# Supporting Information

# H<sub>2</sub>O<sub>2</sub>/HBr system - several directions but one choice: oxidation-bromination of secondary alcohols into mono- or dibromo ketones

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#### General materials and methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE II 300 spectrometer (300.13 and 75.48 MHz, respectively) in CDCl<sub>3</sub>. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: <sup>1</sup>H (CDCl<sub>3</sub>  $\delta$ =7.26 ppm), <sup>13</sup>C (CDCl<sub>3</sub>  $\delta$ =77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

High resolution mass spectra (HR-MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). A syringe injection was used for all acetonitrile solutions (flow rate 3  $\mu$ L/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

GC analysis was performed on a Chrom-5 chromatograph with the flame-ionization detector and 3x3000 mm analytical glass columns with 5% SE-30 and 5% FFAP on Chromaton N-AW-HMDS (0.16-0.20 mm). The product yields were determined by an internal standard method with the empirical correlation coefficients.

The TLC analysis was carried out on standard silica gel chromatography plates (DC-Fertigfolien ALUGRAM<sup>R</sup> Xtra SIL G/UV<sub>254</sub>). Column chromatography was performed using silica gel (0.060-0.200 mm, 60 A, CAS 7631-86-9, Acros).

Petroleum ether (PE, 40/70), MeOH, THF, dichloroethane (DCE) were distilled prior to use. MeCN were distilled over  $P_2O_5$ . EtOAc were purchased from commercial sources and were used as is.

Pentan-3-ol (1a), 2,4-dimethylpentan-3-ol (1h), nonan-4-ol (1f), 2-methyloctan-3-ol (1g), 1phenylhexan-1-ol (4c), HBr (48% solution in water),  $H_2O_2$  (35% aqueous solution),  $Na_2SO_4$ ,  $Na_2SO_3$  were commercial reagents (Acros, Sigma-Aldrich). Other secondary alcohols were synthesized according to the literature<sup>1</sup>.

## **Experimental for Table 1**

To a solution of alcohol **1a** (1 mmol, 88.2 mg) and HBr (48% aqueous, 1.2-6 mmol, 0.136-0.679 ml) in 1 ml of solvent at 65-70 °C and vigorous stirring, a solution of  $H_2O_2$  (35% aqueous, 10-15

mmol, 0.860-1.290 ml) was added portionwise (0.2-0.3 ml) during 6-10 h. After the addition of the first portion, brown vapors and a bright orange color of the reaction mass were observed. The next portions of  $H_2O_2$  were added after the decolorization of the reaction mixture (a pale-yellow color), then the reaction mass was cooled, diethyl ether (15 mL) and Na<sub>2</sub>SO<sub>3</sub> (1 g) were added. The organic layer was decanted and washed with water (5 ml), then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated in a vacuum of a water jet pump (20 mmHg). Yields **2a**, **3a** and **7a** were determined by GLC using heptan-4-one and undecane-6-one as the internal standards.

#### **Experimental for the Table 2**

To a solution of alcohol **1a-h**, **4a-e** (1 mmol, 88.2-256.5 mg) and HBr (48% aqueous, 1.2 mmol, 0.136 ml) in CH<sub>3</sub>CN (1 ml) at 65-70 °C and vigorous stirring, a solution of H<sub>2</sub>O<sub>2</sub> (35% aqueous, 10 mmol, 0.860 ml) in CH<sub>3</sub>CN (1 ml) was added portionwise (0.2-0.3 ml) for 6 hours. After the addition of the first portion, brown vapors and a bright orange color of the reaction mass were observed. The next portions of H<sub>2</sub>O<sub>2</sub> were added after the decolorization of the reaction mixture (a pale-yellow color), then the reaction mass was cooled, diethyl ether (15 mL) and Na<sub>2</sub>SO<sub>3</sub> (1 g) were added. The organic layer was decanted and washed with water (5 ml), then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated in a vacuum of a water jet pump (20 mmHg). The products **2a-h** and **5a-e** were isolated by column chromatography on silica gel in a solvent system PE: EA (100:1).

#### **Experimental for the Table 3**

To a solution of alcohol **1a-h**, **4a-e** (1 mmol, 88.2-256.5 mg) and HBr (48% aqueous, 6 mmol, 0.679 ml) in CH<sub>3</sub>CN (1 ml) at 65-70 °C and vigorous stirring, a solution of H<sub>2</sub>O<sub>2</sub> (35% aqueous, 15 mmol, 1.290 ml) in CH<sub>3</sub>CN (1 ml) was added portionwise (0.2-0.3 ml) for 6 hours. After the addition of the first portion, brown vapors and a bright orange color of the reaction mass were observed. The next portion of hydrogen peroxide was added after the decolorization of the reaction mixture (a pale-yellow color), then the reaction mass was cooled, diethyl ether (15 mL) and Na<sub>2</sub>SO<sub>3</sub> (1 g) were added. The organic layer was decanted and washed with water (5 ml) and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated in a vacuum of a water jet pump (20 mmHg). The products **3a-g** and **6a,b,d,e** were isolated by column chromatography on silica gel in a solvent system PE: EA (100:1).

### **Characterization of the products**

All the new compounds were characterized using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, HR-MS spectroscopy. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the known compounds were in agreement with the literature data<sup>2-11</sup>.

### 2-Bromopentan-3-one, 2a9



Colorless oil (130 mg, 79%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 1.10 (t, 3H, CH<sub>3</sub>, *J* = 7.2 Hz), 1.72 (d, 3H, <u>CH<sub>3</sub></u>CHBr, *J* = 6.9 Hz), 2.51-2.65 (m, 1H, CH<sub>2</sub>), 2.78-2.92 (m, 1H, CH<sub>2</sub>), 4.40 (q, CHBr, *J* = 6.9 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 8.17 (CH<sub>3</sub>), 20.14 (<u>CH<sub>3</sub>CHBr</u>), 31.95 (CH<sub>2</sub>), 47.26 (CHBr), 205.09 (CO).

3-Bromoheptan-4-one, 2b<sup>10</sup>



Colorless oil (158 mg, 82%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.93 (t, 3H, CH<sub>3</sub>, J = 7.3 Hz), 1.00 (t, 3H, CH<sub>3</sub>, J = 7.3 Hz), 1.58-1.70 (m, 2H, CH<sub>2</sub>), 1.90-2.07 (m, 2H, <u>CH<sub>2</sub>CHBr</u>), 2.57-2.71 (m, 2H, CH<sub>2</sub>CO), 4.16 (dd, 1H, CHBr, J = 6.4 Hz, J = 8.0 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 11.97 (CH<sub>3</sub>), 13.58 (CH<sub>3</sub>), 17.39 (CH<sub>2</sub>), 26.88 (<u>C</u>H<sub>2</sub>CHBr), 40.90 (<u>C</u>H<sub>2</sub>CO), 55.48 (CHBr), 204.21 (CO).

