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Supporting Information

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# **Unsaturated Aldehydes as Alkene Equivalents in the Diels-Alder Reaction**

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## General methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 instrument. Chemical shifts were correlated relative to chloroform (7.26 ppm and 77.00 ppm, respectively). The data were processed with MestReC 4.7.4.0 software. GC-MS analysis was performed on a Shimadzu Spectachrom QP5000 GC-MS with a Supelco Equity-1 column (30 m in length, an inner diameter of 0.25 mm, and an inner film of dimethyl polysiloxane). Optical rotation was measured on a Perkin-Elmer 241 Polarimeter.

Reactions were carried out using flame dried glassware and a protective argon atmosphere in all cases. Argon atmosphere was achieved with a manifold system by first evacuating the reaction flask and then allowing for an inflow of argon. This cycle was repeated 5 times. All chemicals were used as received, except where otherwise noted.

Silica gel 60 (220-440 mesh, Fluka) was used for column chromatography. The same silica was used for TLC (Silica gel 60 F<sub>254</sub>, Merck). TLC's of aldehydes were processed by using 2,4-dinitro-phenylhydrazine and TLC's of olefins were processed by using KMnO<sub>4</sub>.

DMF and diethyl ether were dried over 4Å molecular sieves. Diglyme was used as received (water content of up to 100 ppm is not detrimental to the Diels-Alder reaction, but a higher water concentration will hydrolyze boron trifluoride and significantly lower the reaction rate).

Acrolein, methacrolein and crotonaldehyde form low-boiling azeotropes with water and were therefore purified by two distillations, the final one over flame dried calcium sulfate (1:1 weight ratio). They were stored in a dark bottle over a small amount of hydroquinone (~0.1%). Furthermore, methacrolein and crotonaldehyde were stored at 5 °C. The aldehydes are stable for many months when stored in this way, and no special precautions are necessary when opening the flasks and taking out a sample. Cinnamaldehyde was vacuum distilled once and the same batch was used for many weeks.

All dienes were stored in a refrigerator. Isoprene, myrcene, 2-phenyl-1,3-butadiene and 2-(butoxymethyl)-1,3-butadiene are not stable for many weeks, and were thus distilled prior to use. Myrcene and (1*R*)-nopadiene contain some isomeric impurities that could not be separated (less than 10%). Some of these impurities remain in the final products, as they do not participate in the reaction. Based on GC-MS and NMR data, the percentage of impurities present was determined and subtracted to give the product yield.

High resolution mass spectrometry was carried out at the Department of Physics and Chemistry, University of Southern Denmark while microanalyses were conducted at the Institute of Physical Chemistry, University of Vienna.

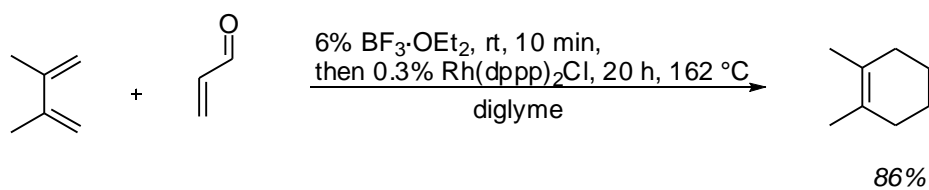
## Rh(dppp)<sub>2</sub>Cl

### Procedure

A 25 mL round bottomed flask was charged with RhCl<sub>3</sub>·3H<sub>2</sub>O (29.3 mg, 0.111 mmol), dppp (95.6 mg, 0.225 mmol) and 96% ethanol (10 mL). The mixture was degassed (5 × vacuum/argon) and then refluxed for 30 min during which time the color changed from burgundy red to pale yellow.

The reaction mixture was then cooled to room temperature under argon and vacuum (15 mm Hg) was applied in order to evaporate ethanol and acetaldehyde. The catalyst deposited as a yellow layer on the inside of the flask. The catalyst was dissolved in 1 – 3 mL of diglyme and transferred to the reaction mixture containing the aldehyde.

## 1,2-Dimethylcyclohexene



### Procedure

A 100 mL round bottomed flask was charged with diglyme (40 mL), 2,3-dimethyl-1,3-butadiene (3.269 g, 39 mmol) and acrolein (4.0 mL, 60 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.30 mL, 2.4 mmol, 6%) under stirring. The mixture was stirred at room temperature (water bath) for 10 min and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (0.60 g, 2.4 mmol) and water (0.25 mL).

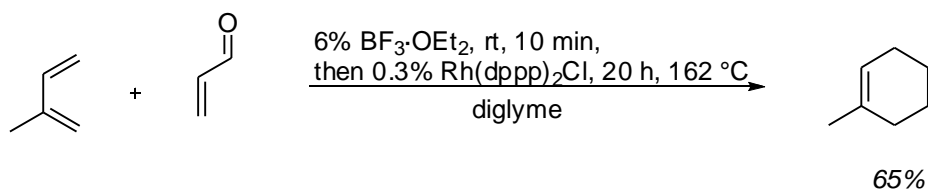
0.3% Rh(dppp)<sub>2</sub>Cl (0.111 mmol) dissolved in 3 mL of diglyme was transferred to the reaction mixture and the solution was degassed (5 × argon/vacuum). The reaction flask was placed in a 175 °C hot oil bath for 20 h.

The flask was cooled to room temperature and water (50 mL) was added. The mixture was extracted with pentane (2 × 50 mL) and the combined organic extracts were washed with water (5 × 50 mL). The organic layer was dried with anhydrous sodium sulfate and pentane was slowly distilled off with a 55 °C hot oil bath. The residue was distilled at 134-136 °C to afford a colorless oil.

Yield: 3.700 g (86%).

**1,2-Dimethylcyclohexene.** Bp: 134-136 °C (lit.<sup>1</sup> bp: 135-136 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 1.50-1.60 (m, 4H), 1.61 (s, 6H), 1.86-1.97 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 19.14, 23.46, 31.71, 125.60 ppm. MS: 110 41%, 95 88%, 81 77%, 67 100%. NMR data are in accordance with literature values.<sup>1,2</sup>

## 1-Methylcyclohexene



### Procedure

A 100 mL round bottomed flask was charged with diglyme (30 mL), isoprene (2.735 g, 40.2 mmol) and acrolein (4.0 mL, 60 mmol) followed by addition of BF<sub>3</sub>·OEt<sub>2</sub> (0.30 mL, 2.4 mmol, 6%) under stirring. The mixture was stirred at room temperature (water bath) for 10 min and then quenched with K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (0.6 g, 2.6 mmol) and water (0.15 mL).

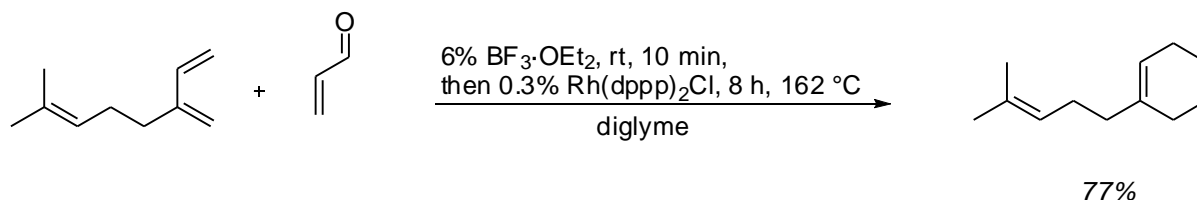
0.3% Rh(dppp)<sub>2</sub>Cl (0.11 mmol) dissolved in 3 mL of diglyme was transferred to the reaction mixture and the solution was degassed (5 × argon/vacuum). The reaction flask was placed in a 175 °C hot oil bath for 20 h.

The flask was cooled to room temperature and water (50 mL) was added. The mixture was extracted with pentane (2 × 50 mL) and the combined organic extracts were washed with water (5 × 50 mL). The organic layer was dried with anhydrous sodium sulfate and pentane was slowly distilled off with a 55 °C hot oil bath. The residue was distilled at 107-110 °C to afford a colorless oil.

Yield: 2.52 g (65%).

**1-Methylcyclohexene.** Bp: 107-110 °C (lit.<sup>3</sup> bp: 106-110 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 1.49-1.67 (m, 4H), 1.64 (s, 3H), 1.87-2.01 (m, 4H), 5.36-5.42 (tdd, 1H, *J* = 1.5 Hz, *J* = 3.4 Hz, *J* = 5.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 22.37, 22.99, 23.94, 25.28, 30.02, 121.10, 134.05 ppm. MS: 96 46%, 81 100%, 68 48%, 67 71%. NMR data are in accordance with literature values.<sup>3</sup>

### 1-(4-Methyl-3-pentenyl)cyclohexene



### Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), myrcene (1.499 g, 10.0 mmol, 91% pure) and acrolein (1.0 mL, 15 mmol) followed by addition of BF<sub>3</sub>·OEt<sub>2</sub> (0.075 mL, 0.6 mmol, 6%) under stirring. The mixture was stirred at room temperature (water bath)

for 10 min and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (150 mg, 0.66 mmol) and water (0.10 mL).

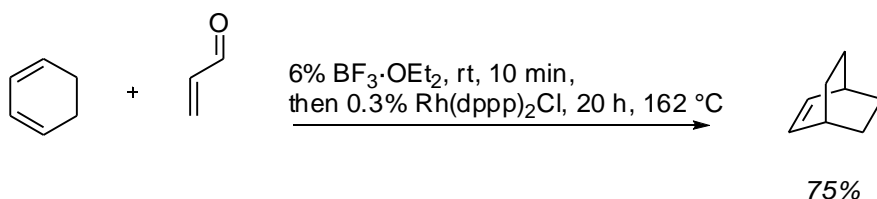
0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.31 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $190^\circ\text{C}$  hot oil bath for 8 h.

The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with pentane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was removed with a  $55^\circ\text{C}$  hot oil bath. The residue was distilled ( $100\text{-}102^\circ\text{C}$  at 17 mm Hg) to afford 1.390 g of a colorless oil, that was 91% pure by GC-MS (myrcene impurities, such as pinene, that do not participate in the reaction, account for the remaining 9%).

Yield: 1.265 g (77%).

**1-(4-Methyl-3-pentenyl)cyclohexene.** Bp:  $100\text{-}102^\circ\text{C}$  at 17 mm Hg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.48-1.66 (m, 4H), 1.60 (s, 3H), 1.68 (s, 3H), 1.88-2.12 (m, 8H), 5.06-5.15 (m, 1H), 5.37-5.42 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 17.65, 22.57, 23.02, 25.23, 25.69, 26.46, 28.37, 38.09, 120.66, 124.47, 131.23, 137.72 ppm. MS: 164 5%, 149 8%, 121 43%, 95 38%, 69 100%, 67 50%. NMR data are in accordance with literature values.<sup>2</sup>

### Bicyclo[2,2,2]-2-octene



### Procedure

A 100 mL round bottomed flask was charged with diglyme (30 mL), 1,3-cyclohexadiene (3.323 g, 40.3 mmol) and acrolein (4.0 mL, 60 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.30



mL, 2.4 mmol, 6%) under stirring. The mixture was stirred at room temperature (water bath) for 10 min and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (600 mg, 2.6 mmol) and water (0.15 mL).

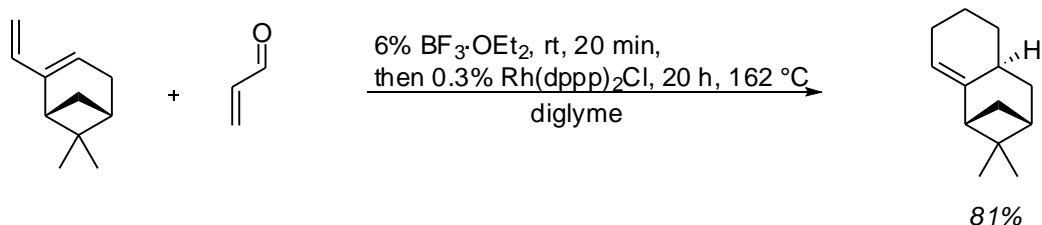
0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.11 mmol) dissolved in 3 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $175^\circ\text{C}$  hot oil bath for 20 h.

The flask was cooled to room temperature and water (50 mL) was added. The mixture was extracted with pentane ( $2 \times 50$  mL) and the combined organic extracts were washed with water ( $5 \times 50$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was slowly distilled off with a  $55^\circ\text{C}$  hot oil bath. The solid residue was bulb-to-bulb sublimed at 1 atm to afford colorless crystals. The remaining pentane traces were carefully removed *in vacuo*.

Yield: 3.29 g (75%).

**Bicyclo[2,2,2]-2-octene.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.10-1.19 (m, 4H), 1.36-1.46 (m, 4H), 2.35-2.43 (m, 2H), 6.12-6.19 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 25.75, 29.46, 134.21 ppm. MS: 108 7%, 80 100%, 79 46%, 67 7%, 51 13%. NMR data are in accordance with literature values.<sup>2</sup>

### 9,9-Dimethyltricyclo[4,4,0,1<sup>8,10</sup>]-1-undecene



### Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), (1*R*)-nopadiene<sup>4</sup> (1.550 g, 10.0 mmol, 96% pure) and acrolein (1.0 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$

(0.075 mL, 0.6 mmol, 6%) under stirring. The temperature of the flask increased to about 30 °C. After 20 min, the mixture was quenched with  $K_2HPO_4 \cdot 3H_2O$  (150 mg, 0.6 mmol) and water (0.10 mL). GC-MS showed conversion of about 94% (longer reaction times lowered the final yield of the product).

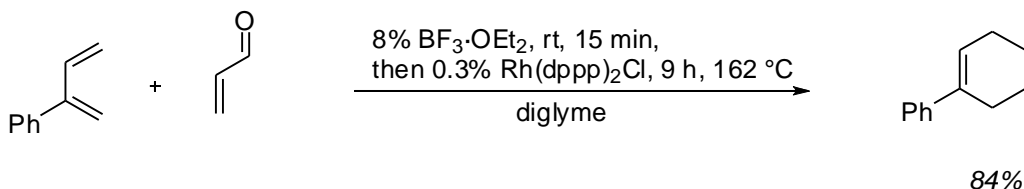
0.3%  $Rh(dppp)_2Cl$  (0.033 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a 190 °C hot oil bath for 20 h.

The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with pentane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). The organic layer was dried with anhydrous sodium sulfate and filtered through a plug of silica (5-6 cm). Pentane was distilled off with a 55 °C hot oil bath and the residue was distilled (115-120 °C at 15 mm Hg) to afford 1.566 g of a colorless oil which was 91% pure according to GC-MS.

Yield: 1.426 g (81%).

**9,9-Dimethyltricyclo[4,4,0,1<sup>8,10</sup>]-1-undecene.** Bp: 115-120 °C at 15 mm Hg (lit.<sup>2</sup> bp: 118-123 °C at 15 mm Hg).  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 0.84 (d, 1H,  $J = 9.3$  Hz), 0.97 (s, 3H), 1.13-1.23 (m, 1H), 1.25 (s, 3H), 1.40-1.48 (m, 1H), 1.56-1.71 (m, 1H), 1.76-1.90 (m, 2H), 1.94-2.11 (m, 3H), 2.11-2.24 (m, 1H), 2.41 (t, 1H,  $J = 5.8$  Hz), 2.45-2.61 (m, 2H), 5.14 (q, 1H,  $J = 3.3$  Hz).  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 22.79, 23.57, 24.53, 27.19, 32.56, 33.37, 33.55, 35.59, 39.56, 42.17, 52.22, 116.88, 146.73 ppm. MS: 176 8%, 161 3%, 133 78%, 107 17%, 105 27%, 91 100%, 79 91%, 69 34%, 55 26%.  $[\alpha]_D^{20} = -29.9$  ( $c = 2.2$ ,  $CH_2Cl_2$ ).  $^1H$  NMR data are in accordance with literature values.<sup>2</sup>

## 1-Phenylcyclohexene



### Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), 2-phenyl-1,3-butadiene<sup>5</sup> (1.294 g, 9.95 mmol) and acrolein (1.0 mL, 15 mmol) followed by addition of  $BF_3 \cdot OEt_2$  (0.10 mL, 0.8 mmol, 8%) under stirring. The temperature of the flask increased to 40-50 °C. After

15 min the reaction was quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (200 mg, 0.9 mmol) and water (0.05 mL).

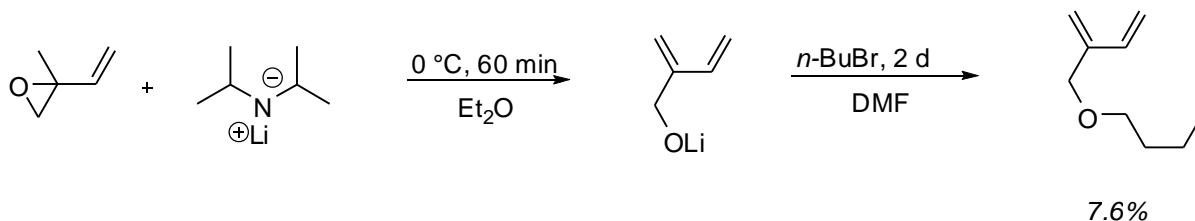
0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.032 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $180^\circ\text{C}$  hot oil bath for 9 h.

The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with pentane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was removed *in vacuo*. The residue was purified by flash chromatography (EtOAc 1, hexane 99) to afford a colorless oil.

Yield: 1.322 g (84%).

**1-Phenylcyclohexene.** Bp:  $122\text{-}125^\circ\text{C}$  at 13 mm Hg (lit.<sup>6</sup> bp:  $128^\circ\text{C}$  at 16 mm Hg).  $R_f$ : 0.45 (EtOAc 1, hexane 99).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.63-1.73 (m, 2H), 1.75-1.84 (m, 2H), 2.18-2.27 (m, 2H), 2.39-2.47 (m, 2H), 5.13-5.19 (m, 1H), 7.19-7.42 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 22.40, 23.31, 26.12, 27.63, 125.00, 125.16, 126.73, 128.40, 136.80, 142.92 ppm. MS: 130 94%, 129 100%, 128 56%, 127 22%, 115 75%, 102 21%, 91 14%, 77 25%, 63 25%, 51 50%.

## 2-(Butoxymethyl)-1,3-butadiene



### Procedure

A 100 mL round bottomed flask was charged with diethyl ether (30 mL) and lithium diisopropyl amide (1.8 M solution in THF/heptane/ethylbenzene, 33.3 mL, 60 mmol). The

mixture was cooled to 0 °C and 2-methyl-2-vinylloxirane<sup>7</sup> (5.75 g, 68 mmol) was added drop wise over 10 min.

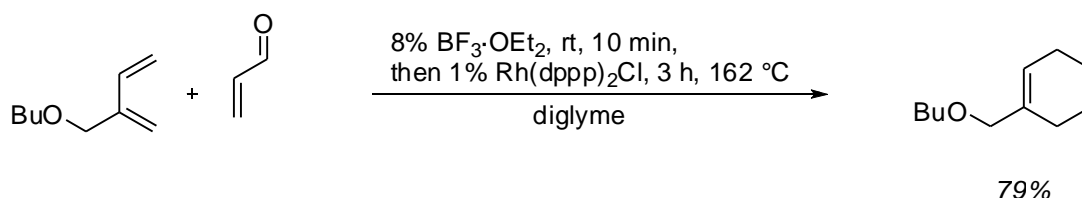
After one hour, the reaction was concentrated *in vacuo*. To the residue was added DMF (30 mL) followed by *n*-butyl bromide (6.4 mL, 8.2 g, 60 mmol). The reaction was then stirred for 2 days.

The mixture was diluted with water (50 mL) and extracted with pentane (2 × 50 mL). The combined pentane layers were washed successively with water (2 × 50 mL), 2 M hydrochloric acid (2 × 25 mL), water (50 mL), saturated sodium bicarbonate (50 mL) and brine (50 mL). The organic layer was dried over anhydrous magnesium sulfate and pentane was removed *in vacuo*. The yellow residual oil consisted of mostly ethyl benzene and the desired product. The oil was purified by flash chromatography (3.5 cm in diameter, 20 cm silica) eluting first with pure pentane ( $R_f$ : 0.15) then with 10% diethyl ether in pentane ( $R_f$ : 1). This afforded *ca.* 1 g of a yellow oil, which was further purified by distillation (56-59 °C at 12 mm Hg).

Yield: 725 mg (7.6%) of a colorless oil.

**2-(Butoxymethyl)-1,3-butadiene.** Bp: 56-59 °C at 12 mm Hg.  $R_f$ : 0.15 (pentane). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ : 0.92 (t, 3H,  $J$  = 7.3 Hz), 1.30-1.46 (m, 2H), 1.52-1.65 (m, 2H), 3.44 (t, 2H,  $J$  = 6.6 Hz), 4.14 (s, 2H), 5.07-5.35 (m, 4H), 6.32-6.44 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$ : 13.93, 19.38, 31.82, 70.25, 70.47, 114.23, 116.99, 136.64, 142.74 ppm. MS: 125 1%, 111 1%, 97 3%, 83 17%, 71 15%, 69 15%, 68 100%, 67 79%, 65 17%, 57 54%, 56 30%, 55 40%.

