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SUPPLEMENTARY INFORMATION FOR

Rhodium-catalyzed Regio- and Stereoselective Oxyamination of Dienes via Tandem Aziridination-Ring-opening of Dienyl Carbamates

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General methods. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of argon. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. The solvents were freshly dried and purified under argon before use by standard procedures.[1]

^{1}H and ^{13}C NMR spectra were recorded on a Varian® Mercury VX 400 (400 MHz and 100.6 MHz respectively), a Varian 400-MR or a Bruker® Advance III (600 MHz and 150.9 MHz respectively) spectrometer in $CDCl_3$ as solvent, with chemical shifts (δ) referenced to internal standards $CDCl_3$ (7.26 ppm ^{1}H, 77.23 ppm ^{13}C) or Me_4Si as an internal reference (0.00 ppm). ESI MS were run on an Agilent® 1100 Series LC/MSD instrument. IR spectra were recorded on a JASCO FT/IR-600 plus Fourier Transform Infrared Spectrometer ATR Specac Golden Gate. Melting points were determined by calorimetric analyses on a Mettler DSC-822e thermal analyzer from 30ºC to 300ºC at a heating rate of 10ºC/min.

Reactions were monitored by TLC carried out on 0.25 mm E. Merck® silica gel 60 F_{254} glass or aluminum plates. Developed TLC plates were visualized under a short-wave UV lamp (250 nm) and by heating plates that were dipped in ethanol/H_2SO_4 (15:1) and basic solution of potassium permanganate. Flash column chromatography was carried out using forced flow of the indicated solvent on Fluka® or Merck® silica gel 60 (230-400 mesh). Radial chromatography was performed on 1 or 2 mm plates of Kieselgel 60 PF_{254} silica gel, depending on the amount of product.

General procedure for the conversion of allylic dienols to carbamates. A solution of trichloroacetyl isocyanate (TAI) (1 mL, 8.4 mmol) in dry benzene (8 mL) was added to a solution of dienol (8.0 mmol) in dry dichloromethane (16 mL). The mixture was left at room temperature until TLC showed complete consumption of the starting dienol. Then a solution of K_2CO_3 in methanol was added and the mixture was stirred at room temperature during 3 hours. After solvent evaporation, the residue was dissolved in a 1:1 mixture of dichloromethane and brine. The aqueous phase was extracted with dichloromethane and the combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure.

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1 Perrin D.D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd. ed., Pergamon Press, Oxford, **1989**.

The dienols used in this study are depicted in figure S1.

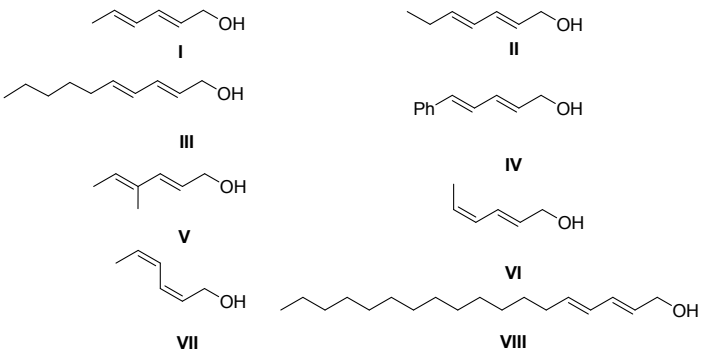
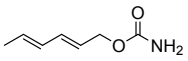


Figure S1

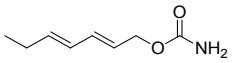
(2*E*,4*E*)-Hexa-2,4-dien-1-yl carbamate (1).



The title compound was synthesized following the general carbamoylation procedure starting from **I** (0.78 g, 8.0 mmol) and TAI (1 mL, 8.4 mmol). The crude was purified by flash chromatography (2:8 AcOEt/hexanes) to afford (0.92 g, 81 %) of pure carbamate **1** as a white powder.

Mp: 86 ºC. **FT-IR (ATR)** ν in cm^{-1}: 3441, 3300, 3212, 2923, 2852, 1663, 1615, 1437, 1354, 1114, 991. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 6.24 (dd, 1H, *J* = 15.1, 10.6 Hz), 6.04 (ddd, 1H, *J* = 15.1, 10.6, 1.4 Hz), 5.74 (dq, 1H, *J* = 15.1, 6.8 Hz), 5.62 (dt, 1H, *J* = 15.1, 6.6 Hz), 4.91 (brs, 2H), 4.64 (d, 2H, *J* = 6.6 Hz), 1.75 (d, 3H, *J* = 6.8 Hz).**^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 157.1, 134.8, 131.4, 130.6, 124.2, 65.7, 18.3. **ESI-TOF** [M+1] calc for $C_7H_{10}O_2$: 142.0790, found: 142.0105.

(2*E*,4*E*)-Hepta-2,4-dien-1-yl carbamate (8).

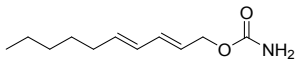


The title compound was synthesized following the general carbamoylation procedure starting from **II** (1 g, 8.9 mmol) and TAI (1.17 mL, 9.8 mmol). The crude was purified by flash chromatography (1:9 AcOEt/hexanes to 2:8 AcOEt/hexanes) to afford (1.04 g, 76 %) of carbamate **8** as a white powder.

Mp: 70 ºC. **FT-IR (ATR)** ν in cm^{-1}: 3437, 3334, 3273, 3215, 3021, 2966, 2935, 2875, 1687, 1606, 1461, 1415, 1342, 1321, 1047, 984. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 6.25 (dd, 1H, *J* = 14.0, 10.4 Hz), 6.02 (dd, 1H, *J* = 15.2, 10.4 Hz), 5.77 (dt, 1H, *J*

= 14.0, 6.0 Hz), 5.63 (dt, 1H, *J* = 15.2, 7.2 Hz), 4.92 (brs, 2H), 4.55 (d, 2H, *J* = 6.0 Hz), 2.09 (qt, 2H, *J* = 7.6 Hz), 0.99 (t, 3H, *J* = 7.6 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 157.1, 138.4, 134.9, 128.3, 124.4, 65.7, 25.8, 13.5. **ESI-TOF** [M+23] calc for $C_8H_{13}NO_2Na$: 178.0946, found: 178.0875.

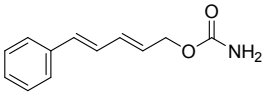
(2*E*,4*E*)-Deca-2,4-dien-1-yl carbamate (9).



The title compound was synthesized following the general carbamoylation procedure starting from **III** (1 g, 6.4 mmol) and TAI (0.85 mL, 7.1 mmol). The crude was purified by flash chromatography (1:9 AcOEt/hexanes to 2:8 AcOEt/hexanes) to afford (0.92 g, 72 %) of carbamate **9** as a white powder.

Mp: 61 ºC. **FT-IR (ATR)** ν in cm^{-1}: 3432, 3322, 3258, 3198, 3020, 2952, 2923, 2870, 2852, 1687, 1606, 1465, 1416, 1338, 1319, 1053, 986. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 6.24 (dd, 1H, *J* = 15.2, 10.4 Hz), 6.02 (dd, 1H, *J* = 15.2, 10.4 Hz), 5.73 (dt, 1H, *J* = 15.2, 6.8 Hz), 5.63 (dt, 1H, *J* = 15.2, 6.4 Hz), 4.81 (brs, 2H), 4.56 (d, 2H, *J* = 6.8 Hz), 2.06 (q, 2H, *J* = 6.8 Hz), 1.44-1.20 (m, 6H), 0.87 (t, 3H, *J* = 6.8 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 156.8, 136.9, 134.8, 129.0, 124.1, 65.6, 32.6, 32.3, 28.8, 22.5, 14.0. **ESI-TOF** [M+23] calc for $C_{11}H_{19}NO_2Na$: 220.1416, found: 220.1317.

(2*E*,4*E*)-5-Phenylpenta-2,4-dien-1-yl carbamate (10).

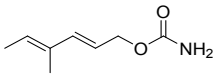


The title compound was synthesized following the general carbamoylation procedure starting from **IV** (0.20 g, 1.3 mmol) and TAI (0.17 mL, 1.4 mmol). The crude was purified by flash chromatography (2:8 AcOEt/hexanes) to afford (0.21 g, 80 %) of pure carbamate **10** as a white powder.

Mp: 137 ºC. **FT-IR (ATR)** ν in cm^{-1}: 3445, 3345, 3282, 3031, 2920, 2853, 2364, 1646, 1608, 1426, 1353, 1096, 1052, 990. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.40 (d, 2H, *J* = 7.4 Hz), 7.32 (t, 2H, *J* = 7.4 Hz), 7.24 (t, 1H, *J* = 7.4 Hz), 6.78 (dd, 1H, *J* = 15.6, 10.4 Hz), 6.59 (d, 1H, *J* = 15.6 Hz), 6.46 (dd, 1H, *J* = 15.2, 10.4 Hz), 5.89 (dt, 1H, *J* = 15.2, 6.2 Hz), 4.69 (brs, 2H, $CONH_2$), 4.67 (d, 2H, *J* = 6.2 Hz). **^{13}C NMR** (100

MHz, $CDCl_3$, δ in ppm): 156.9, 137.1, 134.4, 133.9, 128.8, 128.0, 127.9, 127.5, 126.7, 65.6.

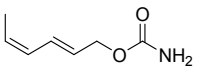
(2*E*,4*E*)-4-Methylhexa-2,4-dien-1-yl carbamate (11).



The title compound was synthesized following the general carbamoylation procedure starting from **V** (0.45 g, 4.0 mmol) and TAI (0.53 mL, 4.4 mmol). The crude was purified by flash chromatography (2:8 AcOEt/hexanes) to afford (0.492 g, 78 %) of pure carbamate **11** as a white solid.

MP: decomposes. **FT-IR (ATR)** ν in cm^{-1}: 3421, 3343, 3260, 3208, 2359, 1684, 1615, 1426, 1126, 1069, 1350, 963 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 6.31 (d, 1H, *J* = 15.6 Hz), 5.62 (m, 2H), 4.66 (brs, 2H), 4.61 (d, 2H, *J* = 6.8 Hz), 1.74 (s, 3H), 1.73 (d, 3H, *J* = 6.4 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 157.1, 139.6, 133.8, 128.8, 119.9, 66.3, 14.1, 12.1.

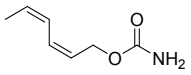
(2*E*,4*Z*)-Hexa-2,4-dien-1-yl carbamate (12).



The title compound was synthesized following the general carbamoylation procedure starting from **VI** (0.24 g, 2.5 mmol) and TAI (0.33 mL, 2.8 mmol). The crude was purified by flash chromatography (1:9 AcOEt/hexanes) to afford (0.29 g, 84 %) of pure carbamate **12** as a white solid.

Mp: 67 ºC. **FT-IR (ATR)** ν in cm^{-1}: 3429, 3337, 3275, 3212, 3022, 2947, 2915, 2855, 1681, 1610, 1427, 1405, 1346, 1103, 1066, 988 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 6.59 (ddt, 1H, *J* = 15.2, 12.3, 1.2 Hz), 6.00 (t, 1H, *J* = 10.8 Hz), 5.73 (dt, 1H, *J* = 15.2, 6.4 Hz), 5.57 (dq, 1H, *J* = 10.8, 6.8 Hz), 4.61 (d, 2H, *J* = 6.4 Hz), 1.76 (d, 3H, *J* = 6.8 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 156.9, 129.5, 128.4, 128.3, 126.5, 65.8, 13.6. **ESI-TOF** [M+1] calc for $C_7H_{10}NO_2$: 142.0790, found: 142.0129.

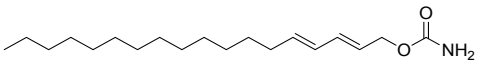
(2*Z*,4*Z*)-Hexa-2,4-dien-1-yl carbamate (13).



The title compound was synthesized following the general carbamoylation procedure starting from **VII** (0.10 g, 1.0 mmol) and TAI (0.14 mL, 1.1 mmol). The crude was purified by flash chromatography (2:8 AcOEt/hexanes) to afford (0.11 g, 75 %) of pure carbamate **13** as a white solid.

MP: decomposes. **FT-IR (ATR)** ν in cm^{-1}: 3422, 3332, 3267, 3211, 3044, 2914, 2855, 1684, 1612, 1408, 1355, 1321, 1082. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 6.47 (t, 1H, *J* = 11.4 Hz), 6.26 (t, 1H, *J* = 11.4 Hz), 5.66 (dq, 1H, *J* = 10.8, 7.2 Hz), 5.54 (dt, 1H, *J* = 10.8, 6.8 Hz), 4.95 (brs, 2H), 4.72 (d, 2H, *J* = 6.8 Hz), 1.75 (d, 3H, *J* = 7.2 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 157.2, 129.6, 127.4, 124.1, 123.7, 61.1, 13.4. **ESI-TOF** [M+23] calc for $C_7H_{11}NO_2Na$: 164.0790, found: 164.0688.

(2*E*,4*E*)-Octadeca-2,4-dien-1-yl carbamate (25).



The title compound was synthesized following the general carbamoylation procedure starting from **VIII** (0.57 g, 2.2 mmol) and TAI (0.29 mL, 2.4 mmol). The crude was purified by flash chromatography (2:8 AcOEt/hexanes) to afford (0.50 g, 72 %) of pure carbamate **25** as a white crystalline solid.

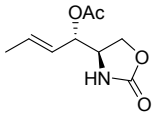
Mp: 87 ºC. **FT-IR (ATR)** ν in cm^{-1}: 3435, 3289, 3018, 2954, 2917, 2848, 1691, 1606, 1472, 1461, 1438, 1073, 982. **^{1}H NMR** (400 MHz,$CDCl_3$, δ in ppm): 6.26 (dd, 1H, *J* = 15.2, 10.4 Hz), 6.03 (dd, 1H, *J* = 15.2, 10.4 Hz), 5.74 (dt, 1H, *J* = 15.2, 6.8 Hz), 5.64 (dt, 1H, *J* = 15.2, 6.4 Hz), 4.57 (d, 2H, *J* = 6.4 Hz), 4.56 (brs, 2H), 2.07 (q, 2H, *J* = 7.2 Hz), 1.42-1.15 (m, 22H), 0.88 (t, 3H, *J* = 6.4 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 156.9, 137.1, 135.0, 129.2, 124.3, 65.8, 32.8, 32.1, 29.9, 29.9, 29.9, 29.8, 29.7, 29.6, 29.4, 29.3, 22.9, 21.3, 14.3. **ESI-TOF** [M+23] calc for $C_{19}H_{35}NO_2Na$: 332.2668, found: 332.2575.

General procedure for the tandem intramolecular aziridination-ring opening of allyl carbamates (Procedure A). The corresponding carbamate (0.1 mmol), bis(*tert*-butylcarbonyloxy)iodobenzene, $PhI(OPiv)_2$ (0.2 mmol), activated MgO (0.33 mmol) and rhodium(II) dimer, $Rh_2(OAc)_4$ (0.01 mmol) were placed in a 10 mL flame dried

Schlenk. Then dichloromethane (2 mL) was added and the mixture was stirred at room temperature until TLC showed complete consumption of the starting material. The reaction mixture was initially purified through a short silicagel column (2-3 cm), washing with hexanes to hexanes/ethyl acetate 1:1, to afford an essentially pure mixture of isomers. Separation of isomers was achieved by column chromatography, although yields dropped significantly after prolonged contact with silicagel.

General for the tandem intramolecular aziridination-ring opening of allyl carbamates (Procedure B). The corresponding carbamate (0.1 mmol), iodobenzene diacetate, $PhI(OAc)_2$ (0.2 mmol), activated MgO (0.33 mmol) and $Rh_2(OPiv)_4$ (0.01 mmol) were placed in a 10 mL flame dried Schlenk. Then dichloromethane (0.05 M solution of the carbamate) was added and the mixture was stirred at 5ºC until TLC showed complete consumption of the starting material. The reaction mixture was initially purified through a short silicagel column (2-3 cm), washing with hexanes to hexanes/ethyl acetate 1:1, to afford an essentially pure mixture of isomers. Separation of isomers was achieved by column chromatography, although yields dropped significantly after prolonged contact with silicagel.

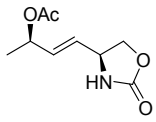
(*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl acetate (3a).



Compound **3a** was synthesized from carbamate **1** according to the general procedure A. Starting from 14 mg (0.1 mmol) of carbamate **1**, products **3a,b** (17 mg, 87%) was obtained as a 75:25 mixture of regioisomers. The mixture was further purified for characterization purposes, using 10% ethyl acetate-hexanes to 40% ethyl acetate–hexanes as the eluent. The title compound **3a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3297, 2922, 2851, 1741, 1229. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.92 (dq, 1H, *J* = 14.8, 6.5 Hz), 5.37 (ddq, 1H, *J* = 14.8, 7.6, 1.8 Hz), 5.24 (dd, 1H, *J* = 7.6, 5.0 Hz), 5.16 (brs, 1H), 4.44 (t, 1H, *J* = 8.9 Hz), 4.23 (dd, 1H, *J* = 8.9, 5.0 Hz), 3.99 (m, 1H), 2.09 (s, 3H), 1.75 (dd, 3H, J = 6.5, 1.8 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.2, 157.1, 134.4, 123.6, 74.8, 66.3, 54.7, 29.9, 18.2. **ESI-TOF** [M+23] calc for $C_9H_{12}NO_4Na$: 222.0845, found: 222.0733.

(*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (3b).



Compound **3b** has been synthesized from two different carbamates according to the general procedure B.

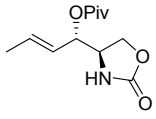
a) Starting from 14 mg (0.1 mmol) of carbamate **1**, compounds **3a,b** (15 mg, 74 %) were obtained as a <5:>95 mixture.

b) Starting from 14 mg (0.1 mmol) of carbamate **13**, compound **24a** and **3b** (13 mg, 71 %) were obtained as a 36:64 mixture of regioisomers.

The purification was accomplished by means of column chromatography employing hexanes 10% ethyl acetate-hexanes to 40% ethyl acetate–hexanes as the eluent. The title compound **3b** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3295, 2922, 1733, 1371, 1234, 1022 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.76 (dd, 1H, *J* = 15.6, 5.4 Hz), 5.67 (ddd, 1H, *J* = 15.6, 7.3, 1.0 Hz), 5.39 (brs, 1H), 5.35 (m, 1H), 4.54 (t, 1H, *J* = 8.8 Hz), 4.39 (m, 1H), 4.06 (dd, 1H, *J* = 8.8, 6.4 Hz), 2.07 (s, 3H), 1.31 (d, 3H, *J* = 6.7 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.0, 159.1, 134.1, 128.7, 69.9, 69.3, 54.1, 21.2, 20.0. **ESI-TOF** [M+23] calc for CH_9NO_4Na: 222.0845, found: 222.0731.

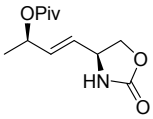
(*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (4a).



Compound **4a** was synthesized from carbamate **1** according to general procedure A. Starting from 14 mg (0.1 mmol) of carbamate **1**, products **4a,b** (21 mg, 89%) were obtained as a 91:9 mixture of regioisomers. Purification was accomplished by means of column chromatography using 10% ethyl acetate-hexanes to 40% ethyl acetate–hexane as the eluent. The title compound **4a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3288, 2971, 2936, 2920, 2893, 1753, 1727, 1480, 1398, 1278, 1229, 1148. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.88 (dq, 1H, *J* = 15.2, 6.5 Hz), 5.35 (ddq, 1H, *J* = 15.2, 7.0, 1.7 Hz), 5.26 (dd, 1H, *J* = 7.0, 4.4 Hz), 4.42 (t, 1H, *J* = 8.9 Hz), 4.27 (dd, 1H, *J* = 8.9, 4.4 Hz), 3.99 (m, 1H), 1.75 (dd, 3H, *J* = 6.5, 1.7 Hz), 1.21 (s, 9H). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 177.8, 159.1, 133.4, 123.8, 73.9, 66.1, 54.9, 27.3, 18.3. **ESI-TOF** [M+23] calc for $C_{12}H_{19}NO_4Na$: 264.1314, found: 264.1205.

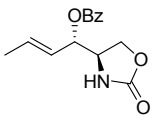
(*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl pivalate (4b).



Compound **4b** was synthesized from carbamate **1** according to general procedure B and employing $PhI(OPiv)_2$ instead of $PhI(OAc)_2$. Starting from 14 mg (0.1 mmol) of carbamate **1**, products **4a,b** (14 mg, 61%) were obtained as a 15:85 mixture of regioisomers. A small fraction was further purified by column chromatography using 10% ethyl acetate-hexanes to 30% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **4b** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3319, 2978, 1756, 1725, 1480, 1398, 1281, 1230, 1164, 1041 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.77 (dd, 1H, *J* = 15.3, 5.2 Hz), 5.65 (ddd, 1H, *J* = 15.3, 7.7, 1.2 Hz), 5.32 (m, 1H), 4.53 (t, 1H, *J* = 8.6 Hz), 4.39 (m, 1H), 4.03 (dd, 1H, *J* = 8.6, 6.7 Hz), 1.29 (d, 3H, *J* = 6.7 Hz), 1.20 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz, δ ppm): 177.8, 159.2, 134.8, 128.4, 70.2, 69.1, 54.4, 23.7, 20.2. **ESI-TOF** [M+1] calc for $C_{12}H_{19}NO_4Na$: 242.1314, found: 242.2855.

(*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl benzoate (5a).



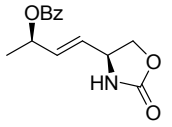
Compound **5a** was synthesized from carbamate **1** according to general procedure A employing $PhI(OCOPh)_2$ instead of $PhI(OPiv)_2$.[2] Starting from 14 mg (0.1 mmol) of carbamate **1**, product **5** (24 mg, 91% yield) was obtained as a 66:34 mixture of regioisomers. The mixture was further purified using 20% ethyl acetate – hexanes as the

[2] Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.* **1988**, *110*, 3272-3278.

eluent for characterization purposes. The title compound **5a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3292, 2922, 2853, 1754, 1720, 1267, 1109, 712 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 8.02 (d, 2H, *J* = 7.2Hz), 7.60 (t, 1H, *J* = 7.2 Hz), 7.46 (t, 2H, *J* = 7.2 Hz), 6.00 (dq, 1H, *J* = 14.0, 6.8 Hz), 5.44 (m, 2H), 5.33 (brs, 1H), 4.91 (t, 1H, *J* = 8.8 Hz), 4.26 (dd, 1H, *J* = 8.8, 4.8 Hz), 4.10 (m, 1H), 1.75 (d, 3H, *J* = 6.8 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 165.6, 160.2, 134.0, 133.5, 129.9, 128.6, 123.6, 75.4, 66.3, 55.0, 18.1. **ESI-TOF** [M+1] calc for $C_{12}H_{20}NO_4$: 242.1314, found: 242. 2831.

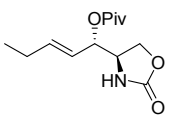
(*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl benzoate (5b).



Compound **5b** was synthesized from carbamate **1** according to general procedure B employing $PhI(OCOPh)_2$ instead of $PhI(OAc)_2$. Starting from 14 mg (0.1 mmol) of carbamate **1**, product **5** (21 mg, 82% yield) was obtained as a 14:86 mixture of regioisomers. The mixture was further purified using 20% ethyl acetate – hexane as the eluent for characterization purposes. The title compound **5b** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3324, 2923, 2852, 1753, 1716, 1272, 1113, 712 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 8.05 (d, 2H, *J* = 7.9 Hz), 7.58 (t, 1H, *J* = 7.3 Hz), 7.46 (dd, 2H, *J* = 7.9, 7.3 Hz), 5.98 (dd, 1H, *J* = 15.3, 5.2 Hz), 5.76 (dd, 1H, *J* = 15.3, 7.3 Hz), 5.62 (m, 1H), 5.37 (brs, 1H), 4.54 (t, 1H, *J* = 8.6 Hz), 4.41 (m, 1H), 4.06 (dd, 1H, *J* = 8.6, 6.8 Hz), 1.45 (d, 3H, *J* = 6.7 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 165.1, 159.3, 134.5, 133.4, 130.3, 129.8, 129.0, 128.7, 70.2, 70.1, 54.5, 20.4. **ESI-TOF** [M+23] calc for $C_{12}H_{19}NO_4Na$: 284.1001, found: 284.0845.

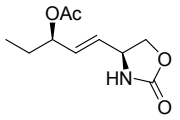
(*E*)-1-(2-Oxo-oxazolidin-4-yl)pent-2-en-1-yl pivalate (14a).



Compound **14a** was synthesized from carbamate **8** according to general procedure A. Starting from 16 mg (0.1 mmol) of carbamate **8**, products **14a,b** (19 mg, 72%) were obtained as a 86:14 mixture of regioisomers. The mixture was further purified by column chromatography using 10% ethyl acetate-hexanes to 30% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **14a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3289, 2967, 2933, 2873, 1756, 1733, 1480, 1398, 1279, 1229, 1031, 970. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.91 (dt, 1H, *J* = 14.4, 10.4 Hz), 5.38 (brs, 1H), 5.36-5.26 (m, 2H), 4.42 (t, 1H, *J* = 8.8 Hz), 4.27 (dd, 1H, *J* = 8.8, 4.8 Hz), 3.99 (m, 1H), 2.09 (qt, 2H, *J* = 7.6 Hz), 1.21 (s, 9H), 0.99 (t, 3H, *J* = 7.6 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 177.5, 158.9, 139.7, 121.3, 73.7, 65.8, 54.7, 39.0, 27.0, 25.4, 13.0. **ESI-TOF** [M+23] calc for $C_{13}H_{21}NO_4Na$: 278.1471, found: 278.1384.

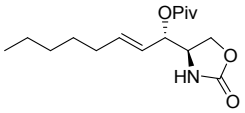
(*E*)-1-(2-Oxo-oxazolidin-4-yl)pent-1-en-3-yl acetate (15b).



Compound **15b** was synthesized from carbamate **8** according to general procedure B. Starting from 16 mg (0.1 mmol) of carbamate **8**, products **15a,b** (14 mg, 65%) were obtained as a 10:90 mixture. A small fraction was further purified by column chromatography using 10% ethyl acetate-hexanes to 30% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **15b** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3305, 2968, 2928, 1735, 1588, 1423, 1372, 1238, 1024, 968. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.72 (dd, 1H, *J* = 15.6, 5.6 Hz), 5.67 (dd, 1H, *J* = 15.6, 6.0 Hz), 5.25 (brs, 1H), 5.18 (m, 1H), 4.55 (t, 1H, *J* = 8.8 Hz), 4.40 (m, 1H), 4.06 (dd, 1H, *J* = 8.8, 6.4 Hz), 2.08 (s, 3H), 1.63 (m, 2H), 0.89 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.4, 159.4, 132.9, 74.3, 70.2, 54.3, 27.3, 21.3, 9.5. **ESI-TOF** [M+23] calc for $C_{10}H_{15}NO_4Na$: 236.1001, found: 236.0907.

