Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information

Low Temperature *n*-Butyllithium-Induced [3,3]-Sigmatropic Rearrangement/Electrophile Trapping Reactions of Allyl-1,1-Dichlorovinyl Ethers. Synthesis of β-,γ-,and δ-lactones.

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General Methods. Distilled water was used in all of the experiments. Organic extracts were dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator at aspirator pressure (20-30mmHg). Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, 230-400 mesh). ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ at 400 MHz and 100 MHz, respectively, using Me_4Si as internal standard. Chemical shifts are reported in ppm downfield (δ) from Me_4Si.

A. General procedure for [3,3] sigmatropic rearrangement/ketone trapping of allyl-1,1-dichlorovinyl ethers to form **β**-lactones **3a-3j**.

The allyl-1,1-dichlorovinyl ether **2a** (188 mg, 0.85 mmol) was dissolved in THF (5 mL) and cooled to -78°C. *n*-BuLi (1.27 mL, 2M in cyclohexane, 2.54 mmol, 3 equivalents) was added dropwise at -78°C and the dark-colored solution was stirred at this temperature for 45 minutes. Then the ketone (1.7 mmol, 2 equivalents) was added and the mixture was stirred at -78°C for another 45 minutes. A solution of saturated $NaHCO_3$ (5 mL) was added, followed by ether (5 mL) and the mixture was allowed to warm to room temperature. The phases were separated and the aqueous layer was further extracted with ether (2 x 25 mL). The combined organic extracts were once washed with 20 ml sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude oil. Purification of the residue by flash chromatography afforded **β**-lactones **3**.

B. General procedure for [3,3] sigmatropic rearrangement/ketone trapping of allyl-1,1-dichlorovinyl ethers to form **γ** and δ-lactones **3l-3r**.

The allyl-1,1-dichlorovinyl ether **2a** (188 mg, 0.85 mmol) was dissolved in THF (5 mL) and cooled to -78°C. *n*-BuLi (1.27 mL, 2M in cyclohexane, 2.54 mmol, 3 equivalents) was added dropwise at -78°C and the dark-colored solution was stirred at this temperature for 45 minutes. Then the epoxide or oxetane (1.7 mmol, 2 equivalents) was added, followed by BF_3•OEt_2 (1.7 mmol, 2 equivalents) and the mixture was stirred at -78°C for another 45 minutes. A solution of saturated $NaHCO_3$ (5 mL) was added, followed by ether (5 mL) and the mixture was allowed to warm to room temperature. The phases were separated and the aqueous layer was further extracted with ether (2 x 25 mL). The combined organic extracts were once washed with 20 ml sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude oil. Purification of the residue by flash chromatography afforded **γ**- or δ–lactones **3**.

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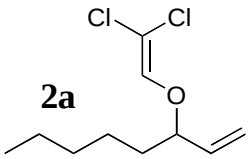

2a

Compound **2a** was prepared from 1-octene-2-ol in 68% overall yield according to the procedure in main text reference 4.

See spectra on page S24

^{1}H NMR: (400 MHz, $CDCl_3$)

6.55 (s, 1H); 5.77 (m, 1H); 5.28 (d, *J*=5.2 Hz, 1H); 5.24 (s, 1H); 4.12 (q, *J*=6.8 Hz, 1H); 1.73 (m, 1H); 1.59 (m, 1H); 1.42-1.27 (m, 6H); 0.91 (t, *J*=6.4 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

141.8; 137.1; 118.1; 103.9; 84.7; 34.7; 31.5; 24.6; 22.6; 22.4; 13.9.

HRMS (ESI): calculated for $C_{10}H_{17}Cl_2O_8$ 223.0656, found 223.0682 $(M+H)^+$

MS spectra were difficult to obtain because dichlorovinyl ethers undergo facile [3,3] sigmatropic rearrangement reactions upon exposure to thermal, ionizing or acidic conditions (*Org Lett*. **2006**, *8*, 451). As a result, the $[M+H]^+$ and $[M+Na]^+$ signals for dichlorovinyl ethers **2a**, **2e**, **2h** and **2j** are very weak. The thermal rearrangement of allyl-1,1-dichlorovinyl ethers is known (*Synthesis* **1981**, 308).

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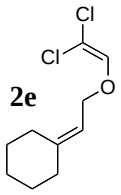

2e

Compound **2e** was prepared from 2-cyclohexylideneethanol[a] in 51% overall yield according to the procedure in main text reference 4.

See spectra on page S25

^{1}H NMR: (400 MHz, $CDCl_3$)

6.55 (s, 1H); 5.32 (t, *J*=6.2 Hz, 1H); 4.42 (s, 1H); 4.40 (s, 1H); 2.22 (m, 2H); 2.16 (m, 1H); 1.73 (m, 2H); 1.58 (m, 4H).

^{13}C NMR: (100 MHz, $CDCl_3$)

148.0; 143.3; 142.5; 115.5; 72.0; 68.7; 37.0; 34.2; 33.1; 29.1; 28.3; 27.7; 26.5; 26.4; 26.1.

HRMS (ESI): calculated for $C_{10}H_{14}Cl_2ONa$ 243.0319, found 243.0314 $(M+H)^+$

[a]Koo, J.; Park, H.-S; Shin, S. *Tetrahedron Lett.* **2013**, *54*, 834.

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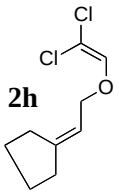

2h

Compound **2h** was prepared from 2-cyclopentylideneethanol[b] in 62% overall yield according to the procedure in main text reference 4.

See spectra on page S26

^{1}H NMR: (400 MHz, $CDCl_3$)

6.55 (s, 1H); 5.47 (m, 1H); 4.39 (s, 1H); 4.37 (s, 1H); 2.34 (t, *J*=7.0 Hz, 2H); 2.27 (t, *J*=7.4 Hz, 2H); 1.66 (m, 4H).

^{13}C NMR: (100 MHz, $CDCl_3$)

151.5; 142.7; 114.4; 71.1; 33.8; 29.0; 26.2; 25.9.

HRMS (ESI): calculated for $C_9H_{13}Cl_2O$ 207.0343, found 207.0385 $(M+H)^+$

[b]Rigoli, J.W.; Moyer, S.A.; Pearce, S.D.; Schomaker, J.M. *Org. Biomol. Chem.* **2012**, *10*, 1746.

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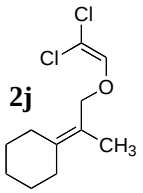

2j

Compound **2j** was prepared from 2-cyclohexylidenepropan-1-ol[c] in 90% overall yield according to the procedure in main text reference 4.

See spectra on page S27

^{1}H NMR: (400 MHz, $CDCl_3$)
6.51 (s, 1H); 4.43 (s, 2H); 2.25 (m, 4H); 1.74 (s, 3H); 1.57 (m, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$)
142.3; 141.3; 119.9; 104.6; 73.1; 30.9; 30.4; 28.4; 27.8; 26.6; 15.8.

HRMS (ESI): calculated for $C_{11}H_{16}Cl_2NaO$ 257.0476, found 257.0467 $(M+Na)^+$

[c]Kuroda, C.; Koshio, H; Koito, A.; Sumiya, H.; Murase, A.; Hirono, Y. *Tetrahedron* **2000**, *56*, 6441.

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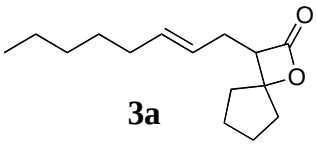

3a

Compound **3a** was prepared from **2a** in 70% yield according to general procedure **A** outlined above.

See spectra on page S28

^{1}H NMR: (400 MHz, $CDCl_3$)

5.52 (m, 1H); 5.39 (m, 1H); 3.54 (dd, *J*=9.6, 6.3 Hz, 2H); 2.52 (m, 1H); 2.41 (m, 1H); 2.15 (m, 1H); 2.05-1.71 (m, 8H); 1.40-1.25 (m, 6H); 0.91 (t, *J*=6.8 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

171.3; 133.5; 125.0; 91.3; 54.4; 37.8; 32.4; 32.0; 31.3; 28.9; 28.8; 23.5; 23.4; 22.4; 13.9.

HRMS (ESI): calculated for $C_{15}H_{25}O_2$ 237.1855, found 237.1876 $(M+H)^+$

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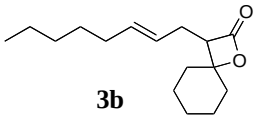

3b

Compound **3b** was prepared from **2a** in 56% yield according to general procedure **A** outlined above.

See spectra on page S29

^{1}H NMR: (400 MHz, $CDCl_3$)

5.51 (m, 1H); 5.42 (m, 1H); 3.19 (t, *J*=6.7 Hz, 2H); 2.48 (m, 2H); 2.04 (q, *J*=6.9 Hz, 2H);1.94 (m, 1H); 1.75-1.60 (m, 10H); 1.38-1.27 (m, 8H); 0.93 (t, *J*=4.0 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

171.6; 133.4; 125.5; 82.4; 57.8; 37.4; 32.4; 31.4; 31.3; 31.1; 28.9; 27.0; 25.3; 24.9; 22.8; 22.7; 22.5; 22.4; 22.0; 14.0.

HRMS (ESI): calculated for $C_{16}H_{26}NaO_2$ 273.1830, found 273.1819 $(M+Na)^+$

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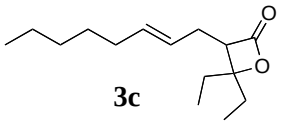


3c

Compound **3c** was prepared from **2a** in 85% yield according to the general procedure **A** outlined above.

See spectra on page S30

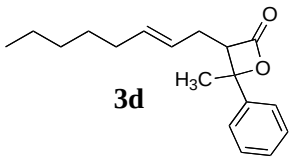
^{1}H NMR: (400 MHz, $CDCl_3$)

5.54 (dt, *J*=15.2, 7.0 Hz, 1H); 5.38 (dt, *J*=13.5, 7.5 Hz, 1H); 3.27 (dd, *J*=9.5, 6.6 Hz, 2H); 2.50 (m, 1H); 2.41 (m, 1H); 2.03 (m, 2H); 1.86-1.68 (m, 3H); 1.37-1.24 (m, 9H); 1.00 (t, *J*=7.5 Hz, 3H); 0.94 (m, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$)

171.5; 133.7; 125.6; 85.2; 56.8; 32.3; 31.3; 29.1; 28.9; 27.4; 24.5; 22.4; 14.0; 8.1; 7.3.

HRMS (ESI): calculated for $C_{15}H_{26}NaO_2$ 261.1830, found 261.1846 $(M+Na)^+$



3d

Compound **3d** was prepared from **2a** in 71% yield according to the general procedure **A** outlined above.

See spectra on page S31; **product obtained as a mixture of diastereomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.36 (m, 5H); 5.22 (m, 2H); 3.59 (t, *J*=8.2 Hz, 1H); 1.97 (s, 3H); 2.05-1.90 (m, 4H); 1.28 (m, 6H); 0.91 (t, *J*=6.7 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

170.7; 138.8; 133.5; 128.3; 128.0; 125.3; 124.3; 82.3; 60.5; 32.3; 31.3; 29.3; 28.9; 27.7; 22.4; 14.0.

HRMS (ESI): calculated for $C_{18}H_{24}NaO_2$ 295.1674, found 295.1669 $(M+Na)^+$

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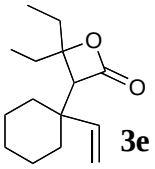

3e

Compound **3e** was prepared from **2e** in 81% yield according to the general procedure **A** outlined above.

See spectra on page S32

^{1}H NMR: (400 MHz, $CDCl_3$)

5.81 (dd, *J*=17.8, 11.0, 1H); 5.30 (d, *J*=11.0 Hz, 1H); 5.20 (d, *J*=13.8 Hz, 1H); 3.23 (s, 1H); 2.21 (m, *J*=6.4 Hz, 1H); 2.07 (m, 1H); 2.01 (m, *J*=6.4 Hz, 1H); 1.84 (m, *J*=7.3 Hz, 1H); 1.72 (m, 1H); 1.55 (m, 8H); 1.26 (m, 1H); 0.93 (t, *J*=7.3 Hz, 3H); 0.89 (t, *J*=6.4 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

170.5; 142.2; 116.4; 87.2; 67.7; 40.3; 34.9; 30.2; 25.7; 25.2; 21.9; 21.4; 8.3; 7.5.

HRMS (ESI): calculated for $C_{15}H_{24}NaO_2$ 259.1674, found 259.1635 $(M+Na)^+$

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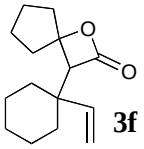

3f

Compound **3f** was prepared from **2e** in 84% yield according to the general procedure **A** outlined above.

See spectra on page S33

^{1}H NMR: (400 MHz, $CDCl_3$)

5.84 (d, *J*=11.2 Hz, 1H); 5.79 (d, *J*=10.8 Hz, 1H); 5.24 (d, *J*=10.8 Hz, 1H); 5.17 (d, *J*=18.8 Hz, 1H); 3.56 (s, 1H); 2.08 (m, 2H); 1.98 (m, 1H); 1.88-1.42 (m, 14H; 1.30 (m, 1H).

^{13}C NMR: (100 MHz, $CDCl_3$)

170.5; 141.6; 116.1; 91.5; 63.9; 40.3; 39.7; 34.4; 33.3; 33.2; 25.6; 23.9; 22.1; 21.8; 21.4.

HRMS (ESI): calculated for $C_{15}H_{22}NaO_2$ 257.1517, found 257.1521 $(M+Na)^+$

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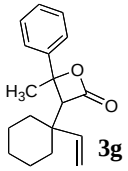

3g

Compound **3g** was prepared from **2e** in 56% yield according to the general procedure **A** outlined above.

See spectra on page S34; **product obtained as a mixture of diastereomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.41-7.28 (m, 5H); 5.28 (d, *J*=11 Hz, 1H); 5.23 (d, *J*=10.9 Hz, 1H); 5.06 (d, *J*=10.9 Hz, 1H); 4.88 (d, *J*=18.6 Hz, 1H); 3.64 (s, 1H); 1.92 (s, 3H); 1.66-1.10 (m, 10H)

^{13}C NMR: (100 MHz, $CDCl_3$)

168.9; 141.1; 139.5; 128.0; 127.7; 126.7; 123.6; 115.8; 82.8; 71.9; 40.5; 35.6;34.6; 33.1; 32.6; 29.9; 26.1; 25.5; 22.0; 21.6; 21.3.

HRMS (ESI): calculated for $C_{18}H_{22}NaO_2$ 293.1517, found 293.1515 $(M+Na)^+$

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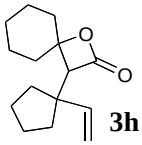

3h

Compound **3h** was prepared from **2h** in 62% yield according to the general procedure **A** outlined above.

