

# Electronic Supporting Information

## Efficient and sustainable tandem annulation-decarboxylation reaction using ecocatalysis

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## 1. Characterisation of ecocatalysts<sup>®</sup>

### 1.1. MP-AES analyses of ecocatalysts<sup>®</sup>

Table S1. Elemental composition of ecocatalysts<sup>®</sup> determined by MP-AES.

Ecocatalyst <sup>®</sup>	mean of wt(%) (standard deviation)												
	Al	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
Eco1-E-Salix <i>alba</i>	0.07 (0.03)	19.4 (2.8)	0.01 (0.01)	0 (0)	0 (0)	0.12 (0.03)	13.1 (5.9)	3.00 (0.89)	0.02 (0.01)	0.26 (0.03)	0 (0)	0,01 (0.02)	0,21 (0.04)
Eco1-E-Fallopia <i>japonica</i>	0.13 (0.04)	8.93 (2.02)	0.007 (0.01)	0 (0)	0 (0)	0.13 (0.03)	29.2 (1.8)	3.98 (0.23)	0.06 (0.02)	0.14 (0.04)	0 (0)	0 (0)	0.04 (0.05)
Eco1-E-Arundo <i>donax</i>	0.01 (0)	1.37 (0.51)	0.03 (0.02)	0 (0)	0.01 (0.07)	0.025 (0.01)	36.2 (4.3)	1.01 (0.06)	0.03 (0.01)	0.08 (0.05)	0 (0)	0 (0)	0.01 (0.01)
Eco1-E-spent <i>Coffea arabica</i>	0.19 (0.11)	21.49 (1.66)	0.01 (0.01)	0 (0)	0.15 (0.02)	0.39 (0.09)	4.93 (2.70)	7.33 (0.28)	0.19 (0.02)	1.97 (0.56)	0 (0)	0 (0)	0.05 (0.01)

