

## Supporting information

### **Aerobic Oxidation and EATA-Based Highly Enantioselective Synthesis of Lamnallenic Acid**

Xingguo Jiang,<sup>a</sup> Yufeng Xue,<sup>a</sup> and Shengming Ma<sup>\*a,b</sup>

<sup>a</sup> State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

<sup>b</sup> Department of Chemistry, Fudan University, 220 Handan Lu, Shanghai 200433, P. R. China

E-mail: [masm@sioc.ac.cn](mailto:masm@sioc.ac.cn)

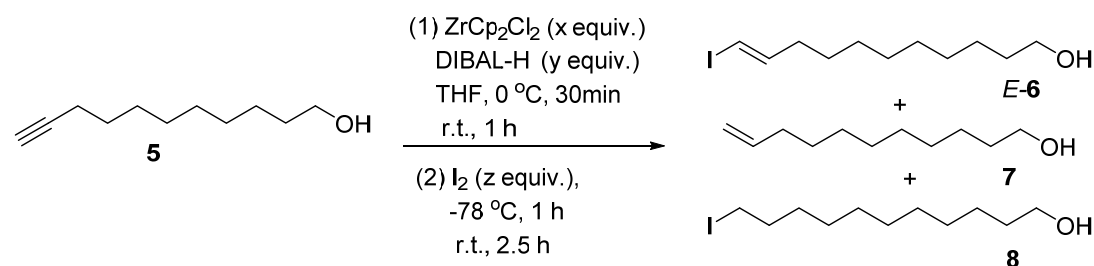
Fax: (+86)21-64167510

<b>The initial attempts to construct the C=C double bond (concluding experimental details and analytical data)</b>	<b>S1-11</b>
<b>Notes and references</b>	<b>S12</b>
<b><sup>1</sup>H, <sup>13</sup>C NMR and HPLC spectra of all the products</b>	<b>S13-61</b>

### The initial attempts to construct the C=C double bond in laballenic acid

In order to construct the C=C double bond with a high *E/Z* ratio, we wished to prepare *E*-alkenyl iodide with a free terminal hydroxy group *E*-**6** first, which could be transformed into (*E*)-10-dodecenol *E*-**16** after cross coupling reaction with ZnMe<sub>2</sub>. However, by applying the ZrCp<sub>2</sub>Cl<sub>2</sub>/DIBAL-H reduction and iodination protocol developed by Negishi et al.,<sup>1</sup> the reaction of terminal alkynol **5** afforded two extra by-products: protonolysis product **7** and the over-reduction product **8**, which were hard to be separated from each other by chromatography on silica gel (entry 1, Table S1). By-products still existed after adjusting the equiv. of ZrCp<sub>2</sub>Cl<sub>2</sub> and DIBAL-H (entries 2 and 3, Table S1).

**Table S1** ZrCp<sub>2</sub>Cl<sub>2</sub>/DIBAL-H reduction and iodization of 10-undecynol **5**.

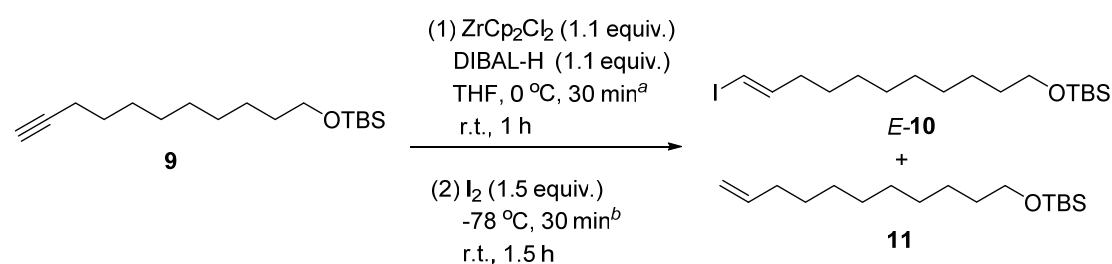


Entry	x	y	z	Yield (%) <sup>a</sup>		
				<i>E</i> - <b>6</b>	<b>7</b>	<b>8</b>
1	1.5	1.5	1.5	59	17	7
2	2.1	2.1	2.5	58	3	18
3	1.1	2.1	2.5	31	9	24

<sup>a</sup>NMR yield.

We reasoned that the hydroxyl group might assist the side reaction. Then its TBS ether **9** was treated with 1.1 equiv. each of ZrCp<sub>2</sub>Cl<sub>2</sub> and DIBAL-H. No over reduction was observed, but protonolysis by-product **11** still existed (entry 1, Table S2). After enlarging the reaction scale from 0.5 mmol to 5.0 mmol, the ratio of *E*-10/11 was improved from 7.2:1 to 14.0:1 (entry 2, Table S2).

**Table S2** ZrCp<sub>2</sub>Cl<sub>2</sub>/DIBAL-H reduction and iodization of TBS-protected 10-undecynol **9**.

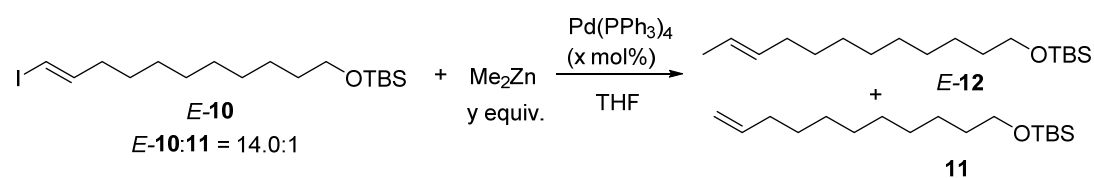


Entry	Scale (mmol)	4Å MS	Yield of <i>E</i> -10 (%)	Ratio of <i>E</i> -10: <b>11</b>
1	0.5	-	72	7.2:1
2	5.0	-	62	14.0:1
3	0.5	100 mg	70	6.6:1

<sup>a</sup>45 min for 5.0 mmol scale (entry 2); <sup>b</sup>1 h for 5.0 mmol scale (entry 2).

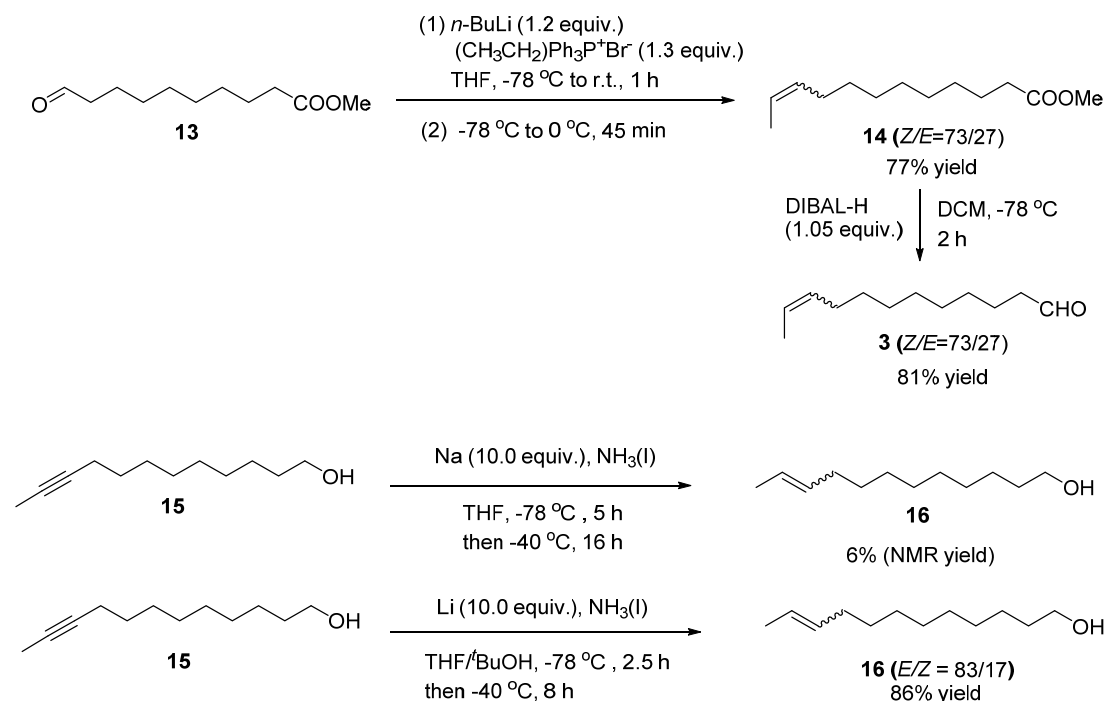
The cross coupling reaction of the mixture of this alkenyl iodide *E*-10 and **11** with 1.2 equiv. of Me<sub>2</sub>Zn<sup>2</sup> with 10 mol% of Pd(PPh<sub>3</sub>)<sub>4</sub> at room temperature afforded a 7.2:1 mixture of *E*-alkene *E*-12 and the protonolysis by-product **11** (entry 1, Table S3). When we reduced the loading of Pd(PPh<sub>3</sub>)<sub>4</sub> to 5 mol% and raised the amount of Me<sub>2</sub>Zn to 1.5 equiv., an 11.1:1 mixture of *E*-alkene *E*-12 and **11** was afforded at 40 °C for 5 hours (entry 2, Table S3), which are hard to be separated from each other due to their similar polarities on silica gel. We had to look for a better solution.

**Table S3** Cross coupling reaction of *E*-10 and Me<sub>2</sub>Zn.



Entry	<i>x</i>	<i>y</i>	Time (h)	Temp. (°C)	Yield of <i>E</i> -12 (%)	Ratio of <i>E</i> -12: <b>11</b>
1	10	1.2	6	r.t.	76	7.2:1
2	5	1.5	5	40	88	11.1:1

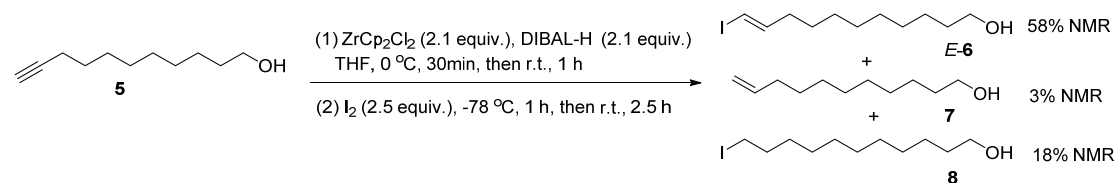
Furthermore, attempts to form the *trans* C=C bond by Wittig reaction of aldehyde **13** were tried and a 73/27 mixture of the *Z* and *E* isomers of **14** was afforded (Scheme S1). Then, Na/ NH<sub>3</sub> (l) reduction was applied to construct this *trans* C=C double bond.<sup>3</sup> Only 6% of the product **16** was detected by NMR analysis. With Li/NH<sub>3</sub> (l) reduction,<sup>4</sup> 86% yield of 10-dodecenol **16** was obtained with 83/17 of *E/Z* ratio, which was still NOT good enough for a highly stereoselective synthesis.



**Scheme S1** Attempts to construct the *trans* C=C bond.

## Experimental details and analytical data for the initial attempts to construct the C=C double bond

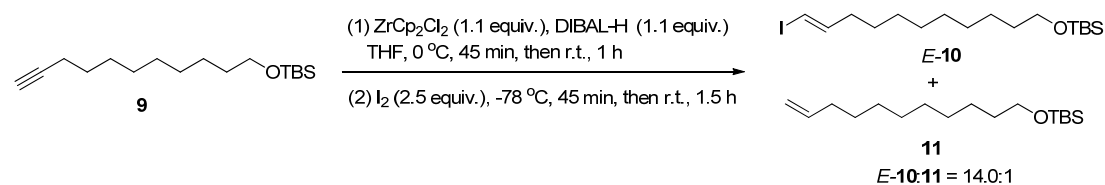
### (*E*)-11-Iodo-10-undecen-1-ol<sup>1a</sup> (**E-6**) (jxg-4-164)



To a flame dried Schlenk tube were added ZrCp<sub>2</sub>Cl<sub>2</sub> (307.3 mg, 1.05 mmol) and anhydrous THF (1.5 mL). DIBAL-H (1M in toluene, 1.05 mL, 1.05 mmol) was added dropwise at 0 °C under Ar atmosphere. After 30 min, a solution of **5** (84.4 mg, 0.5 mmol) in THF (0.5 mL) was added dropwise. The mixture was then allowed to warm

up to room temperature. After being stirred for 1 h, the resulting mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  followed by addition of a solution of  $\text{I}_2$  (317.8 mg, 1.25 mmol) in THF (0.8 mL) dropwise. After being stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, the resulting mixture was warmed up to room temperature and stirred for 2.5 h until the completion of the reaction as monitored by TLC. After being cooled to  $-78\text{ }^{\circ}\text{C}$ , 1M HCl (3 mL) was added to quench the reaction. Then  $\text{Et}_2\text{O}$  (20 mL) was added to separate the organic layer. The aqueous phase was extracted by ethyl ether (10 mL). The combined organic layer was washed sequentially with a saturated  $\text{NaHCO}_3$  aqueous solution (10 mL), a saturated  $\text{Na}_2\text{S}_2\text{O}_3$  aqueous solution (10 mL), and brine. After being dried over anhydrous  $\text{Na}_2\text{SO}_4$ , the mixture was filtrated and evaporated. 48  $\mu\text{L}$  of mesitylene was added to the residue as the internal standard. 58% yield of *E*-**6**,<sup>5</sup> 3% yield of **7**,<sup>6</sup> and 18% yield of **8**<sup>7</sup> were detected by NMR analysis of the crude product. The mixture was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford a 65:1:20 mixture of *E*-**6**, **7** and **8** (118.1 mg) as an oil: *E*-**6**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.55-6.46 (m, 1 H, =CH), 5.97 (d,  $J = 14.4$  Hz, 1 H, =CH), 3.63 (t,  $J = 6.6$  Hz, 2 H,  $\text{OCH}_2$ ), 2.09-2.00 (m, 2 H,  $\text{CH}_2$ ), 1.61-1.45 (m, 3 H,  $\text{CH}_2 + \text{OH}$ ), 1.43-1.18 (m, 12 H,  $12 \times \text{CH}_2$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.7, 74.3, 62.95, 36.0, 32.7, 29.41, 29.2, 28.8, 28.3, 25.7, 7.4. The following signals are discernible for **7**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.87-5.74 (m, 1 H, =CH), 5.03-4.89 (m, 2 H, = $\text{CH}_2$ ). The following signals are discernible for **8**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.19 (t,  $J = 7.0$  Hz,  $\text{CH}_2$ ), 1.82 (quint,  $J = 7.2$  Hz,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  62.96, 33.5, 30.4, 29.5, 29.40, 29.34, 29.31, 28.5.

**(*E*)-tert-Butyldimethyl (11-iodo-10-undecen-1-yloxy) silane<sup>1a</sup> (*E*-**10**) (jxg-4-180)**

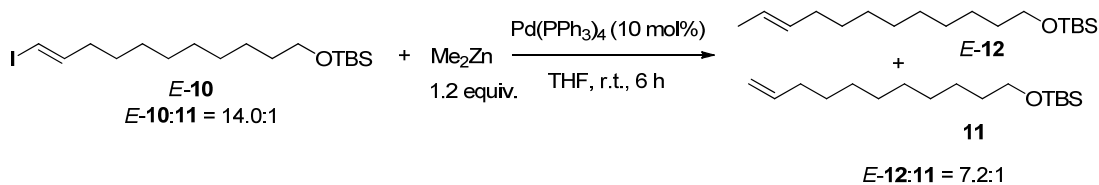


To a flame dried Schlenk tube were added  $\text{ZrCp}_2\text{Cl}_2$  (1.6084 g, 5.5 mmol) and anhydrous THF (12.5 mL). DIBAL-H (1M in Toluene, 5.5 mL, 5.5 mmol) was added

dropwise at 0 °C under Ar atmosphere. After 45 min, a solution of **9**<sup>8</sup> (1.4130 g) in THF (2.5 mL) was added dropwise in 20 min. The mixture was then allowed to warm up to room temperature and stirred for 1 h and cooled to -78 °C, followed by addition of a solution of I<sub>2</sub> (1.9049 g, 7.5 mmol) in THF (7.5 mL) dropwise in 10 min at this temperature. After being stirred at -78 °C for 1 h, the resulting mixture was warmed up to room temperature and stirred at rt for 1.5 h until the completion of the reaction monitored by TLC. After being cooled to -78 °C, 1M HCl (30 mL) was added to quench the reaction. Et<sub>2</sub>O (80 mL) was added to separate the organic layer. The aqueous phase was extracted by ethyl ether (20 × 3 mL). The combined organic layer was washed sequentially with a saturated NaHCO<sub>3</sub> aqueous solution (30 mL), a saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution (30 mL), and brine. After being dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the mixture was filtrated and evaporated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 100/1) to afford a 14.0:1 mixture of *E*-**10**<sup>1c</sup> and **11**<sup>9</sup> (1.3343 g) as an oil: *E*-**10** (62% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.56-6.46 (m, 1 H, =CH), 6.00-5.93 (d, *J* = 6.6 Hz, 1 H, =CH), 3.60 (t, *J* = 6.6 Hz, 2 H, OCH<sub>2</sub>), 2.09-2.00 (m, 2 H, CH<sub>2</sub>), 1.50 (m, 2 H, CH<sub>2</sub>), 1.43-1.33 (m, 2 H, CH<sub>2</sub>), 1.33-1.22 (m, 10 H, 5 × CH<sub>2</sub>), 0.89 (s, 9 H, 3 × CH<sub>3</sub>), 0.67 (s, 6 H, 2 × CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.8, 74.3, 63.3, 36.0, 32.8, 29.5, 29.4, 29.3, 28.9, 28.3, 26.0, 25.8, 18.4, -5.3; IR (neat) ν (cm<sup>-1</sup>) 2927, 2855, 1606, 1463, 1388, 1361, 1254, 1097, 1006, 942, 834, 774; MS (ESI) *m/z* (%): 411 ((M+H)<sup>+</sup>). The following signals are discernible for **11**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.87-5.74 (m, 1 H, =CH), 5.03-4.90 (m, 2 H, =CH<sub>2</sub>).

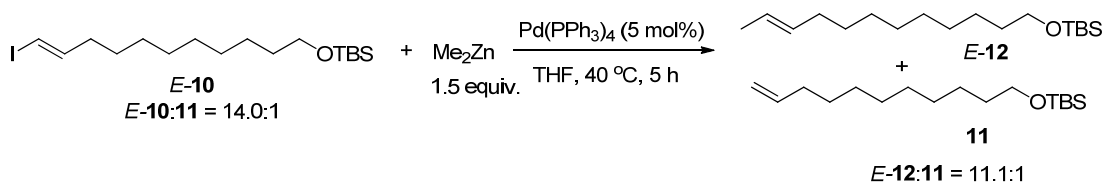
The molar ratio of *E*-**10**:**11** was 14.0:1. Thus *E*-**10** in the product was calculated to be  $1.3343 \text{ g} \times (410.46 \times 14.0 / (410.46 \times 14.0 + 284.56 \times 1.0)) = 1.2713 \text{ g}$ . Yield (*E*-**10**) =  $1.2713 \text{ g} / 410.46 / (1.4130 \text{ g} / 282.54) \times 100\% = 62\%$ .

**(*E*)-tert-Butyldimethyl (10-dodecen-1-yloxy) silane<sup>2</sup> (*E*-**12**) (jxg-4-184, jxg-5-9)**



To a flame dried Schlenk tube were added Pd(PPh<sub>3</sub>)<sub>4</sub> (57.8 mg, 0.05 mmol), *E-10* (205.8 mg, 0.5 mmol), and anhydrous THF (2.5 mL) sequentially under Ar atmosphere at room temperature. Me<sub>2</sub>Zn (0.6 mL, 0.6 mmol, 1M in toluene) was added dropwise. The reaction was then conducted at room temperature for 6 h until the completion of the reaction monitored by TLC (petroleum ether). H<sub>2</sub>O (10 mL) was added to quench the reaction. Then ethyl acetate (20 mL) was added to separate the organic layer. The aqueous phase was extracted by ethyl acetate (5 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford a 7.2:1 mixture of *E-12* and **11** (123.2 mg) as an oil: *E-12* (76% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.47-5.34 (m, 2 H, CH=CH), 3.60 (t, *J* = 6.8 Hz, 2 H), 2.00-1.90 (m, 2 H, CH<sub>2</sub>), 1.66-1.62 (m, 3 H, CH<sub>3</sub>), 1.55-1.45 (m, 2 H, CH<sub>2</sub>), 1.38-1.20 (m, 12 H, 6 × CH<sub>2</sub>), 0.90 (s, 9 H, 3 × CH<sub>3</sub>), 0.05 (s, 6 H, 2 × CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 131.7, 124.5, 63.3, 32.9, 32.6, 29.6, 29.48, 29.44, 29.2, 26.0, 25.8, 18.4, 17.9, -5.3. The following signals are discernible for **11**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.86-5.75 (m, 1 H, =CH), 5.02-4.90 (m, 2 H, =CH<sub>2</sub>), 2.04 (q, *J* = 7.1 Hz, 2 H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.2, 114.1, 33.8, 29.59, 29.1, 28.9.

The molar ratio of *E-12:11* was 7.2:1. Thus *E-10* in the substrate was calculated to be 205.8 mg × (410.46 × 14.0 / (410.46 × 14.0 + 284.56 × 1.0)) = 196.1 mg. The molar ratio of *E-12:11* was 7.2:1. Thus *E-12* in the product was calculated to be 123.2 mg × (298.59 × 7.2 / (298.59 × 7.2 + 284.56 × 1.0)) = 108.8 mg. Yield (*E-12*) = 108.8 mg / 298.59 / (196.1 mg / 410.46) × 100% = 76%.

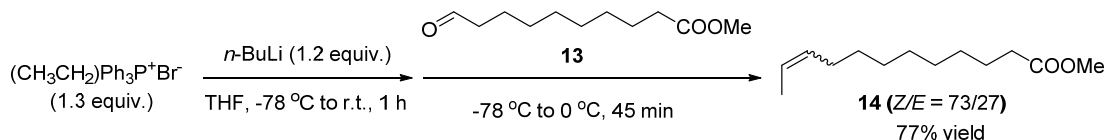


To a flame dried Schlenk tube were added Pd(PPh<sub>3</sub>)<sub>4</sub> (29.0 mg, 5 mol%), *E*-**10** (205.3 mg, 0.5 mmol), and anhydrous THF (2.5 mL) sequentially under Ar atmosphere at room temperature. Me<sub>2</sub>Zn (0.75 mL, 0.75 mmol, 1 M in toluene) was added dropwise in 5 min. The reaction was then conducted at 40 °C for 5 h until the completion of the reaction monitored by TLC (petroleum ether). When the reaction mixture was cooled to room temperature, 1M HCl (3 mL) was added to quench the reaction. Ethyl acetate (20 mL) was added to separate the organic layer. The aqueous phase was extracted by ethyl acetate (5 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 500/1) to afford a 11.1:1 mixture of *E*-**12** and **11** (136.3 mg) as an oil: *E*-**12** (88% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.47-5.35 (m, 2 H, CH=CH), 3.60 (t, *J* = 6.8 Hz, 2 H), 2.00-1.89 (m, 2 H, CH=CHCH<sub>2</sub>), 1.67-1.61 (m, 3 H, CH<sub>3</sub>), 1.56-1.46 (m, 2 H, CH<sub>2</sub>), 1.38-1.21 (m, 12 H, 6 × CH<sub>2</sub>), 0.90 (s, 9 H, 3 × CH<sub>3</sub>), 0.05 (s, 6 H, 2 × CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 131.7, 124.5, 63.3, 32.9, 32.6, 29.6, 29.48, 29.44, 29.2, 26.0, 25.8, 18.4, 17.9, -5.3; IR (neat) ν (cm<sup>-1</sup>) 2926, 2855, 1463, 1387, 1361, 1254, 1098, 1007, 965, 834, 774; MS (ESI) *m/z* (%): 299 ((M+H)<sup>+</sup>); HRMS calcd for C<sub>19</sub>H<sub>39</sub>OSi ((M+H)<sup>+</sup>): 299.2765; found: 299.2765. The following signals are discernible for **11**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.87-5.75 (m, 1 H, =CH), 5.02-4.90 (m, 2 H, =CH<sub>2</sub>), 2.04 (q, *J* = 6.9 Hz, 2 H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 114.1, 33.8, 29.6, 29.1, 28.9.

The molar ratio of *E*-**12**:**11** was 11.1:1. Thus *E*-**12** in the substrate was calculated to be 205.3 mg × (410.46 × 14.0 / (410.46 × 14.0 + 284.56 × 1.0)) = 195.6 mg. The molar ratio of *E*-**12**:**11** was 11.1:1. Thus *E*-**12** in the product was calculated to be 136.3 mg × (298.59 × 11.1 / (298.59 × 11.1 + 284.56 × 1.0)) = 125.5 mg. Yield (*E*-**12**) = 125.5 mg / 298.59 / (195.6 mg / 410.46) × 100% = 88%.

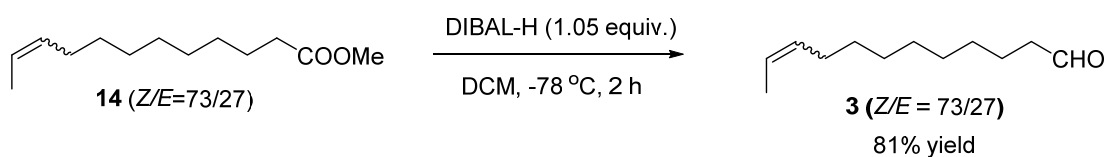
#### **(Z/E)-Methyl 10-dodecenate (14) (jxg-1-101)**





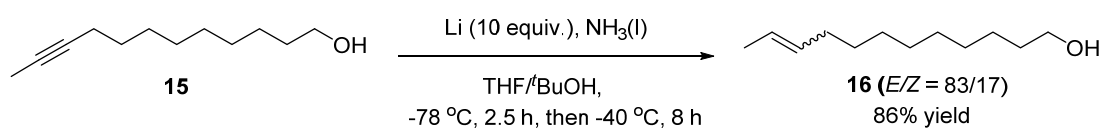
To a flame dried Schlenk tube were added  $(\text{CH}_3\text{CH}_2)_3\text{P}^+\text{Br}^-$  (241.8 mg, 0.65 mmol) and anhydrous THF (2 mL). After the mixture was cooled to  $-78\text{ }^\circ\text{C}$ ,  $n\text{-BuLi}$  (2.5 M in toluene, 0.24 mL, 0.60 mmol) was added dropwise in 5 min. The resulting mixture was then warmed up to room temperature and stirred for 1 h. After being cooled to  $-78\text{ }^\circ\text{C}$  again, a solution of **13**<sup>10</sup> (99.7 mg, 0.5 mmol) in THF (2 mL) was added dropwise. The reaction was then allowed to warm up to  $0\text{ }^\circ\text{C}$  and stirred for 45 min until the completion of the reaction monitored by TLC (petroleum ether/ethyl acetate = 5/1). The colour of the mixture changed from orange to white. A saturated  $\text{NH}_4\text{Cl}$  solution (2 mL) was added to quench the reaction at  $0\text{ }^\circ\text{C}$ . Ethyl ether (20 mL) and  $\text{H}_2\text{O}$  (10 mL) were added. The aqueous phase was extracted by ethyl ether (5 mL  $\times$  3). The combined organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) to afford **14**<sup>11</sup> ( $Z/E = 73/27$ ) (81.9 mg, 77%) as an oil: **14** (*Z*):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.48-5.33 (m, 2 H,  $\text{CH}=\text{CH}$ ), 3.67 (s, 3 H,  $\text{CH}_3$ ), 2.30 (t,  $J = 7.6$  Hz, 2 H), 2.06-1.99 (m, 2 H,  $\text{CH}_2$ ), 1.67-1.56 (m, 5 H,  $\text{CH}_3 + \text{CH}_2$ ), 1.39-1.20 (m, 10 H,  $5 \times \text{CH}_2$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 130.8, 123.6, 51.4, 34.0, 29.47, 29.29, 29.19, 29.16, 29.1, 26.8, 24.9, 12.7; IR (neat)  $\nu$  ( $\text{cm}^{-1}$ ) 3013, 2926, 2855, 1741, 1456, 1363, 1259, 1195, 1170, 1017; MS (EI)  $m/z$  (%): 212 ( $\text{M}^+$ , 5.44), 55 (100). The following signals are discernible for **14** (*E*):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.99-1.92 (m, 2 H,  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  131.6, 124.5, 32.5, 29.52, 29.26, 29.17, 29.0, 17.9.

#### (*Z/E*)-10-Dodecenal (**3**) (jxg-1-111)



To a flame dried Schlenk tube were added **14** (*Z/E* = 73/27) (743.4 mg, 3.5 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10.5 mL). DIBAL-H (1 M in Toluene, 3.68 mL, 3.68 mmol) was added dropwise at -78 °C in 10 min. The reaction was carried out at -78 °C for 2 h until the completion of the reaction monitored by TLC (petroleum ether/ethyl ether = 20/1). A saturated potassium sodium tartrate aqueous solution (10 mL) was added to quench the reaction at -78 °C. The mixture was warmed up to room temperature and stirred. CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added to separate the organic layer. The aqueous phase was extracted by ethyl ether (10 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to afford **3**<sup>12</sup> (*Z/E* = 73/27) (513.9 mg, 81%) as an oil: **3** (*Z*): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.77 (t, *J* = 2.0 Hz, 1 H, CHO), 5.48-5.33 (m, 2 H, CH=CH), 2.42 (td, *J*<sub>1</sub> = 7.4, *J*<sub>2</sub> = 2.0 Hz, 2 H, CH<sub>2</sub>), 2.06-1.99 (m, 2 H, CH<sub>2</sub>), 1.67-1.57 (m, 5 H, CH<sub>3</sub> + CH<sub>2</sub>), 1.39-1.22 (m, 10 H, 5 × CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.0, 130.7, 123.6, 43.9, 29.50, 29.28, 29.27, 29.13, 29.09, 26.7, 22.0, 12.7; IR (neat) ν (cm<sup>-1</sup>) 3013, 2924, 2854, 2714, 1727, 1463, 1405, 1368, 1259, 1014; MS (EI) *m/z* (%): 182 (M<sup>+</sup>, 0.83), 55 (100). The following signals are discernible for **3** (*E*): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.99-1.92 (m, 2 H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 131.5, 124.5, 32.5, 29.46, 29.24, 29.03, 17.9.

**(*E/Z*)-10-Dodecen-1-ol<sup>4</sup> (16) (jxg-1-150)**



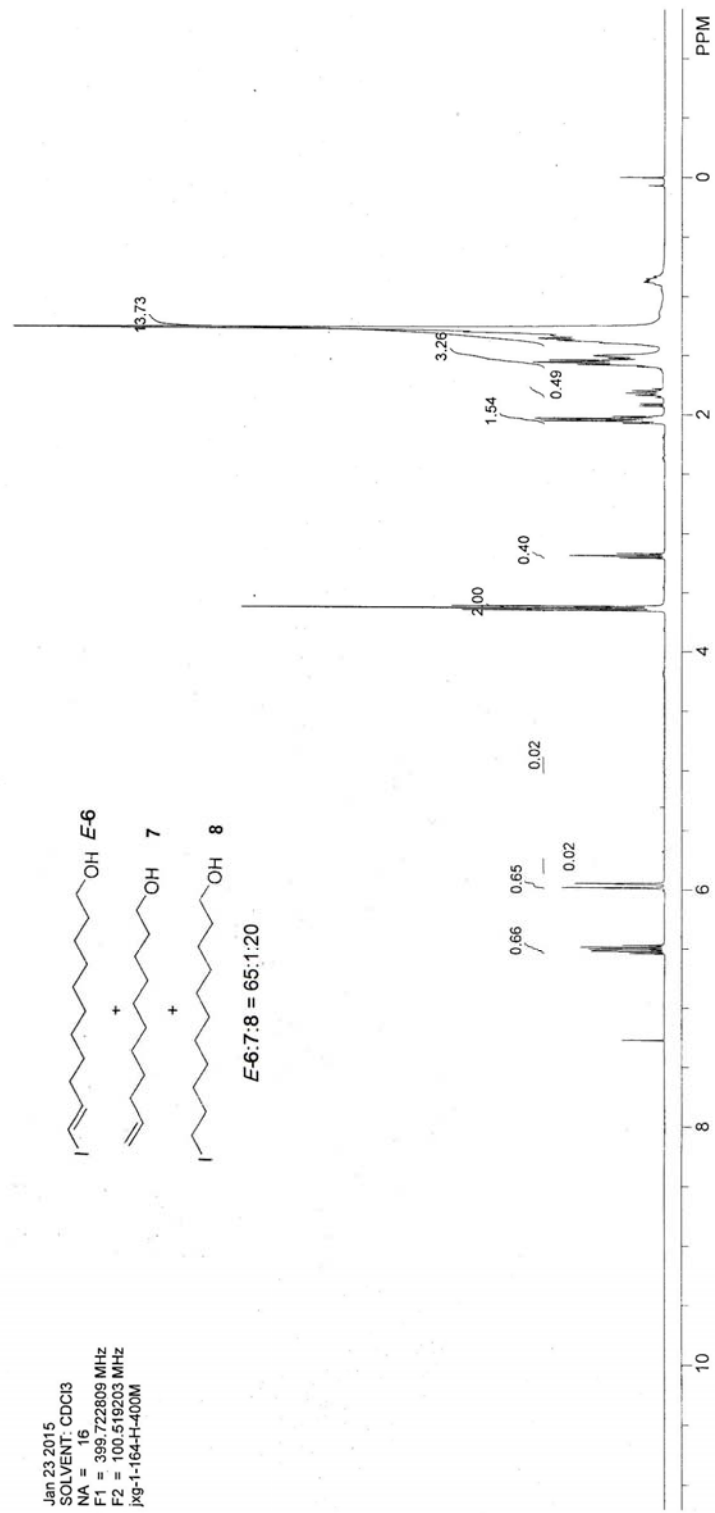
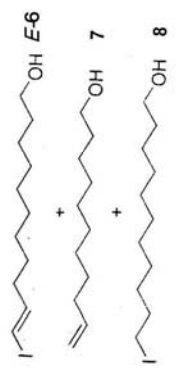
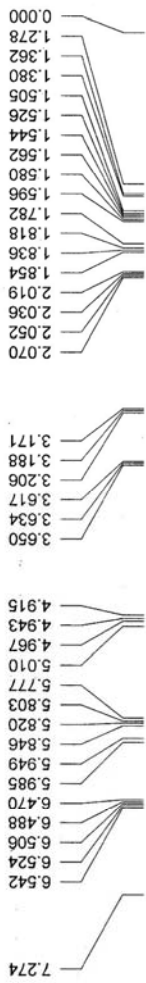
To a flame dried Schlenk tube was introduced NH<sub>3</sub> (gas) at -78 °C to collect 10 mL of NH<sub>3</sub> liquid. A solution of **15**<sup>4</sup> (182.0 mg) in a mixed solvent (7.2 mL, THF/<sup>t</sup>BuOH = 5/3 by volume). Then Li rod (70.1 mg, 10.0 mmol) was added. The resulting mixture was stirred at -78 °C for 2.5 h and warmed up to -40 °C with stirring for 8 h until the completion of the reaction as monitored by TLC (petroleum ether/ethyl acetate = 5/1). A saturated NH<sub>4</sub>Cl solution (2 mL) was added to quench the reaction. The flask was opened to air overnight to allow the NH<sub>3</sub> (l) to evaporate completely.

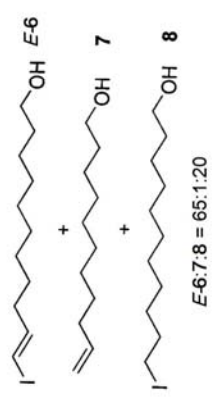
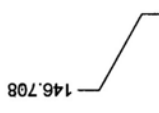
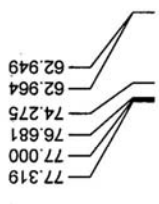
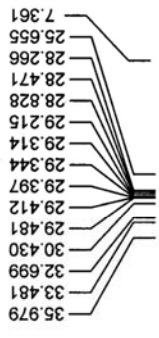
Et<sub>2</sub>O (20 mL) and H<sub>2</sub>O (10 mL) were added. The aqueous phase was extracted by ethyl ether (10 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) to afford **16**<sup>4</sup> (*E/Z* = 83/17) (158.7 mg, 86%) as an oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.47-5.34 (m, 2 H, CH=CH), 3.62 (t, *J* = 6.6 Hz, 2 H, OCH<sub>2</sub>), 1.99-1.92 (m, 2 H, CH<sub>2</sub>), 1.77 (brs, 1 H, OH), 1.64 (dd, 3 H, *J*<sub>1</sub> = 3.4 Hz, *J*<sub>2</sub> = 1.0 Hz, CH<sub>3</sub>), 1.62-1.50 (m, 2 H, CH<sub>2</sub>), 1.39-1.22 (m, 12 H, 6×CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 131.6, 124.5, 62.9, 32.7, 32.5, 29.56, 29.53, 29.41, 29.38, 29.1, 26.7, 25.7, 17.9. The following signals are discernible for **16** (*Z*): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.06-2.00 (m, 2 H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 130.8, 123.6, 29.50, 29.44, 29.2, 12.7.

## Notes and references

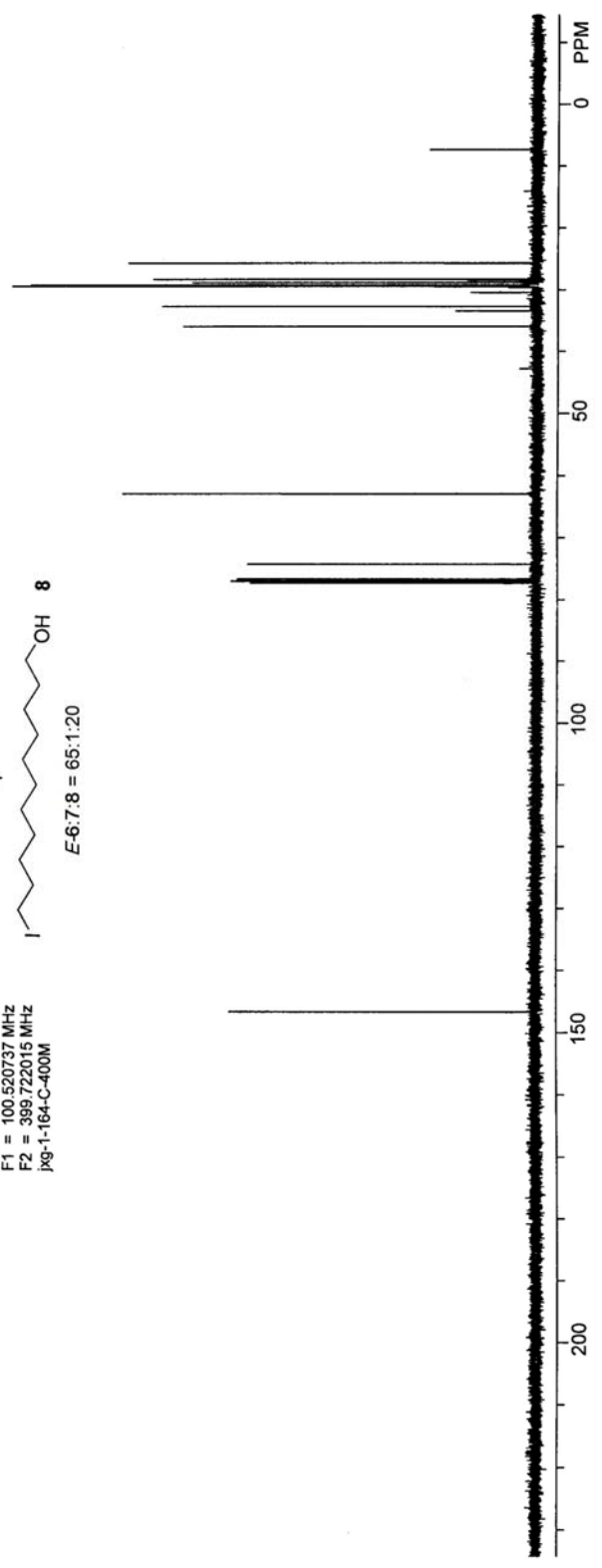
1. (a) Z. Huang and E.-i. Negishi, *Org. Lett.*, 2006, **8**, 3676; (b) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, 1974, **96**, 8115; some other reports to synthesize *E*-alkenyl iodides: (c) A. Kalivretenos, J. K. Stille and L. S. Hegedus, *J. Org. Chem.*, 1991, **56**, 2883; (d) G. Hikosaka, Y. Hattori and H. Makabe, *Tetrahedron: Asymmetry*, 2014, **25**, 1367; (e) A. Darwish and J. M. Chong, *Tetrahedron*, 2012, **68**, 654.
2. P. Wipf and M. J. Soth, *Org. Lett.*, 2002, **4**, 1787.
3. J. Wang, J. Chen, C. W. Kee, C.-H. Tan, *Angew. Chem. Int. Ed.*, 2012, **51**, 2382.
4. M. J. Cryle, P. Y. Hayes and J. J. De Voss, *Chem. Eur. J.*, 2012, **18**, 15994.
5. J. K. Stille and J. H. Simpson, *J. Am. Chem. Soc.*, 1987, **109**, 2138.
6. D. Peng, M. Zhang and Z. Huang, *Chem. Eur. J.*, 2015, **21**, 14737.
7. M. Bérubé, F. Kamal, J. Roy and D. Poirier, *Synthesis*, 2006, **18**, 3085.
8. X. Lu, S. Cseh, H. S. Byun, G. Tigyi and R. Bittman, *J. Org. Chem.*, 2003, **68**, 7046.
9. S. C. Sinha, A. Sinha-Bagchi and E. Keinan, *J. Org. Chem.*, 1993, **58**, 7789.
10. P. D. Gokhale, V. S. Dalavoy, A. S. C. Prakasa Rao, U. R. Nayak and S. Dev, *Synthesis*, 1974, 718.
11. X. Guan, M. B. Fisher, D. H. Lang, Y.-M. Zheng, D. R. Koop and A. E. Rettie, *Chem. Biol. Interact.*, 1998, **110**, 103.
12. G. W. Kabalka, S. Yu and N.-S. Li, *Can. J. Chem.*, 1998, **76**, 800.

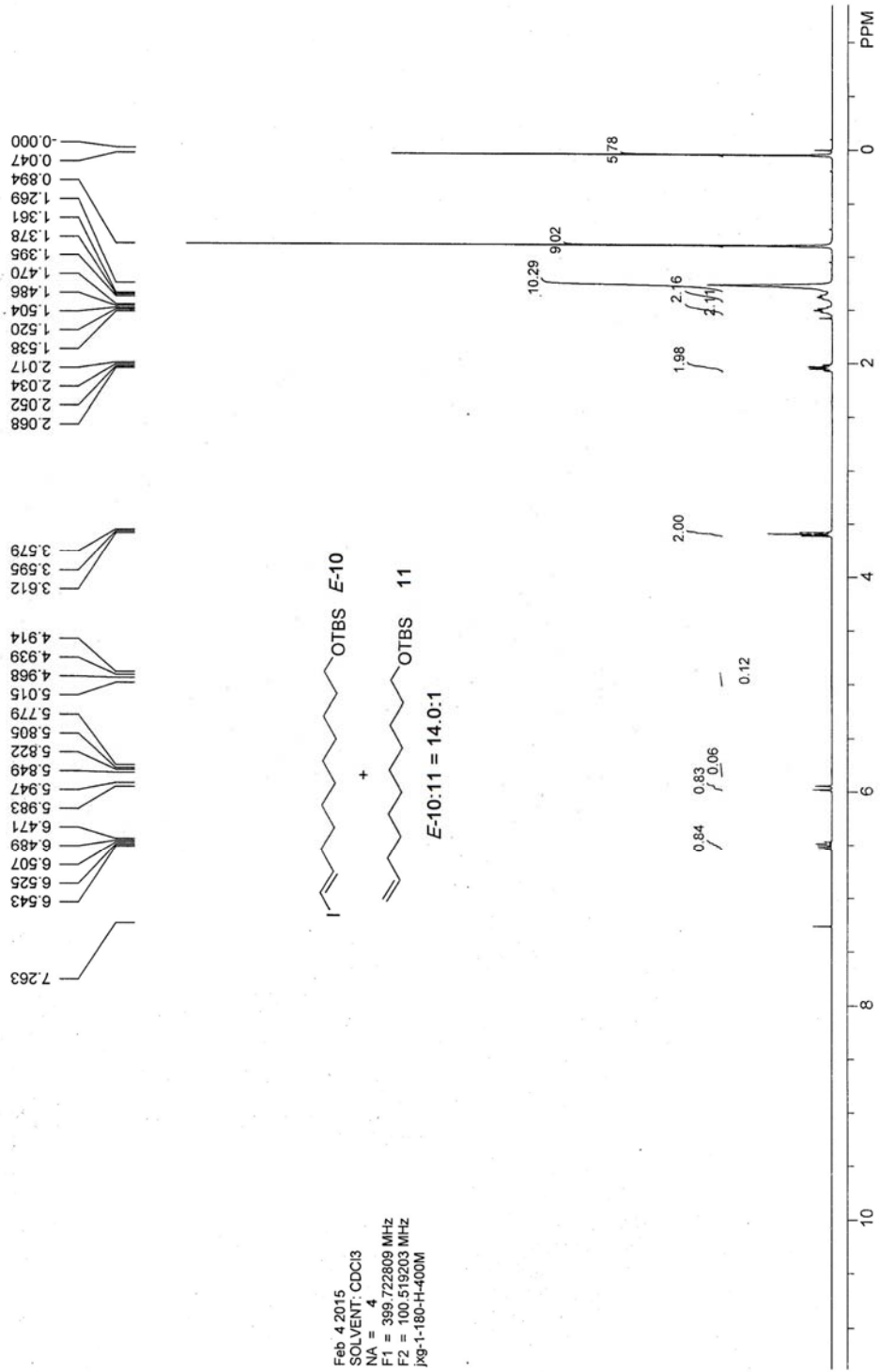
Jan 23 2015  
 SOLVENT: CDCl3  
 NA = 16  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 jrg-1-164-H-400M

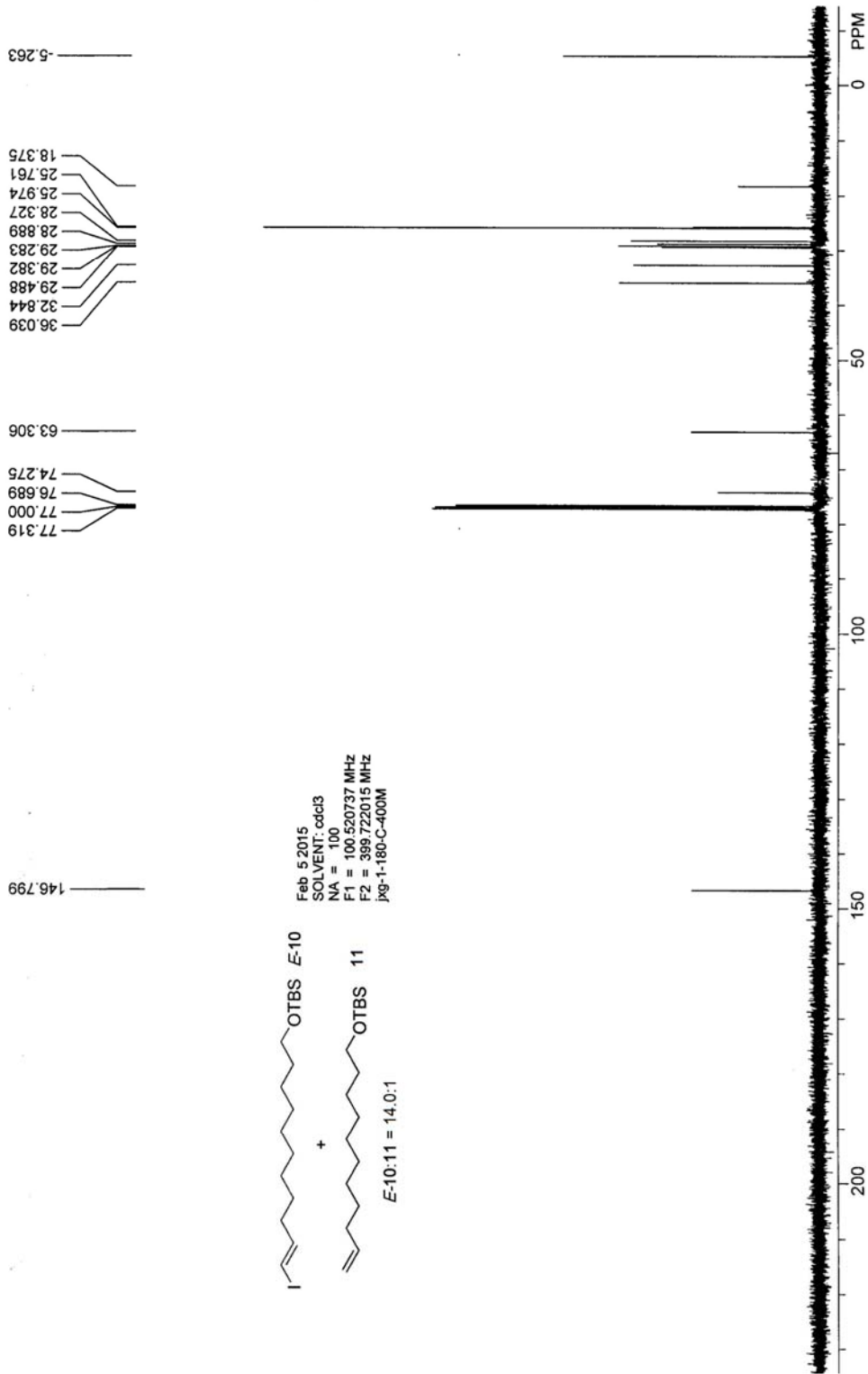




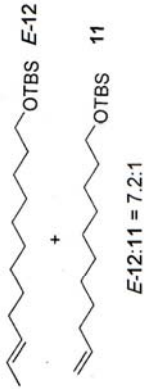
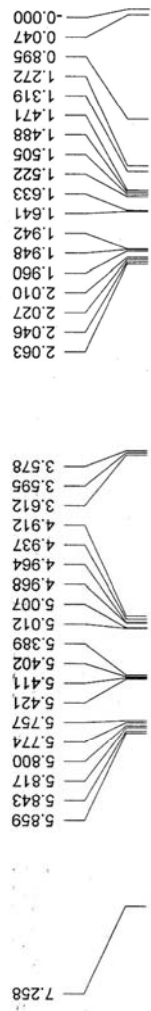
Jan 23 2015  
 SOLVENT: cdcl3  
 NA = 204  
 F1 = 100.520737 MHz  
 F2 = 399.722015 MHz  
 jxg-1-164-C-400M





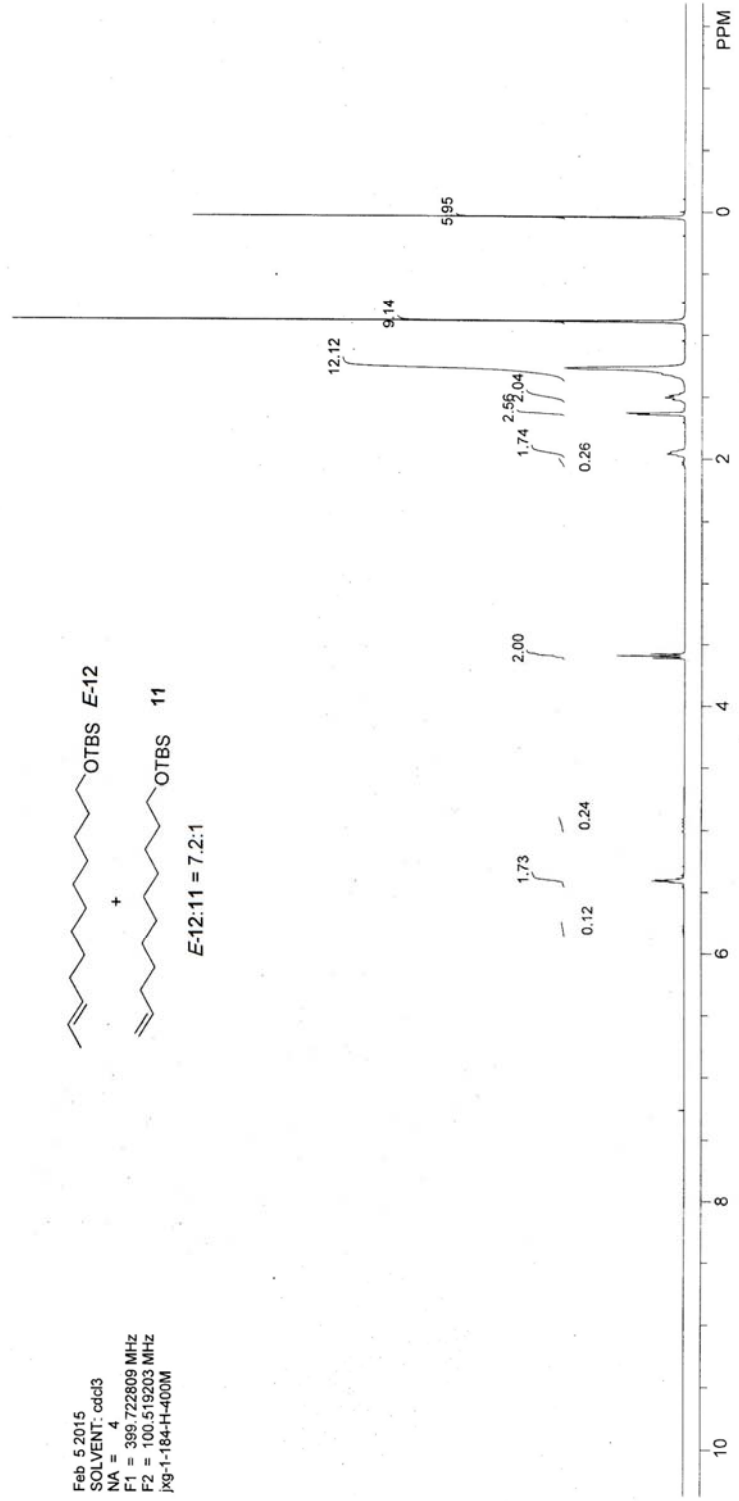


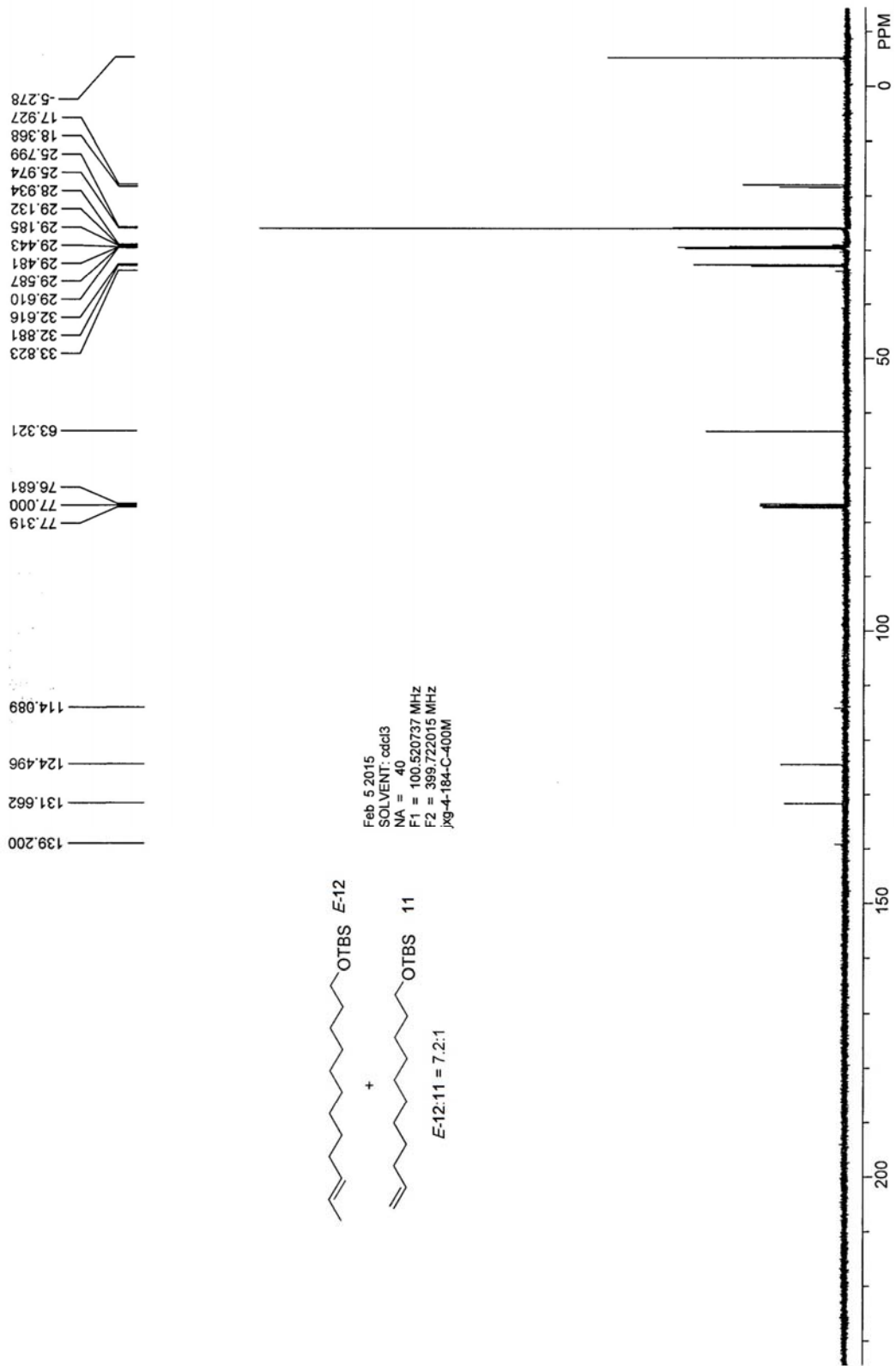


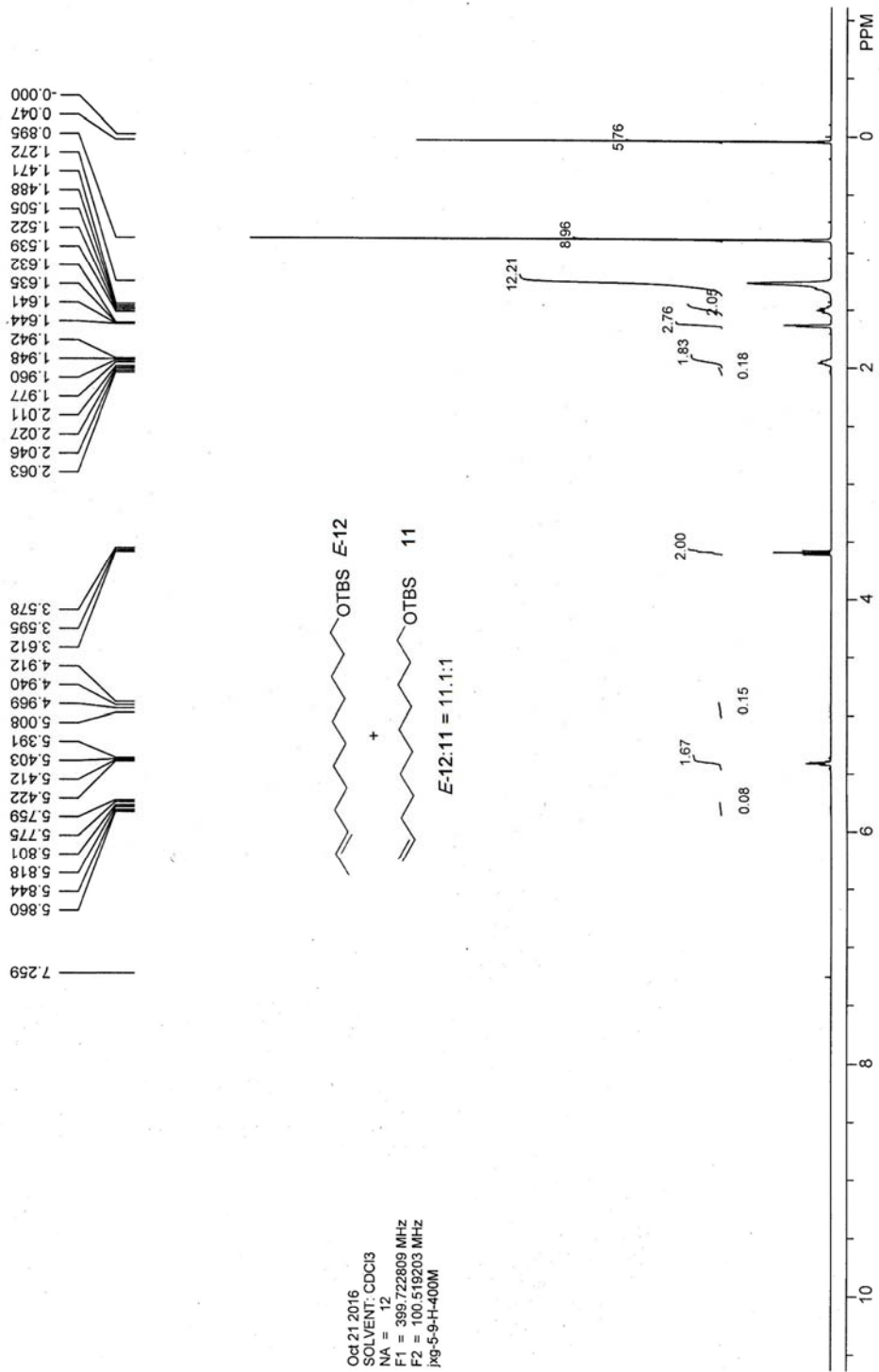


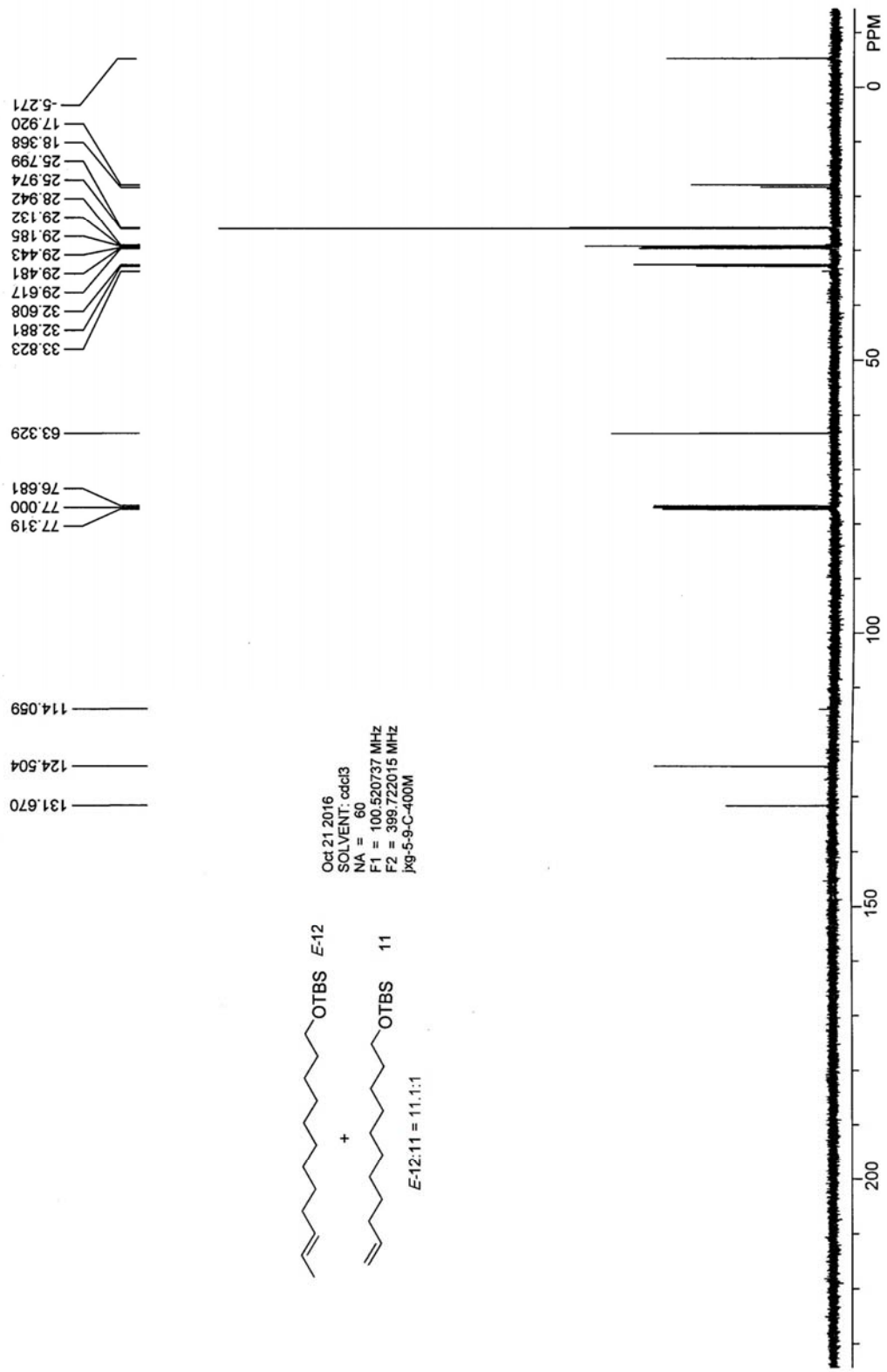
*E*-12:11 = 7.2:1

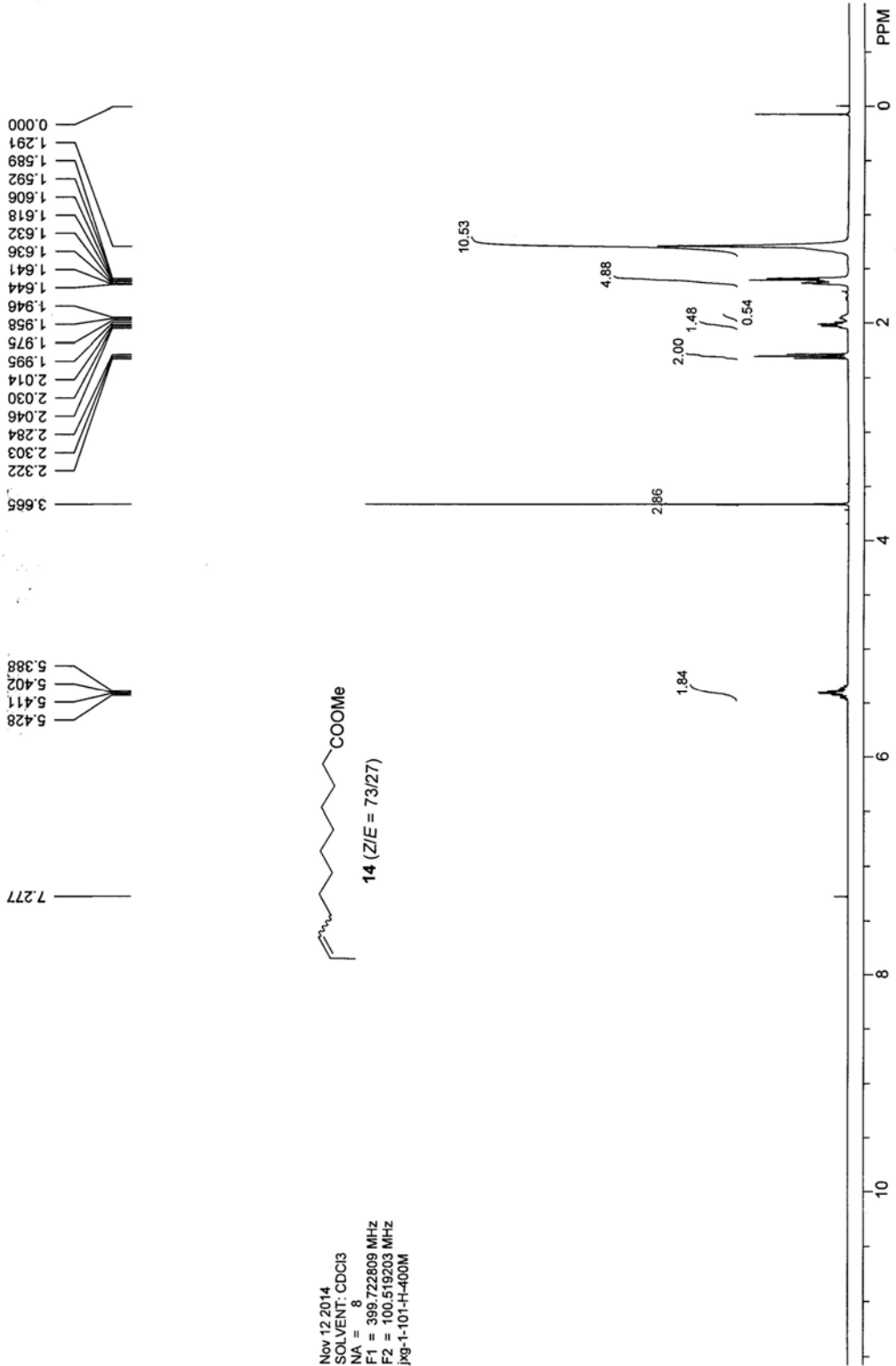
Feb 5 2015  
 SOLVENT: cddc3  
 NA = 4  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 JRG-1-184-H-400M

