Supplementary Information

for

Enantioselective Construction of Acyclic Quaternary Carbon Stereocenters: Palladium-Catalyzed Decarboxylative Allylic Alkylation of Fully-Substituted Amide Enolates

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Contents

1 General

Technion Data

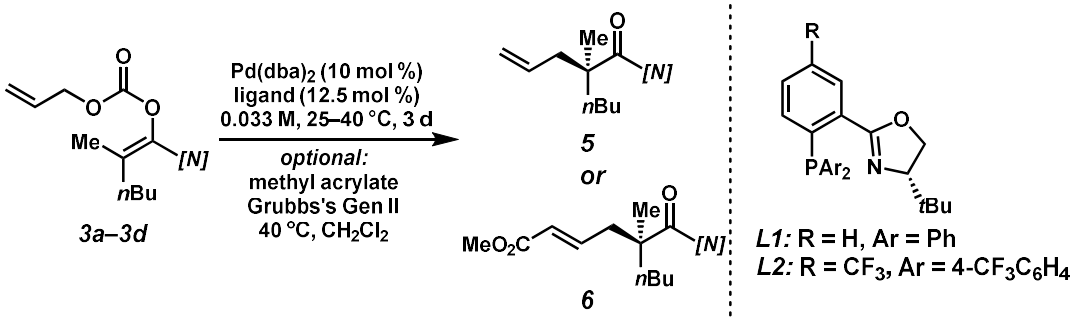
All reactions were carried out in dry glassware under positive pressure of argon. THF and Et_2O were used following purification from a zeolite drying apparatus (Pure-Solv® Purification System; Innovative Technology©). All Grignard reagents (incl. MeMgBr solution in Et_2O purchased from Sigma–Aldrich; others prepared in-house) were titrated with *tert*-butanol solution in toluene with 1,10-phenanthroline as indicator. All other chemicals were used as supplied. Chromatographic separations were performed on Bio-Lab silica gel 60Å (40–63 μm). Thin–layer chromatography was performed on Merck© TLC Silica gel 60 F_{254} and visualised by UV (254 nm), $KMnO_4$ and/or phosphomolybdic acid: ^1H and ^{13}C NMR spectra were recorded on Bruker© Avance 500, 400, and 300 spectrometers. Residual solvent peaks were used as internal standards.[1] Chemical shifts are quoted in ppm using the following abbreviations: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *qn* quintet; *sx* sextet; *non* nonet, *m* multiplet; *br*, broad; or a combination thereof. The coupling constants *J* are measured in Hz. Mass spectra (APCI or ESI) were recorded at the Schulich Faculty of Chemistry, Technion–Israel Institute of Technology.

Caltech Data

Unless stated otherwise, reactions were performed at ambient temperature (23 °C) in flame-dried glassware under a nitrogen atmosphere using dry, deoxygentated solvents (distilled or passed over a column of activated alumina).[2] Commercially available reagents were used as received. Reactions requiring external heat were modulated to the specified temperatures using an IKAmag temperature controller. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (250 nm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 μm) was used for flash chromatography. (*S*)-*t*-BuPHOX,[3] (*S*)-(CF_3)-*t*-BuPHOX,[4] and bis(dibenzylideneacetone) palladium(0) ($Pd(dba)_2$) were prepared by known methods. Commercially available C-2 symmetric ligands ((*R*,*R*)-DACH-naphthyl Trost ligand, (*R*,*R*)-DACH-phenyl Trost ligand, (*R,R*)-ANDEN-Phenyl Trost Ligand) were purchased from Sigma Aldrich, used as received, and stored in a glovebox. Grubbs's Generation II catalyst was purchased from Materia Inc. and used as received. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (500 MHz and 126 MHz, respectively) and are reported in terms of chemical shift relative to $CHCl_3$ (δ 7.26 and 77.16, respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Infrared (IR) spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). Analytical chiral SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system with Chiralpak AD-H column, OD-H column, and OJ-H column obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using a JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) or electron ionization (EI+) mode, or from the Caltech Center for Catalysis and Chemical Synthesis using an Agilent 6200 series TOF with an Agilent G1978A Multimode source in mixed (Multimode ESI/APCI) ionization mode. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm.

2 Supplementary Tables

Table 1. Evaluation of PHOX-ligands.



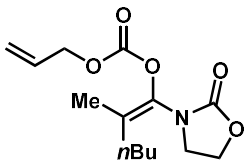
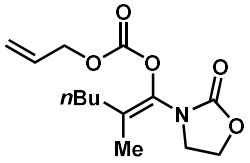
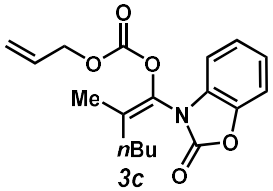
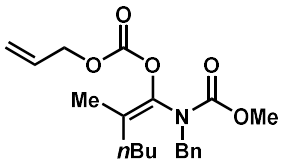
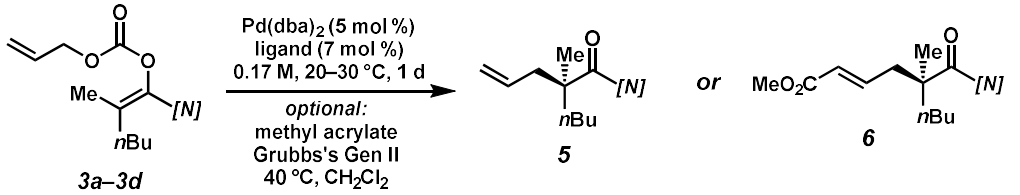
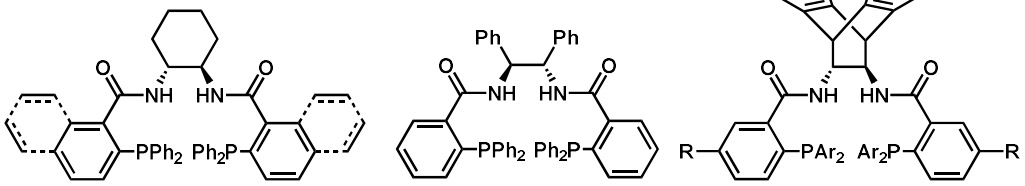
entry	substrate	ligand	solvent	ee%
1	 3a	L1	THF	0
2			MTBE	1
3			PhMe	0
4		L2	THF	15
5			MTBE	28
6			PhMe	15
7	 3b	L1	THF	–10
8			PhMe	–10
9			EtOAc	–4
10		L2	THE	–50
11			PhMe	–52
12			EtOAc	–34
13	 3c	L1	THF	1
14			MTBE	4
15			PhMe	5
16		L2	THF	9
17			MTBE	2
18			PhMe	6
19	 3d	L1	THF	4
20			MTBE	8
21			PhMe	12
22		L2	THF	24
23			MTBE	24
24			PhMe	38

Table 2. Evaluation of C_2-symmetric ligands.



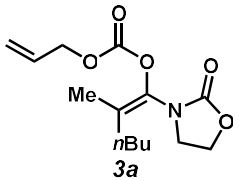
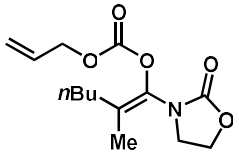
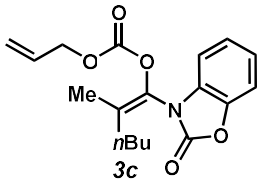
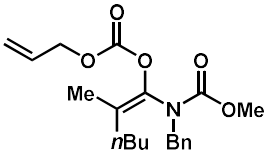
C_2-Symmetric Allylic Alkylation Ligands



L3, phenyl
L4, naphthyl

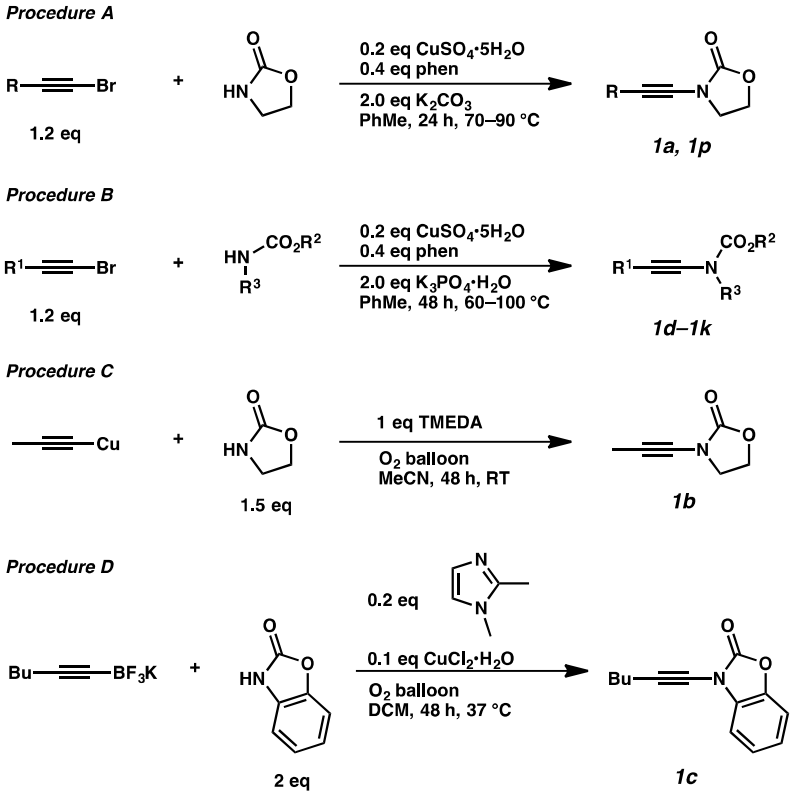
L5

L6, R = H, Ar = Ph
L7, R = CF_3, Ar = 4-$CF_3C_6H_4$
L8, R = H, Ar = 2-$CH_3C_6H_4$

entry	substrate	ligand	solvent	ee%
1	 *3a*	L3	DO	54
2			THF	64
3		L4	DO	70
4			THF	75
5		L5	THF	–70
6		L6	THF	70
7			EtOAc	72
8		L7	THF	70
9			EtOAc	62
10		L8	THF	NR
11	 *3b*	L5	THF	47
12			EtOAc	46
13		L6	THF	–30
14			EtOAc	–36
15	 *3c*	L4	THF	32
16		L6	THF	57
17	 *3d*	L3	THF	–72
18		L4	THF	–74
19		L5	THF	60
20			EtOAc	68
21		L6	THF	–85
22			EtOAc	–84
23		L7	THF	–85
24			EtOAc	–94
25		L8	THF	NR

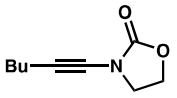
3 Procedures

3.1 Ynecarbamates



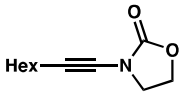
Representative Procedure A [Hsung coupling with cyclic carbamates][5]

A slurry of ynecarbamate (1.0 equiv), 1-bromoalkyne (1.2 equiv), $CuSO_4 \cdot 5H_2O$ (0.2 equiv) 1,10-phenanthroline monohydrate (0.4 equiv), and K_2CO_3 (2.0 equiv) in toluene (50–60 mL) was stirred at 70–90 °C for 24 h. The mixture was cooled to room temperature, diluted with DCM and filtered through silica, washed with DCM, concentrated under reduced pressure and the crude residue was purified by flash chromatography with EtOAc/Hex (1:5) to give the product.



3-(Hex-1-yn-1-yl)oxazolidin-2-one (1a)[5]

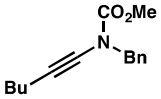
Representative Procedure A. Prepared from oxazolidin-2-one (2.4150 g, 27.7 mmol, 1.0 equiv) and 1-bromohex-1-yne (5.362 g, 33.3 mmol, 1.2 equiv) using K_2CO_3 (7.66 g. 55.5 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (1.383 g, 5.55 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (2.220 g, 11.1 mmol, 0.4 equiv) and toluene (55 mL) at 70 °C to give the desired product as a pale yellow oil (4.417 g, 26.4 mmol, 95%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.39 (t, 2H, J = 7.9), 3.85 (t, 2H, J = 7.9), 2.28 (t. 2H, J = 6.9), 1.49 (qn, 2H, J = 6.9), 1.38 (sx, 2H, J = 6.9); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.8, 71.2, 70.1, 62.9, 47.1, 30.9, 22.0, 18.1, 13.6. HRMS (ESI) for $C_9H_{14}NO_2$ $[M+H]^+$ found 168.1011, calc. 168.1019.



3-(Oct-1-yn-1-yl)oxazolidin-2-one (1p)[7]

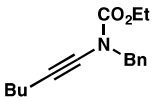
Representative Procedure A. Prepared from oxazolidin-2-one (3.1075 g, 35.7 mmol, 1.0 equiv) and 1-bromooct-1-yne (8.097 g, 42.8 mmol, 1.2 equiv) using K_2CO_3 (9.858 g. 71.4 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (1.782 g, 7.1 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (2.829 g, 14.3 mmol, 0.4 equiv) and toluene (60 mL) at 90 °C to give the desired product as a pale yellow oil (6.178 g, 31.6 mmol, 89%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.40 (t, 2H. *J* = 8.2), 3.87 (t, 2H, *J* = 8.2), 2.29 (t, 2H, *J* = 7.0), 1.52 (qn, 2H, *J* =7.0), 1.40–1.20 (6H), 0.89 (t, 2H, *J* =7.0); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.8, 71.4, 70.1, 62.9, 47.2, 31.5, 28.9, 28.7, 22.7, 18.5, 14.2. HRMS (ESI) for $C_{11}H_{18}NO_2$ $[M+H]^+$ found 196.1343, calc. 196.1332.

Representative Procedure B [Hsung coupling with acyclic carbamates]:[Error! Bookmark not defined.] A slurry of ynecarbamate (1.0 equiv), 1-bromoalkyne (1.2 equiv), $CuSO_4 \cdot 5H_2O$ (0.2 equiv) 1,10-phenanthroline monohydrate (0.4 equiv), and $K_3PO_4 \cdot H_2O$ (2.0 equiv) in toluene (50–60 mL) was stirred at 70–90 °C for 48 h. The mixture was cooled to room temperature, diluted with DCM and filtered through silica, washed with DCM, concentrated under reduced pressure and the crude residue was purified by flash chromatography with EtOAc/hexane or Et_2O/hexane (1:20 to 1:10) to give the product.



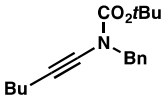
Methyl benzyl(hex-1-yn-1-yl)carbamate (1d)[Error! Bookmark not defined.]

Representative Procedure B. Prepared from methyl benzylcarbamate (6.955 g, 42.1 mmol, 1.0 equiv) and 1-bromohex-1-yne (8.136 g, 50.5 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (19.39 g. 84.2 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (2.103 g, 8.42 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (3.338 g, 16.8 mmol, 0.4 eq) and toluene (60 mL) at 80 °C to give the desired product as a pale yellow oil (7.277 g, 29.7 mmol, 70%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39–7.27 (m, 5H), 4.59 (s, 2H), 3.80 (s, 3H), 2.25 (t, 2H, *J* = 7.3), 1.43 (qn, 2H, *J* = 7.3), 1.32 (sx, 2H, *J* = 7.3), 0.89 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 136.4, 128.6, 128.0, 73.9, 70.8, 54.1, 31.1, 21.9, 18.3, 13.7, two peaks not observed/overlapped. HRMS (ESI) for $C_{15}H_{20}NO_2$ $[M+H]^+$ found 246.1480, calc. 246.1489.



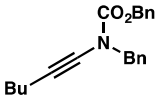
Ethyl benzyl(hex-1-yn-1-yl)carbamate (1e)

Representative Procedure B. Prepared from ethyl benzylcarbamate (5.077 g, 28.3 mmol, 1.0 equiv) and 1-bromohex-1-yne (5.477 g, 34.0 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (13.05 g. 56.7 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (1.409 g, 5.67 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (2.246 g, 11.3 mmol, 0.4 equiv) and toluene (60 mL) at 80 °C to give the desired product as a pale yellow oil (3.9024 g, 15.0 mmol, 53%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.3–7.1 (m, 5H), 4.51 (s, 2H), 4.15 (q, 2H, *J* = 7.0), 2.17 (t, 2H, *J* = 6.6), 1.40–1.17 (m, 4H), 0.80 (t, 3H, *J* = 6.6); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.9, 136.6, 128.5, 128.4, 127.9, 74.1, 70.5, 63.1, 53.8, 31.1, 21.9, 18.2, 14.5, 13.7; HRMS (ESI) for $C_{16}H_{22}NO_2$ $[M+H]^+$ found 260.1655, calc. 260.1645.



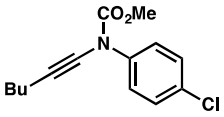
***tert*-Butyl benzyl(hex-1-yn-1-yl)carbamate (1f)**

Representative Procedure B. Prepared from *tert*-butyl benzylcarbamate (4.972 g, 24.0 mmol, 1.0 equiv) and 1-bromohex-1-yne (4.64 g, 28.8 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (11.05 g. 48.0 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (1.20 g, 4.80 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (1.90 g, 9.60 mmol, 0.4 equiv) and toluene (80 mL) at 90 °C to give the desired product as a pale yellow oil (3.833 g, 13.3 mmol, 56%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.20 (m, 5H), 4.50 (s, 2H), 2.20 (m, 2H), 1.50–1.35 (m, 2H), 1.30 (sx, 2H, J = 7.2), 0.83 (t, 3H, J = 7.2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 137.0, 128.5, 128.2, 127.7, 82.1, 74.9, 69.8, 53.2, 31.1, 28.2, 21.9, 18.2, 13.7; HRMS (ESI) for $C_{18}H_{25}NO_2Na$ $[M+Na]^+$ found 310.1776, calc. 310.1783.



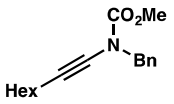
Benzyl benzyl(hex-1-yn-1-yl)carbamate (1g)

Representative Procedure B. Prepared form benzyl benzylcarbamate (4.3935 g, 18.2 mmol, 1.0 equiv) and 1-bromohex-1-yne (3.5187 g, 21.8 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (8.386 g, 36.4 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (0.9093 g, 3.64 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (1.4437 g, 7.28 mmol, 0.4 equiv) and toluene (40 mL) at 80 °C to give the desired product as a yellow oil 3.6119 g, 11.2 mmol, 62%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50–7.30 (m, 10 H), 5.30 (s, 2H), 4.69 (s, 2H), 2.31 (m, 2H), 1.55–1.45 (qn, 2H, J = 7.2), 1.45–1.35 (sx, 2H, J = 7.2), 0.94 (t, 3H, J = 7.2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.7, 136.3, 135.9, 128.48, 128.47, 128.4, 128.2, 127.9, 127.7, 73.7, 70.6, 68.3, 53.8, 31.0, 21.8, 18.1, 13.6; HRMS (ESI) for $C_{21}H_{23}NO_2Na$ $[M+Na]^+$ found 344.1620, calc. 344.1621.



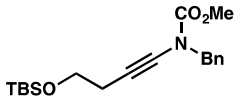
Methyl (4-chlorophenyl)(hex-1-yn-1-yl)carbamate (1h)

Representative Procedure B. Prepared from methyl (4-chlorophenyl)carbamate (5.466 g, 29.5 mmol, 1.0 equiv) and 1-bromohex-1-yne (5.69 g, 35.3 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (13.56 g, 58.9 mmol, 2.4 equiv), $CuSO_4 \cdot 5H_2O$ (1.471 g, 5.89 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (2.335 g, 11.8 mmol, 0.4 equiv) and toluene (60 mL) at 80 °C to give the desired product as an organge oil (4.585 g, 17.3 mmol, 59%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, 2H, J = 8.6), 7.28 (d, 2H, J = 8.6), 3.81 (s, 3H), 2.29 (t, 2H, J = 6.9), 1.48 (qn, 2H, J = 6.9), 1.38 (sx, 2H, J = 6.9), 0.87 (t, 3H, J = 6.9); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 138.7, 132.1, 129.0, 125.6, 73.3, 70.5, 64.4, 31.0, 22.1, 18.2, 13.7; HRMS for $C_{14}H_{17}ClNO_2$ $[M+H]^+$ found 266.0932, calc. 266.0942.



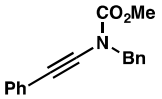
Methyl benzyl(oct-1-yn-1-yl)carbamate (1i)[Error! Bookmark not defined.]

Representative Procedure B. Prepared using methyl benzylcarbamate (6.465 g, 39.1 mmol, 1.0 equiv) and 1-bromooct-1-yne (8.880 g, 47.0 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (18.02 g, 78.3 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (1.954 g, 7.83 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (3.103 g, 15.7 mmol, 0.4 equiv) and toluene (60 mL) at 100 °C to give the desired product as a yellow oil (6.2891 g, 23.0 mmol, 59%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.19 (t, 2H, J = 7.0), 1.51 (qn, 2H, J = 7.0), 1.42–1.20 (m, 6H), 0.89 (3H, t, J = 7.0); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 136.4, 128.5, 128.4, 127.9, 73.9, 70.7, 54.0, 53.5, 31.4, 29.0, 28.5, 22.7, 18.5, 14.1. HRMS (ESI) for $C_{17}H_{24}NO_2$ $[M+H]^+$ found 274.1798, calc. 274.1802.



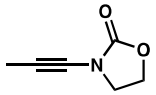
Methyl benzyl(4-((tert-butyldimethylsilyl)oxy)but-1-yn-1-yl)carbamate (1j)

Representative Procedure B. Prepared from methyl benzylcarbamate (2.197 g, 13.3 mmol, 1.0 equiv) and ((4-bromobut-3-yn-1-yl)oxy)(tert-butyl)dimethylsilane (4.2021 g, 16.0 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (7.352 g, 31.9 mmol, 2.4 equiv), $CuSO_4 \cdot 5H_2O$ (0.664 g, 2.66 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (1.0545 g, 5.32 mmol, 0.4 equiv) and toluene (50 mL) at 100 °C to give the desired product as a yellow oil (2.4914 g, 7.17 mmol, 54%) of product. Yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.20 (m, 5H), 4.54 (s, 2H), 3.74 (s,3H), 3.60 (d, 2H, J = 7.1), 2.42 (d, 2H, J = 7.1), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 136.3, 128.5, 128.4, 128.0, 74.8, 67.6, 62.2, 54.0, 26.0, 22.9, 18.4, -5.24, one carbon not observed (Ph*C*H$_2$); HRMS (ESI) for $C_{19}H_{30}NO_3Si$ $[M+H]^+$ found 348.1990, calc. 348.1989.



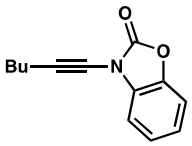
Methyl benzyl(phenylethynyl)carbamate (1k)[8]

Representative Procedure B. Prepared from methyl benzylcarbamate (3.1557 g, 19.1 mmol, 1.0 equiv) and (bromoethynyl)benzene (4.1500 g, 22.9 mmol, 1.2 equiv) using $K_3PO_4 \cdot H_2O$ (8.798 g, 38.2 mmol, 2.0 equiv), $CuSO_4 \cdot 5H_2O$ (0.9540 g, 3.82 mmol, 0.2 equiv), 1,10-phenanthroline monohydrate (1.5147 g, 7.64 mmol, 0.4 equiv) and toluene (60 mL) at 100 °C to give the desired product as a yellow oil (3.660 g, 13.8 mmol, 72%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50–7.20 (m, 10H), 4.76 (s, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.7, 136.0, 131.3, 128.7, 128.3, 128.2, 127.7, 123.2, 83.1, 71.3, 54.3, 54.2, one carbon not observed (Ar). HRMS (ESI) for $C_{17}H_{16}NO_2$ $[M+H]^+$ found 266.1156, calc. 266.1176.



3-(Prop-1-yn-1-yl)oxazolidin-2-one (1b):[9]

Procedure C [Evano *N*-alkynylation using alkynylcopper reagent]:[10] A slurry of oxazolidin-2-one (5.930 g, 67.8 mmol, 1.5 equiv), prop-1-yn-1-ylcopper (4.64 g, 45.2 mmol, 1.0 equiv), and TMEDA (6.81 mL, 45.2 mmol 1.0 equiv) in acetonitrile (20 mL) was stirred at RT for 48 h under dioxygen atmosphere (balloon). The mixture was filtered through a short silica plug, washed with DCM, concentrated under reduced pressure and the crude residue was purified by flash chromatography with EtOAc/hexane (1:5) to give the product as a colourless oil (4.1232 g, 33.0 mmol, 73%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.32 (t, 2H, J = 7.8), 3.78 (t, 2H, J = 7.8), 1.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.7, 69.0, 66.3, 62.9, 46.7, 2.9. HRMS (ESI) for $C_6H_8NO_2$ $[M+H]^+$ found 126.0553, calc. 126.0550.

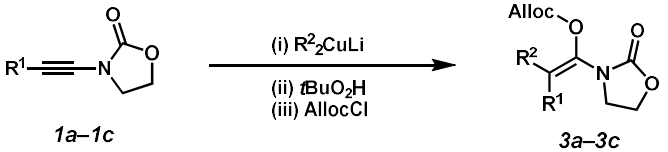


3-(Hex-1-yn-1-yl)benzo*[d]*oxazol-2*(3H)*-one (1c)

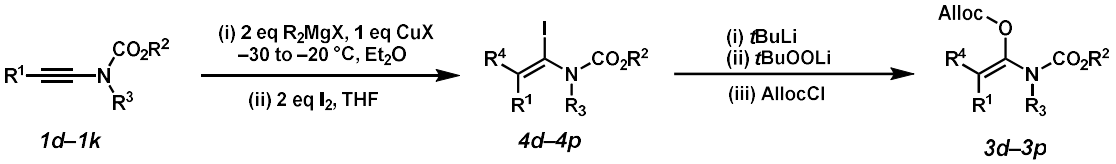
Procedure D [Evano *N*-alkynylation using potassium alkynyltrifluoroborates]:[11] A slurry of potassium 1-hexynyltrifluoroborate (6.589 g, 35.0 mmol, 1 equiv), 2-benzoxazolinone (9.470 g, 70.1 mmol, 2 equiv), 1,2-dimethylimidazole (1.24 mL, 14.0, 0.2 equiv), $CuCl_2$-$2H_2O$ (1.20 g, 7.01 mmol, 0.1 equiv) was stirred in DCM (20 mL) under dioxygen atmosphere (balloon) at 37 ºC for 48 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (EtOAc/Hex 1:40) to give the product as a yellow oil (1.5354 g, 7.13 mmol. 20%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.2–7.0 (m, 4H, Ar*H*), 2.40 (t, 2H, *J* = 7.0, CH_2C≡C), 1.55 (qn, 2H, *J* = 7.0, CH_2CH$_2$C≡C), 1.43 (sx, 2H, *J* = 7.0, CH$_3$CH_2), 0.88 (t, 2H, *J* = 7.0, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 142.0, 130.0, 124.5, 124.1, 110.3, 110.1, 76.6, 64.9, 30.5, 21.9, 18.2, 13.6; HRMS for $C_{13}H_{14}NO_2$ $[M+H]^+$ found 216.1022, calc. 216.1019.

3.2 Formation of Stereodefined Enolates

One-Pot: Procedure E
[only for cyclic carbamates]



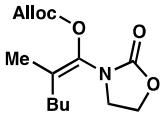
Two-Step: Procedure F
[general method]



3.2.1 One-Pot Procedure using Gilman Reagents

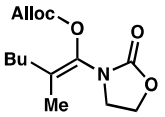
Representative Procedure E

A solution of MeLi in Et_2O (2–2.4 equiv) was added dropwise to a suspension of CuBr·DMS (1.0–1.1 equiv) in Et_2O (15–30 mL) at –30 °C. Once the solution became colourless (after 10 min), a solution of ynecarbamate (1.0 equiv) in Et_2O (5–10 mL) was added and the mixture left to stir gradually warming up to –10 °C. When carbometallation was complete (30 min), the mixture was cooled down to –80 °C and ca. 5.5 M *t*BuOOH (TBHP) solution in decane (1.0 equiv) was added dropwise and left to stir at –80 °C. After 30 min, allyl chloroformate (2.5–4.0 equiv) was added and the reaction mixture was allowed to warm to room temperature. It was quenched with 1 M HCl solution, extracted with Et_2O (2×), the combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography (EtOAc/hexane 1:10) to give the desired product.



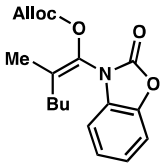
***(E)*-Allyl (2-methyl-1-(2-oxooxazolidin-3-yl)hex-1-en-1-yl) carbonate (3a)**

Representative Procedure E. Prepared from 3-(hex-1-yn-1-yl)oxazolidin-2-one (1.784 g, 10.7 mmol, 1 equiv) using MeLi (1.6 M in Et_2O; 13.33 mL, 21.3 mmol, 2 equiv), CuBr·DMS (2.1934 g, 10.7 mmol, 1 equiv), TBHP (5.5 M in decane; 1.94 mL, 10.7 mmol, 1 equiv) and AllocCl (2.84 mL, 26.7 mmol, 2.5 equiv) to give the desired product as a pale yellow oil (2.101 g, 7.42 mmol, 70%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.93 (ddt, 1H, *J* = 16.6, 10.4, 5.7), 5.37 (d, 1H, *J* = 16.6), 5.28 (d, 1H, *J* = 10.4), 4.65 (d, 2H, *J* = 5.7), 4.37 (t, 2H, *J* = 7.9), 3.77 (t, 2H, *J* = 7.9), 2.05 (t, 2H, *J* = 7.0), 1.68 (s, 3H), 1.42 (qn, 2H, *J* = 7.0), 1.29 (sx, 2H, *J* = 7.0), 0.88 (t, 3H, *J* = 7.0); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 152.6, 131.0, 130.1, 125.8, 118.7, 68.4, 61.7, 44.3, 30.1, 28.3, 21.6, 15.2, 13.0. HRMS for $C_{14}H_{22}NO_5$ $[M+H]^+$ found 284.1490, calc. 284.1492.



***(Z)*-Allyl (2-methyl-1-(2-oxooxazolidin-3-yl)hex-1-en-1-yl) carbonate (3b)**

Representative Procedure E. Prepared from 3-(prop-1-yn-1-yl)oxazolidin-2-one (1.6736 g, 13.4 mmol, 1 equiv) using BuLi (1.6 M in hexanes; 16.7 mL, 26.7 mmol, 2 equiv), CuBr·DMS (2.750 g, 13.4 mmol, 1 equiv), TBHP (5.5 M in decane; 2.43 mL, 13.4 mmol, 1 equiv) and AllocCl (3.55 mL, 33.4 mmol, 2.5 equiv) to give the desired product as a yellow oil (1.964 g, 6.93 mmol, 52%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.95 (ddt, 1H, *J* = 17.2, 10.4, 5.8), 5.40 (d, 1H, *J* = 17.2), 5.30 (dd, 1H, *J* = 10.4, 1.3), 4.68 (d, 2H, *J* = 5.8), 4.40 (t, 2H, *J* = 7.8), 3.82 (t, 2H, *J* = 7.8), 2.08 (t, 2H, *J* = 7.2), 1.71 (s, 3H), 1.42 (qn, 2H, *J* = 7.2), 1.32 (sx, 2H, *J* = 7.2), 0.90 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 152.6, 131.0, 130.1, 125.8, 118.7, 68.4, 61.7, 44.3, 30.1, 28.3, 21.6, 15.2, 13.0; HRMS for $C_{14}H_{22}NO_5$ $[M+H]^+$ found 284.1495, calc. 284.1492.



***(E)*-Allyl (2-methyl-1-(2-oxobenzo[d]oxazol-3(2H)-yl)hex-1-en-1-yl) carbonate (3c)**

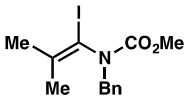
Representative Procedure E. Prepared from 3-(hex-1-yn-1-yl)benzo[*d*]oxazol-2(3*H*)-one (130 g, 0.604 mmol, 1 equiv) using MeLi (1.6 M in Et_2O; 906 µL, 1.45 mmol, 2.4 equiv), CuBr·DMS (150 mg, 0.730 mmol, 1.2 equiv), TBHP (5.5 M in decane; 132 µL, 0.730 mmol, 1.2 equiv) and AllocCl (257 µL, 2.42 mmol, 4 equiv) to give the desired product as a yellow oil (97.6 mg, 0.295 mmol, 49%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22–7.12 (m, 4H), 5.89 (ddt, 1H, *J* = 17.3, 10.5, 5.8), 5.34 (dqt, 1H, *J* = 17.3, 1.3), 5.26 (dqt, 1H, *J* = 10.5, 1.23), 4.62 (dqt, 2H, *J* = 5.8, 1.3), 2.00 (td, 2H, *J* = 7.6, 3.6), 1.88 (s, 3H), 1.50–1.30 (m, 2H), 1.21 (sx, 2H, *J* = 7.5), 0.79 (t, 3H, *J* = 7.5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.6, 152.4, 142.7, 131.0, 130.8, 130.5, 128.0, 124.2, 123.4, 119.7, 110.8, 110.3, 69.6, 31.8, 29.2, 22.4, 15.5, 13.8; HRMS (APCI) for $C_{18}H_{22}NO_5$ $[M+H]^+$ found 332.1515, calc. 332.1492.

3.2.2 Two-Step Procedure Using Grignard Reagents

3.2.2.1 Carbometallation–Iodination Products

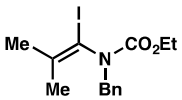
Representative Procedure F

Carbometallation–Iodination: A solution of ynecarbamate (1 equiv) in Et_2O (5–10 mL) was added to a suspension of CuI (1 equiv) and RMgBr (in Et_2O; 2 equiv) in Et_2O (15–25 mL) at – 30 °C and the mixture was left to stir gradually warming up to –10 °C. After 1 h, a solution of iodine (2 equiv) in THF (10–20 mL) was added dropwise at –10 °C and the mixture left for 15 min. It was then quenched with sat. aq. $Na_2S_2O_3$ solution and extracted with Et_2O (2×), the combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography Et_2O/hexane or Et_2O/pentane (1:20 to 1:10) to give the desired product.



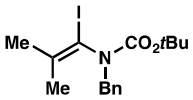
***(E)*-Methyl benzyl(1-iodo-2-methylhex-1-en-1-yl)carbamate (4d)**

Representative Procedure F. Prepared from methyl benzyl(hex-1-yn-1-yl)carbamate (200 mg, 0.815 mmol, 1 equiv) using CuI (155 mg, 0.815 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 0.69 mL, 1.63 mmol, 2 equiv) and iodine (424 mg, 1.63 mmol, 2 equiv) to give the desired product as a pale yellow oil (316 mg, 0.815 mmol, quant): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.25 (m, 5H), 4.98 (d, 1H, *J* = 14.2), 4.05 (d, 1H, *J* = 14.2), 3.81 (s, 3H), 1.77 (s, 3H), 1.70 (td, 1H, *J* = 13.2, 5.2), 1.55 (m, 1H), 1.15–1.05 (m, 1H), 1.05–0.90 (m, 2H), 0.73 (t, 3H, *J* = 7.2), 0.65–0.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.5, 146.2, 135.8, 129.9, 128.3, 127.8, 95.3, 53.6, 52.2, 33.5, 29.1, 25.9, 22.7, 13.8; HRMS (APCI) for $C_{20}H_{31}INO_2$ $[M+H]^+$ found 338.0770, calc. 338.0768.



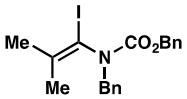
***(E)*-Ethyl benzyl(1-iodo-2-methylhex-1-en-1-yl)carbamate (4e)**

Representative Procedure F. Prepared from ethyl benzyl(hex-1-yn-1-yl)carbamate (1.5237 g, 5.88 mmol, 1 equiv) using CuI (1.119 g, 5.88 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 3.92 mL, 11.8 mmol, 2 equiv) and iodine (2.982 mg, 11.8 mmol, 2 equiv) to give the desired product as a yellow oil (1.728 g, 4.31 mmol, 73%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31–7.13 (m, 5H), 4.87 (d, 1H, *J* = 14.2), 4.24–4.07 (m, 2H), 3.91 (d, 1H, *J* = 14.2), 1.69 (s, 3H), 1.63–1.53 (m, 1H), 1.57–1.37 (m, 1H), 1.20 (m, 3H, *J* = 7.0), 0.62 (t, 3H, *J* = 7.2), 0.50–0.33 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.0, 145.8, 135.9, 129.9, 128.3, 127.7, 95.7, 62.4, 52.0, 33.5, 29.2, 25.8, 22.7, 14.7, 13.8; HRMS for $C_{17}H_{25}INO_2$ $[M+H]^+$ found 402.0975, calc. 402.0924.



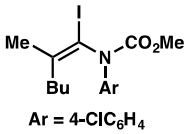
***(E)*-*tert*-Butyl benzyl(1-iodo-2-methylhex-1-en-1-yl)carbamate (4f)**

Representative Procedure F. Prepared from *tert*-butyl benzyl(hex-1-yn-1-yl)carbamate (1.022 g, 3.56 mmol, 1 equiv) using CuI (0.677 g, 3.56 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 2.37 mL, 7.11 mmol, 2 equiv) and iodine (1.805 g, 7.11 mmol, 2 equiv) to give the desired product as a pale yellow oil (1.1732 g, 2.73 mmol, 77%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30–7.10 (m, 5H), 4.80 (d, 1H, *J* = 13.9), 3.83 (d, 1H, *J* = 13.9), 1.65–1.55 (m, 4H), 1.40 (s, 9H), 1.10–0.95 (m, 1H), 0.89 (qn, 2H, *J* = 7.2), 0.85–0.75 (m, 1H), 0.63 (t, 3H, *J* = 7.2), 0.55–0.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 144.7, 136.2, 129.8, 128.1, 127.5, 97.4, 80.9, 51.6, 33.4, 29.1, 28.2, 25.7, 22.7, 13.7; HRMS (APCI) for $C_{19}H_{29}INO_2$ $[M+H]^+$ found 430.1217, calc. 430.1237.



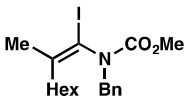
***(E)*-Benzyl benzyl(1-iodo-2-methylhex-1-en-1-yl)carbamate (4g)**

Representative Procedure F. Prepared from benzyl benzyl(hex-1-yn-1-yl)carbamate (0.618 g, 1.92 mmol, 1 equiv) using CuI (0.366 g, 1.92 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 1.28 mL, 3.85 mmol, 2 equiv) and iodine (0.976 g, 3.85 mmol, 2 equiv) to give the desired product as a pale yellow oil (0.891 g, 1.92 mmol, quant): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.10 (m, 10H), 5.20–5.05 (m, 2H), 4.90 (d, 1H, *J* = 13.9), 3.95 (d, 1H, *J* =13.9), 1.64 (s, 3H), 1.60-1.45 (m, 2H), 1.00–0.65 (m, 3H), 0.60–0.50 (m, 3H), 0.40–0.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.9, 146.3, 136.3, 135.7, 129.9, 128.4, 128.3, 128.0, 127.8, 95.0, 68.0, 52.2, 33.6, 29.1, 25.8, 22.7, 13.7, one carbon not observed (Ar); HRMS (APCI) for $C_{22}H_{27}INO_2$ $[M+H]^+$ found 464.1073, calc. 464.1081.



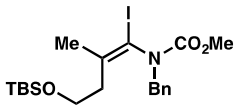
***(E)*-Methyl (4-chlorophenyl)(2-methyl-1-iodohex-1-en-1-yl)carbamate (4h)**

Representative Procedure F. Prepared from benzyl methyl (4-chlorophenyl)(hex-1-yn-1-yl)carbamate (0.710 g, 2.67 mmol, 1 equiv) using CuI (0.509 g, 2.67 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 1.78 mL, 5.34 mmol, 2 equiv) and iodine (1.356 g, 5.34 mmol, 2 equiv) to give the desired product as a yellow oil (0.949 g, 2.33 mmol, 87%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.30 (m, 4H), 3.83 (s, 3H), 2.35–2.25 (m, 1H), 2.18 (td, 1H, *J* = 10.3, 4.4), 1.94 (s, 3H), 1.45–1.35 (m, 1H), 1.35–1.15 (m, 3H), 0.88 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.0, 146.6, 139.1, 131.5, 128.9, 125.5, 92.9, 53.7, 33.4, 29.2, 26.1, 22.8, 13.9; HRMS (ESI) for $C_{15}H_{20}ClNIO_2$ $[M+H]^+$ found 408.0221, calc. 408.0222.



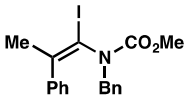
***(E)*-Methyl benzyl(1-iodo-2-methyloct-1-en-1-yl)carbamate (4i)**

Representative Procedure F. Prepared from methyl benzyl(oct-1-yn-1-yl)carbamate (0.675 g, 2.47 mmol, 1 equiv) using CuI (0.470 g, 2.47 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 1.65 mL, 4.94 mmol, 2 equiv) and iodine (1.253 g, 4.94 mmol, 2 equiv) to give the desired product as a pale yellow oil (1.025 g, 2.47 mmol, quant): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46–7.10 (m, 5H), 4.87 (d, 1H, *J* = 14.0), 3.93 (d, 1H, *J* = 14.0), 3.68 (s, 3H), 1.66 (s, 3H), 1.59 (td, 1H, *J* = 12.0, 5.5), 1.50–1.36 (m, 1H), 1.10 (qn, 2H, *J* = 7.2), 1.05–0.91 (m, 3H), 0.87–0.78 (m, 2H), 0.76 (t, 3H, *J* =7.2), 0.53–0.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.5, 146.1, 135.7, 129.9, 128.3, 127.8, 95.3, 53.6, 52.2, 33.7, 31.5, 29.3, 27.0, 25.8, 22.5, 14.1; HRMS (APCI) for $C_{18}H_{27}INO_2$ $[M+H]^+$ found 416.1083, calc. 416.1081.



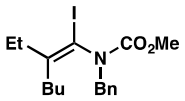
***(E)*-Methyl benzyl(4-((tert-butyldimethylsilyl)oxy)-1-iodo-2-methylbut-1-en-1-yl)carbamate (4j)**

Representative Procedure F. Prepared from methyl benzyl(4-((tert-butyldimethylsilyl)oxy)but-1-yn-1-yl)carbamate (0.542 g, 1.56 mmol, 1 equiv) using CuI (0.297 g, 1.56 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 1.04 mL, 3.12 mmol, 2 equiv) and iodine (0.792 g, 3.12 mmol, 2 equiv) to give the desired product as a pale yellow oil (0.703 g, 1.44 mmol, 92%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.20 (m, 5H), 4.95 (d, 1H, J =13.9), 4.12 (d, 1H, J = 13.9), 3.81 (s, 3H), 3.30–3.10 (m, 2H), 2.10–2.00 (m, 2H), 1.92–1.78 (m, 4H), 0.88 (s, 9H), 0.0074 (s, 3H), –0.0001 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 143.4, 135.4, 130.0, 128.3, 127.9, 97.1, 60.8, 53.6, 52.6, 36.9, 26.6, 25.9, 18.2, –5.35l; HRMS (APCI) for $C_{20}H_{33}INO_3Si$ $[M+H]^+$ found 490.1282, calc. 490.1269.



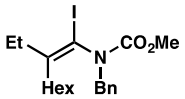
***(E)*-Methyl benzyl(1-iodo-2-phenylprop-1-en-1-yl)carbamate (4k)**

Representative Procedure F. Prepared from methyl benzyl(phenylethynyl)carbamate (0.500 g, 1.88 mmol, 1 equiv) using CuI (0.359 g, 1.88 mmol, 1 equiv), MeMgBr (3 M in Et_2O; 1.26 mL, 3.77 mmol, 2 equiv) and iodine (0.957 g, 3.77 mmol, 2 equiv) to give the desired product as a pale yellow oil (0.551 g, 1.35 mmol, 72%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20–6.95 (m, 6H), 6.95–6.80 (m, 2H), 6.70–6.50 (m, 2H), 4.31 (d, 1H, *J* = 13.9), 4.04 (d, 1H, *J* =13.9), 3.71 (s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 144.8, 139.4, 134.8, 129.6, 128.1, 127.4, 127.1, 126.6, 98.1, 53.6, 53.1, 29.6, one carbon not observed (overlapped in Ar); HRMS (APCI) for $C_{18}H_{19}INO_2$ $[M+H]^+$ found 408.0447, calc. 408.0455.



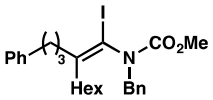
***(E)*-Methyl benzyl(2-ethyl-1-iodohex-1-en-1-yl)carbamate (4l)**

Representative Procedure F. Prepared from methyl benzyl(hex-1-yn-1-yl)carbamate (0.471 g, 1.92 mmol, 1 equiv) using CuI (0.366 g, 1.92 mmol, 1 equiv), EtMgBr (1.9 M in Et_2O; 2.02 mL, 3.84 mmol, 2 equiv) and iodine (0.975 g, 3.84 mmol, 2 equiv) to give the desired product as a pale yellow oil (0.564 g, 1.41 mmol, 73%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.15 (m, 5H), 4.89 (d, 1H, *J* = 13.8), 3.92 (d, 1H, *J* = 13.8), 3.69 (s, 3H), 2.12–2.02 (m, 1H), 2.02–1.90 (m, 1H), 1.58 (td, 1H, *J* = 13.3, 4.8), 1.45–1.35 (m, 1H), 1.05–0.85 (m, 3H), 0.81 (t, 3H, *J* = 7.4), 0.63 (t, 3H, *J* = 7.2), 0.55–0.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.6, 150.9, 135.6, 130.2, 128.4, 127.9, 94.9, 53.6, 52.1, 31.7, 31.0, 29.3, 22.9, 13.8, 11.6; HRMS (APCI) for $C_{17}H_{25}INO_2$ $[M+H]^+$ found 402.0911, calc. 402.0924.



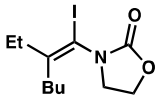
***(E)*-Methyl benzyl(2-ethyl-1-iodooct-1-en-1-yl)carbamate (4m)**

Representative Procedure F. Prepared from methyl benzyl(oct-1-yn-1-yl)carbamate (0.464 g, 1.69 mmol, 1 equiv) using CuI (0.323 g, 1.69 mmol, 1 equiv), EtMgBr (1.9 M in Et_2O; 1.78 mL, 3.39 mmol, 2 equiv) and iodine (0.860 g, 3.39 mmol, 2 equiv) to give the desired product as a pale yellow oil (0.621 g, 1.45 mmol, 85%): 1H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.25 (m, 5H), 4.98 (d, 1H, *J* = 13.5), 4.02 (d, 1H, *J* = 13.5), 3.79 (s, 3H), 2.25–2.15 (m, 1H), 2.15–2.05 (m, 1H), 1.68 (td, 1H, *J* =13.1, 4.9), 1.55–1.40 (m, 1H), 1.30–1.25 (m, 2H), 1.15–0.90 (m, 5H), 0.90 (t, 3H, *J* = 7.4), 0.87 (t, 3H, *J* = 7.3), 0.70–0.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.9, 135.6, 130.2, 128.3, 127.9, 53.6, 52.1, 31.7, 31.6, 31.3, 29.5, 27.1, 22.6, 14.2, 11.7, two carbons not observed (*C*=*C*); HRMS (APCI) for $C_{19}H_{29}INO_2$ $[M+H]^+$ found 430.1237, calc. 430.1240.



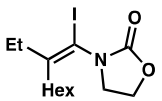
Methyl *(Z)*-benzyl(1-iodo-2-(3-phenylpropyl)oct-1-en-1-yl)carbamate (4n)

Representative Procedure F. Prepared from methyl benzyl(oct-1-yn-1-yl)carbamate (1.029 g, 3.76 mmol, 1 equiv) using CuI (0.717 g, 3.76 mmol, 1 equiv), $Ph(CH_2)_3MgBr$ (2.3 M in Et_2O; 3.27 mL, 7.53 mmol, 2 equiv) and iodine (1.911 g, 7.53 mmol, 2 equiv) to give the desired product as a yellow oil (1.801 g, 3.47 mmol, 92%): ^1H NMR ($CDCl_3$, 500 MHz) δ 7.41–7.37 (m, 2H), 7.37–7.29 (m, 5H), 7.26–7.20 (m, 3H), 5.05 (br d, 1H, *J* = 13.5), 4.05 (br d, 1H, *J* = 13.5), 3.82 (s, 3H), 2.64 (td, *J* = 7.6, 1.6), 2.27–2.10 (m, 2H), 1.77–1.60 (m, 2H), 1.58–1.48 (br s, 1H), 1.24 (qn, 2H, *J* = 7.4), 1.13–0.92 (m, 6H), 0.90 (m, 3H, *J* = 7.4), 0.63–0.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.6, 149.4, 142.1, 135.6, 130.1, 128.5, 128.37, 128.35, 127.9, 125.9, 95.8, 53.6, 52.1, 37.9, 35.7, 31.6, 31.5, 29.4, 28.9, 27.1, 22.6, 14.2; HRMS (APCI) for $C_{26}H_{35}INO_2$ $[M+H]^+$ found 520.1711, calc. 520.1707.