### 1.2. XRPD diffractograms of ecocatalysts<sup>®</sup>

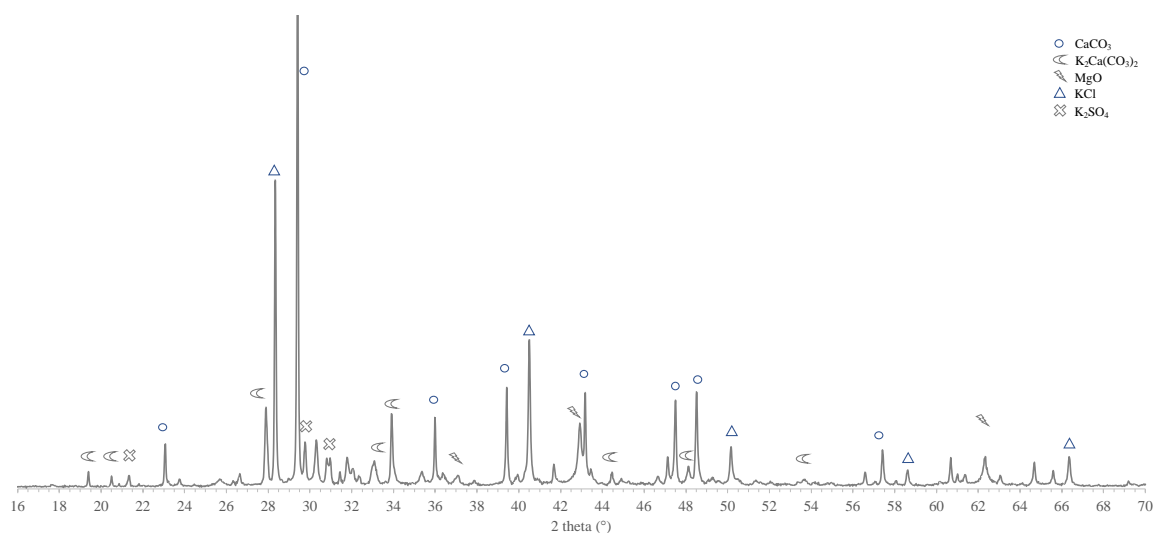


Figure S1. XRPD of Eco1-E-F. japonica

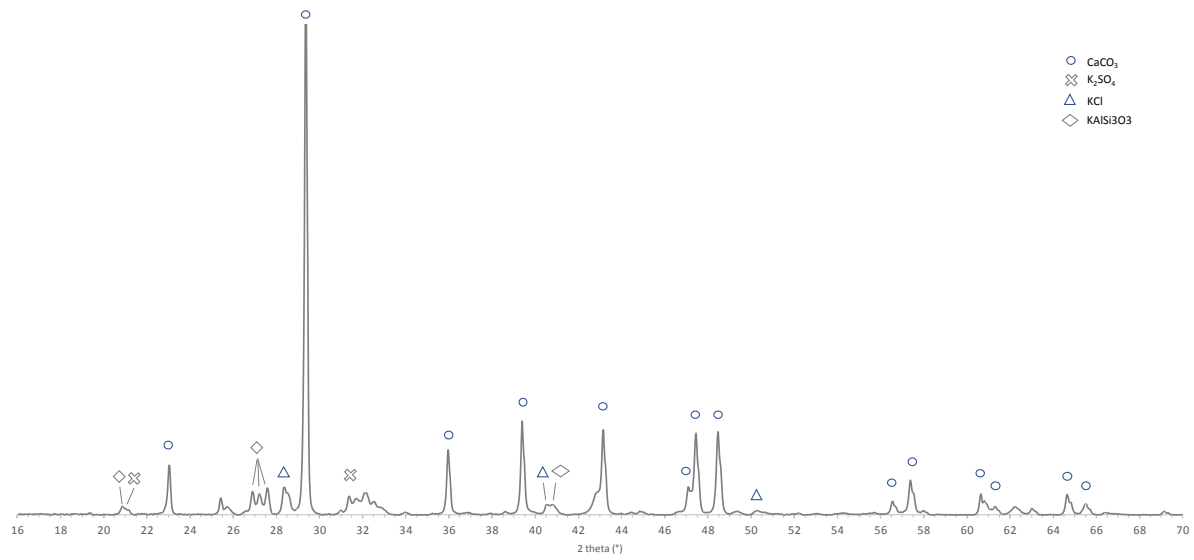


Figure S2. XRPD of *Eco1-E-S. alba*

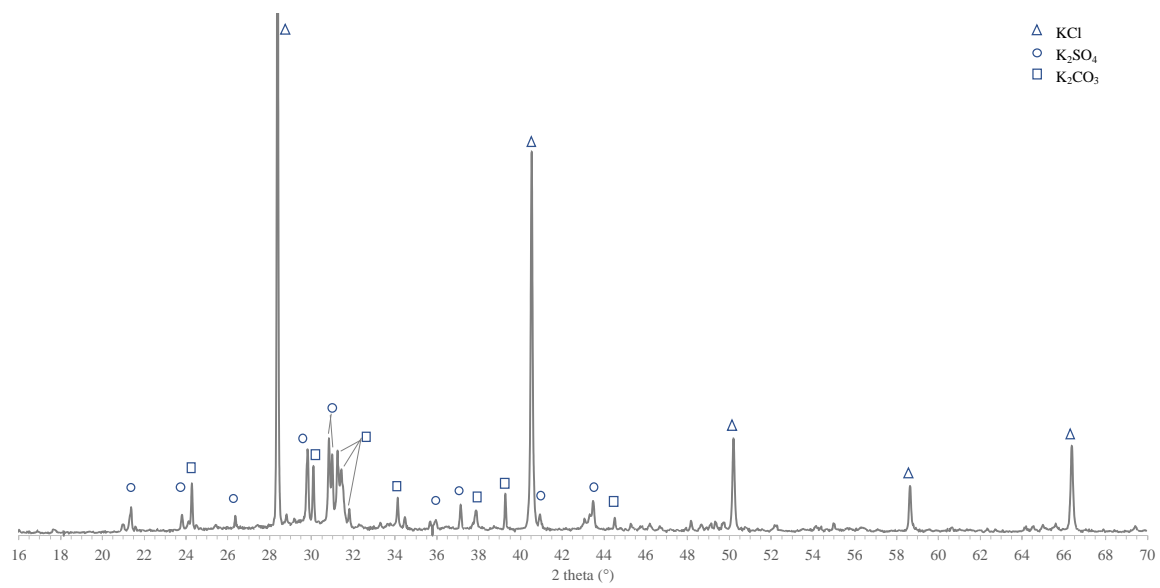


Figure S3. XRPD of *Eco1-E-A. donax*

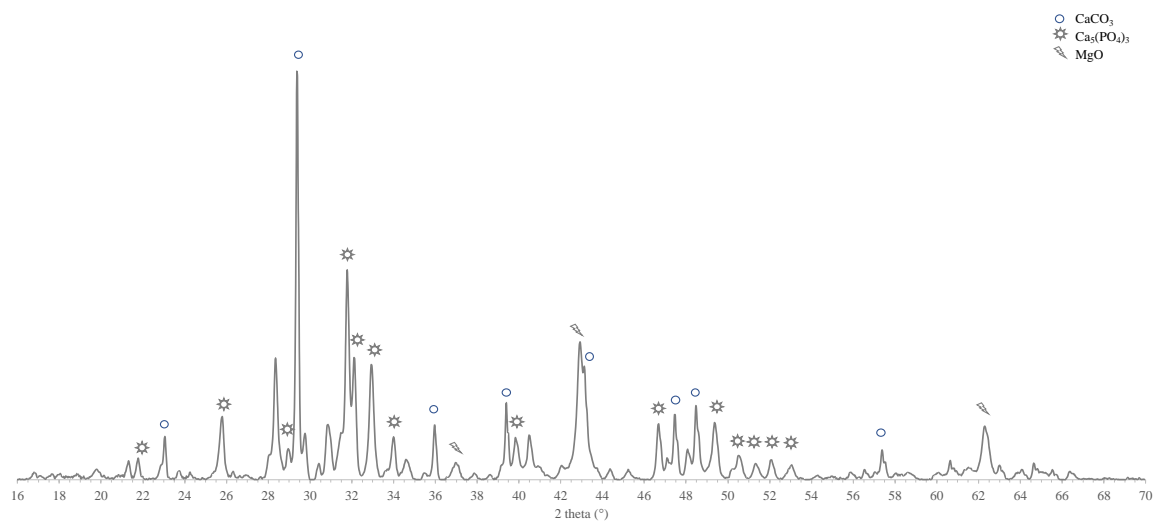


Figure S4. XRPD of Eco1-E-spent *C. arabica*

## 2. Synthesis and characterisation of cyclohexenones

### 2.1. Synthesis of 3-methyl-2-cyclohexenone: experimental conditions used for the Spearman correlation matrix

Table S2. Details of experimental conditions of 38 reactions used for calculating the Spearman correlation matrix. \*These conditions have been reproduced 9 times and the yield corresponds to the mean of the 9 yields.

Exp.	(eco)catalyst	K (eq.)	Mg (eq.)	Ca (eq.)	Na (eq.)	cat. (g/mol)	temp. (°C)	time (min)	glycerol (eq.)	yield (%)
1		0,0019	0,0027	0,0041	0,0007	1	180	30	0,5	45
2	Eco1-E-spent	0,0038	0,0054	0,0081	0,0014	2	180	30	0,5	61
3	<i>C. arabica</i>	0,0150	0,0218	0,0323	0,0058	7	180	30	0,5	65
4		0,0345	0,0500	0,0743	0,0132	16	180	30	0,5	77
5		0,0000	0,0017	0,0000	0,0000	0	180	30	0,5	30
6		0,0000	0,0033	0,0000	0,0000	0	180	30	0,5	60
7	MgO	0,0000	0,0066	0,0000	0,0000	0	180	30	0,5	55
8		0,0000	0,0131	0,0000	0,0000	1	180	30	0,5	71
9		0,0000	0,0525	0,0000	0,0000	2	180	30	0,5	67
10		0,0000	0,1000	0,0000	0,0000	4	180	30	0,5	88
11		0,0109	0,0000	0,0000	0,0000	1	180	30	0,5	45
12	K <sub>2</sub> CO <sub>3</sub>	0,0263	0,0000	0,0000	0,0000	2	180	30	0,5	62
13		0,0526	0,0000	0,0000	0,0000	4	180	30	0,5	60
14		0,1000	0,0000	0,0000	0,0000	7	180	30	0,5	72
15	Eco1-E-A. <i>donax</i>	0,2137	0,0110	0,0109	0,0004	25	180	30	0,5	65
16	Eco1-E-S. <i>alba</i>	0,0406	0,0110	0,0660	0,0004	10	180	30	0,5	67
17	Eco1-E-F. <i>japonica</i>	0,0479	0,0110	0,0110	0,0051	11	180	30	0,5	68
18	Eco1-E-A. <i>donax</i>	0,0499	0,0026	0,0025	0,0001	5,86	180	30	0,5	57
19	MgO	0,0000	0,0131	0,0000	0,0000	1	180	30	0,5	71
20	CaCO <sub>3</sub>	0,0000	0,0000	0,0440	0,0000	4	180	30	0,5	14
21	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	0,0000	0,0000	0,0440	0,0000	4	180	30	0,5	0
22	MgO & CaCO <sub>3</sub> & Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	0,0000	0,0130	0,0320	0,0000	4	180	30	0,5	82
23	Eco1-E-spent <i>C. arabica</i> (350 °C)	0,0085	0,0181	0,0293	0,0263	36	180	90	0,5	57
24	Eco1-E-spent <i>C. arabica</i> (no TT)	0,0030	0,0027	0,0066	0,0103	131	180	30	0,5	5
25	K <sub>2</sub> CO <sub>3</sub>	0,0109	0,0000	0,0000	0,0000	1	180	30	0	29
26	K <sub>2</sub> CO <sub>3</sub>	0,0109	0,0000	0,0000	0,0000	1	180	30	0,5	45
27	Eco1-E-spent <i>C. arabica</i>	0,0075	0,0109	0,0162	0,0029	4	180	30	0	34
28		0,0075	0,0109	0,0162	0,0029	4	100	30	0,5	0
29		0,0075	0,0109	0,0162	0,0029	4	120	30	0,5	0
30	Eco1-E-spent <i>C. arabica</i>	0,0075	0,0109	0,0162	0,0029	4	140	30	0,5	16
31		0,0075	0,0109	0,0162	0,0029	4	160	30	0,5	56
32		0,0075	0,0109	0,0162	0,0029	4	200	30	0,5	84

33		<b>0,0075</b>	<b>0,0109</b>	<b>0,0162</b>	<b>0,0029</b>	<b>4</b>	<b>220</b>	<b>30</b>	<b>0,5</b>	<b>92</b>
34	Eco1-E-spent <i>C. arabica</i>	0,0075	0,0109	0,0162	0,0029	4	180	90	0,5	82
35		<b>0,0075</b>	<b>0,0109</b>	<b>0,0162</b>	<b>0,0029</b>	<b>4</b>	<b>220</b>	<b>45</b>	<b>0,5</b>	<b>92</b>
36		0,0075	0,0109	0,0162	0,0029	4	220	90	0,5	72
37*	Eco1-E-spent <i>C. arabica</i>	0,0075	0,0109	0,0162	0,0029	4	180	30	0,5	81*
38	-	0,0000	0,0000	0,0000	0,0000	0	180	30	0,5	0

## 2.2. Synthesis of 3-methyl-2-cyclohexenone using Eco1-E-spent *C. arabica* from different spent coffee grounds

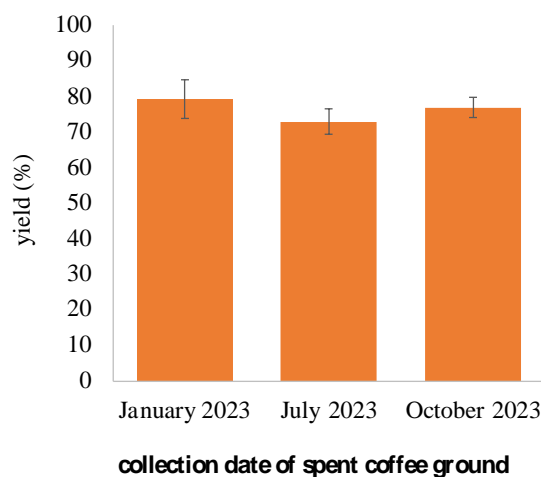


Figure S5: Yield comparison for the synthesis of 3-methyl-2-cyclohexenone using Eco1-E-spent *C. arabica* from spent coffee grounds collected at different seasons. Conditions of the reaction: ethylacetoacetate (2 equiv.), Eco1-E-spent *C. arabica* (0.01 equiv. of Mg), butenone (1 equiv.) and glycerol (0.5 equiv.), 180 °C, 30 min. Yields were quantified by GC-FID analysis.

## 2.3. Recycling and reuse of ecocatalysts<sup>®</sup>

Table S3. Experimental conditions for the recycling of Eco1-E-spent *C. arabica*

run	ecocatalyst <sup>®</sup>	temp. (°C)	time (min)	yield (%)
1				72
2				63
3	Eco1-E-spent <i>C. arabica</i>	220	45	63
4				37
5				38

## 2.4. Method of calculation of green metrics

### E-factor

$$E_{\text{factor}} = \frac{\text{total mass of all wastes (for all runs, reaction and workup)}}{\text{total mass of final product (for all runs)}}$$

### Process Mass Intensity (PMI)

$$\text{PMI} = \frac{\text{total mass of reactants}}{\text{mass of final product}}$$

### Energy

$$E (\text{h.}^\circ\text{C}) = (\text{reaction time}) \times (\text{reaction temperature})$$

Since data of electric power are not available for each electric equipment used to perform a chemical reaction followed by its workup in literature, the calculation of energy could not be done in Joules and was simplified.

