

## Supplemental Information

### Cross-metathesis approach to $\alpha$ , $\omega$ -bifunctional compounds from methyl oleate and *cis*-2-butene-1,4-diol

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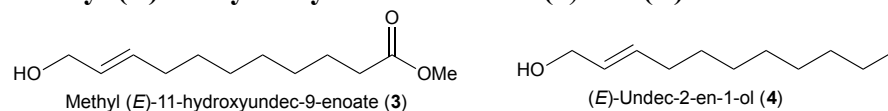


## [1] Experimental Section:

### General:

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were acquired in  $\text{CDCl}_3$  on either Varian Unity Inova 600 (600 MHz) or Bruker Avance 600 (600 MHz) NMR spectrometers. Chemical shifts ( $\delta$ ) were reported as parts per million (ppm) with reference to tetramethylsilane (TMS) or residual solvent unless otherwise stated. The coupling constants ( $J$ ) are reported in Hz. Mass spectra were obtained with Hewlett-Packard Esquire Ion Trap LCMS (electrospray). GC analyses were performed with HP 5890 series II equipped with FID, an auto sampler (HP controller 7672A), and MXT®-Biodiesel TG column (Siltek-treated stainless steel, 15 m, 0.32 mm ID and 0.10  $\mu\text{m}$   $d_f$ ). Samples were analyzed with the following method: 60  $^\circ\text{C}$  to 370  $^\circ\text{C}$ , at 10  $^\circ\text{C}/\text{min}$  and 6 min hold. Most reagents were purchased from commercial suppliers and used without further purification. Olefin metathesis catalysts were purchased from the following manufacturers: **C1** (“Hoveyda-Grubbs II”), **C4** (“Stewart-Grubbs”), **C5**, **C7**, **C8**, **C9**, **C10**, **C12**, **C13**: Sigma-Aldrich, **C2** (“Grela catalyst”), **C3** (“StickyCat C1”), **C6**, **C11** (“GreenCat”),: Strem Chemical, Inc. Thin layer chromatography (TLC) was carried out on glass backed silica plates, purchased from Sorbent Technology. The plates were visualized under UV (254 nm) light, and by staining with potassium permanganate and gentle heating. Silica gel column chromatography was carried out using 20–60 micron dry silica purchased from Sorbent Technology.

### Methyl (*E*)-11-hydroxyundec-9-enoate (**3**) and (*E*)-2-Undecen-1-ol (**4**)

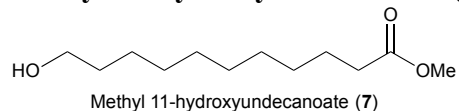


Methyl oleate (**1**, 955 mg, 3.22 mmol) and *cis*-2-butene-1,4-diol (**2**, 1426 mg, 16.19 mmol) were taken in a 25 mL three-neck flask. The mixture was stirred at 0  $^\circ\text{C}$  in an ice bath under argon atmosphere. After 20 min, a solution of dichloro[1,3-bis(2-methylphenyl)-2-imidazolidynylidene](2-isopropoxyphenylmethylene)ruthenium(II) (4.6 mg, 0.008 mmol) in 5.0 mL of ethyl acetate was added dropwise for 1 hour using a syringe pump. After 6 hours of stirring at 0  $^\circ\text{C}$ , 1 mL of ethyl vinyl ether was added and the reaction mixture was warmed to room temperature. The reaction mixture was then passed through a short plug of silica gel with 4.0 mL of ethyl acetate. The filtrate was concentrated and purified by column chromatography (ethyl acetate:hexanes, 1:9→3:7) to obtain methyl (*E*)-11-hydroxyundec-9-enoate (**3**) as a clear colorless liquid (493 mg, 71.5%, 83.3% BORSM) and (*E*)-2-Undecen-1-ol (**4**) as a colorless liquid (386 mg, 70.4%, 82.0% BORSM). During the purification, 135 mg of unreacted methyl oleate was recovered.

Compound **3**:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.61–5.69 (m, 2H), 4.08 (t,  $J$  = 5.6 Hz, 2H), 3.66 (s, 3H), 2.30 (t,  $J$  = 7.5 Hz, 2H), 2.01–2.05 (m, 2H), 1.59–1.63 (m, 2H), 1.27–1.37 (m, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  174.5, 133.6, 129.0, 64.0, 51.6, 34.2, 32.3, 29.2, 29.14, 29.08, 29.0, 25.0.

Compound **4**:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.55–5.72 (m, 2H), 4.07–4.09 (m, 2H), 2.02–2.07 (m, 2H), 1.23–1.38 (m, 13H), 0.88 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.8, 128.9, 64.0, 32.4, 32.0, 29.6, 29.4, 29.34, 29.28, 22.8, 14.3.

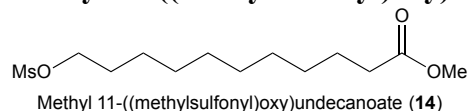
### Methyl 11-hydroxyundecanoate (7)



A mixture of 5% palladium on calcium carbonate (140 mg, 0.07 mmol, poisoned with lead), 5.0 mL of methanol, and methyl (*E*)-11-hydroxyundec-9-enoate (493 mg, 2.30 mmol) was pressurized (43 psi) and charged with hydrogen gas in a Parr shaker for 7 hours at room temperature. At the end of the reaction, the reaction mixture was passed through a Celite® pad and concentrated using a rotary evaporator. Finally, the residue was purified by column chromatography (ethyl acetate:hexanes, 3:7) to obtain the desired product as a white solid. (452.8 mg, 91% yield).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.66 (s, 3H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.54-1.63 (m, 4H), 1.26-1.35 (m, 12H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>): δ 174.5, 63.2, 51.6, 34.2, 32.9, 29.6, 29.51, 29.48, 29.35, 29.3, 25.8, 25.1.

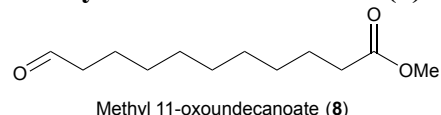
### Methyl 11-((methylsulfonyl)oxy)undecanoate (14)



To a stirred mixture of crude saturated alcohol (79 mg, 0.37 mmol) dissolved in anhydrous dichloromethane (0.5 mL) and triethylamine (0.15 mL) was slowly added methanesulfonylchloride (0.042 mL, 0.54 mmol) at 0 °C. Stirring was continued at 0 °C for additional 6 hours and thereafter, the mixture was allowed to warm to room temperature. After 7 hours (total reaction time), the reaction was quenched by addition of water (2 mL) and organic phase was separated. Aqueous phase was further extracted with ethyl acetate (2 mL x 3). The organic layers were combined and washed with saturated sodium chloride, dried with anhydrous magnesium sulfate, filtered and concentrated. Crude methansulfonyl ester was purified by column chromatography (ethyl acetate: hexanes, 1:4) to yield pure product as a white solid (96.3 mg, 90%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 4.21 (t, *J* = 6.6 Hz, 2H), 3.66 (s, 3H), 3.00 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.71-1.76 (m, 2H), 1.57-1.64 (m, 2H), 1.28-1.41 (m, 12 H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 174.5, 70.3, 51.6, 37.5, 34.2, 29.5, 29.4, 29.3, 29.25, 29.24, 29.1, 25.5, 25.1.

### Methyl 11-oxoundecanoate (8) – by isomerization of (*E*)-11-hydroxyundec-9-enoate (3)

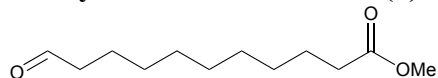


A solution of methyl (*E*)-11-hydroxyundec-9-enoate (33.6 mg, 0.16 mmol) in anhydrous toluene (1 mL) and a solution of (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium catalyst (0.5 mg, 0.0008 mmol) in toluene (1 mL) were added to a microwave vial. After adding a stir bar, the vial was sealed with a crimp-top lid and heated at 150 °C for 24 hours. Ethyl vinyl ether (1 mL) was added to quench the reaction and the reaction mixture was cooled to room temperature. The mixture was then passed through a short plug of silica gel with 2.0 mL of ethyl acetate. The filtrate was concentrated and purified by

column chromatography (ethyl acetate:hexanes, 1:9) to obtain aldehyde **8** as a clear colorless liquid (30 mg, 89 %).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.77 (t,  $J = 1.86$  Hz, 1H), 3.66 (s, 3H), 2.41 (td,  $J = 7.3$  Hz, and  $J = 1.9$  Hz, 2H), 2.30 (t,  $J = 7.5$  Hz, 2H), 1.58–1.63 (m, 4H), 1.28–1.33 (m, 10H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.1, 174.5, 51.6, 44.0, 34.2, 29.4, 29.33, 29.29, 29.25, 29.22, 25.0, 22.2.

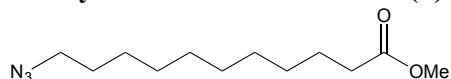
### Methyl 11-oxoundecanoate (**8**) – by oxidation of Ethyl 11-hydroxyundecanoate (**7**)



Methyl 11-oxoundecanoate (**8**)

A solution of crude saturated alcohol (~30 mg, 0.14 mmol) in dichloromethane:DMSO (2:1, 2.0 mL) were added  $\text{SO}_3 \cdot \text{pyridine}$  (88 mg, 0.56 mmol) and triethylamine (56  $\mu\text{L}$ ) at ambient temperature and stirred for 2 hours. The mixture was quenched with water (6 mL) and extracted with ethyl acetate (10 mL x 4). The combined organic phases was dried over  $\text{MgSO}_4$ , filtered, concentrated, and purified by column chromatography (ethyl acetate: hexanes, 1:9) to obtain aldehyde **8** (14 mg, 47%).

### Methyl 11-azidoundecanoate (**9**)



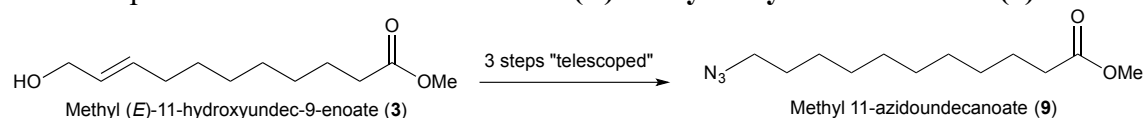
Methyl 11-azidoundecanoate (**9**)

Sodium azide (200 mg) was added to a solution of methyl 11-((methylsulfonyl)oxy)undecanoate (300 mg, 1.02 mmol) in anhydrous dimethylformamide (4 mL) and stirred at 50  $^\circ\text{C}$  for 18 h. After completion of the reaction, the mixture was poured over 4 mL of distilled water and extracted three times with ethyl acetate (5 mL x 3). The solution consisting of combined organic layers was dried with anhydrous magnesium sulfate, filtered, and concentrated. The crude azide was purified by column chromatography (ethyl acetate: hexanes, 1:9) to obtain azide **9** as a colorless clear liquid (240 mg, 97%).

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data were consistent with the previously reported values.<sup>1</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.66 (s, 3H), 3.25 (t,  $J = 7.0$  Hz, 2H), 2.30 (t,  $J = 7.5$  Hz, 2H), 1.55–1.63 (m, 4H), 1.28–1.37 (m, 12 H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  174.5, 51.6, 34.2, 29.5, 29.45, 29.35, 29.32, 29.26, 29.0, 26.8, 25.1.

### Methyl 11-azidoundecanoate (**9**) – “Telescoped” procedure: Three steps carried out without isolation/purification of intermediates from (*E*)-11-hydroxyundec-9-enoate (**3**)



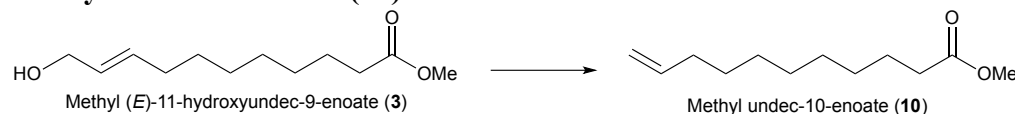
A mixture of 5% palladium on calcium carbonate (140 mg, 0.07 mmol, poisoned with lead), 8.0 mL of methanol, and methyl (*E*)-11-hydroxyundec-9-enoate (**3**) (501.4 mg, 2.34 mmol) was pressurized with  $\text{H}_2$  (43 psi) in a Parr reactor and mixed for 5 h at room temperature. The reaction mixture was passed through a Celite® pad and concentrated using a rotary evaporator. To a stirred mixture of crude saturated alcohol dissolved in anhydrous dichloromethane (5 mL) and triethylamine (0.975 mL), methanesulfonylchloride (0.265 mL, 3.42 mmol) was added dropwise at 0  $^\circ\text{C}$  for 30 min. Stirring was continued at 0  $^\circ\text{C}$  for additional 5.5 hours and allowed to warm to room temperature. After 16 hours (total reaction time), the reaction was quenched by

addition of water (10 mL) and the organic phase was separated. The aqueous phase was further extracted with ethyl acetate (15 mL x 3). Combined organic layers were washed with saturated sodium chloride, dried with anhydrous magnesium sulfate, filtered and concentrated. Sodium azide (453 mg, 6.97 mmol) was added to a solution of the crude mesylate in anhydrous dimethylformamide (10 mL) and stirred at 50 °C for 16 hours. After completion of the reaction, the mixture was poured over 10 mL of distilled water and extracted three times with ethyl acetate (3 x 15 mL). Combined organic layers was dried with anhydrous magnesium sulfate, filtered, and concentrated. Crude azide was purified by column chromatography (ethyl acetate: hexanes, 1:9) to obtain azide **9** as a colorless clear liquid (489 mg, 87%, 3 steps).

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data were consistent with the previously reported values.<sup>1</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.66 (s, 3H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.55–1.63 (m, 4H), 1.28–1.37 (m, 12 H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 174.5, 51.6, 34.2, 29.5, 29.45, 29.35, 29.32, 29.26, 29.0, 26.8, 25.1.

### Methyl undec-10-enoate (**10**)

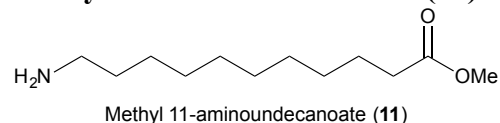


A mixture of methyl 11-hydroxyundec-9-enoate (202.4 mg, 0.94 mmol), formic acid (0.88 mL), and toluene (1.76 mL) was heated at 70 °C with stirring under a reduced pressure (360 mmHg) for 45 min. Toluene and excess formic acid were evaporated by applying full vacuum. A solution of crude formylated product and triphenylphosphine (74 mg, 0.28 mmol) in toluene (15 mL) was heated to 80 °C for 5 min, and palladium diacetate (1.5 mg, 0.0067 mmol) dissolved in dimethoxyethane (3 mL) was added. After 20 minutes, the crude reaction mixture was passed through a plug of silica gel (~2 cm) and ethyl acetate (~2 mL) was used to rinse the silica gel plug. After the solvent evaporation under reduced pressure, the crude product was purified by column chromatography (hexanes → ethyl acetate:hexanes, 1:49) to afford the title compound as a colorless liquid (136.4 mg, 73%).

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data were consistent with the previously reported values.<sup>2</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 5.78–5.83 (m, 1H), 4.91–5.01 (m, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.01–2.05 (m, 2H), 1.59–1.64 (m, 2H), 1.29–1.38 (m, 10H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 174.5, 139.3, 114.3, 51.6, 34.3, 33.9, 29.4, 29.34, 29.27, 29.2, 29.0, 25.1.

### Methyl 11-aminoundecanoate (**11**)



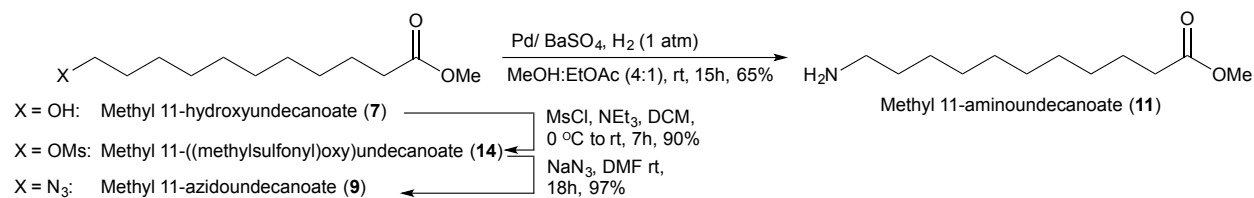
Palladium on barium sulfate (17 mg) was added to a solution of methyl azidoundecanoate (97 mg) in methanol:ethyl acetate (4:1, 4 mL) solvent mixture and stirred under hydrogen atmosphere (1 atm, using a balloon) at room temperature for 15 hours. The reaction mixture was passed through a Celite® bed, concentrated and purified by column chromatography (dichloromethane:methanol, 9:1) to afford the desired product as a white solid (57 mg, 65%).

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data were consistent with the previously reported values.<sup>3</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.66 (s, 3H), 2.68 (t, *J* = 7.1 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.67 (s, 2H), 1.60–1.62 (m, 2H), 1.42–1.47 (m, 2H), 1.27–1.31 (m, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 174.5, 51.6, 42.3, 34.2, 33.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.0, 25.1.

## [2] An alternative route to Methyl 11-aminoundecanoate (**11**) from Methyl 11-hydroxyundecanoate (**7**):

In parallel with the approaches described in the main text, we have studied a more conventional approach from **7** to amino ester **11**, which involves formation of mesylate, azide displacement and reduction (Scheme E1). Transformation of alcohol **7** to azide **9** was accomplished via mesylation of the hydroxyl group and its displacement through standard procedures, in 90 and 97% yield, respectively. The three-step sequence was also carried out without intermediate isolation to provide 87% overall yield. Finally, the azide was hydrogenated by Pd/BaSO<sub>4</sub> under hydrogen atmosphere to amino ester **11** in 65% yield.

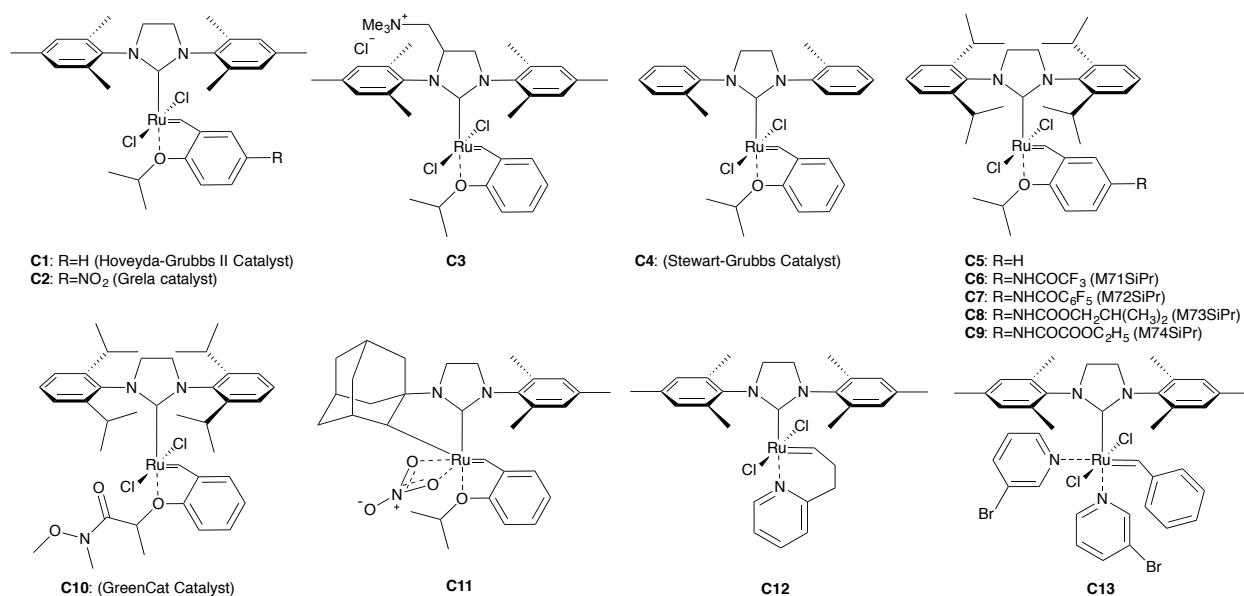


**Scheme E1:** Synthesis of amino-ester **11** from saturated alcohol **7**.

## [3] Metathesis catalyst screening:

The complete list of catalysts that was evaluated is shown below. The results are summarized in Table E2.

(a) Bench-mark catalyst: Hoveyda-Grubbs II (**C1**),<sup>4</sup> (b) “Fast initiating” or “highly active”: Grela catalyst (**C2**);<sup>5-7</sup> Umicore M7 series:<sup>8-10</sup> M71SiPr (**C6**), M72SiPr (**C7**), M73SiPr (**C8**), M74SiPr (**C9**); (c) Catalysts effective with unreactive or hindered olefins: Stewart-Grubbs catalyst (**C4**),<sup>11-12</sup> (**C5**),<sup>12</sup> (**C13**).<sup>13</sup> (d) Others: Affinity to silica gel that aids in recovery: (**C3**);<sup>14</sup> GreenCat catalyst (**C10**);<sup>15</sup> Z olefin selective: (**C11**);<sup>16</sup> (**C12**).<sup>17</sup>



**Table E1.** Screening study of metathesis catalysts<sup>[a]</sup>

Entry	Catalyst	Conversion /% <sup>[b]</sup>	<b>3</b> /% <sup>[b]</sup>	<b>4</b> /% <sup>[b]</sup>	<b>6</b> /% <sup>[b]</sup>
1	<b>C1</b>	92.6	50.2	67.9	7.7
2	<b>C2</b>	91.2	59.7	71.5	8.1
3	<b>C3</b>	62.3	44.1	46.5	8.5
4	<b>C4</b>	92.6	69.6	72.9	8.0
5	<b>C5</b>	88.2	33.2	58.5	11.0
6	<b>C6</b>	91.6	48.3	70.0	8.7
7	<b>C7</b>	85.4	35.8	58.5	11.2
8	<b>C8</b>	95.2	34.8	59.9	10.9
9	<b>C9</b>	89.8	38.4	65.0	10.9
10	<b>C10</b>	90.1	47.0	68.0	9.6
11	<b>C11</b>	<5	<5	<5	<5
12	<b>C12</b>	<5	<5	<5	<5
13	<b>C13</b>	6.0	<5	<5	<5

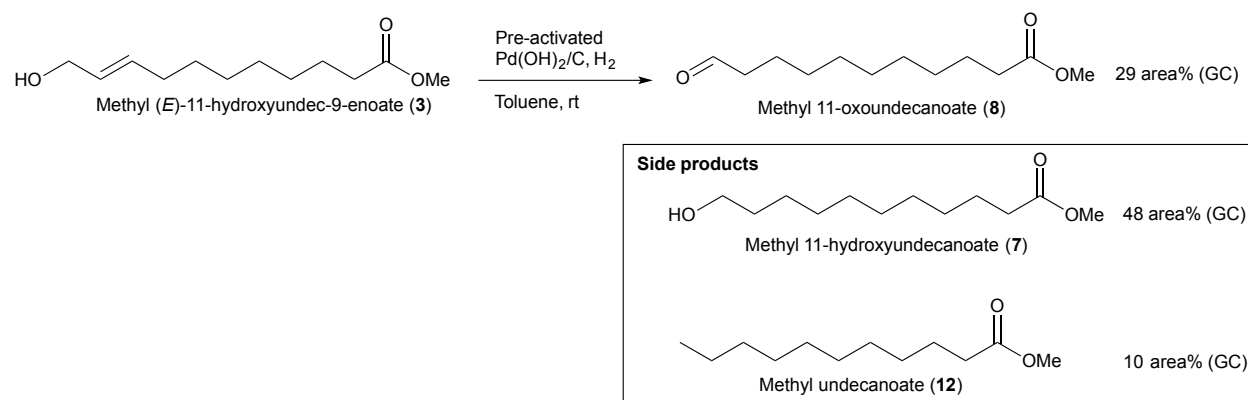
<sup>[a]</sup> To a flask containing methyl oleate (**1**, 1 eq) and *cis*-2-butene-1,4-diol (**2**, 5 eq) at 0 °C was added a solution of the catalyst (2 mol%) in ethyl acetate (4.3 mg/2 mL) over 1 h. The reaction was stirred at 0 °C for 10 hours before analysis. <sup>[b]</sup> Determined by GC using methyl palmitate as an internal standard.



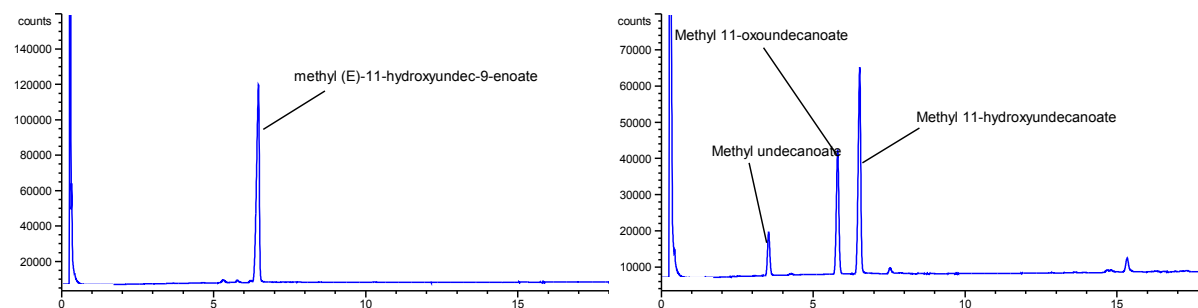
#### [4] Additional studies on allyl alcohol isomerization to aldehyde:

##### Palladium-catalyzed isomerization of Methyl (*E*)-11-hydroxyundec-9-enoate (**3**) to Methyl 11-oxoundecanoate (**8**):

In prior to attempting the ruthenium catalyzed procedure (described in the main text), we examined a method reported by Sabitha and co-workers<sup>18</sup> in which a palladium catalyst was used to promote conversion of primary allylic alcohols to the corresponding saturated aldehydes. When isolated and purified **3** was subjected to the procedure, however, a mixture of products including saturated alcohol-ester **7**, de-hydroxylated saturated ester **12**, and desired aldehyde **8** were obtained in low yields (Scheme S1, Figure S1). Changing the catalyst, solvent or reaction time did not improve the reaction outcome.

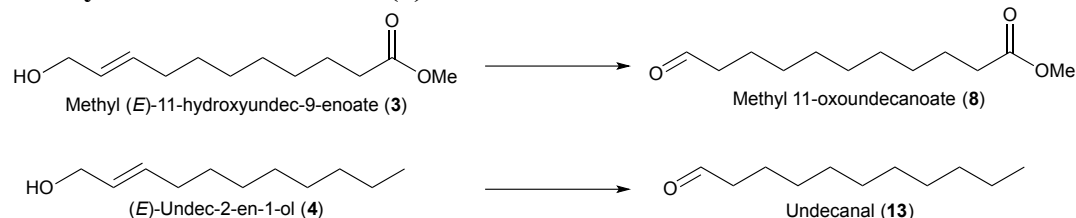


**Scheme S1.** Attempted allyl alcohol isomerization of **3** with Pd(OH)<sub>2</sub>/H<sub>2</sub>.



**Figure S1:** GC chromatogram of crude reaction mixture after the attempted allyl alcohol isomerization of **3** with Pd(OH)<sub>2</sub>/H<sub>2</sub>.

**[5] Ruthenium-catalyzed isomerization of Methyl (*E*)-11-hydroxyundec-9-enoate (**3**) to Methyl 11-oxoundecanoate (**8**):**

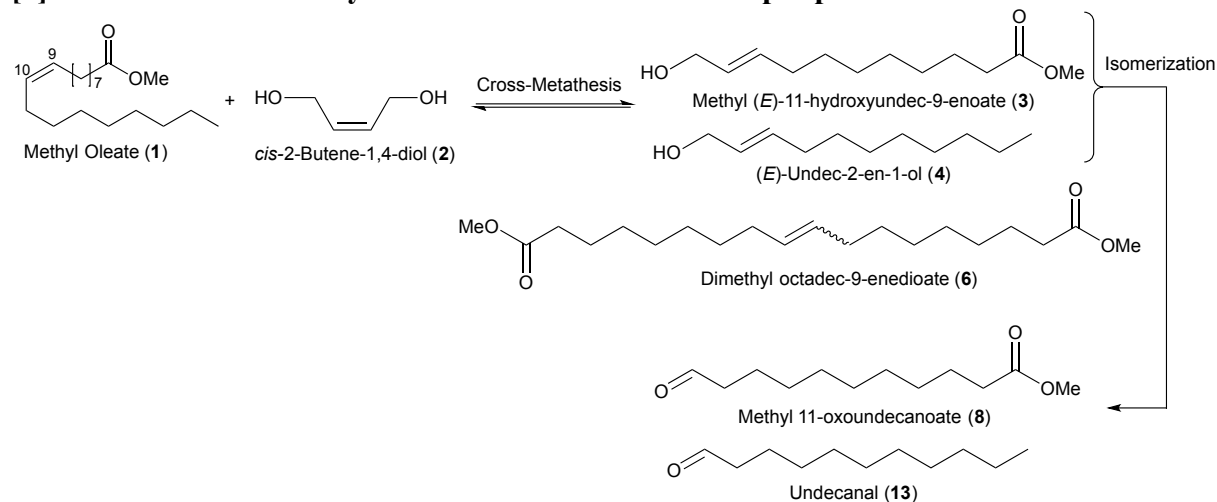


**Table E2: Ruthenium-catalyzed allyl alcohol isomerization<sup>[a]</sup>**

Entry	Substrate	Catalyst	Solvent	Time /h	Temp. /°C	Yield <sup>[b]</sup>	
						Alcohol	Aldehyde
1	<b>3</b>	<b>C1</b>	Toluene	3	150		89.6
2	<b>4</b>	<b>C1</b>	Toluene	24	150		79.4
3 <sup>[c]</sup>	<b>4</b>	<b>C4</b>	Toluene	24	150	(14)	(55)
4	<b>4</b>	<b>C1</b>	Toluene	19	150		~85
5	<b>4</b>	<b>C1</b>	Toluene	19	150	(4)	(91)
6	<b>3</b>	<b>C1</b>	Toluene	1	Microwave	(88)	(8)
7	<b>4</b>	NA <sup>[d]</sup>	THF <sup>[e]</sup>	5	80	(~7)	(71)
8	<b>3</b>	<b>C1</b>	Toluene	3	150		81.2
9	<b>4</b>	<b>C1</b>	Toluene	3	150		87.0
10 <sup>[f]</sup>	<b>4</b>	<b>C1</b>	EtOAc	5	150	(13)	(73)
11	<b>4</b>	<b>C4</b> <sup>[g]</sup>	Toluene	4	150	(69)	(20)
				24	150	(35)	(46)
				125	150	(20)	(53)

[a] Reaction conditions: See the representative reaction conditions in the experimental section. [b] Isolated % yield; GC area% in parenthesis. [c] Dimer **5** (31 area%) was also formed, which is likely formed during reaction heating. [d] A portion of undecanal was lost due to its volatility. [e] Grubbs II (2 mol%) and sodium formate (0.2 equiv) was used. [f] 0.19M. [g] Dimer **5** (17 area%) was also formed. [g] No external catalyst was added. There is likely residual ruthenium catalyst left in the isolated substrate.

**[6] Cross-metathesis / allyl alcohol isomerization – one-pot procedure**



Methyl oleate (100.2 mg, 0.34 mmol), *cis*-2-butene-1,4-diol (121.2 mg, 1.38 mmol), and methyl palmitate (24.7 mg, internal standard) were added to a 5-mL crimp-top microwave reaction vial. A stir bar was added and the vial was sealed. The vial was cooled to 0 °C and a solution of dichloro[1,3-bis(2-methylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II) (Stewart-Grubbs catalyst, **C4**; 1.0 mg, 0.0018 mmol, in 0.5 mL ethyl acetate) was added drop wise over 30 minutes. The mixture was stirred at this temperature for 6 hours (total reaction time) while monitoring the reaction using TLC and GC-FID. After 6 hours, the reaction vial was transferred to an oil bath preheated to 150 °C. The reaction progress was monitored by GC-FID. After 16 hours stirring at 150 °C, the vial was cooled to room temperature and 1 mL of ethyl vinyl ether was added. The reaction mixture was passed through a small plug of silica gel and analyzed by GC-FID.

The products after cross-metathesis as well as isomerization were quantified using methyl palmitate as an internal standard.

After cross-metathesis: Methyl (*E*)-11-hydroxyundec-9-enoate (**3**, 67 mg, 63 %); (*E*)-2-Undecen-1-ol (**4**, 79 mg, 74 %); Dimethyl octadec-9-enedioate (**6**, 3.8 mg, 7 %); unreacted methyl oleate (**1**, 14 mg, 14 %; 86 % conversion).

