17=1.08333068\ a15=110.24564892\ a16=110.32818832\ a17=105.74044258\ d15=59.69165861\ d16=-60.85977655\ d17=-180.58797913\ r18=1.08860894\ r19=1.08666357\ r20=1.08721168\ a18=109.958701\ a19=110.94787015\ a20=109.72436021\ d18=63.35096584\ d19=-57.66035436\ d20=182.98457886\ r21=1.08675639\ r22=1.0866708\ r23=1.08906891\ a21=111.47669032\ a22=110.03021242\ a23=109.61455196\ d21=57.41055988\ d22=-63.06111346\ d23=177.75196144\ \Version=x86-Linux-G03RevB.05\ HF=-574.6288483\ RMSD=3.352e-09\ RMSF=3.967e-05\ Dipole=-1.0902332,0.3949109,0.3040963\ PG=C01 [X(C7H12O4)]\ \@

Dimethyl dimethylmalonate anion radical (s6, R¹ = R² = Me)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C7H12O4(1,2)\HIROSHI\02-Nov-2008\1\#BB95/6-31+G* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimethyl dimethylmalonate anion radical BB1K another\1\2\C\C,1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,10,r21,1,a21,2,d21,0\H,10,r22,1,a22,2,d22,0\H,10,r23,1,a23,2,d23,0\ r2=1.49690308\ r3=1.20954863\ a3=126.71840874\ r4=1.34451256\ a4=120.76645709\ d4=180.83149175\ r5=1.55585906\ a5=109.74045748\ d5=-64.11044514\ r6=1.26272246\ a6=117.68339404\ d6=184.59313541\ r7=1.4419937\ a7=105.01389717\ d7=-42.0337073\ r8=1.38619873\ a8=112.45335521\ d8=185.19937544\ r9=1.52333194\ r10=1.52239068\ a9=110.83552506\ a10=109.14367382\ d9=54.28022509\ d10=175.78

405416\r11=1.09102431\r12=1.09868555\r13=1.09144611\al1=107.61620462\al2=111.12400671\al3=111.469779
01\d11=178.18974794\d12=-62.50510512\d13=57.74745681\r14=1.4033295\al4=114.9721078\d14=-184.93657219
\r15=1.0894606\r16=1.08820156\r17=1.08628573\al5=111.21320823\al6=110.68837166\al7=106.03066048\d15=
62.83386177\d16=-57.80708532\d17=-177.35736516\r18=1.09341168\r19=1.08792228\r20=1.08907692\al8=111.6
4973819\al9=110.75007898\al20=107.59055065\d18=65.13783272\d19=-56.85327859\d20=185.00788707\r21=1.0
8778966\r22=1.09250796\r23=1.08907456\al21=110.34983832\al22=111.9340721\al23=107.91002054\d21=57.5034
755\d22=-63.16112087\d23=176.06487785\\Version=x86-Linux-G03RevB.05\HF=-574.5899042\S2=0.754272\S2-
1=0.\S2A=0.75001\RMSD=4.575e-09\RMSF=1.066e-04\Dipole=-0.2357474,0.7920542,1.9283771\PG=C01 [X(C7
H12O4)]\@

1-Hydroxy-1-methoxy-2-methoxycarbonyl-2-methylpropan-1-yl radical (s7, $R^1 = R^2 = \text{Me}$)

