

**Enantioselective allylic alkylation of stereodefined polysubstituted copper enolate as
an entry to acyclic quaternary carbon stereocentre†**

Zackaria Nairoukh, Gunda GKS Narayana Kumar, Yury Minko and Ilan Marek*

The Mallat Family Laboratory of Organic Chemistry, Schulich Faculty of Chemistry and
Lise MeitnerMinerva Center for Computational Quantum Chemistry, Technion-Israel
Institute of Technology, Technion City, Haifa 32000, Israel

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General methods

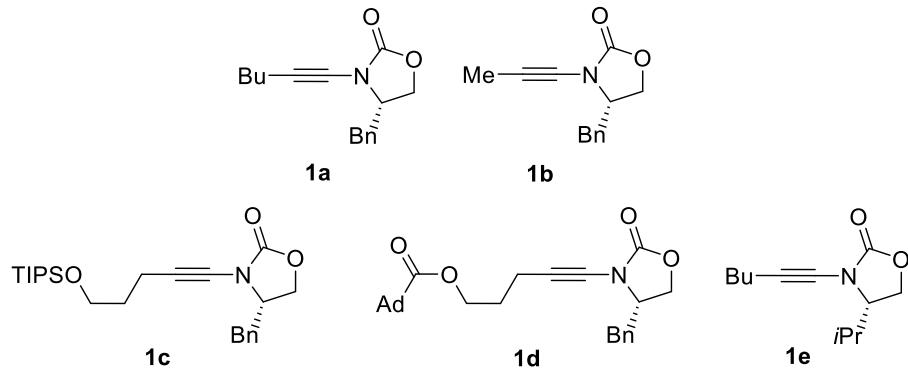
All reactions were carried out in a flame-dried glassware under positive pressure of argon in dry solvents using standard Schlenk techniques unless otherwise indicated. Progress of the reactions was monitored by analytical TLC using glass plates pre-coated with silica gel with F254 indicator (Merck). Visualization of spots was done using UV light (254 nm), iodine, *p*-anisaldehyde, phosphomolybdic acid (PMA), and Hanessian's (cerium ammonium molybdate) stains. All organometallic compounds, dry solvents and reagents were transferred using plastic single-use graduated syringes and oven-dried stainless steel needles. Purification of crude mixtures was accomplished by preparative flash column chromatography on silica gel 60A (GraceResolv), aluminum oxide 90 neutral (Merck) or Florisil® Adsorbent 100-200 mesh (Fluka) using gradient mixtures of ethyl acetate / *n*-hexane (unless otherwise indicated). ¹H and ¹³C NMR spectra were measured on Bruker Avance 200 (200 MHz ¹H, 50 MHz ¹³C), Bruker Avance 300 (300 MHz ¹H, 75 MHz ¹³C) or Bruker Avance AV 400 (400 MHz ¹H, 100 MHz ¹³C) spectrometers. Chemical shifts values (δ) are reported in ppm (calibration of spectra to the residual peak of chloroform: δ = 7.26 ppm (s) for ¹H NMR; δ = 77.00 ppm for ¹³C NMR). All the proton spectra reported as following: δ value (multiplicity, J coupling constant (in Hz), number of nuclei). Multiplicity contractions used: (s) – singlet, (d) – doublet, (dd) – doublet of doublet, (t) – triplet, (q) – quartet, (m) – multiplet, and (br) – broad signal. Melting point of solid crystalline compounds was measured on Stuart® SMP11 apparatus. Optical specific rotations are measured with an UniPol L 1000 polarimeter (Na-vapor lamp, λ = 589 nm), calculated using the equation $[\alpha]_D^t = \frac{\alpha_{measured}}{l \cdot (c \cdot 10^{-3})}$, where (l , dm ; c , $\frac{g}{dl}$), and reported as following: $[\alpha]_D^t$ value (c M, solvent). High performance liquid chromatography (HPLC) spectra were recorded on Agilent™ 1100 Series equipment with a variable wavelength UV analytical detector. Analytical separation of diastereomers from each sample was done using CHIRALPAK® AD-H 4.6 mm x 250 mmL, CHIRALCEL® OZ-H 10 mm x 250 mmL or CHIRALCEL OD 4.6 mm x 250 mm analytical HPLC column and isocratic mixtures of isopropyl alcohol and *n*-hexane (LiChrosolv® HPLC grade, Merck). MS and HRMS mass spectrometry was carried out on a APCI instrument by Maxis Impact (Bruker) and on a LCT Premier (Waters).

Reagents and materials

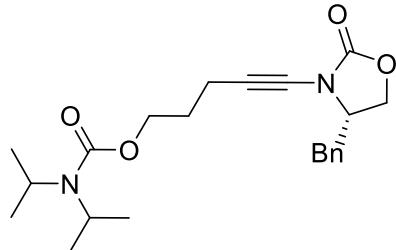
All solvents were purified and dried immediately prior to use: THF and diethyl ether (HPLC grade, non-stabilized, BioLab) were dried using Innovative Technology PureSolv PS-MD-2 solvent purifier (aluminum oxide columns) and kept under positive pressure of nitrogen (99.9999% purity grade); toluene was distilled from sodium metal under argon. Methylolithium solution in diethyl ether (1.60 M), *n*-butyllithium solution in hexane (1.60 M), *n*-pentyllithium solution in heptane (2.20M) and *n*-hexyllithium solution in hexane (2.30M) were purchased from Aldrich and used as received. *tert*-Butylhydroperoxide (TBHP) solution in nonane (5.5 M, over 4Å MS) was purchased from Aldrich. Terminal alkynes, ethyl acrylate, acryloyl chloride, 3-buten-2-one, 1-adamantanecarbonyl chloride, 2-methylpropanoyl chloride, N,N-diisopropylcarbamoyl chloride, *N*-bromosuccinimide, silver nitrate, iodine, (*S*)-4-benzyl-2-oxazolidinone, copper (I) bromide, copper (I) bromide – dimethylsulfide complex, copper(II) sulfate pentahydrate, 1,10-phenanthroline were purchased from commercial suppliers. (*S*)-4-isopropyl-2-oxazolidinone was prepared from commercially available starting materials and reagents according to published procedure.^[1] But-3-yn-1-yl isobutyrate, pent-4-yn-1-yl adamantine-1-carboxylate and but-3-yn-1-yl diisopropylcarbamate were prepared by reaction of the corresponding commercially available acyl chlorides with commercially available 4-pentyn-1-ol and 3-butyn-1-ol in presence of a stoichiometric amount of pyridine in diethyl ether. TIPS-protected 4-pentyn-1-ol was prepared according to previously reported procedure.^[2] All bromoalkynes were prepared according to a previously published procedure.^[3] Purification of the corresponding compounds was accomplished using a short-path silica gel column in *n*-hexane or 10% of ethyl acetate in *n*-hexane as eluent. Cyclopropyllithium,^[4] ethyl 2-(bromomethyl)acrylate,^[5] benzyl 2-(bromomethyl)acrylate^[6] and 3-(bromomethyl)but-3-en-2-one^[7] were prepared according to a previously published procedure.

General protocol for the preparation of starting chiral ynamides

All starting chiral ynamides **1a-h** were prepared on a multi-gram scale according to a modified literature procedure.^[8-9] NMR spectra of pure products **1a-e** were consistent with previously reported data.^[8-9]

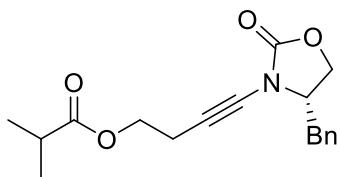


(*S*)-4-(4-benzyl-2-oxooxazolidin-3-yl)but-3-yn-1-yl diisopropylcarbamate (**1f**)



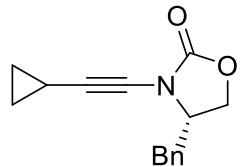
The product was obtained as a colorless oil (78%). ¹H NMR (400 MHz, CDCl₃) δ = 7.37 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 4.31 (t, *J* = 8.3 Hz, 1H), 4.26 – 4.16 (m, 3H), 4.10 - 3.94 (dd overlapped with bs, *J* = 8.4 Hz, 5.5, 2H), 3.79 (bs, 1H), 3.21 (dd, *J*¹ = 13.9 Hz, *J*² = 3.9 Hz, 1H), 2.93 (dd, *J*¹ = 13.9 Hz, *J*² = 8.1 Hz, 1H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.97 – 1.86 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 155.98, 155.36, 134.27, 129.28 (*2), 128.73 (*2), 127.19, 71.83, 69.54, 67.10, 63.06, 58.05, 45.43 (*2), 37.57, 28.30, 20.95 (*4), 15.51; HRMS TOF MS ES+: [MH]⁺ calcd. for C₂₂H₃₁N₂O₄ 387.2284; found 387.2234.

(*S*)-4-(4-benzyl-2-oxooxazolidin-3-yl)but-3-yn-1-yl isobutyrate (**1g**)



The product was obtained as a colorless oil (60%). ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.27 (m, 3H), 7.25 – 7.18 (m, 2H), 4.32 (t, $J = 8.3$ Hz, 1H), 4.26 – 4.18 (m, 3H), 4.14 – 4.08 (m, 1H), 3.20 (dd, $J^1 = 13.9$ Hz, $J^2 = 3.9$ Hz, 1H), 2.93 (dd, $J^1 = 13.9$ Hz, $J^2 = 8.1$ Hz, 1H), 2.71 (t, $J = 6.8$ Hz, 2H), 2.58 (dt, $J^1 = 14.0$ Hz, $J^2 = 7.0$ Hz, 1H), 1.19 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.97, 156.09, 134.31, 129.45 (*2), 129.08 (*2), 127.58, 70.43, 69.27, 67.37, 62.20, 58.28, 37.84, 34.00, 19.23, 19.05 (*2); HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{18}\text{H}_{22}\text{NO}_4$ 316.1549; found 316.1515.

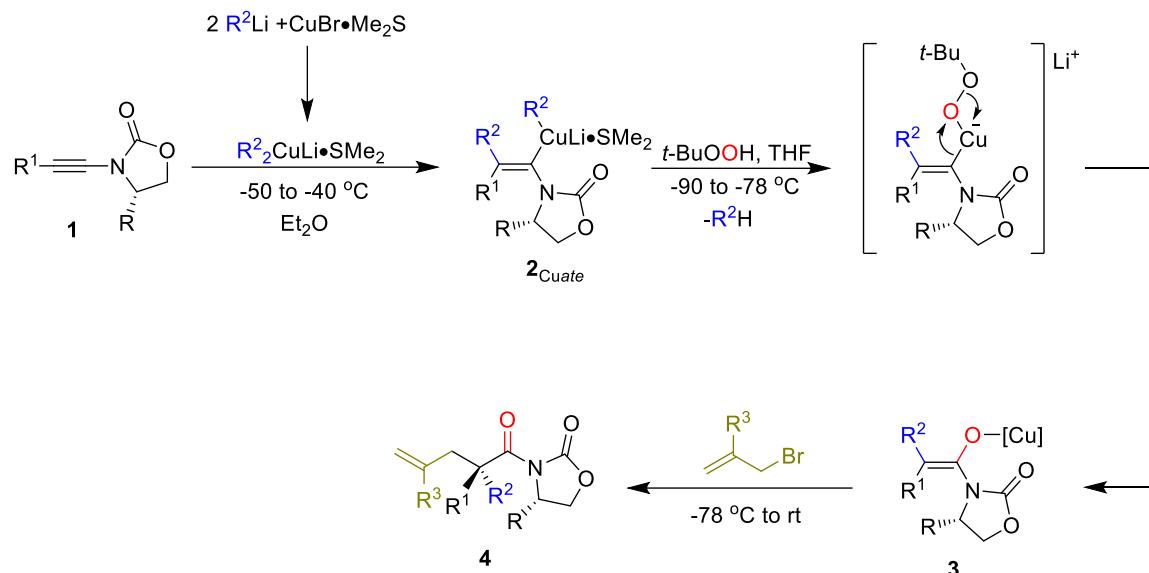
(*S*)-4-benzyl-3-(cyclopropylethynyl)oxazolidin-2-one (**1h**)



The product was obtained as a white solid (65%). mp: 46 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.26 (m, 3H), 7.22 (d, $J = 6.9$ Hz, 2H), 4.30 (t, $J = 8.3$ Hz, 1H), 4.26 – 4.16 (m, 1H), 4.09 (dd, $J^1 = 8.5$ Hz, $J^2 = 5.7$ Hz, 1H), 3.22 (dd, $J^1 = 13.9$ Hz, $J^2 = 3.9$ Hz, 1H), 2.92 (dd, $J^1 = 13.9$ Hz, $J^2 = 8.3$ Hz, 1H), 1.41 (tt, $J^1 = 8.1$ Hz, $J^2 = 4.9$ Hz, 1H), 0.91 – 0.82 (m, 2H), 0.80 – 0.70 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 156.34, 134.47, 129.41 (*2), 128.93 (*2), 127.39, 77.37, 67.20, 64.52, 58.30, 37.77, 8.94, 8.89, -0.73; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{15}\text{H}_{16}\text{NO}_2$ 242.1181; found 242.1173.

General procedures for the allylation of stereodefined trisubstituted copper enolate

1- One-pot carbocupration/oxidation with *t*-BuOOH/allylation sequence (Method A)

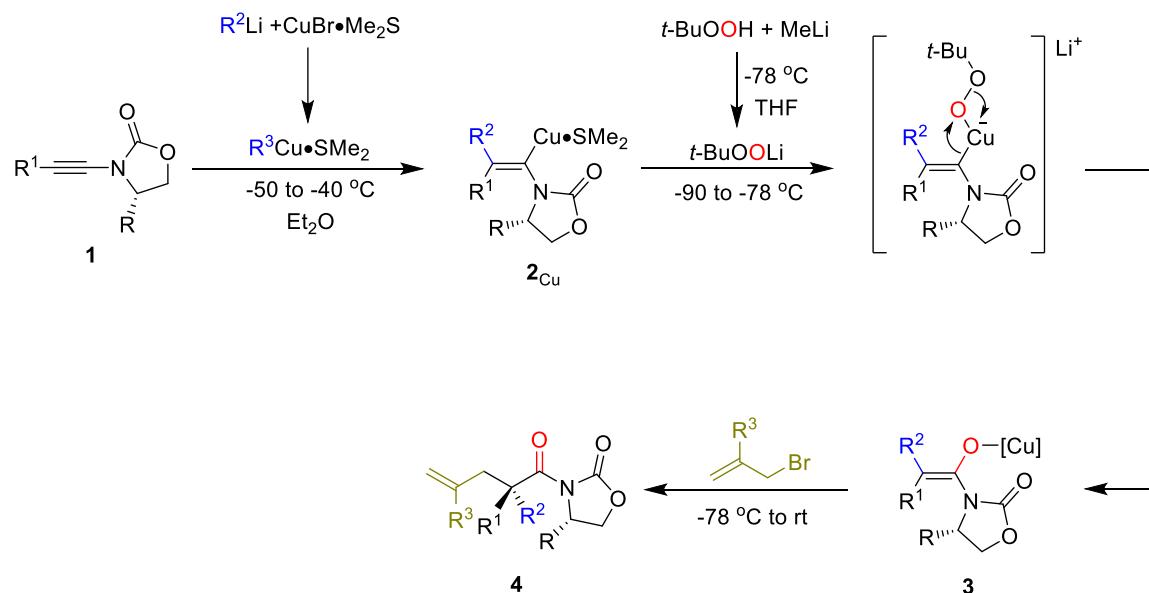


Supplementary Figure 1: One-pot sequence of carbocupration, direct oxidation with *t*-BuOOH and allylation of the stereodefined copper enolate (Method A).

$CuBr \bullet Me_2S$ complex (1.10 mmol, 1.1 equiv) was placed into a flame-dried three-necked round-bottomed flask equipped with a magnetic stirring bar and connected to an argon line. Dry diethyl ether (10 ml) was added through a septum, and the system was cooled to $-50^\circ C$ using acetone-liquid nitrogen bath. A solution of alkylolithium (2.20 mmol, 2.2 equiv), was added dropwise, and the reaction mixture was allowed to warm to $-40^\circ C$ and stirred for 30 min at this temperature to form a clear colourless or pale-yellow solution of dimethyl cuprate – lithium bromide complex. The reaction mixture was cooled to $-50^\circ C$ and a solution of the starting alkynyl carbamate **1** (1.00 mmol, 1.0 equiv) in 3 ml of diethyl ether was added dropwise; the reaction mixture was allowed to warm to $-40^\circ C$ and stirred at this temperature for 1 h (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent) to form a pale-yellow clear solution of vinylcuprate (Supplementary Fig. 1, first step). Upon completion of the first step, the reaction mixture was cooled to $-90^\circ C$ and THF (5 ml) followed by solution of *tert*-butylhydroperoxide in nonane (1.20 mmol, 1.2 equiv) were added. The resulting reaction mixture was allowed to warm up slowly to $-78^\circ C$, and stirred at the indicated temperature for 2 h (monitored by

TLC on silica gel using 20% ethyl acetate in hexane as eluent) to form a dark-brown opaque solution (Supplementary Fig. 1, second step). Upon completion of the second step, allyl bromide derivative (3.00 mmol, 3.00 equiv.) was added neat to the reaction mixture at -78 °C and stirring was continued at the indicated temperature for 2 h (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent). The reaction was allowed to warm to room temperature and was quenched with a 2:1 mixture of aqueous saturated solution of NH₄Cl and NH₄OH (30%). Phases were separated, and the aqueous phase was extracted three times with diethyl ether (10 ml). The combined organic phases were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (solvent gradient 0-20% ethyl acetate in hexane unless otherwise indicated).

2- Carbocupration/oxidation with *t*-BuOOLi/allylation sequence (Method B)



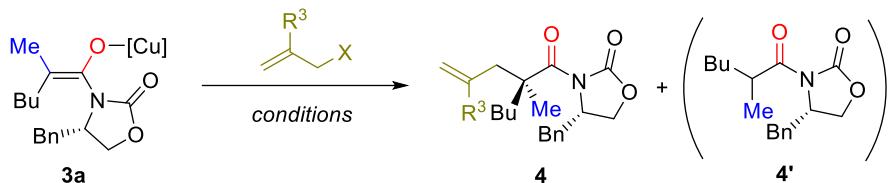
Supplementary Figure 2: One-pot sequence of carbocupration, oxidation with *t*-BuOOt-BuLi and allylation of the stereodefined copper enolate (Method B).

CuBr•Me₂S complex (1.10 mmol, 1.1 equiv) was placed into a flame-dried three-necked round-bottomed flask equipped with a magnetic stirring bar and connected to an argon line. Dry diethyl ether (10.0 ml) was added through a septum, and the system was cooled to -50 °C using acetone-liquid nitrogen bath. A solution of alkyllithium (1.30 mmol,

1.3 equiv), was added dropwise, and the reaction mixture was allowed to warm to -40 °C and stirred for 30 min at this temperature to form a bright-yellow opaque solution in case of methylolithium, dark-yellow in case of *n*-butyllithium, orange to dark-brown in case of *n*-pentyl and *n*-hexyllithium. The reaction mixture was cooled to -50 °C and a solution of the starting alkynyl carbamate **1** (1.00 mmol, 1.0 equiv) in 3 ml of diethyl ether was added dropwise; the reaction mixture was allowed to warm to -40 °C, and stirred at this temperature for 1 h (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent) to form a solution of vinylcuprate (Supplementary Fig. 2, first step).

In a separate flask connected to an argon line, a solution of 1.54 mmol (1.54 equiv) of *t*-BuOOLi was prepared as follow. Dry THF (5.0 ml) was added to flame-dried three-necked round-bottomed flask *via* a syringe followed by addition of a solution of *tert*-butyl hydroperoxide in nonane (0.28 ml of commercially available 5.5 M solution; 1.54 equiv, 1.54 mmol). The resulting solution was cooled to -90 °C and a solution of methylolithium (1.60 M in diethyl ether, 1.80 mmol, 1.80 equiv) was added dropwise keeping the indicated temperature. The resulting solution of lithium *tert*-butylperoxide was allowed to warm to -80 °C and stir for 10 min prior to use in the following reaction step. Upon completion of the first step, the reaction mixture was cooled to -90 °C and the freshly prepared solution of lithium *tert*-butylperoxide in THF (1.54 mmol, 1.54 equiv) was transferred *via* a cannula. The resulting reaction mixture was allowed to warm up slowly to -78 °C and stirred at the indicated temperature for 2 h (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent) to form a brown opaque solution (Supplementary Fig. 2, second step). Upon completion of the second step, allyl bromide derivative (3.00 mmol, 3.00 equiv.) was added neat to the reaction mixture at -78 °C and stirring was continued at the indicated temperature for 2 h (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent). Upon the completion of the third step the reaction mixture was warmed to room temperature and handled as mentioned in Path A.

Optimization reactions



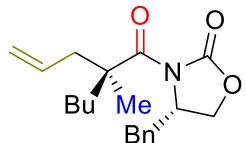
Entry ^[a]	$\text{R}^3\text{-X}^{\text{[b]}}$	Additive	Conditions	Conv. ^[c,d]	d.r. ^[e]
1		none	-78 °C to r.t. 12h	n.r.	-
2		THF (5 ml)	-78 °C to r.t. 12h	n.r.	-
3		TMEDA (2 ml)	-78 °C to r.t. 12h	n.r.	-
4		HMPA (2 ml)	-78 °C to r.t. 12h	n.r.	-
5		none	-78 °C to r.t. 12h	n.r.	-
6		THF (5 ml)	-78 °C to r.t. 12h	n.r.	-
7		DMPU (2 ml)	-78 °C to r.t. 12h	n.r.	-
8		TMEDA (2 ml)	-78 °C to r.t. 12h	>20%	n.d.
9		HMPA (5 equiv.)	-78 °C to r.t. 3h	>90%	50:50
10		HMPA (2 ml)	-78 °C to r.t. 2h	>99%	75:25
11		HMPA (5 ml)	-78 °C to r.t. 2h	>99%	75:25
12		none	-50 to -20 °C 2h	>99%	96:4
13		DMPU (4 equiv.)	-50 to -20 °C 2h	>99%	87:13
14		none	-78 °C to r.t. 2h	>99%	99:1

[a] General procedure 2 for the allylic alkylation was followed. [b] 3.00 equiv. of the electrophile was added.

[c] Conversion and diastereomeric ratio (*d.r.*) were determined by NMR and HPLC analysis of the crude.
[d] In case of no reaction (n.r.), the hydrolyzed product **4'** was isolated.

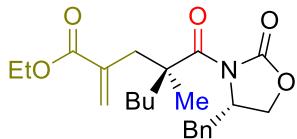
Products of the enantioselective allylic alkylation reaction

(*S*)-3-((*S*)-2-allyl-2-methylhexanoyl)-4-benzyloxazolidin-2-one (**4a**)



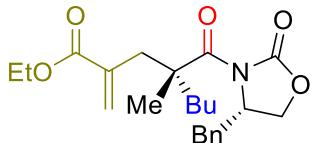
The product was obtained as a colorless oil and inseparable mixture of diastereomers (Method B: 62%, *d.r.* 75:25). Major diastereomer: ¹H NMR (300 MHz, CDCl₃) δ 7.35 – 7.16 (m, 5H), 5.85 – 5.62 (m, 1H), 5.13 – 4.95 (m, 2H), 4.71 – 4.56 (m, 1H), 4.14 – 4.03 (m, 2H), 3.27 (dd, *J*¹ = 13.1 Hz, *J*² = 3.1 Hz, 1H), 2.85 (dd, *J*¹ = 14.2 Hz, *J*² = 7.9 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.41 – 2.29 (m, 1H), 2.26 – 2.14 (m, 1H), 1.65 (m, 1H), 1.40 – 1.21 (m, 6H), 1.19 – 1.06 (m, 1H), 0.87 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 176.88, 152.35, 135.76, 134.45, 129.45, 128.93, 127.26, 117.83, 66.18, 57.97, 49.20, 40.87, 38.06, 35.98, 26.90, 23.20, 22.73, 14.11.

Ethyl-(*S*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-methyl-2-methyleneoctanoate (**4b**)



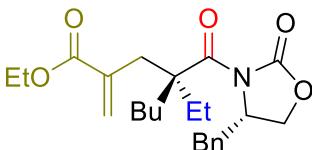
The product was obtained as a colorless oil (Method A: 65%, *d.r.* 99:1; Method B: 78%, *d.r.* 99:1). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 6.15 (d, *J* = 1.3 Hz, 1H), 5.51 (s, 1H), 4.57 (qd, *J*¹ = 6.6 Hz, *J*² = 3.1 Hz, 1H), 4.16 – 4.00 (m, 4H), 3.27 (d, *J* = 14.4 Hz, 2H), 2.75 (d, *J* = 14.0 Hz, 1H), 2.60 (dd, *J*¹ = 13.2 Hz, *J*² = 10.6 Hz, 1H), 2.19 – 2.03 (m, 1H), 1.47 – 1.34 (m, 1H), 1.28 – 1.14 (m, 9H), 1.05 – 0.93 (m, 1H), 0.81 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.70, 167.48, 152.63, 137.74, 136.11, 129.43 (*2), 128.90 (*2), 128.10, 127.17, 66.29, 60.75, 58.19, 49.07, 38.01, 37.88, 36.65, 27.00, 23.15, 22.35, 14.16, 14.03; HRMS TOF MS ES+: [MH]⁺ calcd. for C₂₃H₃₂NO₅ 402.2280; found 402.2258; HPLC: t_R(major) = 8.632 min; t_R (minor) = 9.304 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (*R*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-methyl-2-methyleneoctanoate
(4c)



The product was obtained as a colorless oil (Method A: 60%, *d.r.* 99:1; Method B: 87%, *d.r.* 99:1). ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.22 (m, 2H), 7.21 – 7.15 (m, 3H), 6.13 (d, $J = 1.5$ Hz, 1H), 5.49 (s, 1H), 4.57 (ddt, $J^1 = 10.5$ Hz, $J^2 = 7.5$ Hz, $J^3 = 2.9$ Hz, 1H), 4.16 (t, $J^1 = 8.1$ Hz, 1H), 4.08 – 4.01 (m, 3H), 3.39 (d, $J = 14.1$ Hz, 1H), 3.24 (dd, $J^1 = 13.1$ Hz, $J^2 = 3.1$ Hz, 1H), 2.59 (dd, $J^1 = 13.1$ Hz, $J^2 = 10.5$ Hz, 1H), 2.50 – 2.36 (m, 2H), 1.45 – 1.36 (m, 1H), 1.31 – 1.22 (m, 3H), 1.21 – 1.14 (m, 7H), 1.11 – 1.01 (m, 1H), 0.83 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.32, 167.26, 152.79, 137.45, 135.91, 129.31 (*2), 128.75 (*2), 128.25, 127.03, 66.10, 60.60, 57.97, 48.67, 38.21, 38.04, 36.83, 26.88, 23.06, 22.78, 14.02, 13.93; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{23}\text{H}_{32}\text{NO}_5$ 402.2280; found 402.2251; HPLC: t_{R} (major) = 9.284 min; t_{R} (minor) = 8.640 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

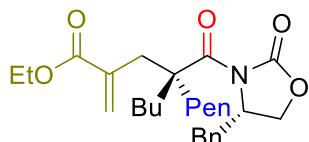
Ethyl (*S*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-ethyl-2-methyleneoctanoate
(4d)



The product was obtained as a colorless oil (Method A: 61%, *d.r.* 97:3). ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.22 (m, 2H), 7.22 – 7.15 (m, 3H), 6.13 (s, 1H), 5.48 (s, 1H), 4.58 (qd, $J^1 = 6.4$ Hz, $J^2 = 2.9$ Hz, 1H), 4.14 – 3.99 (m, 4H), 3.28 (dd, $J^1 = 13.1$ Hz, $J^2 = 3.0$ Hz, 1H), 3.09 (d, $J = 14.5$ Hz, 1H), 2.86 (d, $J = 14.5$ Hz, 1H), 2.57 (dd, $J^1 = 13.0$ Hz, $J^2 = 10.8$ Hz, 1H), 2.08 (dq, $J^1 = 14.8$ Hz, $J^2 = 7.4$ Hz, 1H), 1.88 – 1.76 (m, 1H), 1.75 – 1.67 (m, 1H), 1.67 – 1.58 (m, 1H), 1.26 – 1.14 (m, 6H), 1.11 – 1.04 (m, 1H), 0.83 (t, $J = 7.2$ Hz, 3H), 0.78 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.83, 167.51, 152.80, 137.94, 136.17, 129.40 (*2), 128.89 (*2), 127.70, 127.14, 66.23, 60.74, 58.38, 52.22, 38.11, 34.09, 31.37, 26.05, 24.72, 23.16, 14.14, 14.10, 8.62; HRMS TOF MS ES+: $[\text{M}+\text{Na}]^+$ calcd. for

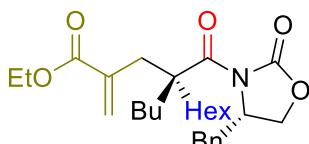
$C_{24}H_{33}NO_5Na$ 438.2256; found 438.2259; HPLC: t_R (major) = 6.151 min; t_R (minor) = 7.116 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (*R*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-butyl-2-methylenenonanoate
(4e)



The product was obtained as a colorless oil (Method B: 76%, *d.r.* 94:6). 1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.21 – 7.14 (m, 3H), 6.12 (d, J = 1.5 Hz, 1H), 5.46 (d, J = 0.9 Hz, 1H), 4.58 (ddt, J^1 = 7.3 Hz, J^2 = 6.1 Hz, J^3 = 3.0 Hz, 1H), 4.15 – 3.98 (m, 4H), 3.27 (dd, J^1 = 13.1 Hz, J^2 = 3.2 Hz, 1H), 3.11 (d, J = 14.5 Hz, 1H), 2.83 (d, J = 14.5 Hz, 1H), 2.57 (dd, J^1 = 13.1 Hz, J^2 = 10.7 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.85 – 1.74 (m, 1H), 1.70 – 1.57 (m, 2H), 1.27 – 1.06 (m, 13H), 0.86 – 0.78 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.90, 167.49, 152.78, 137.95, 136.16, 129.41 (*2), 128.88 (*2), 127.67, 127.13, 66.20, 60.73, 58.35, 51.88, 38.08, 34.48, 32.29, 32.05, 31.94, 26.06, 23.83, 23.15, 22.57, 14.14, 14.11, 14.08; HRMS TOF MS ES+: $[M+Na]^+$ calcd. for $C_{27}H_{39}NO_5Na$ 480.2726; found 480.2720; HPLC: t_R (major) = 8.004 min; t_R (minor) = 7.615 min; CHIRALPAK® AD-H (98:2 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

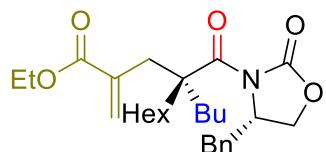
Ethyl (*R*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-butyl-2-methylenedecanoate
(4f)



The product was obtained as a colorless oil (Method B: 76%, *d.r.* 92:8). 1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.20 – 7.16 (m, 3H), 6.12 (d, J = 1.4 Hz, 1H), 5.46 (s, 1H), 4.58 (tt, J^1 = 7.1 Hz, J^2 = 2.9 Hz, 1H), 4.16 – 3.97 (m, 4H), 3.27 (dd, J^1 = 13.1 Hz, J^2 = 3.0 Hz, 1H), 3.11 (d, J = 14.5 Hz, 1H), 2.83 (d, J = 14.5 Hz, 1H), 2.57 (dd, J^1 = 13.0 Hz, J^2 = 10.8 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.87 – 1.74 (m, 1H), 1.69 – 1.58 (m, 2H), 1.27 – 1.05 (m, 15H), 0.87 – 0.77 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.93, 167.51, 152.78,

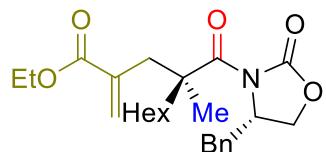
137.95, 136.17, 129.42 (*2), 128.89 (*2), 127.68, 127.14, 66.21, 60.75, 58.37, 51.90, 38.08, 34.47, 32.12, 31.94, 31.74, 29.78, 26.08, 24.12, 23.16, 22.67, 14.15, 14.12, 14.07; HRMS TOF MS ES+: [MH]⁺ calcd. for C₂₈H₄₂NO₅ 472.3062; found 472.3063; HPLC: t_R(major) = 6.502 min; t_R (minor) = 5.809 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (S)-4-((S)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-butyl-2-methylenedecanoate
(4g)



The product was obtained as a colorless oil (Method B: 79%, *d.r.* 94:6). ¹H NMR (300 MHz, CDCl₃) δ 7.35 – 7.27 (m, 2H), 7.27 – 7.14 (m, 3H), 6.17 (s, 1H), 5.51 (s, 1H), 4.62 (ddd, *J*¹ = 10.2 Hz, *J*² = 6.2 Hz, *J*³ = 2.9 Hz, 1H), 4.23 – 4.04 (m, 4H), 3.32 (dd, *J*¹ = 13.1 Hz, *J*² = 3.2 Hz, 1H), 3.14 (d, *J* = 14.5 Hz, 1H), 2.90 (d, *J* = 14.5 Hz, 1H), 2.66 – 2.56 (m, 1H), 2.16 – 2.00 (m, 1H), 1.91 – 1.79 (m, 1H), 1.75 – 1.60 (m, 2H), 1.40 – 1.01 (m, 15H), 0.91 – 0.82 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 176.81, 167.36, 152.65, 137.76, 136.03, 129.29 (*2), 128.76 (*2), 127.62, 127.01, 66.08, 60.63, 58.26, 51.74, 37.92, 34.31, 32.05, 31.64, 29.64, 26.21, 23.68, 23.03, 22.56, 14.03, 13.98, 13.95; HRMS TOF MS ES+: [MH]⁺ calcd. for C₂₈H₄₂NO₅ 472.3062; found 472.3072; HPLC: t_R(major) = 5.830 min; t_R (minor) = 6.542 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

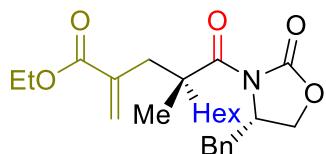
Ethyl (S)-4-((S)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-methyl-2-methylenedecanoate
(4h)



The product was obtained as a colorless oil (Method B: 81%, *d.r.* 98:2). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.22 (m, 2H), 7.22 – 7.15 (m, 3H), 6.15 (d, *J* = 1.4 Hz, 1H), 5.50 (s, 1H), 4.57 (qd, *J*¹ = 6.6 Hz, *J*² = 3.2 Hz, 1H), 4.16 – 3.99 (m, 4H), 3.27 (d, *J* = 13.8 Hz, 2H), 2.74 (d, *J* = 14.0 Hz, 1H), 2.60 (dd, *J*¹ = 13.2 Hz, *J*² = 10.6 Hz, 1H), 2.20 – 2.03 (m, 1H),

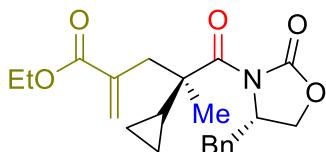
1.44 – 1.35 (m, 1H), 1.30 – 1.15 (m, 13H), 1.07 – 0.95 (m, 1H), 0.79 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.79, 167.57, 152.72, 137.85, 136.22, 129.53 (*2), 129.00 (*2), 128.18, 127.26, 66.38, 60.84, 58.29, 49.21, 38.13, 37.97, 37.04, 31.78, 29.85, 24.83, 22.70, 22.45, 14.26, 14.14; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{25}\text{H}_{36}\text{NO}_5$ 430.2593; found 430.2593; HPLC: t_{R} (major) = 7.610 min; t_{R} (minor) = 8.433 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (*R*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-methyl-2-methylenedecanoate (**4i**)



The product was obtained as a colorless oil (Method B: 83%, *d.r.* 99:1). ^1H NMR (300 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.20 (m, 3H), 6.18 (s, 1H), 5.53 (s, 1H), 4.61 (qd, J^1 = 6.9 Hz, J^2 = 3.2 Hz, 1H), 4.20 (t, J = 8.1 Hz, 1H), 4.13 – 4.05 (m, 3H), 3.44 (d, J = 14.1 Hz, 1H), 3.28 (dd, J^1 = 13.1 Hz, J^2 = 3.5 Hz, 1H), 2.63 (dd, J^1 = 13.3 Hz, J^2 = 10.3 Hz, 1H), 2.56 – 2.35 (m, 2H), 1.50 – 1.37 (m, 1H), 1.36 – 1.15 (m, 13H), 1.15 – 1.00 (m, 1H), 0.85 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.31, 167.25, 152.79, 137.45, 135.92, 129.31 (*2), 128.75 (*2), 128.24, 127.03, 66.10, 60.59, 57.96, 48.70, 38.23, 38.03, 37.12, 31.60, 29.66, 24.65, 22.79, 22.50, 14.02, 13.96; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{25}\text{H}_{36}\text{NO}_5$ 430.2593; found 430.2560; HPLC: t_{R} (major) = 8.483 min; t_{R} (minor) = 7.669 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

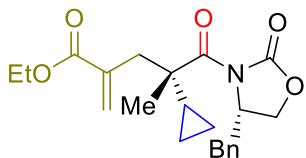
Ethyl (*R*)-5-((*S*)-4-benzyl-2-oxooxazolidin-3-yl)-4-cyclopropyl-4-methyl-2-methylene-5-oxopentanoate (**4j**)



The product was obtained as a colorless oil (Method B: 74%, *d.r.* 99:1). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.14 (m, J = 6.8 Hz, 3H), 6.15 (s, 1H), 5.55 (s, 1H), 4.57 (td, J^1 = 7.4 Hz, J^2 = 3.6 Hz, 1H), 4.17 – 4.00 (m, 4H), 3.38 (d, J = 13.8 Hz, 1H),

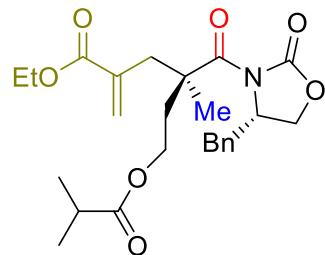
3.27 (dd, $J^1 = 13.2$ Hz, $J^2 = 2.8$ Hz, 1H), 2.93 (d, $J = 13.8$ Hz, 1H), 2.66 (dd, $J^1 = 13.1$ Hz, $J^2 = 10.6$ Hz, 1H), 1.72 – 1.64 (m, 1H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.82 (s, 3H), 0.38 – 0.28 (m, 3H), 0.17 – 0.09 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.10, 167.45, 152.88, 137.72, 136.28, 129.57 (*2), 128.97 (*2), 128.27, 127.23, 66.36, 60.81, 58.47, 48.14, 38.66, 37.88, 17.32, 15.86, 14.27, 1.90, 1.21; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{22}\text{H}_{28}\text{NO}_5$ 386.1967; found 386.1967; HPLC: t_{R} (major) = 12.974 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (*S*)-5-((*S*)-4-benzyl-2-oxooxazolidin-3-yl)-4-cyclopropyl-4-methyl-2-methylene-5-oxopentanoate (**4k**)



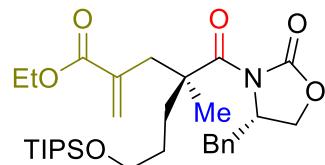
The product was obtained as a colorless oil (Method B: 70%, *d.r.* 97:3). ^1H NMR (400 MHz, CDCl_3) δ 7.12 – 7.07 (m, 2H), 7.06 – 7.00 (m, 3H), 5.99 (dd, $J^1 = 7.6$ Hz, $J^2 = 1.6$ Hz, 1H), 5.36 (s, 1H), 4.47 (ddt, $J^1 = 10.5$ Hz, $J^2 = 7.6$ Hz, $J^3 = 3.0$ Hz, 1H), 4.03 (t, $J = 8.2$ Hz, 1H), 3.95 – 3.85 (m, 3H), 3.41 (d, $J = 14.1$ Hz, 1H), 3.02 (dd, $J^1 = 13.3$ Hz, $J^2 = 3.2$ Hz, 1H), 2.56 – 2.43 (m, 2H), 1.94 – 1.83 (m, 1H), 1.03 (t, $J = 7.1$ Hz, 3H), 0.59 (s, 3H), 0.25 – 0.15 (m, 3H), 0.05 – -0.04 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.71, 167.38, 153.09, 137.69, 136.04, 129.57 (*2), 128.93 (*2), 128.38, 127.24, 66.33, 60.78, 57.97, 47.78, 38.83, 38.24, 17.50, 15.60, 14.24, 1.76, 1.03; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{22}\text{H}_{27}\text{NO}_5\text{Na}$ 408.1787; found 408.1736; HPLC: t_{R} (major) = 16.420 min; t_{R} (minor) = 13.241 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (R)-4-((S)-4-benzyl-2-oxooxazolidine-3-carbonyl)-6-(isobutyryloxy)-4-methyl-2-methylenehexanoate (**4l**)



The product was obtained as a colorless oil (Method B: 60%, *d.r.* 95:5). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 6.19 (d, $J = 1.4$ Hz, 1H), 5.54 (s, 1H), 4.59 (ddt, $J^1 = 7.3$ Hz, $J^2 = 6.2$ Hz, $J^3 = 3.0$ Hz, 1H), 4.18 (t, $J = 8.2$ Hz, 1H), 4.13 – 3.98 (m, 5H), 3.25 (dd, $J^1 = 13.2$ Hz, $J^2 = 3.2$ Hz, 1H), 3.17 (d, $J = 14.0$ Hz, 1H), 2.92 (d, $J = 13.9$ Hz, 1H), 2.66 – 2.51 (m, 2H), 2.45 – 2.34 (m, 1H), 1.72 (dt, $J^1 = 14.2$ Hz, $J^2 = 7.0$ Hz, 1H), 1.29 (s, 3H), 1.22 – 1.18 (t, $J = 7.11$ Hz, 3H), 1.07 (dd, $J^1 = 7.0$ Hz, $J^2 = 0.4$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.30, 177.11, 175.87, 167.36, 152.92, 137.18, 136.08, 129.52 (*2), 129.03 (*2), 128.91, 127.32, 66.55, 61.33, 60.96, 58.25, 47.77, 38.30, 38.08, 35.86, 34.07, 22.38, 19.05, 19.04, 14.25; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{25}\text{H}_{34}\text{NO}_5$ 460.2335; found 460.2384; HPLC: t_{R} (major) = 10.634 min; t_{R} (minor) = 9.775 min; CHIRALPAK[®] AD-H (90:10 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

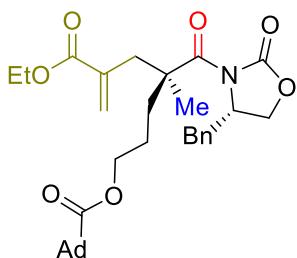
Ethyl (S)-4-((S)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-methyl-2-methylene-7-((triisopropylsilyl)oxy)heptanoate (**4m**)



The product was obtained as a colorless oil (Method B: 85%, *d.r.* 99:1). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 6.16 (d, $J = 1.5$ Hz, 1H), 5.52 (s, 1H), 4.57 (qd, $J^1 = 6.7$ Hz, $J^2 = 3.2$ Hz, 1H), 4.14 – 3.99 (m, 4H), 3.63 – 3.50 (m, 2H), 3.30 – 3.20 (m, 2H), 2.81 (d, $J = 14.0$ Hz, 1H), 2.60 (dd, $J^1 = 13.2$ Hz, $J^2 = 10.5$ Hz, 1H), 2.21 – 2.10 (m, 1H), 1.62 – 1.38 (m, 3H), 1.37 – 1.27 (m, 1H), 1.25 (s, 3H), 1.20 (m, 4H), 1.04 – 1.00 (m, 1H), 0.99 – 0.94 (m, 18H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.65, 167.55, 152.72, 137.73, 136.23, 129.55 (*2), 129.02 (*2), 128.35, 127.29, 66.40, 63.68, 60.87,

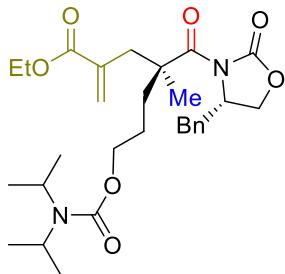
58.25, 48.90, 38.19, 38.04, 33.43, 28.64, 22.48, 18.15 (*6), 14.28, 12.11 (*3); HRMS TOF MS ES+: $[M+H]^+$ calcd. for $C_{31}H_{50}NO_6Si$ 560.3407; found 560.3420; HPLC: t_R (major) = 12.913 min; t_R (minor) = 12.371 min; CHIRALCEL® OZ-H (99:1 *n*-hexane – *i*-PrOH), flow rate 0.7 ml/min.

