

Solvent free silica gel mediated decarboxylation of C–O coupling products of β -diketones and β -oxo esters with malonyl peroxides

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General Information

Caution: Although malonyl peroxides possess sufficient thermostability, safety precautions should be applied.

The commercially available (Acros Organic, cat. no. 240370300) silica gel was used for reactions: CAS 7631-86-9, 60-200 μm , 60 \AA , appearance (color) – white, appearance (form) – powder, pH - 6.5 to 7.5 (10% w/w suspension), specific surface area 470 to 530 $\text{m}^2 \text{g}^{-1}$, pore diameter 58 to 68 \AA , pore volume 0.70 to 0.85 ml g^{-1} , volatile matter 3 to 6 % (160 $^\circ\text{C}$), particle size 5.0% max. (under size), 5.0% max. (over size).

CDCl_3 was used as solvent for recording NMR spectra (^1H NMR - 300.13 MHz, ^{13}C NMR - 75.48 MHz). Electrospray ionization (ESI) method was applied for obtaining HRMS data [S1]. A positive ion mode (interface capillary voltage 4500 V) was applied for the measurements; the mass ratio was from m/z 50 to 3000 Da; Electrospray Calibrant Solution was used for external/internal calibration. A syringe injection (flow rate 3 $\mu\text{l min}^{-1}$) was carried out for solutions in MeCN. Nitrogen was applied as a dry gas; interface temperature was 180 $^\circ\text{C}$.

Column chromatography and reactions was performed on silica gel (0.060-0.200 mm, 60 \AA , CAS 7631-86-9). Thin-layer chromatography (TLC) was carried out using standard silica gel plates coated with fluorescent indicator F254. All solvents were distilled before use using standard procedures.

Starting dicarbonyl compounds **1a**, [S2] **1b**, [S3] **1c**, [S4] **1f**, [S5] **1h**, [S5] **1i**, [S6] **1j**, [S7] and malonyl peroxides **2a-d** [S8] were synthesized according to the literature procedures. Starting dicarbonyl compounds **1d**, **1e**, **1g**, **1k**, **1l**, **1m**, 2,2-diethyl malonic acid were purchased from commercial sources and was used as is.

Scanning electron microscopy (SEM) data

The field-emission scanning electron microscopy (FE-SEM) study of used silica gel (60-200 μm) showed that sample contains particles with a size of about 100 μm (Figure S1). The surface of silica gel is irregular.

Target-oriented approach was utilized for the optimization of the analytic measurements [S9]. Before measurements the samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive tape. Metal coating with a thin film (7 nm) of gold/palladium alloy (60/40) was performed using magnetron sputtering method as described earlier [S10]. The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 2 kV accelerating voltage and at working distance 4-5 mm. Morphology of the samples was studied taking into account possible influence of metal coating on the surface [S10].

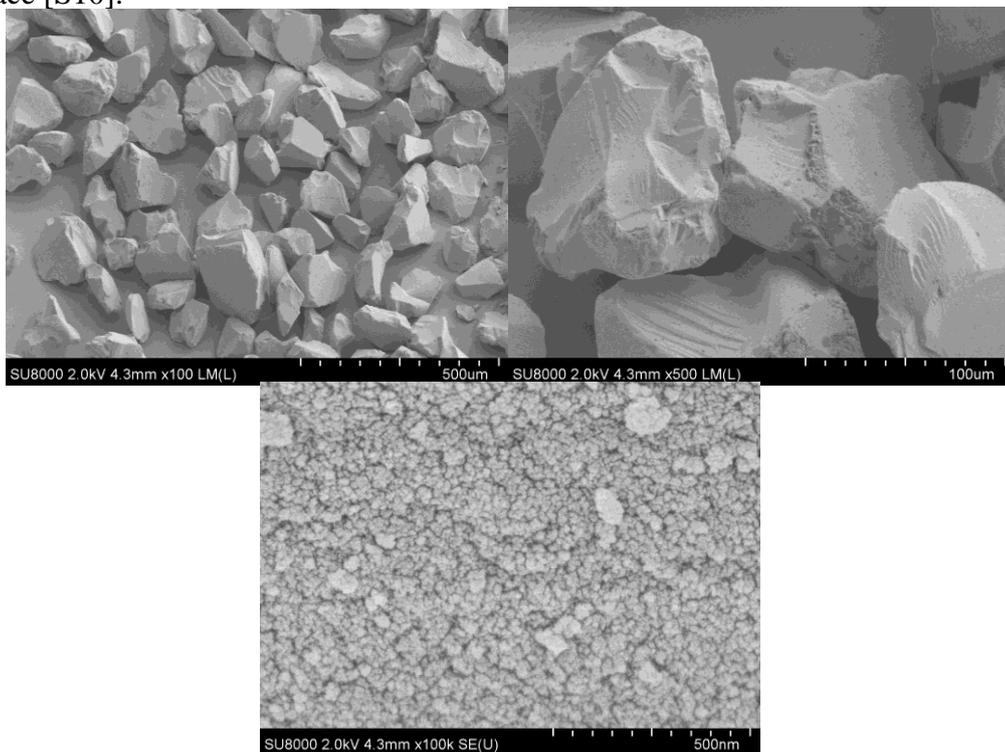


Figure S1. SEM images of silica gel 60-200 μm

The energy dispersive X-ray microanalysis (EDX) showed that tested silica gel sample did not contain impurities of heavy metals (Figure S2).

The X-ray microanalysis was carried out using energy-dispersive X-ray spectrometer OxfordInstruments X-max. The background signals of carbon (support, sputtering) and aluminum (support) are observed in addition to the main signals of Si and O in all spectra. The elemental composition of the sample is calculated with the use of data shown on the spectrum (the carbon is ignored because of the carbon deposition is used in accordance with program settings).



Figure S2. Energy-dispersive X-ray (EDX) spectra of silica gel 60-200 μm .

EXPERIMENTAL SECTION

Caution: Safety precautions should be applied in working with peroxides.

Experimental Procedures for Table 1. SiO₂ - mediated decarboxylation of tetracarbonyl compound 3ja prepared *in situ* from β-oxo ester 1j and malonyl peroxide 2a.

Experimental Procedure for entries 2, 4-7, 9: β-Oxo ester **1j** (100.0 mg, 0.45 mmol, 1.0 eq.) was mixed with SiO₂ (54.4 mg, 0.9 mmol, 2.0 eq.). Then into well-stirred reaction mixture malonyl peroxide **2a** (107.6 mg, 0.68 mmol, 1.5 eq.) was slowly loaded within 5 min. The reaction mass was stirred from 2 to 24 h at the temperature 25-200 °C. Then CH₂Cl₂ (10 ml) was added, the formed precipitate was separated, rinsed with CH₂Cl₂ (3 × 3 ml). The organic layers were combined and concentrated *in vacuo* (10-20 Torr). Products **3j** and **4j** were isolated by column chromatography on silica gel with eluent: petroleum ether (40-70) / EtOAc (volume ratio = from 20:1 to 2:1).

Experimental Procedure for entries 1, 3, 8: To well-stirred β-oxo ester **1j** (100.0 mg, 0.45 mmol, 1.0 eq.) malonyl peroxide **2a** (107.6 mg, 0.68 mmol, 1.5 eq.) was slowly loaded for 5 min. The reaction mass was stirred from 2 to 24 h at the temperature 25-200 °C. Products **3j** and **4j** were isolated by column chromatography on silica gel with eluent: petroleum ether (40-70) / EtOAc (volume ratio = from 20:1 to 2:1).

Experiments for proving of the reaction pathway: preparation of decarboxylation products 4a, 4h, 4j from preliminary synthesized C-O coupling products 3a, 3h, 3j.

Prepared according to literature procedure [S11] C-O coupling product **3a** (179.2 mg, 0.50 mmol, 1.0 eq.), **3h** (172.2 mg, 0.50 mmol, 1.0 eq.), **3j** (189.2 mg, 0.50 mmol, 1.0 eq.) was mixed with SiO₂ (60.0 mg, 1.0 mmol, 2.0 eq.). The reaction mass was stirred for 2 h at the temperature of 120 °C. Decarboxylation products **4a, 4h, 4j** were isolated by column chromatography on silica gel with eluent: petroleum ether (40-70) / EtOAc (volume ratio = from 20:1 to 2:1).

Experimental Procedure for Scheme 1. Synthesis C-O coupling/decarboxylation products 4a-s.

β-Diketone **1a-f** (500.0 mg, 2.23-3.96 mmol, 1.0 eq.), β-oxo ester **1g-l** (500.0 mg, 2.27-3.47 mmol, 1.0 eq.) or lactone **1m** (500.0 mg, 3.90 mmol, 1.0 eq.) was mixed with SiO₂ (267.0-475.6 mg, 4.45-7.93 mmol, 2.0 eq.). Then into well-stirred reaction mixture malonyl peroxide **2a-d** (505.7-1028.8 mg, 3.34-5.95 mmol, 1.5 eq.) was slowly loaded for 5 min. The reaction mass was mixed for 2 h at the temperature 120 °C. Then CH₂Cl₂ (10 ml) was added, the formed precipitate was separated and rinsed with CH₂Cl₂ (3 × 3 ml). The organic layers were combined and concentrated *in vacuo* (10-20 Torr). Decarboxylation products **4a-s** were isolated by column chromatography on silica gel with eluent: petroleum ether (40-70) / EtOAc (volume ratio = from 20:1 to 2:1).

Characterization data of C-O coupling/decarboxylation products 4.

Ethyl 4-acetyl-4-(2-ethylbutanoyloxy)-5-oxohexanoate, 4a

643 mg (2.05 mmol, 82 %).

Colorless oil. R_f = 0.88 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH).

¹H NMR (300.13 MHz; CDCl₃; 25 °C): δ = 0.96 (t, *J* = 7.3 Hz, 6H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.53-1.75 (m, 4H), 2.14-2.31 (m, 9H), 2.57 (t, *J* = 7.7 Hz, 2H), 4.09 ppm (q, *J* = 7.3 Hz, 2H);

¹³C NMR (75.48 MHz; CDCl₃; 25 °C): δ = 11.6, 14.1, 24.5, 26.6, 28.1, 28.5, 48.3, 60.8, 92.3, 171.9, 174.8, 201.5 ppm;

HRMS (ESI) *m/z* [M+Na]⁺: Calcd for [C₁₆H₂₆NaO₆]⁺: 337.1622. Found: 337.1615;

Anal.: Calcd (%) for C₁₆H₂₆O₆ (314.37): C 61.13, H 8.34; found: C 61.23, H 8.19.

3-Benzyl-2,4-dioxopentan-3-yl 2-ethylbutanoate, 4b

630 mg (2.07 mmol, 79 %).

Colorless oil. $R_f = 0.88$ (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);
 $^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 0.92$ (t, 6H, $J = 7.3$ Hz), 1.51-1.68 (m, 4H), 2.16 (s, 6H), 2.23-2.27 (m, 1H), 3.61 (s, 2H), 7.05-7.07 (m, 2H), 7.23-7.25 ppm (m, 3H);
 $^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 11.6, 24.1, 27.3, 39.3, 48.1, 93.6, 127.3, 128.4, 129.9, 134.2, 175.0, 202.4$ ppm;
HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{18}\text{H}_{25}\text{O}_4]^+$: 305.1747. Found: 305.1754;
Anal.: Calcd (%) for $\text{C}_{18}\text{H}_{24}\text{O}_4$ (304.39): C 71.03, H 7.95; found: C 71.07, H 8.01.

3-(4-Chlorobenzyl)-2,4-dioxopentan-3-yl 2-ethylbutanoate, 4c

590 mg (1.74 mmol, 78 %).

Colorless oil. $R_f = 0.87$ (eluent: petroleum ether (40-70) / EtOAc 10:1 with 2% AcOH);
 $^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 0.92$ (t, $J = 7.3$ Hz, 6H), 1.51-1.70 (m, 4H), 2.15 (s, 6H), 2.22-2.26 (m, 1H), 3.58 (s, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.21 ppm (d, $J = 8.8$ Hz, 2H);
 $^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 11.6, 24.1, 27.2, 38.5, 48.1, 93.6, 128.6, 131.3, 132.7, 133.3, 174.9, 202.0$ ppm;
HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{18}\text{H}_{23}\text{ClNaO}_4]^+$: 361.1177. Found: 361.1179;
Anal.: Calcd (%) for $\text{C}_{18}\text{H}_{23}\text{ClO}_4$ (338.83): C 63.81, H 6.84, Cl 10.46; found: C 63.77, H 6.91, Cl 10.28.

1-Acetyl-2-oxocyclopentyl 2-ethylbutanoate, 4d

812 mg (3.38 mmol, 85 %).

Colorless oil. $R_f = 0.89$ (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);
 $^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 0.90$ -0.96 (m, 6H), 1.51-1.68 (m, 4H), 1.96-2.18 (m, 3H), 2.28-2.35 (m, 5H), 2.50-2.68 ppm (m, 2H);
 $^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 11.5, 11.7, 18.4, 24.9, 25.1, 26.1, 31.6, 36.0, 48.3, 89.9, 174.6, 203.2, 209.3$ ppm;
HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{13}\text{H}_{20}\text{NaO}_4]^+$: 263.1254. Found: 263.1255;
Anal.: Calcd (%) for $\text{C}_{13}\text{H}_{20}\text{O}_4$ (240.30): C 64.98, H 8.39; found: C 65.05, H 8.48.

1-Acetyl-2-oxocyclohexyl 2-ethylbutanoate, 4e

792 mg (3.11 mmol, 87 %).

Colorless oil. $R_f = 0.83$ (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);
 $^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 0.97$ (t, $J = 7.3$ Hz, 6H), 1.52-1.79 (m, 7H), 1.94-1.99 (m, 1H), 2.06-2.32 (m, 6H), 2.57-2.75 ppm (m, 2H);
 $^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 11.7, 21.3, 24.6, 25.4, 26.1, 34.4, 41.0, 48.3, 89.7, 174.9, 202.6, 202.8$ ppm;
HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{14}\text{H}_{22}\text{NaO}_4]^+$: 277.1410. Found: 277.1407;
Anal.: Calcd (%) for $\text{C}_{14}\text{H}_{22}\text{O}_4$ (254.32): C 66.12, H 8.72; found: C 65.95, H 8.68.

3-Acetyl-2,6-dioxoheptan-3-yl 2-ethylbutanoate, 4f

578 mg (2.03 mmol, 69 %).

Colorless oil. $R_f = 0.53$ (eluent: petroleum ether (40-70) / EtOAc 10:1 with 2% AcOH);
 $^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 0.95$ (t, $J = 7.3$ Hz, 6H), 1.52-1.74 (m, 4H), 2.09 (s, 3H), 2.23 (s, 6H), 2.30-2.38 (m, 3H), 2.44-2.49 ppm (m, 2H);
 $^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 11.7, 24.5, 26.6, 26.9, 29.8, 37.3, 48.3, 92.1, 174.8, 201.7, 206.2$ ppm;
HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{15}\text{H}_{24}\text{NaO}_5]^+$: 307.1516. Found: 307.1503;
Anal.: Calcd (%) for $\text{C}_{15}\text{H}_{24}\text{O}_5$ (284.35): C 63.36, H 8.51; found: C 63.40, H 8.63.

Ethyl 2-(2-ethylbutanoyloxy)-2-methyl-3-oxobutanoate, 4g

772 mg (2.99 mmol, 86 %).

Colorless oil. $R_f = 0.87$ (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);
 $^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 0.90$ -0.96 (m, 6H), 1.23 (t, $J = 7.3$ Hz, 3H), 1.53-1.66 (m, 7H), 2.22-2.28 (m, 1H), 2.33 (s, 3H), 4.19 ppm (q, $J = 7.3$ Hz, 2H);

^{13}C NMR (75.48 MHz; CDCl_3 ; 25 °C): δ = 11.57, 11.60, 13.8, 19.8, 24.9, 25.0, 25.9, 48.5, 62.0, 85.0, 167.5, 174.5, 201.7 ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{13}\text{H}_{22}\text{NaO}_5]^+$: 281.1359. Found: 281.1365;

Anal.: Calcd (%) for $\text{C}_{13}\text{H}_{22}\text{O}_5$ (258.31): C 60.45, H 8.58; found: C 60.34, H 8.55.

Ethyl 2-acetyl-2-(2-ethylbutanoyloxy)hexanoate, 4h

633 mg (2.11 mmol, 79 %).

Colorless oil. R_f = 0.88 (eluent: petroleum ether (40-70) / EtOAc 10:1 with 2% AcOH);

^1H NMR (300.13 MHz; CDCl_3 ; 25 °C): δ = 0.85 (t, J = 6.9 Hz, 3H), 0.92-0.97 (m, 6H), 1.20-1.29 (m, 7H), 1.49-1.73 (m, 4H), 2.08-2.14 (m, 2H), 2.24-2.33 (m, 4H), 4.19 ppm (q, J = 7.3 Hz, 2H);

^{13}C NMR (75.48 MHz; CDCl_3 ; 25 °C): δ = 11.57, 11.61, 13.7, 13.9, 22.5, 24.7, 24.9, 25.4, 27.2, 33.7, 48.4, 61.9, 87.5, 167.6, 174.7, 201.3 ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{16}\text{H}_{28}\text{NaO}_5]^+$: 323.1829. Found: 323.1817;

Anal.: Calcd (%) for $\text{C}_{16}\text{H}_{28}\text{O}_5$ (300.39): C 63.97, H 9.40; found: C 64.21, H 9.28.

Ethyl 2-acetyl-4-cyano-2-(2-ethylbutanoyloxy)butanoate, 4i

493 mg (1.66 mmol, 61 %).

Colorless oil. R_f = 0.58 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

^1H NMR (300.13 MHz; CDCl_3 ; 25 °C): δ = 0.92-0.98 (m, 6H), 1.25 (t, J = 7.3 Hz, 3H), 1.53-1.74 (m, 4H), 2.31-2.38 (m, 6H), 2.42-2.65 (m, 2H), 4.22 ppm (q, J = 7.3 Hz, 2H);

^{13}C NMR (75.48 MHz; CDCl_3 ; 25 °C): δ = 11.5, 11.6, 12.0, 13.8, 24.4, 24.7, 26.9, 28.9, 48.1, 62.7, 85.6, 118.2, 166.1, 174.5, 200.2 ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{15}\text{H}_{20}\text{NNaO}_5]^+$: 320.1468. Found: 320.1467;

Anal.: Calcd (%) for $\text{C}_{15}\text{H}_{20}\text{NO}_5$ (297.35): C 60.59, H 7.80, N 4.71; found: C 60.51, H 8.05, N 4.67.

Ethyl 2-benzyl-2-(2-ethylbutanoyloxy)-3-oxobutanoate, 4j

658 mg (1.97 mmol, 87 %).

Colorless oil. R_f = 0.40 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

^1H NMR (300.13 MHz; CDCl_3 ; 25 °C): δ = 0.92-0.97 (m, 6H), 1.18 (t, J = 7.3 Hz, 3H), 1.50-1.77 (m, 4H), 2.12-2.36 (m, 4H), 3.46 (d, J = 13.9 Hz, 1H, CH_2), 3.54 (d, J = 13.9 Hz, 1H, CH_2), 4.16 (q, J = 7.3 Hz, 2H), 7.11-7.14 (m, 2H), 7.23-7.28 ppm (m, 3H);

^{13}C NMR (75.48 MHz; CDCl_3 ; 25 °C): δ = 11.5, 11.7, 13.8, 24.3, 24.6, 27.8, 39.7, 48.2, 62.1, 87.6, 127.3, 128.2, 130.1, 134.1, 166.9, 174.7, 202.2 ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{19}\text{H}_{26}\text{NaO}_5]^+$: 357.1672. Found: 357.1667

Anal.: Calcd (%) for $\text{C}_{19}\text{H}_{26}\text{O}_5$ (334.41): C 68.24, H 7.84; found: C 68.43, H 7.75.

Ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclopentanecarboxylate, 4k

697 mg (2.58 mmol, 81 %).

Colorless oil. R_f = 0.78 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

^1H NMR (300.13 MHz; CDCl_3 ; 25 °C): δ = 0.86-0.93 (m, 6H), 1.23 (t, J = 7.3 Hz, 3H), 1.47-1.68 (m, 4H), 2.06-2.31 (m, 4H), 2.38-2.59 (m, 2H), 2.72-2.80 (m, 1H), 4.19 ppm (q, J = 7.3 Hz, 2H);

^{13}C NMR (75.48 MHz; CDCl_3 ; 25 °C): δ = 11.5, 11.6, 13.9, 18.3, 24.8, 24.9, 33.6, 35.8, 48.1, 62.1, 83.6, 167.0, 174.9, 208.0 ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{14}\text{H}_{22}\text{NaO}_5]^+$: 293.1359. Found: 293.1363;

Anal.: Calcd (%) for $\text{C}_{14}\text{H}_{22}\text{O}_5$ (270.32): C 62.20, H 8.20; found: C 62.26, H 8.21.

Ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclohexanecarboxylate, 4l

743 mg (2.61 mmol, 89 %).

Colorless oil. R_f = 0.80 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

^1H NMR (300.13 MHz; CDCl_3 ; 25 °C): δ = 0.92-0.99 (m, 6H), 1.25 (t, J = 7.3 Hz, 3H), 1.46-1.80 (m, 7H), 1.93-2.00 (m, 1H), 2.06-2.14 (m, 1H), 2.23-2.32 (m, 1H), 2.38-2.43 (m, 1H), 2.56-2.63 (m, 1H), 2.89-2.99 (m, 1H), 4.22 ppm (q, J = 7.3 Hz, 2H).

^{13}C NMR (75.48 MHz; CDCl_3 ; 25 °C): δ = 11.6, 13.9, 21.0, 24.8, 24.9, 27.3, 36.4, 40.4, 48.4, 61.8, 85.1, 168.1, 174.5, 201.4 ppm;

HRMS (ESI) m/z $[M+Na]^+$: Calcd for $[C_{15}H_{24}NaO_5]^+$: 307.1516. Found: 307.1518;
Anal.: Calcd (%) for $C_{15}H_{24}O_5$ (284.35): C 63.36, H 8.51; found: C 63.35, H 8.68.

3-Acetyl-2-oxotetrahydrofuran-3-yl 2-ethylbutanoate, 4m

432 mg (1.78 mmol, 46 %).

Colorless oil. R_f = 0.55 (eluent: petroleum ether (40-70) / EtOAc 10:1 with 2% AcOH);

1H NMR (300.13 MHz; $CDCl_3$; 25 °C): δ = 0.91-0.97 (m, 6H), 1.52-1.74 (m, 4H), 2.30-2.42 (m, 5H), 2.99-3.07 (m, 1H), 4.35-4.43 (m, 1H), 4.48-4.55 ppm (m, 1H);

^{13}C NMR (75.48 MHz; $CDCl_3$; 25 °C): δ = 11.5, 11.7, 24.7, 25.0, 25.3, 30.6, 48.3, 66.2, 84.4, 169.7, 174.8, 200.8 ppm;

HRMS (ESI) m/z $[M+Na]^+$: Calcd for $[C_{12}H_{18}NaO_5]^+$: 265.1046. Found: 265.1037;

Anal.: Calcd (%) for $C_{12}H_{18}O_5$ (242.27): C 59.49, H 7.49; found: C 59.33, H 7.61.

Ethyl 1-(2-butylhexanoyloxy)-2-oxocyclopentanecarboxylate, 4n

616 mg (1.89 mmol, 59 %).

Colorless oil. R_f = 0.83 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

1H NMR (300.13 MHz; $CDCl_3$; 25 °C): δ = 0.86 (t, J = 7.3 Hz, 6H), 1.22-1.28 (m, 11H), 1.40-1.45 (m, 2H), 1.55-1.67 (m, 2H), 2.07-2.25 (m, 3H), 2.34-2.60 (m, 3H), 2.71-2.80 (m, 1H), 4.19 ppm (q, J = 7.3 Hz, 2H);

^{13}C NMR (75.48 MHz; $CDCl_3$; 25 °C): δ = 13.8, 18.3, 22.5, 29.2, 31.8, 31.9, 33.6, 35.8, 44.9, 62.1, 83.6, 167.1, 175.2, 208.0 ppm;

HRMS (ESI) m/z $[M+Na]^+$: Calcd for $[C_{18}H_{31}O_5]^+$: 327.2166. Found: 327.2152;

Anal.: Calcd (%) for $C_{18}H_{30}O_5$ (326.43): C 66.23, H 9.26; found: C 66.21, H 9.26.

1-Benzyl-1-ethoxycarbonyl-2-oxopropyl cyclobutanecarboxylate, 4o

261 mg (0.82 mmol, 36 %).

Colorless oil. R_f = 0.43 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

1H NMR (300.13 MHz; $CDCl_3$; 25 °C): δ = 1.20 (t, J = 7.3 Hz, 3H), 1.85-2.03 (m, 2H), 2.13-2.31 (m, 7H), 3.15-3.26 (m, 1H), 3.50 (d, J = 14.3 Hz, 1H, CH_2), 3.56 (d, J = 14.3 Hz, 1H, CH_2), 4.17 (q, J = 7.3 Hz, 2H), 7.06-7.08 (m, 2H), 7.23-7.26 ppm (m, 3H);

^{13}C NMR (75.48 MHz; $CDCl_3$; 25 °C): δ = 13.8, 18.4, 24.9, 27.4, 37.8, 39.1, 62.1, 87.8, 127.2, 128.3, 130.1, 134.2, 168.7, 173.9, 202.2 ppm;

HRMS (ESI) m/z $[M+Na]^+$: Calcd for $[C_{18}H_{22}NaO_5]^+$: 341.1359. Found: 341.1363;

Anal.: Calcd (%) for $C_{18}H_{22}O_5$ (318.37): C 67.91, H 6.97; found: C 67.85, H 6.99.

Ethyl 1-cyclobutylcarbonyloxy-2-oxocyclohexanecarboxylate, 4p

301 mg (1.12 mmol, 38 %).

Colorless oil. R_f = 0.57 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

1H NMR (300.13 MHz; $CDCl_3$; 25 °C): δ = 1.25 (t, J = 7.3 Hz, 3H), 1.66-1.79 (m, 3H), 1.88-2.40 (m, 9H), 2.54-2.60 (m, 1H), 2.85-2.94 (m, 1H), 3.16-3.27 (m, 1H), 4.22 ppm (q, J = 7.3 Hz, 2H);

^{13}C NMR (75.48 MHz; $CDCl_3$; 25 °C): δ = 13.9, 18.4, 21.0, 24.9, 25.1, 27.3, 36.3, 37.6, 40.2, 61.8, 85.1, 168.1, 173.8, 201.6 ppm;

HRMS (ESI) m/z $[M+Na]^+$: Calcd for $[C_{14}H_{20}NaO_5]^+$: 291.1203. Found: 291.1208;

Anal.: Calcd (%) for $C_{14}H_{20}O_5$ (268.31): C 62.67, H 7.51; found: C 62.65, H 7.53.

1-Acetyl-1-benzyl-2-oxopropyl cyclopentanecarboxylate, 4q

288 mg (0.95 mmol, 36 %).

Colorless oil. R_f = 0.71 (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

1H NMR (300.13 MHz; $CDCl_3$; 25 °C): δ = 1.57-1.87 (m, 8H), 2.12 (s, 6H), 2.74-2.84 (m, 1H), 3.60 (s, 2H), 7.01-7.04 (m, 2H), 7.23-7.25 ppm (m, 3H);

^{13}C NMR (75.48 MHz; $CDCl_3$; 25 °C): δ = 25.7, 27.0, 29.6, 39.0, 43.7, 93.8, 127.2, 128.4, 129.9, 134.3, 175.4, 202.0 ppm;

HRMS (ESI) m/z $[M+Na]^+$: Calcd for $[C_{18}H_{22}NaO_4]^+$: 325.1410. Found: 325.1397;

Anal.: Calcd (%) for $C_{18}H_{22}O_4$ (302.15): C 71.50, H 7.33; found: C 71.52, H 7.35.

1-Benzyl-1-ethoxycarbonyl-2-oxopropyl cyclopentanecarboxylate, 4r

356 mg (1.07 mmol, 47 %).

Colorless oil. $R_f = 0.46$ (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

$^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 1.18$ (t, $J = 7.3$ Hz, 3H), 1.54-1.67 (m, 4H), 1.80-1.90 (m, 4H), 2.18 (s, 3H), 2.75-2.86 (m, 1H), 3.49 (d, $J = 14.3$ Hz, 1H, CH_2), 3.56 (d, $J = 14.3$ Hz, 1H, CH_2), 4.11-4.19 (m, 2H), 7.06-7.09 (m, 2H), 7.23-7.25 ppm (m, 3H);

$^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 13.8, 25.7, 27.5, 29.6, 39.2, 43.5, 62.0, 87.8, 127.2, 128.2, 130.1, 134.2, 168.7, 175.1, 202.2$ ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{19}\text{H}_{24}\text{NaO}_5]^+$: 355.1516. Found: 355.1511;

Anal.: Calcd (%) for $\text{C}_{19}\text{H}_{24}\text{O}_5$ (332.39): C 68.66, H 7.28; found: C 68.63, H 7.28.

Ethyl 1-cyclopentylcarbonyloxy-2-oxocyclohexanecarboxylate, 4s

425 mg (1.51 mmol, 51 %).

Colorless oil. $R_f = 0.54$ (eluent: petroleum ether (40-70) / EtOAc 5:1 with 2% AcOH);

$^1\text{H NMR}$ (300.13 MHz; CDCl_3 ; 25 °C): $\delta = 1.20$ (t, $J = 7.3$ Hz, 3H), 1.51-1.90 (m, 12H), 2.03-2.11 (m, 1H), 2.32-2.37 (m, 1H), 2.50-2.58 (m, 1H), 2.74-2.90 (m, 2H), 4.13-4.21 ppm (m, 2H);

$^{13}\text{C NMR}$ (75.48 MHz; CDCl_3 ; 25 °C): $\delta = 13.8, 20.8, 25.6, 27.2, 29.6, 29.7, 36.2, 40.1, 43.1, 61.6, 84.9, 167.9, 174.9, 201.4$ ppm;

HRMS (ESI) m/z $[\text{M}+\text{Na}]^+$: Calcd for $[\text{C}_{15}\text{H}_{22}\text{NaO}_5]^+$: 305.1359. Found: 305.1354;

Anal.: Calcd (%) for $\text{C}_{15}\text{H}_{22}\text{O}_5$ (282.34): C 63.81, H 7.85; found: C 63.77, H 7.86.

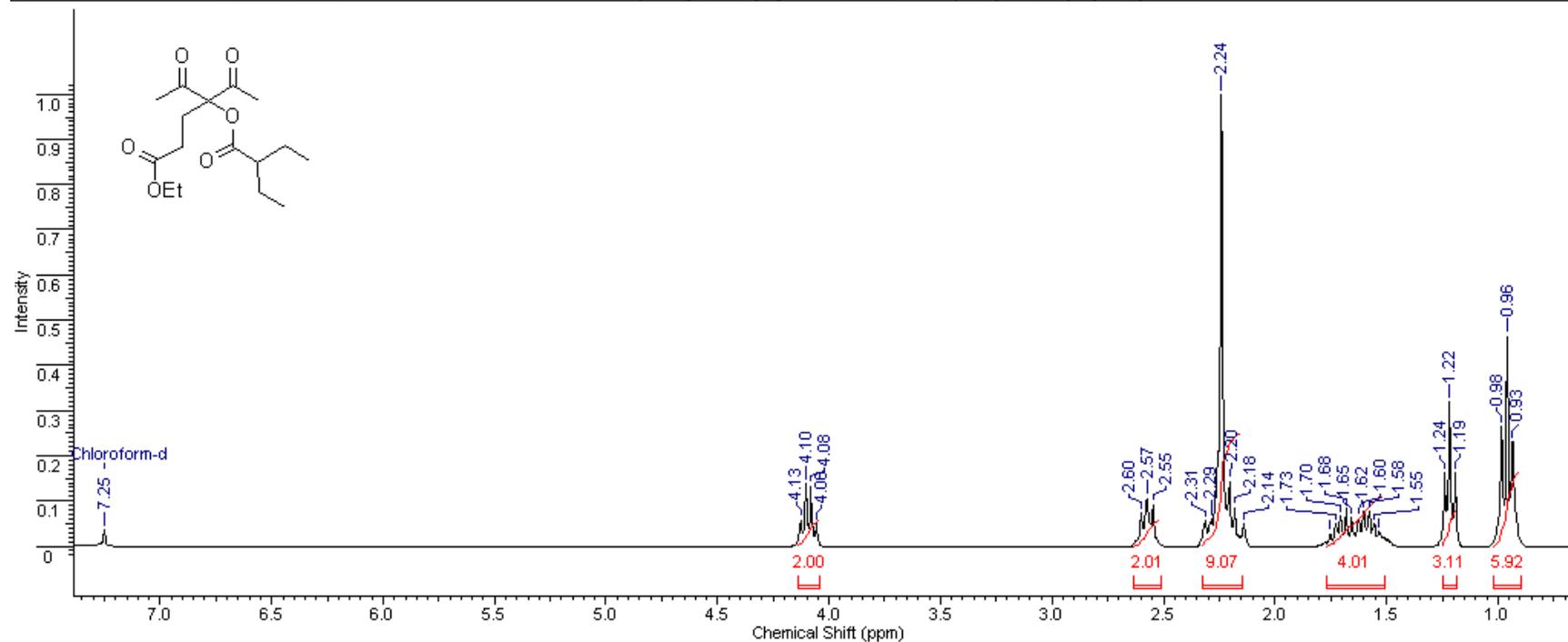
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¹H and ¹³C NMR Spectra

¹H NMR of ethyl 4-acetyl-4-(2-ethylbutanoyloxy)-5-oxohexanoate, **4a**

| | | | | | |
|-------------------------------|--------------|------------------------------|---------|-------------------------------|----------------------|
| Acquisition Time (sec) | 1.0832 | Frequency (MHz) | 300.13 | Date | 11 Apr 2016 09:08:16 |
| Number of Transients | 1 | Original Points Count | 8124 | Nucleus | ¹ H |
| Solvent | CHLOROFORM-D | Points Count | 8192 | Pulse Sequence | zg |
| | | Sweep Width (Hz) | 7500.00 | Temperature (degree C) | 26.900 |



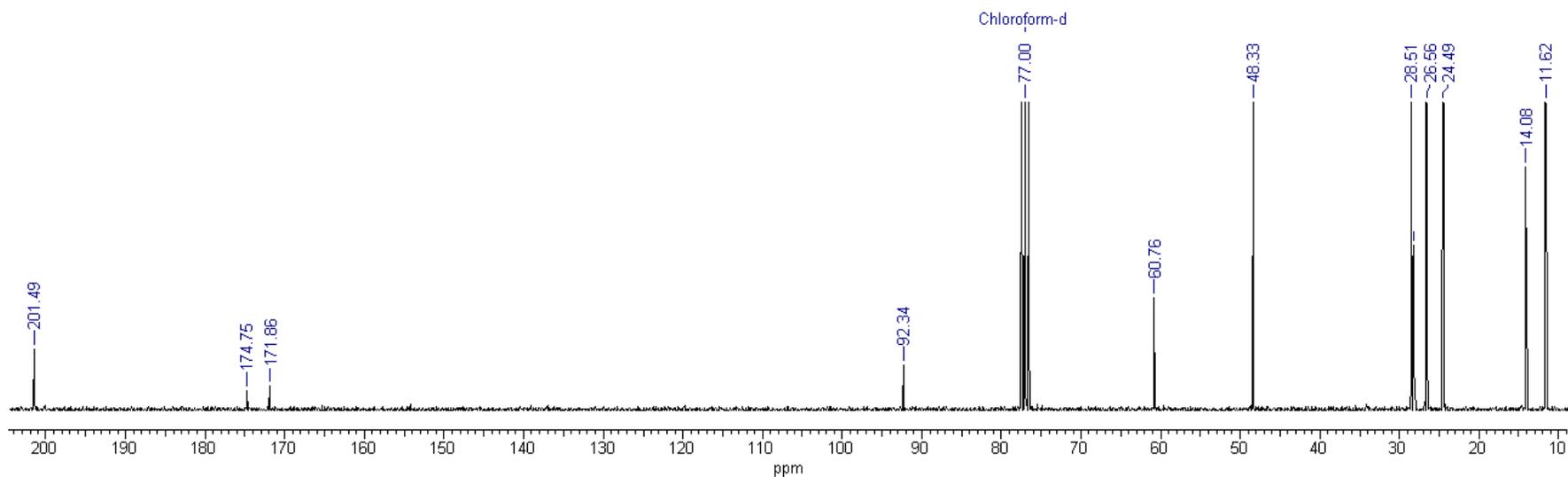
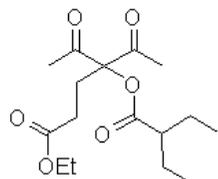
| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.93 | 280.6 | 0.2308 | 11 | 1.62 | 486.6 | 0.0608 | 21 | 2.29 | 686.2 | 0.0606 |
| 2 | 0.96 | 287.9 | 0.4644 | 12 | 1.65 | 496.7 | 0.0634 | 22 | 2.31 | 694.5 | 0.0569 |
| 3 | 0.98 | 295.2 | 0.2655 | 13 | 1.68 | 504.0 | 0.0826 | 23 | 2.55 | 764.0 | 0.0920 |
| 4 | 1.19 | 357.5 | 0.1623 | 14 | 1.70 | 511.3 | 0.0672 | 24 | 2.57 | 772.3 | 0.1057 |
| 5 | 1.22 | 364.8 | 0.3177 | 15 | 1.73 | 517.7 | 0.0490 | 25 | 2.60 | 779.6 | 0.0739 |
| 6 | 1.24 | 372.2 | 0.1617 | 16 | 1.75 | 526.0 | 0.0275 | 26 | 4.06 | 1217.3 | 0.0503 |
| 7 | 1.53 | 460.1 | 0.0315 | 17 | 2.14 | 641.3 | 0.0500 | 27 | 4.08 | 1224.6 | 0.1336 |
| 8 | 1.55 | 466.5 | 0.0493 | 18 | 2.18 | 654.2 | 0.0847 | 28 | 4.10 | 1231.0 | 0.1372 |
| 9 | 1.58 | 473.8 | 0.0754 | 19 | 2.20 | 661.5 | 0.1435 | 29 | 4.13 | 1238.3 | 0.0582 |
| 10 | 1.60 | 480.2 | 0.0770 | 20 | 2.24 | 672.5 | 1.0000 | 30 | 7.25 | 2176.0 | 0.0356 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value | Absolute Value |
|-----|----------------|-------|----------------|
| 1 | [0.90 .. 1.02] | 5.916 | 3.14874e+8 |
| 2 | [1.19 .. 1.25] | 3.108 | 1.65444e+8 |
| 3 | [1.51 .. 1.77] | 4.014 | 2.13642e+8 |
| 4 | [2.15 .. 2.33] | 9.074 | 4.82969e+8 |
| 5 | [2.51 .. 2.63] | 2.014 | 1.07189e+8 |
| 6 | [4.04 .. 4.14] | 2.000 | 1.06449e+8 |

¹³C NMR of ethyl 4-acetyl-4-(2-ethylbutanoyloxy)-5-oxohexanoate, **4a**

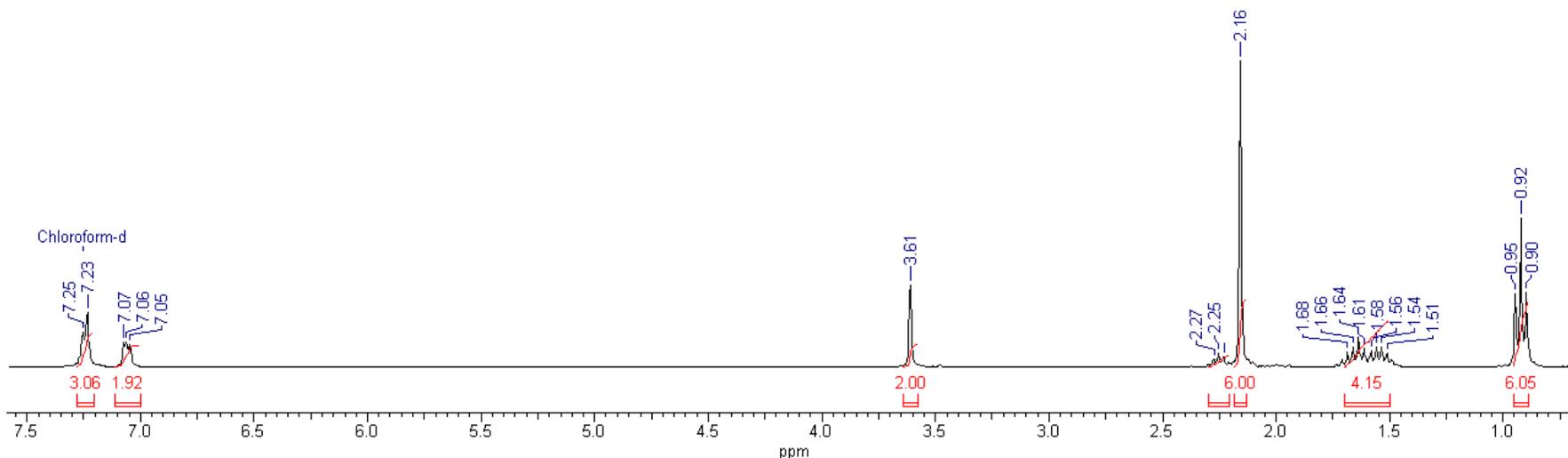
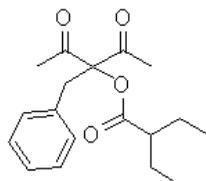
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|-------------------------------|------------|------------------------------|----------------------|
| Acquisition Time (sec) | 0.4340 | Date | 11 Apr 2016 09:10:24 |
| Nucleus | 13C | Number of Transients | 46 |
| Pulse Sequence | zgpg60base | Original Points Count | 16316 |
| Temperature (degree C) | 27.000 | Solvent | CHLOROFORM-D |
| | | Frequency (MHz) | 75.48 |
| | | Points Count | 16384 |
| | | Sweep Width (Hz) | 18796.99 |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.62 | 876.9 | 0.9383 | 8 | 60.76 | 4586.2 | 0.1428 | 1 | Chloroform-d | 77.00 |
| 2 | 14.08 | 1062.7 | 0.3091 | 9 | 77.00 | 5811.6 | 0.5122 | | | |
| 3 | 24.49 | 1848.7 | 1.0000 | 10 | 92.34 | 6989.3 | 0.0577 | | | |
| 4 | 26.56 | 2004.7 | 0.4973 | 11 | 171.86 | 12971.1 | 0.0304 | | | |
| 5 | 28.14 | 2124.0 | 0.2096 | 12 | 174.75 | 13189.1 | 0.0244 | | | |
| 6 | 28.51 | 2151.6 | 0.4248 | 13 | 201.49 | 15207.2 | 0.0779 | | | |
| 7 | 48.33 | 3647.7 | 0.4049 | | | | | | | |

¹H NMR of 3-benzyl-2,4-dioxopentan-3-yl 2-ethylbutanoate, **4b**

| | | | | | |
|------------------------|---------|------------------------|----------------------|-----------------|--------------|
| Acquisition Time (sec) | 0.6759 | Date | 16 Jun 2016 16:08:32 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 23.100 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zg |
| | | | | Solvent | CHLOROFORM-D |
| | | | | Nucleus | 1H |



| No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|
| 1 | 0.90 | 269.2 | 0.2418 |
| 2 | 0.92 | 276.6 | 0.4842 |
| 3 | 0.95 | 283.9 | 0.2401 |
| 4 | 1.51 | 453.4 | 0.0434 |
| 5 | 1.54 | 460.7 | 0.0642 |
| 6 | 1.56 | 467.3 | 0.0642 |
| 7 | 1.58 | 474.7 | 0.0522 |

| No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|
| 8 | 1.61 | 484.2 | 0.0609 |
| 9 | 1.64 | 491.5 | 0.0958 |
| 10 | 1.66 | 498.9 | 0.0638 |
| 11 | 1.68 | 505.5 | 0.0462 |
| 12 | 2.16 | 647.8 | 1.0000 |
| 13 | 2.23 | 669.1 | 0.0345 |
| 14 | 2.25 | 676.4 | 0.0430 |

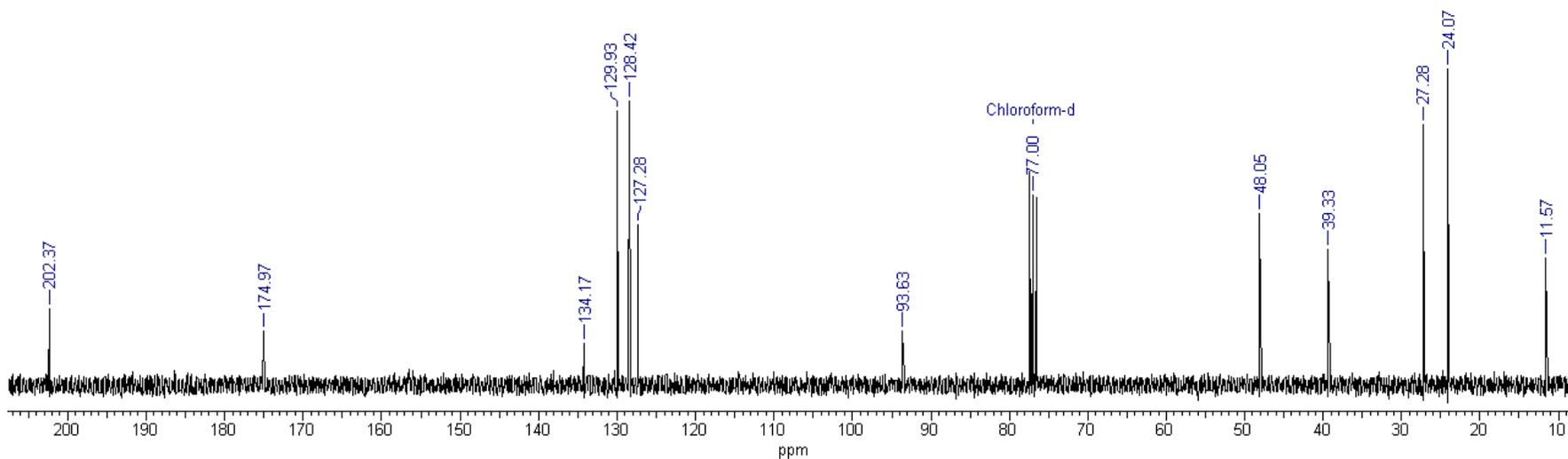
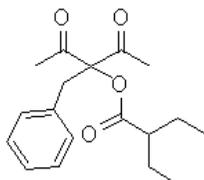
| No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|
| 15 | 2.27 | 682.3 | 0.0243 |
| 16 | 3.61 | 1083.6 | 0.2674 |
| 17 | 7.05 | 2115.9 | 0.0737 |
| 18 | 7.06 | 2119.6 | 0.0790 |
| 19 | 7.07 | 2123.3 | 0.0794 |
| 20 | 7.23 | 2170.9 | 0.1765 |
| 21 | 7.25 | 2176.1 | 0.1125 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value |
|-----|------------|-------|
| 1 | .89 .. 0.9 | 6.054 |
| 2 | .50 .. 1.7 | 4.147 |
| 3 | .13 .. 2.1 | 6.004 |
| 4 | .20 .. 2.3 | 1.021 |
| 5 | .57 .. 3.6 | 2.000 |
| 6 | .00 .. 7.1 | 1.919 |
| 7 | .20 .. 7.2 | 3.062 |

¹³C NMR of 3-benzyl-2,4-dioxopentan-3-yl 2-ethylbutanoate, **4b**

| | | | | | | | | |
|-------------------------------|--------------|------------------------------|-------|---------------------|-------------------------|------------------------|-------------------------------|--------|
| Acquisition Time (sec) | 0.4503 | | | | Date | 16 Jun 2016 16:08:32 | | |
| | | Original Points Count | 16316 | Points Count | 16384 | Frequency (MHz) | 75.48 | |
| Number of Transients | 121 | | | | Pulse Sequence | zgpg30 | Nucleus | 13C |
| Solvent | CHLOROFORM-D | | | | Sweep Width (Hz) | 18115.94 | Temperature (degree C) | 23.100 |



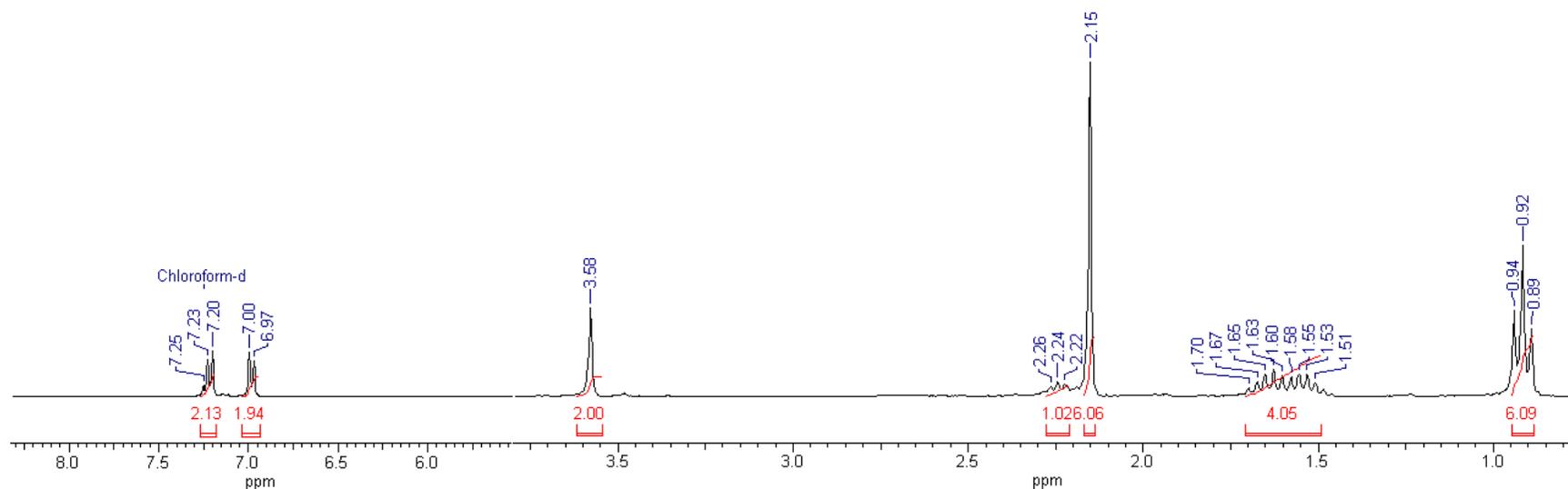
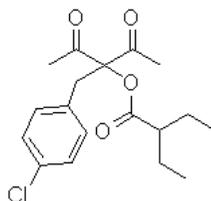
| No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|
| 1 | 11.57 | 873.3 | 0.4036 |
| 2 | 24.07 | 1816.5 | 1.0000 |
| 3 | 27.28 | 2058.7 | 0.8240 |
| 4 | 39.33 | 2968.7 | 0.4299 |
| 5 | 48.05 | 3626.7 | 0.5432 |
| 6 | 77.00 | 5811.7 | 0.6029 |
| 7 | 93.63 | 7066.7 | 0.1738 |

| No. | (ppm) | (Hz) | Height |
|-----|--------|---------|--------|
| 8 | 127.28 | 9606.7 | 0.5099 |
| 9 | 128.42 | 9693.0 | 0.8976 |
| 10 | 129.93 | 9806.9 | 0.8692 |
| 11 | 134.17 | 10126.4 | 0.1348 |
| 12 | 174.97 | 13206.0 | 0.1706 |
| 13 | 202.37 | 15273.8 | 0.2436 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of 3-(4-chlorobenzyl)-2,4-dioxopentan-3-yl 2-ethylbutanoate, **4c**

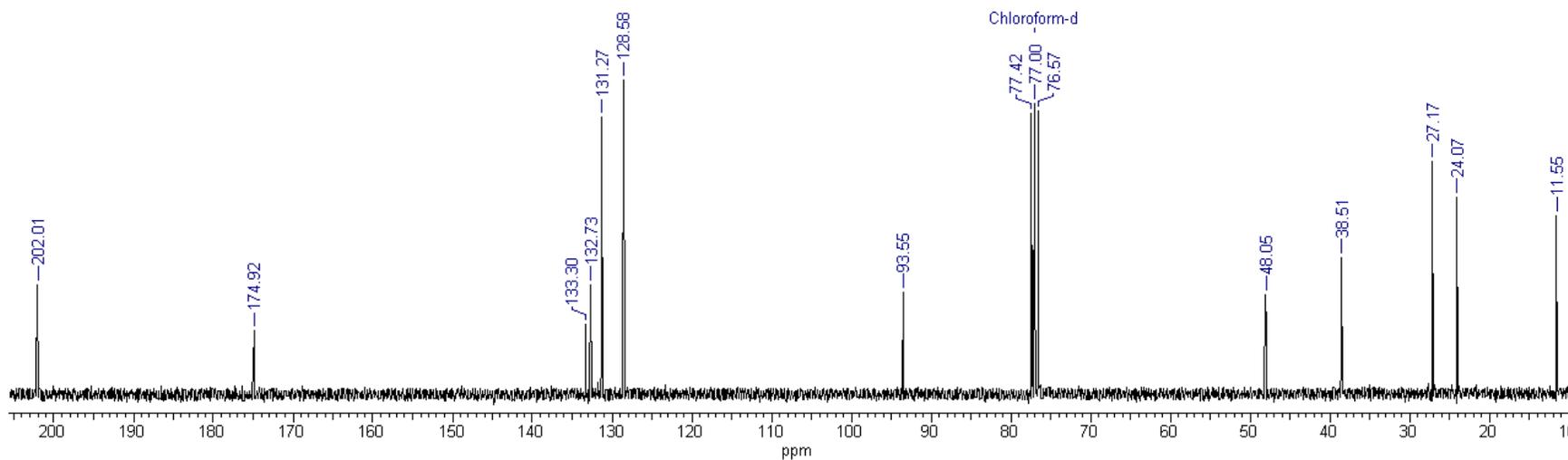
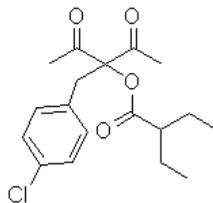
| | | | | | |
|------------------------|---------|------------------------|----------------------|-----------------|--------------|
| Acquisition Time (sec) | 0.6759 | Date | 08 Jun 2016 15:53:36 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 24.100 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zq |
| | | | | Nucleus | 1H |
| | | | | Solvent | CHLOROFORM-D |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) | No. | (ppm) | Value |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|-----|--------------|-------|-----|------------|-------|
| 1 | 0.89 | 267.7 | 0.2009 | 9 | 1.63 | 488.5 | 0.0808 | 17 | 3.58 | 1074.0 | 0.2654 | 1 | Chloroform-d | 7.25 | 1 | 88 .. 0.9 | 6.095 |
| 2 | 0.92 | 275.0 | 0.4514 | 10 | 1.65 | 495.9 | 0.0668 | 18 | 6.97 | 2090.9 | 0.1024 | 2 | | | 2 | .49 .. 1.7 | 4.048 |
| 3 | 0.94 | 282.4 | 0.2561 | 11 | 1.67 | 502.5 | 0.0450 | 19 | 7.00 | 2099.7 | 0.1256 | 3 | | | 3 | .14 .. 2.1 | 6.056 |
| 4 | 1.51 | 452.6 | 0.0410 | 12 | 1.70 | 509.8 | 0.0259 | 20 | 7.20 | 2160.6 | 0.1323 | 4 | | | 4 | .21 .. 2.2 | 1.024 |
| 5 | 1.53 | 459.9 | 0.0645 | 13 | 2.15 | 645.5 | 1.0000 | 21 | 7.23 | 2169.4 | 0.1074 | 5 | | | 5 | .54 .. 3.6 | 2.000 |
| 6 | 1.55 | 466.5 | 0.0642 | 14 | 2.22 | 667.6 | 0.0346 | 22 | 7.25 | 2176.0 | 0.0323 | 6 | | | 6 | .94 .. 7.0 | 1.945 |
| 7 | 1.58 | 473.1 | 0.0582 | 15 | 2.24 | 673.4 | 0.0456 | | | | | 7 | | | 7 | .18 .. 7.2 | 2.132 |
| 8 | 1.60 | 481.2 | 0.0613 | 16 | 2.26 | 679.3 | 0.0280 | | | | | | | | | | |

¹³C NMR of 3-(4-chlorobenzyl)-2,4-dioxopentan-3-yl 2-ethylbutanoate, **4c**

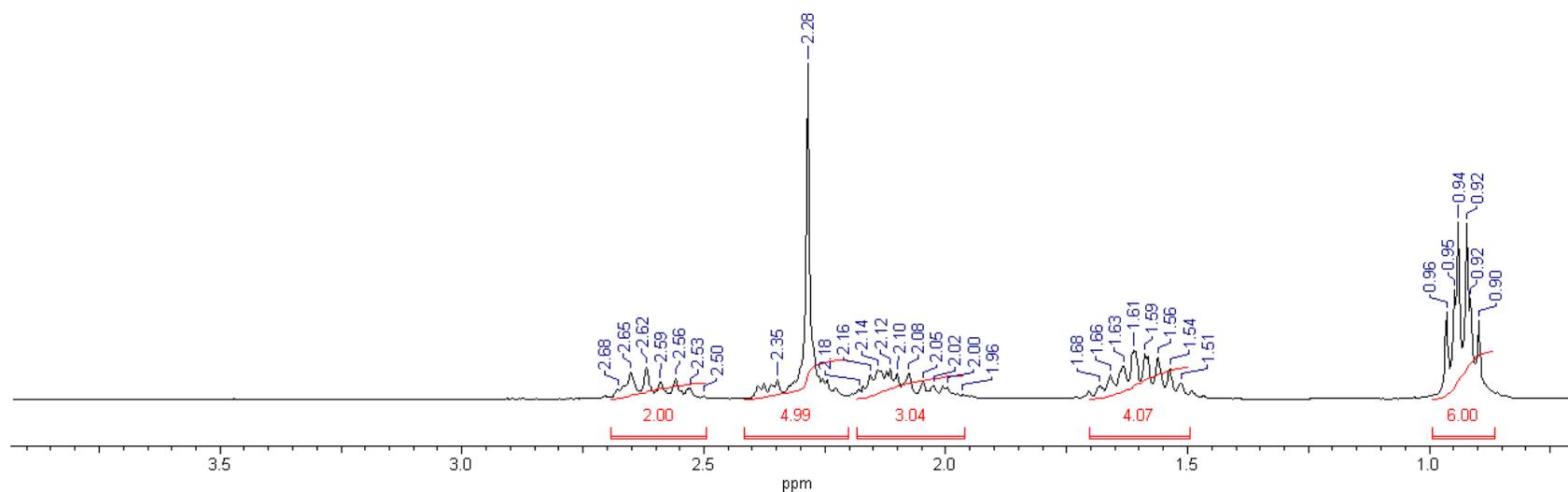
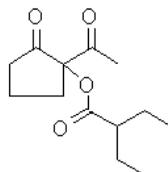
| | | | | | |
|------------------------|--------------|-----------------------|----------|------------------------|----------------------|
| Acquisition Time (sec) | 0.4503 | | | Date | 08 Jun 2016 15:53:36 |
| Number of Transients | 332 | Original Points Count | 16316 | Points Count | 16384 |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Pulse Sequence | zgpg30 |
| | | | | Temperature (degree C) | 24.100 |
| | | | | Frequency (MHz) | 75.48 |
| | | | | Nucleus | 13C |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.55 | 872.1 | 0.5668 | 9 | 93.55 | 7061.2 | 0.3219 | 1 | Chloroform-d | 77.00 |
| 2 | 24.07 | 1816.5 | 0.6252 | 10 | 128.58 | 9705.1 | 1.0000 | | | |
| 3 | 27.17 | 2050.9 | 0.7396 | 11 | 131.27 | 9907.4 | 0.8826 | | | |
| 4 | 38.51 | 2906.7 | 0.4303 | 12 | 132.73 | 10018.0 | 0.3443 | | | |
| 5 | 48.05 | 3626.6 | 0.3124 | 13 | 133.30 | 10061.1 | 0.2153 | | | |
| 6 | 76.57 | 5779.6 | 0.9016 | 14 | 174.92 | 13202.6 | 0.1962 | | | |
| 7 | 77.00 | 5811.6 | 0.9274 | 15 | 202.01 | 15247.2 | 0.3464 | | | |
| 8 | 77.42 | 5843.7 | 0.8949 | | | | | | | |

¹H NMR of 1-acetyl-2-oxocyclopentyl 2-ethylbutanoate, **4d**

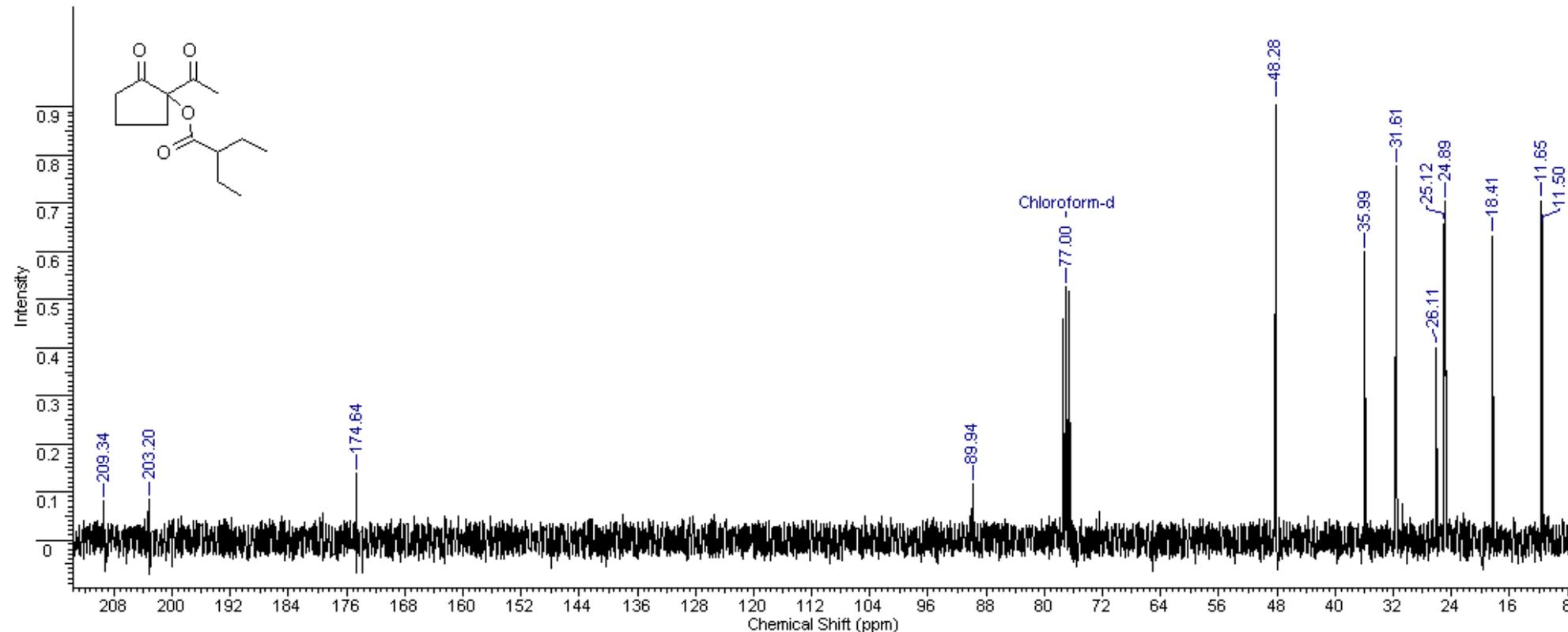
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|------------------------|--------------|-----------------------|------|------------------------|----------------------|-----------------|--------|---------|----|
| Acquisition Time (sec) | 0.6759 | | | Date | 16 May 2016 16:42:40 | | | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 | Frequency (MHz) | 300.13 | Nucleus | 1H |
| Solvent | CHLOROFORM-D | | | Sweep Width (Hz) | 6009.62 | Pulse Sequence | zg | | |
| | | | | Temperature (degree C) | 23.000 | | | | |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) | No. | (ppm) | Value |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|-----|--------------|-------|-----|-------------|-------|
| 1 | 0.90 | 269.7 | 0.2335 | 10 | 1.59 | 476.6 | 0.1345 | 19 | 2.08 | 623.4 | 0.0767 | 28 | 2.53 | 758.4 | 0.0337 | 1 | Chloroform-d | 7.25 | 1 | .86 .. 0.9 | 6.000 |
| 2 | 0.92 | 274.9 | 0.3019 | 11 | 1.61 | 484.0 | 0.1456 | 20 | 2.10 | 630.0 | 0.0752 | 29 | 2.56 | 767.9 | 0.0611 | 2 | | | 2 | .50 .. 1.71 | 4.070 |
| 3 | 0.92 | 277.1 | 0.5226 | 12 | 1.63 | 489.8 | 0.0994 | 21 | 2.12 | 635.1 | 0.0924 | 30 | 2.58 | 777.4 | 0.0517 | 3 | | | 3 | .96 .. 2.11 | 3.035 |
| 4 | 0.94 | 282.2 | 0.5274 | 13 | 1.66 | 497.9 | 0.0747 | 22 | 2.14 | 642.4 | 0.0891 | 31 | 2.62 | 786.2 | 0.0966 | 4 | | | 4 | .20 .. 2.4 | 4.990 |
| 5 | 0.95 | 284.4 | 0.3250 | 14 | 1.68 | 504.5 | 0.0391 | 23 | 2.16 | 646.8 | 0.0721 | 32 | 2.66 | 795.8 | 0.0812 | 5 | | | 5 | .49 .. 2.6 | 2.004 |
| 6 | 0.96 | 289.5 | 0.2585 | 15 | 1.96 | 589.6 | 0.0137 | 24 | 2.18 | 654.2 | 0.0306 | 33 | 2.68 | 803.1 | 0.0307 | | | | | | |
| 7 | 1.51 | 453.9 | 0.0480 | 16 | 2.00 | 599.2 | 0.0365 | 25 | 2.28 | 685.7 | 1.0000 | 34 | 7.25 | 2175.8 | 0.0794 | | | | | | |
| 8 | 1.54 | 461.2 | 0.0935 | 17 | 2.02 | 607.2 | 0.0422 | 26 | 2.35 | 704.8 | 0.0578 | | | | | | | | | | |
| 9 | 1.56 | 468.6 | 0.1258 | 18 | 2.05 | 614.6 | 0.0513 | 27 | 2.50 | 750.3 | 0.0100 | | | | | | | | | | |

¹³C NMR of 1-acetyl-2-oxocyclopentyl 2-ethylbutanoate, **4d**

| | | | | |
|--------------------------------------|--|------------------------------------|--------------------------------------|--------------------|
| Acquisition Time (sec) 0.8680 | | Date 10 May 2016 09:33:52 | | |
| Number of Transients 57 | | Original Points Count 16316 | Frequency (MHz) 75.48 | Nucleus 13C |
| Solvent CHLOROFORM-D | | Points Count 16384 | Pulse Sequence zgpg60base | |
| | | Sweep Width (Hz) 18796.99 | Temperature (degree C) 23.300 | |

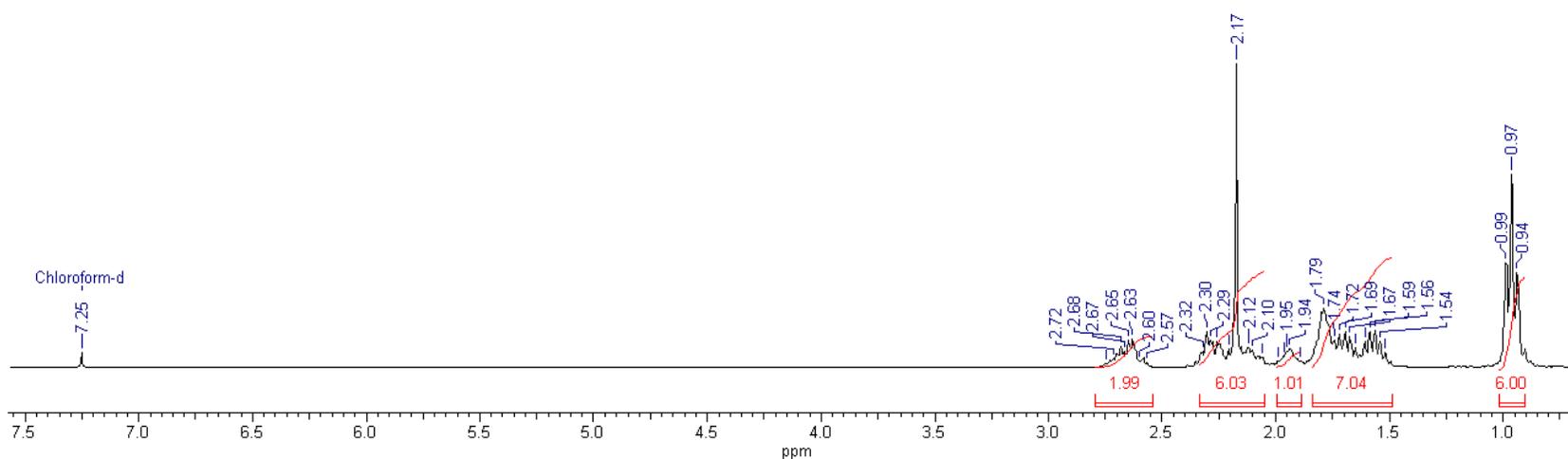
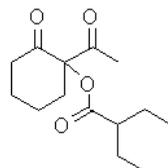


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 11.50 | 867.7 | 0.6508 | 8 | 35.99 | 2716.1 | 0.5999 |
| 2 | 11.65 | 879.2 | 0.7060 | 9 | 48.28 | 3644.3 | 1.0000 |
| 3 | 18.41 | 1389.7 | 0.6327 | 10 | 77.00 | 5811.6 | 0.5269 |
| 4 | 24.89 | 1878.5 | 0.7049 | 11 | 89.94 | 6788.0 | 0.1167 |
| 5 | 25.12 | 1895.7 | 0.6579 | 12 | 174.64 | 13181.0 | 0.1391 |
| 6 | 26.11 | 1970.3 | 0.4006 | 13 | 203.20 | 15336.9 | 0.0841 |
| 7 | 31.61 | 2385.6 | 0.7755 | 14 | 209.34 | 15800.4 | 0.0801 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of 1-acetyl-2-oxocyclohexyl 2-ethylbutanoate, **4e**

| | | | | | | | |
|-------------------------------|---------|-------------------------------|--------|------------------------|----------------------|----------------|--------------|
| Acquisition Time (sec) | 0.6759 | | | Date | 04 May 2016 11:26:56 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Frequency (MHz) | 300.13 | Nucleus | 1H |
| Sweep Width (Hz) | 6009.62 | Points Count | 8192 | Pulse Sequence | zg | Solvent | CHLOROFORM-D |
| | | Temperature (degree C) | 22.000 | | | | |

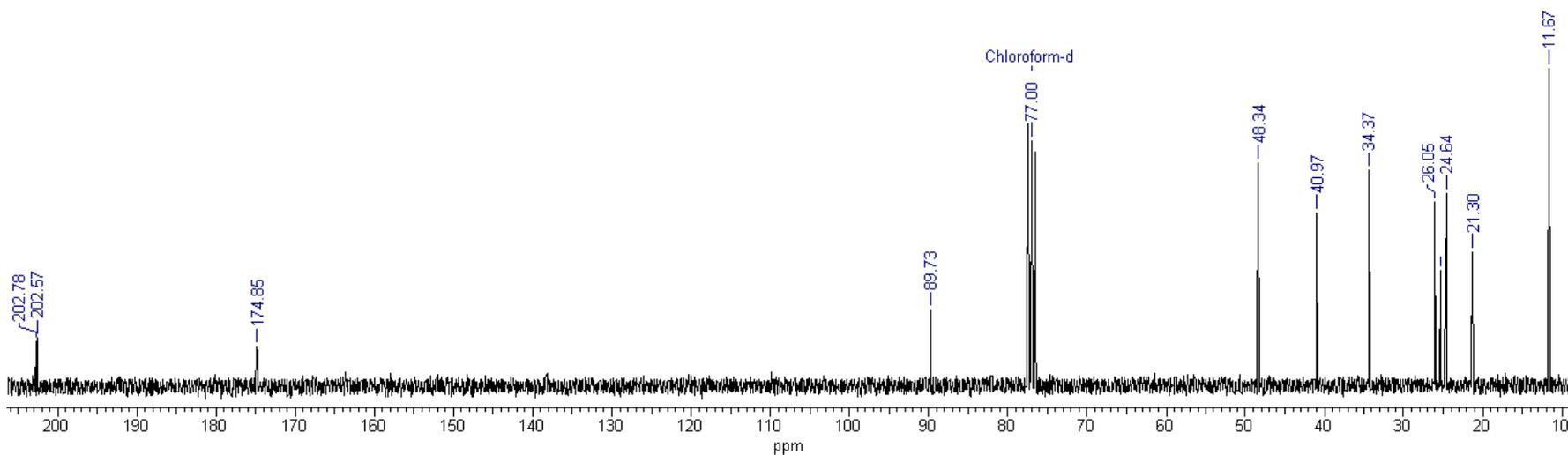
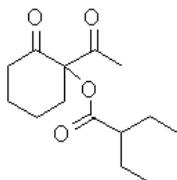


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.94 | 282.4 | 0.3150 | 11 | 1.69 | 508.3 | 0.1203 | 21 | 2.10 | 630.9 | 0.0564 | 31 | 2.63 | 789.3 | 0.0925 |
| 2 | 0.97 | 289.7 | 0.6352 | 12 | 1.72 | 515.7 | 0.1086 | 22 | 2.12 | 636.0 | 0.0668 | 32 | 2.65 | 794.5 | 0.0909 |
| 3 | 0.99 | 297.0 | 0.3464 | 13 | 1.74 | 522.3 | 0.0890 | 23 | 2.17 | 652.1 | 1.0000 | 33 | 2.67 | 800.4 | 0.0553 |
| 4 | 1.52 | 455.5 | 0.0509 | 14 | 1.79 | 537.0 | 0.1956 | 24 | 2.21 | 662.4 | 0.0592 | 34 | 2.68 | 804.8 | 0.0896 |
| 5 | 1.54 | 462.1 | 0.0860 | 15 | 1.89 | 567.8 | 0.0230 | 25 | 2.26 | 677.8 | 0.0851 | 35 | 2.72 | 815.0 | 0.0278 |
| 6 | 1.56 | 469.5 | 0.1225 | 16 | 1.94 | 581.7 | 0.0616 | 26 | 2.29 | 685.9 | 0.0909 | 36 | 2.75 | 824.6 | 0.0141 |
| 7 | 1.59 | 476.1 | 0.1189 | 17 | 1.95 | 586.1 | 0.0521 | 27 | 2.30 | 691.8 | 0.1174 | 37 | 7.25 | 2176.0 | 0.0495 |
| 8 | 1.61 | 482.7 | 0.0853 | 18 | 1.97 | 589.8 | 0.0370 | 28 | 2.32 | 696.9 | 0.0541 | | | | |
| 9 | 1.65 | 495.1 | 0.0666 | 19 | 1.99 | 597.1 | 0.0221 | 29 | 2.57 | 770.3 | 0.0171 | | | | |
| 10 | 1.67 | 502.5 | 0.1012 | 20 | 2.06 | 618.4 | 0.0339 | 30 | 2.60 | 779.8 | 0.0225 | | | | |

| No. | Annotation | (ppm) | No. | (ppm) | Value |
|-----|--------------|-------|-----|-----------|-------|
| 1 | Chloroform-d | 7.25 | 1 | 90 .. 1.0 | 6.000 |
| | | | 2 | 49 .. 1.8 | 7.040 |
| | | | 3 | 89 .. 1.9 | 1.011 |
| | | | 4 | 05 .. 2.3 | 6.033 |
| | | | 5 | 54 .. 2.7 | 1.987 |

¹³C NMR of 1-acetyl-2-oxocyclohexyl 2-ethylbutanoate, **4e**

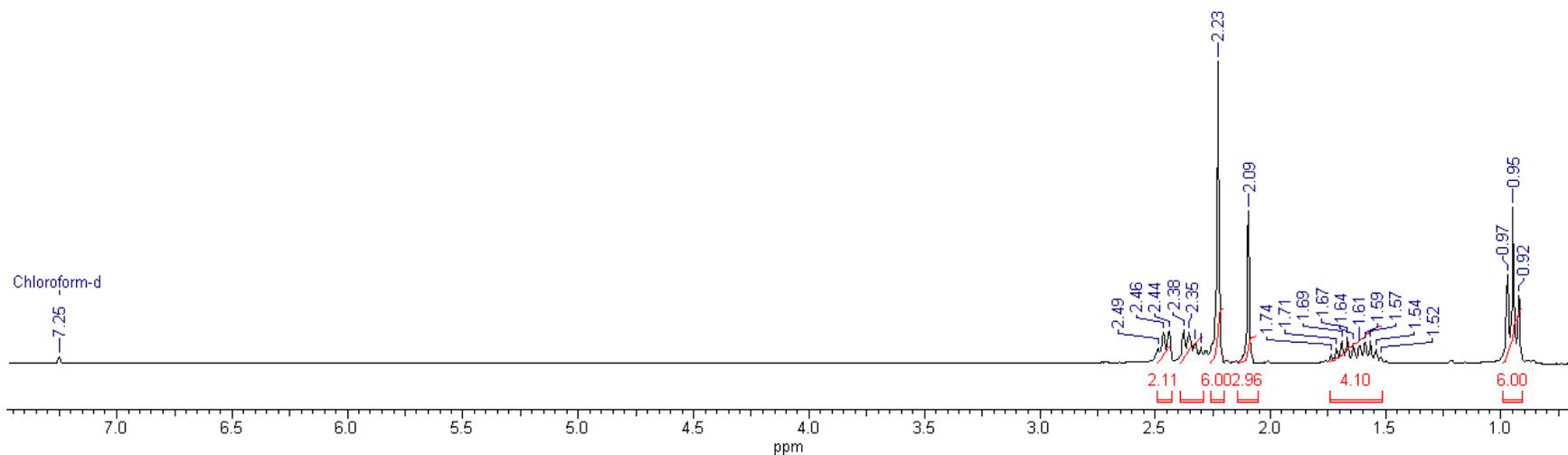
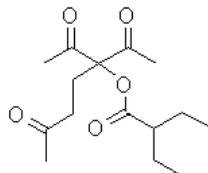
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|-------------------------------|--------|------------------------------|-------------------------|-------------------------------|----------------------|
| Acquisition Time (sec) | 0.4503 | | | Date | 04 May 2016 11:29:04 |
| | | | | Frequency (MHz) | 75.48 |
| | | | | Nucleus | 13C |
| Number of Transients | 169 | Original Points Count | 16316 | Points Count | 16384 |
| Solvent | | CHLOROFORM-D | Sweep Width (Hz) | | 18115.94 |
| | | | | Pulse Sequence | zgpg30 |
| | | | | Temperature (degree C) | 22.100 |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.67 | 881.0 | 1.0000 | 8 | 48.34 | 3648.8 | 0.7037 | 1 | Chloroform-d | 77.00 |
| 2 | 21.30 | 1607.5 | 0.4238 | 9 | 77.00 | 5811.7 | 0.7739 | | | |
| 3 | 24.64 | 1859.6 | 0.6078 | 10 | 89.73 | 6772.6 | 0.2431 | | | |
| 4 | 25.37 | 1914.9 | 0.3668 | 11 | 174.85 | 13197.2 | 0.1288 | | | |
| 5 | 26.05 | 1965.8 | 0.5802 | 12 | 202.57 | 15289.3 | 0.1545 | | | |
| 6 | 34.37 | 2593.9 | 0.6811 | 13 | 202.78 | 15304.8 | 0.1445 | | | |
| 7 | 40.97 | 3092.6 | 0.5480 | | | | | | | |

¹H NMR of 3-acetyl-2,6-dioxoheptan-3-yl 2-ethylbutanoate, **4f**

| | | | | | |
|------------------------|---------|------------------------|----------------------|-----------------|--------------|
| Acquisition Time (sec) | 0.6759 | Date | 25 Apr 2016 12:03:12 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 21.500 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zq |
| | | | | Nucleus | 1H |
| | | | | Solvent | CHLOROFORM-D |



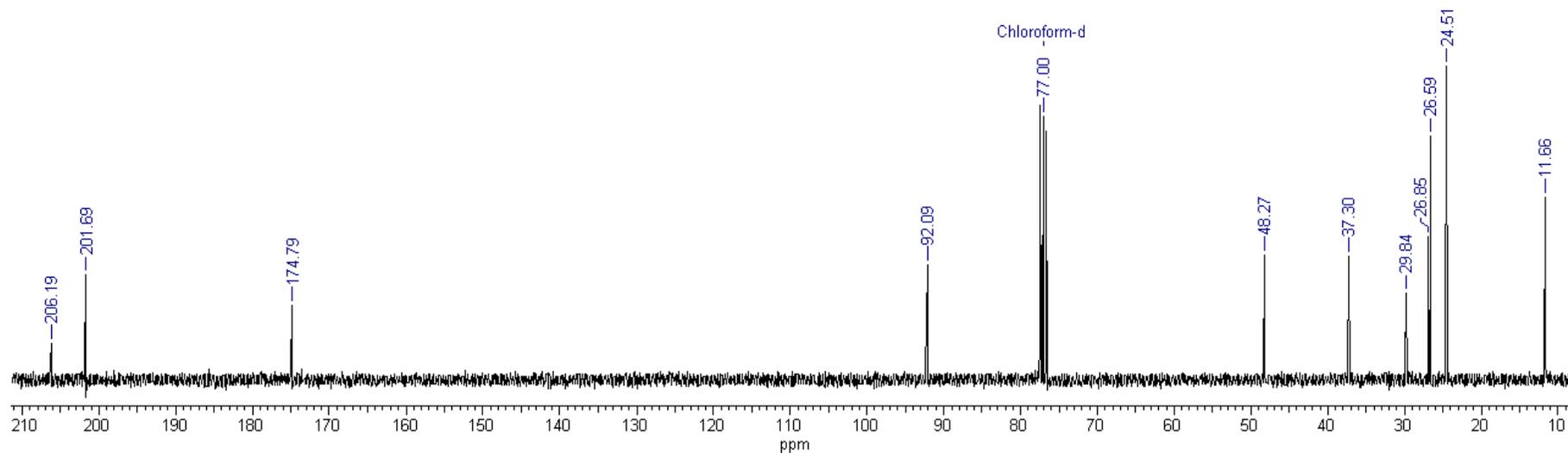
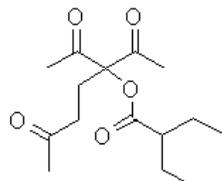
| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.92 | 277.2 | 0.2229 | 9 | 1.64 | 492.2 | 0.0656 | 17 | 2.33 | 698.4 | 0.0672 |
| 2 | 0.95 | 284.6 | 0.5173 | 10 | 1.67 | 500.3 | 0.0866 | 18 | 2.36 | 705.7 | 0.1042 |
| 3 | 0.97 | 291.9 | 0.2944 | 11 | 1.69 | 507.6 | 0.0722 | 19 | 2.38 | 713.0 | 0.1095 |
| 4 | 1.52 | 456.3 | 0.0227 | 12 | 1.71 | 514.2 | 0.0508 | 20 | 2.44 | 731.4 | 0.1053 |
| 5 | 1.54 | 462.9 | 0.0448 | 13 | 1.74 | 521.6 | 0.0294 | 21 | 2.46 | 739.5 | 0.1025 |
| 6 | 1.57 | 470.2 | 0.0718 | 14 | 2.09 | 628.7 | 0.5028 | 22 | 2.49 | 746.1 | 0.0508 |
| 7 | 1.59 | 476.8 | 0.0717 | 15 | 2.23 | 669.0 | 1.0000 | 23 | 7.25 | 2176.0 | 0.0228 |
| 8 | 1.61 | 484.1 | 0.0590 | 16 | 2.30 | 691.0 | 0.0539 | | | | |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value |
|-----|------------|-------|
| 1 | .91 .. 0.9 | 6.000 |
| 2 | .51 .. 1.7 | 4.096 |
| 3 | .05 .. 2.1 | 2.969 |
| 4 | .20 .. 2.2 | 6.002 |
| 5 | .29 .. 2.3 | 2.992 |
| 6 | .43 .. 2.4 | 2.110 |

¹³C NMR of 3-acetyl-2,6-dioxoheptan-3-yl 2-ethylbutanoate, **4f**

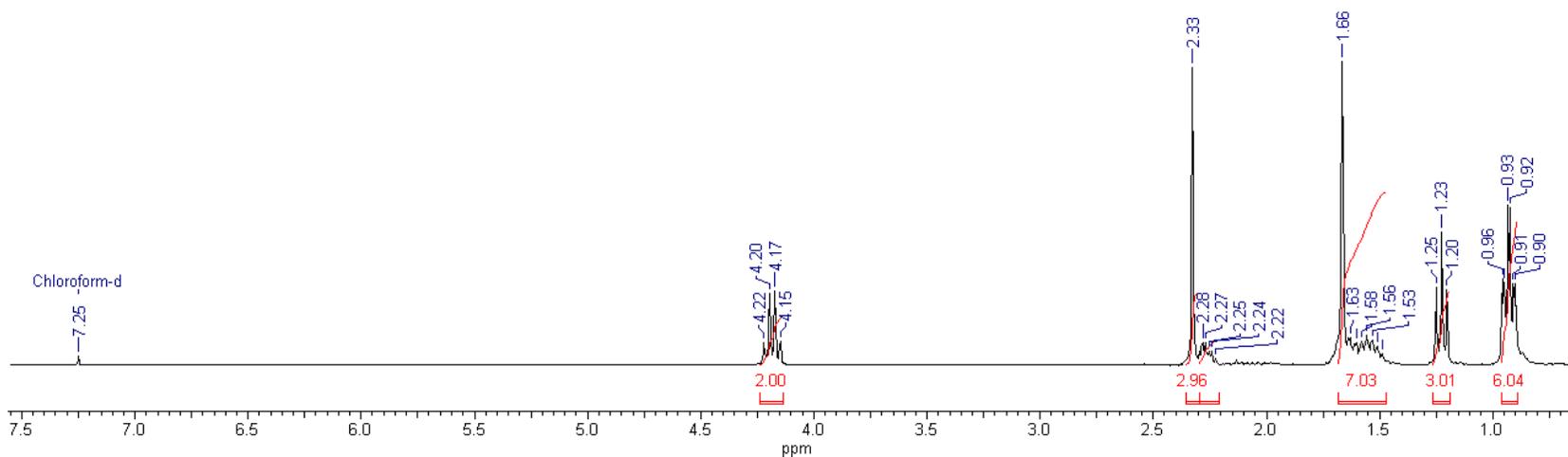
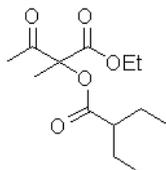
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|------------------------|--------------|-----------------------|----------|------------------------|----------------------|
| Acquisition Time (sec) | 0.4503 | | | Date | 21 Apr 2016 15:23:44 |
| | | Original Points Count | 16316 | Points Count | 16384 |
| Number of Transients | 299 | | | Pulse Sequence | zgpg30 |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Temperature (degree C) | 20.500 |
| | | | | Frequency (MHz) | 75.48 |
| | | | | Nucleus | 13C |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.66 | 879.9 | 0.5829 | 7 | 48.27 | 3643.3 | 0.4001 | 1 | Chloroform-d | 77.00 |
| 2 | 24.51 | 1849.7 | 1.0000 | 8 | 77.00 | 5811.7 | 0.8420 | | | |
| 3 | 26.59 | 2006.7 | 0.7762 | 9 | 92.09 | 6950.6 | 0.3692 | | | |
| 4 | 26.85 | 2026.6 | 0.4579 | 10 | 174.79 | 13192.7 | 0.2398 | | | |
| 5 | 29.84 | 2252.2 | 0.2778 | 11 | 201.69 | 15222.9 | 0.3366 | | | |
| 6 | 37.30 | 2815.0 | 0.3978 | 12 | 206.19 | 15562.4 | 0.1191 | | | |

¹H NMR of ethyl 2-(2-ethylbutanoyloxy)-2-methyl-3-oxobutanoate, **4g**

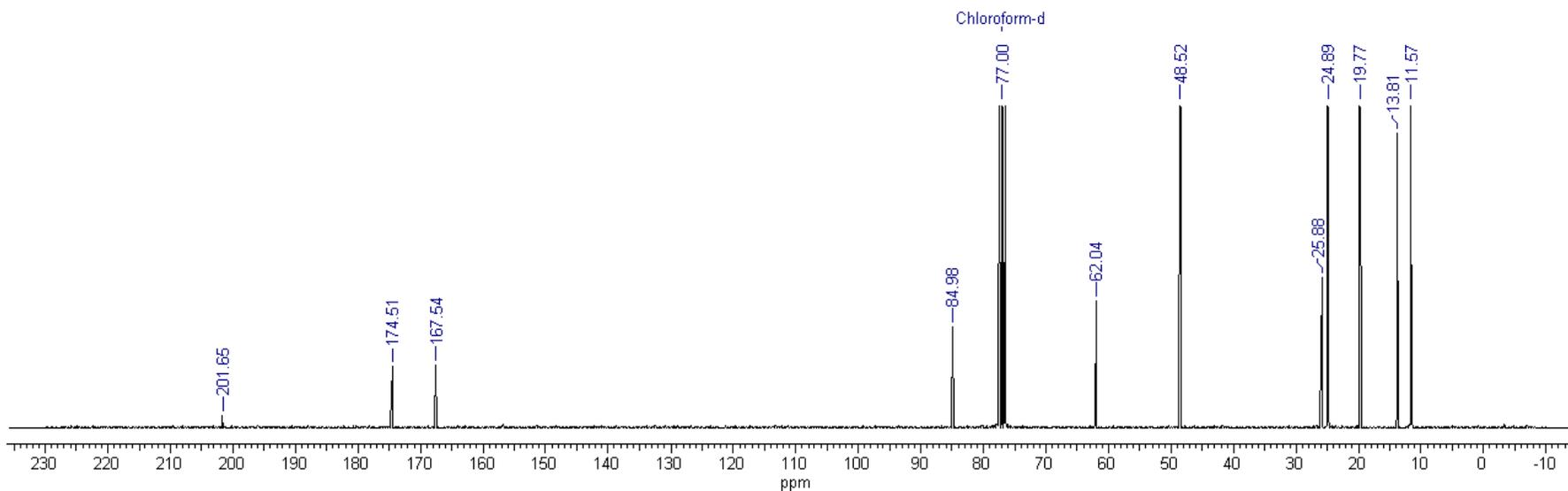
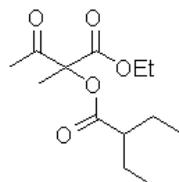
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|------------------------|---------|------------------------|----------------------|-----------------|----------------|
| Acquisition Time (sec) | 0.6759 | Date | 13 Apr 2016 14:24:00 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 23.800 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zg |
| | | | | Nucleus | ¹ H |
| | | | | Solvent | CHLOROFORM-D |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) | No. | (ppm) | Value |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|-----|--------------|-------|-----|-----------|-------|
| 1 | 0.90 | 269.7 | 0.2681 | 11 | 1.51 | 453.2 | 0.0609 | 21 | 2.27 | 681.3 | 0.0726 | 1 | Chloroform-d | 7.25 | 1 | 89 .. 0.9 | 6.040 |
| 2 | 0.91 | 272.7 | 0.2667 | 12 | 1.53 | 459.0 | 0.0631 | 22 | 2.28 | 685.0 | 0.0740 | 2 | | | 2 | 19 .. 1.2 | 3.011 |
| 3 | 0.92 | 277.1 | 0.5214 | 13 | 1.56 | 467.1 | 0.0963 | 23 | 2.33 | 698.2 | 0.9816 | 3 | | | 3 | 47 .. 1.6 | 7.028 |
| 4 | 0.93 | 280.0 | 0.5255 | 14 | 1.58 | 474.4 | 0.0764 | 24 | 4.15 | 1244.8 | 0.0787 | 4 | | | 4 | 21 .. 2.2 | 0.996 |
| 5 | 0.95 | 284.4 | 0.2727 | 15 | 1.60 | 481.0 | 0.0738 | 25 | 4.17 | 1252.1 | 0.2441 | 5 | | | 5 | 30 .. 2.3 | 2.962 |
| 6 | 0.96 | 287.3 | 0.2820 | 16 | 1.63 | 489.1 | 0.0879 | 26 | 4.20 | 1259.5 | 0.2341 | 6 | | | 6 | 13 .. 4.2 | 2.000 |
| 7 | 1.20 | 360.7 | 0.2484 | 17 | 1.66 | 499.4 | 1.0000 | 27 | 4.22 | 1266.8 | 0.0724 | | | | | | |
| 8 | 1.23 | 368.0 | 0.4373 | 18 | 2.22 | 667.4 | 0.0223 | 28 | 7.25 | 2175.8 | 0.0293 | | | | | | |
| 9 | 1.25 | 374.6 | 0.2556 | 19 | 2.24 | 672.5 | 0.0438 | | | | | | | | | | |
| 10 | 1.49 | 445.8 | 0.0355 | 20 | 2.25 | 675.5 | 0.0450 | | | | | | | | | | |

¹³C NMR of ethyl 2-(2-ethylbutanoyloxy)-2-methyl-3-oxobutanoate, **4g**

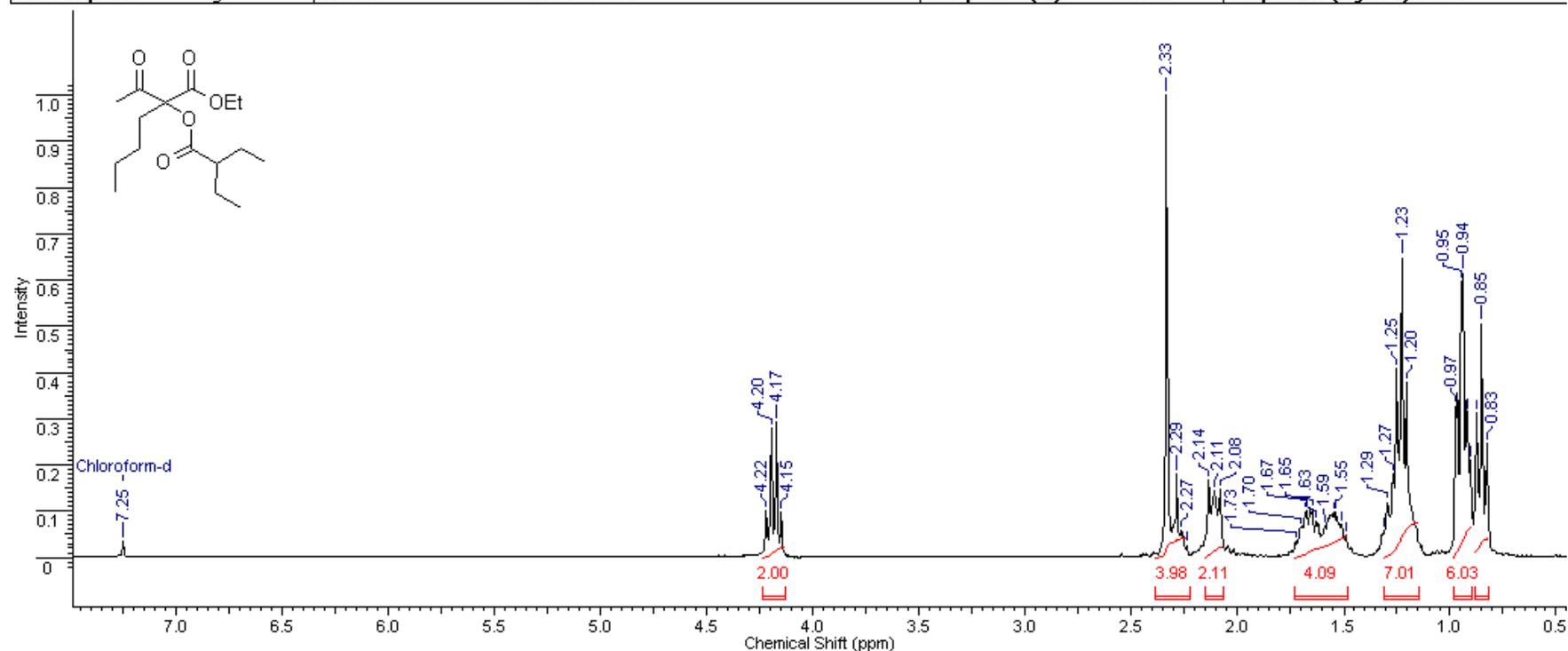
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|-------------------------------|--------------|------------------------------|----------|-------------------------------|----------------------|
| Acquisition Time (sec) | 0.4503 | | | Date | 13 Apr 2016 14:30:24 |
| Number of Transients | 112 | Original Points Count | 16316 | Frequency (MHz) | 75.48 |
| Solvent | CHLOROFORM-D | Points Count | 16384 | Pulse Sequence | zpgg30 |
| | | Sweep Width (Hz) | 18115.94 | Temperature (degree C) | 23.800 |
| | | | | Nucleus | 13C |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.57 | 873.2 | 0.5131 | 8 | 48.52 | 3662.0 | 0.6838 | 1 | Chloroform-d | 77.00 |
| 2 | 11.60 | 875.4 | 0.5419 | 9 | 62.04 | 4682.6 | 0.2008 | | | |
| 3 | 13.81 | 1042.4 | 0.4648 | 10 | 77.00 | 5811.6 | 0.9529 | | | |
| 4 | 19.77 | 1492.5 | 1.0000 | 11 | 84.98 | 6414.3 | 0.1802 | | | |
| 5 | 24.89 | 1878.4 | 0.6400 | 12 | 167.54 | 12645.3 | 0.1007 | | | |
| 6 | 24.96 | 1883.9 | 0.6322 | 13 | 174.51 | 13171.7 | 0.0975 | | | |
| 7 | 25.88 | 1953.6 | 0.2387 | 14 | 201.65 | 15219.6 | 0.0197 | | | |

¹H NMR of ethyl 2-acetyl-2-(2-ethylbutanoyloxy)hexanoate, **4h**

| | | | | | | | | | |
|------------------------|--------|---------|----------------------|----------------------|-----------------------|------------------|--------------|------------------------|--------|
| Acquisition Time (sec) | 1.3518 | Date | 07 Apr 2016 14:47:28 | | Original Points Count | 8124 | Points Count | 8192 | |
| Frequency (MHz) | 300.13 | Nucleus | 1H | Number of Transients | 1 | Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 25.200 |
| Pulse Sequence | zg | Solvent | CHLOROFORM-D | | | | | | |



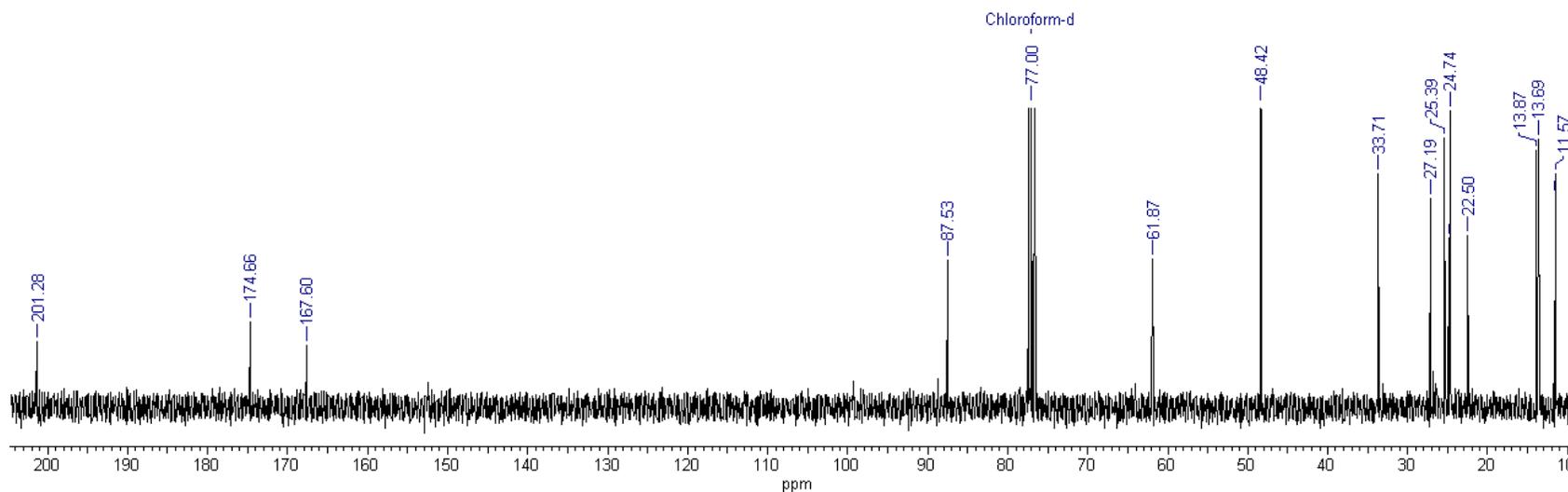
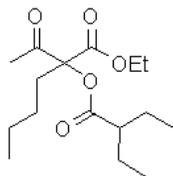
| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.83 | 247.8 | 0.2452 | 13 | 1.29 | 388.0 | 0.1185 | 25 | 2.08 | 624.9 | 0.1471 |
| 2 | 0.85 | 255.2 | 0.5054 | 14 | 1.31 | 393.8 | 0.0557 | 26 | 2.11 | 632.3 | 0.1441 |
| 3 | 0.87 | 261.8 | 0.3106 | 15 | 1.49 | 446.7 | 0.0465 | 27 | 2.14 | 641.1 | 0.1665 |
| 4 | 0.90 | 271.3 | 0.2109 | 16 | 1.51 | 453.3 | 0.0697 | 28 | 2.24 | 671.9 | 0.0269 |
| 5 | 0.92 | 275.0 | 0.3132 | 17 | 1.53 | 460.6 | 0.0962 | 29 | 2.27 | 680.0 | 0.0568 |
| 6 | 0.94 | 282.3 | 0.6147 | 18 | 1.55 | 464.3 | 0.0971 | 30 | 2.29 | 685.8 | 0.1809 |
| 7 | 0.95 | 284.5 | 0.5981 | 19 | 1.59 | 476.7 | 0.0674 | 31 | 2.33 | 700.5 | 1.0000 |
| 8 | 0.97 | 291.9 | 0.3265 | 20 | 1.63 | 490.0 | 0.0786 | 32 | 4.15 | 1244.9 | 0.0982 |
| 9 | 1.20 | 361.6 | 0.3779 | 21 | 1.65 | 494.4 | 0.1038 | 33 | 4.17 | 1252.3 | 0.2922 |
| 10 | 1.23 | 368.2 | 0.6477 | 22 | 1.67 | 502.4 | 0.1016 | 34 | 4.20 | 1259.6 | 0.2779 |
| 11 | 1.25 | 375.5 | 0.4078 | 23 | 1.70 | 510.5 | 0.0643 | 35 | 4.22 | 1266.2 | 0.0995 |
| 12 | 1.27 | 380.6 | 0.1787 | 24 | 1.73 | 518.6 | 0.0338 | 36 | 7.25 | 2176.0 | 0.0354 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value | Absolute Value |
|-----|----------------|-------|----------------|
| 1 | [0.82 .. 0.88] | 3.099 | 1.43275e+8 |
| 2 | [0.90 .. 0.98] | 6.030 | 2.78785e+8 |
| 3 | [1.14 .. 1.31] | 7.011 | 3.24125e+8 |
| 4 | [1.48 .. 1.73] | 4.089 | 1.89026e+8 |
| 5 | [2.07 .. 2.15] | 2.106 | 9.73777e+7 |
| 6 | [2.22 .. 2.39] | 3.985 | 1.84215e+8 |
| 7 | [4.13 .. 4.24] | 2.000 | 9.24619e+7 |

¹³C NMR of ethyl 2-acetyl-2-(2-ethylbutanoyloxy)hexanoate, **4h**

| | | | | | |
|-------------------------------|--------------|------------------------------|----------|-------------------------------|----------------------|
| Acquisition Time (sec) | 0.4503 | | | Date | 07 Apr 2016 13:11:28 |
| Number of Transients | 111 | Original Points Count | 16316 | Frequency (MHz) | 75.48 |
| Solvent | CHLOROFORM-D | Points Count | 16384 | Pulse Sequence | zgpg30 |
| | | Sweep Width (Hz) | 18115.94 | Temperature (degree C) | 25.700 |
| | | | | Nucleus | 13C |

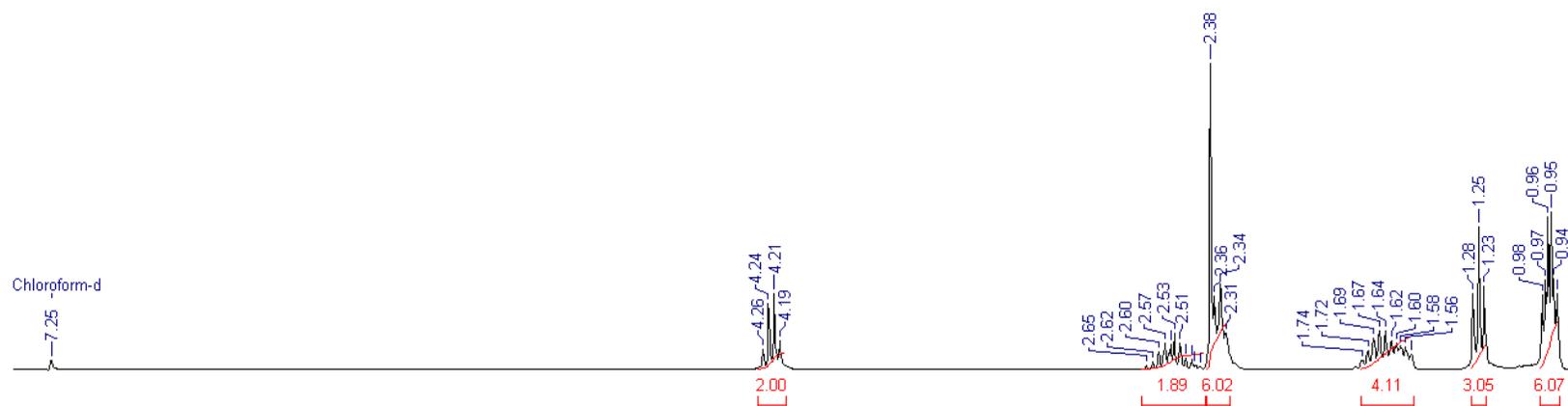
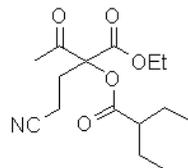


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 11.57 | 873.3 | 0.5662 | 10 | 33.71 | 2544.1 | 0.5679 |
| 2 | 11.61 | 876.6 | 0.5186 | 11 | 48.42 | 3654.3 | 1.0000 |
| 3 | 13.69 | 1033.6 | 0.6517 | 12 | 61.87 | 4689.4 | 0.3641 |
| 4 | 13.87 | 1046.9 | 0.6235 | 13 | 77.00 | 5811.7 | 0.9248 |
| 5 | 22.50 | 1698.2 | 0.4189 | 14 | 87.53 | 6606.7 | 0.3611 |
| 6 | 24.74 | 1867.4 | 0.7198 | 15 | 167.60 | 12649.8 | 0.1553 |
| 7 | 24.89 | 1878.4 | 0.4116 | 16 | 174.66 | 13182.8 | 0.2123 |
| 8 | 25.39 | 1916.0 | 0.6551 | 17 | 201.28 | 15192.0 | 0.1627 |
| 9 | 27.19 | 2052.0 | 0.5089 | | | | |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of ethyl 2-acetyl-4-cyano-2-(2-ethylbutanoyloxy)butanoate, **4i**

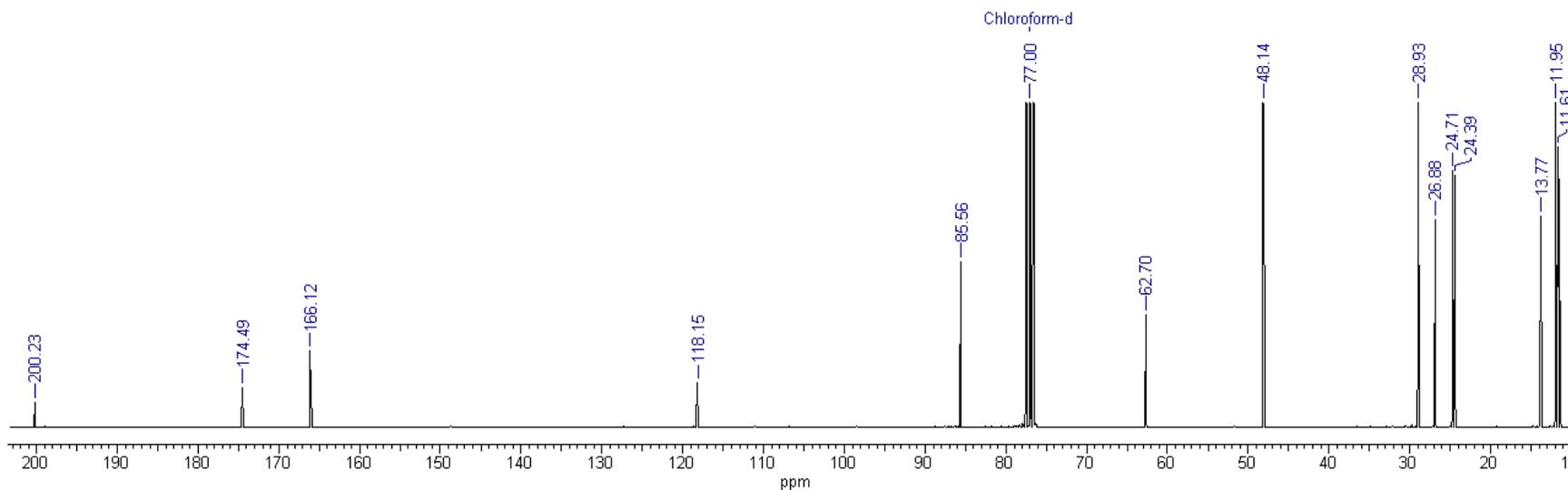
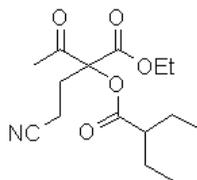
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|------------------------|---------|------------------------|----------------------|-----------------|--------------|
| Acquisition Time (sec) | 0.6759 | Date | 29 Mar 2016 12:22:24 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 25.600 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zg |
| | | | | Nucleus | 1H |
| | | | | Solvent | CHLOROFORM-D |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) | No. | (ppm) | Value | |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|-----|--------------|-------|-----|-------------|-------|--|
| 1 | 0.92 | 277.2 | 0.2445 | 11 | 1.56 | 468.0 | 0.0725 | 21 | 2.34 | 702.0 | 0.2804 | 31 | 2.57 | 771.7 | 0.0837 | 1 | Chloroform-d | 7.25 | 1 | .91 ... 0.9 | 6.070 | |
| 2 | 0.94 | 280.9 | 0.2961 | 12 | 1.58 | 473.9 | 0.0784 | 22 | 2.36 | 709.4 | 0.2398 | 32 | 2.60 | 779.8 | 0.0549 | 2 | | | 2 | .22 ... 1.2 | 3.047 | |
| 3 | 0.95 | 284.6 | 0.5121 | 13 | 1.60 | 479.7 | 0.0841 | 23 | 2.38 | 714.5 | 1.0000 | 33 | 2.62 | 786.4 | 0.0236 | 3 | | | 3 | .53 ... 1.7 | 4.115 | |
| 4 | 0.96 | 288.2 | 0.5000 | 14 | 1.62 | 485.6 | 0.0938 | 24 | 2.42 | 727.0 | 0.0068 | 34 | 2.65 | 794.5 | 0.0092 | 4 | | | 4 | .30 ... 2.3 | 6.025 | |
| 5 | 0.97 | 291.9 | 0.2915 | 15 | 1.64 | 492.9 | 0.1244 | 25 | 2.44 | 733.6 | 0.0097 | 35 | 4.19 | 1257.4 | 0.0941 | 5 | | | 5 | .40 ... 2.6 | 1.892 | |
| 6 | 0.98 | 295.6 | 0.2412 | 16 | 1.67 | 501.0 | 0.1232 | 26 | 2.46 | 738.0 | 0.0307 | 36 | 4.21 | 1264.8 | 0.2475 | 6 | | | 6 | .17 ... 4.2 | 2.000 | |
| 7 | 1.23 | 368.9 | 0.2689 | 17 | 1.69 | 508.3 | 0.1005 | 27 | 2.48 | 745.3 | 0.0367 | 37 | 4.24 | 1272.1 | 0.2155 | | | | | | | |
| 8 | 1.25 | 376.3 | 0.4643 | 18 | 1.72 | 515.7 | 0.0992 | 28 | 2.51 | 752.7 | 0.0851 | 38 | 4.26 | 1278.7 | 0.0644 | | | | | | | |
| 9 | 1.28 | 382.9 | 0.2480 | 19 | 1.74 | 522.3 | 0.0287 | 29 | 2.53 | 760.0 | 0.1148 | 39 | 7.25 | 2176.0 | 0.0280 | | | | | | | |
| 10 | 1.53 | 460.7 | 0.0486 | 20 | 2.31 | 694.7 | 0.1188 | 30 | 2.55 | 764.4 | 0.0790 | | | | | | | | | | | |

¹³C NMR of ethyl 2-acetyl-4-cyano-2-(2-ethylbutanoyloxy)butanoate, **4i**

| | | | | | | | |
|------------------------|--------------|-----------------------|----------------------|------------------------|--------|----------------|---------|
| Acquisition Time (sec) | 0.4503 | Date | 29 Mar 2016 14:24:00 | Frequency (MHz) | 75.48 | Nucleus | 13C |
| Number of Transients | 231 | Original Points Count | 16316 | Points Count | 16384 | Pulse Sequence | zpgpg30 |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Temperature (degree C) | 25.200 | | |

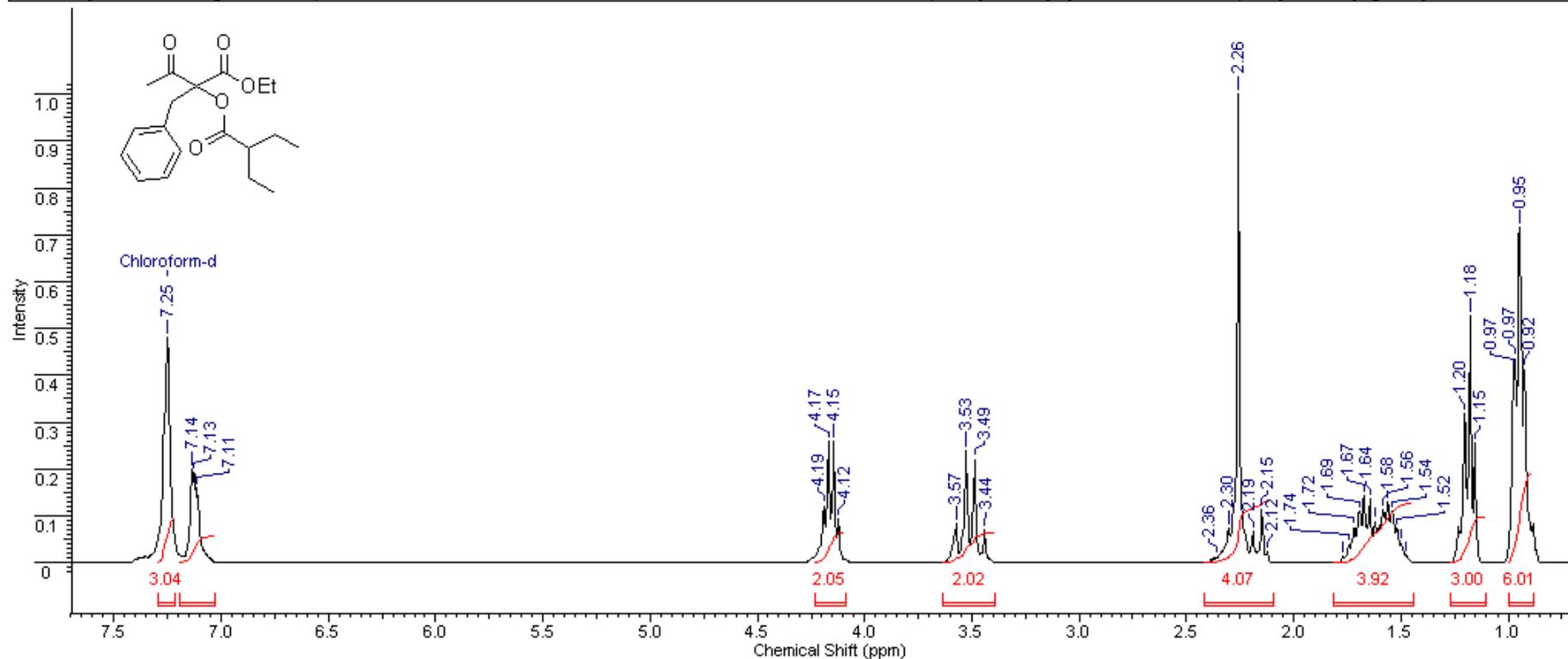


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 11.47 | 865.5 | 0.3861 | 9 | 48.14 | 3633.3 | 0.8462 |
| 2 | 11.61 | 876.6 | 0.4351 | 10 | 62.70 | 4732.4 | 0.1758 |
| 3 | 11.95 | 902.0 | 0.7499 | 11 | 77.00 | 5811.7 | 1.0000 |
| 4 | 13.77 | 1039.1 | 0.3291 | 12 | 85.56 | 6457.4 | 0.2580 |
| 5 | 24.39 | 1840.8 | 0.3917 | 13 | 118.15 | 8917.8 | 0.0895 |
| 6 | 24.71 | 1865.2 | 0.3990 | 14 | 166.12 | 12538.1 | 0.1187 |
| 7 | 26.88 | 2028.8 | 0.3230 | 15 | 174.49 | 13169.5 | 0.0621 |
| 8 | 28.93 | 2183.6 | 0.5066 | 16 | 200.23 | 15112.4 | 0.0397 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of ethyl 2-benzyl-2-(2-ethylbutanoyloxy)-3-oxobutanoate, **4j**

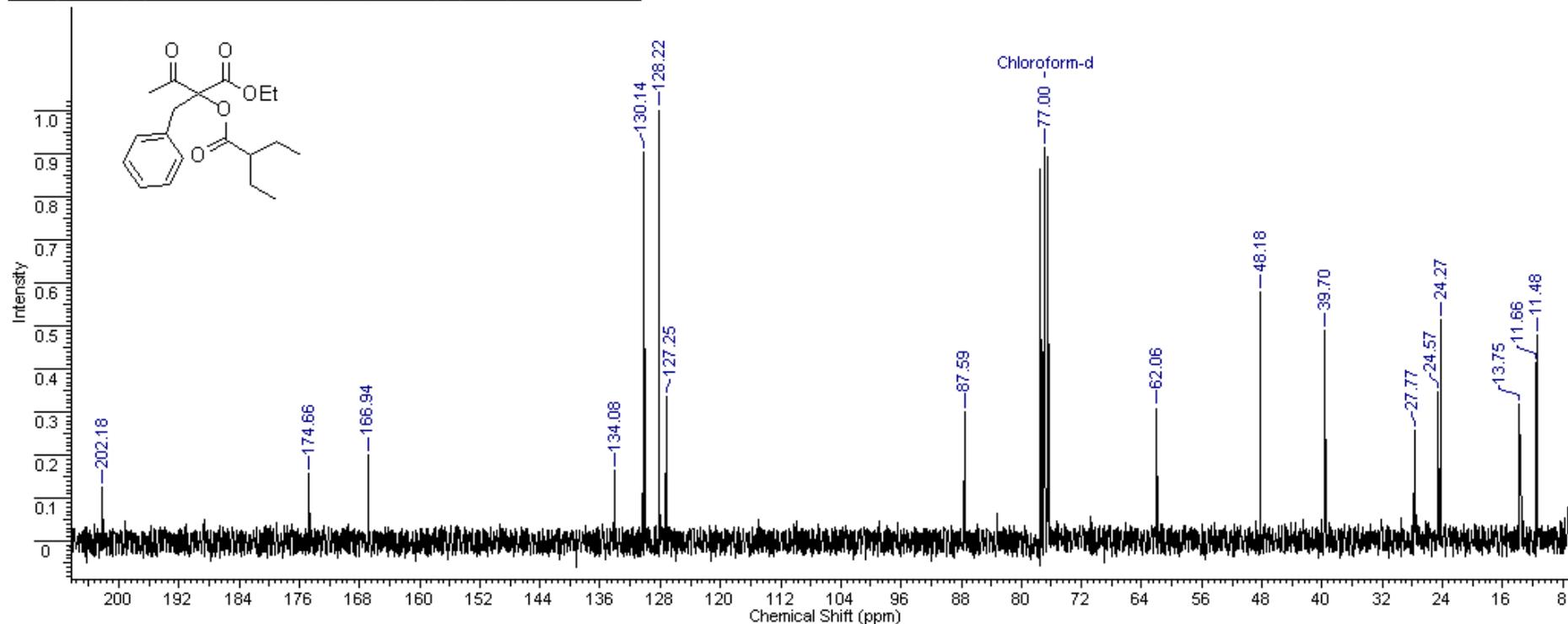
| | | | | | | | | | |
|------------------------|--------|---------|----------------------|----------------------|-----------------------|------------------|--------------|------------------------|--------|
| Acquisition Time (sec) | 1.3518 | Date | 20 Apr 2016 15:00:16 | | Original Points Count | 8124 | Points Count | 8192 | |
| Frequency (MHz) | 300.13 | Nucleus | 1H | Number of Transients | 1 | Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 22.100 |
| Pulse Sequence | zg3 | Solvent | CHLOROFORM-D | | | | | | |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | Value | Absolute Value |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|-----|-------|--------|--------|-----|-----------------|-------|----------------|
| 1 | 0.92 | 277.2 | 0.4113 | 11 | 1.52 | 455.5 | 0.0734 | 21 | 1.77 | 531.0 | 0.0143 | 31 | 3.57 | 1072.5 | 0.0819 | 1 | Chloroform-d | 7.25 | |
| 2 | 0.94 | 283.1 | 0.6866 | 12 | 1.54 | 462.8 | 0.1099 | 22 | 2.12 | 636.7 | 0.0243 | 32 | 4.12 | 1236.8 | 0.0940 | 2 | [1.10 ... 1.27] | 6.012 | 3.60890e+8 |
| 3 | 0.95 | 284.5 | 0.7141 | 13 | 1.56 | 467.9 | 0.1283 | 23 | 2.15 | 644.8 | 0.1138 | 33 | 4.15 | 1244.2 | 0.2590 | 3 | [1.44 ... 1.81] | 3.923 | 2.35506e+8 |
| 4 | 0.97 | 290.4 | 0.4360 | 14 | 1.58 | 475.3 | 0.1138 | 24 | 2.19 | 656.5 | 0.0661 | 34 | 4.17 | 1250.8 | 0.2589 | 4 | [2.10 ... 2.41] | 4.074 | 2.44570e+8 |
| 5 | 0.97 | 291.9 | 0.4122 | 15 | 1.62 | 486.3 | 0.0888 | 25 | 2.26 | 677.0 | 1.0000 | 35 | 4.19 | 1258.1 | 0.1207 | 5 | [3.39 ... 3.64] | 2.019 | 1.21170e+8 |
| 6 | 1.15 | 346.1 | 0.2545 | 16 | 1.64 | 493.6 | 0.1357 | 26 | 2.30 | 690.2 | 0.0737 | 36 | 7.11 | 2134.9 | 0.1608 | 6 | [4.09 ... 4.23] | 2.048 | 1.22956e+8 |
| 7 | 1.18 | 353.5 | 0.5258 | 17 | 1.67 | 501.7 | 0.1435 | 27 | 2.36 | 707.9 | 0.0118 | 37 | 7.13 | 2139.3 | 0.1909 | 7 | [7.03 ... 7.20] | 1.733 | 1.04058e+8 |
| 8 | 1.20 | 360.8 | 0.3180 | 18 | 1.69 | 508.3 | 0.1099 | 28 | 3.44 | 1032.1 | 0.0693 | 38 | 7.14 | 2142.2 | 0.1981 | 8 | [7.22 ... 7.29] | 3.043 | 1.82654e+8 |
| 9 | 1.47 | 442.3 | 0.0163 | 19 | 1.72 | 515.6 | 0.0749 | 29 | 3.49 | 1046.1 | 0.2211 | 39 | 7.25 | 2176.0 | 0.4802 | | | | |
| 10 | 1.50 | 449.6 | 0.0414 | 20 | 1.74 | 523.0 | 0.0384 | 30 | 3.53 | 1058.6 | 0.2393 | | | | | | | | |

¹³C NMR of ethyl 2-benzyl-2-(2-ethylbutanoyloxy)-3-oxobutanoate, **4j**

| | | | | | |
|------------------------|----------|------------------------|----------------------|-----------------------|--------------|
| Acquisition Time (sec) | 0.9006 | Date | 20 Apr 2016 11:56:48 | | |
| Frequency (MHz) | 75.48 | Nucleus | 13C | Number of Transients | 209 |
| Points Count | 16384 | Pulse Sequence | zgpg30 | Solvent | CHLOROFORM-D |
| Sweep Width (Hz) | 18115.94 | Temperature (degree C) | 21.800 | Original Points Count | 16316 |

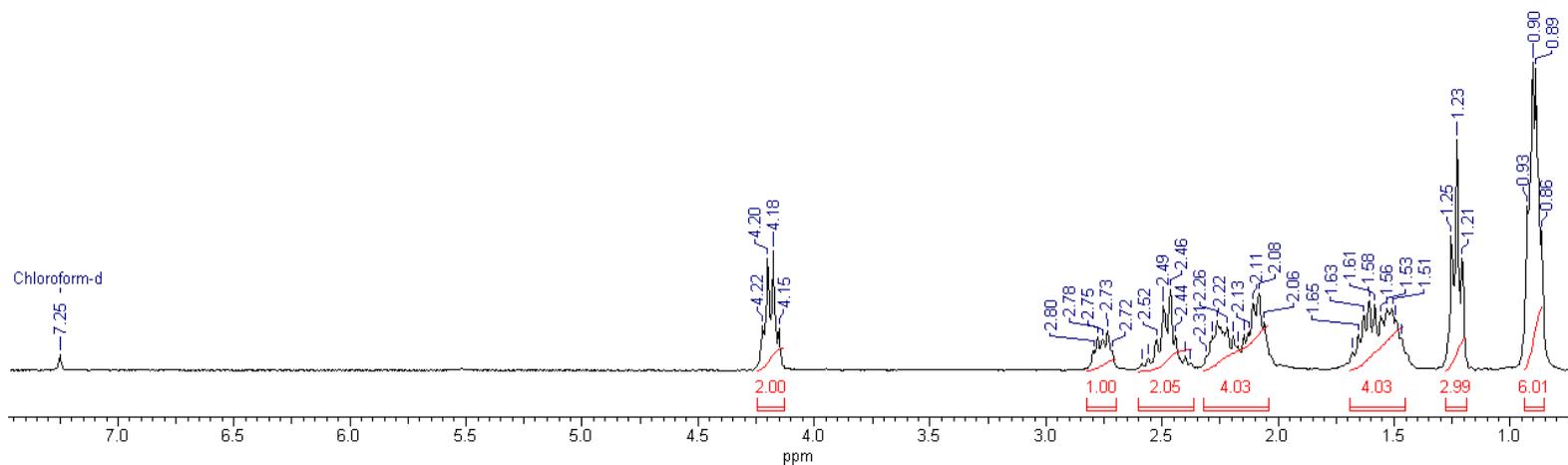
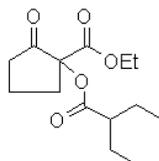


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 11.48 | 866.6 | 0.4783 | 10 | 77.00 | 5811.7 | 0.9135 |
| 2 | 11.66 | 879.9 | 0.4141 | 11 | 87.59 | 6611.1 | 0.3011 |
| 3 | 13.75 | 1038.0 | 0.3184 | 12 | 127.25 | 9604.5 | 0.3352 |
| 4 | 24.27 | 1832.0 | 0.5130 | 13 | 128.22 | 9677.5 | 1.0000 |
| 5 | 24.57 | 1854.1 | 0.3468 | 14 | 130.14 | 9822.3 | 0.9031 |
| 6 | 27.77 | 2096.2 | 0.2582 | 15 | 134.08 | 10119.8 | 0.1628 |
| 7 | 39.70 | 2996.3 | 0.4881 | 16 | 166.94 | 12600.0 | 0.1994 |
| 8 | 48.18 | 3636.6 | 0.5773 | 17 | 174.66 | 13182.8 | 0.1560 |
| 9 | 62.06 | 4683.8 | 0.3090 | 18 | 202.18 | 15259.4 | 0.1246 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclopentanecarboxylate, **4k**

| | | | | | |
|------------------------|---------|------------------------|----------------------|-----------------|----------------|
| Acquisition Time (sec) | 0.6759 | Date | 14 Apr 2016 13:02:56 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 23.600 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zg |
| | | | | Solvent | CHLOROFORM-D |
| | | | | Nucleus | ¹ H |

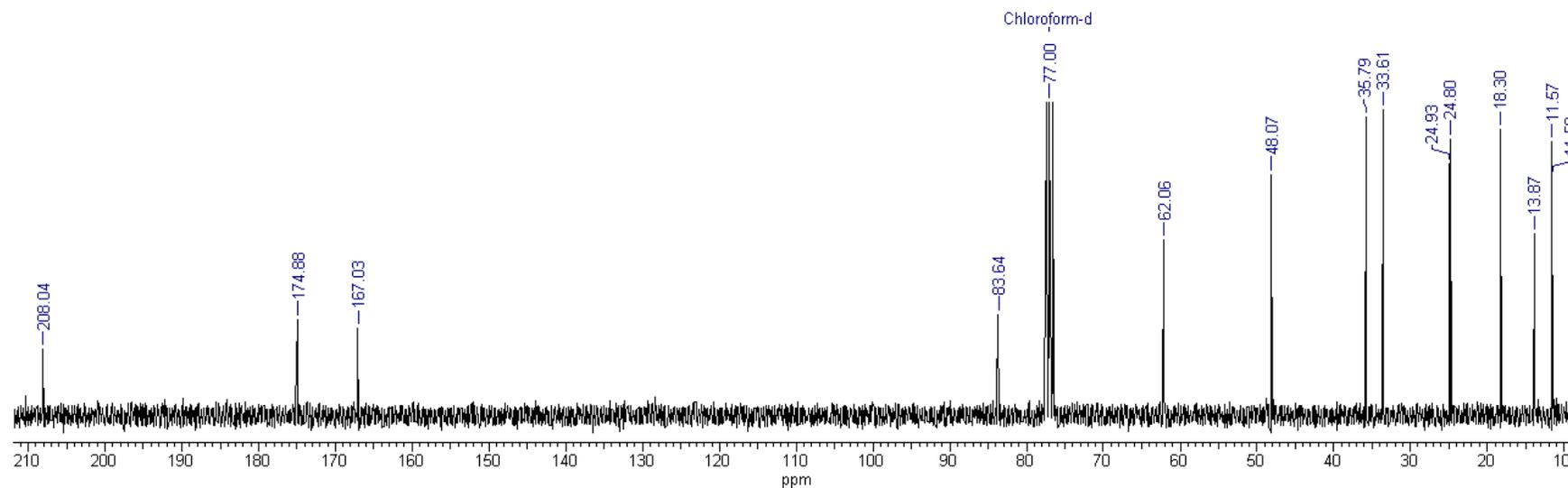
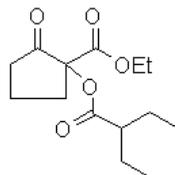


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.86 | 259.5 | 0.4525 | 13 | 1.58 | 475.2 | 0.2131 | 25 | 2.22 | 665.9 | 0.1419 | 37 | 2.72 | 814.9 | 0.0648 |
| 2 | 0.89 | 266.8 | 0.9776 | 14 | 1.61 | 482.5 | 0.2243 | 26 | 2.26 | 679.1 | 0.1612 | 38 | 2.73 | 820.7 | 0.1270 |
| 3 | 0.90 | 270.5 | 1.0000 | 15 | 1.63 | 489.8 | 0.1785 | 27 | 2.28 | 685.0 | 0.1103 | 39 | 2.75 | 826.6 | 0.1009 |
| 4 | 0.93 | 277.8 | 0.5335 | 16 | 1.65 | 496.4 | 0.1174 | 28 | 2.31 | 693.1 | 0.0475 | 40 | 2.78 | 833.9 | 0.1096 |
| 5 | 1.21 | 362.2 | 0.3634 | 17 | 1.68 | 503.8 | 0.0585 | 29 | 2.38 | 713.6 | 0.0255 | 41 | 2.80 | 839.1 | 0.0620 |
| 6 | 1.23 | 368.8 | 0.7478 | 18 | 2.06 | 618.2 | 0.1571 | 30 | 2.40 | 720.2 | 0.0464 | 42 | 4.15 | 1246.3 | 0.1390 |
| 7 | 1.25 | 376.1 | 0.4384 | 19 | 2.08 | 625.6 | 0.2521 | 31 | 2.44 | 732.7 | 0.1133 | 43 | 4.18 | 1253.6 | 0.3896 |
| 8 | 1.47 | 440.7 | 0.1058 | 20 | 2.11 | 632.9 | 0.2173 | 32 | 2.46 | 739.3 | 0.2633 | 44 | 4.20 | 1260.9 | 0.3658 |
| 9 | 1.49 | 448.0 | 0.1658 | 21 | 2.13 | 638.8 | 0.1254 | 33 | 2.49 | 748.8 | 0.2098 | 45 | 4.22 | 1267.5 | 0.1452 |
| 10 | 1.51 | 452.4 | 0.2033 | 22 | 2.15 | 644.6 | 0.1156 | 34 | 2.52 | 757.6 | 0.0988 | 46 | 7.25 | 2175.8 | 0.0506 |
| 11 | 1.53 | 459.8 | 0.2018 | 23 | 2.17 | 652.7 | 0.0806 | 35 | 2.56 | 767.9 | 0.0417 | | | | |
| 12 | 1.56 | 467.8 | 0.1796 | 24 | 2.19 | 658.6 | 0.1110 | 36 | 2.59 | 776.7 | 0.0217 | | | | |

| No. | Annotation | (ppm) | No. | (ppm) | Value |
|-----|--------------|-------|-----|------------|-------|
| 1 | Chloroform-d | 7.25 | 1 | 85 .. 0.9 | 6.008 |
| | | | 2 | .19 .. 1.2 | 2.992 |
| | | | 3 | .45 .. 1.6 | 4.028 |
| | | | 4 | .04 .. 2.3 | 4.033 |
| | | | 5 | .37 .. 2.6 | 2.047 |
| | | | 6 | .70 .. 2.8 | 0.998 |
| | | | 7 | .13 .. 4.2 | 2.000 |

¹³C NMR of ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclopentanecarboxylate, **4k**

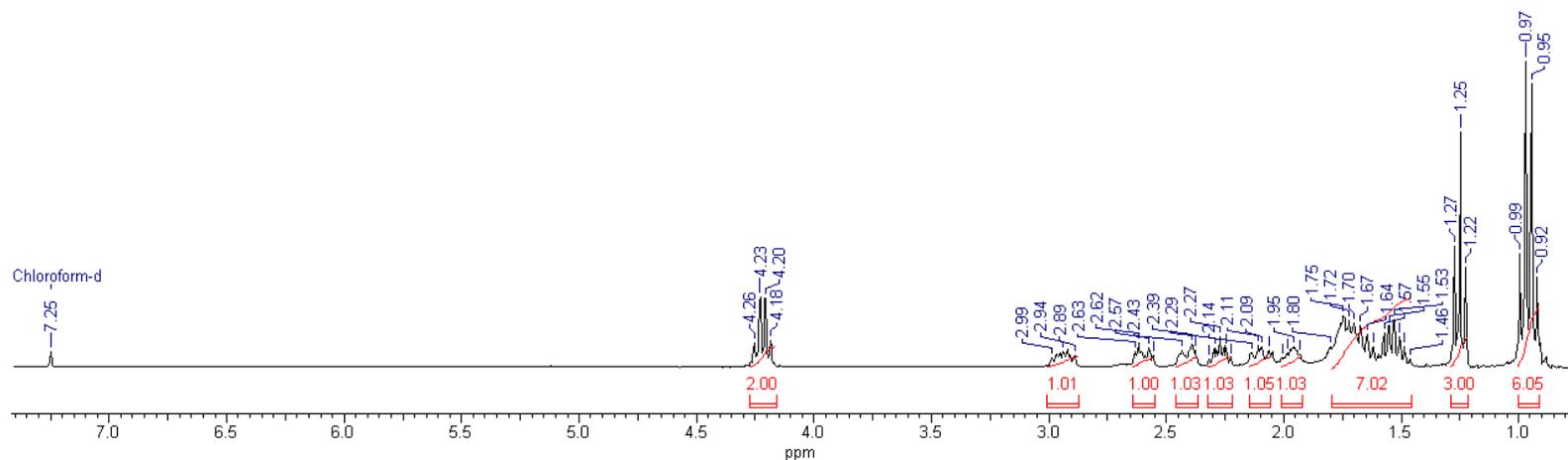
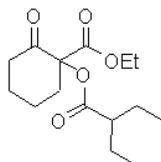
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|------------------------|--------------|-----------------------|----------|------------------------|----------------------|
| Acquisition Time (sec) | 0.4503 | | | Date | 14 Apr 2016 13:02:56 |
| Number of Transients | 155 | Original Points Count | 16316 | Points Count | 16384 |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Pulse Sequence | zgpg30 |
| | | | | Frequency (MHz) | 75.48 |
| | | | | Nucleus | 13C |
| | | | | Temperature (degree C) | 23.600 |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.50 | 867.8 | 0.6943 | 9 | 48.07 | 3627.8 | 0.6981 | 1 | Chloroform-d | 77.00 |
| 2 | 11.57 | 873.3 | 0.7920 | 10 | 62.06 | 4683.8 | 0.5092 | | | |
| 3 | 13.87 | 1046.9 | 0.5254 | 11 | 77.00 | 5811.7 | 1.0000 | | | |
| 4 | 18.30 | 1380.8 | 0.8273 | 12 | 83.64 | 6312.6 | 0.2940 | | | |
| 5 | 24.80 | 1871.8 | 0.8017 | 13 | 167.03 | 12606.7 | 0.2538 | | | |
| 6 | 24.93 | 1881.8 | 0.7312 | 14 | 174.88 | 13199.4 | 0.2799 | | | |
| 7 | 33.61 | 2536.4 | 0.8841 | 15 | 208.04 | 15701.8 | 0.1927 | | | |
| 8 | 35.79 | 2701.1 | 0.8637 | | | | | | | |

¹H NMR of ethyl 1-(2-ethylbutanoxy)-2-oxocyclohexanecarboxylate, **4l**

| | | | | | |
|--------------------------------------|--|-----------------------------------|--|--------------------------------------|--|
| Acquisition Time (sec) 0.6759 | | | | Date 30 Sep 2015 10:37:52 | |
| Number of Transients 1 | | Original Points Count 8124 | | Frequency (MHz) 300.13 | |
| Solvent CHLOROFORM-D | | Points Count 8192 | | Nucleus 1H | |
| | | Sweep Width (Hz) 6009.62 | | Pulse Sequence zg | |
| | | | | Temperature (degree C) 24.200 | |



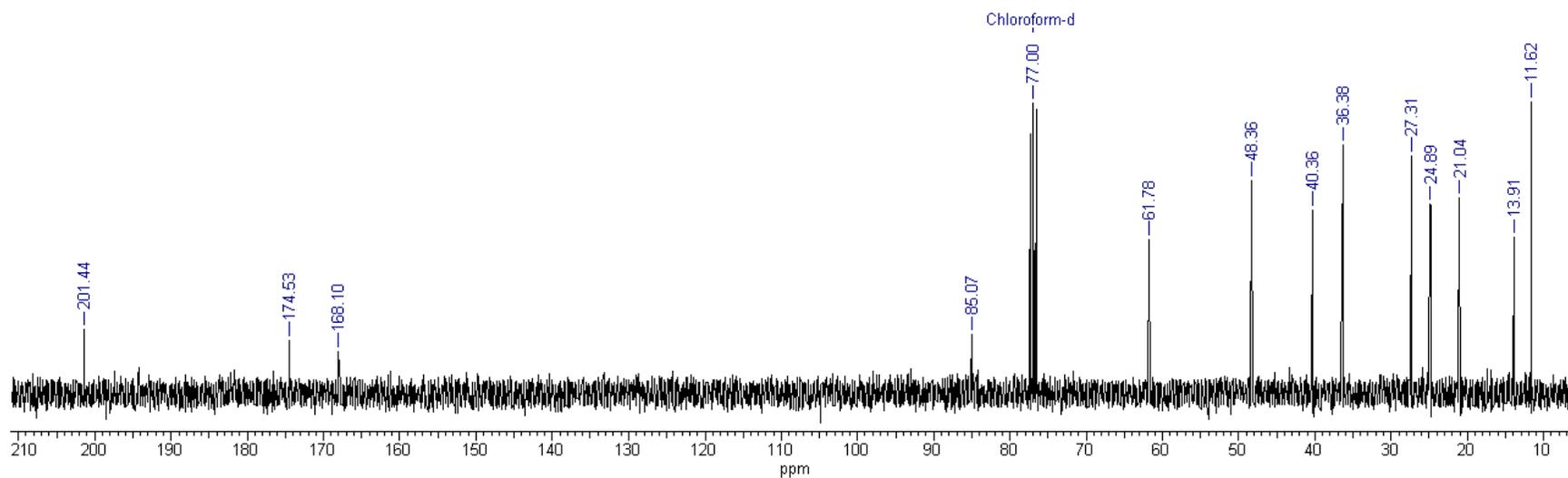
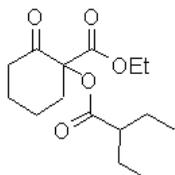
| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.92 | 276.3 | 0.2924 | 13 | 1.57 | 472.2 | 0.1117 | 25 | 2.06 | 619.7 | 0.0522 | 37 | 2.56 | 767.2 | 0.0367 |
| 2 | 0.95 | 283.7 | 0.9266 | 14 | 1.62 | 485.4 | 0.0674 | 26 | 2.09 | 628.5 | 0.0662 | 38 | 2.57 | 772.3 | 0.0621 |
| 3 | 0.97 | 291.0 | 1.0000 | 15 | 1.64 | 493.5 | 0.1068 | 27 | 2.11 | 632.9 | 0.0681 | 39 | 2.62 | 785.5 | 0.0803 |
| 4 | 0.99 | 298.3 | 0.3716 | 16 | 1.67 | 502.3 | 0.1359 | 28 | 2.14 | 641.7 | 0.0465 | 40 | 2.63 | 789.9 | 0.0497 |
| 5 | 1.22 | 367.3 | 0.3262 | 17 | 1.70 | 510.4 | 0.1450 | 29 | 2.23 | 668.1 | 0.0318 | 41 | 2.89 | 866.9 | 0.0378 |
| 6 | 1.25 | 374.6 | 0.7667 | 18 | 1.72 | 516.2 | 0.1496 | 30 | 2.24 | 673.2 | 0.0609 | 42 | 2.94 | 882.3 | 0.0507 |
| 7 | 1.27 | 382.0 | 0.3931 | 19 | 1.75 | 524.3 | 0.1654 | 31 | 2.27 | 682.1 | 0.1000 | 43 | 2.99 | 896.3 | 0.0305 |
| 8 | 1.46 | 438.5 | 0.0267 | 20 | 1.80 | 540.5 | 0.0672 | 32 | 2.29 | 687.2 | 0.0805 | 44 | 4.18 | 1255.8 | 0.0851 |
| 9 | 1.49 | 445.8 | 0.0672 | 21 | 1.93 | 580.1 | 0.0415 | 33 | 2.32 | 695.3 | 0.0252 | 45 | 4.20 | 1261.7 | 0.2268 |
| 10 | 1.50 | 451.7 | 0.0971 | 22 | 1.95 | 586.7 | 0.0669 | 34 | 2.36 | 713.6 | 0.0528 | 46 | 4.23 | 1269.0 | 0.2301 |
| 11 | 1.53 | 459.0 | 0.1548 | 23 | 1.98 | 595.5 | 0.0453 | 35 | 2.39 | 717.3 | 0.0748 | 47 | 4.26 | 1277.1 | 0.0784 |
| 12 | 1.55 | 464.9 | 0.1343 | 24 | 2.00 | 601.3 | 0.0296 | 36 | 2.43 | 730.5 | 0.0527 | 48 | 7.25 | 2175.8 | 0.0514 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value | No. | (ppm) | Value |
|-----|-----------|-------|-----|-----------|-------|
| 1 | 91 .. 1.0 | 6.049 | 6 | 22 .. 2.3 | 1.035 |
| 2 | 21 .. 1.2 | 3.001 | 7 | 37 .. 2.4 | 1.033 |
| 3 | 45 .. 1.7 | 7.023 | 8 | 55 .. 2.6 | 1.005 |
| 4 | 92 .. 2.0 | 1.033 | 9 | 87 .. 3.0 | 1.015 |
| 5 | 05 .. 2.1 | 1.053 | 10 | 16 .. 4.2 | 2.000 |

¹³C NMR of ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclohexanecarboxylate, **41**

| | | | | | |
|-------------------------------|-----------------|-----------------------------|----------------------|------------------------------|----------|
| Acquisition Time (sec) | 0.4340 | Date | 28 Mar 2016 08:12:48 | | |
| Nucleus | ¹³ C | Number of Transients | 53 | Original Points Count | 16316 |
| Pulse Sequence | zgpg60base | Solvent | CHLOROFORM-D | Frequency (MHz) | 75.48 |
| Temperature (degree C) | 27.400 | | | Points Count | 16384 |
| | | | | Sweep Width (Hz) | 18796.99 |



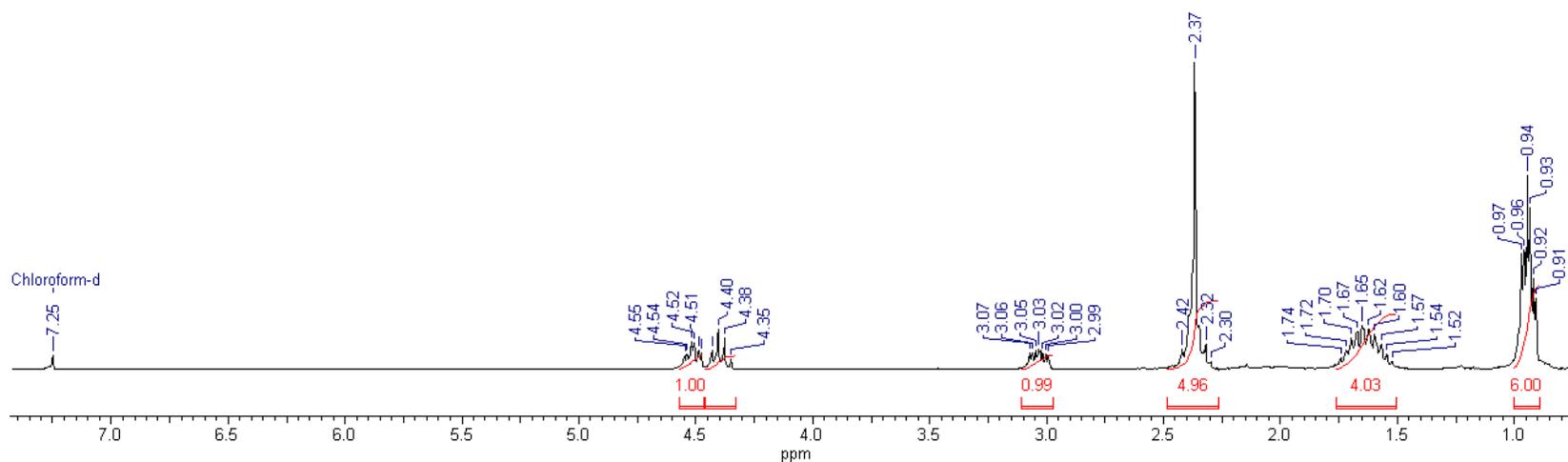
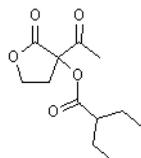
| No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|
| 1 | 11.62 | 876.9 | 1.0000 |
| 2 | 13.91 | 1050.1 | 0.5341 |
| 3 | 21.04 | 1588.2 | 0.6685 |
| 4 | 24.84 | 1875.1 | 0.6455 |
| 5 | 24.89 | 1878.5 | 0.6483 |
| 6 | 27.31 | 2060.9 | 0.8132 |
| 7 | 36.38 | 2745.9 | 0.8507 |
| 8 | 40.36 | 3046.5 | 0.6278 |

| No. | (ppm) | (Hz) | Height |
|-----|--------|---------|--------|
| 9 | 48.36 | 3650.0 | 0.7294 |
| 10 | 61.78 | 4663.1 | 0.5283 |
| 11 | 77.00 | 5811.6 | 0.9945 |
| 12 | 85.07 | 6420.9 | 0.2017 |
| 13 | 168.10 | 12687.7 | 0.1443 |
| 14 | 174.53 | 13173.0 | 0.1815 |
| 15 | 201.44 | 15203.8 | 0.2189 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of 3-acetyl-2-oxotetrahydrofuran-3-yl 2-ethylbutanoate, **4m**

| | | | | | |
|------------------------|---------|------------------------|----------------------|--------------|--------------|
| Acquisition Time (sec) | 0.5416 | Date | 20 Jun 2016 08:08:32 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 7500.00 | Temperature (degree C) | 25.100 | | |
| | | Frequency (MHz) | 300.13 | Nucleus | 1H |
| | | Pulse Sequence | zg | Solvent | CHLOROFORM-D |

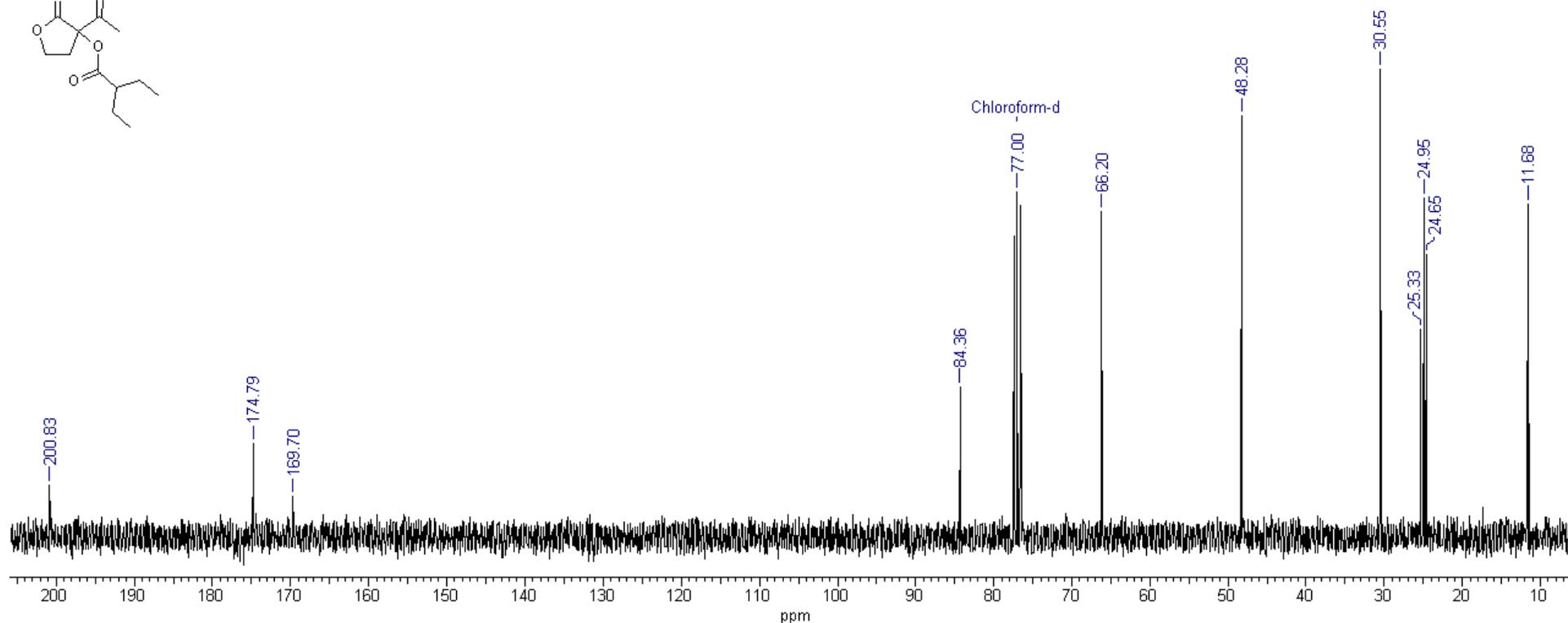
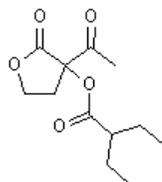


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|-----|-------|--------|--------|
| 1 | 0.91 | 272.3 | 0.2318 | 11 | 1.62 | 487.5 | 0.1312 | 21 | 2.99 | 897.7 | 0.0439 | 31 | 4.43 | 1329.8 | 0.0621 |
| 2 | 0.92 | 275.9 | 0.2955 | 12 | 1.65 | 495.7 | 0.1430 | 22 | 3.00 | 901.3 | 0.0505 | 32 | 4.48 | 1343.6 | 0.0520 |
| 3 | 0.93 | 279.6 | 0.5252 | 13 | 1.67 | 502.1 | 0.1225 | 23 | 3.02 | 905.9 | 0.0527 | 33 | 4.49 | 1346.3 | 0.0623 |
| 4 | 0.94 | 283.3 | 0.6349 | 14 | 1.70 | 509.4 | 0.1020 | 24 | 3.03 | 910.5 | 0.0639 | 34 | 4.51 | 1352.7 | 0.0871 |
| 5 | 0.96 | 287.9 | 0.3875 | 15 | 1.72 | 515.8 | 0.0601 | 25 | 3.05 | 914.1 | 0.0599 | 35 | 4.52 | 1356.4 | 0.0902 |
| 6 | 0.97 | 290.6 | 0.3768 | 16 | 1.74 | 523.2 | 0.0357 | 26 | 3.06 | 918.7 | 0.0540 | 36 | 4.54 | 1361.9 | 0.0507 |
| 7 | 1.52 | 456.3 | 0.0247 | 17 | 2.30 | 689.8 | 0.0265 | 27 | 3.07 | 922.4 | 0.0531 | 37 | 4.55 | 1364.6 | 0.0445 |
| 8 | 1.54 | 463.7 | 0.0481 | 18 | 2.32 | 695.3 | 0.0793 | 28 | 4.35 | 1305.1 | 0.0331 | 38 | 7.25 | 2175.9 | 0.0458 |
| 9 | 1.57 | 471.0 | 0.0803 | 19 | 2.37 | 710.0 | 1.0000 | 29 | 4.38 | 1313.4 | 0.1029 | | | | |
| 10 | 1.60 | 479.2 | 0.1158 | 20 | 2.42 | 726.4 | 0.0655 | 30 | 4.40 | 1321.6 | 0.1281 | | | | |

| No. | Annotation | (ppm) | No. | (ppm) | Value |
|-----|--------------|-------|-----|------------|-------|
| 1 | Chloroform-d | 7.25 | 1 | .89 .. 1.0 | 6.000 |
| | | | 2 | .51 .. 1.7 | 4.030 |
| | | | 3 | .26 .. 2.4 | 4.960 |
| | | | 4 | .97 .. 3.1 | 0.987 |
| | | | 5 | .33 .. 4.4 | 0.971 |
| | | | 6 | .46 .. 4.5 | 1.002 |

¹³C NMR of 3-acetyl-2-oxotetrahydrofuran-3-yl 2-ethylbutanoate, **4m**

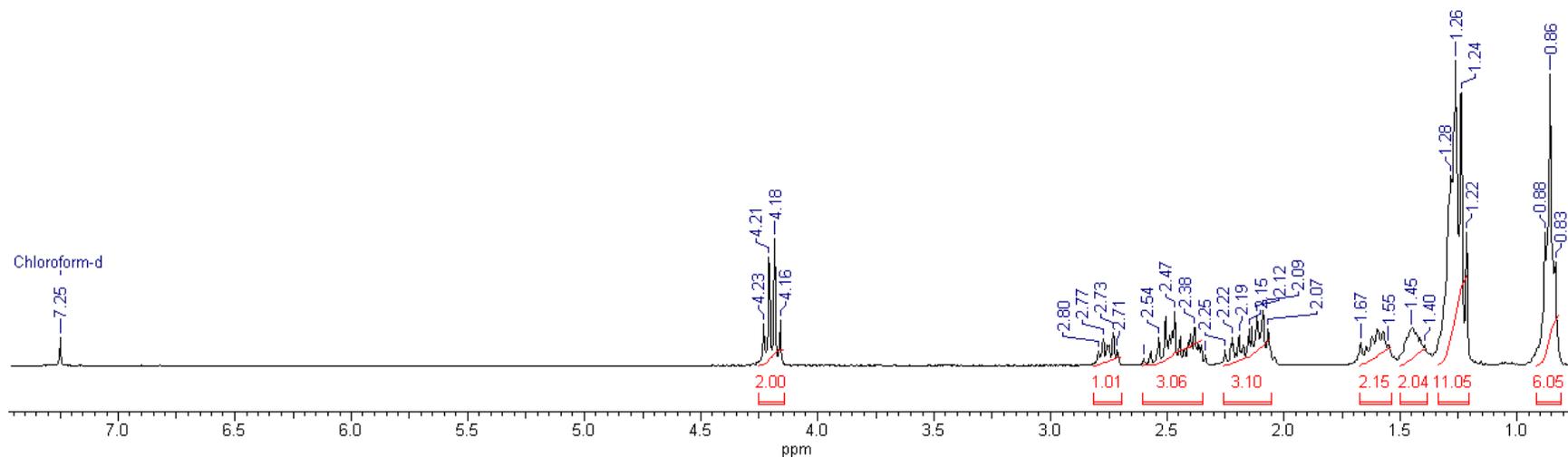
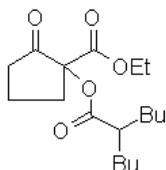
| | | | | | | | | |
|-------------------------------|--------------|------------------------------|-------------------------|---------------------|-------------------------------|-----------------------|----------------|-----|
| Acquisition Time (sec) | 0.4322 | Date | 20 Jun 2016 08:19:12 | | Frequency (MHz) | 75.48 | Nucleus | 13C |
| Number of Transients | 137 | Original Points Count | 16308 | Points Count | 16384 | Pulse Sequence | zgpg60base | |
| Solvent | CHLOROFORM-D | | Sweep Width (Hz) | 18867.92 | Temperature (degree C) | 25.700 | | |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 11.52 | 869.8 | 0.5253 | 8 | 66.20 | 4996.3 | 0.6954 | 1 | Chloroform-d | 77.00 |
| 2 | 11.68 | 881.3 | 0.7116 | 9 | 77.00 | 5811.7 | 0.7387 | | | |
| 3 | 24.65 | 1860.3 | 0.6026 | 10 | 84.36 | 6366.8 | 0.3211 | | | |
| 4 | 24.95 | 1883.3 | 0.7245 | 11 | 169.70 | 12808.1 | 0.0667 | | | |
| 5 | 25.33 | 1912.1 | 0.4434 | 12 | 174.79 | 13192.8 | 0.1985 | | | |
| 6 | 30.55 | 2306.0 | 1.0000 | 13 | 200.83 | 15157.5 | 0.1110 | | | |
| 7 | 48.28 | 3644.2 | 0.9001 | | | | | | | |

¹H NMR of ethyl 1-(2-butylhexanoyloxy)-2-oxocyclopentanecarboxylate, **4n**

| | | | | | | | |
|-------------------------------|--------------|------------------------------|---------|-------------------------------|----------------------|----------------|----|
| Acquisition Time (sec) | 0.5416 | | | Date | 23 May 2016 10:12:16 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Frequency (MHz) | 300.13 | Nucleus | 1H |
| Solvent | CHLOROFORM-D | Points Count | 8192 | Pulse Sequence | zg | | |
| | | Sweep Width (Hz) | 7500.00 | Temperature (degree C) | 22.900 | | |



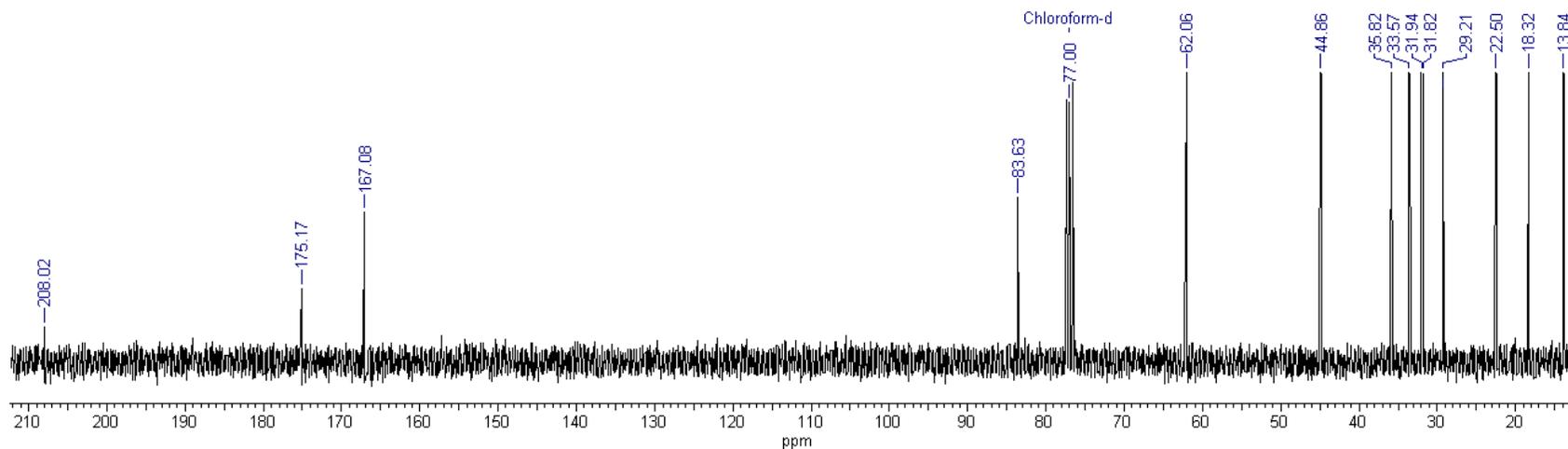
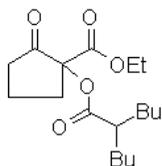
| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 0.83 | 250.3 | 0.3407 | 9 | 1.45 | 436.2 | 0.1211 | 17 | 2.22 | 666.0 | 0.0904 | 25 | 2.73 | 819.9 | 0.1084 |
| 2 | 0.86 | 256.7 | 0.9568 | 10 | 1.55 | 465.5 | 0.0690 | 18 | 2.25 | 675.2 | 0.0500 | 26 | 2.77 | 832.7 | 0.0695 |
| 3 | 0.88 | 263.1 | 0.4354 | 11 | 1.67 | 501.2 | 0.0763 | 19 | 2.34 | 700.8 | 0.0335 | 27 | 2.80 | 839.1 | 0.0488 |
| 4 | 1.22 | 364.8 | 0.4377 | 12 | 2.07 | 620.2 | 0.1196 | 20 | 2.38 | 715.5 | 0.1270 | 28 | 4.16 | 1248.4 | 0.1495 |
| 5 | 1.24 | 371.2 | 0.8959 | 13 | 2.09 | 626.7 | 0.1819 | 21 | 2.47 | 740.2 | 0.1762 | 29 | 4.18 | 1255.7 | 0.4153 |
| 6 | 1.26 | 378.5 | 1.0000 | 14 | 2.12 | 634.9 | 0.1643 | 22 | 2.54 | 761.3 | 0.0904 | 30 | 4.21 | 1263.0 | 0.3961 |
| 7 | 1.28 | 384.9 | 0.6233 | 15 | 2.15 | 645.0 | 0.1213 | 23 | 2.60 | 780.5 | 0.0240 | 31 | 4.23 | 1269.4 | 0.1380 |
| 8 | 1.40 | 418.8 | 0.0666 | 16 | 2.19 | 657.8 | 0.1008 | 24 | 2.71 | 814.4 | 0.0515 | 32 | 7.25 | 2175.9 | 0.0930 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value |
|-----|------------|--------|
| 1 | .81 .. 0.9 | 6.045 |
| 2 | .21 .. 1.3 | 11.045 |
| 3 | .38 .. 1.5 | 2.036 |
| 4 | .54 .. 1.6 | 2.149 |
| 5 | .05 .. 2.2 | 3.099 |
| 6 | .35 .. 2.6 | 3.063 |
| 7 | .70 .. 2.8 | 1.011 |
| 8 | .14 .. 4.2 | 2.000 |

¹³C NMR of ethyl 1-(2-butylhexanoyloxy)-2-oxocyclopentanecarboxylate, **4n**

| | | | | | |
|-------------------------------|------------|------------------------------|----------------------|-------------------------|----------|
| Acquisition Time (sec) | 0.4340 | Date | 23 May 2016 10:16:32 | | |
| Nucleus | 13C | Number of Transients | 127 | Frequency (MHz) | 75.48 |
| Pulse Sequence | zgpg60base | Original Points Count | 16316 | Points Count | 16384 |
| Temperature (degree C) | 23.400 | Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18796.99 |

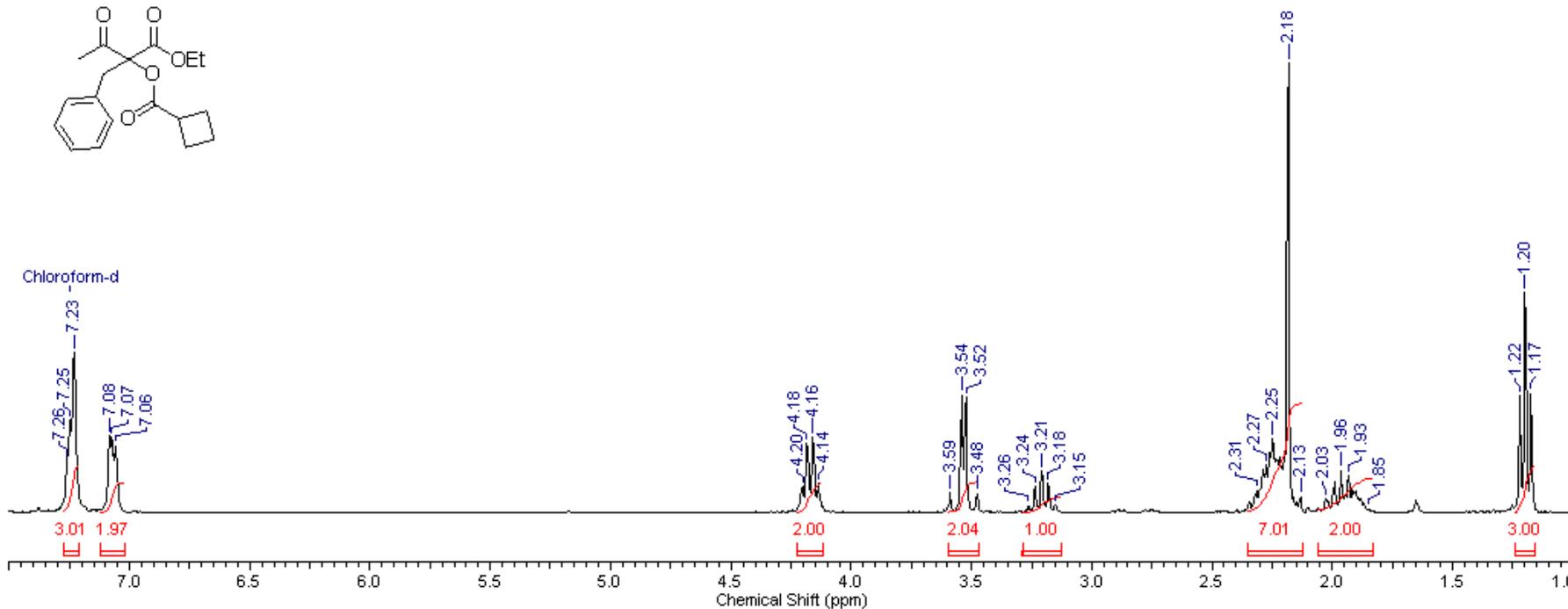
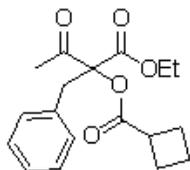


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 13.84 | 1044.4 | 0.8679 | 10 | 33.57 | 2533.7 | 0.9071 |
| 2 | 13.90 | 1049.0 | 0.6605 | 11 | 35.82 | 2703.5 | 0.5848 |
| 3 | 18.32 | 1382.9 | 0.7621 | 12 | 44.86 | 3386.1 | 1.0000 |
| 4 | 22.50 | 1698.4 | 0.7061 | 13 | 62.06 | 4683.8 | 0.4817 |
| 5 | 22.56 | 1703.0 | 0.7717 | 14 | 77.00 | 5811.6 | 0.4085 |
| 6 | 29.21 | 2204.4 | 0.8306 | 15 | 83.63 | 6311.9 | 0.2589 |
| 7 | 29.30 | 2211.3 | 0.4247 | 16 | 167.08 | 12610.8 | 0.2349 |
| 8 | 31.82 | 2401.7 | 0.7204 | 17 | 175.17 | 13221.2 | 0.1155 |
| 9 | 31.94 | 2410.9 | 0.6676 | 18 | 208.02 | 15700.6 | 0.0554 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of 1-benzyl-1-(ethoxycarbonyl)-2-oxopropyl cyclobutanecarboxylate, **4o**

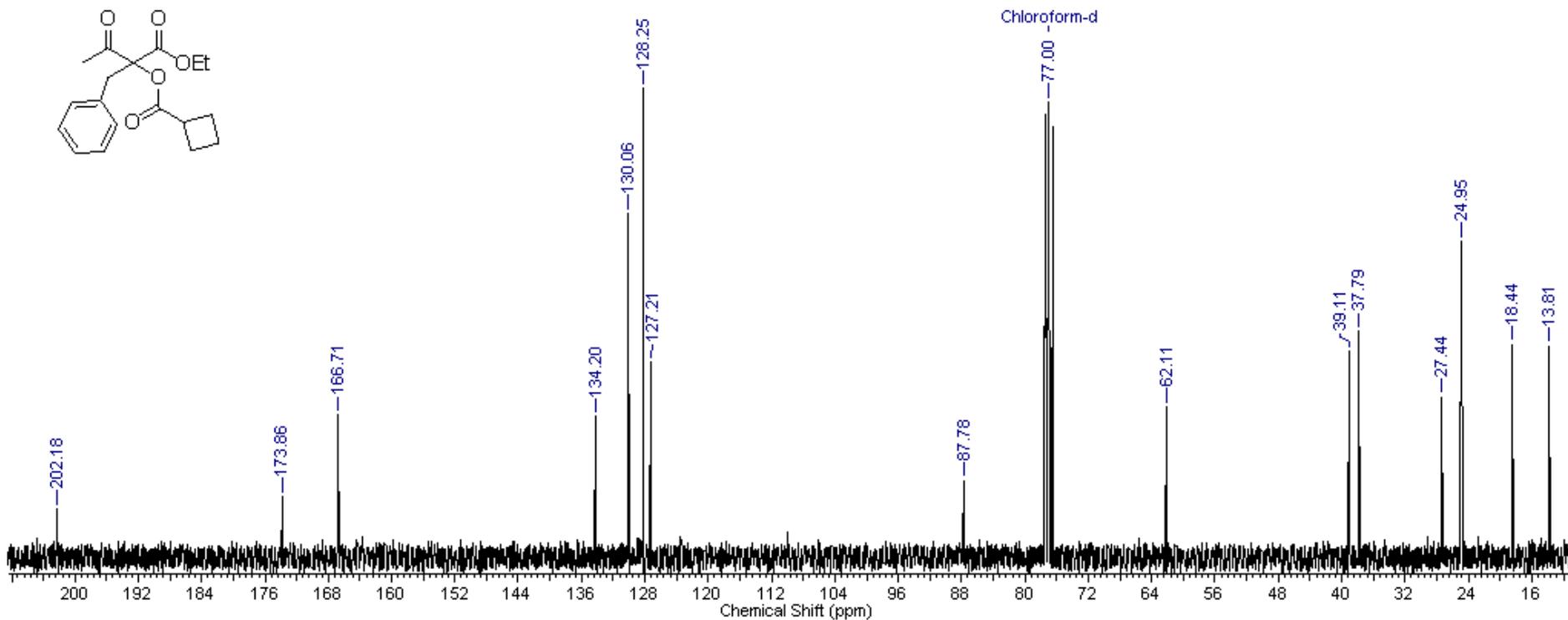
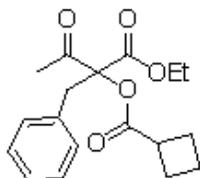
| | | | | | |
|--------------------------------------|-------------------------------|-----------------------------------|--------------------------------------|-------------------------------|--|
| Acquisition Time (sec) 1.3518 | | | | Frequency (MHz) 300.13 | |
| Nucleus 1H | Number of Transients 1 | Original Points Count 8124 | Points Count 8192 | | |
| Pulse Sequence zg | Solvent CHLOROFORM-D | Sweep Width (Hz) 6009.62 | Temperature (degree C) 25.600 | | |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | Value | Absolute Value |
|-----|-------|-------|--------|-----|-------|--------|--------|-----|-------|--------|--------|-----|----------------|-------|----------------|
| 1 | 1.17 | 352.0 | 0.2641 | 12 | 2.31 | 694.6 | 0.0501 | 23 | 4.16 | 1248.6 | 0.1686 | 1 | [1.16 .. 1.24] | 3.000 | 1.97774e+8 |
| 2 | 1.20 | 359.4 | 0.4887 | 13 | 3.15 | 945.6 | 0.0186 | 24 | 4.18 | 1255.9 | 0.1543 | 2 | [1.83 .. 2.06] | 2.000 | 1.31850e+8 |
| 3 | 1.22 | 366.0 | 0.2600 | 14 | 3.18 | 954.4 | 0.0662 | 25 | 4.20 | 1261.1 | 0.0581 | 3 | [2.12 .. 2.35] | 7.005 | 4.61828e+8 |
| 4 | 1.85 | 555.2 | 0.0098 | 15 | 3.21 | 962.4 | 0.0921 | 26 | 7.06 | 2118.7 | 0.1490 | 4 | [3.12 .. 3.29] | 0.999 | 6.58371e+7 |
| 5 | 1.93 | 580.2 | 0.0840 | 16 | 3.24 | 971.2 | 0.0589 | 27 | 7.07 | 2123.1 | 0.1677 | 5 | [3.47 .. 3.60] | 2.043 | 1.34685e+8 |
| 6 | 1.96 | 588.3 | 0.0951 | 17 | 3.26 | 979.3 | 0.0159 | 28 | 7.08 | 2126.1 | 0.1710 | 6 | [4.12 .. 4.22] | 2.001 | 1.31918e+8 |
| 7 | 2.03 | 608.1 | 0.0316 | 18 | 3.48 | 1043.1 | 0.0430 | 29 | 7.23 | 2169.4 | 0.3396 | 7 | [7.02 .. 7.12] | 1.969 | 1.29811e+8 |
| 8 | 2.13 | 639.6 | 0.0373 | 19 | 3.52 | 1057.1 | 0.2567 | 30 | 7.23 | 2170.8 | 0.3555 | 8 | [7.21 .. 7.27] | 3.007 | 1.98221e+8 |
| 9 | 2.18 | 655.0 | 1.0000 | 20 | 3.54 | 1062.2 | 0.2620 | 31 | 7.25 | 2176.0 | 0.2047 | | | | |
| 10 | 2.25 | 674.1 | 0.1632 | 21 | 3.59 | 1076.9 | 0.0449 | 32 | 7.26 | 2178.9 | 0.1172 | | | | |
| 11 | 2.27 | 682.2 | 0.1081 | 22 | 4.14 | 1241.2 | 0.0647 | | | | | | | | |

¹³C NMR of 1-benzyl-1-(ethoxycarbonyl)-2-oxopropyl cyclobutanecarboxylate, **4o**

| | | | | | |
|--------------------------------------|---------------------------------|------------------------------------|--|--|--------------------------------------|
| Acquisition Time (sec) 0.9006 | | | | | Frequency (MHz) 75.48 |
| Nucleus 13C | Number of Transients 145 | Original Points Count 16316 | | | Points Count 16384 |
| Pulse Sequence zgpg30 | Solvent CHLOROFORM-D | Sweep Width (Hz) 18115.94 | | | Temperature (degree C) 25.500 |

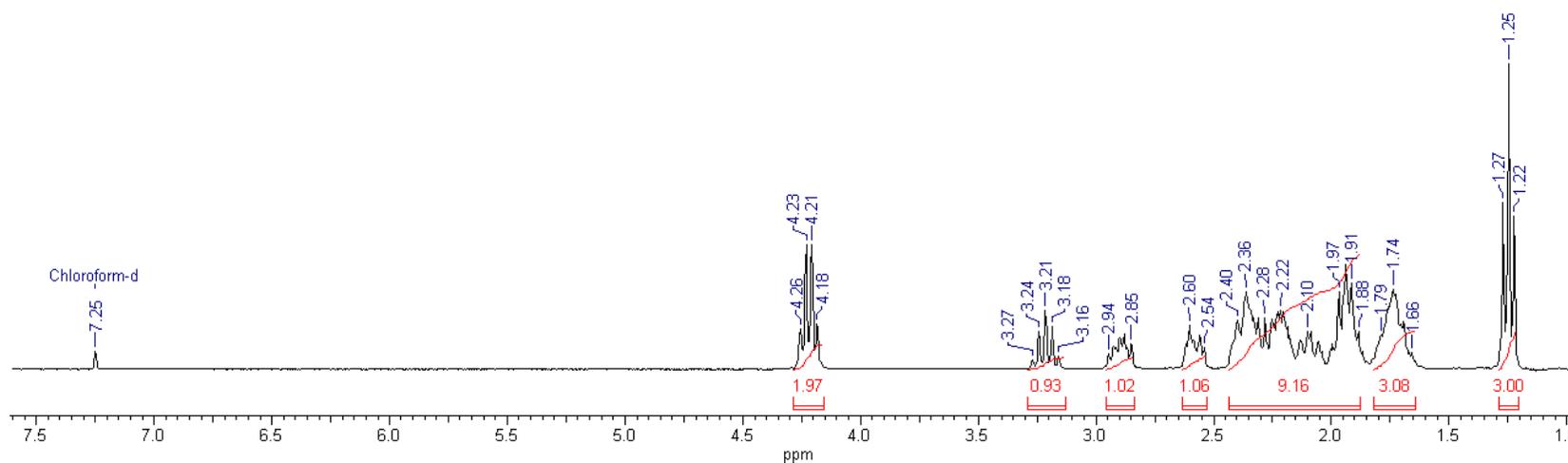
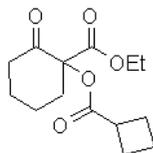


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 13.81 | 1042.4 | 0.4548 | 10 | 87.78 | 6625.5 | 0.1709 |
| 2 | 18.44 | 1391.9 | 0.4596 | 11 | 127.21 | 9601.2 | 0.4217 |
| 3 | 24.87 | 1877.3 | 0.6318 | 12 | 128.25 | 9679.7 | 1.0000 |
| 4 | 24.95 | 1882.8 | 0.6786 | 13 | 130.06 | 9816.8 | 0.7370 |
| 5 | 27.44 | 2070.8 | 0.3483 | 14 | 134.20 | 10128.6 | 0.3063 |
| 6 | 37.79 | 2852.6 | 0.4861 | 15 | 166.71 | 12582.3 | 0.3099 |
| 7 | 39.11 | 2952.1 | 0.4445 | 16 | 173.86 | 13121.9 | 0.1370 |
| 8 | 62.11 | 4688.2 | 0.3274 | 17 | 202.18 | 15259.4 | 0.1117 |
| 9 | 77.00 | 5811.7 | 0.9725 | | | | |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of ethyl 1-(cyclobutanecarbonyloxy)-2-oxocyclohexanecarboxylate, **4p**

| | | | | | |
|------------------------|---------|------------------------|----------------------|-----------------|----------------|
| Acquisition Time (sec) | 0.6759 | Date | 26 Oct 2016 16:38:24 | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 25.400 | Frequency (MHz) | 300.13 |
| | | | | Pulse Sequence | zg |
| | | | | Nucleus | ¹ H |
| | | | | Solvent | CHLOROFORM-D |



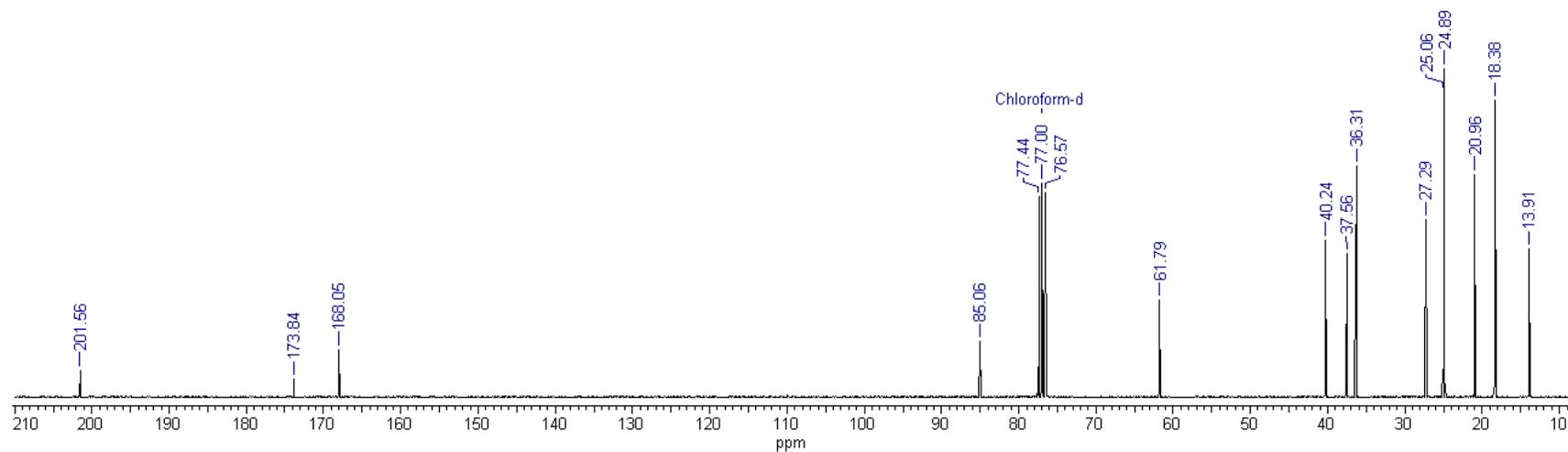
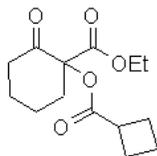
| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|-----|-------|-------|--------|-----|-------|--------|--------|
| 1 | 1.22 | 367.3 | 0.5013 | 11 | 2.22 | 665.2 | 0.1928 | 21 | 3.21 | 964.6 | 0.1931 |
| 2 | 1.25 | 373.9 | 1.0000 | 12 | 2.28 | 685.0 | 0.1891 | 22 | 3.24 | 972.6 | 0.1226 |
| 3 | 1.27 | 381.3 | 0.5457 | 13 | 2.36 | 708.5 | 0.2534 | 23 | 3.27 | 980.7 | 0.0312 |
| 4 | 1.66 | 497.2 | 0.0552 | 14 | 2.40 | 720.2 | 0.1617 | 24 | 4.18 | 1255.8 | 0.1473 |
| 5 | 1.74 | 521.4 | 0.2638 | 15 | 2.54 | 762.1 | 0.0714 | 25 | 4.21 | 1262.4 | 0.4104 |
| 6 | 1.79 | 536.8 | 0.1124 | 16 | 2.60 | 781.1 | 0.1441 | 26 | 4.23 | 1269.8 | 0.4092 |
| 7 | 1.88 | 565.4 | 0.1225 | 17 | 2.85 | 855.2 | 0.0846 | 27 | 4.26 | 1277.1 | 0.1329 |
| 8 | 1.91 | 574.2 | 0.2832 | 18 | 2.94 | 883.8 | 0.0534 | 28 | 7.25 | 2175.9 | 0.0602 |
| 9 | 1.97 | 590.4 | 0.2547 | 19 | 3.16 | 947.7 | 0.0437 | | | | |
| 10 | 2.10 | 630.7 | 0.1223 | 20 | 3.18 | 955.7 | 0.1398 | | | | |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value |
|-----|-----------|-------|
| 1 | 21 .. 1.2 | 3.000 |
| 2 | 64 .. 1.8 | 3.081 |
| 3 | 88 .. 2.4 | 9.160 |
| 4 | 53 .. 2.6 | 1.056 |
| 5 | 83 .. 2.9 | 1.023 |
| 6 | 13 .. 3.2 | 0.930 |
| 7 | 16 .. 4.2 | 1.971 |

¹³C NMR of ethyl 1-(cyclobutanecarbonyloxy)-2-oxocyclohexanecarboxylate, **4p**

| | | | | | | |
|-------------------------------|--------------|------------------------------|----------------------|-------------------------------|----------------|-----|
| Acquisition Time (sec) | 0.4503 | Date | 26 Oct 2016 16:40:32 | | | |
| Number of Transients | 147 | Original Points Count | 16316 | Points Count | 16384 | |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Frequency (MHz) | 75.48 | |
| | | Pulse Sequence | zgpg30 | Temperature (degree C) | 25.400 | |
| | | | | | Nucleus | 13C |

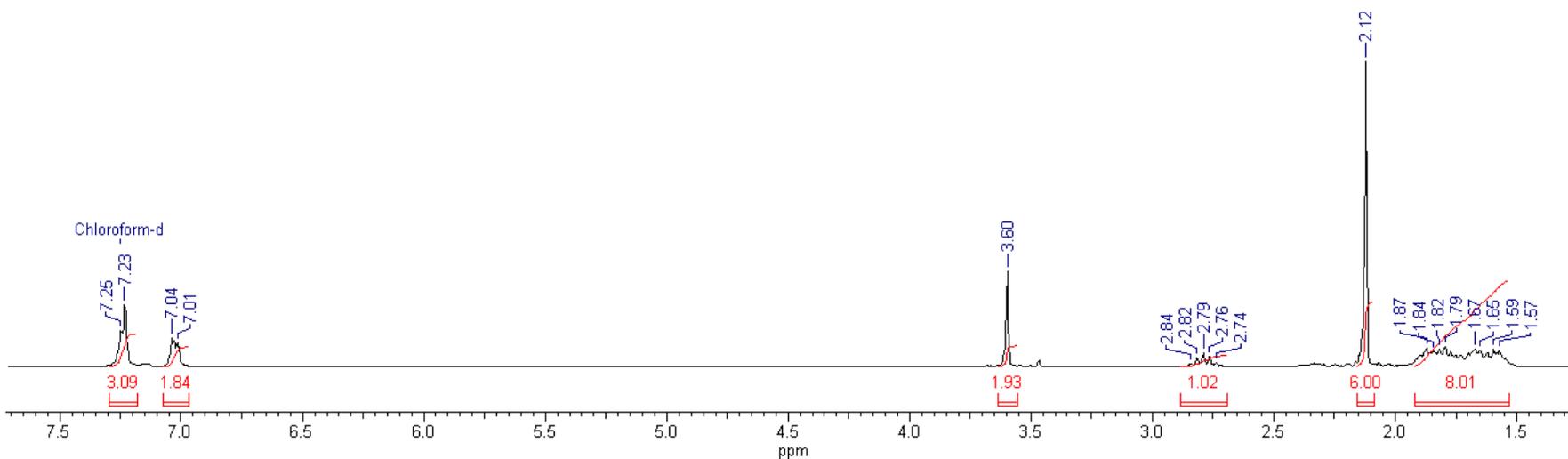
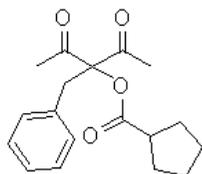


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 13.91 | 1050.1 | 0.4505 | 10 | 61.79 | 4663.8 | 0.2955 |
| 2 | 18.38 | 1387.4 | 0.9020 | 11 | 76.57 | 5779.6 | 0.6202 |
| 3 | 20.96 | 1582.0 | 0.6771 | 12 | 77.00 | 5811.6 | 0.6521 |
| 4 | 24.89 | 1878.4 | 1.0000 | 13 | 77.44 | 5844.8 | 0.6113 |
| 5 | 25.06 | 1891.6 | 0.9265 | 14 | 85.06 | 6419.8 | 0.1689 |
| 6 | 27.29 | 2059.7 | 0.5387 | 15 | 168.05 | 12684.0 | 0.1440 |
| 7 | 36.31 | 2740.9 | 0.7019 | 16 | 173.84 | 13120.8 | 0.0540 |
| 8 | 37.56 | 2834.9 | 0.4360 | 17 | 201.56 | 15212.9 | 0.0813 |
| 9 | 40.24 | 3037.2 | 0.4766 | | | | |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of 3-benzyl-2,4-dioxopentan-3-yl cyclopentanecarboxylate, **4q**

| | | | | | | | |
|------------------------|---------|------------------------|----------------------|-----------------|--------|----------------|----------------|
| Acquisition Time (sec) | 0.6759 | Date | 02 Nov 2016 13:13:36 | Frequency (MHz) | 300.13 | Nucleus | ¹ H |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 | Pulse Sequence | zq |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 24.800 | | | Solvent | CHLOROFORM-D |



| No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|
| 1 | 1.57 | 471.6 | 0.0517 |
| 2 | 1.59 | 478.2 | 0.0592 |
| 3 | 1.65 | 495.0 | 0.0549 |
| 4 | 1.67 | 501.6 | 0.0565 |
| 5 | 1.79 | 538.3 | 0.0672 |
| 6 | 1.82 | 544.9 | 0.0578 |
| 7 | 1.84 | 553.0 | 0.0506 |

| No. | (ppm) | (Hz) | Height |
|-----|-------|-------|--------|
| 8 | 1.87 | 561.1 | 0.0609 |
| 9 | 2.12 | 636.6 | 1.0000 |
| 10 | 2.74 | 821.5 | 0.0143 |
| 11 | 2.76 | 829.6 | 0.0348 |
| 12 | 2.79 | 836.9 | 0.0471 |
| 13 | 2.82 | 845.0 | 0.0285 |
| 14 | 2.84 | 853.1 | 0.0095 |

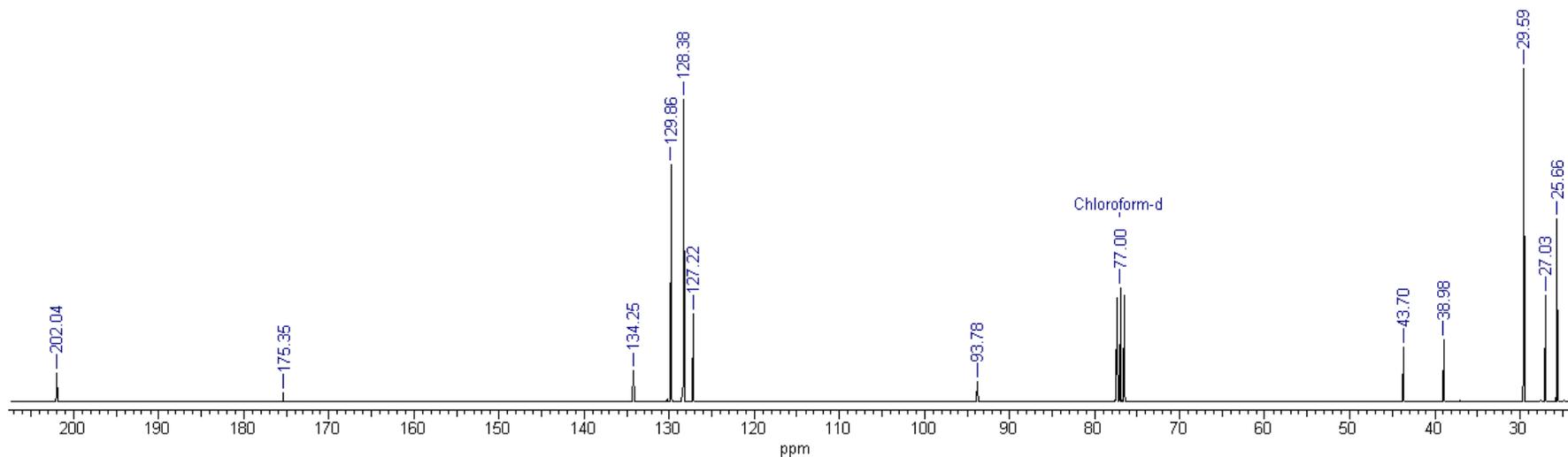
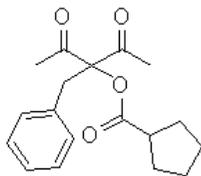
| No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|
| 15 | 3.60 | 1079.8 | 0.3113 |
| 16 | 7.01 | 2104.7 | 0.0790 |
| 17 | 7.04 | 2112.8 | 0.0938 |
| 18 | 7.23 | 2170.8 | 0.2018 |
| 19 | 7.25 | 2175.9 | 0.1189 |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 7.25 |

| No. | (ppm) | Value |
|-----|------------|-------|
| 1 | .53 .. 1.9 | 8.007 |
| 2 | .09 .. 2.1 | 6.000 |
| 3 | .69 .. 2.8 | 1.018 |
| 4 | .56 .. 3.6 | 1.932 |
| 5 | .97 .. 7.0 | 1.845 |
| 6 | .18 .. 7.2 | 3.090 |

¹³C NMR of 3-benzyl-2,4-dioxopentan-3-yl cyclopentanecarboxylate, **4q**

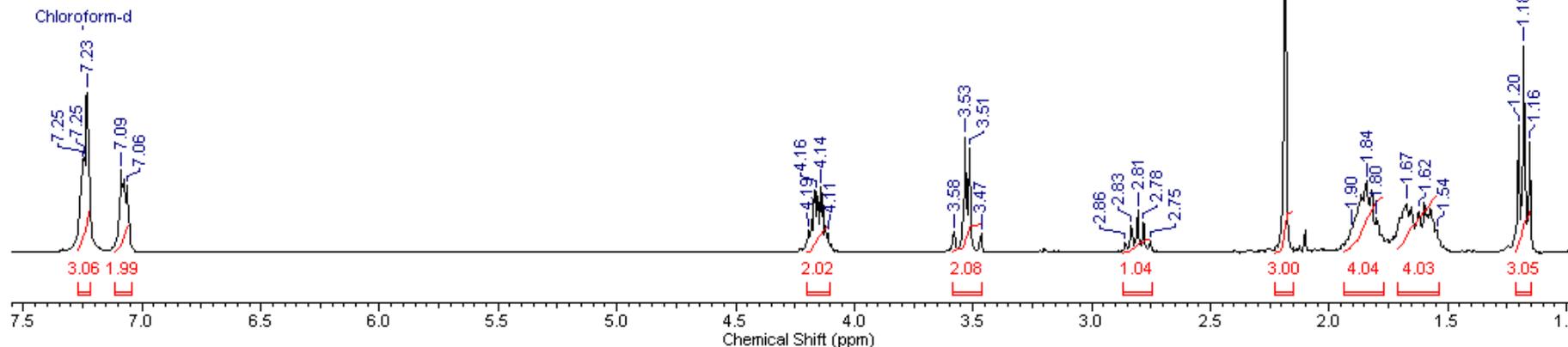
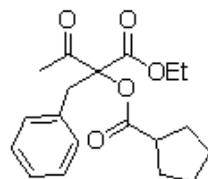
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|------------------------|--------------|-----------------------|----------------------|----------------|---------|------------------------|--------|
| Acquisition Time (sec) | 0.4503 | Date | 02 Nov 2016 13:15:44 | | Nucleus | 13C | |
| Number of Transients | 250 | Original Points Count | 16316 | Points Count | 16384 | Frequency (MHz) | 75.48 |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Pulse Sequence | zgpg30 | Temperature (degree C) | 24.800 |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 25.66 | 1937.0 | 0.5473 | 8 | 127.22 | 9602.3 | 0.2639 | 1 | Chloroform-d | 77.00 |
| 2 | 27.03 | 2039.8 | 0.3204 | 9 | 128.36 | 9689.6 | 0.9063 | | | |
| 3 | 29.59 | 2233.4 | 1.0000 | 10 | 129.86 | 9801.3 | 0.7097 | | | |
| 4 | 38.98 | 2942.2 | 0.1863 | 11 | 134.25 | 10133.0 | 0.0921 | | | |
| 5 | 43.70 | 3298.2 | 0.1635 | 12 | 175.35 | 13234.7 | 0.0270 | | | |
| 6 | 77.00 | 5811.7 | 0.3410 | 13 | 202.04 | 15249.5 | 0.0859 | | | |
| 7 | 93.78 | 7077.8 | 0.0598 | | | | | | | |

¹H NMR of 1-benzyl-1-(ethoxycarbonyl)-2-oxopropyl cyclopentanecarboxylate, **4r**

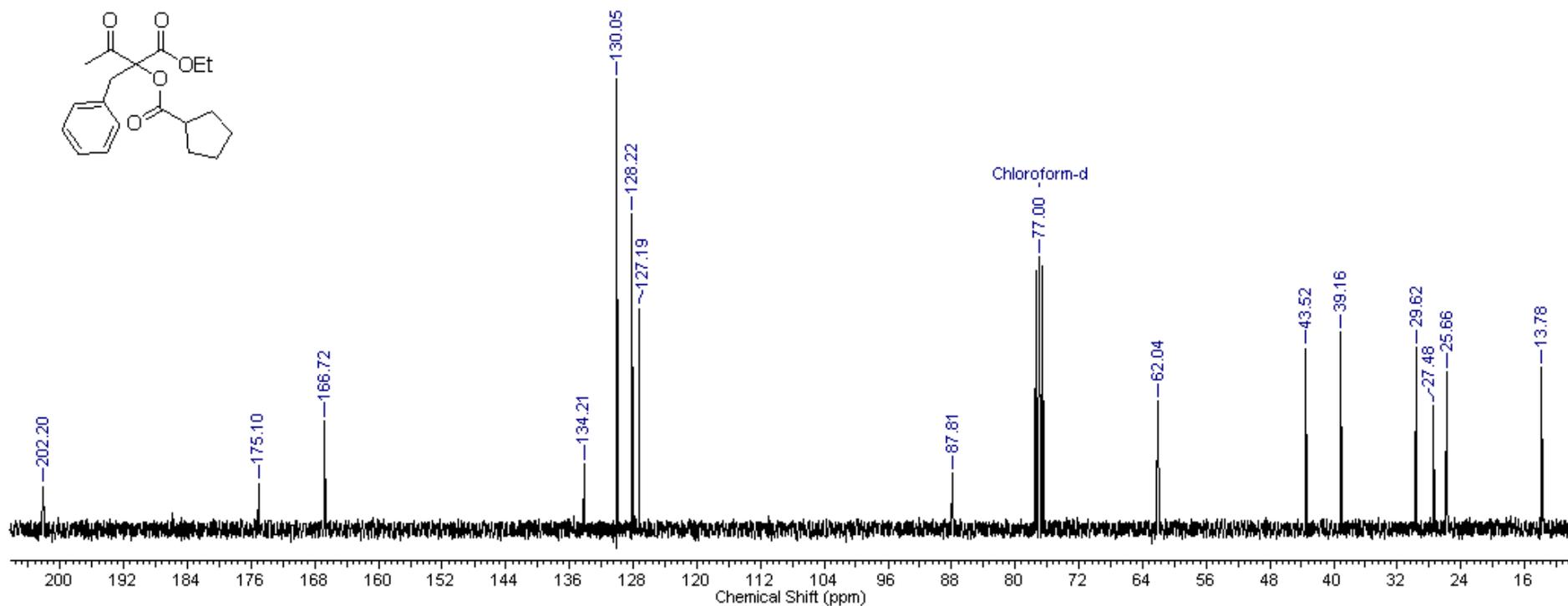
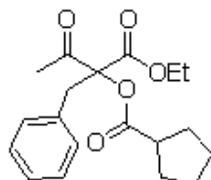
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|--------------------------------------|-------------------------------|-----------------------------------|--|--|--------------------------------------|
| Acquisition Time (sec) 1.3518 | | | | | Frequency (MHz) 300.13 |
| Nucleus 1H | Number of Transients 1 | Original Points Count 8124 | | | Points Count 8192 |
| Pulse Sequence zg | Solvent CHLOROFORM-D | Sweep Width (Hz) 6009.62 | | | Temperature (degree C) 26.000 |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) | No. | (ppm) | Value | Absolute Value |
|-----|-------|-------|--------|-----|-------|--------|--------|-----|-------|--------|--------|-----|--------------|-------|-----|---------------|-------|----------------|
| 1 | 1.16 | 346.9 | 0.2439 | 11 | 2.75 | 826.7 | 0.0252 | 21 | 4.14 | 1243.4 | 0.1442 | 1 | Chloroform-d | 7.25 | 1 | [1.15 ..1.21] | 3.050 | 1.62879e+8 |
| 2 | 1.18 | 353.5 | 0.4574 | 12 | 2.78 | 834.8 | 0.0667 | 22 | 4.16 | 1247.8 | 0.1358 | 2 | | | 2 | [1.53 ..1.71] | 4.032 | 2.15338e+8 |
| 3 | 1.20 | 360.8 | 0.2806 | 13 | 2.81 | 842.1 | 0.0944 | 23 | 4.19 | 1258.1 | 0.0494 | 3 | | | 3 | [1.77 ..1.94] | 4.039 | 2.15680e+8 |
| 4 | 1.54 | 463.5 | 0.0505 | 14 | 2.83 | 850.2 | 0.0596 | 24 | 7.06 | 2120.2 | 0.1479 | 4 | | | 4 | [2.15 ..2.22] | 3.000 | 1.60203e+8 |
| 5 | 1.62 | 487.0 | 0.0919 | 15 | 2.86 | 858.3 | 0.0201 | 25 | 7.09 | 2127.5 | 0.1822 | 5 | | | 5 | [2.74 ..2.87] | 1.037 | 5.53718e+7 |
| 6 | 1.67 | 502.4 | 0.1091 | 16 | 3.47 | 1040.2 | 0.0439 | 26 | 7.23 | 2170.8 | 0.3556 | 6 | | | 6 | [3.46 ..3.59] | 2.085 | 1.11336e+8 |
| 7 | 1.80 | 539.8 | 0.0758 | 17 | 3.51 | 1054.2 | 0.2299 | 27 | 7.25 | 2174.5 | 0.2105 | 7 | | | 7 | [4.10 ..4.20] | 2.021 | 1.07931e+8 |
| 8 | 1.84 | 553.0 | 0.1571 | 18 | 3.53 | 1060.0 | 0.2561 | 28 | 7.25 | 2176.0 | 0.2016 | 8 | | | 8 | [7.04 ..7.11] | 1.990 | 1.06243e+8 |
| 9 | 1.90 | 571.4 | 0.0538 | 19 | 3.58 | 1074.7 | 0.0458 | | | | | 9 | | | 9 | [7.22 ..7.27] | 3.062 | 1.63514e+8 |
| 10 | 2.18 | 655.8 | 1.0000 | 20 | 4.11 | 1233.2 | 0.0434 | | | | | | | | | | | |

¹³C NMR of 1-benzyl-1-(ethoxycarbonyl)-2-oxopropyl cyclopentanecarboxylate, **4r**

| | | | | | |
|--------------------------------------|---------------------------------|------------------------------------|--|--|--------------------------------------|
| Acquisition Time (sec) 0.9006 | | | | | Frequency (MHz) 75.48 |
| Nucleus 13C | Number of Transients 109 | Original Points Count 16316 | | | Points Count 16384 |
| Pulse Sequence zgpg30 | Solvent CHLOROFORM-D | Sweep Width (Hz) 18115.94 | | | Temperature (degree C) 25.900 |

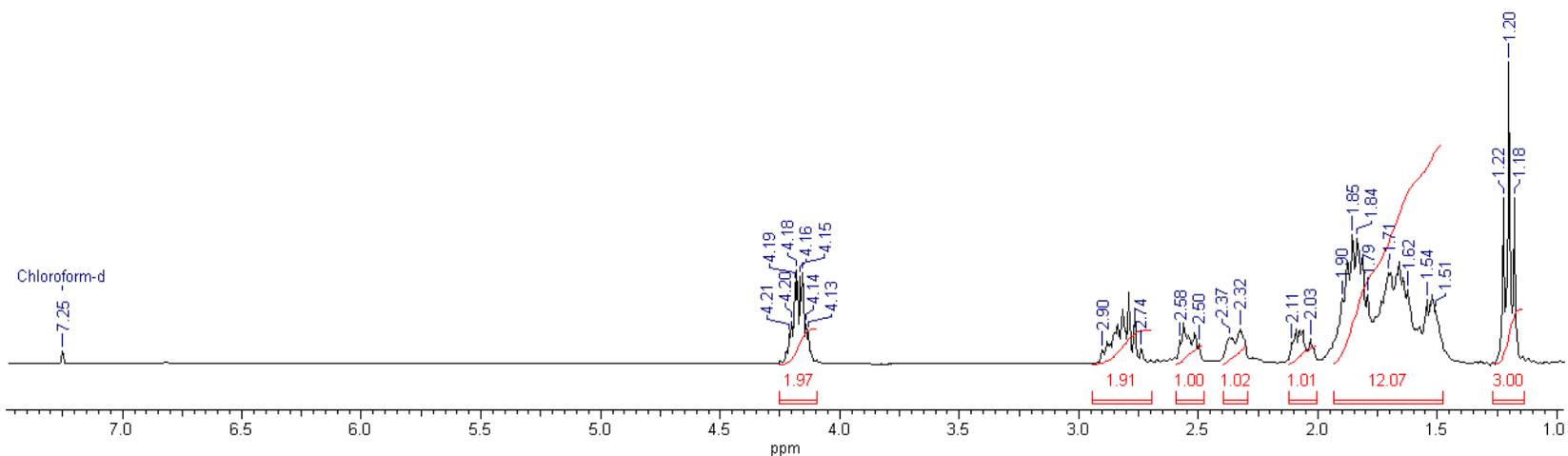
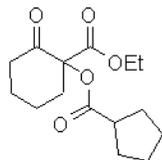


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|-----|-------|--------|--------|-----|--------|---------|--------|
| 1 | 13.78 | 1040.2 | 0.3590 | 10 | 87.81 | 6627.7 | 0.1225 |
| 2 | 25.66 | 1937.0 | 0.3493 | 11 | 127.19 | 9600.0 | 0.4903 |
| 3 | 27.48 | 2074.1 | 0.2723 | 12 | 128.22 | 9677.5 | 0.7003 |
| 4 | 29.53 | 2228.9 | 0.3317 | 13 | 130.05 | 9815.7 | 1.0000 |
| 5 | 29.62 | 2235.6 | 0.4029 | 14 | 134.21 | 10129.7 | 0.1444 |
| 6 | 39.16 | 2955.4 | 0.4366 | 15 | 166.72 | 12583.4 | 0.2392 |
| 7 | 43.52 | 3285.0 | 0.4009 | 16 | 175.10 | 13215.9 | 0.1000 |
| 8 | 62.04 | 4682.7 | 0.2828 | 17 | 202.20 | 15261.6 | 0.0942 |
| 9 | 77.00 | 5811.7 | 0.6037 | | | | |

| No. | Annotation | (ppm) |
|-----|--------------|-------|
| 1 | Chloroform-d | 77.00 |

¹H NMR of ethyl 1-(cyclopentanecarbonyloxy)-2-oxocyclohexanecarboxylate, **4s**

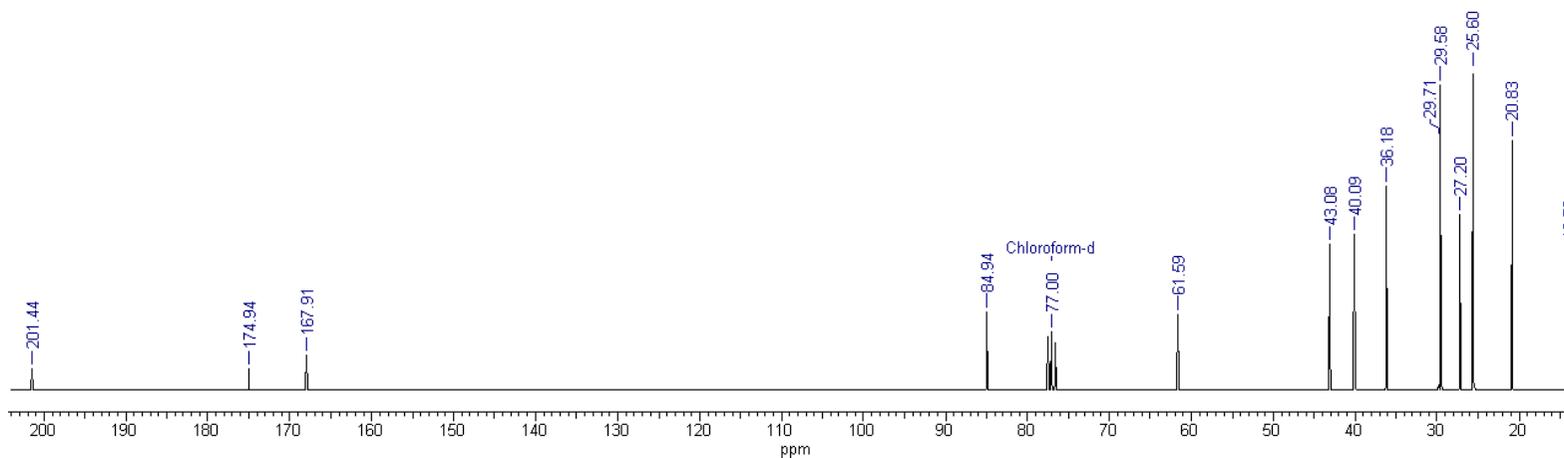
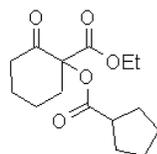
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|------------------------|---------|------------------------|----------------------|--------------|----------------|-----------------|--------|---------|--------------|
| Acquisition Time (sec) | 0.6759 | Date | 27 Oct 2016 14:32:32 | | | | | | |
| Number of Transients | 1 | Original Points Count | 8124 | Points Count | 8192 | Frequency (MHz) | 300.13 | Nucleus | 1H |
| Sweep Width (Hz) | 6009.62 | Temperature (degree C) | 25.000 | | Pulse Sequence | zg | | Solvent | CHLOROFORM-D |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | Value |
|-----|-------|-------|--------|-----|-------|--------|--------|-----|-------|--------|--------|-----|-------------|--------|
| 1 | 1.18 | 353.4 | 0.5516 | 11 | 1.90 | 569.1 | 0.2175 | 21 | 4.14 | 1242.6 | 0.1348 | 1 | 7.25 | 3.000 |
| 2 | 1.20 | 360.7 | 1.0000 | 12 | 2.03 | 609.4 | 0.0851 | 22 | 4.15 | 1247.0 | 0.3044 | 2 | 1.14 .. 1.2 | 12.072 |
| 3 | 1.22 | 367.3 | 0.5496 | 13 | 2.11 | 632.9 | 0.0734 | 23 | 4.16 | 1250.0 | 0.2912 | 3 | .00 .. 2.1 | 1.009 |
| 4 | 1.51 | 451.7 | 0.1775 | 14 | 2.32 | 697.5 | 0.1195 | 24 | 4.18 | 1254.4 | 0.3098 | 4 | .29 .. 2.4 | 1.015 |
| 5 | 1.54 | 463.4 | 0.2130 | 15 | 2.37 | 711.4 | 0.0900 | 25 | 4.19 | 1256.6 | 0.2723 | 5 | .48 .. 2.5 | 1.003 |
| 6 | 1.62 | 486.9 | 0.2468 | 16 | 2.50 | 749.6 | 0.0709 | 26 | 4.20 | 1261.0 | 0.1438 | 6 | .69 .. 2.9 | 1.909 |
| 7 | 1.71 | 511.9 | 0.3040 | 17 | 2.68 | 773.1 | 0.0804 | 27 | 4.21 | 1263.9 | 0.1007 | 7 | .09 .. 4.2 | 1.972 |
| 8 | 1.79 | 537.5 | 0.2294 | 18 | 2.74 | 822.2 | 0.0519 | 28 | 7.25 | 2175.9 | 0.0420 | | | |
| 9 | 1.84 | 550.8 | 0.4151 | 19 | 2.90 | 870.6 | 0.0495 | | | | | | | |
| 10 | 1.85 | 556.6 | 0.4300 | 20 | 4.13 | 1239.7 | 0.1072 | | | | | | | |

¹³C NMR of ethyl 1-(cyclopentanecarbonyloxy)-2-oxocyclohexanecarboxylate, **4s**

| | | | | | | |
|-------------------------------|--------------|------------------------------|----------------------|-------------------------------|----------------|-----|
| Acquisition Time (sec) | 0.4503 | Date | 27 Oct 2016 14:34:40 | | | |
| Number of Transients | 289 | Original Points Count | 16316 | Points Count | 16384 | |
| Solvent | CHLOROFORM-D | Sweep Width (Hz) | 18115.94 | Frequency (MHz) | 75.48 | |
| | | | | Pulse Sequence | zgpg30 | |
| | | | | Temperature (degree C) | 25.000 | |
| | | | | | Nucleus | 13C |



| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | Annotation | (ppm) |
|-----|-------|--------|--------|-----|--------|---------|--------|-----|--------------|-------|
| 1 | 13.78 | 1040.2 | 0.1548 | 9 | 43.08 | 3251.7 | 0.1711 | 1 | Chloroform-d | 77.00 |
| 2 | 20.83 | 1572.1 | 0.2942 | 10 | 61.59 | 4648.3 | 0.0895 | | | |
| 3 | 25.60 | 1932.6 | 1.0000 | 11 | 77.00 | 5811.6 | 0.0686 | | | |
| 4 | 27.20 | 2053.1 | 0.2058 | 12 | 84.94 | 6411.0 | 0.0921 | | | |
| 5 | 29.58 | 2232.2 | 0.3591 | 13 | 167.91 | 12673.0 | 0.0407 | | | |
| 6 | 29.71 | 2242.2 | 0.2971 | 14 | 174.94 | 13203.7 | 0.0252 | | | |
| 7 | 36.18 | 2730.9 | 0.2401 | 15 | 201.44 | 15204.1 | 0.0249 | | | |
| 8 | 40.09 | 3026.2 | 0.1829 | | | | | | | |

HRMS spectra

HRMS of ethyl 4-acetyl-4-(2-ethylbutanoxy)-5-oxohexanoate, **4a**

Display Report

Analysis Info

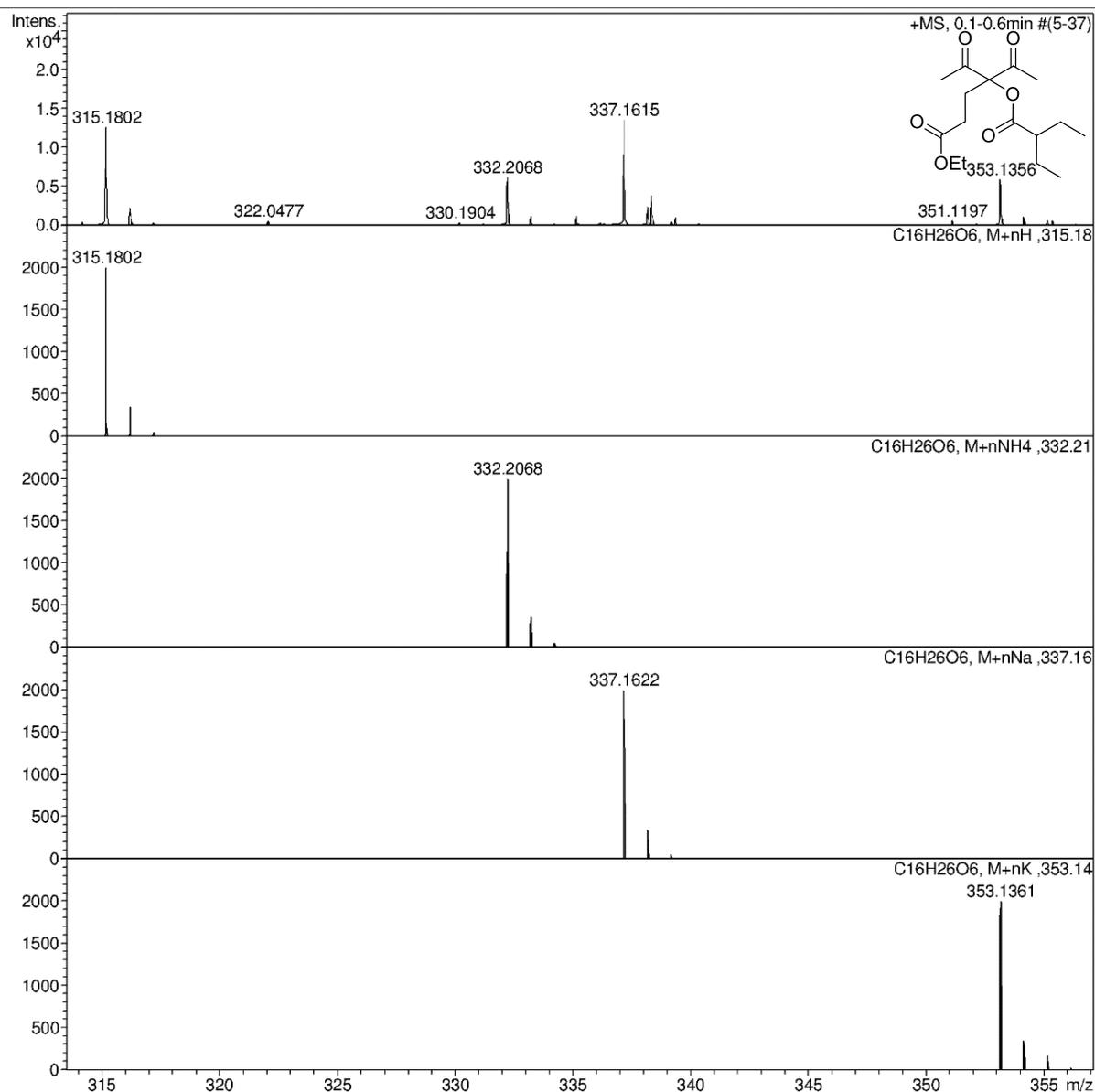
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Sample Name /TERN OZ289_21-24
Comment C16H26O6 mw 314.17 calibrant added

Acquisition Date 14.04.2016 14:28:28

Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 3-benzyl-2,4-dioxopentan-3-yl 2-ethylbutanoate, **4b**

Display Report

Analysis Info

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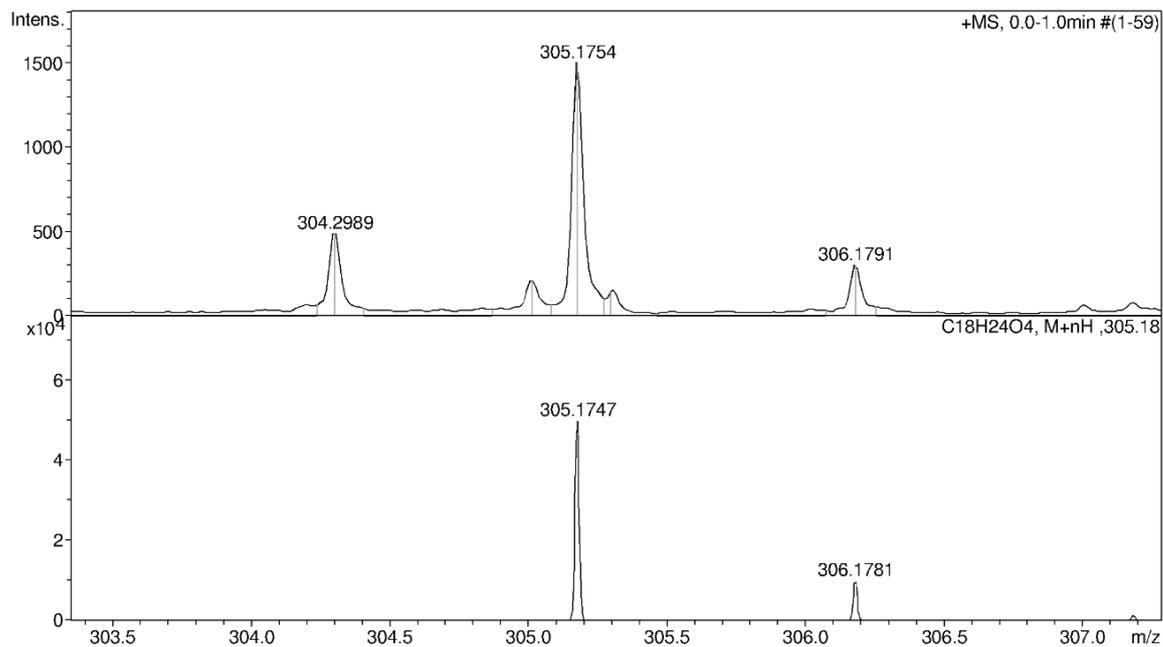
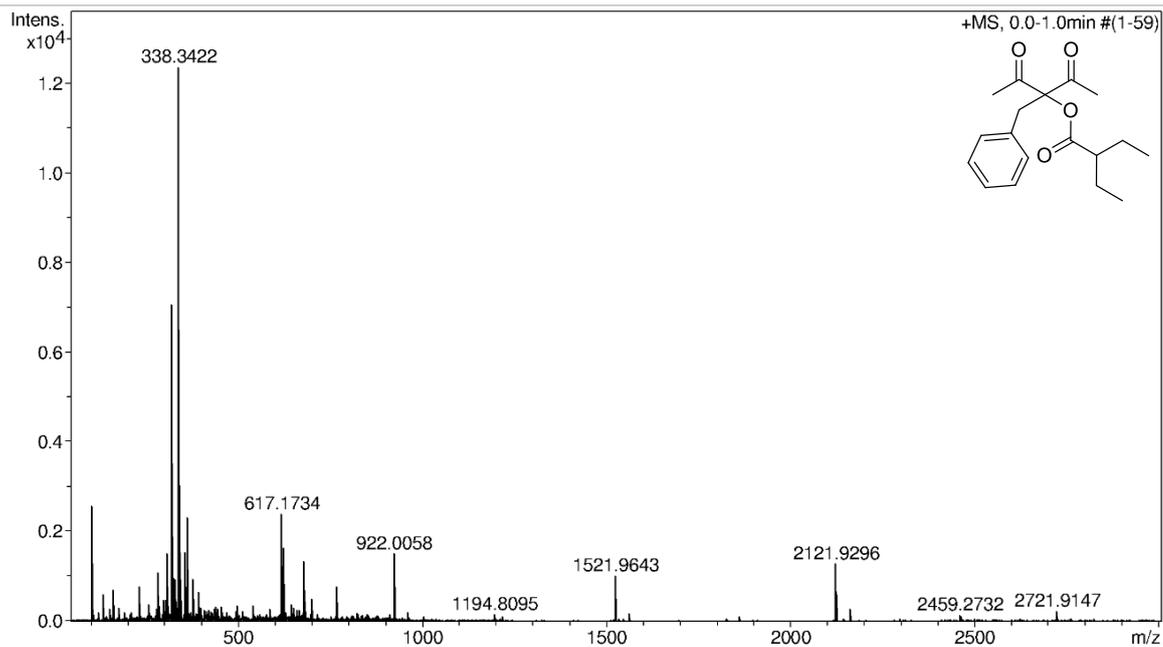
Acquisition Date 17.06.2016 16:50:51

Operator BDAL@DE

Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 3-(4-chlorobenzyl)-2,4-dioxopentan-3-yl 2-ethylbutanoate, **4c**

Display Report

Analysis Info

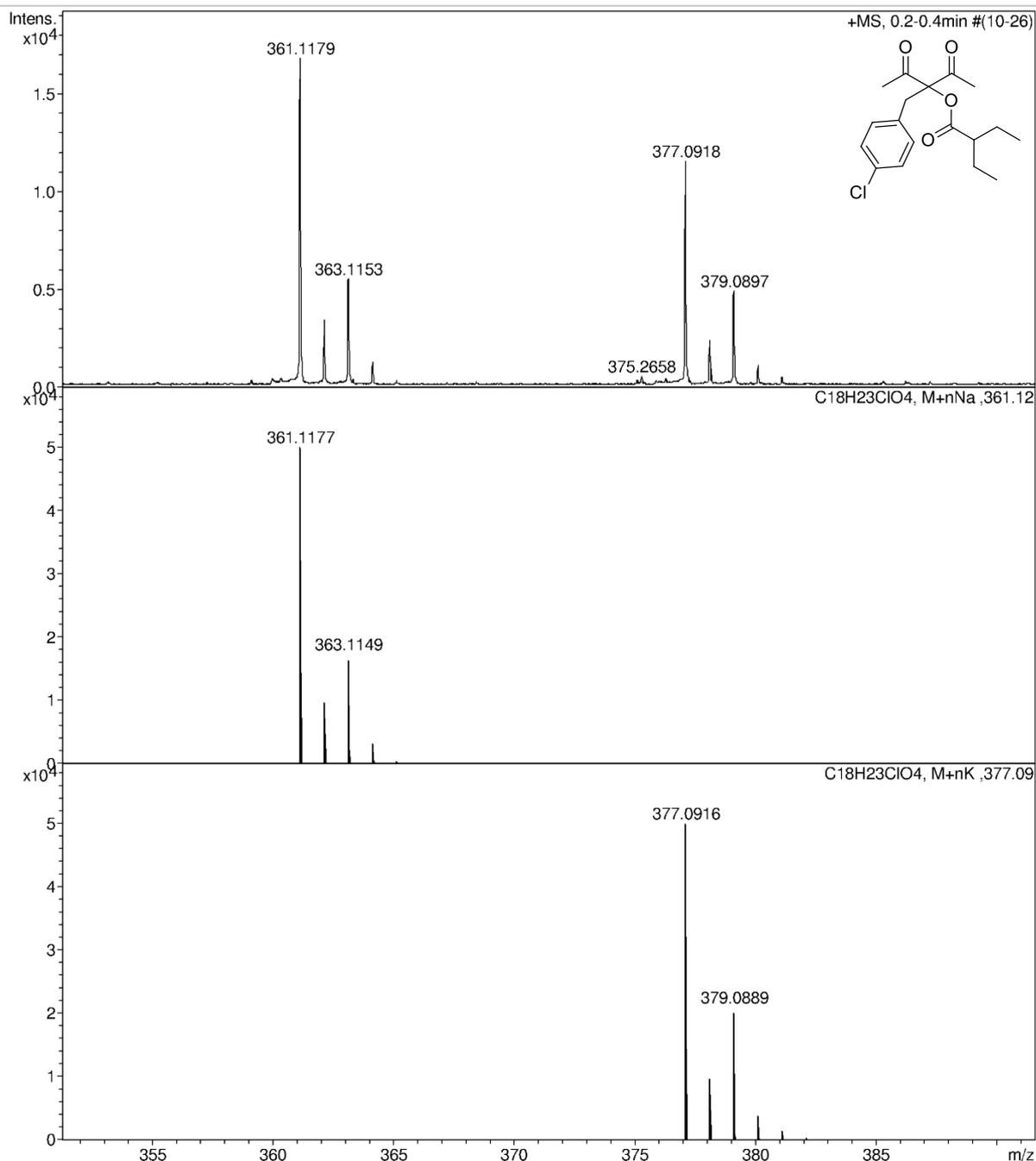
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 Sample Name /TERN OB361_7-9
 Comment C18H23ClO4 mw 339.135 clb added

Acquisition Date 15.06.2016 18:02:42

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 1-acetyl-2-oxocyclopentyl 2-ethylbutanoate, **4d**

Display Report

Analysis Info

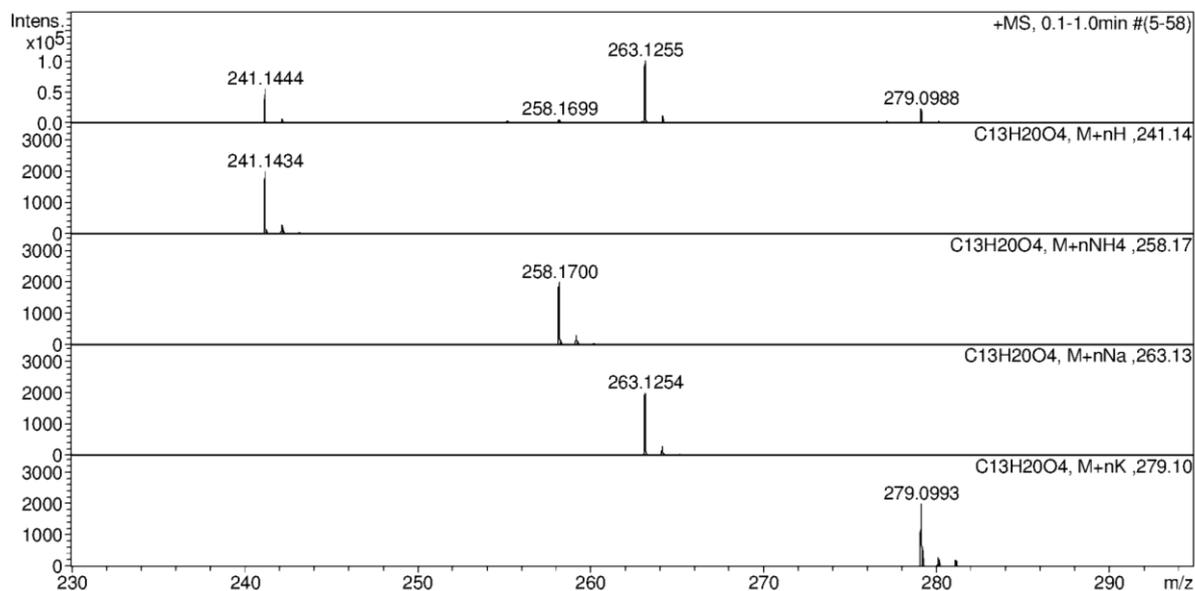
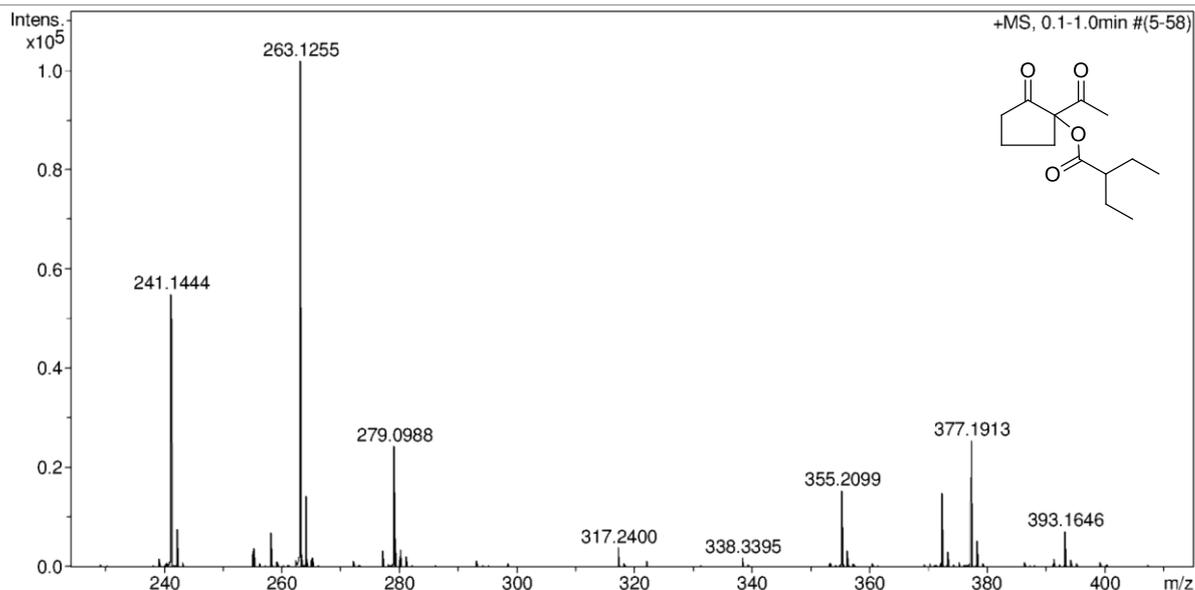
Analysis Name D:\Data\Kolotyrkina\2016\Bitukov\0517012.d
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 Sample Name /TERN 013506_9-11
 Comment C13H20O4 mwH 241.14 clb added

Acquisition Date 17.05.2016 14:28:42

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 1-acetyl-2-oxocyclohexyl 2-ethylbutanoate, 4e

Display Report

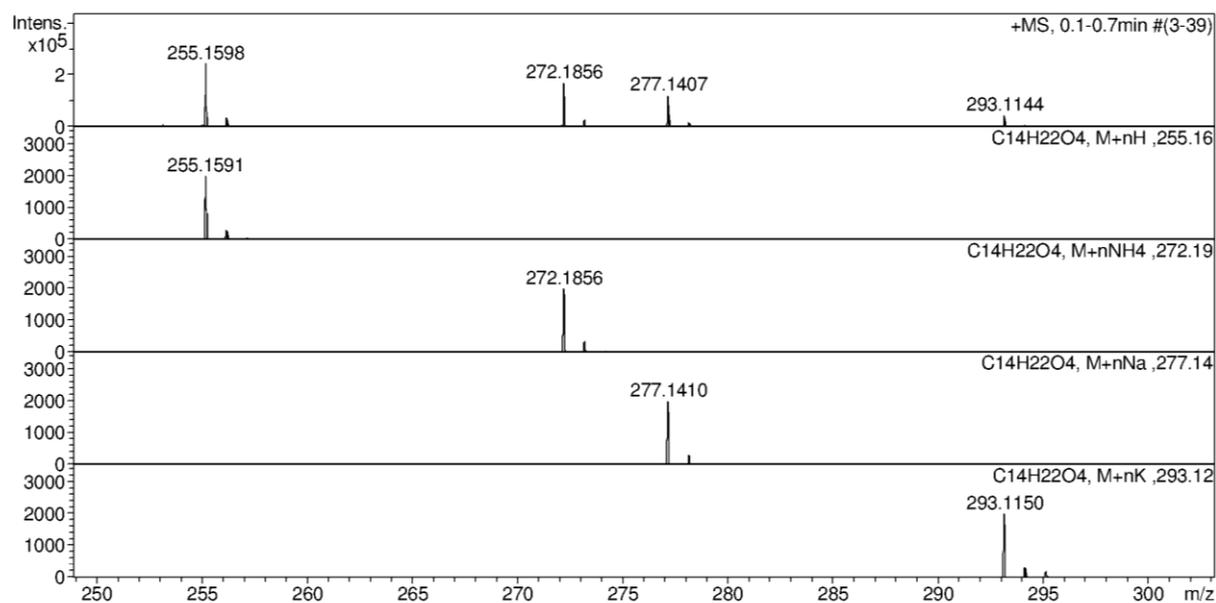
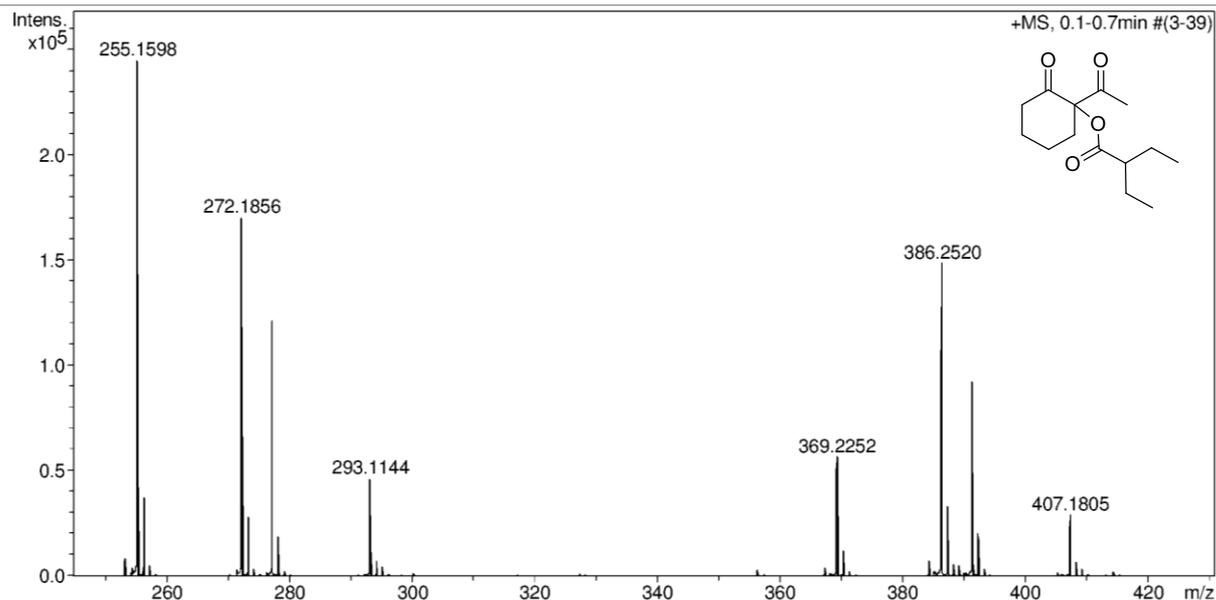
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Acquisition Date 17.05.2016 14:15:26
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

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|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 3-acetyl-2,6-dioxoheptan-3-yl 2-ethylbutanoate, **4f**

Display Report

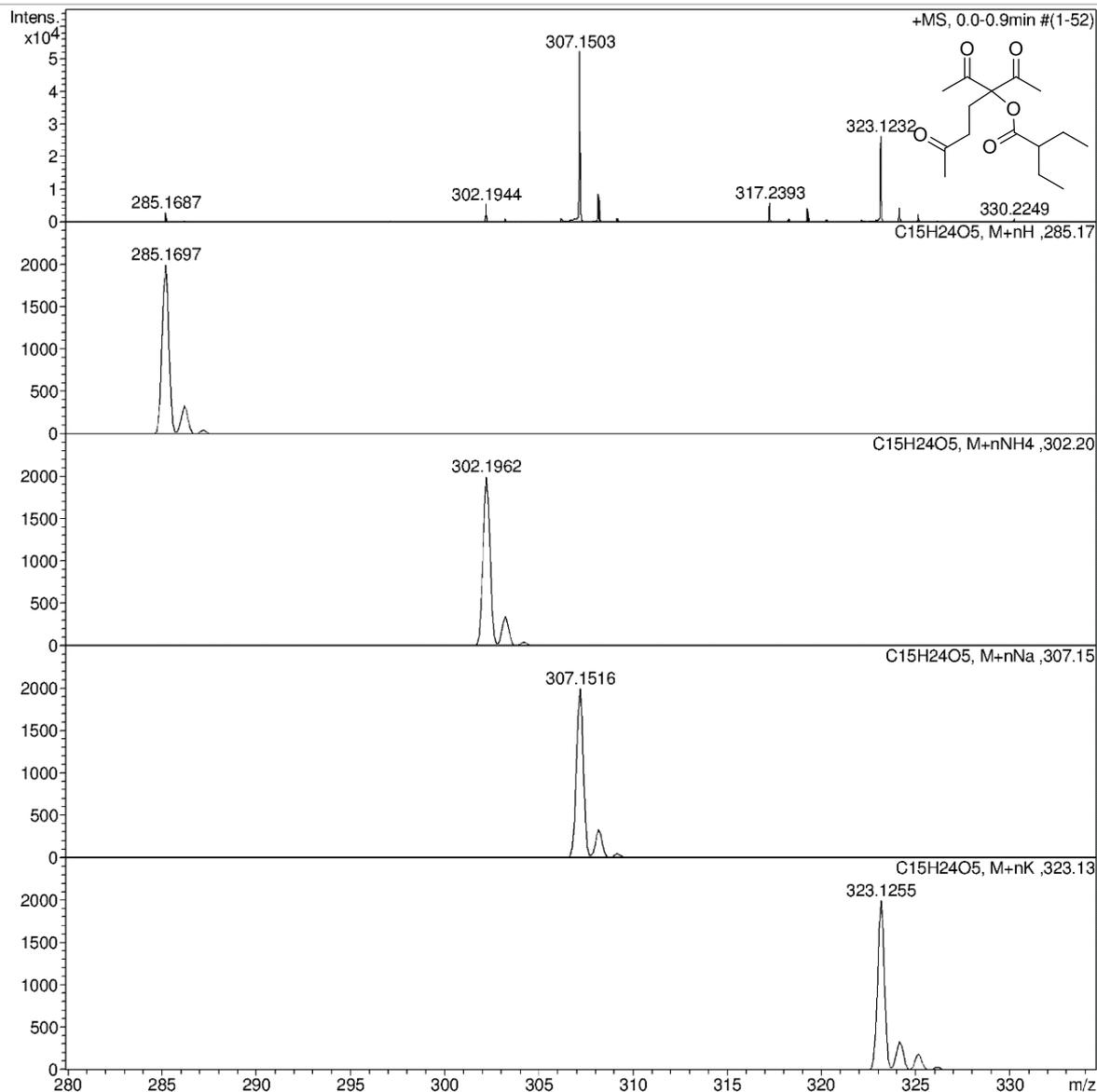
Analysis Info

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 Sample Name /TERN OB304_25_27
 Comment C15H24O5 mw 284.161 calibrant added

Acquisition Date 26.04.2016 12:02:16
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 2-(2-ethylbutanoyloxy)-2-methyl-3-oxobutanoate, 4g

Display Report

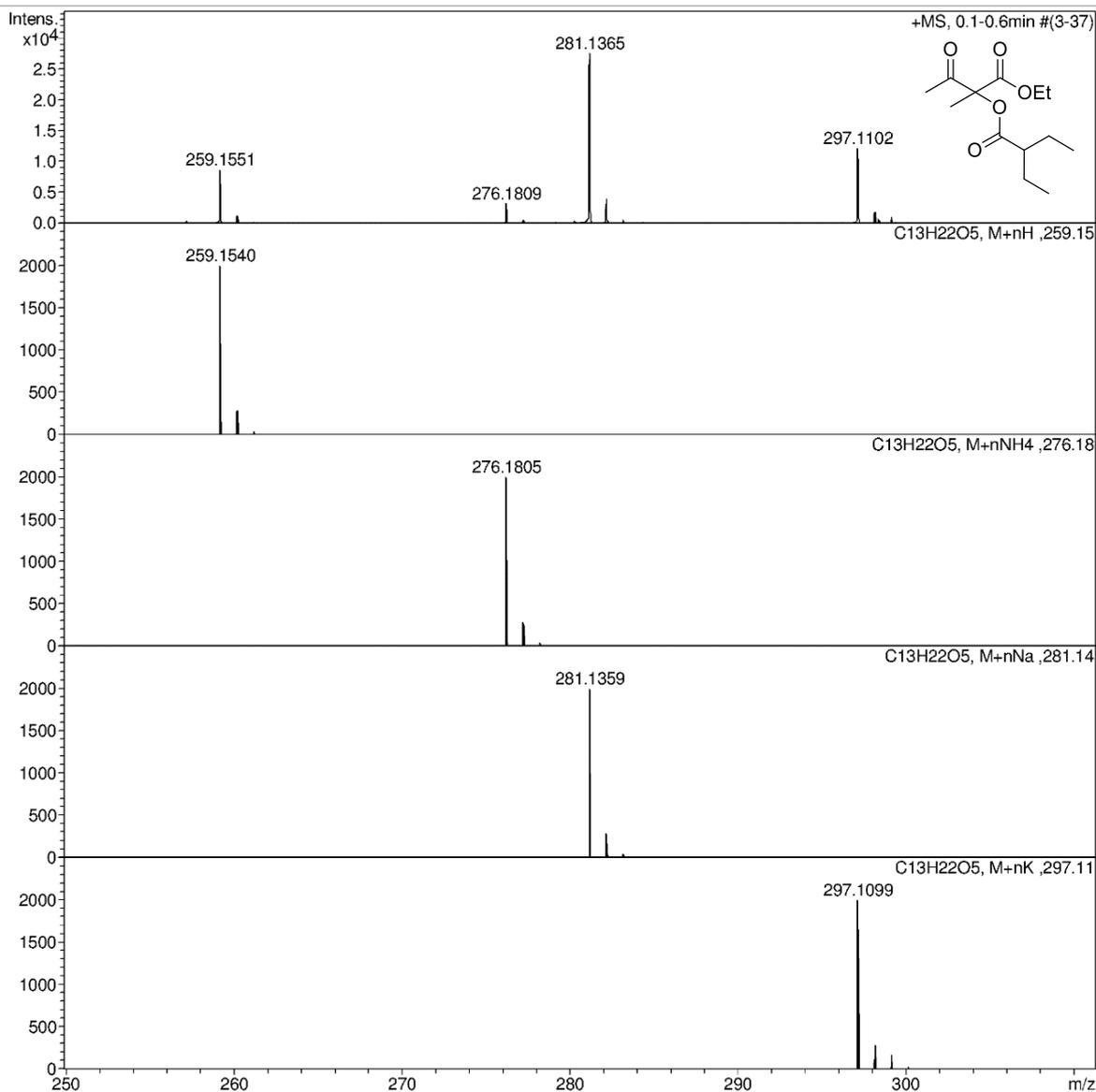
Analysis Info

Analysis Name D:\Data\Kolotyrykina\2016\Bitukov\0414016.d
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 Comment C13H22O5 mw 258.146 calibrant added

Acquisition Date 14.04.2016 14:20:43
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 2-acetyl-2-(2-ethylbutanoyloxy)hexanoate, **4h**

Display Report

Analysis Info

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 Sample Name /TERN ob288
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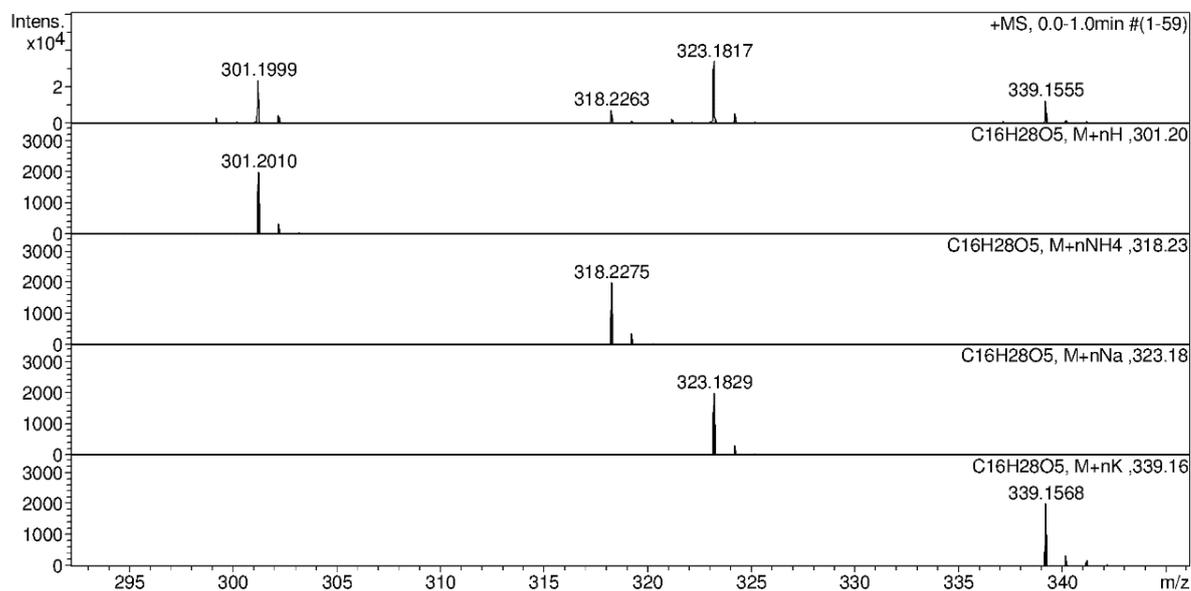
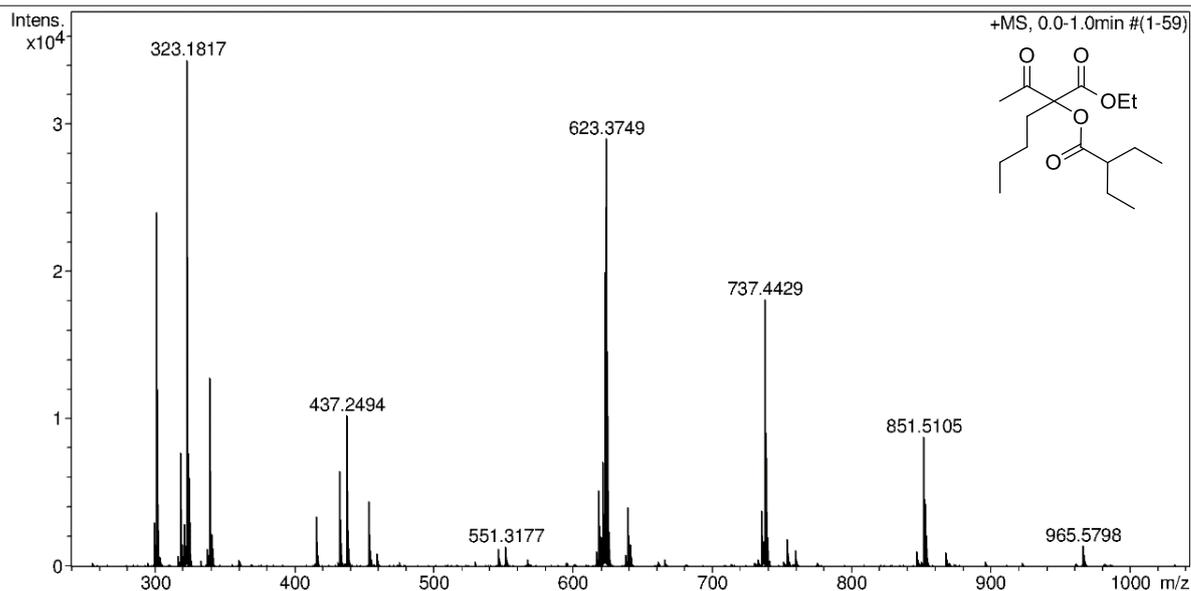
Acquisition Date 09.04.2016 14:42:05

Operator BDAL@DE

Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 2-acetyl-4-cyano-2-(2-ethylbutanoyloxy)butanoate, **4i**

Display Report

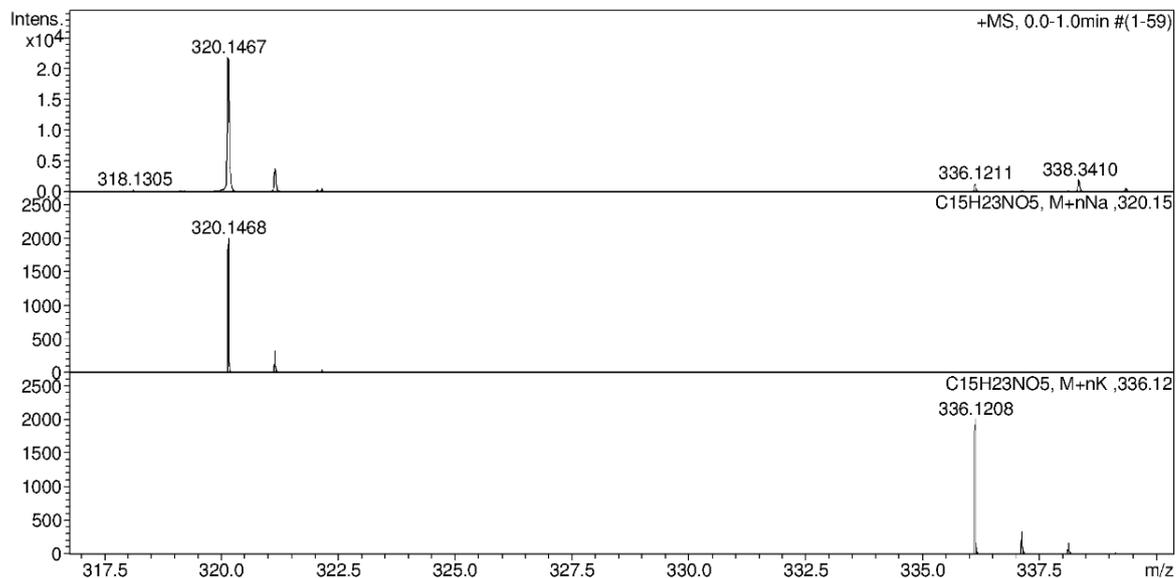
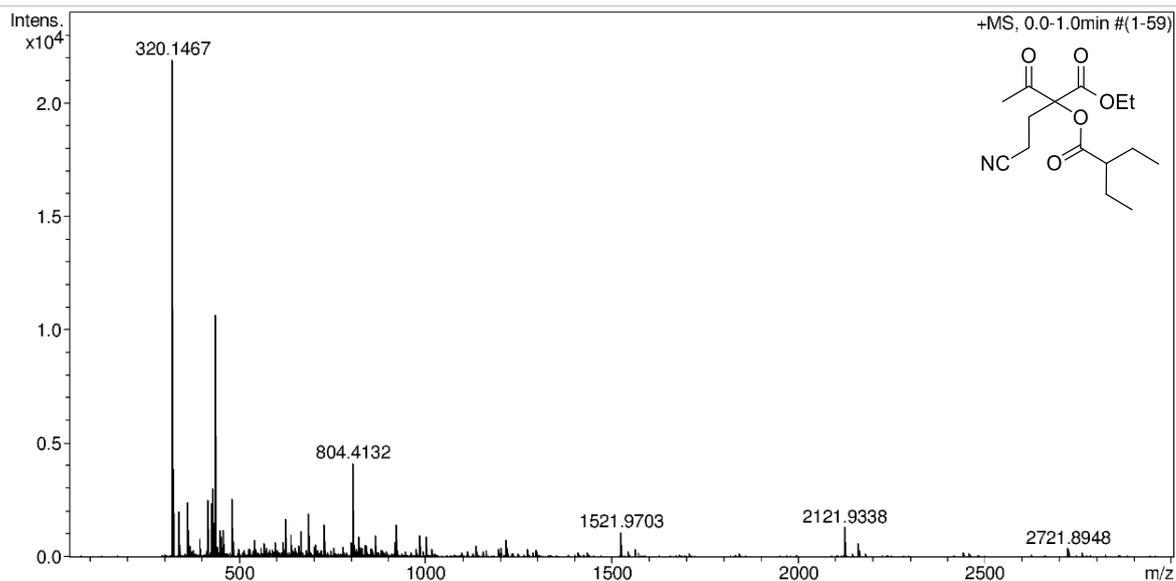
Analysis Info

Analysis Name D:\Data\Chizhov\Terentiev\Bityukov\ob278_22-25_&clblow.d
 Method tune_wide.m
 Sample Name /TERN OB278-22-25
 Comment CH3CN 100 %, dil. 200, calibrant added

Acquisition Date 01.04.2016 16:49:21
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 2-benzyl-2-(2-ethylbutanoyloxy)-3-oxobutanoate, 4j

Display Report

Analysis Info

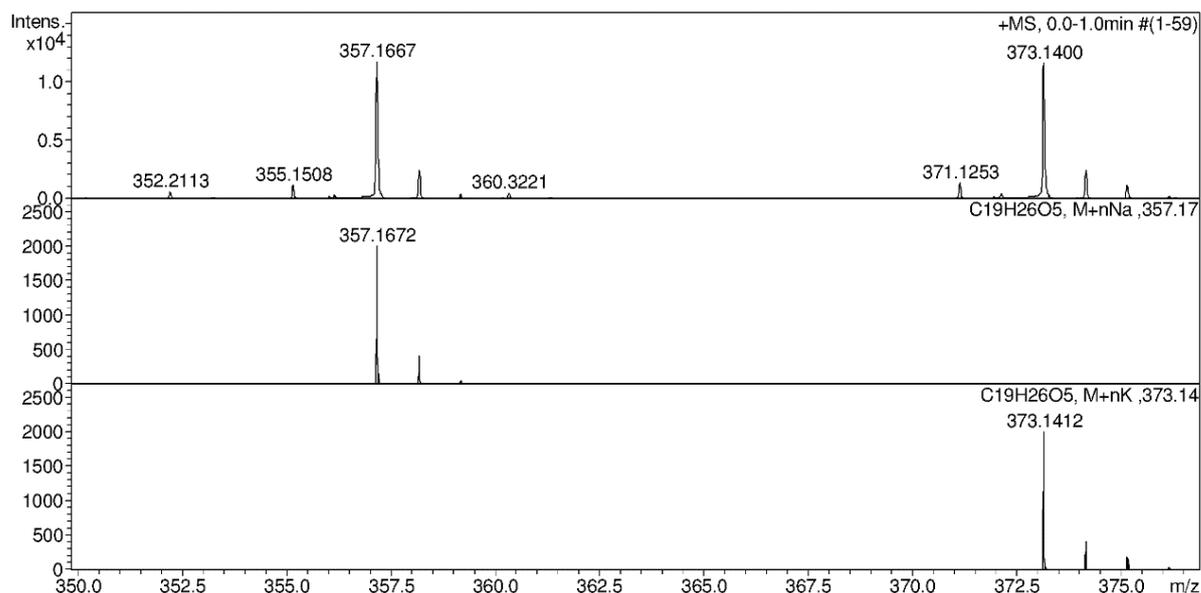
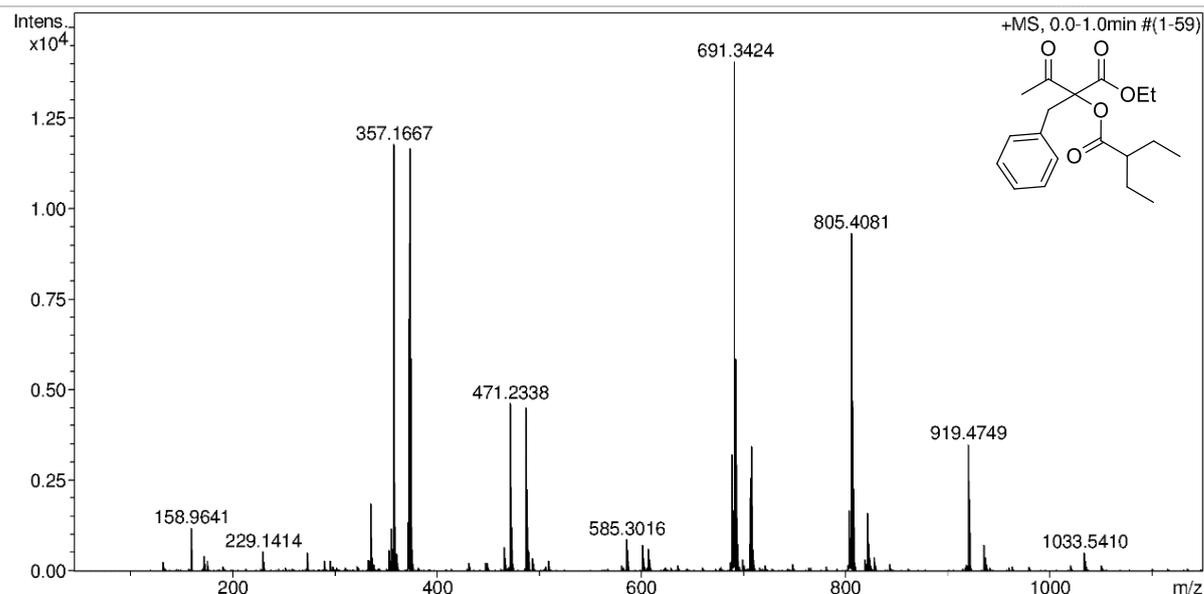
Analysis Name D:\Data\Chizhov\Terentiev\Bityukov\ob286-8-r_&clblow.d
 Method tune_low.m
 Sample Name /TERN OB-286(8-R)
 Comment CH3CN 100 %, dil. 200, calibrant added

Acquisition Date 25.04.2016 15:44:12

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclopentanecarboxylate, 4k

Display Report

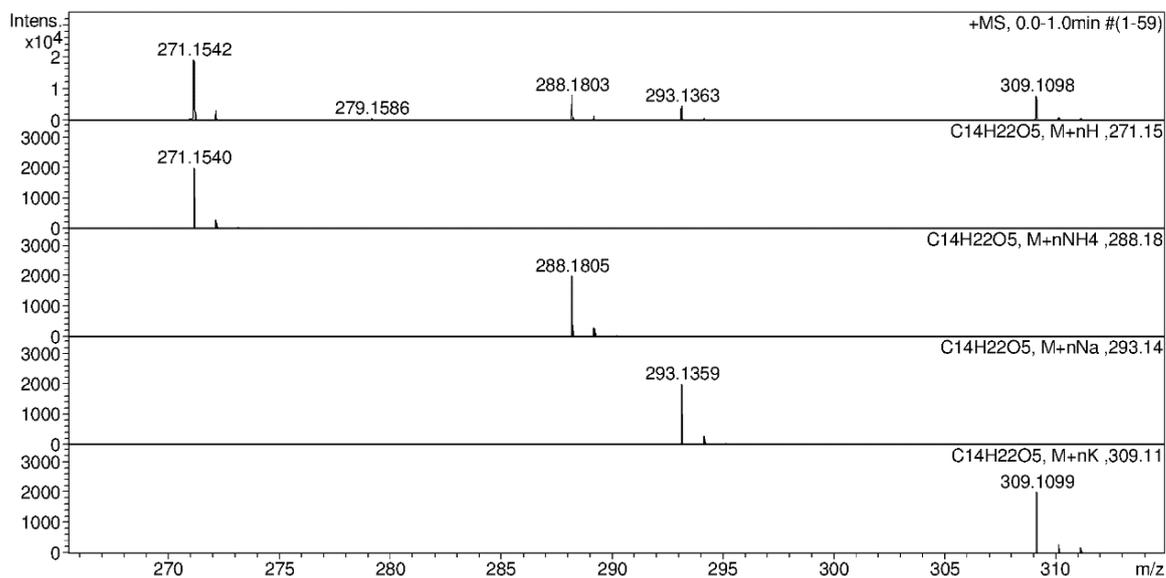
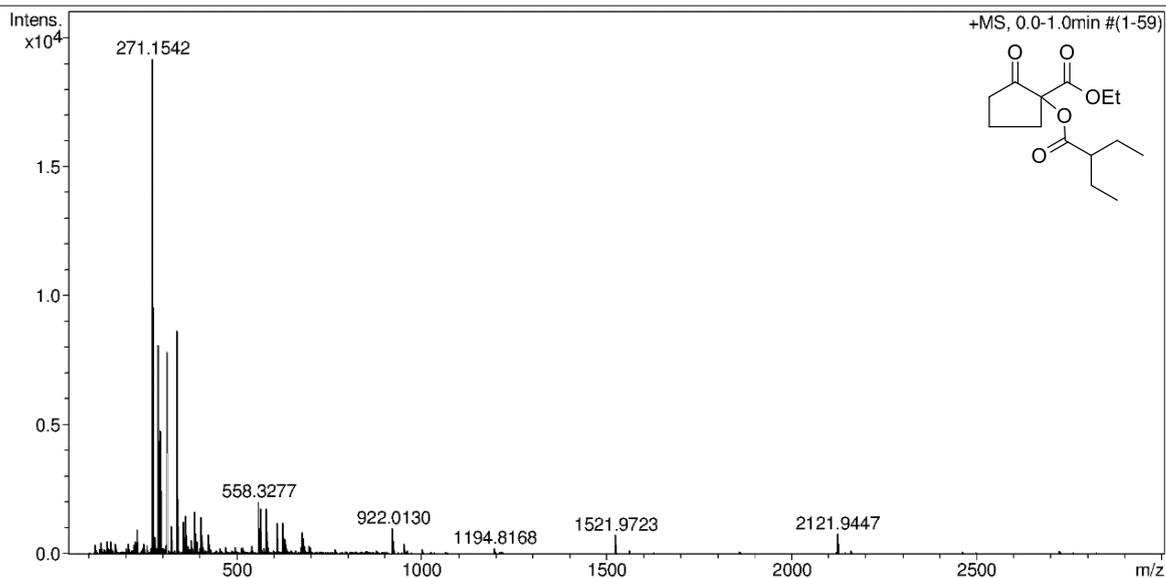
Analysis Info

Analysis Name D:\Data\Chizhov\Terentiev\Bityukov\ob290-13-16_&clb\$low.d
 Method tune_low.m
 Sample Name /TERN OB290(13-16)
 Comment CH3CN 100 %, dil. 2000, calibrant added

Acquisition Date 18.04.2016 16:25:51
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 1-(2-ethylbutanoyloxy)-2-oxocyclohexanecarboxylate, 4l

Display Report

Analysis Info

Analysis Name D:\Data\Chizhov\Terentiev\Bityukov\ob-279-14-17_\&clblow.d
 Method tune_low.m
 Sample Name /TERN OB-279-14-17
 Comment CH3CN 100 %, dil. 200, calibrant added

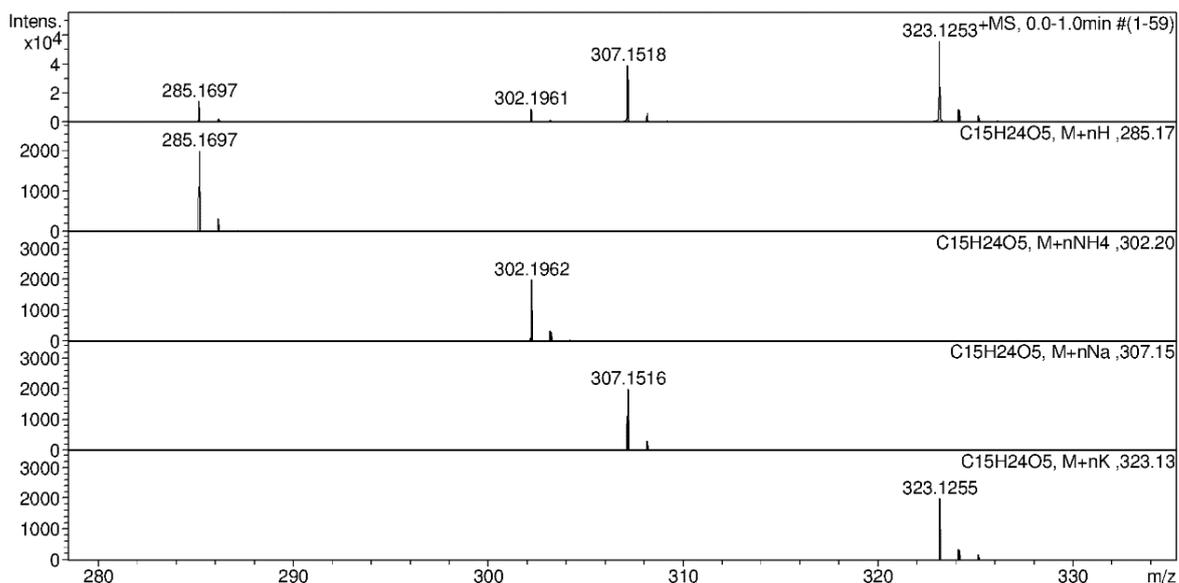
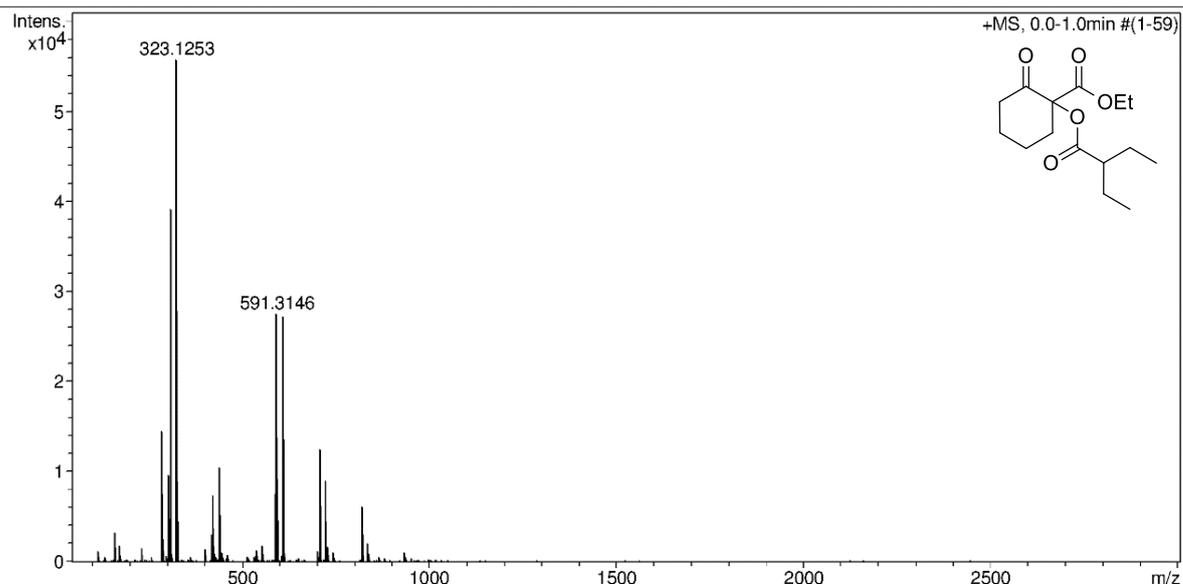
Acquisition Date 04.04.2016 13:54:18

Operator BDAL@DE

Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 3-acetyl-2-oxotetrahydrofuran-3-yl 2-ethylbutanoate, **4m**

Display Report

Analysis Info

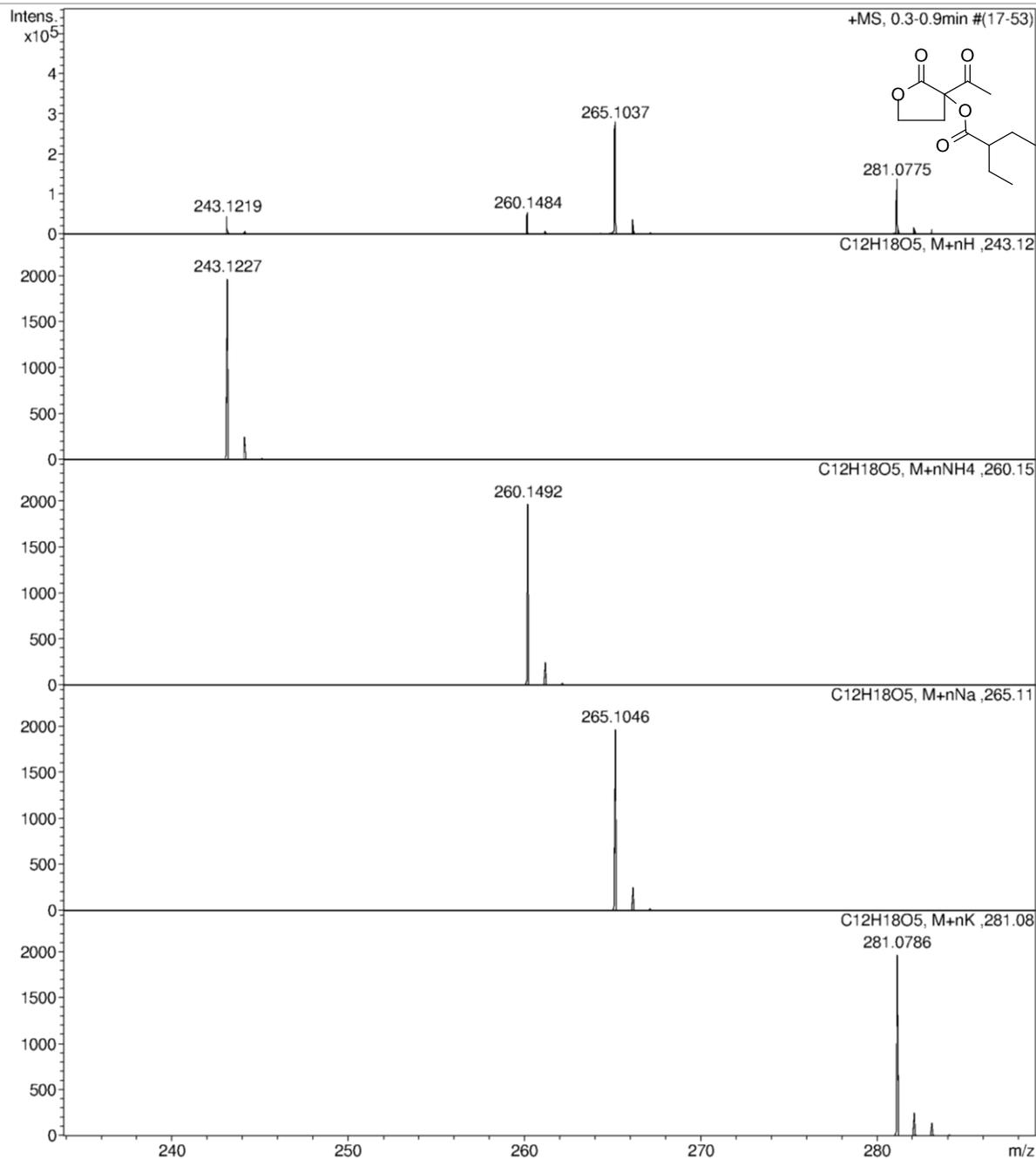
Analysis Name D:\Data\Kolotyrykina\2016\Bitukov\0721011.d
 Method tune_low.m
 Sample Name /TERN OB378
 Comment C12H18O5 mH 243.122 clb added

Acquisition Date 21.07.2016 15:55:18

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 1-(2-butylhexanoyloxy)-2-oxocyclopentanecarboxylate, **4n**

Display Report

Analysis Info

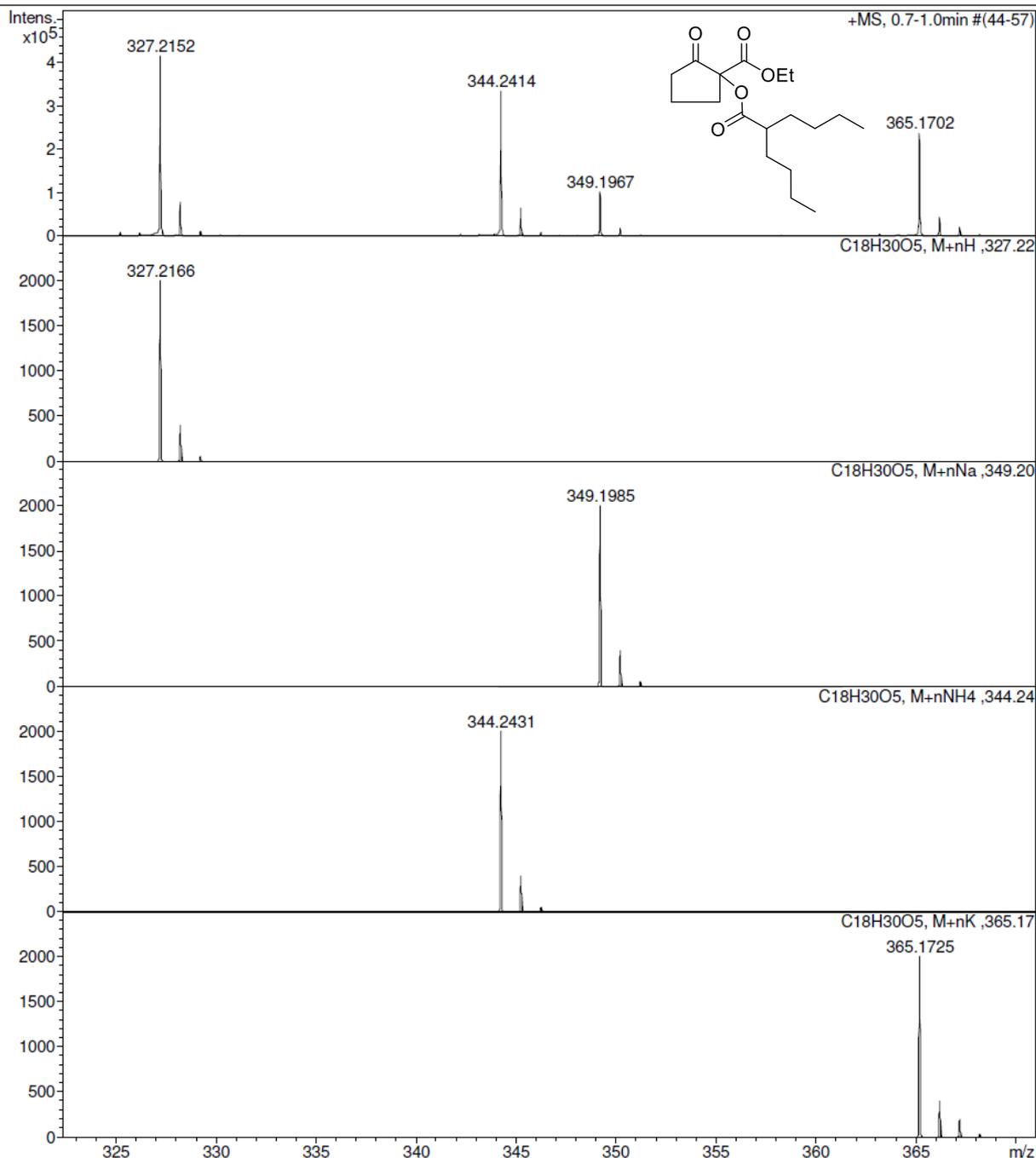
Analysis Name D:\Data\Kolotyrkina\2016\Bitukov\0526022.d
 Method tune_low.m
 Sample Name /TERN OB326_8-10
 Comment C18H305 mH-327.216 clb added

Acquisition Date 26.05.2016 16:35:43

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



Display Report

Analysis Info

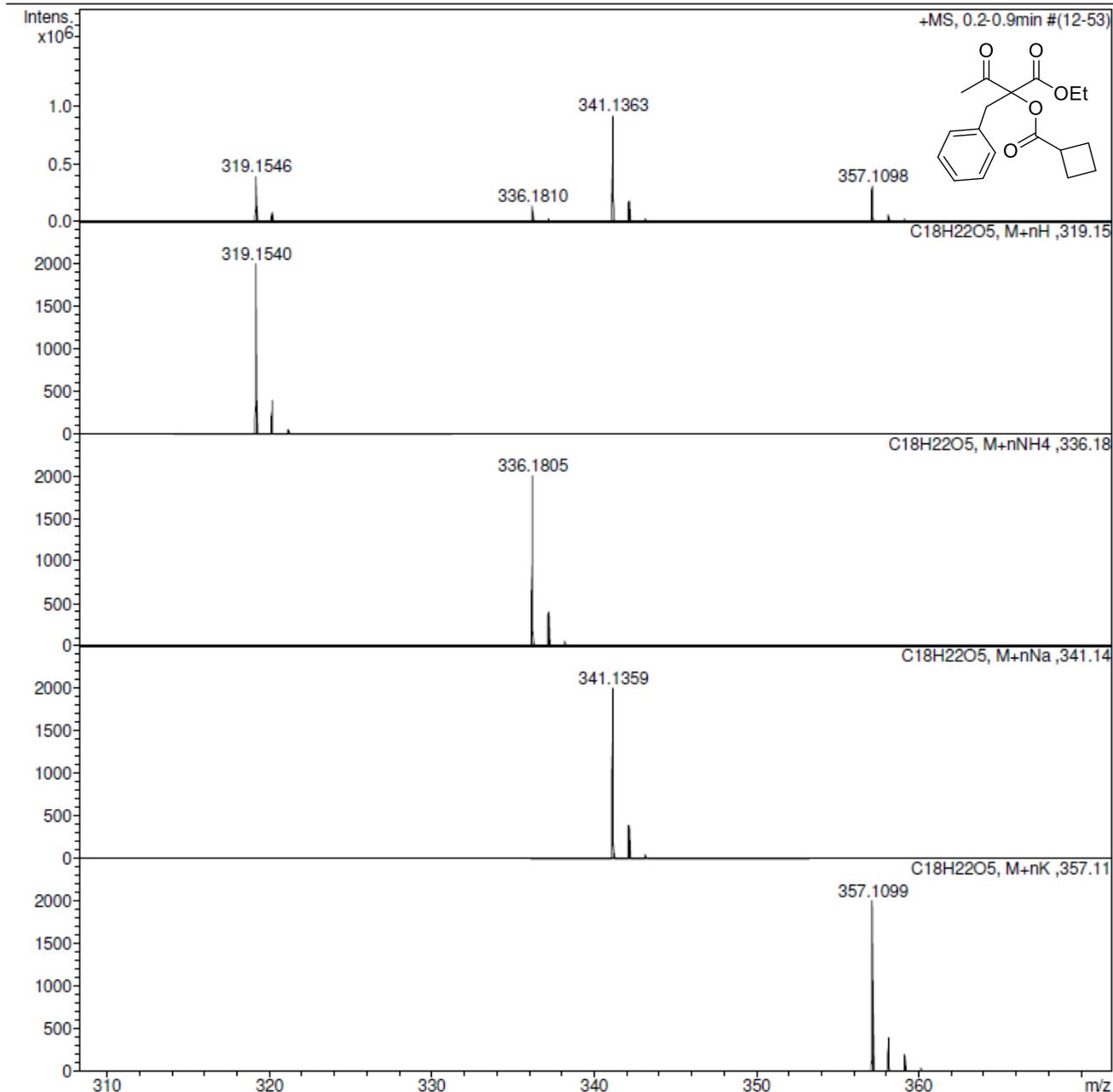
Analysis Name D:\Data\Kolotyrkina\2018\Bitukov\0213053.d
 Method tune_low.m
 Sample Name /TERN OB519_1
 Comment C18H22O5 mH 319.1540 calibrant added CH3CN

Acquisition Date 13.02.2018 20:01:19

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



Display Report

Analysis Info

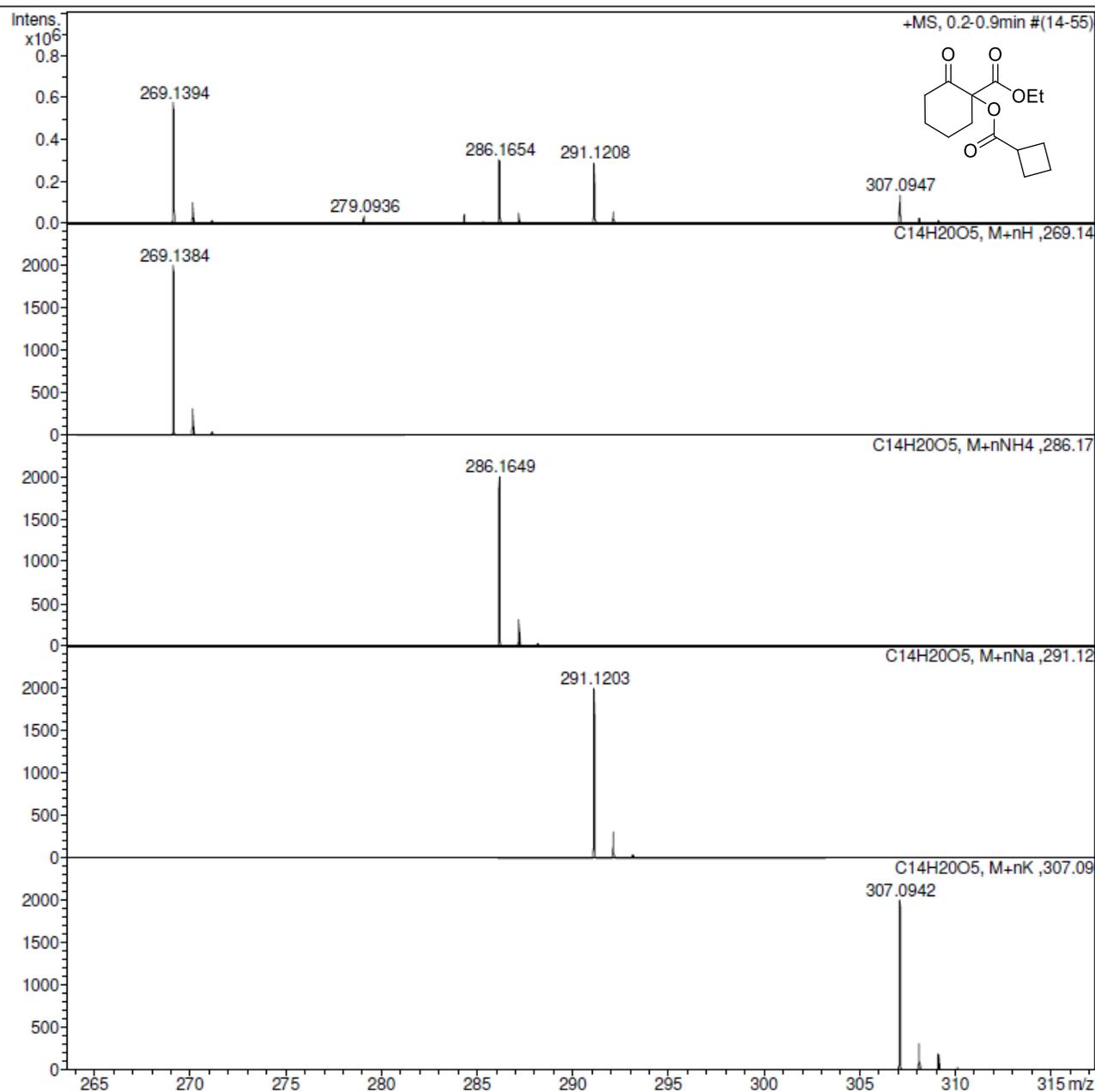
Analysis Name D:\Data\Kolotyrkina\2018\Bitukov\0213052.d
 Method tune_low.m
 Sample Name /TERN OB545
 Comment C14H20O5 mH 269.1383 calibrant added CH3CN

Acquisition Date 13.02.2018 19:54:49

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 1-acetyl-1-benzyl-2-oxopropyl cyclopentanecarboxylate, **4q**

Display Report

Analysis Info

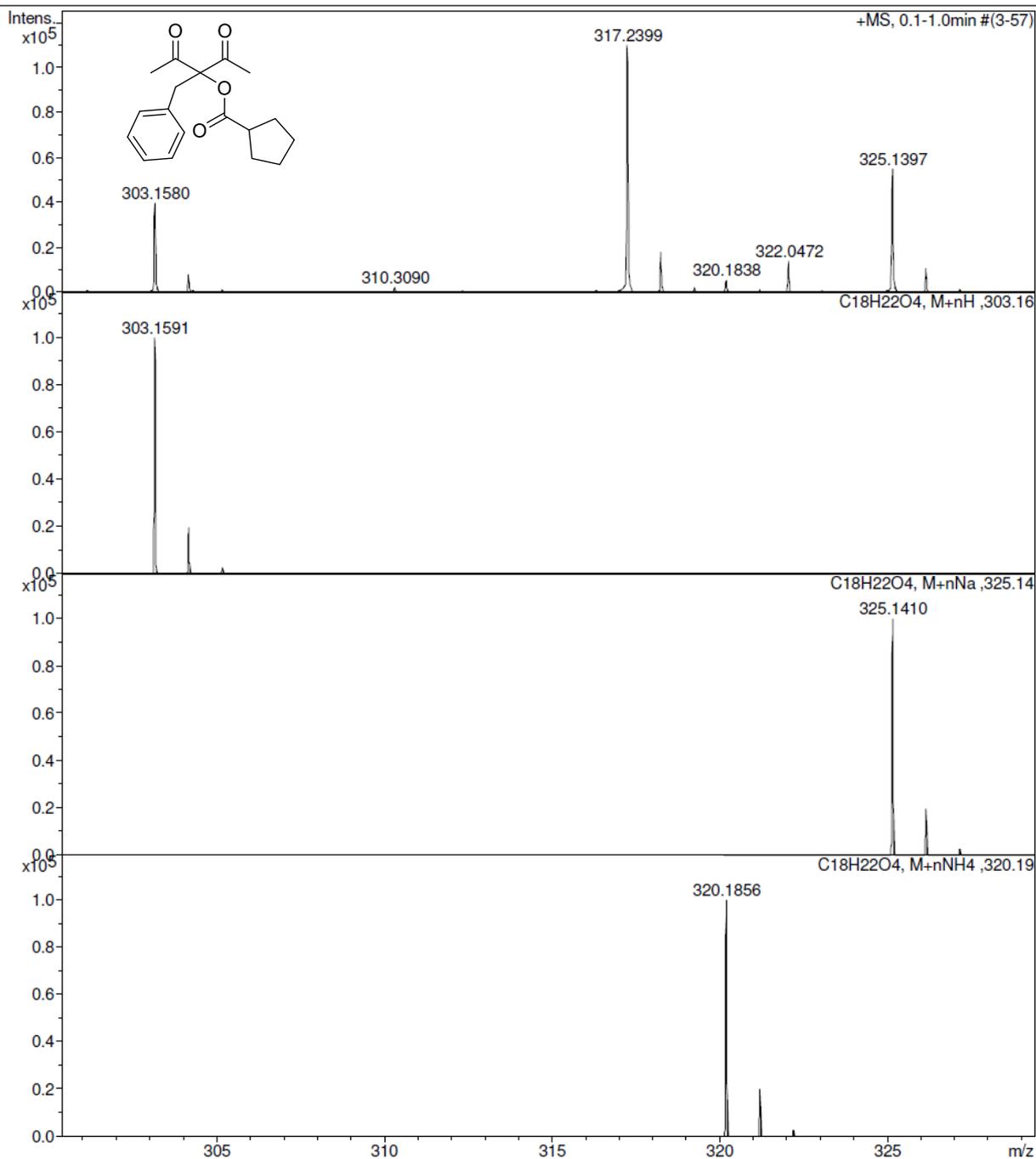
Analysis Name D:\Data\Kolotyrkina\2016\Bitukov\1110015.d
 Method tune_low.m
 Sample Name /TERN OB547_8-9
 Comment C18H22O4 mH 303.1590 clb added

Acquisition Date 10.11.2016 15:47:04

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of 1-benzyl-1-ethoxycarbonyl-2-oxopropyl cyclopentanecarboxylate, **4r**

Display Report

Analysis Info

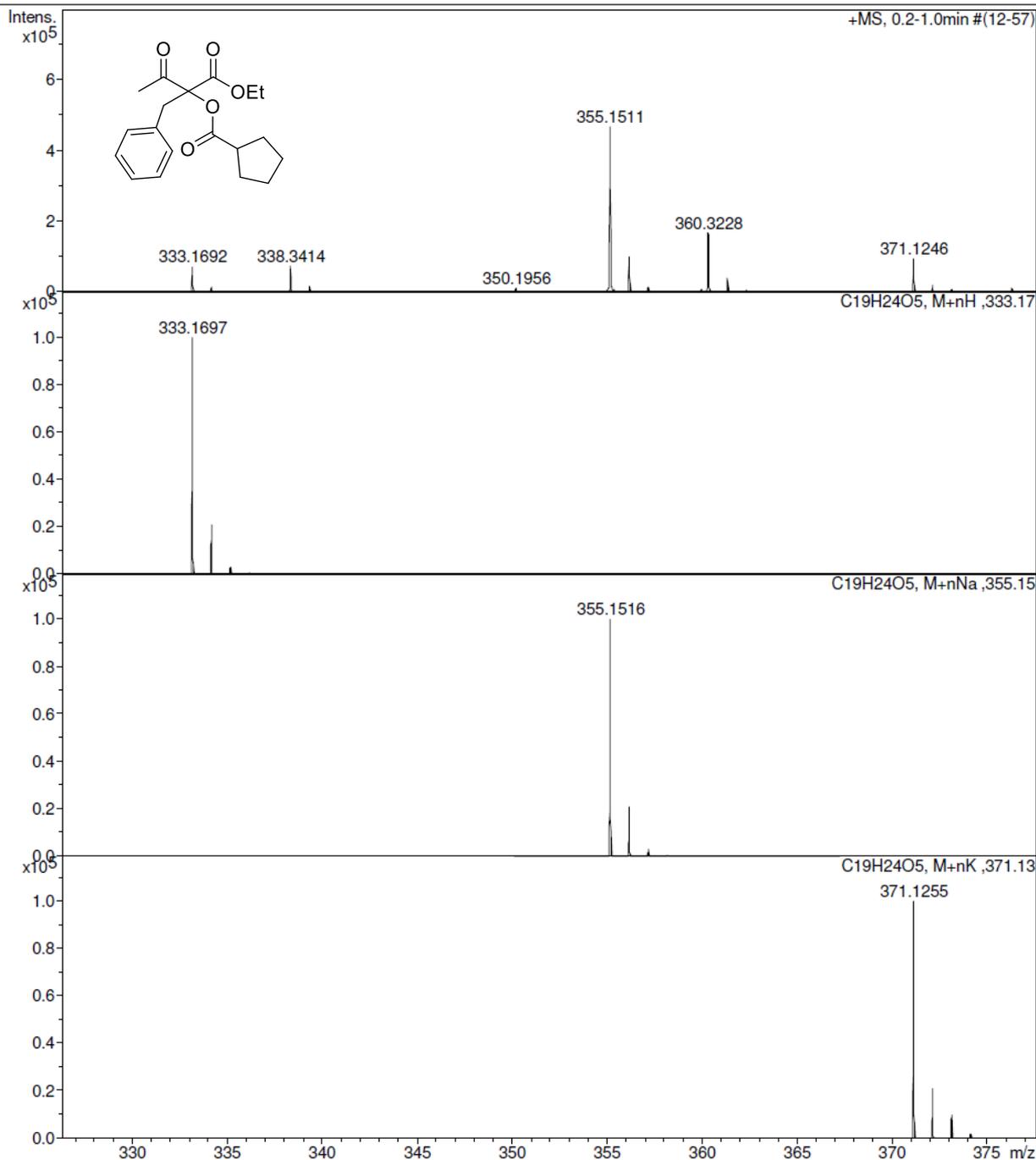
Analysis Name D:\Data\Kolotyrkina\2016\Bitukov\1026010.d
 Method tune_low.m
 Sample Name /TERN OB511_2
 Comment C19H24O5 mH 333.1696 calibrant added

Acquisition Date 26.10.2016 12:28:30

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |



HRMS of ethyl 1-cyclopentylcarbonyloxy-2-oxocyclohexanecarboxylate, 4s

Display Report

Analysis Info

| | | | |
|---------------|---|-------------------|---------------------|
| Analysis Name | D:\Data\Chizhov\Terentiev\Bityukov\ob546-10-12_&clblow%.d | Acquisition Date | 03.11.2016 11:52:31 |
| Method | tune_low.m | Operator | BDAL@DE |
| Sample Name | /TERN OB546(10-12) | Instrument / Ser# | microTOF 10248 |
| Comment | CH3CN 100 %, dil. 2000000, calibrant added | | |

Acquisition Parameter

| | | | | | |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Waste |