See spectra on page S35

^{1}H NMR: (400 MHz, $CDCl_3$)

5.82 (d, *J*=10.7 Hz, 1H); 5.80 (d, *J*=10.7, Hz, 1H); 5.12 (d, *J*=10.7 Hz, 1H); 5.09 (d, *J*=8.6 Hz, 1H); 3.32 (s, 1H); 2.19 (m, 1H); 1.89 (m, 3H); 1.65 (m, 15H).

^{13}C NMR: (100 MHz, $CDCl_3$)

170.9; 142.9; 113.4; 84.1; 67.1; 48.0; 38.3; 36.1; 34.9; 31.6; 24.9; 23.1; 22.5; 21.6

HRMS (ESI): calculated for $C_{15}H_{22}NaO_2$ 257.1517, found 257.1574 $(M+Na)^+$

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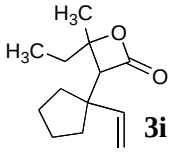

3i

Compound **3i** was prepared from **2h** in 91% yield according to general procedure **A** outlined above.

***See spectra on page S36*; product obtained as a mixture of diastereomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

5.83 (m, 2H); 5.14-5.01 (m, 4H); 5.52 (s, 1H); 3.49 (s, 1H); 2.02 (m, 1H); 1.95-1.62 (m, 19H); 1.55 (s, 3H); 1.51 (s, 3H); 0.99 (q, *J*=7.4 Hz, 3H)

^{13}C NMR: (100 MHz, $CDCl_3$)

170.6; 170.4; 142.8; 142.5; 113.7; 113.3; 84.5; 84.2; 67.6; 65.0; 48.1; 37.5; 37.1; 35.1; 34.3; 28.0; 25.0; 24.6; 24.5; 22.5; 22.4; 19.7; 8.4; 7.8.

HRMS (ESI): calculated for $C_{13}H_{21}NaO_2$ 231.1361, found 231.1311 $(M+Na)^+$

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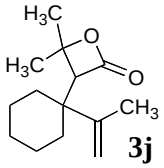

3j

Compound **3j** was prepared from **2j** in 93% yield according to general procedure **A** outlined above.

See spectra on page S37

^{1}H NMR: (400 MHz, $CDCl_3$)
5.19 (s, 1H); 4.98 (s, 1H); 3.37 (s, 1H); 2.26 (m, 2H); 1.76 (s, 3H); 1.79-1.70 (m, 3H); 1.60 (s, 3H); 1.58 (m, 3H); 1.49 (s, 3H); 1.25 (m, 2H)

^{13}C NMR: (100 MHz, $CDCl_3$)
170.8; 143.2; 116.1; 81.9; 65.7; 43.2; 34.2; 30.9; 29.7; 25.7; 22.6; 22.0; 21.6; 19.6.

IR: 1807, 1222, 1069, 899, 802 cm^{-1}

HRMS (ESI): calculated for $C_{14}H_{22}NaO_2$ 245.1517, found 245.1509 $(M+Na)^+$

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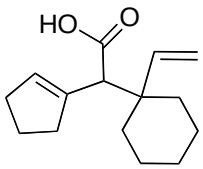

4f

Compound **4f** was prepared from **3f** in >95% yield by the following procedure:

Compound **3f** (45 mg, 0.19 mmol) was dissolved in CH_2Cl_2 (1 mL) and cooled to -78°C. Then allyltrimethylsilane (0.08 ml, 0.5 mmol) was added, followed by TMSOTf (0.1 mL, 0.5 mmol). The reaction was stirred 10 minutes at -78°C and then saturated aqueous $NaHCO_3$ solution (5 mL) and ether (5 mL) was added. The phases were separated and the aqueous layer was further extracted with ether (2 x 25 mL). The combined organic extracts were once washed with 20 ml sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude oil. ^{1}H NMR of the crude oil indicated that product **4f** was >95% pure.

See spectra on page S38

^{1}H NMR: (400 MHz, $CDCl_3$)

5.88 (dd, *J*=17.8, 11.0 Hz, 1H); 5.67 (m, 1H); 5.23 (d, *J*=11.0 Hz, 1H); 5.03 (d, *J*=17.8 Hz, 1H); 3.29 (s, 1H); 2.42 (m, 2H); 2.35 (m, 2H); 1.85 (m, 3H); 1.65-1.39 (m, 9H).

^{13}C NMR: (100 MHz, $CDCl_3$)

178.4; 142.9; 137.9; 131.0; 115.1; 57.4; 42.7; 36.5; 34.5; 32.8; 30.3; 29.6; 26.1; 23.6; 22.1; 21.9.

HRMS (ESI): calculated for $C_{15}H_{22}NaO_2$ 257.1517, found 257.1548 $(M+Na)^+$

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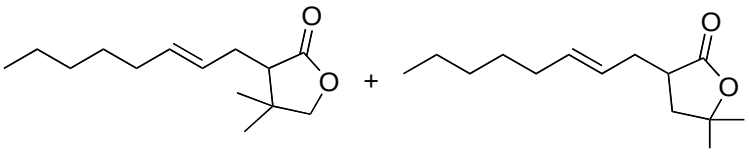

3l

Compounds **3l** were prepared from **2a** in 56% yield according to general procedure **B** outlined above.

***See spectra on page S39*; product obtained as a mixture of regioisomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

5.46 (dt, *J*=8.4, 0.8 Hz, 1H); 5.29 (dt, *J*=8.0, 6.8 Hz, 1H); 4.05 (m, 2H); 2.59 (m, 1H); 2.28 (m, 1H); 2.14 (m, 1H); 2.01-1.93 (m, 2H); 1.63-1.50 (m, 2H); 1.42-1.13 (m, 6H); 1.20 (s, 3H); 1.19 (s, H); 0.92 (t, *J*=7.6 Hz, 3H)

^{13}C NMR: (100 MHz, $CDCl_3$)

177.0; 133.5; 126.2; 70.4; 64.3; 44.8; 41.6; 37.1; 32.4; 31.3; 30.6; 30.5; 29.0; 28.4; 22.5; 19.1; 14.0; 13.6.

HRMS (ESI): calculated for $C_{14}H_{25}O_2$ 225.1855, found 225.1817 $(M+H)^+$

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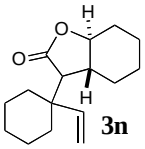

3n

Compound **3n** was prepared from **2e** in 78% yield according to general procedure **B** outlined above.

***See spectra on page S41*; product obtained as a mixture of diastereomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

5.82 (dd, *J*=17.8, 11.0 Hz, 1H); 5.26 (d, *J*=11.0 Hz, 1H); 5.11 (d, *J*=17.8 Hz, 1H); 3.63 (td, *J*=10.7, 3.5 Hz, 1H); 2.36 (d, *J*=12.0 Hz, 1H); 2.17 (m, 3H); 1.87-1.63 (m, 6H); 1.52-1.40 (m, 7H); 1.39-1.28 (m, 3H)

^{13}C NMR: (100 MHz, $CDCl_3$)

176.2; 142.5; 115.8; 81.9; 54.3; 45.7; 41.7; 34.2; 33.6; 30.6; 30.1; 26.1; 25.5; 23.9; 21.9; 21.8.

IR: 1770, 1080, 1035, 912 cm^{-1}

HRMS (ESI): calculated for $C_{16}H_{24}NaO_2$ 271.1674, found 271.1689 $(M+Na)^+$

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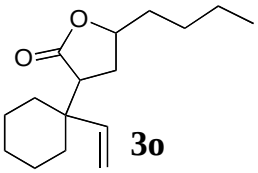

3o

Compound **3o** was prepared from **2e** in 89% yield according to general procedure **B** outlined above.

See spectra on page S42: **product obtained as a mixture of diastereomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

5.77 (dd, *J*=17.8, 11.0 Hz, 1H); 5.26 (dd, *J*=11.0, 1.2 Hz, 1H); 5.08 (dd, *J*=17.8, 1.3 Hz, 1H); 4.23 (m, 1H); 2.67 (dd, *J*=12.4, 8.6 Hz, 1H); 2.21 (m, 1H); 2.16 (m, 1H); 1.69-1.31 (m, 10H); 0.92 (t, *J*=6.8 Hz, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

176.4; 141.7; 116.1; 48.8; 40.8; 35.8; 35.1; 33.7; 33.2; 30.7; 29.6. 27.3; 26.0; 22.4; 21.9; 21.8; 13.8.

HRMS (ESI): calculated for $C_{16}H_{26}NaO_2$ 273.1830, found 273.1842 $(M+Na)^+$

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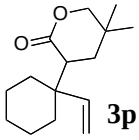

3p

Compound **3p** was prepared from **2e** in 65% yield according to general procedure **B** outlined above.

See spectra on page S43

^{1}H NMR: (400 MHz, $CDCl_3$)

5.83 (dd, *J*=17.8, 11.0 Hz, 1H); 5.26 (d, *J*=6.5, 1.3 Hz, 1H); 5.07 (d, *J*=17.8, 1.3 Hz, 1H); 3.86 (m, 2H); 2.60 (dd, *J*=10.8, 8.4 Hz, 1H); 2.00-1.31 (m, 12H); 1.06 (s, 3H); 0.99 (s, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

172.1; 142.1; 115.7; 70.1; 45.3; 42.4; 35.0; 35.4; 34.6; 32.4; 31.9; 30.6; 30.5; 28.5; 28.2; 26.8; 26.1; 24.0; 22.6; 22.1; 21.9; 14.0.

IR: 2927, 1727, 1141.6, 1073, 914 cm^{-1}

HRMS (ESI): calculated for $C_{15}H_{24}NaO_2$ 259.1674, found 259.1626 $(M+Na)^+$

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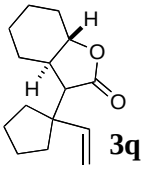

3q

Compound **3q** was prepared from **2h** in 71% yield according to general procedure **B** outlined above.

***See spectra on page S44*: product obtained as a mixture of diastereomers**

^{1}H NMR: (400 MHz, $CDCl_3$)

5.81 (dd, *J*=17.4, 10.7 Hz, 1H); 5.17 (d, *J*=10.7 Hz, 1H); 5.09 (d, *J*=17.5 Hz, 1H); 3.67 (td, *J*=14.7, 3.5 Hz, 1H); 2.28 (d, *J*=12.3 Hz, 1H); 2.19 (m, 1H); 1.91 (m, 2H); 1.78 (m, 2H); 1.65 (m, 4H); 1.57-1.40 (m, 3H); 1.37-1.24 (m, 4H).

^{13}C NMR: (100 MHz, $CDCl_3$)

176.4; 141.3; 114.7; 82.2; 56.3; 49.7; 47.1; 39.0; 37.0; 35.2; 30.1; 29.2; 25.3; 23.3; 22.9.

HRMS (ESI): calculated for $C_{15}H_{242}NaO_2$ 257.1517, found 257.1491 $(M+Na)^+$

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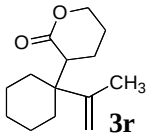

3r

Compound **3r** was prepared from **2j** in 68% yield according to general procedure **B** outlined above.

See spectra on page S45

^{1}H NMR: (400 MHz, $CDCl_3$)

5.15 (s, 1H); 4.86 (s, 1H); 4.29 (m, 1H); 4.16 (m, 1H); 2.56 (t, *J*=9.6 Hz, 1H); 1.97-1.73 (m, 6H); 1.68 (s, 3H); 1.58-1.46 (m, 5H); 1.27 (m, 3H).

^{13}C NMR: (100 MHz, $CDCl_3$)

172.3; 145.0; 115.8; 68.9; 46.6; 33.2; 31.3; 30.7; 26.0; 23.1; 22.4; 21.1; 22.0; 20.1.

HRMS (ESI): calculated for $C_{14}H_{22}NaO_2$ 245.1517, found 245.1573 $(M+Na)^+$

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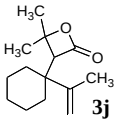
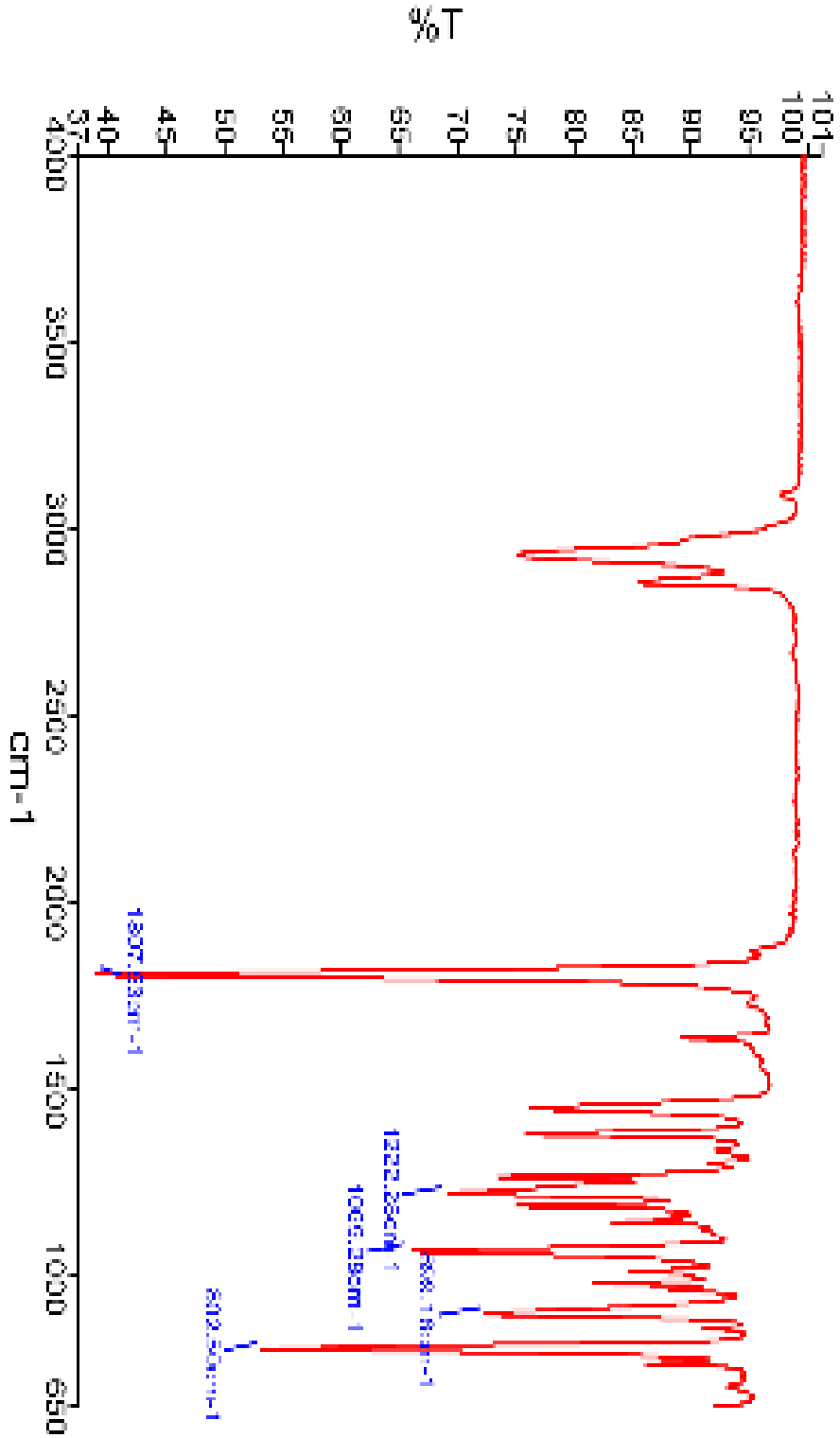