(S)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-6-(ethoxycarbonyl)-4-methylhept-6-en-1-yl (*3R*)-adamantane-1-carboxylate (**4n**)



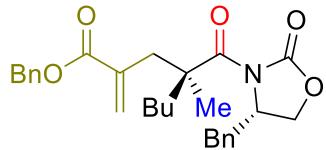
The product was obtained as a colorless oil (Method B: 71%, *d.r.* 99:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 6.17 (s, 1H), 5.52 (s, 1H), 4.58 (td, $J^1 = 7.4$ Hz, $J^2 = 3.7$ Hz, 1H), 4.17 – 4.02 (m, 4H), 3.94 (t, $J = 5.9$ Hz, 2H), 3.30 – 3.17 (m, 2H), 2.84 (d, $J = 14.0$ Hz, 1H), 2.61 (dd, $J^1 = 13.0$ Hz, $J^2 = 10.6$ Hz, 1H), 2.19 (t, $J = 10.9$ Hz, 1H), 1.98 – 1.87 (m, 3H), 1.84 – 1.75 (m, 6H), 1.67 – 1.58 (m, 6H), 1.50 – 1.38 (m, 3H), 1.26 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.77, 176.28, 167.40, 152.69, 137.55, 136.11, 129.49 (*2), 128.97 (*2), 128.40, 127.26, 66.42, 64.19, 60.85, 58.17, 48.71, 40.78, 38.89 (*3), 38.07, 37.99, 36.59 (*3), 33.50, 28.04 (*3), 24.33, 22.27, 14.23; HRMS TOF MS ES+: $[M+H]^+$ calcd. for $C_{33}H_{44}NO_7$ 566.3118; found 566.3132; HPLC: t_R (major) = 15.557 min; t_R (minor) = 13.951 min; CHIRALPAK® AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Ethyl (*R*)-4-((*S*)-4-benzyl-2-oxooxazolidine-3-carbonyl)-6-((diisopropylcarbamoyl)oxy)-4-methyl-2-methylenehexanoate (**4o**)



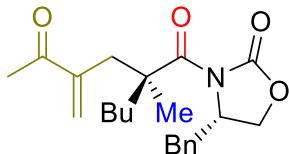
The product was obtained as a colorless oil (Method A: 52%, *d.r.* 98:2). ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.22 (m, 2H), 7.21 – 7.14 (m, 3H), 6.16 (d, $J = 1.4$ Hz, 1H), 5.52 (s, 1H), 4.58 (qd, $J^1 = 6.3$ Hz, $J^2 = 3.0$ Hz, 1H), 4.18 – 3.89 (m, 7H), 3.72 (bs, 1H), 3.30 – 3.16 (m, 2H), 2.85 (d, $J = 14.0$ Hz, 1H), 2.61 (dd, $J^1 = 13.2$ Hz, $J^2 = 10.5$ Hz, 1H), 2.23 (t, $J = 10.7$ Hz, 1H), 1.64 – 1.56 (m, 1H), 1.52 – 1.37 (m, 2H), 1.26 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H), 1.13 (dd, $J^1 = 6.8$ Hz, $J^2 = 1.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.34, 167.40, 155.70, 152.69, 137.53, 136.11, 129.49 (*2), 128.96 (*2), 128.40, 127.23, 66.41, 64.78, 60.83, 58.15, 48.72, 46.12 (*2), 38.13, 37.96, 33.89, 24.70, 22.31, 20.88 (*4), 14.23; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{29}\text{H}_{42}\text{N}_2\text{O}_7$ 531.3070; found 531.3070; HPLC: t_{R} (major) = 18.730 min; t_{R} (minor) = 16.692 min; CHIRALPAK[®] AD-H (97:3 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Benzyl (S)-4-((S)-4-benzyl-2-oxooxazolidine-3-carbonyl)-4-methyl-2-methyleneoctanoate (**4p**)



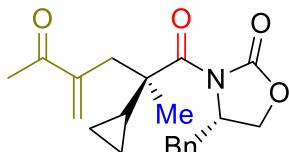
The product was obtained as a white solid (Method B: 84%, *d.r.* 99:1). mp: 56 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.08 (m, 10H), 6.22 (d, $J = 1.4$ Hz, 1H), 5.55 (s, 1H), 5.11 – 5.01 (m, 2H), 4.55 – 4.42 (m, 1H), 4.07 – 3.95 (m, 2H), 3.30 – 3.19 (m, 2H), 2.79 (d, $J = 14.0$ Hz, 1H), 2.57 (dd, $J^1 = 13.1$ Hz, $J^2 = 10.6$ Hz, 1H), 2.14 – 2.03 (m, 1H), 1.47 – 1.34 (m, 1H), 1.28 – 1.14 (m, 6H), 1.07 – 0.92 (m, 1H), 0.80 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.70, 167.33, 152.75, 137.51, 136.19, 136.12, 129.53 (*2), 128.96 (*2), 128.88, 128.61 (*2), 128.22, 128.08 (*2), 127.24, 66.61, 66.38, 58.20, 49.06, 38.17, 37.96, 36.85, 27.06, 23.24, 22.41, 14.14; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{28}\text{H}_{34}\text{NO}_5$ 464.2437; found 464.2490; HPLC: t_{R} (major) = 10.547 min; t_{R} (minor) = 11.442 min; CHIRALPAK[®] AD-H (95:5 *n*-hexane – *i*-PrOH), flow rate 1 ml/min. Single crystals of the title compound **4p** suitable for X-ray diffraction analysis were obtained by crystallization at room temperature from (1:1) mixture of *n*-hexane and ethyl acetate (slow evaporation of solvents). Detailed crystallographic data reported in the corresponding section of the Supplementary Information.

(S)-1-((*S*)-4-benzyl-2-oxooxazolidin-3-yl)-2-butyl-2-methyl-4-methylenehexane-1,5-dione (**4q**)



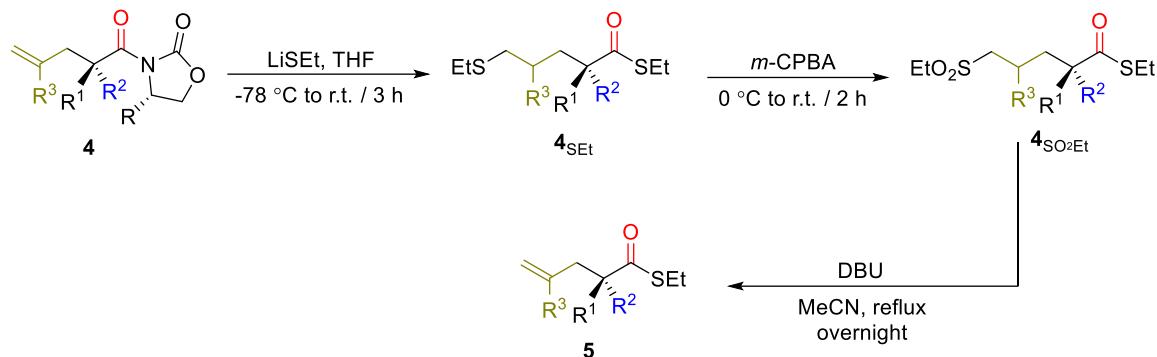
The product was obtained as a white solid (Method B: 67%, *d.r.* 99:1). mp: 63 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.13 (m, 3H), 6.01 (s, 1H), 5.73 (s, 1H), 4.56 (ddd, *J*¹ = 10.3 Hz, *J*² = 7.0 Hz, *J*³ = 3.3 Hz, 1H), 4.15 – 4.01 (m, 2H), 3.31 – 3.19 (m, 2H), 2.74 – 2.58 (m, 2H), 2.22 (s, 3H), 2.14 – 2.04 (m, 1H), 1.36 – 1.19 (m, 4H), 1.16 (s, 3H), 1.04 – 0.92 (m, 1H), 0.80 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 199.86, 176.81, 152.77, 146.34, 136.29, 129.53 (*2), 128.93 (*2), 128.46, 127.18, 66.36, 58.21, 48.71, 37.97, 37.35, 37.17, 27.08, 25.91, 23.25, 22.64, 14.11; HRMS TOF MS ES+: [MH]⁺ calcd. for C₂₂H₂₉NO₄ 372.2175; found 372.2160; HPLC: t_R(major) = 7.970 min; t_R (minor) = 7.437 min; CHIRALCEL OD (90:10 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

(R)-1-((*S*)-4-benzyl-2-oxooxazolidin-3-yl)-2-cyclopropyl-2-methyl-4-methylenehexane-1,5-dione (**4r**)



The product was obtained as a colorless oil (Method B: 60%, *d.r.* 99:1). ¹H NMR (400 MHz, CDCl₃) δ 7.15 – 7.09 (m, 2H), 7.07 – 7.01 (m, 3H), 5.89 (s, 1H), 5.65 (s, 1H), 4.50 – 4.39 (m, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 3.93 (dd, *J*¹ = 8.8 Hz, *J*² = 2.3 Hz, 1H), 3.21 (d, *J*¹ = 13.6 Hz, 1H), 3.14 (dd, *J*¹ = 13.3 Hz, *J*² = 3.0 Hz, 1H), 2.73 (d, *J* = 13.6 Hz, 1H), 2.56 (dd, *J*¹ = 13.2 Hz, *J*² = 10.6 Hz, 1H), 2.09 (s, 3H), 1.50 (dq, *J*¹ = 7.8 Hz, *J*² = 6.2 Hz, 1H), 0.63 (s, 3H), 0.27 – 0.11 (m, 3H), 0.04 – -0.07 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 198.49, 175.83, 151.59, 144.83, 135.02, 128.24 (*2), 127.58 (*2), 127.41, 125.82, 65.00, 57.10, 46.38, 36.60, 36.53, 24.56, 16.07, 14.75, 0.43, 0.00; HRMS TOF MS ES+: [MH]⁺ calcd. for C₂₁H₂₅NO₄ 356.1862; found 356.1836; HPLC: t_R(major) = 9.327 min; t_R (minor) = 9.868 min; CHIRALPAK® AD-H (90:10 *n*-hexane – *i*-PrOH), flow rate 1 ml/min.

Cleavage of oxazolidinone moiety **4**



Supplementary Figure 3: Removal of the chiral auxiliary, oxidation and elimination sequence

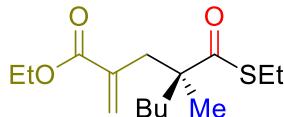
5 was prepared according to a modified literature procedure.^[10] To a suspension of ethanethiol (7.00 equiv.) in THF (0.4 M) at -78°C was slowly added $n\text{-BuLi}$ (6.50 equiv., 1.6 M in hexane). After 30 min, a solution of **4** (1.00 equiv.) in THF (5 mL) was slowly added to the reaction mixture at -78°C , and the contents were allowed to gradually warm up to room temperature over 3 h. Upon completion of the first step (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent), the reaction mixture was quenched with sat. NaHCO_3 (15 mL) and extracted with Et_2O (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure affording thioester **4_{SEt}**.

The thioester crude **4_{SEt}** was then dissolved in DCM (0.1 M) and cooled to 0°C followed by the addition of $m\text{-CPBA}$ (5.00 equiv.). The resulting mixture was slowly warm up to room temperature over 2 h. Upon completion of the second step (monitored by TLC on silica gel using 20% ethyl acetate in hexane as eluent), a solution of 10% Na_2SO_4 was added and the mixture was stirred at room temperature for 20 min. Phases were separated, and the aqueous phase was extracted three times with chloroform (10 ml). The combined organic phases were dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure affording **4_{SO₂Et}**.

Then, **4_{SO₂Et}** was dissolved in acetonitrile (0.1 M) followed by the addition of 1,8-diazabicycloundec-7-ene (1.10 equiv., DBU). After refluxing for 6 h, the reaction mixture was cooled to room temperature and a solution of 5% HCl was added (20 ml). Phases were

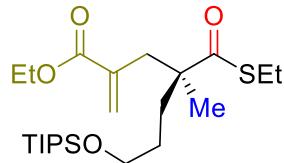
separated and the aqueous phase was extracted three times with chloroform (10 ml). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (solvent gradient 0–10% ethyl acetate in hexane).

Ethyl (*S*)-4-((ethylthio)carbonyl)-4-methyl-2-methyleneoctanoate (5b**)**



The product was obtained as a colorless oil (76% over 3 steps, *e.r.* 99:1). $[\alpha]_D^{20} = -0.61$ ($c = 0.56$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 6.18 (d, $J = 1.5$ Hz, 1H), 5.49 (d, $J = 0.7$ Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2H), 2.81 (q, $J = 7.4$ Hz, 2H), 2.63 (q, $J = 13.7$ Hz, 2H), 1.75 – 1.62 (m, 1H), 1.43 – 1.32 (m, 1H), 1.30 – 1.17 (m, 10H), 1.13 (s, 3H), 0.85 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.79, 167.77, 137.17, 128.15, 60.96, 53.72, 40.07, 39.68, 26.49, 23.33, 23.24, 20.50, 14.76, 14.30, 14.08, 1.16; HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{15}\text{H}_{27}\text{O}_3\text{S}$ 287.1681; found 287.1655.

Ethyl (*S*)-4-((ethylthio)carbonyl)-4-methyl-2-methylene-7-((triisopropylsilyl)oxy)heptanoate (5m**)**

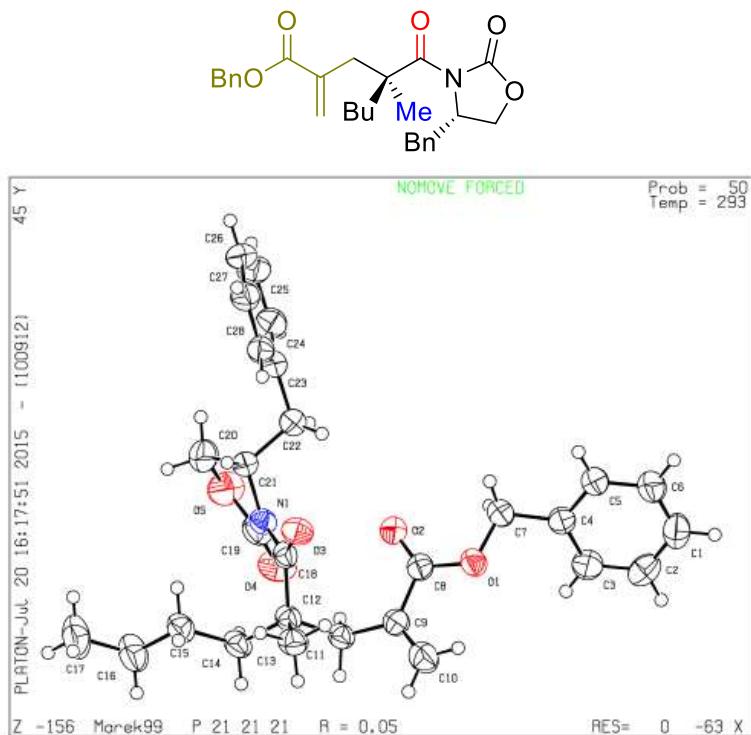


The product was obtained as a colorless oil (72% over 3 steps, *e.r.* 99:1). $[\alpha]_D^{20} = +0.98$ ($c = 0.64$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 6.19 (d, $J = 1.5$ Hz, 1H), 5.51 (s, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.67 – 3.54 (m, 2H), 2.80 (q, $J = 7.4$ Hz, 2H), 2.64 (dd, $J^1 = 32.9$ Hz, $J^2 = 13.7$ Hz, 2H), 1.82 – 1.66 (m, 1H), 1.55 – 1.36 (m, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.4$ Hz, 3H), 1.14 (s, 3H), 1.05 – 0.94 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 205.60, 167.70, 137.05, 128.26, 63.62, 60.95, 53.44, 40.00, 36.10, 27.95, 23.24, 20.56, 18.15 (*6), 14.74, 14.29, 12.08 (*3); HRMS TOF MS ES+: $[\text{MH}]^+$ calcd. for $\text{C}_{23}\text{H}_{45}\text{O}_4\text{SSi}$ 445.2808; found 445.2813.

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X-Ray crystallographic analysis data of 4p



Supplementary Figure 4: Crystal structure of compound 4p

Table 1. Crystal data and structure refinement for Marek99.

Identification code	Marek99
Empirical formula	C ₂₈ H ₃₃ N ₁ O ₅
Formula weight	463.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 6.003(6) Å alpha = 90 deg. b = 14.84(3) Å beta = 90 deg. c = 28.93(3) Å gamma = 90 deg.
Volume	2577(7) Å ³

Z, Calculated density 4, 1.195 Mg/m³
 Absorption coefficient 0.081 mm⁻¹
 F(000) 992
 Crystal size 0.45 x 0.21 x 0.18 mm
 Theta range for data collection 1.41 to 24.14 deg.
 Limiting indices 0<=h<=6, 0<=k<=16, 0<=l<=32
 Reflections collected / unique 2210 / 2210 [R(int) = 0.0650]
 Completeness to theta = 24.14 99.1 %
 Absorption correction Semi-empirical from equivalents
 Max. and min. transmission 0.9655 and 0.9643
 Refinement method Full-matrix least-squares on F²
 Data / restraints / parameters 2210 / 0 / 309
 Goodness-of-fit on F² 1.070
 Final R indices [I>2sigma(I)] R1 = 0.0460, wR2 = 0.1174
 R indices (all data) R1 = 0.0611, wR2 = 0.1403
 Absolute structure parameter 0.0
 Largest diff. peak and hole 0.196 and -0.214 e.A⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for shelxl. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	-2690(4)	5907(2)	4144(1)	47(1)
O(2)	-1210(4)	4686(2)	3794(1)	50(1)
O(3)	3850(4)	5024(2)	3511(1)	49(1)
O(4)	-839(5)	3511(2)	2745(1)	66(1)
O(5)	1619(6)	2428(2)	2923(1)	71(1)

N(1)	2471(5)	3824(2)	3150(1)	43(1)
C(1)	-8088(8)	6678(3)	5386(2)	62(1)
C(2)	-8446(7)	6626(3)	4918(2)	63(1)
C(3)	-6905(7)	6205(3)	4635(1)	56(1)
C(4)	-4993(6)	5831(2)	4818(1)	45(1)
C(5)	-4643(7)	5894(3)	5292(1)	51(1)
C(6)	-6211(8)	6309(3)	5571(1)	61(1)
C(7)	-3373(7)	5334(3)	4520(1)	51(1)
C(8)	-1709(6)	5479(3)	3790(1)	42(1)
C(9)	-1325(6)	6077(3)	3382(1)	43(1)
C(10)	-1545(8)	6964(3)	3418(2)	64(1)
C(11)	-781(6)	5611(3)	2934(1)	43(1)
C(12)	1741(6)	5424(3)	2837(1)	41(1)
C(13)	3008(6)	6318(3)	2888(1)	49(1)
C(14)	1959(6)	5082(3)	2335(1)	49(1)
C(15)	4296(7)	4795(3)	2181(1)	53(1)
C(16)	4344(8)	4432(4)	1692(1)	72(1)
C(17)	6664(9)	4136(4)	1536(2)	92(2)
C(18)	2695(6)	4765(2)	3195(1)	41(1)
C(19)	916(8)	3294(3)	2917(1)	55(1)
C(20)	3870(8)	2402(3)	3113(2)	69(1)
C(21)	3975(7)	3225(3)	3416(1)	46(1)
C(22)	3129(6)	3047(3)	3908(1)	48(1)
C(23)	4662(6)	2441(3)	4178(1)	45(1)
C(24)	4097(7)	1554(3)	4280(1)	57(1)
C(25)	5538(8)	1005(3)	4528(2)	67(1)
C(26)	7563(8)	1337(3)	4682(2)	63(1)
C(27)	8143(7)	2221(3)	4584(1)	54(1)
C(28)	6721(6)	2756(3)	4329(1)	47(1)

Table 3. Bond lengths [Å] and angles [deg] for shelxl.

O(1)-C(8)	1.342(4)
O(1)-C(7)	1.440(5)
O(2)-C(8)	1.214(5)
O(3)-C(18)	1.210(4)
O(4)-C(19)	1.208(5)
O(5)-C(19)	1.354(6)
O(5)-C(20)	1.459(6)
N(1)-C(19)	1.394(5)
N(1)-C(18)	1.409(6)
N(1)-C(21)	1.482(5)
C(1)-C(6)	1.363(6)
C(1)-C(2)	1.373(6)
C(1)-H(1)	0.9300
C(2)-C(3)	1.383(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.381(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.389(5)
C(4)-C(7)	1.495(5)
C(5)-C(6)	1.386(6)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.494(5)
C(9)-C(10)	1.327(6)
C(9)-C(11)	1.506(5)
C(10)-H(10A)	0.9300

C(10)-H(10B)	0.9300
C(11)-C(12)	1.564(5)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(18)	1.536(5)
C(12)-C(13)	1.536(6)
C(12)-C(14)	1.543(5)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.533(6)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.514(6)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.528(7)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(20)-C(21)	1.505(6)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.533(5)
C(21)-H(21)	0.9800
C(22)-C(23)	1.506(5)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(24)	1.390(6)

C(23)-C(28)	1.392(6)
C(24)-C(25)	1.387(6)
C(24)-H(24)	0.9300
C(25)-C(26)	1.386(7)
C(25)-H(25)	0.9300
C(26)-C(27)	1.385(7)
C(26)-H(26)	0.9300
C(27)-C(28)	1.379(5)
C(27)-H(27)	0.9300
C(28)-H(28)	0.9300

C(8)-O(1)-C(7)	115.0(3)
C(19)-O(5)-C(20)	108.6(4)
C(19)-N(1)-C(18)	131.8(3)
C(19)-N(1)-C(21)	108.8(3)
C(18)-N(1)-C(21)	119.2(3)
C(6)-C(1)-C(2)	119.7(4)
C(6)-C(1)-H(1)	120.2
C(2)-C(1)-H(1)	120.2
C(1)-C(2)-C(3)	120.2(4)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	120.7(4)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	118.5(4)
C(3)-C(4)-C(7)	121.1(3)
C(5)-C(4)-C(7)	120.3(4)
C(6)-C(5)-C(4)	120.2(4)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9

C(1)-C(6)-C(5)	120.7(4)
C(1)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
O(1)-C(7)-C(4)	109.3(3)
O(1)-C(7)-H(7A)	109.8
C(4)-C(7)-H(7A)	109.8
O(1)-C(7)-H(7B)	109.8
C(4)-C(7)-H(7B)	109.8
H(7A)-C(7)-H(7B)	108.3
O(2)-C(8)-O(1)	124.0(3)
O(2)-C(8)-C(9)	123.2(3)
O(1)-C(8)-C(9)	112.9(3)
C(10)-C(9)-C(8)	120.9(4)
C(10)-C(9)-C(11)	123.0(3)
C(8)-C(9)-C(11)	116.1(3)
C(9)-C(10)-H(10A)	120.0
C(9)-C(10)-H(10B)	120.0
H(10A)-C(10)-H(10B)	120.0
C(9)-C(11)-C(12)	116.4(3)
C(9)-C(11)-H(11A)	108.2
C(12)-C(11)-H(11A)	108.2
C(9)-C(11)-H(11B)	108.2
C(12)-C(11)-H(11B)	108.2
H(11A)-C(11)-H(11B)	107.3
C(18)-C(12)-C(13)	107.5(3)
C(18)-C(12)-C(14)	113.1(3)
C(13)-C(12)-C(14)	109.4(3)
C(18)-C(12)-C(11)	110.7(3)
C(13)-C(12)-C(11)	108.0(3)
C(14)-C(12)-C(11)	108.0(3)
C(12)-C(13)-H(13A)	109.5

C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(12)	116.3(3)
C(15)-C(14)-H(14A)	108.2
C(12)-C(14)-H(14A)	108.2
C(15)-C(14)-H(14B)	108.2
C(12)-C(14)-H(14B)	108.2
H(14A)-C(14)-H(14B)	107.4
C(16)-C(15)-C(14)	112.9(3)
C(16)-C(15)-H(15A)	109.0
C(14)-C(15)-H(15A)	109.0
C(16)-C(15)-H(15B)	109.0
C(14)-C(15)-H(15B)	109.0
H(15A)-C(15)-H(15B)	107.8
C(15)-C(16)-C(17)	113.3(4)
C(15)-C(16)-H(16A)	108.9
C(17)-C(16)-H(16A)	108.9
C(15)-C(16)-H(16B)	108.9
C(17)-C(16)-H(16B)	108.9
H(16A)-C(16)-H(16B)	107.7
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(3)-C(18)-N(1)	116.1(3)
O(3)-C(18)-C(12)	121.3(3)

N(1)-C(18)-C(12)	122.3(3)
O(4)-C(19)-O(5)	122.0(4)
O(4)-C(19)-N(1)	129.3(4)
O(5)-C(19)-N(1)	108.7(4)
O(5)-C(20)-C(21)	103.7(3)
O(5)-C(20)-H(20A)	111.0
C(21)-C(20)-H(20A)	111.0
O(5)-C(20)-H(20B)	111.0
C(21)-C(20)-H(20B)	111.0
H(20A)-C(20)-H(20B)	109.0
N(1)-C(21)-C(20)	99.1(3)
N(1)-C(21)-C(22)	112.5(3)
C(20)-C(21)-C(22)	112.7(4)
N(1)-C(21)-H(21)	110.7
C(20)-C(21)-H(21)	110.7
C(22)-C(21)-H(21)	110.7
C(23)-C(22)-C(21)	112.5(3)
C(23)-C(22)-H(22A)	109.1
C(21)-C(22)-H(22A)	109.1
C(23)-C(22)-H(22B)	109.1
C(21)-C(22)-H(22B)	109.1
H(22A)-C(22)-H(22B)	107.8
C(24)-C(23)-C(28)	117.9(4)
C(24)-C(23)-C(22)	121.8(4)
C(28)-C(23)-C(22)	120.3(4)
C(25)-C(24)-C(23)	120.9(4)
C(25)-C(24)-H(24)	119.6
C(23)-C(24)-H(24)	119.6
C(26)-C(25)-C(24)	120.3(4)
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9

C(27)-C(26)-C(25)	119.4(4)
C(27)-C(26)-H(26)	120.3
C(25)-C(26)-H(26)	120.3
C(28)-C(27)-C(26)	119.9(4)
C(28)-C(27)-H(27)	120.0
C(26)-C(27)-H(27)	120.0
C(27)-C(28)-C(23)	121.6(4)
C(27)-C(28)-H(28)	119.2
C(23)-C(28)-H(28)	119.2

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{A}^2 \times 10^3$) for shelxl. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	57(2)	47(1)	38(1)	-3(1)	4(1)	2(1)
O(2)	51(2)	49(2)	49(2)	5(1)	8(1)	7(1)
O(3)	49(2)	56(2)	41(1)	2(1)	-13(1)	-5(1)
O(4)	68(2)	68(2)	61(2)	1(2)	-20(2)	-16(2)
O(5)	98(2)	54(2)	62(2)	-16(2)	-19(2)	4(2)
N(1)	48(2)	47(2)	36(2)	0(1)	-4(1)	-1(2)
C(1)	62(3)	58(3)	67(3)	-9(2)	17(2)	3(2)
C(2)	48(2)	58(3)	82(3)	0(2)	-5(2)	7(2)
C(3)	55(2)	60(3)	53(2)	-2(2)	-5(2)	0(2)
C(4)	52(2)	37(2)	47(2)	1(2)	5(2)	-1(2)
C(5)	56(2)	52(2)	43(2)	-1(2)	2(2)	6(2)
C(6)	76(3)	60(3)	47(2)	-5(2)	6(2)	8(2)
C(7)	61(2)	50(2)	42(2)	3(2)	9(2)	6(2)
C(8)	36(2)	49(2)	42(2)	-2(2)	-3(2)	0(2)
C(9)	38(2)	47(2)	42(2)	2(2)	-1(2)	0(2)
C(10)	76(3)	59(3)	57(2)	6(2)	16(2)	0(2)
C(11)	41(2)	52(2)	36(2)	4(2)	-2(2)	0(2)
C(12)	36(2)	53(2)	35(2)	2(2)	-2(2)	-1(2)
C(13)	43(2)	54(2)	51(2)	9(2)	-1(2)	-2(2)
C(14)	44(2)	68(3)	34(2)	4(2)	-3(2)	0(2)
C(15)	53(2)	68(3)	39(2)	0(2)	1(2)	2(2)

C(16)	66(3)	100(4)	49(2)	-14(3)	5(2)	-1(3)
C(17)	83(3)	135(5)	59(3)	-26(3)	14(3)	15(4)
C(18)	34(2)	50(2)	38(2)	-1(2)	4(2)	-1(2)
C(19)	71(3)	54(3)	41(2)	-5(2)	-2(2)	-3(2)
C(20)	85(4)	67(3)	56(2)	-10(2)	3(2)	21(3)
C(21)	46(2)	50(2)	42(2)	6(2)	2(2)	10(2)
C(22)	47(2)	52(2)	43(2)	4(2)	3(2)	5(2)
C(23)	47(2)	47(2)	39(2)	1(2)	6(2)	6(2)
C(24)	57(2)	50(2)	64(2)	6(2)	5(2)	-6(2)
C(25)	75(3)	48(2)	77(3)	18(2)	11(3)	3(2)
C(26)	67(3)	59(3)	62(3)	20(2)	7(2)	18(2)
C(27)	50(2)	65(3)	48(2)	4(2)	-3(2)	5(2)
C(28)	51(2)	42(2)	48(2)	3(2)	6(2)	0(2)

Table 5. Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å² x 10³) for shelxl.

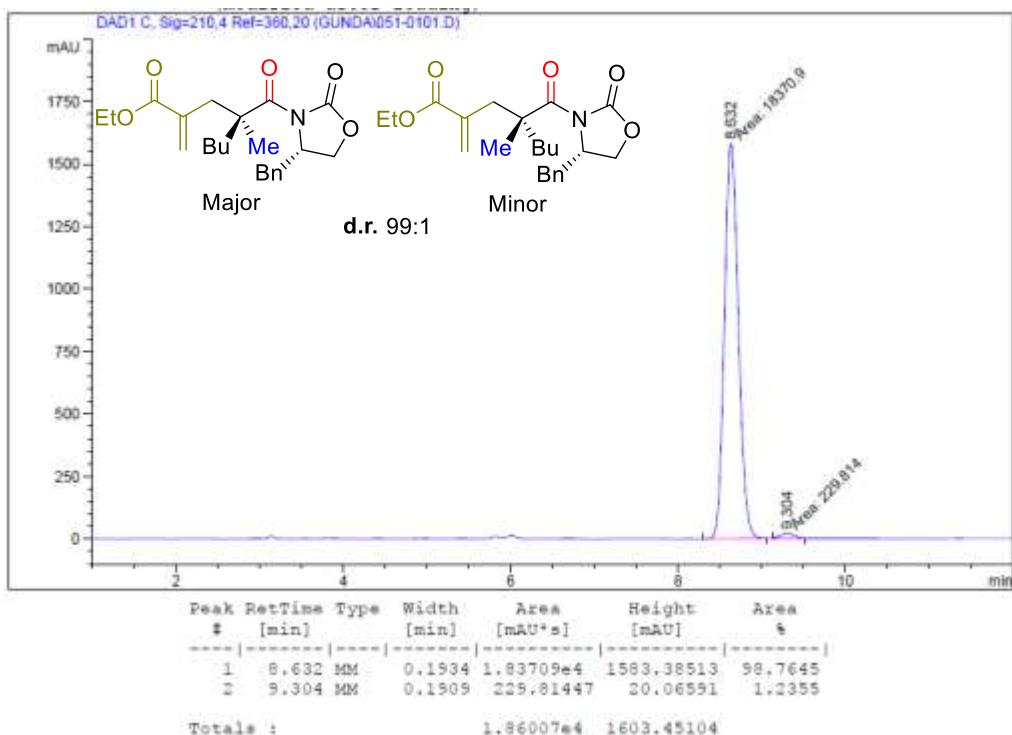
	x	y	z	U(eq)
H(1)	-9122	6964	5575	75
H(2)	-9727	6876	4790	75
H(3)	-7161	6172	4319	67
H(5)	-3352	5657	5422	61
H(6)	-5981	6337	5889	73
H(7A)	-2083	5159	4701	61
H(7B)	-4063	4793	4399	61
H(10A)	-1943	7220	3699	77
H(10B)	-1301	7329	3162	77
H(11A)	-1362	5974	2682	51
H(11B)	-1565	5039	2928	51
H(13A)	4550	6226	2814	74
H(13B)	2882	6529	3201	74
H(13C)	2384	6757	2682	74
H(14A)	965	4572	2297	58
H(14B)	1446	5554	2129	58
H(15A)	5289	5309	2201	64
H(15B)	4847	4335	2390	64
H(16A)	3803	4893	1483	86
H(16B)	3339	3921	1671	86
H(17A)	6578	3887	1230	138
H(17B)	7225	3687	1745	138
H(17C)	7645	4646	1535	138
H(20A)	4976	2431	2869	83

H(20B)	4106	1858	3292	83
H(21)	5490	3471	3423	55
H(22A)	2979	3616	4069	57
H(22B)	1666	2772	3891	57
H(24)	2734	1327	4182	69
H(25)	5144	412	4590	80
H(26)	8524	971	4850	75
H(27)	9489	2452	4689	65
H(28)	7147	3342	4257	56

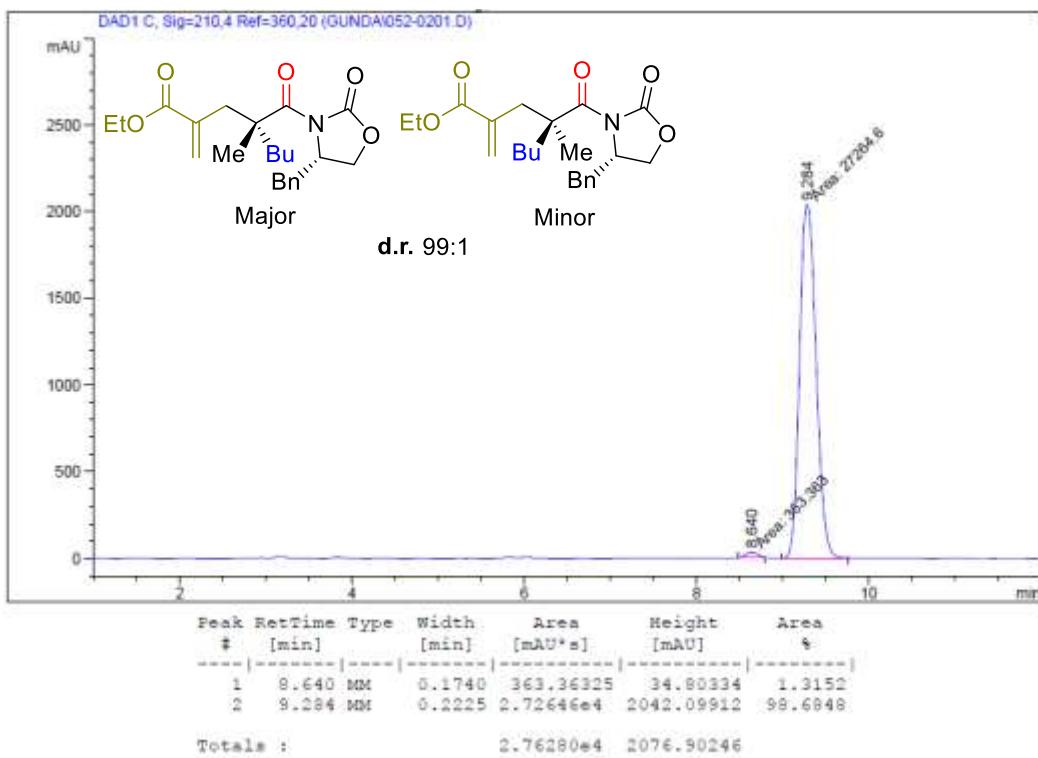
Table 6. Torsion angles [deg] for shelxl.

Analytical HPLC analysis data for the products of enantioselective allylic alkylation