### 1-(Butoxymethyl)cyclohexene



### Procedure

A 25 mL round bottomed flask was charged with diglyme (5 mL), 2-(butoxymethyl)-1,3-butadiene (0.689 g, 4.92 mmol) and acrolein (0.5 mL, 7.5 mmol) followed by addition of BF<sub>3</sub>·OEt<sub>2</sub> (0.05 mL, 0.4 mmol, 8%) under stirring. The mixture was stirred at room

temperature for 10 min and then quenched with  $K_2HPO_4 \cdot 3H_2O$  (150 mg, 0.6 mmol) and water (0.05 mL). TLC showed full conversion.

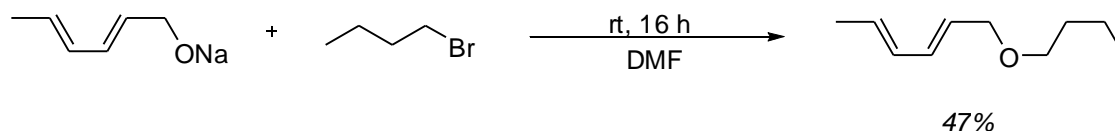
1%  $Rh(dppp)_2Cl$  (0.050 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a 180 °C hot oil bath for 3 h.

The flask was cooled to room temperature and brine (10 mL) was added. The mixture was extracted with pentane ( $2 \times 6$  mL). The combined organic extracts were washed successively with brine ( $3 \times 10$  mL) and water ( $3 \times 10$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was distilled off with a 55 °C hot oil bath. The residue was distilled (95-102 °C at 15 mm Hg) to afford a colorless oil.

Yield: 0.652 g (79%).

**1-(Butoxymethyl)cyclohexene.** Bp: 95-102 °C at 15 mm Hg.  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 0.90 (t, 3H,  $J = 7.3$  Hz), 1.30-1.43 (m, 2H), 1.49-1.68 (m, 6H), 1.93-2.05 (m, 4H), 3.35 (t, 2H,  $J = 6.6$  Hz), 3.78-3.80 (m, 2H), 5.63-5.69 (m, 1H).  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 13.92, 19.39, 22.42, 22.52, 24.97, 25.86, 31.85, 69.62, 75.56, 124.47, 135.21 ppm. MS: 168 22%, 112 59%, 95 49%, 94 64%, 81 72%, 79 100%, 67 88%, 57 86%. HRMS calcd for  $C_{11}H_{20}ONa$ : 191.1412 [ $M + Na$ ] $^+$ ; found: 191.1403.

### (2E,4E)-1-Butoxy-2,4-hexadiene



### Procedure

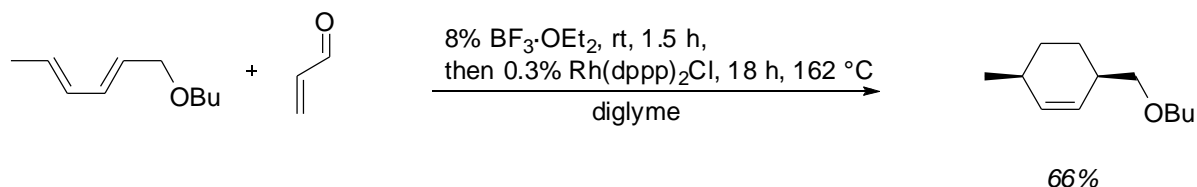
A 100 mL round bottomed flask was charged with DMF (50 mL) and NaH (55% mineral oil suspension, 1.50 g, 34 mmol). Over the course of 10 min, 2,4-hexadien-1-ol (3.42 g, 35 mmol) was added drop wise and the mixture was stirred for an additional 30 min. *n*-Butyl bromide (4.8 g, 35 mmol) was then added drop wise over 5 min followed by stirring for 16 h.

The reaction mixture was poured into a 250 mL separatory funnel containing 50 mL of ice-water. The mixture was extracted with pentane ( $2 \times 50$  mL) and the combined organic extracts were washed with water ( $3 \times 50$  mL). The organic layer was dried with anhydrous magnesium sulfate and pentane was removed *in vacuo*. The slightly yellow residual oil was purified by distillation (88-92 °C at 15 mm Hg) to afford a colorless oil.

Yield: 2.56 g (47%).

**(2E,4E)-1-Butoxy-2,4-hexadiene.** Bp: 88-92 °C at 15 mm Hg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 0.91 (t, 3H,  $J = 7.3$  Hz), 1.29-1.43 (m, 2H), 1.50-1.61 (m, 2H), 1.74 (d, 3H,  $J = 6.9$  Hz), 3.40 (t, 2H,  $J = 6.7$  Hz), 3.96 (d, 2H,  $J = 2.9$  Hz), 5.56-5.76 (m, 2H), 5.99-6.25 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 13.92, 18.08, 19.34, 31.84, 68.96, 71.16, 127.02, 129.73, 130.83, 132.85 ppm. MS: 154 19%, 139 1%, 125 2%, 111 7%, 98 40%, 97 15%, 83 54%, 81 54%, 80 20%, 79 40%, 70 39%, 69 100%, 67 22%, 57 69%, 56 41%, 55 46%, 53 29%.

### 3-(Butoxymethyl)-6-methylcyclohexene



#### Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), (2E,4E)-1-butoxy-2,4-hexadiene (1.539 g, 10.0 mmol, freshly distilled) and acrolein (1.0 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.10 mL, 0.8 mmol, 8%) under stirring. The mixture was stirred at

room temperature for 90 min and then quenched with  $K_2HPO_4 \cdot 3H_2O$  (200 mg, 0.9 mmol) and water (0.10 mL). TLC showed only a trace of the diene.

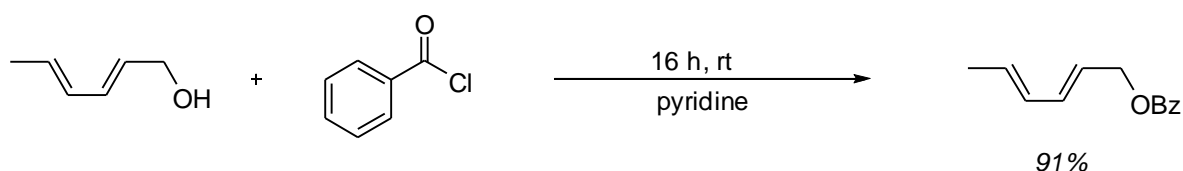
0.3%  $Rh(dppp)_2Cl$  (0.030 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $180^\circ C$  hot oil bath for 18 h.

The flask was cooled to room temperature and brine (50 mL) was added. The mixture was extracted with pentane ( $2 \times 20$  mL) and the combined organic extracts were washed successively with brine ( $2 \times 30$  mL) and water ( $2 \times 30$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was removed *in vacuo*. The residue was purified by flash chromatography ( $Et_2O$  1, pentane 19) to afford a slightly yellow oil.

Yield: 1.20 g (66%).

**3-(Butoxymethyl)-6-methylcyclohexene.**  $R_f$ : 0.67 ( $Et_2O$  1, pentane 19).  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$ : 0.87-0.97 (m, 6H), 1.21-1.45 (m, 3H), 1.48-1.72 (m, 5H), 2.09-2.39 (m, 2H), 3.19-3.31 (m, 2H), 3.36-3.46 (m, 2H), 5.52-5.66 (m, 2H).  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$ : 13.94, 19.37, 21.43, 23.15, 27.95, 29.99, 31.81, 35.26, 70.81, 74.56, 127.25, 134.88 ppm. MS: 139 13%, 108 8%, 95 14%, 93 13%, 79 13%, 67 16%, 57 100%. HRMS calcd for  $C_{12}H_{22}ONa$ : 205.1568 [ $M + Na$ ] $^+$ ; found: 205.1563.

### (2E,4E)-2,4-Hexadienyl benzoate



### Procedure

A 100 mL round bottomed flask was charged with pyridine (20 mL) and cooled to  $0^\circ C$ . Benzoyl chloride (3.23 g, 23 mmol) was added slowly followed by drop wise addition of 2,4-

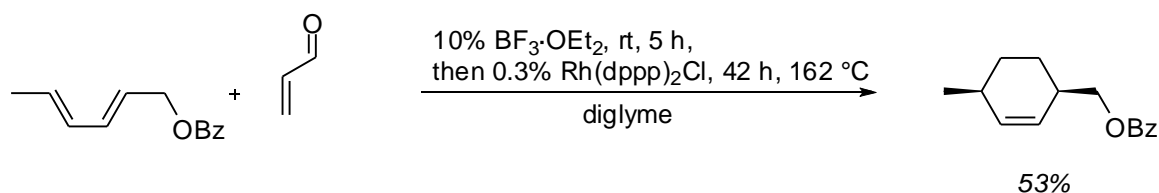
hexadien-1-ol (1.5 g, 15.3 mmol) over 5 min. The ice bath was removed and the reaction was stirred for 16 h.

The solution was slowly poured into a beaker containing 250 mL of ice cold 2 M hydrochloric acid. The resulting mixture was extracted with dichloromethane (4 × 60 mL) and the combined organic extracts were washed successively with 4 M hydrochloric acid (2 × 60 mL) and saturated sodium bicarbonate (3 × 60 mL). The organic phase was dried over anhydrous magnesium sulfate and dichloromethane was removed *in vacuo*. The residue was purified by flash chromatography (EtOAc 1, heptane 4) to afford a colorless oil.

Yield: 2.83 g (91%).

**(2E,4E)-2,4-Hexadienyl benzoate.** Bp: 133-134 °C at 3 mm Hg (lit.<sup>8</sup> bp: 130 °C at 1 mm Hg). R<sub>f</sub>: 0.47 (EtOAc 1, heptane 4). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 1.77 (d, 3H, *J* = 3.4 Hz), 4.83 (d, 2H, *J* = 3.3 Hz), 5.69-5.86 (m, 2H), 6.03-6.15 (m, 1H), 6.29-6.40 (m, 1H), 7.40-7.47 (m, 2H), 7.52-7.60 (m, 1H), 8.03-8.09 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 18.13, 65.39, 123.70, 128.28, 129.57, 130.24, 130.40, 131.30, 132.85, 134.91, 166.34 ppm. MS: 202 5%, 173 2%, 122 8%, 106 8%, 105 100%, 80 24%, 79 62%, 77 61%, 51 25%. NMR data are in accordance with literature values.<sup>8</sup>

### (4-Methyl-2-cyclohexenyl)methyl benzoate



### Procedure



A 50 mL round bottomed flask was charged with diglyme (15 mL), (2*E*,4*E*)-2,4-hexadienyl benzoate (3.016 g, 15.0 mmol) and acrolein (1.5 mL, 22.5 mmol) followed by addition of BF<sub>3</sub>·OEt<sub>2</sub> (0.19 mL, 1.5 mmol, 10%) under stirring. The reaction was stirred at room temperature for 5 h and then quenched with K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (200 mg, 0.9 mmol) and water (0.10 mL).

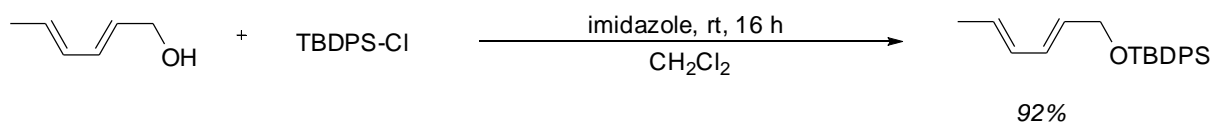
0.3% Rh(dppp)<sub>2</sub>Cl (0.046 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed (5 × argon/vacuum). The reaction flask was placed in a 180 °C hot oil bath for 42 h.

The flask was cooled to room temperature and water (50 mL) was added. The mixture was extracted with pentane (2 × 30 mL) and the combined organic extracts were washed with water (5 × 30 mL). The organic layer was dried with anhydrous sodium sulfate and pentane was removed *in vacuo*. The residue was purified by dry column chromatography<sup>9</sup> (6 cm silica, 4 cm in diameter, EtOAc 1, heptane 99) to afford a slightly yellow oil, which solidified upon standing.

Yield: 1.825 g (53%).

**(4-Methyl-2-cyclohexenyl)methyl benzoate.** R<sub>f</sub>: 0.55 (EtOAc 1, heptane 99). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 1.00 (d, 3H, *J* = 7.1 Hz), 1.30-1.45 (m, 1H), 1.56-1.79 (m, 3H), 2.15-2.27 (m, 1H), 2.50-2.61 (m, 1H), 4.20 (d, 1H, *J* = 1.3 Hz), 4.22 (s, 1H), 5.58-5.76 (m, 2H), 7.40-7.59 (m, 3H), 8.03-8.08 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 21.27, 23.03, 27.73, 29.82, 34.42, 67.90, 125.81, 128.29, 129.51, 130.36, 132.81, 135.95, 166.56 ppm. MS: 108 97%, 105 100%, 93 99%, 91 15%, 80 17%, 79 30%, 77 72%, 67 12%, 51 21%. HRMS calcd for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>Na: 253.1205 [*M* + Na]<sup>+</sup>; found: 253.1206.

### *tert*-Butyl((2*E*,4*E*)-2,4-hexadienyloxy)diphenylsilane



### Procedure

A 250 mL round bottomed flask was charged with CH<sub>2</sub>Cl<sub>2</sub> (100 mL), 2,4-hexadien-1-ol (3.0 g, 30.6 mmol) and imidazole (4.2 g, 61.3 mmol). The mixture was stirred followed by

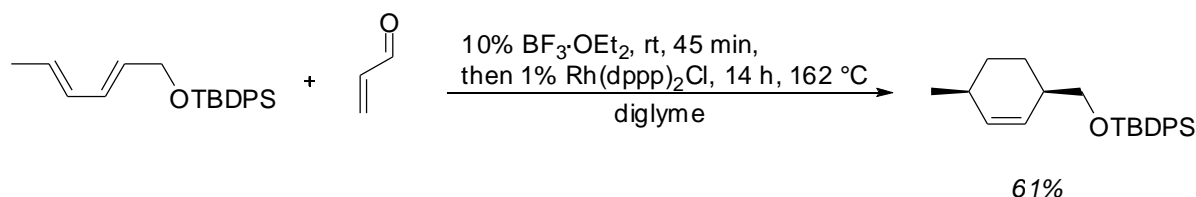
addition of *tert*-butylchlorodiphenylsilane (12.6 g, 45.9 mmol) and stirring for an additional 16 h.

The reaction was diluted with diethyl ether (100 mL) and washed with 1 M hydrochloric acid (100 mL) and brine (100 mL). Removal of the solvents *in vacuo* afforded 14.38 g of a crude product which was purified by flash chromatography (EtOAc 1, heptane 4) to give a colorless oil.

Yield: 9.48 g (92%).

***tert*-Butyl((2*E*,4*E*)-2,4-hexadienyloxy)diphenylsilane.**  $R_f$ : 0.51 (EtOAc 1, heptane 4).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.11 (s, 9H), 1.79 (d, 3H,  $J = 3.4$  Hz), 4.27 (d, 2H,  $J = 2.6$  Hz), 5.63-5.78 (m, 2H), 6.05-6.17 (m, 1H), 6.22-6.34 (m, 1H), 7.38-7.50 (m, 6H), 7.70-7.77 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.11, 19.22, 26.80, 64.22, 127.61, 128.95, 129.40, 129.57, 130.10, 131.02, 133.69, 135.52 ppm. MS: 280 7%, 279 27%, 200 19%, 199 100%, 181 9%, 77 26%, 57 14%.

### *tert*-Butyl((4-methyl-2-cyclohexenyl)methoxy)diphenylsilane



### Procedure

A 50 mL round bottomed flask was charged with diglyme (6.6 mL), *tert*-butyl((2*E*,4*E*)-2,4-hexadienyloxy)diphenylsilane (2.205 g, 6.6 mmol) and acrolein (0.66 mL, 10 mmol) followed by addition of BF<sub>3</sub>·OEt<sub>2</sub> (0.07 mL, 0.6 mmol, 10%) under stirring. The reaction was stirred at room temperature for 45 min and then quenched with K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (150 mg, 0.6 mmol) and water (0.06 mL). TLC showed only a trace of the diene.

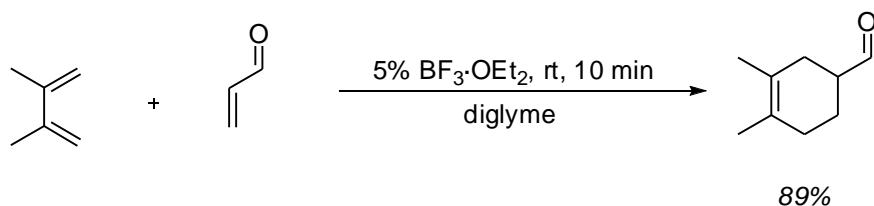
1% Rh(dppp)<sub>2</sub>Cl (0.066 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed (5 × argon/vacuum). The reaction flask was placed in a 180 °C hot oil bath for 14 h.

The flask was cooled to room temperature and most of the diglyme was distilled off (15 mm Hg, 55 °C). The residue was purified by flash chromatography (EtOAc 1, heptane 39) to afford a viscous oil.

Yield: 1.47 g (61%).

***tert*-Butyl((4-methyl-2-cyclohexenyl)methoxy)diphenylsilane.** R<sub>f</sub>: 0.30 (EtOAc 1, heptane 39). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 0.99 (d, 3H, *J* = 3.7 Hz), 1.11 (s, 9H), 1.22-1.34 (m, 1H), 1.63-1.75 (m, 3H), 2.13-2.42 (m, 2H), 3.50-3.65 (m, 2H), 5.57-5.70 (m, 2H), 7.37-7.49 (m, 6H), 7.70-7.76 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 19.30, 21.39, 22.72, 26.87, 27.97, 29.99, 37.74, 67.32, 127.28, 127.56, 129.48, 133.98, 134.89, 135.60. MS: 307 20%, 230 9%, 229 46%, 200 20%, 199 100%, 181 19%, 135 20%, 77 34%, 57 21%. HRMS calcd for C<sub>24</sub>H<sub>32</sub>OSiNa: 387.2120 [*M* + Na]<sup>+</sup>; found: 387.2120.

### 3,4-Dimethyl-3-cyclohexene-1-carbaldehyde



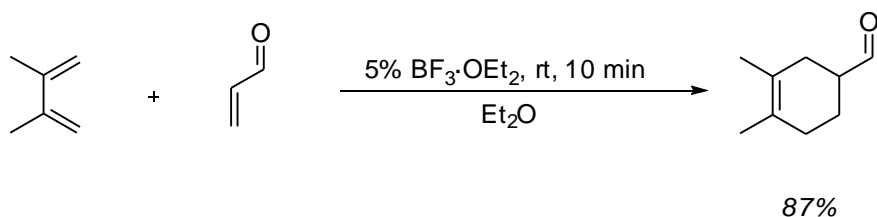
### Procedure

A 50 mL round bottomed flask was charged with diglyme (30 mL), 2,3-dimethyl-1,3-butadiene (2.54 g, 30.0 mmol) and acrolein (3.0 mL, 45 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.19 mL, 1.5 mmol, 5%) under stirring. The reaction was stirred at room temperature (water bath) for 10 min.

The reaction mixture was transferred to a 250 mL separatory funnel containing saturated sodium bicarbonate (50 mL) and pentane (50 mL). The phases were separated and the organic phase was washed with saturated sodium bicarbonate (50 mL) and water ( $3 \times 50$  mL) and then dried over anhydrous sodium sulfate. Pentane was removed *in vacuo* and the residual, slightly cloudy oil purified by distillation (85-87 °C at 15 mm Hg).

Yield: 3.70 g (89%).

**3,4-Dimethyl-3-cyclohexene-1-carbaldehyde.** Bp: 85-87 °C at 15 mm Hg (lit.<sup>10</sup> bp: 92-94 °C at 25 mm Hg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.54-1.68 (m, 7H), 1.86-2.24 (m, 5H), 2.40-2.52 (m, 1H), 9.67 (d, 1H,  $J = 0.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.92, 19.05, 22.82, 30.13, 30.50, 46.95, 123.42, 125.84, 204.81 ppm. MS: 138 53%, 123 25%, 109 55%, 107 41%, 105 31%, 95 39%, 93 31%, 91 43%, 81 34%, 79 46%, 77 28%, 67 100%, 55 39%. NMR data are in accordance with literature data.<sup>10</sup>



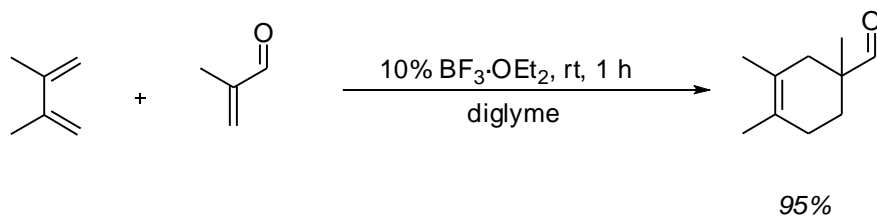
### Procedure

A 100 mL round bottomed flask was charged with diethyl ether (50 mL), 2,3-dimethyl-1,3-butadiene (4.23 g, 50 mmol) and acrolein (5.0 mL, 75 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.32 mL, 2.5 mmol, 5%) under stirring. The reaction was stirred at room temperature (water bath) for 10 min.

