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Supplementary Material

General Experimental Conditions

All reactions were carried out in flame-dried glassware under an inert atmosphere (nitrogen or argon), unless stated otherwise. Temperatures indicated refer to an external bath. All reactions were magnetically stirred.

All organic solvents were distilled and dried following known procedures.¹ All aldehydes were either distilled or chromatographed on SiO₂ prior to use. Other commercial reagents were purchased from Aldrich Chemicals (Milwaukee) and used without further purification.

Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated glass plates (0.25 mm). Visualization was effected by short wave UV illumination, KMnO₄ dip or phosphomolybdic acid/ethanol solution followed by development on a hot plate. Flash chromatography was performed according to the procedure of Still² using Merck silica gel (230-400 mesh).

Melting points were measured on a Gallenkamp melting point apparatus and temperatures are reported in °C and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B Infrared Spectrometer and are reported in wavenumbers (cm⁻¹) and were run in CHCl₃ unless stated otherwise. All ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL200 (200 MHz) or Varian Unity-400 (400 MHz) spectrometer. Unless indicated otherwise, all spectra were obtained in CDCl₃ (Me₄Si internal standard) with chemical shifts reported in ppm and coupling constants in Hz. Low and high resolution mass spectra were measured on a Kratos MS50TC mass spectrometer.

¹ Perrin, D.D. and Armarego, W.L.F.; *Purification of Laboratory Chemicals*, 3rd. Ed.; Pergamon Press: Toronto, 1988.

² Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, 43, 2923.

General procedure for generating benzyltrimethylammonium 2-proposed.

Methoxide (35 wt. % solution in methanol, 2.33 g, 4.5 mmol) and 2-propanol (100 ml) were placed in a 250 ml three necked round bottom flask. The flask was then connected to an oil vacuum pump, the volatile solvents were removed to dryness, and the residue was then dissolved in 15 to 25 ml of the *tert*-butyl alcohol. An aliquot (1 ml) of the resultant solution was taken and benzoyl chloride (29 μ l, 0.25 mmol) was added and stirred for 15 minutes. This aliquot was then washed with water and dried over MgSO_4 . Removal of the solvent under vacuo afforded the crude 2-propyl benzoate. The ^1H NMR spectrum of the crude benzoate was taken using methanol as an internal standard, to determine the molarity of the solution.

General procedure for alkylations of various aldehydes bearing only one α -proton using benzyltrimethylammonium 2-propoxide.

Freshly prepared benzyltrimethylammonium 2-propoxide (1.2-1.4 mmol) in 10 ml of *tert*-butyl alcohol was put in a 25 ml round bottom flask. The appropriate aldehydes (1mmol) and alkyl halides (3 mmol) were dissolved in 2 ml of *tert*-butyl alcohol and added to the solution of 2-propoxide in one portion. The mixture was stirred for 30 minutes, unless indicated otherwise, at ambient temperature. Progress was monitored by TLC, and by ^1H NMR spectra of an aliquot to ensure the complete consumption of starting material. The precipitated salt was filtered, and the filtrate was added to a solution of 2,4-dinitrophenyl hydrazine in ethanol containing a catalytic amount of concentrated sulfuric acid. Following stirring for 30 minutes, the hydrazone was dissolved in methylene chloride and washed with water, dried over MgSO_4 , filtered and solvent evaporated in vacuo. The crude product was purified by SiO_2 chromatography using hexane:ethyl acetate (17:1) as eluent.

(1-benzyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 3:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and benzyl bromide in 100% yield.

¹H NMR : 1.41-1.68 (m, 8H), 1.91-1.97 (m, 2H), 2.8 (s, 2H), 7.04-7.09 (m, 2H), 7.2-7.28 (m, 3H), 7.29 (s, 1H), 7.78 (d, 1H, J=9.6), 8.27 (dd, 1H, J=9.5, 2.5), 9.12 (d, J=2.5), 10.99 (s, 1H).

¹³C NMR : 22.5 (2C), 25.9 (1C), 34.3 (2C), 42.9 (1C), 47.7 (1C), 116.6 (1C), 123.4 (1C), 126.4 (1C), 127.9 (2C), 128.7 (1C), 129.9 (1C), 130.5 (2C), 136.7 (1C), 137.7 (1C), 145.2 (1C), 158.4 (1C).

IR : 3300 (m), 2920 (m), 1620 (s), 1590 (s), 1330 (s).

HREIMS: m⁺/z: calc. : 382.1642, found: 382.1639

M.P.: 162.5° - 163.5°C

(1-Allyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 4:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and allyl bromide in 98% yield.

¹H NMR : 1.43-1.60 (m, 8H), 1.83-1.9 (m, 2H), 2.28 (d, 2H, J=7.3), 5.04 (d, 1H, J=4.7), 5.1 (s, 1H), 5.67-5.83 (m, 1H), 7.34 (s, 1H), 7.91 (d, 1H, J=9.6), 8.31 (dd, 1H, J=9.5, 2.5), 9.2 (d, 1H, J=2.5), 10.98 (s, 1H).

¹³C NMR : 22.2 (2C), 25.9 (1C), 33.9 (2C), 41.8 (1C), 44.2 (1C), 116.6 (1C), 118.2 (1C), 123.4 (1C), 128.7 (1C), 129.9 (1C), 133.3 (1C), 137.7 (1C), 145.2 (1C), 158.4 (1C).

IR: 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1330 (s).

HREIMS: m⁺/z: calc. : 332.1486, found: 332.1462

M.P.: 155.3° - 156.4°C

(1-Crotyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 5:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and crotyl bromide in 98% yield.

¹H NMR : 1.33-1.67 (m, 11H), 1.80-1.87 (m, 2H), 2.17-2.23 (m, 2H), 5.40-5.46 (m, 2H), 7.33 (s, 1H), 7.92 (d, 1H, J=9.7), 8.31 (dd, 1H, J=9.7, 2.6), 9.13 (d, 1H, J=2.6), 10.99 (s, 1H).

¹³C NMR : 18.0 (1C), 22.2 (2C), 25.9 (1C), 33.9 (2C), 42.0 (1C), 116.6 (2C), 123.5 (2C), 125.5 (1C), 128.7 (1C), 129.9 (2C), 145.3 (1C), 158.8 (1C).

IR: 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1330 (s).

HREIMS: m⁺/z: calc. : 346.1642, found: 346.1649.

M.P.: 139.5° - 141°C

(1-Methyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 6:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and methyl iodide in 92% yield.

¹H NMR: 1.16 (s, 3H), 1.37-1.56 (m, 8H), 1.76-1.85 (m, 2H), 7.4 (s, 1H), 7.92 (d, 1H, J=9.6), 8.31 (dd, 1H, J=9.7, 2.5), 9.13 (d, 1H, J=2.5), 10.97 (s, 1H).

¹³C NMR: 22.2 (2C), 25.8 (2C), 35.8 (2C), 38.7 (1C), 116.5 (1C), 123.5 (1C), 128.7 (1C), 129.9 (1C), 137.6 (1C), 145.3 (1C), 159.6 (1C).

IR : 3300 (m), 2920 (m), 1625 (s), 1590 (s), 1335 (s).

HREIMS: m⁺/z: calc. : 306.1329, found: 306.1318.

M.P.: 157.9° - 159.6°C

(1-Ethyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 7:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and ethyl iodide in 82% yield.

¹H NMR : 0.85 (t, 3H, J=7.4), 1.35-1.60 (m, 10H), 1.83-1.89 (m, 2H), 7.29 (s, 1H), 7.92 (d, 1H, J=9.5), 8.31 (dd, 1H, J=9.7, 2.5), 9.13 (d, 1H, J=2.5), 10.99 (s, 1H).

¹³C NMR : 14.0 (1C), 22.3 (2C), 23.3 (1C), 25.7 (1C), 34.1 (2C), 41.8 (1C), 116.6 (1C), 123.5 (1C), 128.7 (1C), 129.9 (1C), 137.6 (1C), 145.3 (1C), 159.0 (1C).

IR : 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1335 (s).

HREIMS: m⁺/z: calc. : 320.1486, found: 320.1458.

M.P.: 153.6° - 155°C

(1-Butyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 8:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and butyl iodide in 80% yield.

¹H NMR : 0.89 (t, 3H, J=7), 1.2-1.58 (m, 14H), 1.83-1.88 (m, 2H) 7.3 (s, 1H), 7.92 (d, 1H, J=9.6), 8.3 (dd, 1H, J=9.7, 2.5), 9.13 (d, 1H, J=2.5), 11.01 (s, 1H).

¹³C NMR : 13.9 (1C), 22.3 (2C), 23.4 (1C), 25.7 (1C), 26.1 (1C), 34.2 (2C), 39.8 (1C), 41.8 (1C), 116.6 (1C), 123.5 (1C), 128.7 (1C), 129.9 (1C), 137.6 (1C), 145.3 (1C), 159.0 (1C).

IR : 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1335 (s).

HREIMS: m⁺/z: calc. : 348.1799, found: 348.1795.

M.P.: 164.4° - 165.5°C.

(1-Isopropyl-1-cyclohexanecarboxaldehyde)-2,4-dinitrophenyl hydrazone 9:

Prepared following the above procedure from cyclohexanecarboxaldehyde **1** and isopropyl iodide in 72% yield.

¹H NMR : 0.92 (d, 6H, J=6.8), 1.37-1.42 (m, 4H), 1.62-1.70 (m, 5H), 1.97-2.0 (m, 2H), 7.29 (s, 1H), 7.93 (d, 1H, J=9.5), 8.29 (dd, 1H, J=9.5, 2.5), 9.14 (d, 1H, J=2.5), 11.04 (s, 1H).

¹³C NMR : 17.3 (2C), 22.6 (2C), 26.0 (1C), 31.9 (2C), 36.9 (1C), 44.5 (1C), 116.6 (1C), 123.5 (1C), 128.7 (1C), 130.0 (1C), 137.6 (1C), 145.3 (1C), 157.8 (1C).

IR : 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1335 (s).

HREIMS: m⁺/z: calc. : 334.1642, found: 334.1652.

M.P.: 154° - 156.2° C.

Trimethyl-acetaldehyde-2,4-dinitrophenyl hydrazone :

Prepared following the above procedure from isobutyraldehyde **10** and methyl iodide in 96% yield.

¹H NMR : 1.22 (s, 9H), 7.44 (s, 1H), 7.93 (d, 1H, J=9.6), 8.28 (dd, 1H, J=9.6, 2.6), 9.12 (d, 1H, J=2.6), 10.94 (s, 1H).

¹³C NMR : 27.3 (3C), 35.5 (1C), 116.5 (1C), 125.5 (1C), 128.5 (1C), 129.8 (1C), 137.6 (1C), 145.3 (1C), 159.7 (1C).

IR : 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1335 (s).

HREIMS: m⁺/z: calc. : 266.1016, found: 266.1014.

M.P.: 205.1° - 205.4°C

(1-Methyl-1-cyclopentanecarboxaldehyde)-2,4-dinitrophenyl hydrazone :

Prepared following the above procedure from cyclopentanecarboxaldehyde **11** and methyl iodide in 92% yield.

¹H NMR : 1.27 (s, 3H), 1.52-1.94 (m, 8H), 7.48 (s, 1H), 7.93 (d, 1H, J=9.6), 8.28 (dd, 1H, J=9.6, 2.5), 9.12 (d, 1H, J=2.5), 10.97 (s, 1H).

¹³C NMR : 24.1 (1C), 24.6 (2C), 37.8 (2C), 46.6 (1C), 116.5 (1C), 123.5 (1C), 128.7 (1C), 129.9 (1C), 137.6 (1C), 145.3 (1C), 159.3 (1C).

IR : 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1330 (s).

HREIMS: m⁺/z: calc. : 292.1172, found: 292.1124.

M.P.: 149.4° - 150.6°C

(1-Methyl-myrtanal)-2,4-dinitrophenyl hydrazone 13:

Prepared following the above procedure from myrtanal **12** and methyl iodide. The reaction was stirred for 12 hours to produce the corresponding hydrazone of C-methylated myrtanal in 60% yield.

¹H NMR : 0.86 (s, 3H), 1.25 (s, 3H), 1.37 (s, 3H), 1.52 (d, 1H, J=9), 2.2-2.51 (m, 3H), 5.75 (dd, 1H, J=9, 1.8), 6.3 (q, 1H, J=6.45), 7.53 (s, 1H), 7.93 (d, 1H, J=9.6), 8.31 (dd, 1H, J=9.6, 2.5), 9.12 (d, 1H, J=2.5), 11.04 (s, 1H).

¹³C NMR : 24.7 (1C), 25.9 (1C), 27.2 (1C), 31.2 (1C), 42.0 (1C), 42.4 (1C), 46.9 (1C), 50.8 (1C), 116.4 (1C), 123.5 (1C), 127.9 (1C), 128.8 (1C), 129.9 (1C), 136.8 (1C), 137.7 (1C), 145.2 (1C), 158.2 (1C).

IR : 3300 (m), 2920 (m), 1615 (s), 1590 (s), 1330 (s).

HREIMS: m⁺/z: calc. : 344.1486, found: 344.1478.

M.P.: 205.2° - 206.7°C.

8-Formyl-2,4,8-trimethylbicyclo[3.2.1]octan-3-one 16:

Prepared following the above procedure from aldehyde **15** and methyl iodide. The reaction was stirred for 2 hours to give the ketoaldehyde **16** in 71% yield.

¹H NMR : 1.05 (d, 6H, J=6.8), 1.21 (s, 3H), 2.62-2.75 (m, 4H), 6.13 (d, 2H, J=1.3), 9.95 (s, 1H).

¹³C NMR : 13.9 (2C), 23.6 (1C), 46.7 (2C), 52.4 (2C), 56.6 (1C), 134.4 (2C), 160.1 (1C), 181.9 (1C).

IR: 1700 (s)

HREIMS: m⁺/z : calc. (for C₁₁H₁₅O): 163.1123, found: 163.1057