Supporting Information

A Mild Lewis Acid Mediated Epoxy-Ester to Bicyclic Ortho Ester Rearrangement

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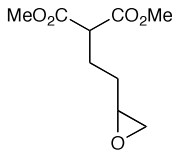
Experimental section

General Information. High resolution mass spectroscopy was carried out on a Jeol SX 102 machine, using fast atom bombardment (FAB^+) ionisation technique. Nuclear magnetic resonance spectroscopy was carried out using a Brucker DPX 400 instrument. The spectra were calibrated where possible to the signals of tetramethylsilane or the small quantity of $CHCl_3$ present in $CDCl_3$. Where possible, coupling constants (*J*) are shown denoting the multiplicity as a singlet (s), doublet (d), triplet (t), quarter (q), multiplet (m). The size of the coupling constant is given in Hertz (Hz). Fourrier transformation Infra Red spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrophotometer in the range of 3500-600 cm^{-1} following a standard background correction. Flash silica column chromatography was used as a standard purification procedure using Fluka Kiesel gel 60, 0.04-0.063 mm particle size. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given reaction. TLC plates used were Merck aluminium backed sheets with Kiesel gel 60 F_{254} silica coating. DCM was distilled over CaH_2 for anhydrous reactions. Petrol was distilled collecting the fraction distilling below 60 °C. THF was dried over sodium/benzophenone and freshly distilled before use. Diethyl ether was purchased from Fischer Scientific (99+ %) and used without purification. Ethyl acetate was distilled over $CaCl_2$ for general use.

General procedure for the epoxidation of malonic olefins.

To a solution of malonic olefins in DCM, at 0 °C, *m*-CPBA was added. The reaction mixture was allowed to stir for eight hours at 0 °C and then quenched with 0.1M NaOH solution (80 mL). The organic layer was separated and aqueous layer extracted with DCM (2×25 mL). The combined organic layers were washed again with 0.1M NaOH (2×50 mL) solution, dried over $MgSO_4$, filtered and concentrated under *vacuo* to afford neat epoxides.



(**2**)

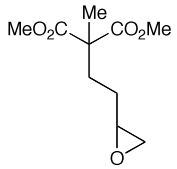
2-(2-Oxiranylethyl)malonic acid dimethyl ester (2) was obtained as colourless oil (1.50 g, 7.42 mmol, 92 %).

ν_{max} (film)/cm^{-1} 2923s, 2853s, 1738s, 1458m, 1375w, 1268w.

δH (400 MHz; $CDCl_3$) 1.53-1.66 (2H, m, C$\underline{H}_2$), 2.05-2.12 (2H, m, C$\underline{H}_2$), 2.49 (1H, dd, J 2.8 Hz, 4.8 Hz, C$\underline{H}_2$), 2.76 (1H, t, J 4.4 Hz, C$\underline{H}_2$), 2.91-2.94 (1H, m, C$\underline{H}$), 3.45 (1H, t, J 7.4 C$\underline{H}$), 3.75 (6H, s, OC$\underline{H}_3$).

δC (100 MHz; $CDCl_3$) 25.28 (C$\underline{H}_2$), 30.08 (C$\underline{H}_2$), 46.80 (C$\underline{H}_2$), 51.11 (C$\underline{H}$), 51.51 (C$\underline{H}$), 52.61 (OC$\underline{H}_3$), 52.62 (OC$\underline{H}_3$), 169.55 ($\underline{C}O_2CH_3$), 169.57 ($\underline{C}O_2CH_3$).

m/z (ESI) Calculated for $C_9H_{14}O_5(Na^+)$ requires 225.0733; found 225.0728 and $C_9H_{14}O_5(H^+)$ requires 203.0914 found 203.0910.



(**3**)

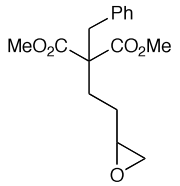
2-Methyl-2-(2-oxiranylethyl)malonic acid dimethyl ester (3) was obtained as colourless oil (1.05 g, 4.86 mmol, 97 %).

ν_{max} (film)/cm^{-1} 2970m, 2954s, 1731s, 1434m, 1380w, 1236br, 1115m, 876w.

δH (400 MHz; $CDCl_3$) 1.42 (3H, s, C$\underline{H}_3$), 1.48-1.54 (2H, m, C$\underline{H}_2$), 1.95-2.06 (2H, m, C$\underline{H}_2$), 2.47 (1H, dd, J 2.8 Hz, 4.8 Hz, C$\underline{H}_2$), 2.75 (1H, t, J 4.8 Hz, C$\underline{H}_2$), 2.89-2.94 (1H, m, C$\underline{H}$), 3.73 (6H, s, OC$\underline{H}_3$).

δC (100 MHz; $CDCl_3$) 20.01 (C$\underline{H}_3$), 27.65 (C$\underline{H}_2$), 31.86 (C$\underline{H}_2$), 46.90 (C$\underline{H}_2$), 51.86 (C$\underline{H}$), 52.52 (OC$\underline{H}_3$), 52.54 (OC$\underline{H}_3$), 53.24 ($\underline{C}$), 172.42 ($\underline{C}O_2CH_3$), 172.46 ($\underline{C}O_2CH_3$).

m/z (ESI) Calculated for $C_{10}H_{16}O_5(Na^+)$ requires 239.0890; found 239.0886.



(**4**)

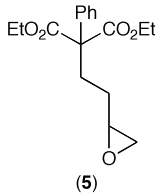
2-Benzyl-2-(2-oxiranylethyl)malonic acid dimethyl ester (4) was obtained as colourless oil (1.20 g, 4.11 mmol, 98 %).

ν_{max} (film)/cm^{-1} 3086w, 3061w, 3031w, 2995w, 2952m, 2869w, 1734s, 1496w, 1434s, 1327s, 1269s, 1207s, 1179s, 1157s, 1123s, 1092w, 1031w.

δH (400 MHz; $CDCl_3$) 1.51-1.57 (2H, m, C$\underline{H}_2$), 1.87-2.03 (2H, m, C$\underline{H}_2$), 2.46 (1H, dd, J 2.8 Hz, 4.8 Hz, C$\underline{H}_2$), 2.74 (1H, t, J 4.8 Hz, C$\underline{H}_2$), 2.87-2.90 (1H, m, C$\underline{H}$), 3.24 (2H, s, C$\underline{H}_2$), 3.71 (3H, s, OC$\underline{H}_3$), 3.72 (3H, s, OC$\underline{H}_3$), 7.04-7.07 (2H, m, ArC$\underline{H}$), 7.23-7.29 (3H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 27.68 (C$\underline{H}_2$), 28.35 (C$\underline{H}_2$), 38.62 (C$\underline{H}_2$), 46.96 (C$\underline{H}_2$), 51.83 (C$\underline{H}$), 52.45 (OC$\underline{H}_3$), 52.46 (OC$\underline{H}_3$), 58.52 (C$\underline{}$), 127.15 (ArC$\underline{H}$), 128.41 (ArC$\underline{H}$), 129.79 (ArC$\underline{H}$), 135.67 (ArC$\underline{}$), 171.35 (C$\underline{O}_2CH_3$), 171.43 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_{16}H_{20}O_5(Na^+)$ requires 315.1203; found 315.1197 and $C_{16}H_{20}O_5(H^+)$ requires 293.1384 found 293.1379.



(**5**)

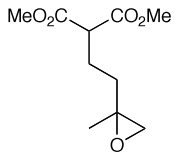
2-(2-Oxiranyl-ethyl)-2-phenyl-malonic acid diethyl ester (5) was obtained as colourless oil (0.63g, 2.06 mmol, 98 %).

ν_{max} (film)/cm^{-1} 3058w, 2982s, 2937m, 1732s, 1499m, 1447s, 1412m, 1389m, 1367w, 1184s, 1122m, 1049m, 943w, 916w, 841m.

δH (400 MHz; $CDCl_3$) 1.24 (6H, t, J 7.2 Hz, C$\underline{H}_3$), 1.43-1.59 (2H, m, C$\underline{H}_2$), 2.37-2.53 (3H, m, C$\underline{H}_2$), 2.72 (1H, t, J 4.4 Hz, C$\underline{H}_2$), 2.88-2.91 (1H, m, C$\underline{H}$), 4.21-4.27 (4H, m, C$\underline{H}_2$), 7.26-7.40 (5H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 13.98 (C$\underline{H}_3$), 27.98 (C$\underline{H}_2$), 32.02 (C$\underline{H}_2$), 46.92 (C$\underline{H}_2$), 51.97 (C$\underline{H}$), 61.65 (C$\underline{H}_2$), 62.19 (C$\underline{}$), 127.58 (ArC$\underline{H}$), 127.95 (ArC$\underline{H}$), 128.21 (ArC$\underline{H}$), 136.66 (ArC$\underline{}$), 170.47 (C$\underline{O}_2$Et), 170.51 (C$\underline{O}_2CH_2CH_3$).

m/z (ESI) Calculated for $C_{17}H_{22}O_5(Na^+)$ requires 329.1359; found 329.1359 (-0.1010ppm) and $C_{17}H_{22}O_5(H^+)$ requires 307.1540 found 307.1541 (0.3416ppm).



(**9**)

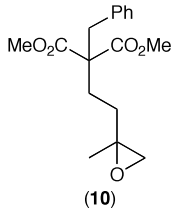
2-[2-(2-Methyloxiranyl)ethyl]malonic acid dimethyl ester (9) was obtained as colourless oil (1.55 g, 7.17 mmol, 96 %).

ν_{max} (film)/cm^{-1} 2956m, 1735s, 1436s, 1346s, 1227br, 1157s, 1101w, 1042w, 892w, 806w.

δH (400 MHz; $CDCl_3$) 1.33 (3H, s, CH_3), 1.54-1.63 (2H, m, CH_2), 2.01 (2H, q, J 7.2 Hz, CH_2), 2.58 (1H, d, J 4.6 Hz, CH_2) 2.63 (1H, d, J 4.6 Hz, CH_2), 3.39 (1H, t, J 7.2 Hz, CH), 3.74 (3H, s, OCH_3), 3.75 (3H, s, OCH_3).

δC (100 MHz; $CDCl_3$) 20.79 (CH_3), 24.48 (CH_2), 34.10 (CH_2), 51.29 (CH), 52.54 (OCH_3), 52.56 (OCH_3), 53.48 (CH_2), 56.32 (C), 169.55 (CO_2CH_3), 169.58 (CO_2CH_3).

m/z (ESI) Calculated for $C_{10}H_{16}O_5(Na^+)$ requires 239.0890; found 239.0888 and $C_{10}H_{16}O_5(H^+)$ requires 217.1071 found 217.1069.



(**10**)

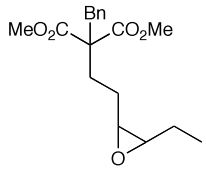
2-Benzyl-2-[2-(2-methyloxiranyl)ethyl]malonic acid dimethyl ester (10) was obtained as colourless oil (1.60 g, 5.23 mmol, 99 %).

ν_{max} (film)/cm^{-1} 3087w, 3061w, 3031s, 2952s, 2886w, 2844w, 1734s, 1604w, 1496s, 1435s, 1392m, 1328m, 1231s, 1198s, 1177s, 1109s, 1024s, 976s, 900m.

δH (400 MHz; $CDCl_3$) 1.29 (3H, s, CH_3), 1.43-1.50 (1H, m, CH_2), 1.56-1.60 (1H, m, CH_2), 1.86-1.90 (2H, m, CH_2), 2.56 (2H, q, J 5 Hz, CH_2), 3.23 (2H, s, CH_2), 3.71 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 7.05-7.07 (2H, m, ArCH), 7.20-7.30 (3H, m, ArCH).

δC (100 MHz; $CDCl_3$) 20.83(CH_3), 27.59 (CH_2), 31.58 (CH_2), 38.37 (CH_2), 52.42 (OCH_3), 53.61 (CH_2), 56.54 (C), 58.54 (C), 127.13 (ArCH), 128.38 (ArCH), 129.78 (ArCH), 135.72 (ArC), 171.38 (CO_2CH_3), 171.42 (CO_2CH_3).

m/z (ESI) Calculated for $C_{17}H_{22}O_5(Na^+)$ requires 329.1359; found 329.1357 and $C_{17}H_{22}O_5(H^+)$ requires 307.1540 found 307.1539.



(**13**)

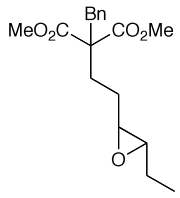
***syn*-2-Benzyl-2-[2-(3-ethyloxiranyl)ethyl]malonic acid dimethyl ester (13)** was obtained as colourless oil (1.62 g, 5.12 mmol, 99 %).

ν_{max} (film)/cm^{-1} 3087m, 3063s, 3030s, 2970s, 2877s, 2844m, 1732s, 1604w, 1454s, 1434s, 1389s, 1309s, 1203br, 1108s, 1031s, 818s.

δH (400 MHz; $CDCl_3$) 1.02 (3H, t, J 7.6 Hz, C$\underline{H}_3$), 1.42-1.59 (4H, m, C$\underline{H}_2$), 1.85-2.02 (2H, m, C$\underline{H}_2$), 2.84-2.88 (2H, m, C$\underline{H}$), 3.26 (2H, s, C$\underline{H}_2$), 3.72 (3H, s, OC$\underline{H}_3$), 3.73 (3H, s, OC$\underline{H}_3$), 7.07 (2H, d, J 8 Hz, ArC$\underline{H}$), 7.21-7.29 (3H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 10.61 (C$\underline{H}_3$), 21.00 (C$\underline{H}_2$), 23.08 (C$\underline{H}_2$), 28.96 (C$\underline{H}_2$), 38.68 (C$\underline{H}_2$), 52.43 (C$\underline{)}$, 56.68 (OC$\underline{H}_3$), 58.39 (C$\underline{H}$), 58.66 (C$\underline{H}$), 127.13 (ArC$\underline{H}$), 128.41 (ArC$\underline{H}$), 129.78 (ArC$\underline{H}$), 135.69 (ArC$\underline{)}$, 171.36 (C$\underline{O}_2CH_3$), 171.45 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_{18}H_{24}O_5(Na^+)$ requires 343.1516; found 343.1510 and $C_{18}H_{24}O_5(H^+)$ requires 321.1697 found 321.1693.



(**14**)

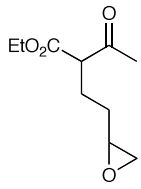
***anti*-2-Benzyl-2-[2-(3-ethyloxiranyl)ethyl]malonic acid dimethyl ester (14)** was obtained as colourless oil (0.57 g, 1.78 mmol, 97 %).

ν_{max} (film)/cm^{-1} 3087w, 3063w, 3030w, 2968s, 2876w, 2844w, 1735s, 1604w, 1496w, 1455s, 1434s, 1269s, 1232s, 1203s, 1179s, 1097w, 892w.

δH (400 MHz; $CDCl_3$) 0.97 (3H, t, J 7.6 Hz, C$\underline{H}_3$), 1.49-1.58 (4H, m, C$\underline{H}_2$), 1.85-1.98 (2H, m, C$\underline{H}_2$), 2.62-2.66 (2H, m, C$\underline{H}$), 3.24 (2H, s, C$\underline{H}_2$), 3.71 (3H, s, OC$\underline{H}_3$), 3.72 (3H, s, OC$\underline{H}_3$), 7.06 (2H, d, J 8 Hz, ArC$\underline{H}$), 7.23-7.28 (3H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 9.83 (C$\underline{H}_3$), 24.99 (C$\underline{H}_2$), 27.34 (C$\underline{H}_2$), 28.42 (C$\underline{H}_2$), 38.58 (C$\underline{H}_2$), 52.41 (OC$\underline{H}_3$), 57.83 (C$\underline{H}$), 58.56 (C$\underline{)}$, 59.80 (C$\underline{H}$), 127.12 (ArC$\underline{H}$), 128.38 (ArC$\underline{H}$), 129.80 (ArC$\underline{H}$), 135.72 (ArC$\underline{)}$, 171.36 (C$\underline{O}_2CH_3$), 171.42 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_{18}H_{24}O_5(Na^+)$ requires 343.1527; found 343.1509 and $C_{18}H_{24}O_5(H^+)$ requires 321.1707 found 321.1691.



(**17a-b**)

2-(2-Oxiranylethyl)-3-oxobutyric acid ethyl ester (17a-b) was purified by flash chromatography on silica gel eluting with light petrol/Et_2O (9:1) to afford a mixture (1:1) of inseparable diastereoisomers (1.20 g, 6.00 mmol, 86 %) as colourless oil.

ν_{max} (film)/cm^{-1} 2983m, 2936m, 1740s, 1715s, 1621w, 1447w, 1361w, 1246m, 1151m, 1097w, 1069w, 856w, 837w.

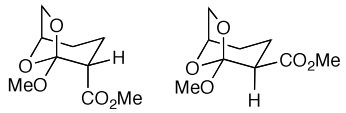
δH (400 MHz; $CDCl_3$) 1.28 (6H, t, J 7.2 Hz, C$\underline{H}_3$), 1.42-1.50 (2H, m, C$\underline{H}_2$), 1.62-1.68 (2H, m, C$\underline{H}_2$), 2.02 (4H, q, J 7.6 Hz, C$\underline{H}_2$), 2.25 (3H, s, C$\underline{H}_3$), 2.26 (3H, s, C$\underline{H}_3$), 2.45-2.48 (2H, m, C$\underline{H}_2$), 2.74 (2H, t, J 4.4 Hz, C$\underline{H}_2$), 2.87-2.93 (2H, m, C$\underline{H}$), 3.52 (2H, dt, J 7.2 Hz, 21.6 Hz, C$\underline{H}$), 4.20 (4H, q, J 7.2 Hz, C$\underline{H}_2$).

δC (100 MHz; $CDCl_3$) 14.03 (C$\underline{H}_3$), 24.39 (C$\underline{H}_2$), 24.43 (C$\underline{H}_2$), 28.83 (C$\underline{H}_3$), 29.21 (C$\underline{H}_3$), 29.89 (C$\underline{H}_2$), 30.19 (C$\underline{H}_2$), 46.62 (C$\underline{H}_2$), 46.72 (C$\underline{H}_2$), 51.53 (C$\underline{H}$), 51.61 (C$\underline{H}$), 58.75 (C$\underline{H}$), 59.16 (C$\underline{H}$), 61.40 (C$\underline{H}_2$), 169.43 (C$\underline{O}_2$Et), 202.63 (C$\underline{O}$CH$_3$), 202.70 (C$\underline{O}$CH$_3$).

m/z (ESI) Calculated for $C_{10}H_{16}O_4(Na^+)$ requires 223.0941; found 223.0941 and $C_{10}H_{16}O_4(H^+)$ requires 201.1121 found 201.1121.

General procedure for Lewis acid catalysed cyclisation of malonyl epoxides.

To the solution of malonyl epoxide in DCM was added zinc bromide. The reaction mixture was allowed to stir at room temperature for eight hours and then quenched with water. The organic layer was separated and aqueous layer extracted with (3×30 mL) DCM. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure.



(**1a**) (**1b**)

5-Methoxy-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid methyl ester (1a and 1b) was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (9:1).

1a was obtained as white crystalline solid (50 mg, 0.25 mmol, 17 %), recrystallised from MeOH at 0 °C m.p. 69-71 °C.

ν_{max} (film)/cm^{-1} 2953s, 2894m, 2863w, 1735s, 1434m, 1369m, 1329m, 1290s, 1218s, 1138s, 1003, 1025s, 920s.

δH (400 MHz; $CDCl_3$) 1.46 (1H, dd, J 5.8 Hz, 14 Hz, C$\underline{H}_2$), 1.89 (1H,dd, J 6.2 Hz, 14 Hz, C$\underline{H}_2$), 1.99-2.07 (1H, m, C$\underline{H}_2$), 2.32-2.36 (1H, m, C$\underline{H}_2$), 2.92 (1H, d, J 6.2 Hz, C$\underline{H}$), 3.41 (3H, s, OC$\underline{H}_3$), 3.72 (3H, s, OC$\underline{H}_3$), 3.86 (1H, d, J 7 Hz, C$\underline{H}_2$), 4.00 (1H, t, J 7 Hz, C$\underline{H}_2$), 4.72 (1H, s, C$\underline{H}$).

δC (100 MHz; $CDCl_3$) 21.17 (C$\underline{H}_2$), 25.59 (C$\underline{H}_2$), 47.35 (C$\underline{H}$), 49.02 (OC$\underline{H}_3$), 51.92 (OC$\underline{H}_3$), 68.14 (C$\underline{H}_2$), 75.57 (C$\underline{H}$), 118.90 (C), 171.80 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_9H_{14}O_5(Na^+)$ requires 225.0733; found 225.0729.

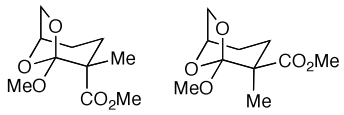
1b was obtained as white crystalline solid (0.19 g, 0.94 mmol, 63 %), recrystallised from MeOH at 0 °C m.p. 65.5 °C.

ν_{max} (DCM)/cm^{-1} 2993m, 2954m, 2922m, 2900s, 2853m, 1741s, 1490s, 1435s, 1362s, 1341m, 1291m, 1227m, 1162s, 994s, 960s.

δH (400 MHz; $CDCl_3$) 1.62 (1H, dd, J 6 Hz, 12.4 Hz, C$\underline{H}_2$), 1.86-1.93 (1H, m, C$\underline{H}_2$), 1.86-1.93 (1H, m, C$\underline{H}_2$), 2.15-2.24 (1H, m, C$\underline{H}_2$), 2.94 (1H, dd, J 4.8 Hz, 12.4 Hz, C$\underline{H}$), 3.40 (3H, s, OC$\underline{H}_3$), 3.71 (3H, s, OC$\underline{H}_3$), 3.96 (1H, d, J 7 Hz, C$\underline{H}_2$), 4.05 (1H, t, J 7 Hz, C$\underline{H}_2$), 4.63 (1H, s, C$\underline{H}$).

δC (100 MHz; $CDCl_3$) 21.66 (C$\underline{H}_2$), 27.71 (C$\underline{H}_2$), 48.92 (C$\underline{H}$), 49.85 (OC$\underline{H}_3$), 51.93 (OC$\underline{H}_3$), 69.12 (C$\underline{H}_2$), 74.73 (C$\underline{H}$), 119.08 (C), 171.79 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_9H_{14}O_5(Na^+)$ requires 225.0733; found 225.0732.



(**6a**) (**6b**)

5-methoxy-4-methyl-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid methyl ester (6a and 6b) was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (97:3).

6a was obtained as colourless oil (0.17 g, 0.79 mmol, 17 %).

ν_{max} (film)/cm^{-1} 2976s, 2950s, 2891m, 2844w, 1728s, 1459m, 1438m, 1375w, 1339w, 1233s, 1282s, 1262s, 1203s, 1168s, 1130s, 1042s, 836w, 648w.

δH (400 MHz; $CDCl_3$) 1.26 (3H, s, C$\underline{H}_3$), 1.45 (1H, dd, J 6 Hz, 13.6 Hz, C$\underline{H}_2$), 1.63 (1H, dt, J 6 Hz, 13.6 Hz, C$\underline{H}_2$), 2.03 (1H, dd, J 6 Hz, 13.6 Hz, C$\underline{H}_2$), 2.23-2.35 (1H, m, C$\underline{H}_2$), 3.38 (3H, s, OC$\underline{H}_3$), 3.71 (3H, s, OC$\underline{H}_3$), 3.80 (1H, d, J 7.2 Hz, C$\underline{H}_2$), 3.99 (1H, t, J 7.2 Hz, C$\underline{H}_2$), 4.66 (1H, s, C$\underline{H}$).

δC (100 MHz; $CDCl_3$) 20.81 (C$\underline{H}_3$), 27.42 (C$\underline{H}_2$), 30.09 (C$\underline{H}_2$), 48.87 (OC$\underline{H}_3$), 50.99 (C), 52.02 (OC$\underline{H}_3$), 68.54 (C$\underline{H}_2$), 75.45 (C$\underline{H}$), 120.71 (C), 173.97 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_{10}H_{16}O_5(Na^+)$ requires 239.0890; found 239.0888.

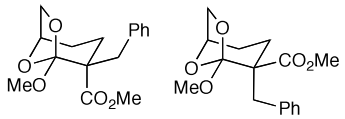
6b was obtained as white crystalline solid (0.63 g, 2.92 mmol, 63 %) recrystallised in MeOH at 0 °C. m.p. 42.5 °C.

V_{max} (film)/cm^{-1} 2984s, 2951s, 2893m, 2843w, 1729s, 1465s, 1438w, 1338w, 1329s, 1262s, 1239s, 1198s, 1182s, 1129s, 1070s.

δH (400 MHz; $CDCl_3$) 1.38 (3H, s, C$\underline{H}_3$), 1.49-1.57 (2H, m, C$\underline{H}_2$), 1.95-2.05 (1H, m, C$\underline{H}_2$), 2.41-2.52 (1H, m, C$\underline{H}_2$), 3.36 (3H, s, OC$\underline{H}_3$), 3.71 (3H, s, OC$\underline{H}_3$), 3.91 (1H, d, J 7.2 Hz, C$\underline{H}_2$), 3.99-4.03 (1H, m, C$\underline{H}_2$), 4.61 (1H, s, C$\underline{H}$).

δC (100 MHz; $CDCl_3$) 17.95 (C$\underline{H}_3$), 25.23 (C$\underline{H}_2$), 28.35 (C$\underline{H}_2$), 48.88 (OC$\underline{H}_3$), 50.96 (C), 52.09 (OC$\underline{H}_3$), 68.53 (C$\underline{H}_2$), 57.07 (C$\underline{H}$), 120.88 (C), 174.17 (C$\underline{O}_2$CH$_3$).

m/z (ESI) Calculated for $C_{10}H_{16}O_5(Na^+)$ requires 239.0890; found 239.0890.



(**7a**) (**7b**)

4-Benzyl-5-methoxy-6,8-dioxa-bicyclo[3.2.1]octane-4-carboxylic acid methyl ester (7a and 7b) was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (97:3).

7a was obtained as colourless oil (0.15 g, 0.51 mmol, 15 %).

V_{max} (film)/cm^{-1} 3085m, 3061m, 3028s, 2974s, 2949s, 2891s, 2843m, 1728s, 1603m, 1495s, 1439s, 1343s, 1231br, 1201s, 1075s, 690s, 945s,869m.

δH (400 MHz; $CDCl_3$) 1.43 (1H, dd, J 6 Hz, 13.6 Hz, C$\underline{H}_2$), 1.60-1.69 (1H, m, C$\underline{H}_2$), 1.76 (1H, dd, J 6 Hz, 13.6 Hz, C$\underline{H}_2$), 2.15-2.26 (1H, m, C$\underline{H}_2$), 2.69 (1H, d, J 13.6 Hz, C$\underline{H}_2$), 3.44 (3H, s, OC$\underline{H}_3$), 3.55 (1H, d, J 13.6 Hz, C$\underline{H}_2$), 3.72 (3H, s, OC$\underline{H}_3$), 3.85 (1H, d, J 6.8 Hz, C$\underline{H}_2$), 4.03 (1H, t, J 6.8 Hz, C$\underline{H}_2$), 4.64 (1H, s, C$\underline{H}$), 7.08 (2H, d, J 7.2 Hz, ArC$\underline{H}$), 7.17-7.25 (3H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 27.22 (C$\underline{H}_2$), 27.36 (C$\underline{H}_2$), 39.74 (C$\underline{H}_2$), 49.09 (OC$\underline{H}_3$), 51.85 (OC$\underline{H}_3$), 56.47 (C), 69.04 (C$\underline{H}_2$), 75.77 (C$\underline{H}$), 120.69 (C), 126.46 (ArC$\underline{H}$), 128.09 (ArC$\underline{H}$), 130.01 (ArC$\underline{H}$), 136.84 (ArC$\underline{H}$), 172.53 (C$\underline{O}_2$CH$_3$).

m/z (ESI) Calculated for $C_{16}H_{20}O_5(Na^+)$ requires 315.1203; found 315.1206 and $C_{16}H_{20}O_5(H^+)$ requires 293.1384 found 293.1387.

7b was obtained as white crystalline solid (0.63 g, 2.16 mmol, 63 %) recrystallised from MeOH at 0 °C. m.p. 98.2-99.7 °C.

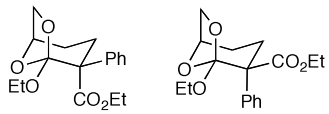
V_{max} (film)/cm^{-1} 3085w, 3061w, 3027w, 2950s, 2892m, 2847w, 1727s, 1496w, 1455m, 1437m, 1310w, 1254m, 1195s, 1178s, 994s.

δH (400 MHz; $CDCl_3$) 1.50 (1H, dd, J 5.6 Hz, 14 Hz, C$\underline{H}_2$), 1.59 (1H, dd, J 5.6 Hz, 14 Hz, C$\underline{H}_2$), 2.00-2.11 (1H, m, C$\underline{H}_2$), 2.24-2.38 (1H, m, C$\underline{H}_2$), 3.09 (1H, d, J 14, C$\underline{H}_2$), 3.42 (3H, s, OC$\underline{H}_3$), 3.52 (1H, d, J

14 Hz, C$\underline{H}_2$), 3.71 (3H, s, OC$\underline{H}_3$), 3.91 (1H, d, J 7 Hz, C$\underline{H}_2$), 4.02 (1H, t, J 7 Hz, C$\underline{H}_2$), 4.67 (1H, s, C$\underline{H}$), 7.12 (2H, d, J 7.2 Hz, ArC$\underline{H}$), 7.18-7.26 (3H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 21.07 (C$\underline{H}_2$), 22.32 (C$\underline{H}_2$), 35.79 (C$\underline{H}_2$), 49.18 (OC$\underline{H}_3$), 52.06 (OC$\underline{H}_3$), 56.37 (C$\underline{H}_2$), 68.72 (C$\underline{H}_2$), 75.15 (C$\underline{H}$), 121.02 (C$\underline{H}$), 126.43 (ArC$\underline{H}$), 128.19 (ArC$\underline{H}$), 130.15 (ArC$\underline{H}$), 138.01 (ArC$\underline{H}$), 172.59 (C$\underline{O}_2CH_3$).

m/z (ESI) Calculated for $C_{16}H_{20}O_5(Na^+)$ requires 315.1203; found 315.1206 and $C_{16}H_{20}O_5(H^+)$ requires 293.1384 found 293.1387.