The reaction mixture was transferred to a 250 mL separatory funnel containing saturated sodium bicarbonate (50 mL). The phases were separated and the organic phase was washed with saturated sodium bicarbonate (50 mL) and water (50 mL) and then dried over anhydrous sodium sulfate. Diethyl ether was removed *in vacuo* and the residual, slightly cloudy oil purified by distillation (85-87 °C at 15 mm Hg).

Yield: 6.02 g (87%).

### 1,3,4-Trimethyl-3-cyclohexene-1-carbaldehyde



### Procedure

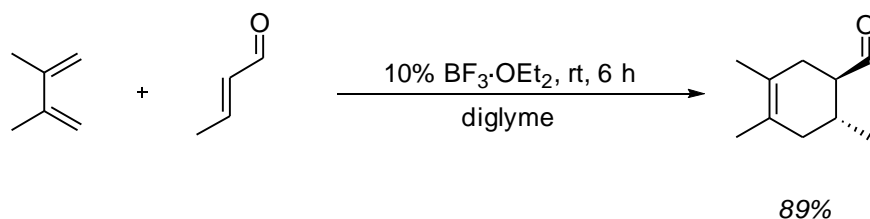
A 50 mL round bottomed flask was charged with diglyme (20 mL), 2,3-dimethyl-1,3-butadiene (1.64 g, 19.4 mmol) and methacrolein (2.5 mL, 30 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.25 mL, 2.0 mmol, 10%) under stirring. The reaction was stirred at room temperature (water bath) for 1 h.

The reaction mixture was transferred to a 250 mL separatory funnel containing saturated sodium bicarbonate (50 mL) and pentane (50 mL). The phases were separated and the organic phase was washed with saturated sodium bicarbonate (50 mL) and water ( $3 \times 50$  mL) and then dried over anhydrous sodium sulfate. Pentane was removed *in vacuo* and the residual, slightly cloudy oil purified by distillation (89-81 °C at 18 mm Hg).

Yield: 2.80 g (95%).

**1,3,4-Trimethyl-3-cyclohexene-1-carbaldehyde.** Bp: 89-91 °C at 18 mm Hg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.02 (s, 3H), 1.39-1.52 (m, 1H), 1.58 (s, 3H), 1.63 (s, 3H), 1.69-1.83 (m, 2H), 1.91-2.01 (m, 2H), 2.19-2.29 (m, 1H), 9.45 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.77, 19.18, 20.70, 28.40, 29.20, 37.81, 45.24, 122.98, 125.07, 206.22 ppm. MS: 152 22%, 137 18%, 123 54%, 109 78%, 91 32%, 82 37%, 81 75%, 67 100%, 55 46%. NMR data are in accordance with literature values.<sup>11</sup>

3,4,6-Trimethyl-3-cyclohexene-1-carbaldehyde



### Procedure

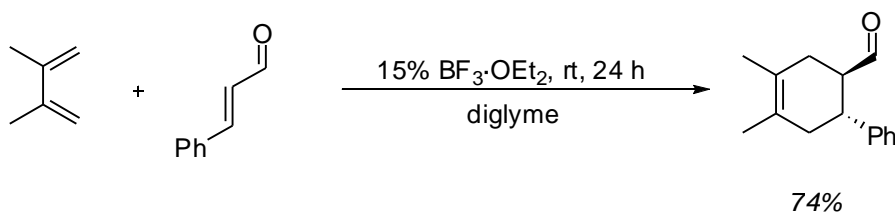
A 50 mL round bottomed flask was charged with diglyme (20 mL), 2,3-dimethyl-1,3-butadiene (1.68 g, 19.8 mmol) and crotonaldehyde (2.5 mL, 30 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.25 mL, 2.0 mmol, 10%) under stirring. The reaction was stirred at room temperature for 6 h.

The reaction mixture was transferred to a 250 mL separatory funnel containing saturated sodium bicarbonate (50 mL) and pentane (50 mL). The phases were separated and the organic phase was washed with saturated sodium bicarbonate (50 mL) and water ( $3 \times 50$  mL) and then dried over anhydrous sodium sulfate. Pentane was removed *in vacuo* and the residual, slightly cloudy oil was purified by distillation (91-92 °C at 14 mm Hg).

Yield: 2.68 g (89%).

**3,4,6-Trimethyl-3-cyclohexene-1-carbaldehyde.** Bp: 91-92 °C at 14 mm Hg (lit.<sup>12</sup> bp: 89 °C at 12 mm Hg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 0.99 (d, 3H,  $J = 3.2$  Hz), 1.59 (s, 3H), 1.63 (s, 3H), 1.64-1.77 (m, 1H), 1.90-2.25 (m, 5H), 9.60 (d, 1H,  $J = 1.5$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.64, 18.85, 19.55, 28.75, 30.30, 38.88, 53.49, 122.55, 125.07, 205.34 ppm. MS: 152 44%, 137 12%, 123 30%, 121 100%, 119 29%, 110 27%, 109 28%, 107 55%, 105 37%, 95 39%, 91 44%, 81 69%, 79 41%, 67 92%, 55 58%.

3,4-Dimethyl-6-phenyl-3-cyclohexene-1-carbaldehyde



### Procedure

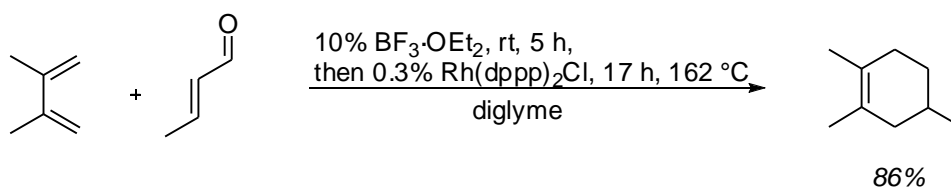
A 50 mL round bottomed flask was charged with diglyme (20 mL), 2,3-dimethyl-1,3-butadiene (1.65 g, 19.5 mmol) and cinnamaldehyde (3.8 mL, 30 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.38 mL, 3.0 mmol, 15%) under stirring. The reaction was stirred at room temperature for 24 h.

The reaction mixture was transferred to a 250 mL separatory funnel containing saturated sodium bicarbonate (50 mL) and pentane (50 mL). The phases were separated and the organic phase was washed with saturated sodium bicarbonate (50 mL) and water ( $3 \times 50$  mL) and then dried over anhydrous sodium sulfate. Pentane was removed *in vacuo* and the residual oil purified by flash chromatography (EtOAc 1, heptane 19).

Yield: 3.19 g (74%).

**3,4-Dimethyl-6-phenyl-3-cyclohexene-1-carbaldehyde.** Bp: 110-113 °C at 0.1 mm Hg (lit.<sup>13</sup> bp: 171-173 °C at 3.5 mm Hg).  $R_f$ : 0.25 (EtOAc 1, heptane 19).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.66 (s, 3H), 1.70 (s, 3H), 1.99-2.37 (m, 4H), 2.74-2.87 (m, 1H), 3.02-3.15 (m, 1H), 7.17-7.36 (m, 5H), 9.47 (d, 1H,  $J = 1.5$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.73, 18.75, 30.98, 39.42, 41.37, 52.00, 123.33, 125.56, 126.66, 127.37, 128.69, 143.42, 204.48 ppm. MS: 214 40%, 199 3%, 183 55%, 172 33%, 131 32%, 115 29%, 95 40%, 94 61%, 91 100%, 82 50%, 77 37%, 67 97%.

### 1,2,4-Trimethylcyclohexene



## Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), 2,3-dimethyl-1,3-butadiene (807 mg, 9.6 mmol) and crotonaldehyde (1.23 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.125 mL, 0.99 mmol, 10%) under stirring. The mixture was stirred at room temperature (water bath) for 5 h and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (200 mg, 0.88 mmol) and water (0.10 mL). GC-MS showed conversion of about 96%.

0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.032 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a 185 °C hot oil bath for 17 h.

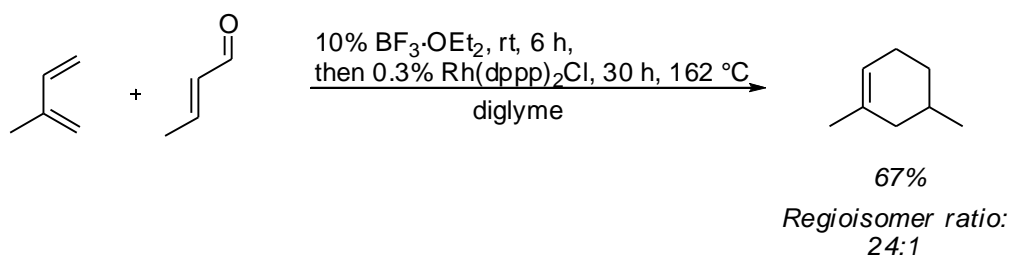
The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with pentane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was slowly distilled off with a 55 °C hot oil bath. The residue was distilled at 110 mm Hg to afford a colorless oil.

Yield: 1.020 g (86%).

**1,2,4-Trimethylcyclohexene.** Bp: 150-154 °C (lit.<sup>10</sup> bp: 154 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 0.94 (d, 3H,  $J = 2.6$  Hz), 1.08-1.23 (m, 1H), 1.24-1.70 (m, 9H), 1.85-2.11 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.86, 19.10, 21.95, 29.32, 31.73, 31.98, 40.53, 125.14, 125.16 ppm. MS: 124 28%, 109 43%, 95 27%, 82 74%, 81 21%, 69 18%, 67 100%, 55 15%. NMR data are in accordance with literature values.<sup>10</sup>

## 1,5-Dimethylcyclohexene





## Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), isoprene (1.0 mL, 10.0 mmol) and crotonaldehyde (1.23 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.125 mL, 0.99 mmol, 10%) under stirring. The mixture was stirred at room temperature for 6 h and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (200 mg, 0.88 mmol) and water (0.10 mL).

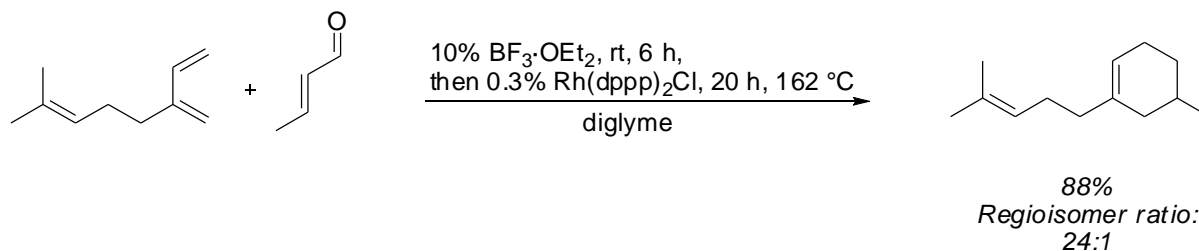
0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.035 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $190^\circ\text{C}$  hot oil bath for 30 h.

The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with pentane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). The organic layer was dried with anhydrous sodium sulfate and pentane was distilled off with a  $55^\circ\text{C}$  hot oil bath. The residue was distilled at  $132\text{--}133^\circ\text{C}$  to afford a colorless oil. Two products with mass 110 were identified by GC-MS in a ratio of 24:1.

Yield: 0.732 g (67%).

**1,5-Dimethylcyclohexene.** Bp:  $132\text{--}133^\circ\text{C}$  (lit.<sup>14</sup> bp:  $127\text{--}129^\circ\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 0.93-0.98 (m, 3H), 1.03-1.19 (m, 1H), 1.51-1.73 (m, 6H), 1.87-2.06 (m, 3H), 5.33-5.40 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 21.97, 23.74, 25.36, 28.89, 30.63, 38.73, 120.64, 133.65 ppm. MS: 110 28%, 95 95%, 81 24%, 68 69%, 67 100%, 55 51%, 53 33%. MS of minor isomer: 110 39%, 95 83%, 81 24%, 68 100% (retro Diels-Alder in MS), 67 96%, 55 41%, 53 48%.

## 5-Methyl-1-(4-methyl-3-pentenyl)cyclohexene



## Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), myrcene (1.459 g, 9.8 mmol, 91% pure) and crotonaldehyde (1.23 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.125 mL, 0.99 mmol, 10%) under stirring. The mixture was stirred at room temperature for 6 h and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (200 mg, 0.88 mmol) and water (0.10 mL).

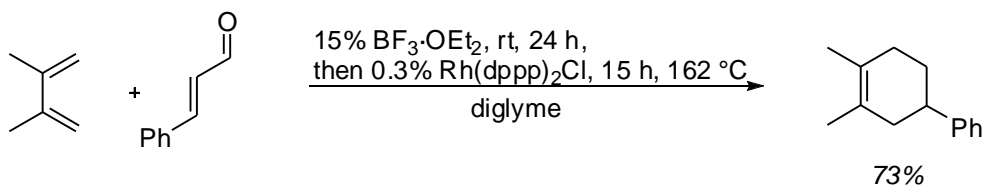
0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.032 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a 190 °C hot oil bath for 20 h.

The flask was cooled to room temperature and water (25 ml) was added. The mixture was extracted with pentane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). Pentane was removed *in vacuo* and the orange residual oil was purified by flash chromatography (10 cm silica, pentane) to afford 1.596 g of a colorless oil, which was 96% pure by GC-MS (myrcene impurities present). Two products with mass 178 were identified by GC-MS in a ratio of 24:1.

Yield: 1.532 (88%).

**5-Methyl-1-(4-methyl-3-pentenyl)cyclohexene.** Bp: 107-108 °C at 12 mm Hg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 0.96 (d, 3H,  $J = 2.7$  Hz), 1.05-1.22 (m, 1H), 1.54-1.75 (m, 9H), 1.87-2.13 (m, 7H), 5.06-5.16 (m, 1H), 5.35-5.41 (s, br, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 17.67, 22.00, 25.33, 25.70, 26.49, 28.92, 30.83, 37.07, 37.91, 120.26, 124.47, 131.22, 137.29 ppm. MS: 178 5%, 163 6%, 135 33%, 122 7%, 109 23%, 95 14%, 93 20%, 91 10%, 81 20%, 79 22%, 77 12%, 69 100%, 68 12%, 67 66%, 55 29%, 53 27%. MS of minor isomer: 163 15%, 135 43%, 109 17%, 93 23%, 79 24%, 69 100%, 67 74%. Elemental analysis (%) calcd for  $\text{C}_{13}\text{H}_{22}$ : C 87.56, H 12.44; found: C 86.60, H 12.17.

## 1,2-Dimethyl-4-phenylcyclohexene



## Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), 2,3-dimethyl-1,3-butadiene (836 mg, 10.0 mmol) and cinnamaldehyde (1.9 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.19 mL, 1.50 mmol, 15%) under stirring. The mixture was stirred at room temperature for 24 h and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (300 mg, 1.3 mmol) and water (0.10 mL).

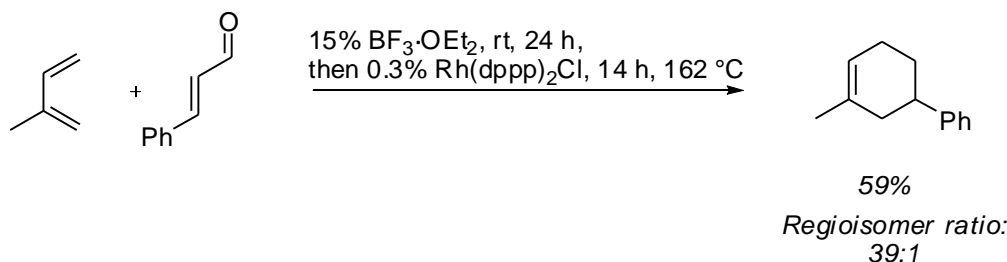
0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.032 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $190 \text{ }^\circ\text{C}$  hot oil bath for 15 h.

The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with heptane ( $2 \times 25 \text{ mL}$ ) and the combined organic extracts were washed with water ( $5 \times 25 \text{ mL}$ ). The organic layer was dried with anhydrous sodium sulfate and heptane was removed *in vacuo*. The orange residual oil was purified by flash chromatography (15 cm silica, heptane) to afford a colorless oil.

Yield: 1.355 g (73%).

**1,2-Dimethyl-4-phenylcyclohexene.** Bp:  $130\text{-}131 \text{ }^\circ\text{C}$  at 13 mm Hg (lit.<sup>15</sup> bp:  $128\text{-}130 \text{ }^\circ\text{C}$  at 11 mm Hg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.65-1.70 (m, 6H), 1.71-2.29 (m, 6H), 2.73-2.86 (m, 1H), 7.18-7.38 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 18.87, 19.05, 30.29, 32.35, 40.05, 40.91, 125.32, 125.48, 125.85, 126.84, 128.28, 147.32 ppm. MS: 186 23%, 171 6%, 143 6%, 129 7%, 115 7%, 104 100%, 91 17%, 82 33%, 67 27%.

## 1-Methyl-5-phenylcyclohexene



## Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), isoprene (0.679 g, 10.0 mmol) and cinnamaldehyde (1.9 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.19 mL, 1.5 mmol, 15%) under stirring. The flask was sealed with a stopper (due to volatile isoprene) and stirred at room temperature for 24 h. The reaction was then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (300 mg, 1.3 mmol) and water (0.10 mL).

0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.033 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a  $190 \text{ }^\circ\text{C}$  hot oil bath for 14 h.

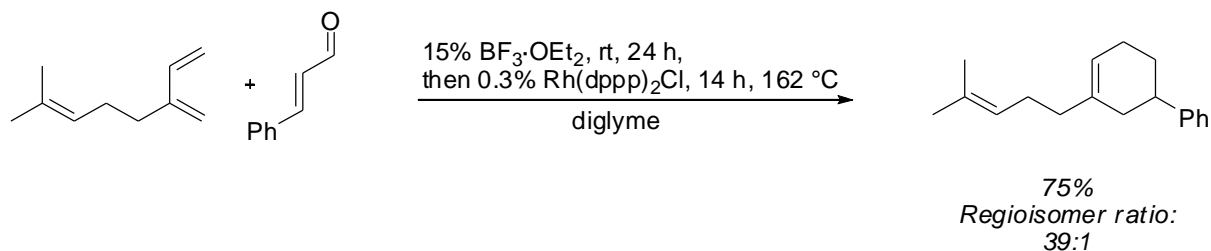
The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with pentane ( $2 \times 25 \text{ mL}$ ) and the combined organic extracts were washed with water ( $5 \times 25 \text{ mL}$ ). The organic layer was dried with anhydrous sodium sulfate and most of the pentane was removed *in vacuo*. The orange residual oil was purified by flash column chromatography (10 cm silica, pentane) to afford a colorless oil. Two products with mass 172 were identified by GC-MS in a ratio of 39:1.

Yield: 1.018 g (59%).

**1-Methyl-5-phenylcyclohexene.** Bp:  $122\text{-}123 \text{ }^\circ\text{C}$  at 13 mm Hg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.58-1.74 (m, 1H), 1.68 (s, 3H), 1.83-1.93 (m, 1H), 2.01-2.20 (m, 4H), 2.78-2.90 (m, 1H), 5.42-5.49 (s, br, 1H), 7.14-7.33 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 23.62, 25.82, 29.45, 38.31, 40.54, 120.86, 125.91, 126.86, 128.32, 133.77, 147.30 ppm. MS: 172 14%, 129 5%, 115 5%, 105 9%, 104 100%, 78 10%, 77 8%.  $^{13}\text{C}$  NMR data are in accordance with literature data.<sup>16</sup>

MS of minor isomer: 172 17%, 105 13%, 104 100% (retro Diels-Alder in MS), 91 11%, 78 10%.

## 5-Phenyl-1-(4-methyl-3-pentenyl)cyclohexene



## Procedure

A 50 mL round bottomed flask was charged with diglyme (10 mL), myrcene (1.461 g, 9.8 mmol, 91% pure) and cinnamaldehyde (1.9 mL, 15 mmol) followed by addition of  $\text{BF}_3 \cdot \text{OEt}_2$  (0.19 mL, 1.5 mmol, 15%) under stirring. The mixture was stirred at room temperature for 24 h and then quenched with  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (300 mg, 1.3 mmol) and water (0.10 mL).

0.3%  $\text{Rh}(\text{dppp})_2\text{Cl}$  (0.033 mmol) dissolved in 1 mL of diglyme was transferred to the reaction mixture and the solution was degassed ( $5 \times$  argon/vacuum). The reaction flask was placed in a 190 °C hot oil bath for 14 h.

