

## Supporting Information

### Chlorocyclization/Cycloreversion of Allylic Alcohols to Vinyl Chlorides

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#### Contents:

I. General information.....	1
II. Synthesis and characterization of <b>2a</b> .....	2
III. General Procedure for the synthesis of alcohol .....	4
IV. Characterization of compound <b>4</b> .....	4
V. Synthesis and characterization of <b>5</b> .....	14
VI. General Procedure for the synthesis of ketones.....	15
VII. Characterization of Compounds <b>7</b> .....	15
VIII. Synthesis and characterization of <b>8</b> .....	24
IX. X-Ray Crystallographic Data .....	28
X. References.....	32
XI. NMR Spectra .....	33

## I. General information

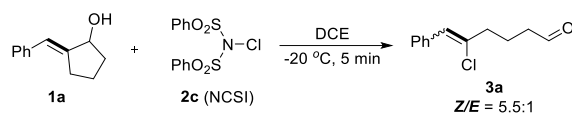
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded respectively on a Bruker 14A04336 (600 MHz) and a Bruker 14A04336 (151 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform  $\delta$  7.26), carbon (chloroform  $\delta$  77.0) or tetramethylsilane (TMS  $\delta$  0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz).

High resolution mass spectra (HRMS) were recorded on a Bruker 19A01643 Q-TOF LC/MS with Electron Spray Ionization (ESI) resource. The single crystal diffraction data was performed on an Agilent SuperNova E 15A11181.

For thin layer chromatography (TLC), Qingdao Haiyang Chemical was used. Visualization on TLC was achieved by use UV light (254 nm). Further visualization was achieved by staining with 2,4-dinitrophenylhydrazine, or phosphomolybdic acid followed by heating using a heat gun. Flash chromatography separations were performed on Qingdao Haiyang Chemical 300-400 mesh silica gel.

All commercially available reagents were used as received for the reactions without any purification. The starting material, allylic alcohols, were known and were simply prepared by the aldol reaction by aldehydes and ketones,<sup>1</sup> following by the addition of  $\text{NaBH}_4$  or  $\text{LiCH}_3$ . The  $\text{NCSl}^2$  and  $\text{NCSc}^3$  were synthesized according to the known procedures respectively.

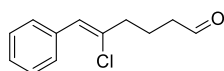
## II. Synthesis and characterization of 2a



### 5-Chloro-6-phenylhex-5-enal (**2a**)

To a 15 mL tube equipped with magnetic stir bar was added allylic alcohol **1a** (57.4 mg, 0.33 mmol) and 3 mL of DCE. Then the tube was equipped with a rubber septum, and placed in a pre-cooled low-temperature reactor. After stirred for 5 min at the specified temperature, NCSI (99.5 mg, 0.30 mmol) was further added into the tube. The reaction mixture was vigorously stirred for additional 5 min. After taken to room temperature, the crude reaction mixture was filtered through celite and the filtrate was concentrated to dryness and then directly analyzed by <sup>1</sup>H NMR to determine the Z/E ratio. The residue was then purified by column chromatography (hexane:ethyl acetate = 40:1) to yield the product **3a** in 73% yield as an oil.

#### **3a-maj:** (Z)-5-Chloro-6-phenylhex-5-enal

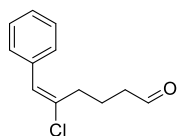


<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.80 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 6.48 (s, 1H), 2.56-2.50 (m, 4H), 2.04-1.98 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 201.71, 134.83, 133.42, 128.99, 128.18, 127.67, 125.48, 42.35, 40.15, 19.99.

HRMS (ESI): C<sub>12</sub>H<sub>14</sub>ClO [M+H]<sup>+</sup> calculated:209.0728, found:209.0725.

#### **3a-min:** (E)-5-Chloro-6-phenylhex-5-enal

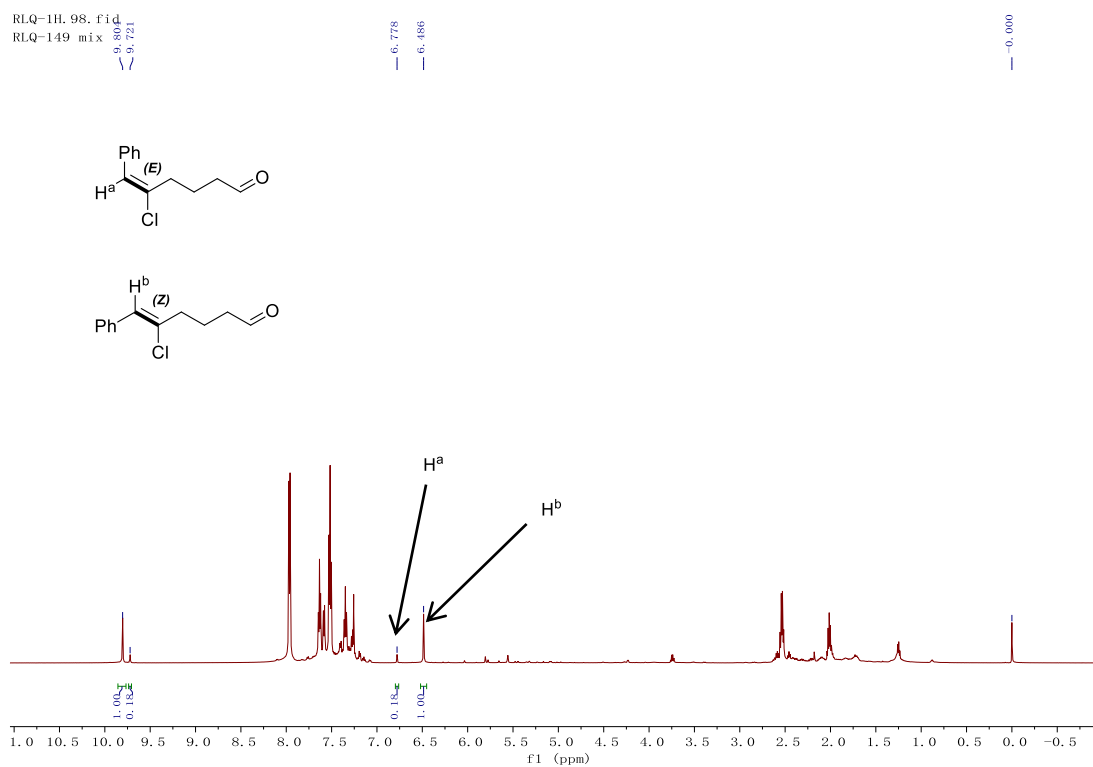


<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 9.73 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 5.4 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.45 (td, *J* = 7.2 Hz, 1.2 Hz, 2H), 2.02-1.96 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 201.47, 136.73, 135.50, 129.20, 128.54, 128.29, 127.38, 42.61, 33.46, 20.06.

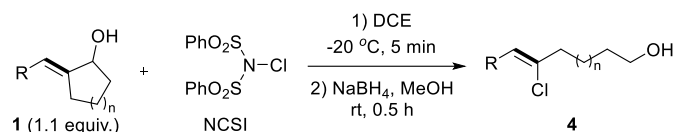
HRMS (ESI): C<sub>14</sub>H<sub>12</sub>ClO [M+H]<sup>+</sup> calculated:231.0571, found:231.0563.

The *Z/E* configuration of **3a** (5.5:1) was determined by <sup>1</sup>H NMR measurement as shown below. The *Z/E* configuration of **3a** (3.1:1) calculated by isolated yield is less probably because of the consumption of the major product in column chromatography and a little hidden solvent in the minor product.





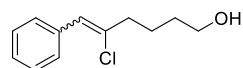
### III. General Procedure for the synthesis of alcohol



To a 15 mL tube equipped with magnetic stir bar was added allylic alcohol **1** (0.33 mmol) and 3 mL of DCE. Then the tube was equipped with a rubber septum, and placed in a pre-cooled low-temperature reactor. After stirred for 5 min at the specified temperature, NCSI (0.30 mmol) was further added into the tube. The reaction mixture was vigorously stirred for additional 5 min. After taken to room temperature, 1 mL of methanol was then added followed by NaBH<sub>4</sub> (0.6 mmol). The resulting mixture was allowed to stir at ambient temperature for 0.5 h, quenched by saturate brine, extracted with ethyl acetate, concentrated and purified by silica gel chromatography (hexanes:ethyl acetate) to afford the pure products **4** with two geometrical isomers.

### IV. Characterization of compound 4

#### 5-Chloro-6-phenylhex-5-en-1-ol (**4a**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4a-min** (8.1 mg and 13%) and **4a-maj** (44.4 mg and 70%) were isolated separately as a colorless oil.

#### **4a-min**: (*E*)-5-Chloro-6-phenylhex-5-en-1-ol

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.74 (s, 1H), 3.62 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.78-1.71 (m, 2H), 1.61-1.55 (m, 3H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.87, 135.81, 128.46, 128.41, 128.32, 127.20, 62.53, 34.01, 31.75, 23.89.

HRMS (ESI): C<sub>12</sub>H<sub>15</sub>ClNaO [M+Na]<sup>+</sup> calculated: 233.0704, found: 233.0702.

#### **4a-maj**: (*Z*)-5-Chloro-6-phenylhex-5-en-1-ol

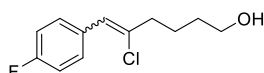
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.25

(t,  $J = 7.8$  Hz, 1H), 6.48 (s, 1H), 3.68 (t,  $J = 7.2$  Hz, 2H), 2.52 (t,  $J = 7.2$  Hz, 2H), 1.77-1.73 (m, 2H), 1.65-1.61 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  135.12, 134.55, 128.98, 128.13, 127.47, 124.65, 62.62, 40.87, 31.62, 23.87.

**HRMS (ESI):**  $\text{C}_{12}\text{H}_{15}\text{ClNaO}$   $[\text{M}+\text{Na}]^+$  calculated: 233.0704, found: 233.0703.

#### 5-Chloro-6-(4-fluorophenyl)hex-5-en-1-ol (4b)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4b-min** (8 mg and 12%) and **4b-maj** (50 mg and 72%) were isolated separately as a colorless oil.

#### **4b-maj: (Z)-5-Chloro-6-(4-fluorophenyl)hex-5-en-1-ol**

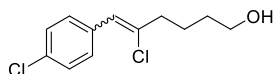
$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.56 (dd,  $J = 5.4$  Hz, 8.4 Hz, 2H), 7.03 (t,  $J = 8.4$  Hz, 2H), 6.44 (s, 1H), 3.69 (t,  $J = 7.2$  Hz, 2H), 2.51 (t,  $J = 7.2$  Hz, 2H), 1.77-1.72 (m, 2H), 1.66-1.60 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  161.87 (d,  $J = 247.6$  Hz), 131.16 (d,  $J = 3.8$  Hz), 130.67 (d,  $J = 8.0$  Hz), 123.52, 115.05 (d,  $J = 21.5$  Hz), 62.60, 40.78, 31.61, 23.85.

$^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -113.85.

**HRMS (ESI):**  $\text{C}_{12}\text{H}_{14}\text{ClFNaO}$   $[\text{M}+\text{Na}]^+$  calculated: 251.0609, found: 251.0606.

#### 5-Chloro-6-(4-chlorophenyl)hex-5-en-1-ol (4c)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4c-min** (9 mg and 13%) and **4c-maj** (40 mg and 54%) were isolated separately as a colorless oil.

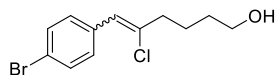
#### **4c-maj: (Z)-5-Chloro-6-(4-chlorophenyl)hex-5-en-1-ol**

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.52 (d,  $J = 8.4$  Hz, 2H), 7.3 (d,  $J = 8.4$  Hz, 2H), 6.42 (s, 1H), 3.69 (t,  $J = 7.2$  Hz, 2H), 2.51 (t,  $J = 7.2$  Hz, 2H), 1.78-1.72 (m, 2H), 1.66-1.60 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  135.37, 133.53, 133.12, 130.24, 128.32, 123.50, 62.60, 40.86, 31.61, 23.85.

**HRMS (ESI):** C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>NaO [M+Na]<sup>+</sup> calculated: 267.0314, found: 267.0309.

#### 6-(4-bromophenyl)-5-Chlorohex-5-en-1-ol (**4d**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4d-min** (12 mg and 13%) and **4d-maj** (45 mg and 52%) were isolated separately as a colorless oil.

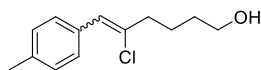
#### **4d-maj: (Z)-6-(4-bromophenyl)-5-Chlorohex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.45 (s, 4H), 6.41 (s, 1H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.78-1.71 (m, 2H), 1.65-1.60 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 135.51, 133.99, 131.28, 130.54, 123.55, 121.32, 62.58, 40.89, 31.61, 23.83.

**HRMS (ESI):** C<sub>12</sub>H<sub>14</sub>BrClNaO [M+Na]<sup>+</sup> calculated: 310.9809, found: 310.9803.

#### 5-Chloro-6-(*p*-tolyl)hex-5-en-1-ol (**4e**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4e-min** (4 mg and 6%) and **4e-maj** (39 mg and 57%) were isolated separately as a colorless oil.

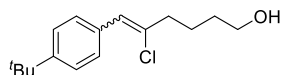
#### **4e-maj: (Z)-5-Chloro-6-(*p*-tolyl)hex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.44 (s, 1H), 3.68 (t, *J* = 6.6 Hz, 2H), 2.50 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 1.77-1.70 (m, 2H), 1.65-1.60 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.32, 133.71, 132.27, 128.83, 128.88, 124.52, 62.65, 40.85, 31.64, 23.88, 21.22.

**HRMS (ESI):** C<sub>13</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 247.0860, found: 247.0860.

#### 6-(4-(*tert*-Butyl)phenyl)-5-chlorohex-5-en-1-ol (**4f**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed

using hexanes and ethyl acetate (20:1 to 4:1), **4f-min** (5 mg and 7%) and **4f-maj** (54 mg and 67%) were isolated separately as a colorless oil.

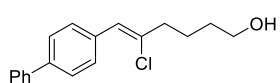
**4f-maj: (Z)-6-(4-(tert-Butyl)phenyl)-5-chlorohex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.37 (s, 1H), 3.60 (dd, *J* = 7.2 Hz, 1.2 Hz, 2H), 2.43 (t, *J* = 7.8 Hz, 2H), 1.69-1.64 (m, 2H), 1.58-1.52 (m, 2H), 1.24 (s, 9H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 150.55, 133.76, 132.23, 128.72, 125.07, 124.43, 62.65, 40.91, 34.61, 31.62, 31.26, 23.88.

HRMS (ESI): C<sub>16</sub>H<sub>23</sub>ClNaO [M+Na]<sup>+</sup> calculated: 289.1330, found: 289.1239.

**6-([1,1'-Biphenyl]-4-yl)-5-chlorohex-5-en-1-ol (4g)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4g-min** (4 mg and 4%) and **4g-maj** (56 mg and 65%) were isolated separately as a white solid.

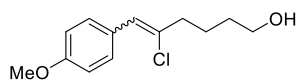
**4g-maj: (Z)-6-([1,1'-Biphenyl]-4-yl)-5-chlorohex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.60 (dd, *J* = 7.8 Hz, 13.1 Hz, 4H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.51 (s, 1H), 3.70 (t, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.80-1.74 (m, 2H), 1.67-1.60 (m, 2H), 1.38 (s, 1H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 140.67, 140.20, 134.71, 134.11, 129.42, 128.78, 127.36, 127.00, 126.81, 124.27, 62.66, 40.99, 31.65, 23.91.

HRMS (ESI): C<sub>18</sub>H<sub>19</sub>ClNaO [M+Na]<sup>+</sup> calculated: 309.1017, found: 309.1016.

**5-Chloro-6-(4-methoxyphenyl)hex-5-en-1-ol (4h)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (15:1 to 3:1), **4h-min** (trace) and **4h-maj** (32 mg and 44%) were isolated as a colorless oil.

**4h-maj: (Z)-5-Chloro-6-(4-methoxyphenyl)hex-5-en-1-ol**

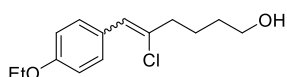
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.40

(s, 1H), 3.81 (s, 3H), 3.68 (t,  $J = 6.6$  Hz, 2H), 2.50 (t,  $J = 7.2$  Hz, 2H), 1.76-1.70 (m, 2H), 1.65-1.59 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  158.86, 132.64, 130.28, 127.75, 124.04, 113.58, 62.65, 55.25, 40.84, 31.64, 23.90.

**HRMS (ESI):**  $\text{C}_{13}\text{H}_{17}\text{ClNaO}_2$   $[\text{M}+\text{Na}]^+$  calculated: 263.0809, found: 263.0803.

#### 5-Chloro-6-(4-ethoxyphenyl)hex-5-en-1-ol (**4i**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (15:1 to 3:1), **4i-min** (trace) and **4i-maj** (32 mg and 42%) were isolated as a colorless oil.

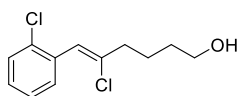
#### **4i-maj: (Z)-5-Chloro-6-(4-ethoxyphenyl)hex-5-en-1-ol**

$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.54 (d,  $J = 8.4$  Hz, 2H), 6.86 (d,  $J = 8.4$  Hz, 2H), 6.40 (s, 1H), 4.03 (q,  $J = 7.2$  Hz, 2H), 3.67 (t,  $J = 6.6$  Hz, 2H), 2.50 (t,  $J = 7.2$  Hz, 2H), 1.76-1.67 (m, 2H), 1.65-1.59 (m, 2H), 1.40 (t,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  158.24, 132.48, 130.27, 127.58, 124.09, 114.13, 63.44, 62.65, 40.86, 31.64, 23.90, 14.81.

**HRMS (ESI):**  $\text{C}_{14}\text{H}_{19}\text{ClNaO}_2$   $[\text{M}+\text{Na}]^+$  calculated: 277.0966, found: 277.0966.

#### 5-Chloro-6-(2-chlorophenyl)hex-5-en-1-ol (**4j**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4j-min** (9 mg and 12%) and **4j-maj** (18 mg and 24%) were isolated separately as a colorless oil.

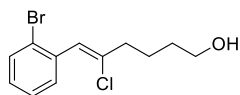
#### **4j-maj: (Z)-5-Chloro-6-(2-chlorophenyl)hex-5-en-1-ol**

$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.72 (d,  $J = 7.8$  Hz, 1H), 7.37 (d,  $J = 7.8$  Hz, 1H), 7.25 (t,  $J = 7.8$  Hz, 1H), 7.21 (t,  $J = 7.8$  Hz, 1H), 6.64 (s, 1H), 3.71 (t,  $J = 6.6$  Hz, 2H), 2.57 (t,  $J = 7.2$  Hz, 2H), 1.81-1.75 (m, 2H), 1.70-1.64 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  137.06, 133.61, 133.48, 130.81, 129.18, 128.65, 126.22, 122.00, 62.61, 40.35, 31.54, 23.68.

**HRMS (ESI):** C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>NaO [M+Na]<sup>+</sup> calculated: 267.0314, found: 267.0311.

#### 6-(2-bromophenyl)-5-Chlorohex-5-en-1-ol (**4k**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4k-min** (8 mg and 7%) and **4k-maj** (22 mg and 26%) were isolated separately as a colorless oil.

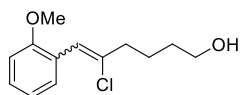
#### **4k-maj: (Z)-6-(2-Bromophenyl)-5-chlorohex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.56 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.30 (td, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.13 (td, *J* = 7.8 Hz, 1.8 Hz, 1H), 6.59 (s, 1H), 3.72 (t, *J* = 6.6 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.81-1.75 (m, 2H), 1.71-1.65 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 136.91, 135.49, 132.37, 131.03, 128.88, 126.85, 124.43, 123.85, 62.62, 40.18, 31.53, 23.63.

**HRMS (ESI):** C<sub>12</sub>H<sub>14</sub>BrClNaO [M+Na]<sup>+</sup> calculated: 310.9809, found: 310.9805.

#### 5-Chloro-6-(2-methoxyphenyl)hex-5-en-1-ol (**4l**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (15:1 to 3:1), **4l-min** (trace) and **4l-maj** (23 mg and 32%) were isolated as a colorless oil.

#### **4l-maj: (Z)-5-Chloro-6-(2-methoxyphenyl)hex-5-en-1-ol**

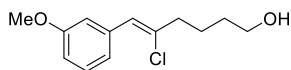
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 1.8 Hz, 7.8 Hz, 1H), 7.25 (td, *J* = 1.8 Hz, 5.4 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 3.82 (s, 3H), 3.69 (t, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.79-1.73 (m, 2H), 1.68-1.62 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 156.84, 134.89, 129.96, 128.74, 124.12, 120.07, 119.84, 110.36, 62.68, 55.50, 40.73, 31.66, 23.85.

**HRMS (ESI):** C<sub>13</sub>H<sub>17</sub>ClNaO<sub>2</sub> [M+Na]<sup>+</sup> calculated: 263.0809, found: 263.0804.

#### 5-Chloro-6-(3-methoxyphenyl)hex-5-en-1-ol (**4m**)

The title compound was prepared according to the general procedure as described, Silica gel



flash column chromatography was performed using hexanes and ethyl acetate (15:1 to 3:1), **4m-min** (7 mg and 10%) and **4m-maj** (36 mg and 49%) were isolated separately as a colorless oil.

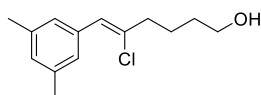
**4m-maj: (Z)-5-Chloro-6-(3-methoxyphenyl)hex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.25 (t, *J* = 7.8 Hz, 1H), 7.20 (s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.81 (dd, *J* = 8.4 Hz, 3.0 Hz, 1H), 6.46 (t, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 3.68 (t, *J* = 6.6 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.77-1.71 (m, 2H), 1.65-1.60 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 159.36, 136.39, 134.79, 129.07, 124.52, 121.69, 114.32, 113.30, 62.61, 55.24, 40.90, 31.62, 23.87.

HRMS (ESI): C<sub>13</sub>H<sub>18</sub>ClO<sub>2</sub> [M+Na]<sup>+</sup> calculated: 241.0990, found: 241.1001.

**5-Chloro-6-(3,5-dimethylphenyl)hex-5-en-1-ol (4n)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4n-min** (7 mg and 10%) and **4n-maj** (46 mg and 64%) were isolated separately as a colorless oil.

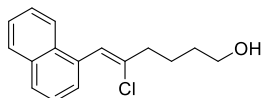
**4n-maj: (Z)-5-Chloro-6-(3,5-dimethylphenyl)hex-5-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.20 (s, 2H), 6.90 (s, 1H), 6.42 (s, 1H), 3.69 (t, *J* = 6.6 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 6H), 1.77-1.70 (m, 2H), 1.65-1.59 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.57, 134.98, 134.06, 129.19, 126.77, 124.84, 62.66, 40.86, 31.62, 23.85, 21.31.

HRMS (ESI): C<sub>14</sub>H<sub>19</sub>ClNaO [M+Na]<sup>+</sup> calculated: 261.1017, found: 261.1018.

**5-Chloro-6-(naphthalen-1-yl)hex-5-en-1-ol (4o)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4o-min** (trace) and **4o-maj** (50 mg and 64%) were isolated as a colorless oil.

**4o-maj: (Z)-5-Chloro-6-(naphthalen-1-yl)hex-5-en-1-ol**

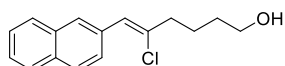
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.2 Hz, 1H), 7.85 (dd, *J* = 7.2 Hz, 3.0 Hz,

1H), 7.79 (d,  $J = 7.8$  Hz, 1H), 7.62 (d,  $J = 7.2$  Hz, 1H), 7.51-7.46 (m, 3H), 6.96 (s, 1H), 3.74 (t,  $J = 6.6$  Hz, 2H), 2.65 (t,  $J = 7.8$  Hz, 2H), 1.87-1.81 (m, 2H), 1.75-1.69 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  137.38, 133.49, 132.56, 131.49, 128.54, 127.89, 127.21, 126.05, 125.79, 125.24, 124.41, 122.99, 62.68, 40.20, 31.75, 23.94.

**HRMS (ESI):**  $\text{C}_{16}\text{H}_{17}\text{ClNaO}$  [ $\text{M}+\text{Na}$ ] $^{+}$  calculated: 283.0860, found: 283.0860.

#### 5-Chloro-6-(naphthalen-2-yl)hex-5-en-1-ol (4p)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4p-min** (6 mg and 7%) and **4p-maj** (46 mg and 59%) were isolated separately as a white solid.

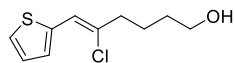
#### **4p-maj: 5-Chloro-6-(naphthalen-2-yl)hex-5-en-1-ol**

$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  8.05 (s, 1H), 7.83-7.78 (m, 3H), 7.70 (dd Hz,  $J = 1.8$ , 8.4 Hz, 1H), 7.47-7.43 (m, 2H), 6.63 (s, 1H), 3.70 (t,  $J = 6.6$  Hz, 2H), 2.57 (t,  $J = 7.8$  Hz, 2H), 1.81-1.75 (m, 2H), 1.68-1.61 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  134.96, 133.22, 132.64, 132.62, 128.21, 128.15, 127.58, 127.56, 126.89, 126.12, 124.72, 62.66, 40.98, 31.67, 23.93.

**HRMS (ESI):**  $\text{C}_{16}\text{H}_{17}\text{ClNaO}$  [ $\text{M}+\text{Na}$ ] $^{+}$  calculated: 283.0860, found: 283.0860.

#### 5-Chloro-6-(thiophen-2-yl)hex-5-en-1-ol (4q)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4q-min** (2 mg and 3%) and **4q-maj** (21 mg and 33%) were isolated separately as a yellow oil.

#### **4q-maj: (Z)-5-Chloro-6-(thiophen-2-yl)hex-5-en-1-ol**

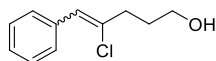
$^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.29 (d,  $J = 5.4$  Hz, 1H), 7.16 (d,  $J = 3.6$  Hz, 1H), 7.01 (dd,  $J = 3.6$  Hz, 5.4 Hz, 1H), 6.71 (s, 1H), 3.67 (t,  $J = 6.6$  Hz, 2H), 2.53 (t,  $J = 7.8$  Hz, 2H), 1.77-1.71 (m, 2H), 1.64-1.58 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform- $d$ )  $\delta$  138.23, 132.52, 128.40, 126.19, 125.94, 119.09, 62.61, 40.13, 31.61, 23.99.



**HRMS (ESI):** C<sub>10</sub>H<sub>13</sub>ClNaOS [M+Na]<sup>+</sup> calculated: 239.0268, found: 239.0264.

#### 4-chloro-5-phenylpent-4-en-1-ol (4r)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4r-min** (24 mg and 40%) and **4r-maj** (31 mg and 53%) were isolated separately as a colorless oil.

#### **4r-maj: (Z)-4-chloro-5-phenylpent-4-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 6.6 Hz, 1H), 6.51 (s, 1H), 3.72 (t, *J* = 6.6 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.95-1.90 (m, 2H), 1.52 (s, 1H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 135.05, 134.13, 128.98, 128.15, 127.53, 124.88, 61.58, 37.52, 30.57.

**HRMS (ESI):** C<sub>11</sub>H<sub>14</sub>ClO [M+H]<sup>+</sup> calculated: 197.0728, found: 197.0730.

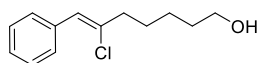
#### **4r-min: (E)-4-chloro-5-phenylpent-4-en-1-ol**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.75 (s, 1H), 3.65 (t, *J* = 6.6 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.94-1.89 (m, 2H), 1.38 (s, 1H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.40, 135.67, 128.69, 128.54, 128.30, 127.29, 61.72, 30.89, 30.61.

**HRMS (ESI):** C<sub>11</sub>H<sub>14</sub>ClO [M+H]<sup>+</sup> calculated: 197.0728, found: 197.0737.

#### 6-Chloro-7-phenylhept-6-en-1-ol (4s)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (20:1 to 4:1), **4s-min** (3 mg and 4%) and **4s-maj** (31 mg and 46%) were isolated separately as a colorless oil.

#### **4s-maj: (Z)-6-Chloro-7-phenylhept-6-en-1-ol**

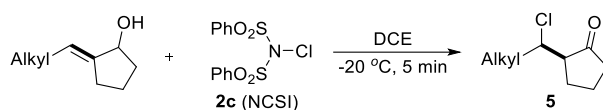
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.47 (t, 1H), 3.66 (t, *J* = 6.6 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.73-1.67 (m,

2H), 1.65-1.59 (m, 2H), 1.46-1.40 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 135.17, 134.76, 128.98, 128.12, 127.42, 124.47, 62.81, 41.10, 32.50, 27.38, 24.77.

**HRMS (ESI):** C<sub>13</sub>H<sub>17</sub>ClO [M+Na]<sup>+</sup> calculated: 247.0860, found: 247.0859.

## V. Synthesis and characterization of **5**



To a 15 mL tube equipped with magnetic stir bar was added allylic alcohol (0.33 mmol) and 3 mL of DCE. Then the tube was equipped with a rubber septum, and placed in a pre-cooled low-temperature reactor. After stirred for 5 min at the specified temperature, NCSI (99.5 mg, 0.30 mmol) was further added into the tube. The reaction mixture was vigorously stirred for additional 5 min, and was then quenched by a small amount of silica gel. After taken to room temperature, the crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to yield the product **5** in pure form as oil.

### 2-(1-Chlorobutyl)cyclopentan-1-one (**5a**)

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 4.46-4.42 (m, 1H), 2.40-2.30 (m, 2H), 2.20-2.07 (m, 4H), 1.80-1.73 (m, 2H), 1.71-1.64 (m, 1H), 1.57-1.52 (m, 1H), 1.44-1.39 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 217.35, 61.00, 54.04, 38.99, 38.68, 23.46, 20.43, 19.94, 13.40.

HRMS (ESI): C<sub>9</sub>H<sub>16</sub>ClO [M+H]<sup>+</sup> calculated: 175.0884, found: 175.0884.

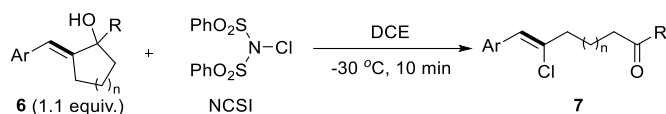
### 2-(Chloro(cyclohexyl)methyl)cyclopentan-1-one (**5b**)

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 4.21 (dd, *J* = 3.0 Hz, 9.0 Hz, 1H), 2.54-2.49 (m, 1H), 2.34-2.29 (m, 1H), 2.13-2.10 (m, 5H), 1.80-1.70 (m, 5H), 1.58-1.55 (m, 1H), 1.27-1.20 (m, 2H), 1.16-1.12 (m, 1H), 1.05-0.98 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 218.19, 67.12, 51.70, 42.87, 38.64, 30.38, 30.17, 26.05, 25.77, 23.68, 20.52.