(**8a**) (**8b**)

5-Ethoxy-4-phenyl-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid ethyl ester (8a and 8b) was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (97:3).

8a was obtained as colourless oil (44 mg, 0.16 mmol, 9 %).

V_{max} (film)/cm^{-1} 2978s, 2896m, 1720s, 1602w, 1499m, 1445m, 1366m, 1262s, 1225s, 1185s, 1154s, 1044s, 1003s, 1056s, 974s, 950m, 770w.

δH (400 MHz; $CDCl_3$) 1.20-1.25 (6H, m, C$\underline{H}_3$), 1.53 (1H, ddt, J 1.4 Hz, 4.8 Hz, 13.2 Hz, C$\underline{H}_2$), 1.95-2.03 (1H, m, C$\underline{H}_2$), 2.27-2.37 (1H, m, C$\underline{H}_2$), 2.45 (1H, ddt, J, 1.4 Hz, 4.8 Hz, 13.2 Hz, C$\underline{H}_2$), 3.75-3.86 (2H, m, C$\underline{H}_2$), 3.89 (1H, d, J 6.8 Hz, C$\underline{H}_2$), 4.05-4.08 (1H, m, C$\underline{H}_2$), 4.13-4.21 (1H, m, C$\underline{H}_2$), 4.24-4.33 (1H, m, C$\underline{H}_2$), 4.69 (1H, t, J 4 Hz, C$\underline{H}$), 7.18-7.22 (1H, m, ArC$\underline{H}$), 7.25-7.30 (2H, m, ArC$\underline{H}$), 7.43-7.45 (2H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 14.06 (C$\underline{H}_3$), 15.58 (C$\underline{H}_3$), 27.83 (C$\underline{H}_2$), 32.34 (C$\underline{H}_2$), 57.62 (C$\underline{H}_2$), 60.70 (C$\underline{H}_2$), 61.08 (C$\underline{H}_2$), 69.17 (C$\underline{H}_2$), 75.56 (C$\underline{H}$), 120.99 (C$\underline{H}$), 126.66 (ArC$\underline{H}$), 127.15 (ArC$\underline{H}$), 128.12 (ArC$\underline{H}$), 140.56 (ArC$\underline{H}$), 172.12 (C$\underline{O}_2CH_2CH_3$).

m/z (ESI) Calculated for $C_{17}H_{22}O_5(Na^+)$ requires 329.1359; found 329.1350 and $C_{17}H_{22}O_5(H^+)$ requires 307.1540 found 307.1532.

8b as white crystalline solid (0.15 g, 0.49 mmol, 30 %) recrystallised from MeOH at 0 °C m.p. 84.5-85.6 °C.

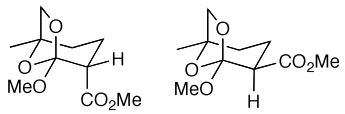
V_{max} (film)/cm^{-1} 2978m, 1720s, 1606w, 1445w, 1365w, 1251s, 1160m, 1088m, 1028s, 995m, 938w, 753s.

δH (400 MHz; $CDCl_3$) 1.15 (3H, t, J 7.2 Hz, C$\underline{H}_3$), 1.24 (3H, t, J 7.2 Hz, C$\underline{H}_3$), 1.52 (1H, ddt, J 1.6 Hz, 5.6 Hz, 14 Hz, C$\underline{H}_2$), 1.82-1.90 (1H, m, C$\underline{H}_2$), 2.23 (1H, ddt, J 1.6 Hz, 5.6 Hz, 14.4 Hz, C$\underline{H}_2$), 2.71-2.79 (1H, m, C$\underline{H}_2$), 3.79-3.89 (2H, m, C$\underline{H}_2$), 3.94 (1H, d, J 7.2 Hz, C$\underline{H}_2$), 4.00-4.03 (1H, m, C$\underline{H}_2$), 4.07-4.20

(2H, m, C<u>H</u>$_2$), 4.61 (1H, t, J 3.6 Hz, C<u>H</u>), 7.19-7.24 (1H, m, ArC<u>H</u>), 7.26-7.31 (2H, m, ArC<u>H</u>), 7.54-7.57 (2H, m, ArC<u>H</u>).

δC (100 MHz; CDCl$_3$) 14.02 (<u>C</u>H$_3$), 15.41 (<u>C</u>H$_3$), 26.25 (<u>C</u>H$_2$), 29.65 (<u>C</u>H$_2$), 57.51 (<u>C</u>H$_2$), 59.49 (<u>C</u>), 60.95 (<u>C</u>H$_2$), 68.41 (<u>C</u>H$_2$), 74.97 (1<u>C</u>H), 120.70 (<u>C</u>), 126.53 (Ar<u>C</u>H), 127.66 (Ar<u>C</u>H), 128.79 (Ar<u>C</u>H), 139.28 (Ar<u>C</u>), 172.55 (<u>C</u>O$_2$CH$_2$CH$_3$).

m/z (ESI) Calculated for $C_{17}H_{22}O_5(Na^+)$ requires 329.1359; found 329.1352 and $C_{17}H_{22}O_5(H^+)$ requires 307.1540 found 307.1533.



(**11a**) (**11b**)

5-Methoxy-1-methyl-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid methyl ester (11a and 11b) was purified by flash chromatography on silica gel eluting with light petrol/Et$_2$O (97:3).

11a was obtained as colourless oil (60 mg, 0.28 mmol, 20 %).

V$_{max}$ (film)/cm^{-1} 2951s, 2884s, 2846m, 1736s, 1437s, 1361m, 1323s, 1300, 1242s, 1160s, 1140s, 1100s, 994s, 973s, 894s, 795m.

δH (400 MHz; CDCl$_3$) 1.41 (3H, s, C<u>H</u>$_3$), 1.48-1.53 (1H, m, C<u>H</u>$_2$), 1.91-1.94 (1H, m, C<u>H</u>$_2$), 1.98-2.08 (1H, m, C<u>H</u>$_2$), 2.11-2.20 (1H, m, C<u>H</u>$_2$), 2.88 (1H, d, J 6 Hz, C<u>H</u>), 3.42 (3H, s, OC<u>H</u>$_3$), 3.56 (1H, dd, J 1.8 Hz, 6.8 Hz, C<u>H</u>$_2$), 3.71 (3H, s, OC<u>H</u>$_3$), 3.86 (1H, d, J 6.8 Hz, C<u>H</u>$_2$).

δC (100 MHz; CDCl$_3$) 22.18 (<u>C</u>H$_2$), 22.36 (<u>C</u>H$_3$), 31.45 (<u>C</u>H$_2$), 46.40 (<u>C</u>H), 48.88 (O<u>C</u>H$_3$), 51.87 (O<u>C</u>H$_3$), 73.38 (<u>C</u>H$_2$), 81.37 (<u>C</u>), 119.33 (<u>C</u>), 171.77 (<u>C</u>O$_2$CH$_3$).

m/z (ESI) Calculated for $C_{10}H_{16}O_5(Na^+)$ requires 239.0890; found 239.0888 and $C_{10}H_{16}O_5(H^+)$ requires 217.1071 found 217.1069.

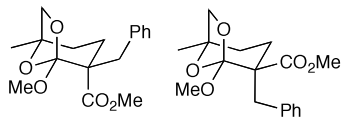
11b was obtained as colourless oil (0.17 g, 0.79 mmol, 57 %).

V$_{max}$ (film)/cm^{-1} 2951s, 2884s, 2846m, 1736s, 1437s, 1382s, 1364s, 1321s, 1256s, 1235s, 1210s, 1170s, 1106s, 1044s, 1012s, 978m, 922s, 893s.

δH (400 MHz; CDCl$_3$) 1.38 (3H, s, C<u>H</u>$_3$), 1.65-1.70 (2H, m, C<u>H</u>$_2$), 1.88-1.93 (1H, m, C<u>H</u>$_2$), 2.15-2.25 (1H, m, C<u>H</u>$_2$), 2.88 (1H, dd, J 5.2 Hz, 12 Hz, C<u>H</u>), 3.41 (3H, m, OC<u>H</u>$_3$), 3.63 (1H, dd, J 1.2 Hz, 7 Hz, C<u>H</u>$_2$), 3.71 (3H, s, OC<u>H</u>$_3$), 3.98 (1H, d, J 7 Hz, C<u>H</u>$_2$).

δC (100 MHz; CDCl$_3$) 22.15 (<u>C</u>H$_3$), 22.84 (<u>C</u>H$_2$), 33.61 (<u>C</u>H$_2$), 48.79 (<u>C</u>H), 49.09 (O<u>C</u>H$_3$), 51.92 (O<u>C</u>H$_3$), 74.35 (<u>C</u>H$_2$), 80.48 (<u>C</u>), 119.38 (<u>C</u>), 171.97 (<u>C</u>O$_2$CH$_3$).

m/z (ESI) Calculated for $C_{10}H_{16}O_5(Na^+)$ requires 239.0890; found 239.0887 and $C_{10}H_{16}O_5(H^+)$ requires 217.1071 found 217.1069.



(**12a**) (**12b**)

4-Benzyl-5-methoxy-1-methyl-6,8-dioxa-bicyclo[3.2.1]octane-4-carboxylic acid methyl ester (12a and 12b) was purified by flash chromatography on silica gel eluting with light petrol/Et_2O (97:3).

12a was obtained as white crystalline solid (0.27 g, 0.88 mmol, 30 %) recrystallised from methanol at 0 °C m.p. 79.2-80.2 °C.

V_{max} (film)/cm^{-1} 3061w, 3029w, 2974s, 2948s, 2881m, 2843w, 1730s, 1604w, 1480w, 1382m, 1374s, 1318s, 1296m, 1228s, 1214s, 1157s, 1103s, 1080s, 971s.

δH (400 MHz; $CDCl_3$) 1.35 (3H, s, CH_3), 1.45-1.50 (1H, m, CH_2), 1.63-1.71 (1H, m, CH_2), 1.75-1.81 (1H, m, CH_2), 1.95-2.05 (1H, m, CH_2), 2.67 (1H, d, J 13.6 Hz, CH_2), 3.46 (3H, s, OCH_3), 3.53 (1H, d, J 13.6 Hz, CH_2), 3.61 (1H, dd, J 2.4 Hz, 6.8 Hz, CH_2), 3.71 (3H, s, OCH_3), 3.86 (1H, d, J 6.8 Hz, CH_2), 7.08 (2H, d, J 7.6 Hz, ArCH), 7.18-7.25 (3H, m, ArCH).

δC (100 MHz; $CDCl_3$) 21.88 (CH_3), 28.17 (CH_2), 33.22 (CH_2), 39.54 (CH_2), 48.95 (OCH_3), 51.81 (OCH_3), 55.52 (C), 74.17 (CH_2), 81.58 (C), 120.20 (C), 126.44 (ArCH), 128.07 (ArCH), 129.97 (ArCH), 136.99 (ArC), 172.47 (CO_2CH_3).

m/z (ESI) Calculated for $C_{17}H_{22}O_5(Na^+)$ requires 329.1359; found 329.1351 and $C_{17}H_{22}O_5(H^+)$ requires 307.1540 found 307.1533.

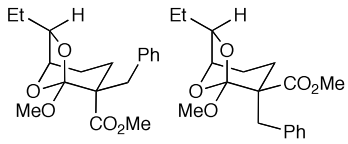
12b was obtained as white crystalline solid (0.60 g, 1.96 mmol, 60 %) recrystallised from methanol at 0 °C m.p. 86.6-87.2 °C.

V_{max} (film)/cm^{-1} 3086w, 3061w, 3027m, 2975s, 2949s, 2884s, 2844s, 1728s, 1603w, 1496s, 1436s, 1382s, 1293s, 1258s, 1109s, 1093s, 1010s, 990s, 955m, 902m.

δH (400 MHz; $CDCl_3$) 1.43 (3H, s, CH_3), 1.53-1.64 (1H, m, CH_2), 1.53-1.64 (1H, m, CH_2), 1.80-1.89 (1H, m, CH_2), 2.30-2.40 (1H, m, CH_2), 3.05 (1H, d, J 14 Hz, CH_2), 3.44 (3H, s, OCH_3), 3.52 (1H, d, J 14 Hz, CH_2), 3.60 (1H, dd, J 2 Hz, 6.8 Hz, CH_2), 3.71 (3H, s, OCH_3), 3.93 (1H, d, J 6.8 Hz, CH_2), 7.13 (2H, d, J 7.6 Hz, ArCH), 7.16-7.25 (3H, m, ArCH).

δC (100 MHz; $CDCl_3$) 22.18 (CH_3), 23.40 (CH_2), 31.59 (CH_2), 35.71 (CH_2), 49.04 (OCH_3), 52.03 (OCH_3), 55.46 (C), 73.93 (CH_2), 80.93 (C), 121.27 (C), 126.39 (ArCH), 128.16 (ArCH), 130.15 (ArCH), 138.05 (ArC), 172.66 (CO_2CH_3).

m/z (ESI) Calculated for $C_{17}H_{22}O_5(Na^+)$ requires 329.1359; found 329.1351 and $C_{17}H_{22}O_5(H^+)$ requires 307.1540 found 307.1533.



(**15a**) (**15b**)

***exo*-4-Benzyl-7-ethyl-5-methoxy-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid methyl ester (15a and 15b)** was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (19:1) affording a chromatographically inseparable mixture of diastereoisomers. **15b** was separated by recrystallization in hexane at 0 °C as white solid, leaving a 2:1 mixture of **15a** and **15b** in the mother liquor.

15a and 15b was obtained as colourless oil (0.10 g, 0.31 mmol, 19 %).

ν_{max} (film)/cm^{-1} 3086w, 3062w, 3028m, 2951s, 2253w, 1731s, 1603w, 1496s, 1437s, 1337s, 1225br, 1131s, 913s, 849w, 809w, 735w.

δH (400 MHz; $CDCl_3$) 0.95 (3H, t, J 7.2 Hz, C$\underline{H}_3$), 0.98 (3H, t, J 7.2 Hz, C$\underline{H}_3$), 1.39-1.44 (1H, m, C$\underline{H}_2$), 1.46-1.51 (1H, m, C$\underline{H}_2$), 1.56-1.76 (7H, m, C$\underline{H}_2$), 2.01-2.06 (1H, m, C$\underline{H}_2$), 2.14-2.23 (1H, m, C$\underline{H}_2$), 2.29-2.38 (1H, m, C$\underline{H}_2$), 2.68 (1H, d, J 14 Hz, C$\underline{H}_2$), 3.08 (1H, d, J 14 Hz, C$\underline{H}_2$), 3.43 (3H, s, OC$\underline{H}_3$), 3.45 (3H, s, OC$\underline{H}_3$), 3.56 (2H, d, J 14 Hz, C$\underline{H}_2$), 3.70 (3H, s, OC$\underline{H}_3$), 3.71 (3H, s, OC$\underline{H}_3$), 3.80 (1H, t, J 7 Hz, C$\underline{H}$), 3.87 (1H, t, J 7 Hz, C$\underline{H}$), 4.23 (1H, t, J 1.8 Hz, C$\underline{H}$), 4.26 (1H, t, 1.8 Hz, C$\underline{H}$), 7.08-7.24 (10H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 9.89 (C$\underline{H}_3$), 9.95 (C$\underline{H}_3$), 22.42 (C$\underline{H}_2$), 25.43 (C$\underline{H}_2$), 27.25 (C$\underline{H}_2$), 27.55 (C$\underline{H}_2$), 27.57 (C$\underline{H}_2$), 35.71 (C$\underline{H}_2$), 39.70 (C$\underline{H}_2$), 49.02 (OC$\underline{H}_3$), 49.07 (OC$\underline{H}_3$), 51.80 (OC$\underline{H}_3$), 52.02 (OC$\underline{H}_3$), 56.00 (C), 56.09 (C), 78.24 (C$\underline{H}$), 78.82 (C$\underline{H}$), 80.44 (C$\underline{H}$), 80.74 (C$\underline{H}$), 120.90 (C), 121.28 (C), 126.39 (ArC$\underline{H}$), 126.41 (ArC$\underline{H}$), 128.06 (ArC$\underline{H}$), 128.17 (ArC$\underline{H}$), 130.03 (ArC$\underline{H}$), 130.14 (ArC$\underline{H}$), 136.97 (ArC), 138.10 (ArC), 172.63 ($\underline{C}O_2CH_3$).

m/z (ESI) Calculated for $C_{18}H_{24}O_5(Na^+)$ requires 343.1516; found 343.1512 and $C_{18}H_{24}O_5(H^+)$ requires 321.1697 found 321.1694.

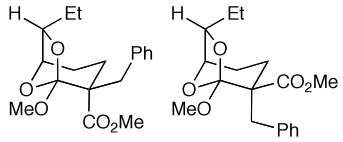
15b was obtained as white solid (0.38 g, 1.19 mmol, 73 %) recrystallized from methanol at 0 °C m.p. 100-101 °C.

ν_{max} (film)/cm^{-1} 3085w, 3061w, 3027s, 2950s, 2877s, 2843m, 1723s, 1603m, 1495s, 1436, 1335s, 915s, 865w, 817w, 796m.

δH (400 MHz; $CDCl_3$) 0.95 (3H, t, J 7.6 Hz, C$\underline{H}_3$), 1.46-1.51 (1H, m, C$\underline{H}_2$), 1.54-1.61 (2H, m, C$\underline{H}_2$), 1.68-1.75 (1H, m, C$\underline{H}_2$), 1.96-2.08 (1H, m, C$\underline{H}_2$), 2.28-2.39 (1H, m, C$\underline{H}_2$), 3.08 (1H, d, J 14 Hz, C$\underline{H}_2$), 3.43 (3H, s, OC$\underline{H}_3$), 3.52 (1H, d, J 14 Hz, C$\underline{H}_2$), 3.71 (3H, s, OC$\underline{H}_3$), 3.87 (1H, t, J 7 Hz, C$\underline{H}$), 4.26 (1H, t, J 1.6 Hz, C$\underline{H}$), 7.12 (2H, d, J 7.6 Hz, ArC$\underline{H}$), 7.17-7.25 (3H, m, ArC$\underline{H}$).

δC (100 MHz; $CDCl_3$) 9.89 ($\underline{C}H_3$), 22.42 ($\underline{C}H_2$), 25.43 ($\underline{C}H_2$), 27.55 ($\underline{C}H_2$), 35.72 ($\underline{C}H_2$), 49.07 ($O\underline{C}H_3$), 52.02 ($O\underline{C}H_3$), 56.00 ($\underline{C}$), 78.24 ($\underline{C}H$), 80.44 ($\underline{C}H$), 121.28 ($\underline{C}$), 126.38 ($Ar\underline{C}H$), 128.17 ($Ar\underline{C}H$), 130.14 ($Ar\underline{C}H$), 138.10 ($Ar\underline{C}$), 172.67 ($\underline{C}O_2CH_3$).

m/z (ESI) Calculated for $C_{18}H_{24}O_5(Na^+)$ requires 343.1516; found 343.1511.



(**16a**) (**16b**)

***endo*-4-Benzyl-7-ethyl-5-methoxy-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid methyl ester (16a and 16b)** was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (19:1) affording a chromatographically inseparable mixture of diastereoisomers. **16b** was separated by recrystallization in hexane at 0 °C as white granules, leaving pure **16a** in the mother liquor.

16a was obtained as colourless oil (0.11g, 0.34 mmol, 21 %).

V_{max} (film)/cm^{-1} 3085w, 3061w, 3028w, 2967s, 2949s, 1730s, 1603w, 1496w, 1453s, 1277s, 1177s, 1134s, 1115s, 1072s, 1012s, 914s, 868w, 807w.

δH (400 MHz; $CDCl_3$) 1.02 (3H, t, J 7.4 Hz, $C\underline{H}_3$), 1.50-1.58 (2H, m, $C\underline{H}_2$), 1.66-1.71 (2H, m, $C\underline{H}_2$), 1.80-1.87 (1H, m, $C\underline{H}_2$), 2.11-2.20 (1H, m, $C\underline{H}_2$), 2.65 (1H, d, J 13.6 Hz, $C\underline{H}_2$), 3.46 (3H, s, $OC\underline{H}_3$), 3.55 (1H, d, J 13.6 Hz, $C\underline{H}_2$), 3.72 (3H, s, $OC\underline{H}_3$), 4.10-4.14 (1H, m, $C\underline{H}$), 4.40 (1H, t, J 3.8 Hz, $C\underline{H}$), 7.07 (2H, d, J 6.8 Hz, $ArC\underline{H}$), 7.17-7.25 (3H, m, $ArC\underline{H}$).

δC (100 MHz; $CDCl_3$) 10.50 ($\underline{C}H_3$), 22.06 ($\underline{C}H_2$), 22.86 ($\underline{C}H_2$), 28.38 ($\underline{C}H_2$), 39.51 ($\underline{C}H_2$), 48.85 ($O\underline{C}H_3$), 51.83 ($O\underline{C}H_3$), 55.87 ($\underline{C}$), 78.05 ($\underline{C}H$), 81.72 ($\underline{C}H$), 120.12 ($\underline{C}$), 126.38 ($Ar\underline{C}H$), 128.05 ($Ar\underline{C}H$), 130.01 ($Ar\underline{C}H$), 136.97 ($Ar\underline{C}$), 172.89 ($\underline{C}O_2CH_3$).

m/z (ESI) Calculated for $C_{18}H_{24}O_5(Na^+)$ requires 343.1516; found 343.1510 and $C_{18}H_{24}O_5(H^+)$ requires 321.1697 found 321.1692.

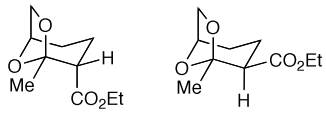
16b was obtained as white granules (0.27 g, 0.84 mmol, 52 %) recrystallized from methanol at 0 °C m.p. 92-94 °C.

V_{max} (film)/cm^{-1} 3085w, 3061w, 3027m, 2967s, 2949s, 2878s, 2842w, 1728s, 1603w, 1496s, 1433s, 1272s, 1227s, 1127s, 1114s, 957s.

δH (400 MHz; $CDCl_3$) 0.98 (3H, t, J 7.2 Hz, $C\underline{H}_3$), 1.52-1.63 (3H, m, $C\underline{H}_2$), 1.83-1.88 (1H, m, $C\underline{H}_2$), 1.90-2.02 (1H, m, $C\underline{H}_2$), 2.34-2.43 (1H, m, $C\underline{H}_2$), 3.10 (1H, d, J 14 Hz, $C\underline{H}_2$), 3.44 (3H, s, $OC\underline{H}_3$), 3.52 (1H, d, J 14 Hz, $C\underline{H}_2$), 3.70 (3H, s, $OC\underline{H}_3$), 4.11-4.17 (1H, m, $C\underline{H}$), 4.43 (1H, t, J 4 Hz, $C\underline{H}$), 7.12 (2H, d, J 7.6 Hz, $ArC\underline{H}$), 2.16-2.26 (3H, m, $ArC\underline{H}$).

δC (100 MHz; $CDCl_3$) 10.54 ($\underline{C}H_3$), 21.60 ($\underline{C}H_2$), 21.82 ($\underline{C}H_2$), 23.34 ($\underline{C}H_2$), 36.33 ($\underline{C}H_2$), 48.95 ($O\underline{C}H_3$), 51.96 ($O\underline{C}H_3$), 55.68 ($\underline{C}$), 77.34 ($\underline{C}H$), 81.98 ($\underline{C}H$), 120.58 ($\underline{C}$), 126.36 ($Ar\underline{C}H$), 128.15 ($Ar\underline{C}H$), 130.19 ($Ar\underline{C}H$), 138.27 ($Ar\underline{C}$), 172.57 ($\underline{C}O_2CH_3$).

m/z (ESI) Calculated for $C_{18}H_{24}O_5(Na^+)$ requires 343.1516; found 343.1510.



(**18a**) (**18b**)

5-Methyl-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid ethyl ester (18a and 18b) was purified by flash chromatography on silica gel eluting with light petrol/Et_2O (19:1).

18a was obtained as colourless oil (0.40 g, 2.00 mmol, 40 %)**.**

V_{max} (film)/cm^{-1} 2978s, 2942s, 2889s, 1734s, 1479w, 1449m, 1372s, 1324s, 1253s, 1243s, 1324s, 1204s, 1154s, 1112s, 1067s, 891s, 876s.

δH (400 MHz; $CDCl_3$) 1.28 (3H, t, J 7.2 Hz, $C\underline{H}_3$), 1.43 (1H, dd, J 6 Hz, 14 Hz, $C\underline{H}_2$), 1.54 (3H, s, $C\underline{H}_3$), 1.85 (1H, dd, J 6 Hz, 14 Hz, $C\underline{H}_2$), 1.98-2.08 (1H, m, $C\underline{H}_2$), 2.25-2.36 (1H, m, $C\underline{H}_2$), 2.65 (1H, d, J 6, $C\underline{H}$), 3.86-3.90 (2H, m, $C\underline{H}_2$), 4.12-4.22 (2H, m, $C\underline{H}_2$), 4.61 (1H, s, $C\underline{H}$).

δC (100 MHz; $CDCl_3$) 14.18 ($\underline{C}H_3$), 20.05 ($\underline{C}H_2$), 23.60 ($\underline{C}H_3$), 25.55 ($\underline{C}H_2$), 48.45 ($\underline{C}H$), 60.41 ($\underline{C}H_2$), 68.48 ($\underline{C}H_2$), 75.58 ($\underline{C}H$), 106.34 ($\underline{C}$), 172.23 ($\underline{C}O_2Et$).

m/z (ESI) Calculated for $C_{10}H_{16}O_4(Na^+)$ requires 223.0941; found 223.0938 and $C_{10}H_{16}O_4(H^+)$ requires 201.1121 found 201.1119.

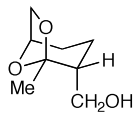
18b was obtained as colourless oil (0.40 g, 2.00 mmol, 40 %)**.**

V_{max} (film)/cm^{-1} 2979s, 2941s, 2891m, 1736s, 1448w, 1384s, 1337s, 1257s, 1154s, 1036s, 943s, 867w, 829w.

δH (400 MHz; $CDCl_3$) 1.26 (3H, t, J 7.2 Hz, $C\underline{H}_3$), 1.49 (3H, s, $C\underline{H}_3$), 1.59 (1H, dd, J 6 Hz, 13.6 Hz, $C\underline{H}_2$), 1.80-1.87 (1H, m, $C\underline{H}_2$), 1.80-1.87 (1H, m, $C\underline{H}_2$), 2.10-2.20 (1H, m, $C\underline{H}_2$), 2.69 (1H, dd, J 5 Hz, 11.8 Hz, $C\underline{H}$), 3.90-3.94 (1H, m, $C\underline{H}_2$), 3.99 (1H, d, J 6.8 Hz, $C\underline{H}_2$), 4.10-4.20 (2H, m, $C\underline{H}_2$), 4.55 (1H, s, $C\underline{H}$).

δC (100 MHz; $CDCl_3$) 14.21 ($\underline{C}H_3$), 20.52 ($\underline{C}H_2$), 22.91 ($\underline{C}H_3$), 27.80 ($\underline{C}H_2$), 50.95 ($\underline{C}H$), 60.45 ($\underline{C}H_2$), 69.57 ($\underline{C}H_2$), 74.53 ($\underline{C}H$), 106.40 ($\underline{C}$), 172.33 ($\underline{C}O_2Et$).

m/z (ESI) Calculated for $C_{10}H_{16}O_4(Na^+)$ requires 223.0941; found 223.0937 and $C_{10}H_{16}O_4(H^+)$ requires 201.1121 found 201.1118.



(**19a**)

(5-Methyl-6,8-dioxabicyclo[3.2.1]oct-4-yl)methanol (19a)

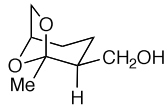
To the solution of 5-methyl-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid ethyl ester **18a** (0.25 g, 1.25 mmol) in THF (13 mL) at RT was added $LiAlH_4$ (80 mg, 2.10 mmol). The reaction mixture was allowed to stir for one hour and then quenched with methanol (5 mL) and washed with water (10 mL). The organic layer was extracted with DCM (2×20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure affording (5-methyl-6,8-dioxabicyclo[3.2.1]oct-4-yl)methanol **19a** (0.14 g, 0.86 mmol, 70 %) as colourless oil.

V_{max} (film)/cm^{-1} 3400br, 2940s, 1457s, 1384s, 1327s, 1295s, 1190s, 1168s, 1116s, 1015s, 950s, 887s, 847s.

δH (400 MHz; $CDCl_3$) 1.41-1.44 (1H, m, C$\underline{H}_2$), 1.48 (3H, s, C$\underline{H}_3$), 1.72-1.79 (2H, m, C$\underline{H}$, C$\underline{H}_2$), 1.99-2.09 (2H, m, C$\underline{H}_2$), 2.37 (1H, s, O$\underline{H}$), 3.73 (1H, dd, J 3.6 Hz, 11.2 Hz, C$\underline{H}_2$), 3.80 (1H, dd, J 6 Hz, 11.2 Hz, C$\underline{H}_2$), 3.85-3.91 (2H, m, C$\underline{H}_2$), 4.56 (1H, m, C$\underline{H}$).