The flask was cooled to room temperature and water (25 mL) was added. The mixture was extracted with heptane ( $2 \times 25$  mL) and the combined organic extracts were washed with water ( $5 \times 25$  mL). The organic layer was dried with anhydrous sodium sulfate and most of the heptane removed *in vacuo*. The orange residual oil was purified by flash column chromatography (10 cm silica, heptane) to afford a colorless oil. The remaining myrcene impurities were removed at high vacuum ( $< 1$  mm Hg). GC-MS analysis showed that only traces of the myrcene impurities remained. Two products with mass 240 were identified by GC-MS in a ratio of 39:1.

Yield: 1.771 g (75%).

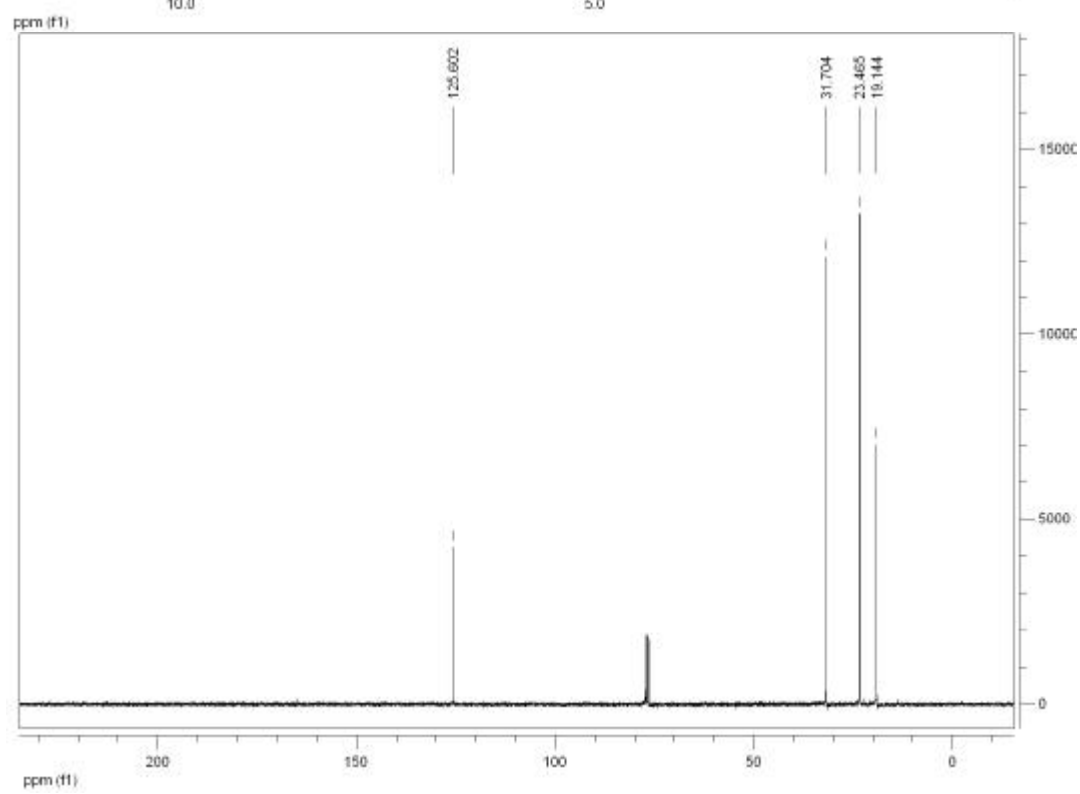
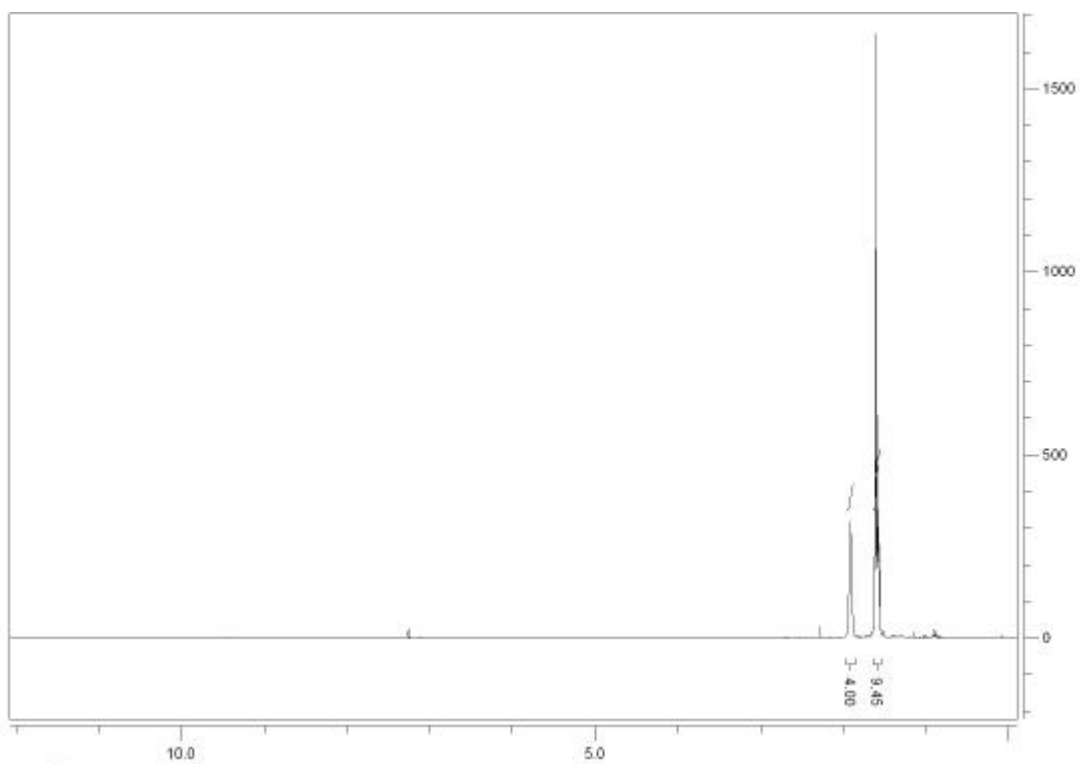
**5-Phenyl-1-(4-methyl-3-pentenyl)cyclohexene.** Bp: 113-115 °C at 0.1 mm Hg.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.65 (s, 3H), 1.74 (s, 3H), 1.67-1.80 (m, 1H), 1.90-2.27 (m, 9H), 2.76-2.90 (m, 1H), 5.13-5.21 (m, 1H), 5.53 (s, br, 1H), 7.20-7.39 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 17.70, 25.71, 25.83, 26.45, 29.61, 36.81, 37.79, 40.59, 120.47, 124.30, 125.91, 126.86, 128.32, 131.38, 137.45, 147.37 ppm. MS: 240 10%, 225 4%, 197 24%, 183 5%, 170 12%, 155 8%, 143 9%, 129 27%, 115 13%, 104 39%, 93 25%, 91 88%, 77 19%, 69 100%, 67 19%, 53 15%.

MS of minor isomer: 197 23%, 142 12%, 104 22% (retro Diels-Alder in MS), 91 100%, 69 88%.

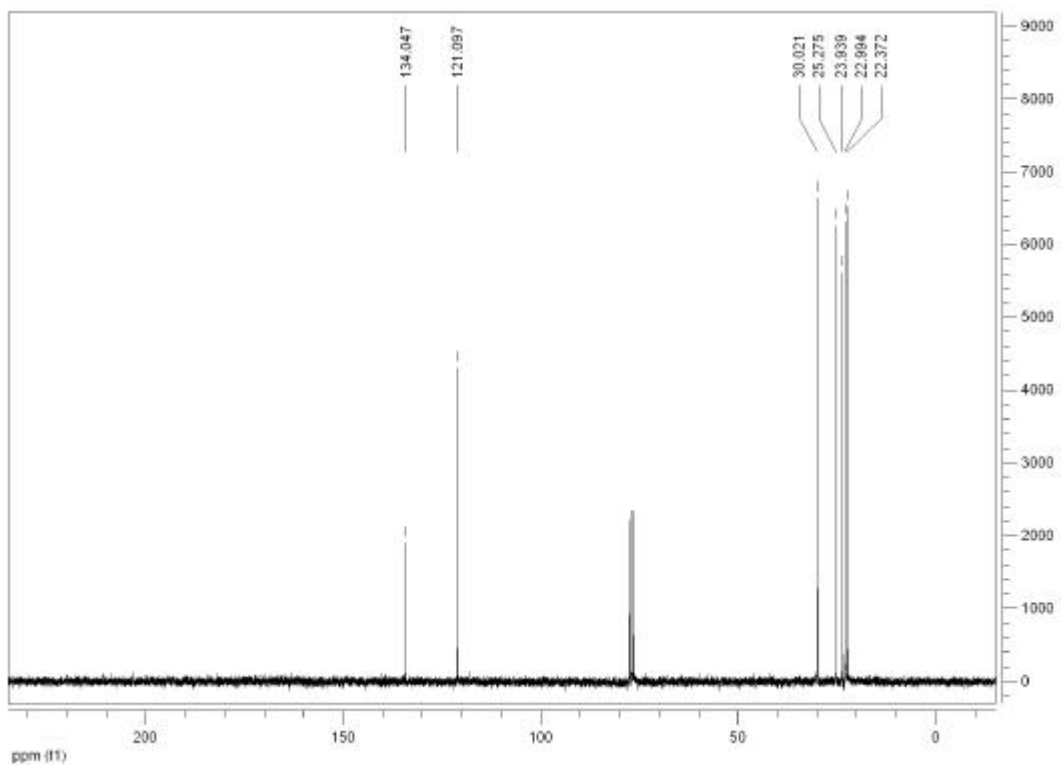
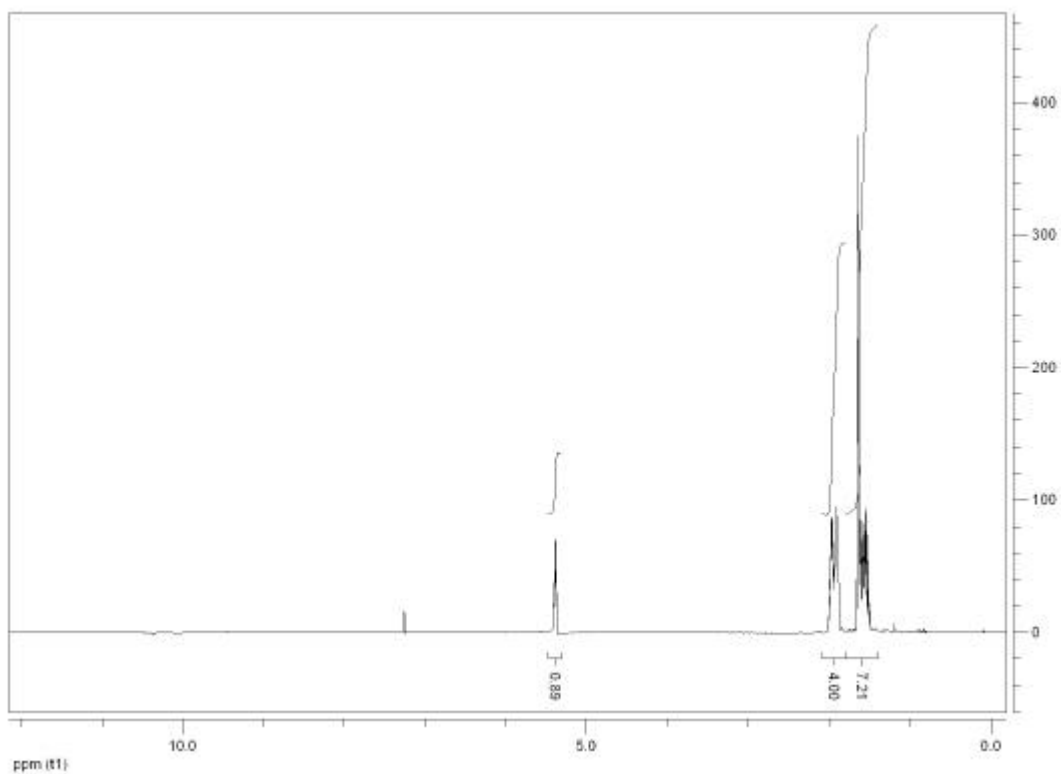
Elemental analysis (%) calcd for  $\text{C}_{18}\text{H}_{24}$ : C 89.94, H 10.06; found: C 89.58, H 10.12.

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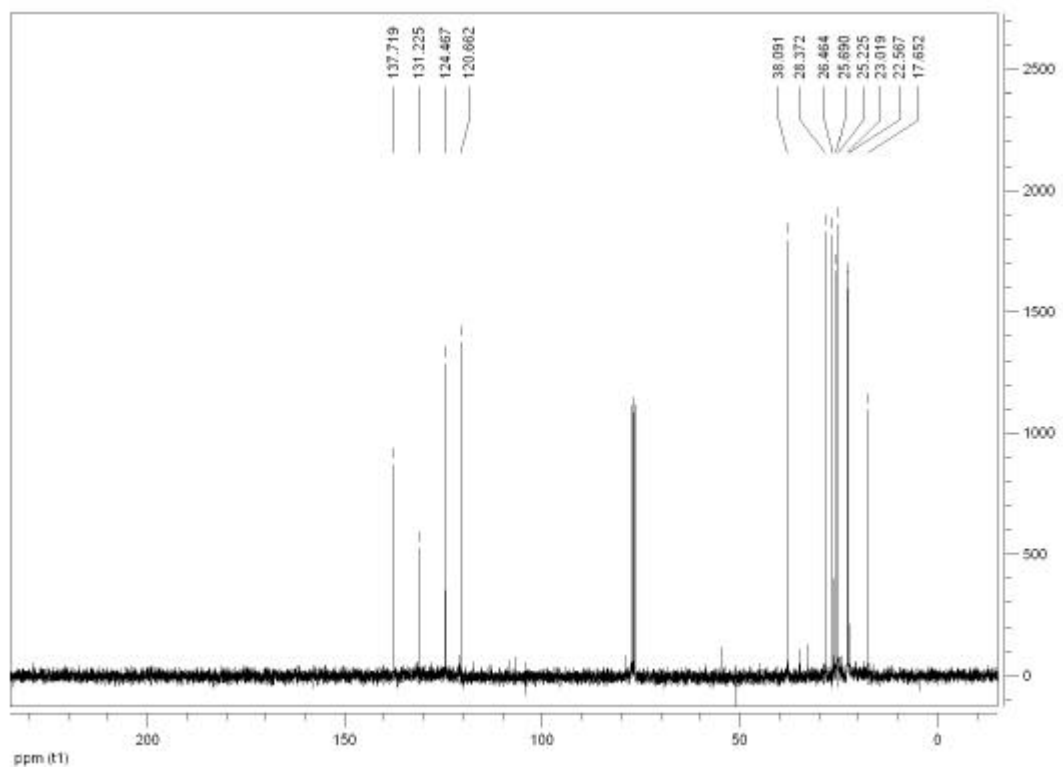
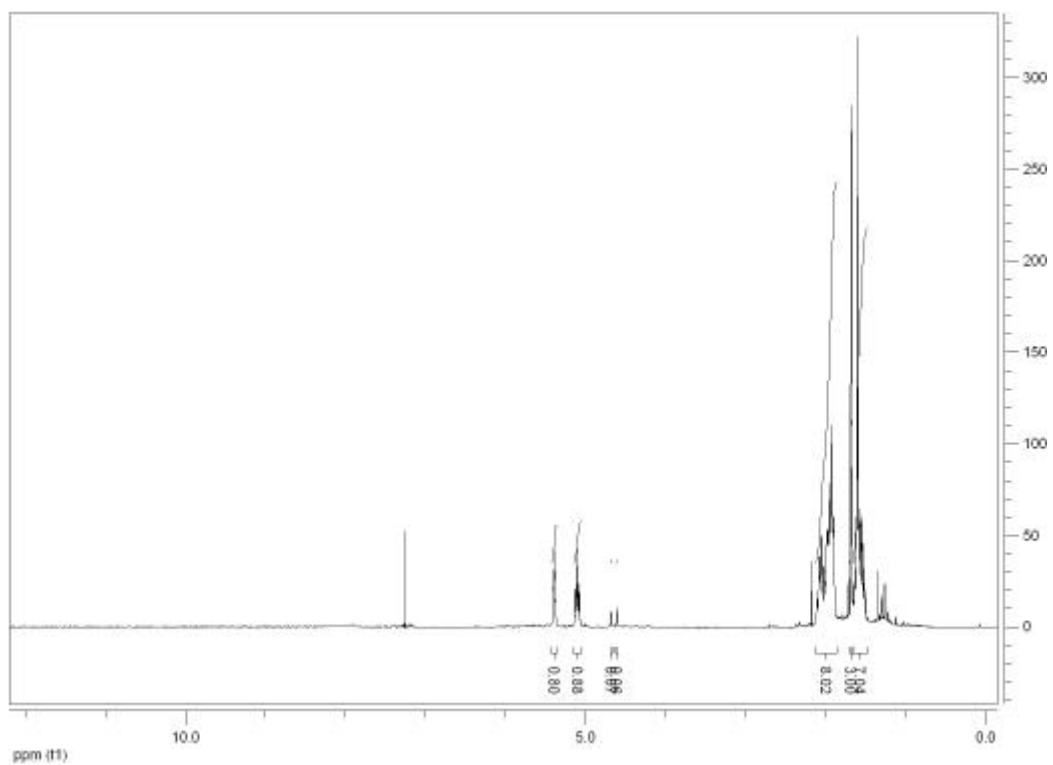


**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1-methylcyclohexene**

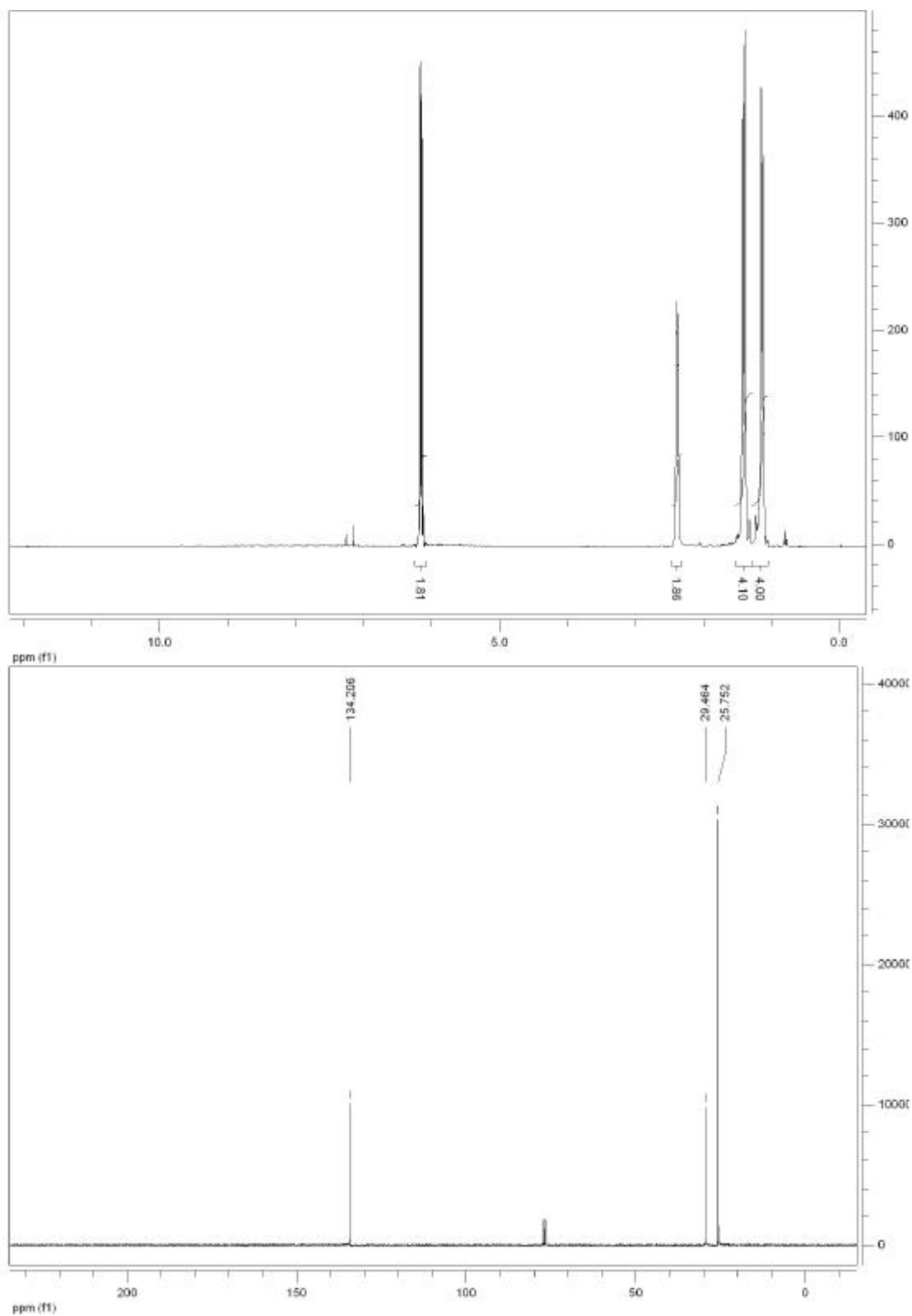


**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1-(4-methyl-3-pentenyl)cyclohexene**

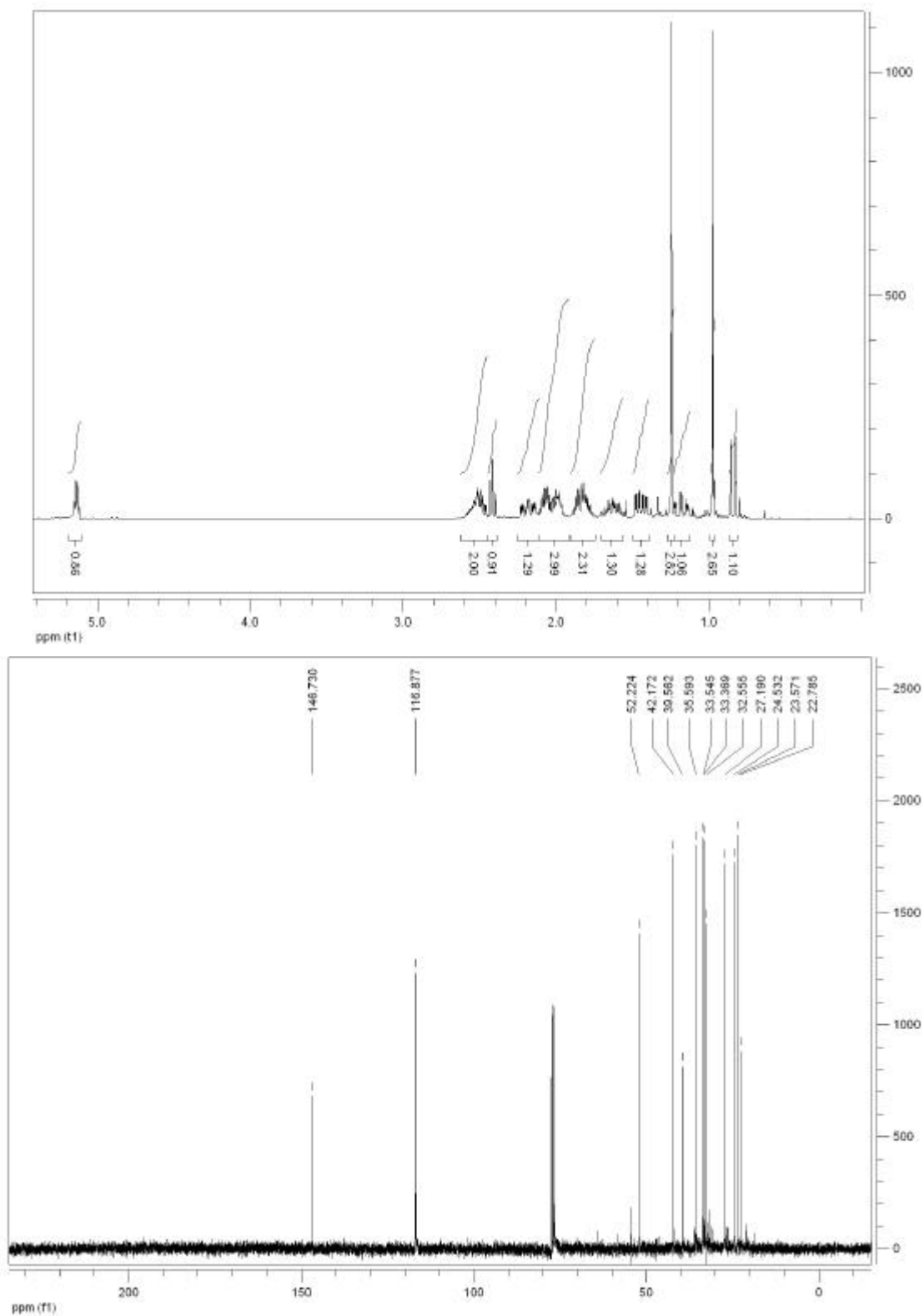




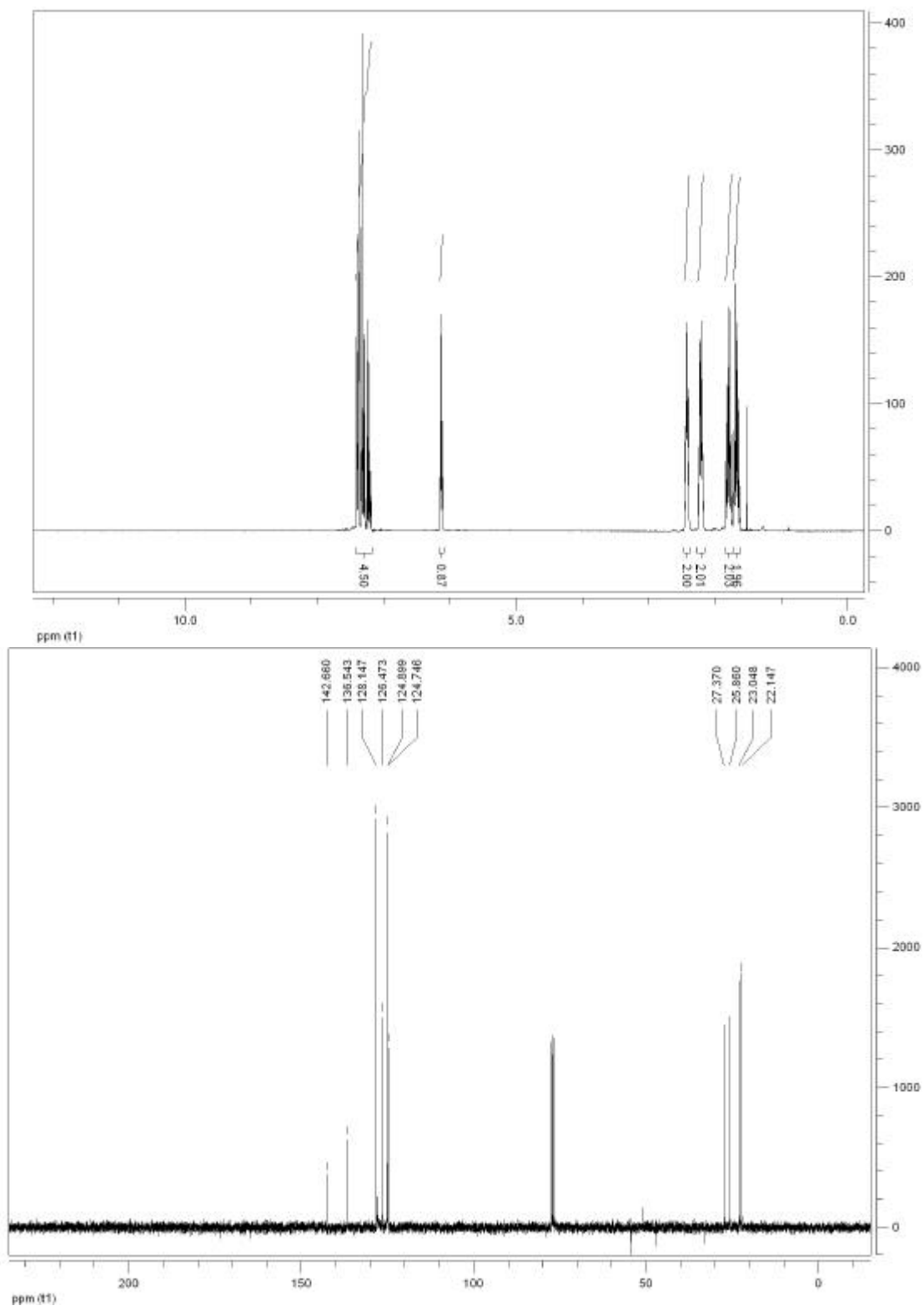
**<sup>1</sup>H and <sup>13</sup>C NMR of bicyclo[2,2,2]-2-octene**



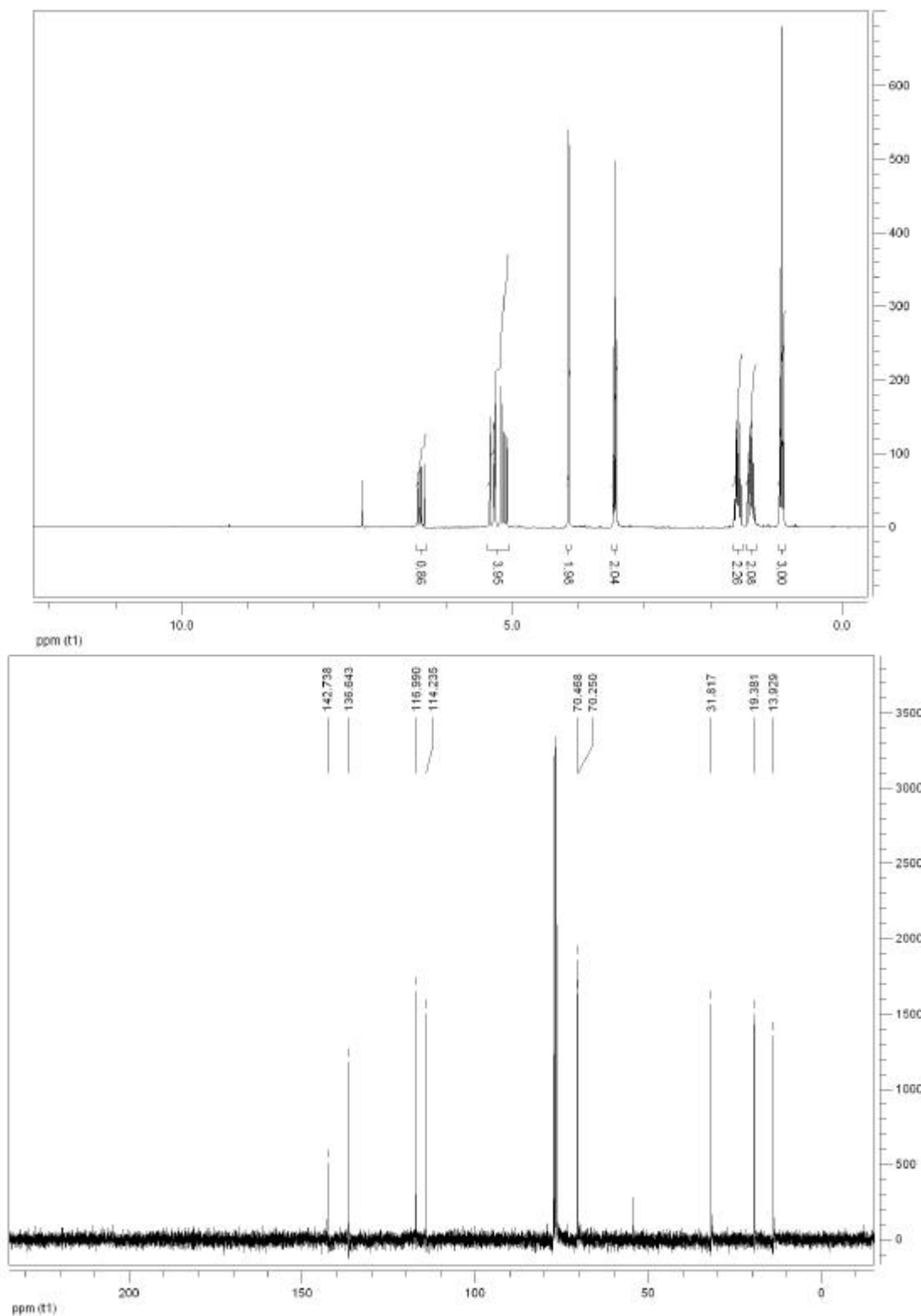
**<sup>1</sup>H and <sup>13</sup>C NMR of 9,9-dimethyltricyclo[4,4,0,1<sup>8,10</sup>]-1-undecene**



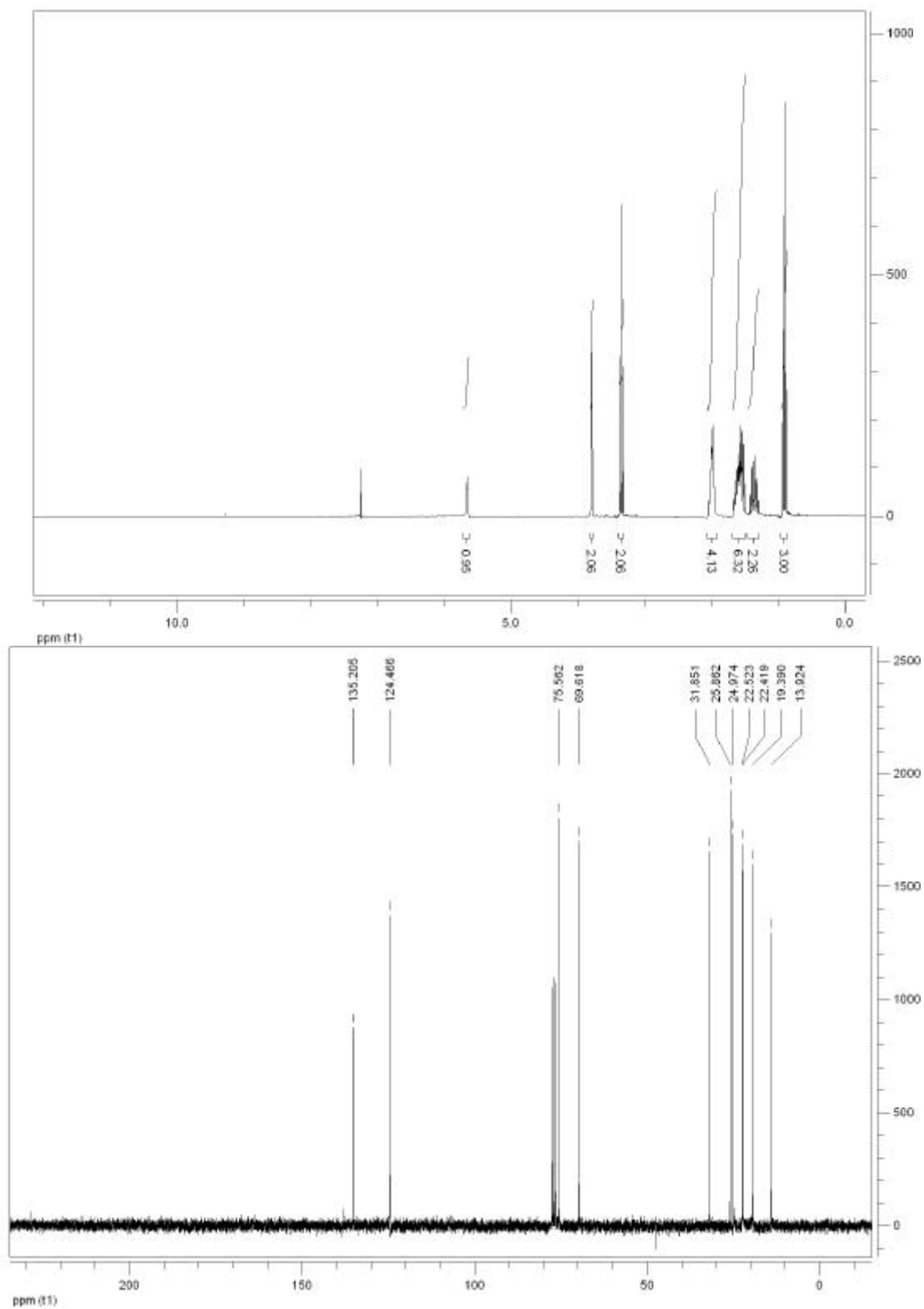
**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1-phenylcyclohexene**



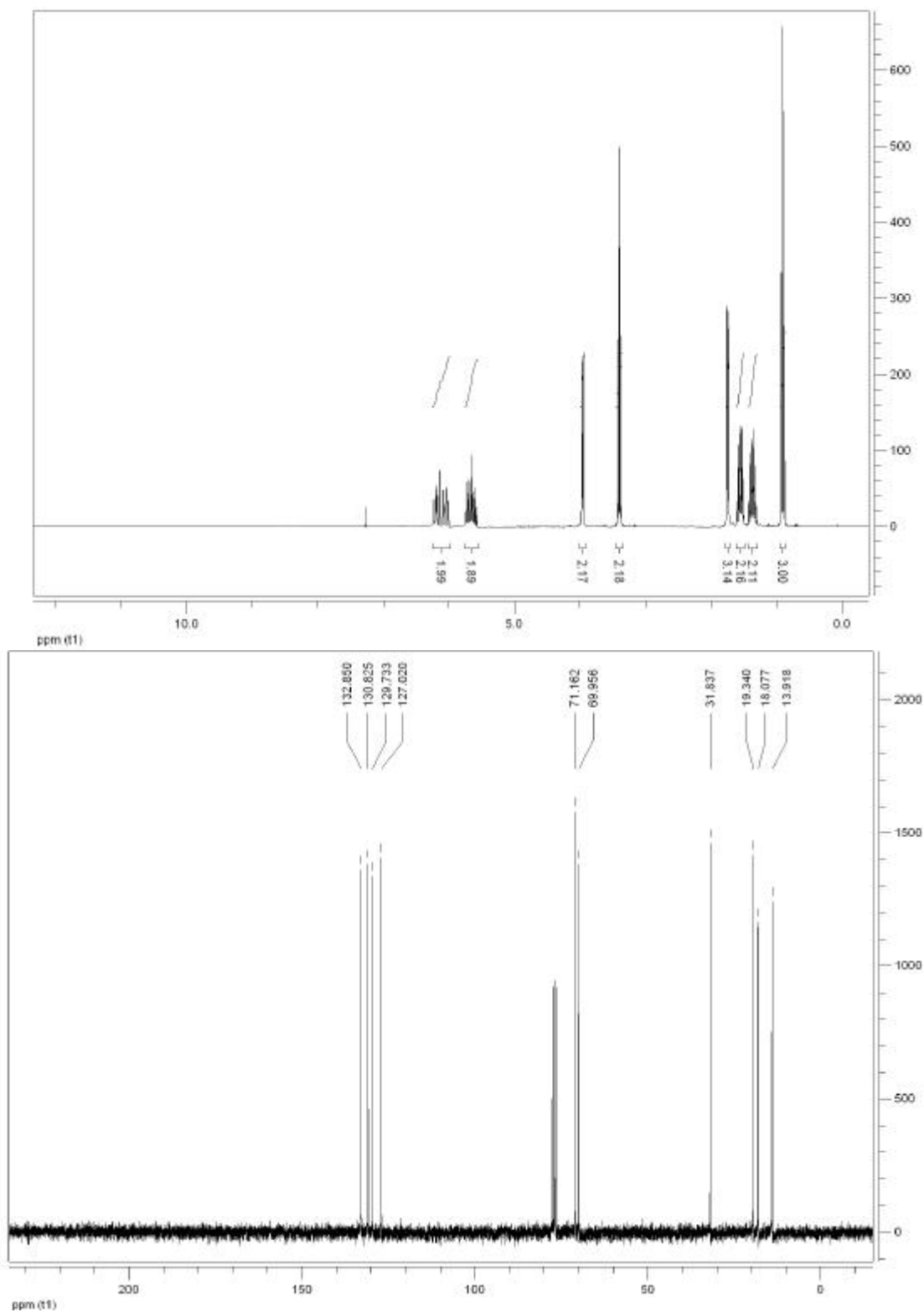
$^1\text{H}$  and  $^{13}\text{C}$  NMR of 2-(butoxymethyl)-1,3-butadiene



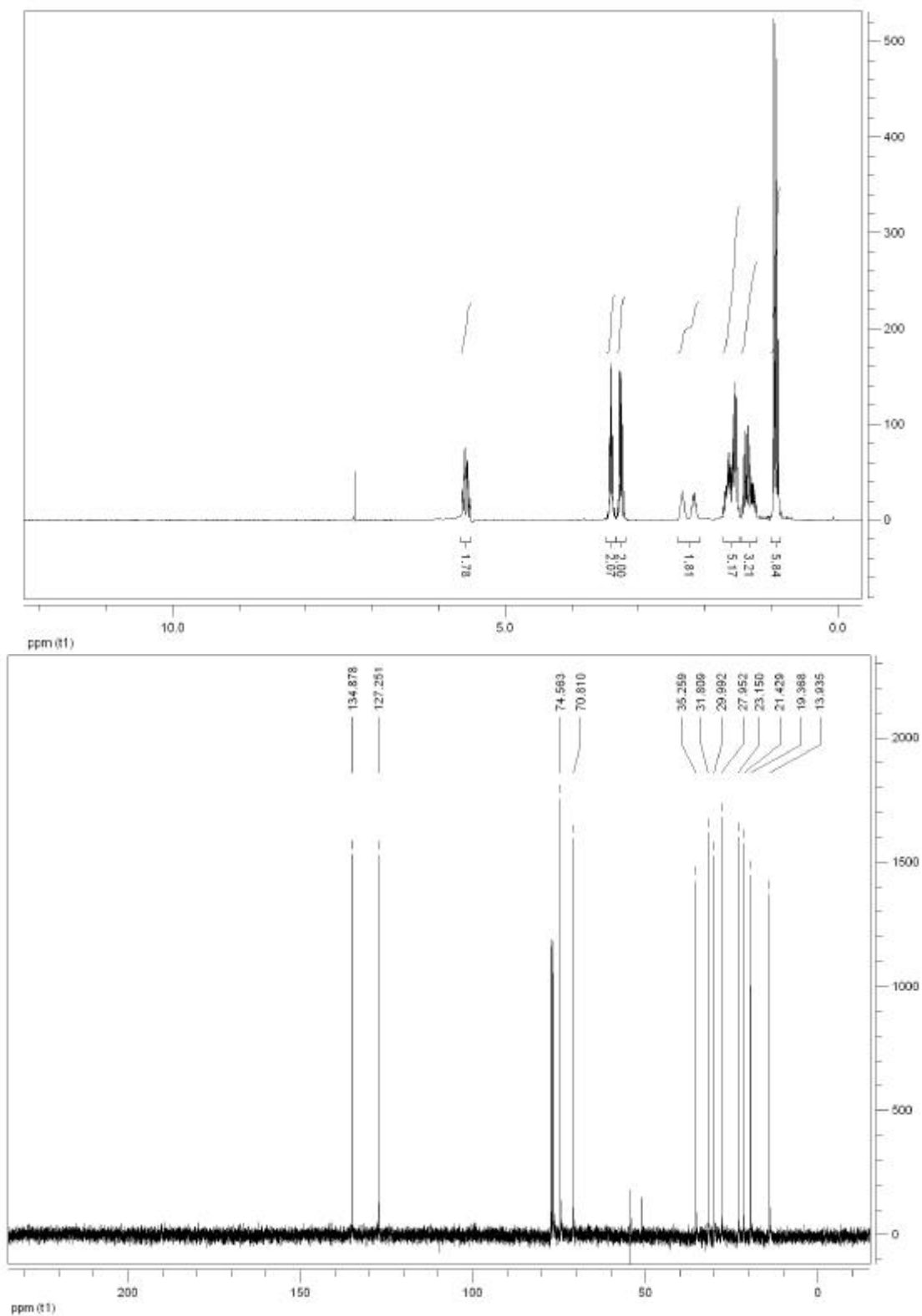
$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1-(butoxymethyl)cyclohexene



$^1\text{H}$  and  $^{13}\text{C}$  NMR of (2E,4E)-1-butoxy-2,4-hexadiene

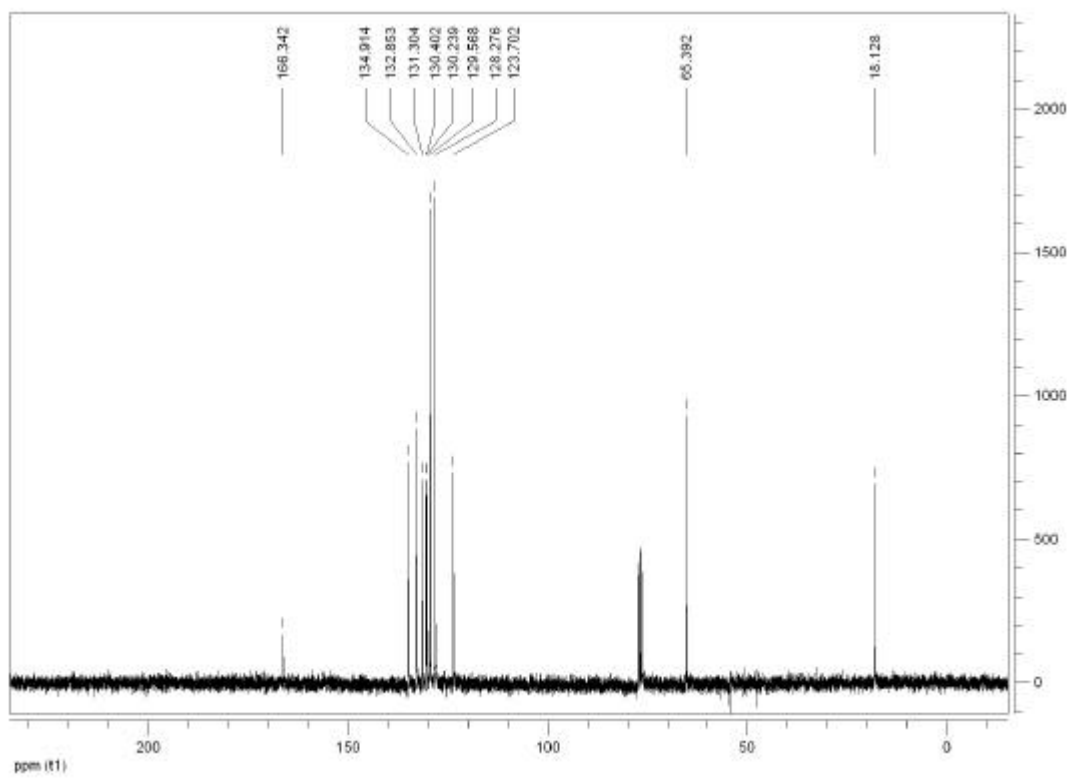
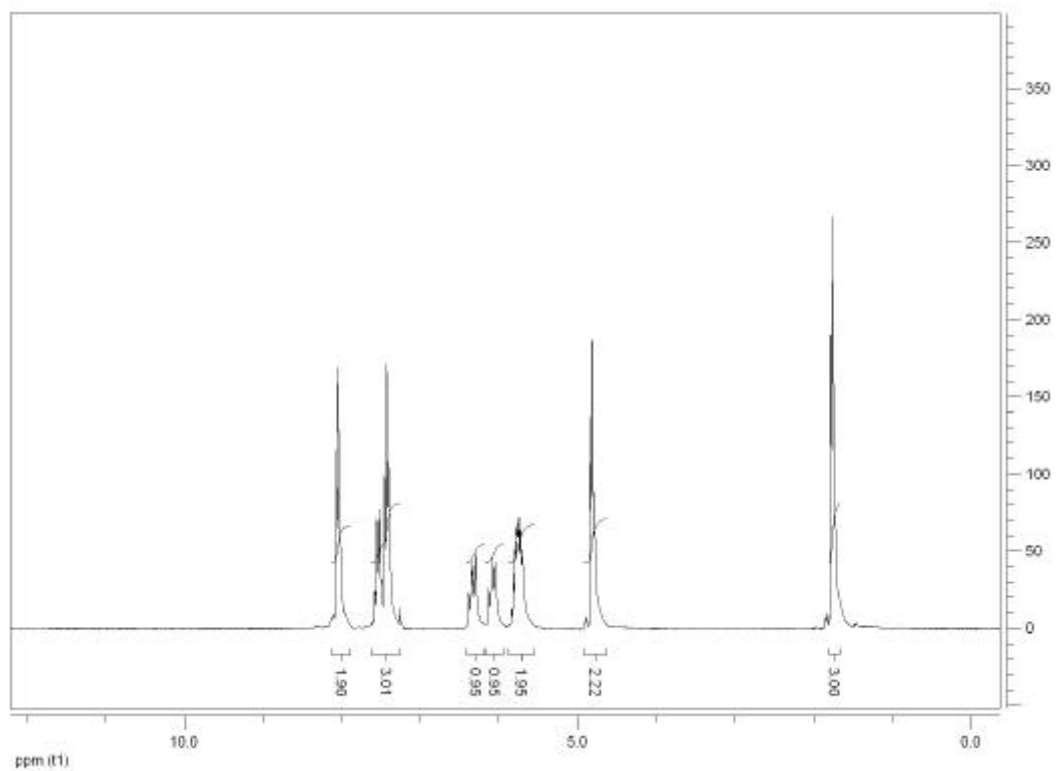


$^1\text{H}$  and  $^{13}\text{C}$  NMR of 3-(butoxymethyl)-6-methylcyclohexene

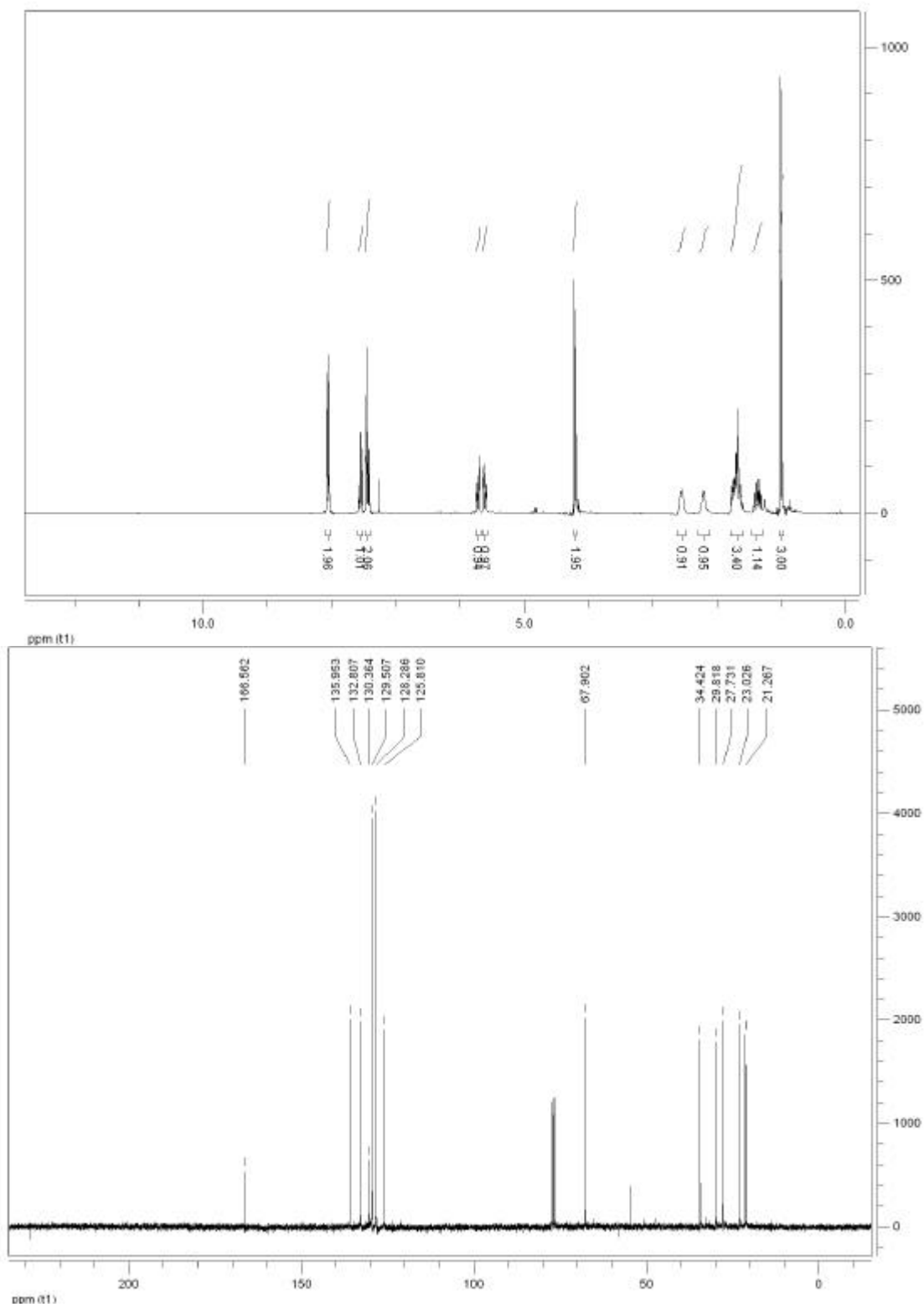


**<sup>1</sup>H and <sup>13</sup>C NMR of (2E,4E)-2,4-hexadienyl benzoate**

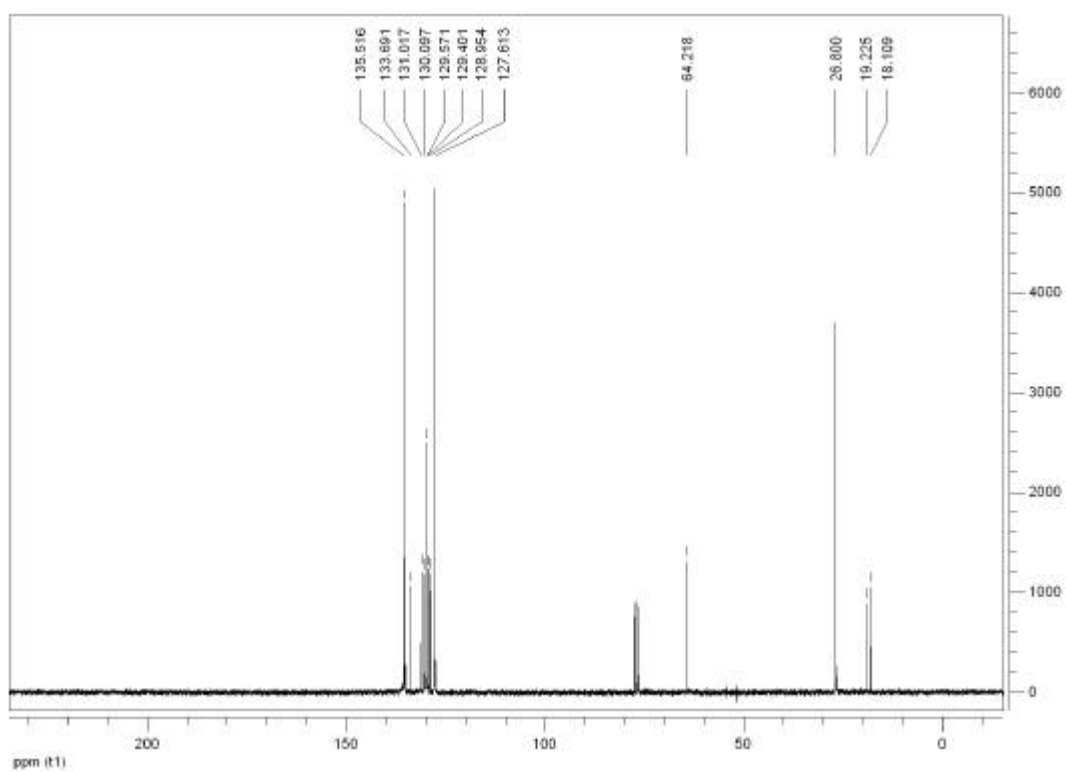
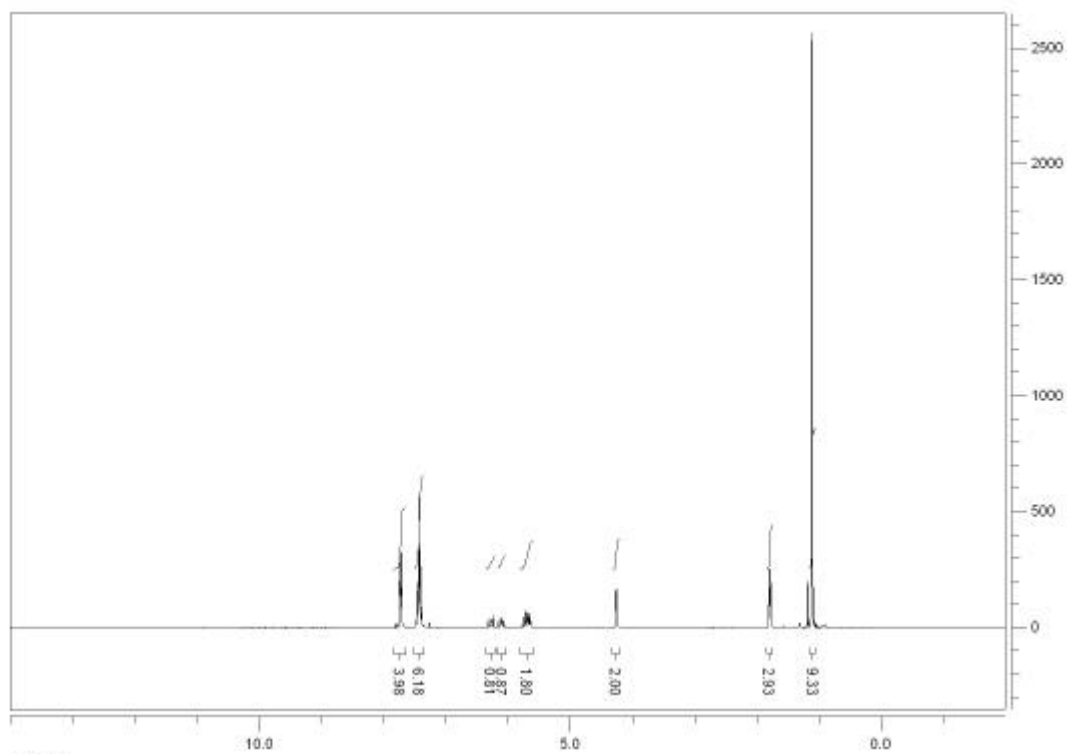




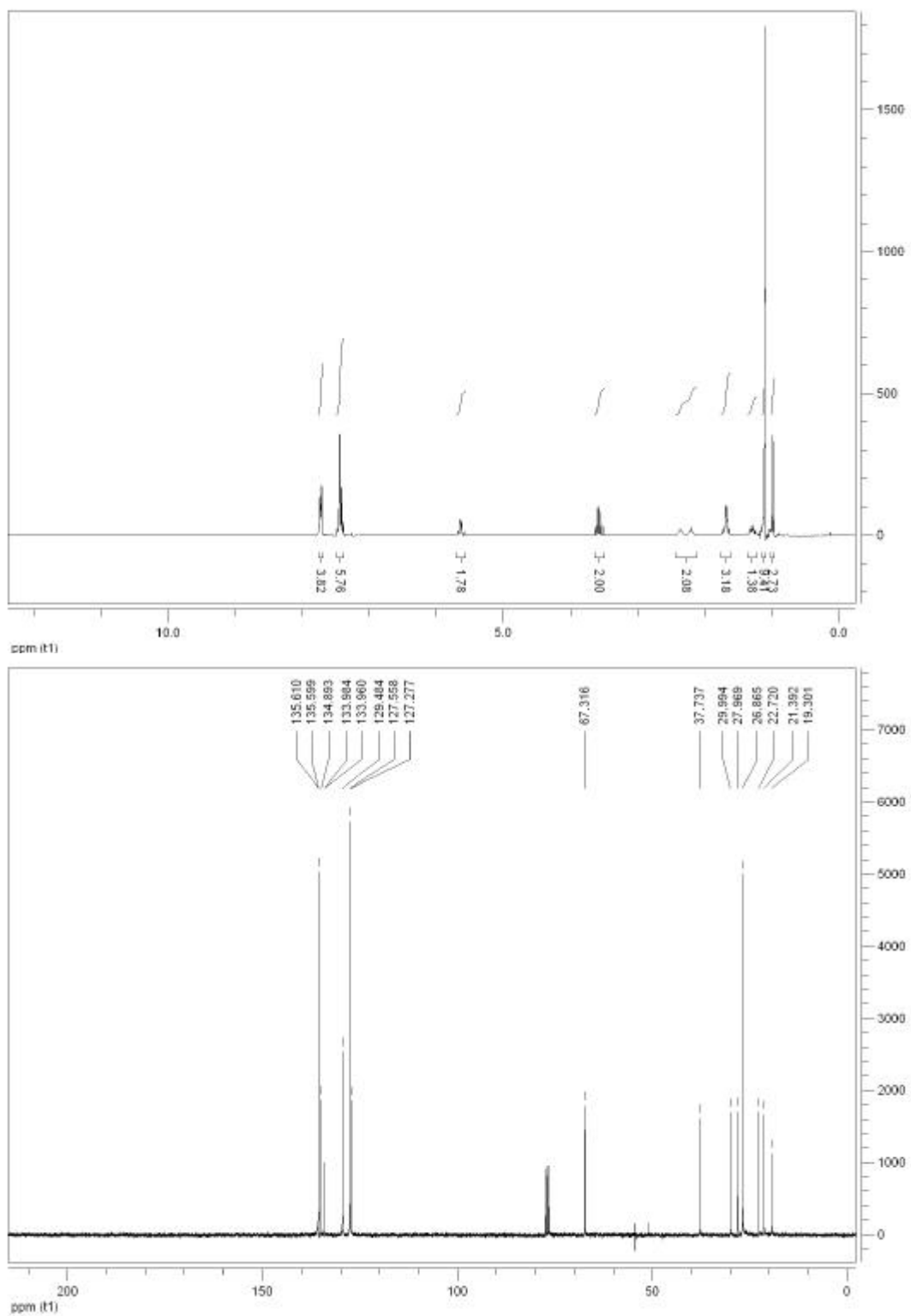
$^1\text{H}$  and  $^{13}\text{C}$  NMR of (4-methyl-2-cyclohexenyl)methyl benzoate



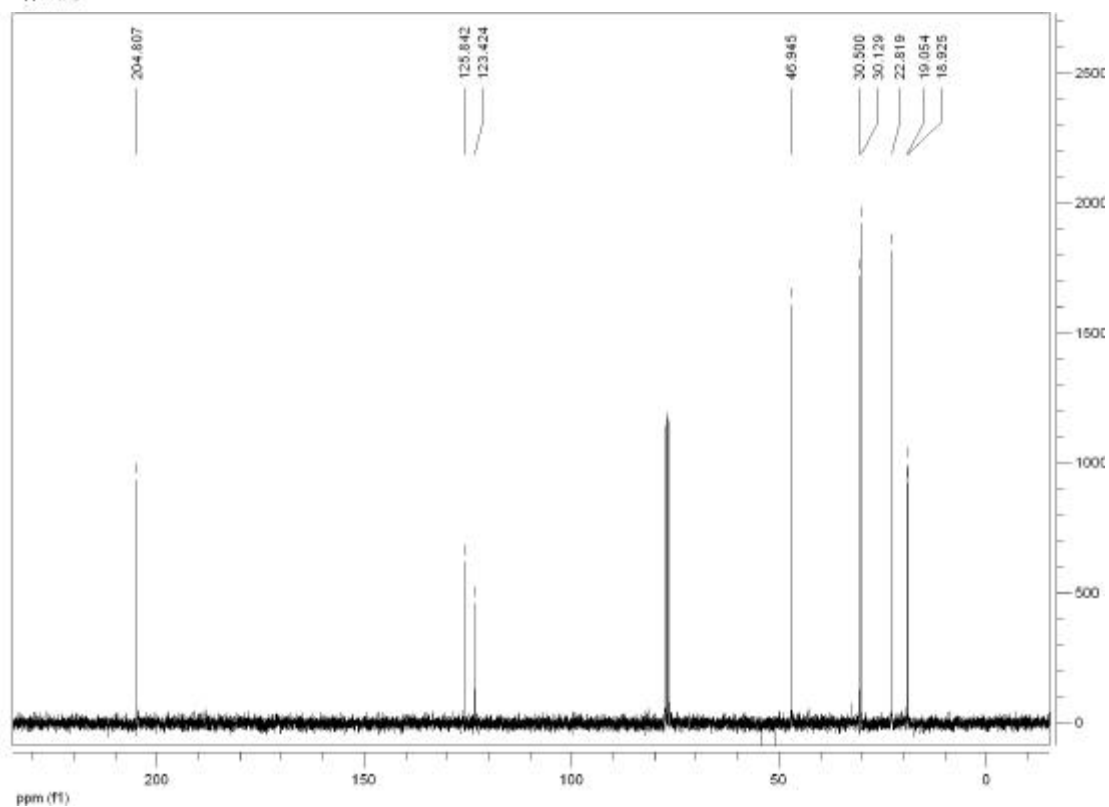
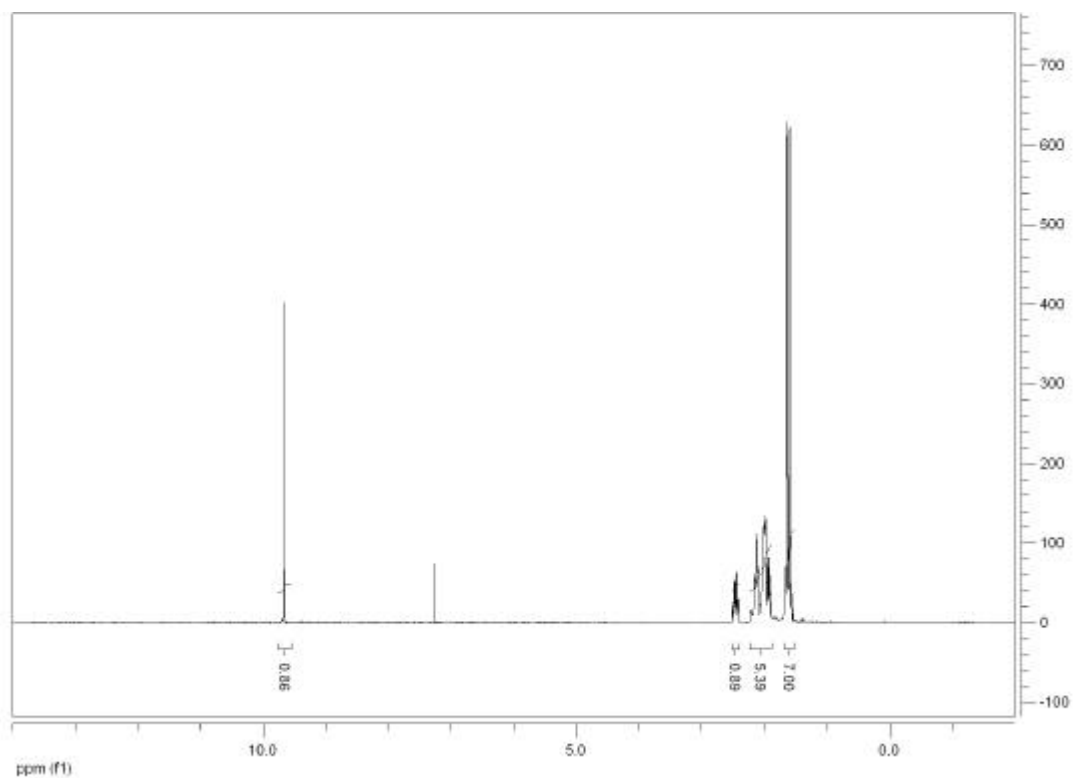
**<sup>1</sup>H and <sup>13</sup>C NMR of *tert*-butyl((*2E,4E*)-2,4-hexadienyloxy)diphenylsilane**



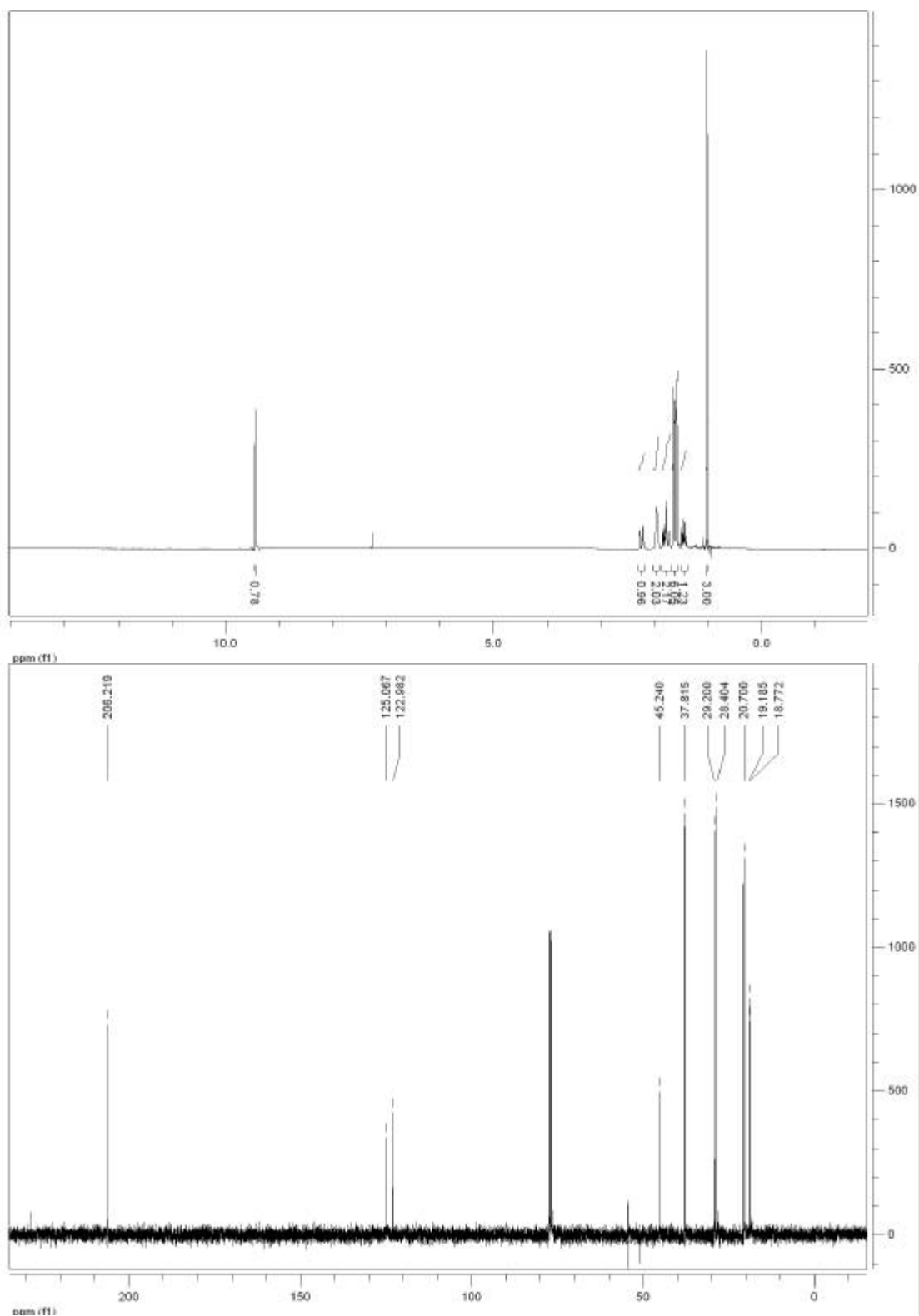
<sup>1</sup>H and <sup>13</sup>C NMR of *tert*-butyl((4-methyl-2-cyclohexenyl)methoxy)diphenylsilane



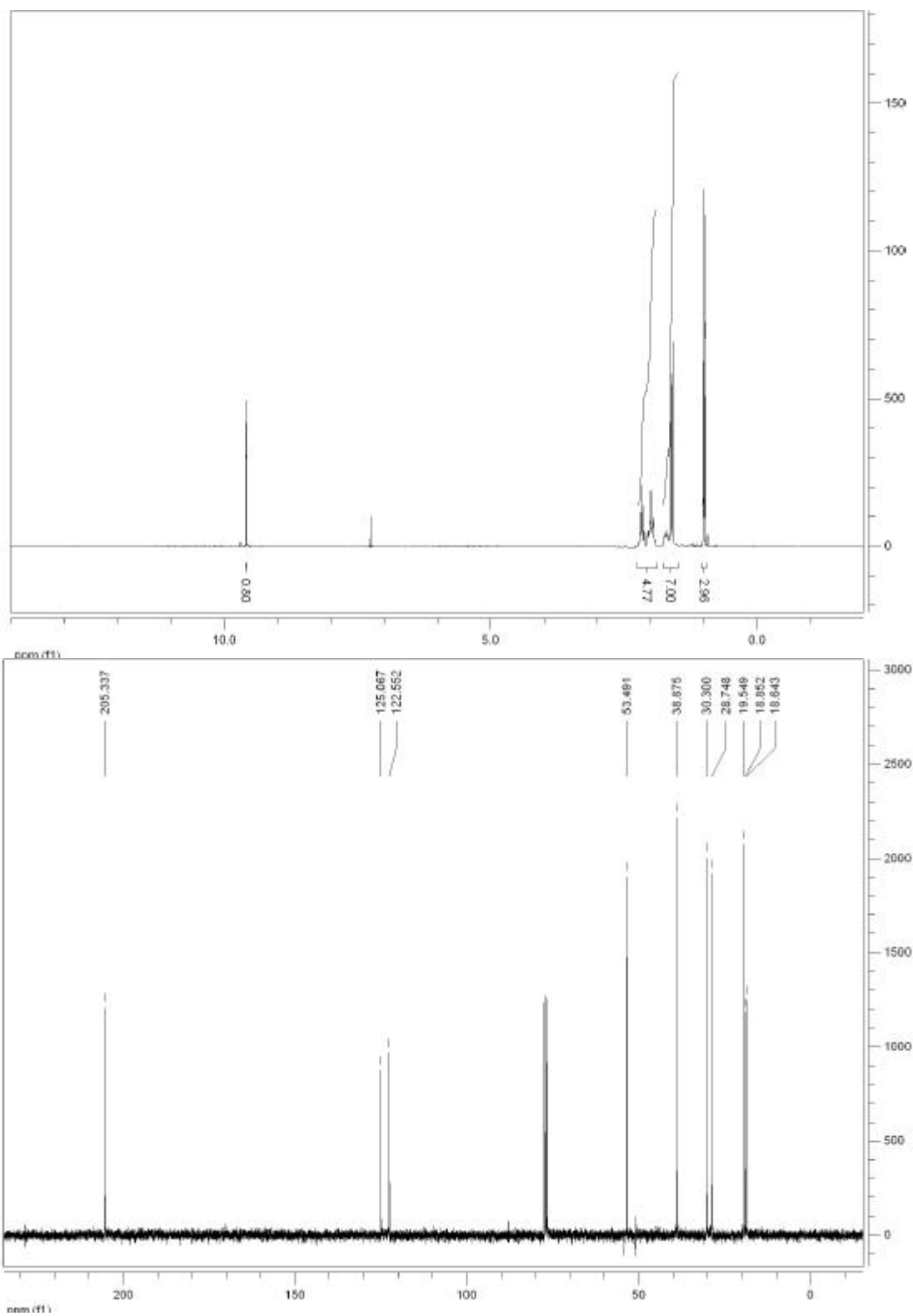
$^1\text{H}$  and  $^{13}\text{C}$  NMR of 3,4-dimethyl-3-cyclohexene-1-carbaldehyde



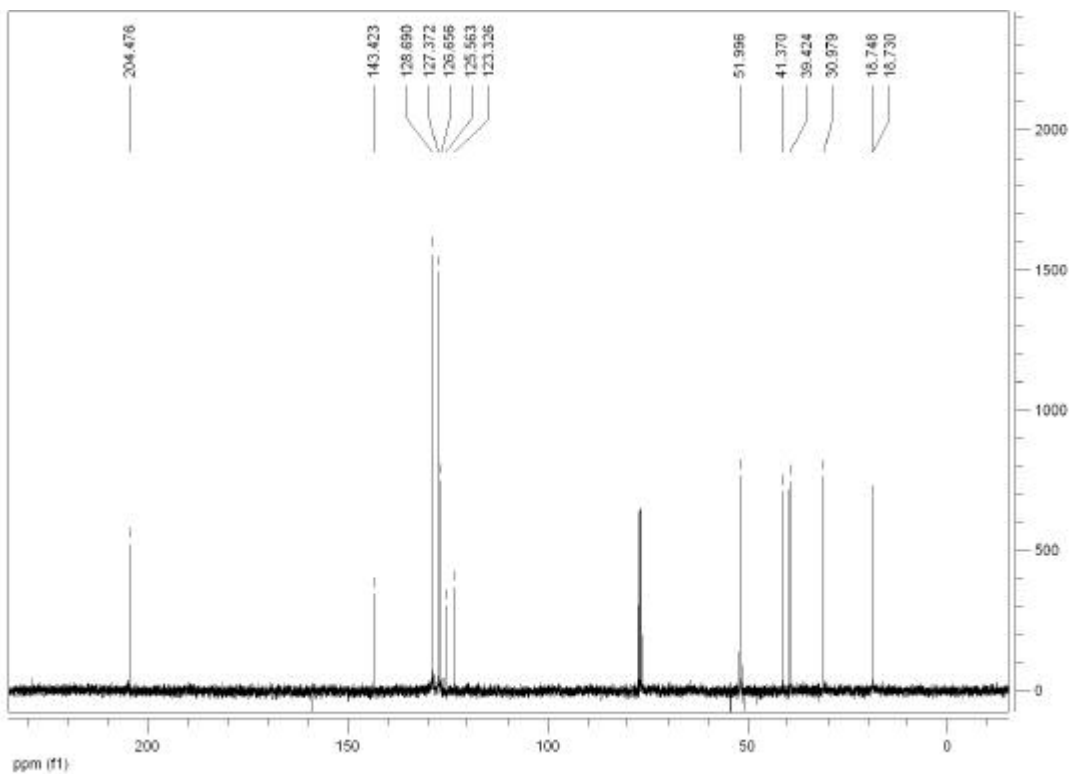
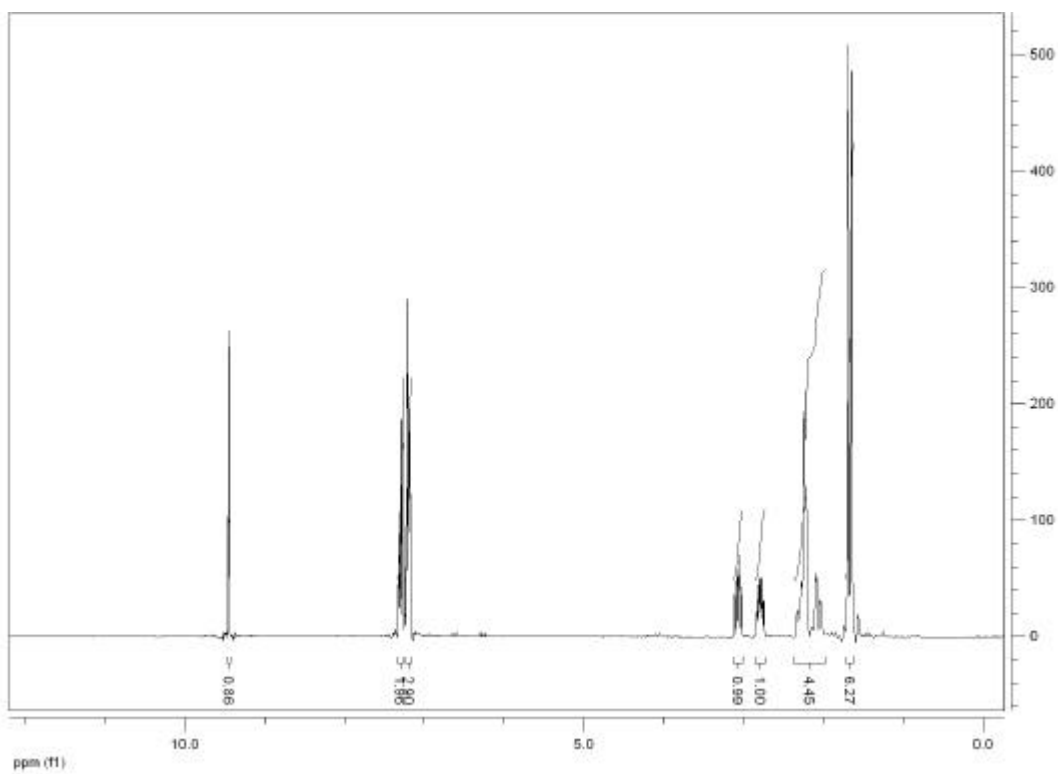
**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1,3,4-trimethyl-3-cyclohexene-1-carbaldehyde**



$^1\text{H}$  and  $^{13}\text{C}$  NMR of 3,4,6-trimethyl-3-cyclohexene-1-carbaldehyde

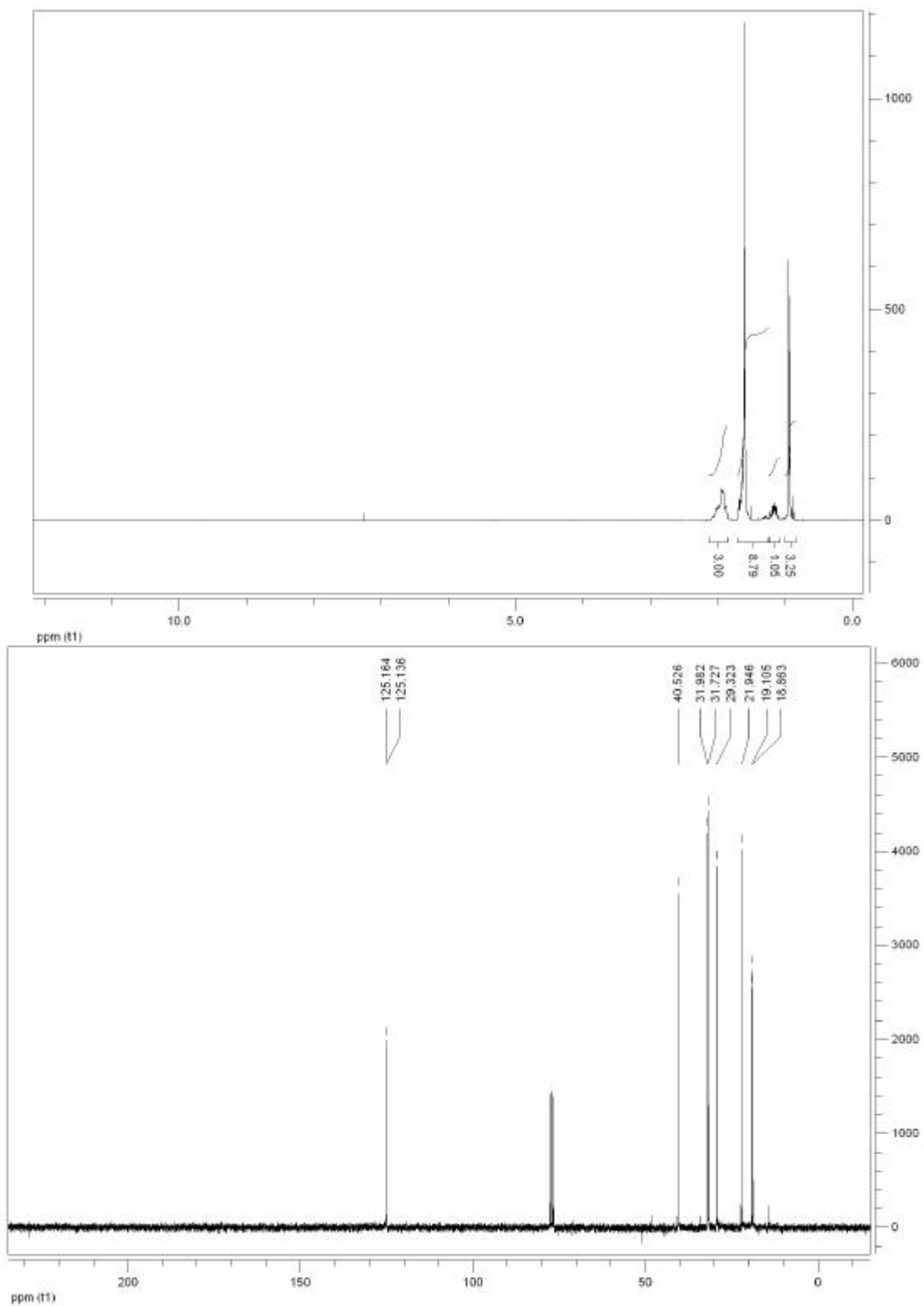


$^1\text{H}$  and  $^{13}\text{C}$  NMR of 3,4-dimethyl-6-phenyl-3-cyclohexene-1-carbaldehyde

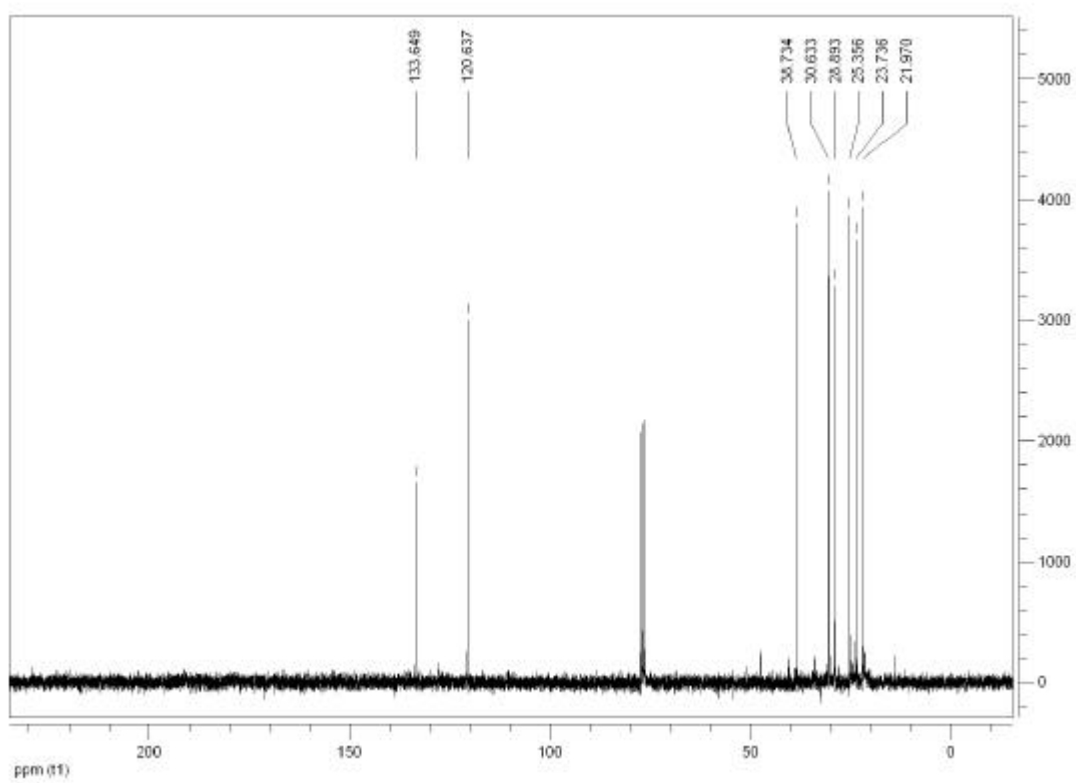
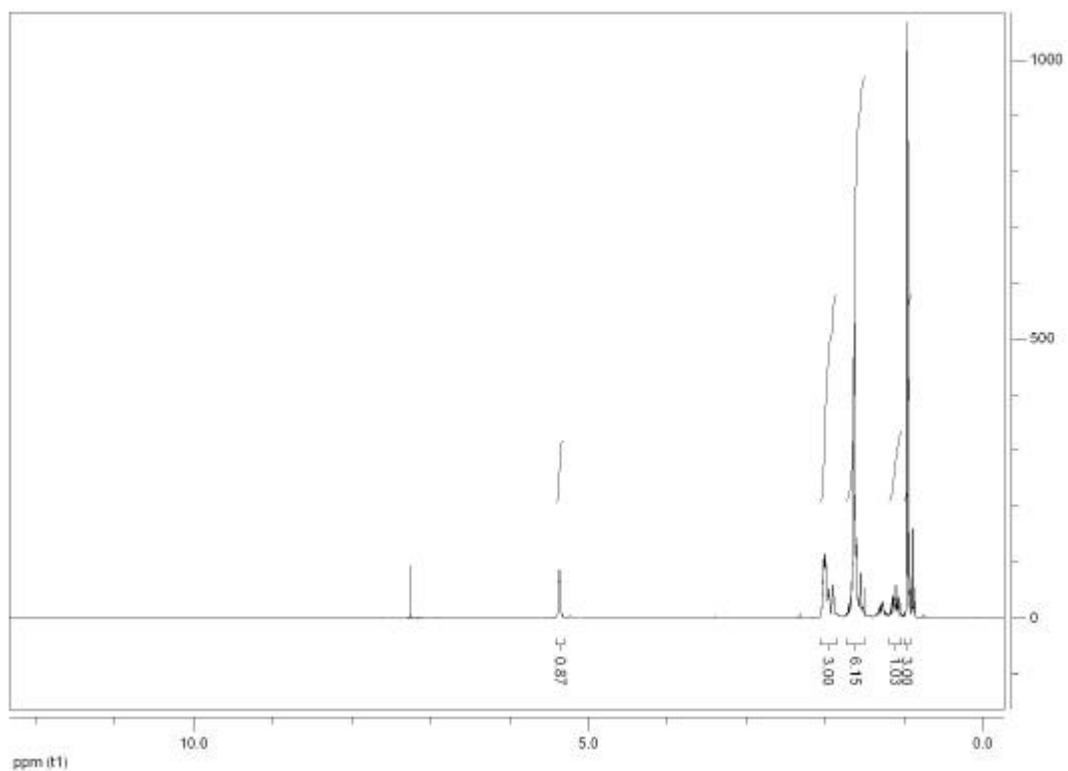


**<sup>1</sup>H and <sup>13</sup>C NMR of 1,2,4-trimethylcyclohexene**

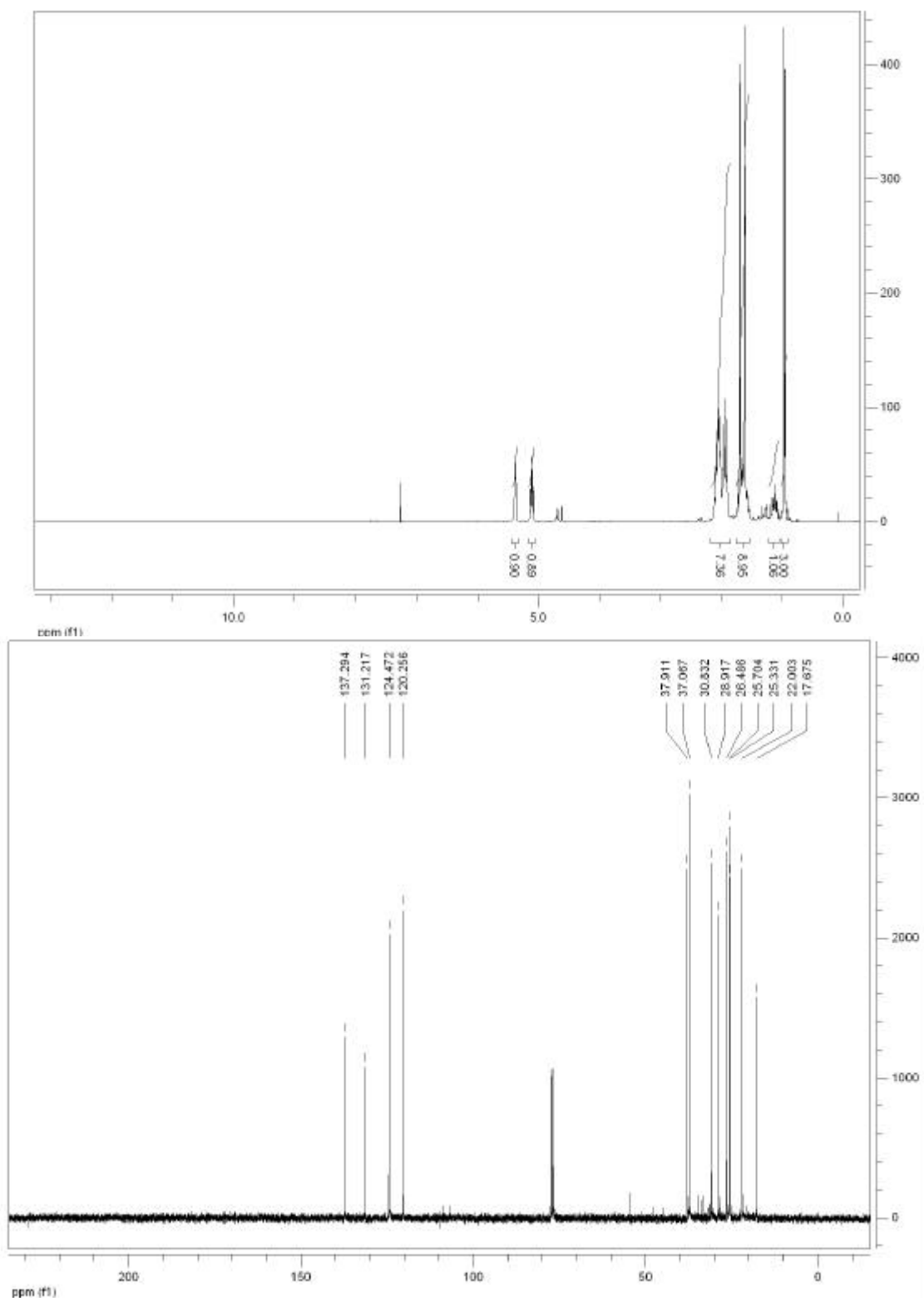




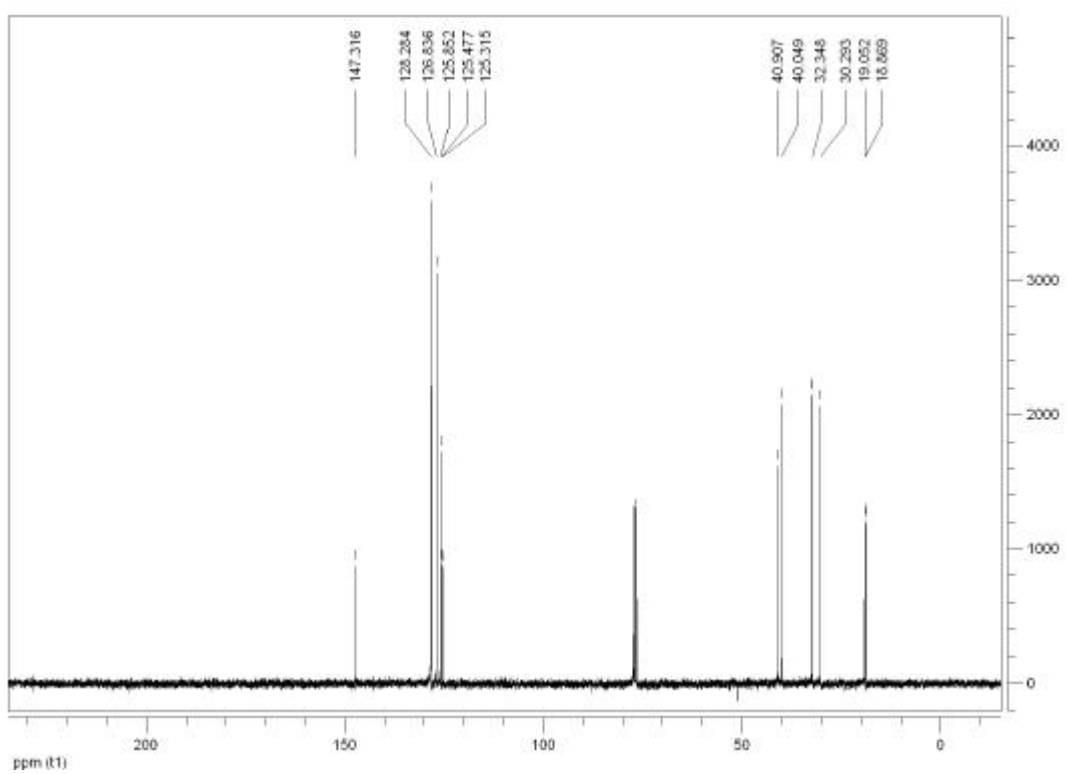
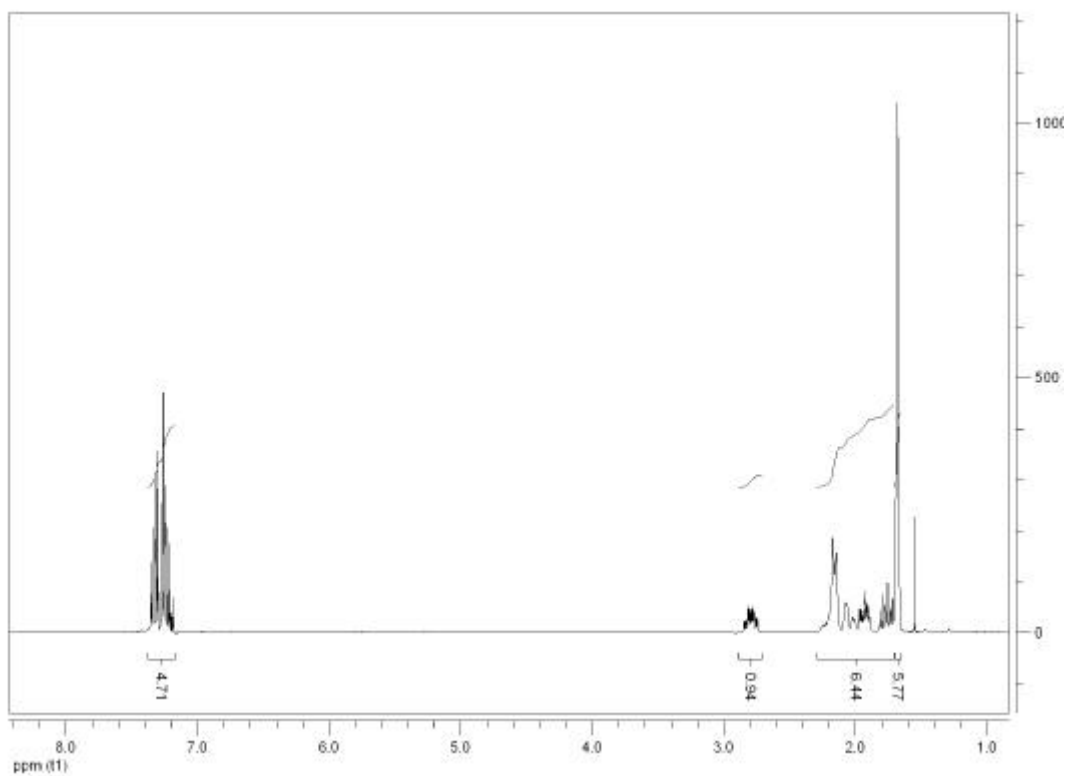
**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1,5-dimethylcyclohexene**



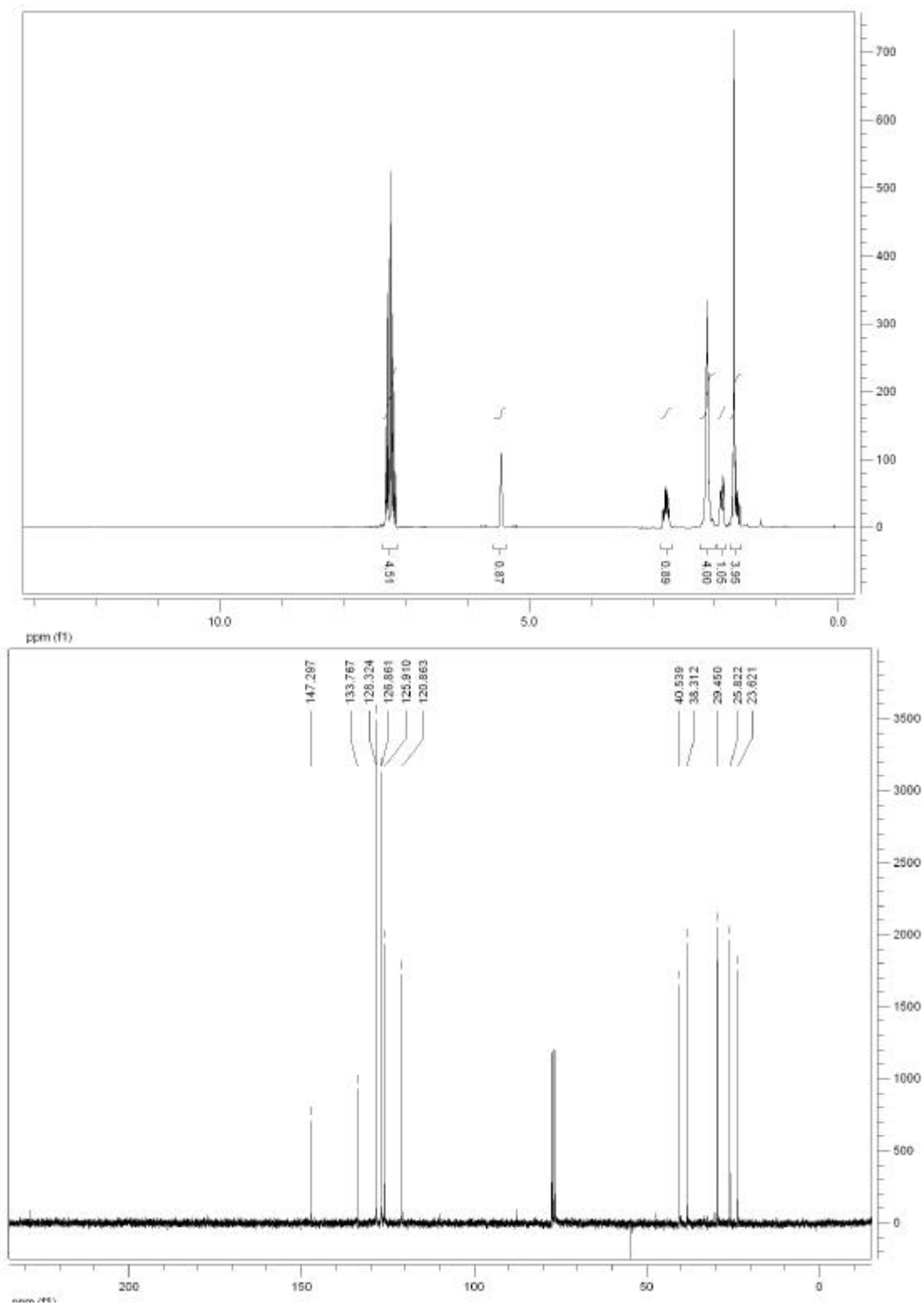
**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 5-methyl-1-(4-methyl-3-pentenyl)cyclohexene**



$^1\text{H}$  and  $^{13}\text{C}$  NMR of 1,2-dimethyl-4-phenylcyclohexene



**<sup>1</sup>H and <sup>13</sup>C NMR of 1-methyl-5-phenylcyclohexene**



**$^1\text{H}$  and  $^{13}\text{C}$  NMR of 5-phenyl-1-(4-methyl-3-pentenyl)cyclohexene**