### Space Time Yield (STY)

$$\text{STY} (\text{g. h}^{-1} \cdot \text{L}^{-1}) = \frac{\text{masse of product}}{\text{volume of reactor} \times \text{reaction time}}$$

### Turn-Over Number (TON)

$$\text{TON} = \frac{\text{total moles of limiting reactants of all runs}}{\text{moies of catalysts used for all runs}} \times \text{mean of all yields}$$

### Turn-Over Frequency (TOF)

$$\text{TOF} (\text{h}^{-1}) = \frac{\text{TON}}{\text{reaction time of all catalysed reactions}}$$

## 2.5. Procedure and characterisation of cyclohexenones

### 2.5.1. General procedure for the scope of isolated cyclohexenones

The  $\beta$ -keto ester (2 equiv.), Eco1-E-spent *C. arabica* (0.011 equiv. of Mg), conjugated enone (or enal) (1 equiv.) and glycerol (0.5 equiv.) were mixed in a micro-wave reactor (CEM Discover<sup>®</sup> 2.0). The reaction mixture was ramped to temperature for 10 minutes until 180 °C, then was stirred for 45 minutes at 180 °C. The reaction procedure was repeated four times for subsequent purification. After cooling to room temperature, the Eco1-E-spent *C. arabica* was filtered through sinter with ethyl acetate (20 mL) and the collected solution was concentrated under reduced pressure. The crude product was purified by distillation under vaccum.

**3-methyl-2-cyclohexen-1-one (3).** The reaction of ethyl acetoacetate (30 mmol, 3.83 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), 3-buten-2-one (15 mmol, 1.39 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **3** in 65% yield/70% purity. The product was isolated by liquid-liquid extraction with NaOH 0.5M (3 x 18 mL) and ethyl acetate (25 mL). The product **3** was isolated in 55% yield as a light yellow liquid by distillation. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.86 (bs, 1H), 2.32 (m, 2H), 2.27 (t, J = 6.0 Hz, 2H), 2.00-1.95 (m, 2H), 1.94 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 199.8, 162.9, 126.7, 37.1, 31.0, 24.5, 22.6.

**3-ethyl-2-cyclohexen-1-one (7).** The reaction of ethyl acetoacetate (30 mmol, 3.83 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), 1-penten-3-one (15 mmol, 1.53 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **7** in 73% yield/76% purity. The crude product was isolated by liquid-liquid extraction with NaOH 0.5M (3 x 18mL) and ethyl acetate (25 mL). The product **7** was isolated in 63% yield as a light yellow liquid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 5.87 (s, 1H), 2.35 (m, 2H), 2.28 (t, J = 6.0 Hz, 2H), 2.25-2.21 (q, J = 7.4 Hz, 2H), 2.00-1.95 (m, 2H), 1.10-1.07 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 200.0, 167.9, 124.5, 37.3, 30.8, 29.6, 22.6, 11.2.

**3,6-dimethyl-2-cyclohexen-1-one (8).** The reaction of ethyl 2-methylacetoacetate (30 mmol, 4.24 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), 3-buten-2-one (15 mmol, 1.39 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **8** in 69% yield/75% purity. The crude product was isolated by liquid-liquid extraction with NaOH 0.5M (5 x 18mL) and ethyl acetate (25 mL). The product **8** was isolated

in 67% yield as a light yellow liquid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.81 (s, 1H), 2.36-2.21 (m, 3H), 2.04-2.00 (m, 1H), 1.91 (s, 3H), 1.70-1.64 (m, 1H), 1.10 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 202.5, 161.9, 126.4, 40.7, 31.0, 30.9, 24.5, 15.4.

**2,3-dimethyl-2-cyclohexen-1-one (9).** The reaction of ethyl 3-oxovalerate (30mmol, 4.29mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), 3-buten-2-one (15 mmol, 1.39 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **9** in in 79% yield/72% purity. The crude product was isolated by liquid-liquid extraction with NaOH 0.5M (3 x 24 mL) and ethyl acetate (30 mL). The product **9** was isolated in 74% yield as a light yellow liquid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.37 (m, 2H), 2.33-2.31 (m, 2H), 1.94-1.90 (m, 5H), 1.75 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.3, 155.3, 131.2, 37.7, 32.9, 22.4, 21.6, 10.9.

**3,5-dimethyl-2-cyclohexen-1-one (10).** The reaction of ethyl acetoacetate (30 mmol, 3.83 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), 3-penten-2-one (15 mmol, 2.31 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **10** in 90% yield/100% purity as a light yellow liquid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.83 (s, 1H), 2.38 (dd,  $J = 16.2, 3.6$  Hz, 1H), 2.27 (dd,  $J = 18.0, 4.2$  Hz, 1H), 2.20-2.12 (m, 1H), 2.01-1.96 (m, 2H), 1.92 (s, 3H), 1.04 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.3, 162.2, 126.5, 45.4, 39.6, 30.2, 24.5, 21.3.

**Isophorone (11).** The reaction of ethyl acetoacetate (30 mmol, 3.83 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), mesityl oxide (15 mmol, 1.81 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **11** in 6% yield/68% purity. The crude product was isolated by liquid-liquid extraction with NaOH 0.5M (3x6mL) and ethyl acetate (8 mL). The product **11** was isolated in 6% yield as a light yellow liquid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.86 (m, 1H), 2.18 (s, 2H), 2.15 (s, 2H), 1.92 (s, 3H), 1.01 (s, 6H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.1, 160.5, 125.6, 50.9, 45.4, 33.7, 28.4, 24.7.

**5-Methyl-2-cyclohexen-1-one (12).** The reaction of ethyl acetoacetate (30 mmol, 3.83 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), crotonaldehyde (15 mmol, 1.39 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **12** in 33% yield/100% purity as a light yellow liquid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.95 (ddd,  $J = 15.0, 10.2, 8.4$  Hz, 1H), 6.02-5.98 (m, 1H), 2.50-2.37 (m, 2H), 2.28-2.16 (m, 1H), 2.14-1.98 (m, 2H), 1.06 (d,  $J = 10.2$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.2, 150.0, 129.7, 46.4, 34.1, 30.5, 21.3.

**4-methyl-2-cyclohexen-1-one (13).** The reaction of ethyl acetoacetate (30 mmol, 3.83 mL, 2 equiv.), Eco1-E-spent *C. arabica* (0.17 mmol, 53 mg, 0.011 equiv. of Mg), methacrolein (15 mmol, 1.39 mL, 1 equiv.) and glycerol (7.5 mmol, 0.6 mL, 0.5 equiv.) provided **13** in 33% yield/80% purity.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.78 (ddd,  $J = 10.2, 2.4, 1.2$  Hz, 1H), 5.92 (ddd,  $J = 10.2, 2.4, 1.2$  Hz, 1H), 2.54-2.52 (m, 1H), 2.47-2.44 (m, 1H), 2.36-2.31 (m, 1H), 2.10-2.07 (m, 1H), 1.68-1.61 (dddd,  $J = 16.8, 13.2, 9.0, 4.2$  Hz, 1H), 1.13 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.1, 156.6, 128.9, 37.2, 31.4, 31.2, 20.5.