δC (100 MHz; $CDCl_3$) 20.06 (C$\underline{H}_2$), 22.78 (C$\underline{H}_3$), 25.88 (C$\underline{H}_2$), 44.39 (C$\underline{H}$), 63.83 (C$\underline{H}_2$), 68.35 (C$\underline{H}_2$), 75.64 (C$\underline{H}$), 108.52 (C$\underline{}$).

m/z (ESI) Calculated for $C_8H_{14}O_3(Na^+)$ requires 181.0835; found 181.0832 and $C_8H_{14}O_3(H^+)$ requires 159.1016 found 159.1013.



(**19b**)

(5-Methyl-6,8-dioxabicyclo[3.2.1]oct-4-yl)methanol (19b)

To the solution of 5-methyl-6,8-dioxabicyclo[3.2.1]octane-4-carboxylic acid ethyl ester **18b** (0.20 g, 0.10 mmol) in THF (10 mL) at RT was added $LiAlH_4$ (64 mg, 1.70 mmol). The reaction mixture was allowed to stir for one hour and then quenched with methanol (5 mL) and washed with water (10 mL). The organic layer was extracted with DCM (2×20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with light petrol/EtOAc (8:1) affording (5-methyl-6,8-dioxabicyclo[3.2.1]oct-4-yl)methanol **19b** (0.12 g, 0.86 mmol, 75 %) as colourless oil.

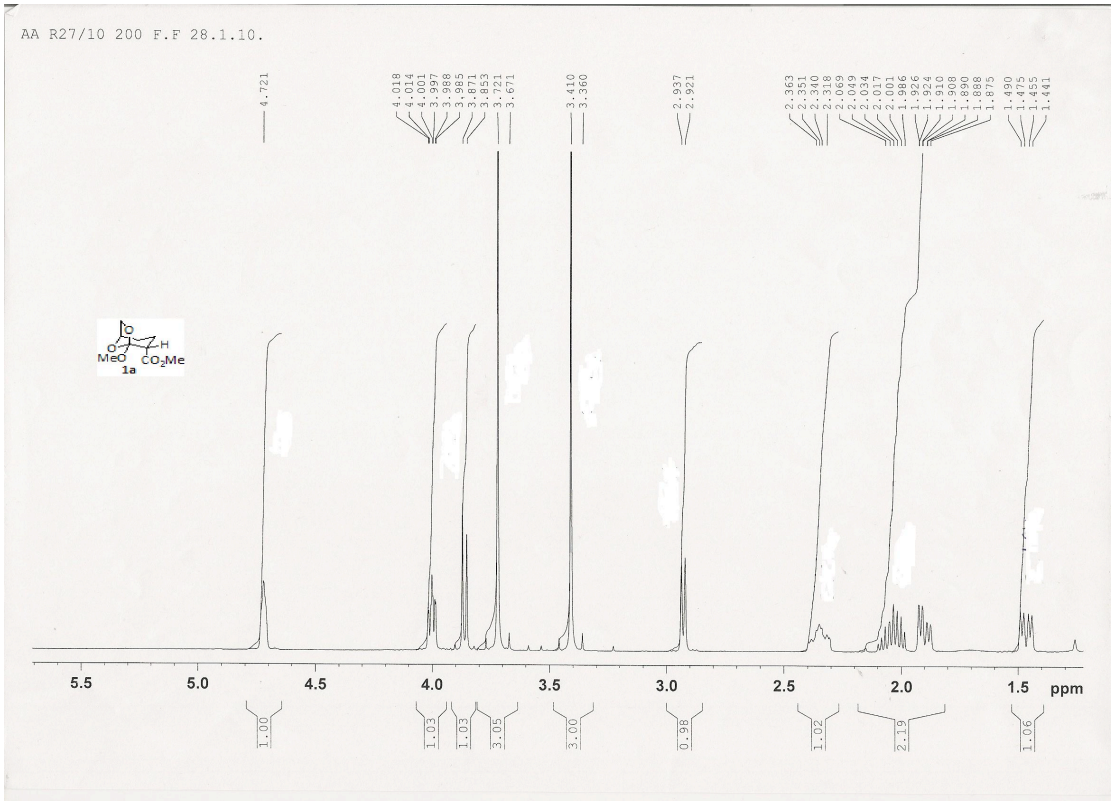
V_{max} (film)/cm^{-1} 3434br, 2940s, 2888s, 1484m, 1453s, 1384s, 1333s, 1213s, 1170s, 1121s, 1074s, 1016s, 959s, 889s, 849s, 739w.

δH (400 MHz; $CDCl_3$) 1.51 (3H, s, C<u>H</u>$_3$), 1.58-1.68 (2H, m, C<u>H</u>$_2$), 1.81-1.95 (3H, m, C<u>H</u>$_2$, C<u>H</u>), 2.41 (1H, s, O<u>H</u>), 3.50 (1H, d, J 10.4 Hz, C<u>H</u>$_2$), 3.74 (1H, dd, J 3.6 Hz, 11.2 Hz, C<u>H</u>$_2$), 3.85-3.90 (2H, m, C<u>H</u>$_2$), 4.54-4.55 (1H, m, C<u>H</u>).

δC (100 MHz; $CDCl_3$) 19.64 (<u>C</u>H$_2$), 22.25 (<u>C</u>H$_3$), 28.50 (<u>C</u>H$_2$), 44.80 (<u>C</u>H), 63.64 (<u>C</u>H$_2$), 68.87 (<u>C</u>H$_2$), 74.60 (<u>C</u>H), 109.14 (<u>C</u>).

m/z (ESI) Calculated for $C_8H_{14}O_3(Na^+)$ requires 181.0835; found 181.0835 and $C_8H_{14}O_3(H^+)$ requires 159.1016 found 159.1016.

1a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3.671
3.410
3.360
2.937
2.921
2.363
2.351
2.340
2.318
2.069
2.049
2.034
2.017
2.001
1.986
1.924
1.910
1.908
1.890
1.888
1.875
1.490
1.475
1.455
1.441
MeO
CO2Me
1a
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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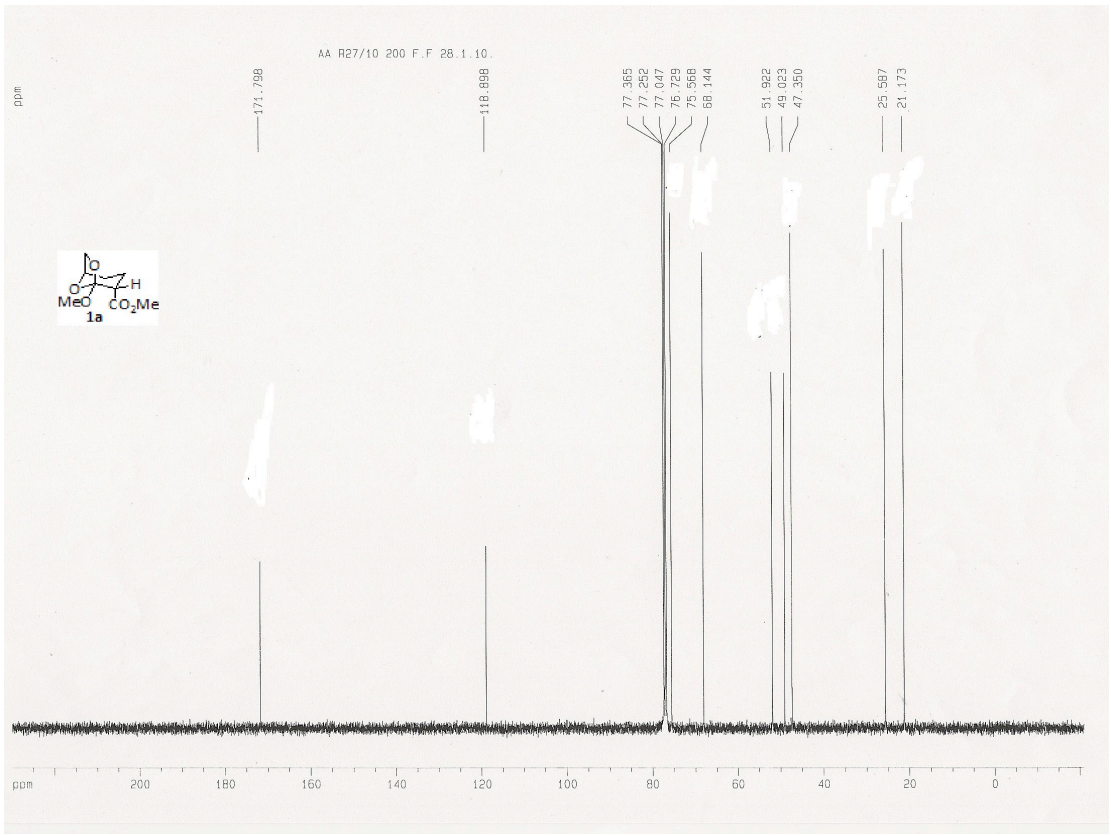
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49.023
47.350
25.587
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120
100
80
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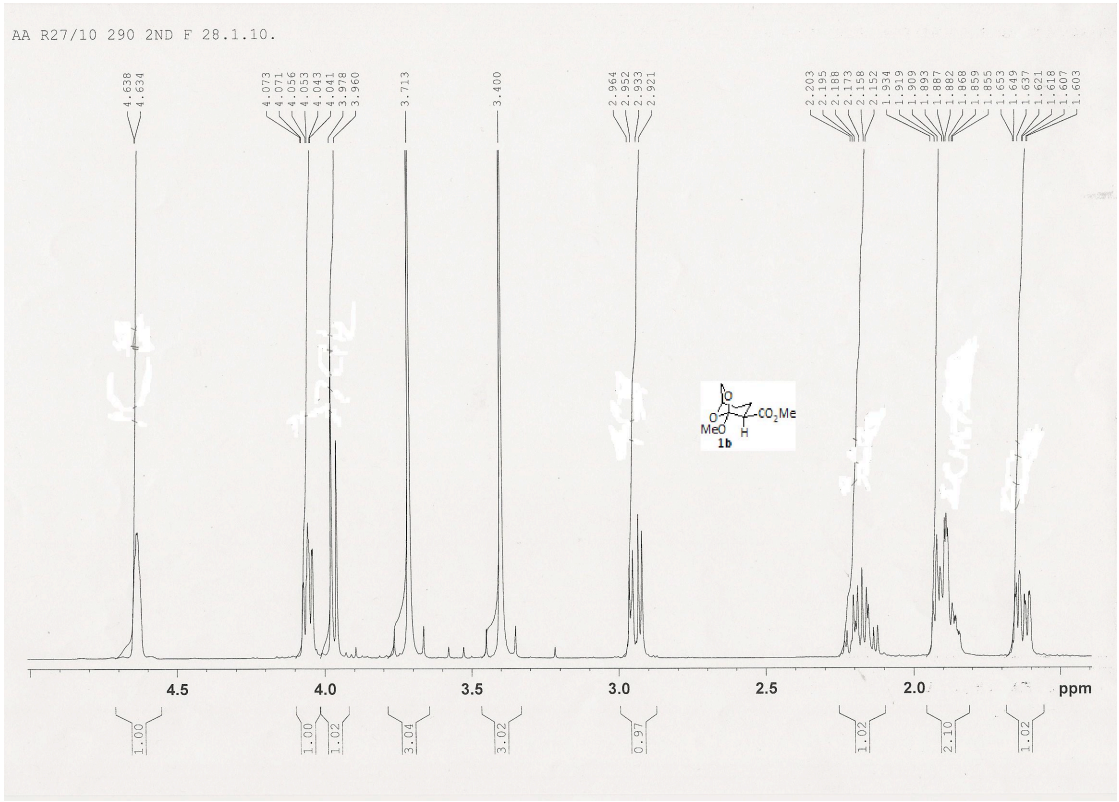
40
20
0

1b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3.400
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2.952
2.933
2.921
2.203
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2.158
2.152
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1.919
1.909
1.893
1.887
1.882
1.868
1.859
1.855
1.653
1.649
1.637
1.621
1.618
1.607
1.603
CO2Me
MeO
H
1b
4.5
4.0
3.5
3.0
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3.02
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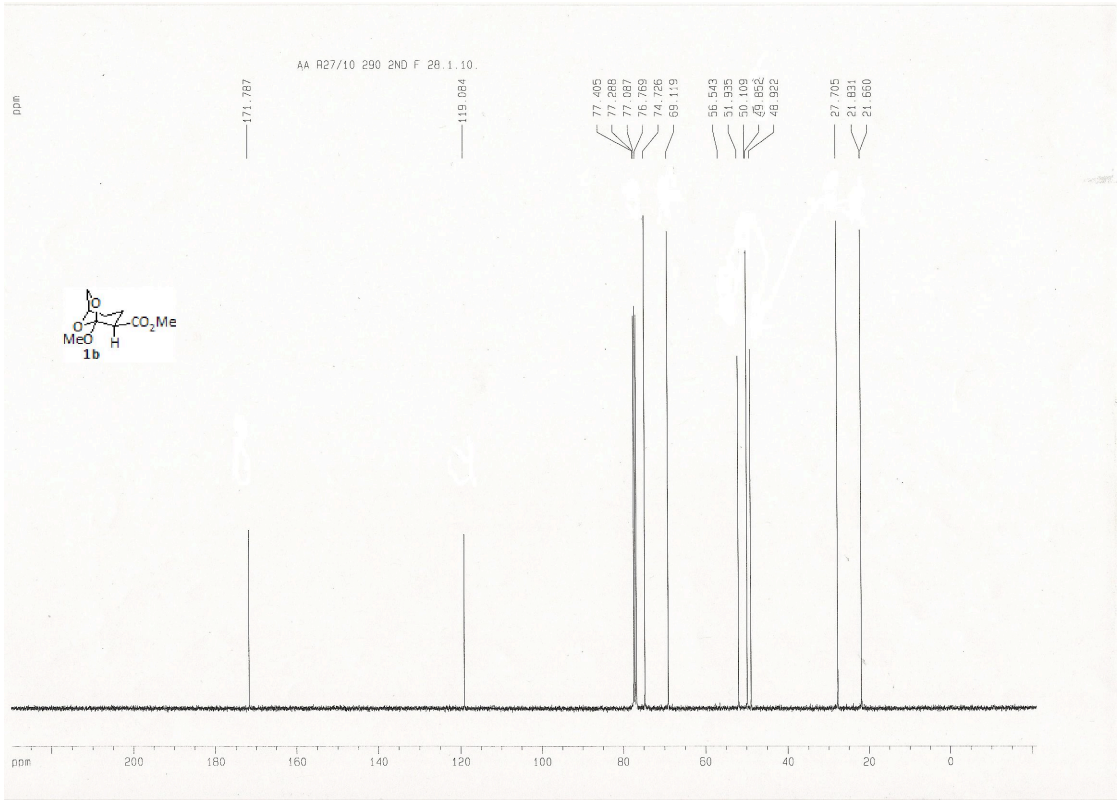
1.02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51.935
50.109
49.852
48.922
27.705
21.831
21.660
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MeO
H
1b
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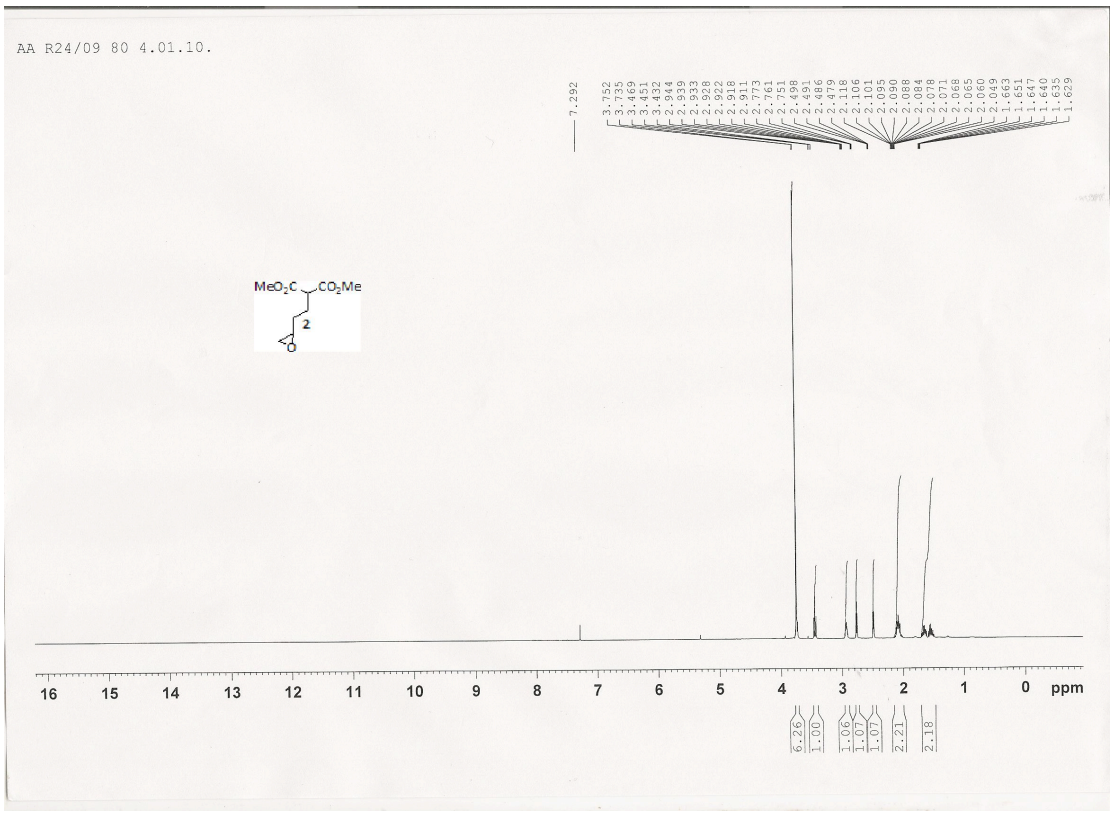
140
120
100
80
60
40
20
0

2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3.735
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3.432
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2.939
2.933
2.928
2.922
2.918
2.911
2.773
2.761
2.751
2.498
2.491
2.486
2.479
2.118
2.106
2.101
2.095
2.090
2.088
2.084
2.078
2.071
2.068
2.065
2.060
2.049
1.663
1.651
1.647
1.640
1.635
1.629
MeO2C
CO2Me
2
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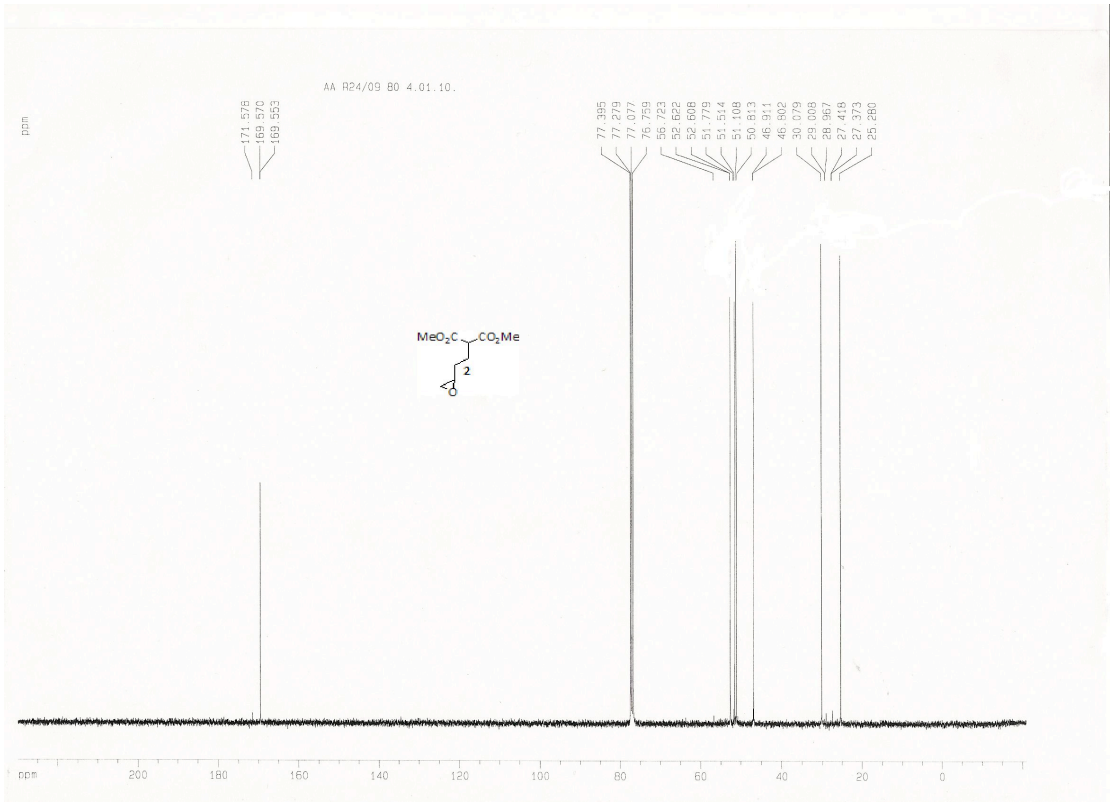
1.06
1.07
1.07
2.21
2.18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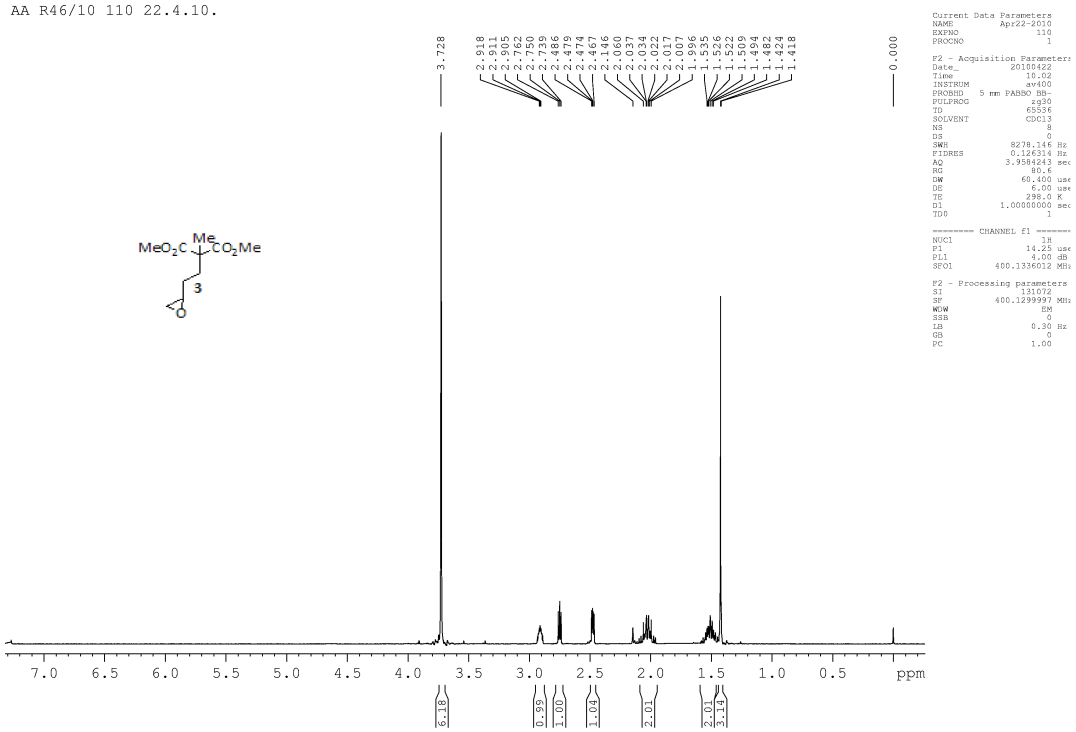
3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2.739
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2.479
2.474
2.467
2.146
2.060
2.037
2.034
2.022
2.017
2.007
1.996
1.535
1.526
1.522
1.489
1.482
1.424
1.418
0.000
MeO2C
Me
CO2Me
3
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.04
2.01
2.01
3.14
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NAME Apr22-2010
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PROCNO 1
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Time 10.02
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PULPROG zg30
TD 65536
SOLVENT CDCl3
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FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 80.6
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
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PL1 4.00 dB
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SF 400.1299997 MHz
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SSB 0
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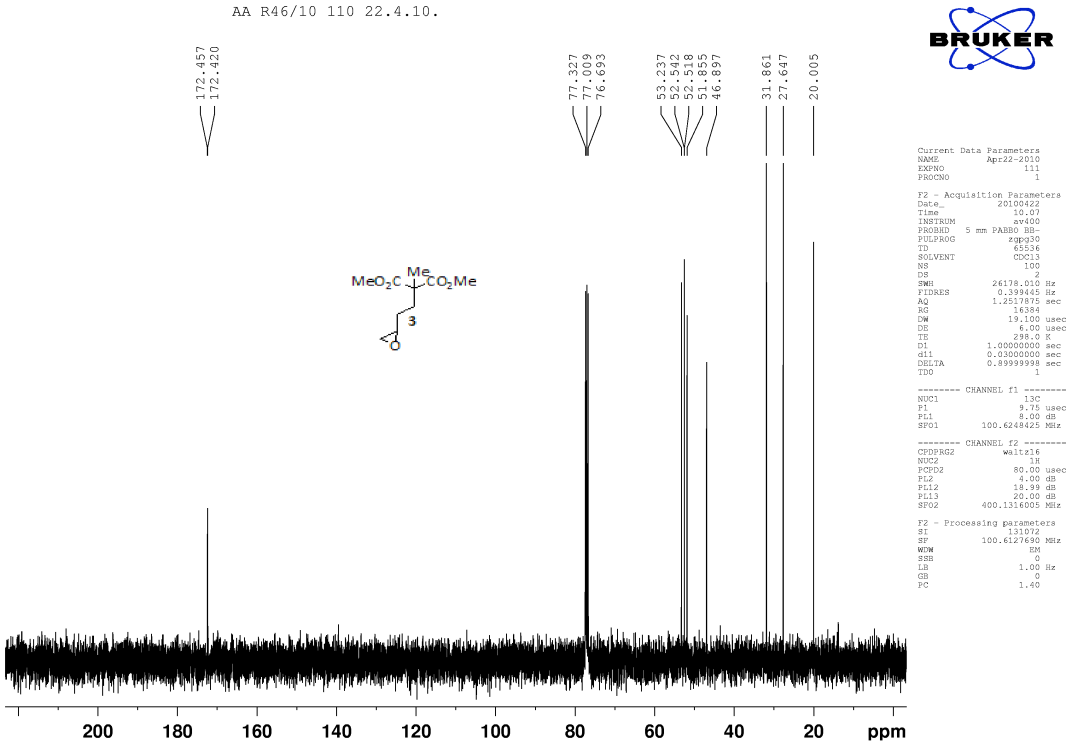
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CO2Me
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160
140
120
100
80
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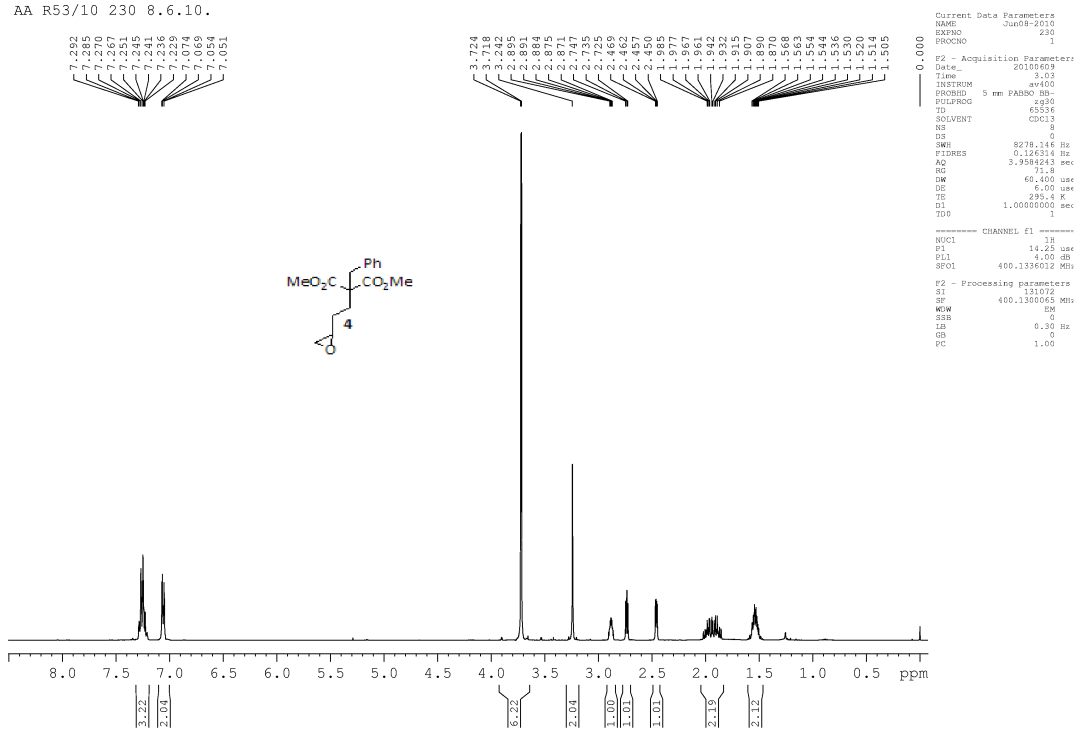
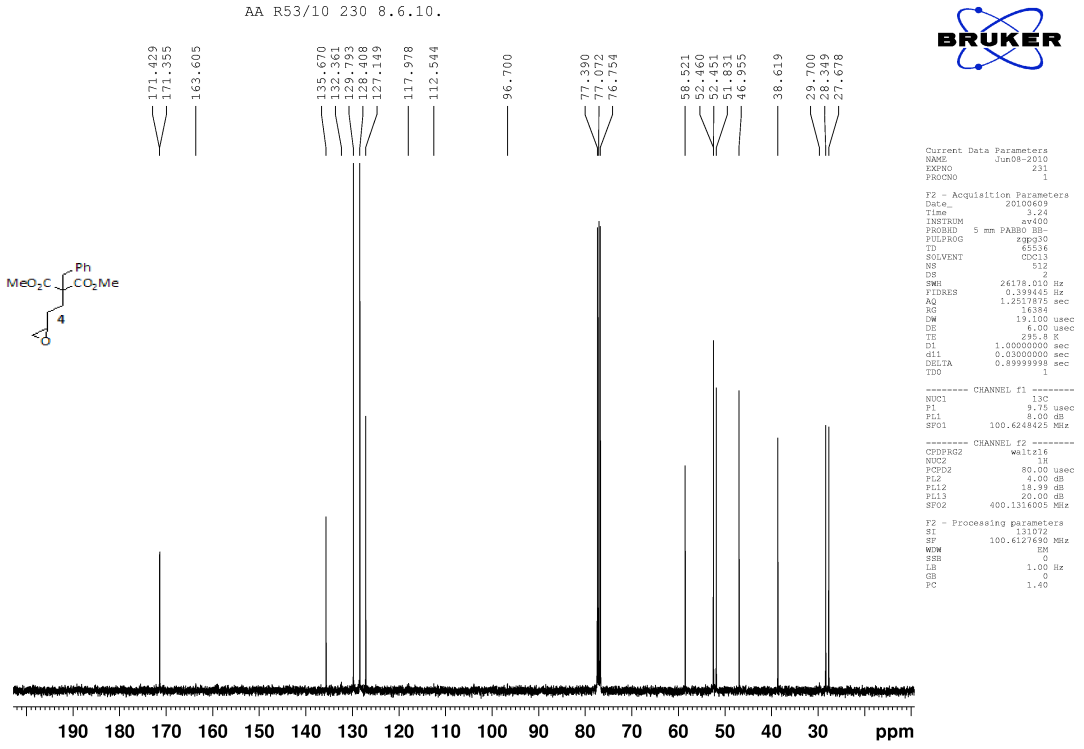
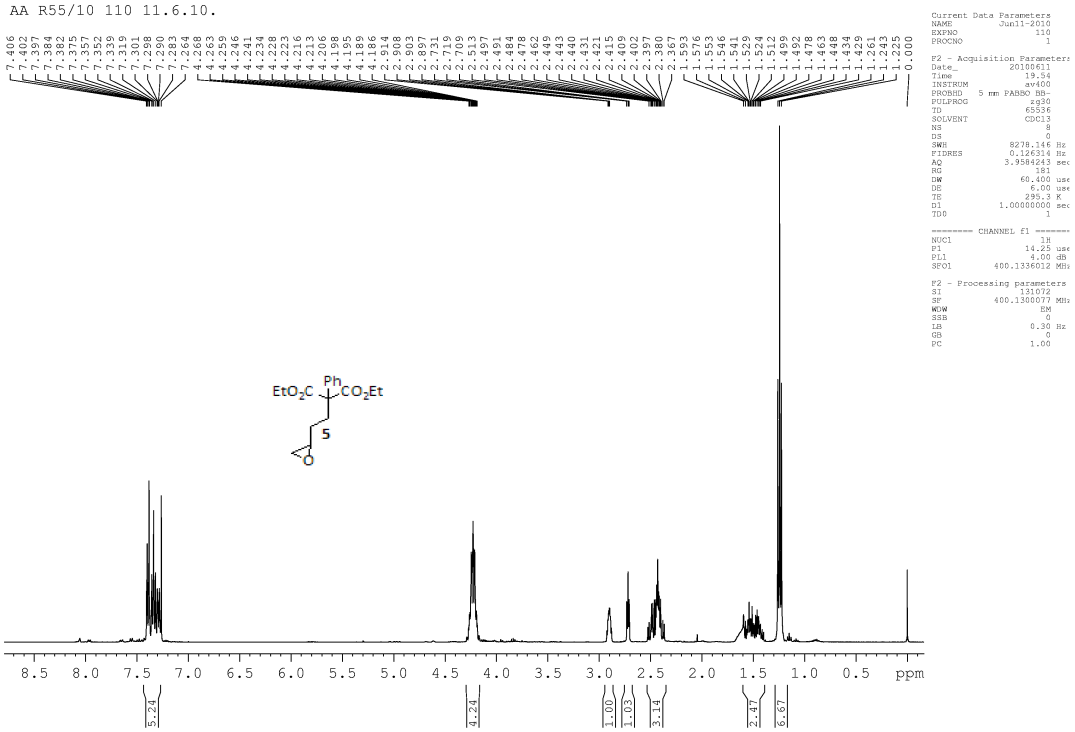
40
20
ppm
Current Data Parameters
NAME Apr22-2010
EXPNO 111
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100422
Time 10.07
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

