

# Supporting Information

## Acyl Radicals from Acylsilanes: Photoredox Catalyzed Synthesis of Unsymmetrical Ketones

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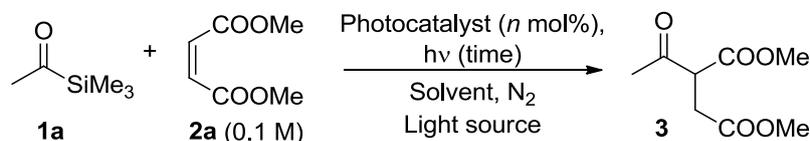
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### CONTENT

<b>1. Optimization of Conditions</b>	<b>p. S2</b>
<b>2. ON-OFF Experiments</b>	<b>p. S3</b>
<b>3. Electrochemical Data</b>	<b>p. S4</b>
<b>4. Spectroscopic Data</b>	<b>p. S5</b>
<b>5. Chemical Quenching Experiments</b>	<b>p. S7</b>
<b>6. Experimental Section</b>	<b>p. S8</b>
<b>7. References</b>	<b>p. S17</b>
<b>8. Copy of <math>^1\text{H}</math> and <math>^{13}\text{C}</math> NMR</b>	<b>p. S18</b>

# 1 Optimization of Conditions

**Table S1.** Optimization of the reaction conditions.<sup>a</sup>

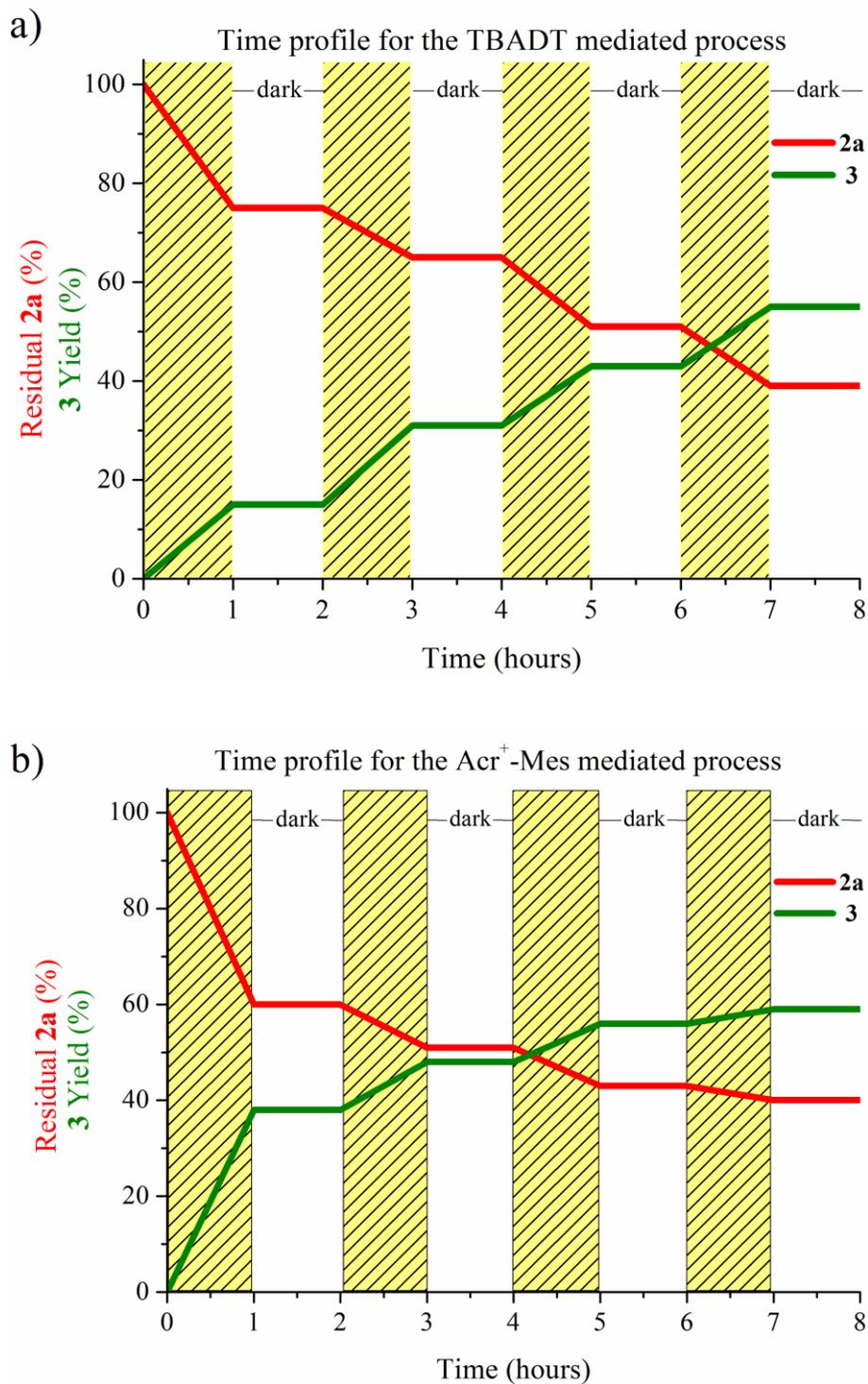


Entry	Photocatalyst	<b>1a</b> (M)	Solvent	Irradiation Time (h)	Light Source	<b>2a</b> Consumption (%)	<b>3</b> Yield (%) <sup>b</sup>
1	TBADT (2 mol%)	0.1	MeCN	8	310 nm	30	62 <sup>c</sup>
2	TBADT (2 mol%)	0.1	MeCN-H <sub>2</sub> O 5/1	8	310 nm	72	71
3	TBADT (2 mol%)	0.1	0.5 M LiClO <sub>4</sub> MeCN-H <sub>2</sub> O 5/1	8	310 nm	100	57 <sup>d</sup>
<b>4</b>	<b>TBADT (2 mol%)</b>	<b>0.12</b>	<b>MeCN-H<sub>2</sub>O 5/1</b>	<b>8</b>	<b>310 nm</b>	<b>100</b>	<b>72</b>
5	TBADT (2 mol%)	0.12	MeCN-H <sub>2</sub> O 2/1	8	310 nm	100	47
6	TBADT (2 mol%)	0.12	MeCN-TFE 5/1	8	310 nm	32	5
7	TBADT (2 mol%)	0.12	MeCOMe-H <sub>2</sub> O 5/1	8	310 nm	100	52
8	TBADT (1 mol%)	0.12	MeCN-H <sub>2</sub> O 5/1	8	310 nm	70	55 <sup>d</sup>
9	TBADT (2 mol%)	0.12	MeCN-H <sub>2</sub> O 5/1	8	366 nm	65	52
10	TBADT (2 mol%)	0.12	MeCN-H <sub>2</sub> O 5/1	8	SolarBox <sup>e</sup>	100	63
11	-	0.12	MeCN-H <sub>2</sub> O 5/1	8	310 nm	100	4
12	TBADT (2 mol%)	0.12	MeCN-H <sub>2</sub> O 5/1	8	-	< 5	n.d.
13	Acr <sup>+</sup> -Mes (5 mol%)	0.12	CHCl <sub>3</sub>	48	410 nm	< 5	Traces
14	Acr <sup>+</sup> -Mes (5 mol%)	0.12	CH <sub>2</sub> Cl <sub>2</sub> -MeOH 9/1	48	410 nm	13	4
15 <sup>f</sup>	Acr <sup>+</sup> -Mes (5 mol%)	0.12	CH <sub>2</sub> Cl <sub>2</sub> -MeOH 9/1	48	410 nm	14	6
16 <sup>g</sup>	Acr <sup>+</sup> -Mes (5 mol%)	0.12	CH <sub>2</sub> Cl <sub>2</sub> -MeOH 9/1	48	410 nm	30	21
17	Acr <sup>+</sup> -Mes (5 mol%)	0.12	CH <sub>2</sub> Cl <sub>2</sub> -MeOH 1/1	48	410 nm	23	20
18	Acr <sup>+</sup> -Mes (5 mol%)	0.12	MeOH	48	410 nm	52	41
19	Acr <sup>+</sup> -Mes (5 mol%)	0.15	MeOH	48	410 nm	68	65
20	Acr <sup>+</sup> -Mes (10 mol%)	0.15	MeOH	48	410 nm	85	75
<b>21<sup>h</sup></b>	<b>Acr<sup>+</sup>-Mes (10 mol%)</b>	<b>0.15</b>	<b>MeOH</b>	<b>48</b>	<b>410 nm</b>	<b>100</b>	<b>81</b>
22	TPT (2 mol%)	0.12	MeCN	24	410 nm	< 5	n.d.
23	TPT (2 mol%)	0.12	MeCN-H <sub>2</sub> O 5/1	24	410 nm	< 5	n.d. <sup>c</sup>
24 <sup>i</sup>	Ru(bpz) <sub>3</sub> <sup>2+</sup> (5 mol%)	0.12	MeCN-H <sub>2</sub> O 5/1	24	450 nm	< 5	n.d.
25	DCA (0.75 mol%)	0.12	MeCN	24	410 nm	19	n.d.
26	DCA (5 mol%)	0.12	CHCl <sub>3</sub>	24	410 nm	39	9

<sup>a</sup> Reaction conditions: **1a** (0.1-0.15 M), **2a** (0.1 M), photocatalyst (*n* mol%) in 1 mL of the chosen solvent under deaerated conditions. TBADT = (*n*Bu<sub>4</sub>N)<sub>4</sub>[W<sub>10</sub>O<sub>32</sub>]; Acr<sup>+</sup>-Mes = 9-mesityl-10-methylacridinium; TPT = 2,4,6-triphenylpyrylium tetrafluoroborate; DCA: 9,10-dicyanoanthracene.

<sup>b</sup> Gas Chromatography (GC) yields referred to the consumption of the limiting reagent (**2a**), using *n*-dodecane as internal standard. <sup>c</sup> A complex mixture was formed. <sup>d</sup> Some filming on the tube walls has been observed. <sup>e</sup> Irradiation carried out with a solar simulator equipped with a 1.5 kW Xe lamp (500 W·m<sup>-2</sup>). <sup>f</sup> Reaction performed in the presence of 0.1 M Hantzsch ester. <sup>g</sup> Reaction performed in the presence of 0.02 M thiophenol. <sup>h</sup> Air-equilibrated solution. <sup>i</sup> Three cycles of freeze-pump-thaw were performed prior to irradiation.

## 2 ON-OFF Experiments



**Figure S1.** Time profile for the reaction of **1a** with **2a** to give **3** in the presence of: (a) TBADT and (b) Acr<sup>+</sup>-Mes under optimized reaction conditions (see Table 1). Light was switched off during the "dark" periods.

### 3 Electrochemical Data

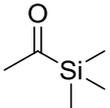
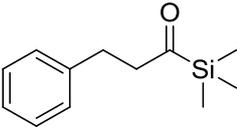
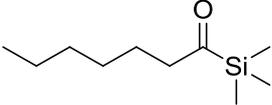
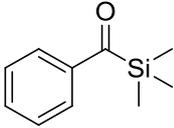
The electrochemical measurements were carried out by a BASi computer-controlled electrochemical analyzer. Electrochemical measurements (cyclic voltammetry) were performed in a three-electrode cell (volume 5 mL; acetonitrile/water 5:1 as solvent,  $n\text{Bu}_4\text{NPF}_6$  0.05 M as the supporting electrolyte, 2 mM concentration of the tested compound) at glassy carbon (diameter 2 mm, BASi) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (3 M NaCl) as the reference electrode. Scan speed was  $100 \text{ mV}\cdot\text{s}^{-1}$ .

The potential range investigated was 0/+1.80 V vs Ag/AgCl (3 M NaCl). The potentials measured were then referred to SCE by applying the equation:

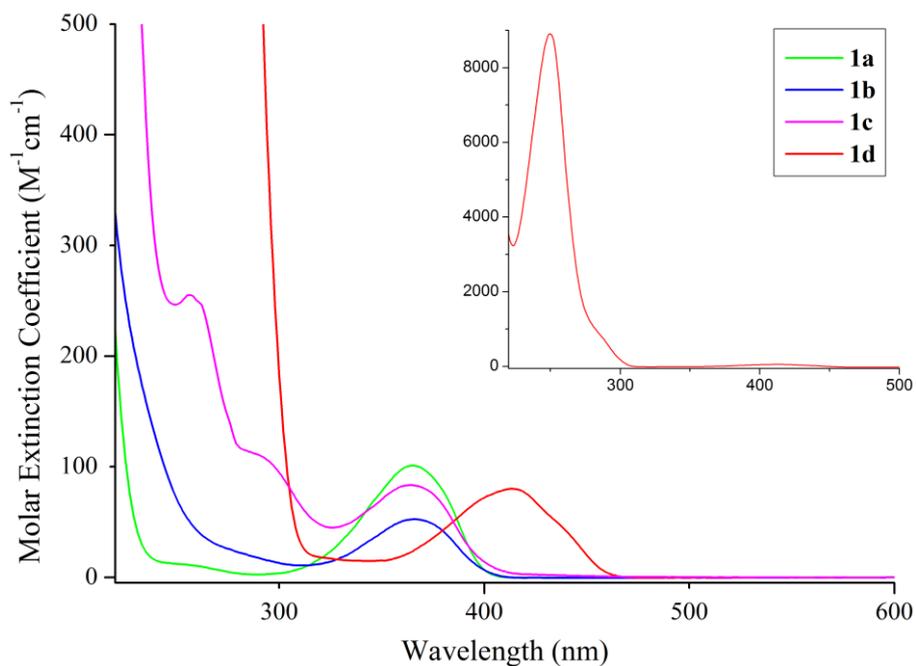
$$E (\text{vs SCE}) = E (\text{vs Ag/AgCl; 3 M NaCl}) - 35 \text{ mV}$$

All examined compounds showed a quasi-reversible or reversible behavior.

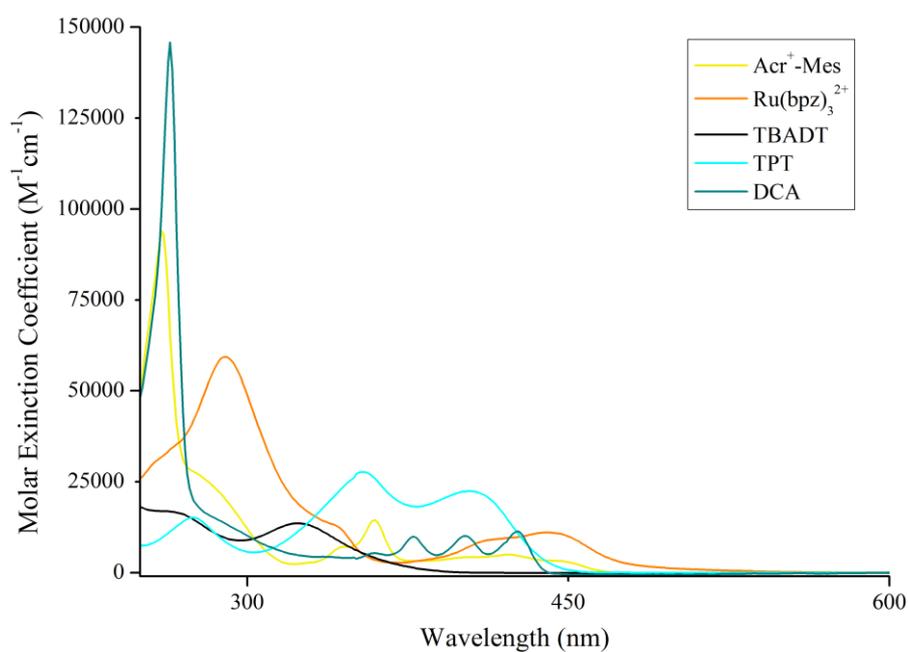
**Table S2.** Oxidation potentials (V vs SCE) of compounds **1a-d**.

<b>1a</b>		+1.46	<b>1c</b>		+1.26
<b>1b</b>		+1.31	<b>1d</b>		+1.51

## 4 Spectroscopic Data



**Figure S2.** UV-Vis spectra of acylsilanes used in this work (from 1 mM solutions in MeCN). The inset shows the full spectrum of **1d** (from a 1 mM solution in MeCN).



**Figure S3.** UV-Vis spectra of photocatalysts used in this work from  $5 \times 10^{-6}$  M solutions in MeCN or CHCl<sub>3</sub> (only for DCA).

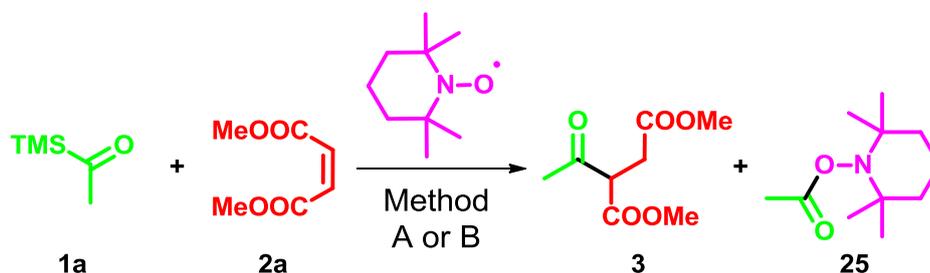
**Table S3.** Photophysical and electrochemical properties of photocatalysts used in this work. All energy values are in eV; potentials are in V vs SCE and wavelength is expressed in nanometers.<sup>S1-S3</sup>

	<sup>1</sup> PC <i>excited state energy, eV</i>	<sup>3</sup> PC <i>excited state energy, eV</i>	<sup>1</sup> PC <i>excited state redox potential E (<sup>1</sup>PC/PC<sup>+</sup>), V vs SCE</i>	<sup>3</sup> PC <i>excited state redox potential E (<sup>3</sup>PC/PC<sup>+</sup>), V vs SCE</i>	<b>Absorption maximum (<math>\lambda_{\max}</math>), nm</b>
<b>TBADT</b>	-	3.41	-	+2.44	323
<b>Acr<sup>+</sup>-Mes</b>	LE: 2.67 CT: 2.57	LE: 1.94	LE: +2.18 CT: +2.08	LE: +1.45 CT: +1.88	425
<b>Ru<sup>II</sup>(bpz)<sub>3</sub></b>	-	2.12	-	+1.45	443
<b>TPT</b>	2.83	2.30	+2.55	+2.02	415
<b>DCA</b>	2.90	1.81	+1.99	+0.90	422

LE: Locally Excited; CT: Charge Transfer. See Ref. S1.

## 5 Chemical Quenching Experiments

**Table S4.** Chemical Quenching Experiments.



Photocatalyst	Method	2a	3 Yield, <sup>a</sup> %	25 Yield, <sup>b</sup> %	2a Consumption, %
TBADT	A	yes	42	30	> 95
TBADT	A	no	-	30	-
Acr <sup>+</sup> -Mes	B	yes	n.d.	46	80
Acr <sup>+</sup> -Mes	B	no	-	19	-

<sup>a</sup> The yield has been calculated by considering **2a** as the limiting reagent.

<sup>b</sup> The yield has been calculated by considering TEMPO as the limiting reagent.

Trapping experiments were carried out both in the presence and the absence of olefin **2a**.

**Method A:** **1a** (0.12 M), [**2a** (0.1 M)], TBADT (2 mol%) and TEMPO (0.1 M) in 1 mL of MeCN-H<sub>2</sub>O 5/1 irradiated at 310 nm.

**Method B:** **1a** (0.15 M), [**2a** (0.1 M)], Acr<sup>+</sup>-Mes (10 mol%) and TEMPO (0.1 M) in 1 mL of MeOH irradiated at 410 nm.

Compound **25** was quantified by means of a calibration curve using an authentic sample synthesized as described in the literature (GC analysis; internal standard: dodecane).<sup>S4</sup>

## 6 Experimental Section

**General:** Acetylsilane **1a** was commercially available and used as received, while acylsilanes **1b**,<sup>S5</sup> **1c**<sup>S5</sup> and **1d**<sup>S6</sup> were prepared according to procedures adapted from the literature (see below). The photocatalyst TBADT has been prepared according to a published procedure,<sup>S7</sup> while Acr<sup>+</sup>-Mes tetrafluoroborate, TPT, Ru(bpz)<sub>3</sub>[PF<sub>6</sub>]<sub>2</sub> and DCA were commercially available. All solvents were of HPLC purity grade and employed for photochemical reactions as received. NMR spectra were recorded on a 300 (for <sup>1</sup>H) or 75 (for <sup>13</sup>C) MHz spectrometer; the attributions were made on the basis of <sup>1</sup>H and <sup>13</sup>C NMR. Data for <sup>1</sup>H NMR are reported as follows: chemical shift referred to TMS ( $\delta$  ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sext = sextuplet, m = multiplet), coupling constant (Hz) and integration. Data for <sup>13</sup>C NMR are reported in terms of chemical shift.

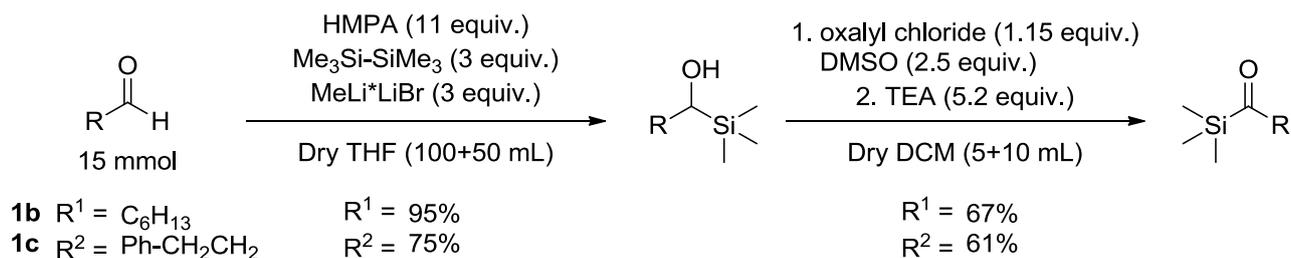
Reactions were monitored by gas chromatographic (GC) analyses (HP-5 capillary column), using *n*-dodecane as external standard. Chromatographic purification of products was accomplished using flash chromatography on 60 Å, 230-400 mesh silica gel. Thin-layer chromatography (TLC) was performed on silica gel 60 F-254 plates. Visualization of the developed plates was performed by fluorescence quenching or by KMnO<sub>4</sub> staining. UV-Vis spectra were recorded with a double beam spectrophotometer equipped with Deuterium lamp (190-350 nm) and Halogen lamp (330-900 nm) and a Photomultiplier R928. Quantum yields of product formation for Acr<sup>+</sup>-Mes<sup>S8</sup> and TBADT<sup>S9</sup> mediated processes were determined according to procedures already available in the literature.

### General procedure for the photoredox catalyzed acylation of electron-poor olefins.

**Method A:** The olefin **2** (0.1 M) and TBADT (2 mol%) were dissolved in 15 mL of a MeCN/H<sub>2</sub>O 5:1 mixture in a quartz tube. The resulting solution was N<sub>2</sub>-flushed for five minutes and then acylsilane **1** (0.12 M) was added. In case of particularly volatile compounds (e.g. acetyltrimethylsilane or methyl vinyl ketone), these were added at the end of the N<sub>2</sub>-flushing. The quartz tube was capped with a septum and the reaction mixture was irradiated in a multi-lamp apparatus fitted with 10×15 W phosphor-coated lamps (emission centered at 310 nm) for 8 h. The solvent was then removed under reduced pressure and the residue was purified through flash chromatography to give the purified product.

**Method B:** The acylsilane **1** (0.15 M) and the olefin **2** (0.1 M) were dissolved in 10 mL of MeOH in a vial; 9-mesityl-10-methylacridinium tetrafluoroborate (Acr<sup>+</sup>-Mes, 10 mol%) was then added. The resulting air-equilibrated solution was divided into 10 vials and irradiated with 10×1 W LEDs (410 nm) for 48 h. The resulting mixtures were reunited, the solvent evaporated under reduced pressure and the residue purified through flash chromatography to give the purified product.