2.5.2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of cyclohexenones

**3-methyl-2-cyclohexen-1-one (3)**

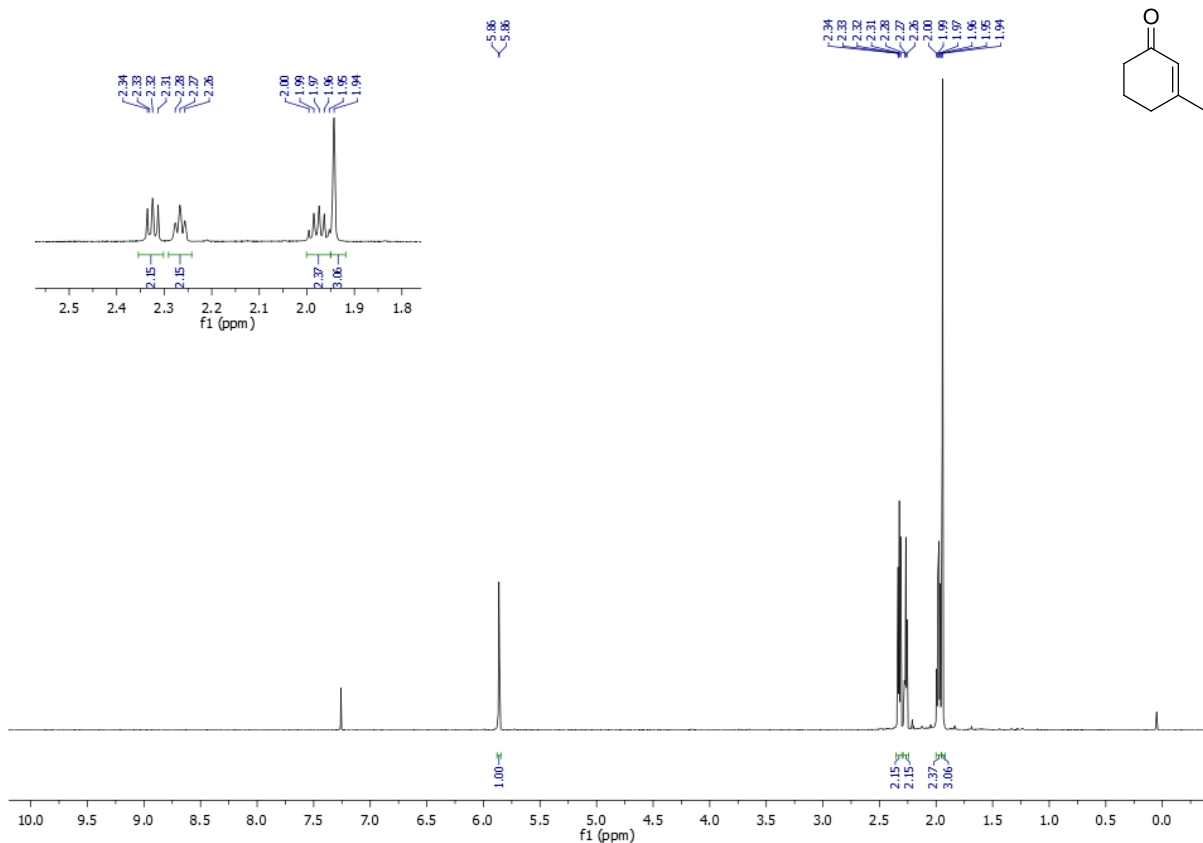


Figure 6.  $^1\text{H}$  NMR spectrum (600MHz,  $\text{CDCl}_3$ ) of 3

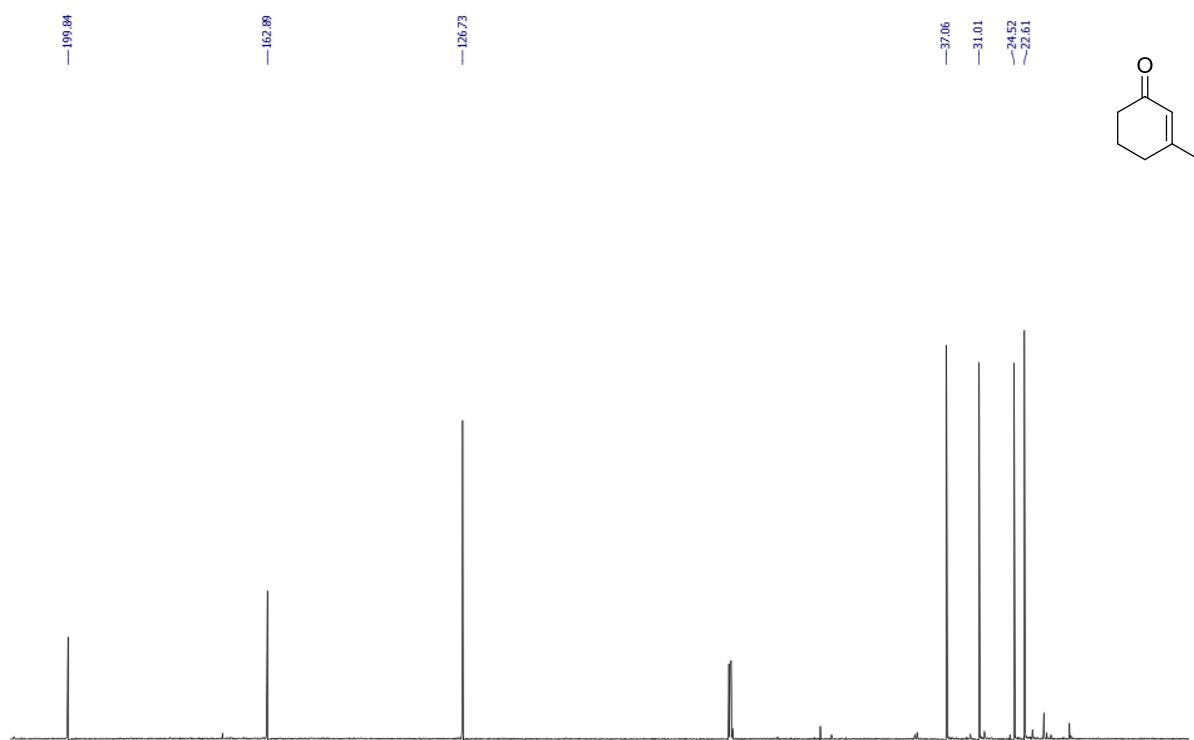


Figure 7.  $^{13}\text{C}$  NMR spectrum (150MHz,  $\text{CDCl}_3$ ) of 3

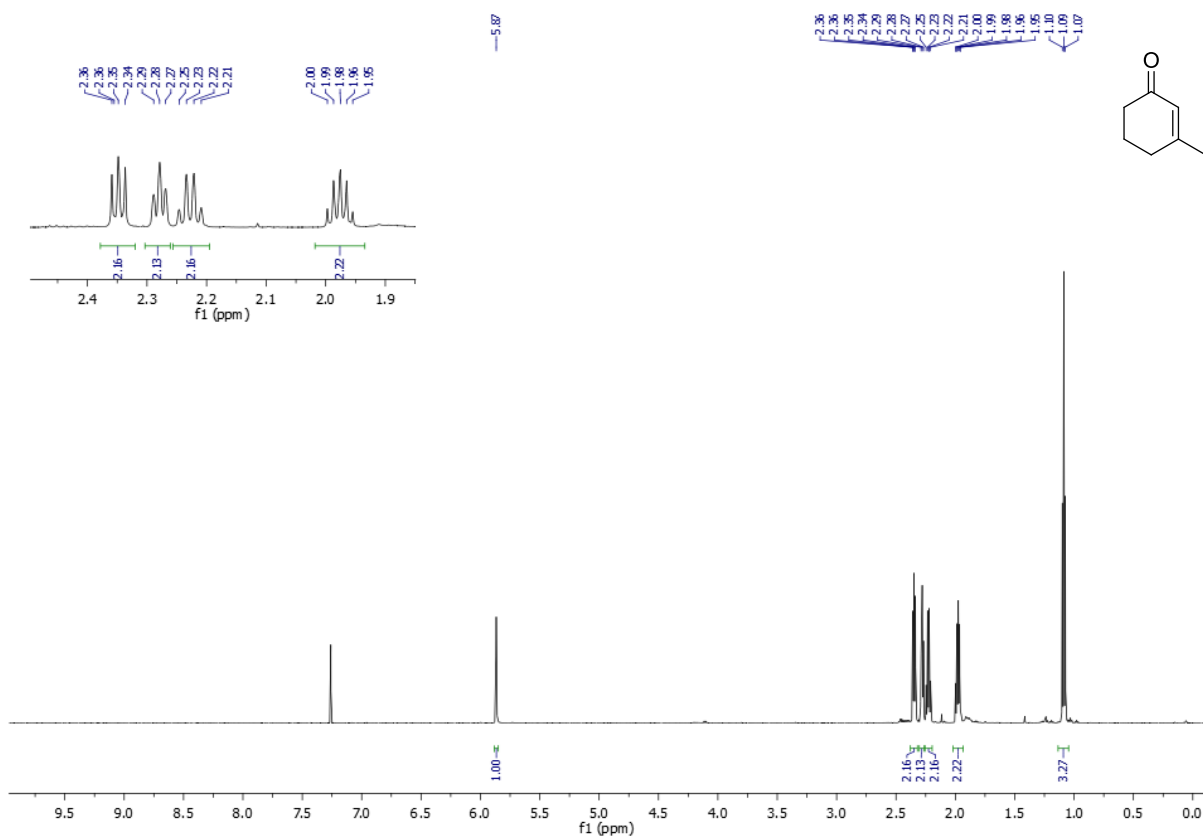