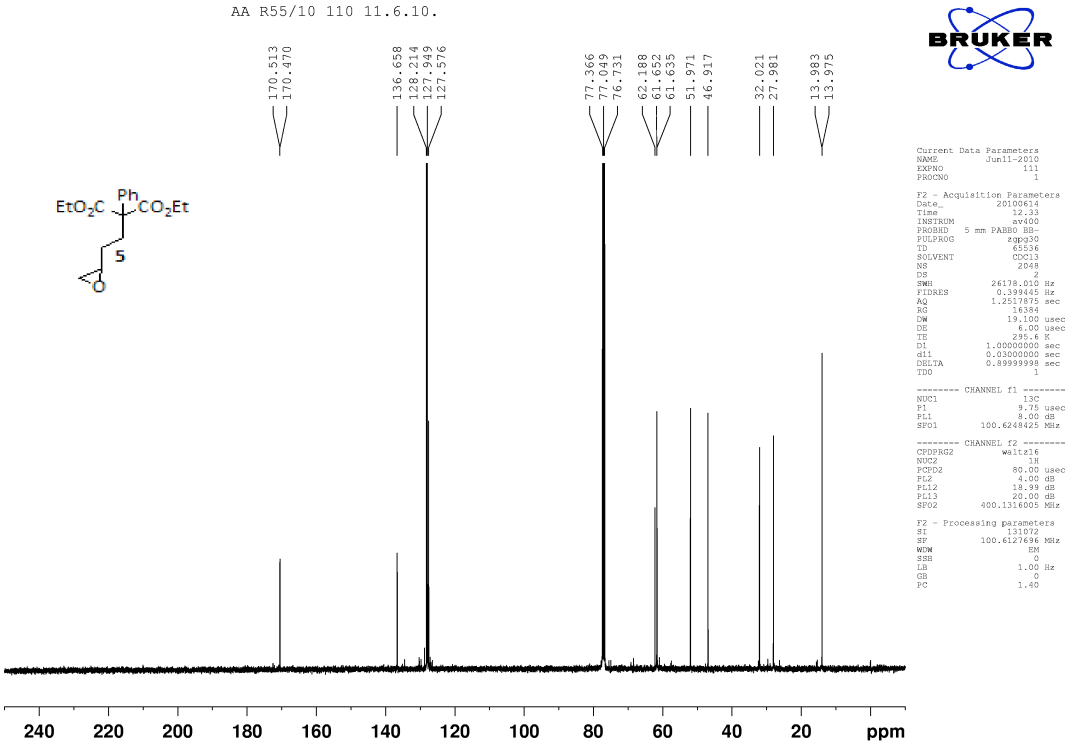
4


AA R53/10 230 8.6.10.
Ph
MeO2C
CO2Me
4
O
ppm

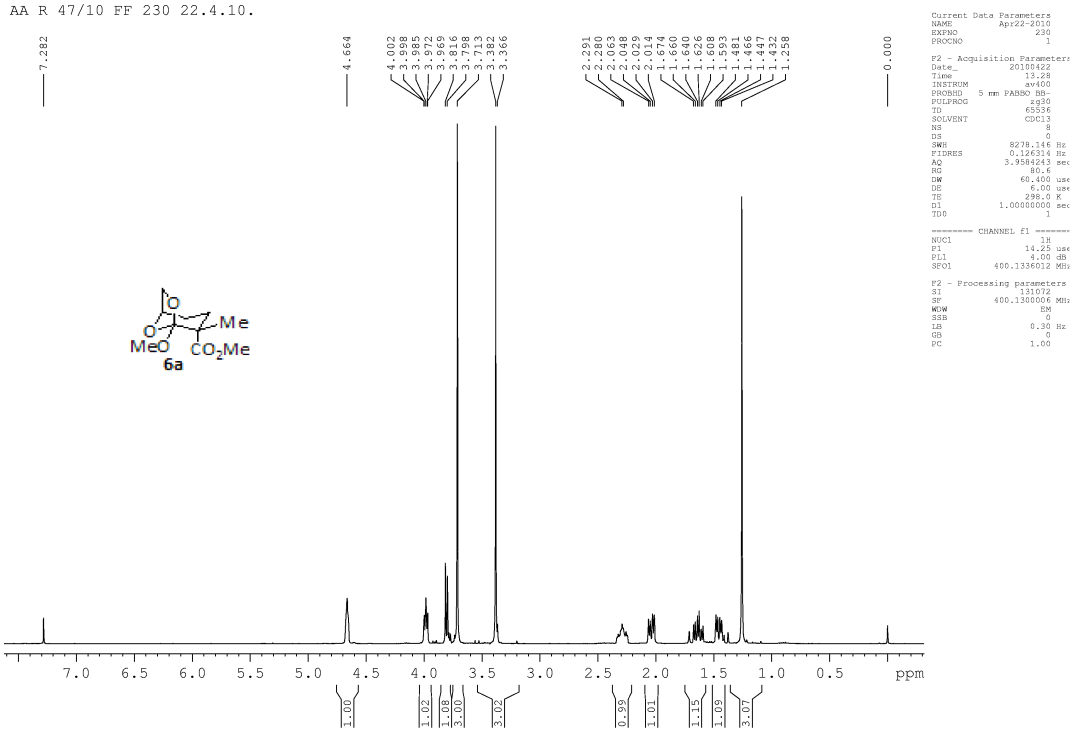

AA R53/10 230 8.6.10.
BRUKER
Ph
MeO2C
CO2Me
4
O
ppm

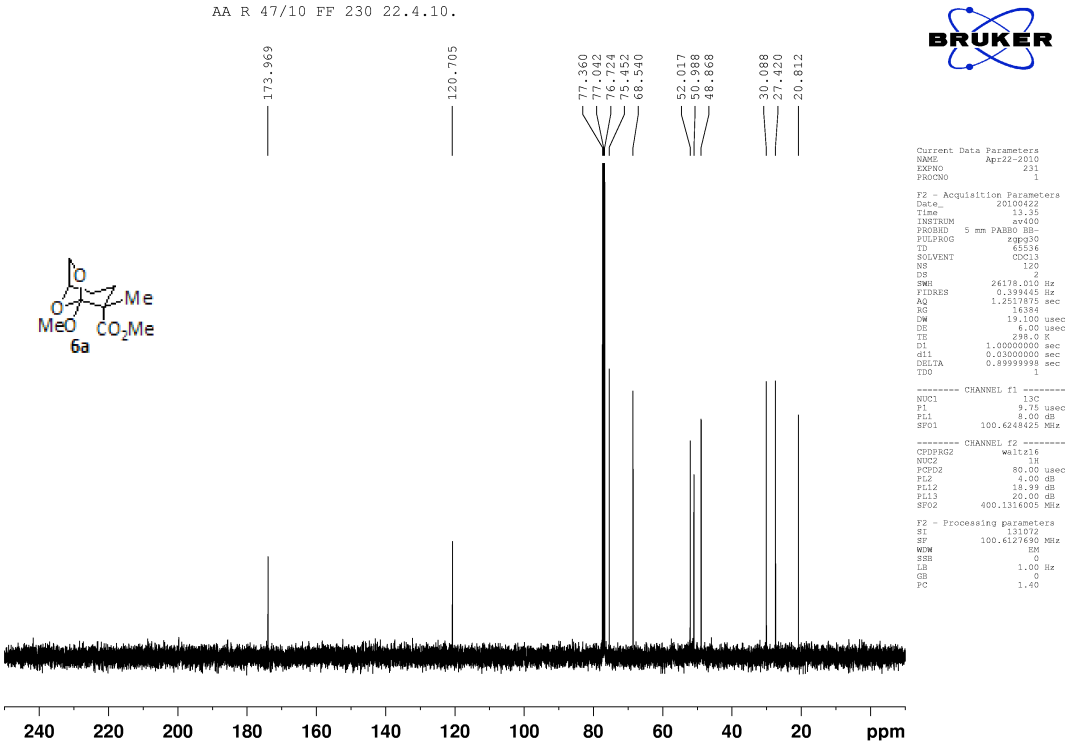
5


AA R55/10 110 11.6.10.
EtO2C
Ph
CO2Et
5
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.24
4.24
1.00
1.03
3.14
2.47
6.67

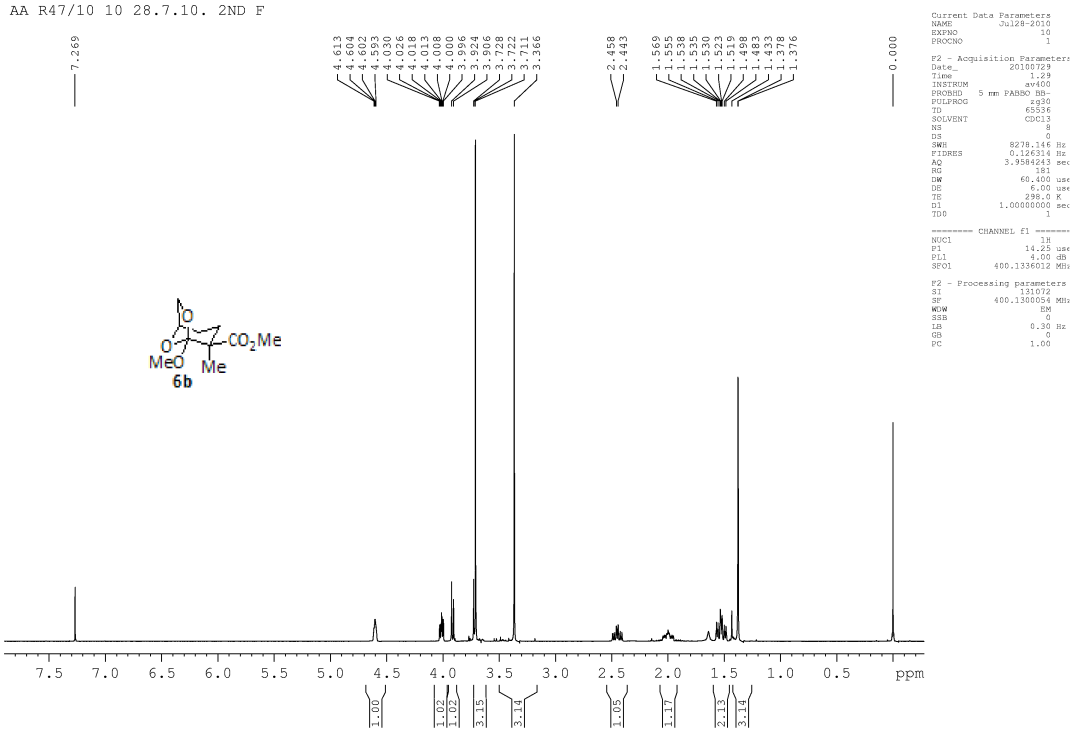

AA R55/10 110 11.6.10.
EtO2C
Ph
CO2Et
5
O
240 220 200 180 160 140 120 100 80 60 40 20 ppm

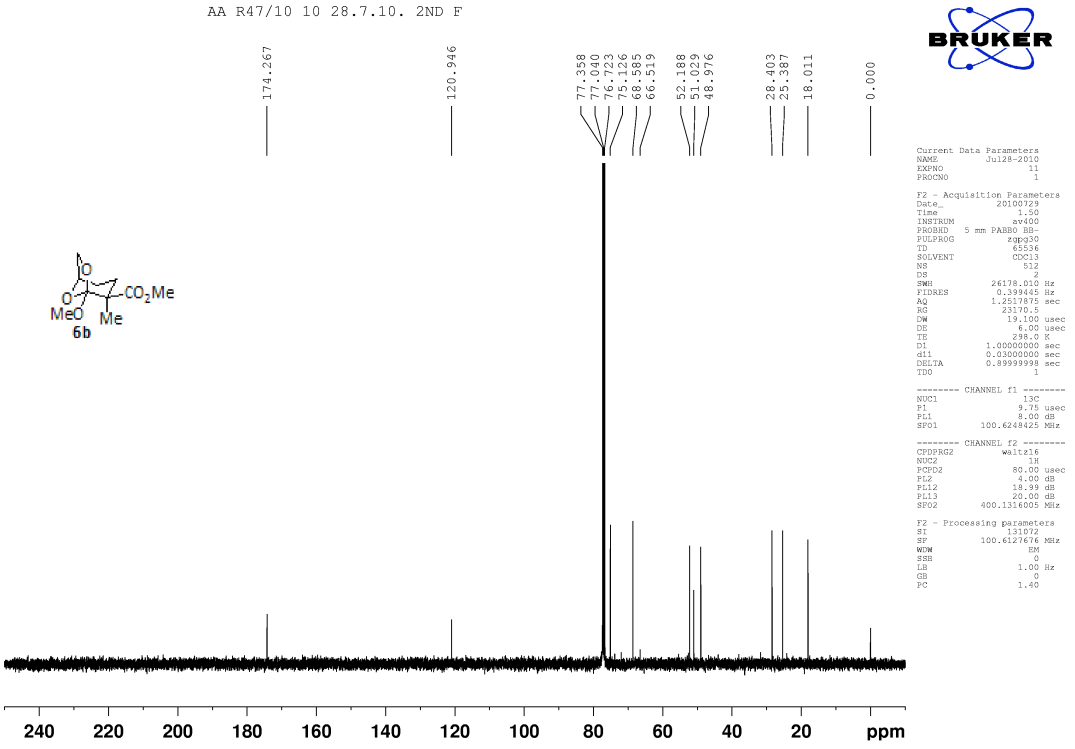
6a


AA R 47/10 FF 230 22.4.10.
7.282
4.664
4.002
3.988
3.985
3.972
3.969
3.816
3.798
3.713
3.382
3.366
2.291
2.280
2.063
2.048
2.029
2.014
1.674
1.660
1.640
1.626
1.608
1.593
1.481
1.466
1.447
1.432
1.258
0.000
Me
MeO
CO2Me
6a
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.02
1.08
3.00
3.02
0.99
1.01
1.15
1.09
3.07

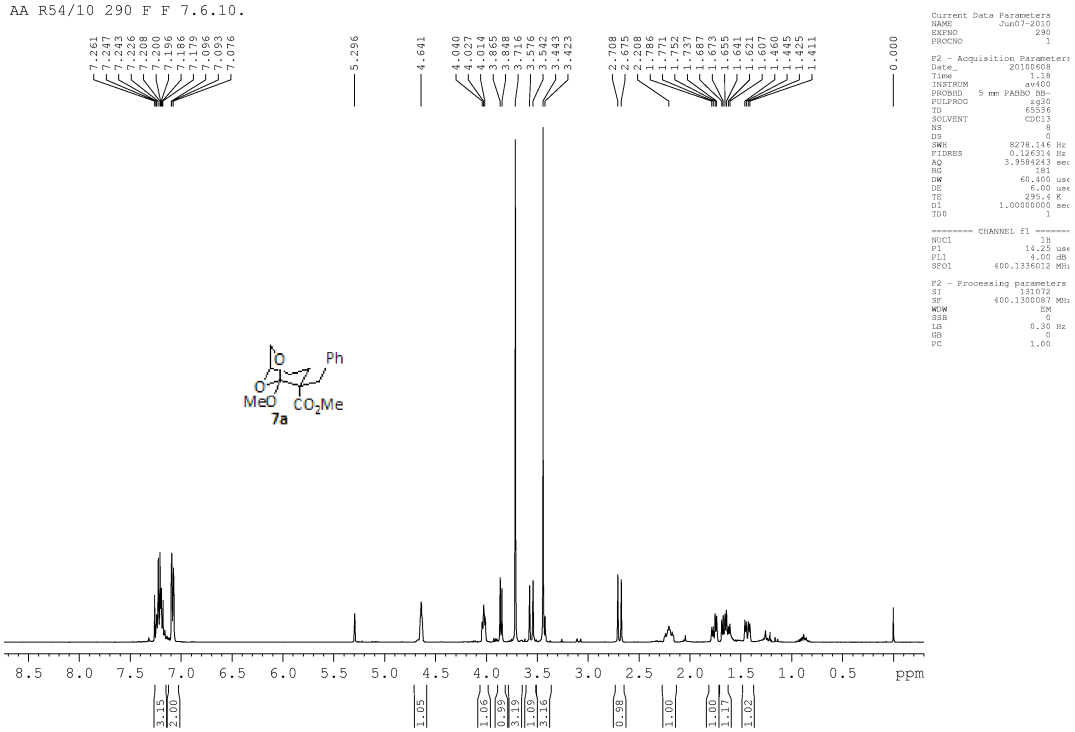

AA R 47/10 FF 230 22.4.10.
173.969
120.705
77.360
77.042
76.724
75.452
68.540
52.017
50.988
48.868
30.088
27.420
20.812
Me
MeO
CO2Me
6a
240
220
200
180
160
140
120
100
80
60
40
20
ppm

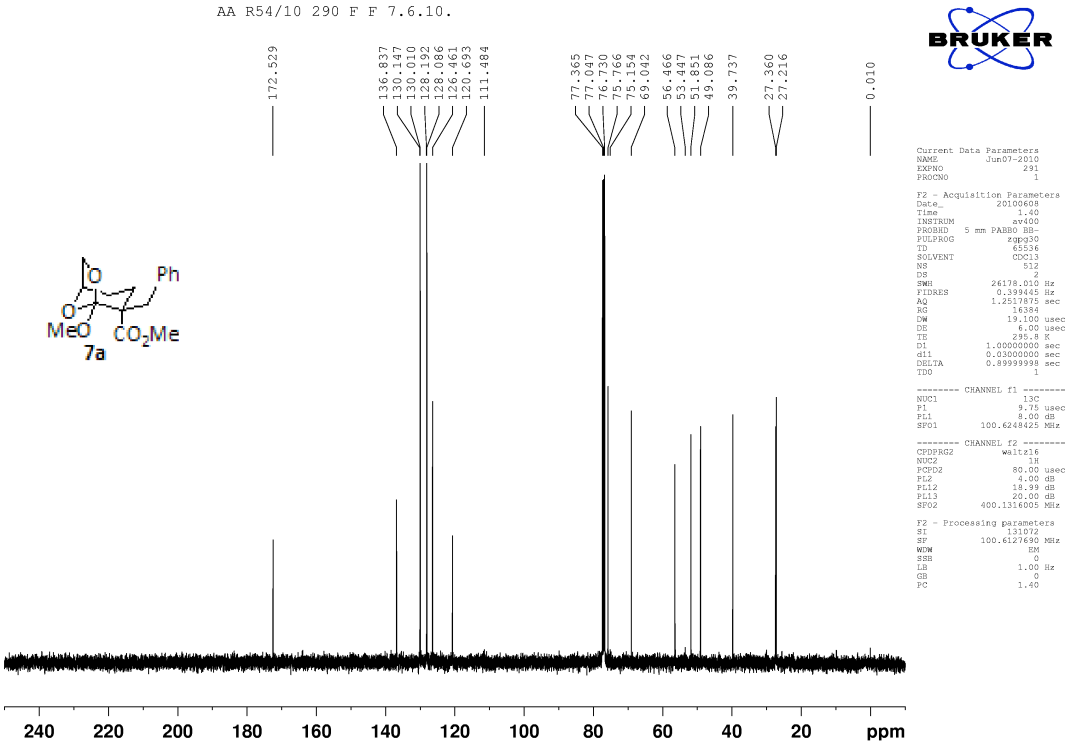
6b


AA R47/10 10 28.7.10. 2ND F
7.269
4.613
4.604
4.602
4.593
4.030
4.026
4.018
4.013
4.008
4.000
3.996
3.984
3.966
3.728
3.722
3.711
3.366
2.458
2.443
1.569
1.555
1.538
1.535
1.530
1.523
1.519
1.498
1.483
1.433
1.378
1.376
0.000
Current Data Parameters
NAME Jul28-2010
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100729
Time 1.29
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
MeO
CO2Me
Me
6b
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.02
1.02
3.15
3.14
1.05
1.17
2.13
3.14

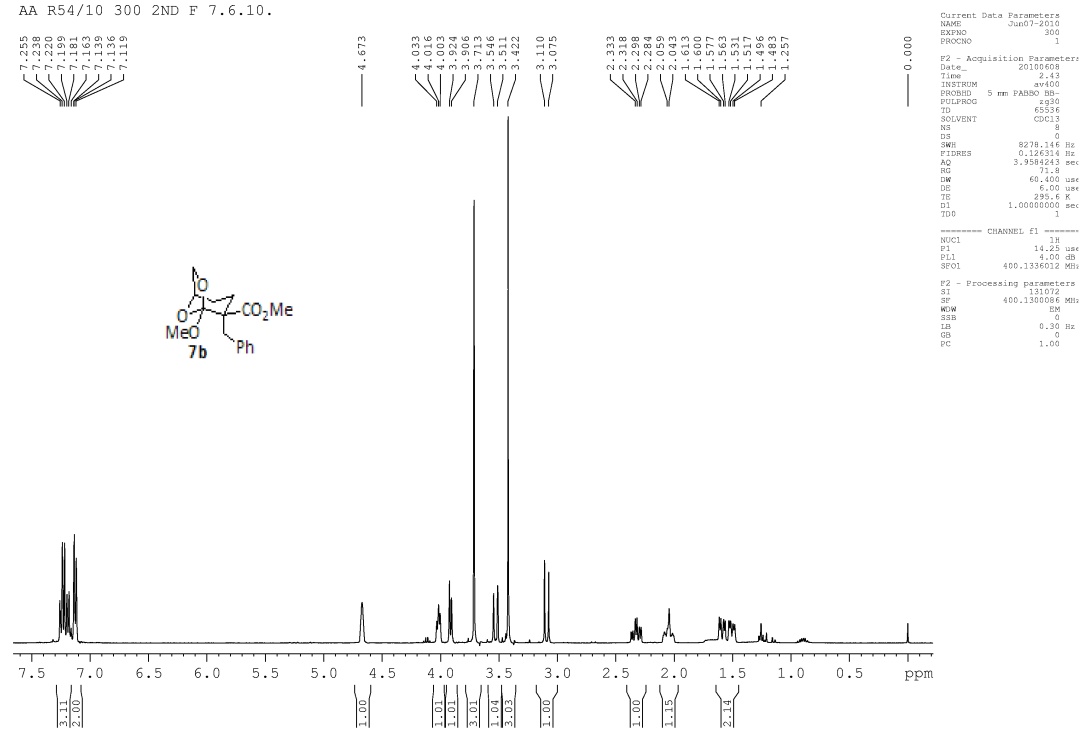

AA R47/10 10 28.7.10. 2ND F
BRUKER
174.267
120.946
77.358
77.040
76.723
75.126
68.585
66.519
52.188
51.029
48.976
28.403
25.387
18.011
0.000
Current Data Parameters
NAME Jul28-2010
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100729
Time 1.50
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 23170.5
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127676 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
MeO
CO2Me
Me
6b
240 220 200 180 160 140 120 100 80 60 40 20 ppm

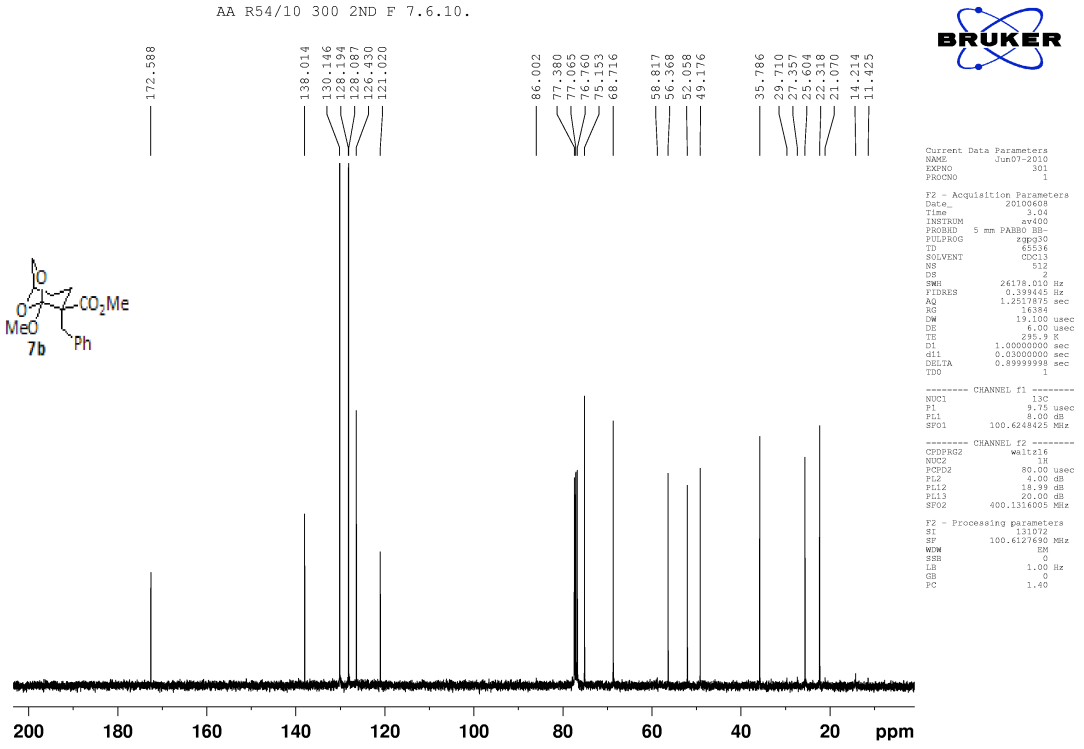
7a


AA R54/10 290 F F 7.6.10.
7.261 7.247 7.243 7.226 7.208 7.200 7.196 7.179 7.096 7.093 7.076
5.296
4.641
4.040 4.027 4.014 3.865 3.848 3.716 3.576 3.542 3.443 3.423
2.708 2.675 2.208 1.786 1.771 1.752 1.737 1.687 1.663 1.655 1.641 1.621 1.607 1.460 1.445 1.425 1.411
0.000
Current Data Parameters
NAME Jun07-2010
EXPNO 290
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100608
Time 1.18
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
Ph
O
MeO
CO2Me
7a
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.15 2.00 1.05 1.06 0.99 3.19 1.06 1.16 0.98 1.00 1.00 1.17 1.02

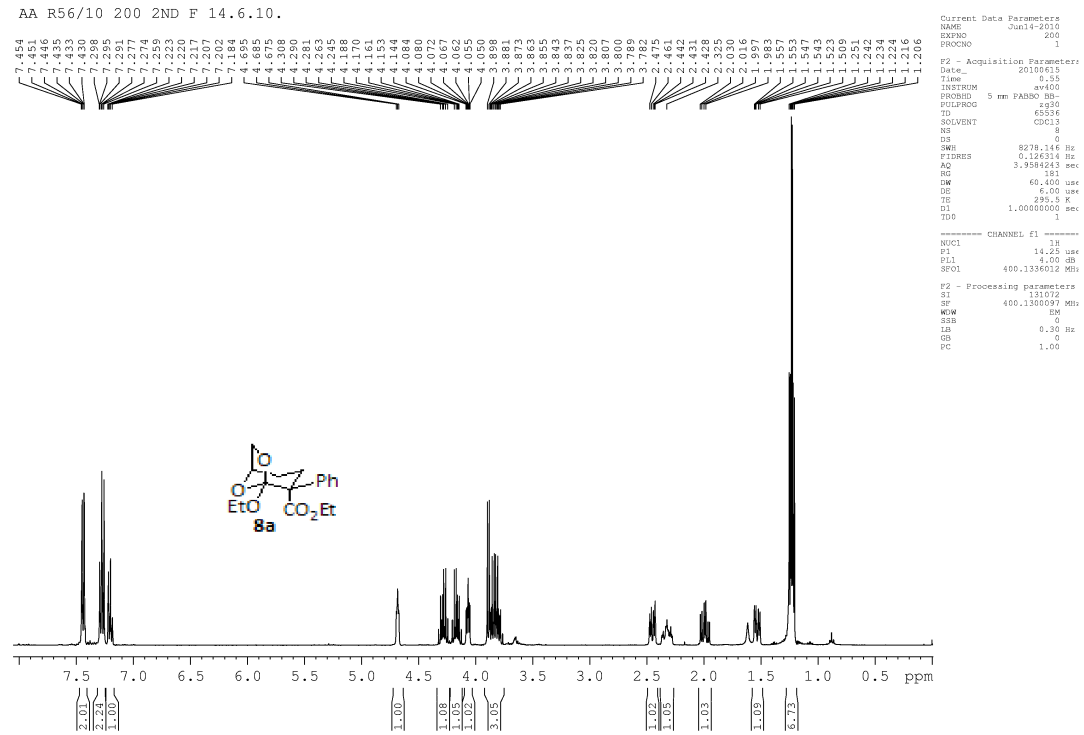

AA R54/10 290 F F 7.6.10.
BRUKER
172.529
136.837 130.147 130.010 128.192 128.086 126.461 120.693 111.484
77.365 77.047 76.730 75.766 75.154 69.042
56.466 53.447 51.851 49.086
39.737
27.360 27.216
0.010
Current Data Parameters
NAME Jun07-2010
EXPNO 291
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100608
Time 1.40
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 295.8 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
Ph
O
MeO
CO2Me
7a
240 220 200 180 160 140 120 100 80 60 40 20 ppm

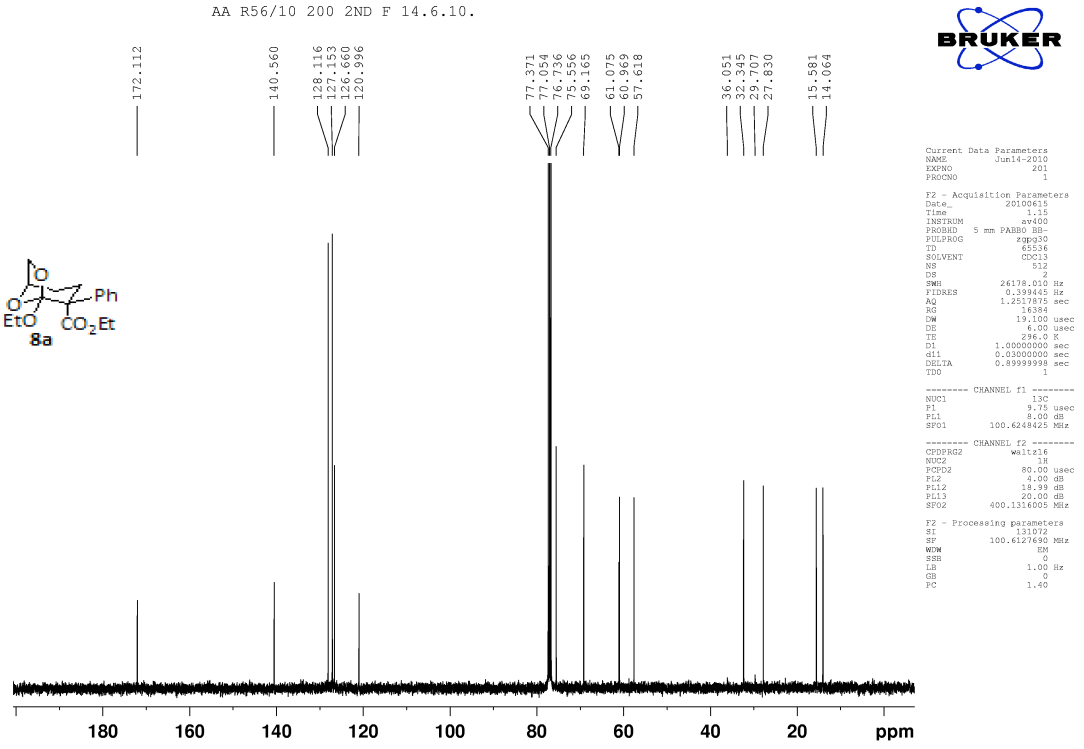
7b


AA R54/10 300 2ND F 7.6.10.
7.255
7.238
7.220
7.199
7.181
7.163
7.139
7.136
7.119
4.673
4.033
4.016
4.003
3.924
3.906
3.713
3.546
3.511
3.422
3.110
3.075
2.333
2.318
2.298
2.284
2.059
2.043
1.613
1.600
1.577
1.553
1.531
1.517
1.496
1.483
1.257
0.000
MeO
CO2Me
Ph
7b
ppm

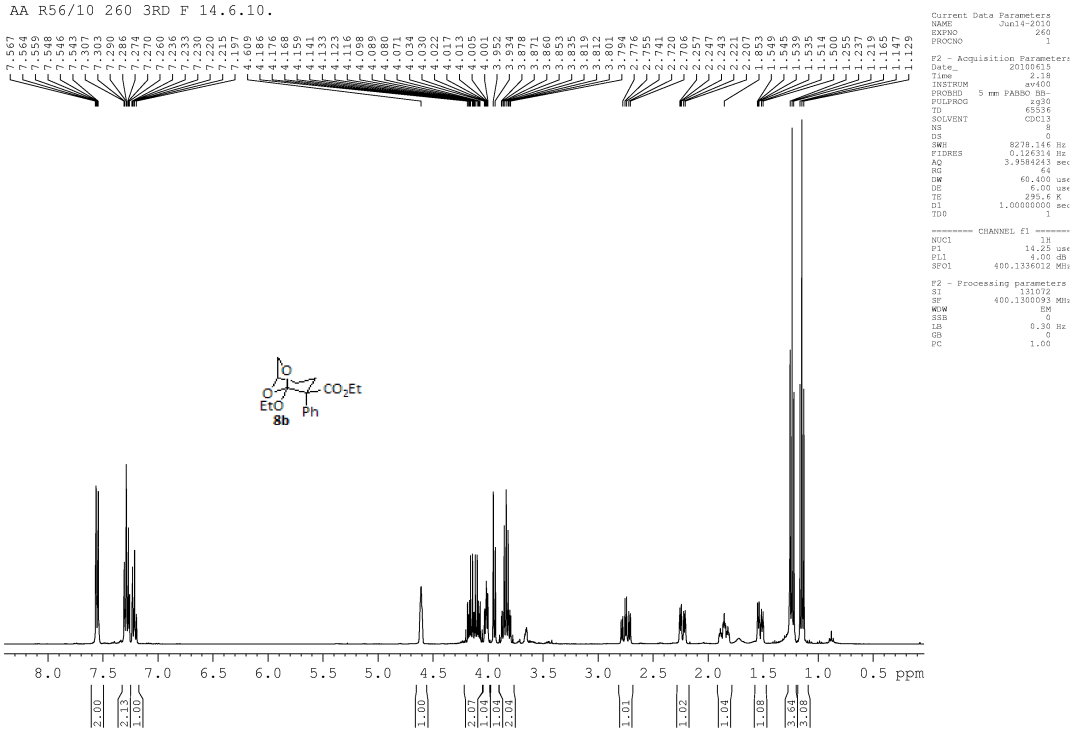

AA R54/10 300 2ND F 7.6.10.
172.588
138.014
130.146
128.194
128.087
126.430
121.020
86.002
77.380
77.065
76.760
75.153
68.716
58.817
56.368
52.058
49.176
35.786
29.710
27.357
25.604
22.318
21.070
14.214
11.425
MeO
CO2Me
Ph
7b
ppm

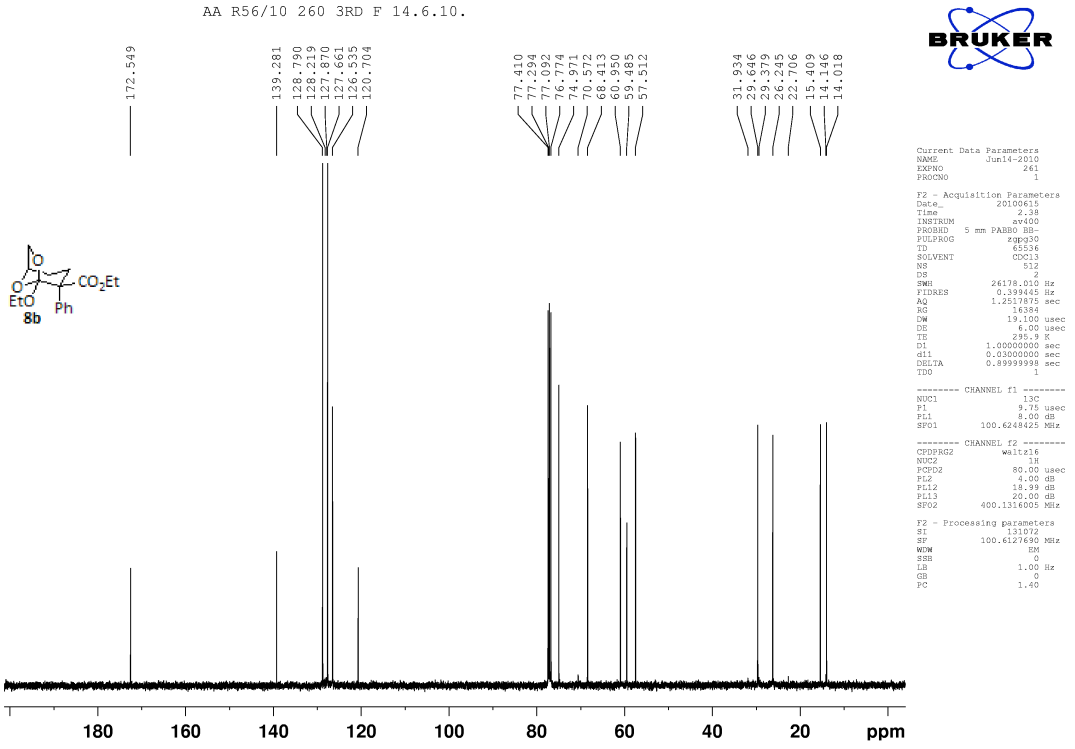
8a

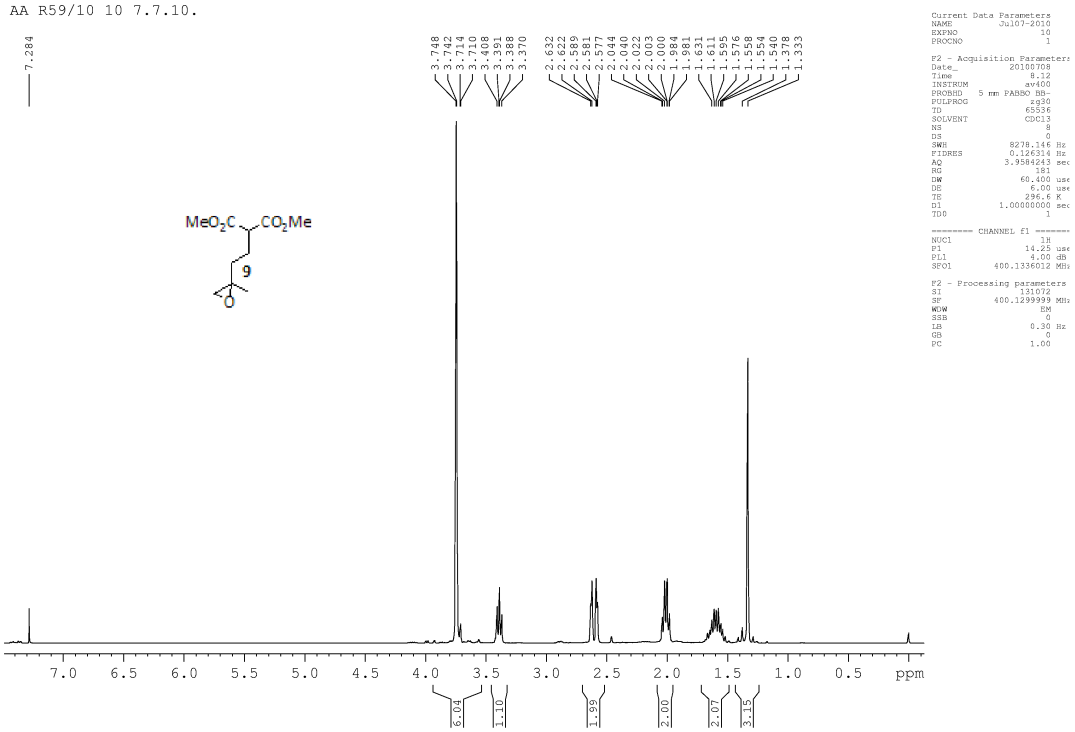

AA R56/10 200 2ND F 14.6.10.
Ph
EtO
CO2Et
8a
ppm

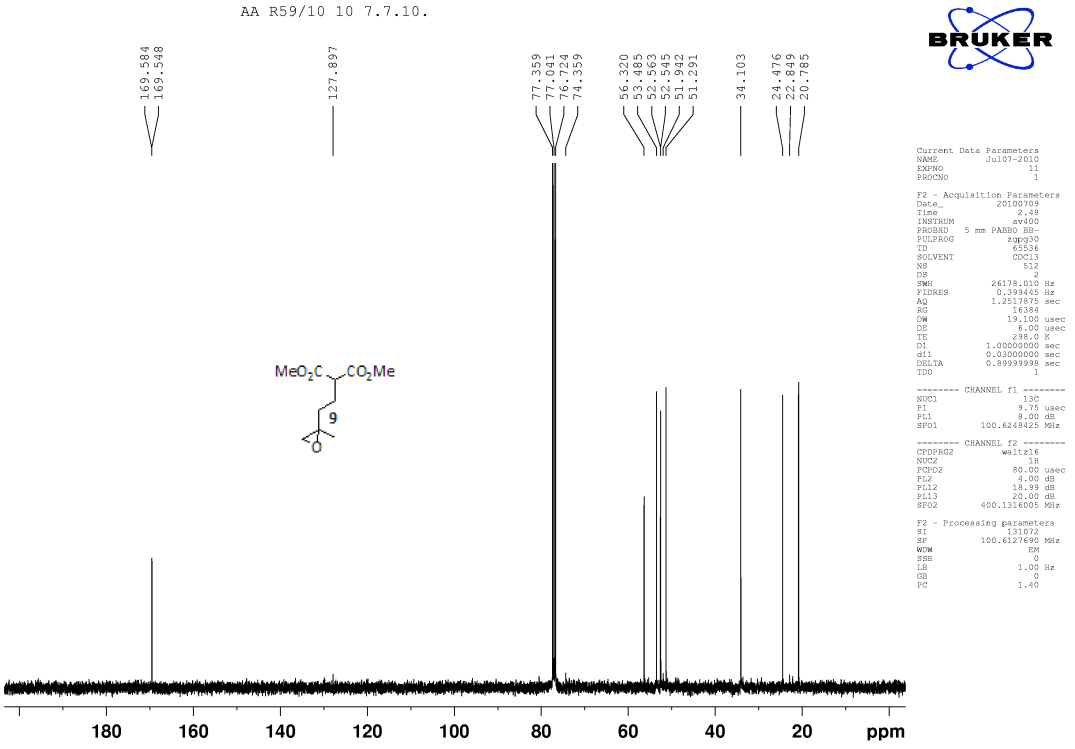

AA R56/10 200 2ND F 14.6.10.
BRUKER
Ph
EtO
CO2Et
8a
ppm

8b

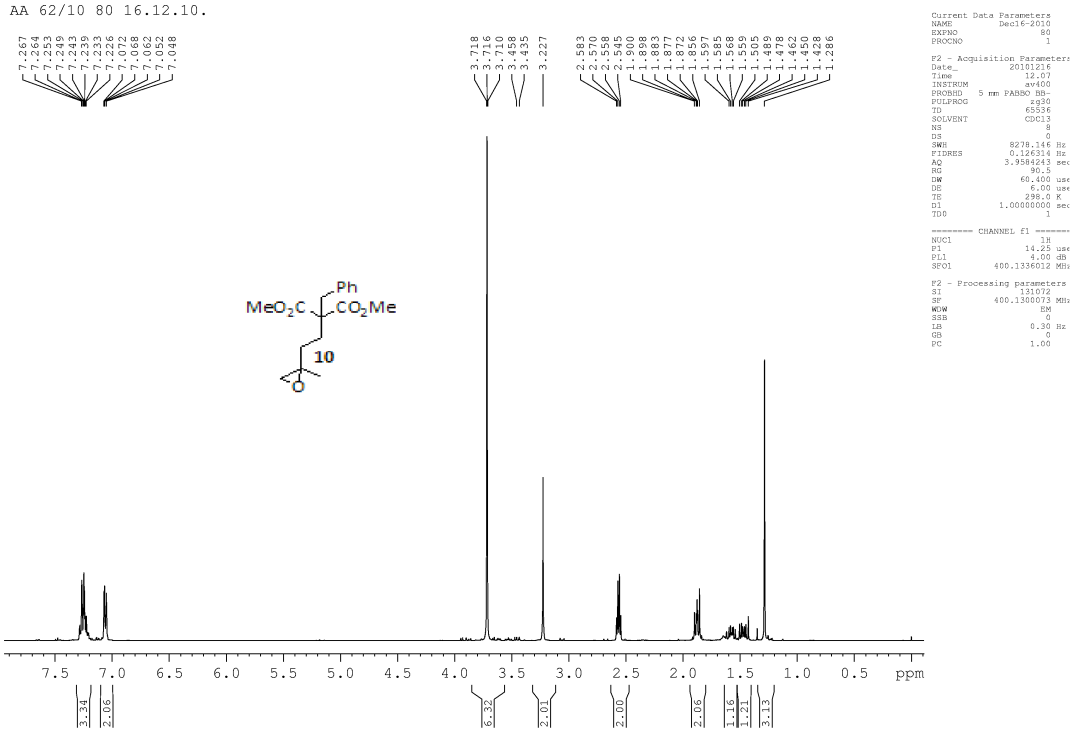

AA R56/10 260 3RD F 14.6.10.
8b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


AA R56/10 260 3RD F 14.6.10.
8b
180 160 140 120 100 80 60 40 20 ppm


AA R59/10 10 7.7.10.
7.284
3.748
3.742
3.714
3.710
3.408
3.391
3.388
3.370
2.632
2.622
2.589
2.581
2.577
2.044
2.040
2.022
2.003
2.000
1.984
1.981
1.621
1.611
1.565
1.558
1.554
1.540
1.378
1.333
MeO2C
CO2Me
9
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.04
1.10
1.99
2.00
2.07
3.15
Current Data Parameters
NAME Ju107-2010
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100708
Time 8.12
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1299999 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


AA R59/10 10 7.7.10.
169.584
169.548
127.897
77.359
77.041
76.724
74.359
56.320
53.485
52.563
52.545
51.942
51.291
34.103
24.476
22.849
20.785
MeO2C
CO2Me
9
O
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Ju107-2010
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100709
Time 2.48
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

10

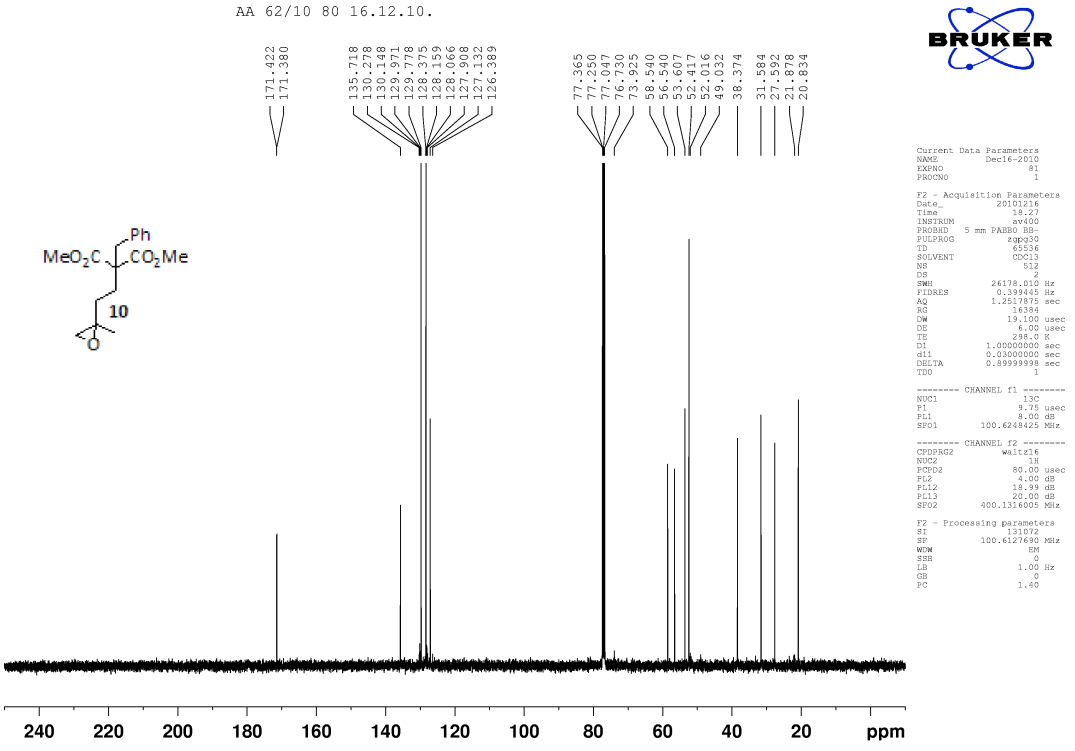


Current Data Parameters
NAME Dec16-2010
EXPNO 80
PROCNO 1

F2 - Acquisition Parameters
Date_ 20101216
Time 12.07
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 131072
SF 400.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME Dec16-2010
EXPNO 81
PROCNO 1

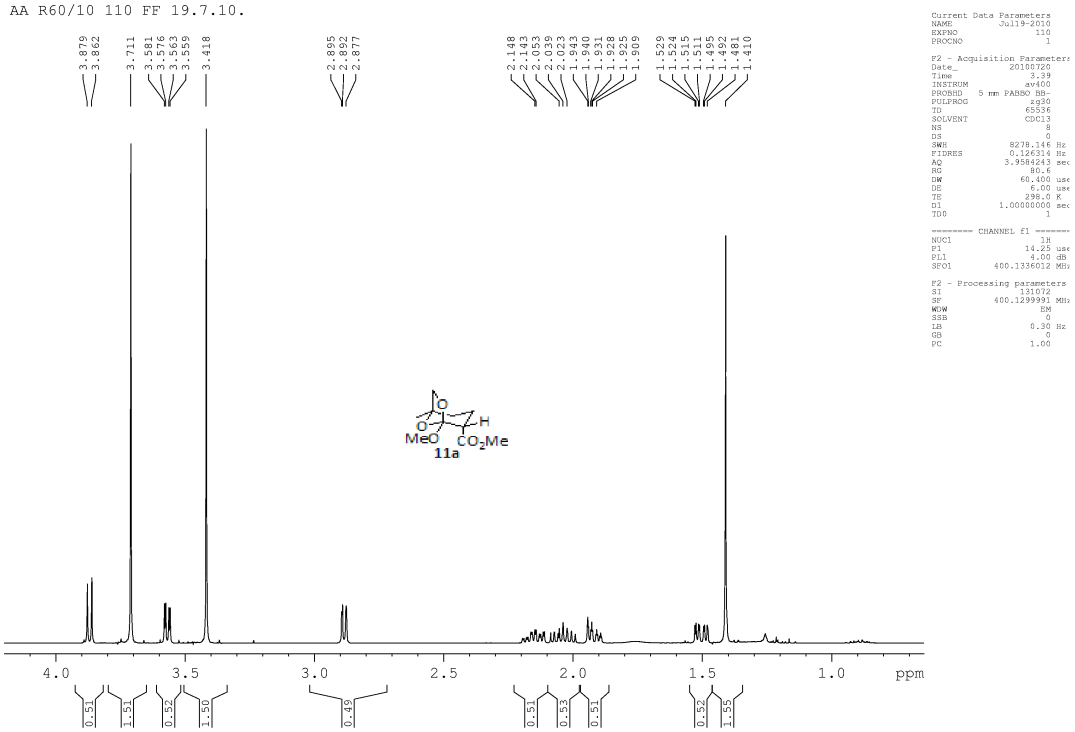
F2 - Acquisition Parameters
Date_ 20101216
Time 19.27
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

11a

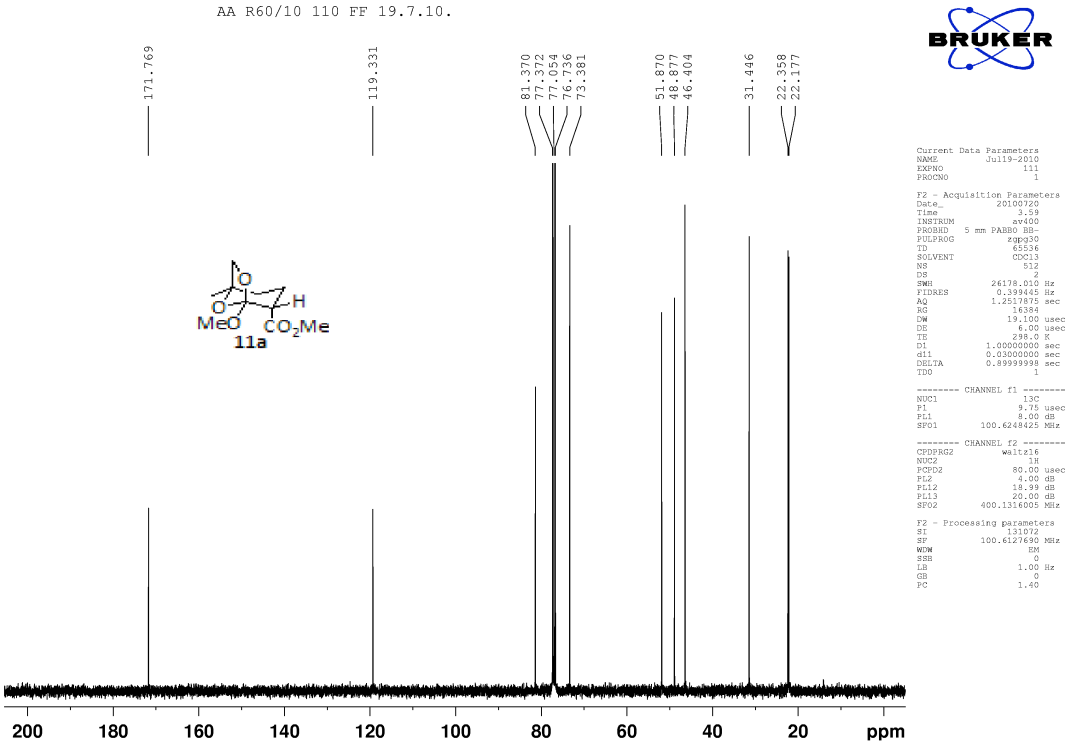


Current Data Parameters
NAME Jul19-2010
EXPNO 110
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100720
Time 3.39
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 80.6
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 131072
SF 400.1299991 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME Jul19-2010
EXPNO 111
PROCNO 1

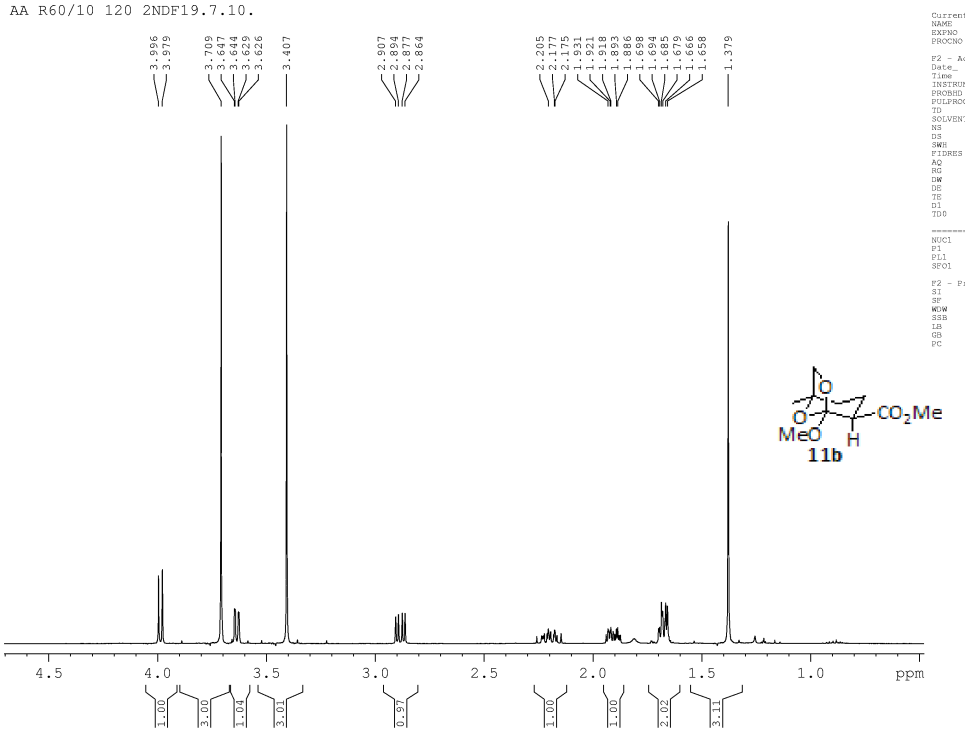
F2 - Acquisition Parameters
Date_ 20100720
Time 3.59
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

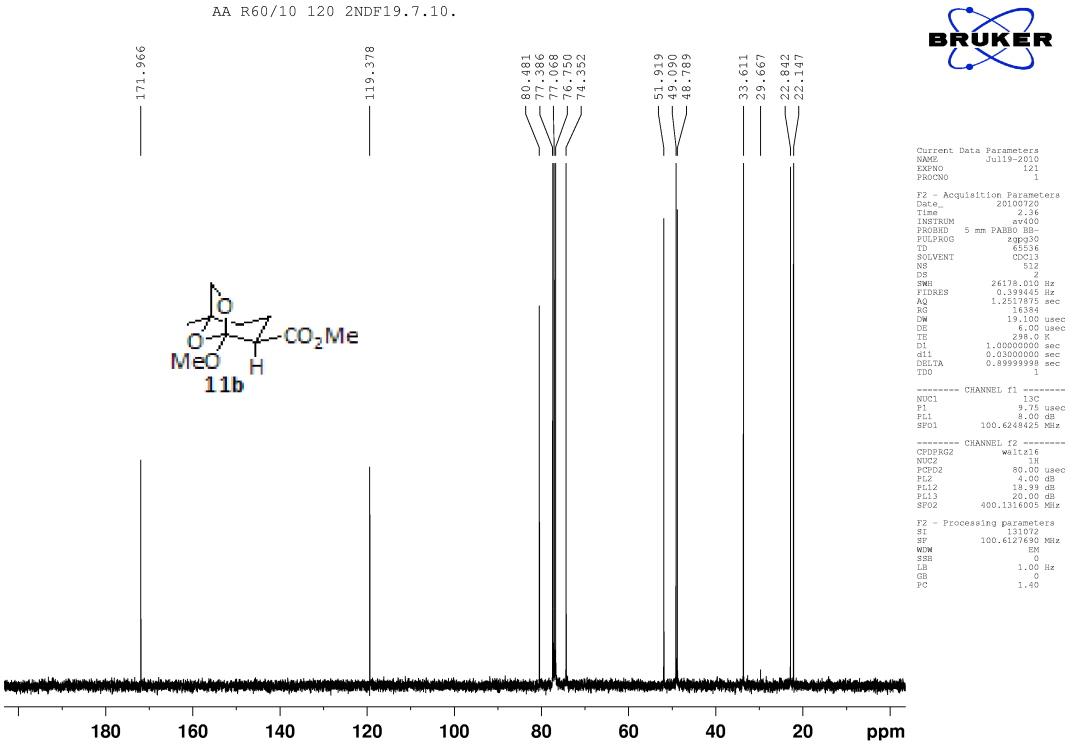
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

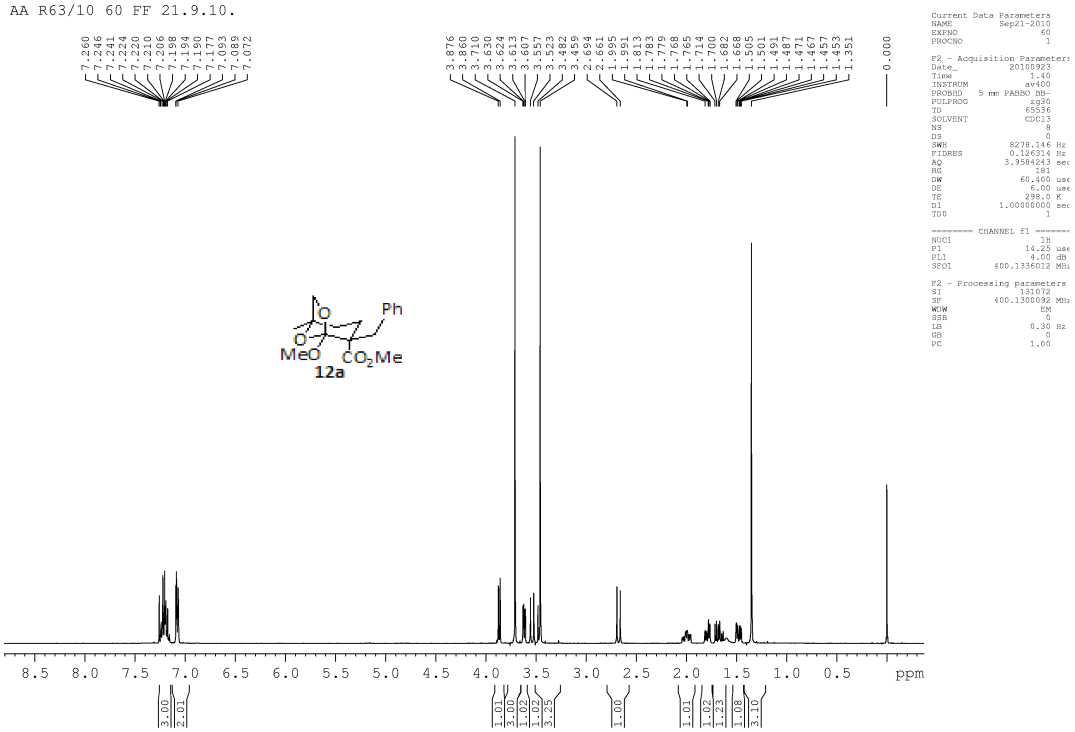
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

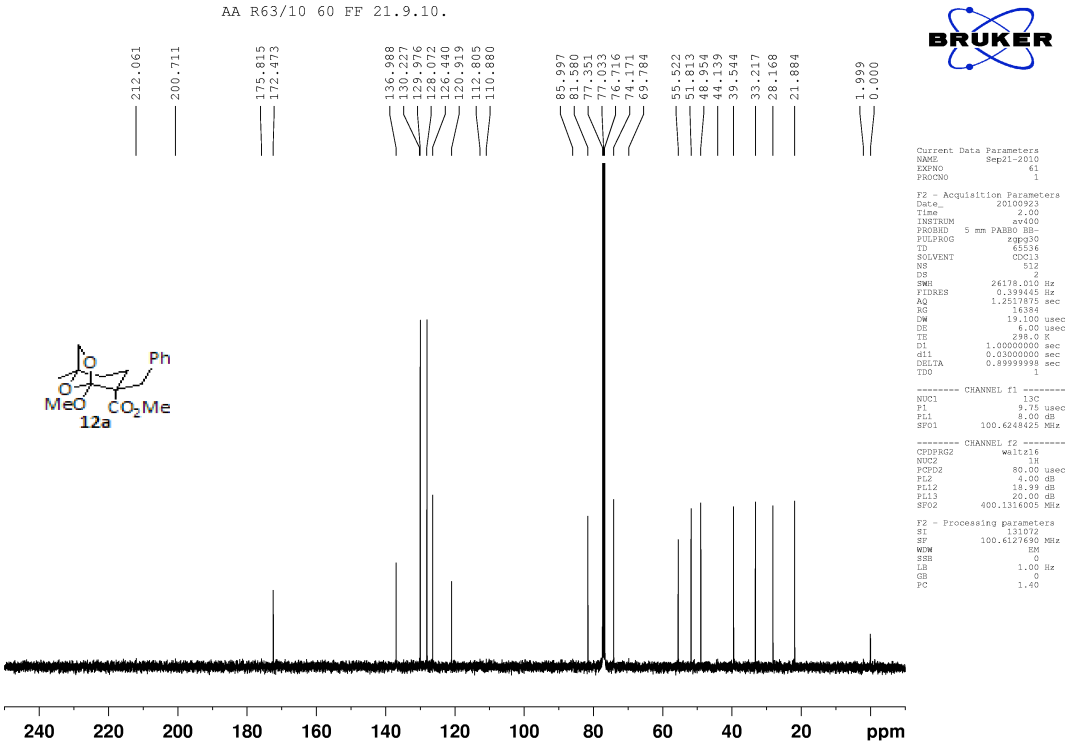
11b


AA R60/10 120 2NDF19.7.10.
3.996
3.979
3.709
3.647
3.644
3.629
3.626
3.407
2.907
2.894
2.877
2.864
2.205
2.177
2.175
1.931
1.921
1.918
1.883
1.886
1.698
1.694
1.685
1.679
1.666
1.658
1.379
Current Data Parameters
NAME Jul19-2010
EXPNO 120
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100720
Time 2.15
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 71.8
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1299965 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
CO2Me
MeO
H
11b
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
3.00
1.04
3.01
0.97
1.00
1.00
2.02
3.11

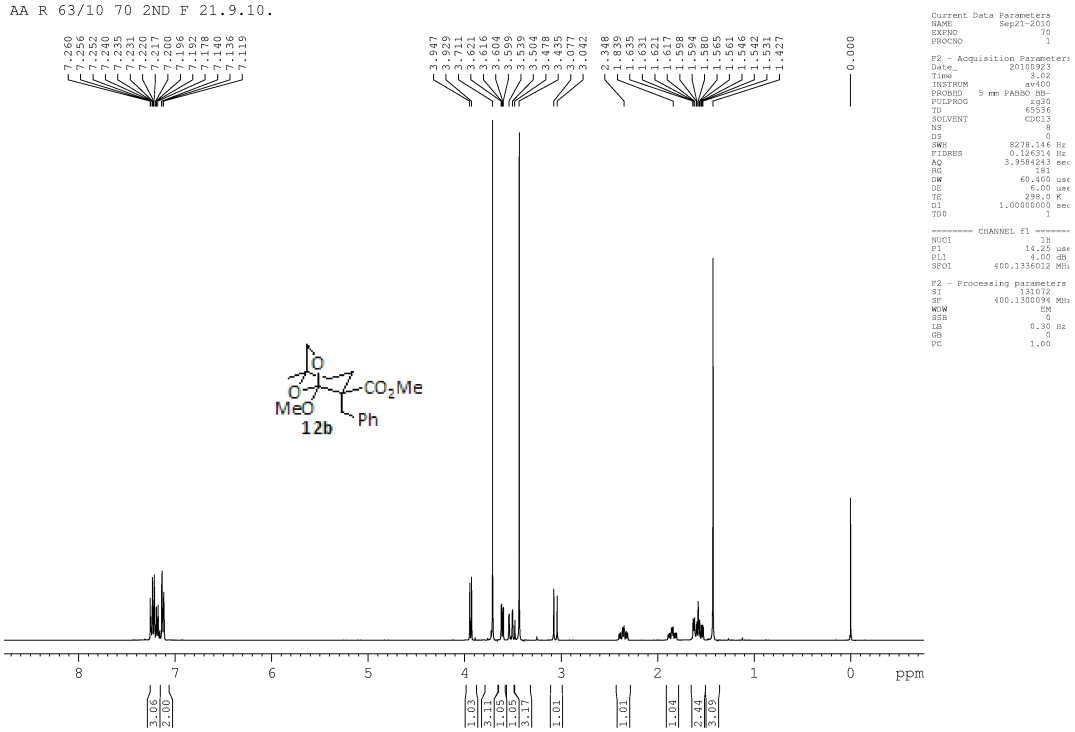

AA R60/10 120 2NDF19.7.10.
171.966
119.378
80.481
77.386
77.068
76.750
74.352
51.919
49.090
48.789
33.611
29.667
22.842
22.147
BRUKER
Current Data Parameters
NAME Jul19-2010
EXPNO 121
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100720
Time 2.36
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
CO2Me
MeO
H
11b
180
160
140
120
100
80
60
40
20
ppm

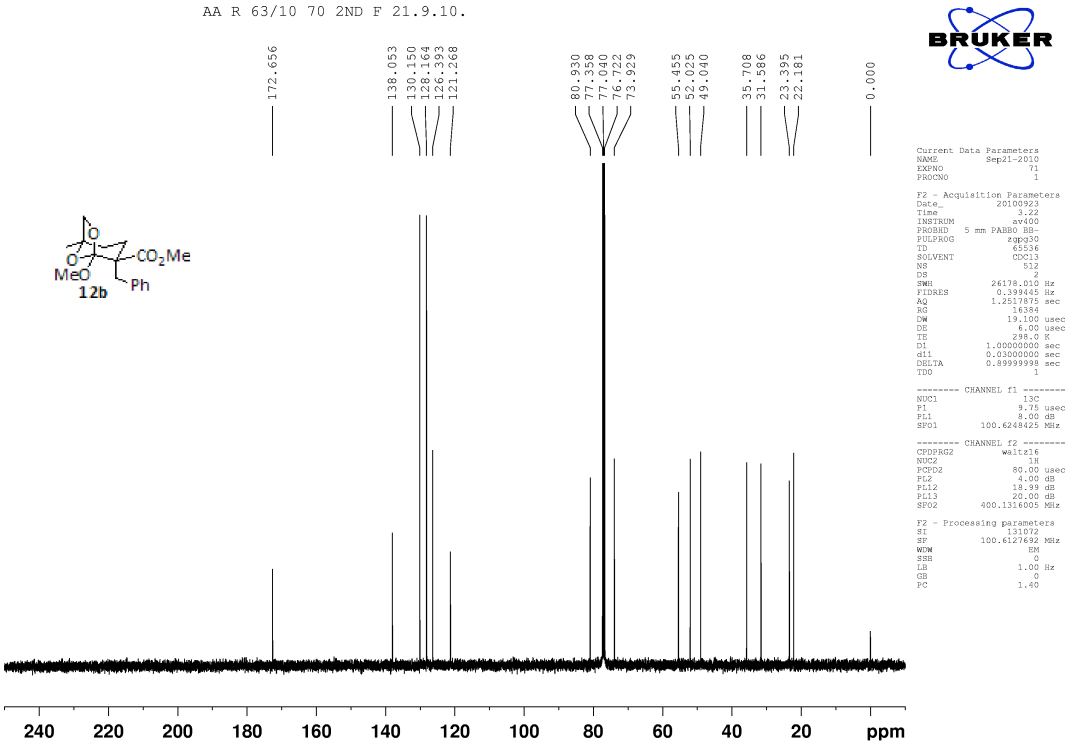
12a

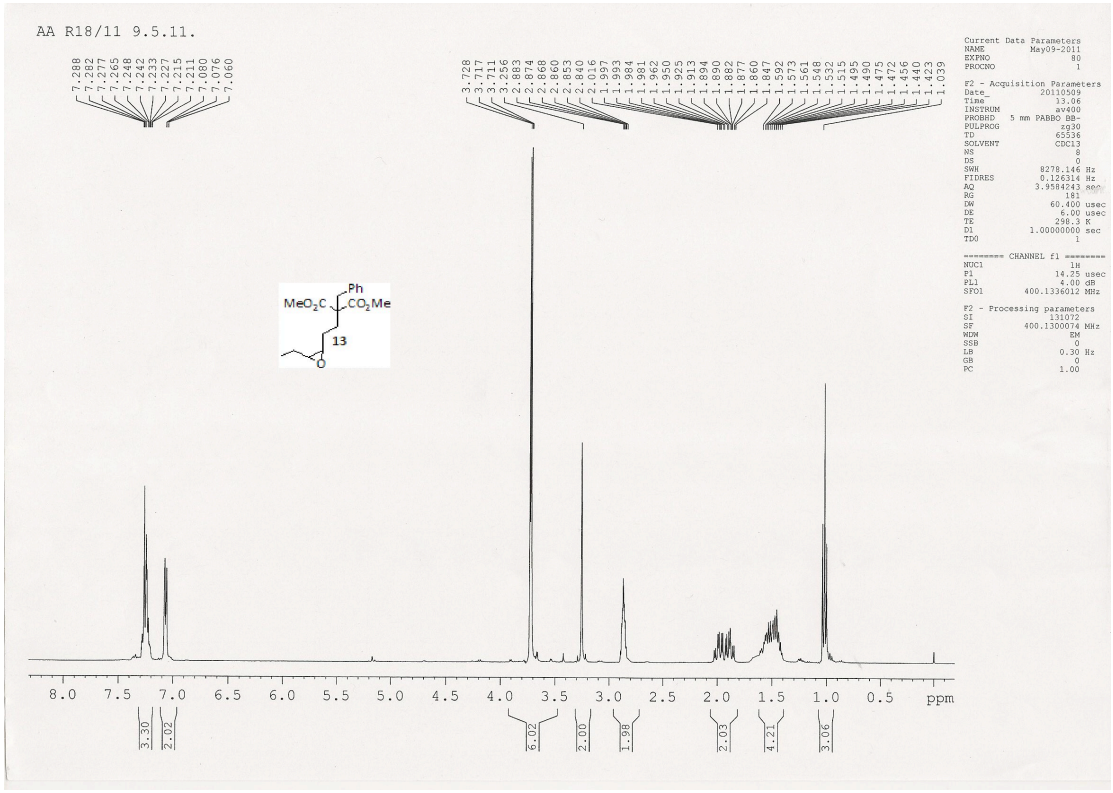

AA R63/10 60 FF 21.9.10.
Ph
MeO
CO2Me
12a
ppm

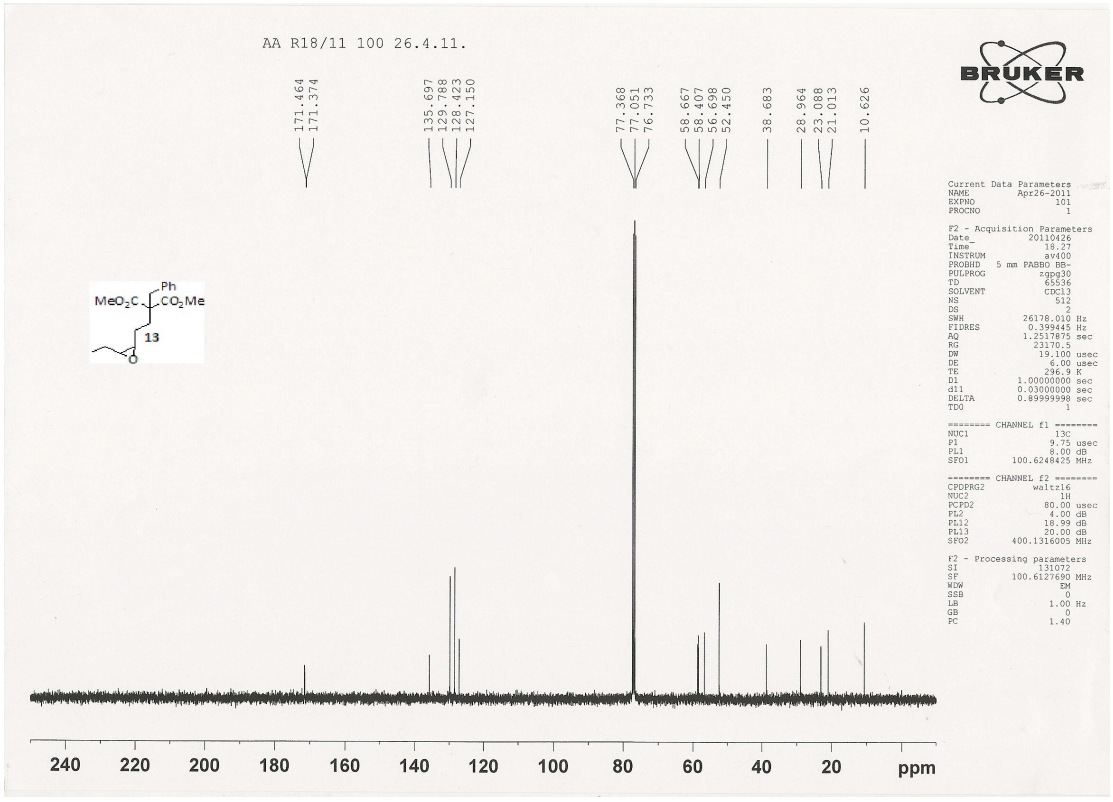

AA R63/10 60 FF 21.9.10.
Ph
MeO
CO2Me
12a
ppm

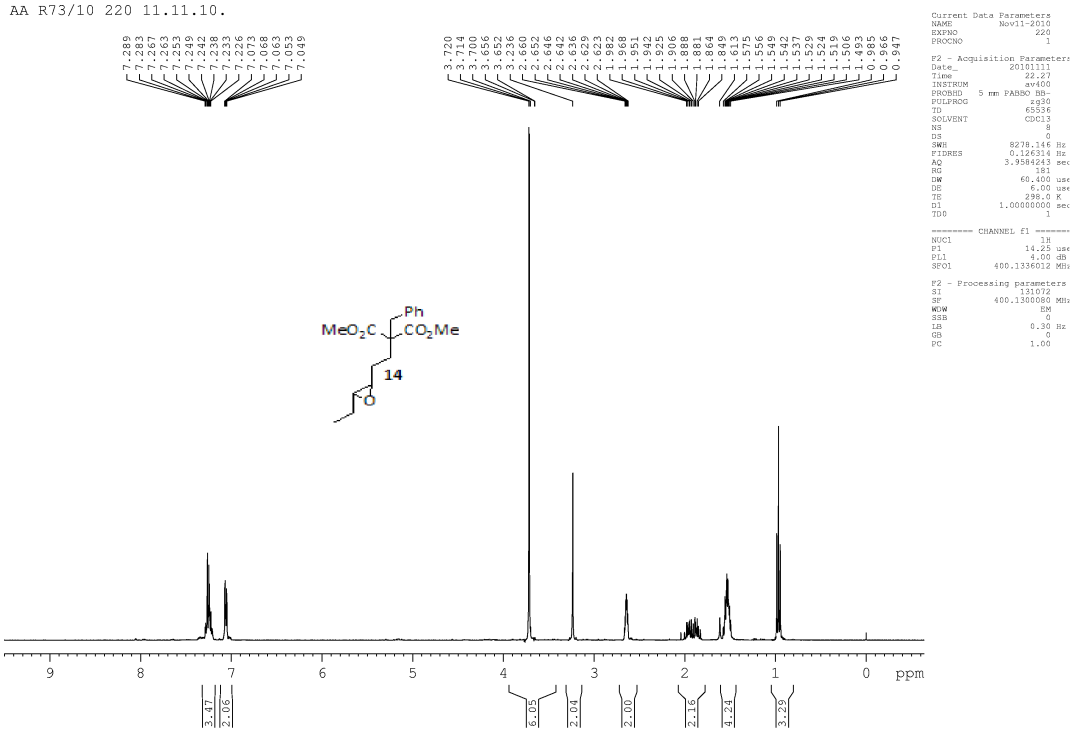
12b

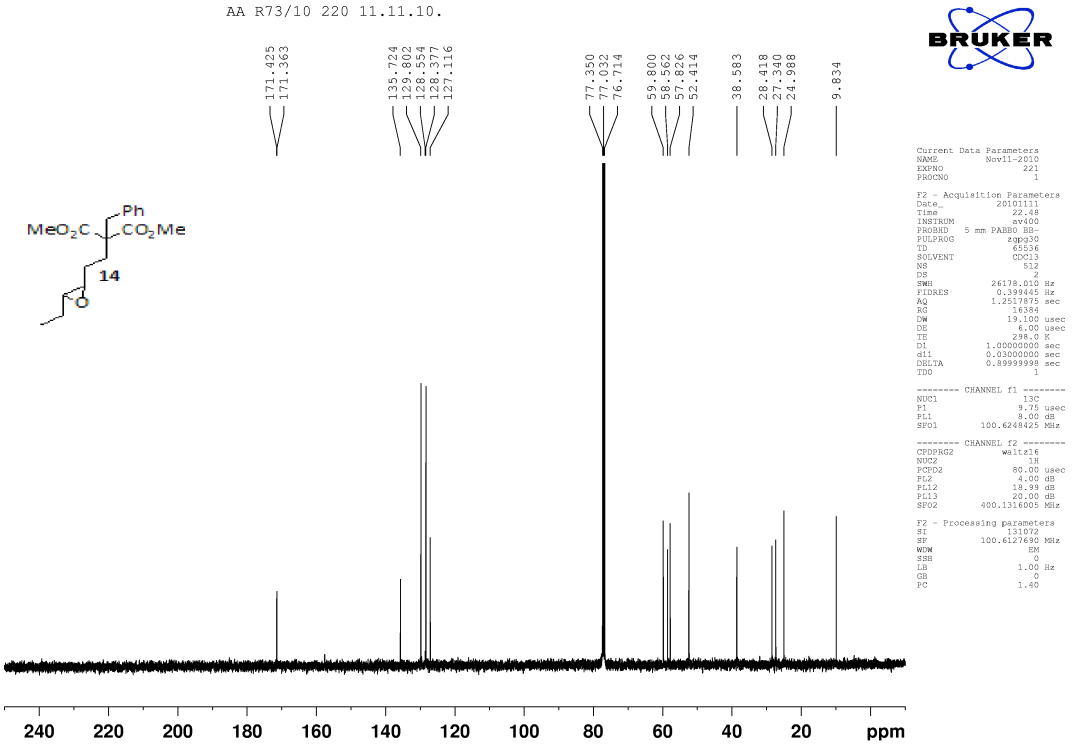

AA R 63/10 70 2ND F 21.9.10.
7.260
7.256
7.252
7.240
7.235
7.231
7.220
7.217
7.200
7.196
7.192
7.178
7.140
7.136
7.119
3.947
3.939
3.711
3.621
3.616
3.604
3.599
3.539
3.504
3.478
3.435
3.077
3.042
2.348
1.839
1.635
1.631
1.621
1.617
1.598
1.594
1.580
1.565
1.561
1.546
1.542
1.531
1.427
0.000
O
O
MeO
CO2Me
Ph
12b
8
7
6
5
4
3
2
1
0
ppm
3.06
2.00
1.03
3.11
1.05
1.05
3.17
1.01
1.01
1.04
2.44
3.09
Current Data Parameters
NAME Sep21-2010
EXPNO 70
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100923
Time 3.02
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


AA R 63/10 70 2ND F 21.9.10.
BRUKER
172.656
138.053
130.150
128.164
126.393
121.268
80.930
77.358
77.040
76.722
73.929
55.455
52.025
49.040
35.708
31.586
23.395
22.181
0.000
O
O
MeO
CO2Me
Ph
12b
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Sep21-2010
EXPNO 71
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100923
Time 3.22
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127692 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

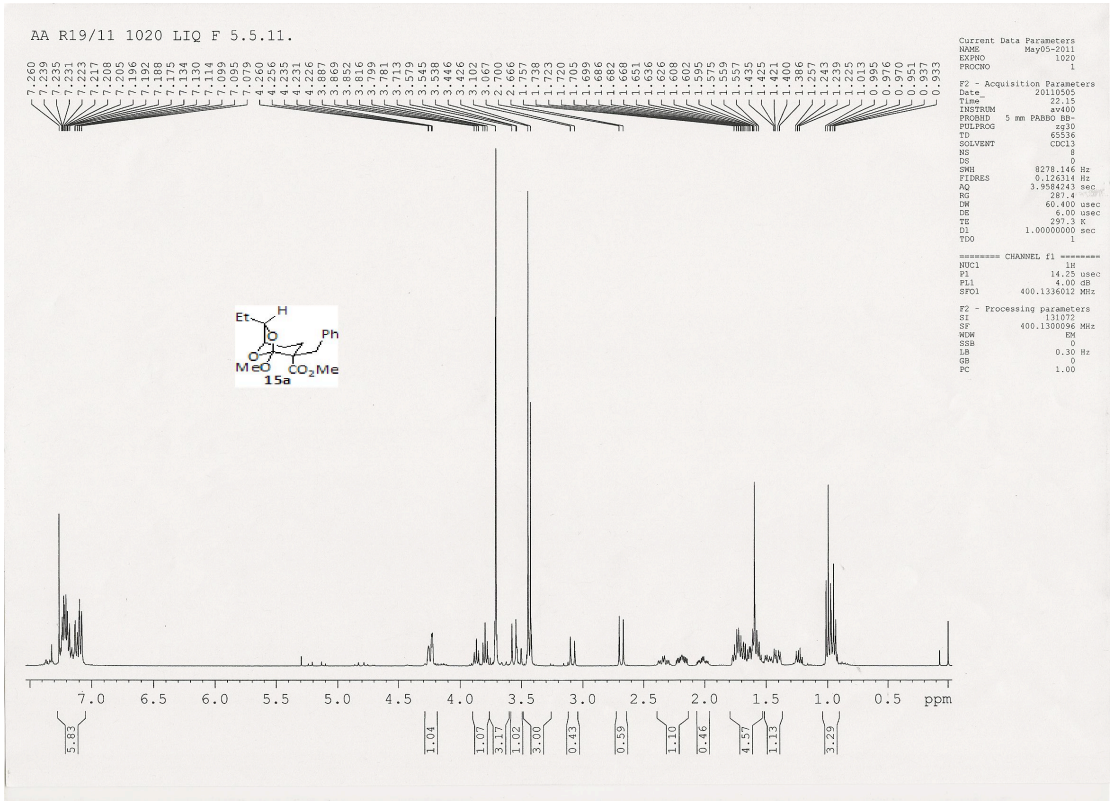

AA R18/11 9.5.11.
7.298
7.282
7.277
7.265
7.248
7.242
7.233
7.227
7.215
7.211
7.080
7.076
7.060
3.728
3.717
3.711
3.256
2.883
2.874
2.868
2.860
2.853
2.016
1.997
1.993
1.984
1.981
1.962
1.950
1.935
1.913
1.894
1.890
1.882
1.877
1.860
1.847
1.592
1.573
1.561
1.548
1.532
1.515
1.495
1.490
1.475
1.472
1.436
1.430
1.423
1.039
Ph
MeO2C
CO2Me
13
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.30
2.02
6.02
2.00
1.98
2.03
4.21
3.06
Current Data Parameters
NAME May09-2011
EXPNO 80
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110509
Time 13.06
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584743 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

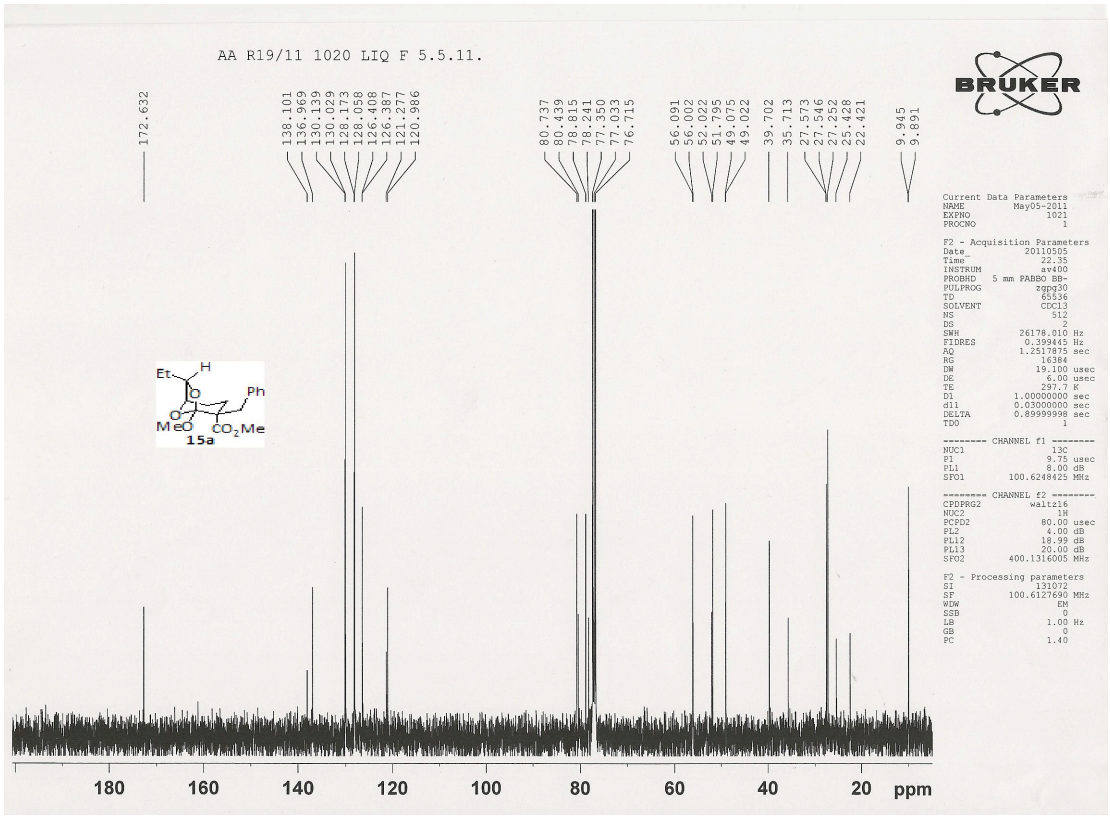

AA R18/11 100 26.4.11.
BRUKER
171.464
171.374
135.697
129.788
128.423
127.150
77.368
77.051
76.733
58.667
58.407
56.698
52.450
38.683
28.964
23.088
21.013
10.626
Ph
MeO2C
CO2Me
13
O
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Apr26-2011
EXPNO 101
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110426
Time 18.27
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 23170.5
DW 19.100 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


AA R73/10 220 11.11.10.
Ph
MeO2C
CO2Me
14
O
ppm

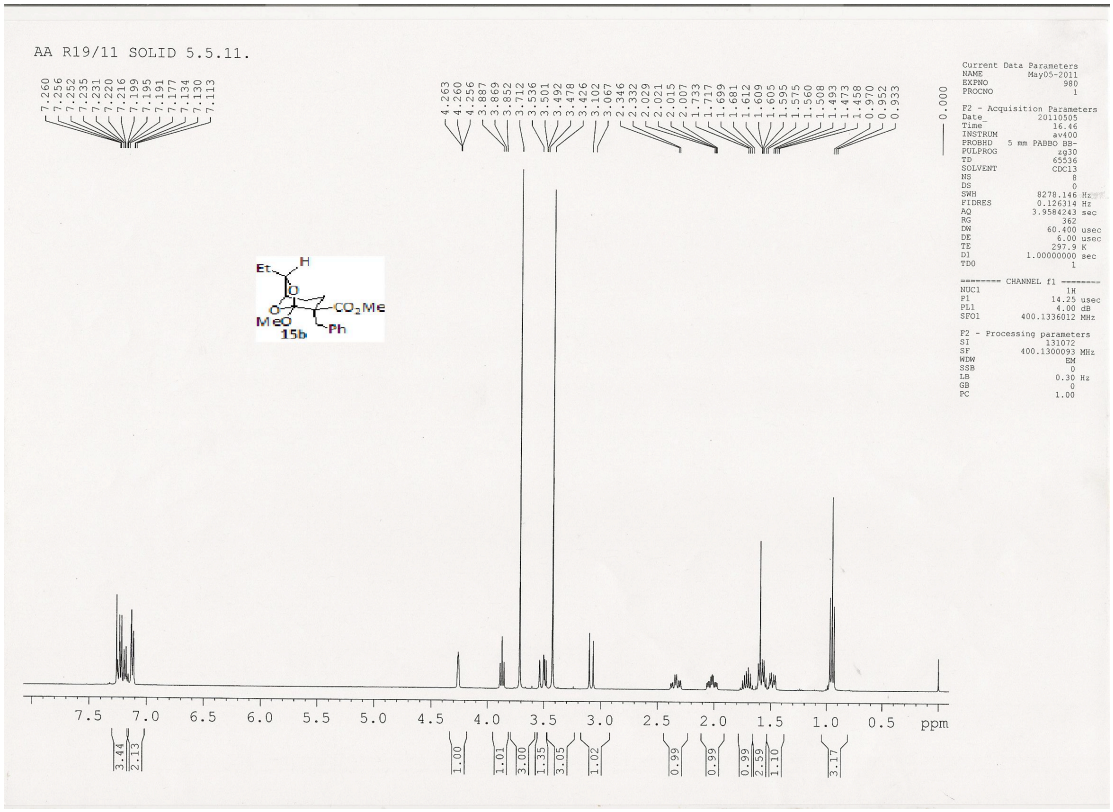

AA R73/10 220 11.11.10.
Ph
MeO2C
CO2Me
14
O
ppm

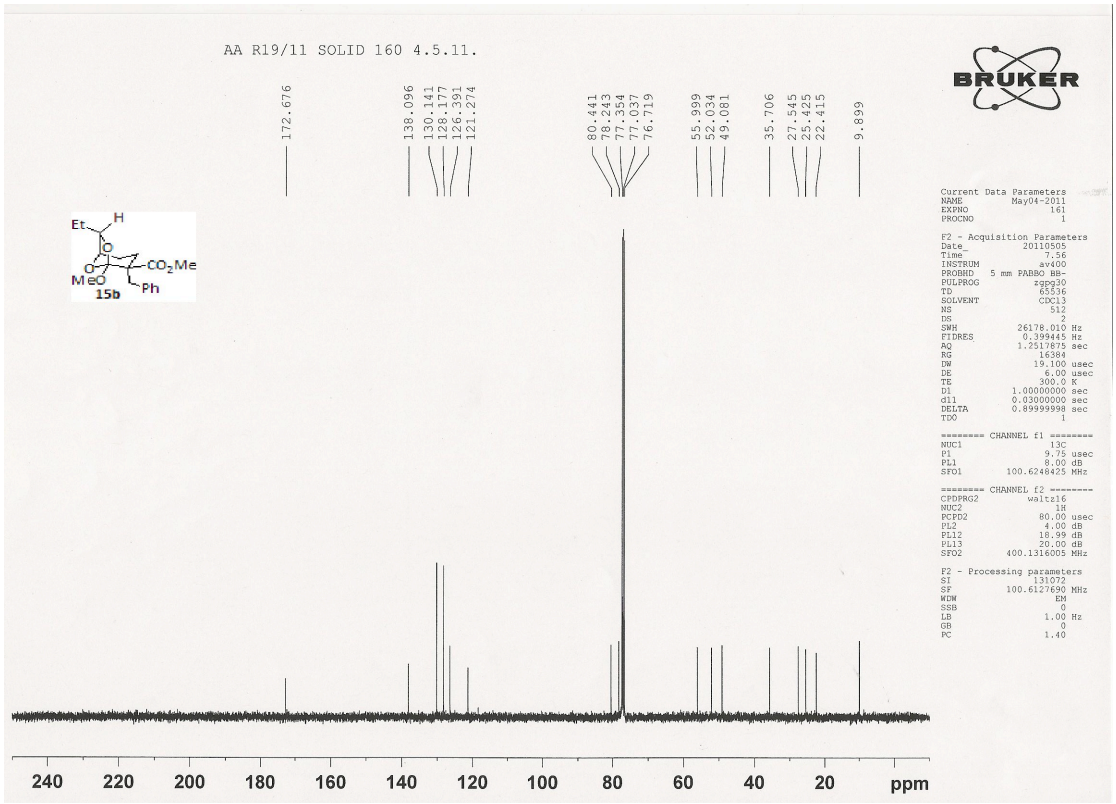
15a


AA R19/11 1020 LIQ F 5.5.11.
15a
ppm

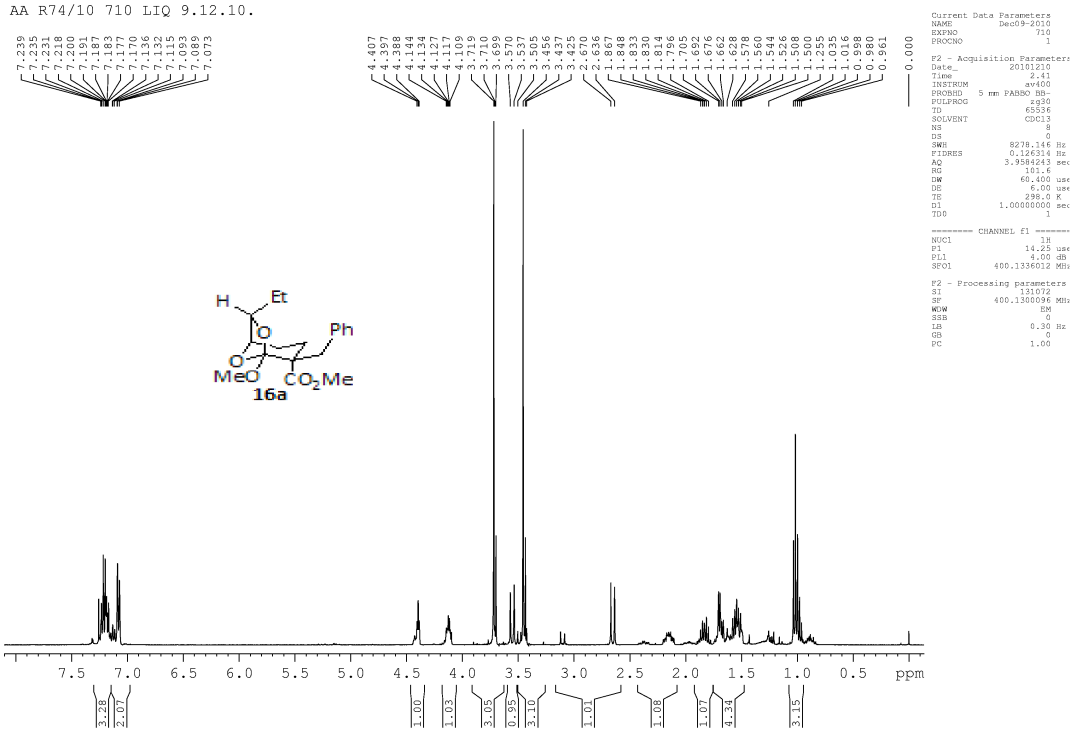

AA R19/11 1020 LIQ F 5.5.11.
BRUKER
15a
ppm

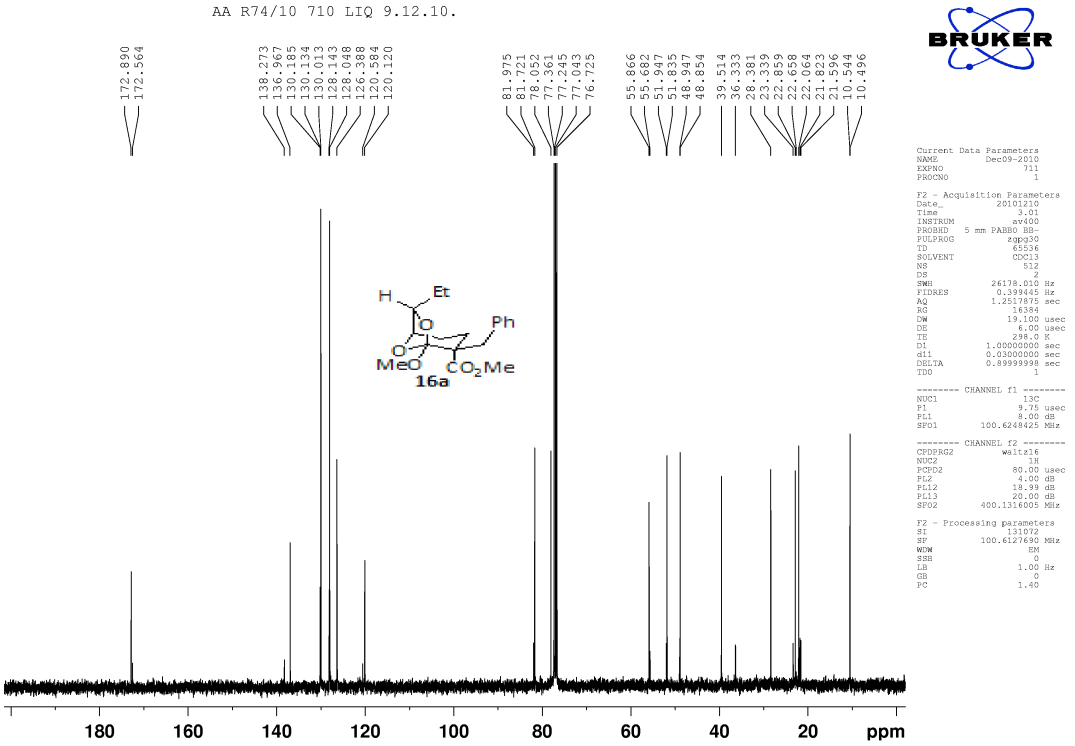
15b


AA R19/11 SOLID 5.5.11.
7.260
7.256
7.252
7.235
7.231
7.220
7.216
7.199
7.195
7.191
7.177
7.134
7.130
7.113
4.263
4.260
4.256
3.887
3.869
3.852
3.712
3.536
3.501
3.492
3.478
3.426
3.102
3.067
2.346
2.332
2.029
2.021
2.015
2.007
1.733
1.717
1.699
1.681
1.612
1.609
1.605
1.595
1.575
1.560
1.508
1.493
1.473
1.458
0.970
0.952
0.933
0.000
Et
H
O
O
MeO
CO2Me
Ph
15b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.44
2.13
1.00
1.01
3.00
1.35
3.05
1.02
0.99
0.99
0.99
2.59
1.10
3.17
Current Data Parameters
NAME May05-2011
EXPNO 980
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110505
Time 16.46
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 362
DW 60.400 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

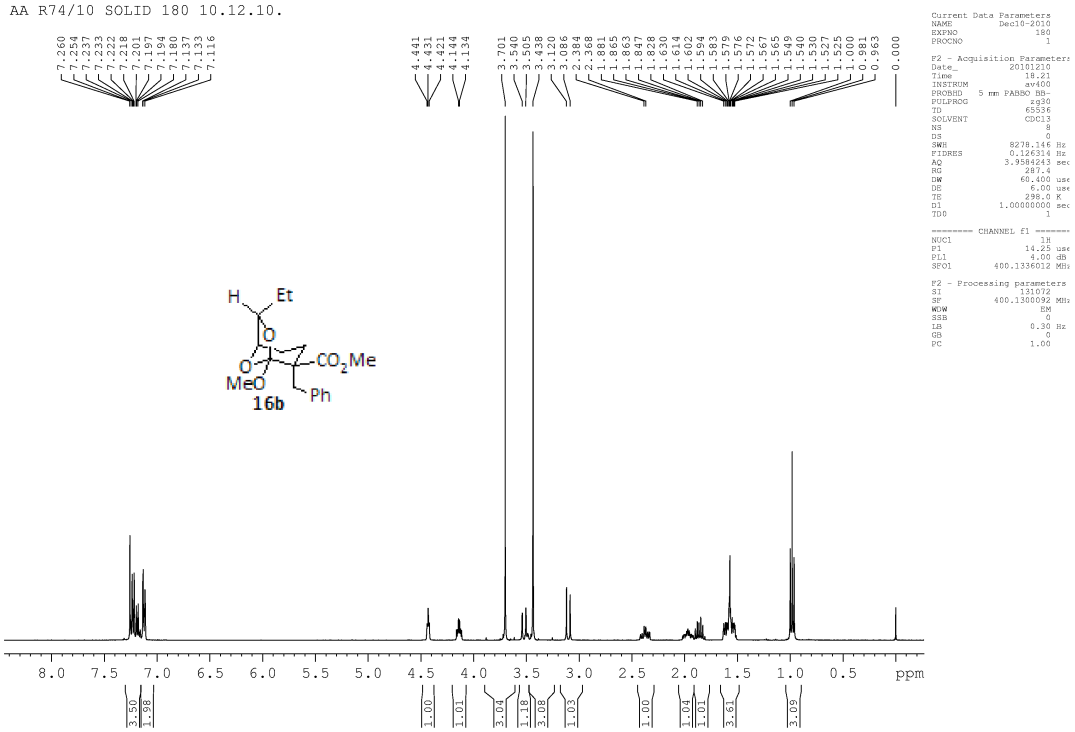

AA R19/11 SOLID 160 4.5.11.
BRUKER
172.676
138.096
130.141
128.177
126.391
121.274
80.441
78.243
77.354
77.037
76.719
55.999
52.034
49.081
35.706
27.545
25.425
22.415
9.899
Et
H
O
O
MeO
CO2Me
Ph
15b
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME May04-2011
EXPNO 161
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110505
Time 7.56
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

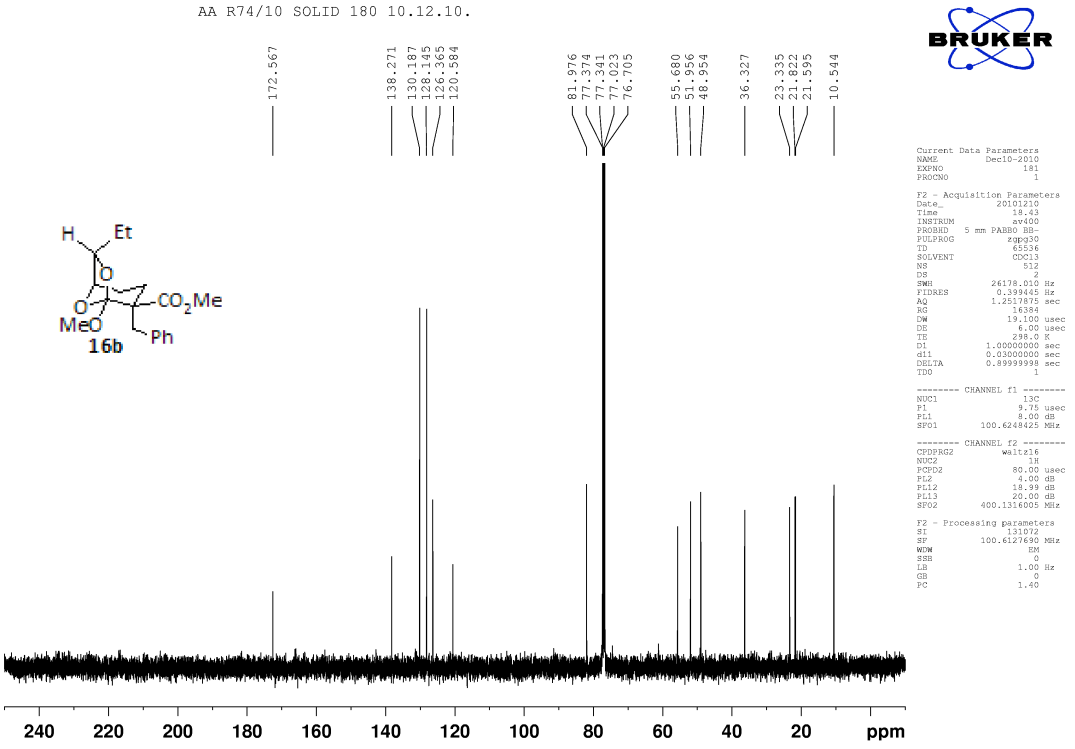
16a


AA R74/10 710 LIQ 9.12.10.
H
Et
O
Ph
O
MeO
CO2Me
16a
ppm

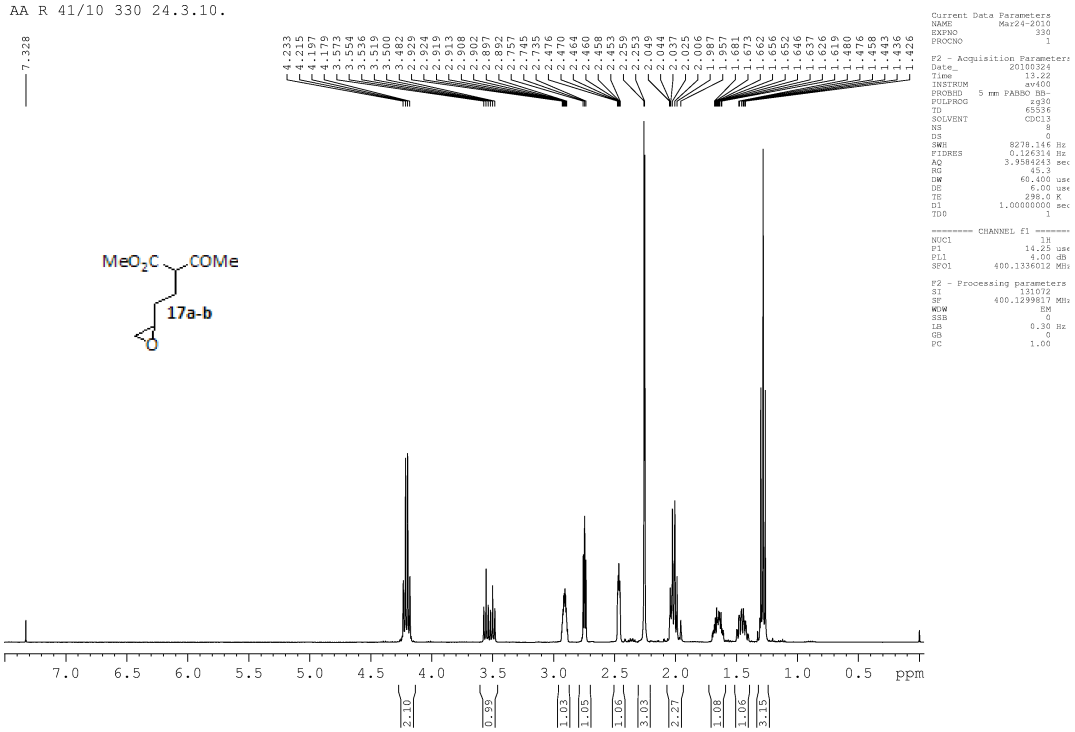

AA R74/10 710 LIQ 9.12.10.
BRUKER
H
Et
O
Ph
O
MeO
CO2Me
16a
ppm

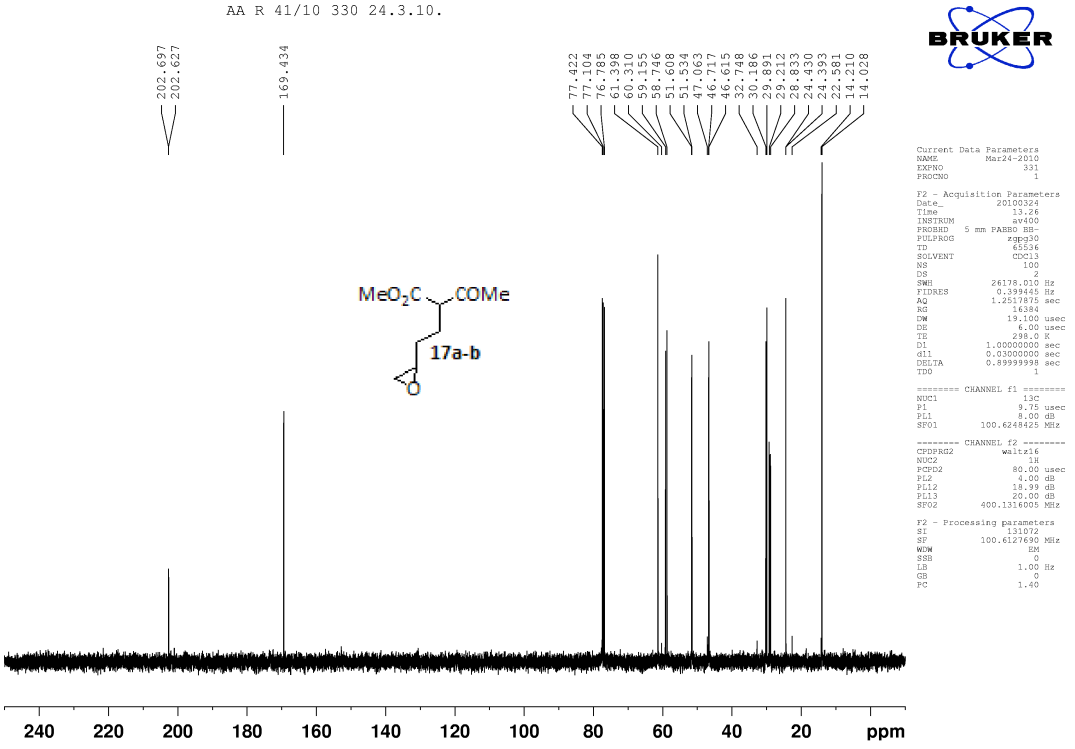
16b


AA R74/10 SOLID 180 10.12.10.
16b
ppm

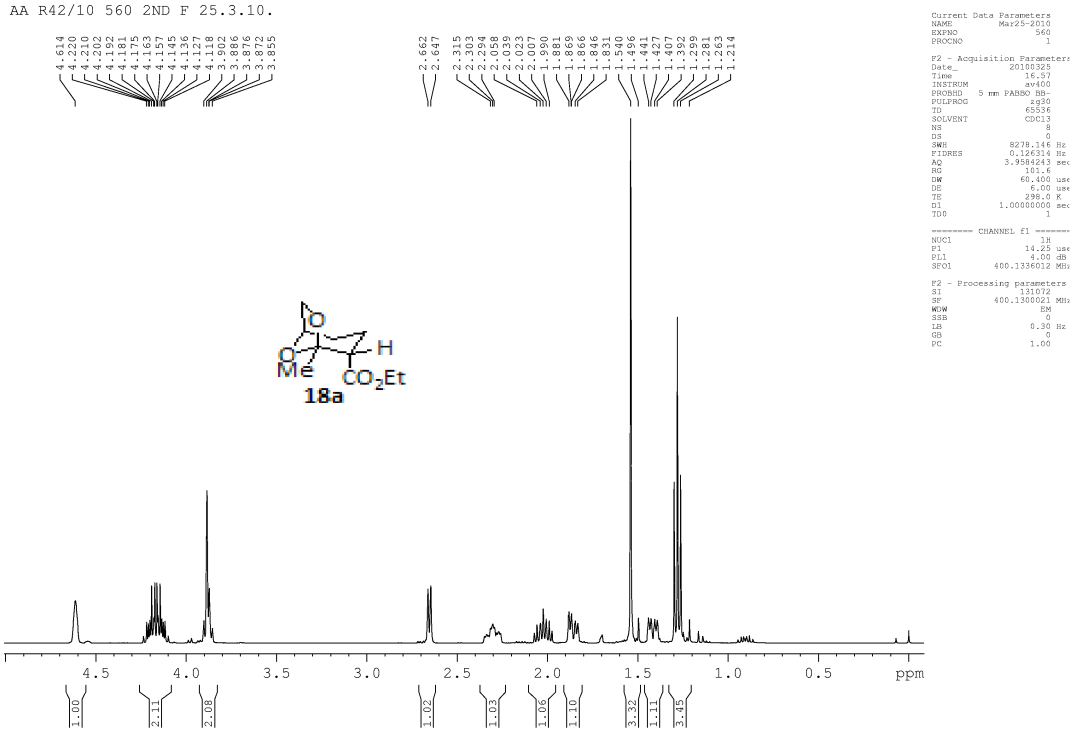

AA R74/10 SOLID 180 10.12.10.
16b
ppm

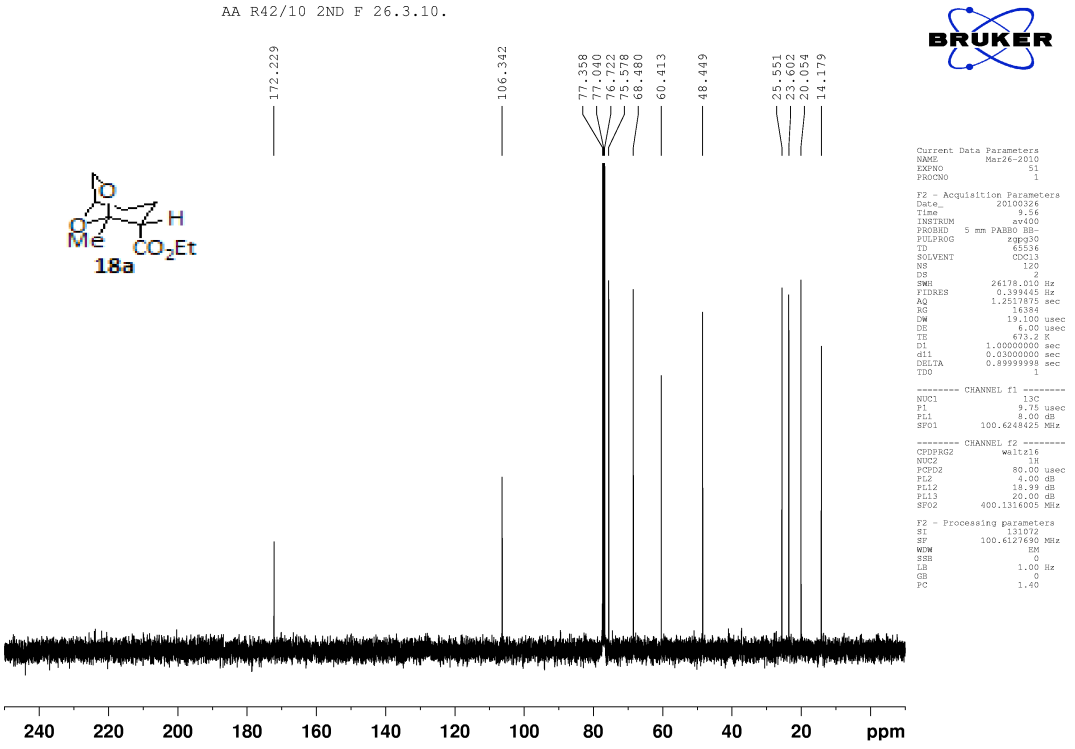
17a-b


AA R 41/10 330 24.3.10.
MeO2C
COMe
17a-b
O
ppm

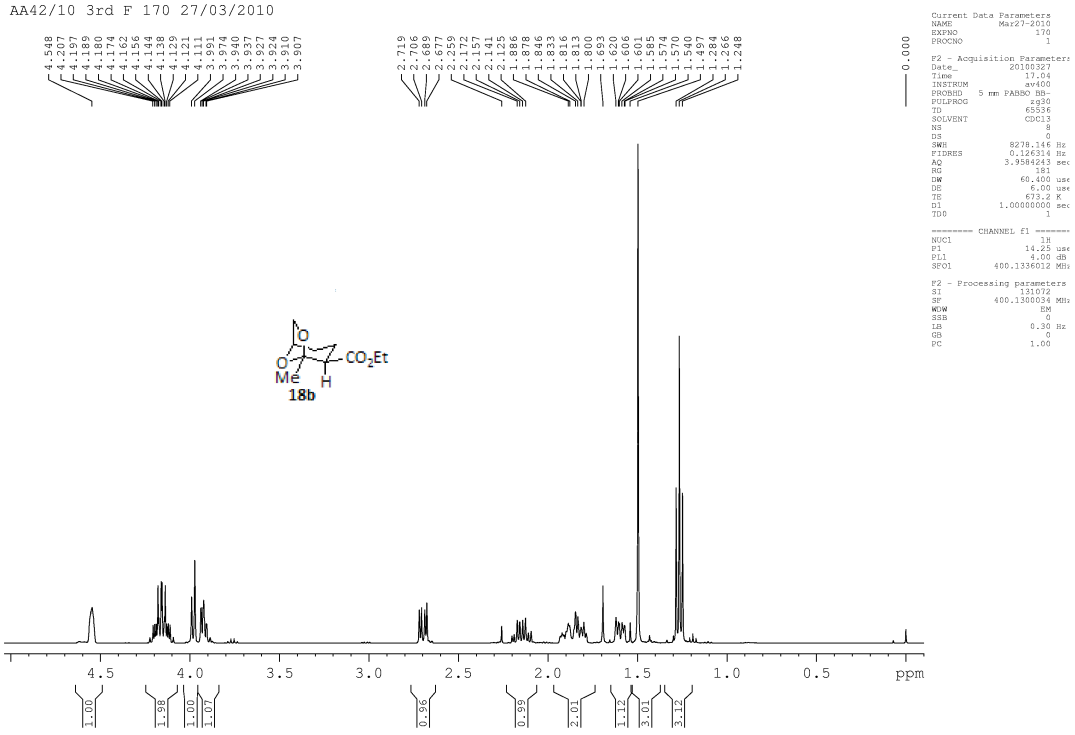

AA R 41/10 330 24.3.10.
BRUKER
MeO2C
COMe
17a-b
O
ppm

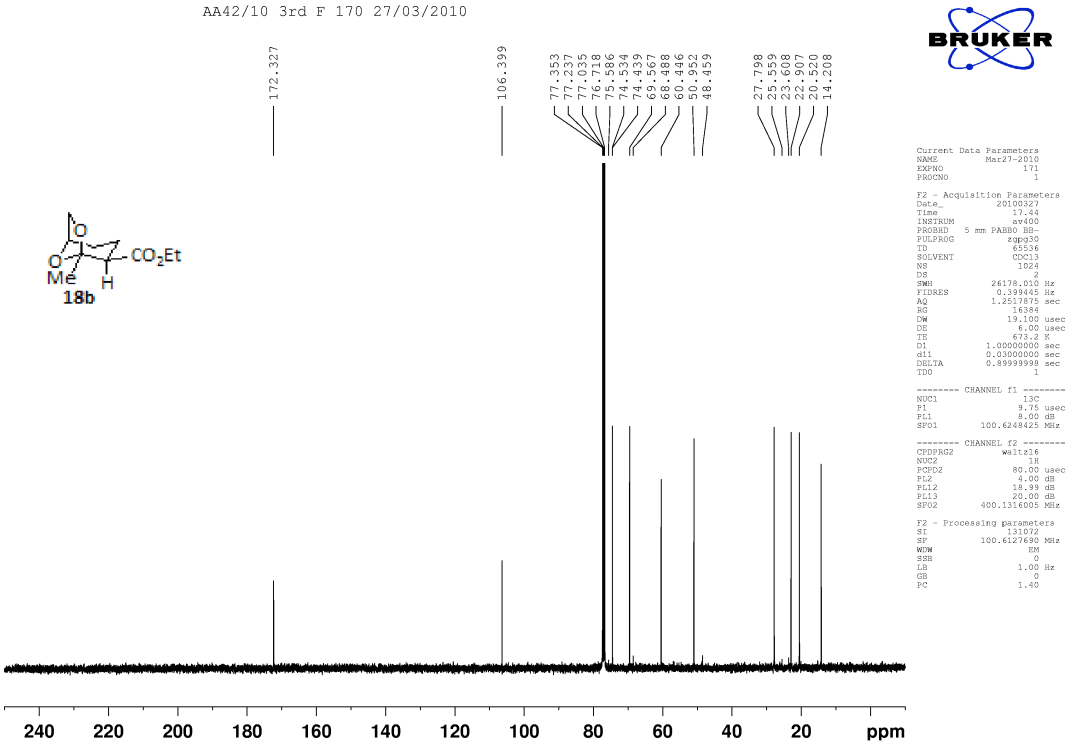
18a


AA R42/10 560 2ND F 25.3.10.
4.614
4.220
4.210
4.202
4.182
4.181
4.175
4.163
4.157
4.145
4.136
4.127
4.118
4.102
3.886
3.876
3.872
3.855
2.662
2.647
2.315
2.303
2.294
2.058
2.039
2.023
2.007
2.000
1.881
1.869
1.866
1.846
1.831
1.540
1.496
1.441
1.427
1.407
1.392
1.299
1.281
1.263
1.214
O
O
Me
H
CO2Et
18a
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.11
2.08
1.02
1.03
1.06
1.10
3.32
1.11
3.45
Current Data Parameters
NAME Mar25-2010
EXPNO 560
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100325
Time 16.57
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181.6
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300021 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

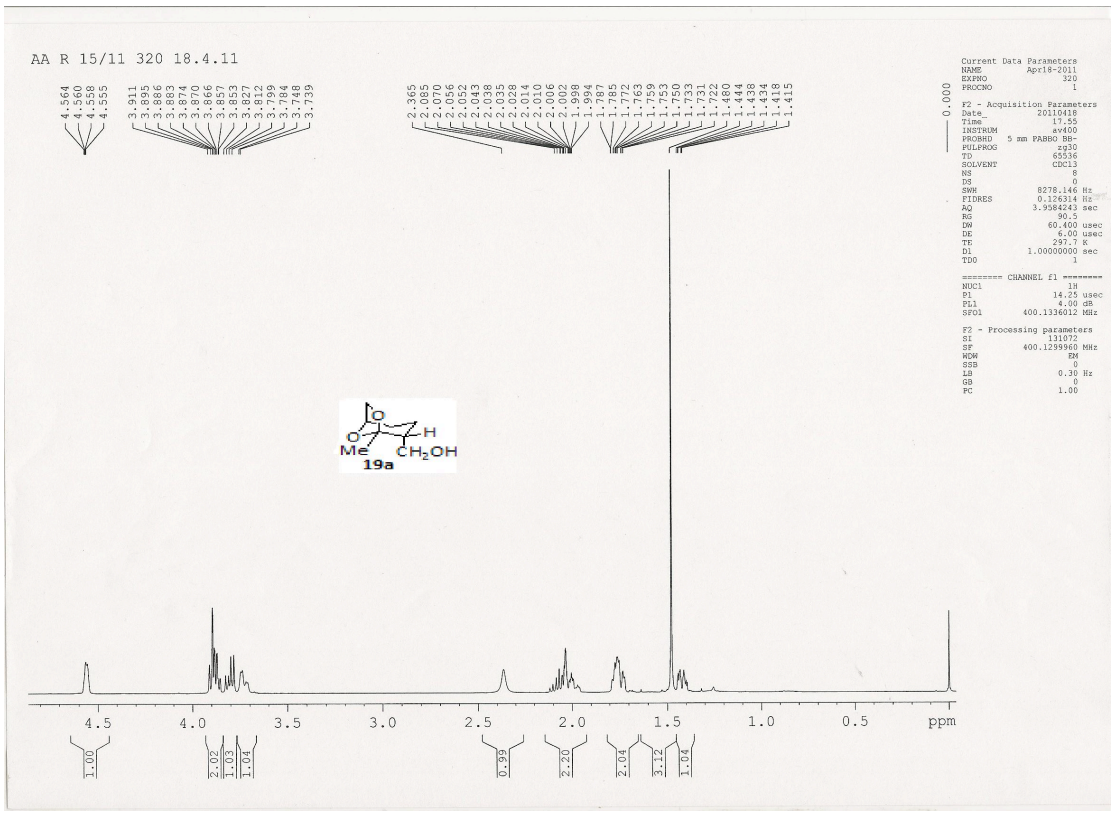

AA R42/10 2ND F 26.3.10.
BRUKER
172.229
106.342
77.358
77.040
76.722
75.578
68.480
60.413
48.449
25.551
23.602
20.054
14.179
O
O
Me
H
CO2Et
18a
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Mar26-2010
EXPNO 51
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100326
Time 9.56
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 120
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

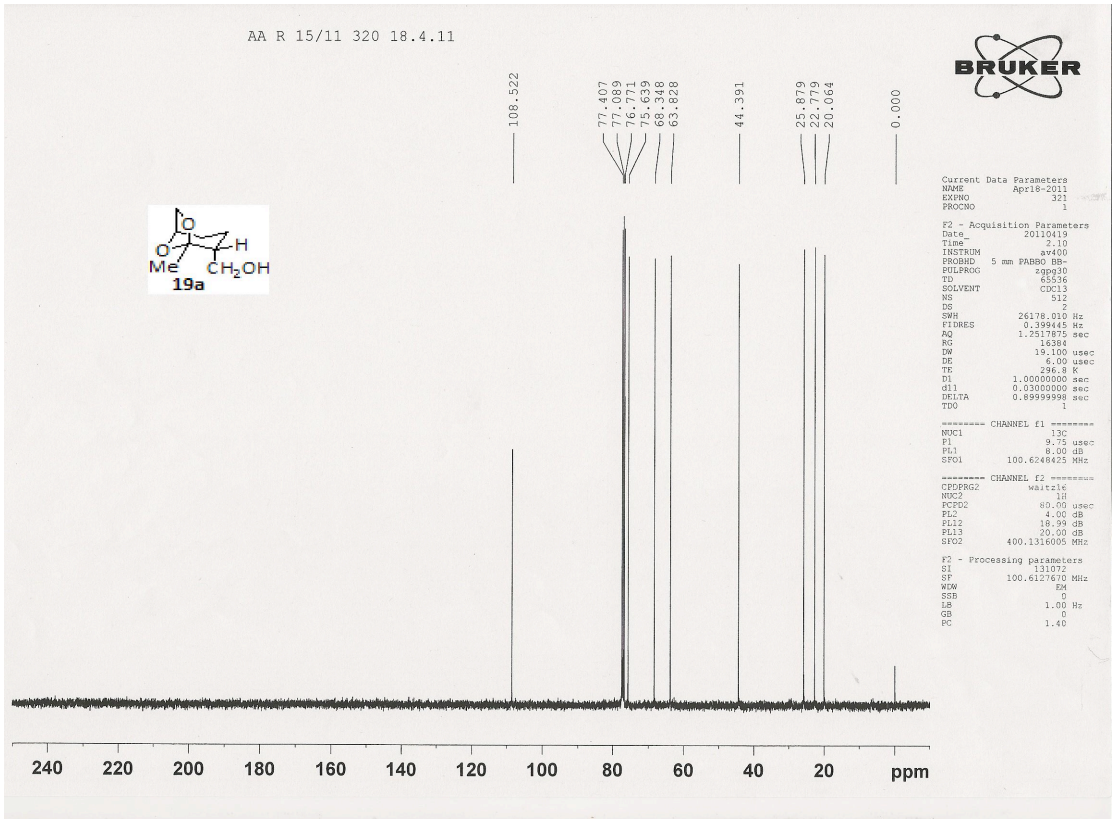
18b


AA42/10 3rd F 170 27/03/2010
4.548
4.207
4.197
4.189
4.180
4.174
4.162
4.156
4.144
4.138
4.129
4.121
4.111
3.991
3.974
3.940
3.937
3.927
3.924
3.910
3.907
2.719
2.706
2.689
2.677
2.259
2.172
2.157
2.111
2.125
1.886
1.878
1.846
1.833
1.816
1.813
1.800
1.663
1.620
1.606
1.601
1.585
1.574
1.570
1.540
1.497
1.284
1.266
1.248
0.000
O
O
Me
H
CO2Et
18b
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.98
1.00
1.07
0.96
0.99
2.01
1.12
3.01
3.12
Current Data Parameters
NAME Mar27-2010
EXPNO 170
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100327
Time 17.04
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1300034 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

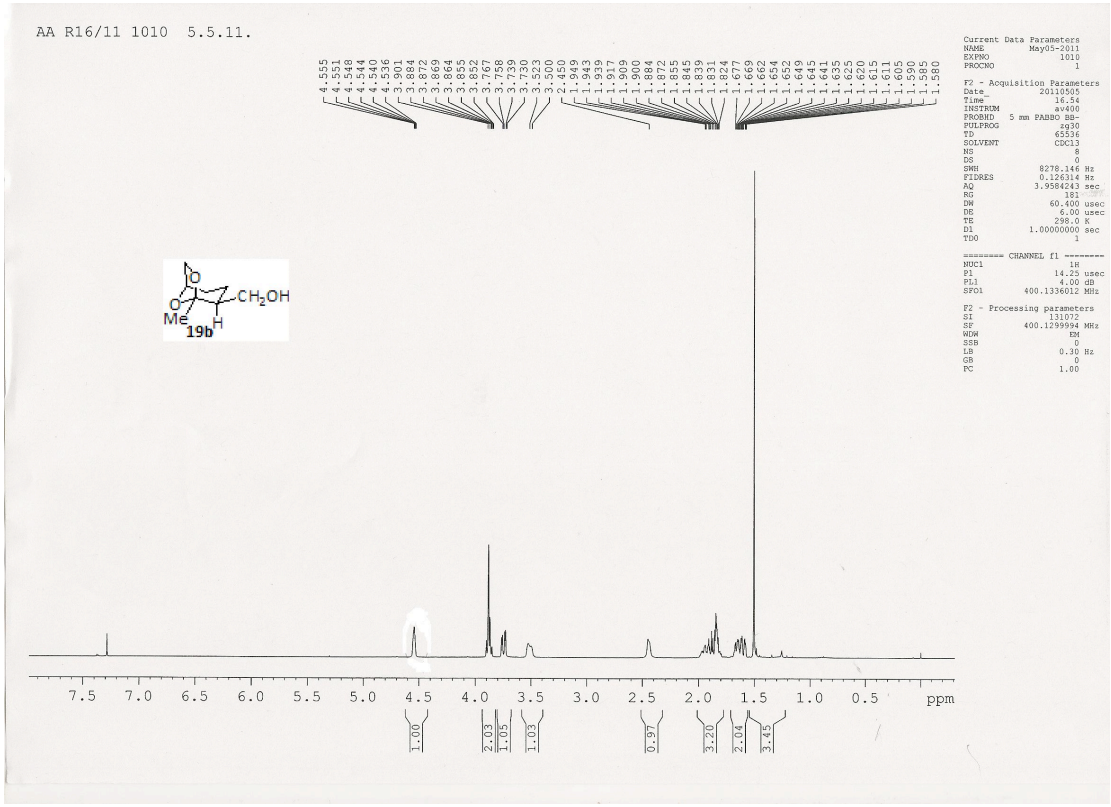

AA42/10 3rd F 170 27/03/2010
172.327
106.399
77.353
77.237
77.035
76.718
75.586
74.534
74.439
69.567
68.488
60.446
50.952
48.459
27.798
25.559
23.608
22.907
20.520
14.208
O
O
Me
H
CO2Et
18b
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Mar27-2010
EXPNO 171
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100327
Time 17.44
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

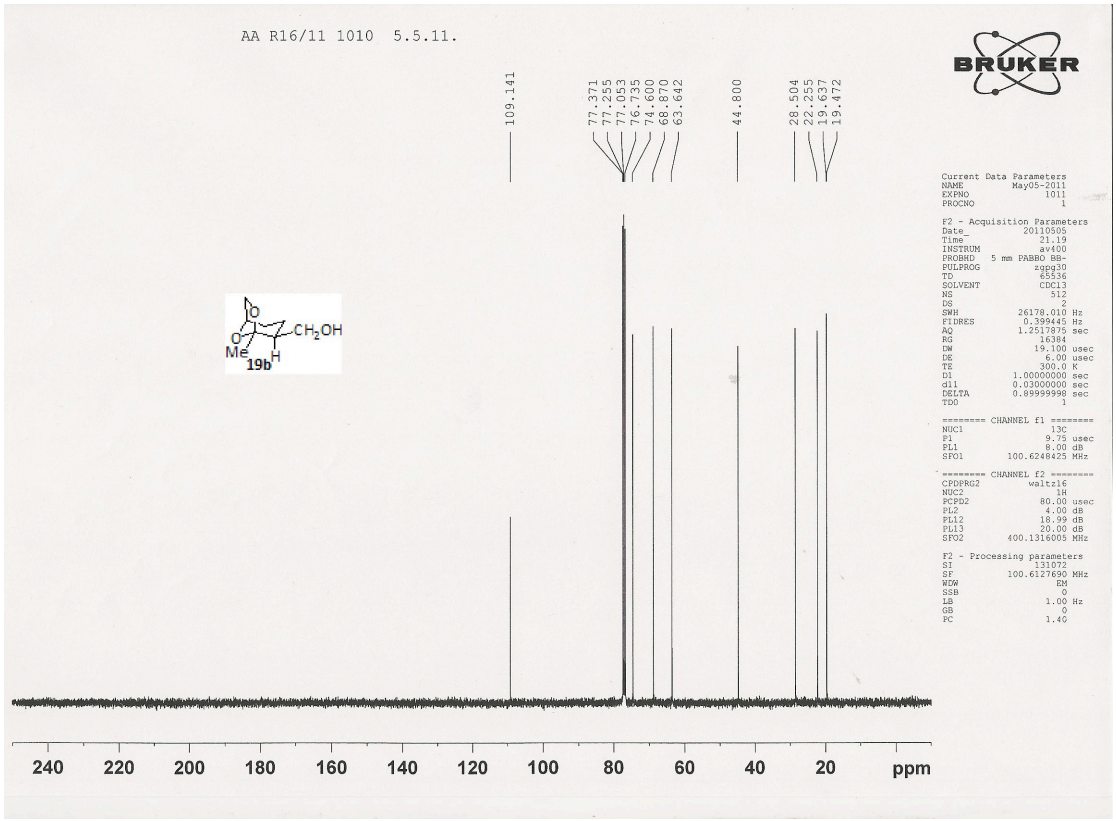
19a



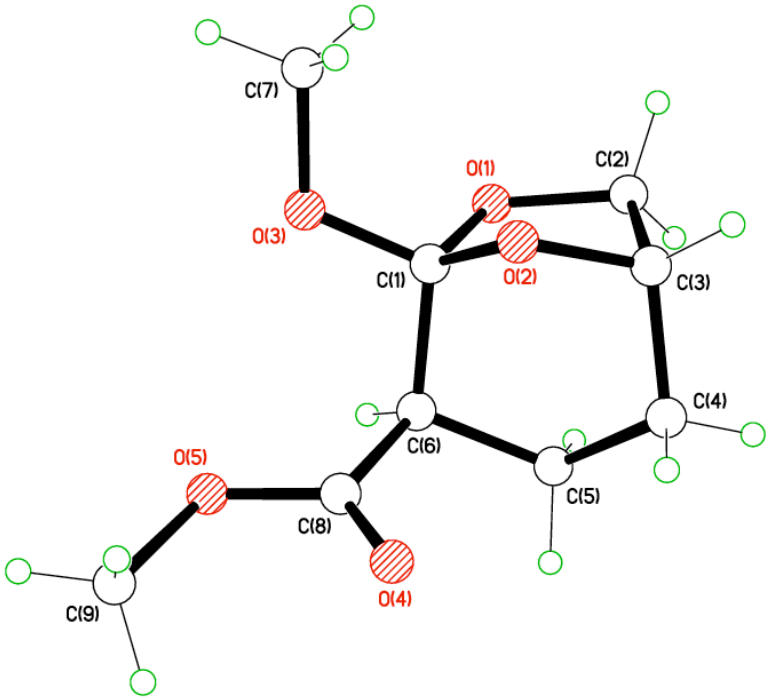


19b

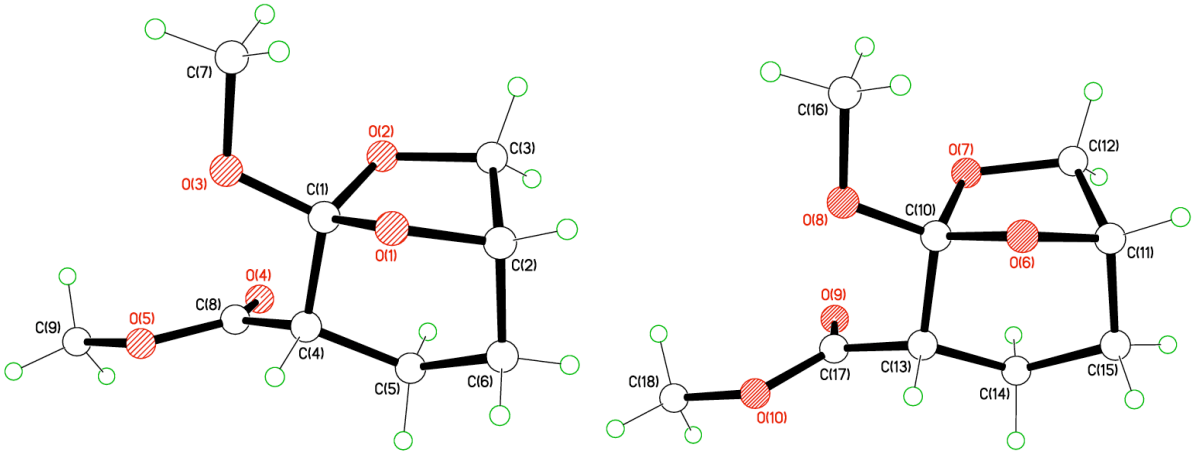

AA R16/11 1010 5.5.11.
4.555
4.551
4.548
4.544
4.540
4.536
3.901
3.884
3.872
3.869
3.864
3.855
3.852
3.767
3.758
3.739
3.730
3.523
3.500
2.450
1.949
1.943
1.939
1.917
1.909
1.900
1.888
1.872
1.855
1.845
1.839
1.831
1.824
1.677
1.669
1.662
1.654
1.652
1.649
1.645
1.641
1.635
1.625
1.620
1.615
1.611
1.605
1.590
1.585
1.580
CH2OH
Me
H
19b
Current Data Parameters
NAME May05-2011
EXPNO 1010
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110505
Time 16.54
INSTRUM av400
PROBHD 5 mm PABBO BA-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.25 usec
PL1 4.00 dB
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 131072
SF 400.1299994 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.03
1.05
1.03
0.97
3.20
2.04
3.45


AA R16/11 1010 5.5.11.
BRUKER
109.141
77.371
77.255
77.053
76.735
74.600
68.870
63.642
44.800
28.504
22.255
19.637
19.472
CH2OH
Me
H
19b
Current Data Parameters
NAME May05-2011
EXPNO 1011
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110505
Time 21.19
INSTRUM av400
PROBHD 5 mm PABBO BA-
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 512
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
240 220 200 180 160 140 120 100 80 60 40 20 ppm

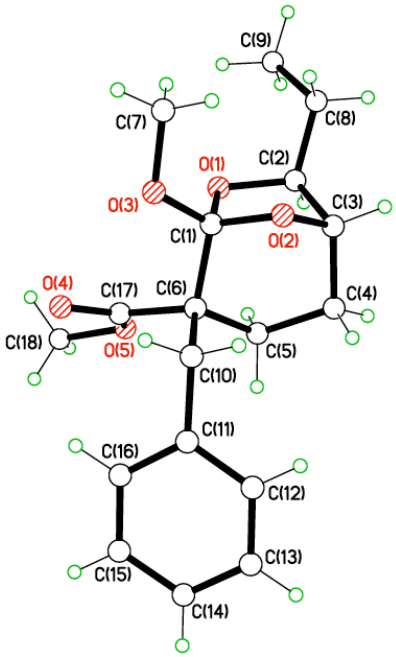
Figures for X-ray Structures.



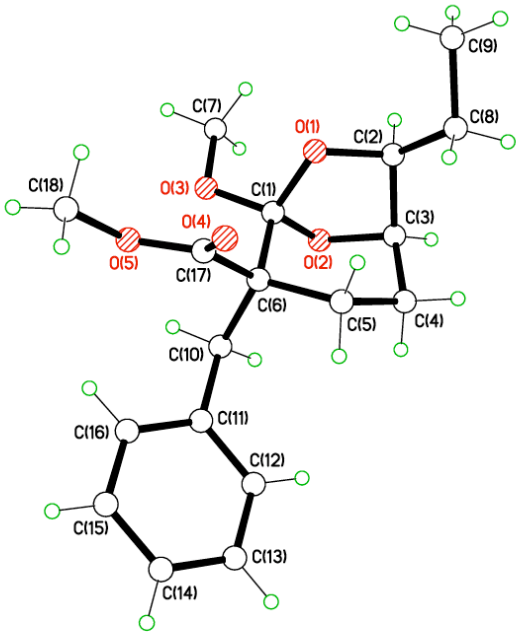
Crystal structure of compound **1a**.



Crystal structure of compound **1b** with two molecules in the asymmetric unit.



Crystal structure of compound **15b**.



Crystal structure of compound **16b.**

X-ray Experimental.

The diffraction data were collected at 150K on a Bruker Apex 2 CCD diffractometer equipped with MoKα radiation[1]. Data were corrected for absorption and Lp effects[1], solved by direct methods[2,3], and refined[2,3] by full-matrix least-squares on F^2. H atoms were included in a riding model. Structure solutions were routine. In **16b** Friedel pairs were merged as there was no indication as to absolute structure from the diffraction data. Further numerical details in the main paper.

1. SAINT and APEX 2 (2009) software for CCD diffractometers. Bruker AXS Inc., Madison, USA.
2. Sheldrick, G.M., (2008), *Acta Crystallogr*. A64, 112-122.
3. G.M. Sheldrick, SHELXTL user manual, version 6.12. Bruker AXS Inc., Madison, WI, USA, (2001).