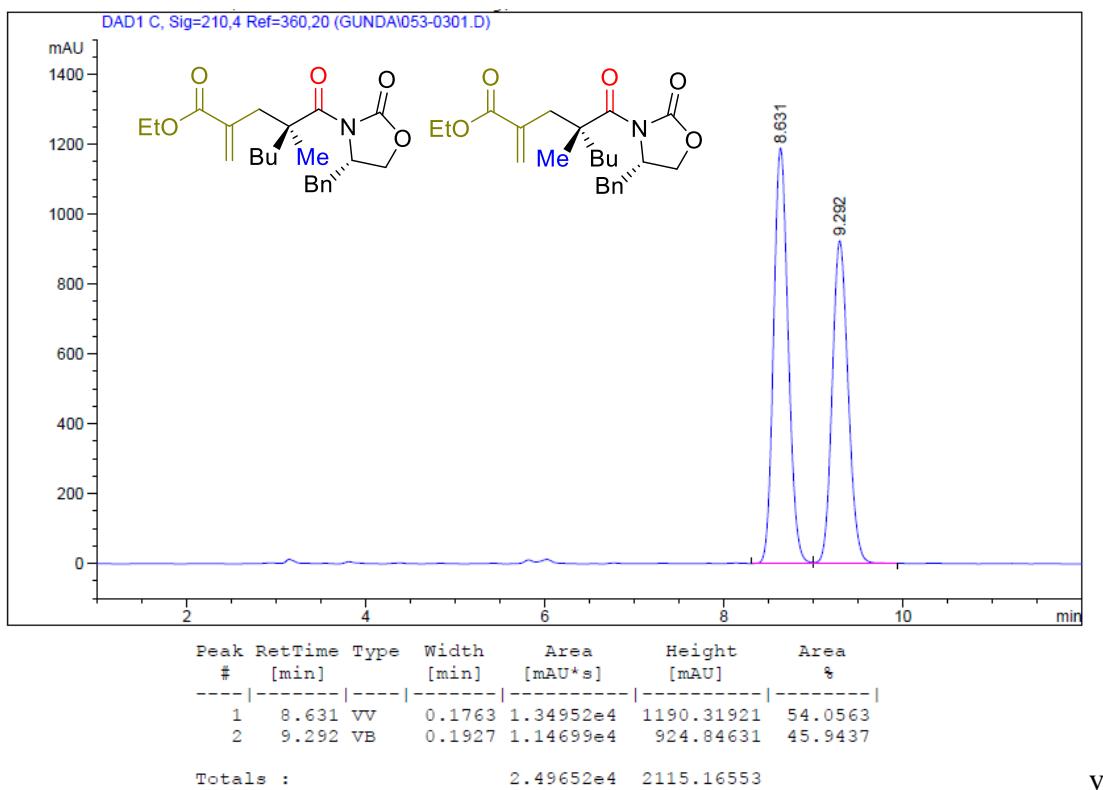
Compound 4b



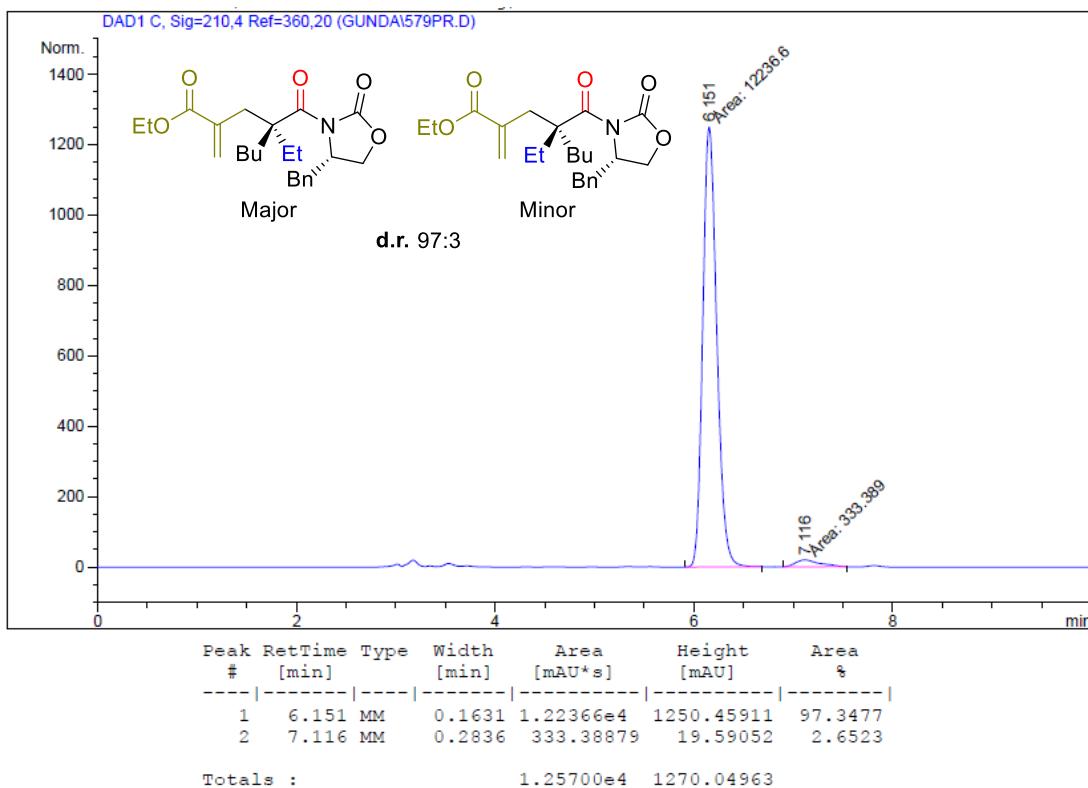
Compound 4c



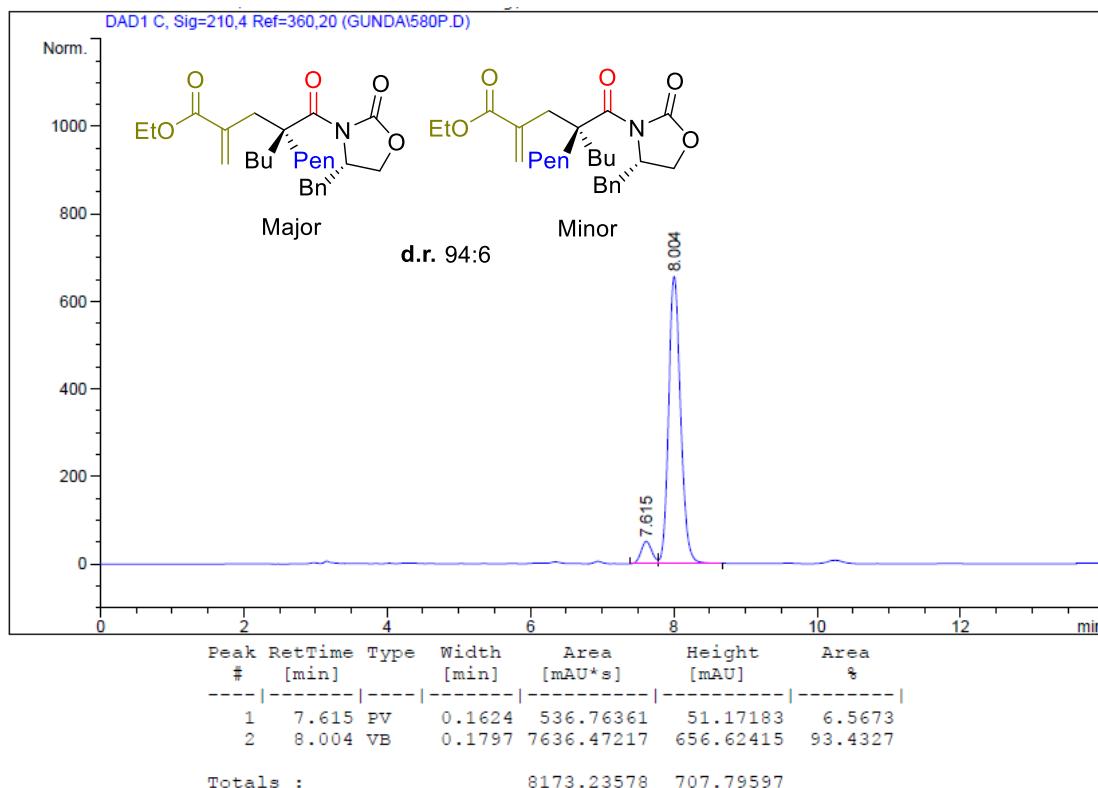
Compound **4b** and **4c**



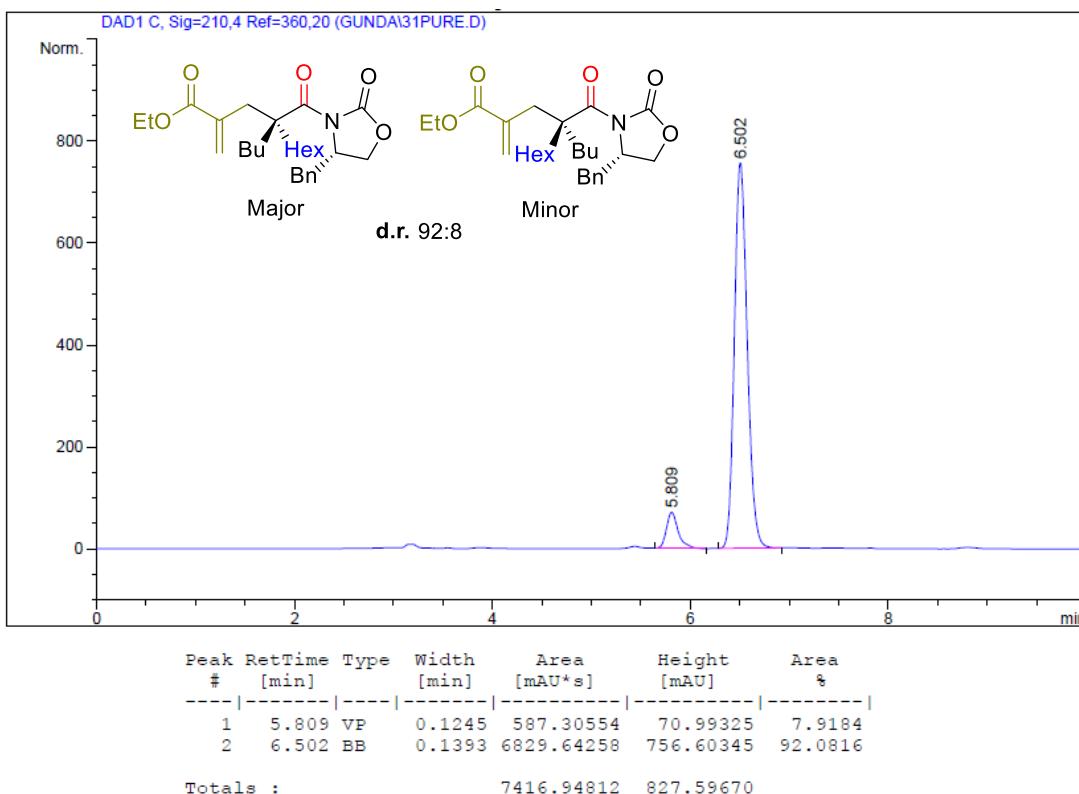
Compound 4d



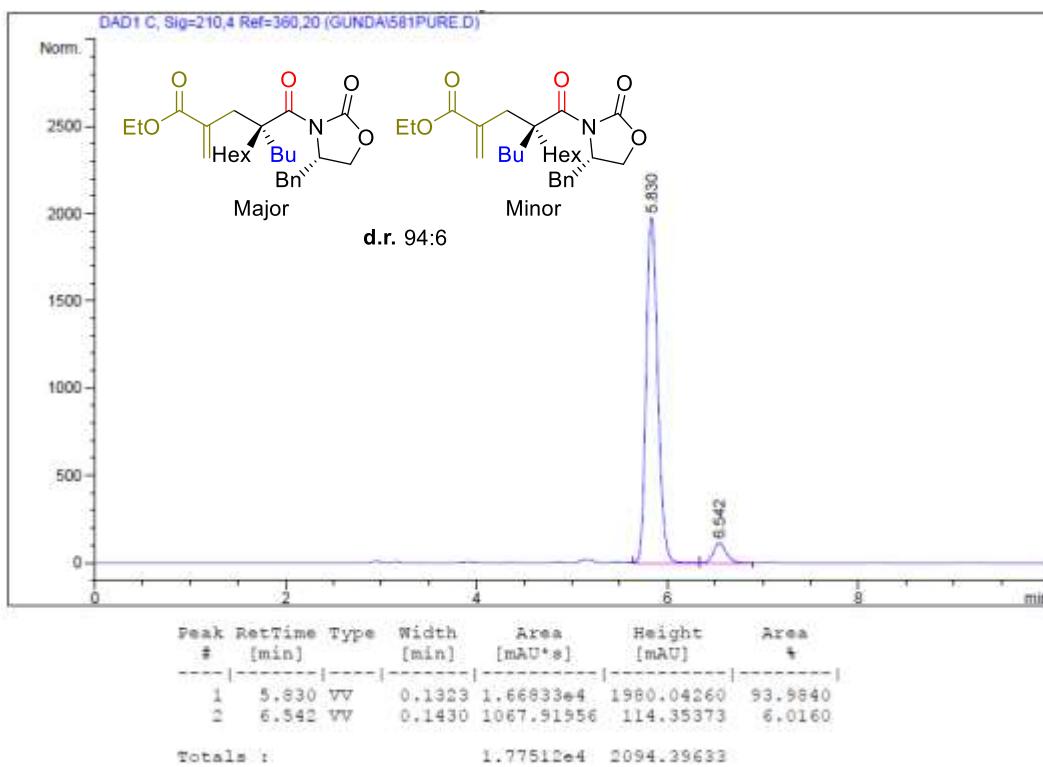
Compound 4e



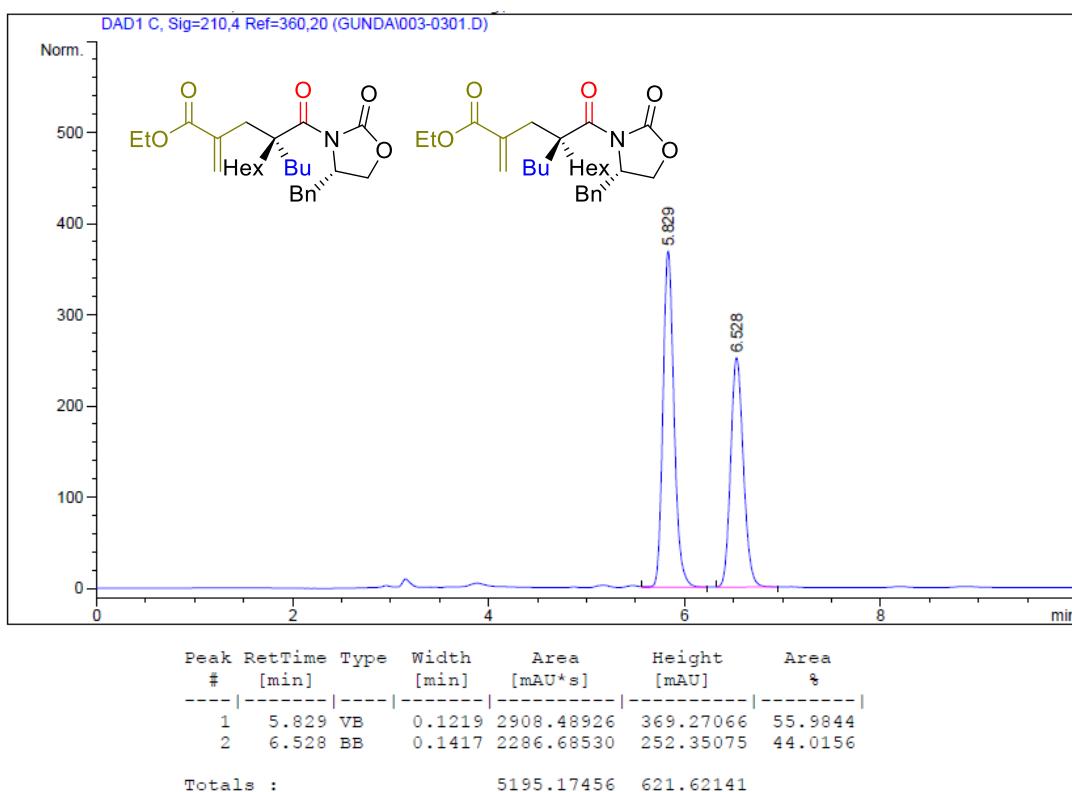
Compound 4f



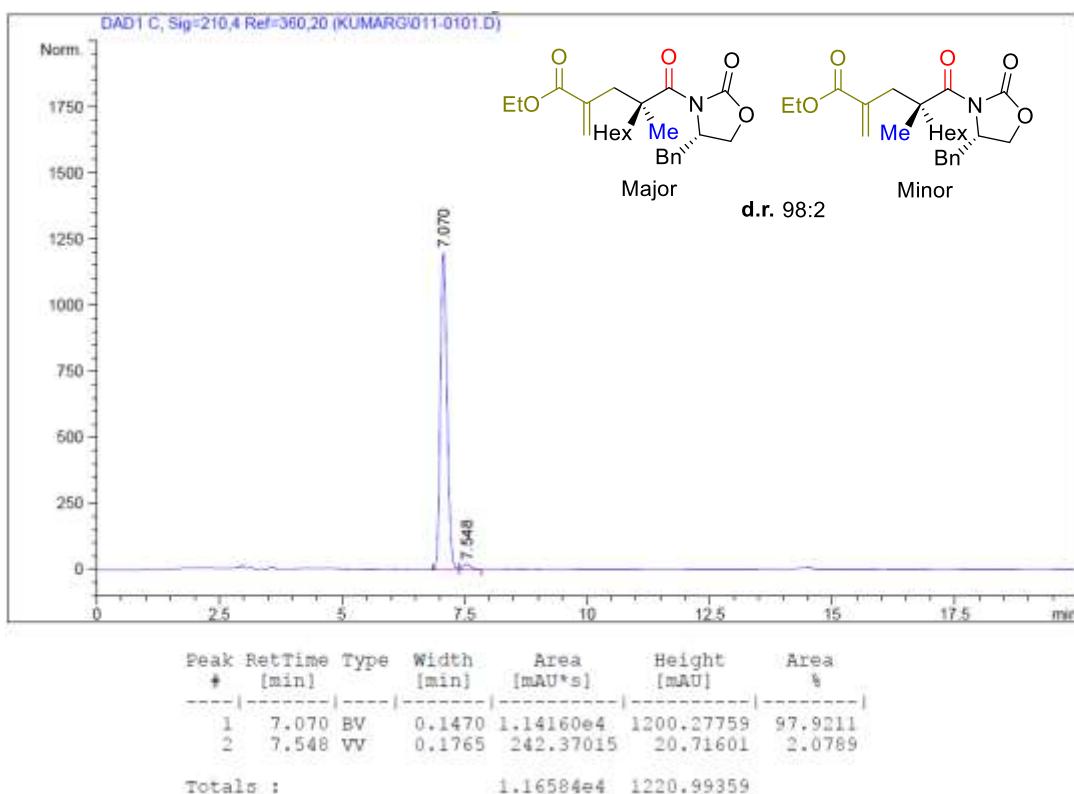
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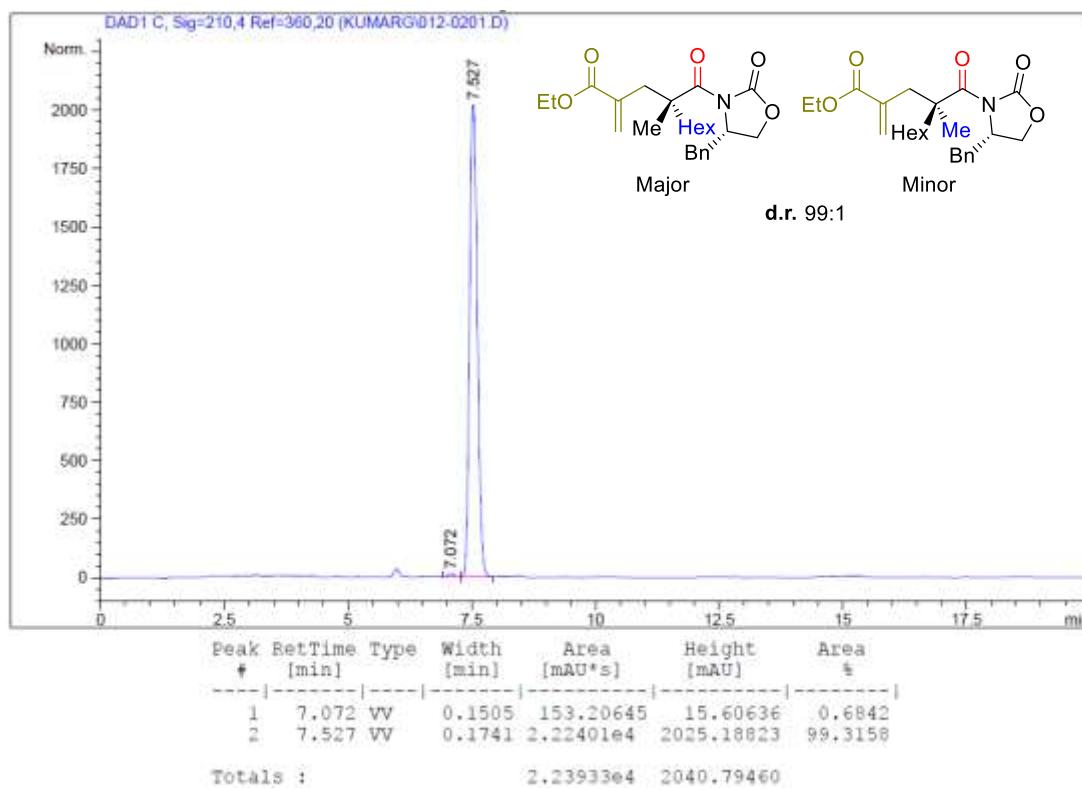
Compounds **4g** and **4f**



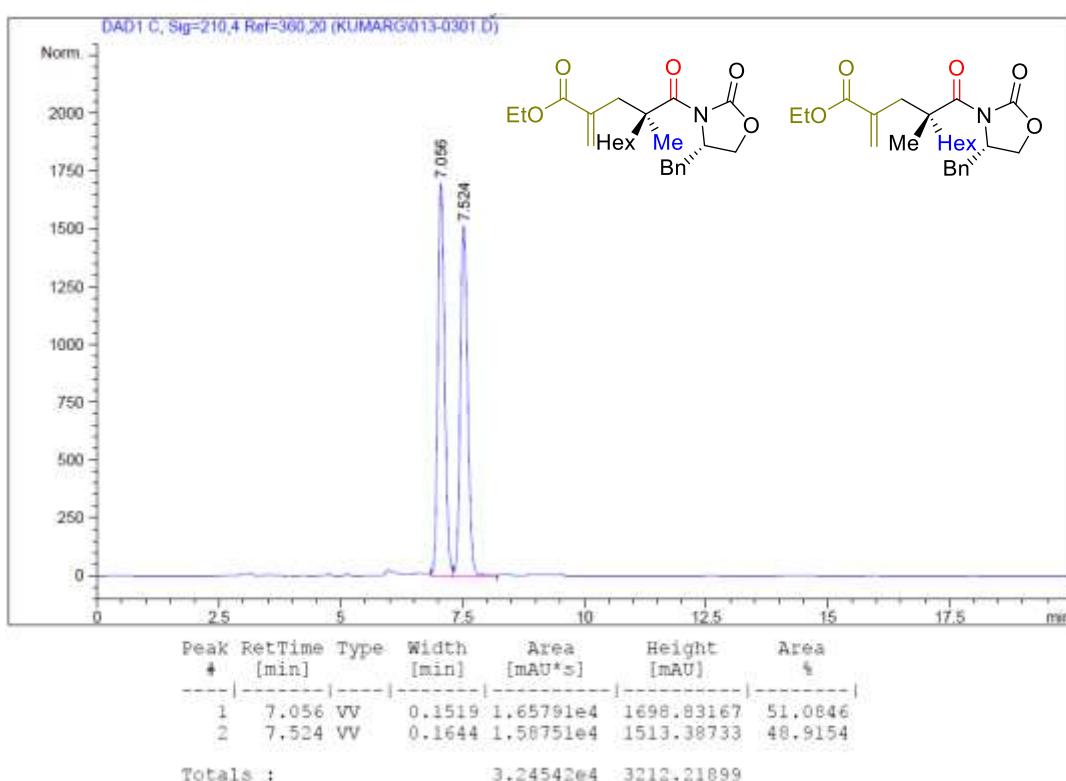
Compound 4h



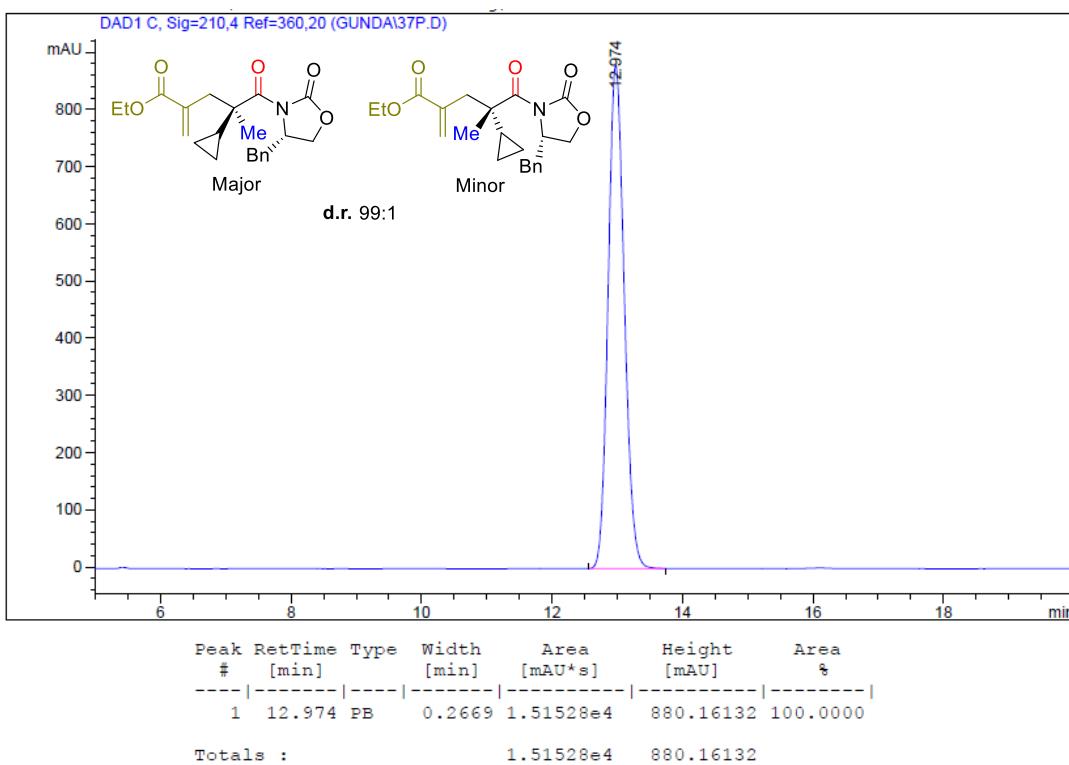
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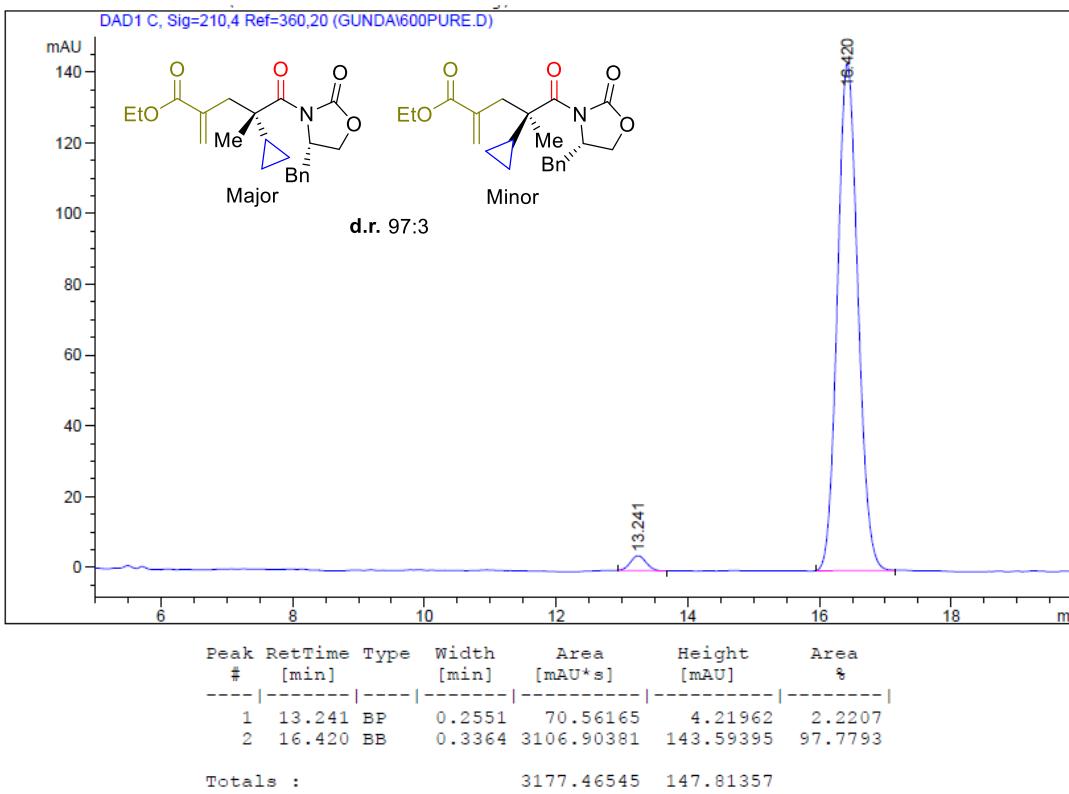
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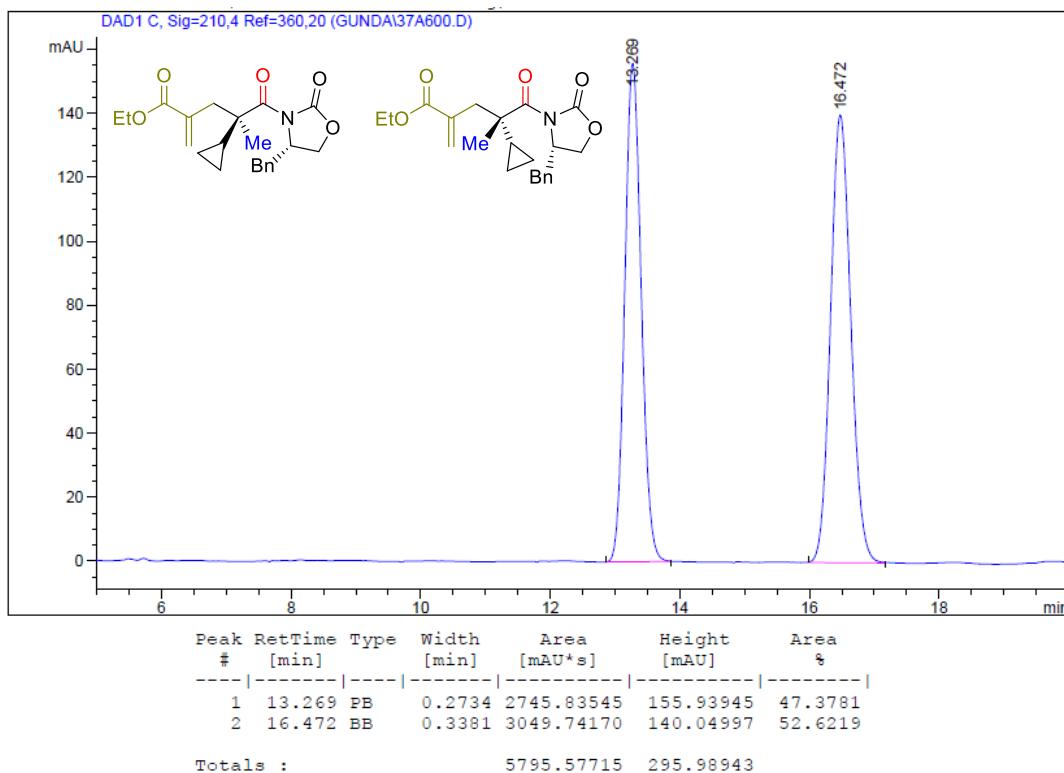
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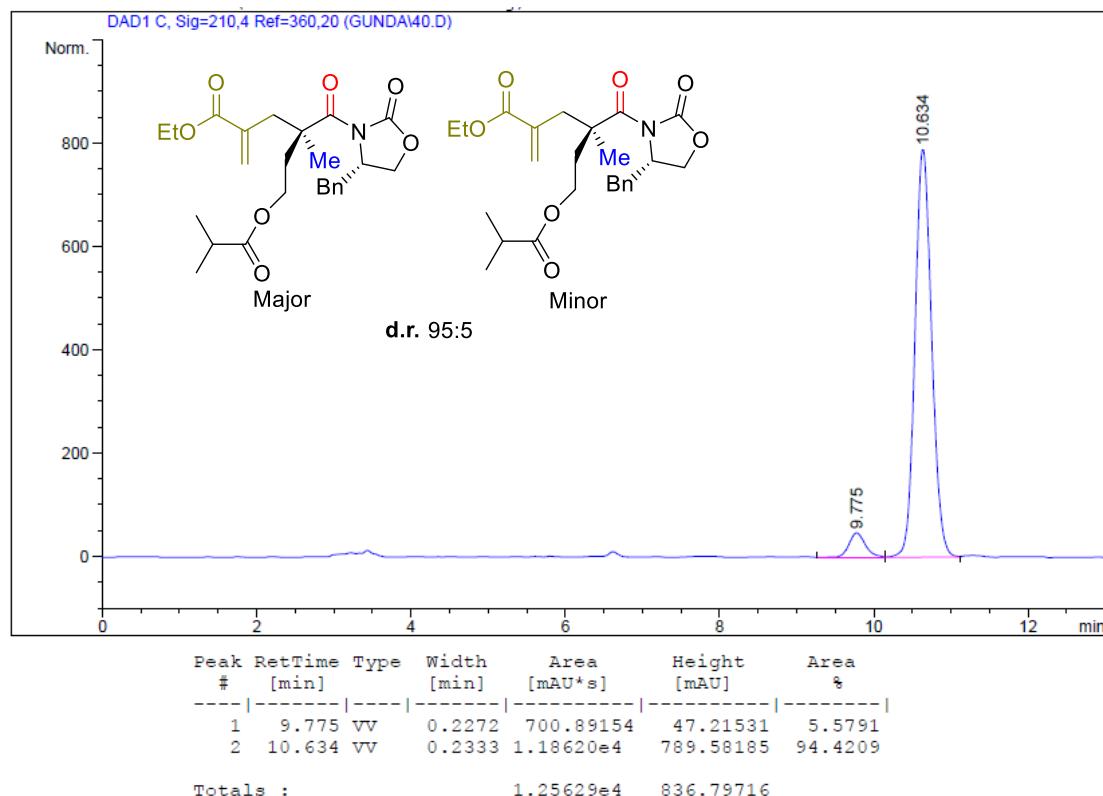
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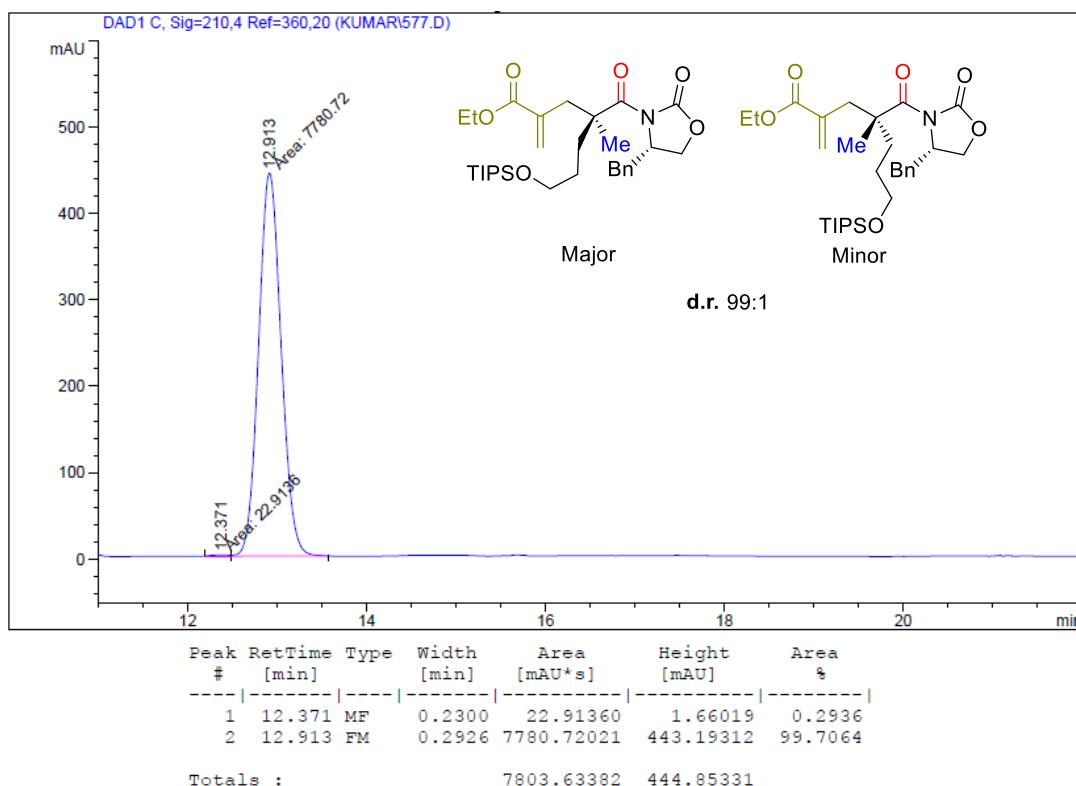
Compound **4j** and **4k**



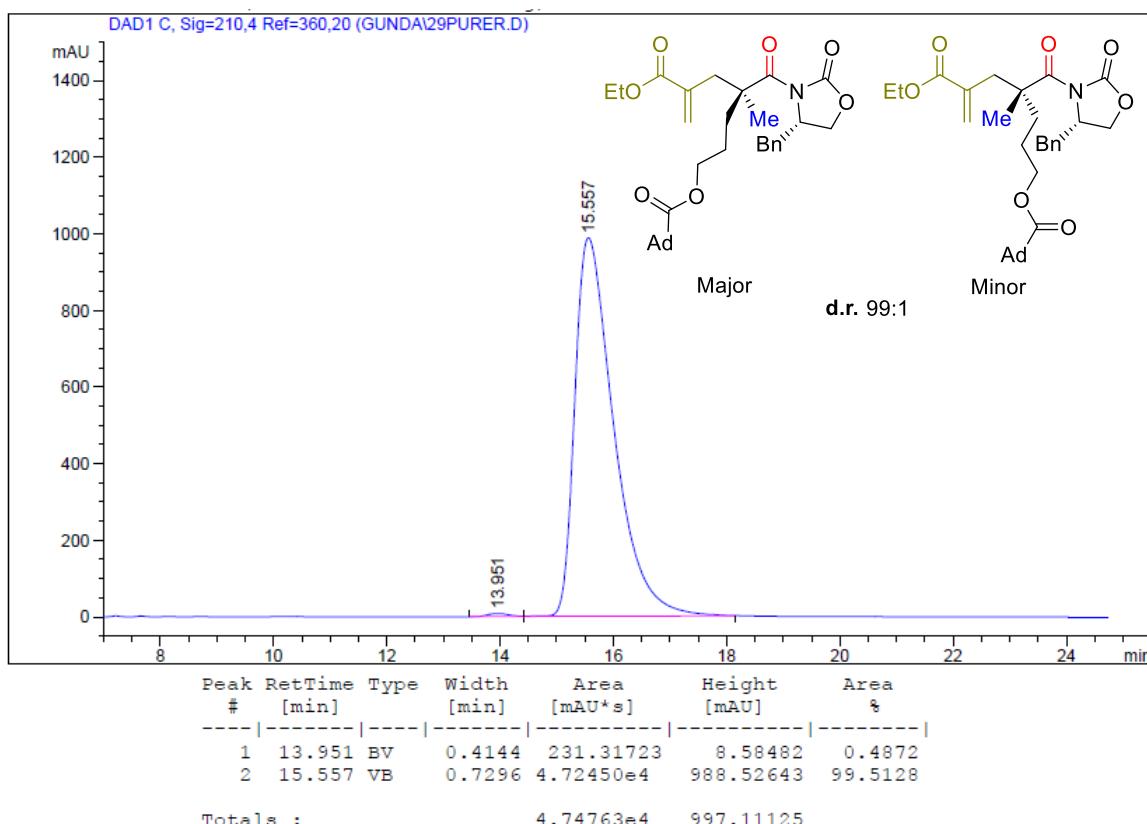
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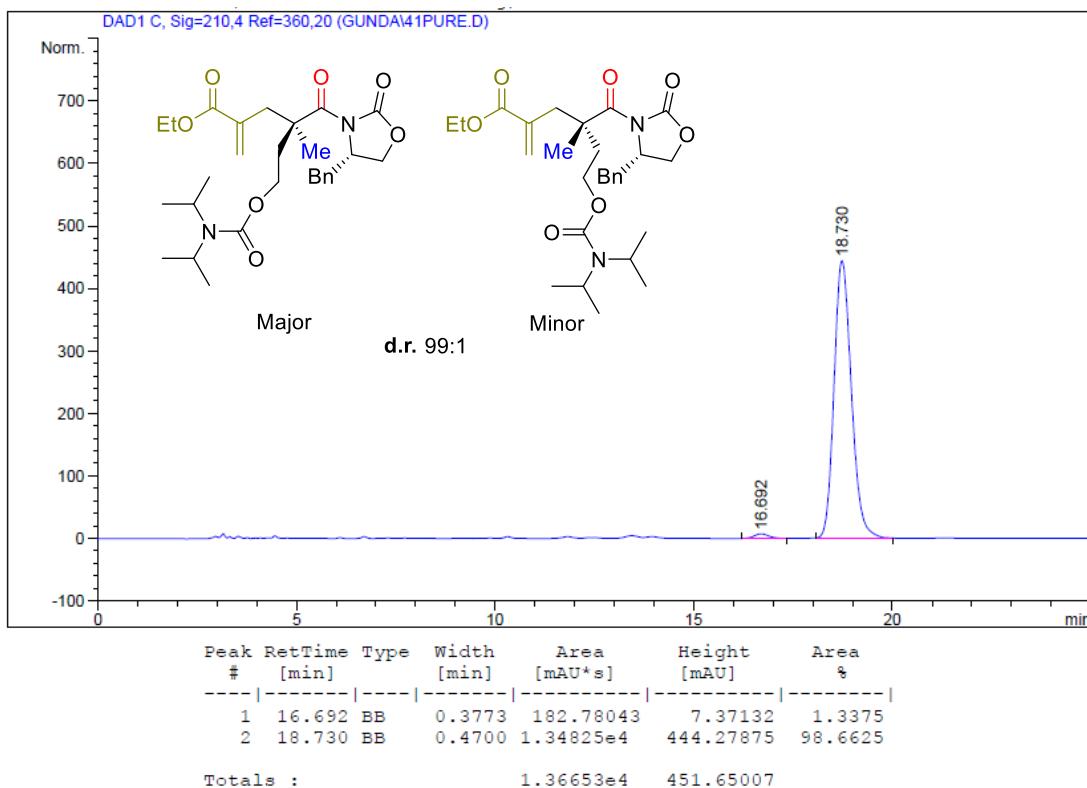
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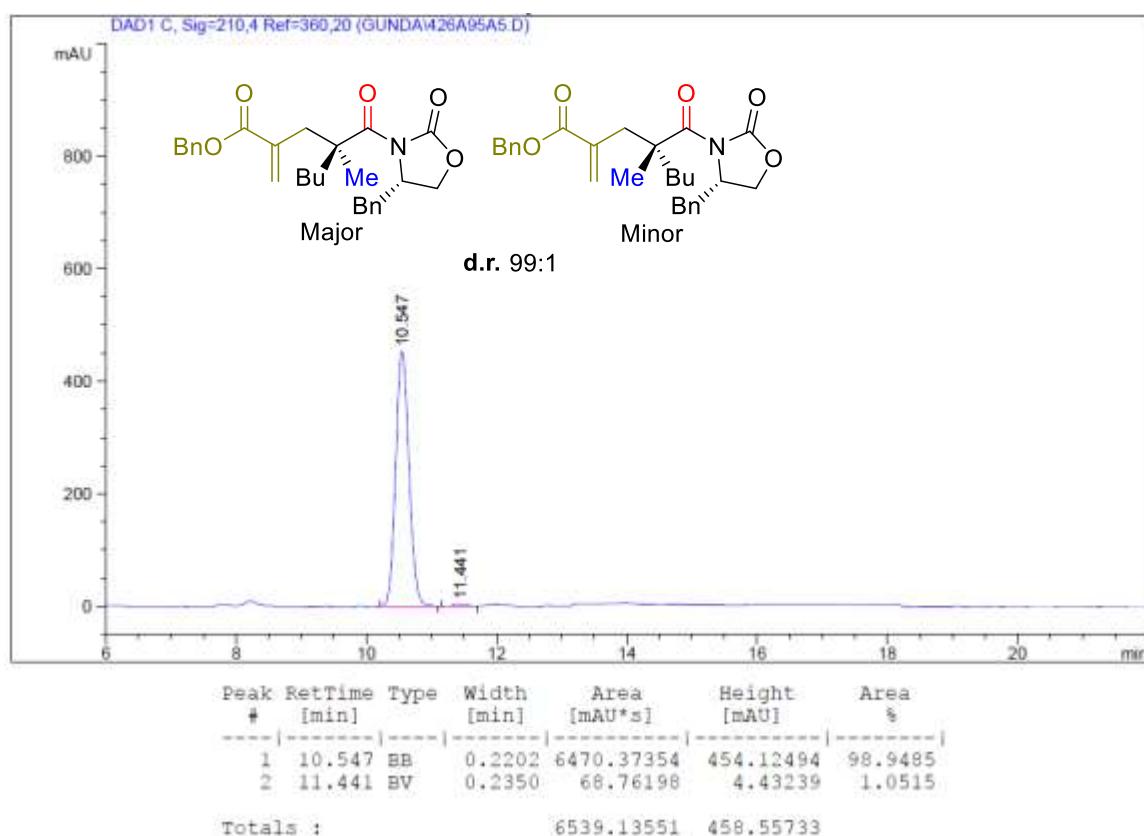
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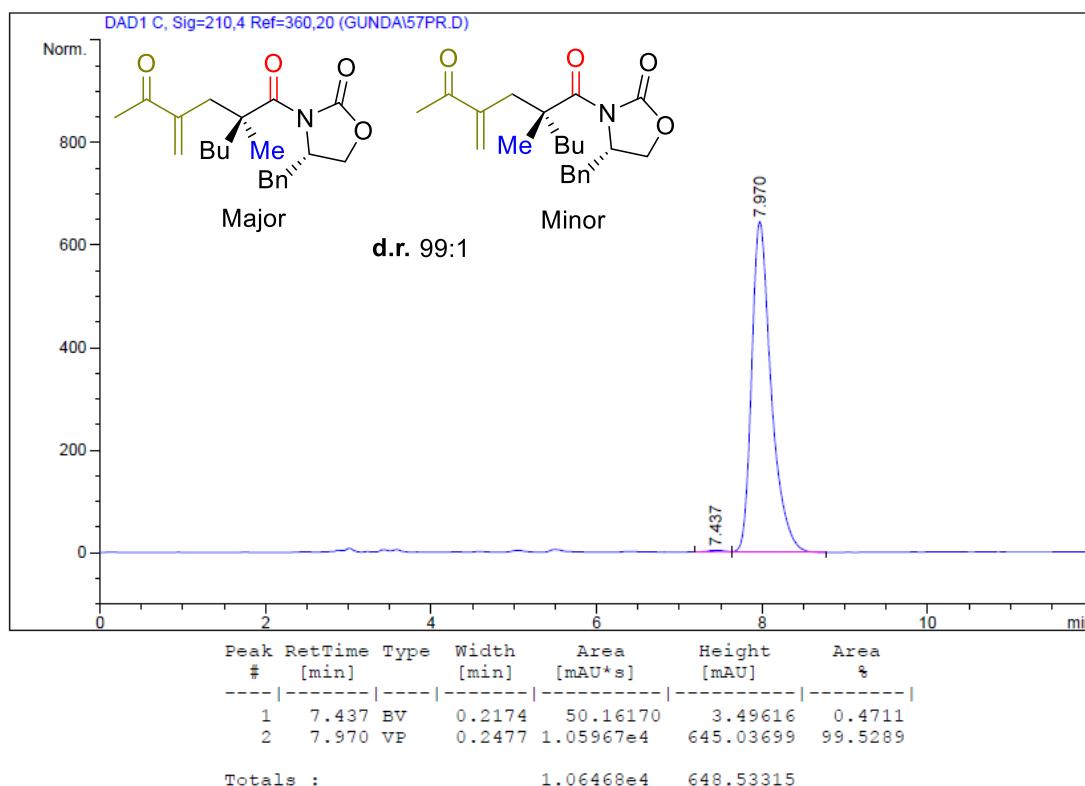
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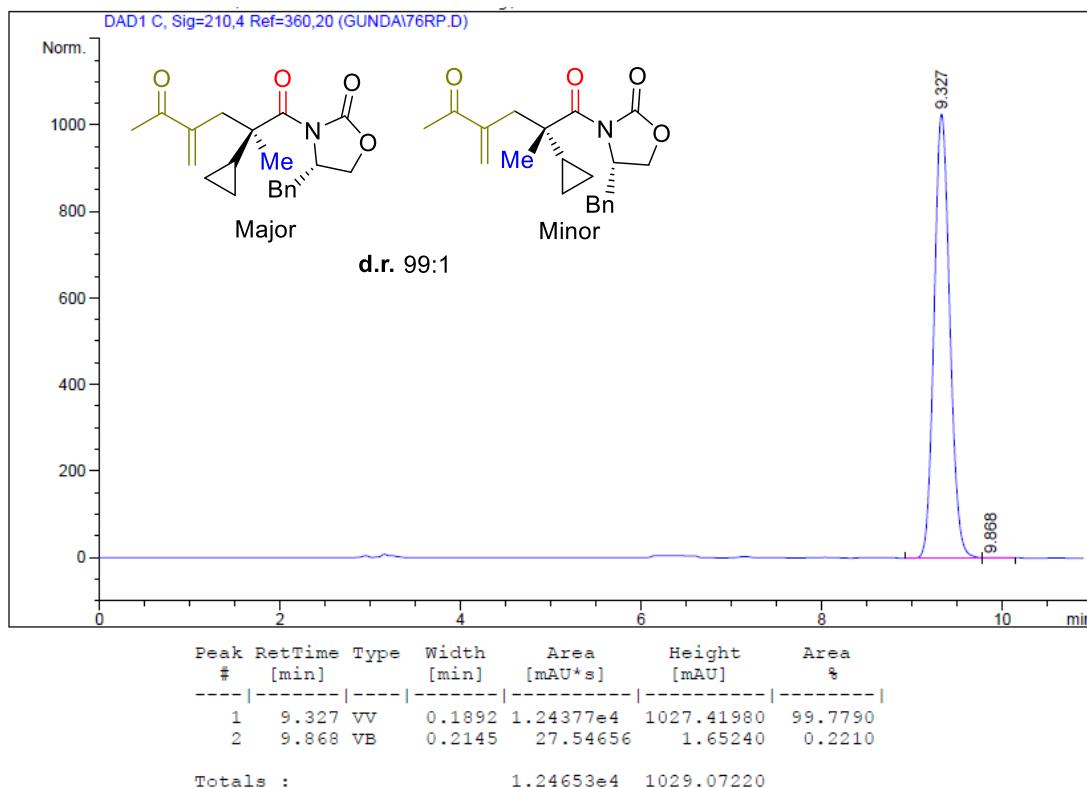
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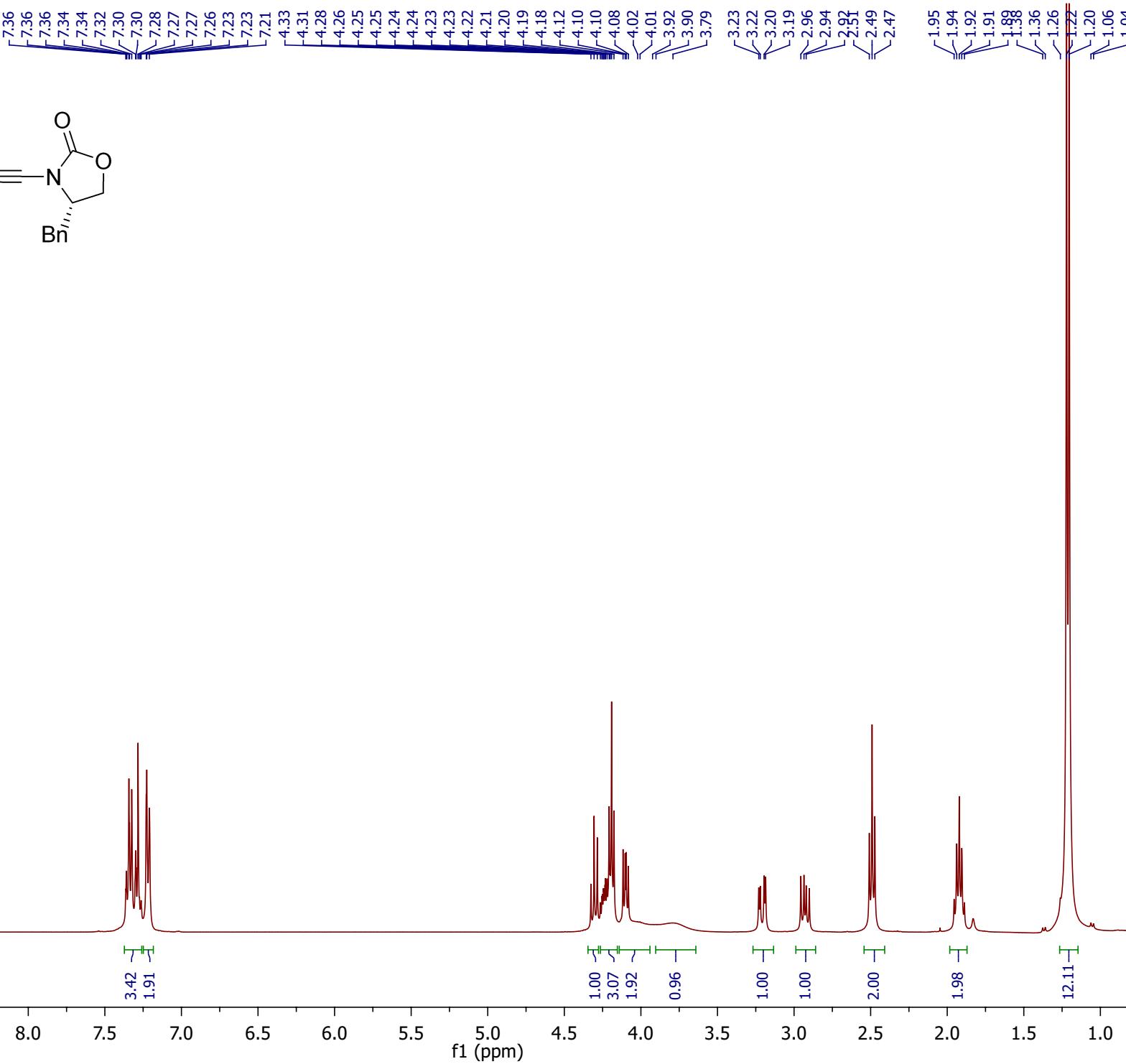
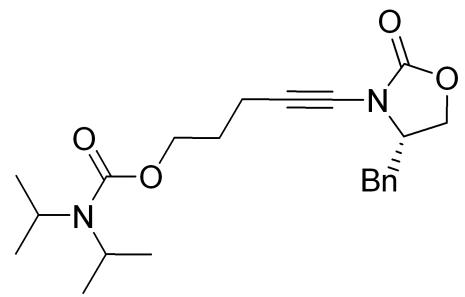