1\1\ GINC-DUAL1\FOpt\UBB95\6-31+G(d)\C7H13O4(2)\HIROSHI\05-Sep-2003\1\#BB95/6-31+G* OPT=(Z-M
ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimet
hyl dimethylmalonate OH radical BB1K\0,2\C\1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,
2,d6,0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,
7,a12,5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,
4,a17,2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,10,r21,1,a21,2,d21,0\H,10,r22,1,
a22,2,d22,0\H,10,r23,1,a23,2,d23,0\H,6,r24,5,a24,1,d24,0\r2=1.51604951\r3=1.20110029\al3=124.91872676\r4=1.3
3156814\al4=123.00785367\d4=182.35380532\r5=1.50968875\al5=108.31132928\d5=-54.29668537\r6=1.37093033\
a6=117.09919632\d6=173.09503686\r7=1.34360445\al7=111.81893188\d7=-55.45985185\r8=1.41054459\al8=116.2
2877622\d8=176.70548987\r9=1.52824231\r10=1.52476009\al9=108.32777927\al10=109.26294356\d9=64.7653376
3\d10=185.04058055\r11=1.0845013\r12=1.08990943\r13=1.08689371\al11=106.1787535\al12=110.30928616\al13=
110.96086611\d11=185.75199119\d12=-55.30966045\d13=66.29327111\r14=1.41644685\al14=115.32811066\d14=-
179.52846548\r15=1.08685779\r16=1.08652981\r17=1.08369831\al15=110.54155385\al16=110.3675372\al17=105.8
0742128\d15=61.32807731\d16=-59.3208065\d17=-178.97218076\r18=1.08866503\r19=1.08852668\r20=1.090279
75\al8=110.4624924\al9=111.42264658\al20=110.01214557\d18=56.81225085\d19=-63.75359446\d20=174.74465
577\r21=1.08631161\r22=1.08796548\r23=1.08858881\al21=110.74889946\al22=110.46609472\al23=109.50861096\
d21=58.28070109\d22=-61.47248809\d23=178.36444383\r24=0.95920152\al24=109.0150832\d24=-68.46694801\\V
ersion=x86-Linux-G03RevB.05\HF=-575.1467683\S2=0.752862\S2-1=0.\S2A=0.750006\RMSD=5.651e-09\RMSF
=3.355e-05\Dipole=-1.1440099,0.2363499,-0.3139119\PG=C01 [X(C7H13O4)]\@

1-Hydroxy-1-methoxy-2-methoxycarbonyl-2-methylpropan-1-ide anion (s8, $R^1 = R^2 = \text{Me}$)

1\1\ GINC-DUAL1\FOpt\RBB95\6-31+G(d)\C7H13O4(1-)\HIROSHI\11-Nov-2008\1\#BB95/6-31+G* OPT=(Z-M
ATRIX,READFC,MAXCYCLE=100) NOSYMM IOP(3/76=0580004200) GEOM=CHECK GUESS=READ\dimet
hyl dimethylmalonate anion BB1K\1,1\C\1,r2\O,2,r3,1,a3\O,2,r4,3,a4,1,d4,0\C,1,r5,2,a5,4,d5,0\O,5,r6,1,a6,2,d6,
0\O,5,r7,1,a7,2,d7,0\C,7,r8,5,a8,1,d8,0\C,1,r9,2,a9,4,d9,0\C,1,r10,2,a10,4,d10,0\H,8,r11,7,a11,5,d11,0\H,8,r12,7,a12,
5,d12,0\H,8,r13,7,a13,5,d13,0\C,4,r14,2,a14,1,d14,0\H,14,r15,4,a15,2,d15,0\H,14,r16,4,a16,2,d16,0\H,14,r17,4,a17,
2,d17,0\H,9,r18,1,a18,2,d18,0\H,9,r19,1,a19,2,d19,0\H,9,r20,1,a20,2,d20,0\H,10,r21,1,a21,2,d21,0\H,10,r22,1,a22,2,
d22,0\H,10,r23,1,a23,2,d23,0\H,6,r24,5,a24,1,d24,0\r2=1.50204337\r3=1.2093697\al3=126.59883741\r4=1.3444149
1\al4=120.32500587\d4=181.59509952\r5=1.55760564\al5=107.9002179\d5=-64.73608548\r6=1.46340286\al6=103.8
2205168\d6=191.77583335\r7=1.44252625\al7=101.44858452\d7=-59.41909332\r8=1.37967961\al8=112.24032613\
d8=168.49547146\r9=1.52405923\r10=1.52538151\al9=109.56934962\al10=108.22572852\d9=52.55211582\d10=17
2.39135249\r11=1.0939365\r12=1.09727866\r13=1.0972685\al11=108.19451154\al12=110.90956876\al13=111.9025
3055\d11=187.03449997\d12=-52.47136202\d13=68.03897042\r14=1.40245633\al14=114.95919522\d14=-183.2554
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\d15=63.19722091\d16=-57.39992415\d17=-177.0008776\r18=1.09438379\r19=1.08778891\r20=1.08970726\al18=1
11.94071183\al19=110.30144653\al20=107.93605673\d18=60.85713412\d19=-61.36356936\d20=180.25644461\r21
=1.08701855\r22=1.0929328\r23=1.08859328\al21=110.21603188\al22=111.78245312\al23=108.42385849\d21=59.3
8728029\d22=-61.23272385\d23=178.13654626\r24=0.95204688\al24=103.38546157\d24=-132.98003525\\Version
=x86-Linux-G03RevB.05\HF=-575.1507011\RMSD=7.854e-09\RMSF=7.038e-05\Dipole=-0.5686817,0.6276096,1.
0522025\PG=C01 [X(C7H13O4)]\@