Figure 3.  $^1\text{H NMR}$  spectrum (600 MHz,  $\text{CDCl}_3$ ) of 7

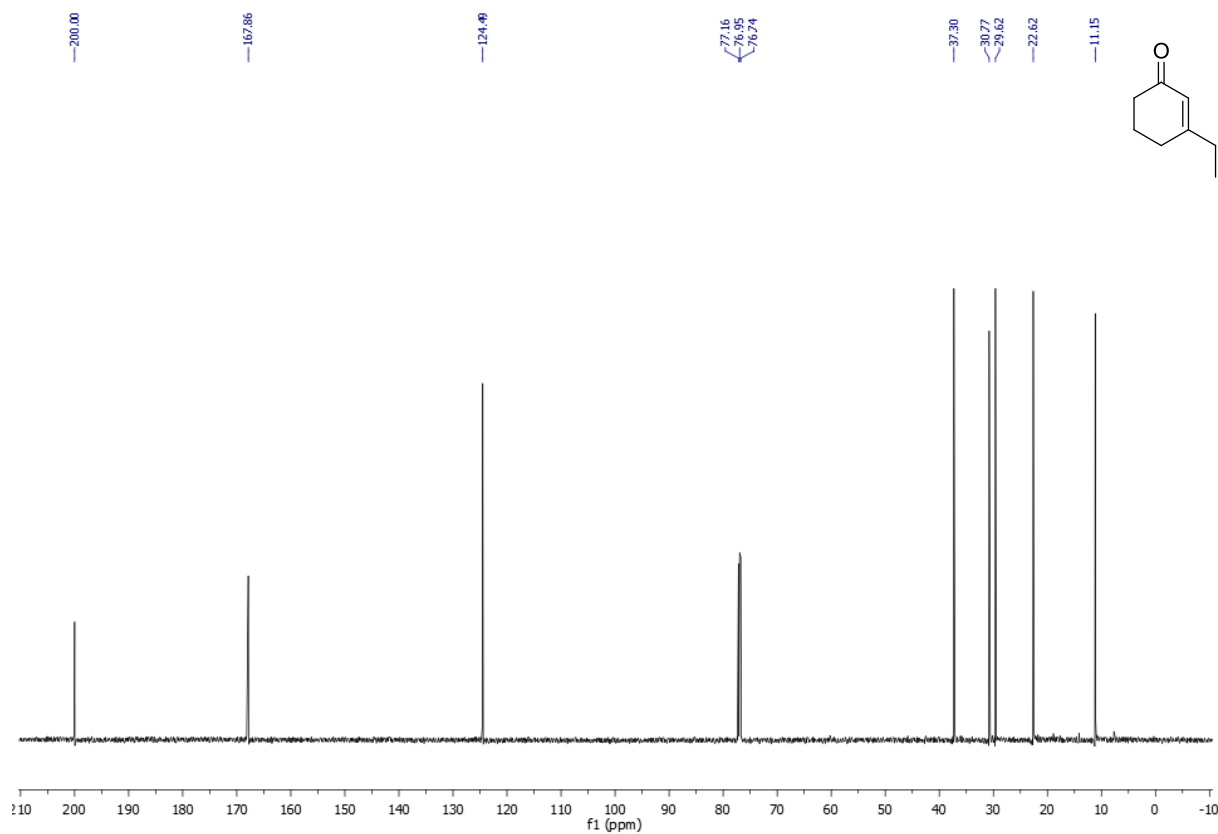


Figure 4.  $^{13}\text{C NMR}$  spectrum (150 MHz,  $\text{CDCl}_3$ ) of 7

**3-ethyl-2-cyclohexen-1-one (7)**

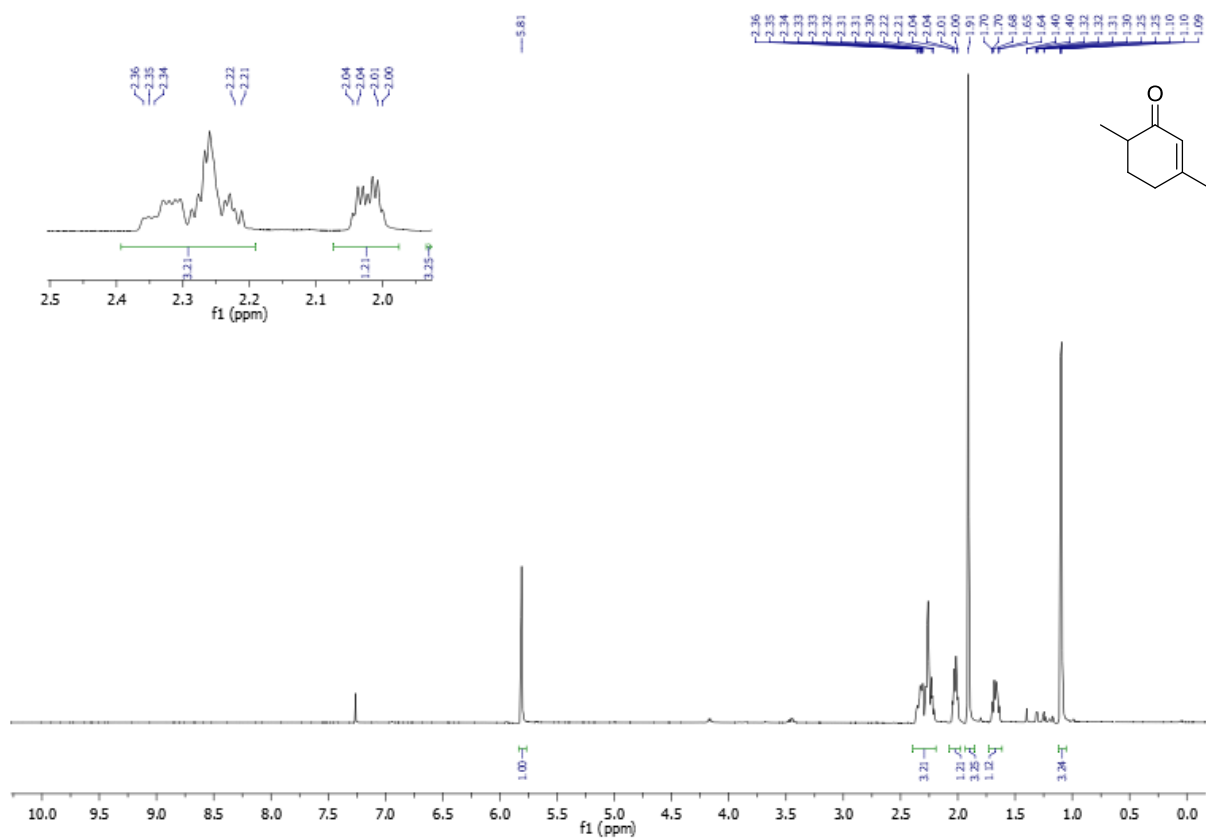


Figure 5. <sup>1</sup>H NMR spectrum (600MHz, CDCl<sub>3</sub>) of 8

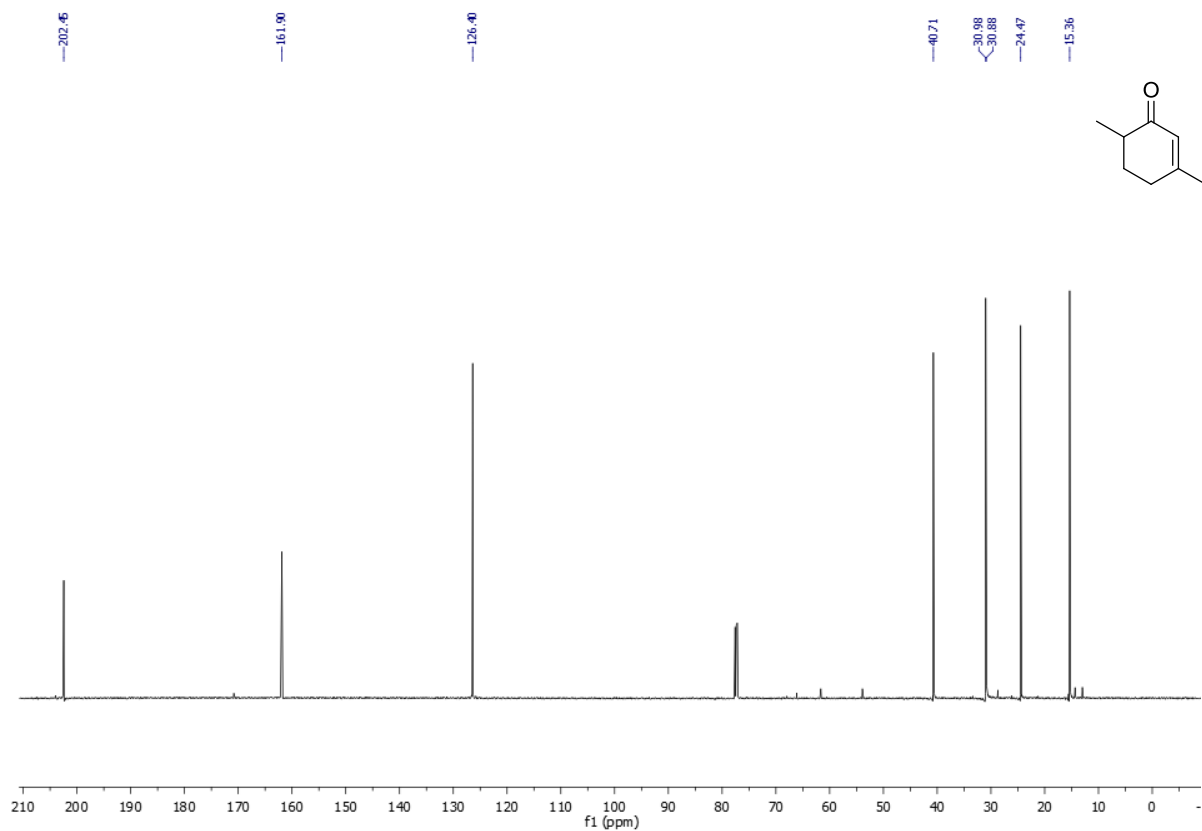