3j



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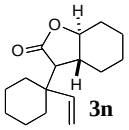
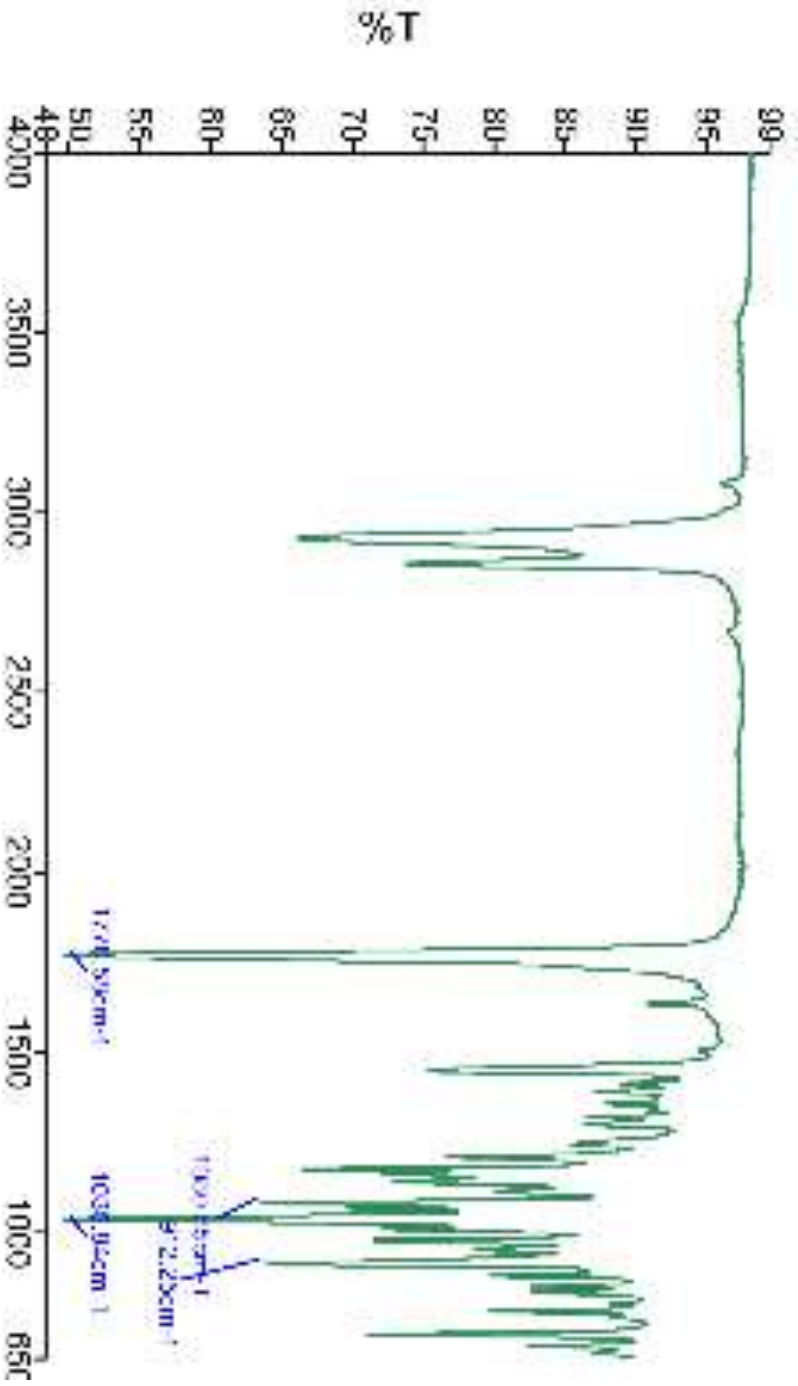


3n



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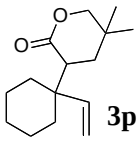
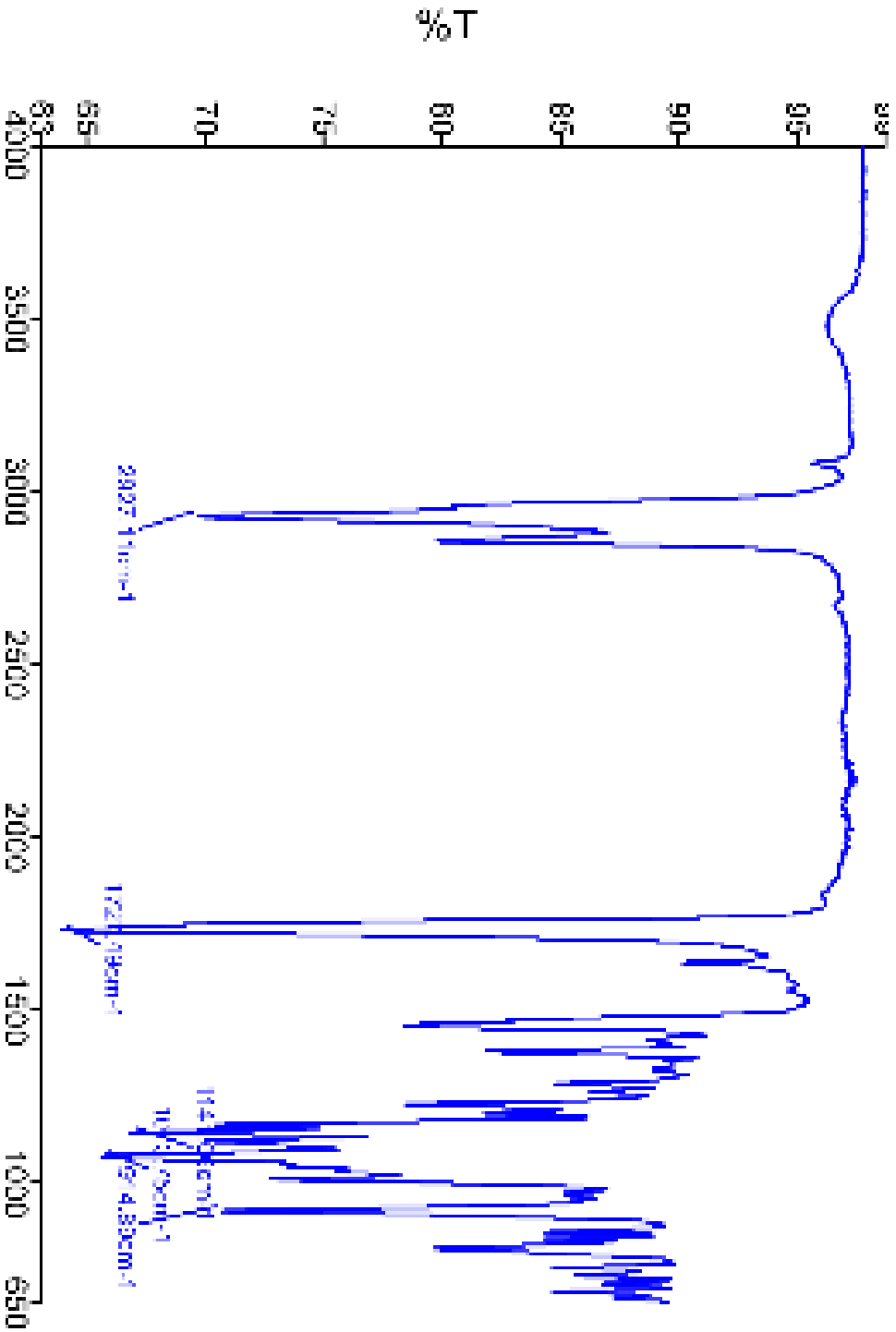


3p



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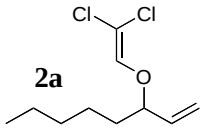
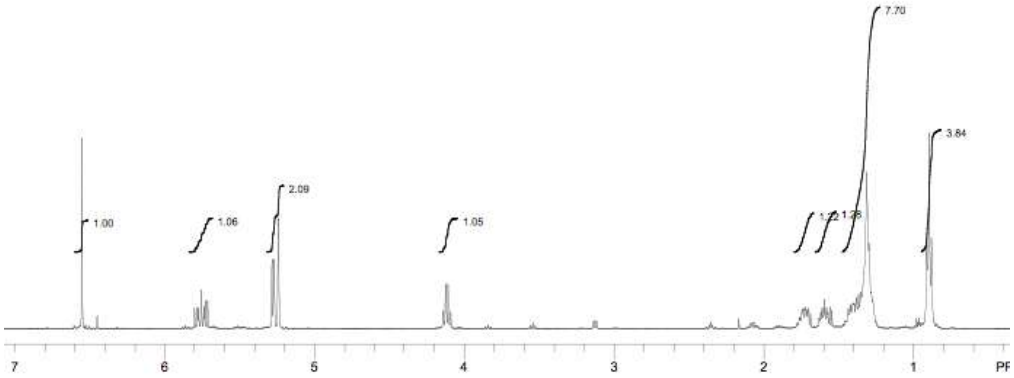
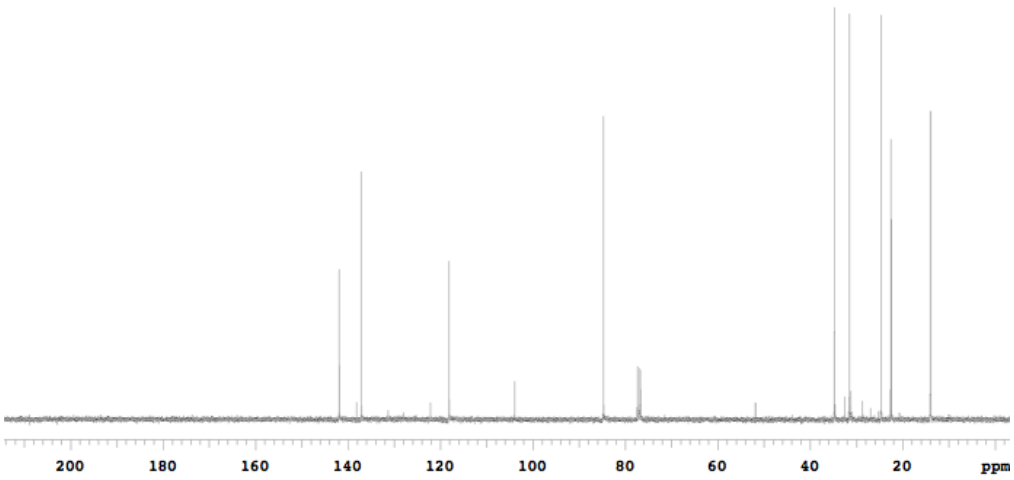


2a ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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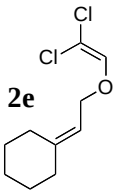
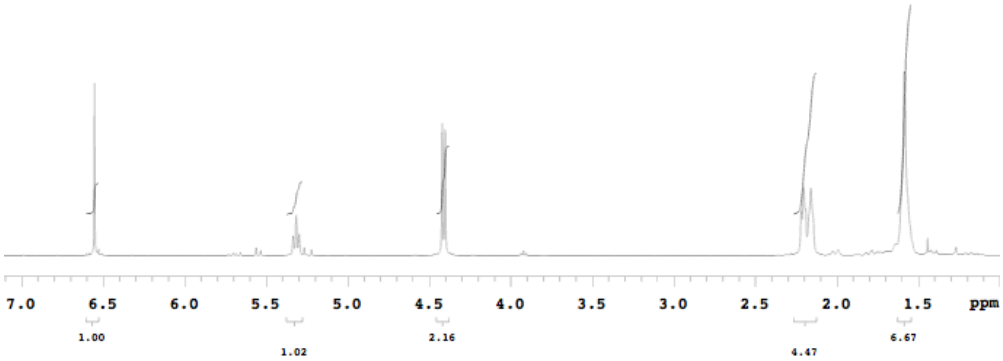
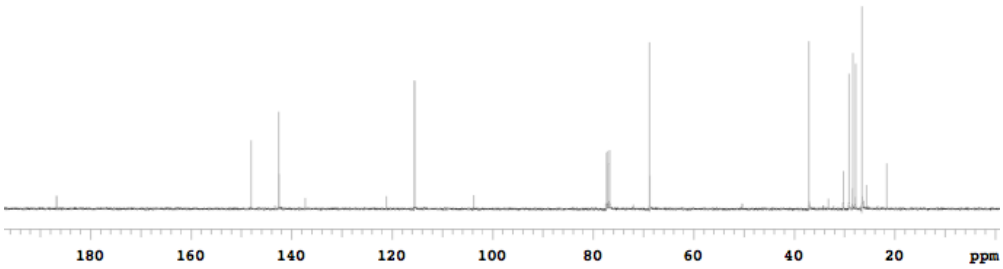