***(E)*-3-(2-Ethyl-1-iodohex-1-en-1-yl)oxazolidin-2-one (4o)**

Representative Procedure F. Prepared from 3-(hex-1-yn-1-yl)oxazolidin-2-one (0.920 g, 5.50 mmol, 1 equiv) using CuI (1.049 g, 5.50 mmol, 1 equiv), EtMgBr (2.7 M in Et_2O; 4.08 mL, 11.0 mmol, 2 equiv) and iodine (2.793 g, 11.0 mmol, 2 equiv) to give the desired product as a yellow oil (1.630 g, 5.04 mmol, 92%): ^1H NMR ($CDCl_3$, 300 MHz) δ 4.45–4.25 (m, 2H), 3.64 (q, 1H, *J* = 9.5), 3.40–3.25 (m, 1H), 2.30–2.10 (m, 4H), 1.50–1.15 (m, 4H), 1.00 (t, 3H, *J* = 7.3), 0.85 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.8, 153.5, 90.1, 62.0, 46.6, 32.0, 31.3, 30.1, 22.7, 13.8, 11.7; HRMS (ESI) for $C_{11}H_{19}INO_2$ $[M+H]^+$ found 324.0450, calc. 324.0455.



***(E)*-3-(2-Ethyl-1-iodooct-1-en-1-yl)oxazolidin-2-one (4p)**

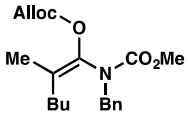
Representative Procedure F. Prepared from 3-(oct-1-yn-1-yl)oxazolidin-2-one (0.9911 g, 5.08 mmol, 1 equiv) using CuI (0.9667 g, 5.08 mmol, 1 equiv), EtMgBr (2.7 M in Et_2O; 3.76 mL, 10.15 mmol, 2 equiv) and iodine (2.577 g, 10.15 mmol, 2 equiv) to give the desired product as a yellow oil (1.5244 g, 4.34 mmol, 86%): ^1H NMR ($CDCl_3$, 300 MHz) δ 4.42–4.24 (m, 2H), 3.63 (q, 1H, *J* = 9.5), 3.35–3.23 (m, 1H), 2.22–2.06 (m, 4H), 1.47–1.24 (m, 2H), 1.24–1.12 (m, 8H), 0.97 (t, 3H, *J* = 7.3), 0.80 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.7, 153.3, 90.1, 62.0, 46.5, 31.9, 31.5, 31.4, 29.2, 27.8, 22.4, 14.0, 11.6; HRMS (ESI) for $C_{13}H_{23}INO_2$ $[M+H]^+$ found 352.0740, calc. 352.0768.

3.2.2.2 Regioretentive Formation of Alloc-Trapped Products

Representative Procedure G

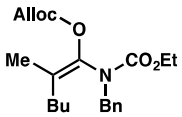
Representative Procedure for Regioretentive Formation of Alloc-Trapped Products: A solution of MeLi in Et_2O (2.1 equiv) was added dropwise to a solution of *t*BuOOH (5.5 M in decane; 1.8 equiv) in THF (15 mL) at –80 °C. After the addition of base was complete, the mixture was stirred for additional 15–30 min prior to be used as an *in situ* prepared oxidant.

A solution of *t*BuLi in hexane (2.1 equiv) was added dropwise to a solution of vinyl iodide **5** (1 equiv) in Et_2O at –80 °C. After 15 min, a solution of freshly prepared *t*BuOOLi (see above; ca. 1.5 equiv) was added *via* syringe at –80 °C and the mixture was left to stir warming up to –40 °C. After 1 h, AllocCl (4.5 equiv) was added and the reaction mixture was allowed to warm to room temperature. It was quenched with 1 M HCl solution, extracted with Et_2O (2×), the combined organic layers were dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography (Et_2O/hexane or EtOAc/hexane) to give the desired product.



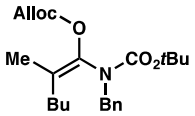
***(E)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3d)**

Representative Procedure G. Prepared from vinyl iodide **4d** (1.611 g, 4.16 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 4.89 mL, 8.32 mmol, 2.0 equiv), TBHP (5.5 M in decane; 1.51 mL, 8.32 mmol, 2.0 equiv) using MeLi (1.6 M in Et_2O; 5.98 mL, 9.57 mmol, 2.3 equiv) and AllocCl (1.77 µL, 16.64 mmol, 4.0 equiv) to give the desired product as a yellow oil (1.082 g, 2.99 mmol, 72%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.4–7.10 (m, 5H), 5.83 (ddt, 1H, *J* = 17.2, 10.4, 5.5), 5.30 (d, 1H, *J* = 17.2), 5.22 (d, 1H, *J* = 10.4), 4.66 (d, 1H, *J* = 14.6), 4.51 (d, 2H, *J* = 5.5), 4.41 (d, 1H, *J* = 14.6), 3.71 (s, 3H), 1.75–1.60 (m, 2H), 1.55 (s, 3H), 1.10–0.90 (m, 2H), 0.90–0.75 (m, 2H), 0.72 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 152.7, 137.5, 134.8, 131.2, 128.8, 128.3, 127.4, 126.1, 119.2, 68.9, 53.3, 51.2, 32.0, 28.9, 22.7, 14.9, 13.9; HRMS (ESI) for $C_{20}H_{28}NO_5$ $[M+H]^+$ found 362.1960, calc. 362.1962.



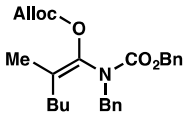
***(E)*-Ethyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3e)**

Representative Procedure G. Prepared from vinyl iodide **4e** (0.879 g, 2.19 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 2.58 mL, 4.38 mmol, 2.0 equiv), TBHP (5.5 M in decane; 797 µL, 4.38 mmol, 2.0 equiv) using MeLi (1.6 M in Et_2O; 3.15 mL, 5.04 mmol, 2.3 equiv) and AllocCl (916 µL, 8.76 mmol, 4.0 equiv) to give the desired product as a yellow oil (0.632 g, 1.68 mmol, 77%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45–7.10 (m, 5H), 5.81 (ddt, 1H, *J* = 17.2, 10.4, 5.7), 5.28 (d, 1H, *J* = 17.2), 5.20 (d, 1H, *J* = 10.4), 4.67 (d, 1H, *J* = 14.6), 4.49 (d, 2H, *J* = 5.7), 4.38 (d, 1H, *J* = 14.6), 4.20–4.05 (m, 2H), 1.70–1.57 (m, 2H), 1.51 (s, 3H), 1.18 (t, 3H, *J* = 7.1), 1.05–0.90 (m, 2H), 0.90–0.75 (m, 2H), 0.70 (t, 3H, *J* = 7.1); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 152.8, 137.7, 135.0, 131.3, 128.8, 128.3, 127.4, 125.9, 119.2, 68.9, 62.2, 51.1, 32.1, 29.0, 22.7, 14.9, 14.6, 13.9; HRMS (ESI) for $C_{21}H_{30}NO_5$ $[M+H]^+$ found 376.2097, calc. 376.2118.



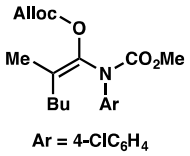
***(E)-tert*-Butyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3f)**

Representative Procedure G. Prepared from vinyl iodide **4f** (0.300 g, 0.70 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 822 µL, 1.40 mmol, 2.0 equiv), TBHP (5.5 M in decane; 254 µL, 1.40 mmol, 2.0 equiv) using MeLi (1.6 M in Et_2O; 1.00 mL, 1.61 mmol, 2.3 equiv) and AllocCl (334 µL, 3.14 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.230 g, 0.57 mmol, 82%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45–7.10 (m, 5H), 5.81 (ddt, 1H, *J* = 17.2, 10.4, 5.6), 5.27 (d, 1H, *J* = 17.2), 5.18 (d, 1H, *J* = 10.4), 4.67 (br s, 1H), 4.48 (d, 2H, *J* = 5.6), 4.33 (d, 1H, *J* = 14.5), 1.7–1.55 (m, 2H), 1.54 (s, 3H), 1.38 (s, 9H), 1.25–0.80 (m, 4H), 0.70 (t, 3H, *J* = 7.0); ^{13}C NMR ($CDCl_3$, 125 MHz) δ NMR 154.7, 152.9, 138.1, 135.5, 131.4, 128.7, 128.3, 127.2, 119.2, 80.8, 77.4, 68.9, 50.5, 32.3, 29.1, 28.3, 22.8, 14.0; HRMS (ESI) for $C_{23}H_{34}NO_5$ $[M+H]^+$ found 404.2433, calc. 404.2431.



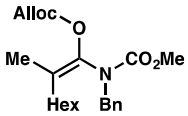
***(E)*-Benzyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3g)**

Representative Procedure G. Prepared from vinyl iodide **4g** (0.517 g, 1.12 mmol, 1 equiv) using *t*BuLi (1.6 M in hexane; 1.40 mL, 2.23 mmol, 2.0 equiv), TBHP (5.5 M in decane; 365 µL, 2.01 mmol, 1.8 equiv) using MeLi (1.24 M in Et_2O; 1.89 mL, 2.34 mmol, 2.1 equiv) and AllocCl (534 µL, 5.02 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.383 g, 0.875, 78%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45–7.10 (m, 10H), 5.79 (ddt, 1H, *J* = 17.1, 10.4, 5.7), 5.26 (dd, 1H, *J* = 17.1, 1.3), 5.19 (d, 1H, *J* = 10.4), 5.20–5.10 (m, 2H), 4.64 (br d, 1H, *J* = 14.6), 4.47 (d, 1H, *J* =5.7), 4.40 (br d, 1H, *J* = 14.6), 1.60–1.45 (m, 5H), 1.10–0.75 (m, 4H), 0.75–0.55 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.7, 152.8, 137.5, 136.4, 134.7, 131.3, 128.8, 128.4, 128.3, 128.0, 127.9, 127.4, 126.2, 119.2, 69.0, 67.9, 51.3, 32.2, 28.9, 22.7, 15.0, 13.9; HRMS (ESI) for $C_{26}H_{32}NO_5$ $[M+H]^+$ found 438.2269, calc. 438.2275.



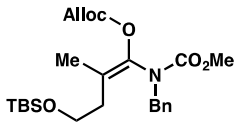
***(E)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(4-chlorophenyl)carbamate (3h)**

Representative Procedure G. Prepared from vinyl iodide **4h** (0.909 g, 2.23 mmol, 1 equiv) using *t*BuLi (1.6 M in hexane; 2.79 mL, 4.46 mmol, 2.0 equiv), TBHP (5.5 M in decane; 0.730 mL, 4.01 mmol, 1.8 equiv) using MeLi (1.24 M in Et_2O; 3.78 mL, 4.68 mmol, 2.1 equiv) and AllocCl (1.07 mL, 10.0 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.610 g, 1.60 mmol, 72%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30–7.15 (m, 4H), 5.79 (ddt, 1H, *J* = 17.2, 10.4, 5.7), 5.23 (dd, 1H, *J* = 17.2, 1.2), 5.17 (d, 1H, *J* = 10.4), 4.51 (d, 2H, *J* = 5.7), 2.00 (t, 2H, *J* = 7.2), 1.61 (s, 3H), 1.35–1.10 (m, 4H), 0.79 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 152.0, 138.6, 135.0, 131.8, 131.1, 128.9, 126.7, 126.0, 119.3, 68.9, 53.5, 32.2, 28.8, 22.8, 15.4, 14.0; HRMS (ESI) for $C_{19}H_{25}ClNO_5$ $[M+H]^+$ found 382.1441, calc. 382.1416.



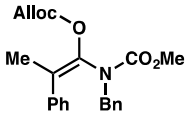
***(E)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-methyloct-1-en-1-yl)(benzyl)carbamate (3i)**

Representative Procedure G. Prepared from vinyl iodide **4i** (0.509 g, 1.23 mmol, 1 equiv) using *t*BuLi (1.6 M in hexane; 1.53 mL, 2.45 mmol, 2.0 equiv), TBHP (5.5 M in decane; 401 µL, 2.21 mmol, 1.8 equiv) using MeLi (1.24 M in Et_2O; 2.08 mL, 2.57 mmol, 2.1 equiv) and AllocCl (586 µL, 5.52 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.387 g, 0.99 mmol, 81%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.10 (m, 5H), 5.79 (ddt, 1H, *J* = 17.1, 10.4, 5.7), 5.26 (dd, 1H, *J* = 17.1, 1.2), 5.18 (d, 1H, *J* = 10.4), 4.63 (br d, 2H, *J* = 14.5), 4.47 (d, 1H, *J* = 5.7), 4.37 (br d, *J* = 14.5), 3.67 (s, 3H), 1.70–1.55 (m, 2H), 1.51 (s, 3H), 1.25–1.10 (m, 4H), 1.04 (qn, 2H, *J* = 7.2), 1.00–0.90 (m, 2H), 0.85 (t, 3H, *J* = 7.3), 0.78 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 152.7, 137.5, 134.8, 131.2, 128.8, 128.3, 127.4, 126.0, 119.15, 68.9, 53.3, 51.2, 32.2, 31.7, 29.3, 26.7, 22.6, 14.9, 14.1; HRMS (ESI) for $C_{22}H_{32}NO_5$ $[M+H]^+$ found 390.2288, calc. 390.2275.



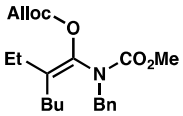
Methyl *(E)*-benzyl(2,2,3,3,7-pentamethyl-10-oxo-4,9,11-trioxa-3-silatetradeca-7,13-dien-8-yl)carbamate (3j)

Representative Procedure G. Prepared from vinyl iodide **4j** (0.802 g, 1.64 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 1.93 mL, 3.28 mmol, 2.0 equiv), TBHP (5.5 M in decane; 596 µL, 3.28 mmol, 2.0 equiv) using MeLi (1.24 M in Et_2O; 3.04 mL, 3.77 mmol, 2.3 equiv) and AllocCl (784 µL, 7.37 mmol, 4.5 equiv) to give the desired product as a pale yellow oil (677g, 1.46 mmol, 89%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38–7.21 (m, 5H), 5.85 (ddt, 1H, *J* = 17.2, 10.4, 5.7), 5.33 (dqt, 1H, *J* = 17.2, 1.2), 5.26 (dd, 1H, *J* = 10.5, 1.2), 4.67–4-52 (br m, 2H) 4.52 (d, 2H, *J* = 5.7), 3.76 (s, 3H) 2.00 (t, 2H, *J* = 7.2), 3.52–3.30 (br m, 2H), 2.07–1.91 (br m, 2H), 1.63 (s, 3H), 0.86 (s, 9H), –0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.3, 152.5, 137.5, 136.3, 131.3, 128.8, 128.4, 127.5, 123.5, 119.4, 69.1, 60.9, 53.5, 51.7, 35.7, 26.0, 18.4, 15.7, –5.27; HRMS (ACPI) for $C_{24}H_{38}NO_6Si$ $[M+H]^+$ found 464.2452, calc. 464.2463.



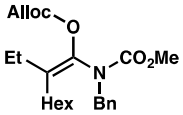
Methyl *(E)*-(1-(((allyloxy)carbonyl)oxy)-2-phenylprop-1-en-1-yl)(benzyl)carbamate (3k)

Representative Procedure G. Prepared from vinyl iodide **4k** (1.036 g, 2.54 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 3.00 mL, 5.09 mmol, 2.0 equiv), TBHP (5.5 M in decane; 833 µL, 4.58 mmol, 1.8 equiv) using MeLi (1.2 M in Et_2O; 4.45 mL, 5.34 mmol, 2.1 equiv) and AllocCl (1.22 mL, 11.45 mmol, 4.5 equiv) to give the desired product as a yellow oil (836 g, 2.11 mmol, 85%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30–7.00 (m, 10 H), 5.91 (*J* = 17.3, 10.3, 5.4)5.38 (d, 1H, *J* = 17.3), 5.31 (d, 1H, *J* = 10.5), 4.70–4.50 (br signal, 1H), 4.57 (d, 2H, *J* = 5.4), 4.40–4.20 (br signal, 1H) 3.63 (s,3H), (2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.9, 152.2, 138.7, 137.6, 137.3, 131.2, 128.4, 128.3, 127.5, 127.3, 127.2 124.9, 119.5, 69.2, 53.3, 52.5, 18.5; HRMS (APCI) for $C_{22}H_{24}NO_5$ $[M+H]^+$ found 382.1633, calc. 382.1649.



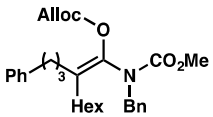
Methyl *(E)*-(1-(((allyloxy)carbonyl)oxy)-2-ethylhex-1-en-1-yl)(benzyl)carbamate (3l)

Representative Procedure G. Prepared from vinyl iodide **4l** (0.395 g, 0.984 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 1.16 mL, 1.97 mmol, 2.0 equiv), TBHP (5.5 M in decane; 358 µL, 1.97 mmol, 2.0 equiv) using MeLi (1.25 M in Et_2O; 1.81 mL, 2.26 mmol, 2.1 equiv) and AllocCl (470 µL, 4.43 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.317 g, 0.844 mmol, 86%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.10 (m, 5H), 5.81 (ddt, 1H, *J* = 17.2, 10.4, 5.7), 5.28 (d, 1H, *J* = 17.2, 1.2), 5.20 (d, 1H, *J* = 10.4, 1.2), 4.67 (br d, 2H, *J* = 14.2), 4.48 (dt, 1H, *J* = 5.7, 1.2), 4.37 (br d, *J* = 14.2), 3.68 (s, 3H), 1.93 (q, 2H, *J* = 7.3), 1.70–1.40 (m, 2H), 1.25–0.94 (m, 4H), 0.86 (t, 3H, *J* = 7.3), 0.70 (t, 3H, *J* = 7.3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.1, 137.5, 134.5, 131.4, 131.2, 129.0, 128.4, 127.5, 119.3, 69.1, 53.4, 51.3, 29.3, 28.9, 23.0, 21.7, 14.0, 11.8, one of the *C*=O peaks not observed; HRMS (APCI) for $C_{21}H_{30}NO_5$ $[M+H]^+$ found 376.2104, calc. 376.2118.



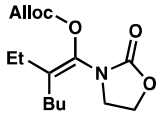
Methyl *(E)*-(1-(((allyloxy)carbonyl)oxy)-2-ethyloct-1-en-1-yl)(benzyl)carbamate (3m)

Representative Procedure G. Prepared from vinyl iodide **4m** (0.352 g, 0.820 mmol, 1 equiv) using *t*BuLi (1.6 M in hexane; 1.02 mL, 1.64 mmol, 2.0 equiv), TBHP (5.5 M in decane; 268 µL, 1.48 mmol, 1.8 equiv) using MeLi (1.24 M in Et_2O; 1.39 mL, 1.72 mmol, 2.1 equiv) and AllocCl (392 µL, 3.69 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.299 g, 0.75 mmol, 90%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.10 (m, 5H), 5.80 (ddt, 1H, *J* = 17.2, 10.4, 5.6), 5.26 (d, 1H, *J* = 17.2), 5.19 (d, 1H, *J* = 10.4), 4.66 (br d, 2H, *J* = 14.5), 4.47 (d, 1H, *J* = 5.6), 4.36 (br d, *J* = 14.5), 3.67 (s, 3H), 1.92 (q, 2H, *J* = 7.2), 1.70–1.40 (m, 2H), 1.25–1.10 (m, 4H), 1.04 (qn, 2H, *J* = 7.2), 1.00–0.90 (m, 2H), 0.85 (t, 3H, *J* = 7.3), 0.78 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4, 153.0, 137.4, 134.4, 131.3, 131.1, 128.9, 128.3, 127.5, 119.2, 68.9, 53.3, 51.1, 31.7, 29.50, 29.45, 26.7, 22.6, 21.6, 14.1, 11.7; HRMS (ESI) for $C_{23}H_{34}NO_5$ $[M+H]^+$ found 404.2435, calc. 404.2435.



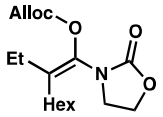
Methyl *(Z)*-(1-(((allyloxy)carbonyl)oxy)-2-(3-phenylpropyl)oct-1-en-1-yl)(benzyl)carbamate (3n)

Representative Procedure G. Prepared from vinyl iodide **4o** (0.868 g, 1.67 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 1.97 mL, 3.34 mmol, 2.0 equiv), TBHP (5.5 M in decane; 607 µL, 3.34 mmol, 2.0 equiv) using MeLi (1.2 M in Et_2O; 3.20 mL, 3.84 mmol, 2.3 equiv) and AllocCl (888 µL, 8.35 mmol, 5.0 equiv) to give the desired product as a yellow oil (0.681 g, 1.38 mmol, 82%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39–7.31 (m, 2H), 7.31–7.21 (m, 5H), 7.21–7.12 (m, 3H), 5.87 (ddt, 1H, *J* = 17.2, 10.4, 5.6), 5.34 (dqt, 1H, *J* = 17.2, 1.2), 5.28 (dd, 1H, *J* = 10.4, 1.2), 4.76 (br d, 2H, *J* = 14.6), 4.52 (dd, 1H, *J* = 5.6, 1.2), 4.41 (br d, *J* = 14.6), 3.75 (s, 3H), 2.62–2.46 (m, 2H), 2.07–1.94 (m, 2H), 1.75–1.57 (m, 4H), 1.24–1.15 (m, 4H), 1.13–1.05 (m, 2H), 1.03–0.97 (m, 2H), 0.86 (t, 3H, *J* = 7.2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.4, 152.9, 142.2, 137.3, 135.0, 131.3, 129.4, 129.0, 128.5, 128.4, 127.5, 125.8, 119.3, 69.0, 53.4, 51.0, 35.6, 31.7, 30.4, 29.8, 29.7, 29.5, 28.8, 27.9, 26.8, 22.6, 14.2; HRMS (ESI) for $C_{30}H_{40}NO_5$ $[M+H]^+$ found 494.2918, calc. 494.2901.



***(E)*-Allyl (2-ethyl-1-(2-oxooxazolidin-3-yl)hex-1-en-1-yl) carbonate (3o)**

Representative Procedure G. Prepared from vinyl iodide **4p** (1.625 g, 5.03 mmol, 1 equiv) using *t*BuLi (1.56 M in hexane; 6.45 mL, 10.06 mmol, 2.0 equiv), TBHP (5.5 M in decane; 1.83 mL, 10.06 mmol, 2.0 equiv) using MeLi (1.6 M in Et_2O; 7.23 mL, 11.57 mmol, 2.3 equiv) and AllocCl (2.41 mL, 22.6 mmol, 4.5 equiv) to give the desired product as a yellow oil (1.188 g, 4.11 mmol, 79%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.87 (ddt, 1H, *J* = 17.2, 10.8, 5.7), 5.31 (d, 1H, *J* = 17.2, 1.3), 5.22 (d, 1H, *J* = 10.8, 1.3), 4.59 (dt, 2H, *J* = 5.7, 1.2), 4.31 (t, 2H, *J* = 7.7), 3.74 (d, 2H, *J* = 7.7), 2.10–1.95 (m, 4H), 1.36 (qn, 2H, *J* = 6.9), 1.25 (sx, 2H, *J* = 6.9), 1.01 (t, 3H, *J* = 7.6), 0.87 (t, 3H, *J* = 6.9); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 153.3, 132.1, 131.7, 130.9, 119.2, 69.0, 62.5, 45.6, 29.3, 29.1, 22.6, 21.9, 13.8, 11.9; HRMS for $C_{15}H_{24}NO_5$ $[M+H]^+$ found 298.1623, calc. 298.1649.

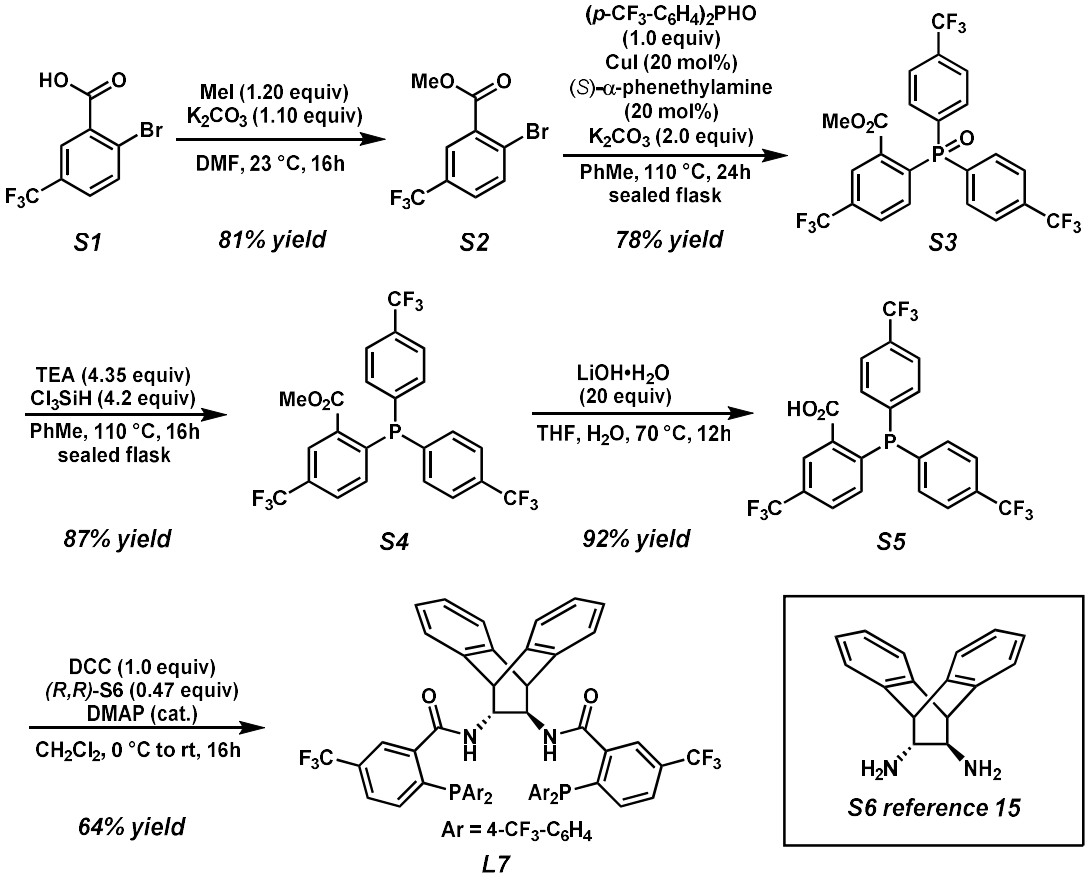


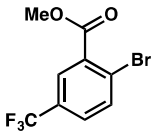
***(E)*-Allyl (2-ethyl-1-(2-oxooxazolidin-3-yl)oct-1-en-1-yl) carbonate (3p)**

Representative Procedure G. Prepared from vinyl iodide **4q** (0.416 g, 1.18 mmol, 1 equiv) using *t*BuLi (1.7 M in hexane; 1.39 mL, 2.37 mmol, 2.0 equiv), TBHP (5.5 M in decane; 431 µL, 2.37 mmol, 2.0 equiv) using MeLi (1.6 M in Et_2O; 1.70 mL, 2.72 mmol, 2.3 equiv) and AllocCl (566 µL, 5.33 mmol, 4.5 equiv) to give the desired product as a yellow oil (0.327 g, 1.00 mmol, 85%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.93 (ddt, 1H, *J* = 17.2, 10.4, 5.8), 5.38 (d, 1H, *J* = 17.2, 1.2), 5.30 (d, 1H, *J* = 10.4, 1.2), 4.66 (d, 2H, *J* = 5.8), 4.38 (t, 2H, *J* = 7.7), 3.81 (d, 2H, *J* = 7.7), 2.20–2.00 (m, 4H), 1.50–1.40 (m, 2H), 1.40–1.20 (m, 6H), 1.01 (t, 3H, *J* = 7.6), 0.87 (t, 3H, *J* = 6.9); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.9, 153.6, 132.6, 131.8, 131.1, 119.5, 69.3, 62.7, 45.9, 31.7, 29.6, 29.5, 27.4, 22.7, 22.2, 14.2, 12.1; HRMS for $C_{17}H_{28}NO_5$ $[M+H]^+$ found 326.1935, calc. 326.1962.

3.3 Decarboxylative Allylic Alkylation

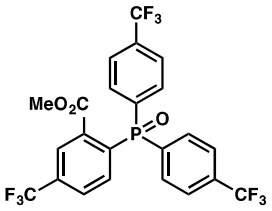
3.3.1 Ligand Synthesis





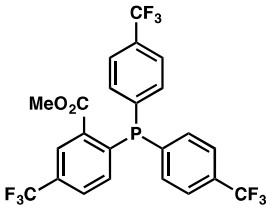
Methyl 2-bromo-5-(trifluoromethyl)benzoate (S2)

To an oven-dried round-bottom flask and magnetic stir bar was added 2-bromo-5-(trifluoromethyl)benzoic acid **(S1)**[12] (1.91 g, 7.10 mmol) followed by anhydrous DMF (20.0 mL). The solution was stirred under nitrogen at room temperature. Solid potassium carbonate (1.08 g, 7.81 mmol) was added in one portion followed by methyl iodide (0.53 mL, 8.52 mmol) dropwise by syringe. The reaction was stirred at room temperature for 16h. Afterward, the reaction mixture was poured into water (300 mL) and extracted with ethyl acetate (3 x 80 mL). The combined organic layers were washed with brine (50 mL), dried with sodium sulfate, filtered and concentrated in vacuo to afford the product (1.83 g, 91% yield), which was not purified further. Characterization data matched literature values:[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.59 –7.56 (m, 1H), 3.97 (s, 3H).



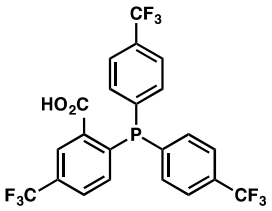
Methyl 2-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-5-(trifluoromethyl)benzoate (S3)

Procedure adapted from Stankevič and Włodarcyk.[14] To an oven dried Schlenk tube equipped with a magnetic stir bar was added CuI (0.145 g, 0.761 mmol). The tube was purged with nitrogen and (*S*)-α-phenylethylamine (0.100 mL, 0.760 mmol) was added with a micro-syringe followed by **S2** (1.09 g, 3.8 mmol) dissolved in toluene (19.0 mL) with a syringe. The reaction mixture was stirred under nitrogen for 5 minutes at room temperature. Bis(4-(trifluoromethyl)phenyl)phosphine oxide[Error! Bookmark not defined.] (1.30 g, 3.84 mmol) was added to the reaction mixture in one portion and stirring continued for five minutes. Potassium carbonate (1.05 g, 7.60 mmol) was added to the reaction mixture and the tube was sealed with a Teflon cap and electrical tape and heated to 110 °C behind a blast shield for 24 hours. The mixture was cooled to room temperature and the mixture was filtered through a pad of celite, eluting with dichloromethane. This mixture was concentrated in vacuo and purified by flash chromatography (30:70 to 35/65, EtOAc/hexanes) to provide the product as an amorphous white solid (1.61 g, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.22 (m, 1H), 7.95 – 7.87 (m, 2H), 7.84 – 7.73 (m, 8H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7 (d, *J* = 2.5 Hz), 136.7 – 136.6 (m), 136.2 (d, *J* = 6.3 Hz), 135.8 (d, *J* = 10.4 Hz), 135.8 (m), 134.9 (qd, *J* = 34.2, 2.4 Hz), 134.2 (qd, *J* = 32.9, 3.0 Hz), 132.3 (d, *J* = 10.4 Hz), 128.5 (dq, *J* = 11.9, 3.6 Hz), 127.9 (dq, *J* = 7.2, 3.5 Hz), 125.7 (dq, *J* = 12.8, 3.7 Hz), 123.5 (q, *J* = 272.6 Hz), 123.0 (q, *J* = 273.1 Hz), 53.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.2, -63.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 28.7; IR (Neat Film, NaCl) 1737, 1440, 1324, 1269, 1131, 715 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{15}F_9O_3P$ $[M+H]^+$: 541.0610, found 541.0616.



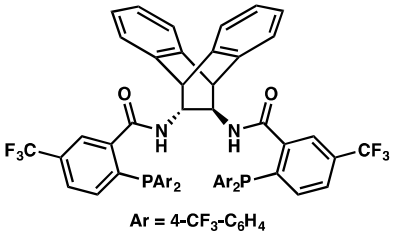
Methyl 2-(bis(4-(trifluoromethyl)phenyl)phosphanyl)-5-(trifluoromethyl)benzoate (S4)

To an oven-dried Schlenk flask equipped with a magnetic stir bar was added **S3** (0.650 g, 1.20 mmol) in toluene (17.5 mL). The mixture was stirred under flow of nitrogen at room temperature. Triethylamine (0.730 mL, 5.22 mmol) was added to the reaction mixture followed by trichlorosilane (0.510 mL, 5.04 mmol) with a syringe. At this stage, the reaction mixture was heated to 110 °C behind a blast shield for 16 hours. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (40 mL), and quenched with a solution of saturated sodium bicarbonate (0.5 mL). The mixture was filtered through celite and eluted with ethyl acetate followed by drying with sodium sulfate. The mixture was filtered, concentrated in vacuo and purified by flash chromatography (2:98 to 4:96, EtOAc/hexanes) to provide the product as a slightly yellow oil that solidified at –20 °C and remained solid at room temperature (0.55 g, 87% yield). The purified product slowly oxidizes in the time it takes to characterize; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (ddt, *J* = 3.6, 2.1, 0.7 Hz, 1H), 7.68 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.64 – 7.59 (m, 4H), 7.36 (dddd, *J* = 7.3, 6.5, 1.7, 0.8 Hz, 4H), 7.02 (ddt, *J* = 8.1, 3.3, 0.7 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (d, *J* = 2.4 Hz), 143.9 (d, *J* = 29.8 Hz), 141.4 (d, *J* = 13.7 Hz), 135.8 (d, *J* = 10.5 Hz), 134.9, 134.2 (d, *J* = 21.3 Hz), 131.5 (q, *J* = 32.6 Hz), 131.5 (q, *J* = 33.2 Hz), 128.9 (q, *J* = 3.5 Hz), 128.1 – 127.8 (m), 125.7 (dq, *J* = 7.5, 3.7 Hz), 124.0 (q, *J* = 272.4 Hz), 123.5 (q, *J* = 272.7 Hz), 53.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9, –63.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ –5.0; IR (Neat Film, NaCl) 1723, 1324, 1257, 1128, 832 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{15}F_9O_2P$ $[M+H]^+$: 525.0660, found 525.0646.



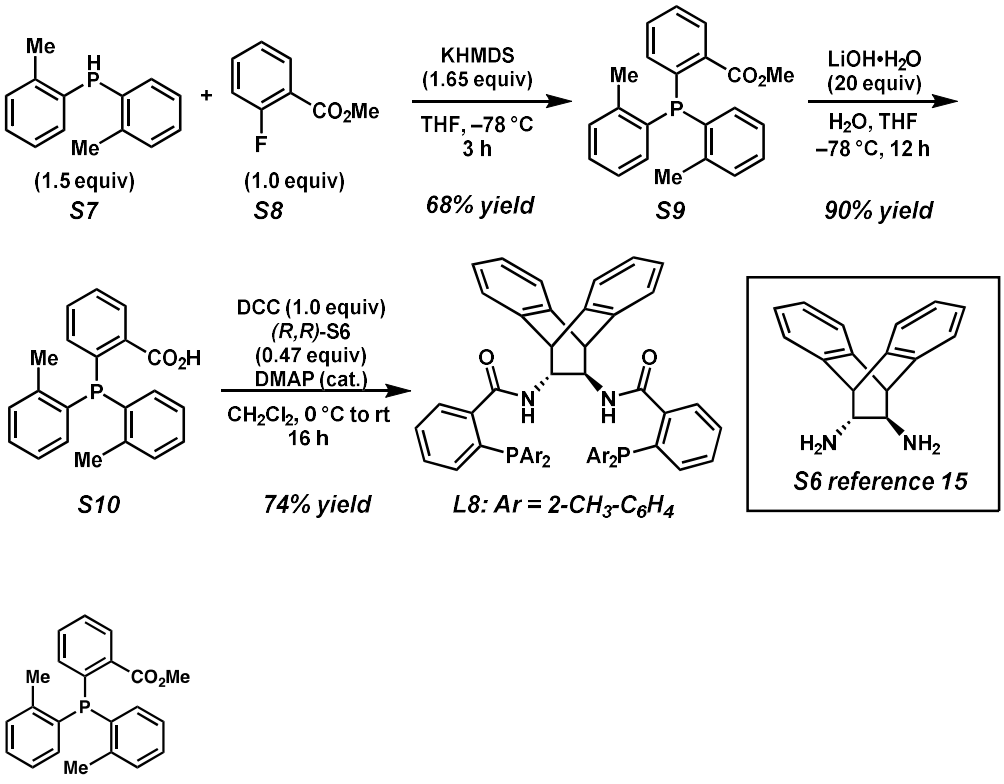
2-(Bis(4-(trifluoromethyl)phenyl)phosphanyl)-5-(trifluoromethyl)benzoic acid (S5)

Compound **S4** (0.550 g, 1.05 mmol) was charged into a round bottom flask equipped with a magnetic stir bar and was dissolved in THF (4.2 mL) at room temperature. Water (4.2 mL) was added to this solution followed by lithium hydroxide monohydrate (0.882 g, 21.0 mmol). The reaction mixture was sealed with a Teflon cap, stirred and heated to 70 °C for 12 hours. The mixture was cooled to room temperature and diluted with ethyl acetate (50 mL). This mixture was added to a 10% aqueous citric acid solution (50 mL) and this phase was extracted with ethyl acetate (2 x 50 mL). The combined organic phases were washed with brine, dried with sodium sulfate, filtered and concentrated in vacuo. The crude material was purified by flash chromatography (3:97 to 5:95, MeOH:CH_2Cl_2) to provide the product as a white amorphous solid (0.492 g, 92% yield); ^{1}H NMR (300 MHz, CD_3OD) δ 8.39 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.07 (dd, *J* = 8.1, 3.4 Hz, 1H); ^{13}C NMR (126 MHz, CD_3OD) δ 168.5 (d, *J* = 5.1 Hz), 145.4 (d, *J* = 30.2 Hz), 143.9 (d, *J* = 14.6 Hz), 137.2 (d, *J* = 20.7 Hz), 136.0, 135.5 (d, *J* = 21.6 Hz), 132.1 (q, *J* = 32.3 Hz), 132.1 (q, *J* = 33.0 Hz), 129.5 (q, *J* = 3.4 Hz), 128.7 – 128.5 (m), 126.5 (dq, *J* = 7.4, 3.7 Hz), 125.5 (q, *J* = 271.5 Hz), 125.1 (q, *J* = 271.6 Hz); ^{19}F NMR (282 MHz, cd_3od) δ -64.3, -64.5; ^{31}P NMR (121 MHz, MeOD) δ -4.9; IR (Neat Film, NaCl) 1698, 1324, 1127, 832 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{11}F_9O_2P$ $[M-H]^-$: 509.0358, found 509.0369.



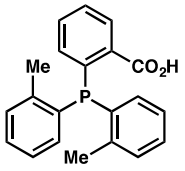
Electron deficient *C*$_2$-symmetric ligand (L7)

To an oven-dried flask equipped with a magnetic stir bar was added chiral diamine **S6**[15] (0.035 g, 0.149 mmol) and dichloromethane (2.6 mL) at room temperature under nitrogen. Benzoic acid **S5** (0.160 g, 0.313 mmol) was added to the reaction and an insoluble mixture was formed. The reaction mixture was cooled to 0 °C and a single crystal of DMAP was added. DCC (0.065 g, 0.313 mmol) was added in one portion and the mixture was slowly allowed to warm to room temperature overnight (12 hours). At this time, the cloudy mixture was filtered through celite, eluting with dichloromethane, and concentrated. The crude material was suspended in a small amount of diethylether and filtered once again through a pad of celite. This mixture was concentrated and purified by flash chromatography (8:92 to 10:90, EtOAc:hexanes) to provide the product as a white amorphous solid (0.116 g, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 8H), 7.56 (d, *J* = 8.0 Hz, 4H), 7.40 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.34 – 7.28 (m, 10H), 7.25 – 7.15 (m, 4H), 7.08 (dd, *J* = 8.1, 3.1 Hz, 2H), 5.82 (d, *J* = 7.7 Hz, 2H), 4.49 (d, *J* = 2.4 Hz, 2H), 4.15 – 4.08 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 141.7 (d, *J* = 28.3 Hz), 141.1 (dd, *J* = 25.5, 14.6 Hz), 140.6 , 140.3 (d, *J* = 25.0 Hz), 138.5, 135.5, 133.9 (dd, *J* = 20.8, 7.0 Hz), 131.9 (q, *J* = 33.3 Hz), 131.5 (qd, *J* = 32.6, 1.3 Hz), 127.5 (q, *J* = 3.4 Hz), 127.4, 127.1, 125.9, 125.7 (dt, *J* = 6.9, 3.6 Hz), 125.3, 124.3 – 123.9 (m), 123.97 (qd, *J* = 272.3, 5.8 Hz), 123.3 (q, *J* = 272.8 Hz), 57.8, 48.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9, –62.9, –63.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ –10.70; IR (Neat Film, NaCl) 1659, 1509, 1397, 1325, 1172, 1130, 1061, 832 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{60}H_{37}F_{18}N_2O_2P_2$ $[M+H]^+$: 1221.2037, found 1221.2039; $[\alpha]^{25}$ –55.0 (*c* 3.17 $CHCl_3$).



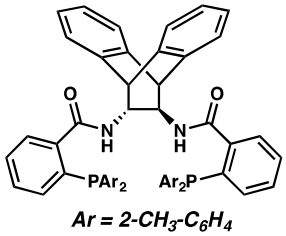
Methyl 2-(di-*o*-tolylphosphanyl)benzoate (S9)

In a nitrogen filled glove box, an oven-dried round-bottom flask equipped with a magnetic stir bar was charged with di-(*o*-tolyl)phosphine (**S7**) (0.321 g, 1.50 mmol). The flask was sealed with a cap equipped with a septa and electrical tape and removed from the glove box. The flask was then charged with THF (8.0 mL) under positive nitrogen pressure. This mixture was cooled to –78 °C in a dry ice/acetone bath. A freshly prepared solution of KHMDS (2.00 mL, 1.65 mmol, 0.825 M) was added to the mixture dropwise by syringe. The reaction mixture was stirred at this temperature for 30 min and then warmed to room temperature. Methyl-2-fluorobenzoate (**S8**) (0.13 mL, 1.0 mmol) was added dropwise and the mixture was stirred for 2.5 hours. A precipitate formed and the reaction turned black in color. The mixture was quenched and diluted with water (10 mL). The aqueous phase was extracted with ethyl acetate (3 x 30 mL) and the combined organic layers were dried with sodium sulfate, filtered and evaporated in vacuo. The crude material was purified by flash chromatography (5:95, EtOAc:hexanes) to provide the product as a white amorphous solid (0.238 g, 68% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (ddd, J = 7.2, 3.9, 1.8 Hz, 1H), 7.42 (pd, J = 7.4, 1.7 Hz, 2H), 7.33 – 7.21 (m, 4H), 7.08 (td, J = 7.0, 6.5, 2.3 Hz, 2H), 6.97 (ddt, J = 7.7, 3.6, 1.6 Hz, 1H), 6.75 (ddd, J = 7.5, 4.3, 1.2 Hz, 2H), 3.77 (s, 3H), 2.44 (d, J = 1.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3 (d, J = 1.9 Hz), 142.6 (d, J = 27.7 Hz), 139.5 (d, J = 25.4 Hz), 136.1 (d, J = 11.4 Hz), 134.9 (d, J = 20.3 Hz), 134.5, 133.2, 132.2, 131.0 (d, J = 3.0 Hz), 130.2 (d, J = 4.8 Hz), 128.8, 128.4, 126.2, 52.2, 21.4 (d, J = 22.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ –20.4; IR (Neat Film, NaCl) 3055, 1721, 1452, 1269, 1107, 749 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{22}O_2P$ $[M+H]^+$: 349.1352, found 349.1362.



2-(Di-*o*-tolylphosphanyl)benzoic acid (S10)

Compound **S9** (0.238 g, 0.683 mmol) was charged into a round bottom flask equipped with a magnetic stir bar and was dissolved in THF (2.8 mL) at room temperature. Water (2.8 mL) was added to this solution followed by lithium hydroxide monohydrate (0.574 g, 13.7 mmol). The reaction mixture was sealed with a Teflon cap, stirred and heated to 70 °C for 12 hours. The mixture was cooled to room temperature and diluted with ethyl acetate (30 mL). This mixture was added to a 10% aqueous citric acid solution (50 mL) and this phase was extracted with ethyl acetate (2 x 30 mL). The combined organic phases were washed with brine, dried with sodium sulfate, filtered and concentrated in vacuo. The crude material was purified by flash chromatography (40:60, EtOAc:hexanes) to provide the product as a white amorphous solid (0.205 g, 90% yield). Characterization data matched literature values.[16] ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.14–8.20 (m, 1H), 7.38–7.45 (m, 2H), 7.18–7.27 (m, 4H), 7.05 (t, J = 7.5 Hz, 2H), 6.96–7.01 (m, 1H), 6.68–6.72 (m, 2H), 2.40 (s, 6H); HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{18}O_2P$ $[M-H]^-$: 333.1044, found 333.1050.



Sterically hindered *C*$_2$-symmetric ligand (L8)

To an oven-dried flask equipped with a magnetic stir bar was added **S6**[Error! Bookmark not defined.] (0.050 g, 0.212 mmol) and dichloromethane (3.0 mL) at room temperature under nitrogen. Benzoic acid **S10** (0.150 g, 0.450 mmol) was added to the reaction and an insoluble mixture was formed. The reaction mixture was cooled to 0 °C and a single crystal of DMAP was added. DCC (0.093 g, 0.45 mmol) was added all at once and the mixture was slowly allowed to warm to room temperature overnight (12 hours). At this time, the cloudy mixture was filtered through celite, eluting with dichloromethane, and concentrated. The crude material was suspended in a small amount of diethylether and filtered once again through a pad of celite. This mixture was concentrated and purified by flash chromatography (20:80 to 40:60, Et_2O:pentane) to provide the product as a white amorphous solid (0.136 g, 74% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.39 – 7.20 (m, 14H), 7.15 – 7.06 (m, 4H), 7.04 – 6.93 (m, 6H), 6.88 (ddd, *J* = 7.5, 4.2, 1.3 Hz, 2H), 6.75 – 6.68 (m, 2H), 6.65 (dd, *J* = 7.6, 4.3 Hz, 2H), 5.74 (d, *J* = 7.1 Hz, 2H), 4.36 (s, 2H), 3.83 (d, *J* = 7.0 Hz, 2H), 2.35 (d, *J* = 4.6 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1 (d, *J* = 1.8 Hz), 142.6 – 142.2 (m), 141.0, 138.7, 135.3 (d, *J* = 10.8 Hz), 134.9, 134.2 (d, *J* = 18.4 Hz), 132.9 (d, *J* = 62.2 Hz), 130.5 (dd, *J* = 14.7, 4.6 Hz), 130.4, 129.2, 128.9 (d, *J* = 10.1 Hz), 128.0 (d, *J* = 6.1 Hz), 126.7 (d, *J* = 11.0 Hz), 126.4 (d, *J* = 30.4 Hz), 125.9, 124.8, 57.9, 48.6, 21.5 (dd, *J* = 21.6, 9.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ –26.5; IR (Neat Film, NaCl) 3054, 1658, 1501, 908, 748 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{58}H_{51}N_2O_2P_2$ $[M+H]^+$: 869.3420, found 869.3433; $[\alpha]^{25}$ –84.1 (*c* 1.83, $CHCl_3$).