## Synthesis of 1-(trimethylsilyl)heptan-1-one (**1b**) and 3-phenyl-1-(trimethylsilyl)propan-1-one (**1c**)



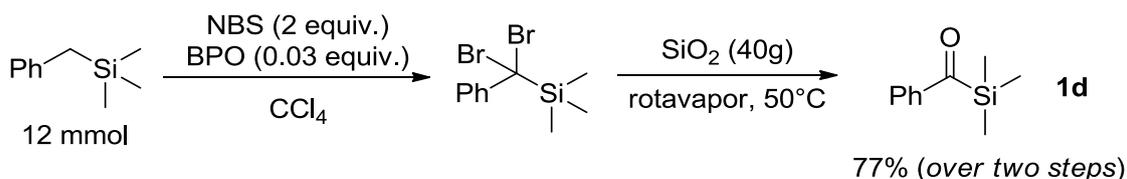
A brief description of the synthetic procedures is reported here. The first step is the silylation of the aldehyde.<sup>S10</sup>

To a mixture of hexamethylphosphoramide (HMPA) and hexamethyldisilane kept under nitrogen at 0 °C placed in a 3-necks round-bottom flask equipped with a pressure-equalizing dropping funnel MeLi·LiBr was added. The resulting brick red solution was stirred for 5 min and tetrahydrofuran was added. The solution was cooled down at -78 °C and the aldehyde was added dropwise. The mixture was stirred overnight and quenched with water and washed with acidic water. After neutralization, the organic phases were collected, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The raw product was used without any further purification.

The second step consists in the Swern oxidation of the silyl alcohol intermediate.<sup>S11</sup>

Anhydrous dimethylsulfoxide (DMSO) in dichloromethane was added dropwise by means of a pressure-equalizing dropping funnel to a solution of oxalyl chloride in dichloromethane kept under nitrogen at -78 °C placed in a 3-necks round-bottom flask equipped with two pressure-equalizing dropping funnels. Then, the alcohol was dissolved in dichloromethane and added dropwise through a second pressure-equalizing dropping funnel. Finally, triethylamine (TEA) was added by means of a syringe. After 3 h, the mixture was extracted with petroleum ether: the organic phases were collected, dried, the solvent removed under reduced pressure and the residue was distilled under reduced pressure to afford the desired product. The spectroscopic data of **1b** and **1c** were in accordance with the literature.<sup>S5,S6</sup>

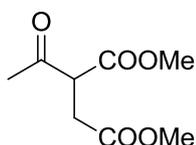
## Synthesis of phenyl(trimethylsilyl)methanone (**1d**)



The first step consists in the dibromination of the benzylsilane. In a 3-neck round-bottom flask, a mixture of benzyltrimethylsilane, *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) in CCl<sub>4</sub>

was heated to reflux overnight; the formation of a white solid was observed. The mixture was cooled at room temperature and filtered to remove the precipitate, the solvent was removed in vacuo and the raw product was used without any further purification. The second step consists in the oxidation of the resulting  $\alpha,\alpha$ -dibromobenzylsilane. The crude product was dissolved in dichloromethane in the presence of  $\text{SiO}_2$  (60 Å, 230-400 mesh) and the resulting suspension was heated (50 °C) under reduced pressure by means of a rotary evaporator. The solvent was removed within a few minutes, but heating was continued, while the colour of  $\text{SiO}_2$  slowly turned to a bright yellow. After 5 h,  $\text{SiO}_2$  was rinsed several times with diethyl ether to give a solution of pure **1d**.<sup>S12</sup> The spectroscopic data of **1d** were in accordance with the literature.<sup>S6</sup>

### Synthesis of dimethyl 2-acetylsuccinate (**3**)



Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 188  $\mu\text{L}$  (1.5 mmol, 0.1 M) of dimethyl maleate (**2a**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 195 mg of dimethyl 2-acetylsuccinate (**3**, 69% yield) as a colorless oil.



Flow conditions (see image of the apparatus on the left): reactor volume: 12 mL; flow rate: 0.05 mL  $\text{min}^{-1}$ , PTFE tube wrapped around a medium pressure Hg-lamp (**3** yield: 72%).

Sunlight irradiation: 2 days, 8 h per day, in a reaction vessel (see the image on the right) on the window ledge (**3** yield: 73%).

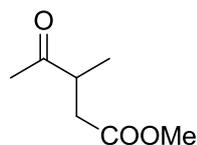


Method B: From 215  $\mu\text{L}$  (1.5 mmol, 0.15 M) of **1a** and 125  $\mu\text{L}$  (1.0 mmol, 0.1 M) of **2a**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 153 mg of dimethyl 2-acetylsuccinate (**3**, 81% yield) as a colorless oil.

Sunlight irradiation: 5 days, 8 h per day, in a reaction vessel on the window ledge (Yield: 71%).

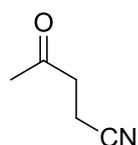
The spectroscopic data of **3** were in accordance with the literature.<sup>S13</sup> Anal. Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_5$ : C, 51.06; H, 6.43. Found: C, 51.1; H, 6.4.

### Synthesis of methyl 3-methyl-4-oxopentanoate (**4**)



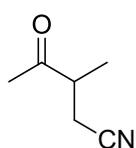
Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 159  $\mu\text{L}$  (1.5 mmol, 0.1 M) of methyl crotonate (**2b**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 130 mg of methyl 3-methyl-4-oxopentanoate (**4**, 60% yield) as a colorless oil. The spectroscopic data of **4** were in accordance with the literature.<sup>S14</sup> Anal. Calcd. for  $\text{C}_7\text{H}_{12}\text{O}_3$ : C, 58.32; H, 8.39. Found: C, 58.3; H, 8.4.

### Synthesis of methyl 4-oxopentanenitrile (**5**)



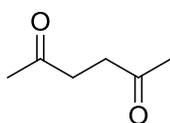
Method A: From 322  $\mu\text{L}$  (2.25 mmol, 0.15 M) of acetyltrimethylsilane (**1a**) and 98  $\mu\text{L}$  (1.5 mmol, 0.1 M) of acrylonitrile (**2c**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 68 mg of methyl 4-oxopentanenitrile (**5**, 47% yield) as a colorless oil. The spectroscopic data of **5** were in accordance with the literature.<sup>S15</sup> Anal. Calcd. for  $\text{C}_5\text{H}_7\text{NO}$ : C, 61.84; H, 7.27; N, 14.42. Found: C, 61.8; H, 7.3; N, 14.4.

### Synthesis of 3-methyl-4-oxopentanenitrile (**6**)



Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 122  $\mu\text{L}$  (1.5 mmol, 0.1 M) of crotonitrile (**2d**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 93 mg of 3-methyl-4-oxopentanenitrile (**6**, 56% yield) as a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 2.85 (sext,  $J = 7$  Hz, 1H), 2.58 (dd,  $J_1 = 17$  Hz,  $J_2 = 6$  Hz, 1H), 2.40 (dd,  $J_1 = 17$  Hz,  $J_2 = 8$  Hz, 1H), 2.20 (s, 3H), 1.31 (d,  $J = 7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 207.8, 118.5, 43.4, 27.9, 19.6, 16.4. Anal. Calcd. for  $\text{C}_6\text{H}_9\text{NO}$ : C, 64.84; H, 8.16; N, 12.60. Found: C, 64.8; H, 8.2; N, 12.6.

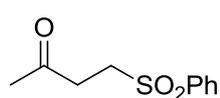
### Synthesis of hexane-2,5-dione (**7**)



Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 125  $\mu\text{L}$  (1.5 mmol, 0.1 M) of methyl vinyl ketone (**2e**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 92 mg of hexane-2,5-dione (**7**, 55% yield) as a colorless oil.

Method B: From 215  $\mu\text{L}$  (1.5 mmol, 0.15 M) of **1a** and 83  $\mu\text{L}$  (1.0 mmol, 0.1 M) of **2e**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 79 mg of hexane-2,5-dione (**7**, 71% yield) as a colorless oil. The spectroscopic data of **7** were in accordance with the literature.<sup>S16,S17</sup> Anal. Calcd. for  $\text{C}_6\text{H}_{10}\text{O}_2$ : C, 63.14; H, 8.83. Found: C, 63.1; H, 8.8.

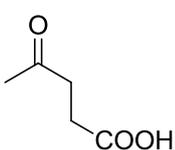
### Synthesis of 4-(phenylsulfonyl)butan-2-one (**8**)



Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 251 mg (1.5 mmol, 0.1 M) of phenyl vinyl sulfone (**2f**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 194 mg of 4-(phenylsulfonyl)butan-2-one (**8**, 61% yield) as a colorless oil.

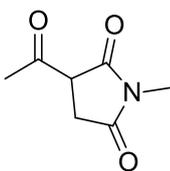
Method B: From 215  $\mu\text{L}$  (1.5 mmol, 0.15 M) of **1a** and 167 mg (1.0 mmol, 0.1 M) of **2f**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 151 mg of 4-(phenylsulfonyl)butan-2-one (**8**, 75% yield) as a colorless oil. The spectroscopic data of **8** were in accordance with the literature.<sup>S18</sup> Anal. Calcd. for  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}$ : C, 56.58; H, 5.70. Found: C, 56.6; H, 5.7.

### Synthesis of 4-oxopentanoic acid (**9**)



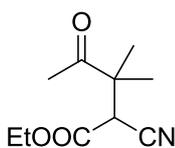
Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 147 mg (1.5 mmol, 0.1 M) of maleic anhydride (**2g**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 110 mg of 4-oxopentanoic acid (**9**, 63% yield) as a colorless oil. The spectroscopic data of **9** were in accordance with the literature.<sup>S19</sup> Anal. Calcd. for  $\text{C}_5\text{H}_8\text{O}_3$ : C, 51.72; H, 6.94. Found: C, 51.7; H, 7.0.

### Synthesis of 3-acetyl-1-methylpyrrolidine-2,5-dione (**10**)



Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 167 mg (1.5 mmol, 0.1 M) of *N*-methylmaleimide (**2h**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 184 mg of 3-acetyl-1-methylpyrrolidine-2,5-dione (**10**, 79% yield) as a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 3.95 (dd,  $J_1 = 9$  Hz,  $J_2 = 4$  Hz, 1H), 3.31 (dd,  $J_1 = 18$  Hz,  $J_2 = 4$  Hz, 1H), 2.96 (s, 3H), 2.65 (dd,  $J_1 = 18$  Hz,  $J_2 = 9$  Hz, 1H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 199.3, 175.6, 172.6, 53.9, 30.3, 29.7, 25.3. Anal. Calcd. for  $\text{C}_7\text{H}_9\text{NO}_3$ : C, 54.19; H, 5.85; N, 9.03. Found: C, 54.2; H, 5.9; N, 9.0.

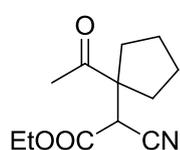
### Synthesis of ethyl 2-cyano-3,3-dimethyl-4-oxopentanoate (**11**)



Method A: From 258  $\mu\text{L}$  (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 230  $\mu\text{L}$  (1.5 mmol, 0.1 M) of ethyl 2-cyano-3-methylbut-2-enoate (**2i**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 186 mg of ethyl 2-cyano-3,3-dimethyl-4-oxopentanoate (**11**, 63% yield) as a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 4.17 (q,  $J = 7$  Hz, 2H), 4.10 (s, 1H), 2.20 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H), 1.25 (t,  $J = 7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 209.3, 164.8, 115.4, 62.9, 48.8, 45.1,

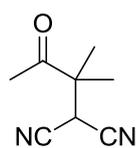
25.3, 24.7, 20.8, 13.9. Anal. Calcd. for C<sub>10</sub>H<sub>15</sub>NO<sub>3</sub>: C, 60.90; H, 7.67; N, 7.10. Found: C, 60.9; H, 7.7; N, 7.1.

### Synthesis of ethyl 2-(1-acetylcyclopentyl)-2-cyanoacetate (**12**)



Method A: From 258  $\mu$ L (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 268  $\mu$ L (1.5 mmol, 0.1 M) of ethyl 2-cyano-2-cyclopentylideneacetate (**2j**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 214 mg of ethyl 2-(1-acetylcyclopentyl)-2-cyanoacetate (**12**, 64% yield) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 4.21 (q,  $J$  = 7 Hz, 2H), 4.16 (s, 1H), 2.39-2.30 (m, 1H), 2.24 (s, 3H), 1.95-1.77 (m, 7H), 1.29 (t,  $J$  = 7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 208.0, 165.0, 116.0, 62.8, 59.3, 44.6, 35.8, 33.2, 26.7, 25.9, 25.0, 13.8. Anal. Calcd. for C<sub>12</sub>H<sub>17</sub>NO<sub>3</sub>: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.5; H, 7.7; N, 6.3.

### Synthesis of 2-(2-methyl-3-oxobutan-2-yl)malononitrile (**13**)



Method A: From 258  $\mu$ L (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 159  $\mu$ L (1.5 mmol, 0.1 M) of 2-(propan-2-ylidene)malononitrile (**2k**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 200 mg of 2-(2-methyl-3-oxobutan-2-yl)malononitrile (**13**, 89% yield) as a colorless oil. <sup>1</sup>H NMR<sup>S18</sup> (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 4.13 (s, 1H), 2.26 (s, 3H), 1.49 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 206.8, 111.8, 51.1, 30.8, 24.3, 22.0. Anal. Calcd. for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.0; H, 6.7; N, 18.6.

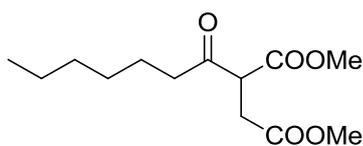
### Synthesis of dimethyl 2-heptanoylsuccinate (**14**)



Method A: From 258  $\mu$ L (1.8 mmol, 0.12 M) of acetyltrimethylsilane (**1a**) and 231 mg (1.5 mmol, 0.1 M) of 2-benzylidenemalononitrile (**2l**). A complex mixture was obtained.

Method B: From 215  $\mu$ L (1.5 mmol, 0.15 M) of **1a** and 154 mg (1.0 mmol, 0.1 M) of **2l**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 7:3 as the eluant) afforded 163 mg of 2-(2-methyl-3-oxobutan-2-yl)malononitrile (**13**, 55% yield) as an oil. <sup>1</sup>H NMR<sup>S20</sup> ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz)  $\delta$ : 8.23 (m, 5H), 5.77 (d,  $J$  = 7 Hz, 1H), 5.99 (d,  $J$  = 7 Hz, 1H), 2.90 (s, 3H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 75 MHz)  $\delta$ : 203.0, 132.9, 130.4, 130.3, 130.0, 113.8, 113.46, 58.5, 28.2, 26.0. Anal. Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O: C, 72.71; H, 5.08; N, 14.13; Found: C, 72.6; H, 5.2; N, 14.0.

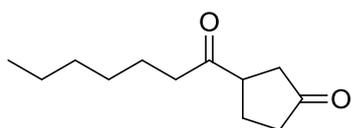
### Synthesis of dimethyl 2-heptanoylsuccinate (**15**)



Method A: From 335 mg (1.8 mmol, 0.12 M) of 1-(trimethylsilyl)heptan-1-one (**1b**) and 188  $\mu$ L (1.5 mmol, 0.1 M) of dimethyl maleate (**2a**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 283 mg of dimethyl 2-heptanoylsuccinate (**15**, 73% yield) as an oil.

Method B: From 280 mg (1.5 mmol, 0.15 M) of **1b** and 125  $\mu$ L (1.0 mmol, 0.1 M) of **2a**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 80 mg of dimethyl 2-heptanoylsuccinate (**15**, 31% yield) as an oil. The spectroscopic data of **15** were in accordance with the literature.<sup>S21</sup> Anal. Calcd. for C<sub>13</sub>H<sub>22</sub>O<sub>5</sub>: C, 60.45; H, 8.58. Found: C, 60.4; H, 8.6.

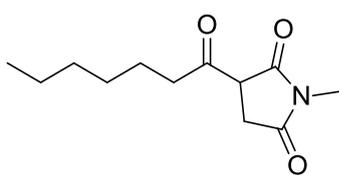
### Synthesis of 3-heptanoylcyclopentanone (**16**)



Method A: From 335 mg (1.8 mmol, 0.12 M) of 1-(trimethylsilyl)heptan-1-one (**1b**) and 125  $\mu$ L (1.5 mmol, 0.1 M) of 2-cyclopenten-1-one (**2m**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 171 mg of 3-heptanoylcyclopentanone (**16**, 58% yield) as an oil.

Method B: From 280 mg (1.5 mmol, 0.15 M) of **1b** and 83  $\mu$ L (1.0 mmol, 0.1 M) of (**2m**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 85 mg of 3-heptanoylcyclopentanone (**16**, 43% yield) as an oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 3.27-3.17 (m, 1H), 2.58-2.39 (m, 3H), 2.37-2.11 (m, 4H), 2.02-1.87 (m, 1H), 1.56 (m, 2H) 1.31-1.26 (m, 6H), 0.84 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 216.8, 210.9, 47.8, 41.8, 40.2, 37.6, 31.7, 29.0, 26.1, 23.6, 22.5, 14.1. Anal. Calcd. for C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>: C, 73.43; H, 10.27. Found: C, 73.4; H, 10.3.

### Synthesis of 3-heptanoyl-1-methylpyrrolidine-2,5-dione (**17**)

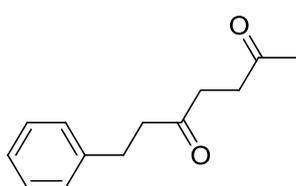


Method A: From 335 mg (1.8 mmol, 0.12 M) of 1-(trimethylsilyl)heptan-1-one (**1b**) and 167 mg (1.5 mmol, 0.1 M) of *N*-methylmaleimide (**2h**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 206 mg of 3-heptanoyl-1-methylpyrrolidine-2,5-dione (**17**, 61% yield) as an oil.

Method B: From 280 mg (1.5 mmol, 0.15 M) of **1b** and 111 mg (1.0 mmol, 0.1 M) of **2h**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 176 mg of 3-heptanoyl-1-methylpyrrolidine-2,5-dione (**17**, 78% yield) as an oil. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 3.92 (dd,  $J_1 = 9$  Hz,  $J_2 = 4$  Hz, 1H), 3.26 (dd,  $J_1 = 18$  Hz,  $J_2 = 4$  Hz, 1H), 3.06-2.97 (m, 1H), 2.93 (s, 3H), 2.68-2.57 (m, 2H), 1.57 (m, 2H), 1.32-1.26 (m, 6H), 0.85 (t,  $J = 7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 201.9, 175.7, 172.8, 53.1, 43.2, 31.6, 30.0, 28.7, 25.3, 23.3, 22.5, 14.1. Anal. Calcd. for C<sub>12</sub>H<sub>19</sub>NO<sub>3</sub>: C, 63.98; H, 8.50; N, 6.22. Found: C, 64.0; H, 8.5; N, 6.2.

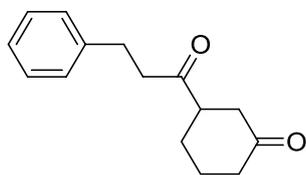
### Synthesis of 7-phenylheptane-2,5-dione (**18**)



Method A: From 371 mg (1.8 mmol, 0.12 M) of 3-phenyl-1-(trimethylsilyl)propan-1-one (**1c**) and 122  $\mu$ L (1.5 mmol, 0.1 M) of methyl vinyl ketone (**2e**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 49 mg of 7-phenylheptane-2,5-dione (**18**, 16% yield) as an oil.

Method B: From 309 mg (1.5 mmol, 0.15 M) of **1c** and 81  $\mu$ L (1.0 mmol, 0.1 M) of **2e**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 9:1 as the eluant) afforded 47 mg of 7-phenylheptane-2,5-dione (**18**, 23% yield) as an oil. The spectroscopic data of **18** were in accordance with the literature.<sup>S22</sup> Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: C, 76.44; H, 7.90. Found: C, 76.4; H, 7.9.

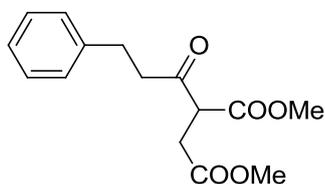
### Synthesis of 3-(3-phenylpropanoyl)cyclohexanone (**19**)



Method A: From 371 mg (1.8 mmol, 0.12 M) of 3-phenyl-1-(trimethylsilyl)propan-1-one (**1c**) and 145  $\mu$ L (1.5 mmol, 0.1 M) of cyclohexen-1-one (**2n**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 35 mg of 3-(3-phenylpropanoyl)cyclohexanone (**19**, 10% yield) as an oil.

Method B: From 309 mg (1.5 mmol, 0.15 M) of **1c** and 97  $\mu$ L (1.0 mmol, 0.1 M) of (**2n**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 70 mg of 3-(3-phenylpropanoyl)cyclohexanone (**19**, 30% yield) as an oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 7.29-7.24 (m, 2H), 7.19-7.14 (m, 3H), 2.92-2.67 (m, 5H), 2.51-2.26 (m, 4H), 2.05-1.95 (m, 2H), 1.74-1.55 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 209.9, 209.7, 140.8, 128.5, 128.2, 126.1, 50.2, 42.5, 42.3, 40.8, 29.6, 27.1, 24.7. Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>: C, 78.23; H, 7.88. Found: C, 78.2; H, 7.9.

### Synthesis of dimethyl 2-(3-phenylpropanoyl)succinate (**20**)

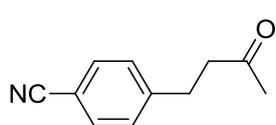


Method A: From 371 mg (1.8 mmol, 0.12 M) of 3-phenyl-1-(trimethylsilyl)propan-1-one (**1c**) and 188  $\mu$ L (1.5 mmol, 0.1 M) of dimethyl maleate (**2a**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded

42 mg of dimethyl 2-(3-phenylpropanoyl)succinate (**20**, 10% yield) as an oil.

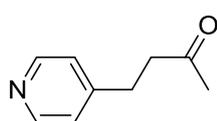
Method B: From 309 mg (1.5 mmol, 0.15 M) of **1c** and 125  $\mu$ L (1.0 mmol, 0.1 M) of **2a**. Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 123 mg of dimethyl 2-(3-phenylpropanoyl)succinate (**20**, 44% yield) as an oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 3.98 (dd,  $J_1 = 8$  Hz,  $J_2 = 6$  Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.15-2.79 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 203.0, 171.8, 168.7, 140.7, 128.5, 128.4, 126.2, 53.9, 52.7, 52.1, 44.4, 32.1, 29.4. Anal. Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_5$ : C, 64.74; H, 6.52. Found: C, 64.7; H, 6.5.

### Synthesis of 4-(3-oxobutyl)benzotrile (**23**)



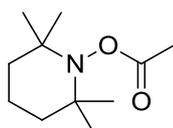
Method B: From 215  $\mu$ L (1.5 mmol, 0.15 M) of acetyltrimethylsilane (**1a**) and 129 mg (1.0 mmol, 0.1 M) of 4-vinylbenzotrile (**2n**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 8:2 as the eluant) afforded 130 mg of 4-(3-oxobutyl)benzotrile (**23**, 75% yield) as a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.56 (d,  $J = 8$  Hz, 2H), 7.30 (d,  $J = 8$  Hz, 2H), 2.95 (t,  $J = 7$  Hz, 2H), 2.78 (t,  $J = 7$  Hz, 2H), 2.15 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 206.8, 146.8, 132.3, 129.3, 119.0, 110.1, 44.2, 30.1, 29.7. Anal. Calcd. for  $\text{C}_{11}\text{H}_{11}\text{NO}$ : C, 76.28; H, 6.40; N, 8.09. Found: C, 76.3; H, 6.4; N, 8.1.