After isomerization: unreacted Methyl (*E*)-11-hydroxyundec-9-enoate (**3**, 12 mg, 17 %); unreacted (*E*)-2-Undecen-1-ol (**4**, 4.4 mg, 7.5 %); Methyl 11-oxoundecanoate (**8**, 47 mg, 64 %); Undecanal (**13**, 26 mg, 46 %); Dimethyl octadec-9-enedioate (**6**, 4.2 mg, 7 %); unreacted methyl oleate (**1**, 12 mg, 11 %; 89 % conversion).

The identical reaction conditions using Hoveyda-Grubbs catalyst (**C1**) provided similar mixture of products after cross-metathesis, however, little reaction was observed when isomerization was attempted (see Table E3, 52% (BORSM)).

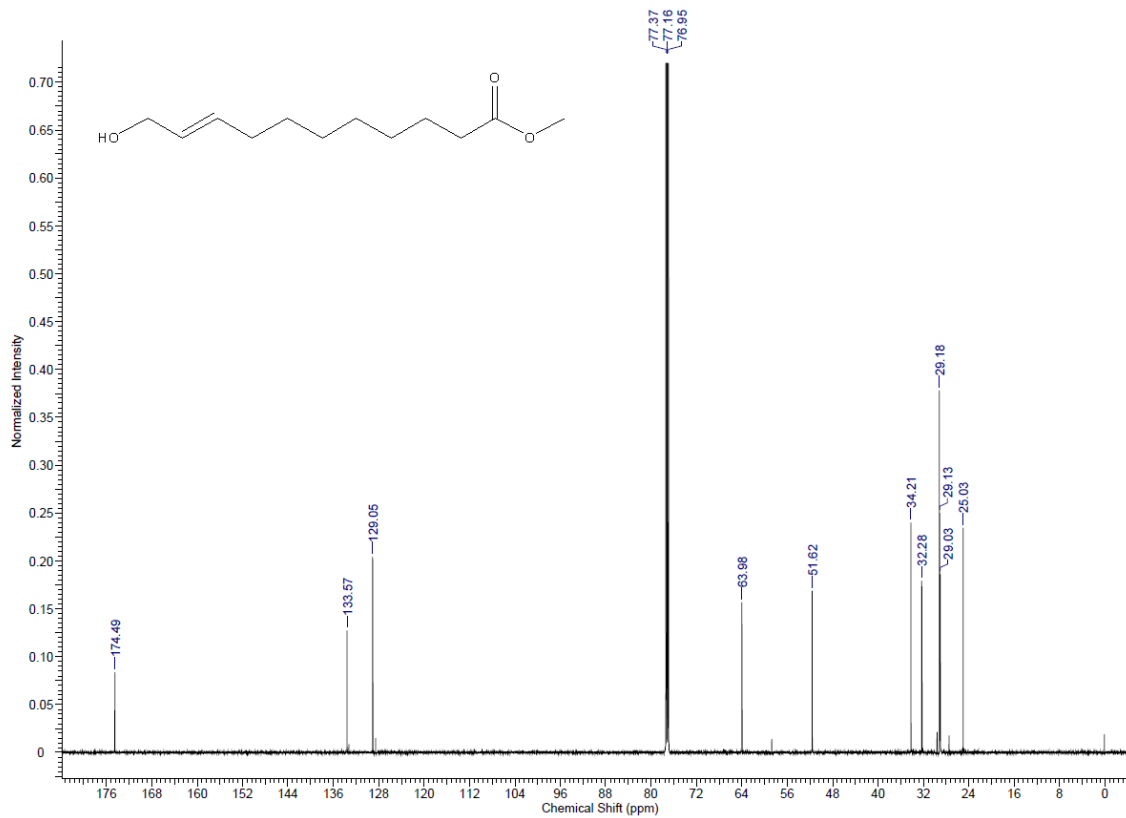
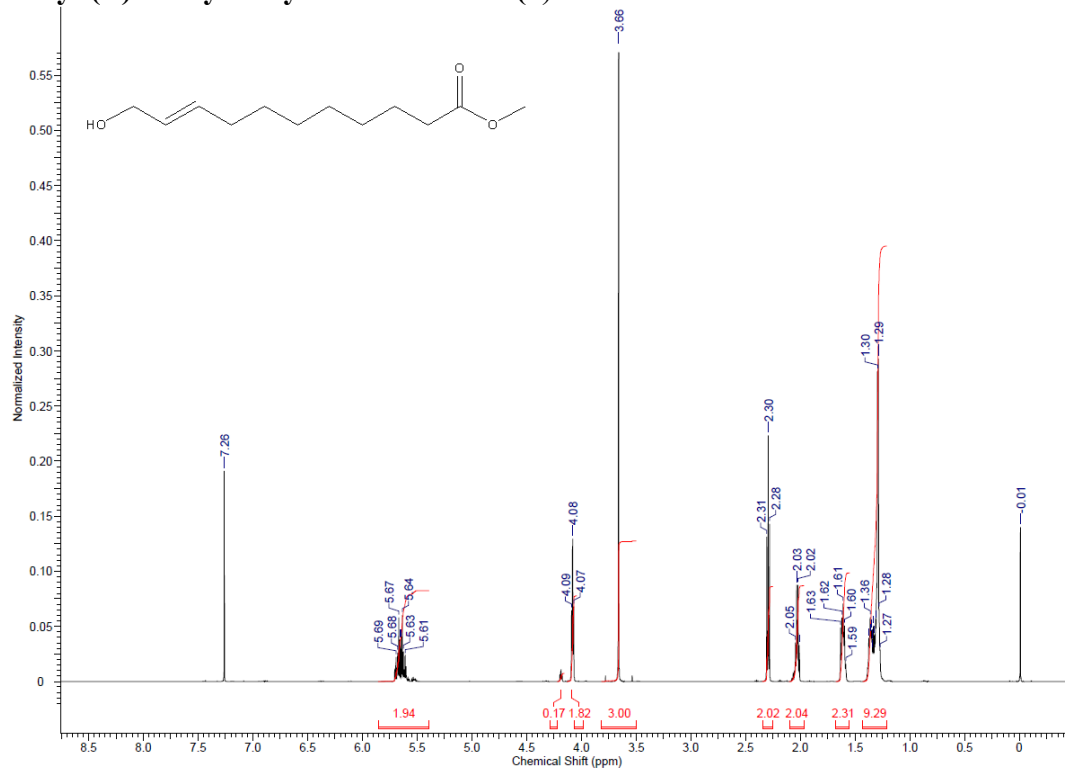
**Table E3:** Tandem cross-metathesis / allyl alcohol isomerization<sup>[a]</sup>

Entry	Steps	Cat.	Solvent	Time /h	Yield (%) <sup>[b]</sup>					
					<b>1</b>	<b>3</b>	<b>4</b>	<b>6</b>	<b>8</b>	<b>13</b> <sup>[d]</sup>
1	CM	<b>C1</b>	EtOAc	6	13.1	52.5	68.1	11.8		
	Isomerization		Toluene	16	12.5	52.8	56.3	11.0	10.3	10.1
2	CM	<b>C4</b>	EtOAc	6	16.1	63.5	67.9	13.3		
	Isomerization		Toluene	16	15.8	8.7	8.7	12.5	57.6	43.9
3 <sup>[c]</sup>	CM	<b>C4</b>	EtOAc	8	12.0	53.7	71.8	13.9		
	Isomerization		EtOAc	16	13.2	26.5	31.0	10.4	36.2	28.3
4	CM	<b>C4</b>	EtOAc	6	14.2	62.8	73.6	6.51		
	Isomerization		EtOAc	16	11.6	7.54	17.0	7.31	64.3	45.6

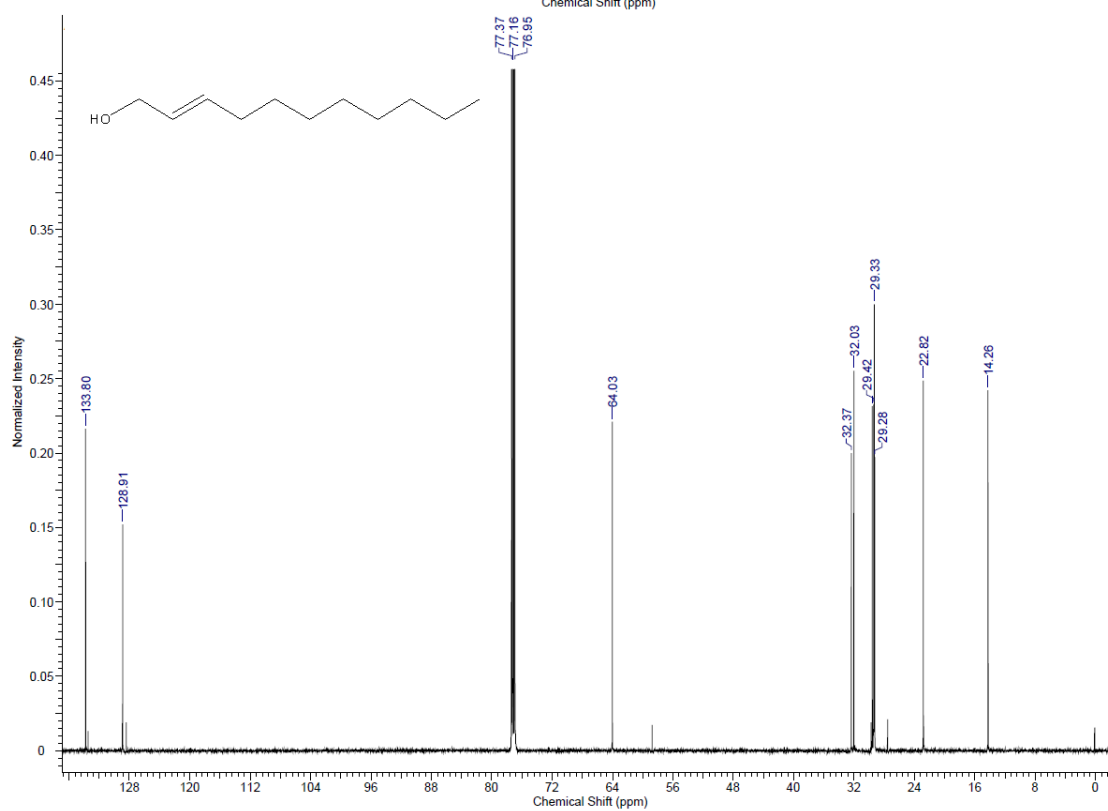
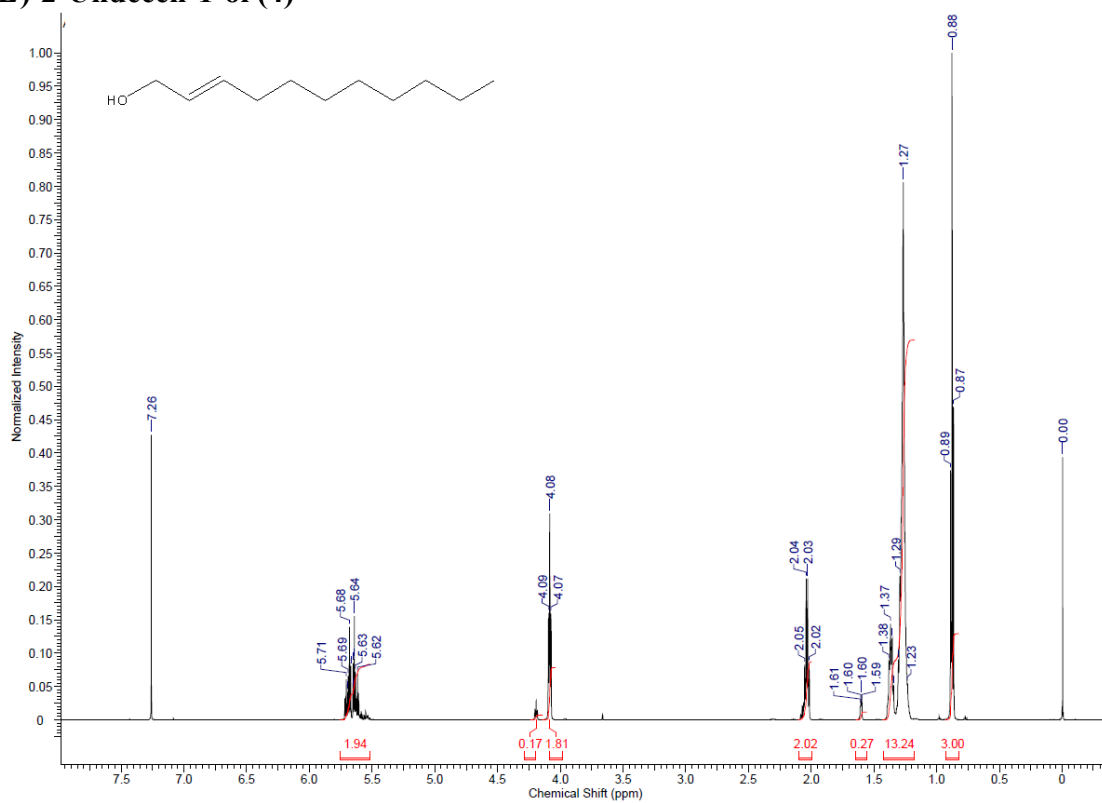
[a] Reaction conditions: See the representative reaction conditions in the experimental section. [b] Calibrated yield using methyl palmitate as an internal reference standard. [c] After cross-metathesis, the reaction mixture was washed with two volumes of water before being carried to the next step. [d] A portion of undecanal was lost due to its volatility.

[7]  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra:

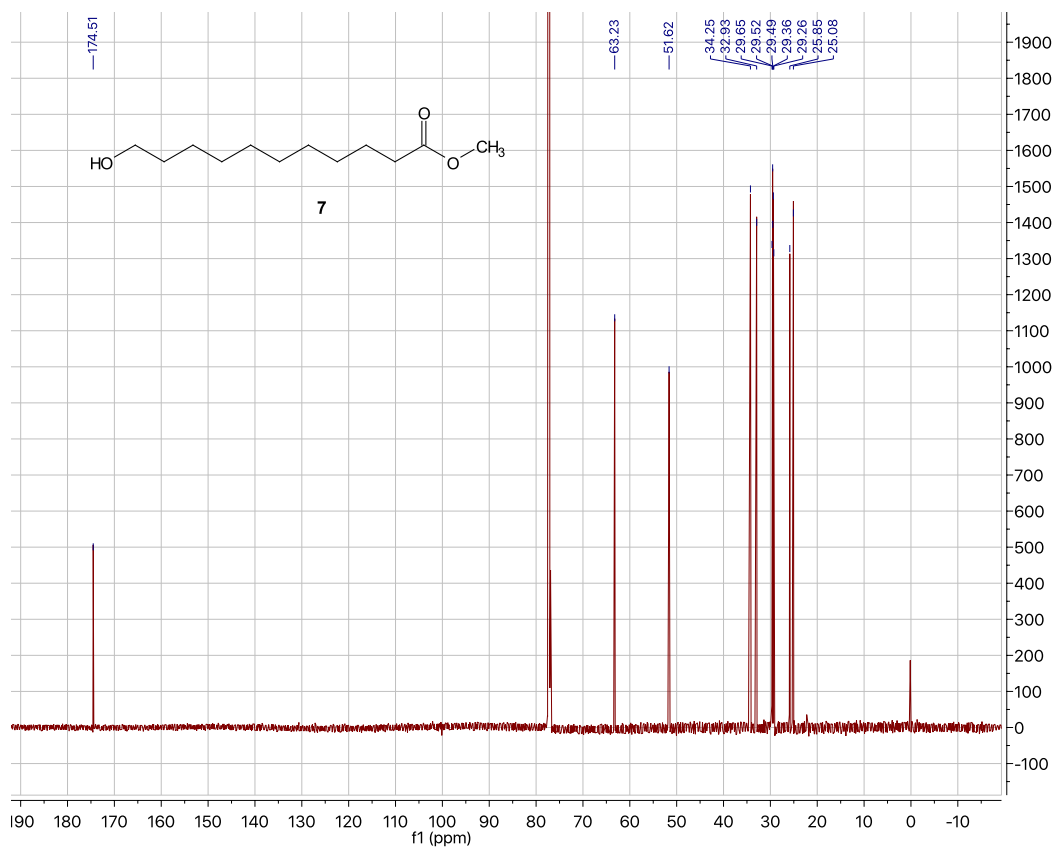
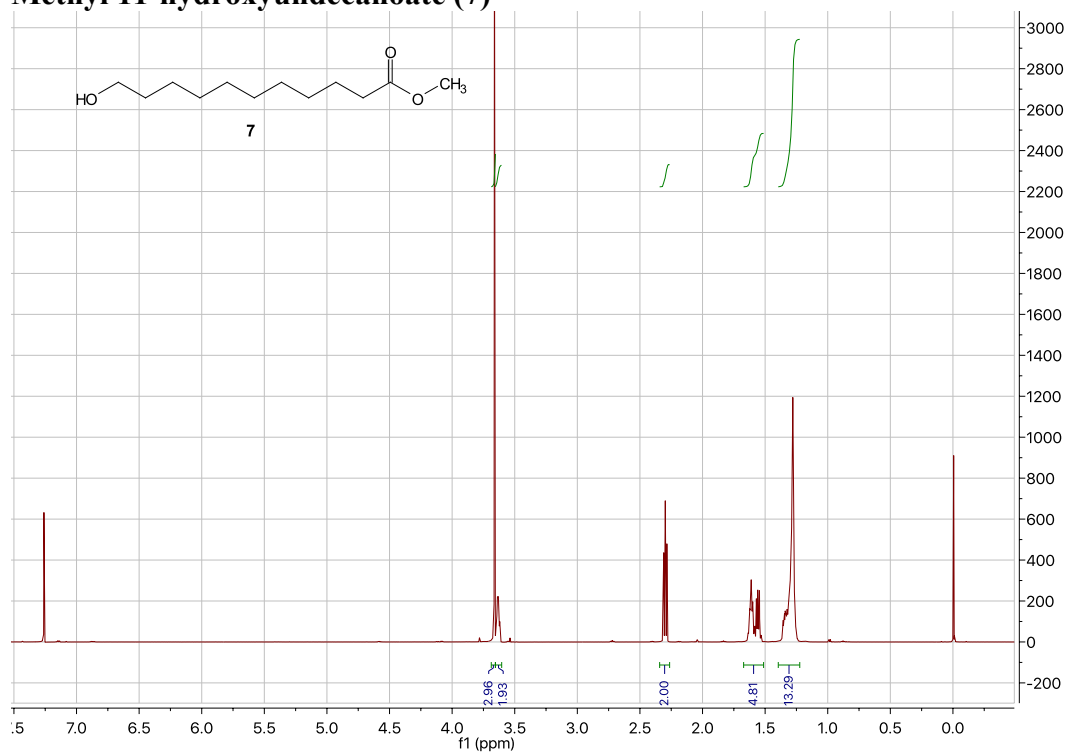
Methyl (*E*)-11-hydroxyundec-9-enoate (3)



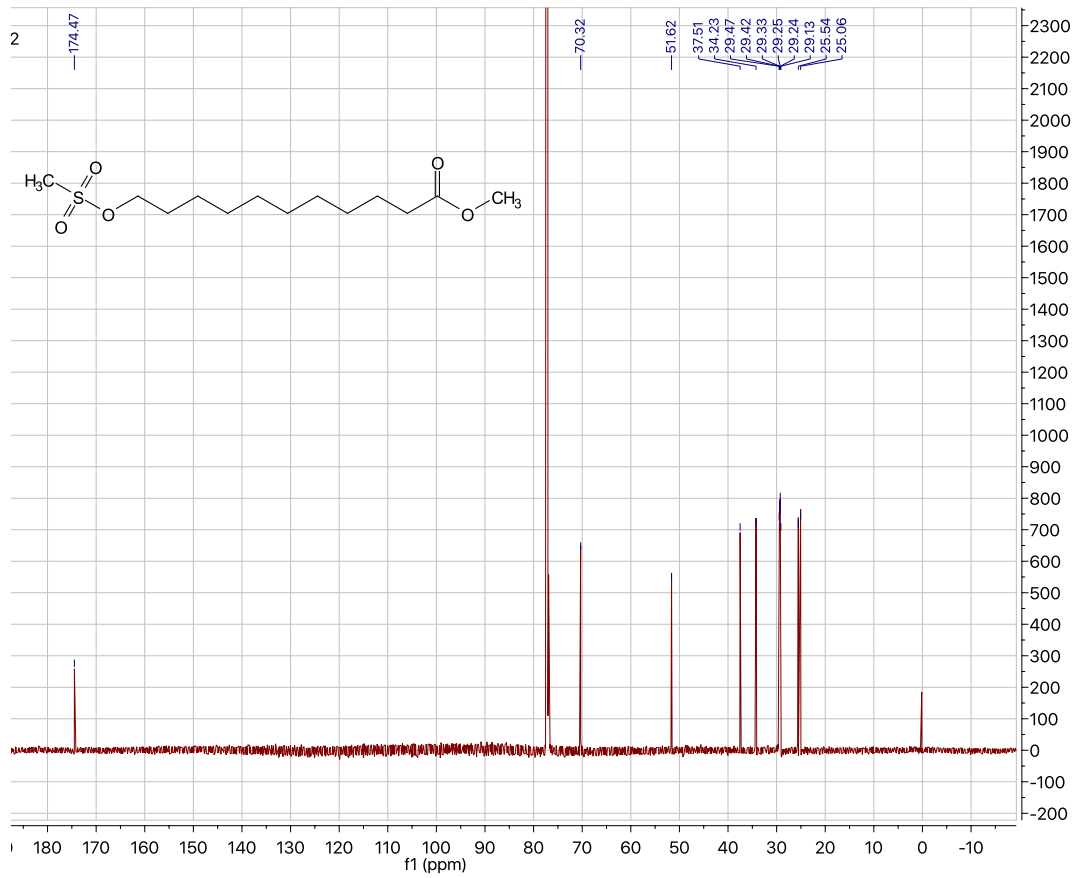
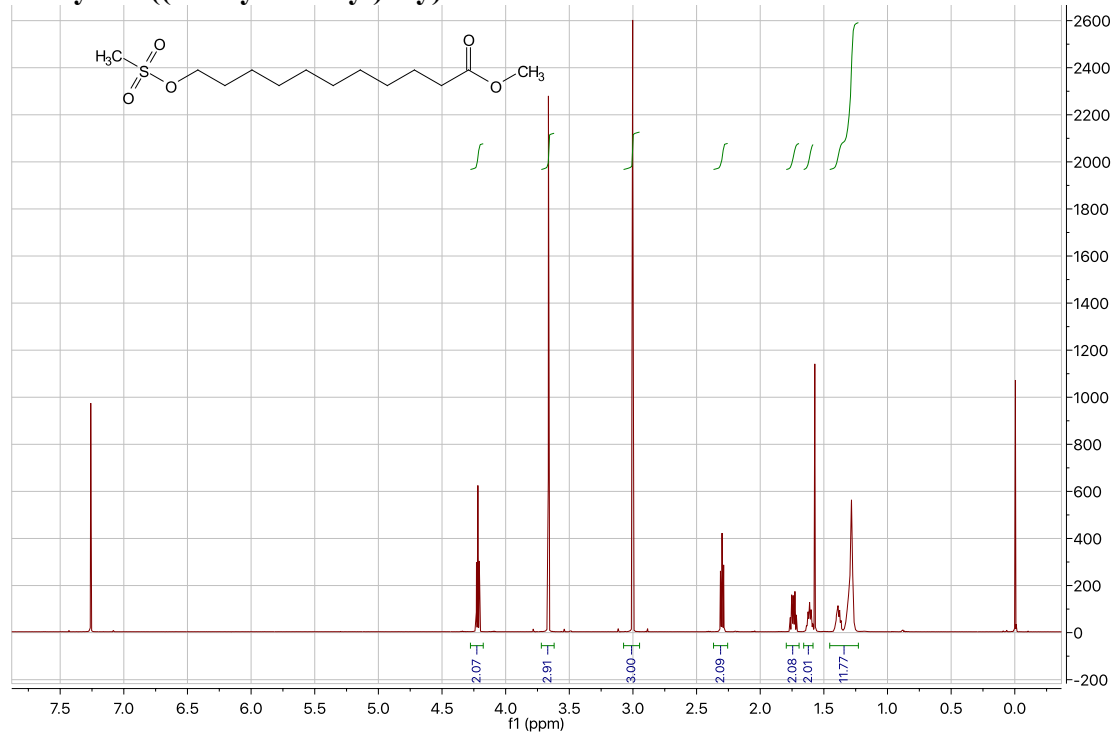
### (E)-2-Undecen-1-ol (4)



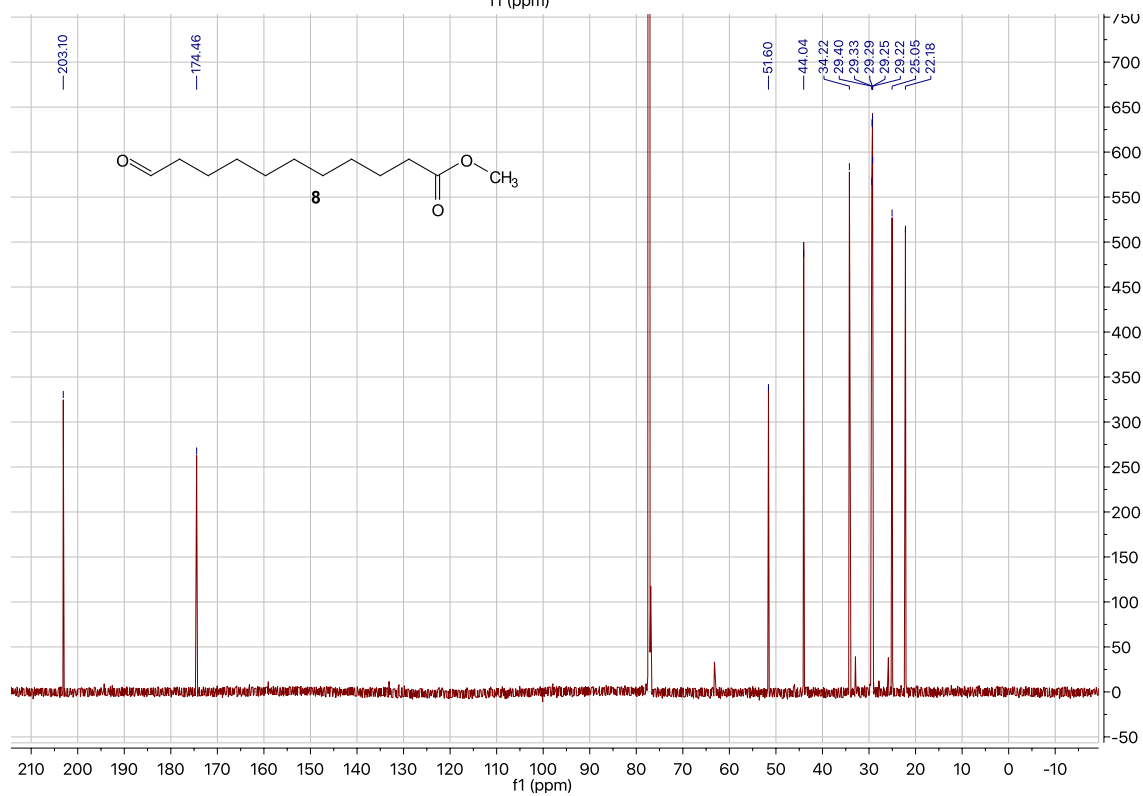
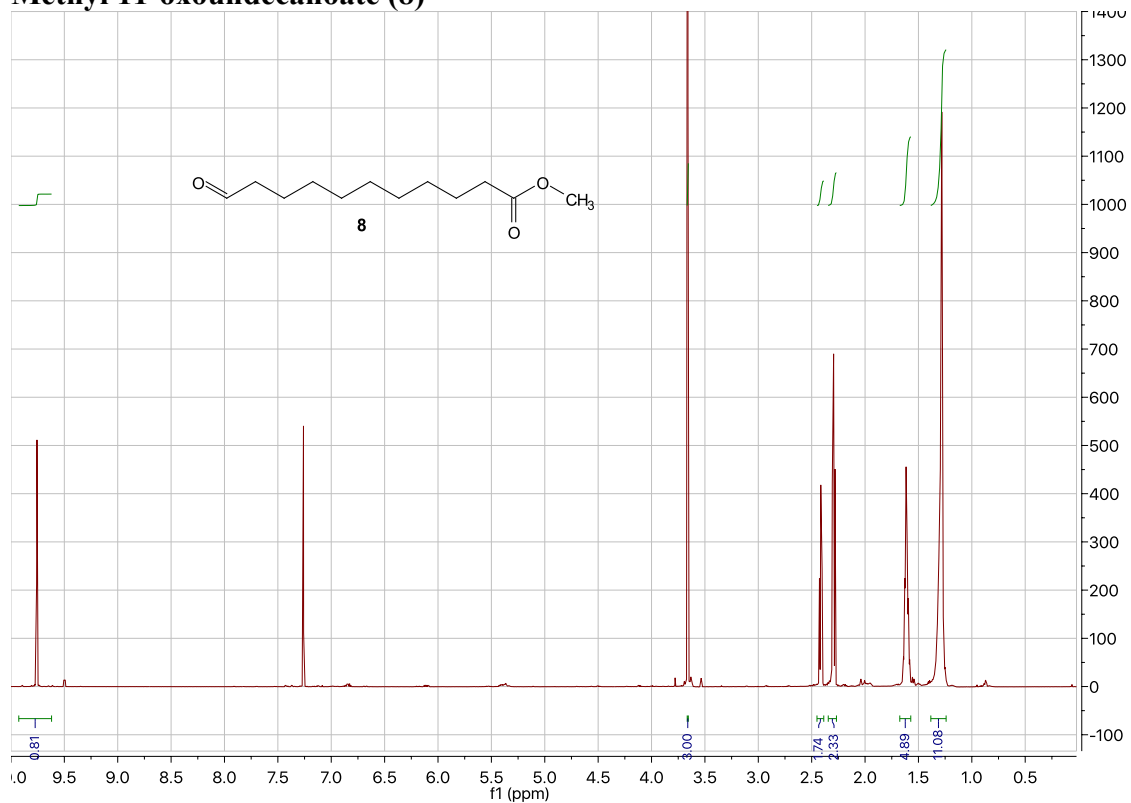
# Methyl 11-hydroxyundecanoate (7)



# Methyl 11-((methylsulfonyl)oxy)undecanoate

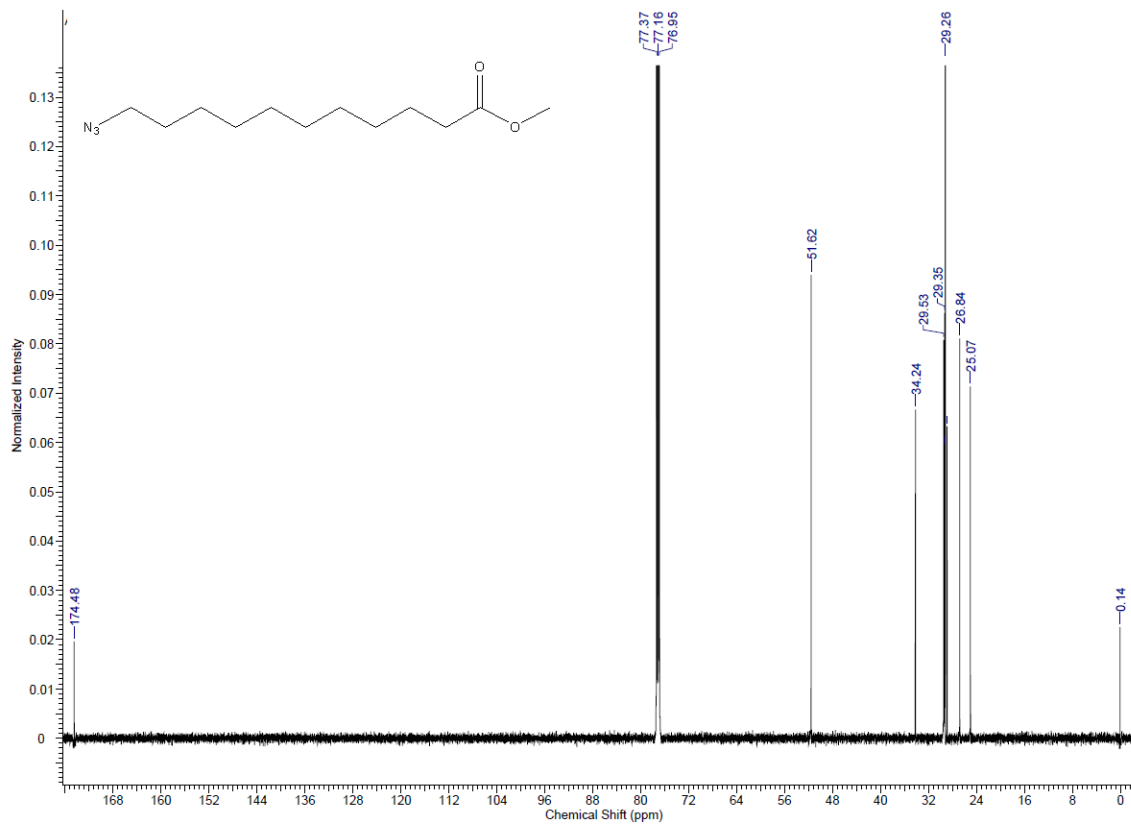
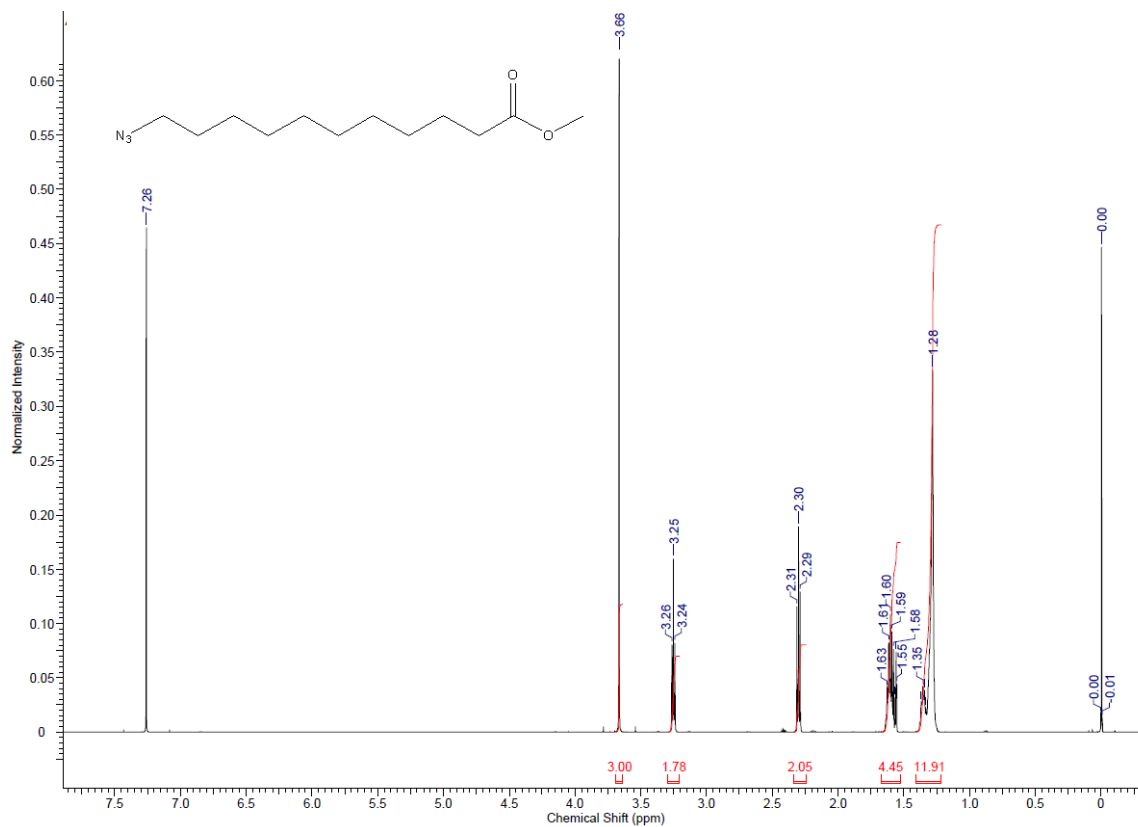


# Methyl 11-oxoundecanoate (8)

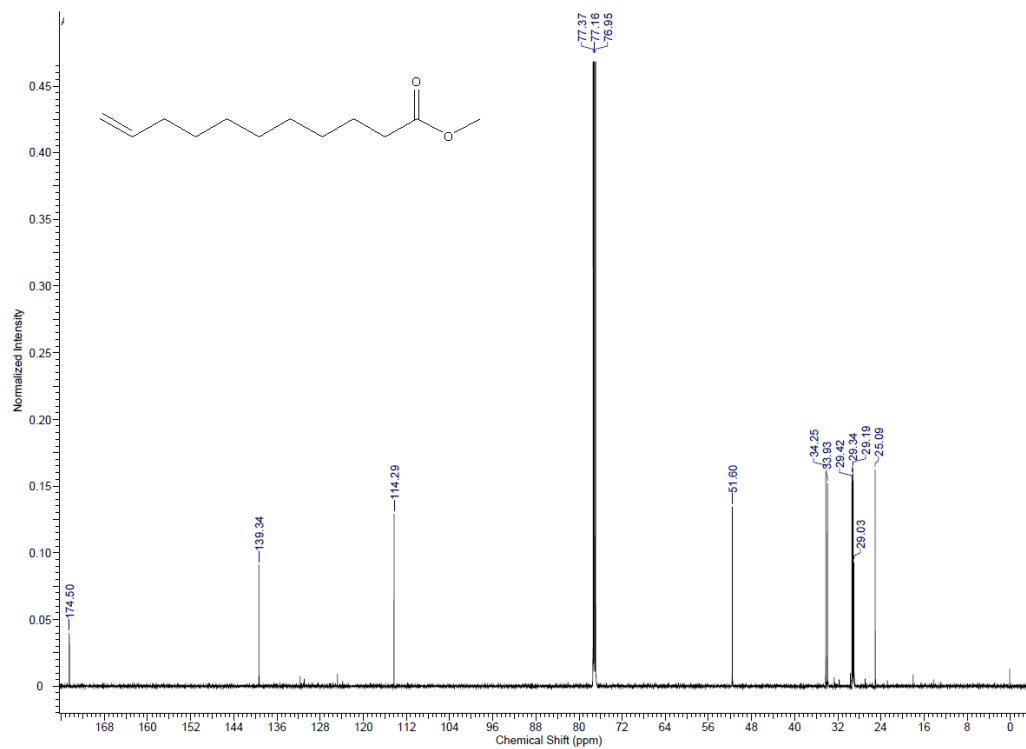
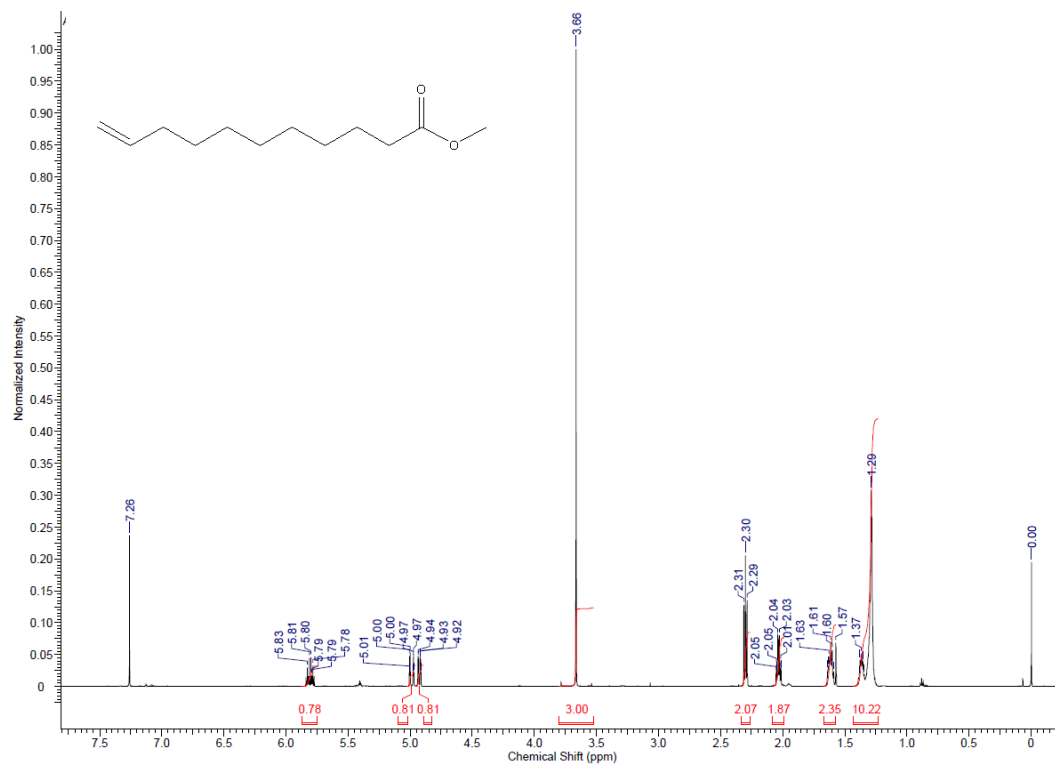


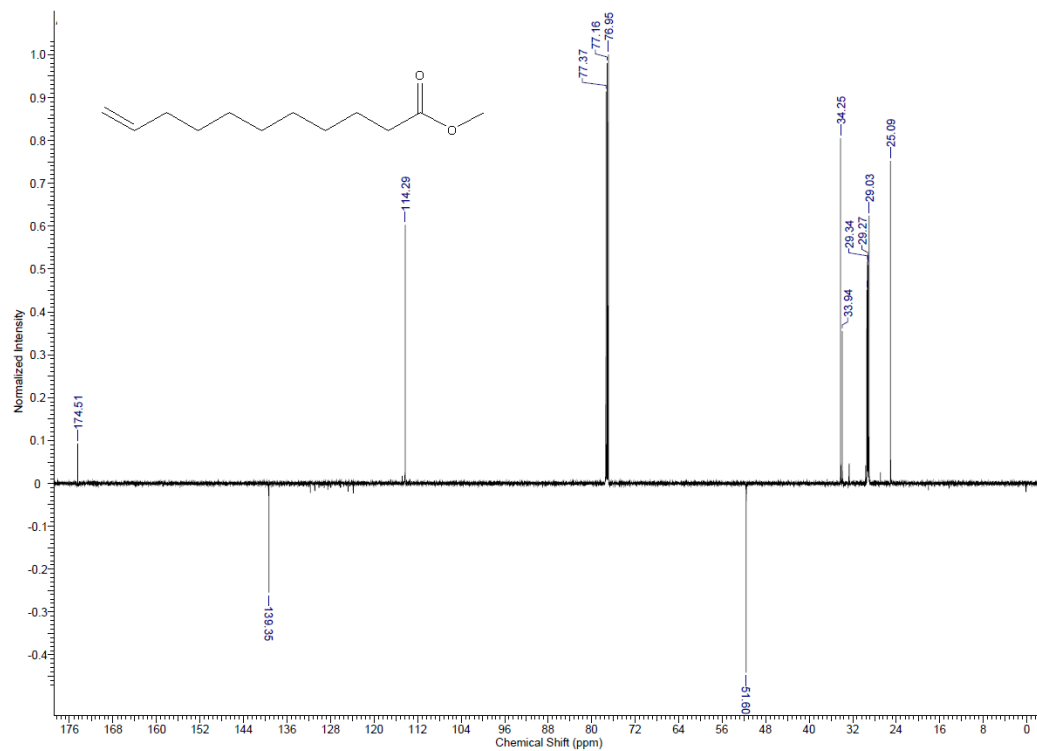


# Methyl 11-azidoundecanoate (9)

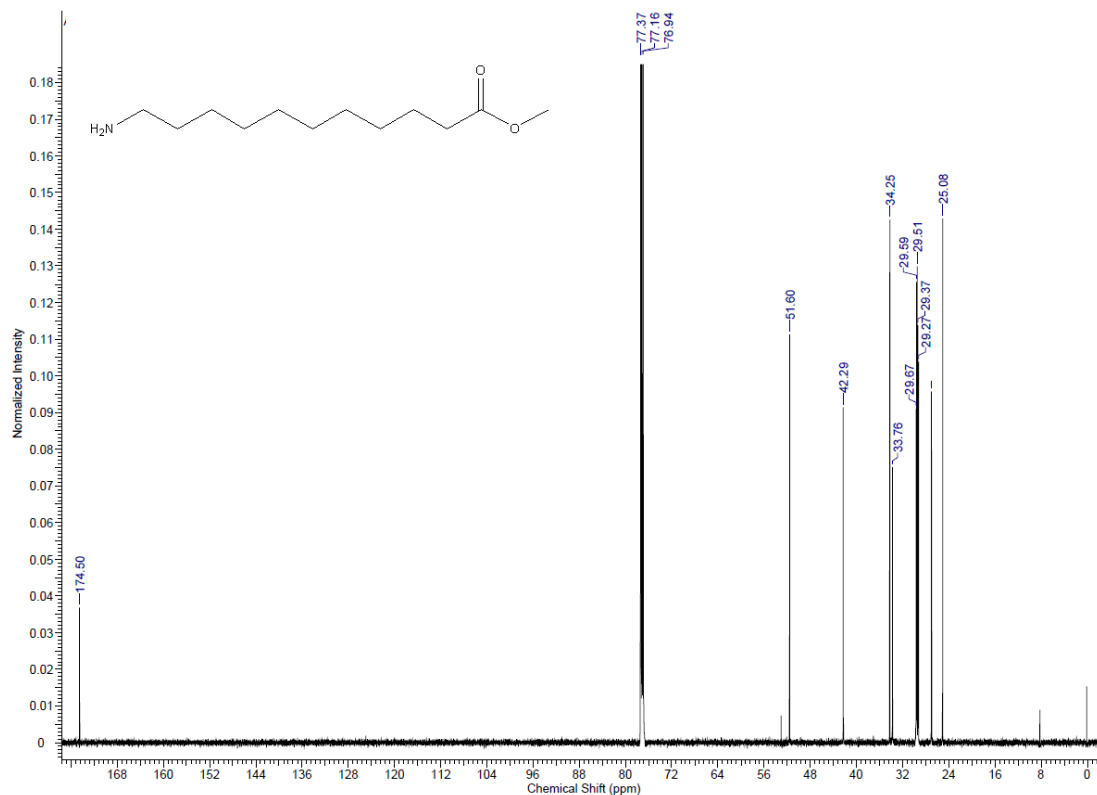
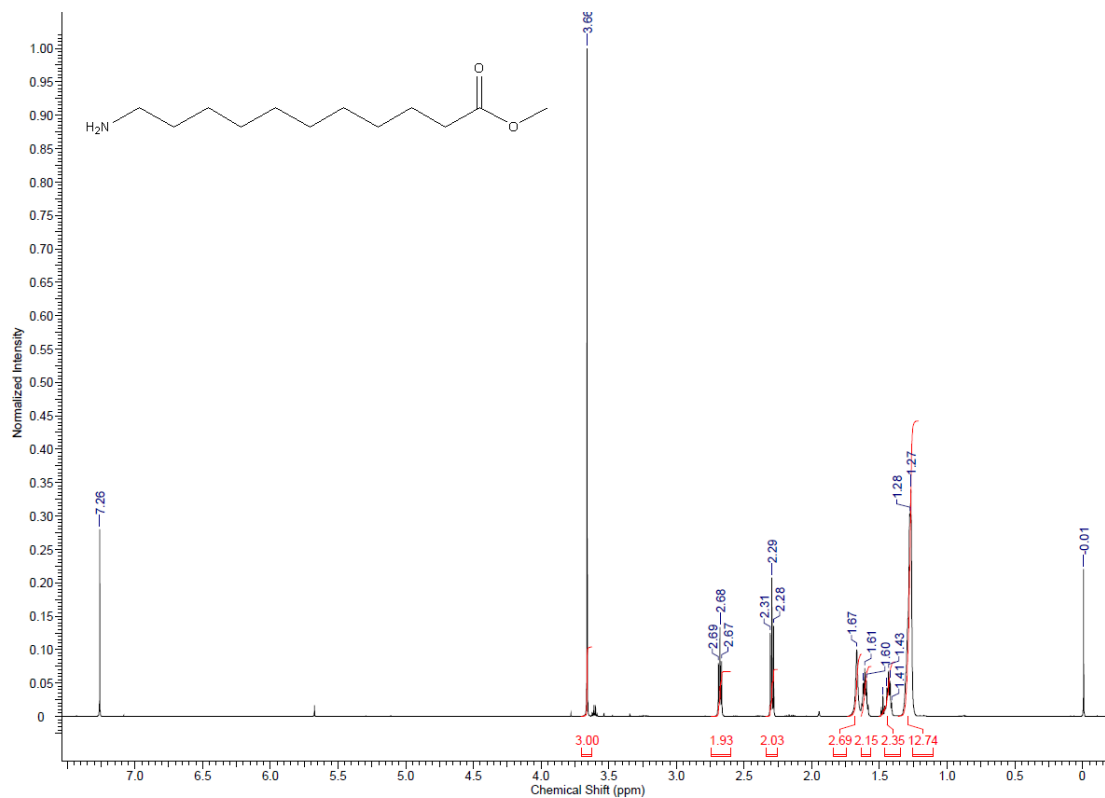


# Methyl undec-10-enoate (10)





# Methyl 11-aminoundecanoate (11)



## References:

- (1) Moon, K.-S.; Lee, E.; Lim, Y.-b.; Lee, M., Bioactive molecular sheets from self-assembly of polymerizable peptides. *Chem. Commun.* **2008**, (34), 4001-4003.
- (2) Minazzi, P.; Lattuada, L.; Menegotto, I. G.; Giovenzana, G. B., An enzymatic approach to bifunctional chelating agents. *Org. Biomol. Chem.* **2014**, *12* (35), 6915-6921.
- (3) Winkler, M.; Meier, M. A. R., Olefin cross-metathesis as a valuable tool for the preparation of renewable polyesters and polyamides from unsaturated fatty acid esters and carbamates. *Green Chem.* **2014**, *16* (6), 3335-3340.
- (4) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H., Efficient and Recyclable Monomeric and Dendritic Ru-Based Metathesis Catalysts. *J. Am. Chem. Soc.* **2000**, *122* (34), 8168-8179.
- (5) Grela, K.; Harutyunyan, S.; Michrowska, A., A Highly Efficient Ruthenium Catalyst for Metathesis Reactions. *Angew. Chem., Int. Ed.* **2002**, *41* (21), 4038-4040.
- (6) Michrowska, A.; Bujok, R.; Harutyunyan, S.; Sashuk, V.; Dolgonos, G.; Grela, K., Nitro-Substituted Hoveyda–Grubbs Ruthenium Carbenes: Enhancement of Catalyst Activity through Electronic Activation. *J. Am. Chem. Soc.* **2004**, *126* (30), 9318-9325.
- (7) Olszewski, T.; Bieniek, M.; Skowerski, K.; Grela, K., A New Tool in the Toolbox: Electron-Withdrawing Group Activated Ruthenium Catalysts for Olefin Metathesis. *Synlett* **2013**, *24* (08), 903-919.
- (8) Mauduit, M.; Clavier, H.; Laurent, I. US008586757B2, February 13, 2013.
- (9) Rix, D.; Caijo, F.; Laurent, I.; Boeda, F.; Clavier, H.; Nolan, S. P.; Mauduit, M., Aminocarbonyl Group Containing Hoveyda–Grubbs-Type Complexes: Synthesis and Activity in Olefin Metathesis Transformations. *J. Org. Chem.* **2008**, *73* (11), 4225-4228.

- (10) Clavier, H.; Caijo, F.; Borré, E.; Rix, D.; Boeda, F.; Nolan, S. P.; Mauduit, M., Towards Long-Living Metathesis Catalysts by Tuning the N-Heterocyclic Carbene (NHC) Ligand on Trifluoroacetamide-Activated Boomerang Ru Complexes. *Liesbig Chem Annalen* **2009**, *2009* (25), 4254-4265.
- (11) Stewart, I. C.; Ung, T.; Pletnev, A. A.; Berlin, J. M.; Grubbs, R. H.; Schrodi, Y., Highly Efficient Ruthenium Catalysts for the Formation of Tetrasubstituted Olefins via Ring-Closing Metathesis. *Org. Lett.* **2007**, *9* (8), 1589-1592.
- (12) Stewart, I. C.; Douglas, C. J.; Grubbs, R. H., Increased Efficiency in Cross-Metathesis Reactions of Sterically Hindered Olefins. *Org. Lett.* **2008**, *10* (3), 441-444.
- (13) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H., A Practical and Highly Active Ruthenium - Based Catalyst that Effects the Cross Metathesis of Acrylonitrile. *Angew. Chem., Int. Ed.* **2002**, *41* (21), 4035-4037.
- (14) Skowerski, K.; Bialecki, J.; Czarnocki, S. J.; Zukowska, K.; Grela, K., Effective immobilisation of a metathesis catalyst bearing an ammonium-tagged NHC ligand on various solid supports. *Beilstein J. Org. Chem.* **2016**, *12*, 5-15.
- (15) Skowerski, K.; Kasprzycki, P.; Bieniek, M.; Olszewski, T. K., Efficient, durable and reusable olefin metathesis catalysts with high affinity to silica gel. *Tetrahedron* **2013**, *69* (35), 7408-7415.
- (16) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H., Improved Ruthenium Catalysts for Z-Selective Olefin Metathesis. *J. Am. Chem. Soc.* **2012**, *134* (1), 693-699.
- (17) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y., Latent Ruthenium Olefin Metathesis Catalysts That Contain an N-Heterocyclic Carbene Ligand. *Organometallics* **2004**, *23* (23), 5399-5401.

(18) Sabitha, G.; Nayak, S.; Bhikshapathi, M.; Yadav, J. S., Palladium hydroxide catalyzed isomerization of primary allylic alcohols to aldehydes: application to the formal synthesis of (-)-brevisamide. *Org. Lett.* **2011**, *13* (3), 382-385.