2e

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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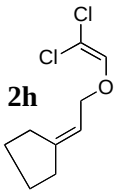
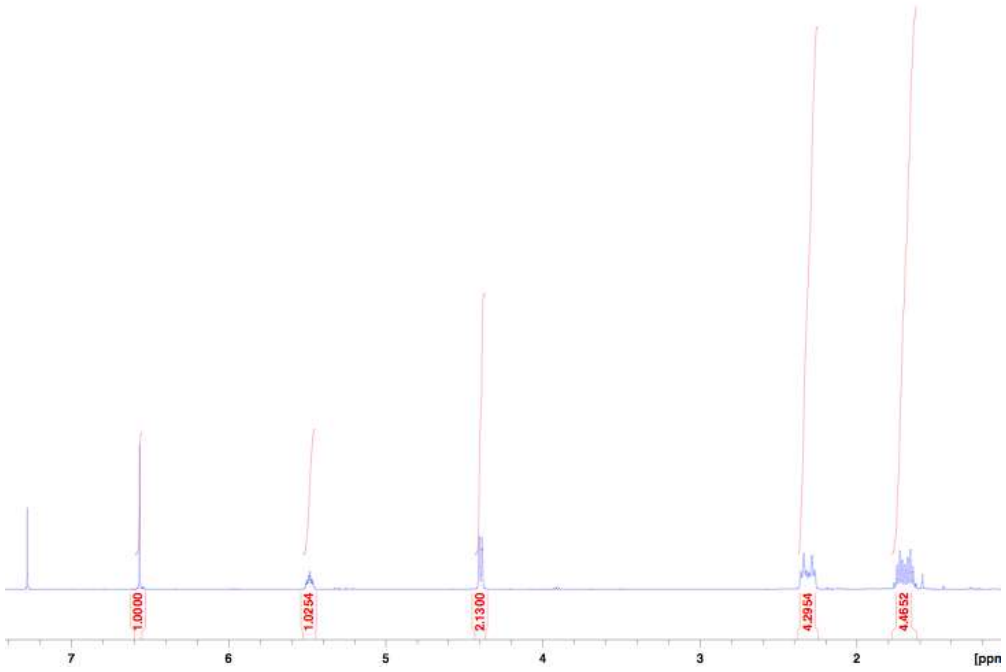
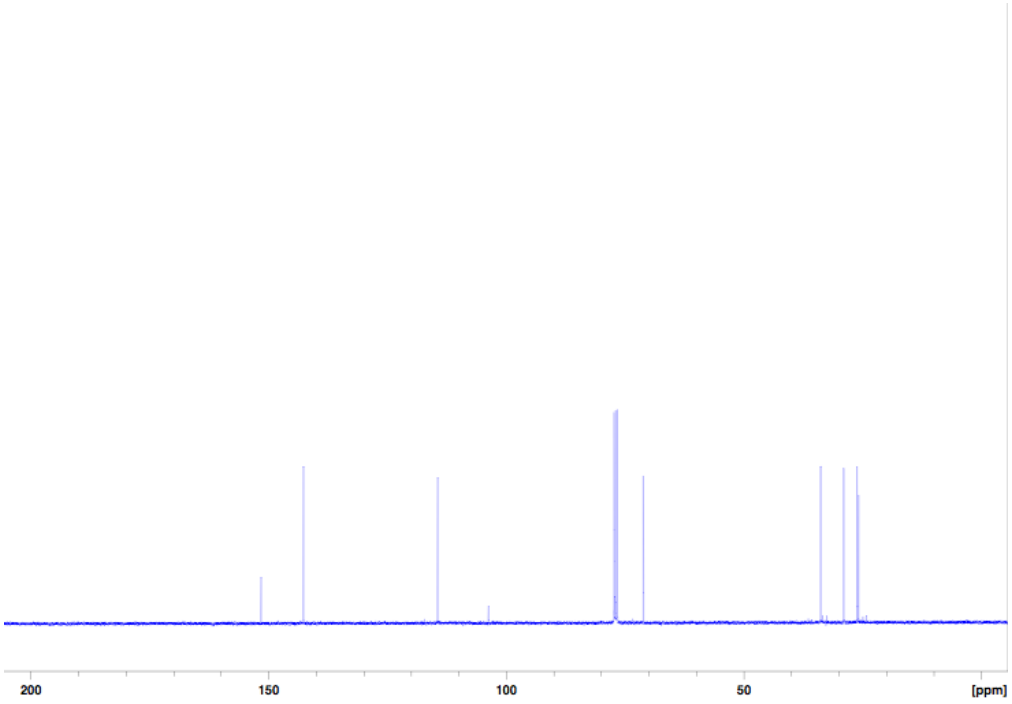


2h

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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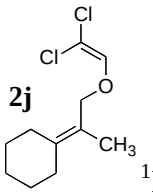
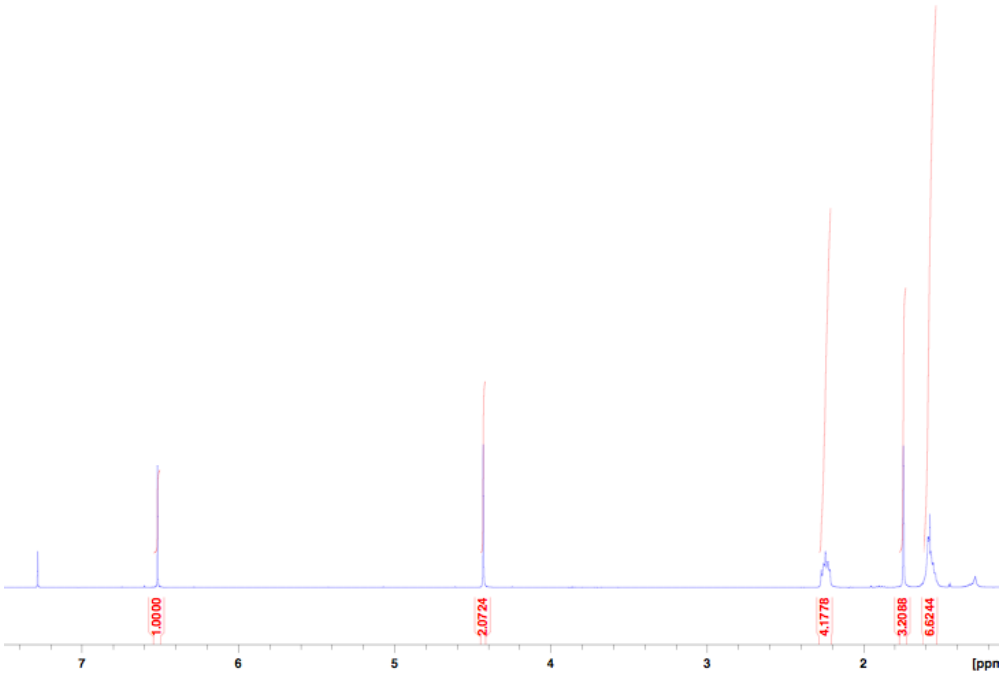
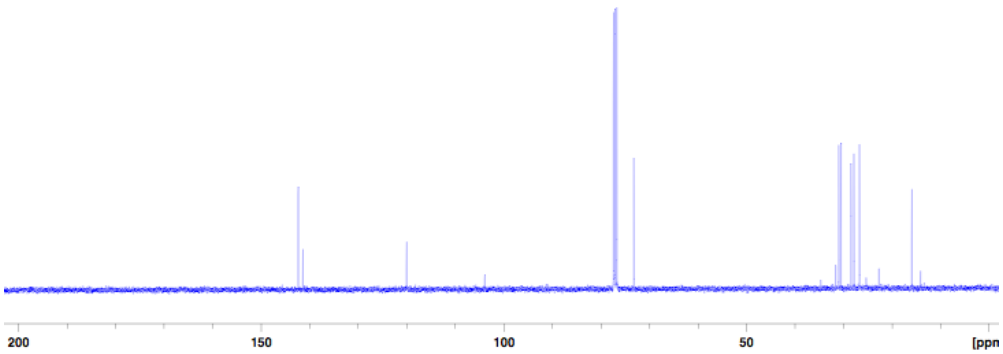


^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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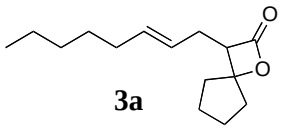
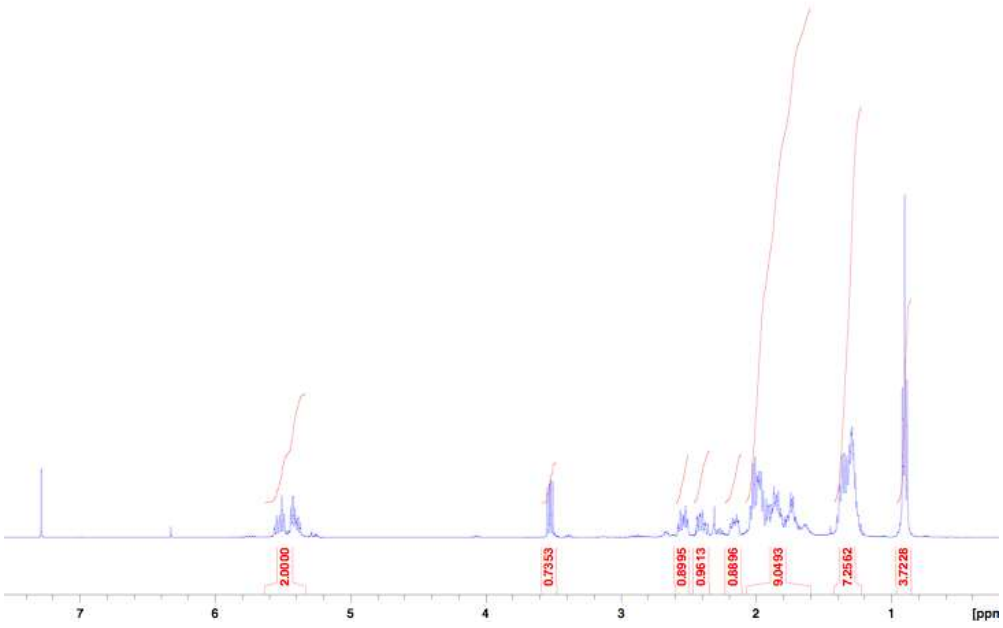
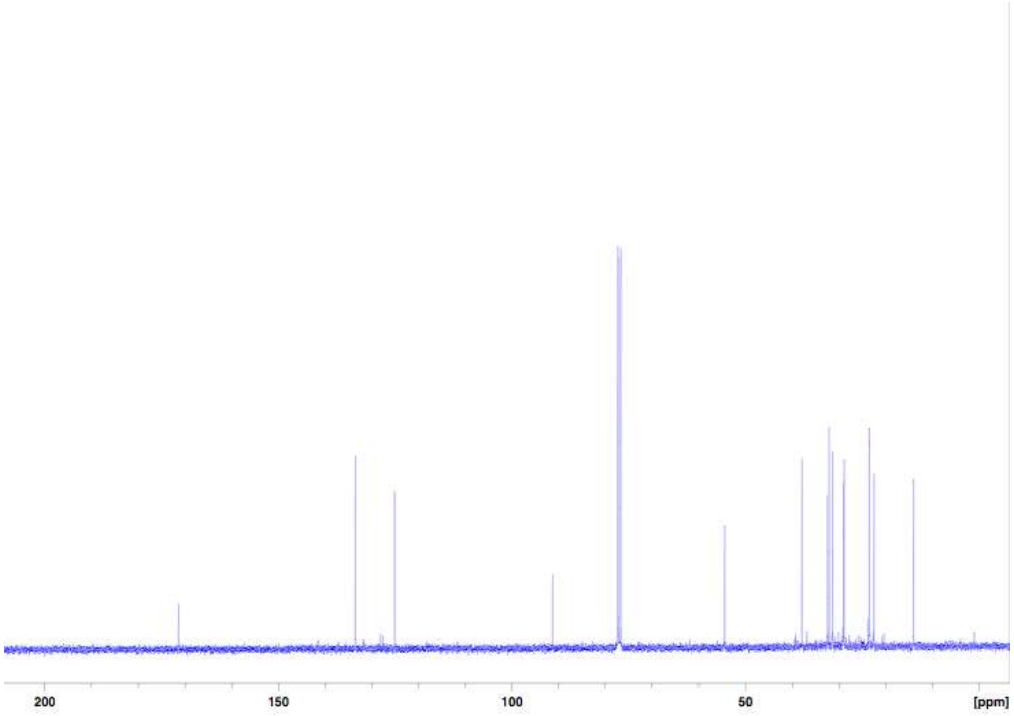
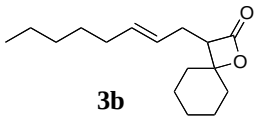


3a

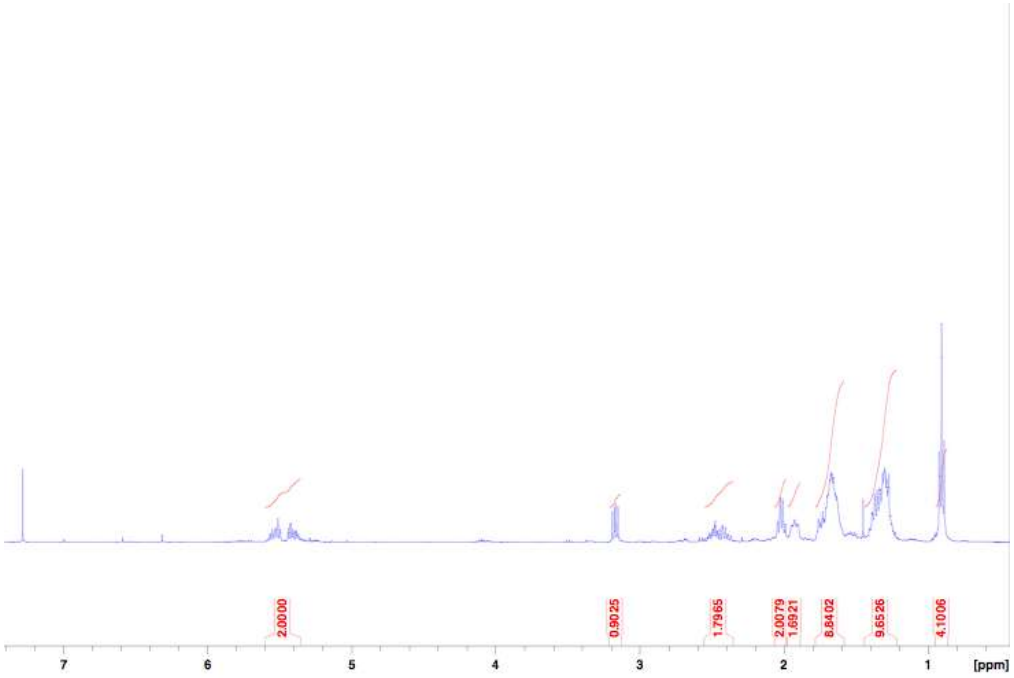
^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra

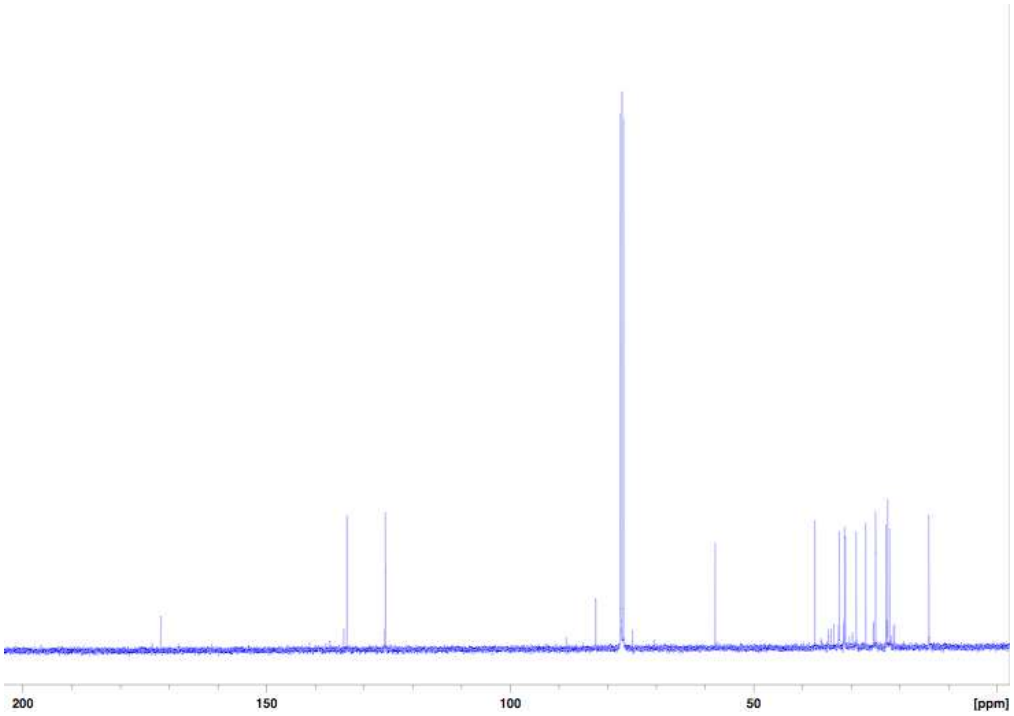


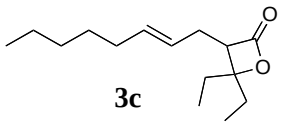




3b ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra

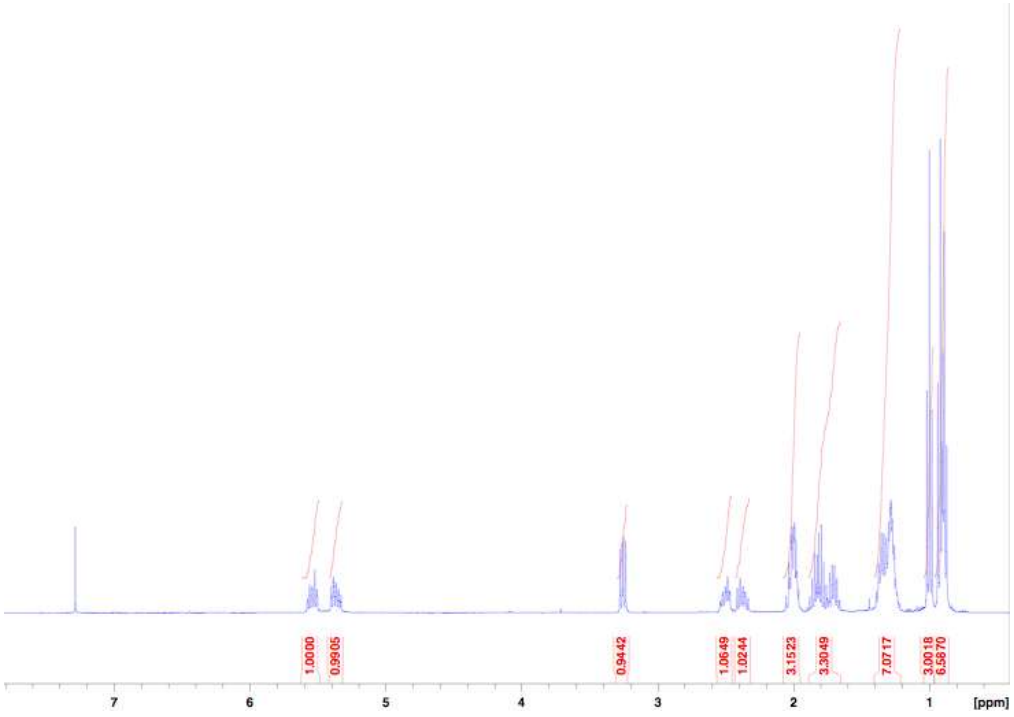


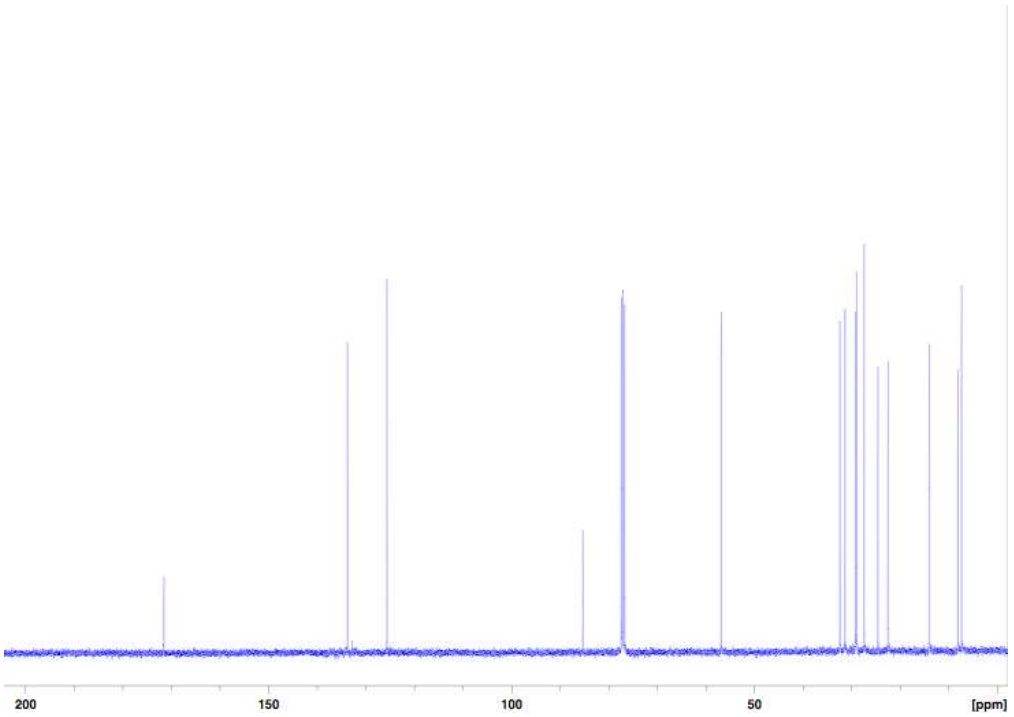




3c

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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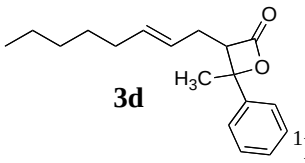
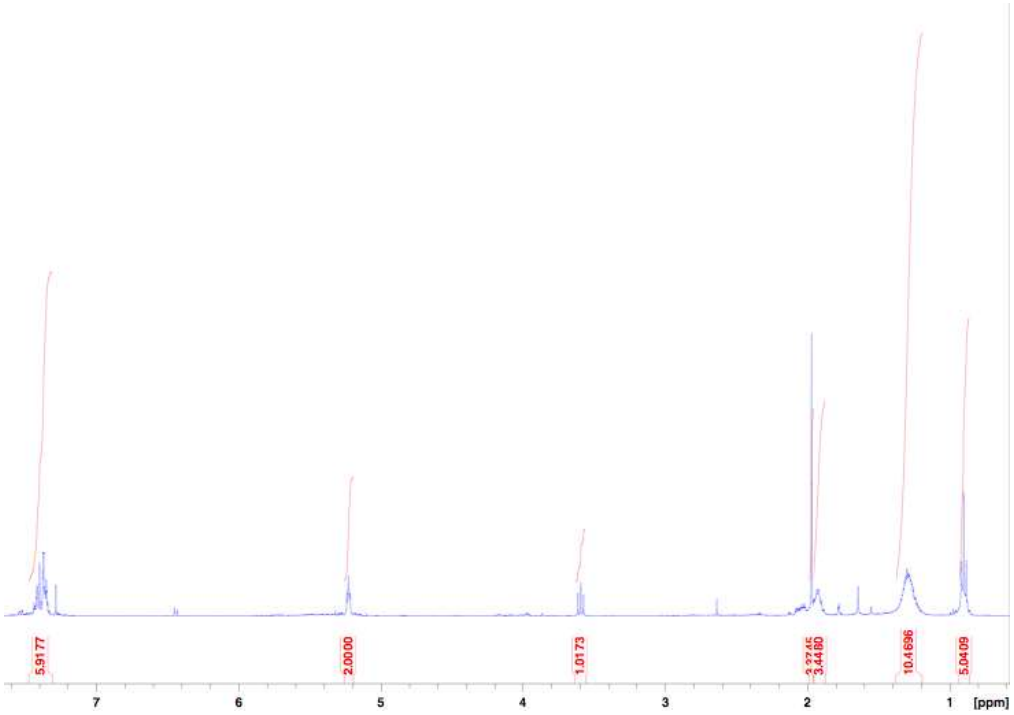
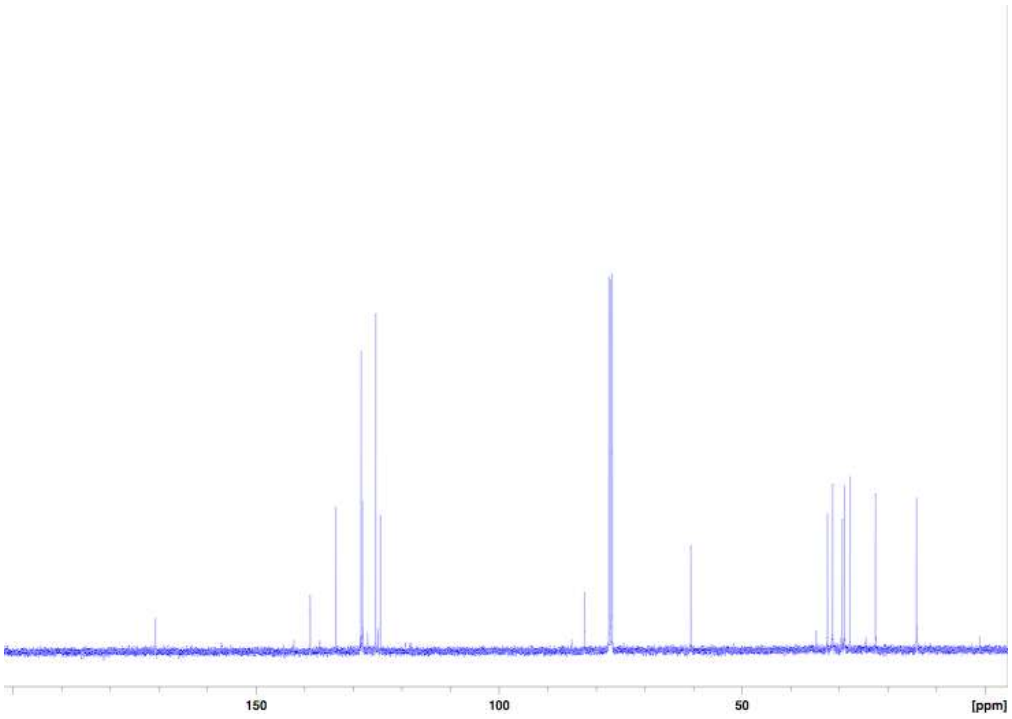


3d

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra; product obtained as a mixture of diastereomers





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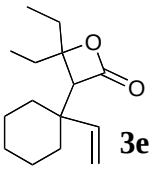
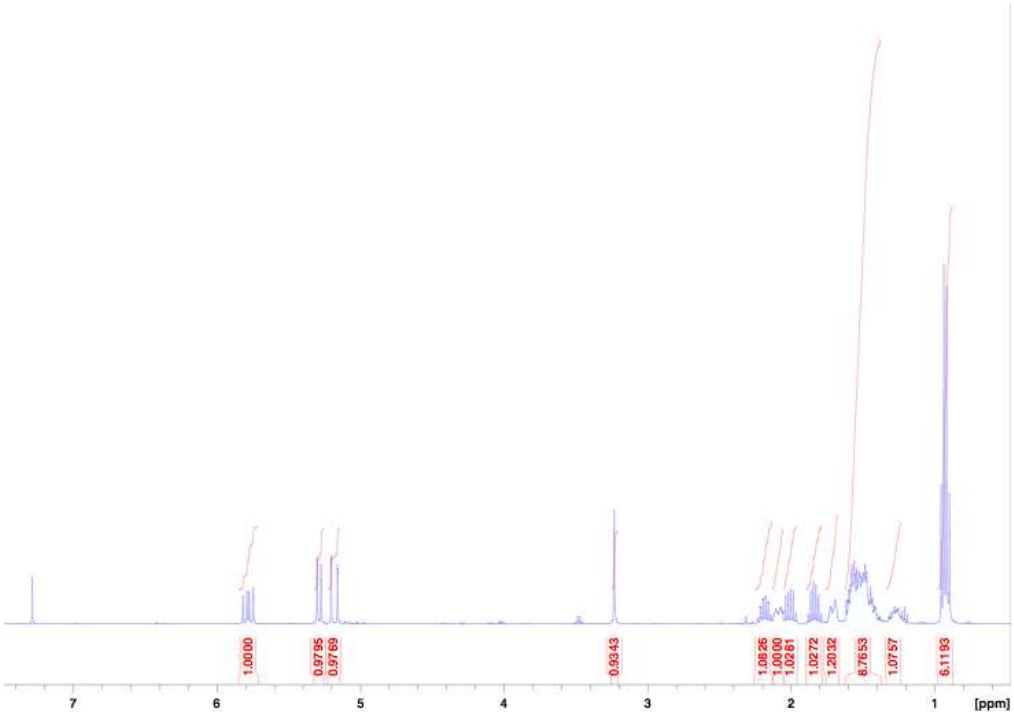
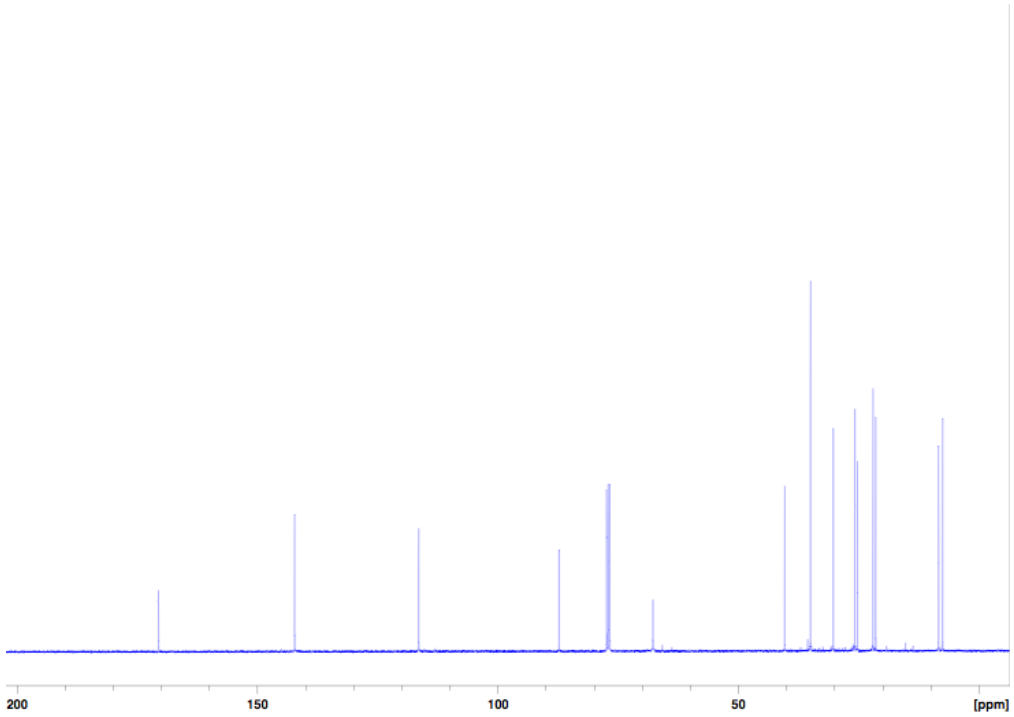