3.3.2 Exploratory Allylic Alkylation Screen

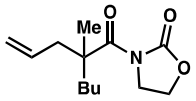
Initially, we ran a series of screens to determine the best combination of ligand and solvent that provided the highest %ee for the allylic alkylation. The following procedure was followed to conduct these screens. This procedure is similar to that previously used by the Stoltz group.[17] To separate enantiomers, the allylic alkylation products were derivitized using a cross metathesis with Grubbs-second generation catalyst and methyl acrylate. This procedure is similar to that previously used by the Stoltz group.[18]

General Screening Procedure (from Table S1 and Table S2):

In a nitrogen-filled glove box, 38.0 mg $Pd(dba)_2$ was taken up in 10 mL THF. To each of 16 half-dram vials, 0.5 mL of this solution (1.90 mg $Pd(dba)_2$, 1.65 μmol, 0.100 equiv) was added. The THF was then removed by evacuation using a Genevac centrifugal evaporator within the glove box. To each of the vials was then added 500 μL of the reaction solvent followed by a small stirring bar. Stock solutions of ligand (0.0165 M) were made in each reaction solvent. From these ligand stock solutions, 250 μL (4.13 μmol, 0.125 equiv) were added to the corresponding reaction vials. The resulting catalyst solutions were stirred in the glove box for 30 minutes at the indicated reaction temperature. Stock solutions of reaction substrate (0.132 M) were made in each reaction solvent. To the stirring catalyst solutions were added 250 μL (33.0 μmol, 1.00 equiv) of the corresponding substrate solution, resulting in a final reaction volume of 1.00 mL (0.033 M with respect to substrate). The reactions were sealed with a Teflon-lined cap and stirred for the indicated reaction duration. The reactions were then removed from the glove box, diluted with 1 mL hexanes and filtered through a silica plug, concentrated in vacuo, taken up in $CDCl_3$ and analyzed by crude ^1H NMR to determine conversion.

The crude reaction mixtures in $CDCl_3$ were concentrated *in vacuo* in half-dram vials and returned to the glove box. To each half-dram vial was added 500 μL of methyl acrylate solution in CH_2Cl_2 (0.66 M, 0.33 mmol, 10 equiv) was added, followed by a small stir bar. The reactions were stirred for approximately 15 minutes. To the resulting solutions were added 500 μL each of a Grubb's second-generation Ru catalyst solution in CH_2Cl_2 (0.004 M, 2 μmol, 0.06 equiv). The reactions were then stirred at 40 °C for 3 hours, removed from the glove box, filtered through a silica plug, concentrated in vacuo and analyzed by crude ^1H NMR to determine conversion and chiral SFC to determine enantiomeric excess. SFC conditions for each substrate can be found in a table at the end of the text portion of the SI.

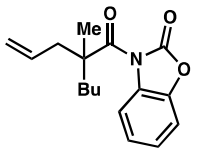
2.3.2.1 Characterization data for 5ab and 5c



3-(2-Allyl-2-methylhexanoyl)oxazolidin-2-one (5ab)

Prepared from **3a or 3b** and **L6** (Table S1, entries 6, 7, 13, 14):

^1H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.10 – 5.01 (m, 2H), 4.42 – 4.34 (m, 2H), 4.09 – 3.98 (m, 2H), 2.92 – 2.84 (m, 1H), 2.36 (ddt, *J* = 14.1, 7.2, 1.2 Hz, 1H), 2.10 (ddd, *J* = 13.7, 11.9, 4.6 Hz, 1H), 1.67 (ddd, *J* = 13.6, 12.4, 4.3 Hz, 1H), 1.31 (s, 3H), 1.30 – 1.19 (m, 3H), 1.15 – 1.03 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 152.4, 134.5, 117.8, 62.3, 49.0, 45.4, 41.0, 35.8, 27.0, 23.2, 22.5, 14.1; IR (Neat Film, NaCl) 2958, 2928, 1777, 1685, 1382, 1200 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{13}H_{22}NO_3$ $[M+H]^+$: 240.1600, found 240.1601.

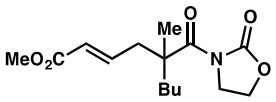


1-(2-Allyl-2-methylhexanoyl)indolin-2-one (5c)

Prepared from **3c** and **L6** (Table S1, entry 16):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 1H), 7.24 – 7.17 (m, 3H), 5.80 – 5.68 (m, 1H), 5.12 – 5.03 (m, 1H), 5.05 – 5.00 (m, 1H), 2.97 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.48 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.18 (td, *J* = 12.6, 11.4, 4.3 Hz, 1H), 1.78 (td, *J* = 14.1, 3.8 Hz, 1H), 1.43 (s, 3H), 1.35 – 1.23 (m, 3H), 1.23 – 1.11 (m, 1H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 150.5, 143.0, 133.9, 129.4, 125.0, 124.6, 118.7, 116.1, 109.9, 50.5, 41.2, 36.1, 27.0, 23.3, 22.4, 14.1; IR (Neat Film, NaCl) 2958, 2932, 1795, 1479, 1299, 1027, 757 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}NO_3$ $[M+H]^+$: 288.1600, found 288.1603.

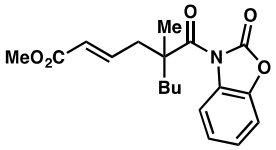
3.3.2.2 Characterization data for 6ab and 6c.



Methyl (*E*)-5-methyl-5-(2-oxooxazolidine-3-carbonyl)non-2-enoate (6ab)

Prepared from **3ab** and **L6** (Table S1, entries 6, 7, 13, 14):

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.86 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.40 (t, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 3.01 (ddd, *J* = 14.5, 7.6, 1.5 Hz, 1H), 2.51 (ddd, *J* = 14.5, 7.9, 1.4 Hz, 1H), 2.01 (ddd, *J* = 13.8, 11.9, 4.8 Hz, 1H), 1.76 (ddd, *J* = 13.8, 12.1, 4.7 Hz, 1H), 1.34 (s, 3H), 1.31 – 1.24 (m, 2H), 1.24 – 1.07 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 166.8, 152.5, 145.4, 123.9, 62.4, 51.6, 49.0, 45.4, 39.8, 35.8, 27.0, 23.2, 22.4, 14.1; IR (Neat Film, NaCl) 2931, 2957, 1778, 1723, 1688, 1274, 1197 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{24}NO_5$ $[M+H]^+$: 298.1654, found 298.1650.



Methyl (*E*)-5-methyl-5-(2-oxo-2,3-dihydrobenzo[*d*]oxazole-3-carbonyl)non-2-enoate (6c)

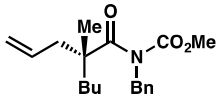
Prepared from **3c** and **L6** (Table S1, entry 16):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.26 – 7.19 (m, 3H), 6.90 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.90 (dt, *J* = 15.5, 1.4 Hz, 1H), 3.70 (s, 3H), 3.08 (ddd, *J* = 14.3, 7.5, 1.4 Hz, 1H), 2.66 (ddd, *J* = 14.3, 7.9, 1.4 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.94 – 1.84 (m, 1H), 1.46 (s, 3H), 1.36 – 1.14 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 166.6, 150.5, 144.5, 143.0, 129.2, 125.2, 124.8, 124.4, 116.2, 110.0, 51.7, 50.3, 39.9, 36.0, 27.0, 23.1, 22.0, 14.0; IR (Neat Film, NaCl) 2256, 1796, 1722, 1479, 1272, cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{24}NO_5$ $[M+H]^+$: 346.1654, found 346.1650.

3.3.3 Allylic Alkylation Substrate Library

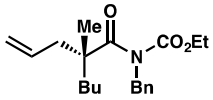
Representative Procedure H. (Compounds 5)

Unless otherwise noted, the allylic alkylation reactions proceeded as follows: Outside of a glove box, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with $Pd(dba)_2$ (2.3 mg, 4.0 μmol, 4 mol %). A second oven-dried two-dram vial was charged with allylenolcarbonate **3d**–**3q** (0.1 mmol). Finally, a third oven-dried 2-dram vial was charged with C-2 symmetric ligand **L6** or **L7** (7.0 μmol). These three uncapped vials were brought into a nitrogen-filled glove box through a small antechamber with 4 x 5 minute vacuum cycles with nitrogen back-filling. To the vial containing compounds **3d**–**3q** was added or THF (0.3 mL) unless otherwise noted. To the vial containing C-2 symmetric ligand (**L6** or **L7**) was added THF (0.3 ml) unless otherwise noted. To the vial containing $Pd(dba)_2$ and a magnetic stir bar was added the entirety of the ligand solution and the reaction was capped, cooled to 20 °C and stirred for 30 min to form the catalyst. At this time, the entirety of the solution containing the substrate (**3d**–**3q**) were added to the catalyst mixture dropwise and the reactions were allowed to stir at 20 °C for 24h. The reaction mixtures were removed from the glove box through the small antechamber and diluted with hexanes (1mL). The mixture was filtered through a short plug of silica gel and eluted with ethyl acetate. The crude material was concentrated and purified by preparative TLC (EtOAc:hexanes mixtures) to provide the products as clear to slightly yellow oils (53–88% yield). Purified products were converted to the corresponding methyl acrylate species via cross metathesis for SFC analysis.



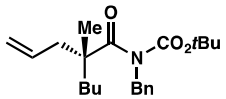
Methyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5d)

Representative Procedure H. Compound **5d** was prepared from allylenolcarbonate **3d** using General Procedure G (27.0 mg, 85% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 5H), 5.63 – 5.53 (m, 1H), 5.03 – 4.93 (m, 2H), 4.76 (s, 2H), 3.76 (s, 3H), 2.58 (ddt, *J* = 13.7, 7.2, 1.3 Hz, 1H), 2.27 (ddt, *J* = 13.7, 7.6, 1.2 Hz, 1H), 1.78 (ddd, *J* = 13.4, 12.3, 4.5 Hz, 1H), 1.52 (ddd, *J* = 13.3, 12.4, 4.5 Hz, 1H), 1.27 – 1.14 (m, 2H), 1.19 (s, 3H), 1.16 – 1.04 (m, 1H), 1.06 – 0.91 (m, 1H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 155.6, 137.8, 134.6, 128.5, 128.3, 127.5, 117.8, 53.5, 50.6, 50.54, 44.1, 39.6, 26.8, 23.4, 22.5, 14.1; IR (Neat Film, NaCl) 2932, 2872, 1738, 1681, 1444, 1156, 998, 916 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{28}NO_3$ $[M+H]^+$: 318.2064, found 318.2064; $[\alpha]^{25}$ –2.36 (*c* 2.40, $CHCl_3$, 92% ee).



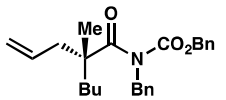
Ethyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5e)

Representative Procedure H. Compound **5e** was prepared from allylenolcarbonate **3e** using General Procedure G (20.5 mg, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.12 (m, 5H), 5.56 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.02 – 4.87 (m, 2H), 4.72 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.57 (ddd, *J* = 13.7, 7.1, 1.3 Hz, 1H), 2.25 (ddd, *J* = 13.7, 7.1, 1.3 Hz, 1H), 1.76 (td, *J* = 12.9, 4.5 Hz, 1H), 1.50 (td, *J* = 12.9, 4.5 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.20 – 1.13 (m, 2H), 1,17 (s, 3H), 1.12 – 1.02 (m, 1H), 1.02 – 0.92 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.1, 155.2, 138.0, 134.7, 128.4, 128.3, 127.4, 117.8, 63.0, 50.6, 50.5, 44.1, 39.5, 26.8, 23.4, 22.5, 14.3, 14.1; IR (Neat Film, NaCl) 2958, 2872, 1738, 1693, 1455, 1376, 1345, 1206, 1018 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{30}NO_3$ $[M+H]^+$: 332.2220, found 332.2219; $[\alpha]^{25}$ –3.19 (*c* 1.70, $CHCl_3$, 94% ee).



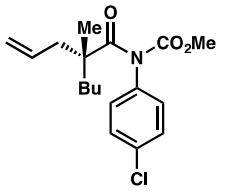
***tert*-Butyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5f)**

Representative Procedure H. Compound **5f** was prepared from allylenolcarbonate **3f** using General Procedure G (10.8 mg, 88% yield, 0.034mmol scale): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 5H), 5.73 – 5.60 (m, 1H), 5.07 – 4.95 (m, 2H), 4.71 (s, 2H), 2.66 (ddt, *J* = 13.6, 7.2, 1.3 Hz, 1H), 2.32 (ddt, *J* = 13.5, 7.6, 1.2 Hz, 1H), 1.84 (ddd, *J* = 13.3, 12.0, 4.4 Hz, 1H), 1.56 (ddd, *J* = 13.2, 12.4, 4.5 Hz, 1H), 1.36 (s, 9H), 1.28 – 1.20 (m, 2H), 1.26 (s, 3H), 1.20 – 1.12 (m, 1H), 1.07 (dddd, *J* = 15.0, 12.6, 7.3, 4.3 Hz, 1H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.3, 153.9, 138.5, 134.9, 128.4, 128.1, 127.3, 117.7, 82.7, 50.8, 50.3, 44.1, 39.5, 27.9, 26.9, 23.4, 22.5, 14.2; IR (Neat Film, NaCl) 2958, 2931, 2872, 1736, 1682, 1368, 1212, 987, 699 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{22}H_{34}NO_3$ $[M+H]^+$: 360.2539, found 360.2527; $[\alpha]^{25}$ -2.89 (*c* 0.8, $CHCl_3$, 90% ee).



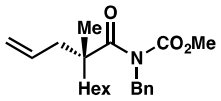
Benzyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5g)

Representative Procedure H. Compound **5g** was prepared from allylenolcarbonate **3g** using General Procedure G (21.0 mg, 53% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 –7.31 (m, 3H), 7.28 – 7.20 (m, 7H), 5.61 – 5.51 (m, 1H), 5.15 (s, 2H), 4.97 – 4.93 (m, 1H), 4.93 – 4.91 (m, 1H), 4.78 (s, 2H), 2.58 (ddt, *J* = 13.6, 7.1, 1.2 Hz, 1H), 2.25 (ddt, *J* = 13.6, 7.7, 1.2 Hz, 1H), 1.75 (ddd, *J* = 13.3, 12.1, 4.4 Hz, 1H), 1.50 (ddd, *J* = 13.3, 12.4, 4.4 Hz, 1H), 1.18 (s, 3H), 1.16 – 1.12 (m, 2H), 1.10 – 1.02 (m, 1H), 1.02 – 0.91 (m, 1H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.1, 155.0, 137.9, 135.0, 134.6, 128.7, 128.7, 128.7, 128.5, 128.3, 127.5, 117.8, 68.7, 50.7, 50.6, 44.0, 39.4, 26.8, 23.3, 22.5, 14.1; IR (Neat Film, NaCl) 3067, 2957, 2932, 2872, 1732, 1696, 1456, 1386, 1347, 1192 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{25}H_{32}NO_3$ $[M+H]^+$: 394.2377, found 394.2376; $[\alpha]^{25}$ –3.88 (*c* 1.91, $CHCl_3$, 93% ee).



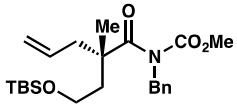
Methyl (*R*)-(2-allyl-2-methylhexanoyl)(4-chlorophenyl)carbamate (5h)

Representative Procedure H. Compound **5h** was prepared from allylenolcarbonate **3h** using General Procedure G (20.7 mg, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.14 – 7.10 (m, 2H), 5.77 – 5.66 (m, 1H), 5.09 – 5.00 (m, 2H), 3.75 (s, 3H), 2.54 (ddt, *J* = 13.8, 7.2, 1.3 Hz, 1H), 2.28 (ddt, *J* = 13.8, 7.5, 1.2 Hz, 1H), 1.76 – 1.65 (m, 1H), 1.55 – 1.47 (m, 1H), 1.29 – 1.20 (m, 4H), 1.19 (s, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 154.8, 137.1, 134.0, 133.9, 129.5, 129.3, 118.5, 53.8, 51.0, 43.4, 39.1, 26.6, 23.3, 22.9, 14.1; IR (Neat Film, NaCl) 2957, 2933, 1742, 1731, 1491, 1439, 1245, 1091 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{25}NO_3Cl$ $[M+H]^+$: 338.1523, found 338.1531; $[\alpha]^{25}$ 2.64 (*c* 1.9, $CHCl_3$, 90% ee).



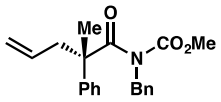
Methyl (*R*)-(2-allyl-2-methyloctanoyl)(benzyl)carbamate (5i)

Representative Procedure H. Compound **5i** was prepared from allylenolcarbonate **3i** using General Procedure G (24.0 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 5.58 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.02 – 4.94 (m, 2H), 4.76 (s, 2H), 3.76 (s, 3H), 2.58 (ddt, *J* = 13.7, 7.0, 1.2 Hz, 1H), 2.27 (ddt, *J* = 13.6, 7.6, 1.2 Hz, 1H), 1.77 (ddd, *J* = 13.3, 12.0, 4.4 Hz, 1H), 1.51 (ddd, *J* = 13.3, 12.0, 4.4 Hz, 1H), 1.19 (s, 3H), 1.28 – 1.14 (m, 6H), 1.16 – 1.06 (m, 1H), 1.05 – 0.95 (m, 1H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.88, 155.63, 137.81, 134.58, 128.45, 128.30, 127.49, 117.79, 53.54, 50.60, 50.57, 44.12, 39.90, 31.79, 29.97, 24.52, 22.73, 22.45, 14.22; IR (Neat Film, NaCl) 3067, 2950, 2930, 2858, 1738, 1694, 1455, 1445, 1351, 1208, 1000 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{32}NO_3$ $[M+H]^+$: 346.2377, found 346.2375; $[\alpha]^{25}$ –2.14 (*c* 2.18, $CHCl_3$, 94% ee).



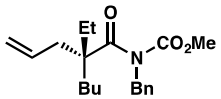
Methyl (*S*)-benzyl(2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-methylpent-4-enoyl)carbamate (5j)

Representative Procedure H. Compound **5j** was prepared from allylenolcarbonate **3j** using General Procedure G (32.1 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 5H), 5.52 (ddt, *J* = 17.2, 10.1, 7.3 Hz, 1H), 4.99 – 4.90 (m, 2H), 4.74 (s, 2H), 3.73 (s, 3H), 3.54 – 3.44 (m, 2H), 2.58 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.27 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.84 – 1.76 (m, 1H), 1.20 (s, 3H), 0.83 (d, *J* = 0.7 Hz, 9H), -0.03 (d, *J* = 1.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.1, 155.5, 137.8, 134.3, 128.5, 128.2, 127.5, 118.1, 59.9, 53.6, 50.6, 49.2, 44.5, 41.9, 26.1, 22.7, 18.4, –5.2, –5.2; IR (Neat Film, NaCl) 2955, 2929, 2857, 1741, 1686, 1444, 1351, 1207, 1095, 837 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{23}H_{38}NO_3$ $[M+H]^+$: 420.2570, found 420.2541; $[\alpha]^{25}$ – 6.23 (*c* 2.91, $CHCl_3$, 94% ee).



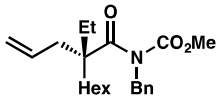
Methyl (*S*)-benzyl(2-methyl-2-phenylpent-4-enoyl)carbamate (5k)

Representative Procedure H. Compound **5k** was prepared from allylenolcarbonate **3k** using General Procedure G (26.0 mg, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.30 – 7.23 (m, 3H), 7.20 – 7.15 (m, 1H), 7.06 – 7.01 (m, 2H), 5.34 (dddd, *J* = 16.8, 10.3, 8.1, 6.5 Hz, 1H), 4.95 (ddt, *J* = 8.7, 2.2, 1.2 Hz, 1H), 4.93 (h, *J* = 1.2 Hz, 1H), 4.88 (s, 2H), 3.22 (s, 3H), 2.90 (ddt, *J* = 13.7, 8.2, 1.0 Hz, 1H), 2.55 (ddt, *J* = 13.6, 6.6, 1.4 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 154.5, 143.7, 137.5, 134.3, 128.6, 128.5, 128.1, 127.6, 126.2, 125.9, 118.5, 54.0, 53.3, 50.1, 47.0, 23.8; IR (Neat Film, NaCl) 3064, 3007, 2954, 1755, 1674 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{23}NO_3$ $[M+H]^+$: 338.1751, found 338.1754; $[\alpha]^{25}$ + 71.01 (*c* 2.36, $CHCl_3$, 76% ee).



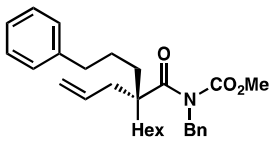
Methyl (*R*)-(2-allyl-2-ethylhexanoyl)(benzyl)carbamate (5l)

Representative Procedure H. Compound **5l** was prepared from allylenolcarbonate **3l** using General Procedure G (8.6 mg, 76% yield, 0.034 mmol scale). Note: this reaction was run in EtOAc and not THF; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 5H), 5.62 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.07 – 4.97 (m, 2H), 4.78 (s, 2H), 3.75 (s, 3H), 2.53 – 2.39 (m, 2H), 1.82 – 1.55 (m, 4H), 1.28 – 1.18 (m, 2H), 1.15 – 1.00 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7, 155.6, 137.9, 134.7, 128.5, 128.3, 127.5, 117.7, 54.0, 53.6, 50.8, 39.1, 35.0, 28.1, 26.7, 23.4, 14.1, 9.0; IR (Neat Film, NaCl) 2958, 2933, 2873, 1741, 1732, 1682, 1443, 1350, 1206, 699 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{29}NO_3$ $[M+H]^+$: 332.2220, found 332.2216; $[\alpha]^{25}$ +0.64 (*c* 0.7, $CHCl_3$, 82% ee).



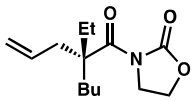
Methyl (*R*)-(2-allyl-2-ethyloctanoyl)(benzyl)carbamate (5m)

Representative Procedure H. Compound **5m** was prepared from allylenolcarbonate **3m** using General Procedure G (24.0 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 5H), 5.62 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.09 – 4.95 (m, 2H), 4.78 (s, 2H), 3.75 (s, 3H), 2.51 – 2.40 (m, 2H), 1.83 – 1.73 (m, 1H), 1.73 – 1.64 (m, 2H), 1.64 – 1.56 (m, 1H), 1.31 – 1.17 (m, 6H), 1.17 – 1.02 (m, 2H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7, 155.6, 137.9, 134.7, 128.5, 128.3, 127.5, 117.7, 54.0, 53.6, 50.8, 39.1, 35.3, 31.8, 30.0, 28.1, 24.4, 22.8, 14.2, 9.0; IR (Neat Film, NaCl)2956, 2872, 1739, 1685, 1443, 1350, 1206, 1183, 998 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{34}NO_3$ $[M+H]^+$: 360.2533, found 360.2530; $[\alpha]^{25}$ +1.25 (*c* 1.90, $CHCl_3$, 93% ee).



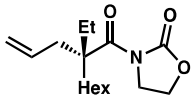
Methyl (*S*)-(2-allyl-2-(3-phenylpropyl)octanoyl)(benzyl)carbamate (5n)

Representative Procedure H. Compound **5n** was prepared from allylenolcarbonate **3n** using General Procedure G (22.4 mg, 56% yield, 0.089 mmol scale); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.09 (m, 10H), 5.61 – 5.52 (m, 1H), 5.01 – 4.98 (m, 1H), 4.97 –4.96 (m, 1H), 4.76 (s, 2H), 3.67 (s, 3H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.43 (dq, *J* = 7.4, 1.3 Hz, 2H), 1.79 – 1.37 (m, 6H), 1.29 – 1.13 (m, 6H), 1.13 – 0.96 (m, 2H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.5, 155.5, 142.4, 137.8, 134.6, 128.6, 128.4, 128.4, 128.3, 127.5, 125.8, 117.8, 53.6, 53.5, 50.8, 39.6, 36.5, 35.7, 35.1, 31.8, 30.0, 26.3, 24.3, 22.7, 14.2; IR (Neat Film, NaCl) 2954, 2930, 1738, 1682, 1444, 1350, 1205, 1176, 699 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{29}H_{40}NO_3$ $[M+H]^+$: 450.3003, found 450.2995; $[\alpha]^{25}$ –0.11 (*c* 2.0, $CHCl_3$, 76% ee).



(*R*)-3-(2-Allyl-2-ethylhexanoyl)oxazolidin-2-one (5o)

Representative Procedure H. Compound **5o** was prepared from allylenolcarbonate **3o** using General Procedure G (16.3 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.11 – 5.01 (m, 2H), 4.38 (dd, *J* = 8.4, 7.6 Hz, 2H), 4.04 (dd, *J* = 8.5, 7.6 Hz, 2H), 2.68 – 2.54 (m, 2H), 2.05 – 1.76 (m, 4H), 1.33 – 1.23 (m, 2H), 1.21 – 1.04 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 152.4, 134.5, 117.9, 62.3, 52.7, 45.6, 36.6, 31.8, 26.6, 25.1, 23.3, 14.2, 8.8; IR (Neat Film, NaCl) 3076, 2960, 2931, 2874, 1778, 1682, 1468, 1384, 1202 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{24}NO_3$ $[M+H]^+$: 254.1756, found 254.1756; $[\alpha]^{25}$ 0.02 (*c* 1.45, $CHCl_3$, 69% ee).



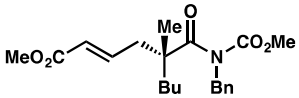
(*R*)-3-(2-Allyl-2-ethyloctanoyl)oxazolidin-2-one (5p)

Representative Procedure H. Compound **5p** was prepared from allylenolcarbonate **3p** using General Procedure G (20.1 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 – 5.58 (m, 1H), 5.14 – 4.96 (m, 2H), 4.38 (t, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 8.0 Hz, 2H), 2.70 – 2.48 (m, 2H), 2.05 – 1.73 (m, 4H), 1.33 – 1.05 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 152.4, 134.5, 117.9, 62.3, 52.8, 45.6, 36.6, 32.1, 31.8, 29.9, 25.1, 24.4, 22.8, 14.2, 8.8; IR (Neat Film, NaCl) 2958, 2926, 1779, 1682, 1467, 1383, 1228, 1194, 1107, 914 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{28}NO_3$ $[M+H]^+$: 282.2069, found 282.2078; $[\alpha]^{25}$ 0.21 (*c* 1.67, $CHCl_3$, 73% ee).

3.3.4 Cross Metathesis Procedure

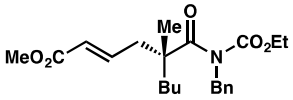
Representative Procedure I. (Compounds 6)

Unless otherwise noted, the cross metathesis procedure was executed as follows: The allylic alkylation substrates were loaded into a 2-dram vial equipped with a magnetic stirring bar and brought into a glove box. A solution of methacrylate (0.06M, 10 equiv.) in dichloromethane was added and the vial was capped with a Teflon lined screw-cap. The reaction mixture was stirred for 30 minutes. A solution of Grubbs generation II catalyst (6.6 mM, 5 mol %) in dichloromethane was added to the reaction. The mixture was sealed the cap and heated to 40 °C with stirring. After 3 hours, the reaction mixture was cooled to room temperature and removed from the glovebox. The reaction mixture was filtered through a silica plug, eluting with diethyl ether, and concentrated. The crude material was purified by preparative TLC (EtOAc/hexanes mobile phase) to afford the product, which was analyzed by SFC to determine the % ee of the allylic alkylation.



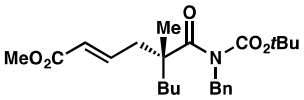
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6d)

Representative Procedure I. Compound **6d** was prepared using General Procedure H with **5d** (26.9 mg, 85 μmol) to afford a clear oil (25.5 mg, 80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 5H), 6.83 (dt, *J* = 15.5, 7.7 Hz, 1H), 5.81 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.77 (s, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.76 (ddd, *J* = 14.0, 7.6, 1.5 Hz, 1H), 2.44 (ddd, *J* = 14.0, 7.9, 1.4 Hz, 1H), 1.77 (ddd, *J* = 13.4, 12.2, 4.4 Hz, 1H), 1.55 (ddd, *J* = 13.4, 12.4, 4.6 Hz, 1H), 1.23 (s, 3H), 1.22 – 1.15 (m, 2H), 1.12 – 1.01 (m, 1H), 0.96 (ttd, *J* = 11.9, 7.4, 4.4 Hz, 1H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.0, 166.7, 155.5, 145.5, 137.6, 128.5, 128.2, 127.6, 123.8, 53.7, 51.6, 50.6, 50.6, 42.3, 39.7, 26.8, 23.3, 22.4, 14.1; IR (Neat Film, NaCl) 2957, 2872, 1726, 1686, 1439, 1350, 1272, 1195, 998 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{21}H_{33}N_2O_5$ $[M+NH_4]^+$: 393.2384, found 393.2376; $[\alpha]^{25}$ +12.17 (*c* 2.3, $CHCl_3$, 92% ee).



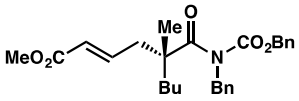
Methyl (*R*,*E*)-5-(benzyl(ethoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6e)

Representative Procedure I. Compound **6e** was prepared using General Procedure H with **5e** (17.4 mg, 53 μmol) to afford a clear oil (17.4 mg, 85% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 6.84 (dt, *J* = 15.5, 7.7 Hz, 1H), 5.82 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.77 (s, 2H), 4.25 – 4.12 (m, 2H), 3.71 (s, 3H), 2.78 (ddd, *J* = 13.9, 7.5, 1.5 Hz, 1H), 2.46 (ddd, *J* = 13.9, 7.9, 1.4 Hz, 1H), 1.80 (ddd, *J* = 13.4, 12.3, 4.4 Hz, 1H), 1.63 – 1.52 (m, 1H), 1.25 (s, 3H), 1.24 (t, *J* = 9.1, 3H), 1.23 – 1.16 (m, 2H), 1.14 – 1.03 (m, 1H), 0.98 (ttd, *J* = 12.4, 7.5, 4.4 Hz, 1H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.1, 166.8, 155.1, 145.6, 137.8, 128.5, 128.2, 127.5, 123.8, 63.1, 51.6, 50.6, 50.5, 42.2, 39.6, 26.8, 23.3, 22.5, 14.3, 14.1; IR (Neat Film, NaCl) 1956, 2873, 1727, 1688, 1436, 1376, 1345, 1272, 1193, 1019, 986 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{22}H_{35}N_2O_5$ $[M+NH_4]^+$: 407.2540, found 407.2538; $[\alpha]^{25}$ +9.70 (*c* 1.5, $CHCl_3$, 94% ee).



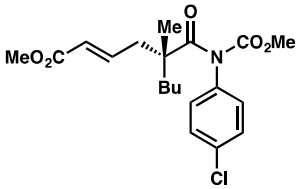
Methyl (*R*,*E*)-5-(benzyl(*tert*-butoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6f)

Representative Procedure I. Compound **6f** was prepared using General Procedure H with **5f** (9.3 mg, 26 μmol) to afford a clear oil (8.5 mg, 79% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 5H), 6.88 (dt, *J* = 15.5, 7.7 Hz, 1H), 5.84 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.71 (s, 2H), 3.72 (s, 3H), 2.83 (ddd, *J* = 13.9, 7.5, 1.5 Hz, 1H), 2.50 (ddd, *J* = 13.9, 7.9, 1.4 Hz, 1H), 1.84 (ddd, *J* = 13.4, 12.1, 4.4 Hz, 1H), 1.59 (ddd, *J* = 13.4, 12.3, 4.5 Hz, 1H), 1.35 (s, 9H), 1.29 (s, 3H), 1.27 – 1.19 (m, 2H), 1.13 (dddd, *J* = 17.0, 7.8, 6.6, 4.6 Hz, 1H), 1.04 (tdd, *J* = 12.4, 8.3, 4.5 Hz, 1H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 166.9, 153.9, 145.9, 138.3, 128.4, 128.0, 127.3, 123.7, 83.0, 51.6, 50.8, 50.3, 42.4, 39.6, 27.9, 26.9, 23.4, 22.5, 14.2; IR (Neat Film, NaCl) 2957, 2933, 1728, 1682, 1370, 1272, 1150, 987, 699 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{36}NO_5$ $[M+H]^+$: 418.2593, found 418.2593; $[\alpha]^{25}$ +10.60 (*c* 0.85, $CHCl_3$, 90% ee).



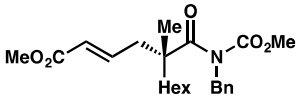
Methyl (*R*,*E*)-5-(benzyl((benzyloxy)carbonyl)carbamoyl)-5-methylnon-2-enoate (6g)

Representative Procedure I. Compound **6g** was prepared using General Procedure H with **5g** (20.9 mg, 53 μmol) to afford a clear oil (18.2 mg, 76% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 3H), 7.29 – 7.20 (m, 7H), 6.81 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.75 (dd, *J* = 15.5, 1.4 Hz, 1H), 5.15 (s, 2H), 4.79 (s, 2H), 3.71 (s, 3H), 2.73 (ddd, *J* = 14.0, 7.6, 1.4 Hz, 1H), 2.43 (ddd, *J* = 13.9, 7.9, 1.5 Hz, 1H), 1.76 (ddd, *J* = 13.5, 12.2, 4.5 Hz, 1H), 1.61 – 1.48 (m, 1H), 1.22 (s, 3H), 1.14 (p, *J* = 7.2 Hz, 2H), 1.10 – 0.99 (m, 1H), 0.94 (ttd, *J* = 12.3, 7.4, 4.3 Hz, 1H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.2, 166.8, 154.9, 145.5, 137.7, 134.9, 128.8, 128.8, 128.7, 128.5, 128.2, 127.5, 123.8, 68.9, 51.6, 50.6, 50.5, 42.1, 39.5, 26.8, 23.2, 22.5, 14.1; IR (Neat Film, NaCl) 2955, 1725, 1688, 1386, 1346, 1272, 1192, 990, 698 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{27}H_{37}N_2O_5$ $[M+NH_4]^+$: 469.2697, found 469.2693; $[\alpha]^{25}$ +5.94 (*c* 1.7, $CHCl_3$, 93% ee).



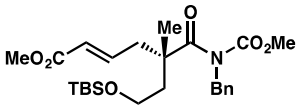
Methyl (*R*,*E*)-5-((4-chlorophenyl)(methoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6h)

Representative Procedure I. Compound **6h** was prepared using General Procedure H with **5h** (19.8 mg, 59 μmol) to afford a clear oil (19.7 mg, 80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.13 – 7.05 (m, 2H), 6.88 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.83 (dt, *J* = 15.3, 1.3 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.73 (ddd, *J* = 14.3, 7.6, 1.5 Hz, 1H), 2.44 (ddd, *J* = 14.1, 7.8, 1.4 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.61 – 1.52 (m, 1H), 1.30 – 1.14 (m, 4H), 1.24 (s, 3H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7, 166.7, 154.7, 144.8, 136.9, 134.1, 129.5, 129.3, 124.2, 54.0, 51.7, 51.2, 41.8, 39.4, 26.6, 23.2, 22.9, 14.1; IR (Neat Film, NaCl) 2956, 2873, 1728, 1658, 1492, 1439, 1272, 1247, 1198, 1092 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{26}NClO_5$ $[M+H-H_2]^+$: 395.1499, found 395.1476; $[\alpha]^{25}$ +7.94 (*c* 1.8, $CHCl_3$, 90% ee).



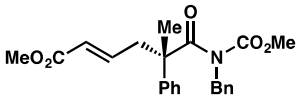
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-methylundec-2-enoate (6i)

Representative Procedure I. Compound **6i** was prepared using General Procedure H with **5i** (17.3 mg, 51 μmol) to afford a clear oil (17.2 mg, 84% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 5H), 6.83 (dt, *J* = 15.5, 7.7 Hz, 1H), 5.81 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.77 (s, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 2.75 (ddd, *J* = 14.0, 7.5, 1.4 Hz, 1H), 2.45 (ddd, *J* = 13.9, 8.0, 1.4 Hz, 1H), 1.77 (ddd, *J* = 13.4, 12.1, 4.4 Hz, 1H), 1.61 – 1.46 (m, 1H), 1.30 – 1.13 (m, 6H), 1.23 (s, 3H), 1.13 – 1.03 (m, 1H), 1.02 – 0.91 (m, 1H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.0, 166.8, 155.5, 145.5, 137.6, 128.5, 128.2, 127.6, 123.8, 53.7, 51.6, 50.6, 50.6, 42.3, 40.0, 31.7, 29.9, 24.5, 22.7, 22.4, 14.2; IR (Neat Film, NaCl) 2954, 2930, 2858, 1728, 1688, 1441, 1350, 1272, 1779, 998 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{23}H_{37}N_2O_5$ $[M+NH_4]^+$: 421.2697, found 421.2688; $[\alpha]^{25}$ +10.91 (*c* 1.6, $CHCl_3$, 94% ee).



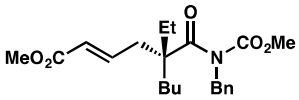
Methyl (*S*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-7-((*tert*-butyldimethylsilyl)oxy)-5-methylhept-2-enoate (6j)

Representative Procedure I. Compound **6j** was prepared using General Procedure H with **5j** (31.7 mg, 76 μmol) to afford a clear oil (28.5 mg, 79% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 5H), 6.79 (dq, *J* = 15.4, 7.8 Hz, 1H), 5.77 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.75 (s, 2H), 3.72 (s, 3H), 3.67 (s, 3H), 3.54 – 3.44 (m, 2H), 2.78 (ddd, *J* = 14.0, 7.6, 1.5 Hz, 1H), 2.47 (ddd, *J* = 14.0, 7.9, 1.5 Hz, 1H), 2.06 (ddd, *J* = 13.9, 7.8, 6.2 Hz, 1H), 1.86 (ddd, *J* = 13.9, 7.9, 6.3 Hz, 1H), 1.24 (s, 3H), 0.82 (s, 9H), -0.03 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.2, 166.7, 155.4, 145.3, 137.6, 128.6, 128.1, 127.6, 124.0, 59.8, 53.7, 51.6, 50.6, 49.3, 42.6, 41.8, 26.1, 22.7, 18.4, -5.2, -5.3; IR (Neat Film, NaCl) 2955, 2857, 1728, 1688, 1440, 1351, 1256, 1195, 1094, 994 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{25}H_{40}NO_6Si$ $[M+H]^+$: 478.2625, found 478.2646; $[\alpha]^{25}$ +2.20 (*c* 2.6, $CHCl_3$, 94% ee).



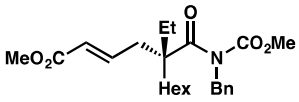
Methyl (*S*,*E*)-6-(benzyl(methoxycarbonyl)amino)-5-methyl-6-oxo-5-phenylhex-2-enoate (6k)

Representative Procedure I. Compound **6k** was prepared using General Procedure H with **4k** (26.0 mg, 77 μmol) to afford a clear oil (23.9 mg, 78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.30 – 7.23 (m, 3H), 7.22 – 7.13 (m, 1H), 7.05 – 6.97 (m, 2H), 6.57 (ddd, *J* = 15.4, 8.3, 6.9 Hz, 1H), 5.71 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.89 (s, 2H), 3.67 (s, 3H), 3.22 (s, 3H), 3.01 (ddd, *J* = 13.9, 8.4, 1.2 Hz, 1H), 2.67 (ddd, *J* = 13.9, 6.9, 1.6 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 166.6, 154.3, 145.1, 142.7, 137.4, 128.5, 128.5, 128.3, 127.7, 126.6, 125.8, 124.3, 54.1, 53.4, 51.5, 50.1, 45.9, 23.4; IR (Neat Film, NaCl) 2953, 1725, 1674, 1496, 1441, 1351, 1315, 1274, 1203, 1004, 700 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{23}H_{29}N_2O_5$ $[M+NH_4]^+$: 413.2071, found 413.2065; $[\alpha]^{25}$ +67.74 (*c* 2.2, $CHCl_3$, 76% ee).



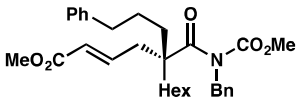
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-ethylnon-2-enoate (6l)

Representative Procedure I. Compound **6l** was prepared using General Procedure H with **5l** (7.3 mg, 22 μmol) to afford a clear oil (7.3 mg, 85% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 5H), 6.83 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.84 (dt, *J* = 15.5, 1.4 Hz, 1H), 4.80 (s, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 2.62 (qdd, *J* = 14.4, 7.7, 1.5 Hz, 2H), 1.84 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.75 (ddd, *J* = 13.8, 12.2, 4.7 Hz, 1H), 1.66 (dt, *J* = 14.3, 7.4 Hz, 1H), 1.59 (ddd, *J* = 13.8, 12.2, 4.7 Hz, 1H), 1.22 (p, *J* = 7.2 Hz, 2H), 1.15 – 0.97 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 166.8, 155.5, 145.8, 137.7, 128.5, 128.2, 127.6, 123.6, 54.2, 53.7, 51.6, 50.8, 37.6, 35.2, 28.3, 26.7, 23.3, 14.1, 9.0; IR (Neat Film, NaCl) 2957, 2874, 1727, 1682, 1442, 1351, 1190, 700 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{22}H_{35}N_2O_5$ $[M+NH_4]^+$: 407.2540, found 407.2537; $[\alpha]^{25}$ +1.32 (*c* 0.66, $CHCl_3$, 82% ee).



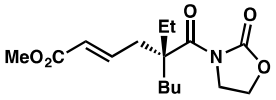
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-ethylundec-2-enoate (6m)

Representative Procedure I. Compound **6m** was prepared using General Procedure H with **5m** (19.0 mg, 53 μmol) to afford a clear oil (18.7 mg, 85% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.14 (m, 5H), 6.83 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.83 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.79 (s, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 2.62 (qdd, *J* = 14.6, 7.7, 1.5 Hz, 2H), 1.84 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.69 – 1.54 (m, 2H), 1.30 – 1.15 (m, 6H), 1.15 – 0.97 (m, 2H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.8, 166.8, 155.5, 145.8, 137.7, 128.5, 128.2, 127.5, 123.6, 54.2, 53.7, 51.6, 50.7, 37.6, 35.5, 31.7, 29.9, 28.3, 24.5, 22.7, 14.2, 9.0; IR (Neat Film, NaCl) 2955, 1727, 1683, 1441, 1351, 1176 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{25}H_{39}N_2O_5$ $[M+NH_4]^+$: 435.2853, found 435.2853; $[\alpha]^{25}$ +2.25 (*c* 1.7, $CHCl_3$, 93% ee).



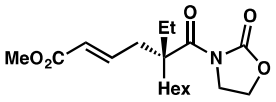
Methyl (*S*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-(3-phenylpropyl)undec-2-enoate (6n)

Representative Procedure I. Compound **6n** was prepared using General Procedure H with **5n** (21.6 mg, 48 □mol) to afford a clear oil (19.8 mg, 84% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 8H), 7.13 – 7.07 (m, 2H), 6.79 (dt, *J* = 15.4, 7.6 Hz, 1H), 5.79 (dt, *J* = 15.4, 1.3 Hz, 1H), 4.78 (s, 2H), 3.72 (s, 3H), 3.67 (s, 3H), 2.60 (dt, *J* = 7.7, 1.3 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 1.84 – 1.68 (m, 2H), 1.65 – 1.51 (m, 2H), 1.51 – 1.35 (m, 2H), 1.29 – 1.13 (m, 6H), 1.12 – 0.93 (m, 2H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.6, 166.7, 155.4, 145.6, 142.1, 137.6, 128.5, 128.5, 128.4, 128.2, 127.6, 125.9, 123.7, 53.8, 53.7, 51.6, 50.7, 38.2, 36.3, 35.8, 35.2, 31.7, 29.9, 26.3, 24.4, 22.7, 14.2; IR (Neat Film, NaCl) 3028, 2930, 2858, 1727, 1683, 1442, 1350, 1273, 1170, 699 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{31}H_{45}N_2O_5$ $[M+NH_4]^+$: 525.3323, found 525.3329; $[\alpha]^{25}$ +0.25 (*c* 1.8, $CHCl_3$, 76% ee).



Methyl (*R*,*E*)-5-ethyl-5-(2-oxooxazolidine-3-carbonyl)non-2-enoate (6o)

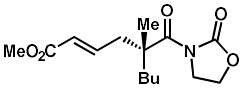
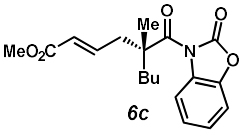
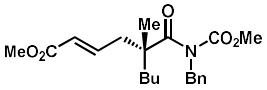
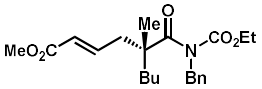
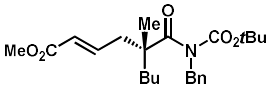
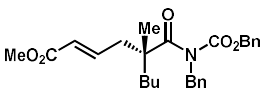
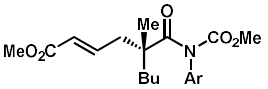
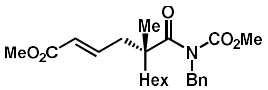
Representative Procedure I. Compound **6o** was prepared using General Procedure H with **5o** (15.2 mg, 60 μmol) to afford a clear oil (14.6 mg, 78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.88 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.48 – 4.31 (m, 2H), 4.05 (dd, *J* = 8.5, 7.6 Hz, 2H), 3.72 (s, 3H), 2.83 – 2.63 (m, 2H), 2.14 – 1.95 (m, 2H), 1.82 – 1.67 (m, 2H), 1.28 (h, *J* = 7.1 Hz, 2H), 1.22 – 1.12 (m, 1H), 1.06 (ttd, *J* = 12.3, 7.3, 4.5 Hz, 1H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 166.8, 152.4, 145.5, 123.8, 62.4, 52.9, 51.6, 45.6, 35.6, 32.2, 26.7, 25.5, 23.2 14.1, 8.8; IR (Neat Film, NaCl) 2959, 2875, 1778, 1722, 1682, 1470, 1436, 1385, 1257, 1195, 1175, 1109, 1045 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{26}NO_5$ $[M+H]^+$: 312.1811, found 312.1791; $[\alpha]^{25}$ +0.50 (*c* 1.3, $CHCl_3$, 69% ee).

