Pd-Catalyzedγ-Arylation of γ,δ-Unsaturated *O*-Carbamates via an Unusual Haptotropic Rearrangement

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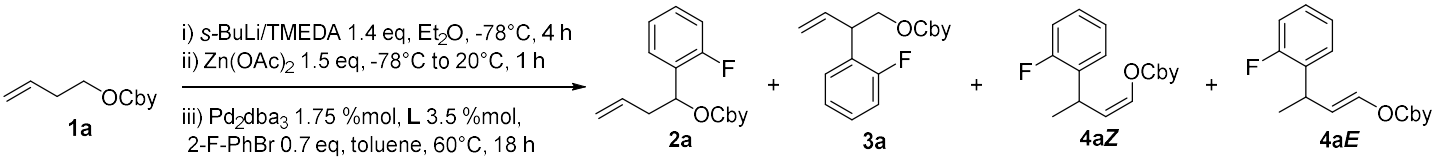
1. General information

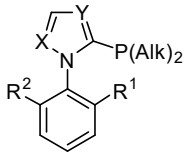
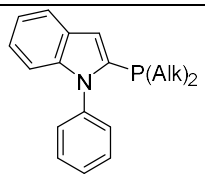
All reactions were performed under an argon atmosphere (unless otherwise noted) in Pyrex glassware equipped with a magnetic stir bar. GC/MS analyses were run on a Shimadzu QP2010 apparatus using aRTx®-5ms column lined with a mass (EI 0.86 kV) detection system.^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a *BrukerAvance III* (400 MHz) spectrometer at 298 K in $CDCl_3$ (residual peaks ^{1}H δ 7.26 ppm, ^{13}C δ 77.16 ppm). Chemical shifts (δ) are reported in ppm relative totetramethylsilane (0.00 ppm). Data are reported as follows: chemical shift in parts per million (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br. for broad), integration value, coupling constant in Hz if applicable. Analytical Thin Layer Chromatography (TLC) was performed using pre-coated *Merck silica gel 60 F254* plates (0.25 mm). Visualization of the developed chromatogram was performed by UV absorbance (254 nm) or TLC stains (Phosphomolybdic acid or $KMnO_4$) Flash chromatographies were performed using *SilicycleSiliaFlash P60* (230-400 mesh) with the indicated solvents. High resolution mass spectrometry recorded by S. Mittelheiser and Dr. M. Pfeffer of the University of Basel on a *BrukermaXis 4G QTOF* ESI mass spectrometer. Infrared spectra were measured on a*ATR Varian Scimitar 800* FT-IR spectrometer and reported in cm^{-1}. HPLC analyses were done using a Shimadzu Prominence system with SIL-20A auto sample, CTO-20AC column oven, LC-20AD pump system, DGU-$20A_3$ degasser and SPD-M20A Diode Array or UV/Vis detector. Chiralcel OD-H, OJ, or OJ-H and Chiralpak AD-H, IA or IC columns from Daicel Corporation were used for separation. Optical rotationwere measured on a Perkin Elmer 341Polarimeter in a 1 mL cuvette (cell length 100 mm) with Na_D-Line (λ = 589 nm) at 20°C. The concentration (c) is given in g/dL.

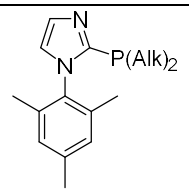
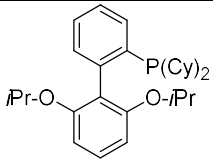
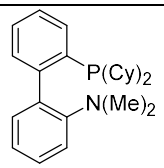
Commercially available reagents were used without further purification unless otherwise stated. Anhydrous solvents (Diethyl ether, THF, Toluene) were purchased form Sigma Aldrich and used as received.Tetramethylethylenediamine (TMEDA) was freshly distilled over CaH_2 under argon atmosphere. (-)-Sparteine and (+)-sparteine were respectively purchased from Sigma Aldrich and Fluorochem, distillated over CaH_2 under argon atmosphere, degassed under high vacuum via freeze-pumping process, and conserved at -30°C. 2-Dicyclohexylphosphino-2',6'-diisopropoxy-biphenyl (RuPhos) was purchased from Strem. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) was purchased from Strem and ABCR. Zinc acetate ($Zn(OAc)_2$)was purchased from Sigma Aldrich and thinly powdered. (RuPhos), ($Pd_2(dba)_3$), and ($Zn(OAc)_2$) were conserved in a glove box.

2. Additional optimization results

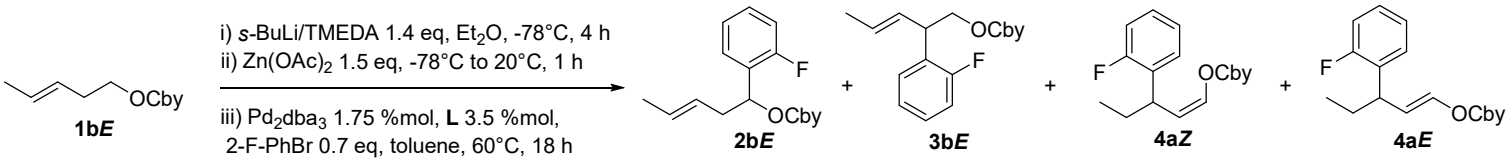
First ligand screen :

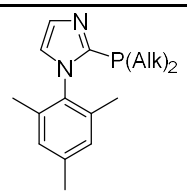
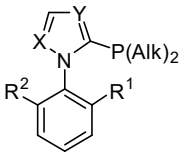
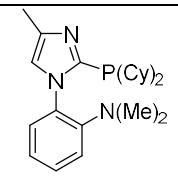
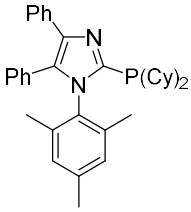


Structure	Ligand	X	Y	R^1	R^2	Alk	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield % (α/β/γZ/γE)
	**L^1**	CH	CH	H	H	*n*Bu	No prod.	n.d.
	L^4	CH	CH	H	H	*i*Bu	No prod.	n.d.
	L^5	CH	CH	H	H	*i*Pr	9/44/16/31	Traces
	L^6	CH	CH	H	H	Cy	12/37/17/33	0/13/0/11
	L^7	CH	CH	H	H	*t*Bu	100/0/0/0	n.d.
	L^8	CH	CH	$N(Me)_2$	H	*i*Pr	24/50/17/8	7.5/20/4/2
	L^9	CH	CH	$N(Me)_2$	H	Cy	27/45/15/11	14/23/7/5
	L^{10}	CH	CH	$N(Me)_2$	H	*t*Bu	23/50/17/10	n.d
	L^{11}	CH	N	$N(Me)_2$	H	Cy	18/36/25/21	7/16/10/8
	L^{12}	CH	N	$N(Me)_2$	H	*t*Bu	100/0/0/0	56/0/0/0
	L^{13}	CH	CH	OMe	H	Cy	29/27/17/27	Traces
	L^{14}	CH	CH	OMe	H	*t*Bu	100/0/0/0	n.d.
	L^{15}	CH	N	O*i*Pr	O*i*Pr	Cy	33/6/51/11	3/0/6/0
	L^{16}	CH	N	O*i*Pr	O*i*Pr	*t*Bu	100/0/0/0	60/0/0/0
	L^{17}	N	CH	O*i*Pr	O*i*Pr	*t*Bu	100/0/0/0	20/0/0/0
	L^{18}	CH	N	$N(Me)_2$	$N(Me)_2$	Cy	88/1/9/3	67/0/0/0
	L^{19}	CH	N	$N(Me)_2$	$N(Me)_2$	*t*Bu	100/0/0/0	31/0/0/0
	L^{20}	N	CH	$N(Me)_2$	$N(Me)_2$	Cy	48/15/30/8	20/6/16/3
	L^{21}	N	CH	$N(Me)_2$	$N(Me)_2$	*t*Bu	100/0/0/0	9/0/0/0
	L^{22}	CH	N	OCy	OCy	*t*Bu	No prod.	n.d
	L^{23}	CH	N	O*i*Pr	O*i*Pr	Ad	100/0/0/0	38/0/0/0
	**L^{24}**	-	-	-	-	Cy	20/36/12/33	3/7/0/3
	L^{25}	-	-	-	-	*t*Bu	100/0/0/0	n.d.

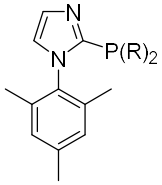
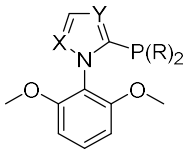
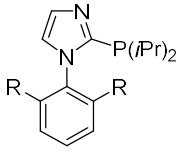
	**L[2]**	-	-	-	-	Cy	18/25/40/48	11/15/21/12
	**L[26]** **RuPhos**	-	-	-	-	-	100/0/0/0	54/0/0/0
	**L[27]** **DavePhos**	-	-	-	-	-	93/7/0/0	n.d.

Second ligand screen :

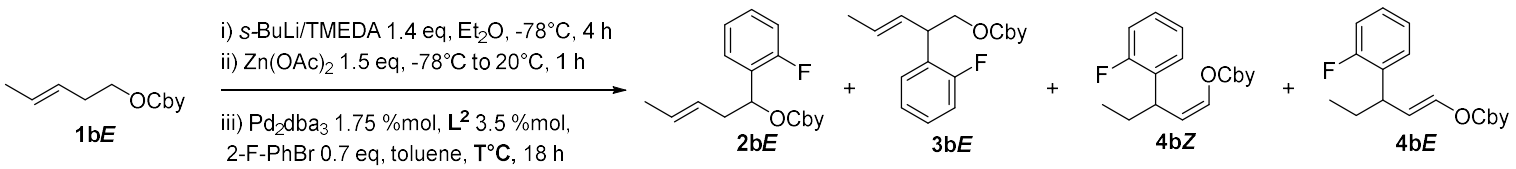


Structure	Ligand	X	Y	R^1	R^2	Alk	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield % γZ/γE
	**L^2**	-	-	-	-	Cy	9/6/64/21	49/12
	**L^9**	CH	CH	$N(Me)_2$	H	Cy	17/33/34/15	12/6
	L^{28}	CH	N	$N(Me)_2$	H	*i*Pr	9/19/46/26	16/6
	L^{29}	CH	N	F	H	Cy	6/9/36/49	9/10
	L^{30}	CH	N	CF_3	H	Cy	4/16/41/39	15/13
	L^{31}	CH	N	*i*Pr	H	Cy	8/5/52/35	20/14
	L^{32}	CH	N	OMe	H	Cy	13/4/47/37	9/6
	L^{33}	CH	N	$N(Et)_2$	H	Cy	7/12/57/24	7/4
	L^{34}	CH	N	Me	H	Cy	7/14/46/33	9/6
	**L^{35}**	-	-	-	-	-	12/14/51/23	14/9
	**L^{36}**	-	-	-	-	-	13/10/57/20	31/10

Third ligand screen :

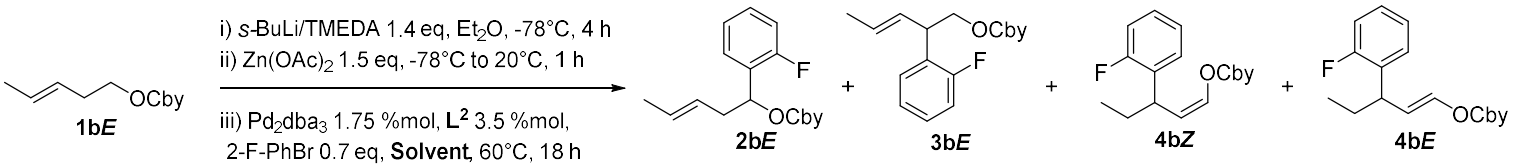
Structure	Ligand	X	Y	R	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield % γZ/γE
	**L^{2}**	-	-	Cy	9/6/65/20	49/12
	L^{37}	-	-	*i*Pr	7/14/60/20	6/2
	**L^{38}**	CH	N	Ph	No traces	n.d.
	L^{39}	CH	N	Cy	16/0/76/8	21/2
	L^{3}	CH	N	*i*Pr	16/1/74/10	39/5
	L^{41}	CH	N	*n*Bu	traces	n.d.
	L^{42}	CH	N	Et	No traces	n.d.
	L^{43}	CH	N	*t*Bu	100/0/0/0	n.d.
	L^{44}	CH	N	*i*Bu	No traces	n.d.
	L^{45}	CH	N	Np	No traces	n.d.
	L^{46}	N	CH	*i*Pr	29/15/46/10	40/10
	**L^{47}**	-	-	OEt	10/1/76/12	45/6
	L^{48}	-	-	O*i*Pr	9/0/79/12	42/6
	L^{49}	-	-	Et	10/12/62/16	41/9
	L^{50}	-	-	F	5/20/44/31	36/17

Temperature screen :



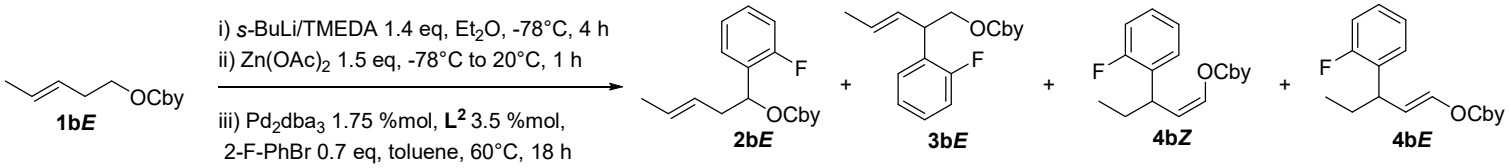
Entry	T°C	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield% (γZ/γE)	Isolated Yield γ-product
1	100	18/8/51/22	32/14	31%, 68/32 Z/E
2	80	11/7/59/22	44/16	33%, 71/29 Z/E
3	60	9/6/64/21	49/12	48%, 75/25 Z/E
4	40	4/6/70/19	40/11	31%, 77/23 Z/E
5	20	traces	<6/1	n.d.
6	0	traces	<2/1	n.d.

Solvent screen :



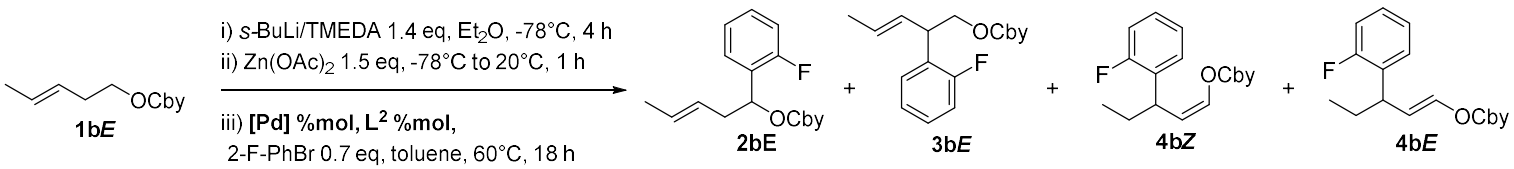
Entry	Solvent	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield% (γZ/γE)	Isolated Yield γ-product
1	toluene	9/6/64/21	49/12	48%, 75/25 Z/E
2	THF	8/4/67/22	31/2	19%, 71/29 Z/E
3	dimethylacetamide	no conversion	n.d.	n.d.
4	1,2-dichloroethane	13/0/75/13	<3/3	n.d.
5	1,2-dimethoxyethane	0/0/86/14	7/<1	n.d.
6	*n*-hexane	10/12/60/19	26/4	29%, 73/27 Z/E
7	1,4-dioxane	no conversion	n.d.	n.d.
8	cyclopentyl methyl ether	10/6/65/19	<2/2	n.d.
9	benzene	7/6/66/21	39/11	47%, 76/24 Z/E
10	cyclohexane	10/6/65/19	<3/3	n.d.
11	α,α,α-trifluorotoluene	8/0/65/27	n.d.	12%, 72/28 Z/E
12	mesitylene	8/8/63/21	20/7	18%, 60/40 Z/E
13	perfluorobenzene	13/8/59/19	20/5	n.d.

Additives/conditions deviations :



Entry	Additive / deviation	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield% (γZ/γE)	Isolated Yield γ-product
1	i) *s*-BuLi/TMEDA 2 eq ii) Zn(OAc) 2,1 eq	6/7/68/16	29/8	31.5%, 74/26 Z/E
2	i) *s*-BuLi/TMEDA 1.05 eq ii) Zn(OAc) 1.1eq	11/5/70/14	42/13	43%, 75/25 Z/E
3	ii) $ZnCl_2$ i/o $Zn(OAc)_2$	8/4/67/21	n.d.	35%, 71/29 Z/E
4	iii) 0.5 eq ArBr	7/7/66/20	38/9	44%, 75/25 Z/E
5	iii) 0.5 eq ArBr, 2.5 %mol cat.	7/5/67/21	42/10	44%, 74/26 Z/E
6	iii) 0.6 eq ArBr	6/6/67/20	32/9	n.d.
7	iii) 1 eq ArBr	8/8/64/20	32/9.5	35%, 75/25 Z/E
8	iii) 1 eq ArBr, 5 %mol cat.	7/6/67/20	33/9.5	35%, 75/25 Z/E
9	iii) 1.5 eq ArBr	8/7/64/21	32/9.5	n.d.
10	iii) 3.5 %mol Pd_2dba_3, 7 %mol **L²**	8/7/67/19	46/14	53.5%, 75/25 Z/E
11	iii) 7 %mol Pd_2dba_3, 14 %mol **L²**	7/7/67/20	44/13	n.d.
12	iii) 1.75 %mol Pd_2dba_3, 5.25 %mol **L²**	8/5/67/20	43/13	42%, 75/25 Z/E
13	iii) 1.75 %mol Pd_2dba_3, 7 %mol **L²**	6/7/66/21	34/10	n.d.
14	iii) reaction 40h	7/7/65/21	44/14	55%, 75/25 Z/E
15	iii) + 12-Crown-4 1.5 eq	8/6/67/20	44/13	n.d.
16	iii) + $MgCl_2$ 1.5 eq	8/7/67/18	41/12	n.d.
17	iii) + ZnF_2 1.5 eq	8/7/67/18	29/10	n.d.
18	iii) + $BF_3.Et_2O$ 1.5 eq	no traces	n.d.	n.d.
19	iii) + CO atmosphere	No reaction, no insertion		
20	iii) + *t*BuNC	Lower conversion, no insertion		

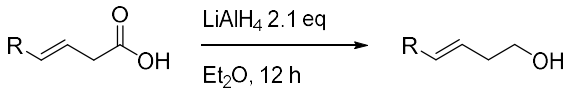
Palladium source screen :



Entry	Additive / deviation	Product ratio GCMS (α/β/γZ/γE)	^{19}F NMR Yield% (γZ/γE)	Isolated Yield γ-product
1	3.5 %mol $Pd(dba)_2$, 3.5 %mol **L²**	6/6/66/21	14/4	n.d.
2	**L²**Pd G3 precatalyst 5 %mol	6/7/67/20	32/10	n.d.
2	3.5 %mol $PdCl_2$, 7 %mol **L²**	6/6/66/21	24/8	n.d.
4	3.5 %mol $Pd(OAc)_2$, 7 %mol **L²**	7/6/67/20	20/6	n.d.
5	1.75 %mol $[CinnamylPdCl]_2$, 7 %mol **L²**	7/7/66/20	35/11	n.d.
6	3.5 %mol $[PdCl_2MeCN_2]$, 7 %mol **L²**	7/7/67/20	45/14	50%, 75/25 Z/E
7	7 %mol $[PdCl_2MeCN_2]$, 14 %mol **L²**	7/5/67/21	43/15	44%, 74/26 Z/E
8	7 %mol $[PdCl_2PhCN_2]$, 14 %mol **L²**	7/6/67/20	45/14	45%, 75/25 Z/E
9	7 %mol $[PdMe_2TMEDA]$, 14 %mol **L²**	7/6/67/20	43/13	n.d.
10	7 %mol $[PdCl_2(SMe)_2]$, 14 %mol **L²**	7/5/67/20	44/14	n.d.
11	7 %mol $[Pd(CH_2SiMe_3)_2$ COD], 14 %mol**L²**	7/6/68/20	44/14	n.d.

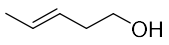
3. Starting material synthesis

- General procedure for the synthesis of homoallyl alcohols **S1-S3** from 3-alkenoic acids



A solution of the corresponding carboxylic acid (1 eq) in Et_2O was added dropwise to a suspension of $LiAlH_4$ (2.1 eq) in Et_2O at 0°C over 30 min. The resulting mixture was stirred at 20°C for 12 h, quenched with 20% aq. NaOH, and then filtrated over celite. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (Pent/Et_2O 95:5 to 50:50) to obtain the corresponding alcohol.

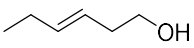
(*E*)-Pent-3-en-1-ol **S1**:



Following the general procedure, (*E*)-pent-3-enoic acid (1.5 mL, 14.7 mmol) in Et_2O (10 mL) was reacted with $LiAlH_4$ (1.2 g, 30.9 mmol) in Et_2O (20 mL) to obtain 1.1 g (87%) of the title alcohol as a colorless oil. The spectral data are consistent with those reported in the literature.[1]

^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 5.62-5.53 (m, 1H), 5.44-5.36 (m, 1H), 3.62 (t, J_3 = 6.3 Hz, 2H), 2.28-2.23 (m, 2H), 1.70-1.67 (m, 3H), 1.49 (br. s, 1H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) :** δ = 128.7, 127.2, 62.1, 36.1, 18.2. **GCMS (EI) m/z (intensity %) :**41 (100), 54 (0.2).**IR neat (υ/cm^{-1}) :** 3330, 3024, 2936, 2363, 1757, 1449, 1045, 966.

(*E*)-Hex-3-en-1-ol **S2**:

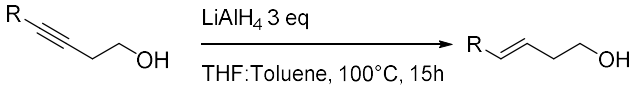


Following the general procedure, (*E*)-hex-3-enoic acid (1.5 g, 12.8 mmol) in Et_2O (10 mL) was reacted with $LiAlH_4$ (1.0 g, 26.9 mmol) in Et_2O (20 mL) to obtain 1.0 g (78%) of the title alcohol as a colorless oil.The spectral data are consistent with those reported in the literature.[2]

[1] Kim, W.-Y.; Kim, B. G.; Kang, T.; Lee, H.-Y. *Chem. Asian J.***2011**, 6, 1931-1935.

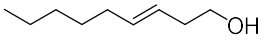
^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 5.64-5.57 (m, 1H), 5.41-5.33 (m, 1H), 3.63 (t, J_3 = 6.3 Hz, 2H), 2.29-2.23 (m, 2H), 2.08-2.00 (m, 2H), 1.48 (br. s, 1H), 0.98 (t, J_3 = 7.4 Hz, 3H).**^{13}C-{^{1}H}NMR ($CDCl_3$, 100 MHz) :**δ = 135.9, 124.9, 62.2, 36.1, 25.8, 13.9. **GCMS (EI) m/z (intensity %) :**43 (100), 61 (34), 89 (27), 70 (25), 45 (20)**.IR neat (υ/cm^{-1}) :** 3342, 2963, 2360, 1441, 1047, 967.

- General procedure for the synthesis of homoallyl alcohols **S3-S5** from homopropargylic alcohols



The homopropargylic alcohol (1 eq) was added dropwise to a suspension of $LiAlH_4$ (3 eq) in THF:Toluene (1:1 v:v) at 0°C. After the addition the mixture was stirred at 100°C for 15 h and then cooled down to room temperature. The reaction was quenched by a sequential addition of water (1µL/mg of $LiAlH_4$), 15% aq. NaOH (1µL/mg of $LiAlH_4$), and water (3µL/mg of $LiAlH_4$). The precipitate was filtered off on celite with Et_2O. The resulting organic phase was dried over $MgSO_4$, filtered, and concentrated under vacuum. The oily residue was purified by silica gel column chromatography (Pent/Et_2O 95:5 to 50:50) the corresponding (*E*)-homoallyl alcohol as an oil.

(*E*)-non-3-en-1-ol **S3**:



Following the general procedure, non-3-yn-1-ol (2.2 g, 15.7 mmol) was reacted with $LiAlH_4$ (reagent grade 95%, 1.9 g, 47.1 mmol) in THF:Toluene (50 mL) to obtain 1.4 g (63%) of the title compound as a colorless oil. The spectral data are consistent with those reported in the literature.[3]

^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 5.59-5.52 (m, 1H), 5.41-5.33 (m, 1H), 3.62 (t, J = 6.3 Hz, 2H), 2.28-2.23 (m, 2H), 2.03-1.98 (m, 2H), 1.48 (br. s., 1H), 1.36-1.25 (m, 6H), 0.88 (t, J = 6.9 Hz, 2H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) :**δ = 134.6, 125.8, 62.1, 36.1, 32.8, 31.5, 29.3, 22.7, 14.2. **GCMS (EI) m/z (intensity %):**41 (100), 55 (93), 69 (68), 81 (42), 95 (24), 124 (5). **IR neat (υ/cm^{-1}) :** 3333, 2924, 2856, 2361, 1461, 1335, 1048, 968.

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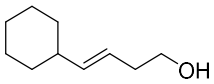
[2] Katritzky, A. R.; Wu, H.; Xie, L. *J. Org. Chem.***1996**, 61, 4035-4039.
[3] Liblikas, I, Mozuraitis, R.; Santangelo, E. M.; Noreika, R.; Borg-Karlson, A.-K. *Chem. Biodivers.***2009**, 6, 1388-1402.

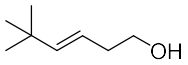
(*E*)-4-cyclohexylbut-3-en-1-ol **S4**:



Following the general procedure, 4-cyclohexylbut-3-yn-1-ol (200 mg, 1.3 mmol) was reacted with $LiAlH_4$ (reagent grade 95%, 157 mg, 3.9 mmol) in THF:Toluene (4 mL) to obtain 190 mg (94%) of the title compound as a colorless oil. The spectral data are consistent with those reported in the literature.[4]

^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 5.54-5.48 (m, 1H), 5.36-5.29 (m, 1H), 3.61 (t, *J* = 6.3 Hz, 2H), 2.27-2.22 (m, 2H), 1.97-1.89 (m, 1H), 1.73-1.62 (m, 5H), 1.48 (s, 1H), 1.31-1.00 (m, 5H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz) :**δ = 140.6, 123.2, 62.2, 40.9, 36.2, 33.3, 26.3, 26.2. **IR neat (υ/cm^{-1}) :** 3328, 2922, 2851, 2362, 1448, 1047, 968.

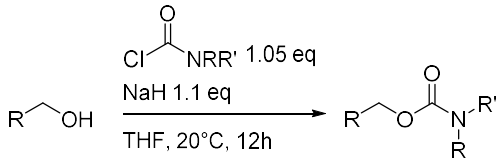
(*E*)-5,5-dimethylhex-3-en-1-ol **S5**:



Following the general procedure, (*E*)-5,5-dimethylhex-3-yn-1-ol (200 mg, 1.6 mmol) was reacted with $LiAlH_4$ (reagent grade 95%, 189 mg, 4.7 mmol) in THF:Toluene (4 mL) to obtain 145 mg (71%) of the title compound as a colorless oil. The spectral data are consistent with those reported in the literature.[4]

^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 5.59 (dt, *J* = 15.6 Hz, *J* = 1.3 Hz, 1H), 5.29 (dt, *J* = 15.6 Hz, *J* = 7.0 Hz, 1H), 3.62 (t, *J* = 6.3 Hz, 2H), 2.29-2.23 (m, 2H), 1.42 (s, 1H), 1.00 (s, 9H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz) :**δ = 145.6, 120.3, 62.2, 36.2, 33.2, 29.9. **IR neat (υ/cm^{-1}) :** 3727, 2956, 2362, 1748, 1634, 1460, 1046, 972.

- General procedure for the synthesis of 2,2,4,4-tetramethyloxazolidine-3-carboxylates **:**

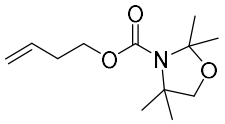


A solution of the corresponding alcohol (1.0 eq) in THF (10 mL) was added dropwise to a suspension of sodium hydride (95% in mineral oil, 1.1 eq) in THF (30 mL) and the mixture

[4] Zeng, X.; Miao, C.; Wang, S.; Xia, C.; Sun, W. *Chem. Commun.* **2013**, 49, 2418-2420.

was stirred for 30 min at room temperature. A solution of 2,2,4,4-tetramethyloxazolidine-3-carbonyl chloride (unless otherwise stated) (1.05 eq) in THF (10 mL) was then added dropwise and the mixture was stirred for 12 h. After quenching with water, the solvent was removed under reduced pressure and Et_2O (50 mL) was added to the crude mixture. The organic phase was washed with sat. aq. $NaHCO_3$ (30 mL), water (30 mL) and brine (30 mL) and dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified by silica gel column chromatography (Pent/Et_2O 98:2 to 80:20).

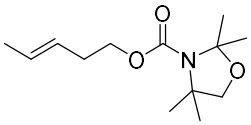
But-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1a**:



Following the general procedure, 3-buten-1-ol (652 µL, 7.5 mmol) gave 1.55 g (91 %) of the corresponding carbamate as a colorless oil. The analytical data were in accordance with the literature.[5]

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.85-5.76 (m, 1H), 5.14-5.05 (m, 2H), 4.16-4.12 (m, 2H), 3.71 (s, 2H), 2.44-2.37 (m, 2H), 1.55 (1.50) (2 br. s, 6H), (1.41) 1.34 (2 br. s, 6H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 152.9/152.2, 134.8, 117.2, 95.9/95.0, 76.5/76.2, 63.8, 60.7/59.9, 33.6, 26.6/25.42, 25.39/24.3. **HRMS (ESI) m/z:**calcd. for $C_{12}H_{21}NO_3Na$ ($[M + Na]^+$): 250.1414; found: 250.1416.**IR neat (ʊ/cm^{-1}) :** 2980, 2361, 1695, 1404, 1343, 1259, 1207, 1068, 991, 768, 652.

(*E*)-Pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1b*E***:



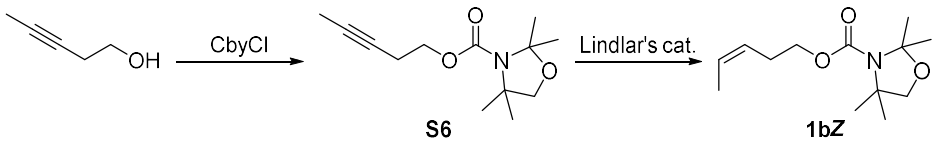
Following the general procedure, (*E*)-pent-3-en-1-ol (1.2 g, 13.9 mmol) gave 3.2 g (95%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.57-5.49 (m, 1H), 5.45-5.39 (m, 1H), 4.11-4.07 (m, 2H), 3.72 (s, 2H), 2.37-2.32 (m, 2H), 1.66 (dd, J_3 = 6.2 Hz, J_4 = 1.1 Hz, 3H), 1.56 (1.51) (2 br. s, 6H), (1.42) 1.35 (2 br. s, 6H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz,**

[5] Royal, T.; Baumgartner, Y.; Baudoin, O. *Org. Lett.* **2017**, *19*, 166-169.

rotamers) :δ = 153.0/152.2, 127.9, 127.2, 95.9/95.0, 76.5/76.2, 64.3, 60.6/59.9, 35.5, 26.5/25.4, 25.3/24.3, 18.1. **HRMS (ESI) m/z:**calcd. for $C_{13}H_{23}NO_3Na$ ($[M + Na]^+$): 264.1570; found: 264.1572**. IR neat (υ/cm^{-1}) :** 2972, 2573, 2361, 1696, 1406, 1343, 1258, 1067, 966.

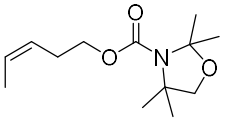
(*Z*)-Pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1b*Z***:



Pent-3-yn-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**S6** :

Following the general procedure, 3-pentyn-1-ol (550 µL, 5.9 mmol) gave 1.3 g (91%) of the carbamate**S6** as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 4.14-4.10 (m, 2H), 3.72 (s, 2H), 2.48-2.43 (m, 2H), 1.74 (t, J_5 = 2.5 Hz, 3H), 1.54 (s, 6H), (1.40) 1.38 (2 br. s, 6H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 152.6/151.9, 95.9/95.2, 77.2, 76.5/76.2, 75.6, 63.0, 60.7/60.0, 26.5/25.4, 25.3/24.2, 19.6, 3.5. **HRMS (ESI) m/z:**calcd. for $C_{13}H_{21}NO_3Na$ ($[M + Na]^+$): 262.1414; found: 262.1418**. IR neat (υ/cm^{-1}) :** 2980, 2870, 2360, 1702, 1408, 1349, 1260, 1099.

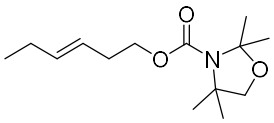


A mixture of pent-3-yn-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **S6** (800 mg, 3.3 mmol, 1 eq), quinoline (200 µL, 1.7 mmol, 0.5 eq) and Lindlar's catalyst (Pd 5% on $CaCO_3$, poisoned with Pb, 50 mg) in ethyl acetate (10 mL) was stirred under hydrogen atmosphere (balloon) at 20°C for 2 h. The reaction mixture was then filtrated through a pad of celite, and washed with 1 M aq. HCl (2x10mL). The organic layer was dried over $MgSO_4$, filtrated and then concentrated under vacuum. The oily residue was purified by silica gel column chromatography (Pent/Et_2O 98:2 to 90:10) to obtain 750 mg (93%) of carbamate **1b*Z*** as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.49-5.41 (m, 1H), 5.32-5.26 (m, 1H), 4.00-3.96 (m, 2H), 3.60 (s, 3H), 2.31-2.28 (m, 2H), 1.52 (d, J = 6.7 Hz, 3H), 1.44 (1.39) (2 br. s, 6H), (1.30) 1.23 (2 br. s, 6H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 152.9/152.2,

126.5/126.4, 126.2, 95.9/95.0, 76.5/76.2, 64.1, 60.6/59.8, 26.9, 26.5/25.4, 25.3/24.2, 13.0. **HRMS (ESI) m/z:** calcd. for $C_{13}H_{23}NO_3Na$ ($[M + Na]^+$): 264.1570; found: 264.1569**. IR neat (υ/cm^{-1}) :** 2979, 2361, 1699, 1407, 1345, 1260, 1208, 1096.

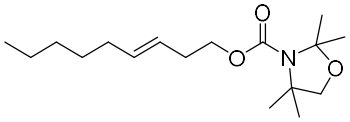
(*E*)-hex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1l**:



Following the general procedure, (*E*)-hex-3-en-1-ol (407 mg, 4.1 mmol) gave 930 mg (90%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.58-5.51 (m, 1H), 5.41-5.33 (m, 1H), 4.10-4.06 (m, 2H), 3.70 (s, 2H), 2.35-2.29 (m, 2H), 2.03-1.96 (m, 2H), 1.54 (1.49) (2 br. s, 6H), (1.40) 1.33 (2 br. s, 6H), 0.94 (t, *J* = 7.5 Hz, 3H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 153.0/152.2, 134.9, 125.0, 95.9/95.0, 76.5/76.2, 64.28/64.23, 60.6/59.8, 32.5, 26.6/25.42, 25.7, 25.36/24.3, 13.8. **HRMS (ESI) m/z:**calcd. for $C_{14}H_{25}NO_3Na$ ($[M + Na]^+$): 278.1727; found: 278.1729**. IR neat (υ/cm^{-1}) :** 2966, 2871, 2361, 1698, 1406, 1342, 1260, 1097, 967.

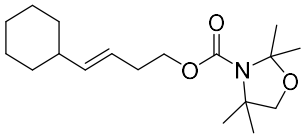
(*E*)-non-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1m**:



Following the general procedure, (*E*)-non-3-en-1-ol (500 mg, 3.52 mmol) gave 940 mg (90%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.55-5.48 (m, 1H), 5.42-5.34 (m, 1H), 4.11-4.07 (m, 2H), 3.72 (s, 2H), 2.37-2.30 (m, 2H), 2.00-1.95 (m, 2H), 1.55 (1.50) (2 br. s, 6H), 1.41-1.23 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 153.0/152.3, 133.5, 125.8, 95.9/95.0, 76.5/76.2, 64.34/64.30, 60.6/59.9, 32.7, 32.5, 31.5, 29.2, 26.6/25.5, 25.4/24.3, 22.7, 14.2. **HRMS (ESI) m/z:**calcd. for $C_{17}H_{31}NO_3Na$ ($[M + Na]^+$): 320.2196; found: 320.2199**. IR neat (υ/cm^{-1}) :** 2930, 2361, 1701, 1407, 1344, 1260, 1098.

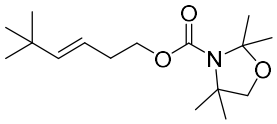
(*E*)-4-cyclohexylbut-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1n**:



Following the general procedure, (*E*)-4-cyclohexylbut-3-en-1-ol (150 mg, 0.97 mmol) gave 230 mg (76%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.49-5.44 (m, 1H), 5.39-5.30 (m, 1H), 4.12-4.07 (m, 2H), 3.72 (s, 2H), 2.36-2.29 (m, 2H), 1.94-1.86 (m, 1H), 1.69-1.65 (m, 5H), 1.55 (1.50) (2 br. s, 6H), (1.41) 1.35 (2 br. s, 6H), 1.30-0.98 (m, 5H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 153.0/152.3, 139.4, 123.44/123.40, 95.9/95.1, 76.5/76.3, 64.4/64.3, 60.6/59.9, 40.9, 33.2, 32.6, 26.7, 26.3, 26.2, 25.5, 24.3. **HRMS (ESI) m/z:**calcd. for $C_{18}H_{31}NO_3Na$ ([M + Na]$^+$): 332.2196; found: 332.2197**. IR neat (υ/cm^{-1}) :** 22925, 2853, 2361, 1697, 1450, 1406, 1343, 1259, 1208, 1097, 969.

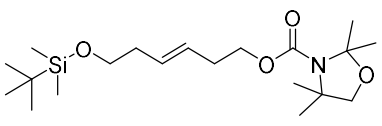
(*E*)-5,5-dimethylhex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1o**:



Following the general procedure, (*E*)-5,5-dimethylhex-3-en-1-ol(125 mg, 0.98 mmol) gave 200 mg (72%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.56-5.52 (m, 1H), 5.35-5.26 (m, 1H), 4.12-4.08 (m, 2H), 3.71 (s, 2H), 2.36-2.30 (m, 2H), 1.55 (1.50) (2 br. s, 6H), (1.41) 1.34 (2 br. s, 6H), 0.97 (s, 9H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 153.0/152.3, 144.3, 120.78/120.74, 95.9/95.0, 765/76.3, 64.4/64.3, 60.6, 59.9, 33.1, 32.6, 29.8, 26.7, 25.5, 24.3. **HRMS (ESI) m/z:**calcd. for $C_{16}H_{29}NO_3Na$ ([M + Na]$^+$): 306.2040; found: 306.2036**. IR neat (υ/cm^{-1}) :** 2957, 2361, 1697, 1509, 1460, 1407, 1344, 1260, 1092, 972.

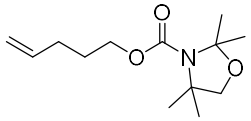
(*E*)-6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1p**:



Following the general procedure, (*E*)-6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-ol(130 mg, 0.56 mmol, *E*:*Z* 85:15) gave 120 mg (55%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.56-5.44 (m, 2H), 4.11-4.08 (m, 2H), 3.72 (s, 2H), 3.61-3.59 (m, 2H), 2.38-2.32 (m, 2H), 2.24-2.20 (m, 2H), 1.55 (1.50) (2 br. s, 6H), (1.41) 1.35 (2 br. s, 6H), 0.88 (s, 9H), -0.04 (s, 6H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 153.0/152.2, 129.5, 128.2, 95.9/95.0, 76.5/76.3, 64.22/64.17, 63.2, 60.7/59.9, 36.5, 32.6, 26.6/25.5, 26.1, 25.4/24.3, 18.5, -5.11. **HRMS (ESI) m/z:**calcd. for $C_{20}H_{39}NO_4SiNa$ ($[M + Na]^+$): 408.2541; found: 408.2546**. IR neat (υ/cm^{-1}) :** 2956, 2361, 1701, 1461, 1407, 1344, 1257, 1098.

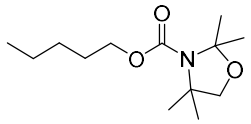
Pent-4-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1q**:



Following the general procedure, Pent-4-en-1-ol (600 µL, 5.8 mmol) gave 1.3 g (93%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.86-5.78 (m, 1H), 5.07-4.98 (m, 2 H), 4.12-4.08 (m, 2H), 3.73 (s, 2H), 2.19-2.12 (m, 2H), 1.80-1.72 (m, 2H), 1.56 (1.53) (2 br. s, 6H), (1.42) 1.37 (2 br. s, 6H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 153.0/152.2, 137.7, 115.4, 95.9/94.9, 76.5/76.2, 64.0, 60.7/59.8, 30.5, 28.3, 26.7, 25.4, 24.3. **HRMS (ESI) m/z:**calcd. for $C_{13}H_{23}NO_3Na$ ($[M + Na]^+$): 264.1570; found: 264.1570**. IR neat (υ/cm^{-1}) :** 2979, 2361, 1695, 1406, 1359, 1259, 1067, 914.

Pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**1r**:

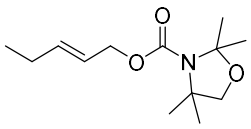


Following the general procedure, pentanol (650 µL, 4 mmol) gave 820 mg (84%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 4.09-4.05 (m, 2H), 3.73 (s, 2H), 1.68-1.63 (m, 2H), 1.56 (1.52) (2 br. s., 6H), 1.44-1.31 (m, 10H), 0.93-0.89 (m, 3H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 153.1/152.4, 95.9/94.9, 76.5/76.2, 64.7, 60.6/59.7, 28.7,

28.5, 26.6/25.43, 25.39/24.3, 22.4, 14.1. **HRMS (ESI) m/z:**calcd. for $C_{13}H_{25}NO_3Na$ ([M + Na]$^+$): 266.1727; found: 266.1729.**IR neat (υ/cm^{-1}) :** 2961, 2867, 2360, 1700, 1408, 1348, 1260, 1096.

(*E*)-Pent-2-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1s**:



Following the general procedure, (*E*)-pent-2-en-1-ol (345 mg, 4 mmol) gave 850 mg (88%) of the corresponding carbamate as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.82-5.78 (m, 1H), 5.61-5.54 (m, 1H) 4.54-4.52 (m, 2H), 3.73 (s, 2H), 2.11-2.04 (m, 2H), 1.56 (1.52) (2 br. s, 6H), (1.42) 1.36 (2 br. s, 6H), 1.00 (t, J_3 = 7.4 Hz, 3H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 152.8/152.1, 137.2/137.1, 123.6/123.6, 95.9/95.0, 76.5/76.26, 65.4, 60.7/59.8, 26.6, 25.4, 24.3, 13.4. **HRMS (ESI) m/z:**calcd. for $C_{13}H_{23}NO_3Na$ ([M + Na]$^+$): 264.1570; found: 264.1575**. IR neat (υ/cm^{-1}) :** 2968, 2871, 2361, 1701, 1405, 1348, 1261, 1065.

4. General procedures for the γ-arylation

General procedure A : arylation with TMEDA

In a tubular reactor (100 mm x 16 mm)capped with a rubber septum, a solution of the carbamate(0.207 mmol, 1 eq) and TMEDA (44 µL, 0.29 mmol, 1.4 eq) in dry diethyl ether (1.5 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (0.29 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (57 mg, 0.31 mmol, 1.5 eq) in dry THF (1.5 mL) was sonicated for 30 min and added dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to warm up to 20°C over 30 min. The solvents were evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (3.3 mg, 3.6 µmol, 1.75 %mol) and **L²** (2.8 mg, 7.3 µmol, 3.5 %mol) in dry toluene (1.5 mL) was added, followed by the aryl bromide (0.15 mmol, 0.7 eq). The mixture was then vigorously stirred and heated to 60°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (2 mL), and the organic phase was diluted with EtOAc (3 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 3 mL). The combined organic layers were dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under vacuum. The residue was purified by preparative reversed-phase HPLC ($MeCN/H_2O$) to afford the γ-arylated products.

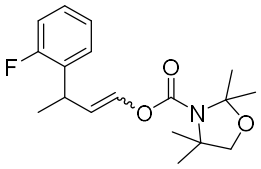
General procedure B : enantioselective arylation with (+)-sparteine

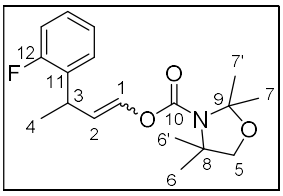
In a tubular reactor (100 mm x 16 mm)capped with a rubber septum, a solution of the carbamate(0.207 mmol, 1 eq) and (+)-sparteine (66 µL, 0.29 mmol, 1.4 eq) in dry diethyl ether (1.5 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (0.29 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (57 mg, 0.31 mmol, 1.5 eq) in dry THF (1.5 mL) was sonicated for 30 min and added dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to heat up to 20°C over 30 min. The solvents were evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (3.3 mg, 3.6 µmol, 1.75 %mol) and **L²** (2.8 mg, 7.3 µmol, 3.5 %mol) (unless otherwise stated) in dry toluene (1.5 mL) was added, followed by the aryl bromide (0.15 mmol, 0.7 eq). The mixture was then vigorously stirred and heated to 60°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (2 mL), and the organic phase was diluted with EtOAc (3 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 3 mL). The combined organic layers were dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under

vacuum. The residue was purified by preparative reversed-phase HPLC ($MeCN/H_2O$) to afford the γ-arylated products.

5. Arylation of **1a** : products **4a** and isomers

3-(2-fluorophenyl)but-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4a**:

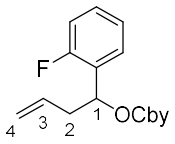




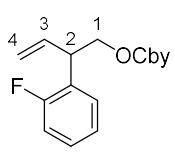
Following the general procedure, but-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (47 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 9.7 mg (21%) of the title compound (64:36 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.29-6.97 (m, 5H, H_1, H_{Ar}), 5.59-5.51 (m, 1H, H_2E), 5.01-4.97 (m, 1H, H_2Z), 4.30-4.19 (m, 1H, H_3Z), 3.95-3.79 (m, 1H, H_3E), 3.76-3.75 (m, 2H, H_5), 1.62-1.28 (m, 15H, H_4, H_6, $H_{6'}$, H_7, $H_{7'}$). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.5/159.5 (d of rotamers, J = 246.4 Hz, C_{12}), 150.2-149.1 (C_{10}), 136.4/136.3 (C_1E), 133.8/133.7 (C_1Z), 133.0-132.8 ($C_{11}Z$), 132.5-132.4 ($C_{11}E$), 128.3-127.7 (2 C_{Ar}), 124.28/124.25 (C_{Ar}), 116.0/115.9 (C_2E), 115.7-115.4 (C_{Ar}), 114.5/114.4 (C_2Z), 96.3-95.4 (C_9), 76.5-76.1 (C_5), 61.1-60.3 (C_8), 31.7 (C_3E), 29.6-24.0 (C_3Z, C_6, $C_{6'}$, C_7, $C_{7'}$), 22.1 (C_4Z), 20.7 (C_4E).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.57/-118.62 ($F_{12}Z$), -118.80/-118.81 ($F_{12}E$). **HRMS (ESI) m/z:**calcd. for $C_{18}H_{24}FNO_3Na$ ($[M + Na]^+$): 344.1632; found: 344.1638.**IR neat (υ/cm^{-1}) :** 2974, 2921, 2361, 1717, 1374, 1241, 1069.

Observation and isolation of α- and β-products **2a** and **3a**:



2a



3a

After arylation, <10% yield of amixture of α- and β-arylated products (ratio 50:50) was isolated for analytical purpose.

α-product **2a** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.07-6.04 (m, 1H, H_1), 5.79-5.69 (m, 1H, H_3), 5.09-5.04 (m, 2H, H_4), 2.75-2.63 (m, 2H, H_2).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 133.5/133.4 (C_3), 118.3 (C_4), 70.74/70.69 (C_1), 40.2/40.1 (C_2).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ =-117.93/-117.96.

β-product **3a** :

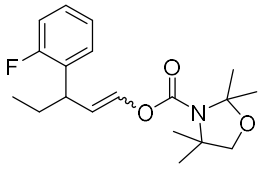
^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.02-5.97 (m, 1H, H_3), 5.19-5.14 (m, 2H, H_4), 4.48-4.43 (m, 1H, H_1), 4.33-4.27 (m, 1H, H_1), 4.10-4.04 (m, 1H, H_2).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 136.7-136.6 (C_3), 117.3 (C_4), 66.3 (C_1), 42.7/42.6 (C_2). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ =-117.51/-117.55.

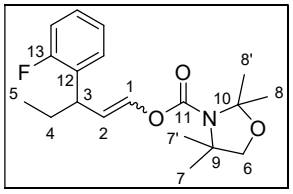
IR neat (υ/cm^{-1}) : 2980, 2361, 1699, 1399, 1347, 1259, 1066.

6. Arylation of carbamate **1bE**: products **4b-k**

- Arylations of **1b*E*** with 1-bromo-2-fluorobenzene : products **4b** and isomers

3-(2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4b** :





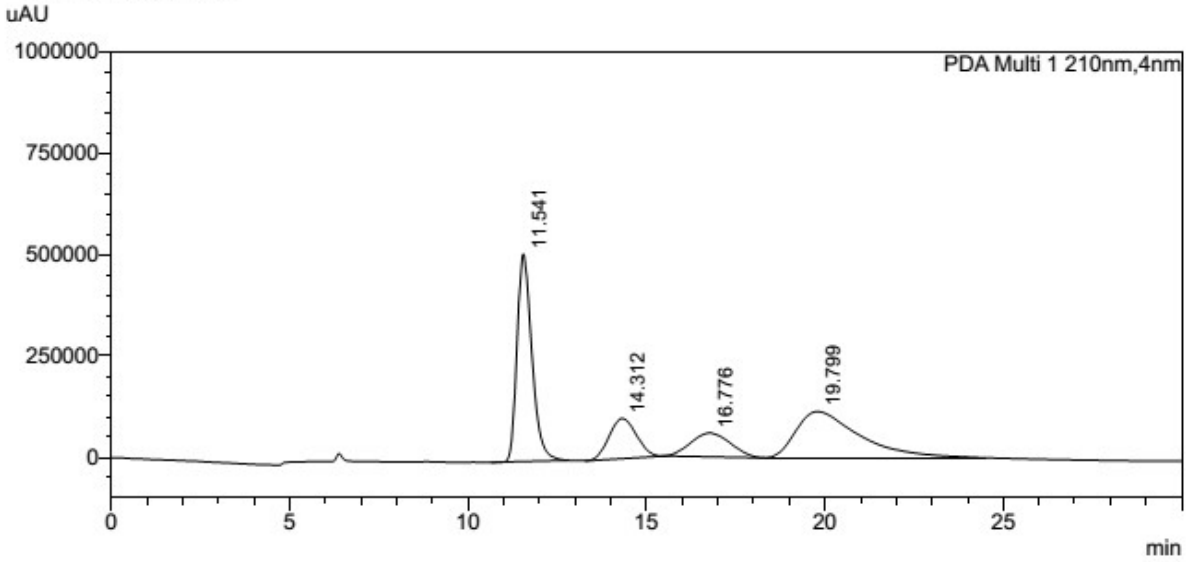
Following the general procedure A, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 29 mg (60%) of the title compound (75:25 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.24-7.06 (m, 4H, H_1, H_{Ar}), 7.02-6.97 (m, 1H, H_{Ar}), 5.54-5.47 (m, 1H, H_2*E*), 4.99-4.95 (m, 1H, H_2*Z*), 4.07-3.96 (m, 1H, H_3*Z*), 3.78-3.73 (m, 2H, H_6), 3.51-3.46 (m, 1H, H_3*E*), 1.79-1.62 (m, 2H, H_4), 1.64-1.32 (m, 12H, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.92-0.87 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 162.0/161.9-159.6/159.5 (d of rotamers, *J* = 245.4 Hz, C_{13}), 150.0/149.1 (C_{11}), 136.8/136.6 (C_1*E*), 134.8/134.7 (C_1*Z*), 131.8/131.7 (C_{12}*Z*), 131.4/131.3 (C_{12}*E*), 128.8-128.5 (C_{Ar}), 127.9-127.6 (C_{Ar}), 124.3-124.2 (C_{Ar}), 115.8/115.4 (C_{Ar}), 114.7/114.6 (C_2*E*), 113.2/113.1 (C_2*Z*),

96.3/96.1/95.4 (C_{10}), 76.6/76.4/76.2 (C_6), 61.2/61.0/60.4/60.3 (C_9), 39.6 (C_3E), 36.63/36.56 (C_3Z), 29.4 (C_4Z), 28.4 (C_4E), 26.9-24.0 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.3 (C_5E), 12.2 (C_5Z).. **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.31/-118.32 ($F_{13}E$), -118.35/-118.41 ($F_{13}Z$). **HPLC separation conditions :** Chiralcel OJ-H column, *n*-heptane/*i*-PrOH 99.5:0.5, flow rate 0.5 mL/min, 25°C, t_R 11.5 min for (*R*,*Z*)-enantiomer, t_R 14.3 min for (*S*,*E*)-enantiomer, t_R 16.8 min for (*R*,*E*)-enantiomer and t_R 19.8 min for (*S*,*Z*)-enantiomer. **HRMS (ESI) m/z:** calcd. for $C_{19}H_{26}FNO_3Na$ ($[M + Na]^+$): 358.1789; found: 358.1794**.IR neat (υ/cm^{-1}) :**2971, 2361, 1717, 1378, 1225, 1089.

References of the racemic products :

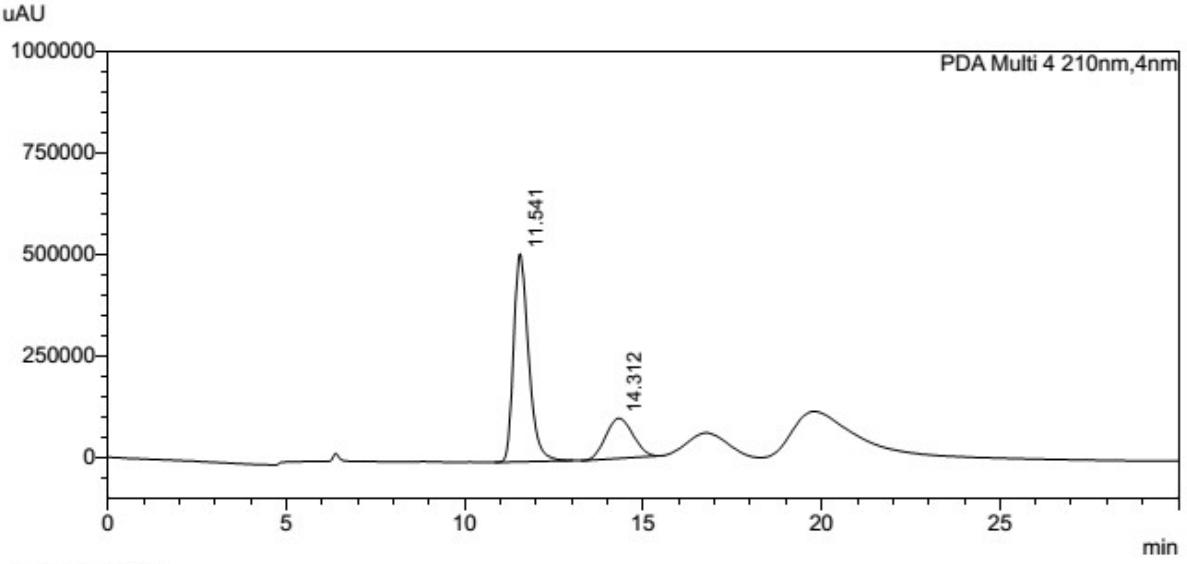
<Chromatogram>



<Peak Table>

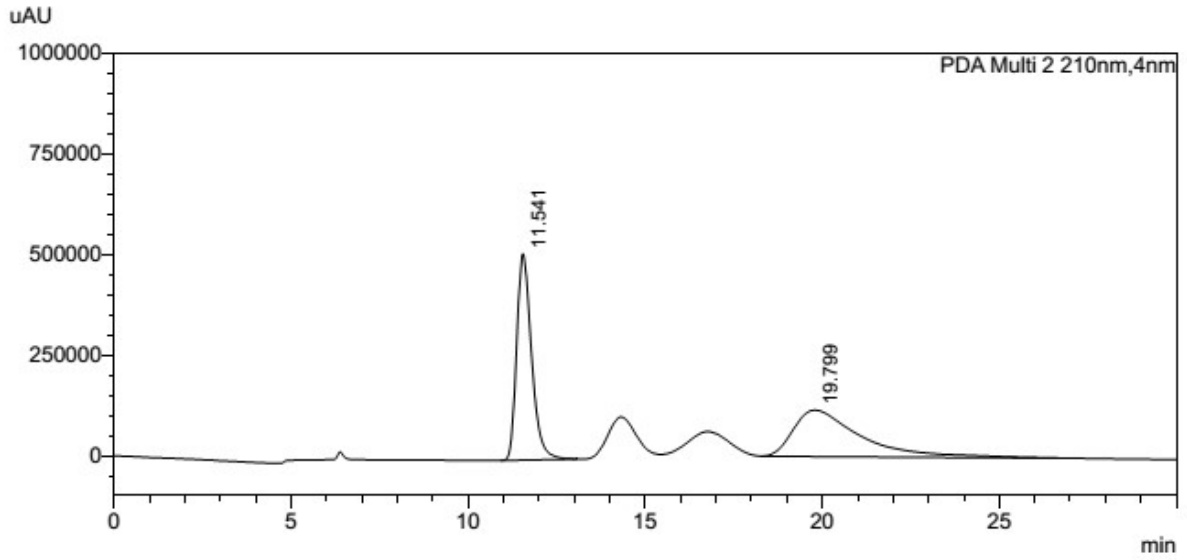
PDA Ch1 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.541	38.373	14891598	511705	38.373		M
2	14.312	13.559	5261849	99023	13.559		M
3	16.776	11.640	4517160	58490	11.640		M
4	19.799	36.428	14137033	114514	36.428		M
Total		100.000	38807641	783732			



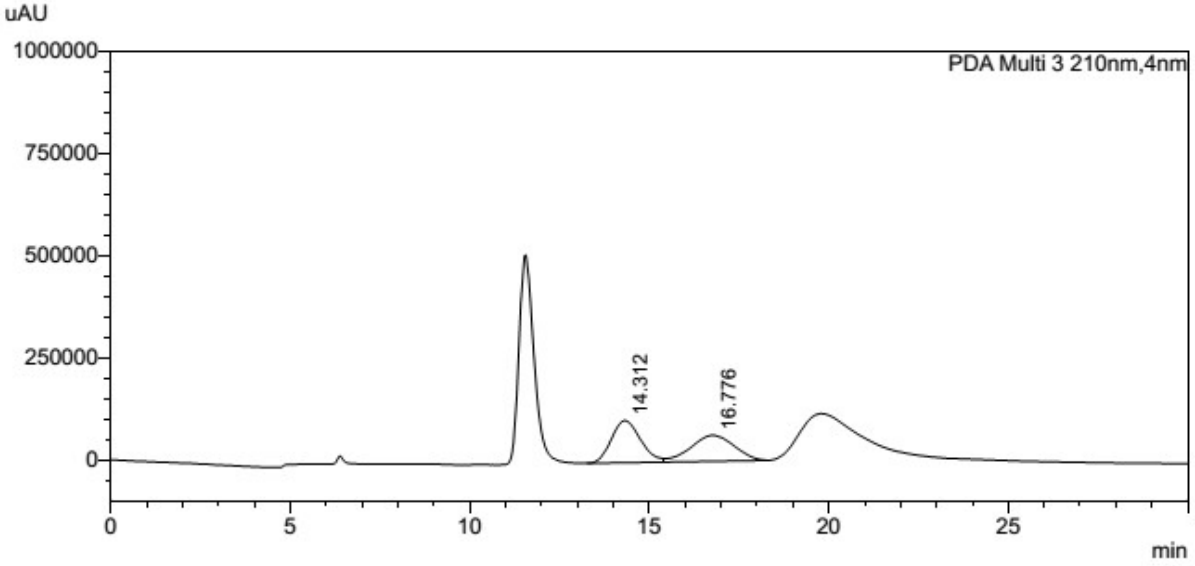
PDA Ch4 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.541	74.166	15022547	512578	74.166		M
2	14.312	25.834	5232829	98826	25.834		M
Total		100.000	20255375	611404			



PDA Ch2 210nm

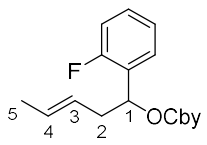
Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.541	49.837	15035407	512614	49.837		M
2	19.799	50.163	15133902	115479	50.163		M
Total		100.000	30169309	628094			



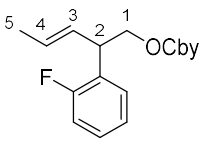
PDA Ch3 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	14.312	52.084	5790262	103097	52.084		M
2	16.776	47.916	5326903	63379	47.916		V M
Total		100.000	11117165	166476			

Observation and isolation of α- and β-products **2b*E*** and **3b*E***:



2b*E*



3b*E*

After arylation following the general procedure A, 6 mg (12%) of amixture of α- and β-arylated products (ratio 47:57) was isolated for analytical purpose.

α-product **2b*E*** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.00-5.98 (m, 1H, H_1), 5.51-5.46 (m, 1H, H_4), 5.39-5.33 (m, 1H, H_3), 2.65-2.57 (m, 2H, H_2), 1.62-1.60 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 125.95/125.89 (C_3), 71.04/70.99 (C_1), 31.11/39.05 (C_2), 18.1 (C_5).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ =-117.65/-117.68.

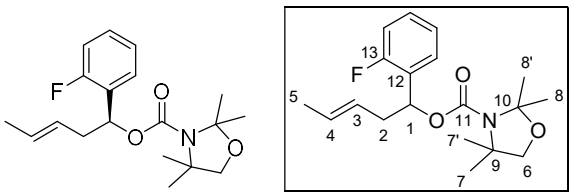
β-product **3b*E***:

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 5.65-5.56 (m, 2H, H_3, H_4), 4.40-4.35 (m, 1H, H_1), 4.28-4.22 (m, 1H, H_1), 4.04-3.97 (m, H_2), 1.68-1.67 (m, 3H, H_5).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 66.7 (C_1), 42.03/41.98 (C_2), 18.2 (C_5). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ =-118.11/-118.13.

IR neat (υ/cm^{-1}) of the mixture : 2978, 2361, 1696, 1398, 1341, 1258, 1064, 966.

Selective α-Arylation of **1b*E*** : synthesis of enantiopure **2b*E*** :

(−)-(*S*,*E*)-1-(2-fluorophenyl)pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate :



Arylation with TMEDA :

In a tubular reactor (100 mm x 16 mm)capped with a rubber septum, a solution of (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg, 0.207 mmol, 1 eq) and TMEDA (44 µL, 0.29 mmol, 1.4 eq) in dry diethyl ether (1.5 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (0.29 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (57 mg, 0.31 mmol, 1.5 eq) in dry THF (1.5 mL) was sonicated for 30 min and added

dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to heat up to 20°C over 30 min. The solvents were evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (3.3 mg, 3.6 µmol, 1.75 %mol) and RuPhos (3.4 mg, 7.3 µmol, 3.5 %mol) in dry toluene (1.5 mL) was added, followed by 1-bromo-2-fluorobenzene (15.8 µL, 0.15 mmol, 0.7 eq). The mixture was then vigorously stirred and heated to 80°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (2 mL), and the organic phase was diluted with EtOAc (3 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 3 mL). The combined organic layers were dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under vacuum. The residue was purified by preparative reversed-phase HPLC ($MeCN/H_2O$) to afford 17 mg (35%) of the racemictitle compound as an oil.

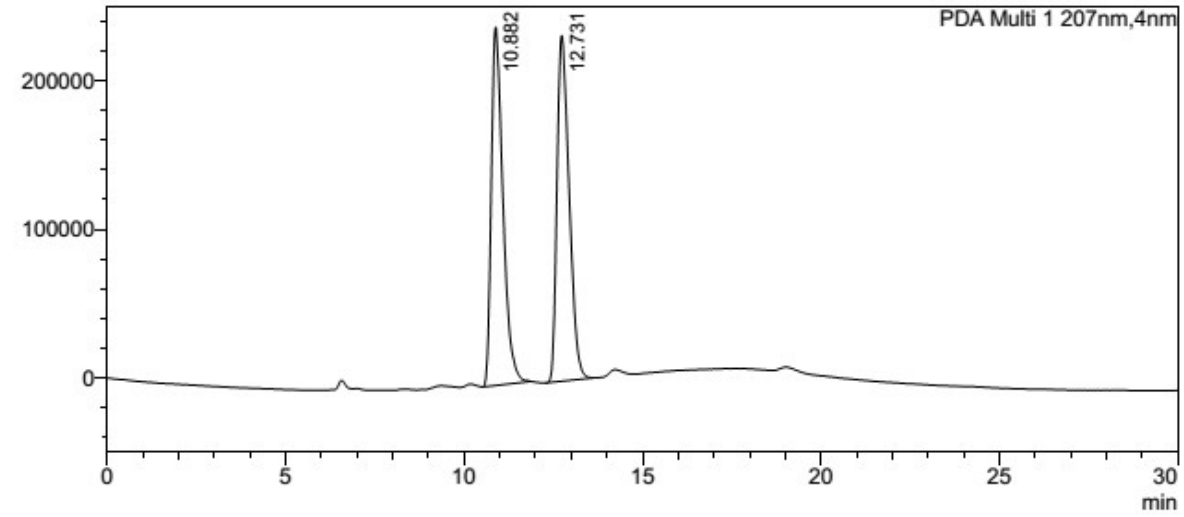
Arylation with (+)-sparteine :

The same procedure as for the arylation with TMEDA was used, using (+)-sparteine (88 µL, 0.29 mmol, 1.4 eq) as the diamine, instead of TMEDA. The crude residue was purified by preparative reversed-phase HPLC ($MeCN/H_2O$) to afford 20.5 mg (42%) of the enantioenriched title compound as an oil (*e.r.* 1:99).

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.34-7.23 (m, 2H, H_{Ar}), 7.13-7.10 (m, 1H, H_{Ar}), 7.05-7.01 (m, 1H, H_{Ar}), 5.99 (t, *J* = 6.6 Hz, 1H, H_1), 5.50-5.32 (m, 2H, H_3, H_4), 3.76-3.70 (m, 2H, H_6, 2.65-2.57 (m, 2H, H_2), 1.62-1.34 (m, 15H, H_5, H_7, H_7', H_8, H_8'). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.0-159.0 (d of rotamers, *J* = 247.6 Hz, C_{13}), 152.0/151.2 (C_{11}), 129.24/129.17 (C_{Ar}), 128.9 (C_4), 128.5-128.2 (C_{12}), 128.1/128.0 (C_{Ar}), 126.0/125.9 (C_3), 124.12/124.09 (C_{Ar}), 115.8/115.7 (C_{Ar}), 96.2/95.1 (C_{10}), 76.6/76.2 (C_6), 71.0 (C_1), 60.9/60.0 (C_9), 39.1/39.0 (C_2), 26.8-24.3 (C_7, $C_{7'}$, C_8, $C_{8'}$), 18.1 (C_5).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -117.62/-117.64 (F_{13}). **HPLC separation conditions :** Chiralpak IC column, *n*-heptane/*i*-PrOH 99:1, flow rate 0.5 mL/min, 25°C, t_R10.9 min for (*R*)-enantiomer (minor) and t_R 12.7 min for (*S*)-enantiomer (major). *e.r.* = 1:99.**HRMS (ESI) m/z:**calcd. for $C_{19}H_{26}NO_3Na$ ($[M + Na]^+$) : 358.1789; found: 358.1784**. IR neat (υ/cm^{-1}) :** 2960, 2361, 1701, 1397, 1258, 10630.**$[\alpha]_D^{20}$ =** -3.1° (c=1, $CHCl_3$).

<Chromatogram>

uAU



<Peak Table>

PDA Ch1 207nm

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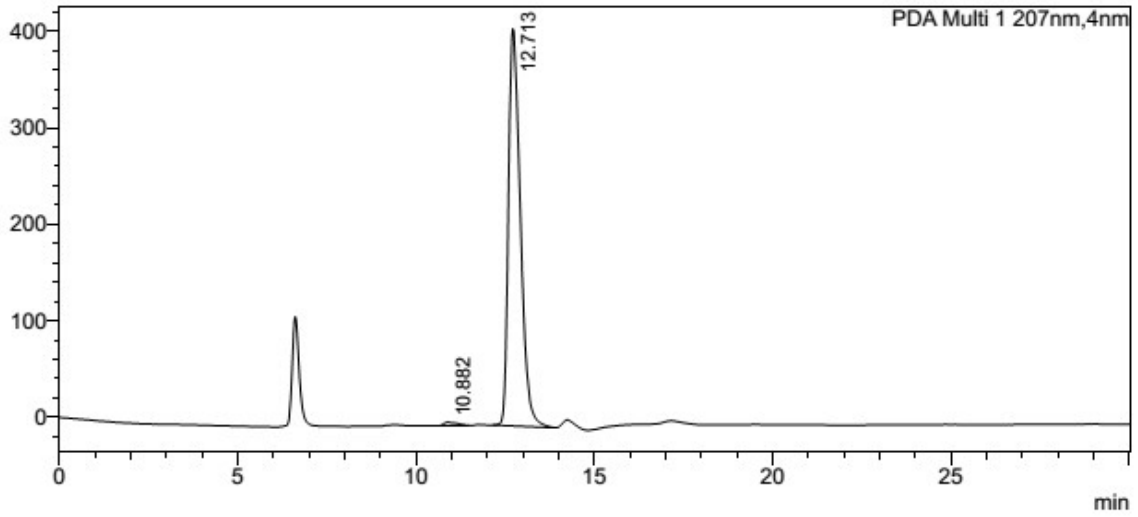
2	12.731	50.200	5492958	232430	50.200		M
Total		100.000	10942161	473279			

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
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2	12.713	99.041	9565229	411603	0.000		M
Total		100.000	9657888	415263			

Scale-up of the racemic arylation of **1b*E*** with $\mathbf{L^2}$

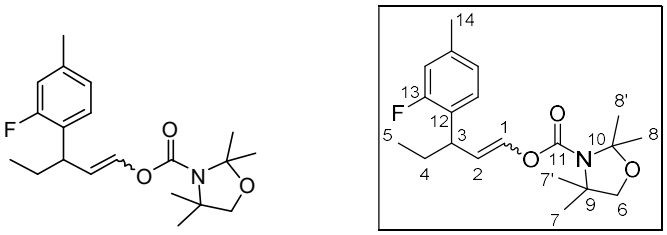
In a oven-dried Schlenck tube (75 mm x 40 mm) set up with a rubber septum, a solution of **1b*E*** (603 mg, 2.5 mmol, 1 eq) and TMEDA (530 µL, 3.5 mmol, 1.4 eq) in dry diethyl ether (10 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (3.5 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (688 mg, 3.8 mmol, 1.5 eq) in dry THF (10 mL) was sonicated for 30 min and added dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to warm-up to 20°C over 30 min. The solvents where evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (40.1 mg, 44 µmol, 1.75 %mol) and $\mathbf{L^2}$ (33.5 mg, 88 µmol, 3.5 %mol) in dry toluene (10 mL) was added to solve the residue, followed by 1-Br-2-F-benzene (191 µL, 1.75 mmol, 0.7 eq). The mixture was then vigorously stirred at60°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (10 mL), and the organic phase was diluted with EtOAc (25 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 25 mL). The combined organic layers were washed with water and dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under vacuum. The residue was purified bypreparative reversed-phase HPLC ($MeCN/H_2O$) to afford 397 mg (68%) of the γ-product **4b** (74:26 *Z*:*E* ratio).

Scale-up of the enantioselective arylation of **1b*E*** with $\mathbf{L^3}$

In a oven-dried Schlenck tube (75 mm x 40 mm) set up with a rubber septum, a solution of **1b*E*** (483 mg, 2 mmol, 1 eq) and (+)-sparteine (643 µL, 2.8 mmol, 1.4 eq) in dry diethyl ether (5 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (2.8 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (550 mg, 3 mmol, 1.5 eq) in dry THF (5 mL) was sonicated for 30 min and added dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to warm-up to 20°C over 30 min. The solvents where evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (32.1 mg, 35 µmol, 1.75 %mol) and $\mathbf{L^3}$ (22.4 mg, 70 µmol, 3.5 %mol) in dry toluene (5 mL) was added to solve the residue, followed by 1-Br-2-F-benzene (153 µL, 1.4 mmol, 0.7 eq). The mixture was then vigorously stirred at 60°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (10 mL), and the organic phase was diluted with EtOAc (25 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 25 mL). The combined organic layers were washed with water and dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under

vacuum. The residue was purified by preparative reversed-phase HPLC (MeCN/H_2O) to afford 255 mg (54%) of the γ-product **4b** (86:14 *Z*:*E* ratio, *e.r.* 2:98 for both isomers).

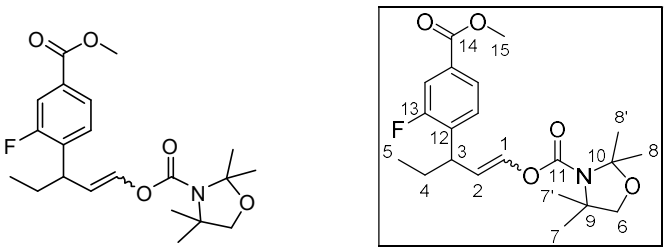
3-(2-fluoro-4-methylphenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4c** :



Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 4-bromo-3-fluorotoluene (18.3 µL) to give 29.9 mg (59%) of the title compound (76:24 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.11-7.05 (m, 2H, H_1, H_{Ar}), 6.90-6.88 (m, 1H, H_{Ar}), 6.84-6.80 (m, 1H, H_{Ar}), 5.53-5.45 (m, 1H, H_2E), 4.98-4.93 (m, 1H, H_2Z), 4.02-3.91 (m, 1H, H_3Z), 3.77-3.74 (m, 2H, H_6), 3.46-3.41 (m, 1H, H_3E), 2.31 (s, 3H, $H_{14}E$), 2.30 (s, 3H, $H_{14}Z$), 1.76-1.34 (m, 14H, H_4, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.91-0.86 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.9/161.7-159.4/159.3 (d of rotamers, *J* = 244.3 Hz, C_{13}), 150.0/149.2 (C_{11}), 138.1-137.9 (C_{Ar}), 136.6/136.5 (C_1E), 134.6/134.5 (C_1Z), 128.6-128.2 (C_{12}, C_{Ar}), 125.0-124.9 (C_{Ar}), 116.3-116.0 (C_{Ar}), 115.0/114.9 (C_2E), 113.5/113.3 (C_2Z), 96.3-95.4 (C_{10}), 76.6-76.2 (C_6), 61.1-60.3 (C_9), 39.3 (C_3E), 36.42/36.36 (C_3Z), 29.4 (C_4Z), 28.4 (C_4E), 26.9-24.0 (C_7, $C_{7'}$, C_8, $C_{8'}$), 21.01/21.99 (C_{14}), 12.3 (C_5E), 12.2 (C_5Z).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -119.3--119.4 (F_{13}).**HRMS (ESI) m/z:**calcd. for $C_{20}H_{28}FNO_3Na$ ($[M + Na]^+$): 372.1945; found: 372.1953**. IR neat (ʊ/cm^{-1}) :**2970, 2361, 1718, 1377, 1258, 1089.

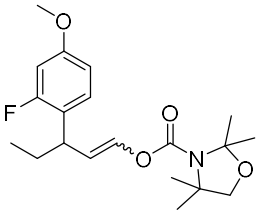
3-(2-fluoro-4-(methoxycarbonyl)phenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4d** :

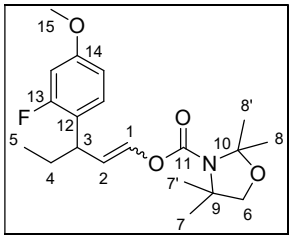


Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with methyl 4-bromo-3-fluorobenzoate (33.8 mg, in 0.5 mL of toluene) to give 31 mg (54%) of the title compound (68:32 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.78-7.75 (m, 1H, H_{Ar}), 7.68-7.64 (m, 1H, H_{Ar}), 7.32-7.25 (m, 1H, H_{Ar}), 7.14-7.11 (m, 1H, H_1), 5.52-5.43 (m, 1H, H_2E), 4.98-4.92 (m, 1H, H_2Z), 4.11-3.99 (m, 1H, H_3Z), 3.90 (s, 3H, H_{15}), 3.75-3.74 (m, 2H, H_6), 3.55-3.48 (m, 1H, H_3E), 1.78-1.66 (m, 2H, H_4), 1.62-1.28 (m, 12H, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.92-0.86 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 166.13/166.10 (C_{14}), 161.6/161.5-159.2/159.0 (d of rotamers, J = 245.3 Hz, C_{13}), 150.0/149.8 ($C_{11}Z$), 149.2/149.0 ($C_{11}E$), 137.4-137.0 (C_{Ar}, C_1E), 135.4/135.3 (C_1Z), 130.2-130.0 (C_{12}), 128.9-128.6 (C_{Ar}), 125.61-125.56 (C_{Ar}), 117.0-116.6 (C_{Ar}), 113.74/113.69 (C_2E), 112.2/112.1 (C_2Z), 96.3-95.3 (C_{10}), 76.5-76.1 (C_6), 61.2-60.3 (C_9), 52.4 (C_{15}), 39.7 (C_3E), 36.8/36.7 (C_3Z), 29.3 (C_4Z), 28.7 (C_4E), 26.7-24.0 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.2 (C_5E), 12.1 (C_5Z).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -117.37--117.38 ($F_{13}E$), -117.47--117.52 ($F_{13}Z$).**HRMS (ESI) m/z:**calcd. for $C_{21}H_{28}FNO_5Na$ ([M + Na]$^+$): 416.1844; found: 416.1838**. IR neat (υ/cm^{-1}) :**2969, 2874, 2361, 1720, 1353, 1290, 1210, 1089.

3-(2-fluoro-4-methoxyphenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4e** :





Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 4-bromo-3-fluoroanisole (29.7 mg) to give 24.1 mg (46%) of the title compound (77:23 *Z*:*E* ratio) as an oil.

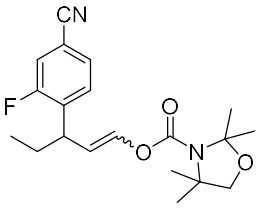
^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.12-7.06 (m, 3H, H_1, $2H_{Ar}$), 6.66-6.63 (m, 1H, H_{Ar}), 6.60-6.56 (m, 1H, H_{Ar}), 5.52-5.44 (m, 1H, H_2E), 4.96-4.91 (m, 1H, H_2Z), 3.97-3.87 (m, 1H, H_3Z), 3.79-3.74 (m, 5H, H_6, H_{14}), 3.43-3.38 (m, 1H, H_3E), 1.75-1.34 (m, 14H, H_4, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.91-0.95 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 162.2/162.1-160.3/160.1 (d of rotamers, J = 244.2 Hz, C_{13}), 159.3-159.1 (C_{15}), 150.2-149.2 (C_{11}), 138.6/138.4 (C_1E), 134.6-134.4 (C_1Z), 129.1-128.8 (C_{Ar}), 123.7-123.6 ($C_{12}Z$), 123.2-123.1 ($C_{12}E$), 115.11/115.06 (C_2E), 113.6/113.5 (C_2Z), 110.1-109.9 (C_{Ar}), 101.9-101.7 (C_{Ar}), 93.3-95.4 (C_{10}), 76.6-76.2 (C_6), 61.2-60.3 (C_9), 55.6 (C_{15}), 40.0 (C_3E), 36.2/36.1 (C_3Z), 29.5 (C_4Z), 28.4 (C_4E), 26.9-24.1 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.3 (C_5E), 12.2

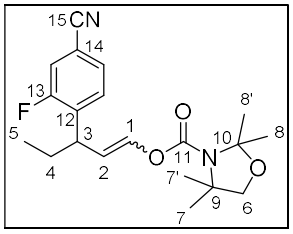
(C_5Z).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -119.28--119.33 (F_{13}).**HRMS (ESI) m/z:**calcd. for $C_{20}H_{28}FNO_4Na$ ([M + Na]$^+$): 388.1895; found: 388.1897**. IR neat (υ/cm^{-1}) :** 2968, 2361, 1714, 1624, 1507, 1376, 1353, 1259, 1090.

- Scale up of the arylation for the synthesis of **4e**

In a oven-dried Schlenck tube (75 mm x 40 mm) set up with a rubber septum, a solution of **2b*E*** (302 mg, 1.25 mmol, 1 eq) and TMEDA (264 µL, 1.75 mmol, 1.4 eq) in dry diethyl ether (10 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (1.75 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (344 mg, 3.8 mmol, 1.5 eq) in dry THF (10 mL) was sonicated for 30 min and added dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to warm-up to 20°C over 30 min. The solvents where evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (20 mg, 22 µmol, 1.75 %mol) and **L^2** (16.7 mg, 88 µmol, 3.5 %mol) in dry toluene (10 mL) was added to solve the residue, followed by 4-Br-3-F-anisole (112 µL, 0.88 mmol, 0.7 eq). The mixture was then vigorously stirred at60°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (10 mL), and the organic phase was diluted with EtOAc (25 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 25 mL). The combined organic layers were washed with water and dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under vacuum. The residue was purified by preparative reversed-phase HPLC (MeCN/H_2O) to afford 200 mg (44%) of the γ-product **4e** (76:24 *Z*:*E* ratio).

3-(4-cyano-2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4f** :

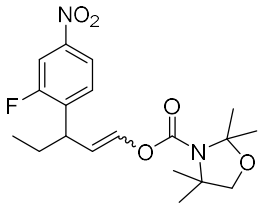


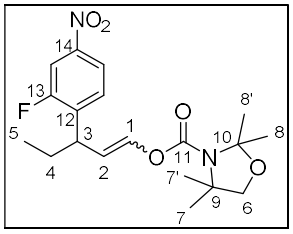


Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 4-bromo-3-fluorobenzonitrile (29 mg) to give 22.5 mg (43%) of the title compound (67:33 *Z*:*E* ratio, contains ~10% α- and β-arylated products) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.42-7.40 (m, 1H, H_{Ar}), 7.37-7.29 (m, 2H, $2H_{Ar}$), 7.15-7.12 (m, 1H, H_1), 5.47-5.39 (m, 1H, H_2E), 4.93-4.88 (m, 1H, H_2Z), 4.10-4.00 (m, H_3Z), 3.78-3.73 (m, 2H, H_6), 3.55-3.50 (m, 1H, H_3E), 1.81-1.65 (m, 2H, H_4), 1.61-1.38 (m, 12H, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.93-0.87 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.2-159.1 (d of rotamers, J = 248.4 Hz, C_{13}), 150.0-148.8 (C_{11}), 138.2-137.8 (C_{12}), 137.6/137.5 (C_1E), 136.0/135.8 (C_1Z), 130.0-129.7 (C_{14}, C_{Ar}), 128.48-128.45 (C_{Ar}), 119.5-119.1 (C_{Ar}), 117.8 (C_{15}), 113.04/112.99 (C_2E), 111.6-111.4 (C_2Z), 96.4-95.3 (C_{10}), 76.5-76.2 (C_6), 61.3-60.3 (C_9), 39.7 (C_3E), 36.72/36.67 (C_3Z), 29.2 (C_4Z), 28.2 (C_4E), 26.9-23.8 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.12 (C_5E), 12.05 (C_5Z).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = [-113.73/-113.74 ($F_{α\text{-prod}}$), -114.4 ($F_{β\text{-prod}}$)], -114.84/-114.85 ($F_{13}E$), -115.0/-115.1 ($F_{13}Z$).**HRMS (ESI) m/z:**calcd. for $C_{20}H_{25}FN_2O_3Na$ ($[M + Na]^+$): 383.1741; found: 383.1739. **IR neat (ʊ/cm^{-1}) :**2970, 2874, 2361, 2234, 1713, 1376, 1257, 1088.

3-(2-fluoro-4-nitrophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4g** :



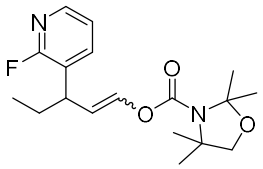


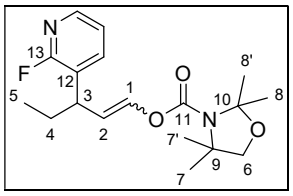
Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 4-bromo-3-fluoronitrobenzene (32 mg) to give 17 mg (31%) of the title compound (65:35 *Z*:*E* ratio, contains ~5% α- and β-arylated products) as an orange oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 8.00-7.98 (m, 1H, H_{Ar}), 7.91-7.88 (m, 1H, H_{Ar}), 7.44-7.37 (m, 1H, H_{Ar}), 7.17-7.14 (m, 1H, H_1), 5.49-5.41 (m, 1H, H_2E), 4.96-4.91 (m, 1H, H_2Z), 4.15-4.04 (m, 1H, H_3Z), 3.78-3.74 (m, 2H, H_6), 3.60-3.55 (m, 1H, H_3E), 1.84-1.71 (m, 2H, H_4), 1.63-1.29 (m, 12H, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.95-0.89 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.1-158.95 (d of rotamers, J = 248.5 Hz, C_{13}), 149.9-148.8 (C_{11}), 147.3-147.1 (C_{14}), 140.0-139.5 (C_{12}), 137.8/137.6 (C_1E), 136.1/136.0 (C_1Z), 129.4-129.2 (C_{Ar}), 119.62/119.59 (C_{Ar}), 112.90/112.86 (C_2E), 111.8-111.2 (C_2Z, C_{Ar}), 96.5-95.3 (C_{10}), 76.5-76.2 (C_6), 61.4-60.3 (C_9), 39.76/39.74 (C_3E), 36.8-36.7 (C_3Z), 29.3 (C_4Z), 28.2 (C_4E), 26.8-24.0 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.14 (C_5E), 12.07 (C_5Z).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = [-112.52/-112.53 ($F_{α\text{-prod}}$), -113.2 ($F_{β\text{-prod}}$)], -113.67/-113.68 ($F_{13}E$), -113.86/-

113.91 ($F_{13}Z$).**HRMS (ESI) m/z:** calcd. for $C_{19}H_{25}FN_2O_5Na$ ([M + Na]$^+$): 403.1640; found: 403.1633**. IR neat (υ/cm^{-1}) :** 2971, 2874, 2361, 1714, 1528, 1351, 1258, 1088.

3-(2-fluoropyridin-3-yl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4h** :

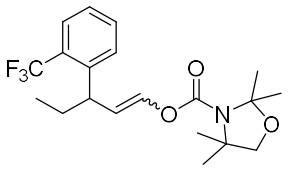


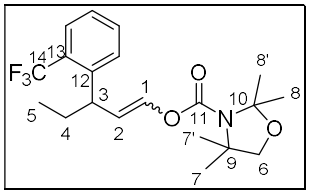


Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 3-bromo-2-fluoropyridine (14.7 µL) to give 25.6 mg (53%) of the title compound (75:25 *Z*:*E* ratio, contains ~10% of other isomers) as an oil.

^{1}H NMR (CDCl$_3$, 400 MHz, rotamers) :δ = 8.07-8.04 (m, 1H, H_{Ar}), 7.66-7.60 (m, 1H, H_{Ar}), 7.15-7.12 (m, 2H, H_1, H_{Ar}), 5.51-5.43 (m, 1H, H_2E), 4.95-4.90 (m, 1H, H_2Z), 4.00-3.89 (m, 1H, H_3Z), 3.77-3.73 (m, 2H, H_6), 3.42-3.37 (m, 1H, H_3E), 1.78-1.25 (m, 14H, H_4, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.94-0.88 (m, 3H, H_5). **^{13}C-{^{1}H} NMR (CDCl$_3$, 125 MHz, rotamers) :**δ = 162.6-160.9 (d of rotamers, *J* = 238.2 Hz, C_{13}), 150.0-148.9 (C_{11}), 145.5-145.2 (C_{Ar}), 139.4-139.0 (C_{Ar}), 137.4/137.3 (C_1E), 135.8-135.6 (C_1Z), 126.9-126.6 (C_{12}), 121.70/121.67 (C_{Ar}), 113.4-113.3 (C_2E), 111.8/111.7 (C_2Z), 96.4-95.4 (C_{10}), 76.5-76.2 (C_6), 61.3-60.4 (C_9), 40.0/39.9 (C_3E), 36.57/36.55 (C_3E), 29.1/29.0 (C_4Z), 28.2 (C_4E), 26.5-25.1 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.2-12.1 (C_5).**^{19}F-{^{1}H} NMR (CDCl$_3$, 376 MHz, rotamers) :** δ = [-69.53--70.2 (F other isomers)], -71.7/-71.8 ($F_{13}E$), -72.3 ($F_{13}Z$).**HRMS (ESI) m/z:** calcd. for $C_{18}H_{25}FN_2O_3Na$ ([M + Na]$^+$): 359.1741; found: 359.1740**. IR neat (υ/cm^{-1}) :** 2970, 2874, 1361, 1713, 1435, 1377, 1257, 1089.

3-(2-(trifluoromethoxy)phenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4i** :

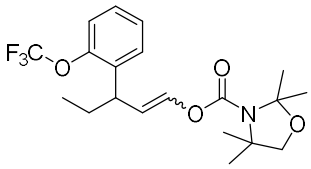


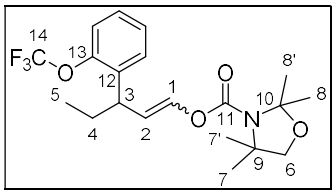


Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-(trifluoromethyl)benzene(20.1 µL) to give 23.6 mg (42%) of the title compound (48:52 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.62-7.60 (m, 1H, H_{Ar}), 7.54-7.41 (m, 2H, H_{Ar}), 7.30-7.27 (m, 1H, H_{Ar}), 7.09-7.06 (m, 1H, H_1E), 7.03-7.01 (m, 1H, H_1Z), 5.50-5.42 (m, 1H, H_2E), 4.93-4.89 (m, 1H, H_2Z), 4.23-4.13 (m, 1H, H_3Z), 3.79-3.74 (m, 2H, H_6), 3.66-3.62 (m, 1H, H_3E), 1.81-1.37 (m, 14H, H_4, C_7, $C_{7'}$, C_8, $C_{8'}$), 0.89-0.84 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 150.2-149.3 (C_{11}), 144.0/143.9 (C_{12}), 136.9/136.8 (C_1E), 134.8/134.7 (C_1Z), 132.3/132.2 (C_{Ar}), 128.5/128.1 (C_{Ar}), 128.3 (q, J = 29.6 Hz, C_{13}), 126.2 (C_{Ar}), 126.1-125.8 (C_{Ar}), 124.7 (q of rotamers, J = 279.8 Hz, C_{14}), 115.52/115.46 (C_2E), 114.64/114.59 (C_2Z), 96.4-95.4 (C_{10}), 76.6-76.1 (C_6), 61.3-60.4 (C_9), 40.9 (C_3E), 38.7 (C_3Z), 31.2 (C_4Z), 29.8 (C_4E), 26.9-24.0 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.13/12.06 (C_5).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -58.30/-58.33(F_{14}).**HRMS (ESI) m/z:**calcd. for $C_{20}H_{26}F_3NO_3Na$ ($[M + Na]^+$): 408.1757; found: 408.1753**. IR neat (ʊ/cm^{-1}) :** 2972, 2361, 1715, 1374, 1314, 1122, 1071.

3-(2-(trifluoromethoxy)phenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4j** :



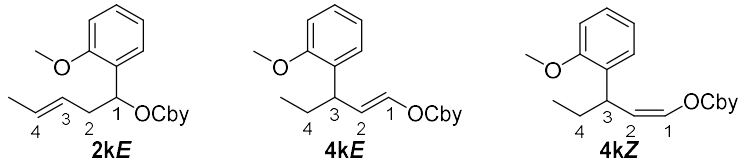


Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-(trifluoromethoxy)benzene (21.6 µL) to give 37 mg (64%) of the title compound (61:39 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.34-7.21 (m, 4H, H_{Ar}), 7.10-7.07 (m, 1H, H_1), 5.48-5.40 (m, 1H, H_2E), 4.93-4.88 (m, 1H, H_2Z), 4.18-4.07 (m, 1H, H_3Z), 3.77-3.74 (m, 2H, H_6), 3.63-3.58 (m, 1H, H_3E), 1.80-1.38 (m, 14H, H_4, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.92-0.85 (m, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 150.2/150.0 ($C_{11}Z$), 149.3/149.2 ($C_{11}E$), 149.2/147.1 (C_{13}), 137.1-136.8 (C_1E, C_{Ar}), 135.0/134.9 (C_1Z), 128.7/128.5 (C_{Ar}), 127.5/127.4 (C_{Ar}), 127.2-126.9 (C_{Ar}), 122.1/122.0-119.52/119.46 (q of rotamers, J = 257 Hz, C_{14}), 120.7/120.0 (C_{Ar}), 96.4-95.4 (C_{10}), 76.6-76.2 (C_6), 61.2-60.4 (C_9), 38.7 (C_3E), 36.3 (C_3Z), 30.0 (C_4E), 29.8 (C_4Z), 26.9-24.0 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.1 (C_5).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -56.41/-56.43($F_{14}Z$), -56.74 ($F_{13}E$).**HRMS (ESI) m/z:**calcd.

for$C_{20}H_{26}F_3NO_4Na$ ([M + Na]$^+$): 424.1706; found: 424.1700**. IR neat (υ/cm^{-1}) :**2972, 2876, 2361, 1718, 1377, 1256, 1164, 1088.

- Arylation of **1b*E*** with 2-bromoanisole : products **4k** and isomers



Following the general procedure, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 2-bromoanisole (18.1 µL) to give 15 mg (30%) of a mixture of isomeric arylated product (NMR ratio : α/γE/γZ 16/54/30). The calculated yield of combined γ-product **4k** was *ca*. 24% (64:36 *Z*:*E* ratio).

<u>α-isomer**2k*E***:</u>

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.16-6.13 (m, 1H, H_1), 5.45-5.39 (m, 2H, H_3, H_4), 2.57-2.49 (m, 2H, H_2). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 71.4/71.3 (C_1), 39.1/39.0 (C_2).

<u>γE-product **4k*E*** :</u>

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 5.53-5.47 (m, 1H, H_2), 3.66-3.61 (m, 1H, H_3). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 38.8 (C_3).

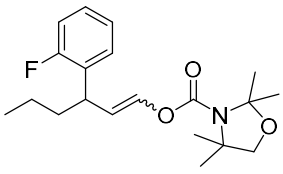
<u>γZ-product **4k*Z***:</u>

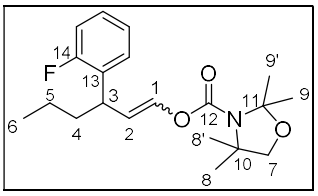
^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 5.01–4.97 (m, 1H, H_2), 4.20-4.09 (m, 1H, H_3), 1.75-1.67 (m, 2H, H_4).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 114.5/114.3 (C_2), 36.62/36.45 (C_3), 29.3/29.2 (C_4).

HRMS (ESI) m/z: calcd. for$C_{20}H_{29}NO_4Na$ ([M + Na]$^+$): 370.1989; found: 370.1989.**IR neat (υ/cm^{-1}) :** 2969, 2361, 1711, 1596, 1377, 1350, 1241, 1091.

7. Arylation of carbamates **1l-p** : products **4l-p**

3-(2-fluorophenyl)hex-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4l** :

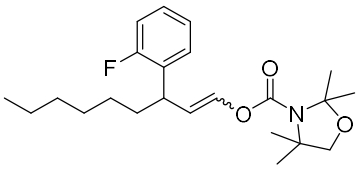


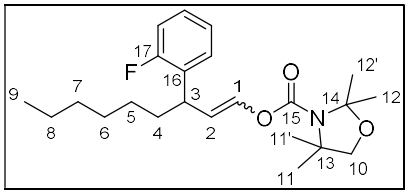


Following the general procedure, (*E*)-hex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (53 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 27.2 mg (54%) of the title compound (76:24 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.24-7.06 (m, 4H, $3H_{Ar}$, H_1), 7.01-6.97 (m, 1H, H_{Ar}), 5.55-5.47 (m, 1H, H_2E), 5.00-4.96 (m, 1H, H_2Z), 4.17-4.07 (m, 1H, H_3Z), 3.76-3.74 (m, 2H, H_7), 3.62-3.57 (m, 1H, H_3E), 1.73-1.21 (m, 16H, H_4, H_5, H_8, $H_{8'}$, H_9, $H_{9'}$), 0.92-0.88 (m, 3H, H_6). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.7/161.6-159.8/159.7 (d of rotamers, J = 245.1 Hz, C_{14}), 150.2/150.0 ($C_{12}Z$), 149.4/149.2 ($C_{12}E$), 136.6/136.5 (C_1E), 134.6/134.5 (C_1Z), 132.0-131.5 (C_{13}), 128.8-128.5 (C_{Ar}), 127.8-127.6 (C_{Ar}), 124.29/124.27 (C_{Ar}), 115.8-115.4 (C_{Ar}), 114.93/114.89 (C_2E), 113.5/113.4 (C_2Z), 96.3-95.4 (C_{11}), 76.6-76.2 (C_7), 61.2-60.4 (C_{10}), 38.7 (C_4Z), 37.6 (C_4E), 37.5 (C_3E), 34.74-34.65 (C_3Z), 26.9-24.0 (C_8, $C_{8'}$, C_9, $C_{9'}$), 20.80/20.76 (C_5), 14.1/14.0 (C_6).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ =-118.31/-118.32 ($F_{14}E$), -118.33/-118.39 ($F_{14}Z$). **HRMS (ESI) m/z:**calcd. for$C_{20}H_{28}FNO_3Na$ ([M + Na]$^{+}$): 372.1945; found: 372.1943**. IR neat (ʊ/cm^{-1}) :**2361, 1712, 1345, 1240, 1225, 1089.

3-(2-fluorophenyl)non-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4m** :

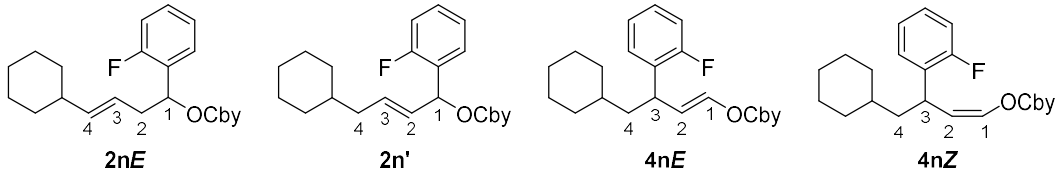




Following the general procedure, (*E*)-oct-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 22.9 mg (45%) of the title compound (77:23 *Z*:*E* ratio) as an oil.

^{1}H NMR ($CDCl_3$, 500 MHz, rotamers) :δ = 7.25-7.06 (m, 4H, H_1, H_{Ar}), 7.02-6.97 (m, 1H, H_{Ar}), 5.54-5.47 (m, 1H, H_2*E*), 5.00-4.95 (m, 1H, H_2*Z*), 4.15-4.04 (m, 1H, H_3*Z*), 3.76-3.74 (m, 2H, H_{10}), 3.59-3.54 (m, 1H, H_3*E*), 1.73-1.23 (m, 22H, H_4, H_5, H_6, H_7, H_8, H_{11}, $H_{11'}$, H_{12}, $H_{12'}$), 0.87-0.84 (m, 3H, H_9). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 161.7/161.6-159.8/159.7 (d of rotamers, *J* = 244.7 Hz, C_{17}), 150.2/150.0 (C_{15}*Z*), 149.4/149.2 (C_{15}*Z*), 136.6/136.5 (C_1*E*), 134.6/134.5 (C_1*Z*), 132.0/131.9 (C_{16}*Z*), 31.6/131.5 (C_{16}*E*), 128.8-128.5 (C_{Ar}), 127.8-127.6 (C_{Ar}), 124.29/124.26 (C_{Ar}), 115.8-115.4 (C_{Ar}), 115.01/115.95 (C_2*E*), 113.6/113.5 (C_2*Z*), 96.3-95.4 (C_{14}), 76.6-76.2 (C_{10}), 61.2-60.3 (C_{13}), 37.80/37.78 (C_3*E*), 36.5 (C_4*Z*), 35.4 (C_4*E*), 35.0-34.9 (C_3*Z*), 31.85/31.82 (C_5), 29.3/29.2 (C_6), 27.64/27.58 (C_7), 26.7-24.0 (C_{11}, $C_{11'}$, C_{12}, $C_{12'}$) 22.8 (C_8), 14.2 (C_9).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.30/-118.31 (F_{17}*E*), -118.34/-118.40 (F_{17}*Z*).**HRMS (ESI) m/z:**calcd. for $C_{23}H_{34}FNO_3Na$ ($[M + Na]^+$): 414.2415; found: 414.2414**. IR neat (υ/cm^{-1}) :**2929, 2361, 1711, 1372, 1258, 1128, 1069.

- Arylation of carbamate **1n** : products **4n** and isomers



Following the general procedure A, (*E*)-4-cyclohexylbut-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (64.1 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 30 mg (52%) of a mixture of isomeric arylated product (NMR ratio : α/α'/γE/γZ 13/2/11/74). The calculated yield of combined γ-product **4n** was *ca*. 44% (87:13 *Z*:*E* ratio).

α-product **2n*E*** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.02-6.00 (m, 1H, H_1), 5.41-5.36 (m, 1H, H_4), 5.31-5.24 (m, 1H, H_3),2.66-2.52 (m, 2H, H_2). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 140.4 (C_4), 122.03/121.95 (C_3), 71.1/71.0 (C_1), 39.1/39.0 (C_2).).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -116.95.

α'-product **2n'** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.41-6.39 (m, 1H, H_1) 5.75-5.63 (m, 2H, H_2, H_3). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 72.0 (C_1). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -117.49/-117.53.

γE-product **4n*E*** :

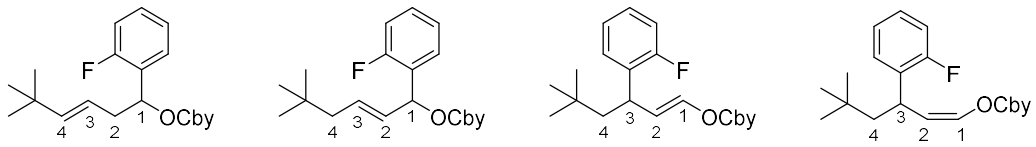
^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 5.52-5.45 (m, 1H, H_2). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 115.3/115.2 (C_2), 34.6 (C_3). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.34/-118.35

γZ-product **4n*Z***:

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 4.97–4.93 (m, 1H, H_2), 4.30-4.19 (m, 1H, H_3). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 114.0/113.9 (C_2), 32.1-32.0 (C_3). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.6/-118.44.

HRMS (ESI) m/z: calcd. for$C_{24}H_{34}FNO_3Na$ ([M + Na]$^+$): 426.2415; found: 426.2412**. IR neat (υ/cm^{-1}) :** 2923, 2852, 2361, 1714, 1349, 1258, 1091.

- Arylation of carbamate **1o**: products **4o** and isomers



Following the general procedure A, (*E*)-5,5-dimethylhex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (58.7 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 23 mg (42%) of a mixture of isomeric arylated product (NMR ratio : α/α'/γE/γZ 24/17/12/47). The calculated yield of combined γ-product was *ca*. 25% (80:20 *Z*:*E* ratio).

α-product **2o*E*** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.04-6.02 (m, 1H, H_1), 5.46-5.42 (m, 1H, H_4), 5.29-5.21 (m, 1H, H_3),2.66-2.51 (m, 2H, H_2). **^{13}C-{^{1}H} NMR ($CDCl_3$,**

125 MHz, rotamers), characteristic peaks :δ = 145.4 (C_4), 119.4/119.3 (C_3), 71.1/71.0 (C_1), 39.1/39.0 (C_2).).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -117.52/-117.57.

α'-product **2o'** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 6.44-6.41 (m, 1H, H_1) 5.82-5.76 (m, 2H, H_2), 5.70-5.65 ((m, 2H, H_3), 1.92 (d, *J* = 7.5 Hz, 1H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 71.9/71.8 (C_1), 132.2/132.1 (C_2), 129.7/129.6 (C_3), 46.8 (C_4). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -116.97/-116.99.

γE-product **4o*E*** :

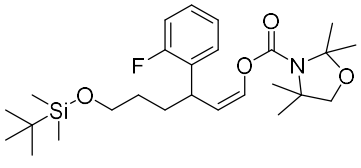
^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 5.57-5.49 (m, 1H, H_2), 1.80 (ddd, *J* = 13.9 Hz, *J* = 7.3 Hz, *J* = 2.4 Hz, 1H, H_4). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 117.0/116.9 (C_2), 49.3 (C_4), 34.68/34.66 (C_3). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -117.99/-118.0.

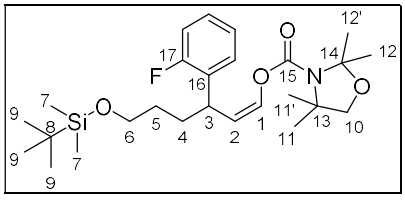
γZ-product **4o*Z*** :

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers), characteristic peaks :δ = 5.07-5.02 (m, 1H, H_2), 4.30-4.21 (m, 1H, H_3). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers), characteristic peaks :**δ = 50.9 (C_4). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -117.86/-117.95.

HRMS (ESI) m/z:calcd. for$C_{22}H_{32}FNO_3Na$ ($[M + Na]^+$): 400.2258; found: 400.2254.**IR neat (υ/cm^{-1}) :**2958, 2361, 1712, 1397, 1259, 1066.

(*Z*)-6-((tert-butyldimethylsilyl)oxy)-3-(2-fluorophenyl)hex-1-en-1-yl 2,2,4,4-tetramethyloxa zolidine-3-carboxylate**4p** :



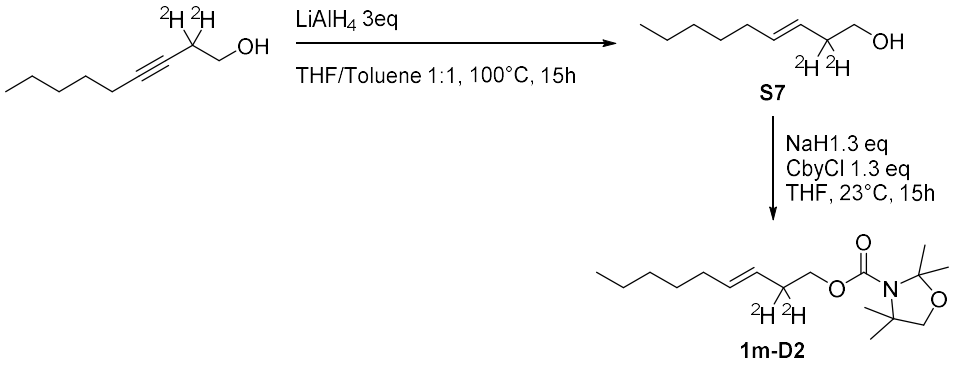


Following the general procedure, (*E*)-6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (80 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 11.5 mg (17%) of the title compound as an oil.

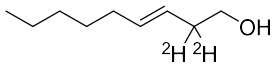
^{1}H NMR ($CDCl_3$, 500 MHz, rotamers) : δ = 7.25-7.20 (m, 1H, H_{Ar}), 7.18-7.14 (m, 1H, H_{Ar}), 7.09-7.06 (m, 2H, H_1, H_{Ar}), 7.01-6.97 (m, 1H, H_{Ar}), 5.00-4.95 (m, 1H, H_2), 4.15-4.04 (m, 1H, H_3), 3.78-3.73 (m, 2H, H_{10}), 3.60-3.57 (m, 2H, H_6), 1.87-1.65 (m, 2H, H_4), 1.64-1.32 (m, 14H, H_5, H_{11}, $H_{11'}$, H_{12}, $H_{12'}$), 0.87 (s, 9H, H_9), 0.01 (m, 6H, H_7). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :** δ = 161.6-159.7 (d of rotamers, J = 244.2 Hz, C_{17}), 150.0/149. (C_{15}), 134.7-134.6 (C_1), 131.8/131.6 (C_{16}), 128.6-128.5 (C_{Ar}), 127.8-127.7 (C_{Ar}), 124.4/124.3 (C_{Ar}), 115.7/115.5 (C_{Ar}), 113.3/113.2 (C_2), 96.3/95.4 (C_{14}), 76.6/76.2 (C_{10}), 63.07/63.05 (C_6), 61.2/60.3 (C_{13}), 34.9/34.8 (C_3), 32.7 (C_4), 31.1 (C_5), 26.8-24.0 (C_{11}, $C_{11'}$, C_{12}, $C_{12'}$), 26.1 (C_9), 18.5 (C_8), -5.2 (C_7).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.21/-118.27 (F_{17}). **HRMS (ESI) m/z:** calcd. for $C_{26}H_{42}FNO_4SiNa$ ($[M + Na]^+$): 502.2759 ; found: 502.2766**. IR neat (υ/cm^{-1}) :** 2935, 2863, 2361, 1719, 1400, 1349, 1256, 1091.

8. Deuterium labeling experiment (Scheme 3b)

- Synthesis of the deuterated substrate **1m-D2**



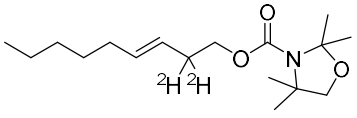
[2,2-$^2H_2$]-non-3(*E*)-en-1-ol **S7** :



$LiAlH_4$ (211 mg, 5.3 mmol, 3 eq) was added portionwise to a solution of [2,2-$^2H_2$] non-3-yn-1-ol[6] (250 mg, 1.8 mmol, 1 eq) in THF/Toluene (5 mL, 1:1 v:v) at 0°C (water, ice) over 5 min. The mixture was stirred at 100°C for 15 h and then cooled down to room temperature. The reaction was quenched by a sequential addition of water (250µL), 15% aq. NaOH (250µL), and water (750 µL). The precipitate was filtered off on celite with Et_2O. The resulting organic phase was dried over $MgSO_4$, filtered, and concentrated under vacuum. The oily residue was purified by silica gel column chromatography (Pent/Et_2O 95:5 to 50:50) to obtain 180 mg (71 %, 100 % (*E*), >98% ^2H int.) of the desired deuterated alcohol as a colorless oil.

^1H NMR ($CDCl_3$, 400 MHz) :δ = 5.55 (dt, *J* = 15.3 Hz, *J* = 6.7 Hz, 1H), 5.36 (br. d, *J* = 15.4 Hz, 1H), 3.60 (s, 2H), 2.03-1.98 (m, 2H), 1.51 (s, 1H), 1.39-1.22 (m, 6H), 0.88 (t, *J* = 6.95 Hz, 3H).**^{13}C-{^1H} NMR ($CDCl_3$, 100 MHz) :** δ = 134.6, 125.7, 62.1, 35.6/35.4/35.2 (<u>C</u>$^2H_2$), 32.8, 31.5, 29.3, 14.2. **GCMS (EI) m/z (intensity %) :** 70 (100), 41 (76), 57 (71), 83 (45), 97 (27), 126 (7), 111 (2), 144 (0.2)**.IR neat (υ/cm^{-1}) :** 2927, 2361, 1394, 1249, 1054.

[2,2-$^2H_2$]-non-3(*E*)-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1m-D2**:

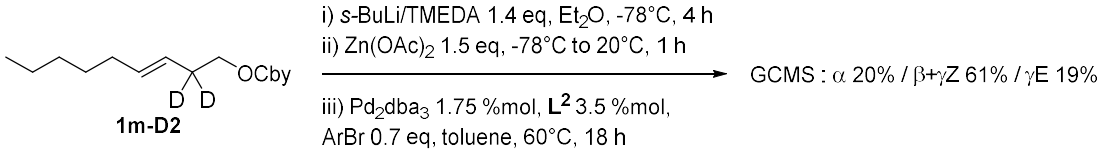


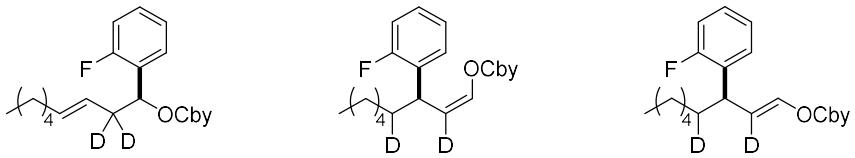
[6] Crombie, L.; Heavers, A. D. *J. Chem. Soc. Perkin Trans.***1992**, 1, 1929-1937.

A solution of [2,2-$^2H_2$] non-3(*E*)-en-1-ol**S7** (150 mg, 1.0 mmol, 1 eq) in THF (1 mL) was added dropwise to a suspension of sodium hydride (34 mg, 1.4 mmol, 1.3 eq) in THF (4 mL) at 0°C (water, ice) over 5 min. The mixture was then stirred for 30 min at room temperature. A solution of 2,2,4,4-tetramethyloxazolidine-3-carbonyl chloride (259 mg, 1.4 eq, 1.3 eq) in THF (1 mL) was added dropwise and the mixture was stirred for 15 h at room temperature. After quenching with water, the solvent was removed under vacuum and the residue was diluted with Et_2O (10 mL). The organic phase was washed with sat. aq. $NaHCO_3$ (10 mL), water (10 mL), brine (10 mL) and then dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (Pent/Et_2O 95:5 to 80:20) to obtain 215 mg (70 %, 100 % (*E*), >98% ^2H int.) of the desired deuterated carbamate as colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 5.55-5.48 (m, 1H), 5.39-5.34 (m, 1H), 4.08-4.07 (m, 2H), 3.71 (s, 2H), 2.00-1.95 (m, 2H), 1.55 (1.50) (2 br. s, 6H), 1.41-1.22 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :** δ = 153.0/152.3, 133.6, 125.7, 95.9/95.0, 76.5/76.2, 64.2, 60.6/59.9, 32.7, 31.8/31.6/31.5 ($\underline{C}^2H_2$ overlapped with CH_2), 29.2, 26.6/25.44, 25.38/24.3, 22.7, 14.2. **HRMS (ESI) m/z:** calcd. for $C_{17}H_{29}D_2NO_3Na$ ($[M + Na]^+$): 322.2322; found: 322.2327.**IR neat (υ/cm^{-1}) :** 2971, 1361, 1701, 1403, 1068.

- Arylation of **1m-D2** : products **2m-D2** and **4m-D2** :



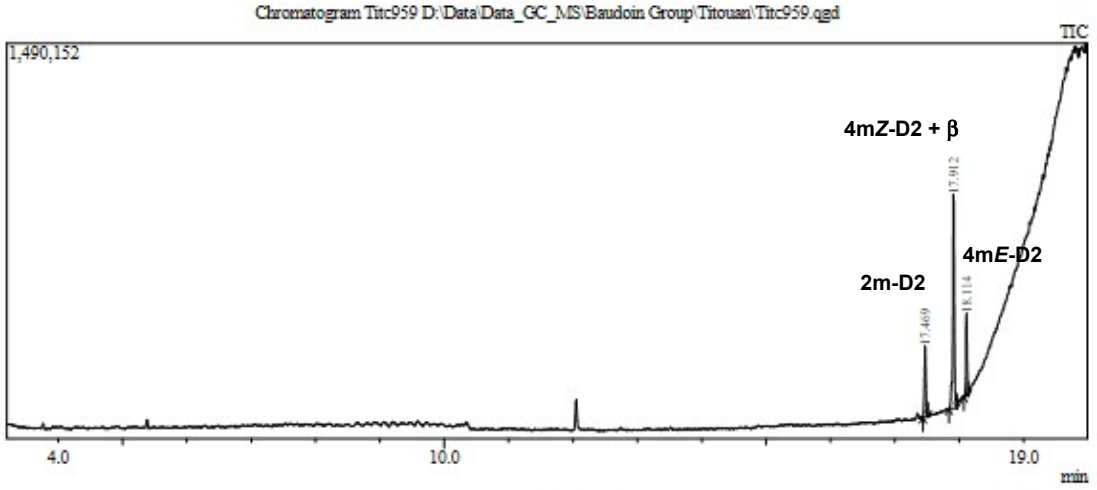


2m-D2, 3.5%
>95% D int.

4m*Z*-D2, 18%
>95% D int.

4m*E*-D2, 5%
>95% D int.

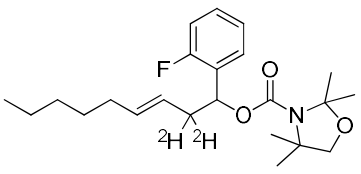
GCMS analysis of the crude reaction mixture

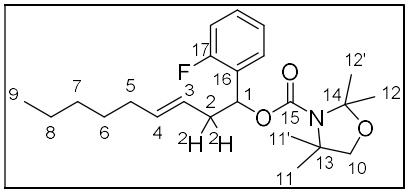


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	17.469	17.433	17.517	435049	19.69	267093	19.28	1.63	MI	
2	17.912	17.842	17.967	1358349	61.48	805227	58.13	1.69	MI	
3	18.114	18.075	18.142	416000	18.83	312801	22.58	1.33	MI	
				2209398	100.00	1385121	100.00			

(*E*)-1-(2-fluorophenyl)-[2,2-$^{2}H_2$]-non-3-en-1-yl 2,2,4,4-tetramethyl oxazolidine-3-carboxylate **2m-D2** :

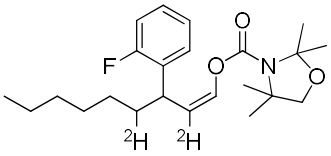


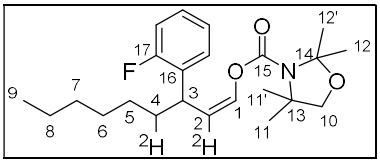


^{1}H NMR (CDCl$_3$, 500 MHz, rotamers) : δ = 7.33-7.28 (m, 1H, H_{Ar}), 7.27-7.23 (m, 1H,H_{Ar}), 7.13-7.10 (m, 1H, H_{Ar}), 7.05-7.01 (m,1H, H_{Ar}), 5.99 (s, 1H, H_1), 5.47-5.42 (m, 1H, H_3), 5.33-5.28 (m, 1H, H_4), 3.76-3.70 (m, 2H, H_{10}), 1.94-1.91 (m, 2H, H_5), 1.62-1.34 (m, 12H, H_{11},

$H_{11'}$, H_{12}, $H_{12'}$), 1.29-1.23 (m, 4H, H_6, H_7), 1.20-1.17 (m, 2H, H_8), 0.86 (t, J = 7.2 Hz, 3H, H_9). **^{2}H NMR ($CHCl_3$, 76 MHz, rotamers) :**δ = 7.62-7.55 (m, 2^2H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :** δ = (C_{17}, C_{16},C_{15}missing), 134.7 (C_3), 129.24/129.16 (C_{Ar}), 128.2/128.1 (C_{Ar}), 124.4/124.3 (C_{Ar}), 124.10/124.07 (C_4), , 115.8/115.7 (C_{Ar}), 96.2/95.1 (C_{14}), 76.6/76.2 (C_{10}), 71.1/71.0 (C_1), 60.9/60.0 (C_{13}), 32.7 (C_5), 31.4 (C_6), 29.9 (C_2), 29.1 (C_7), 26.9-24.3 (C_{11}, $C_{11'}$, C_{12}, $C_{12'}$), 22.7 (C_8), 14.2 (C_9). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = 117.53/117.56 (F_{17}). **HRMS (ESI) m/z:** calcd. for $C_{23}H_{32}D_2FNO_3Na$ ([M + Na]$^+$): 416.2540; found: 416.2547 **. IR neat (υ/cm^{-1}) :** 2969, 2361, 1702, 1395, 1260, 1063.

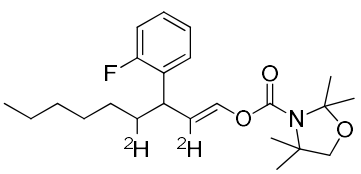
(*Z*)-3-(2-fluorophenyl)-[2,4-$^2H_2$]-non-1-en-1-yl 2,2,4,4-tetramethyl oxazolidine-3-carboxylate **4m*Z*-D2**:

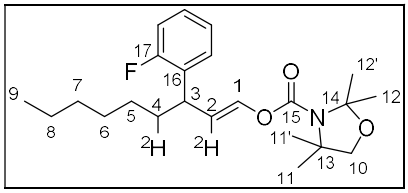




^{1}H NMR ($CDCl_3$, 500 MHz, rotamers) :δ = 7.24-7.20 (m, 1H, H_{Ar}), 7.17-7.14 (m, 1H, H_{Ar}), 7.08-7.06 (m, 2H, H_1, H_{Ar}), 7.00-6.97 (m, 1H, H_{Ar}), 4.12-4.04 (m, 1H, H_3), 3.78-3.72 (m, 2H, H_{10}), 1.64-1.21 (m, 21H, H_4, H_5, H_6, H_7, H_8, H_{11}, $H_{11'}$, H_{12}, $H_{12'}$), 0.86 (t, J = 7.0 Hz, 3H, H_9). **^{2}H NMR ($CHCl_3$, 76 MHz, rotamers) :**δ = 5.02 (s, 1^2H, $^2H_2$), 1.70 (s, 1^2H, $^2H_4$). **^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :** δ = 161.8-159.4 (d, J = 245.7 Hz, C_{17}), 150.0/149.2 (C_{15}), 134.6/134.4 (C_1), 132.0/131.9 (C_{16}), 128.60-128.51 (C_{Ar}), 127.7-127.6 (C_{Ar}), 124.30/124.26 (C_{Ar}), 115.6/115.4 (C_{Ar}), 96.3/95.4 (C_{14}), 76.6/76.2 (C_{10}), 61.2/60.3 (C_{13}), 36.3-36.0 (C_4), 34.84/34.77 (C_3), 31.9 (C_5), 29.2 (C_6), 27.6 (C_7), 26.7-24.0 (C_{11}, $C_{11'}$, C_{12}, $C_{12'}$), 22.8 (C_8), 14.2 (C_9).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = 118.3–118.40 (F_{17}). **HRMS (ESI) m/z:**calcd. for $C_{23}H_{32}D_2FNO_3Na$ ([M + Na]$^+$): 416.2540; found: 416.2548 **. IR neat (υ/cm^{-1}) :** 2926, 2361, 1716, 1375, 1258, 1141, 1087.

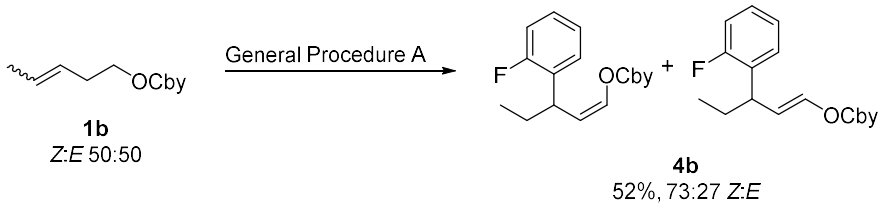
(*E*)-3-(2-fluorophenyl)-[2,4-$^2H_2$]-non-1-en-1-yl 2,2,4,4-tetramethyl oxazolidine-3-carboxylate **4m*E*-D2**:





^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.21-7.15 (m, 2H, H_{Ar}), 7.10-7.07 (m, 2H, H_1, H_{Ar}), 7.02-6.99 (m, 1H, H_{Ar}), 3.76-3.74 (m, 2H, H_{10}), 3.56-3.55 (m, 1H, H_3), 1.70-1.68 (m, 1H, H_4), 1.57-1.21 (m, 20H, H_5, H_6, H_7, H_8, H_{11}, $H_{11'}$, H_{12}, $H_{12'}$) , 0.86 (t, *J* = 7.1 Hz, 3H, H_9). **^{2}H NMR ($CHCl_3$, 76 MHz, rotamers) :**δ = 5.55 (s, 1^2H, $^2H_2$), 1.71 (s, 1^2H, $^2H_4$). **^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :** δ = 161.8-159.8 (d, *J* = 245.6 Hz, C_{17}), 150.2 (C_{15}), 136.6/136.4 (C_1), 131.7/131.5 (C_{16}), 128.84/128.80 (C_{Ar}), 127.8/127.7 (C_{Ar}), 124.32/124.29 (C_{Ar}), 115.8/115.6 (C_{Ar}), 96.2/95.4 (C_{14}), 76.5/76.2 (C_{10}), 61.0/60.4 (C_{13}), 37.68/37.64 (C_3), 35.2-34.9 (C_4), 31.8 (C_5), 29.2 (C_6), 27.5 (C_7), 26.9-24.1 (C_{11}, $C_{11'}$, C_{12}, $C_{12'}$), 22.8 (C_8), 14.2 (C_9). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = 118.31/118.32 (F_{17}). **HRMS (ESI) m/z:**calcd. for $C_{23}H_{32}D_2FNO_3Na$ ($[M + Na]^+$): 416.2540; found: 416.2548 **. IR neat (υ/cm^{-1}) :** 2926, 2361, 1714, 1374, 1258, 1126, 1071.

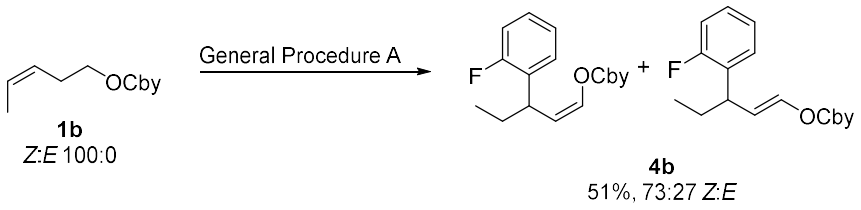
9. Stereoconvergence in the arylation of **1b** (Scheme 3c)



1b
Z:*E* 50:50

4b
52%, 73:27 *Z*:*E*

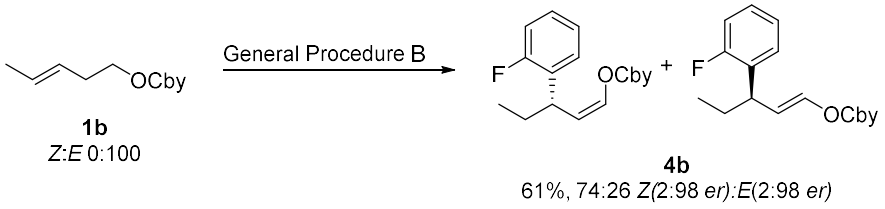
Following the general procedure A, a mixture of (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate and (*Z*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg, ratio 50:50) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 25.1 mg (52%) of the desired compound (73:27 *Z*:*E* ratio) as an oil.



1b
Z:*E* 100:0

4b
51%, 73:27 *Z*:*E*

Following the general procedure A, (*Z*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 24.6 mg (51%) of the desired compound (73:27 *Z*:*E* ratio) as an oil.

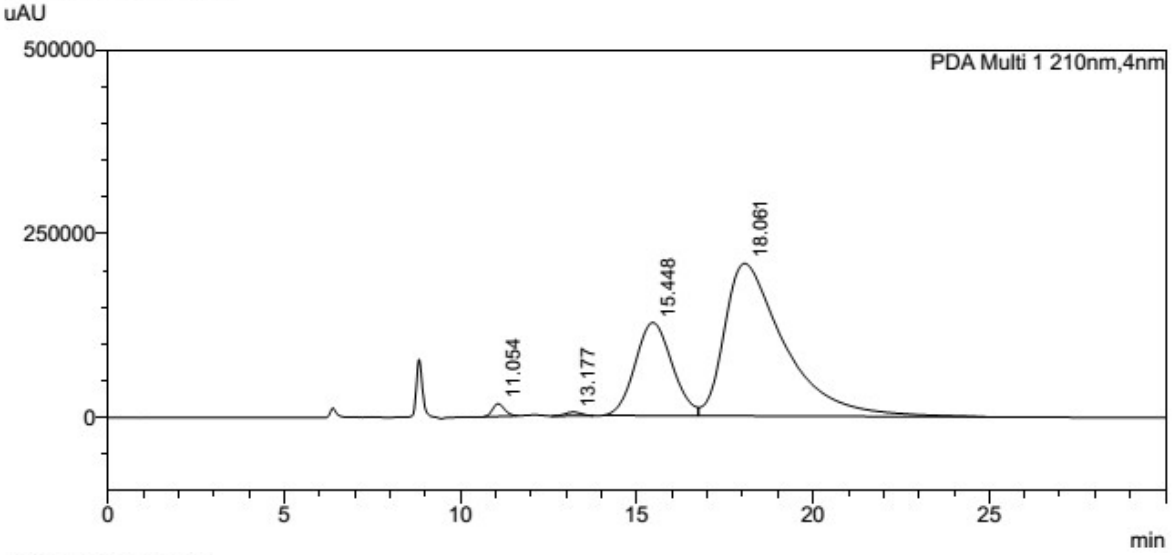


1b
Z:*E* 0:100

4b
61%, 74:26 *Z*(2:98 *er*):*E*(2:98 *er*)

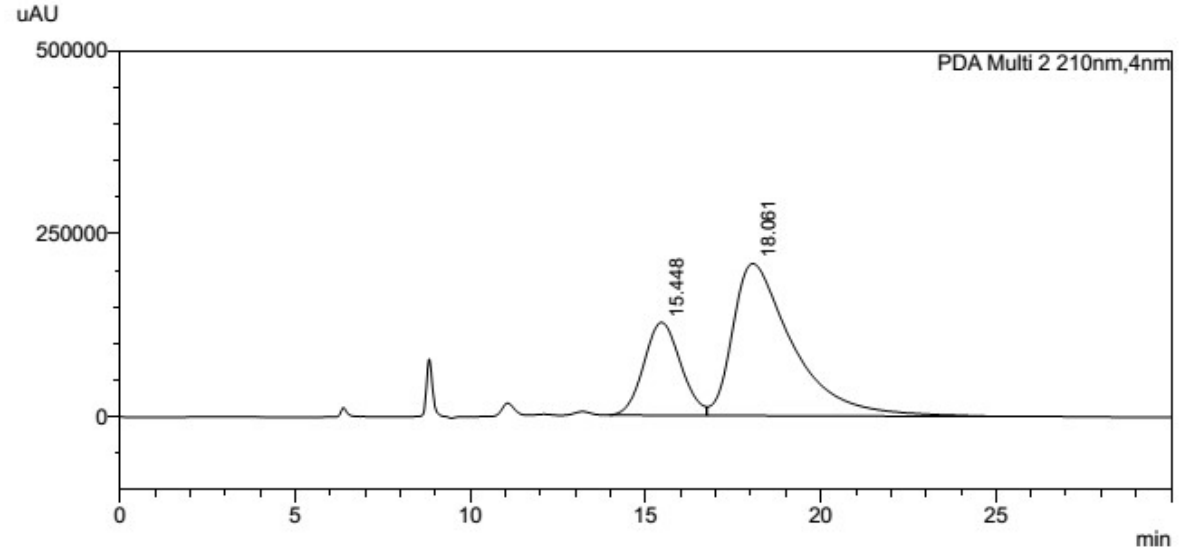
Following the general procedure B, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 29.6 mg (61%) of the desired compound (74:26 *Z*:*E* ratio) as an oil. The *e.r.* were, respectively, 2:98 for the (*S,Z*)-isomer and 2:98 for the (*R,E*)-isomer.

<Chromatogram>



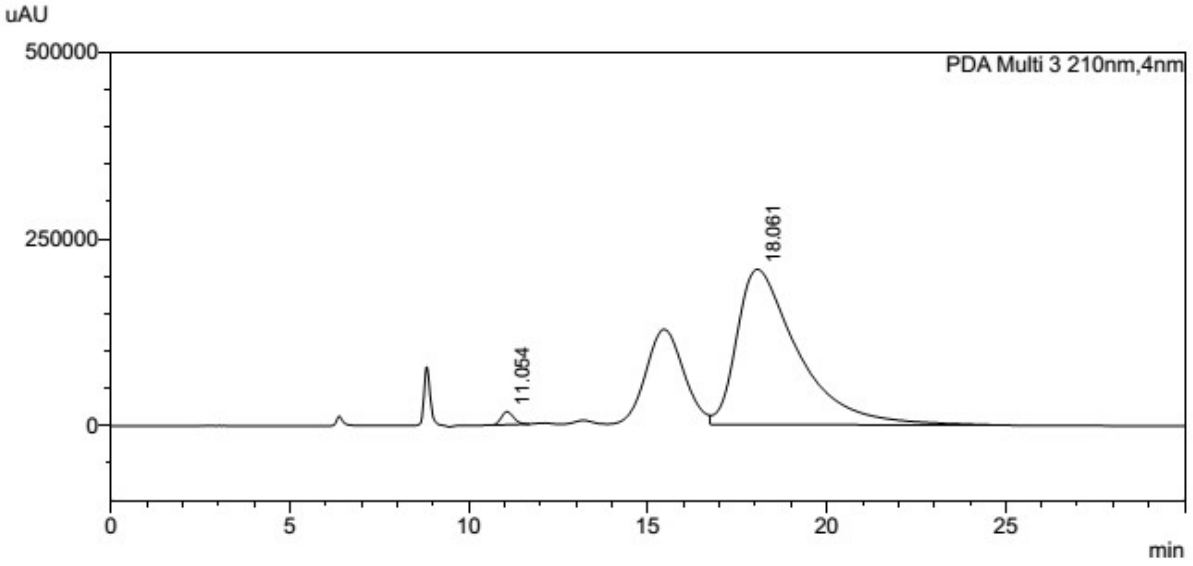
PDA Ch1 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.054	1.188	408688	17272	0.000		M
2	13.177	0.474	163125	5048	0.000		M
3	15.448	26.815	9221055	126552	0.000		M
4	18.061	71.522	24595086	207452	0.000		V M
Total		100.000	34387954	356324			



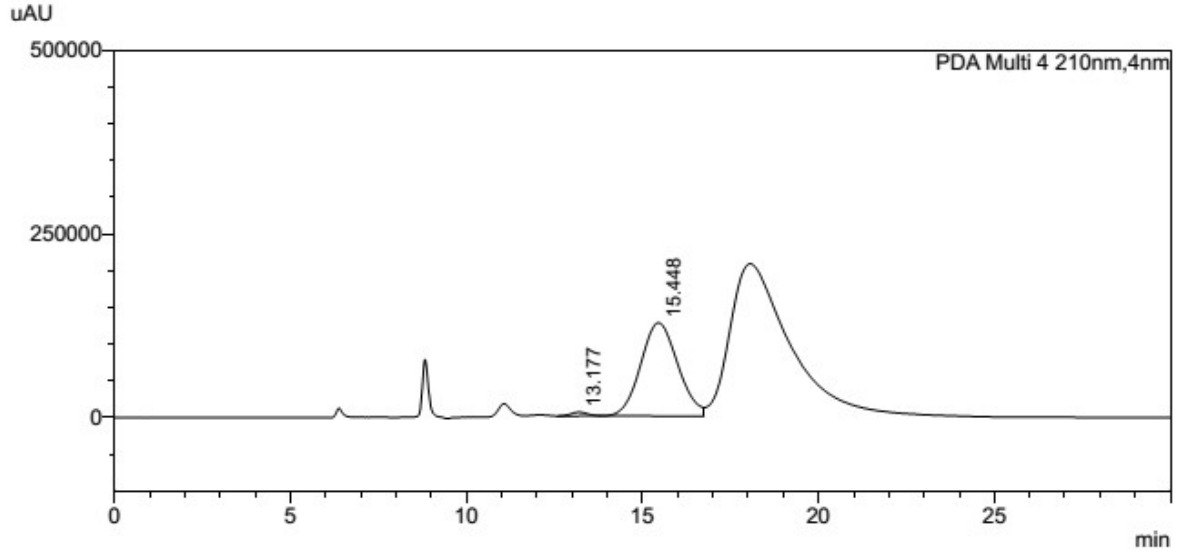
PDA Ch2 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	15.448	27.304	9290901	126976	0.000		M
2	18.061	72.696	24736243	207802	0.000		V M
Total		100.000	34027144	334777			



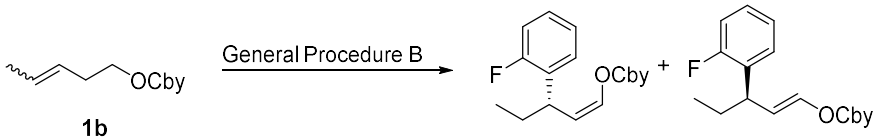
PDA Ch3 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.054	1.652	415247	17379	0.000		M
2	18.061	98.348	24723437	207866	0.000		M
Total		100.000	25138684	225244			



PDA Ch4 210nm

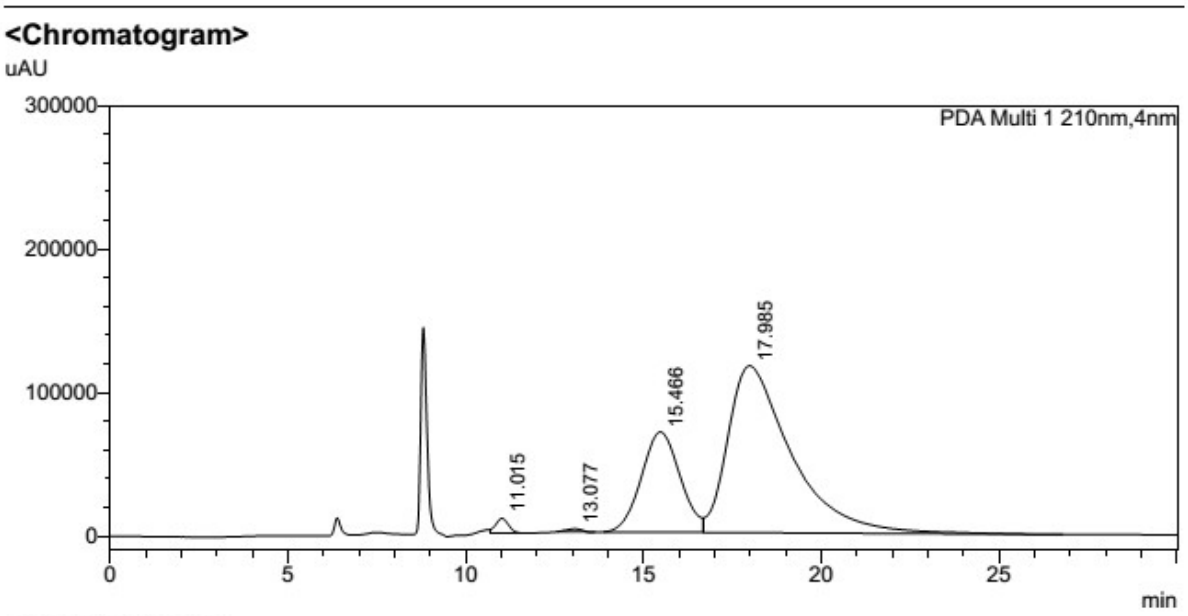
Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	13.177	1.764	167317	5107	0.000		M
2	15.448	98.236	9319113	127141	0.000		M
Total		100.000	9486430	132248			



1b
Z:*E* 50:50

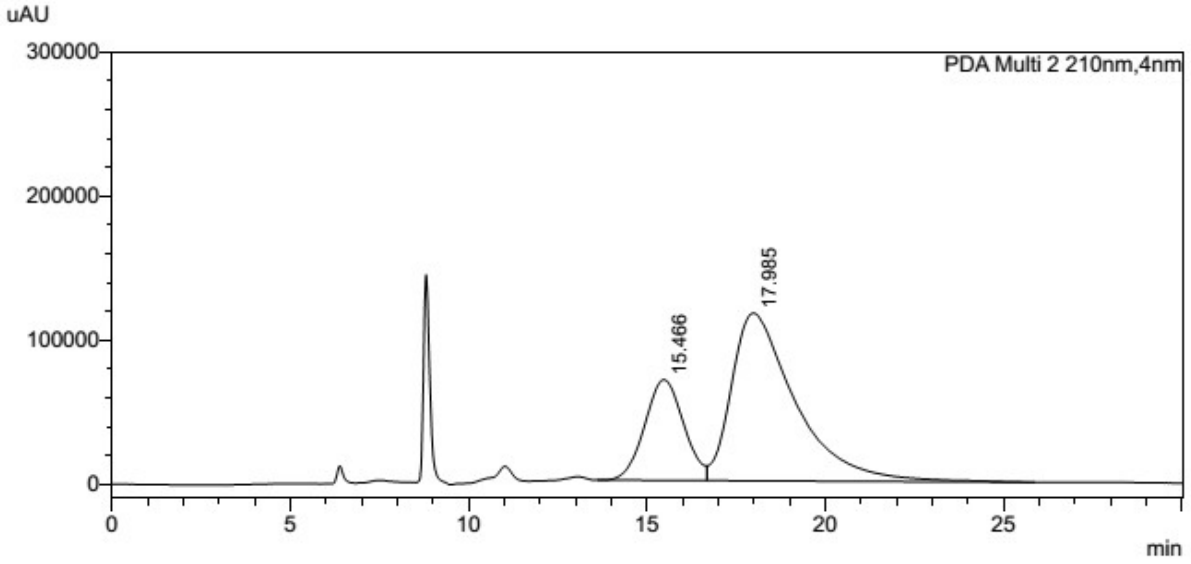
4b
56%, 74:26 *Z*(2:98 *er*):*E*(2:98 *er*)

Following the general procedure B, a mixture of (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate and (*Z*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg, ratio 50:50) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 27.4 mg (56%) of the desired compound (74:26 *Z*:*E* ratio) as an oil. The *e.r.* were, respectively, 2:98 for the (*S,Z*)-isomer and 2:98 for the (*R,E*)-isomer.



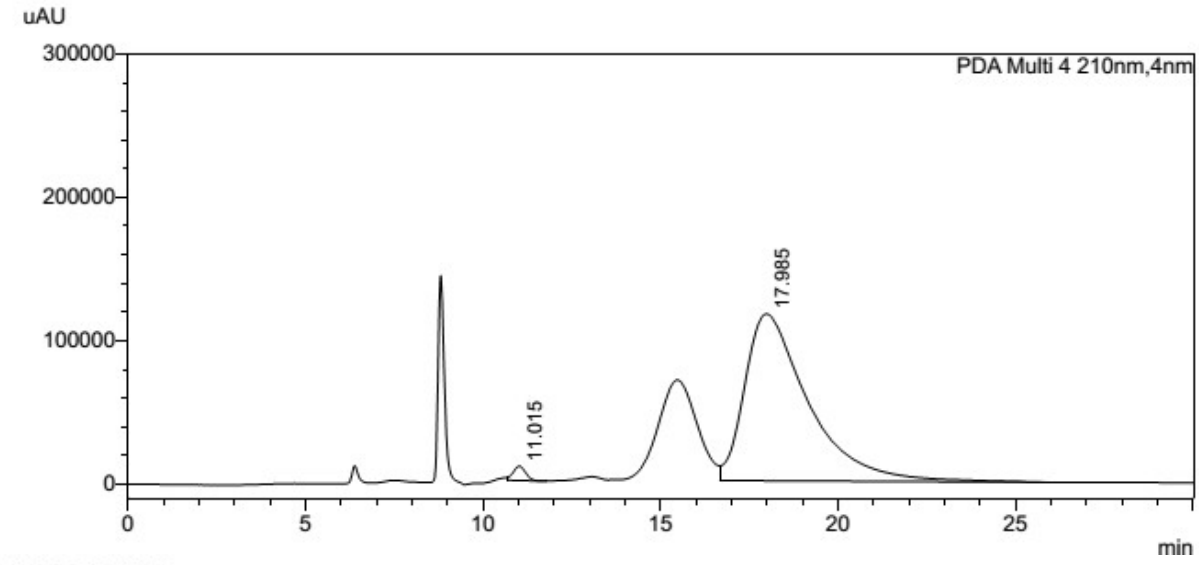
PDA Ch1 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.015	1.320	265741	10497	0.000		M
2	13.077	0.302	60853	2063	0.000		M
3	15.466	26.363	5305621	69837	0.000		M
4	17.985	72.014	14493095	116287	0.000		V M
Total		100.000	20125310	198683			



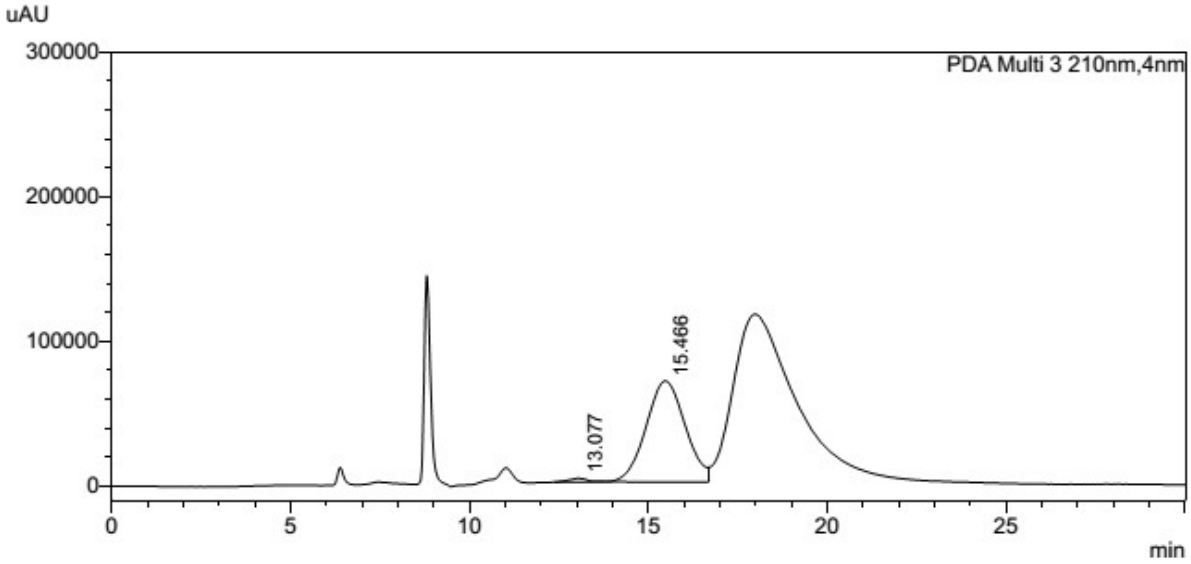
PDA Ch2 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	15.466	26.803	5311787	69872	0.000		M
2	17.985	73.197	14506447	116316	0.000		V M
Total		100.000	19818234	186187			



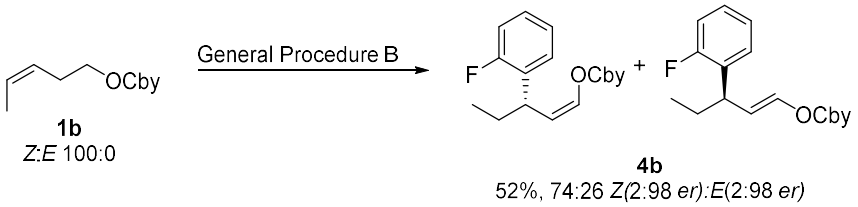
PDA Ch3 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	13.077	1.479	79757	2335	0.000		M
2	15.466	98.521	5311204	69869	0.000		M
Total		100.000	5390960	72205			



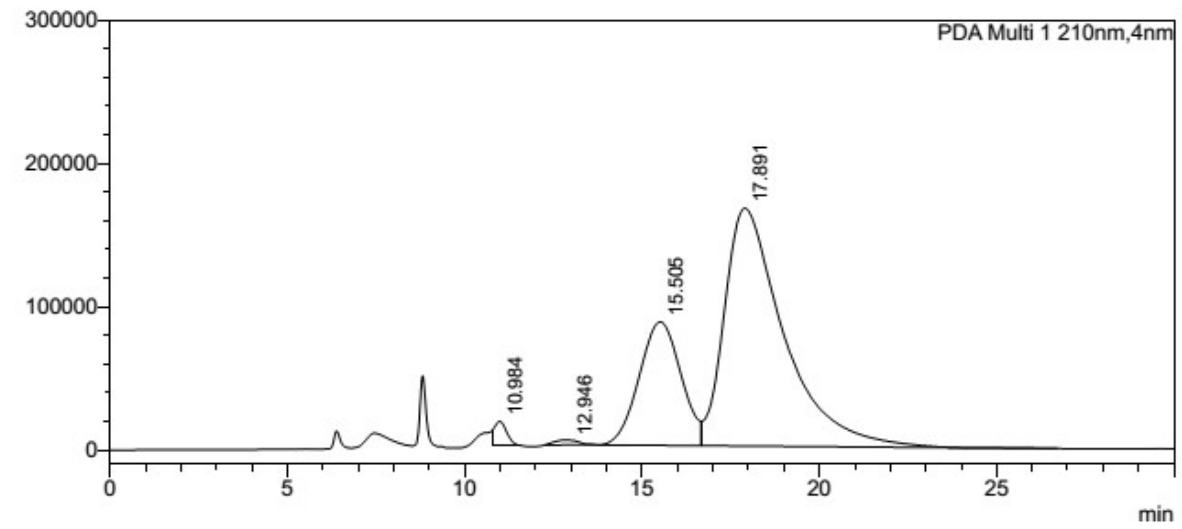
PDA Ch4 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.015	1.653	244013	10042	0.000		M
2	17.985	98.347	14516806	116324	0.000		M
Total		100.000	14760819	126365			



Following the general procedure B, (*Z*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) to give 25.3 mg (52%) of the desired compound (74:26 *Z*:*E* ratio) as an oil. The *e.r.* were, respectively, 2:98 for the (*S,Z*)-isomer and 2:98 for the (*R,E*)-isomer.

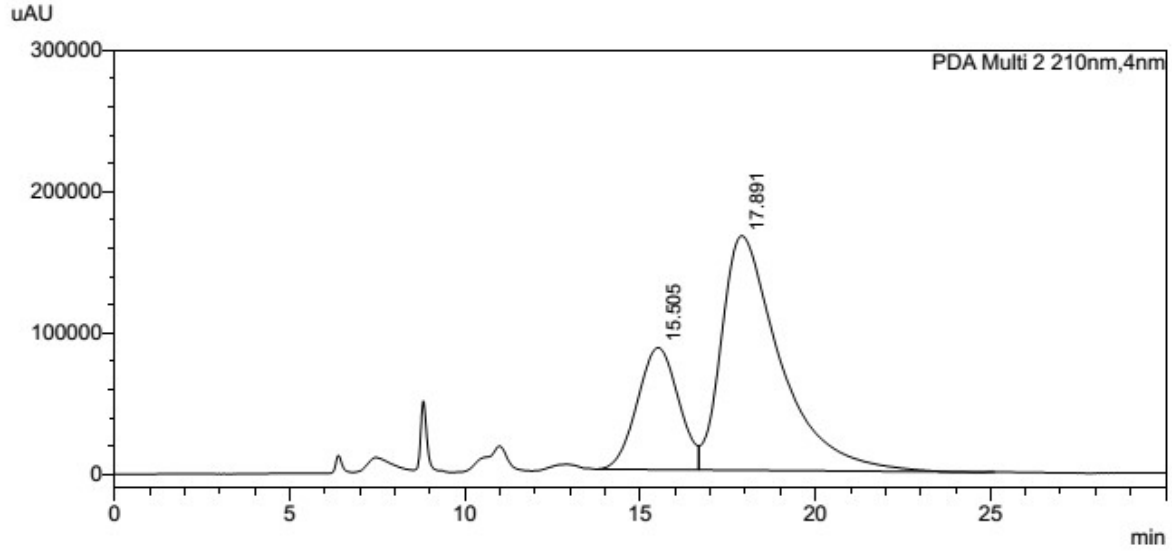
<Chromatogram>



<Peak Table>

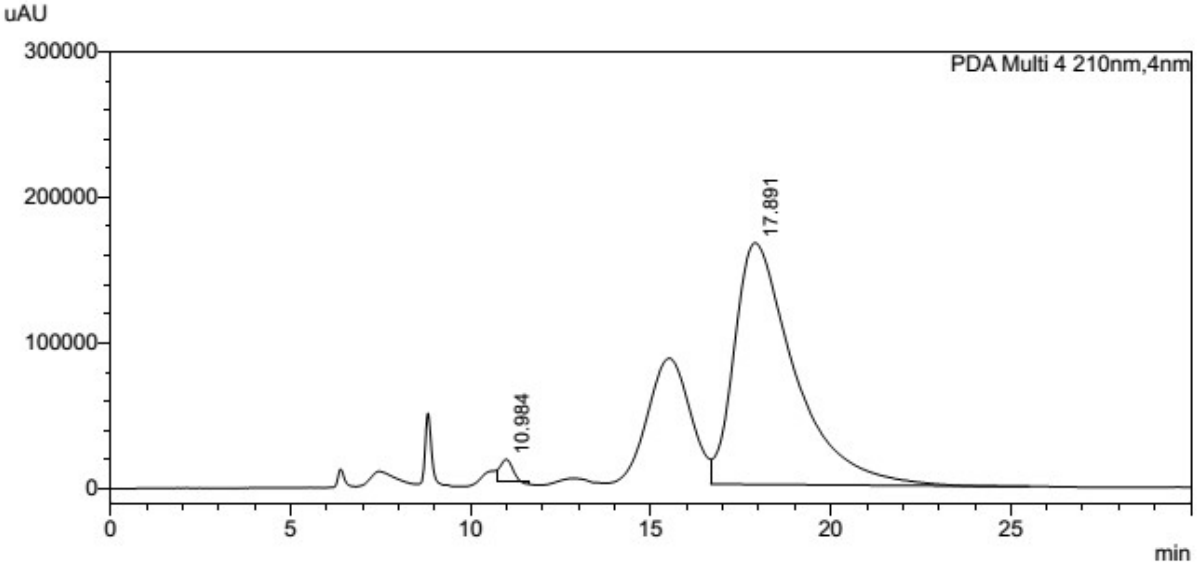
PDA Ch1 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	10.984	1.380	372789	16303	0.000		M
2	12.946	0.604	163017	3385	0.000		M
3	15.505	26.134	7059236	86275	0.000		M
4	17.891	71.882	19416554	165906	0.000		V M
Total		100.000	27011595	271869			



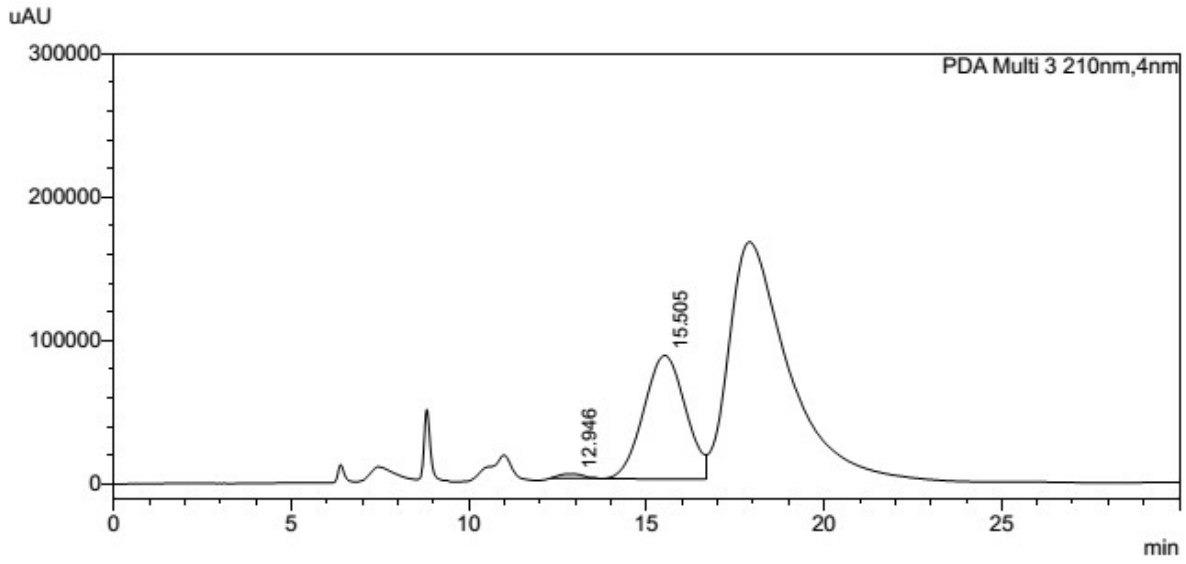
PDA Ch2 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	15.505	26.702	7056746	86258	0.000		M
2	17.891	73.298	19371515	165866	0.000		V M
Total		100.000	26428261	252123			



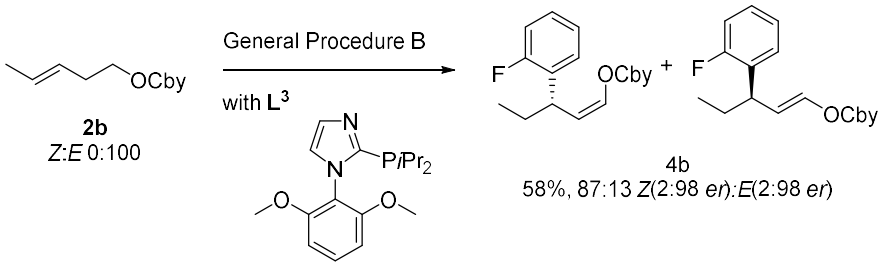
PDA Ch4 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	10.984	1.840	362907	15813	0.000		M
2	17.891	98.160	19356467	165832	0.000		M
Total		100.000	19719373	181646			

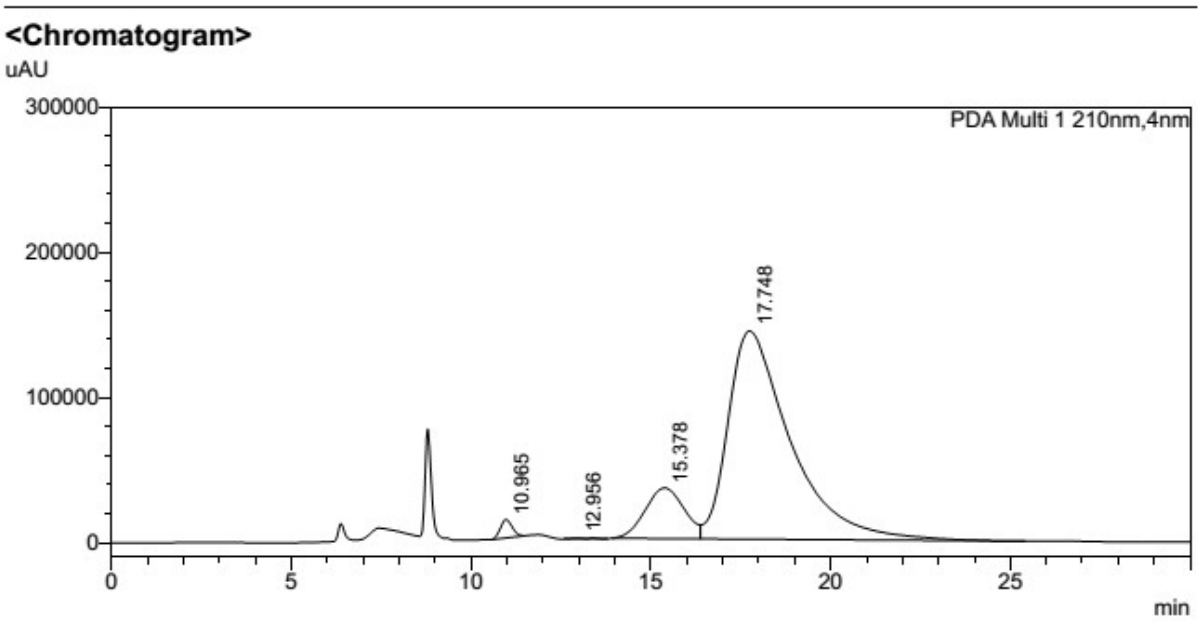


PDA Ch3 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	12.946	1.841	132335	3010	0.000		M
2	15.505	98.159	7056389	86255	0.000		M
Total		100.000	7188724	89265			

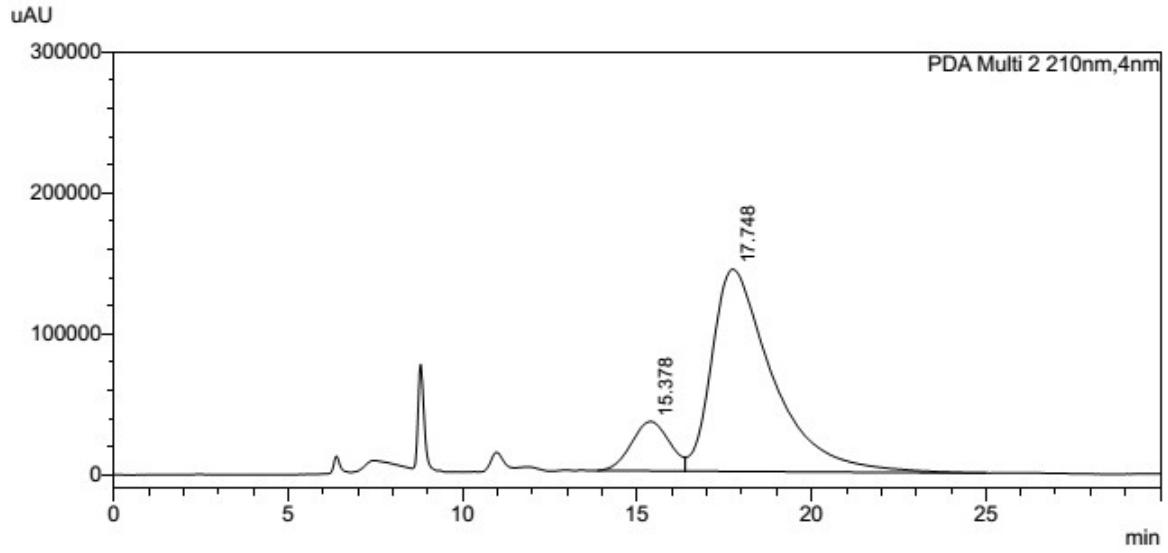


Following the general procedure B, (*E*)-pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (50 mg) was arylated with 1-bromo-2-fluorobenzene (15.8 µL) in presence of **2.L**[44] to give 28 mg (58%) of the desired compound (87:13 *Z*:*E* ratio) as an oil. The *e.r.* were, respectively, 2:98 for the (*S,Z*)-isomer and 2:98 for the (*R,E*)-isomer.



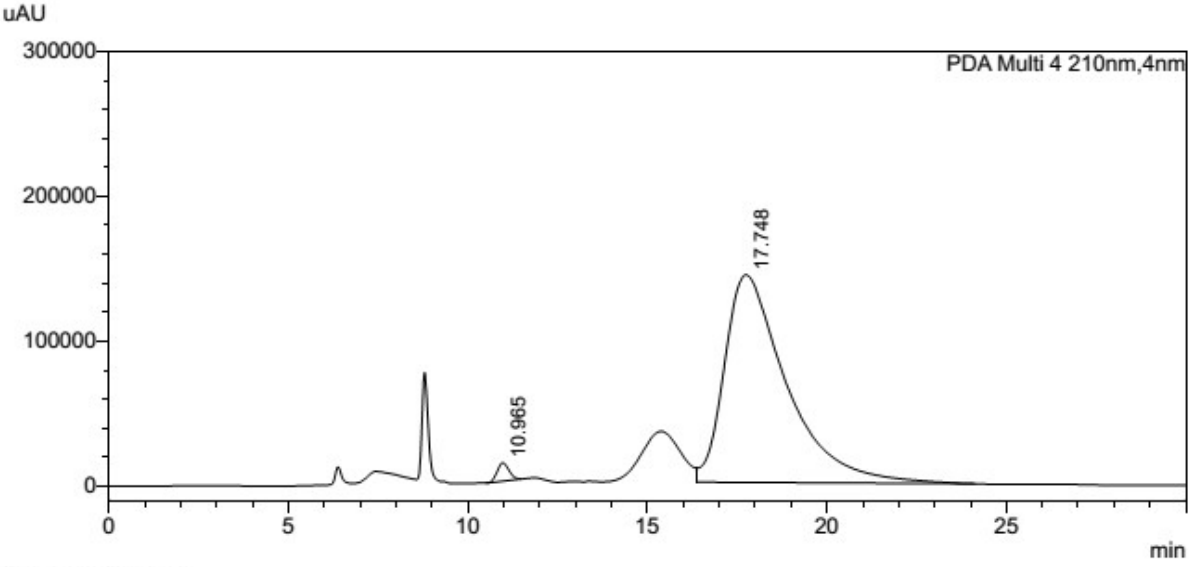
PDA Ch1 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	10.965	1.419	288032	12518	0.000		M
2	12.956	0.101	20531	685	0.000		M
3	15.378	12.998	2638100	34938	0.000		M
4	17.748	85.482	17349918	143372	0.000		V M
Total		100.000	20296582	191514			



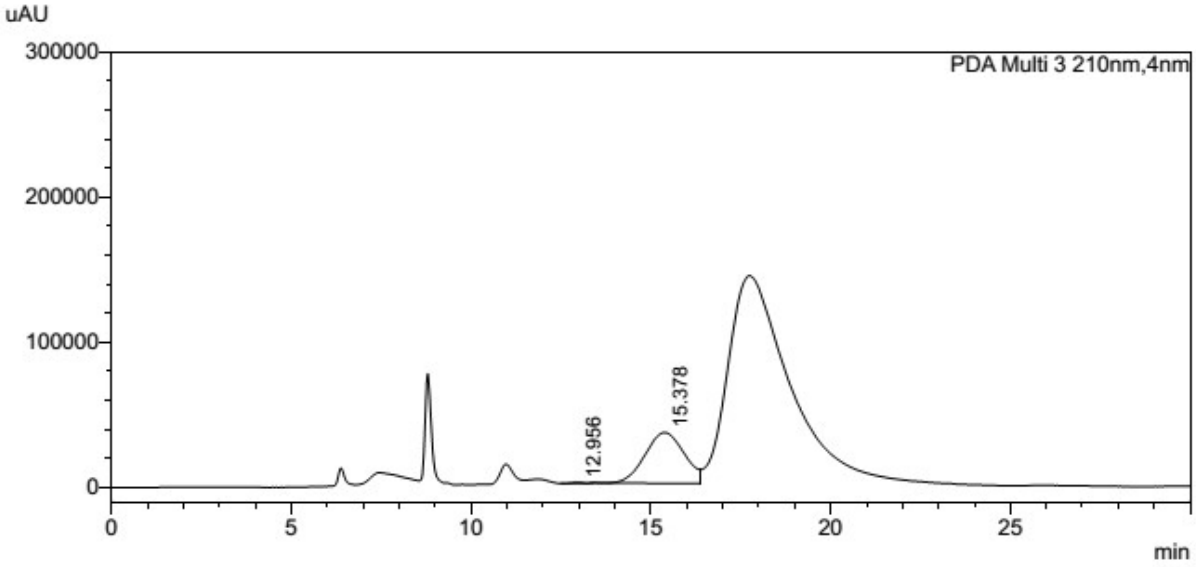
PDA Ch2 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	15.378	13.230	2654391	35047	0.000		M
2	17.748	86.770	17409568	143483	0.000		V M
Total		100.000	20063959	178530			



PDA Ch4 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	10.965	1.636	288032	12518	0.000		M
2	17.748	98.364	17312799	143328	0.000		
Total		100.000	17600832	155847			

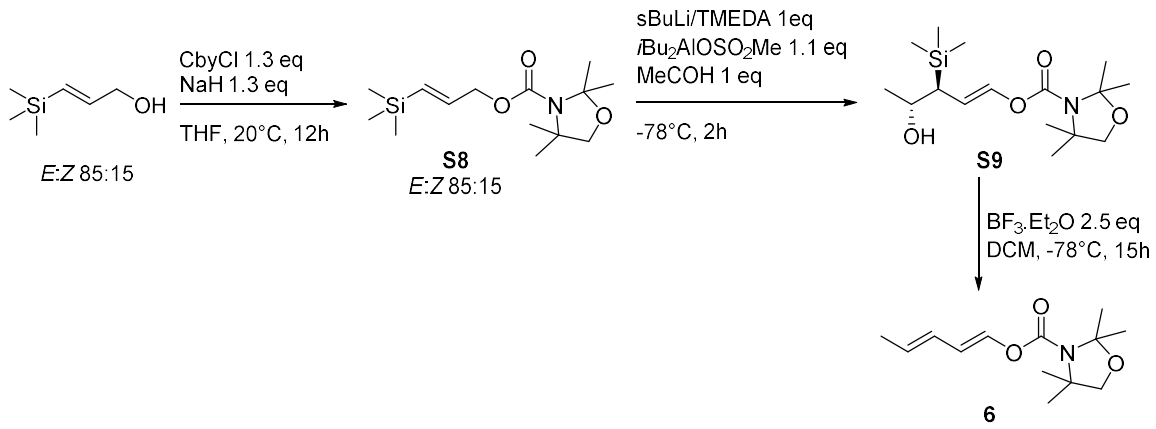


PDA Ch3 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	12.956	0.724	19352	701	0.000		M
2	15.378	99.276	2653216	35038	0.000		M
Total		100.000	2672568	35739			

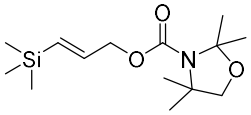
10. Cross-over experiment (Scheme 3e)

- Preparation of the diene **6**



The diene **6** was prepared following a procedure similar to the literature.[7]

3-(trimethylsilyl)allyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **S8** :

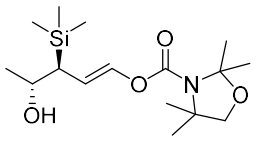


Following the general procedure, (*E*)-3-(trimethylsilyl)prop-2-en-1-ol[8] (621 mg, 5 mmol, *E*:*Z* 85:15) was reacted with sodium hydride (95% in mineral oil, 3 eq)and 2,2,4,4-tetramethyloxazolidine-3-carbonyl chloride (3 eq) to give 1.25 g (88%, *E*:*Z* 85:15) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 6.43-6.36 (m, 1H, mino.), 6.12-6.05 (m, 1H, majo.), 5.95-5.90 (m, 1H, majo.), 5.81-5.79 (m, 1H, mino.), 4.66-4.60 (m, 2H), 3.76-3.73 (m, 2H), 1.60-1.36 (m, 12H), 0.15-0.00 (m, 9H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz, rotamers) :**δ = 152.67/151.95, 142.0/141.9 (mino.), 140.3/140.2 (majo.), 134.4/134.3 (mino.), 132.84/132.75 (mino.), 96.0/95.1, 76.6/76.2 (majo.), 75.3 (mino.), 67.1 (majo.), 64.6/64.5 (mino), 60.8/59.9, 26.78/26.68, 25.5.48/25.46/25.42, 24.5, 24.3, 23.7/23.5, 0.12, -1.3. **HRMS (ESI) m/z:**calcd. for $C_{14}H_{27}NO_3SiNa$ ([M + Na]$^{+}$): 308.1652; found: 308.1658**. IR neat (υ/cm^{-1}) :** 2957, 2361, 1700, 1400, 1338, 1250, 1097.

[7]Van Hulsen, E.; Hoppe, D. *Tet. Lett.* **1985**, 26, 411-414.
[8] A synthesis of this alcohol is described in : Jones, T. K.; Denmark, S. E.; Viti, S. M.; Sharpless, B. K. *Org. Synth.* **1990**, 7, 524 (first edition **1986**, 64, 182).

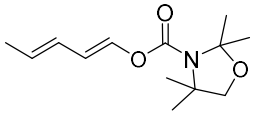
(*E*)-4-hydroxy-3-(trimethylsilyl)pent-1-en-1-yl2,2,4,4-tetramethyloxazolidine-3-carboxylate **S9** :



To a solution of 3-(trimethylsilyl)allyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **S8** (380 mg, 1.3 mmol, 1 eq, 85:15 *E*:*Z*) and TMEDA (199 µL, 1.3 mmol, 1 eq) in dry diethyl ether (5 mL) at -78°C (cryostat, acetone bath) was added *s*-Butyllithium (1.46 mmol, 1.1 eq, solution in hexane) over 5 min. The orange mixture was stirred for 1 h, before the addition of diisobutylaluminium methanesulfonate[9] (1.46 mmol, 1.1 eq, 0.5 M in Toluene:MTBE 1:1). The yellow mixture was then stirred for 1.5 h, before the addition of acetaldehyde (75 µL, 1.33 mmol, 1 eq). After 1 h, the mixture was stirred for 15 min at 20°C before the addition of Seignette's salt (10% in water, 20 mL) to quench the reaction. The aqueous layer was extracted with diethyl ether (3x 10 mL), and the combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under vacuum. The residue was purified by flash column chromatography (Pent/Et_2O 80:20 to 30:70) to give 195 mg (45%) of the desired compound as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz, rotamers) :δ = 6.97-6.94 (dd, *J* = 12.4 Hz, *J* = 2.4 Hz, 1H), 5.32-5.24 (m, 1H), 4.01-3.96 (m, 1H), 3.76-3.75 (m, 2H), 1.58-1.56 (m, 6H), 1.48-1.41 (m, 7H), 1.23-1.22 (m, 3H), 0.06 (m,9H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 150.3/149.5, 136.3/136.1, 109.5/109.4, 96.1/95.4, 76.5/76.2, 68.1, 61.0, 60.4, 37.19/37.17, 26.9/26.8, 25.8/25.7, 25.3/25.2, 24.2/24.1, 23.8, 1.8. **HRMS (ESI) m/z:**calcd. for $C_{16}H_{31}NO_4SiNa$ ($[M + Na]^+$): 352.1915; found: 352.1919**. IR neat (υ/cm^{-1}) :** 2969, 2872, 2361, 1695, 1373, 1255, 1118.

(1*E*,3*E*)-penta-1,3-dien-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **6**:

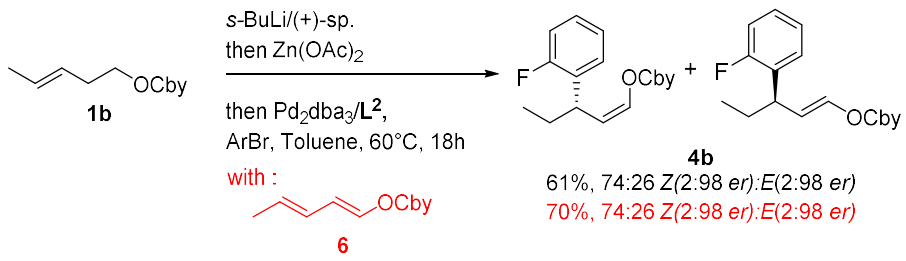


[9] (iBu)$_2$AlOSO$_2$CH$_3$ was freshly prepared by addition of CH_3SO_3H (95 µL, 1.46 mmol, 1.1 eq) to a solution of DIBAL-H (1.46 mL (1M in toluene), 1.46 mmol, 1.1 eq) in MTBE (1.46 mL) at 0°C (ice bath). After addition, the solution was stirred at 20°C for 30 min.

A solution of (*E*)-4-hydroxy-3-(trimethylsilyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**S9** (190 mg, 0.58 mmol, 1 eq) in dichloromethane (1.9 mL) was cooled down to -78°C (cryostat, acetone bath). $BF_3.Et_2O$ (0.38 mL, 1.44 mmol, 2.5 eq) was slowly added and the resulting yellowish mixture was stirred at -78°C for 15 h. The reaction was quenched at -78°C (total degradation of the product was observed when warmed up to 20°C before the quench) by addition of aq. sat. $NaHCO_3$ (1.5 mL) and stirred for 5 min, and then was allowed to warm up to room temperature over 30 min under vigourous stirring. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3x1.5 mL). The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under vacuum. The oily residue was purified by flash column chromatography (Pent/Et_2O 95:5 to 80:20) to give 107 mg (78%) of the desired compound as a colorless oil (the product appears also to be slightly volatile).

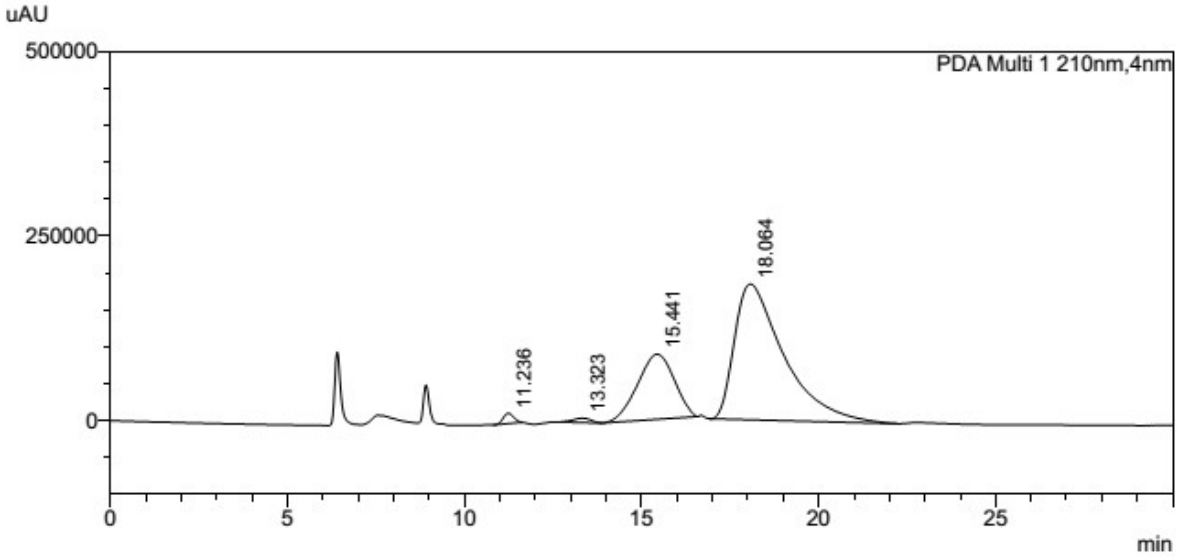
^{1}H NMR ($CDCl_3$, 500 MHz, rotamers) :δ = 7.25-7.21 (m, 1H), 6.00-5.88 (m, 2H), 5.66-5.59 (m, 1H), 3.75 (s, 1H), 1.75-1.74 (m, 3H), 1.57 (1.56) (2 br. s, 6H), (1.43) 1.41 (2 br. s, 6H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 150.00/149.2, 137.3/137.2, 128.13/128.10, 126.2/126.1, 113.72/113.66, 96.2/95.5, 76.4/76.2, 61.1/60.5, 26.9/25.7, 25.2/24.1, 18.4. **HRMS (ESI) m/z:**calcd. for $C_{13}H_{21}NO_3Na$ ([M + Na]$^+$): 262.1414; found: 262.1419**. IR neat (υ/cm^{-1}) :** 2980, 2361, 1716, 1372, 1258, 1133, 1068.

- Procedure for the cross-over experiment :



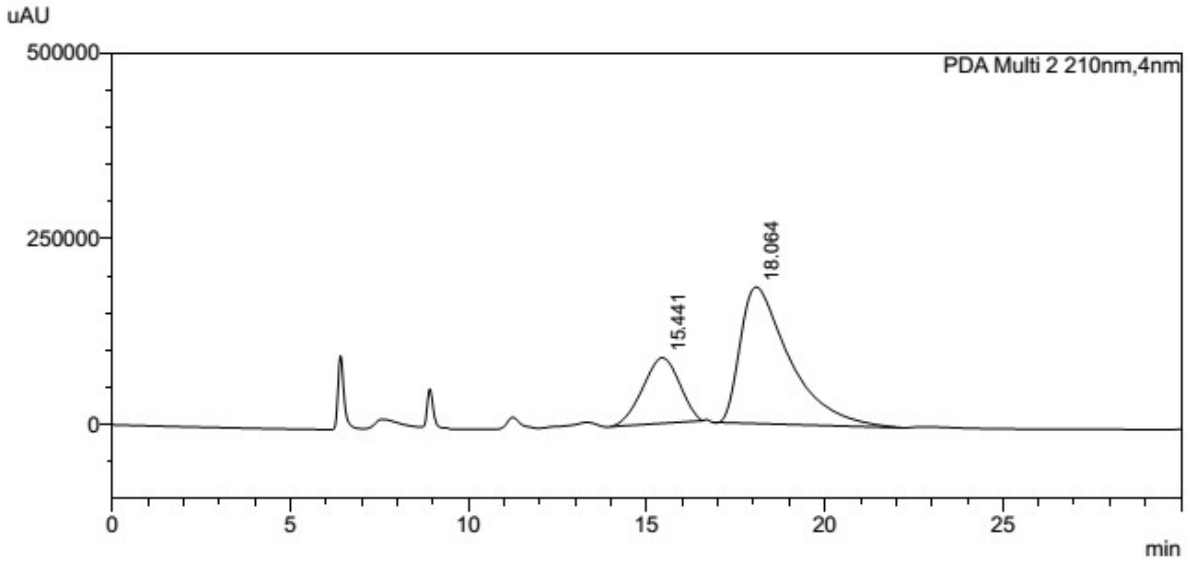
In a tubular reactor (100 mm x 16 mm)capped with a rubber septum, a solution of the carbamate **1b** (50 mg, 0.207 mmol, 1 eq) and (+)-sparteine (67 µL, 0.29 mmol, 1.4 eq) in dry diethyl ether (1.5 mL) under argon was stirred and cooled down to -78°C (acetone bath, cryostat). *s*-Butyllithium (0.29 mmol, 1.4 eq, solution in hexane) was added dropwise, and the mixture was stirred for 4 h. A suspension of zinc acetate (57 mg, 0.31 mmol, 1.5 eq) in dry THF (1.5 mL) was sonicated for 30 min and added dropwise to the mixture. The resulting solution was stirred for 30 min at -78°C, and then allowed to heat up to 20°C over 30 min.

The solvents were evaporated over 30 min under high vacuum, and a solution of $Pd_2(dba)_3$ (3.3 mg, 3.6 µmol, 1.75 %mol) and CataCXium PICy**L**^{2} (2.8 mg, 7.3 µmol, 3.5 %mol) in dry toluene (1.0 mL) was added, followed by the aryl bromide (0.15 mmol, 0.7 eq) and the diene**6** (49.5 mg, 0.207 mmol, 1 eq,) in toluene (0.5 mL). The mixture was then vigorously stirred and heated to 60°C for 18h. After cooling down, the reaction was quenched with sat. aq. NH_4Cl (2 mL), and the organic phase was diluted with EtOAc (3 mL) and separated. The aqueous phase was extracted with EtOAc (2 x 3 mL). The combined organic layers were dried over $MgSO_4$, filtrated over a pad of celite, and evaporated under vacuum. The residue was purified by preparative reversed-phase HPLC (MeCN/H_2O) to afford 34 mg (70%) of **4b** (74:26 *Z*:*E* ratio) as an oil. The *e.r.* were, respectively, 2:98 for the (*S,Z*)-isomer and 2:98 for the (*R,E*)-isomer.



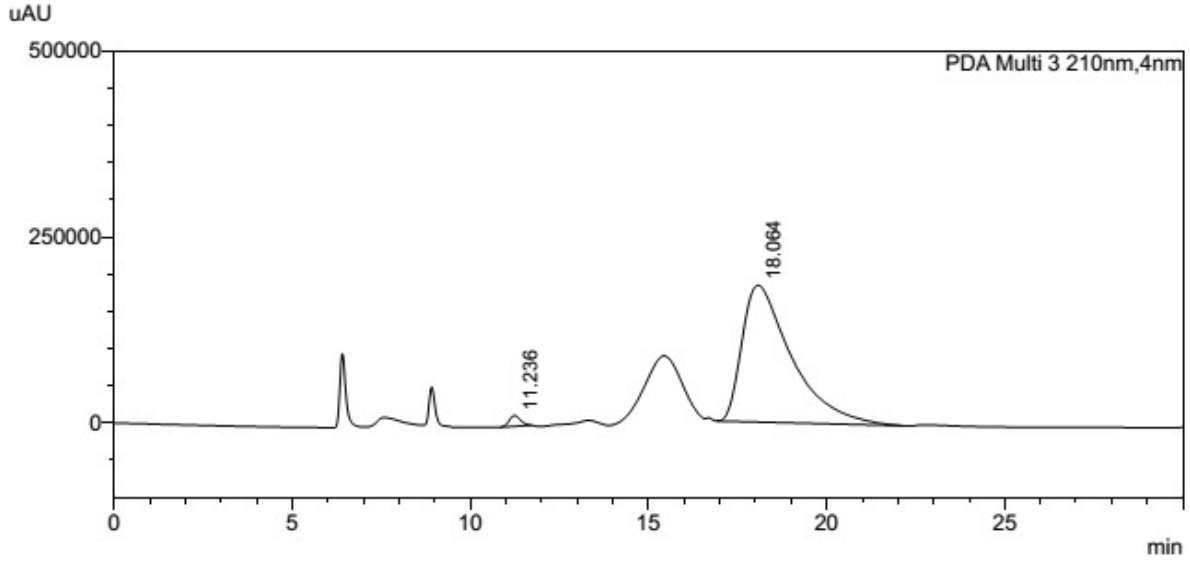
PDA Ch1 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.236	1.181	290984	14040	0.000		M
2	13.323	0.836	206084	5963	0.000		M
3	15.441	25.722	6339415	88209	0.000		M
4	18.064	72.261	17809203	183973	0.000		M
Total		100.000	24645685	292186			



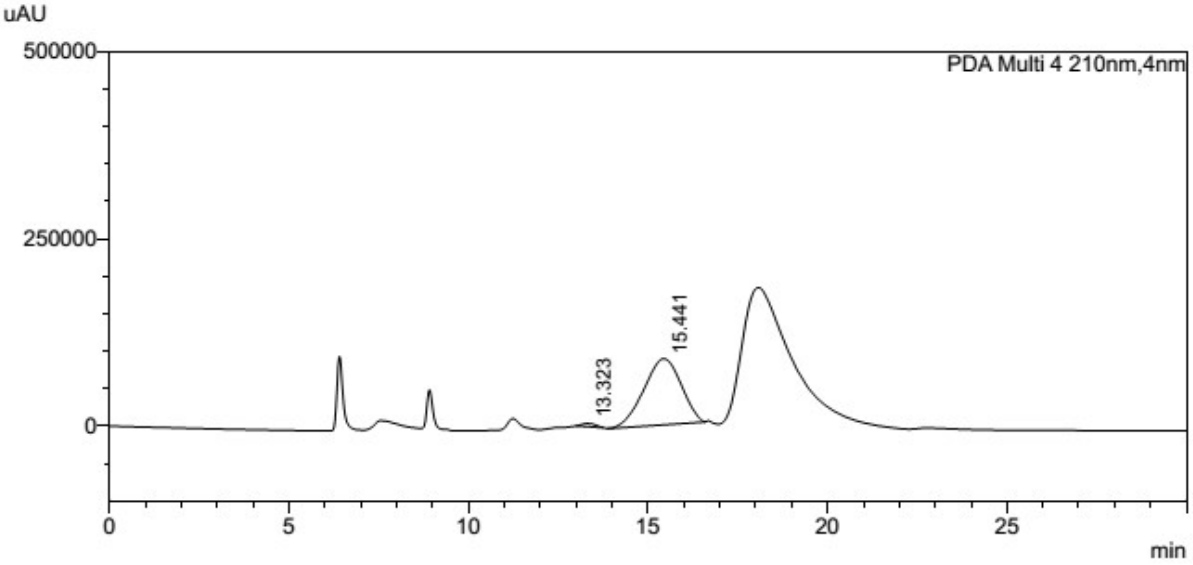
PDA Ch2 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	15.441	26.315	6327776	88138	0.000		M
2	18.064	73.685	17718201	183507	0.000		M
Total		100.000	24045978	271645			



PDA Ch3 210nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	11.236	1.756	317722	14574	0.000		M
2	18.064	98.244	17776643	183975	0.000		M
Total		100.000	18094365	198548			



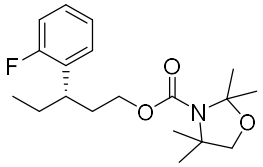
PDA Ch4 210nm

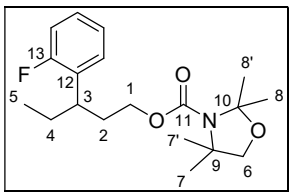
Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	13.323	1.738	112783	4259	0.000		M
2	15.441	98.262	6378143	88434	0.000		M
Total		100.000	6490926	92694			

11. Product derivatization (Scheme 3c)

11.1. Hydrogenation product **5**

(+)-(*S*)-3-(2-fluorophenyl)pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **5** :





rac-3-(2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4b** (75:25 *Z*:*E*) (206 mg, 0.6 mmol, 1 eq) was diluted with dry ethanol (6 mL) in a 10 mL glass vial. Pd/C 10%w/w (20 mg, 10% w/w) was added and the vial was loaded in an autoclave. The mixture was stirred at 50°C under H_2 (50 bar) for 24h. After cooling down, the reaction mixture was filtered on celite and the filtrated solution was concentrated under vacuum. The crude residue was filtered over a pad of silica gel (Pent/Et_2O 85:15) to afford 192 mg (93%) of the desired *rac*-carbamate as an oil.

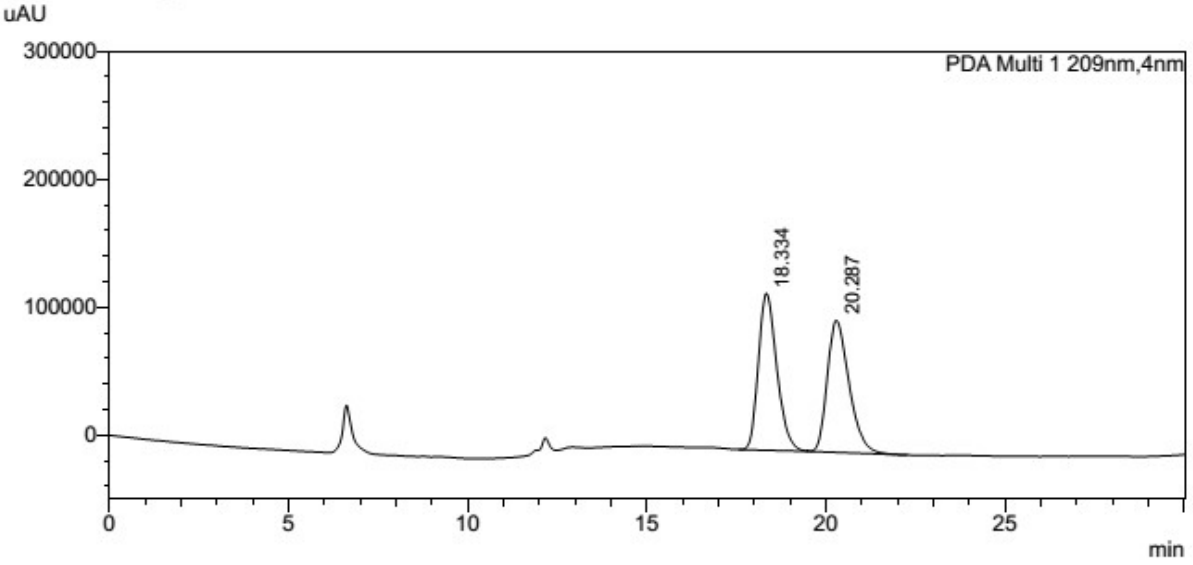
Under the same conditions, an enantioenriched mixture of 3-(2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (75:25 *Z*:*E*, *e.r.* 2:98 respectively) (7 mg, 0.02 mmol, 1 eq) was hydrogenated to give 7 mg (99 %) of the desired enantioenriched carbamate as an oil (*e.r.* 75:25)

Under the same conditions, an enantioenriched mixture of 3-(2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate (87:13 *Z*:*E*, *e.r.* 2:98 respectively) (20.2 mg, 0.06 mmol, 1 eq) was hydrogenated to give 17 mg (84%) of the desired enantioenriched carbamate as an oil (*e.r.* 86:14)

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.17-7.13 (m, 2H, H_{Ar}), 7.09-7.06 (m, 1H, H_{Ar}), 7.01-6.97 (m, 1H, H_{Ar}), 4.06-3.90 (m, 2H, H_1), 3.71 (s, 2H, H_6), 3.03-2.95 (m, 1H, H_3), 2.08-1.90 (m, 2H, H_2), 1.77-1.62 (m, 2H, H_4), 1.62-1.36 (m, 12H, H_7, $H_{7'}$, H_8, $H_{8'}$), 0.80 (t, *J* = 7.4 Hz, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 162.36/160.42 (d of rotamers, *J* = 243.9 Hz, C_{13}), 152.9/152.2 (C_{11}), 131.2/131.1 (C_{12}), 128.7/128.6 (C_{Ar}), 127.72/127.66 (C_{Ar}), 124.32/124.29 (C_{Ar}), 115.7/115.5 (C_{Ar}), 95.9/94.9 (C_{10}), 76.5/76.2 (C_6), 62.9 (C_1), 60.7/59.7 (C_9), 37.3 (C_3), 34.6 (C_2), 28.46/28.45 (C_4), 26.6-24.3 (C_7, $C_{7'}$, C_8, $C_{8'}$), 12.1 (C_5).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.30/-118.33 (F_{13}). **HPLC**

separation conditions : Chiralpak IC column, *n*-heptane/*i*-PrOH 99.5:0.5, flow rate 0.5 mL/min, 25°C, t_R19.4 min for (+)-(*S*)-enantiomer (major) and t_R 21.3 min for (-)-(*R*)-enantiomer (minor). *e.r.* = 86:14. **HRMS (ESI) m/z:**calcd. for $C_{19}H_{28}FNO_3Na$ ($[M + Na]^+$) : 360.1945; found: 360.1946**.IR neat (υ/cm^{-1}) :** 2970, 2361, 1699, 1408, 1364, 1258, 1068. **$[\alpha]_D^{20}$ =** +14.8° (c=0.8, $CHCl_3$, *e.r.* 86:14).

<Chromatogram>

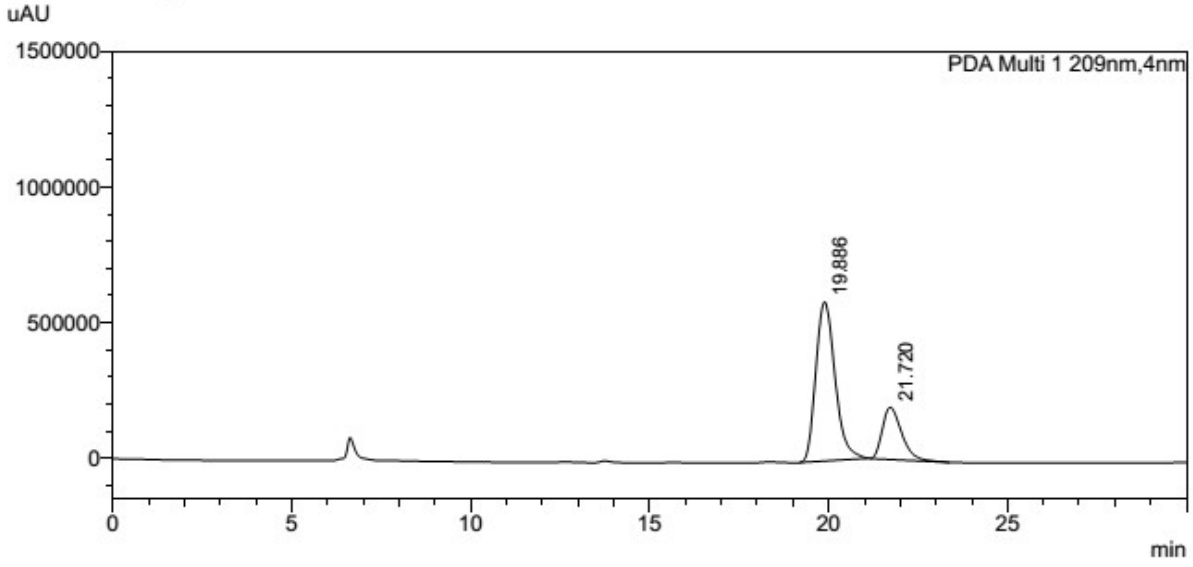


<Peak Table>

PDA Ch1 209nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	18.334	50.099	4377329	122698	50.099		M
2	20.287	49.901	4360114	103154	49.901		M
Total		100.000	8737443	225852			

<Chromatogram>

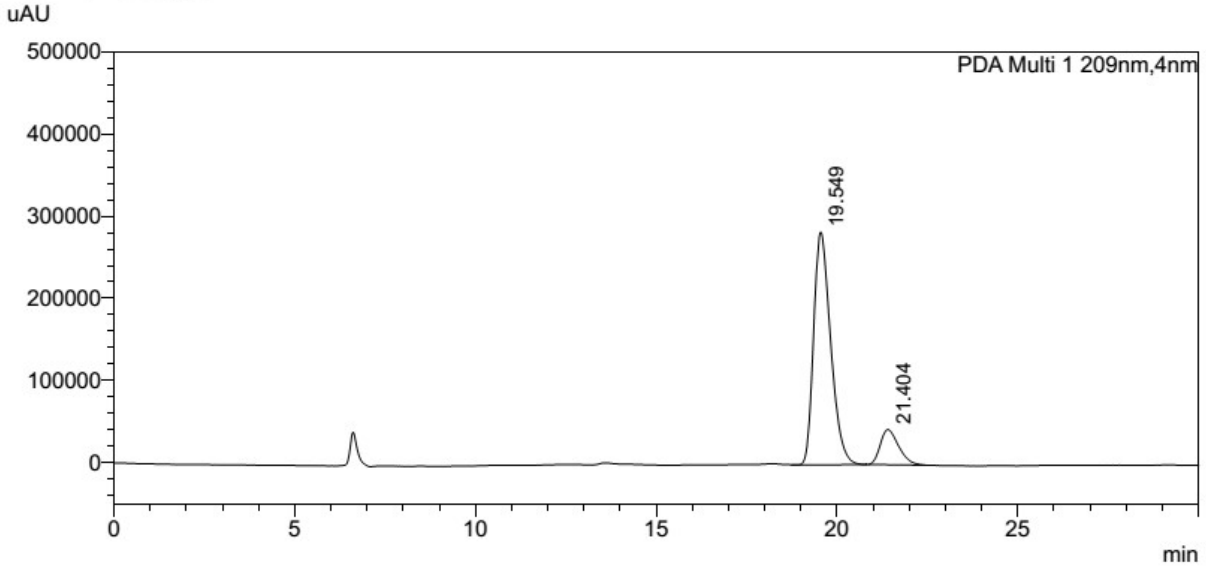


<Peak Table>

PDA Ch1 209nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	19.886	75.264	21939706	586283	75.264		M
2	21.720	24.736	7210596	192432	24.736		M
Total		100.000	29150302	778715			

<Chromatogram>



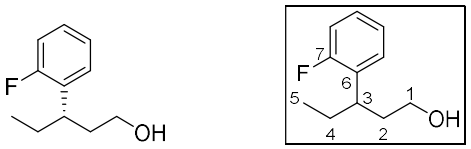
<Peak Table>

PDA Ch1 209nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	19.549	85.973	9272337	283033	0.000		M
2	21.404	14.027	1512837	42873	0.000		M
Total		100.000	10785173	325906			

11.2. Deprotection product **S10**

(+)-(*S*)-3-(2-fluorophenyl)pentan-1-ol **S10** :



rac-3-(2-fluorophenyl)pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **5** (50 mg, 0.15 mmol, 1 eq) was diluted in methanol (1mL) and $MeSO_3H$ (38 µL, 0.59 mmol, 4 eq) was added. The mixture was refluxed for 3.5h, cooled down to 20°C, and $Ba(OH)_2.8H_2O$ (304 mg, 1.78 mmol, 12 eq) was added. The mixture was then refluxed for 18h. After cooling down, the solids were filtrated on a pad silica with Et_2O (5 mL). After evaporation under vacuum, the residue was purified by silica gel column chromatography (Pent/Et_2O 80:20) to give the 25.8 mg (96%) of the racemic alcohol.

Under the same conditions, an enantioenriched mixture of 3-(2-fluorophenyl)pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **5** (*e.r* 86:14) (100 mg, 0.3 mmol, 1 eq) was deprotected to give 50 mg (93%) of the desired enantioenriched alcohol as an oil (*e.r.* 14:86).

H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 7.20-7.15 (m, 2H, H_{Ar}), 7.11-7.08 (m, 1H, H_{Ar}), 7.02-6.99 (m, 1H, H_{Ar}), 3.57-3.45 (m, 2H, H_1), 3.03-2.97 (m, 1H, H_3), 2.01-1.80 (m, 2H, H_2), 1.77-1.60 (m, 2H, H_4), 0.81 (t, *J* = 7.4 Hz, 3H, H_5). **^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 162.47/160.53 (d, *J* = 244.8 Hz, C_7), 131.6/131.4 (C_6), 128.9/128.8 (C_{Ar}), 127.63/127.56 (C_{Ar}), 124.34/124.31 (C_{Ar}), 115.6-115.4 (C_{Ar}), 61.3 (C_1), 38.4 (C_3), 36.92/36.91 (C_2), 28.67/28.66 (C_4), 12.2 (C_5).**^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.54 (F_7). **HPLC separation conditions :** Chiralcel OD-H column, *n*-heptane/*i*-PrOH 99:1, flow rate 0.8 mL/min, 25°C, t_R26.1 min for (-)-(*R*)-enantiomer (minor) and t_R 31.3 min for (+)-(*S*)-enantiomer (major). *e.r.* = 14:86. **HRMS (ESI) m/z:**calcd. for $C_{11}H_{15}FO_3Na$ ([M + Na]$^+$) : 205.0999; found: 205.0998.**IR neat (ʊ/cm^{-1}) :** 3352, 2963, 2361, 1224, 1052. **$[\alpha]_D^{20}$ =** +4.6° (c=1.3, $CHCl_3$, *e.r.*14:86).

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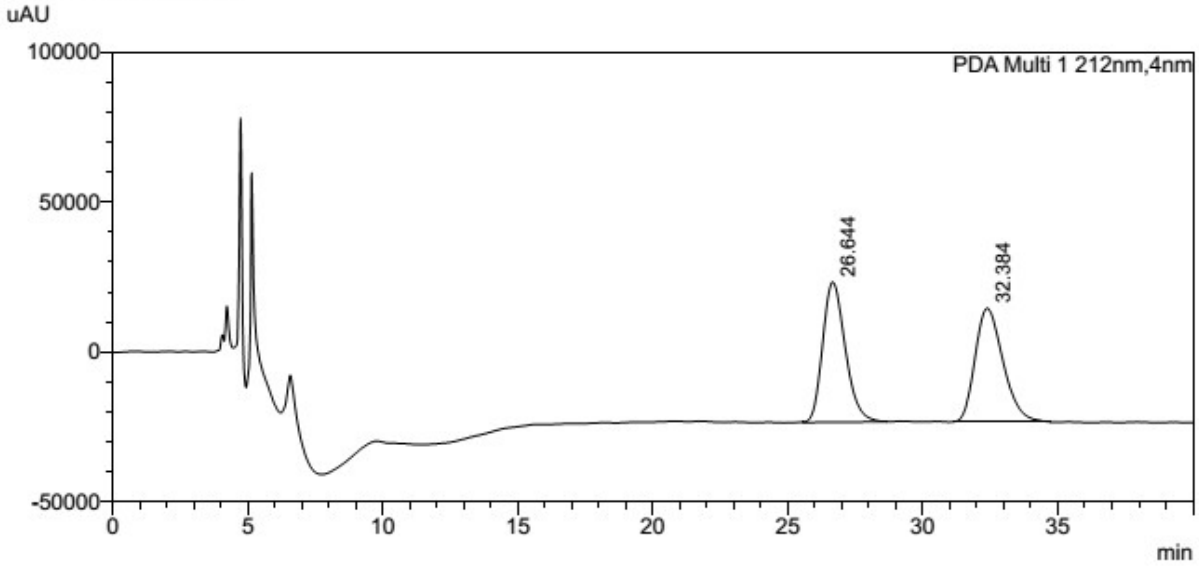

<Peak Table>

PDA Ch1 212nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	26.644	49.818	2723061	46721	49.818		SV
2	32.384	50.182	2742922	38046	50.182		SV
Total		100.000	5465983	84767			

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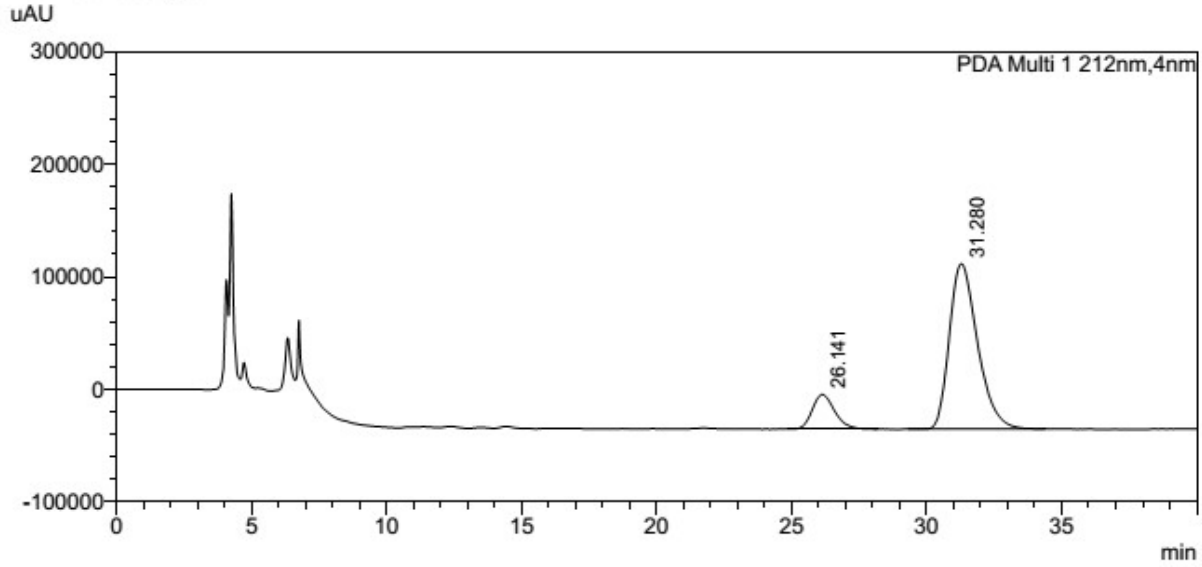


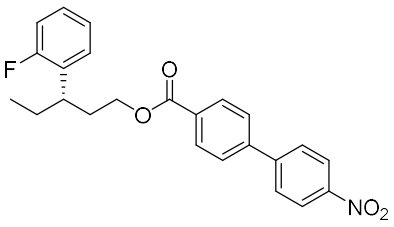
<Peak Table>

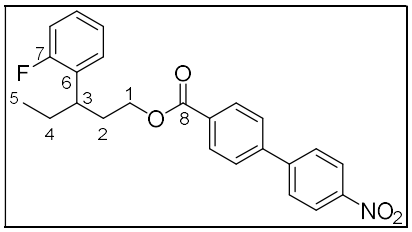
PDA Ch1 212nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	26.141	14.208	1765798	30714	14.208		M
2	31.280	85.792	10662088	146991	85.792		M
Total		100.000	12427886	177705			

11.3. Esterification product **7**

(+)-(*S*)-3-(2-fluorophenyl)pentyl 4'-nitro-[1,1'-biphenyl]-4-carboxylate **7** :





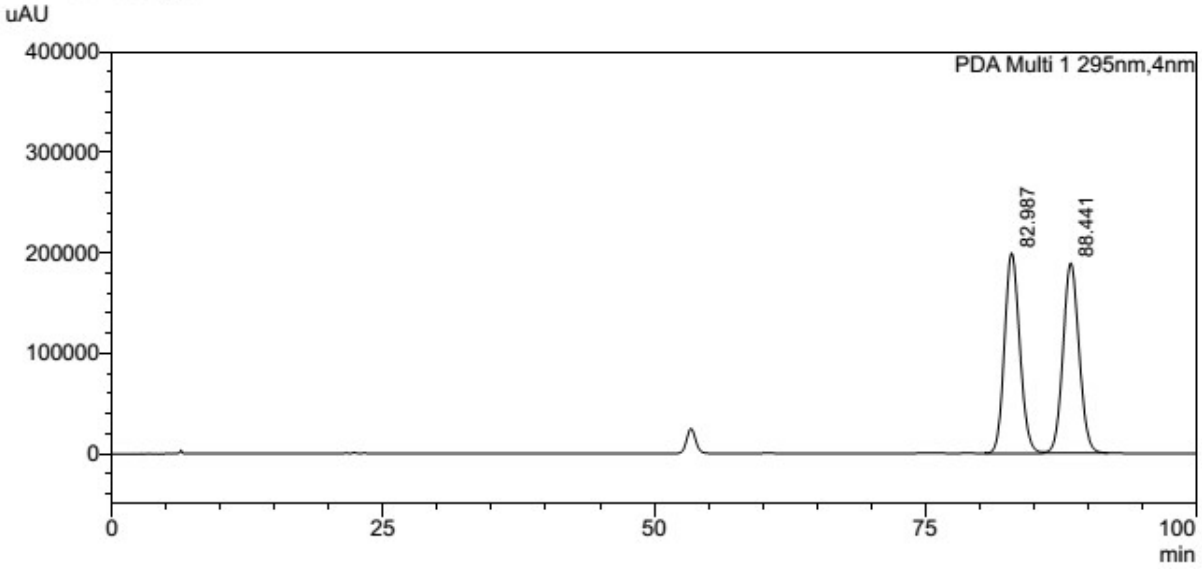
To a solution of *rac*-3-(2-fluorophenyl)pentan-1-ol**7** (25 mg, 0.14 mmol, 1 eq) in CH_2Cl_2 (0.2 mL) were added 4'-nitro-[1,1'-biphenyl]-4-carbonyl chloride[10] (39.4 mg, 0.15 mL, 1.1 eq), triethylamine (57 µL, 0.41 mmol, 3 eq), and DMAP (< 1mg, cat.). The mixture was stirred at 23°C for 45 min. After this time, the volatiles were evaporated under vacuum and the crude residue was purified by column chromatography (EtOAc:Cyclohexane 2.5:97.5) to give 30 mg (54%) of the racemic title compound as a white solid.

Under the same conditions, an enantioenriched mixture of 3-(2-fluorophenyl)pentan-1-ol**7** (*e.r.*14:86) (25 mg, 0.14 mmol, 1 eq) was esterified to give 35 mg (63%) of the desired enantioenriched ester as a crystalline solid (*e.r.* 86:14).

^{1}H NMR ($CDCl_3$, 400 MHz, rotamers) :δ = 8.34-8.32 (m, 2H, H_{Ar}), 8.08-8.07 (m, 2H, H_{Ar}), 7.78-7.76 (m, 2H, H_{Ar}), 7.68-7.66 (m, 2H, H_{Ar}), 7.23-7.16 (m, 2H, $2H_{Ar}$), 7.12-7.03 (m, 1H, H_{Ar}), 7.03-7.00 (m, 1H, H_{Ar}), 4.33-4.28 (m, 1H, H_1), 4.21-4.16 (m, 1H, H_1), .3.12-3.06 (m, 1H, H_3), 2.24-2.17 (m, 1H, H_2), 2.13-2.06 (m, 1H, H_2), 1.82-1.66 (m, 2H, H_4), 0.84 (t, J = 7.4 Hz, 1H).**^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz, rotamers) :**δ = 166.1 (C_8), 162.5/160.5 (d, J = 244.4 Hz, C_7), 147.7 (C_{Ar}), 146.6 (C_{Ar}), 143.1 (C_{Ar}), 131.1/131.0 (C_6), 130.8 (C_{Ar}), 130.5 (C_{Ar}), 128.80/128.76 (C_{Ar}), 128.2 (C_{Ar}), 127.82/127.75 (C_{Ar}), 127.5 (C_{Ar}), 124.41/124.38 (C_{Ar}), 124.35 (C_{Ar}), 115.8/115.6 (C_{Ar}), 63.9 (C_1), 37.6 (C_3), 34.2 (C_2), 28.8 (C_4), 12.2 (C_5). **^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz, rotamers) :** δ = -118.40 (F_7). **HPLC separation conditions :** Chiralpak AD-H column, *n*-heptane/*i*-PrOH 98:2, flow rate 0.5 mL/min, 25°C, t_R 82.7 min for (+)-(*S*)-enantiomer (major) and t_R 88.4 min for (-)-(*R*)-enantiomer (minor). *e.r.* 86:14.**HRMS (ESI) m/z:** $C_{24}H_{22}FO_4Na$ ($[M + Na]^+$) : 430.1425; found: 430.1419**. IR neat (ʊ/cm^{-1}) :** 2963, 2361, 1716, 1598, 1519, 1343, 1275, 1109.**M.p :** 82°C. **$[\alpha]_D^{20}$** =+82.3° (c=0.9, $CHCl_3$, *e.r.* 86:14).

[10] For the synthesis of the corresponding acid : Adachi, Y.; Nakagawa, H.; Matsuo, K.; Suzuki, T; Miyata, N.*Chem. Commun.* **2008**, 5149-5151.

<Chromatogram>



<Peak Table>

PDA Ch1 295nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	82.987	49.926	19513963	199508	49.926		SV
2	88.441	50.074	19571960	189277	50.074		V
Total		100.000	39085924	388786			

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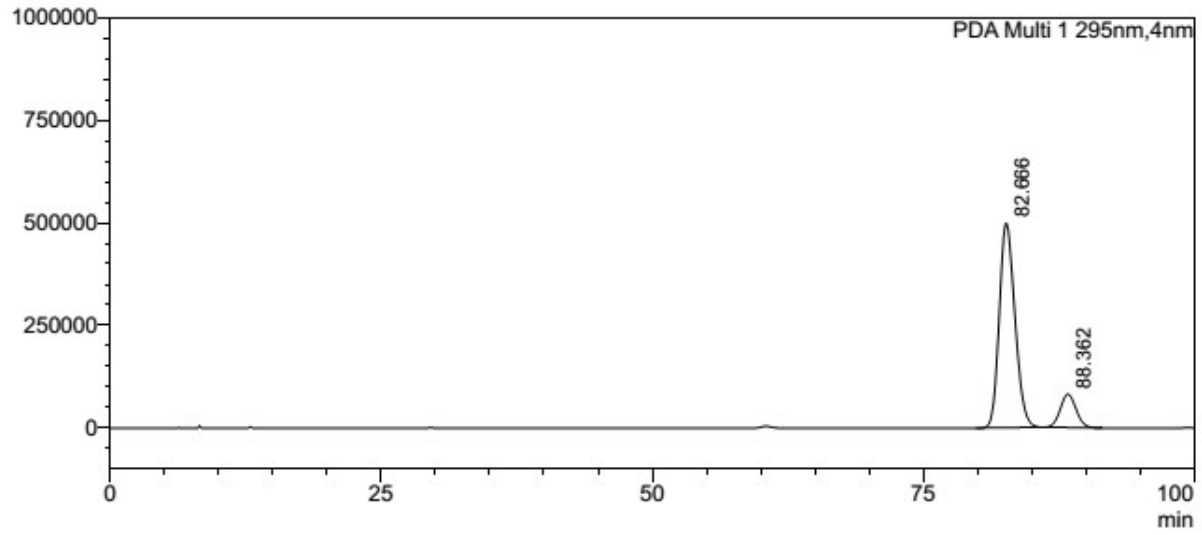


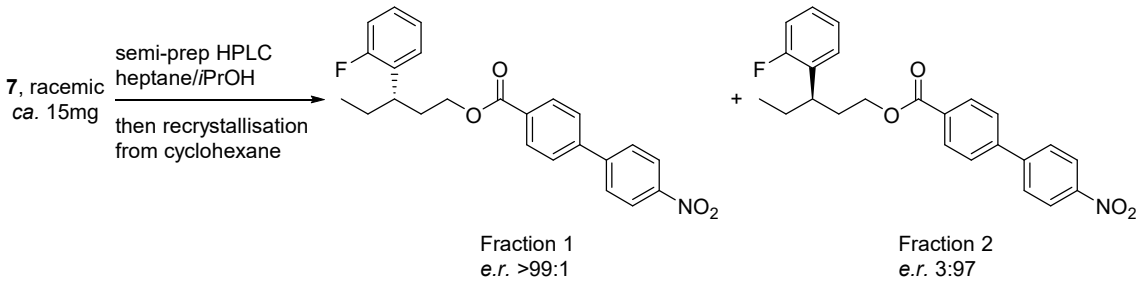
<Peak Table>

PDA Ch1 295nm

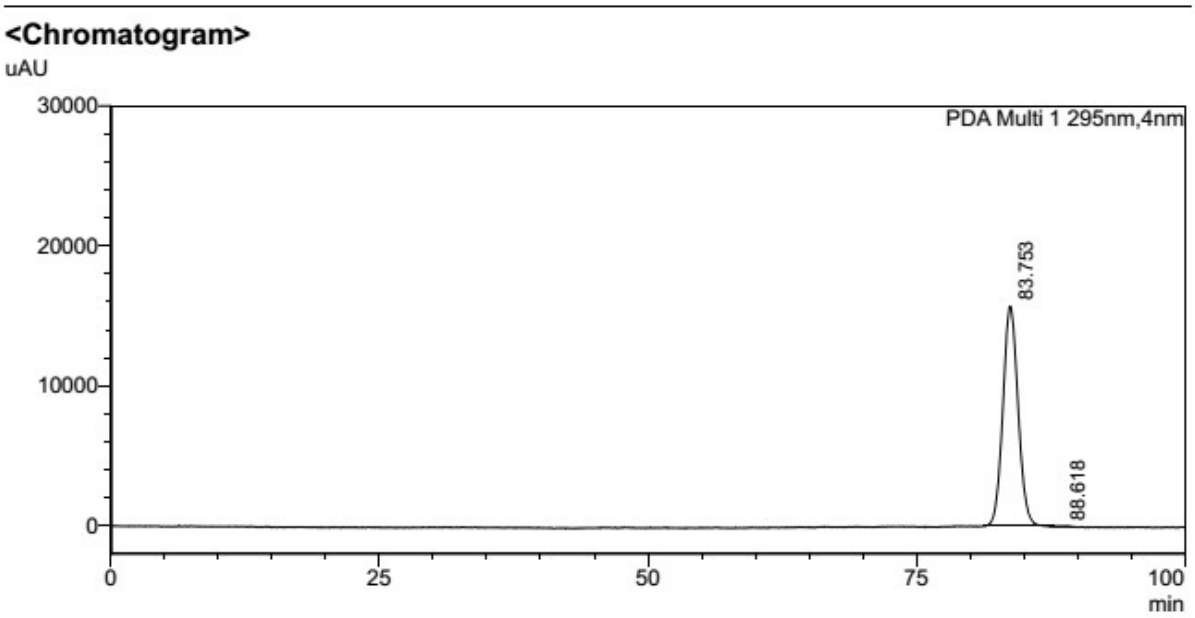
Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	82.666	85.895	49926138	497910	85.895		M
2	88.362	14.105	8198477	80972	14.105		M
Total		100.000	58124615	578882			

12. Determination of the absolute configuration of **7** (Scheme 3c)

A racemic sample of the ester **7** (ca. 15 mg) was separated by semi-preparative HPLC (Chiralpak AD-H semi-prep column, *n*-heptane/*i*-PrOH 97:3, flow rate 2 mL/min, 25°C). After collection, the fractions were combined and evaporated to obtain two enantiopure samples of compound **7** : Fraction 1 (*e.r.* >99:1, t_R 83.7min (majo) by analytical HPLC) and Fraction 2 (*e.r.* 3:97, t_R 88.8 min (majo) by analytical HPLC). The samples were crystallized in a GC vial from pure cyclohexane via slow evaporation process to obtain white needles.



HPLC trace of Fraction 1 :



<Peak Table>

PDA Ch1 295nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	83.753	99.905	1553997	15734	0.000		M
2	88.618	0.095	1479	47	0.000		M
Total		100.000	1555476	15782			

HPLC trace of Fraction 2 :

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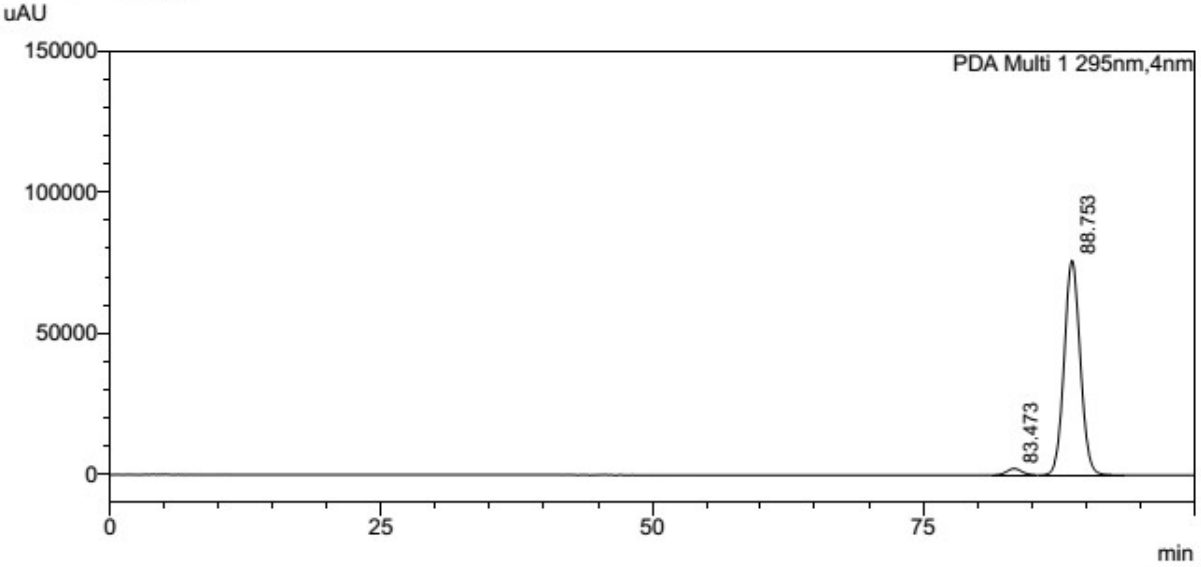
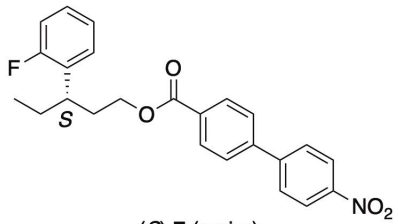


<Peak Table>

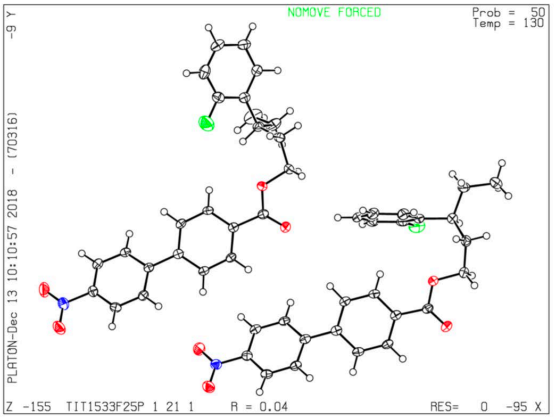
PDA Ch1 295nm

Peak#	Ret. Time	Area%	Area	Height	Conc.	Unit	Mark
1	83.473	2.736	221190	2301	0.000		M
2	88.753	97.264	7864577	76061	0.000		M
Total		100.000	8085767	78363			

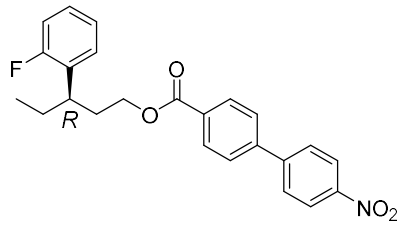
X-Ray structure of Fraction 1:



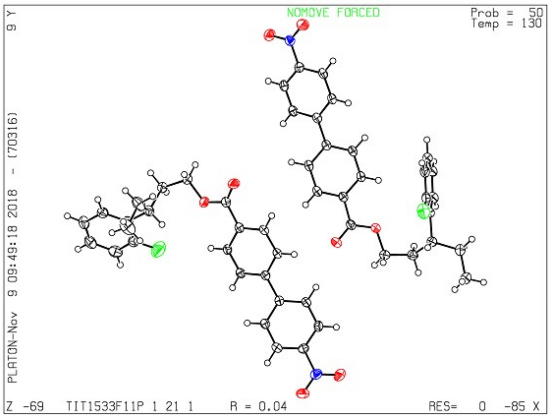
(*S*)-**7** (major)
Fraction 1
e.r. >99:1



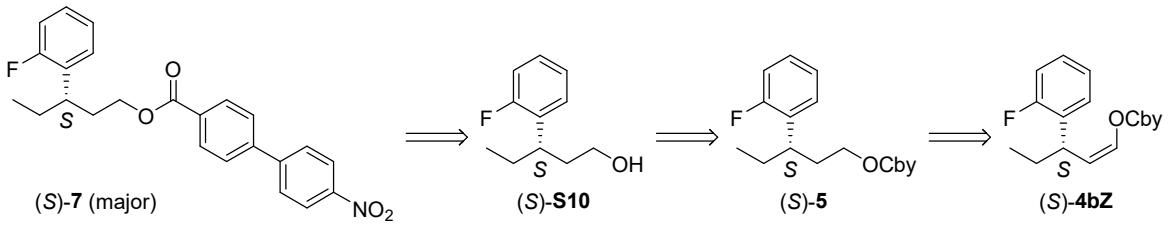
X-Ray structure of Fraction 2:



(*R*)-**7** (minor)
Fraction 2
e.r. 3:97



Absolute configuration of intermediate products :

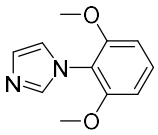


(*S*)-**7** (major) ⟹ (*S*)-**S10** ⟹ (*S*)-**5** ⟹ (*S*)-**4bZ**

13. Preparation of ligand L^3

Synthesis of starting material imidazole **S11**

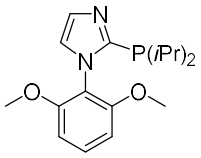
1-(2,6-dimethoxyphenyl)-1*H*-imidazole **S11** :



A 20 mL reaction tube was loaded in a glovebox with imidazole (680 mg, 10 mmol, 1 eq), CuI (286 mg, 1.5 mmol, 0.15 eq), and Cs_2CO_3 (4.89 g, 15 mmol, 1.5 eq). Out of the glovebox, 2-iodo-1,3-dimethoxybenzene (2.64 g, 10 mmol, 1 eq) and DMSO (10 mL) were added. The tube was sealed and placed in a microwave apparatus, stirred for 1 min at ambient temperature, and then stirred and heated at 160°C for 6 h under microwave irradiation. The reaction mixture was diluted with 100 mL of EtOAc:CyHex (50:50) and 100 mL of Brine:Water (50:50) were added. The organic layer was separated and the aqueous layer was extracted 3 times with 100 mL of EtOAc:CyHex (50:50). The combined organic layers were washed with 250 mL of Brine:Water (50:50), dried over $MgSO_4$, filtrated and then concentrated under reduced pressure. The crude residue was purified by column chromatography (EtOAc:MeOH 100:0 to 95:5) to afford 480 mg (24%) of the desired product as an off-white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 7.56 (s, 1H), 7.34-7.30 (m, 1H), 7.17 (s, 1H), 7.02 (s, 1H), 6.68-6.66 (m, 2H), 3.78 (s, 6H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) :**δ = 155.5, 139.2, 139.1, 129.6, 128.2, 121.3, 121.3, 104.6, 69.20. **HRMS (ESI) m/z:** calcd. for $C_{11}H_{12}N_2O_2H$ ([M + H]$^+$): 205.0972; found: 205.0971**. IR neat (ʊ/cm^{-1}) :** 2954, 2877, 2359, 1594, 1449, 1254, 1110. **M.p :** 147°C

2-(diisopropylphosphanyl)-1-(2,6-dimethoxyphenyl)-1*H*-imidazole **L^3** :



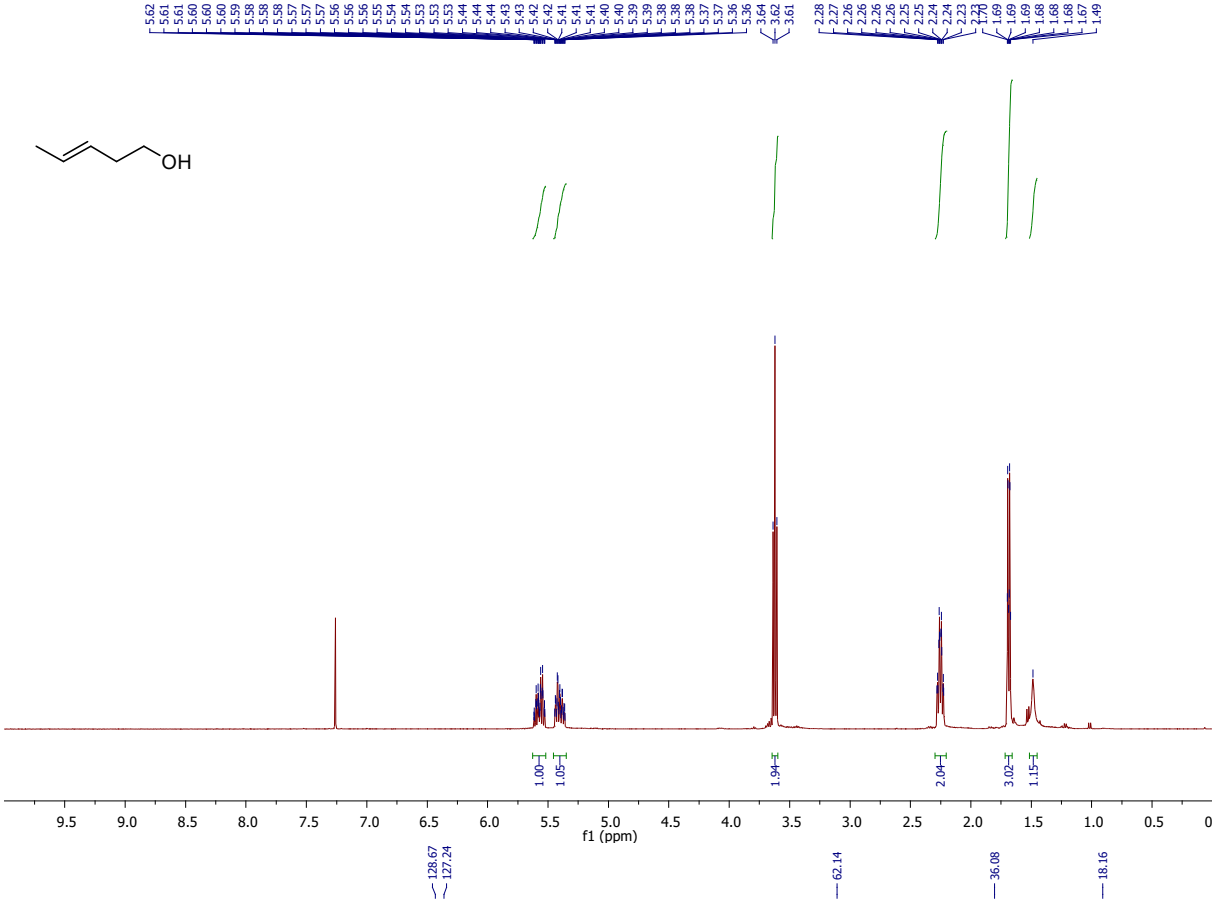
The preparation steps must be carried out under argon atmosphere as much as possible via the use of argon filled balloons and/or a schlenk ramp. A solution of 1-(2,6-dimethoxyphenyl)-1*H*-imidazole **S11** (300 mg, 0.1.47 mmol, 1 eq)in THF (2 mL) was cooled down to -30°C (acetone, cryostat). *s*-Butyllithium (1 eq, solution in hexane) was added dropwise and the mixture was stirred for 30 min before addition of chlorodiisopropylphosphine (236 mg, 0.1.54 mmol, 1.05 eq) in THF (1 mL). The mixture was stirred for 30 min at -30°C and 30 min at 20°C. Then, the mixture was directly concentrated

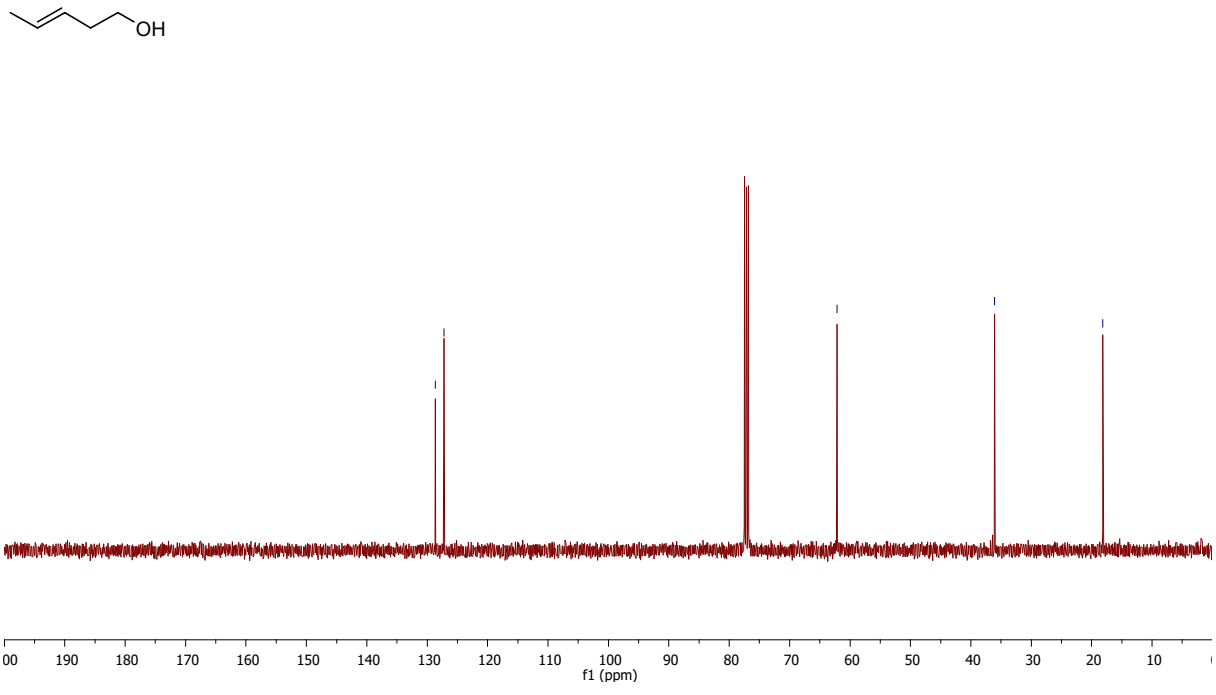
under reduced pressure (using an argon flushed rotavapor) and the residue was purified by column chromatography (Pent/Et_2O 95:5 to 0:100) to afford 310 mg (66%) of the corresponding phosphine ligand as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) :δ = 7.39-7.34 (m, 2H), 6.99-6.98 (m, 1H), 6.64-6.62 (m, 2H), 3.72 (s, 6H), 2.30-2.19 (m, 2H), 1.04-0.96 (m, 12H). **^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) :**δ = 156.2, 130.4, 130.3, 123.5, 103.9, 55.7, 24.6, 24.50, 19.9, 19.7, 19.4, 19.3.. **^{31}P-{^{1}H} NMR ($CDCl_3$, 162 MHz) :**δ = -14.3.**HRMS (ESI) m/z:** $C_{17}H_{25}N_2O_2PH$ ($[M + H]^+$): 321.1726; found: 321.1725. **IR neat (υ/cm^{-1}) :** 2959, 2841, 2359, 1593, 1477, 1257, 1103, 986. **M.p :** 76°C.

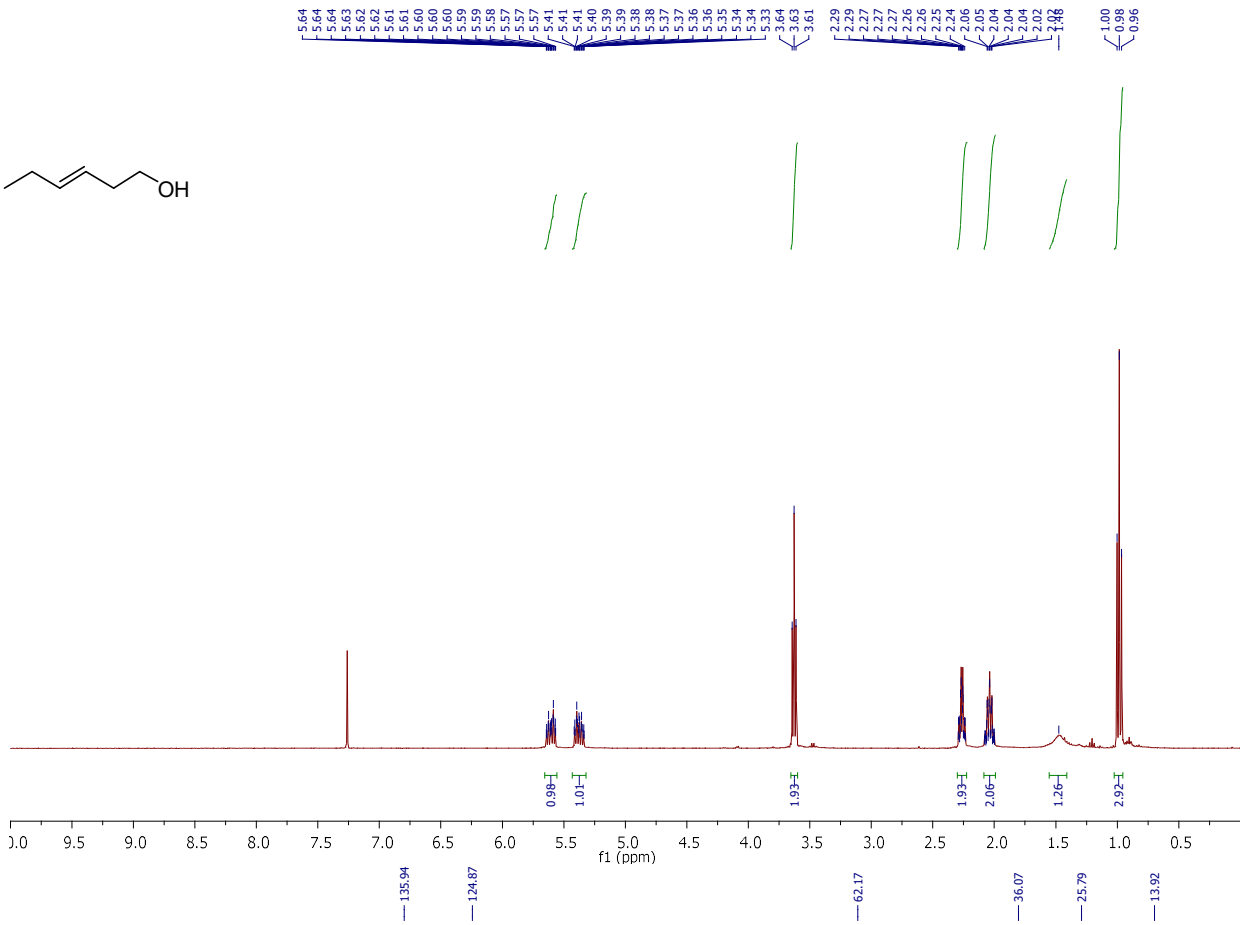
14. NMR Spectra

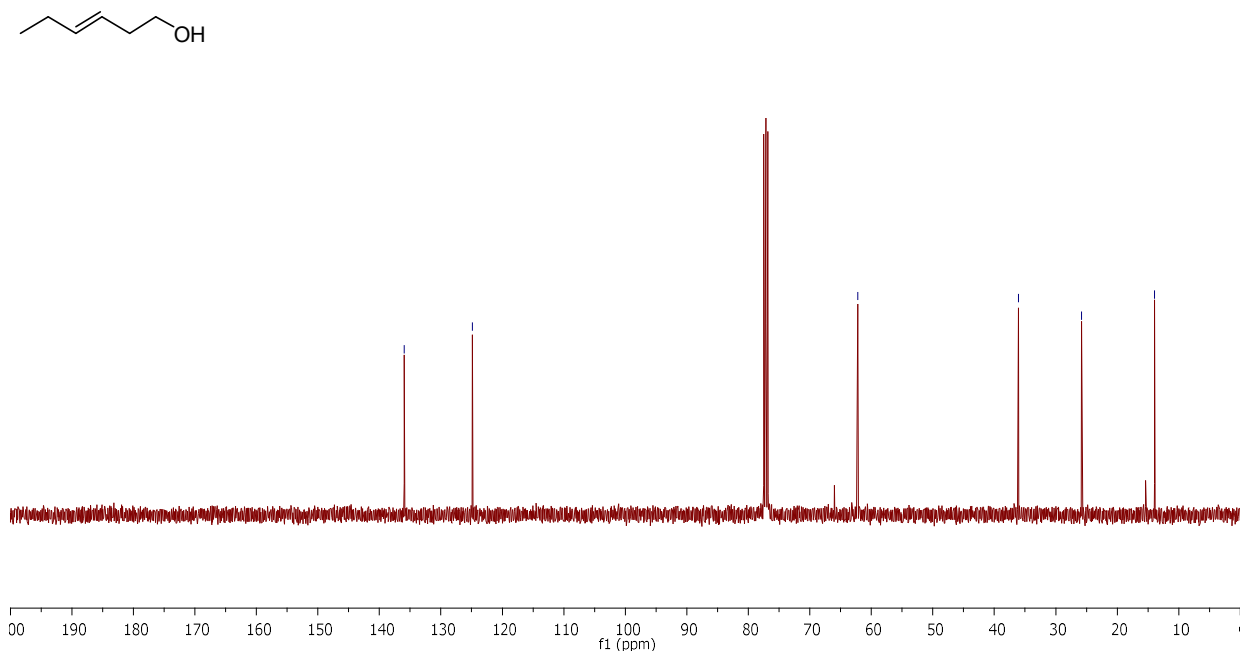
(*E*)-Pent-3-en-1-ol **S1** :



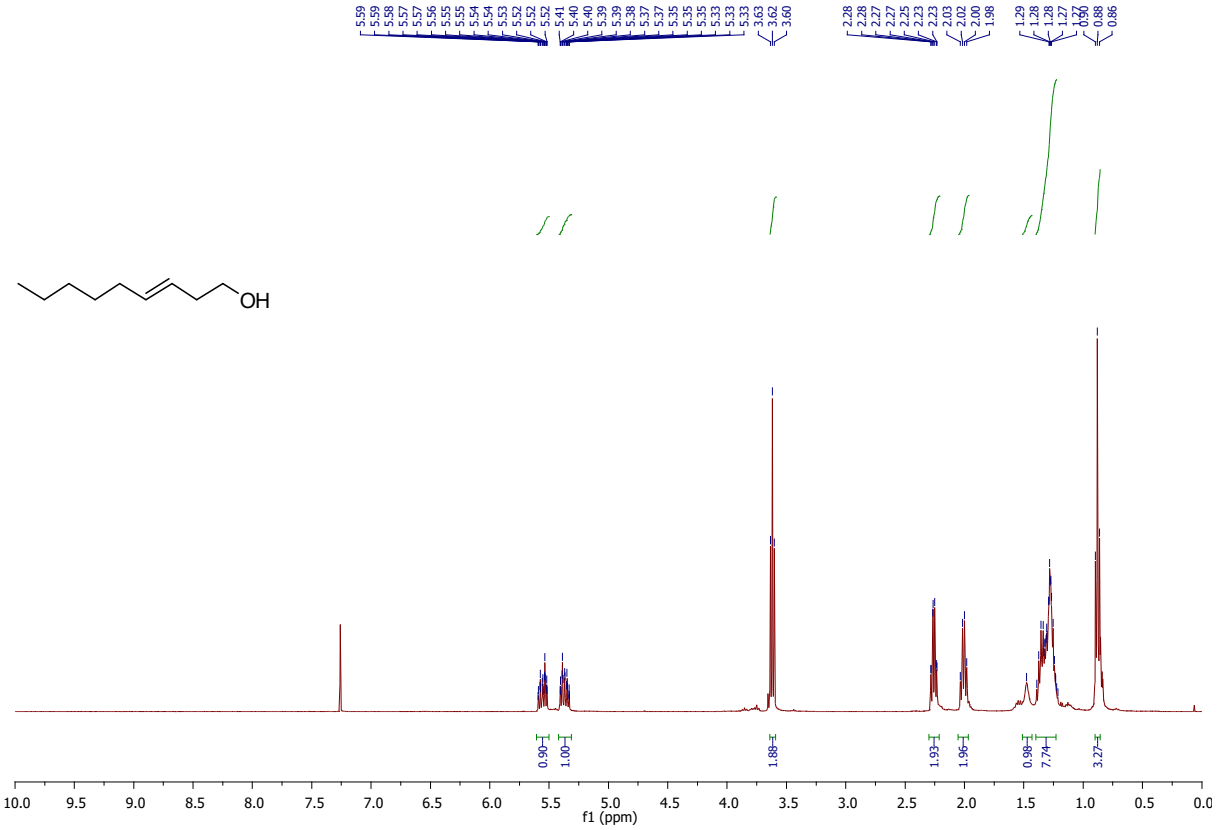


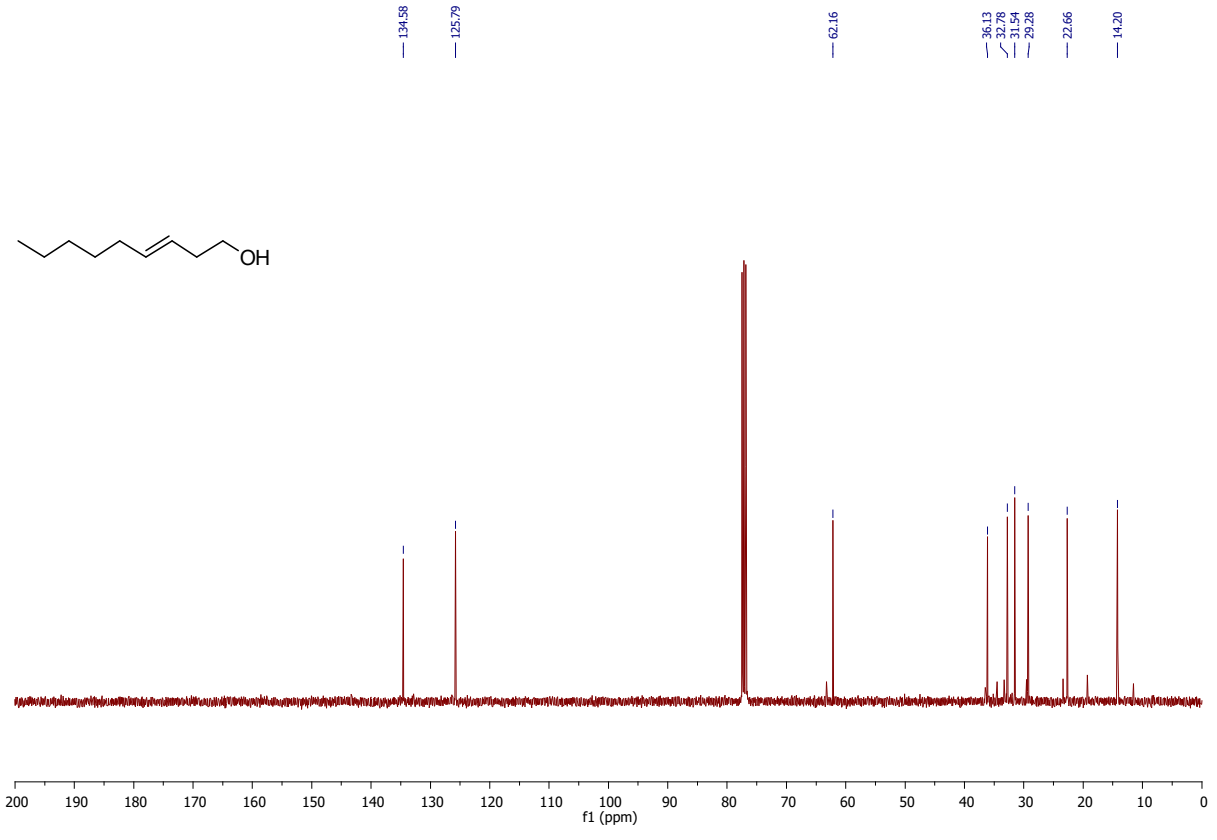
(*E*)-Hex-3-en-1-ol **S2** :



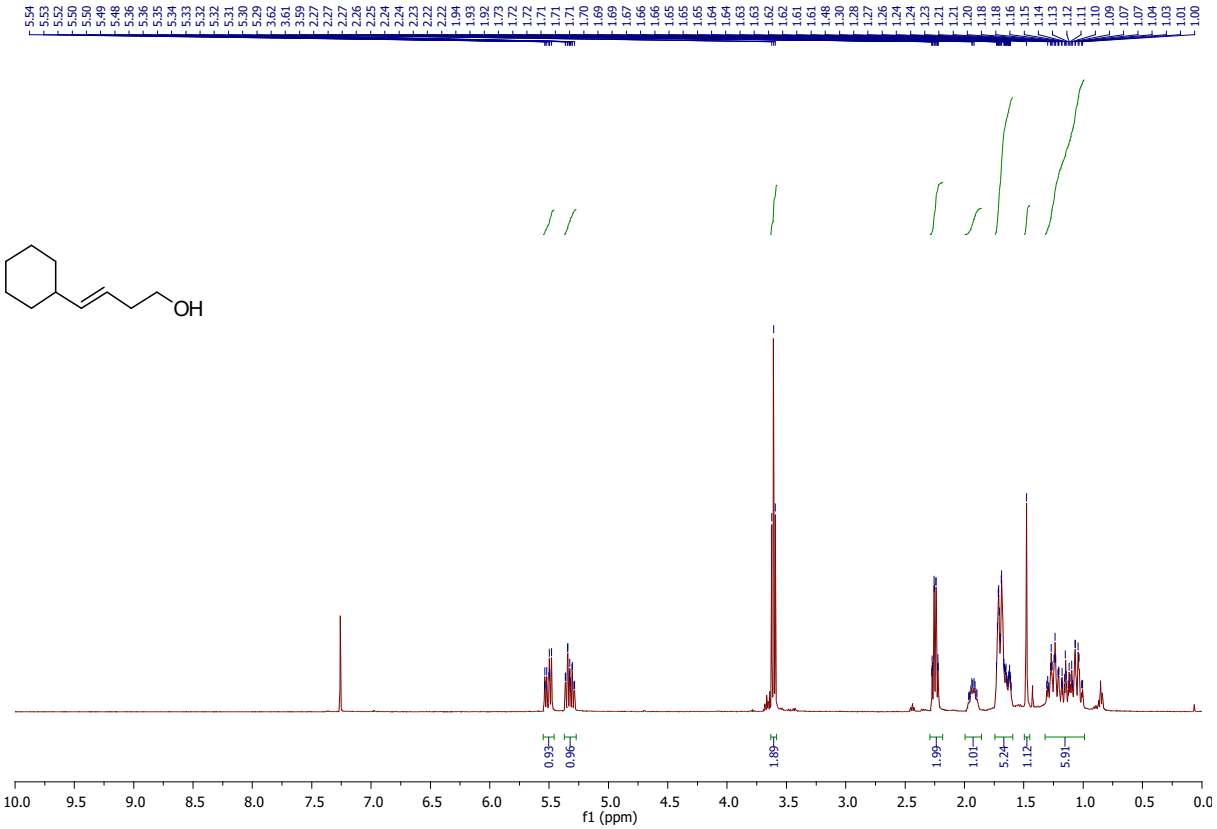


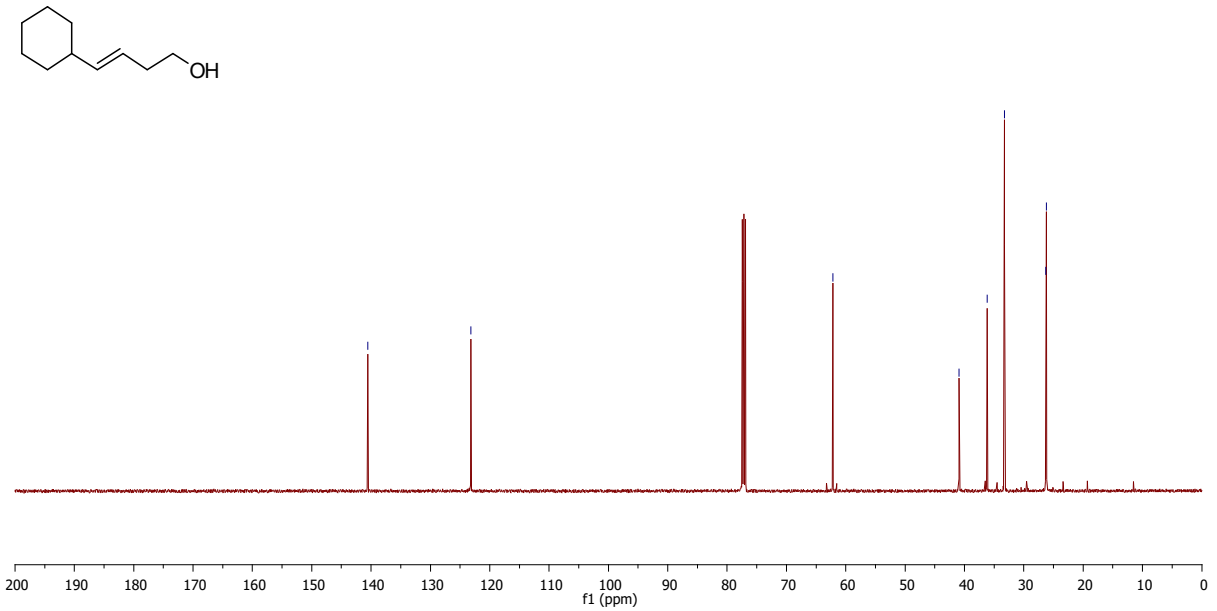
(*E*)-Non-3-en-1-ol **S3** :



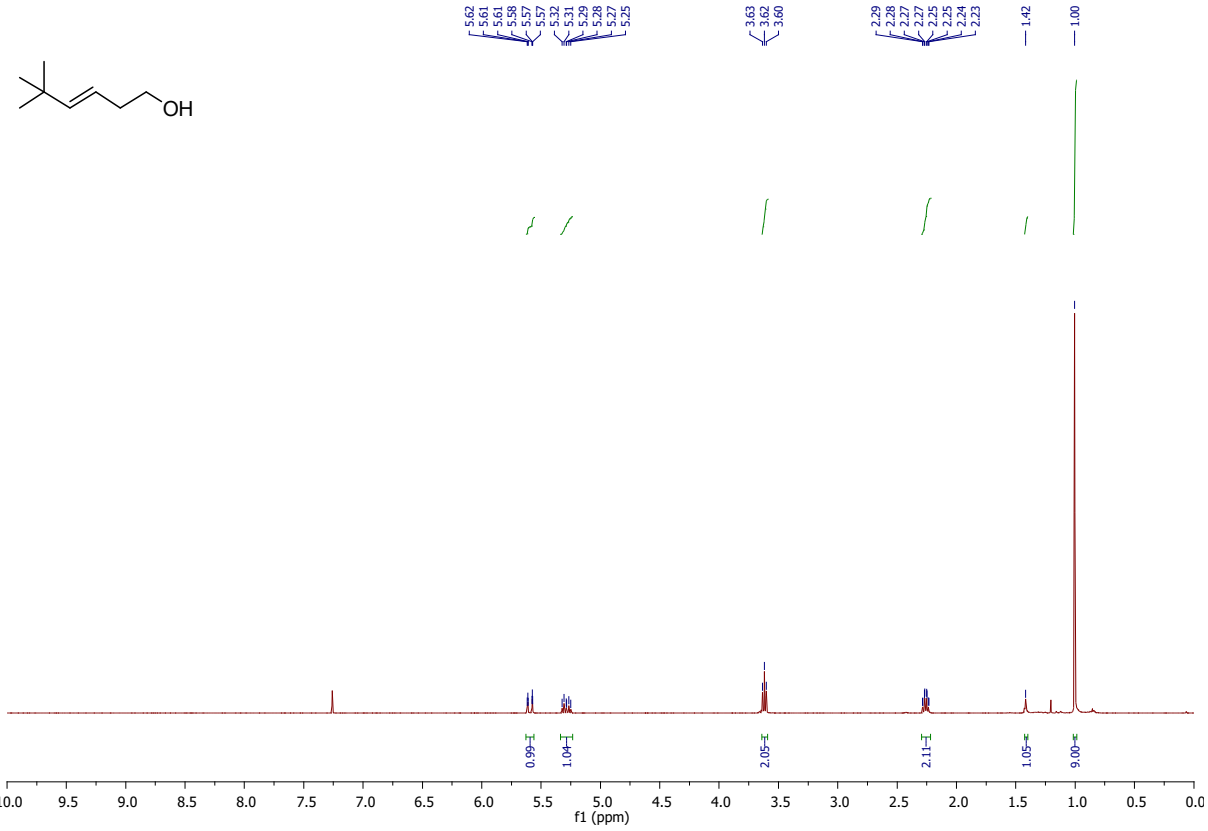


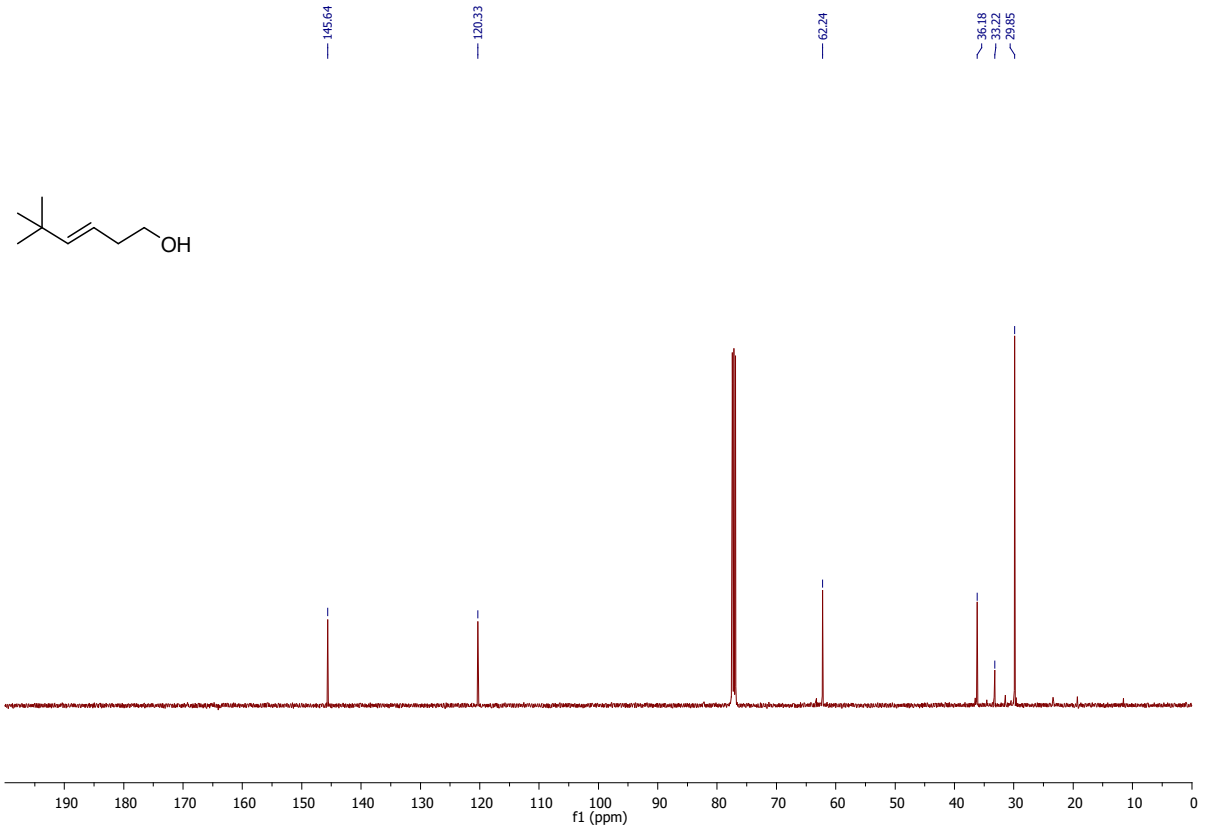
(*E*)-4-cyclohexylbut-3-en-1-ol **S4** :



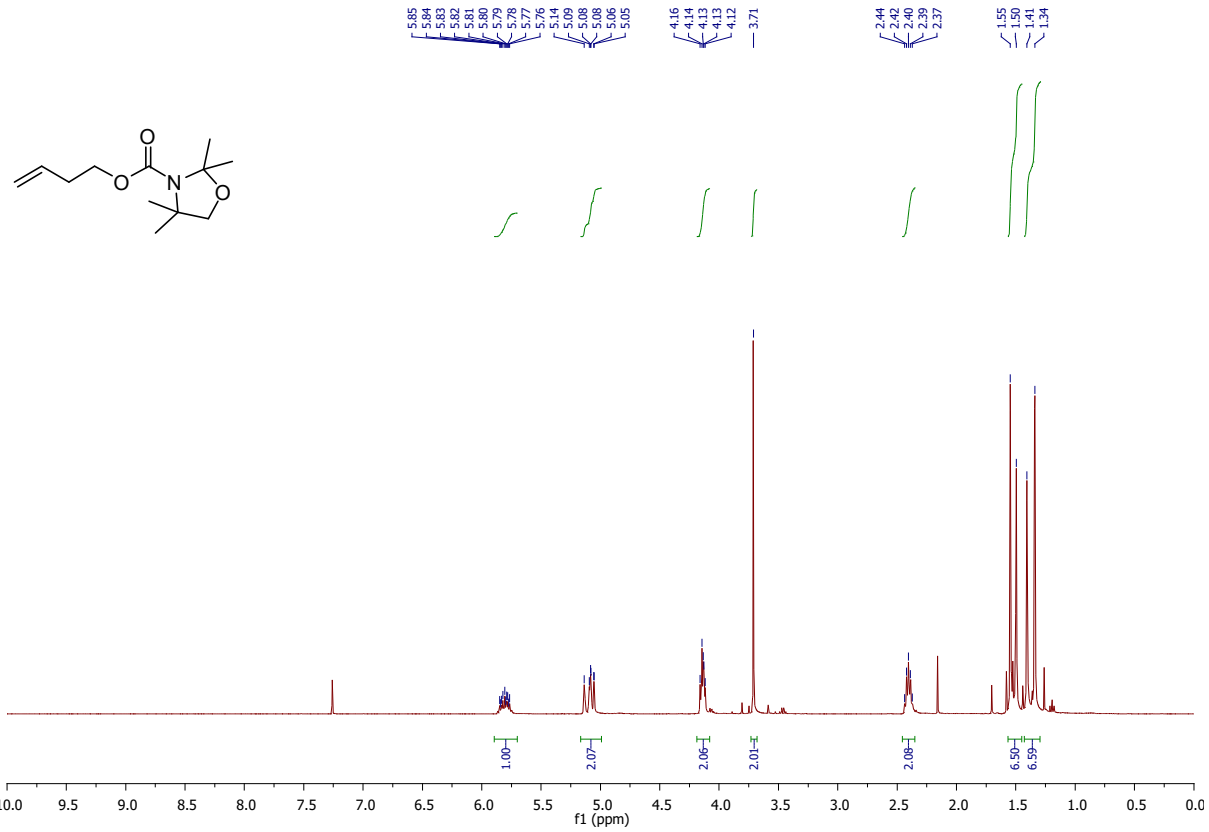


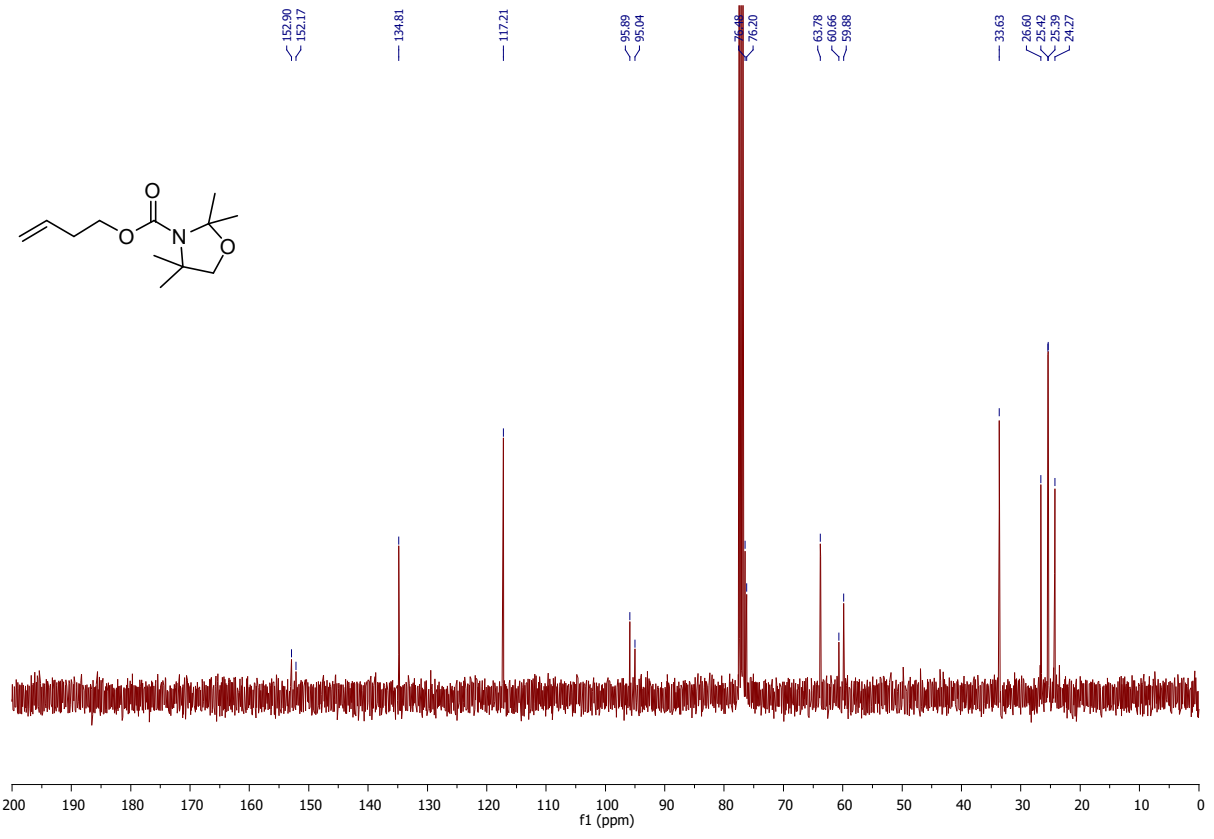
(*E*)-5,5-dimethylhex-3-en-1-ol **S5** :



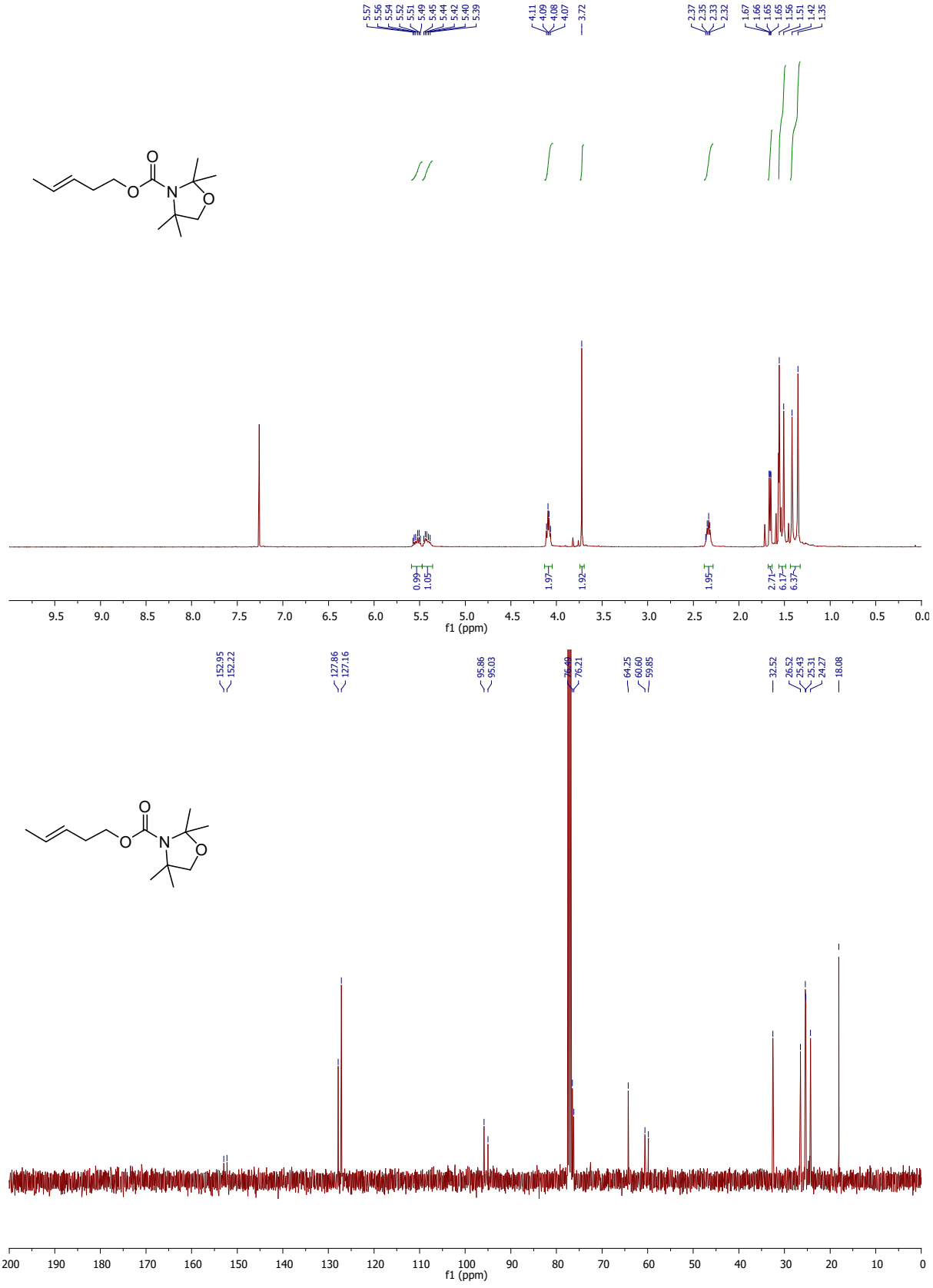


But-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1a** :

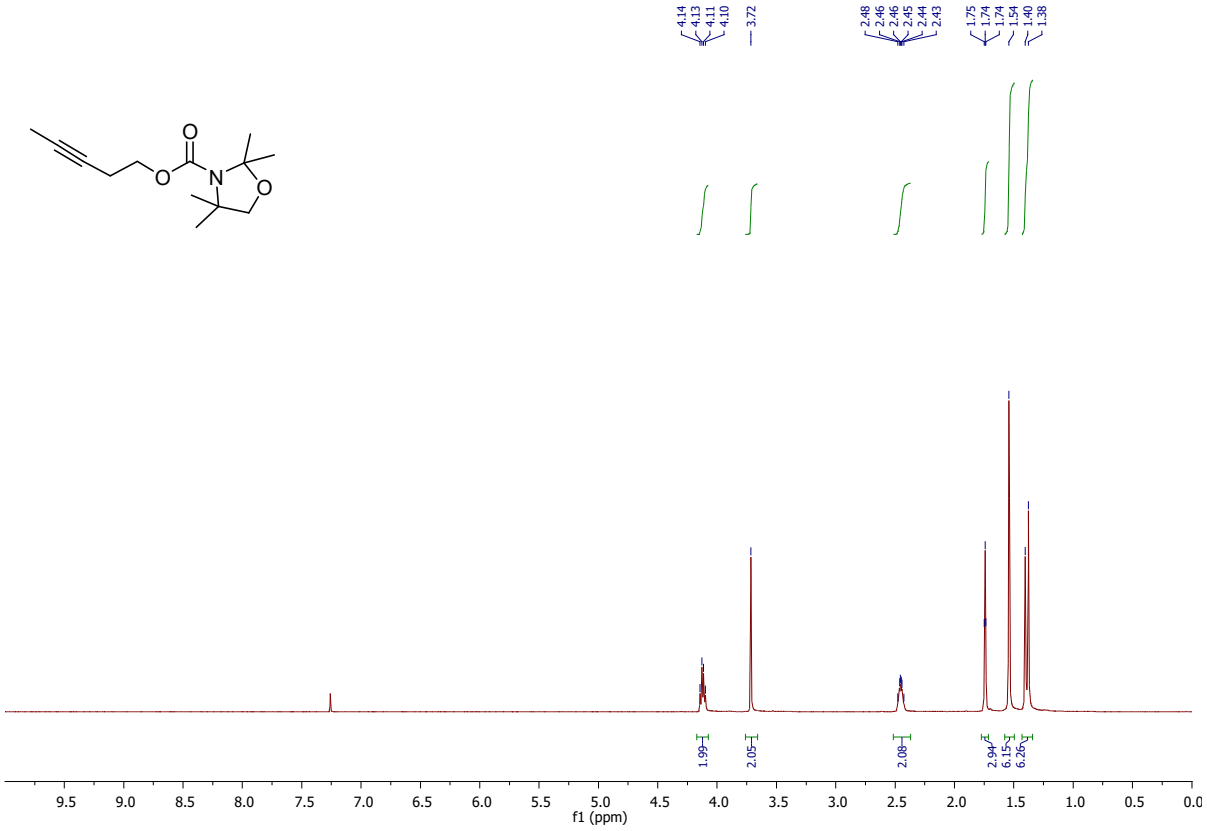


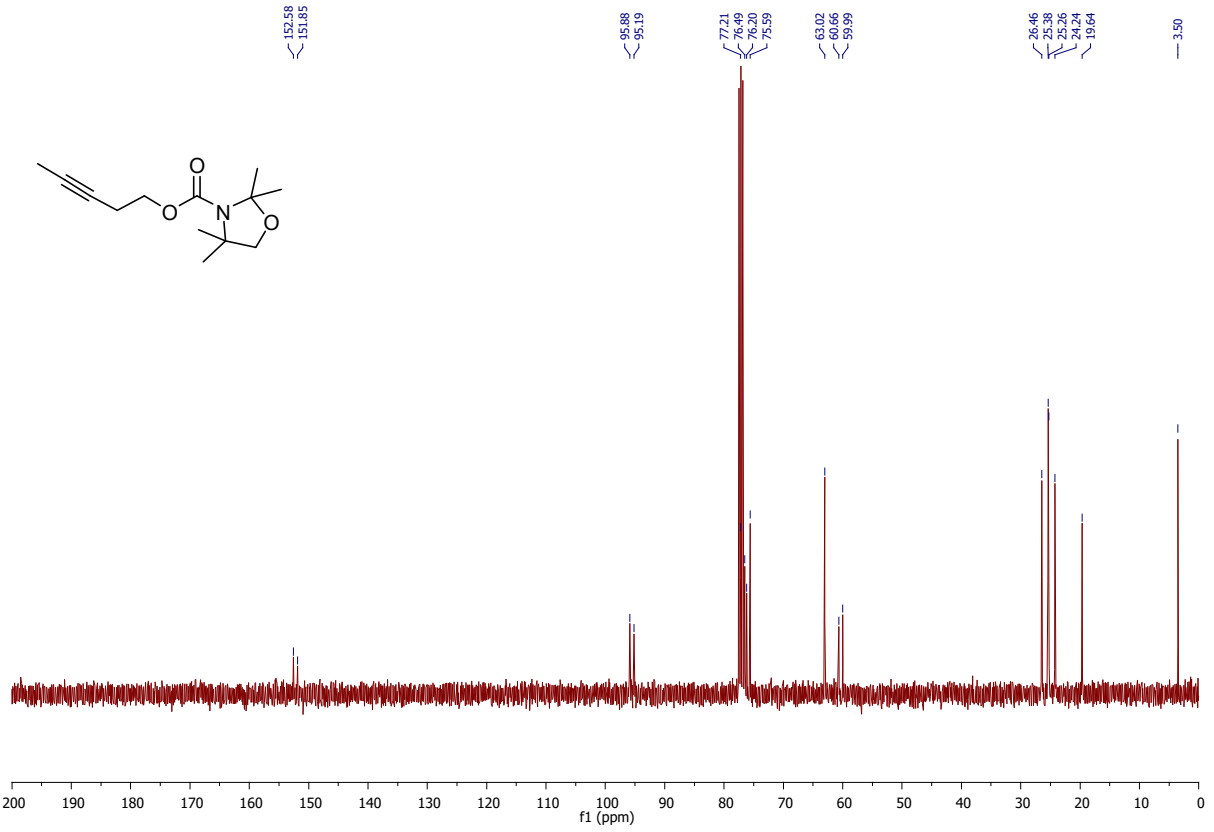


(*E*)-Pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1b*E***:

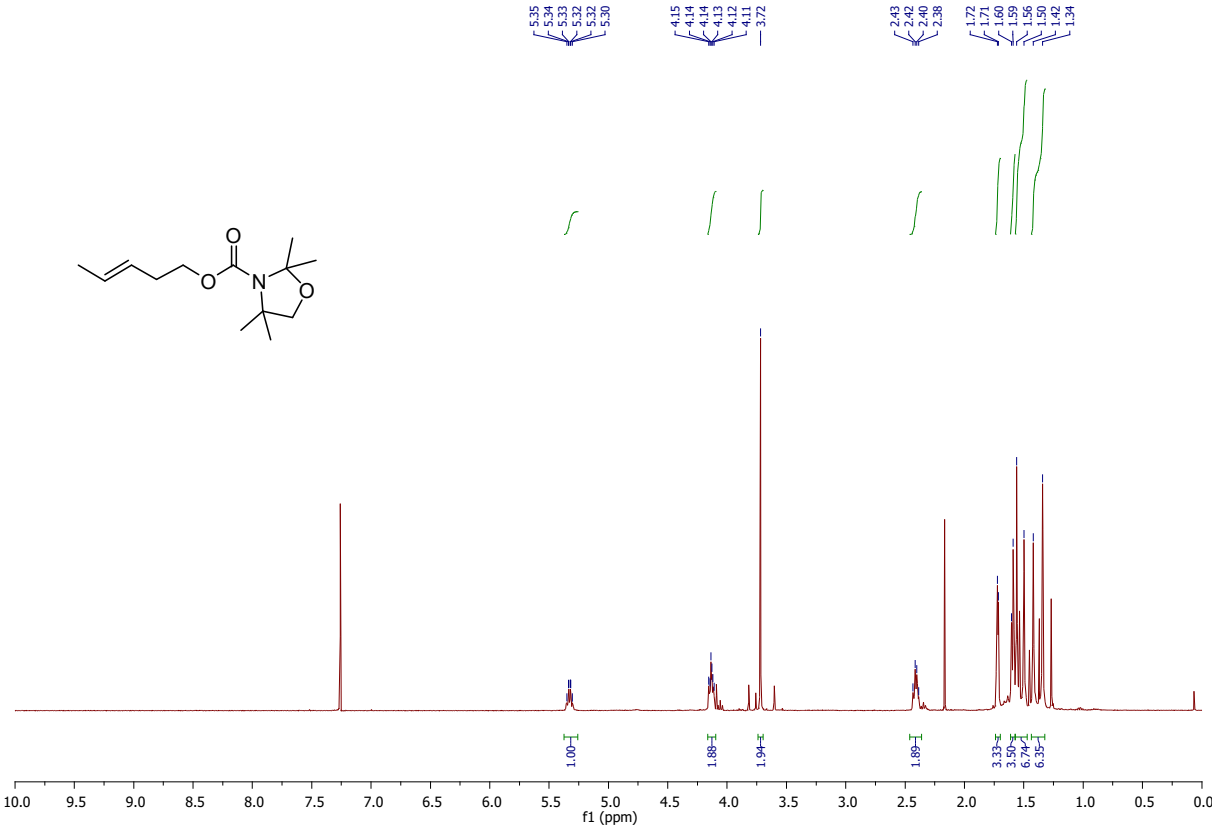


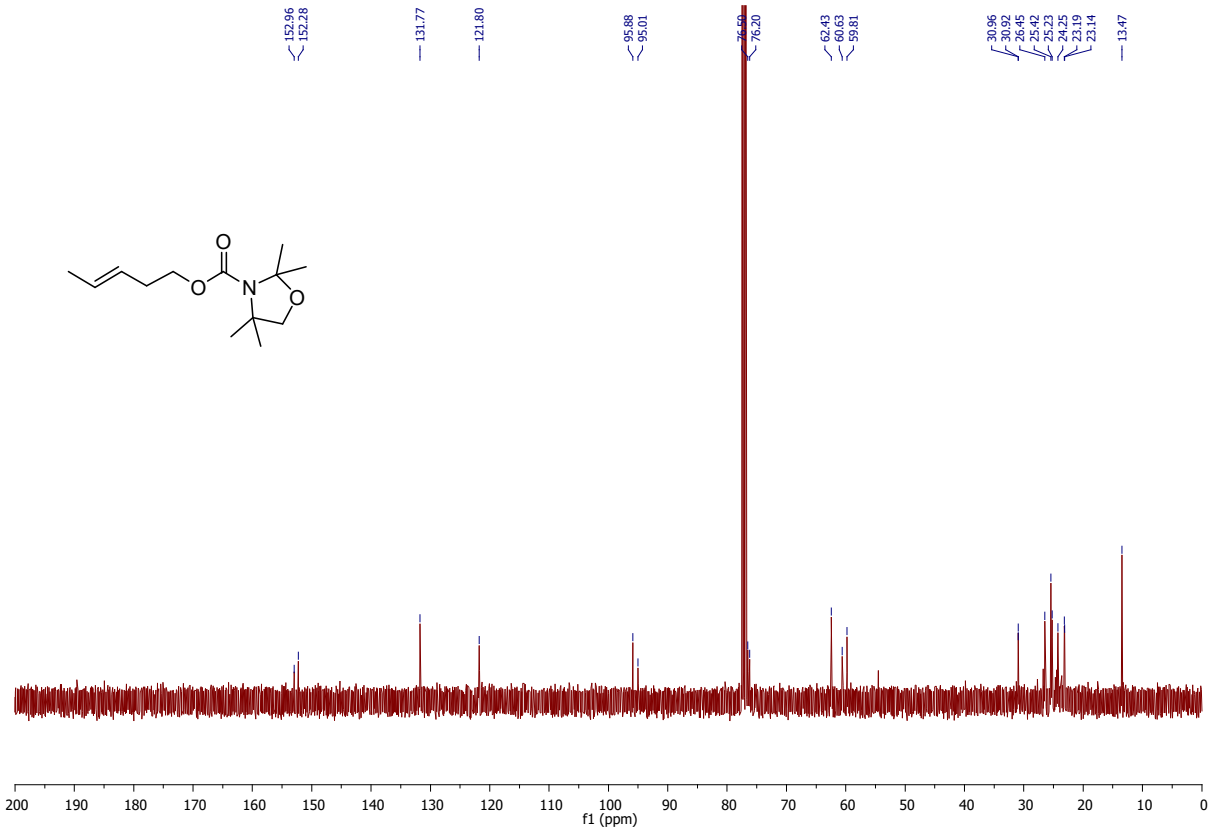
Pent-3-yn-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**S6** :



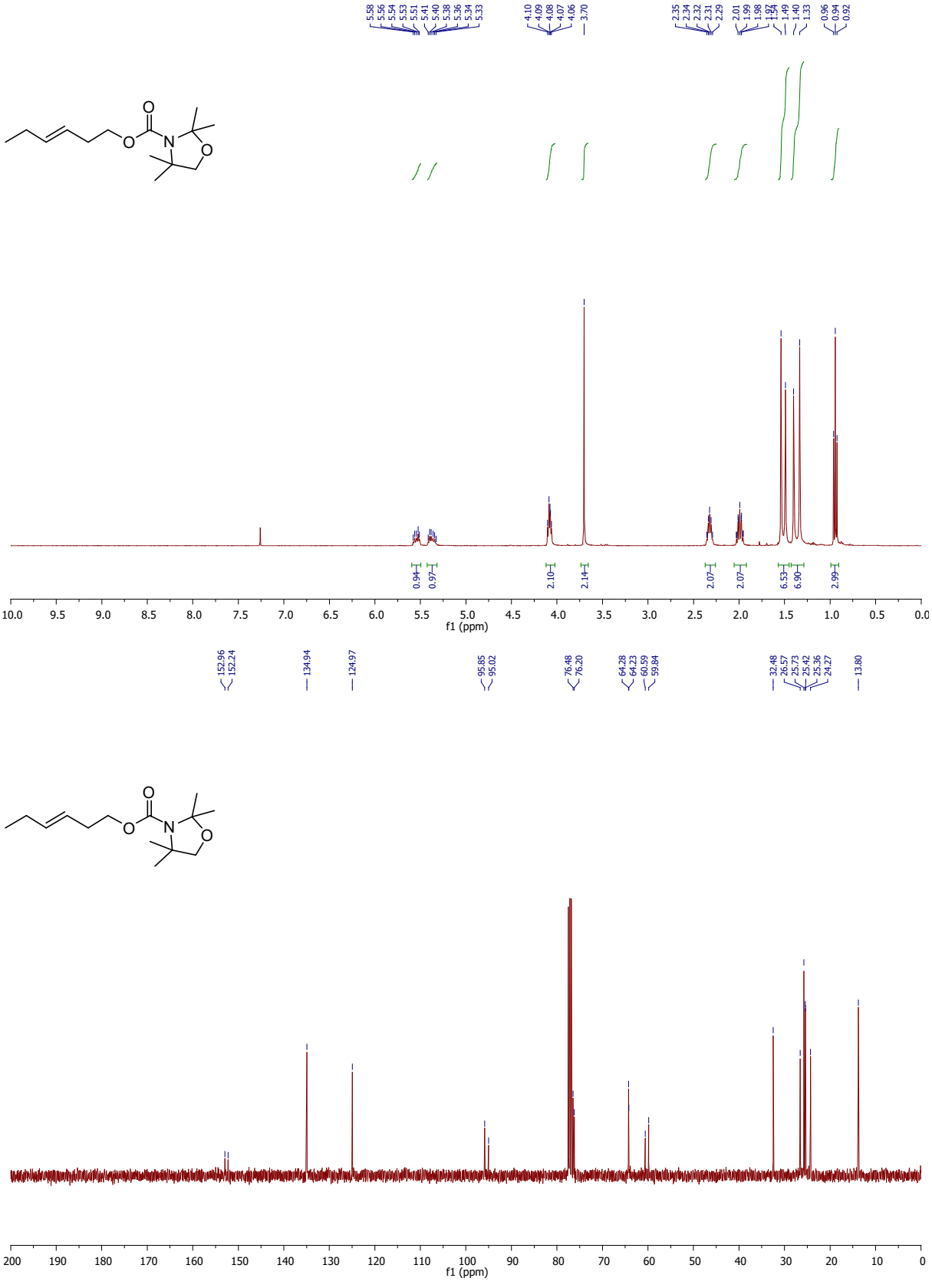


(*Z*)-3-methylpent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **2b*Z*** :

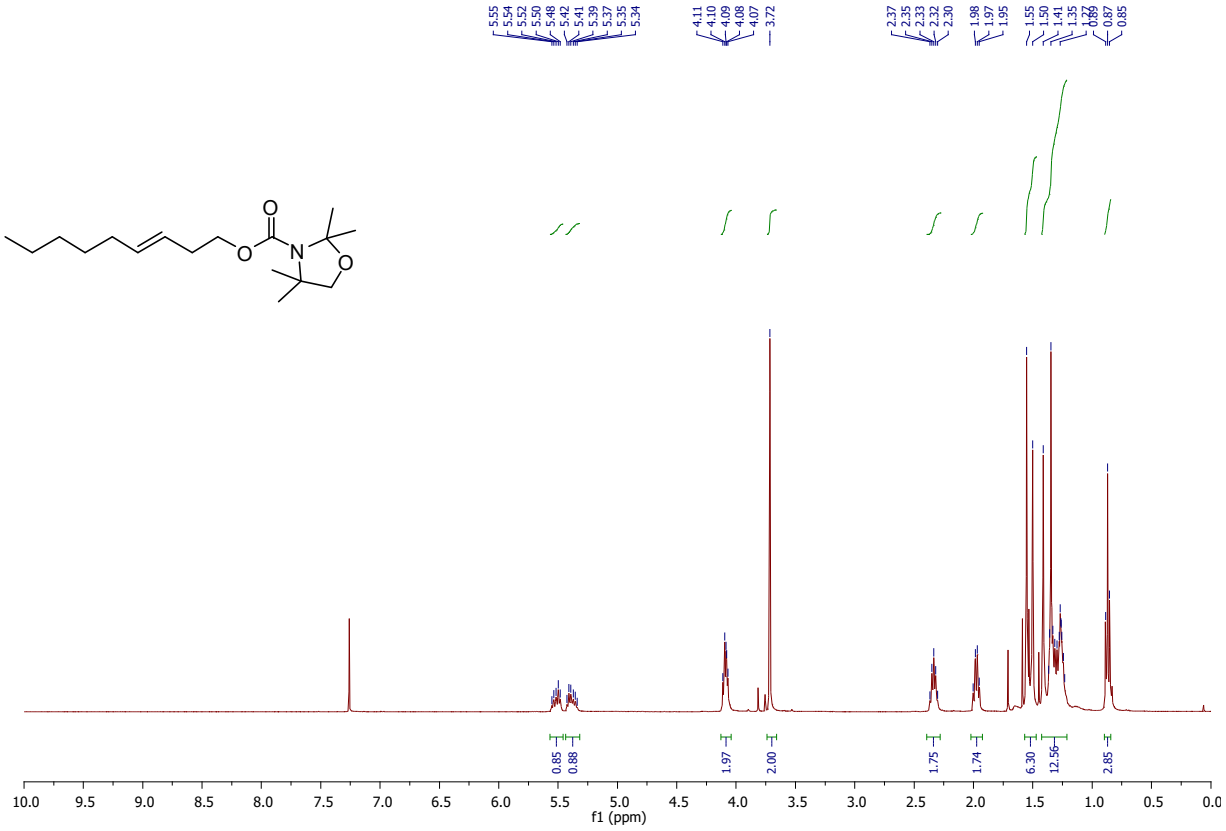


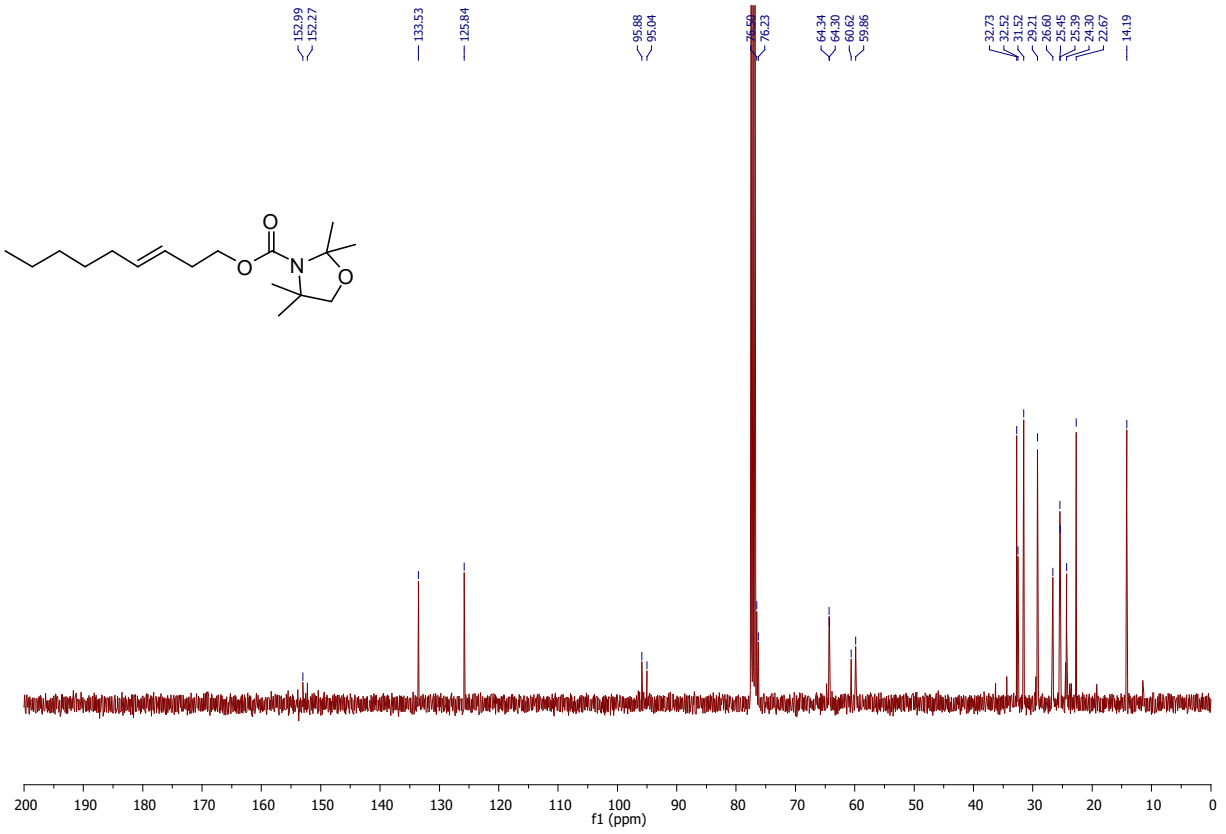


(*E*)-hex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1l** :

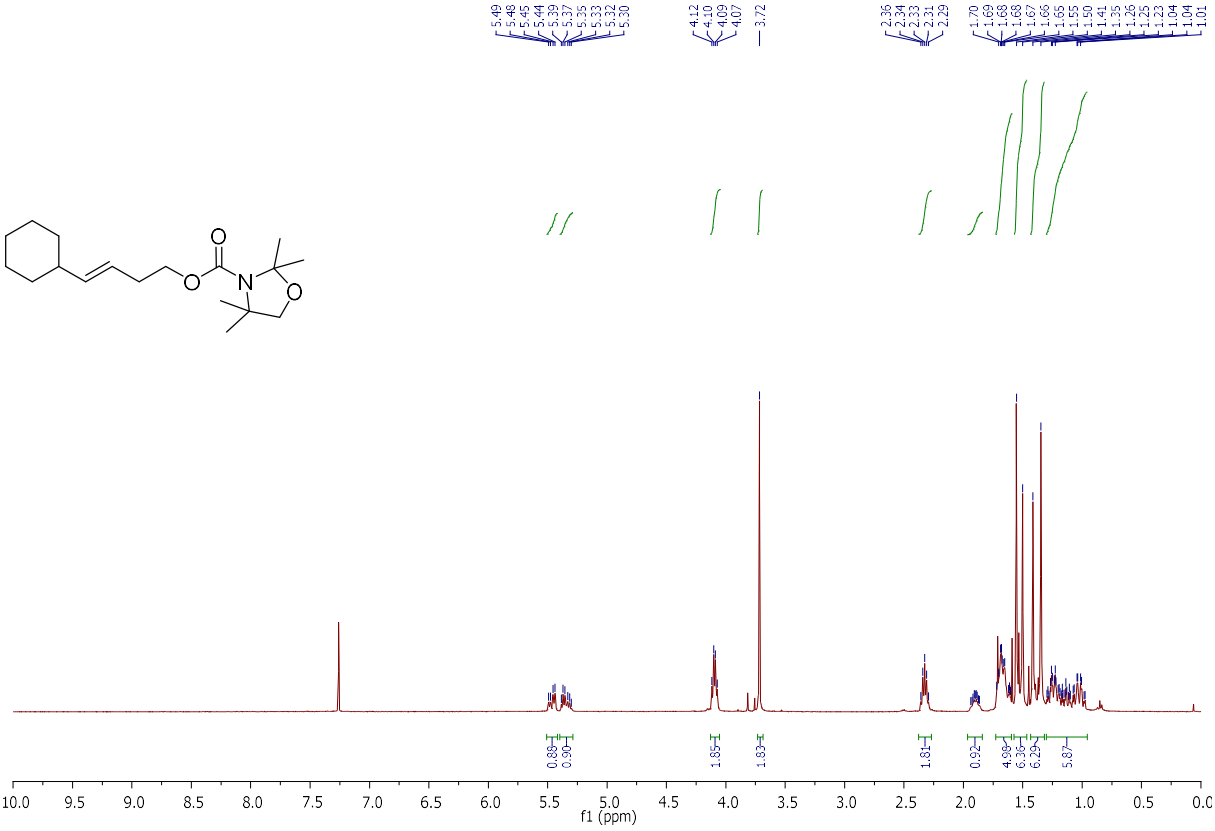


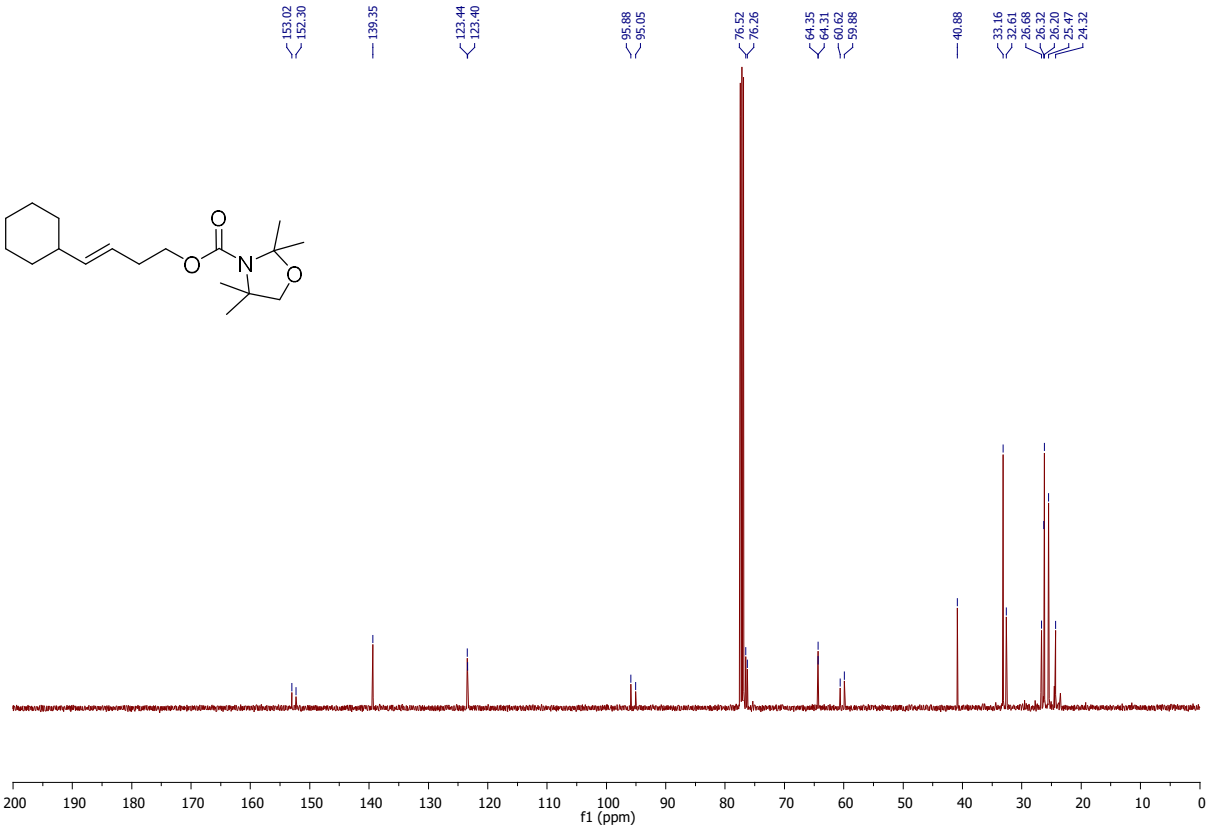
(*E*)-non-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1m** :



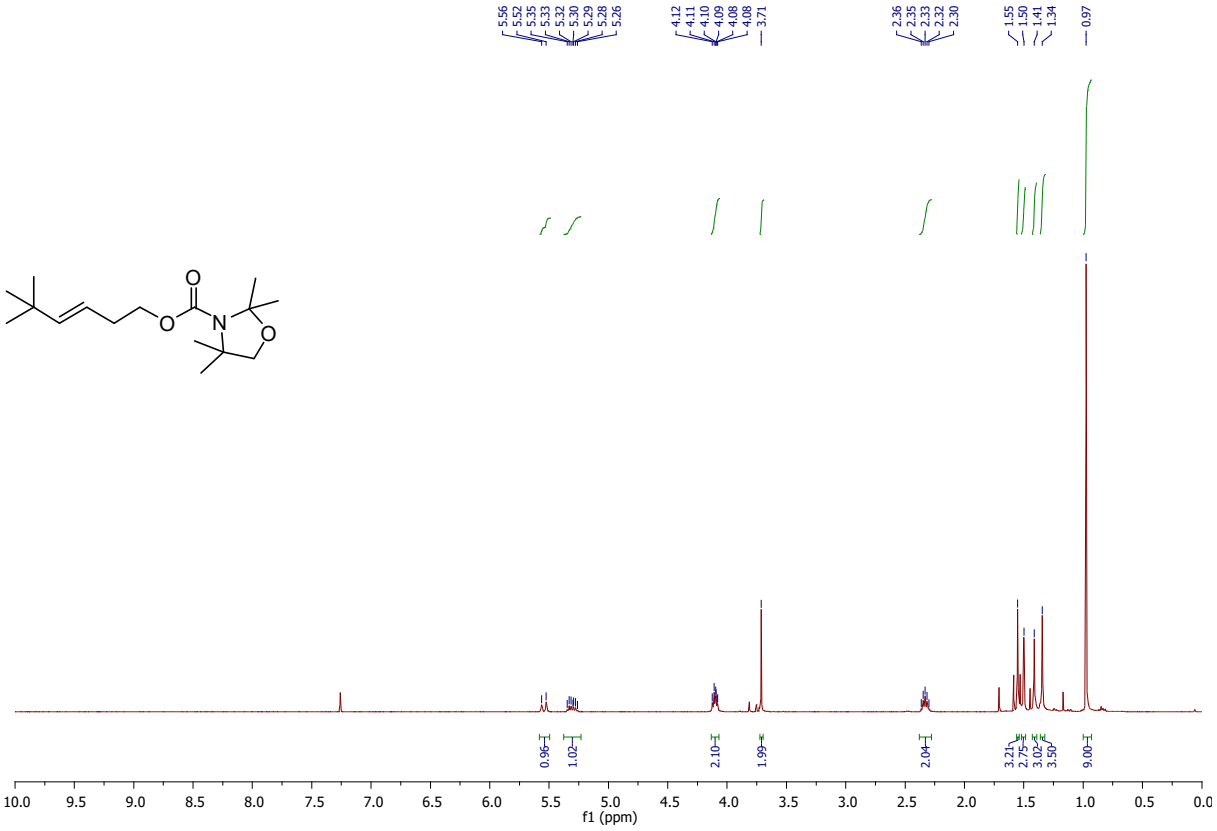


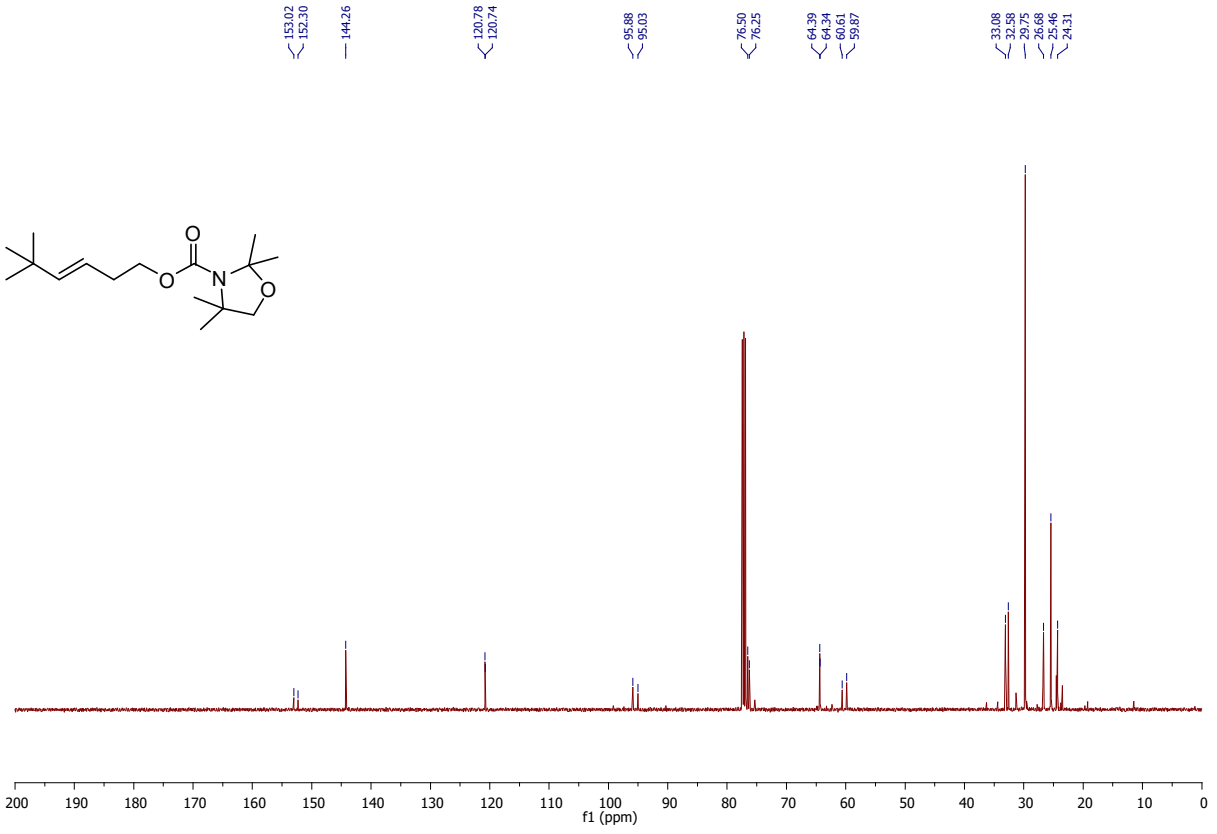
(*E*)-4-cyclohexylbut-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1n** :



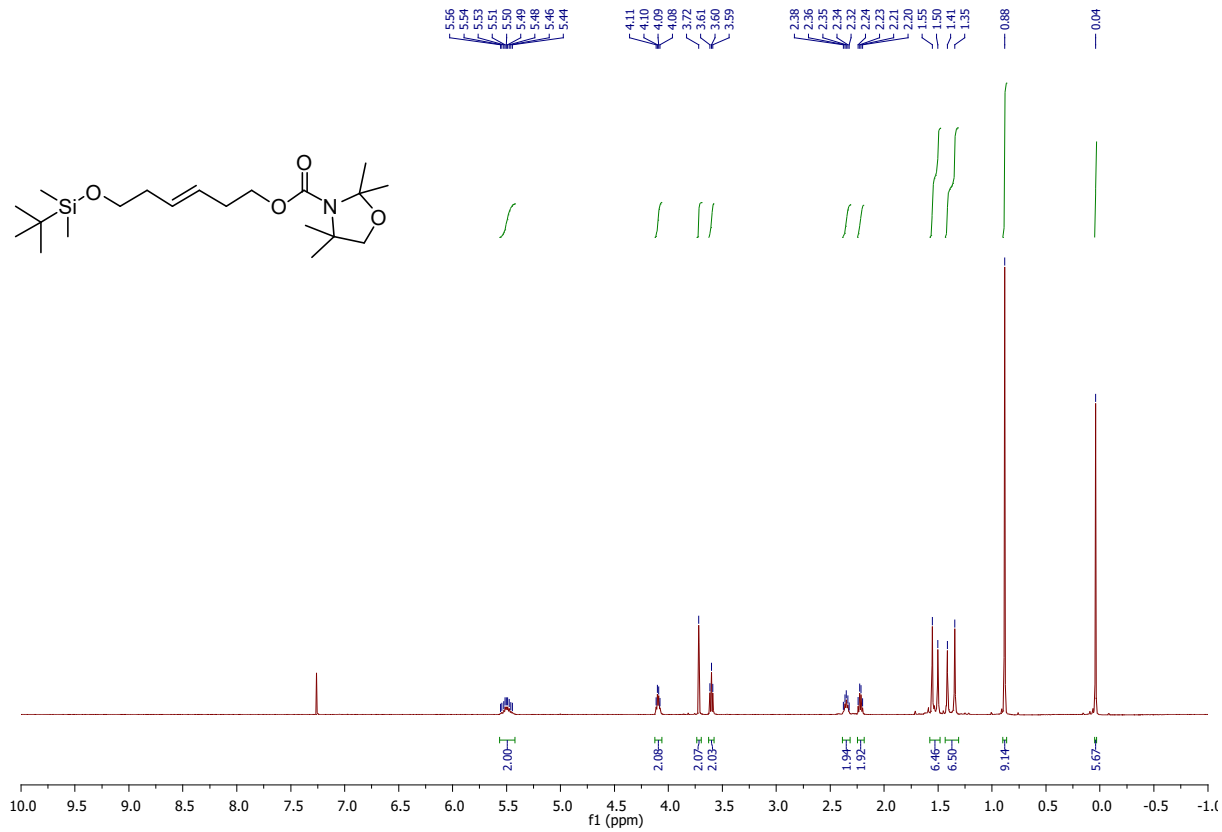


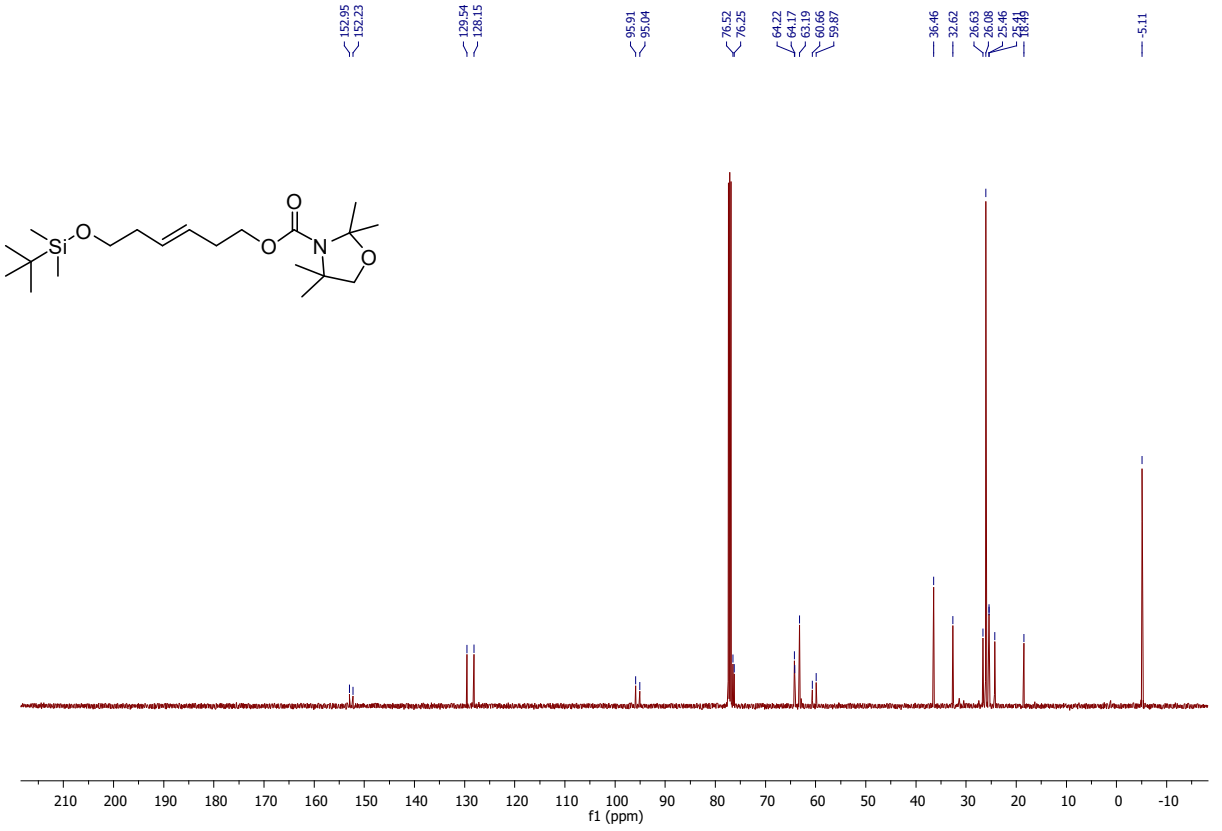
(*E*)-5,5-dimethylhex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1o** :



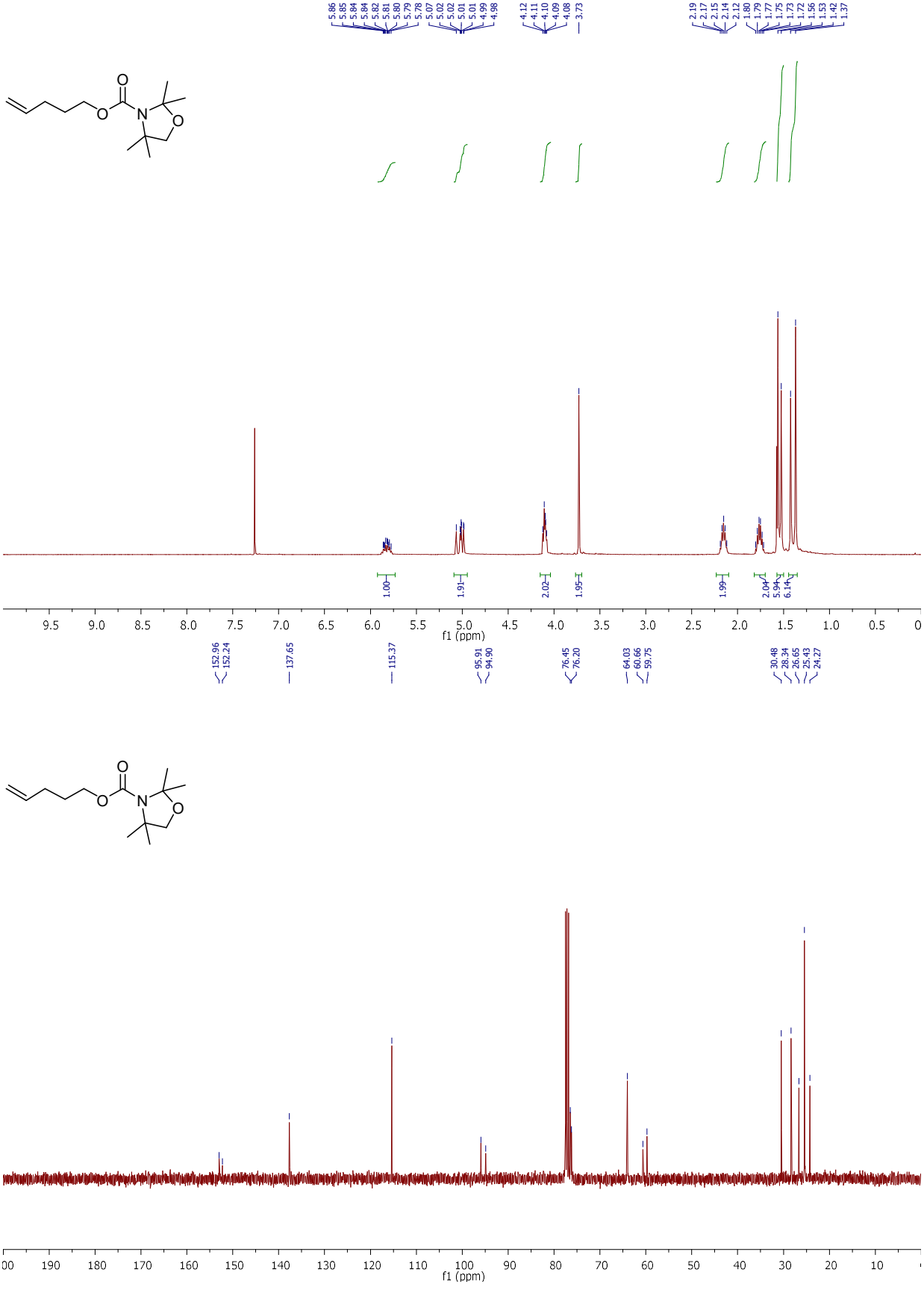


(*E*)-6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1p** :

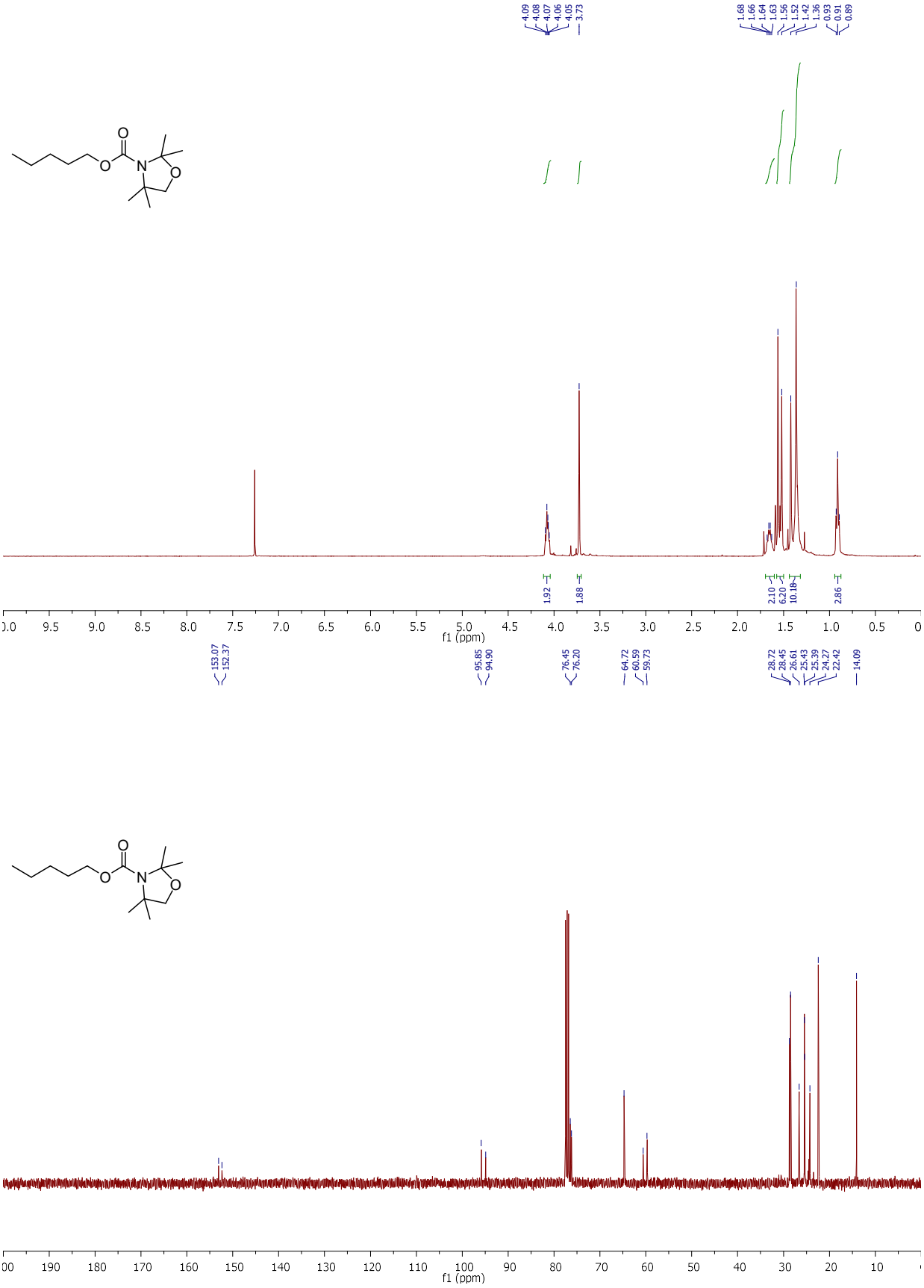




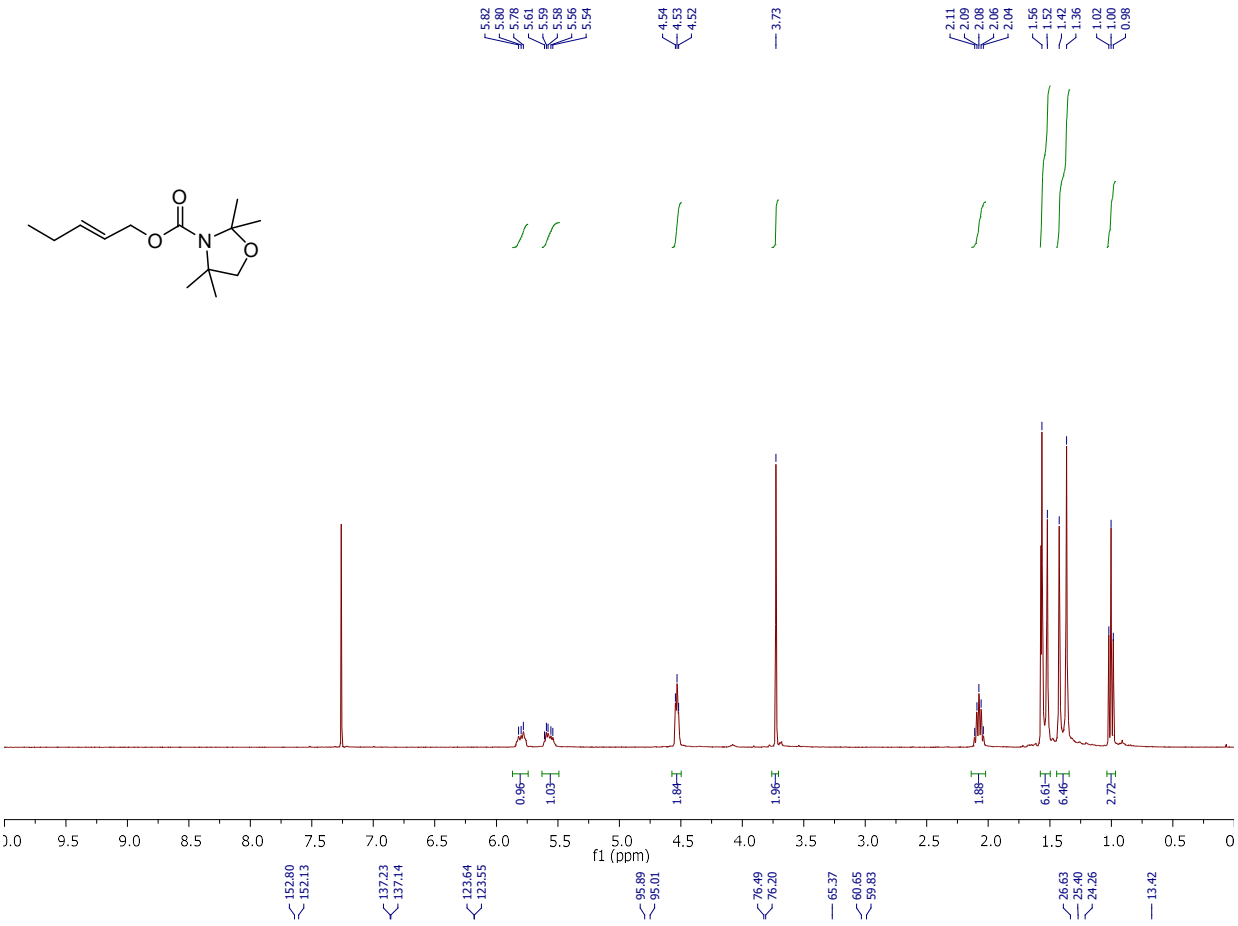
Pent-4-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1q**:

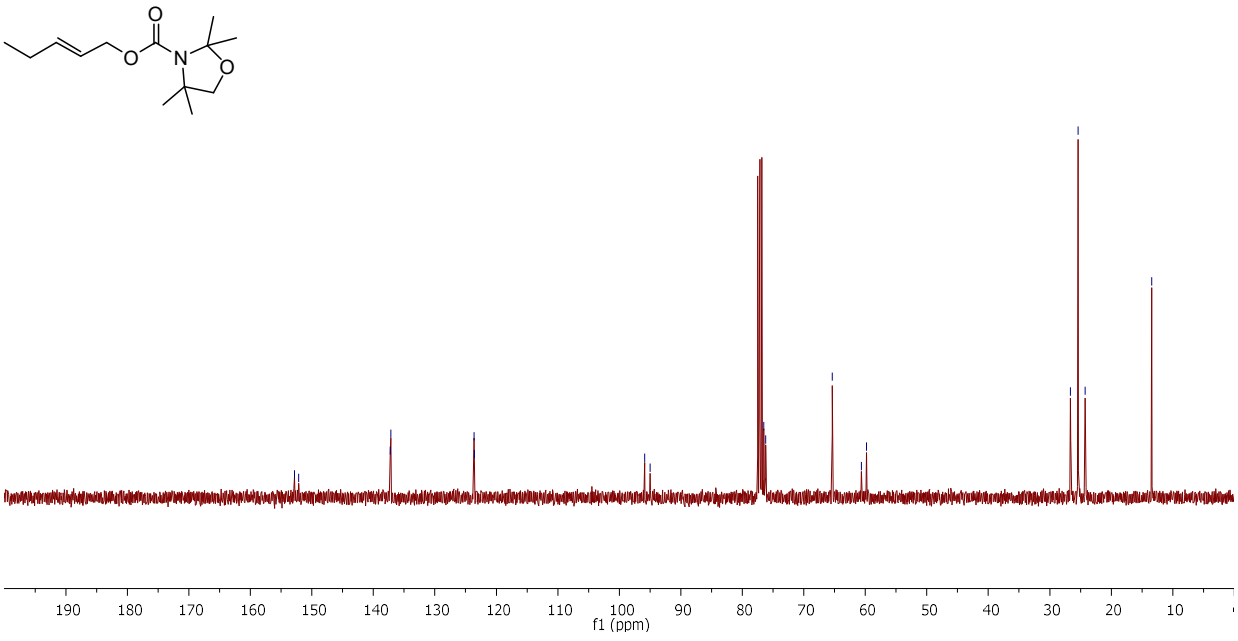


Pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1r** :

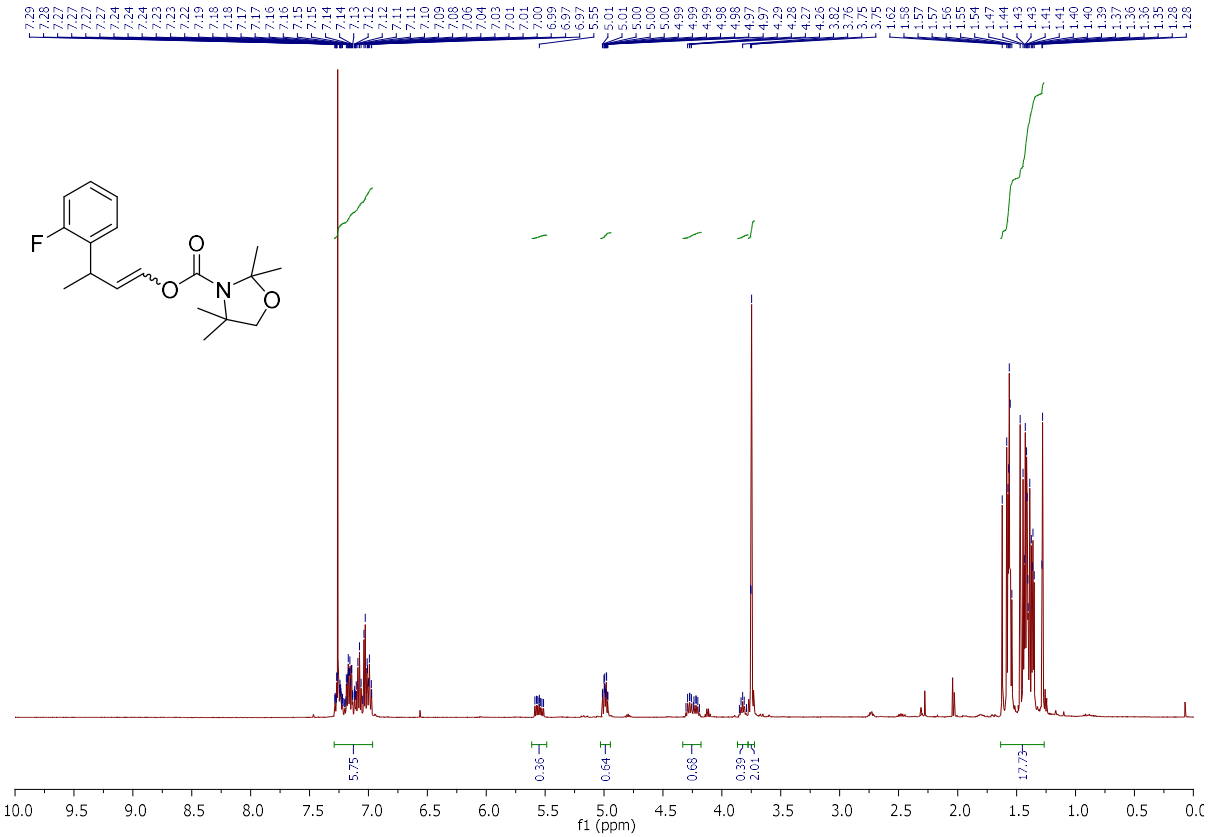


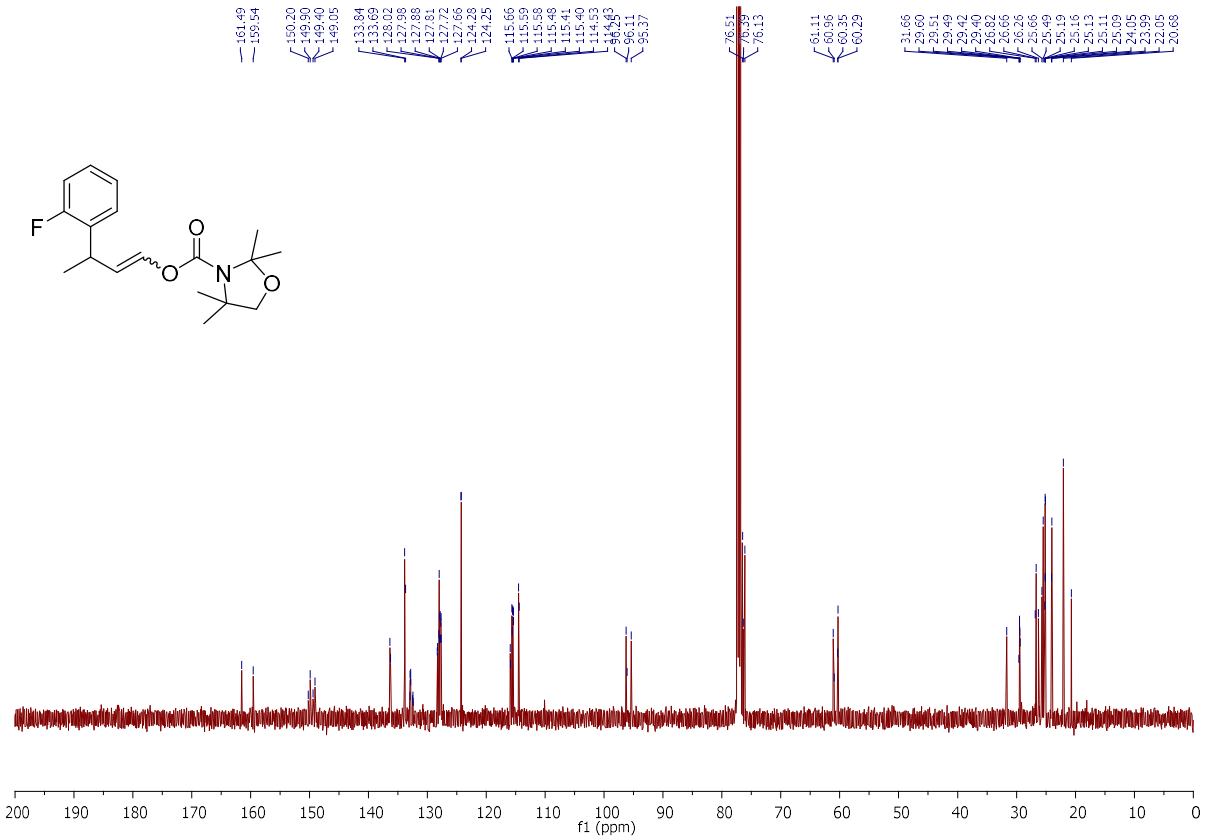
(*E*)-Pent-2-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1s** :



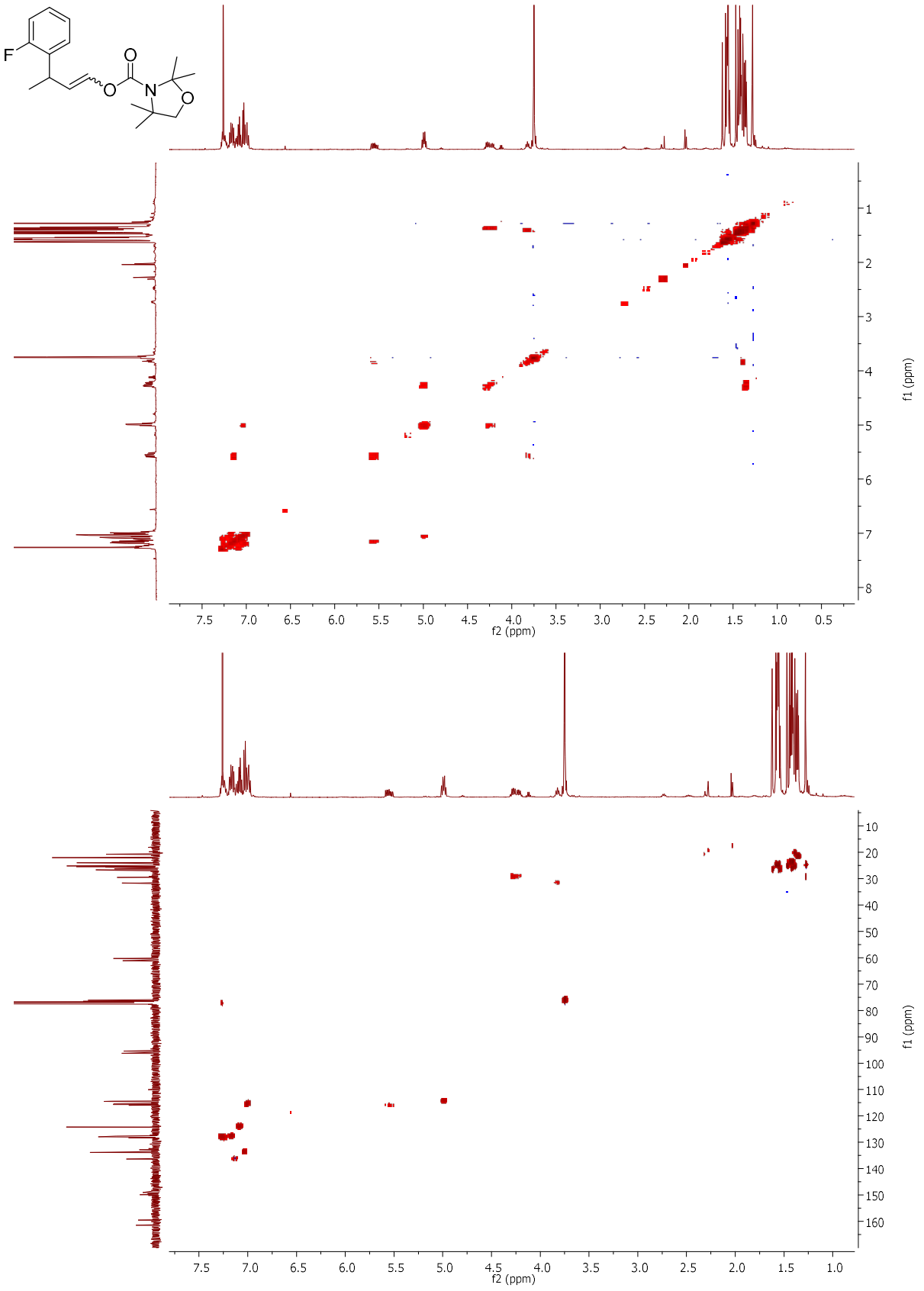


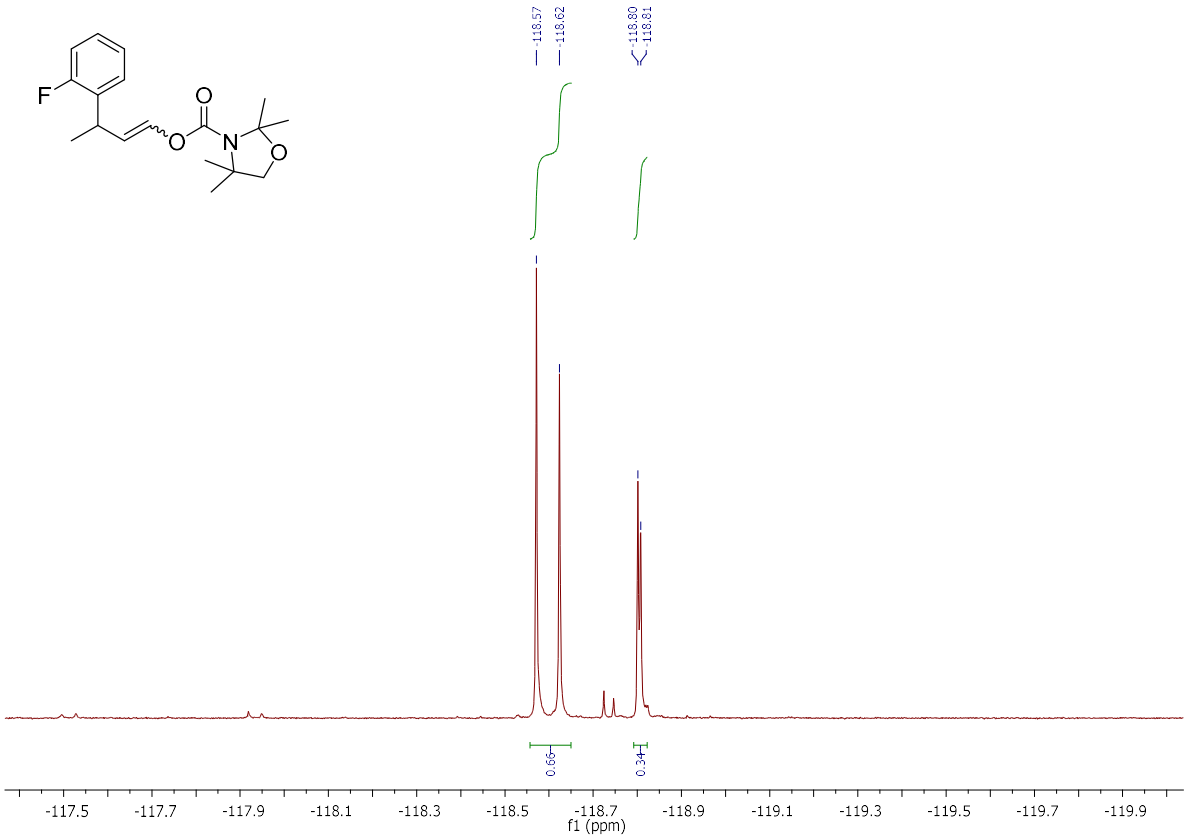
3-(2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4a** :





COSY and HMQC experiments :




F
O
O
N
O
-118.57
-118.62
-118.80
-118.81
0.66
0.34
-117.5
-117.7
-117.9
-118.1
-118.3
-118.5
-118.7
-118.9
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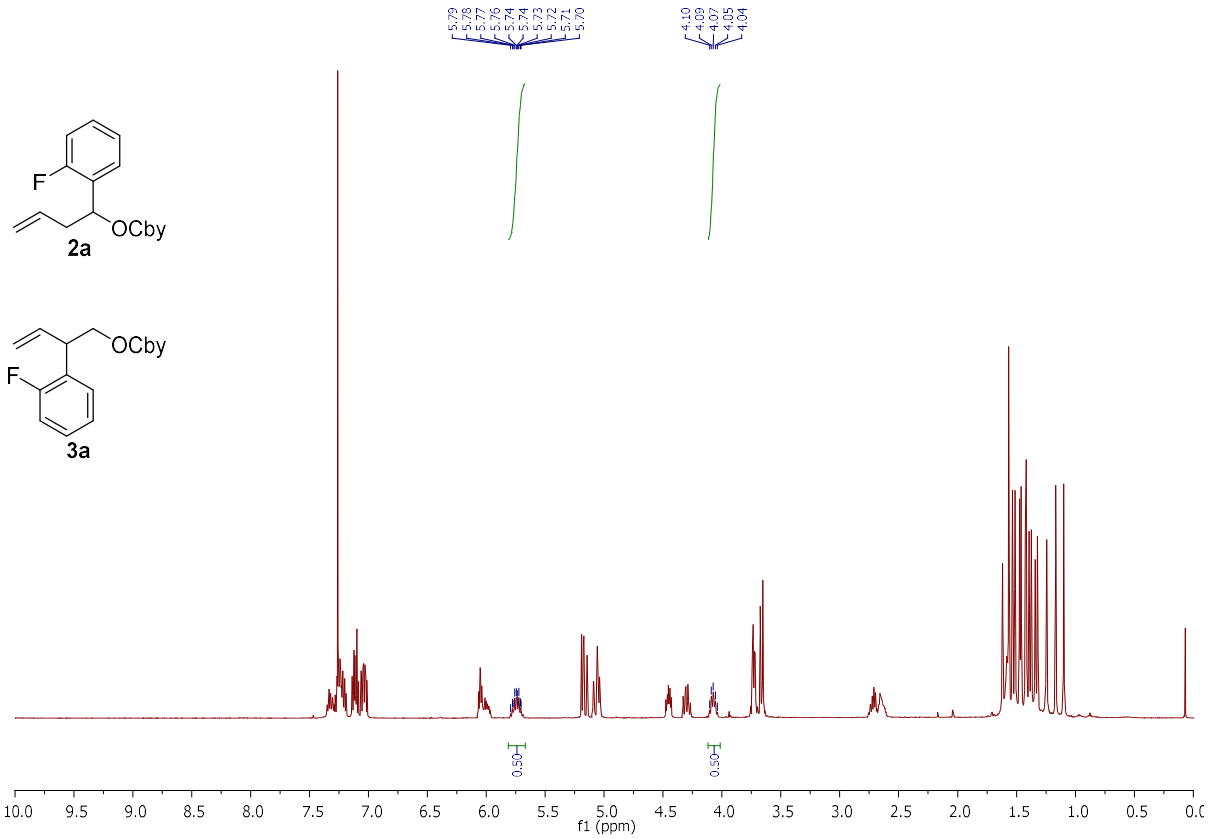
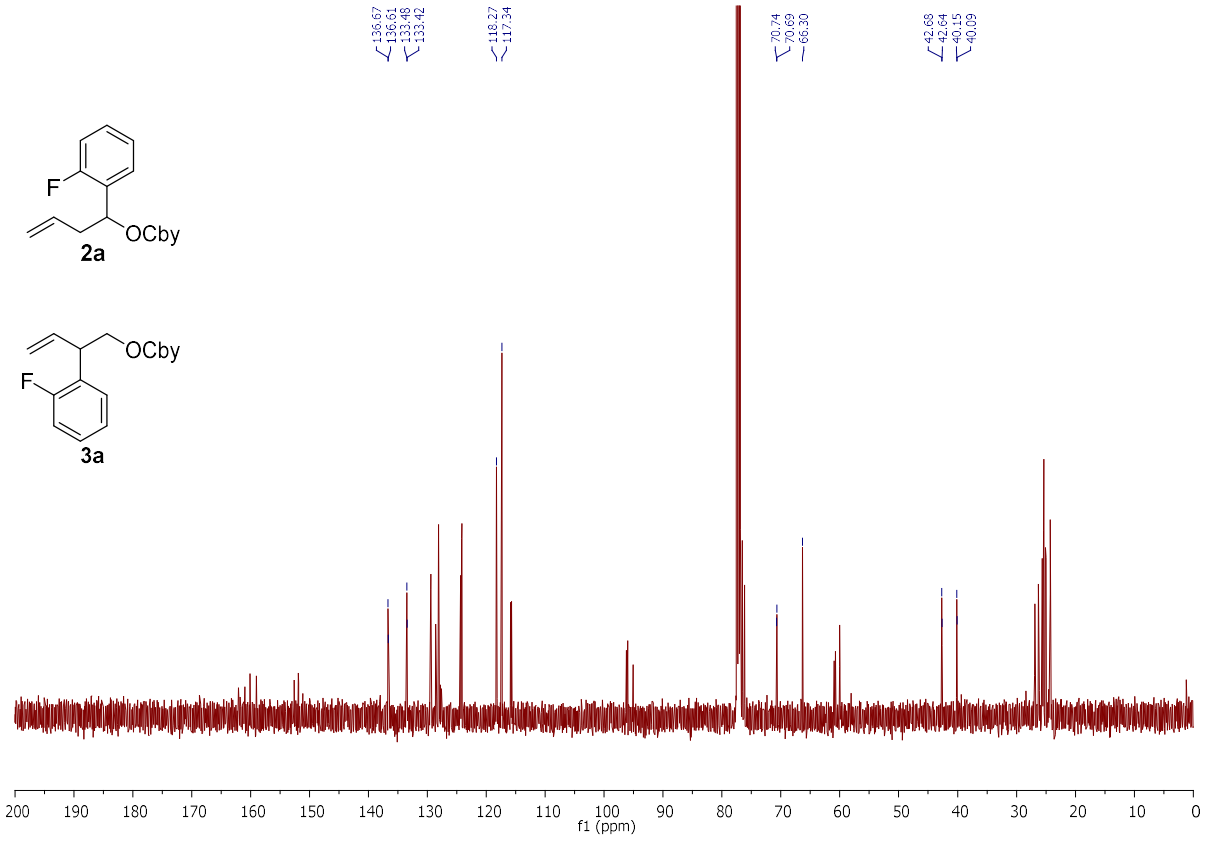
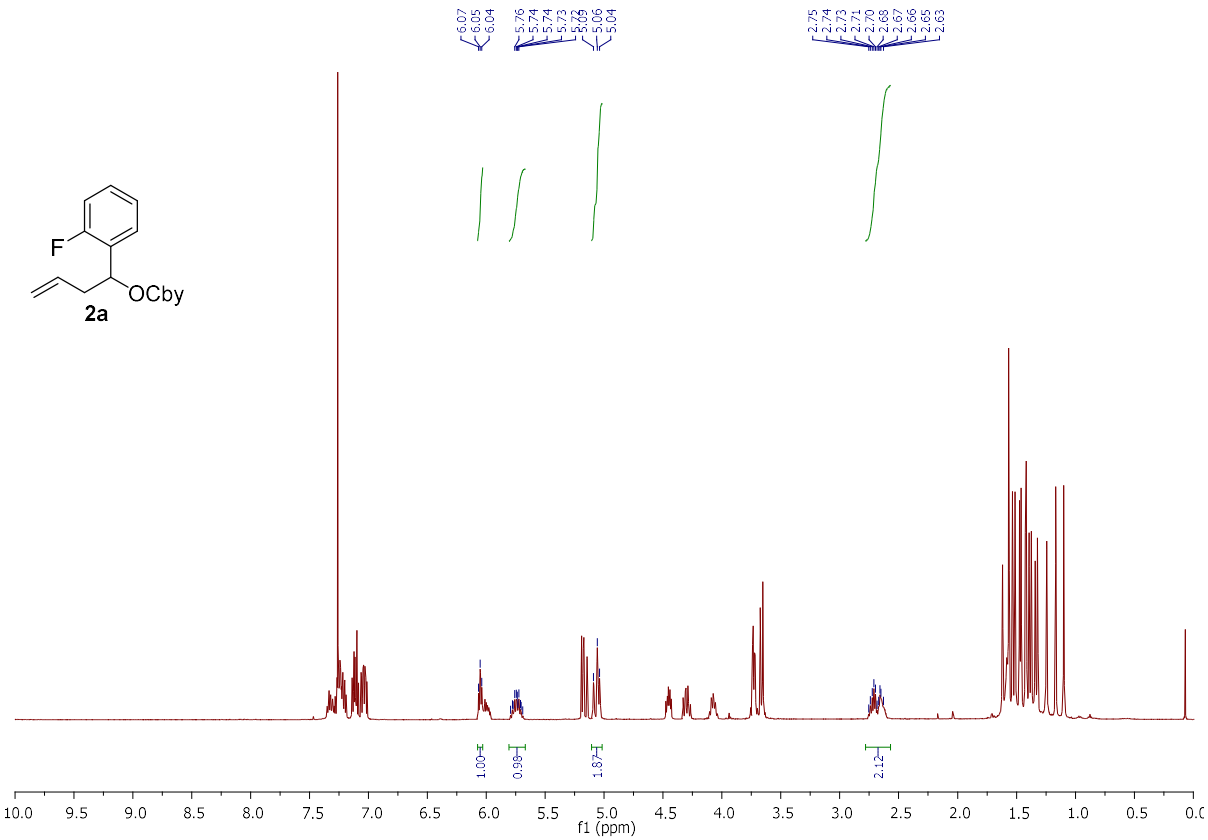
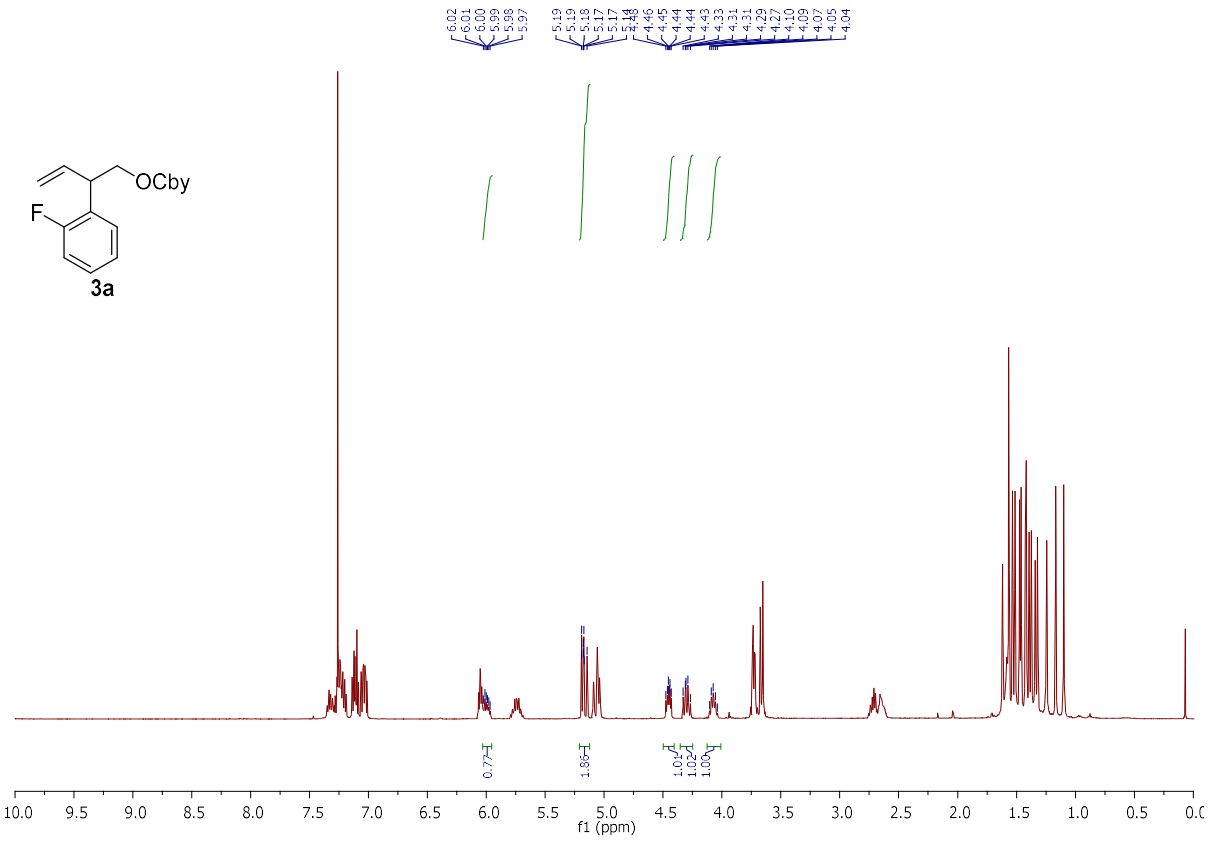
-119.3
-119.5
-119.7
-119.9
f1 (ppm)

α- and β-products**2a** and **3a**:

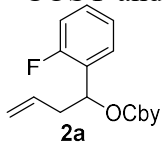




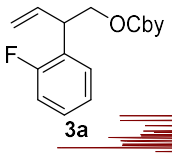

F
OCby
2a
6.07
6.05
6.04
5.76
5.74
5.74
5.73
5.06
5.04
2.75
2.74
2.73
2.71
2.70
2.68
2.67
2.66
2.65
2.63
1.00
0.98
1.87
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OCby
F
3a
6.02
6.01
6.00
5.99
5.98
5.97
5.19
5.19
5.18
5.17
5.17
4.46
4.45
4.44
4.44
4.43
4.33
4.31
4.31
4.29
4.27
4.10
4.09
4.07
4.05
4.04
0.77
1.86
1.02
1.02
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

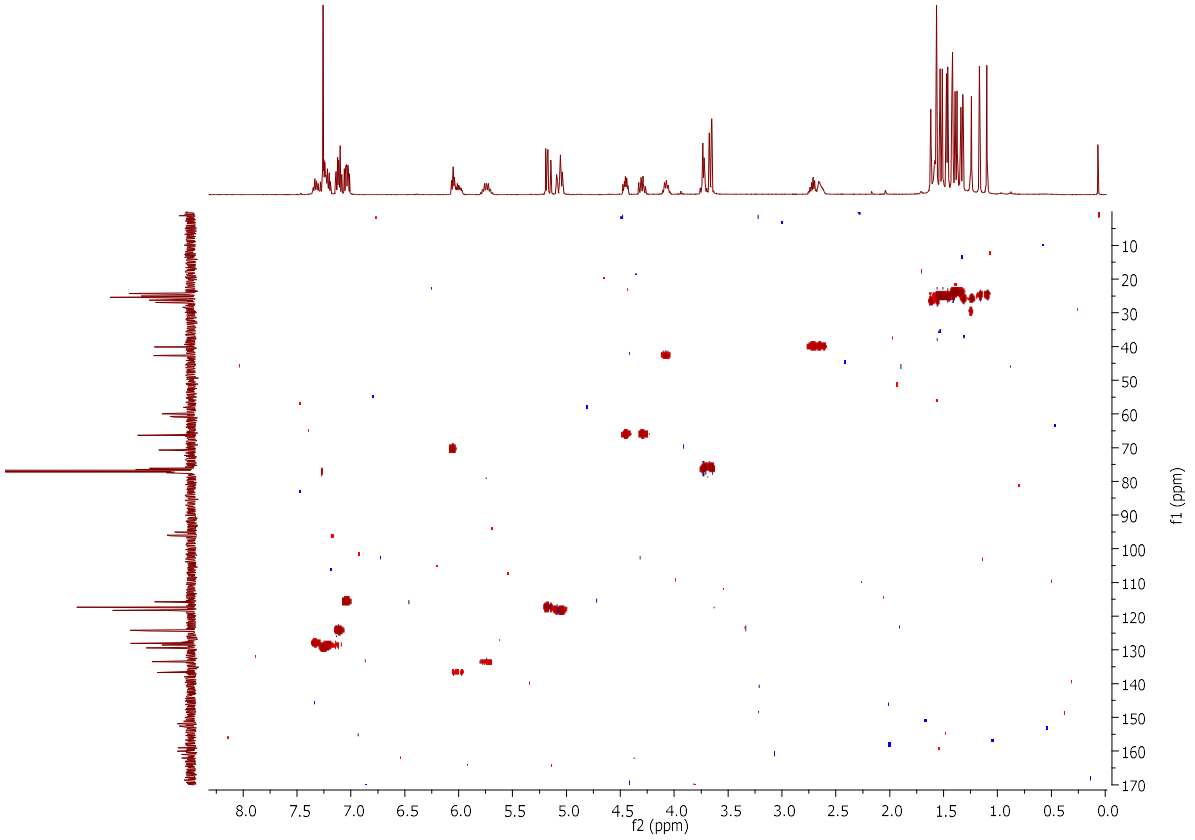
COSY and HMQC experiments :

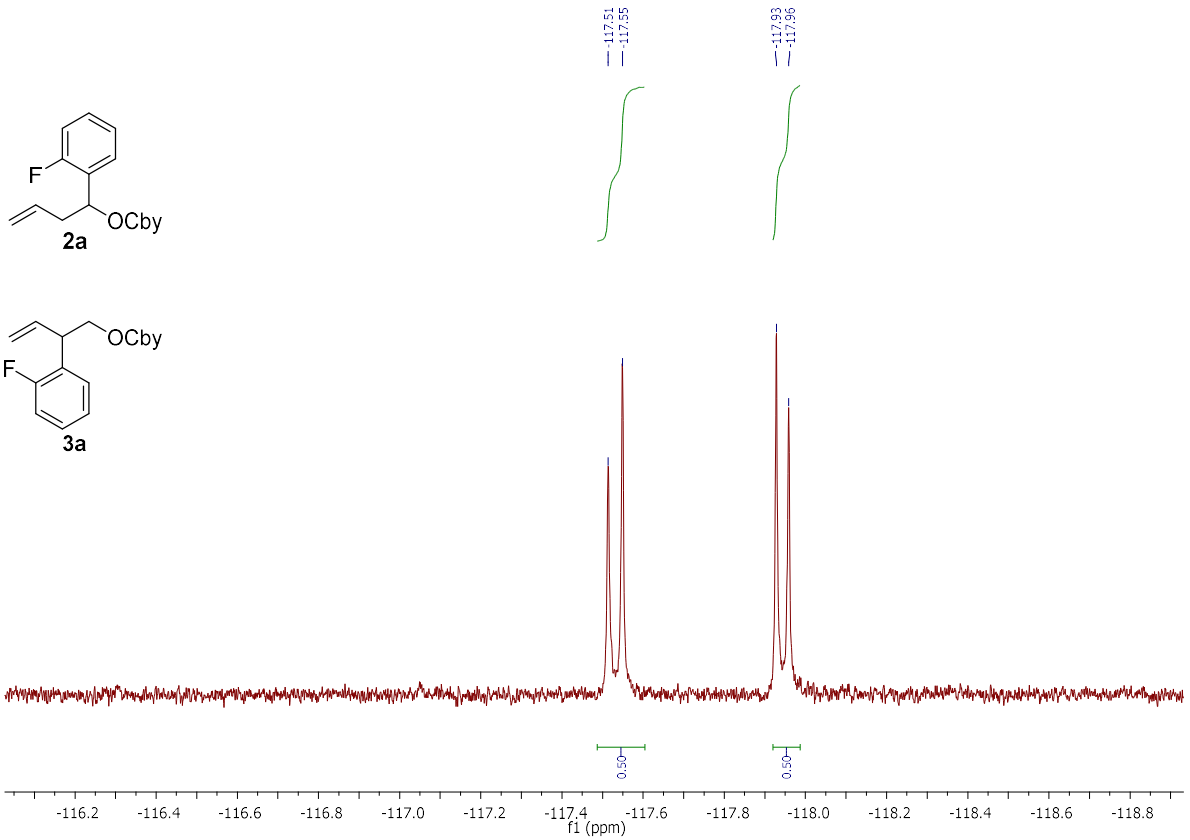


2a

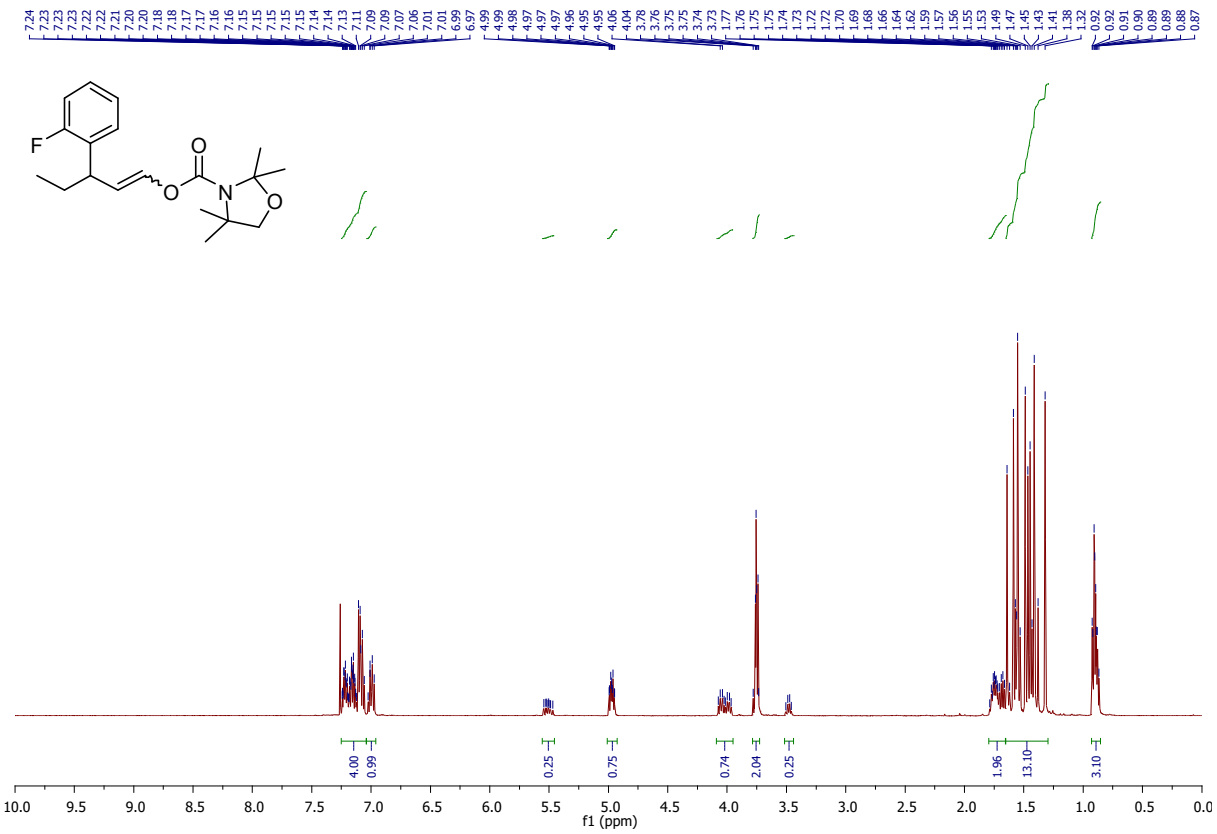


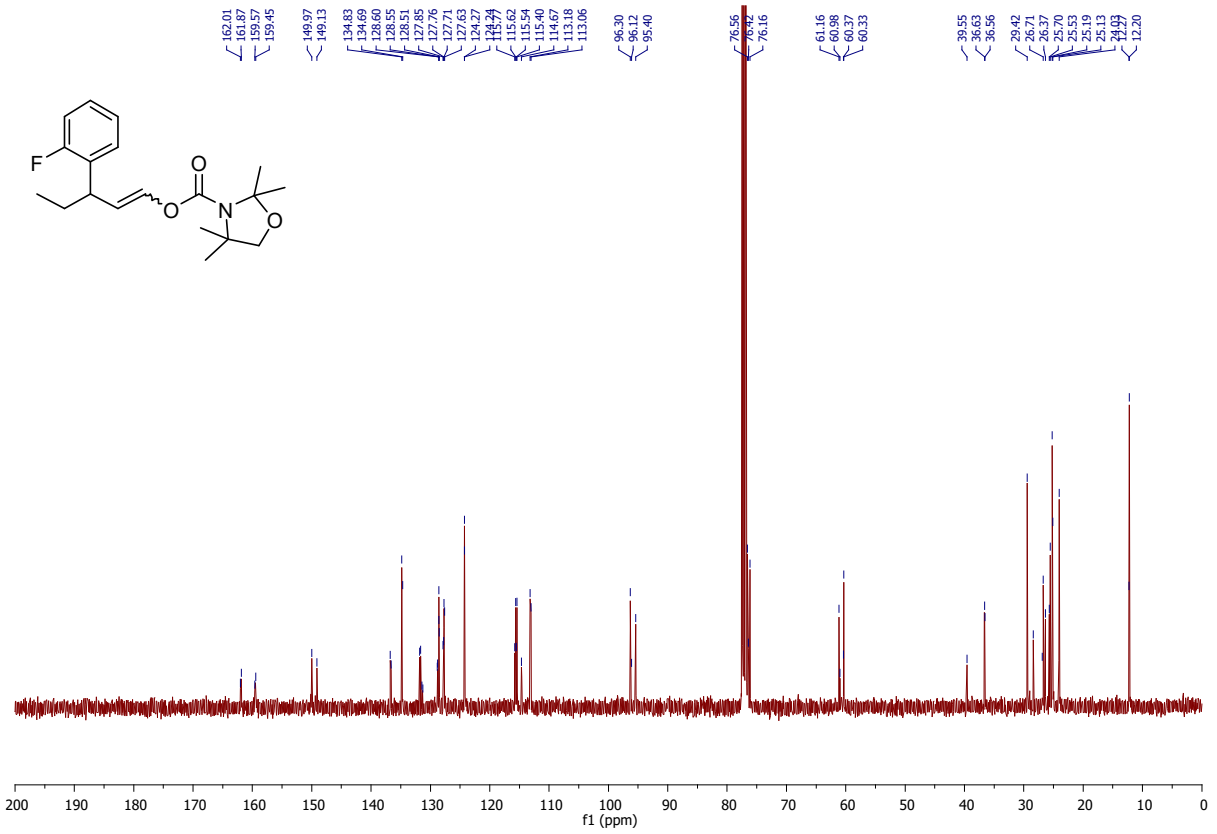
3a



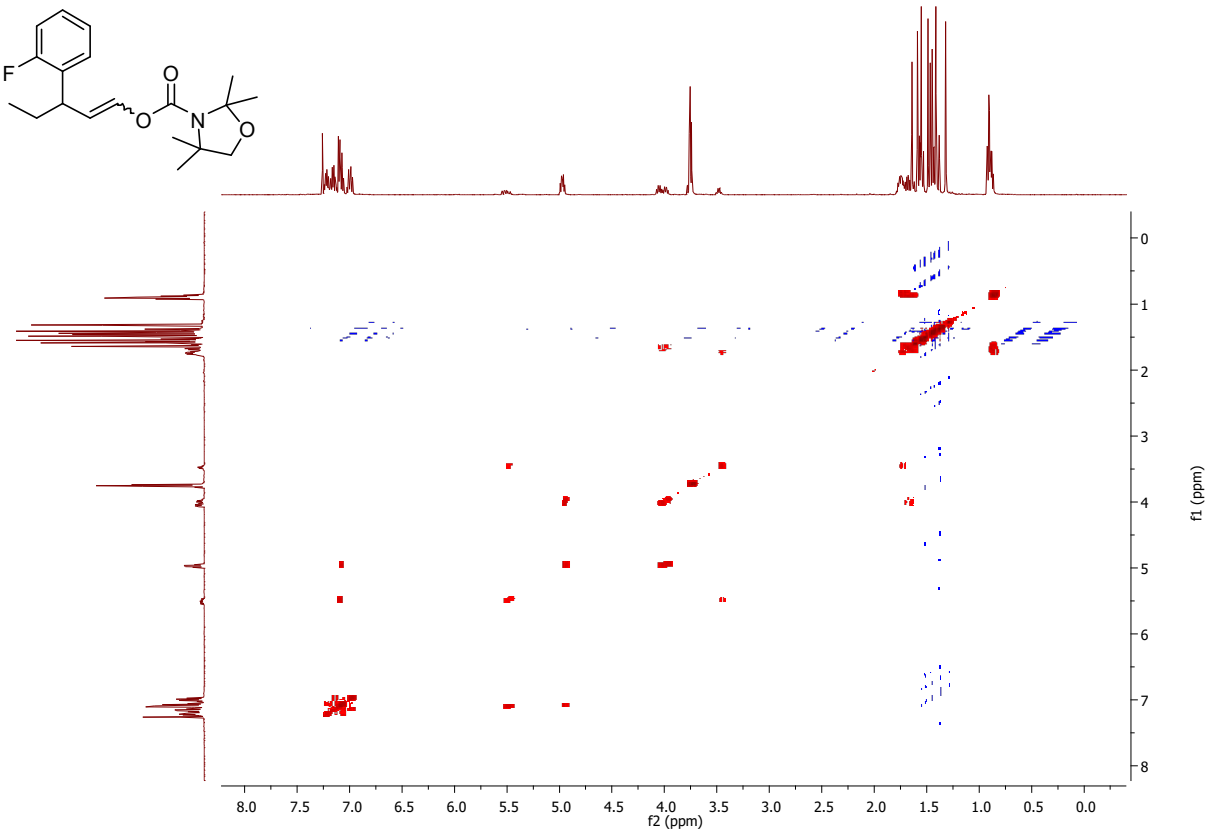

-117.51
-117.55
-117.93
-117.96
F
OCby
2a
OCby
F
3a
0.50
0.50
-116.2
-116.4
-116.6
-116.8
-117.0
-117.2
-117.4
-117.6
-117.8
-118.0
-118.2
-118.4
-118.6
-118.8
f1 (ppm)

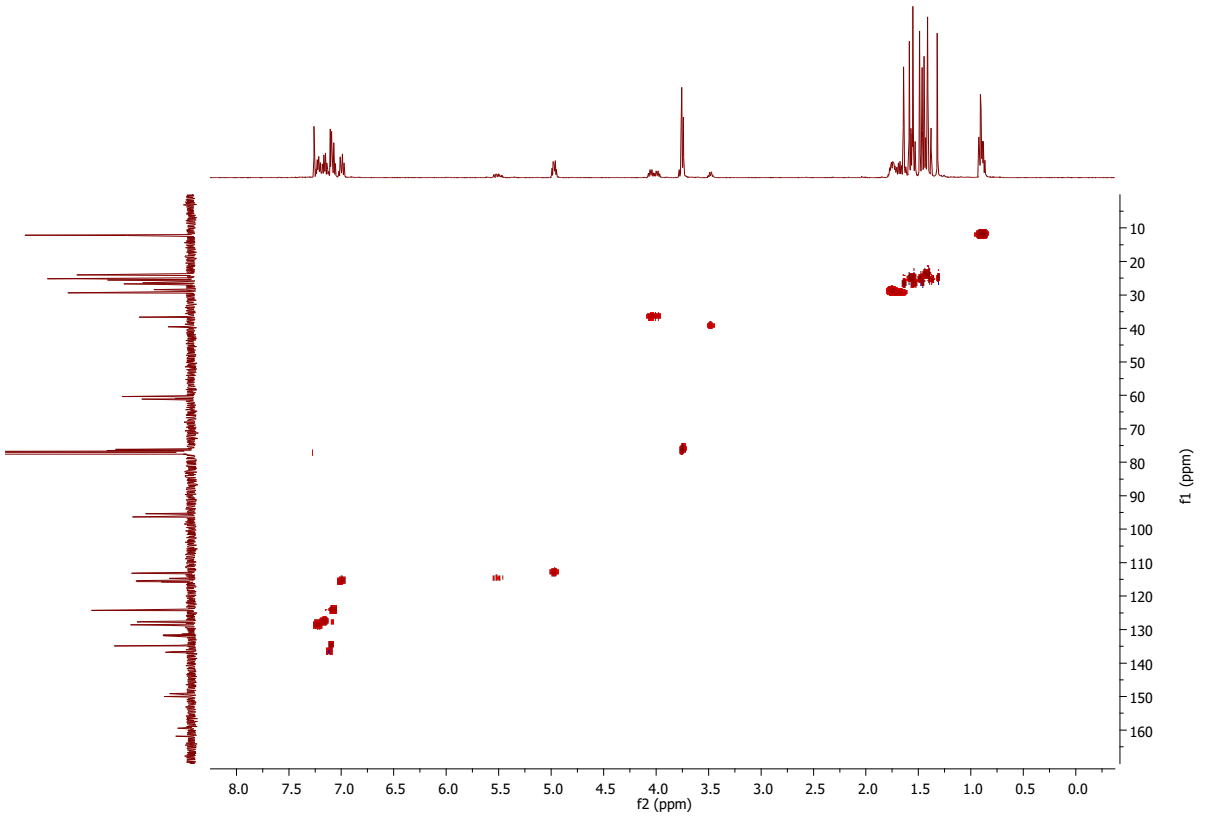
3-(2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4b** :

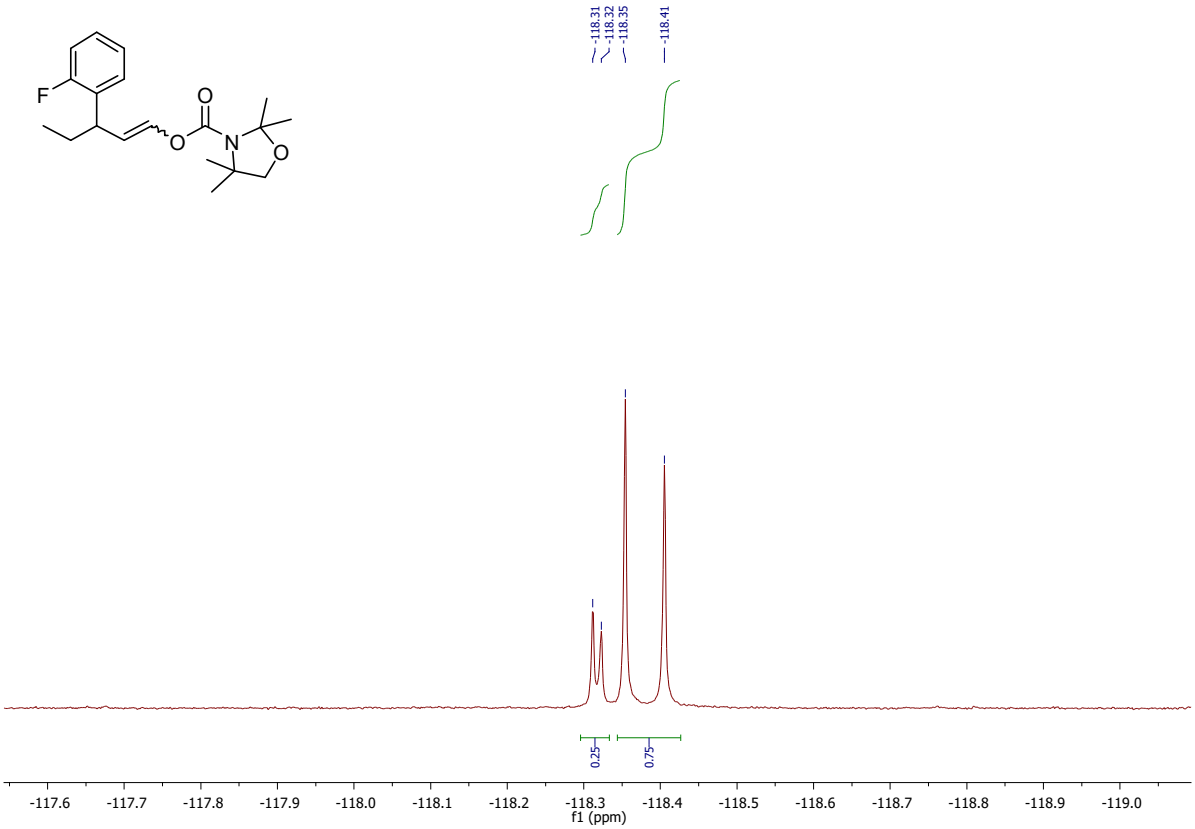




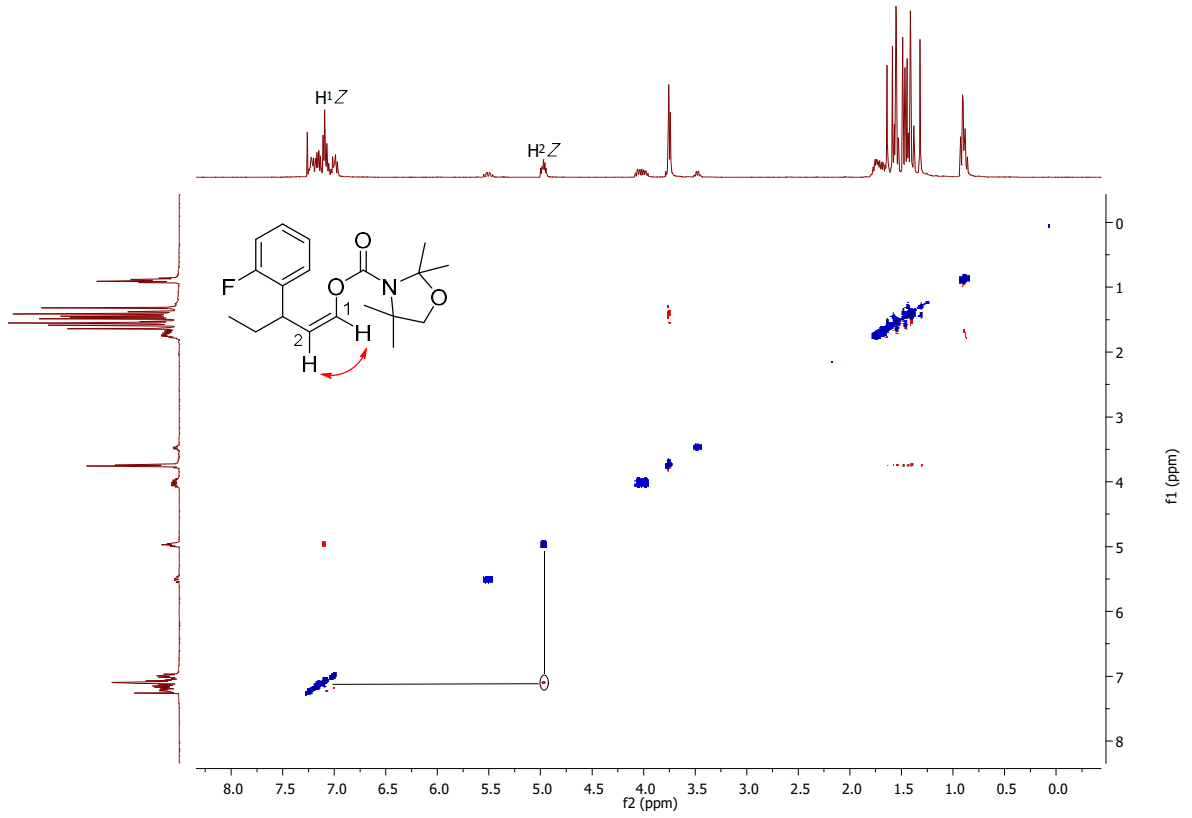
COSY and HMQC experiments :



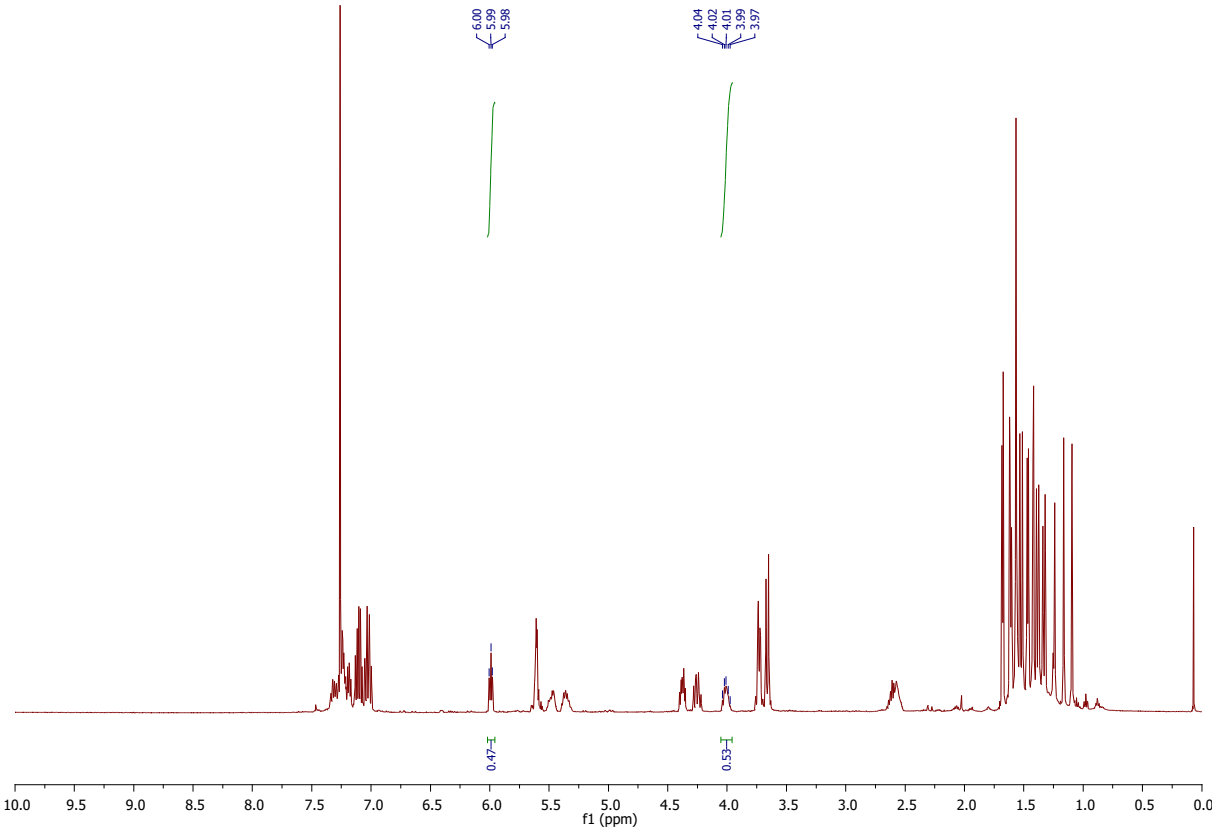


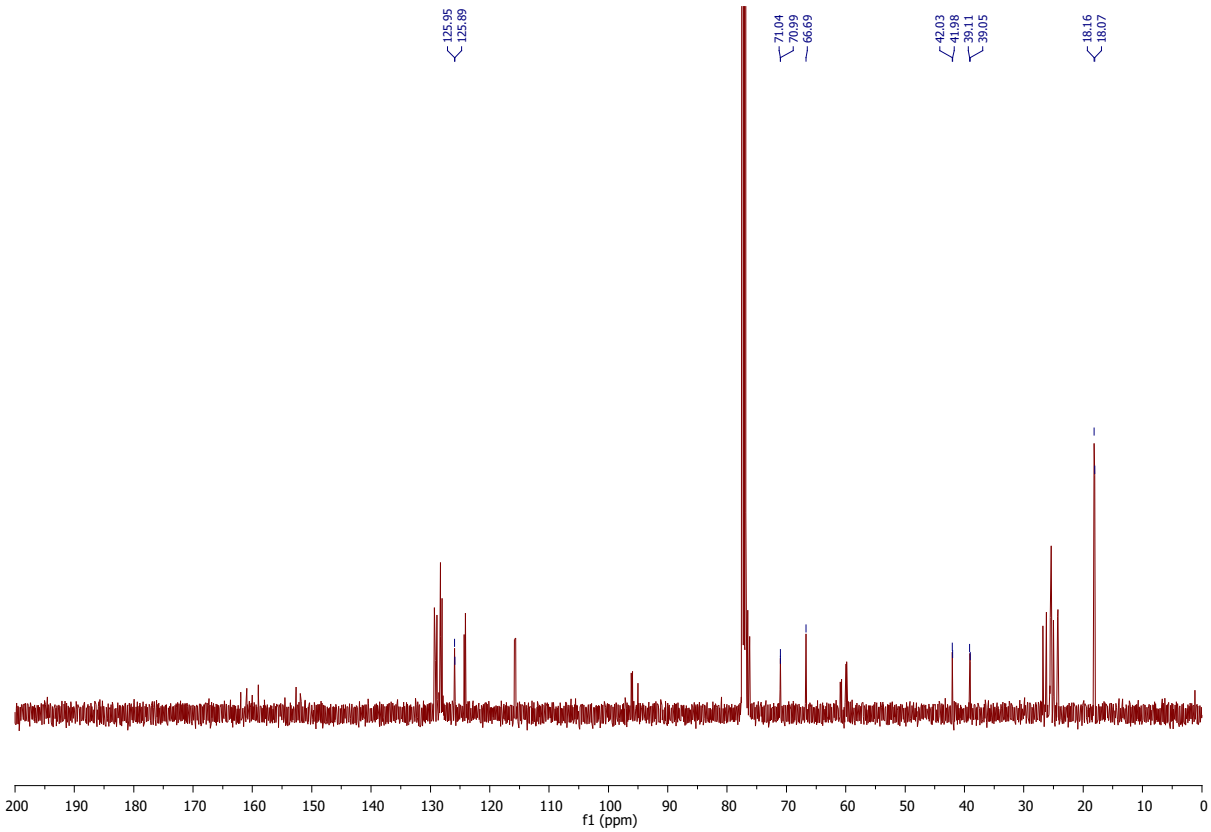


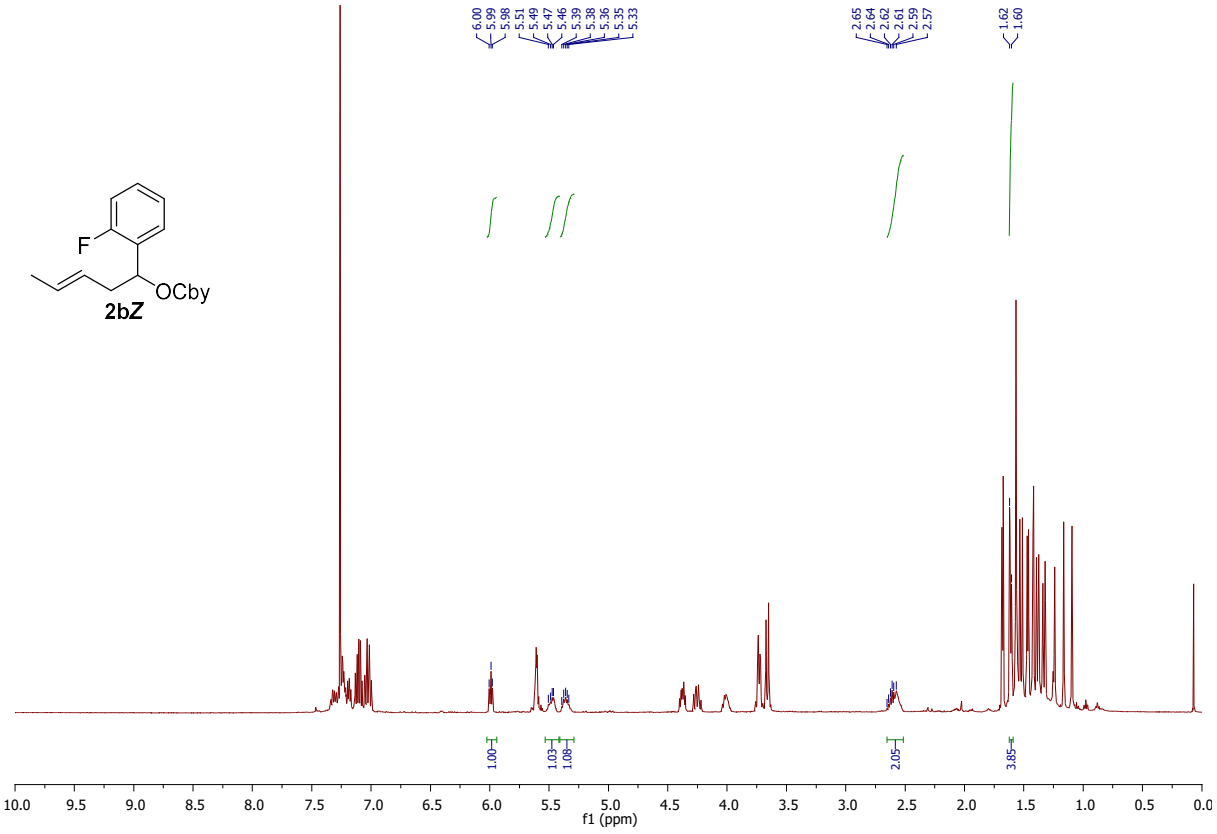
NOESY correlation between H_1Z and H_2Z :