3e ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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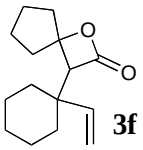
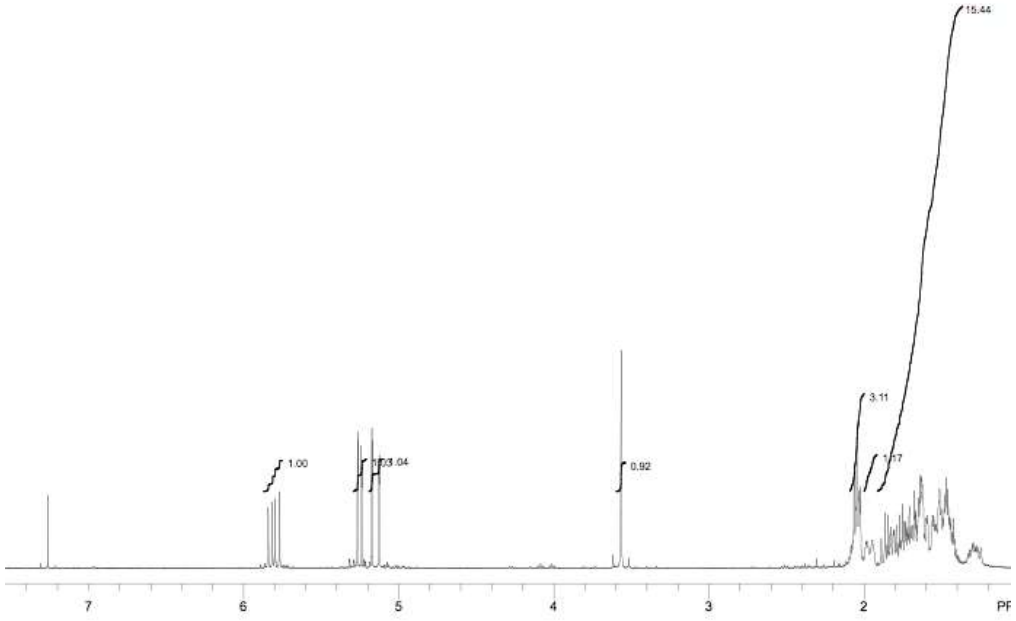
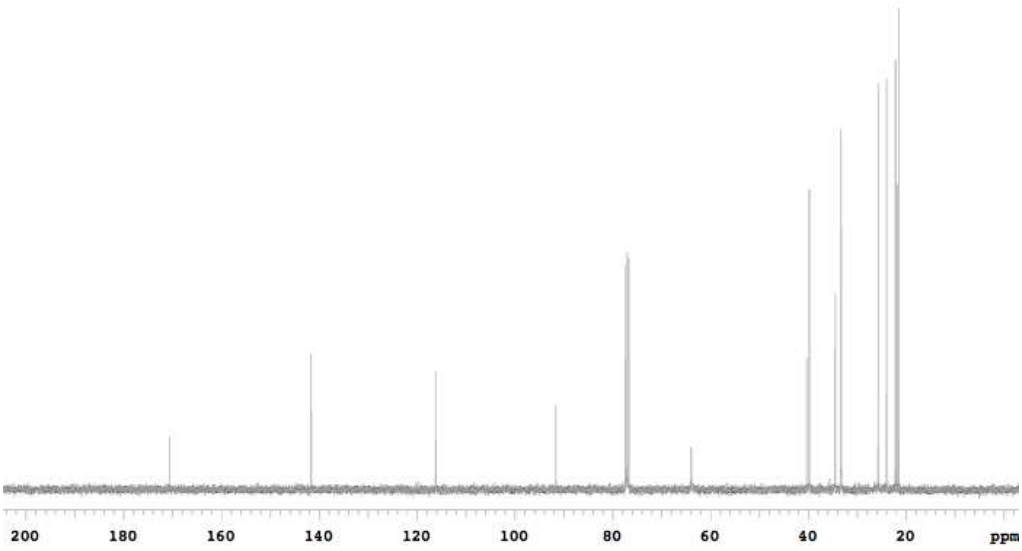


3f ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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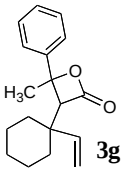
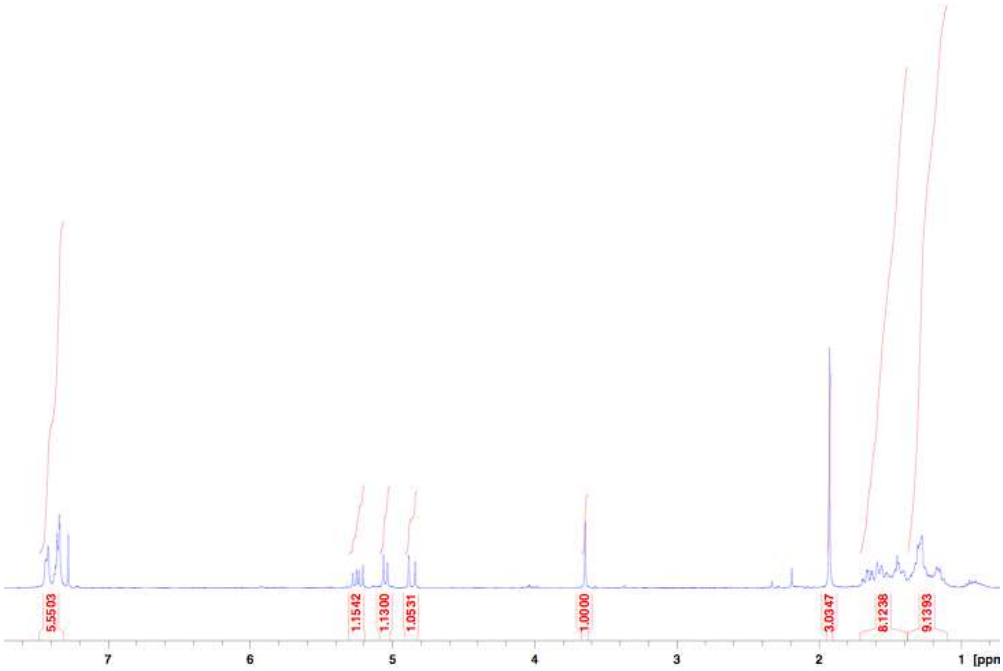
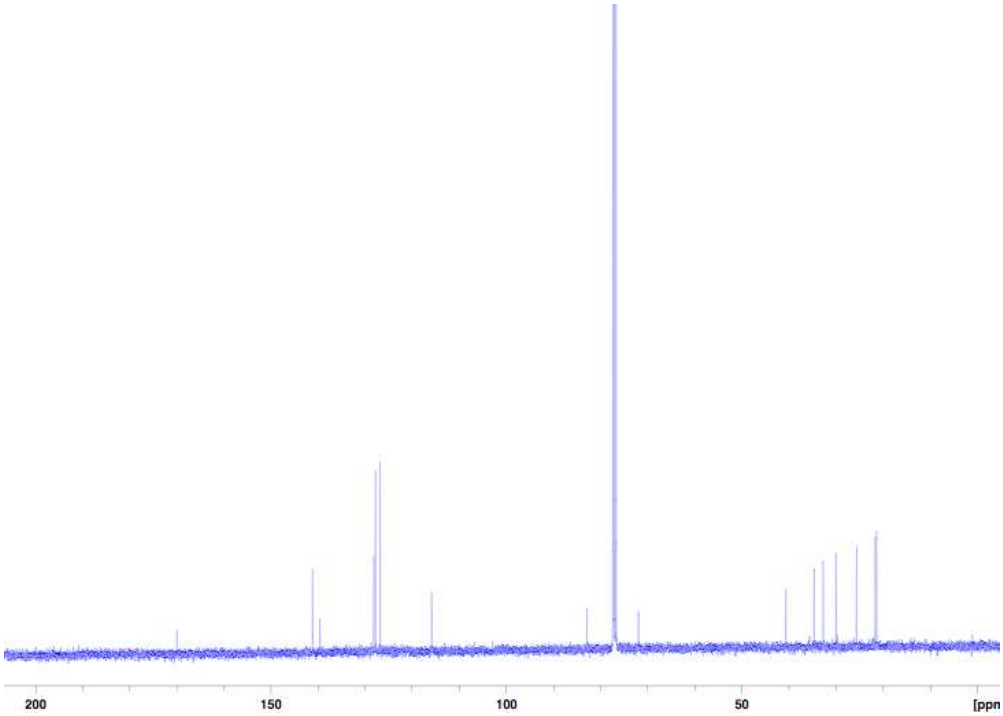


3g ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra; product obtained as a mixture of diastereomers





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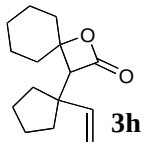
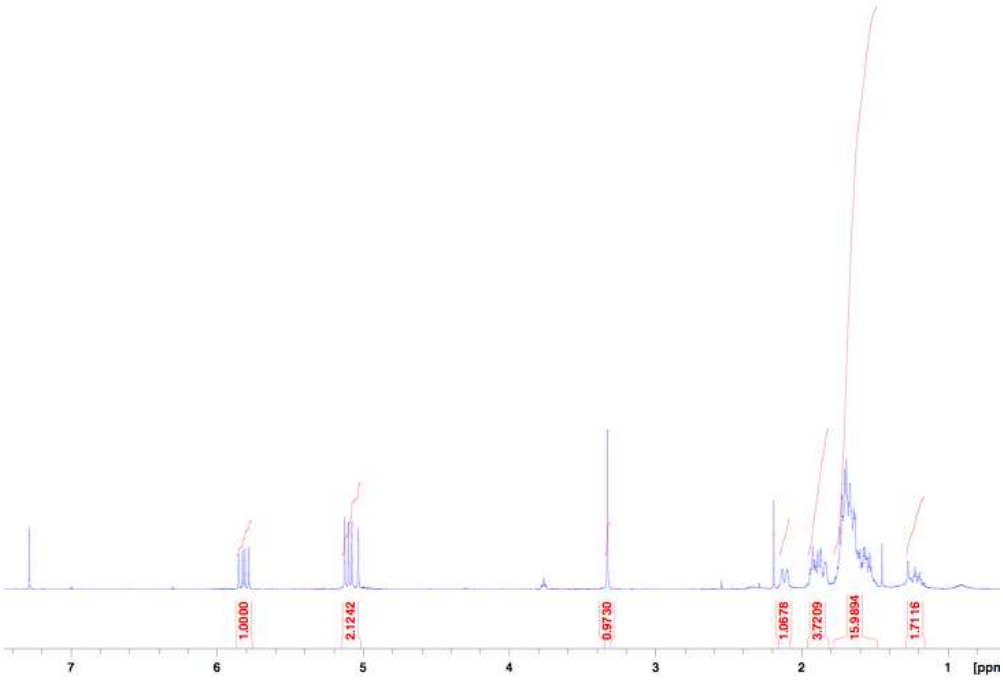
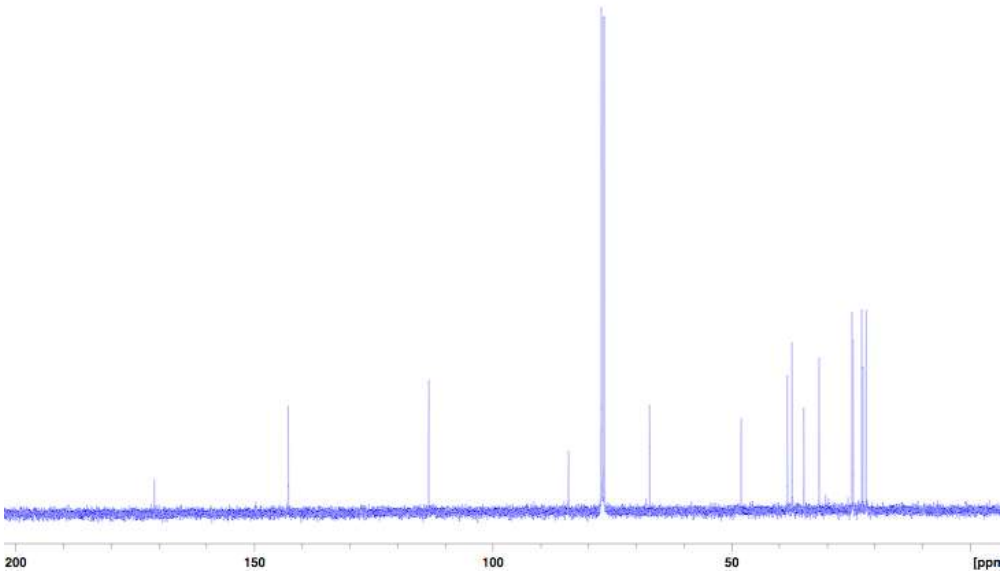


