

Supporting Information

A Powerful tool for acid catalyzed organic addition and substitution reactions

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General

^1H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer operating at 500.1 and 125.8 MHz, respectively. The solvent residual peak was used as a standard for ^1H and ^{13}C measurements in CDCl_3 and CD_3OD (7.26 ppm or 77.16 ppm for CDCl_3 and 3.31 ppm or 49.00 ppm for CD_3OD , respectively),¹ in D_2O 4.79 ppm in ^1H measurements and trimethylsilyl propionic acid sodium salt (TSP) in ^{13}C measurements (0.00 ppm). The proton-coupled ^{13}C NMR spectrum was measured for compound **5a** to confirm the number of protons on each carbon and marked after each carbon by the letters s (singlet), d (doublet), t (triplet), q (quartet) or qv (quintet). The $^nJ_{PP}$ couplings were calculated from the proton spectra and all J values are given in Hz. Mass spectra were recorded on a quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI) with positive ionization mode for compound **27** and negative ionization mode for compound **25**. The purity of the products was determined from ^1H spectrum and was $\geq 95\%$ unless stated otherwise. Ion exchange resins (Dowex[®], Diphonix[®] and Amberlyst[®]) were oven dried for approx. 20 hours at 120°C before use. The used conditions and yields have not been optimized, except in the preparation of **13a** and **17** some conditions optimizations were made. We were unable to measure the correct MS peaks for the compounds **5a** and **5b** probably due to high reactivity or instability of the compounds in used conditions.

Preparation of Dowex[®] D⁺ ion exchange resin: Na^+ form Dowex[®] (approx. 5 g) were stirred for 1 hour in 3.8 M DCl solution (10 ml in D_2O) at room temperature before it was filtered, washed with D_2O and dried *in vacuo*. Dowex[®] D⁺ resin was stored in a desiccator.

Preparation of 3-Iodo-3-methylbutan-1-ol (5a): MgSO_4 dried 3-methyl-3-buten-1-ol (59 μl , 50.2 mg, 0.58 mmol) was dissolved to dry MeOH (4 ml), oven dried NaI (87 mg, 0.58 mmol, 1 eq) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 400 mg) were added and the reaction mixture was stirred for 10-15 min at room temperature. Dowex was filtered off and MeOH was removed by evaporation *in vacuo*. The residue was dissolved in DCM and any solids were removed and DCM evaporated to dryness *in vacuo*. 3-Iodo-3-methyl-butan-1-ol (81 mg, 65%) was obtained as a brownish yellow oil. ^1H NMR (CDCl_3): δ 3.93 (t, 2H, $^3J_{\text{HH}} = 7.0$), 3.57 (br, 1H + some H_2O), 1.99 (t, 2H, $^3J_{\text{HH}} = 7.0$), 1.98 (s, 6H); ^{13}C NMR (CDCl_3): δ 63.2 (t), 51.2 (t), 47.1 (s), 38.7 (q, 2C).

Preparation of deuterated 3-Iodo-3-methylbutan-1-ol (5b): Prepared similarly to **5a**, except Dowex D⁺ was used instead of Dowex H⁺ and CD_3OD instead of MeOH . **5b** (67 mg, 54%) was obtained as a brownish yellow oil. The purity of the compound was approx.

90%. ^1H NMR (CDCl_3): δ 3.97 (t, 2H, $^3J_{\text{HH}} = 7.0$), 2.01 (t, 2H, $^3J_{\text{HH}} = 7.0$), 1.97 (s, 3H), 1.96-1.94 (m, 2H); ^{13}C NMR (CDCl_3): δ 63.2, 51.5, 47.3, 38.9, 38.6 (1:1:1 triplet, $^1J_{\text{CD}} = 19.7$).

Preparation of 3-methoxy-3-methyl-butan-1-ol (8a): Commercially available in many sources. 3-methyl-3-buten-1-ol (59 μl , 50.2 mg, 0.58 mmol) was dissolved in dry MeOH (2.5 ml) followed by adding dry NaI (10 mg, 0.067 mmol, 0.1 eq). The reaction mixture was stirred overnight at 40°C , solids were filtered off and the reaction mixture evaporated to dryness *in vacuo*. 3-Methoxy-3-methyl-butan-1-ol (35 mg, 51%) was obtained as a colourless liquid. ^1H NMR (CDCl_3): δ 3.80 (t, 2H, $^3J_{\text{HH}} = 6.0$), 3.52 (br, 1H), 3.22 (s, 3H), 1.75 (t, 2H, $^3J_{\text{HH}} = 6.0$), 1.23 (s, 6H); ^{13}C NMR (CDCl_3): δ 76.7, 60.1, 49.3, 42.3, 24.5 (2C).

Preparation of 3-butoxy-3-methyl-butan-1-ol (8b): 3-Methyl-3-buten-1-ol (89 μl , 75.7 mg, 0.88 mmol) was dissolved in BuOH (2.5 ml) followed by adding dry NaI (7 mg, 0.047 mmol, 0.05 eq). The reaction mixture was stirred for overnight at 50°C , solids were filtered off and the reaction mixture evaporated to dryness *in vacuo*. 3-butoxy-3-methyl-butan-1-ol (72 mg, 45%) was obtained as colorless liquid. ^1H NMR (CDCl_3): δ 3.80 (t, 2H, $^3J_{\text{HH}} = 6.0$), 3.37 (t, 2H, $^3J_{\text{HH}} = 6.5$), 3.26 (br, 1H), 1.74 (t, 2H, $^3J_{\text{HH}} = 5.5$), 1.52-1.46 (m, 2H), 1.39-1.32 (m, 2H), 1.23 (s, 3H), 0.91 (t, 3H, $^3J_{\text{HH}} = 7.5$); ^{13}C NMR (CDCl_3): δ 76.6, 61.2, 60.1, 42.9, 32.7, 25.0 (2C), 19.6, 14.0.

Preparation of 5-Isopropyl-2-methylphenol, carvacrol (9): Oven dried NaI (96 mg, 0.64 mmol, 1.0 eq) was dissolved in dry acetone (3 ml), *R*-(-)-carvone (100 μl , 96 mg, 0.64 mmol) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 400 mg) was added and the reaction mixture was stirred in the dark overnight at room temperature. Dowex was filtered off and acetone was removed by evaporation *in vacuo*. The crude product was dissolved in DCM (5 ml) and washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate, 4 ml), DCM layer was separated, dried with MgSO_4 and removed by evaporation *in vacuo*. Carvacrol (85 mg, 89%) was obtained as brownish oil. All ^1H and ^{13}C NMR data were comparable with those reported elsewhere.² ^1H NMR (CDCl_3): δ 7.04 (d, 1H, $^3J_{\text{HH}} = 8.0$), 6.73-6.71 (m, 1H), 6.66-6.65 (m, 1H), 4.64 (s, 1H), 2.82 (qv, 1H), 2.21 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (CDCl_3): δ 153.8, 148.7, 131.0, 121.0, 119.0, 113.2, 33.9, 24.2 (2C), 15.5.

Preparation of 5-(1-iodo-1-methyl-ethyl)-2-methyl-cyclohex-2-enone (7): When the synthesis of carvacrol (**9**) was stopped after 2 h, solvent was removed and the crude product purified by TLC using ethyl acetate/hexane (1:9) as eluent, 5-(1-iodo-1-methyl-ethyl)-2-methyl-cyclohex-2-enone (80 mg, 45%, Rf. 0.44) was obtained as a colorless oil. All ^1H NMR data were comparable with those reported elsewhere.³ ^1H NMR (CDCl_3): δ 6.75-6.73 (m, 1H), 2.76-2.71 (m, 1H), 2.63-2.55 (m, 1H), 2.39-2.30 (m, 2H), 1.98 (s, 3H), 1.96 (s, 3H), 1.80-1.78 (m, 3H), 1.28-1.20 (m, 1H). ^{13}C NMR (CDCl_3): δ 198.8, 143.9, 135.3, 56.2, 49.9, 43.1, 36.0, 35.8, 31.2, 15.5.