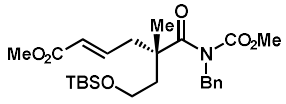
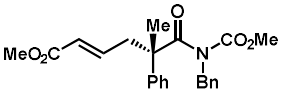
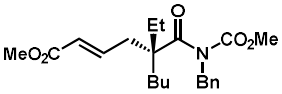
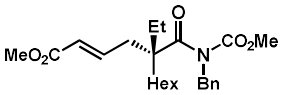
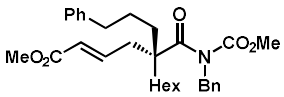
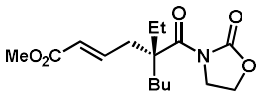
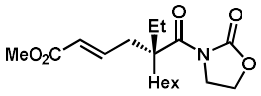


Methyl (*R*,*E*)-5-ethyl-5-(2-oxooxazolidine-3-carbonyl)undec-2-enoate (6p)

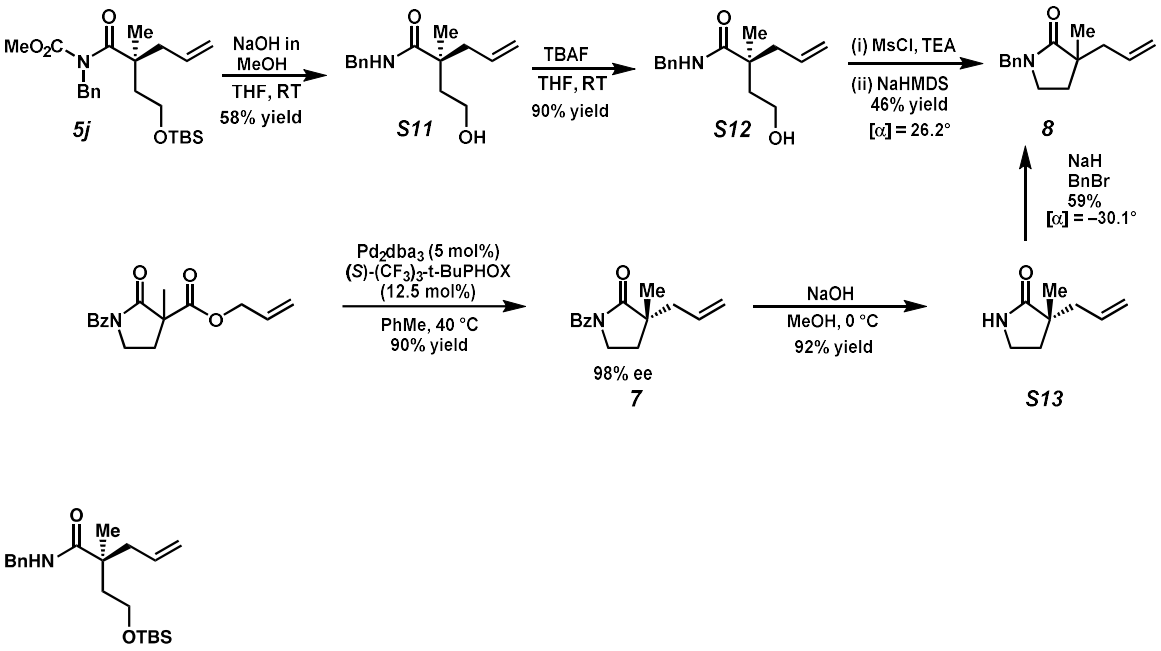
Representative Procedure I. Compound **6p** was prepared using General Procedure H with **5p** (16.5 mg, 59 μmol) to afford a clear oil (16.3 mg, 82% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 – 6.74 (m, 1H), 5.87 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 4.05 (t, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 2.86 – 2.62 (m, 2H), 2.14 – 1.91 (m, 2H), 1.84 – 1.66 (m, 2H), 1.31 – 1.12 (m, 7H), 1.12 – 1.00 (m, 1H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.79 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 166.8, 152.4, 145.6, 123.7, 62.4, 52.9, 51.6, 45.6, 35.6, 32.4, 31.7, 29.7, 25.6, 24.4, 22.7, 14.2, 8.8; IR (Neat Film, NaCl) 2956, 2929, 2858, 1779, 1723, 1682, 1469, 1385, 1254, 1194, 1110, 1046 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{30}NO_5$ $[M+H]^+$: 340.2124, found 340.2116; $[\alpha]^{25}$ +2.41 (*c* 1.5, $CHCl_3$, 73% ee).

Determination of Enantiomeric Excess

entry	compound	assay method and conditions	retention time of minor isomer (min)	retention time of major isomer (min)	%ee
1	 *6ab*	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, AD-H col.	5.31	5.87	*70*
2	 *6c*	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	5.55	6.82	*57**
					*used Ph-ANDEN ligand
3	 *6d*	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	7.00	9.65	*92*
4	 *6e*	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	6.80	9.33	*94*
5	 *6f*	SFC, 2% *i*PrOH in CO_2 2.5 mL/min, OJ-H col.	3.05	3.64	*90*
6	 *6g*	SFC, 15% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	4.45	5.69	*93*
7	 Ar = 4-ClC_6H_4 *6h*	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	6.28	8.73	*90*
8	 *6i*	SFC, 7% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	6.09	8.25	*94*

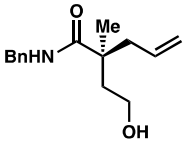
entry	compound	assay method and conditions	retention time of minor isomer (min)	retention time of major isomer (min)	%ee
9	 **6j**	SFC, 10% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	4.00	4.83	*94*
10	 **6k**	SFC, 7% *i*PrOH in CO_2 2.5 mL/min, AD-H col.	8.77	9.66	*76*
11	 **6l**	SFC, 10% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	3.58	4.39	*82*
12	 **6m**	SFC, 7% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	5.67	7.40	*93*
13	 **6n**	SFC, 10% *i*PrOH in CO_2 2.5 mL/min, AD-H col.	6.55	5.71	*76*
14	 **6o**	SFC, 5% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	8.13	10.61	*69*
15	 **6p**	SFC, 6% *i*PrOH in CO_2 2.5 mL/min, OD-H col.	7.73	10.18	*73*

3.4 Evidence of Absolute Stereochemistry



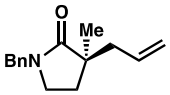
(*S*)-*N*-Benzyl-2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-methylpent-4-enamide (S11)

To an oven-dried round-bottom flask and magnetic stir bar was added **5j** (60 mg, 0.143 mmol) followed by anhydrous THF (1.4 mL). The solution was stirred under nitrogen at room temperature. A solution of NaOH in anhydrous methanol (0.17 mL, 1.0 M) was added dropwise by syringe. The reaction was stirred at room temperature for 45 min. Afterward, the reaction mixture was diluted with ethyl acetate and quenched with water. The mixture was partitioned between water and ethyl acetate and the aqueous layer was extracted two additional times with ethyl acetate. The combined organic layers were washed with brine (50 mL), dried with sodium sulfate and filtered. This mixture was concentrated in vacuo and purified by flash chromatography (10/90 to 12/88 EtOAc/hexanes) to provide the product as an amorphous white solid (30.2 mg, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 6.37 (s, 1H), 5.80 – 5.69 (m, 1H), 5.08 – 5.06 (m, 1H), 5.06 – 5.03 (m, 1H), 4.49 – 4.38 (m, 2H), 3.68 (td, *J* = 6.7, 1.5 Hz, 2H), 2.40 (ddt, *J* = 13.7, 7.1, 1.2 Hz, 1H), 2.27 (ddt, *J* = 13.7, 7.7, 1.1 Hz, 1H), 1.93 (dt, *J* = 13.7, 6.7 Hz, 1H), 1.69 (dt, *J* = 14.1, 6.7 Hz, 1H), 1.20 (s, 3H), 0.86 (s, 9H), 0.02 – -0.00 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 138.8, 134.3, 128.8, 127.9, 127.5, 118.3, 60.1, 44.7, 44.7, 43.7, 41.4, 26.1, 22.3, 18.4, -5.3, -5.3; IR (Neat Film, NaCl) 3343, 2955, 2929, 2856, 1640, 1531, 1254, 1095, 836 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{36}NO_2Si$ $[M+H]^+$: 362.2514, found 362.2515; $[\alpha]^{25}$ –2.93 (*c* 2.5, $CHCl_3$, 94% ee).



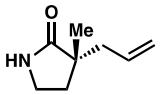
(*S*)-*N*-Benzyl-2-(2-hydroxyethyl)-2-methylpent-4-enamide (S12)

To an oven-dried 2-dram vial and magnetic stir bar was added **S11** (30 mg, 0.083 mmol) followed by anhydrous THF (0.5 mL). The solution was stirred under nitrogen at room temperature. A solution of TBAF in anhydrous THF (0.17 mL, 1.0 M) was added dropwise by syringe. The reaction was stirred at room temperature for 2 h. Afterward, the reaction mixture was quenched with saturated ammonium chloride. The mixture was partitioned between water and dichloromethane and the aqueous layer was extracted two additional times with dichloromethane. The combined organic layers were washed with brine (50 mL), dried with sodium sulfate and filtered. This mixture was concentrated in vacuo and purified by flash chromatography (60/40 EtOAc/hexanes) to provide the product as an oil (19.5 mg, 58% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 6.10 (s, 1H), 5.78 – 5.69 (m, 1H), 5.11 – 5.09 (m, 1H), 5.09 – 5.05 (m, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 3.78 (dt, *J* = 11.8, 6.1 Hz, 1H), 3.74 – 3.65 (m, 1H), 2.56 (s, 1H), 2.48 (ddt, *J* = 13.7, 7.0, 1.3 Hz, 1H), 2.22 (ddt, *J* = 13.7, 7.7, 1.2 Hz, 1H), 2.00 (ddd, *J* = 14.4, 7.3, 5.5 Hz, 1H), 1.70 (ddd, *J* = 14.4, 6.6, 5.4 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 138.3, 133.7, 128.9, 127.9, 127.7, 118.9, 59.3, 44.5, 44.4, 44.0, 41.5, 22.2; IR (Neat Film, NaCl) 3335, 2927, 1634, 1538, 1249 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{15}H_{21}NO_2$ $[M+H]^+$: 248.1645, found 248.1651; $[\alpha]^{25}$ –61.06 (*c* 1.63, $CHCl_3$, 94% ee).



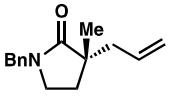
(*S*)-3-Allyl-1-benzyl-3-methylpyrrolidin-2-one ((*S*)-8)

To an oven-dried 2-dram vial and magnetic stir bar was added **S12** (19.5 mg, 0.079 mmol) followed by anhydrous THF (0.20 mL). The solution was stirred under nitrogen at 0 °C. Triethylamine (12 µL, 0.087 mmol) was added dropwise by syringe followed by a solution of methanesulfonyl chloride in THF (0.10 mL, 0.79 M). The reaction was stirred at 0 °C for 0.5 h. A separate oven-dried 2-dram vial and magnetic stir bar was charged with NaHMDS (46 mg, 0.253 mmol) and THF (0.25 mL). The reaction mixture was cannulated into the NaHMDS solution at 0 °C over 5 minutes. This solution was warmed to room temperature and stirred overnight. Afterward, the reaction mixture was quenched with saturated ammonium chloride. The mixture was partitioned between water and ethyl acetate and the aqueous layer was extracted two additional times with ethyl acetate. The combined organic layers were washed with brine (50 mL), dried with sodium sulfate and filtered. This mixture was concentrated in vacuo and purified by preparative TLC (40/60 EtOAc/hexanes) to provide the product as an oil (8.4 mg, 46% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 5H), 5.82 –5.74 (m, 1H), 5.18 – 5.06 (m, 2H), 4.53 – 4.42 (m, 2H), 3.20 – 3.10 (m, 2H), 2.37 (ddt, *J* = 13.7, 6.7, 1.3 Hz, 1H), 2.25 (ddt, *J* = 13.8, 8.2, 1.1 Hz, 1H), 2.03 (ddd, *J* = 12.8, 8.2, 6.4 Hz, 1H), 1.73 (ddd, *J* = 12.9, 8.0, 5.5 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.6, 136.7, 134.1, 128.7, 128.1, 127.6, 118.4, 46.8, 44.1, 43.4, 42.3, 30.4, 23.2; IR (Neat Film, NaCl) 3002, 2962, 1686, 1454, 1431, 1291, 917, 701 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1539, found 230.1549; $[\alpha]^{25}$ 26.10 (*c* 0.70, $CHCl_3$, 94% ee).



(*R*)-3-Allyl-3-methylpyrrolidin-2-one (S13)

To a round-bottom flask and magnetic stir bar was added **7**[17] (98% ee) (80 mg, 0.33 mmol) followed by MeOH (4.0 mL). The solution was stirred under nitrogen at 0 °C. A solution of NaOH (0.61 mL, 2.0 M, 1.2 mmol) was added dropwise by syringe. The reaction was stirred at 0 °C for 1.5 h. The mixture was partitioned between brine and diethyl ether. The organic layer was washed with saturated sodium bicarbonate solution followed by brine, dried with sodium sulfate and filtered. This mixture was concentrated in vacuo and purified by flash chromatography (80/20 to 100/0 EtOAc/hexanes) to provide the product as an amorphous white solid (28.3 mg, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 1H), 5.84 – 5.70 (m, 1H), 5.13 – 5.09 (m, 1H), 5.08 (p, J = 1.2 Hz, 1H), 3.34 – 3.19 (m, 2H), 2.33 – 2.25 (m, 1H), 2.19 (ddt, J = 13.6, 8.2, 1.1 Hz, 1H), 2.15 – 2.06 (m, 1H), 1.86 – 1.76 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 134.1, 118.4, 43.1, 42.0, 39.0, 33.0, 22.8; IR (Neat Film, NaCl) 3233, 3077, 2928, 1697, 1295, 915 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_8H_{14}NO$ $[M+H]^+$: 140.1070, found 140.1071; $[\alpha]^{25}$ –33.10 (*c* 2.27, $CHCl_3$, 98% ee).



(*R*)-3-Allyl-1-benzyl-3-methylpyrrolidin-2-one ((*R*)-8):

To an oven-dried 2-dram vial and magnetic stir bar was added **S13** (28.3 mg, 0.203 mmol) followed by anhydrous DMF (1.0 mL). The solution was stirred under nitrogen at 0 °C. Sodium hydride (8.1 mg, 0.203 mmol) was added portion-wise over two minutes. The reaction was stirred at 0 °C for 40 min. To this solution was added benzyl bromide (30 μL, 0.256 mmol) dropwise through by syringe. This solution was warmed to room temperature and stirred for 2 h. Afterward, the reaction mixture was quenched with saturated ammonium chloride. The mixture was partitioned between water and ethyl acetate and the aqueous layer was extracted two additional times with ethyl acetate. The combined organic layers were washed with brine (50 mL), dried with sodium sulfate and filtered. This mixture was concentrated in vacuo and purified by preparative TLC (40/60 EtOAc/hexanes) to provide the product as an oil (27 mg, 59% yield). Characterization data matched previously synthesized material;[17] $[\alpha]^{25}$ –33.10 (*c* 2.27, $CHCl_3$, 98% ee).

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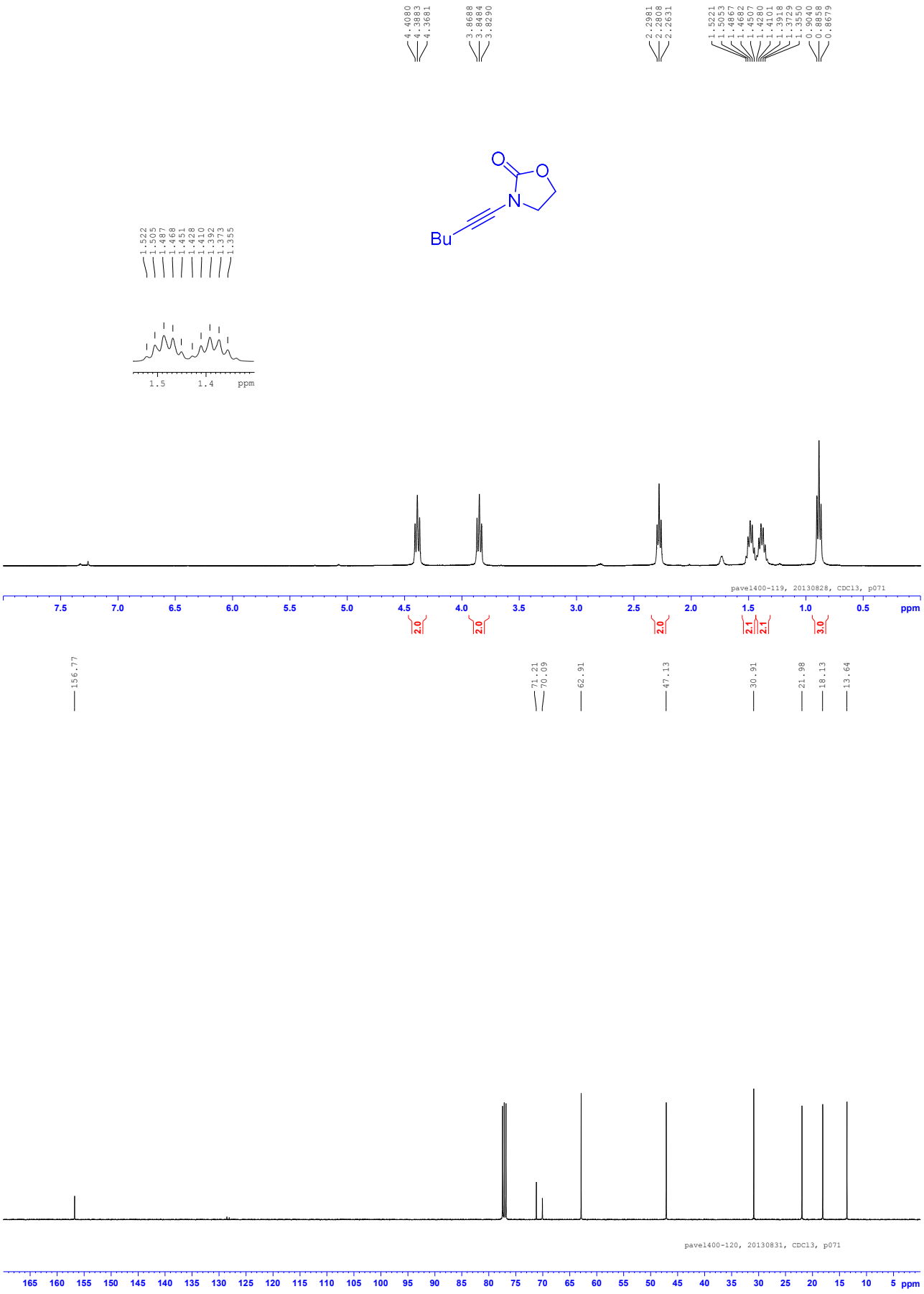
5 Spectra

3-(Hex-1-yn-1-yl)oxazolidin-2-one (1a)



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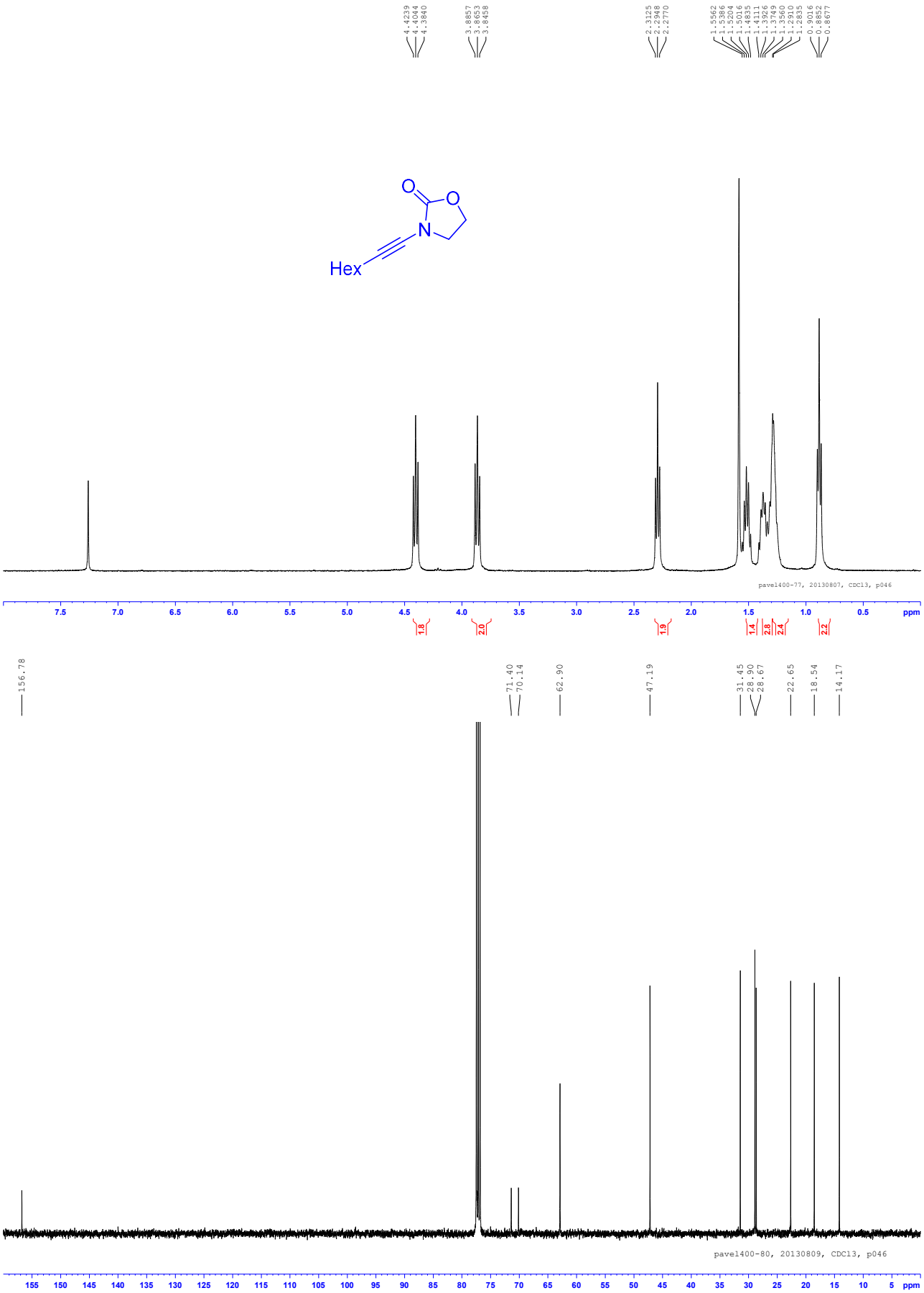

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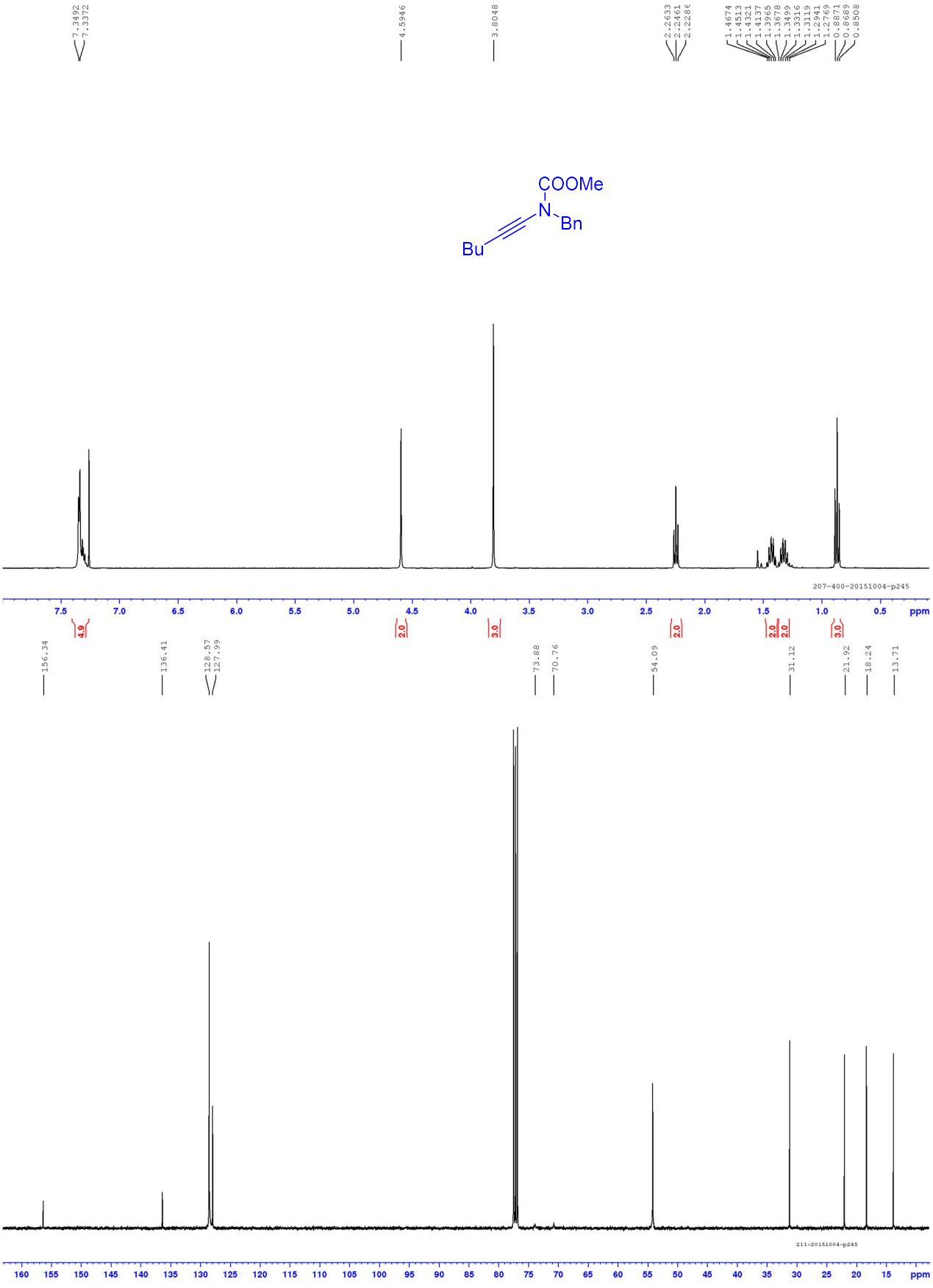

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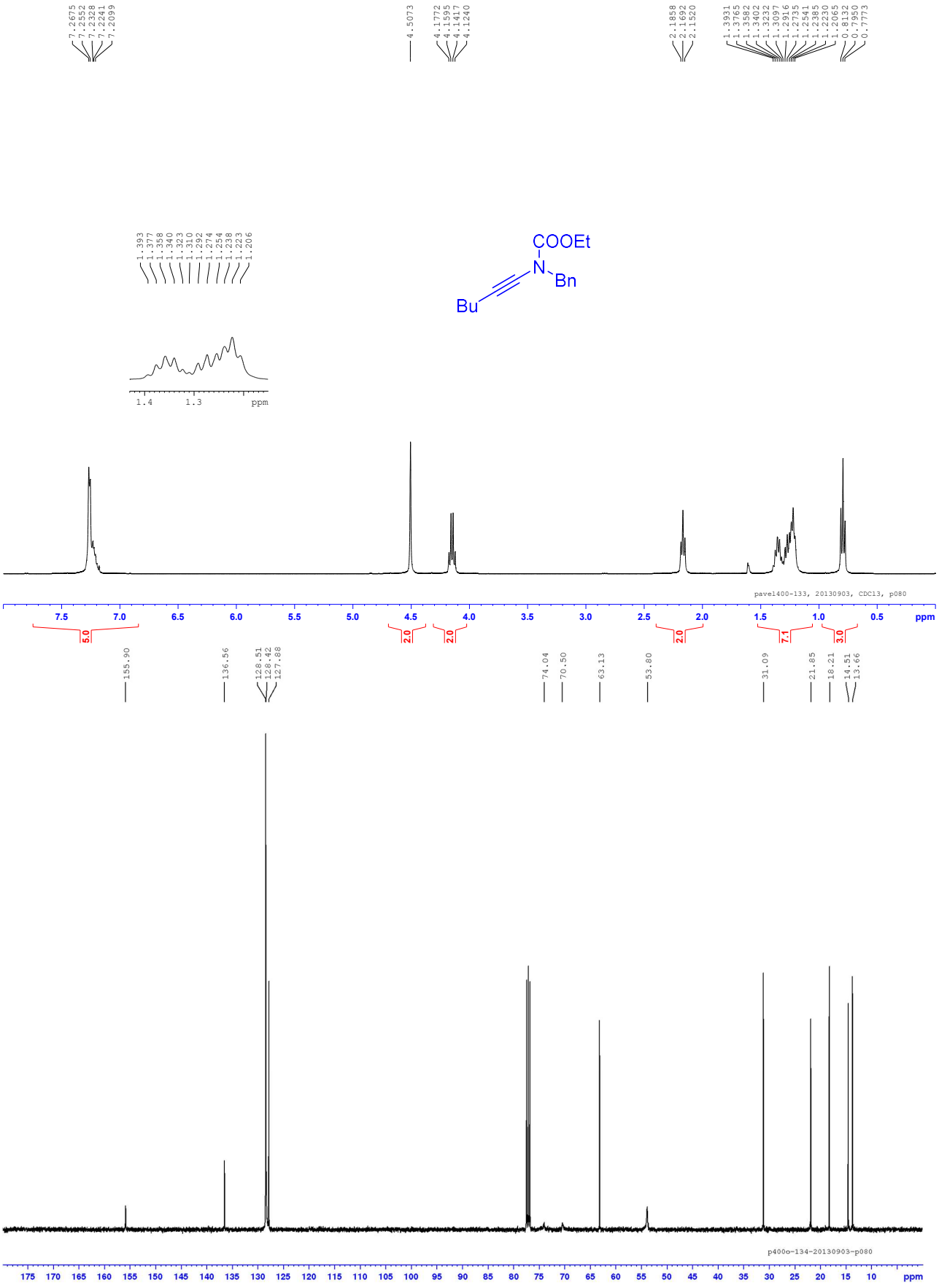

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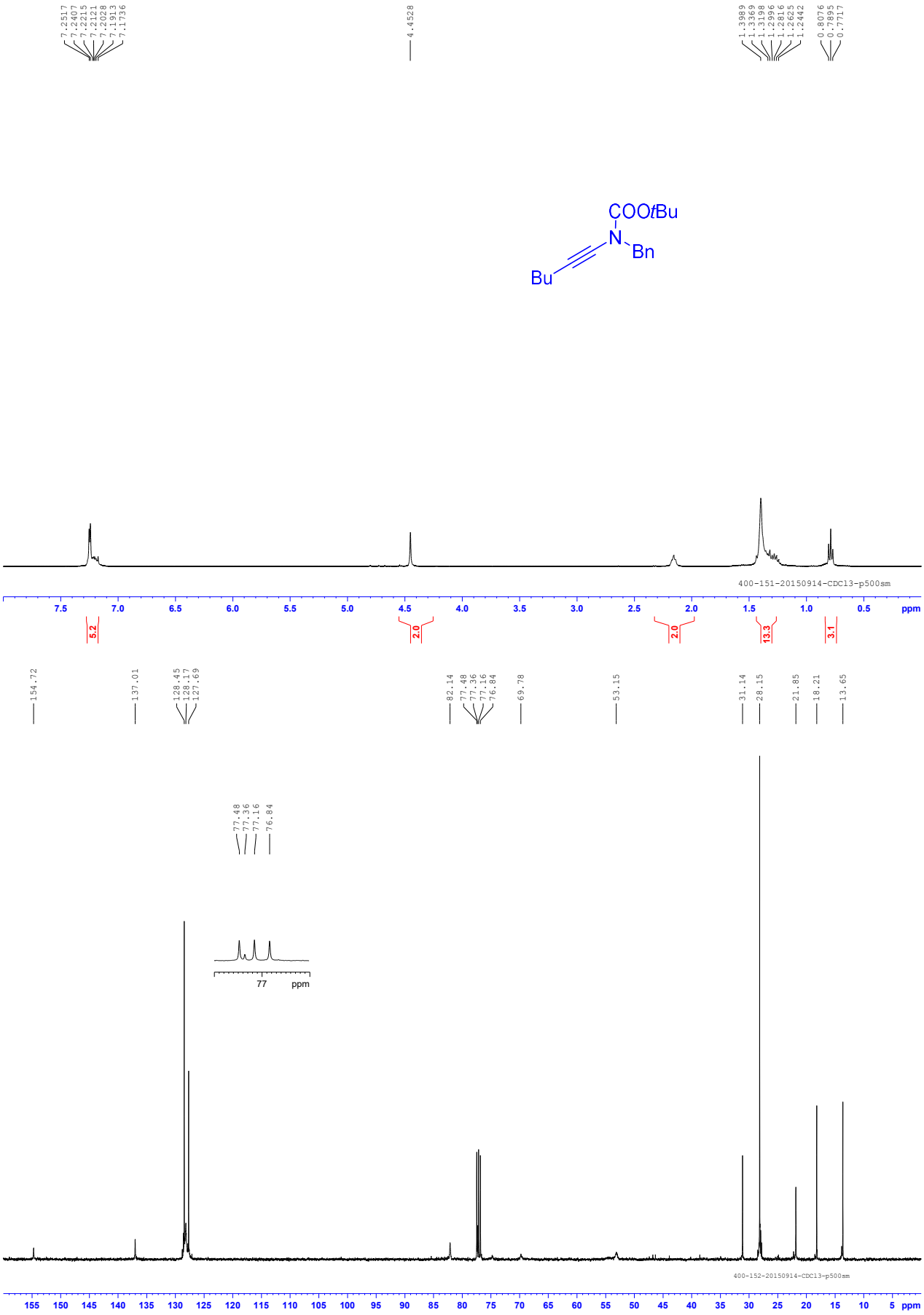
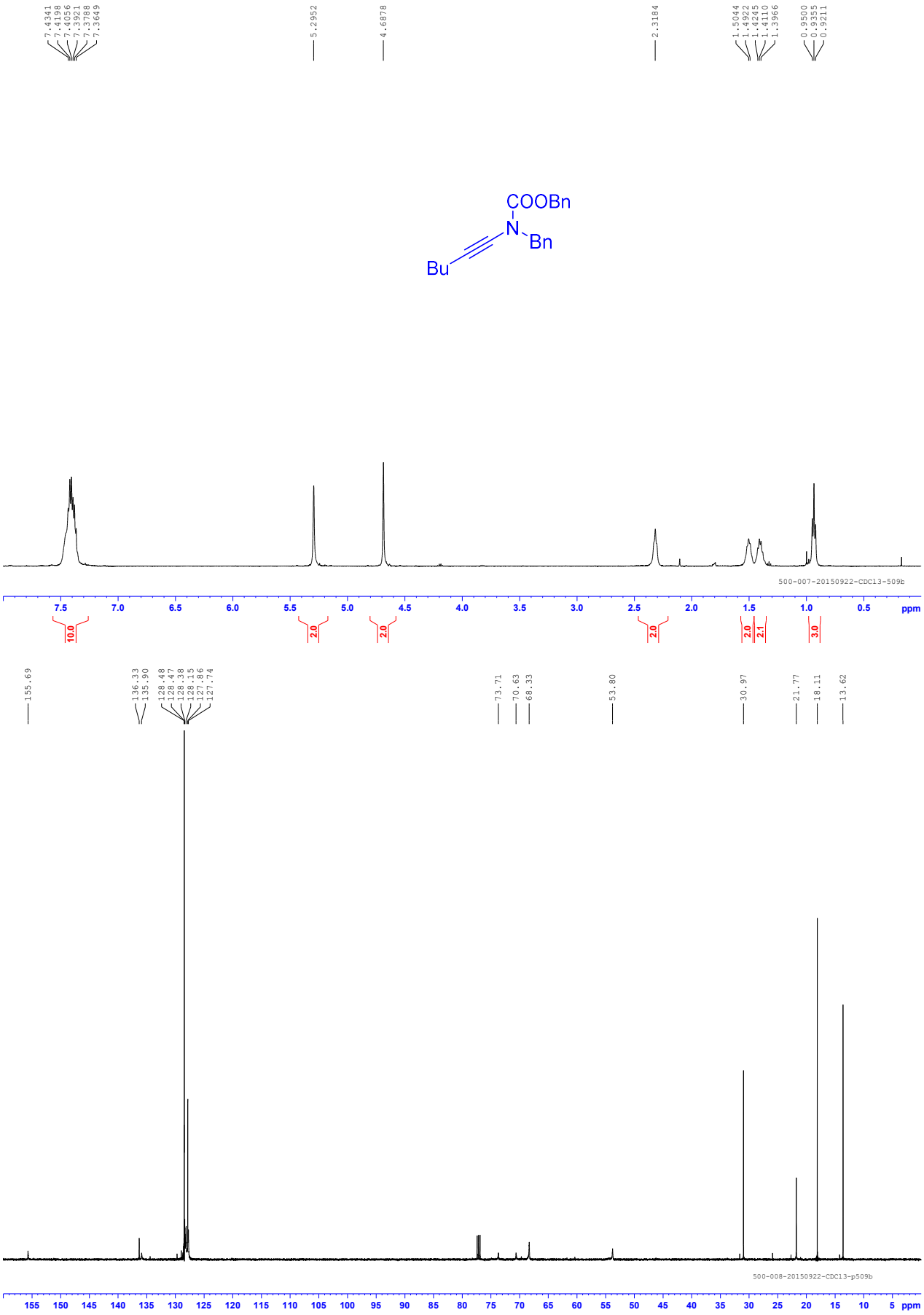
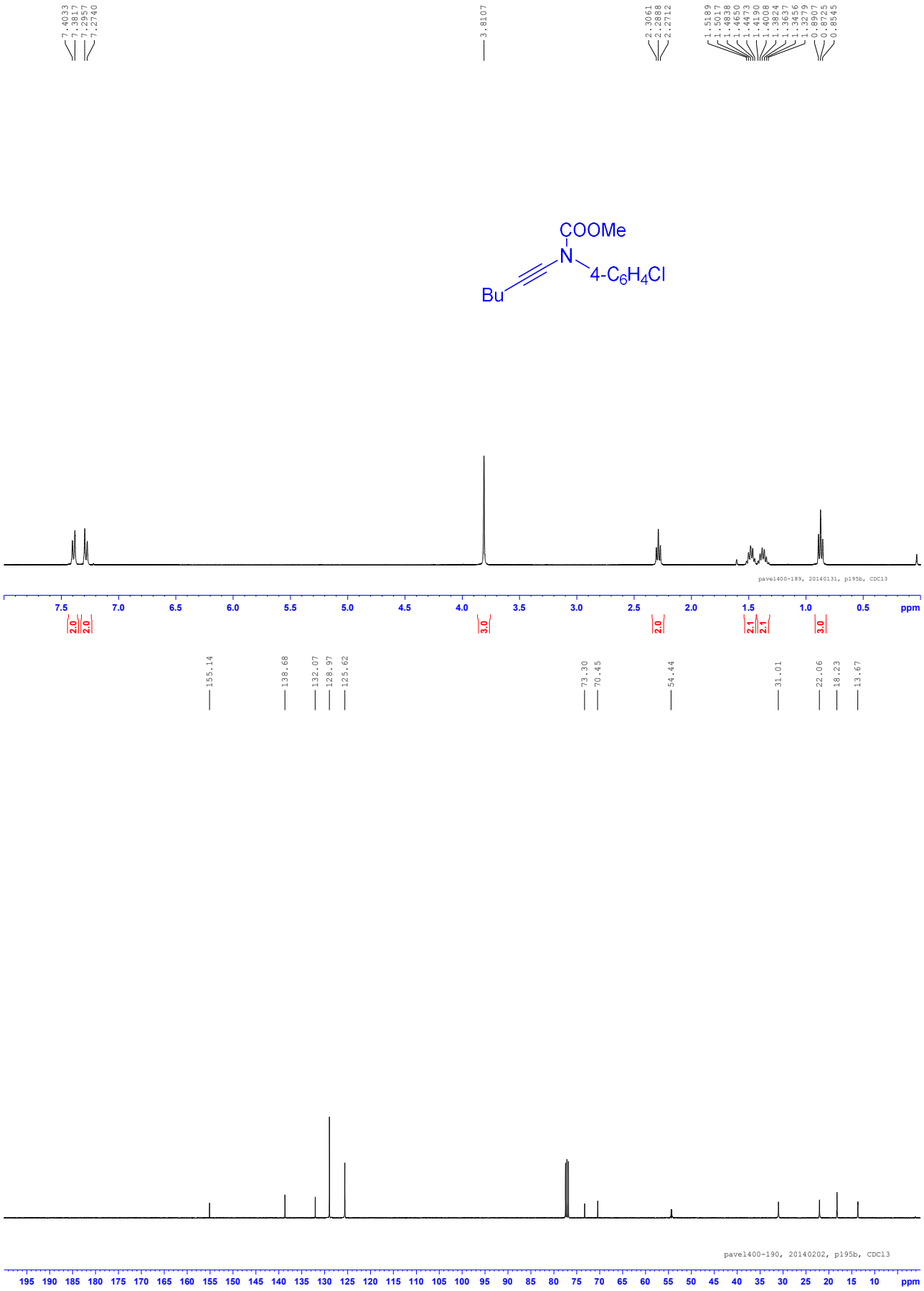


Benzyl benzyl(hex-1-yn-1-yl)carbamate (1g)



Methyl (4-chlorophenyl)(hex-1-yn-1-yl)carbamate (1h)



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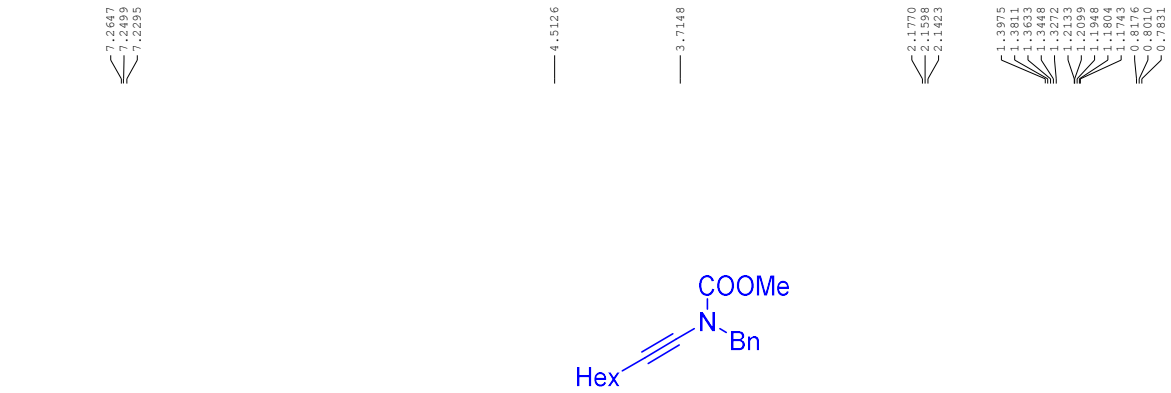

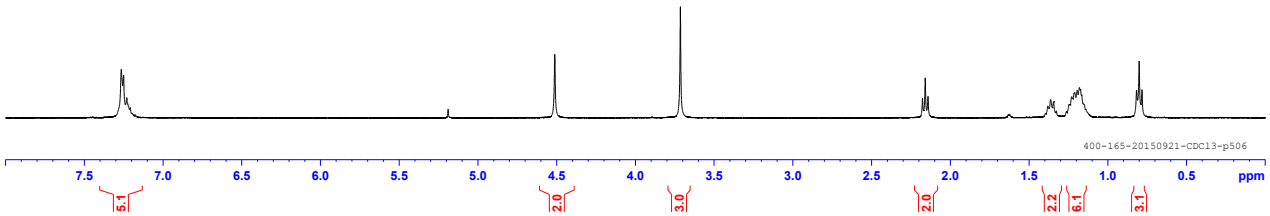

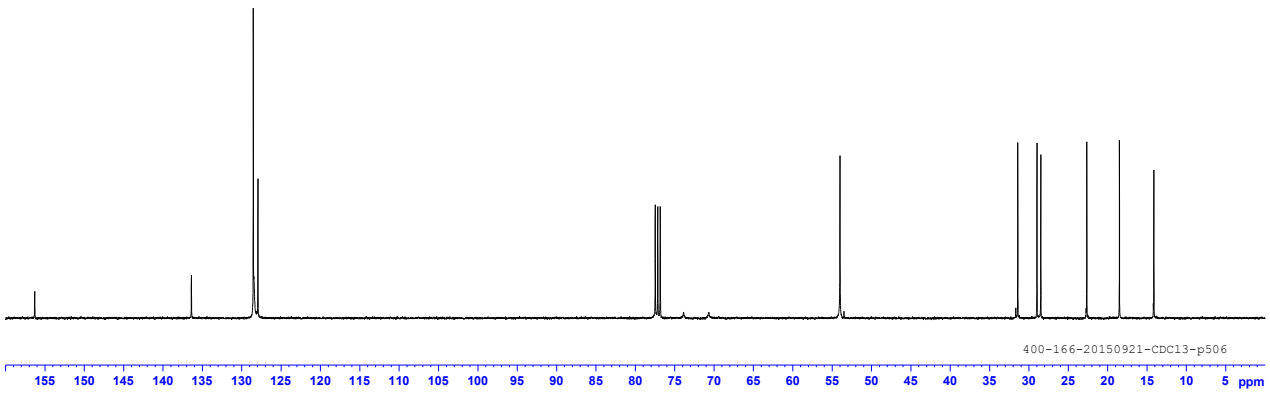

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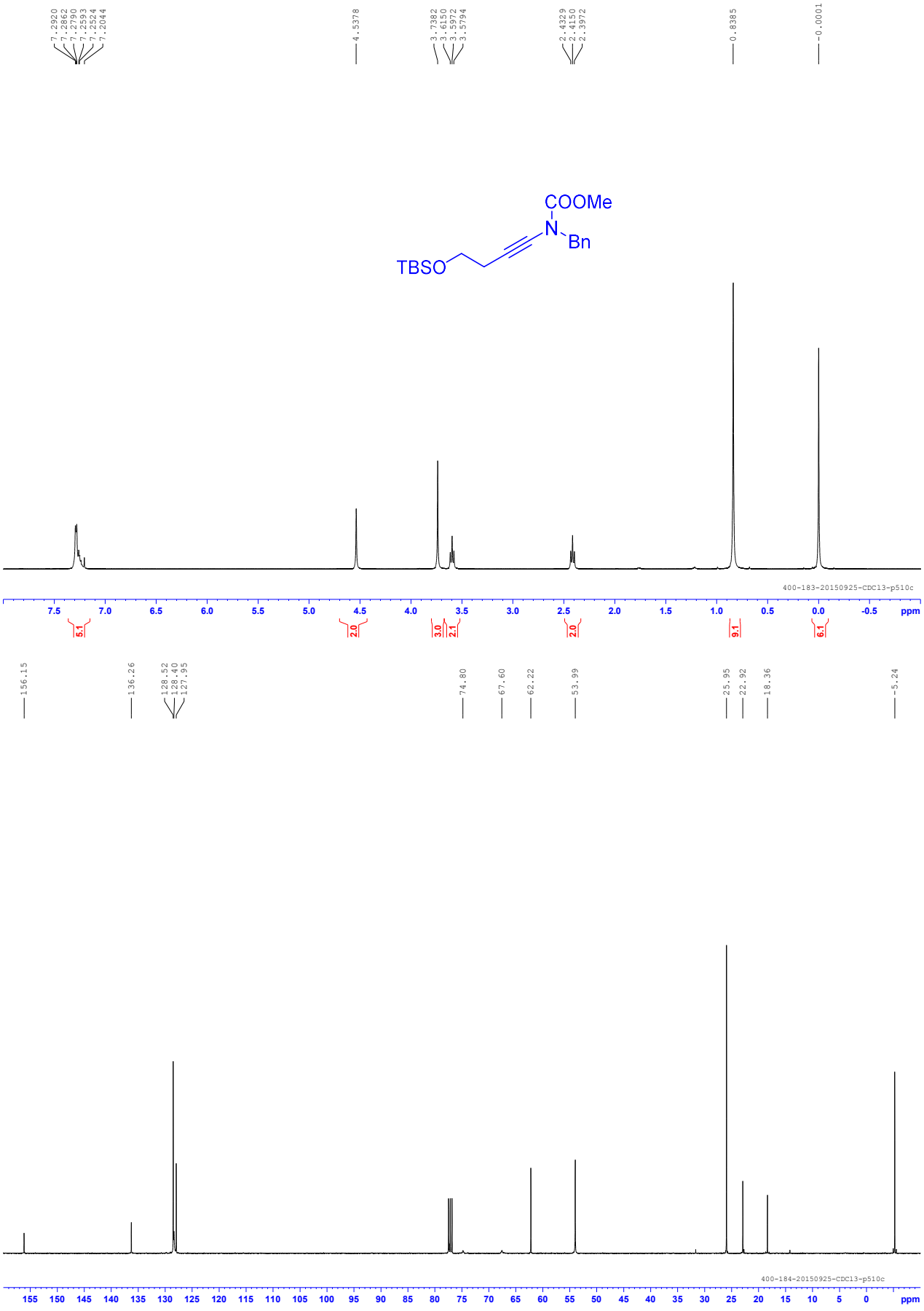
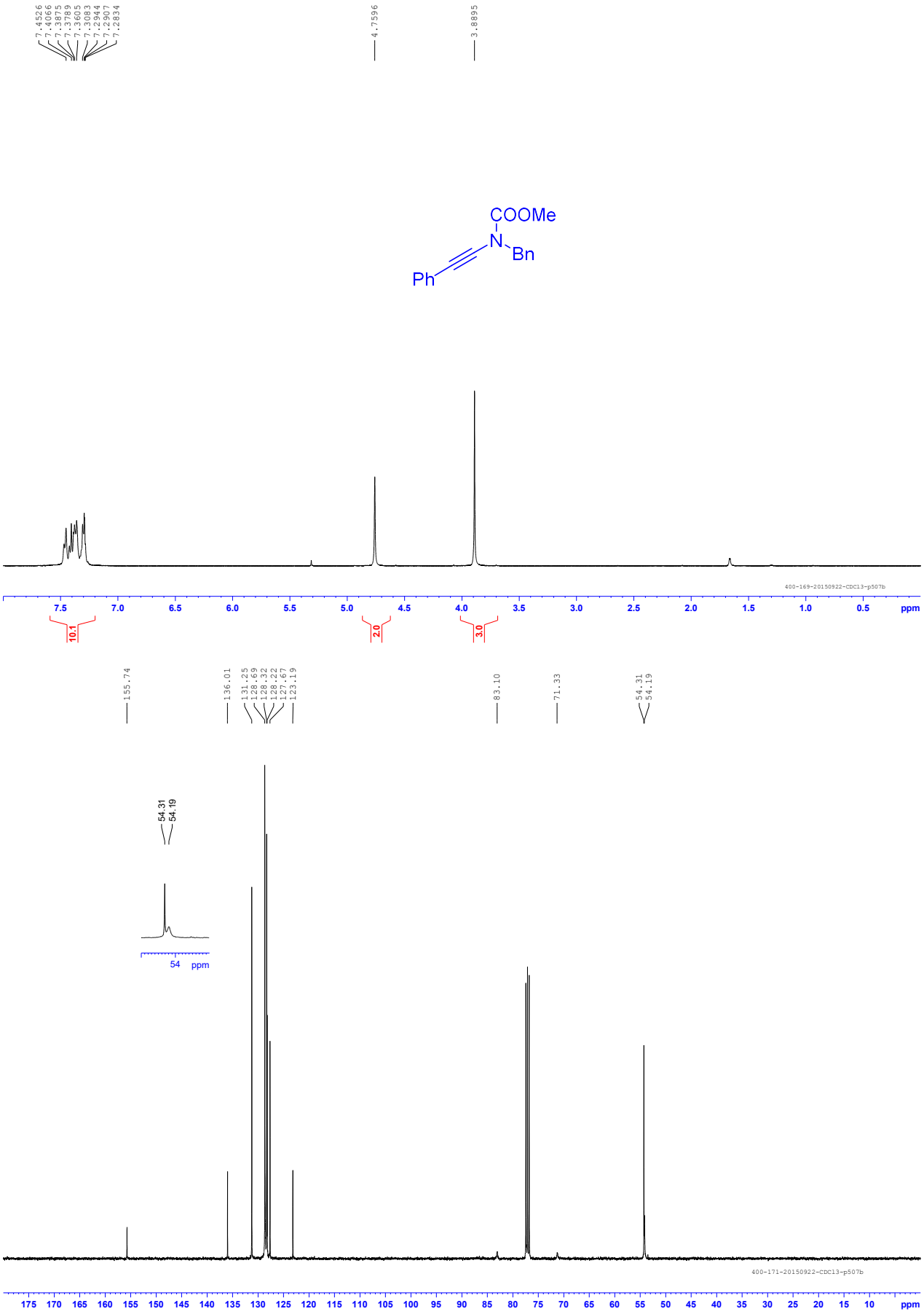


Methyl benzyl(phenylethynyl)carbamate (1k)



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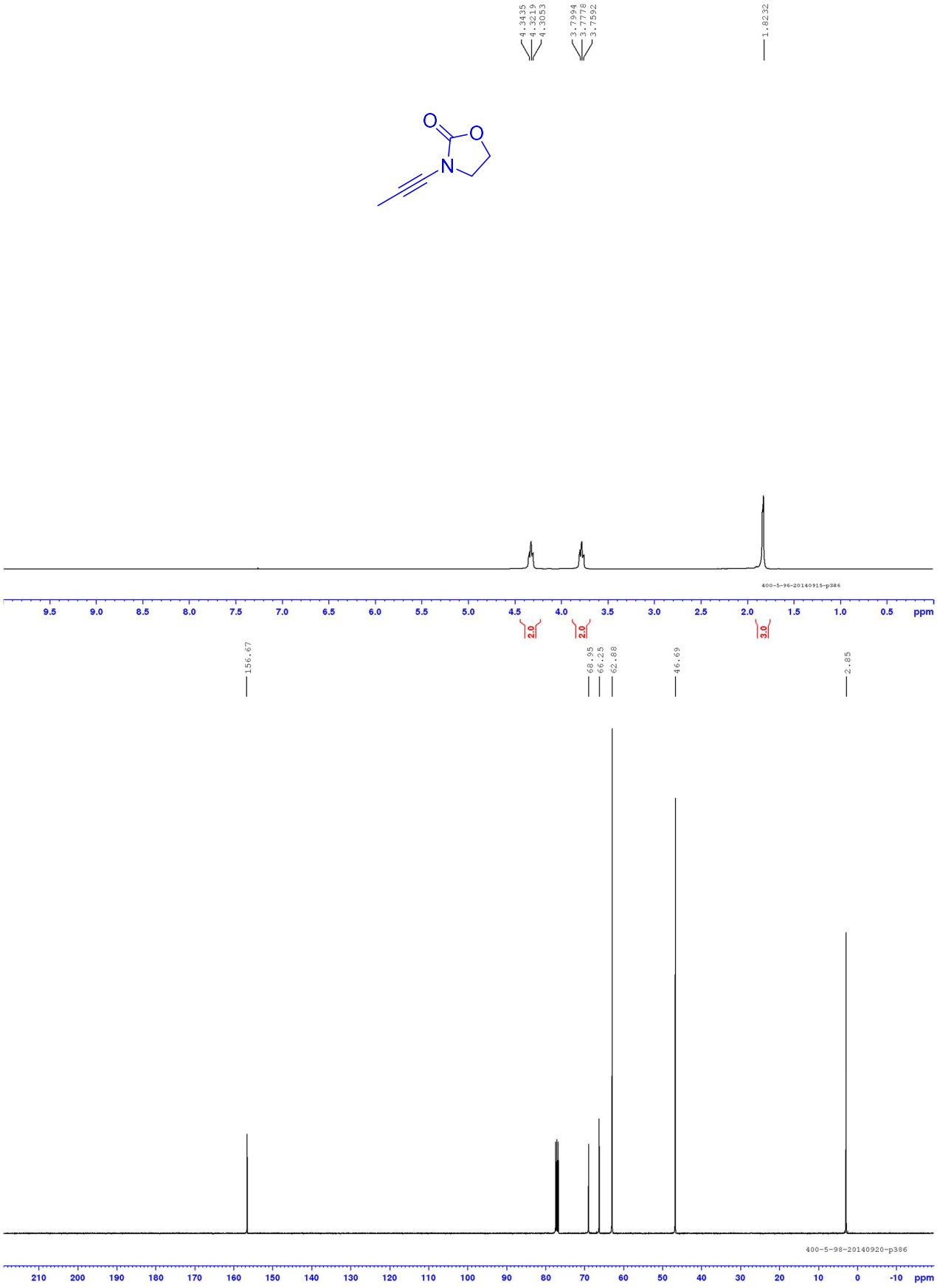
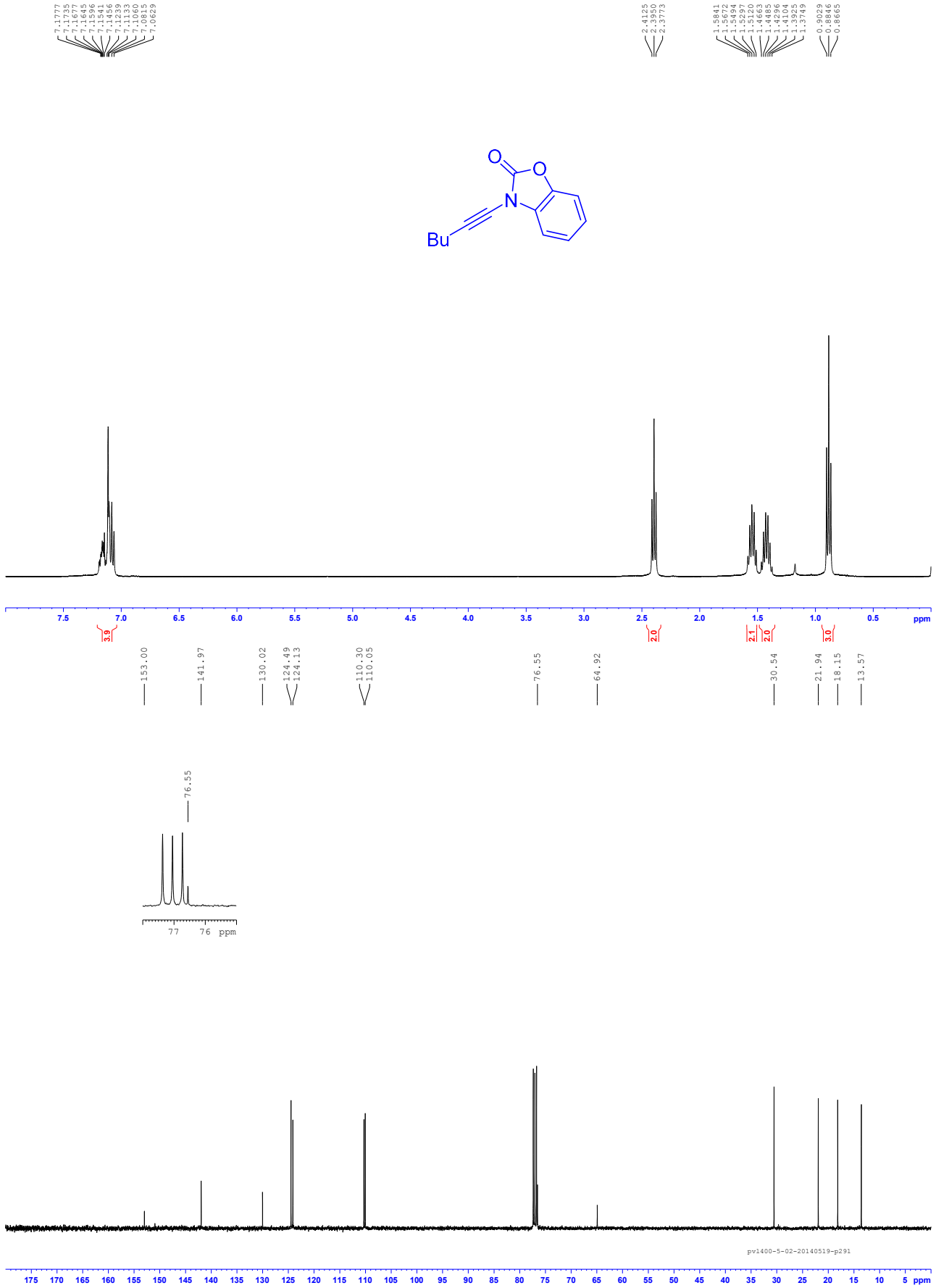


3-(Hex-1-yn-1-yl)benzo[*d*]oxazol-2(3*H*)-one (1c)



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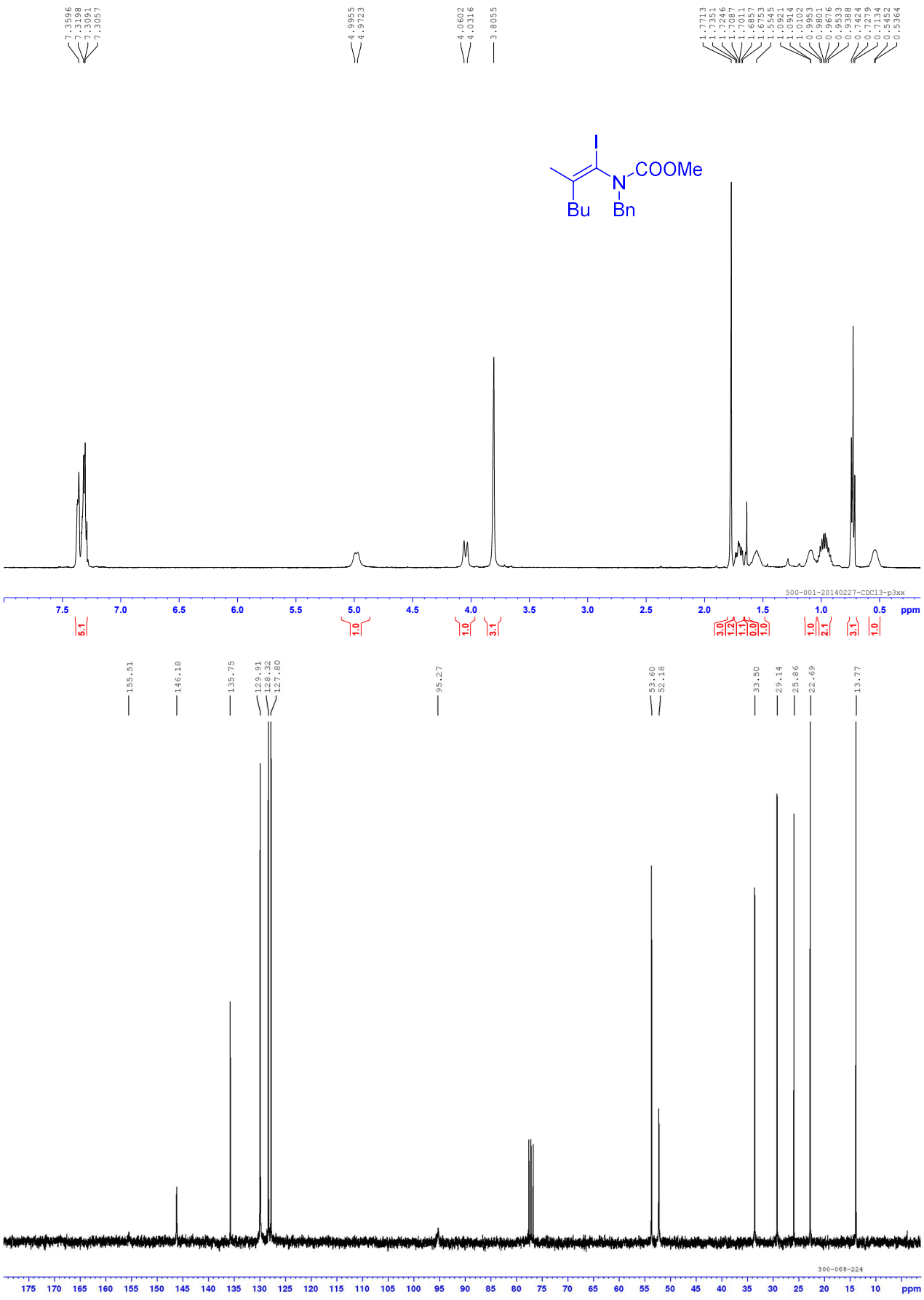
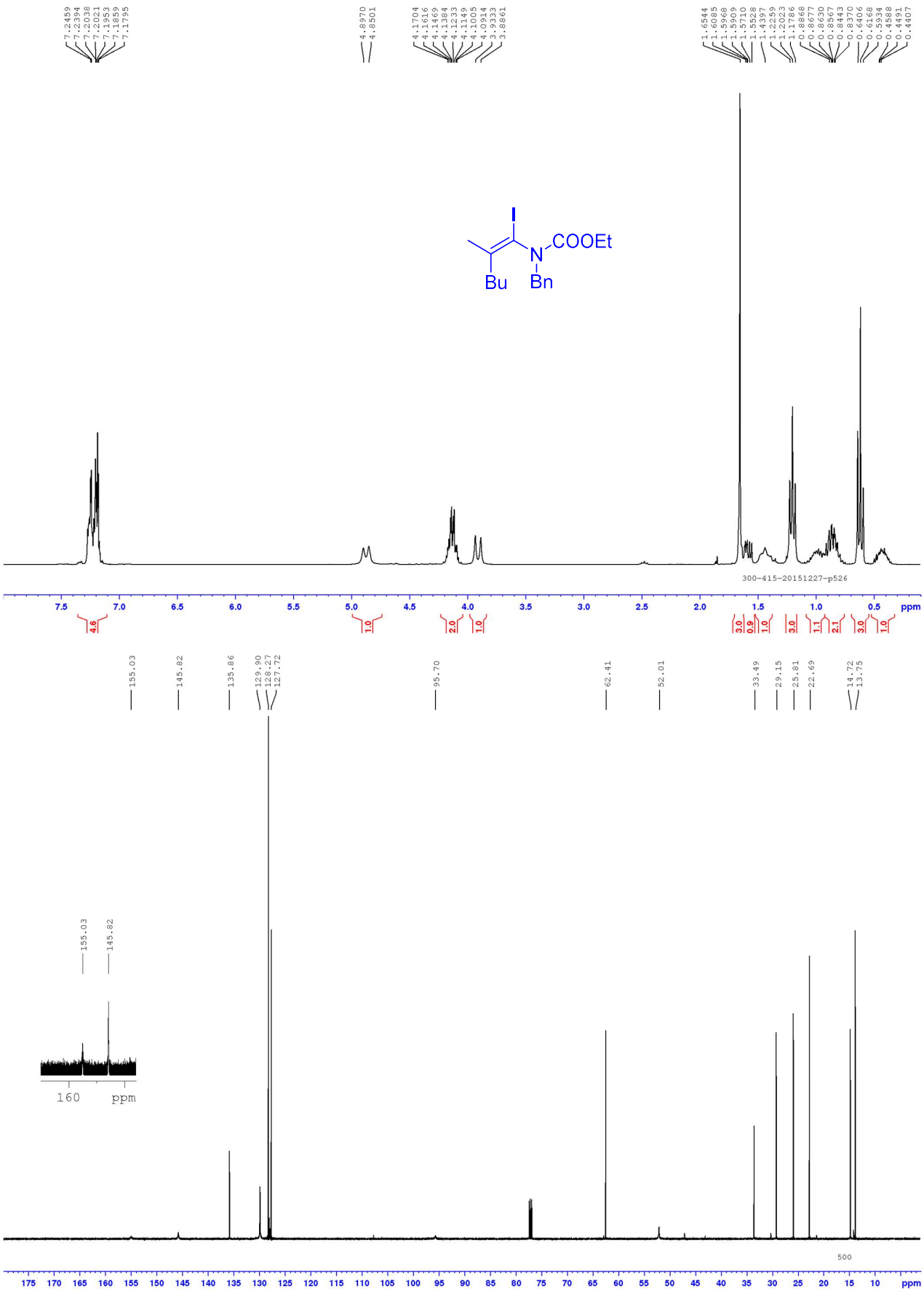


***(E)*-Ethyl benzyl(1-iodo-2-methylhex-1-enyl)carbamate (4e)**



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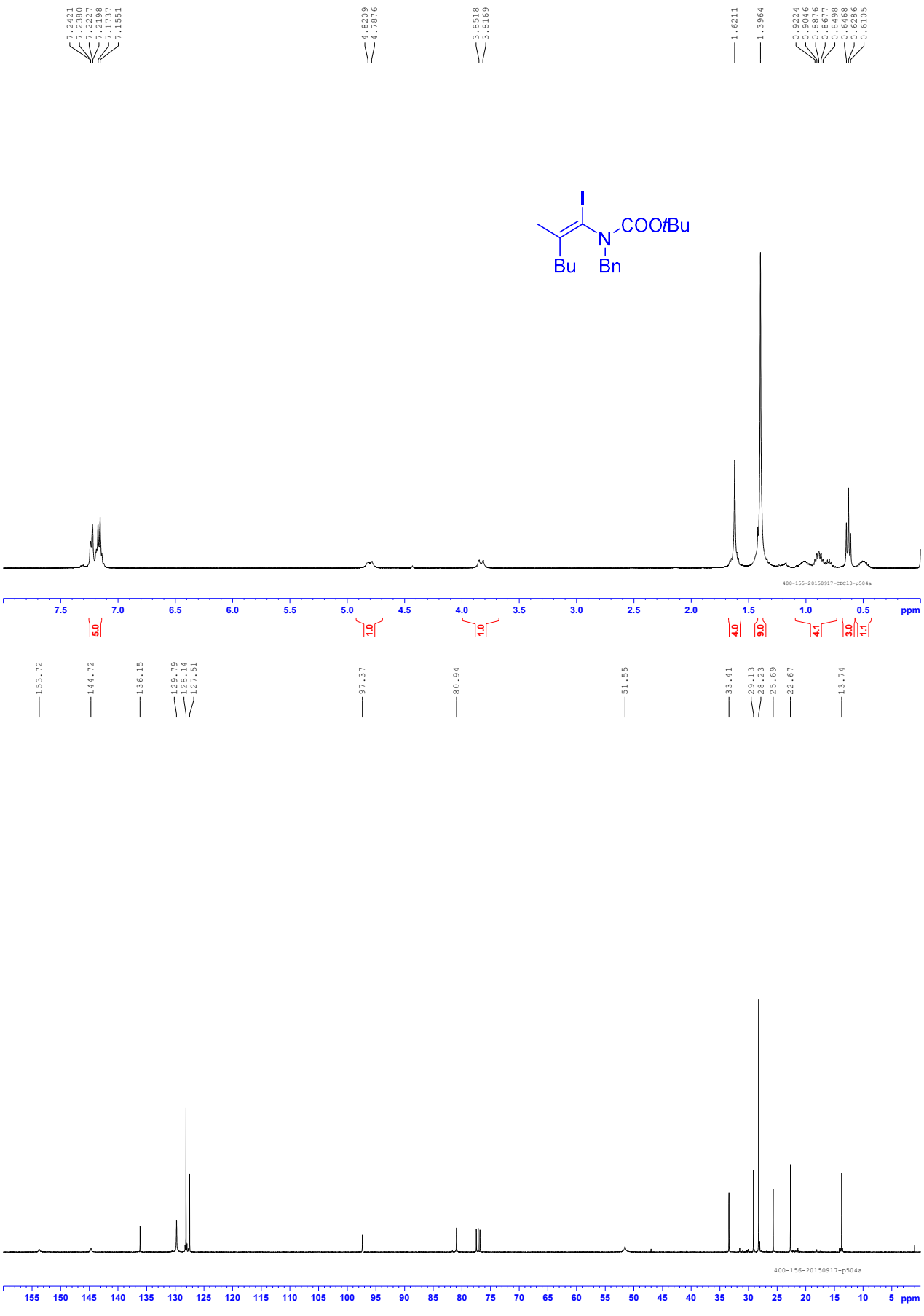
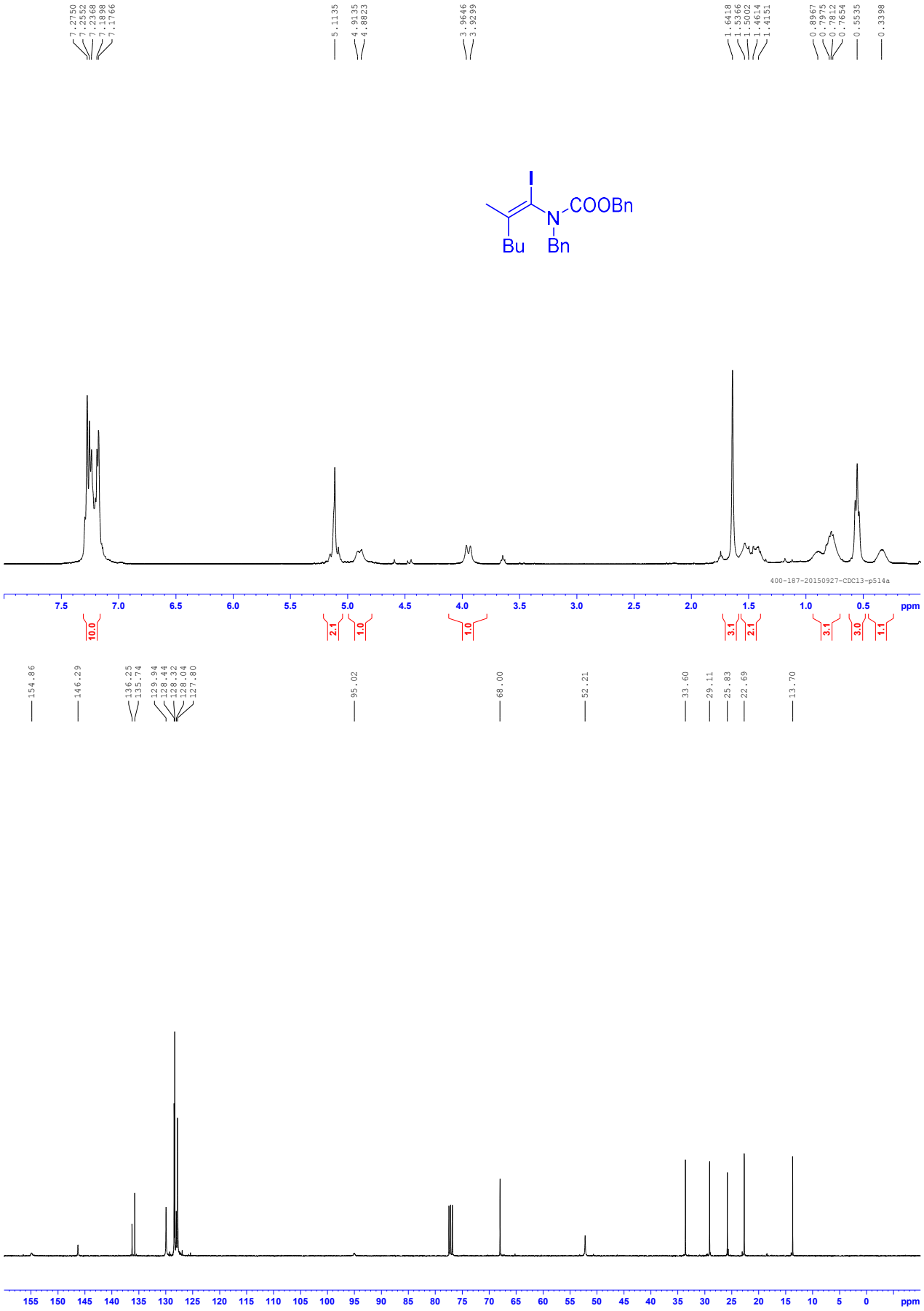
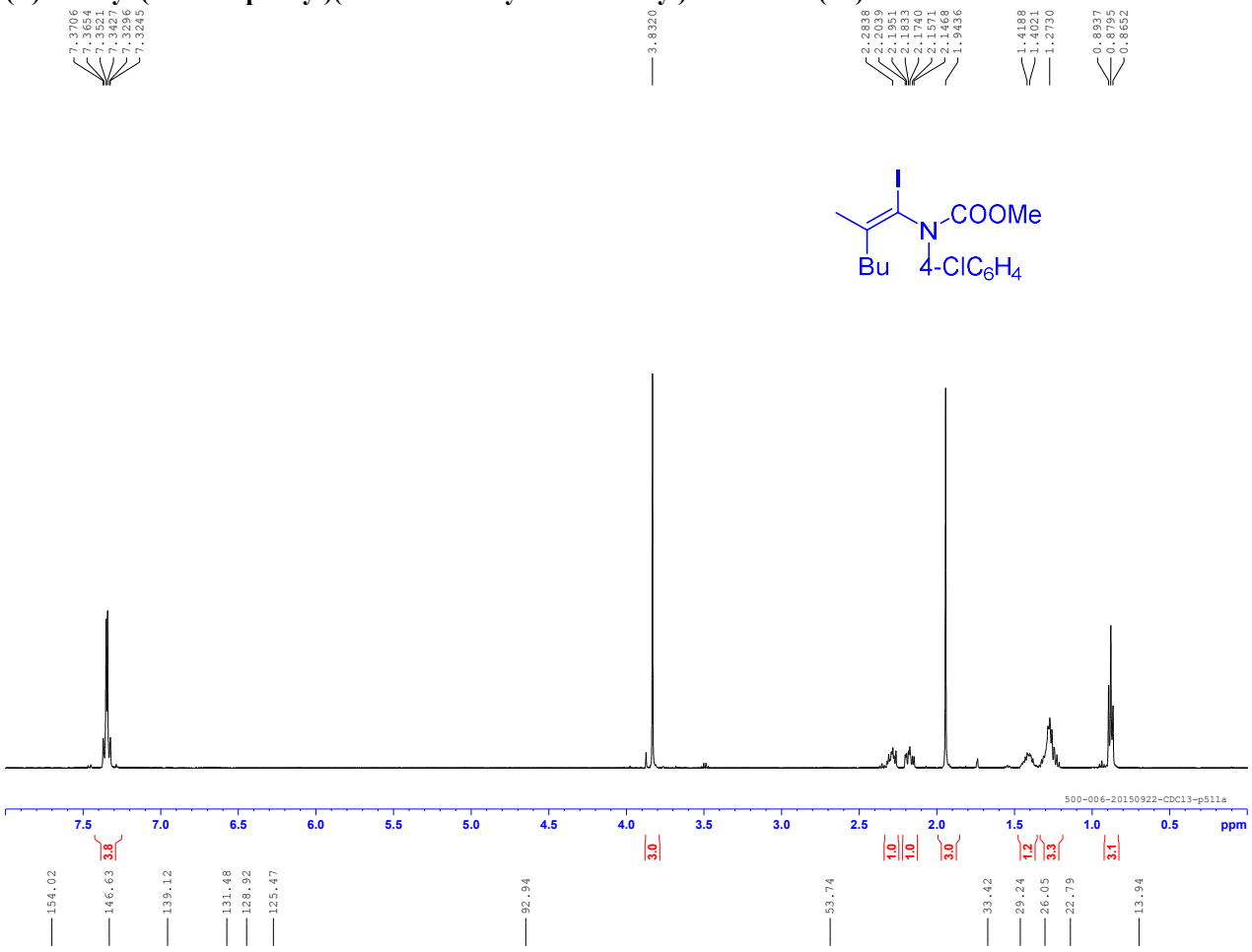


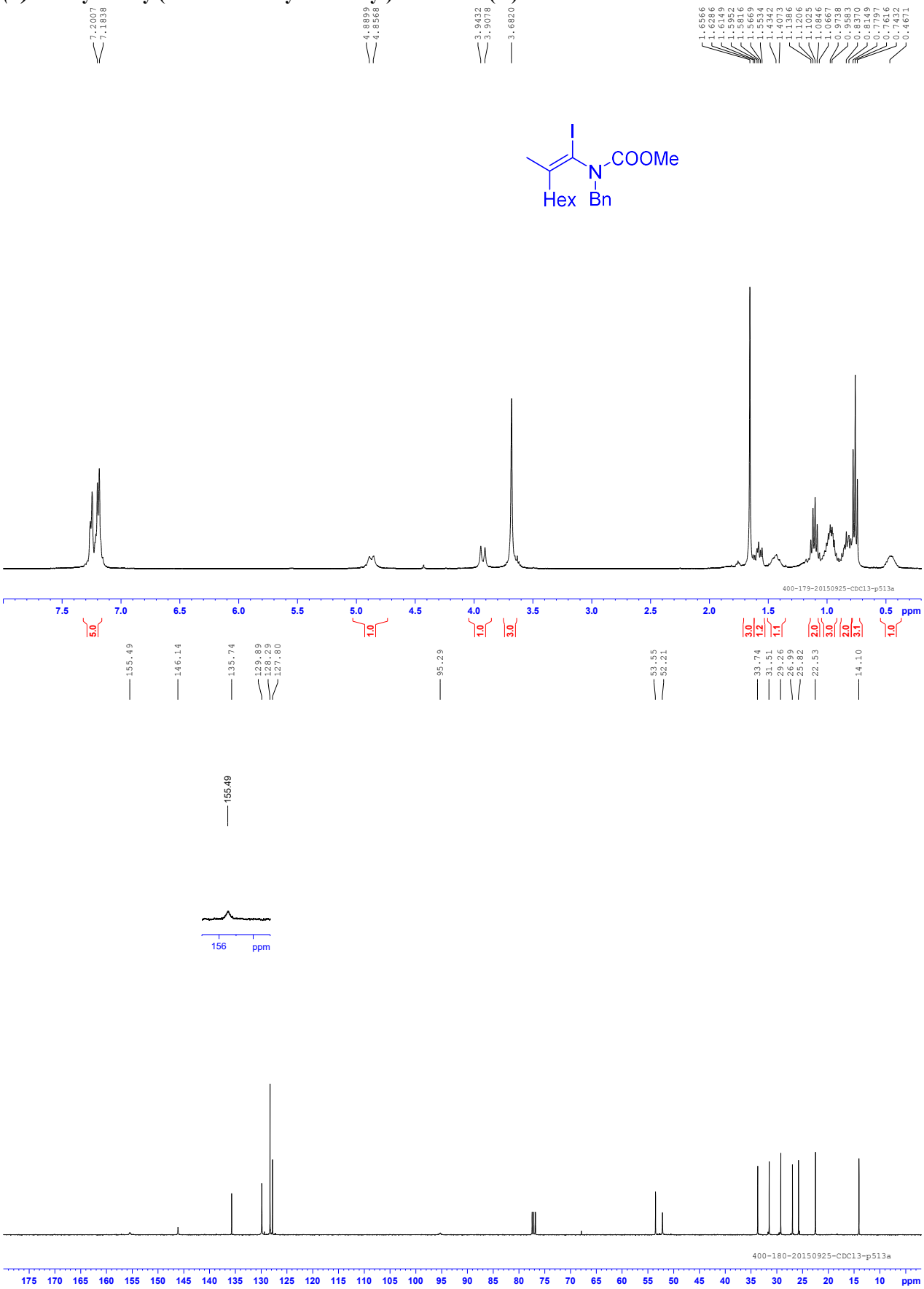
(*E*)-Benzyl benzyl(1-iodo-2-methylhex-1-en-1-yl)carbamate (4g)



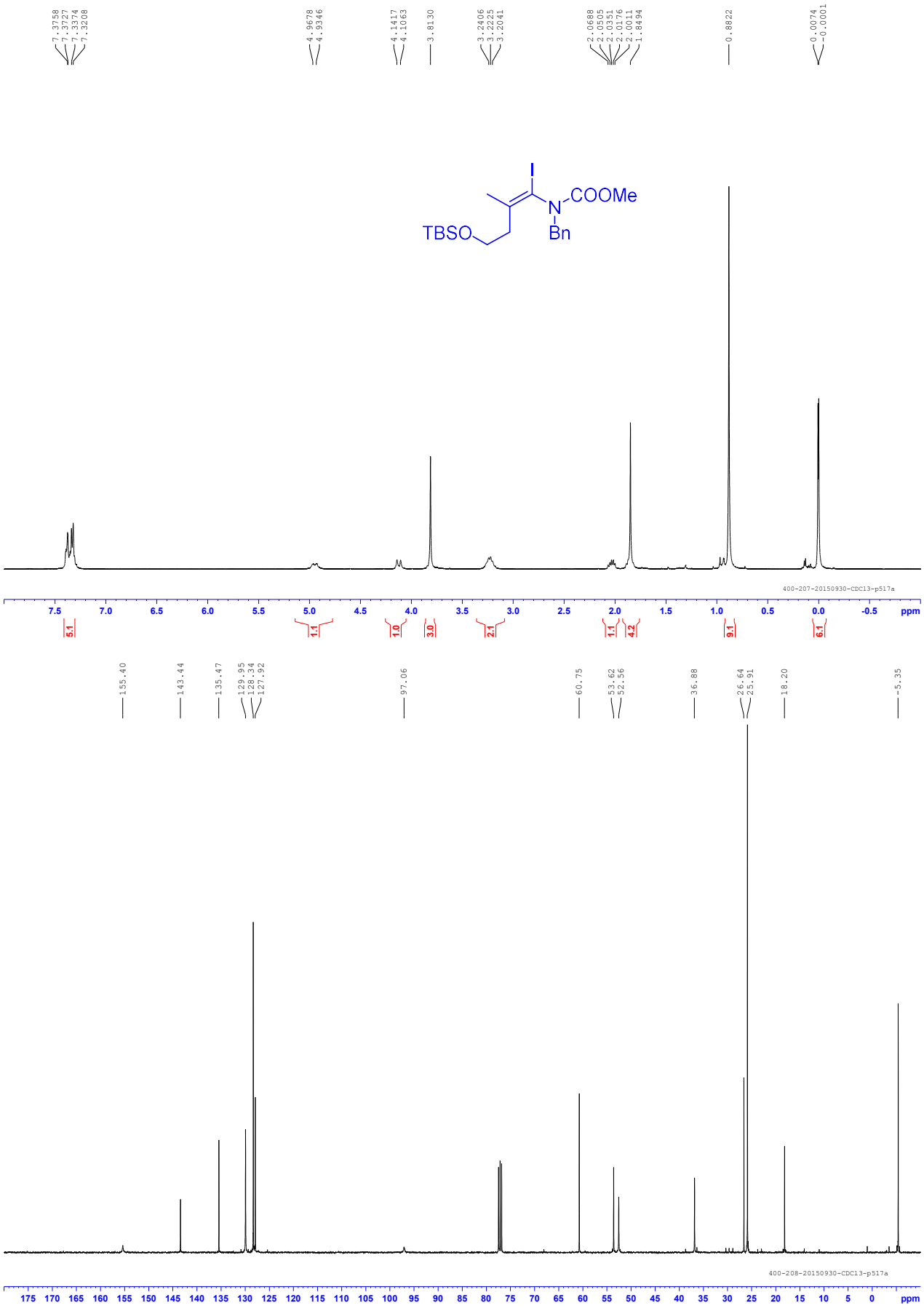
(*E*)-Methyl (4-chlorophenyl)(1-iodo-2-methylhex-1-en-1-yl)carbamate (4h)



_(E)_-Methyl benzyl(1-iodo-2-methyloct-1-enyl)carbamate (4i)

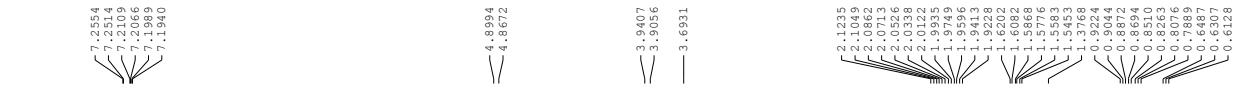


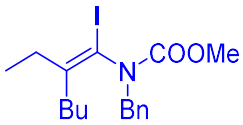
(*E*)-Methyl benzyl(4-((*tert*-butyldimethylsilyl)oxy)-1-iodo-2-methylbut-1-en-1-yl)carbamate (4j)

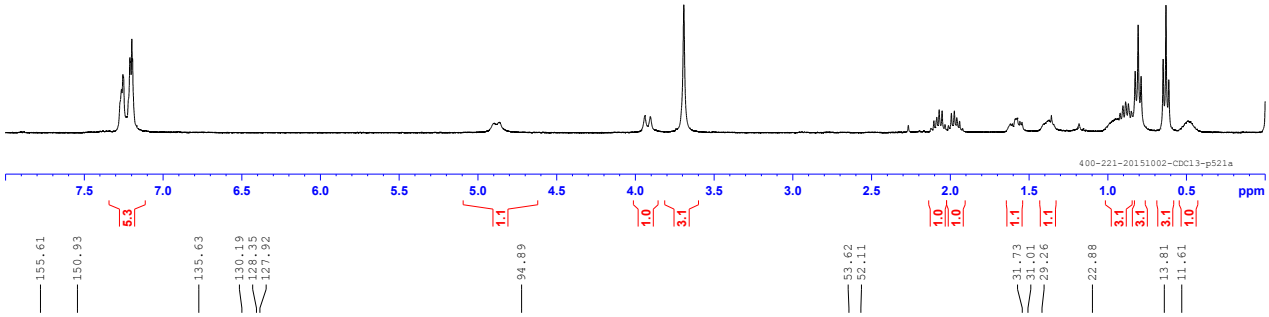


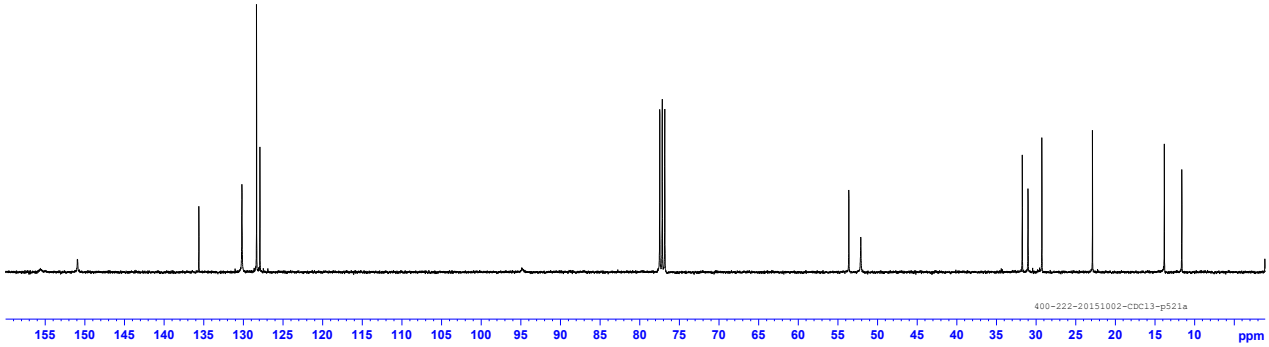
(*E*)-Methyl benzyl(1-iodo-2-phenylprop-1-en-1-yl)carbamate (4k)

(*E*)-Methyl benzyl(2-ethyl-1-iodohex-1-en-1-yl)carbamate (4l)

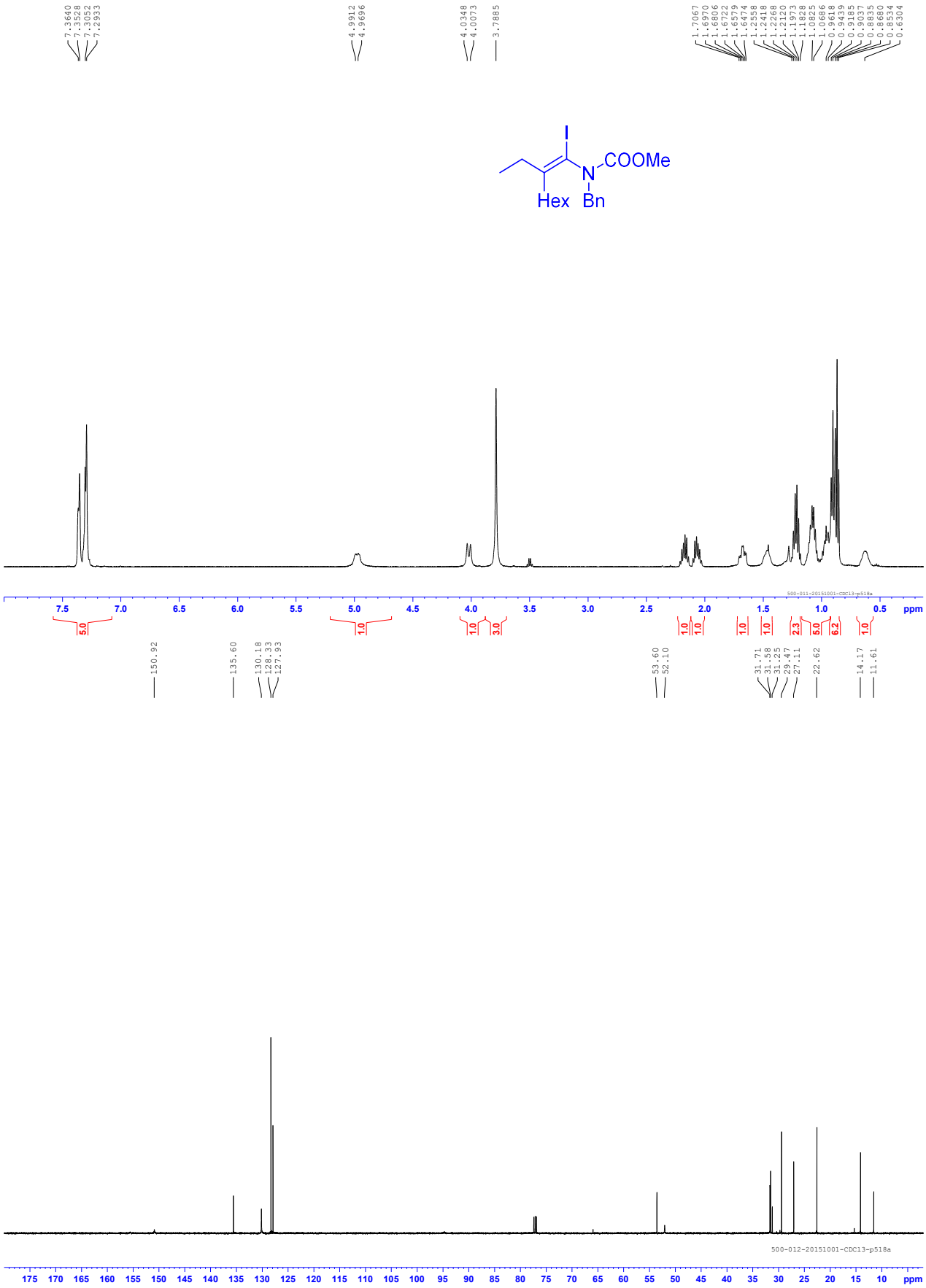




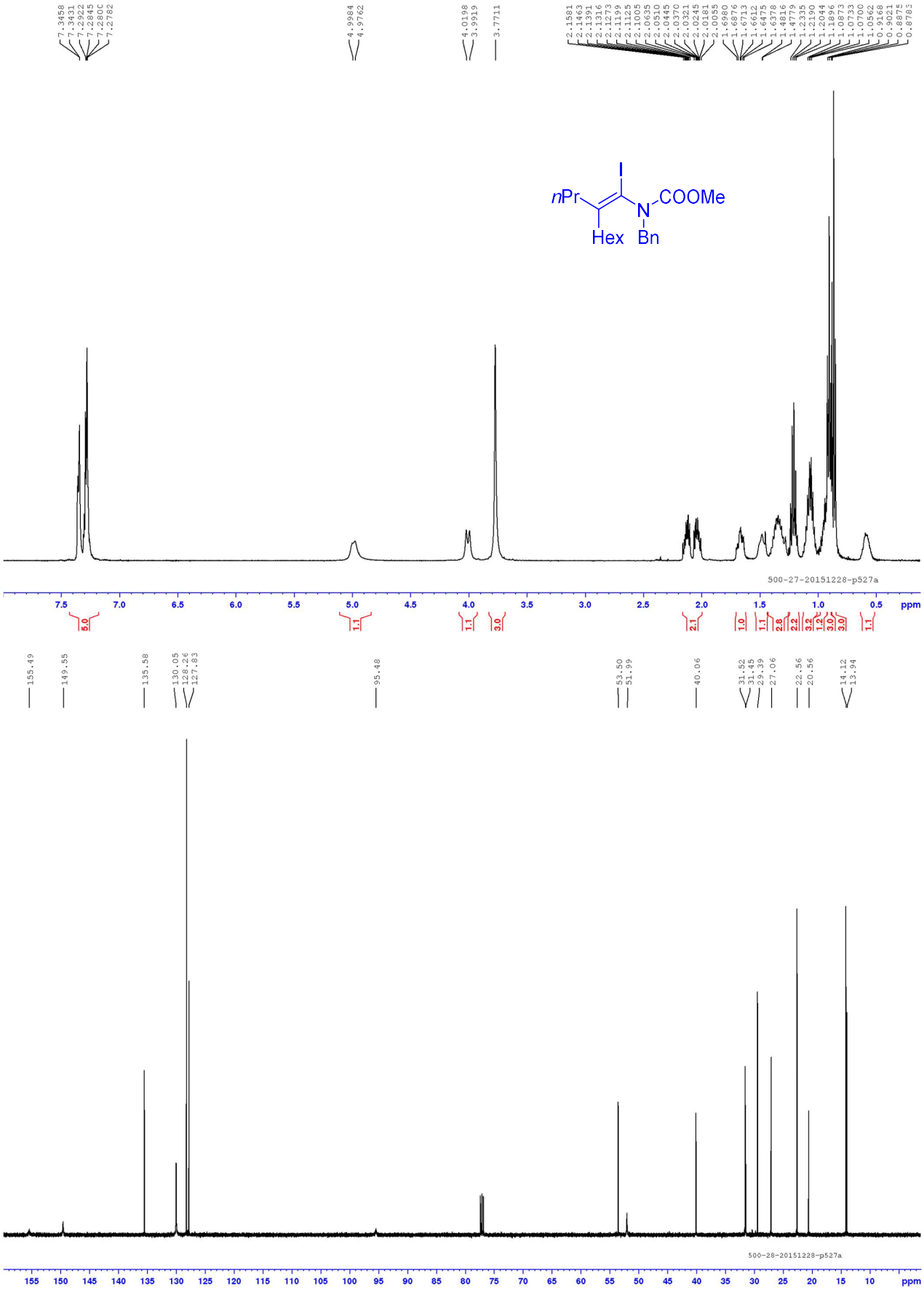




(*E*)-Methyl benzyl(2-ethyl-1-iodooct-1-en-1-yl)carbamate (4m)



***(E)*-Methyl benzyl(1-iodo-2-propyloct-1-en-1-yl)carbamate (4n)**



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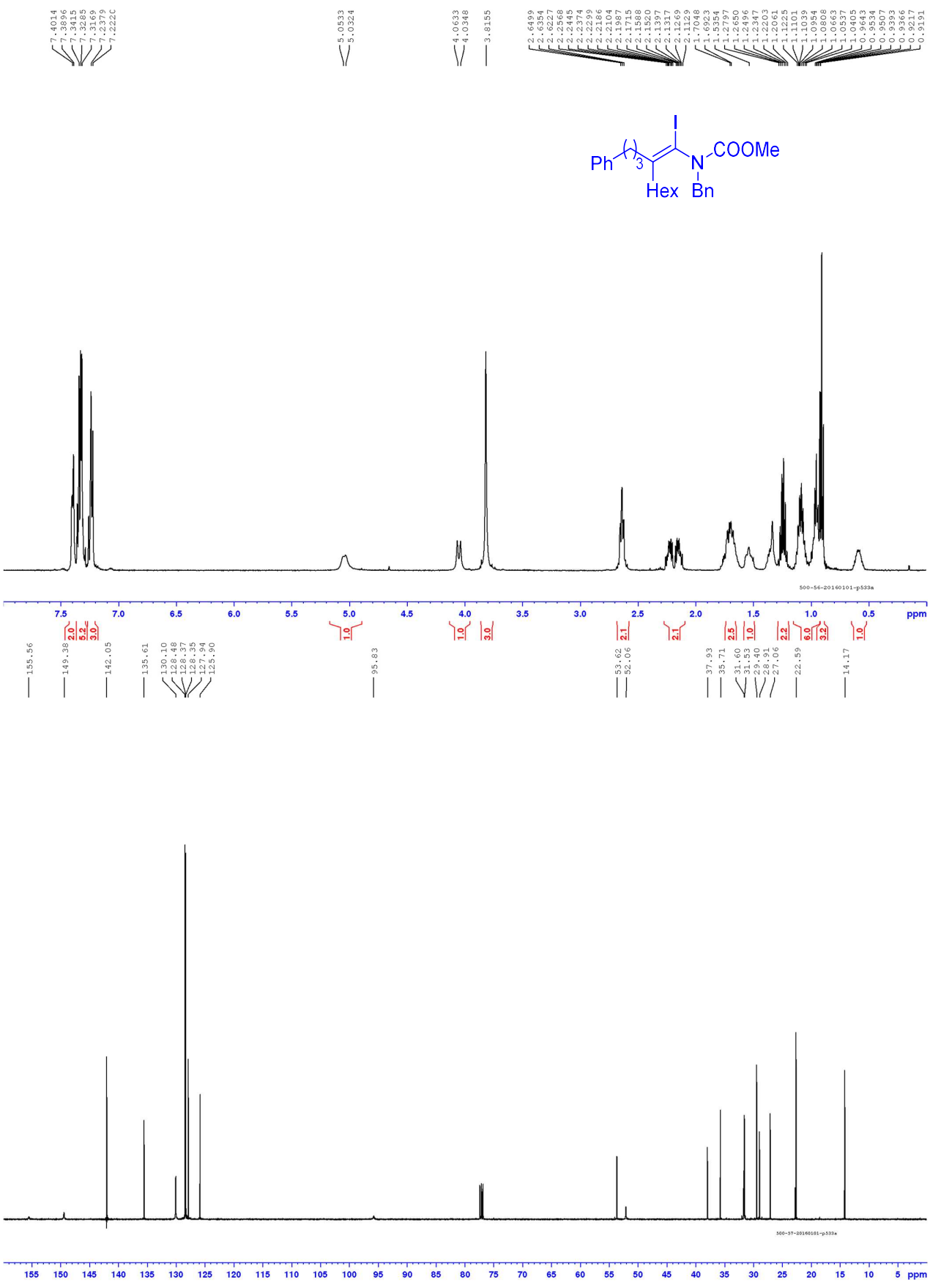
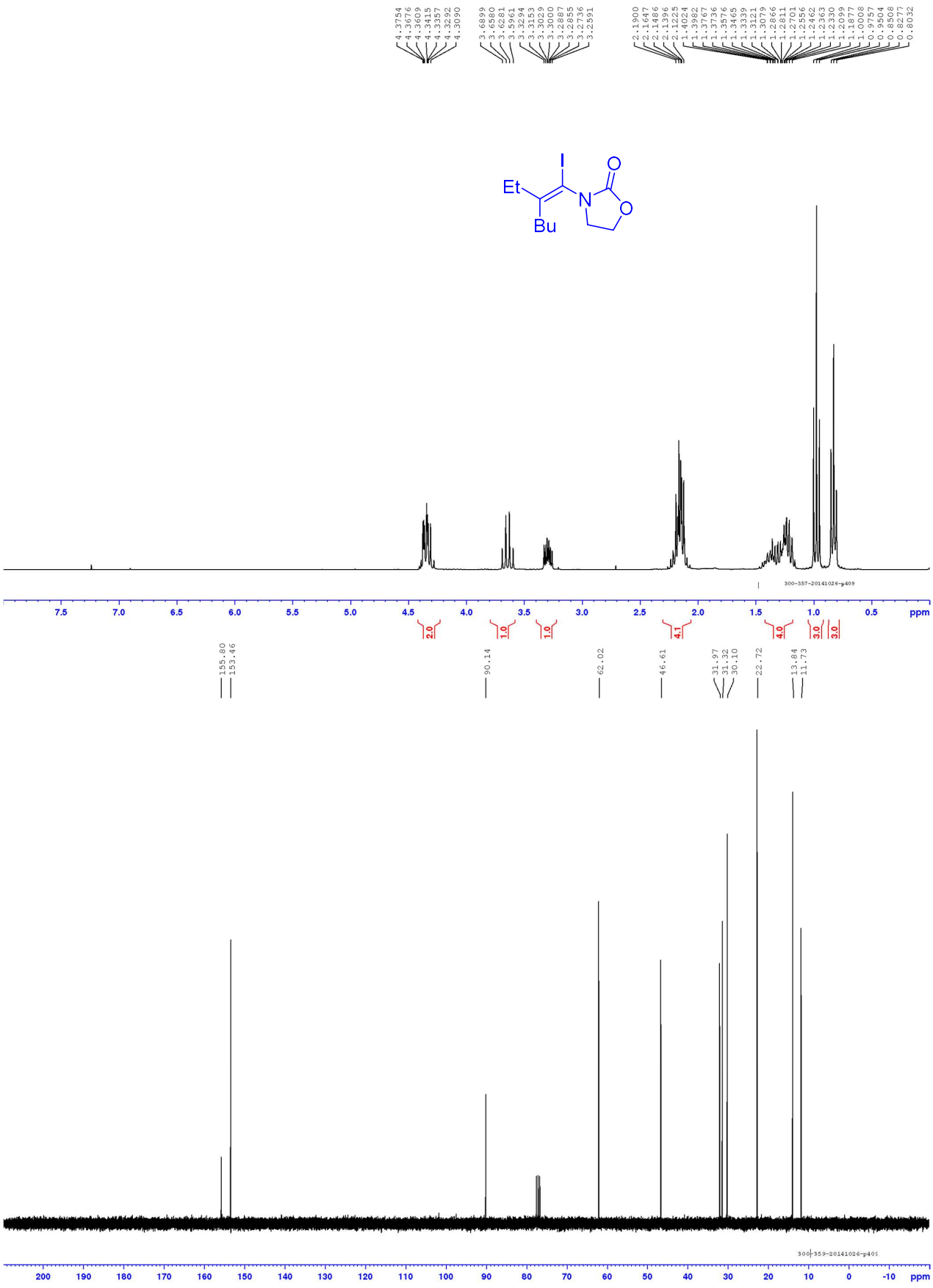
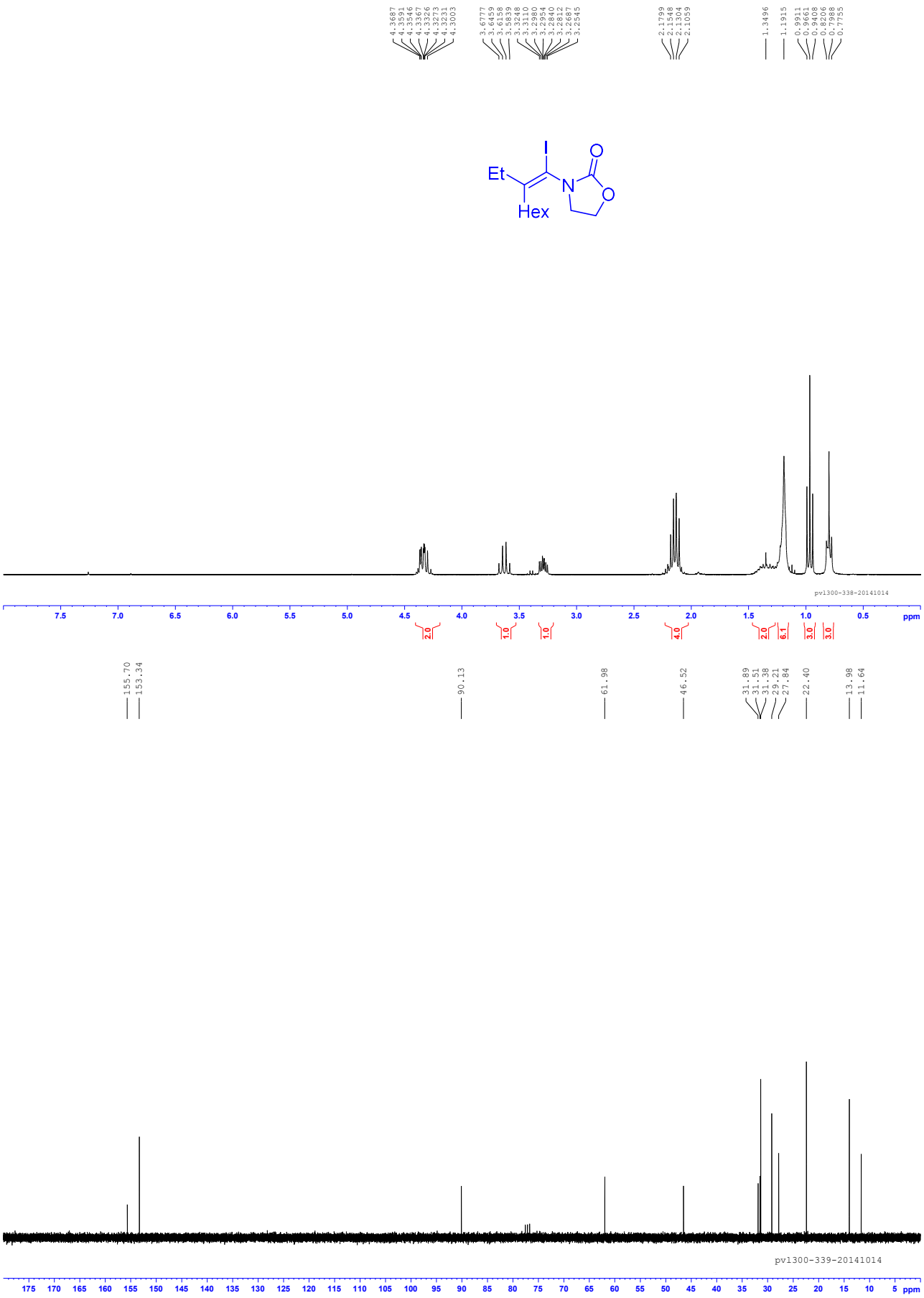


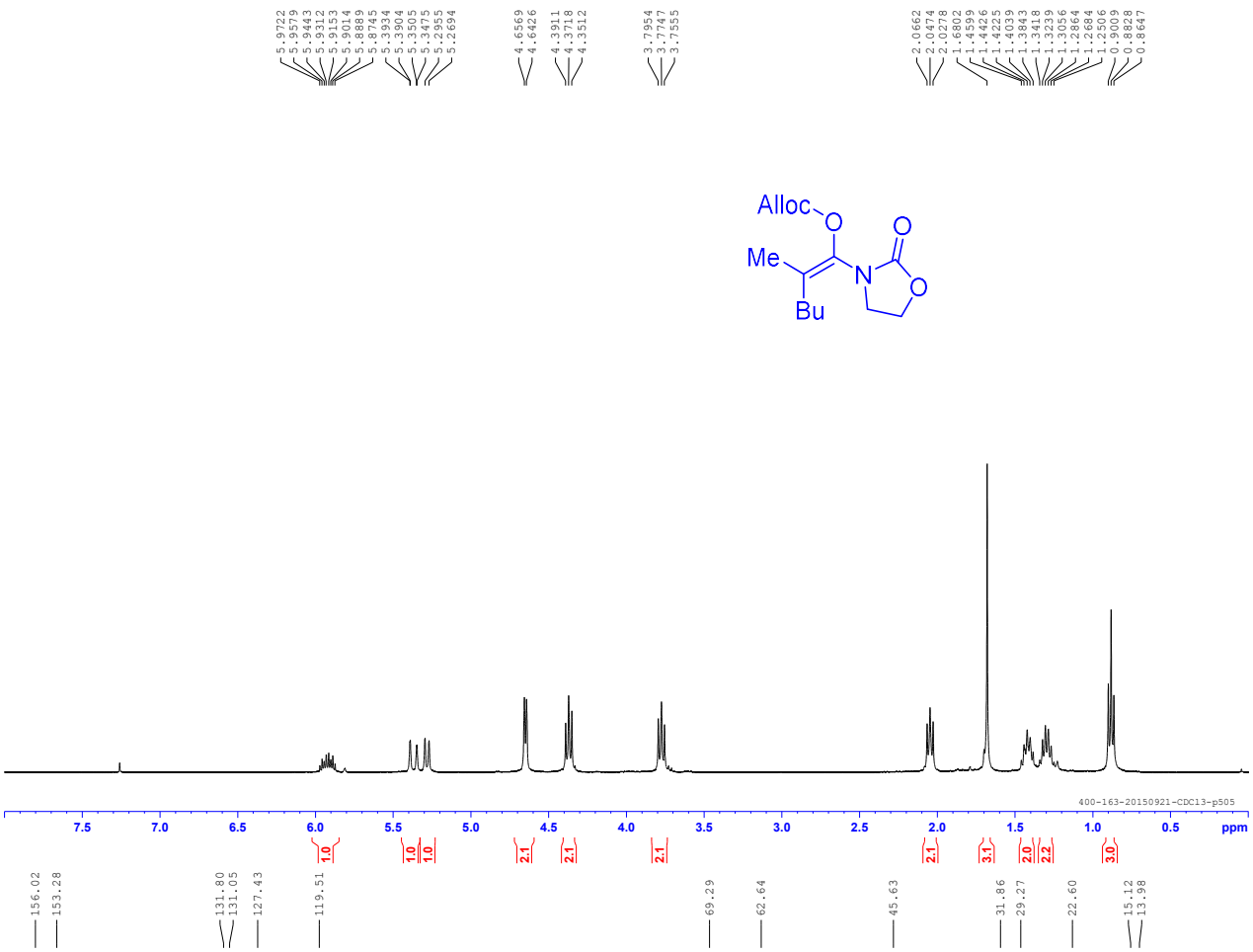
***(E)*-3-(2-Ethyl-1-iodohex-1-en-1-yl)oxazolidin-2-one (4p)**



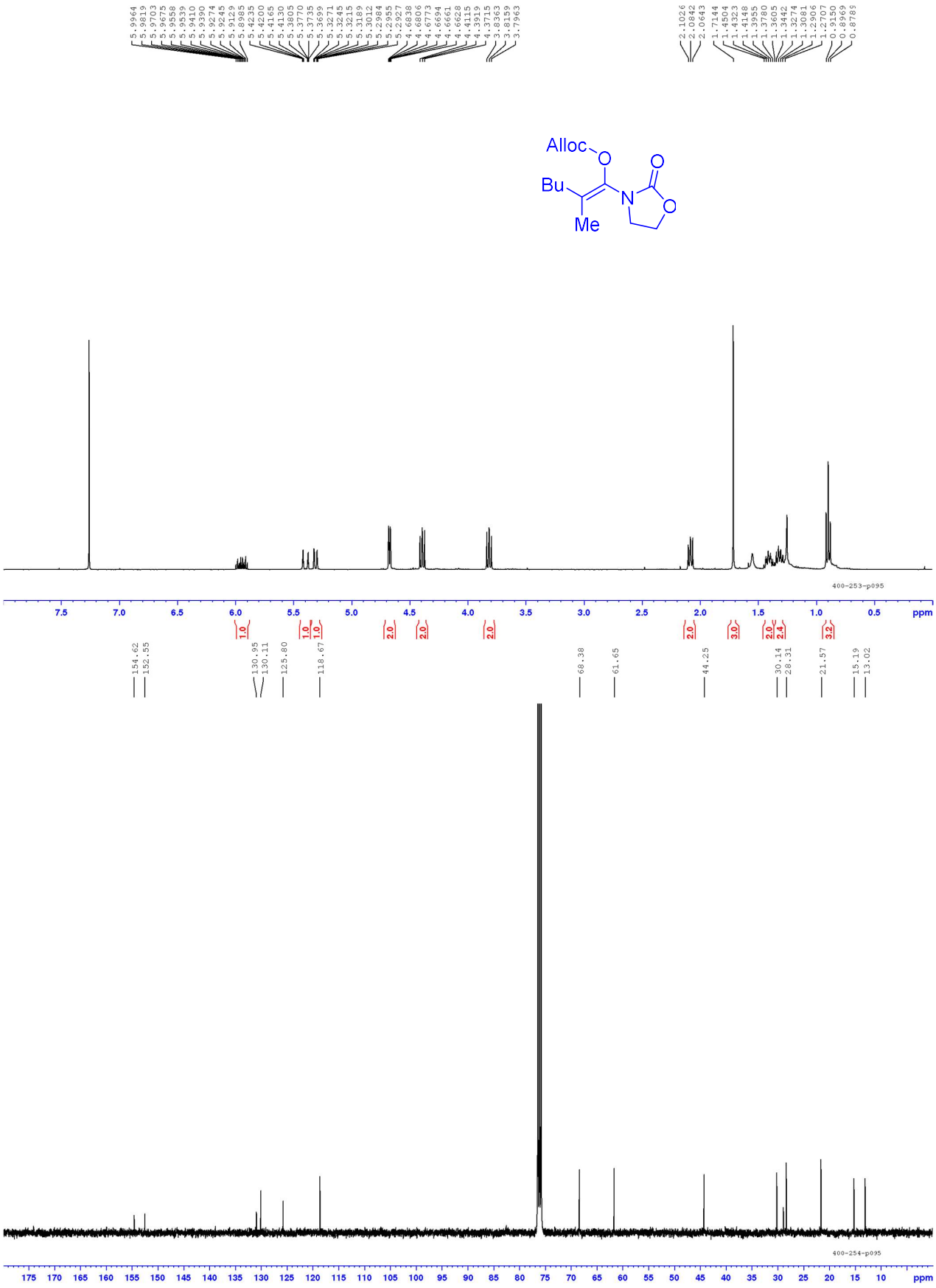
***(E)*-3-(2-Ethyl-1-iodooct-1-en-1-yl)oxazolidin-2-one (4q)**



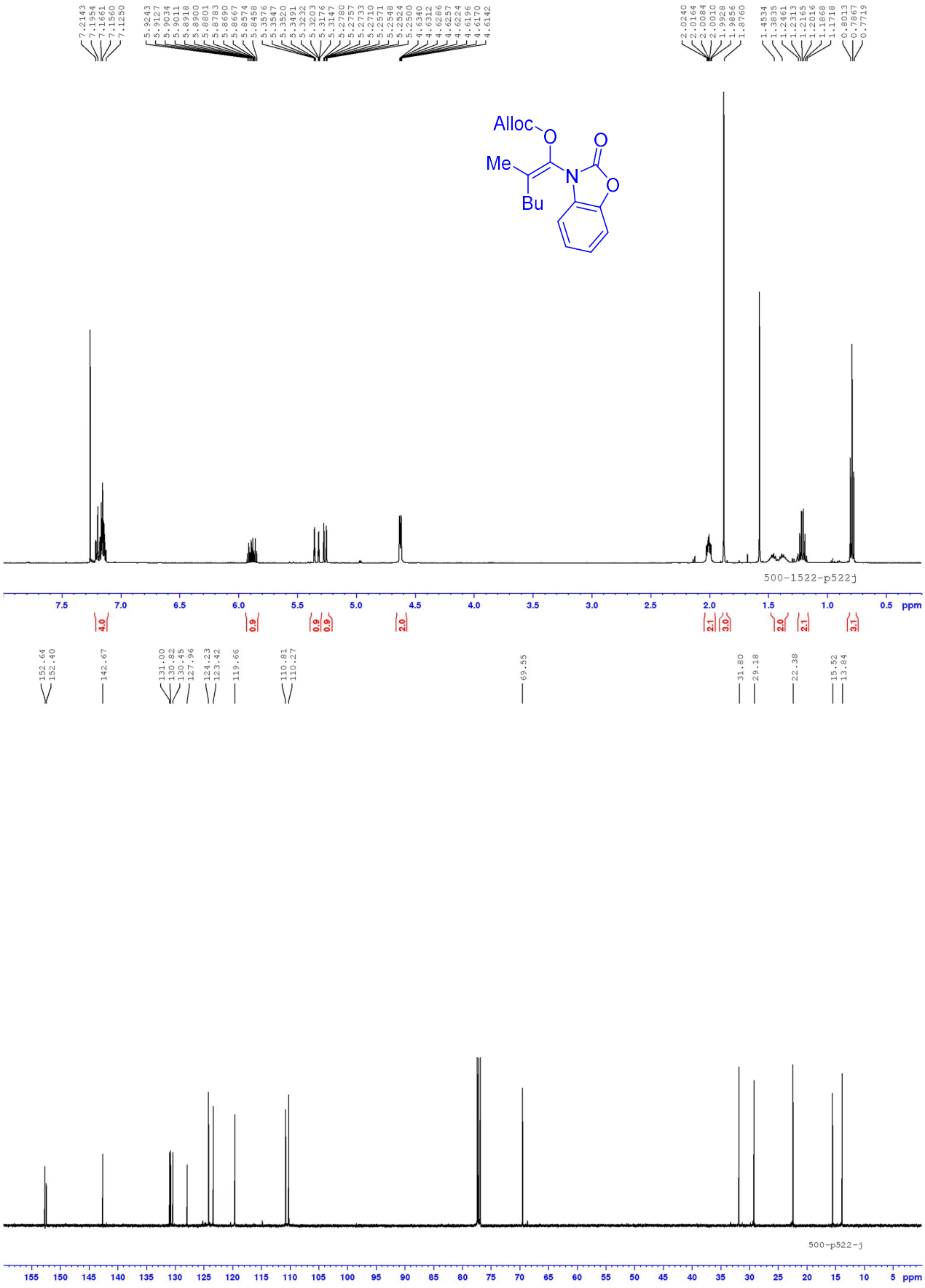
(*E*)-Allyl (2-methyl-1-(2-oxooxazolidin-3-yl)hex-1-en-1-yl) carbonate (3a)



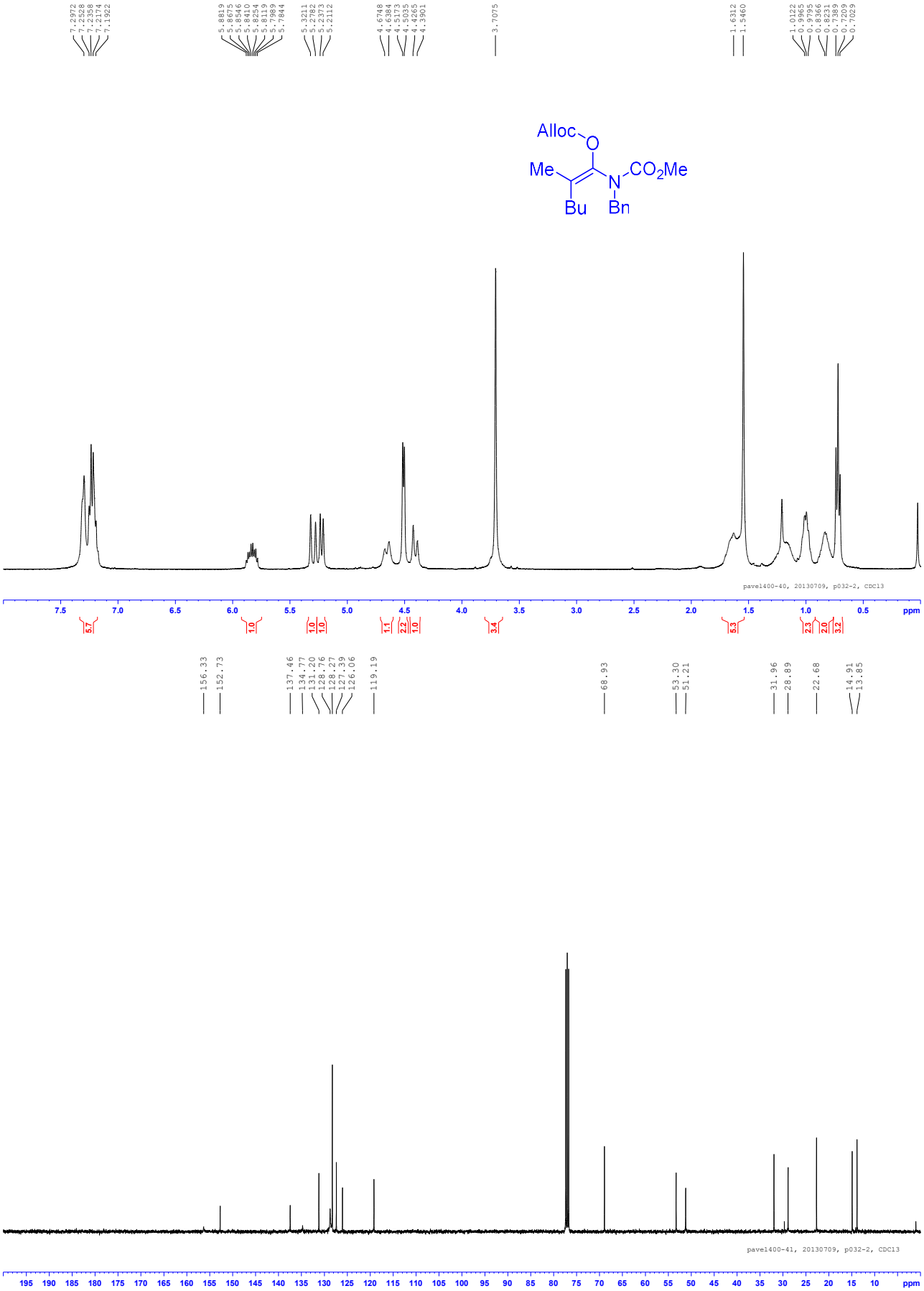
***(Z)*-Allyl (2-methyl-1-(2-oxooxazolidin-3-yl)hex-1-en-1-yl) carbonate (3b)**



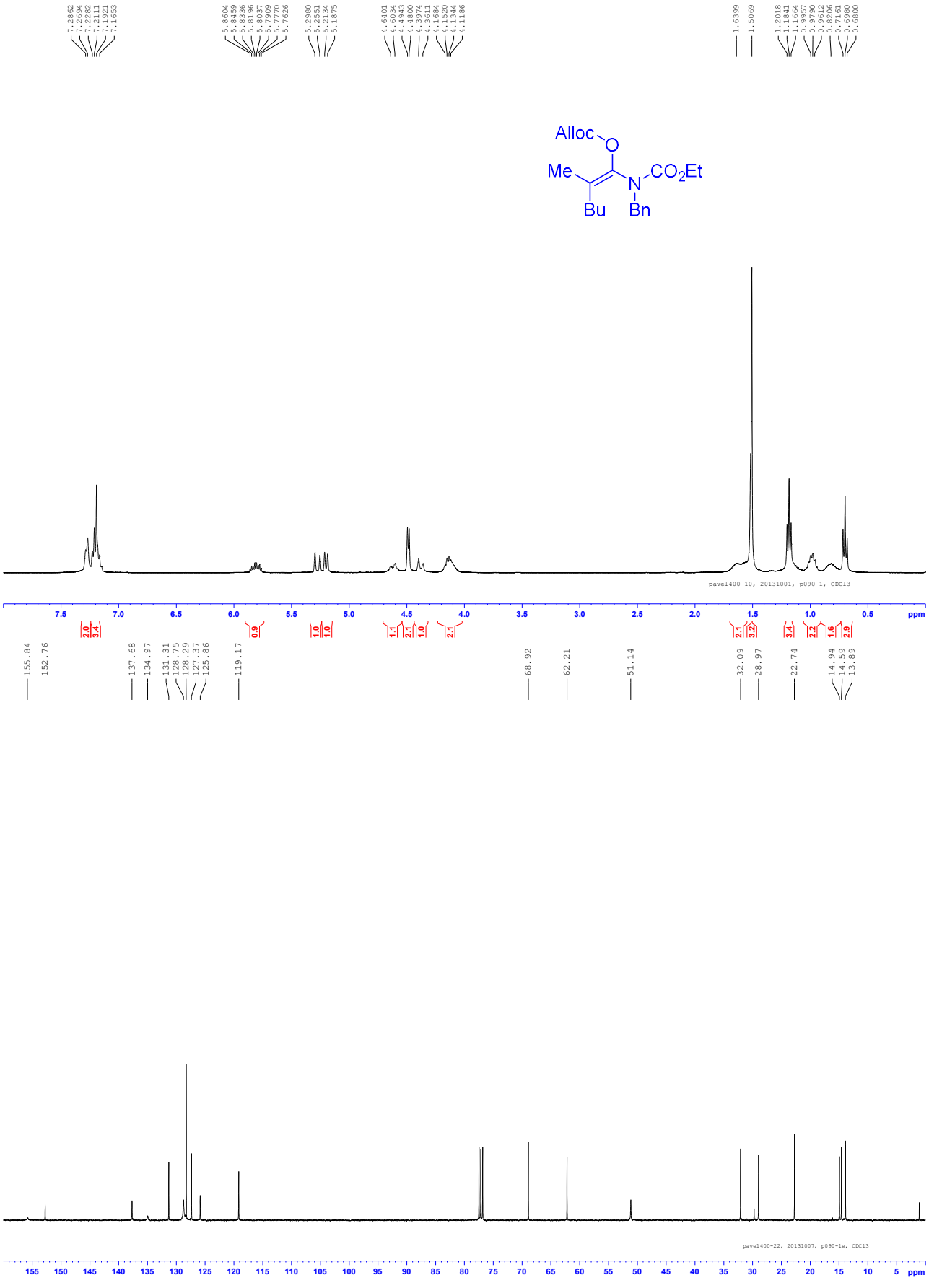
***(E)*-Allyl (2-methyl-1-(2-oxobenzo[d]oxazol-3(2H)-yl)hex-1-en-1-yl) carbonate (3c)**



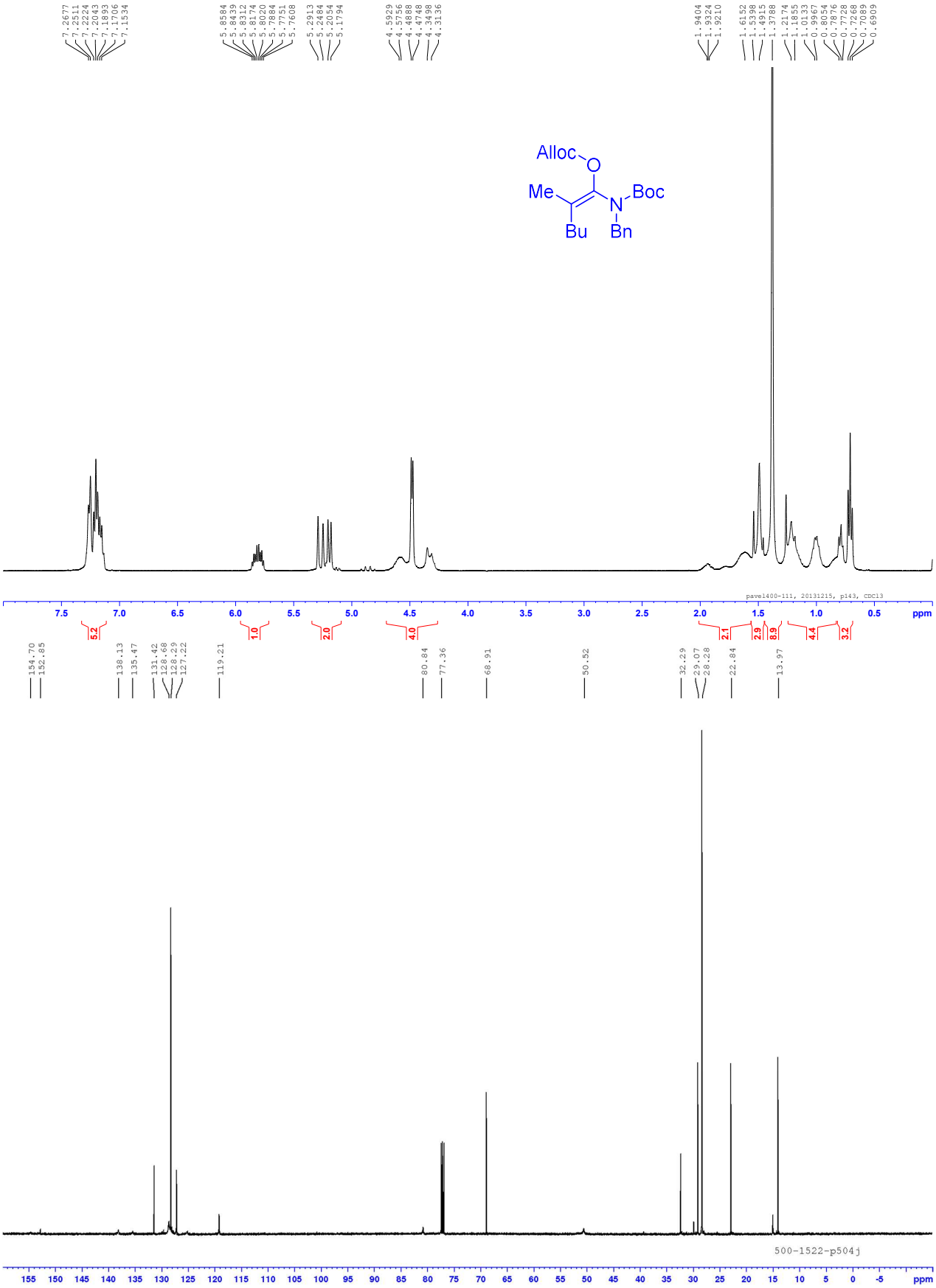
***(E)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3d)**



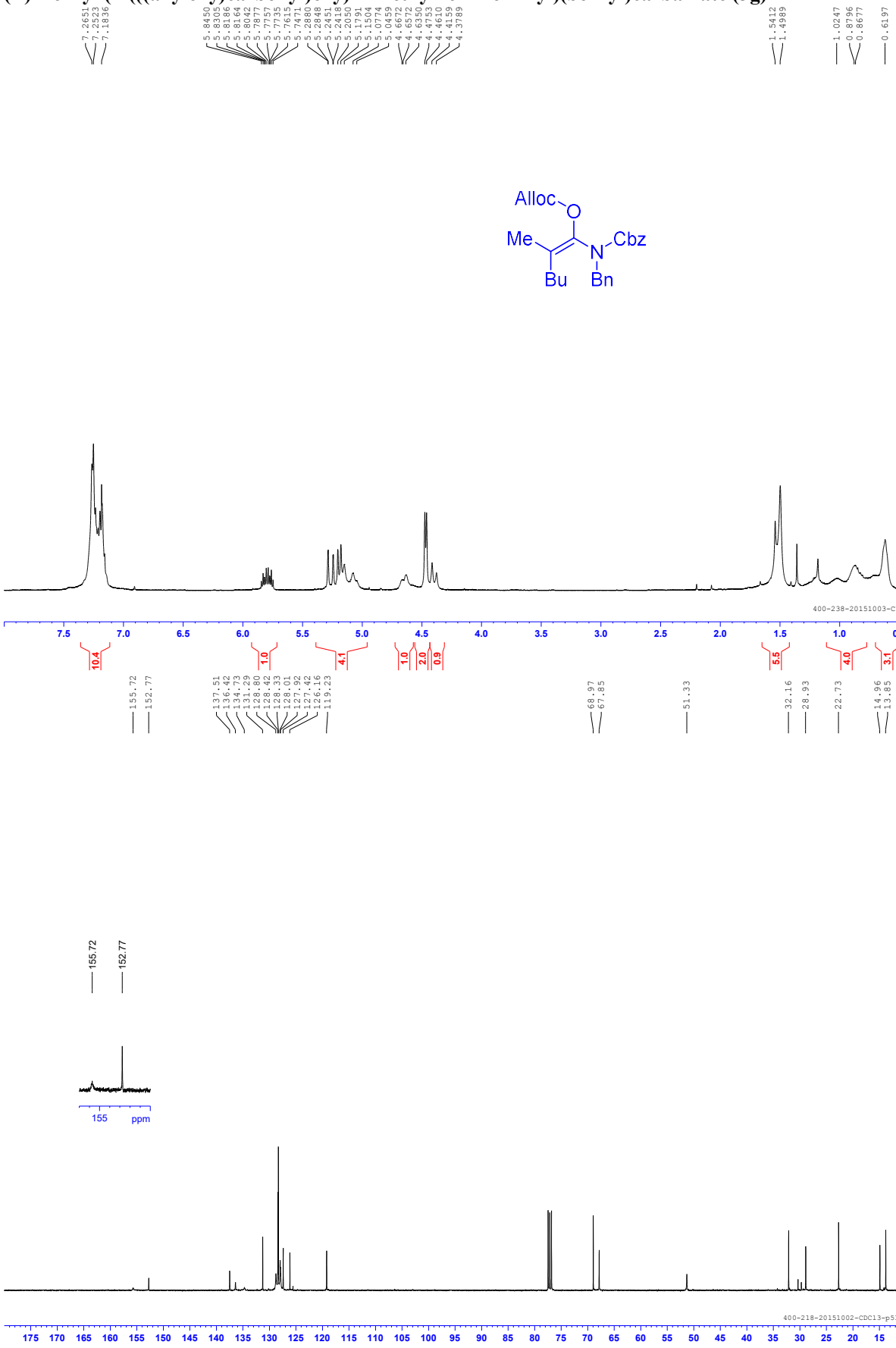
***(E)*-Ethyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3e)**



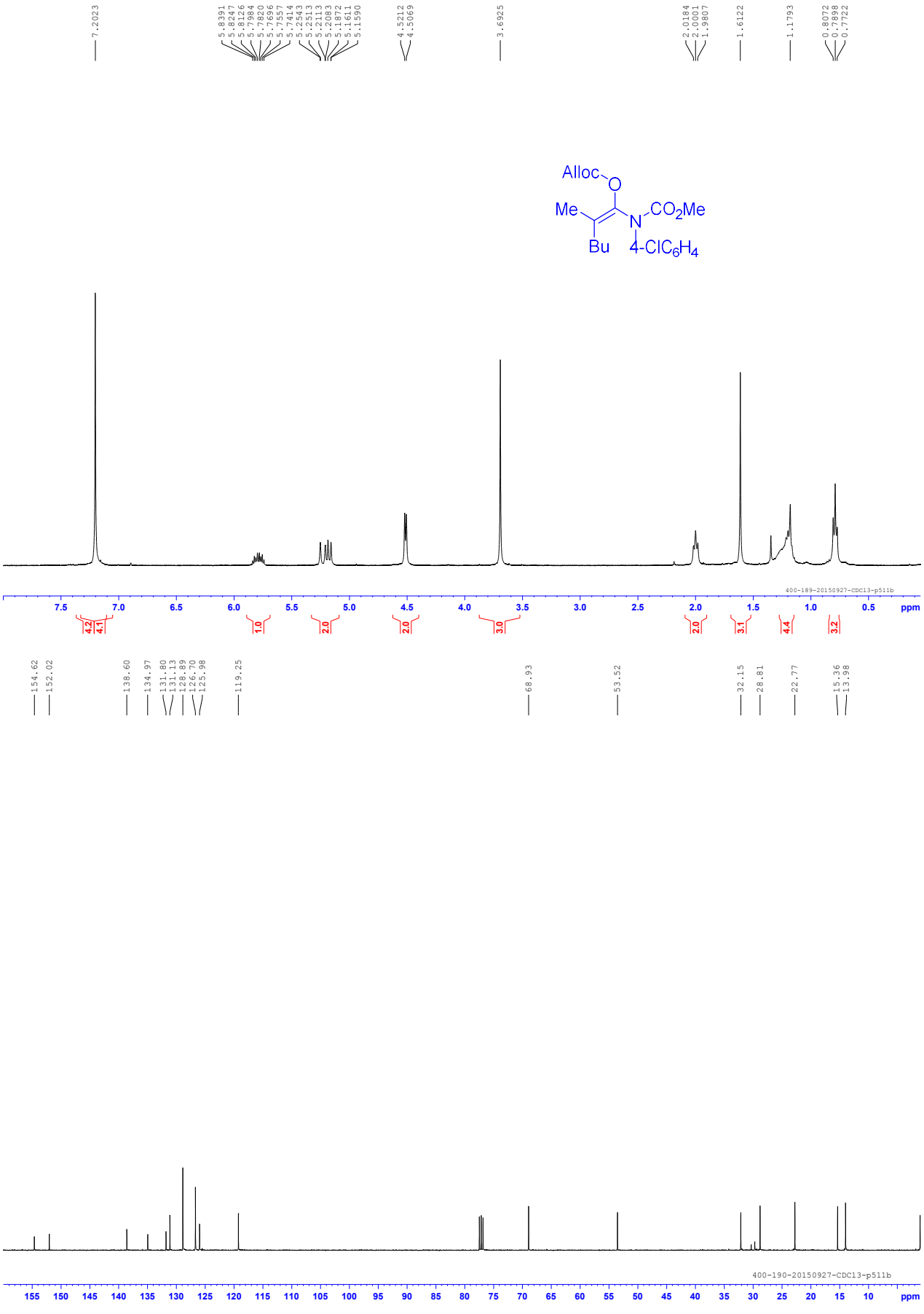
***(E)-tert*-Butyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3f)**



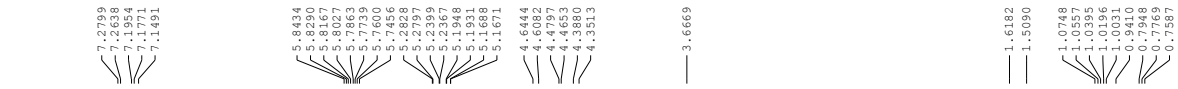
(*E*)-Benzyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(benzyl)carbamate (3g)

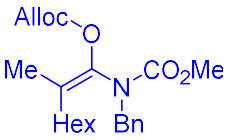


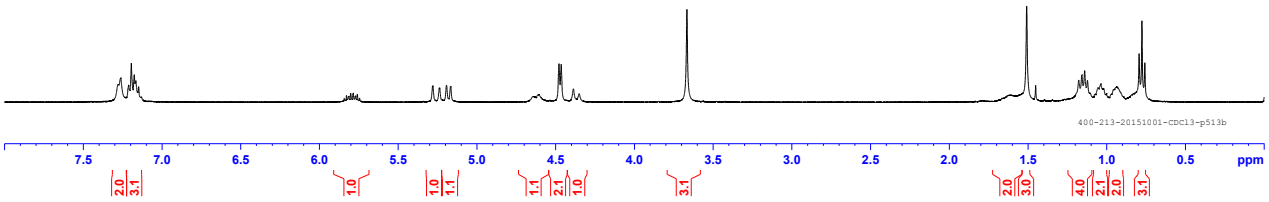
(*E*)-Methyl (1-(((allyloxy)carbonyl)oxy)-2-methylhex-1-en-1-yl)(4-chlorophenyl)carbamate (3h)

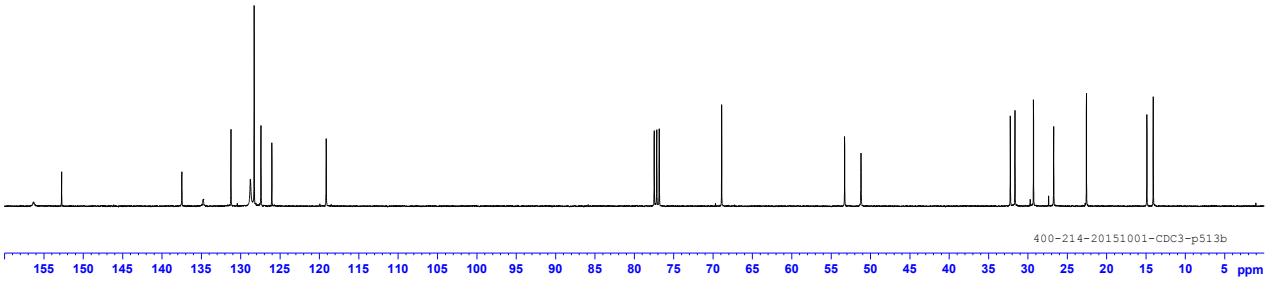


(*E*)-Methyl (1-(((allyloxy)carbonyl)oxy)-2-methyloct-1-en-1-yl)(benzyl)carbamate (3i)

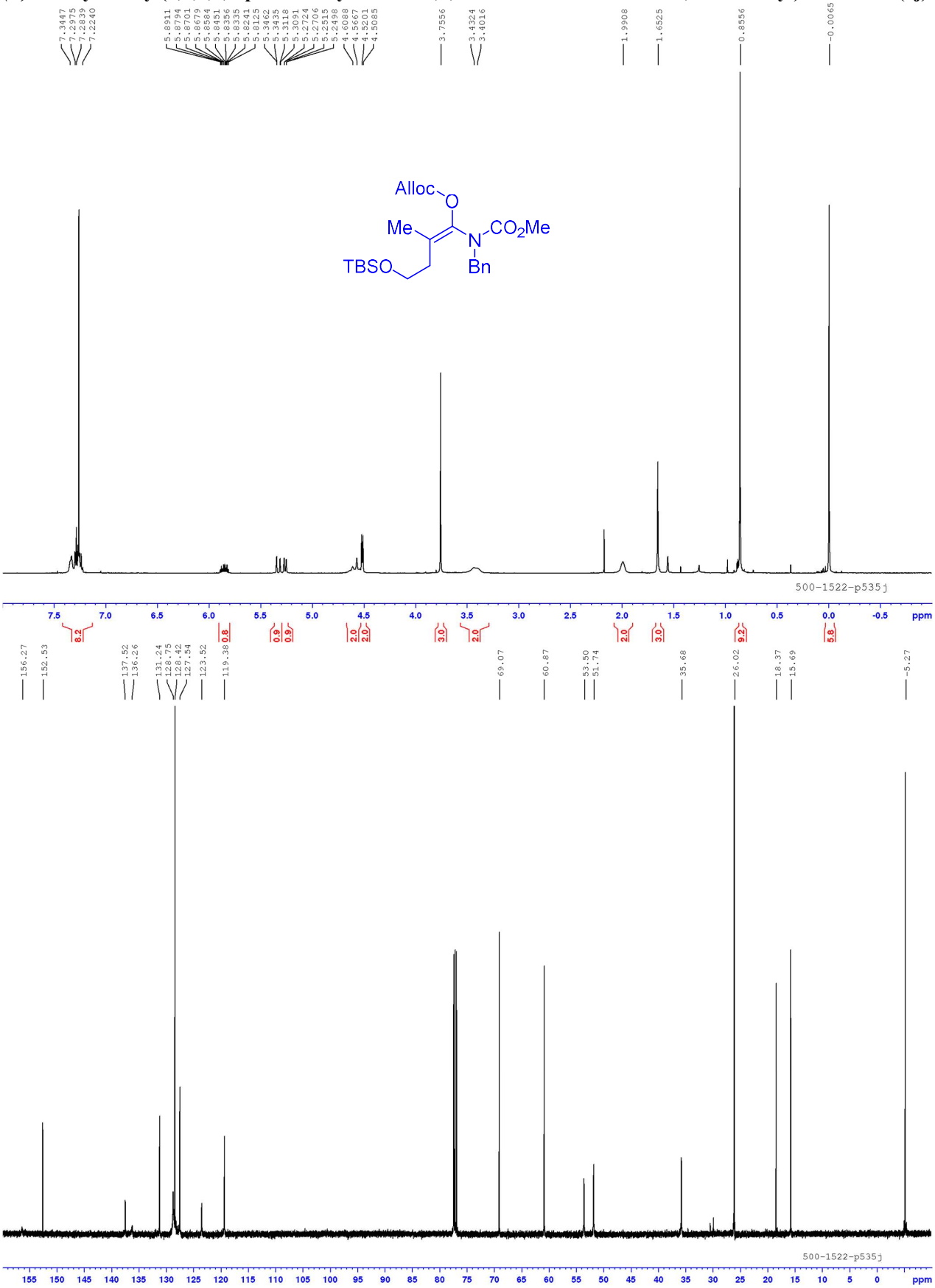




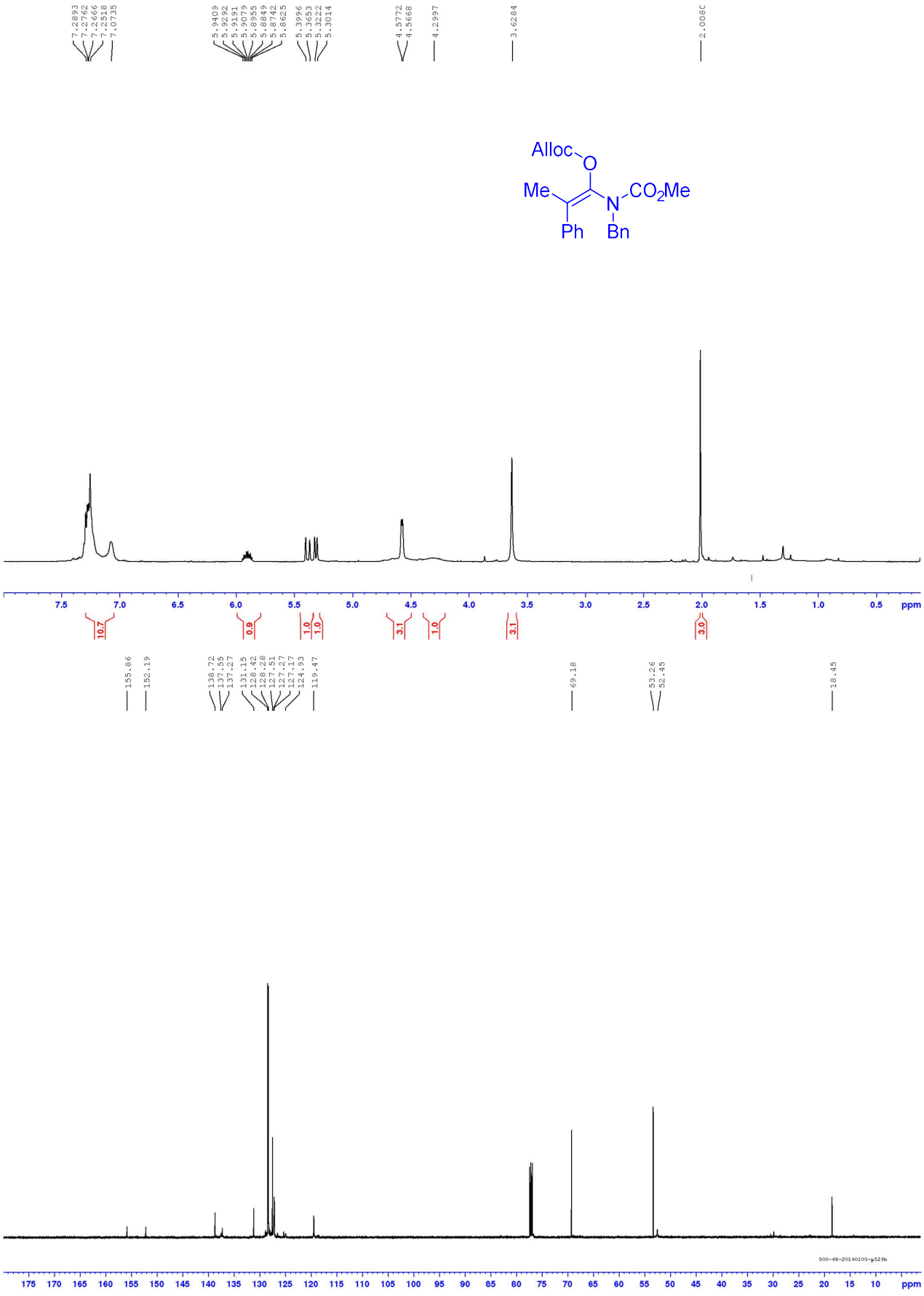




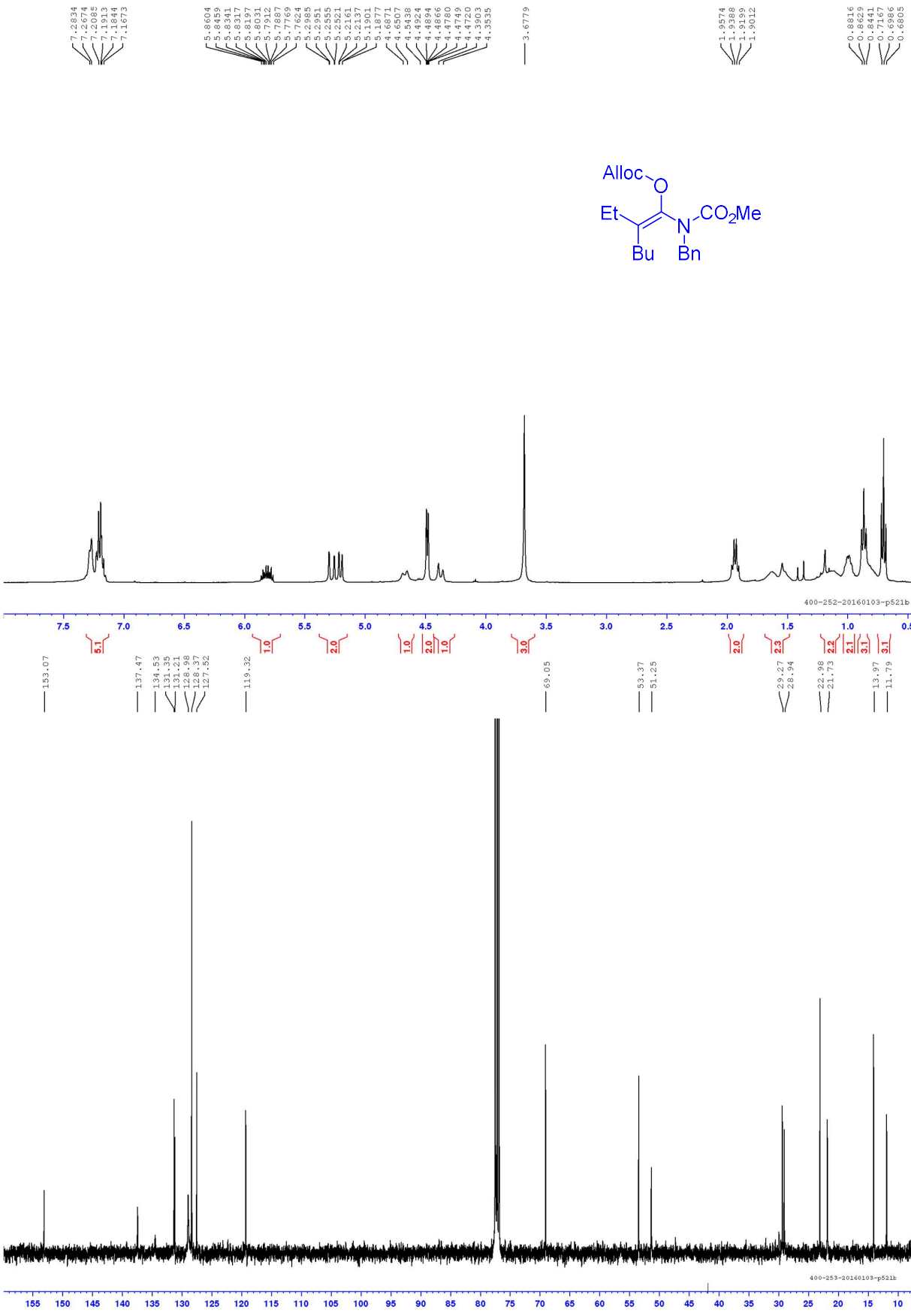
***(E)*-Methyl benzyl(2,2,3,3,7-pentamethyl-10-oxo-4,9,11-trioxa-3-silatetradeca-7,13-dien-8-yl)carbamate (3j)**



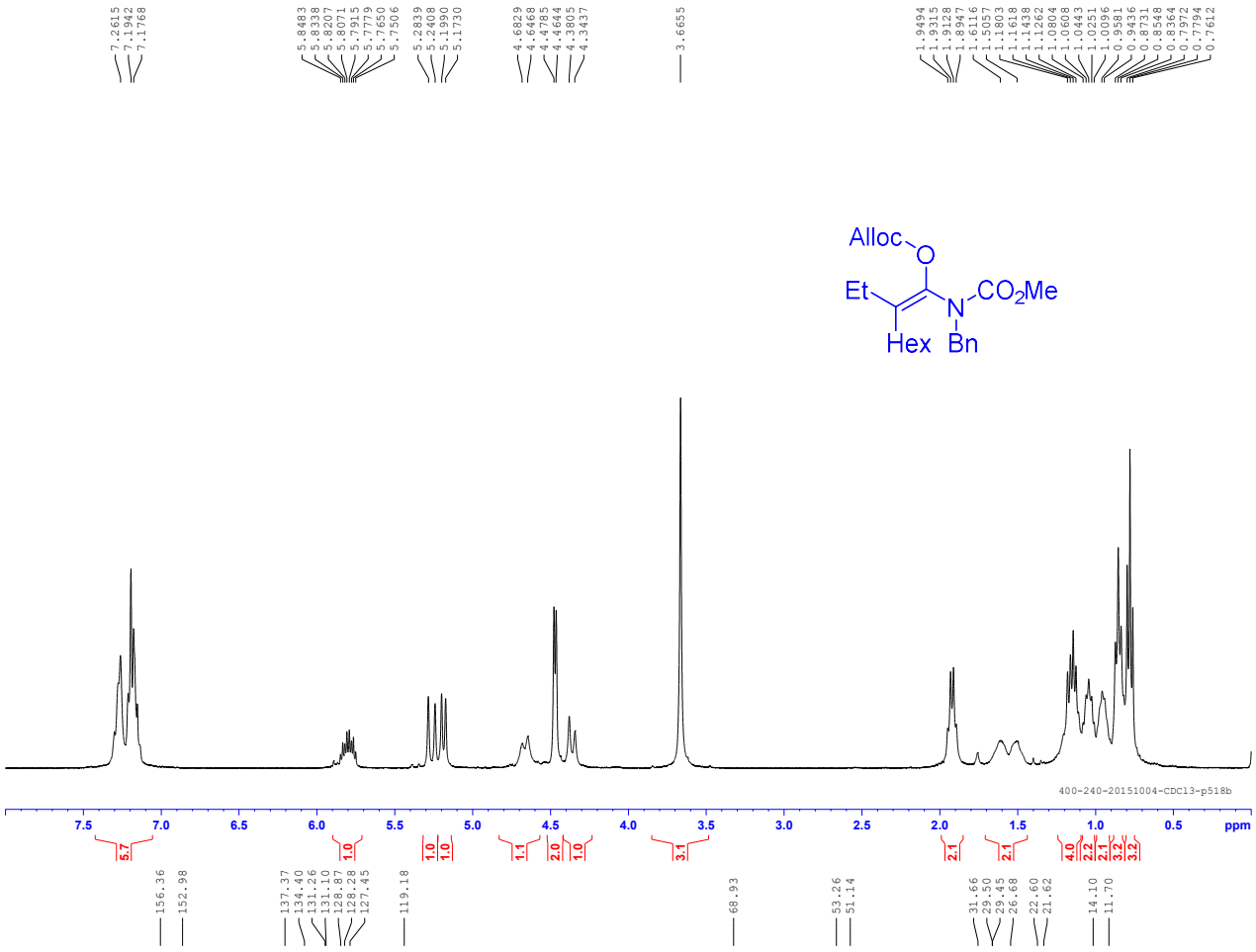
***(E)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-phenylprop-1-en-1-yl)(benzyl)carbamate (3k)**

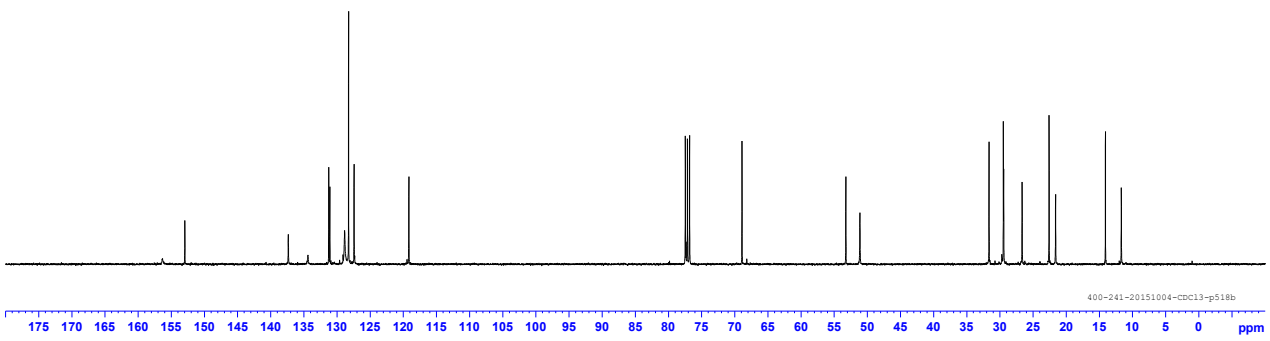


(*E*)-Methyl (1-(((allyloxy)carbonyl)oxy)-2-ethylhex-1-en-1-yl)(benzyl)carbamate (3l)

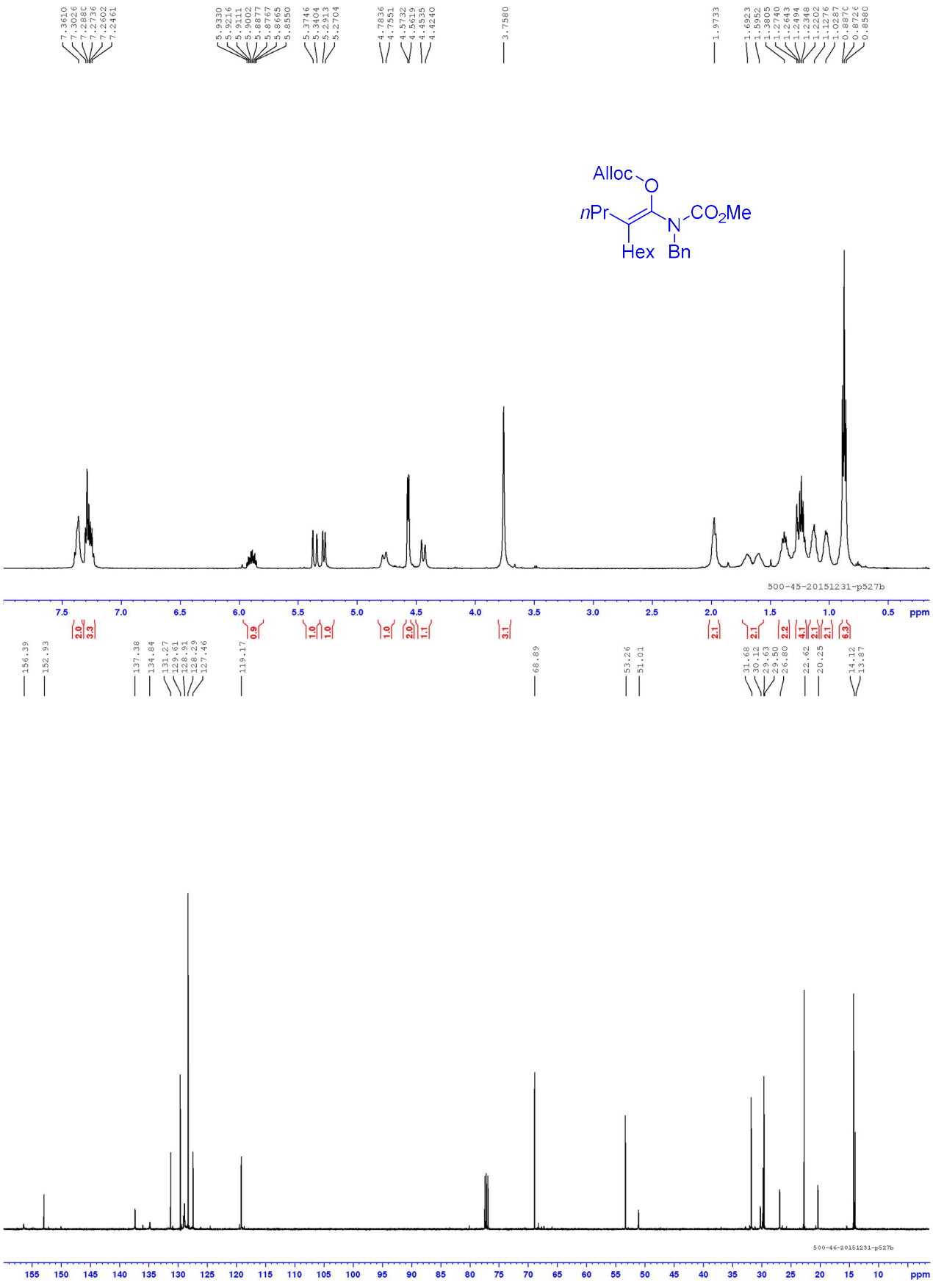


(*E*)-Methyl (1-(((allyloxy)carbonyl)oxy)-2-ethyloct-1-en-1-yl)(benzyl)carbamate (3m)

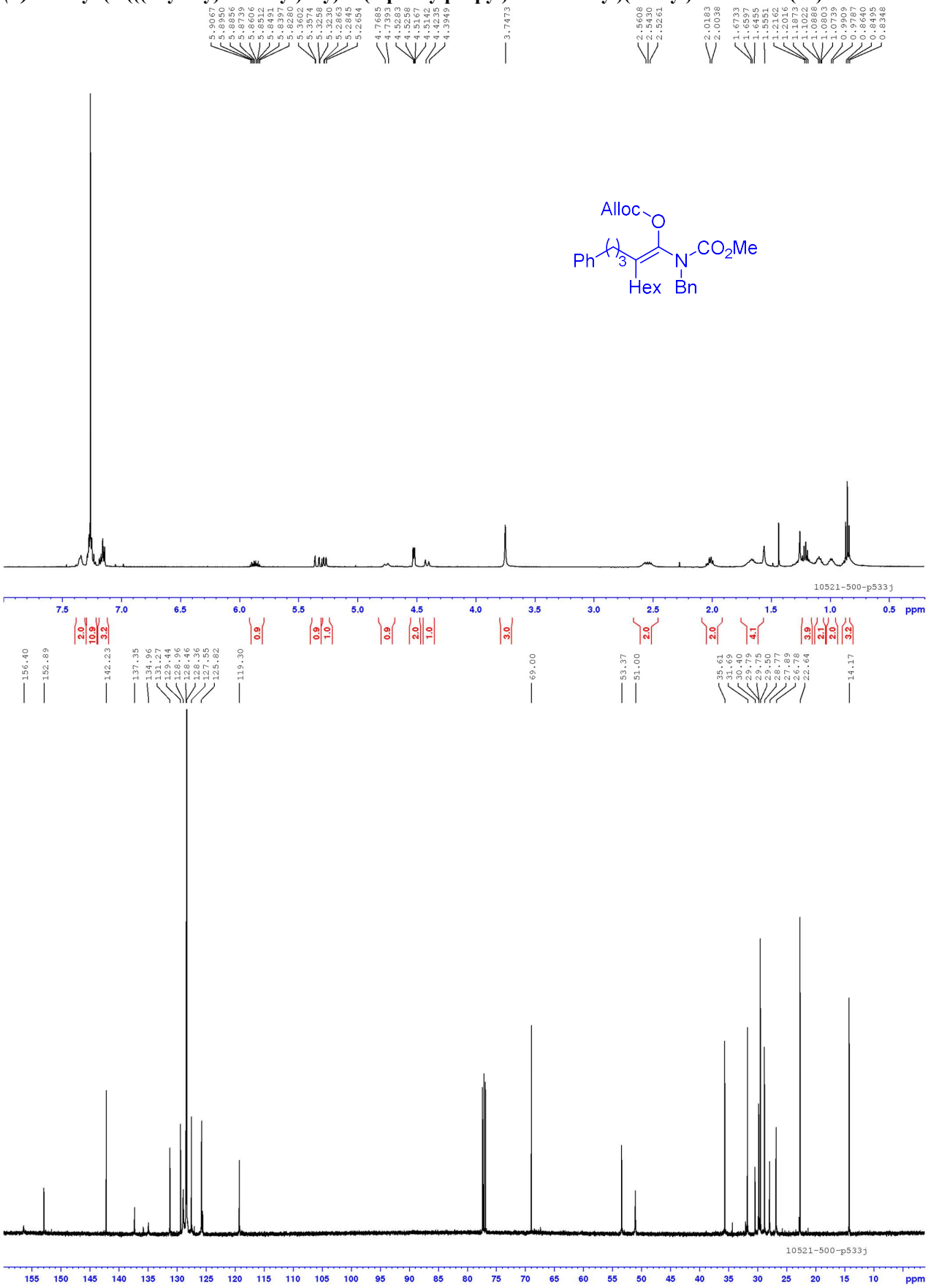




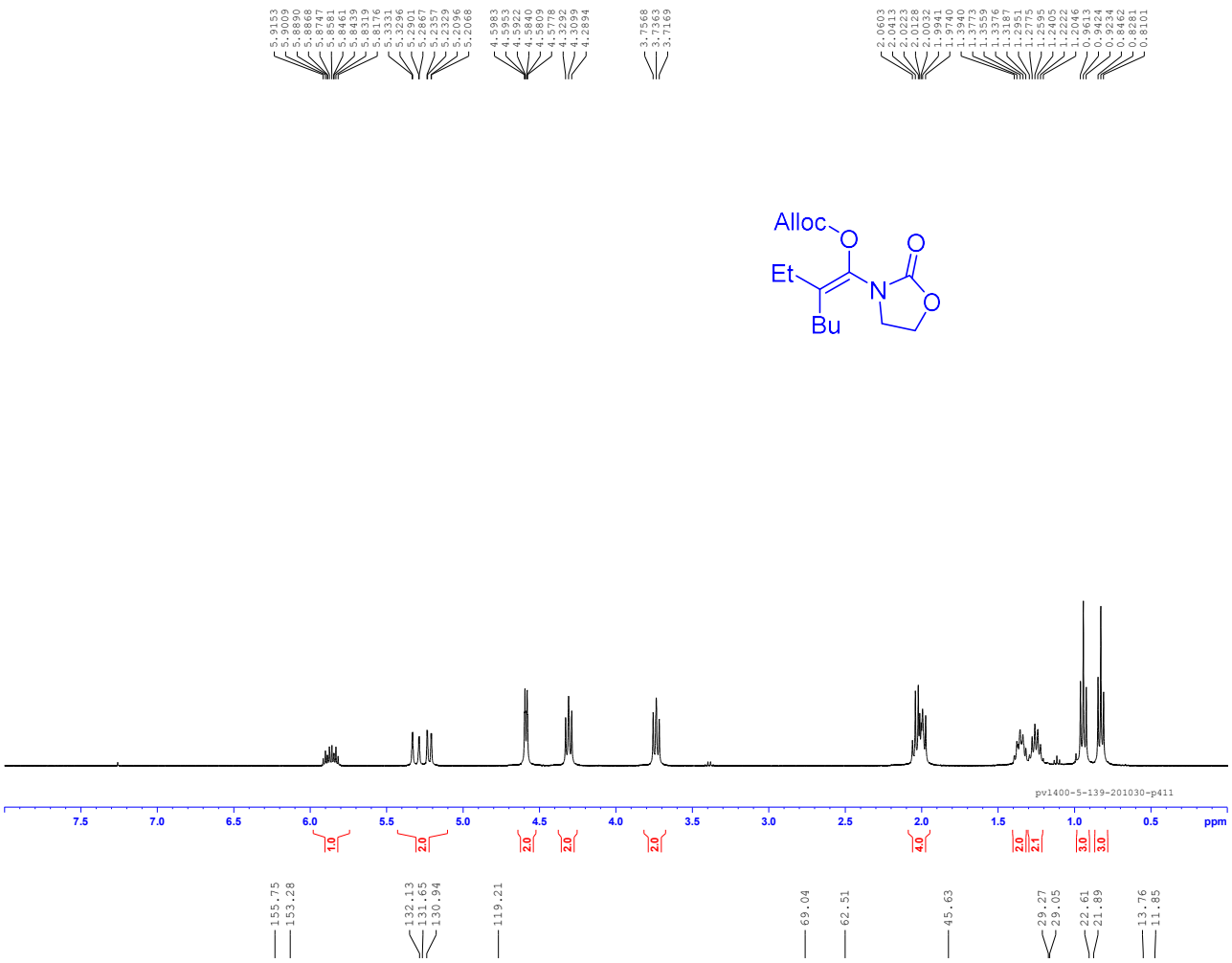
***(E)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-propyloct-1-en-1-yl)(benzyl)carbamate (3n)**



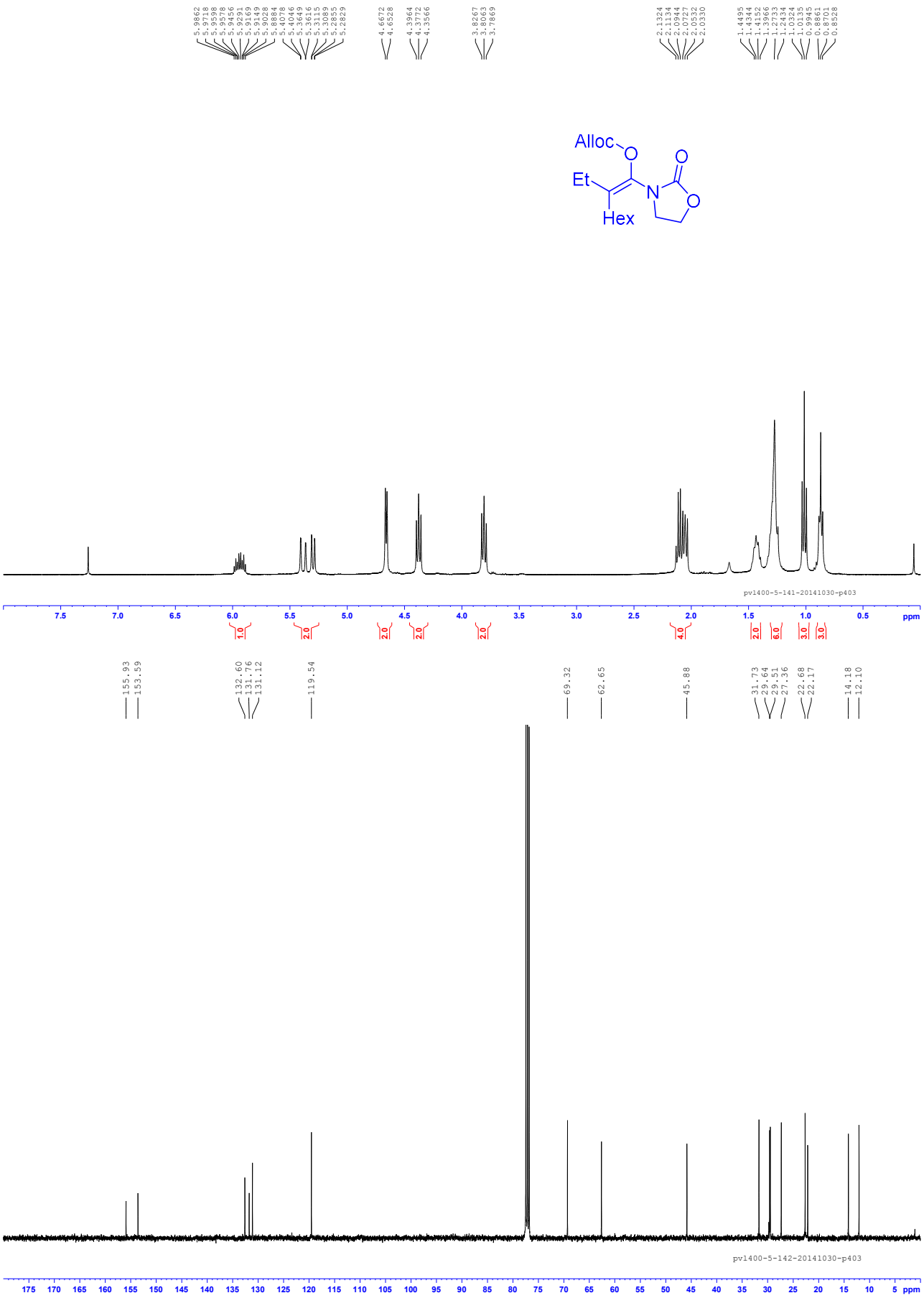
***(Z)*-Methyl (1-(((allyloxy)carbonyl)oxy)-2-(3-phenylpropyl)oct-1-en-1-yl)(benzyl)carbamate (3o)**



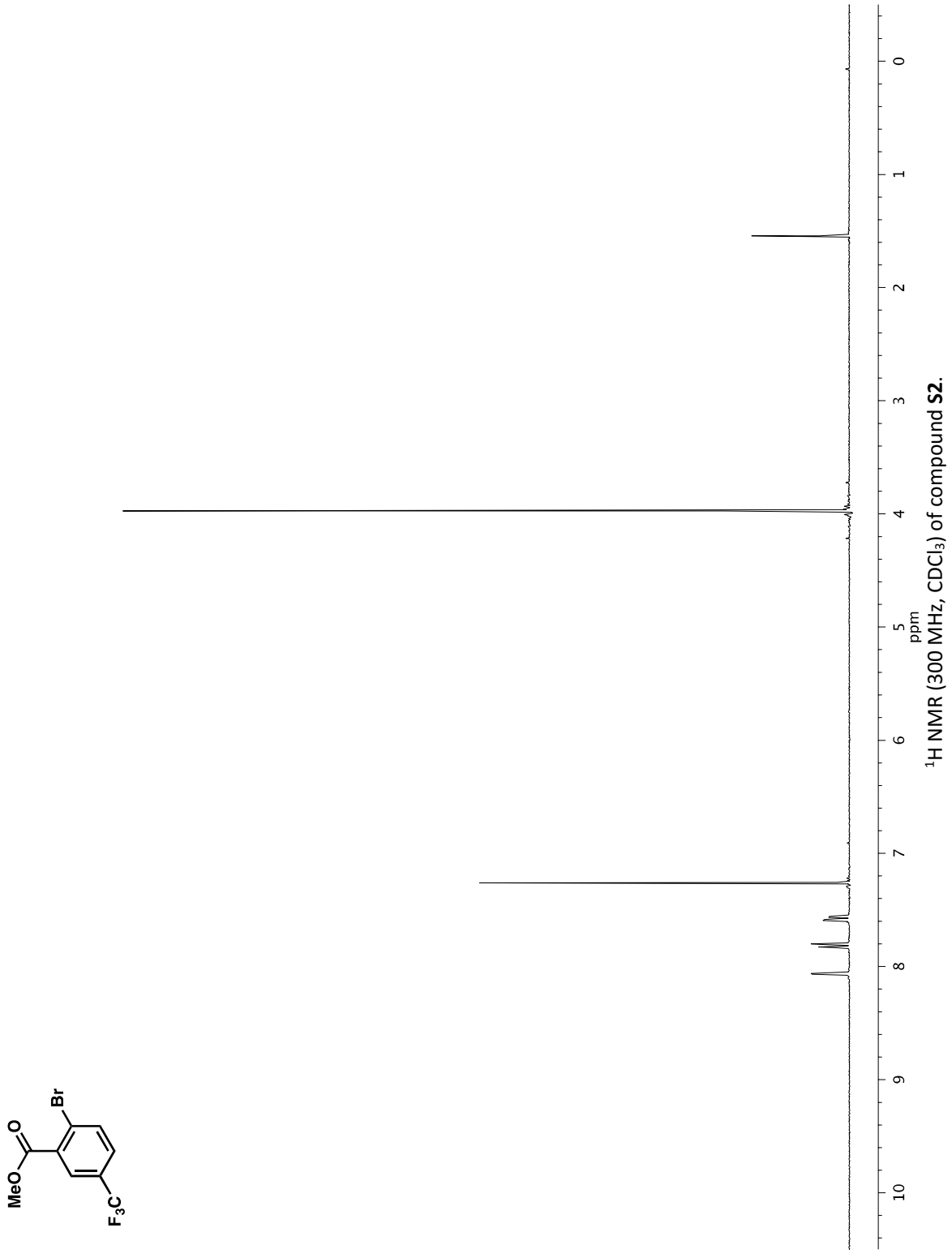
***(E)*-Allyl (2-ethyl-1-(2-oxooxazolidin-3-yl)hex-1-en-1-yl) carbonate (3p)**



***(E)*-Allyl (2-ethyl-1-(2-oxooxazolidin-3-yl)oct-1-en-1-yl) carbonate (3q)**

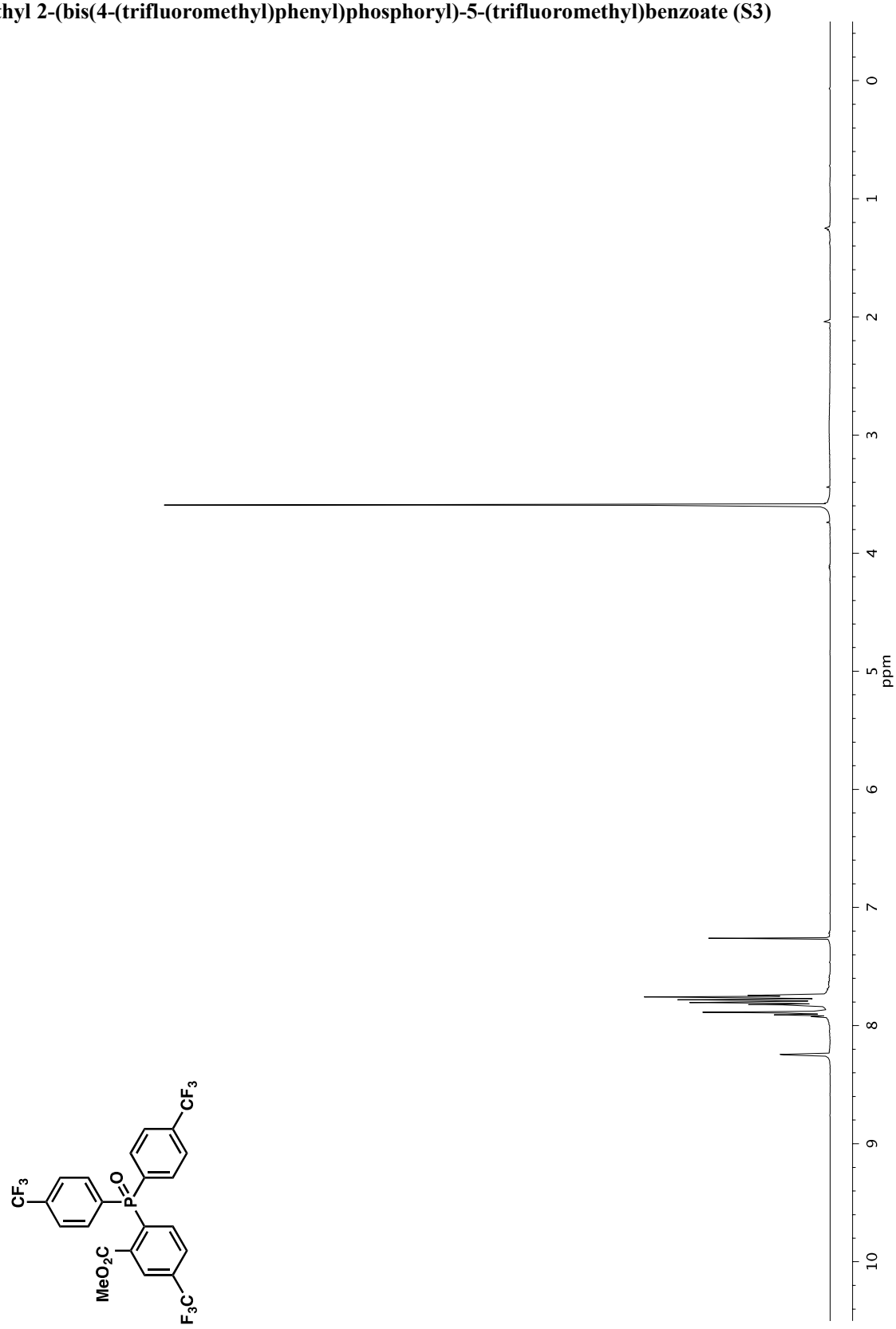


Methyl 2-bromo-5-(trifluoromethyl)benzoate (S2)

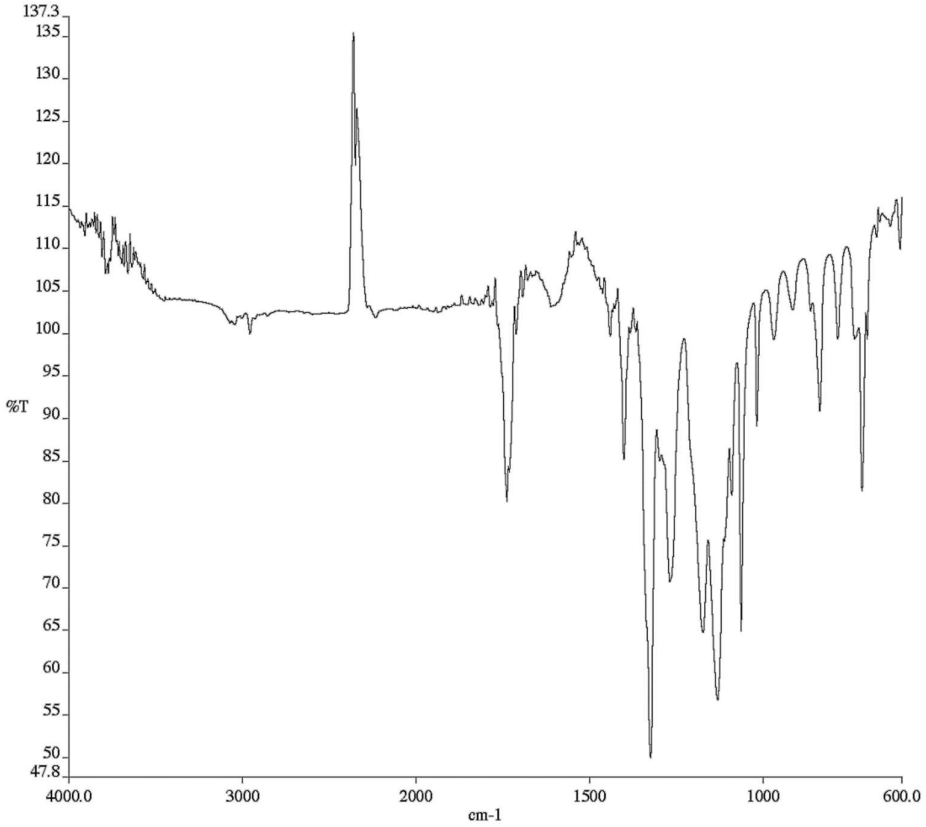


^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2**.

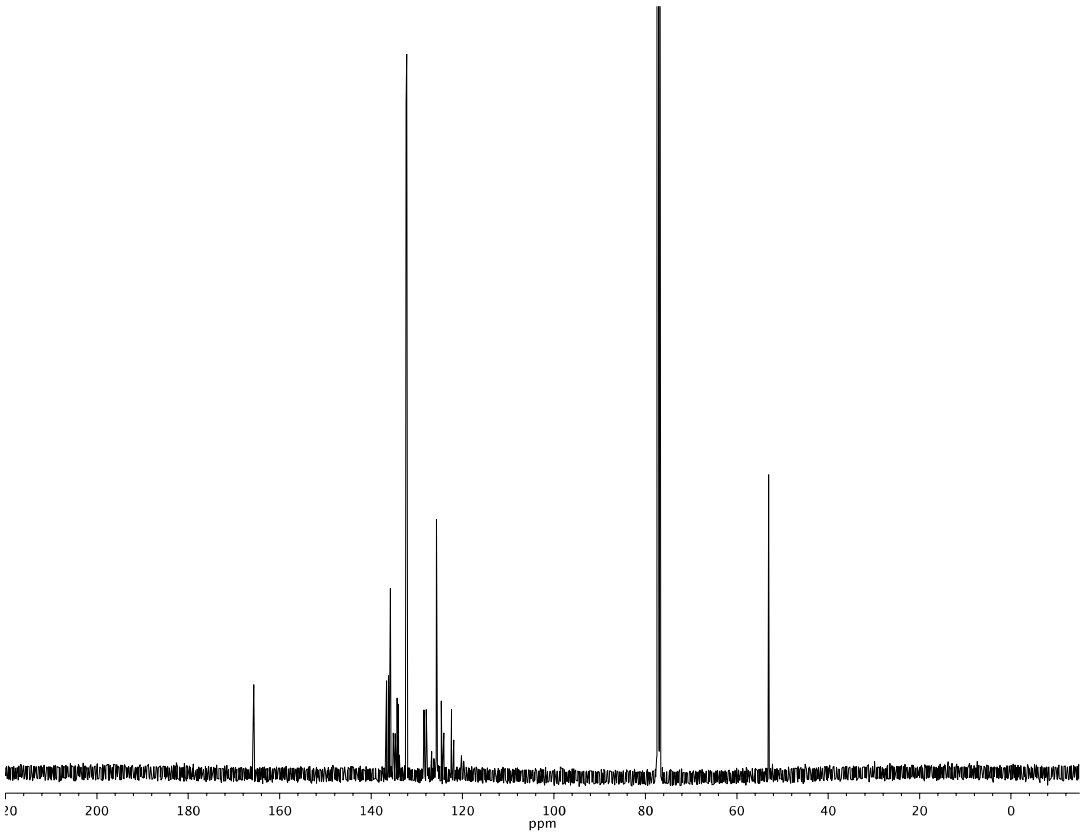
Methyl 2-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-5-(trifluoromethyl)benzoate (S3)



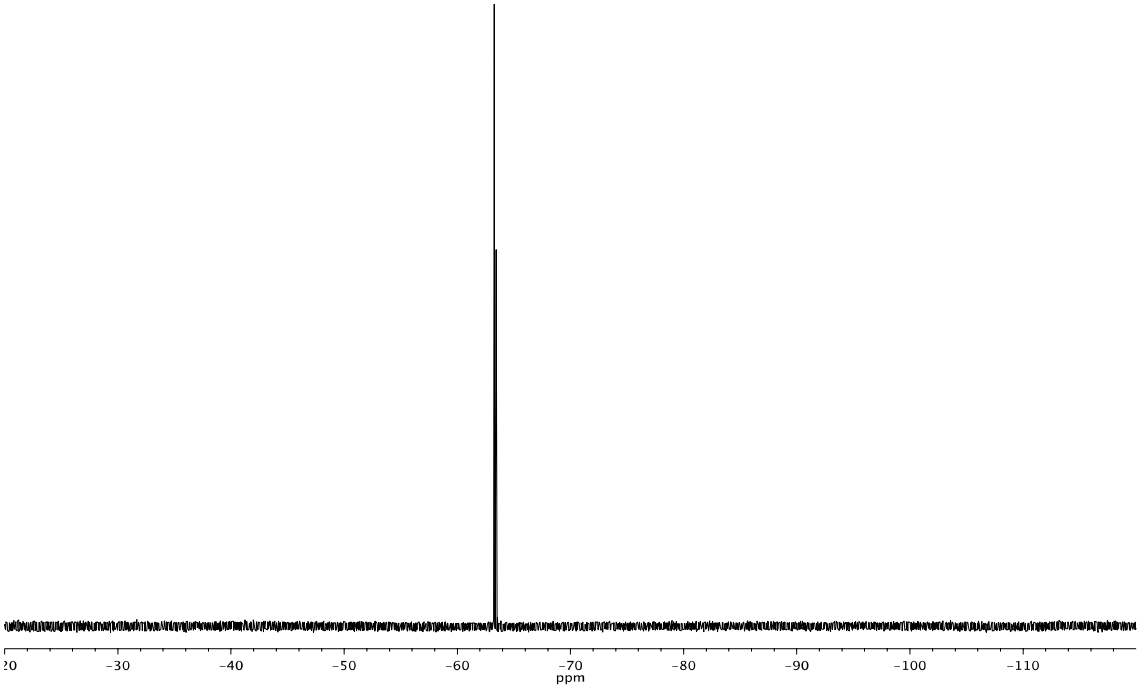
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S3**.



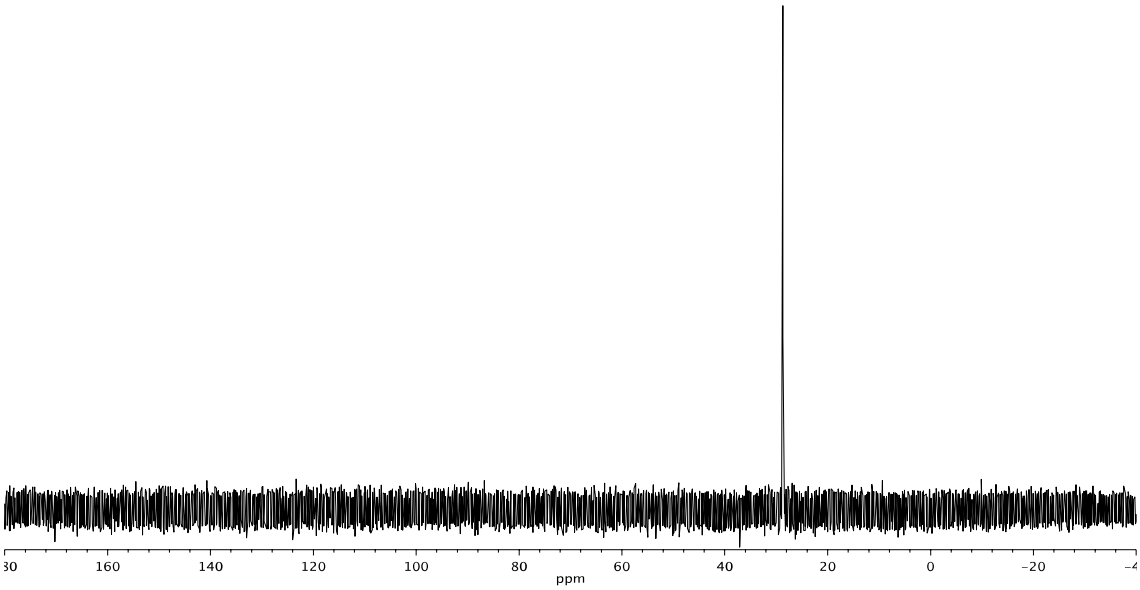
Infrared spectrum (Thin Film, NaCl) of compound **S3**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **S3**.