3h ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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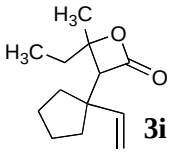
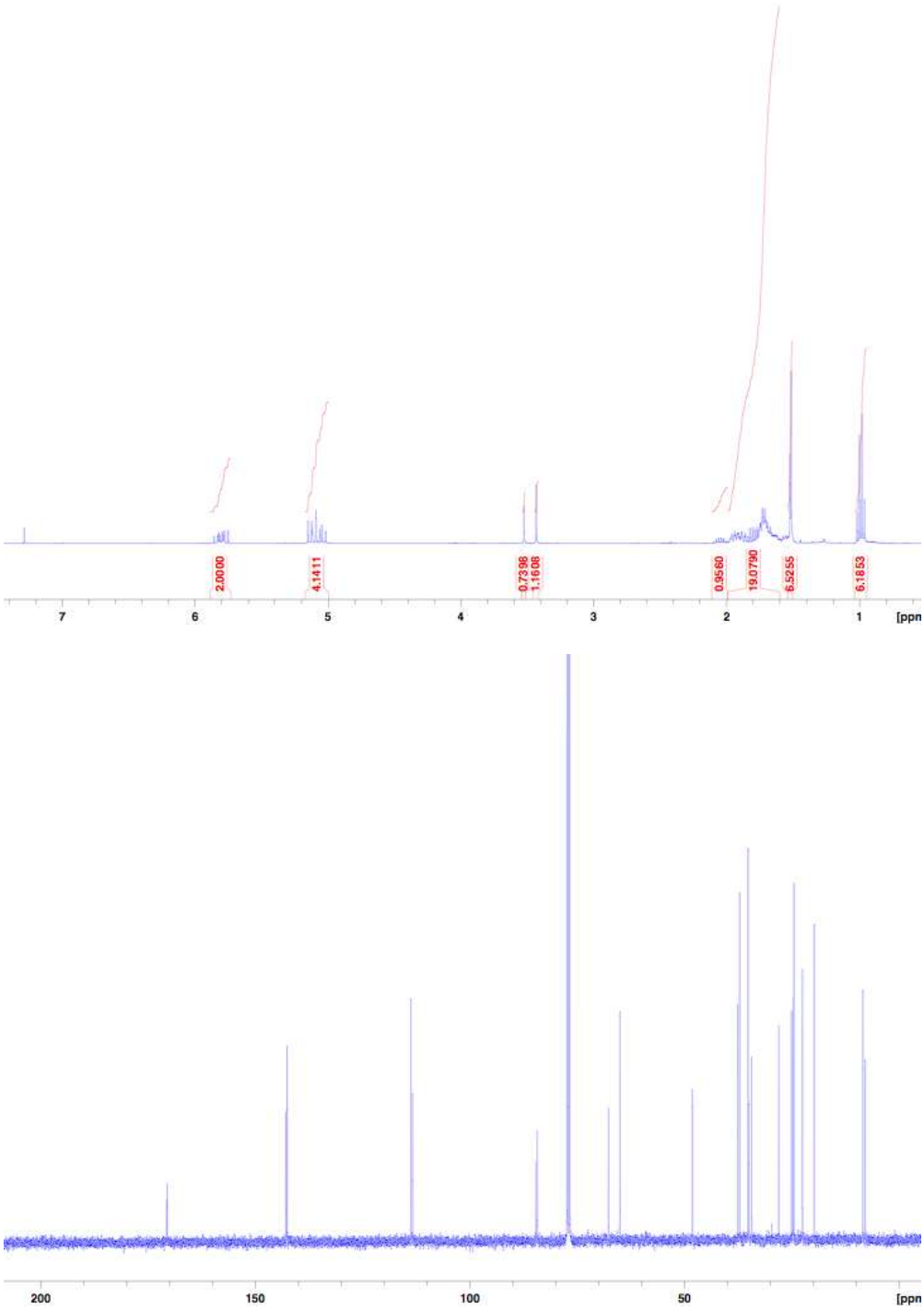


3i ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra product obtained as a mixture of diastereomers



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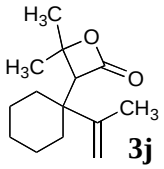
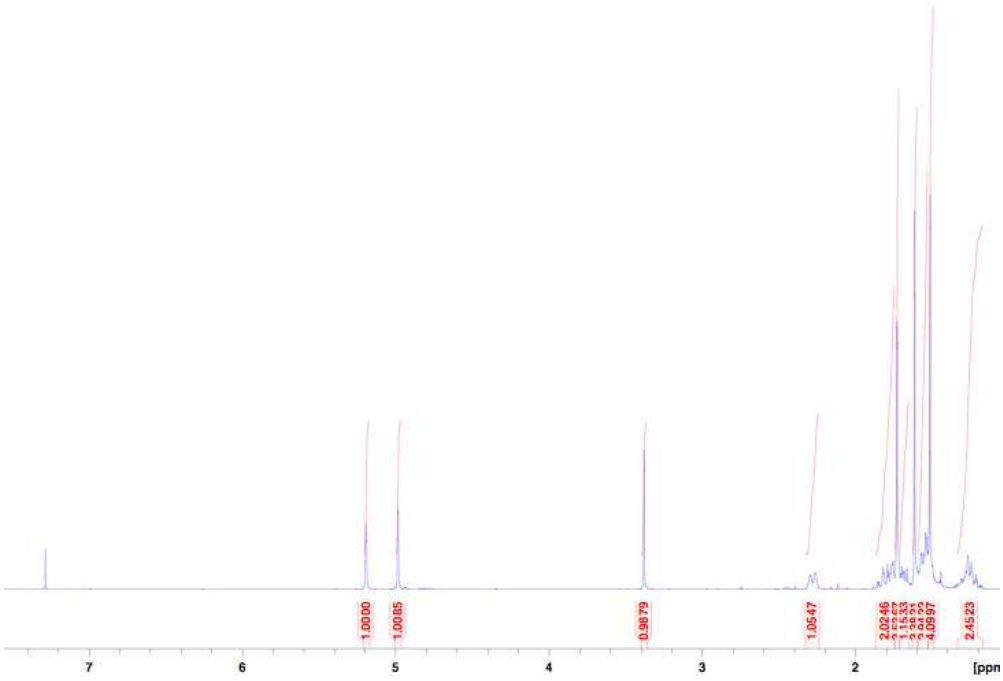
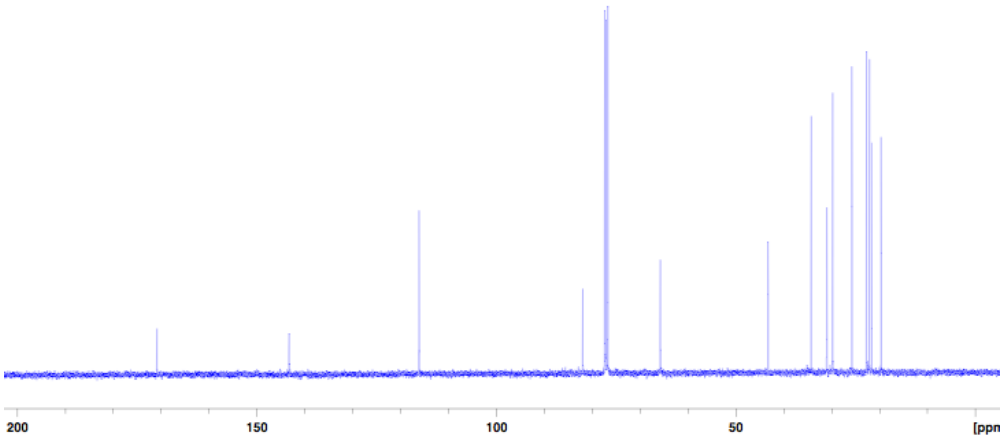


3j ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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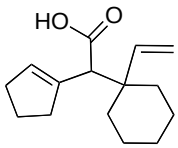
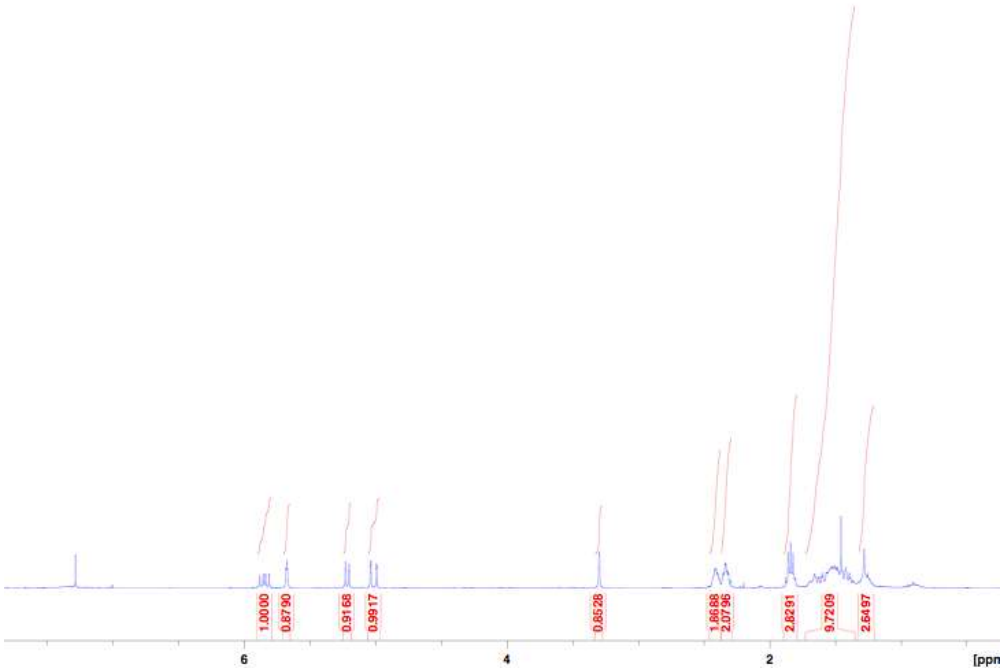
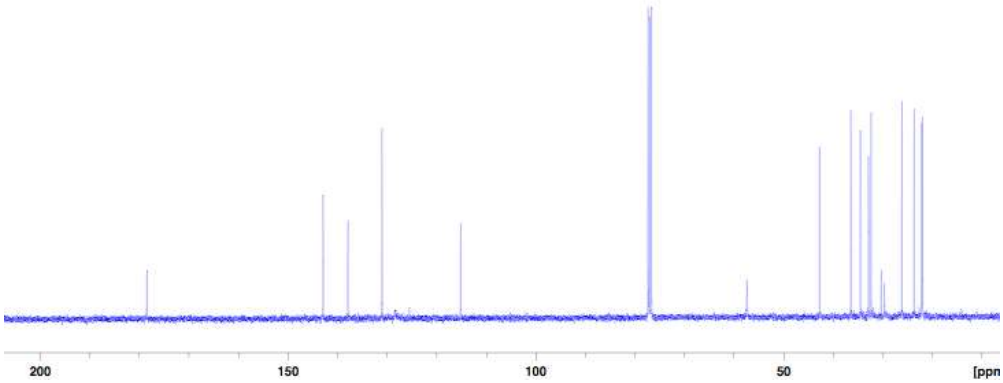


4f

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra





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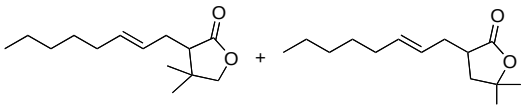
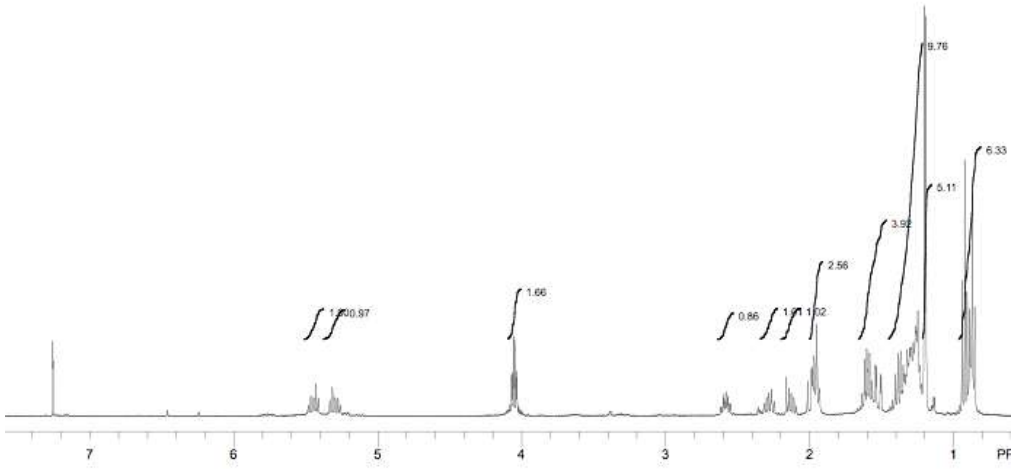
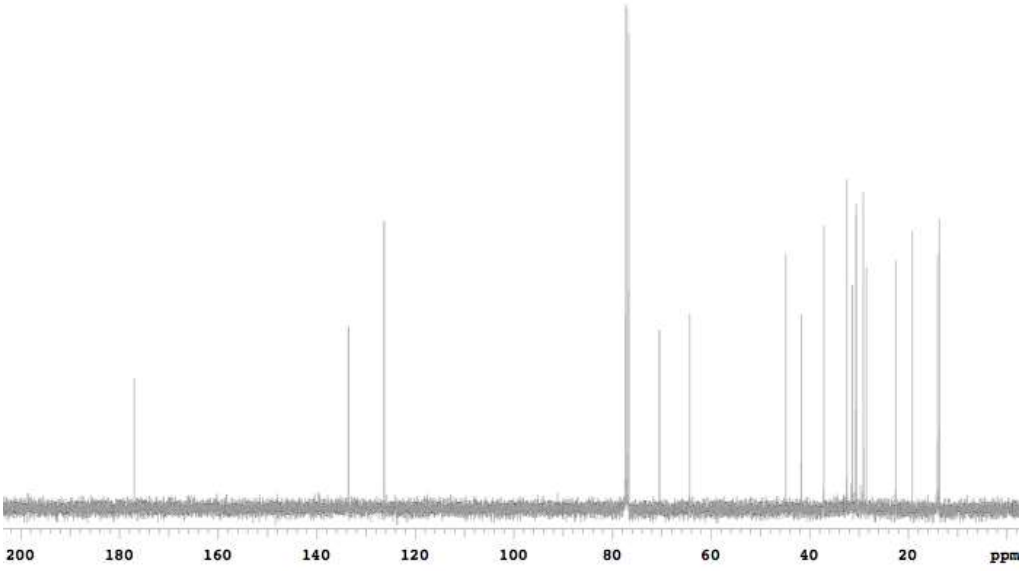


3l

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra product obtained as a mixture of regioisomers