Preparation of (E)-2,3-diiodo-prop-2-en-1-ol (11): Propargyl alcohol (50 μl , 48.2 mg, 0.86 mmol) and oven dried NaI (130 mg, 0.87 mmol, 1 eq) were dissolved to isopropanol (3 ml), oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 500 mg) was added and the reaction mixture was stirred overnight (ca. 16 h) at 65°C . Dowex was filtered off and isopropanol was removed by evaporation *in vacuo*. (E)-2,3-Diiodo-prop-2-en-1-ol (80 mg, 60%) was obtained as a slightly yellow solid. All ^1H and ^{13}C NMR data were comparable with those reported elsewhere.⁴ ^1H NMR (CDCl_3): δ 7.05 (s, 1H), 4.29 (s, 2H), 1.90 (br, 1H). ^{13}C NMR (CDCl_3): δ 104.1, 79.9, 71.0.

Preparation of 5-iodo-pentanol (13a): Oven dried NaI (500 mg, 3.34 mmol), tetrahydropyran (8 ml), and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 2 g) were refluxed for overnight at dark. Dowex was filtered off, the reaction mixture evaporated *in vacuo*. The crude product was dissolved in DCM (10 ml) and washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate, 3 ml), DCM layer was separated, dried with MgSO_4 and removed by evaporation *in vacuo*. The residue was purified by silica column chromatography using ethyl acetate/hexane (1:1) as eluent. 5-Iodo-pentanol (235 mg, 33%) was obtained as a very slightly yellow oil. 1,5-Diiodopentane **13c** was isolated from the same reaction mixture (see below). The total yield was approx. 63% if calculated as both products **13b** (33%) and **13c** (30%) together. It is possible to influence the ratio of the products by the relative amount of tetrahydropyran used in the reaction, as an example, when the following amounts of starting materials were used the calculated yields (not isolated) for **13b** and **13c** were 45% and 23%, respectively, according to the ^1H NMR spectrum: NaI (200 mg), tetrahydropyran (8 ml), and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 800 mg). All ^1H NMR data were comparable with those reported elsewhere.⁵ ^1H NMR (CDCl_3): δ 3.66 (t, 2H, $^3J_{\text{HH}} = 7.0$), 3.20

(t, 2H, $^3J_{\text{HH}} = 7.0$), 1.86 (qv, 2H), 1.63-1.56 (m, 2H), 1.52-1.45 (m, 2H); ^{13}C NMR (CDCl_3): δ 62.9, 33.5, 31.8, 27.0, 7.0.

Preparation of 2-(2-Iodo-ethoxy)-ethanol (13b): Oven dried NaI (1 g, 6.67 mmol), distilled 1,4-dioxane (20 ml), and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 4 g) were refluxed for overnight. Dowex was filtered off, washed with DCM and the reaction mixture with DCM was evaporated *in vacuo*. The crude product was dissolved in DCM (20 ml) and washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate, 6 ml), DCM layer was separated, dried with MgSO_4 and removed by evaporation *in vacuo*. The residue was purified by silica column chromatography using ethyl acetate as eluent. 2-(2-Iodo-ethoxy)-ethanol (980 mg, 68%) was obtained as a very slightly yellow oil. All ^1H NMR data were comparable with those reported elsewhere.⁶ ^1H NMR (CDCl_3): δ 3.79-3.73 (m, 4H), 3.62 (virtual t, 2H), 3.29 (t, 2H, $^3J_{\text{HH}} = 6.5$) 2.00 (t, -OH, $^3J_{\text{HH}} = 6.5$); ^{13}C NMR (CDCl_3): δ 71.7, 71.5, 61.9, 3.1.

Preparation of 1,5-diiodopentane (13c): See the above procedure, 1,5-diiodopentane was isolated as a co-product from the synthesis of **13b**. 1,5-Diiodopentane (160 mg, 30%) was isolated as a very slightly yellow liquid. All ^1H and ^{13}C NMR data were comparable with those reported elsewhere.⁷ ^1H NMR (CDCl_3): δ 3.19 (t, 4H, $^3J_{\text{HH}} = 7.0$), 1.86 (qv, 4H), 1.56-1.49 (m, 2H); ^{13}C NMR (CDCl_3): δ 32.5 (2C), 31.6, 6.3 (2C).

Preparation of octyl iodide (15a): 1-Octanol (183 μl , 151.3 mg, 1.16 mmol) and oven dried NaI (346 mg, 2.31 mmol, 2 eq) were dissolved in di-isopropyl ketone (12 ml), oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.5 g) was added to it and the reaction mixture was stirred for overnight (ca. 16 h) at 100°C . Dowex was filtered off and di-isopropyl ketone was removed by evaporation *in vacuo*. The crude product was purified in a silica column chromatography using hexane/ethyl acetate (9:1) as eluent. Octyl iodide (120 mg, 43%) was obtained as colorless oil. All ^1H NMR data were comparable with those reported elsewhere.⁸ ^1H NMR (CDCl_3): δ 3.19 (t, 2H, $^3J_{\text{HH}} = 7.0$), 1.82 (qv, 2H), 1.43-1.36 (m, 2H), 1.34-1.24 (m, 8H), 0.89 (t, 2H, $^3J_{\text{HH}} = 7.0$); ^{13}C NMR (CDCl_3): δ 33.7, 31.9, 30.7, 29.2, 28.7, 22.8, 14.2, 7.4.

Preparation of 12-Iodo-dodecanoic acid (15b): 12-Hydroxydodecanoic acid (200 mg, 0.92 mmol) was dissolved in dry acetonitrile (8 ml), oven dried NaI (300 mg, 2.0 mmol, 2.15 eq) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.2 g) were added and the

reaction mixture was refluxed for 5 h. Dowex was filtered off and the reaction mixture evaporated to dryness *in vacuo*. The crude product was purified by silica column chromatography using ethyl acetate/hexane (1:3) as eluent. 12-Iodo-dodecanoic acid (215 mg, 71%) was obtained as a yellow solid. All ^1H and ^{13}C NMR data were comparable with those reported elsewhere.^{9,10} ^1H NMR (CDCl_3): δ 3.19 (t, 2H, $^3J_{\text{HH}}=7.0$), 2.35 (t, 2H, $^3J_{\text{HH}}=7.5$), 1.82 (qv, 2H, $^3J_{\text{HH}}=7.5$), 1.67-1.60 (m, 2H), 1.40-1.35 (m, 2H), 1.34-1.24 (m, 12H); ^{13}C NMR (CDCl_3): δ 180.2, 34.2, 33.7, 30.6, 29.6, 29.50, 29.48, 29.3, 29.2, 28.7, 24.8, 7.4.

Preparation of (Z)-Octadec-9-enoic acid methyl ester (17): (Z)-Octadec-9-enoic acid (250 μl , 223.8 mg, 0.79 mmol) was dissolved in MeOH (6 ml), oven dried NaI (12 mg, 0.08 mmol, 0.1 eq) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.0 g) were added and the reaction mixture was stirred for 1 h at room temperature. Dowex was filtered off, washed with MeOH and the liquids evaporated to dryness *in vacuo*. (Z)-Octadec-9-enoic acid methyl ester (232 mg, 99%) was obtained as a colorless oil. All ^1H NMR data were comparable with those reported elsewhere.¹¹ ^1H NMR (CDCl_3): δ 5.38-5.32 (m, 2H), 3.67 (s, 3H), 2.31 (t, 2H, $^3J_{\text{HH}}=7.5$), 2.03-1.98 (m, 4H), 1.65-1.58 (m, 2H), 1.37-1.20 (m, 20H), 0.88 (t, 3H, $^3J_{\text{HH}}=7.0$); ^{13}C NMR (CDCl_3): δ 174.7, 130.2, 129.9, 51.7, 34.3, 32.1, 29.9, 29.8, 29.7, 29.48, 29.47, 29.30, 29.28, 29.24, 27.37, 27.32, 25.1, 22.8, 14.3.

Preparation of 12-hydroxy-dodecanoic acid isopropyl ester (18): 12-hydroxydodecanoic acid (200 mg, 0.92 mmol) was dissolved in 2-propanol (8 ml), oven dried NaI (28 mg, 0.19 mmol, 0.2 eq) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.5 g) were added and the reaction mixture was refluxed for 4 h. Dowex was filtered off and any excess of 2-propanol was removed by evaporation *in vacuo*. The crude product was purified by silica column chromatography using ethyl acetate/hexane (3:2) as eluent. 12-Hydroxy-dodecanoic acid isopropyl ester (168 mg, 70%) was obtained as a white solid. ^1H NMR (CDCl_3): δ 4.99 (qv, 1H, $^3J_{\text{HH}}=6.5$), 3.62 (t, 2H, $^3J_{\text{HH}}=6.5$), 2.24 (t, 2H, $^3J_{\text{HH}}=7.5$), 1.62-1.51 (m, 4H), 1.46 (br, 1H), 1.35-1.23 (m, 14H), 1.21 (d, 6H, $^3J_{\text{HH}}=6.5$); ^{13}C NMR (CDCl_3): δ 173.6, 67.4, 63.2, 34.9, 32.9, 29.7, 29.6, 29.5 (2C), 29.4, 29.2, 25.9, 25.2, 22.0 (2C).