HRMS (ESI): C<sub>12</sub>H<sub>20</sub>ClO [M+H]<sup>+</sup> calculated: 215.1197, found: 215.1196.

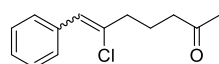
## VI. General Procedure for the synthesis of ketones



To a 15 mL tube equipped with magnetic stir bar was added allylic alcohol **4** (0.33 mmol) and 3 mL of DCE. Then the tube was equipped with a rubber septum, and placed in a pre-cooled low-temperature reactor. After stirred for 10 min at the specified temperature, NCSi (0.30 mmol) was further added into the tube. The reaction mixture was vigorously stirred for additional 5 min, and was then quenched by a small amount of silica gel. After taken to room temperature, the crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography to yield the product **7** in pure form.

## VII. Characterization of Compounds **7**

### 6-Chloro-7-phenylhept-6-en-2-one (**7a**)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7a-maj** (25 mg and 37%) and **7a-min** (18 mg and 27%) were isolated separately as a colorless oil.

#### **7a-maj**: (*E*)-6-Chloro-7-phenylhept-6-en-2-one

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.76 (s, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.07 (s, 3H), 1.96-1.90 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 207.99, 137.15, 135.57, 128.94, 128.52, 128.32, 127.31, 42.21, 33.50, 29.81, 21.58.

HRMS (ESI): C<sub>13</sub>H<sub>15</sub>ClNaO [M+Na]<sup>+</sup> calculated: 245.0704, found: 245.0704.

#### **7a-min**: (*Z*)-6-Chloro-7-phenylhept-6-en-2-one

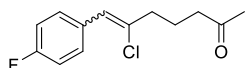
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.47 (s, 1H), 2.51 (dd, *J* = 7.8 Hz, 15 Hz, 4H), 2.15 (s, 3H), 1.98-1.92 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 208.22, 134.94, 133.85, 128.98, 128.17, 127.59, 125.16,

41.91, 40.15, 29.98, 21.51.

**HRMS (ESI):** C<sub>13</sub>H<sub>15</sub>ClNaO [M+Na]<sup>+</sup> calculated: 245.0704, found: 245.0703.

### 6-Chloro-7-(4-fluorophenyl)hept-6-en-2-one (7b)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7b-min** (27.7 mg and 13%) and **7b-maj**, (38.8 mg and 70%) were isolated separately as a colorless oil.

### **7b-maj: (E)-6-Chloro-7-(4-chlorophenyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.18 (dd, *J* = 5.4 Hz, 8.4 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.70 (s, 1H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.95-1.89 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*) δ 207.81, 161.91 (d, *J* = 247.8 Hz), 137.20, 131.57 (d, *J* = 3.4 Hz), 130.00 (d, *J* = 8.0 Hz), 127.79, 115.49 (d, *J* = 21.6 Hz), 42.17, 33.45, 29.80, 21.53.

**<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*) δ -114.30.

**HRMS (ESI):** C<sub>13</sub>H<sub>15</sub>Cl<sub>2</sub>O [M+H]<sup>+</sup> calculated: 257.0494, found: 257.0497.

### **7b-min: (Z)-6-Chloro-7-(4-chlorophenyl)hept-6-en-2-one**

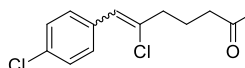
**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 8.4 Hz, 5.4 Hz, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 2.51-2.47 (m, 4H), 2.15 (s, 3H), 1.97-1.91 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*) δ 208.08, 161.93 (d, *J* = 247.8 Hz), 133.74, 131.01 (d, *J* = 3.4 Hz), 130.69 (d, *J* = 7.9 Hz), 124.01, 115.08 (d, *J* = 21.5 Hz), 41.91, 40.08, 29.92, 21.53.

**<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*) δ -113.63.

**HRMS (ESI):** C<sub>13</sub>H<sub>15</sub>Cl<sub>2</sub>O [M+H]<sup>+</sup> calculated: 257.0494, found: 257.0493.

### 6-Chloro-7-(4-chlorophenyl)hept-6-en-2-one (7c)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7c-min** (32.3 mg and 42%) and **7c-maj**, (38.7 mg and 50%) were isolated separately as a colorless oil.

### **7c-maj: (Z)-6-Chloro-7-(4-fluorophenyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.42 (s, 1H), 2.50 (dd, *J* = 6.6 Hz, 13.8 Hz, 4H), 2.15 (s, 3H), 1.97-1.91 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*) δ 208.04, 134.69, 133.36, 133.26, 130.24, 128.35, 123.99, 41.90, 40.15, 29.94, 21.52.

**HRMS (ESI):** C<sub>13</sub>H<sub>18</sub>ClFNO [M+NH<sub>4</sub>]<sup>+</sup> calculated: 258.1055, found: 258.1056.

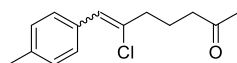
**7c-min: (E)-6-Chloro-7-(4-fluorophenyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 1.95-1.90 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*) δ 207.80, 137.84, 133.95, 133.21, 129.63, 128.73, 127.70, 42.17, 33.56, 28.10, 21.51.

**HRMS (ESI):** C<sub>12</sub>H<sub>14</sub>ClFNaO [M+Na]<sup>+</sup> calculated: 263.0609, found: 263.0610.

**6-Chloro-7-(p-tolyl)hept-6-en-2-one (7d)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7d-min** (13.4 mg and 19%) and **7d-maj** (33.5 mg and 47%) were isolated separately as a colorless oil.

**7d-maj: (Z)-6-Chloro-7-(p-tolyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.43 (s, 1H), 2.51-2.47 (m, 4H), 2.34 (s, 3H), 2.15 (s, 3H), 1.97-1.91 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*) δ 208.26, 137.47, 132.99, 132.08, 128.90, 128.87, 125.05, 41.91, 40.13, 29.96, 21.53, 21.24.

**HRMS (ESI):** C<sub>14</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 259.0860, found: 259.0859.

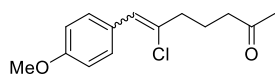
**7d-min: (E)-6-Chloro-7-(p-tolyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.72 (s, 1H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.08 (s, 3H), 1.96-1.90 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*) δ 208.07, 137.13, 136.44, 132.68, 129.20, 128.87, 128.21, 42.25, 33.52, 29.82, 21.59, 21.15.

**HRMS (ESI):** C<sub>14</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 259.0860, found: 259.0859.

### 6-Chloro-7-(4-methoxyphenyl)hept-6-en-2-one (7e)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1 to 10:1), **7e-min** (trace) and **7e-maj**, (61.4 mg and 81%) were isolated separately as an orange oil.

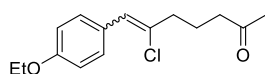
#### **7e-maj: (Z)-6-Chloro-7-(4-methoxyphenyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  7.48 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.32 (s, 1H), 3.74 (s, 3H), 2.41 (t, *J* = 7.2 Hz, 4H), 2.07 (s, 3H), 1.89-1.83 (m, 2H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*)  $\delta$  208.26, 158.97, 131.88, 130.31, 127.56, 124.57, 113.61, 55.25, 41.93, 40.13, 29.95, 21.58.

**HRMS (ESI):** C<sub>14</sub>H<sub>21</sub>ClNO<sub>2</sub> [M+NH<sub>4</sub>]<sup>+</sup> calculated: 270.1255, found: 270.1256.

### 6-Chloro-7-(4-ethoxyphenyl)hept-6-en-2-one (7f)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1 to 10:1), **7f-min** (trace) and **7f-maj** (61.6 mg and 77%) were isolated separately as a colorless oil.

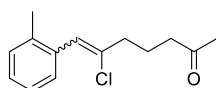
#### **7f-maj: (Z)-6-Chloro-7-(4-ethoxyphenyl)hept-6-en-2-one**

**<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  7.47 (d, *J* = 9 Hz, 2H), 6.79 (d, *J* = 6.6 Hz, 2H), 6.31 (s, 1H), 3.96 (q, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 4H), 2.07 (s, 3H), 1.89-1.83 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR** (151 MHz, Chloroform-*d*)  $\delta$  208.33, 158.33, 131.71, 130.30, 127.38, 124.62, 114.15, 63.44, 41.93, 40.14, 29.97, 21.56, 14.81.

**HRMS (ESI):** C<sub>15</sub>H<sub>19</sub>ClNaO<sub>2</sub> [M+Na]<sup>+</sup> calculated: 289.0966, found: 289.0961.

### 6-Chloro-7-(o-tolyl)hept-6-en-2-one (7g)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7g-min** (24.4 mg and 34%) and **7g-maj**, (36.6 mg and

52%) were isolated separately as a colorless oil.

**7g-maj: (E)-6-Chloro-7-(o-tolyl)hept-6-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.18 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.72 (s, 1H), 2.39 (dt, *J* = 19.2 Hz, 7.2 Hz, 4H), 2.25 (s, 3H), 2.06 (s, 3H), 1.91-1.85 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 207.98, 136.82, 136.31, 134.83, 130.00, 128.73, 128.15, 127.71, 125.81, 42.24, 33.26, 29.72, 21.55, 19.93.

HRMS (ESI): C<sub>14</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 259.0860, found: 259.0858.

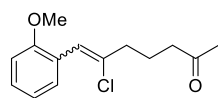
**7g-min: (Z)-6-Chloro-7-(o-tolyl)hept-6-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.48-7.46 (m, 1H), 7.18 (d, *J* = 3.6 Hz, 3H), 6.51 (s, 1H), 2.53 (q, *J* = 7.2 Hz, 4H), 2.26 (s, 3H), 2.17 (s, 3H), 1.99-1.93 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 208.21, 136.17, 135.21, 134.47, 129.79, 129.21, 127.59, 125.43, 124.40, 41.94, 39.38, 29.98, 21.51, 19.92.

HRMS (ESI): C<sub>14</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 259.0860, found: 259.0857.

**6-Chloro-7-(2-methoxyphenyl)hept-6-en-2-one (7h)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7h-min** (8.1 mg and 13%) and **7h-maj** (66.7 mg and 88%) were isolated separately as a colorless oil.

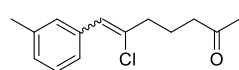
**7h-maj: (Z)-6-Chloro-7-(2-methoxyphenyl)hept-6-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 1.8 Hz, 7.8 Hz, 1H), 7.17 (dt, *J* = 1.8 Hz, 7.8 Hz, 1H), 6.88 (dt, *J* = 1.2 Hz, 7.2 Hz, 1H), 6.79 (dd, *J* = 0.9 Hz, 8.4 Hz, 1H), 6.57 (s, 1H), 3.74 (s, 3H), 2.47-2.41 (m, 4H), 2.08 (s, 3H), 1.90-1.85 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 207.33, 155.83, 133.11, 128.88, 127.83, 122.94, 119.46, 119.05, 109.32, 54.42, 40.80, 38.96, 28.97, 20.43.

HRMS (ESI): C<sub>14</sub>H<sub>17</sub>ClNaO<sub>2</sub> [M+Na]<sup>+</sup> calculated: 275.0809, found: 275.0809.

**6-Chloro-7-(m-tolyl)hept-6-en-2-one (7i)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using



hexanes and ethyl acetate (40:1 to 15:1), **7i-min** (23.1 mg and 33%) and **7i-maj**, (32.3 mg and 46%) were isolated separately as a yellow oil.

**7i-maj: (Z)-6-Chloro-7-(m-tolyl)hept-6-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.42-7.38 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 2.52-2.48 (m, 4H), 2.36 (s, 3H), 2.16 (s, 3H), 1.97-1.92 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 208.27, 137.73, 134.86, 133.58, 129.67, 128.37, 128.06, 126.05, 125.27, 41.90, 40.14, 29.98, 21.50, 21.43.

HRMS (ESI): C<sub>14</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 259.0860, found: 259.0858.

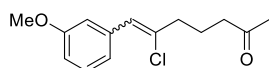
**7i-min: (E)-6-Chloro-7-(m-tolyl)hept-6-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 11.4 Hz, 2H), 6.72 (s, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.08 (s, 3H), 1.96-1.90 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 208.02, 138.17, 136.92, 135.50, 129.04, 128.40, 128.08, 125.34, 42.20, 33.53, 29.82, 21.56, 21.38.

HRMS (ESI): C<sub>14</sub>H<sub>17</sub>ClNaO [M+Na]<sup>+</sup> calculated: 259.0860, found: 259.0859.

**6-Chloro-7-(3-methoxyphenyl)hept-6-en-2-one (7j)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1 to 10:1), **7j-min** (19.5 mg and 26%) and **7j-maj**, (38.9 mg and 51%) were isolated separately as a colorless oil.

**7j-maj: (E)-6-Chloro-7-(3-methoxyphenyl)hept-6-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 8.4 Hz, 1H), 6.80 (td, *J* = 7.8 Hz, 2.4 Hz, 2H), 6.73 (s, 1H), 3.81 (s, 3H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 1.96-1.90 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 207.92, 159.66, 137.40, 136.88, 129.51, 128.81, 120.75, 114.03, 112.82, 55.25, 42.22, 33.58, 29.78, 21.58.

HRMS (ESI): C<sub>14</sub>H<sub>18</sub>ClO<sub>2</sub> [M+H]<sup>+</sup> calculated: 253.0990, found: 253.0992.

**7j-min: (Z)-6-Chloro-7-(3-methoxyphenyl)hept-6-en-2-one**

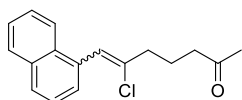
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.8 Hz, 1H), 7.20 (s, 1H), 7.13 (d, *J* = 7.8

Hz, 1H), 6.83 (dd,  $J = 7.8$  Hz, 2.4 Hz, 1H), 6.45 (s, 1H), 3.82 (s, 3H), 2.50 (q,  $J = 7.2$  Hz, 2H), 2.15 (s, 3H), 1.98-1.92 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  208.15, 159.39, 136.21, 134.07, 129.10, 125.05, 121.68, 114.35, 113.40, 55.24, 41.90, 40.18, 29.95, 21.52.

**HRMS (ESI):**  $\text{C}_{14}\text{H}_{17}\text{ClNaO}_2$   $[\text{M}+\text{Na}]^+$  calculated: 275.0809, found: 275.0808.

### 6-Chloro-7-(naphthalen-1-yl)hept-6-en-2-one (7k)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7k-min** (15.6 mg and 19%) and **7k-maj** (49.9 mg and 61%) were isolated separately as a colorless oil.

### **7k-maj: (Z)-6-Chloro-7-(naphthalen-1-yl)hept-6-en-2-one**

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.82 (d,  $J = 7.2$  Hz, 1H), 7.79-7.76 (m, 1H), 7.72 (d,  $J = 7.8$  Hz, 1H), 7.55 (d,  $J = 7.2$  Hz, 1H), 7.44-7.38 (m, 3H), 6.88 (s, 1H), 2.57 (t,  $J = 7.2$  Hz, 2H), 2.50 (t,  $J = 7.2$  Hz, 2H), 2.11 (s, 3H), 1.98-1.93 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  208.22, 136.70, 133.49, 132.34, 131.46, 128.57, 128.00, 127.20, 126.10, 125.82, 125.24, 124.31, 123.51, 42.08, 39.50, 30.01, 21.65.

**HRMS (ESI):**  $\text{C}_{17}\text{H}_{18}\text{ClO}$   $[\text{M}+\text{H}]^+$  calculated: 273.1041, found: 273.1041.

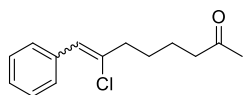
### **7k-min: (E)-6-Chloro-7-(naphthalen-1-yl)hept-6-en-2-one**

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.2$  Hz, 1H), 7.85 (dd,  $J = 7.8$  Hz,  $J = 2.4$  Hz, 1H), 7.80 (d,  $J = 8.4$  Hz, 1H), 7.54-7.49 (m, 2H), 7.45 (t,  $J = 7.2$  Hz, 1H), 7.29 (d,  $J = 6.6$  Hz, 1H), 7.15 (s, 1H), 2.42 (t,  $J = 7.2$  Hz, 2H), 2.30 (t,  $J = 7.2$  Hz, 2H), 1.89 (s, 3H), 1.88-1.83 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  207.90, 138.15, 133.55, 132.83, 131.69, 128.47, 128.13, 127.16, 126.43, 126.29, 126.10, 125.38, 124.71, 42.06, 33.51, 29.56, 21.39.

**HRMS (ESI):**  $\text{C}_{17}\text{H}_{18}\text{ClO}$   $[\text{M}+\text{H}]^+$  calculated: 273.1041, found: 273.1042.

### 7-Chloro-8-phenyloct-7-en-2-one (7l)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (40:1 to 15:1), **7l-min** (4.7 mg and 7%) and **7l-maj**, (39.3 mg and 55%) were isolated separately as a colorless oil.

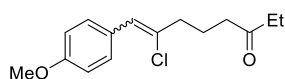
**7l-maj: (Z)-7-Chloro-8-phenyloct-7-en-2-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.48 (s, 1H), 2.51-2.46 (m, 4H), 2.14 (s, 3H), 1.67-1.63 (m, 4H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 208.61, 135.09, 134.35, 128.98, 128.13, 127.47, 124.67, 43.39, 40.95, 29.89, 27.09, 22.74.

HRMS (ESI): C<sub>14</sub>H<sub>18</sub>ClO [M+H]<sup>+</sup> calculated: 237.1041, found: 237.1040.

**7-Chloro-8-(4-methoxyphenyl)oct-7-en-3-one (7m)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1 to 10:1), **7m-min** (trace) and **7m-maj**, (41.6 mg and 52%) were isolated separately as a colorless oil.

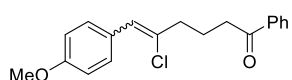
**7m-maj: (Z)-7-Chloro-8-(4-methoxyphenyl)oct-7-en-3-one**

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.39 (s, 1H), 3.81 (s, 3H), 2.50-2.40 (m, 6H), 1.97-1.91 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 211.06, 158.93, 131.97, 130.30, 127.57, 124.51, 113.59, 55.26, 40.56, 40.22, 35.99, 21.62, 7.86.

HRMS (ESI): C<sub>15</sub>H<sub>19</sub>ClNaO<sub>2</sub> [M+Na]<sup>+</sup> calculated: 289.0966, found: 289.0962.

**5-Chloro-6-(4-methoxyphenyl)-1-phenylhex-5-en-1-one (7n)**



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1 to 10:1), **7n-min** (trace) and **7n-maj** (69.0 mg and 73%) were isolated separately as a white solid.

**7n-maj: (Z)-5-Chloro-6-(4-methoxyphenyl)-1-phenylhex-5-en-1-one**

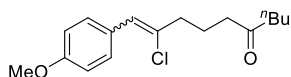
<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.4 Hz, 1.8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz,

3H), 7.37 (t,  $J = 7.8$  Hz, 2H), 6.79 (d,  $J = 9.0$  Hz, 2H), 6.34 (s, 1H), 3.73 (s, 3H), 2.95 (t,  $J = 7.2$  Hz, 2H), 2.51 (t,  $J = 7.2$  Hz, 2H), 2.07-2.01 (m, 2H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  198.76, 157.91, 135.97, 131.99, 130.96, 129.30, 127.57, 127.01, 126.57, 123.64, 112.56, 54.23, 39.28, 35.77, 21.06.

HRMS (ESI):  $\text{C}_{19}\text{H}_{20}\text{ClO}_2$   $[\text{M}+\text{H}]^+$  calculated: 315.1146, found: 315.1140.

### 9-Chloro-10-(4-methoxyphenyl)dec-9-en-5-one (7o)



The title compound was prepared according to the general procedure as described, Silica gel flash column chromatography was performed using hexanes and ethyl acetate (30:1 to 10:1), **7o-min** (trace) and **7o-maj**, (59.3 mg and 67%) were isolated separately as colorless oil.

#### **7o-maj: (Z)-9-Chloro-10-(4-methoxyphenyl)dec-9-en-5-one**

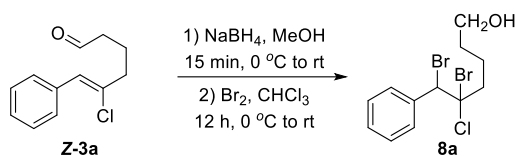
$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.48 (d,  $J = 9.0$  Hz, 2H), 6.80 (d,  $J = 9.0$  Hz, 2H), 6.32 (s, 1H), 3.74 (s, 3H), 2.39 (dt,  $J = 17.4$  Hz, 7.2 Hz, 4H), 2.32 (t,  $J = 7.2$  Hz, 2H), 1.89-1.83 (m, 2H), 1.51-1.45 (m, 2H), 1.27-1.20 (m, 2H), 0.82 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  210.73, 158.92, 131.96, 130.28, 127.56, 124.50, 113.57, 55.23, 42.61, 40.90, 40.18, 25.99, 22.35, 21.55, 13.81.

HRMS (ESI):  $\text{C}_{17}\text{H}_{24}\text{ClO}_2$   $[\text{M}+\text{H}]^+$  calculated: 295.1459, found: 295.1455.

## VIII. Synthesis and characterization of 8

### 5,6-Dibromo-5-chloro-6-phenylhexan-1-ol (**8a**)<sup>4</sup>



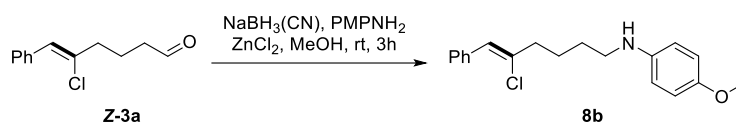
To a solution of **3a** (35 mg, 0.17 mmol) in 1 mL MeOH was added NaBH<sub>4</sub> (2.0 equiv) at 0 °C, the mixture was allowed to stirred for 15 min, quenched by saturate brine, extracted with ethyl acetate. The solvent was evaporated under vacuum, and the resulting residue was re-dissolved in 3 mL CH<sub>3</sub>Cl at 0 °C. Br<sub>2</sub> (2.0 equiv) was added, the mixture was allowed to warm to ambient temperature and stir overnight. The reaction mixture was quenched with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography (hexanes:ethyl acetate = 10:1) to give the corresponding product **8a** in 89 yield as oil.

<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.56 (t, *J* = 4.2 Hz, 2H), 7.29-7.27 (m, 3H), 5.35 (s, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.46-2.42 (m, 2H), 1.83-1.78 (m, 2H), 1.63-1.57 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 137.26, 130.59, 129.22, 127.83, 86.23, 62.47, 48.04, 31.82, 23.12.

HRMS (ESI): C<sub>12</sub>H<sub>15</sub>Br<sub>2</sub>ClNaO [M+Na]<sup>+</sup> calculated: 390.9070, found: 390.9070.

### (*Z*)-N-(5-Chloro-6-phenylhex-5-en-1-yl)-4-methoxyaniline (**8b**)<sup>4</sup>



To a solution of **Z-3a** (42 mg, 0.20 mmol) in 4 mL of MeOH were added PMPNH<sub>2</sub> (99.2 mg, 0.80 mmol). A solution of sodium cyanoborohydride (25.3 mg, 0.4 mmol) and zinc chloride (14 mg, 0.10 mmol) in methane (1 mL) were then added sequentially. The resulting solution was stirred at room temperature for 3 h and was taken up in 0.1 N NaOH (3 mL). After methanol was evaporated under reduced pressure, the aqueous solution was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with water and brine, dried over

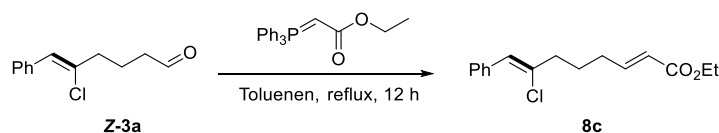
anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The residue was purified by column chromatography (hexanes:ethyl acetate = 10:1) to produce compound **8b** in 77% yield as oil.

$^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  7.50 (d,  $J = 7.2$  Hz, 2H), 7.26 (t,  $J = 7.2$  Hz, 2H), 7.18 (t,  $J = 7.2$  Hz, 2H), 6.69 (dd,  $J = 7.8$  Hz, 0.6 Hz, 2H), 6.50 (d,  $J = 7.8$  Hz, 2H), 6.40 (s, 1H), 3.66 (s, 3H), 3.04 (t,  $J = 7.2$  Hz, 2H), 2.45 (t,  $J = 7.2$  Hz, 2H), 1.73-1.67 (m, 2H), 1.62-1.56 (m, 2H).

$^{13}\text{C NMR}$  (151 MHz, Chloroform-*d*)  $\delta$  152.11, 142.67, 135.08, 134.46, 129.00, 128.16, 127.51, 124.73, 114.98, 114.10, 55.86, 44.76, 40.89, 28.62, 25.18.

**HRMS (ESI):**  $\text{C}_{19}\text{H}_{23}\text{ClNO}$   $[\text{M}+\text{H}]^+$  calculated: 316.1463, found: 316.1462.

#### Ethyl (2*E*,7*Z*)-7-chloro-8-phenylocta-2,7-dienoate (**8c**)<sup>5</sup>



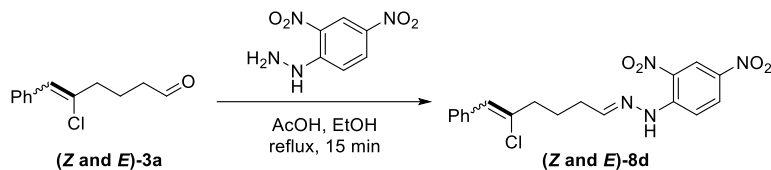
To a solution of **Z-3a** (42 mg, 0.20 mmol) in 4 mL toluene were added PhCOOH (4.9 mg, 0.04 mmol) and ethyl 2-(triphenylphosphanylidene)acetate (37 mg, 0.30 mmol). The resulting solution was heated to reflux for 12 h and then cooled to room temperature. After toluene was evaporated under reduced pressure, the residue was purified by column chromatography (hexanes:ethyl acetate = 20:1) to give compound **8c** in 88% yield as oil.

$^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  7.51 (d,  $J = 7.2$  Hz, 2H), 7.27 (t,  $J = 7.2$  Hz, 2H), 7.20 (d,  $J = 7.2$  Hz, 1H), 6.90 (dt,  $J = 15.6$  Hz, 7.2 Hz, 1H), 6.41 (s, 1H), 5.79 (dt,  $J = 15.6$  Hz, 1.8 Hz, 1H), 4.12 (q,  $J = 7.2$  Hz, 2H), 2.44 (t,  $J = 7.2$  Hz, 2H), 2.19 (q,  $J = 7.2$  Hz, 2H), 1.80-1.75 (m, 2H), 1.22 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C NMR}$  (151 MHz, Chloroform-*d*)  $\delta$  166.56, 148.14, 134.95, 133.86, 128.98, 128.16, 127.57, 125.10, 122.03, 60.22, 40.38, 30.88, 25.83, 14.27.

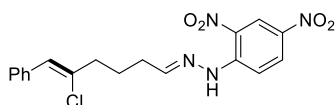
**HRMS (ESI):**  $\text{C}_{16}\text{H}_{20}\text{ClO}_2$   $[\text{M}+\text{H}]^+$  calculated: 279.1146, found: 279.1146.

#### (1*E*)-1-(5-Chloro-6-phenylhex-5-en-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (**8d**)<sup>6</sup>



A mixture of (**Z or E**)-**3a** (62 mg, 0.30 mmol) and 2,4-dinitrophenyl hydrazine (64 mg, 0.32 mmol), dissolved in ethanol (1.6 mL), was added dropwise to AcOH (0.03 mL) while stirring. The reaction mixture was further refluxed at stirring for 15 min. After cooling to room temperature and water (1.6 mL) was added to give a precipitate of crude product. Next, reaction mixture was heated at 60 °C with stirring for 15 min. After cooling to room temperature again, water (10 mL) was added, the aqueous solution was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography (hexanes:ethyl acetate = 15:1) to produce compound (**Z**)-**8d** and (**E**)-**8d** in 81% and 76% yield respectively as an orange solid.

**(E)-1-((Z)-5-Chloro-6-phenylhex-5-en-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (Z-8d)**

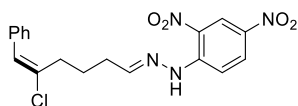


<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 11.02 (s, 1H), 9.10 (d, *J* = 2.4 Hz, 1H), 8.27 (dd, *J* = 9.6 Hz, 3.0Hz, 1H), 7.91 (d, *J* = 9.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 3H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.51 (dt, *J* = 7.2 Hz, 5.4 Hz, 2H), 2.06-2.01 (m, 2H).

<sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 151.33, 145.06, 137.93, 134.75, 133.39, 129.94, 128.94, 128.20, 127.74, 125.58, 123.44, 116.48, 40.46, 31.35, 23.98.

HRMS (ESI): C<sub>18</sub>H<sub>18</sub>ClN<sub>4</sub>O<sub>4</sub> [M+H]<sup>+</sup> calculated: 389.1011, found: 389.1003.

**(E)-1-((E)-5-Chloro-6-phenylhex-5-en-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (E-8d)**



<sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 10.90 (s, 1H), 9.11 (d, *J* = 3.0 Hz, 1H), 8.26 (dd, *J* = 9.6 Hz, 3.0Hz, 1H), 7.83 (d, *J* = 9.6 Hz, 1H), 7.40 (t, *J* = 4.8 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.23

(t,  $J = 7.2$  Hz, 1H), 7.18 (d,  $J = 7.2$  Hz, 2H), 6.81 (s, 1H), 2.69 (t,  $J = 7.2$  Hz, 2H), 2.51 (dt,  $J = 7.2$  Hz, 4.8 Hz, 2H), 2.04-1.98 (m, 2H).

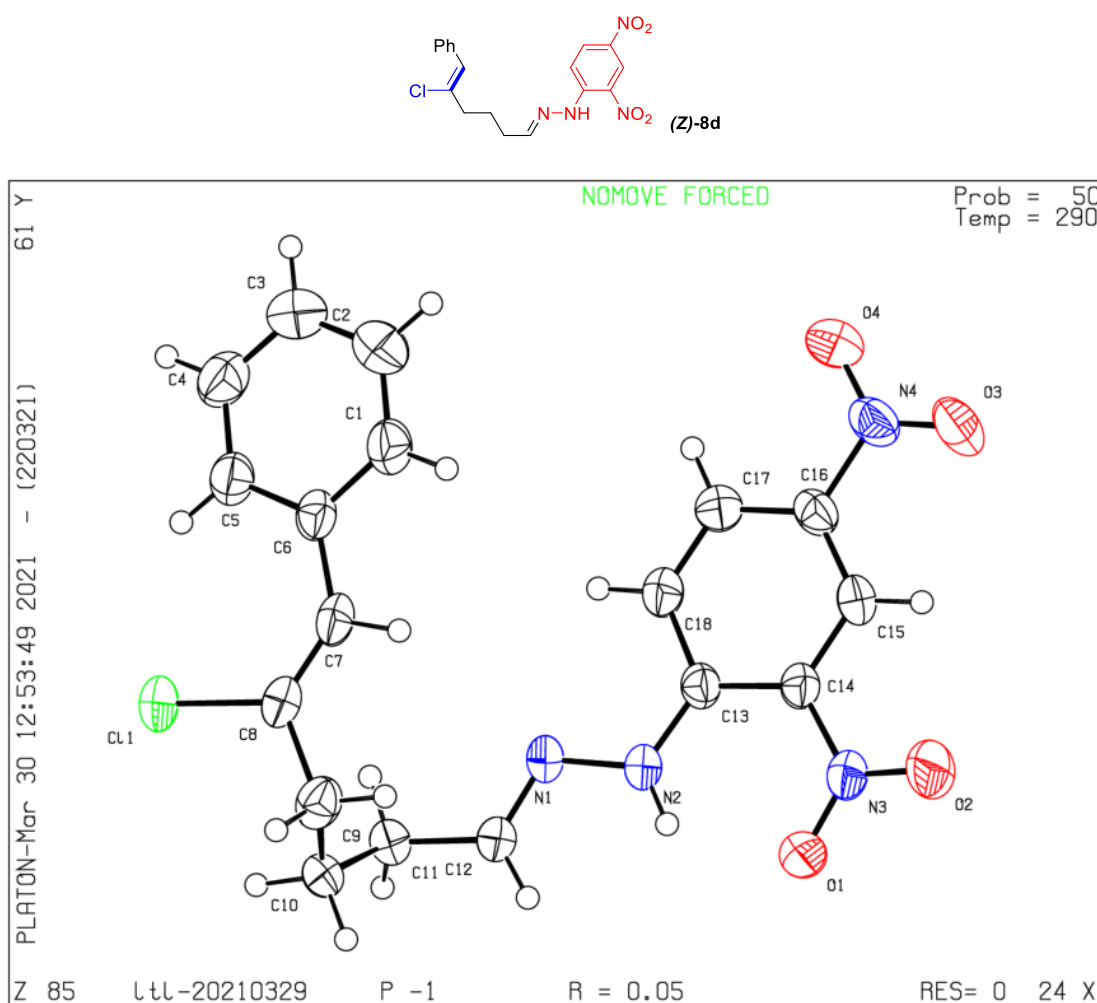
$^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  151.12, 145.01, 137.89, 136.81, 135.60, 129.91, 129.25, 128.52, 128.31, 127.36, 123.41, 116.48, 33.25, 31.12, 23.90.

**HRMS (ESI):**  $\text{C}_{18}\text{H}_{18}\text{ClN}_4\text{O}_4$   $[\text{M}+\text{H}]^+$  calculated: 389.1011, found: 389.1002.



## IX. X-Ray Crystallographic Data

Single crystal suitable for X-ray diffraction of **(Z)-8d** was obtained from a solution of compound **(Z)-8d** in DCM layered with *n*-hexane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Date Centre under reference number CCDC 2083882. Diffraction Data was collected on an Agilent SuperNova E 15A11181. The crystal structure was shown in **Figure S1**. The detailed information was listed in the **Table S1**. **(Z)-8d** was prepared according to the procedure as shown in procedure **VIII**.



**Figure S1. Crystal Structure of (Z)-8d (CCDC 2083882)**

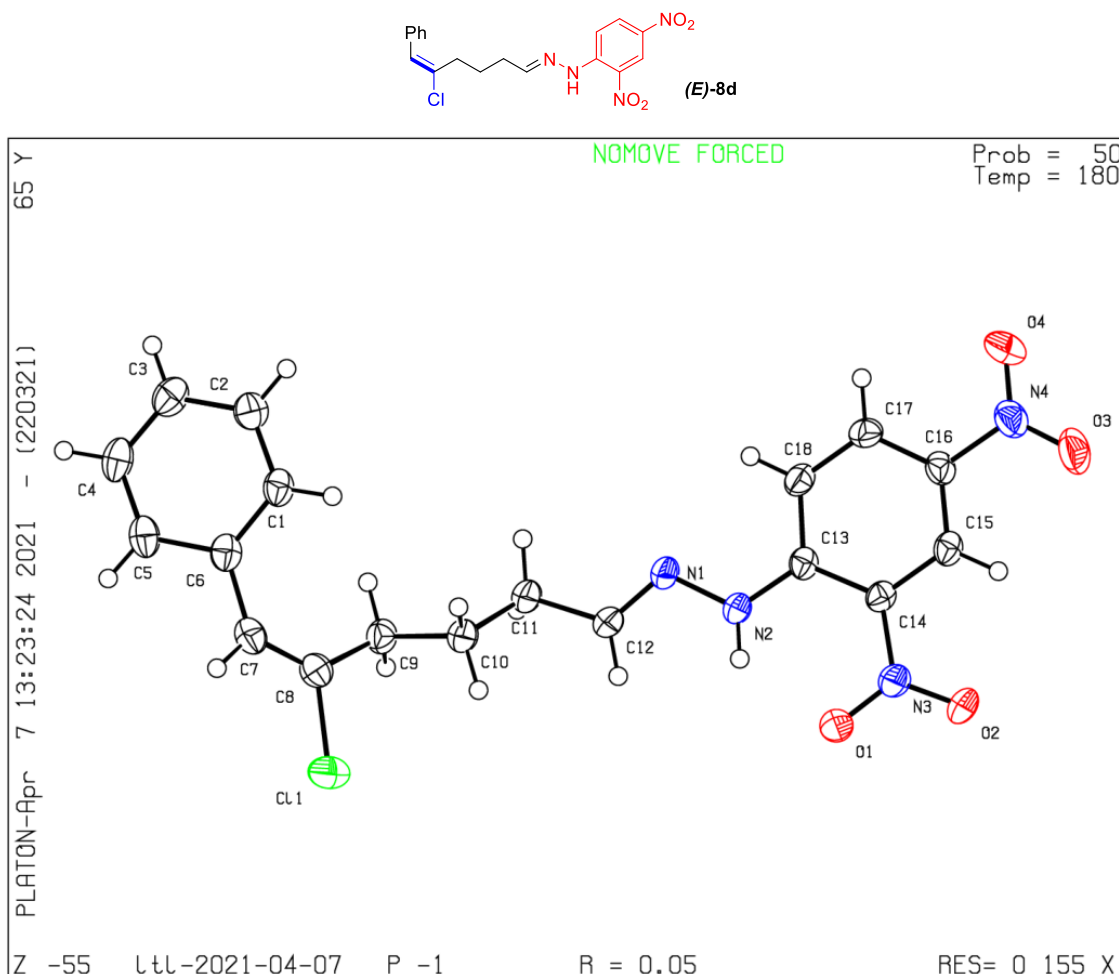
**Table S1. Crystal Data and Structure Refinement of (Z)-8d**

---

Bond precision: C-C = 0.0031 Å	Wavelength=1.54184	
Cell	a = 9.5440 (4) b = 9.6083 (3) c = 10.9794 (4)	
	alpha = 100.755 (3) beta = 109.708 (4) gamma = 99.226 (3)	
Temperature	290 K	
	Calculated	Reported
Volume	903.67 (7)	903.66 (7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H17 Cl N4 O4	C18 H17 Cl N4 O4
Sum formula	C18 H17 Cl N4 O4	C18 H17 Cl N4 O4
Mr	388.81	388.80
Dx, g cm <sup>-3</sup>	1.429	1.429
Z	2	2
Mu (mm <sup>-1</sup> )	2.164	2.164
F000	404.0	404.0
F000'	405.95	
h, k, lmax	11, 11, 13	11, 11, 13
Nref	3572	3502
Tmin, Tmax	0.457, 0.511	0.161, 1.000
Tmin'	0.384	
Correction method = # Reported T Limits: Tmin = 0.161 Tmax = 1.000		
AbsCorr = MULTI-SCAN		
Data completeness = 0.980	Theta (max) = 72.346	
R (reflections) = 0.0535 (3225)	wR2 (reflections) = 0.1512 (3502)	
S = 1.024	Npar = 244	

---

Single crystal suitable for X-ray diffraction of (*E*)-**8d** was obtained from a solution of compound (*E*)-**8d** in DCM layered with *n*-hexane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2083883. Diffraction Data was collected on an Agilent SuperNova E 15A11181. The crystal structure was shown in **Figure S2**. The detailed information was listed in the **Table S2**. (*E*)-**8d** was prepared according to the procedure as shown in procedure **VIII**.



**Figure S2. Crystal Structure of (*E*)-**8d** (CCDC 2083883)**

**Table S2. Crystal Data and Structure Refinement of (E)-8d**

---

Bond precision: C-C = 0.0029 Å	Wavelength=1.54184	
Cell	a = 7.5823 (2) b = 11.0627 (3) c = 11.5599 (4)	
	alpha = 104.955 (3) beta = 101.519 (3) gamma = 98.541 (2)	
Temperature	180 K	
	Calculated	Reported
Volume	897.21 (5)	897.21 (5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H17 Cl N4 O4	C18 H17 Cl N4 O4
Sum formula	C18 H17 Cl N4 O4	C18 H17 Cl N4 O4
Mr	388.81	388.80
Dx, g cm <sup>-3</sup>	1.439	1.439
Z	2	2
Mu (mm <sup>-1</sup> )	2.179	2.179
F000	404.0	404.0
F000'	405.95	
h, k, lmax	9, 13, 14	9, 13, 14
Nref	3528	3484
Tmin, Tmax	0.471, 0.477	0.245, 1.000
Tmin'	0.356	
Correction method = # Reported T Limits: Tmin = 0.245 Tmax = 1.000		
AbsCorr = MULTI-SCAN		
Data completeness = 0.988	Theta (max) = 71.814	
R (reflections) = 0.0523( 3288)	wR2 (reflections) = 0.1477( 3484)	
S = 1.043	Npar = 245	

---

## X. References

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# XI. NMR Spectra

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RLQ-148B

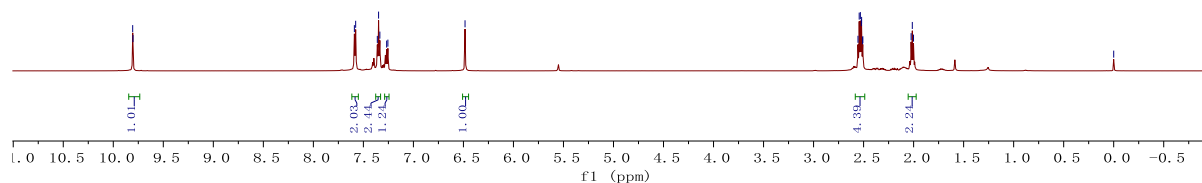
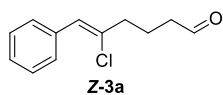
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2.532  
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2.001

0.000



RLQ-13C. 98. fid  
RLQ-148B

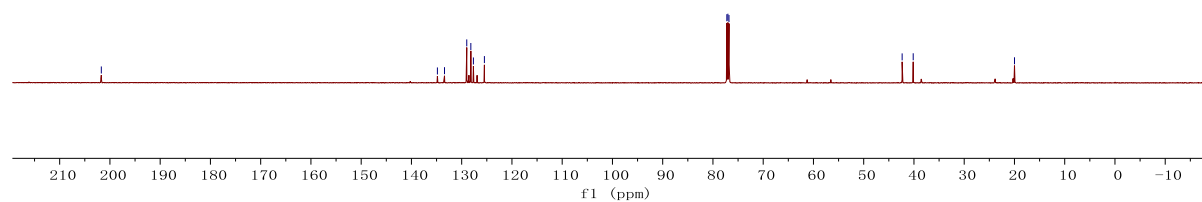
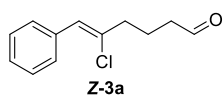
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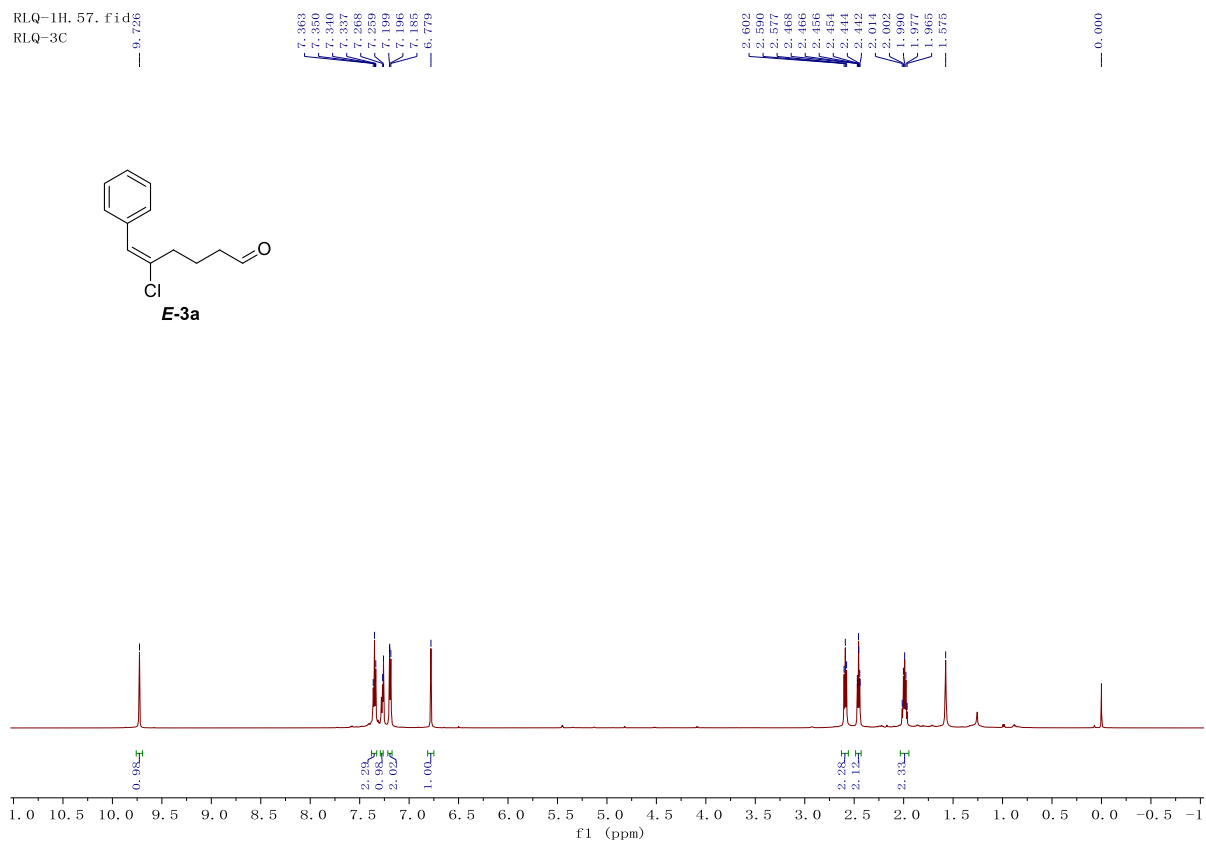
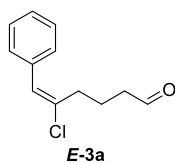
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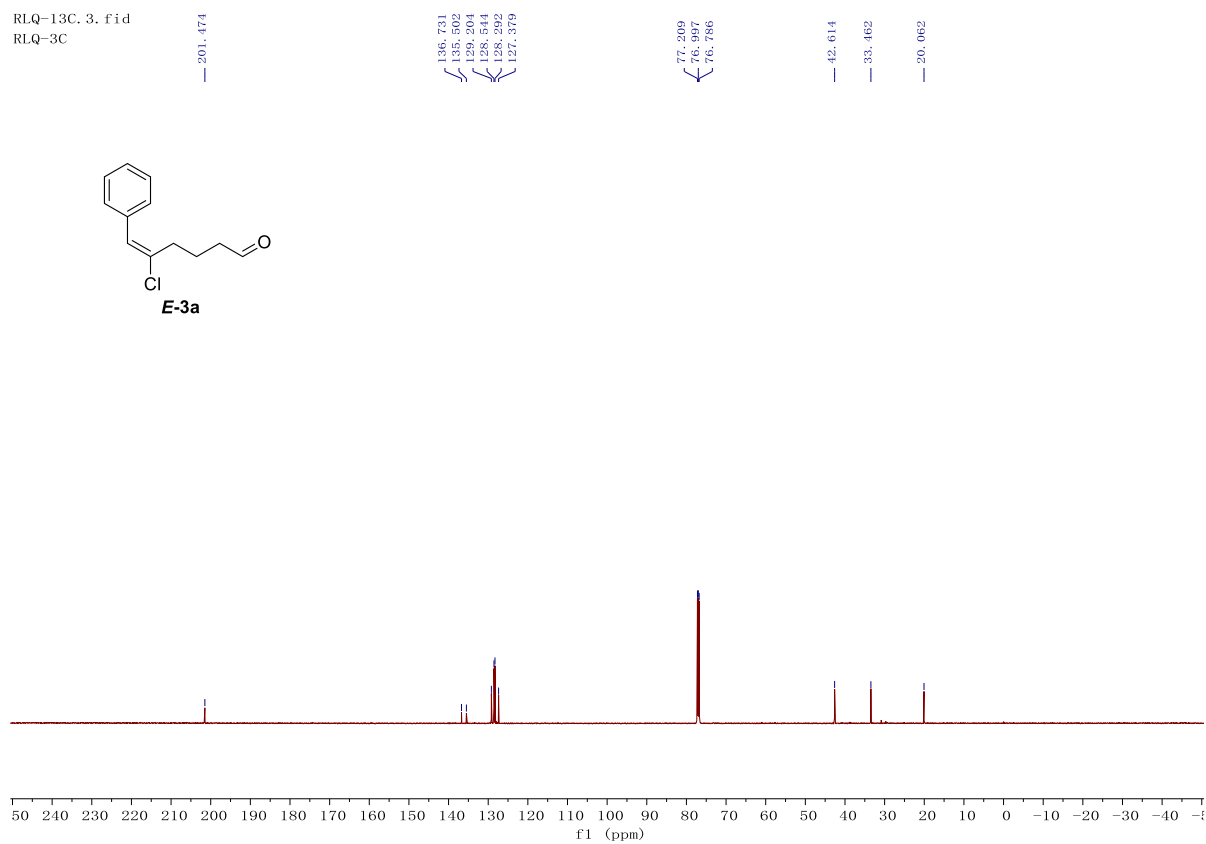
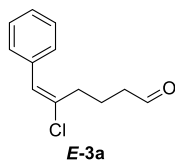
19.992



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RLQ-3C



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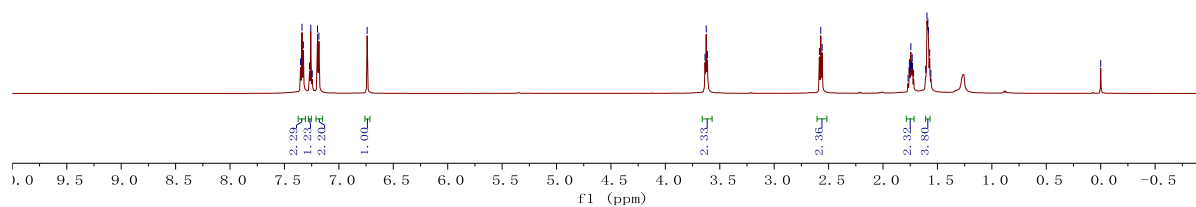
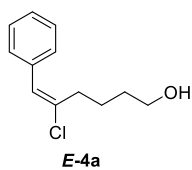


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RLQ-2C

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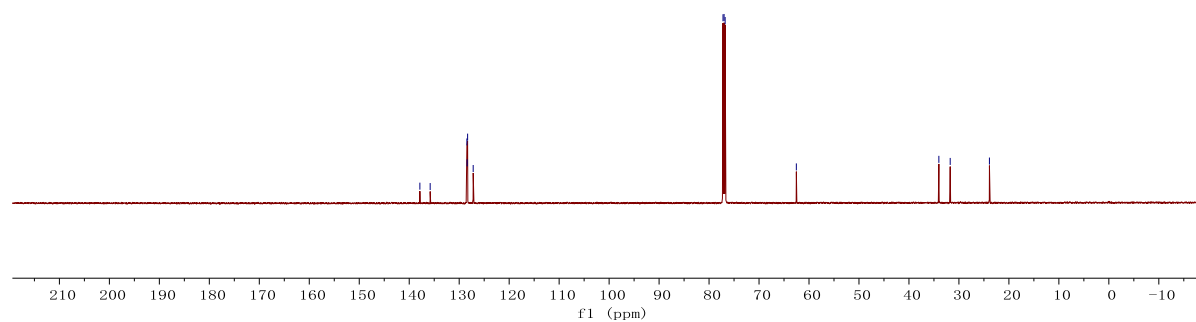
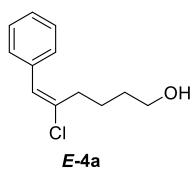
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RLQ-2C

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76.784

62.532

34.014  
31.746  
23.895





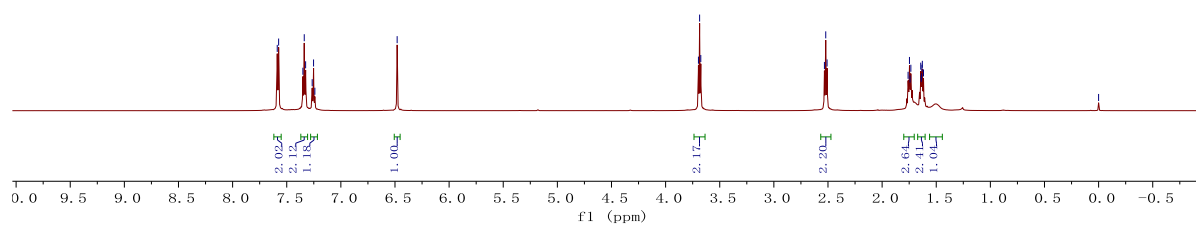
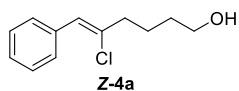
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— 6.480

3.697  
3.686  
3.675

2.533  
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RLQ-2D

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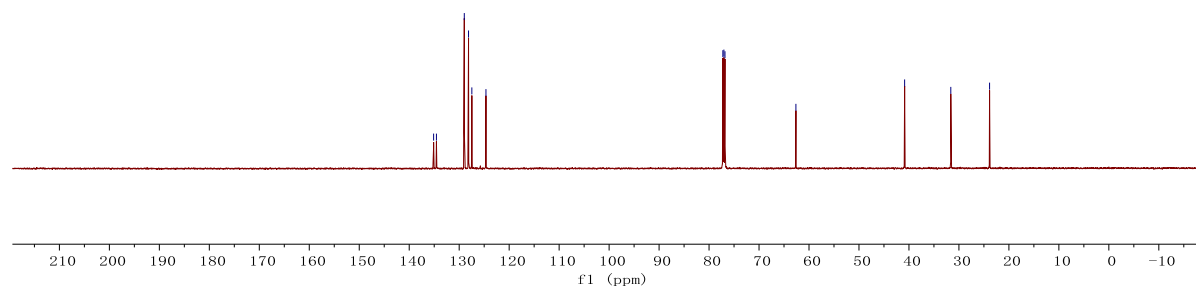
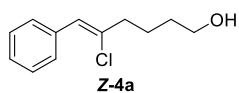
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— 62.621

— 40.865

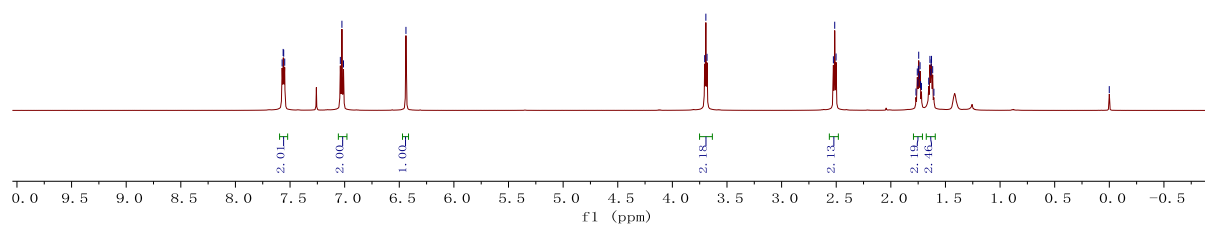
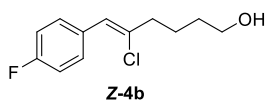
— 31.625

— 23.868



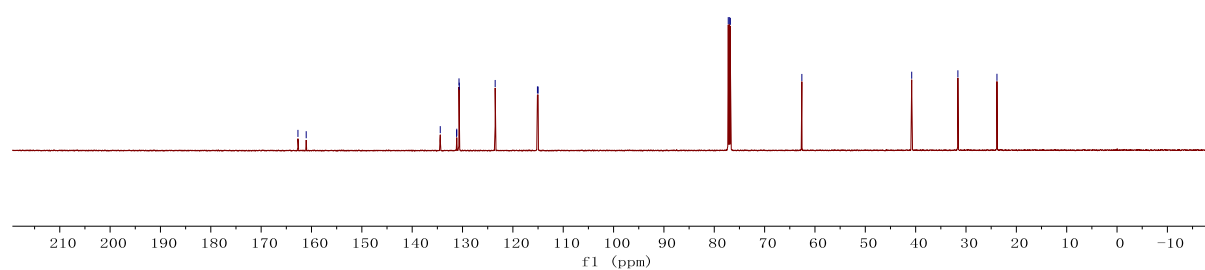
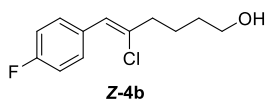
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RLQ-161-2

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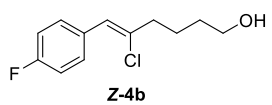


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RLQ-161-2

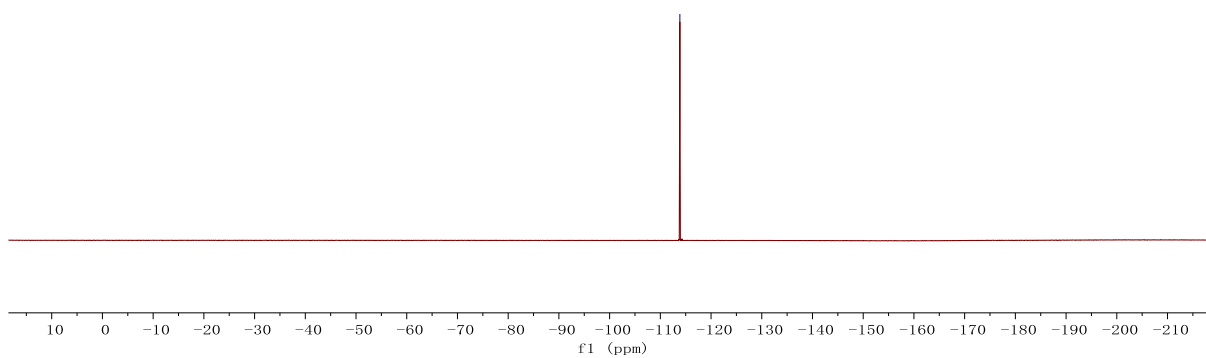
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77.012  
76.800  
62.603  
40.783  
31.611  
23.853



RLQ-266. 1. fid



-113.862



RLQ-1H. 15. fid  
RLQ-155-2

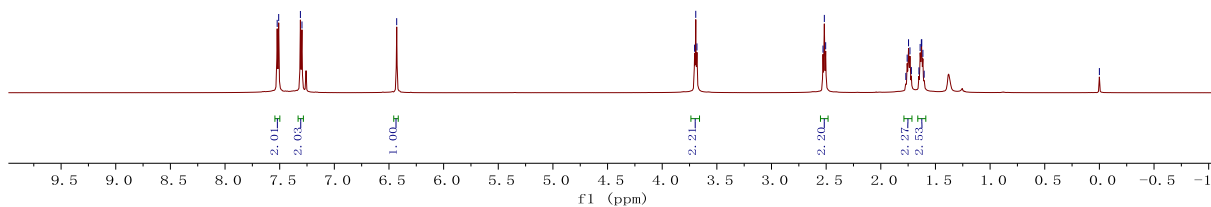
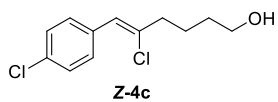
7.523  
7.509  
7.510  
7.256

6.429

3.704  
3.693  
3.682

2.529  
2.517  
2.504  
1.750  
1.746  
1.733  
1.720  
1.651  
1.640  
1.629  
1.615  
1.603

-0.000



RLQ-13C. 20. fid  
RLQ-155-2

135.367  
133.529  
133.524  
130.244  
128.319  
123.504

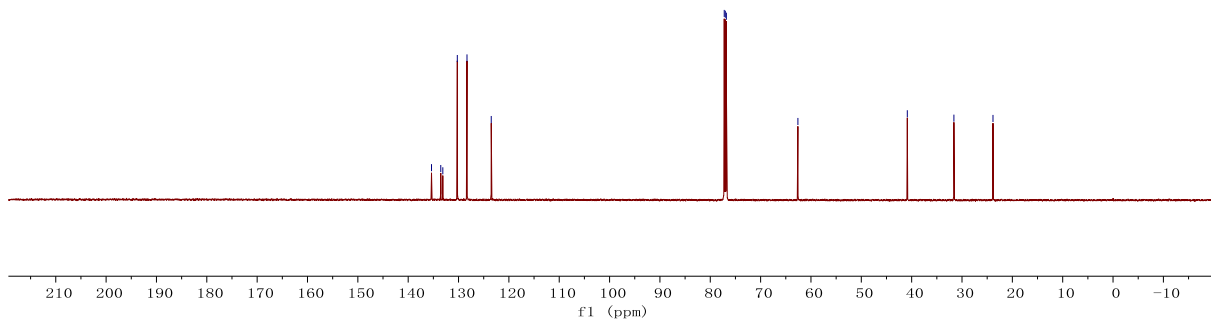
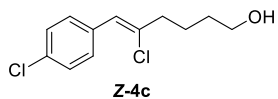
77.226  
77.014  
76.803

62.596

40.864

31.607

23.846



RLQ-1H. 17. fid  
RLQ-156-2

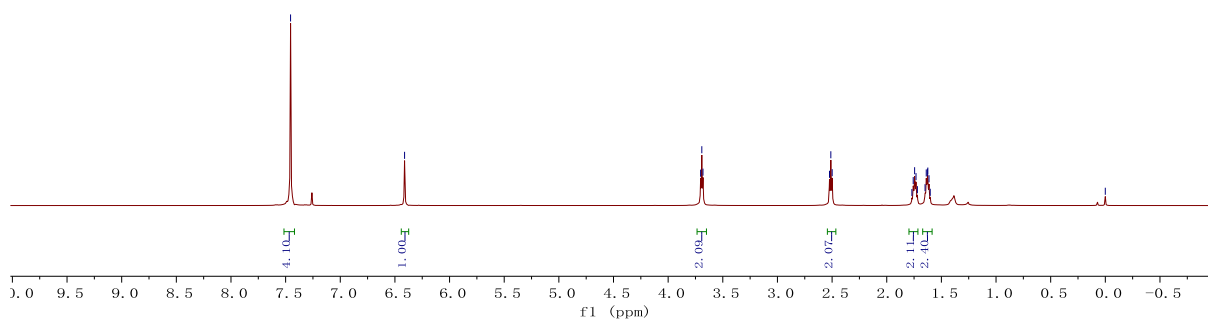
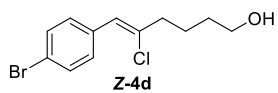
7.455

6.412

3.703  
3.692  
3.681

2.524  
2.511  
2.499  
1.770  
1.758  
1.745  
1.732  
1.720  
1.649  
1.639  
1.628  
1.624  
1.613  
1.602

0.000



RLQ-13C. 21. fid  
RLQ-156-2

135.509  
133.986  
131.280  
130.539  
123.552  
121.317

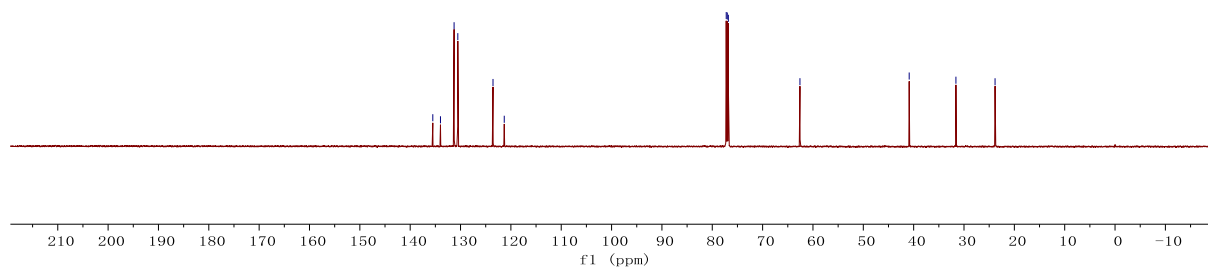
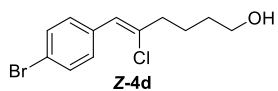
77.229  
77.008  
76.806

62.584

40.886

31.605

23.832

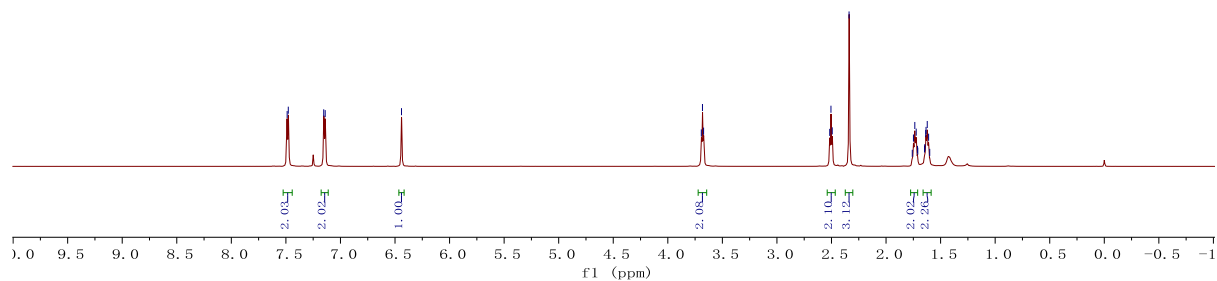
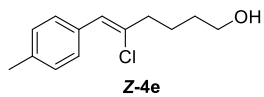


RLQ-1H. 24. fid  
RLQ-162-2

7.488  
7.478  
7.153  
7.140  
6.441

3.693  
3.682  
3.672

2.516  
2.505  
2.493  
2.339  
1.709  
1.708  
1.724  
1.712  
1.709  
1.648  
1.645  
1.637  
1.622  
1.614  
1.600



RLQ-13C. 27. fid  
RLQ-162-2

137.315  
133.712  
132.265  
128.888  
128.838  
124.525

77.240  
77.028  
76.816

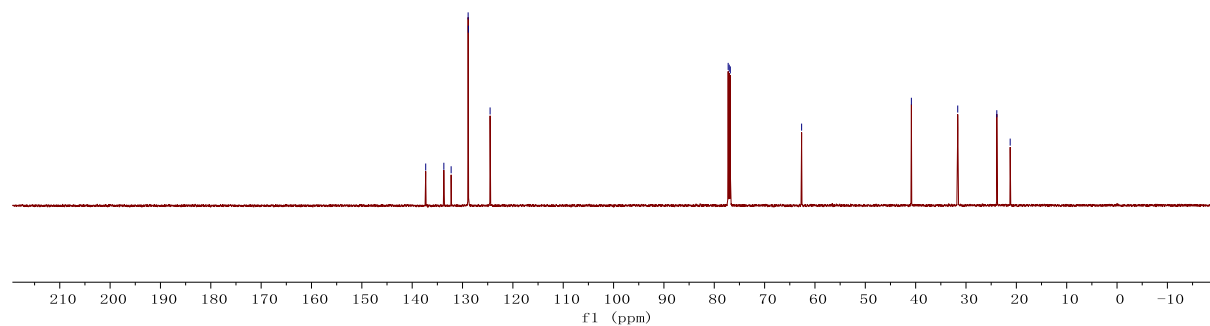
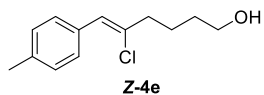
62.650

40.851

31.644

23.881

21.224



RLQ-1H. 3. fid  
RLQ-225-2

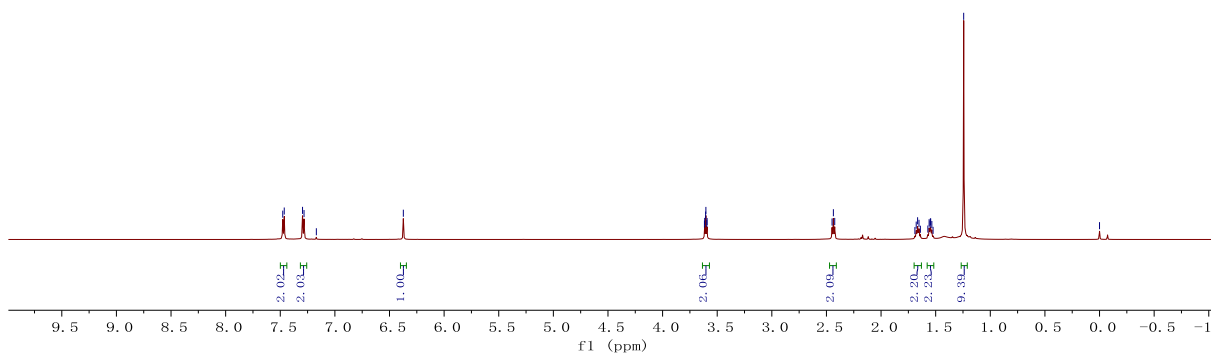
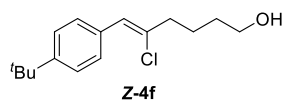
7.477  
7.461  
7.296  
7.282  
7.170

6.373

3.617  
3.614  
3.606  
3.604  
3.595  
3.593

2.449  
2.436  
2.424  
1.690  
1.678  
1.665  
1.653  
1.640  
1.571  
1.564  
1.551  
1.549  
1.546  
1.535  
1.524  
1.244

0.000



RLQ-13C. 51. fid  
RLQ-225-2

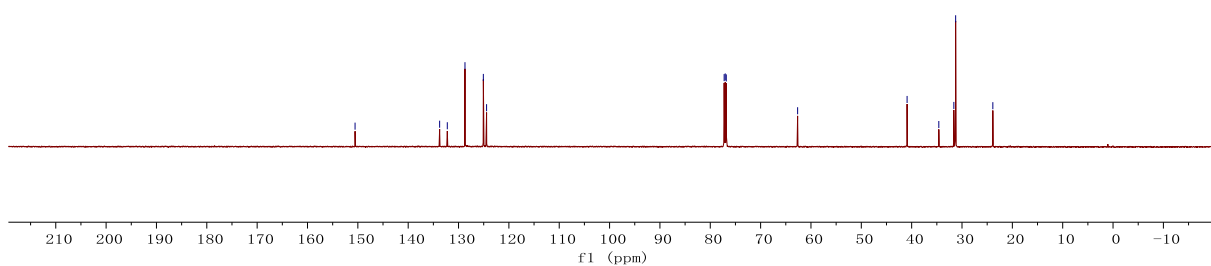
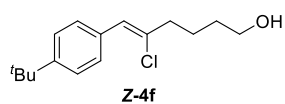
150.551

133.755  
132.932  
128.722  
125.072  
124.430

77.244  
77.035  
76.821

62.651

40.906  
34.606  
31.624  
31.282  
23.876



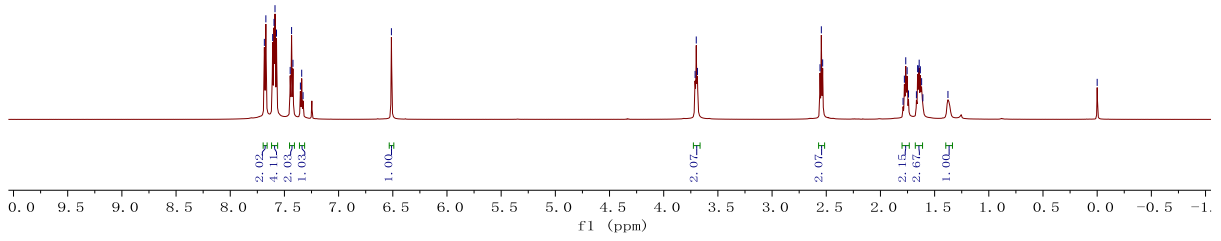
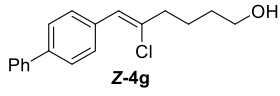
RLQ-1H. 65. fid  
RLQ-188

7.685  
7.671  
7.608  
7.587  
7.587  
7.573  
7.447  
7.434  
7.421  
7.353  
7.341  
7.328  
— 6.513

3.710  
3.700  
3.689

2.558  
2.545  
2.534  
2.520  
1.779  
1.766  
1.754  
1.741  
1.668  
1.657  
1.647  
1.632  
1.620  
1.608  
1.377

— 0.000



RLQ-13C. 36. fid  
RLQ-188

140.671  
140.200  
134.711  
134.111  
133.784  
128.784  
127.361  
126.997  
126.806  
124.274

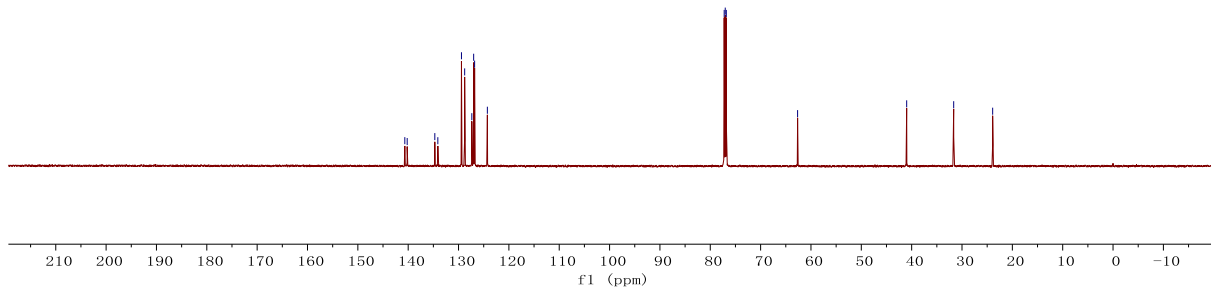
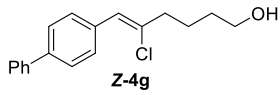
77.238  
77.056  
76.815

— 62.657

— 40.988

— 31.651

— 23.911





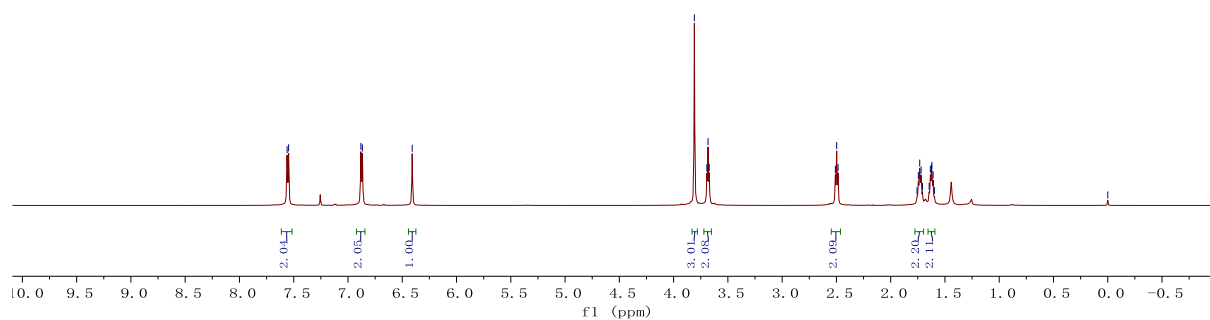
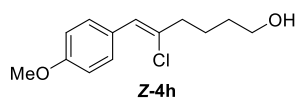
RLQ-1H. 18. fid  
RLQ-158

7.561  
7.517  
6.881  
6.867  
6.408

3.809  
3.693  
3.683  
3.672

2.510  
2.497  
2.485  
1.757  
1.745  
1.733  
1.720  
1.707  
1.696  
1.684  
1.672  
1.650  
1.609  
1.598

0.000



RLQ-13C. 22. fid  
RLQ-158

158.862

132.643  
130.281  
127.745  
124.036

113.578

77.240  
77.028  
76.816

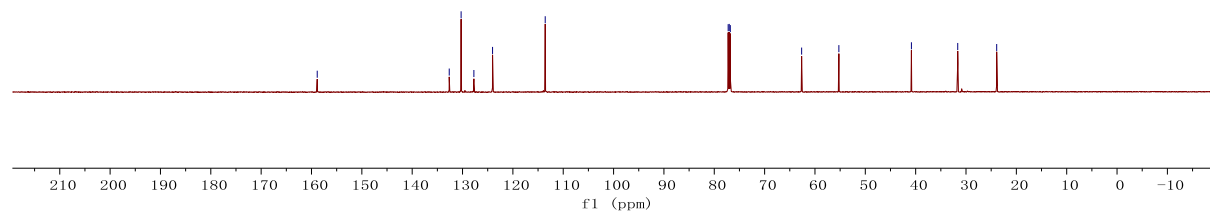
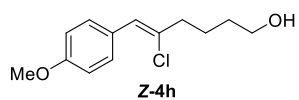
62.646

55.250

40.843

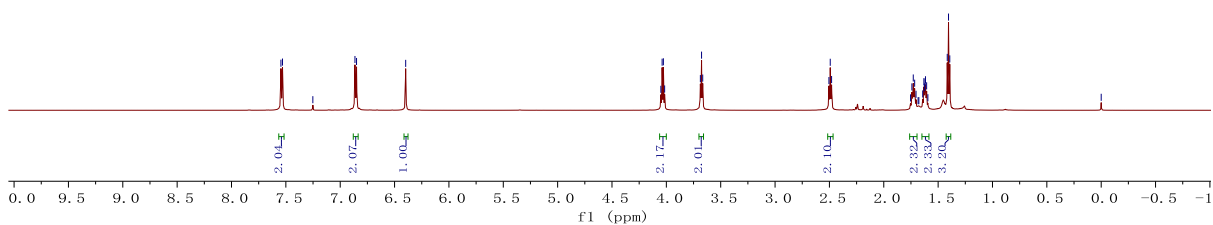
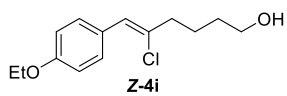
31.644

23.904



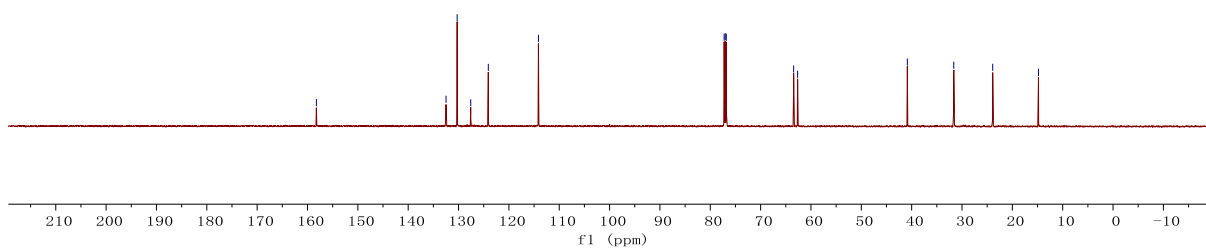
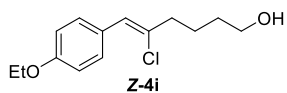
RLQ-1H. 2. fid  
RLQ-224

7.545  
7.531  
7.252  
6.864  
6.850  
6.398  
4.051  
4.039  
4.027  
4.016  
3.987  
3.676  
3.665  
2.504  
2.492  
2.480  
1.754  
1.741  
1.729  
1.716  
1.703  
1.684  
1.672  
1.642  
1.631  
1.627  
1.623  
1.620  
1.616  
1.606  
1.594  
1.416  
1.393  
-0.000



RLQ-13C. 50. fid  
RLQ-224

158.236  
132.484  
130.273  
127.575  
124.087  
114.131  
77.245  
77.023  
76.822  
63.441  
62.653  
40.856  
31.637  
23.901  
14.810



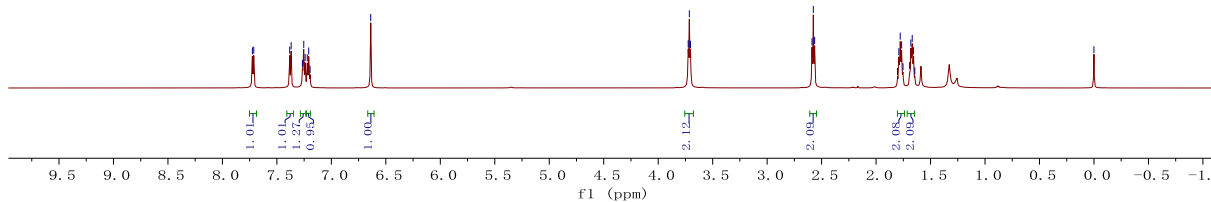
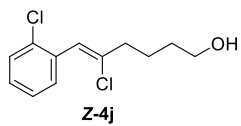
RLQ-1H. 47. fid  
RLQ-177-1

7.725  
7.712  
7.382  
7.369  
7.266  
7.253  
7.241  
7.221  
7.221  
7.195  
6.639

3.725  
3.714  
3.703

2.588  
2.576  
2.564  
1.803  
1.791  
1.778  
1.766  
1.754  
1.692  
1.681  
1.668  
1.656  
1.645

0.000



RLQ-13C. 33. fid  
RLQ-177-1

137.055  
133.615  
133.476  
133.408  
129.177  
128.649  
126.224  
122.003

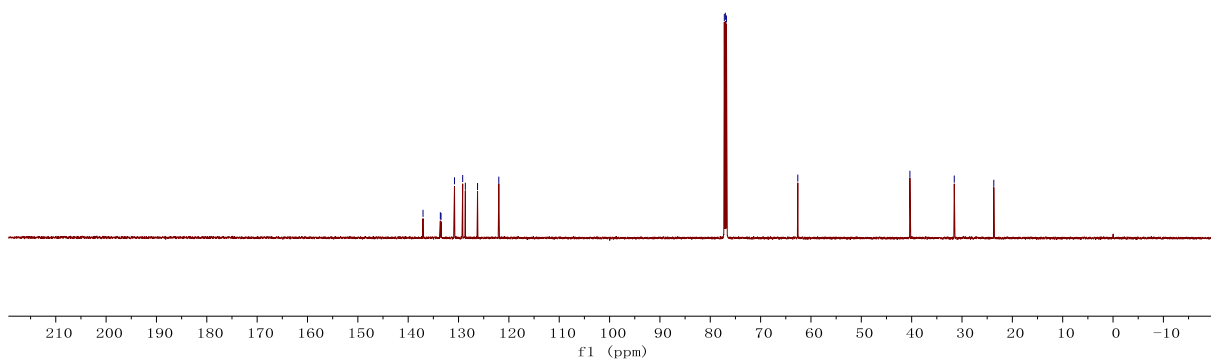
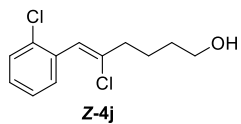
77.211  
76.989  
76.766

62.614

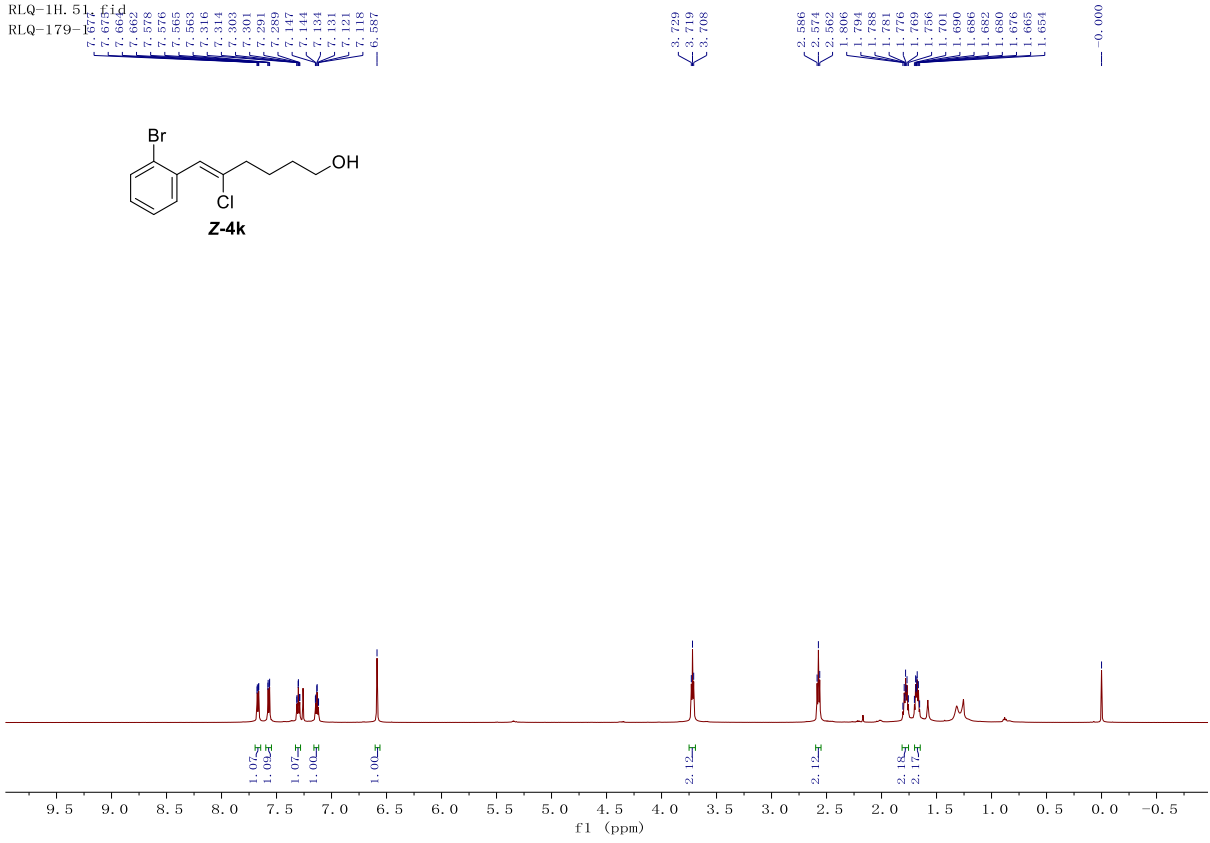
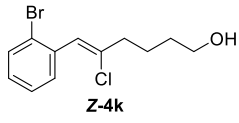
40.349

31.535

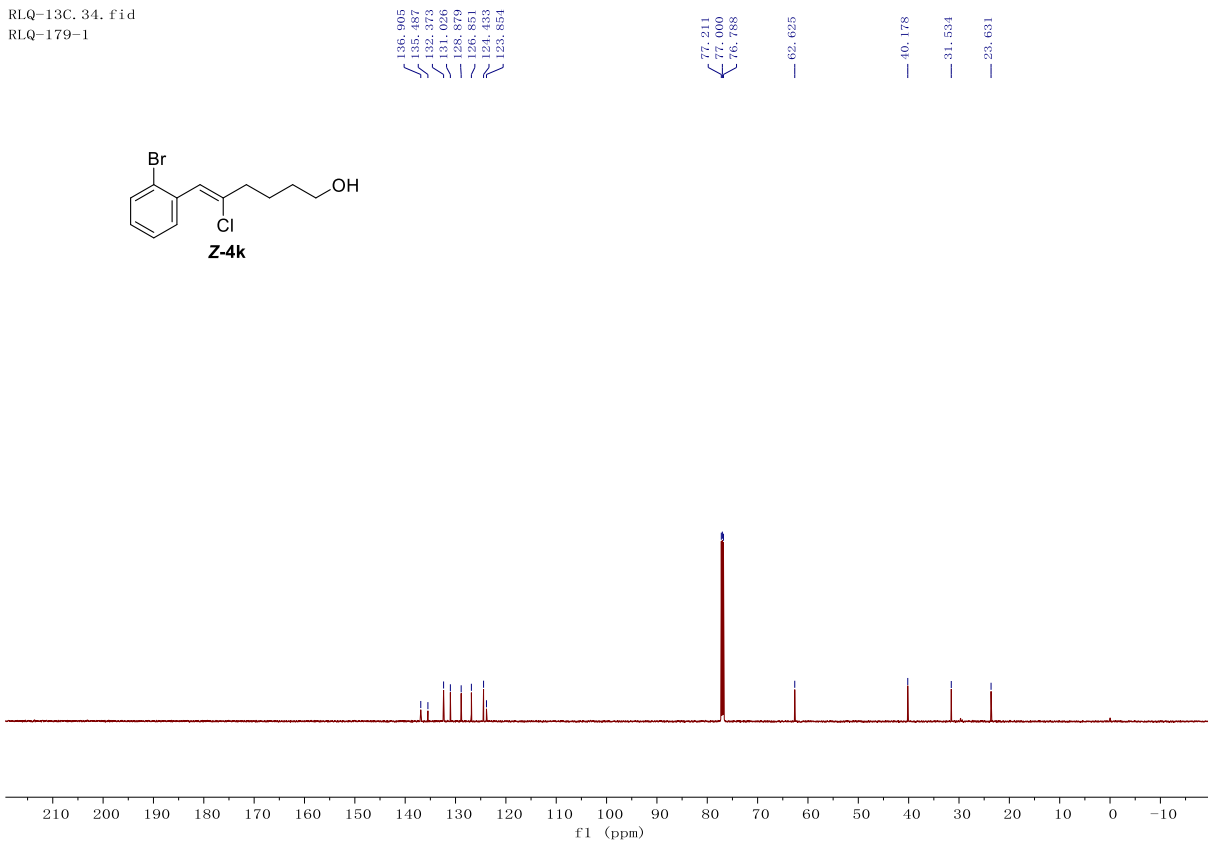
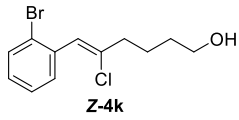
23.684



RLQ-1H. 51  
 RLQ-179-1



RLQ-13C. 34. fid  
 RLQ-179-1



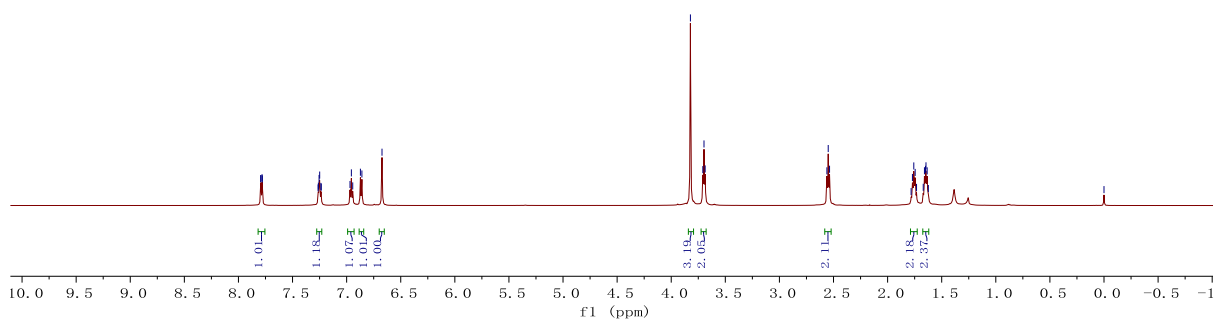
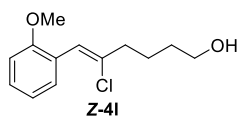
RLQ-1H. 19. fid  
RLQ-159

7.705  
7.732  
7.782  
7.779  
7.264  
7.261  
7.255  
7.249  
7.238  
7.235  
6.969  
6.956  
6.944  
6.873  
6.859  
6.673

3.823  
3.708  
3.697  
3.686

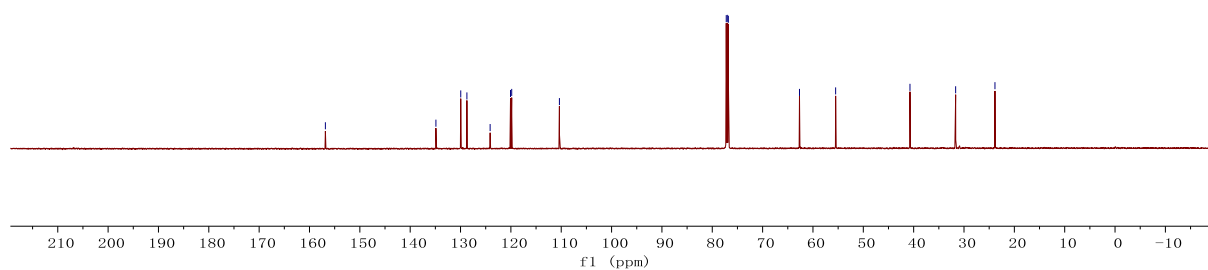
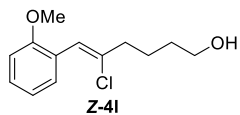
2.561  
2.549  
2.537  
1.783  
1.771  
1.766  
1.745  
1.733  
1.671  
1.659  
1.649  
1.645  
1.635  
1.623

0.000



RLQ-13C. 23. fid  
RLQ-159

156.844  
134.890  
129.956  
128.736  
124.121  
120.073  
119.836  
110.360  
77.226  
77.013  
76.803  
62.677  
55.498  
40.732  
31.680  
23.853

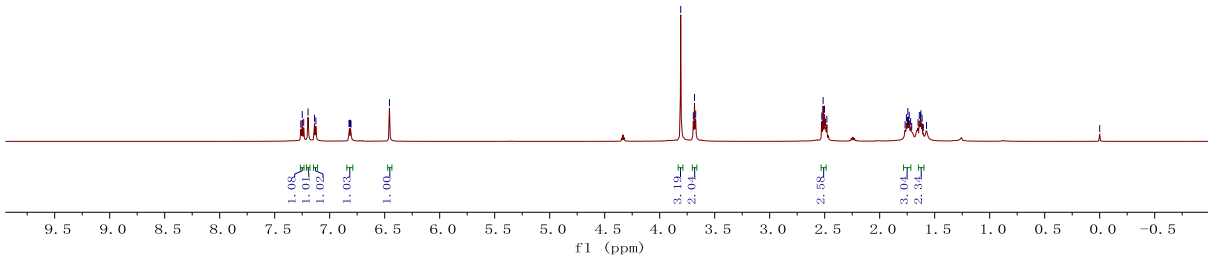
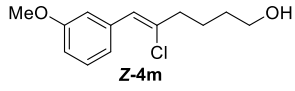


RLQ-1H. 66. fid  
RLQ-176-C

7.2953  
7.2419  
7.2246  
7.1965  
7.1388  
7.1225  
6.8264  
6.8111  
6.8066  
6.457

3.809  
3.694  
3.683  
3.673

2.527  
2.514  
2.502  
2.494  
2.480  
1.709  
1.707  
1.706  
1.704  
1.739  
1.731  
1.719  
1.709  
1.651  
1.640  
1.629  
1.627  
1.614  
1.603  
1.574  
-0.000



RLQ-13C. 46. fid  
RLQ-176-2

159.359

136.390  
134.787  
129.075  
124.523  
121.686  
114.321  
113.298

77.245  
77.035  
76.821

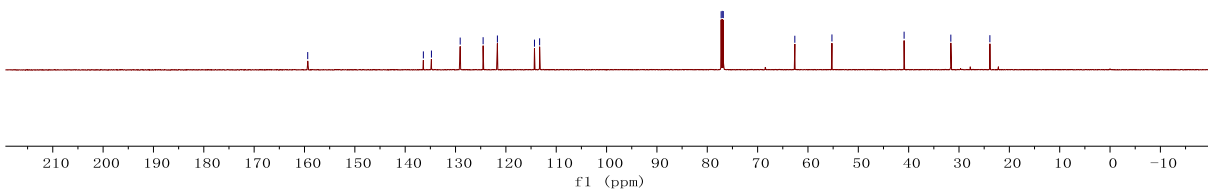
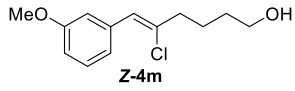
62.609

55.238

40.904

31.623

23.865

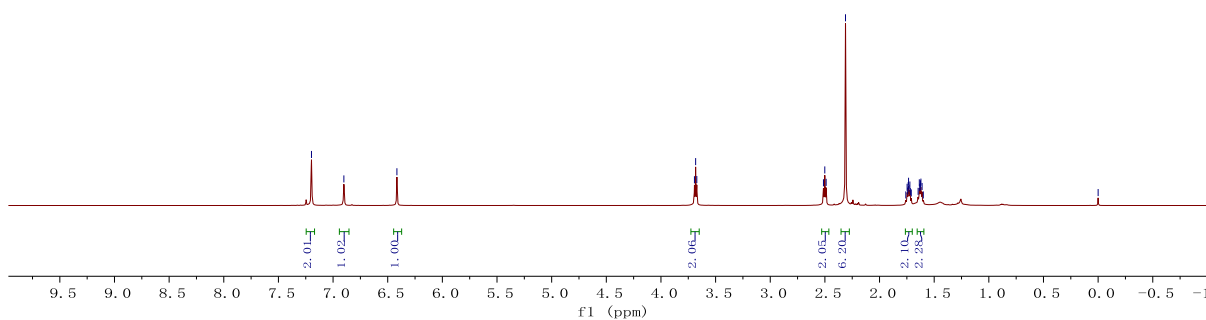
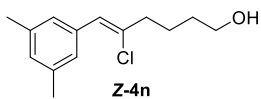


RLQ-1H. 79. fid  
RLQ-203-2

7.198  
6.901  
6.416

3.694  
3.683  
3.672

2.513  
2.501  
2.489  
2.311  
1.760  
1.748  
1.742  
1.737  
1.734  
1.730  
1.722  
1.718  
1.716  
1.647  
1.636  
1.632  
1.628  
1.626  
1.621  
1.611  
1.599  
-0.000



RLQ-13C. 40. fid  
RLQ-203-2

137.572  
134.881  
134.058  
129.192  
126.768  
124.841

77.236  
77.025  
76.814

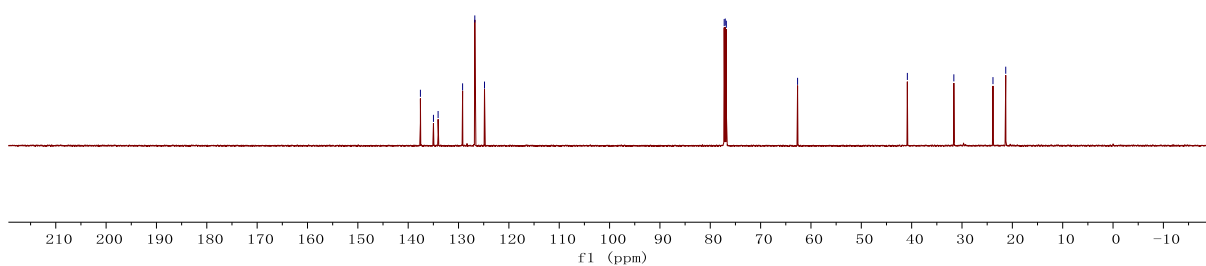
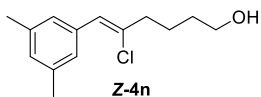
62.657

40.856

31.619

23.850

21.312



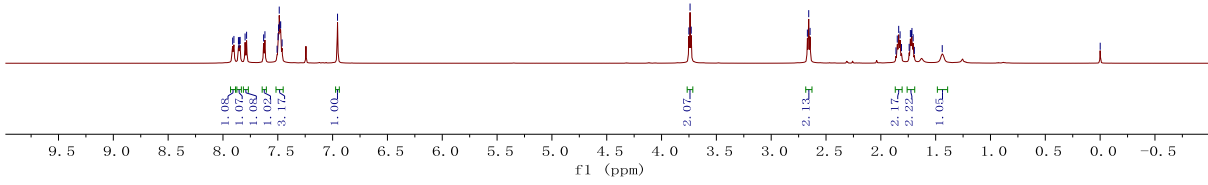
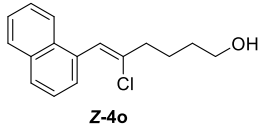
RLQ-1H. 42  
RLQ-175

7.912  
7.900  
7.853  
7.854  
7.848  
7.844  
7.786  
7.785  
7.629  
7.617  
7.506  
7.498  
7.493  
7.487  
7.481  
7.474  
7.461  
6.955

3.751  
3.746  
3.729

2.670  
2.658  
2.645  
1.862  
1.850  
1.837  
1.825  
1.812  
1.792  
1.783  
1.720  
1.716  
1.705  
1.694  
1.440

-0.001



RLQ-13C. 42. fid  
RLQ-175

137.384  
133.493  
132.561  
128.536  
127.893  
127.207  
126.051  
125.786  
125.243  
124.406  
122.990

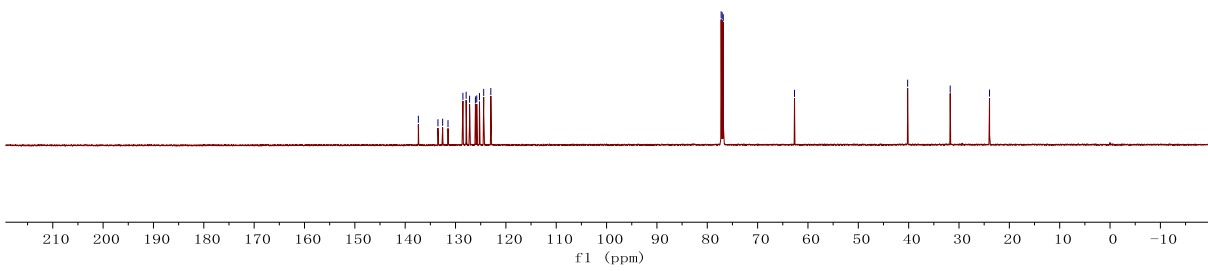
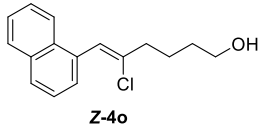
77.246  
77.054  
76.823

62.675

40.200

31.747

23.936



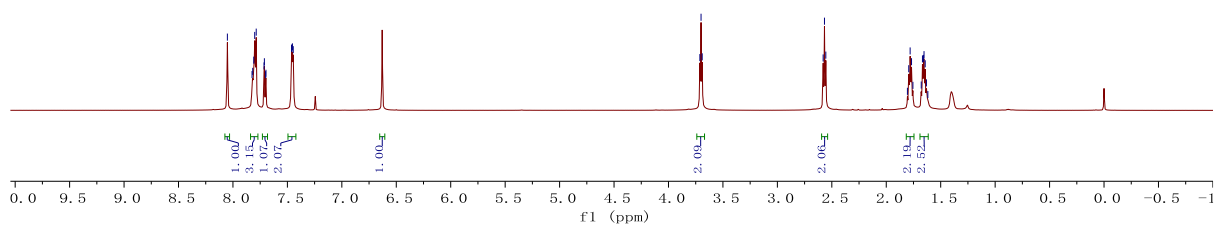
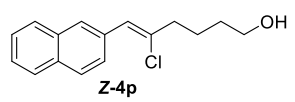


RLQ-1H. 38. fid  
RLQ-173-2

8.051  
7.825  
7.818  
7.809  
7.800  
7.786  
7.714  
7.711  
7.704  
7.697  
7.462  
7.459  
7.454  
7.446

3.712  
3.701  
3.690

2.580  
2.567  
2.558  
2.546  
1.793  
1.781  
1.768  
1.755  
1.679  
1.668  
1.657  
1.653  
1.642  
1.631  
1.618



RLQ-13C. 30. fid  
RLQ-173-2

134.958  
133.220  
132.645  
132.617  
128.208  
128.155  
127.579  
127.559  
126.517  
126.117  
124.717

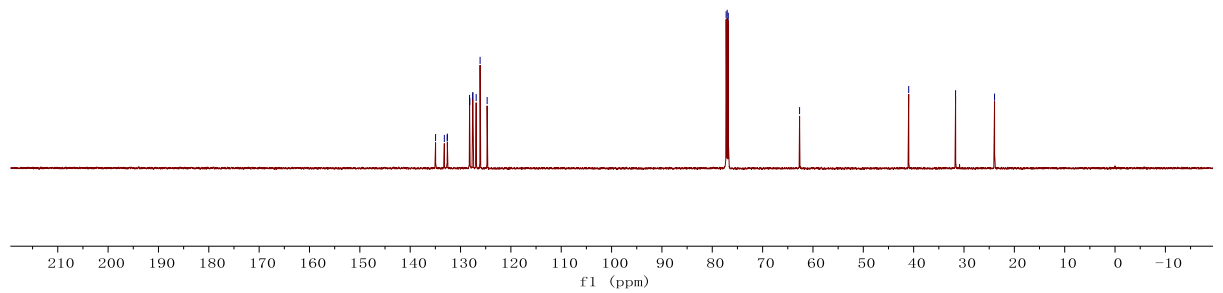
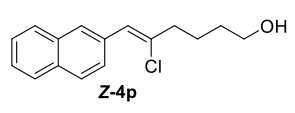
77.245  
77.023  
76.822

62.658

40.984

31.673

23.933



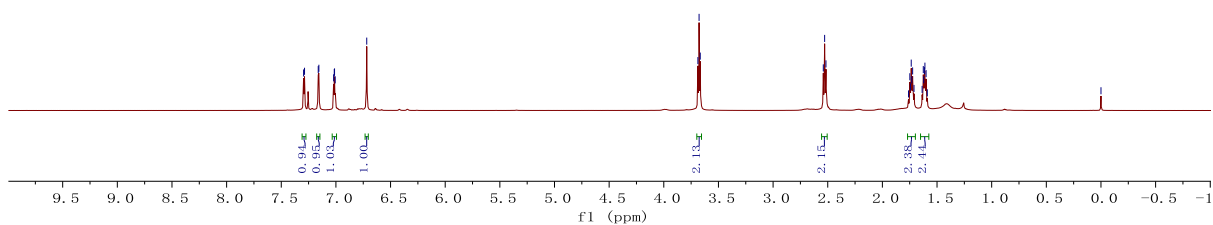
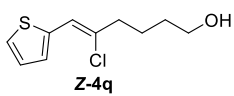
RLQ-1H. 26. fid  
RLQ-164

7.296  
7.287  
7.162  
7.096  
7.022  
7.015  
7.013  
7.006  
6.718

3.688  
3.677  
3.666

2.541  
2.528  
1.761  
1.746  
1.743  
1.736  
1.731  
1.723  
1.711  
1.696  
1.622  
1.613  
1.611  
1.600  
1.589

-0.000



RLQ-13C. 29. fid  
RLQ-164

138.228  
132.523  
128.182  
125.943  
119.085

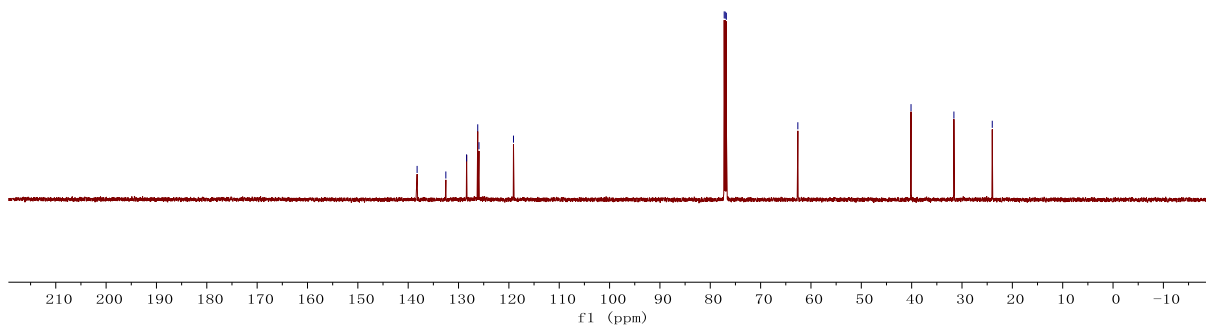
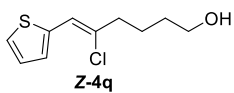
77.233  
77.022  
76.810

62.606

40.127

31.607

23.989



RLQ-1H. 63. fid  
RLQ-187-1

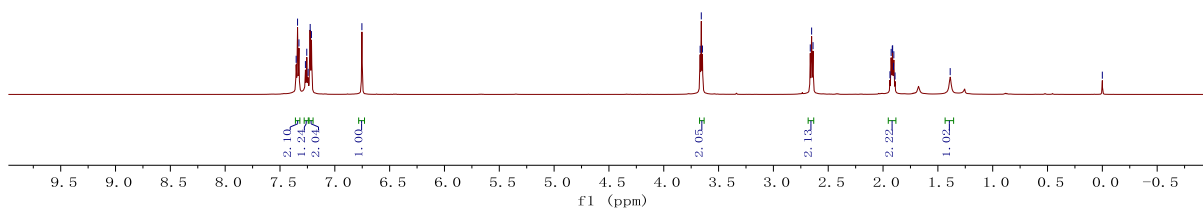
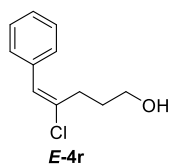
7.353  
7.340  
7.327  
7.268  
7.256  
7.244  
7.225  
7.213  
6.753

3.668  
3.658  
3.647

2.664  
2.651  
2.639

1.937  
1.926  
1.916  
1.912  
1.905  
1.891  
1.888

0.000



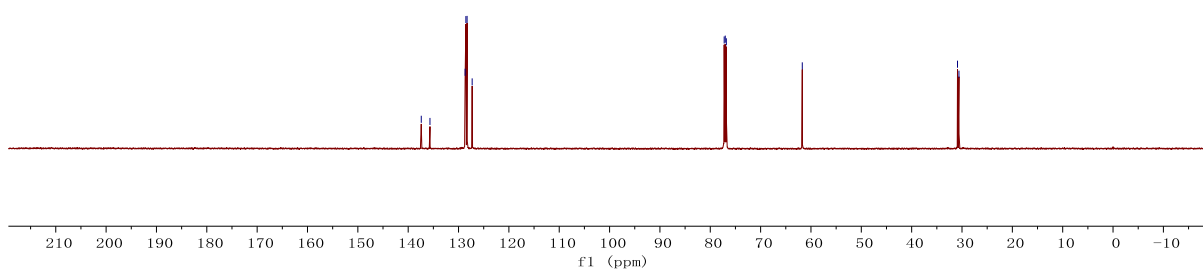
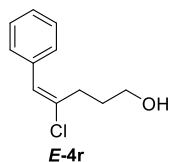
RLQ-13C. 37. fid  
RLQ-187-1

137.404  
135.874  
128.688  
128.639  
128.304  
127.294

77.236  
77.024  
76.813

61.724

30.893  
30.608



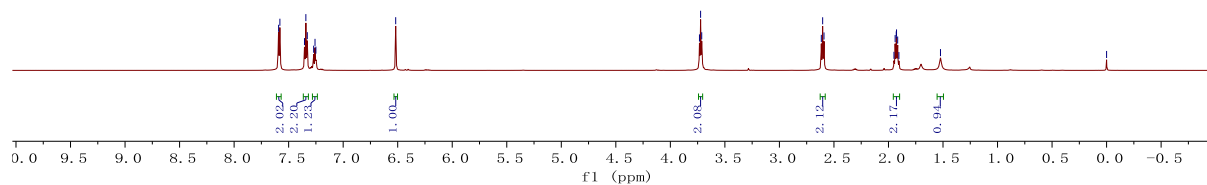
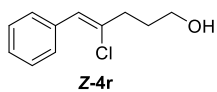
RLQ-1H. 64. fid  
RLQ-187-2

7.592  
7.580  
7.355  
7.342  
7.329  
7.271  
7.258  
7.250  
6.518

3.733  
3.723  
3.712

2.616  
2.604  
2.591  
1.950  
1.939  
1.929  
1.926  
1.916  
1.904  
1.523

0.000



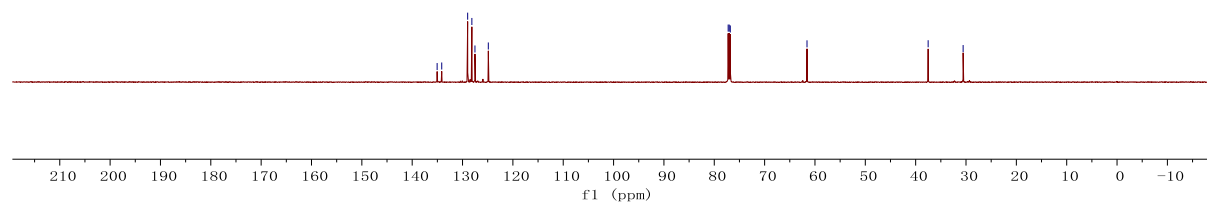
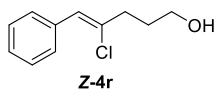
RLQ-13C. 38. fid  
RLQ-187-2

135.045  
134.131  
128.983  
128.149  
127.532  
124.879

77.240  
77.079  
76.917

61.581

37.520  
30.571

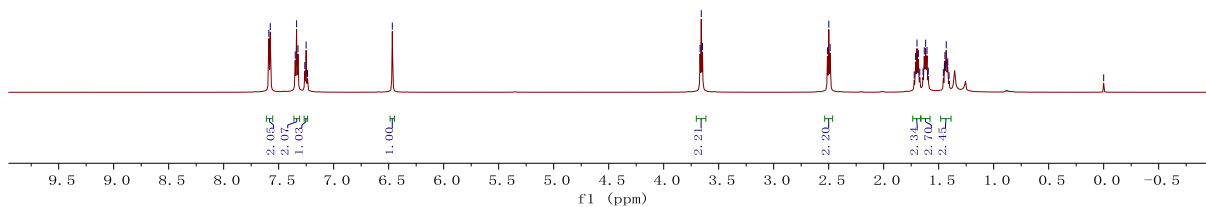
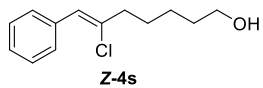


RLQ-1H. 27. fid  
RLQ-163

7.589  
7.576  
7.530  
7.537  
7.537  
7.282  
7.250  
7.238  
— 6.467

3.669  
3.658  
3.647

2.511  
2.499  
2.487  
1.722  
1.710  
1.697  
1.672  
1.672  
1.642  
1.631  
1.619  
1.606  
1.595  
1.457  
1.448  
1.443  
1.433  
1.422  
1.418  
1.406  
— 0.000



RLQ-13C. 28. fid  
RLQ-163

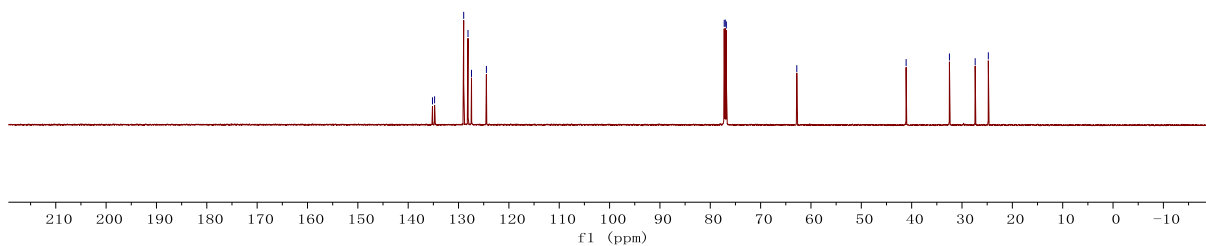
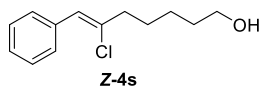
135.174  
134.756  
135.916  
128.118  
127.424  
124.465

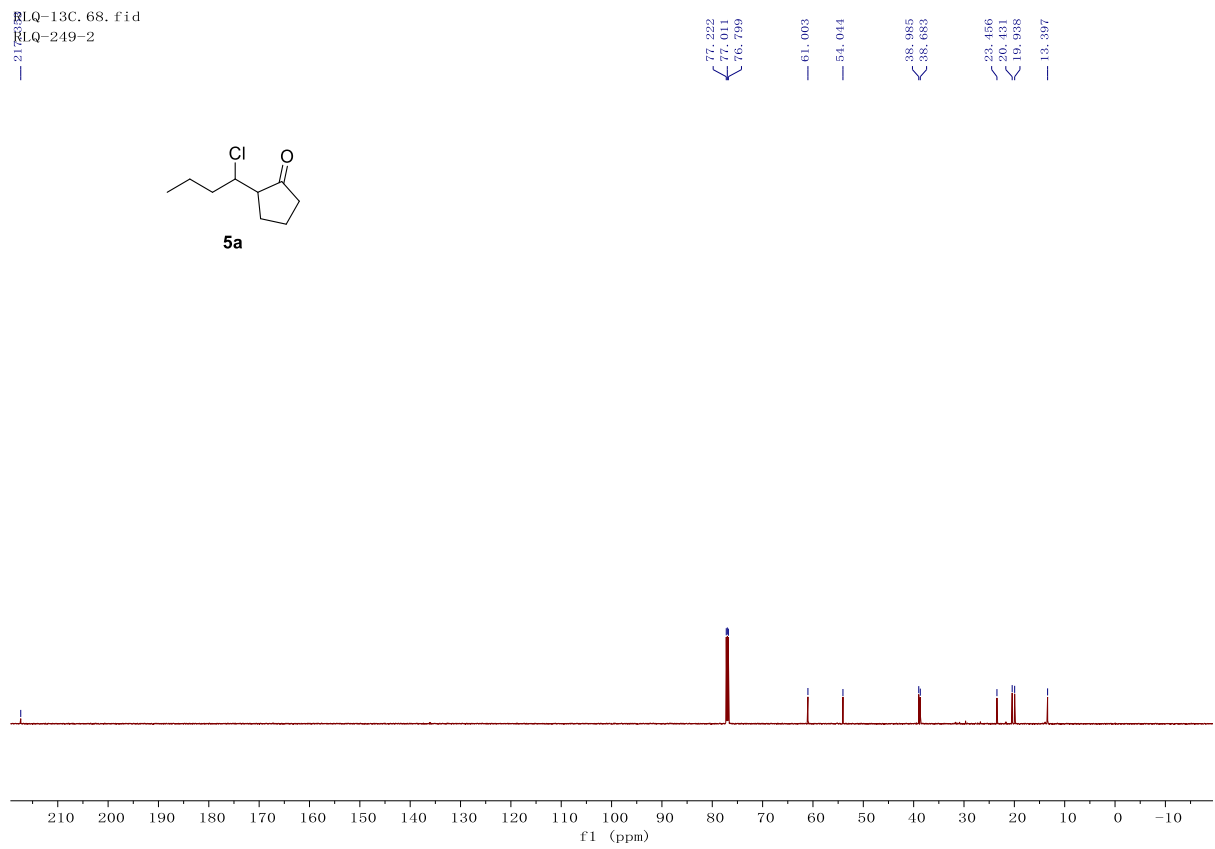
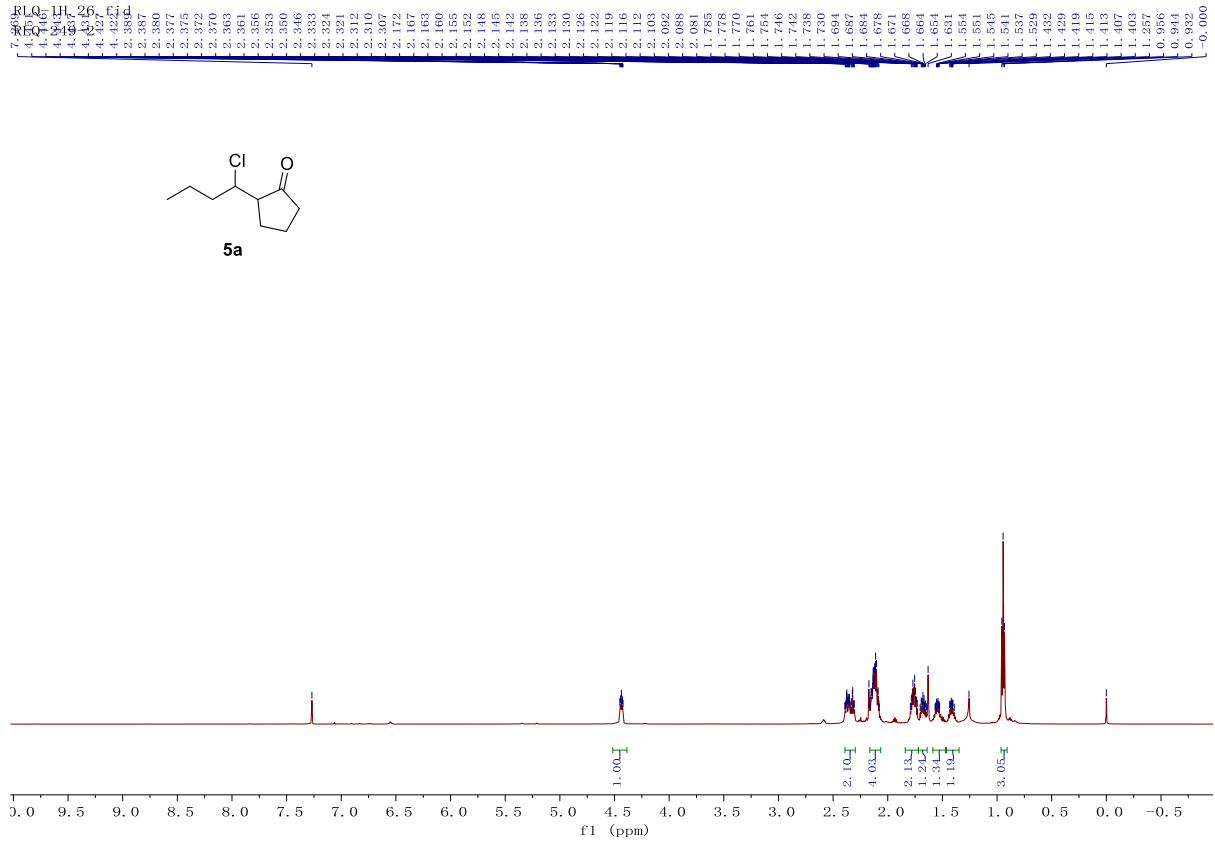
77.230  
77.008  
76.807

— 62.815

— 41.101

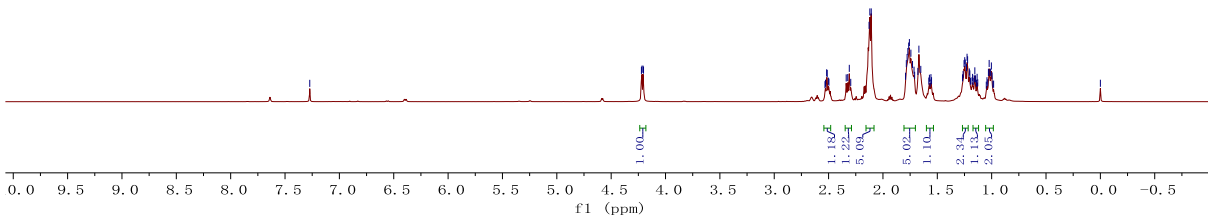
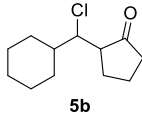
32.487  
27.382  
24.772





RLQ-1H. 28. fid  
RLQ-248

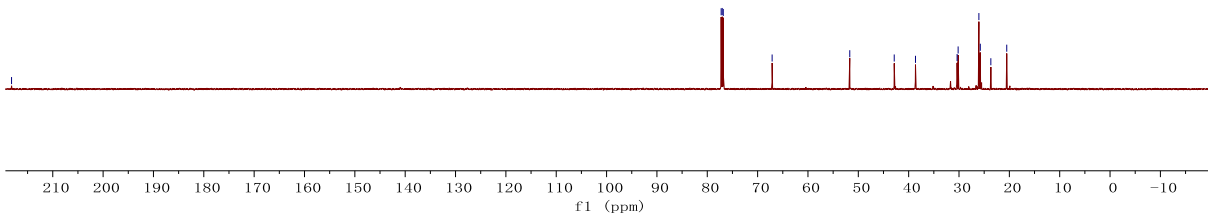
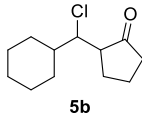
7.273  
4.217  
4.207  
4.202  
2.533  
2.518  
2.513  
2.502  
2.496  
2.338  
2.324  
2.310  
2.296  
2.128  
2.120  
2.108  
1.792  
1.785  
1.771  
1.771  
1.763  
1.757  
1.743  
1.728  
1.714  
1.708  
1.698  
1.688  
1.652  
1.652  
1.578  
1.573  
1.565  
1.558  
1.553  
1.288  
1.283  
1.248  
1.243  
1.232  
1.226  
1.221  
1.206  
1.201  
1.195  
1.175  
1.175  
1.170  
1.161  
1.155  
1.149  
1.140  
1.134  
1.128  
1.114  
1.043  
1.036  
1.030  
1.023  
1.016  
1.010  
1.003  
0.996  
0.988  
0.982  
-0.000



RLQ-13C. 67. fid  
RLQ-248

211  
|

77.244  
77.032  
76.820  
67.117  
51.697  
42.865  
38.644  
30.379  
30.175  
30.076  
25.769  
23.675  
20.517

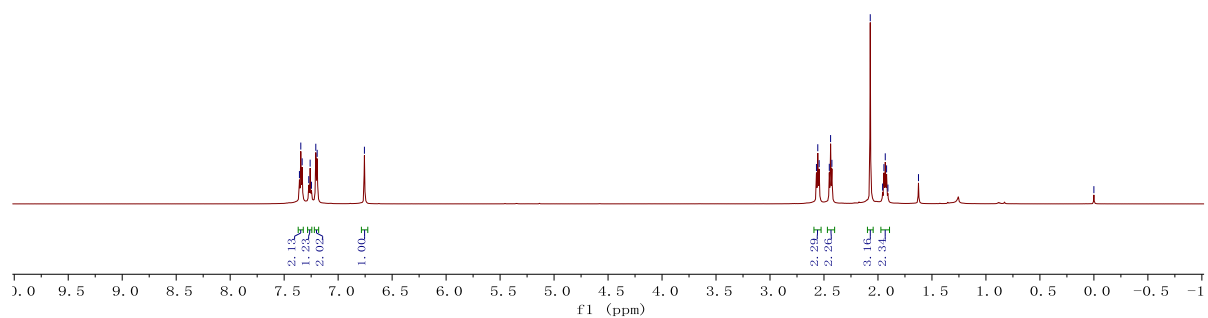
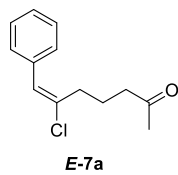


RLQ-1H. 77. fid  
RLQ-128c

7.359  
7.346  
7.333  
7.272  
7.259  
7.247  
7.207  
7.194  
6.757

2.570  
2.557  
2.545  
2.532  
2.439  
2.427  
2.071  
1.957  
1.945  
1.932  
1.920  
1.908  
1.625

0.000



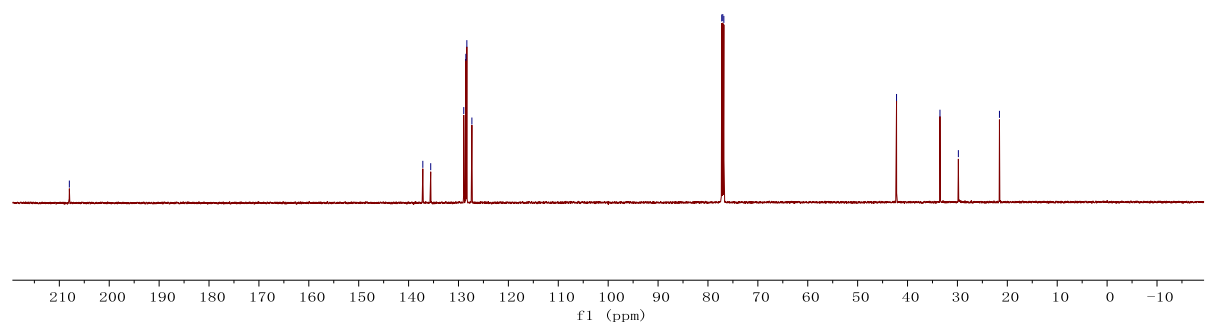
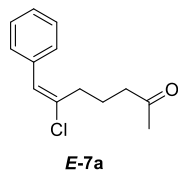
RLQ-13C. 7. fid  
RLQ-128C

203.28

137.149  
135.568  
128.943  
128.523  
128.523  
127.514

77.237  
77.025  
76.814

42.205  
33.498  
29.814  
21.578



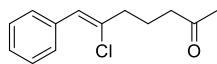


RLQ-1H. 80. fid  
RLQ-128D

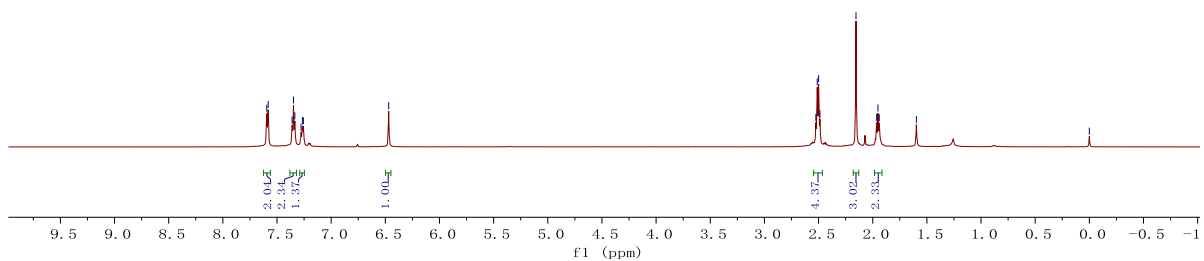
7.594  
7.582  
7.548  
7.348  
7.335  
7.278  
7.265  
7.257  
6.469

2.525  
2.502  
2.487  
2.154  
1.964  
1.952  
1.940  
1.597

0.000



Z-7a



RLQ-13C. 8. fid  
RLQ-128D

208.27

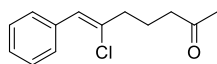
134.937  
133.847  
128.984  
128.165  
127.591  
125.164

77.243  
77.031  
76.819

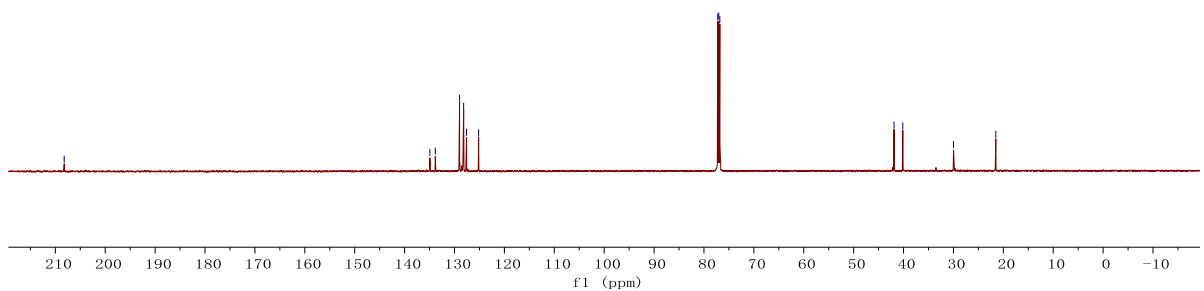
41.907  
40.145

29.978

21.508



Z-7a

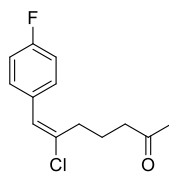


RLQ-1H. 90. fid  
RLQ-209-1

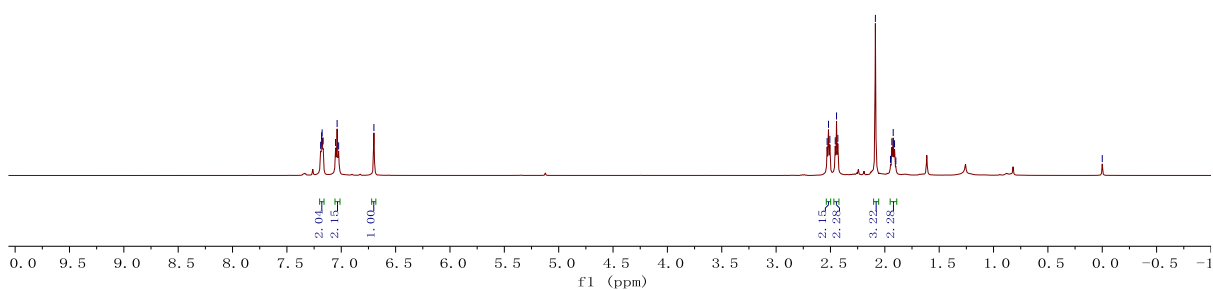
7.190  
7.181  
7.176  
7.167  
7.052  
7.038  
7.024  
6.700

2.531  
2.518  
2.506  
2.496  
2.484  
2.432  
2.087  
1.948  
1.835  
1.823  
1.911  
1.899

-0.000



**E-7b**



RLQ-13C. 44. fid  
RLQ-209-1

162.728  
161.088

137.197  
131.579  
130.574  
130.021  
129.871  
127.794

115.561  
115.418

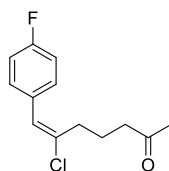
77.214  
77.005  
76.791

42.173

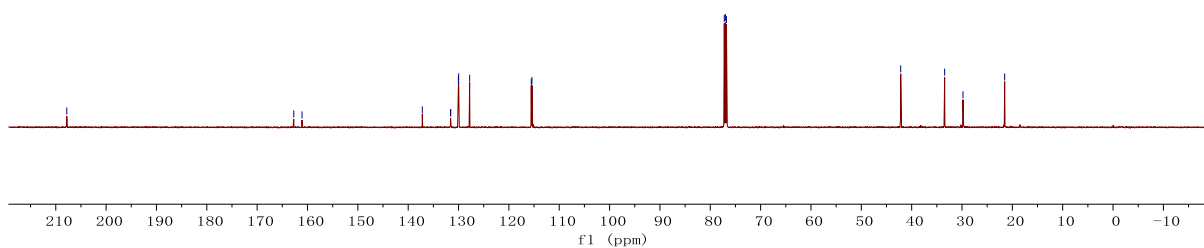
33.449

29.803

21.528

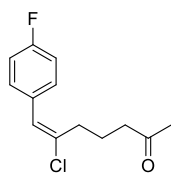


**E-7b**

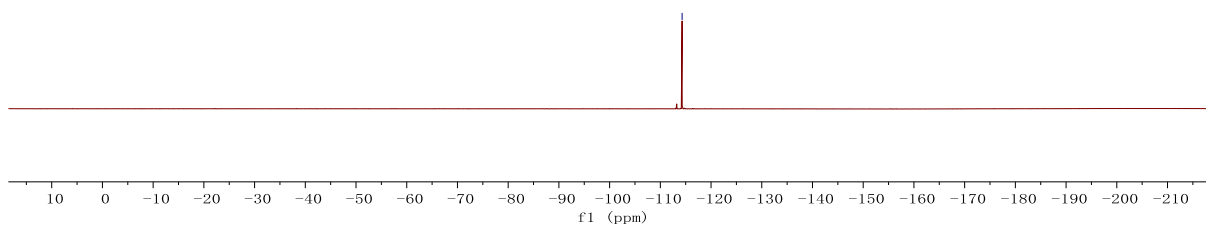


RLQ-265-1. 1. fid

-114.295



**E-7b**



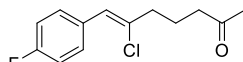
RLQ-1H. 91. fid  
RLQ-209-2

7.575  
7.566  
7.560  
7.551  
7.042  
7.027  
7.015

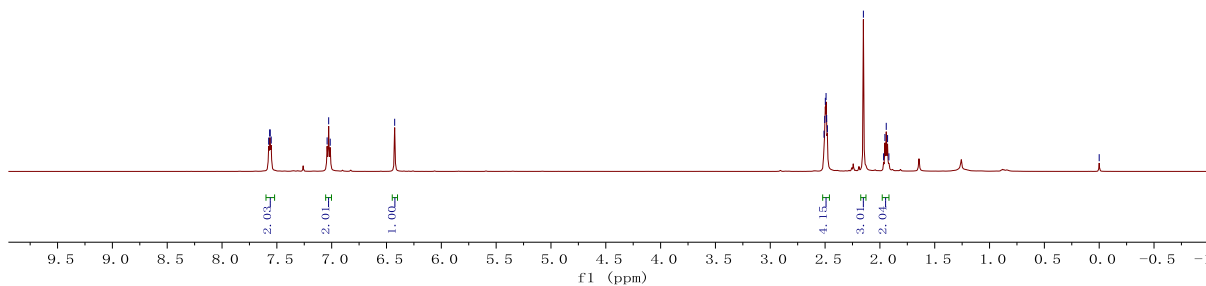
6.425

2.510  
2.503  
2.498  
2.491  
2.486  
2.479  
2.471  
2.466  
1.954  
1.942  
1.930  
1.918

0.000



**Z-7b**



RLQ-193-C. 45. fid

RLQ-209-2

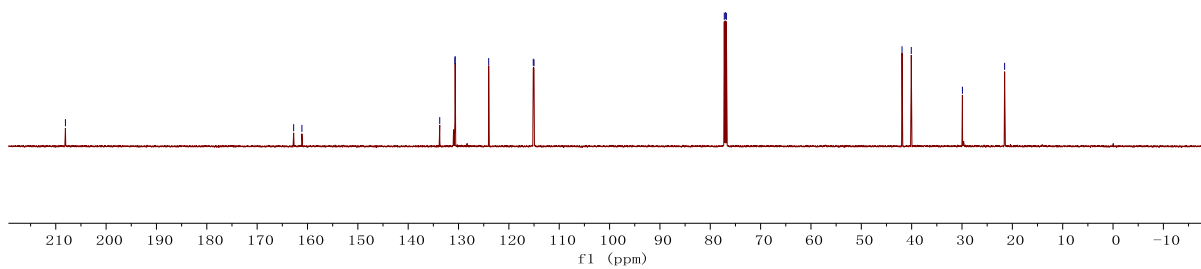
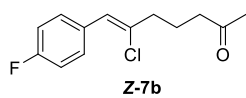
208.838

162.751  
161.109

133.735  
130.719  
130.667  
124.010  
115.155  
115.013

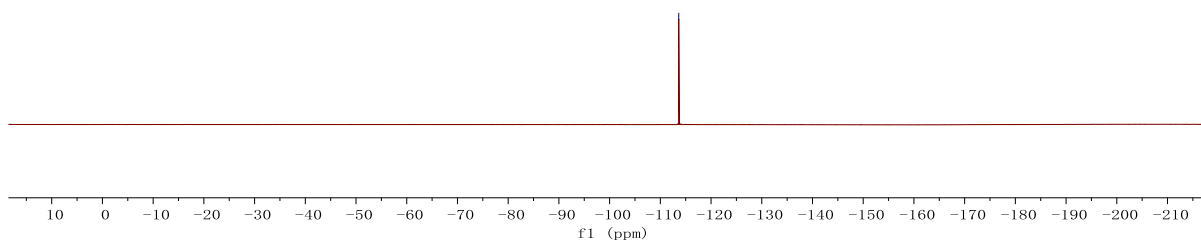
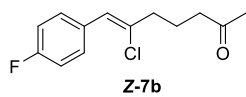
77.219  
77.007  
76.756

41.012  
40.077  
29.920  
21.535



RLQ-265-2. 1. fid

-113.629

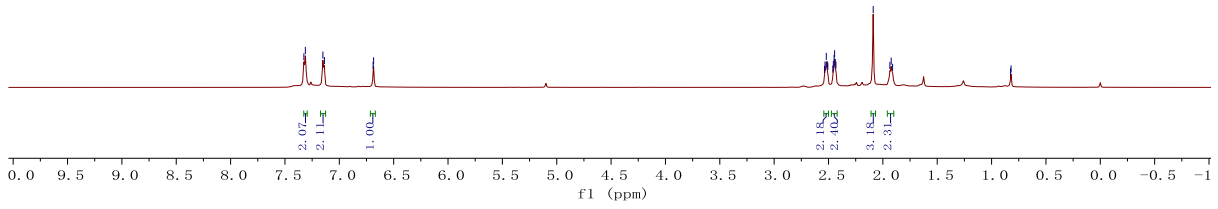
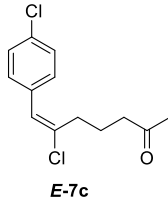


RLQ-1H. 89. fid  
RLQ-210-1

7.326  
7.312  
7.151  
7.137  
6.689  
6.685

2.536  
2.532  
2.520  
2.511  
2.506  
2.460  
2.456  
2.449  
2.438  
2.432  
2.089  
1.936  
1.923  
1.911

0.825  
0.821



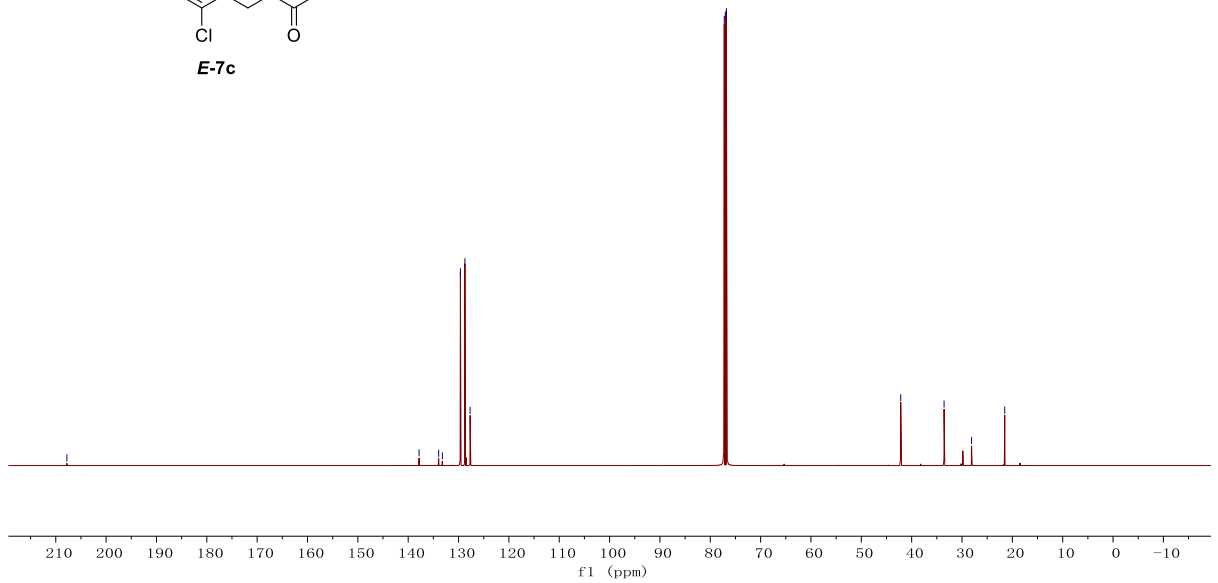
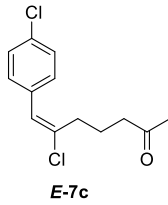
RLQ-13C/70  
RLQ-210-1

200.761

137.836  
135.215  
133.215  
129.630  
128.732  
127.703

77.221  
77.008  
76.795

42.172  
33.561  
28.104  
21.514

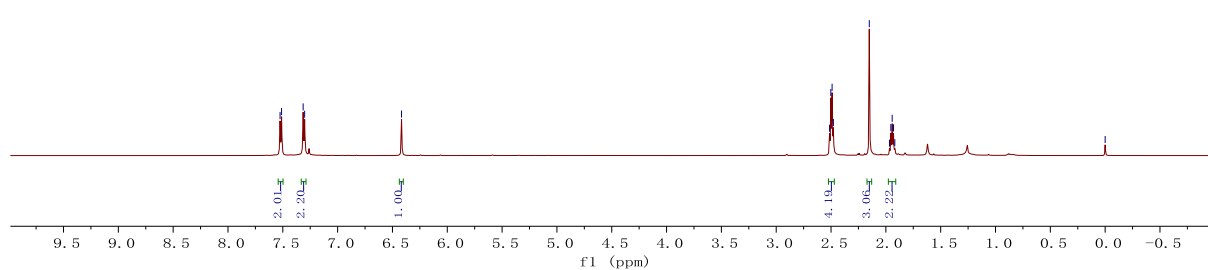
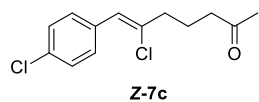


RLQ-1H. 92. fid  
RLQ-210-2

7.525  
7.511  
7.315  
7.301  
6.417

2.513  
2.502  
2.490  
2.479  
2.151  
1.967  
1.855  
1.842  
1.830  
1.918

0.000



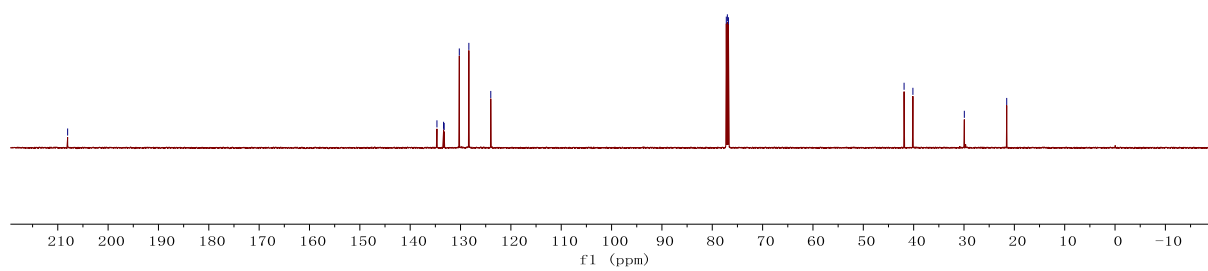
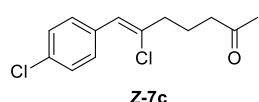
RLQ-13C. 46. fid  
RLQ-210-2

200.000

134.686  
133.385  
132.216  
130.214  
128.316  
123.992

77.214  
77.003  
76.791

41.903  
40.150  
29.937  
21.515

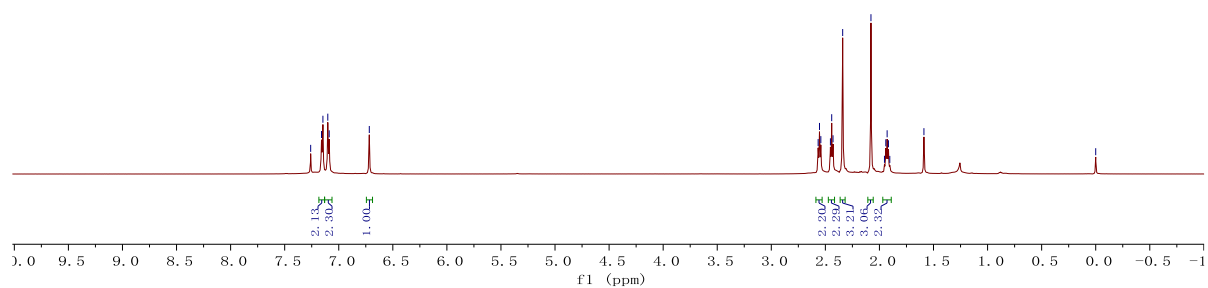
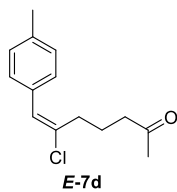


RLQ-1H. 78. fid  
RLQ-129c

7.260  
7.159  
7.146  
7.101  
7.088  
6.718

2.567  
2.554  
2.542  
2.453  
2.441  
2.429  
2.340  
2.308  
2.298  
2.211  
1.953  
1.941  
1.929  
1.917  
1.904  
1.588

0.000



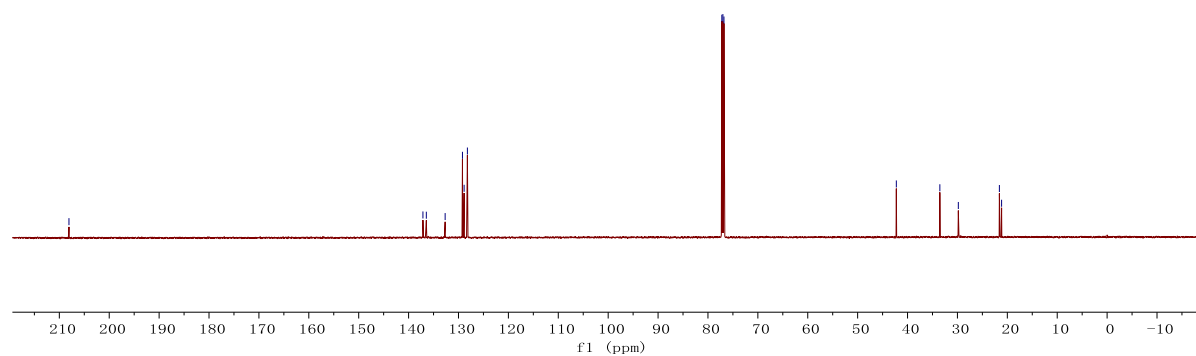
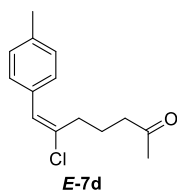
RLQ-13C. 9. fid  
RLQ-129C

208.20

137.128  
136.444  
132.675  
129.205  
128.871  
128.214

77.218  
77.007  
76.795

42.246  
33.524  
29.818  
21.593  
21.149



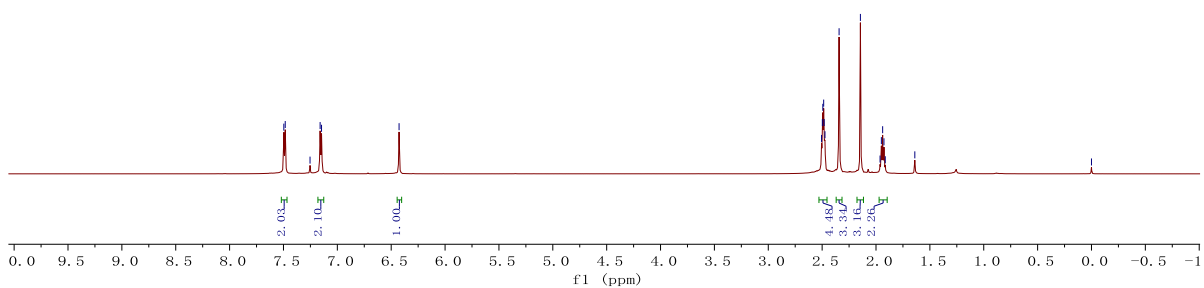
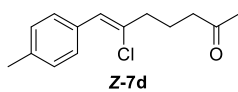
RLQ-1H. 79. fid  
RLQ-129D

7.497  
7.484  
7.253  
7.160  
7.147

6.427

2.506  
2.498  
2.494  
2.486  
2.481  
2.474  
2.343  
2.145  
1.962  
1.950  
1.938  
1.926  
1.911  
1.610

0.000



RLQ-13C. 10. fid  
RLQ-129D

200.257

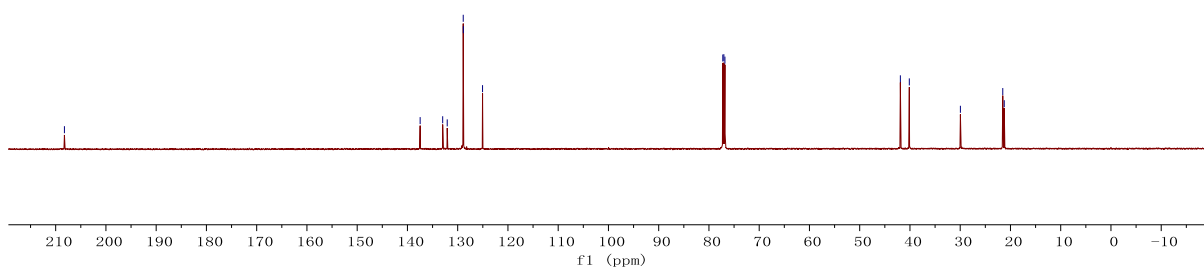
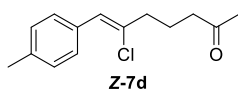
137.471  
132.986  
132.084  
128.896  
128.872  
125.054

77.244  
77.002  
76.821

41.910  
40.128

29.963

21.530  
21.237





RLQ-1H. 69. fid  
RLQ-202

7.492  
7.478

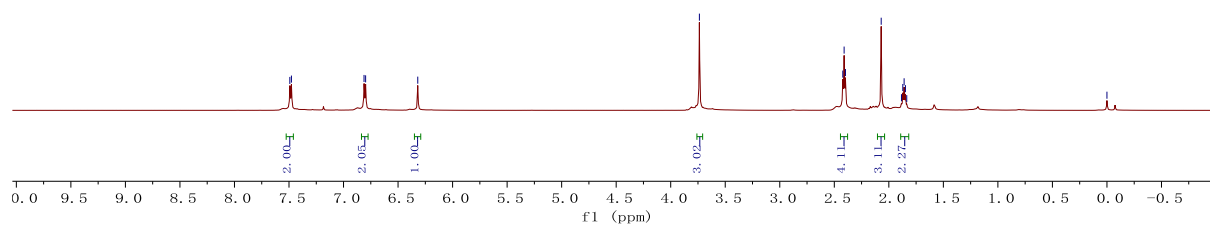
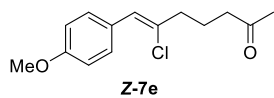
6.812  
6.797

6.319

3.737

2.422  
2.410  
2.398  
2.070  
1.884  
1.872  
1.860  
1.848  
1.836

0.000



RLQ-13C. 39. fid  
RLQ-202

200.383

158.965

131.881  
130.306  
127.560  
124.572

113.608

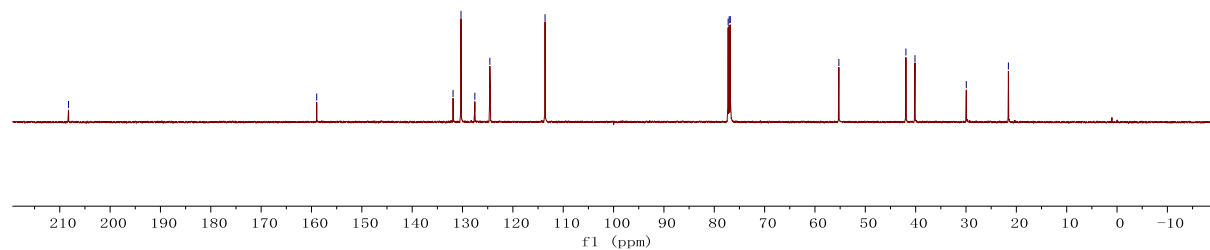
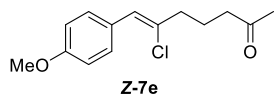
77.244  
77.033  
76.821

55.249

41.932  
40.134

29.945

21.579



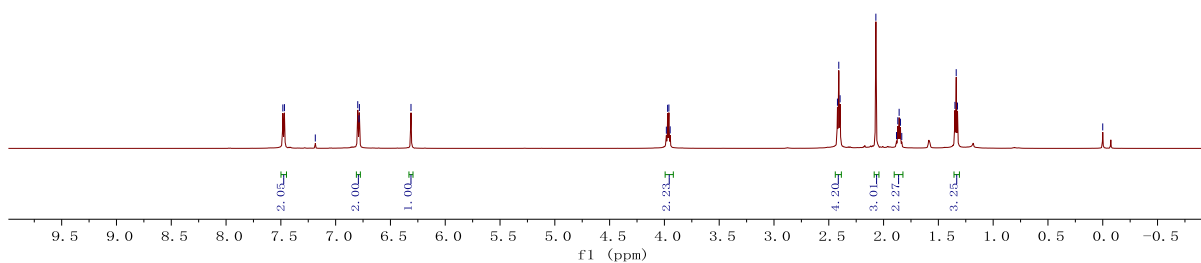
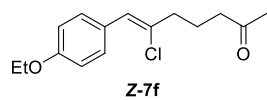
RLQ-1H. 14. fid  
RLQ-237

7.482  
7.467  
7.186  
6.798  
6.787  
6.783  
6.313

3.982  
3.974  
3.959  
3.947

2.421  
2.409  
2.394  
2.070  
1.882  
1.870  
1.858  
1.846  
1.834  
1.389  
1.337  
1.326

0.000



RLQ-13C. 58. fid  
RLQ-237

203.333

158.333

131.714  
130.296  
127.379  
124.820

114.146

77.247  
77.055  
76.824

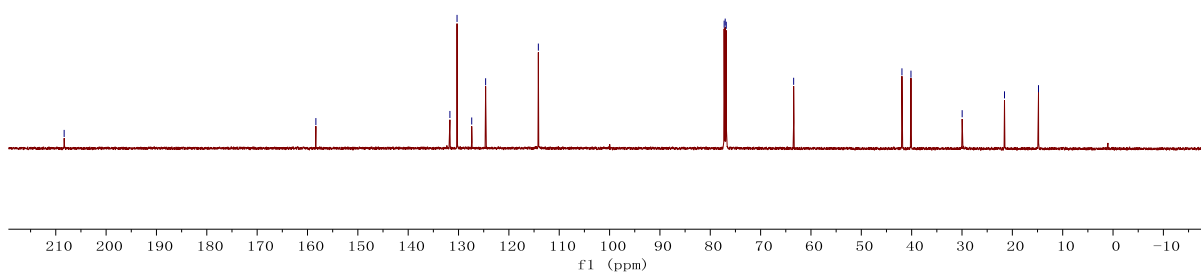
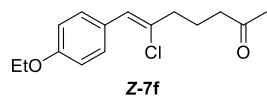
63.437

41.098  
40.138

29.967

21.560

14.806

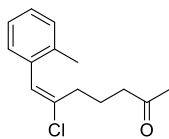


RLQ-1H. 9. fid  
RLQ-236-1

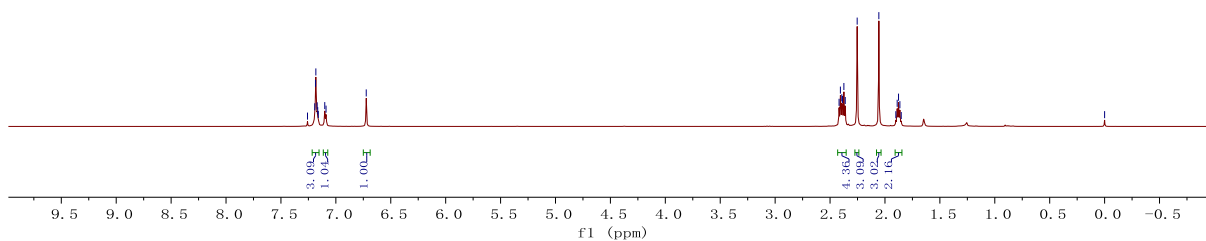
7.258  
7.192  
7.186  
7.152  
7.152  
7.145  
7.160  
7.101  
7.089  
6.723

2.418  
2.406  
2.393  
2.386  
2.374  
2.362  
2.253  
2.056  
1.889  
1.876  
1.864  
1.852

0.000



**E-7g**



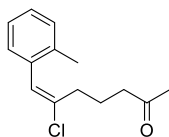
RLQ-13C. 56. fid  
RLQ-236-1

203.38

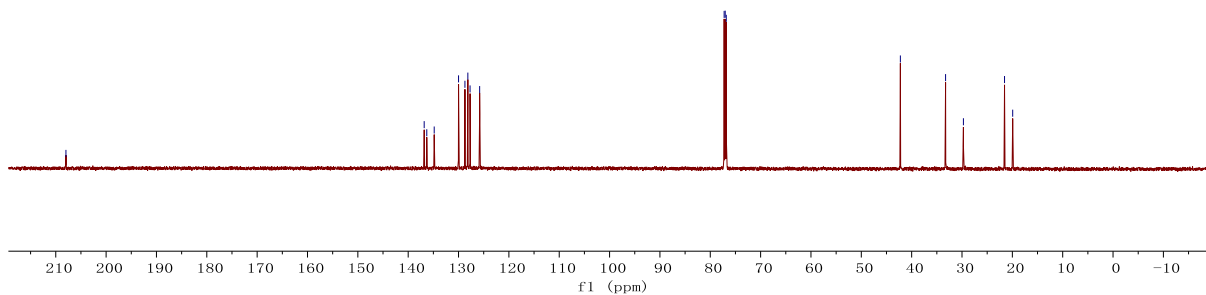
136.823  
136.309  
134.832  
129.897  
128.731  
128.149  
127.711  
123.806

77.244  
77.022  
76.822

42.242  
33.263  
29.719  
21.583  
19.931



**E-7g**

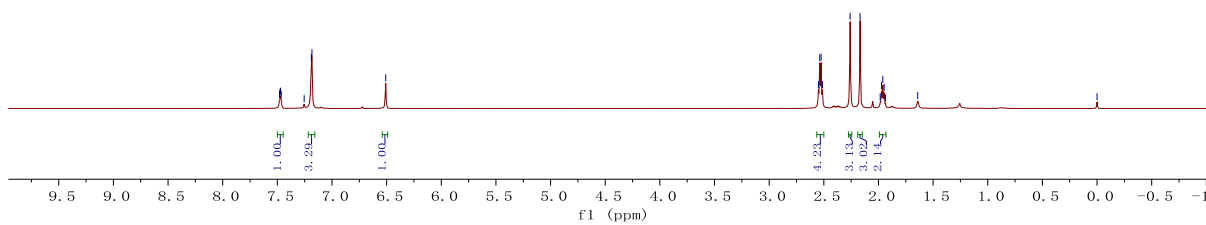
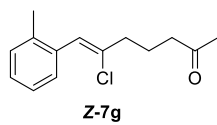


RLQ-1H. 8. fid  
RLQ-236-2

7.480  
7.476  
7.471  
7.466  
7.255  
7.189  
7.183  
6.508

2.549  
2.537  
2.525  
2.512  
2.500  
2.488  
2.1984  
1.972  
1.960  
1.948  
1.936  
1.641

0.000



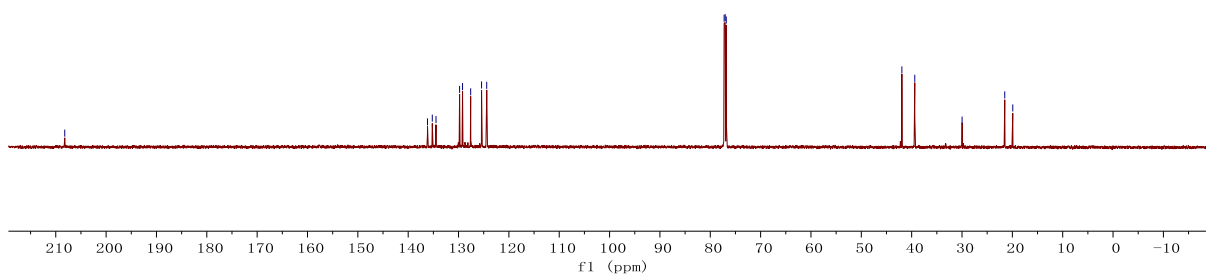
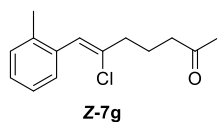
RLQ-13C. 57. fid  
RLQ-236-2

203.22

136.168  
135.216  
134.474  
129.791  
129.205  
127.588  
125.429  
124.401

77.248  
77.036  
76.821

41.943  
39.382  
29.982  
21.509  
19.916



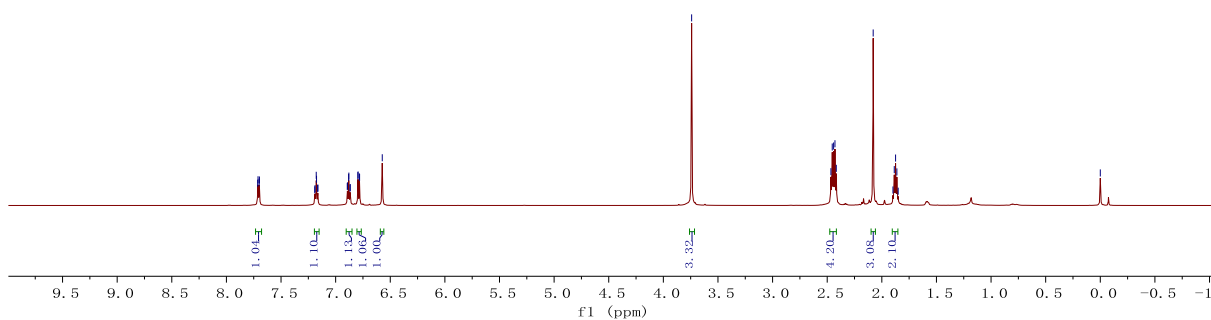
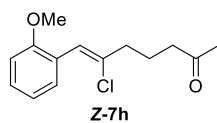
RLQ-1H. 81. fid  
RLQ-205

7.714  
7.711  
7.701  
7.698  
7.191  
7.188  
7.178  
7.175  
7.162  
6.893  
6.892  
6.881  
6.879  
6.869  
6.867  
6.796  
6.783  
6.781  
6.573

3.741

2.466  
2.454  
2.429  
2.417  
2.079  
1.898  
1.886  
1.874  
1.862  
1.850

-0.000



RLQ-13C. 41. fid  
RLQ-205

200.333

155.833

133.105  
128.885  
127.834  
122.941  
119.461  
119.055

109.318

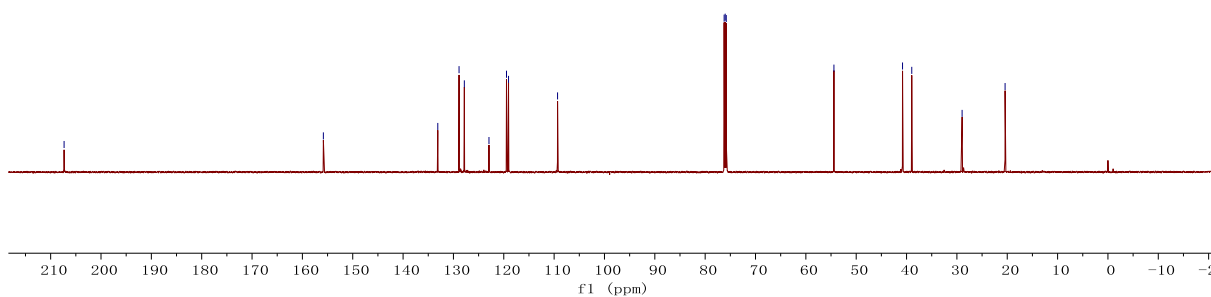
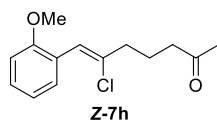
76.232  
75.064  
75.069

54.424

40.769  
38.965

28.965

20.437

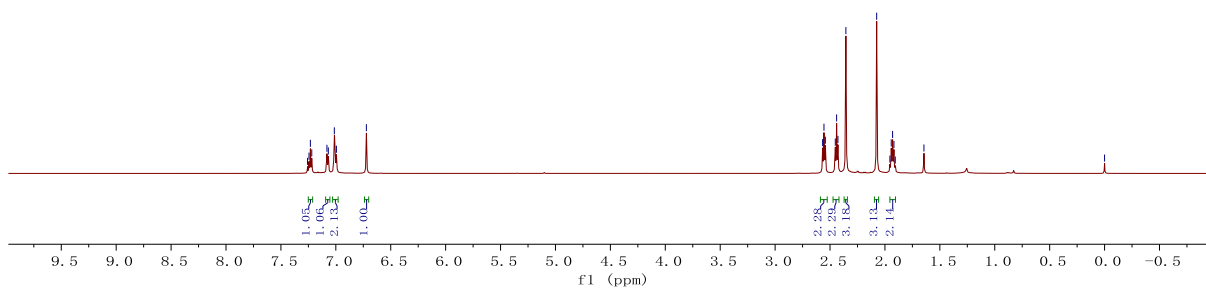
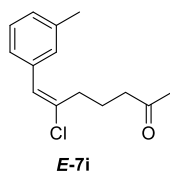


RLQ-1H. 10. fid  
RLQ-235-1

7.258  
7.244  
7.232  
7.218  
7.081  
7.068  
7.014  
6.995  
6.722

2.567  
2.555  
2.543  
2.452  
2.440  
2.428  
2.356  
2.075  
1.955  
1.943  
1.930  
1.918  
1.906  
1.645

0.000



RLQ-13C. 54. fid  
RLQ-2005-1

200.55

138.167  
136.924  
135.926  
129.042  
128.400  
128.076  
125.341

77.244  
77.023  
76.822

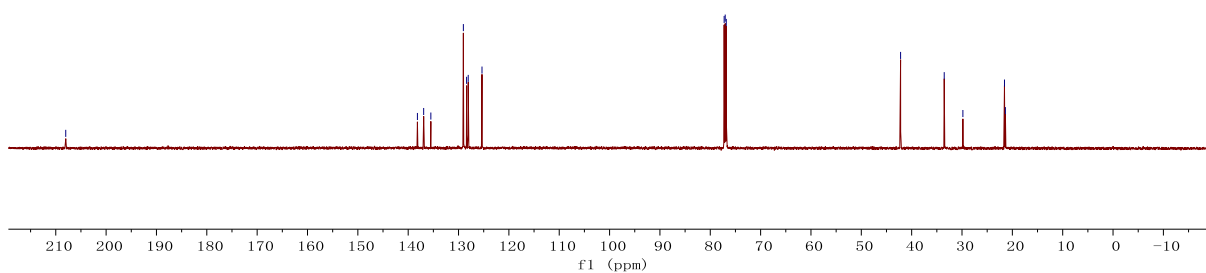
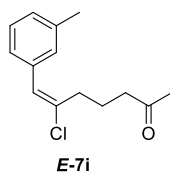
42.198

33.531

29.825

21.562

21.385

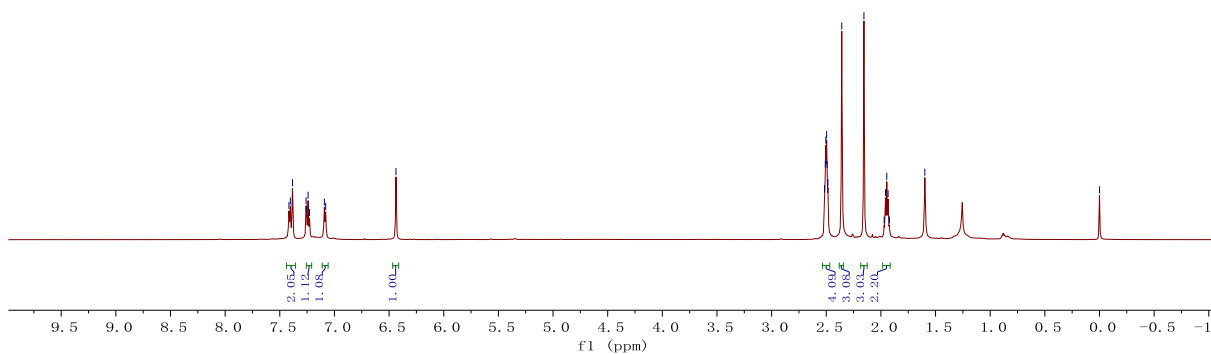
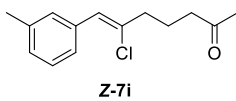


RLQ-1H. 6. fid  
RLQ-235-2

7.416  
7.393  
7.360  
7.254  
7.241  
7.229  
7.092  
7.080  
6.437

2.516  
2.509  
2.504  
2.496  
2.492  
2.484  
2.358  
2.155  
1.970  
1.968  
1.968  
1.934  
1.922  
1.598

0.000



RLQ-13C. 55. fid  
RLQ-235-2

200.328

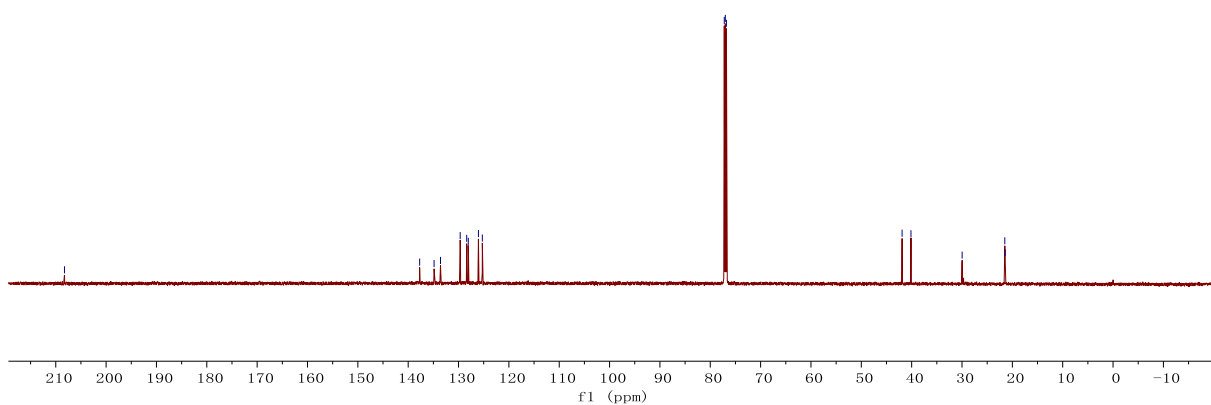
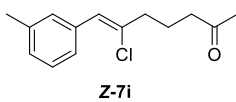
137.726  
134.855  
133.585  
129.673  
128.375  
128.063  
125.672  
123.272

77.219  
77.007  
76.796

41.898  
40.136

29.977

21.499  
21.433

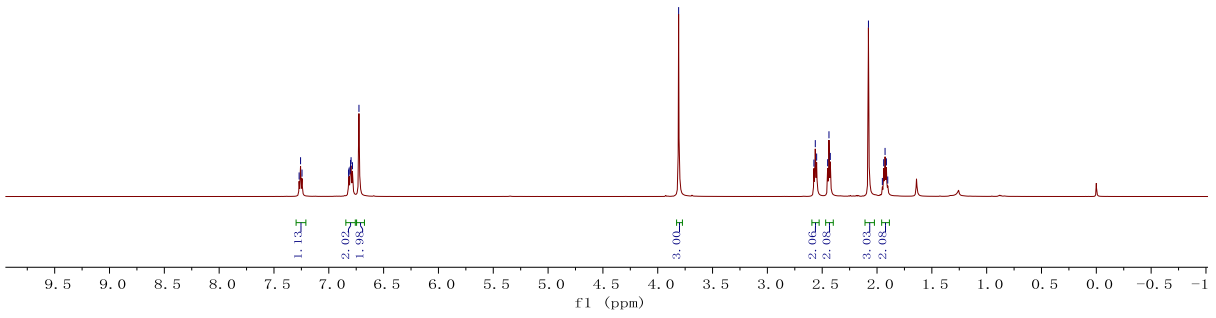
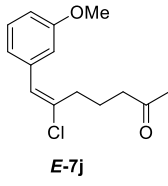


RLQ-1H. 82. fid  
RLQ-206-1

7.271  
7.257  
7.244  
6.819  
6.813  
6.806  
6.800  
6.797  
6.784  
6.725

3.809

2.576  
2.463  
2.450  
2.438  
2.436  
2.078  
1.951  
1.939  
1.927  
1.914  
1.902



RLQ-13C. 42. fid  
RLQ-206-1

200.042

159.862

137.398  
136.885  
129.515  
128.812  
120.751  
114.829  
112.825

77.223  
77.012  
76.800

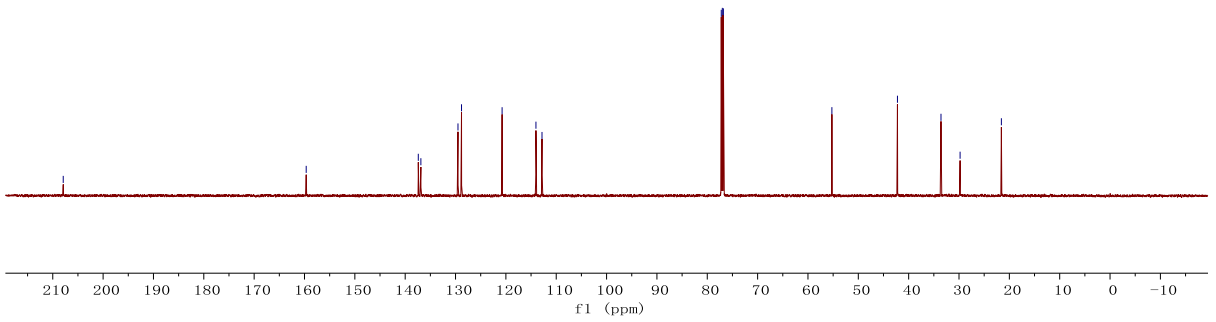
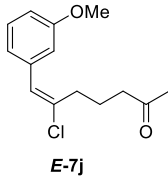
55.247

42.224

33.578

29.785

21.582





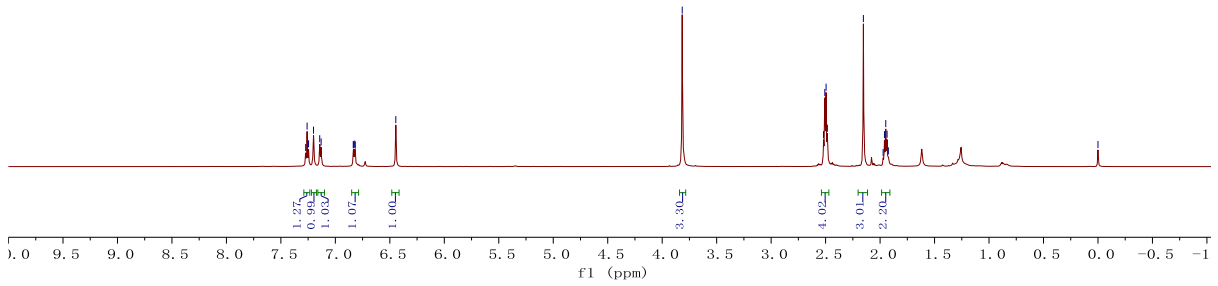
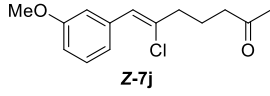
RLQ-1H. 83. fid  
RLQ-206-2

7.272  
7.259  
7.246  
7.200  
7.144  
7.131  
6.836  
6.823  
6.810  
6.818  
6.445

3.815

2.519  
2.507  
2.496  
2.384  
2.375  
2.372  
1.960  
1.948  
1.936  
1.924

0.000



RLQ-13C. 43. fid  
RLQ-206-2

200.1

159.392

136.209  
134.073  
129.103  
125.053  
121.676

114.349  
113.301

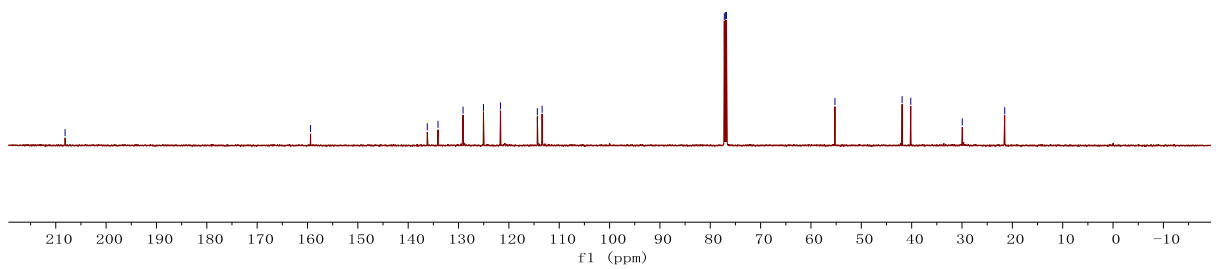
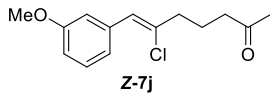
77.216  
77.064  
76.792

55.235

41.896  
40.178

29.948

21.518

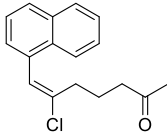


RLQ-1H. 93. f1d  
RLQ-211-1

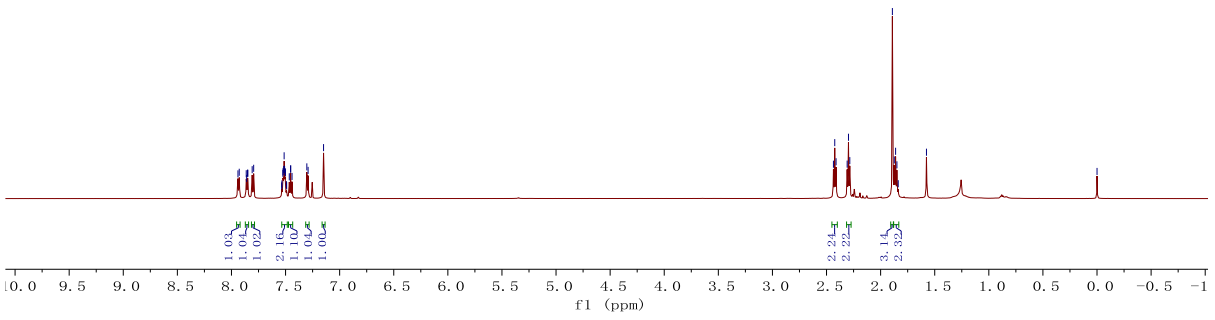
7.9106  
7.8653  
7.8659  
7.8488  
7.8009  
7.7955  
7.5365  
7.5341  
7.5222  
7.5177  
7.5113  
7.5009  
7.5004  
7.5001  
7.4993  
7.4990  
7.4966  
7.4952  
7.4452  
7.4400  
7.3003  
7.2992  
7.1499

2.4386  
2.4324  
2.4112  
2.3309  
2.2987  
2.2967  
1.8901  
1.8774  
1.8652  
1.8449  
1.8377  
1.5776

-0.000



E-7k



RLQ-13C. 47. f1d  
RLQ-211-1

207.388

138.154  
133.554  
132.833  
131.689  
128.469  
128.127  
127.157  
126.334  
125.566  
126.008  
125.377  
124.707

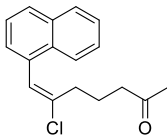
77.224  
77.012  
76.800

42.059

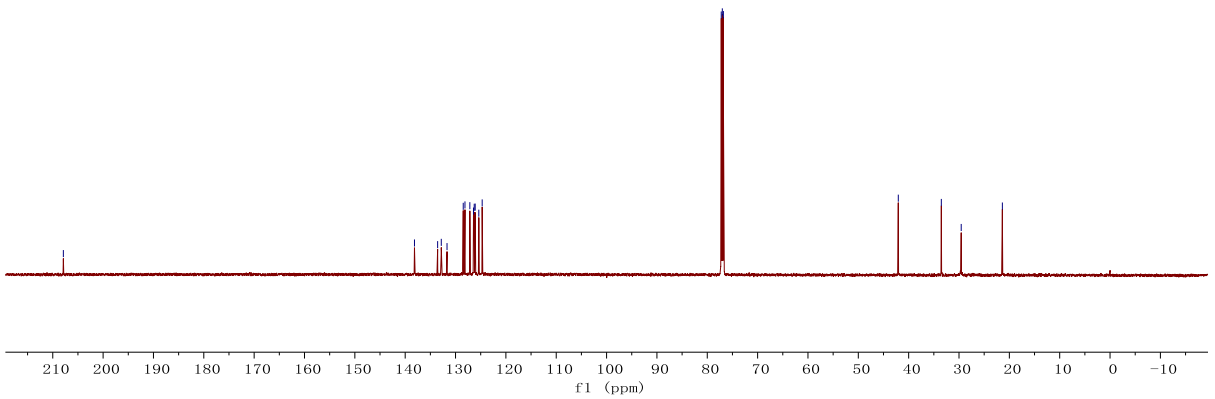
33.510

29.562

21.388



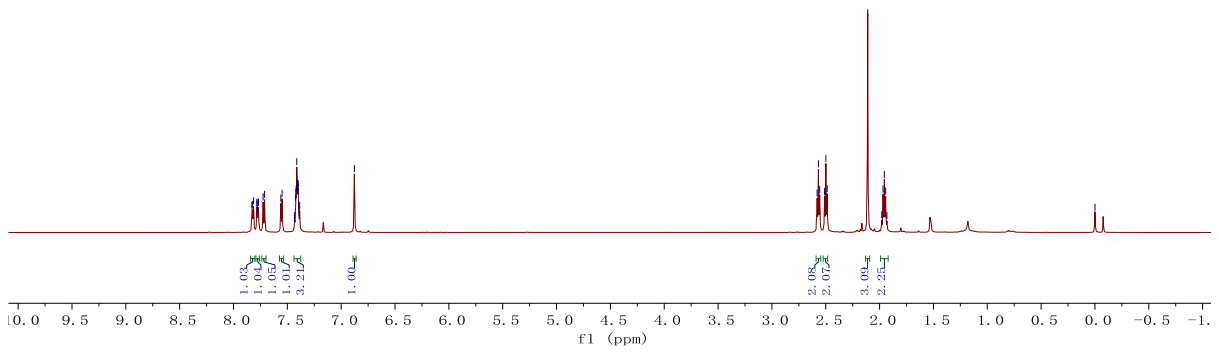
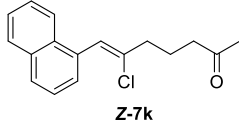
E-7k



RLQ-11.91.fid  
 7.823  
 7.821  
 7.798  
 7.776  
 7.768  
 7.725  
 7.712  
 7.561  
 7.549  
 7.424  
 7.421  
 7.418  
 7.406  
 7.405  
 7.402  
 7.398  
 7.394  
 6.388

2.580  
 2.568  
 2.556  
 2.511  
 2.499  
 2.487  
 2.110  
 1.980  
 1.966  
 1.956  
 1.944  
 1.932

-0.000



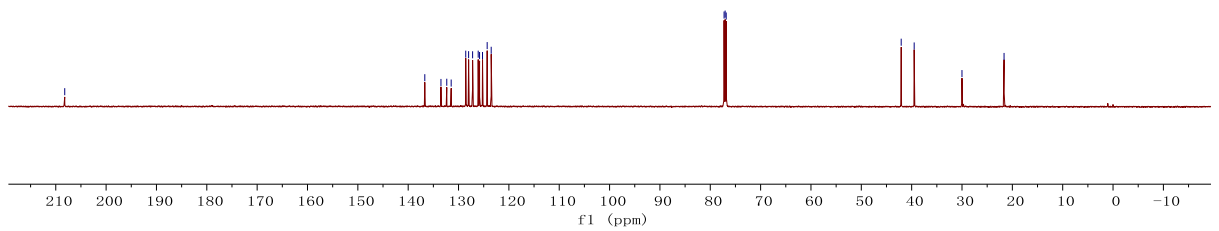
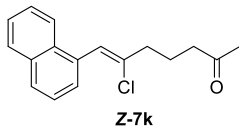
RLQ-12C.48.fid  
 RLQ-21-2

209.23

136.700  
 133.492  
 132.339  
 129.566  
 128.569  
 127.998  
 127.204  
 126.096  
 125.823  
 125.236  
 124.313  
 123.512

77.259  
 77.012  
 76.835

42.077  
 39.500  
 30.005  
 21.646



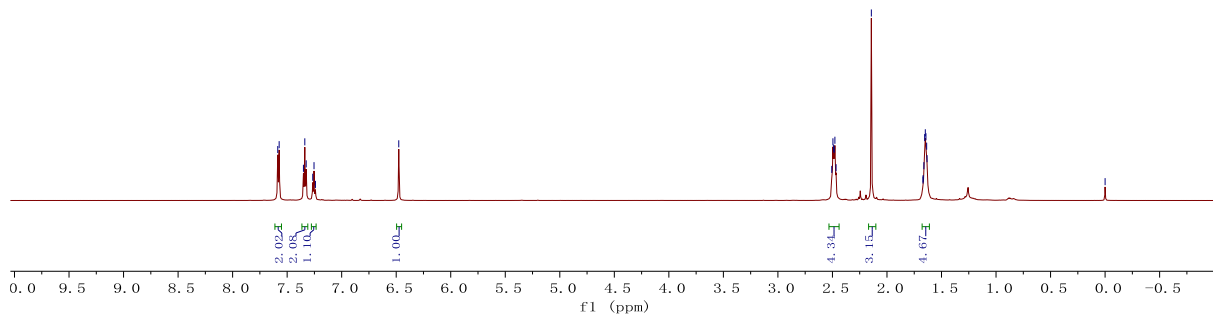
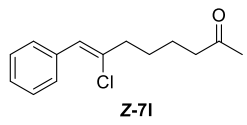
RLQ-1H. 97. fid  
RLQ-216-2

7.5866  
7.5773  
7.3511  
7.3338  
7.3225  
7.2951  
7.2591  
7.2411

6.477

2.5006  
2.4966  
2.4899  
2.4885  
2.4778  
2.467  
2.143  
1.668  
1.652  
1.654  
1.649  
1.643  
1.636  
1.632

-0.000



RLQ-13C. 49. fid  
RLQ-216-2

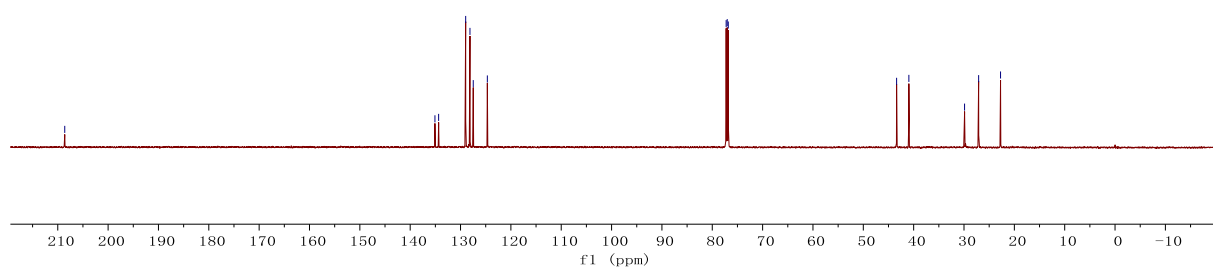
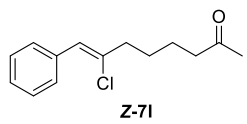
200.36

135.085  
131.951  
128.980  
128.126  
127.474  
124.674

77.203  
77.032  
76.820

43.388  
40.951

29.889  
27.093  
22.741



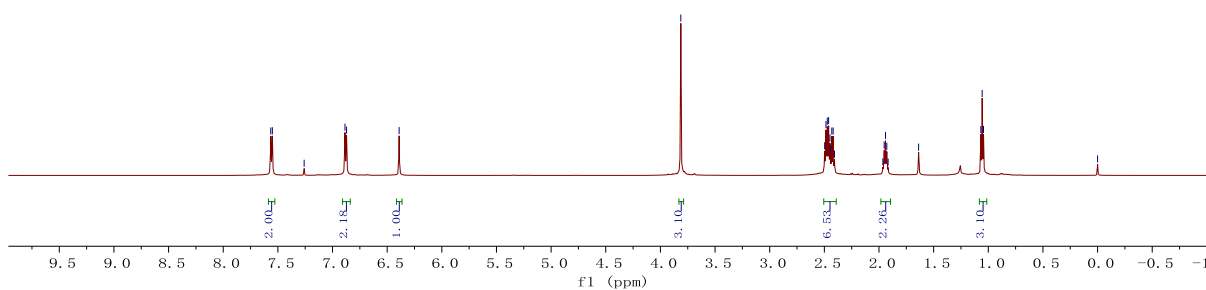
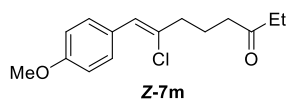
RLQ-1H. 15. fid  
RLQ-238

7.565  
7.550  
7.260  
6.886  
6.871  
6.391

3.813  
2.497  
2.485  
2.473  
2.461  
2.449  
2.444  
2.432  
2.416  
2.407  
1.965  
1.953  
1.941  
1.929  
1.917  
1.637

1.068  
1.056  
1.044

0.000



RLQ-13C. 59. fid  
RLQ-238

211.902  
211.338

158.933

131.969  
130.300  
127.574  
124.513

113.592

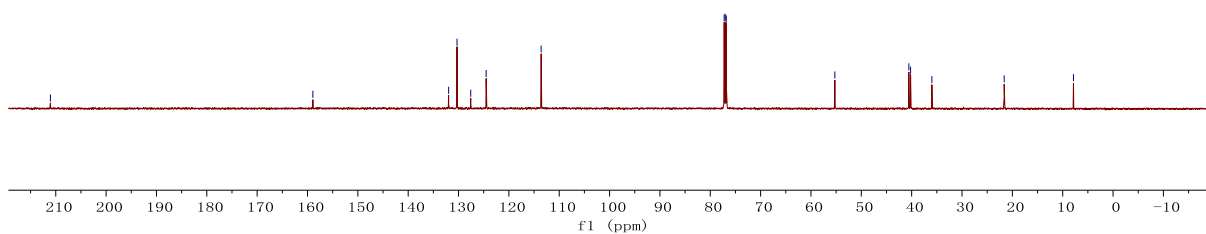
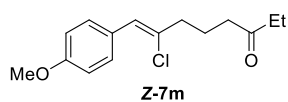
77.239  
77.027  
76.816

55.256

40.558  
40.217  
35.986

21.622

7.863

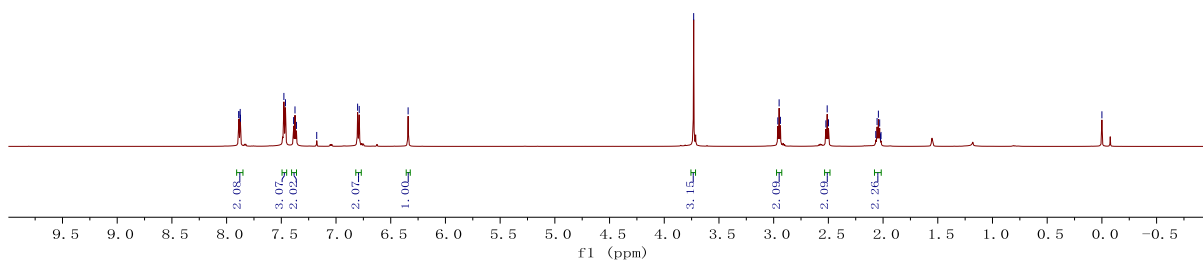
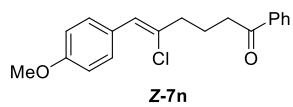


RLQ-1H. 17. fid  
RLQ-239

7.889  
7.887  
7.876  
7.873  
7.476  
7.462  
7.388  
7.375  
7.362  
7.362  
6.803  
6.788  
— 6.341

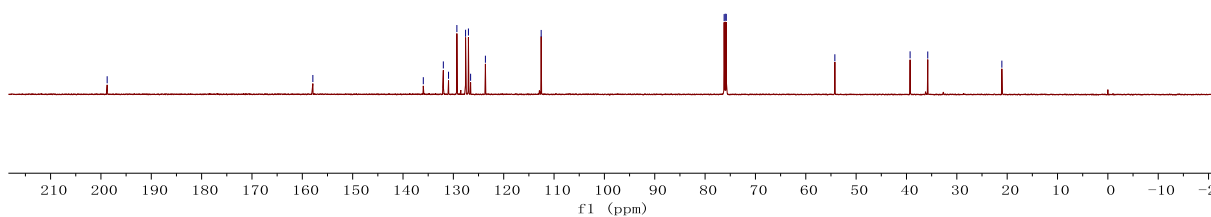
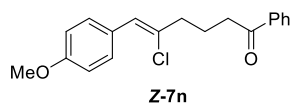
— 3.731  
2.962  
2.950  
2.938  
2.523  
2.511  
2.499  
2.067  
2.055  
2.043  
2.031  
2.023  
2.019

— 0.000



RLQ-13C. 603 fid  
RLQ-239

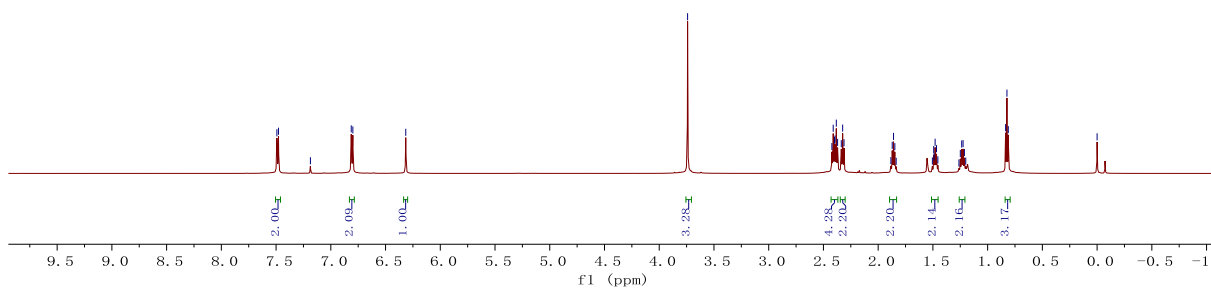
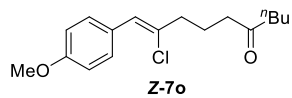
198.763  
— 157.908  
135.972  
131.991  
130.957  
129.300  
127.574  
127.007  
126.574  
123.636  
— 112.659  
76.217  
76.068  
75.794  
— 54.227  
— 39.281  
— 35.774  
— 21.056



RLQ-1H. 18. fid  
RLQ-240

7.493  
7.478  
7.186  
6.813  
6.799  
6.315

3.741  
2.423  
2.411  
2.399  
2.394  
2.382  
2.370  
2.337  
2.324  
2.312  
2.282  
1.872  
1.860  
1.848  
1.836  
1.505  
1.493  
1.489  
1.480  
1.470  
1.455  
1.262  
1.250  
1.237  
1.224  
1.212  
1.200  
0.836  
0.811  
0.811  
0.000



RLQ-13C. 61. fid  
RLQ-740

211.274  
157.440

158.917

131.857  
130.279  
127.564  
124.496

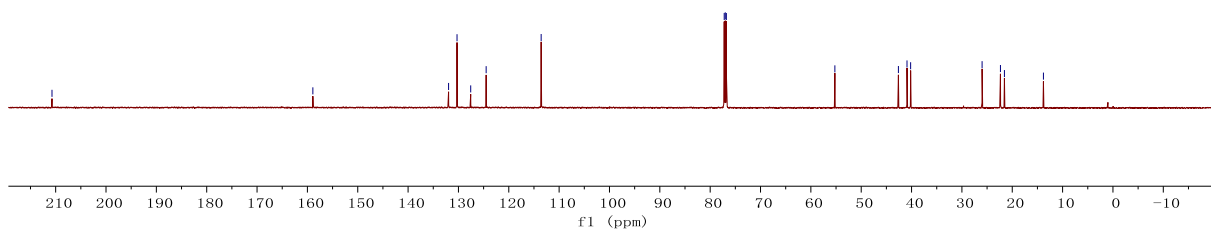
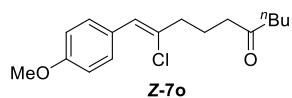
113.572

77.212  
77.000  
76.788

55.231

42.613  
40.904  
40.184

25.989  
22.366  
21.554  
13.808



RLQ-1H. 25. fid  
RLQ-247

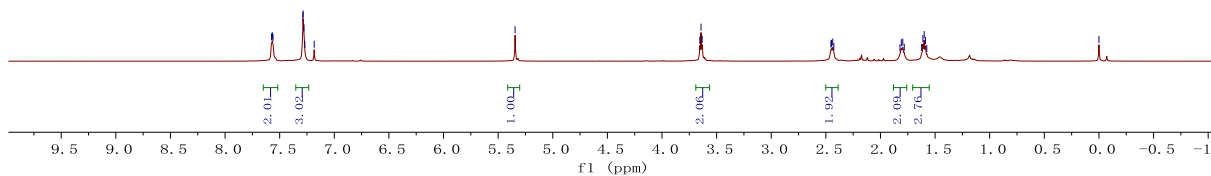
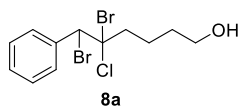
7.574  
7.567  
7.568  
7.588  
7.585  
7.577  
7.270  
7.184

5.345

3.654  
3.643  
3.632

2.453  
2.448  
2.437  
2.427  
1.806  
1.796  
1.782  
1.623  
1.612  
1.600  
1.588  
1.576

0.000



RLQ-13C. 66. fid  
RLQ-247

137.260  
130.587  
129.842  
127.842  
127.832

86.226

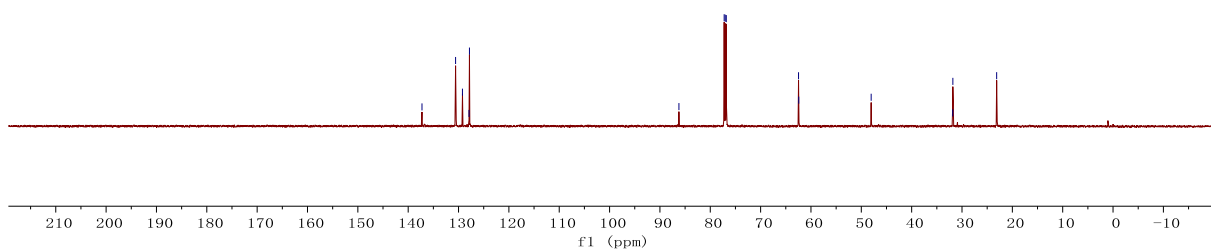
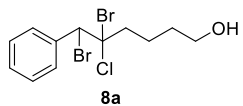
77.241  
77.029  
76.915

62.469  
62.431

48.041

31.841  
31.817

23.117

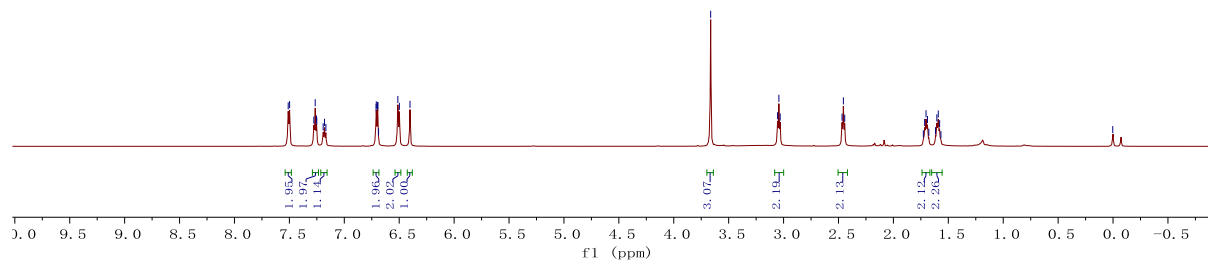
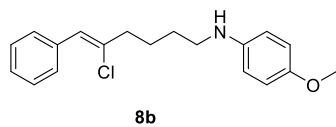




RLQ-1H. 63. fid  
RLQ-244

7.511  
7.498  
7.277  
7.265  
7.253  
7.251  
7.180  
7.168  
6.710  
6.709  
6.697  
6.694  
6.688  
6.512  
6.496  
6.492

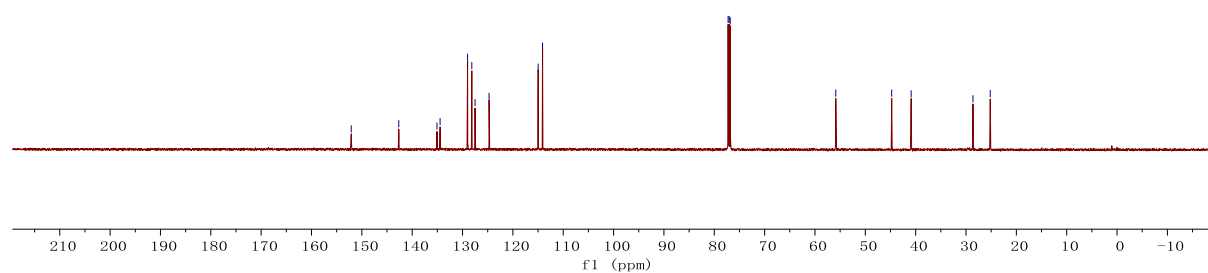
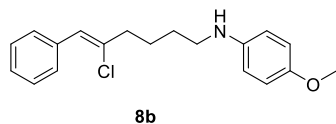
3.664  
3.054  
3.033  
3.031  
2.468  
2.455  
2.433  
1.772  
1.716  
1.703  
1.690  
1.677  
1.617  
1.604  
1.592  
1.579  
1.567  
0.003



RLQ-13C. 63. fid  
RLQ-244

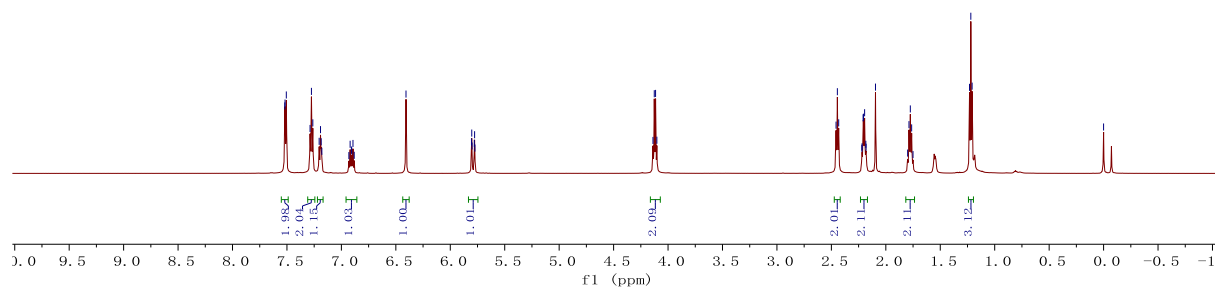
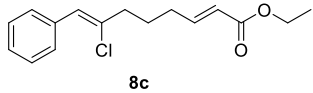
152.106  
142.669  
135.975  
134.957  
128.999  
128.156  
127.514  
124.730  
114.979  
114.103

77.252  
77.004  
76.829  
55.862  
44.761  
40.894  
28.617  
25.184



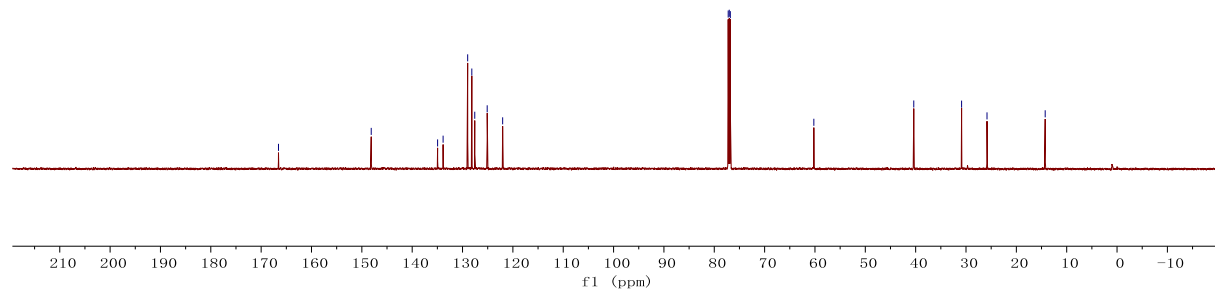
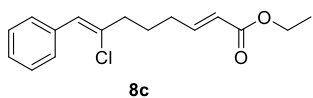
RLQ-1H. 23. fid  
RLQ-243

7.520  
7.518  
7.506  
7.506  
7.508  
7.508  
7.504  
7.504  
7.192  
7.186  
7.180  
6.931  
6.920  
6.908  
6.896  
6.894  
6.882  
6.407  
5.805  
5.803  
5.800  
5.780  
5.777  
5.774  
4.138  
4.127  
4.115  
4.103  
2.457  
2.445  
2.433  
2.220  
2.218  
2.208  
2.206  
2.195  
2.184  
2.181  
2.095  
1.800  
1.787  
1.775  
1.763  
1.750  
1.231  
1.219  
1.208  
0.000

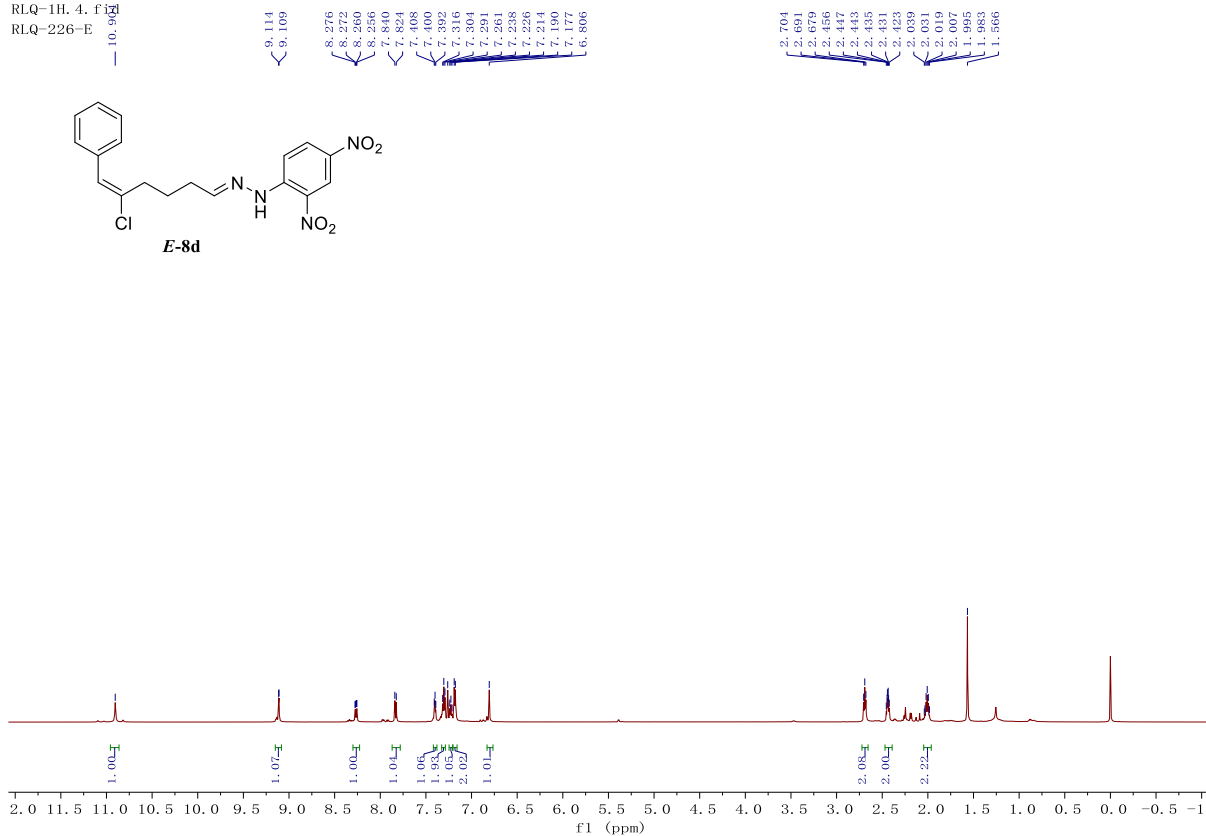
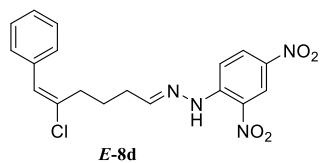


RLQ-13C. 65. fid  
RLQ-243

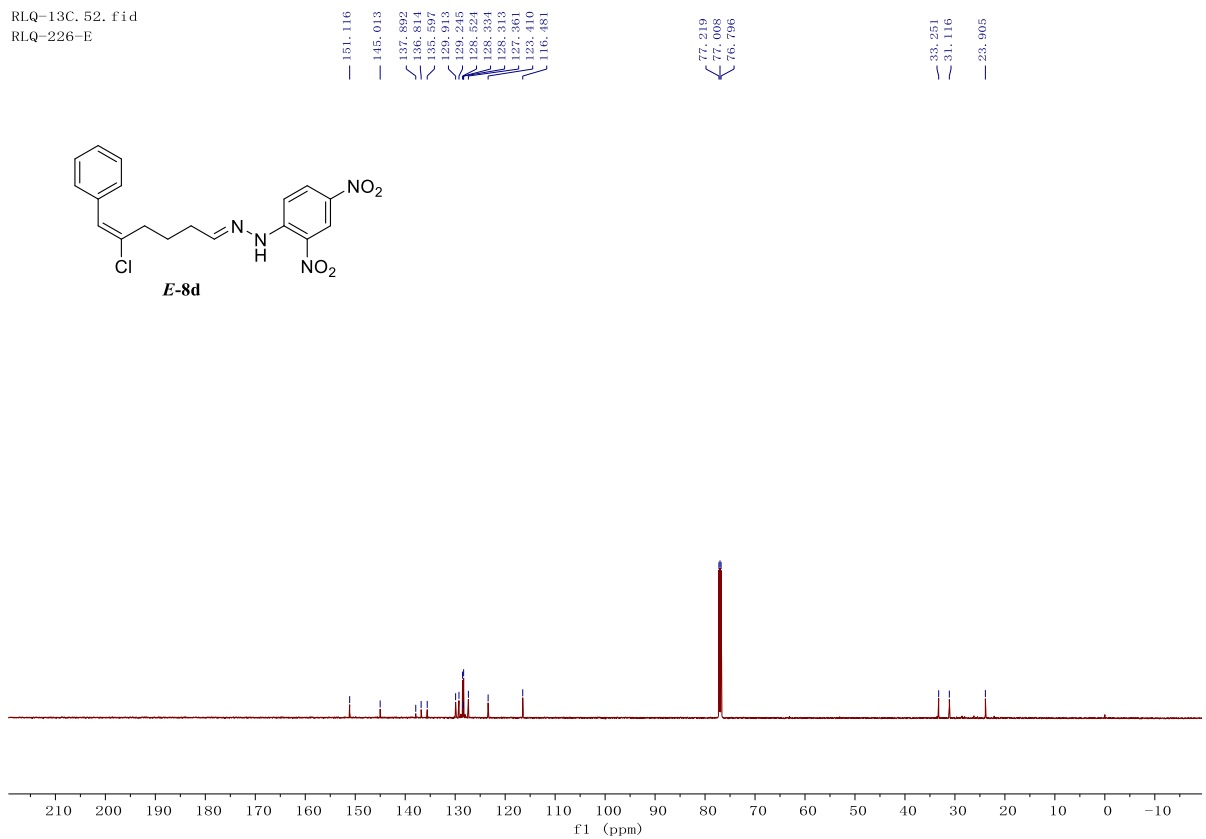
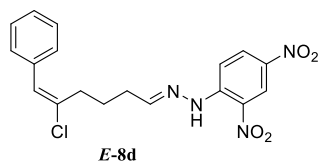
166.556  
148.138  
134.951  
133.861  
128.980  
128.156  
127.573  
125.101  
122.031  
77.235  
77.004  
76.812  
60.222  
40.375  
30.876  
25.828  
14.272



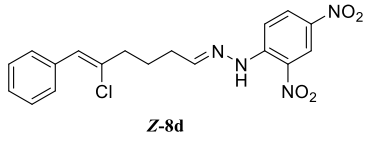
RLQ-1H. 4. f1  
RLQ-226-E



RLQ-13C. 52. f1d  
RLQ-226-E



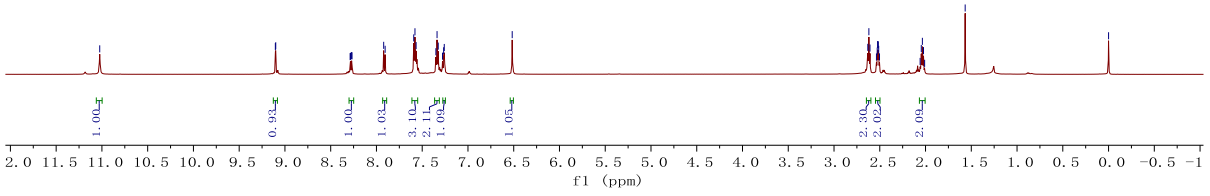
RLQ-1H. 53. fid  
RLQ-227-Z



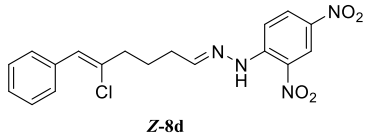
9.105  
9.101  
8.288  
8.283  
8.272  
8.267  
7.921  
7.905  
7.893  
7.887  
7.850  
7.838  
7.825  
7.278  
7.259  
6.517

2.631  
2.619  
2.607  
2.536  
2.528  
2.524  
2.515  
2.512  
2.503  
2.059  
2.046  
2.034  
2.022  
2.010  
1.567

-0.000



RLQ-13C. 53. fid  
RLQ-227-Z



151.331  
145.064  
137.930  
137.446  
133.387  
129.915  
128.940  
128.924  
128.204  
127.737  
125.581  
123.441  
116.476

77.219  
77.007  
76.796

40.463

31.346

23.977