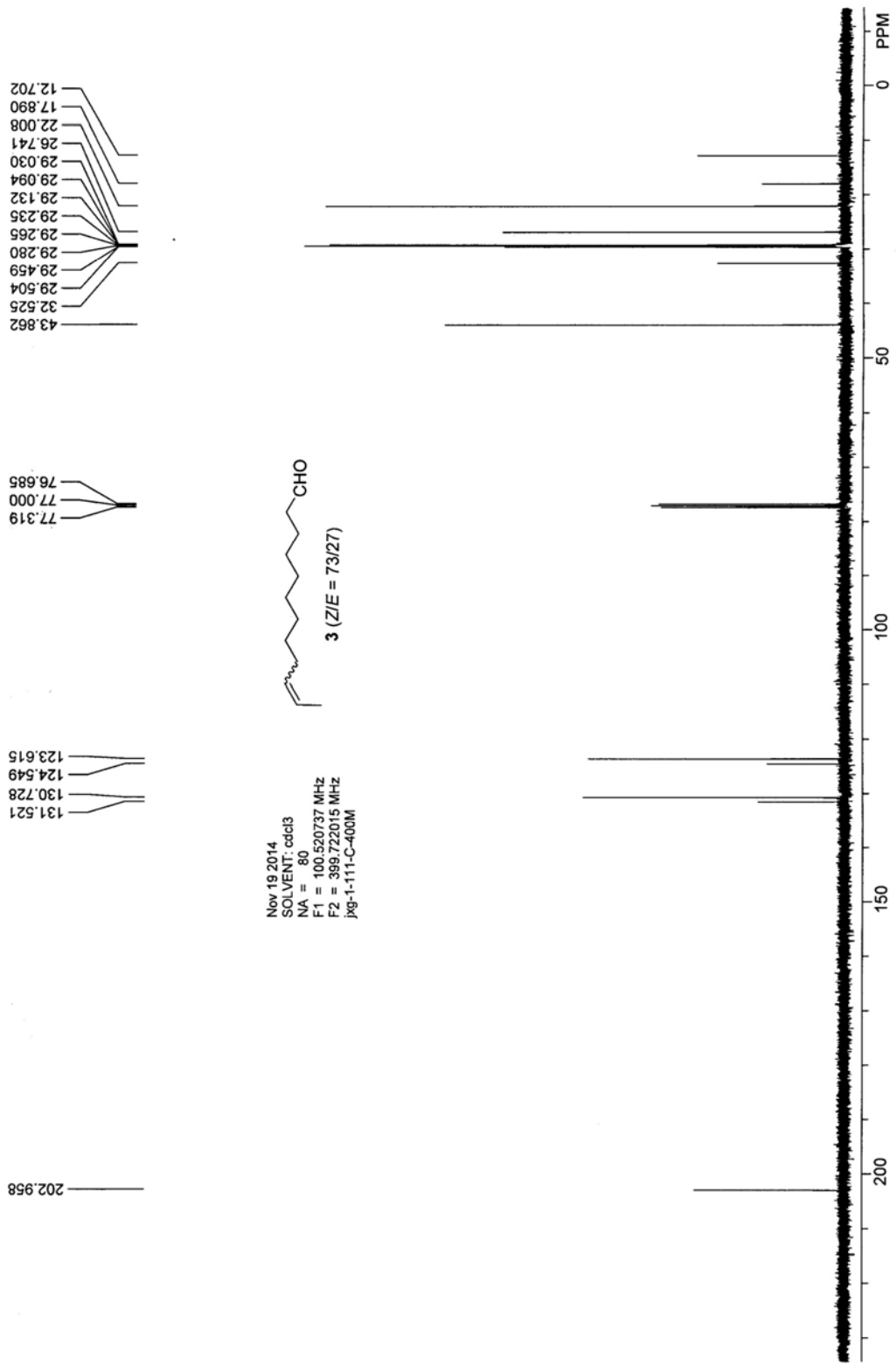


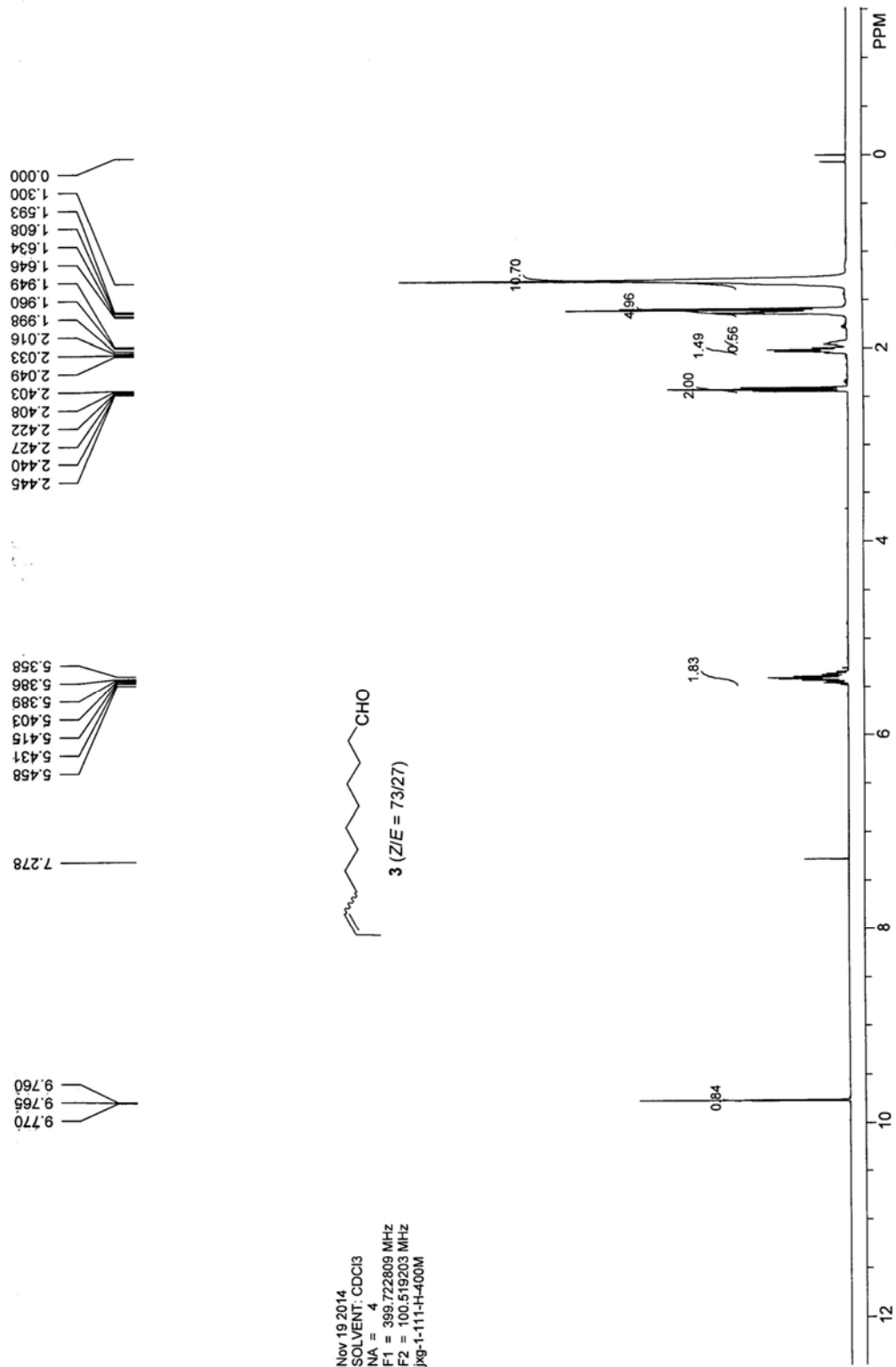


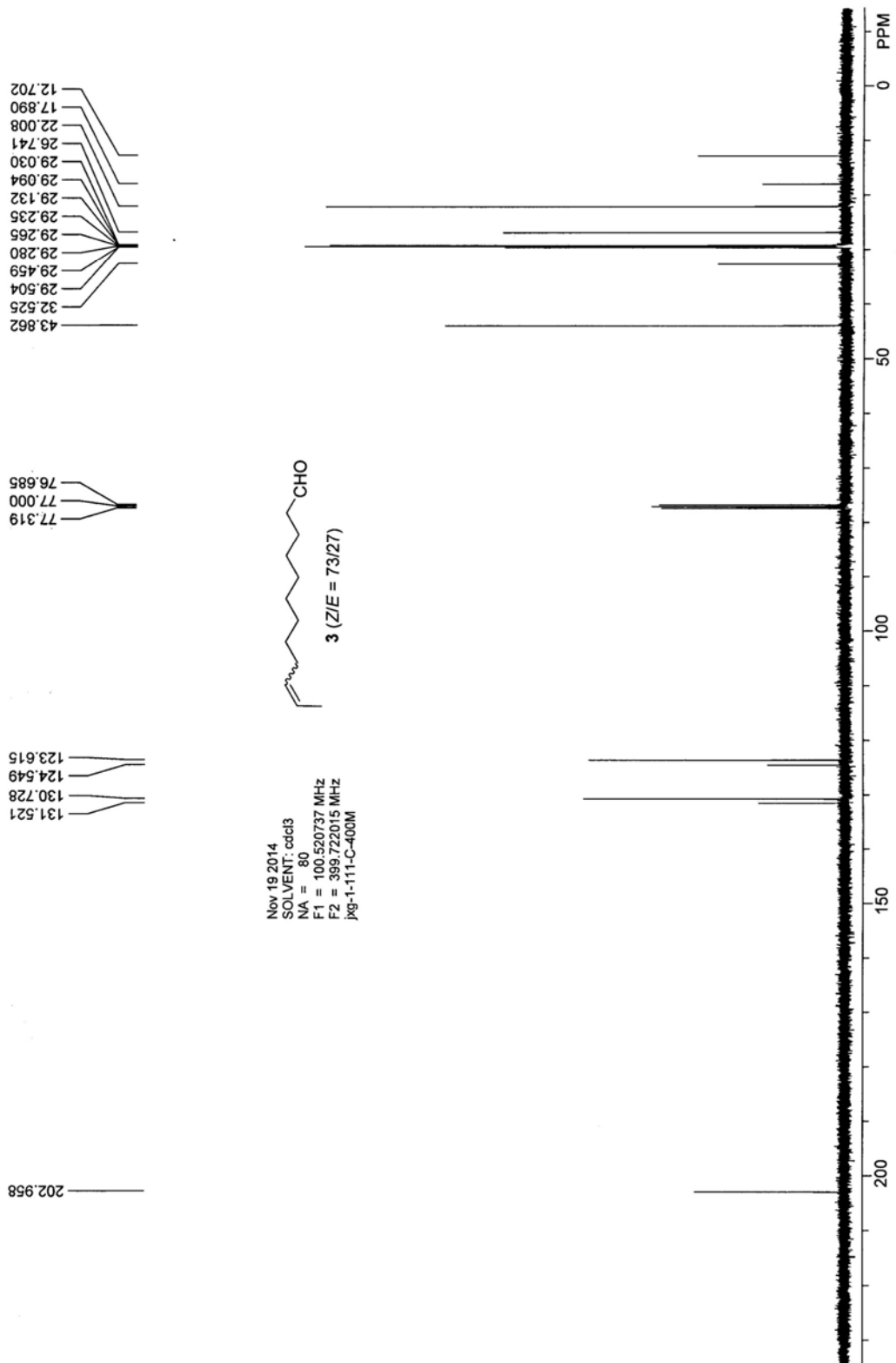










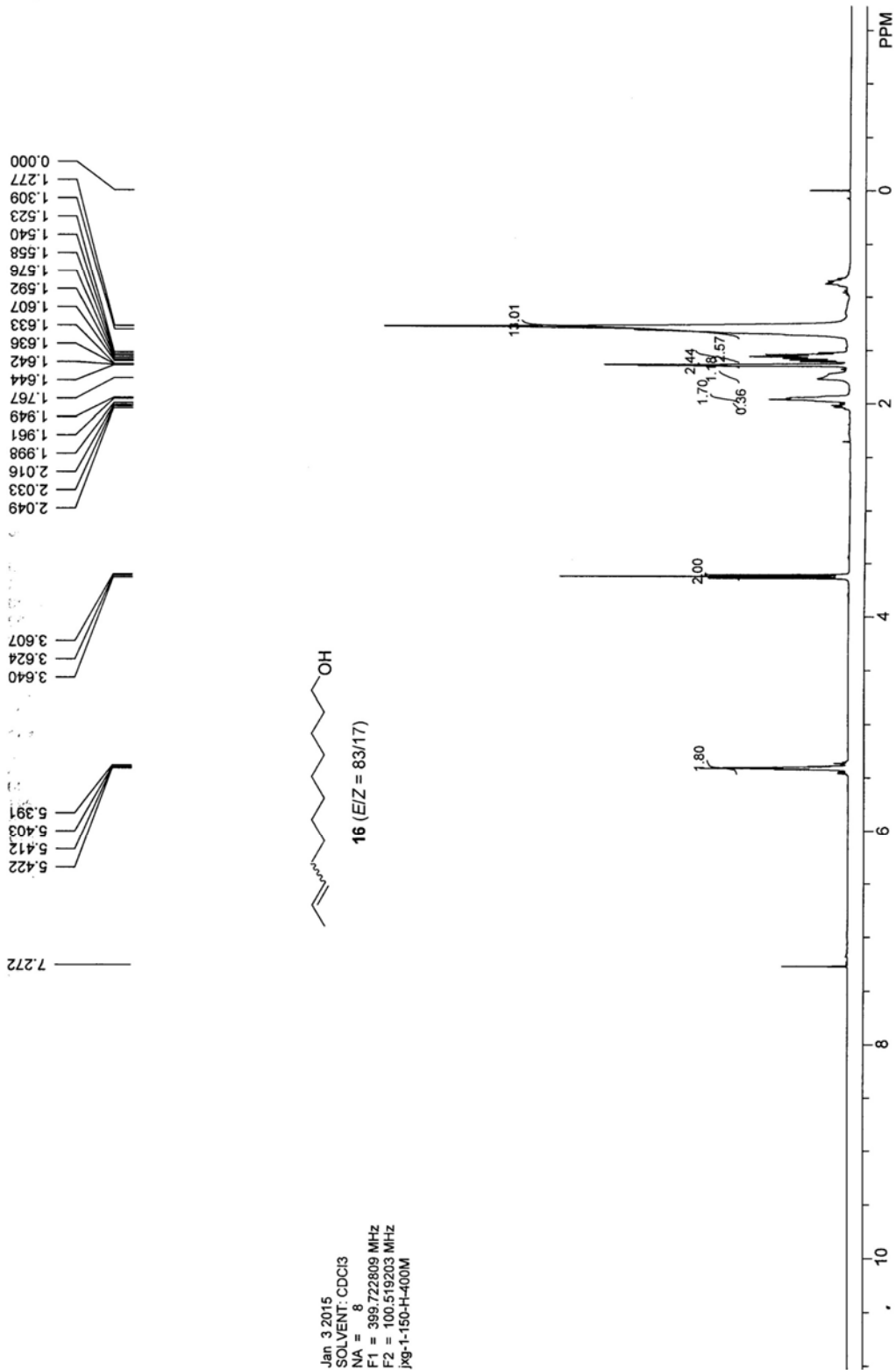


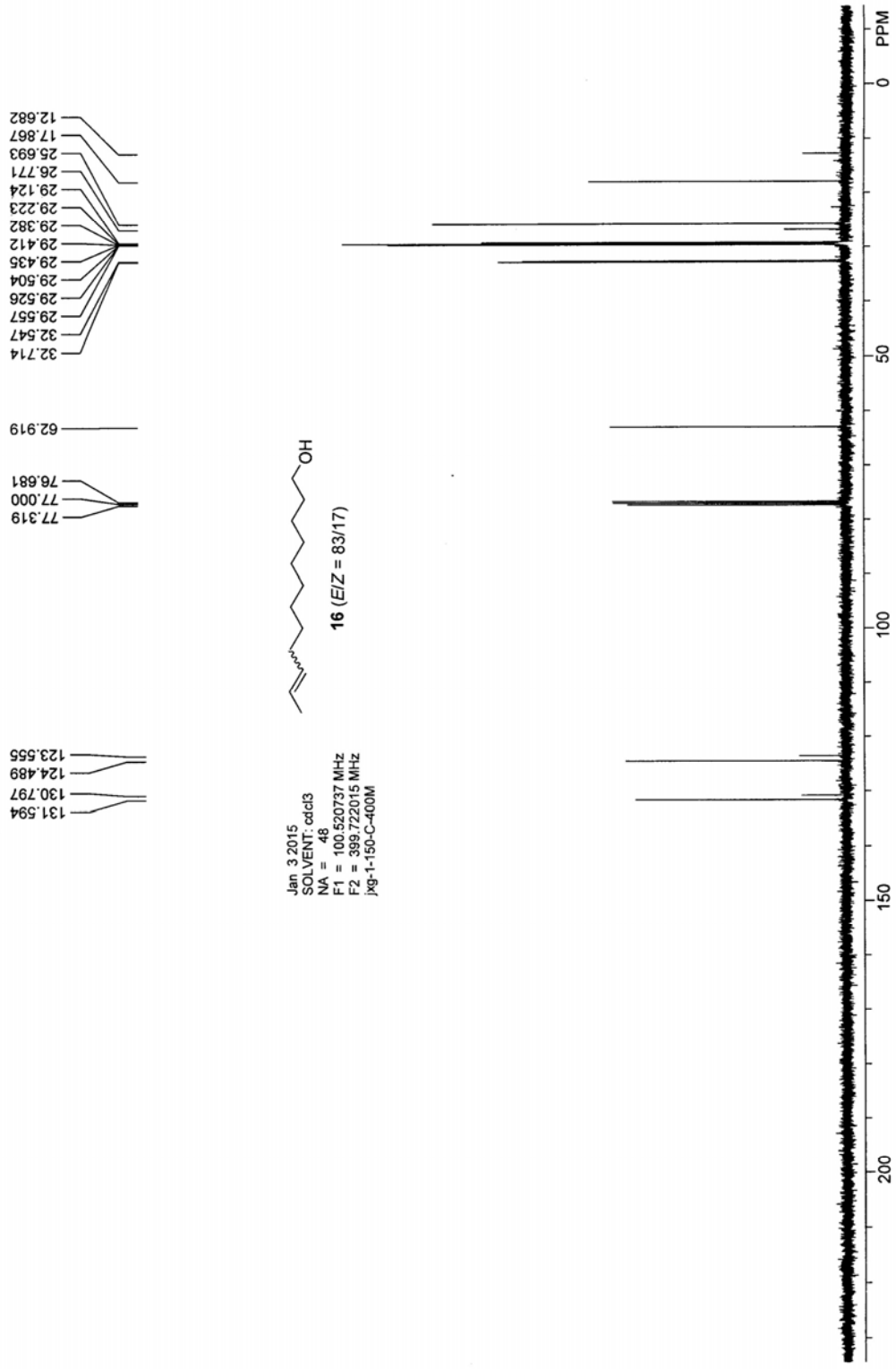


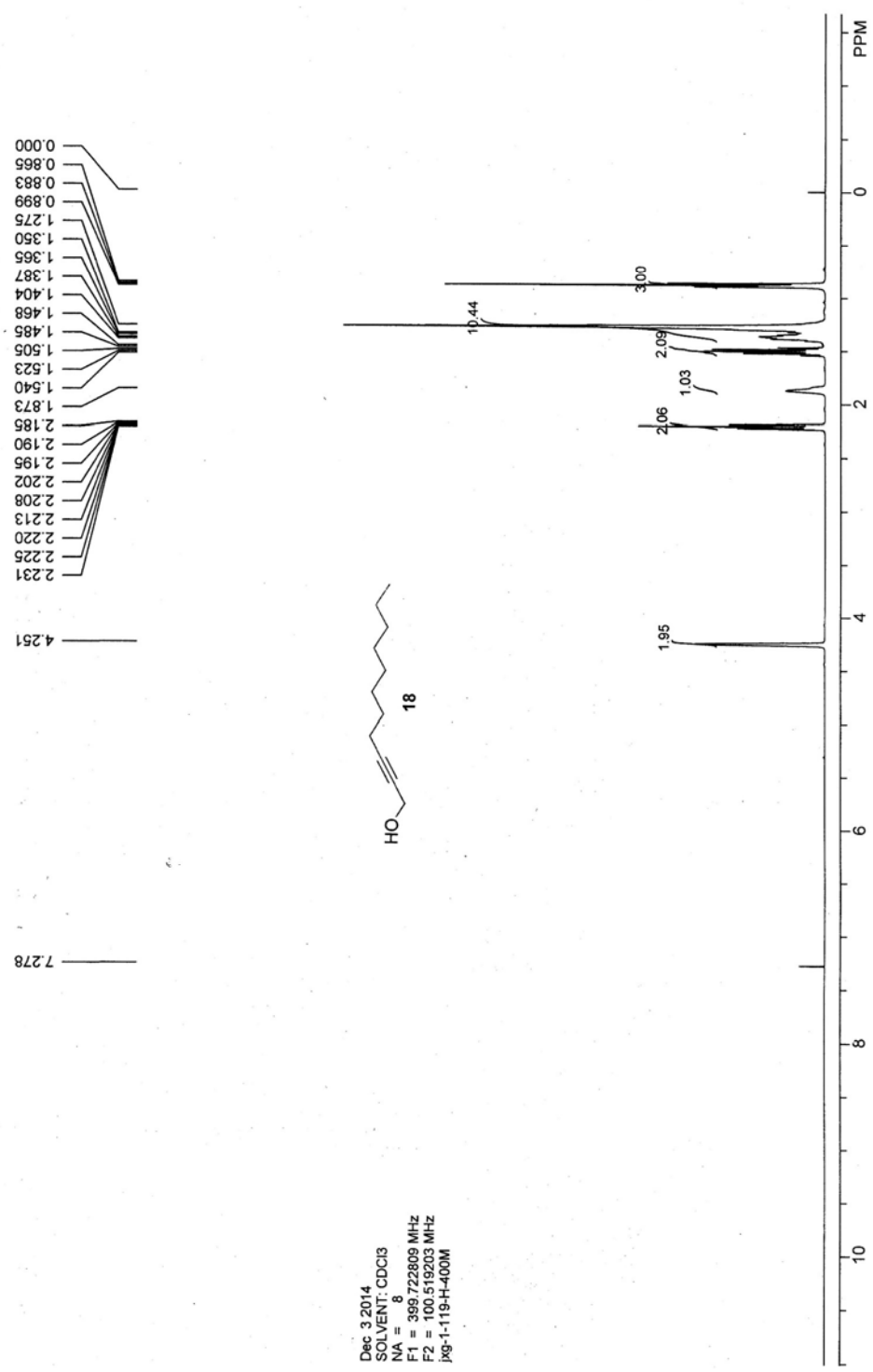
Jan 3 2015  
SOLVENT: CDCl3  
NA = 8  
F1 = 399.722809 MHz  
F2 = 100.519203 MHz  
jg9-1-150-H-400M

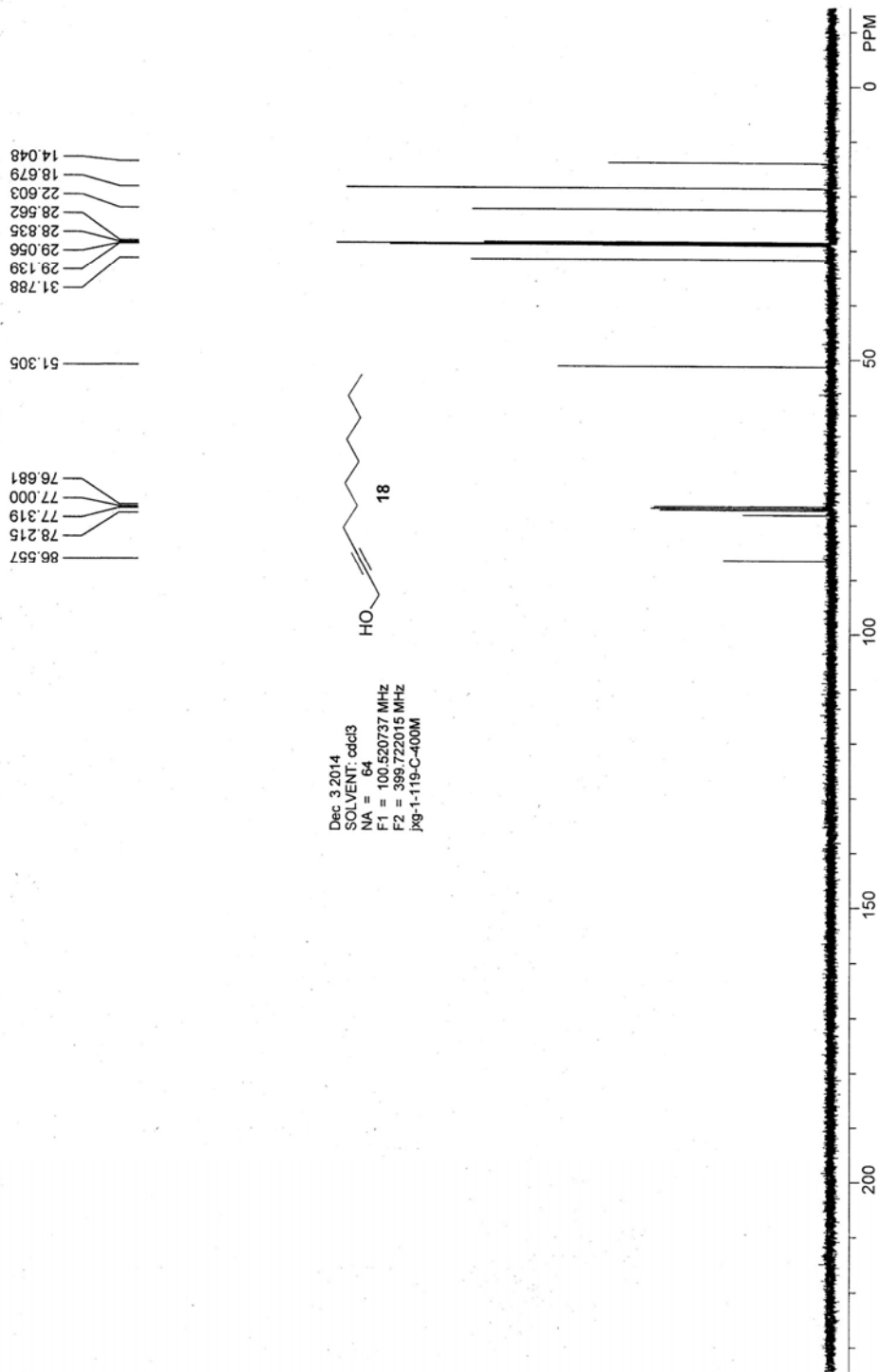


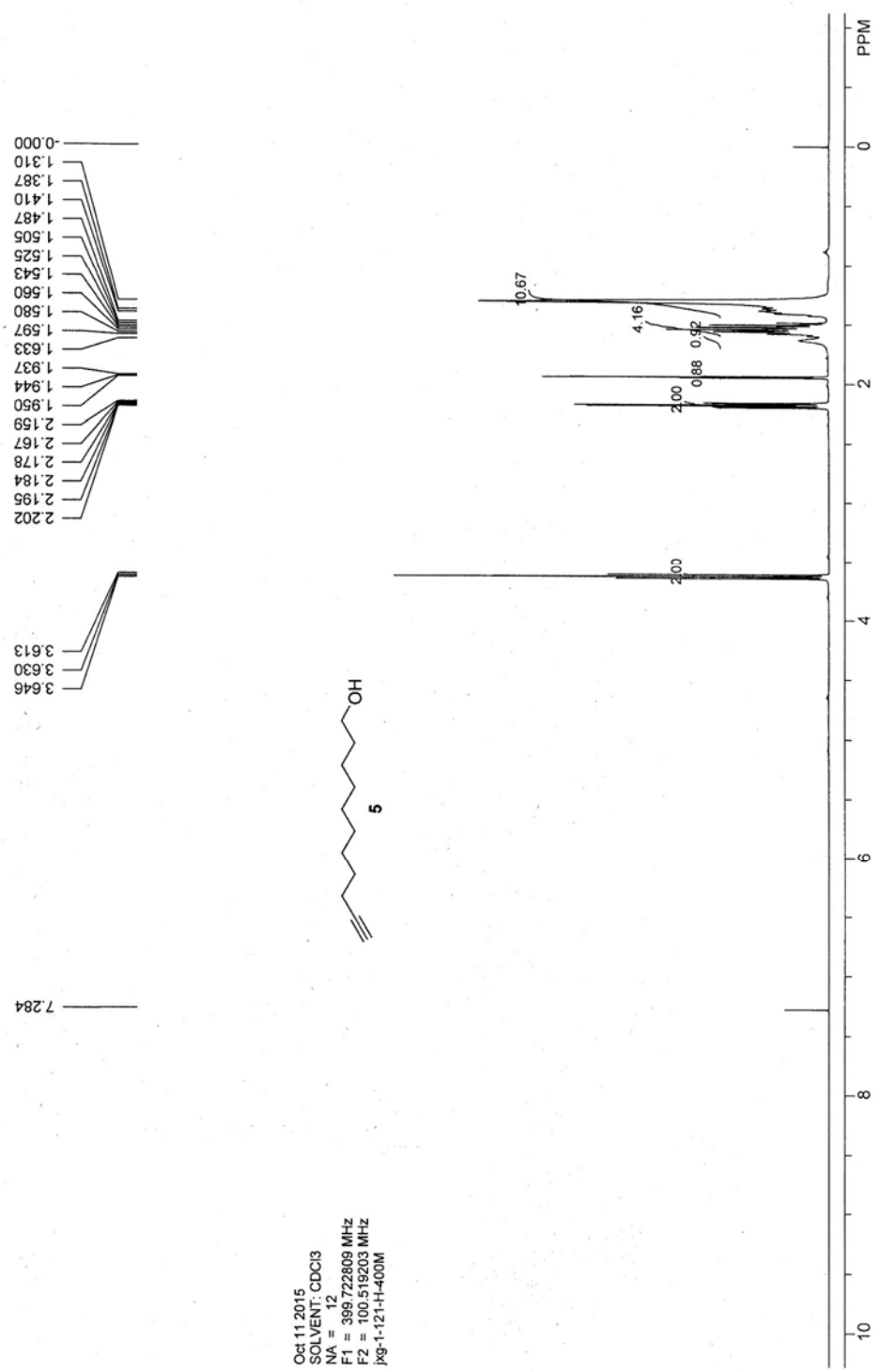
**16** (E/Z = 83/17)



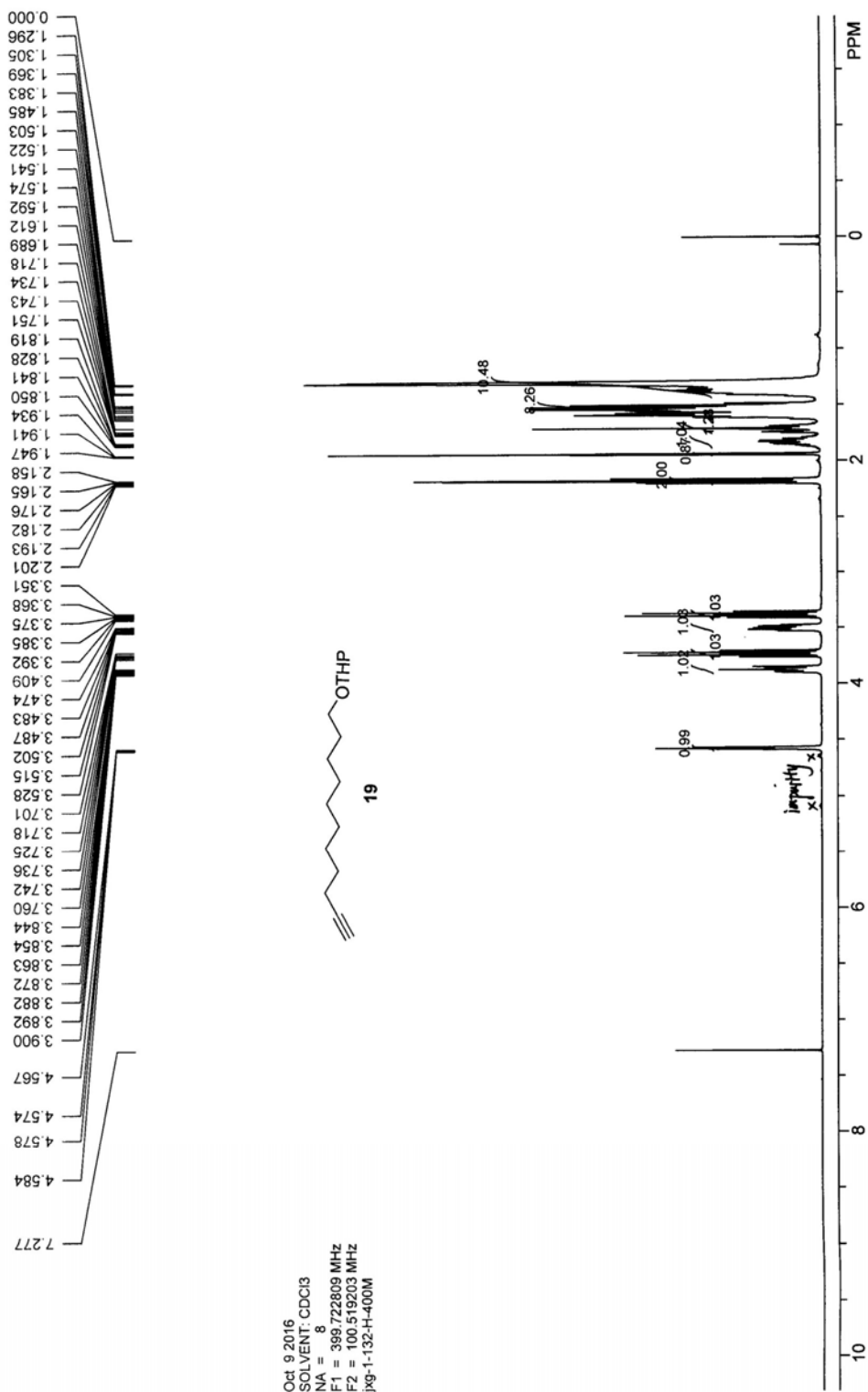








Oct 11, 2015  
 SOLVENT: CDCl3  
 NA = 12  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 JXG-1-121-H-400M

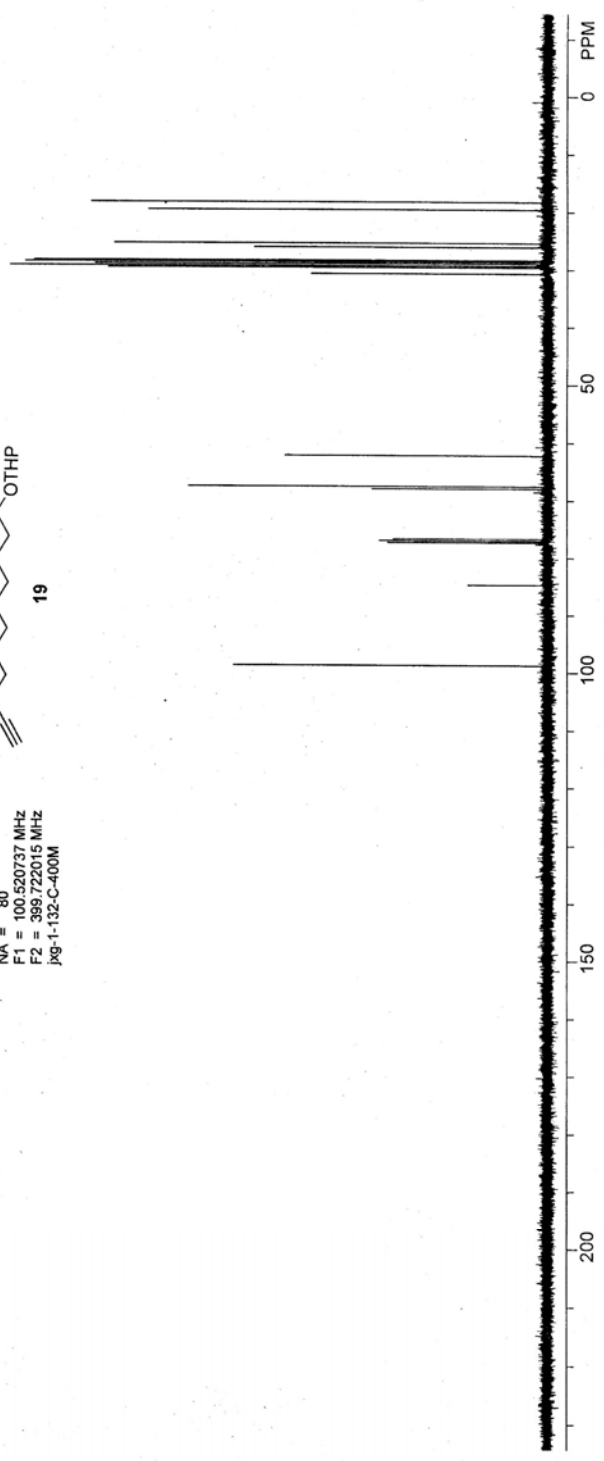
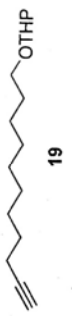


18.322  
19.635  
25.442  
26.148  
28.403  
28.661  
28.980  
29.359  
29.671  
30.718