Preparation of octyl acetate (19a): 1-Octanol (400 μl , 330.8 mg, 2.54 mmol) was dissolved in dry acetonitrile (8 ml), oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.5 g) and H_2O (91 μl , 2 eq) were added and the reaction mixture was refluxed for 48 h. Dowex was

filtered off and acetonitrile was removed by evaporation *in vacuo*. The crude product was purified by silica column chromatography using hexane/ethyl acetate (9:1) as the eluent. Acetic acid octyl ester (175 mg, 40%) was obtained as a colorless oil. All ^1H and ^{13}C NMR data were comparable with those reported elsewhere.¹² ^1H NMR (CDCl_3): δ 4.05 (t, 2H, $^3J_{\text{HH}} = 7.0$), 2.04 (s, 3H), 1.61 (qv, 2H), 1.38-1.22 (m, 10H), 0.88 (t, 3H, $^3J_{\text{HH}} = 7.0$). ^{13}C NMR (CDCl_3): δ 171.4, 64.8, 31.9, 29.36, 29.32, 28.8, 26.1, 22.8, 21.2, 14.2.

Preparation of propionic acid octyl ester (19b): 1-Octanol (400 μl , 330.8 mg, 2.54 mmol) was dissolved in propionitrile (8 ml) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.0 g) was added and the reaction mixture was refluxed overnight. Dowex was filtered off and propionitrile was removed by evaporation *in vacuo*. The crude product was purified by silica column chromatography using hexane/ethyl acetate (9:1) as the eluent. Propionic acid octyl ester (195 mg, 41%) was obtained as a colorless oil. All ^1H and ^{13}C NMR data were comparable with those reported elsewhere.^{13,14} ^1H NMR (CDCl_3): δ 4.06 (t, 2H, $^3J_{\text{HH}} = 7.0$), 2.32 (q, 2H, $^3J_{\text{HH}} = 7.5$), 1.62 (qv, 2H), 1.38-1.22 (m, 10H), 1.14 (t, 3H, $^3J_{\text{HH}} = 7.5$), 0.88 (t, 3H, $^3J_{\text{HH}} = 7.0$). ^{13}C NMR (CDCl_3): δ 171.8, 64.6, 31.9, 29.37, 29.32, 28.8, 27.8, 26.1, 22.8, 14.2, 9.3.

Preparation of isoamyl acetate (21): Isoamyl alcohol (2.0 ml, 1.62 g, 18.4 mmol) was dissolved in acetic acid (2 ml, 2.1 g, 34.9 mmol, 1.9 eq), oven dried NaI (275 mg, 1.83 mmol, 0.1 eq) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 1.0 g) were added and the reaction mixture stirred for 2 h at 50°C . 100%, complete, conversion of isoamyl alcohol to isoamyl acetate was achieved according to the ^1H NMR spectrum. **Isolation of 21:** Dowex was filtered off and the reaction mixture moved to a separation funnel and washed with a saturated NaHCO_3 solution (20 ml) and with 10% $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate, 5 ml). The organic layer was separated and dried over MgSO_4 . Isoamyl acetate (1.53 g, 64%) was obtained as a colorless liquid. All ^1H NMR data were comparable with those reported elsewhere.¹⁵ ^1H NMR (CDCl_3): δ 4.09 (t, 2H, $^3J_{\text{HH}} = 7.0$), 2.03 (s, 3H), 1.72-1.64 (m, 1H), 1.51 (q, 2H, $\Sigma^3J_{\text{HH}} = 7.0$), 0.92 (d, 6H, $^3J_{\text{HH}} = 6.5$).

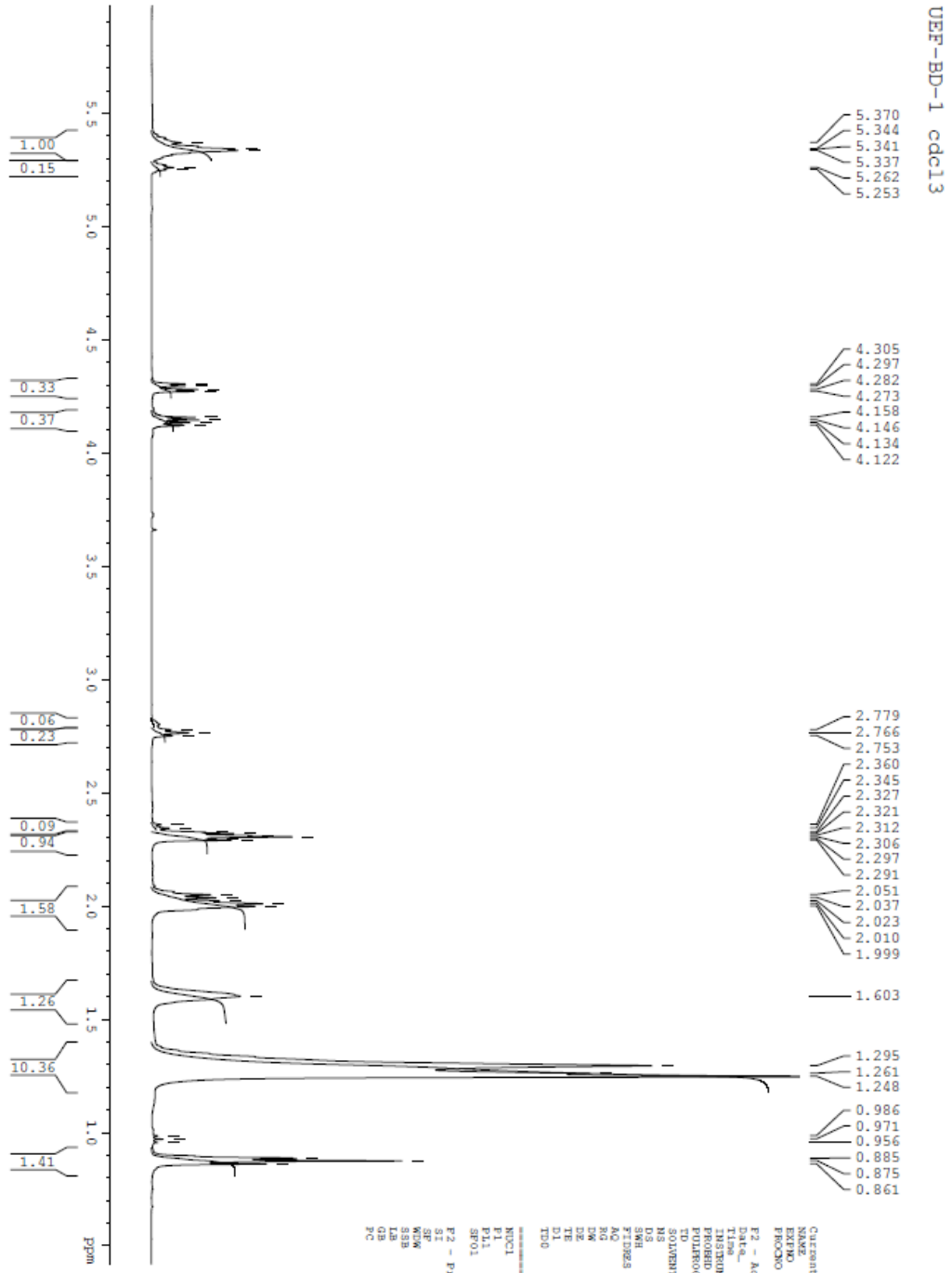
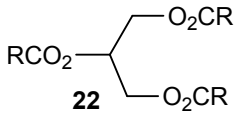
Preparation of biodiesel (23): Used cooking oil (5 g) was dissolved to MeOH (100 ml), oven dried NaI (850 mg, 5.67 mmol,) and oven dried Dowex 50W-X8 ion exchange resin (H^+ -form, 5 g) were added and the reaction mixture was refluxed overnight. Dowex was