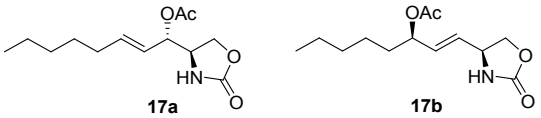
(*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-2-en-1-yl pivalate (16a).



Compound **16a** was synthesized from carbamate **9** according to general procedure A. Starting from 20 mg (0.1 mmol) of carbamate **9**, products **16a,b** (21 mg, 71%) was obtained as a 91:9 mixture of regioisomers. The mixture was further purified by column chromatography using 10% ethyl acetate-hexanes to 30% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **16a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3273, 2958, 2928, 2857, 1757, 1732, 1480, 1399, 1279, 1231, 1152, 1034. **^{1}H NMR** (400 MHz,$CDCl_3$, δ in ppm): 5.86 (dt, 1H, *J* = 15.6, 7.2 Hz), 5.36-5.24 (m, 3H), 4.42 (t, 1H, *J* = 8.8 Hz), 4.27 (dd, 1H, *J* = 8.8, 5.2 Hz), 3.99 (m, 1H), 2.05 (q, 2H, *J* = 7.2 Hz), 1.44-1.09 (m, 16H), 0.88 (t, 3H, *J* = 5.6 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 177.7, 159.2, 138.7, 122.4, 73.9, 66.0, 54.9, 39.2, 32.5, 31.5, 28.6, 27.3, 22.6, 14.2. **ESI-TOF** [M+23] calc for $C_{16}H_{27}NO_4Na$: 320.1940, found: 320.1839.

(*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-2-en-1-yl acetate (17a) and (*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-1-en-3-yl acetate (17b).



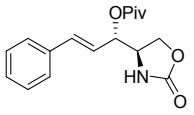
Compounds **17a** and **17b** were synthesized from carbamate **9** according to the general procedure B. Starting from 20 mg (0.1 mmol) of carbamate **9**, products **17a,b** (20 mg, 76 %) were obtained as a 13:87 mixture of regioisomers. Purification of the tittle products was accomplished by means of column chromatography employing hexanes 10% ethyl acetate-hexanes to 30% ethyl acetate–hexanes as the eluent **17a** and **17b** were isolated as colorless oils.

17a (minor): FT-IR (ATR) ν in cm^{-1}: 3306, 2956, 2924, 2853, 1766, 1403, 1243, 1028 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.90 (dt, 1H, *J* = 15.6, 6.8 Hz), 5.27 (dd, 1H, *J* = 15.6, 6.8 Hz), 5.21-5.08 (m, 2H), 4.42 (t, 1H, *J* = 8.8 Hz), 4.17 (dd, 1H, *J* = 8.8, 4.8 Hz), 3.95 (m, 1H), 2.09 (s, 3H), 2.06 (qt, 2H, *J* = 6.4 Hz), 1.42-1.19 (m, 6H), 0.88 (t, 3H, *J* = 6.8 Hz). **ESI-TOF** [M+23] calc for $C_{13}H_{21}NO_4Na$: 278.1451, found: 278.1375.

17b (major): FT-IR (ATR) ν in cm^{-1}: 3298, 2929, 2856, 2361, 2342, 1741, 1466, 1399, 1370, 1237, 1021, 971. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.71 (dd, 1H, *J* = 15.6, 5.6 Hz), 5.66 (dd, 1H, *J* = 15.6, 6.4 Hz), 5.23 (m, 1H), 5.08 (brs, 1H), 4.54 (t, 1H,

J = 8.8 Hz), 4.38 (m, 1H), 4.04 (dd, 1H, *J* = 8.8, 6.4 Hz), 2.07 (s, 3H), 1.37-1.21 (m, 8H), 0.88 (t, 3H, *J* = 6.4 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.3, 154.3, 133.2, 129.3, 70.0, 65.2, 54.1, 34.1, 31.4, 24.7, 22.5, 21.2, 14.0. **ESI-TOF** [M+23] calc for $C_{13}H_{21}NO_4Na$: 278.1451, found: 278.1364.

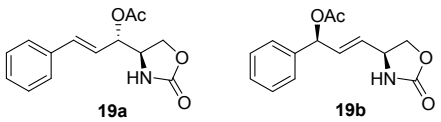
(*E*)-1-(2-Oxo-oxazolidin-4-yl)-3-phenylallyl pivalate (18a).



Compound **18a** was synthesized from carbamate **10** according to general procedure A. Starting from 19 mg (0.1 mmol) of carbamate **10**, product **18** (16 mg, 54%) was obtained as a 70:30 mixture of regioisomers. The mixture was further purified by column chromatography using 10% ethyl acetate-hexanes to 20% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **18a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3270, 3060, 3026, 2973, 2933, 2873, 1753, 1725, 1586, 1480, 1398, 1276, 1144, 1065, 1033, 968. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.41-7.25 (m, 5H), 6.74 (d, 1H, *J* = 16.0 Hz), 6.02 (dd, 1H, *J* = 16.0, 7.2 Hz), 5.67 (brs, 1H), 5.41 (m, 1H), 4.41 (t, 1H, *J* = 8.8 Hz), 4.23 (dd, 1H, *J* = 8.8, 4.4 Hz), 4.1 (m, 1H), 1.25 (s, 9H). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 177.5, 159.0, 135.9, 135.4, 129.0, 127.0, 121.7, 74.9, 66.7, 54.9, 39.3, 27.3. **ESI-TOF** [M+23] calc for $C_{17}H_{21}NO_4Na$: 326.1471, found: 326.1369.

(*E*)-1-(2-Oxo-oxazolidin-4-yl)-3-phenylallyl acetate (19a) and (*E*)-3-(2-Oxo-oxazolidin-4-yl)-1-phenylallyl acetate (19b).

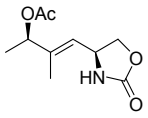


Compounds **19a** and **19b** were obtained from carbamate **10** according to general procedure B. Starting from 19 mg (0.1 mmol) of carbamate **10**, products **19a,b** (16 mg, 60%) were obtained as a 28:72 inseparable mixture of regioisomers. Spectroscopic data extracted from the spectrum of the mixture of compounds.

19a: ^{1}**H NMR** (400 MHz,$CDCl_3$, δ in ppm): 7.42-7.27 (m, 5H), 6.76 (d, 1H, *J* = 15.6 Hz), 6.00 (dd, 1H, *J* = 15.6, 7.6 Hz), 4.46 (t, 1H, *J* = 9.2 Hz), 4.23 (dd, 1H, *J* = 9.2, 4.8 Hz), 4.14-4.09 (m, 1H), 2.14 (s, 3H).

19b: ^{1}**H NMR** (400 MHz,$CDCl_3$, δ in ppm): 7.42-7.27 (m, 5H), 6.25 (d, 1H, *J* = 5.6 Hz), 5.93 (dd, 1H, *J* = 15.2, 5.6 Hz), 5.71 (dd, 1H, *J* = 15.2, 6.4 Hz), 5.39 (brs, 1H), 5.52 (t, 1H, *J* = 8.4 Hz), 4.40 (m, 1H), 4.05 (dd, 1H, *J* = 8.4, 6.4 Hz), 2.12 (s, 3H).

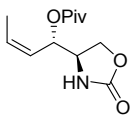
(*E*)-3-Methyl-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (20b).



Compound **20b** was synthesized from carbamate **11** according to general procedure B. Starting from 16 mg (0.1 mmol) of carbamate **11**, products **20a,b (**14 mg, 68%) were obtained as a 10:90 mixture. A small fraction was further purified by column chromatography using 10% ethyl acetate-hexanes to 40% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **20b** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3309, 2981, 2929, 1732, 1675, 1370, 1239, 1075, 1023, 944, 768. ^{1}**H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.48 (d, 1H, *J* = 8.8 Hz), 5.21 (q, 1H, *J* = 6.6 Hz), 5.10 (brs, 1H), 4.68 (m, 1H), 4.53 (t, 1H, *J* = 8.4 Hz), 3.98 (dd, 1H, *J* = 8.4, 6.8 Hz), 2.07 (s, 3H), 1.70 (d, 3H, *J* = 1.6 Hz), 1.30 (d, 3H, *J* = 6.6 Hz). ^{13}**C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.3, 159.3, 141.0, 123.9, 73.8, 70.4, 50.2, 21.5, 19.3, 13.2. **ESI-TOF** [M+23] calc for $C_{10}H_{15}NO_4Na$: 236.1001, found: 236.0909.

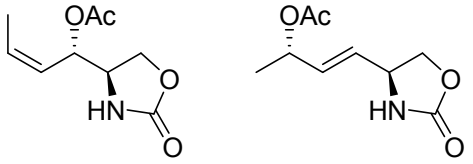
(*Z*)-1-(-2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (21a).



Compounds **21a,b** were synthesized from carbamate **12** according to the general procedure A. Starting from 14 mg (0.1 mmol) of carbamate **12**, products **21a,b** (13 mg, 56%) were obtained as a 90:10 mixture. The reaction mixture was not separable and the spectroscopic data were extracted from the spectrum of the mixture.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 5.88 (dq, 1H, *J* = 10.4, 7.2 Hz), 5.52 (dd, 1H, *J* = 9.2, 4.8 Hz), 5.23 (dd, 1H, *J* = 10.4, 9.2 Hz), 4.97 (brs, 1H), 4.40 (t, 1H, *J* = 8.8 Hz), 4.19 (dd, 1H, *J* = 8.8, 5.2 Hz), 3.96-3.89 (m, 1H), 1.72 (d, 3H, *J* = 7.2 Hz), 1.20 (s, 9H).

(*Z*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl acetate (22a) and (*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (22b).



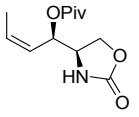
22a **22b**

Compounds **22a** and **22b** have been synthesized from carbamate **12** according to the general procedure B. Starting from 14 mg (0.1 mmol) of carbamate **12**, products **22a,b** (13 mg, 64%) of the product were obtained as a 39:61 mixture. Purification of the title products was accomplished by means of column chromatography employing hexanes 10% ethyl acetate-hexanes to 40% ethyl acetate–hexanes as the eluent. Compounds **22a** and **22b** were isolated as colorless oils.

22a: FT-IR (ATR) ν in cm^{-1}: 3269, 2961, 2922, 1756, 1735, 1482, 1407, 1371, 1227, 1034, 968. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.88 (dqd, 1H, *J* = 10.8, 6.8, 0.8 Hz), 5.56 (brs, 1H), 5.49 (ddd, 1H, *J* = 9.6, 7.2, 0.8 Hz), 5.21 (ddq, 1H, *J* = 10.8, 9.6, 2.0 Hz), 4.41 (t, 1H, *J* = 9.0 Hz), 4.10 (dd, 1H, *J* = 9.0, 4.8 Hz), 3.96 (m, 1H), 2.08 (s, 3H), 1.82 (dd, 3H, *J* = 6.8, 2.0 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.0, 159.1, 133.7, 123.3, 71.5, 66.4, 54.9, 21.2, 14.2. **ESI-TOF** [M+23] calc for CH_9NO_4Na: 222.0845, found: 222.0753.

22b: ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 5.76 (dd, 1H, *J* = 15.6, 5.2 Hz), 5.67 (dd, 1H, *J* = 15.6, 7.2 Hz), 5.35 (m, 1H), 5.34 (brs, 1H), 4.54 (t, 1H, *J* = 8.8 Hz), 4.39 (m, 1H), 4.07 (dd, 1H, *J* = 8.8, 6.8 Hz), 2.06 (s, 3H), 1.31 (d, 3H, *J* = 6.8 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): δ = 170.4, 159.2, 134.4, 129.1, 70.2, 69.6, 54.4, 21.5, 20.2. **ESI-TOF** [M+23] calc for CH_9NO_4Na: 222.0845, found: 222.0712.

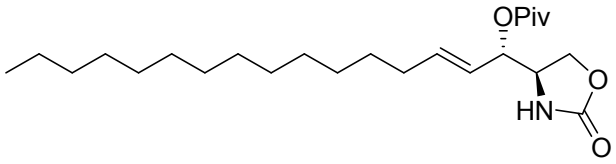
(*Z*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (23a)



Compound **23a** was synthesized from carbamate **13** according to the general procedure A. Starting from 14 mg (0.1 mmol) of carbamate **13**, products **23a,b** (18 mg, 74%) were obtained as a 90:10 mixture. The mixture was further purified by column chromatography using 10% ethyl acetate-hexanes to 20% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **23a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3274, 2962, 2916, 2849, 1757, 1728, 1480, 1398, 1281, 1152, 1036, 937 cm^{-1}. **^{1}H NMR** (400 MHz,$CDCl_3$, δ in ppm): 5.87 (dq, 1H, *J* = 10.8, 7.2 Hz), 5.46 (dd, 1H, *J* = 9.6, 6.8 Hz), 5.30 (brs, 1H), 5.21 (ddd, 1H, *J* = 10.8, 9.6, 1.6 Hz), 4.43 (t, 1H, *J* = 8.8 Hz), 4.11 (dd, 1H, *J* = 8.8, 4.8 Hz), 3.38 (m, 1H), 1.82 (dd, 3H, *J* = 7.2, 1.6 Hz), 1.21 (s, 9H). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): δ = 177.6, 159.0, 133.4, 123.4, 66.5, 64.9, 55.0, 39.1, 27.3, 14.2. **ESI-TOF** [M+23] calc for $C_{12}H_{19}NO_4Na$: 264.1314, found: 264.1207.

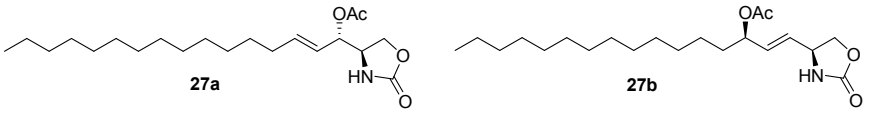
(*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-2-en-1-yl pivalate (26a).



Compound **26a** was synthesized from carbamate **25** according to general procedure A. Starting from 31 mg (0.1 mmol) of carbamate **25**, product **26a** (32 mg, 79%) of the product were obtained as a >98:<2 mixture. It was further purified by column chromatography using 10% ethyl acetate-hexanes to 20% ethyl acetate–hexanes as the eluent for characterization purposes. The title compound **26a** was isolated as colorless oil.

FT-IR (ATR) ν in cm^{-1}: 3277, 2956, 2923, 2853, 1760, 1732, 1480, 1398, 1279, 1149, 1034 cm^{-1}. **^{1}H NMR** (400 MHz,$CDCl_3$, δ in ppm): 5.87 (dt, 1H, *J* = 14.4, 6.8 Hz), 5.30 (m, 2H), 5.02 (brs, 1H), 4.42 (t, 1H, *J* = 8.8 Hz), 4.27 (dd, 1H, *J* = 8.8, 5.2 Hz), 3.99 (m, 1H), 2.05 (q, 2H, *J* = 6.8 Hz), 1.35 (m, 2H), 1.25 (brs, 20H), 1.21 (s, 9H), 0.88 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 177.7, 159.0, 138.8, 122.3, 73.9, 66.0, 58.9, 54.8, 41.6, 39.2, 37.7, 32.6, 32.1, 29.9, 29.9, 29.9, 29.8, 29.6, 29.6, 29.3, 29.0, 28.4, 27.3, 22.9, 20.6, 14.4. **ESI-TOF** [M+23] calc for $C_{24}H_{43}NO_4Na$: 432. 3192, found: 432.3098.

(*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-2-en-1-yl acetate (27a) and (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-1-en-3-yl acetate (27b).



Compounds **27a** and **27b** were obtained from carbamate **25** according to general procedure A. Starting from 31 mg (0.1 mmol) of carbamate **25**, products **27a,b** (28 mg, 76%) were obtained as a 13:87 mixture. Purification of the tittle products was accomplished by means of column chromatography employing 10% hexanes–ethyl acetate-hexanes to 20% ethyl acetate–hexanes as the eluent to afford **27a** and **27b** as colorless oils.

27a: FT-IR (ATR) ν in cm^{-1}: 3278, 2923, 2853, 1763, 1466, 1399, 1234, 1032 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.90 (dt, 1H, *J* = 15.6, 6.8 Hz), 5.27 (ddt, 1H, *J* = 15.6, 7.2, 1.6 Hz), 5.26 (brs, 1H), 5.16 (t, 1H, *J* = 7.2 Hz), 4.41 (t, 1H, *J* = 9.2 Hz), 4.16 (dd, 1H, *J* = 9.2, 4.8 Hz), 3.95 (m, 1H), 2.10 (s, 3H), 2.05 (m, 2H), 1.48-1.16 (m, 22H), 0.88 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.0, 159.0, 139.6, 122.5, 76.0, 66.5, 54.6, 32.6, 32.1, 29.9, 29.9, 29.9, 29.8, 29.6, 29.6, 29.4, 28.9, 22.9, 21.3, 14.4. **ESI-TOF** [M+23] calc for $C_{21}H_{37}NO_4Na$: 390.2723, found: 390.2631.

27b: FT-IR (ATR) ν in cm^{-1}: 3295, 2922, 2853, 1739, 1466, 1399, 1370, 1235, 1023, 969 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 5.71 (dd, 1H, *J* = 15.6, 5.2 Hz), 5.65 (dd, 1H, *J* = 15.6, 6.0 Hz), 5.23 (q, 1H, *J* = 6.0 Hz), 5.13 (brs, 1H), 4.53 (t, 1H, *J* = 8.4 Hz), 4.37 (m, 1H), 4.03 (dd, 1H, *J* = 8.4, 6.4 Hz), 2.07 (s, 3H), 1.59 (m, 2H), 1.39-1.18 (m, 22H), 0.88 (t, 3H, *J* = 6.2 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 170.5, 159.1, 133.4, 129.6, 73.3, 70.2, 54.4, 34.4, 32.1, 29.9, 29.9, 28.9, 28.9, 29.7, 29.6, 29.5, 25.6, 25.3, 22.9, 21.4, 14.4. **ESI-TOF** [M+23] calc for $C_{21}H_{37}NO_4Na$: 390.2723, found: 390.2633.

Synthesis of sphingosine

Pure oxazolidinone **26a** (32 mg, 0.08 mmol) was dissolved in a 10 ml round bottom flask with 3 ml of dioxane and 2 ml of water. Next, $Ba(OH)_2 \cdot 8H_2O$ (76 mg, 2.4 mmol) was added, a reflux condenser was fitted to the flask and the mixture was set to 100 ºC and stirred for 5h. Then the mixture was left to cool to room temperature, filtered and finally the solvent was evaporated. The crude was purified by a short silica gel

chromatography using dichloromethane:methanol:NH_4OH (94:6:1) to afford 16 mg (71%) of racemic sphingosine.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 5.77 (dtd, 1H, *J* = 15.4, 6.8, 1.2 Hz), 5.48 (ddt, 1H, *J* = 15.4, 7.2, 1.6 Hz), 4.04 (t, 1H, *J* = 7.2 Hz), 3.69 (dd, 1H, *J* = 10.4, 4.8 Hz), 3.62 (dd, 1H, *J* = 10.4, 5.8 Hz), 2.88 (td, 1H, *J* = 5.8, 4.8 Hz), 2.05 (dt, 2H, *J* = 7.2, 6.4 Hz), 1.74 (br s, 4H), 1.37 (t, 2H, *J* = 7.2 Hz), 1.32-1.26 (m, 22H), 0.88 (t, 3H, *J* = 6.8 Hz).

^{13}C NMR (100MHz, $CDCl_3$, δ in ppm): 135.2, 129.4, 76.9, 75.9, 64.6, 56.3, 32.6, 32.1, 29.9, 29.9, 29.9, 29.8, 29.7, 29.6, 29.4, 29.3, 22.9, 14.4.

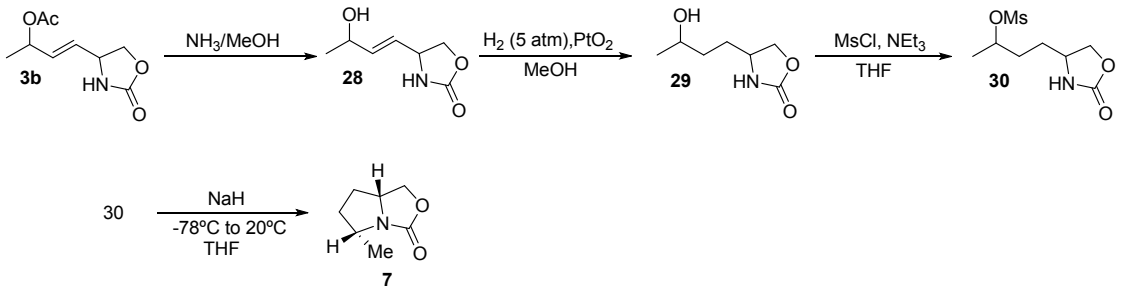
Determination of the relative configuration of product 3b. Preparation of bicyclic compound 7 and NOE experiments.

A 10 mL Shlenk was charged with acetate **3b** (30 mg, 0.15 mmol) and was dissolved in a 7N solution of NH_3 in methanol under argon. The solution was stirred at room temperature overnight resulting in full conversion to the hydrolyzed compound **28**, which easily decomposes in either silica or alumina. Therefore the crude product was used directly in the hydrogenation step. Thus, alcohol **28** dissolved in methanol (2 mL) and PtO_2 (2.3 mg, 0.01 mmol) were introduced in an autoclave, which was then pressurized with hydrogen (5 atm) and the raction mixture was stirred for 5 h at room temperature. After filtration and evaporation of the solvent under vacuum, the saturated alcohol **29** was obtained as the sole product, pure enough to be used directly in the next reaction.

To a stirred solution of **29** and triethylamine (26 μL, 0.18 mmol) in THF (0.5 mL), methanesulfonyl chloride (14 μl, 0.18 mmol) was added at 0ºC. The solution was stirred 2h maintaining the temperature at 0ºC. The reaction was quenched adding a drop of water to eliminate the excess of methanesulfonyl chloride. The solvent was removed and ethyl acetate (1 mL) and water (1 mL) were added. The organic layer was separated and the aqueous phase was extracted repeatedly with 1 mL of ethyl acetate. The combined organic layers were dried with Na_2SO_4, filtered and evaporated to give the mesylated coumpound **30**.

Finally, compound **30** was dissolved in anhydrous THF (2 mL), cooled to -78ºC and NaH (6 mg, 0.15 mmol, as a 60% mixture in mineral oil) was added to the solution. The solution was allowed to warm to room temperature and stirred overnight. A drop of water was added and the solvent evaporated. Afterwards, 1mL of CH_2Cl_2 and 1 mL of

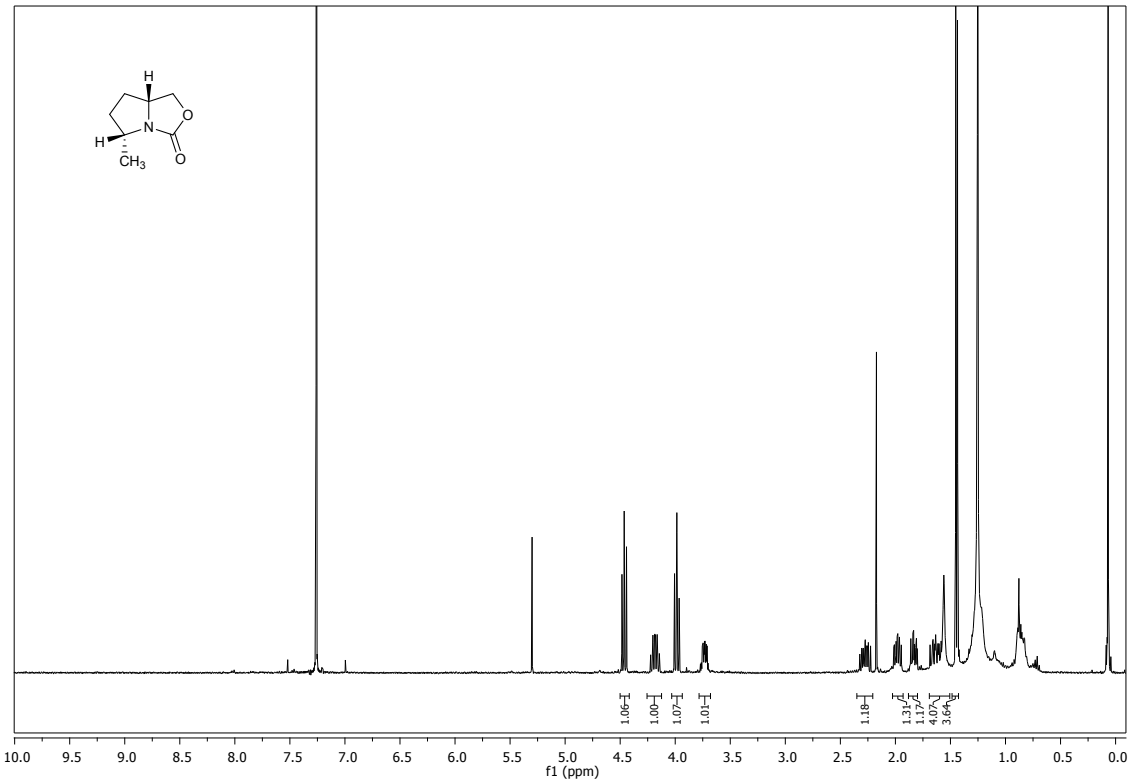
water were added, the organic layer was separated and the aqueous phase extracted with CH_2Cl_2 (3x1 mL). The organic layers were dried and evaporated under vacuum. Final purification was effected by column chromatography employing 20% ethyl acetate–hexanes as the eluent obtaining product **7** as a colorless oil in a 56 % (13 mg) overall yield.