62.258  
67.587  
68.012  
76.681  
77.000  
77.319  
84.674

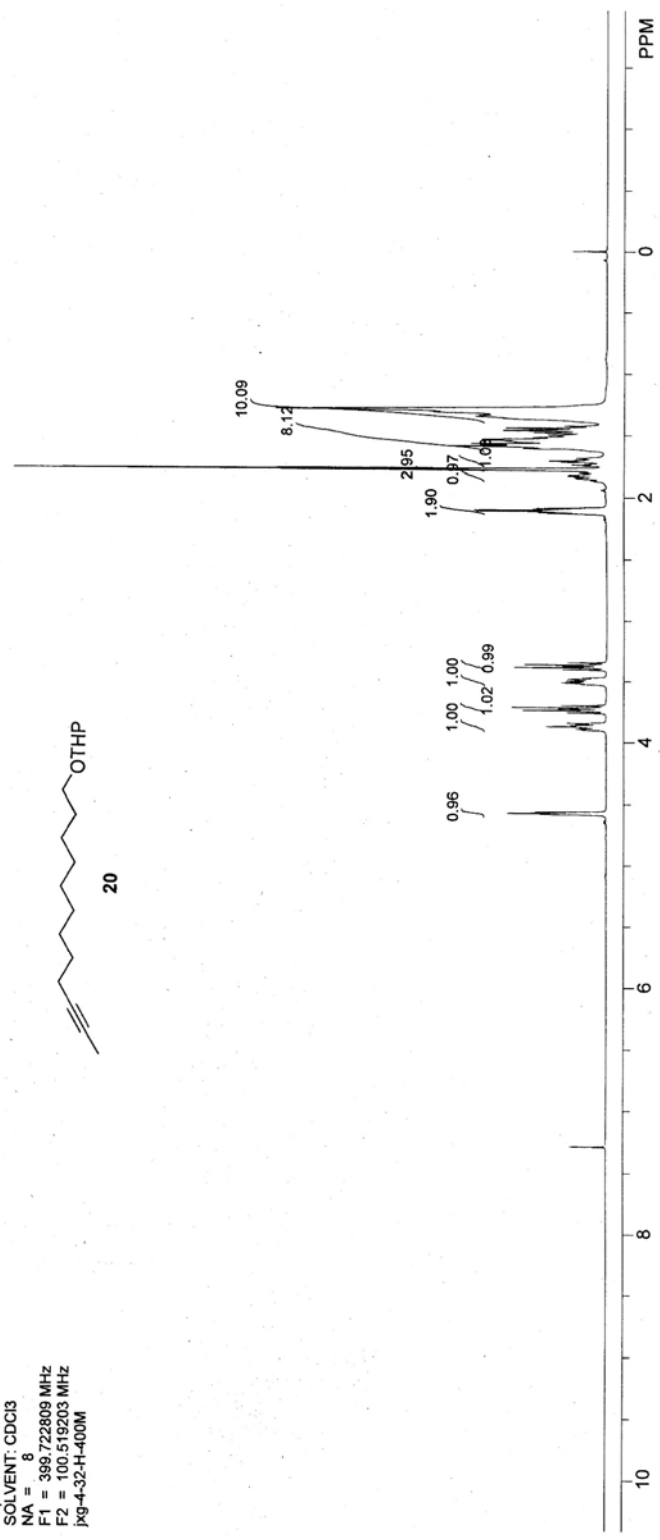
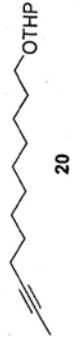
98.763

Dec 16 2014  
SOLVENT: cdcl3  
NA = 80  
F1 = 100.520737 MHz  
F2 = 399.722015 MHz  
jg-1-132-C-400M



7.285  
 4.583  
 4.577  
 4.566  
 3.891  
 3.872  
 3.863  
 3.844  
 3.758  
 3.741  
 3.735  
 3.724  
 3.717  
 3.700  
 3.514  
 3.500  
 3.486  
 3.407  
 3.391  
 3.384  
 3.374  
 3.367  
 3.350  
 2.131  
 2.124  
 2.113  
 2.107  
 2.096  
 2.089  
 1.850  
 1.841  
 1.828  
 1.819  
 1.785  
 1.779  
 1.773  
 1.717  
 1.710  
 1.592  
 1.573  
 1.536  
 1.463  
 1.446  
 1.351  
 1.319  
 1.296  
 0.000

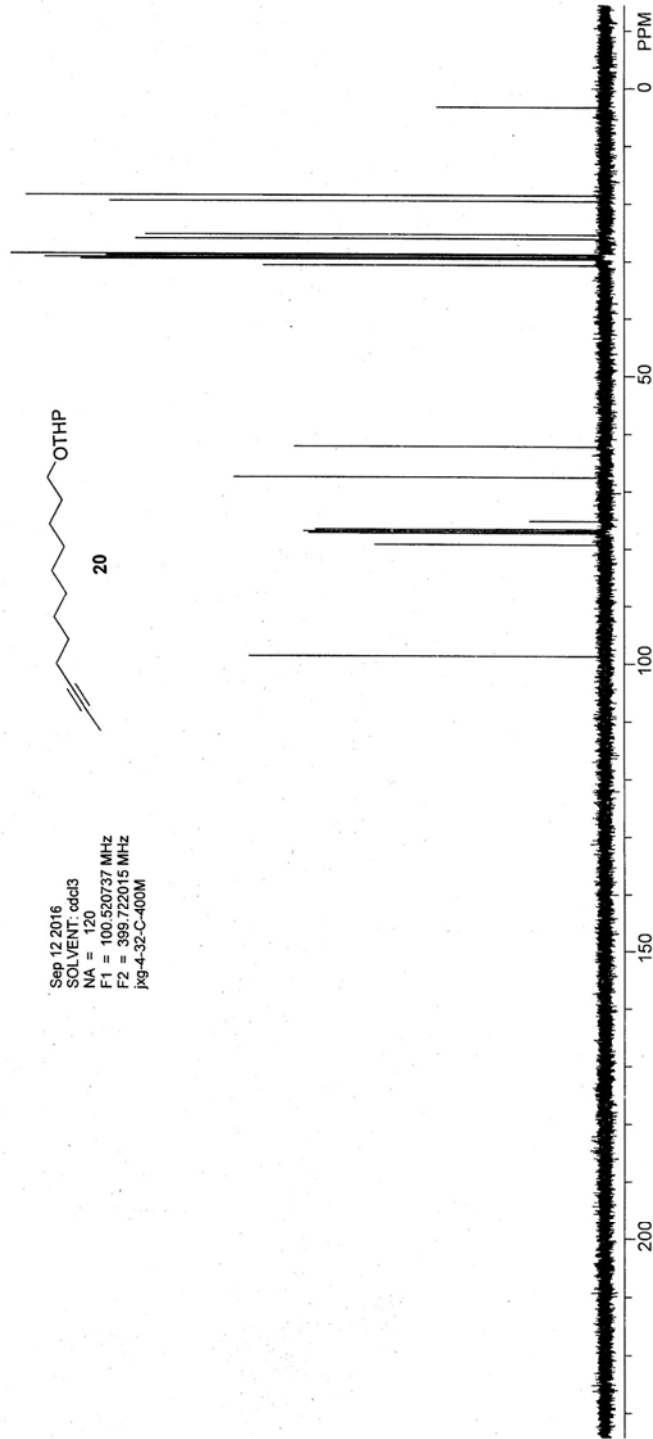
Sep 12 2016  
 SOLVENT: CDCl3  
 NA = 8  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 JXG-4-32-H-400M



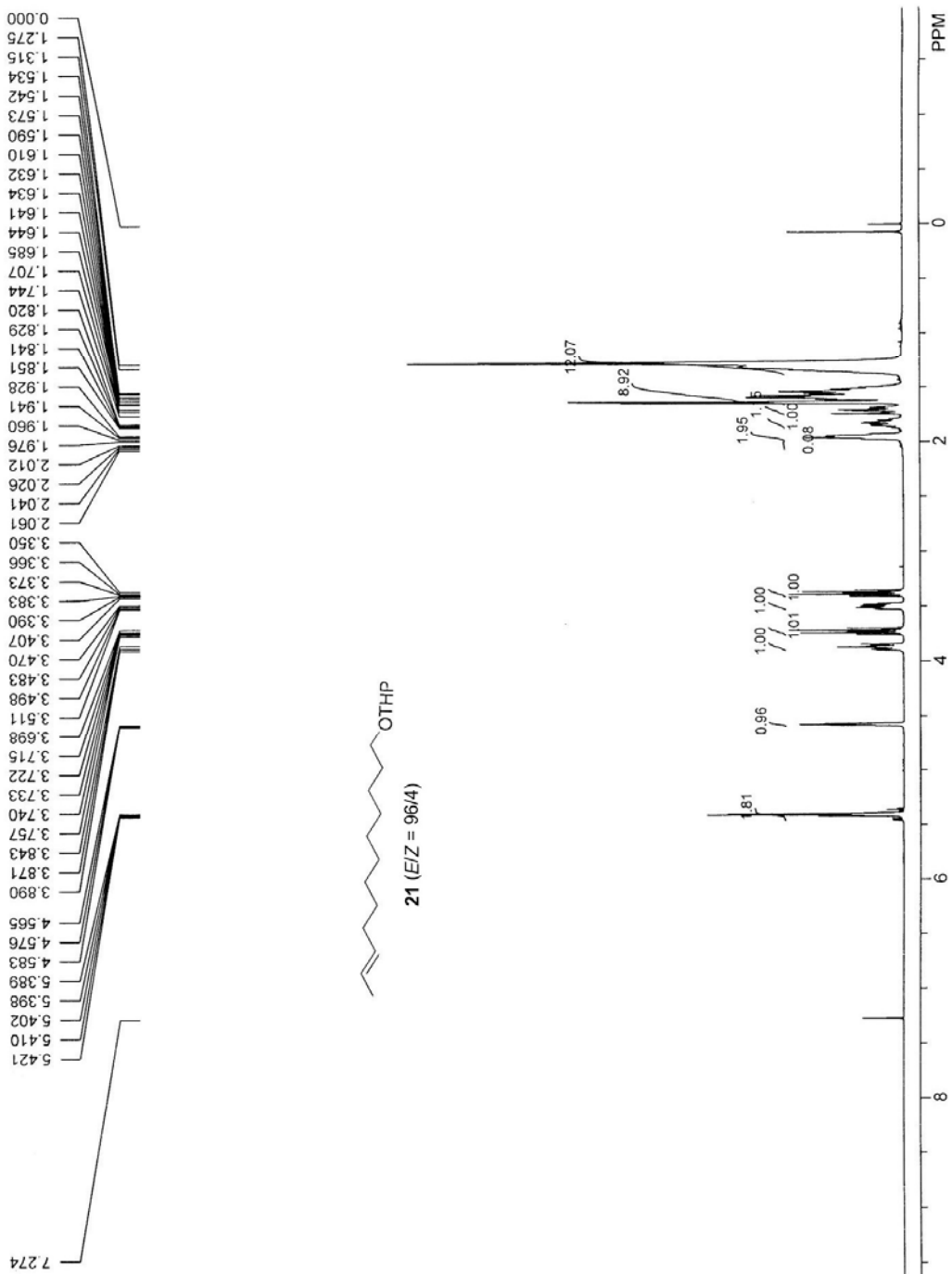


3.406  
18.656  
19.643  
25.450  
26.163  
28.820  
29.018  
29.063  
29.382  
29.412  
29.686  
30.726

62.266  
67.610  
75.239  
76.681  
77.000  
77.319  
79.323  
98.771

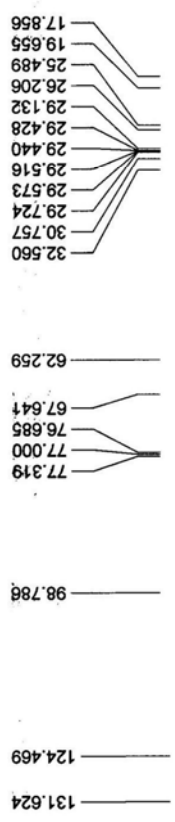


Sep 12 2016  
SOLVENT: cdcl3  
NA = 120  
F1 = 100.520737 MHz  
F2 = 398.722015 MHz  
Jg-4-32-C-400M

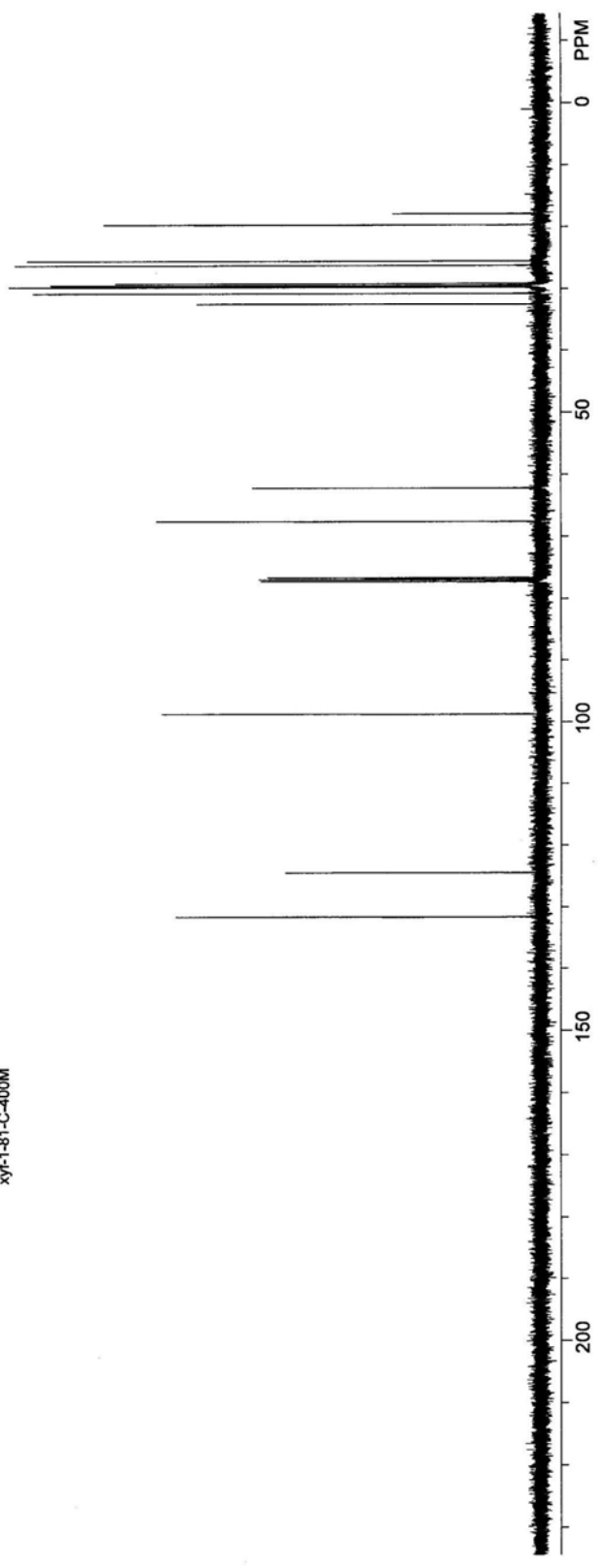
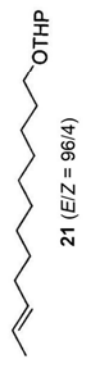


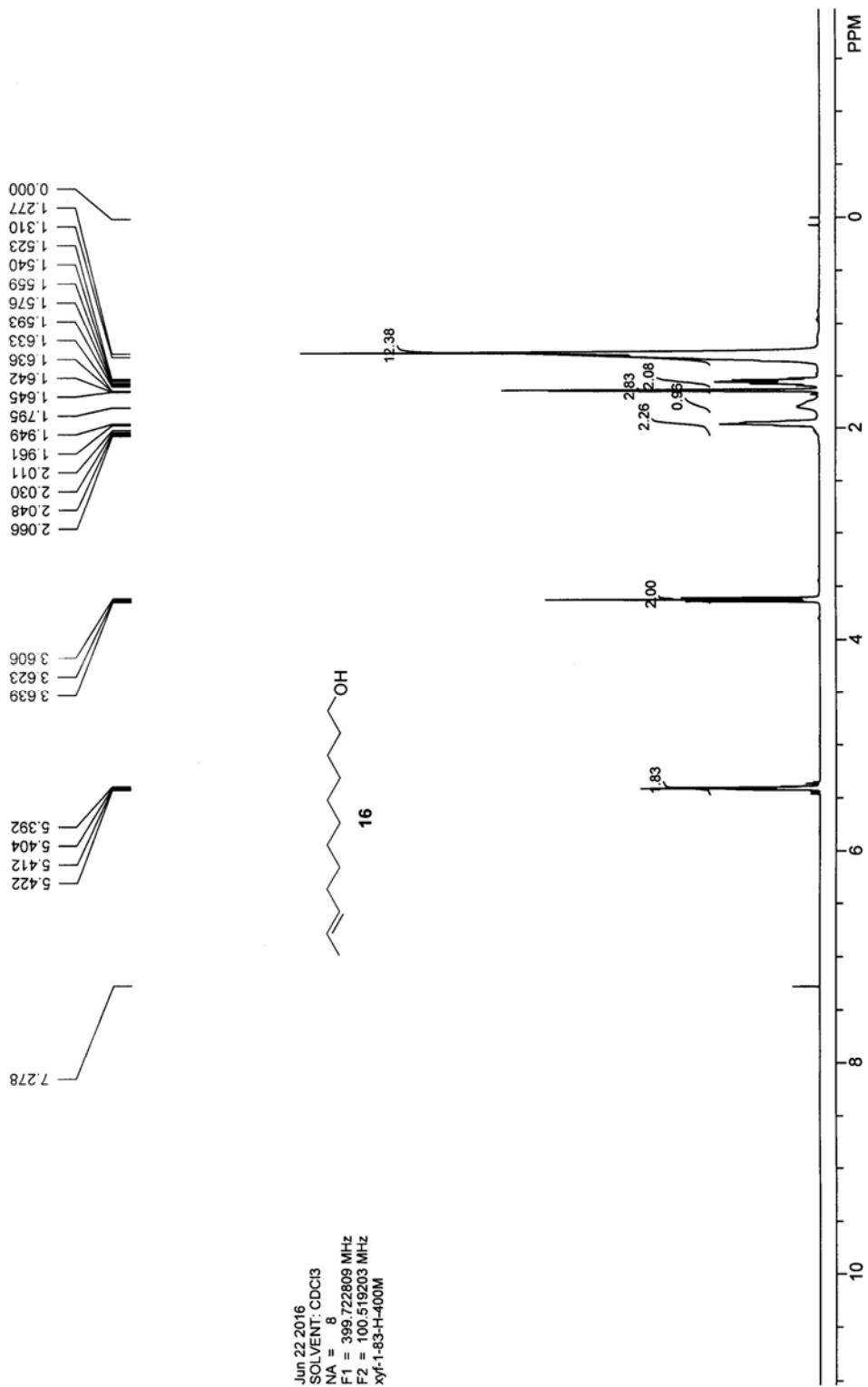
21 (E/Z = 96/4)

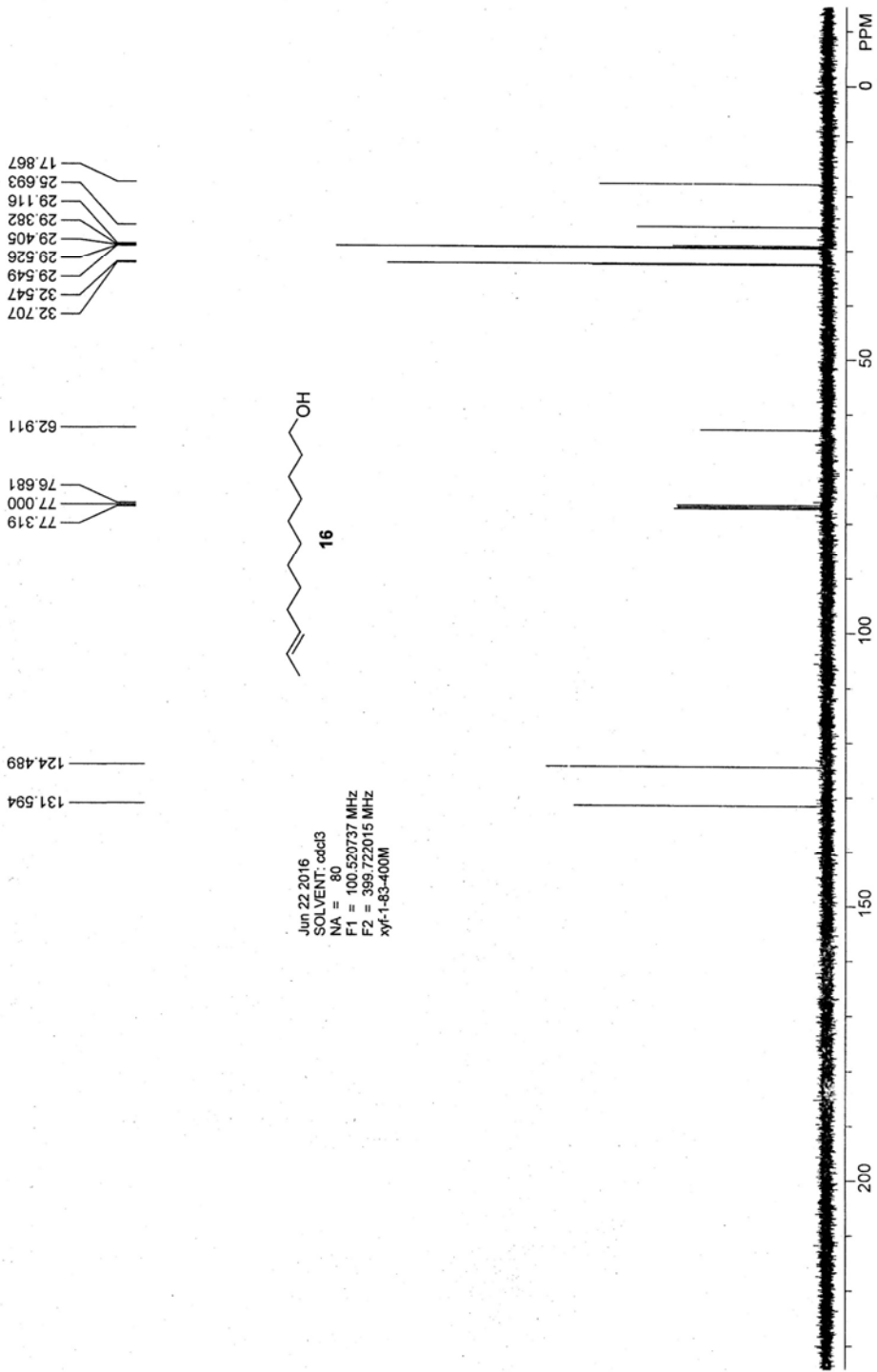
May 13 2016  
 SOLVENT: CDCl3  
 NA = 8  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 xyf-1-81-H-400M

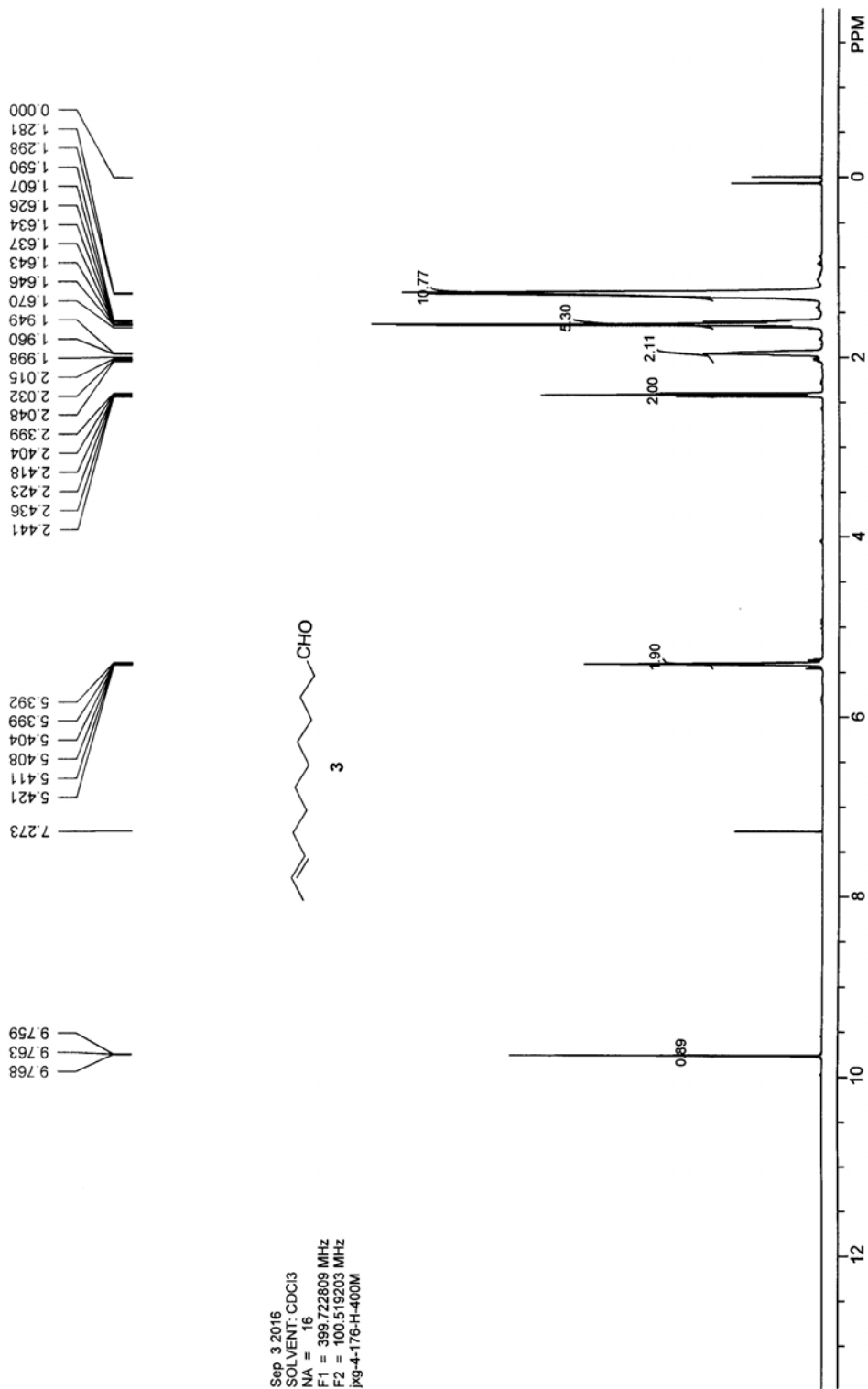


May 13 2016  
 SOLVENT: cdcl3  
 NA = 56  
 F1 = 100.520737 MHz  
 F2 = 399.722015 MHz  
 xyr-1-81-C-400M