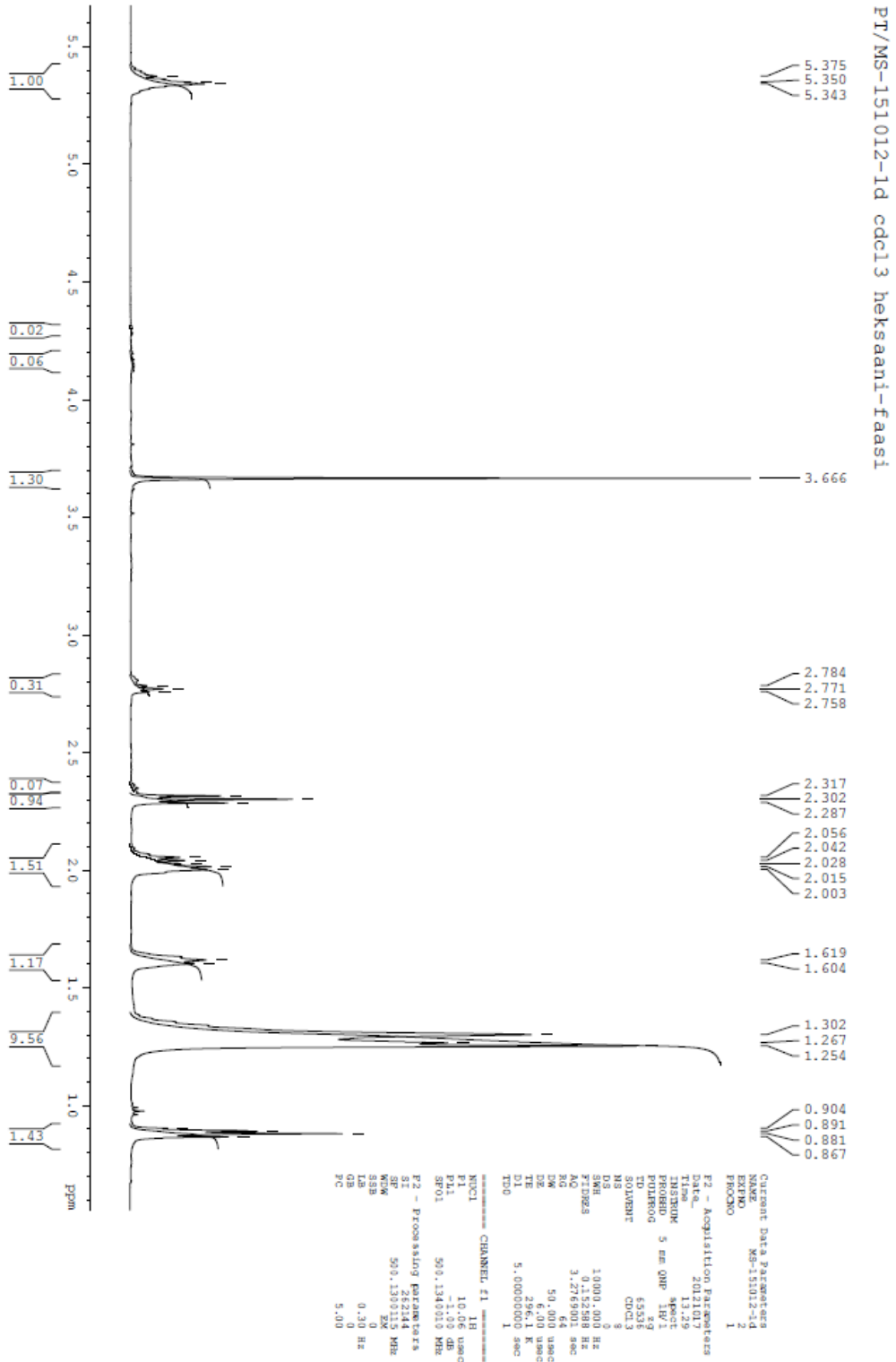
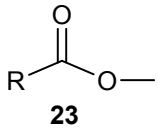
filtered off and MeOH was removed by evaporation *in vacuo*. The residue was dissolved in hexane (20 ml), washed with water (10 ml) and the hexane layer was dried over MgSO₄ before evaporated *in vacuo*. Biodiesel **23** (4.3 g) was obtained as a colorless oil. ¹H NMR (CDCl₃): δ 5.38-5.32 (m), 3.67 (s, 3H), 2.31 (t), 2.03-1.98 (m), 1.65-1.58 (m), 1.37-1.20 (m), 0.88 (t).

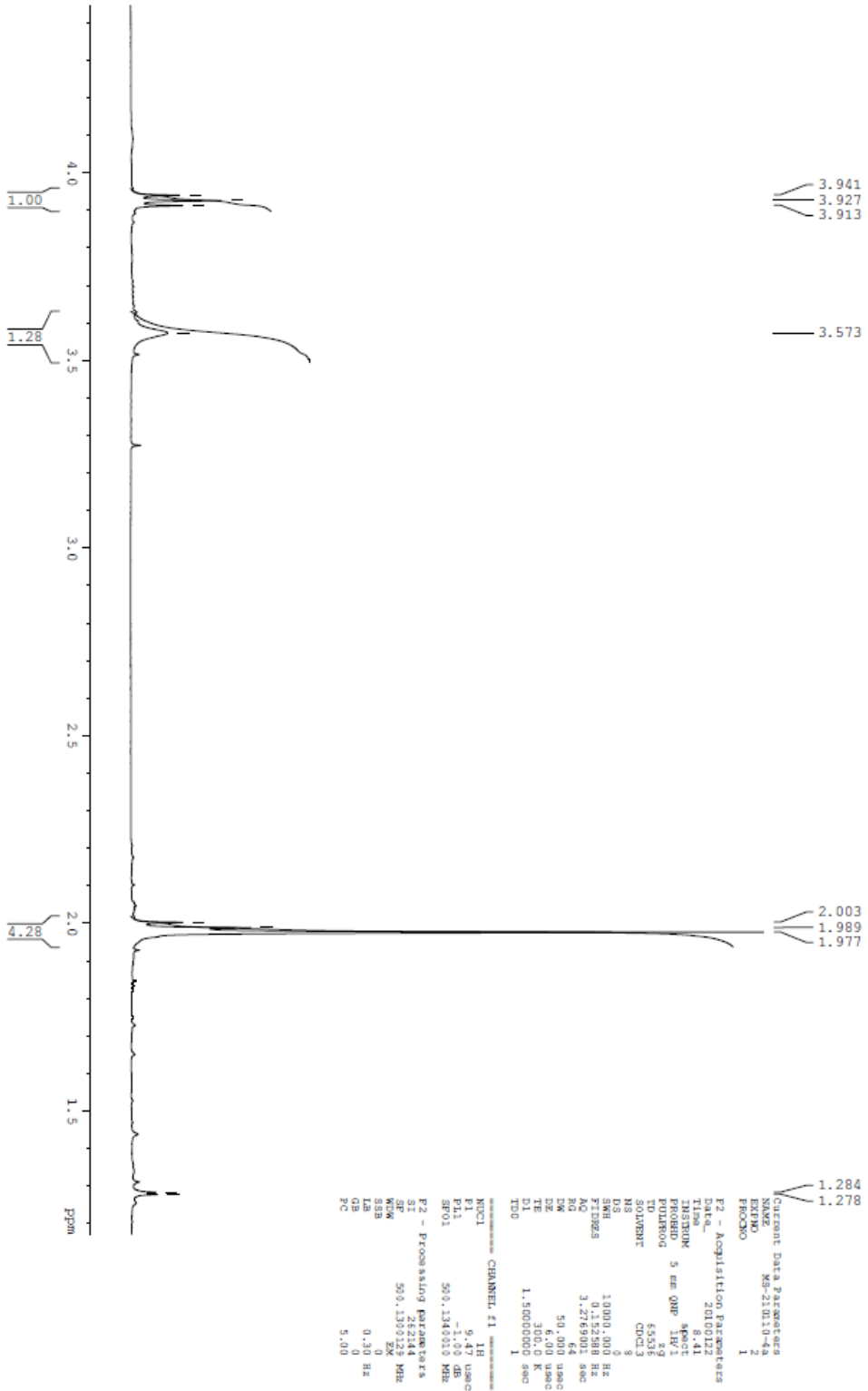
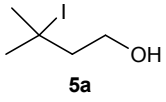
Preparation of 3-(Formyloxy)-2-phenylpropanoic acid (25): Tropic acid (200 mg, 1.20 mmol), dry NaI (180 mg, 1.20 mmol, 1 eq), dried Dowex 50W-X8 ion exchange resin (H⁺-form, 800 mg) and dry DMF (5 ml) were stirred overnight at 115°C followed by evaporation to dryness. The residue was dissolved in DCM (10 ml) and washed with 10% Na₂S₂O₃ (sodium thiosulfate, 5 ml). The aqueous phase was extracted with DCM (5 ml), combined DCM fractions were washed with 0.2 M HCl (7 ml) and water (7 ml) before being dried over MgSO₄ and evaporated to dryness. The residue was dissolved into a mixture of diethyl ether (2 ml) and n-hexane (2 ml) followed by cooling overnight at approx. - 18°C. The precipitate formed was filtered and dried *in vacuo*. 3-(formyloxy)-2-phenylpropanoic acid (131 mg, 56%) was obtained as a white solid. M.p. 69-72°C (decomposed). ¹H NMR (CDCl₃): δ 8.03 (s, 1 H), 7.39-7.32 (m, 5H), 4.68 (t, 3H, ³J_{HH} = 10.0), 4.48-4.43 (m, 1H), 4.03-3.98 (m, 1 H). ¹³C NMR (CDCl₃): δ 176.8, 160.6, 134.0, 129.3 (2C), 128.6, 128.3 (2C), 64.2, 50.5. MS (ESI⁻) calcd. for C₁₀H₉O₄ [M-H]⁻ 193.0501, found: 193.0496.