Figure 6. <sup>13</sup>C NMR spectrum (150MHz, CDCl<sub>3</sub>) of 8

**3,6-dimethyl-2-cyclohexen-1-one (8)**

### 2,3-dimethyl-2-cyclohexen-1-one (9)

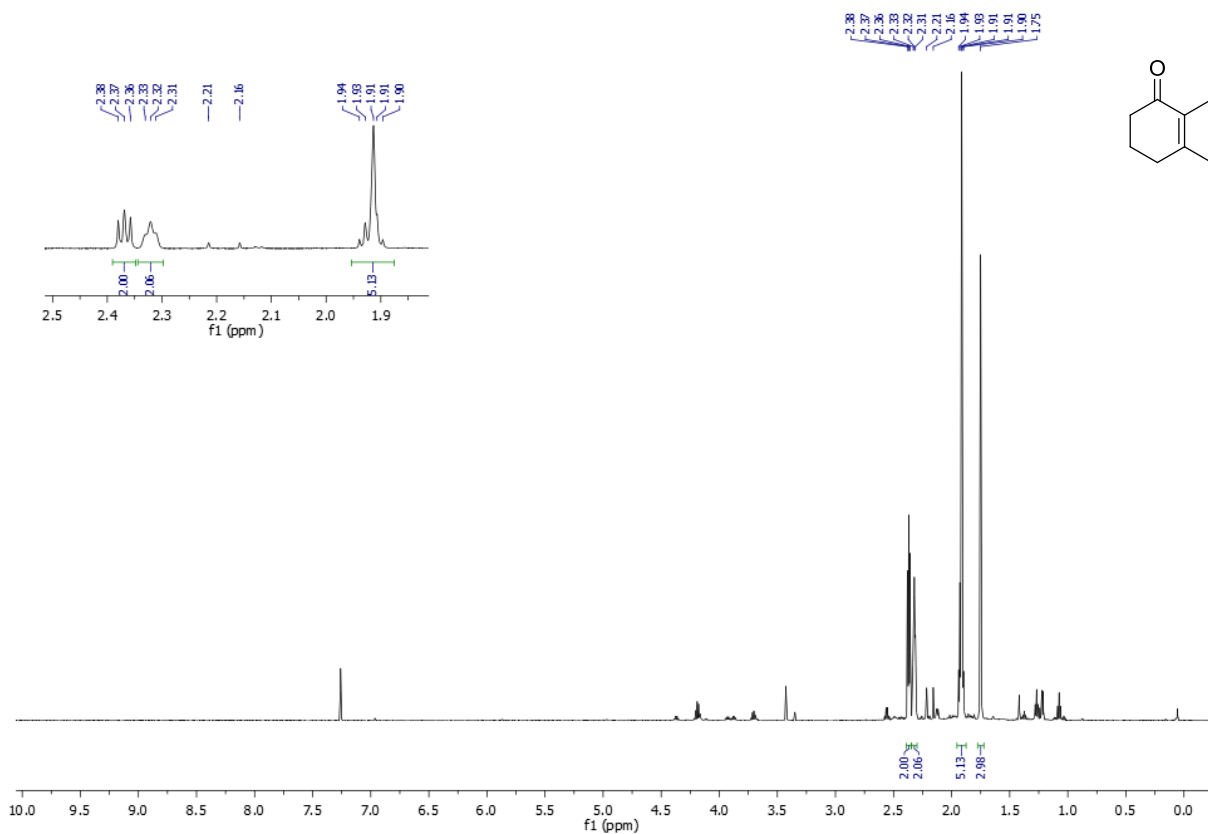


Figure 7.  $^1\text{H}$  NMR spectrum (600MHz,  $\text{CDCl}_3$ ) of 9

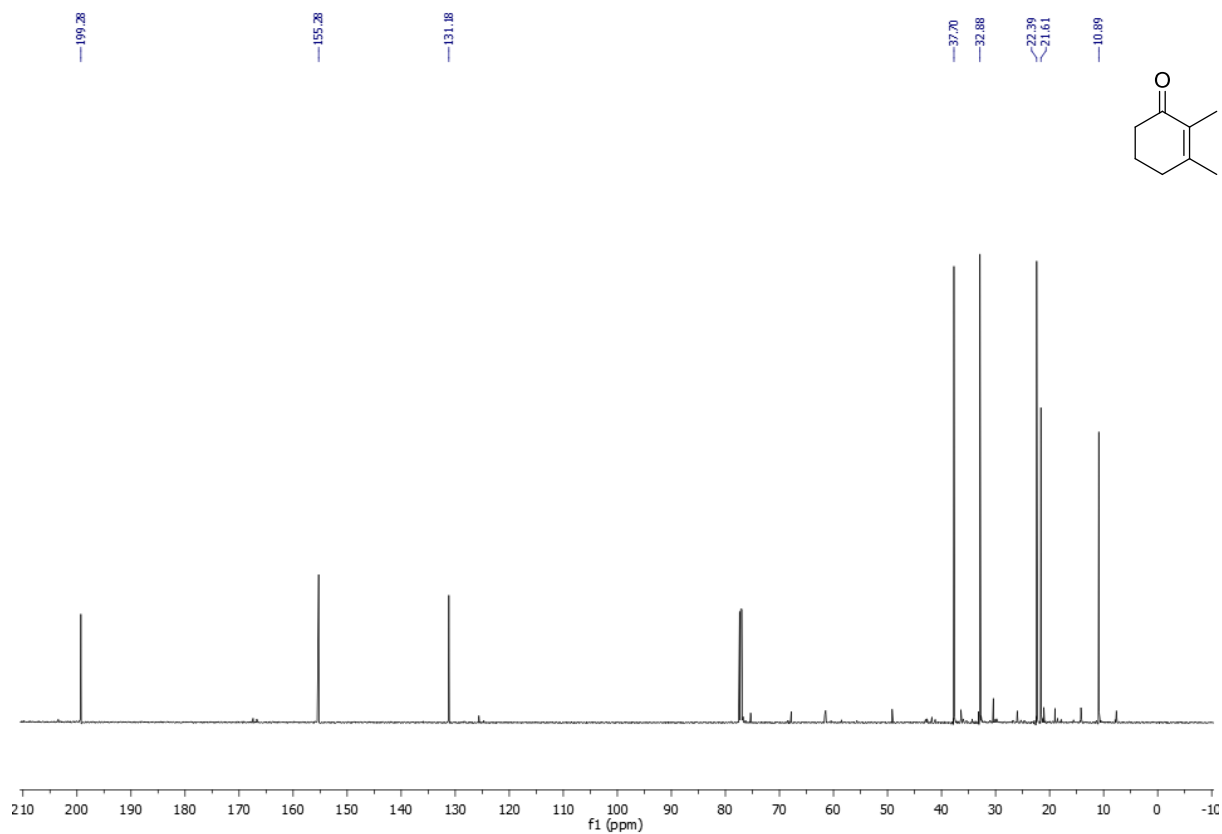


Figure 8.  $^{13}\text{C}$  NMR spectrum (150MHz,  $\text{CDCl}_3$ ) of 9

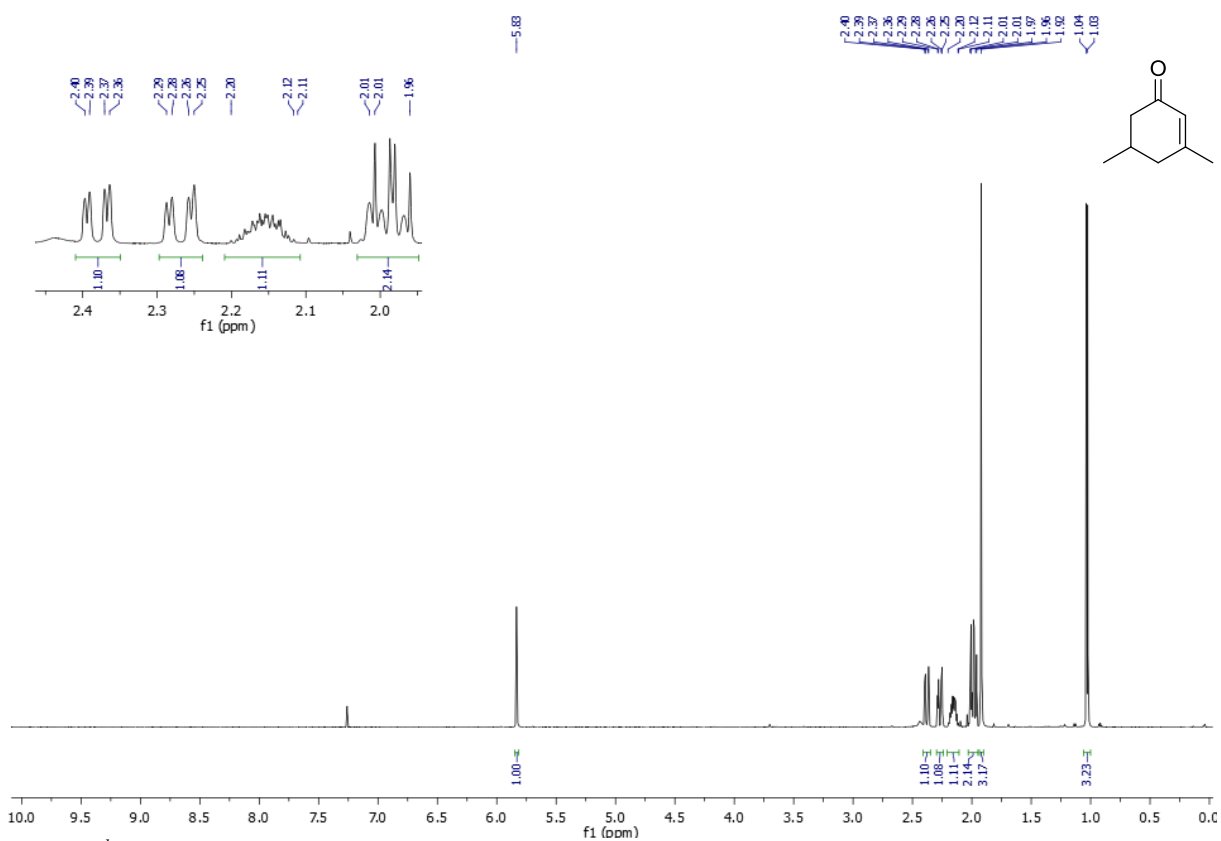


Figure 9.  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of 10

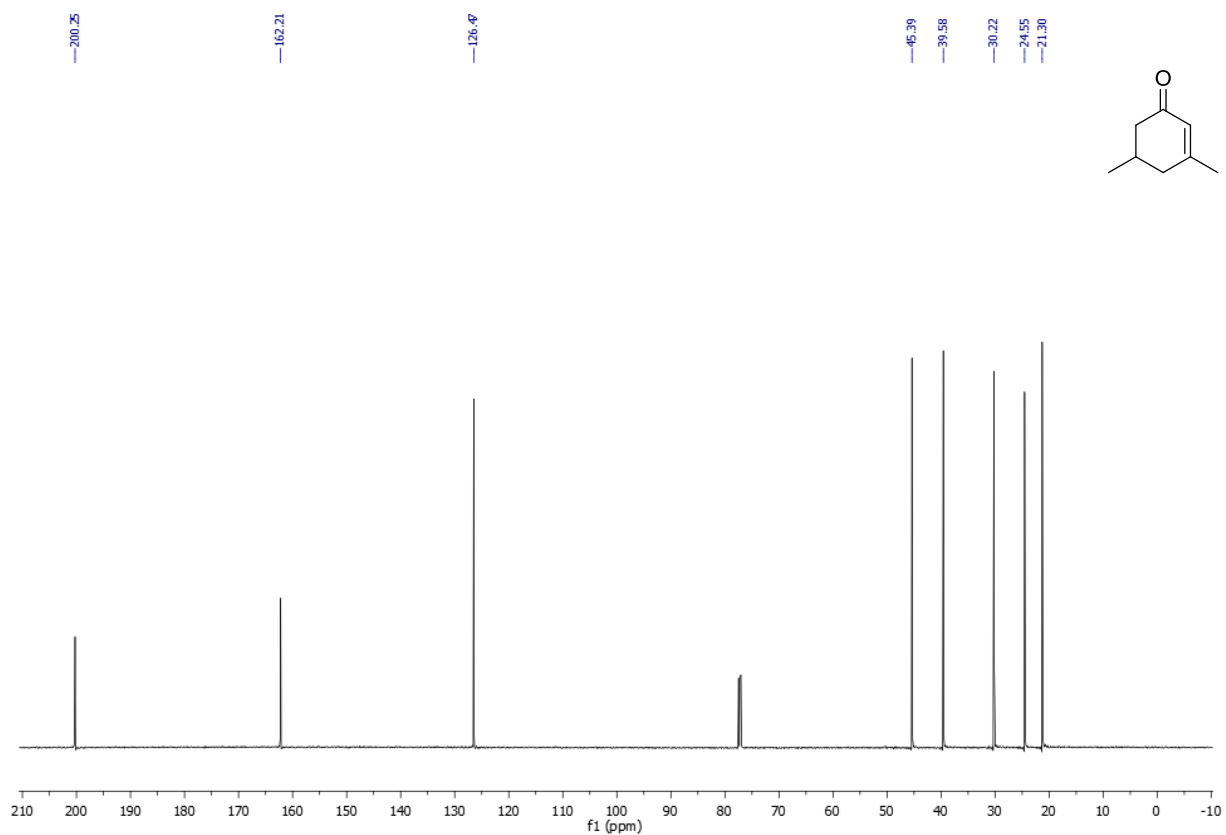


Figure 10.  $^{13}\text{C}$  NMR spectrum (150 MHz,  $\text{CDCl}_3$ ) of 10

**3,5-dimethyl-2-cyclohexen-1-one (10)**



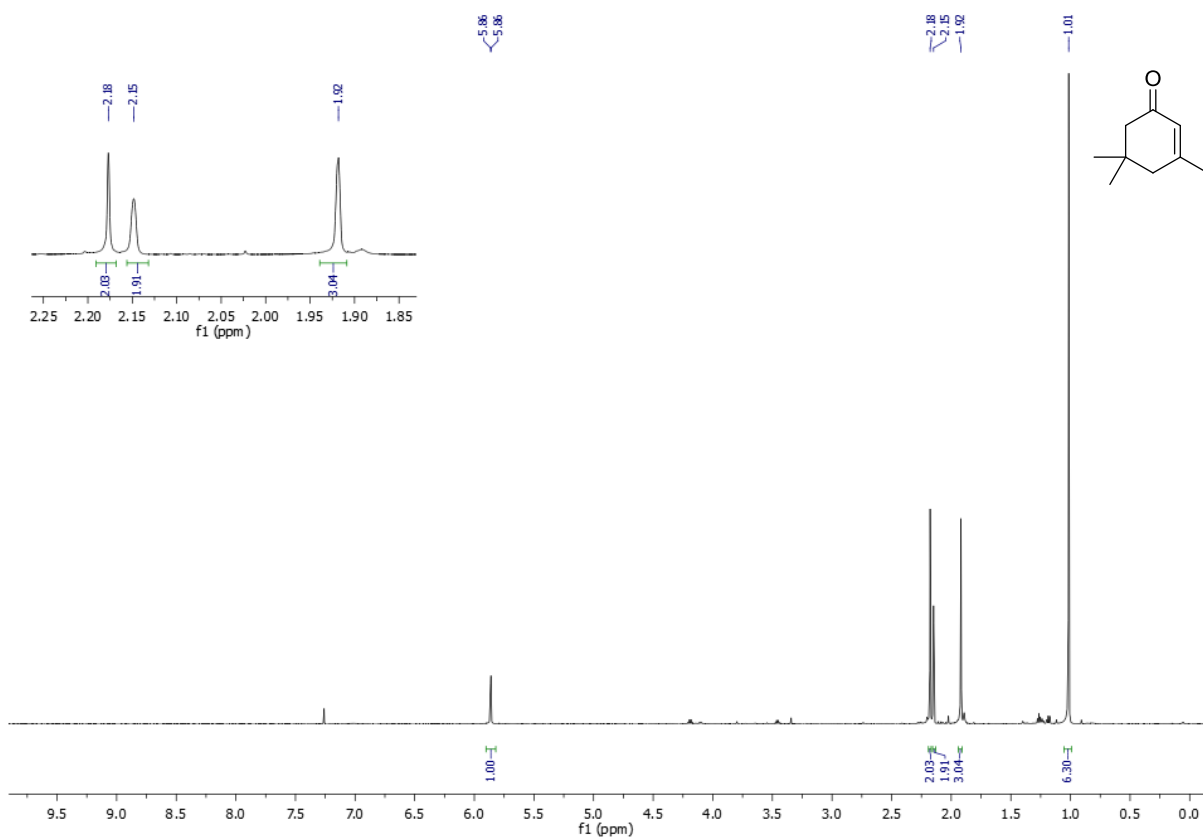


Figure 13.  $^1\text{H}$  NMR spectrum (600MHz,  $\text{CDCl}_3$ ) of 11

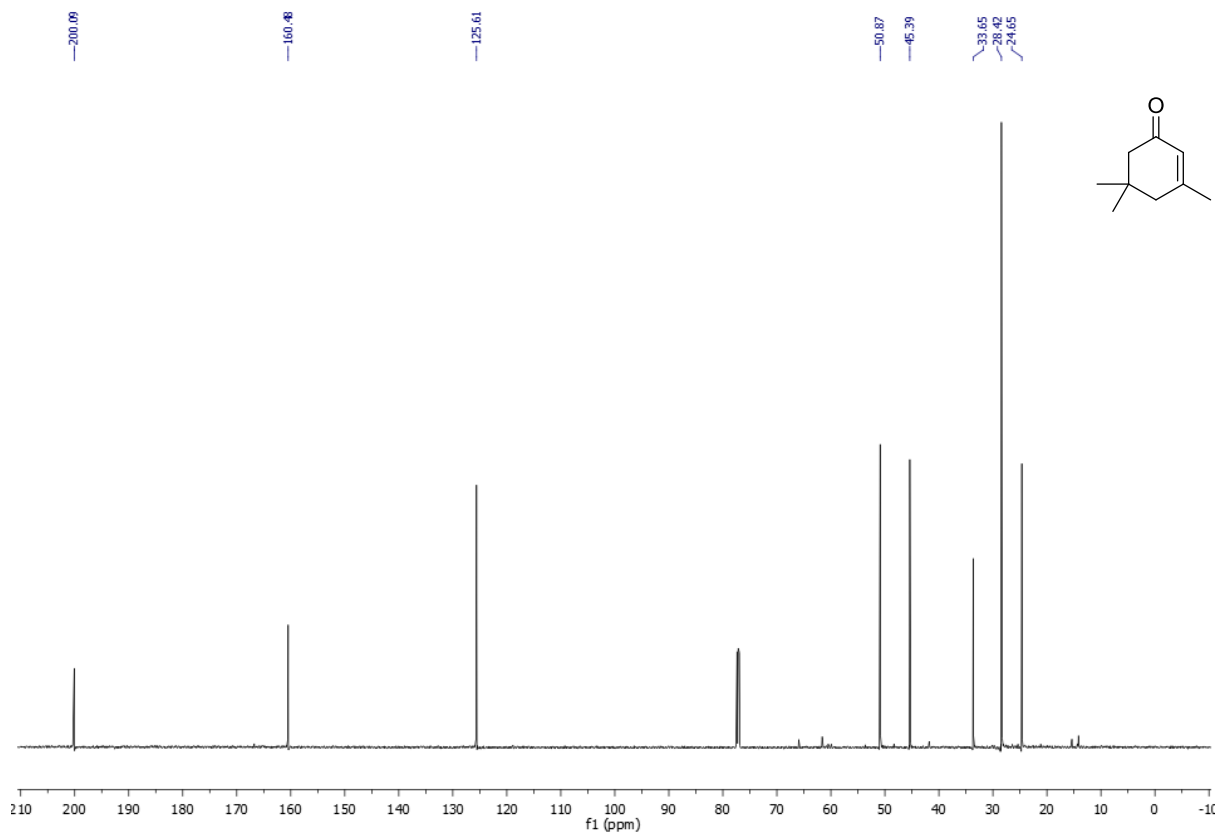