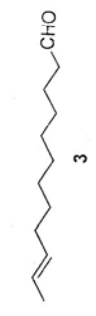


43.881  
32.532  
29.519  
29.276  
29.245  
29.109  
29.040  
22.026  
17.897

77.319  
77.000  
76.681

131.541  
124.565

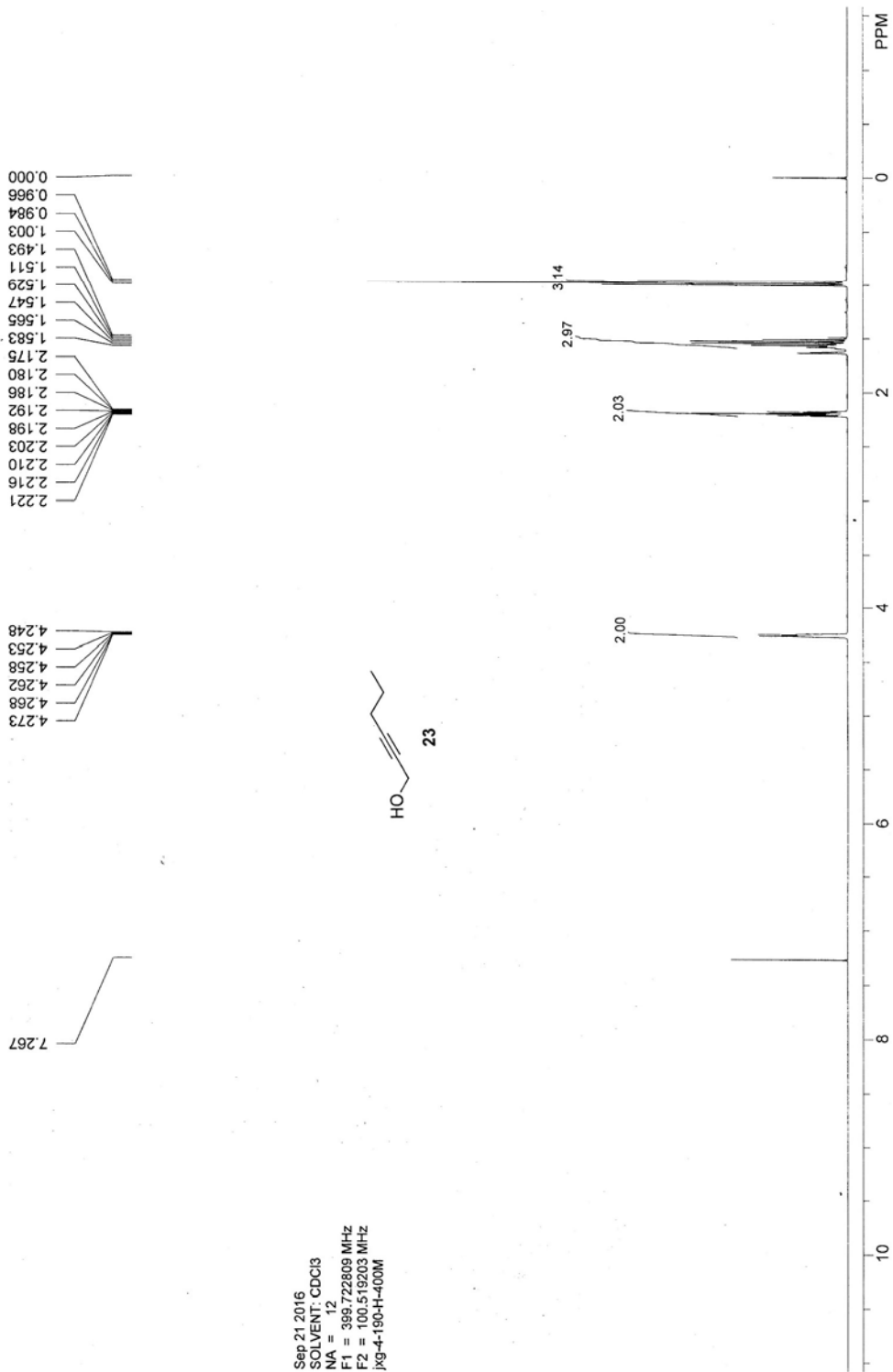
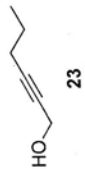
202.964



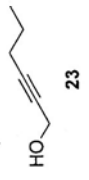
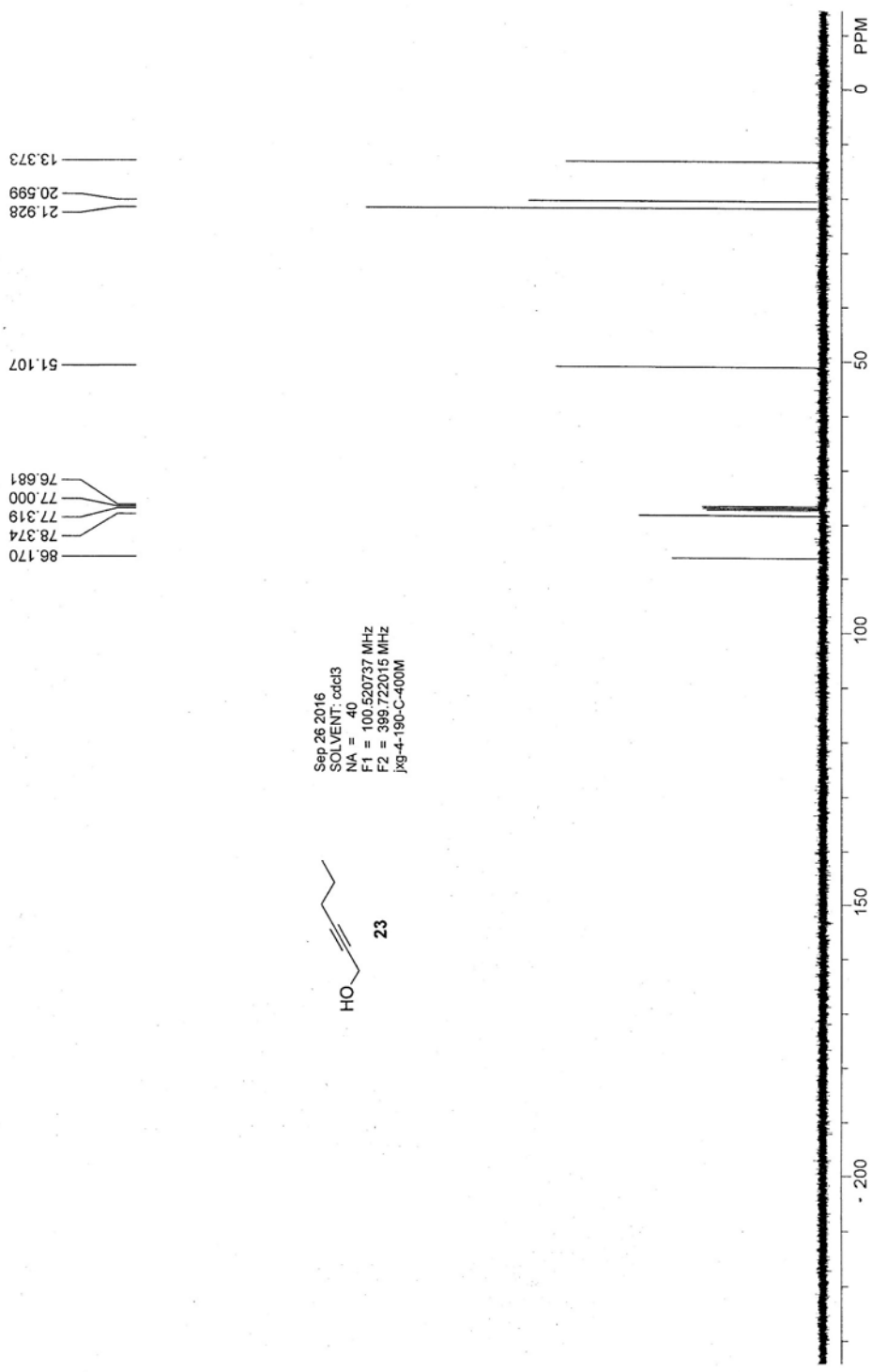
Exp 3\_2016  
SOLVENT: cddc3  
NA = 36  
F1 = 100.520737 MHz  
F2 = 399.722015 MHz  
jrg-4-176-C-400M

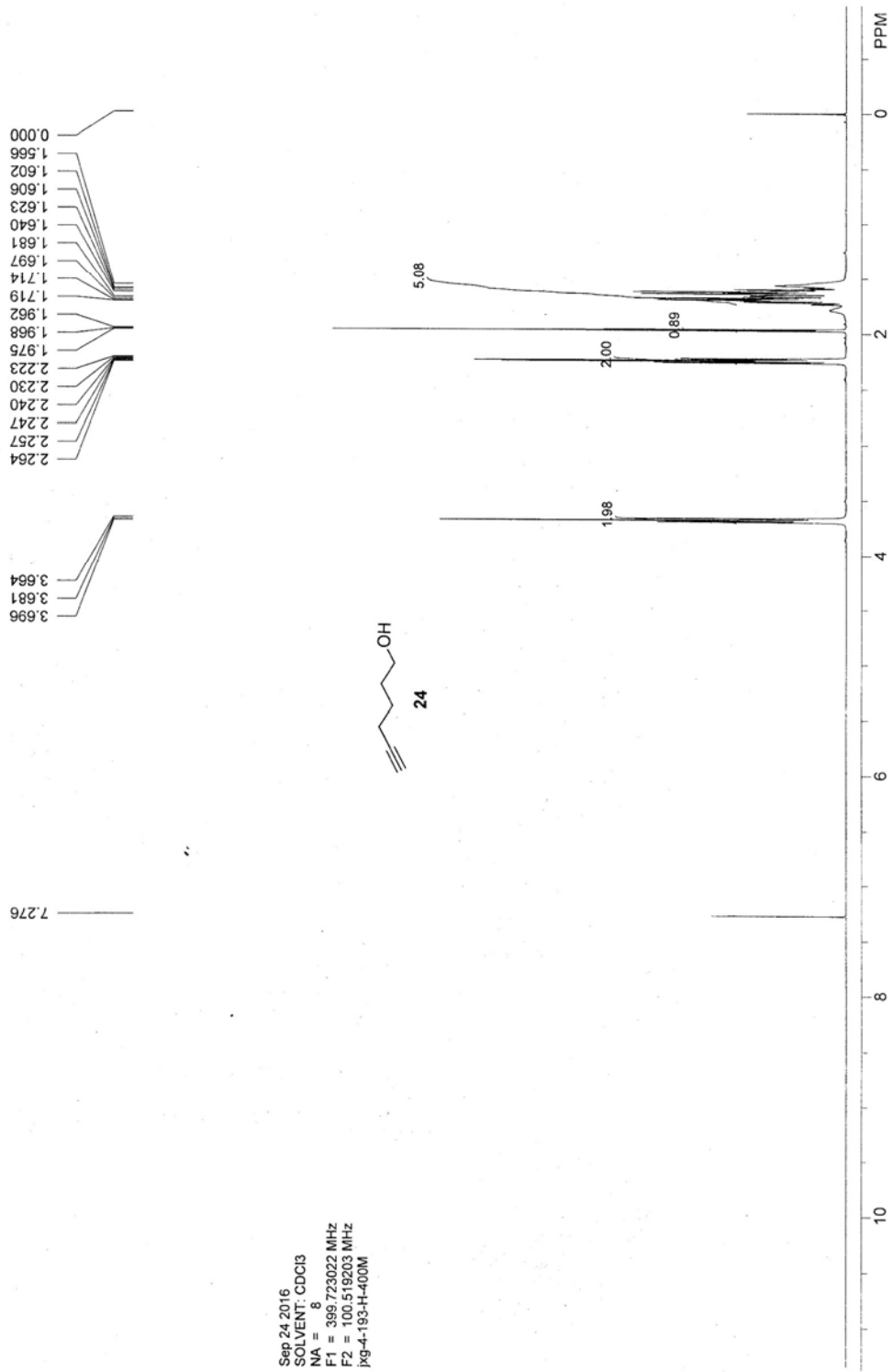


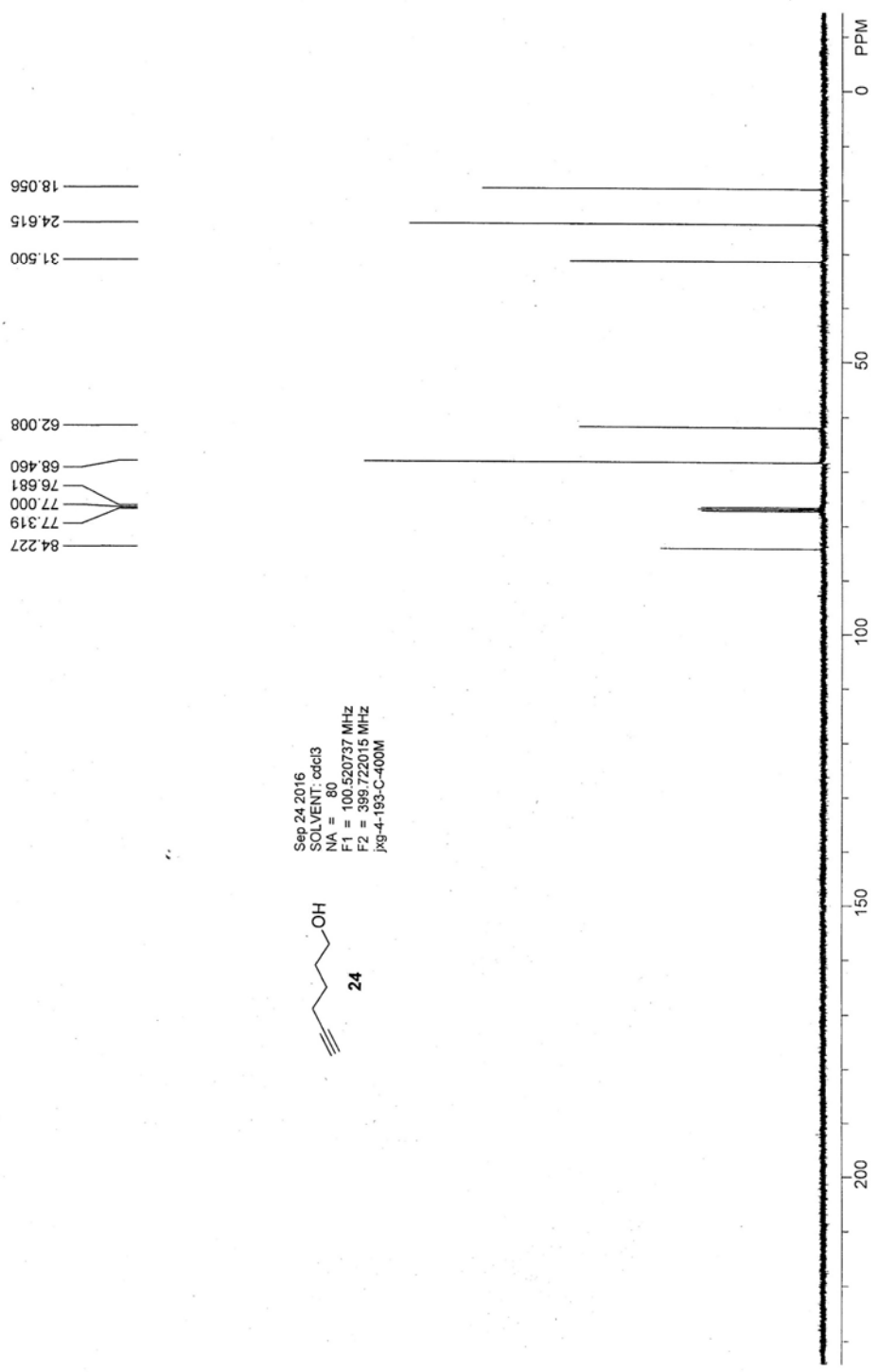
Sep 21 2016  
SOLVENT: CDCl3  
NA = 12  
F1 = 399.722809 MHz  
F2 = 100.519203 MHz  
JXG-4-190H-400M



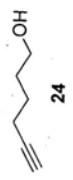


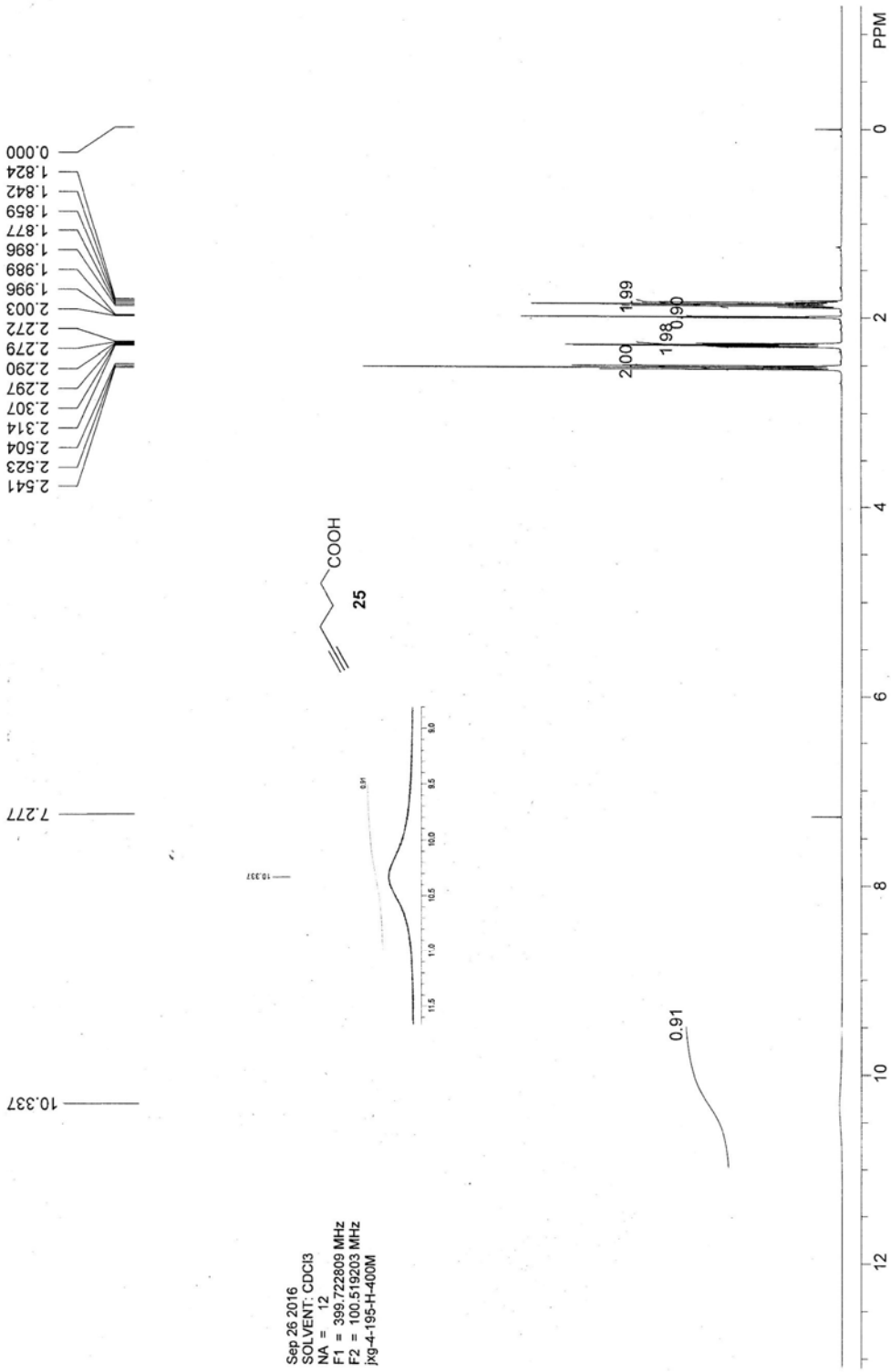




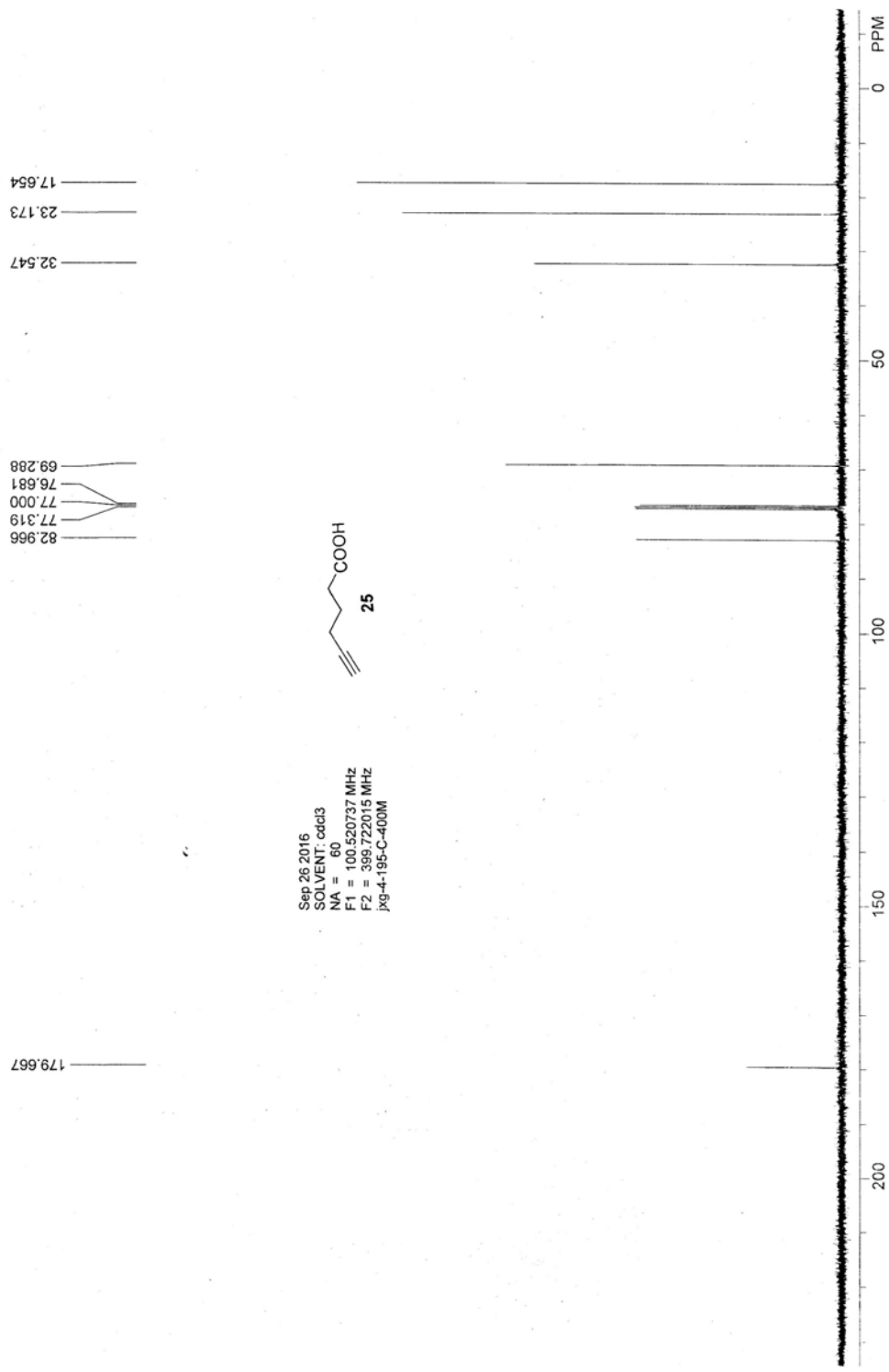


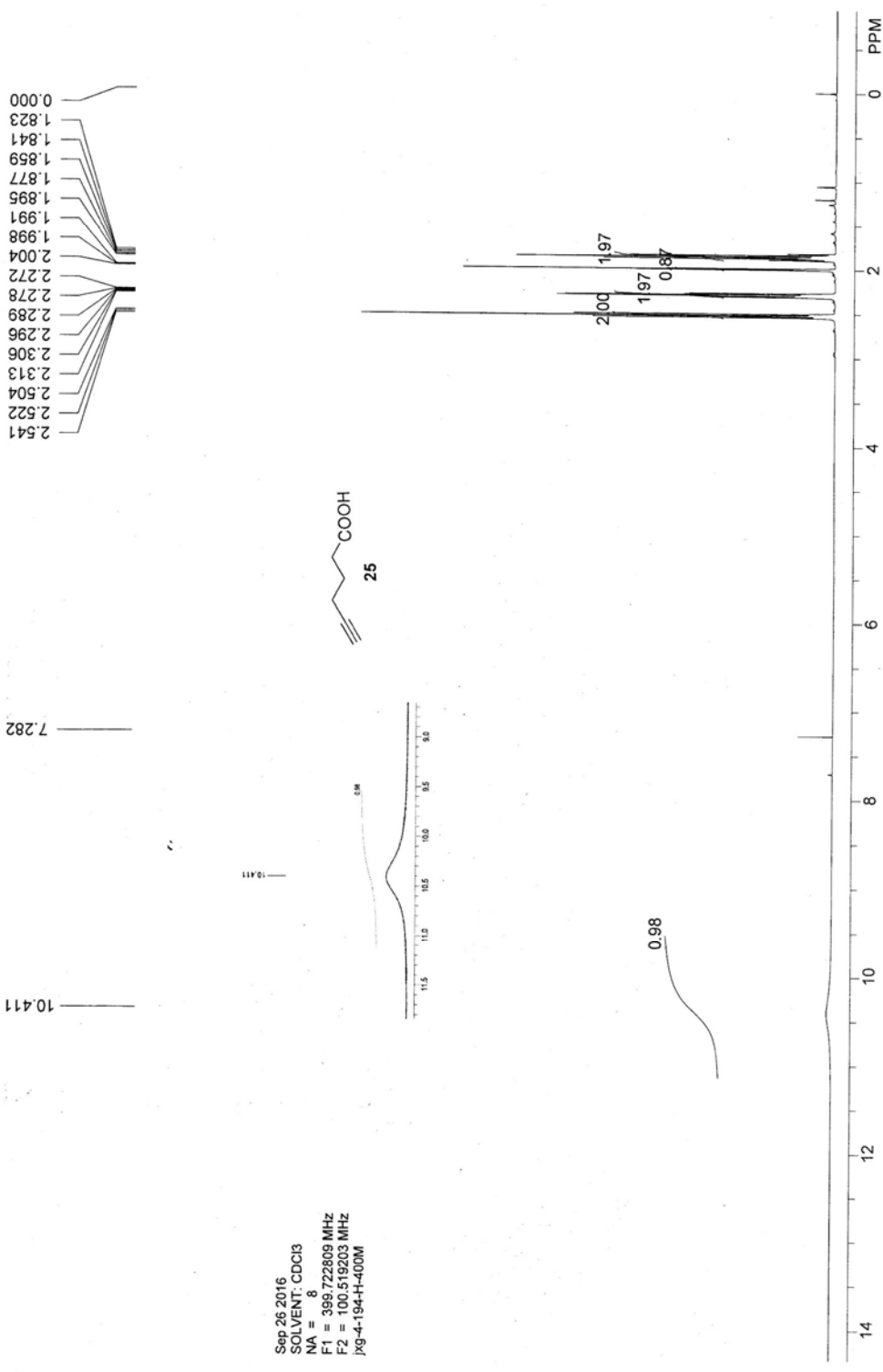
Sep 24, 2016  
 SOLVENT: cdcl3  
 NA = 80  
 F1 = 100.520737 MHz  
 F2 = 399.722015 MHz  
 JRG-4-193-C-400M