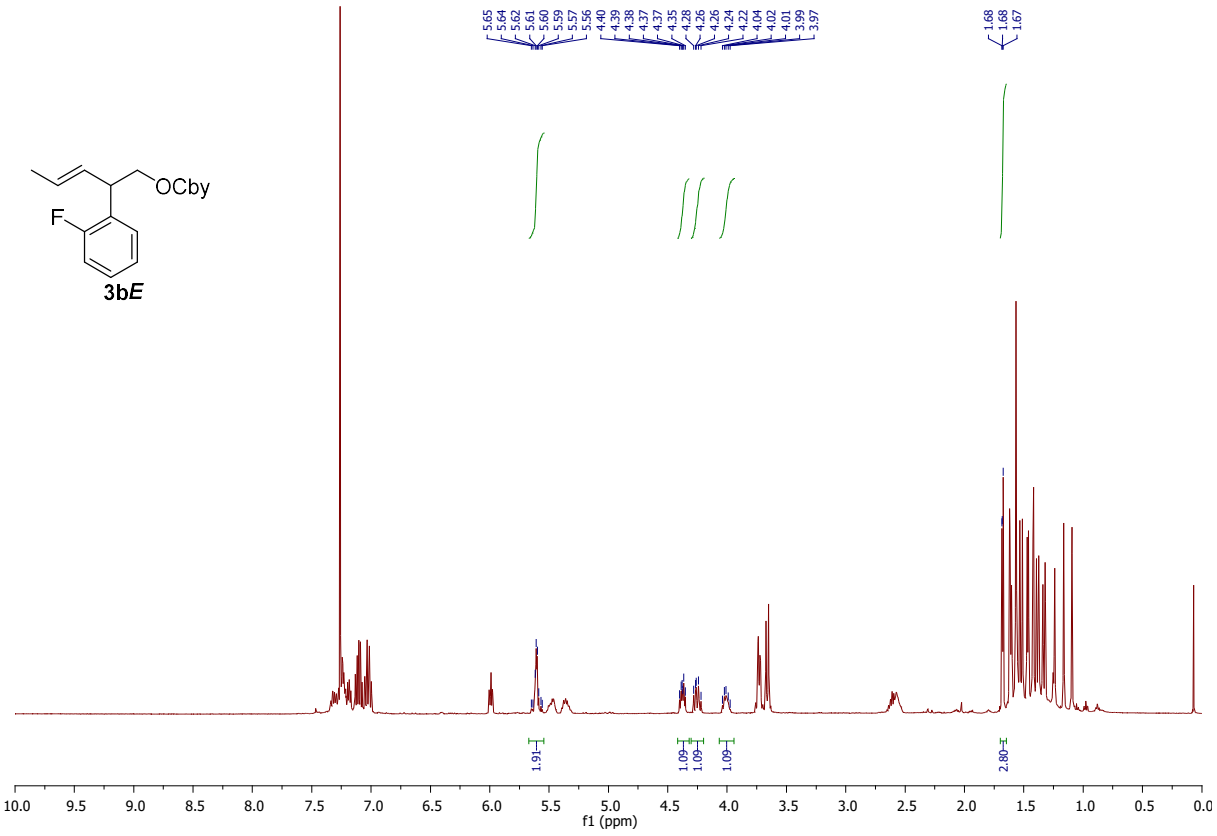


α- and β-products**2b**and **3b** :

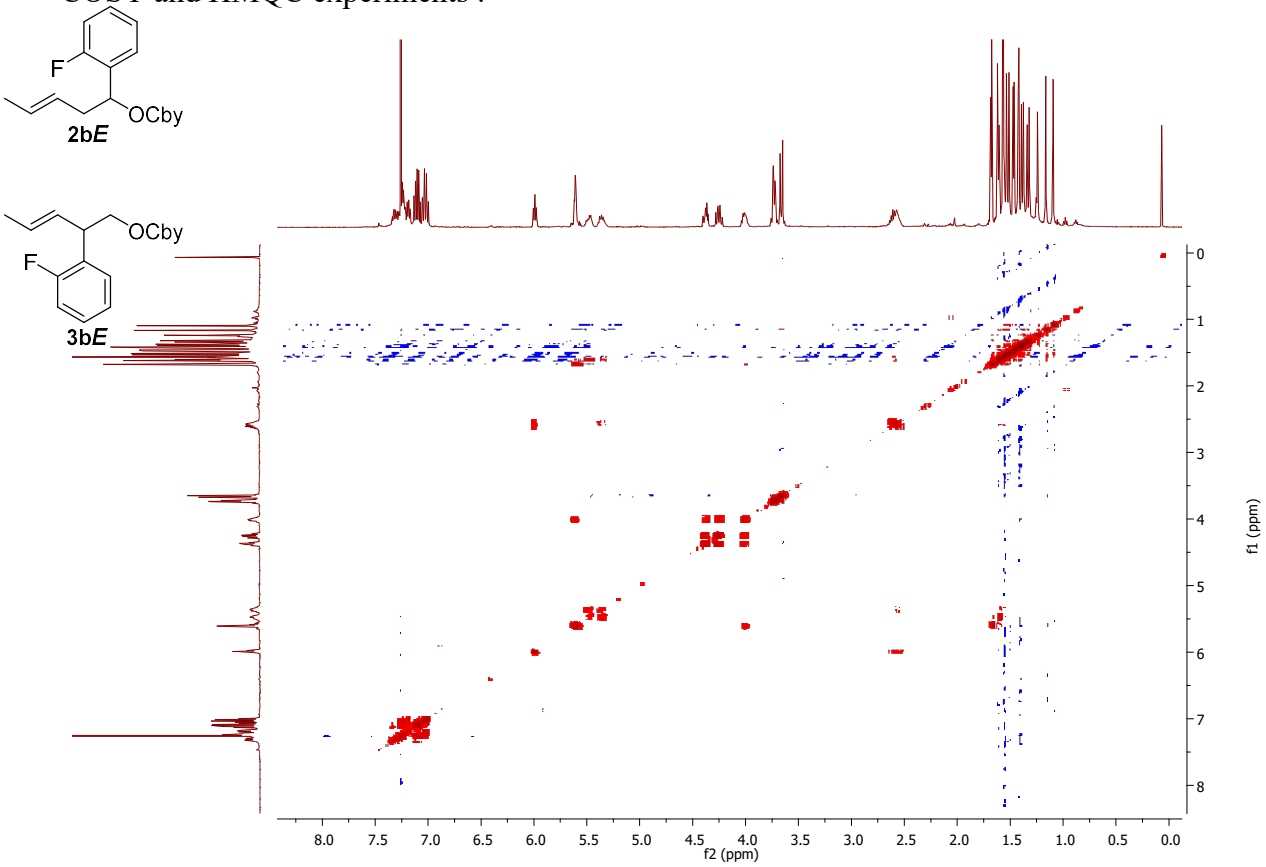


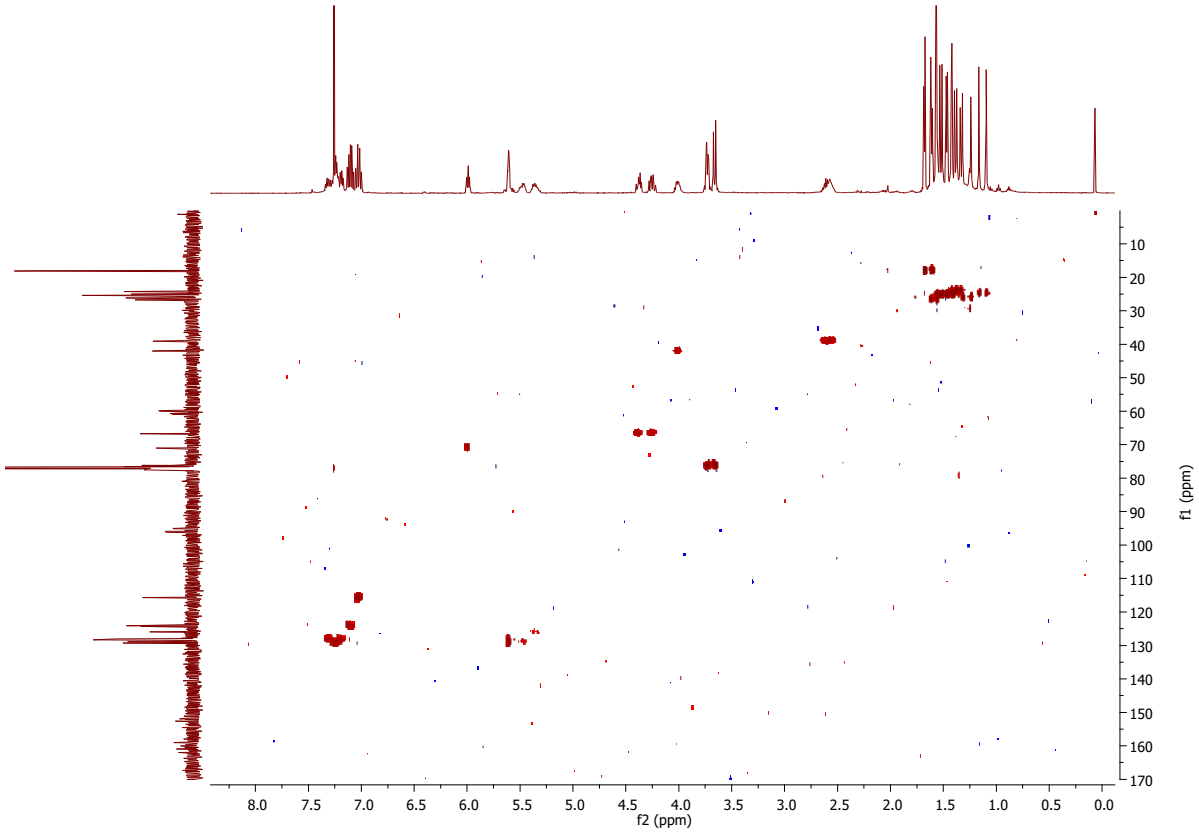


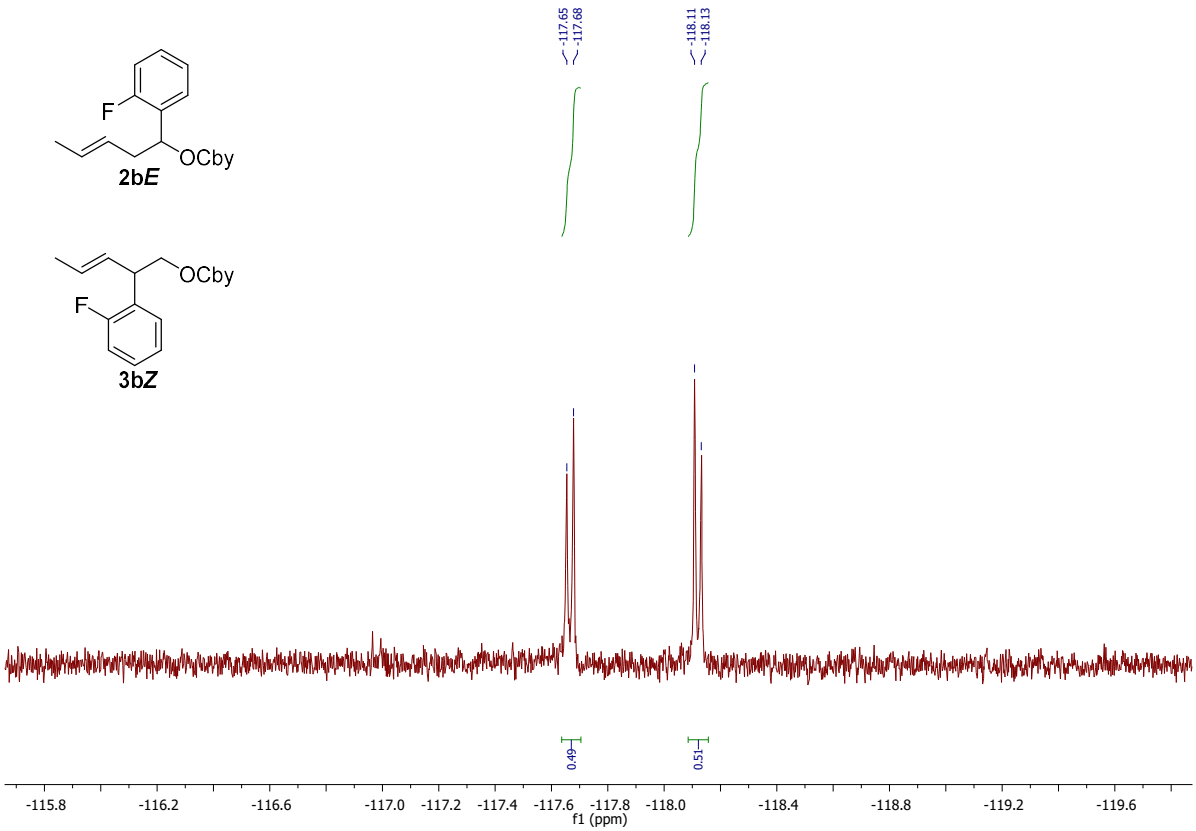

F
OCby
2bZ
6.00
5.99
5.98
5.51
5.49
5.47
5.46
5.39
5.38
5.36
5.35
5.33
2.65
2.64
2.62
2.61
2.59
2.57
1.62
1.60
1.00
1.03
1.08
2.05
3.85
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OCby
F
3bE
5.65
5.64
5.62
5.61
5.60
5.59
5.57
5.56
4.40
4.39
4.38
4.37
4.37
4.35
4.28
4.26
4.26
4.24
4.22
4.04
4.02
4.01
3.99
3.97
1.68
1.68
1.67
1.91
1.09
1.09
1.09
2.80
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

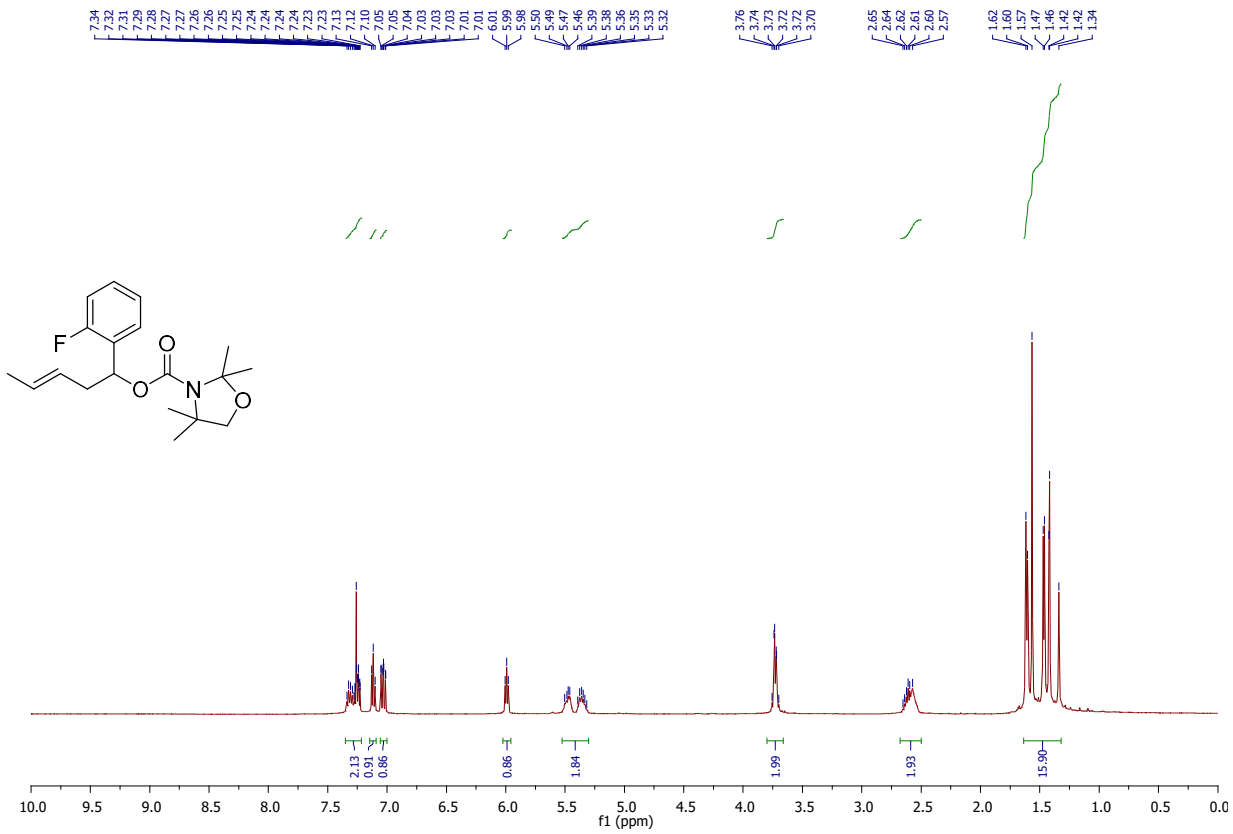
COSY and HMQC experiments :

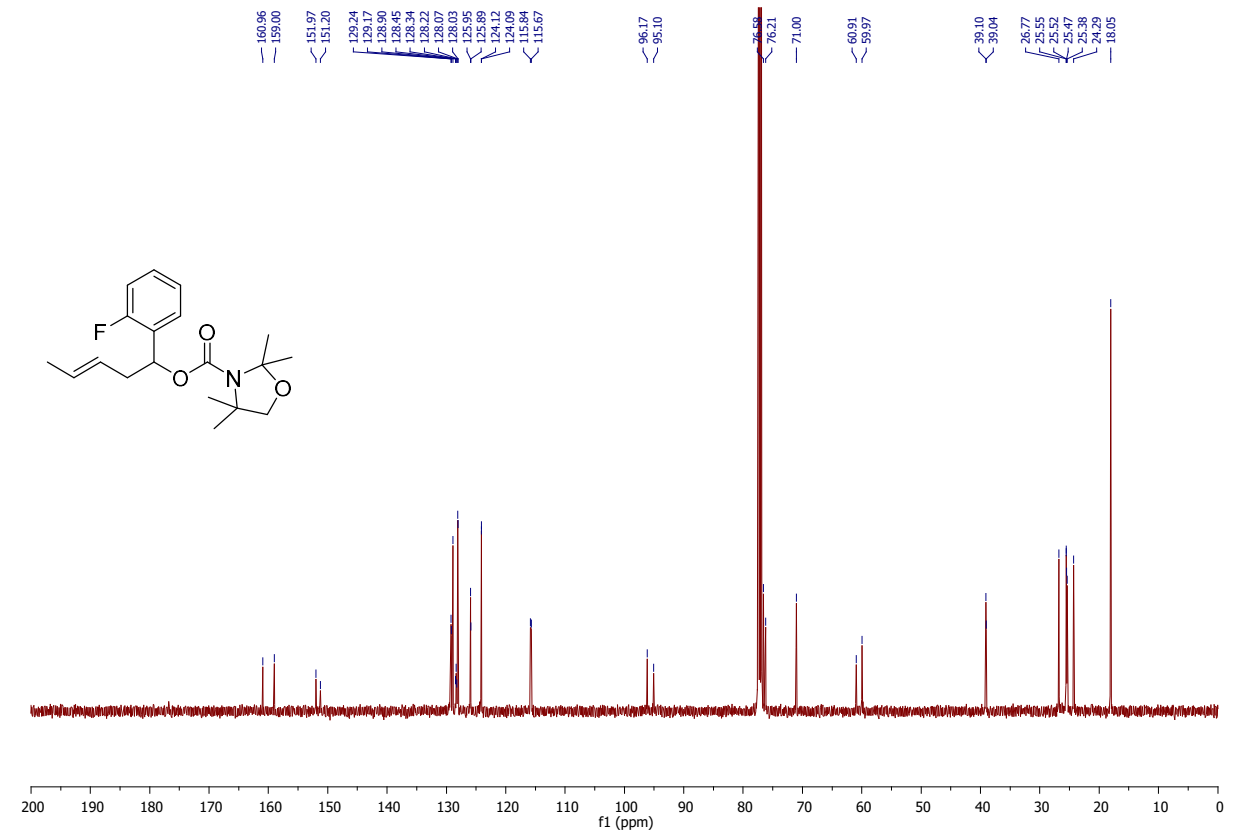




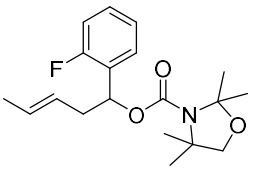

F
OCby
2bE
OCby
F
3bZ
-117.65
-117.68
-118.11
-118.13
0.49
0.51
-115.8
-116.2
-116.6
-117.0
-117.2
-117.4
-117.6
-117.8
-118.0
-118.4
-118.8
-119.2
-119.6
f1 (ppm)

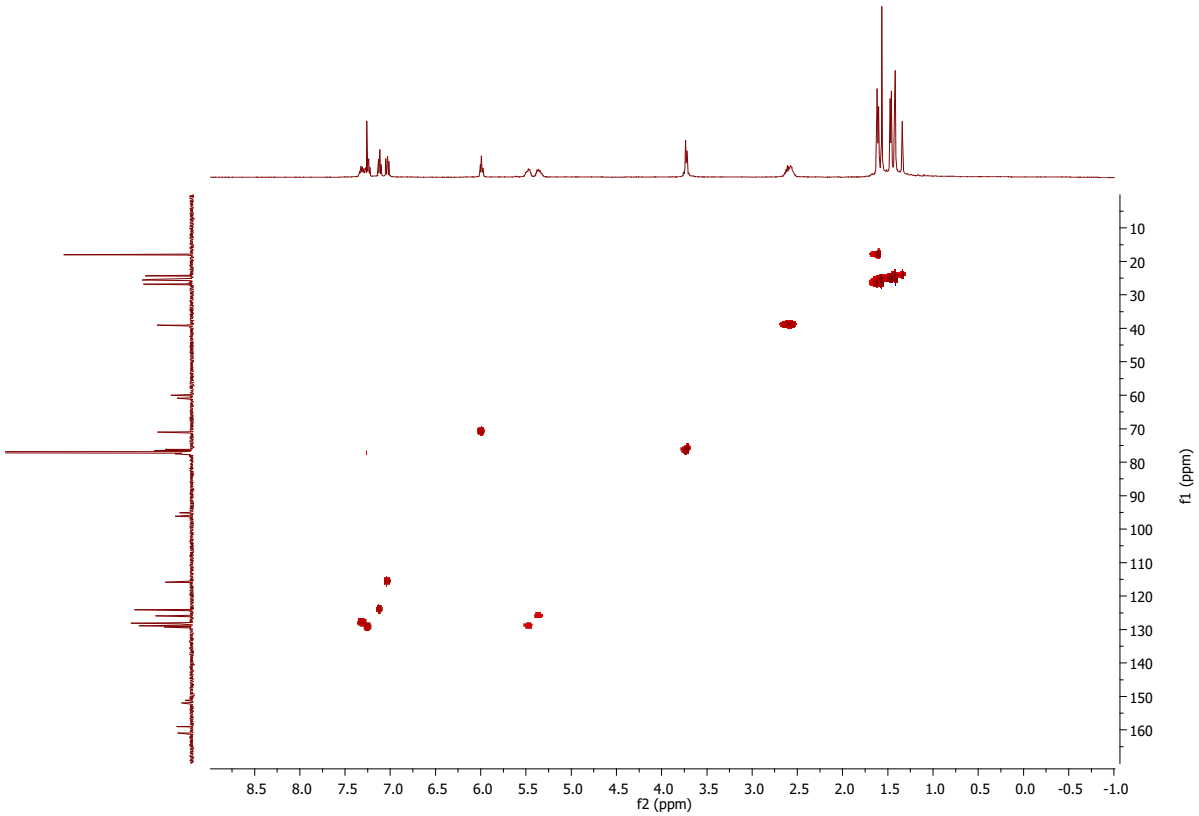
(*E*)-1-(2-fluorophenyl)pent-3-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **2b*E*** :

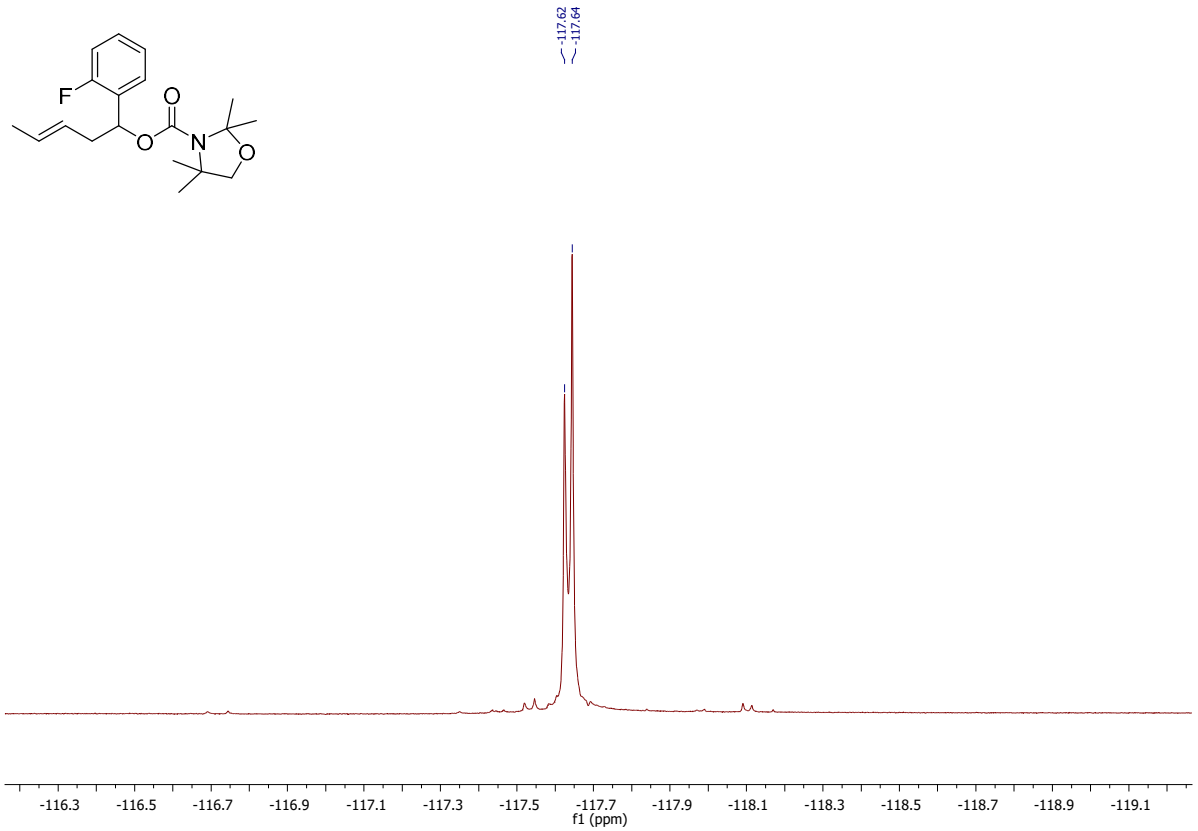




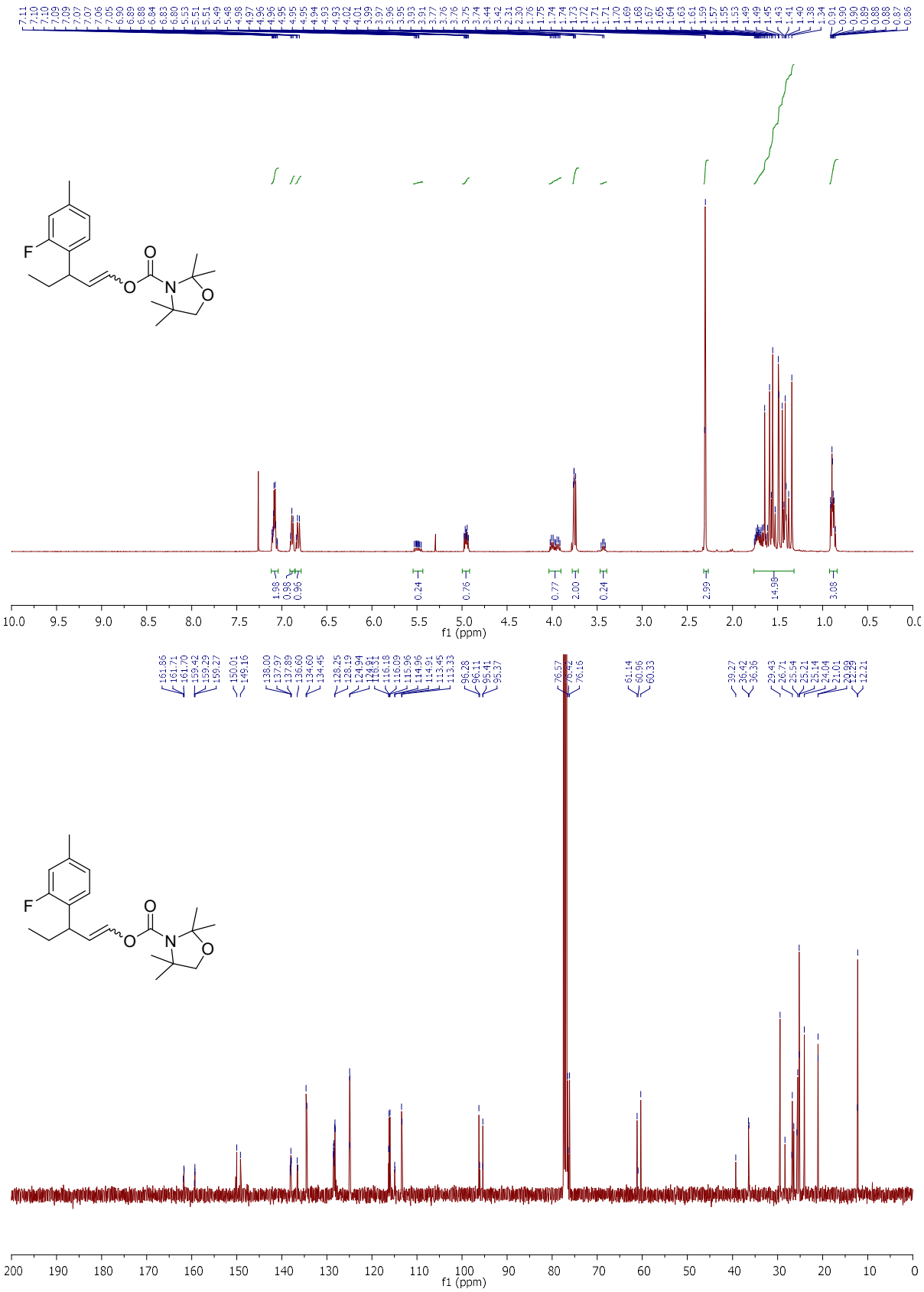
COSY and HMQC experiments :



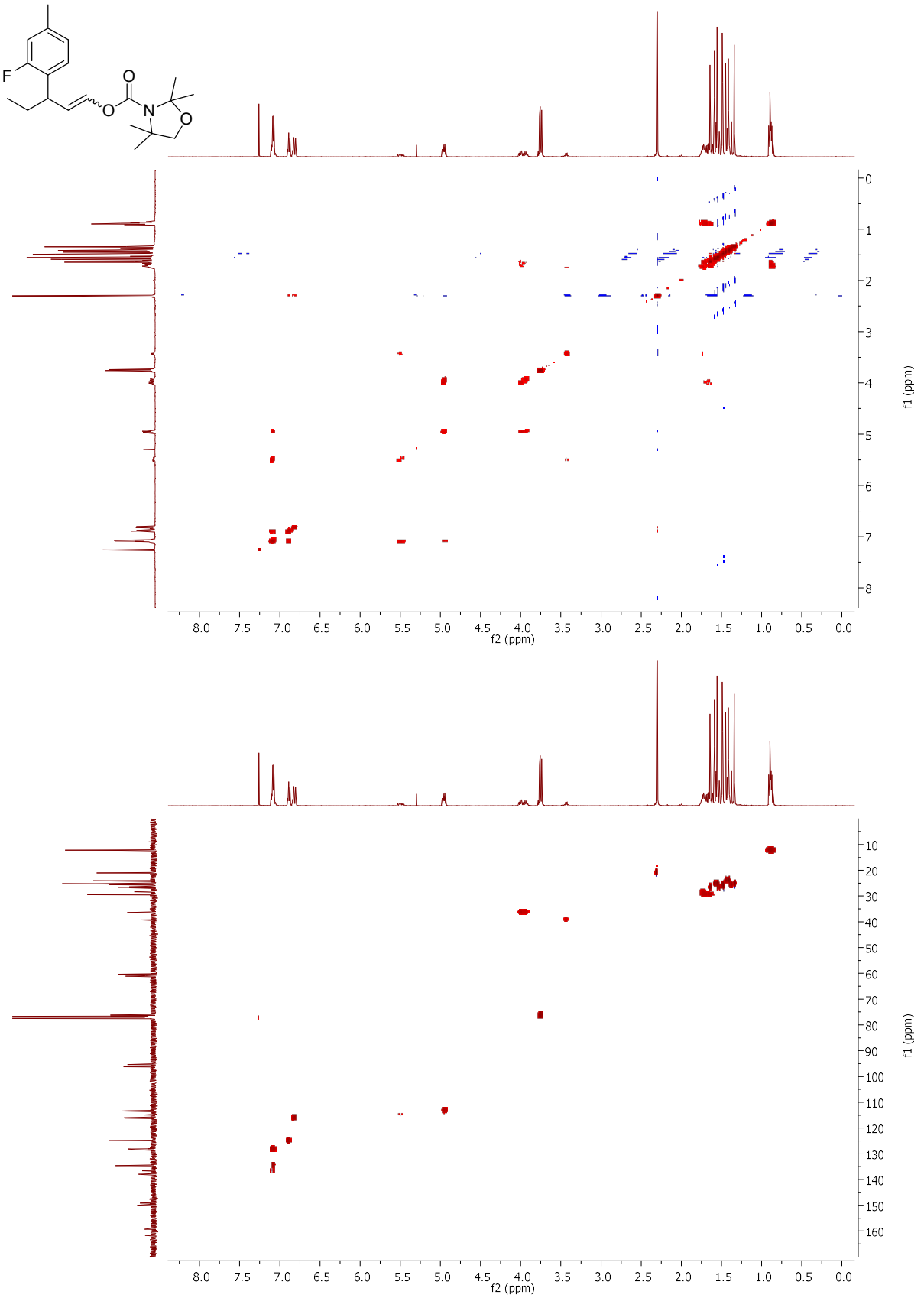


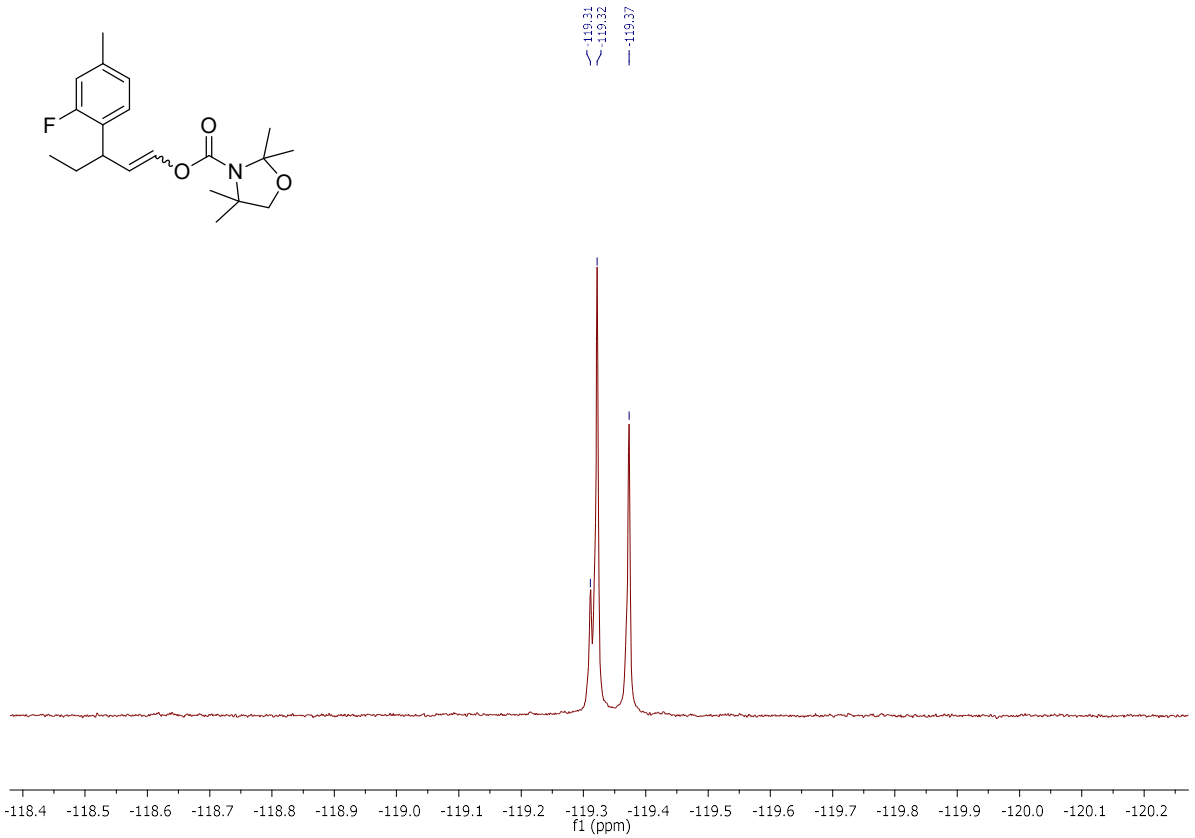

F
O
O
N
O
-117.62
-117.64
-116.3
-116.5
-116.7
-116.9
-117.1
-117.3
-117.5
-117.7
-117.9
-118.1
-118.3
-118.5
-118.7
-118.9
-119.1
f1 (ppm)

3-(2-fluoro-4-methylphenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4c** :

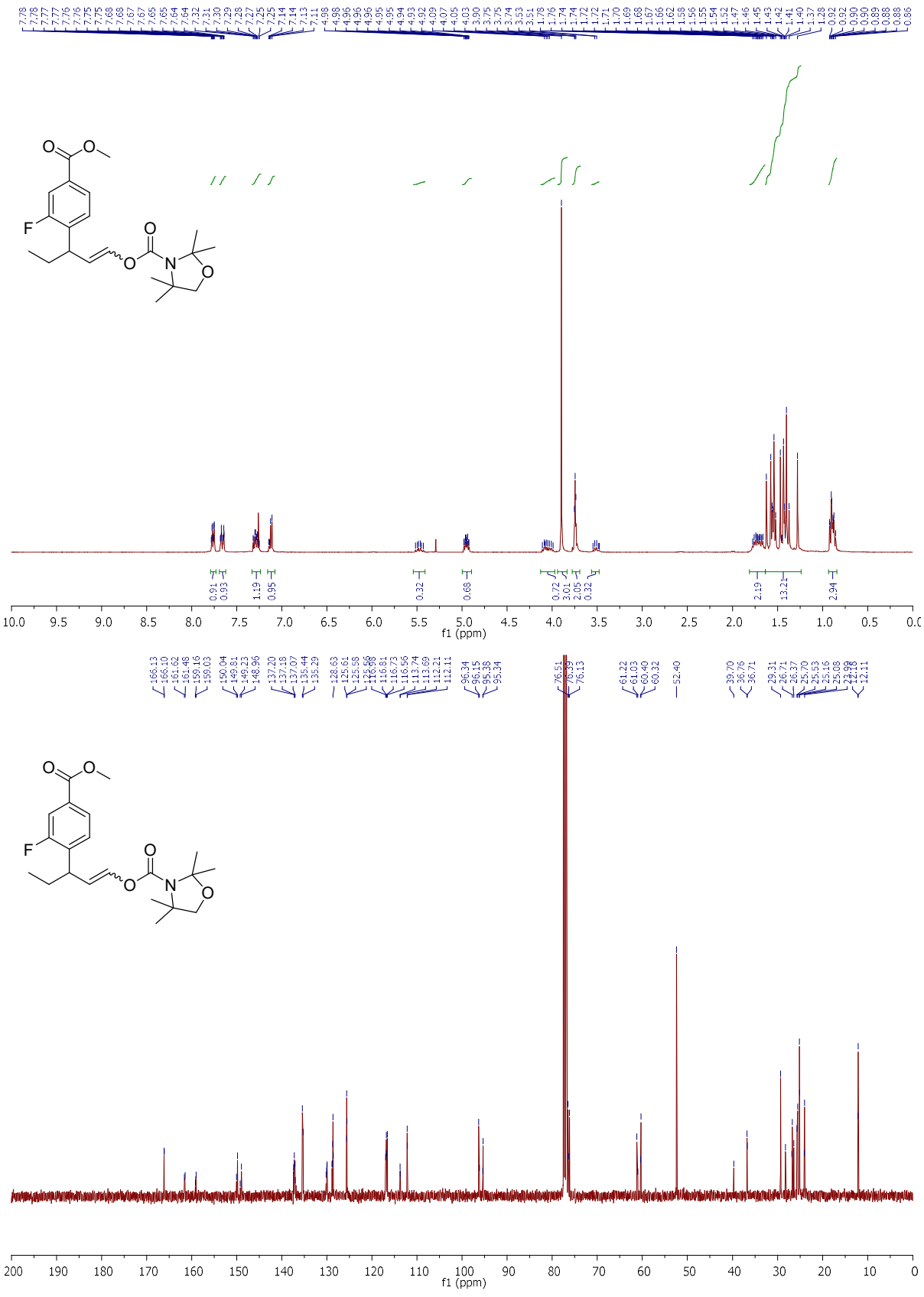


COSY and HMQC experiments :

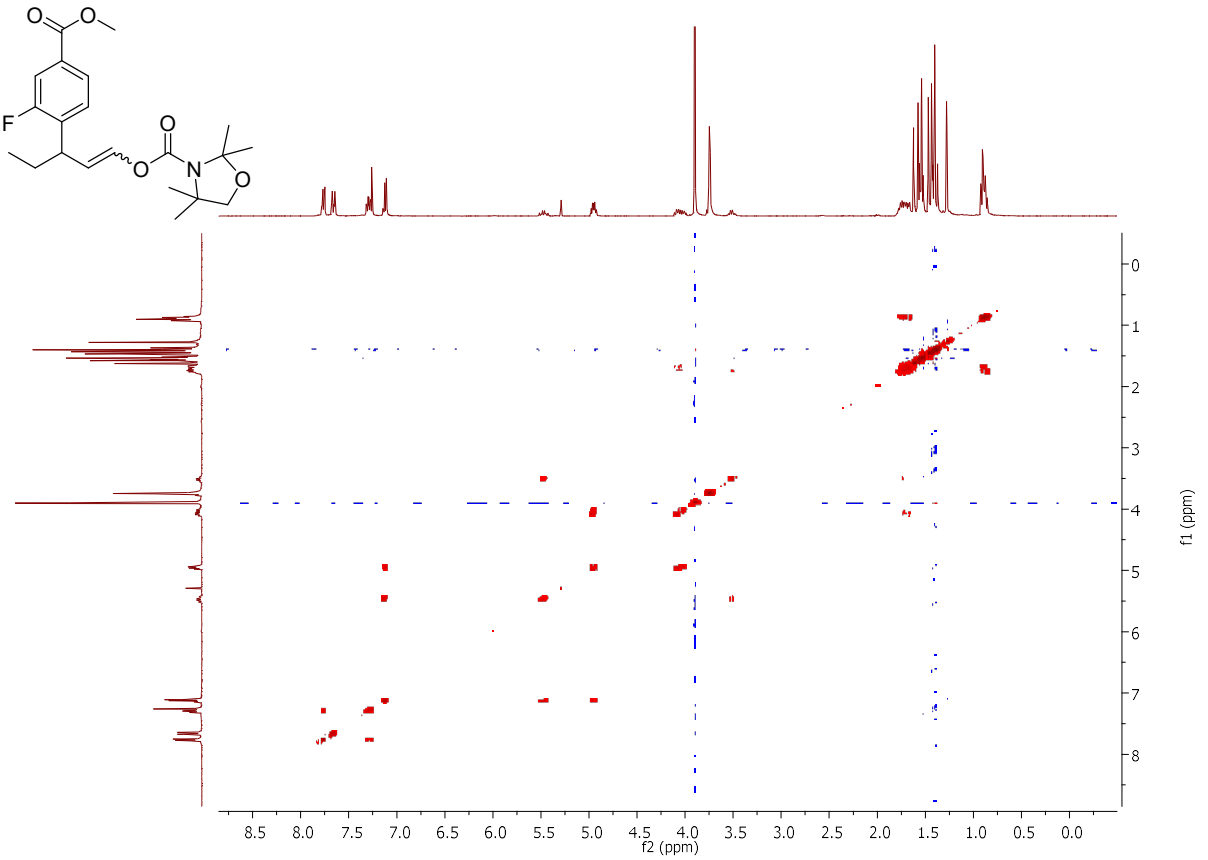


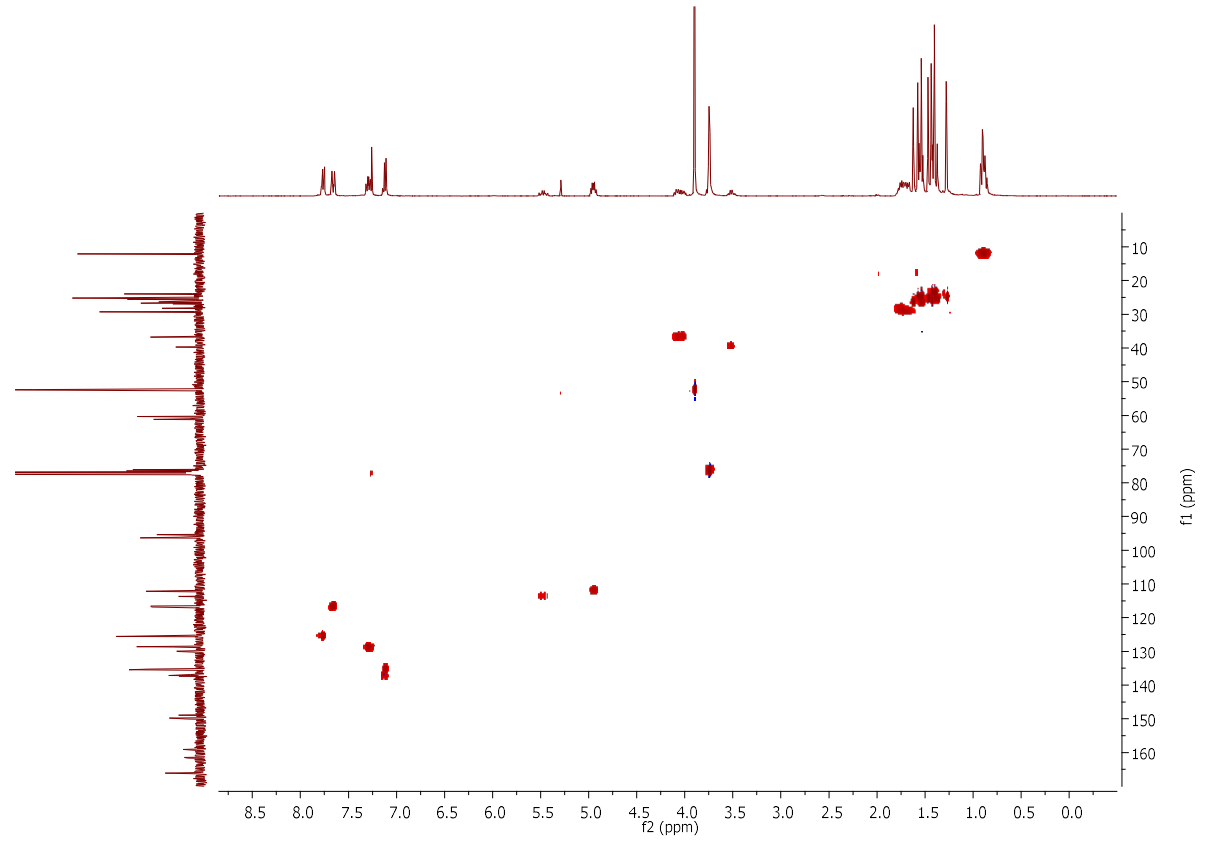

F
O
O
N
O
-119.31
-119.32
-119.37
-118.4
-118.5
-118.6
-118.7
-118.8
-118.9
-119.0
-119.1
-119.2
-119.3
-119.4
-119.5
-119.6
-119.7
-119.8
-119.9
-120.0
-120.1
-120.2
f1 (ppm)

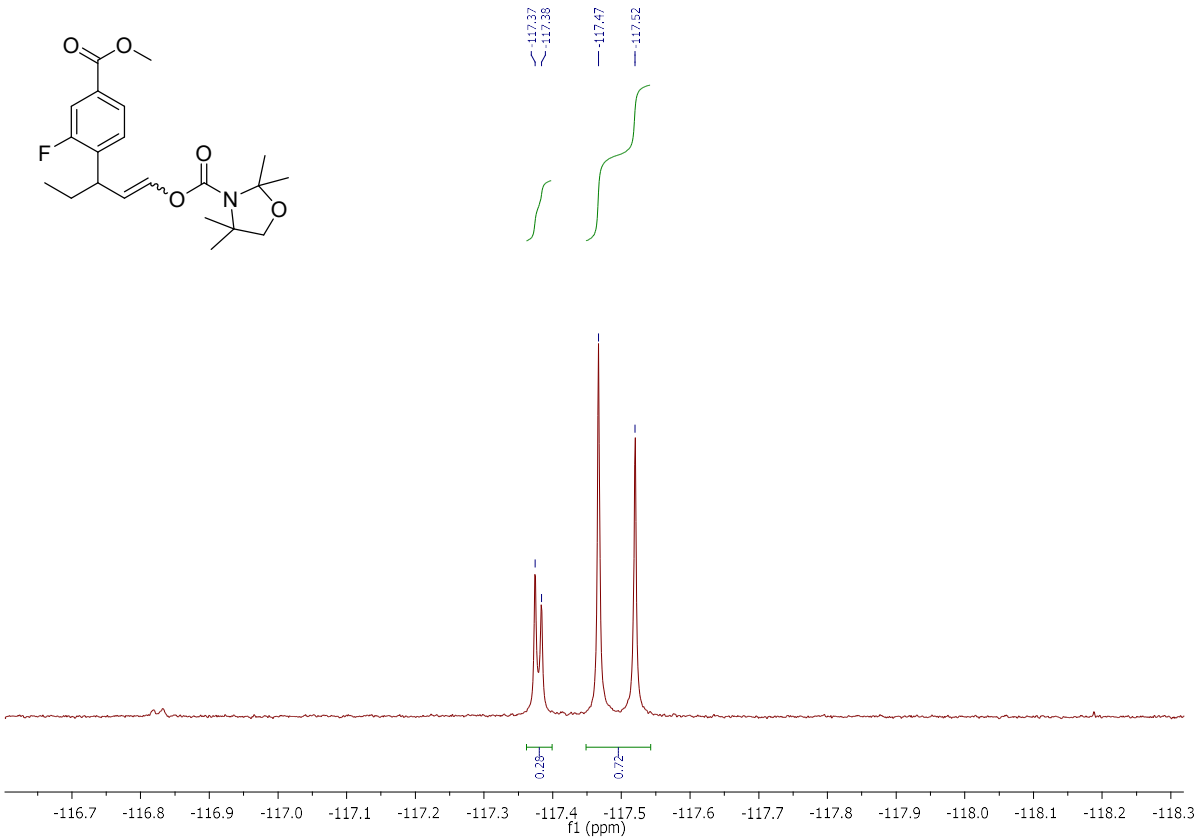
3-(2-fluoro-4-(methoxycarbonyl)phenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4d** :



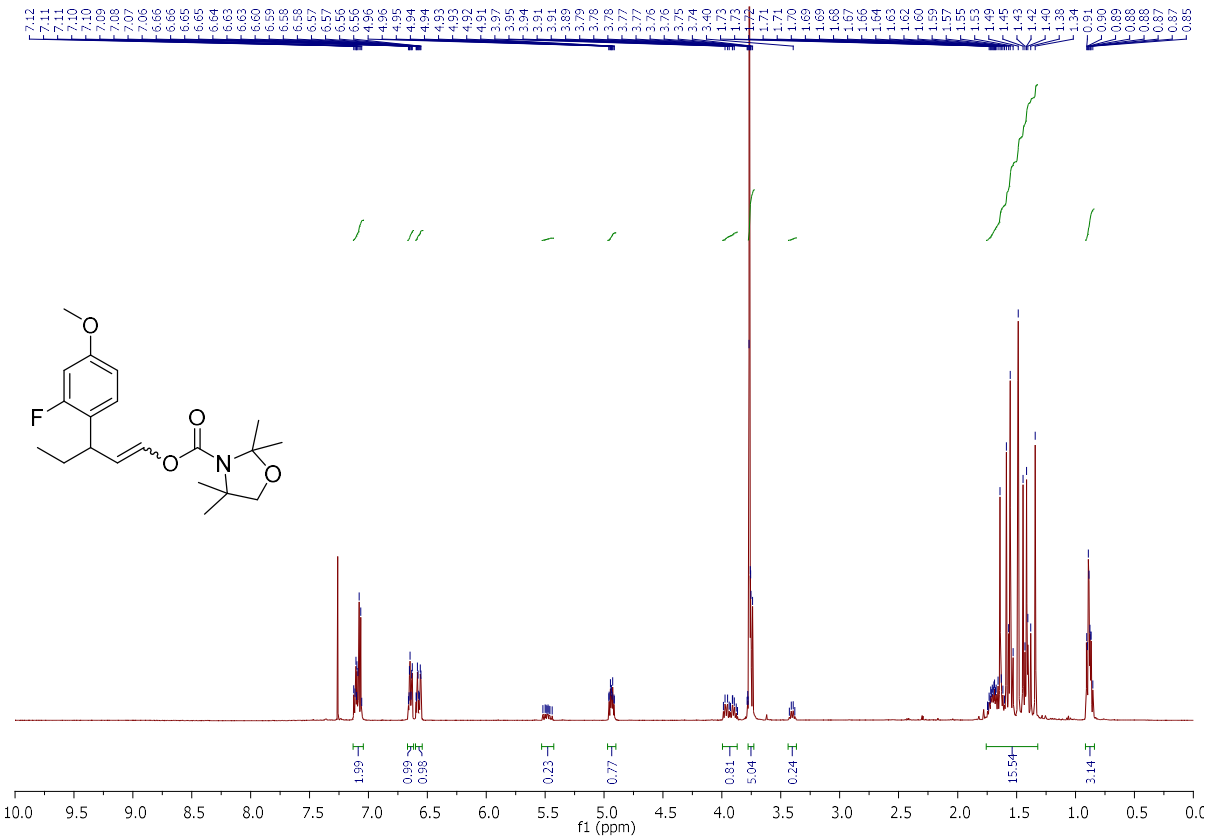
COSY and HMQC experiments :

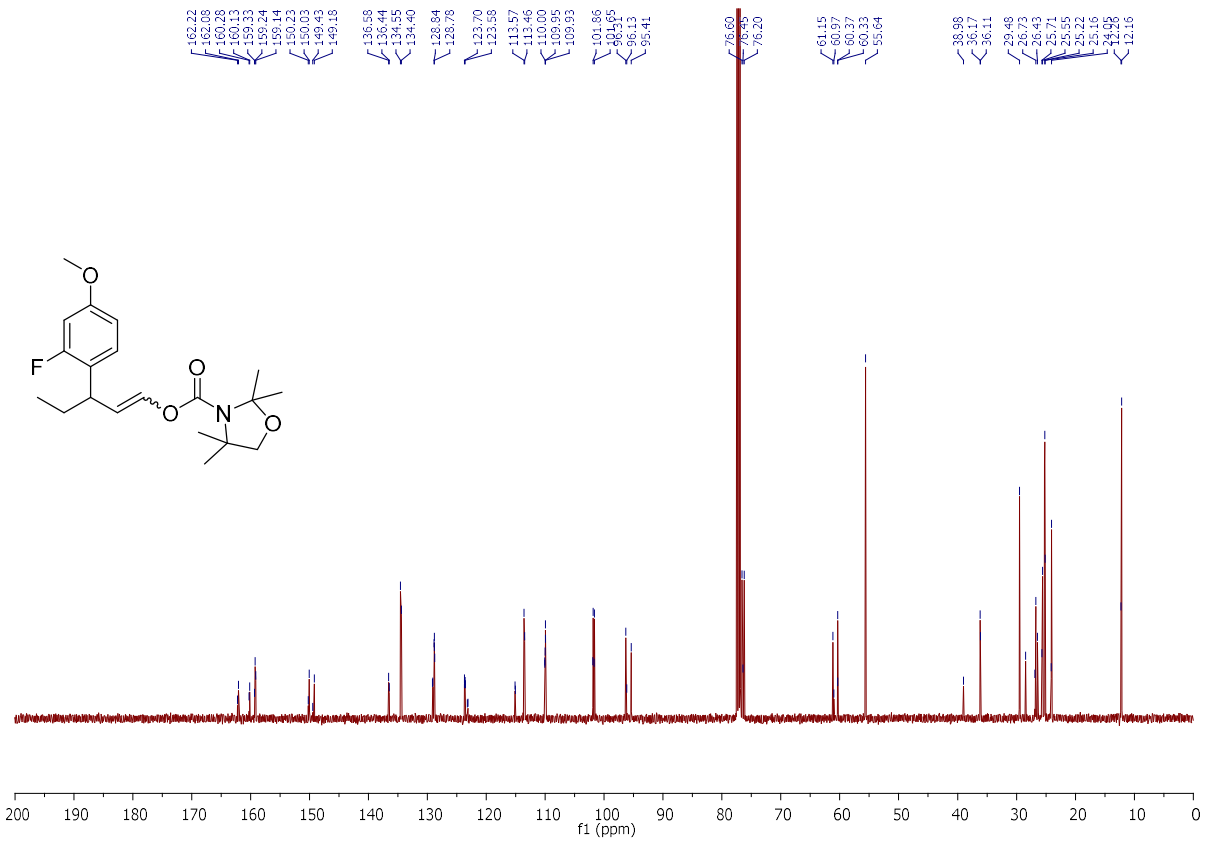




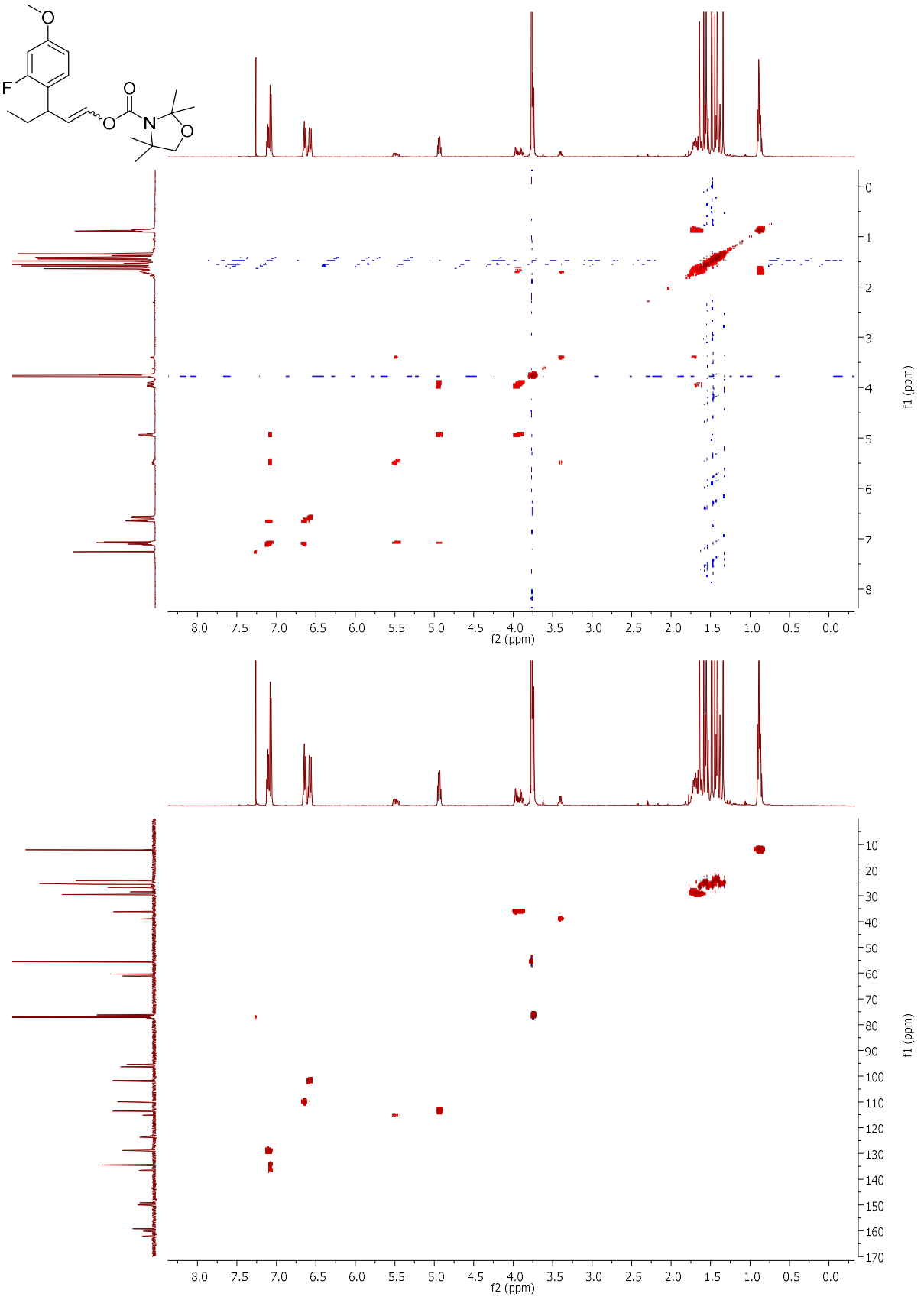

-117.37
-117.38
-117.47
-117.52
0.29
0.72
-116.7
-116.8
-116.9
-117.0
-117.1
-117.2
-117.3
-117.4
-117.5
-117.6
-117.7
-117.8
-117.9
-118.0
-118.1
-118.2
-118.3
f1 (ppm)

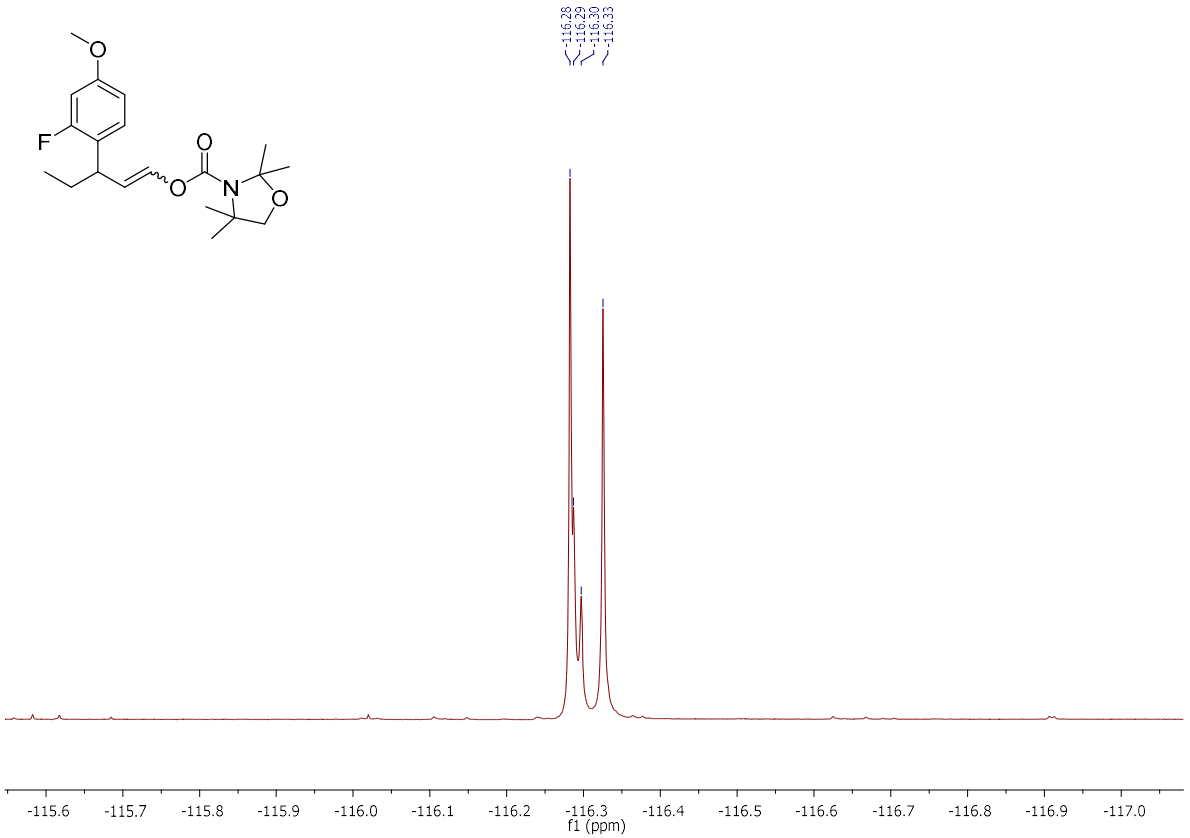
3-(2-fluoro-4-methoxyphenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate**4e** :



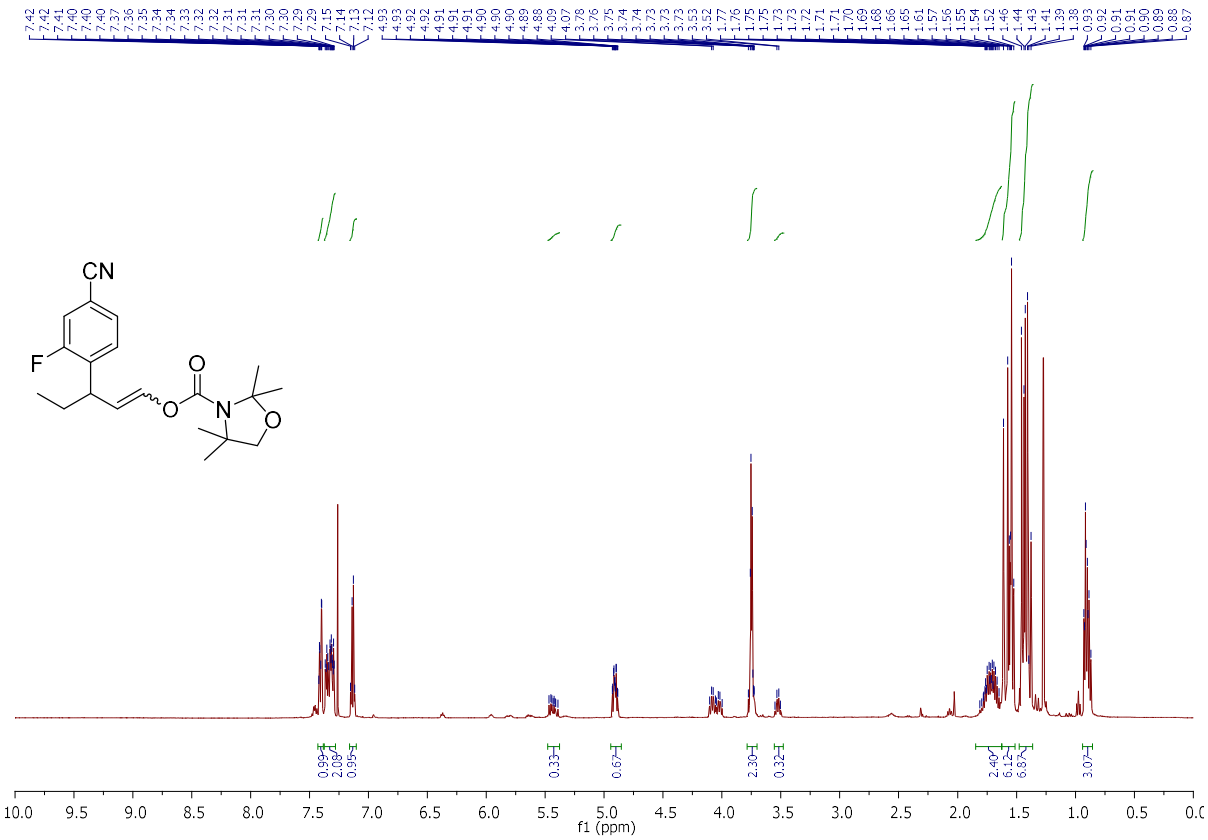


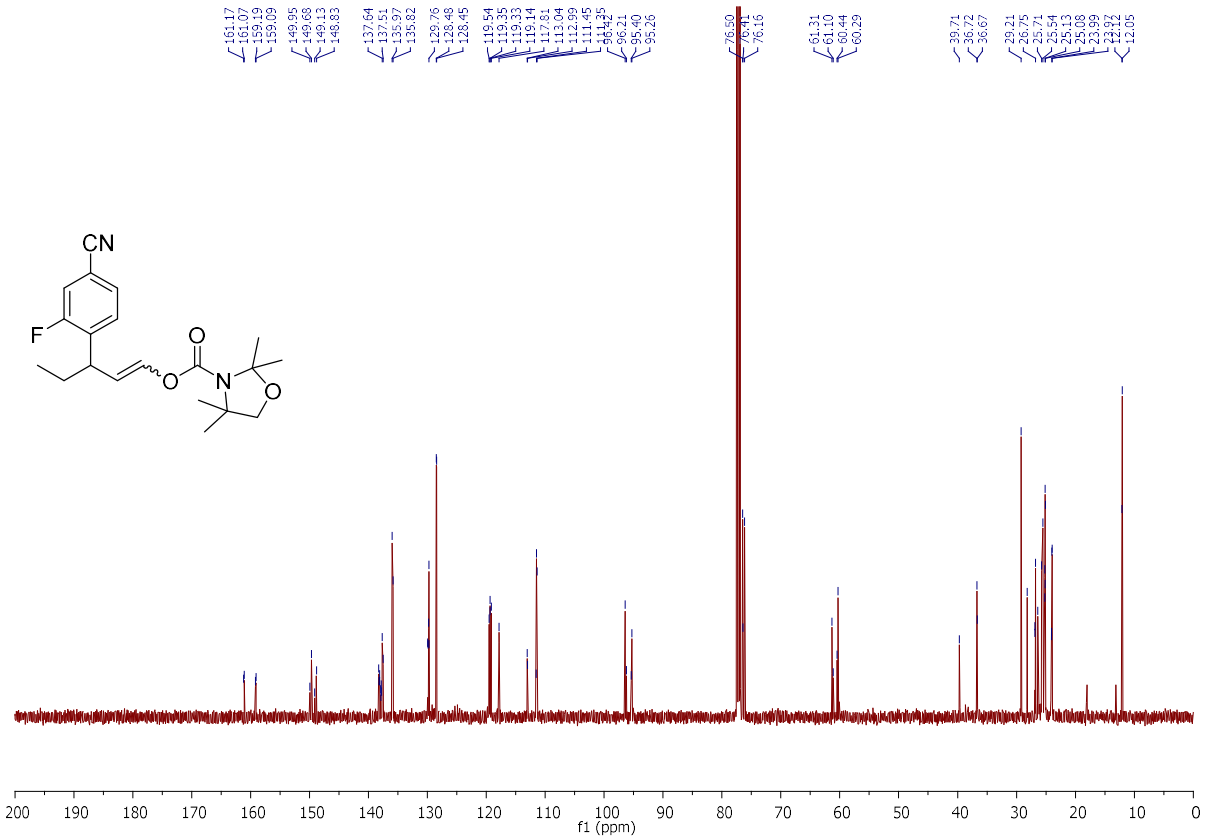
COSY and HMQC experiments :



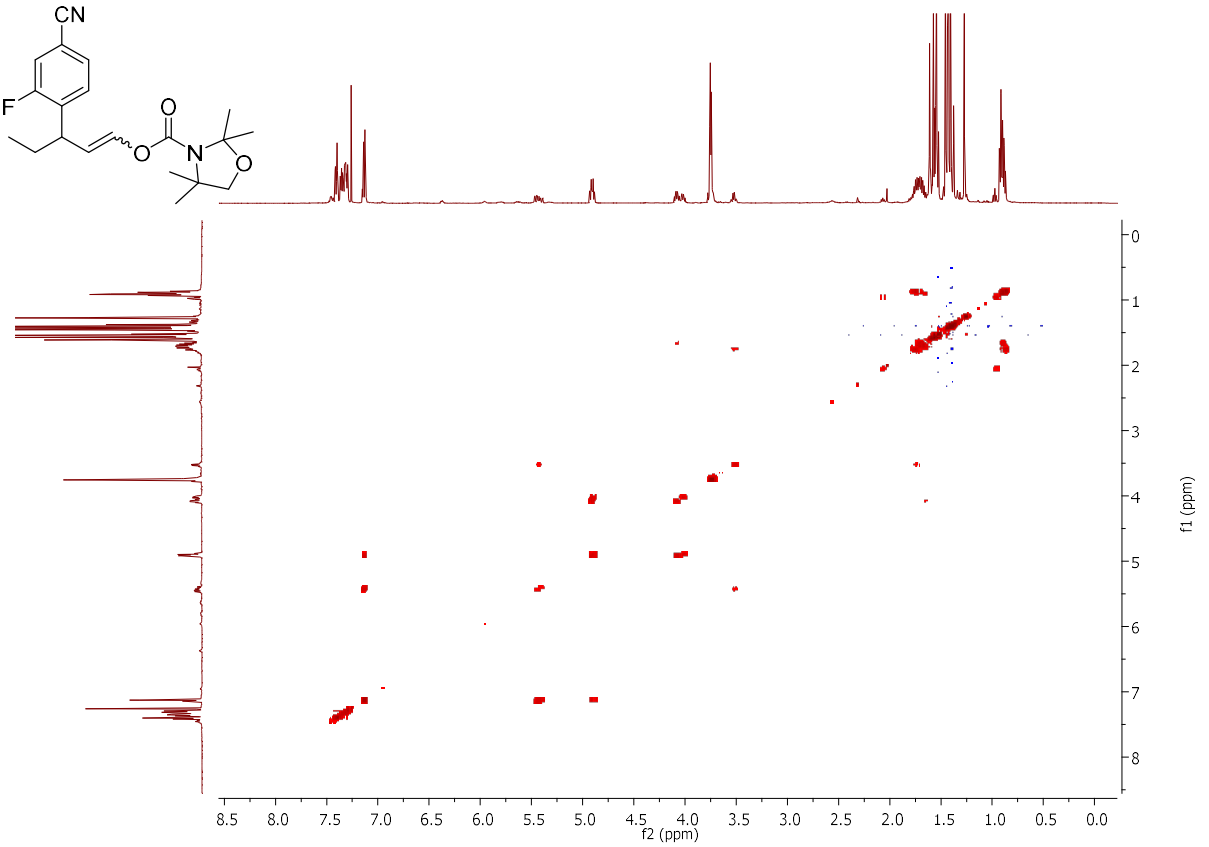

-116.28
-116.29
-116.30
-116.33
F
O
O
O
N
O
-115.6
-115.7
-115.8
-115.9
-116.0
-116.1
-116.2
-116.3
-116.4
-116.5
-116.6
-116.7
-116.8
-116.9
-117.0
f1 (ppm)

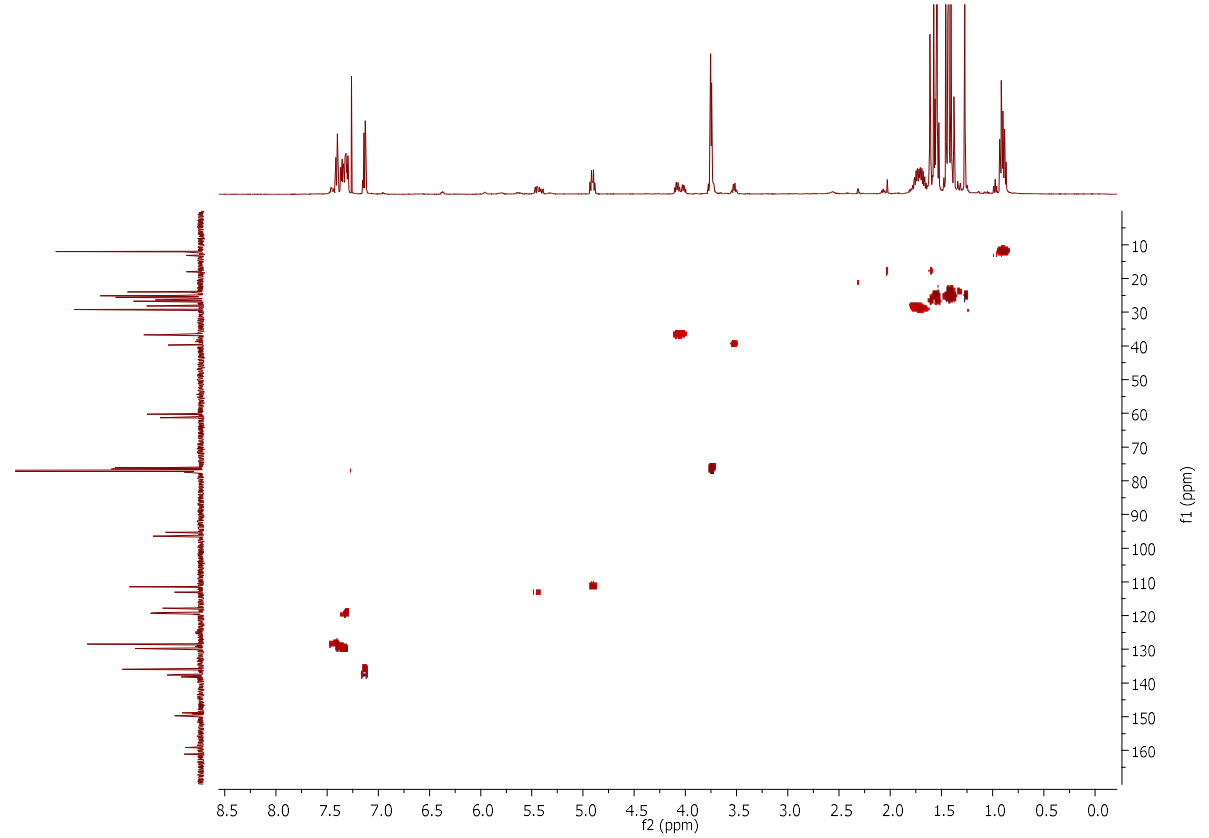
3-(4-cyano-2-fluorophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4f** :

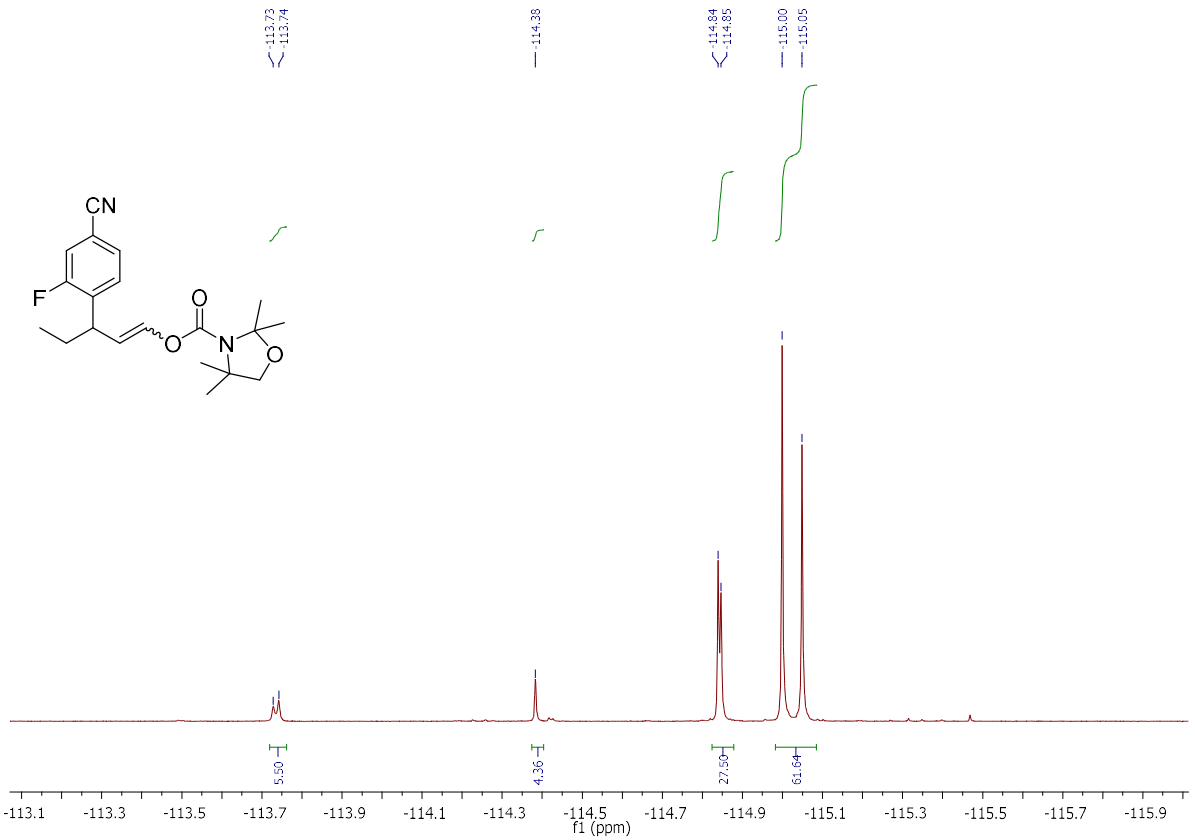




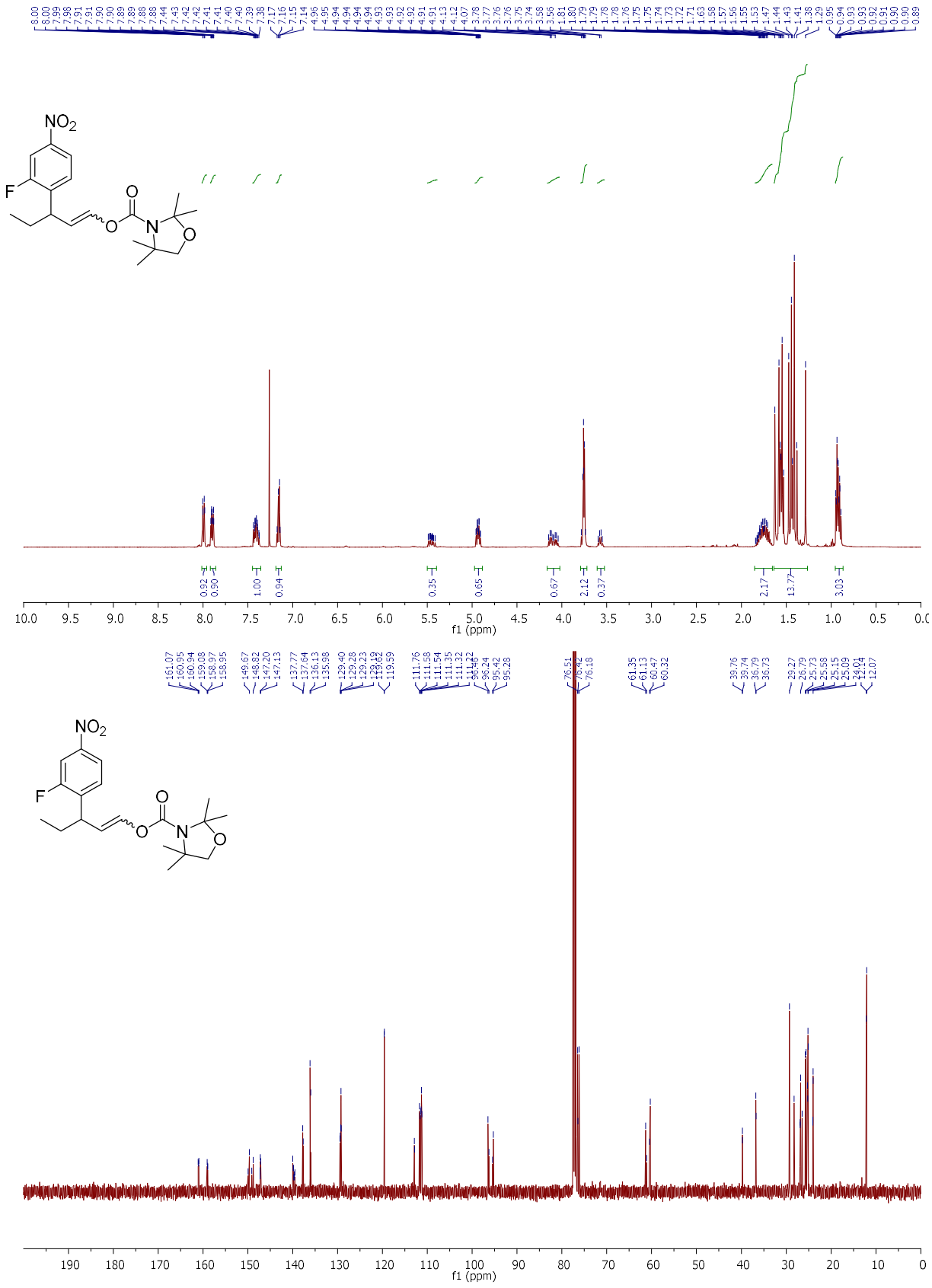
COSY and HMQC experiments :



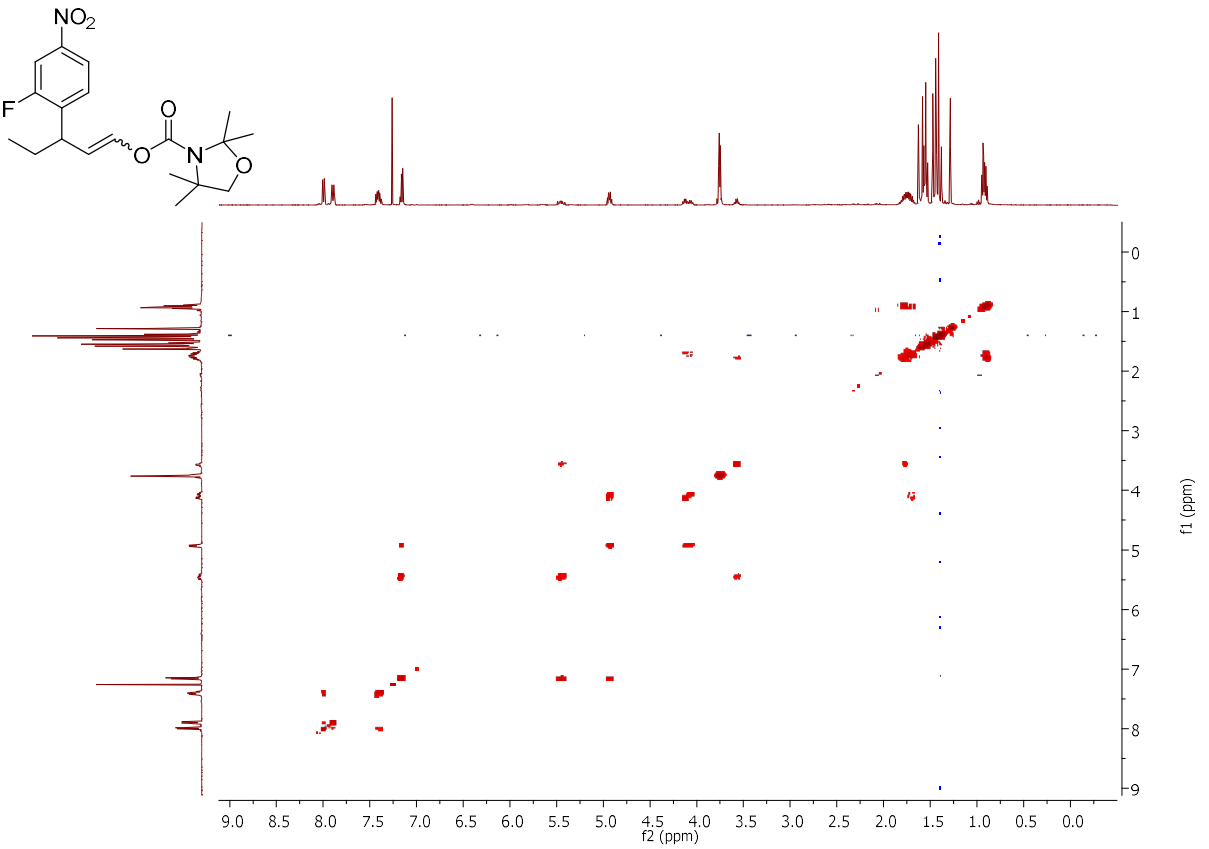


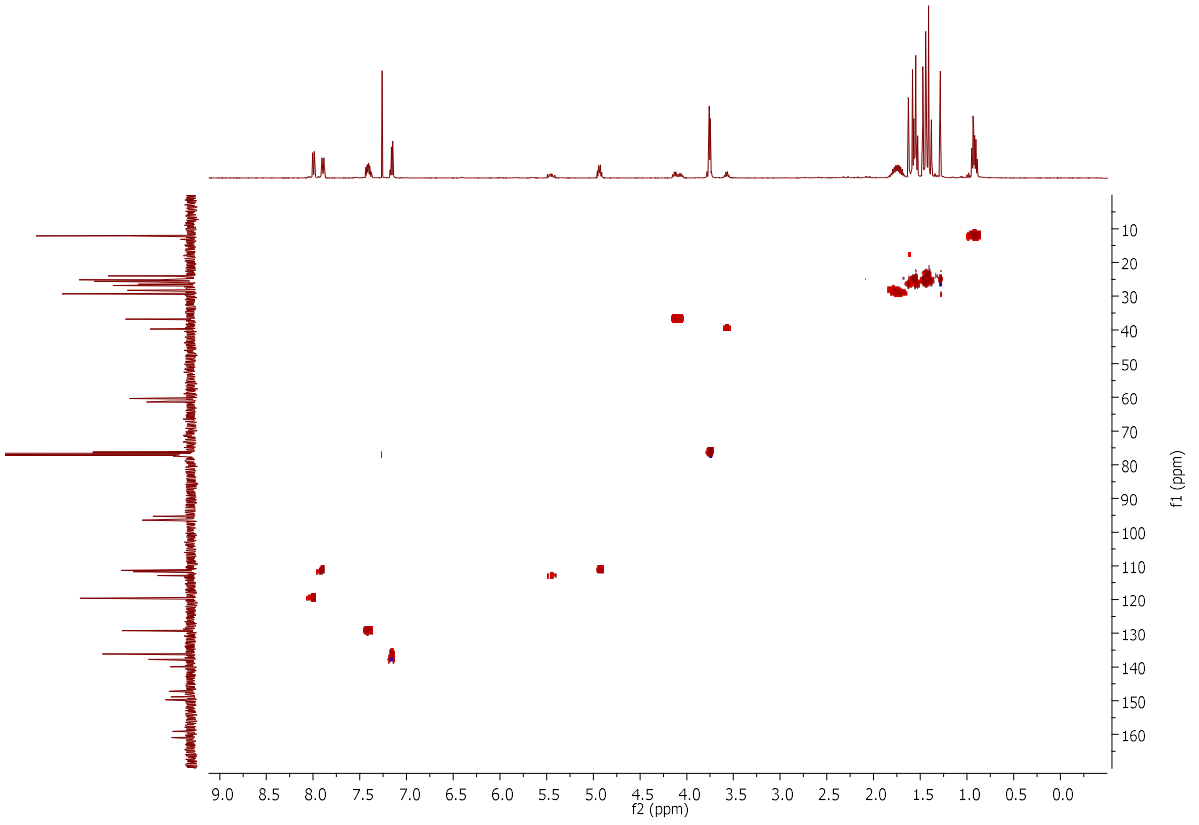

-113.73
-113.74
-114.38
-114.84
-114.85
-115.00
-115.05
CN
F
O
O
N
O
5.50
4.36
27.50
61.64
-113.1
-113.3
-113.5
-113.7
-113.9
-114.1
-114.3
-114.5
-114.7
-114.9
-115.1
-115.3
-115.5
-115.7
-115.9
f1 (ppm)

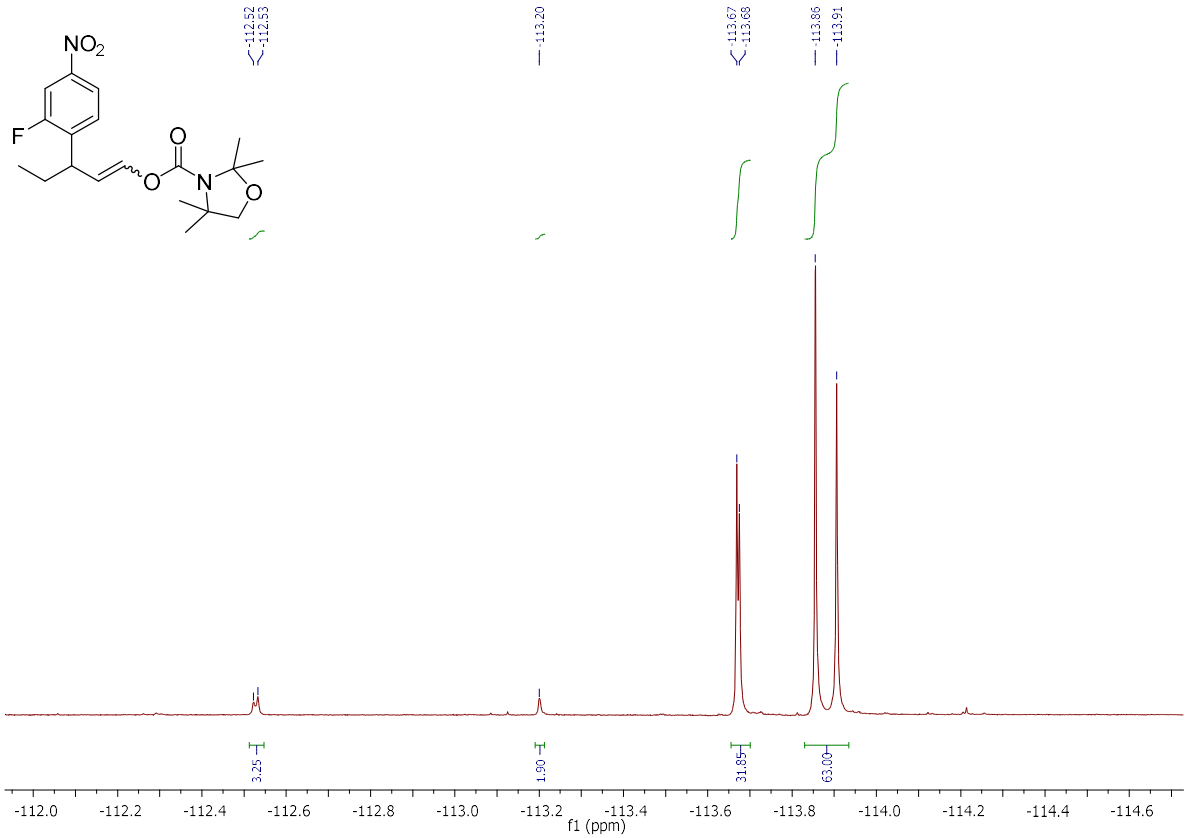
3-(2-fluoro-4-nitrophenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4g** :



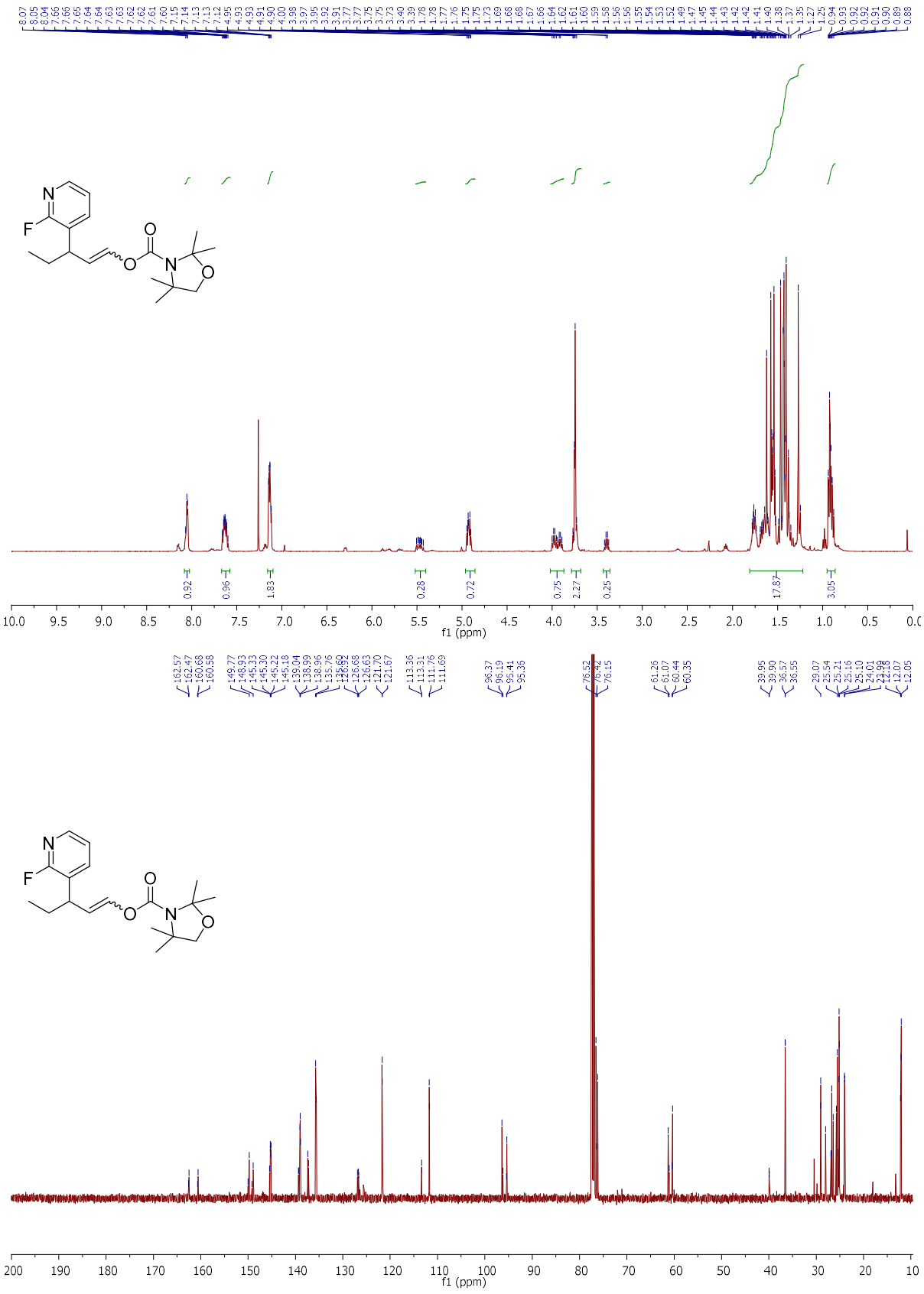
COSY and HMQC experiments :



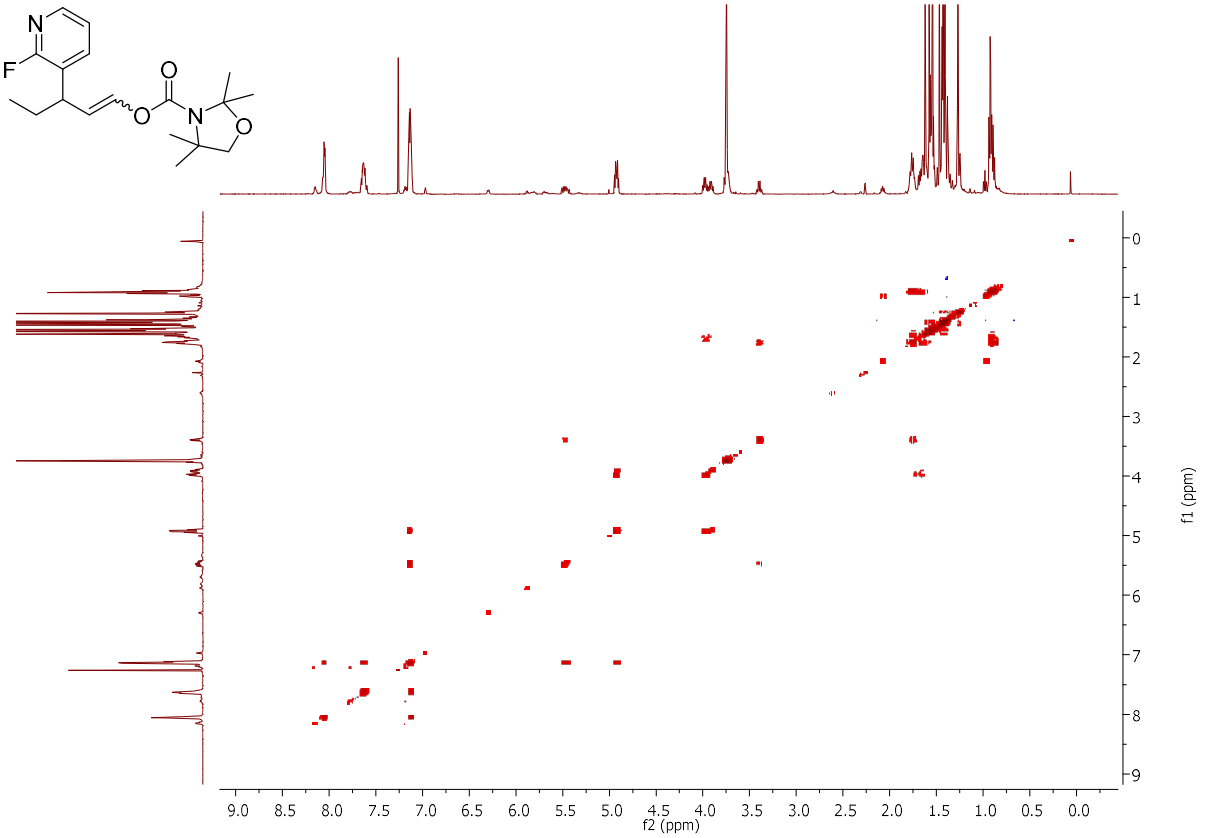


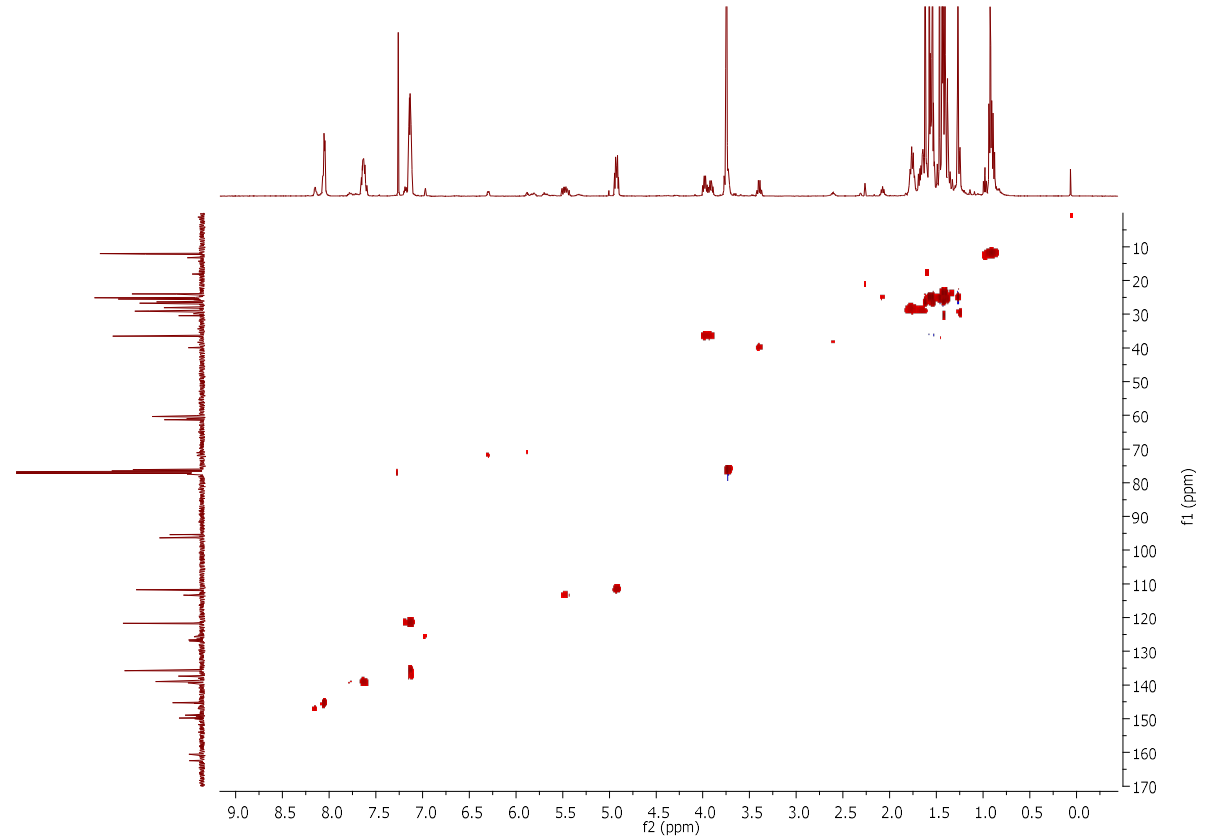

NO2
F
O
O
N
O
-112.52
-112.53
-113.20
-113.67
-113.68
-113.86
-113.91
3.25
1.90
31.85
63.00
-112.0
-112.2
-112.4
-112.6
-112.8
-113.0
-113.2
-113.4
-113.6
-113.8
-114.0
-114.2
-114.4
-114.6
f1 (ppm)

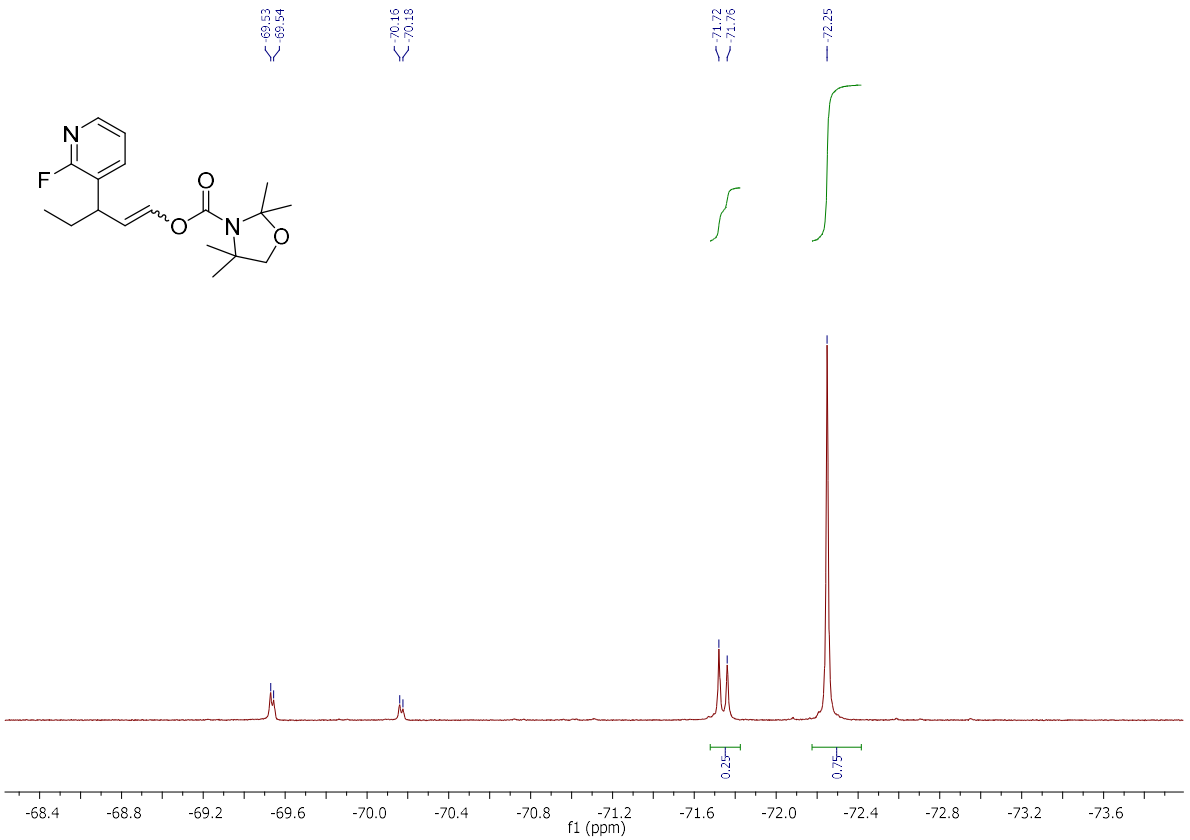
3-(2-fluoropyridin-3-yl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4h** :



COSY and HMQC experiments :

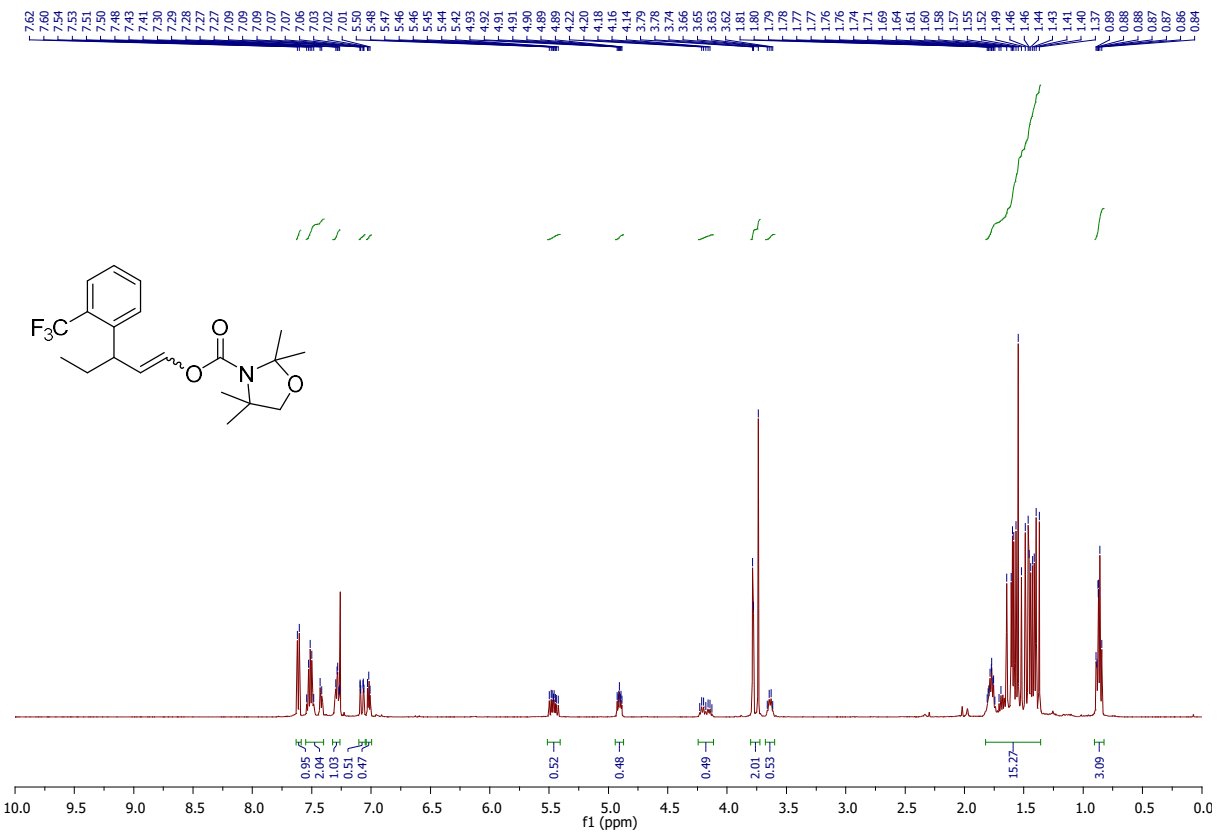


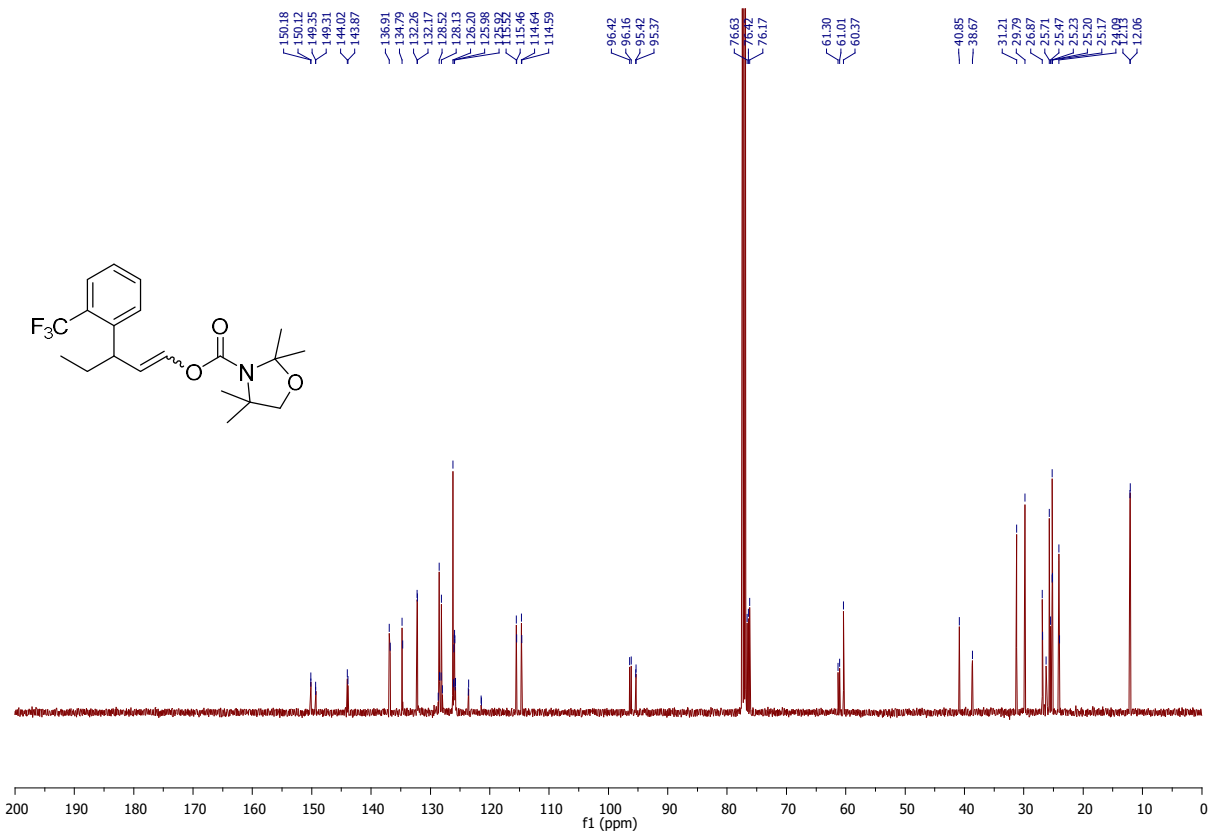



-69.53
-69.54
-70.16
-70.18
-71.72
-71.76
-72.25
N
F
O
O
N
O
0.25
0.75
-68.4
-68.8
-69.2
-69.6
-70.0
-70.4
-70.8
-71.2
-71.6
-72.0
-72.4
-72.8
-73.2
-73.6
f1 (ppm)

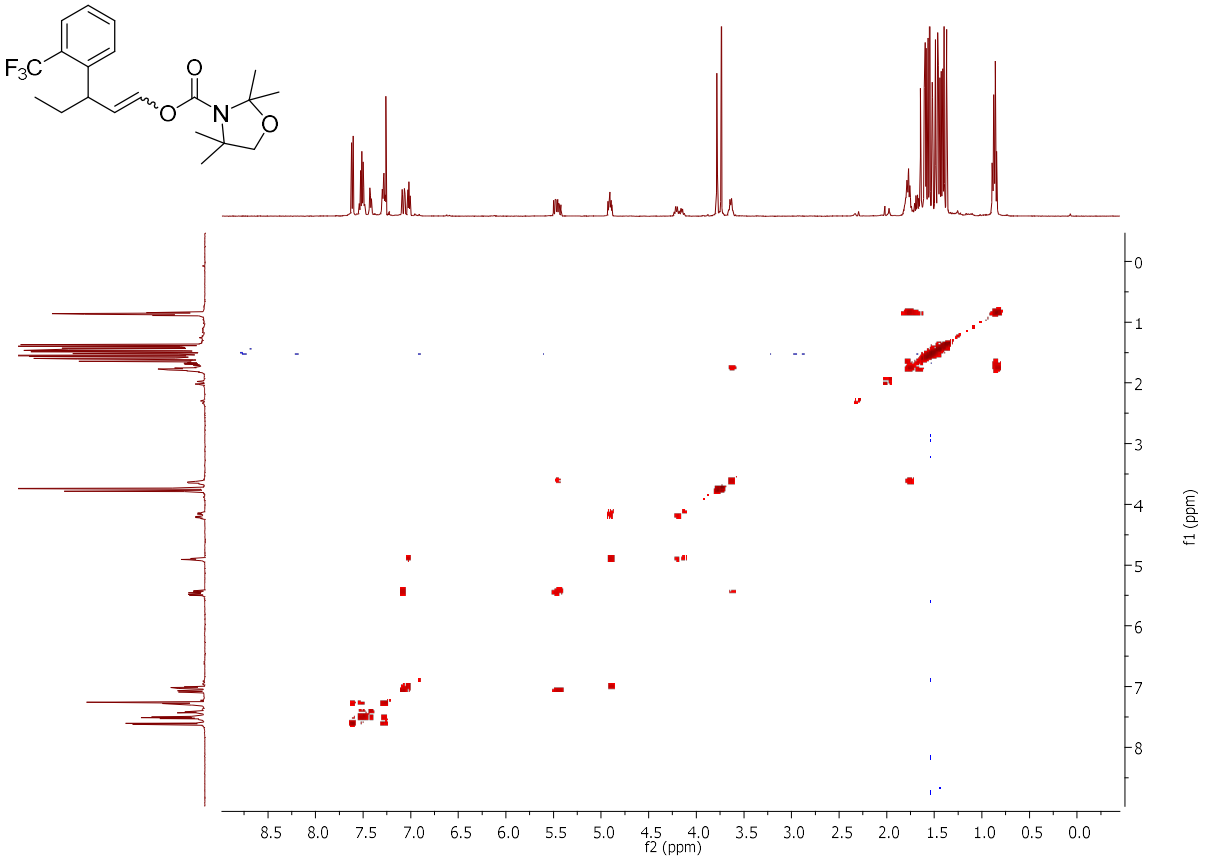
.3-(2-(trifluoromethoxy)phenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate

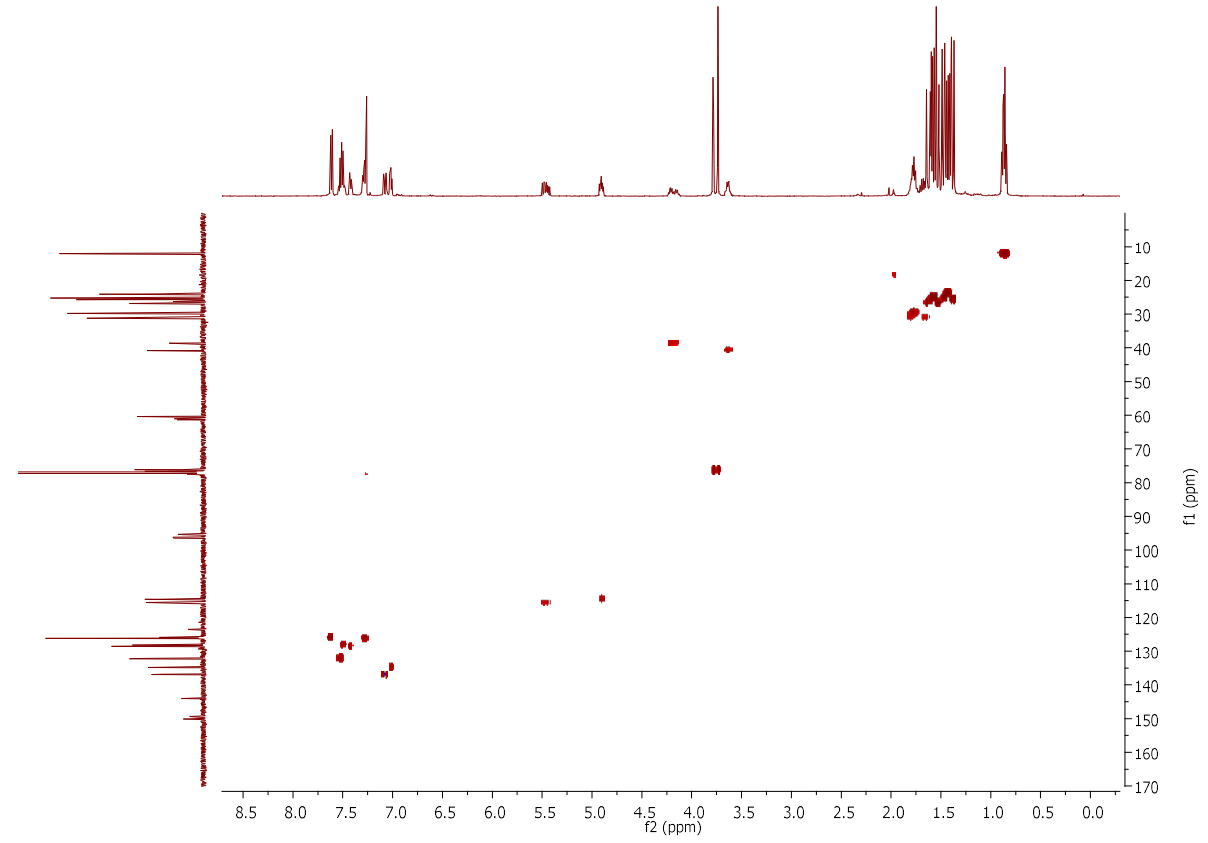
4i :

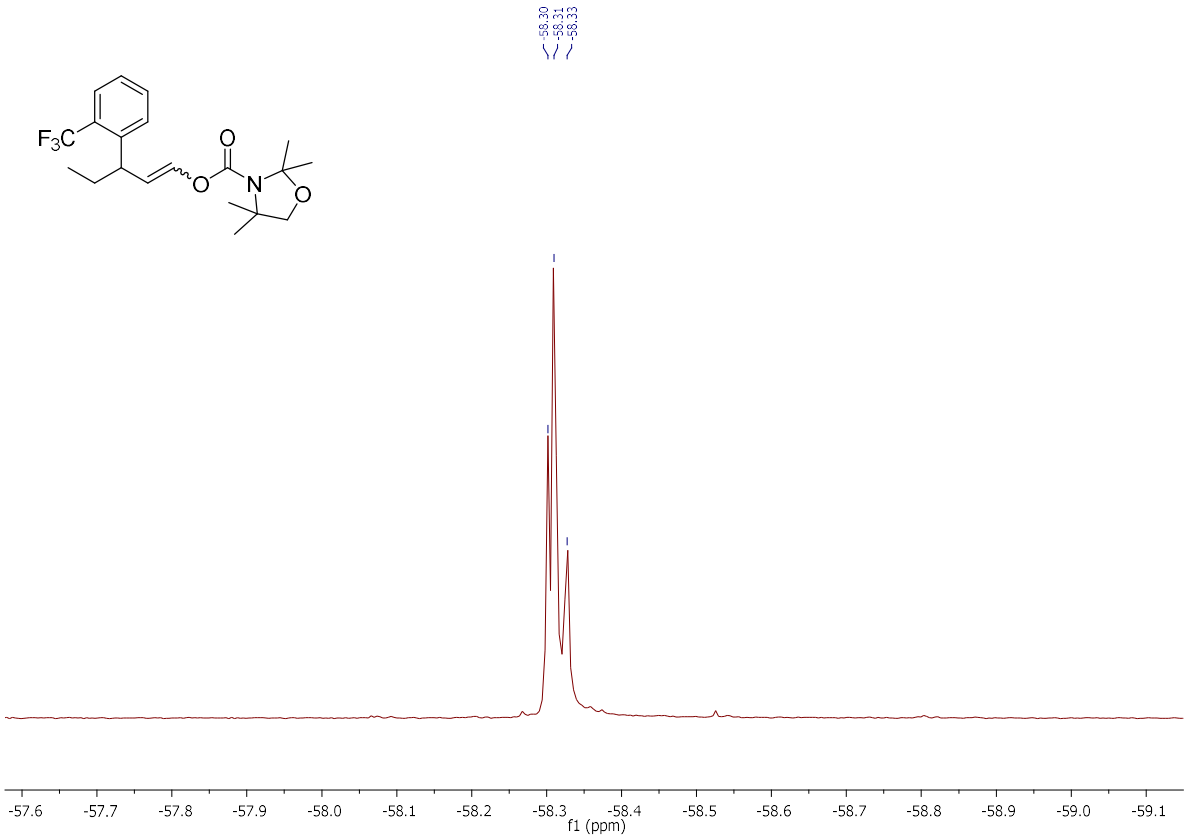




COSY and HMQC experiments :

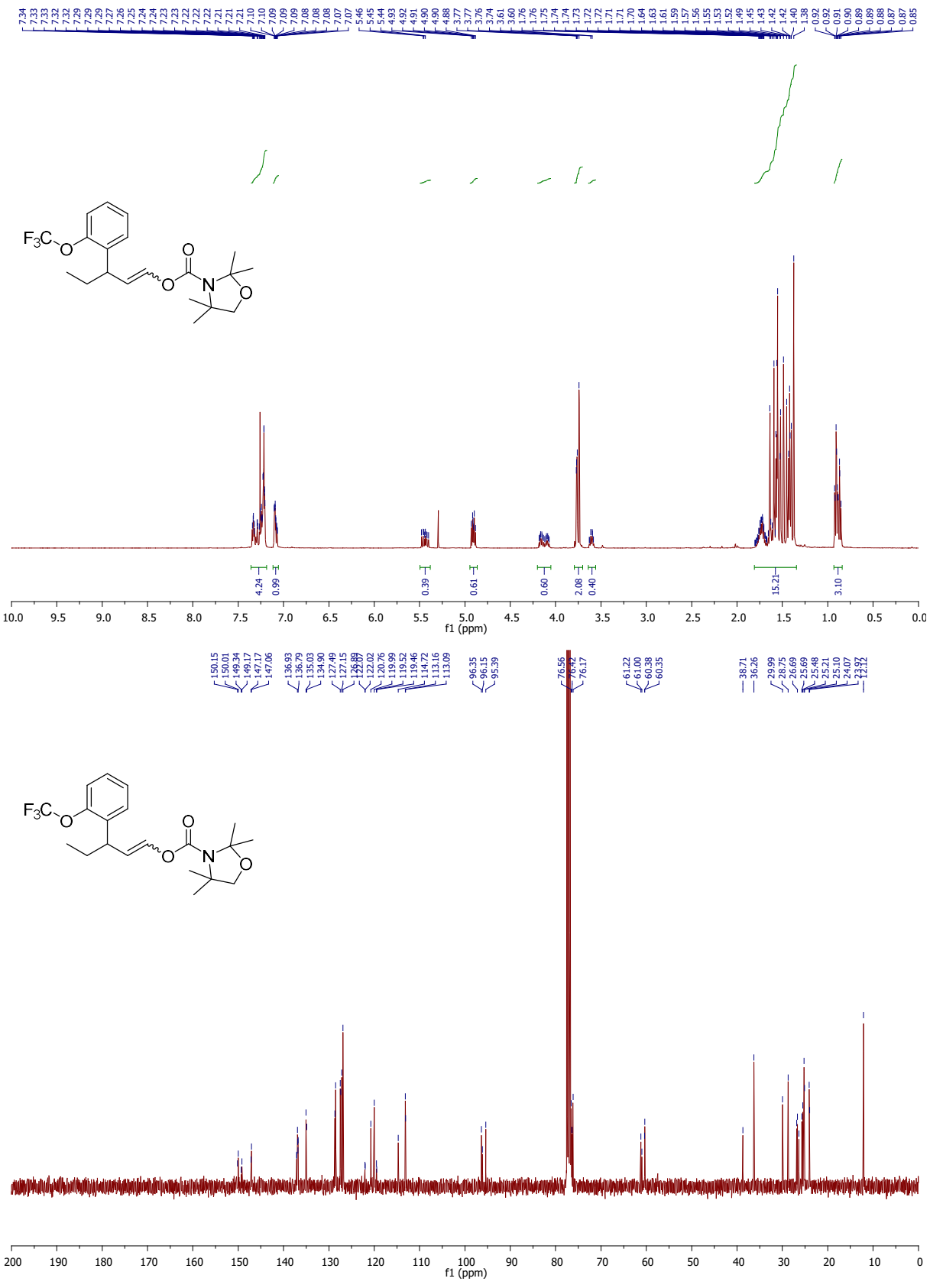




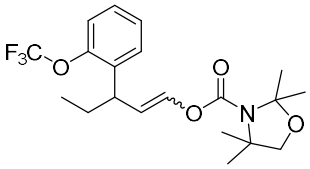

-58.30
-58.31
-58.33
F3C
O
O
N
O
-57.6
-57.7
-57.8
-57.9
-58.0
-58.1
-58.2
-58.3
-58.4
-58.5
-58.6
-58.7
-58.8
-58.9
-59.0
-59.1
f1 (ppm)

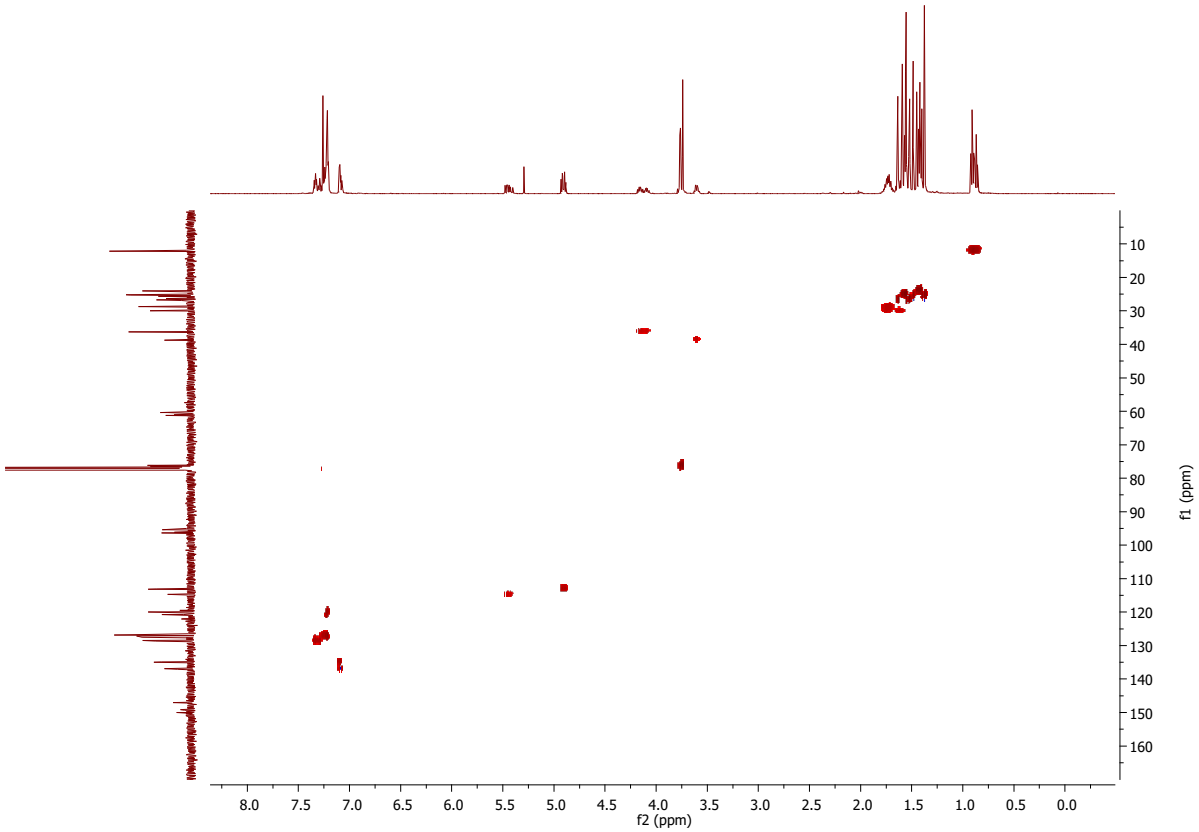
3-(2-(trifluoromethoxy)phenyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate

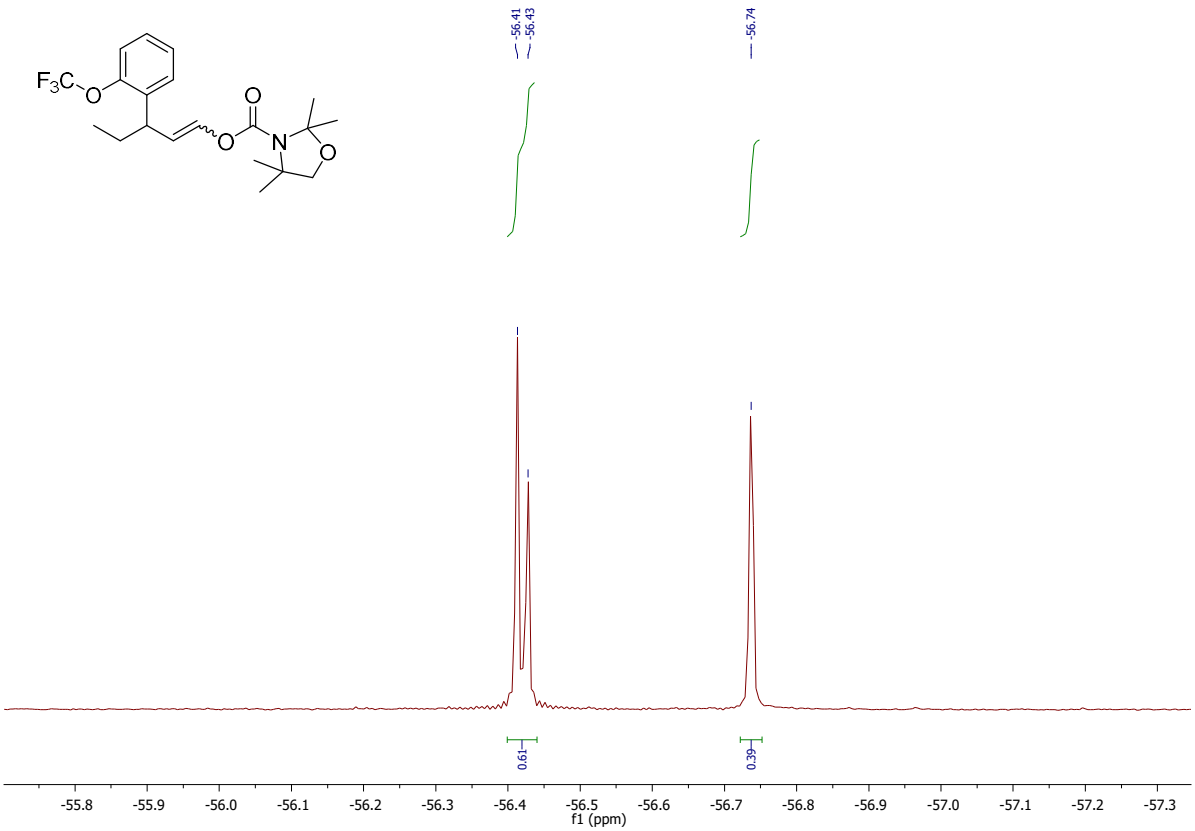
4j :



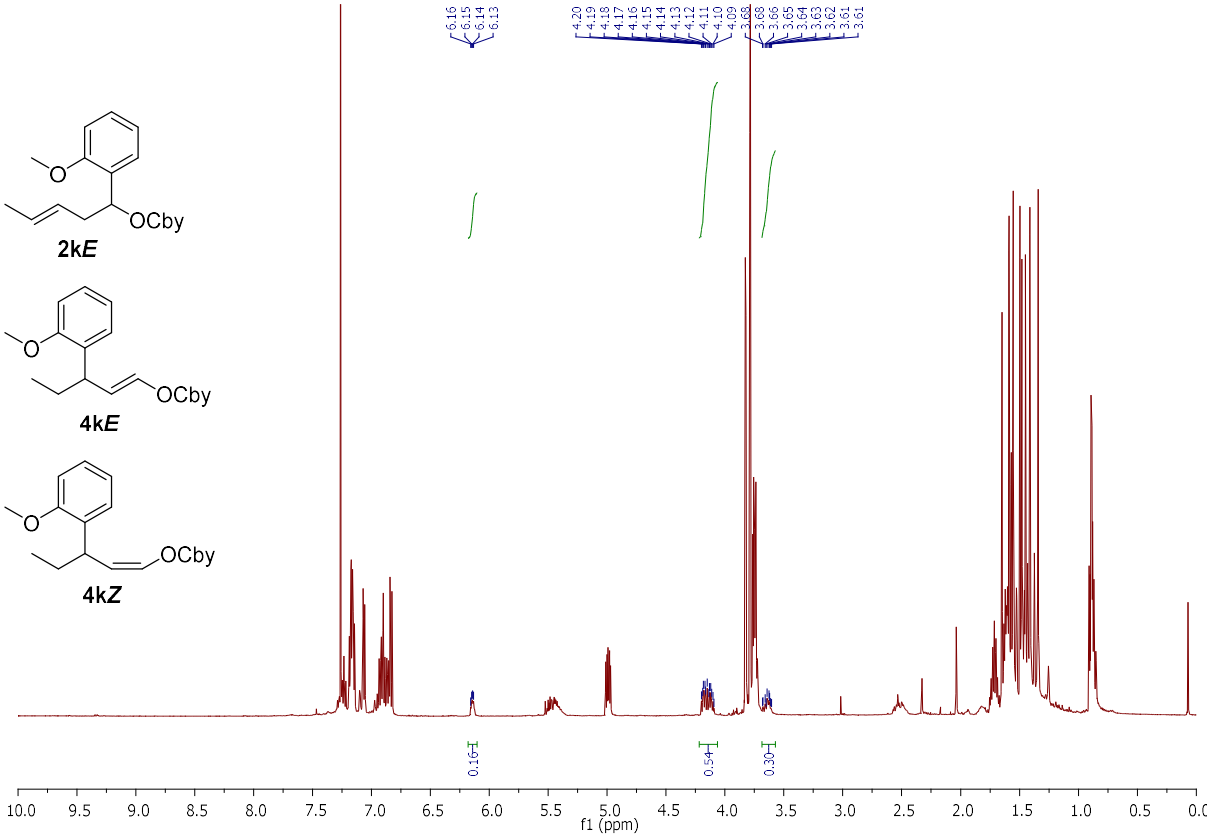
COSY and HMQC experiments :

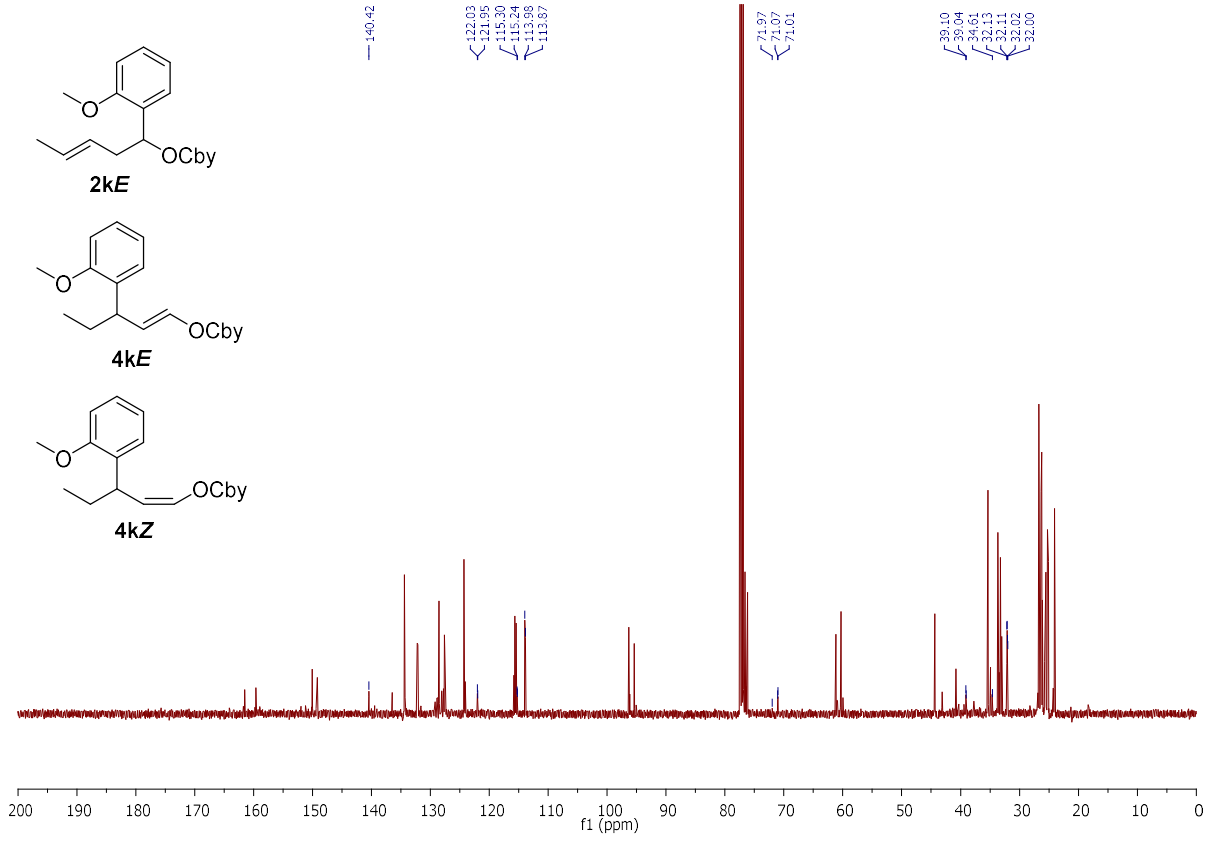


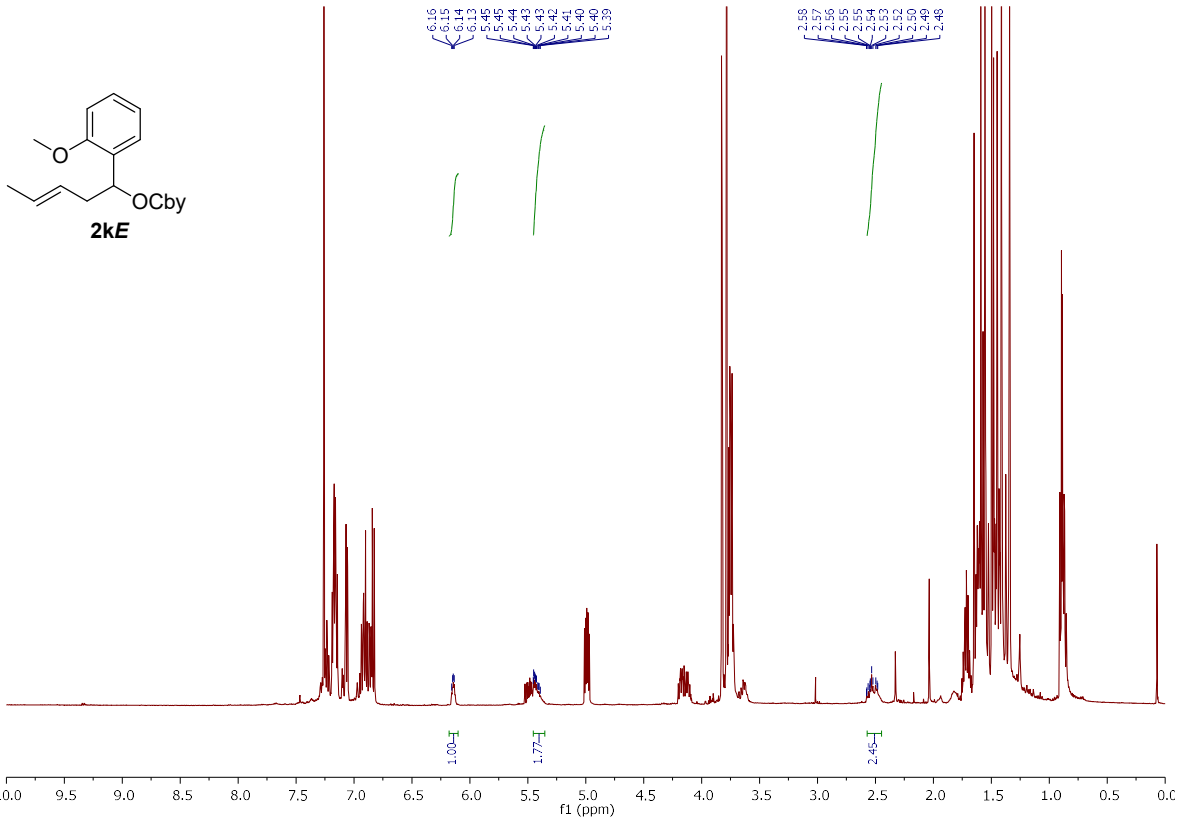


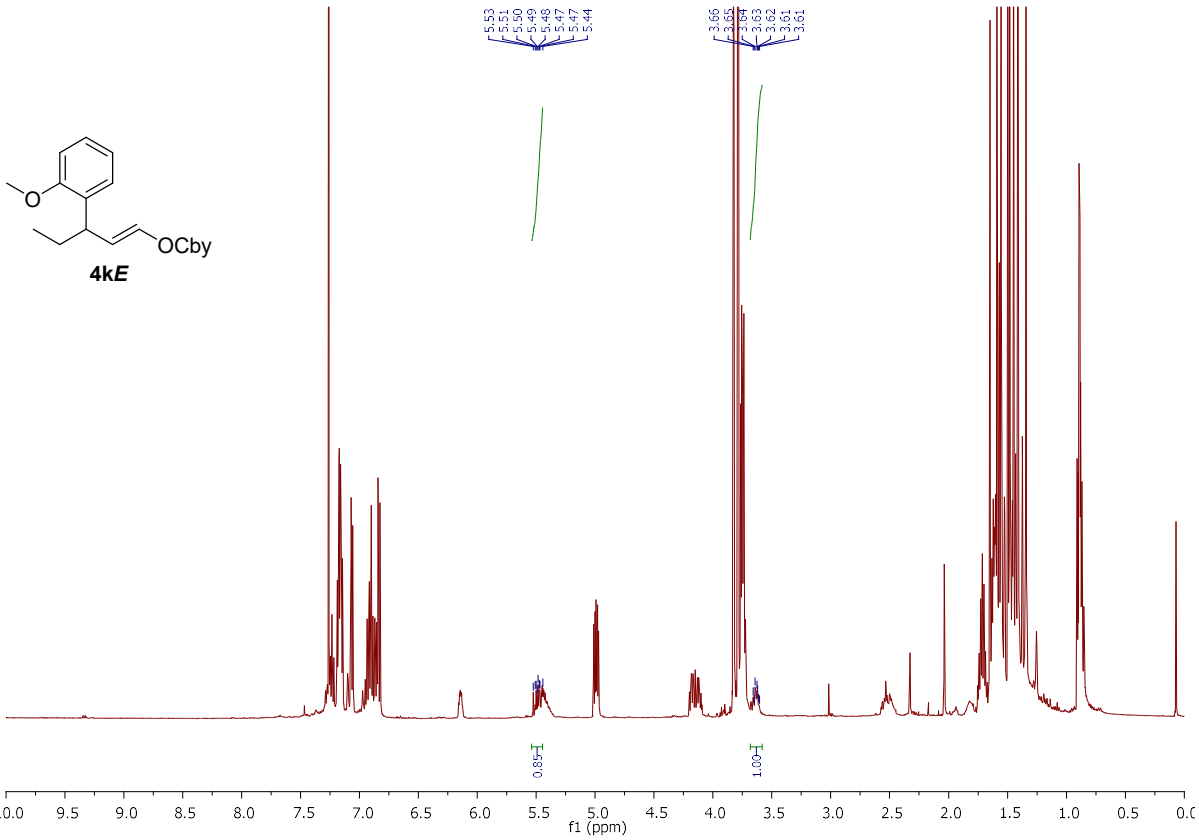

F3C
O
O
O
N
O
-56.41
-56.43
-56.74
0.61
0.39
-55.8
-55.9
-56.0
-56.1
-56.2
-56.3
-56.4
-56.5
-56.6
-56.7
-56.8
-56.9
-57.0
-57.1
-57.2
-57.3
f1 (ppm)

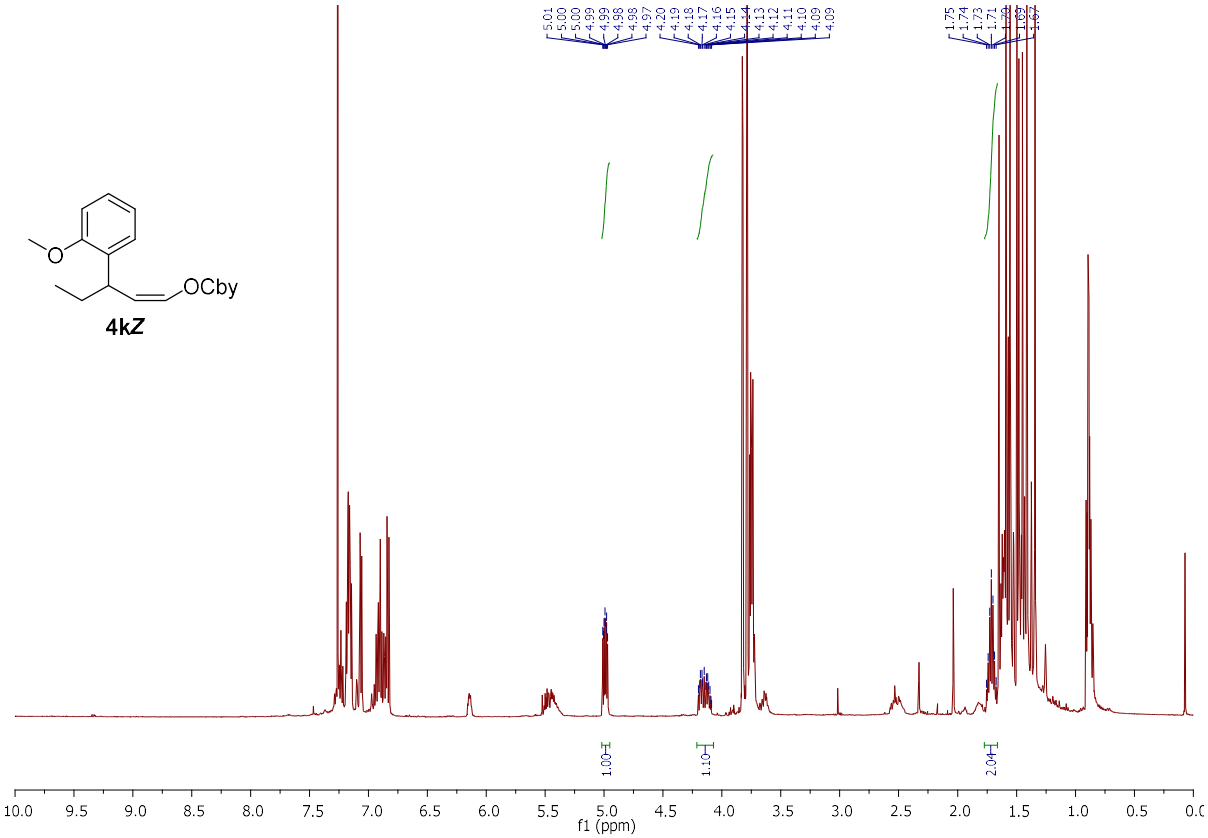
Arylation of **1b*E*** with 2-bromoanisole : product **4k**and isomers



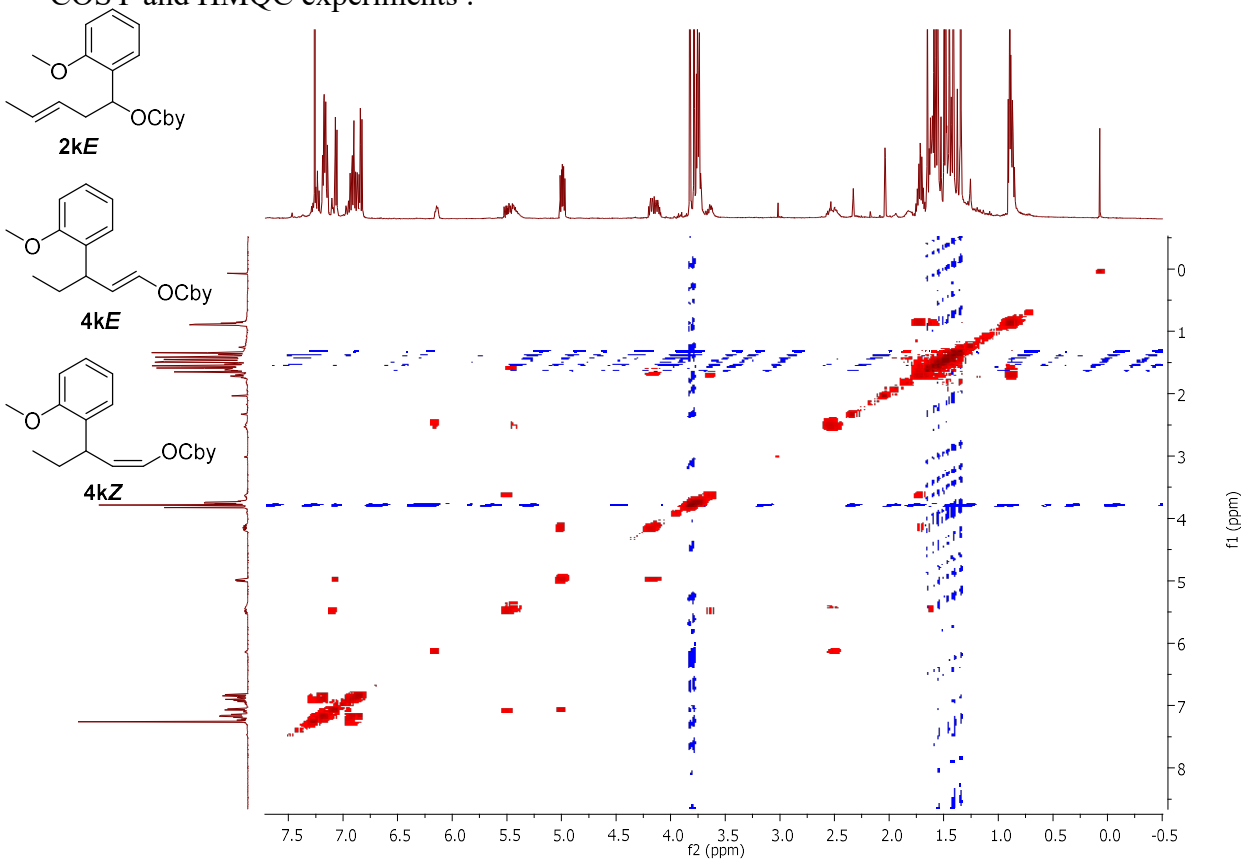


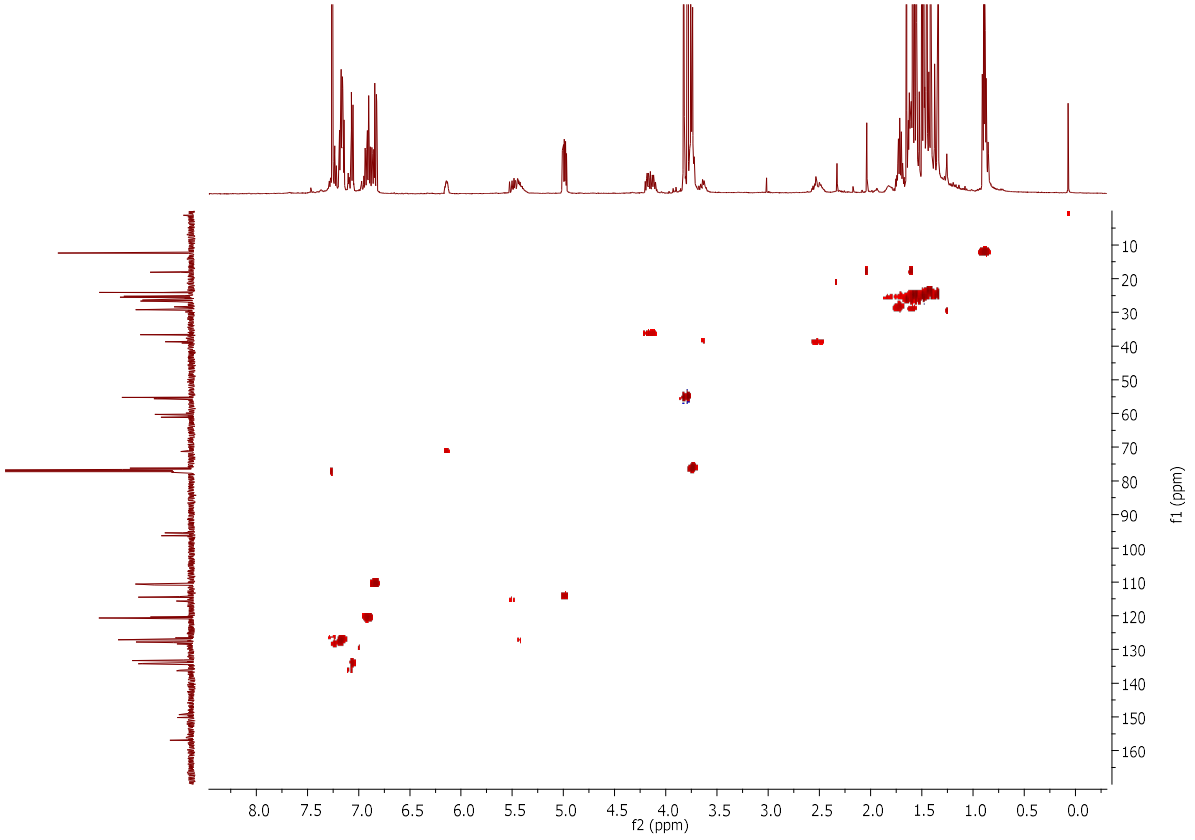

O
OCby
2kE
6.16
6.15
6.14
6.13
5.45
5.45
5.44
5.43
5.42
5.41
5.40
5.39
2.58
2.57
2.56
2.55
2.55
2.54
2.53
2.52
2.50
2.49
2.48
1.00
1.77
2.45
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
OCby
4kE
5.53
5.51
5.50
5.49
5.48
5.47
5.47
5.44
3.66
3.65
3.64
3.63
3.62
3.61
3.61
0.85
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

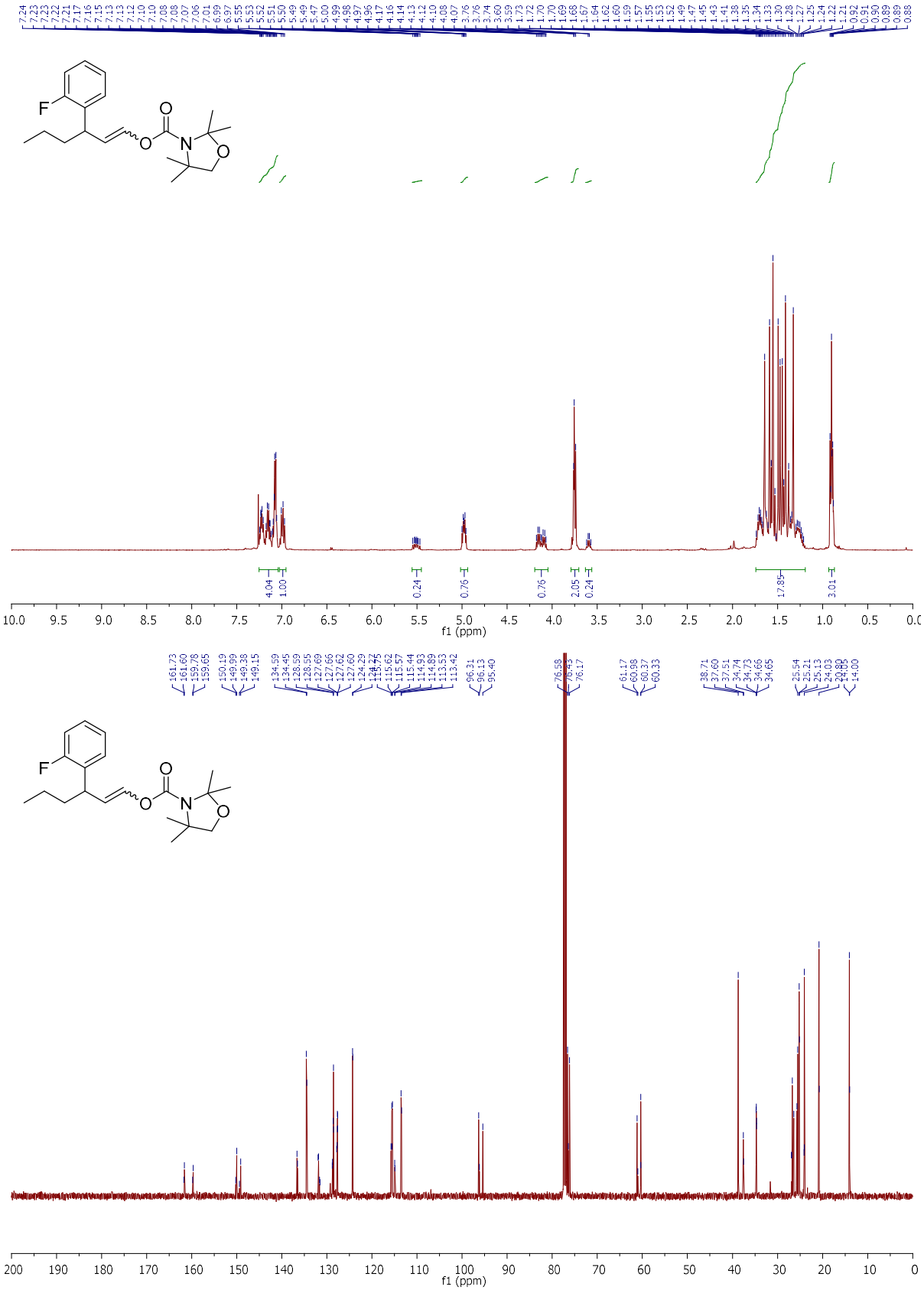

OCby
4kZ
f1 (ppm)

COSY and HMQC experiments :

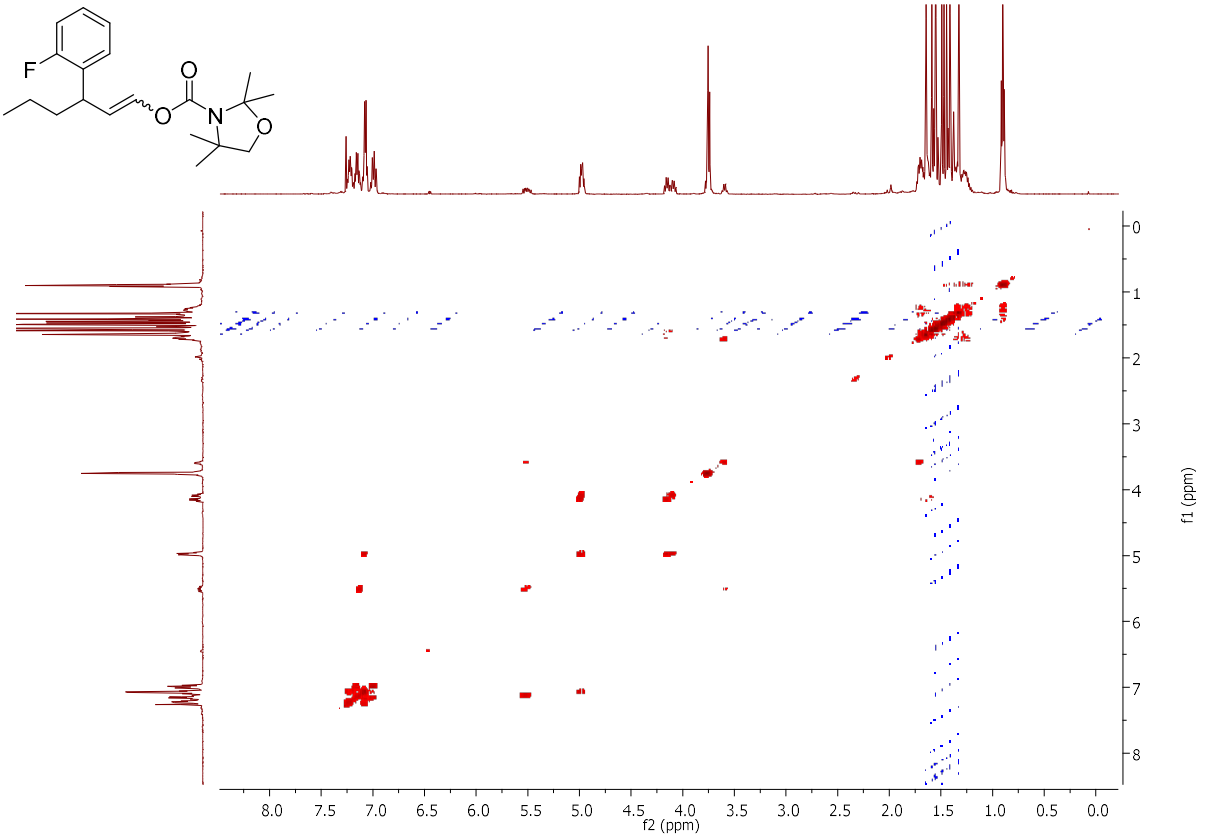


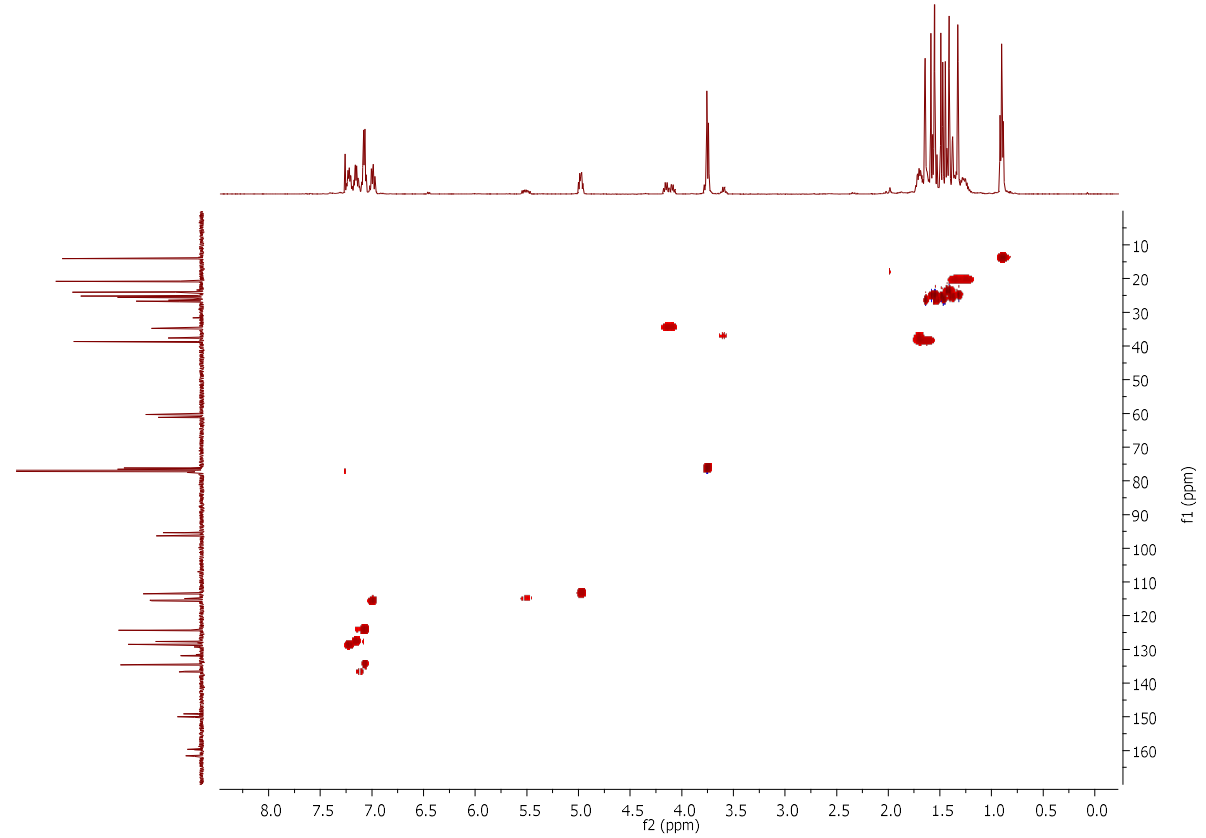


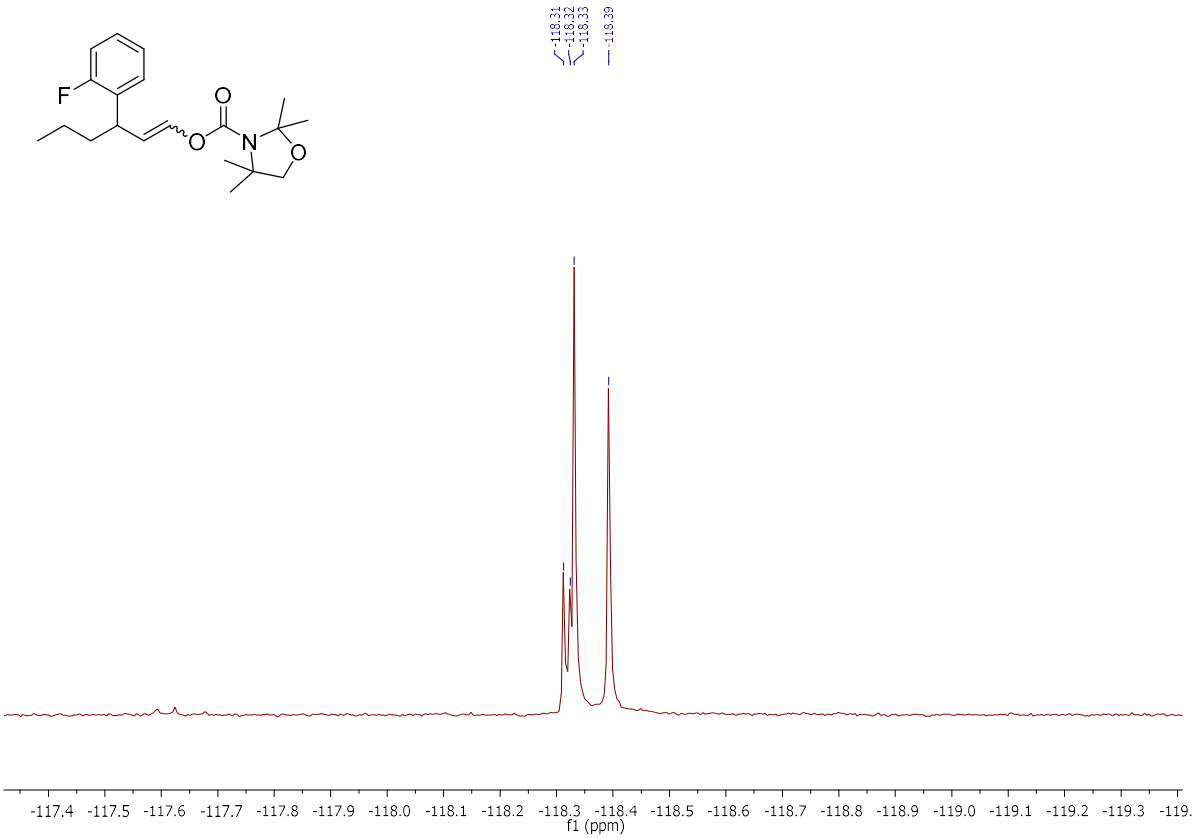
3-(2-fluorophenyl)hex-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4l** :



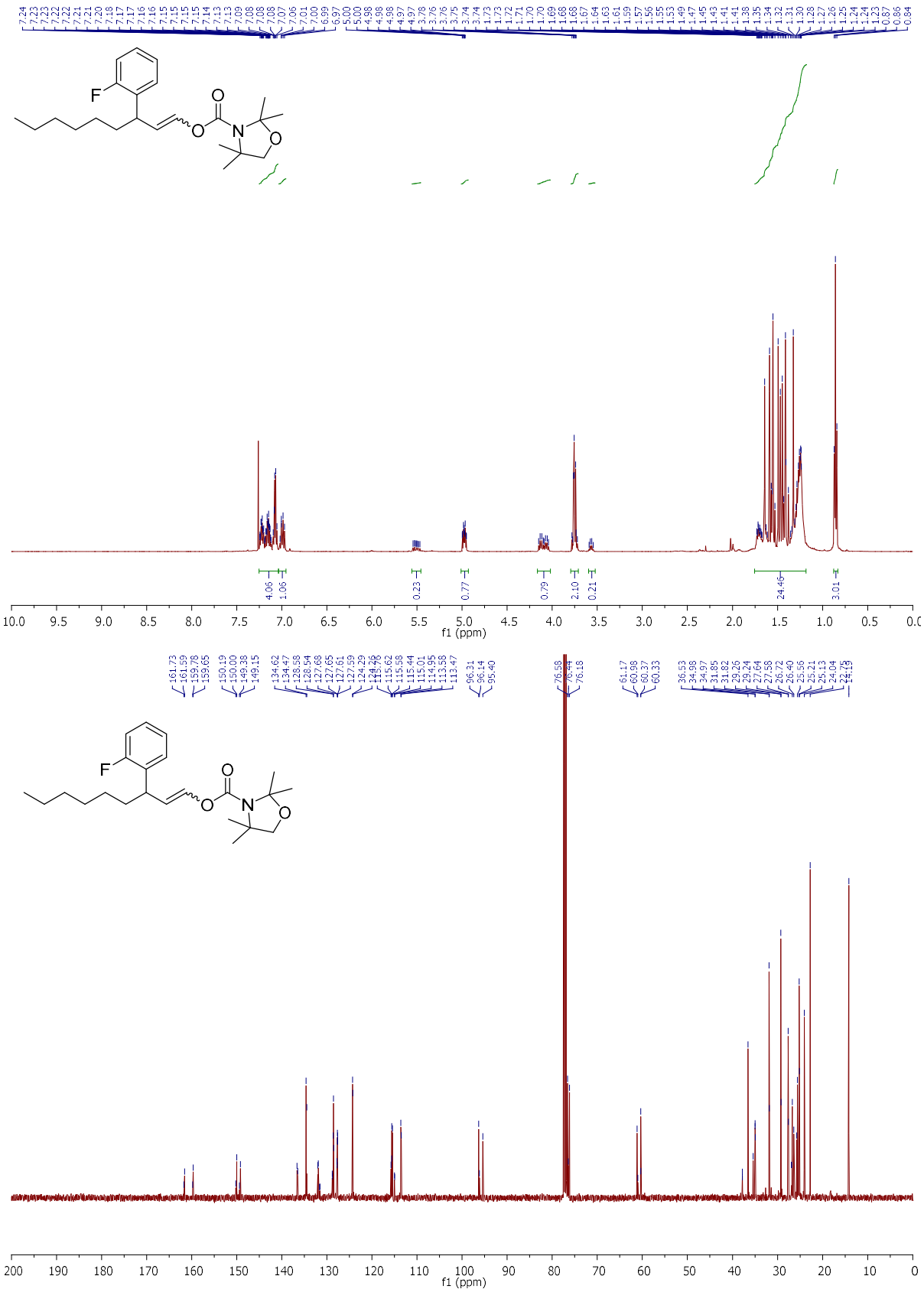
COSY and HMQC experiments :



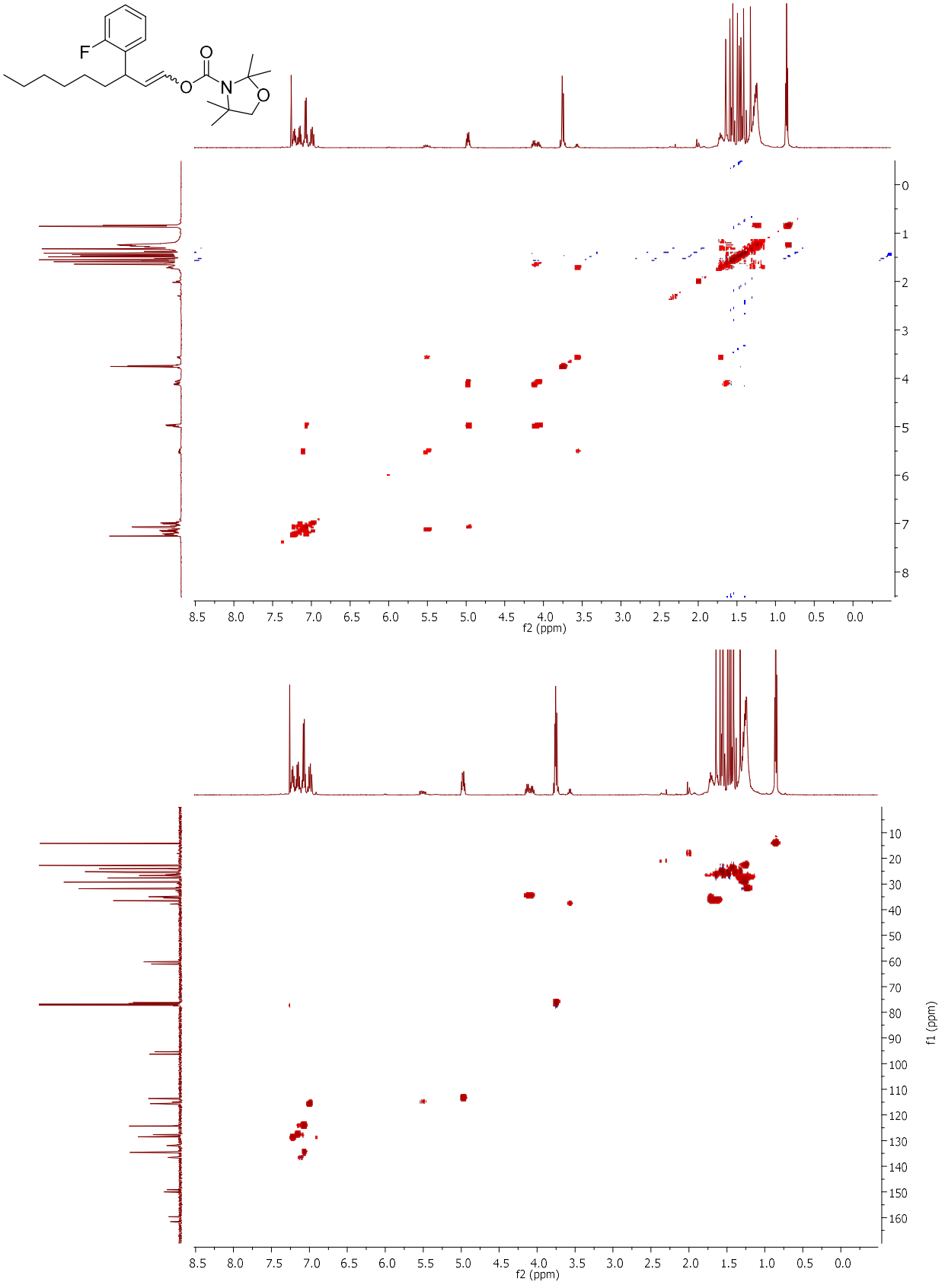


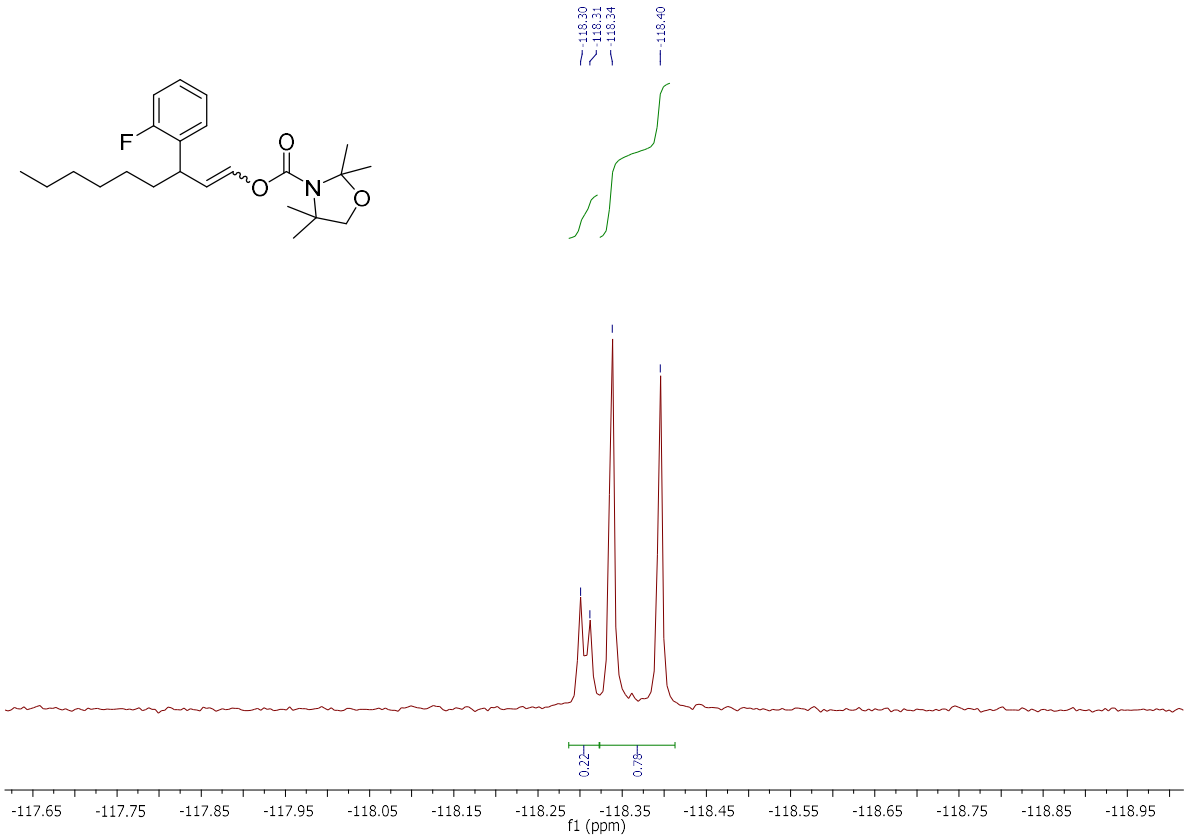

F
O
O
N
O
-118.31
-118.32
-118.33
-118.39
-117.4 -117.5 -117.6 -117.7 -117.8 -117.9 -118.0 -118.1 -118.2 -118.3 -118.4 -118.5 -118.6 -118.7 -118.8 -118.9 -119.0 -119.1 -119.2 -119.3 -119.
f1 (ppm)

3-(2-fluorophenyl)non-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **4m** :

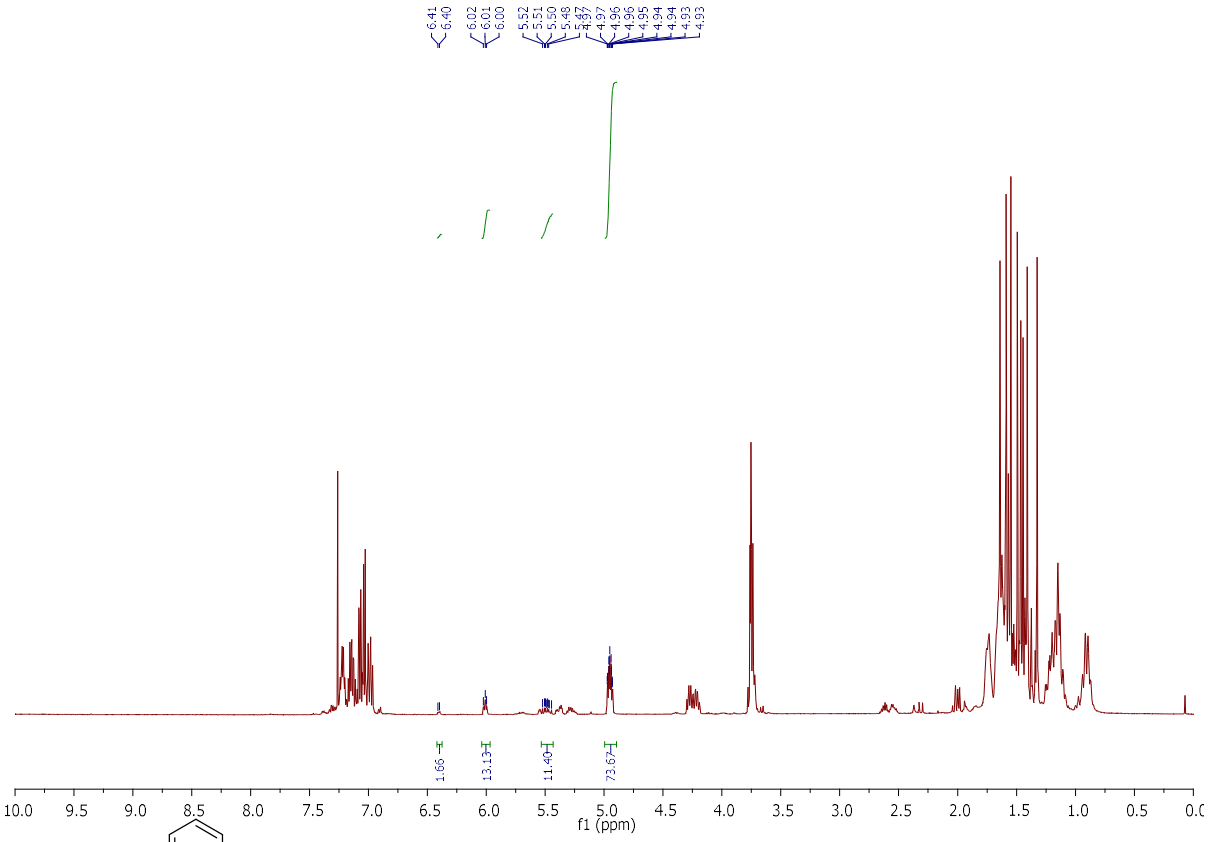


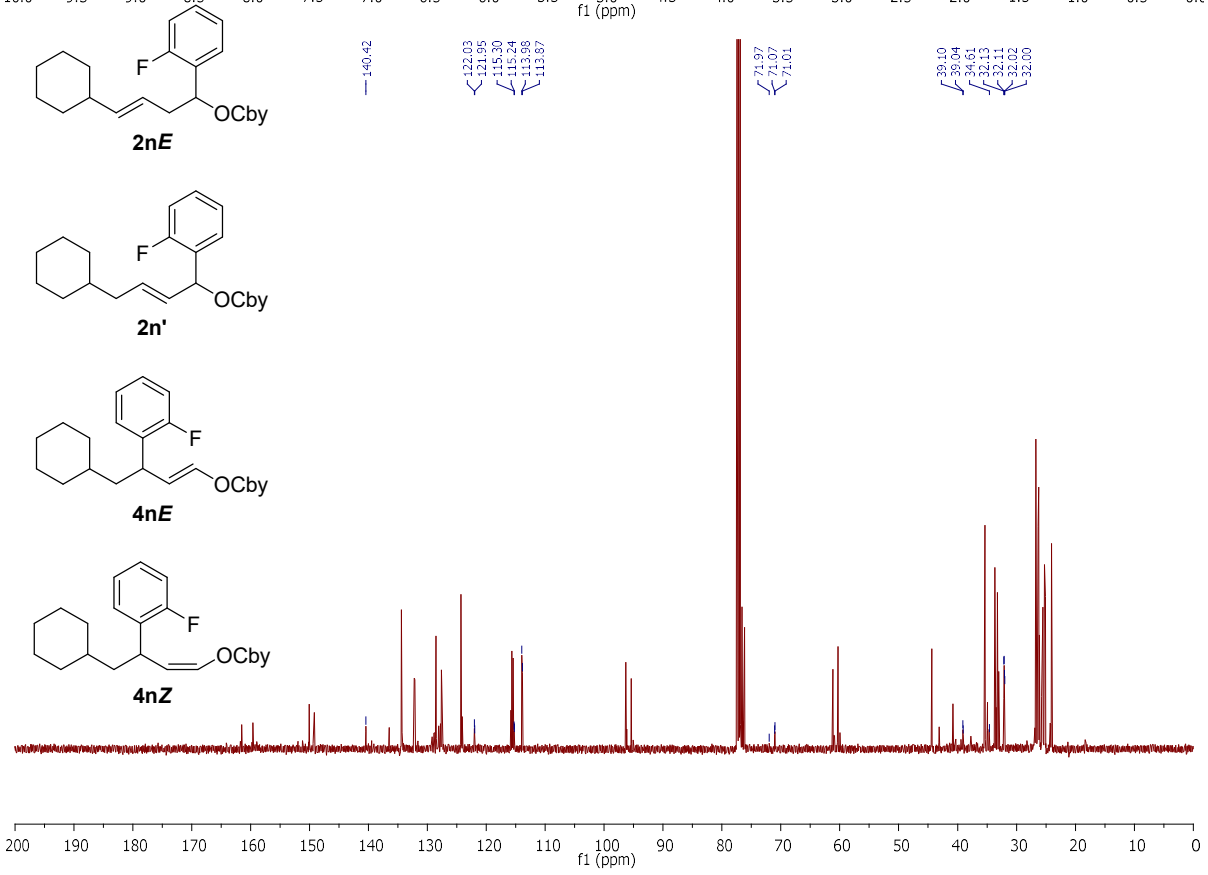
COSY and HMQC experiments :

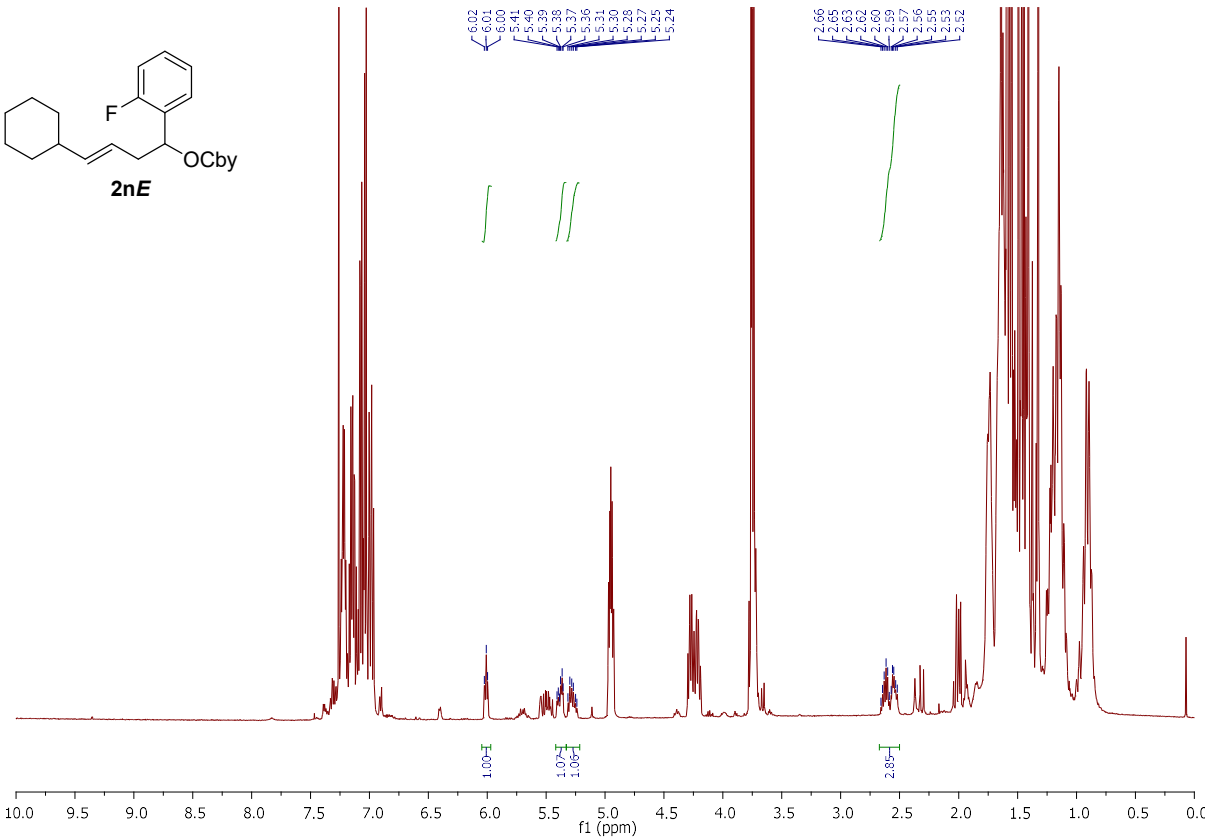


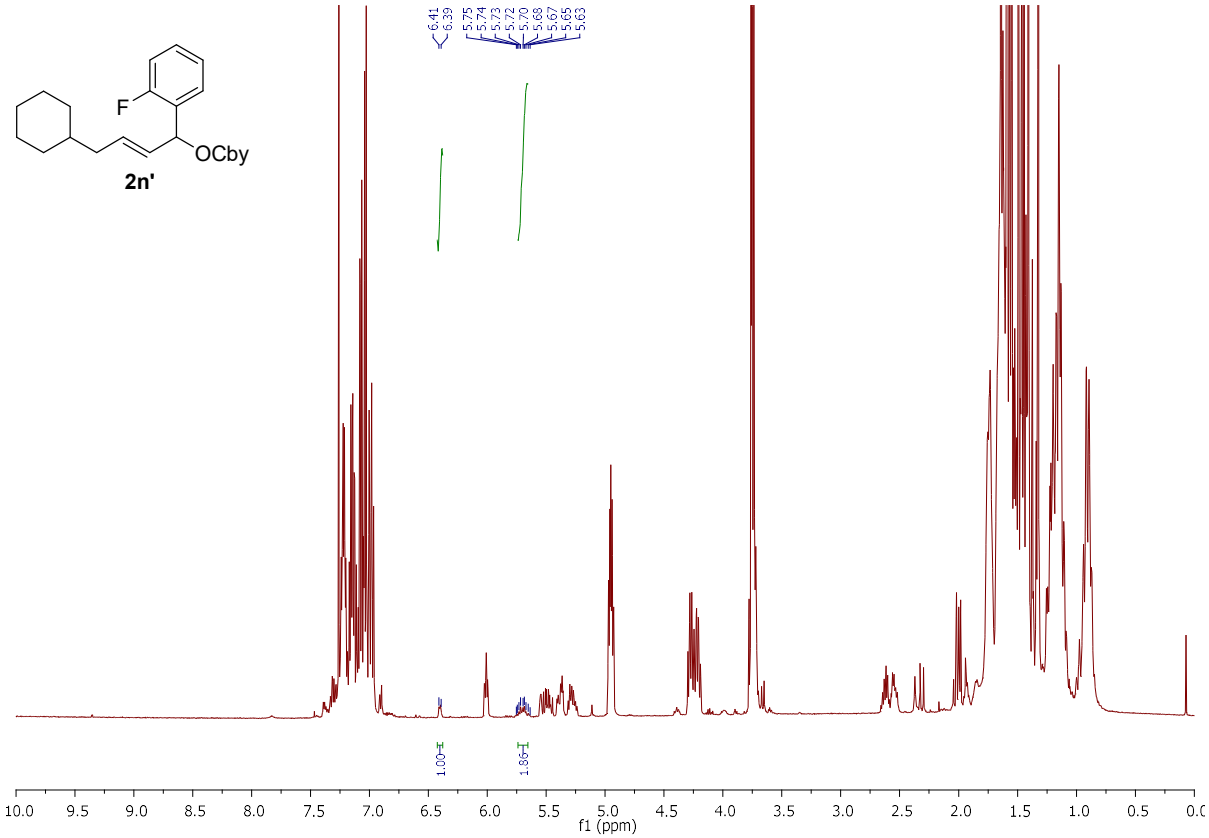

F
O
O
N
O
-118.30
-118.31
-118.34
-118.40
0.22
0.79
-117.65
-117.75
-117.85
-117.95
-118.05
-118.15
-118.25
-118.35
-118.45
-118.55
-118.65
-118.75
-118.85
-118.95
f1 (ppm)

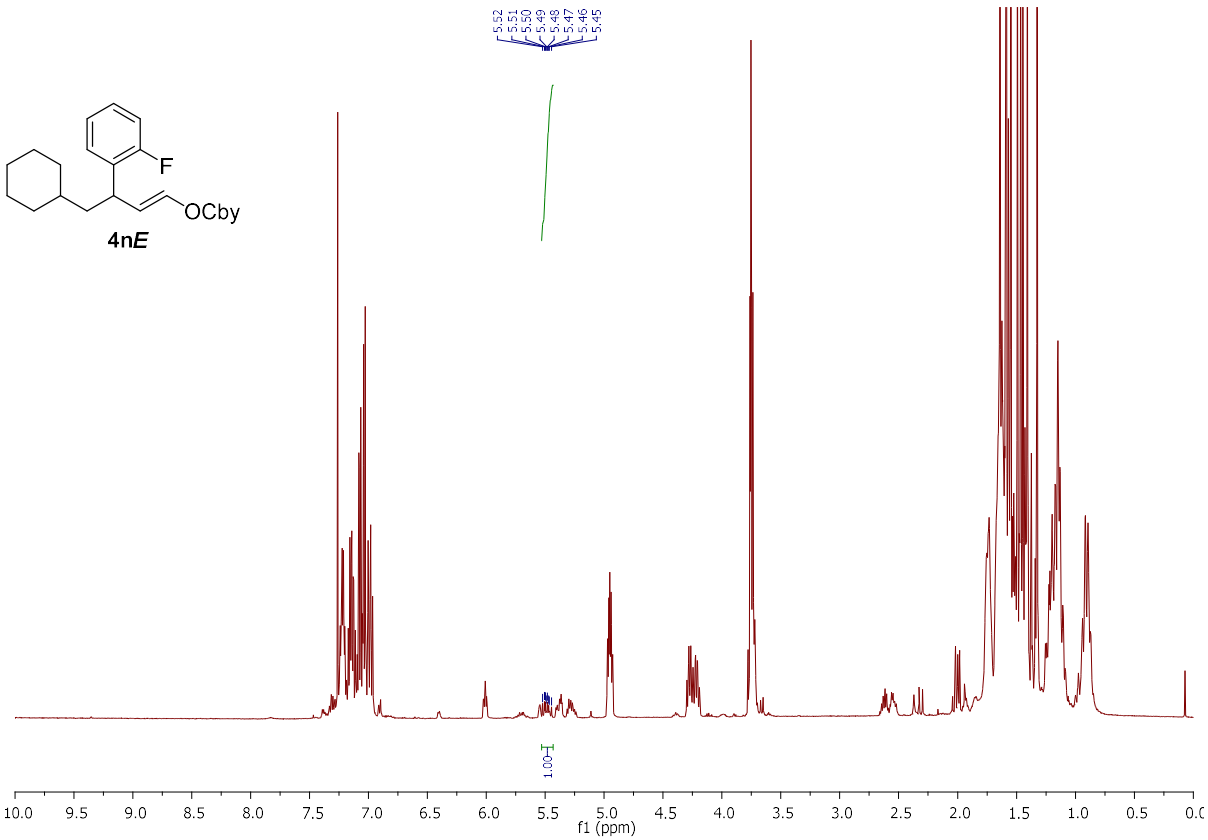
Arylation of **1n** : products **4n** and isomers :

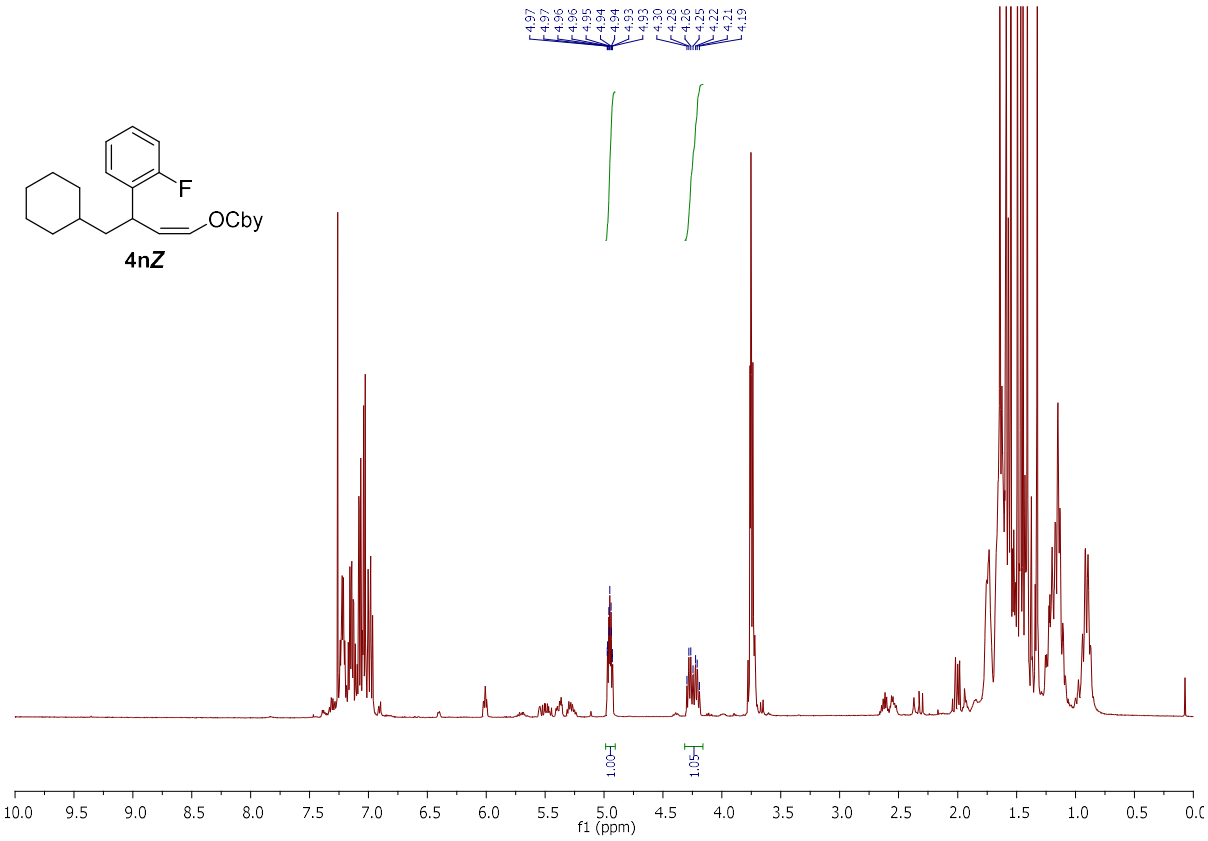




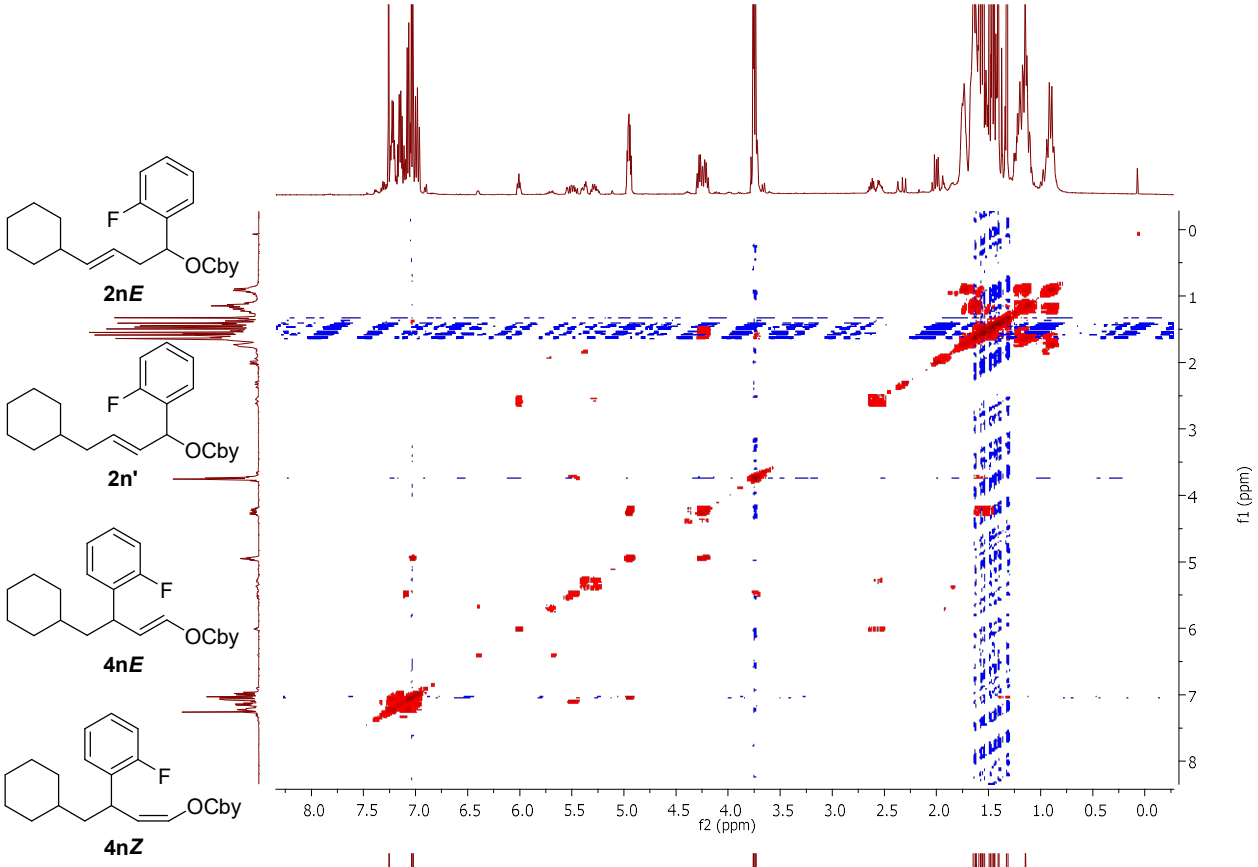

F
OCby
2nE
6.02
6.01
6.00
5.41
5.40
5.39
5.38
5.37
5.36
5.31
5.30
5.28
5.27
5.25
5.24
2.66
2.65
2.63
2.62
2.60
2.59
2.57
2.56
2.55
2.53
2.52
1.00
1.07
1.06
2.85
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

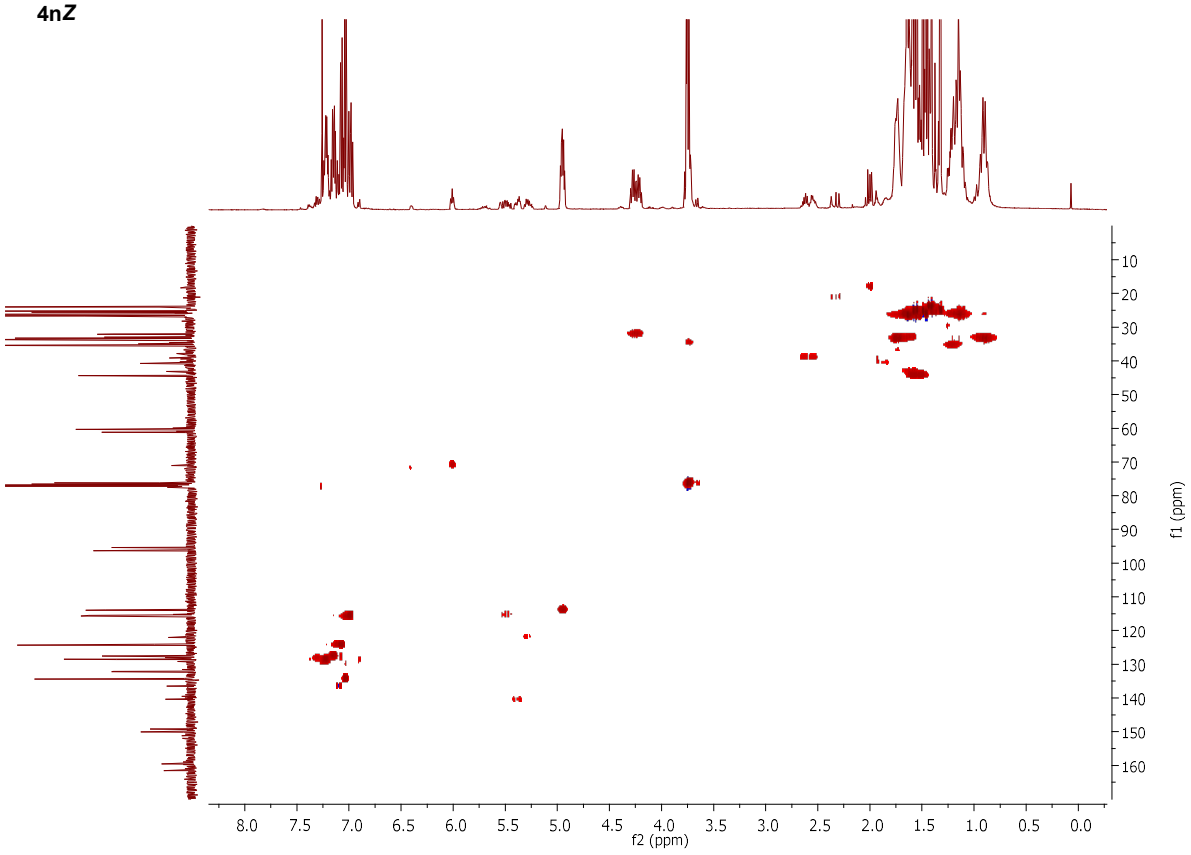

F
OCby
2n'
6.41
6.39
5.75
5.74
5.73
5.72
5.70
5.68
5.67
5.65
5.63
1.00
1.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

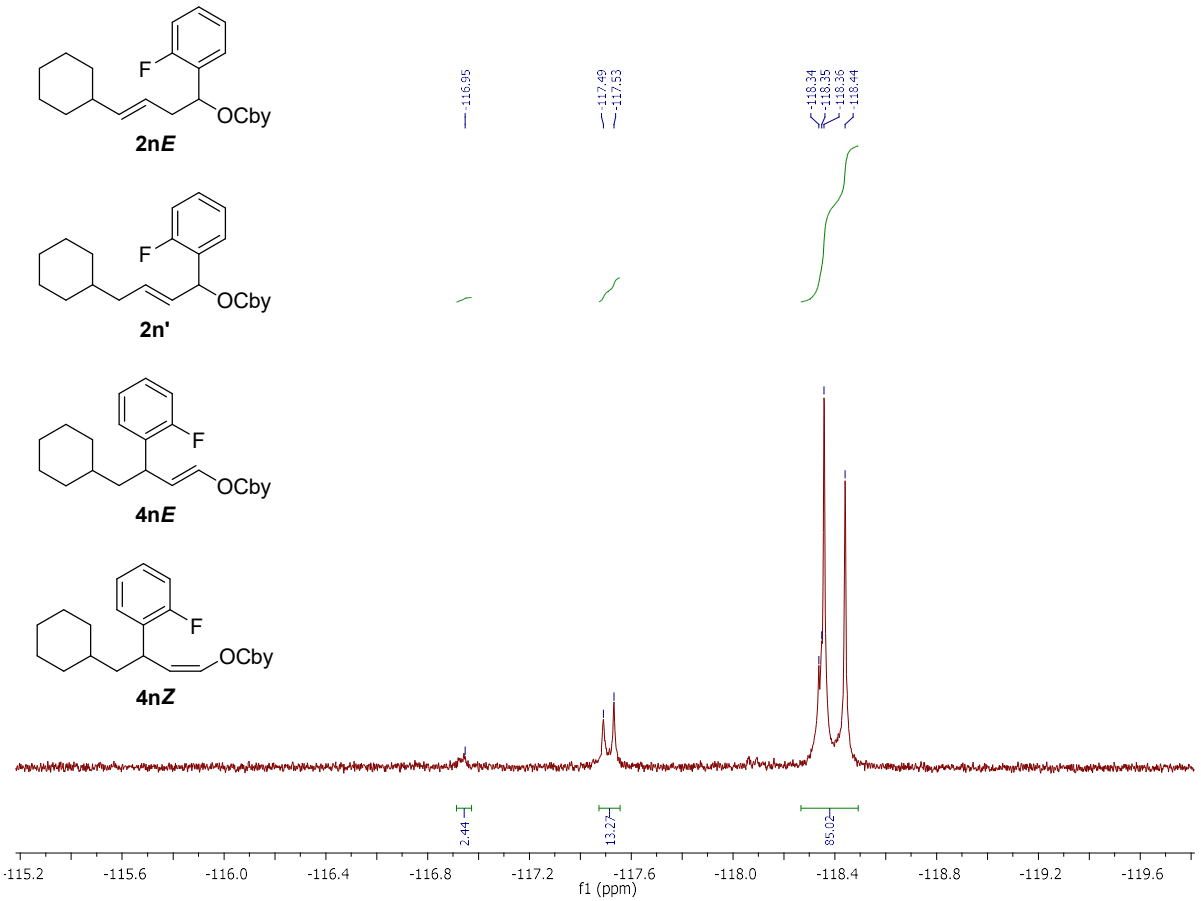

F
OCby
4n*E*
5.52
5.51
5.50
5.49
5.48
5.47
5.46
5.45
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


F
OCby
4n*Z*
4.97
4.97
4.96
4.96
4.95
4.94
4.94
4.93
4.93
4.30
4.28
4.26
4.25
4.22
4.21
4.19
1.00
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

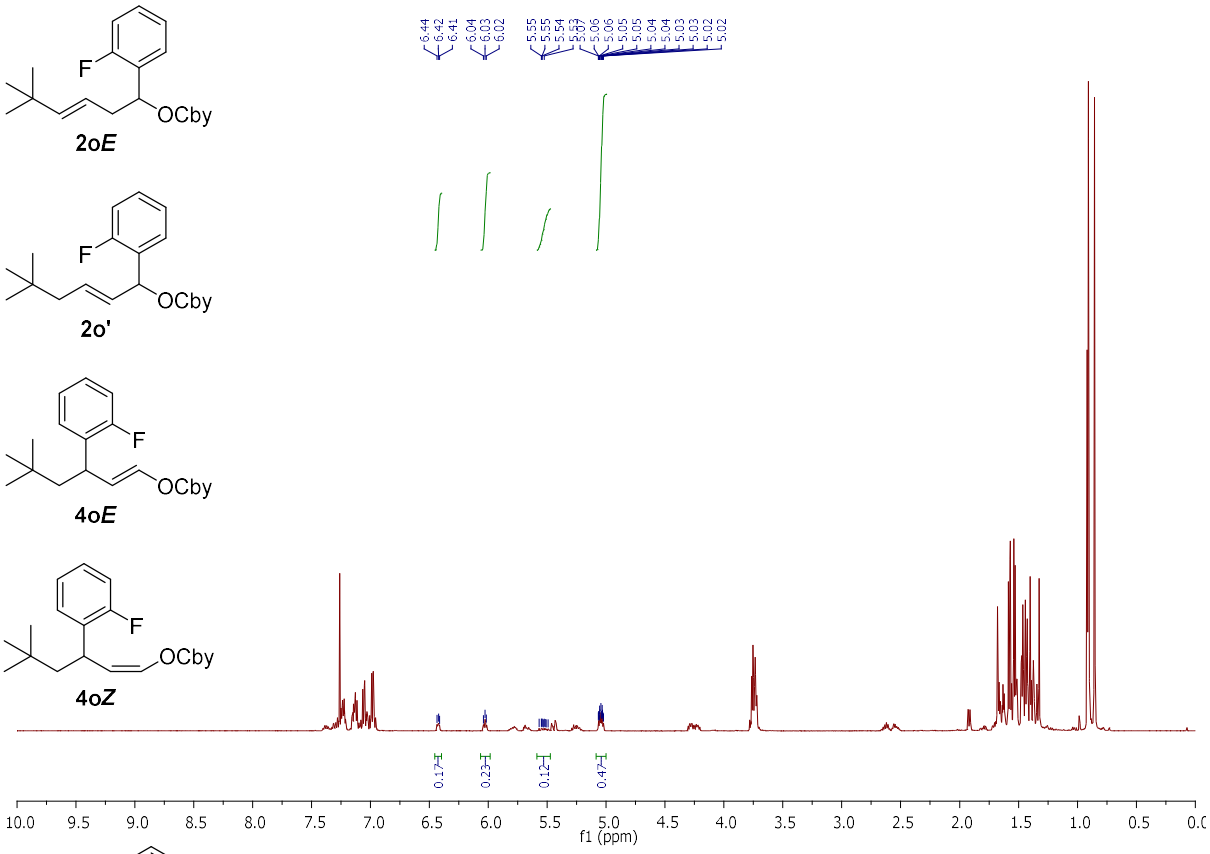
COSY and HMQC experiments :

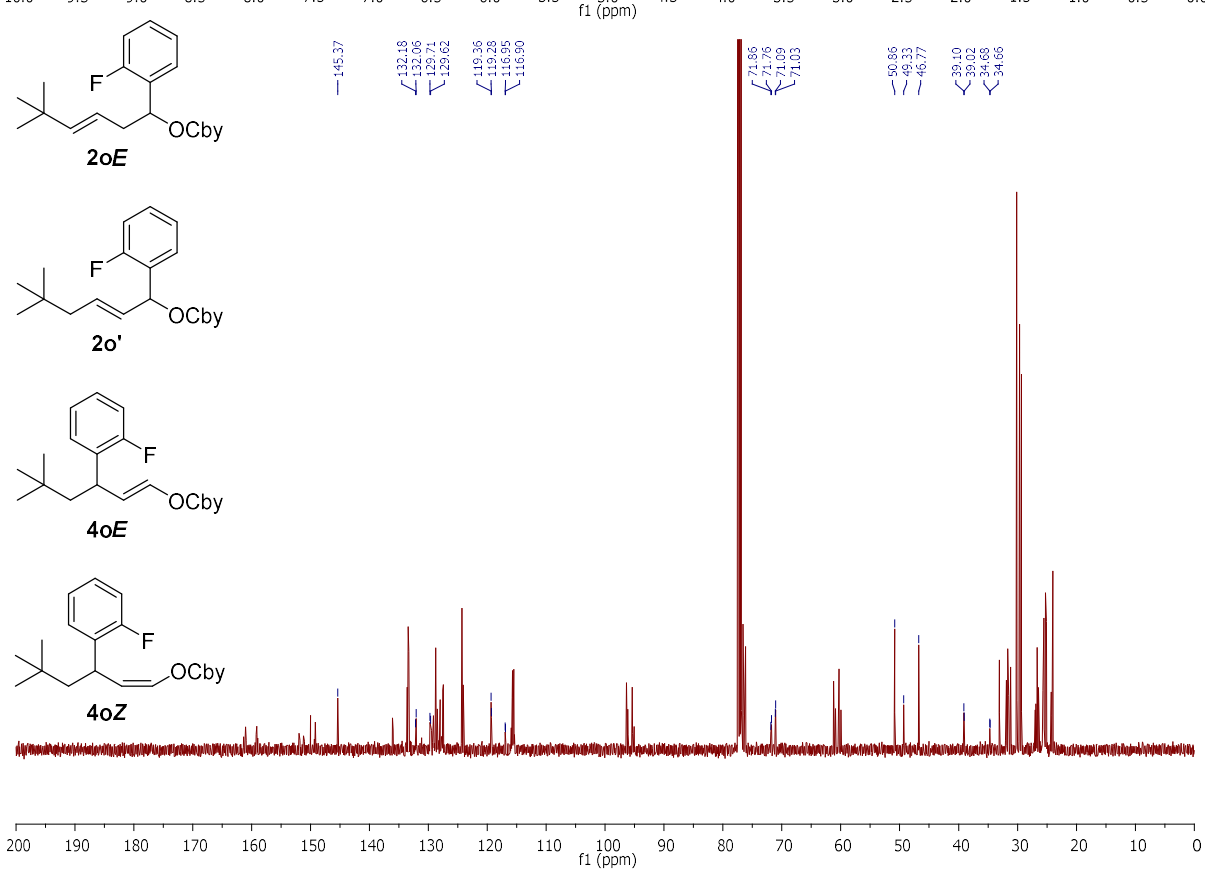


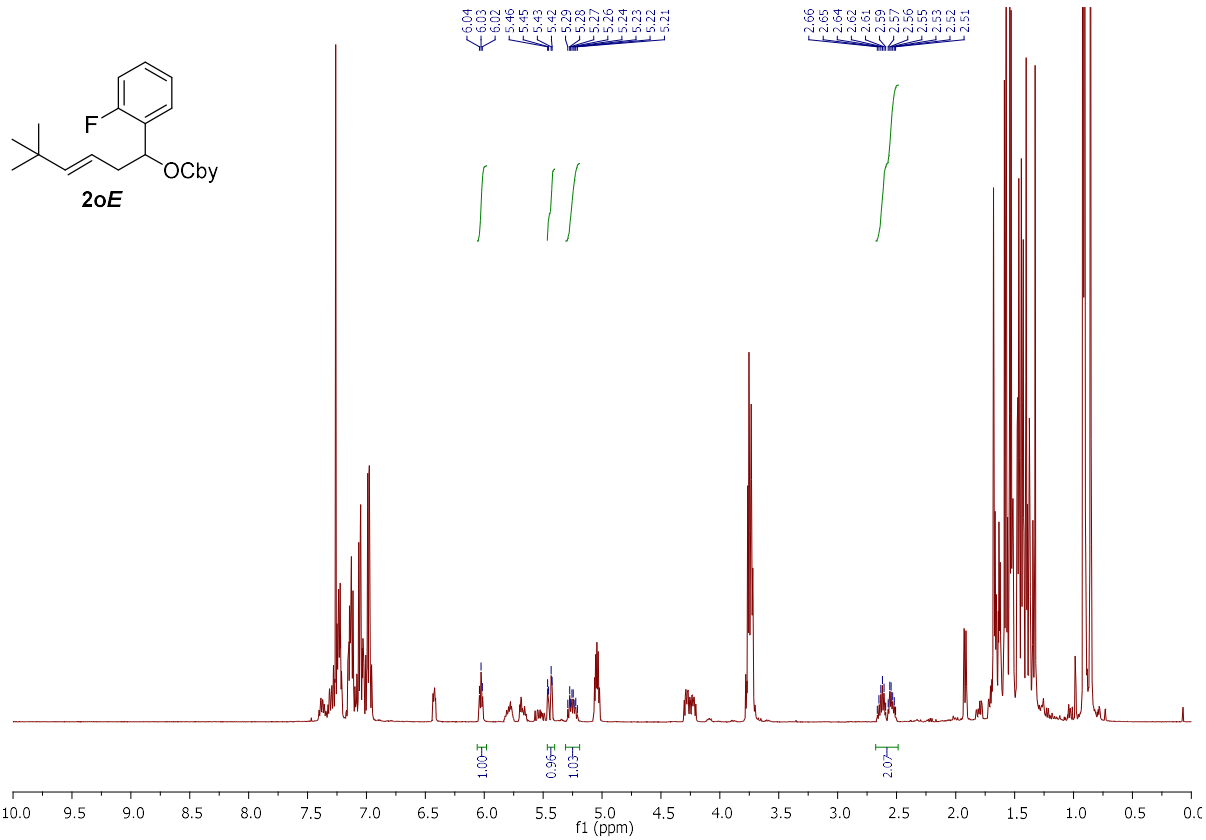


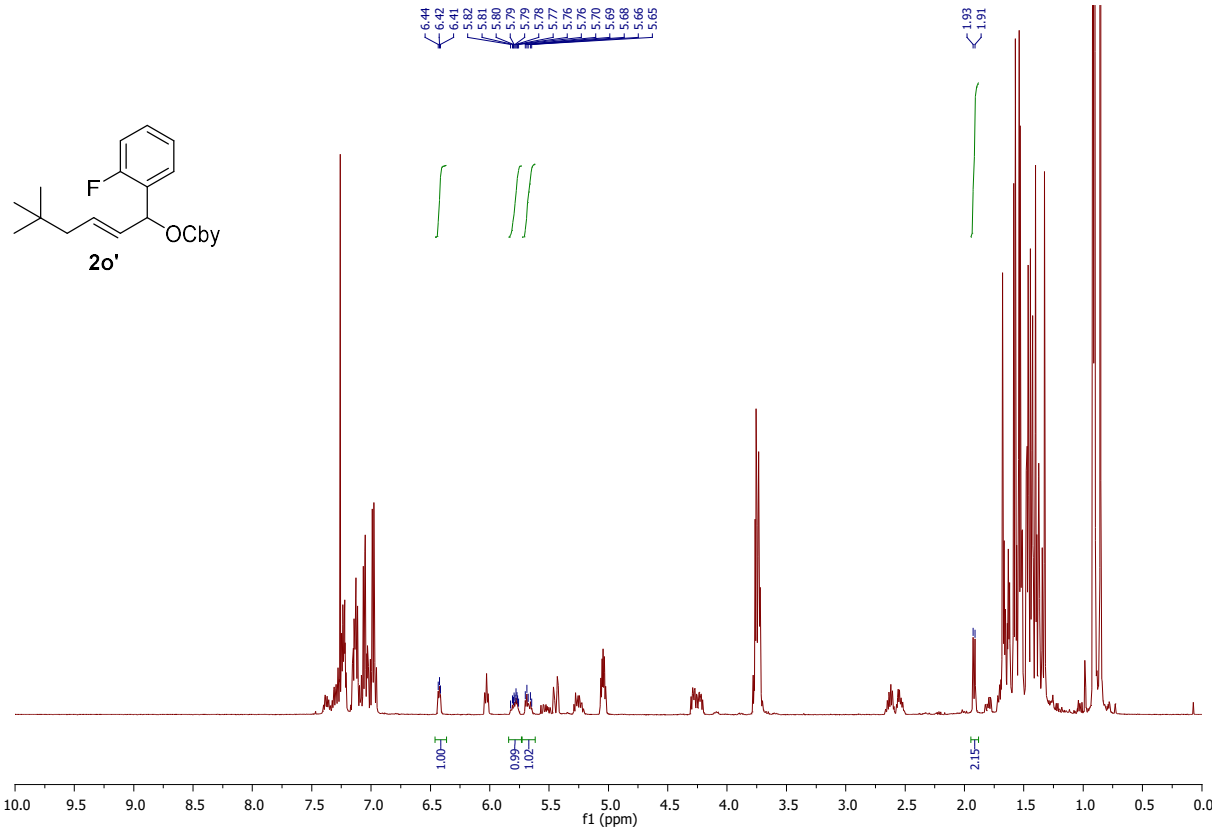

F
OCby
2nE
F
OCby
2n'
F
OCby
4nE
F
OCby
4nZ
-116.95
-117.49
-117.53
-118.34
-118.35
-118.36
-118.44
2.44
13.27
85.02
-115.2
-115.6
-116.0
-116.4
-116.8
-117.2
-117.6
-118.0
-118.4
-118.8
-119.2
-119.6
f1 (ppm)

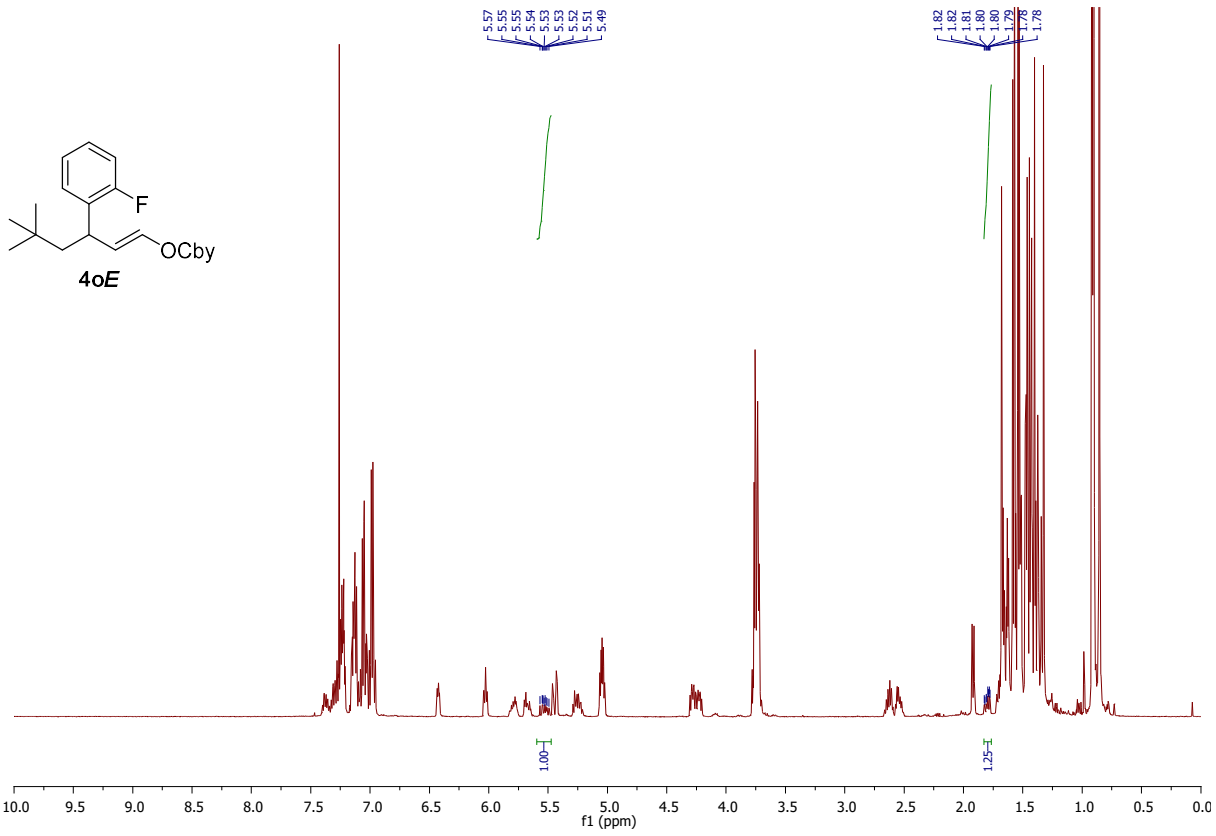
Arylation of **1o** : products **4o**and isomers :

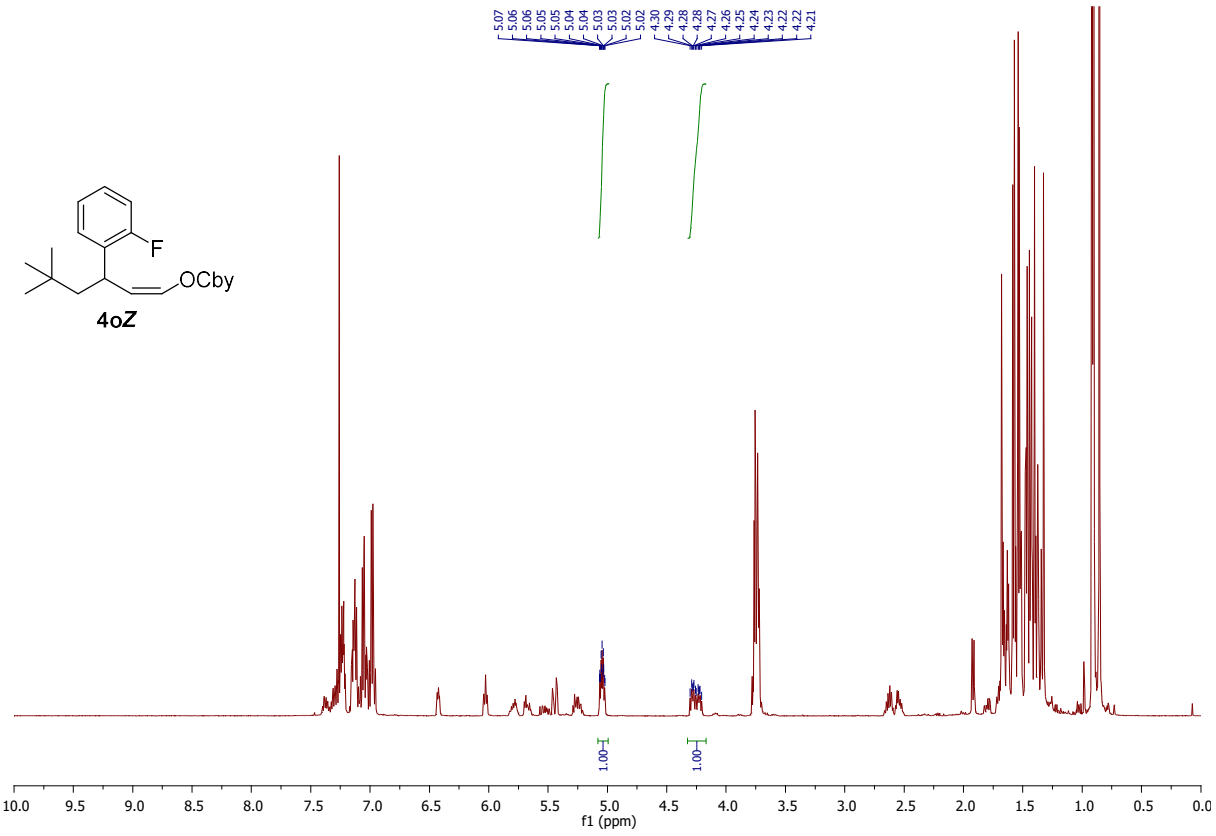




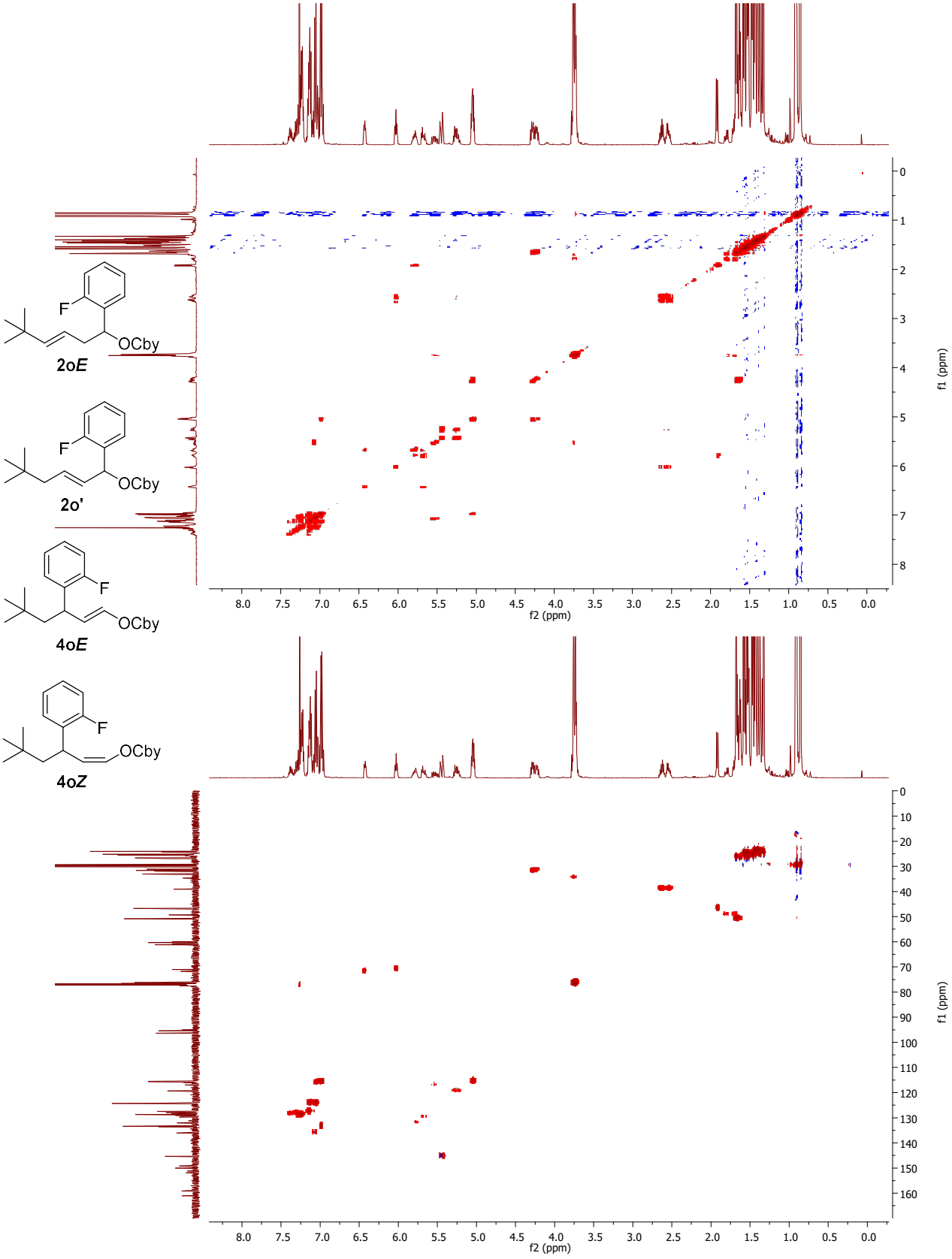

F
OCby
2oE
f1 (ppm)

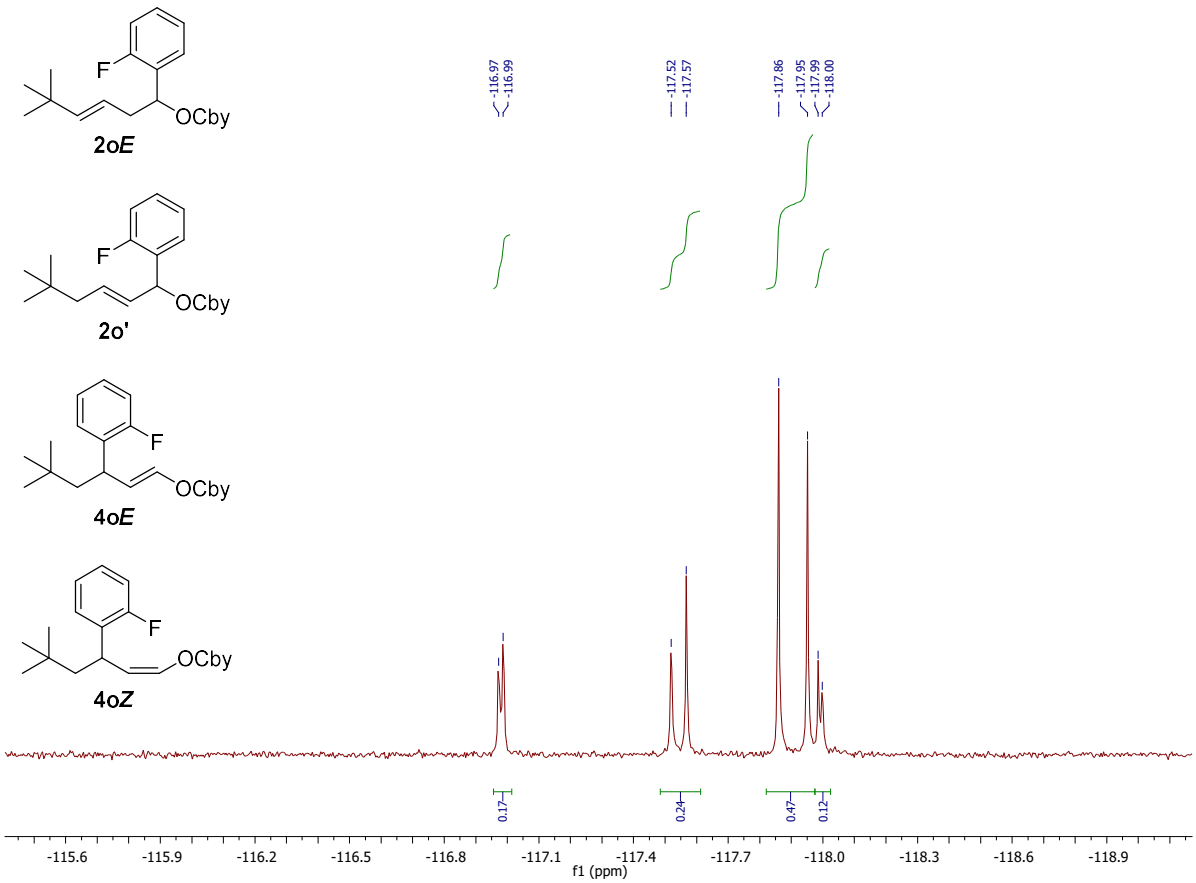

F
OCby
2o'
f1 (ppm)


F
OCby
4oE
5.57
5.55
5.55
5.54
5.53
5.53
5.52
5.51
5.49
1.82
1.82
1.81
1.80
1.80
1.79
1.78
1.78
1.00
1.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

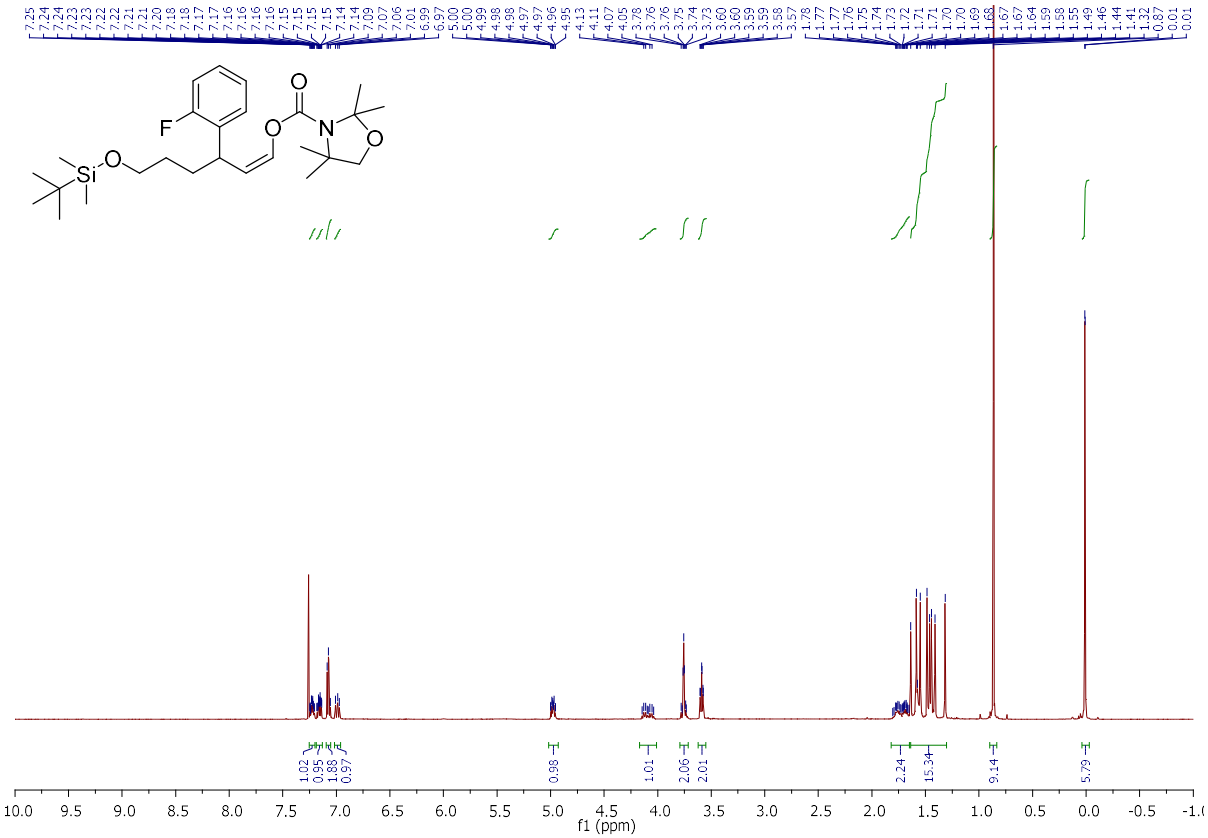

F
OCby
4oZ
5.07
5.06
5.06
5.05
5.05
5.04
5.04
5.03
5.03
5.02
5.02
4.30
4.29
4.28
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.22
4.21
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

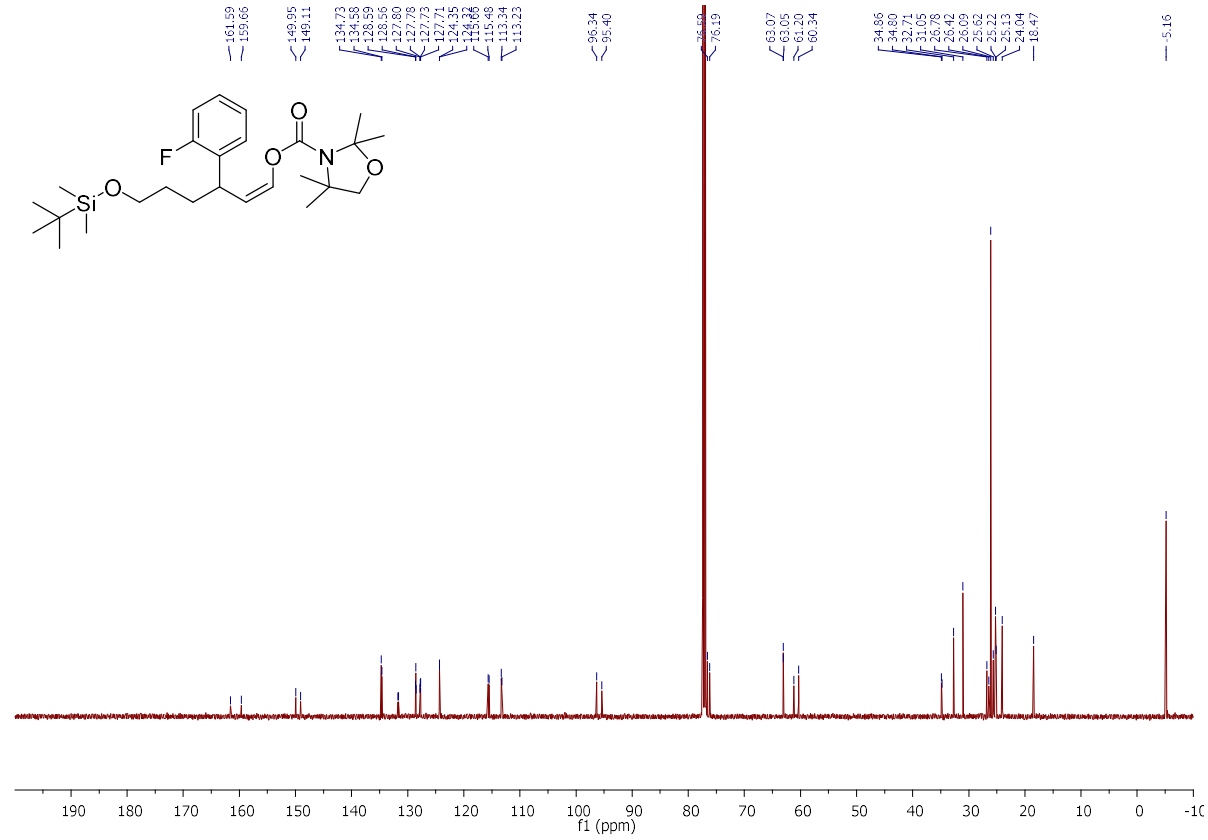
COSY and HMQC experiments :



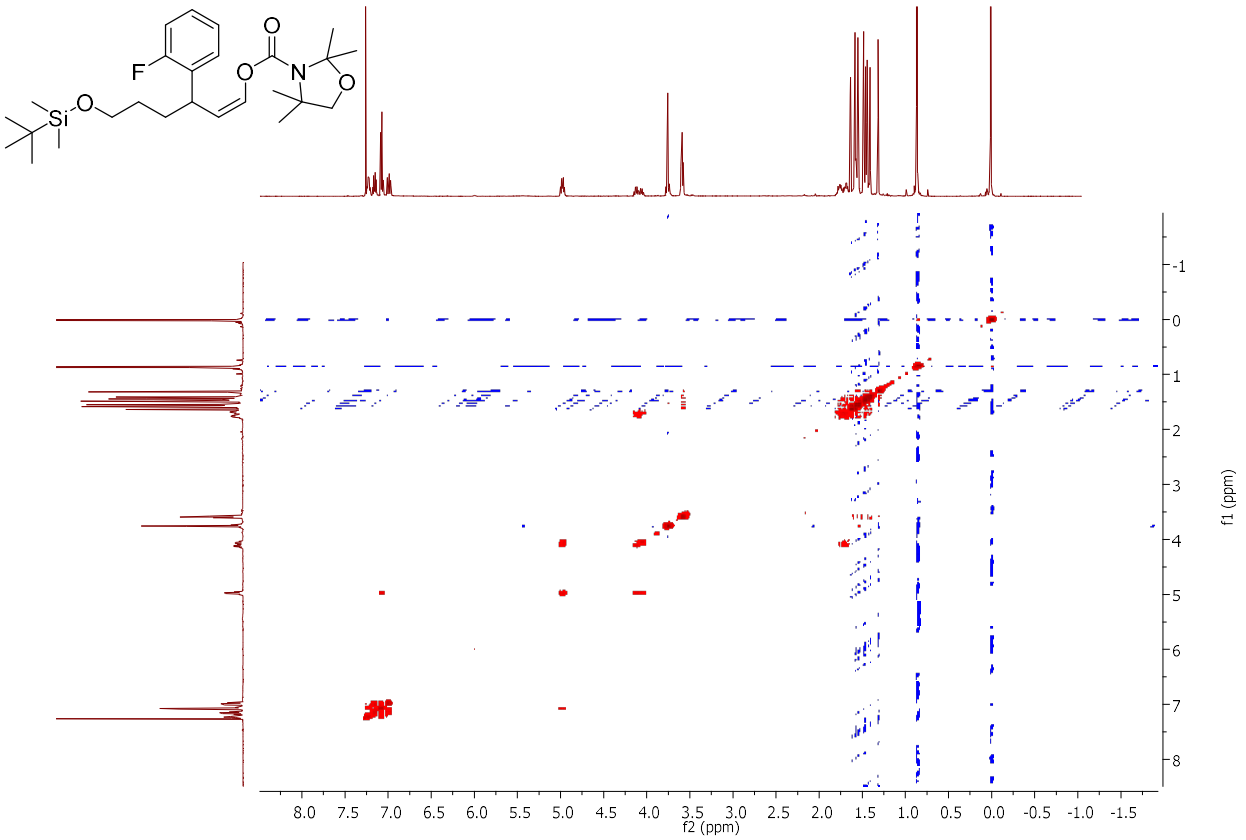

F
OCby
2oE
F
OCby
2o'
F
OCby
4oE
F
OCby
4oZ
-116.97
-116.99
-117.52
-117.57
-117.86
-117.95
-117.99
-118.00
0.17
0.24
0.47
0.12
-115.6
-115.9
-116.2
-116.5
-116.8
-117.1
-117.4
-117.7
-118.0
-118.3
-118.6
-118.9
f1 (ppm)

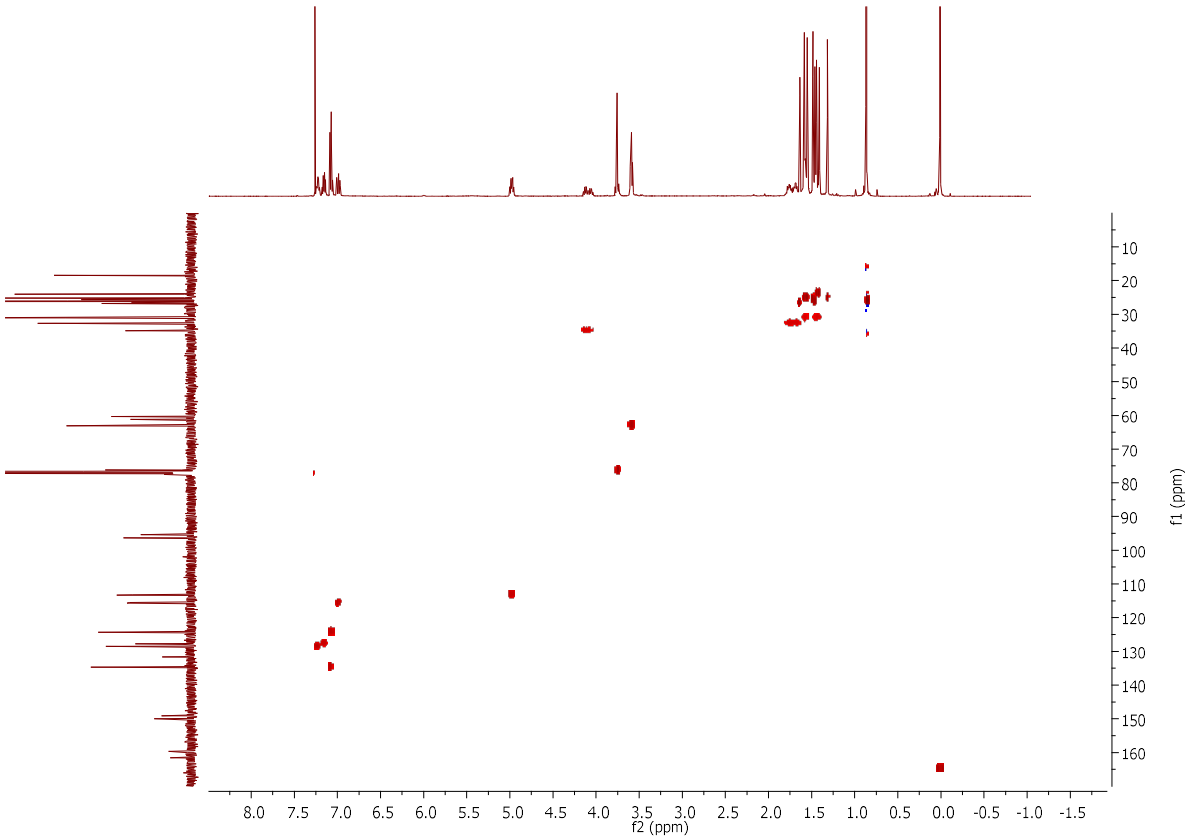
(*Z*)-6-((tert-butyldimethylsilyl)oxy)-3-(2-fluorophenyl)hex-1-en-1-yl2,2,4,4-tetramethyloxazolidine-3-carboxylate **4p** :

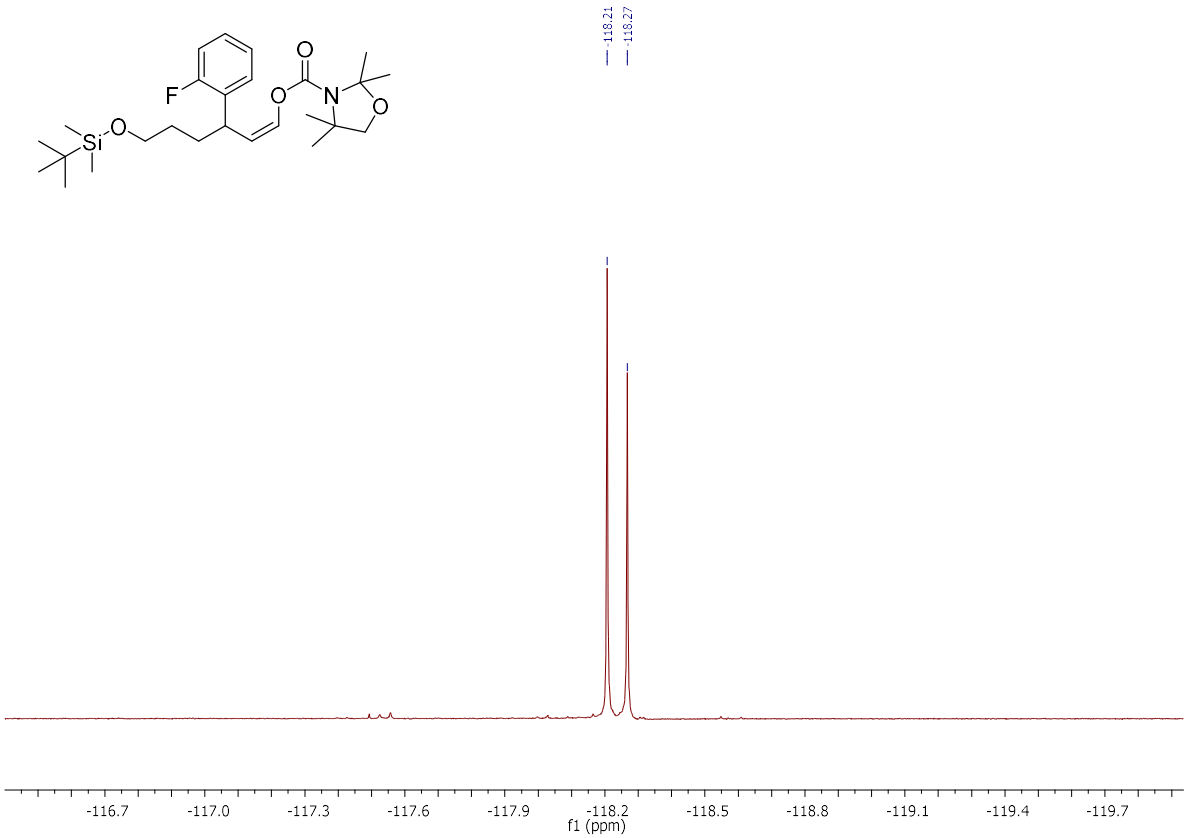




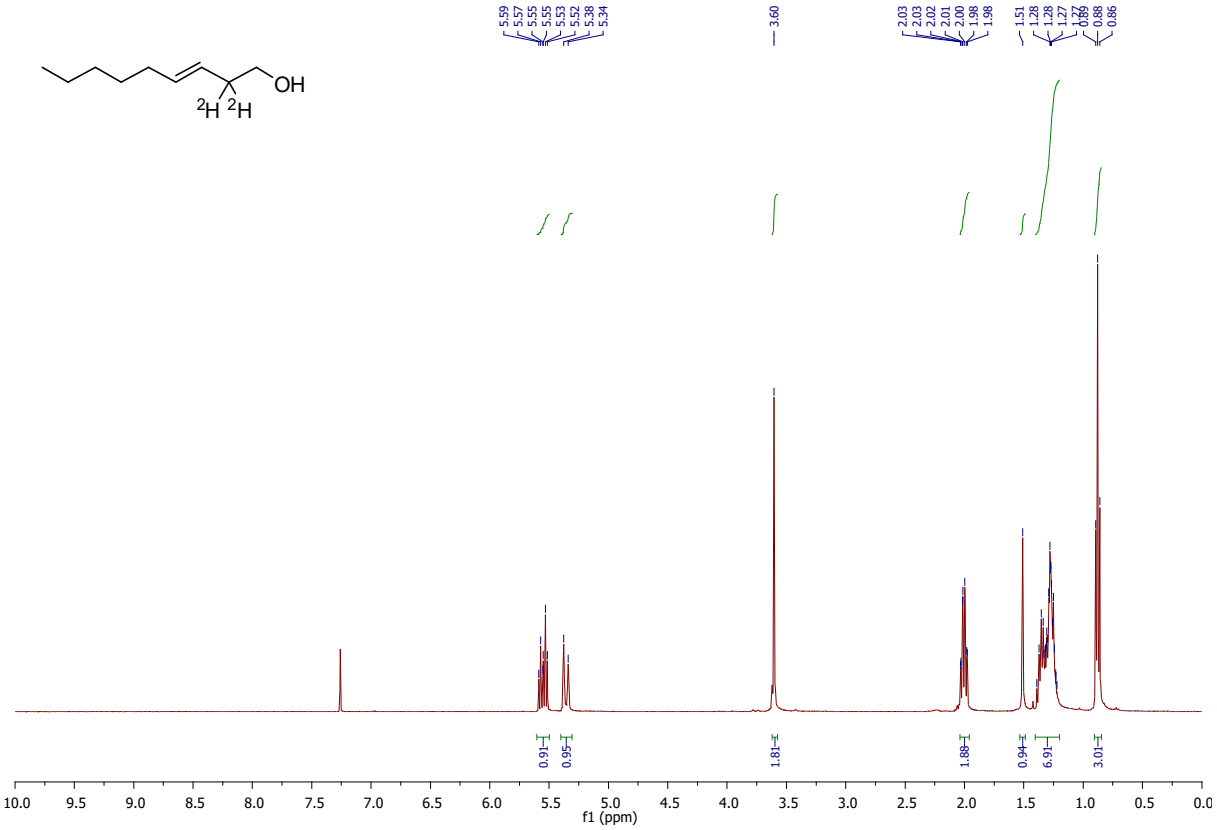
COSY and HMQC experiments :

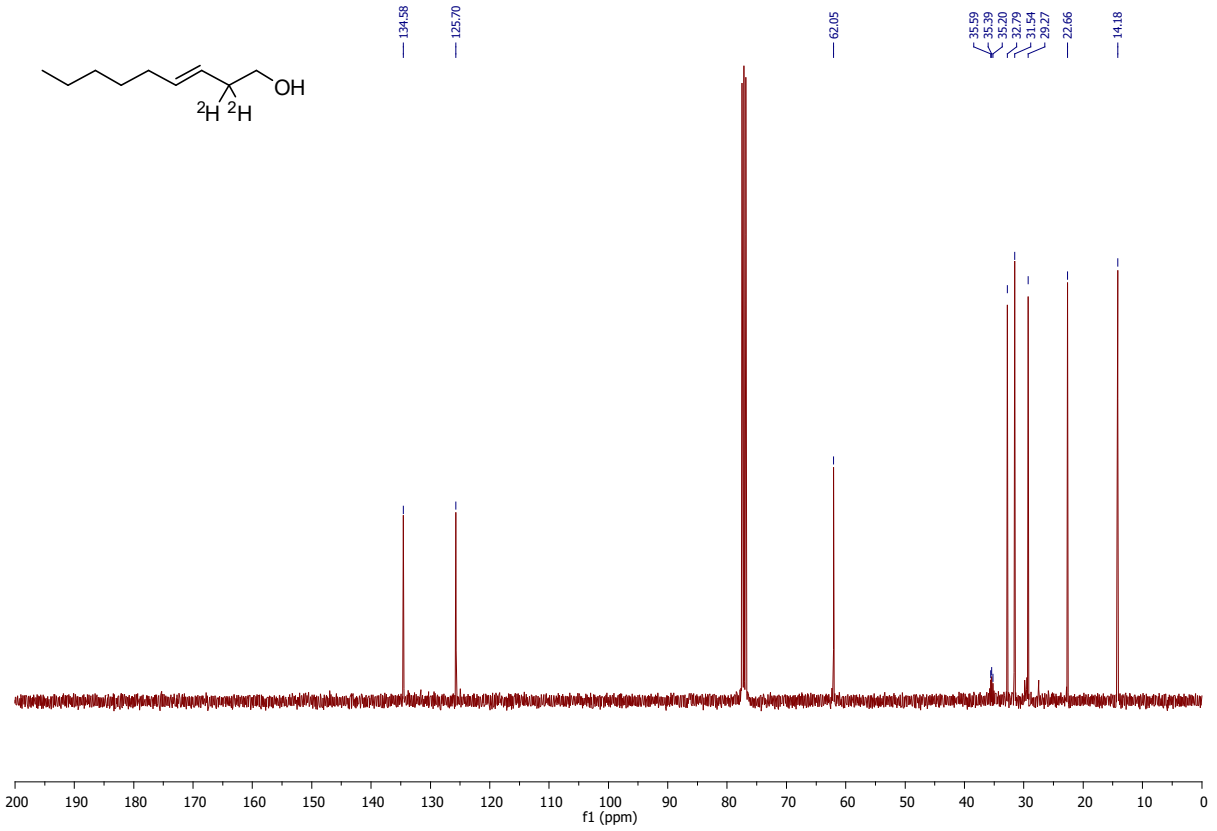




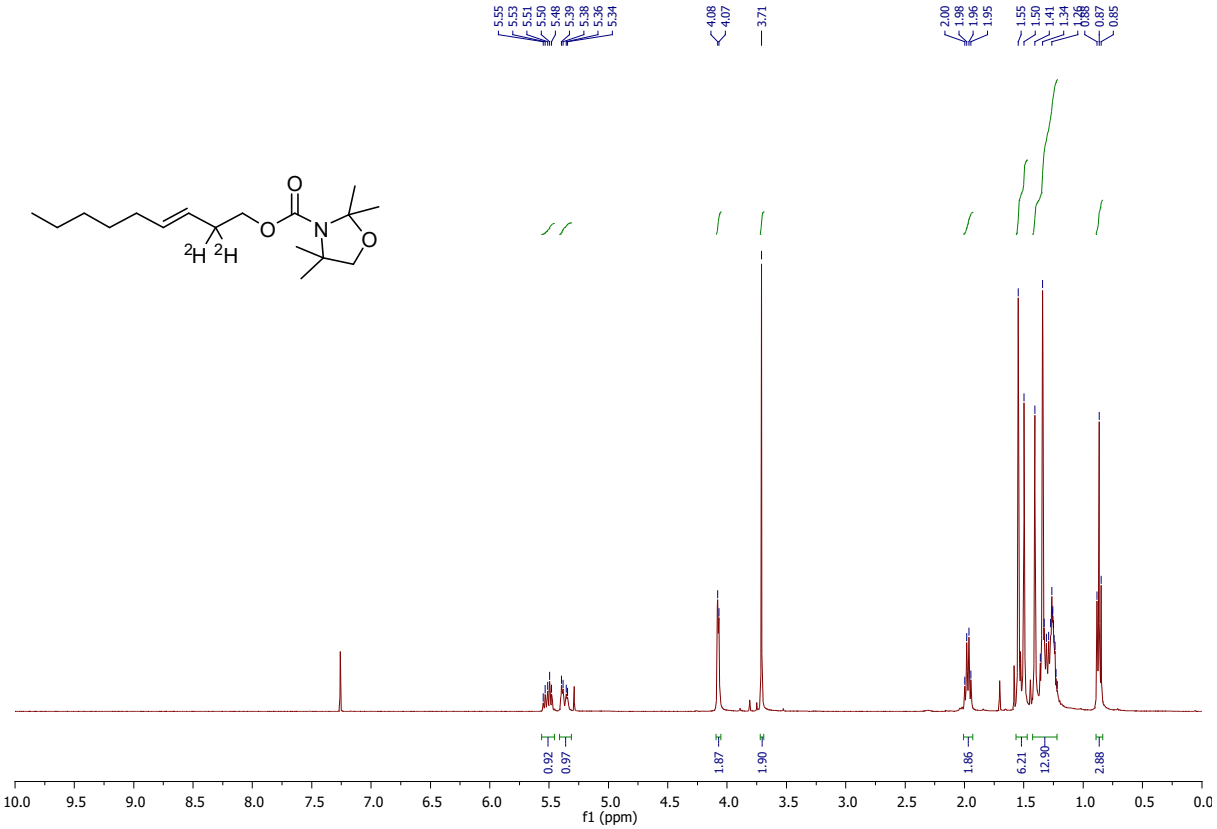

F
O
O
N
O
Si
O
-118.21
-118.27
-116.7
-117.0
-117.3
-117.6
-117.9
-118.2
-118.5
-118.8
-119.1
-119.4
-119.7
f1 (ppm)

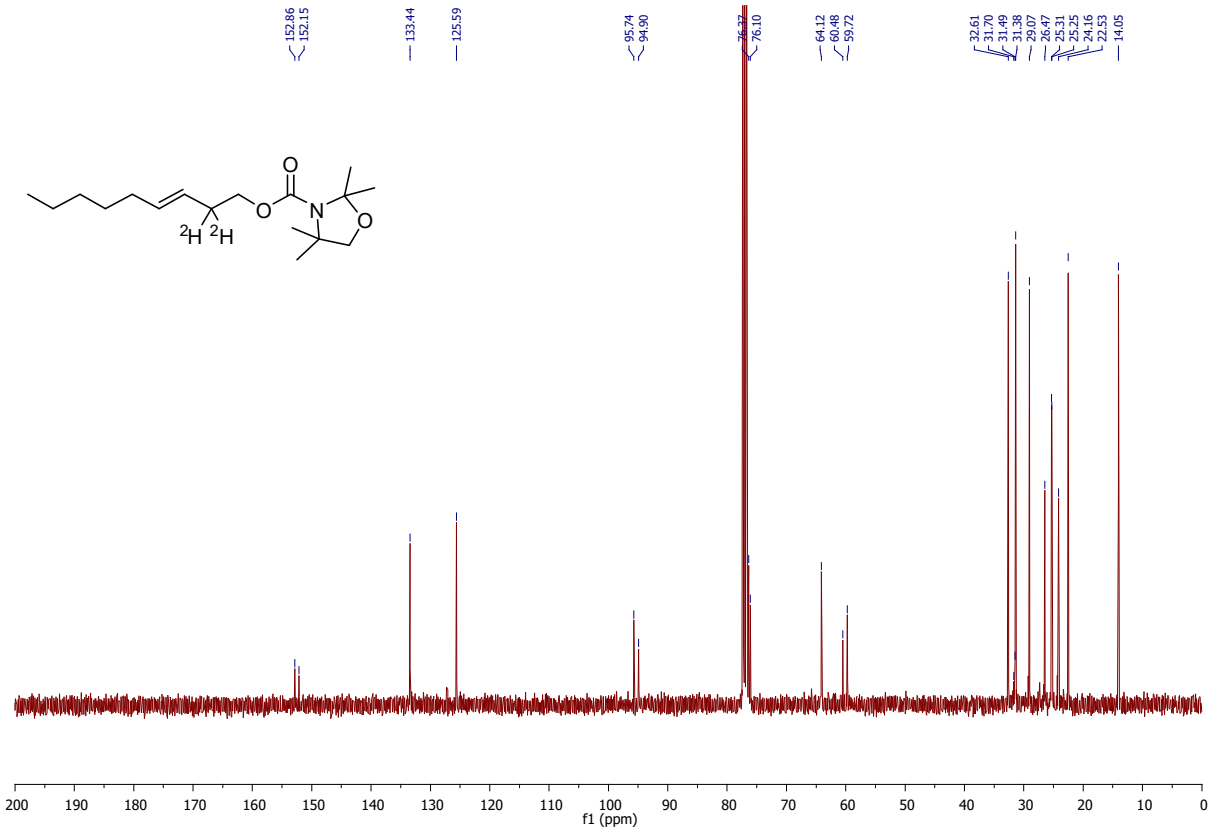
[2,2-$^{2}H_2$]-non-3(*E*)-en-1-ol **S7** :



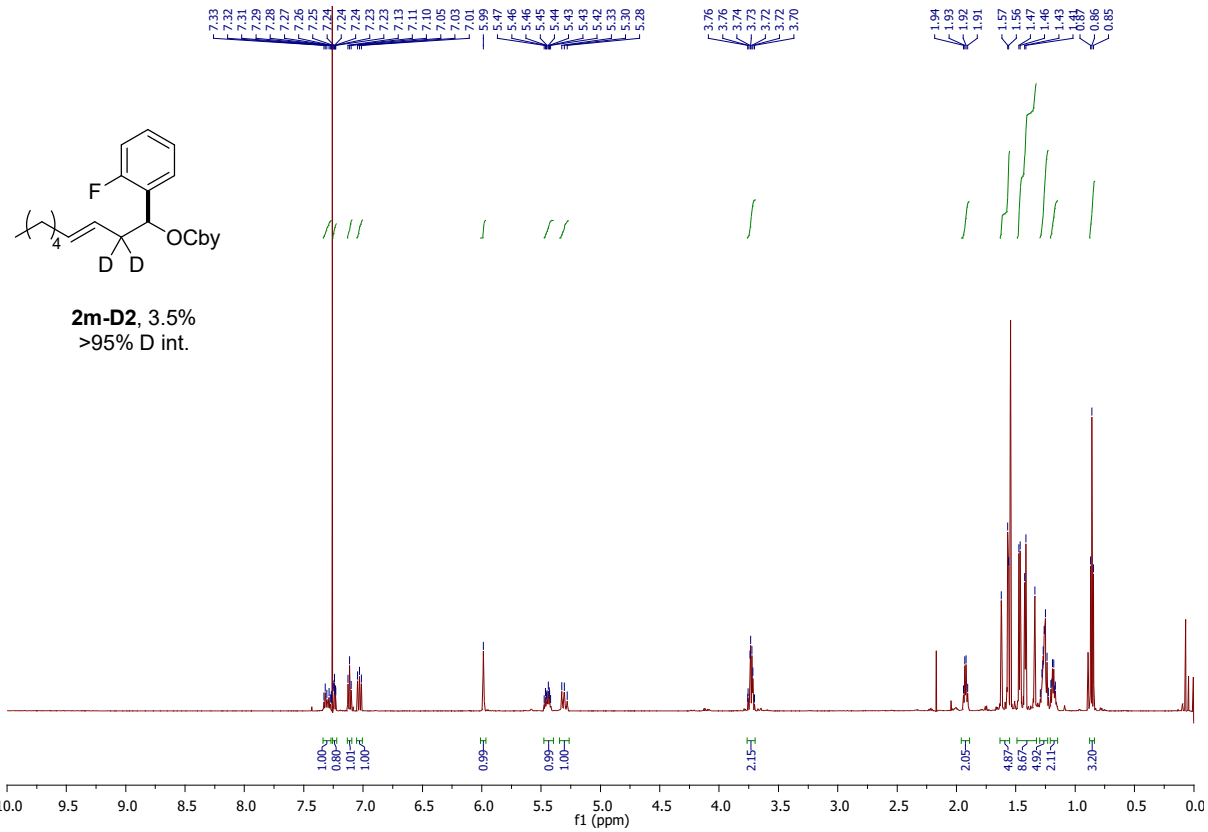


[2,2-$^{2}H_2$]-non-3(*E*)-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **1m-D2** :

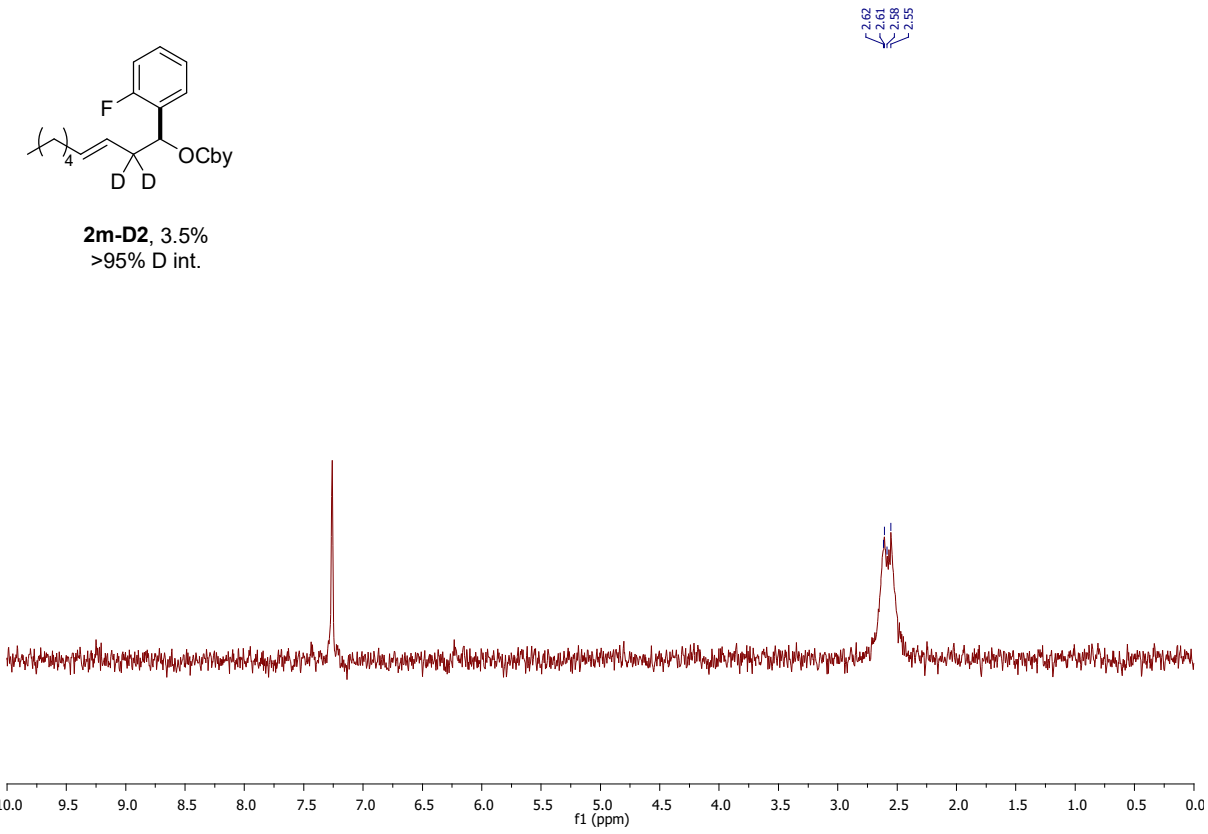




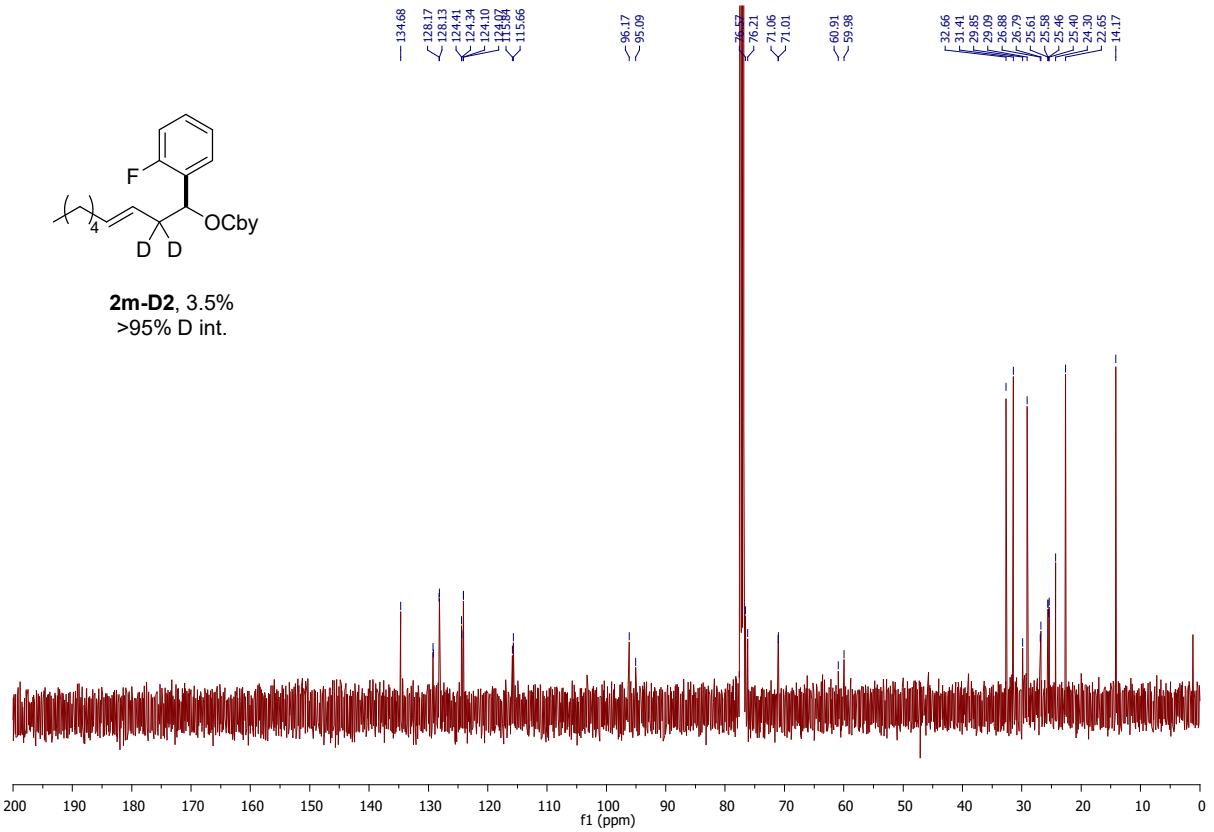
^{1}H NMR of the α-arylated product (rotamers) 2**m-D2**:



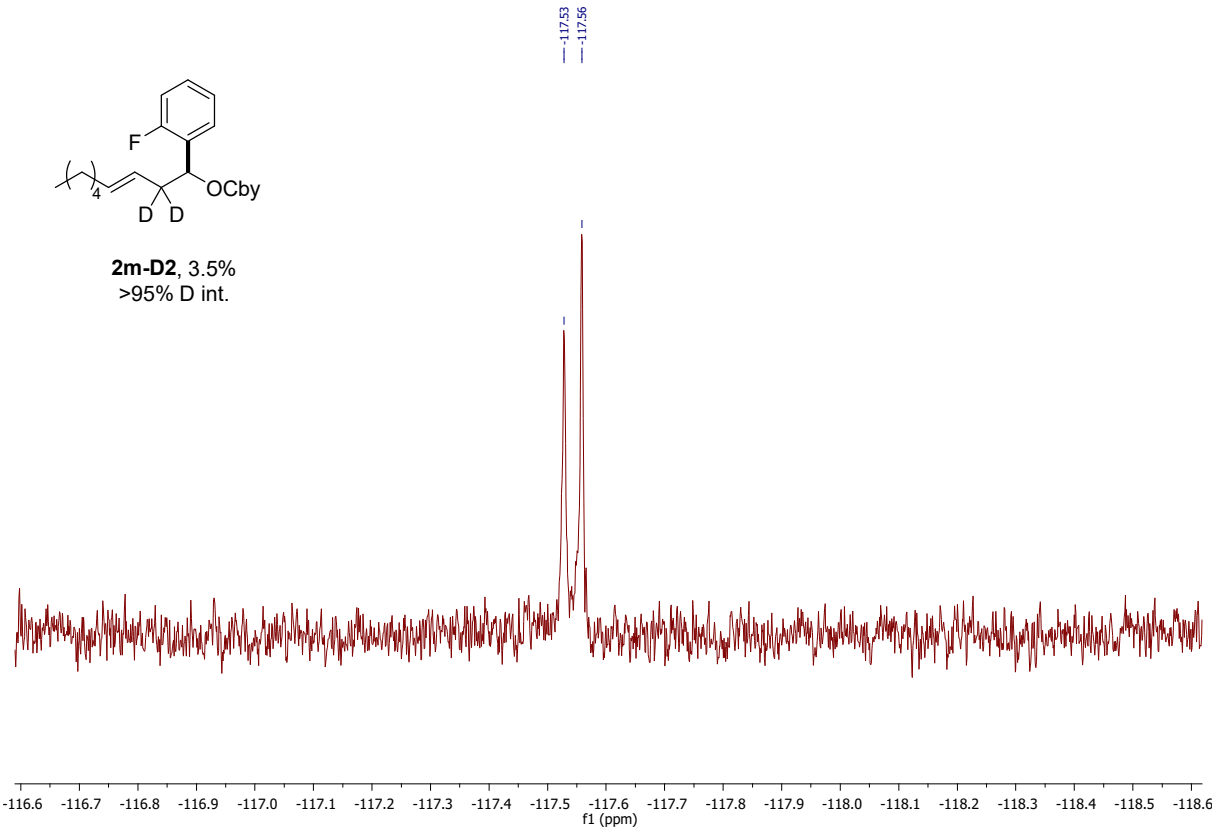
^{2}H NMR of the α-arylated product (rotamers) **2m-D2**:



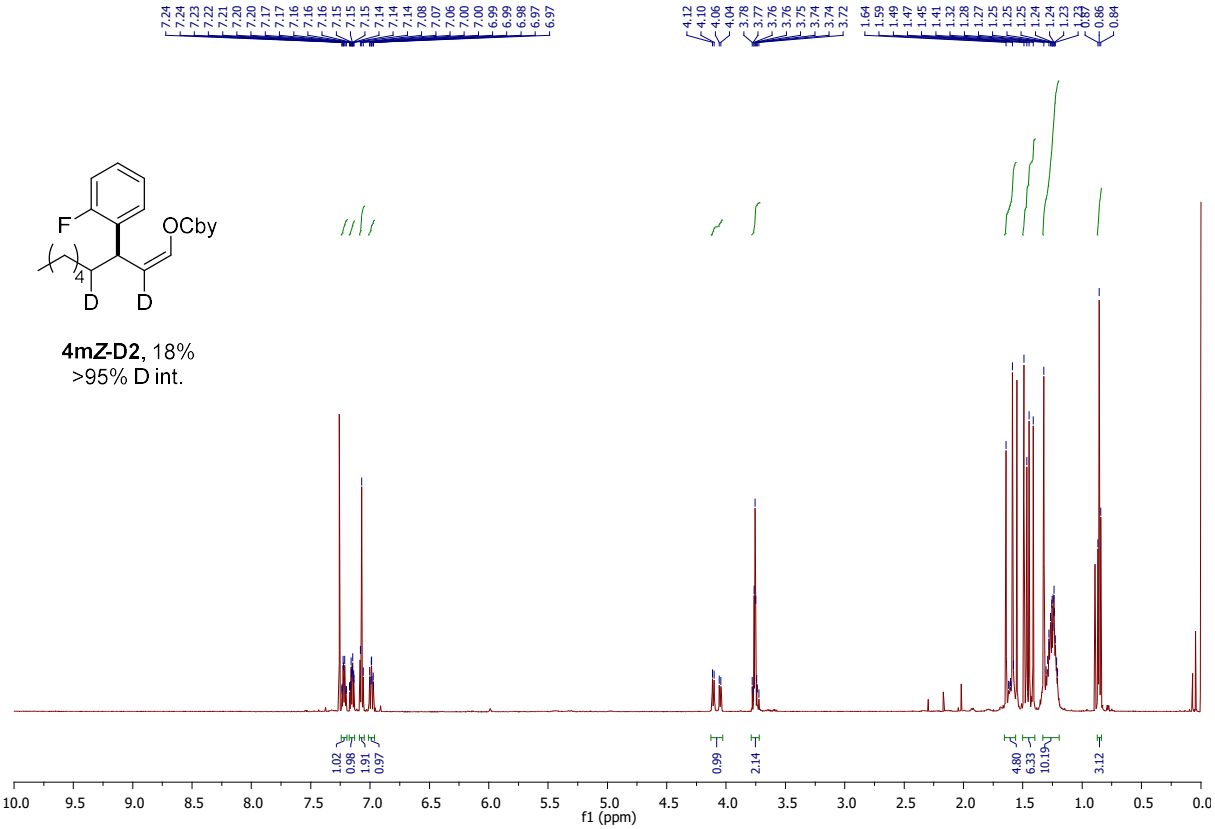
^{13}C NMR of the α-arylated product (rotamers) **2m-D2**:



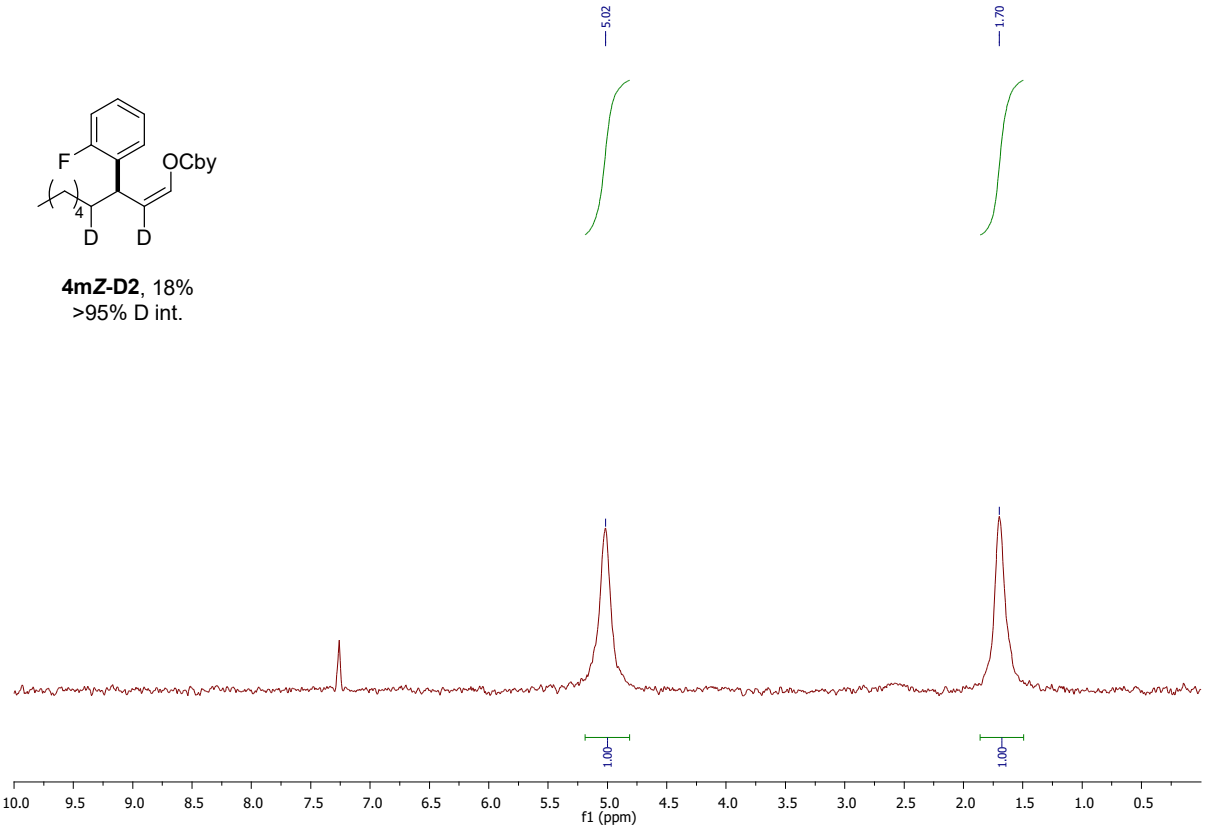
^{19}F NMR of the α-arylated product (rotamers) **2m-D2**:



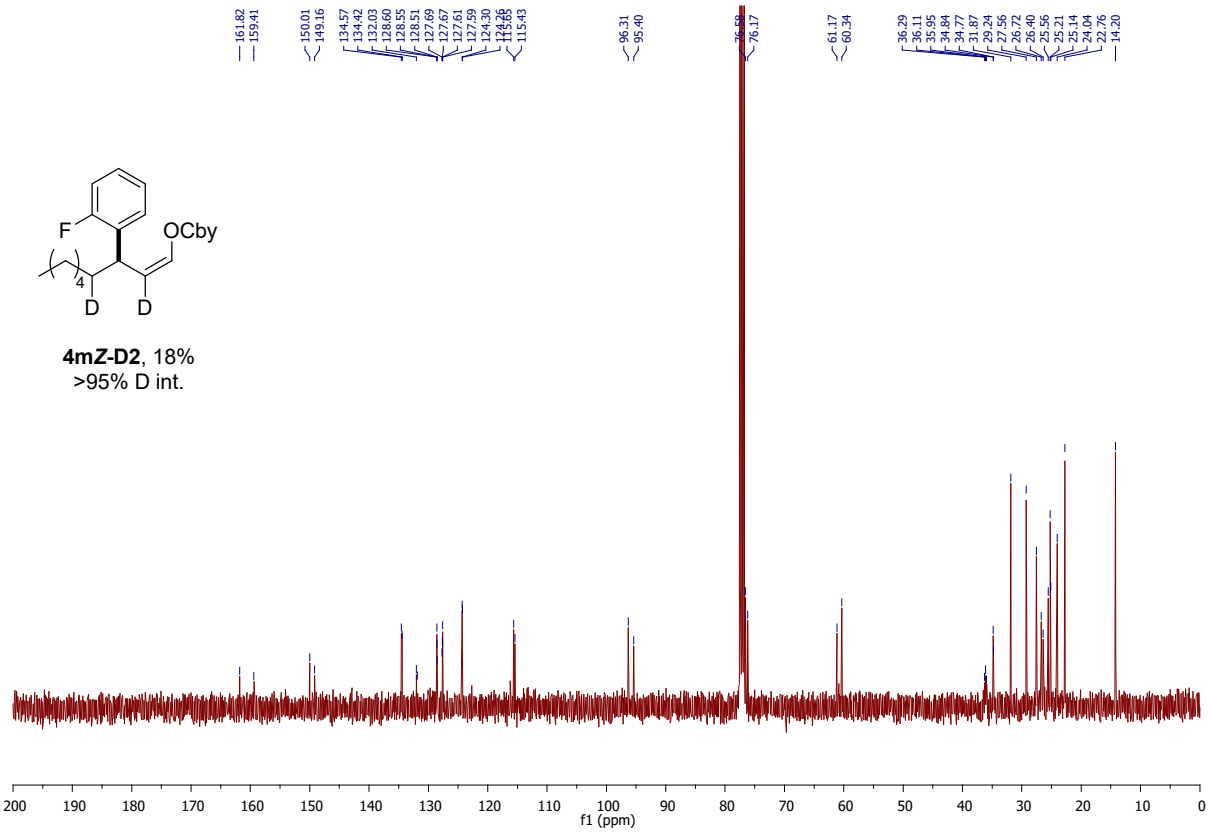
^{1}H NMR of the γ*Z*-arylated product (rotamers) **4m*Z*-D2**:



^{2}H NMR of the γ*Z*-arylated product (rotamers) **4m*Z*-D2**:

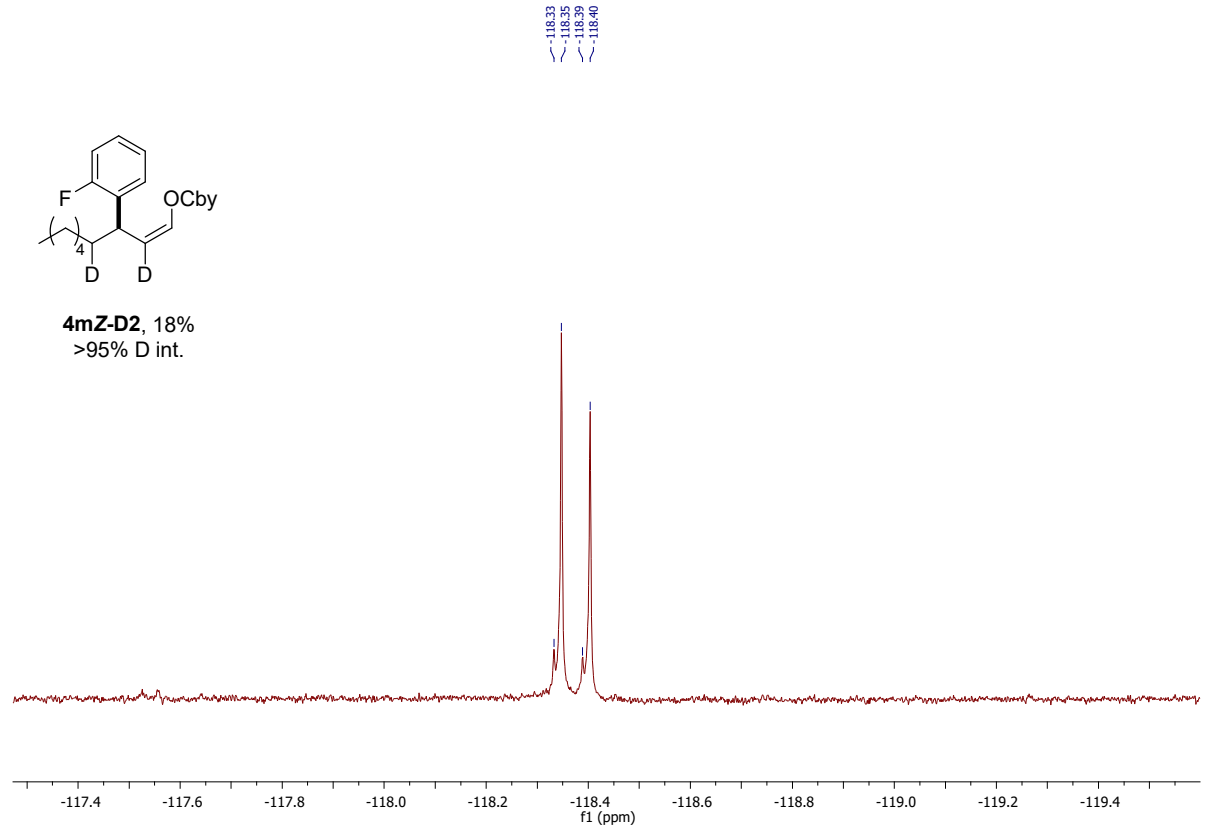


^{13}C NMR of the γ*Z*-arylated product (rotamers) **4m*Z*-D2**:



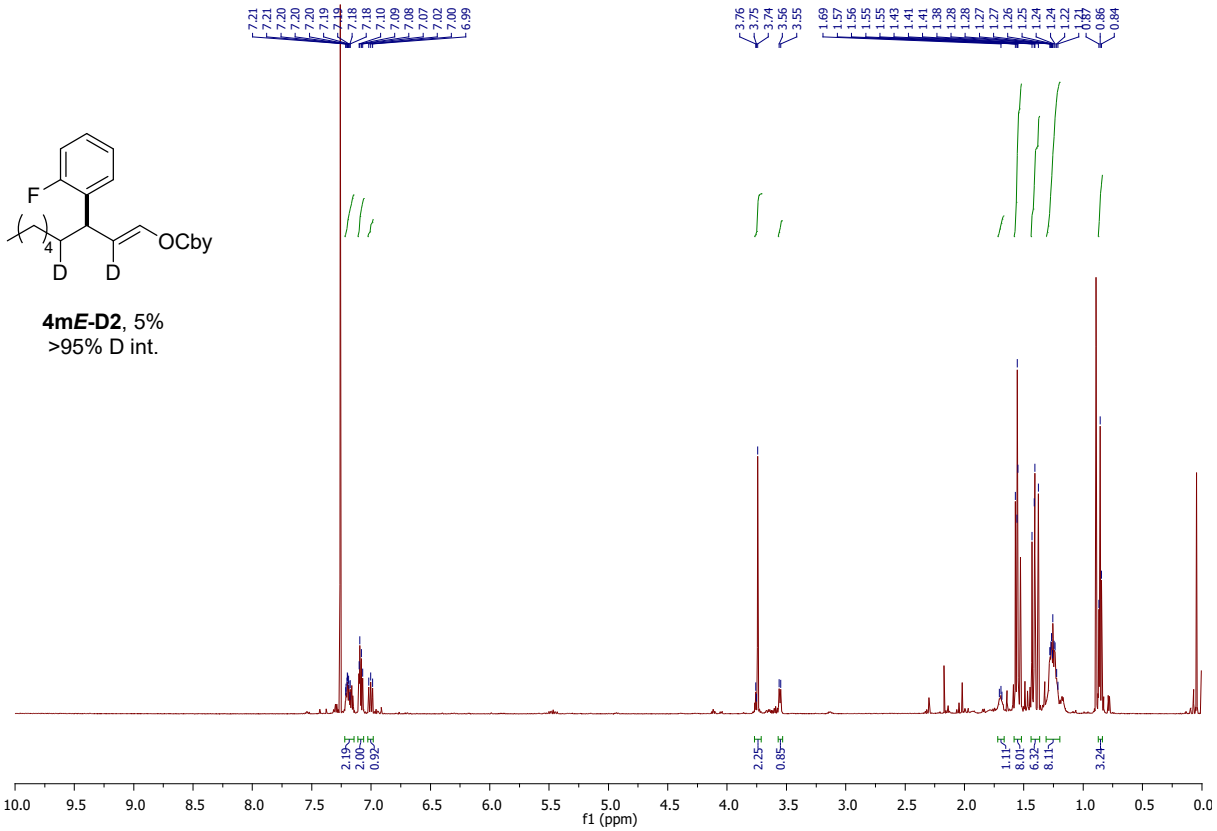
4m*Z*-D2, 18%
>95% D int.

^{19}F NMR of the γ*Z*-arylated product (rotamers) **4m*Z*-D2**:

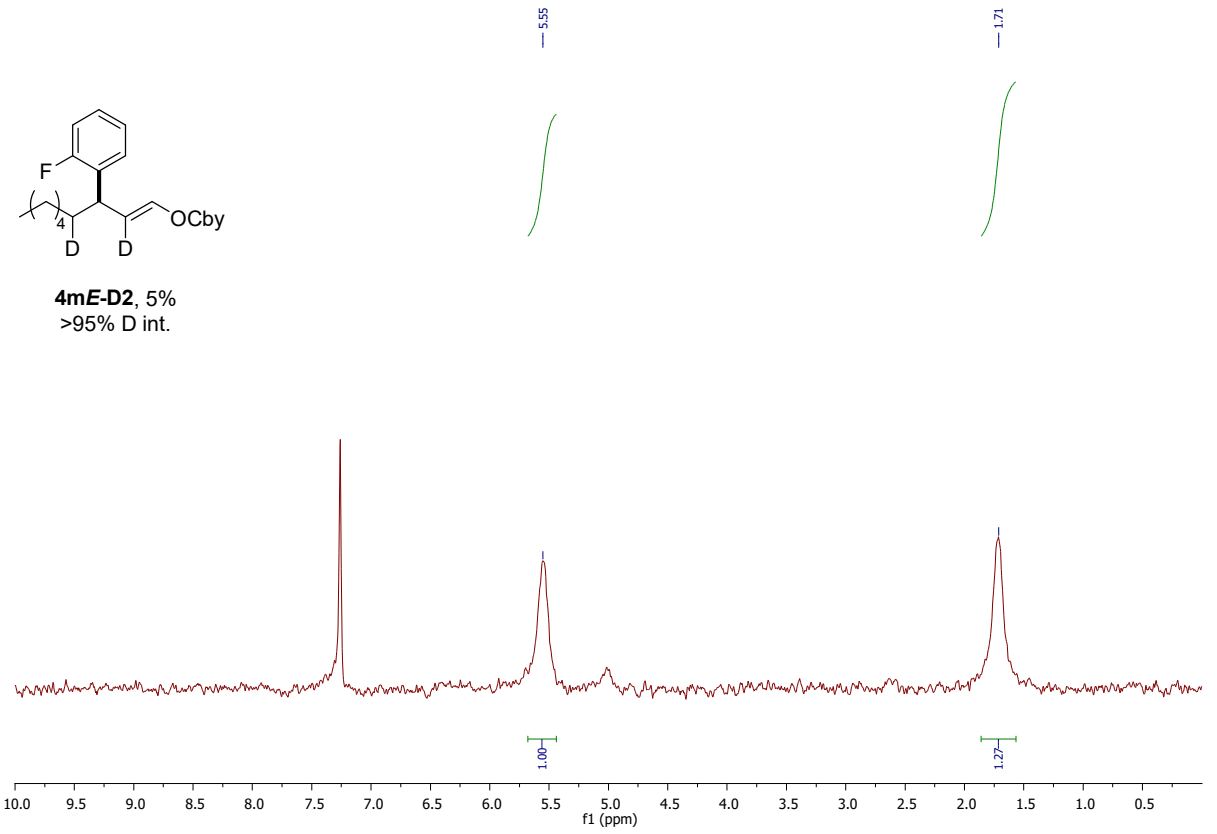


4m*Z*-D2, 18%
>95% D int.

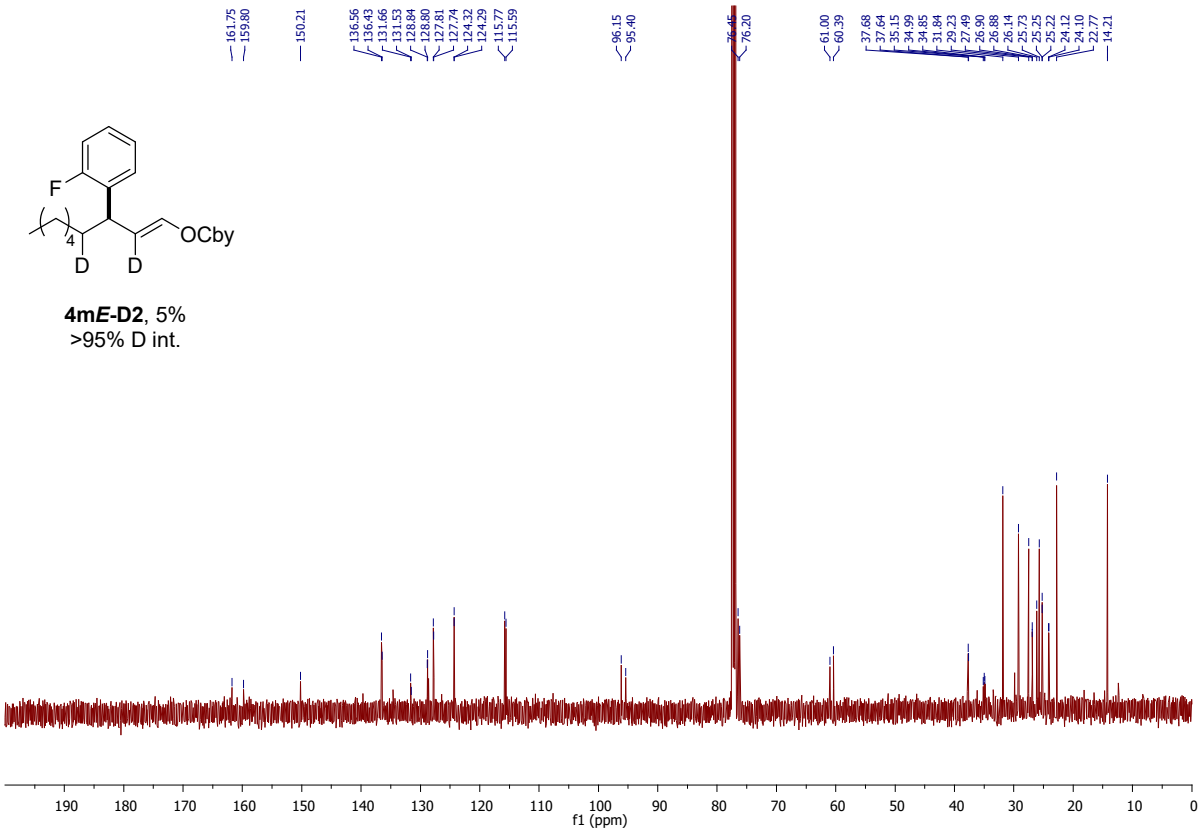
^{1}H NMR of the γ*E*-arylated product **4m*E*-D2** (rotamers, contains γ*Z* product):



^{2}H NMR of the γ*E*-arylated product**4m*E*-D2** (rotamers, contains γ*Z* product):

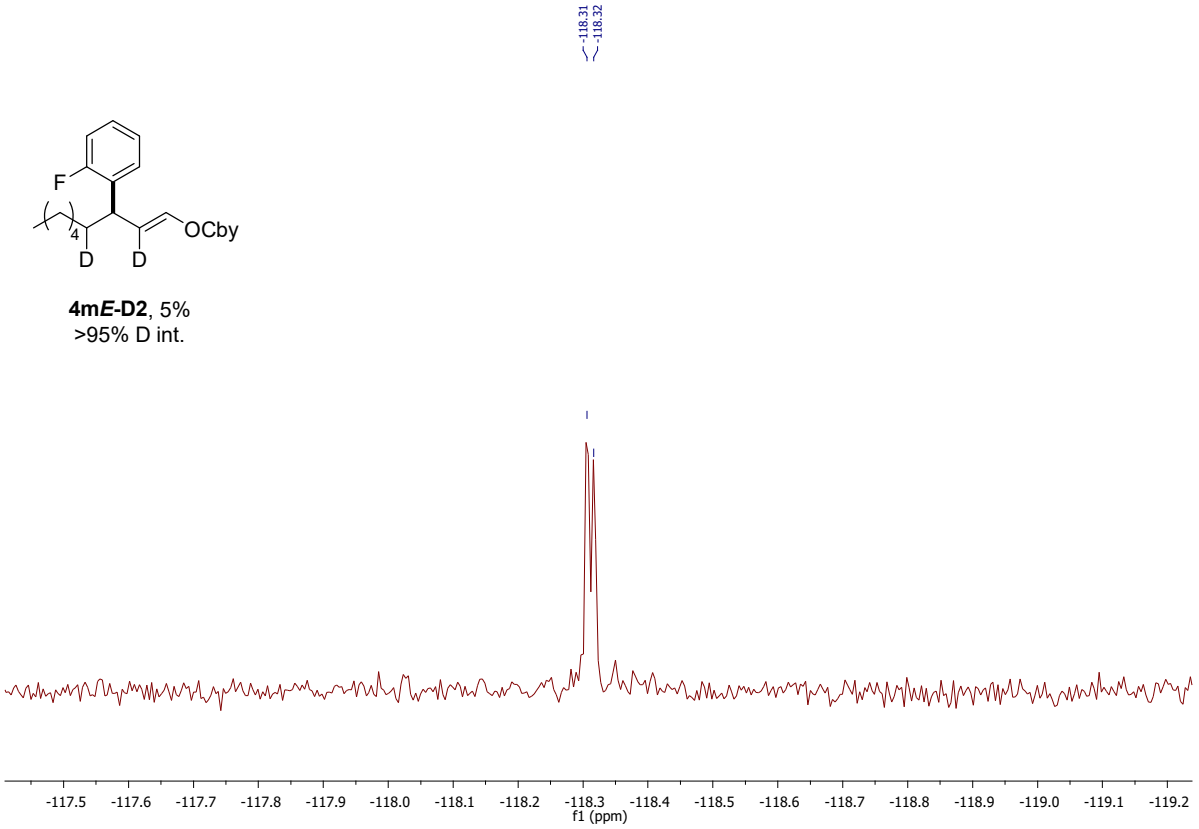


^{13}C NMR of the γ-arylated product**4m*E*-D2** (rotamers, contains γ*Z* product):



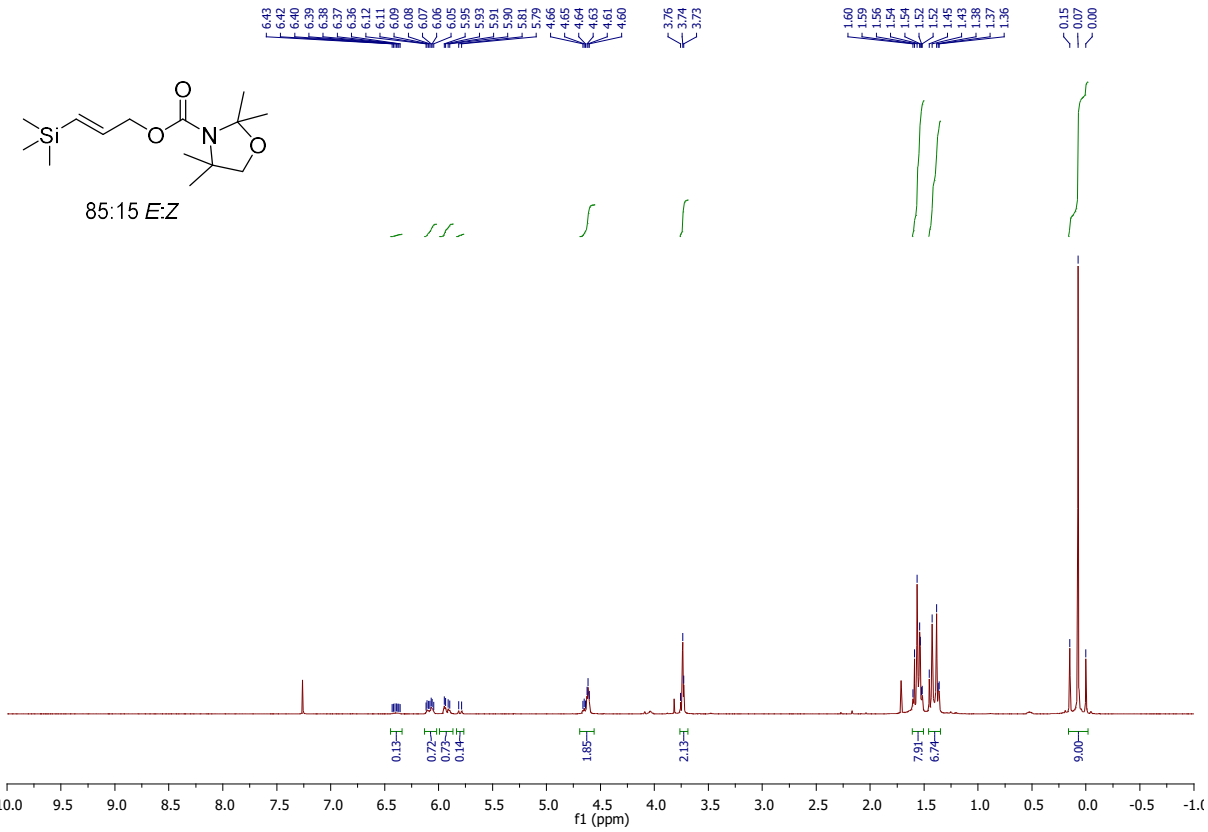
4m*E*-D2, 5%
>95% D int.

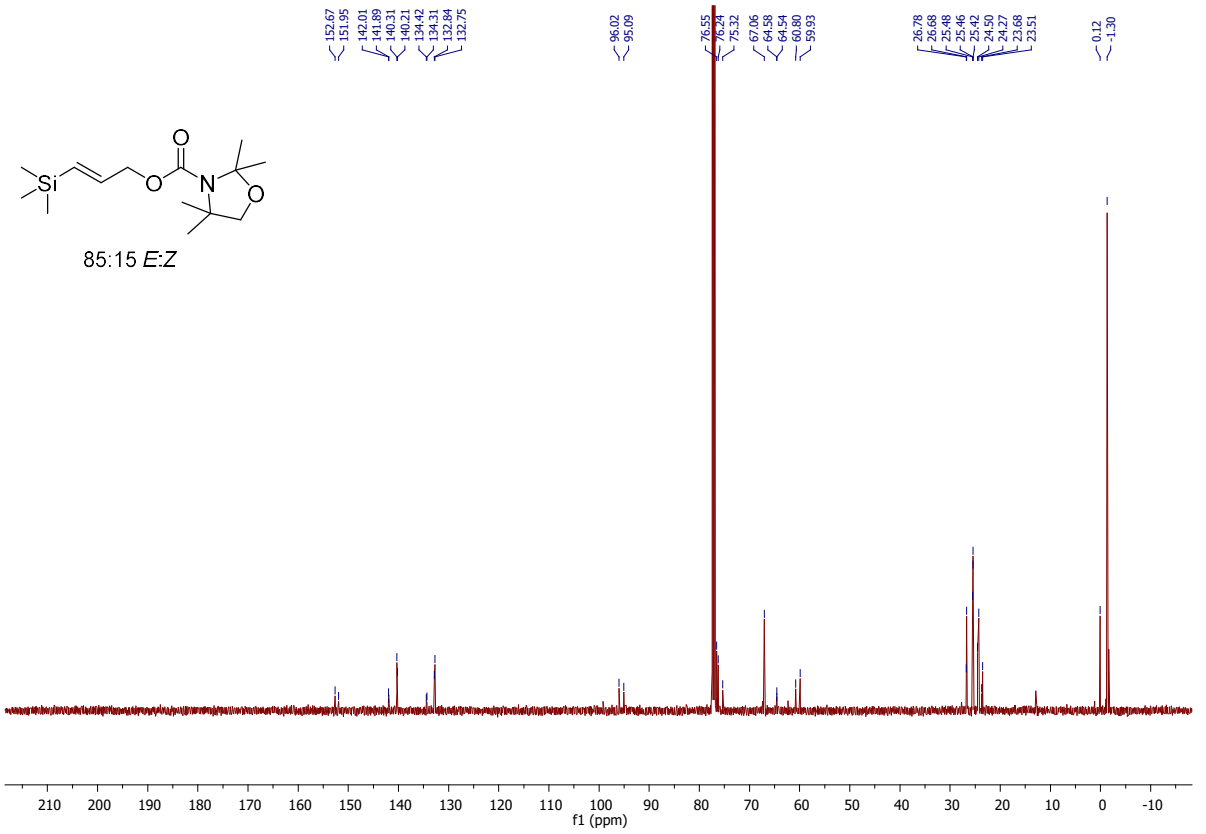
^{19}F NMR of the γ*E*-arylated product **4m*E*-D2**:



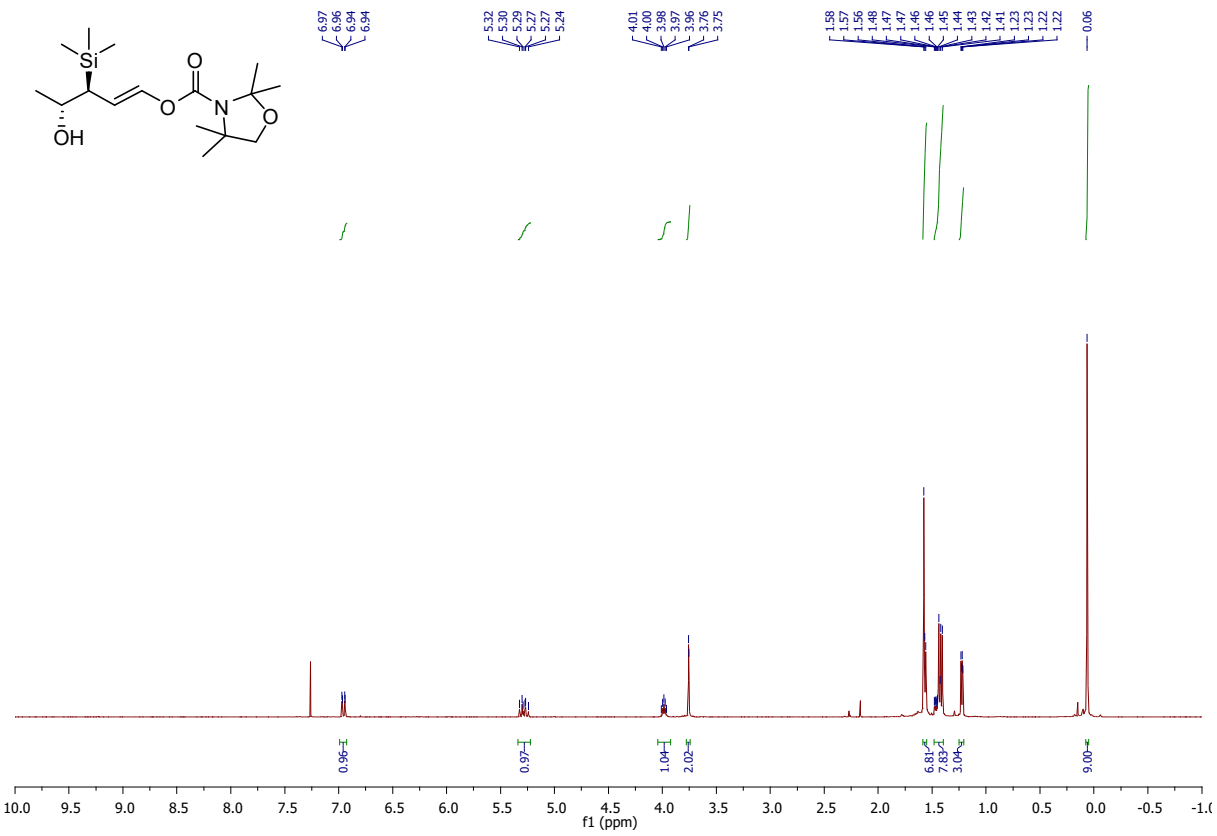
4m*E*-D2, 5%
>95% D int.

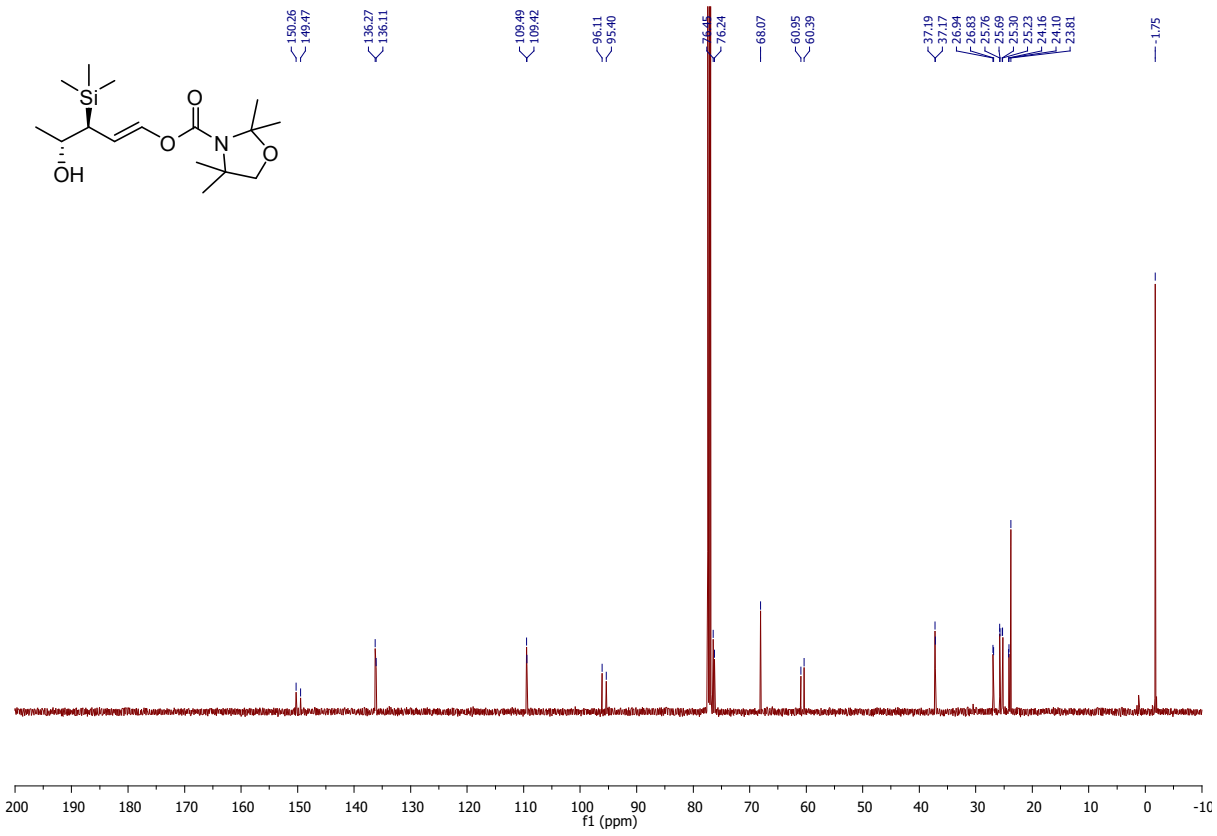
3-(trimethylsilyl)allyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **S8** :



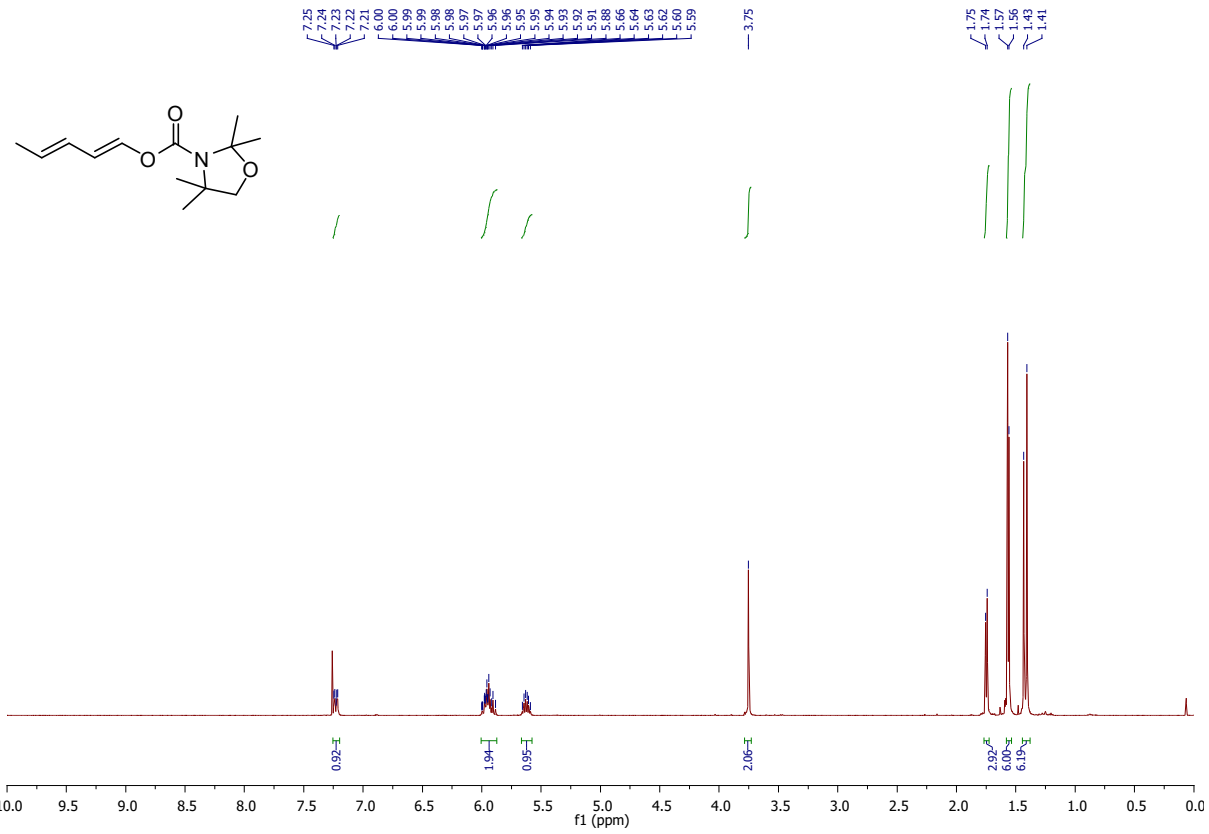


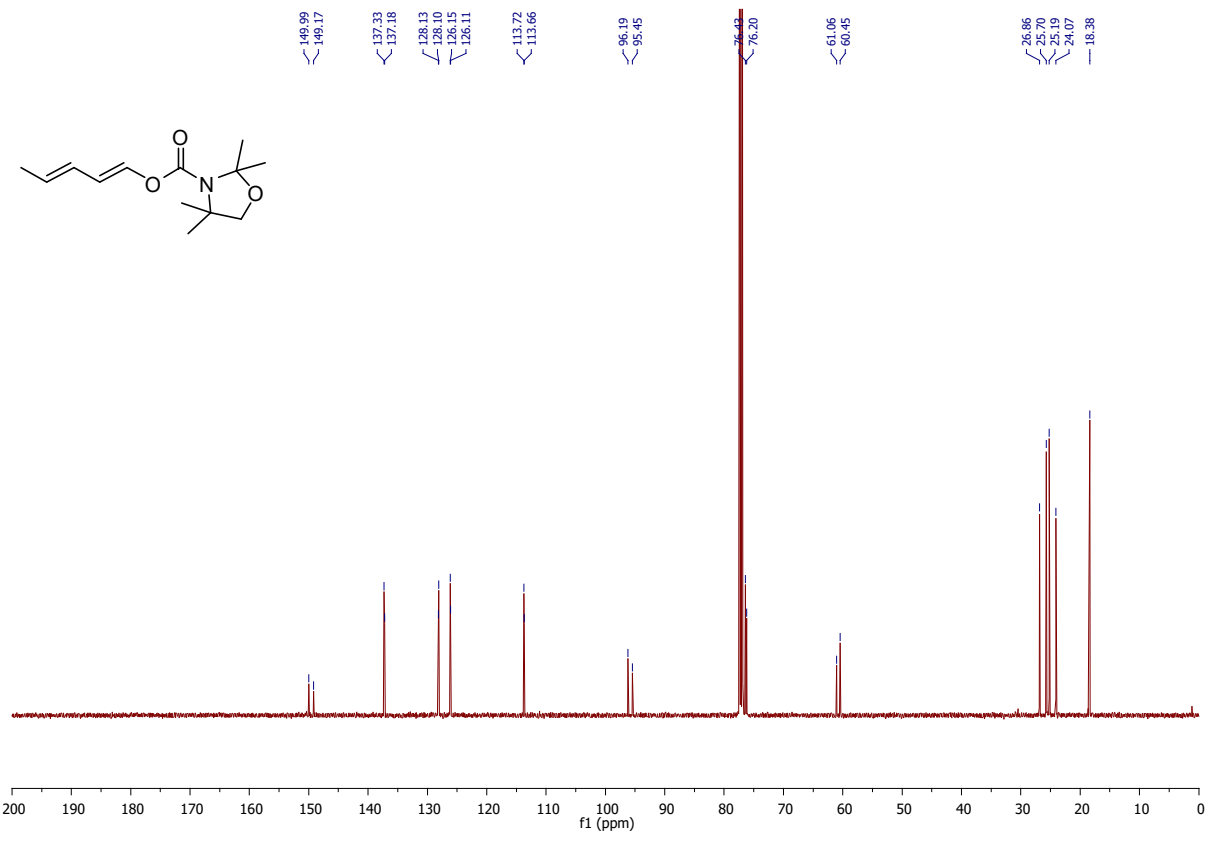
(*E*)-4-hydroxy-3-(trimethylsilyl)pent-1-en-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **S9** :



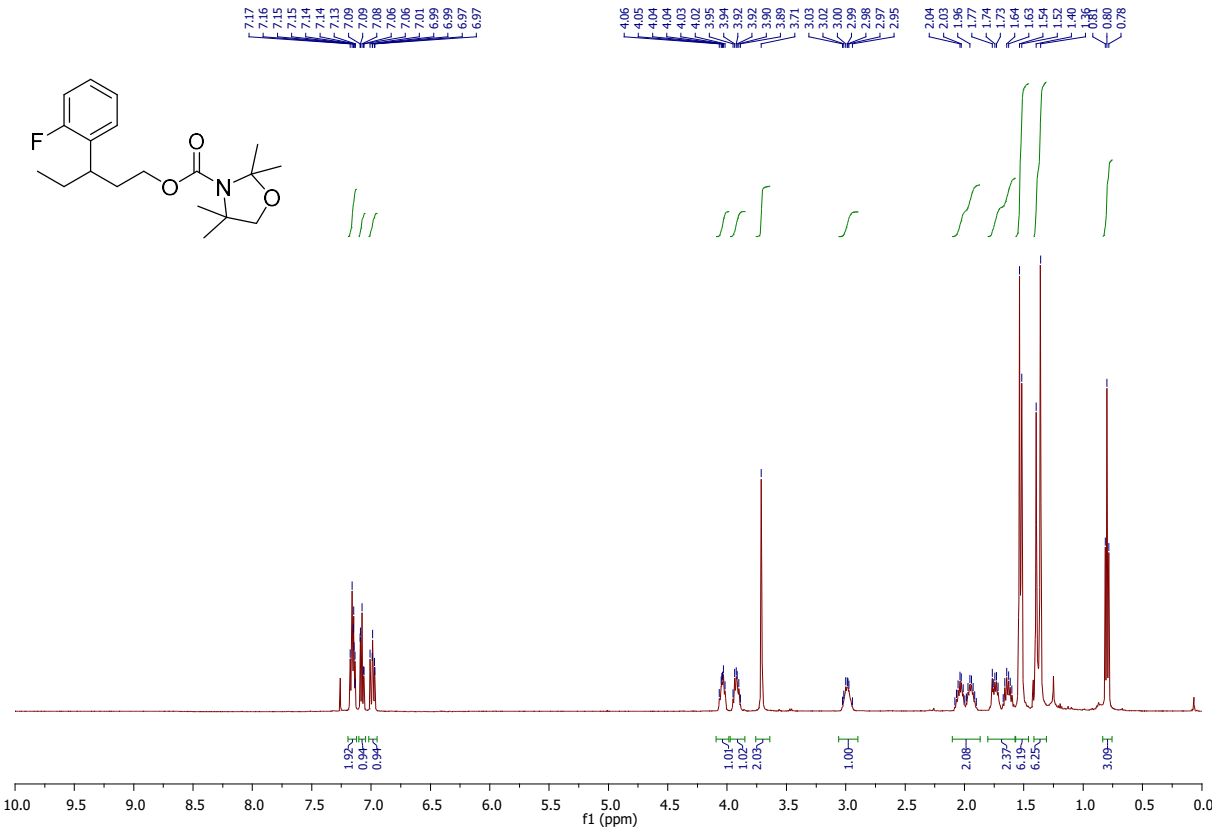


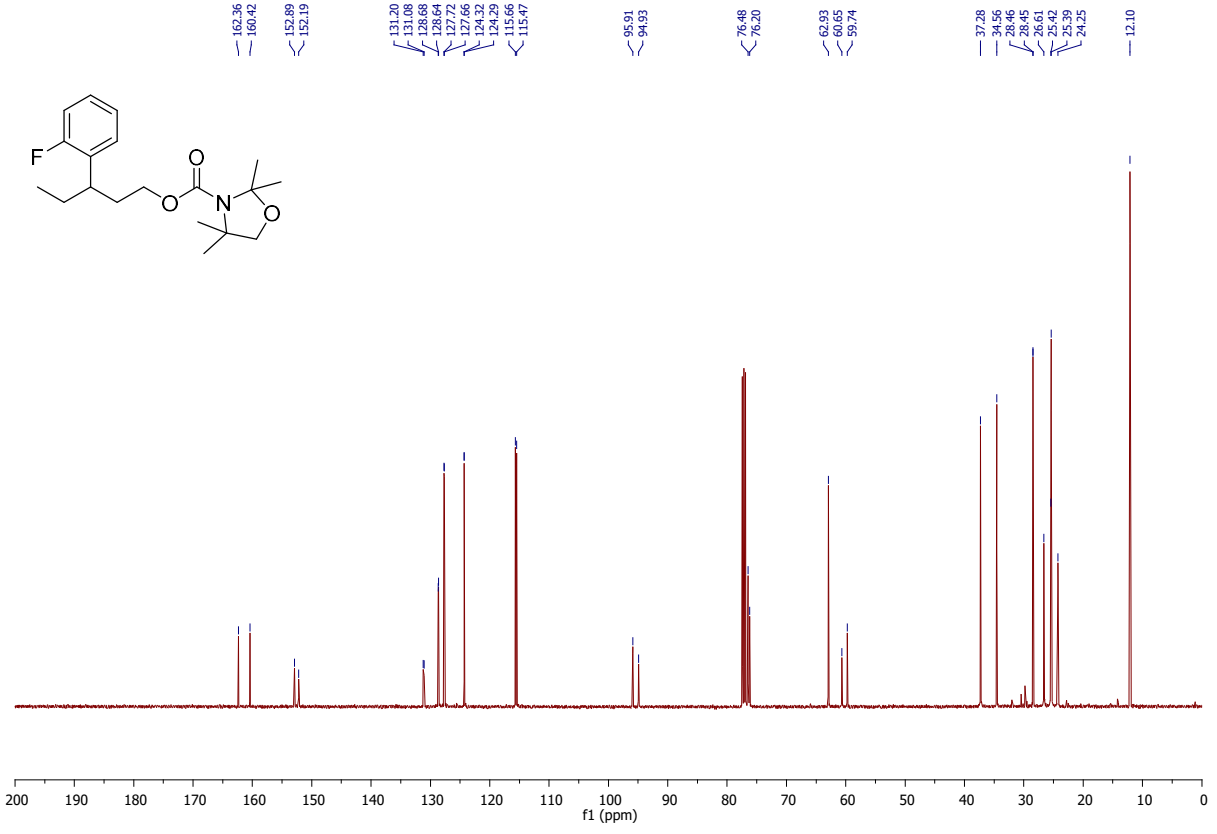
(1*E*,3*E*)-penta-1,3-dien-1-yl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **6** :



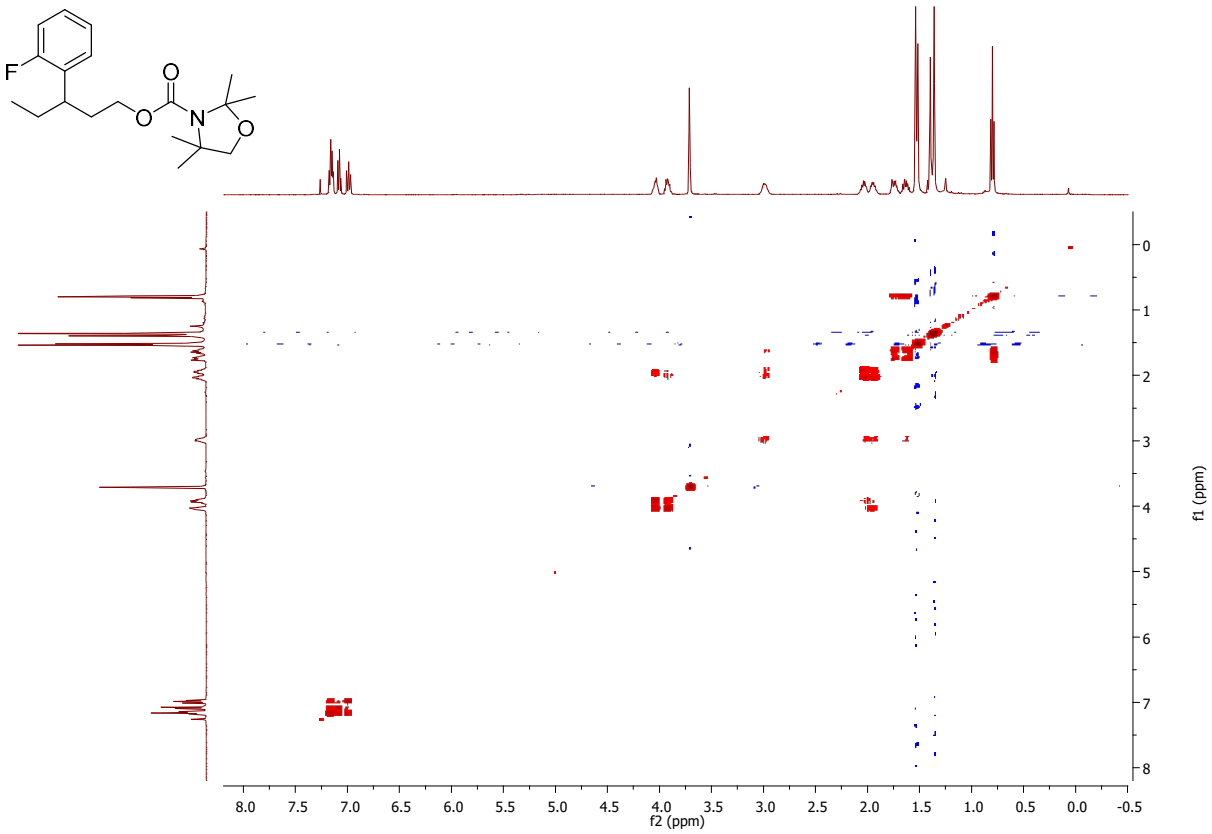


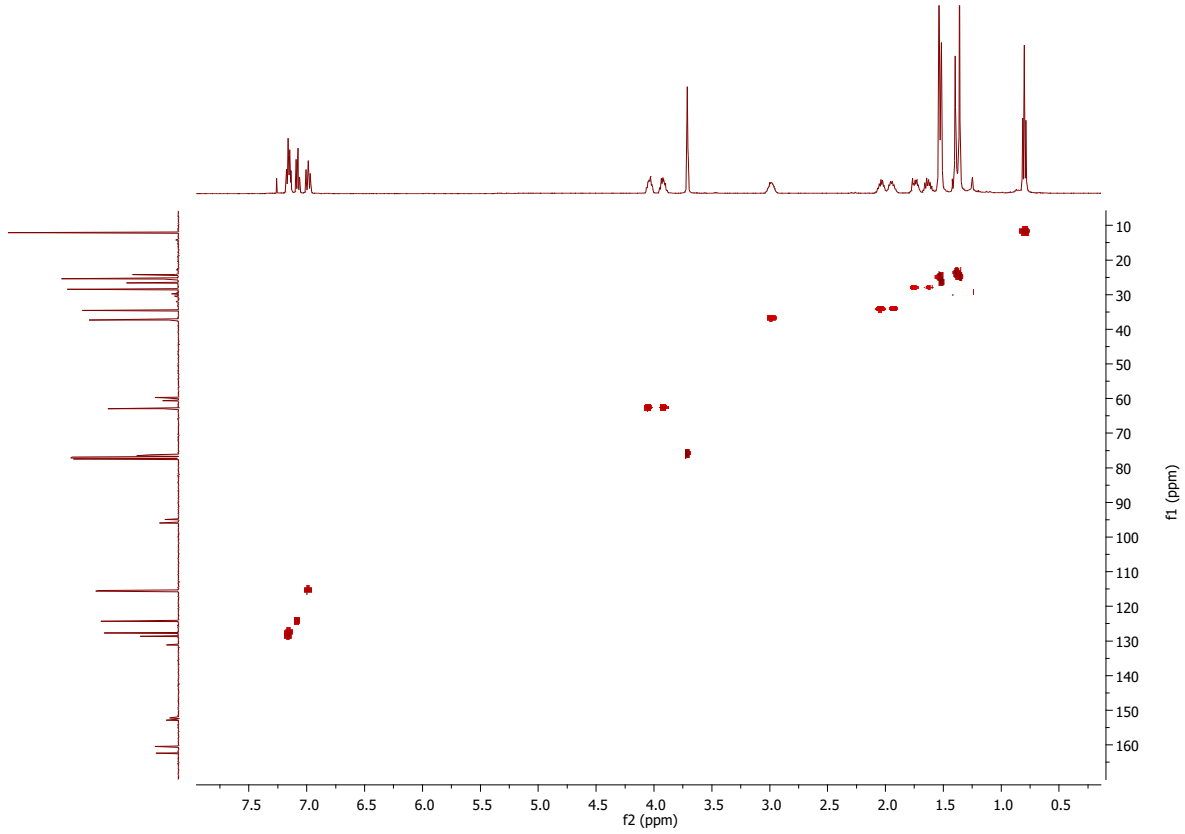
3-(2-fluorophenyl)pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **5**:

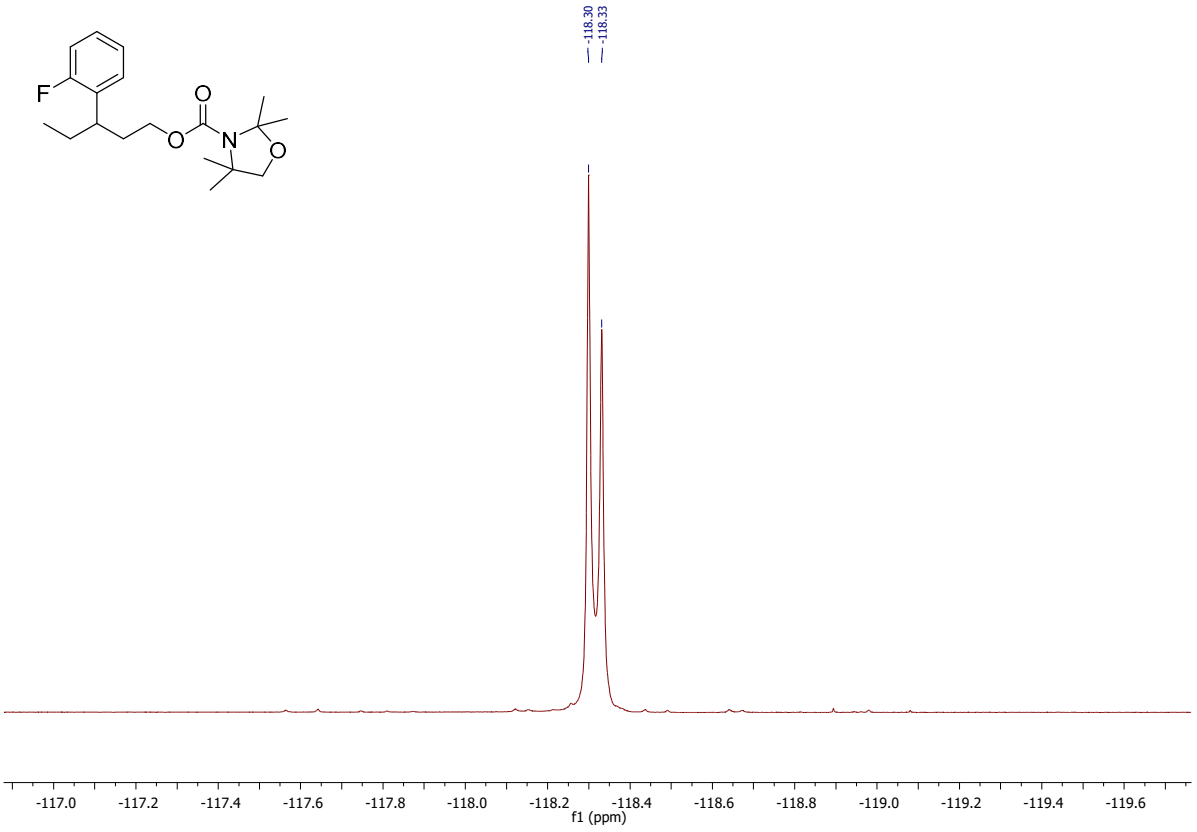




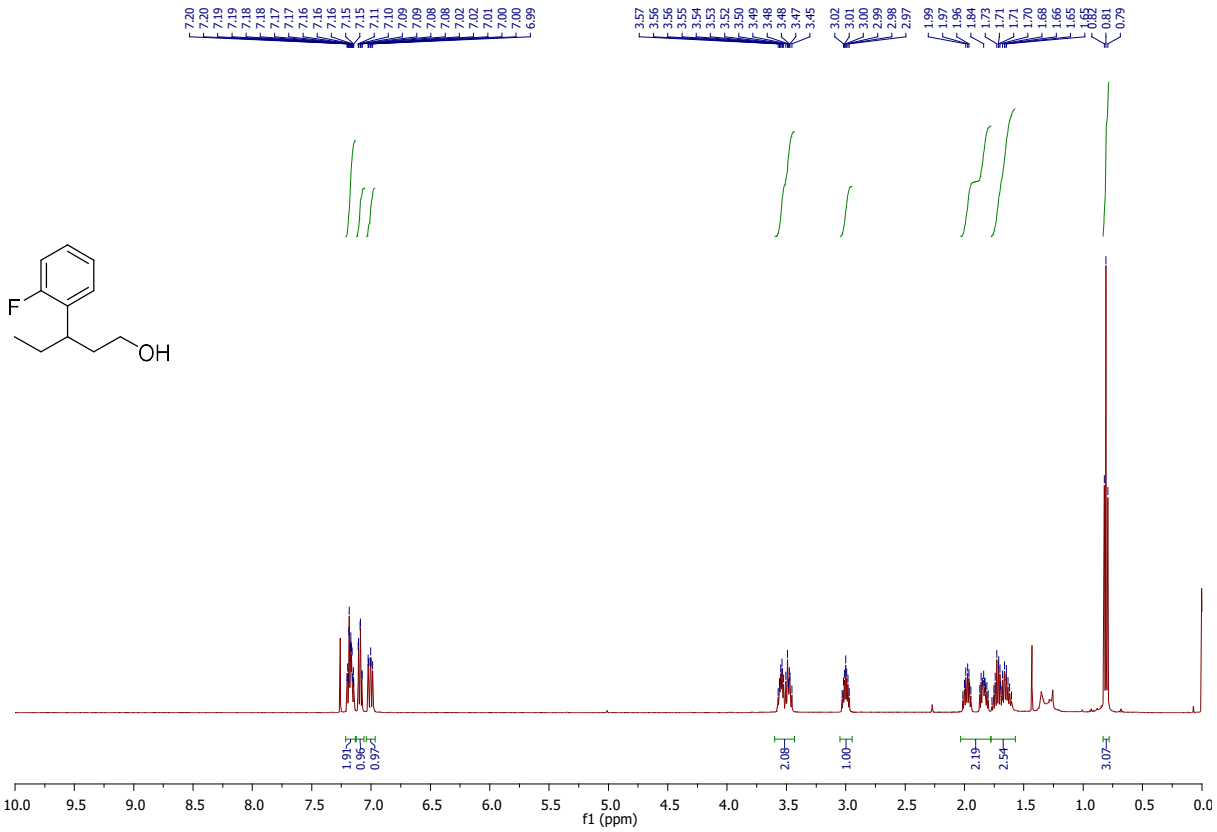
COSY and HMQC experiments :

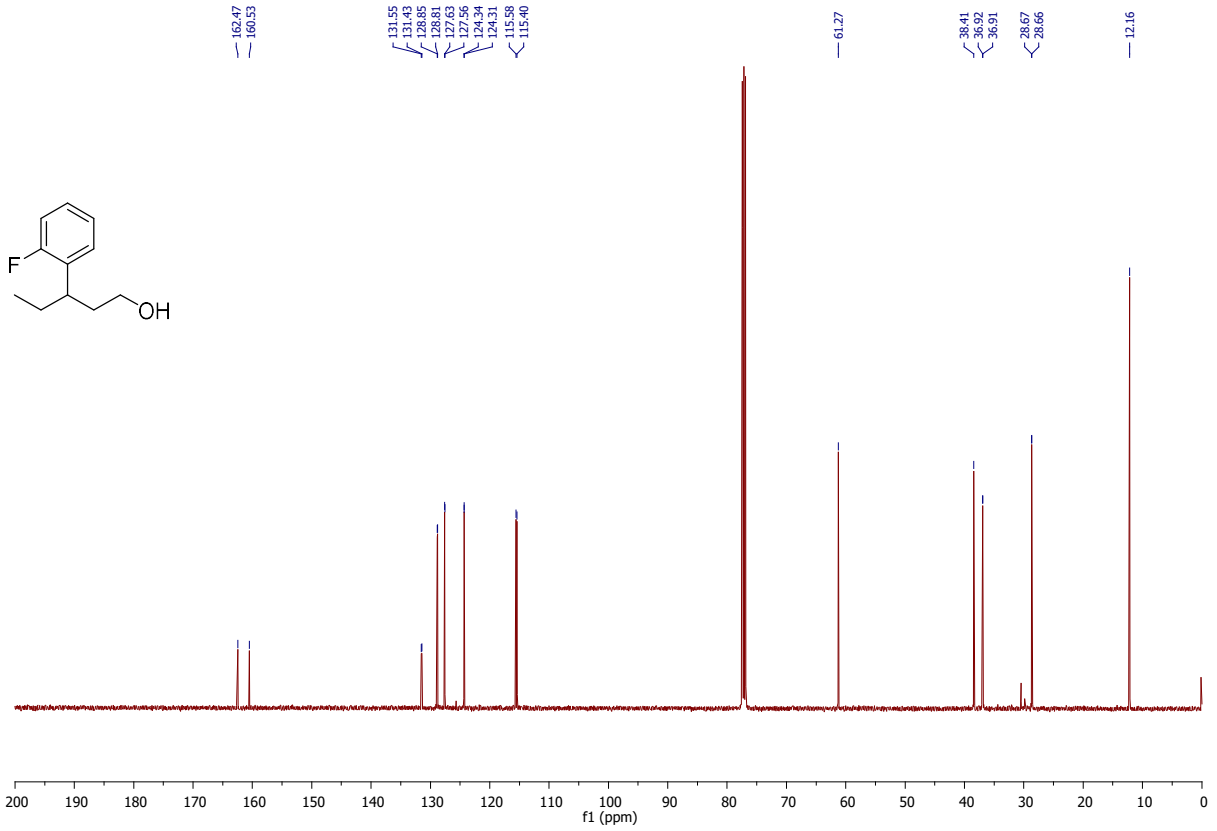




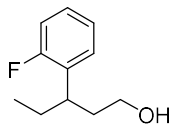

F
O
O
N
O
-118.30
-118.33
-117.0
-117.2
-117.4
-117.6
-117.8
-118.0
-118.2
-118.4
-118.6
-118.8
-119.0
-119.2
-119.4
-119.6
f1 (ppm)

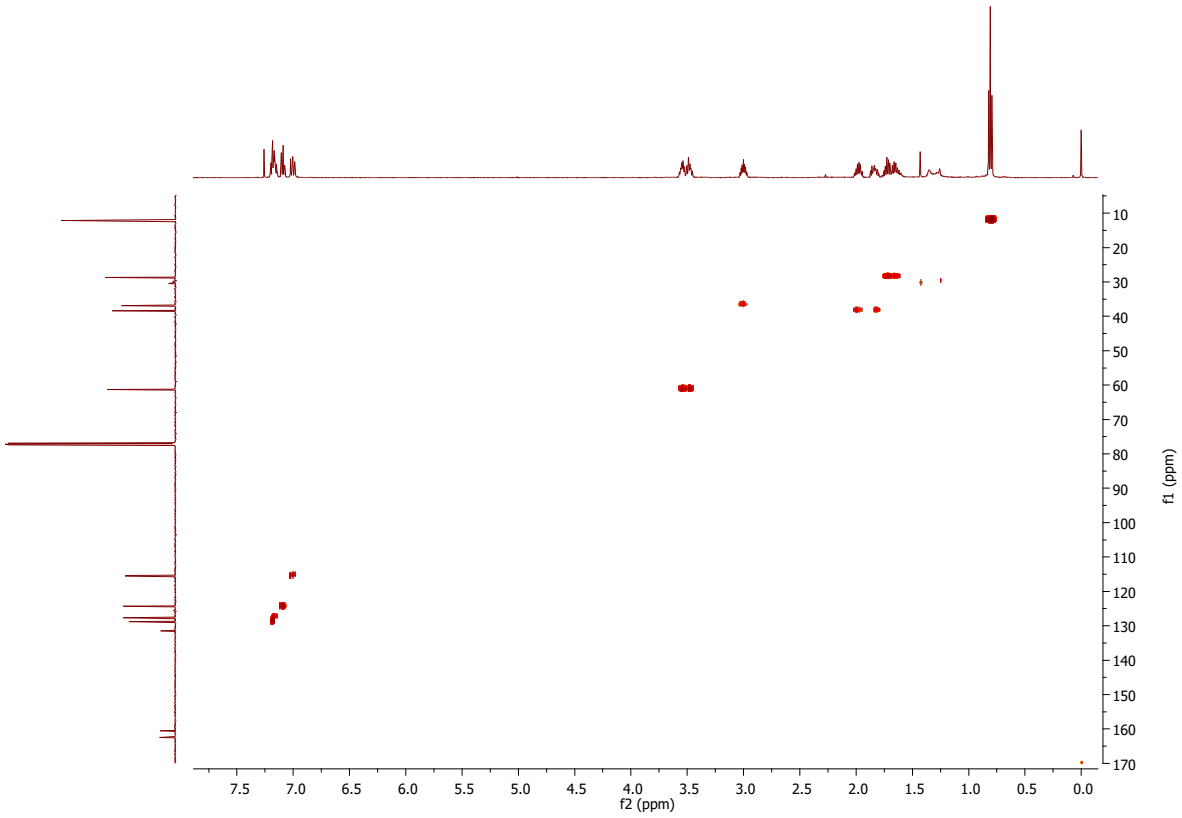
3-(2-fluorophenyl)pentyl 2,2,4,4-tetramethyloxazolidine-3-carboxylate **S10**:

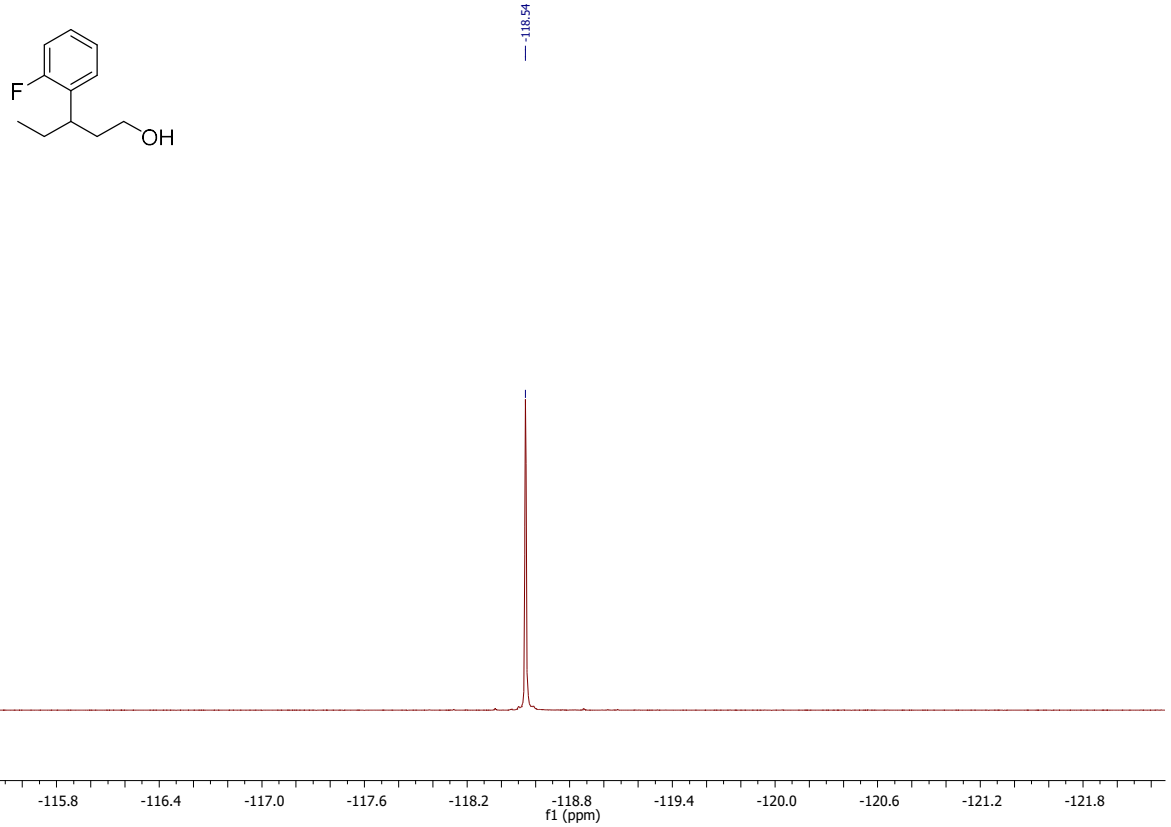




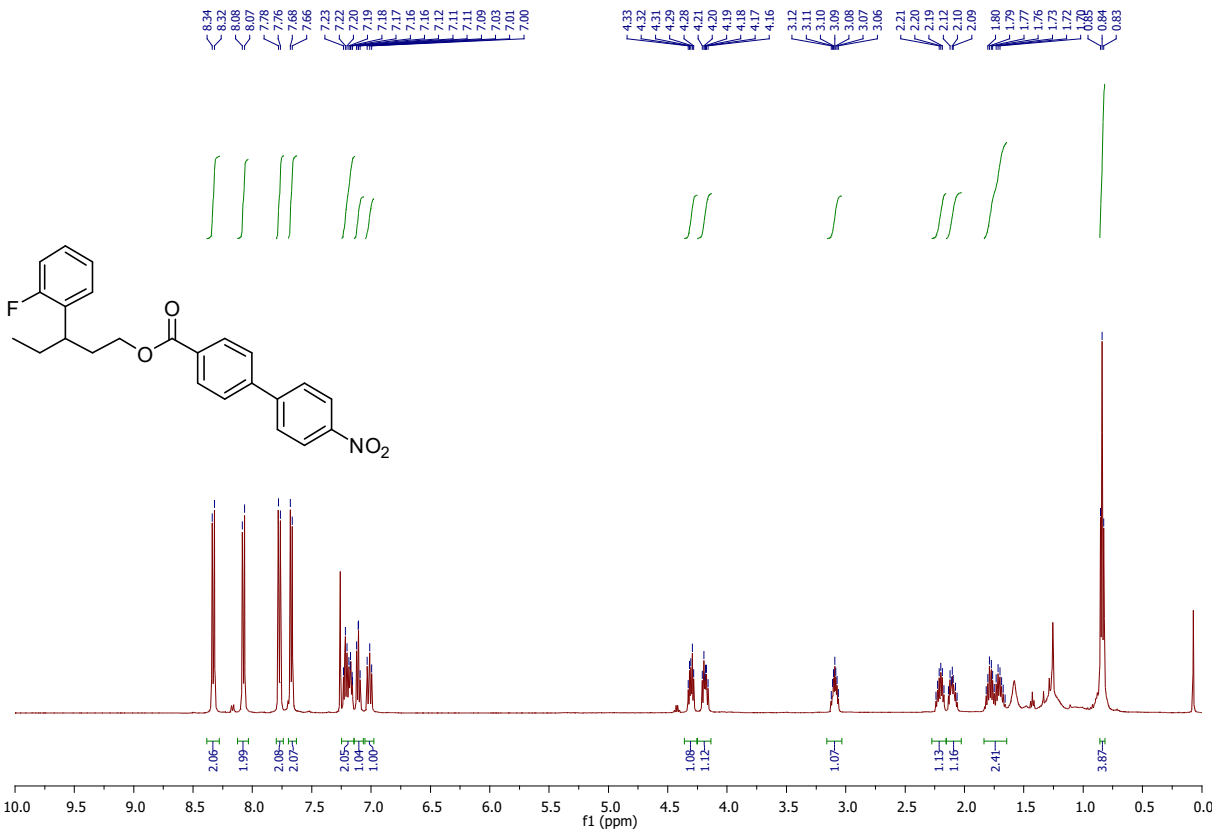
COSY and HMQC experiments :

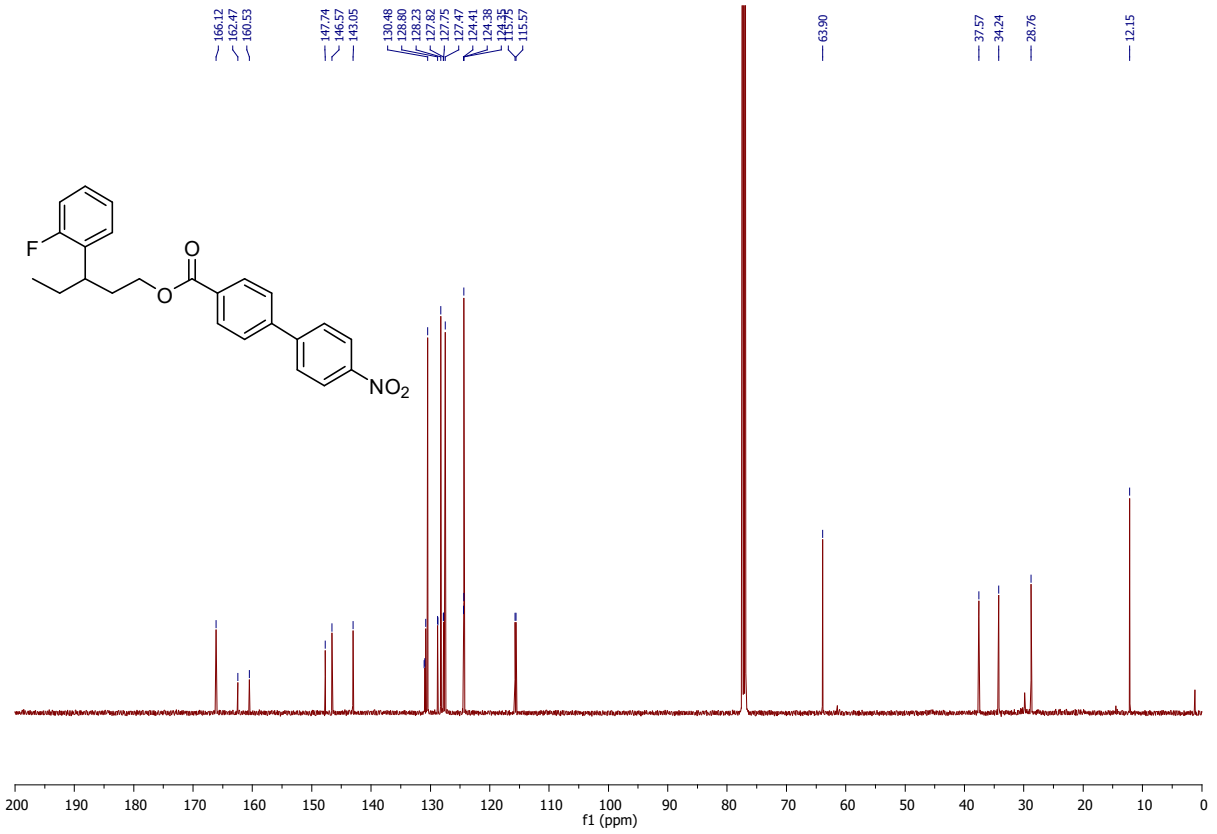




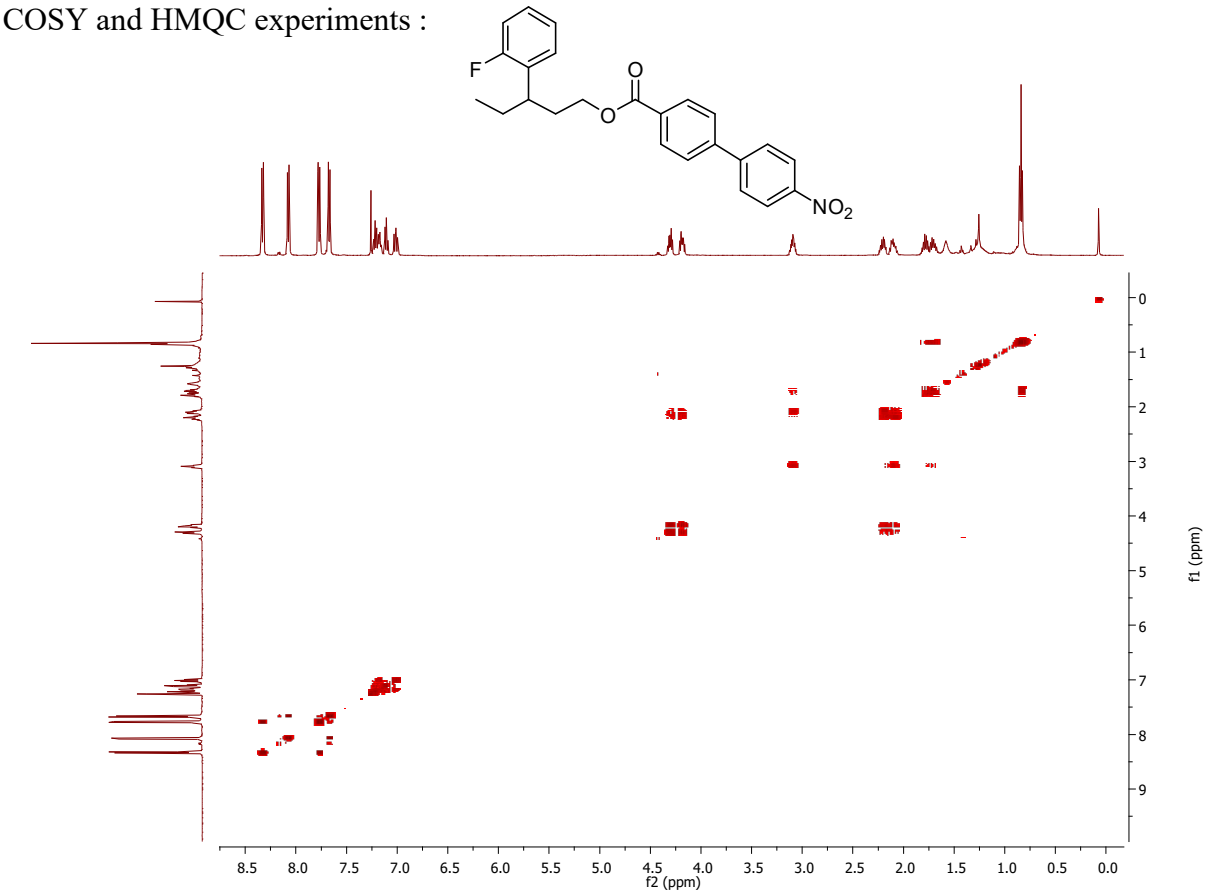

F
OH
-118.54
-115.8
-116.4
-117.0
-117.6
-118.2
-118.8
-119.4
-120.0
-120.6
-121.2
-121.8
f1 (ppm)

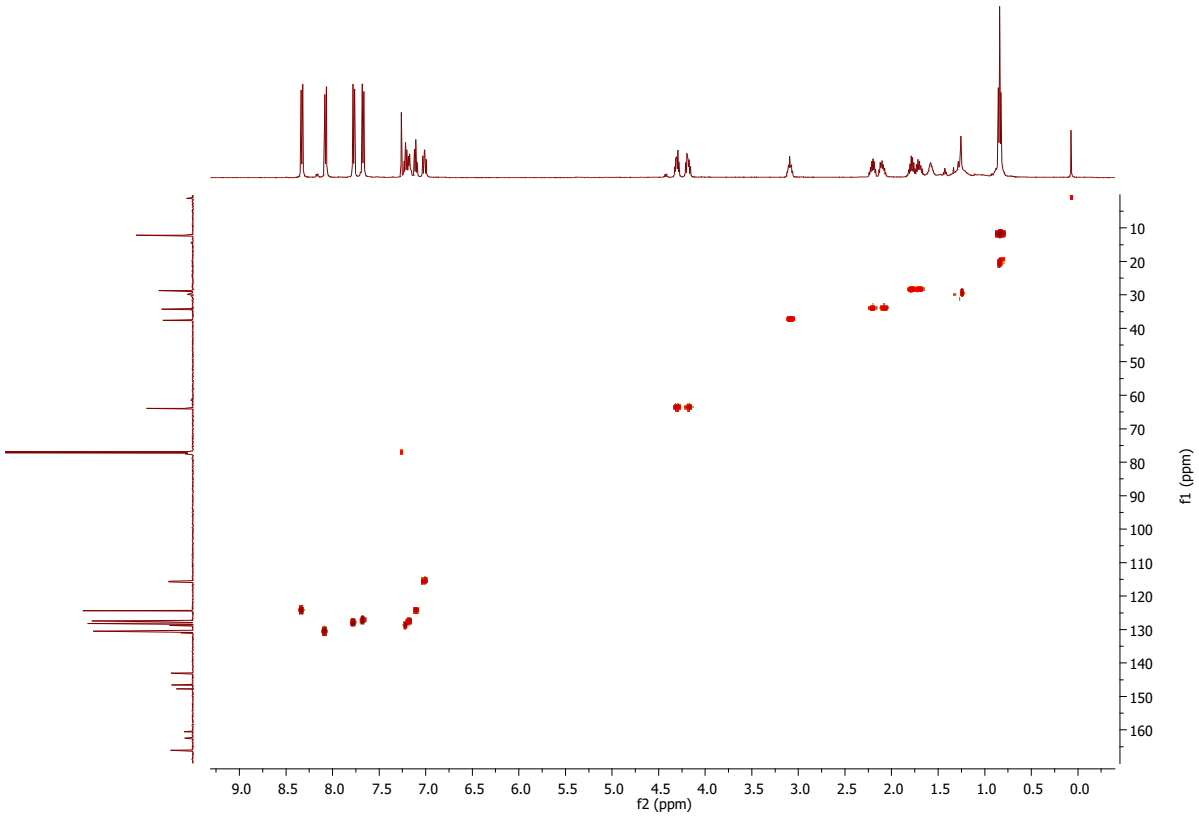
3-(2-fluorophenyl)pentyl 4'-nitro-[1,1'-biphenyl]-4-carboxylate **7** :





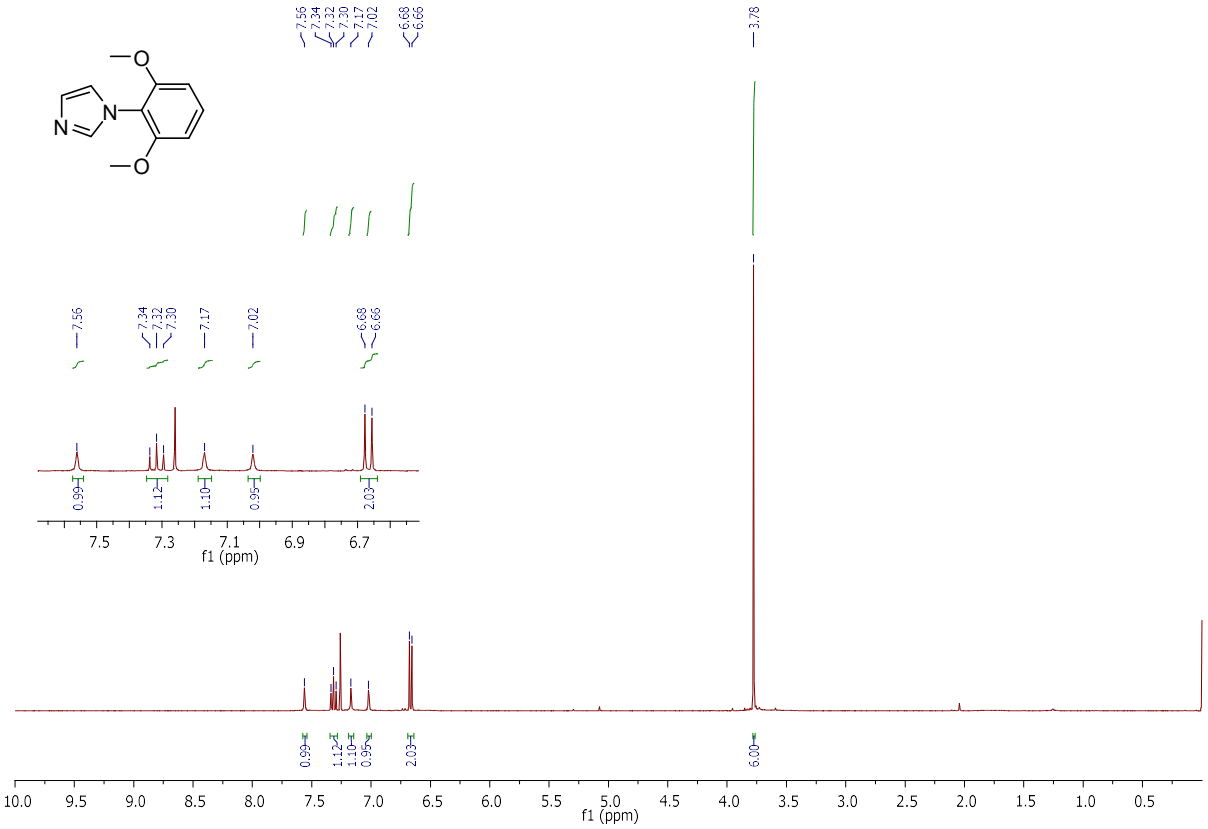
COSY and HMQC experiments :

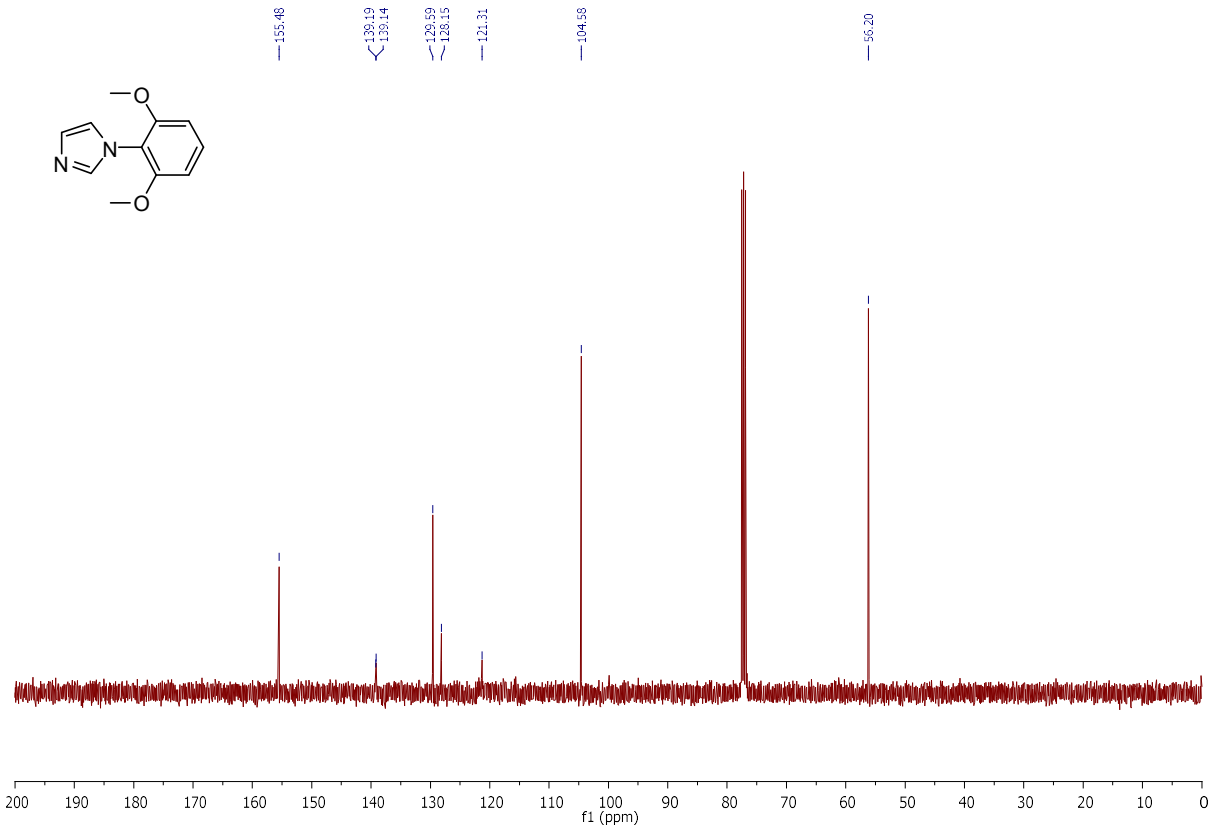




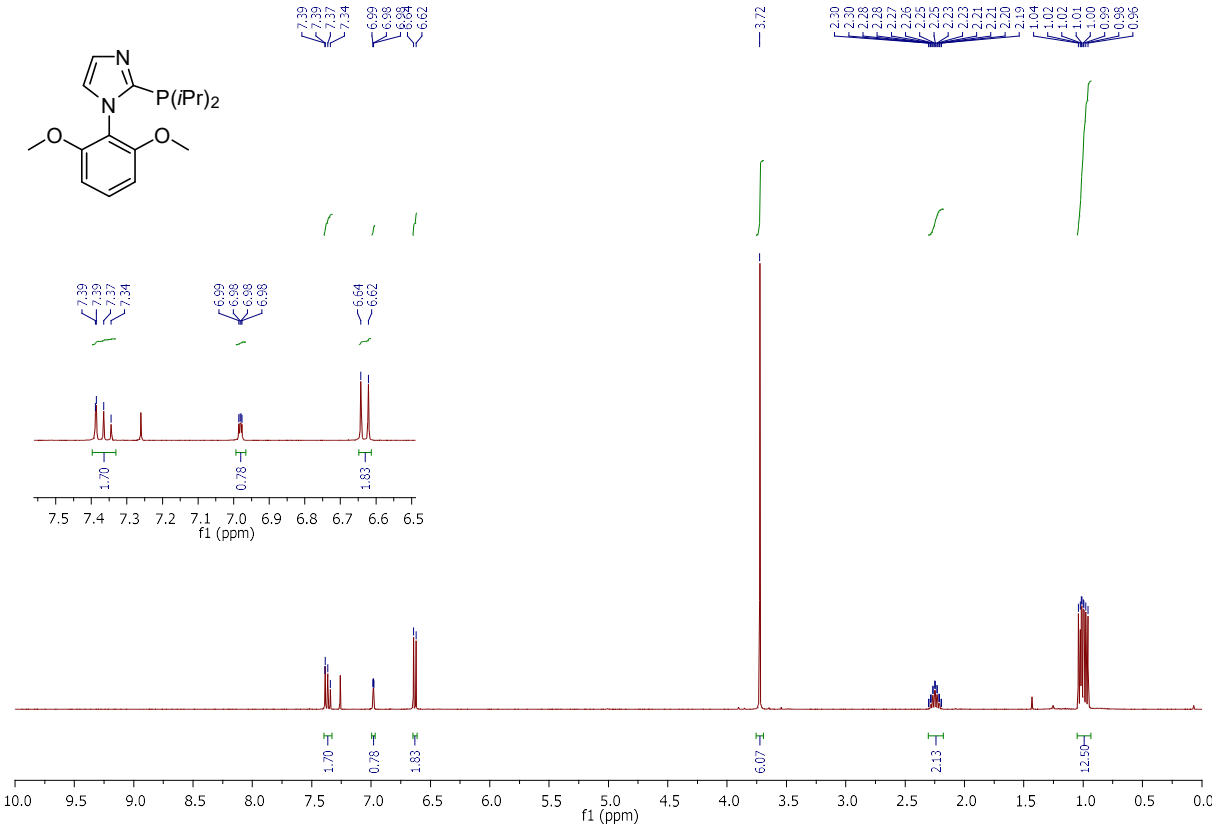

F
O
O
NO2
-118.40
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

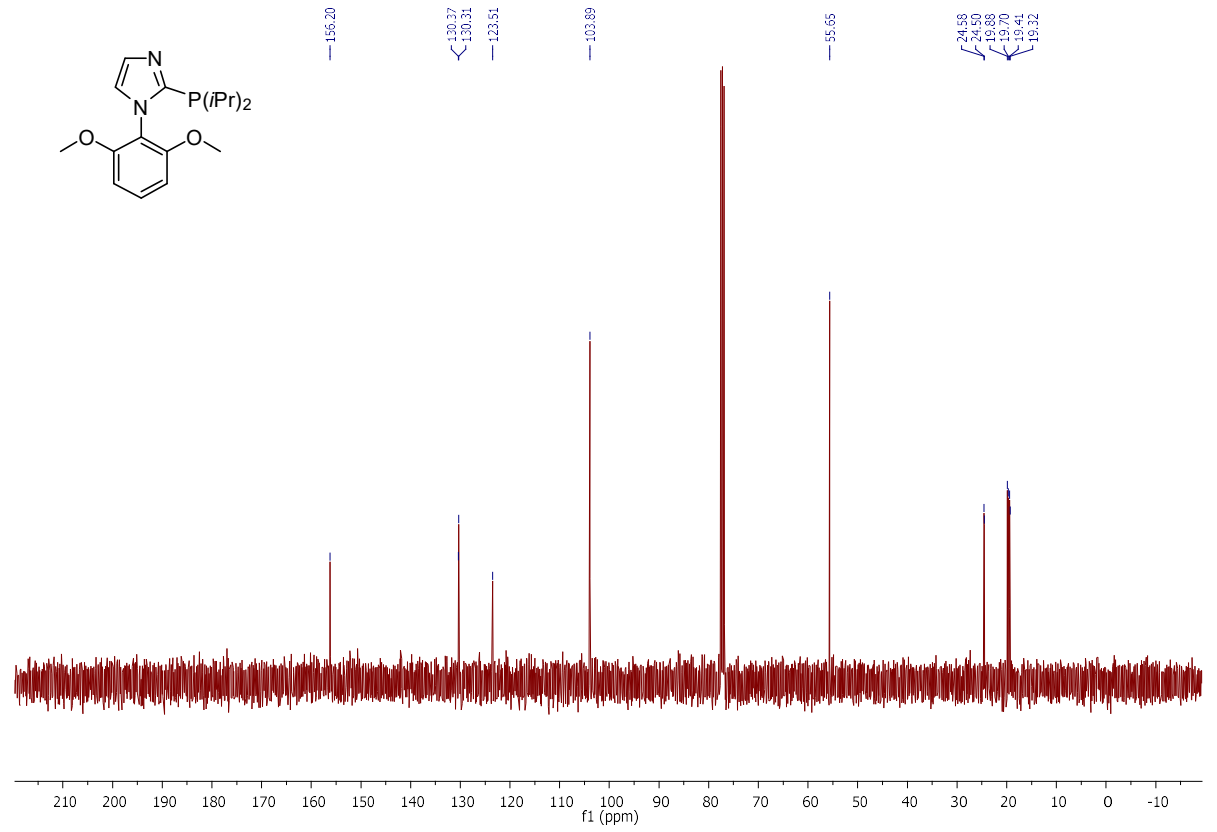
1-(2,6-dimethoxyphenyl)-1*H*-imidazole **S11** :

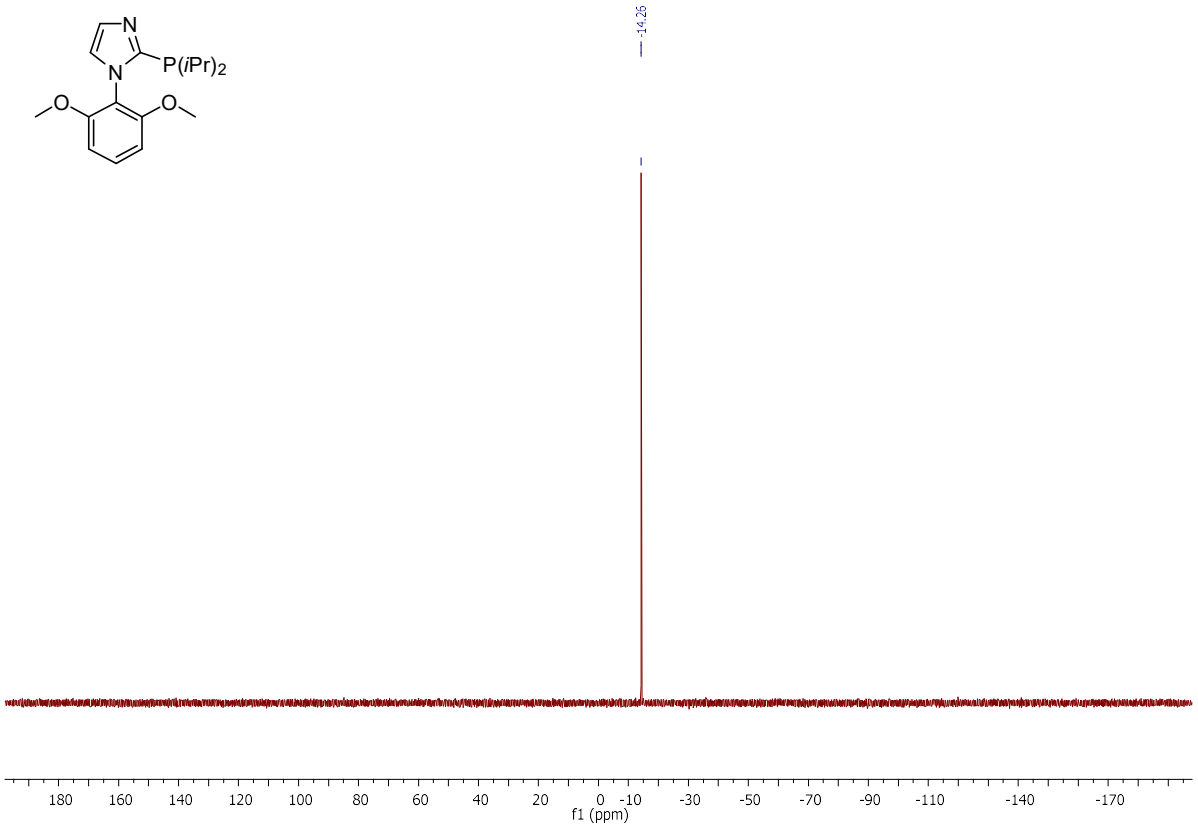




2-(diisopropylphosphanyl)-1-(2,6-dimethoxyphenyl)-1*H*-imidazole $\mathbf{L^3}$:






N
N
P(iPr)2
O
O
-14.26
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
f1 (ppm)