### Synthesis of 4-(pyridin-4-yl)butan-2-one (**24**)



Method B: From 215  $\mu$ L (1.5 mmol, 0.15 M) of acetyltrimethylsilane (**1a**) and 108 mg (1.0 mmol, 0.1 M) of 4-vinylpyridine (**2o**). Purification of the residue by column chromatography (cyclohexane/ethyl acetate 1:1 as the eluant) afforded 102 mg of 4-(pyridin-4-yl)butan-2-one (**24**, 68% yield) as a brownish oil.  $^1\text{H}$  NMR<sup>S23</sup> ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.47 (d,  $J = 6$  Hz, 2H), 7.11 (d,  $J = 6$  Hz, 2H), 2.93 – 2.83 (m, 2H), 2.82 – 2.72 (m, 2H), 2.15 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 206.8, 150.3, 149.8, 123.9, 43.7, 30.1, 28.9. Anal. Calcd. for  $\text{C}_9\text{H}_{11}\text{NO}$ : C, 72.16; H, 7.43; N, 9.39. Found: C, 72.2; H, 7.4; N, 9.4.

### Synthesis of 2,2,6,6-tetramethylpiperidin-1-yl acetate (**25**)

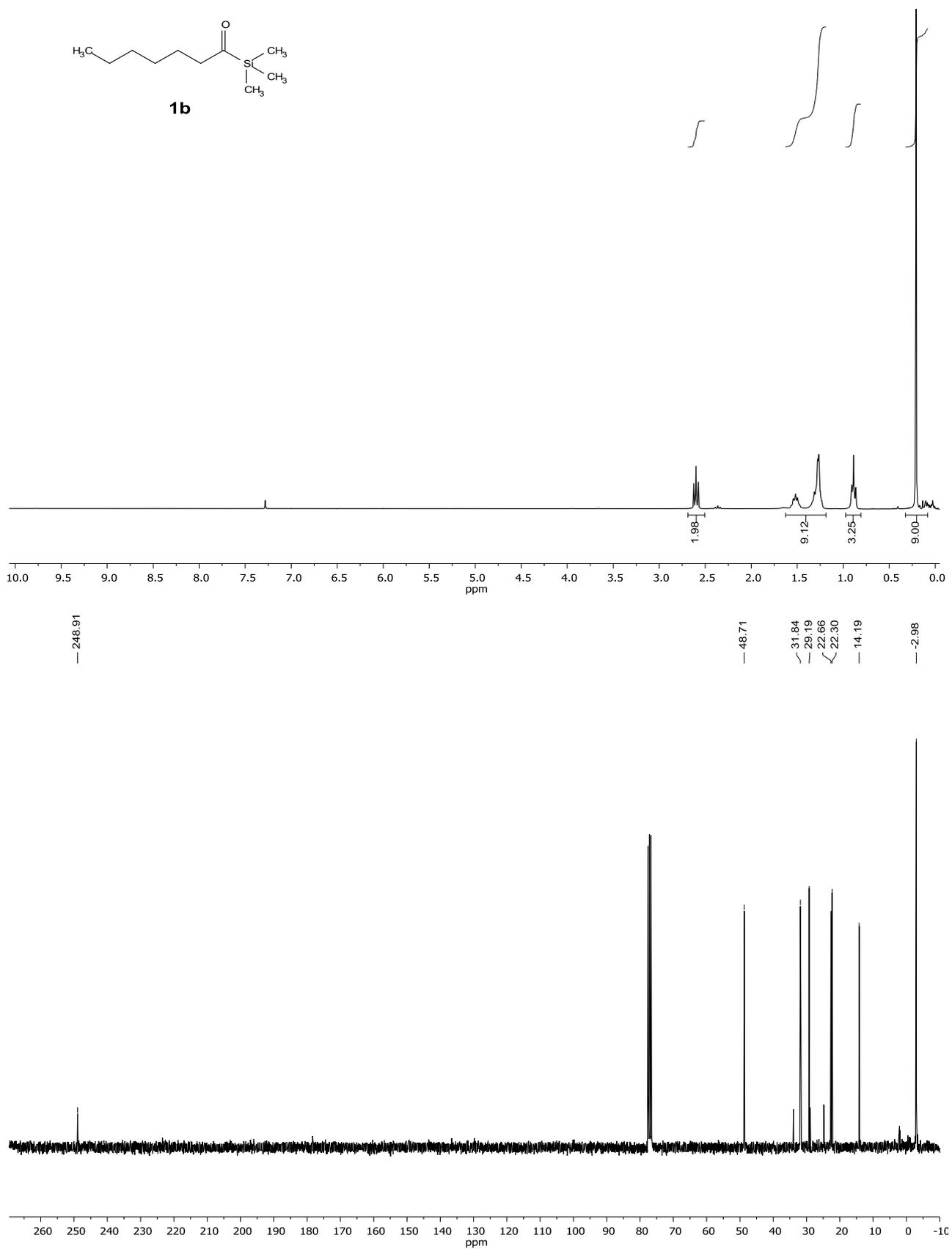


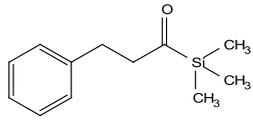
2,2,6,6-tetramethylpiperidin-1-yl acetate was synthesized as reported in the literature. See Section 4 for details.  $^1\text{H}$  NMR<sup>S4</sup> ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 2.09 (s, 3H), 1.75-1.39 (m, 6H), 1.15 (s, 6H), 1.06 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 170.9, 60.1, 39.1, 32.1, 20.6, 19.3, 17.1. Anal. Calcd. for  $\text{C}_{11}\text{H}_{21}\text{NO}_2$ : C, 66.29; H, 10.62; N, 7.03. Found: C, 66.3; H, 10.6; N, 7.0.

## 7 References

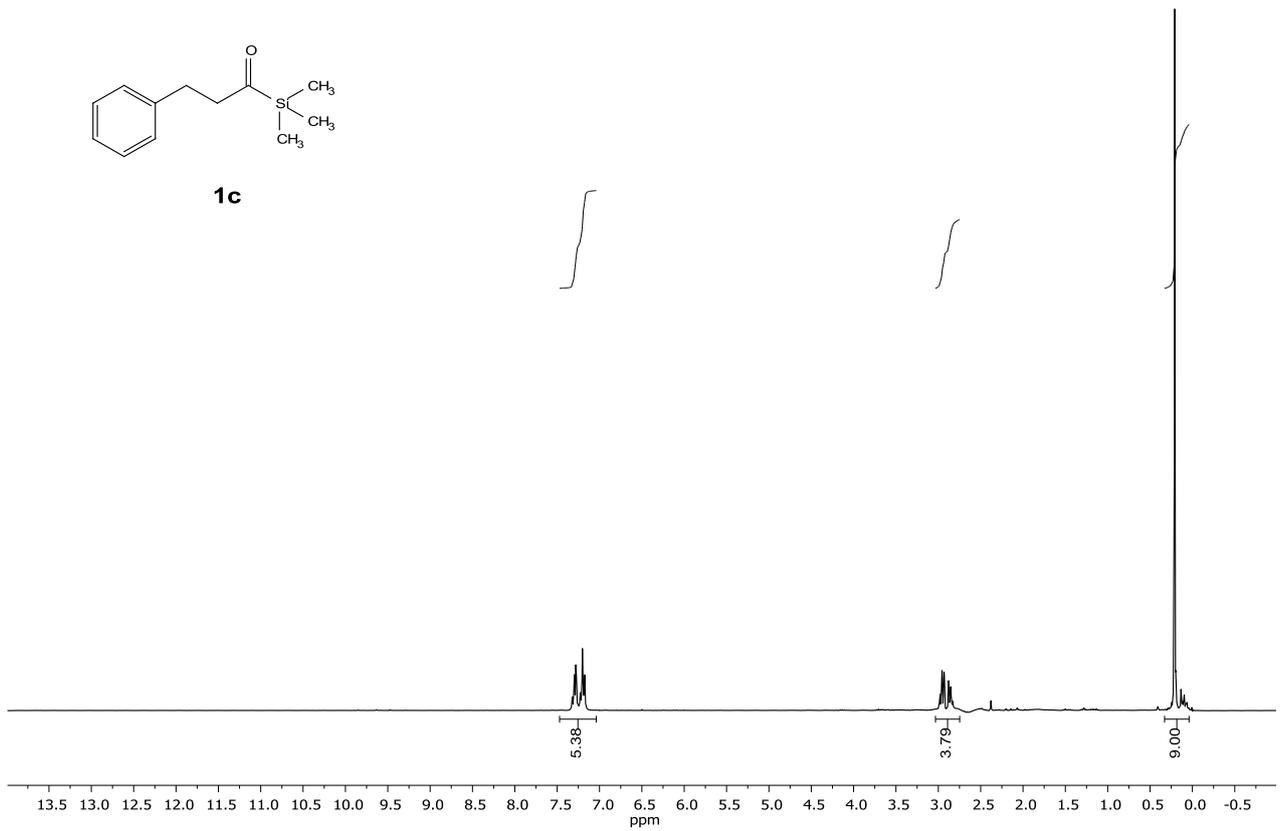
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# 8 Copy of $^1\text{H}$ and $^{13}\text{C}$ NMR of compounds 1b-d, 3-25





**1c**



— 247.20

— 141.81

— 128.58

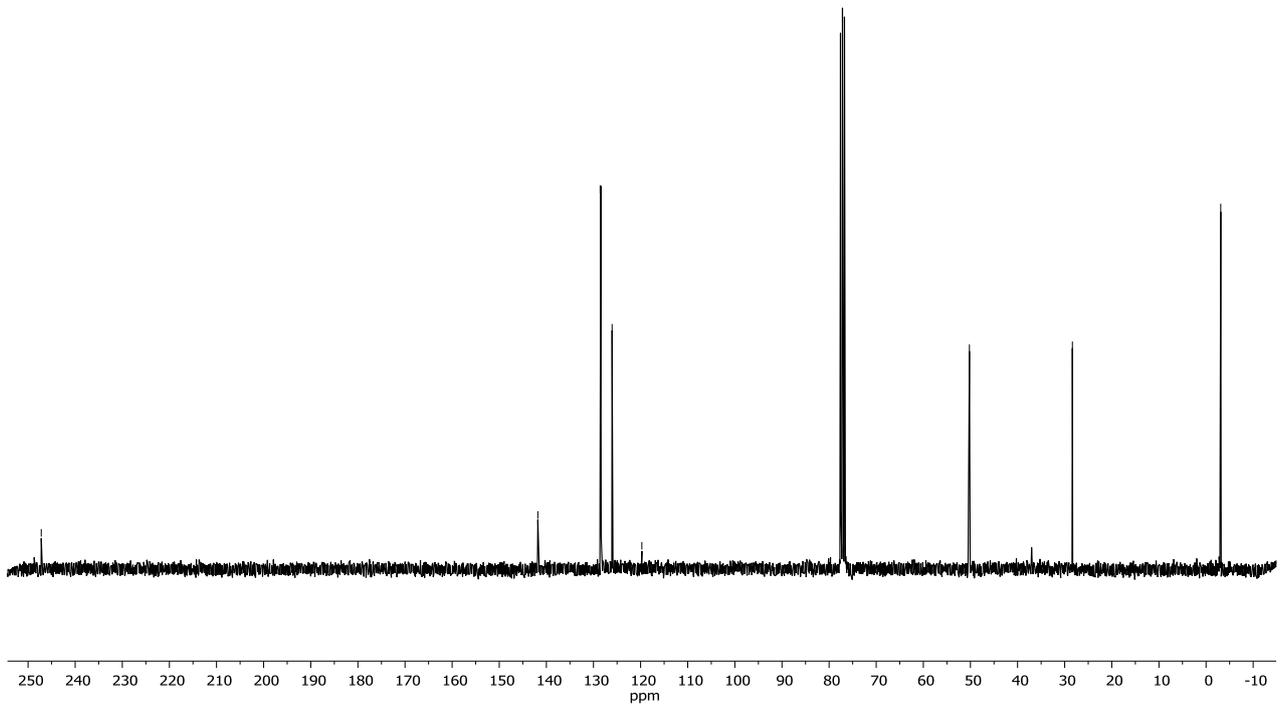
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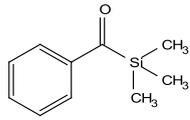
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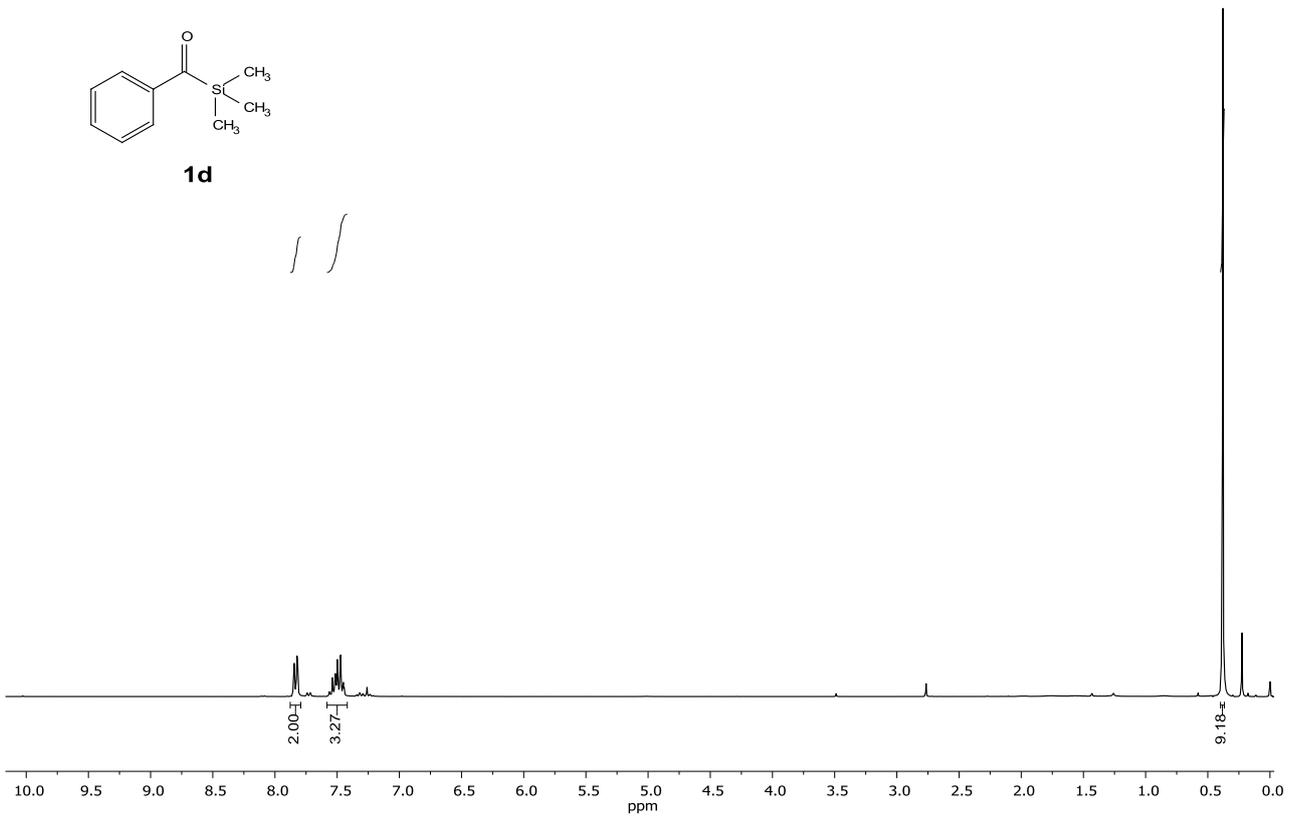
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**1d**

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— 235.92

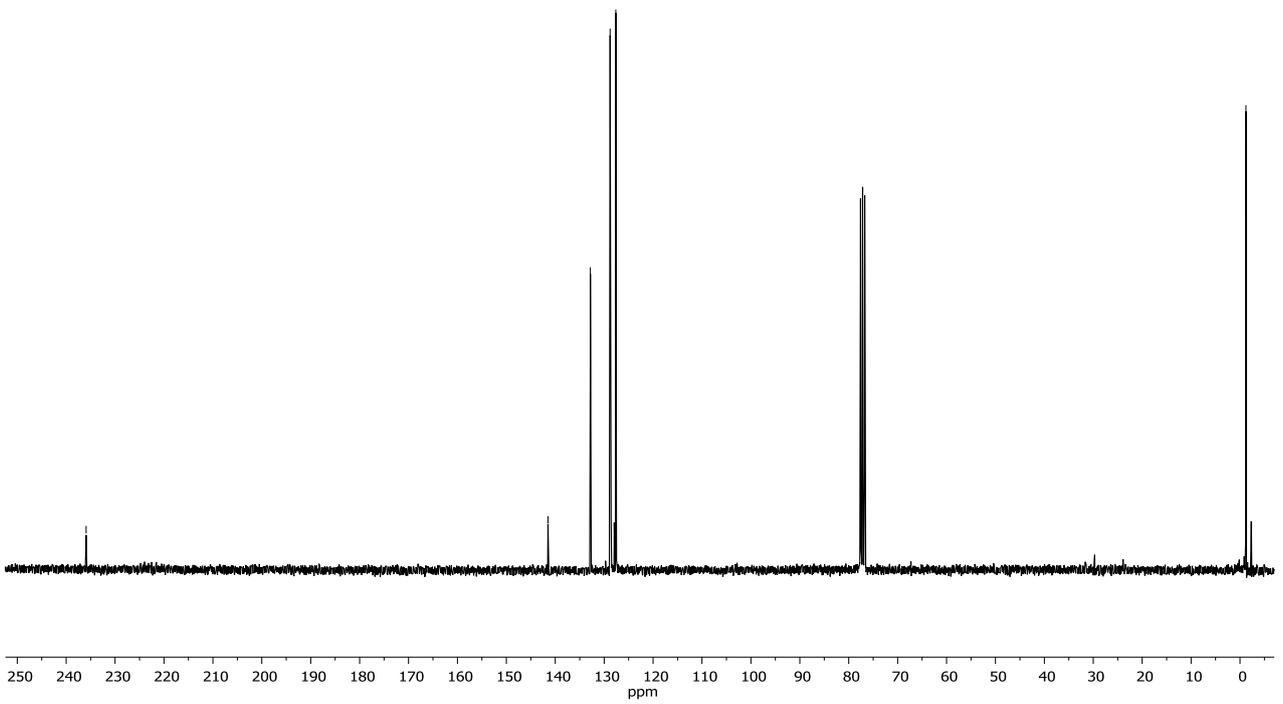
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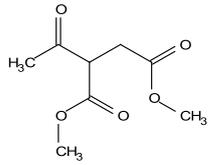
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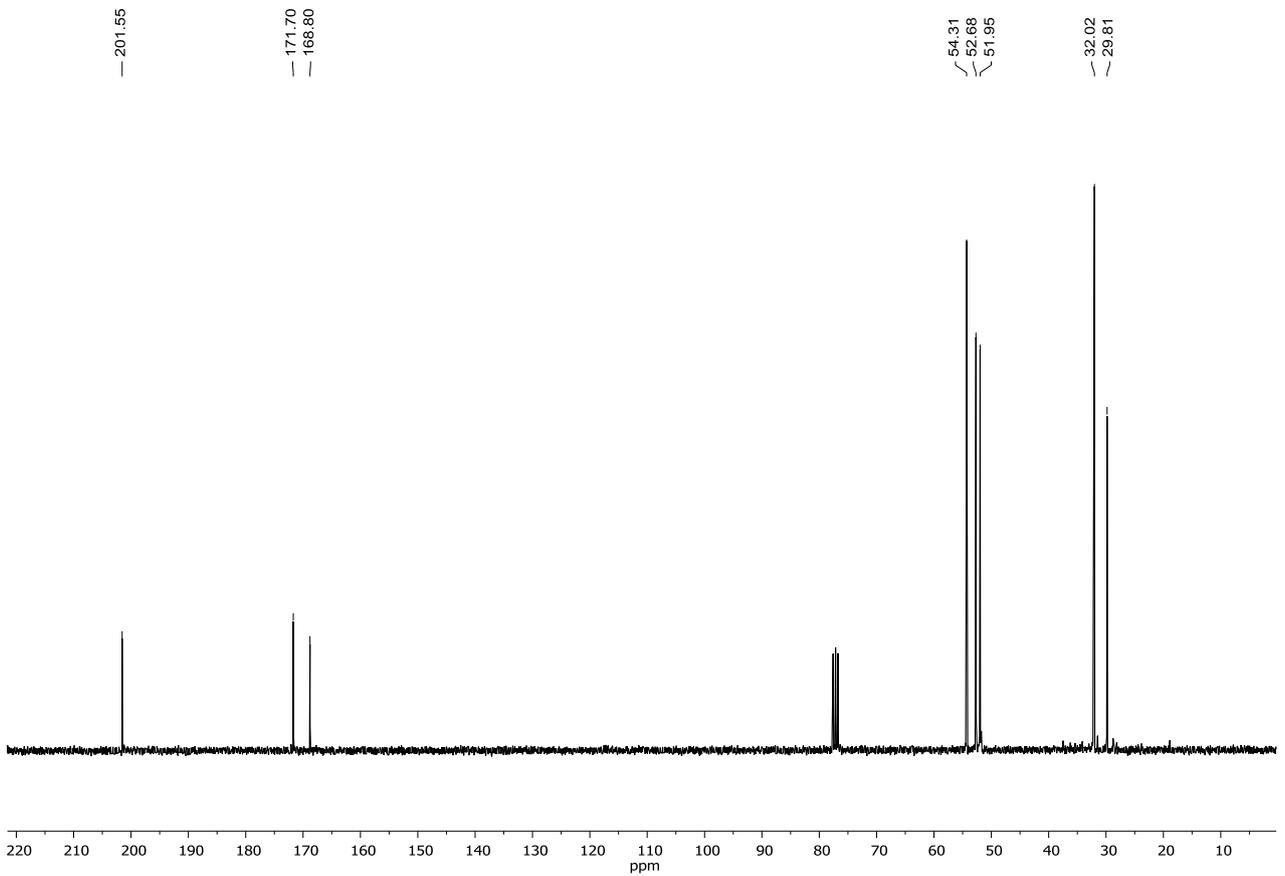
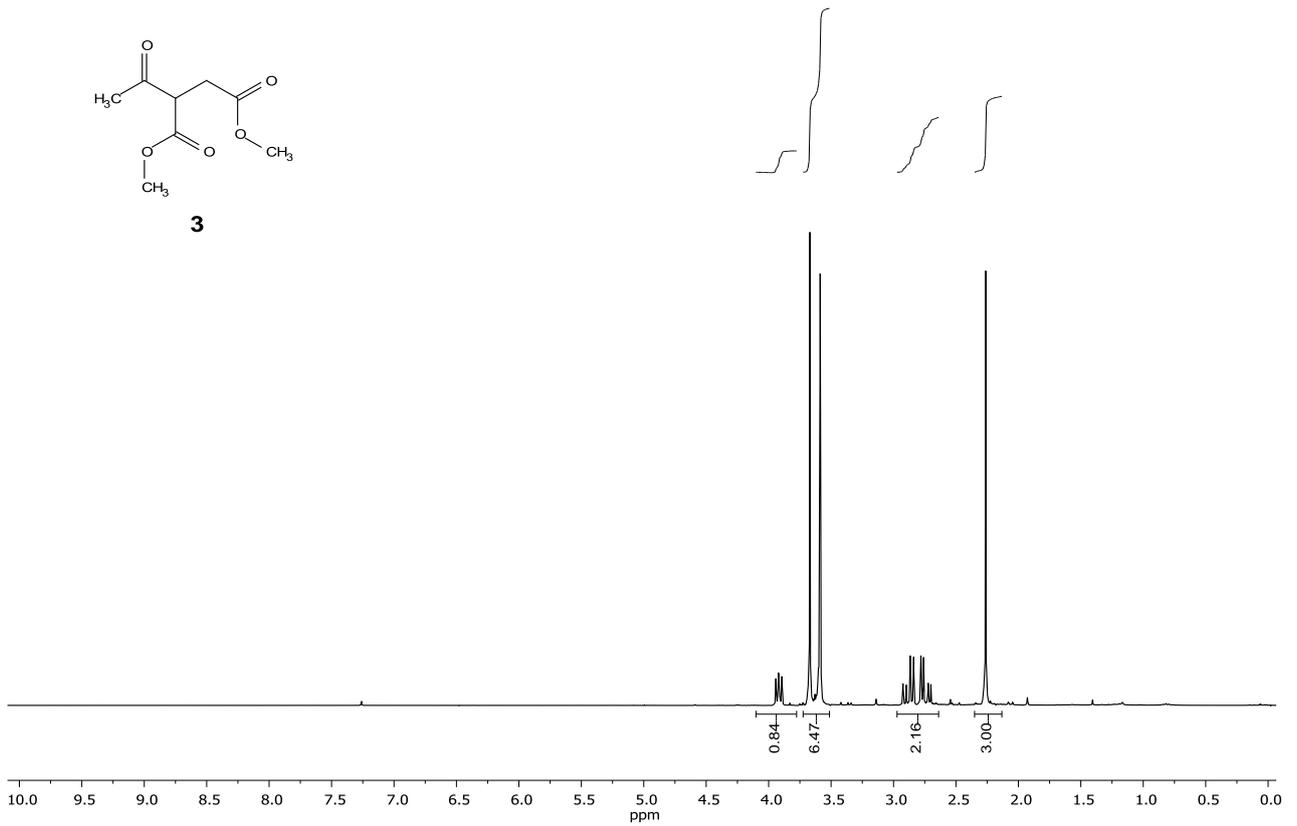
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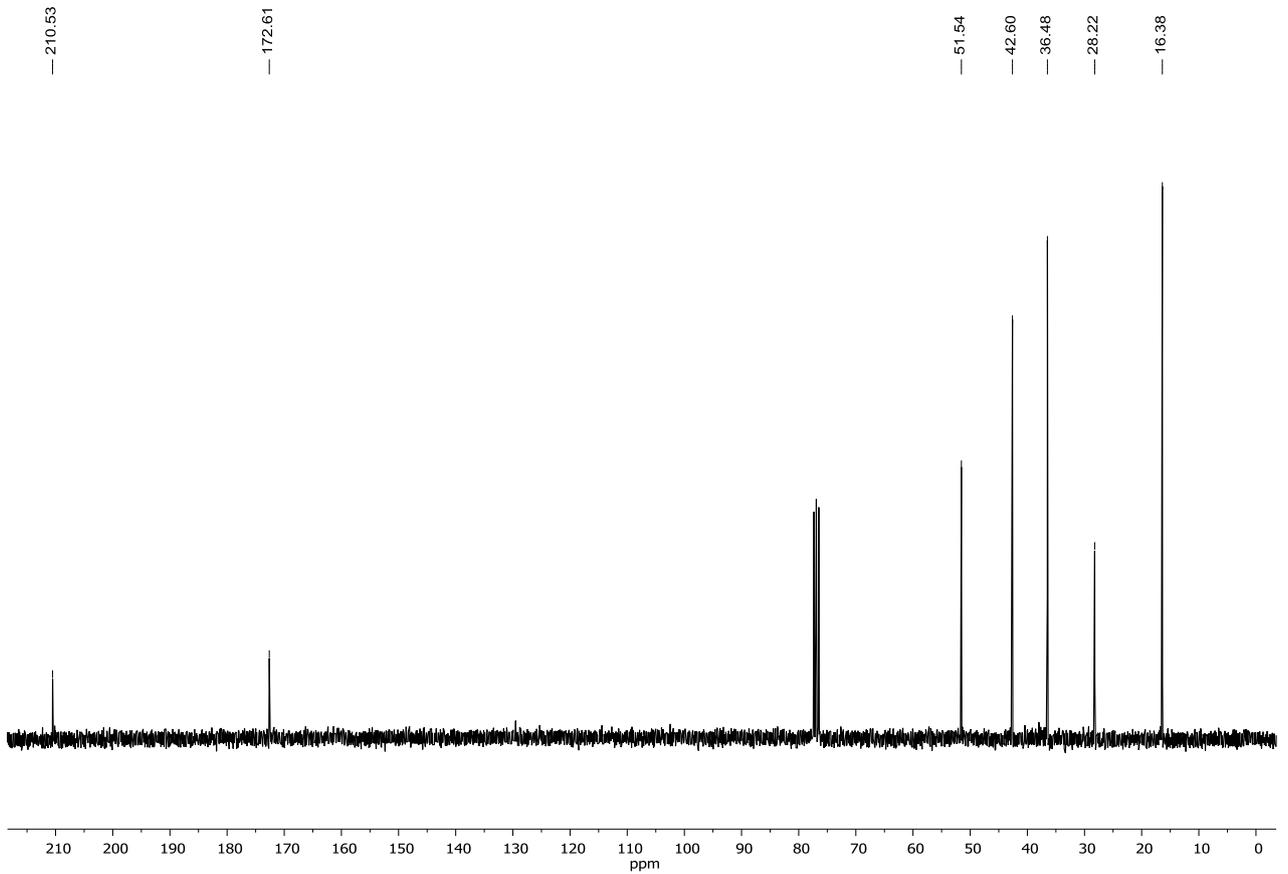
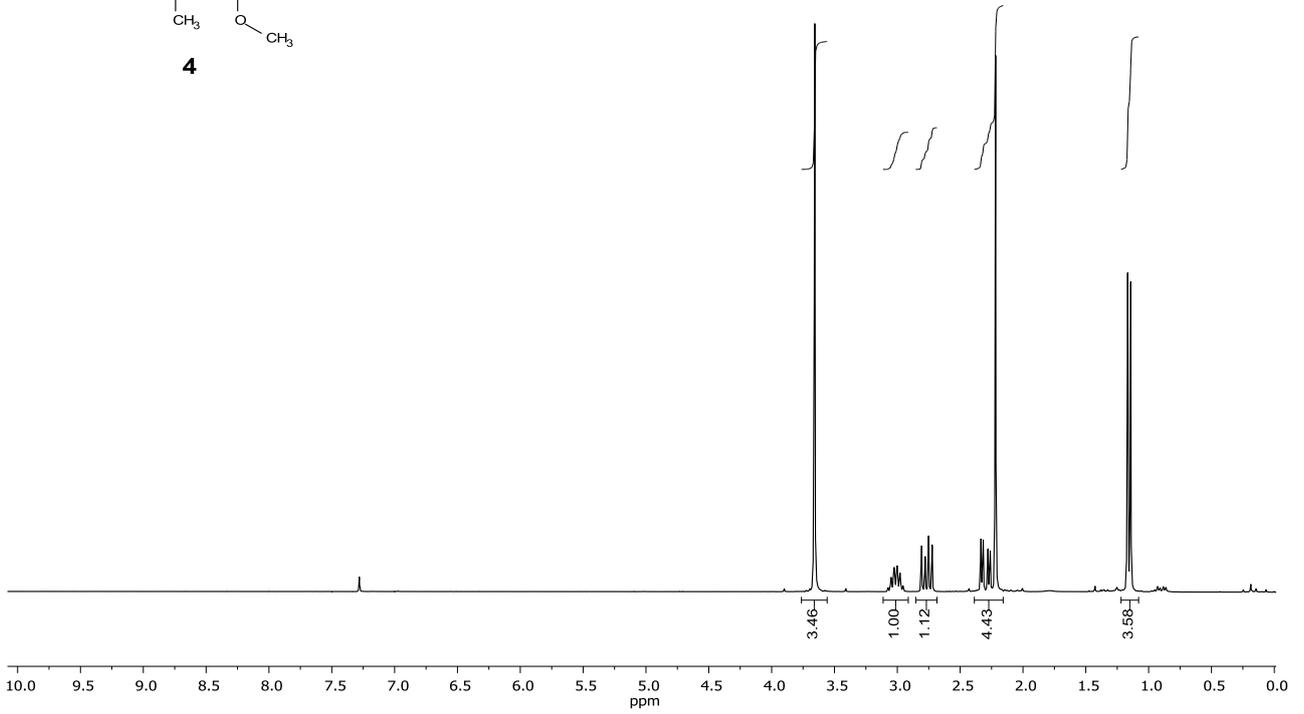
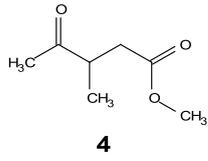
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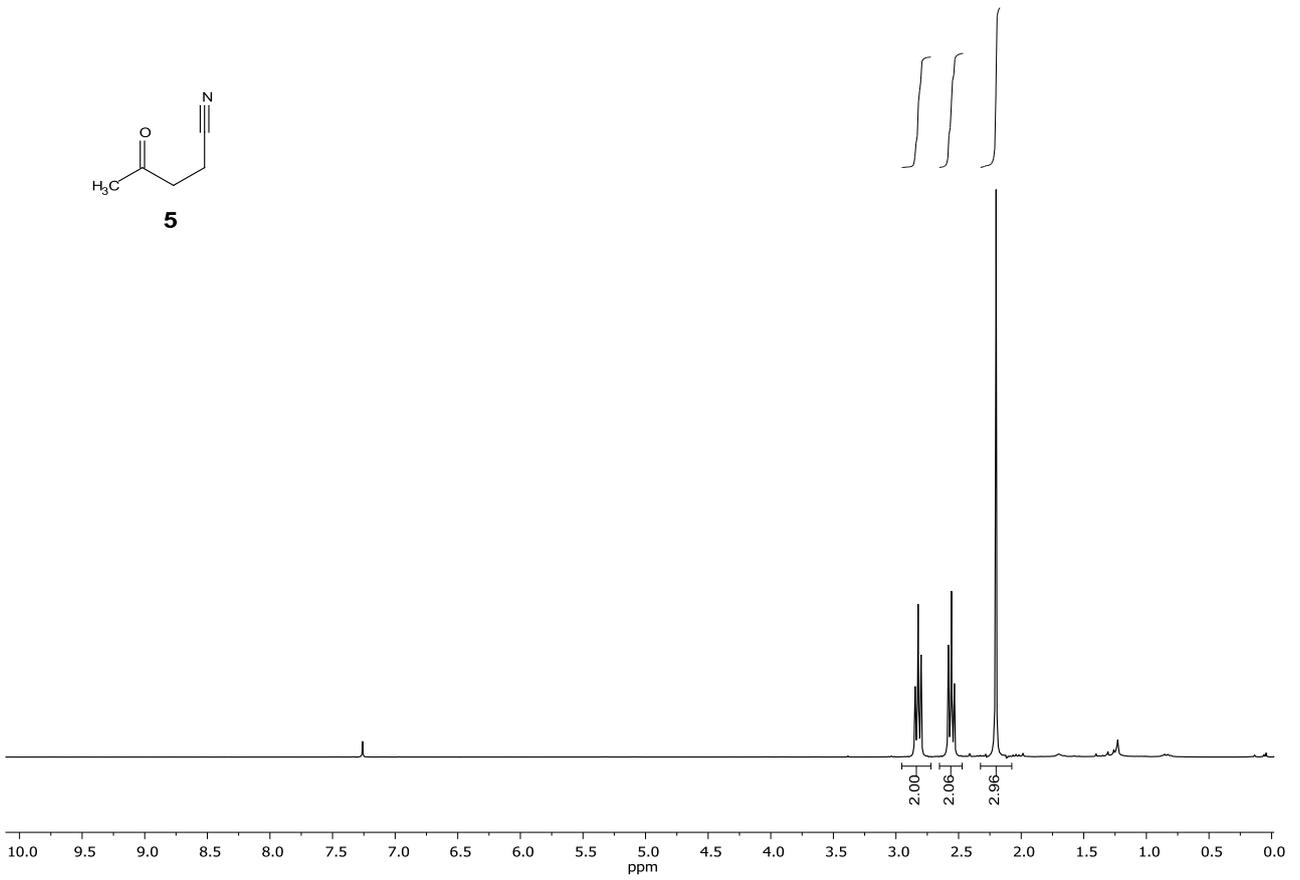
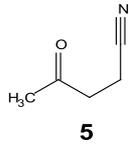




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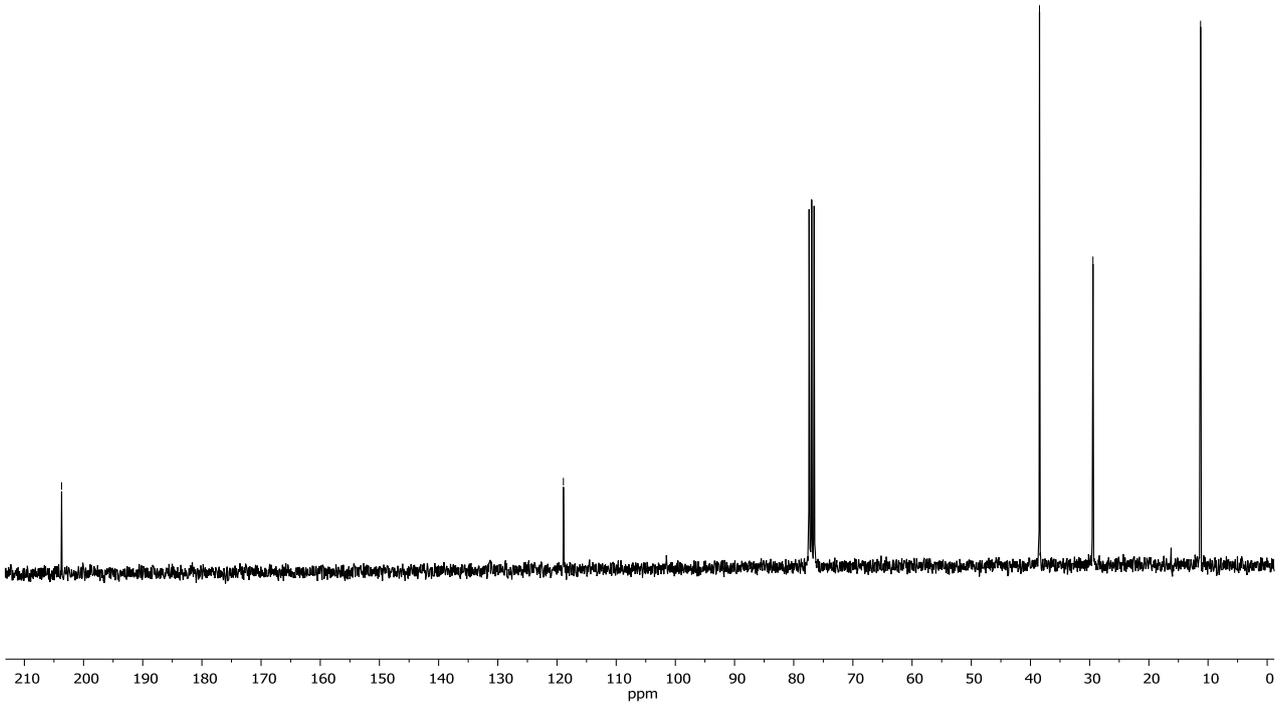
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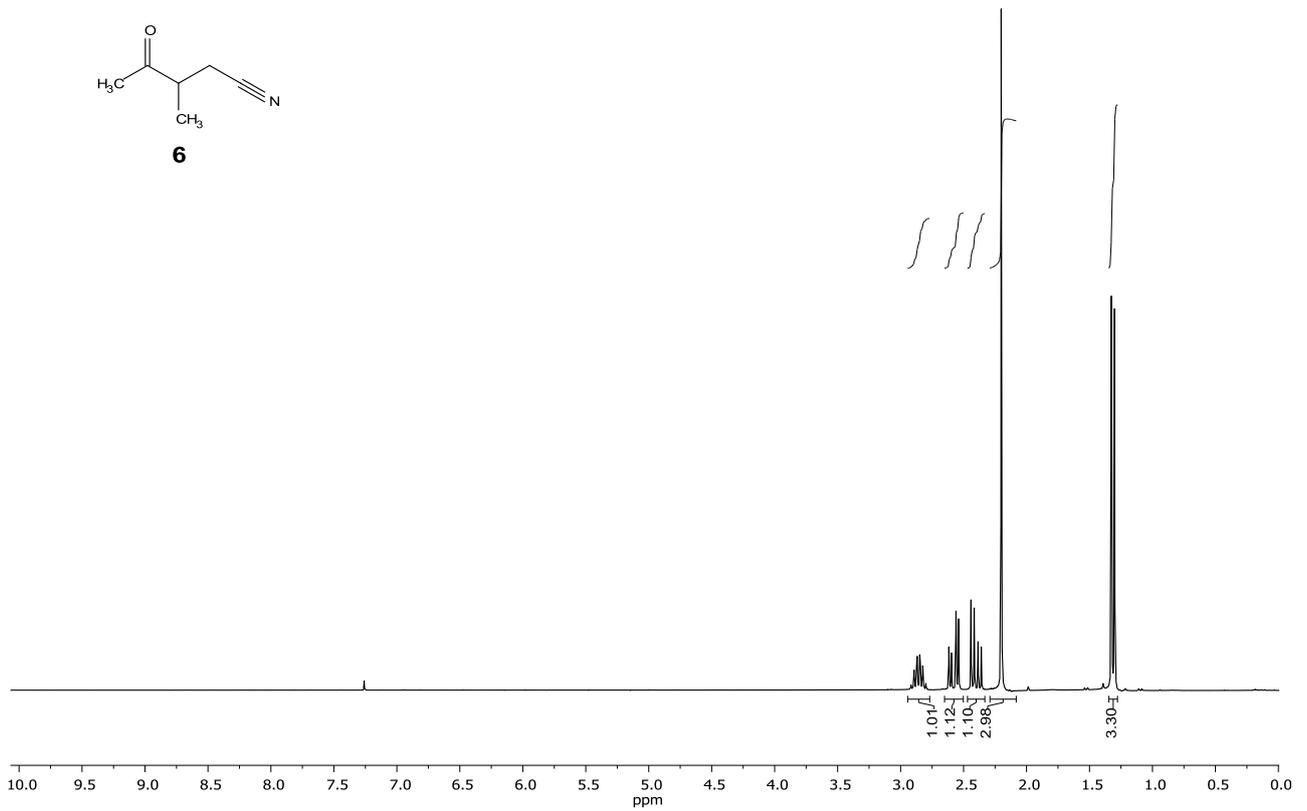
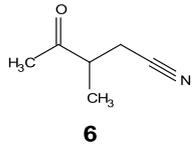
— 118.91

— 38.47

— 29.44

— 11.25





— 207.76

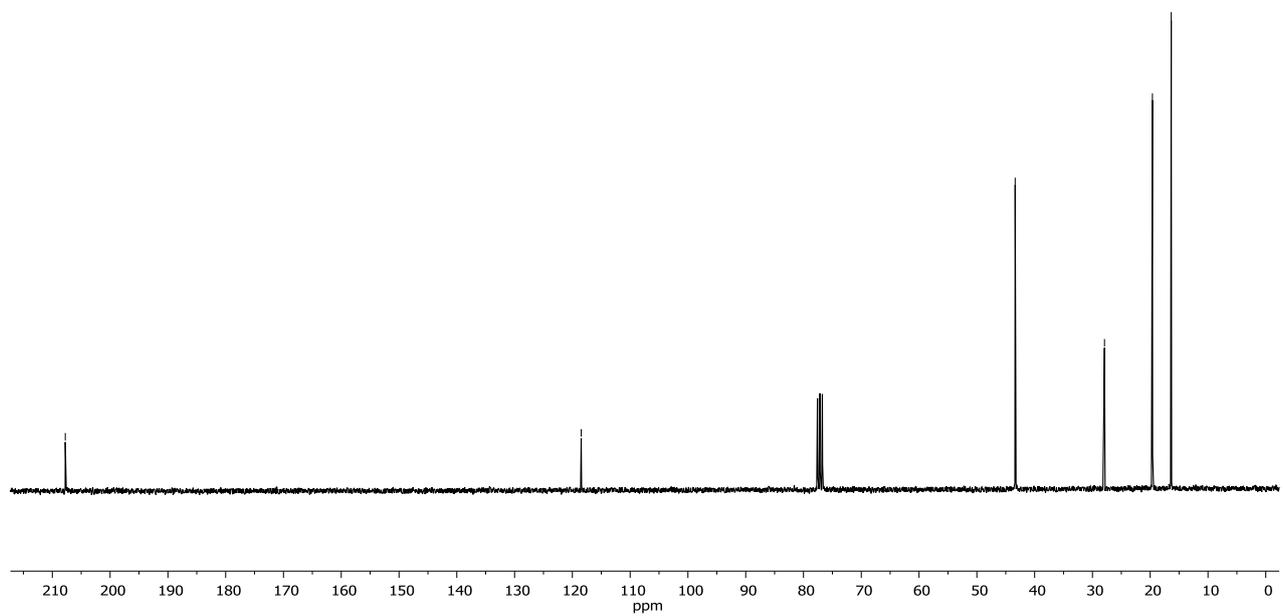
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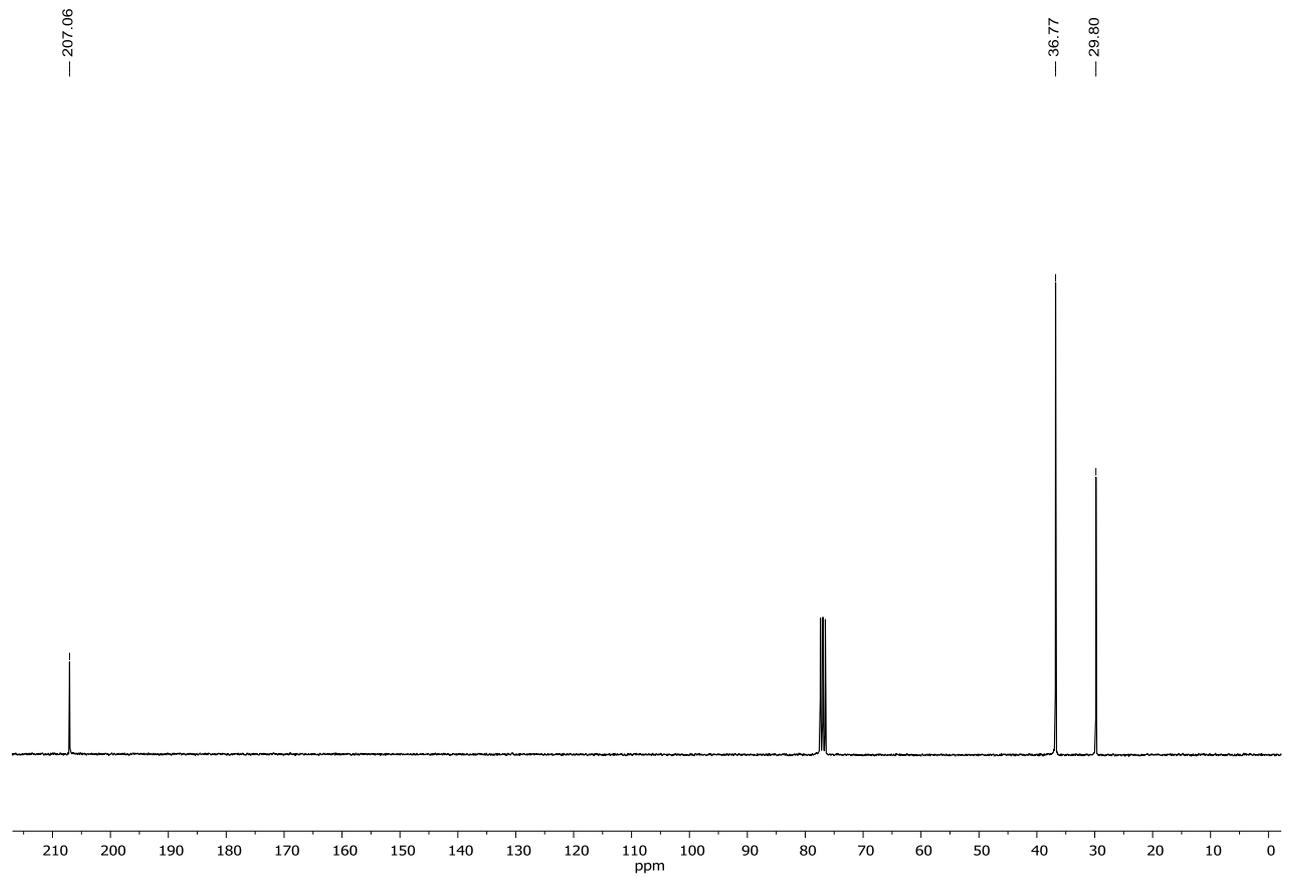
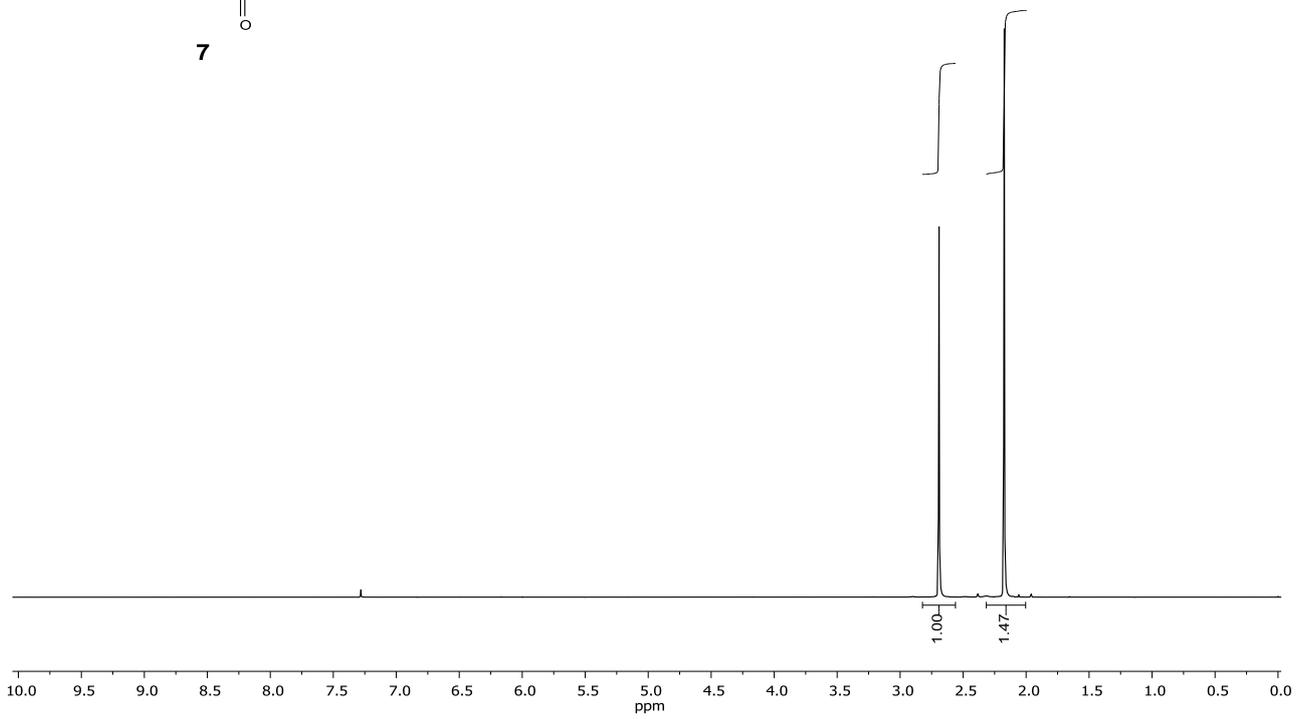
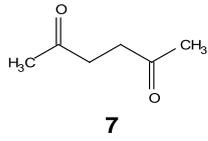
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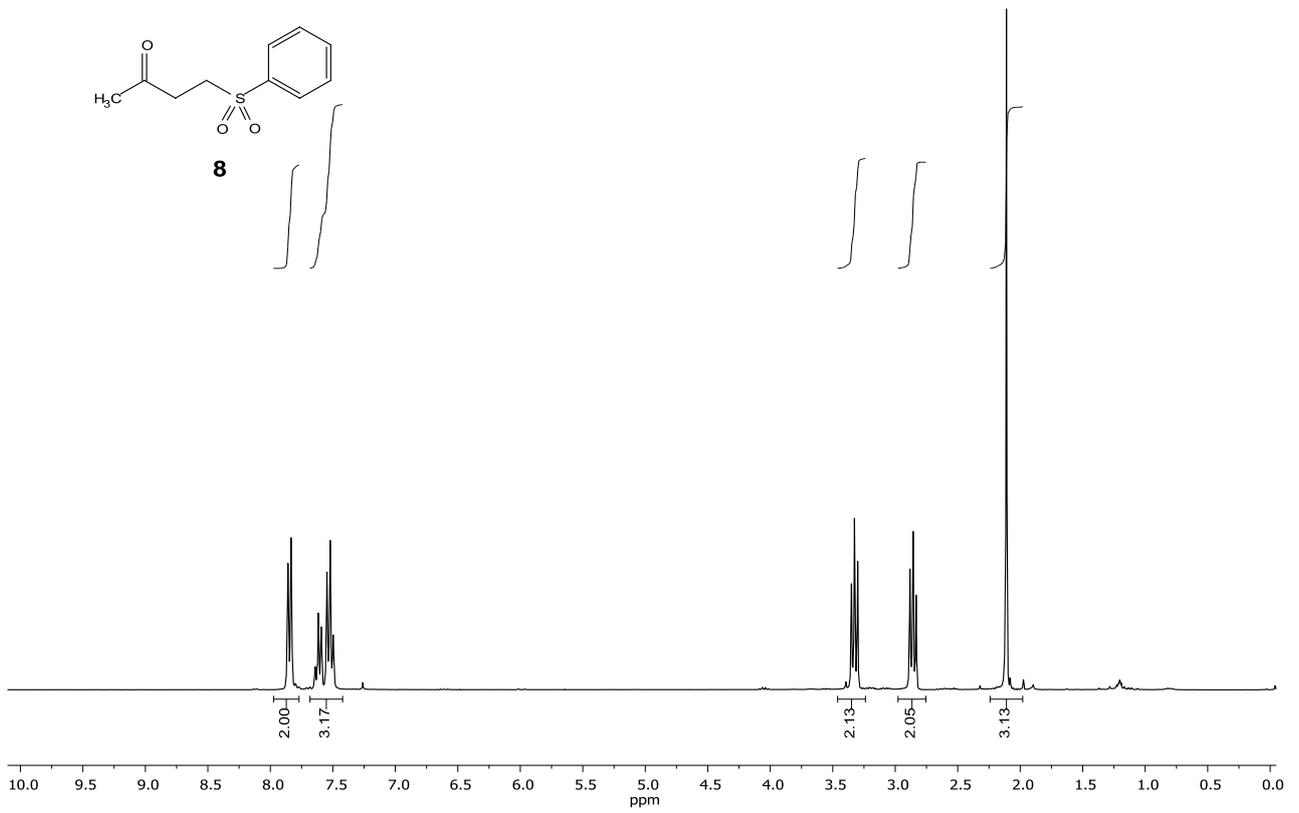
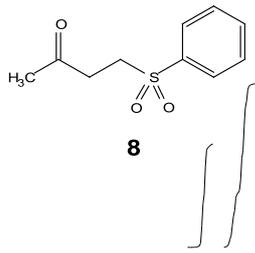
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— 19.62

— 16.36







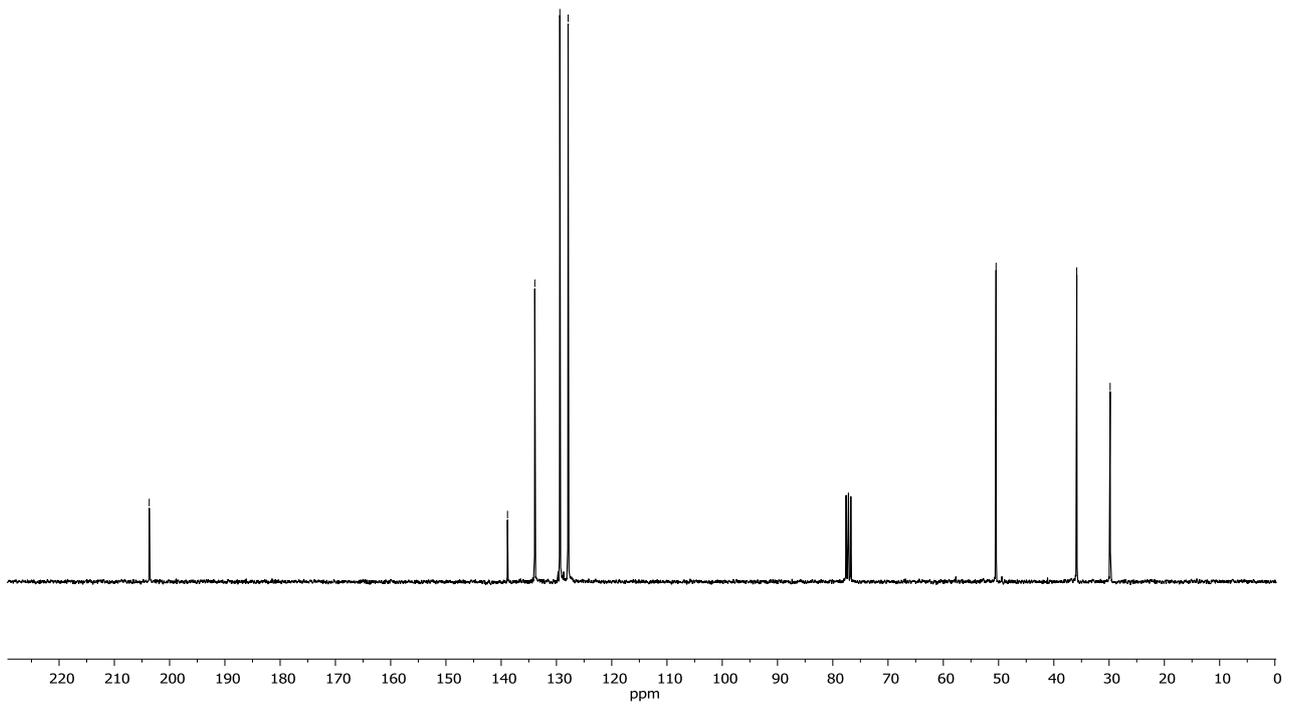
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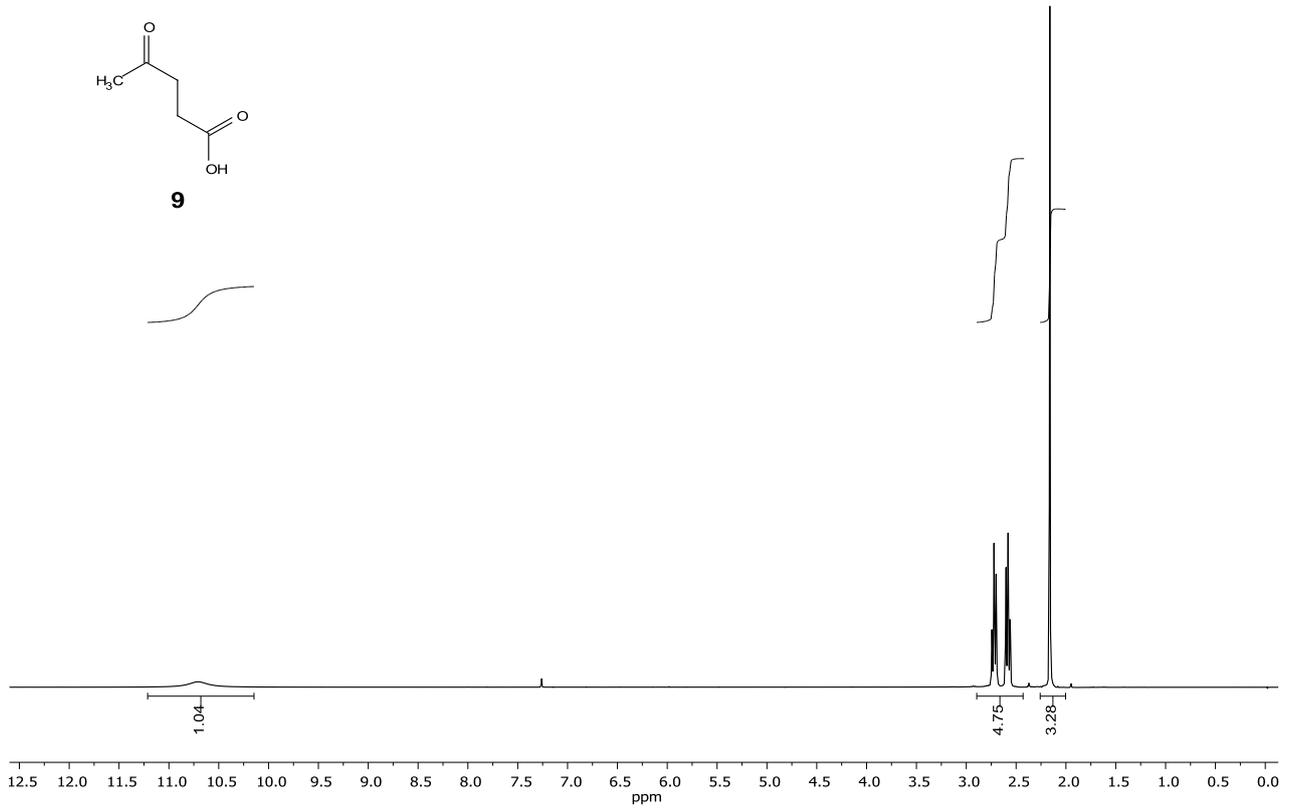
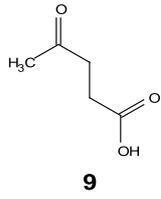
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— 129.39  
— 127.89

— 50.46

— 35.86

— 29.81





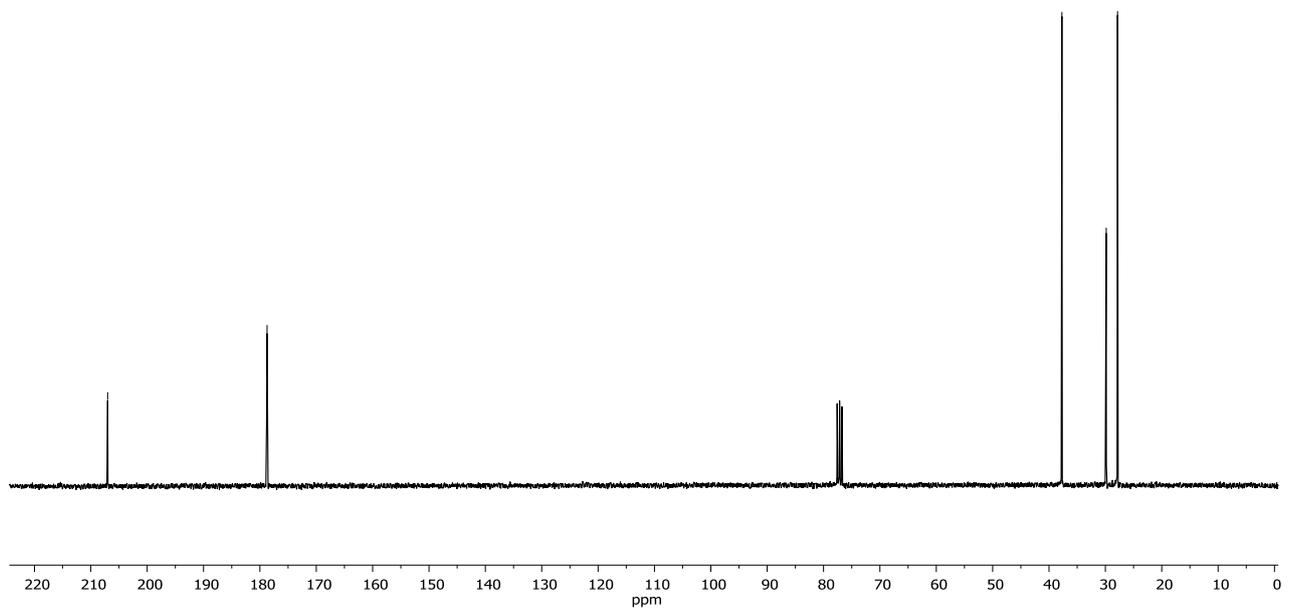
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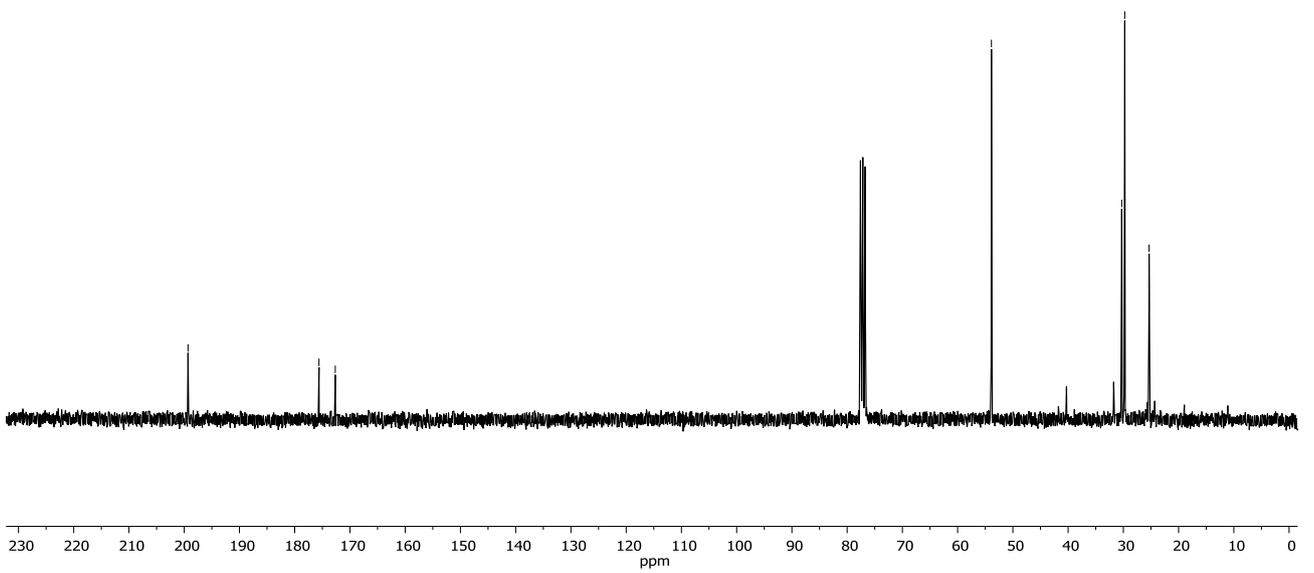
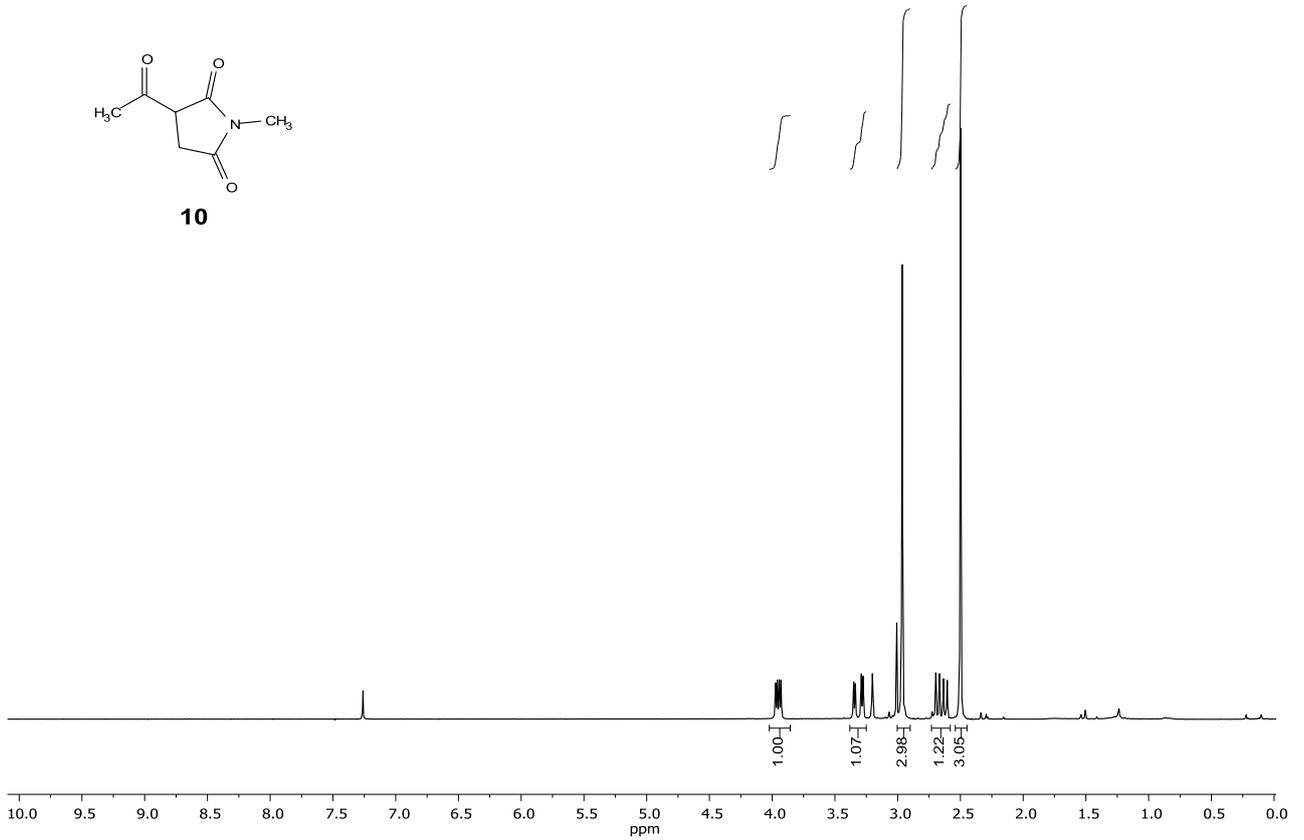
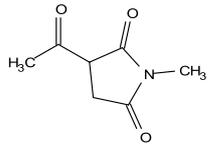
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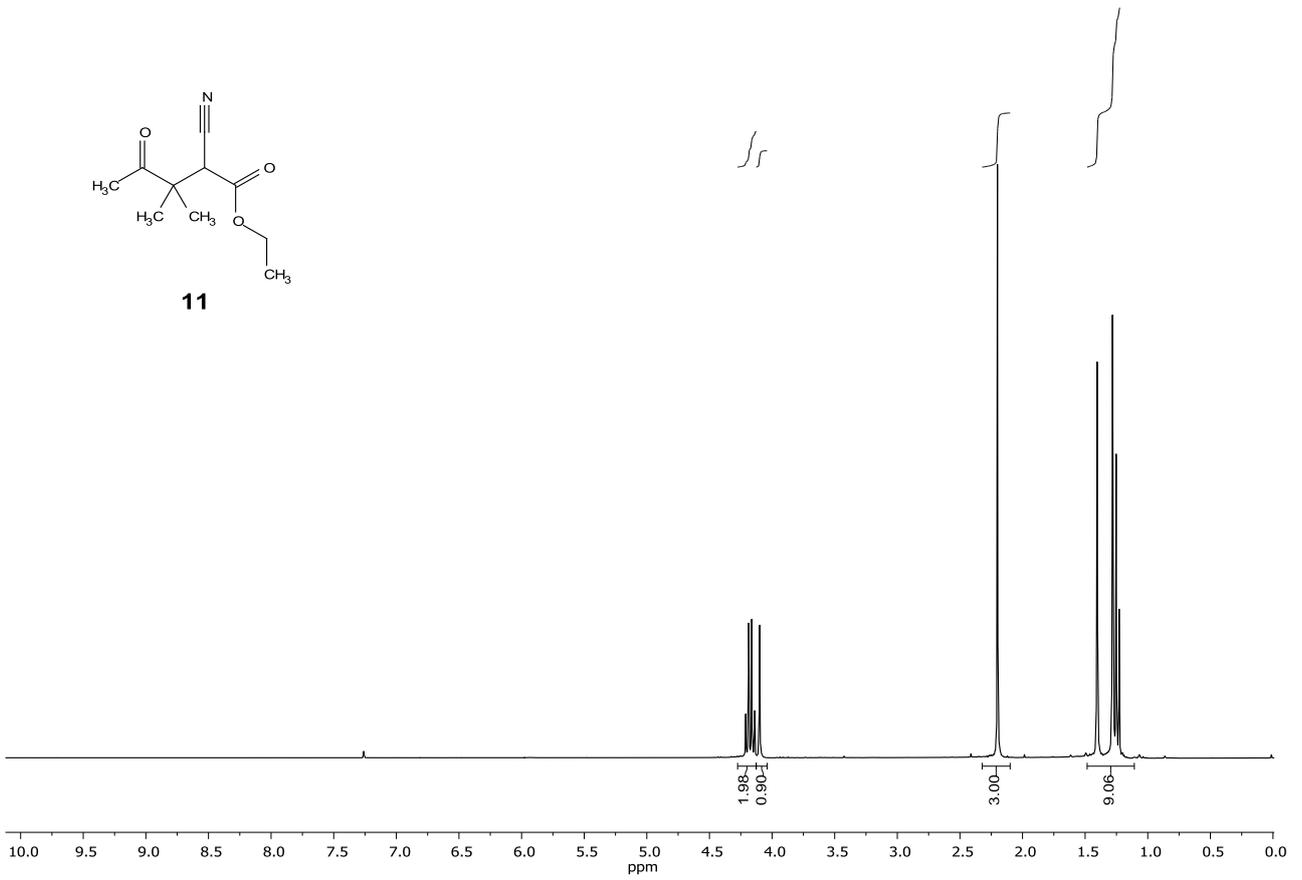
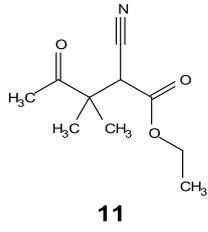
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— 27.84