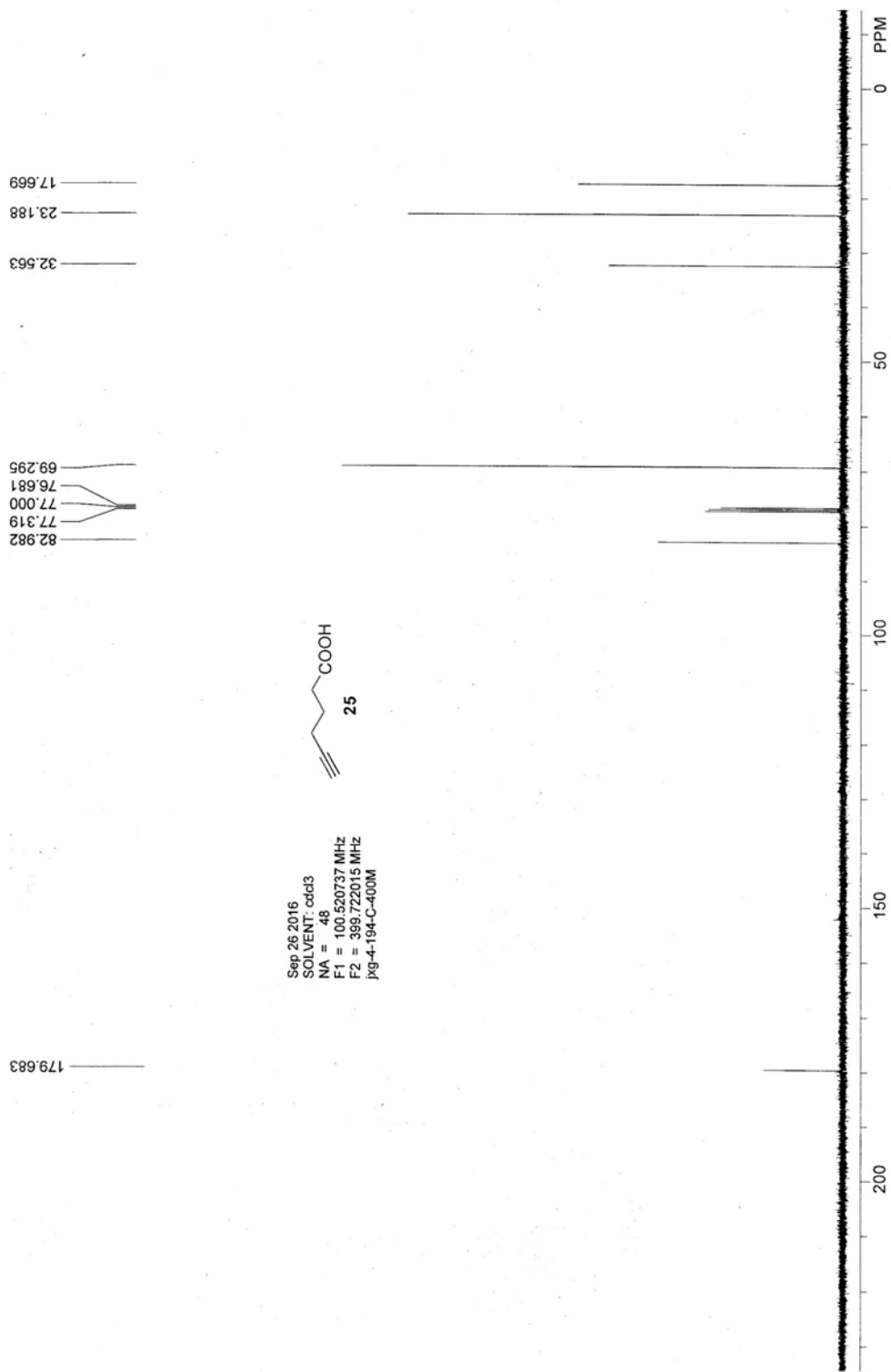




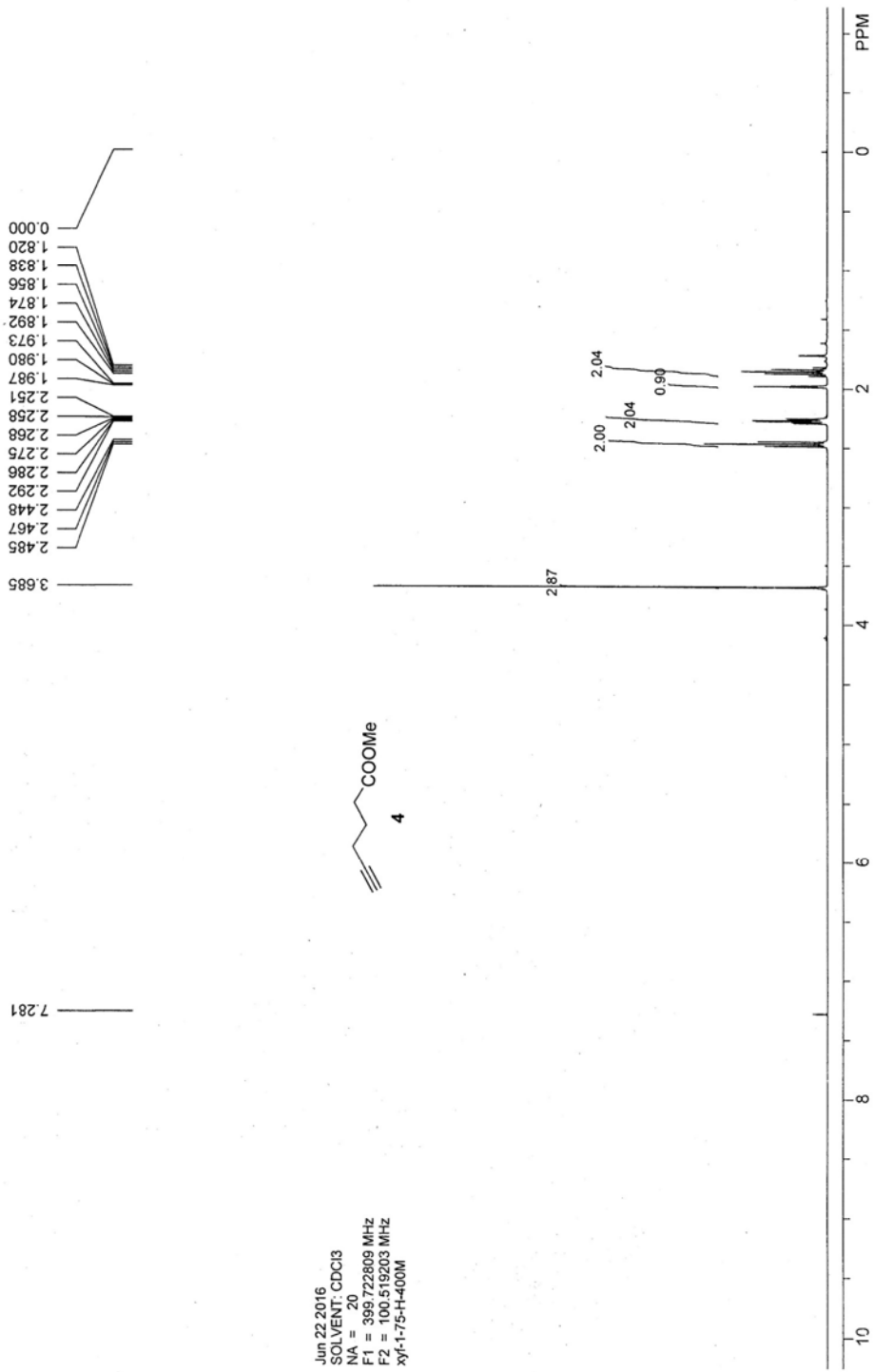
Sep 26 2016  
 SOLVENT: CDCl3  
 NA = 12  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 jg-4-195-H-400M



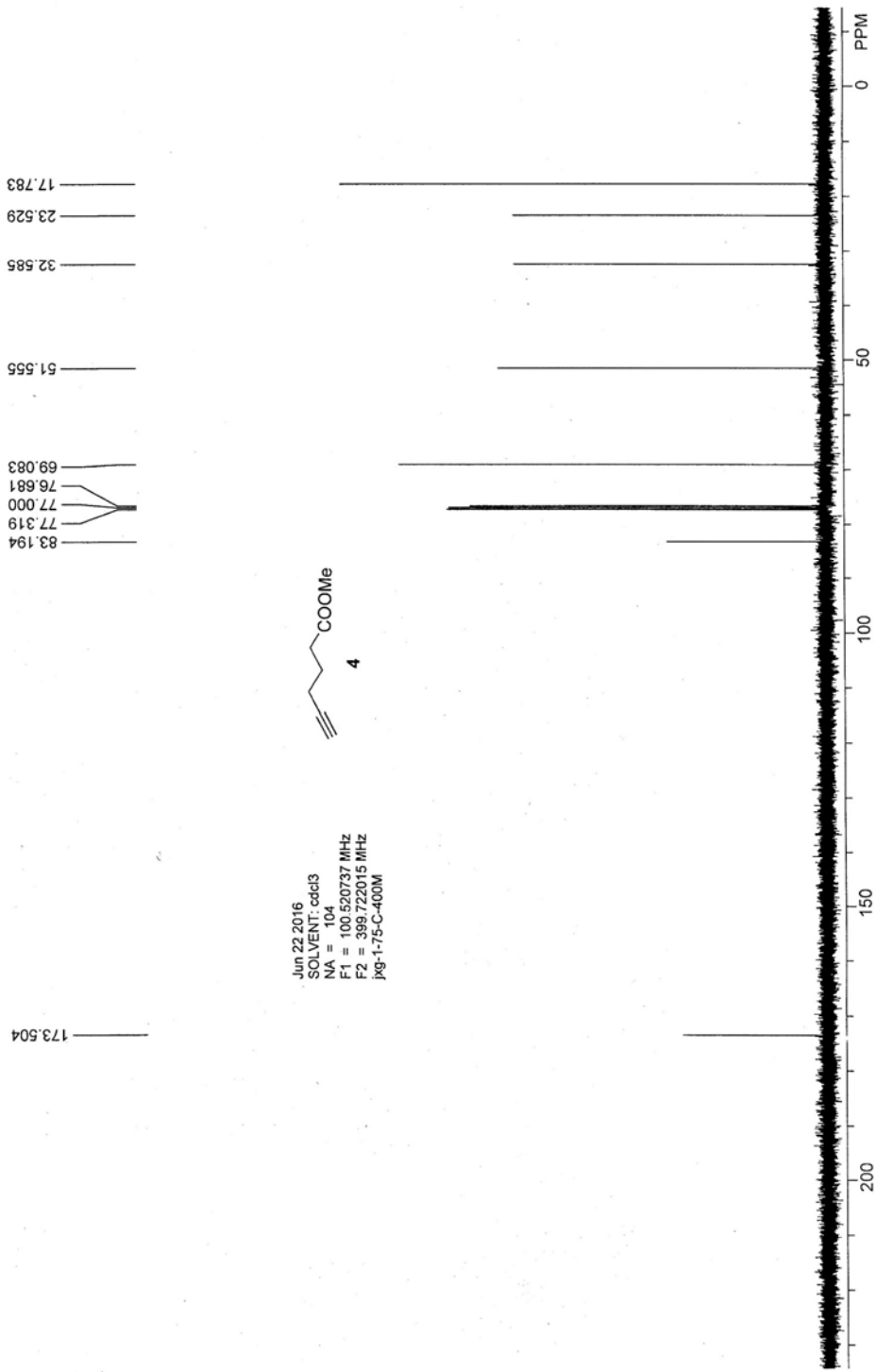


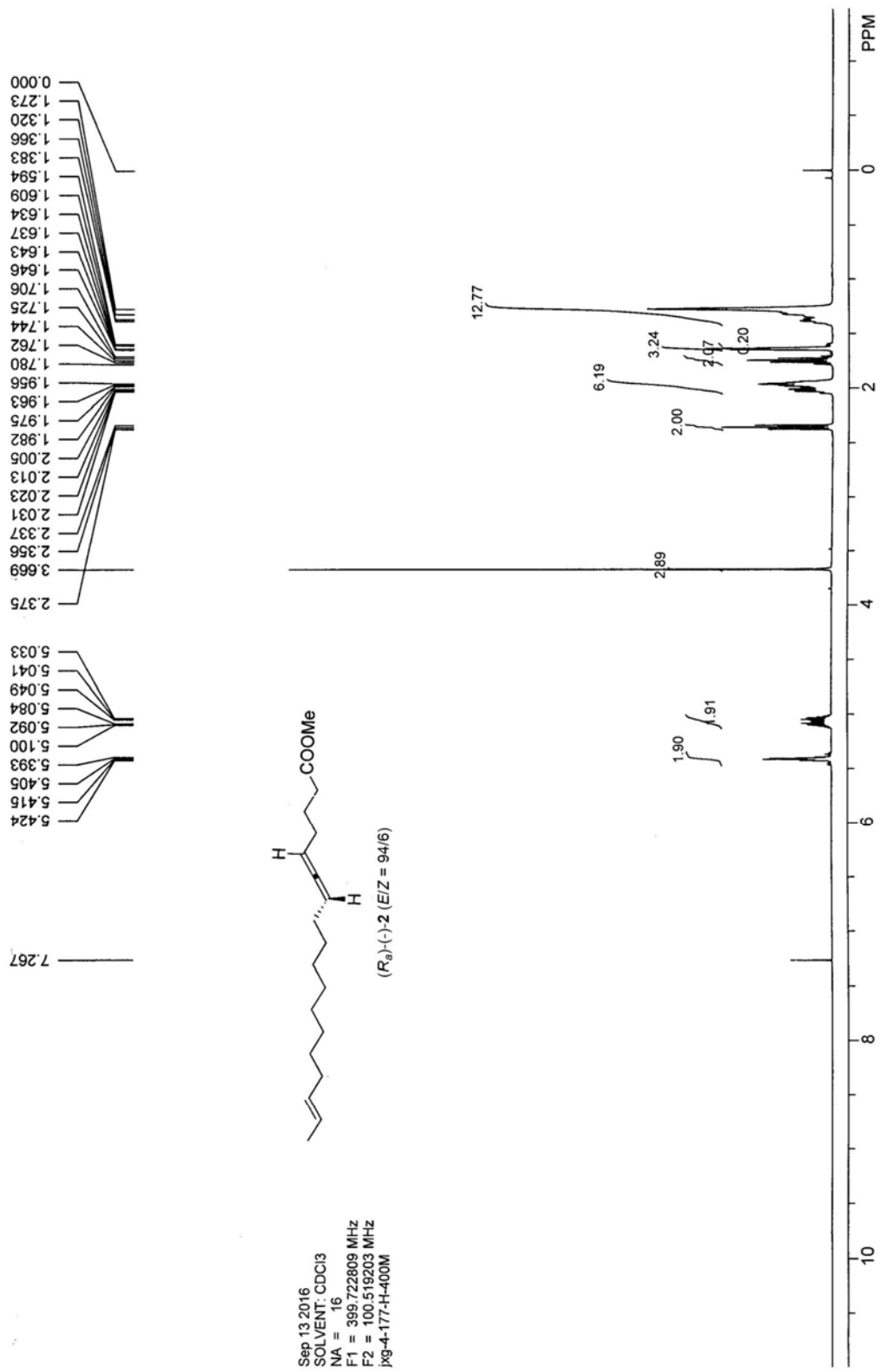


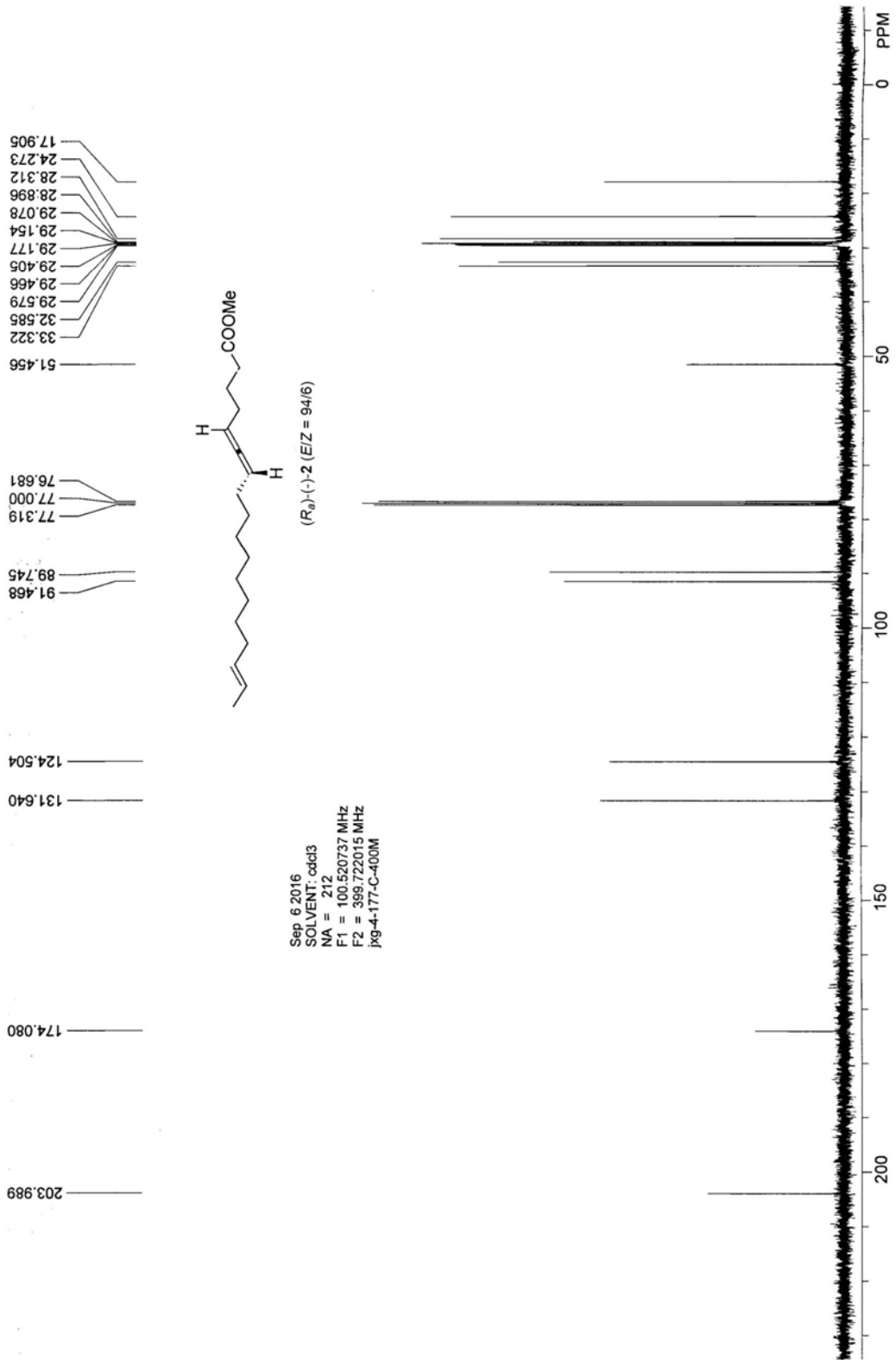
Jun 22 2016  
SOLVENT: CDCl3  
NA = 20  
F1 = 399.722809 MHz  
F2 = 100.519203 MHz  
xyf-175-H-400M









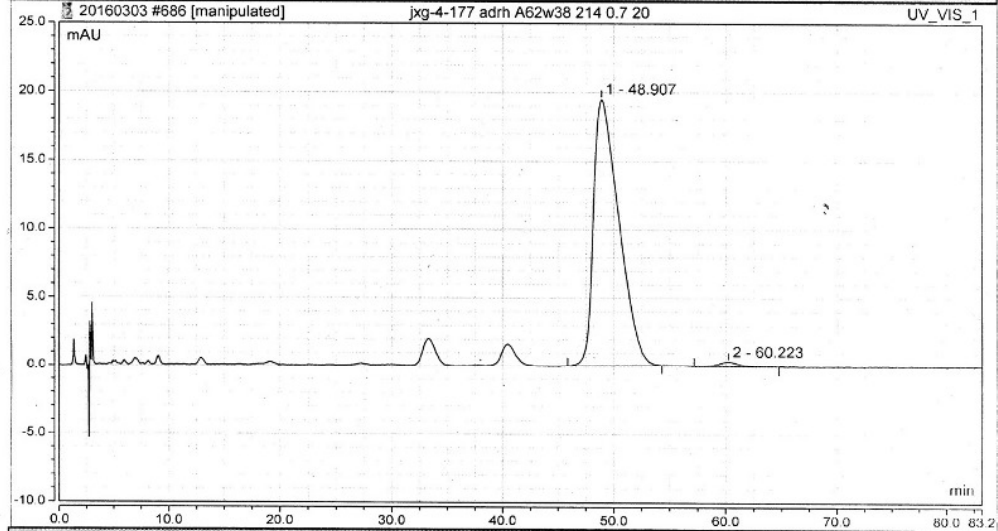


### Chromatogram and Results

#### Injection Details

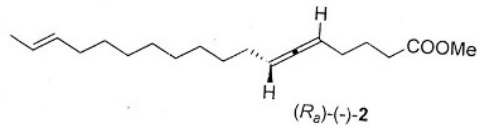
Injection Name:	jxg-4-177 adrh A62w38 214 0.7 20	Run Time (min):	83.20
Vial Number:	RD3	Injection Volume:	3.00
Injection Type:	Unknown	Channel:	UV_VIS_1
Calibration Level:		Wavelength:	214.0
Instrument Method:	20160223-DAD2	Bandwidth:	4
Processing Method:	20160223	Dilution Factor:	1.0000
Injection Date/Time:	20/九月/16 15:30	Sample Weight:	1.0000

#### Chromatogram

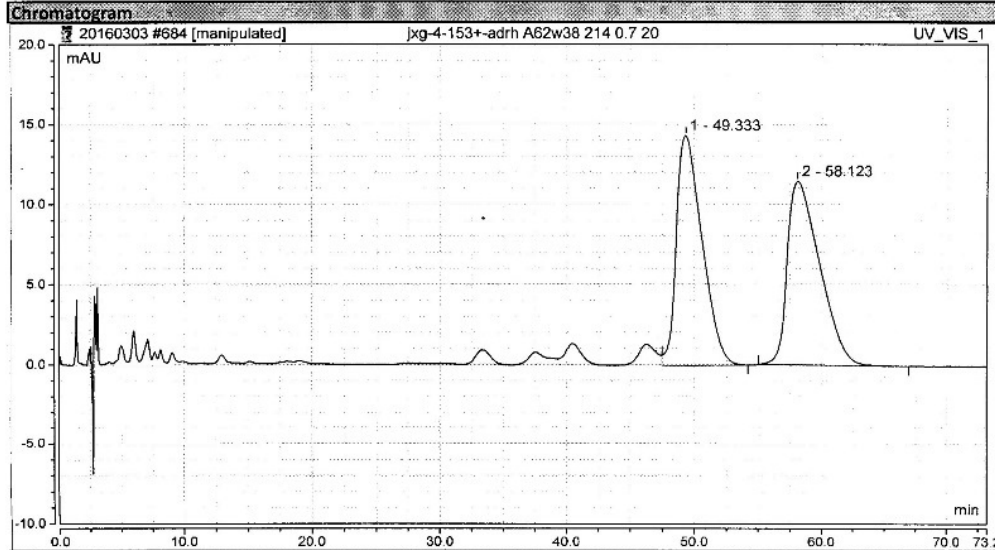


#### Integration Results

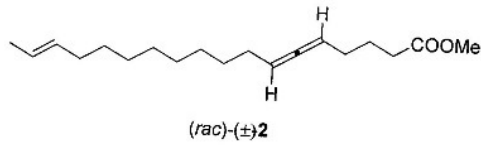
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	48.907	51.507	19.471	98.66
2	60.223	0.697	0.362	1.34
<b>Total:</b>		<b>52.204</b>	<b>19.833</b>	<b>100.00</b>

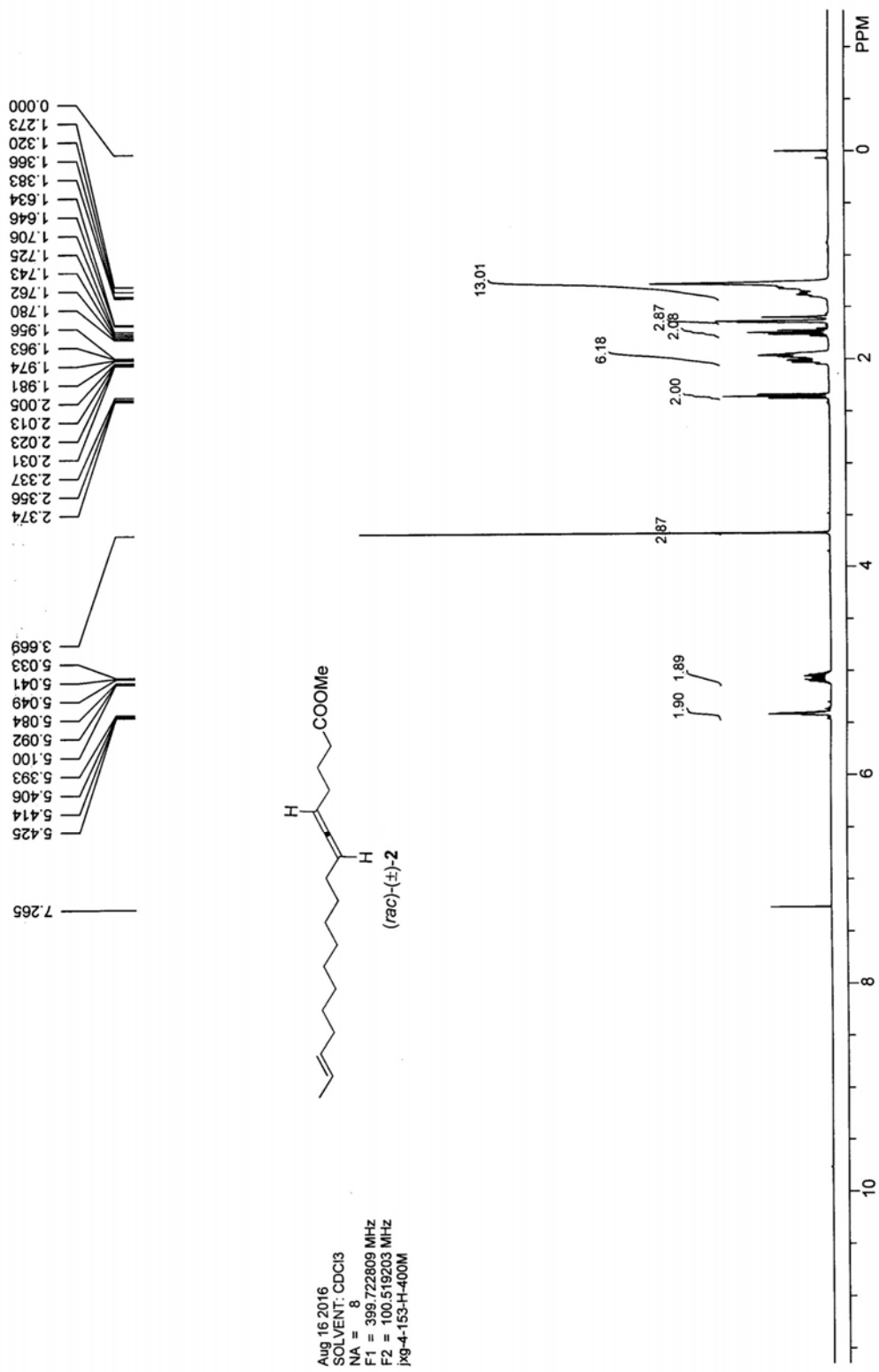


Chromatogram and Results			
<b>Injection Details</b>			
Injection Name:	jxg-4-153+-adrh A62w38 214 0.7 20	Run Time (min):	73.21
Vial Number:	RD1	Injection Volume:	5.00
Injection Type:	Unknown	Channel:	UV_VIS_1
Calibration Level:		Wavelength:	214.0
Instrument Method:	20160223-DAD2	Bandwidth:	4
Processing Method:	20160223	Dilution Factor:	1.0000
Injection Date/Time:	20/九月/16 12:26	Sample Weight:	1.0000



Integration Results				
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	49.333	33.397	14.385	49.55
2	58.123	34.002	11.453	50.45
<b>Total:</b>		<b>67.400</b>	<b>25.838</b>	<b>100.00</b>





51.479  
33.337  
32.593  
29.595  
29.481  
29.420  
29.192  
29.170  
29.094  
28.911  
28.319  
24.281  
17.927

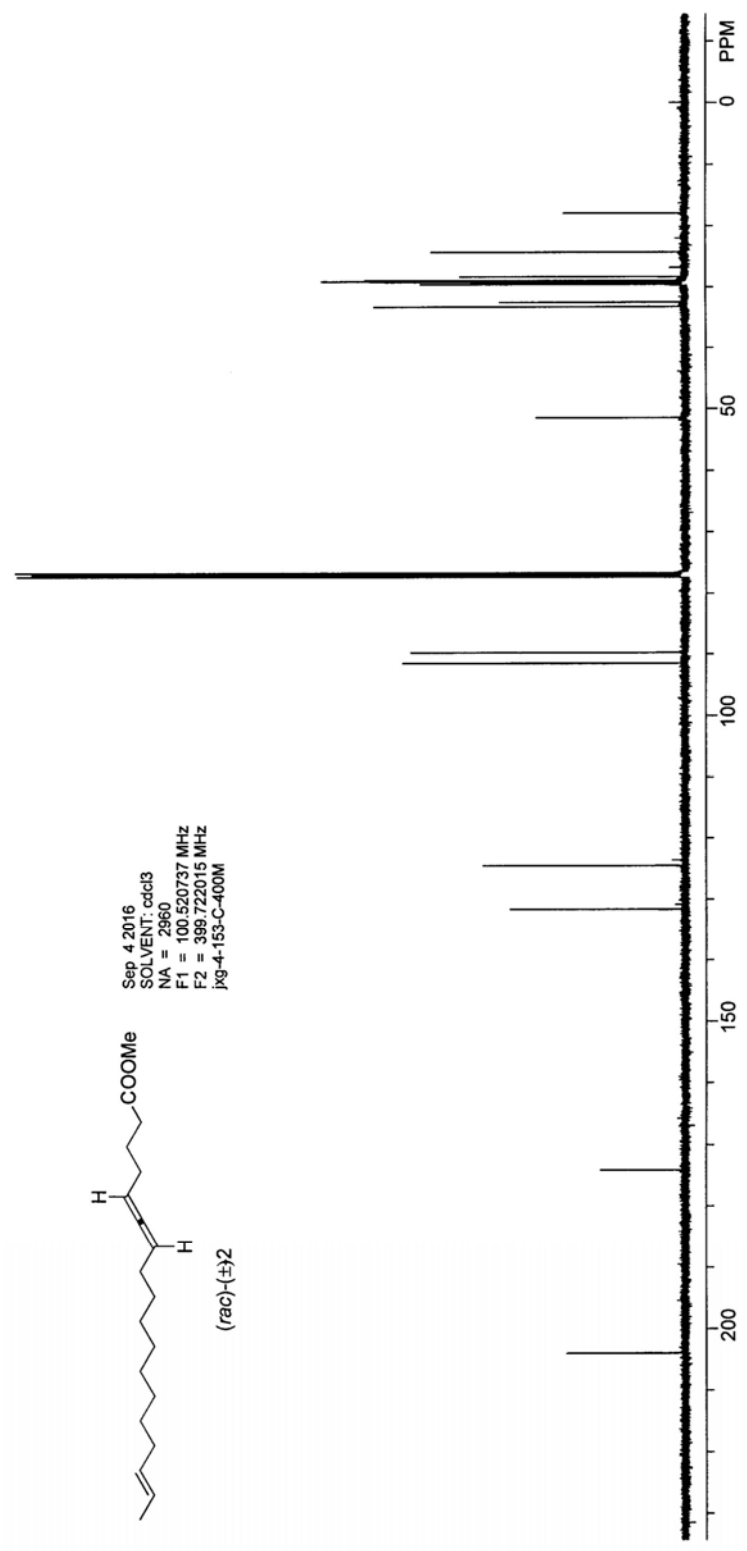
77.319  
77.000  
76.689

91.491  
89.760

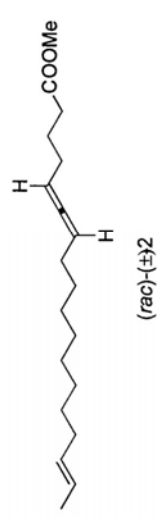
131.655  
124.527

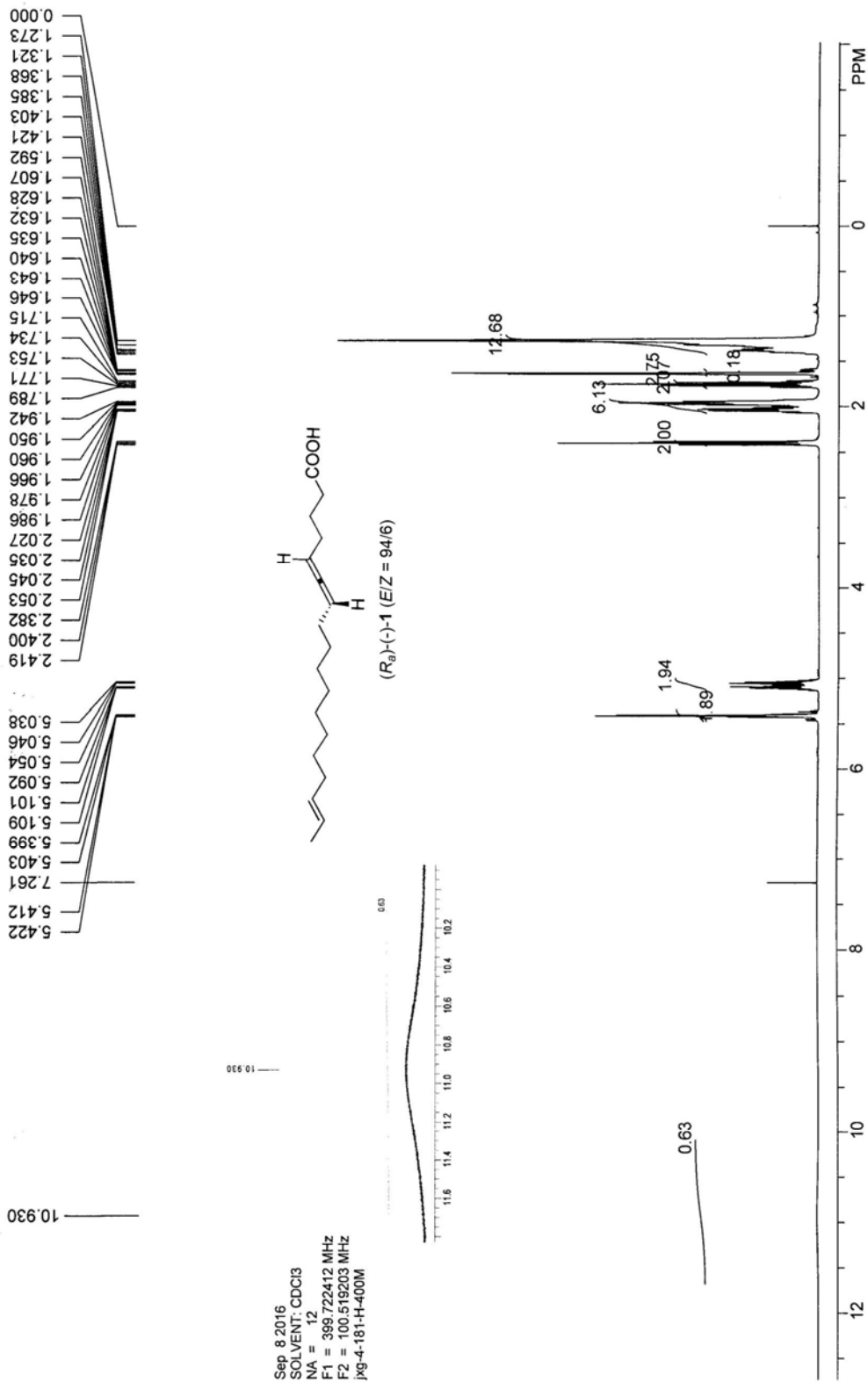
174.118

203.989

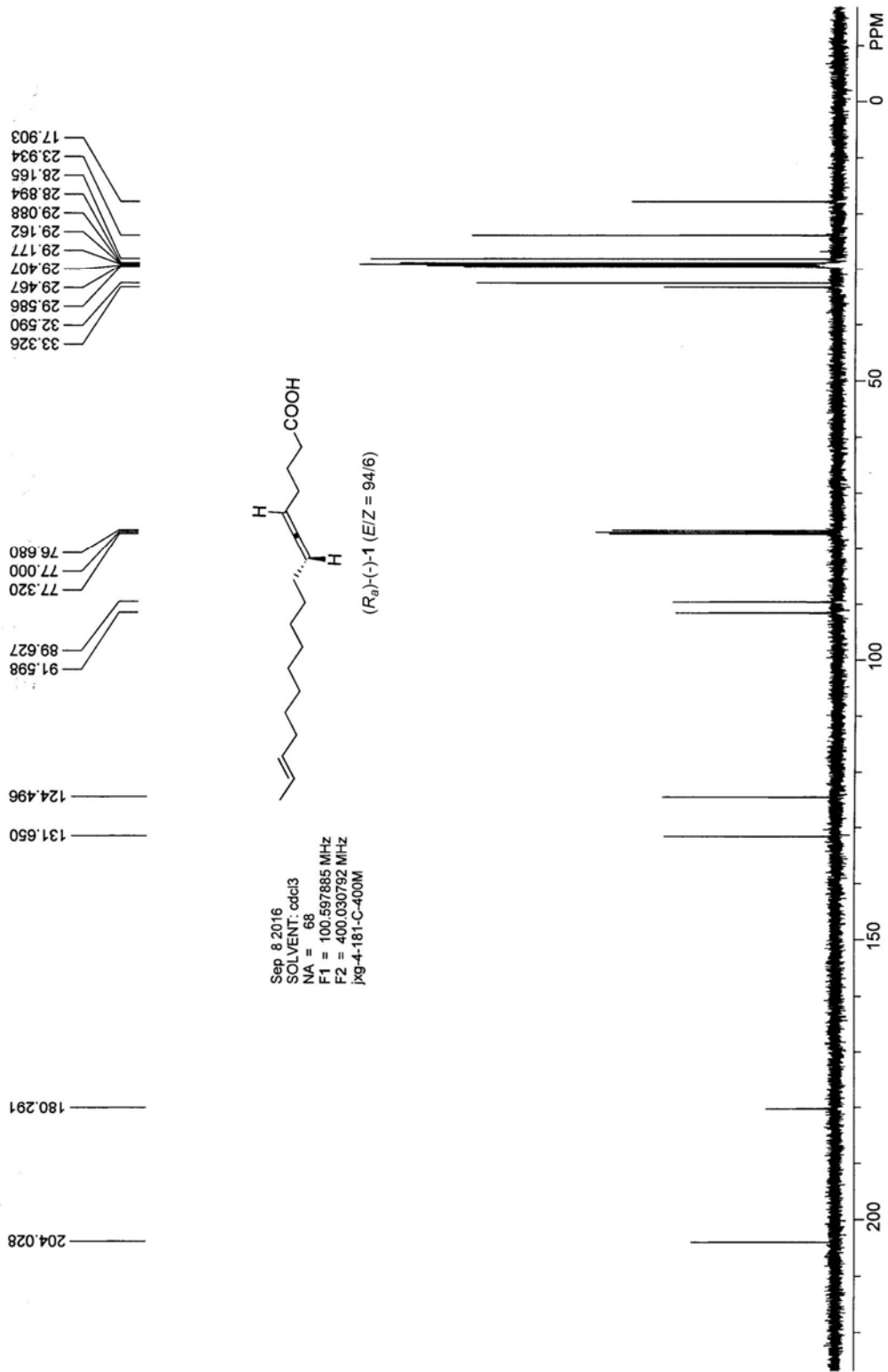


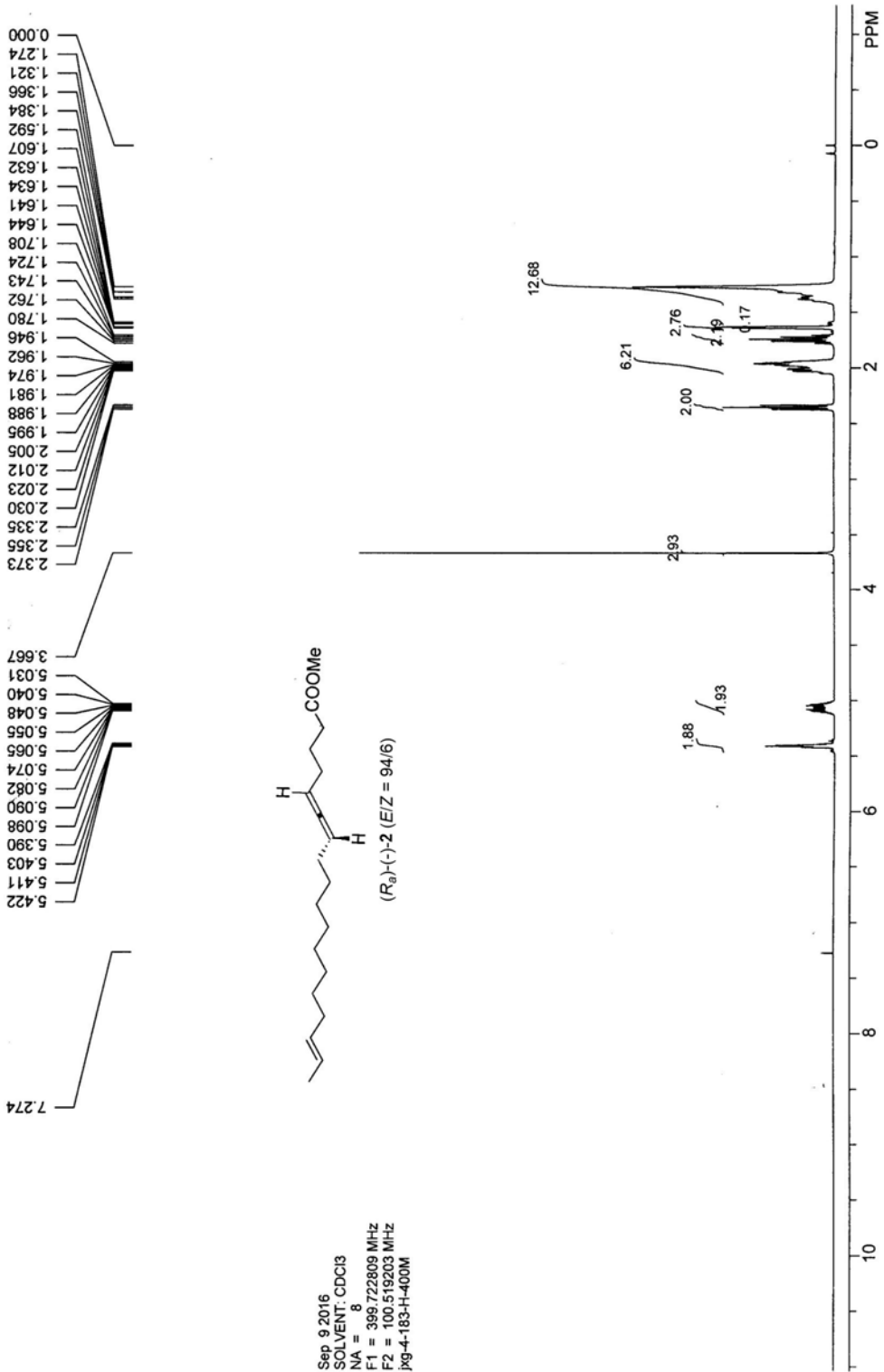
Sep 4 2016  
SOLVENT: cdcl3  
NA = 2960  
F1 = 100.520737 MHz  
F2 = 99.722015 MHz  
J9-4-153-C-400M



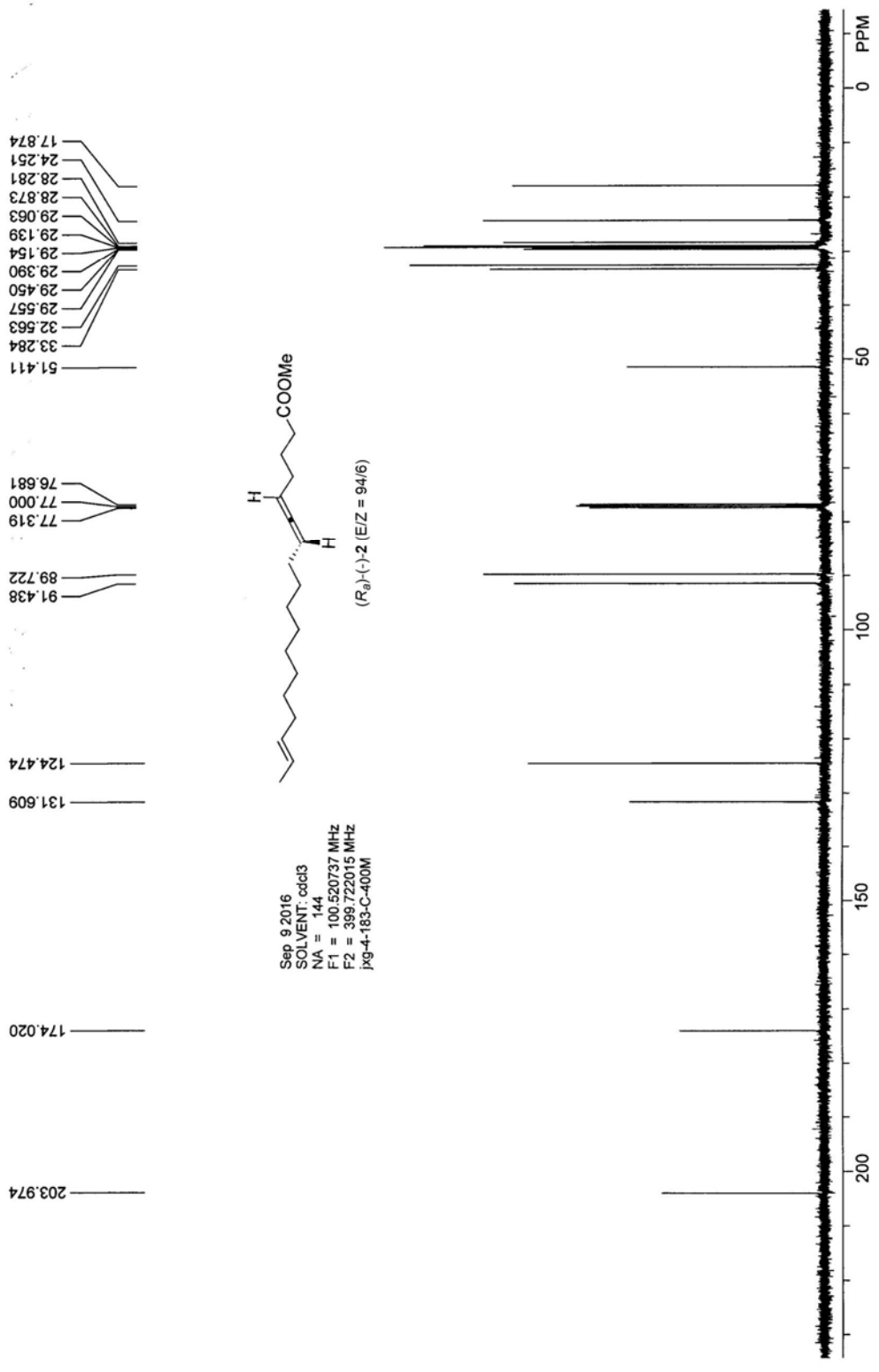








Sep. 9.2016  
 SOLVENT: CDCl3  
 NA = 8  
 F1 = 399.722809 MHz  
 F2 = 100.519203 MHz  
 jpg-4-183-H-400M

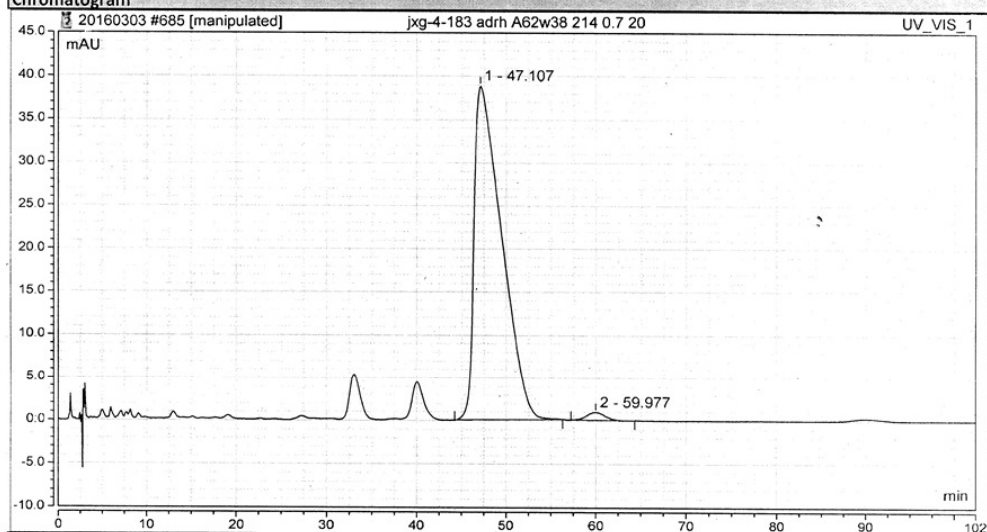


## Chromatogram and Results

## Injection Details

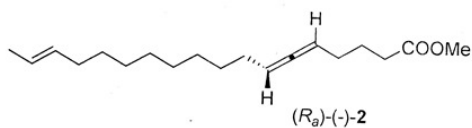
Injection Name:	jxg-4-183 adrh A62w38 214 0.7 20	Run Time (min):	102.43
Vial Number:	RD2	Injection Volume:	3.00
Injection Type:	Unknown	Channel:	UV_VIS_1
Calibration Level:		Wavelength:	214.0
Instrument Method:	20160223-DAD2	Bandwidth:	4
Processing Method:	20160223	Dilution Factor:	1.0000
Injection Date/Time:	20/九月/16 13:43	Sample Weight:	1.0000

## Chromatogram

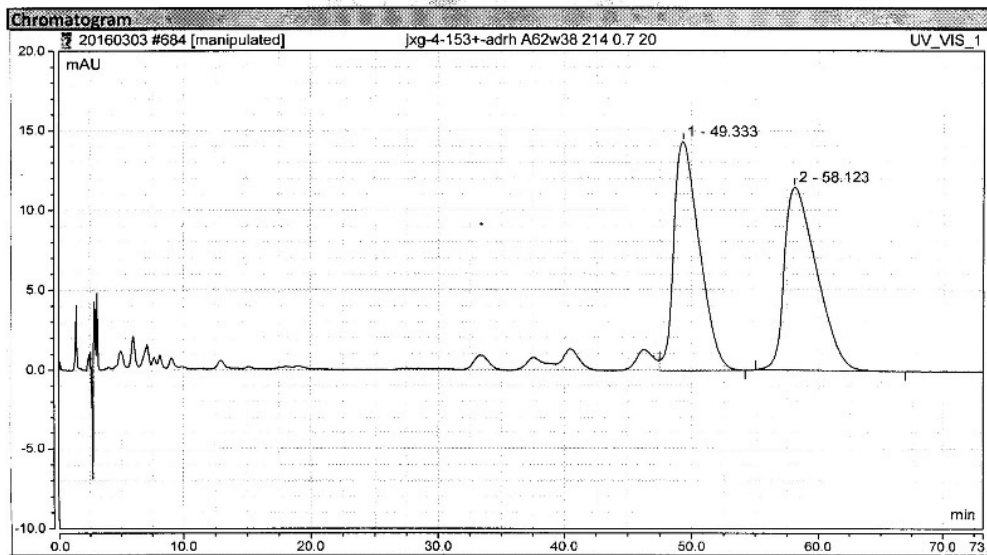


## Integration Results

No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	47.107	138.340	38.802	98.54
2	59.977	2.051	0.910	1.46
Total:		140.391	39.712	100.00



Chromatogram and Results		
<b>Injection Details</b>		
Injection Name:	jxg-4-153+-adrh A62w38 214 0.7 20	Run Time (min): 73.21
Vial Number:	RD1	Injection Volume: 5.00
Injection Type:	Unknown	Channel: UV_VIS_1
Calibration Level:		Wavelength: 214.0
Instrument Method:	20160223-DAD2	Bandwidth: 4
Processing Method:	20160223	Dilution Factor: 1.0000
Injection Date/Time:	2019/9/16 12:26	Sample Weight: 1.0000



Integration Results				
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	49.333	33.397	14.385	49.55
2	58.123	34.002	11.453	50.45
<b>Total:</b>		<b>67.400</b>	<b>25.838</b>	<b>100.00</b>