Preparation of (2S,3R,4S,5S)-6-(isopropoxymethyl)tetrahydro-2H-pyran-2,3,4,5-tetraol (27): D(+)-glucose (100 mg, 0.56 mmol) was dissolved in distilled 2-propanol (4 ml), dry NaI (125 mg, 0.83 mmol, 1.5 eq) and dried Dowex 50W-X8 ion exchange resin (H⁺-form, 500 mg) were added and the reaction mixture was refluxed overnight. Solids were filtered off and 2-propanol was removed by evaporation *in vacuo*. The crude product was purified by silica column chromatography using ethyl acetate/methanol (8:2) as eluent yielding **12** (102 mg, 83%, 1:2 mixture of isomers) as a brownish solid. ¹H NMR (CD₃OD): Major isomer: δ 4.89 (d, 1H, ³J_{HH} = 3.9 Hz), 3.94 (sep, 1H, ³J_{HH} = 6.2 Hz), 3.79 (dd, 1H, ²J_{HH} = 11.3 Hz, ³J_{HH} = 1.9 Hz), 3.68-3.59 (m, 3H), 3.38-3.23 (m, 2H), 1.24 (d, 3H, ³J_{HH} = 6.2 Hz), 1.18 (d, 3H, ³J_{HH} = 6.2 Hz); Minor isomer: 4.33 (d, 1H, ³J_{HH} = 7.8 Hz), 4.04 (sep, 1H, ³J_{HH} = 6.2 Hz), 3.85 (dd, 1H, ²J_{HH} = 11.8 Hz, ³J_{HH} = 2.2 Hz), 3.68 (d, 1H, ²J_{HH} = 11.8 Hz), 3.38-3.23 (m, 3H) 3.16-3.11 (m, 1H), 1.23 (d, 3H, ³J_{HH} = 6.2 Hz), 1.19 (d, 3H, ³J_{HH} = 6.2 Hz). ¹³C NMR (CDCl₃): Major isomer: δ 98.2, 75.1, 73.6, 73.5, 72.0, 70.9, 62.7, 23.7, 21.6; Minor isomer: 102.6,

78.1, 77.9, 75.2, 72.6, 71.7, 62.8, 23.8, 22.0. MS (ESI⁺) calcd. for C₉H₁₈O₆Na [M+Na]⁺
245.1001, found: 245.0995.

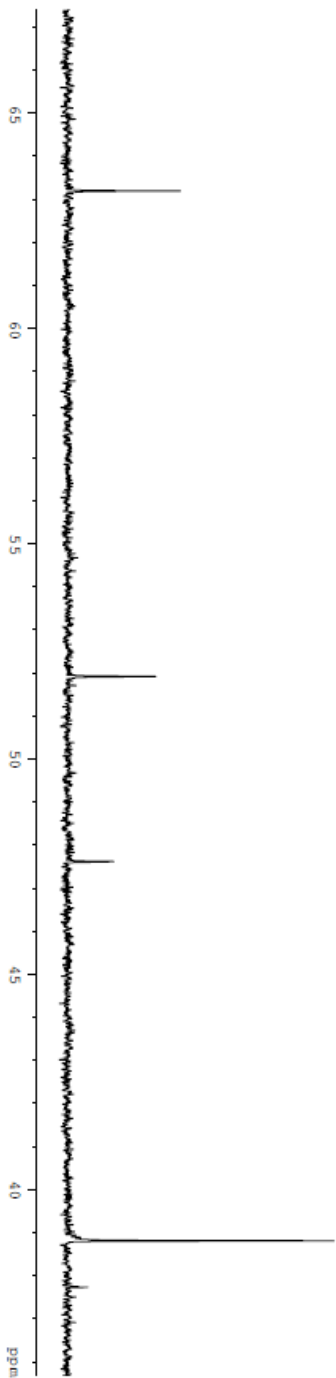






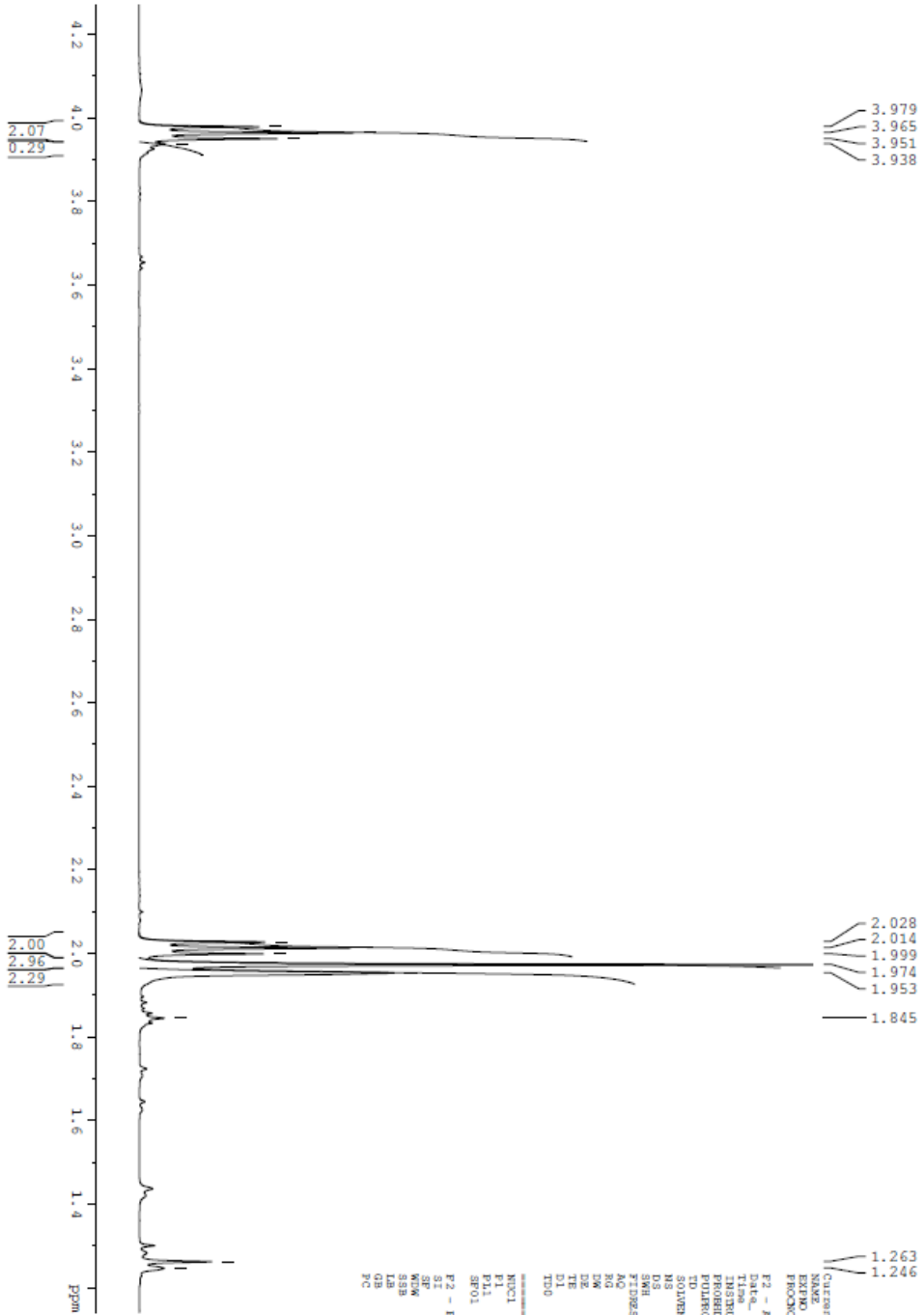
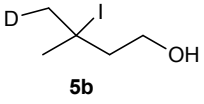
PT/MS-260514-1 cdCl3

63.20
51.92
47.62
38.81

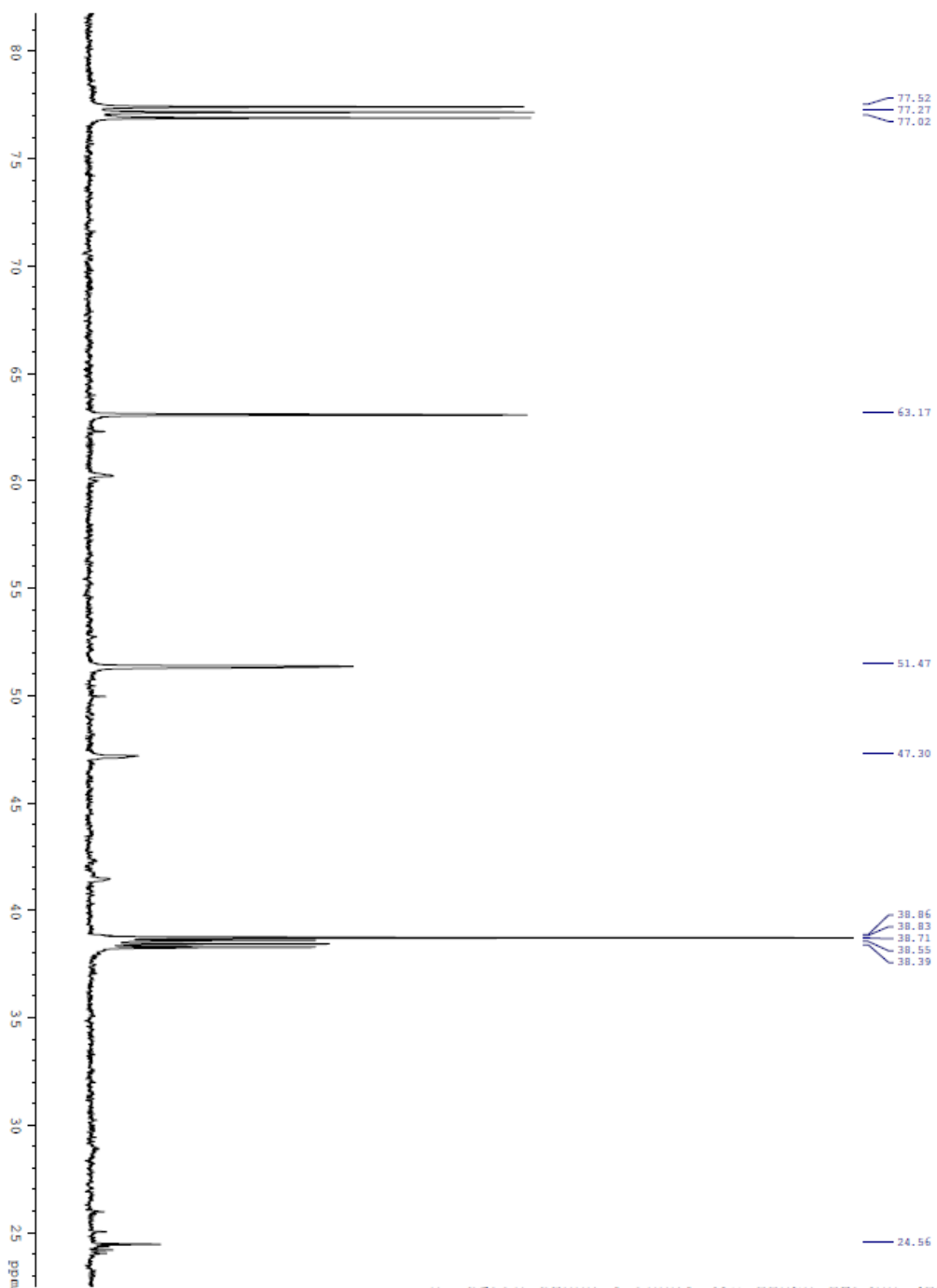


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PROCNO 1
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F2 - Acquisition Parameters
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Time 11:47
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PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 131072
SFO 125.762
AQ 63
SI 63
DS 0
SWH 30303.031 Hz
FIDRES 0.231194 Hz
AQ 2.1627345 sec
RG 654
DE 16.500 usec
DE 6.00 usec
TE 300.0 K
D1 8.00000000 sec
d11 0.03000000 sec
TD0 1
=====
CHANNEL F1
NUC1 13C
P1 1.30 usec
PL1 0.00 dB
SFO1 125.7715724 MHz
=====
CHANNEL F2
NAME16 waltz16
NUC2 13C
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 18.00 dB
SFO2 500.1322506 MHz
=====
F2 - Processing parameters
SI 524288
SF 125.757725 MHz
WDW EM
SSB 0
GB 1.20 Hz
PC 1.40
  
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PT/MS-050310-2 cd c13- liukoinen



Current Data Parameters
 BRNO M-050310-2
 PRONO 1

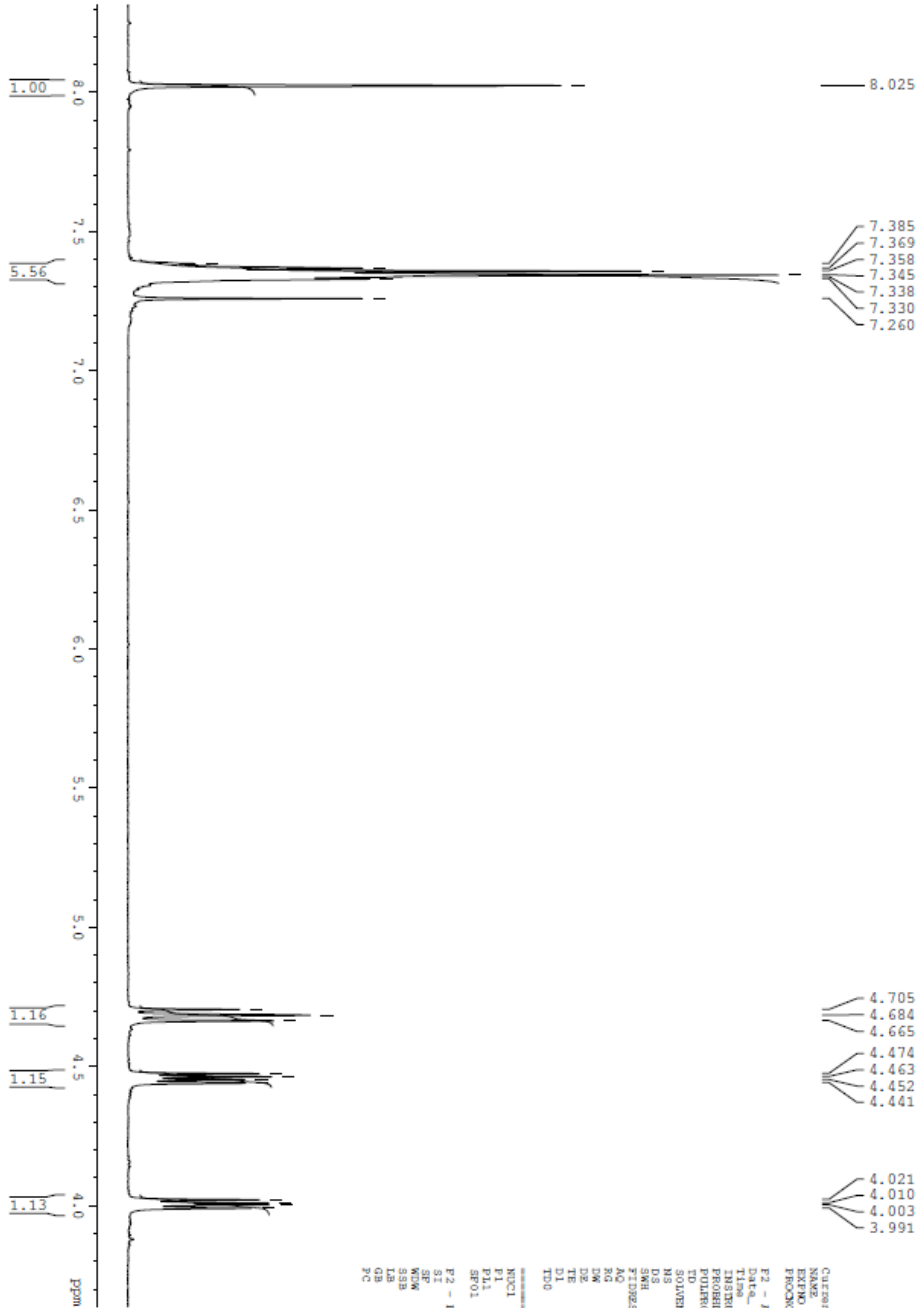
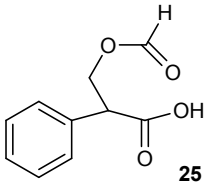
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 Date_ 20100909
 Time 14:41
 INSTRUM spect
 PROBD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 131072
 SFO 125.761171
 SOLVENT CDCl3
 NS 262
 DS 0

SWH 30303.031 Hz
 FIDERS 0.231194 Hz
 RG 2.1623145 sec
 AQC 0.020444 sec
 DW 16.500 usec
 DDE 6.00 usec
 TE 298.1 K
 DT 3.0000000 sec
 D1 0.05000001 sec
 TDO 1

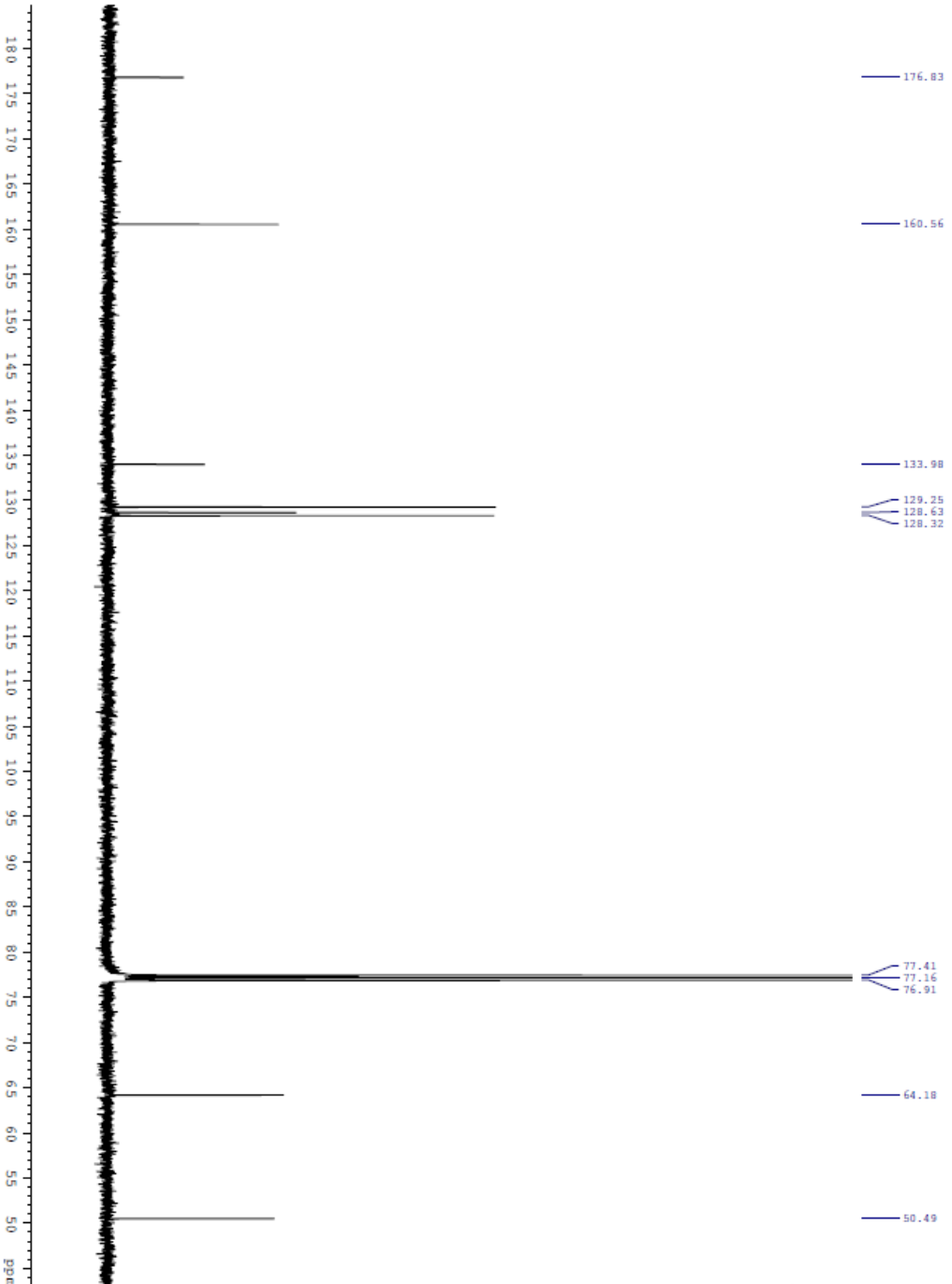
CHANNEL F1
 NUCL 13C
 P2 7.13 usec
 PL 6.00 dB
 SFO 125.7715724 MHz

CHANNEL F2
 PRORG2 waltz16
 NUCL2 13C
 P2 7.13 usec
 PCPD2 90.00 usec
 PL2 -1.00 dB
 PL12 18.56 dB
 SFO2 500.1322906 MHz

F2 - Processing Parameters
 SI 262144
 SF 125.757794 MHz
 WGM SM
 LB 2.00 Hz
 GB 0
 PC 1.40



PT/MS-220812-1a cdcl3 lisse halthd.



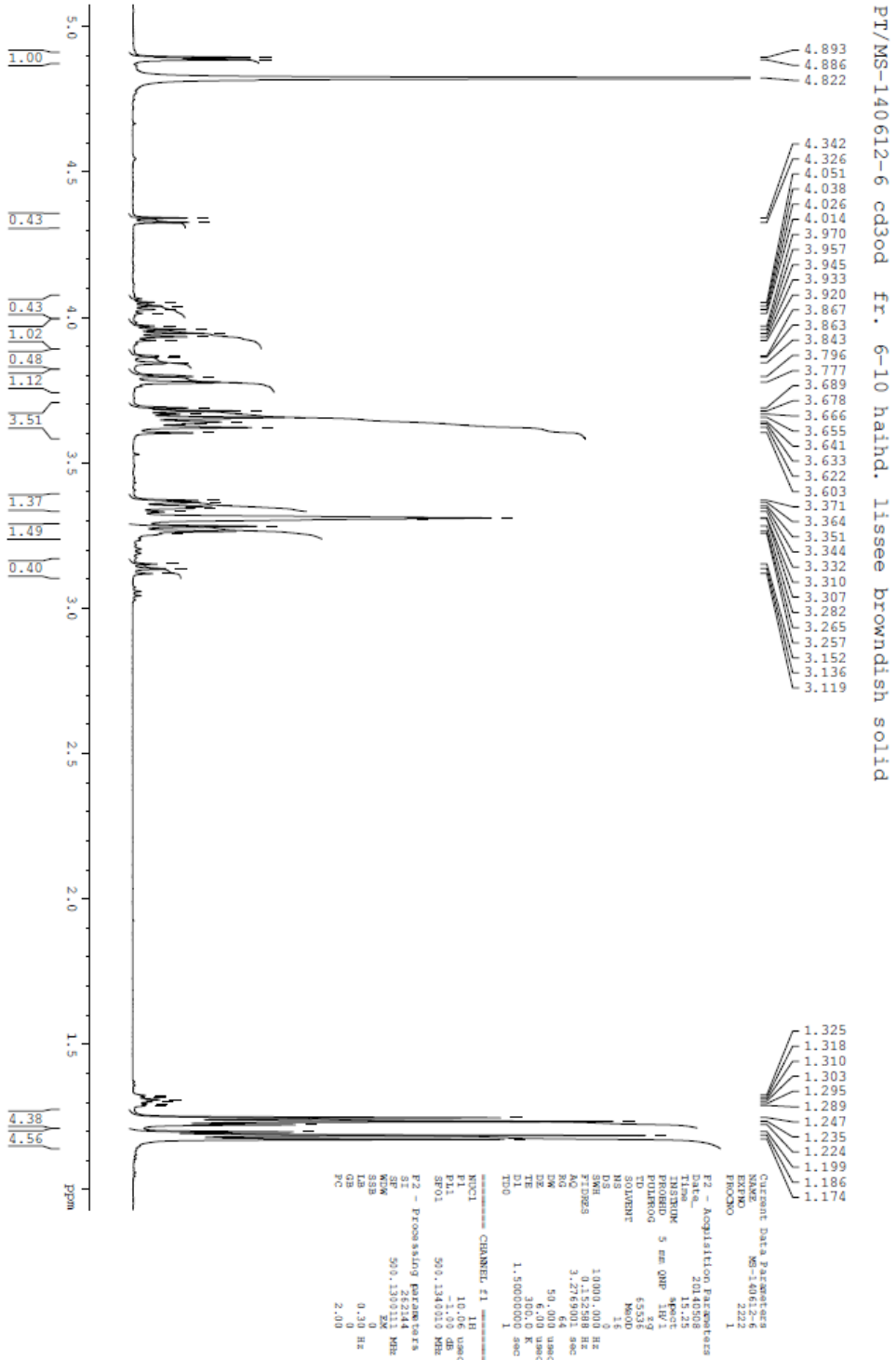
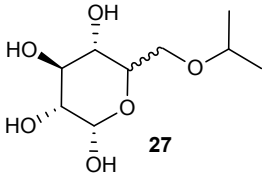
Current Data Parameters
 Name MS-220812-1a
 ExpNO 32
 PROCNO 1
 PROBNM 1

F2 - Acquisition Parameters
 Date_ 20160229
 Time 17:00:00
 INSTRUM spect
 PROBNM 5 mm QNP 1H/1
 PULPROG zgpg
 TD 131072
 SFO 500.132506
 NS 423
 DS 4
 SWH 30933.031 Hz
 FIDRES 0.231194 Hz
 AQ 2.162492 sec
 RG 6145
 CW 16.500 usec
 DE 6.00 usec
 TE 300.0 K
 F2 12.0000000 sec
 d1 0.0300000
 TD0 1

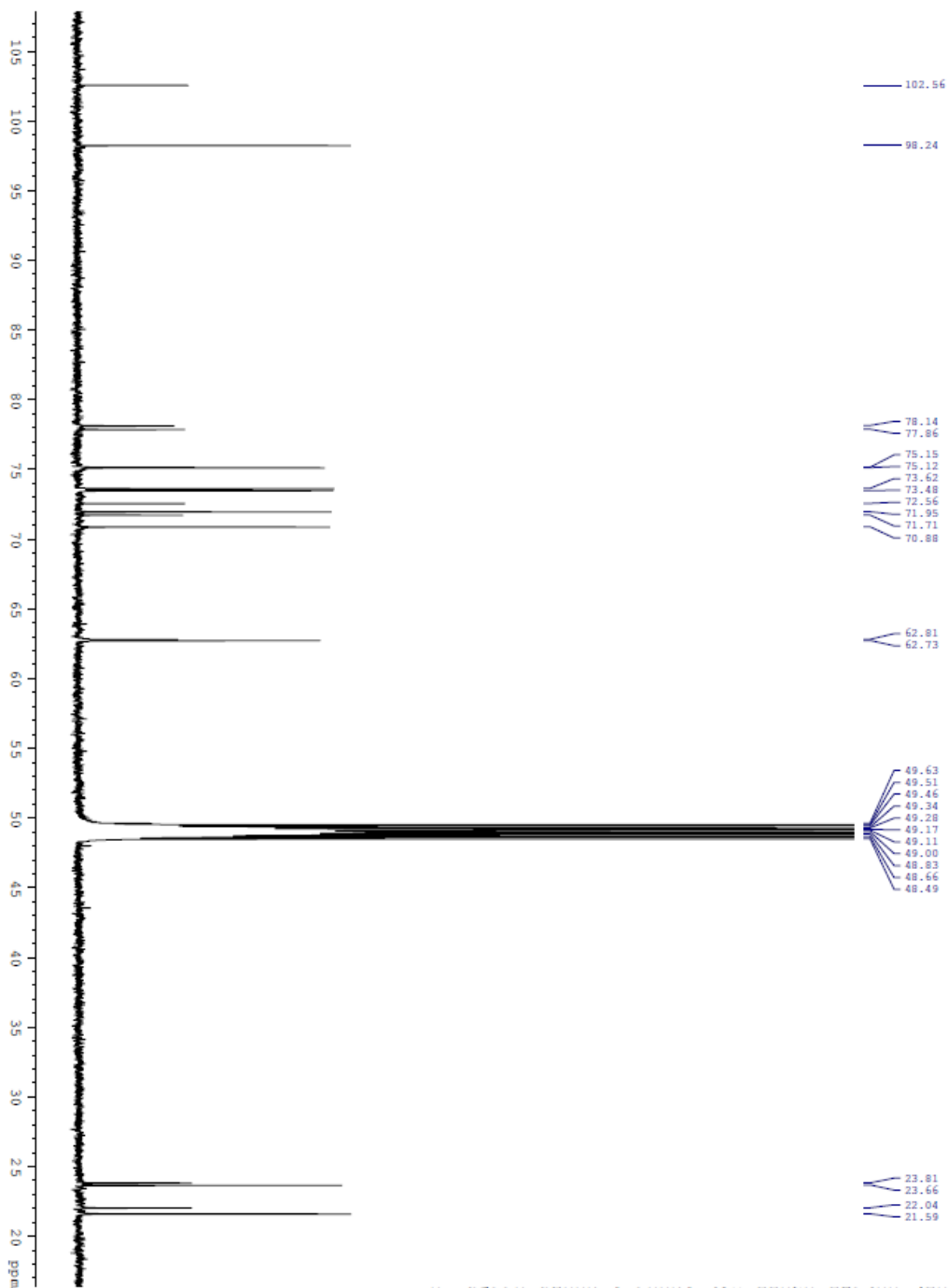
CHANNEL F1
 NUCL1 13C
 P1 1.00 usec
 PL1 0.00 dB
 SFO1 125.771524 MHz

CHANNEL F2
 CHPROG2 waltz16
 NUCL2 1H
 P2 90.00 usec
 PL2 -1.00 dB
 PL12 18.00 dB
 SFO2 500.132506 MHz

F2 - Processing Parameters
 SI 524288
 SF 125.757711 MHz
 KW 64
 SFO 500.132506 MHz
 VB 0
 GB 1.20 Hz
 PC 1.40



PT/MS-140612-6 cd3od fr. 6-10 haihd. lissee brownish solid



Current Data Parameters
 BRNO M-140612
 PRNO 333
 1

F2 - Acquisition Parameters
 Date_ 20140509
 Time_ 11:44
 INSTRM spect
 PROBD 5 mm QNP 1H/1
 aspect
 PULPROG zgpg30
 TD 131072
 SFOURNT 4675
 NS 0
 DS 30303.031 Hz
 SWH 0.231194 Hz
 FIDRES 2.1623145 sec
 AQ 0.00000000
 RG 16.500 usec
 DW 6.00 usec
 DE 300.0 K
 TE 01
 D1 12.0000000 sec
 D11 0.03000001 sec
 TD0 1

CHANNEL F1
 NUCL 13C
 PULPROG zgpg30
 FIDRES 2.1623145 sec
 AQ 0.00000000
 RG 16.500 usec
 DW 6.00 usec
 DE 300.0 K
 TE 01
 D1 12.0000000 sec
 D11 0.03000001 sec
 TD0 1

CHANNEL F2
 NUC1 1H
 PULPROG waltz16
 FIDRES 2.1623145 sec
 AQ 0.00000000
 RG 16.500 usec
 DW 6.00 usec
 DE 300.0 K
 TE 01
 D1 12.0000000 sec
 D11 0.03000001 sec
 TD0 1

F2 - Processing parameters
 SI 534288
 SF 125.7576136 MHz
 WGM EX
 WB 1.20 Hz
 GB 0
 PC 1.40

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