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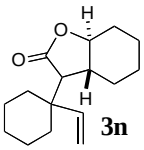
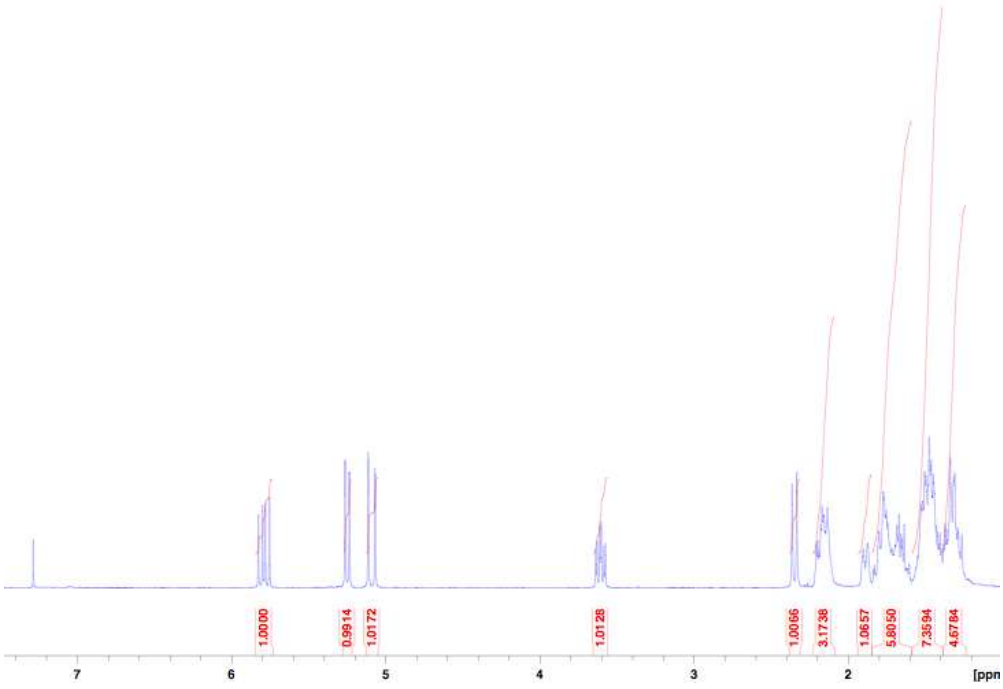
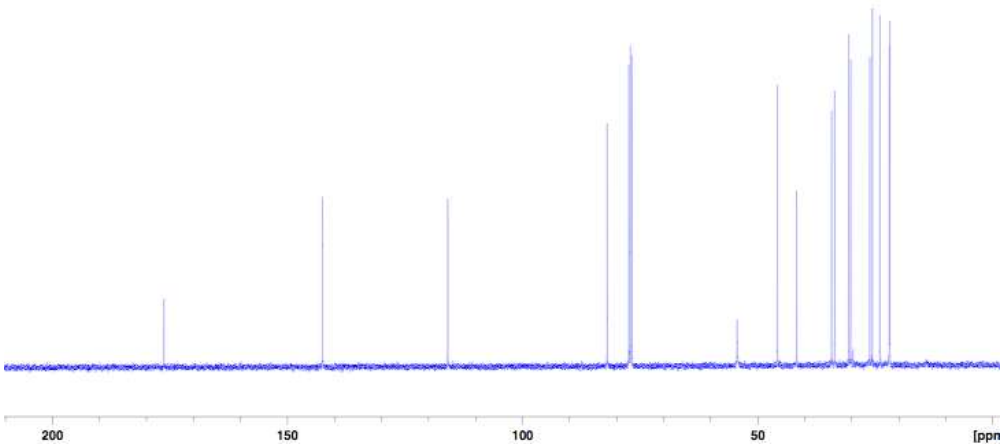


3n ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra product obtained as a mixture of diastereomers





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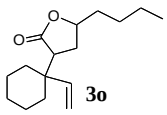
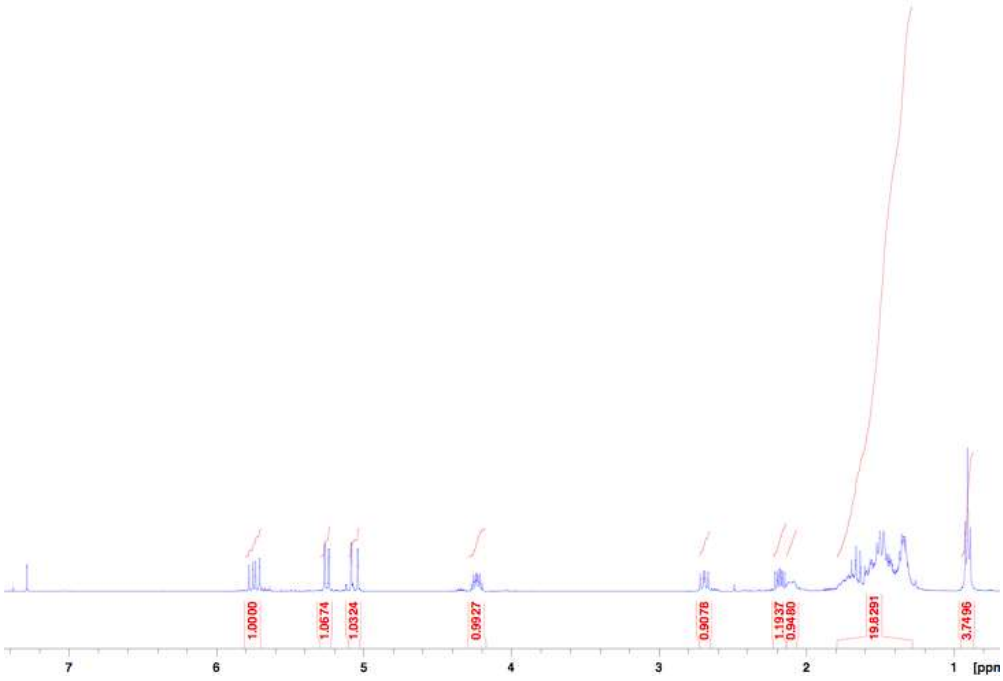
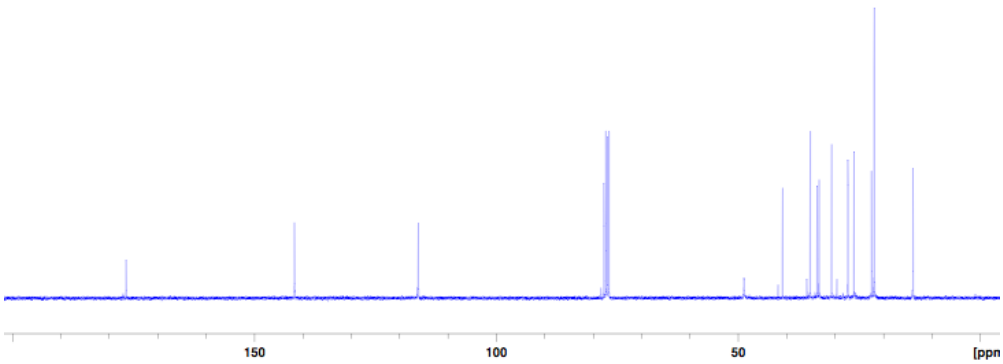


3o ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra product obtained as a mixture of diastereomers





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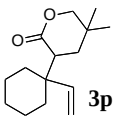
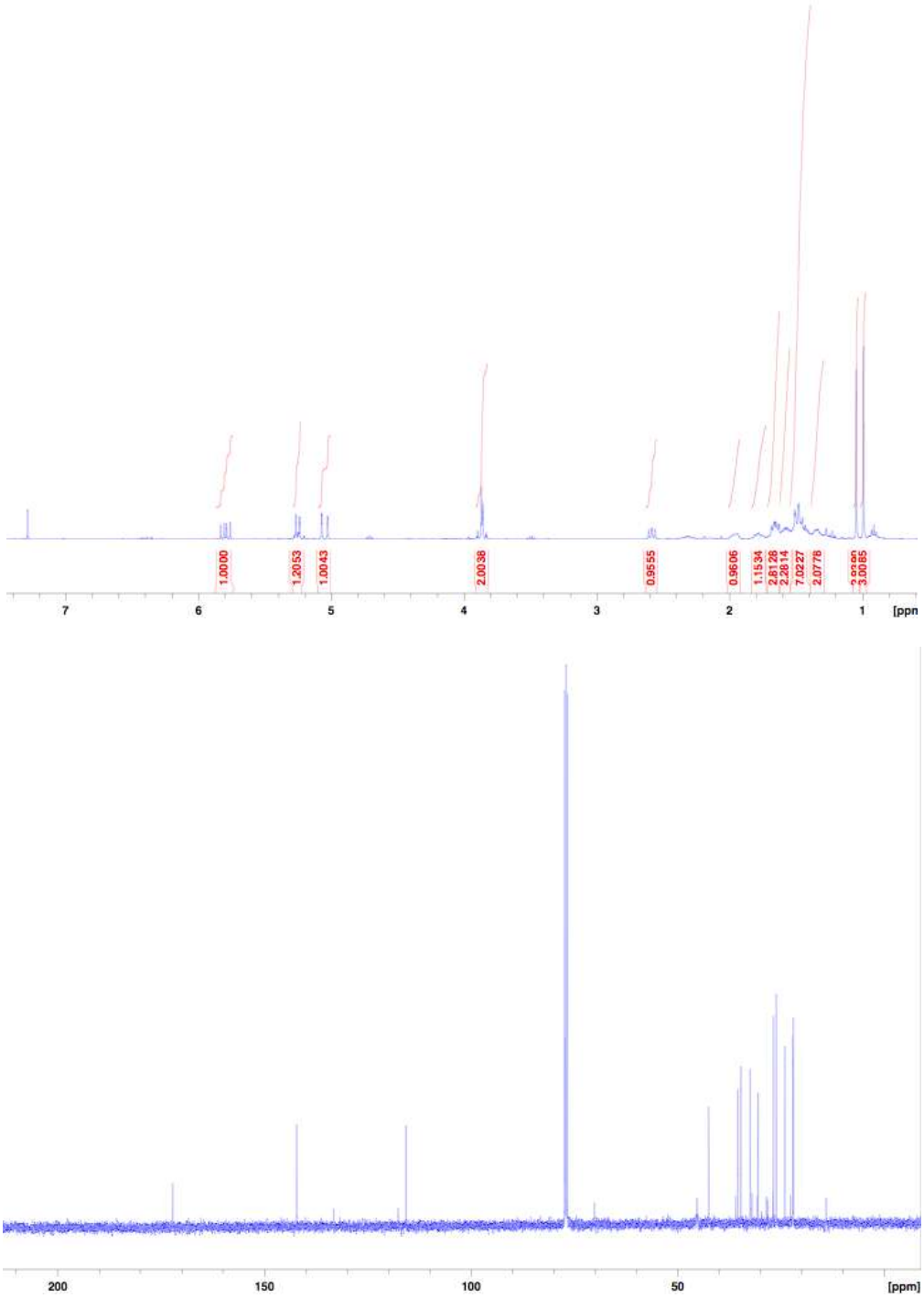


3p ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra



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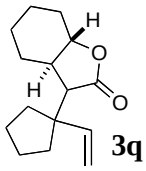
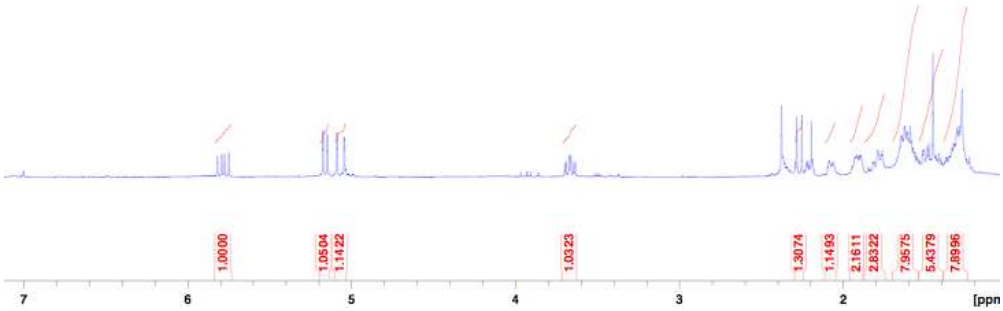
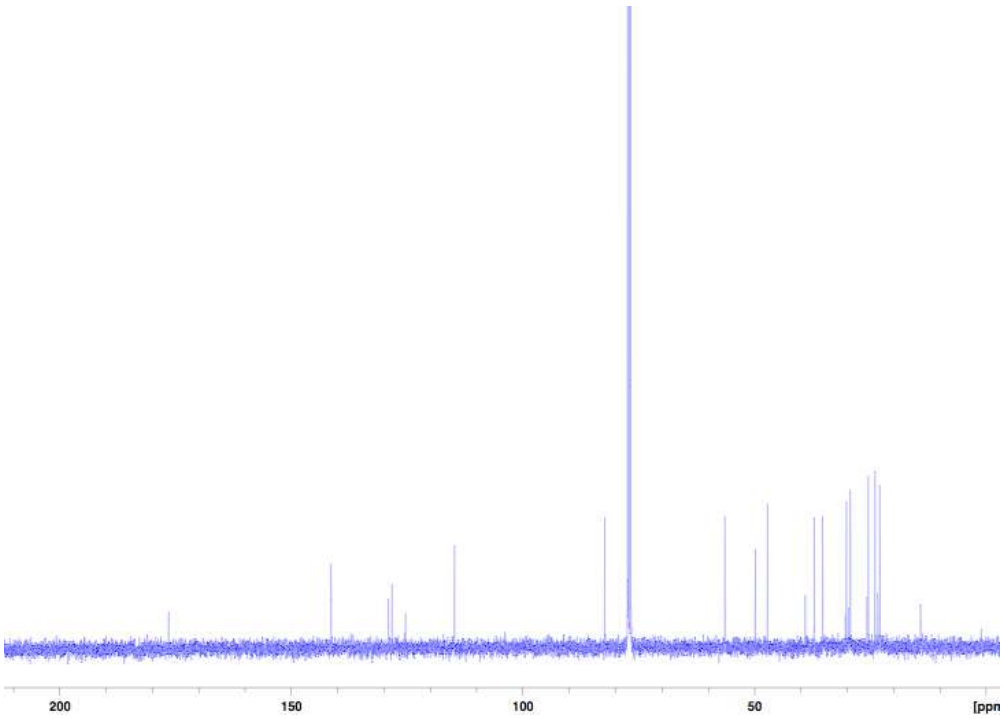


3q ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra product obtained as a mixture of diastereomers





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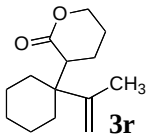

3r ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra