Electronic Supplementary Information

Experimental Part

General Remarks

Starting materials were of the highest commercial quality and were employed as received. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in $CDCl_3$ with a Bruker Ascend 400 spectrometer in $CDCl_3$ solutions with $SiMe_4$ as internal standard.

The peroxide content of CPME was tested employing semi-quantitative test-strips Quantofix®, measuring range 0.5 – 25 mg/L H_2O_2, in agreement with the general indications furnished by the producer.

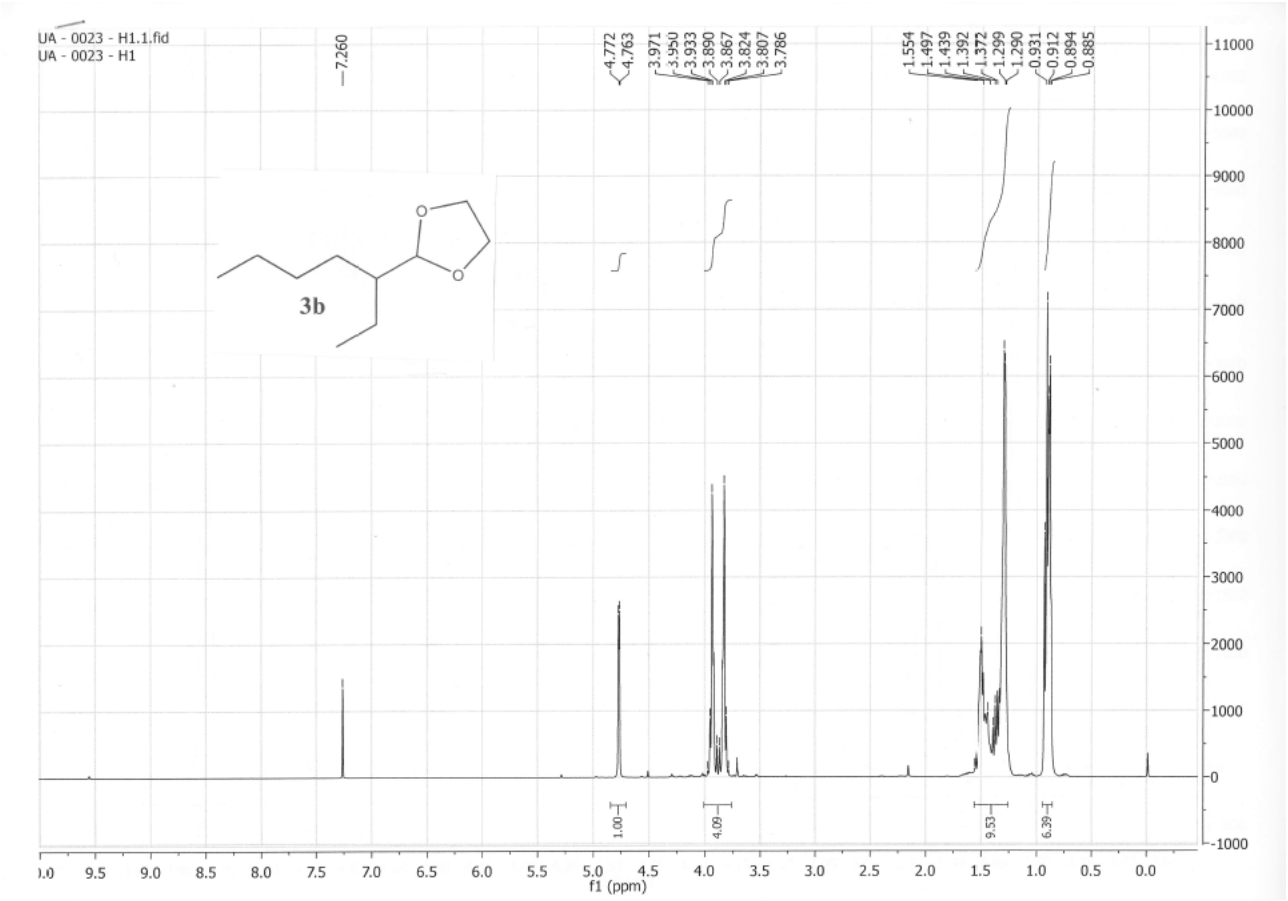
General procedure for the acetalization of carbonyl compounds

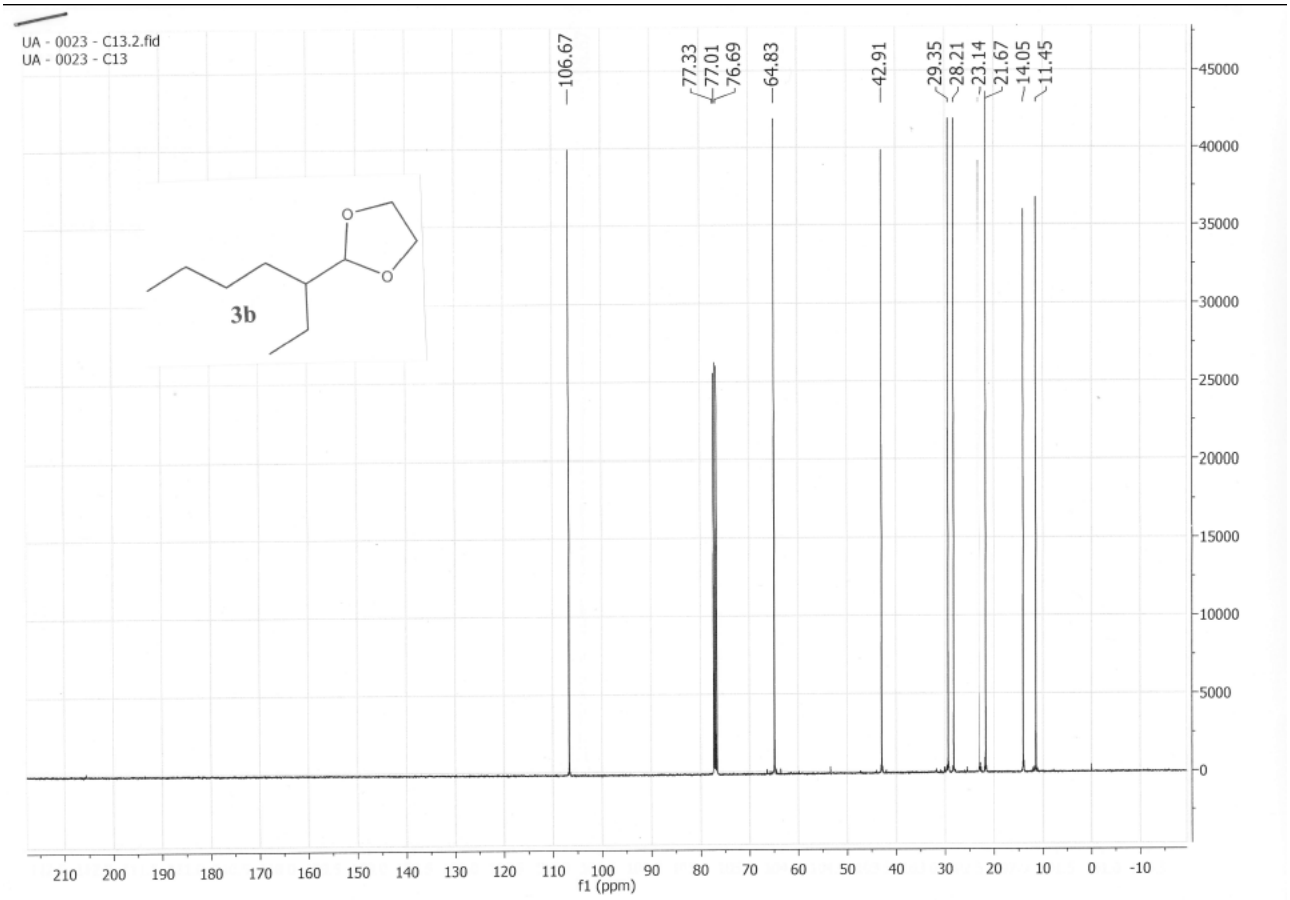
In a 50 mL flask fitted with a Dean-Stark distiller and bubble condenser provided with a calcium chloride valve, the starting material (**1**, 80 mmol) was dissolved in CPME (20 mL) together with the amount of the required diol (88 to 160 mmol, 1.1 to 2.0 equiv) and catalyst (2.4 mmol, 3 mol % of the starting material), as reported in Table 2. The reaction mixture was heated with an oil bath under vigorous stirring and allowed to reflux for the indicated time (Table 2), then cooled to room temperature, the catalyst was decanted and the resulting solution was successively neutralized (K_2CO_3, 1.0 g), stirred for 15 min and filtered. The solvent was evaporated at reduced pressure and the crude product analyzed by means of ^{1}H-NMR spectroscopy. No other product, besides starting material, was detected. Recovery of the catalyst (washed twice with 2 × 5 mL of CPME and dried in vacuo) usually exceeded 90%. Reaction products were identified by comparison with literature data and/or with authentic samples synthesized according to literature procedures, and characterized as follows:

2-Methyl-2-phenyl-1,3-dioxolane (3a):[1,2] white crystals, mp 61-62 °C (CPME); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.66 (3 H, s, CH_3), 3.73-3.83 (2 H, m, CH_2-O), 3.99-4.09 (2 H, m, CH_2-O), 7.29 (1 H, t, J = 7.6 Hz, ArH), 7.35 (2 H, t, J = 7.6 Hz, 2 × ArH), 7.48 (2 H, d, J = 7.6 Hz, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.6, 64.4, 108.8, 125.2, 127.8, 128.1, 143.2.

2-(Heptan-3-yl)-1,3-dioxolane (3b):[3] Purified by fractional distillation, bp 105 °C/30 mmHg, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.85-0.95 (6 H, m, CH_3),

1.25-1.52 (7 H, m, 3 × CH_2, CH), 3.78-3.97 (4 H, m, OCH_2CH_2O), 4.77 (1 H, d, J = 4.0 Hz, O-CH-O); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11. 5, 14.1, 21.7, 23.1, 28.2, 29.4, 42.9, 64.8, 106.7.





(*S*)-7-[1,3]dioxolan-2-yl-2,6-dimethylhept-2-ene, 3c:[5] purified by fractional distillation, bp 152-154 °C/30 mmHg; $[\alpha]_D^{24}$ = - 4.8 (c = 2.07, $CHCl_3$) {lit.[5a] (*R*)-isomer: $[\alpha]_D^{24}$ = + 4.6 (c = 1.96, $CHCl_3$)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.96 (3 H, d, *J* = 6.0 Hz, CH_3), 1.15-1.25 (1 H, m, CH), 1.34-1.55 (2 H, m, CH_2), 1.60 (3 H, s, CH_3), 1.65-1.73 (5 H, m), 1.90-2.07 (2 H, m, CH_2), 3.79-3.88 (2 H, m, 2 × CHO), 3.92-4.01 (2 H, m, 2 × CHO), 4.90 (1 H, t, *J* = 4.8 Hz, CH), 5.10 (1 H, t, *J* = 6.8 Hz, CHO_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 17.6, 19.7, 25.3, 25.7, 29.1, 37.4, 40.9, 64.6, 64.7, 103.8, 124.6, 131.1.

2-Phenyl-1,3-dioxane (3d):[1] purified by fractional distillation, bp 136-138 °C/30 mmHg, light yellow oil which solidifies upon standing; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.44 (1 H, d, *J* = 16.0 Hz, CH*H*), 2.15-2.30 (1 H, m, CH*H*), 3.99 (2 H, td, *J* =12.0, 4 Hz, CH_2-O), 4.27 (2 H, dd, *J* =12.0, 8.0 Hz, CH_2-O), 5.50 (1 H, s, O-CH-O), 7.29-7.39 (3 H, m, 3 × ArH) 7.48 (2 H, d, *J* = 8.0 Hz, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.0, 67.6, 101.9, 126.2, 128.6, 129.1, 139.0.

2-(4-Methoxyphenyl)-1,3-dioxane (3e):[4,6] Can be purified from residual amounts of **1d** by recrystallization from CPME/heptane (for difficulties encountered in this purification by column chromatography, see ref. 7); white powder, mp 46-47 °C (CPME-heptane); ^{1}H

NMR (400 MHz, $CDCl_3$) δ (ppm) 1.43 (1 H, d, J = 16.0 Hz, CH*H*), 2.15-2.28 (1 H, m, CH*H*), 3.80 (3 H, s, CH_3O), 3.97 (2 H, td, J = 12.0, 1.6 Hz, CH_2-O), 4.25 (2 H, dd, J = 12.0, 4.0 Hz, CH_2-O), 5.46 (1 H, s, O-CH-O) 6.86-6.91 (2 H, m, 2 × ArH), 7.38-7.42 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.6, 55.1, 67.2, 101.4, 113.5, 127.2, 131.2, 159.8.

Methyl 4-(1,3-dioxolan-2-yl)benzoate (3f):[8] white powder, mp 31-33 °C (heptane); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.92 (3 H, s, CH_3O), 4.00-4.18 (4 H, m, OCH_2CH_2O), 5.86 (1 H, s, O-CH-O) 7.53-7.57 (2 H, m, 2 × ArH), 8.04-8.07 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 52.1, 65.4, 103.0,126.4, 129.7, 130.8, 142.7, 166.8.

2-(4-Chlorophenyl)-1,3-dioxolane (3g):[9] purified by fractional distillation, bp 145-148 °C/30 mmHg, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.98-4.15 (4 H, m, OCH_2CH_2O), 5.78 (1 H, s, O-CH-O) 7.32-7.38 (2 H, m, 2 × ArH), 7.39-7.44 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz) δ 65.3, 103.1, 127.9, 128.5, 134.9, 136.5.

2-(4-Bromophenyl)-1,3-dioxolane (3h):[6,10] white powder, mp 36-38 °C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.98-4.15 (4 H, m, OCH_2CH_2O), 5.77 (1 H, s, O-CH-O) 7.32-7.38 (2 H, m, 2 × ArH), 7.49-7.54 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz) δ 65.3, 103.0, 123.2, 128.1, 131.5, 137.0.

2-(Nonan-2-yl)-1,3-dioxolane (3i):[11] purified by fractional distillation, bp 116-118 °C/30 mmHg; light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.85-0.90 (3 H, m, CH_3), 1.22-1.44 (13 H, m, 5 × CH_2, CH_3), 3.88-3.98 (4 H, m, OCH_2CH_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 22.6, 23.7, 24.1, 29.3, 29.8, 31.8, 39.2, 64.6, 110.2.

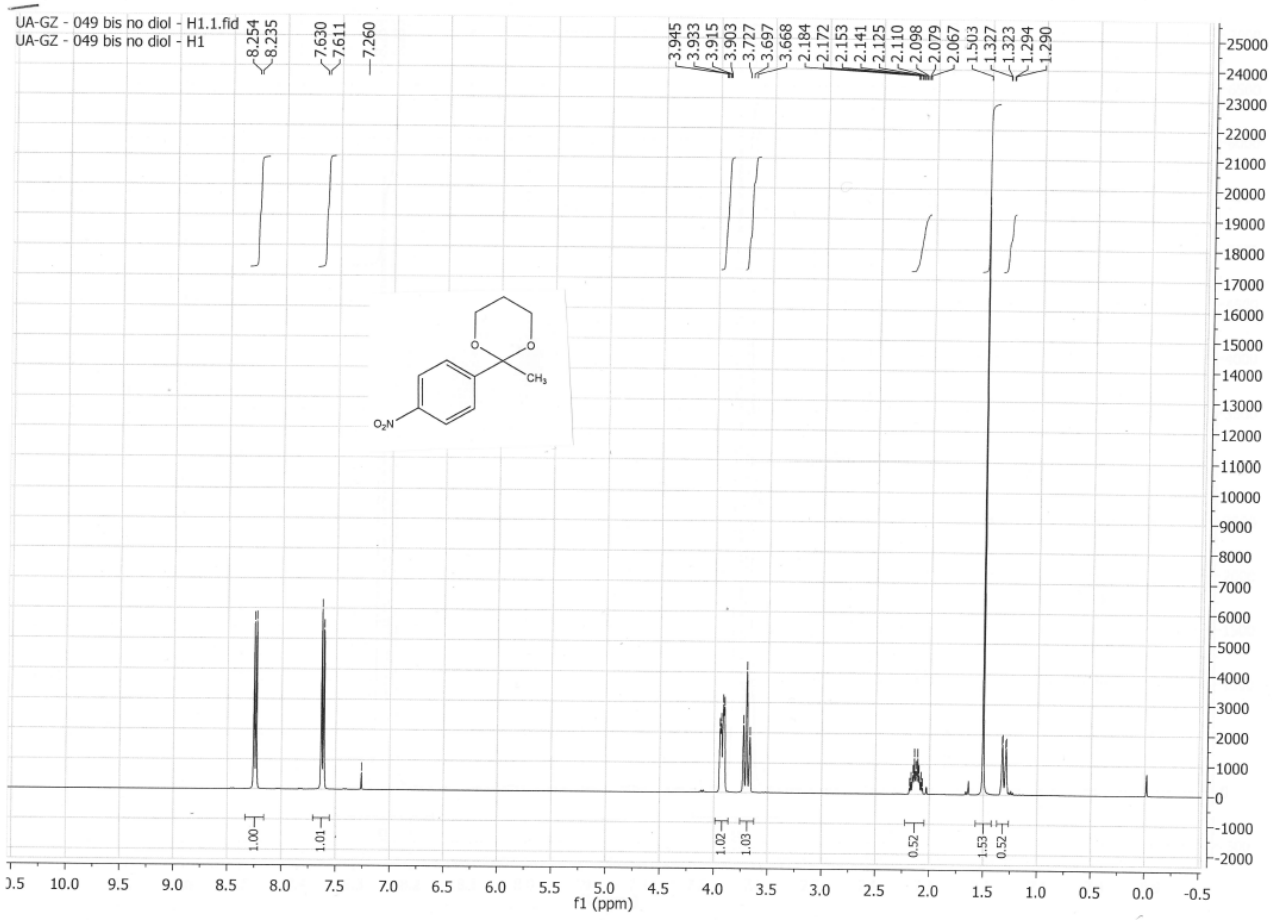
1,4-Dioxaspiro[4.5]decane (3j):[1] purified by fractional distillation, bp 87-89 °C/30 mmHg; ^{1}H NMR ($CDCl_3$; 400 MHz) δ = 1.41 (2 H, br s, CH_2), 1.60 (8 H, s, 4 × CH_2), 3.85 (4 H, s, OCH_2CH_2O); ^{13}C NMR ($CDCl_3$; 100 MHz) δ = 108.9, 64.1, 35.1, 25.1, 23.9.

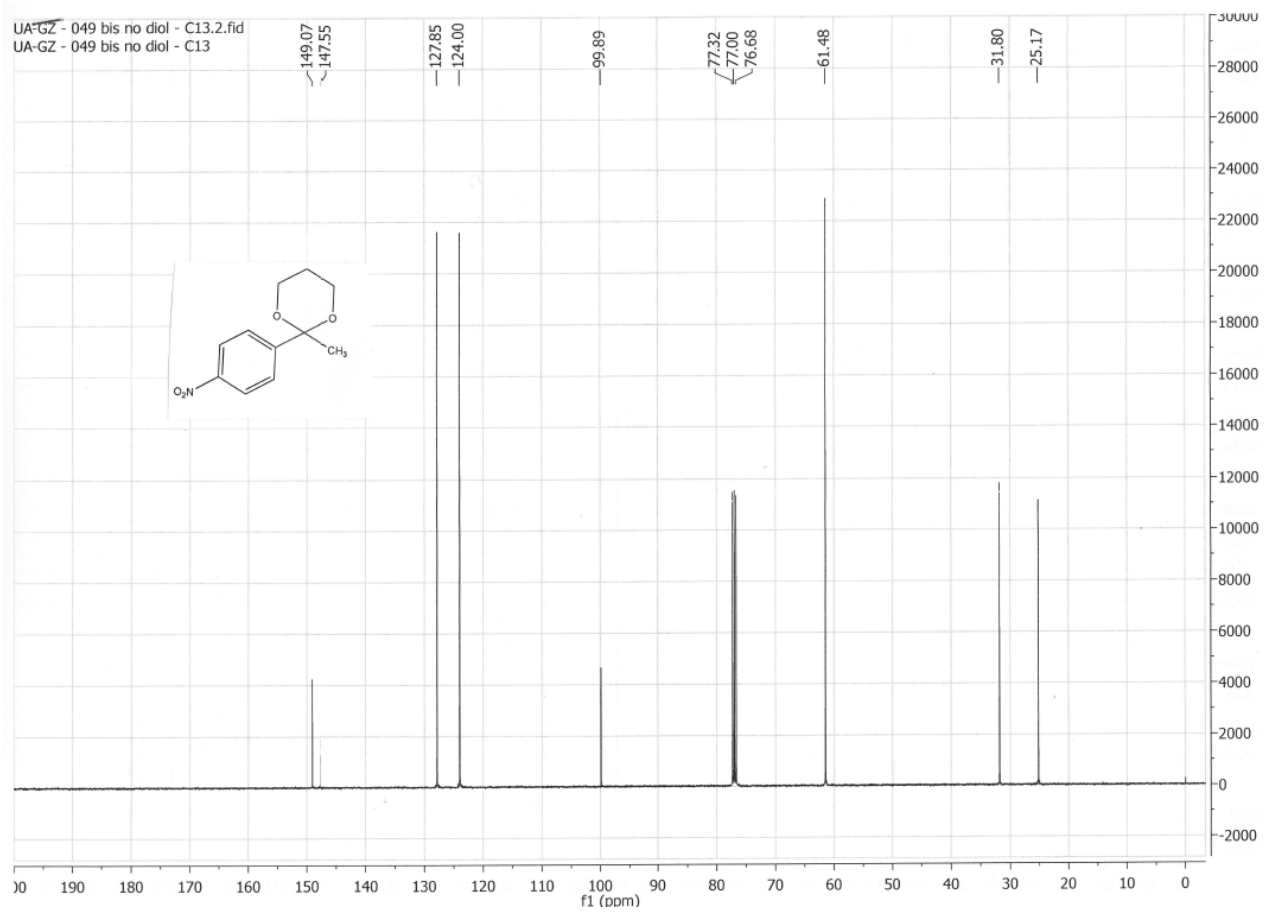
2-Methyl-2-(4-chlorophenyl)-1,3-dioxolane (3k):[12] purified by fractional distillation, bp 151-153 °C/mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.98-4.15 (4 H, m, OCH_2CH_2O), 5.78 (s1 H,, O-CH-O) 7.32-7.38 (2 H, m, 2 × ArH), 7.39-7.44 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz) δ 65.3, 103.1, 127.9, 128.5, 134.9, 136.5.

2-Methyl-2-(4-nitrophenyl)-1,3-dioxolane (3la):[13] white crystals, mp 74-76 °C (CPME); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.66 (3 H, s, CH_3), 3.71-3.82 (2 H, m, OCH_2), 4.02-

4.14 (2 H, m, OCH_2), 7.64-7.68 (2 H, m, 2 × ArH), 8.18-8.22 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.4, 64.7, 108.2, 123.6, 126.4, 147.7, 150.62.

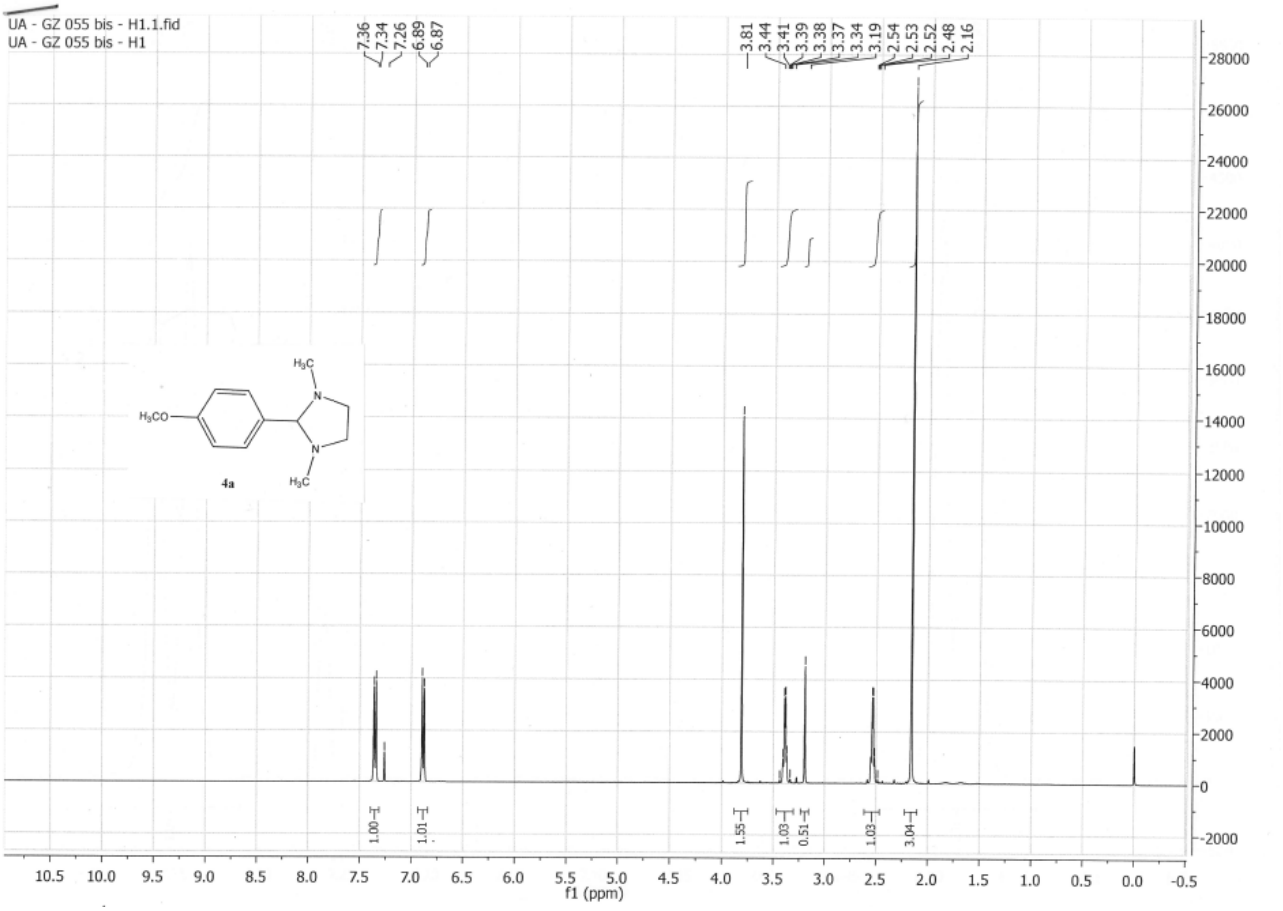
2-Methyl-2-(4-nitrophenyl)-1,3-dioxane (3lb):[14] white crystals, mp 97-99 °C (CPME); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.28-1.34 (1 H, m, CH), 1.50 (3 H, s, CH_3), 2.06-2.19 (1 H, m, CH), 3.70 (t, J = 12.0 Hz, CHO), 3.89-3.95 (1 H, m, CHO), 7.60-7.63 (2 H, m, 2 × ArH), 8.23-8.26 (2H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.1, 31.8, 61.5, 99.9, 124.0, 127.9, 147.6, 149.1.





2-(2-Bromo-1-phenylethyl)-1,3-dioxolane (3m):[15] white powder, mp 57-58 °C (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.66 (2 H, s, CH_2Br), 3.85-3.95 (2 H, m, OCH_2), 4.12-4.24 (2 H, m, OCH_2), 7.31-7.40 (3 H, m, 3 × ArH) 7.51 (2 H, d, J = 7.6 Hz, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 38.2, 65.8, 107.2, 125.9, 128.3, 128.8, 139.6.

2-(4-Methoxyphenyl)-1,3-dimethylimidazolidine, 4a:[16] purified by fractional distillation, bp 92-93 °C/1mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.16 (6 H, s, 2 × CH_3N), 2.48-2.60 (2 H, m, CH_2), 3.19 (1 H, s, CH), 3.34-3.44 (2 H, m, CH_2), 3.81 (3 H, s, CH_3O), 6.86-6.91 (2 H, m, 2 × ArH), 7.33-7.38 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 39.5, 53.2, 55.2, 92.0, 133.6, 129.9, 131.7, 159.8.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3.37
3.34
3.19
2.54
2.53
2.52
2.48
2.16
4a
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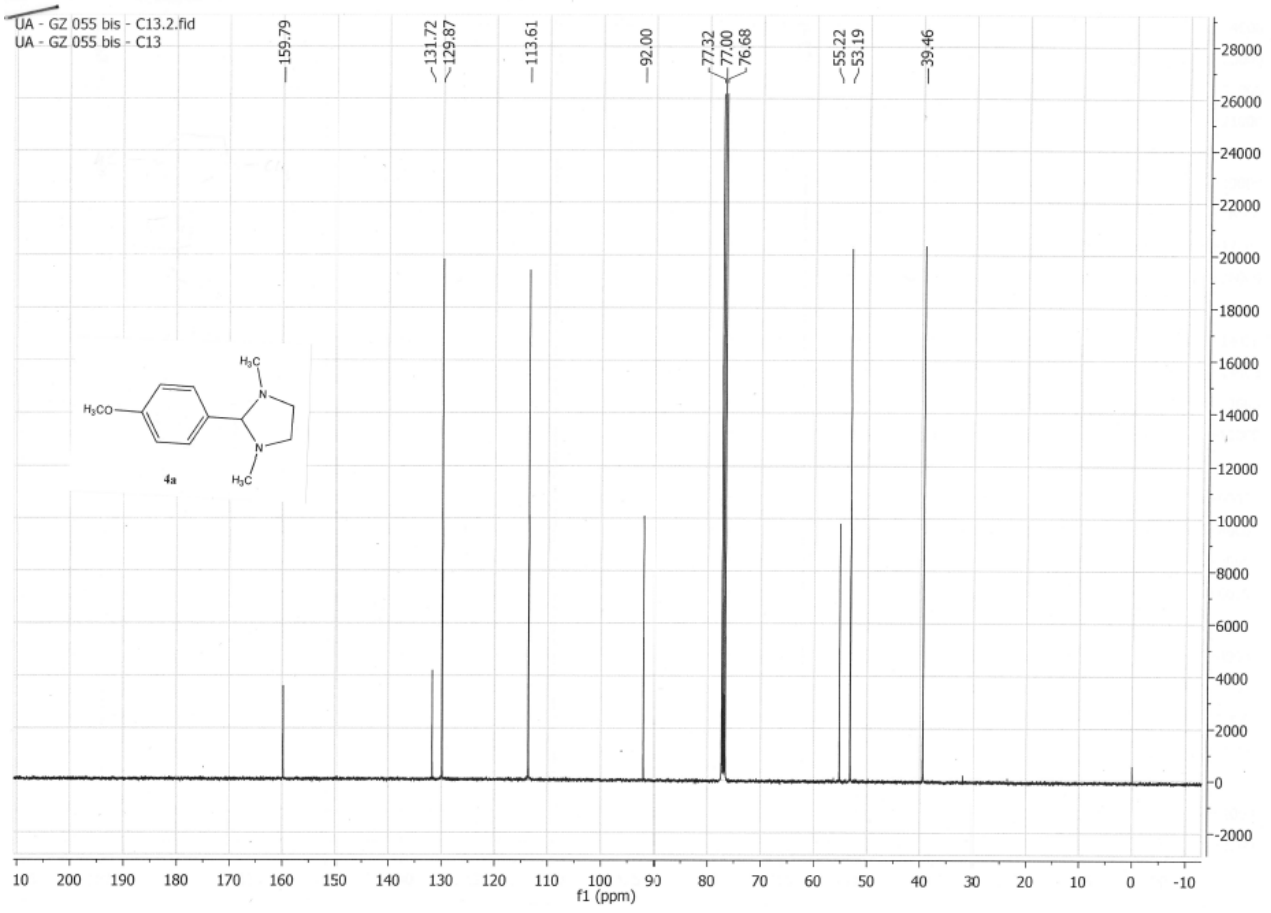
1.01
1.55
1.03
0.51
1.03
3.04
f1 (ppm)


UA - GZ 055 bis - C13.2.fid
UA - GZ 055 bis - C13
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131.72
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113.61
92.00
77.32
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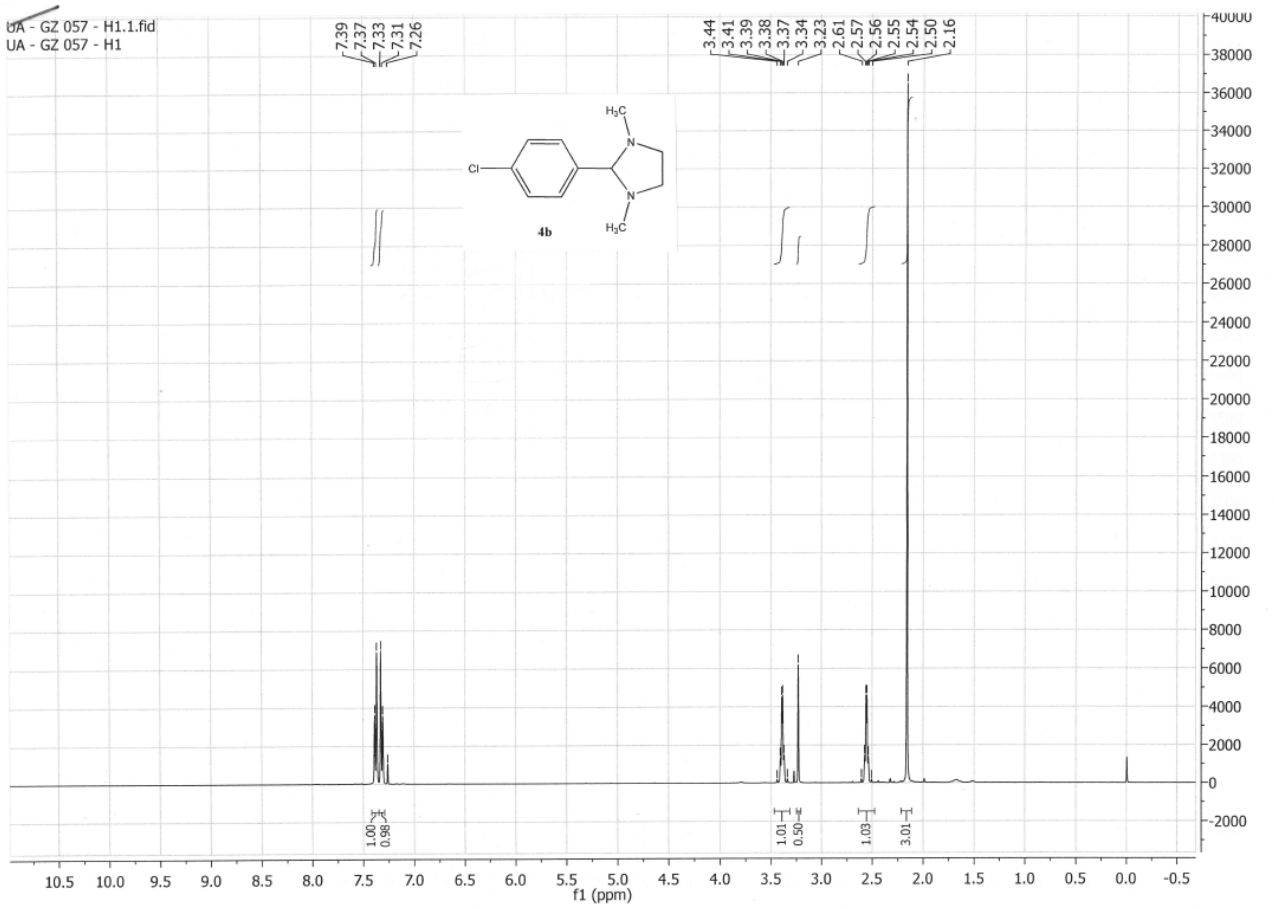
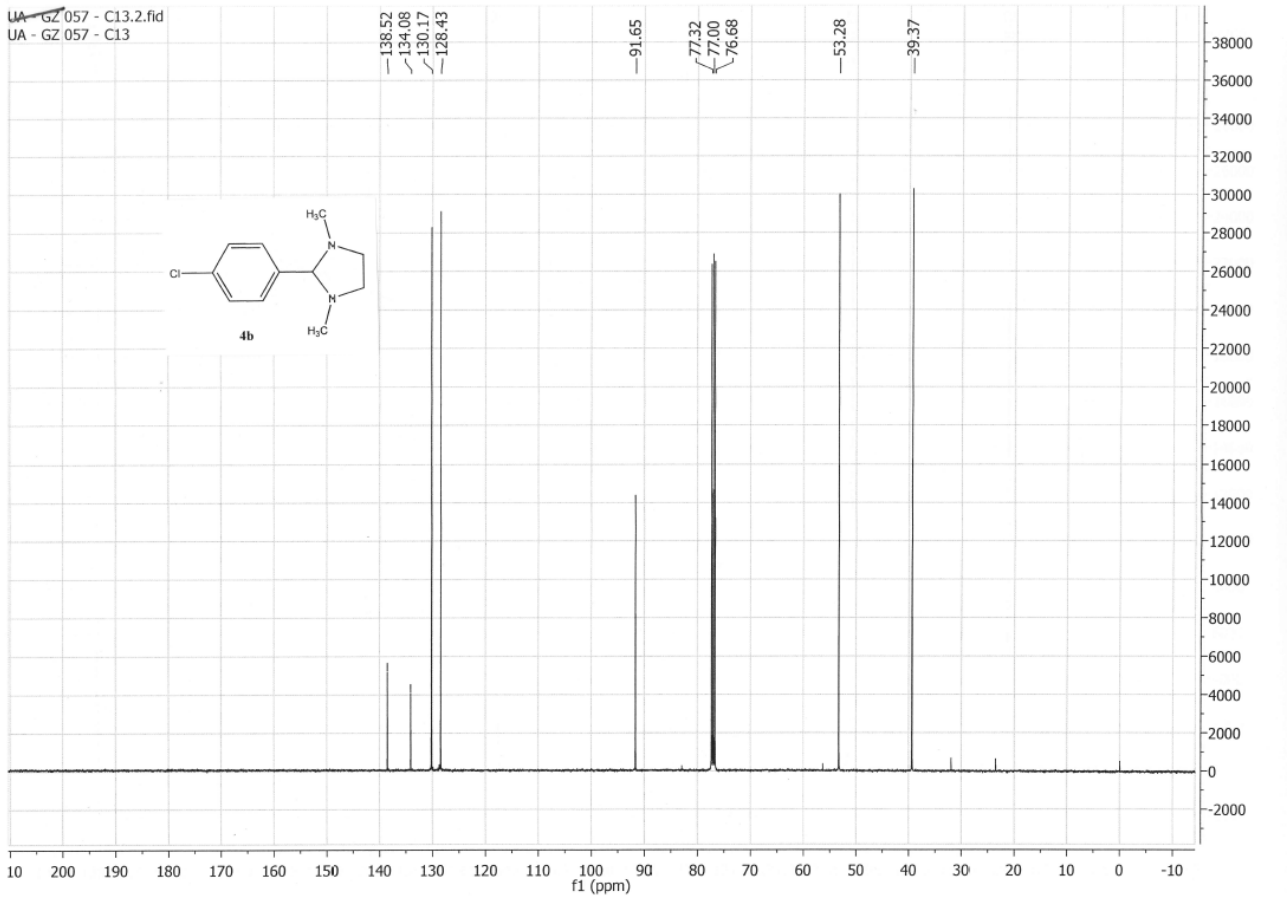
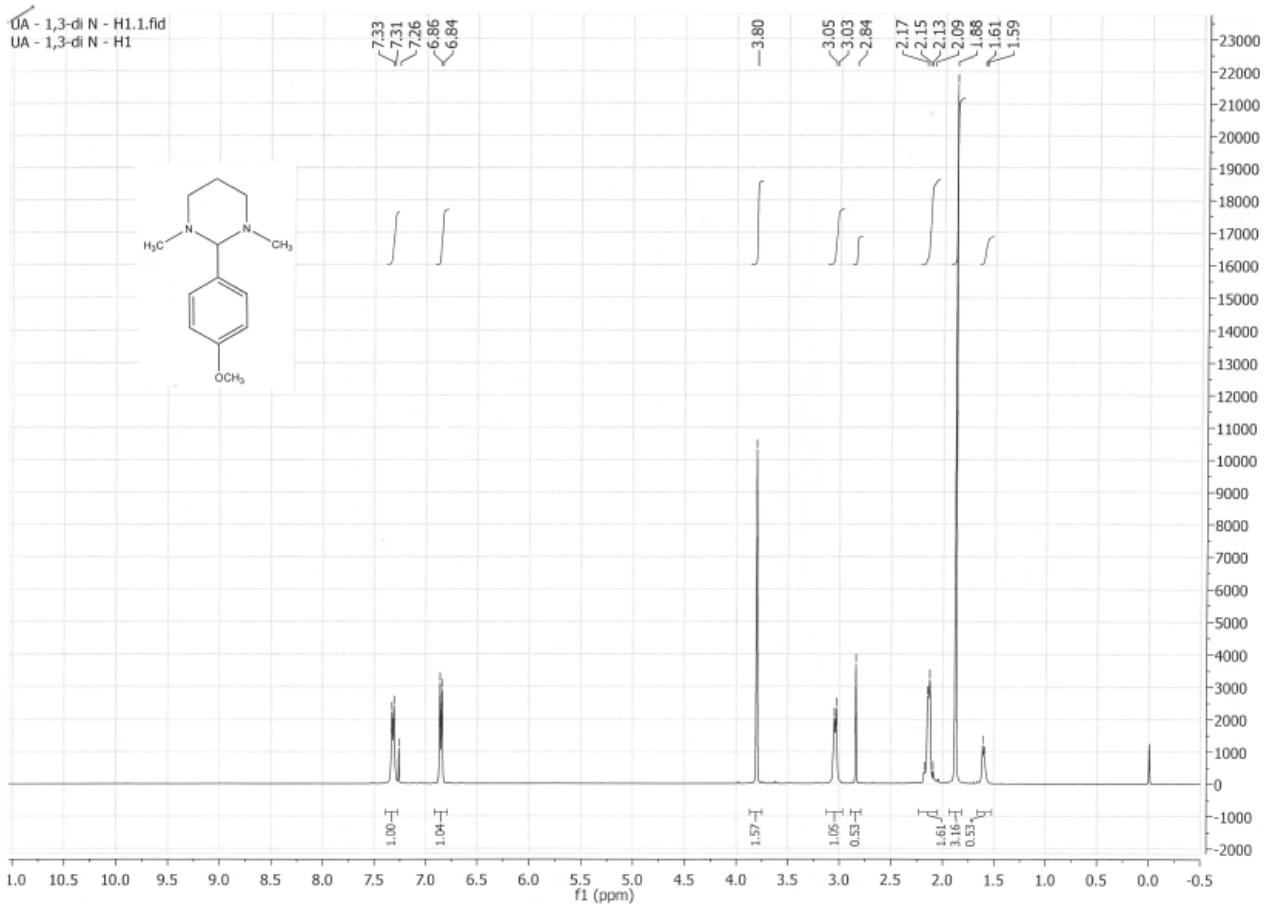
76.68
55.22
53.19
39.46
4a
f1 (ppm)

2-(4-Chlorophenyl)-1,3-dimethylimidazolidine, 4b:[17] purified by fractional distillation, bp 105-107 °C/1mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.16 (6 H, s, 2 × CH_3N), 2.50-2.61 (2 H, m, CH_2), 3.23 (1 H, s, CH), 3.34-3.44 (2 H, m, CH_2), 7.30-7.35 (2 H, m, 2 × ArH), 7.36-7.41 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 39.3, 53.2, 91.6, 128.4, 130.1, 134.0, 138.4.





2-(4-Methoxyphenyl)-1,3-dimethylhexahydropyrimidine, 4c:[18] purified by fractional distillation, bp 148-150 °C/2mmHg (lit.[18] bp 112 °C/0.4 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.55-1.72 (1 H, m, CH), 1.88 (6 H, s, 2 × CH_3N), 2.09-2.18 (3 H, m, 3 × CH), 2.84 (1 H, s, CH), 3.01-3.07 (2 H, m, 2 × CH), 3.80 (3 H, s, CH_3O), 6.83-6.88 (2 H, m, 2 × ArH), 7.28-7.36 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.2, 43.1, 55.2, 55.9, 91.8, 113.5, 129.8, 133.4, 159.4.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3.03
2.84
2.17
2.15
2.13
2.09
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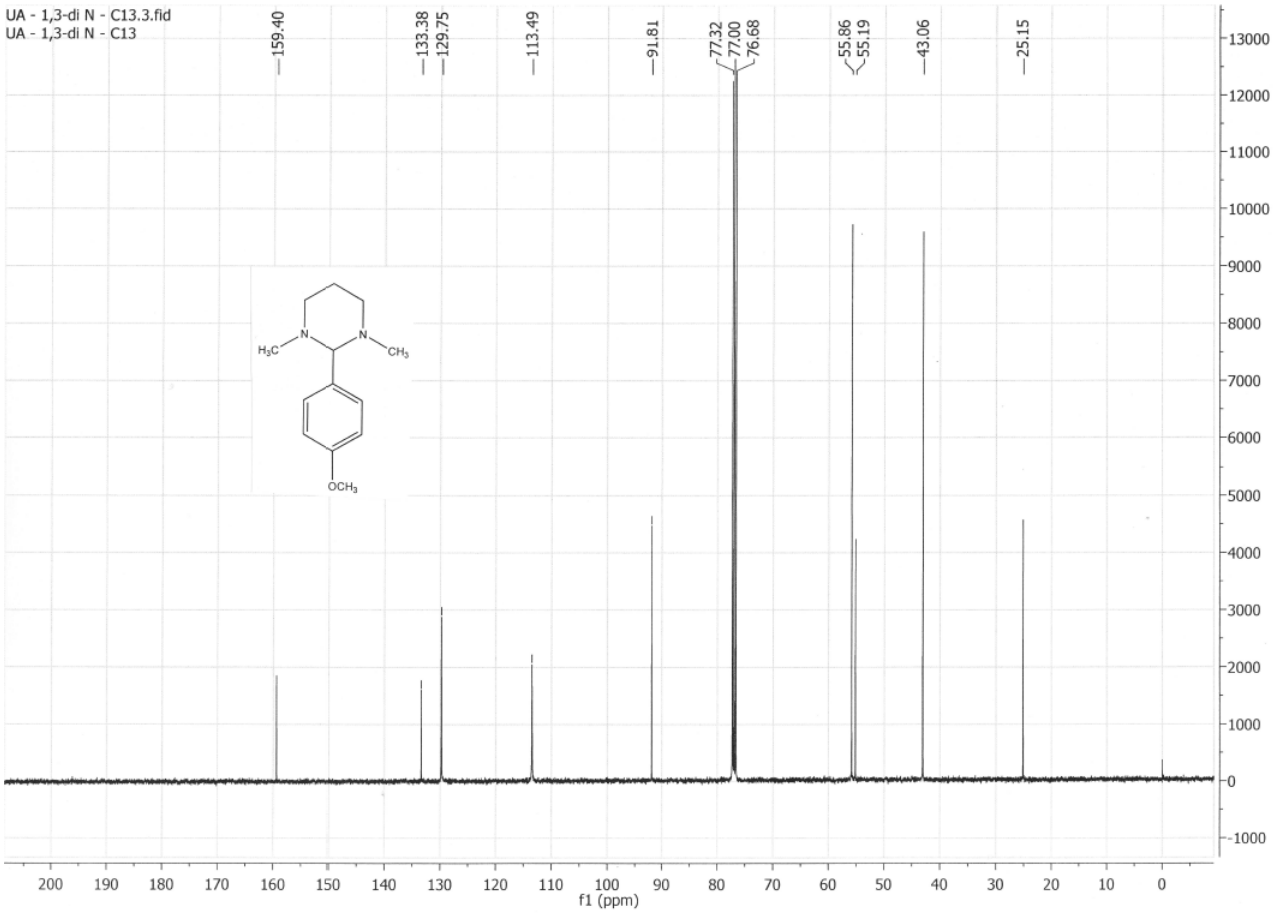
f1 (ppm)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113.49
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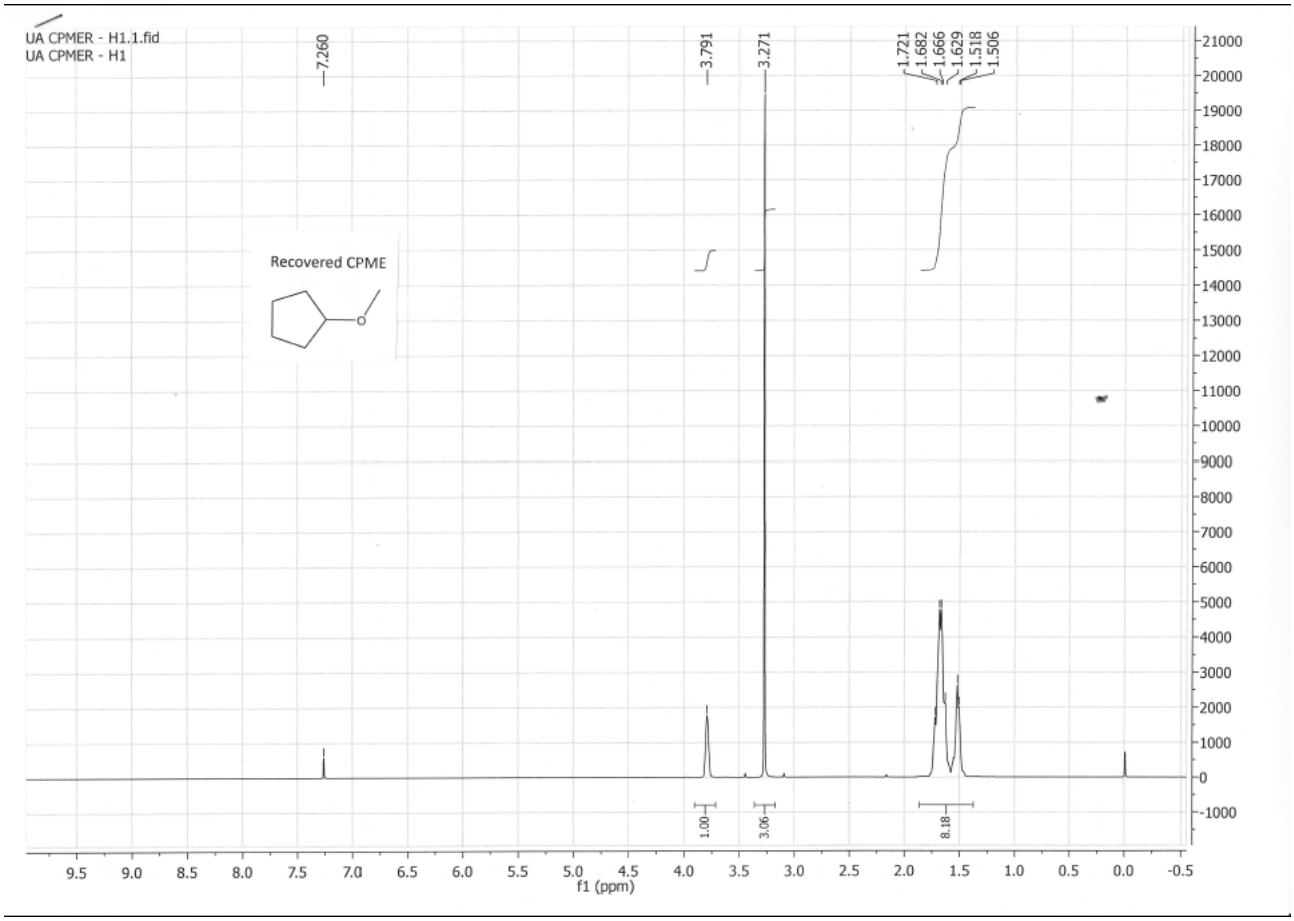
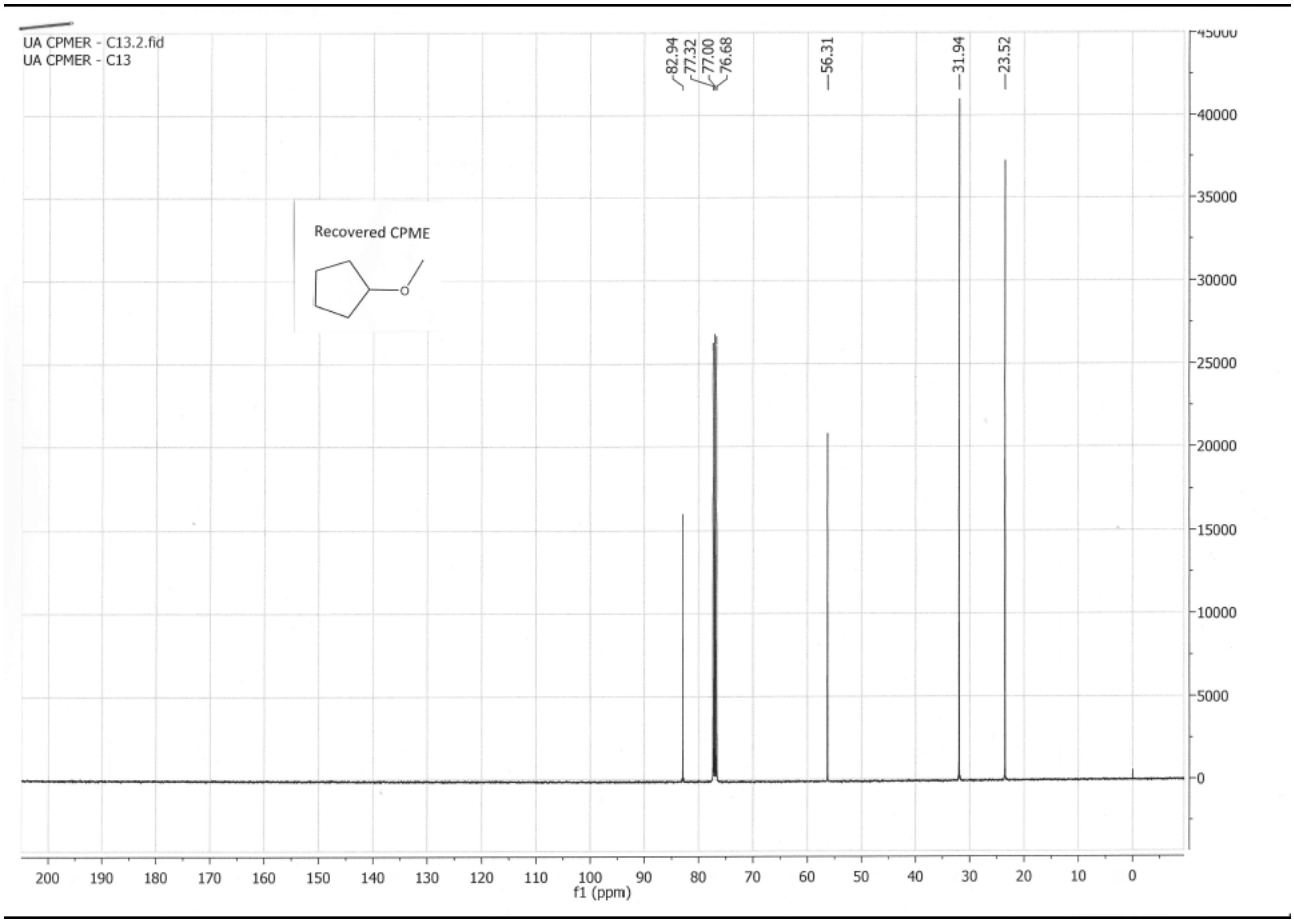
77.00
76.68
55.86
55.19
43.06
25.15
f1 (ppm)

Recovery of CPME

CPME was recovered *via* evaporation of the reaction mixtures obtained as described above. Evaporations were realized employing a rotatory evaporator operating *in vacuo* (*ca.* 50 mmHg), by gently warming (40 – 45 °C) the boiling flask with a water bath, condensing the vapour phase with efficient cooling (-10 °C) and chilling the condensate-collecting flask with an ice-salt bath. The organic solvent recovered from several runs (at least 100 ml) was washed with H_2O, filtered under N_2 pressure (as for flash chromatography) over a small pad of acidic alumina, dried (KOH), distilled at atmospheric pressure ($CaCl_2$ tube), and finally stabilized by addition of 50 ppm of BHT. The recovered solvent (usually 85% mass recovery of the starting material) was analytically pure (^1H and ^{13}C NMR) and identical to a commercial sample.





3-(4-Methoxybenziloxy)-propan-1-ol (5a):[19] In a 10 mL flask fitted with a Dean-Stark distiller and bubble condenser provided with a calcium chloride valve, 4-methoxybenzaldehyde (1.43 g, 10.8 mmol) was dissolved in CPME (3 mL) together with 1,3-propanediol (0.9 g, 11.9 mmol, 1.1 equiv) and NH_4Cl (17 mg, 0.3 mmol, 3% mol). The reaction mixture was heated with an oil bath under vigorous stirring and allowed to reflux during 6 h. The resulting mixture was filtered, dried and neutralized with K_2CO_3 (100 mg), then filtered again. The resulting solution was diluted with CPME (47 mL), transferred under dry Ar into a 100 ml two-necked flask equipped with reflux condenser, dropping funnel and magnetic stirrer, then chilled to 0 °C before adding dropwise, under vigorous stirring, a 1 M solution of DIBAL-H in heptane (22.7 mL, 22.7 mmol). The reaction mixture was additionally stirred during 3 h while allowed to warm to r.t., chilled again to 0 °C and quenched by successive slow dropwise addition of methanol (2.4 mL), and water (2.4 mL). After stirring at r.t. for 1 h, the resulting white precipitate was filtered through a short pad of Celite, washed with CPME (3 × 10 mL) and concentrated to give the monoprotected propanol **3a** (1.53 g, 7.8 mmol, 71%) as a light yellow oil, which was purified by flash chromatography (Et. Pet./AcOEt = 6:4) and characterized as follows: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.85 (2 H, quint, J = 5.6 Hz), 2.61 (1 H, br s), 3.63 (2

H,t, *J* = 5.6 Hz,), 3.77 (2 H, q, *J* = 5.6 Hz), 3.80 (3 H, s, CH_3O), 4.45 (2H, s), 6.86 -6.90 (2 H, m, 2 × ArH), 7.23-7.27 (2 H, m, 2 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 32.0, 55.2, 61.5, 68.8, 72.8, 113.8, 129.2, 130.1, 159.1.

4-(1,3-Dioxolan-2-yl)phenylmethanol (5b):[20]

In a 50 mL flask fitted with a Dean-Stark distiller and bubble condenser provided with a calcium chloride valve, methyl 4-formylbenzoate (7.40 g, 45.1 mmol) was dissolved in CPME (10 mL) together with 1,2-ethanediol (3.92 g, 63.1 mmol, 1.4 equiv) and NH_4HSO_4 (155 mg, 1.35 mmol, 3% mol). The reaction mixture was heated to reflux with an oil bath under vigorous stirring; after 3 h GC analysis showed a conversion of the aldehyde > 99%, the mixture was cooled, filtered, dried and neutralized with K_2CO_3 (0.5 g), then filtered again. The resulting solution was added under vigorous stirring with a dropping funnel to a 100 mL flask at 0°C containing a dispersion of lithium aluminum hydride (3.42 g, 90 mmol) in CPME (20 mL) under dry Ar. The mixture was allowed to reach room temperature and kept under stirring overnight. The mixture was chilled to 0 °C and quenched by very slow addition of water (50 mL, *caution!*). After ceasing of gas evolution the organic phase was separated and collected. The remaining mixture was diluted with a $NaHCO_3$ saturated solution and extracted with dichloromethane (3 × 10 mL). The organic phases were collected, dried (K_2CO_3) and evaporated to give **5b** (5.3 g, 29.4 mmol, 65%) as an oil which was purified by flash chromatography (Et. Pet./AcOEt = 7:3) and solidified on standing at -18°C. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 2.25 (br s, 1H), 3,9. – 4.14 (m, 4H), 4.63 (d, *J* = 8 Hz, 2H), 5.78 (s, 1H), 7.33 (d, *J* = 8 Hz, 2H), 7.44 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 64.8, 65.3, 103.6, 126.7, 126.8, 137.1, 142.1.

[1-(2-Hydroxyethoxy)ethenyl]benzene (5c):[21]

3j (500 mg, 2.1 mmol) was placed under Ar in two-necked flask equipped with a reflux condenser, dropping funnel and magnetic stirrer, dissolved in CPME (10 mL) and chilled to 0 °C. To this mixture, 25 mL of a 0.13 M solution of 1,2-disodiotetraphenylethane (prepared from tetraphenylethane, 1.05 g, 3.2 mmol and Na metal, 0.45 g, 19.2 mmol and filtered from any excess of the metal as described in ref. 22), were added dropwise during 1 h. The resulting deep red mixture was quenched by slow dropwise addition of H_2O (10 mL, *caution!*). After separation of the organic phase, the aqueous phase was extracted with CPME (3 × 10 mL), the roagnic phases were collected, dried (K_2CO_3) and evaporated to

give a crude product which was purified by flash chromatography (AcOEt/Heptane/Et_3N = 5:5:0.5), to afford **5c** (290 mg, 1.8 mmol, 85%) as a light yellow oil; ^{1}H NMR δ (ppm): 1.87 (1 H, br s, OH), 3.90 (br s, 4 H, OCH_2CH_2O), 4.16 (1H, d, *J* = 2.4 Hz), 4.60 (1H, d, *J* = 2.4 Hz), 7.22-7.30 (3 H, m, 3 × ArH), 7.51-7.56 (2 H, m, 2 ×ArH); ^{13}C NMR δ (ppm) 61.2, 69.1, 83.0, 125.4, 128.1, 128.5, 136.3, 159.8.

References to Supplementary Information

1. **3a, 3d, 3j** B. M. Smith, T. M. Kubczyk, A. E. Graham, *Tetrahedron*, 2012, **68**, 7775.
2. **3a** S. Torii, T. Inokuchi, *Chem. Lett.*, 1983, **12**, 1349.
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