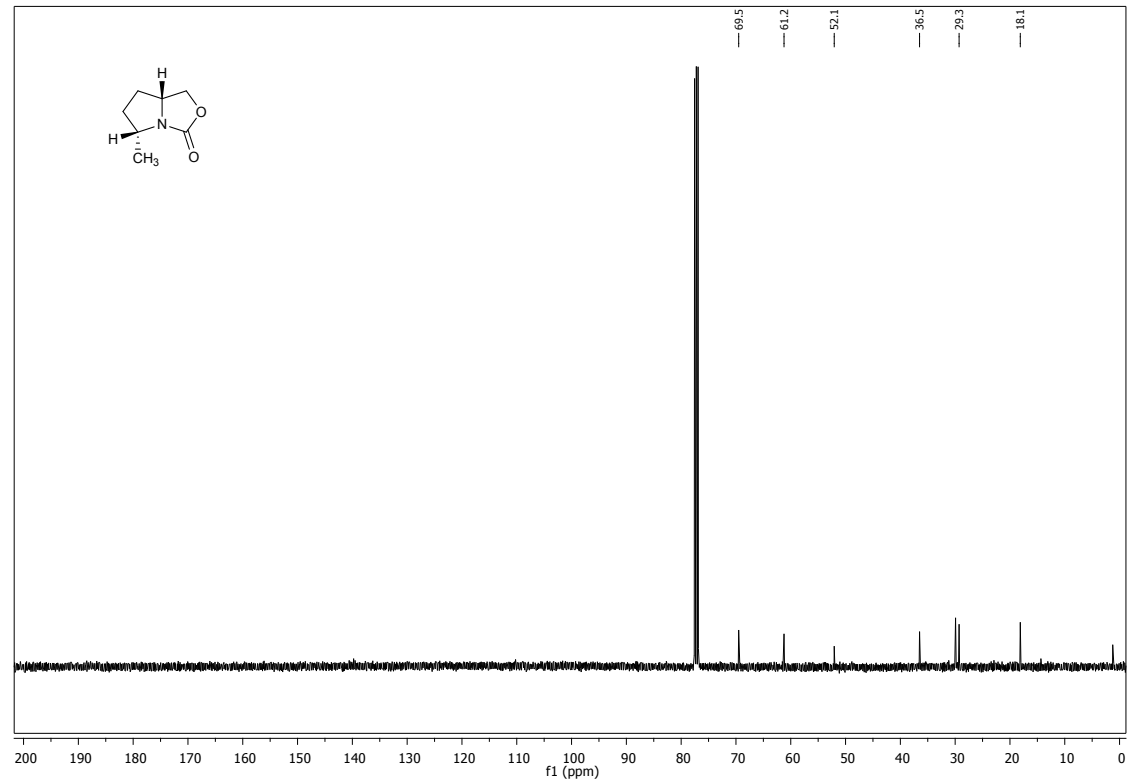
FT-IR (ATR) ν in cm^{-1}: 3346, 2959, 2922, 2853, 2361, 1746, 1456, 1399, 1259, 1024. **^{1}H NMR** (400 MHz,$CDCl_3$, δ in ppm): δ= 4.46 (t, 1H, *J* = 8.0 Hz), 4.18 (m, 1H), 3.98 (t, 1H, *J* = 8.4 Hz), 3.73 (m, 1H), 2.27 (m, 1H), 1.98 (m, 1H), 1.83 (m, 1H), 1.62 (m, 1H), 1.44 (d, 3H, *J* = 6.8 Hz). **^{13}C NMR** (100MHz, $CDCl_3$, δ in ppm): 69.5, 61.2, 52.1, 36.5, 29.3, 18.1. **ESI-TOF** [M+23] calc for $C_7H_{11}NO_2Na$: 164.0790, found: 164.0684.

Signal of CO group was not observed in the ^{13}C NMR. However, the presence of a CO band (1746 cm^{-1}) in the FT-IR spectra in combination with the ESI-TOF, undoubtedly confirm the proposed structure.

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of 5-methyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (7).

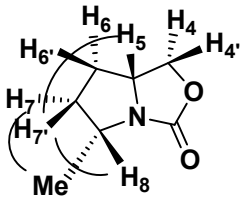


^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of 5-methyltetrahydropyrrolo[1,2-c]oxazol-3(1H)-one (7).



NOESY experiments did not provide any NOE correlation between H_8 and H_5 or between H_9 (Me) and H_5 (Figure S2). Alternatively, the *syn*-disposition of H_8 and H_5 was assigned through the following observations:

- Absence of correlation between the H_5 and H_7 in combination with the NOE correlation observed between H_5 and $H_{7'}$.
- Intense correlation between $H_{7'}$ and H_8 compared with the little correlation existent between H_7 and H_8.
- H_9 (Me) correlates with H_7 but not with $H_{7'}$



7

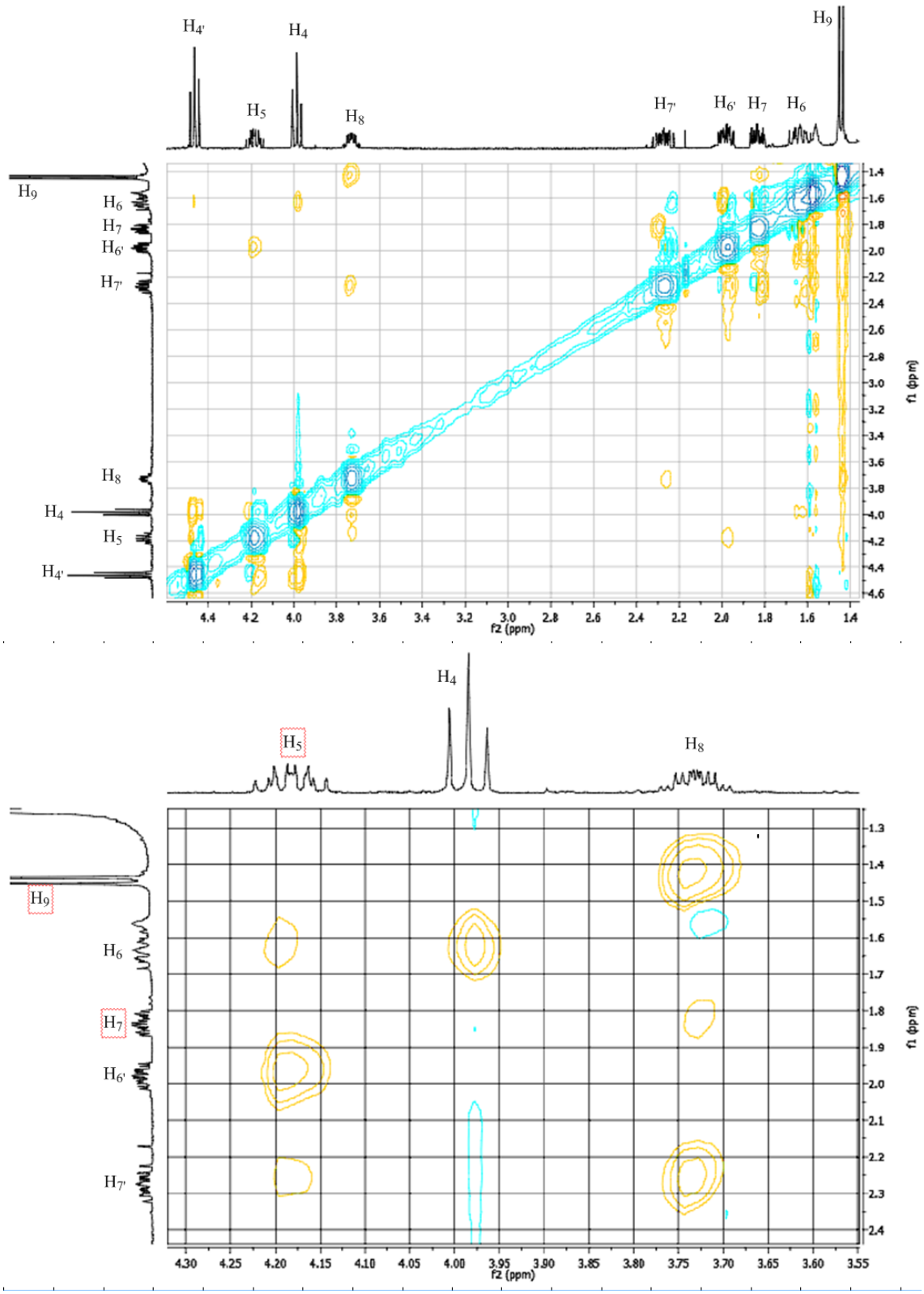
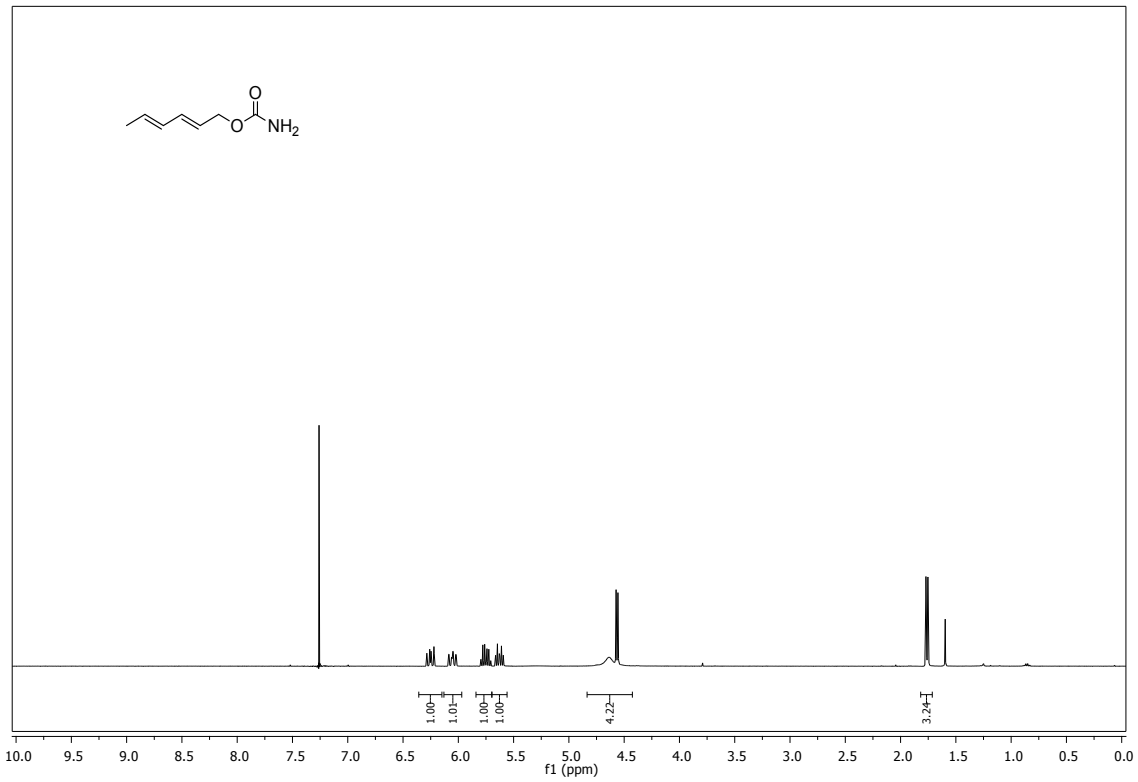
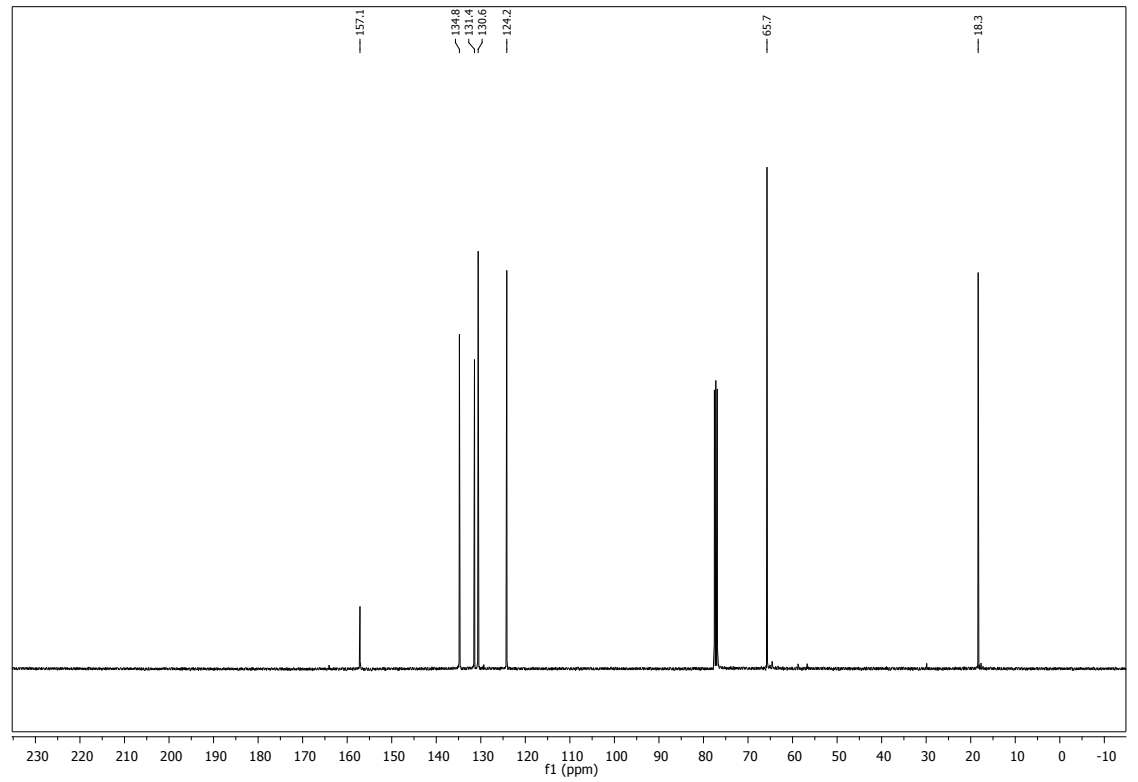


Figure S2

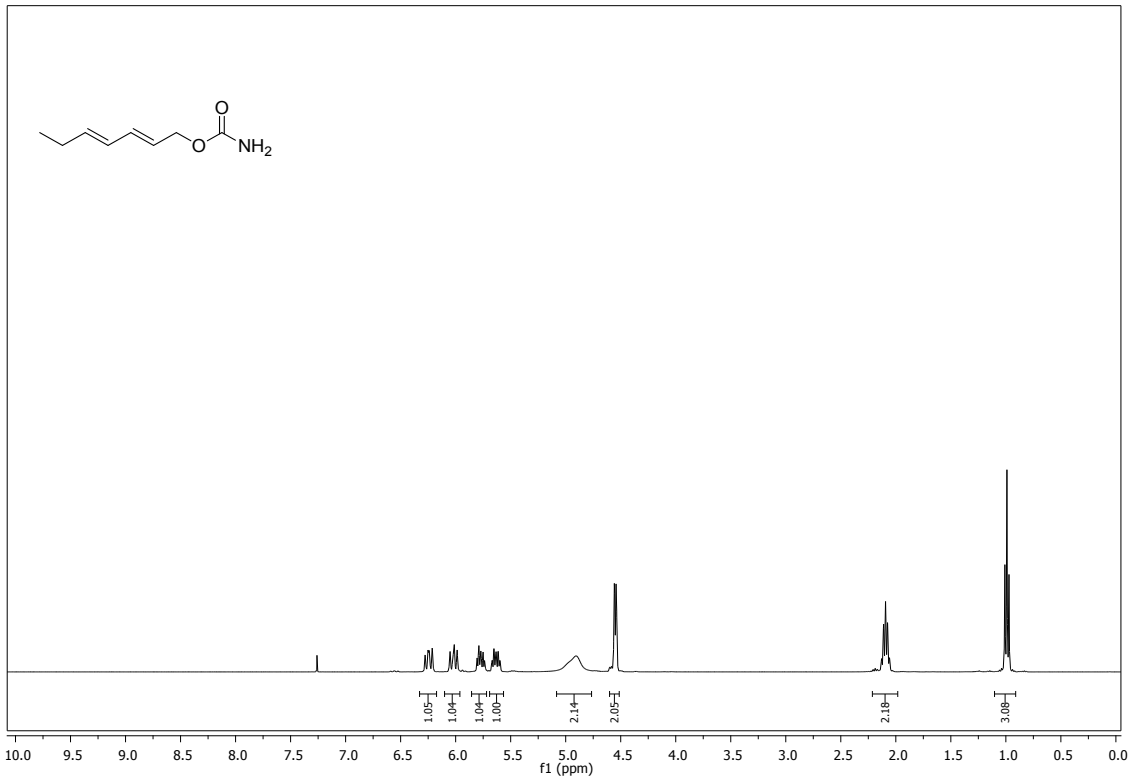
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*E*)-hexa-2,4-dienyl carbamate (1).



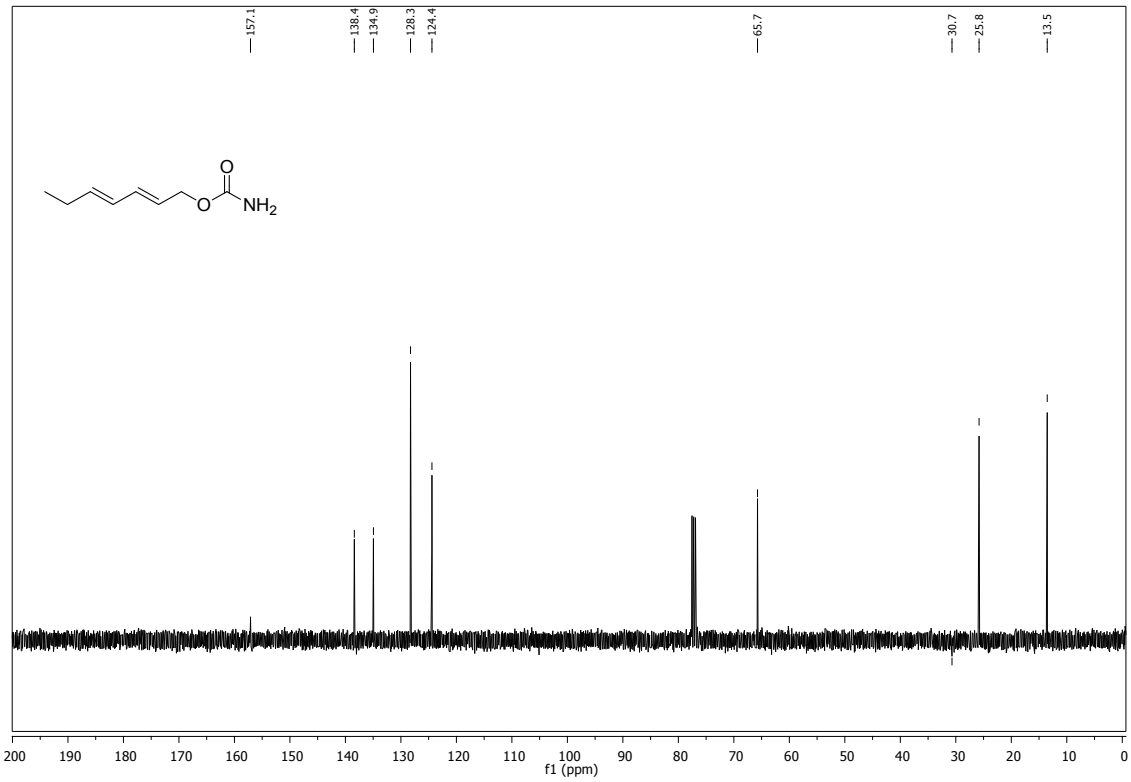
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*E*)-hexa-2,4-dienyl carbamate (1).



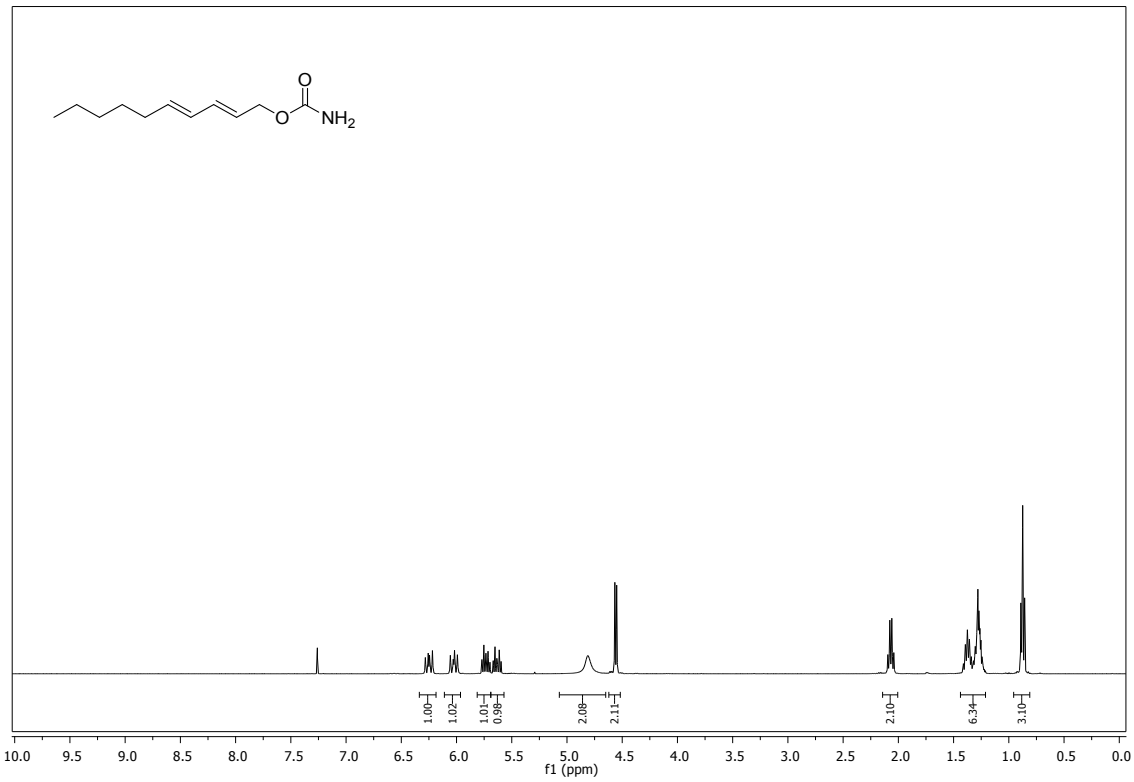
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*E*)-hepta-2,4-dien-1-yl carbamate (8).



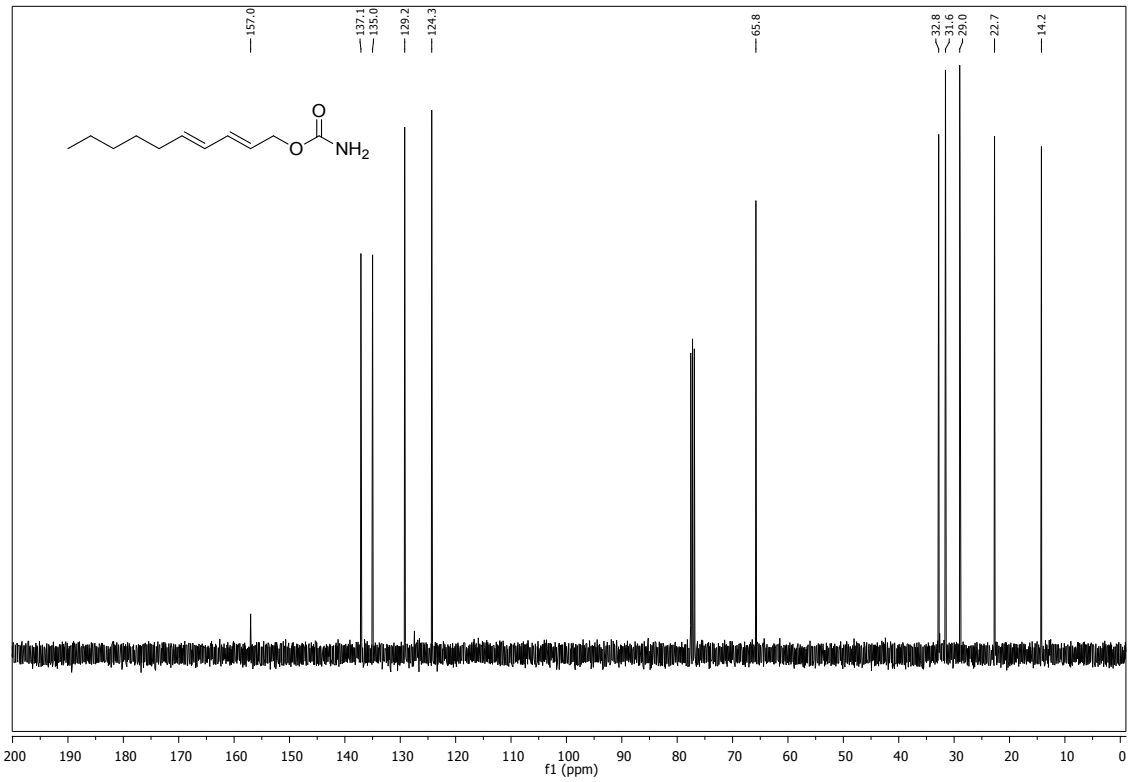
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*E*)-hepta-2,4-dien-1-yl carbamate (8).



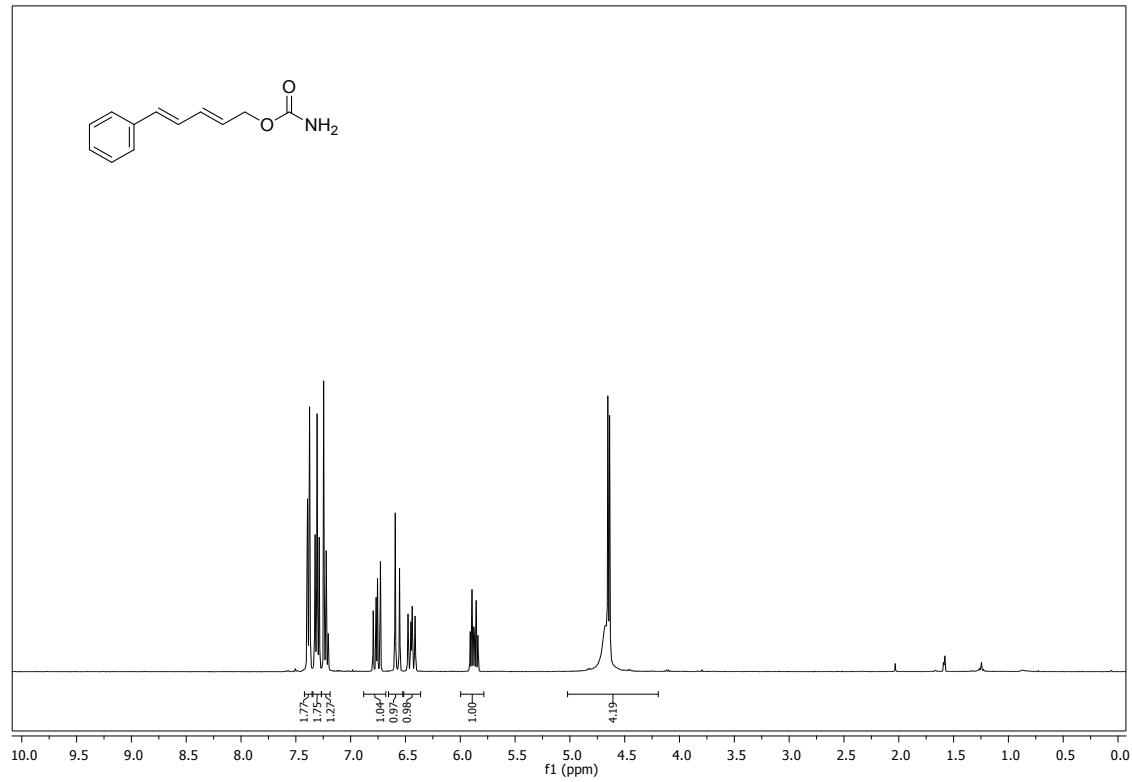
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*E*)-deca-2,4-dien-1-yl carbamate (9).



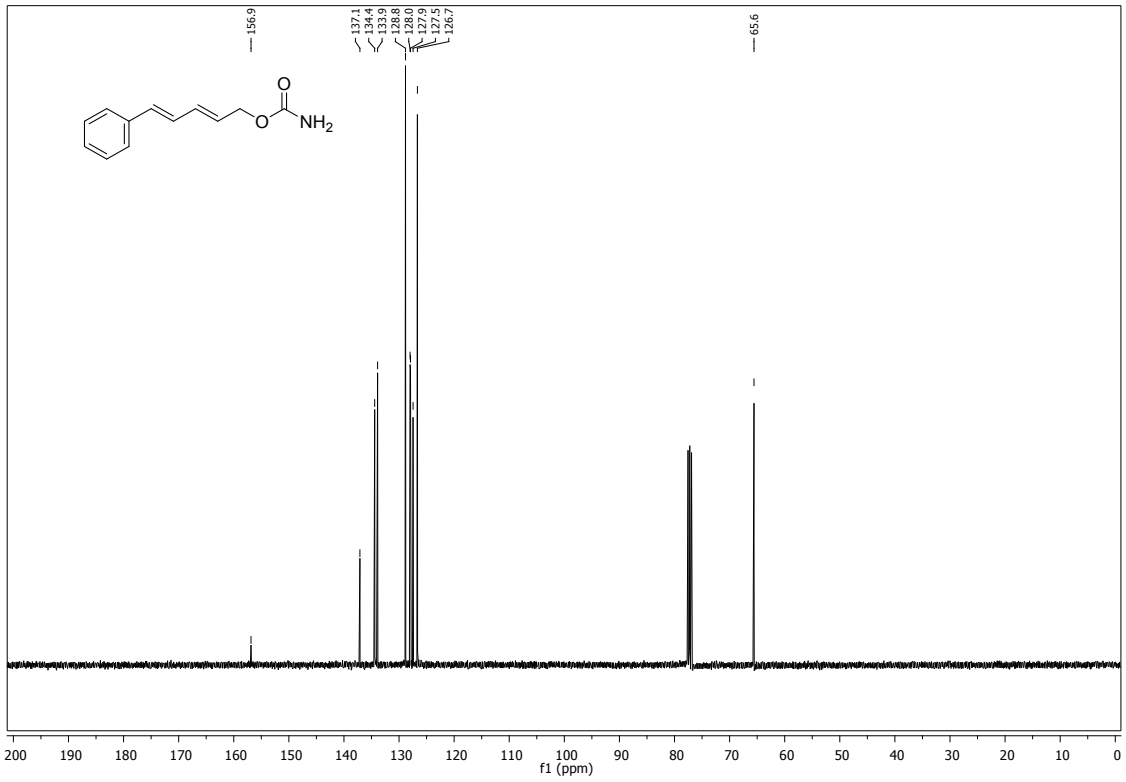
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*E*)-deca-2,4-dien-1-yl carbamate (9).



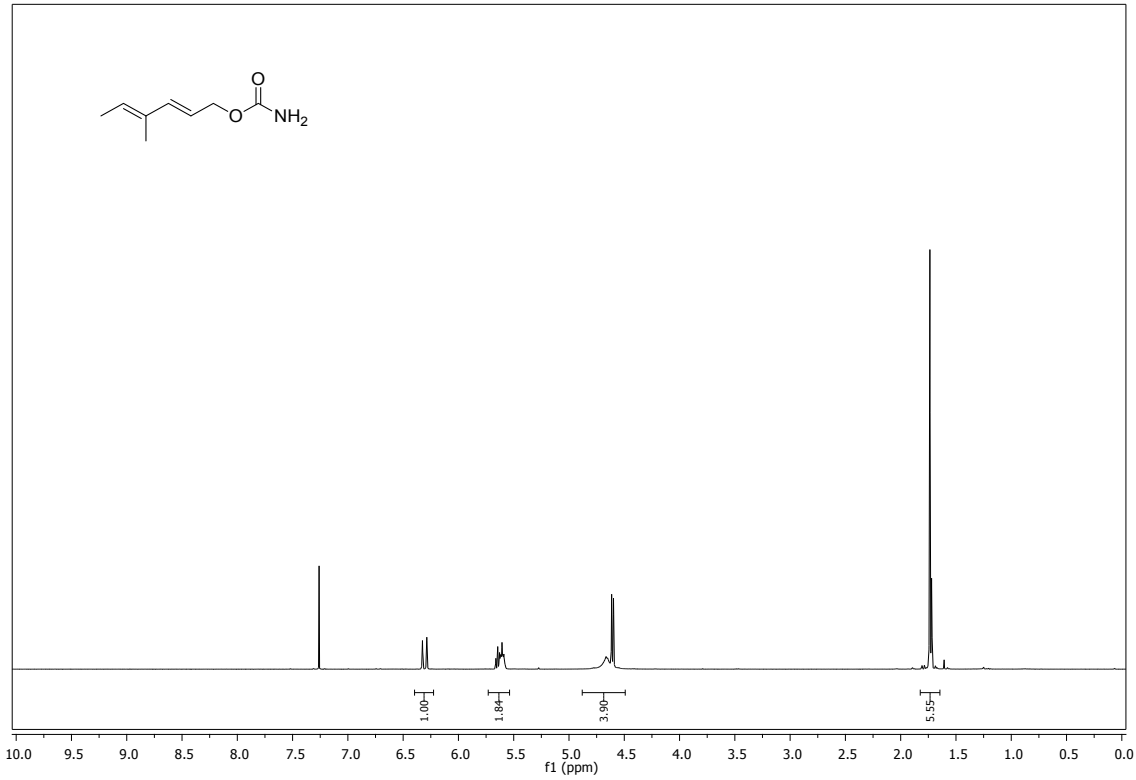
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl carbamate (10).



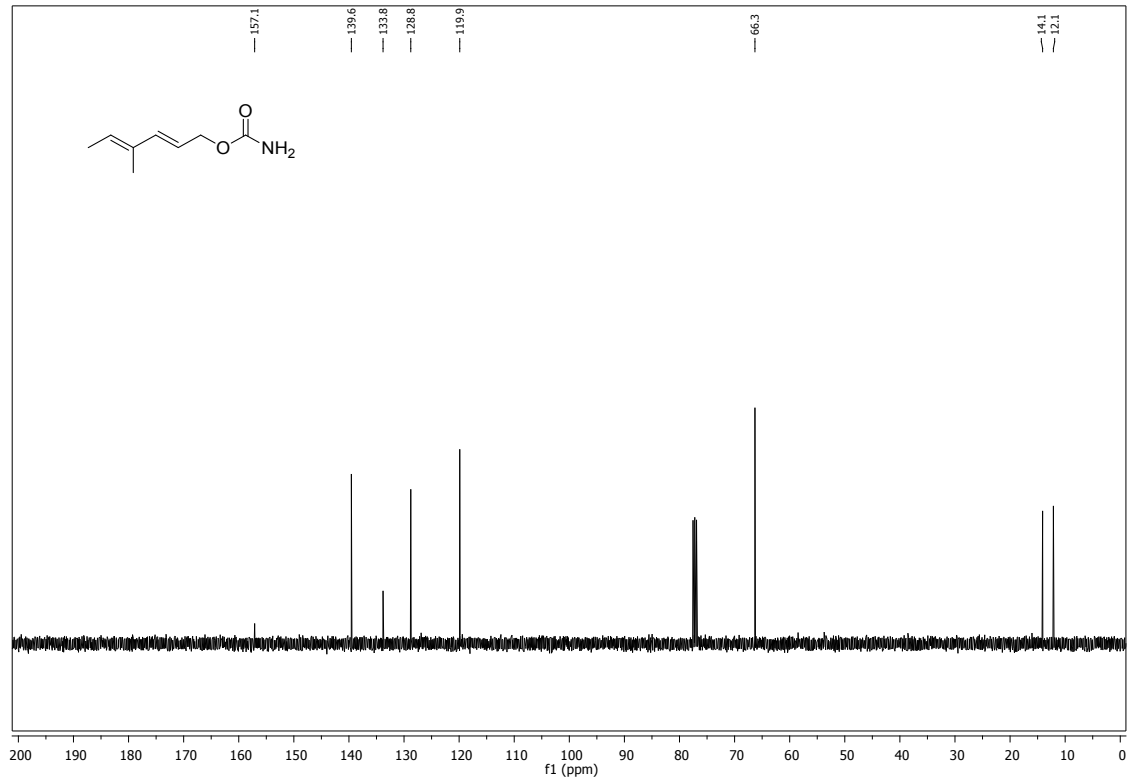
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl carbamate (10).



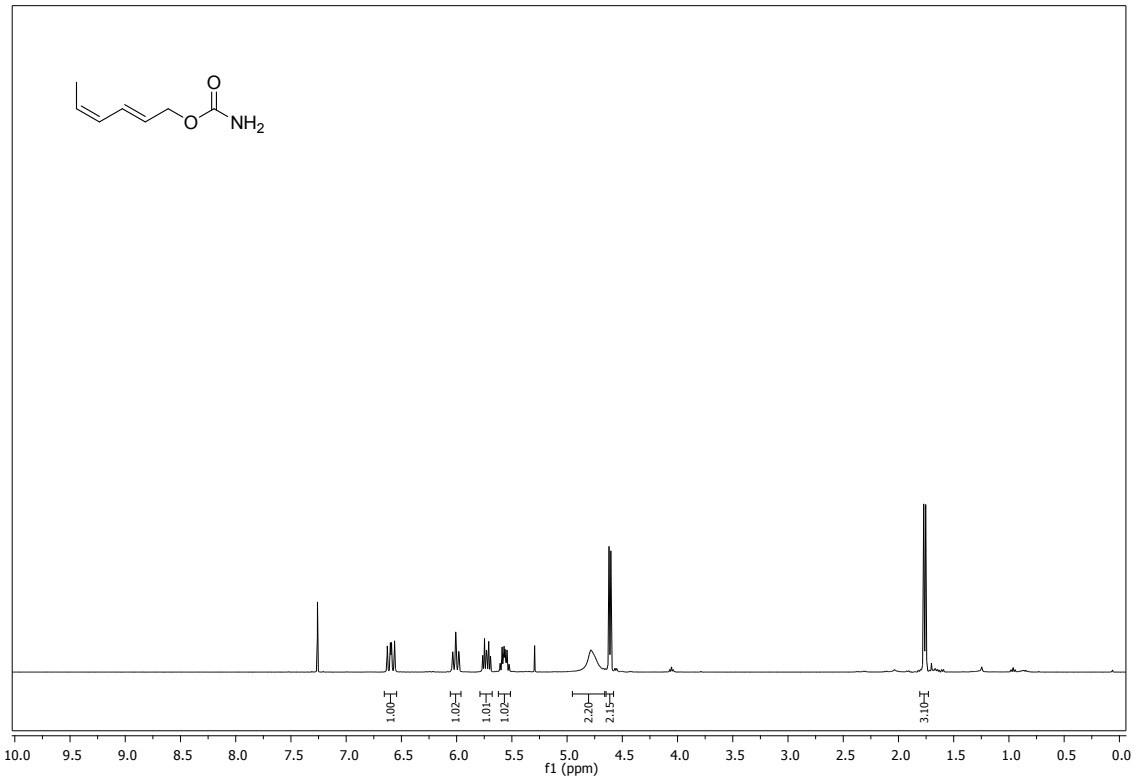
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*E*)-4-methylhexa-2,4-dien-1-yl carbamate (11).



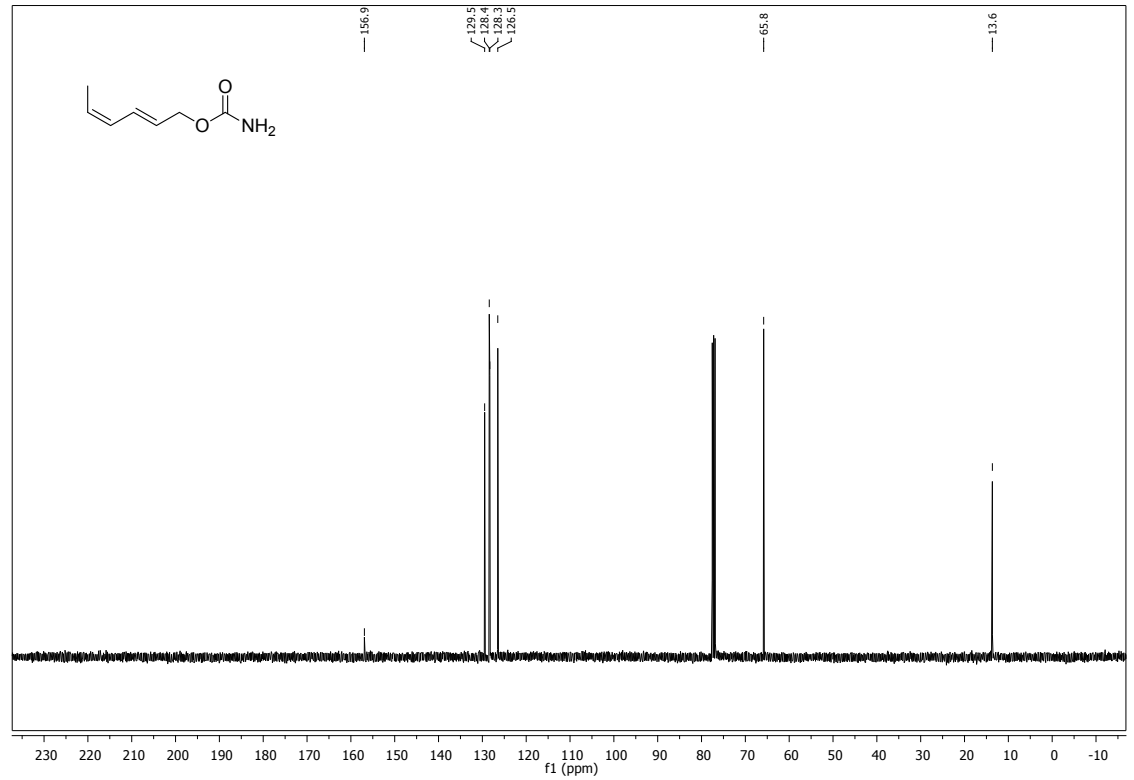
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*E*)-4-methylhexa-2,4-dien-1-yl carbamate (11).



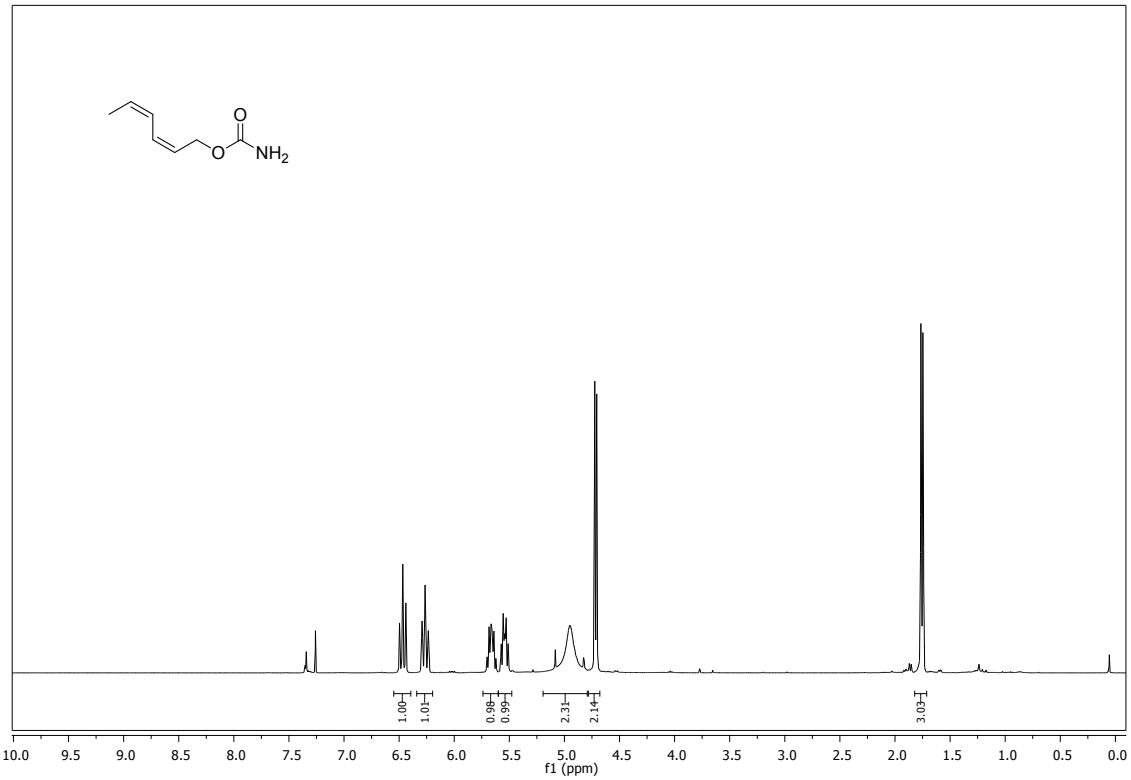
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*Z*)-hexa-2,4-dien-1-yl carbamate (12).



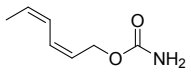
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*Z*)-hexa-2,4-dien-1-yl carbamate (12).

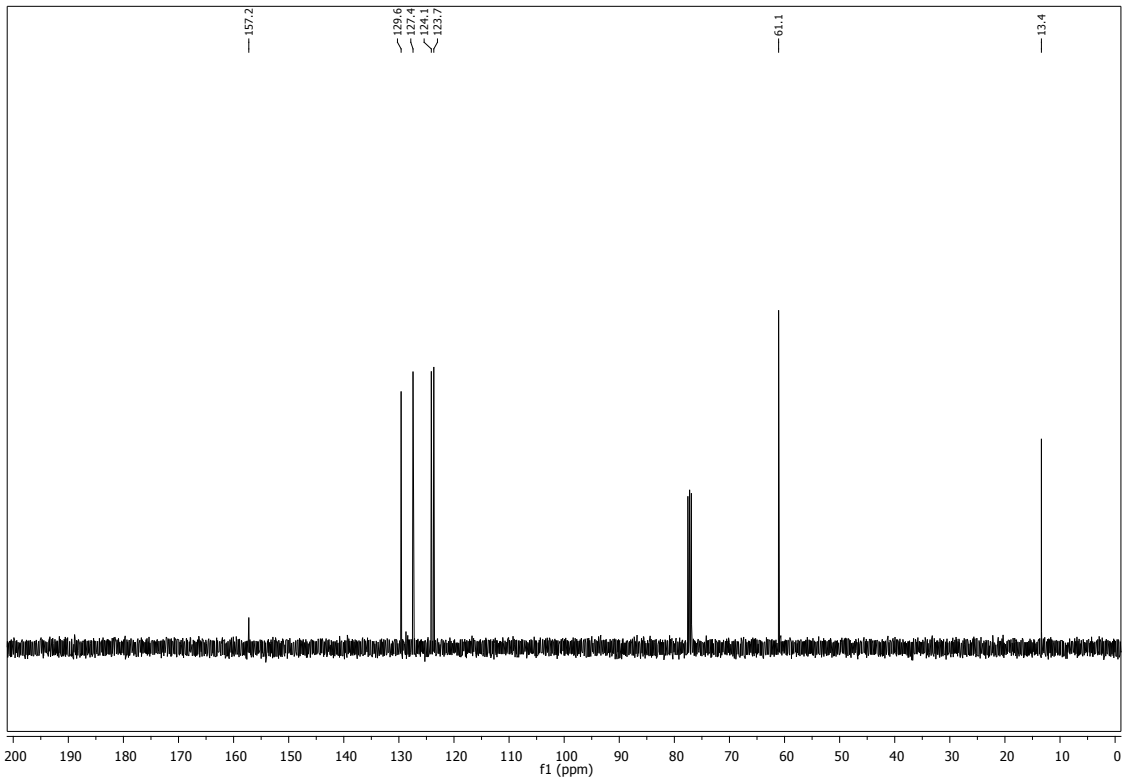


^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*Z*,4*Z*)-hexa-2,4-dien-1-yl carbamate (13).

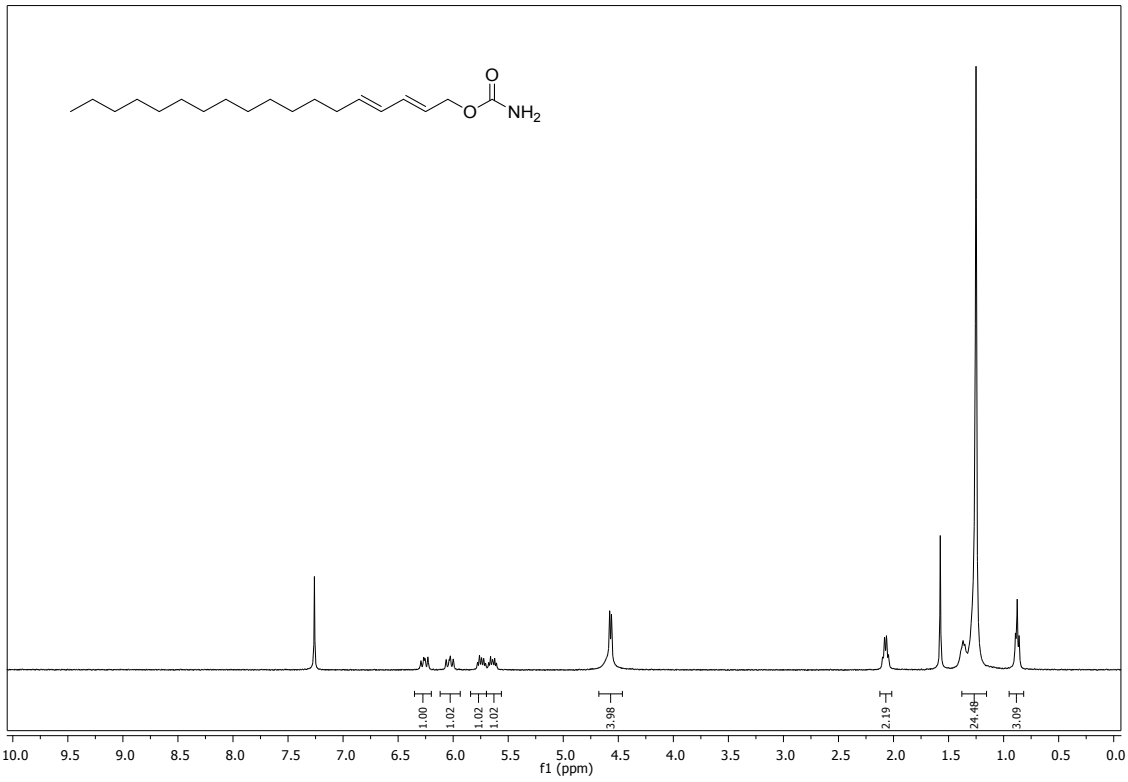


^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*Z*,4*Z*)-hexa-2,4-dien-1-yl carbamate (13).

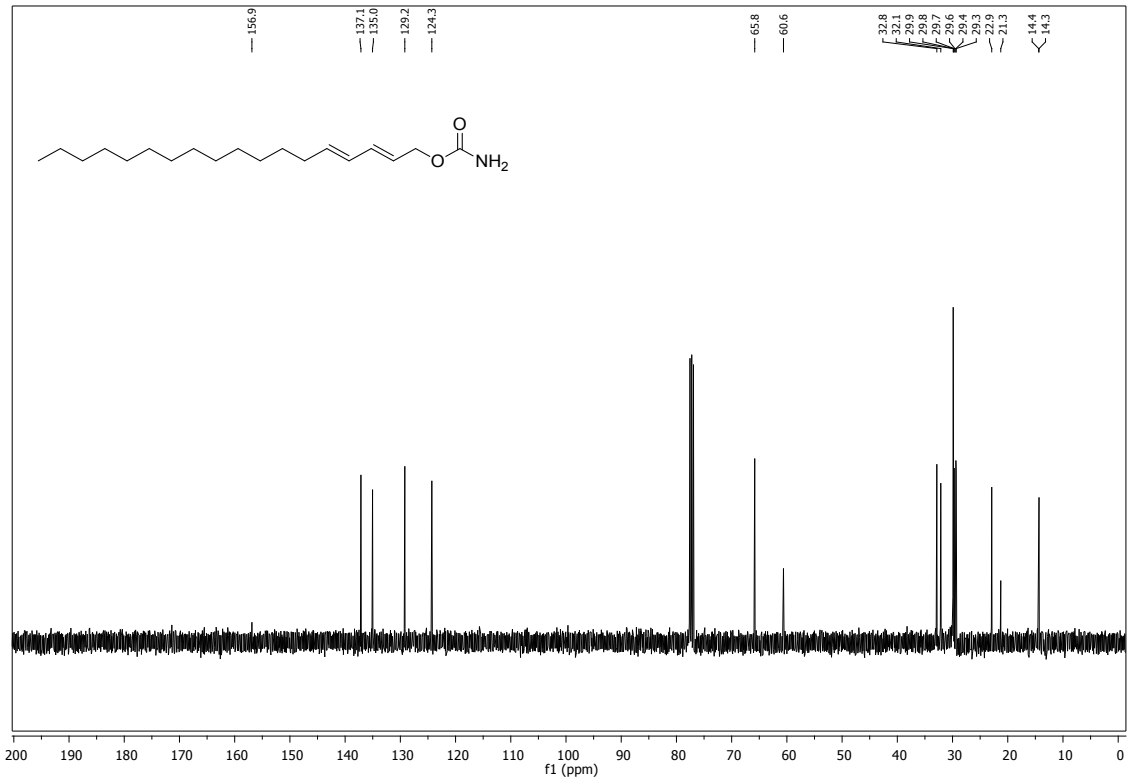




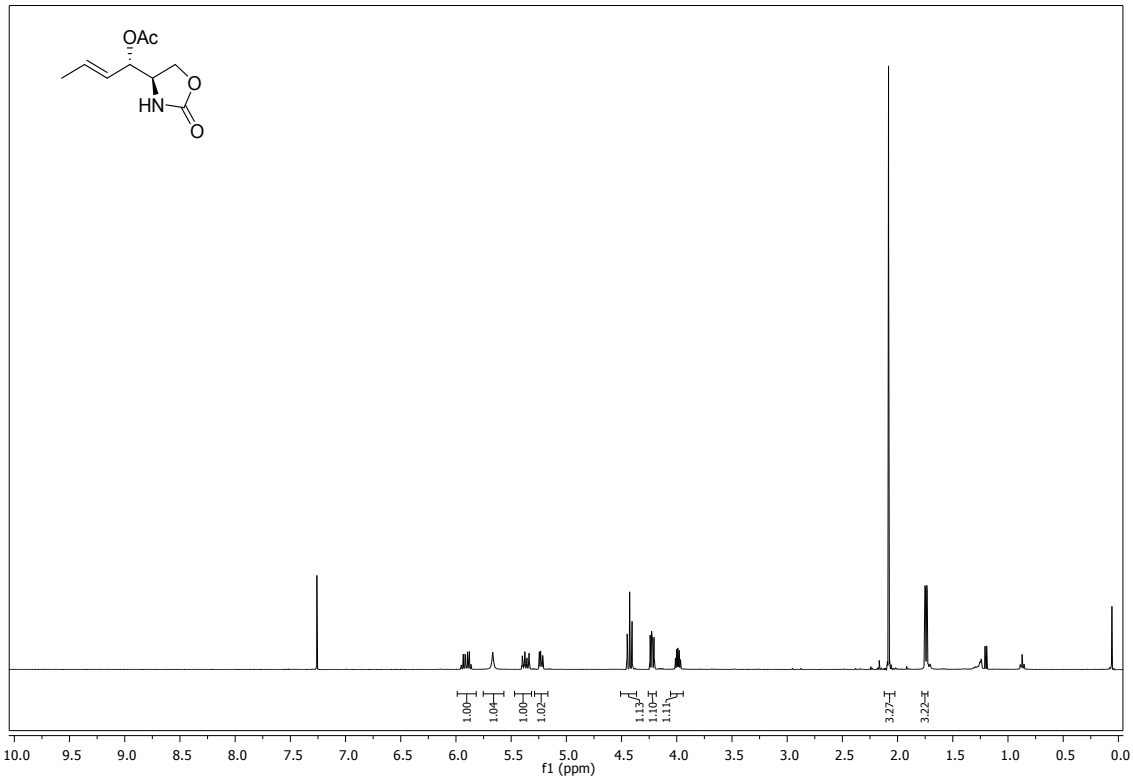
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (2*E*,4*E*)-octadeca-2,4-dien-1-yl carbamate (25).



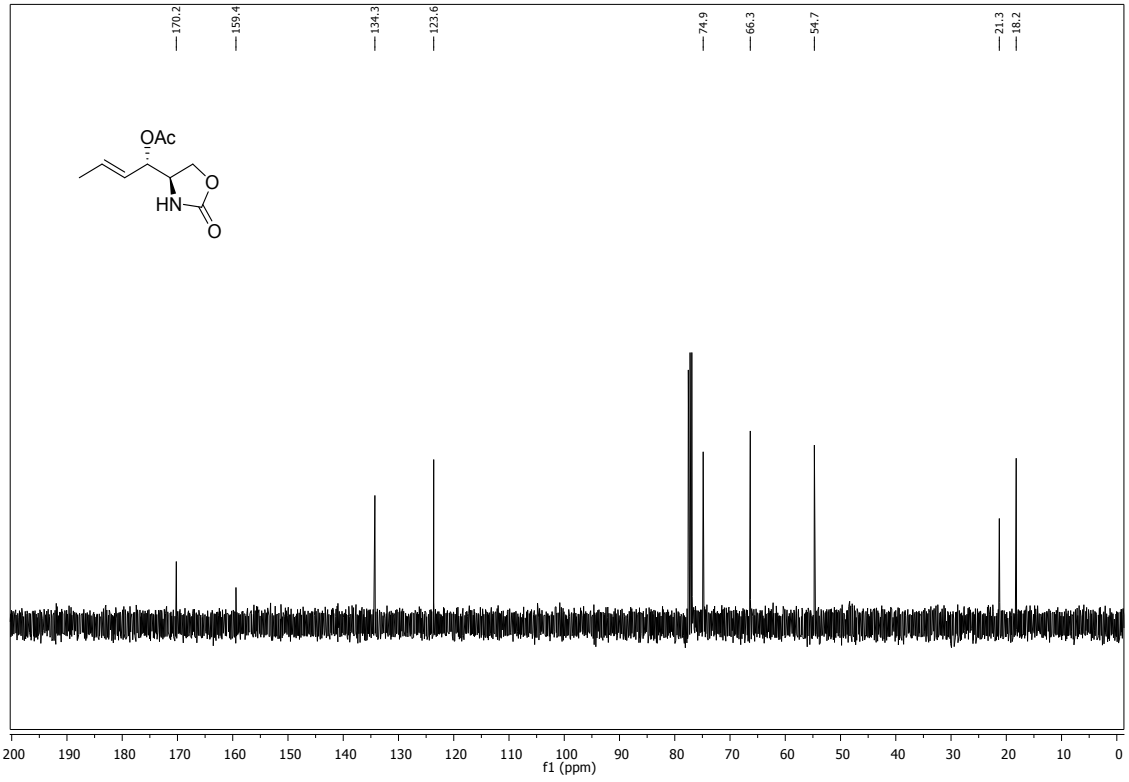
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (2*E*,4*E*)-octadeca-2,4-dien-1-yl carbamate (25).



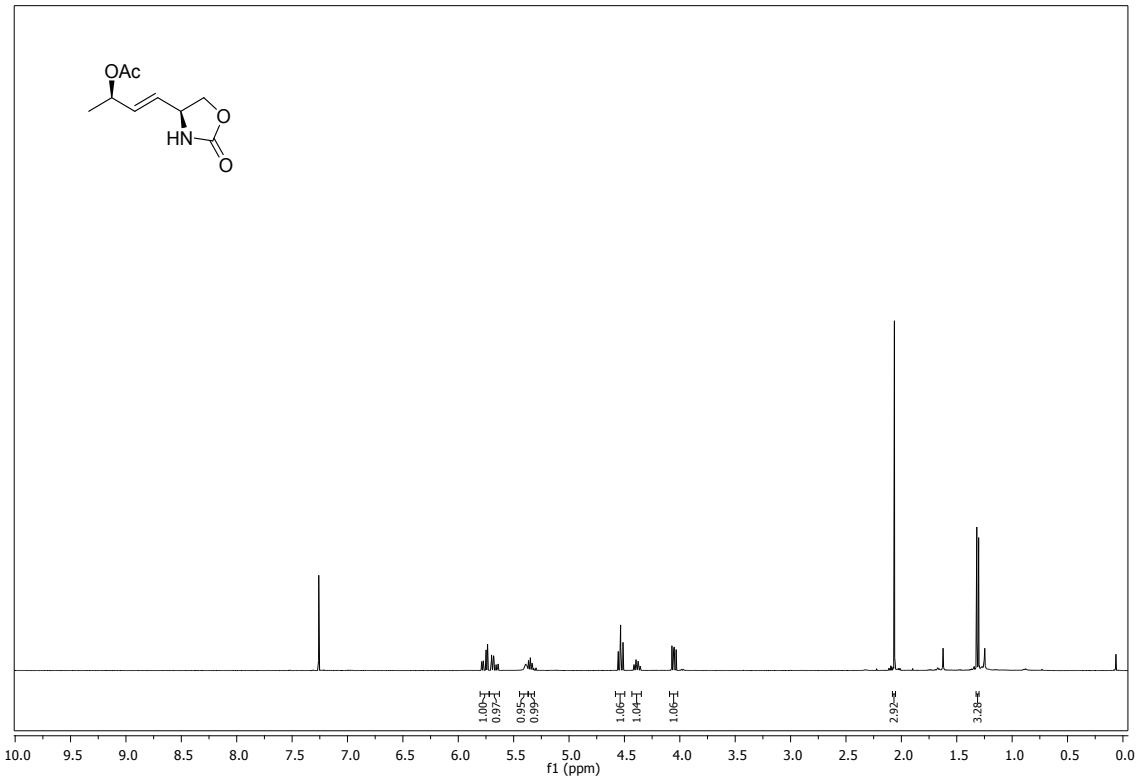
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl acetate (3a).



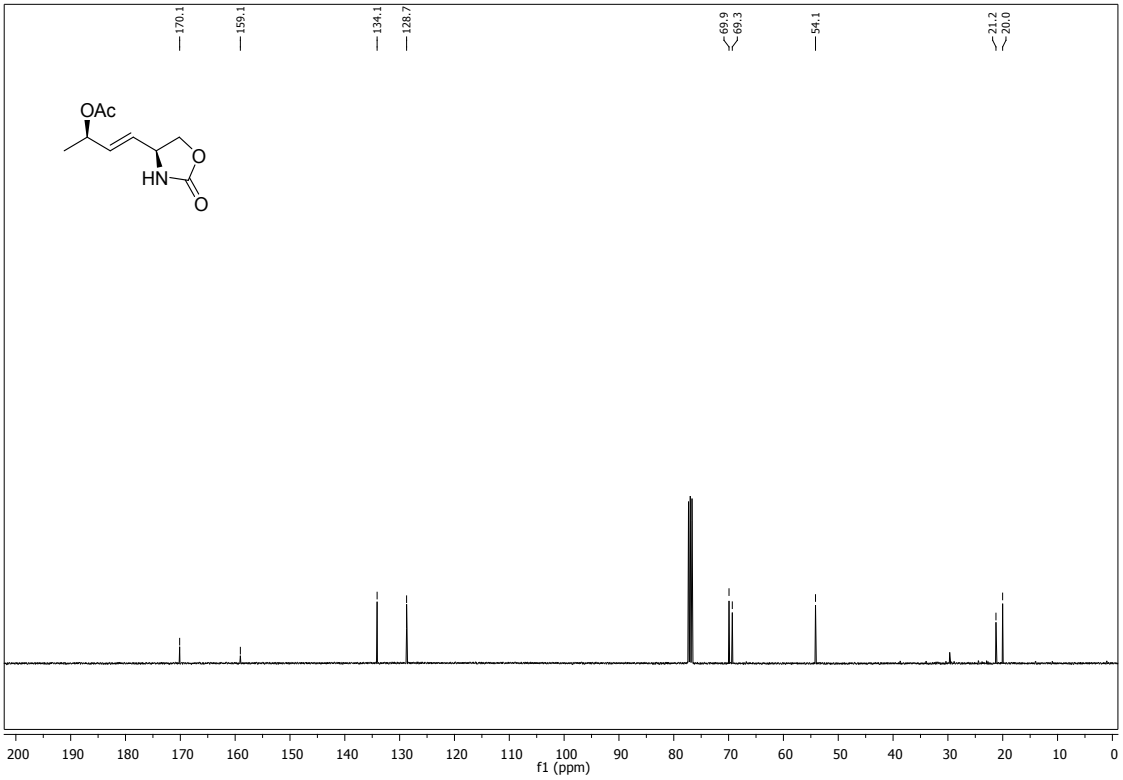
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl acetate (3a).



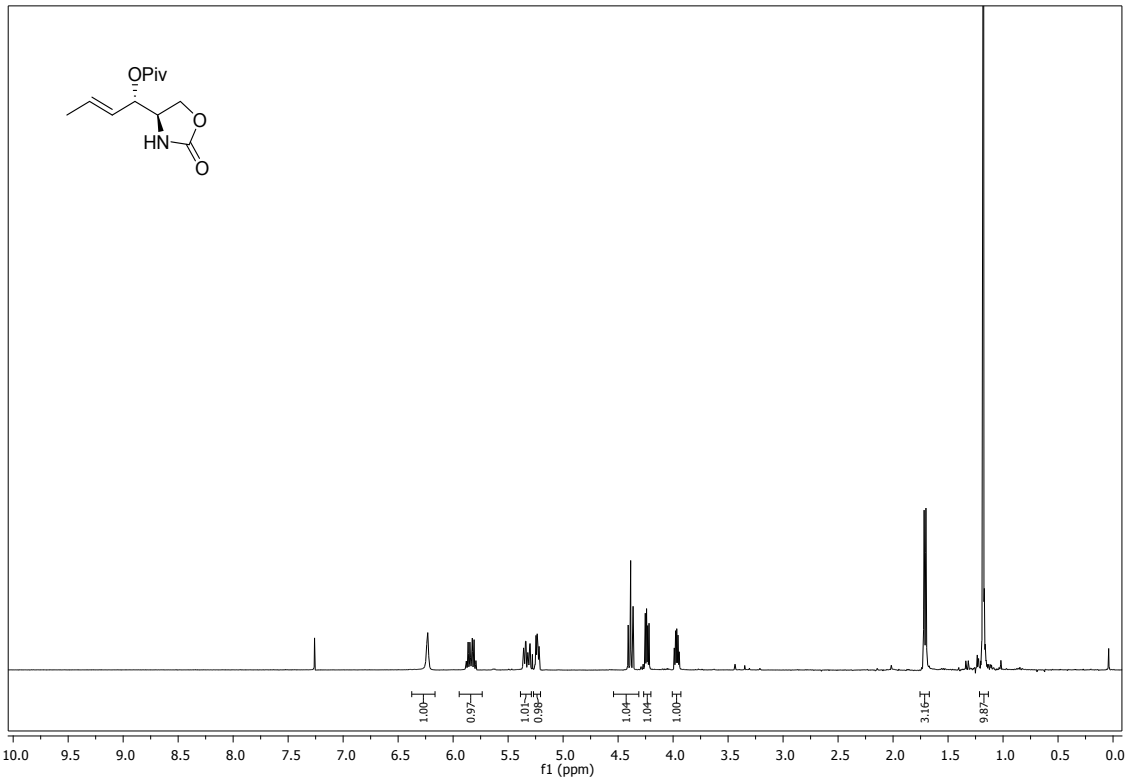
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (E)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (3b).



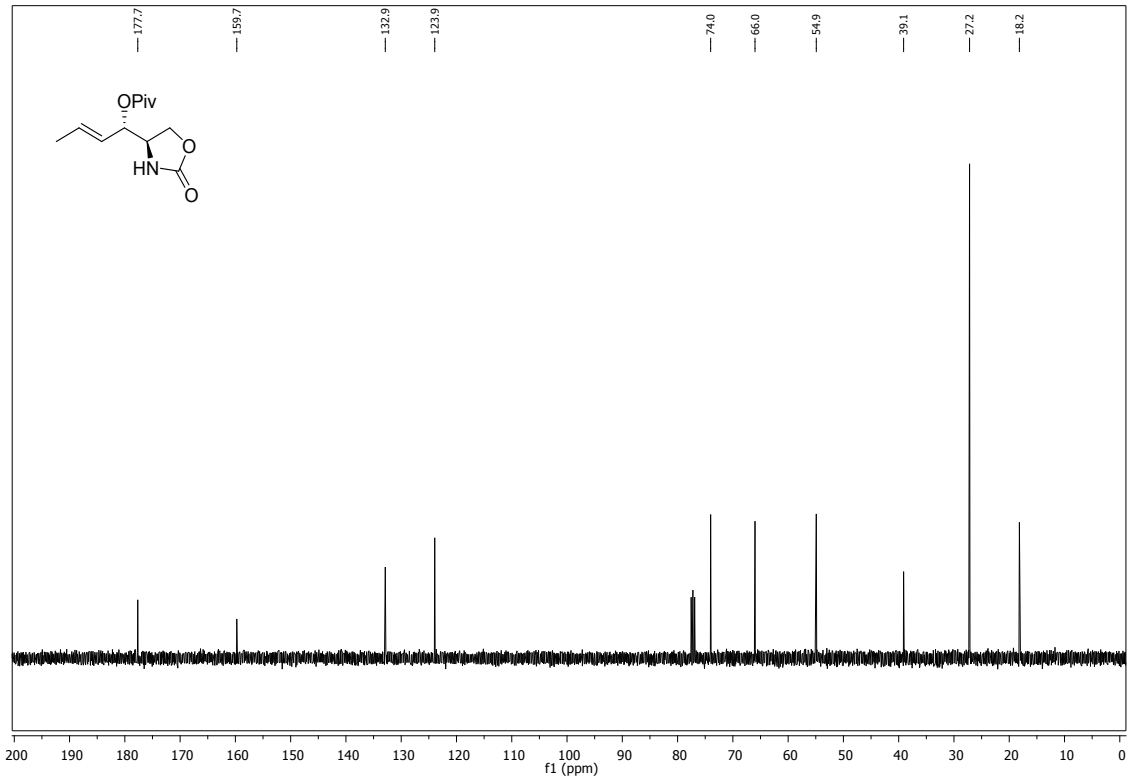
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (E)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (3b).



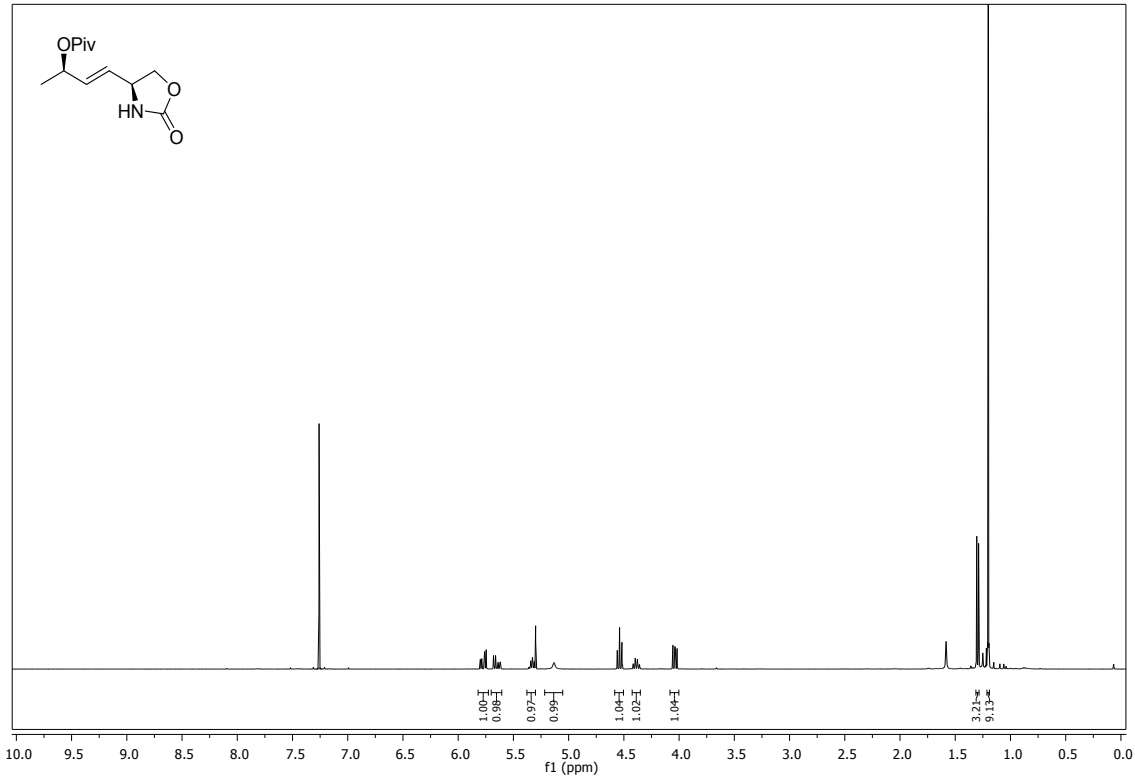
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (4a).



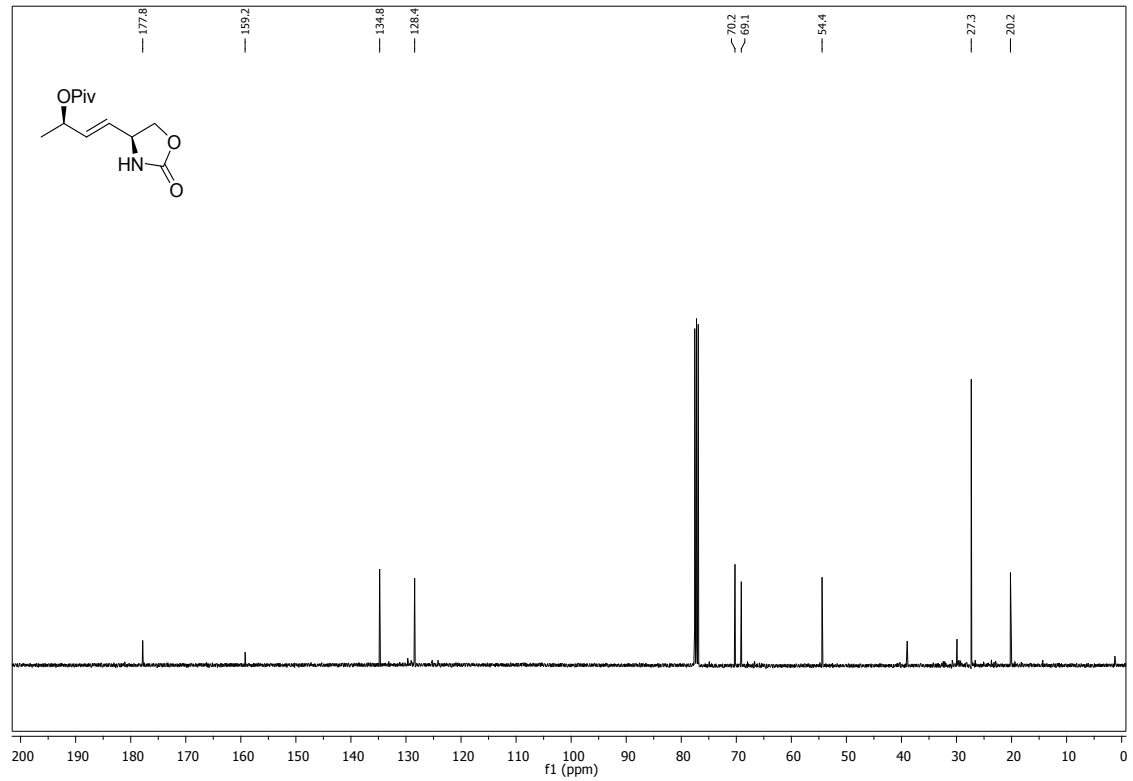
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (4a).



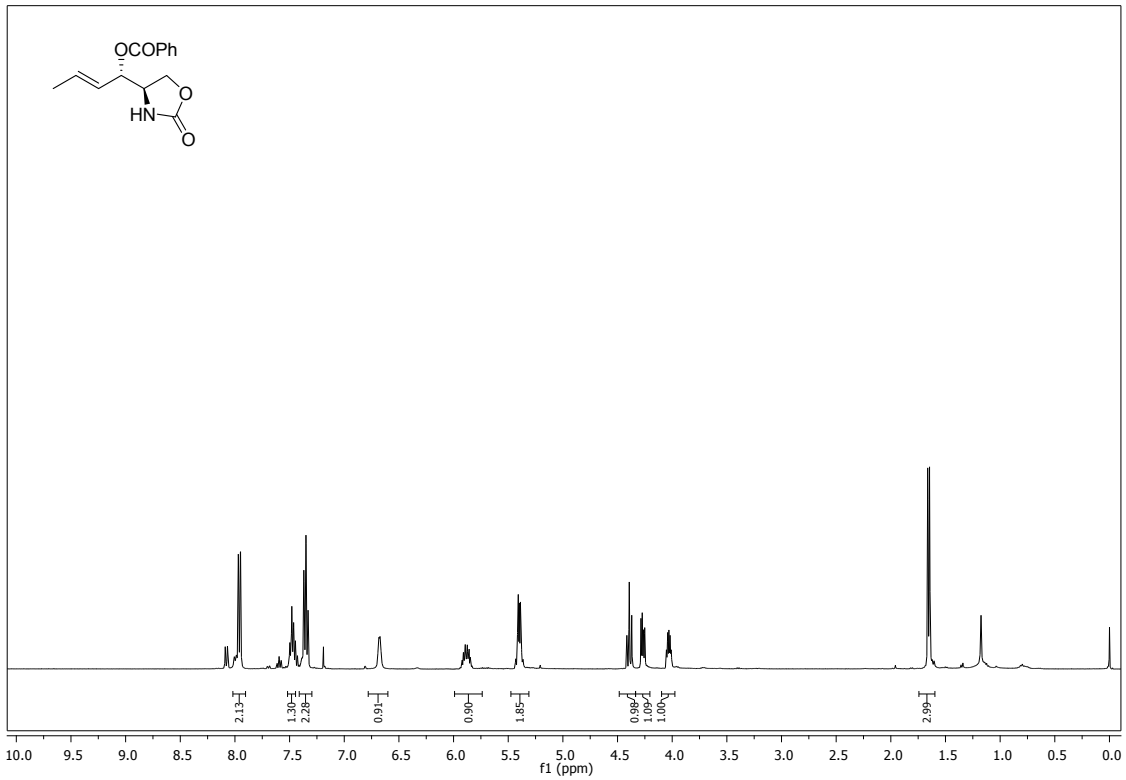
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl pivalate (4b).



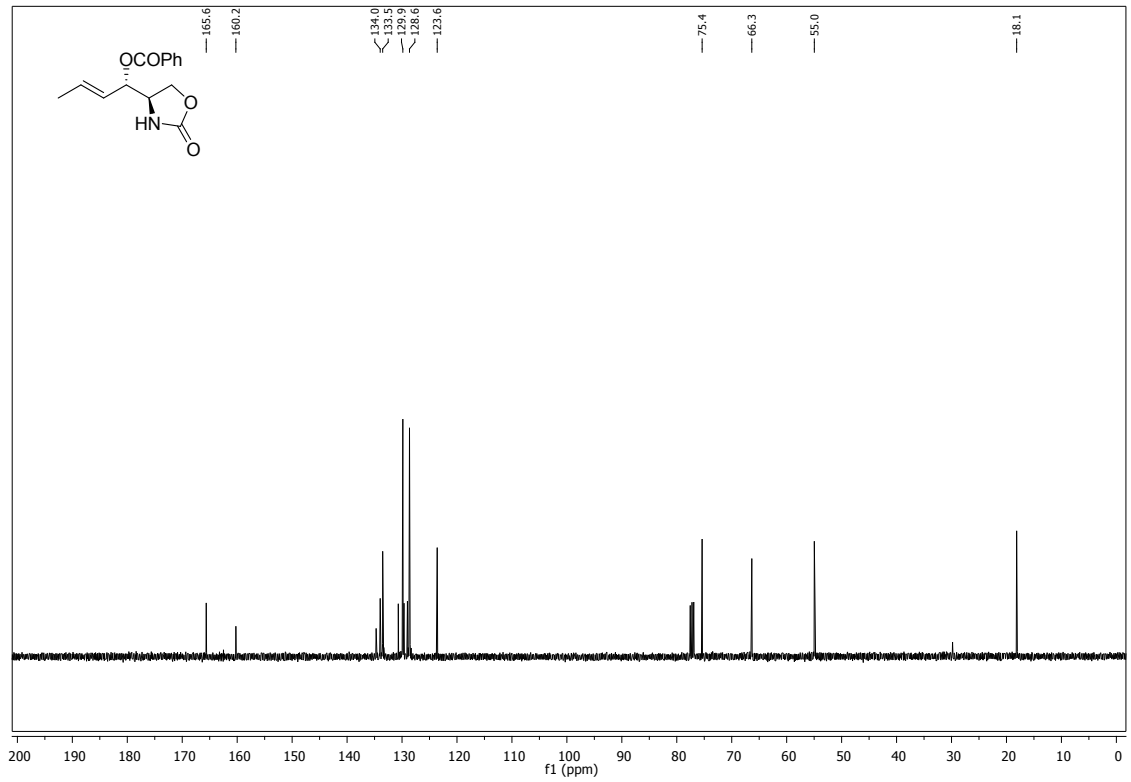
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl pivalate (4b).



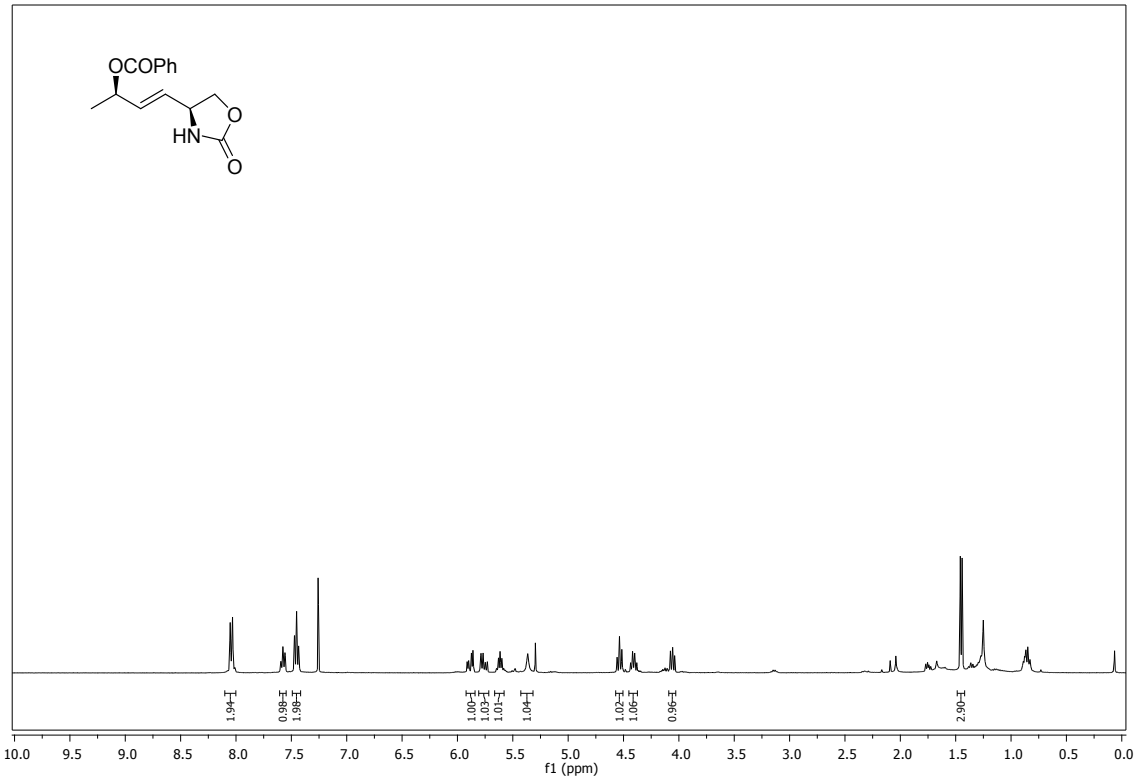
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl benzoate (5a).



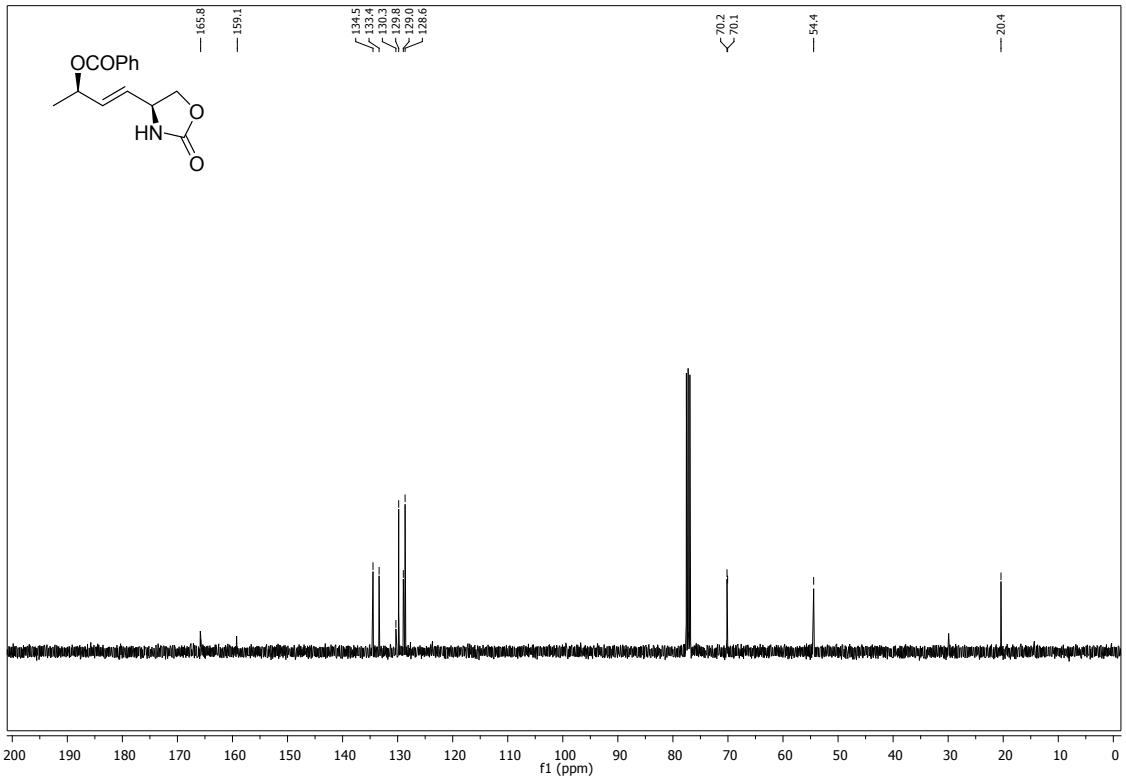
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl benzoate (5a).



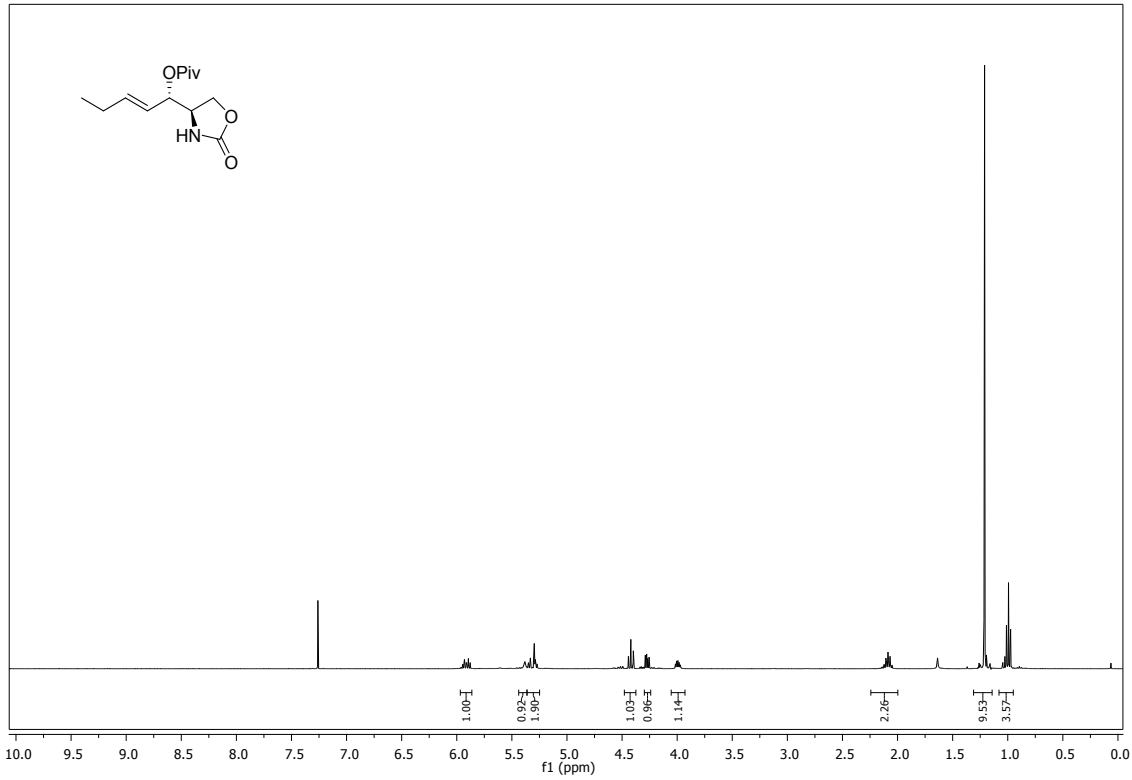
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl benzoate (5b).



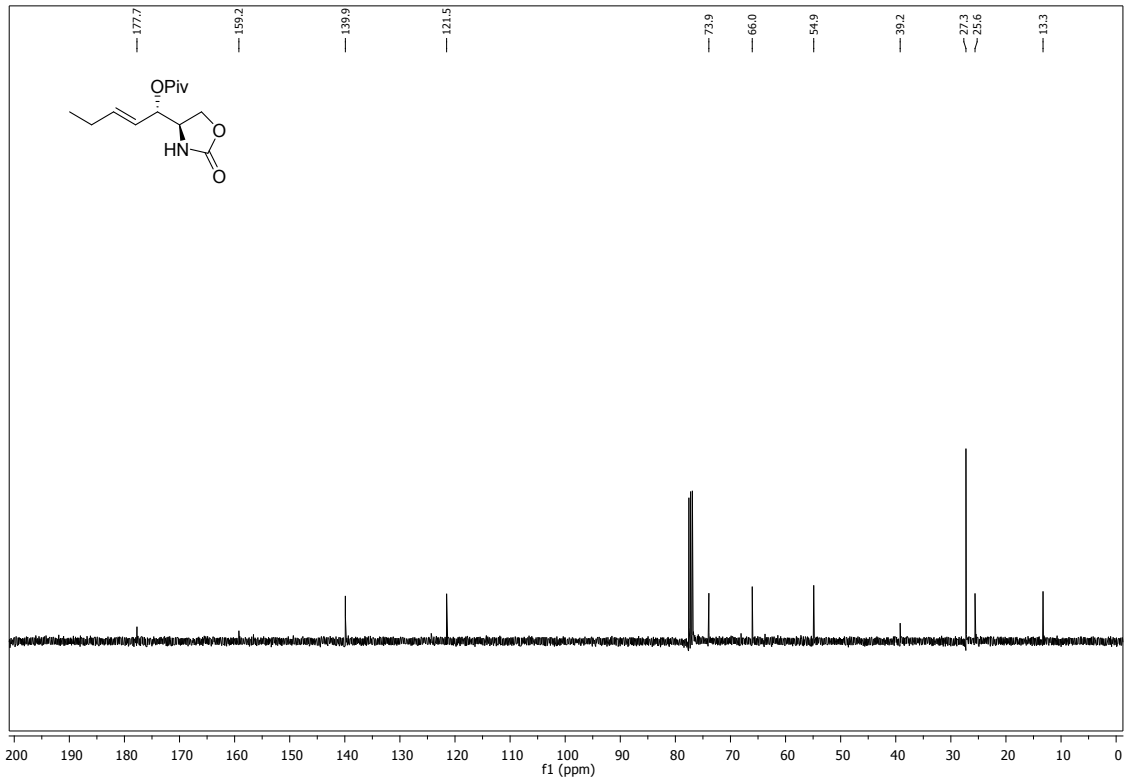
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (E)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl benzoate (5b).



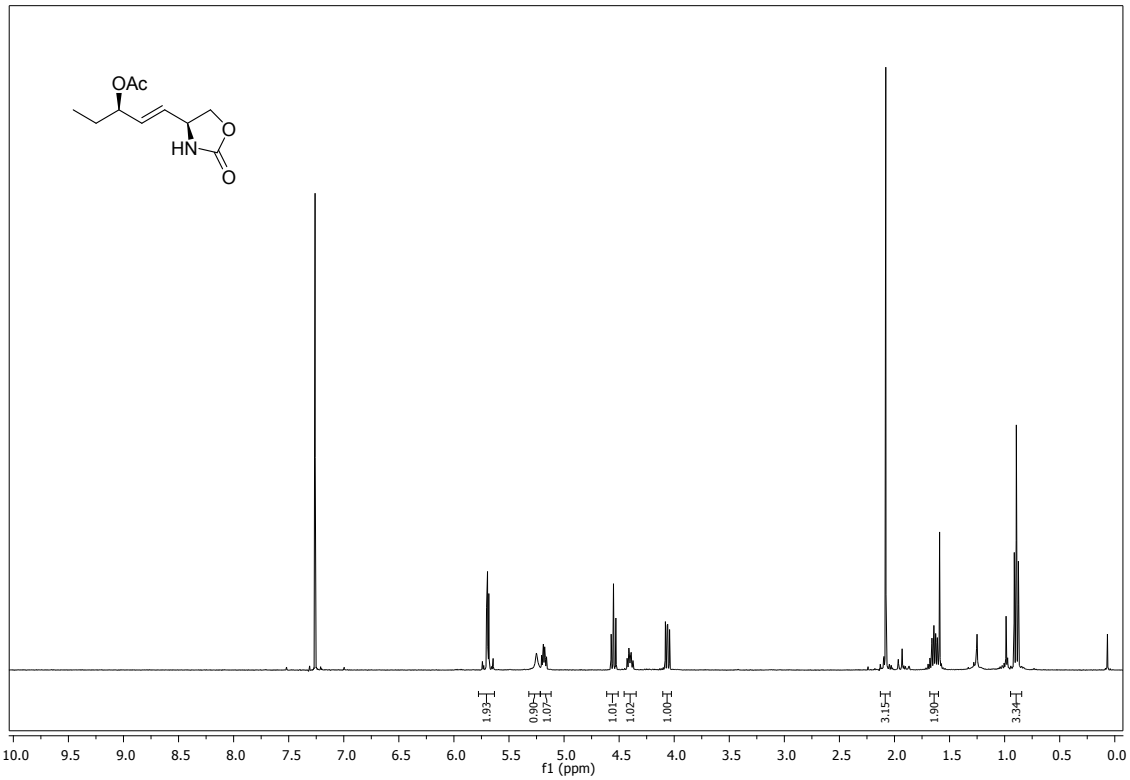
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)pent-2-en-1-yl pivalate (14a).



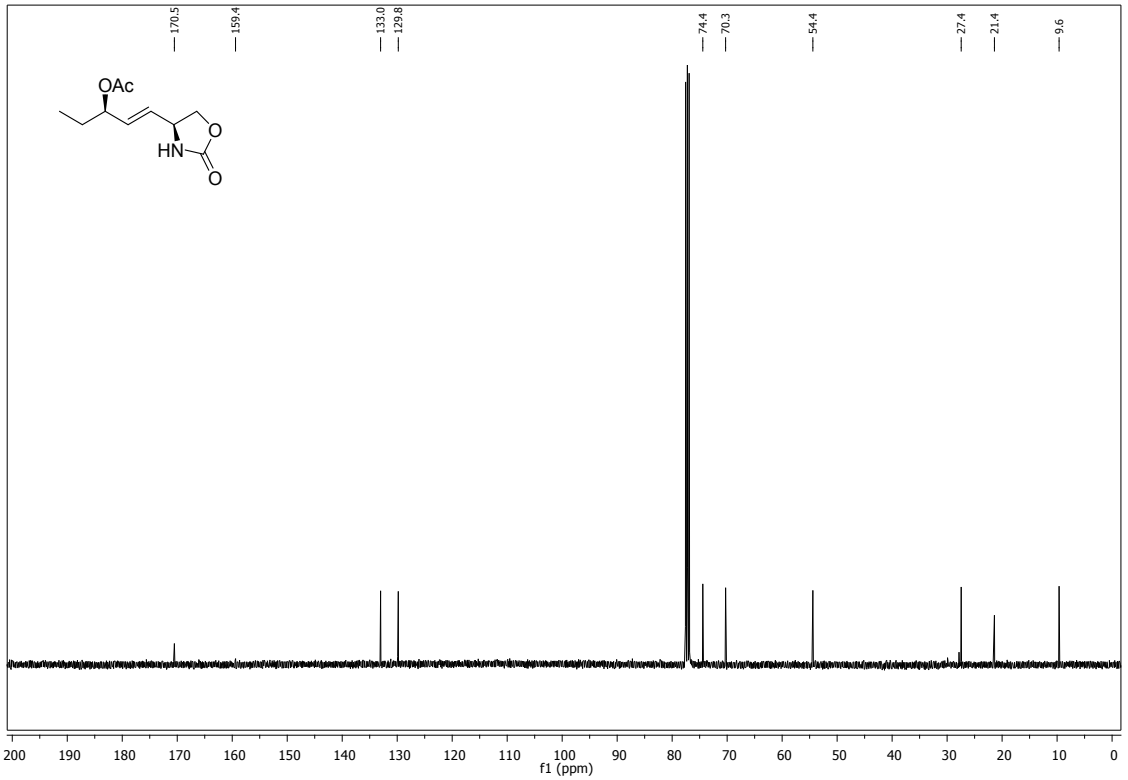
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)pent-2-en-1-yl pivalate (14a).



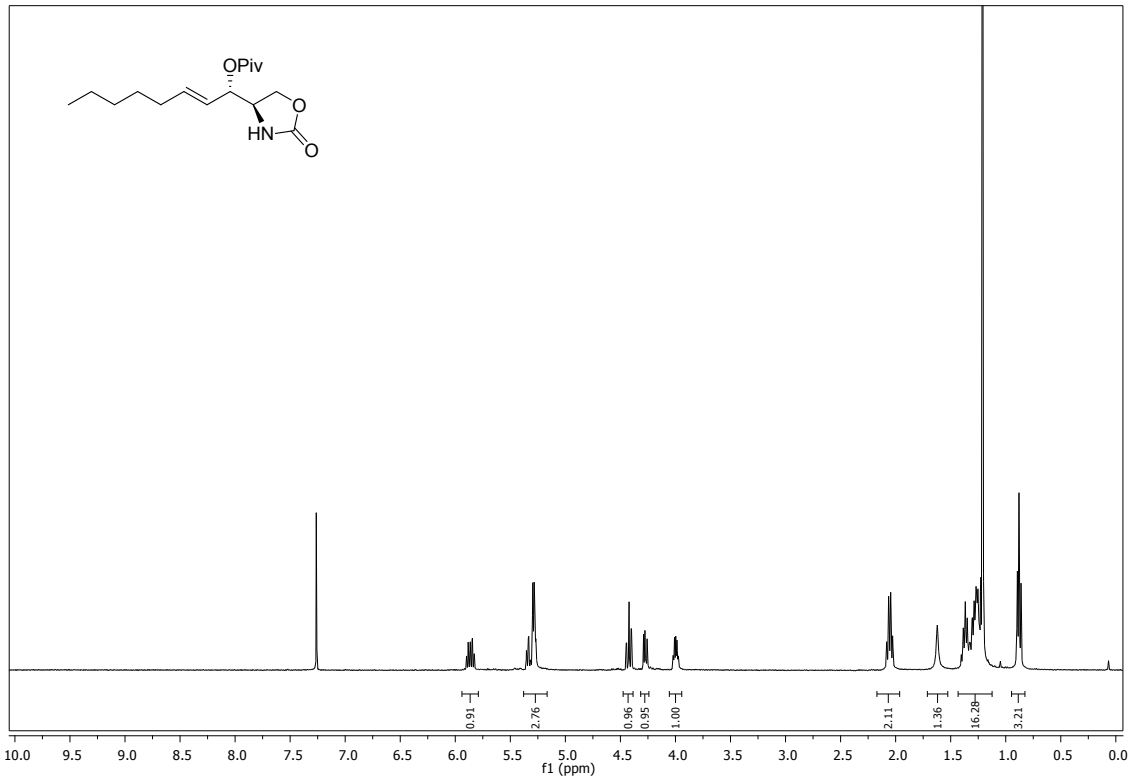
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)pent-1-en-3-yl acetate (15b).



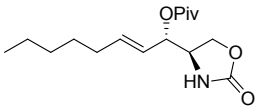
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)pent-1-en-3-yl acetate (15b).

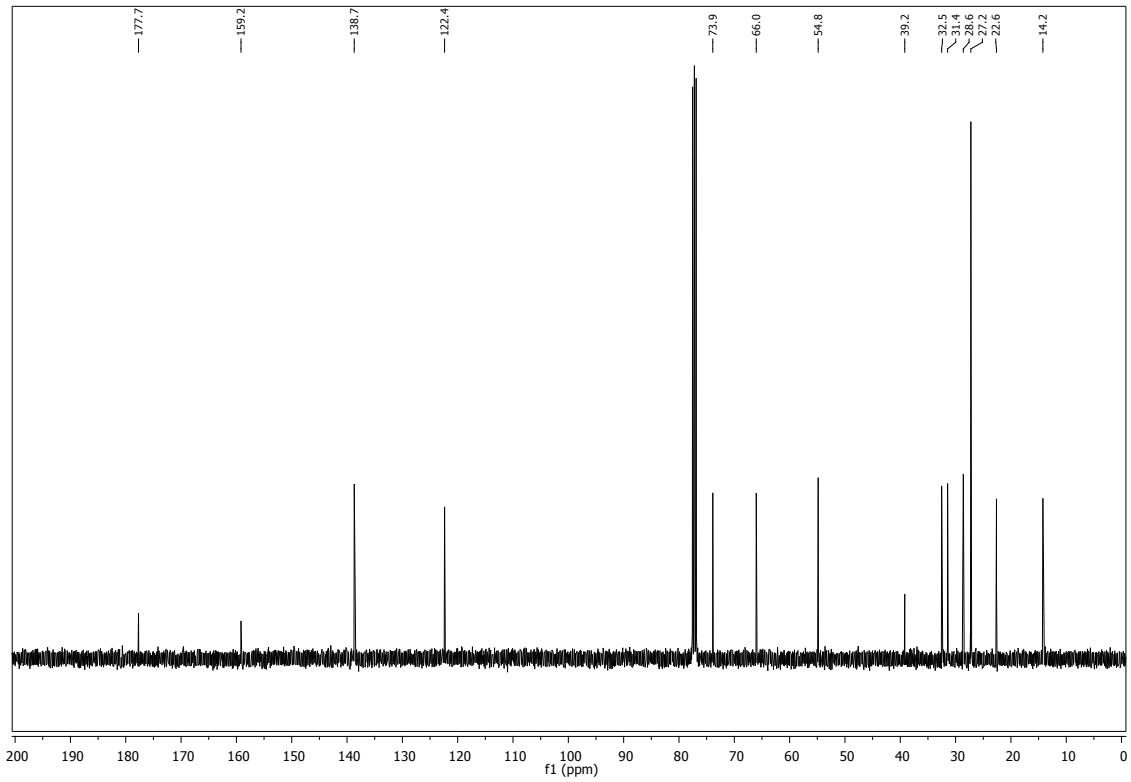


^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-2-en-1-yl pivalate (16a).

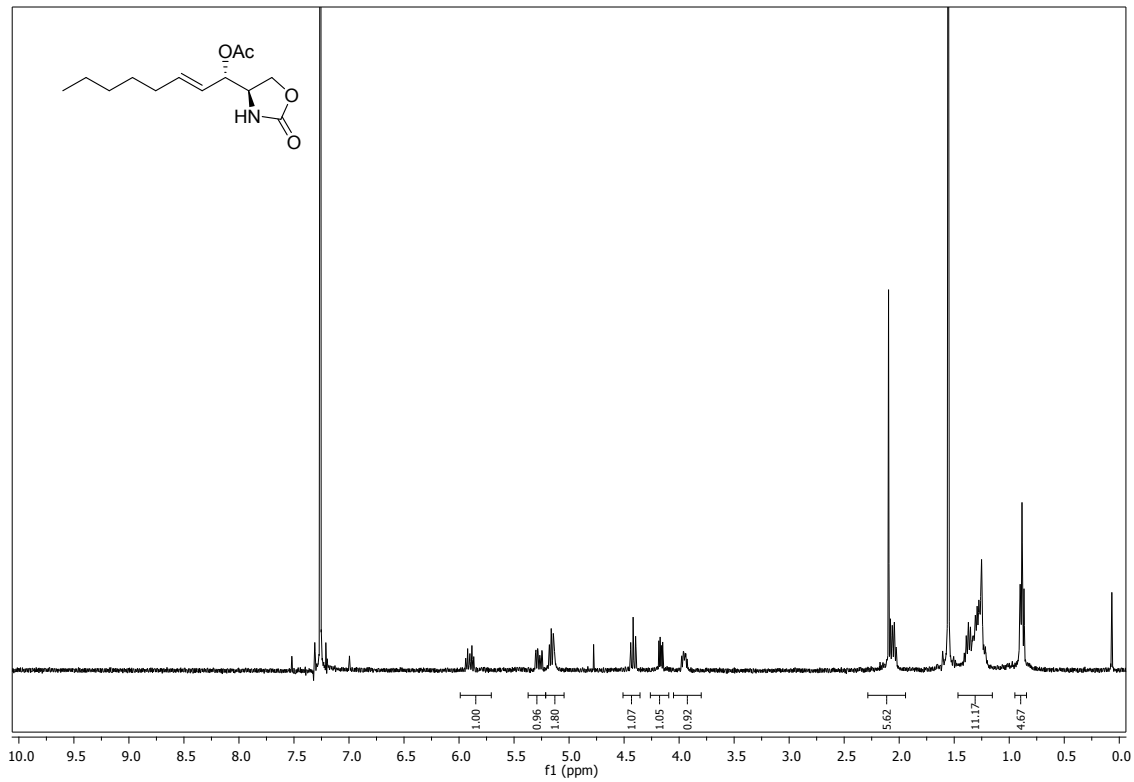


^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-2-en-1-yl pivalate (16a).

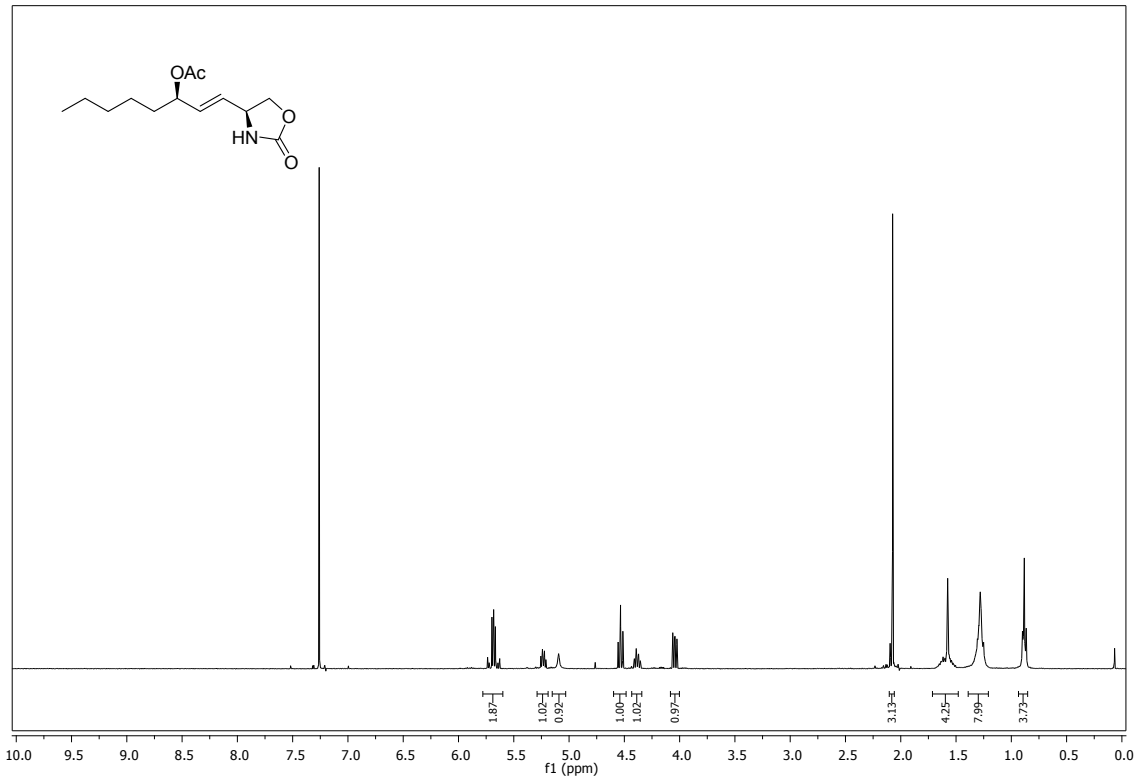




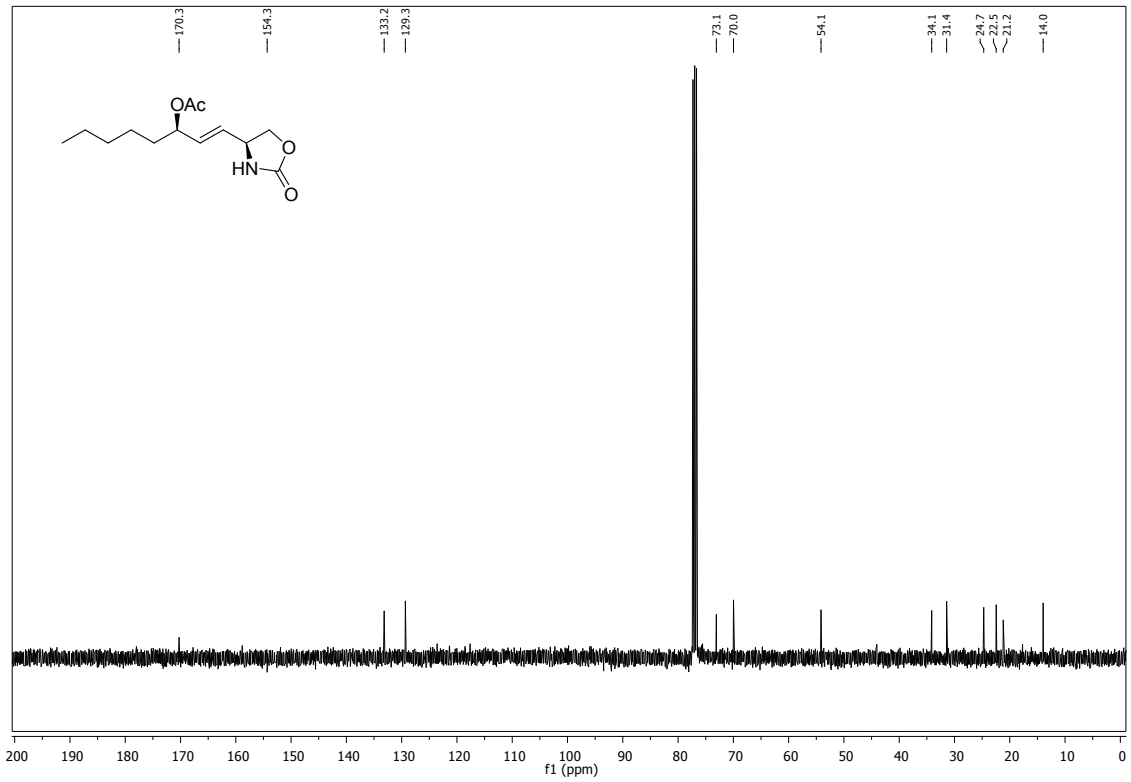
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-2-en-1-yl acetate (17a).



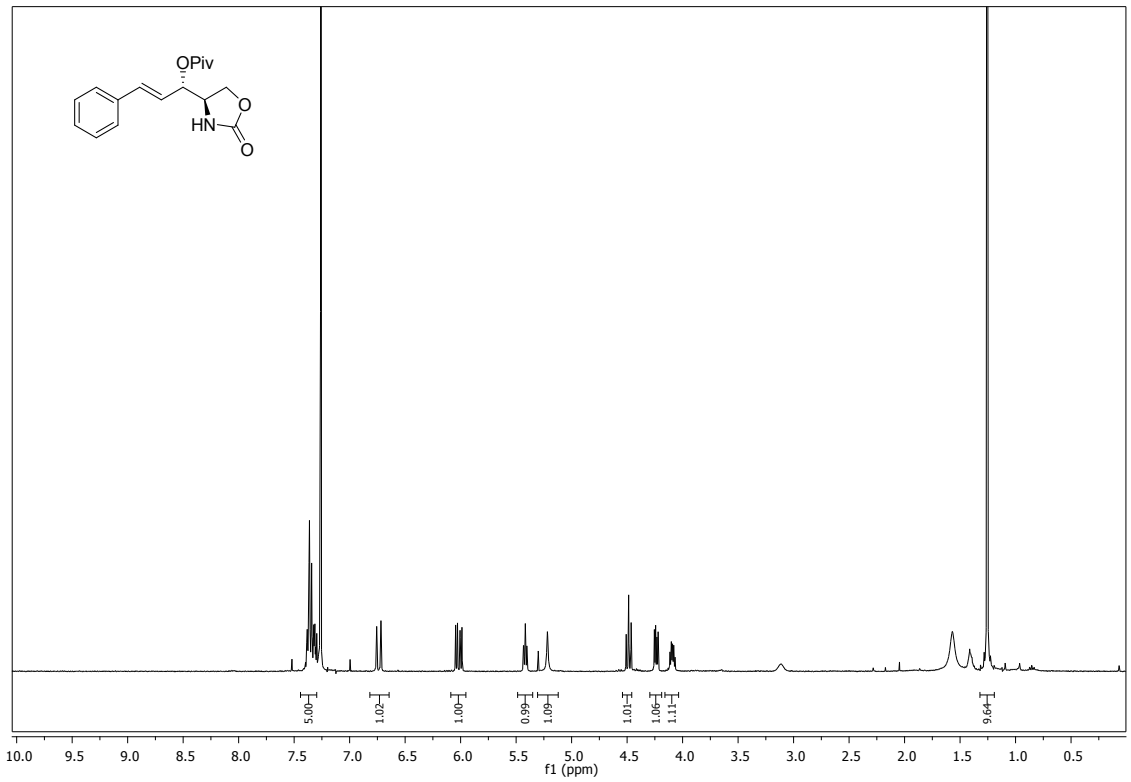
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-1-en-3-yl acetate (17b).



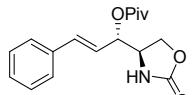
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)oct-1-en-3-yl acetate (17b).



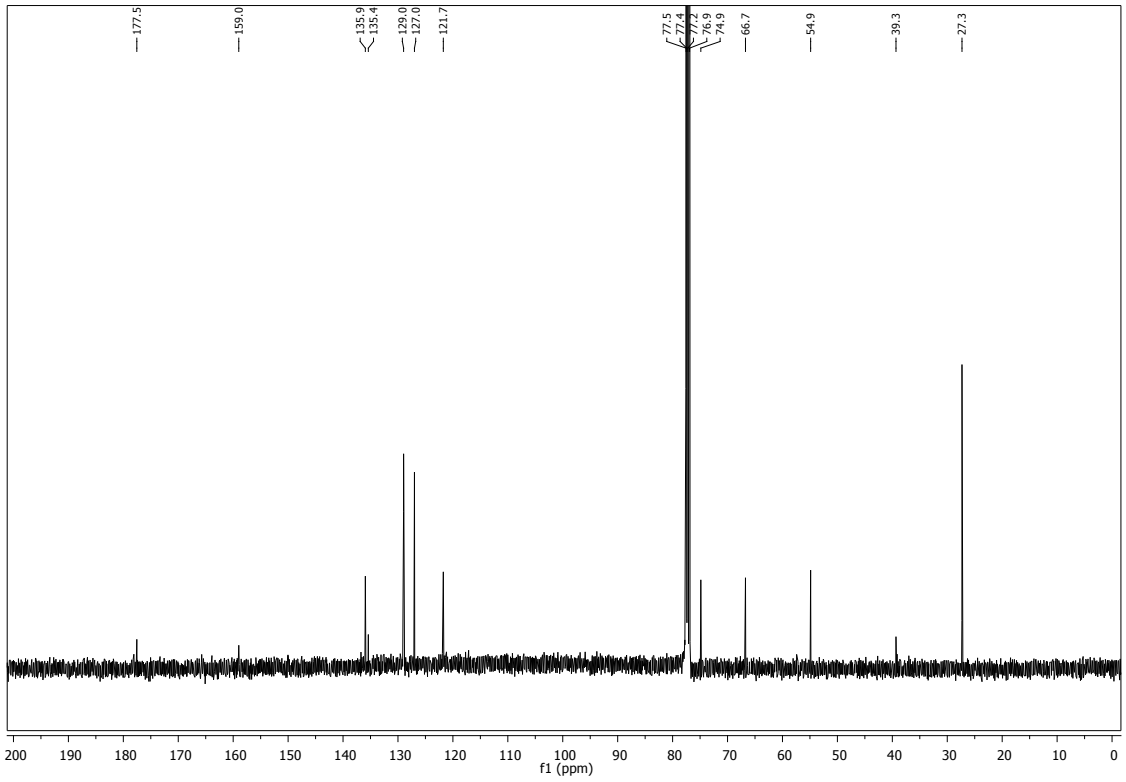
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)-3-phenylallyl pivalate (18a).



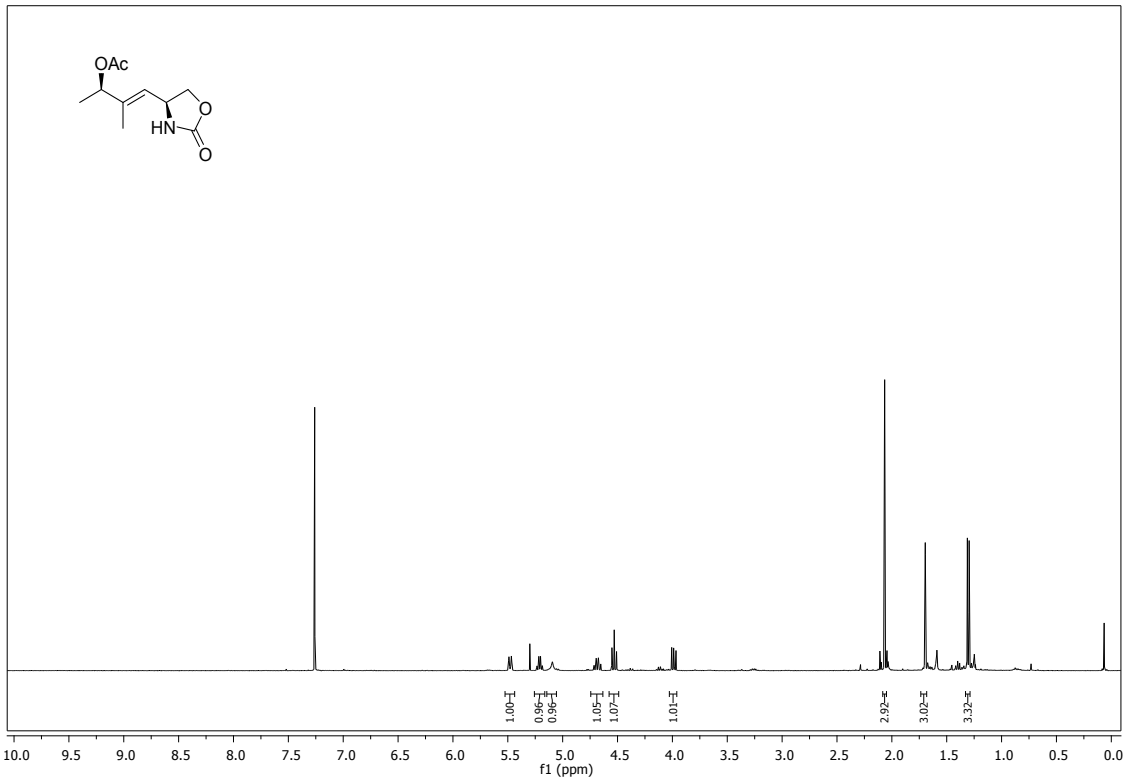
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)-3-



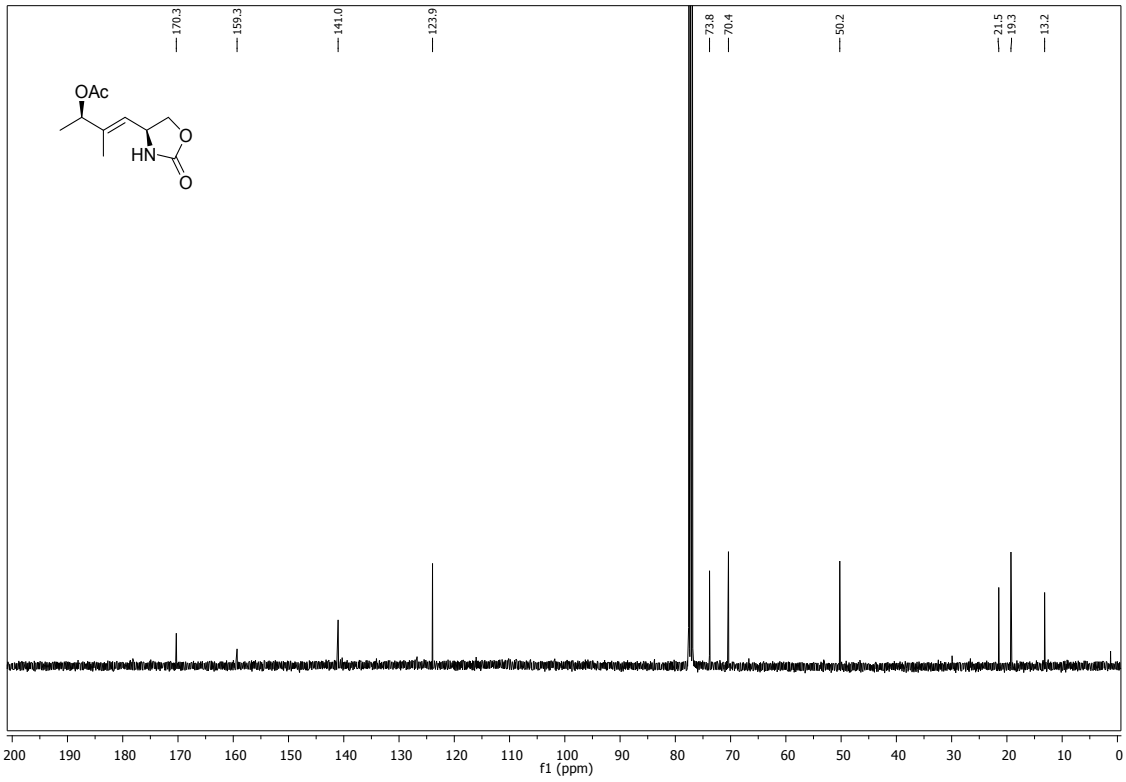
phenylallyl pivalate (18a).



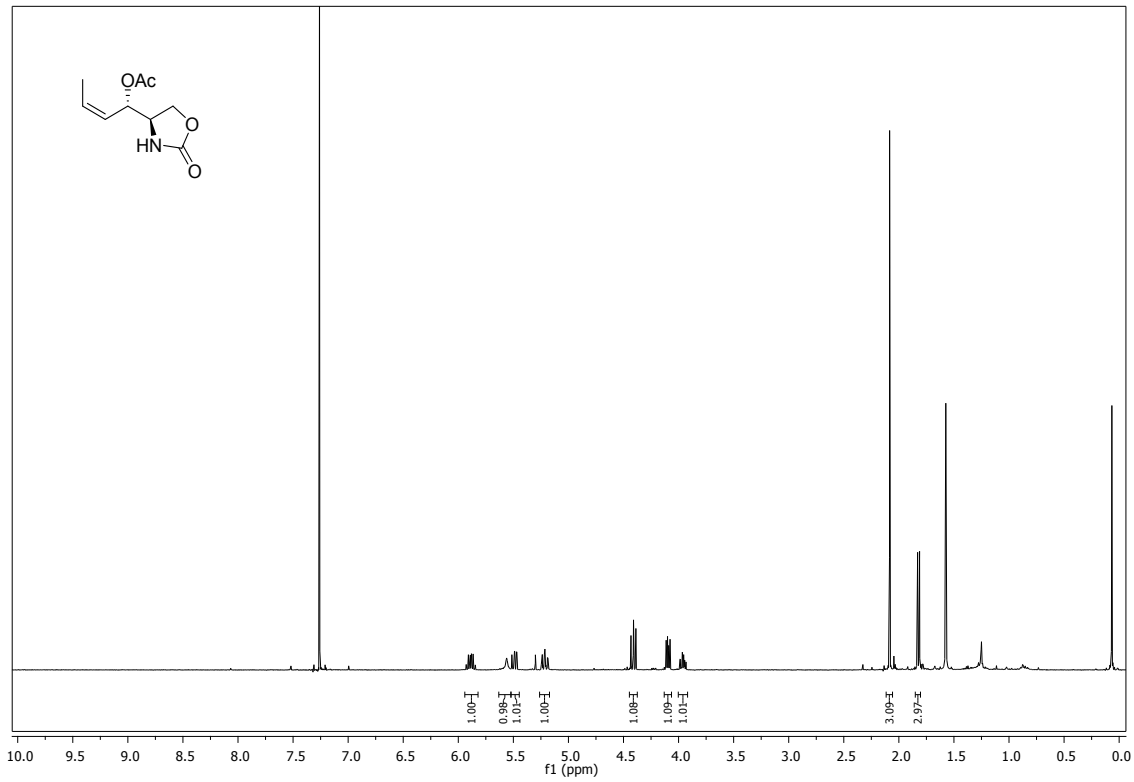
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-3-methyl-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (20b).



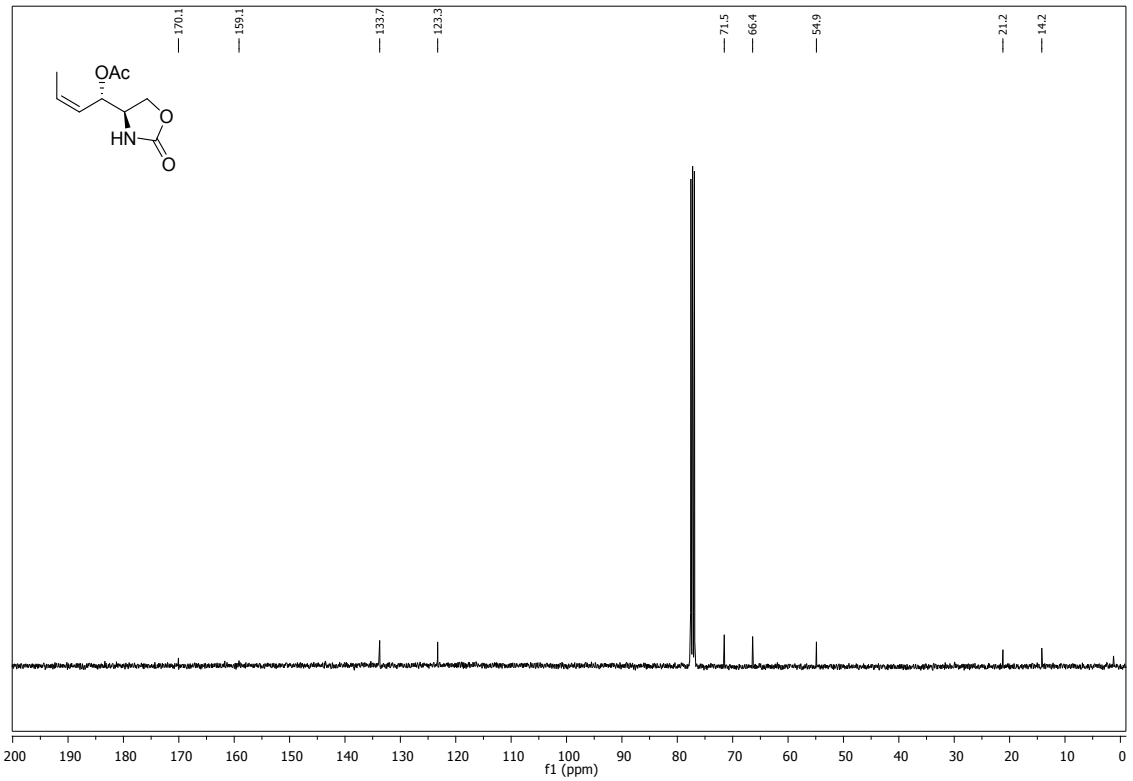
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-3-methyl-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (20b).



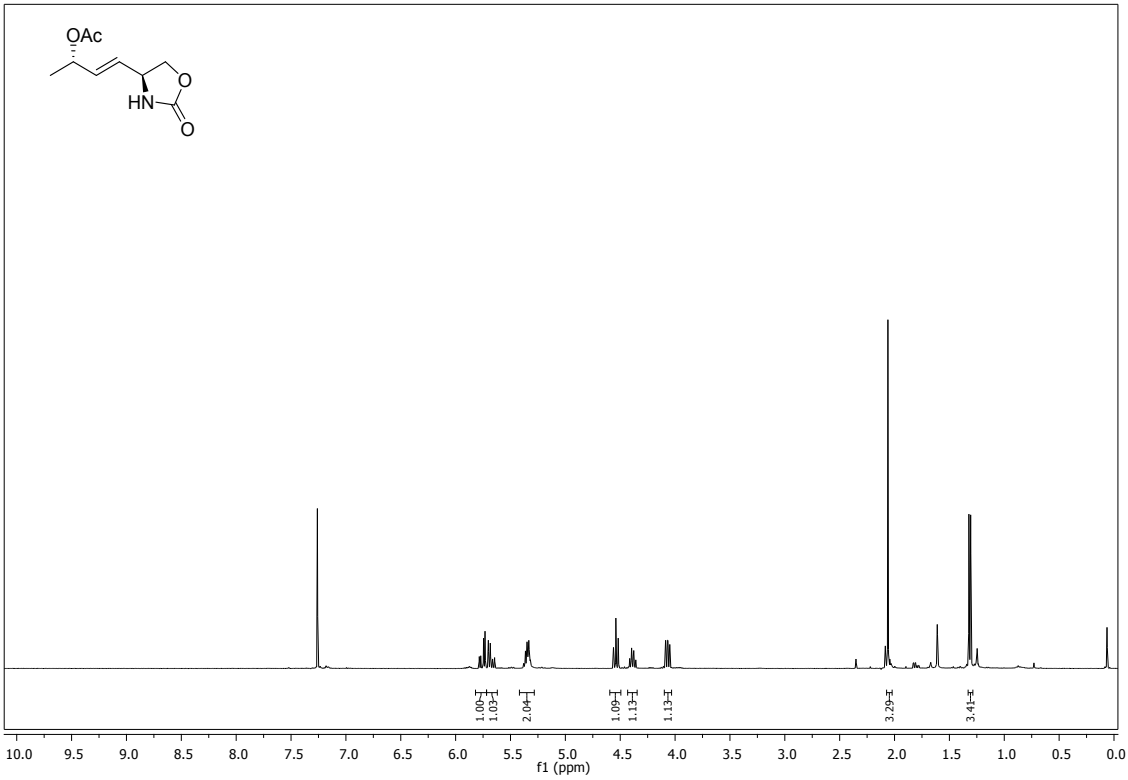
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*Z*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl acetate (22a).



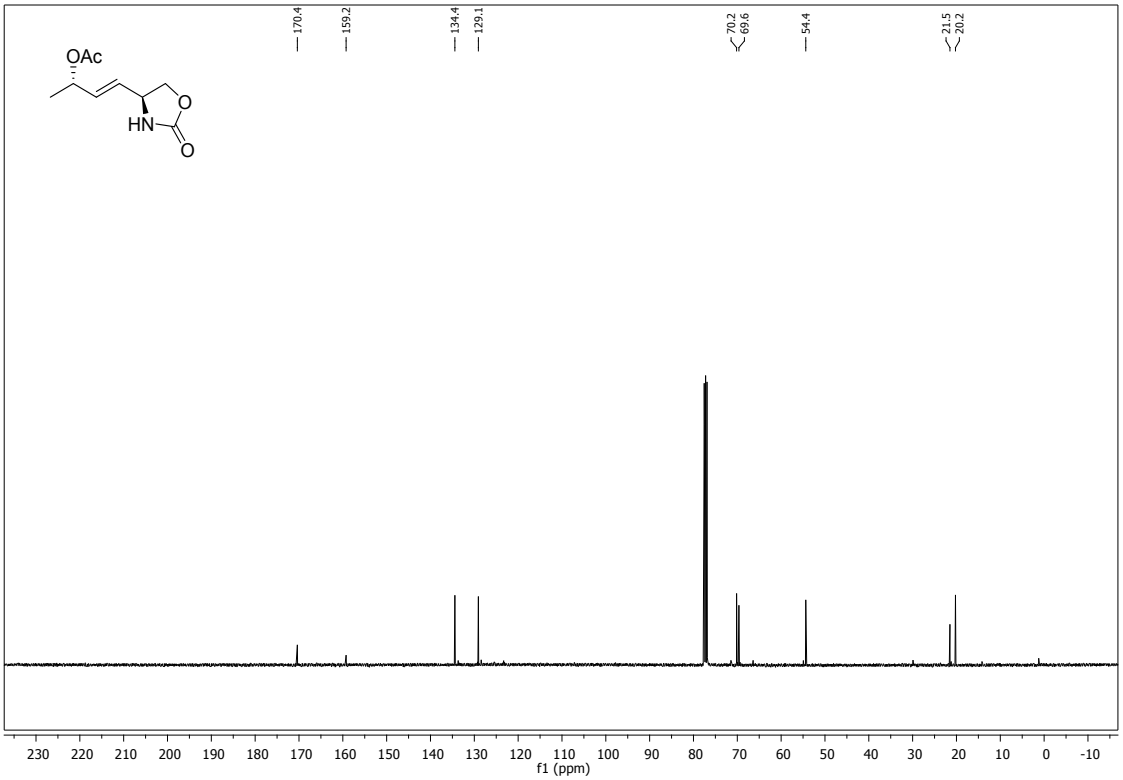
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*Z*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl acetate (22a).



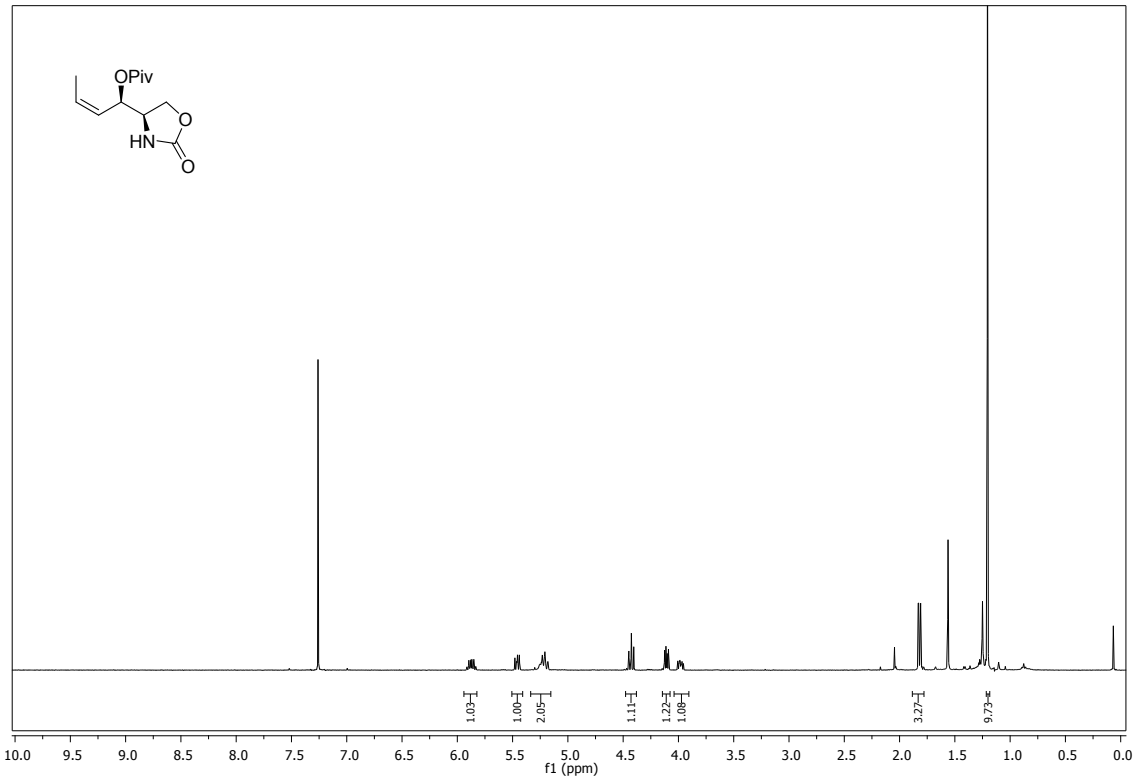
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (22b).



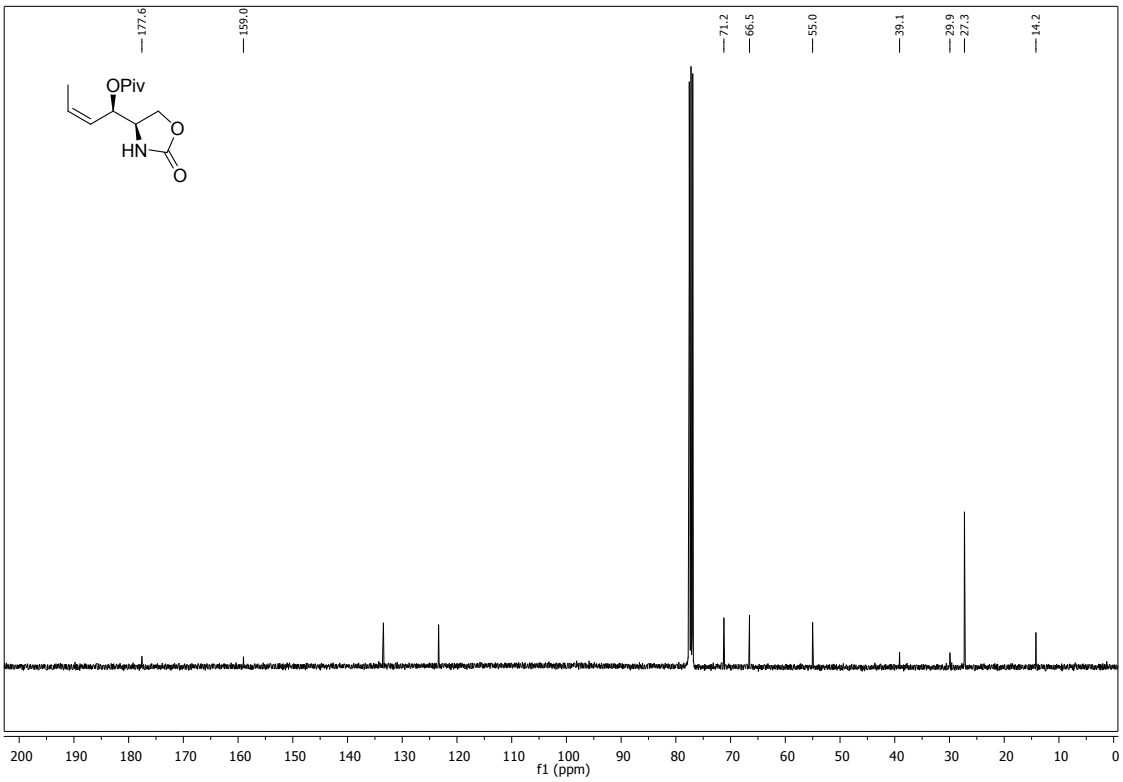
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-4-(2-Oxo-oxazolidin-4-yl)but-3-en-2-yl acetate (22b).



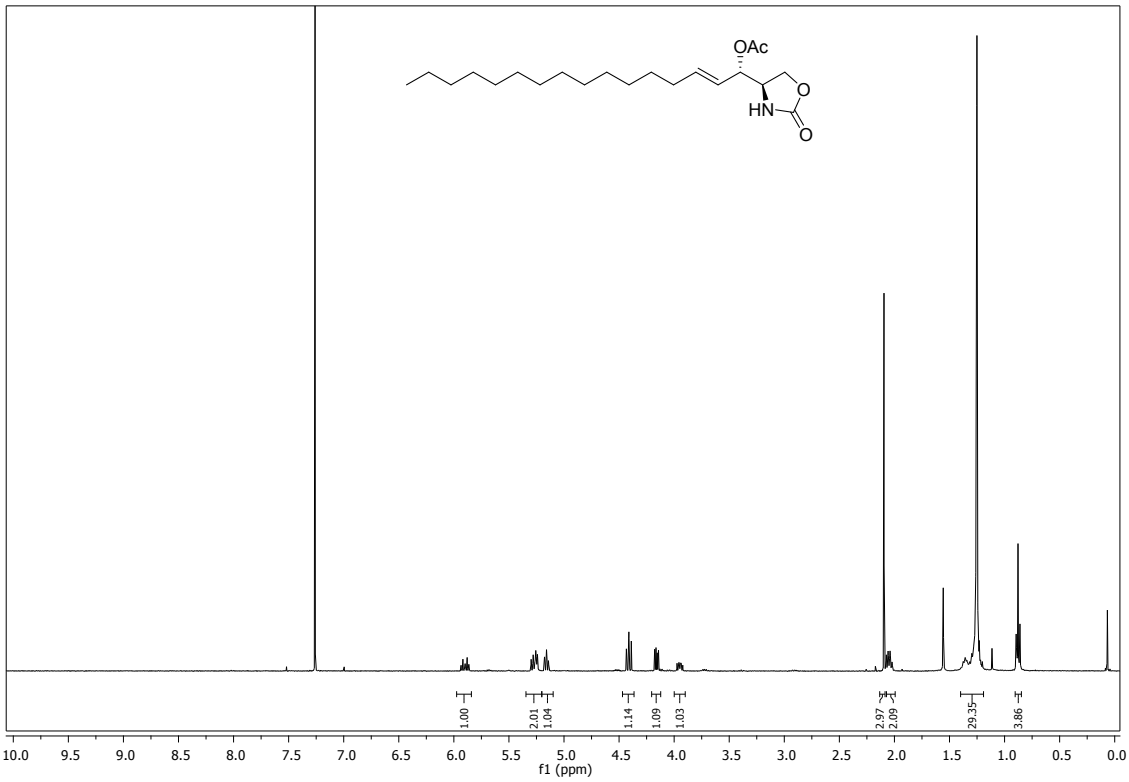
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*Z*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (23a).



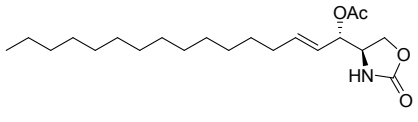
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*Z*)-1-(2-Oxo-oxazolidin-4-yl)but-2-en-1-yl pivalate (23a).

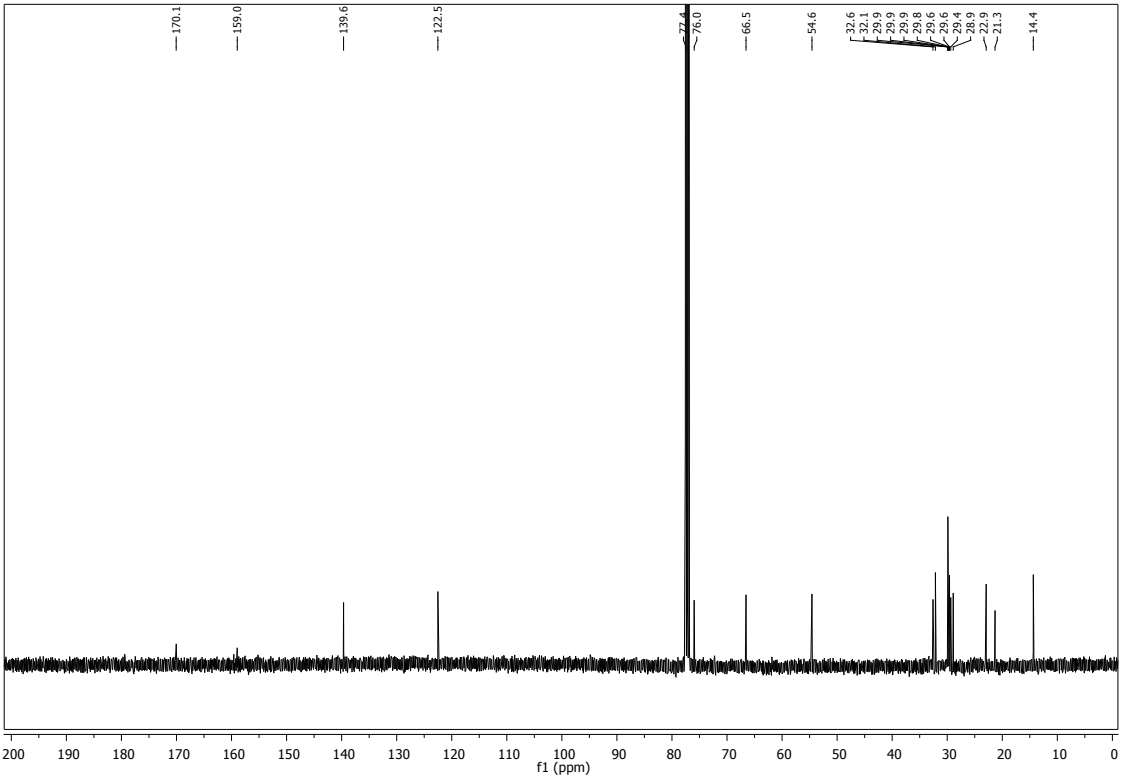


^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-2-en-1-yl acetate (27a).

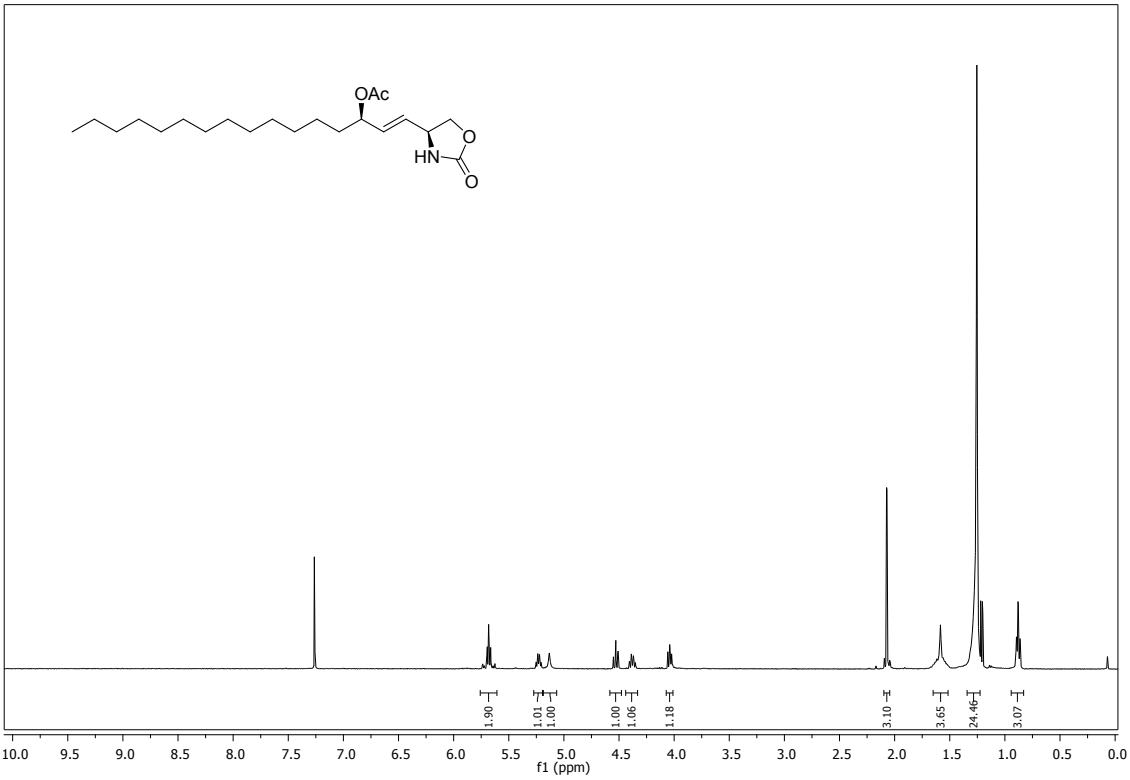


^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-2-en-1-yl acetate (27a)

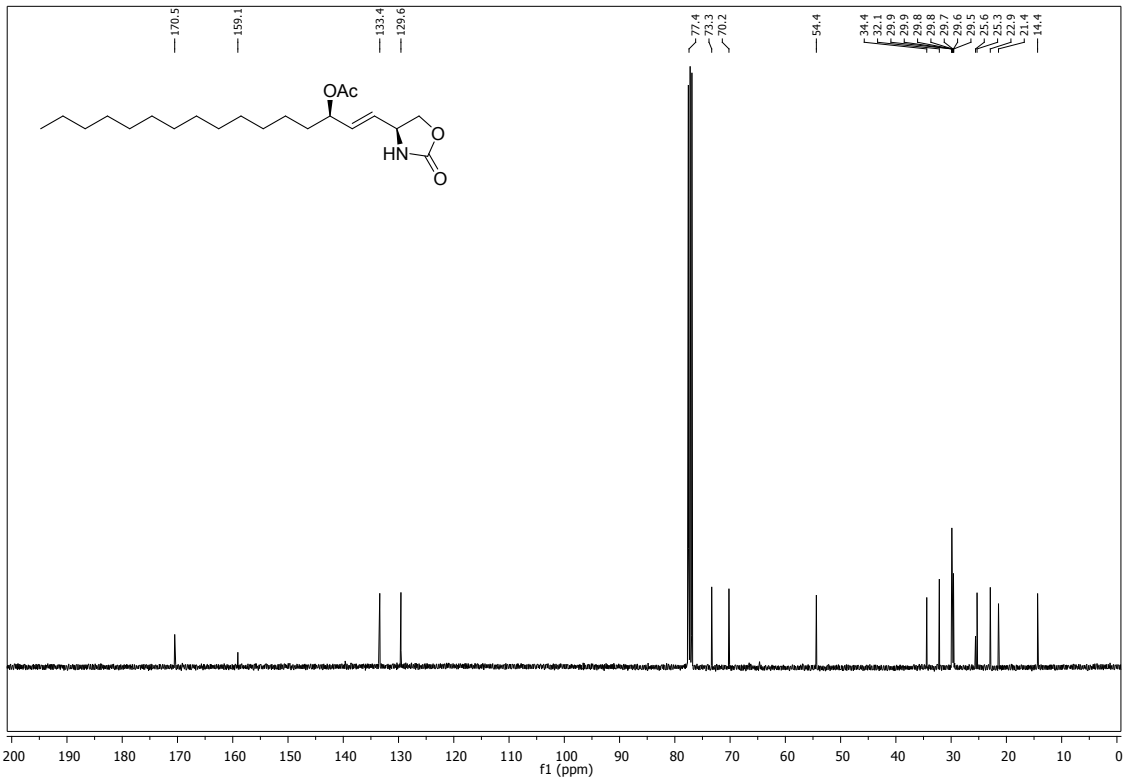




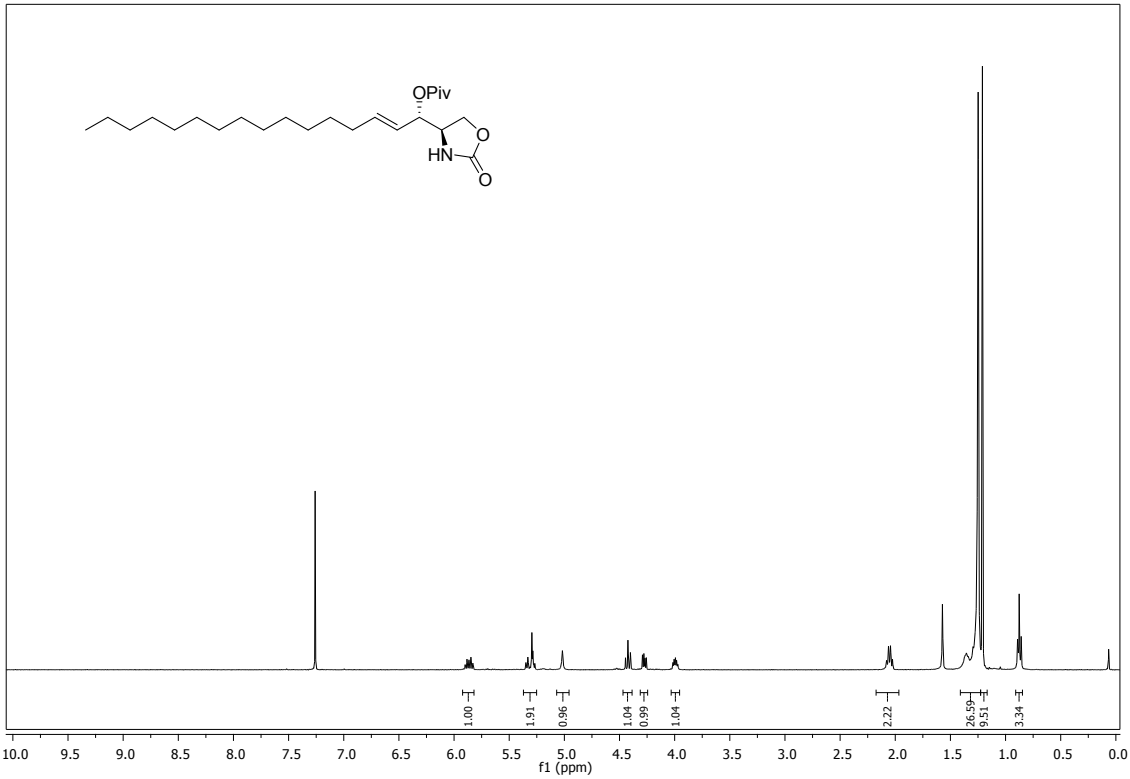
^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-1-en-3-yl acetate (27b).



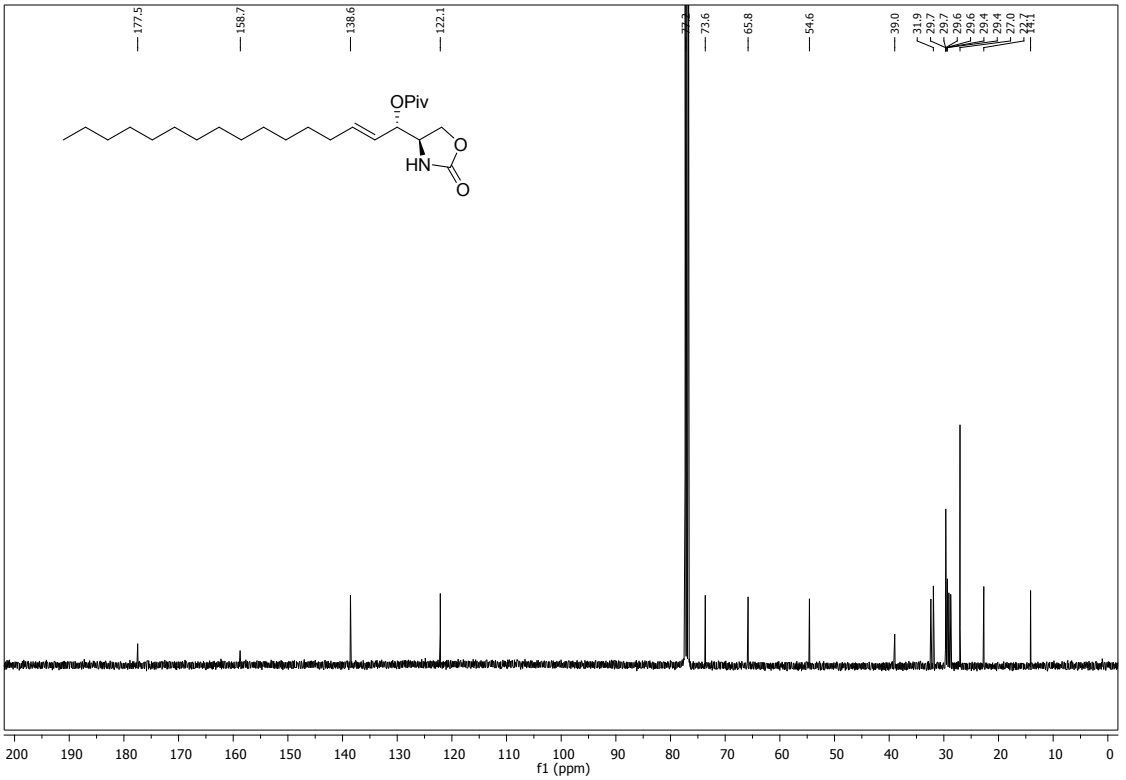
^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-1-en-3-yl acetate (27b).



^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-2-en-1-yl pivalate (26a).



^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm) of (*E*)-1-(2-Oxo-oxazolidin-4-yl)hexadec-2-en-1-yl pivalate (26a).



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