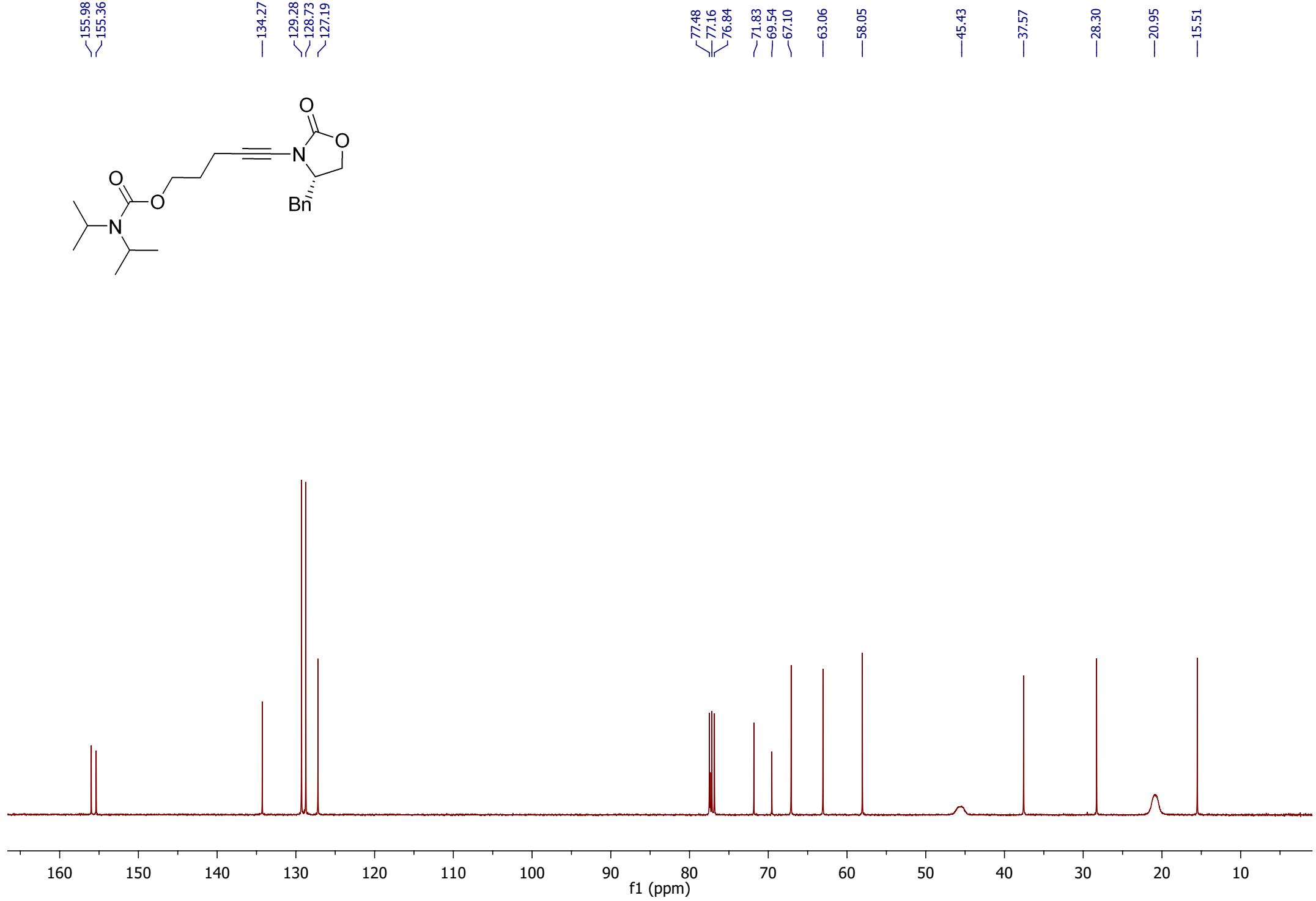
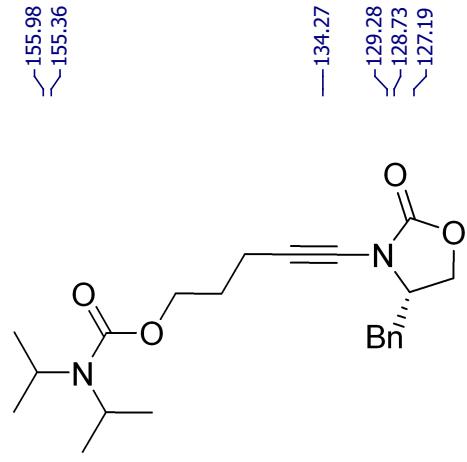
Compound 4q



Compound 4r



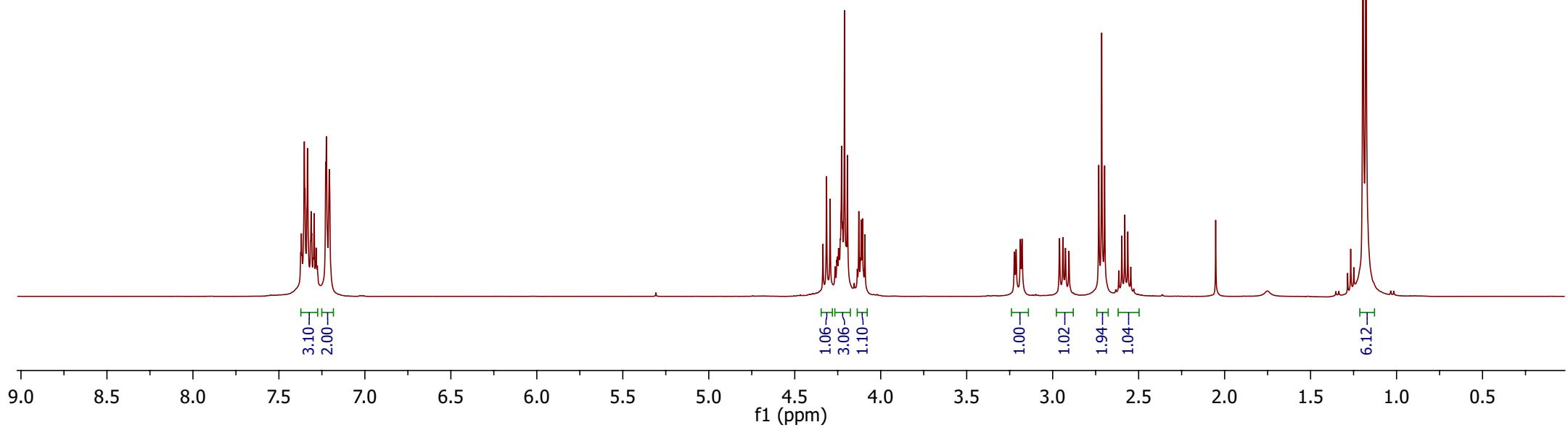
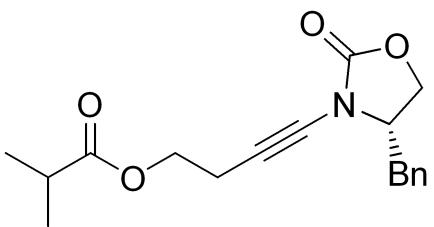




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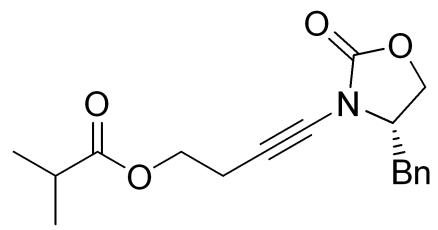
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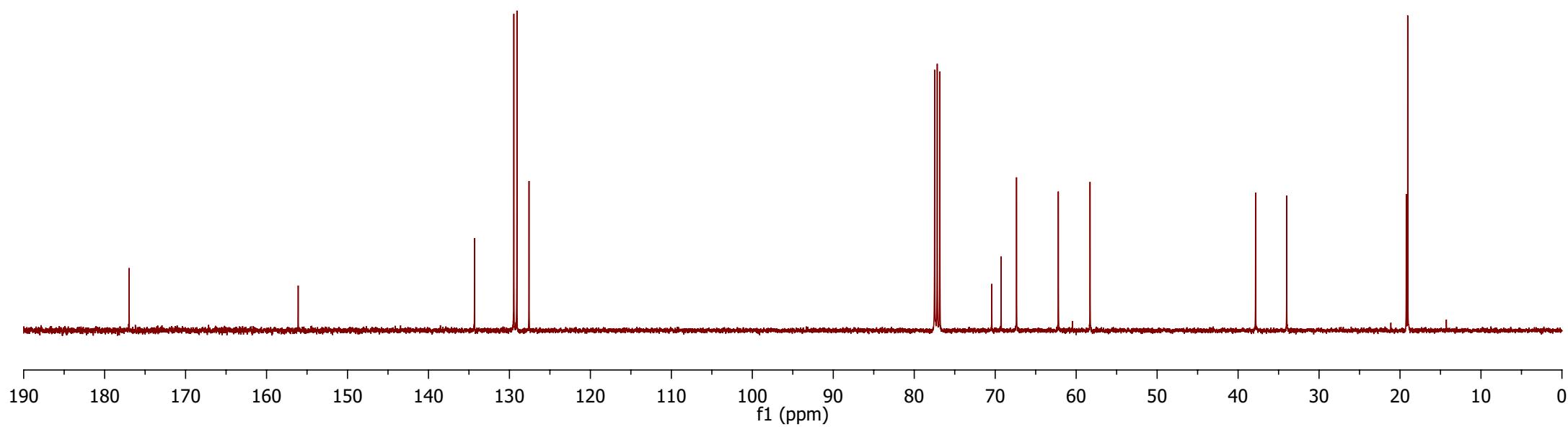
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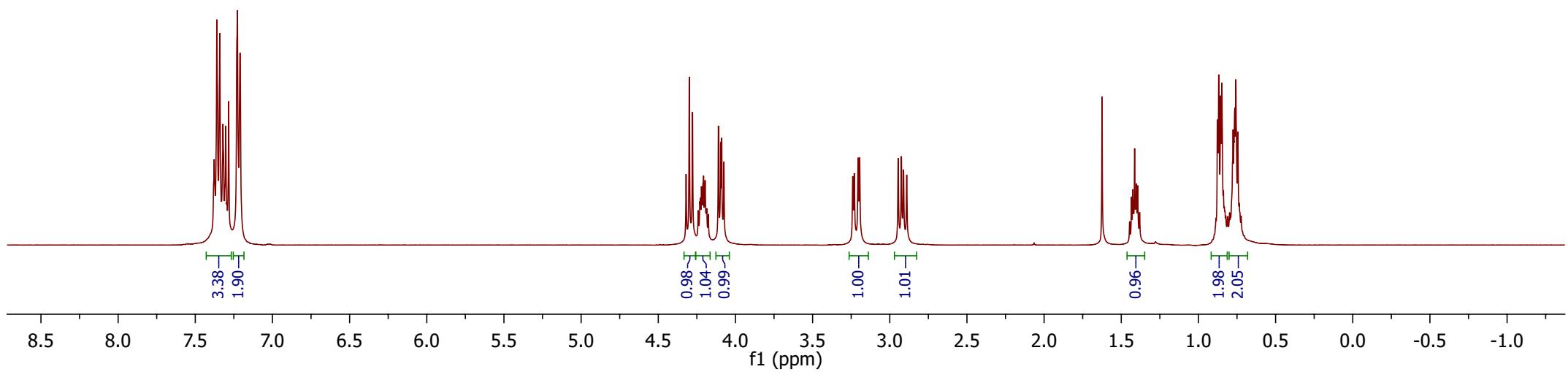
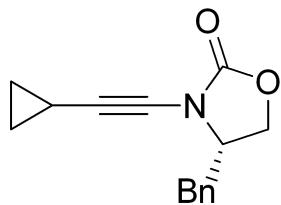
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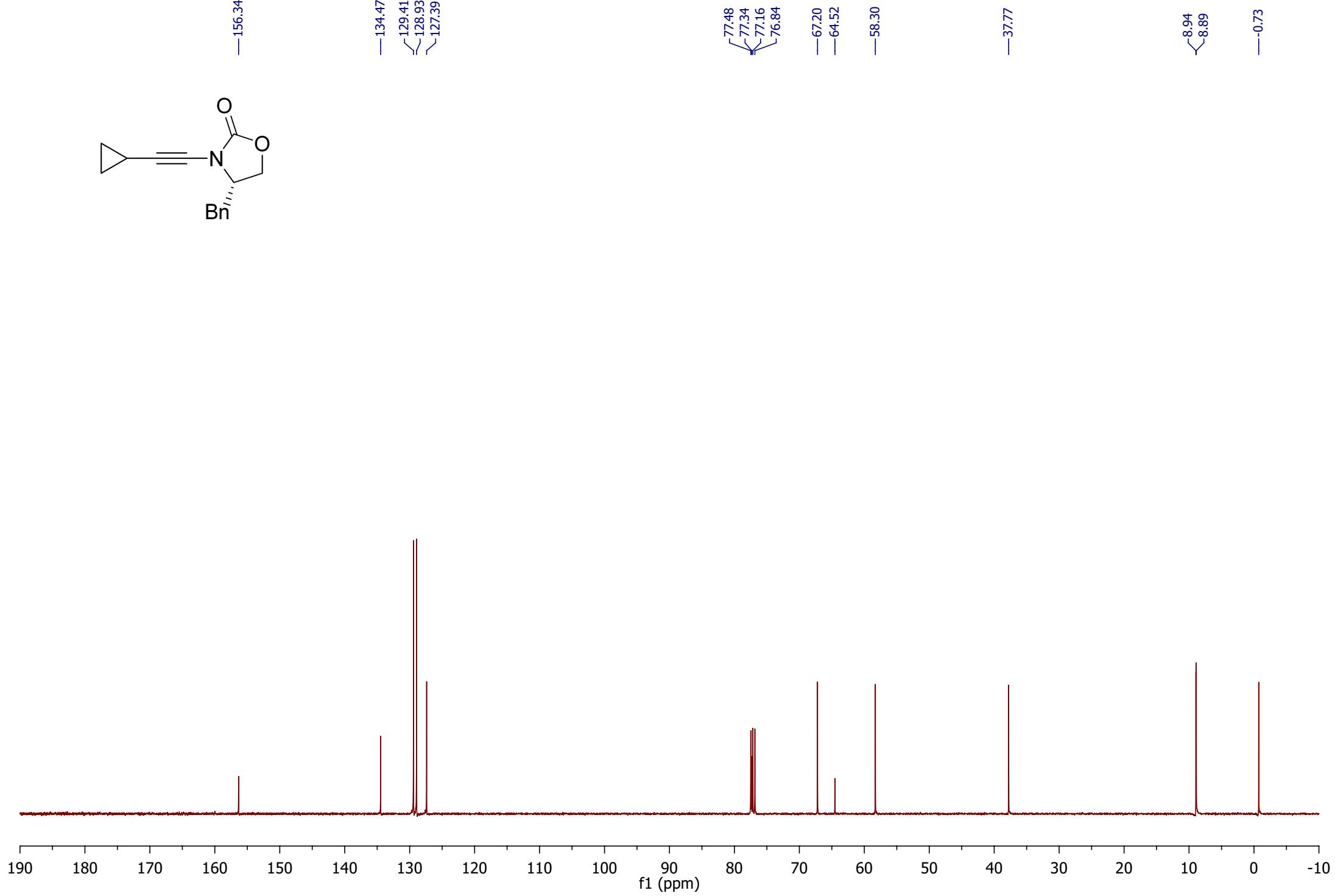
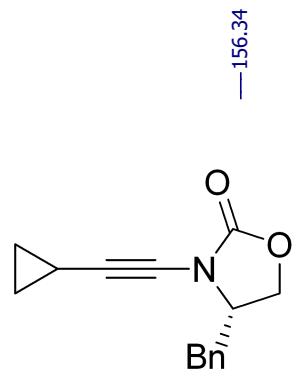


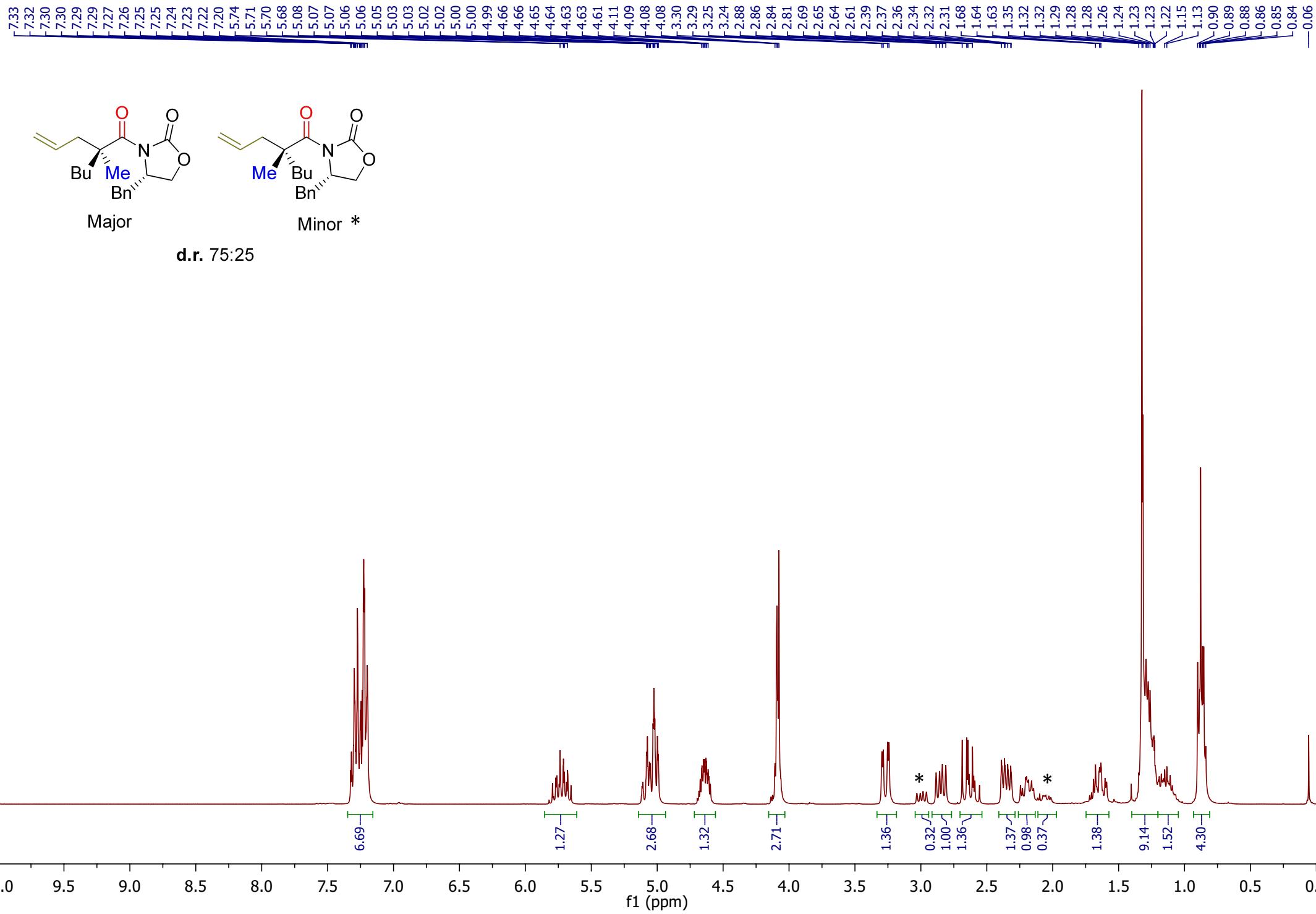
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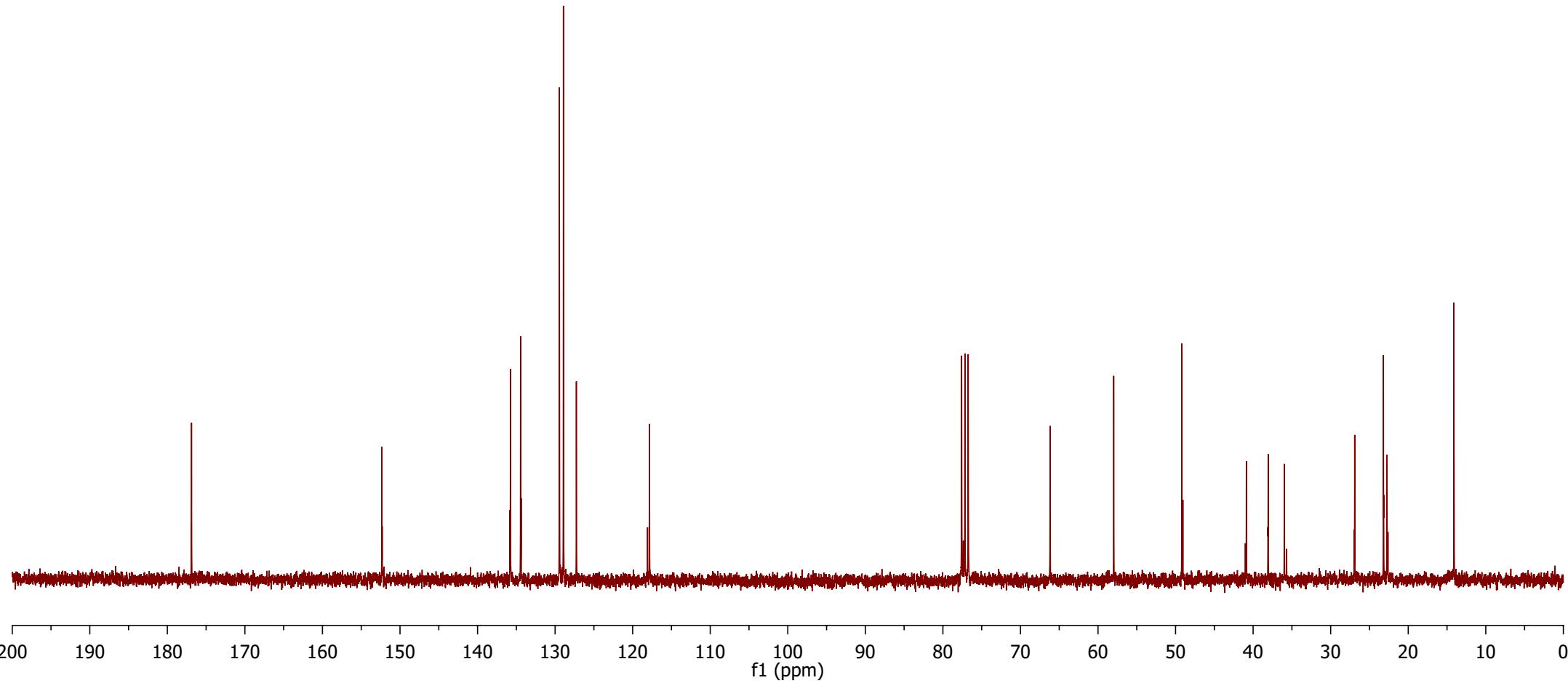
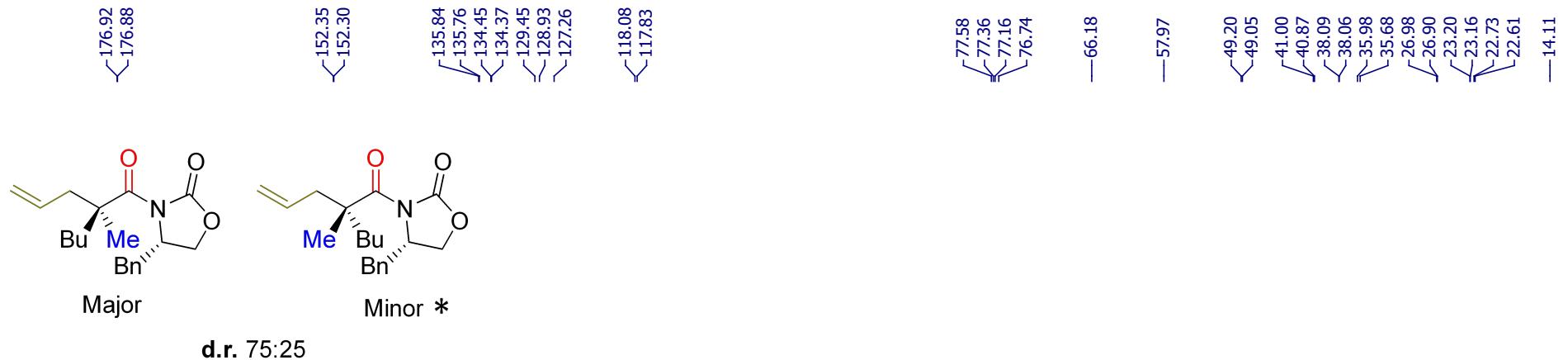
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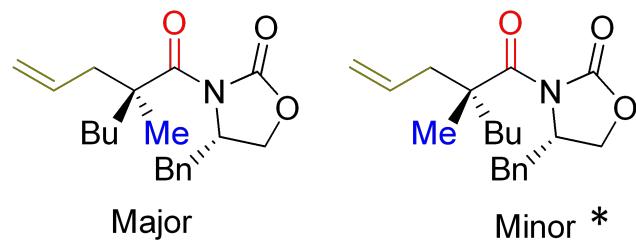






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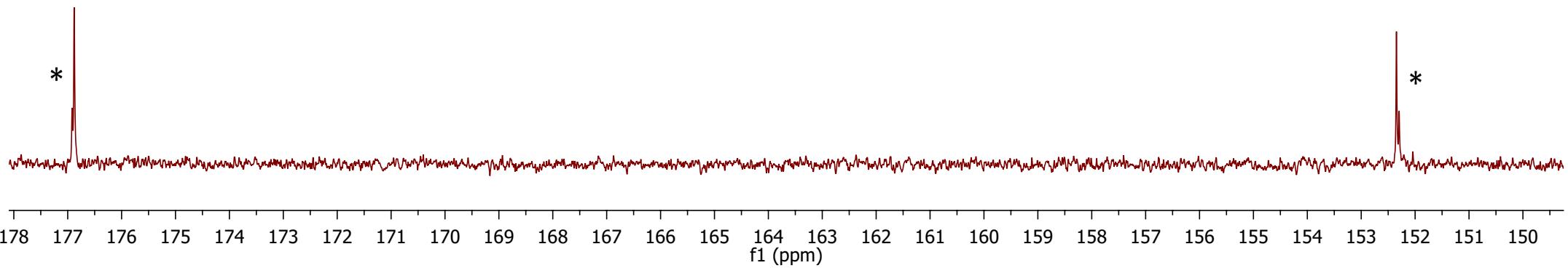
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Minor *

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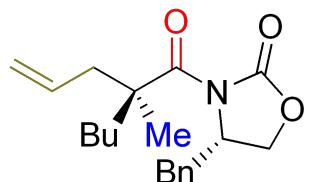
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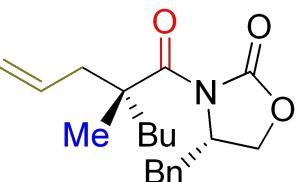
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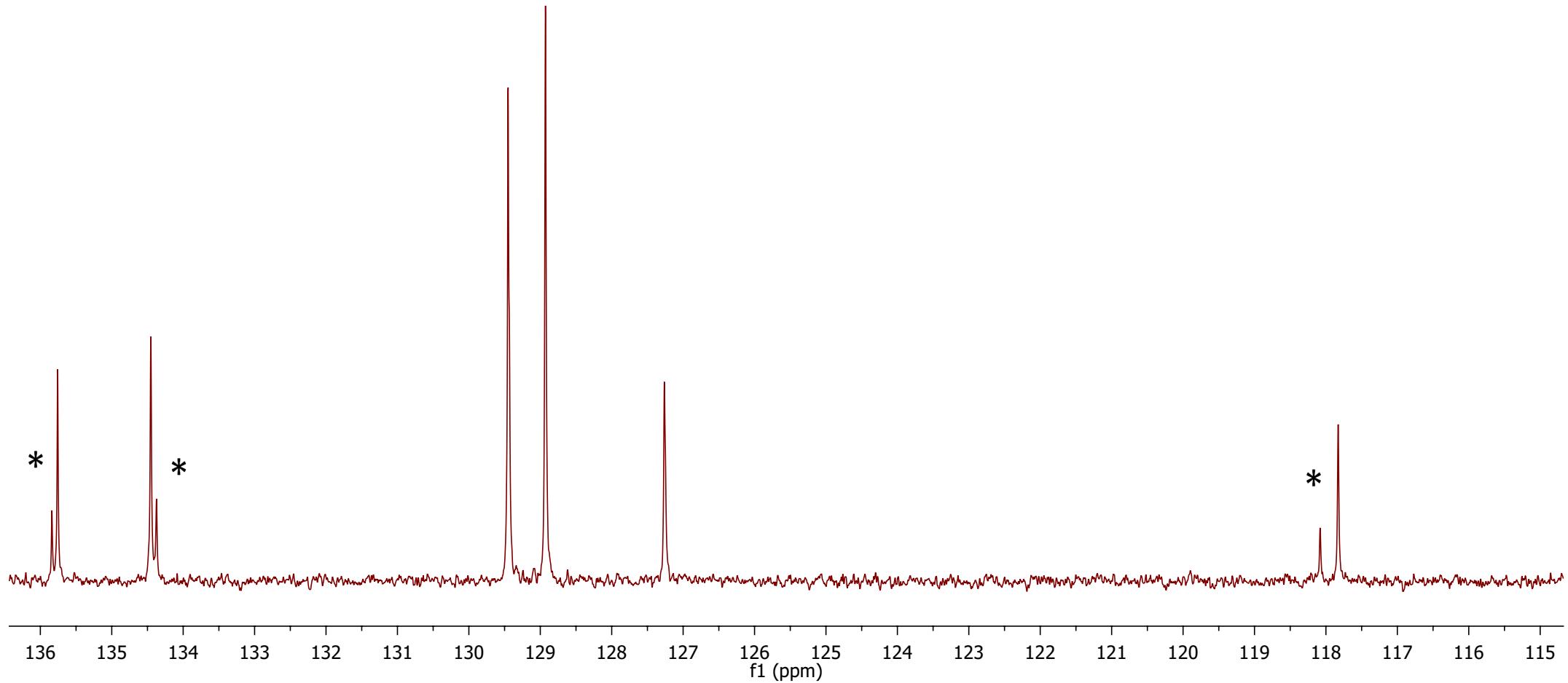
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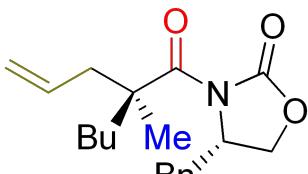
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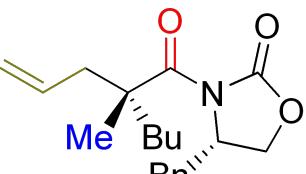


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Major



Minor *

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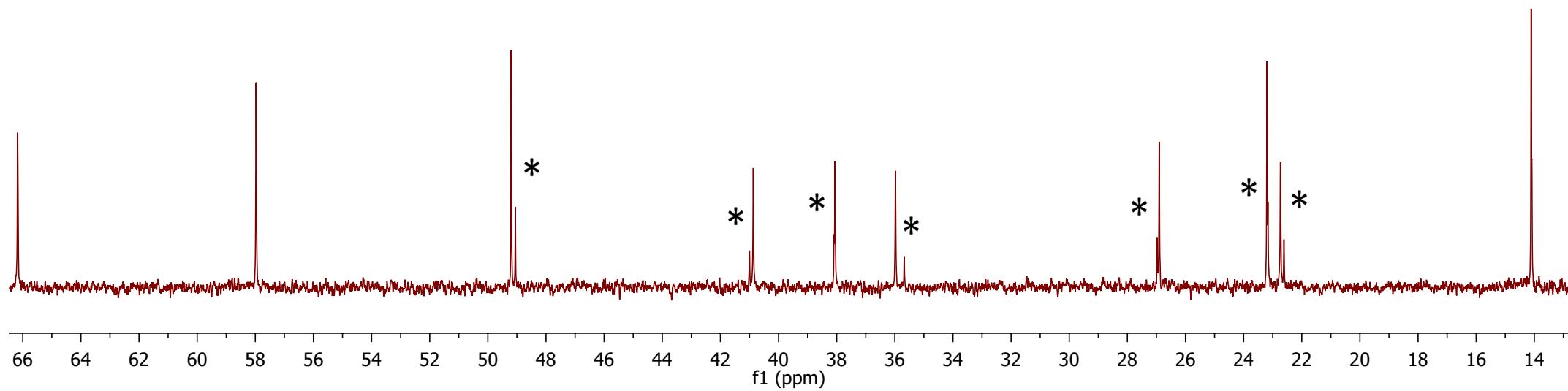
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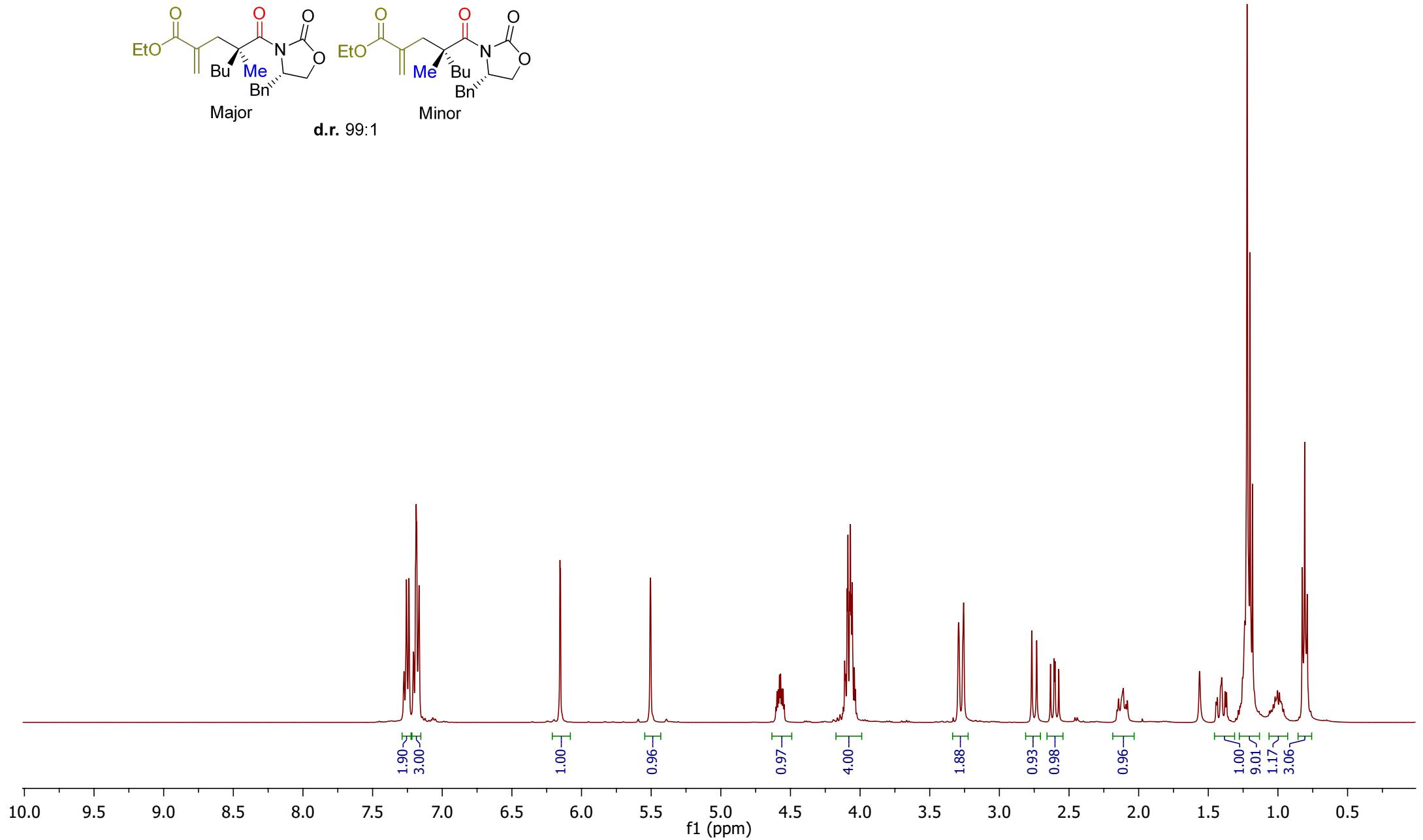
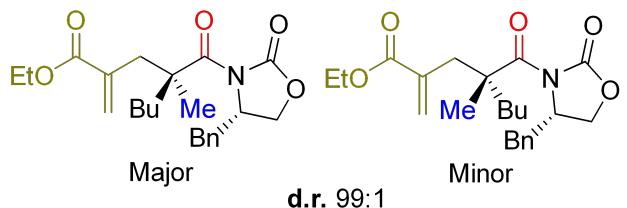
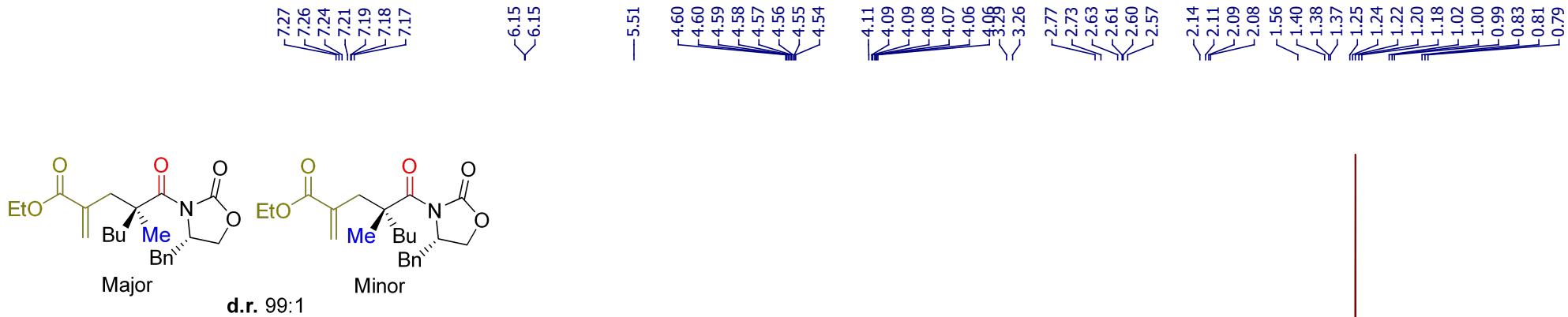
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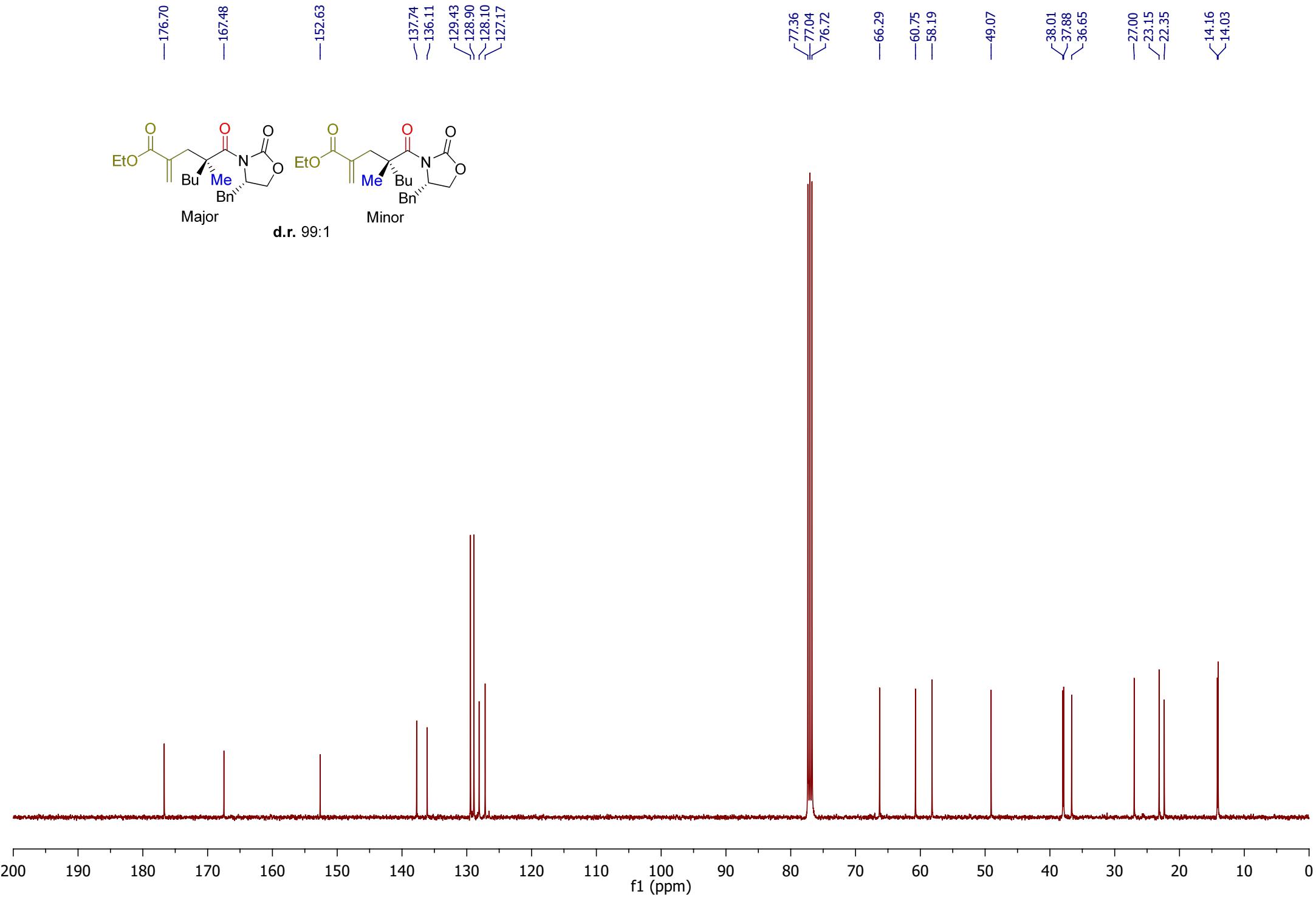
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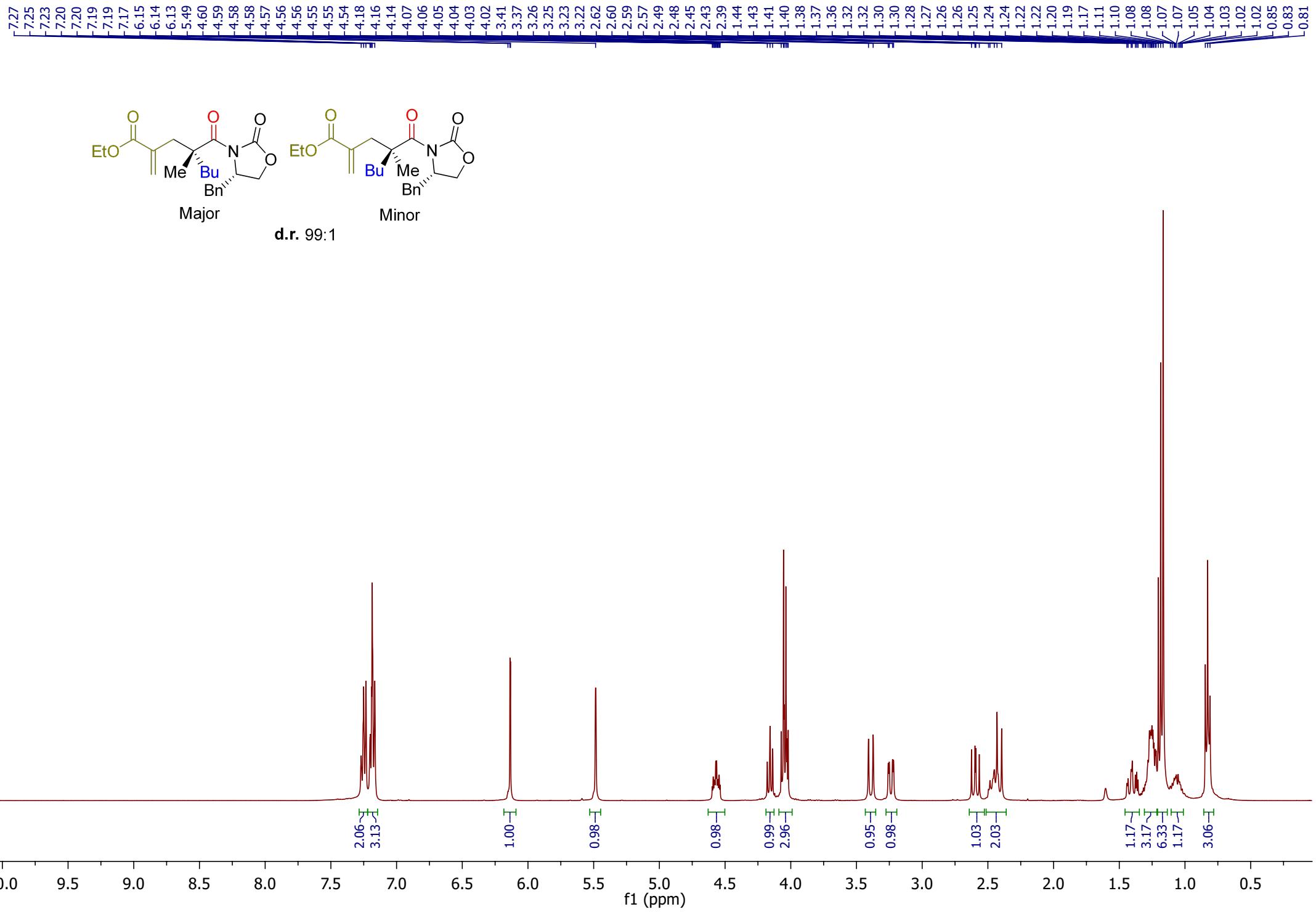
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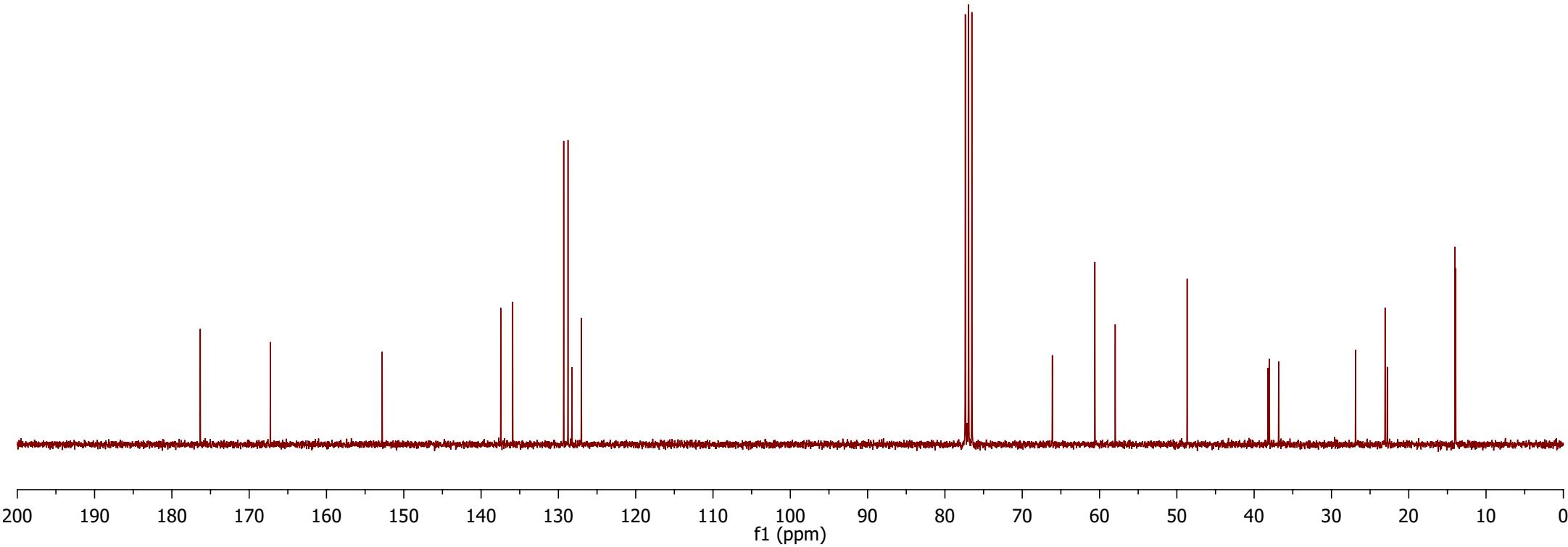
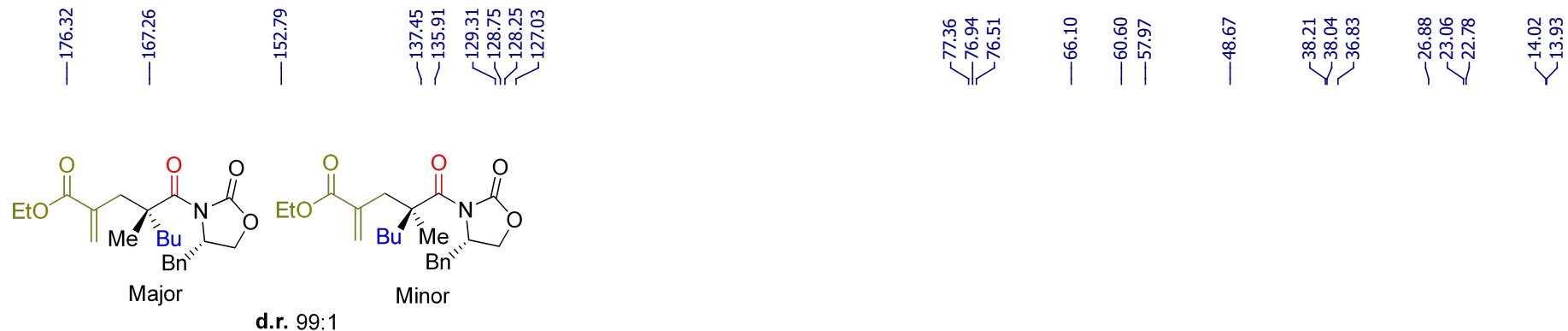
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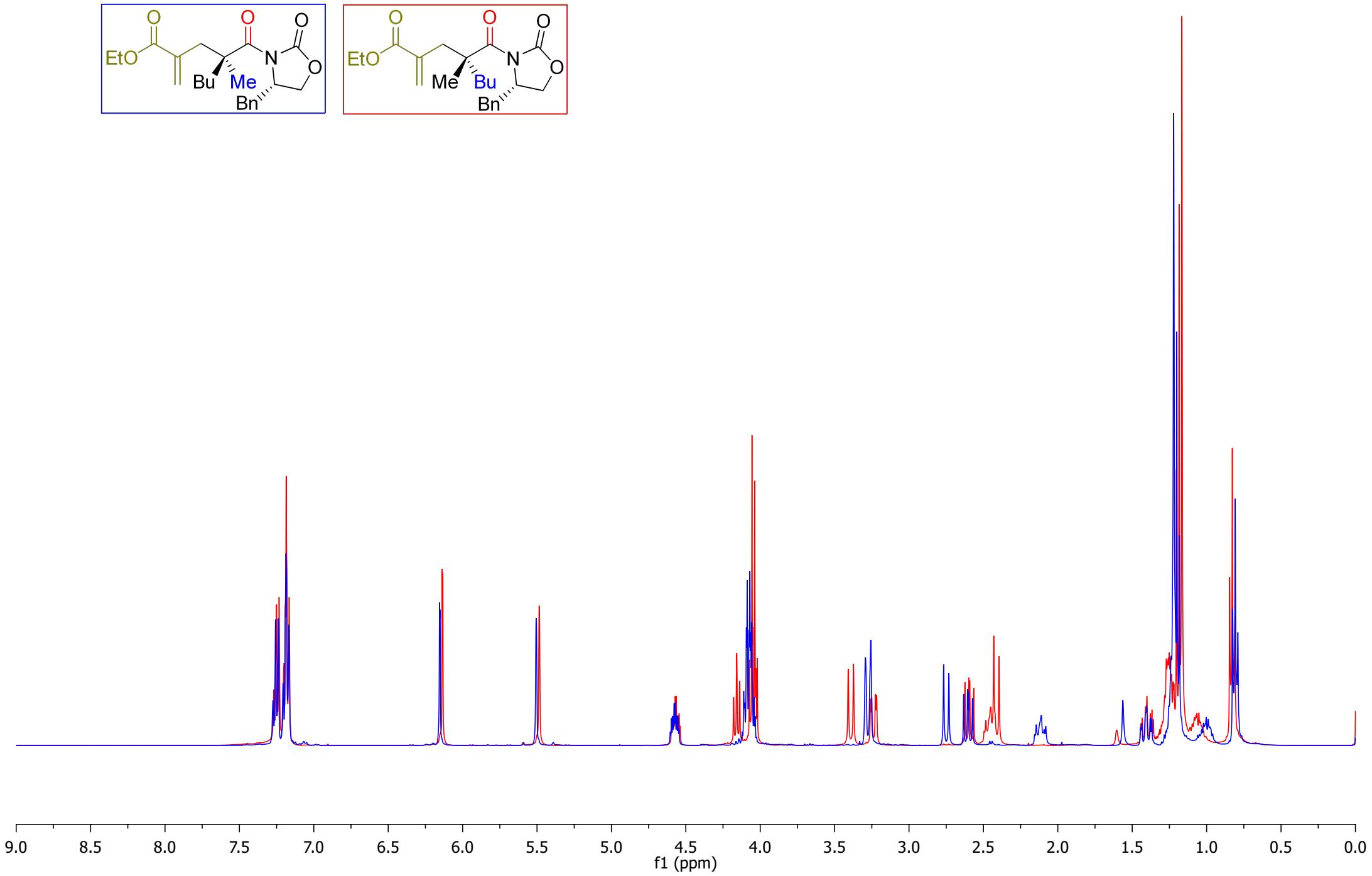
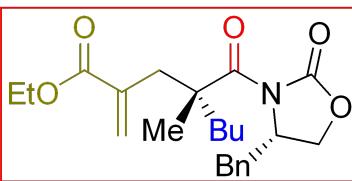
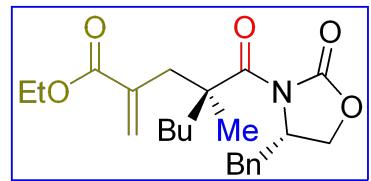


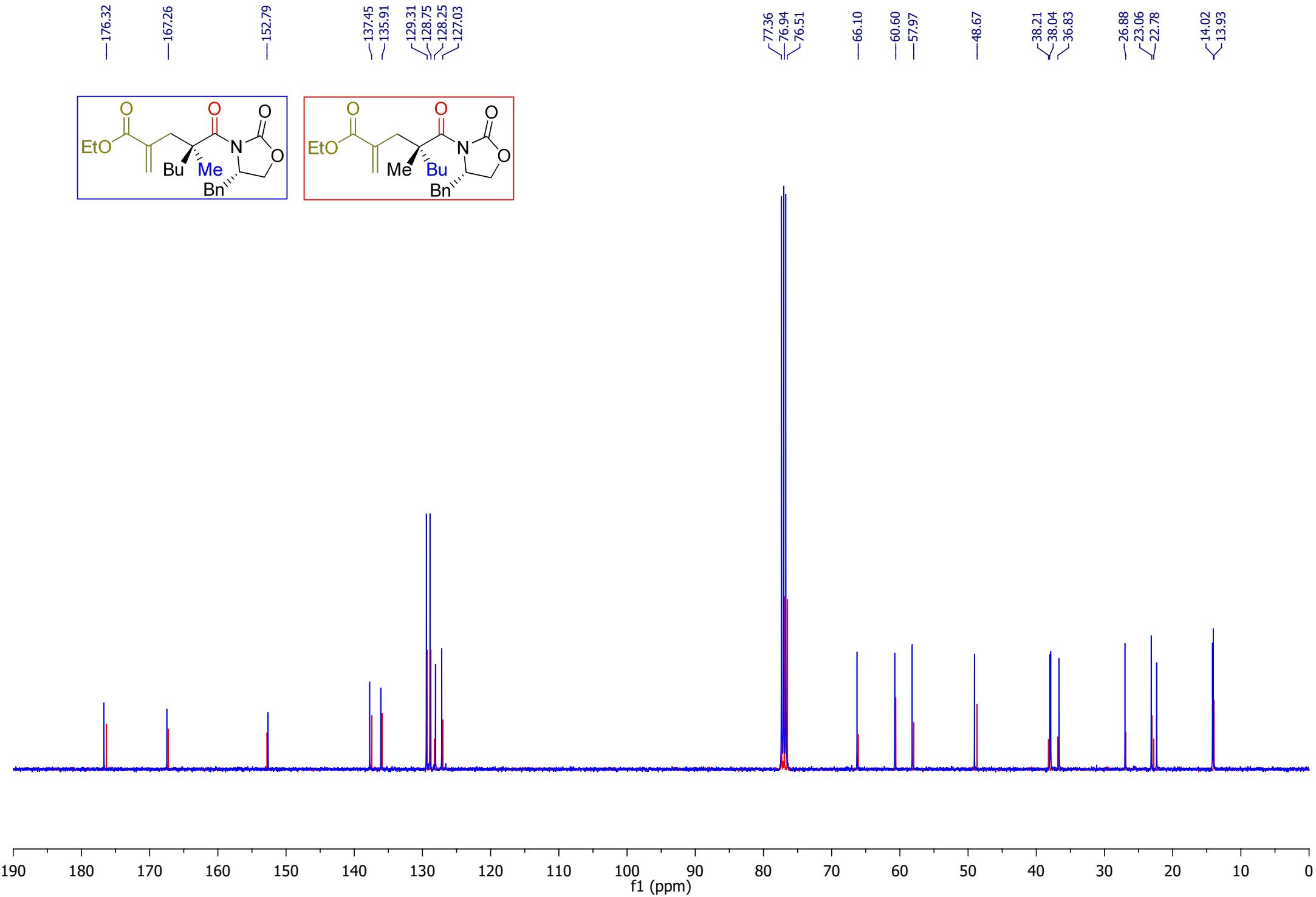




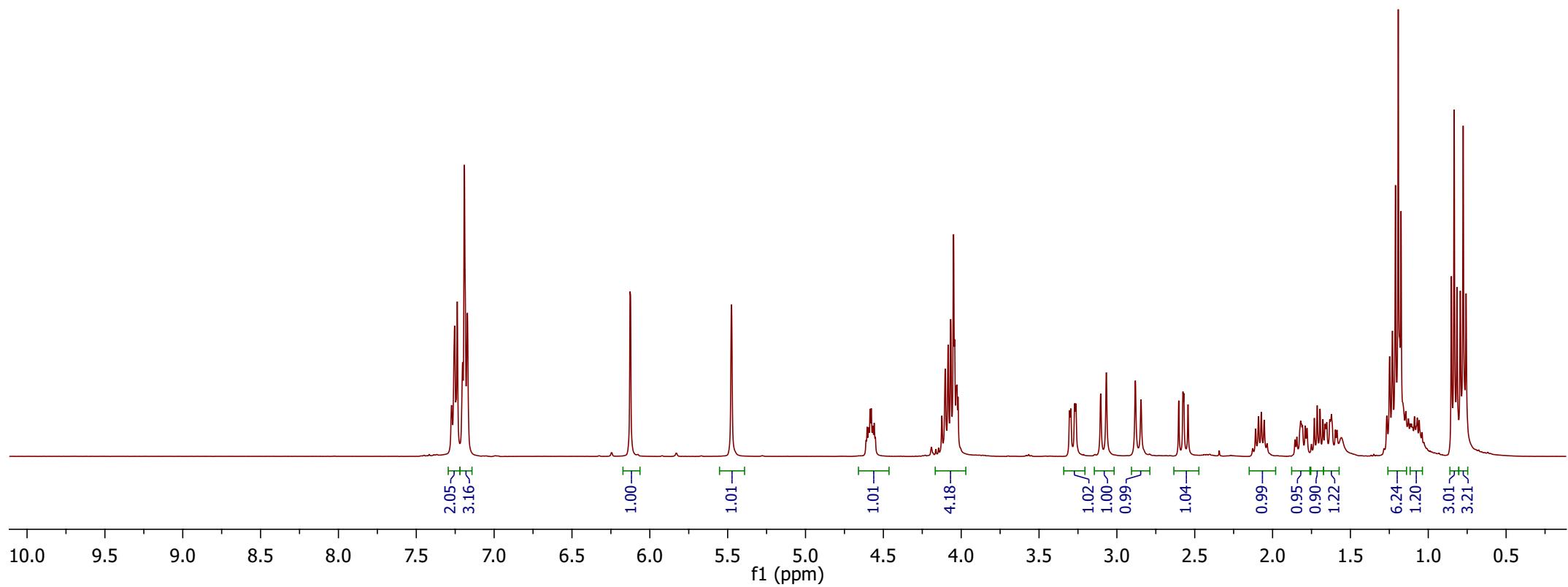
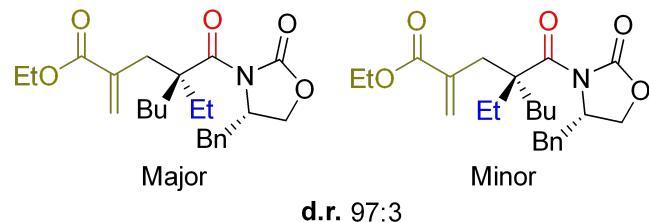


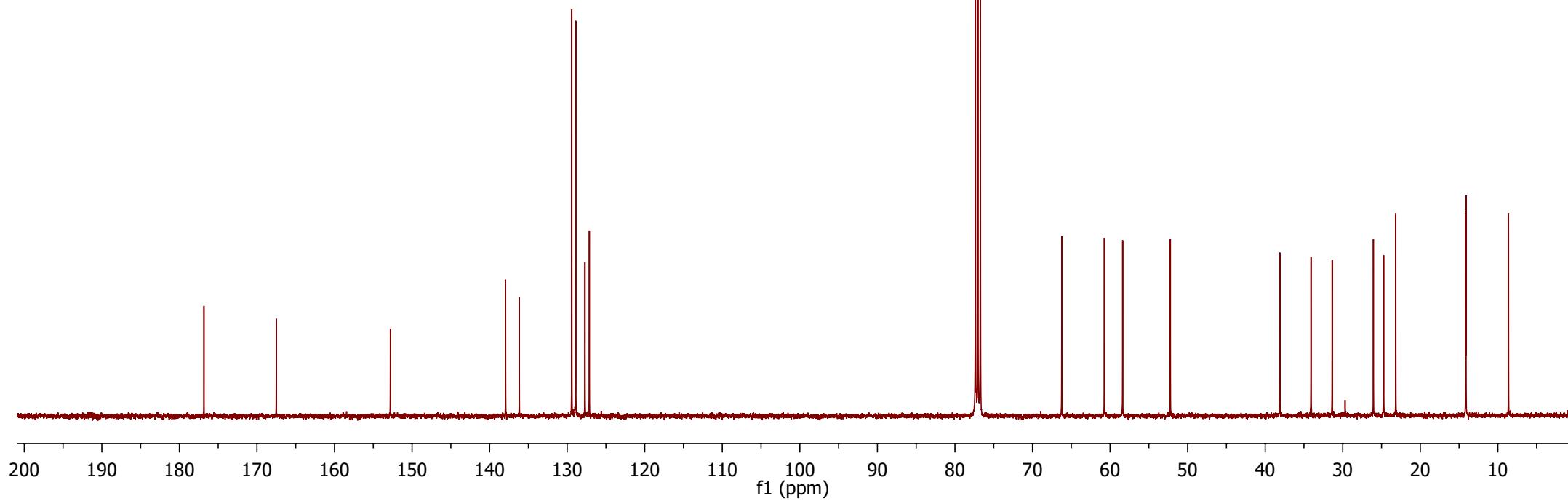
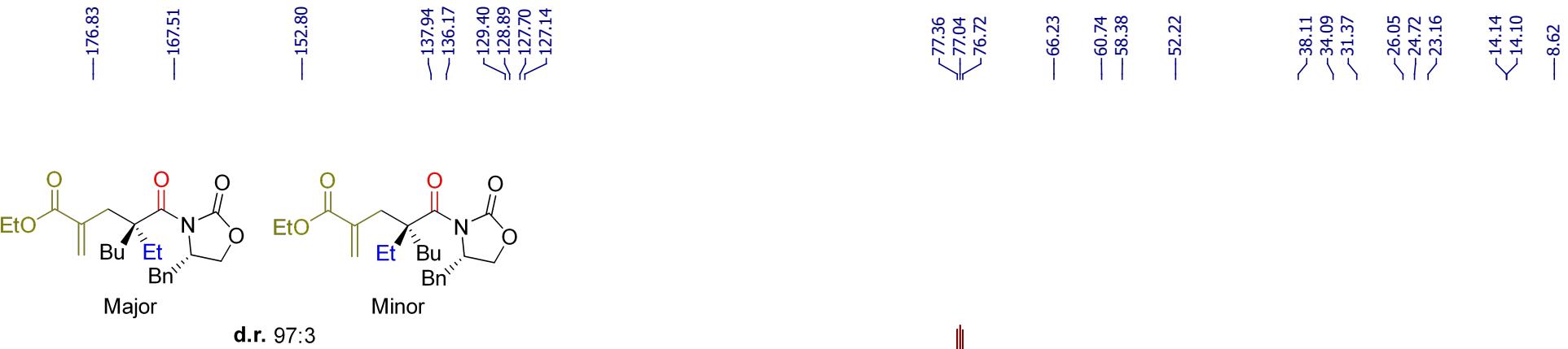


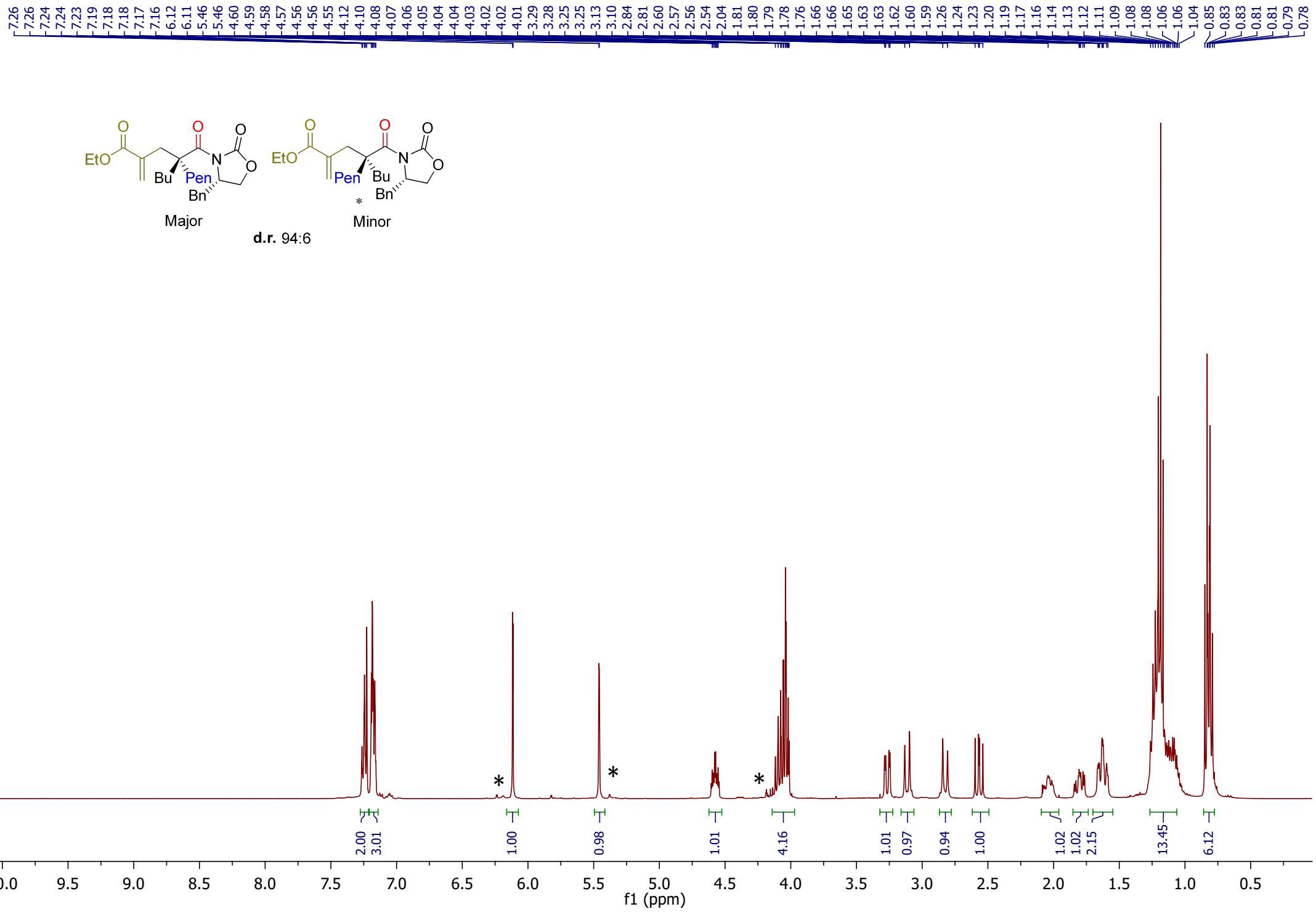


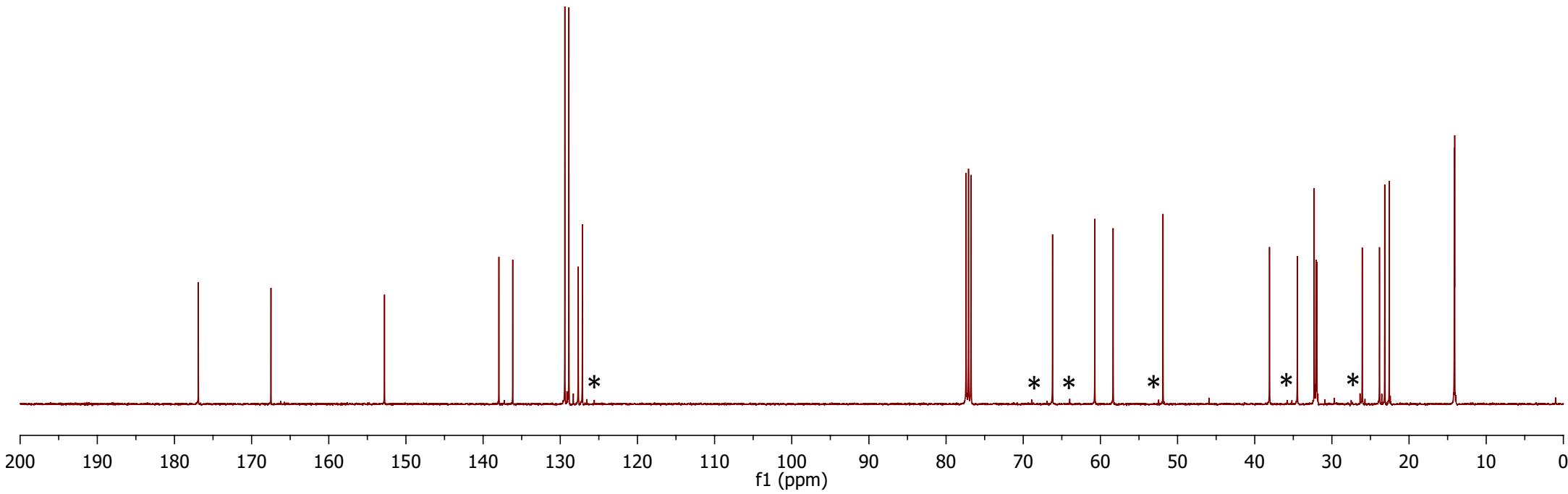


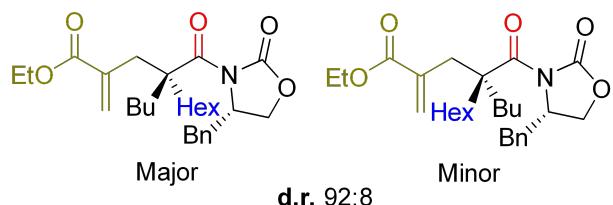
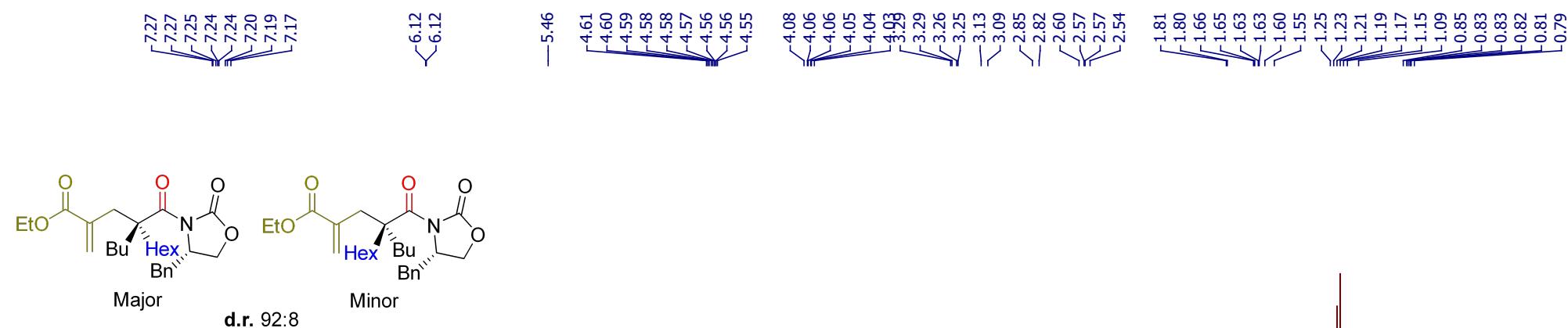
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-4.03	-4.03
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-2.11	-2.09
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-2.04	-2.04
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-1.17	-2.54
-1.14	-2.54
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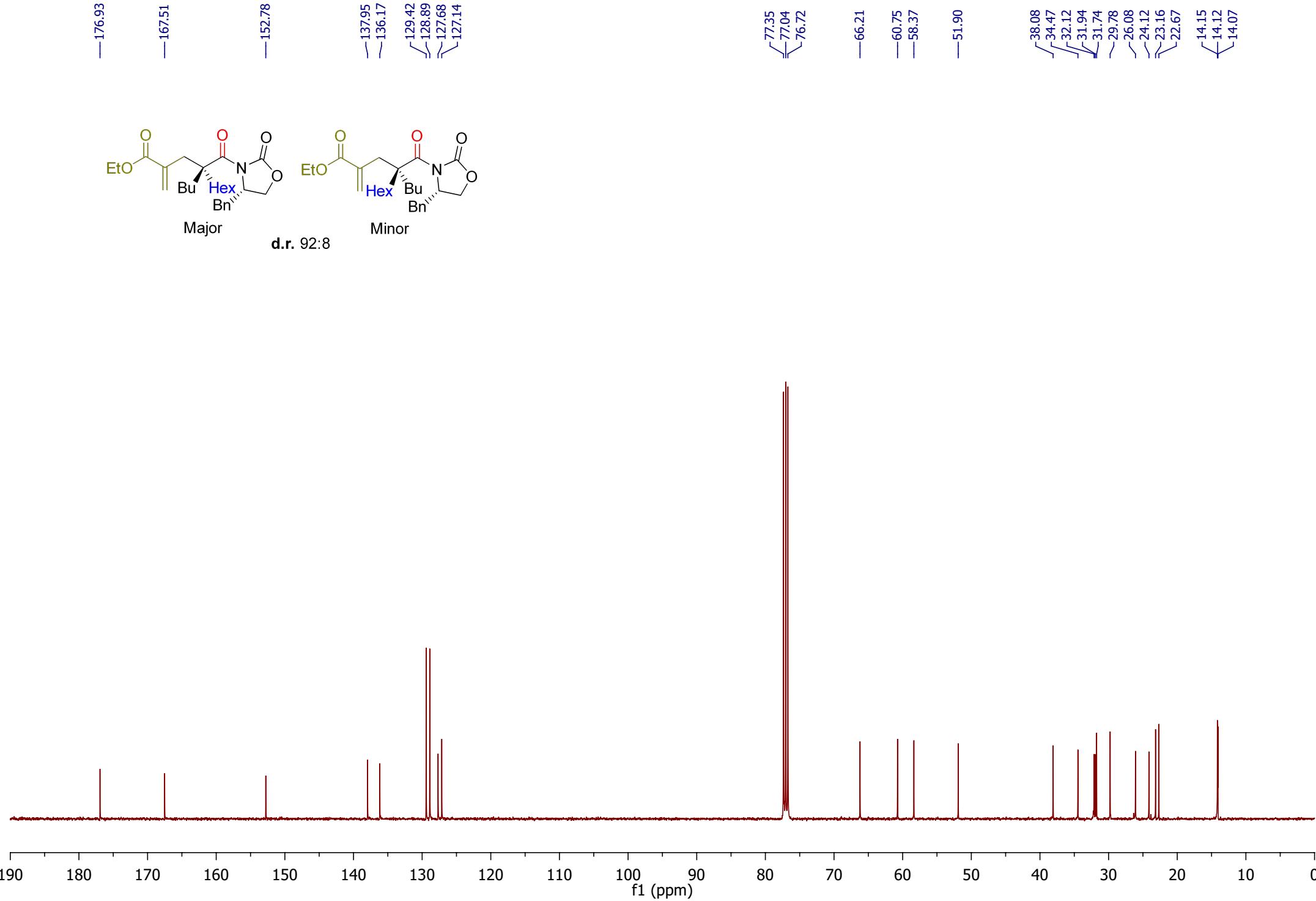


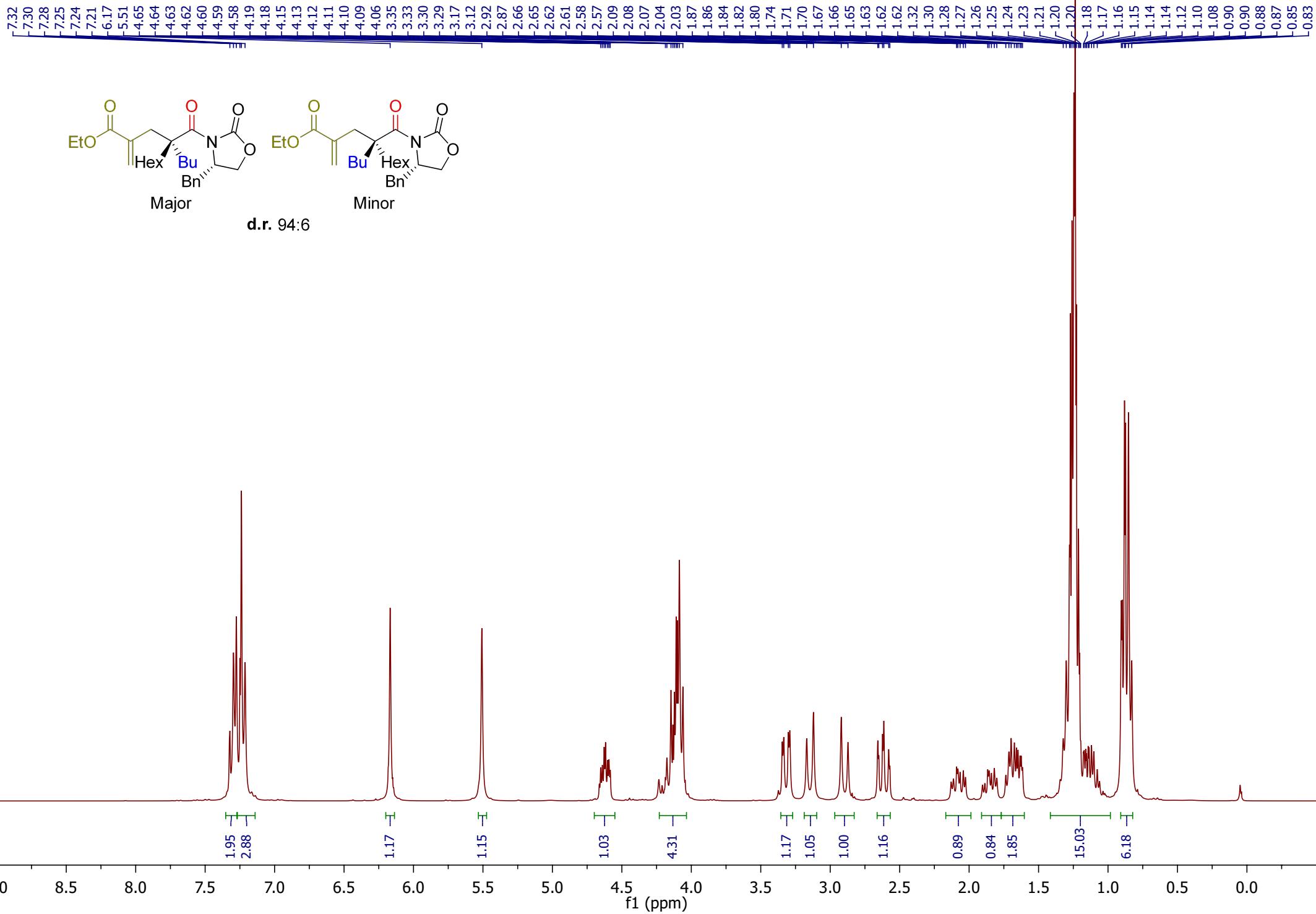


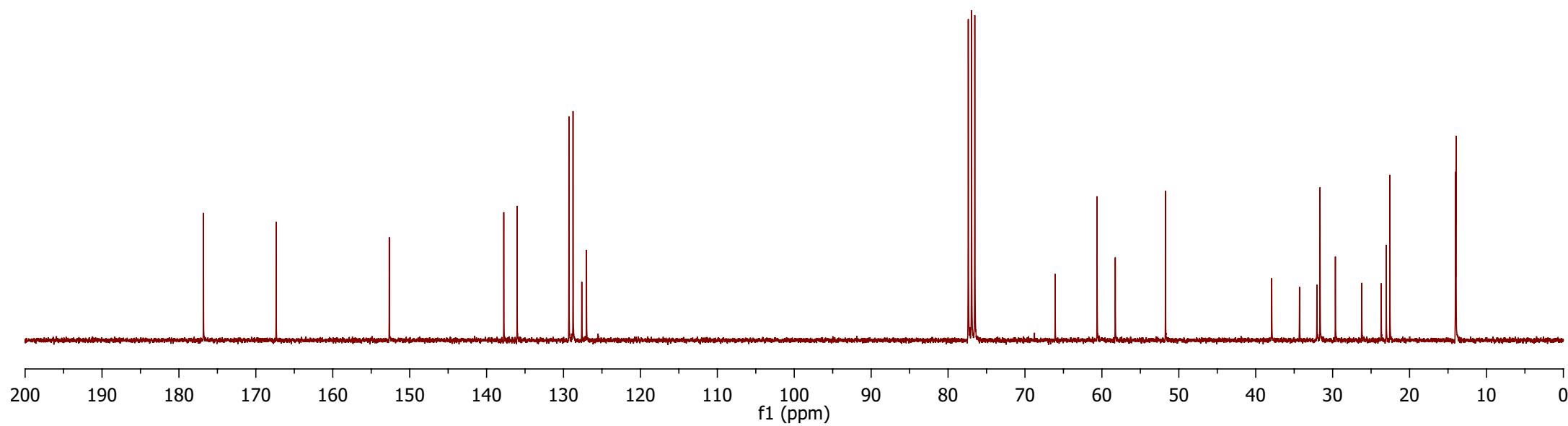


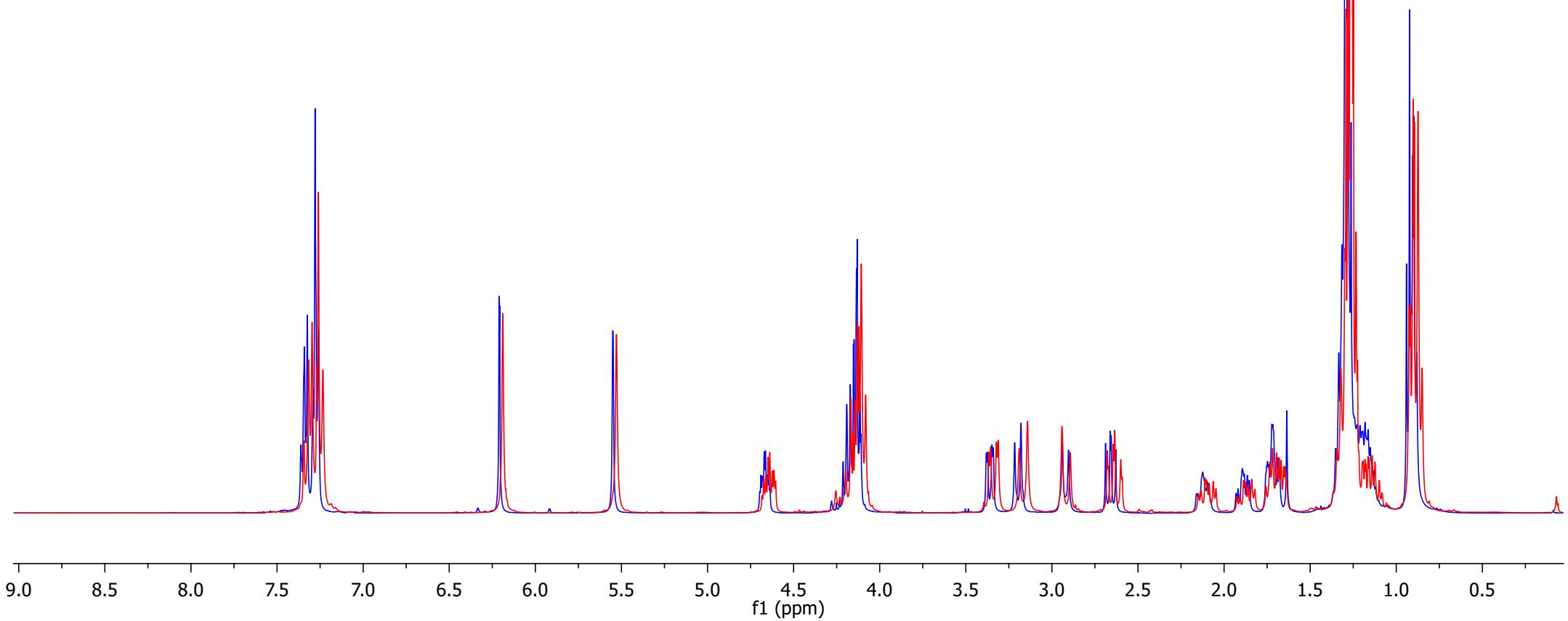
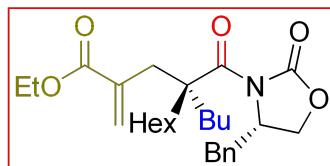
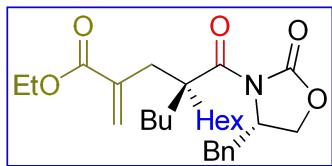


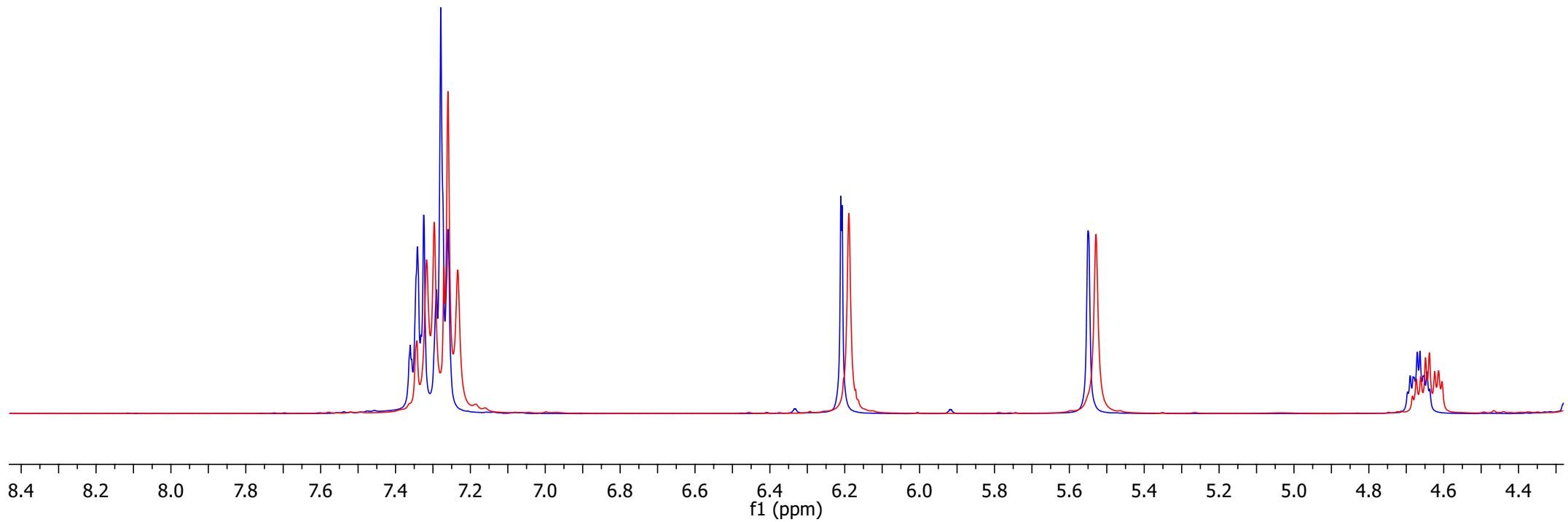
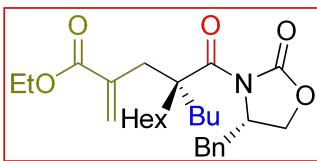
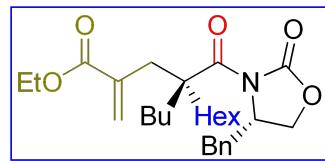


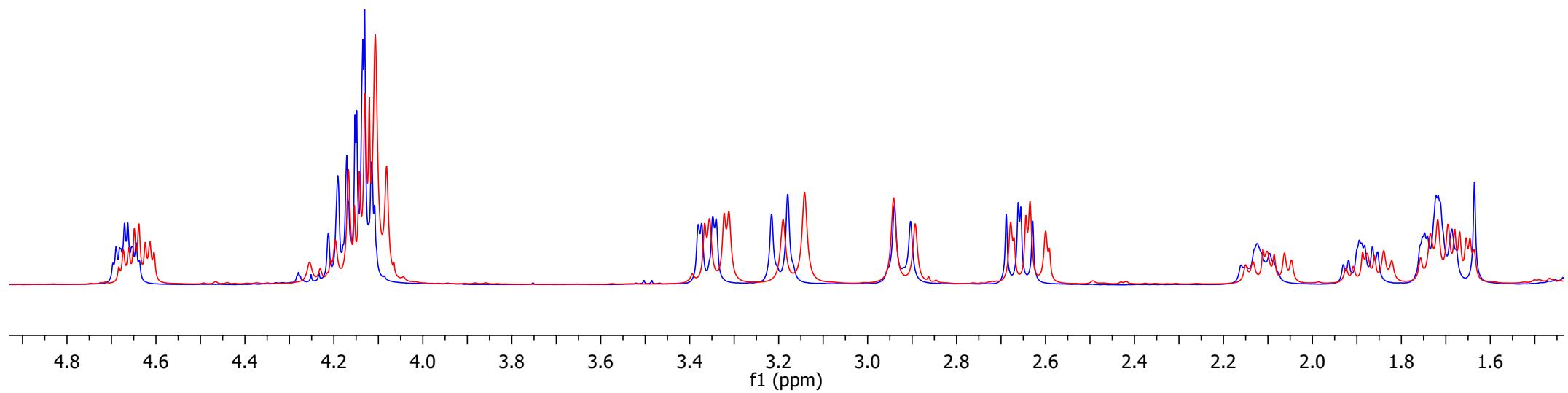
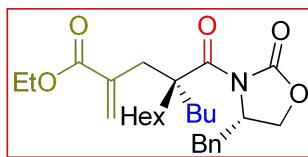
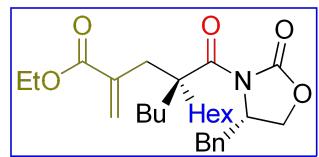


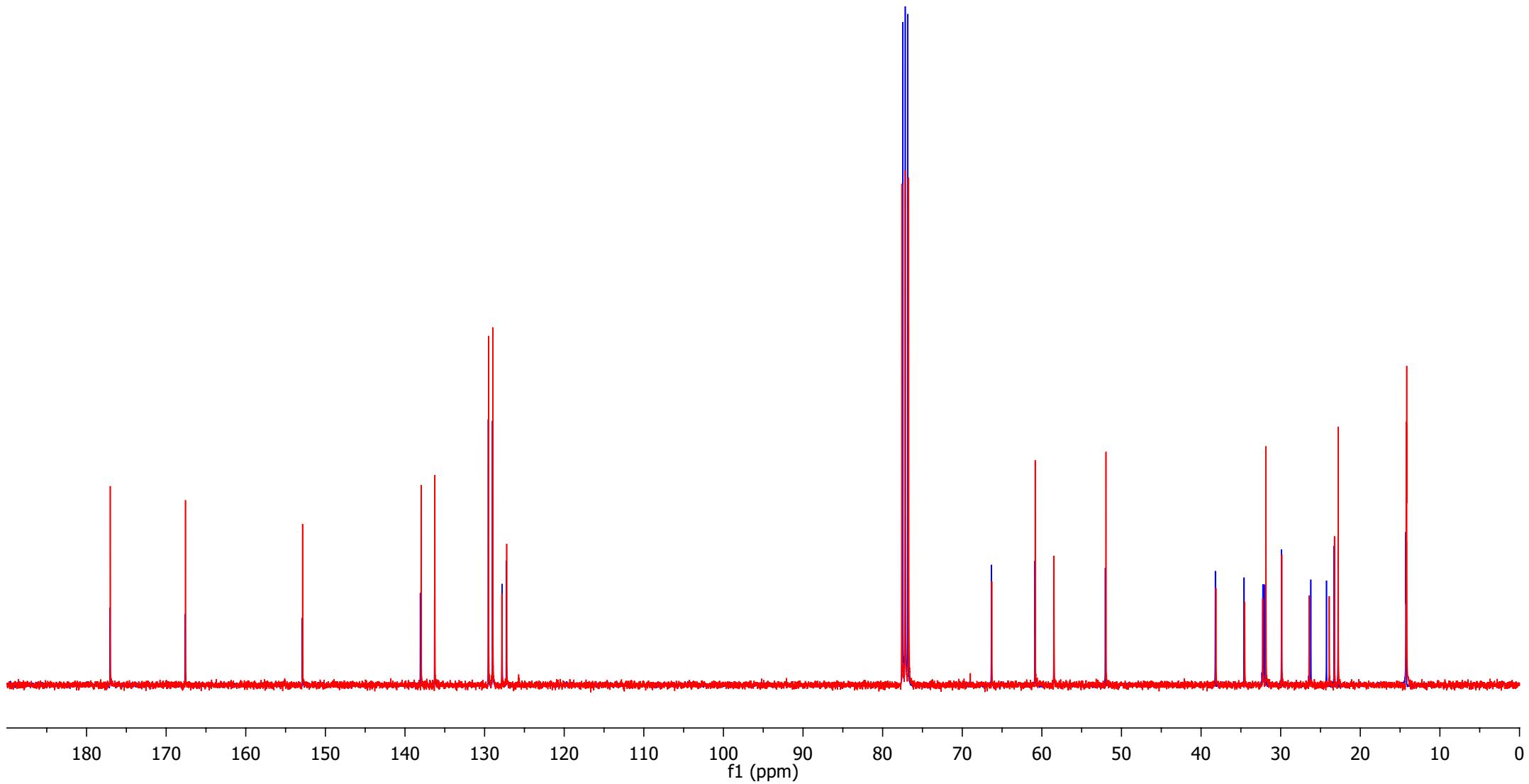
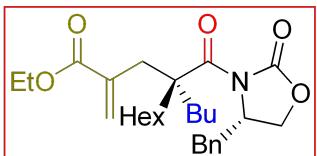
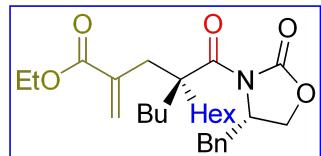


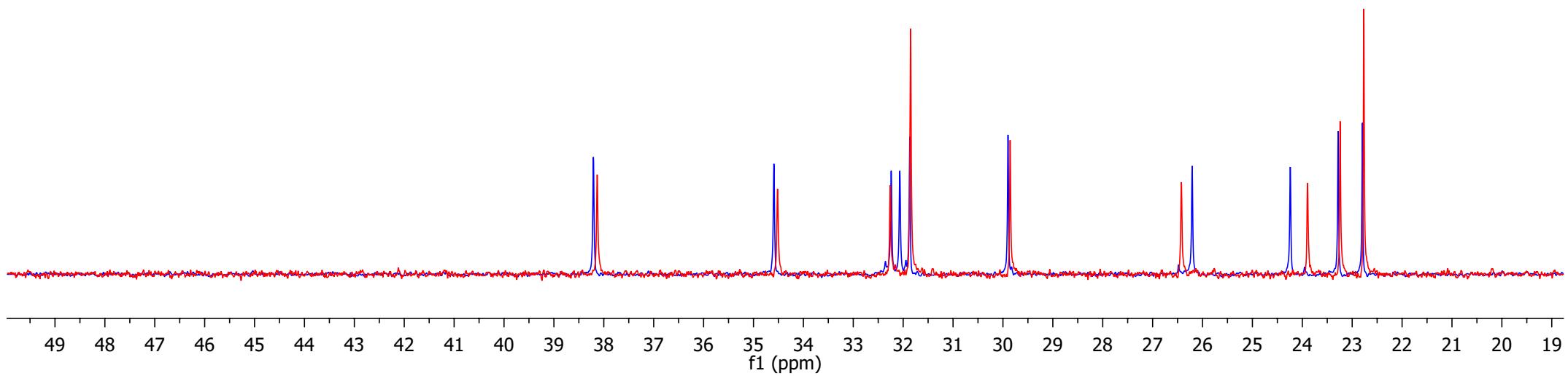
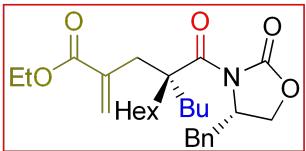
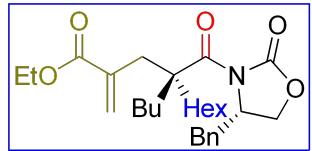


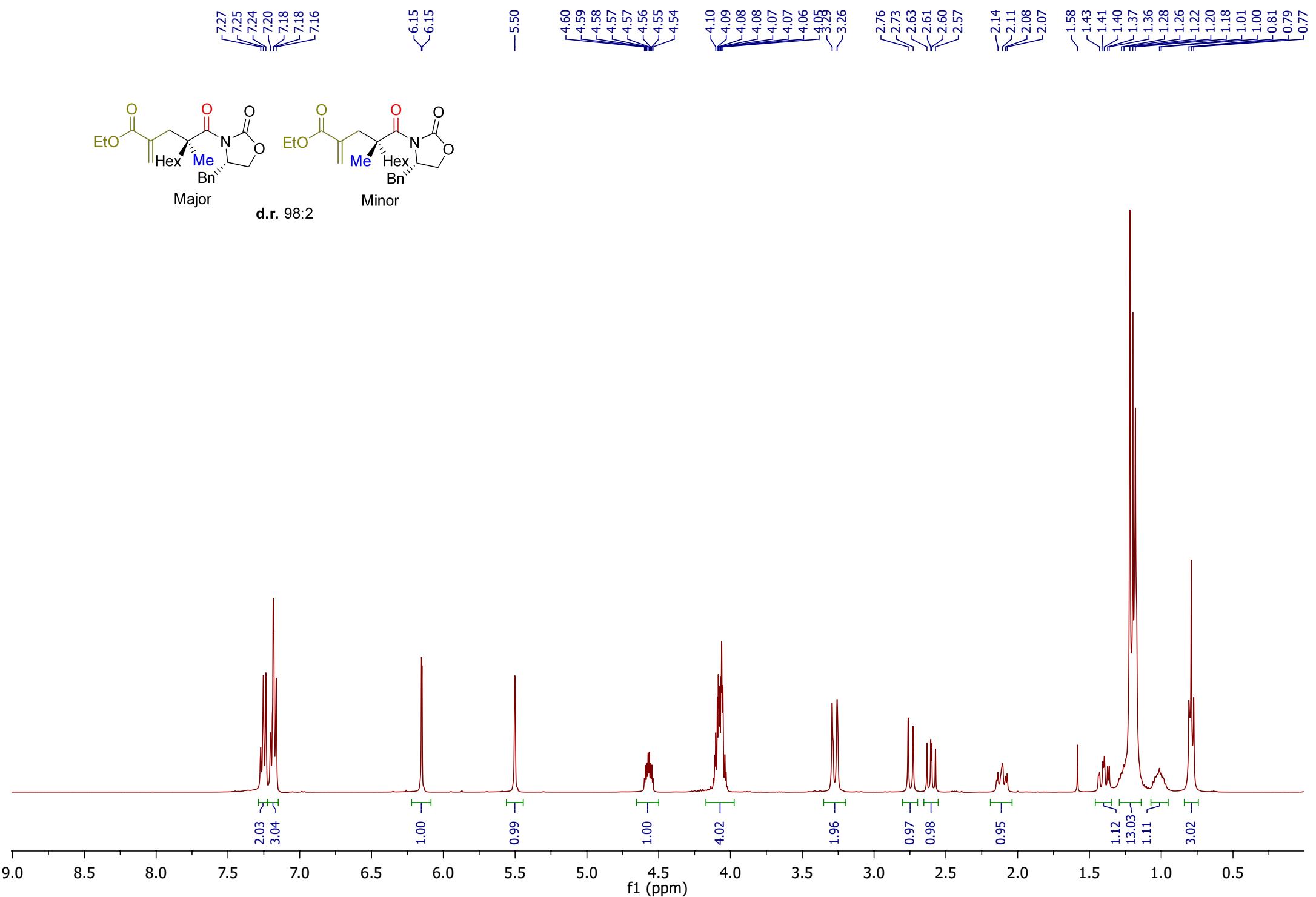


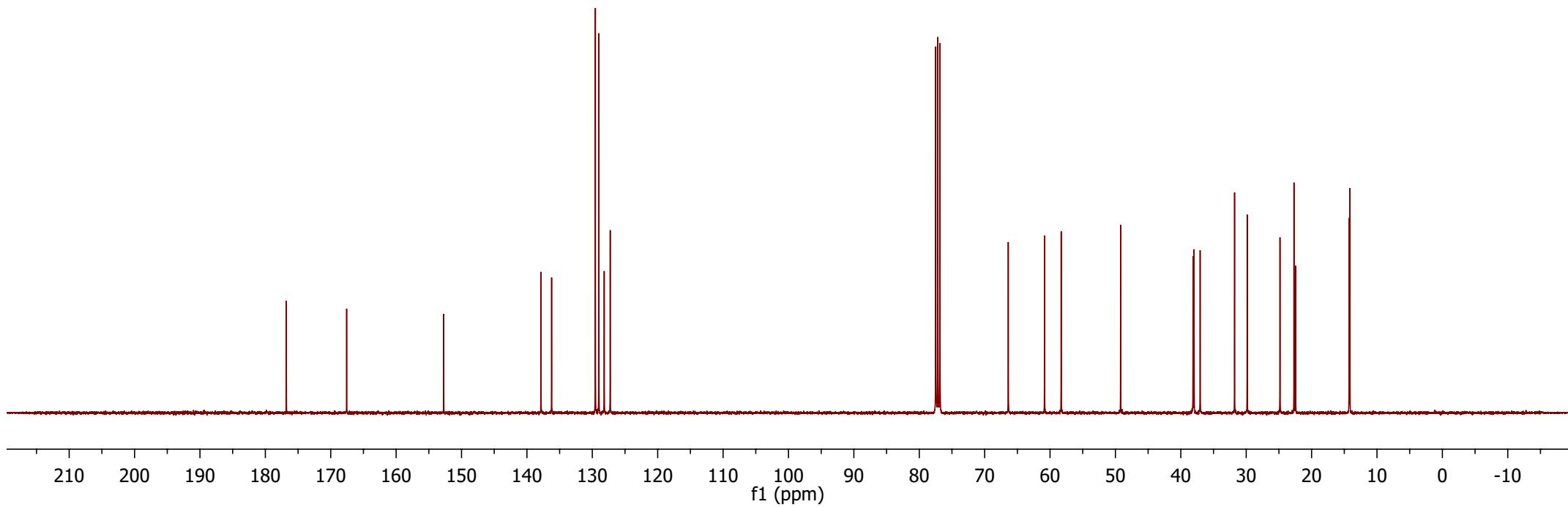
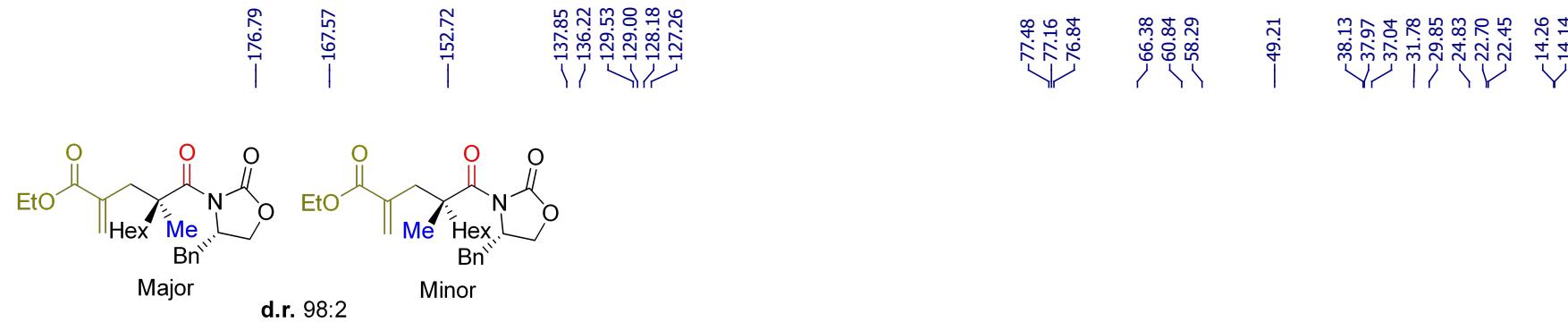


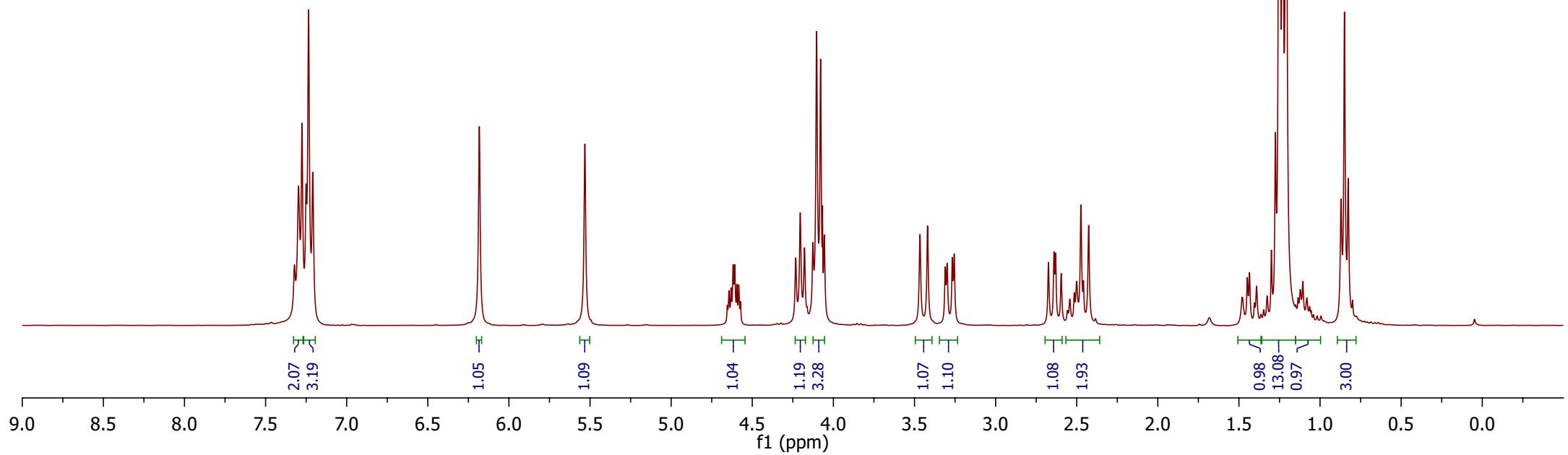
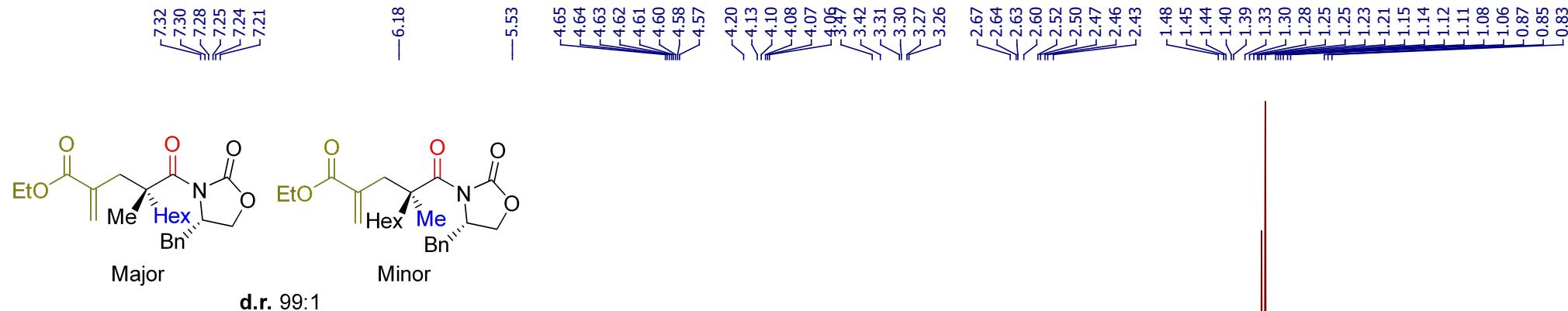


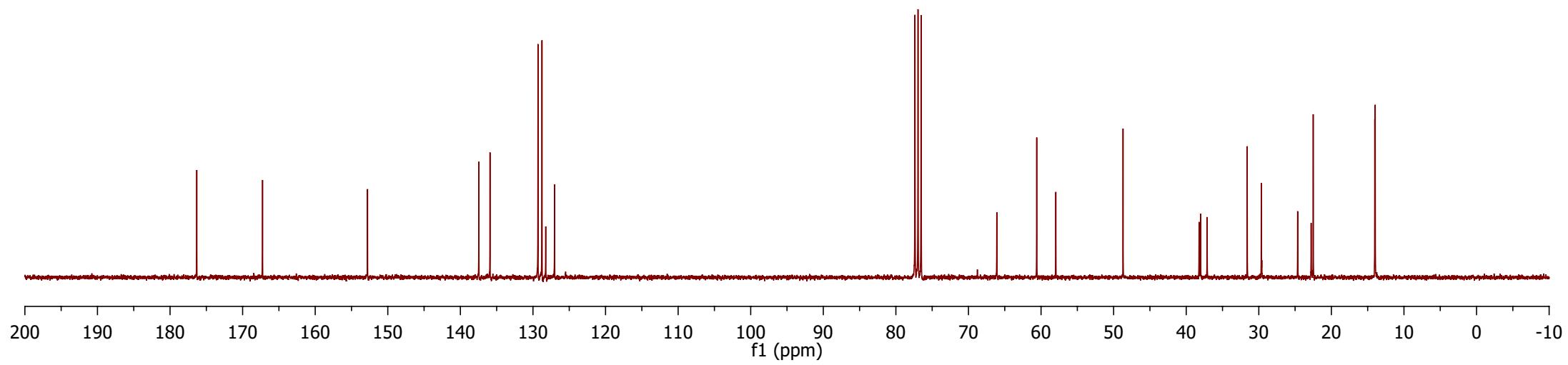


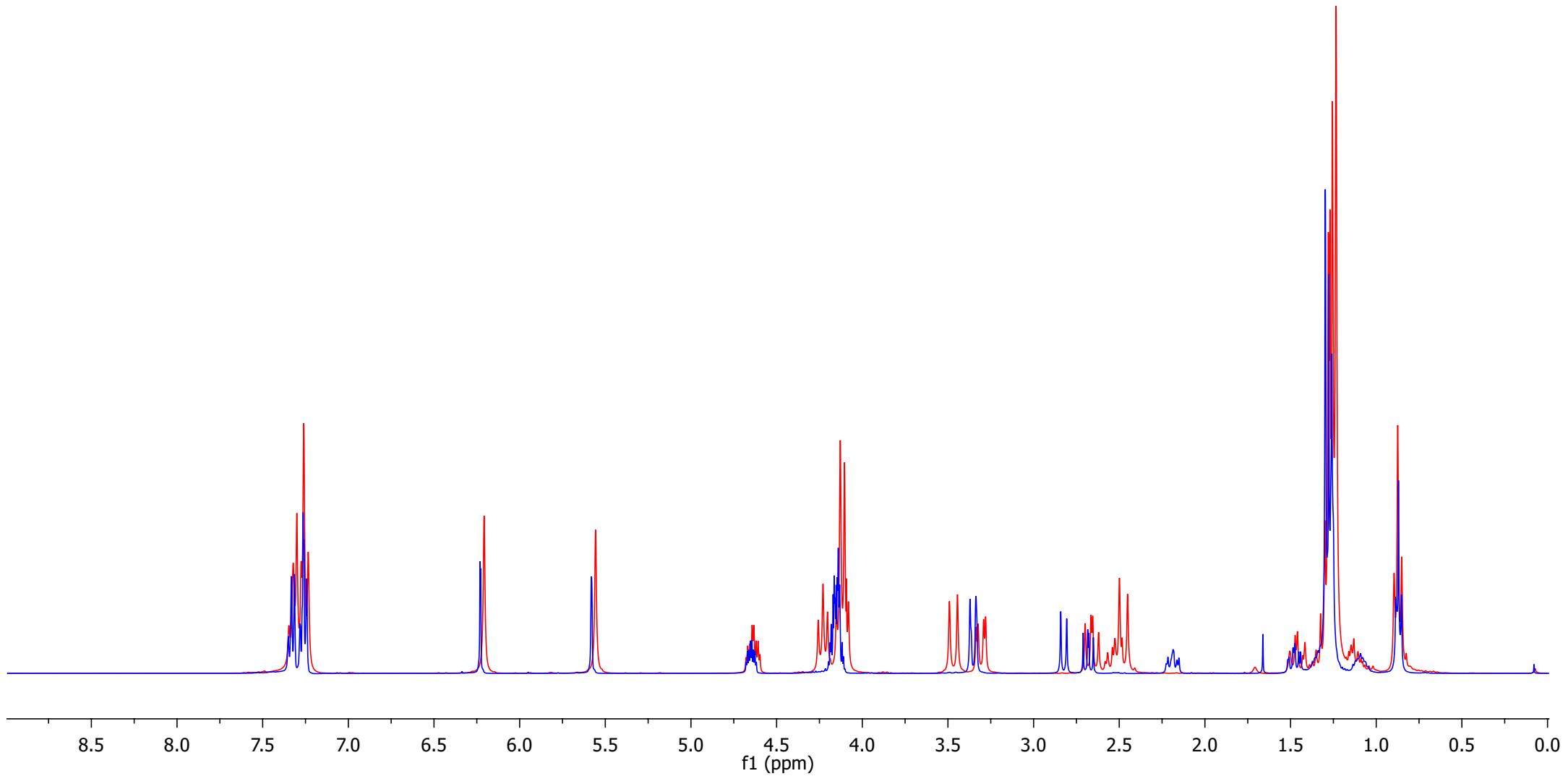
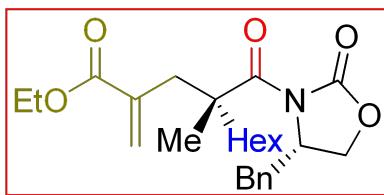
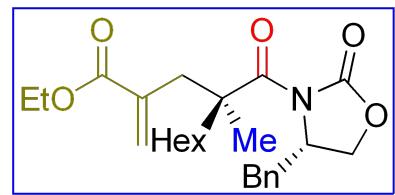


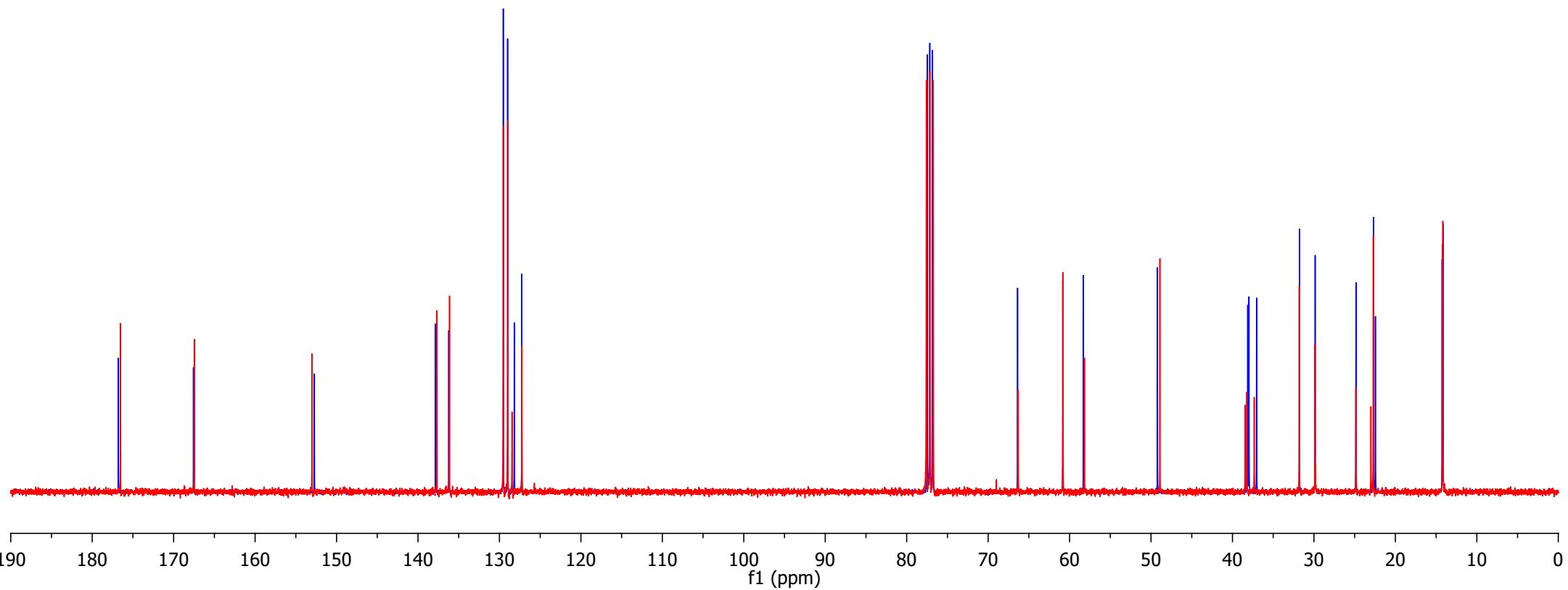
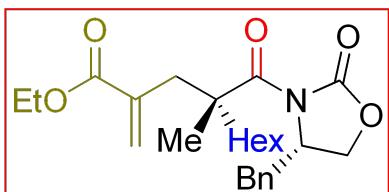
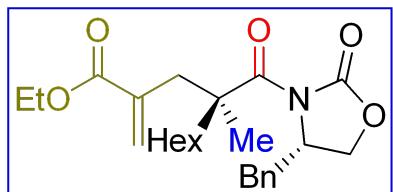


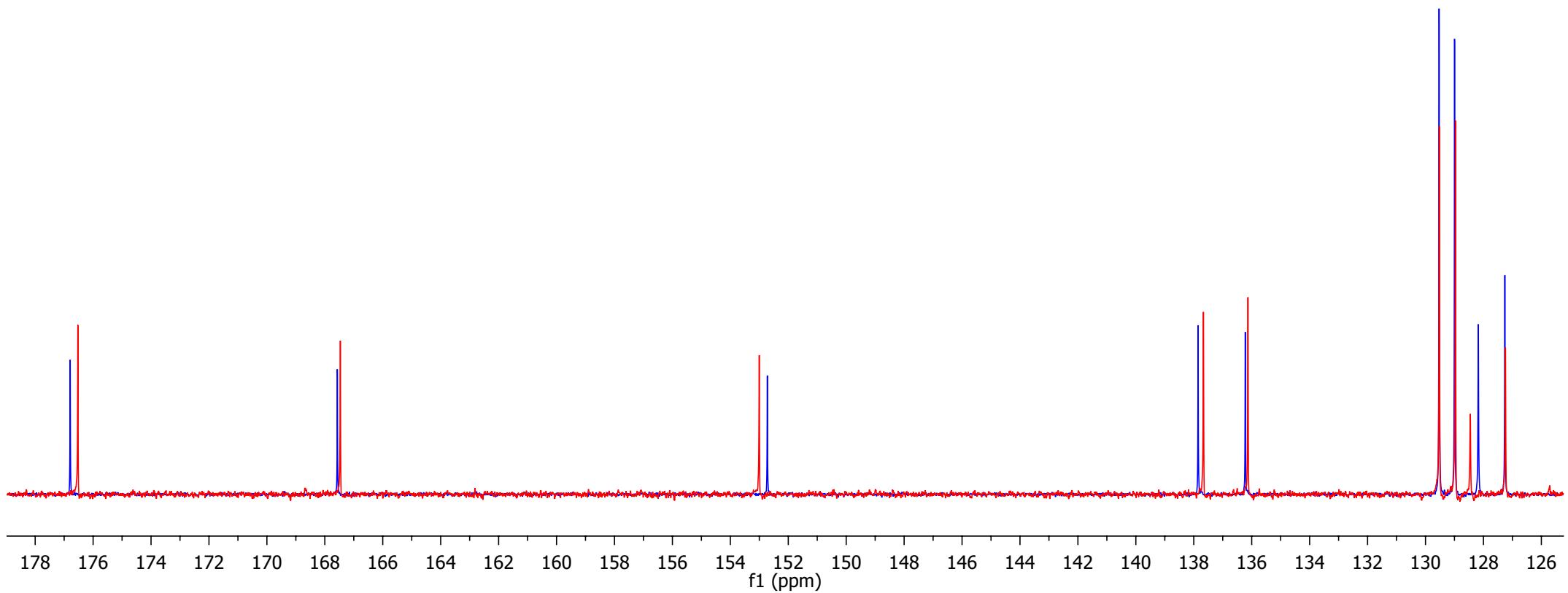
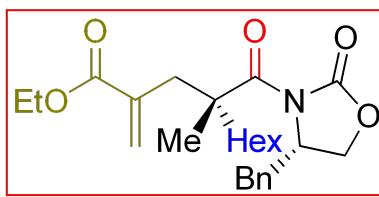
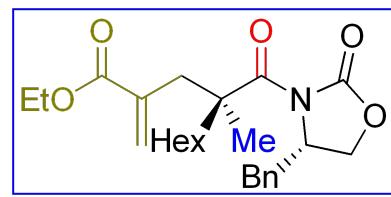


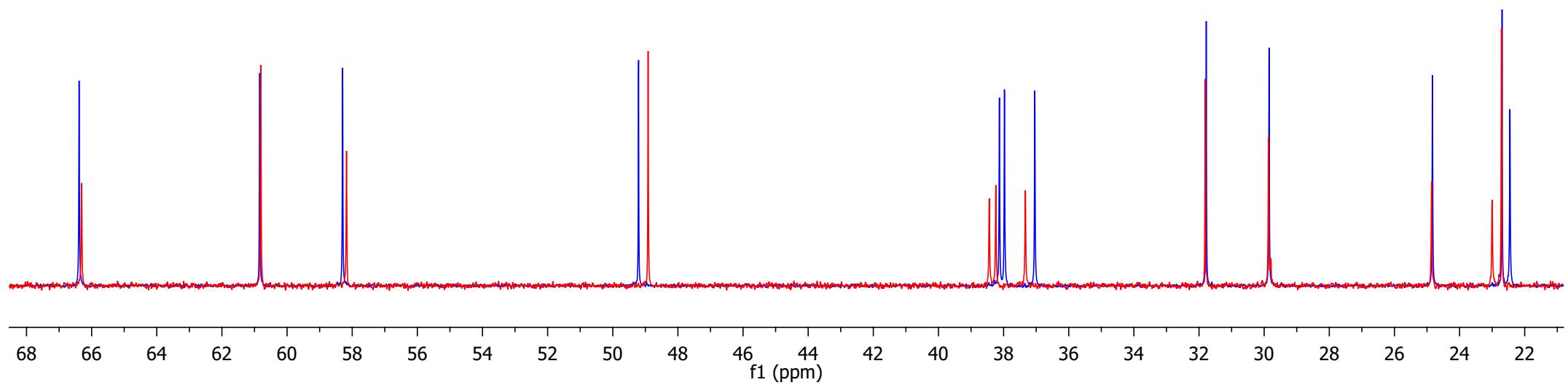
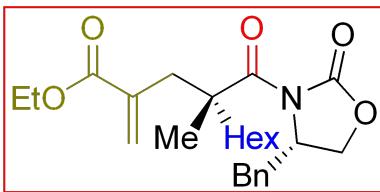
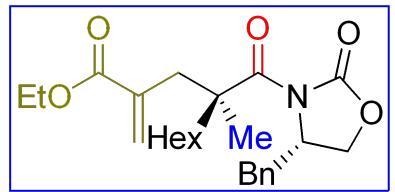


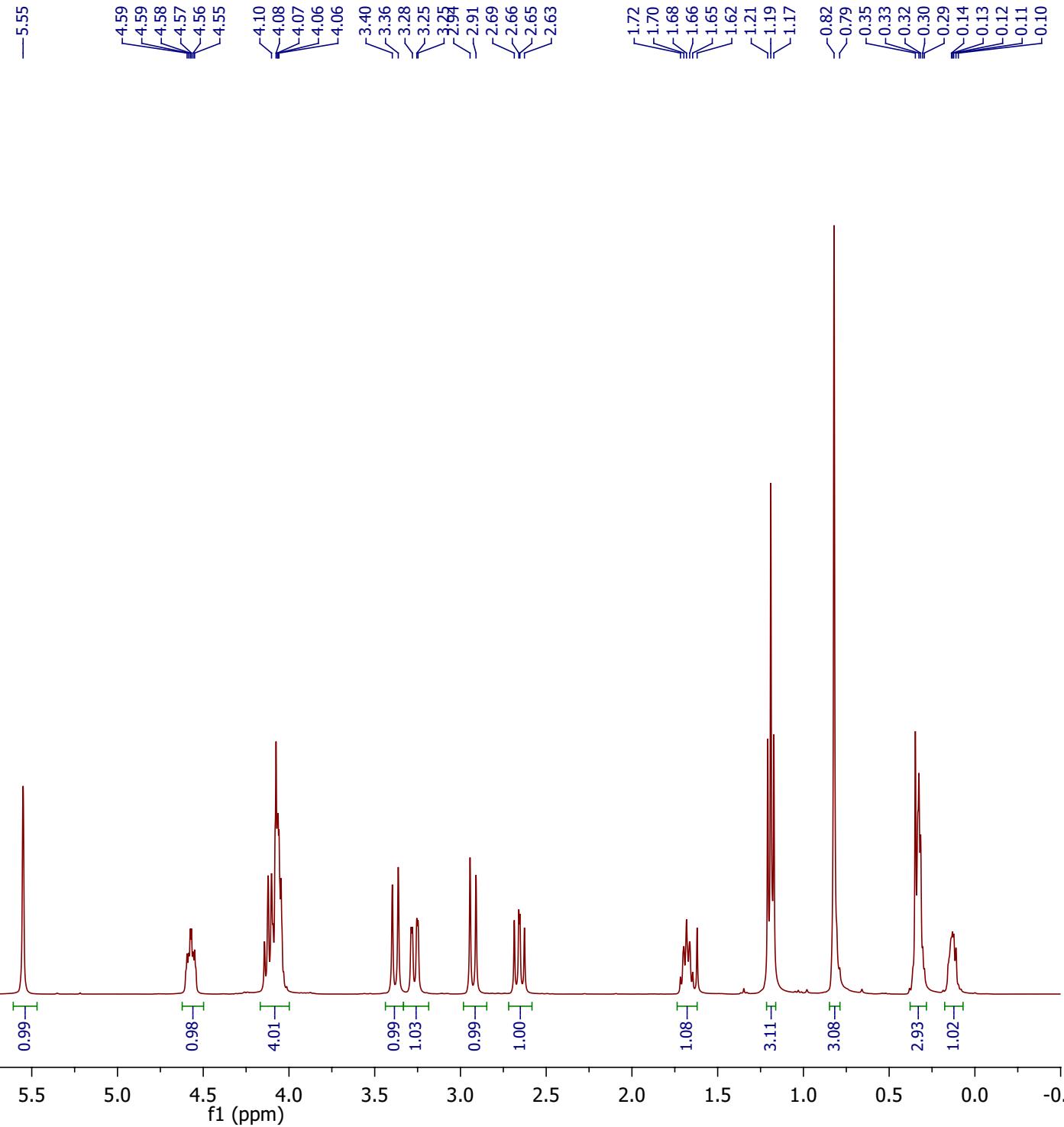
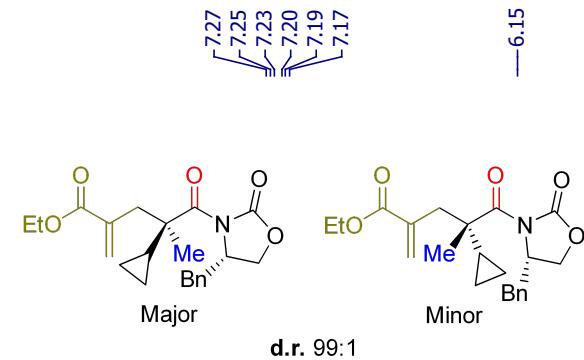


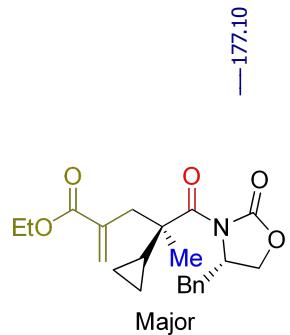




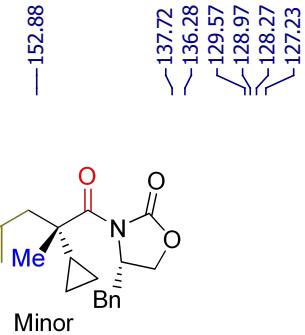








—167.45



d.r. 99:1

—137.72
—136.28
—129.57
—128.97
—128.27
—127.23

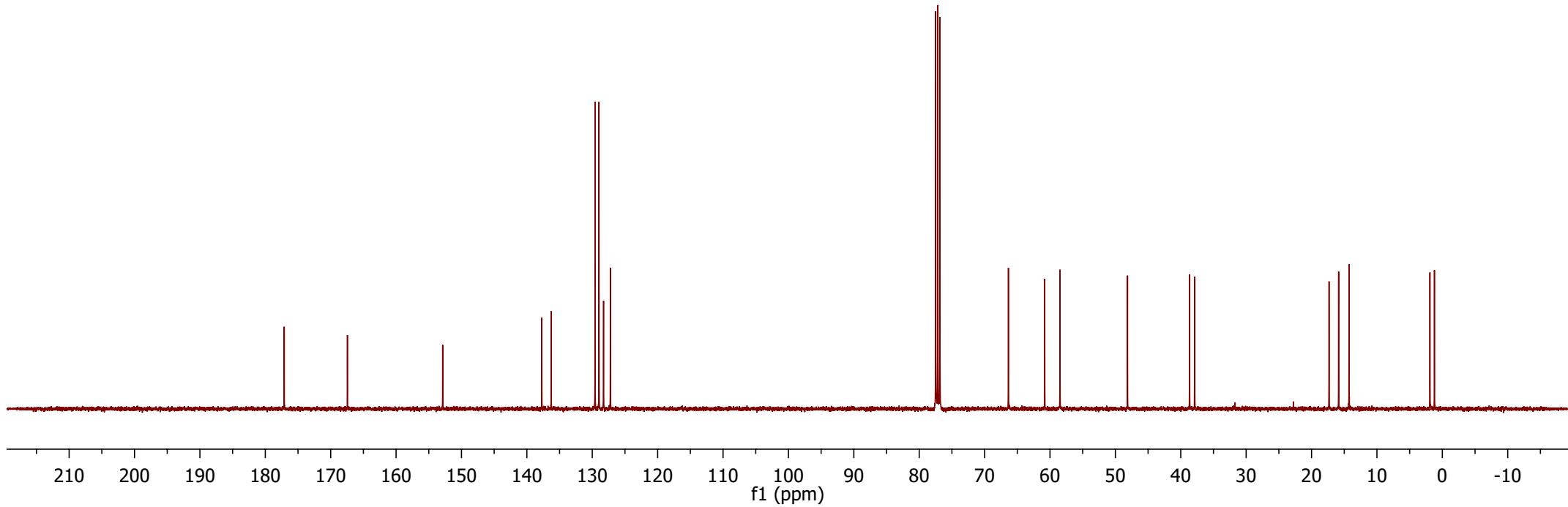
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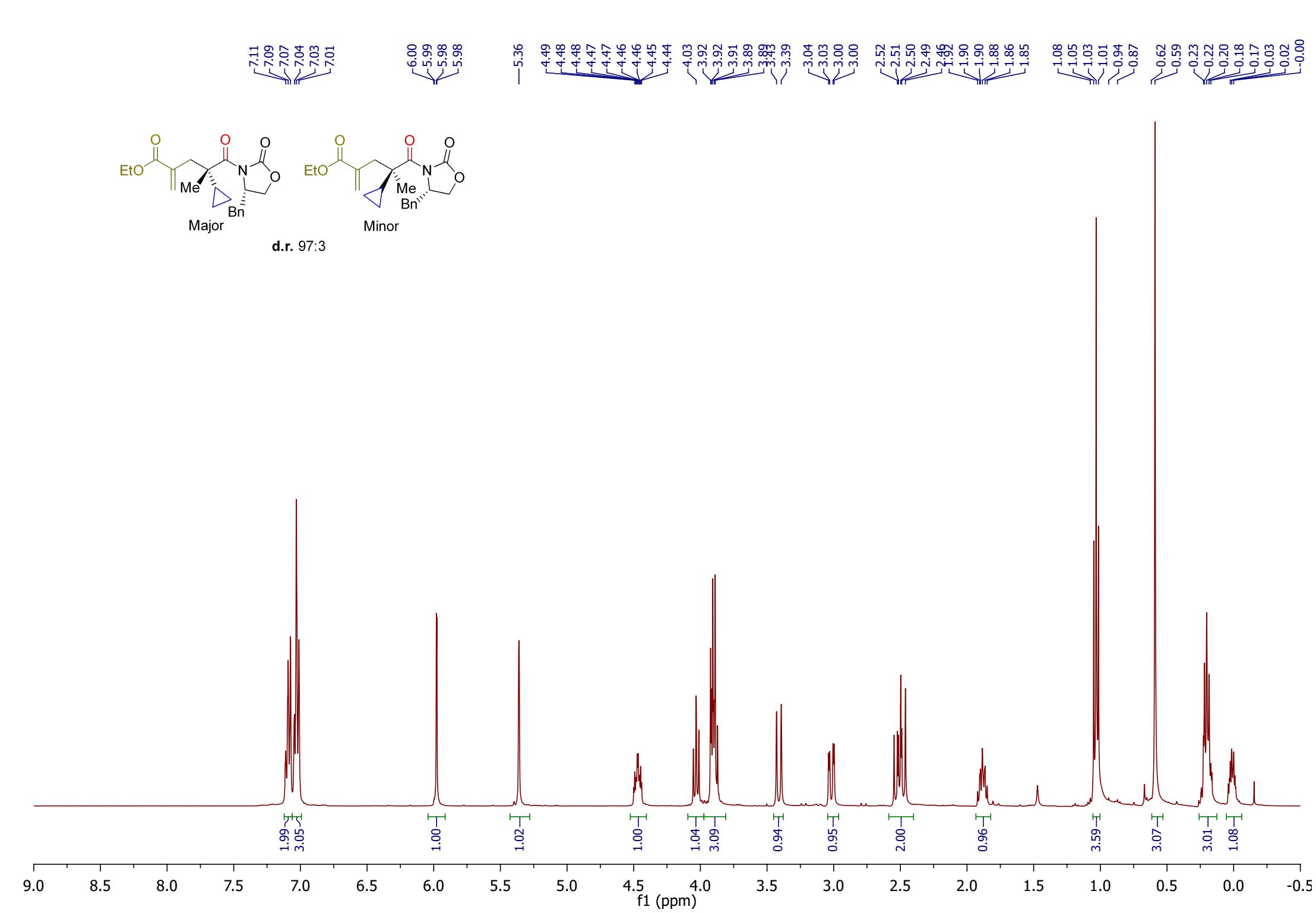
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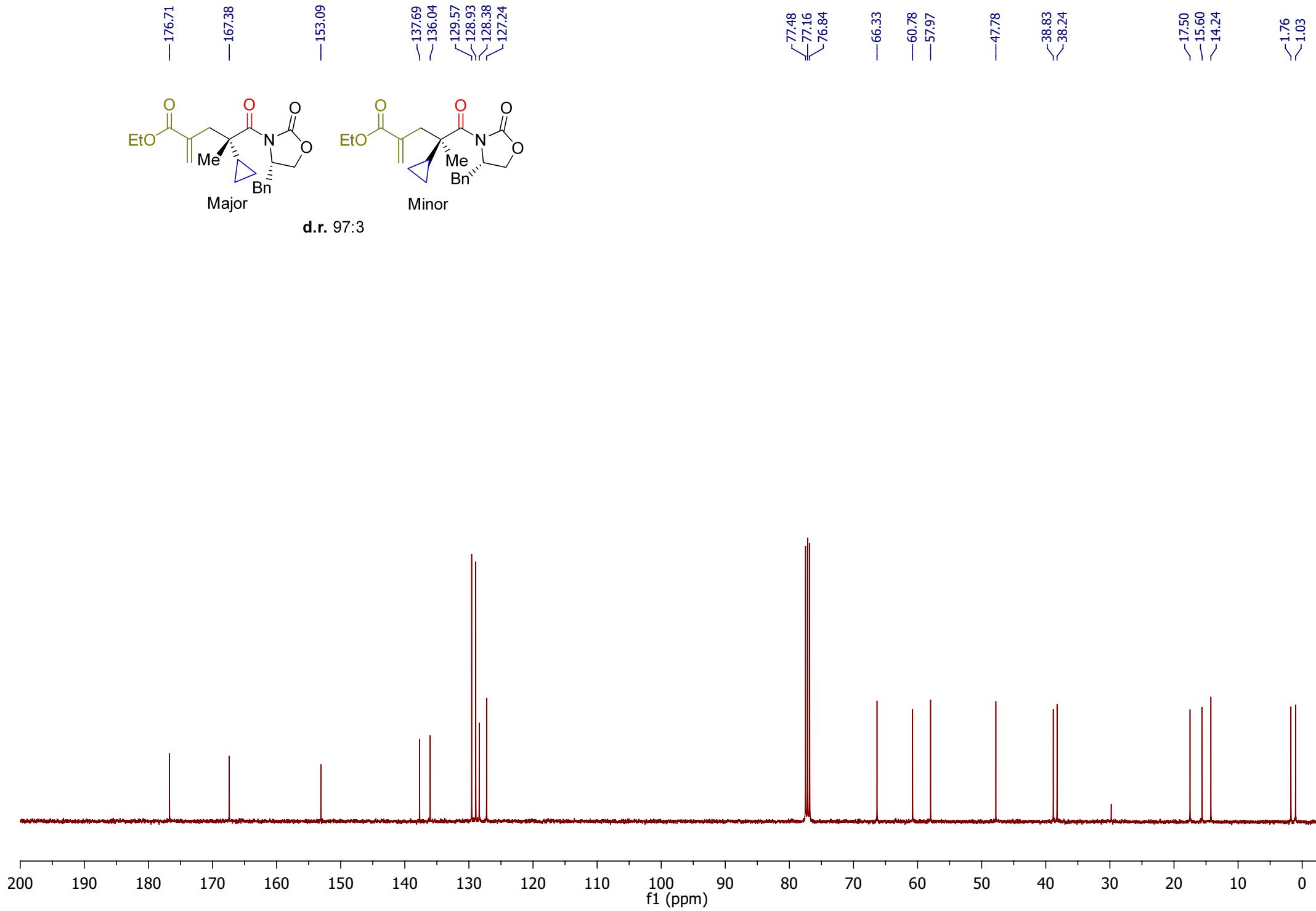
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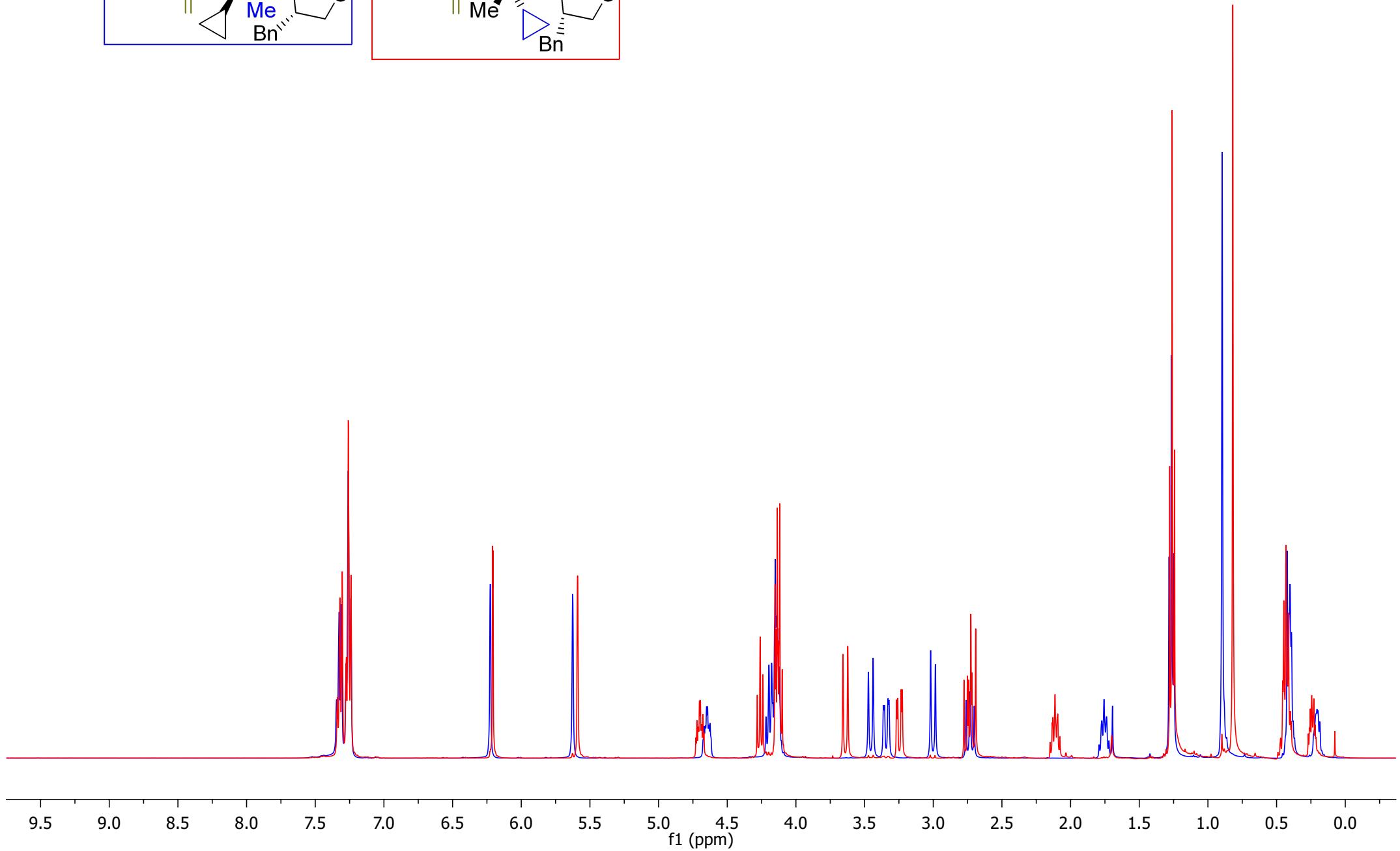
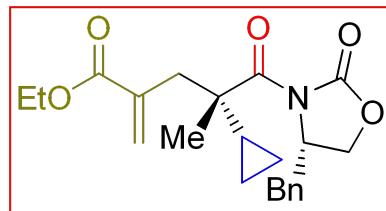
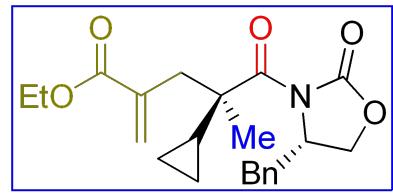
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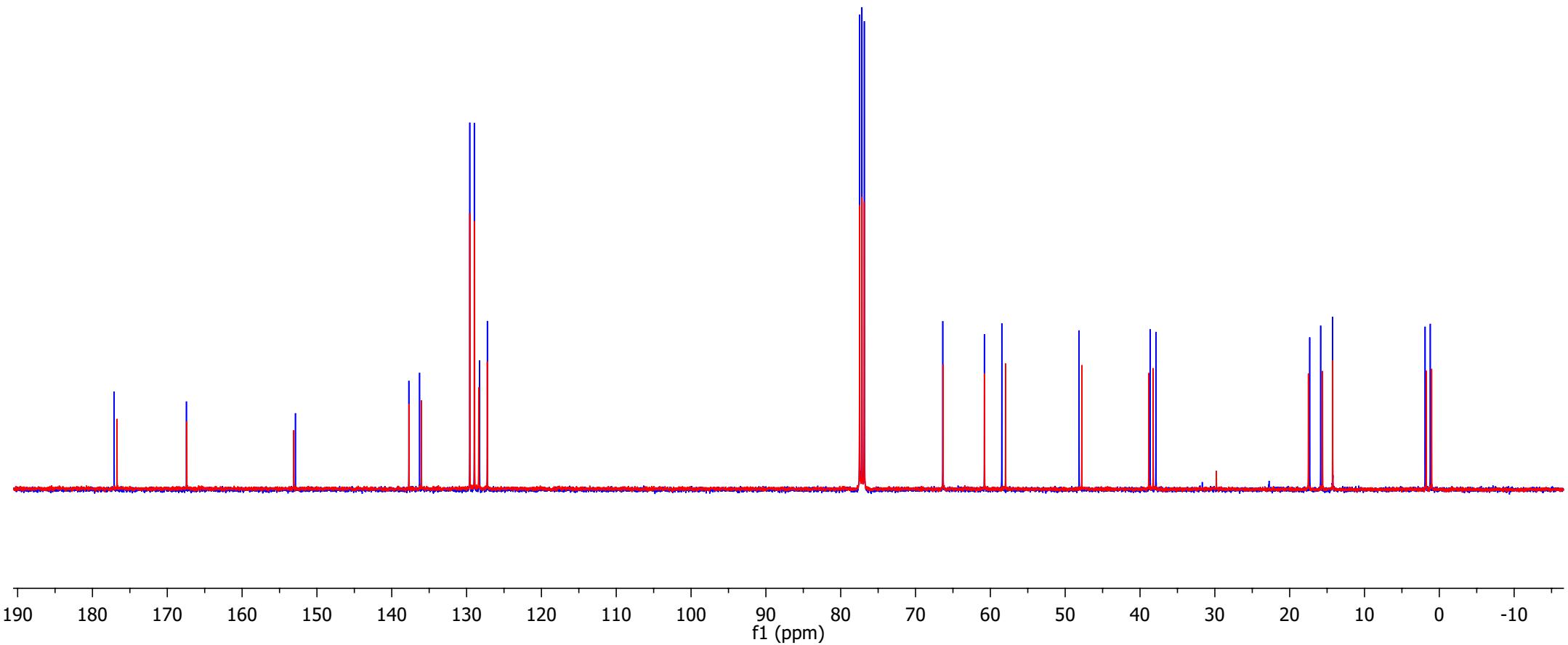
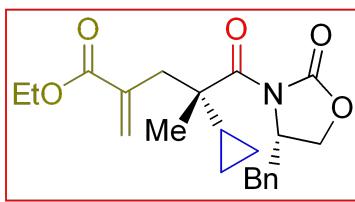
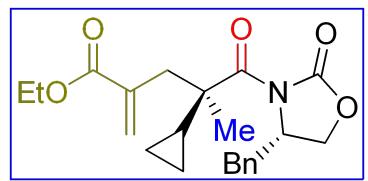
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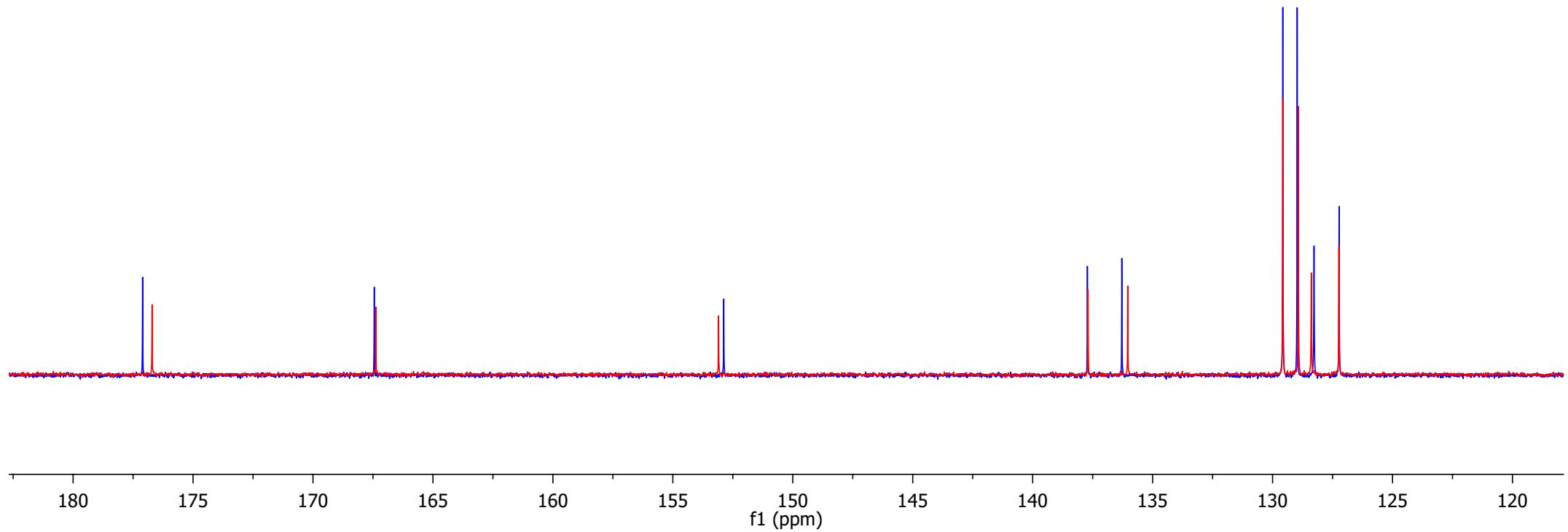
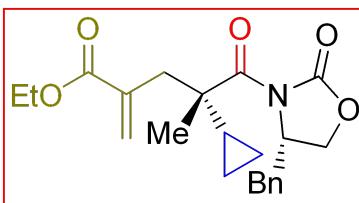
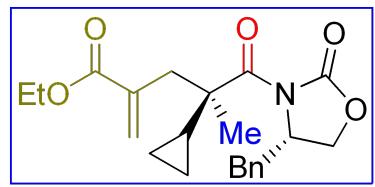


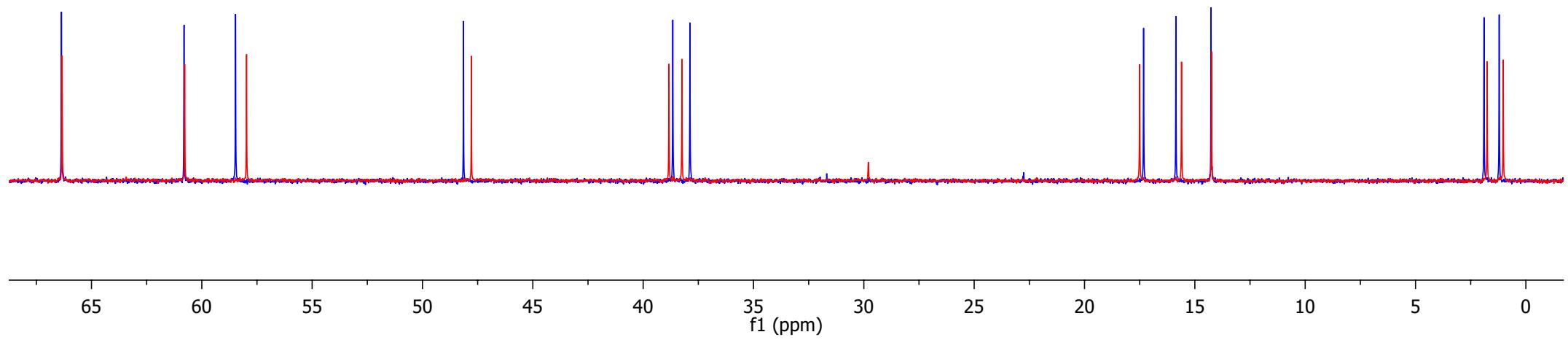
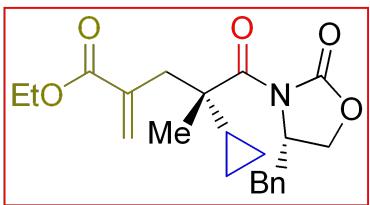
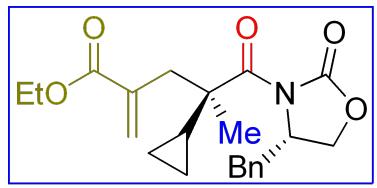


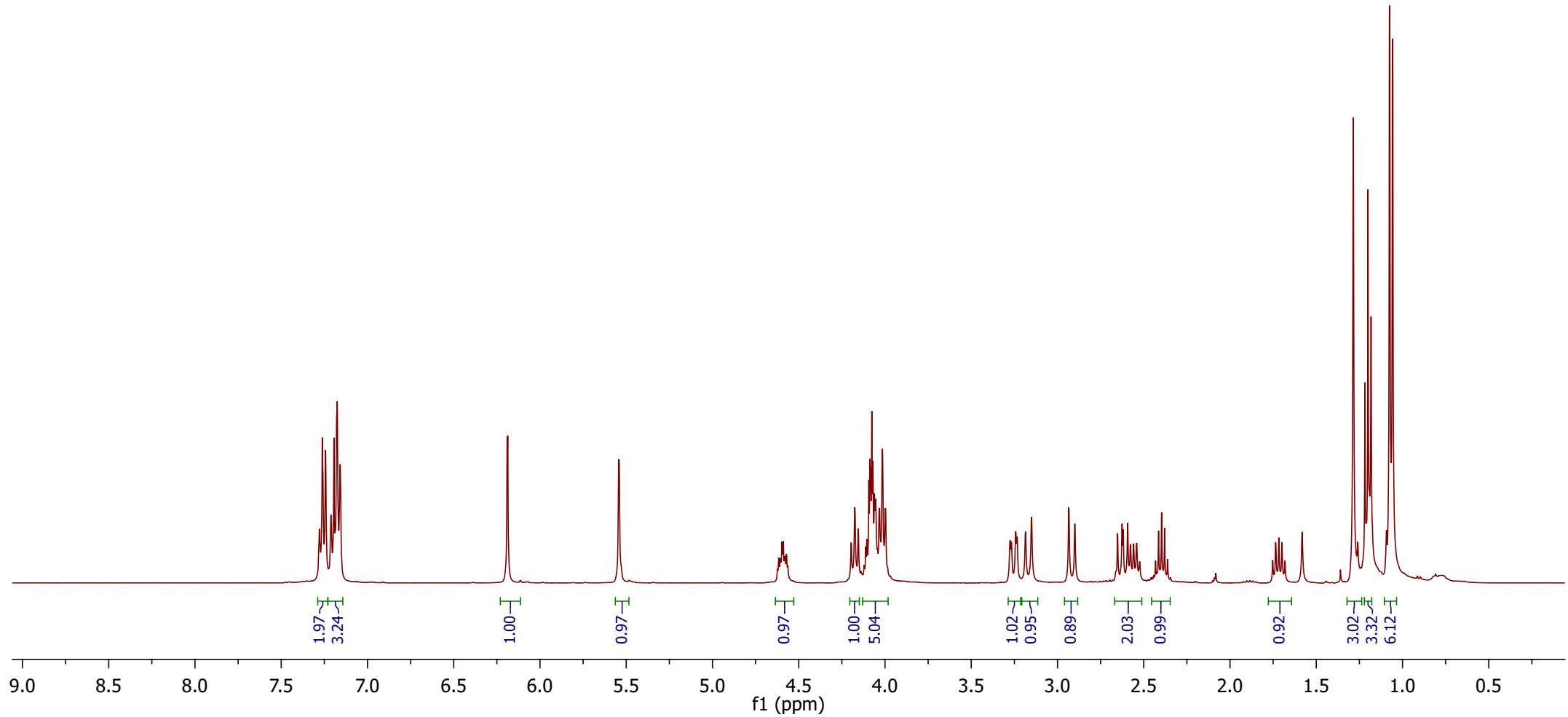
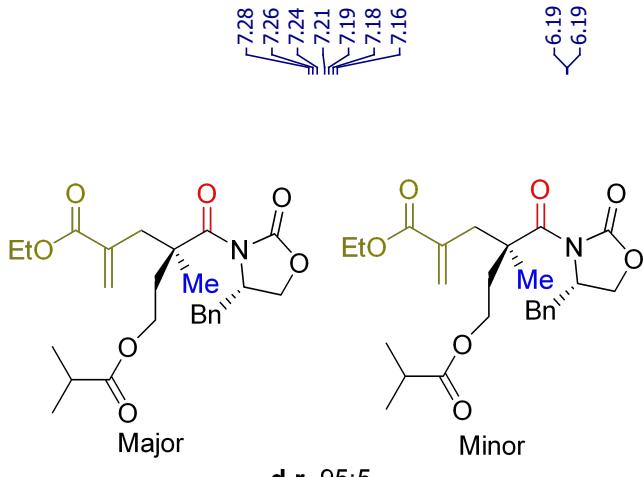


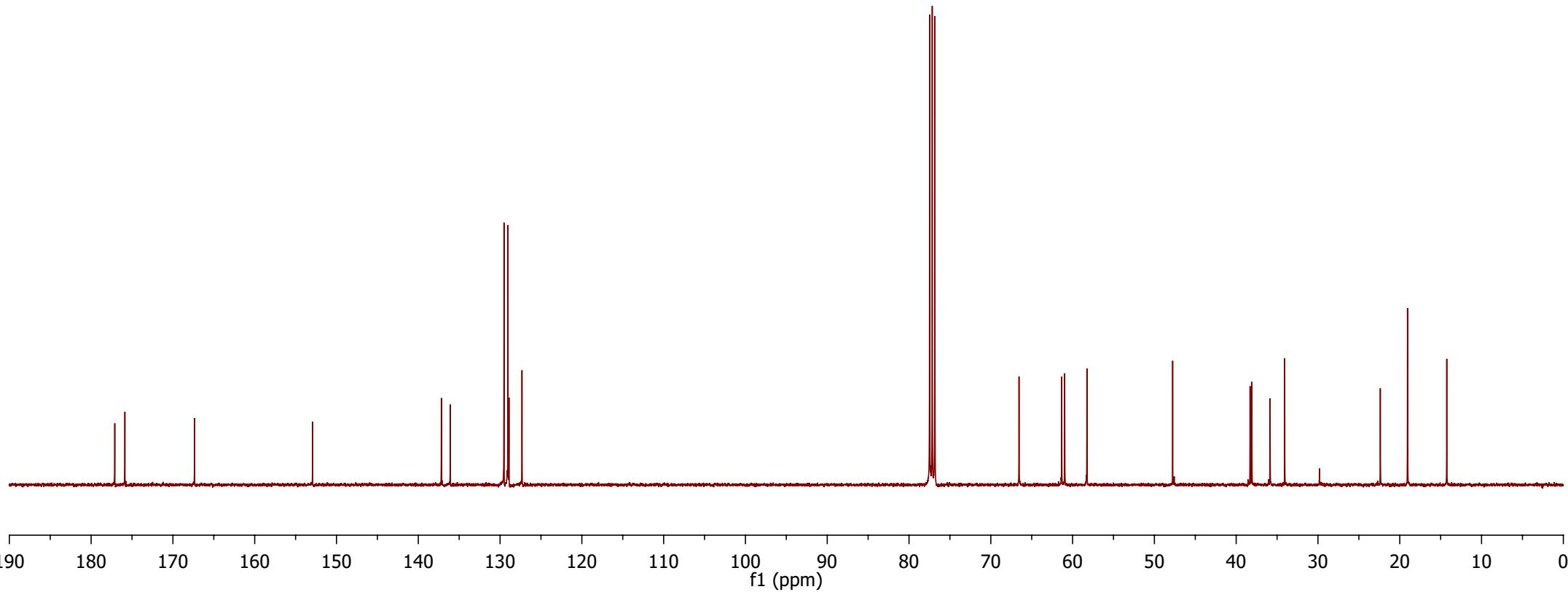
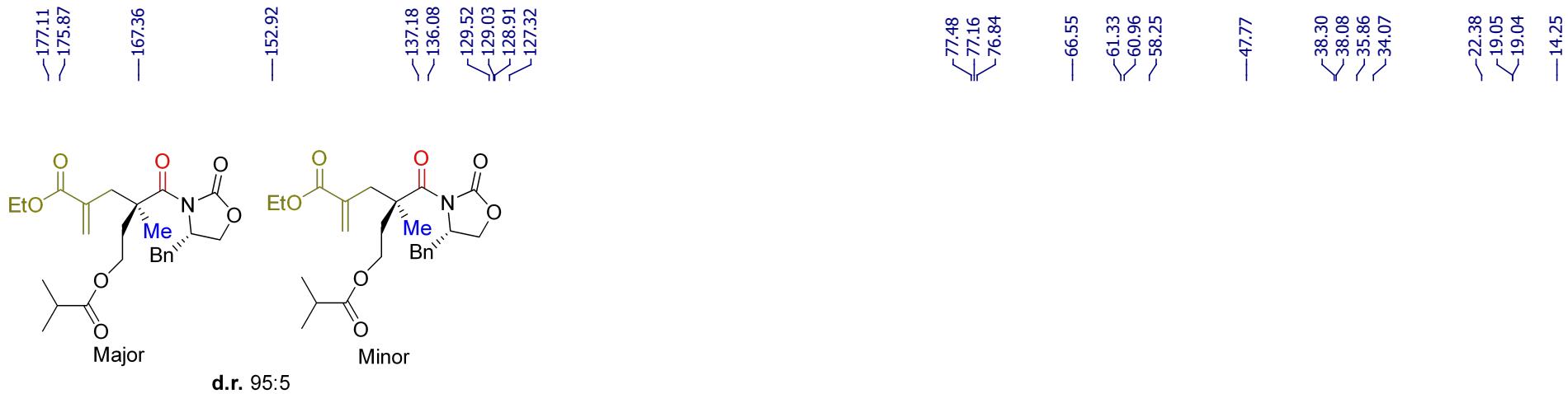


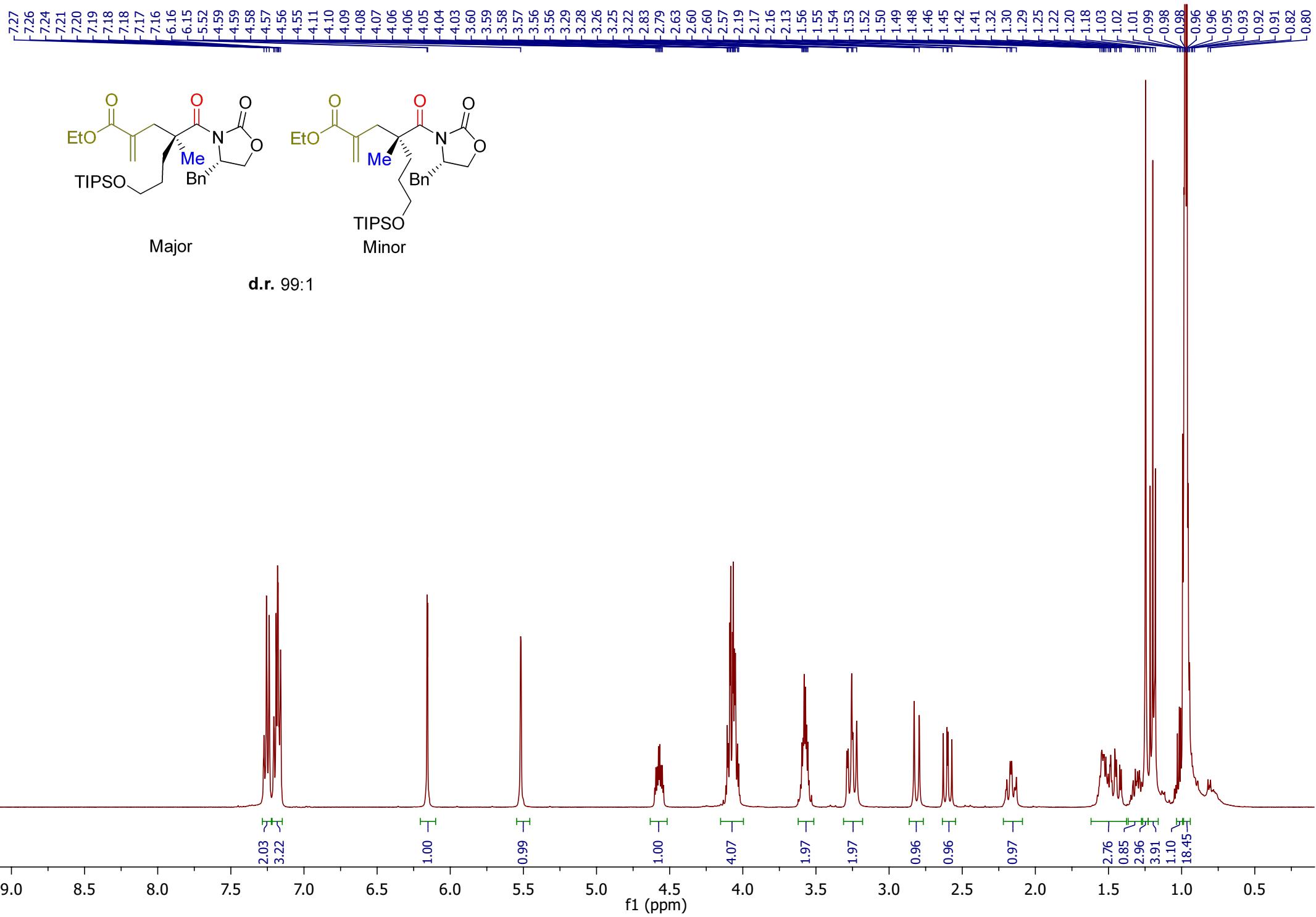


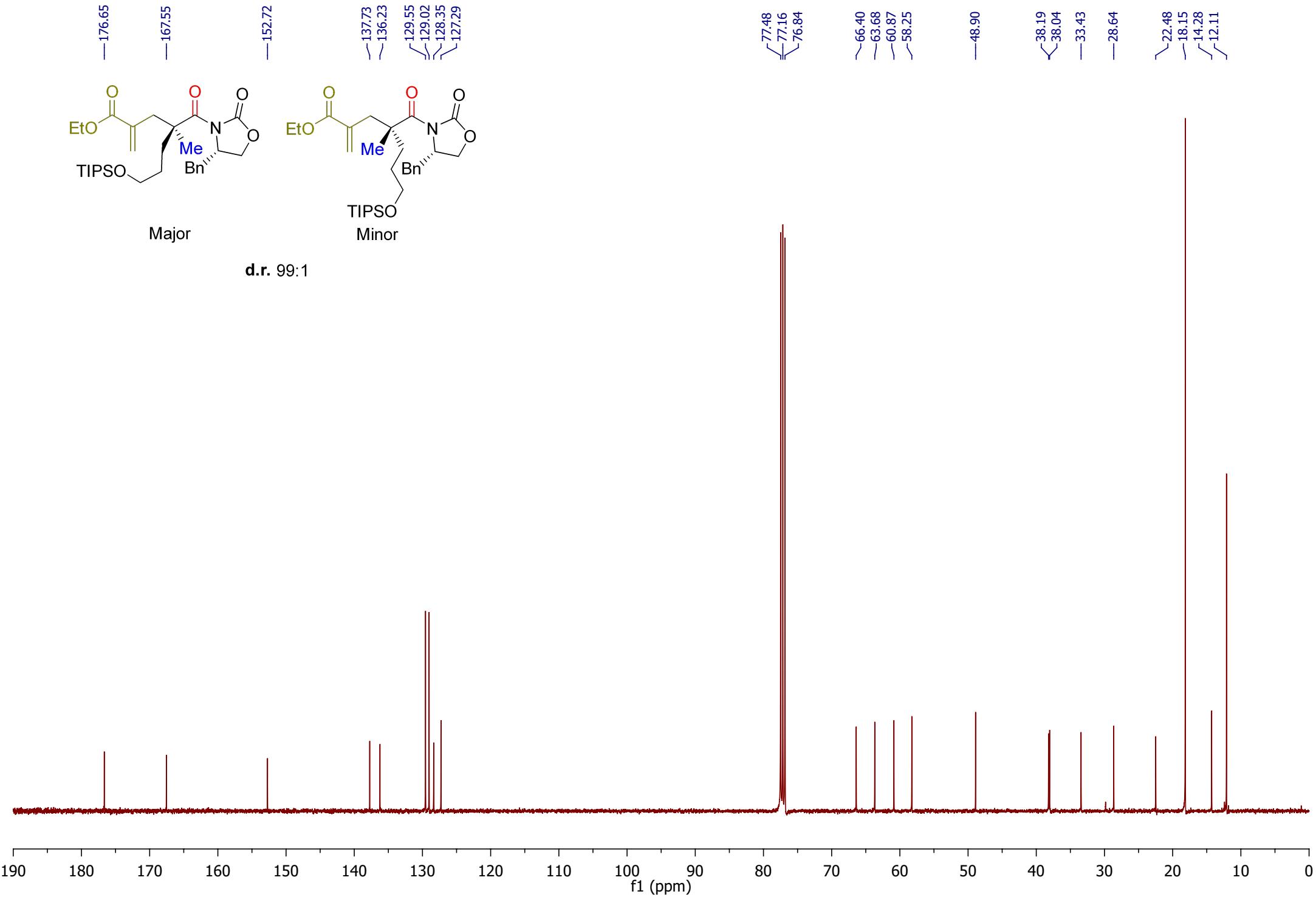


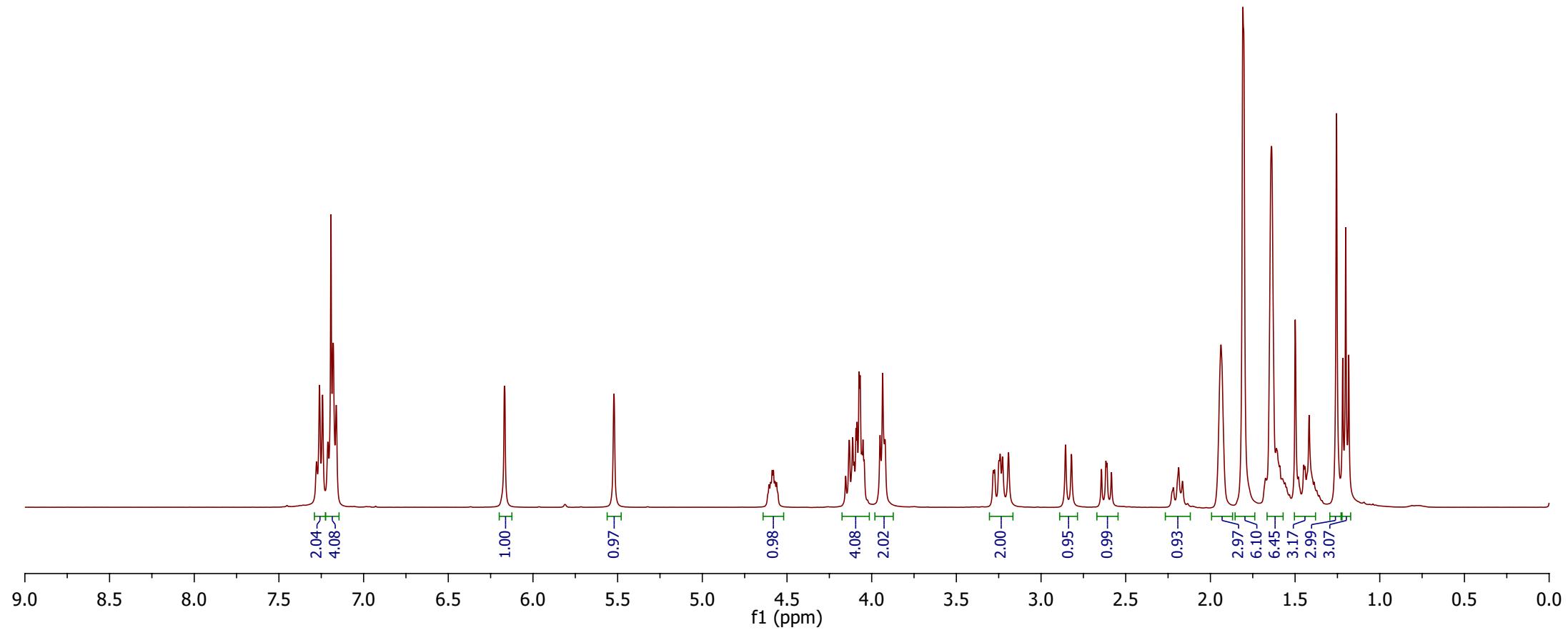
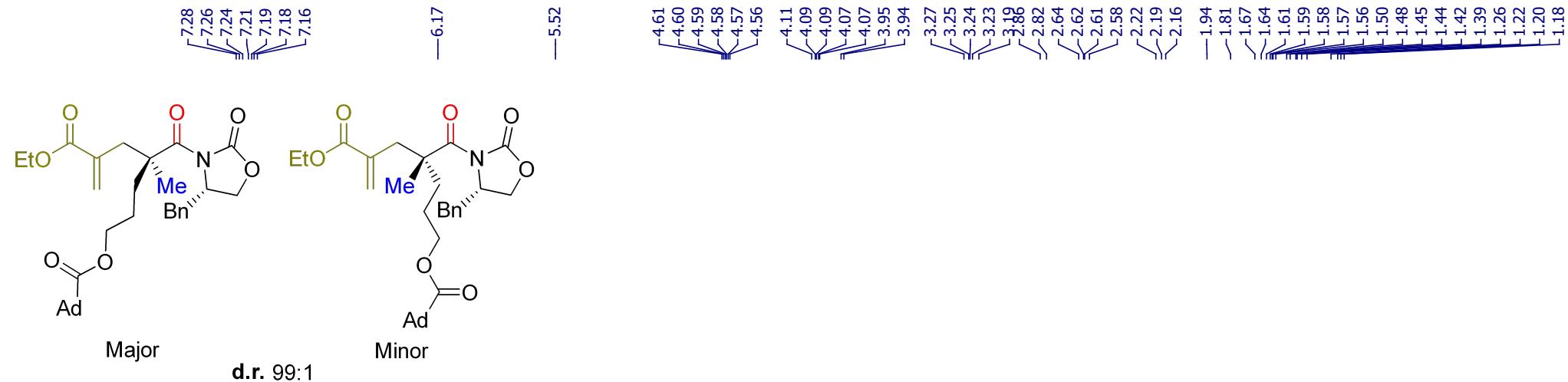




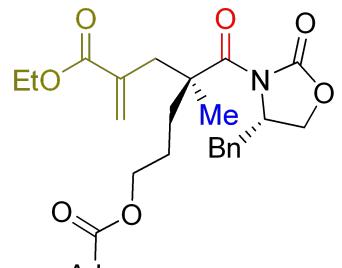




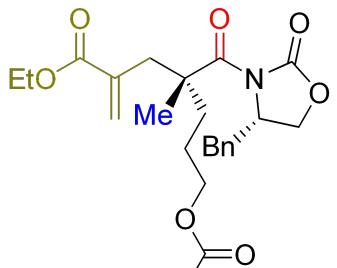




—177.77
 —176.28
 —167.40
 —152.69
 —137.55
 —136.11
 —129.49
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 —127.26
 —48.71
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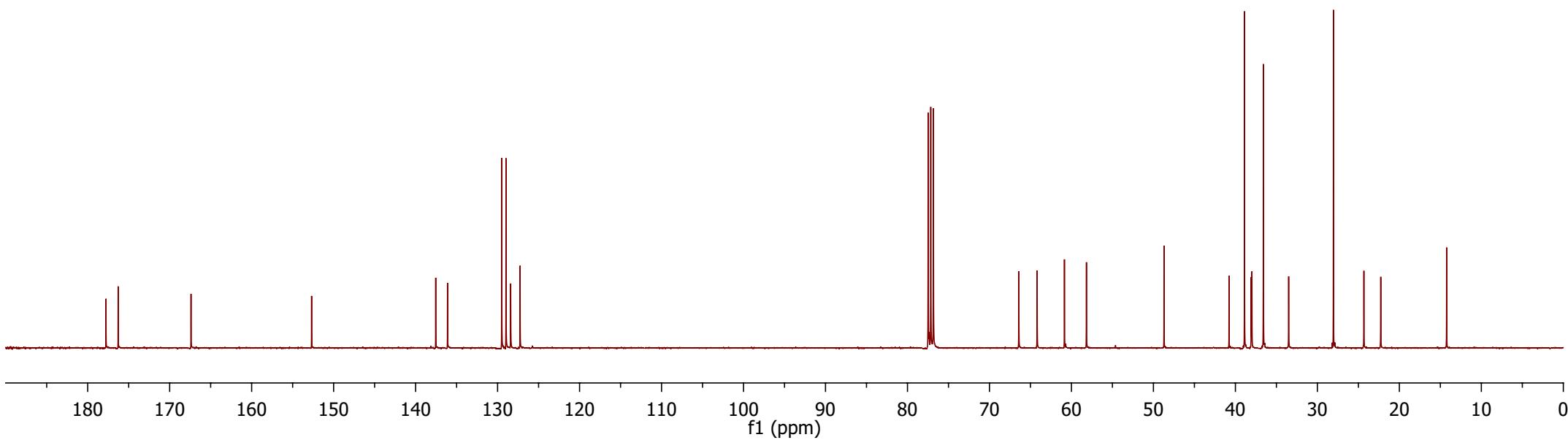


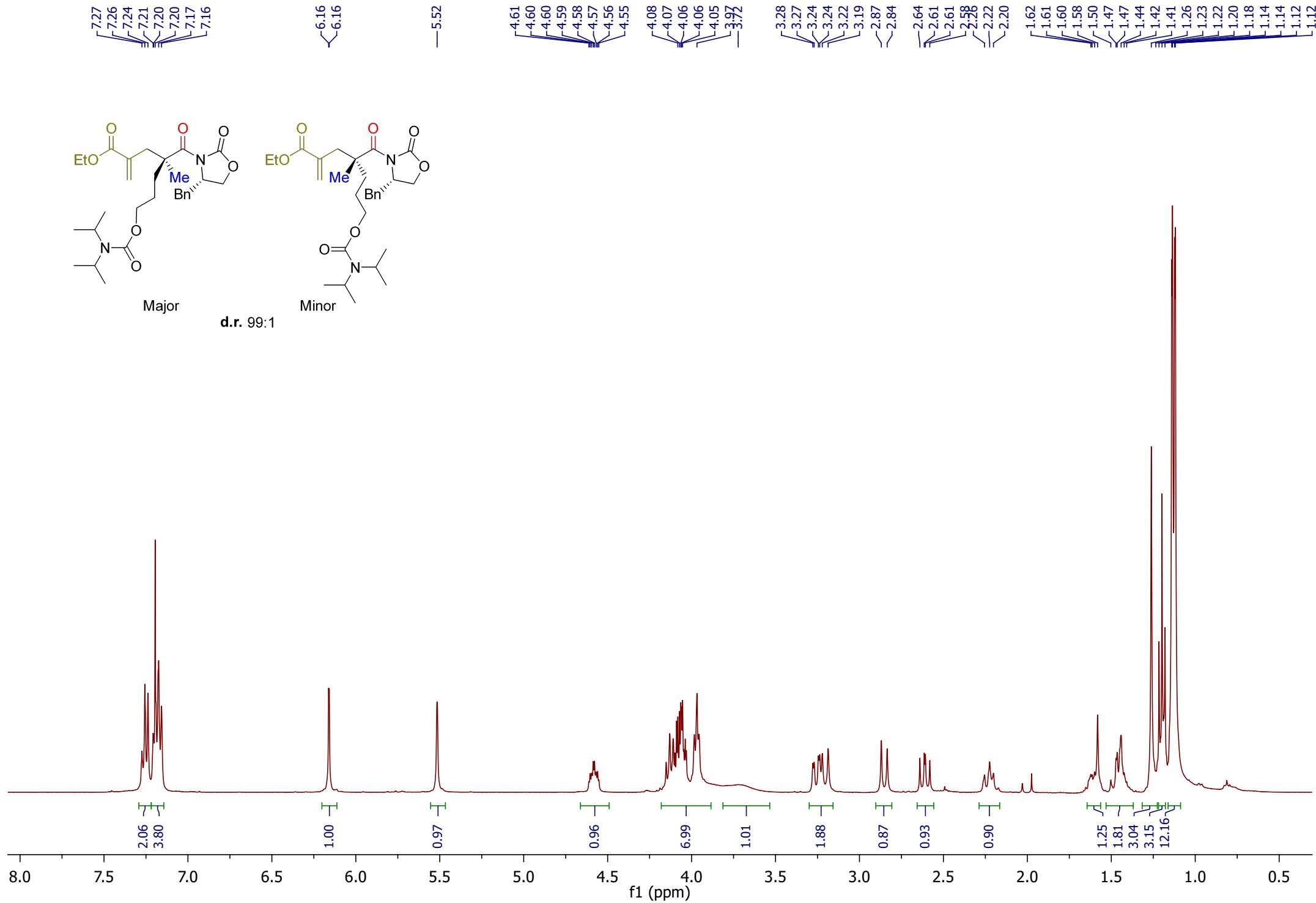
Major



Minor

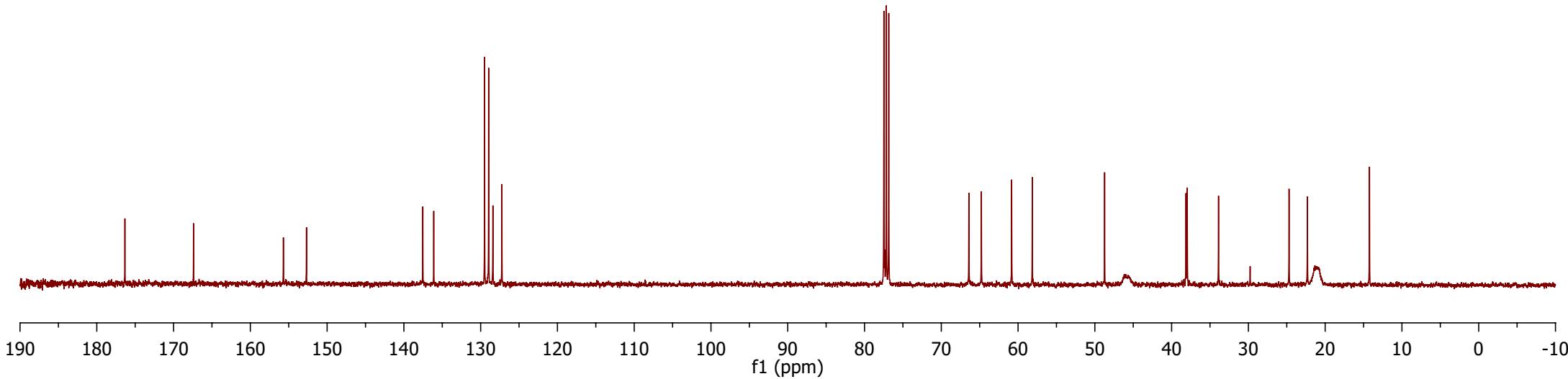
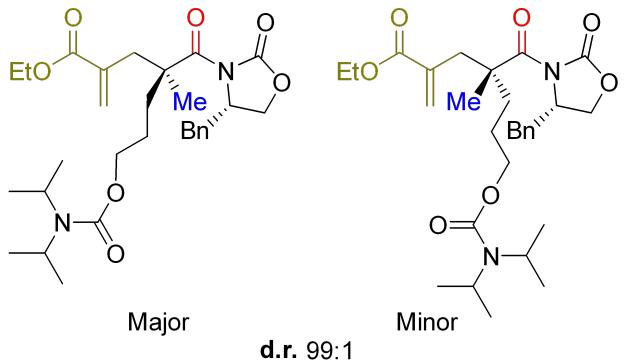
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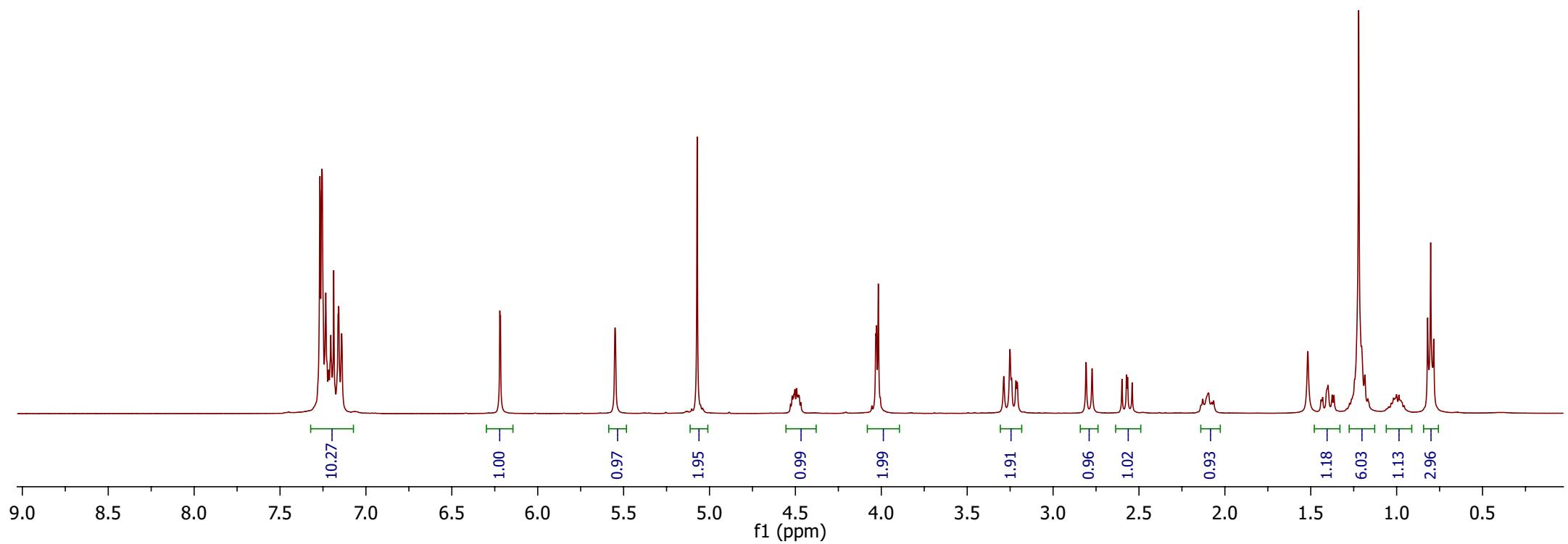
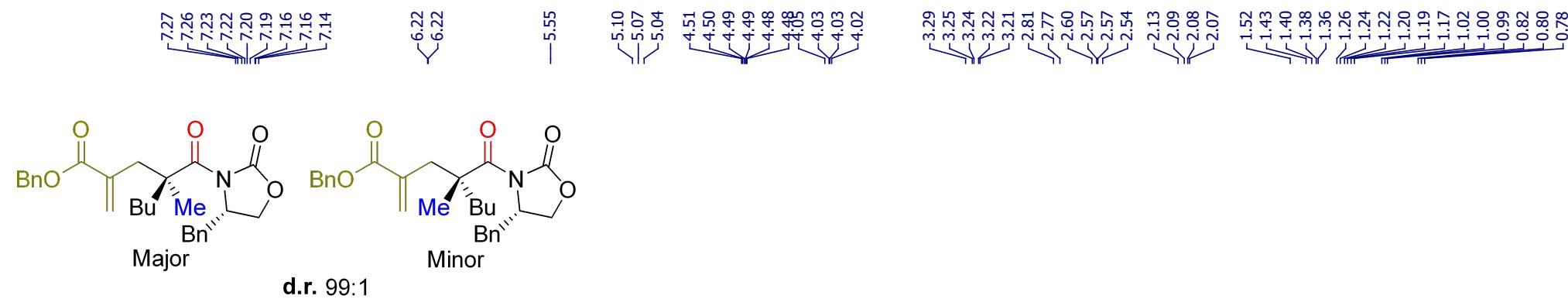


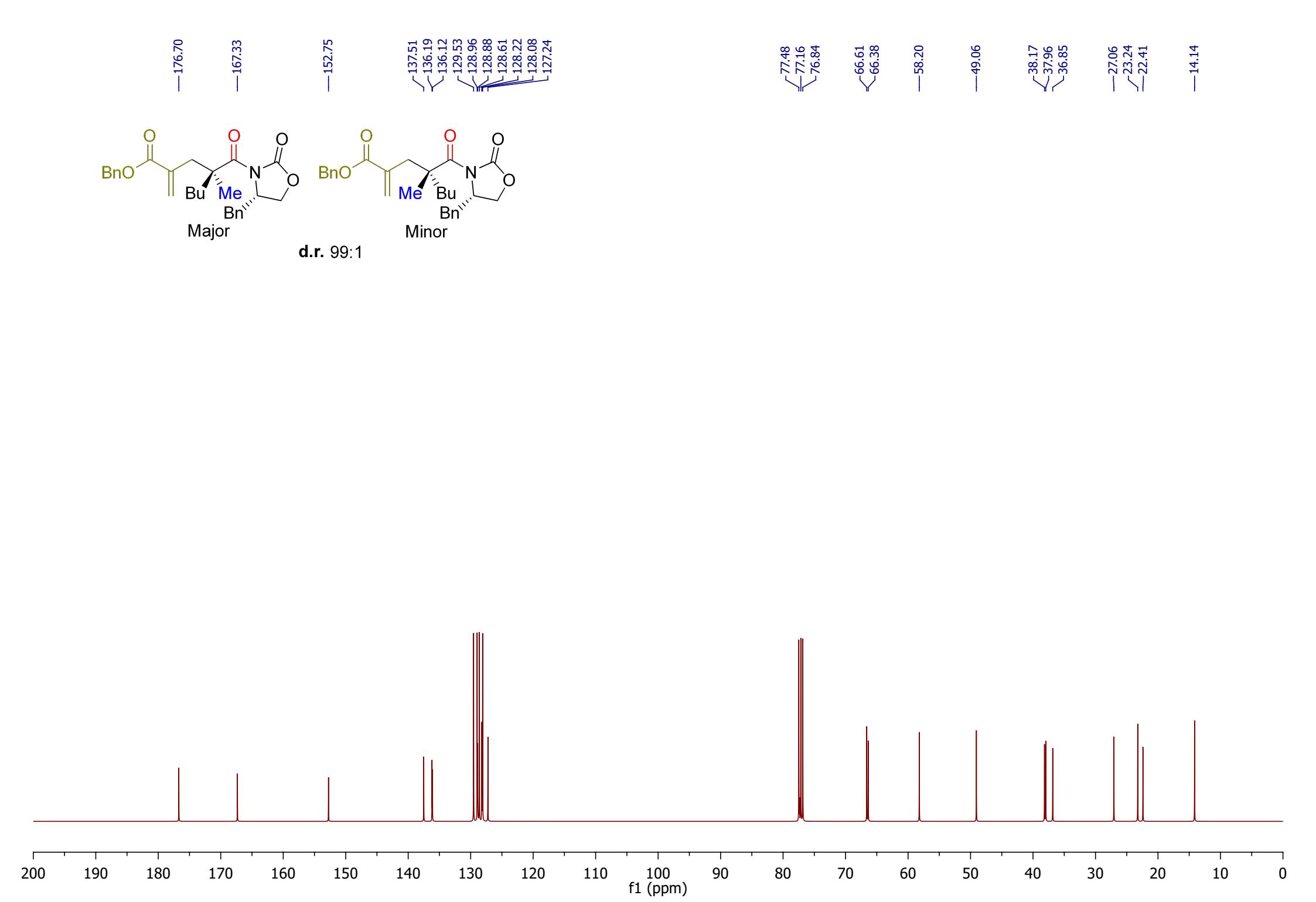


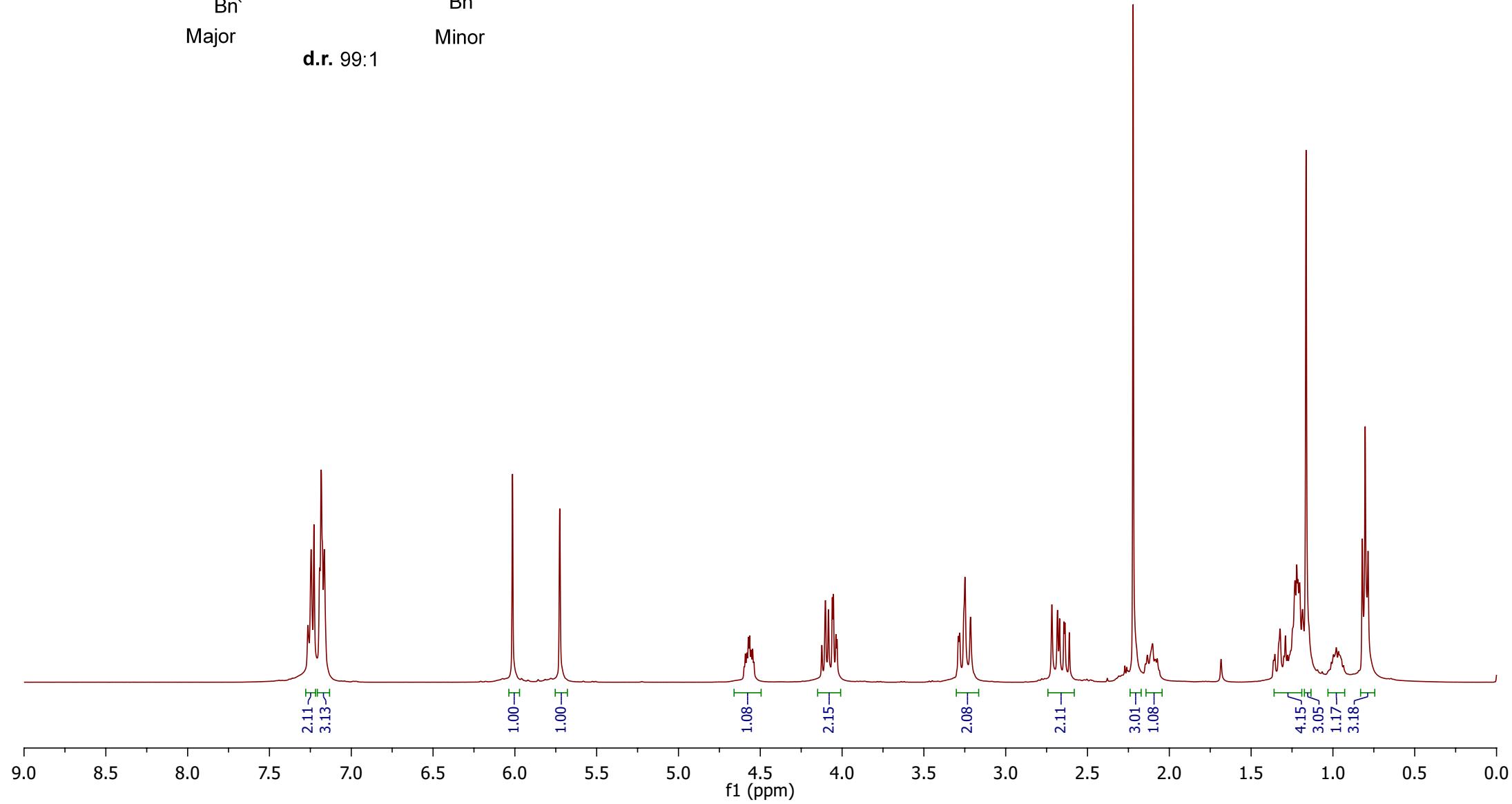
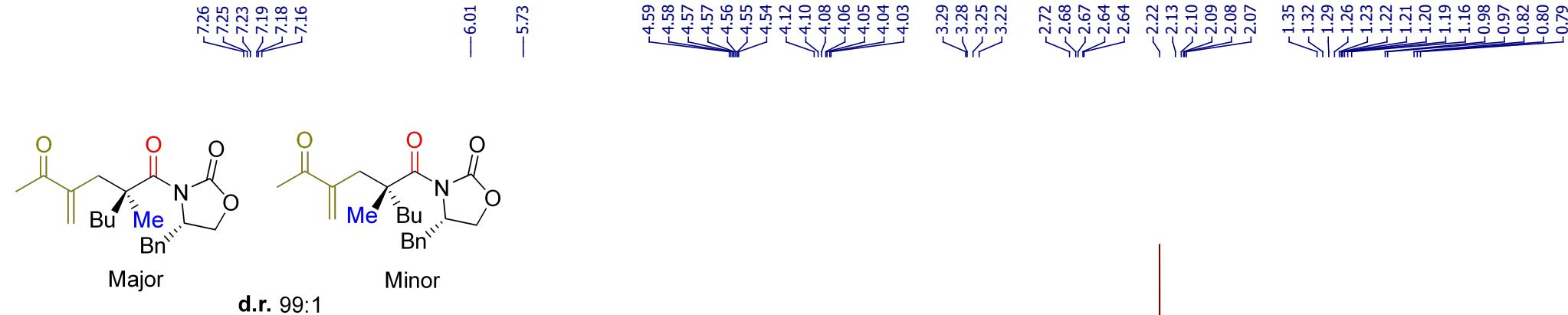
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 128.96
 128.40
 127.23

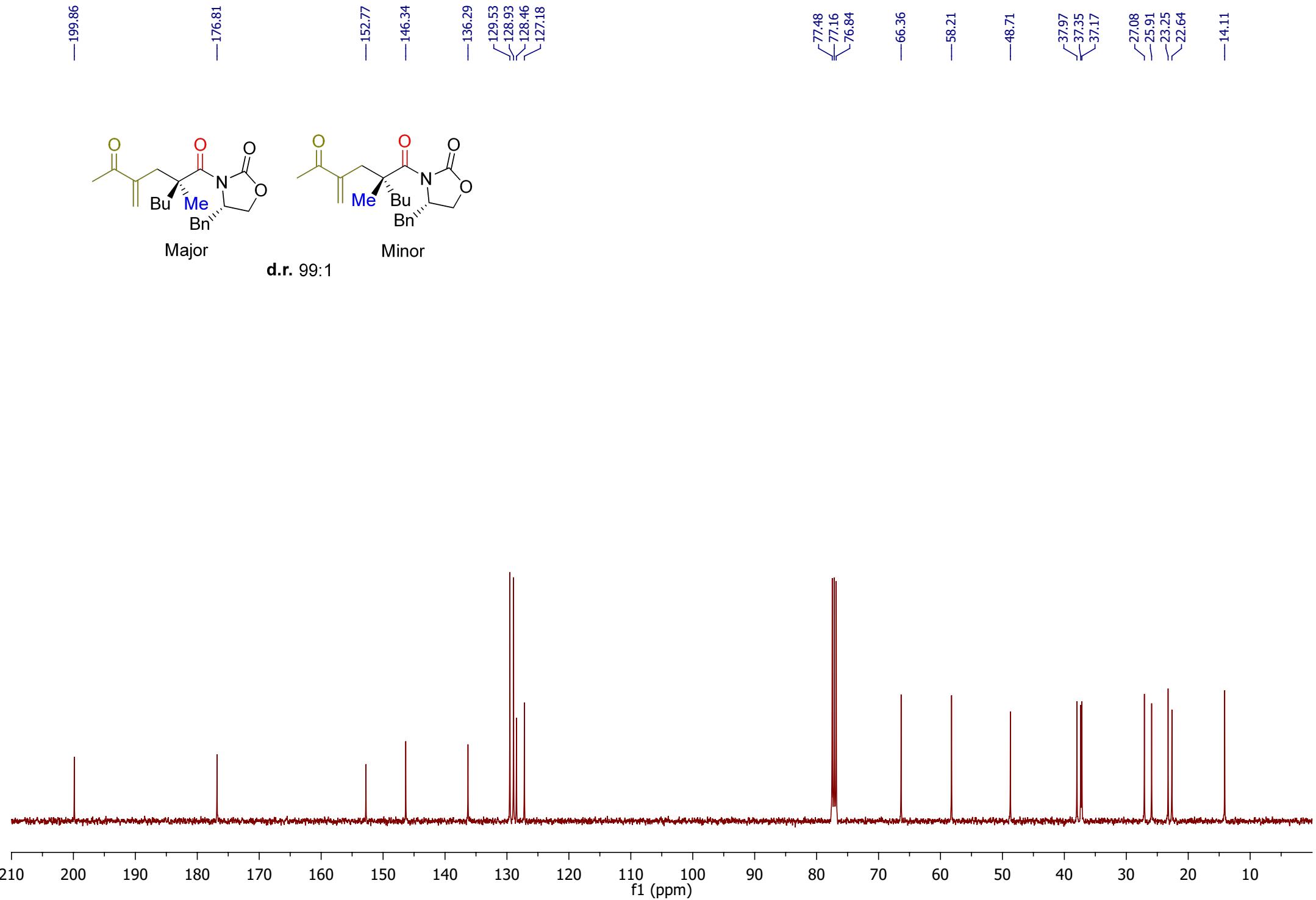
—77.48
 77.16
 76.84
 ~66.41
 ~64.78
 —60.83
 —58.15
 —48.72
 —46.12
 —38.13
 —37.96
 —33.89
 —24.70
 —22.31
 —20.88
 —14.23

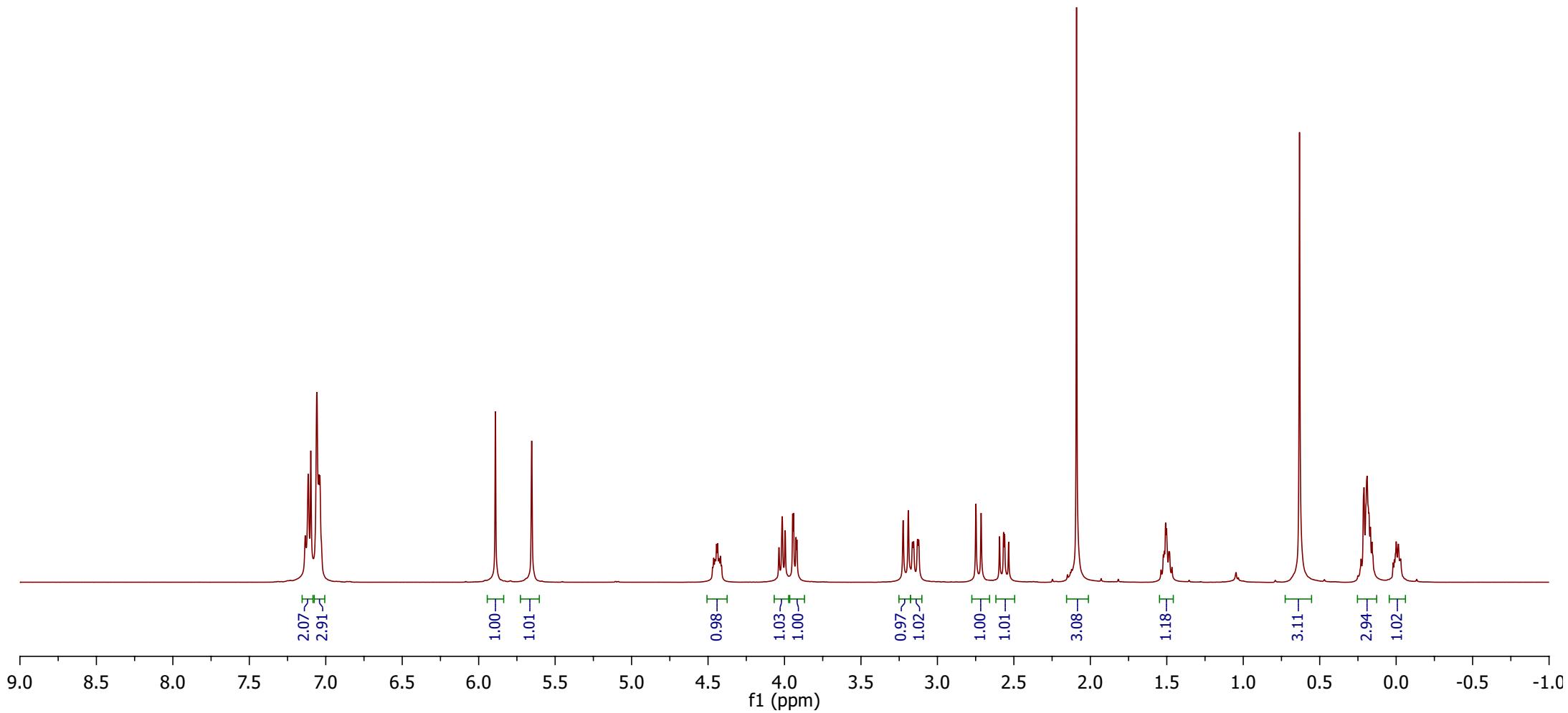
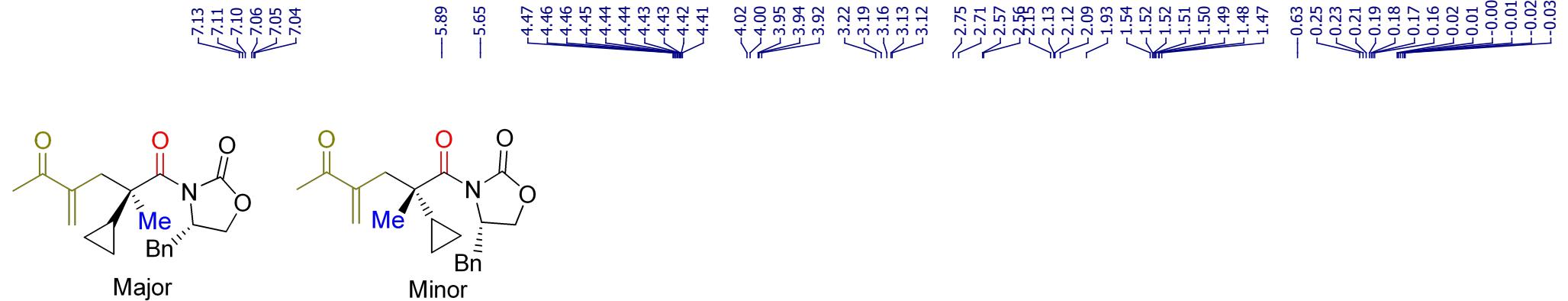


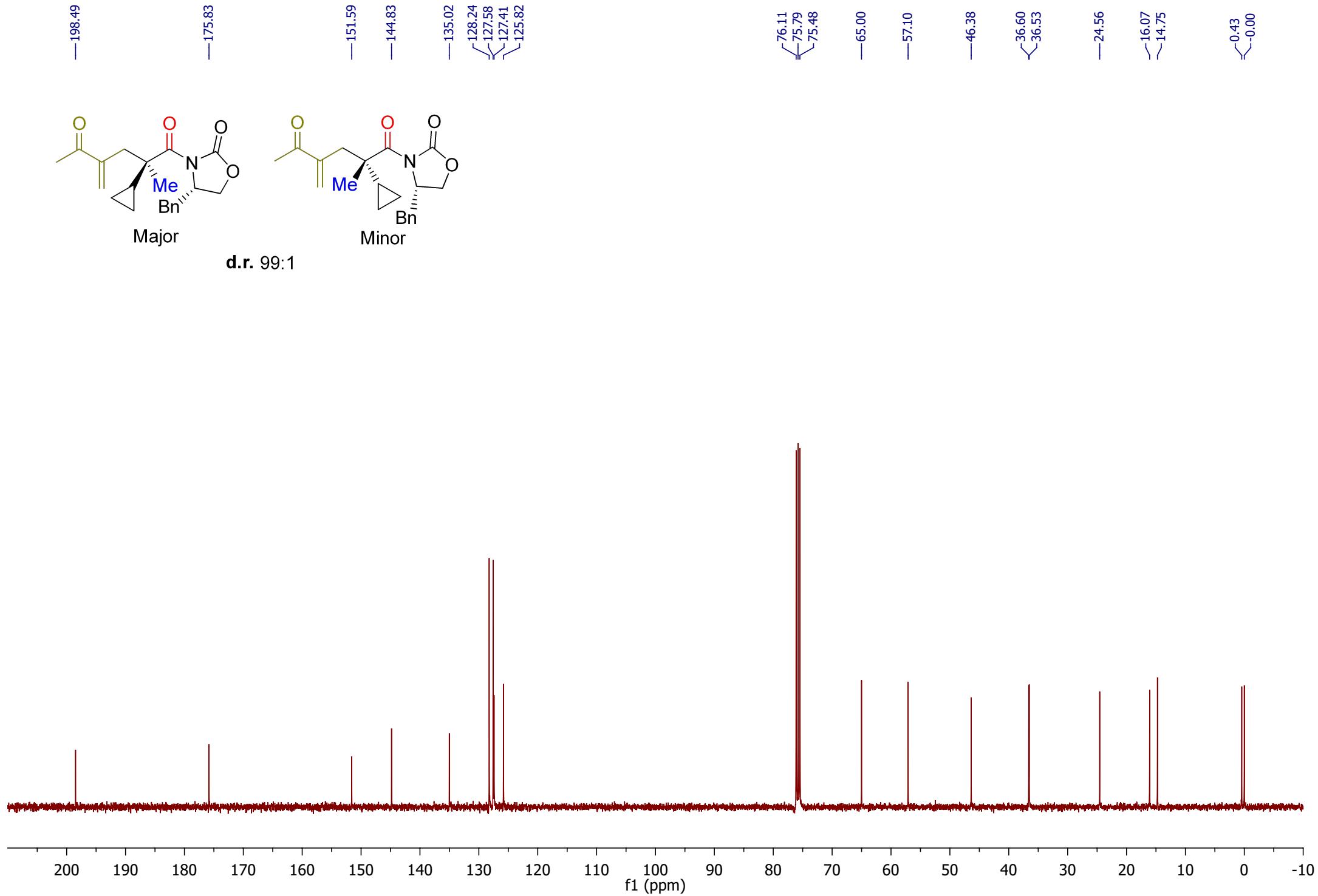


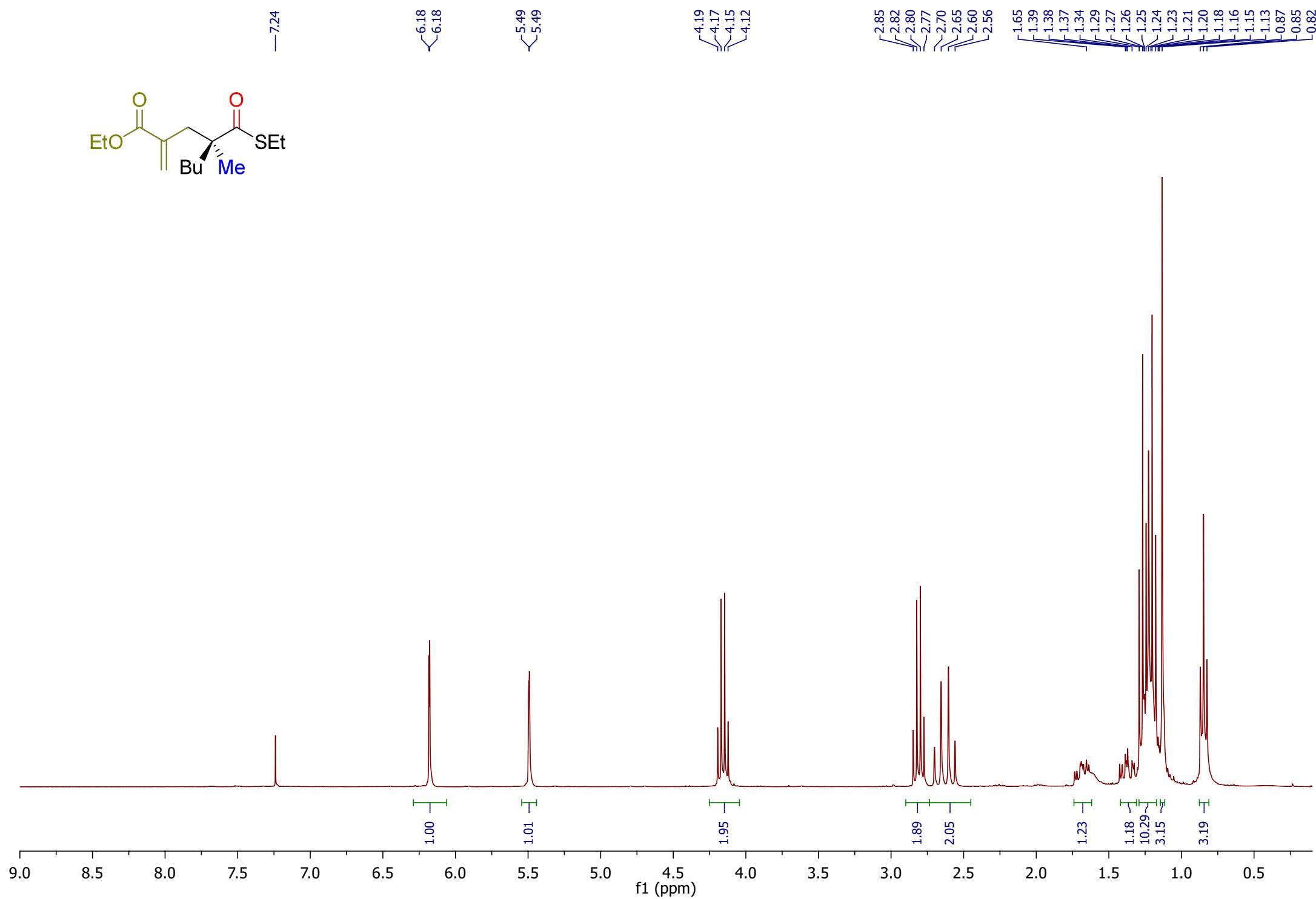
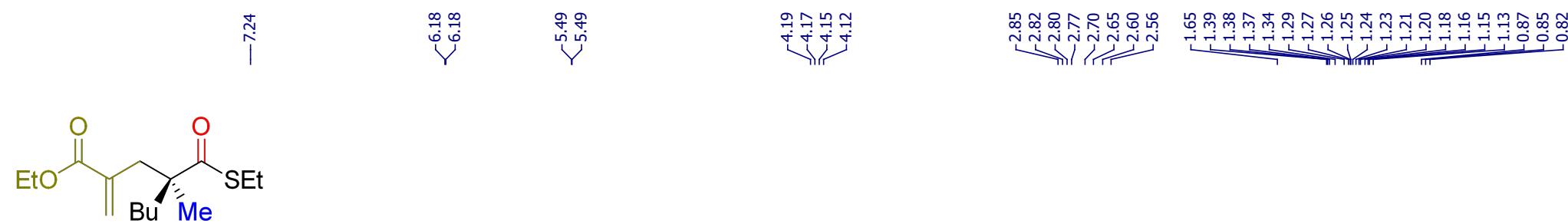












—205.79

—167.77

—137.17

—128.15

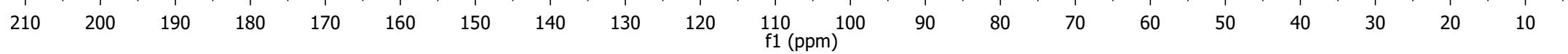
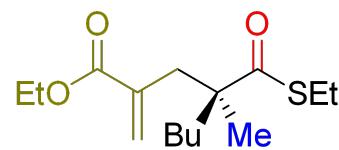
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77.16
76.74

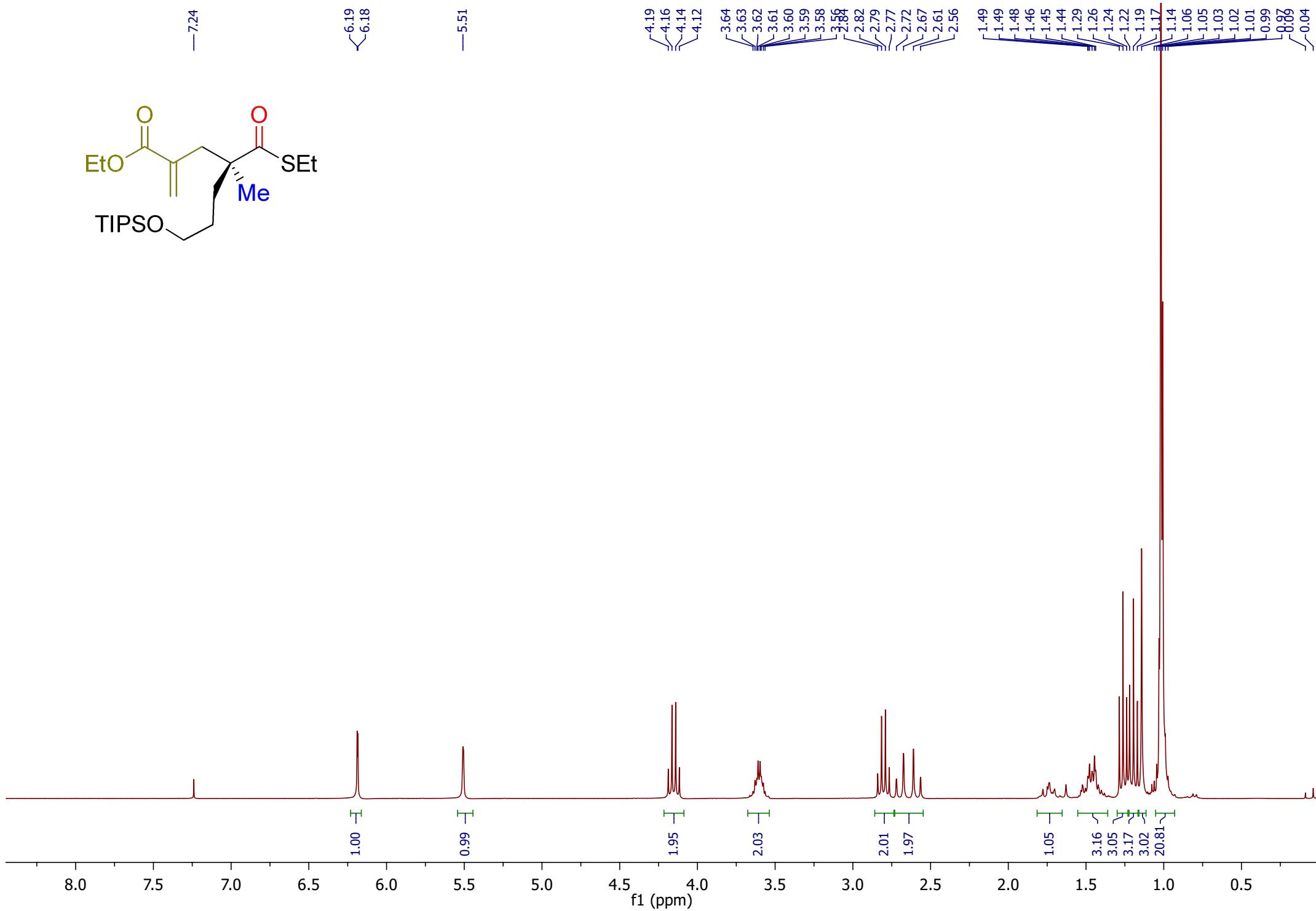
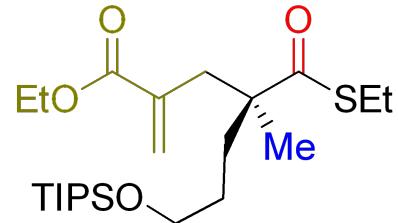
—60.96

—53.72

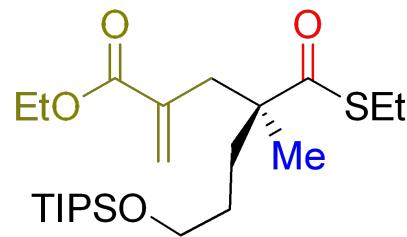
—40.07
—39.68

26.49
23.33
23.24
—20.50
14.76
14.30
14.08





—205.60



—167.70

—137.05

—128.26

77.58
77.16
76.74

—63.62
—60.95

—53.44

—40.00
—36.10

—27.95
—23.24
—20.56
—18.15
—14.74
—14.29
—12.08