4-Bromononan-5-one, 2c<sup>11</sup>



Colorless oil (161 mg, 73%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.88-0.95 (m, 6H, 2CH<sub>3</sub>), 1.28-1.61 (m, 6H, 3CH<sub>2</sub>), 1.84-2.00 (m, 2H, <u>CH<sub>2</sub>CHBr</u>), 2.56-2.75 (m, 2H, CH<sub>2</sub>CO), 4.23 (dd, 1H, CHBr, J = 6.5 Hz, J = 8.0 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>)  $\delta$ : 13.39 (CH<sub>3</sub>), 13.78 (CH<sub>3</sub>), 20.60 (CH<sub>2</sub>), 22.18 (CH<sub>2</sub>), 26.04 (CH<sub>2</sub>), 35.39 (<u>CH<sub>2</sub>CHBr</u>), 38.64 (<u>CH<sub>2</sub>CO</u>), 53.53 (CHBr), 204.37 (CO).

5-Bromoundecan-6-one, 2d<sup>7, 10</sup>



Colorless oil (201 mg, 81%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 0.86-0.92 (m, 6H, 2CH<sub>3</sub>), 1.25-1.46 (m, 8H, 4CH<sub>2</sub>), 1.55-1.65 (m, 2H, CH<sub>2</sub>), 1.85-2.04 (m, 2H, <u>CH<sub>2</sub></u>CHBr), 2.57-2.72 (m, 2H, CH<sub>2</sub>CO), 4.22 (dd, 1H, CHBr, *J* = 6.7 Hz, *J* = 7.9 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 13.80 (CH<sub>3</sub>), 13.87 (CH<sub>3</sub>), 22.10 (CH<sub>2</sub>), 22.40 (CH<sub>2</sub>), 23.64 (CH<sub>2</sub>), 29.47 (CH<sub>2</sub>), 31.23 (CH<sub>2</sub>), 33.18 (<u>C</u>H<sub>2</sub>CHBr), 38.91 (<u>C</u>H<sub>2</sub>CO), 53.79 (CHBr), 204.40 (CO).

8-Bromoheptadecan-9-one, 2e



Colorless oil (213 mg, 64%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 0.87 (t, 6H, 2CH<sub>3</sub>, *J* = 6.6 Hz), 1.27 (m, 20H, CH<sub>2</sub>), 1.58-1.62 (m, 2H CH<sub>2</sub>), 1.88-1.97 (m, 2H, C<u>H</u><sub>2</sub>CHBr), 2.58-2.72 (m, 2H, CH<sub>2</sub>CO), 4.22 (t, 1H, CHBr, *J* = 7.3 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 14.03 (CH<sub>3</sub>), 14.05 (CH<sub>3</sub>), 22.58 (CH<sub>2</sub>), 22.63 (CH<sub>2</sub>), 23.99 (CH<sub>2</sub>), 27.36 (CH<sub>2</sub>), 28.95 (CH<sub>2</sub>), 28.98 (CH<sub>2</sub>), 29.08 (CH<sub>2</sub>), 29.11 (CH<sub>2</sub>), 29.31 (CH<sub>2</sub>), 31.68 (CH<sub>2</sub>), 31.81 (CH<sub>2</sub>), 33.49 (CH<sub>2</sub>), 38.95 (<u>C</u>H<sub>2</sub>CO), 53.84 (CHBr), 204.41 (CO);

HRMS (ESI) m/z [M+Na]<sup>+</sup>: Calcd for [C<sub>17</sub>H<sub>33</sub>BrNaO]<sup>+</sup>: 355.1607. Found: 355.1603.

HRMS-ESI: calculated 355.1607 (<sup>79</sup>Br) and 357.1587 (<sup>81</sup>Br)  $[C_{17}H_{33}BrNaO]^+$  found 355.1603 (<sup>79</sup>Br) and 357.1584 (<sup>81</sup>Br)

#### 2-Bromo-2,4-dimethylpentan-3-one, 2h<sup>10</sup>



Colorless oil (168 mg, 87%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 1.16 (d, 6H, 2CH<sub>3</sub>, *J* = 6.6 Hz), 1.85 (s, 6H, 2CH<sub>3</sub>), 3.37-3.50 (m, 1H CH);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 20.89, 29.30, 34.54, 64.56, 209.93.

Mixture of 3-bromononan-4-one (2f) and 5-bromononan-4-one (2f')<sup>5</sup> (ratio 2f : 2f' according to NMR spectroscopy data  $\sim 1 : 1$ )



Colorless oil (172 mg, 78%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 0.86-0.95 (m, 9H, 3CH<sub>3</sub>), 1.00 (t, 3H, CH<sub>3</sub>, *J* = 7.3 Hz), 1.23-1.39 (m, 8H, 4CH<sub>2</sub>), 1.58-1.70 (m, 4H, 2CH<sub>2</sub>), 1.87-2.08 (m, 4H, 2<u>CH<sub>2</sub></u>CHBr), 2.54-2.75 (m, 4H, 2CH<sub>2</sub>CO), 4.17 (dd, H, CHBr, *J* = 6.4 Hz), 4.21 (dd, H, CHBr, *J* = 6.3 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 11.97 (CH<sub>3</sub>), 13.58 (CH<sub>3</sub>), 13.78 (CH<sub>3</sub>), 13.87 (CH<sub>3</sub>), 17.40 (CH<sub>2</sub>), 22.10 (CH<sub>2</sub>), 22.40 (CH<sub>2</sub>), 23.63 (CH<sub>2</sub>), 26.88 (CH<sub>2</sub>), 29.46 (CH<sub>2</sub>), 31.22 (CH<sub>2</sub>), 33.15 (CH<sub>2</sub>), 39.00 (CH<sub>2</sub>CO), 40.80 (CH<sub>2</sub>CO), 53.78 (CHBr), 55.48 (CHBr), 204.23 (CO), 204.34 (CO).

Mixture of 2-bromo-2-methyloctan-3-one (2g) and 4-bromo-2-methyloctan-3-one (2g') (ratio 2g : 2g' according to NMR spectroscopy data ~ 2 : 1)



Colorless oil (181 mg, 82%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.89 (t, 4.5H, 2CH<sub>3</sub>, J = 6.8 Hz), 1.12 (d, 1.5H, CH<sub>3</sub>, J = 6.9 Hz), 1.16 (d, 1.5H, CH<sub>3</sub>, J = 6.7 Hz), 1.26-1.36 (m, 6H, 4CH<sub>2</sub>), 1.56-1.70 (m, 3H, 2CH<sub>2</sub>), 1.84 (s,

6H, 2CH<sub>3</sub>), 2.78 (t, 2H, CH<sub>2</sub>CO, *J* = 7.3 Hz), 2.97-3.07 (m, 0.5H, CHCO), 4.36 (t, 0.5H, CHBr, *J* = 7.2 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 13.81(CH<sub>3</sub>), 13.90 (CH<sub>3</sub>), 18.65 (CH<sub>2</sub>), 19.36 (CH<sub>2</sub>), 22.18 (CH<sub>3</sub>), 22.45 (CH<sub>2</sub>), 24.44 (CH<sub>2</sub>), 29.57 (CH<sub>3</sub>), 31.24 (CH<sub>2</sub>), 32.98 (CH<sub>2</sub>), 36.04 (<u>C</u>H<sub>2</sub>CO), 37.97 (<u>C</u>HCO), 51.70 (CHBr), 64.03 (CBr), 205.75 (CO), 207.63 (CO).

HRMS-ESI: calculated 243.0355 (<sup>79</sup>Br) and 245.0335 (<sup>81</sup>Br)  $[C_9H_{17}BrNaO]^+$  found 243.0348 (<sup>79</sup>Br) and 245.0340 (<sup>81</sup>Br)

1-Bromo-3,3-dimethylbutan-2-one, 5a9



Colorless oil (163 mg, 91%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 1.21 (s, 9H, CH<sub>3</sub>), 4.16 (s, 2H, CH<sub>2</sub>);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 26.70 (3CH<sub>3</sub>), 31.60 (CH<sub>2</sub>Br), 44.21 (<u>C</u>(CH<sub>3</sub>)<sub>3</sub>), 206.03 (CO).

2-Bromo-1-phenylethanone, 5b<sup>8</sup>



Pale yellow powder (169 mg, 85%); mp = 48-50 °C.

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 4.45 (s, 2H, CH<sub>2</sub>Br), 7.48 (t, 2H, 2CH, *J* = 7.3 Hz), 7.60 (t, 1H, CH, *J* = 7.3 Hz), 7.98 (d, 2H, 2CH, *J* = 7.3 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 30.88 (CH<sub>2</sub>Br), 128.83 (2CH), 128.91 (2CH), 133.93 (2CH), 191.25 (CO).

### 2-Bromo-1-phenylhexan-1-one, 5c<sup>3</sup>



Pale yellow oil (196 mg, 77%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 0.92 (t, 3H, CH<sub>3</sub>, *J* = 7.3 Hz), 1.33-1.53 (m, 4H, 2CH<sub>2</sub>), 2.07-2.27 (m, 2H, <u>CH<sub>2</sub>CHBr</u>), 5.13 (t, 1H, CHBr, *J* = 7.3 Hz), 7.48 (t,2H, 2CH, *J* = 7.3 Hz), 7.59 (t, 1H, CH, *J* = 7.3 Hz), 8.01 (d, 2H, 2CH, *J* = 7.3 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 13.84 (CH<sub>3</sub>), 22.25 (CH<sub>2</sub>), 29.63 (CH<sub>2</sub>), 33.22 (CH<sub>2</sub>), 47.26 (CHBr), 128.73 (2CH), 128.80 (2CH), 133.61(CH), 134.52 (C), 193.27 (CO).

2-Bromo-1-(p-tolyl)ethan-1-one, 5d<sup>12</sup>



White solid (166 mg, 78%); mp 53-54°C

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.41 (s, 3H, CH<sub>3</sub>), 4.41 (s, 2H; CH<sub>2</sub>), 7.27 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 21.71 (CH<sub>3</sub>), 30.90 (CH<sub>2</sub>), 129.01 (CH), 129.50 (CH), 131.44 (C), 144.96 (C), 190.90 (CO).

## 2-Bromo-1-(2-chlorophenyl)ethan-1-one, 5e<sup>13</sup>



Pale yellow oil (121 mg, 52%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 4.51 (s, 2H; CH<sub>2</sub>), 7.34-7.38 (m, 1H), 7.43-7.44 (m, 2H), 7.54-7.56 (m, 1H);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 34.45 (CH<sub>2</sub>), 127.13 (CH), 130.25 (CH), 130.57 (CH), 131.30 (CH), 132.73 (C), 136.24 (C), 194.01 (CO).

## 2,4-Dibromopentan-3-one (mixture of meso- and rac-isomers 1:2), 3a4,9



Colorless oil (192 mg, 79%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : **pair dl (rac)**: 1.79 (d, 3H, CH<sub>3</sub>, *J* = 6.6 Hz), 4.97 (q, 1H, CHBr, *J* = 6.6 Hz), **meso**: 1.86 (d, 3H, CH<sub>3</sub>, *J* = 6.6 Hz), 4.76 (q, 1H, CHBr, *J* = 6.6 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>)  $\delta$ : **pair dl (rac)**: 19.50 (2CH<sub>3</sub>), 43.82 (CHBr), 195.99 (CO), **meso**: 21.74 (2CH<sub>3</sub>), 44.01 (CHBr), 197.99 (CO).

#### 3,5-Dibromoheptan-4-one, 3b<sup>2,9</sup>



Colorless oil (225 mg, 83%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 1.03 (t, 6H, 2CH<sub>3</sub>, *J* = 7.3 Hz), 1.94-2.04 (m, 2H, CH<sub>2</sub>), 2.12-2.21 (m, 2H, CH<sub>2</sub>), 4.65 (t, 2H, CHBr, *J* = 7.3 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 11.88 (2CH<sub>3</sub>), 26.06 (2CH<sub>2</sub>), 51.70 (2CHBr), 194.34(CO).

4,6-Dibromononane-5-one, 3c<sup>6,9</sup>



Colorless oil (264 mg, 88%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 0.97 (t, 6H, CH<sub>3</sub>, *J* = 7.3 Hz), 1.38-1.52 (m, 4H, 2CH<sub>2</sub>), 1.90-2.01 (m, 2H, CH<sub>2</sub>), 2.05-2.15 (m, 2H, CH<sub>2</sub>), 4.73 (t, 2H, 2CHBr, *J* = 7.3 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 13.46 (2CH<sub>3</sub>), 20.52 (2CH<sub>2</sub>), 34.56 (2CH<sub>2</sub>), 49.87 (2CHBr), 194.38 (CO).

5,7-Dibromoundecan-6-one, 3d



Pale yellow oil (242 mg, 74%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 0.91 (t, 6H, 2CH<sub>3</sub>, *J* = 6.6 Hz), 1.38-1.45 (m, 8H, 4CH<sub>2</sub>), 1.92-1.99 (m, 2H, CH<sub>2</sub>), 2.08-2.20 (m, 2H, CH<sub>2</sub>), 4.71 (t, 2H, 2CHBr, *J* = 7.3 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 13.78 (2CH<sub>3</sub>), 22.16 (2CH<sub>2</sub>), 29.30 (2CH<sub>2</sub>), 32.27 (2CH<sub>2</sub>), 50.15 (2CHBr), 194.38 (CO);

HRMS-ESI: calculated 350.9753 (<sup>79</sup>Br) and 352.9732 (<sup>81</sup>Br)  $[C_{11}H_{20}Br_2NaO]^+$  found 350.9749 (<sup>79</sup>Br) and 352.9730 (<sup>81</sup>Br)



Pale yellow oil (276 mg, 67%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : **pair dl (rac):** 0.87 (t, 6H, 2CH<sub>3</sub>, *J* = 6.6 Hz), 1.27-1.39 (m, 20H, 10CH<sub>2</sub>), 1.92-1.98 (m, 2H, CH<sub>2</sub>), 2.07-2.14 (m, 2H, CH<sub>2</sub>), 4.71 (t, 2H, 2CHBr, *J* = 7.3 Hz); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>)  $\delta$ : **pair dl (rac):** 14.05 (2CH<sub>3</sub>), 22.59 (2CH<sub>2</sub>), 27.19 (2CH<sub>2</sub>), 28.98 (2CH<sub>2</sub>), 31.69 (2CH<sub>2</sub>), 32.55 (2CH<sub>2</sub>), 50.19 (2CHBr), 194.40 (CO); HRMS-ESI: calculated 433.0712 (<sup>79</sup>Br) and 435.0692 (<sup>81</sup>Br) [C<sub>17</sub>H<sub>32</sub>Br<sub>2</sub>NaO]<sup>+</sup> found 433.0716

(<sup>79</sup>Br) and 435.0703 (<sup>81</sup>Br)

3,5-Dibromononan-4-one, 3f



Pale yellow oil (216 mg, 72%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : **pair dl (rac):** 0.91 (t, 3H, CH<sub>3</sub>, J = 6.6 Hz), 1.03 (t, 3H, CH<sub>3</sub>, J = 7.3 Hz), 1.36-1.39 (m, 4H, 2CH<sub>2</sub>), 1.92-2.04 (m, 2H, <u>CH<sub>2</sub>CHBr</u>), 2.08-2.21 (m, 2H, <u>CH<sub>2</sub>CHBr</u>), 4.65 (t, 1H, CHBr, J = 7.3 Hz), 4.71 (t, 1H, CHBr, J = 7.3 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: **pair dl (rac):** 11.89 (CH<sub>3</sub>), 13.80 (CH<sub>3</sub>), 22.16 (CH<sub>2</sub>), 26.04 (CH<sub>2</sub>), 29.30 (CH<sub>2</sub>), 32.26 (CH<sub>2</sub>), 50.09 (CHBr), 51.74 (CHBr), 194.35 (CO);

HRMS-ESI: calculated 320.9460 (<sup>79</sup>Br) and 322.9440 (<sup>81</sup>Br)  $[C_9H_{16}Br_2NaO]^+$  found 320.9459 (<sup>79</sup>Br) and 322.9440 (<sup>81</sup>Br)

#### 2,4-Dibromo-2-methyloctan-3-one, 3g

Pale yellow oil (195 mg, 65%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 0.91 (t, 3H, CH<sub>3</sub>, *J* = 6.6 Hz), 1.33-1.54 (m, 4H, 2CH<sub>2</sub>), 1.88 (s, 3H CH<sub>3</sub>), 2.05-2.10 (m, 5H, CH<sub>2</sub>, CH<sub>3</sub>), 4.94 (t, 1H, CHBr, *J* = 7.3 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 13.78 (CH<sub>3</sub>), 22.07 (CH<sub>2</sub>), 29.19 (CH<sub>3</sub>), 29.39 (CH<sub>3</sub>), 31.00 (CH<sub>2</sub>), 34.32 (CH<sub>2</sub>), 45.65 (CHBr), 64.02 ((CH<sub>3</sub>)<sub>2</sub>CBr), 198.04 (CO);

HRMS-ESI: calculated 320.9460 (<sup>79</sup>Br) and 322.9440 (<sup>81</sup>Br)  $[C_9H_{16}Br_2NaO]^+$  found 320.9452 (<sup>79</sup>Br) and 322.9435 (<sup>81</sup>Br)

## 1,1-Dibromo-3,3-dimethylbutan-2-one, 6a9

White crystals (216 mg, 84%); mp = 74-75 °C. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 1.27 (s 9H, 3CH<sub>3</sub>), 6.32 (s, 1H, CHBr<sub>2</sub>); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 26.79 (2CH<sub>3</sub>), 37.34 (CH<sub>3</sub>), 43.98 (CHBr<sub>2</sub>), 201.52 (CO).

### 2,2-Dibromo-1-phenylethanone, 6b<sup>8</sup>



White crystals (222 mg, 80%); mp = 35-36 °C.

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.72 (s, 1H, CHBr<sub>2</sub>), 7.49 (t, 2H, 2CH<sub>ar</sub>, *J* = 7.3 Hz), 7.62 (t, 1H, CH<sub>ar</sub>, *J* = 7.3 Hz), 8.06 (d, 2H, 2CH<sub>ar</sub>, *J* = 7.3 Hz);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 39.71(CHBr<sub>2</sub>), 128.88 (2CH), 129.61 (2CH), 134.39 (2CH), 185.88 (CO).

### 2,2-Dibromo-1-(p-tolyl)ethan-1-one, 6d<sup>8</sup>



White crystals (190 mg, 65%); mp 97-98°C

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 2.44 (s, 3H, CH<sub>3</sub>), 6.68 (s, 1H; CH), 7.29 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 21.81 (CH<sub>3</sub>), 39.81 (CH), 128.10 (C), 129.64 (CH), 129.82 (C), 145.70 (C), 185.62 (CO).

## 2,2-Dibromo-1-(2-chlorophenyl)ethan-1-one, 6e14



Pale yellow oil (146 mg, 47%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>) δ: 6.78 (s, 1H; CH<sub>2</sub>), 7.35-7.40 (m, 1H), 7.43-7.47 (m, 2H), 7.59-7.62 (m, 1H);

<sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) δ: 42.05 (CH), 127.20 (CH), 130.45 (CH), 130.90 (CH), 130.95 (C), 132.97 (CH), 134.07 (C), 188.76 (CO).

## Pentan-3-one, 7a

0 ||

Colorless oil (28 mg, 33%)

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.97 (t, 6H, 2CH<sub>3</sub>, J = 7.3 Hz), 2.35 (t, 4H, 2CH<sub>2</sub>, J = 7.3 Hz).

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## Copies of <sup>1</sup>H, <sup>13</sup>C NMR and HRMS spectra of synthesized products

<sup>1</sup>H NMR of 2-bromopentan-3-one, 2a



## <sup>13</sup>C NMR of 2-bromopentan-3-one, 2a

#### Acquisition Time (sec) 0.9006



No.	(ppm)	(Hz)	Height		No.	Annotation	(ppm)
1	8.17	616.7	0.3504		1	Chloroform-d	77.00
2	20.14	1520.1	0.3913			× •	2
3	31.95	2411.4	0.3224				
4	47.26	3566.9	0.2309	1			
5	77.00	5811.7	0.9903				
6	205.09	15479.5	0.1063				

#### <sup>1</sup>H NMR of 3-bromoheptan-4-one, **2b**

Acquisition Time (sec) 1.3518



## <sup>13</sup>C NMR of 3-bromoheptan-4-one, **2b**

#### Acquisition Time (sec) 0.9006



NU.	(bbui)	(112)	Height	14
1	11.97	903.1	0.2666	
2	13.58	1024.7	0.2838	210
3	17.39	1312.3	0.2039	
4	26.88	2028.8	0.2108	
5	40.90	3087.0	0.1821	
6	55.48	4187.3	0.1457	
7	77.00	5811.7	0.9564	
8	204.21	15413.1	0.0807	

Chloroform-d

77.00

#### <sup>1</sup>H NMR of 4-bromononan-5-one, **2c**

#### Acquisition Time (sec) 1.3518



10 1.38 414.6 0.0759 20 1.84 552.2 0.0176 30 2.64 791.6 0.1980

### <sup>13</sup>C NMR of 4-bromononan-5-one, **2c**

Acquisition Time (sec) 0.9006

7

9

38.64

77.00

8 53.53

2916.1

4040.6

5811.7

10 204.37 15424.8 0.1687

0.6180

0.6095

1.0000



#### <sup>1</sup>H NMR of 5-bromoundecan-6-one, **2d**

#### Acquisition Time (sec) 1.3518



10 1.46 438.6 0.0554 20 2.57 772.4 0.0652

# <sup>13</sup>C NMR of 5-bromoundecan-6-one, **2d**

Acquisition Time (sec) 0.9006

Freq	uency (M	Hz)	75.48		Nicleux	5		13C		Number of Transients	23	D	Orig	inal Points	Count	16316		
Point	ts Count	039	16384		Pulse S	equence		zqpq30		Solvent	CH	LOROFORM-D	Swe	ep Width (f	<b>z</b> )	18115.94		
Temp	oerature (	degree (	27.900															
	Bu			u finik kung palakangan tan kangka					nja ku je ka je	1999 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	- Justie Just	Chloroform-d		62°59-	-38.91			
Innti	200	192	184 17	6 168 1	60 15	2 144	136	6 128	120 112 Chemic:	: 104 96 88 al Shift (ppm.)	8	80 72 64	56	6 48	40	32	24	16 8
No. 1 2 3 4 5 6	(ppm) 13.80 13.87 22.10 22.40 23.64 29.47	(Hz) 1041.3 1046.9 1668.3 1690.4 1784.4 2224.5	Height 0.1695 0.2853 0.1946 0.3270 0.4289 0.2719	No.         (ppm)           7         31.23           8         33.18           9         38.91           10         53.79           11         77.00           12         204.40	(Hz) 2357.2 2504.3 2936.6 4060.1 5811.7 15427.5	Height 0.1618 0.3945 0.3766 0.3547 1.0000 0.0839	No.	Annotation Chloroform-c	(ppm) 1 77.00									

<sup>1</sup>H NMR of 8-bromoheptadecan-9-one, **2e** 

Acquisition Time (sec) 1.3518



10 1.93 579.5 0.0510

#### <sup>13</sup>C NMR of 8-bromoheptadecan-9-one, 2e

#### Acquisition Time (sec) 0.9006



		<sup>1</sup> H NMR	of 2-bromo-2.	4-dimethy	lpentan-3-one.	2h
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#### Acquisition Time (sec) 1.3518

Frequency (NHz) 300	0.13	Nucleus	1H	Number of Transients	1	Original Points Count	8124
Points Count 819	92	Puise Seguence	Zq	Solvent	CHLOROFORM-D	Sweep Width (Hz)	6009.62
Temperature (degree C) 27.	.600						



### <sup>13</sup>C NMR of 2-bromo-2,4-dimethylpentan-3-one, **2h**

#### Acquisition Time (sec) 0.9006



20.03	1010.0	0.4342		1 Cru
29.30	2211.2	0.5723		92
34.54	2607.1	0.1576		
64.56	4872.9	0.0755		
77.00	5811.7	0.9926		
209.93	15844.4	0.0656		

#### <sup>1</sup>H NMR of mixture 3-bromononan-4-one (2f) и 5-bromononan-4-one (2f') 1:1

Acquisition Time (sec) 1.3518



### <sup>13</sup>C NMR of mixture 3-bromononan-4-one (2f) и 5-bromononan-4-one (2f') 1:1

Acquisition Time (sec) 0.9006



10 29.46 2223.4 0.4005

# <sup>1</sup>H NMR of mixture 2-bromo-2-methyloctan-3-one (2g) и 4-bromo-2-methyloctan-3-one (2g') 2:1

Acquisition Time (sec) 1.3518

Freq	uency (I	VHz)	300.13	3		Nux	cieus		ाH	l i		1	umber of Trans	ie <i>nts</i> 1			Original Points Cou	unt	8124	
Point	ts Count	t	65536	;		Pul	se Segue.	nce	zq	19			io ivent	CH	LOROFORM	I-D	Sweep Width (Hz)		6009.62	
Tem	oer <i>a</i> ture	(degree	C) 26.60	0		- 31 31														
2		∽ <sup>Bu</sup>		1		Bu Br												-184		
Chic	proform-o	d									A.39	4.36			73.07 17.3.04 17.3.02 1.3.02	-2.81 -2.78 -2.76			1 167 1 165 1 165 1 162 1 38 1 38 1 38 1 38	115 111 111 0.89 0.89
											0	.51			0.55	2.02		6.0	0 2.90 6.01	1.45 4.46
											<mark>l</mark>	H.			·····	. <mark></mark>				
		7.0	6.	5	6	.0	5.5		5.0	)	4.5 CI	hemic	4.0 al Shift (ppm)	3.5	3.0		2.5 2.	.0	1.5	1.0
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No	. Annotation	(ppm)						
1	0.86	259.6	0.1040	11	1.34	402.8	0.0566	21	2.78	835.D	0.1400	1	Chloro form-d	7.25						
2	0.89	266.4	0.2110	12	1.36	408.5	0.0360	22	2.81	842.3	0.0783									
3	0.91	273.2	0.1073	13	1.56	469.7	0.0209	23	2.97	892.5	0.0080									
4	1.11	332.8	0.1053	14	1.60	480.0	0.0533	24	300	899.3	0.0158									
5	1.15	339.7	0.1047	15	1.62	407.1	0.0735	25	3.02	906.2	0.0191									
7	1.15	350.7	0.1057	17	1.65	494.2 501.3	0.0490	20	3.04	919.9	0.0149									
8	1.26	379.6	0.0525	18	1.70	510.2	0.0056	28	434	1302.2	0.0162									
9	1.29	386.5	0.1081	19	1.84	552.9	1.0000	29	4.36	1309.7	0.0262									
10	1.31	393.8	0.1528	20	2.76	827.6	0.0847	30	4.39	1316.6	0.0160									

#### <sup>13</sup>C NMR of mixture 2-bromo-2-methyloctan-3-one (2g) и 4-bromo-2-methyloctan-3-one (2g') 2:1

Acquisition Time (sec) 0.9006



## <sup>1</sup>H NMR of 1-bromo-3,3-dimethylbutan-2-one, **5a**

#### Acquisition Time (sec) 1.3518

Frequency (NHz) 300.13	Nucleus	ाम	Number of Transients	1	Original Points Count	8124
Points Count 8192	Pulse Sequence	Zq	Solvent	CHLOROFORM-D	Sweep Width (Hz)	6009.62
Temperature (degree C) 26,600						



## <sup>13</sup>C NMR of 1-bromo-3,3-dimethylbutan-2-one, **5a**

Acquisition Time (sec) 0.9006

Frequency (MHz)	75.48	Nucleus	13C	Number of Transients	111	Original Points Count	16316
Points Count	16384	Puise Sequence	zqpq30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	18115.94
Temperature (degree C)	27.500						



5811.7 0.5177 4 77.00 206.03 15550.2 0.0606 5

3

44.21

### <sup>1</sup>H NMR of 2-bromo-1-phenylethanone, **5b**

#### Acquisition Time (sec) 1.3518



# <sup>13</sup>C NMR of 2-bromo-1-phenylethanone, **5b**

Acquisition Time (sec) 0.9006

Frequenc	y (MHz)	75.48	Nucleus	13C	Number of Transients	330	Original Points Count	16316
Points Co	ount	16384	Pulse Sequence	zqpq30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	18115.94
Temperat	ture (degree	<b>C)</b> 24.700						
Br.		<b>C)</b> 24.700				Chloroform-d		
والمادية والمراج		ar de a sta des mais sus Albanematera p	فموار والمردوقة والمردوقة والمروق والمراجع والمردوق	and the state of the second		المراجع والمراجع والمرجع	in the contract of the last of a link of the last of t	in the other tests to be a star of the second
		an dia tanàna mandritra dia					aulantayaa balan fallanaa karaa	ĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸĸ
192	184	176 168 160	152 144 13	36 128 120 1 Chemic	12 104 96 al Shift (ppm)	88 80 72	64 56	48 40 32
No. (pp	om) (Hz)	Height No. Annota	ation (ppm)					
1 30.	.88 2330.7	7 0.2519 1 Chlorof	orm-d 77.00					
2 77.	.00 5811.7	7 0.9618	2.6 E.C.					
3 128	3.83 9723.9	9 0.3605						
4 128	3.91 9729.4	4 0.8657						
5 133	3.93 10108.	7 0.2335						
	05 44404							

#### <sup>1</sup>H NMR of 2-bromo-1-phenylhexan-1-one, **5**c

Acquisition Time (sec) 1.3518



#### <sup>13</sup>C NMR of 2-bromo-1-phenylhexan-1-one, **5**c

Acquisition Time (sec) 0.9006

10

134.52 10152.9 0.1687 11 193.27 14587.1 0.1492



## <sup>1</sup>H NMR of 2-bromo-1-(p-tolyl)ethan-1-one, **5d**

Acquisition Time (sec) 2.7150



## <sup>13</sup>C NMR of 2-bromo-1-(p-tolyl)ethan-1-one, **5d**

Acquisition Time (sec) 0.9050



## <sup>1</sup>H NMR of 2-bromo-1-(2-chlorophenyl)ethan-1-one, **5**e

#### Acquisition Time (sec) 2.7150



10 7.57 2271.7 0.0870

#### <sup>13</sup>C NMR of 2-bromo-1-(2-chlorophenyl)ethan-1-one, 5e

Acquisition Time (sec) 0.9050

6

7

8

9

131.30

132.73

136.24

9909.7 0.0997

10017.6 0.5367 10282.8 0.1471

194.01 14642.8 0.2043



#### <sup>1</sup>H NMR of 2,4-dibromopentan-3-one, **3a** (mixture of *meso-* and *rac-*isomers)

Acquisition Time (sec) 1.3518

6

4.74 1423.9 0.1109 12 5.00

1501.7 0.0823

Frequency (NHz) 300.13	Nucleus 1H	Number of Transients 1	Original Points Count 8124
Points Count 8192	Puise Sequence zo	Solvent CHLOROFORM-D	Sweep Width (Hz) 6009.62
Temperature (degree C) 24,700			



S40

# <sup>13</sup>C NMR of 2,4-dibromopentan-3-one, **3a** (mixture of *meso-* and *rac-*isomers)

Acquisition Time (sec) 0.9006

Frequency (MHz)	75.48	Nucleus	13C	Number of Transients	237	Original Points Count	16316
Points Count	16384	Pulse Sequence	zqpq30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	18115.94
Frequency (IVHz) Points Count Temperature (deque Br Br	75.48 16384 e C) 25.200	Nucleus Pulse Seguence	 	Number of Transients Solvent	237 CHLOROFORM-D Chloroform-d	Original Points Count Sweep Width (Hz)	16316 18115.94 9;61- 10;62- 10
		152 144 11					
No.         (ppm)         (Hz           1         19.50         1471           2         21.74         1640           3         43.82         3307           4         44.01         3321           5         77.00         5811           6         195.99         1479           7         197.99         1494	Height         No.         Annota           .5         0.6282         1         Chlorofo           .7         0.3115         1         Chlorofo           .4         0.1628	tion (ppm) rm-d 77.00	56 126 120 11 Chemic	∠ 104 96 d	30 00 72	04 30 40	40 32 24 16

#### <sup>1</sup>H NMR of 3,5-dibromoheptan-4-one, **3b**

#### Acquisition Time (sec) 1.3518



9 2.12 636.0 0.1158

# <sup>13</sup>C NMR of 3,5-dibromoheptan-4-one, **3b**

#### Acquisition Time (sec) 0.9006

Frequen	ку (MHz)	75.48	Nucleus	13C	Number of Transients	391	Original Points Count	16316
Points (	Count	16384	Pulse Sequence	zqpq30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	18115.94
Tempera	ature (degree	<b>C)</b> 30.700						
Et-	O Er Br					Chloroform-d		
								<u>86.06</u>
								-11.88
-194.34	da a ta san ang	hantilaun, maatanafilisisista satu misyaa	و المحمد المحمد المحمد المحمد من المحمد ا	( اور چیم را شین در شان دون با در آن اور اور اور آن در آن	, al a stability of the state of the	al, any time of a long time at a state of the life of the state of the	teriti metut tetik kenen dan vinanin dan telah meter	an 1 - Ly () H affe an a finistic b. a big fill a star 1 a.
					aran Surah ang tang tang tang tang tang tang tang		, an	
192	2 184	176 168 160	152 144 136	128 120 112 1 Chemic	04 96 88 al Shift (ppm.)	80 72 64	56 48 40	32 24 16 8
No.         (p           1         11           2         26           3         51           4         77           5         19	bpm) (Hz) 1.88 896.5 5.06 1966.9 1.70 3902.0 7.00 5811.7 14.34 14667.8	Height         No.         A           0.4164         1         Ch           0.5491         0.7500         0.9776           0.1700         0.1700         0.1700	Innotation (ppm) Ioroform-d 77.00	Chemic	ar Srint (bhui)			

#### <sup>1</sup>H NMR of 4,6-dibromononane-5-one, **3c**

Acquisition Time (sec) 1.3518



12 1.93 580.2 0.0978 24 7.25 2176.0 0.0516

### <sup>13</sup>C NMR of 4,6-dibromononane-5-one, **3c**

Acquisition Time (sec) 0.9006



5 77.00 5811.7 1.0000 6 194.38 14671.1 0.1827

#### <sup>1</sup>H NMR of 5,7-dibromoundecan-6-one, **3d**

#### Acquisition Time (sec) 1.3518



#### <sup>13</sup>C NMR of 5,7-dibromoundecan-6-one, **3d**

#### Acquisition Time (sec) 0.9006



7 194.38 14671.1 0.1076

#### <sup>1</sup>H NMR of 8,10-dibromoheptadecan-9-one, **3e**

#### Acquisition Time (sec) 1.3518



<sup>13</sup>C NMR of 8,10-dibromoheptadecan-9-one, **3e** 

Acquisition Time (sec) 0.9006



9 194.40 14672.2 0.1154

#### <sup>1</sup>H NMR of 3,5-dibromononan-4-one, **3f**

Acquisition Time (sec) 1.3518



12 2.04 611.0 0.1127

## <sup>13</sup>C NMR of 3,5-dibromononan-4-one, **3f**

Acquisition Time (sec) 0.9006

10 194.35 14668.9 0.1387



### <sup>1</sup>H NMR of 2,4-dibromo-2-methyloctan-3-one, **3g**

Acquisition Time (sec) 1.3518



# <sup>13</sup>C NMR of 2,4-dibromo-2-methyloctan-3-one, **3g**

Acquisition Time (sec) 0.9006

Freq	uency (N	/Hz)	75.48			Nick	us		13C	-	Number of T	rans ients	112		Origina.	l Points	Count	16316	š		
Point	ts Count	- 033	16384			Pulse	Sequence	æ	zqpq30		Solvent		CHLOROFO	RM-D	Sweep	Nidth (H	<b>z</b> )	18115.	94		
Tem	perature	(degree (	26.900																		
-138.04		Br Br									\$\$1 <b>\$4</b> \$4 <b>\$</b> \$4 <b>\$</b> \$ <b></b>		Chloroform-o	-64.02		-45.65		-34.32	-23.19	-13.78	
200	192	184	176	168	160	152	144	136	128	120	112 104 96 Chemical Shift (ppm)	88	80 72	2 64	56	48	40	32	24	16	8
No	(nnm)	(H7)	Height	No	Annota	tion 1	(nnm)														
1	13.78	1040.2	0.4335	1	Chlorofo	rm_d 7	77.00														
2	22.07	1666.1	0.3843			ini-a [ i	1.00														
3	22.01	2203.5	0.6396																		
4	20.10	2203.3	0.0330																		
4	29.39	2217.9	0.7771																		
5	31.00	2339.5	1.0000																		
6	34.32	2590.5	0.8641																		
7	45.65	3445.3	0.8754																		
8	64.02	4831.9	0.2937																		
9	77.00	5811.7	0.8980																		
10	198.04	14947.6	0.2161																		

## <sup>1</sup>H NMR of 1,1-dibromo-3,3-dimethylbutan-2-one, **6a**

#### Acquisition Time (sec) 1.3518

Frequency (NHz) 300.13	Nucleus	ा <b>म</b>	Number of Transients	1	Original Points Count	8124
Points Count 8192	Puise Sequence	ZQ	Solvent	CHLOROFORM-D	Sweep Width (Hz)	6009.62
Temperature (degree C) 27,400						



# <sup>13</sup>C NMR of 1,1-dibromo-3,3-dimethylbutan-2-one, **6a**

Acquisition Time (sec) 0.9006

Frequency (MHz)	75.48	Nucleus	13C	Number of Transients	117	Original Points Count	16316
Points Count	16384	Pulse Sequence	zqpq30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	18115.94
Br	<b>(2)</b> 27.400						-26.79
					Chloroform-d		
8					00.77		
	ler terret gest for let sport for let for the state of th	hand an	analiyada yarahiya dalah kida mayo na jila daga	h fi ya ka	ŧ <b>nadu (</b> 11) fatigation (11) fatigation (11) (11) (11) (11) (11) (11) (11) (11	ĸŧŧŧĸĸŧĸŗŧĸŧŧŧŧŧŧŧĸŧĸŧĸŧĸŧĸŧĸŧĸ	
200 192	Height         No.         Annota	160 152 144	136 128 120 Chemica	112 104 96 al Shift (ppm)	88 80 72	64 56 4	8 40 32 24

No.	(ppm)	(Hz)	Height	No.	Annotation	Γ
1	26.79	2022.2	1.0000	1	Chloroform-d	Γ
2	37.34	2818.3	0.5524	) 	2 · · · · · · · · · · · · · · · · · · ·	1
3	43.98	3319.2	0.3209			
4	77.00	5811.7	0.6810			
5	201.52	15209.7	0.1223			

## <sup>1</sup>H NMR of 2,2-dibromo-1-phenylethanone, **6b**

Acquisition Time (sec) 1.3518



#### <sup>13</sup>C NMR of 2,2-dibromo-1-phenylethanone, **6b**

Acquisition Time (sec) 0.9006



# <sup>1</sup>H NMR of 2,2-dibromo-1-(p-tolyl)ethan-1-one, **6d**

Acquisition Time (sec) 2.7150

Frequency (IVHz)	300.13	Nuckus	1H	Number of Transients	1	Original Points Count	16316
Points Count	16384	Pulse Sequence	ZQ	Solvent	CHLOROFORM-D	Sweep Width (Hz)	6009.62
Temperature (dec	Chloroform-d			30// 6/1		Sweep Vickin (F2)	
1.98	1.99	0.98					3.00
, <mark>,</mark> 8.0	7.5 7.0	6.5 6	.0 5.5 Chemica	 5.0 4. I Shift (αρπ.)	5 4.0	3.5 3.0	2.5
No.         (ppm)         (H           1         2.44         731           2         6.68         200           3         7.25         217           4         7.28         218           5         7.31         219	z)         Height         No.         Annotation           .1         1.0000         1         Chloroform           5.0         0.5349         5.0         0.3806           5.9         0.2286         4.3         0.2445	n (ppm) -d 7.25					

 6
 7.96
 2389.1
 0.3200

 7
 7.99
 2397.5
 0.2861

# <sup>13</sup>C NMR of 2,2-dibromo-1-(p-tolyl)ethan-1-one, **6d**

Acquisition Time (sec) 0.9050

Frequency (MHz)	75.48	Nucleus	13C	Number of Transients 512
Original Points Count	16316	Points Count	16384	Pulse Sequence zapa30
Solvent	CHLOROFORM-D	Sweep Width (Hz)	18028.85	Temperature (degree C) 27.009
			18028.85	Temperature (keqree C) 27.009 Chloroform-d
a han frank ha tra tha tra children a barbara			and and the state of the state	
184         176           No.         (ppm)         (Hz)           1         21.81         1646.4           2         39.81         3004.4           3         77.00         5811.6           4         128.10         9668.7           5         129.64         9784.3           6         129.82         9798.6           7         145.70         10997.0           8         185.62         14010.1	Height         No.         Annotatio           0.1888         1         Chloroform           0.1410         1         Chloroform           1.0000         0.0566         0.2844           0.5257         0.0927         0.0597	144 136 128 n (ppm) ⊷d 77.00	120 112 104 Chemical SI	14 96 88 80 72 64 56 48 40 32 24 16 I Shift (ppm)

# <sup>1</sup>H NMR of 2,2-dibromo-1-(2-chlorophenyl)ethan-1-one, **6e**

#### Acquisition Time (sec) 2.7150

Frequency (	MHz)	300.13		Nucleus		1H		Number of Transients	1	Original Points Count	16316
Points Coun	ıt	16384		Puise Sequence	æ	ZQ		Solvent	CHLOROFORM-D	Sweep Width (Hz)	6009.62
Temperature	e (degree C	27.005									
$\bigcirc$	CI Br	ir				-6.76					
			7.62 7.62 7.47 7.47 7.48	7.35 -7.125 -7.40 -7.35 -7.25 -7.40	1						
				MAL	·····		· · · ··· ·				·····
			1.00 Z			1.00 H					
8.5		8.0	7.5	5	7.0		6.5 Cher	6.0 nical Shift (ppm)	5.5	5.0 4	.5 4.0
No. (ppm)	(Hz) I	Height No.	(ppm) (H	Hz) Height	No.	Annotation	(ppm)				
1 6.76	2027.4 1	1.0000 9	7.43 223	31.0 0.0875	1 (	Chloroform-d	7.25				
2 7.25	2176.0 0	0.4770 10	7.45 223	36.1 0.6107							
3 7.34	2203.8 0	0.0810 11	7.46 223	39.1 0.3184							
4 7.35	2206.8 0	0.0891 12	7.47 224	42.0 0.1696							
5 7.36	2209.7 0	0.1037 13	7.47 224	43.5 0.1524							
6 7.37	2212.3 0	0.1531 14	7.59 227	79.0 0.2639							
7 7.39	2217.4 0	0.1320 15	7.62 228	86.0 0.1855							
8 7.40	2220.0 0	0.1757    16	7.62 228	87.5 0.1832							

# <sup>13</sup>C NMR of 2,2-dibromo-1-(2-chlorophenyl)ethan-1-one, **6e**

#### Acquisition Time (sec) 0.9050

Frequency	(MHz)	75.48	Nuckus	13C	Number of Transients	256	Original Points Count	16316
Points Co.	unt	16384	Puise Sequence	zqpq30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	18028.85
Temperatu	ire (degree C	27.129						
Temperatu	CI Br	<b>3</b> 27.129		<mark>-130.45</mark>		Chlorofo 8, 12 -	rm-d	
and the state of the		<b>******</b> ******************************			«\\\\\ \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\		\\##?\@\###############################	
 192	184	176 168 160	) 152 144	136 128 120 Chemic		 96 88 80		48 40 32
No. (ppr 1 42.0 2 77.0 3 107	n) (Hz) 15 3173.8 10 5811.6	Height No. Annota 0.1968 1 Chlorofo 0.9912	tion (ppm) rm-d 77.00					
4 130	45 9845 9	0.2104						
5 130.4	40 0040.9 00 0880 0	0.4003						
6 130.3	95 9883 3	0.1510						
7 132	97 10036 3	0.1503						
8 134	07 10118.8	0.0731						
0 104.		0.0101						

9 188.76 14246.7 0.0432

<sup>1</sup>H NMR of pentan-3-one, 7a

#### Acquisition Time (sec) 1.3518

Frequency (IVHz) 300.13	Mucleus 1H	Number of Transients 1	Original Points Count 8124
Points Count 8192	Pulse Sequence za	Solvent CHLOROFORM-D	Sweep Width (Hz) 6009.62
Temperature (degree C) 29.200			



7 2.38 715.2 0.1806



### HRMS of 8-bromoheptadecan-9-one, 2e









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#### **Display Report** Analysis Info Acquisition Date 22.03.2018 15:24:46 Analysis Name D:\Data\Kolotyrkina\2018\Kapustina\0322026.d Method tune\_low.m Operator BDAL@DE Sample Name /KAPN 68\_90 Instrument / Ser# micrOTOF 10248 Comment C9H16Br2O mH 298.9640/ clb added, Acquisition Parameter Source Type ESI Ion Polarity Positive Set Nebulizer 0.4 Bar 180 °C Focus Not active Set Dry Heater Scan Begin Scan End Set Capillary Set End Plate Offset 50 m/z 4500 V Set Dry Gas 4.0 l/min Set Divert Valve 3000 m/z -500 V Waste Intens. +MS, 0.2-0.9min #(9-56) x106 1.0 0.8 322.9435 0.6 0.4 320.9452 324.9415 0.2 323.9468 321.9486 320.1301 325.9446 N 0.0 C9H16Br2O, M+nNa ,320.95 322.9440 2000 1500 320.9460 324.9419 1000 500 323.9473 321.9494 325.9453 0 318 320 328 322 326 324 m/z Bruker Compass DataAnalysis 4.0 printed: 22.03.2018 15:27:57 Page 1 of 1

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