Figure 14.  $^{13}\text{C}$  NMR spectrum (150MHz,  $\text{CDCl}_3$ ) of 11

**Isophorone (11)**





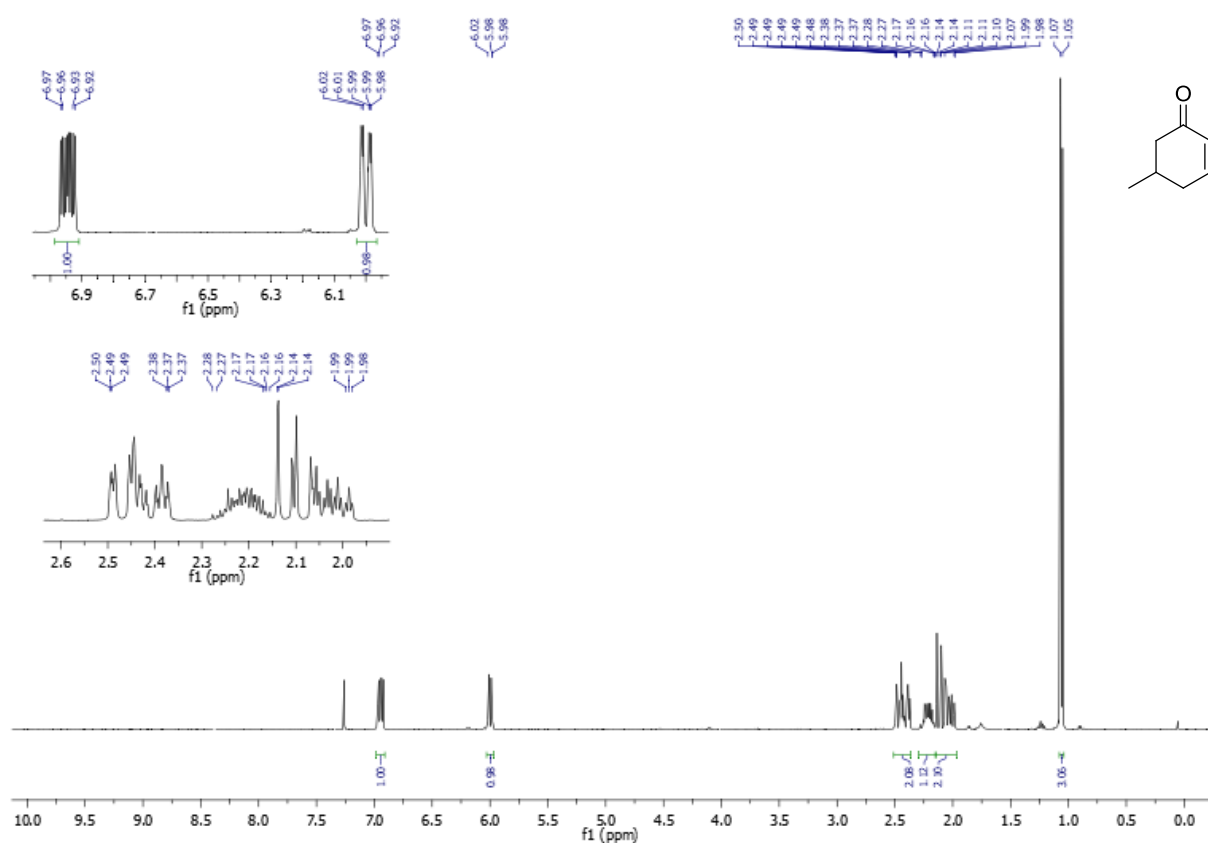


Figure 15. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>) of 12

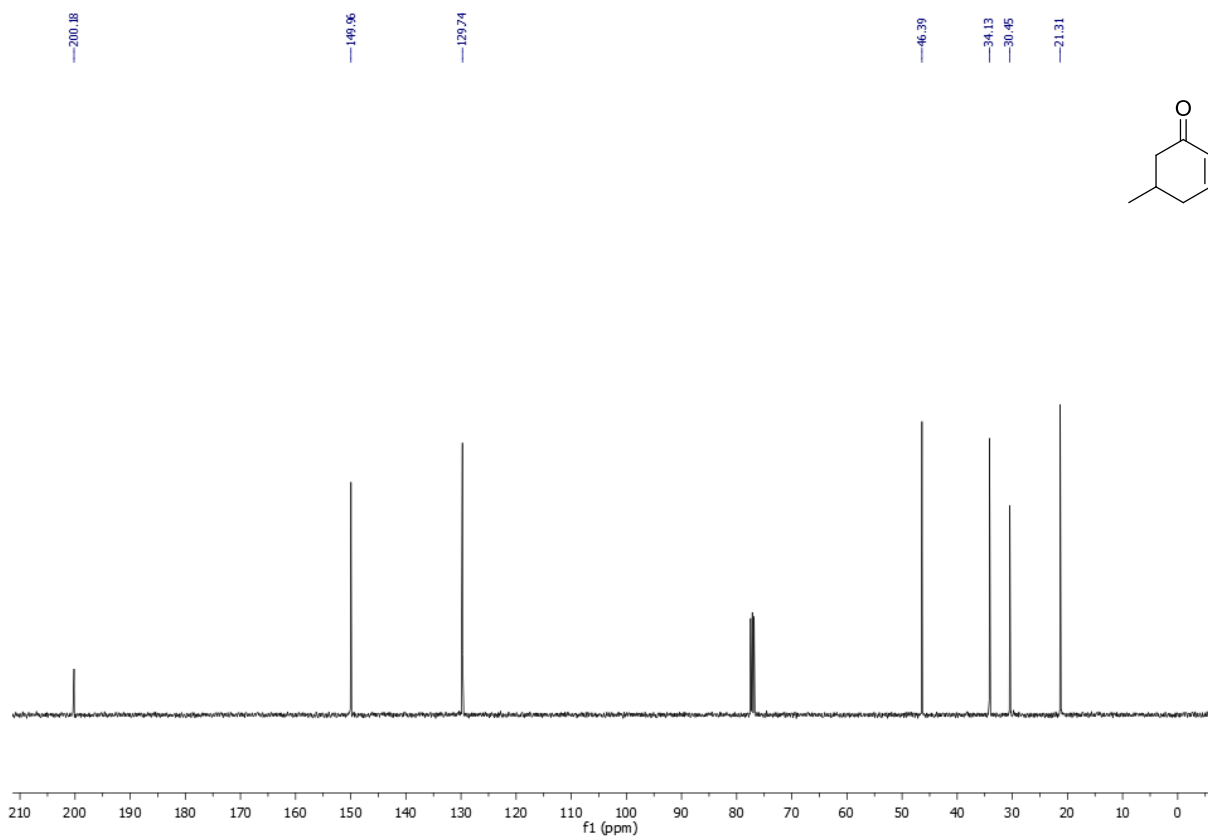


Figure 16. <sup>13</sup>C NMR spectrum (150 MHz, CDCl<sub>3</sub>) of 12

**5-Methyl-2-cyclohexen-1-one (12)**