— 209.33

— 164.79

— 115.45

— 62.87

— 48.85

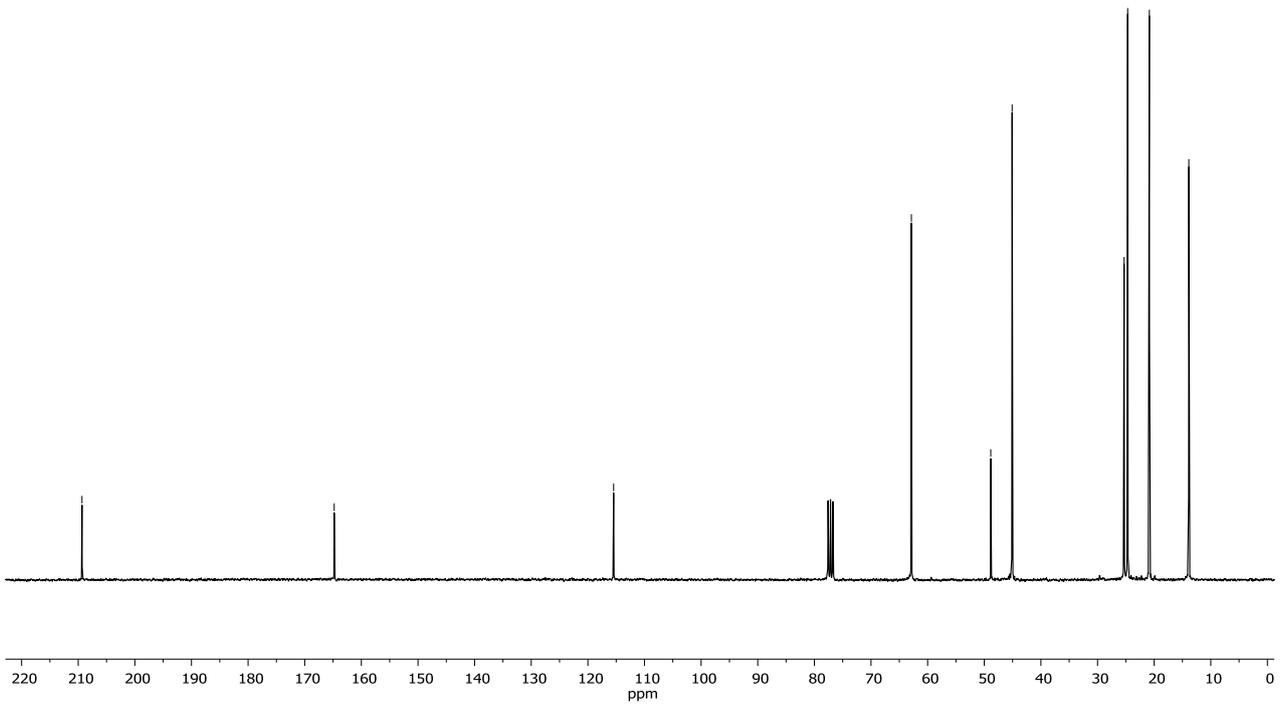
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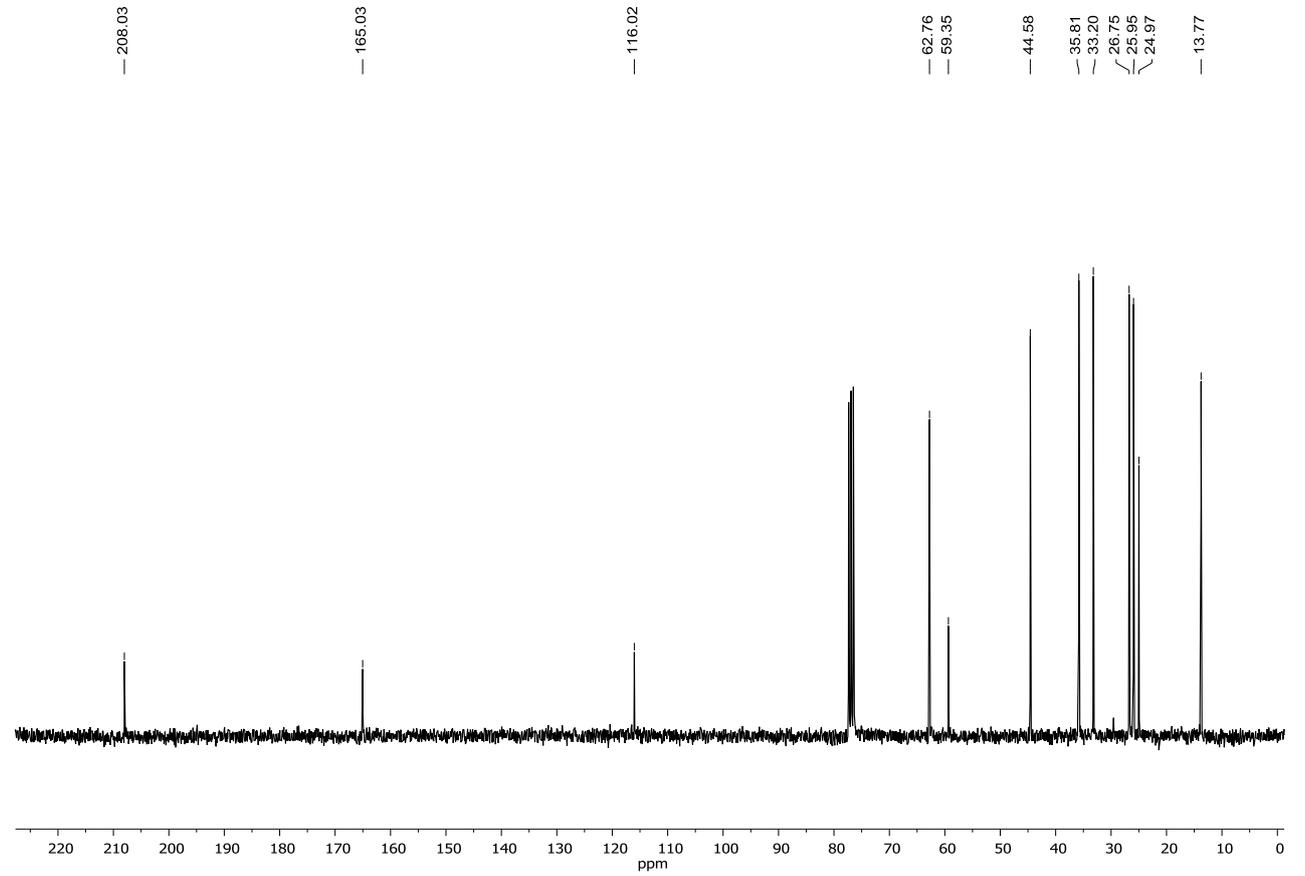
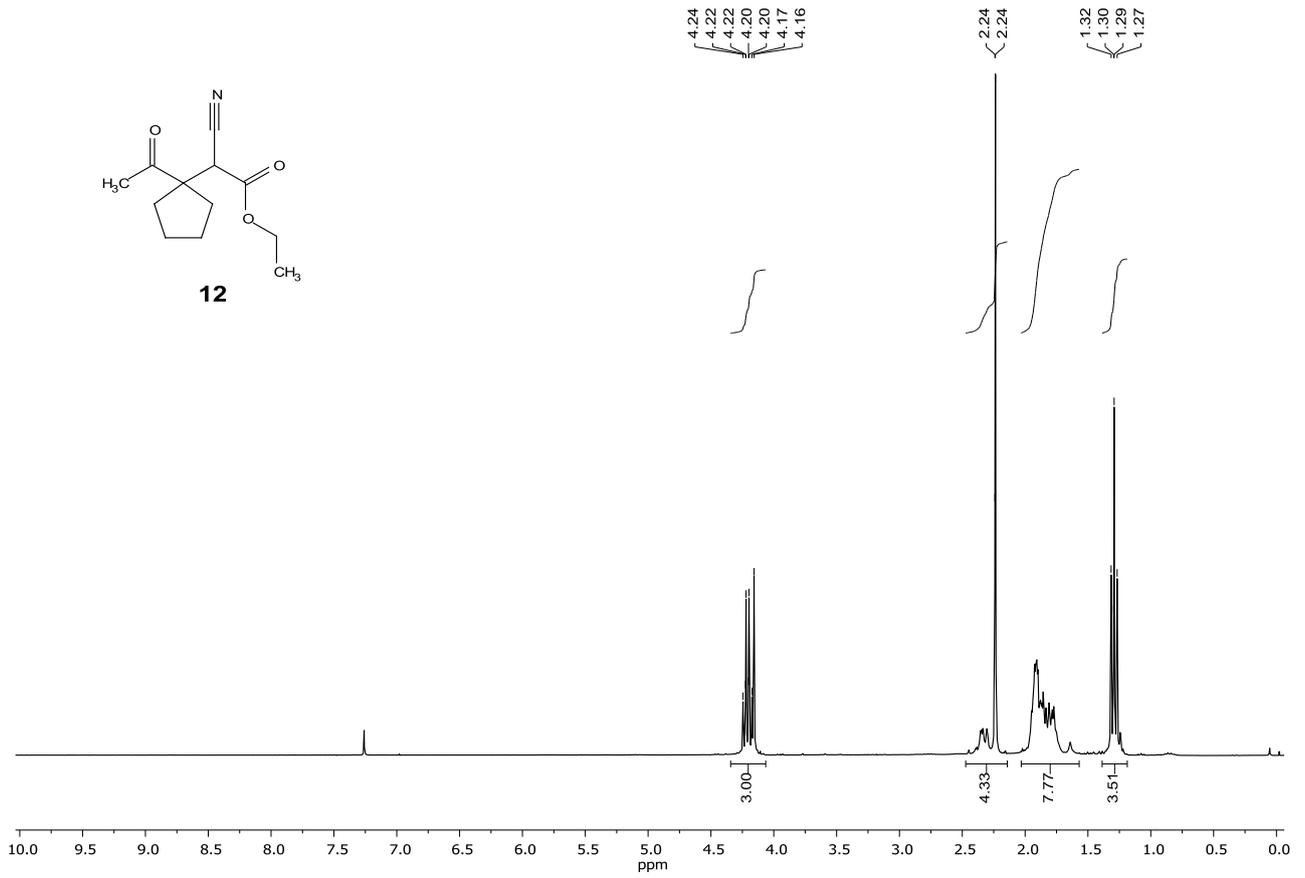
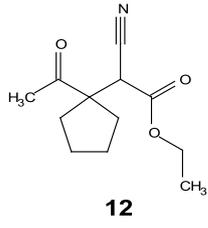
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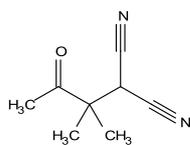
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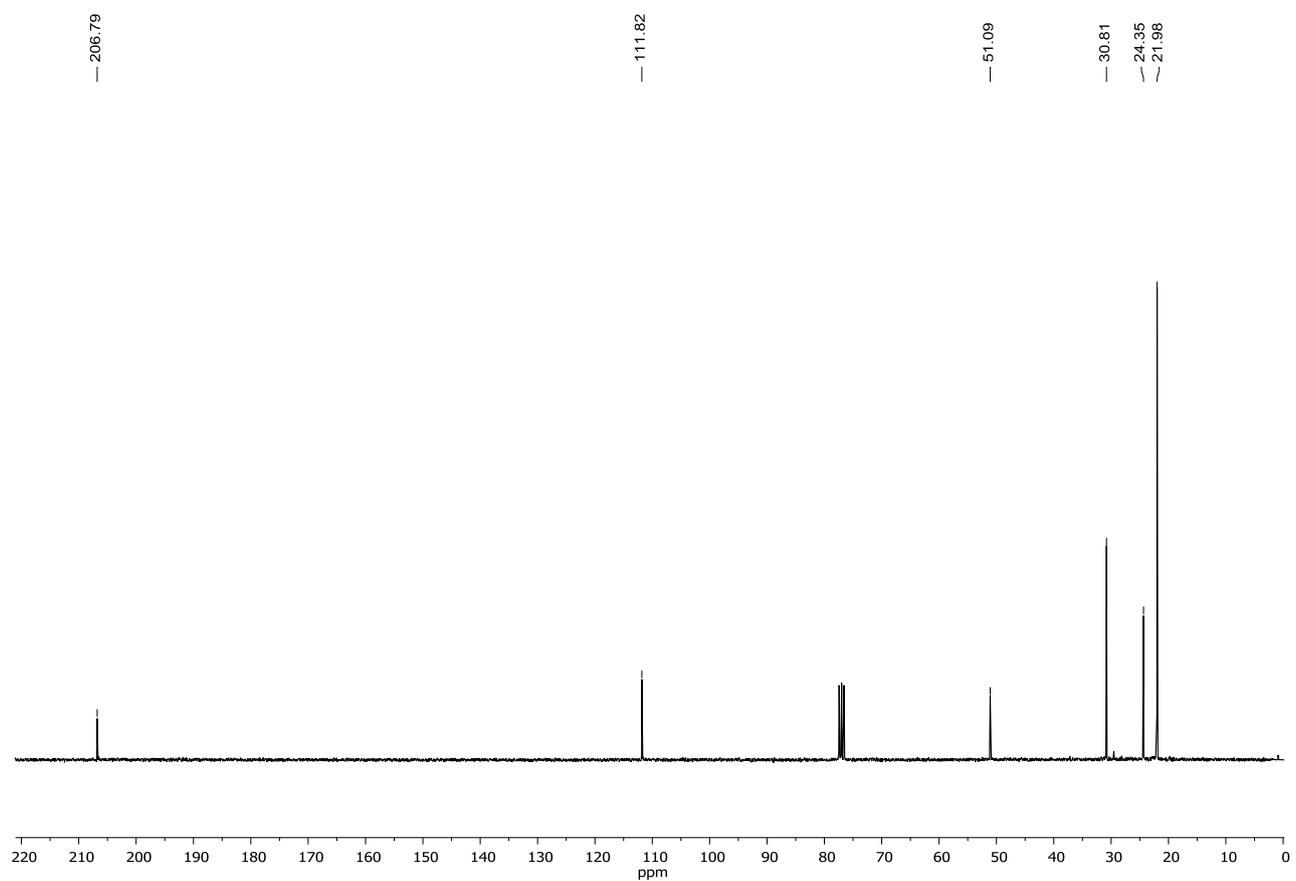
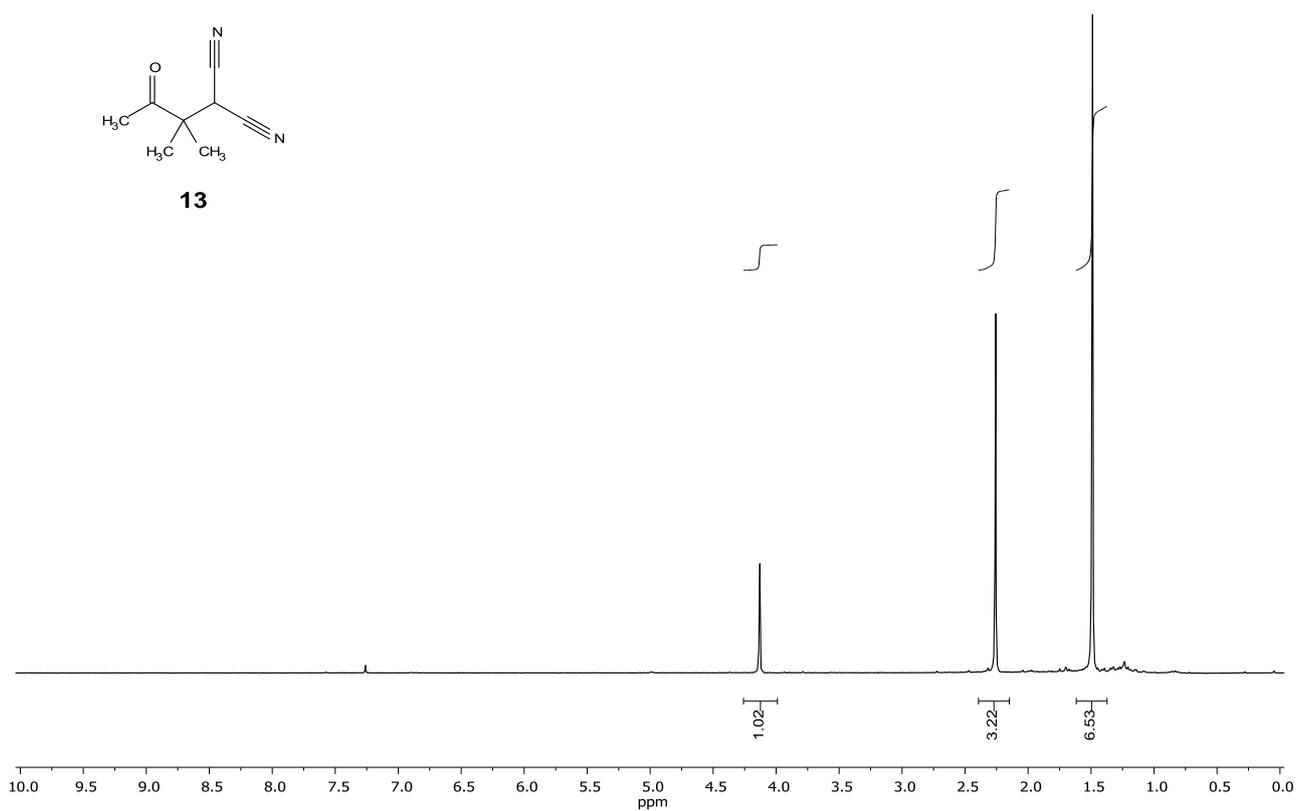
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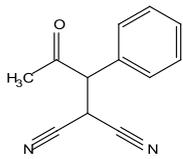




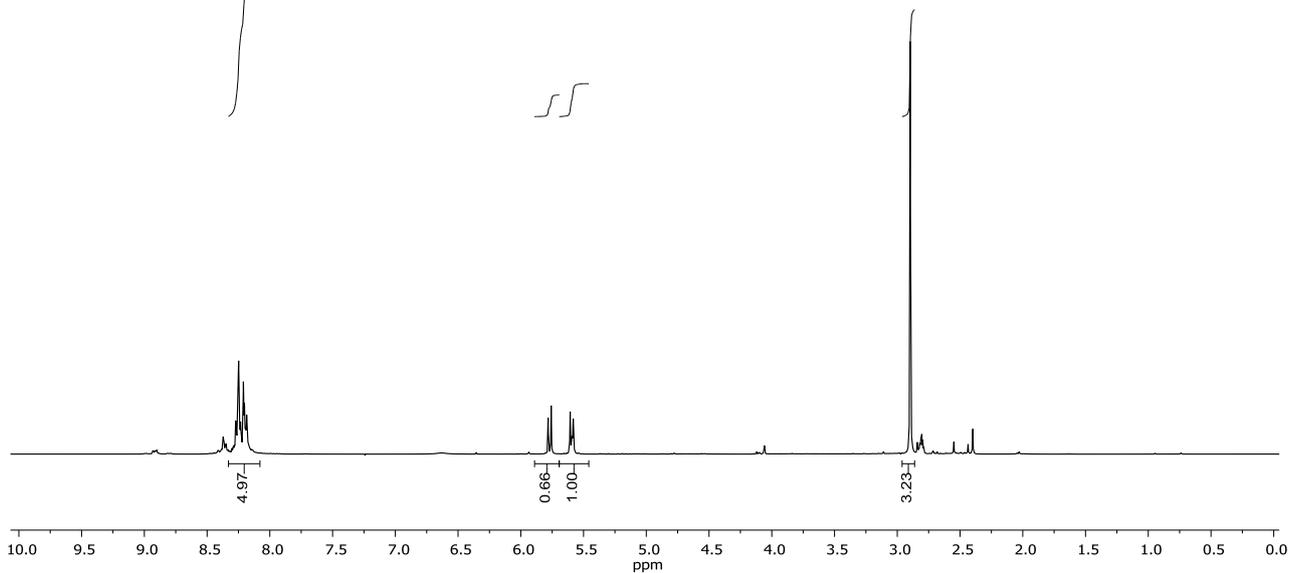


**13**





**14**



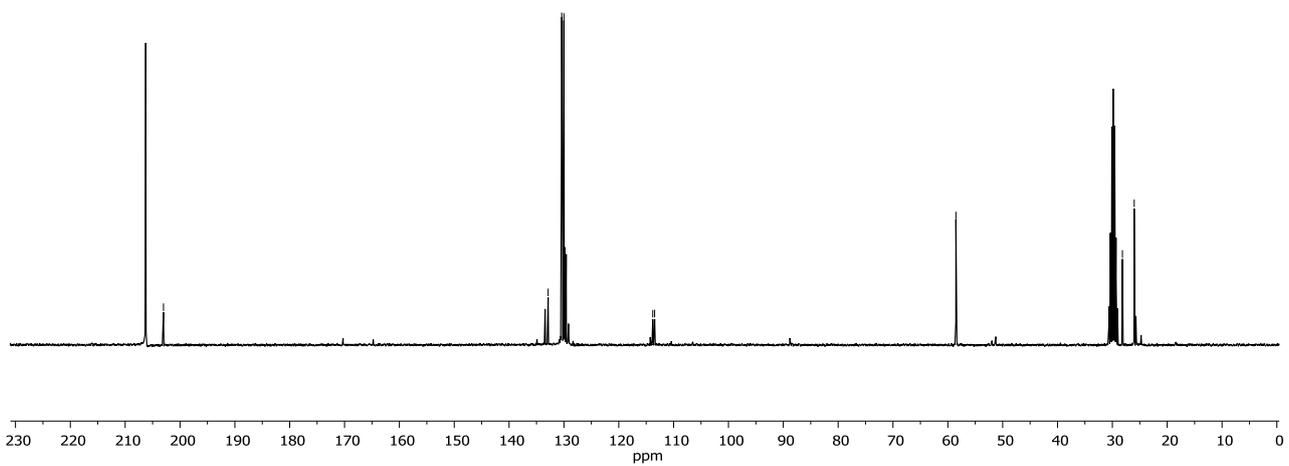
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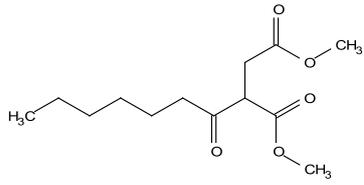
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113.46

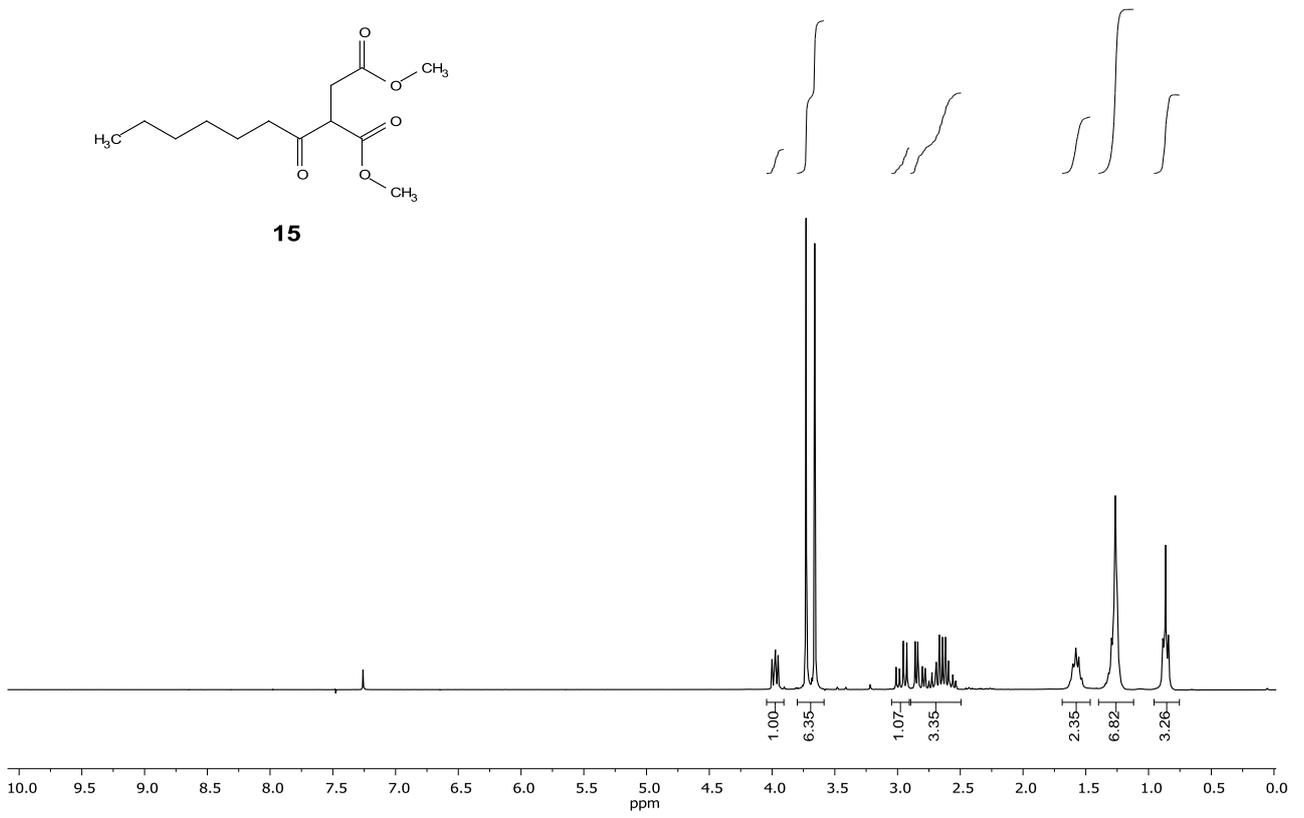
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28.17  
26.01

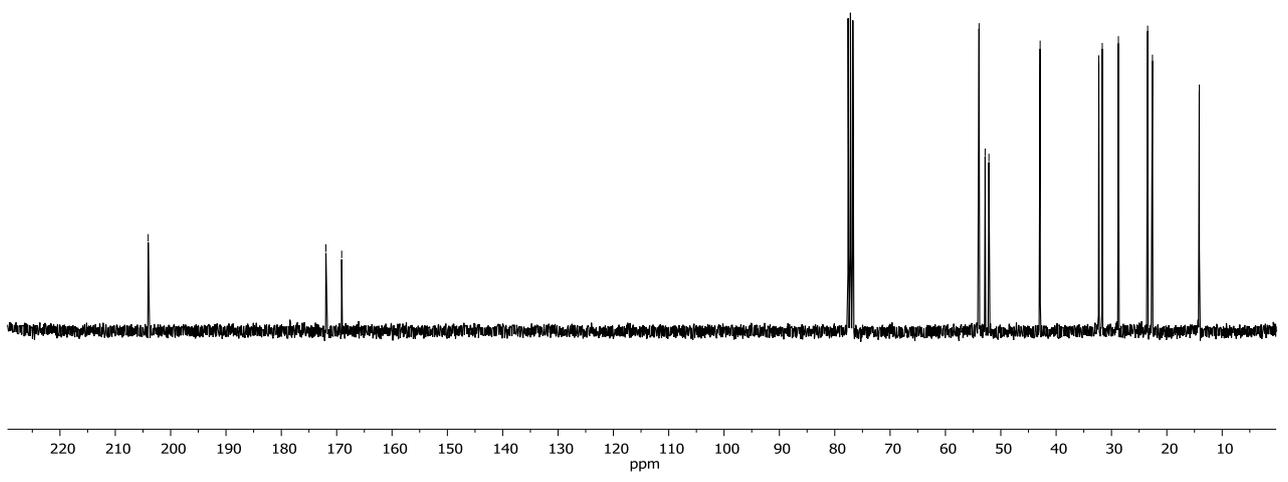


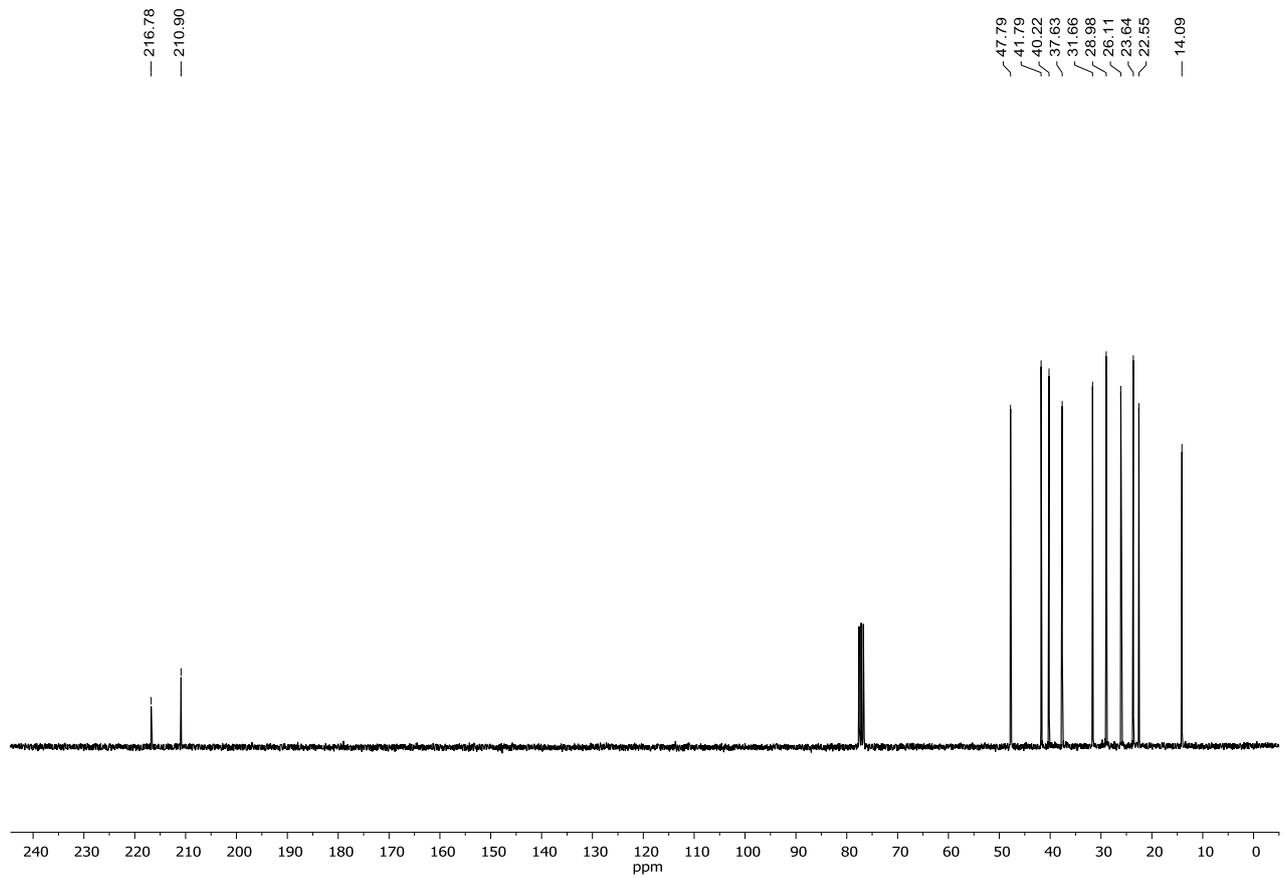
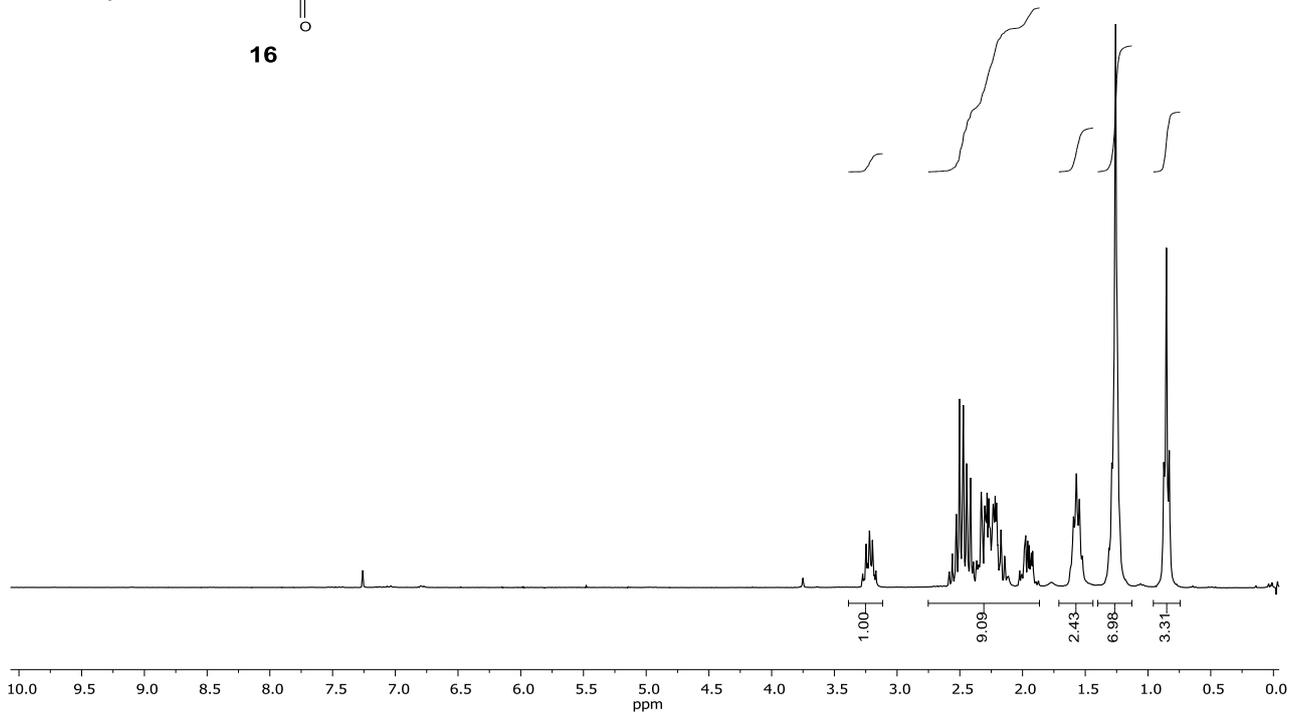
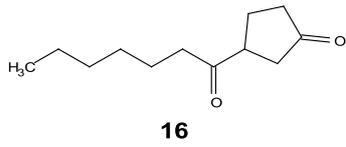


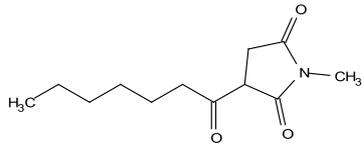
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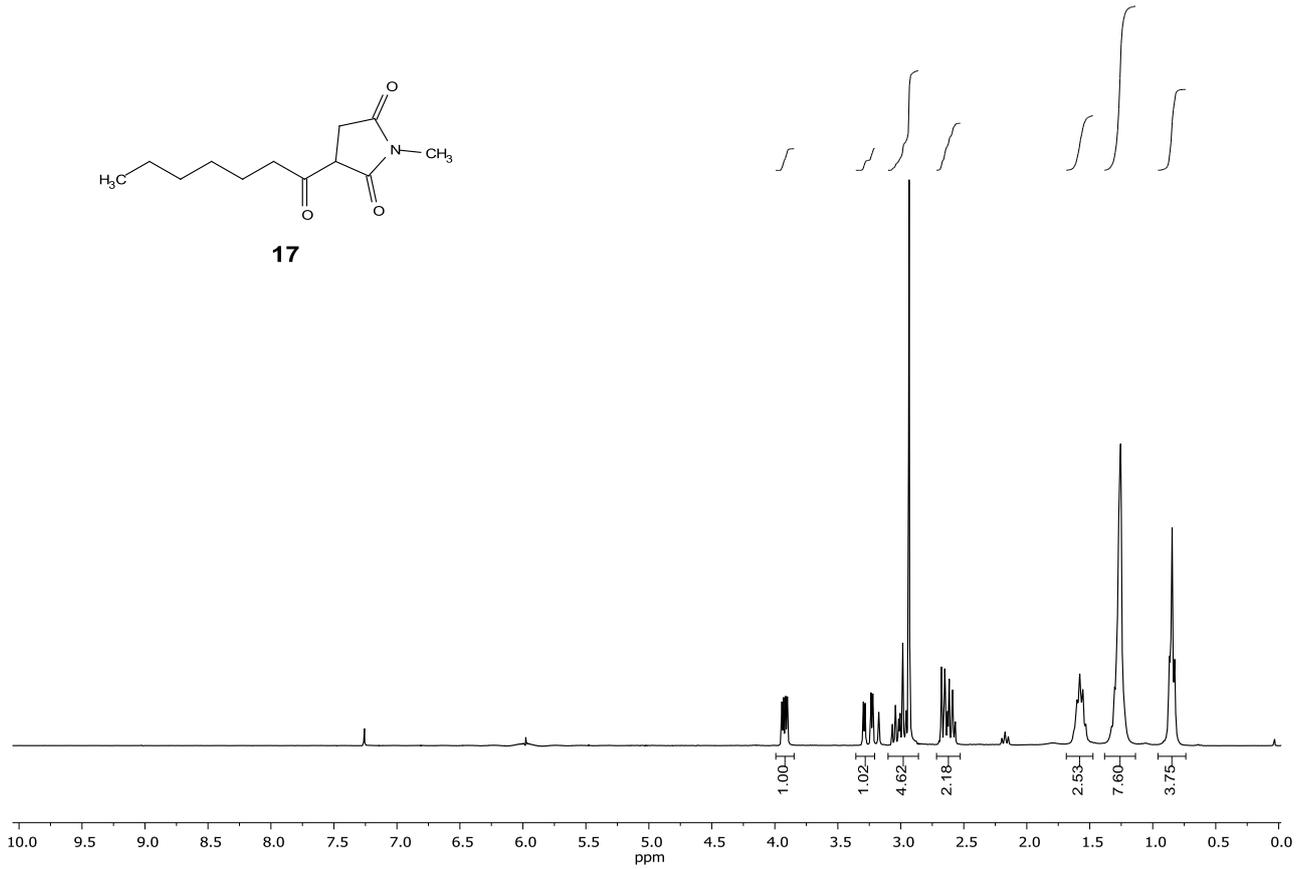
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- 169.09
- 53.93
- 52.83
- 52.15
- 42.89
- 32.29
- 31.66
- 28.75
- 23.46
- 22.59
- 14.13







17



— 201.88

— 175.74  
— 172.84

— 53.05

— 43.24

— 31.60

— 30.00

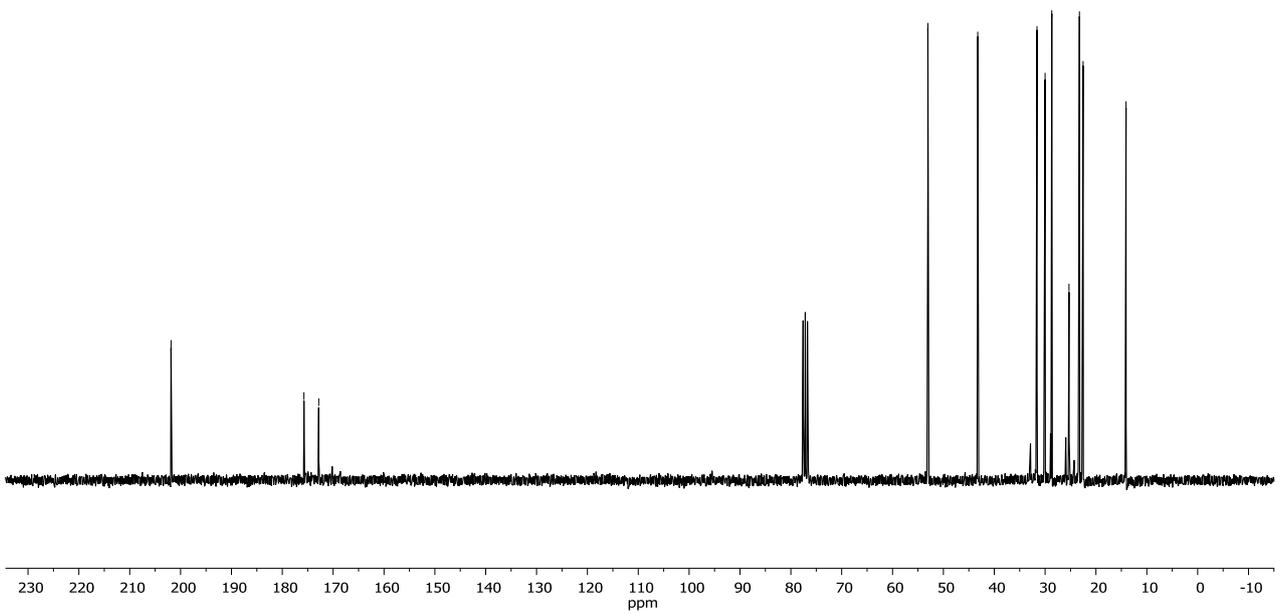
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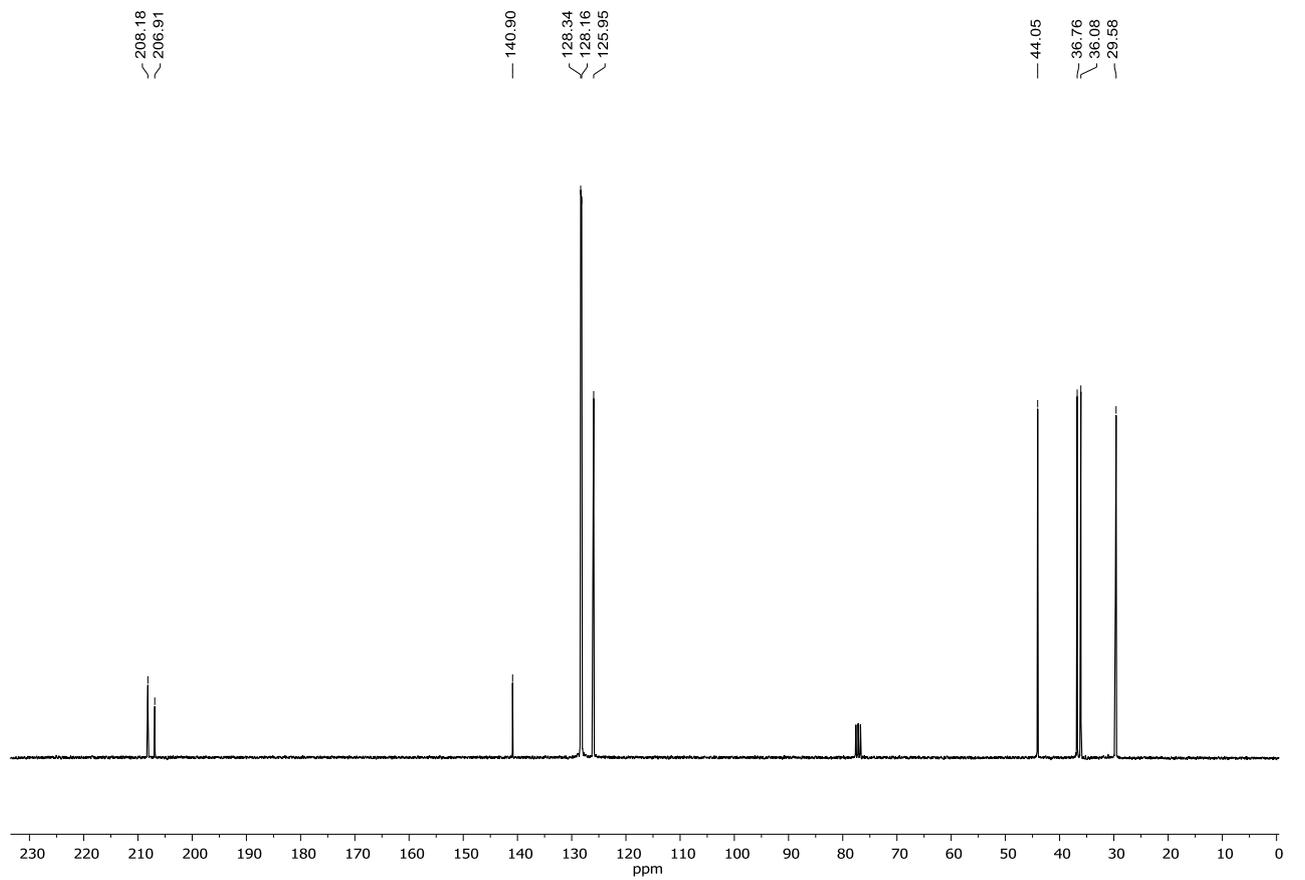
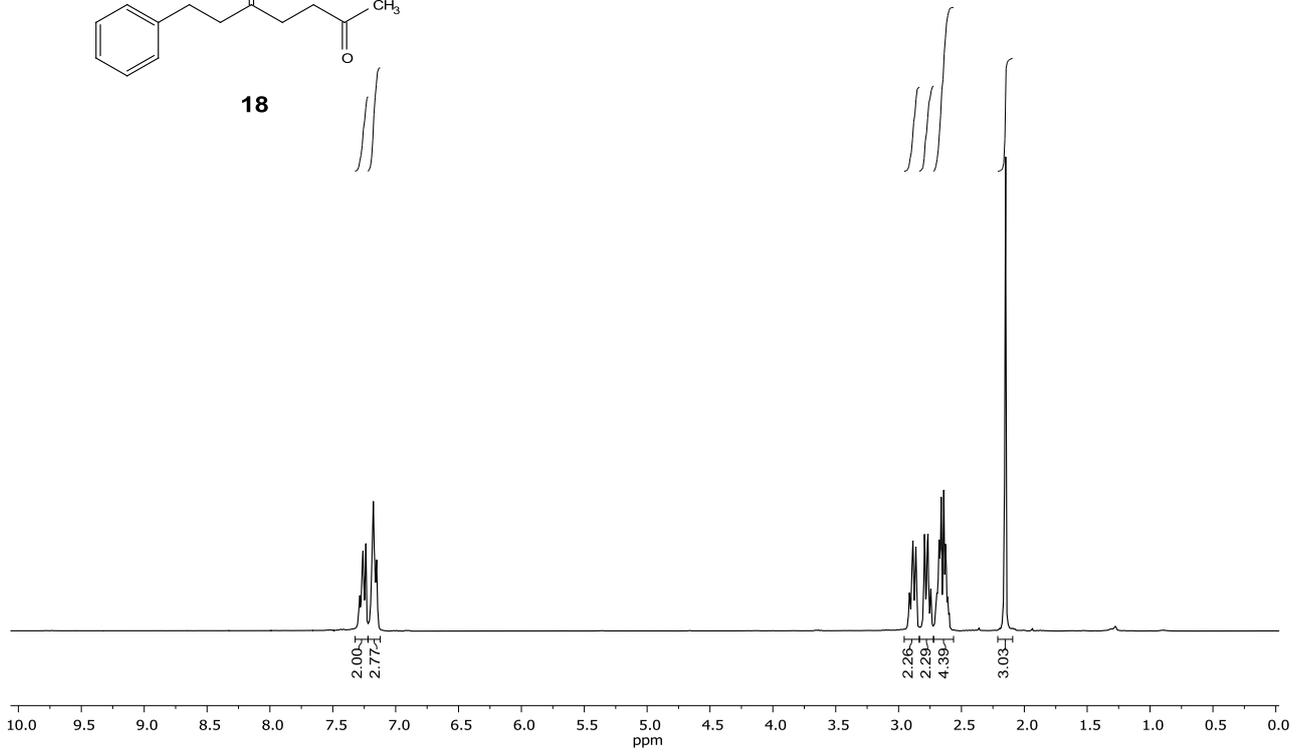
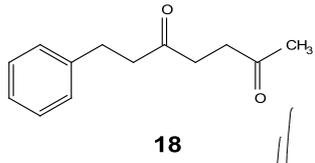
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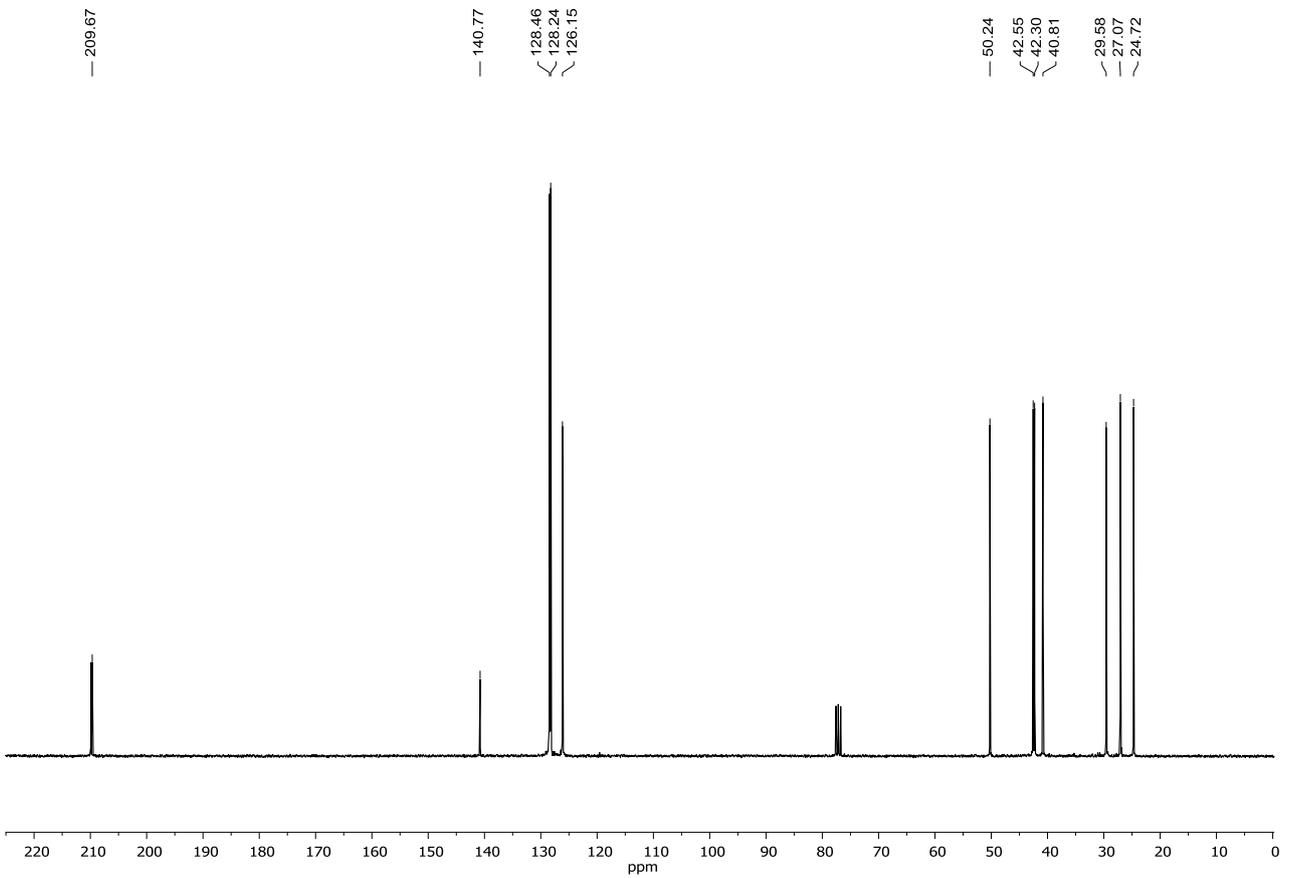
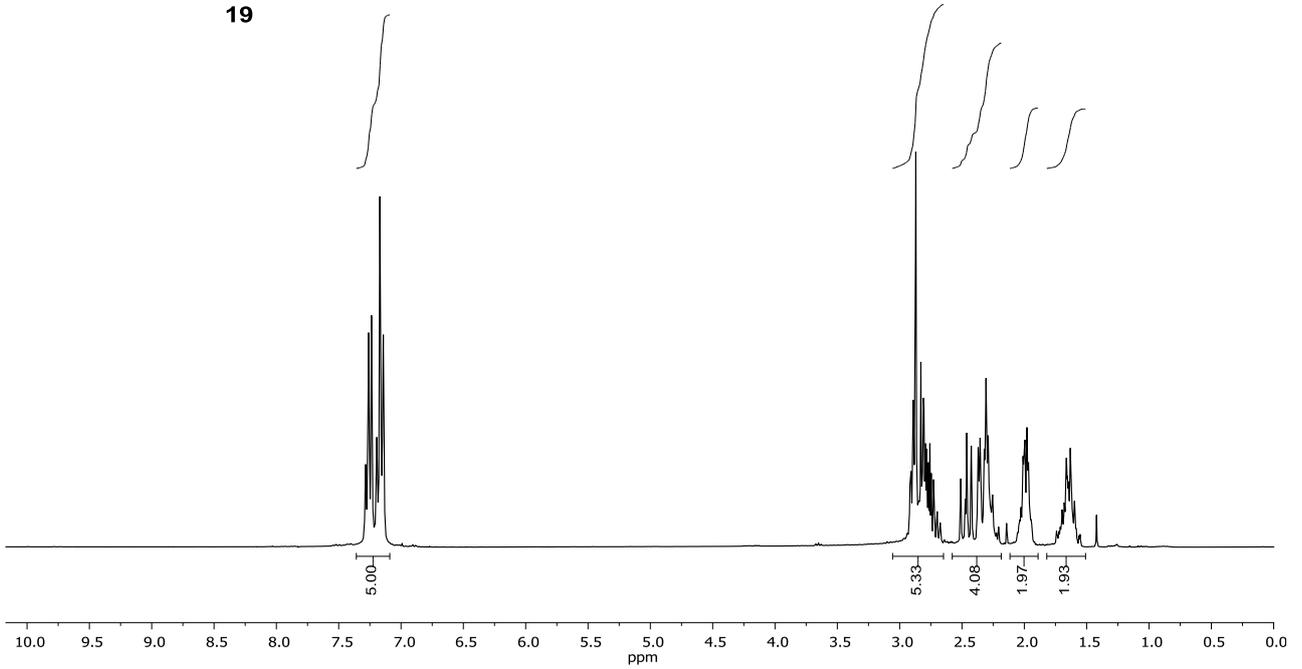
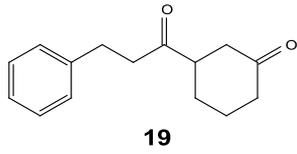
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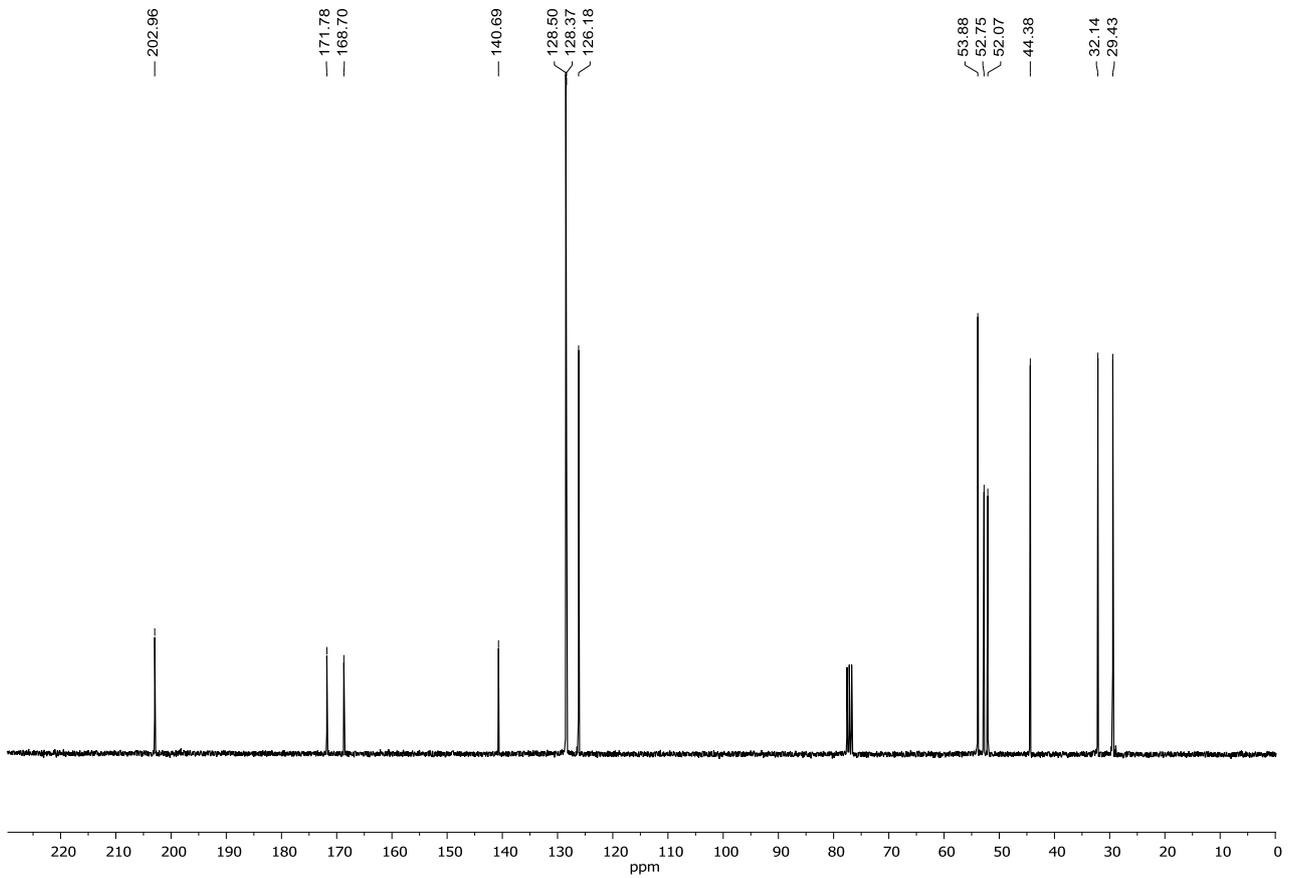
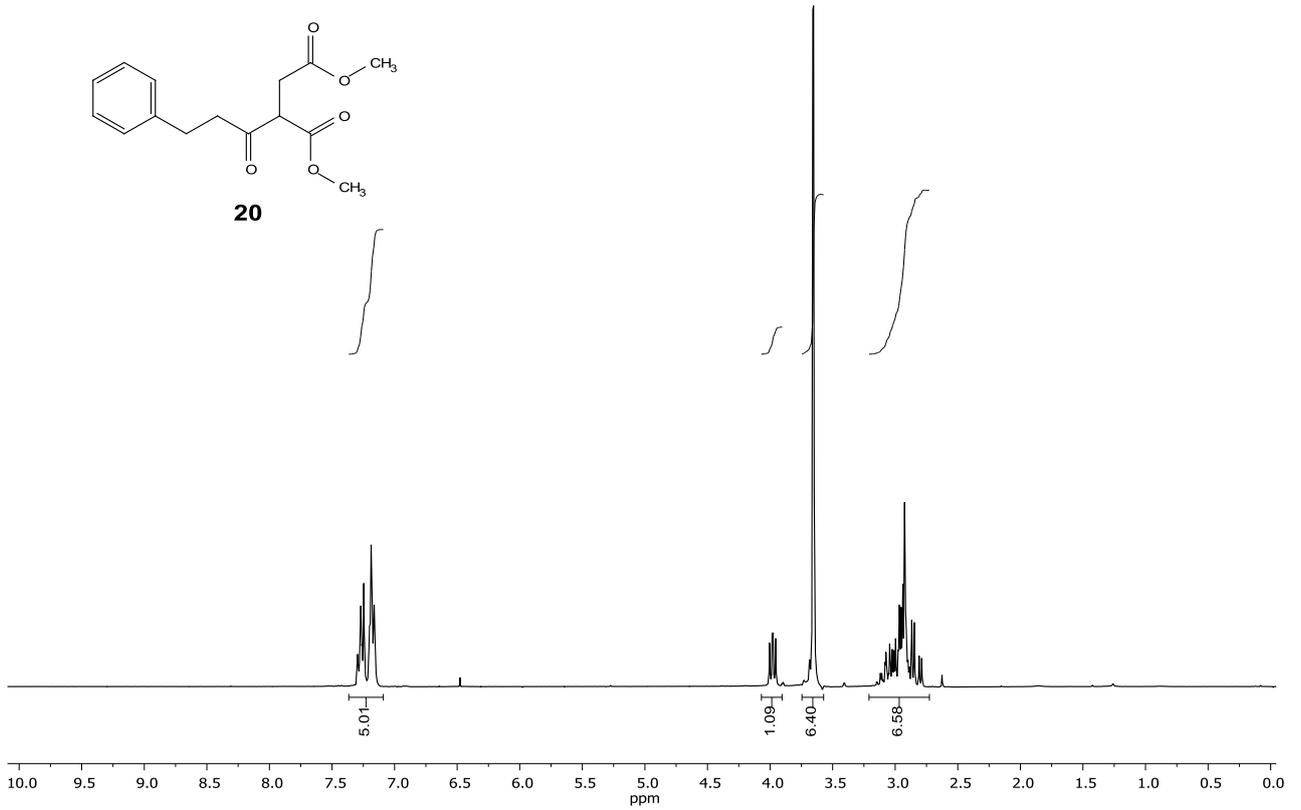
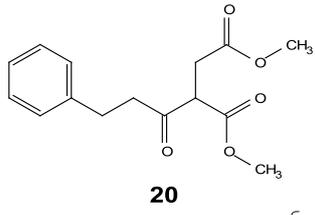
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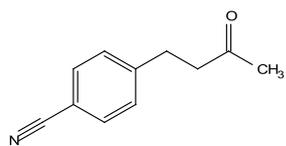
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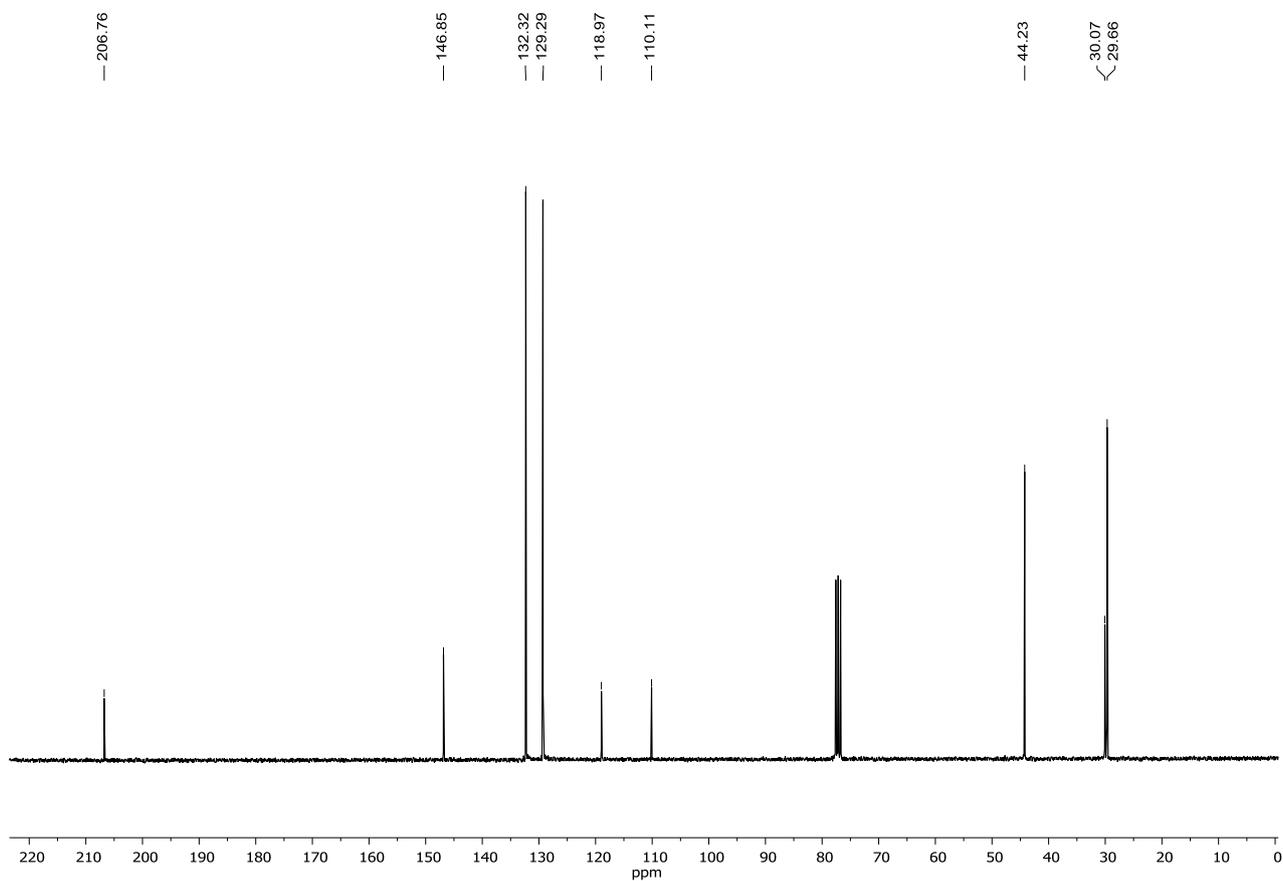
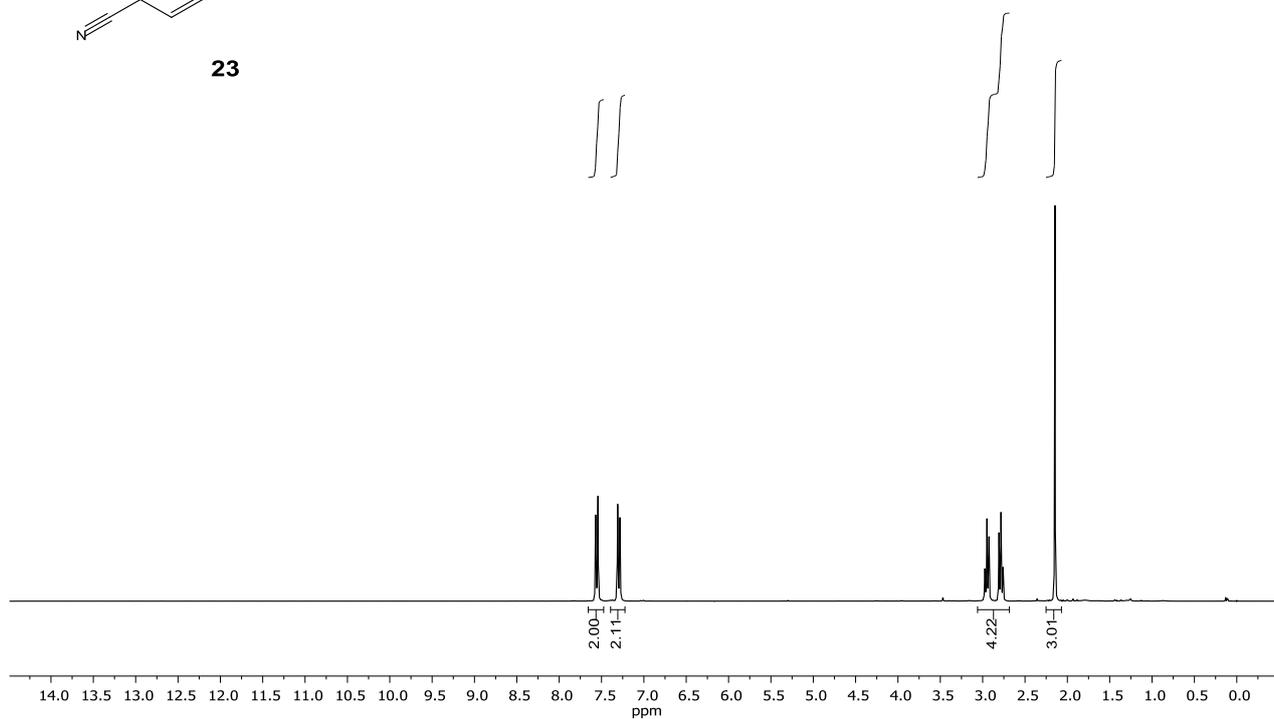


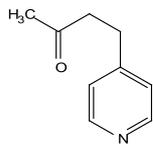






**23**





24