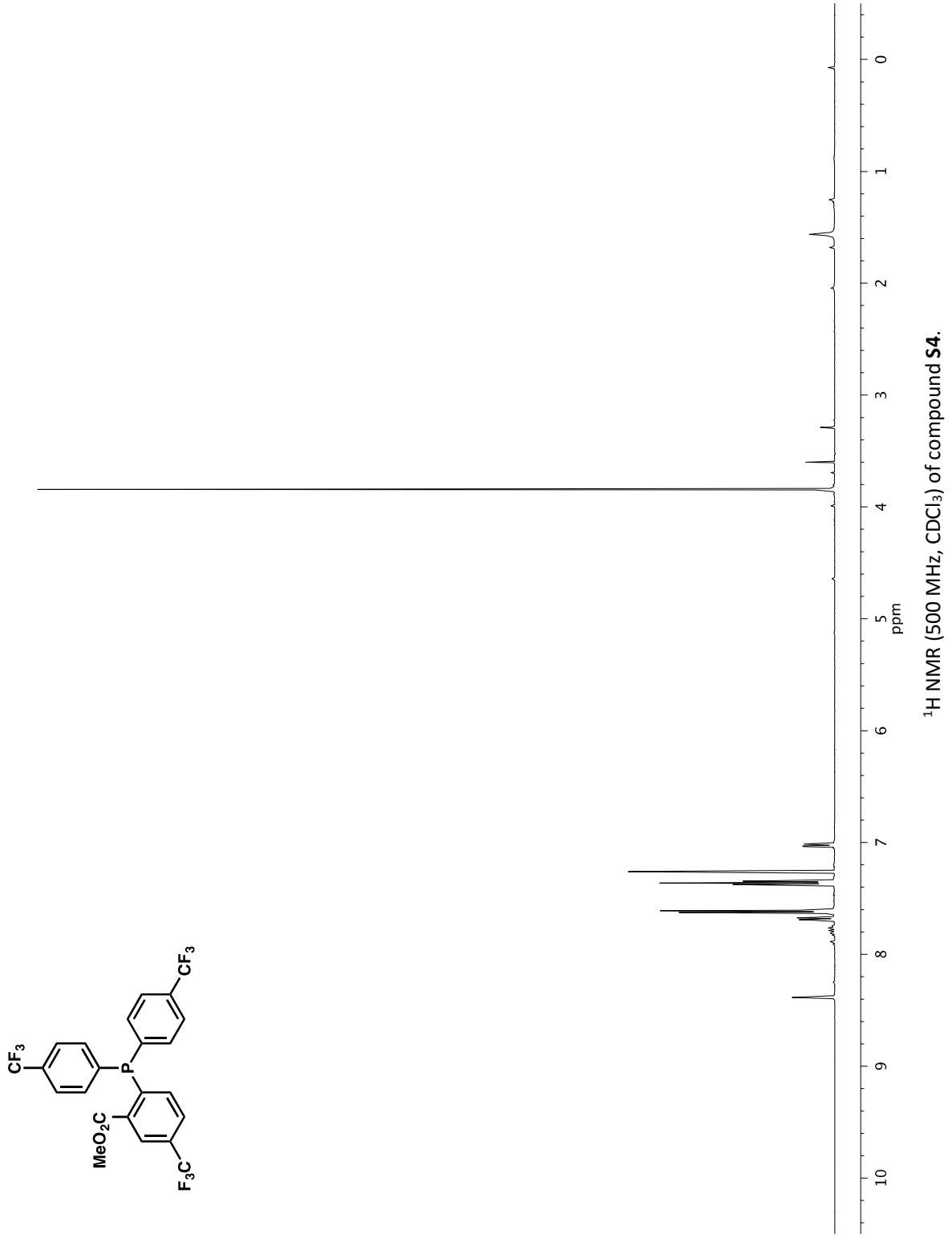


^{19}F NMR (282 MHz, $CDCl_3$) of compound **S3**.

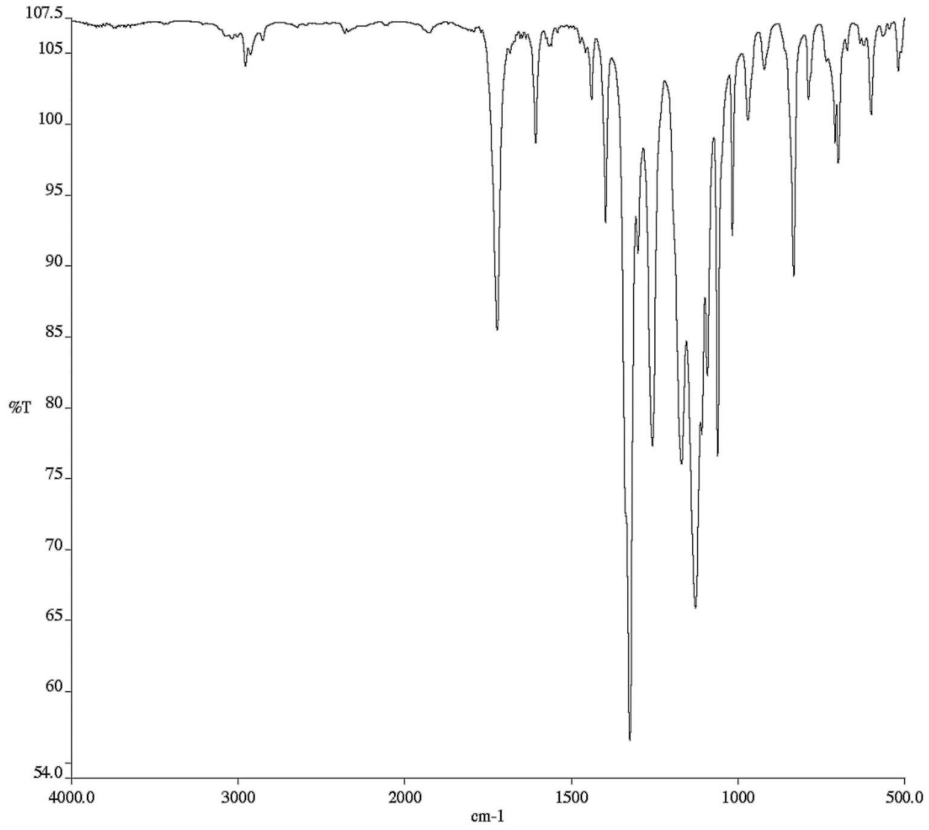


^{31}P NMR (121 MHz, $CDCl_3$) of compound **S3**.

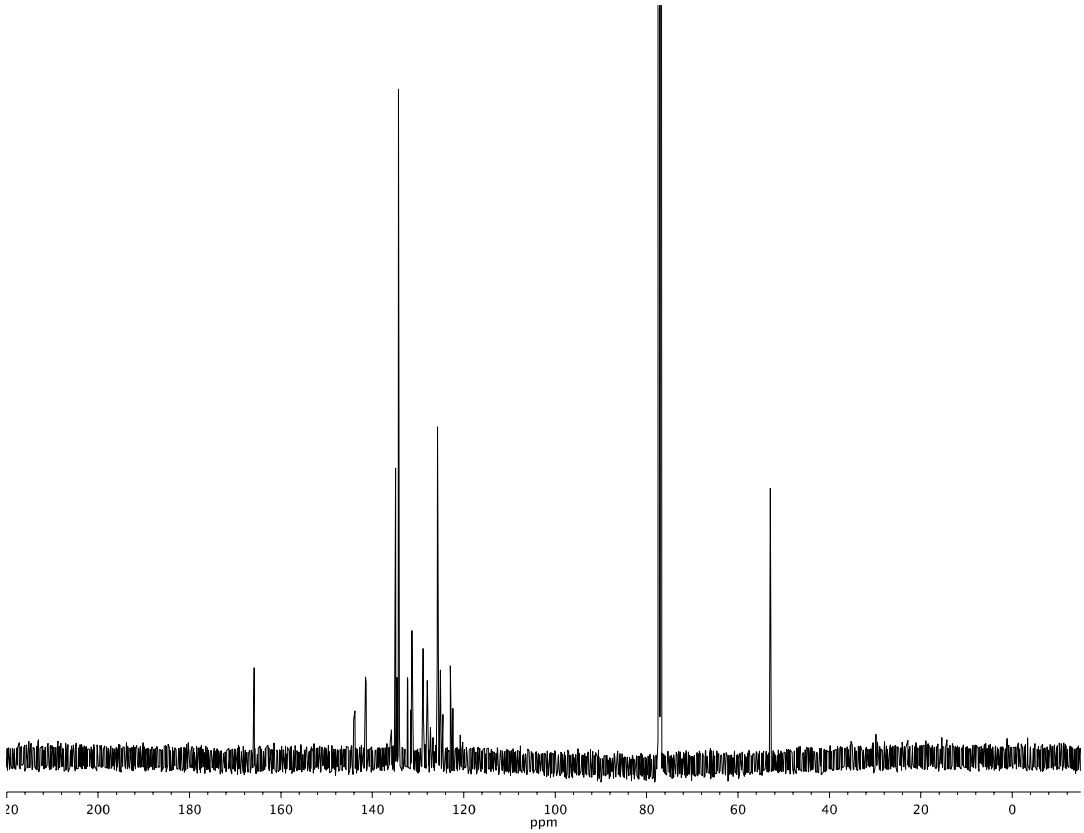
Methyl 2-(bis(4-(trifluoromethyl)phenyl)phosphanyl)-5-(trifluoromethyl)benzoate (S4)



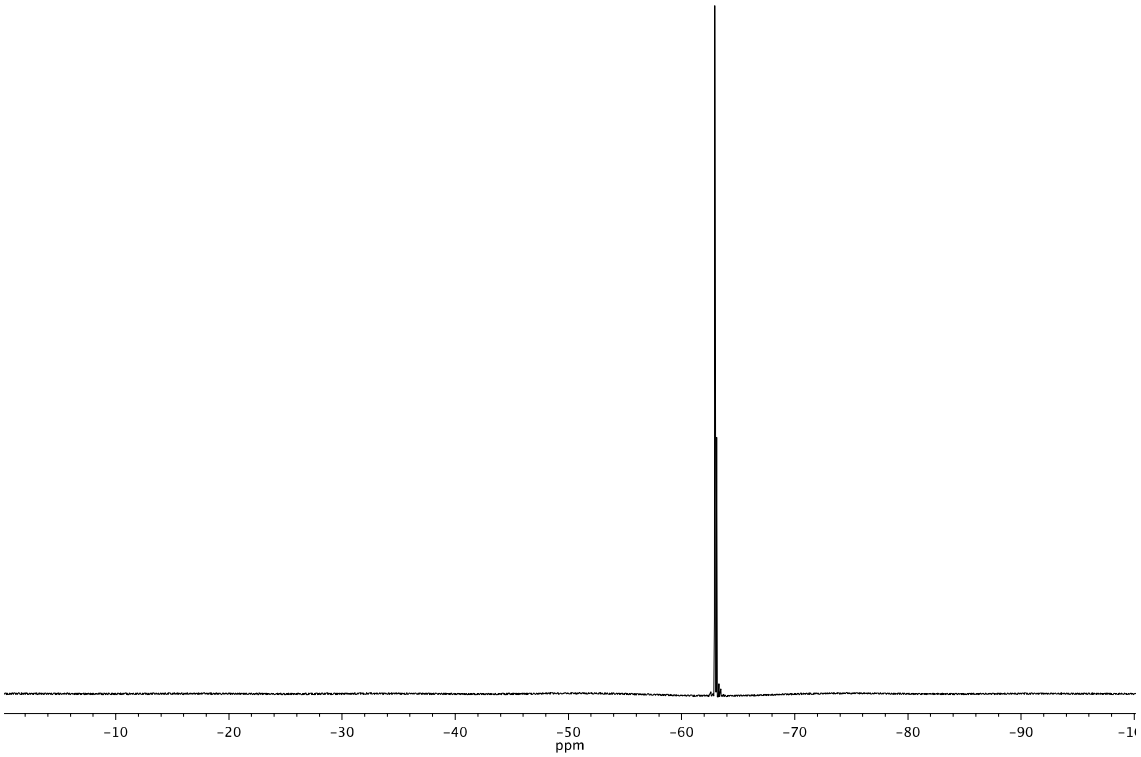
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S4**.



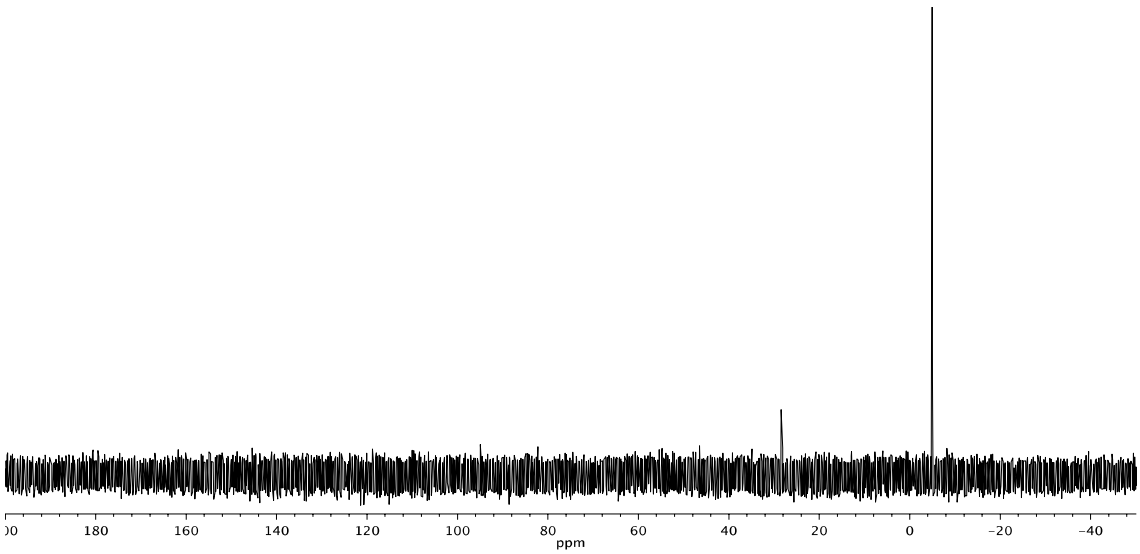
Infrared spectrum (Thin Film, NaCl) of compound **S4**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **S4**.

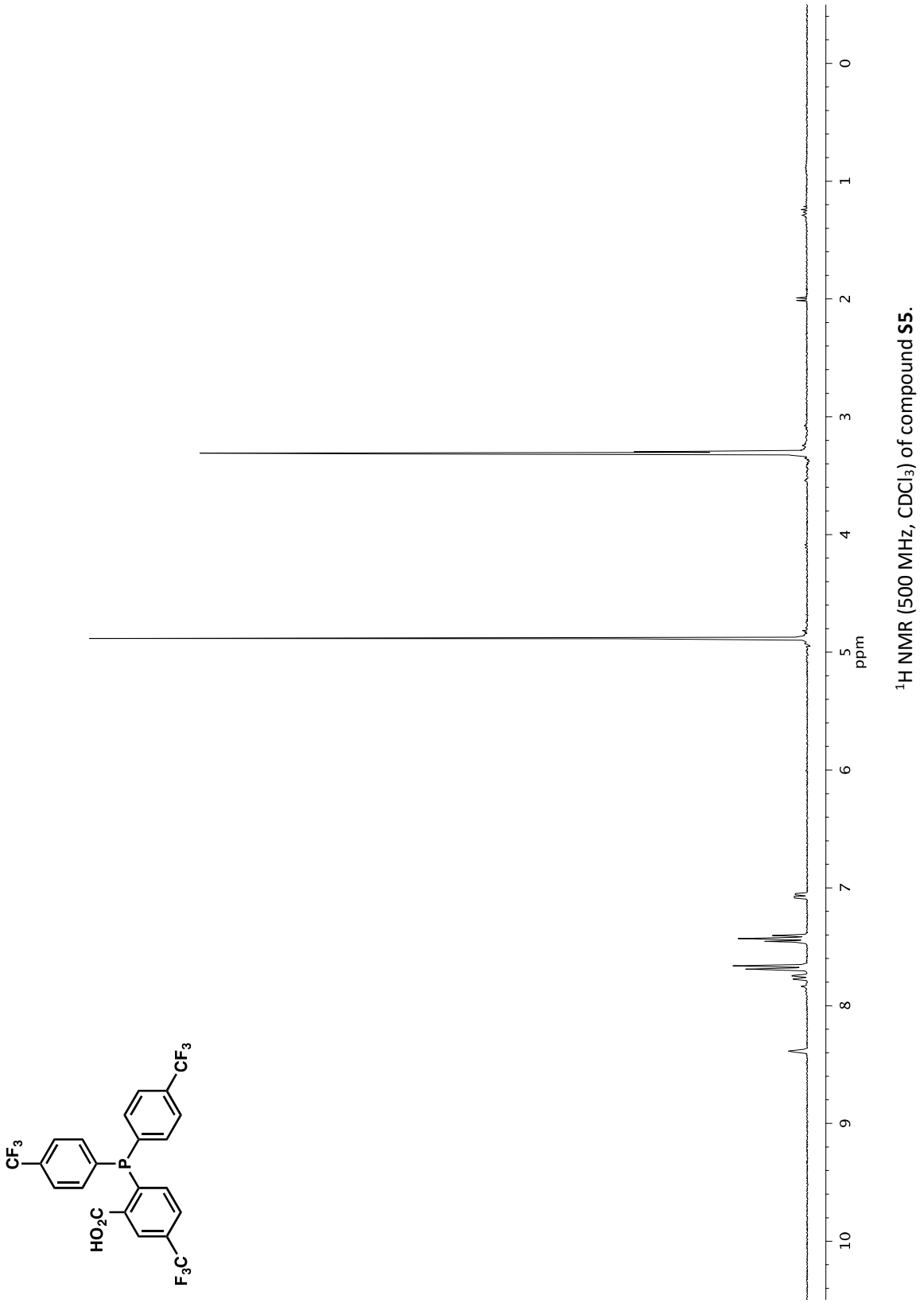


^{19}F NMR (282 MHz, $CDCl_3$) of compound **S4**.

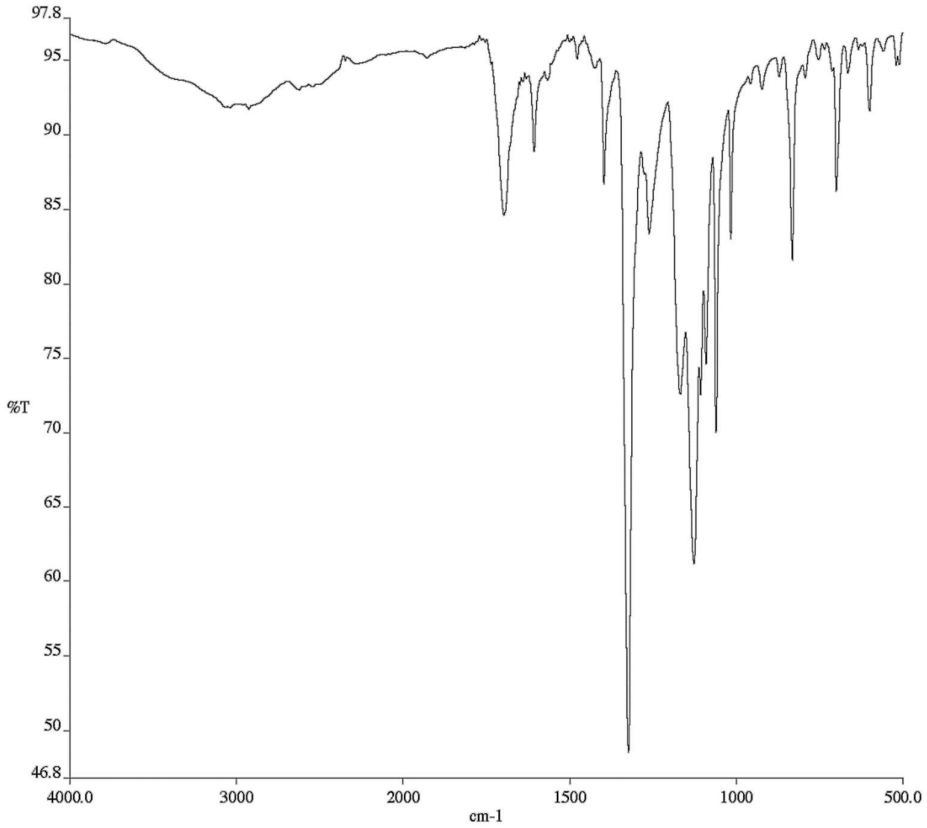


^{31}P NMR (121 MHz, $CDCl_3$) of compound **S4**.

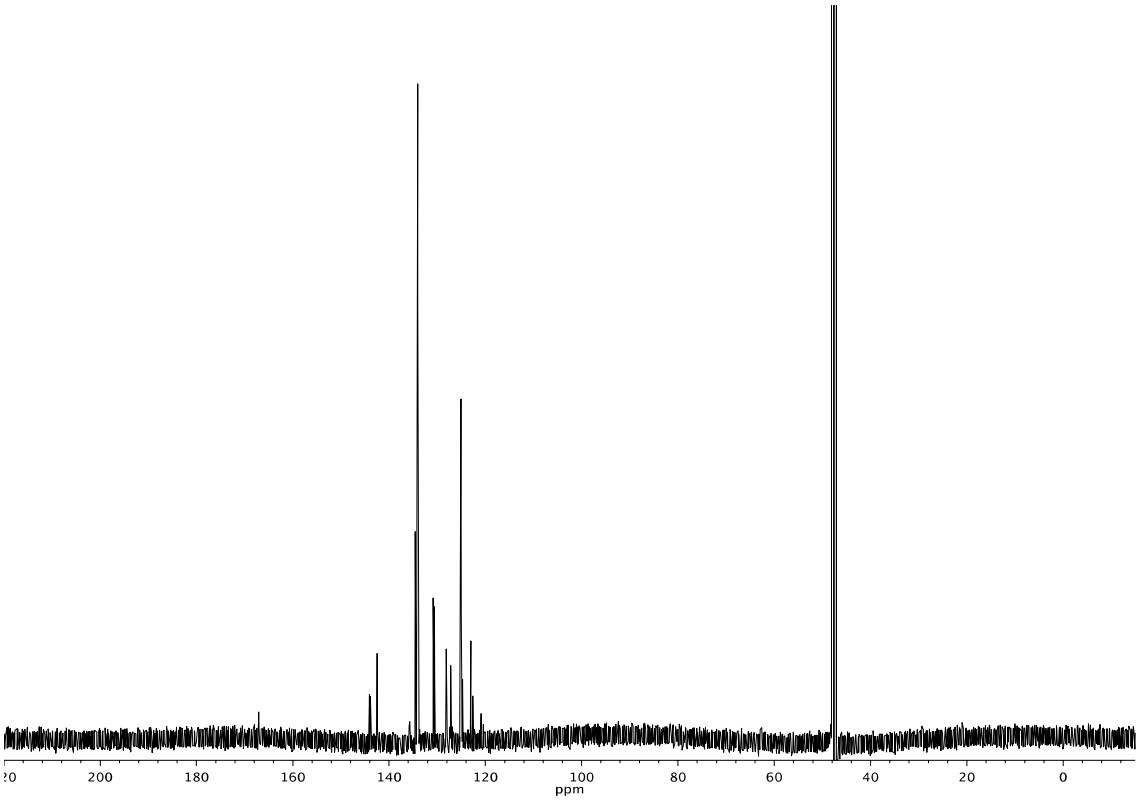
2-(Bis(4-(trifluoromethyl)phenyl)phosphanyl)-5-(trifluoromethyl)benzoic acid (S5)



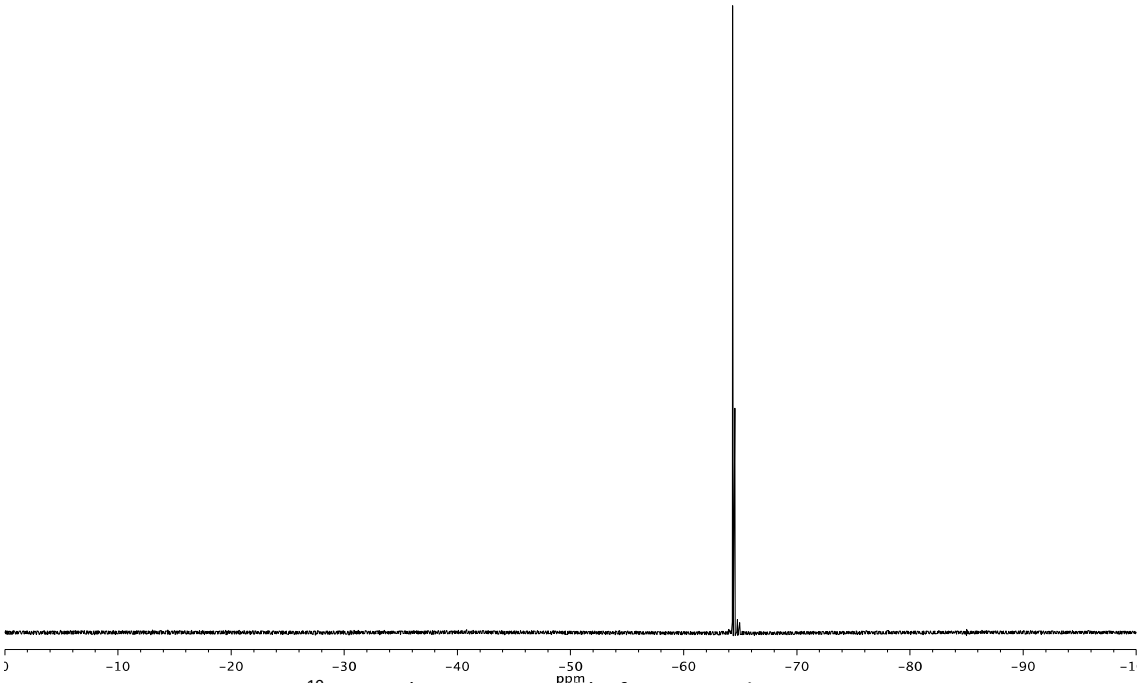
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S5**.



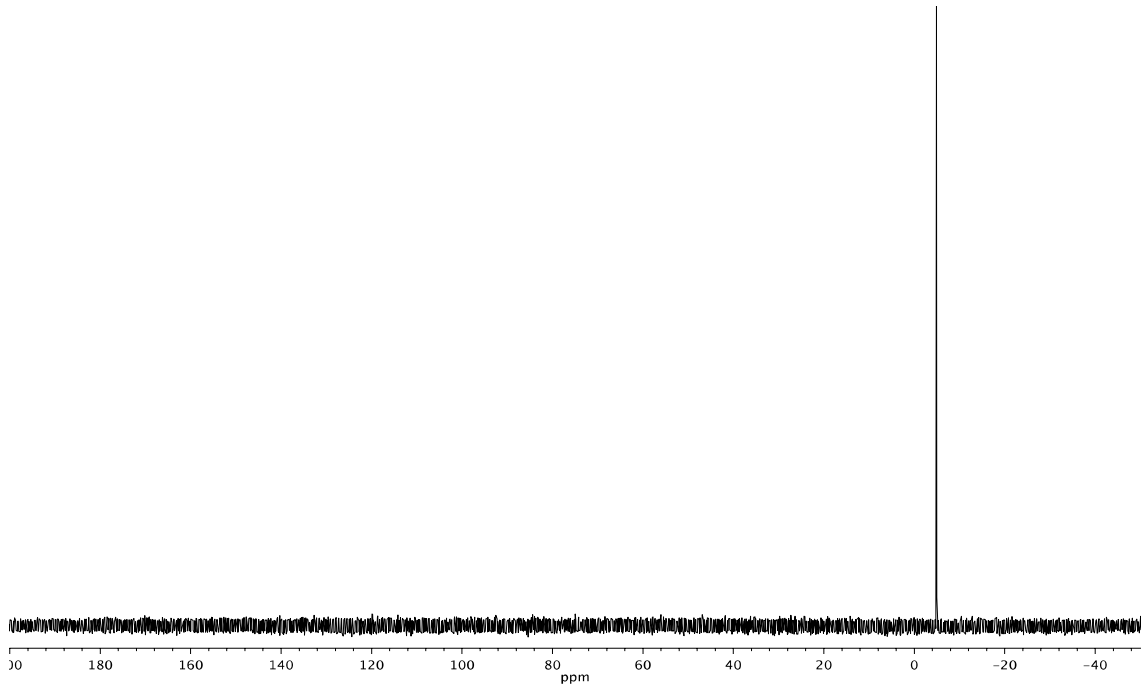
Infrared spectrum (Thin Film, NaCl) of compound **S5**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **S5**.

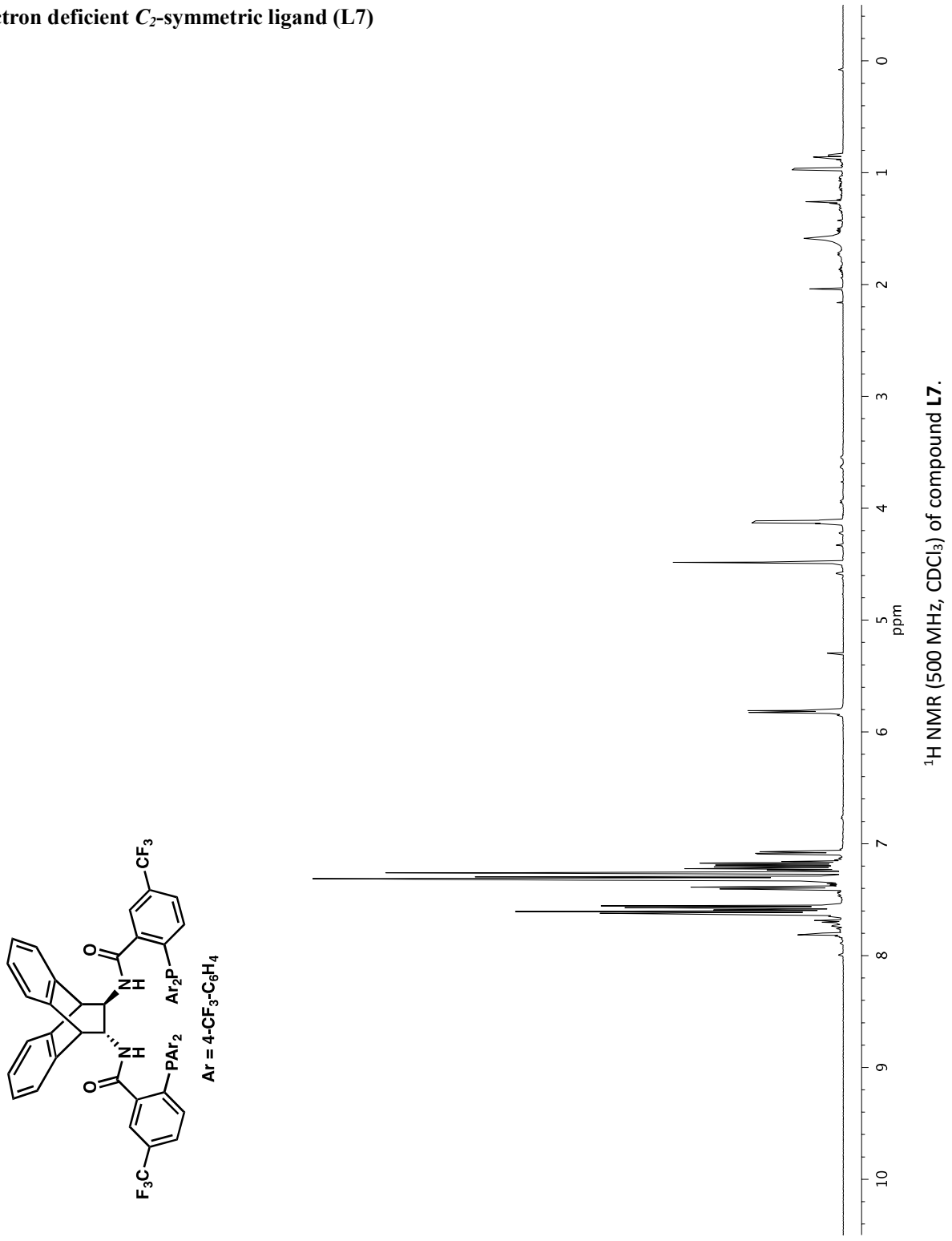


^{19}F NMR (282 MHz, $CDCl_3$) of compound **S5**.

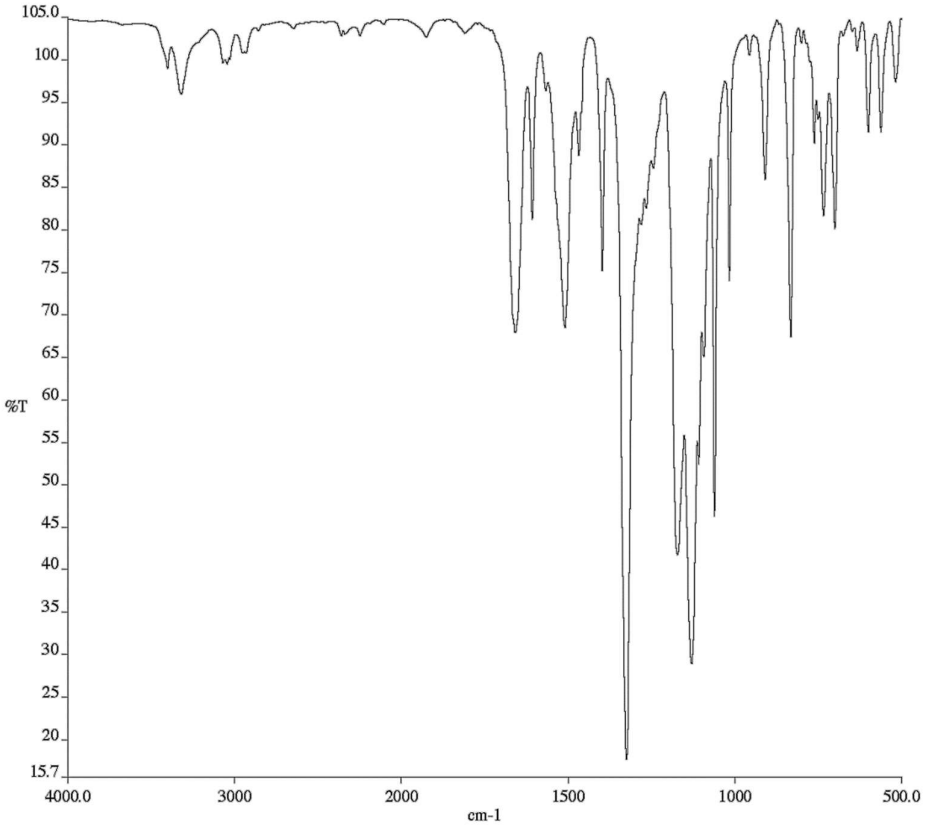


^{31}P NMR (121 MHz, $CDCl_3$) of compound **S5**.

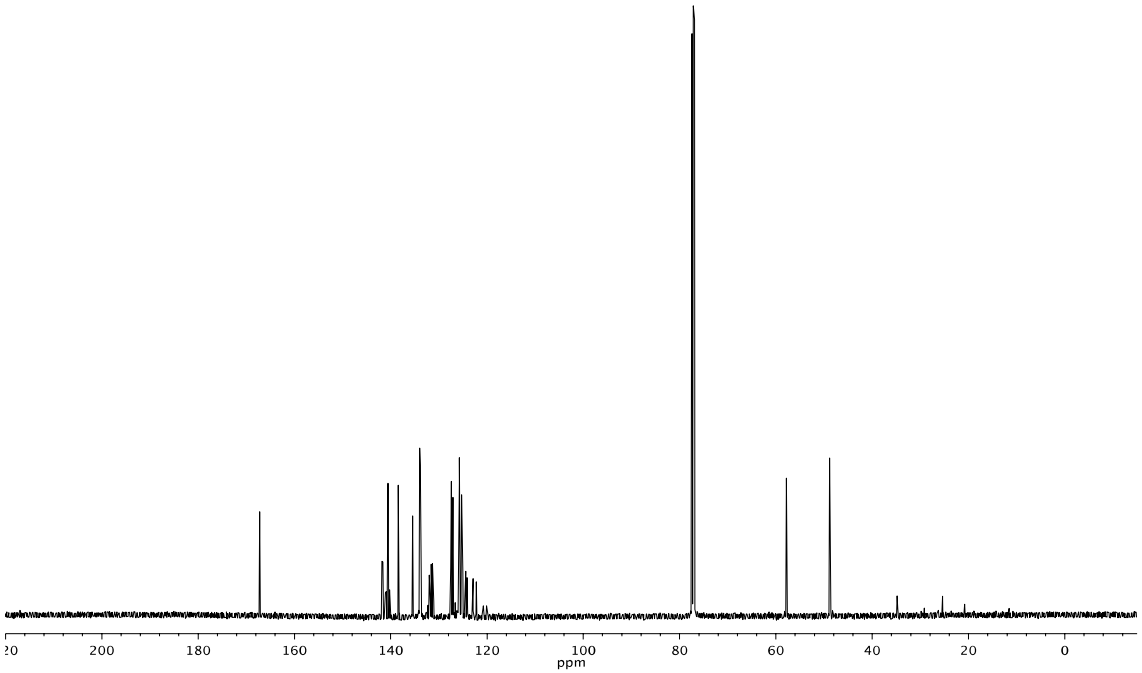
Electron deficient C_2-symmetric ligand (L7)



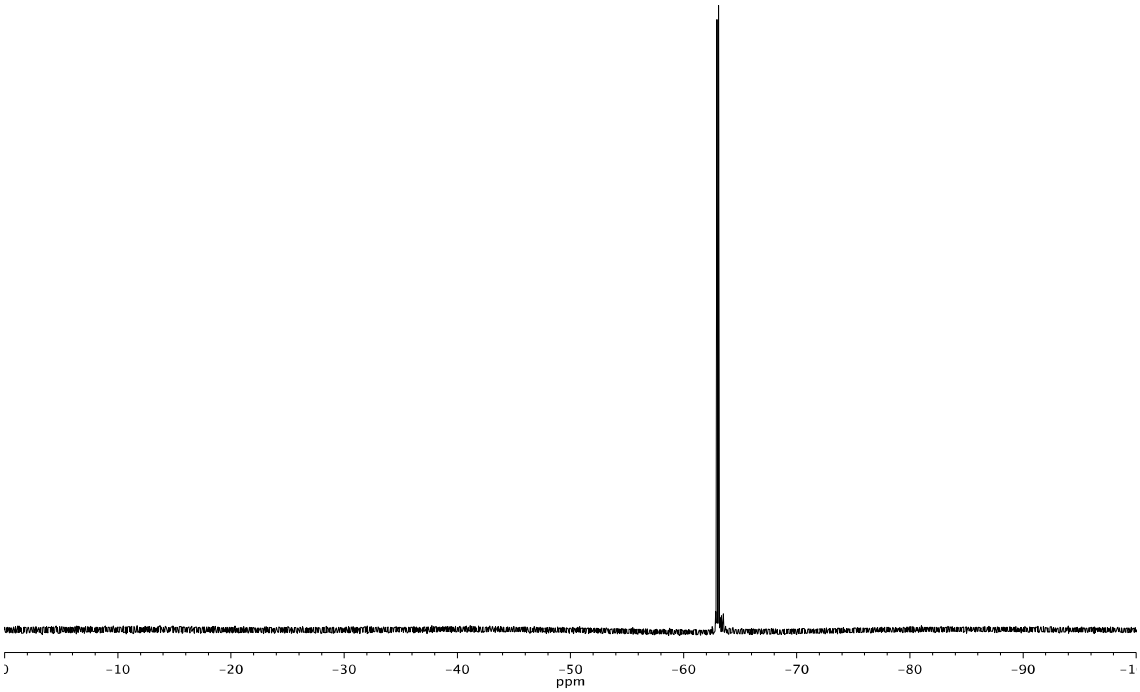
^{1}H NMR (500 MHz, $CDCl_3$) of compound **L7**.



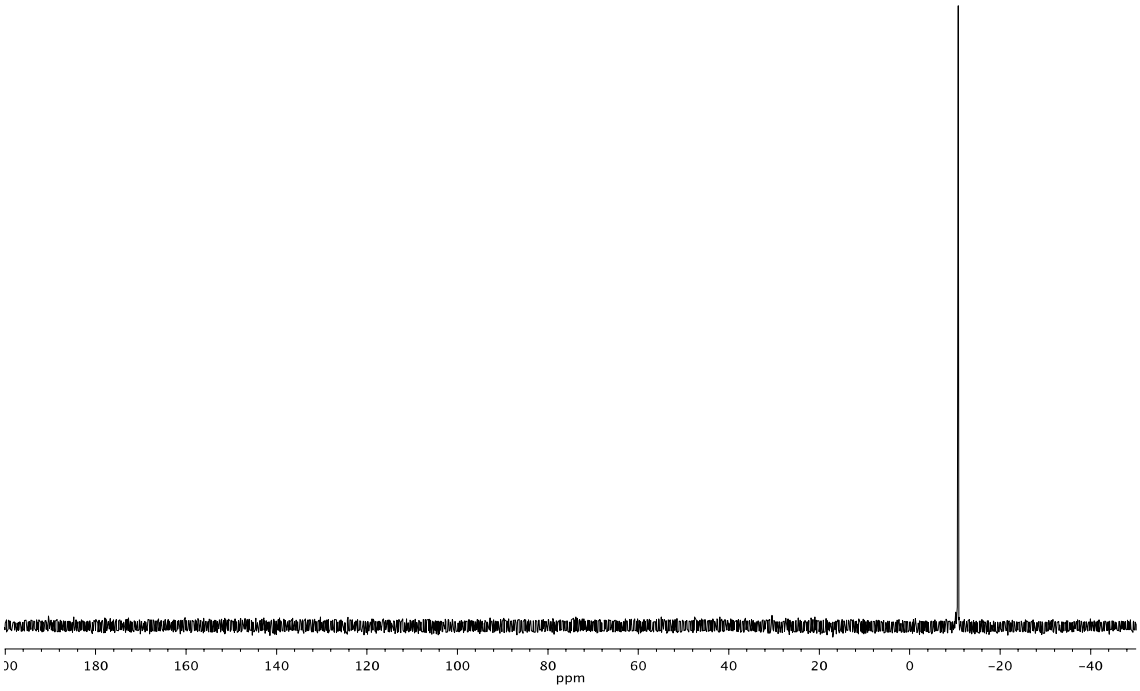
Infrared spectrum (Thin Film, NaCl) of compound **L7**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **L7**.

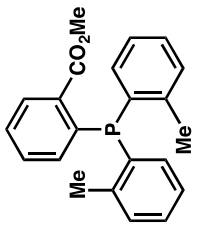


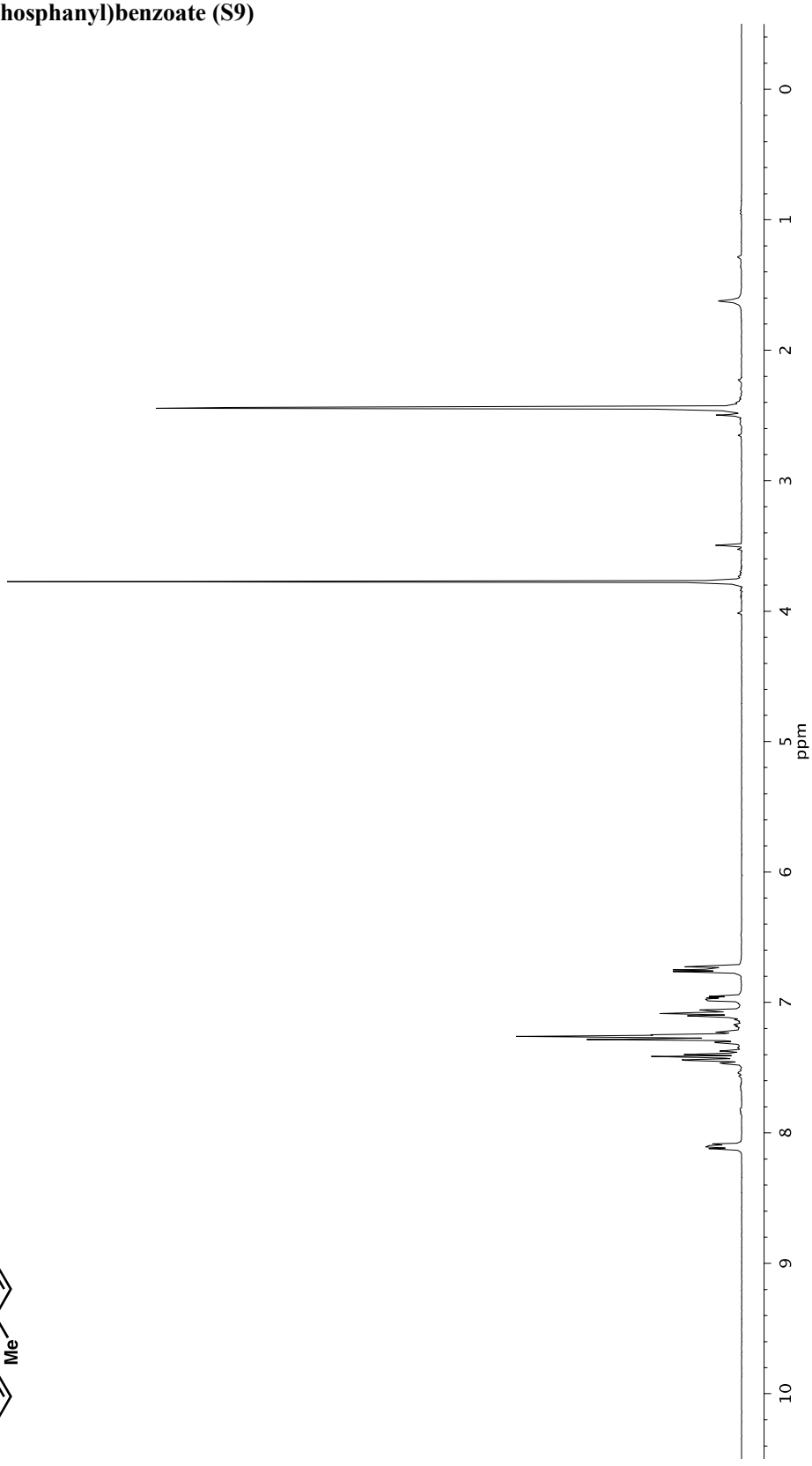
^{19}F NMR (282 MHz, $CDCl_3$) of compound **L7**.



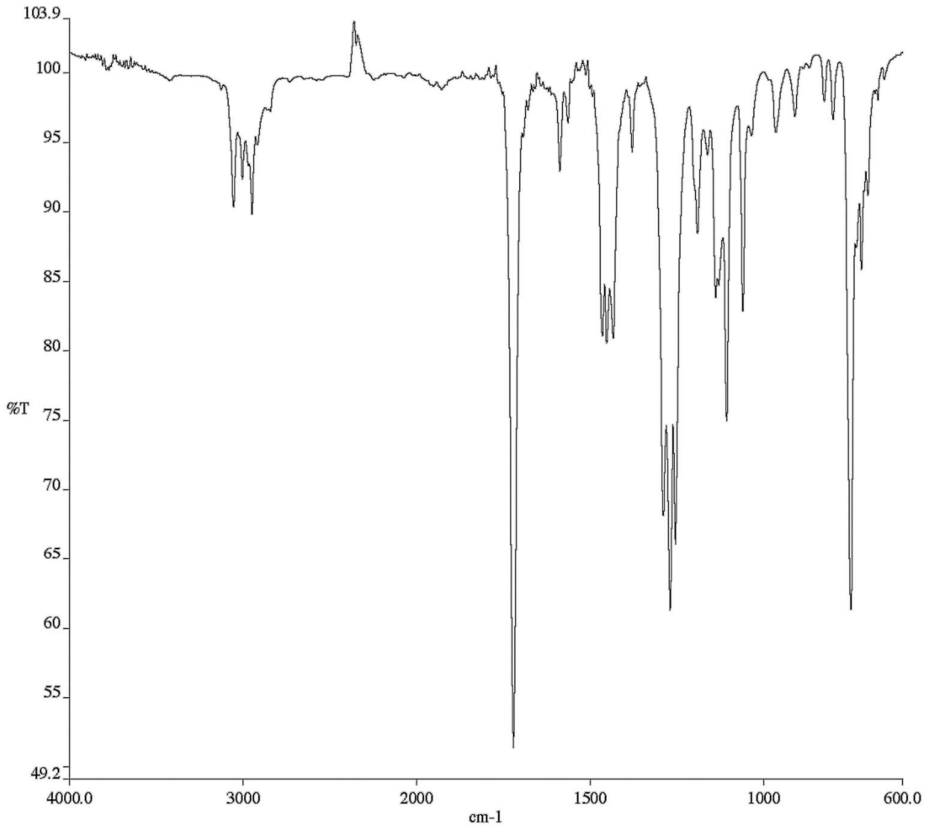
^{31}P NMR (121 MHz, $CDCl_3$) of compound **L7**.

Methyl 2-(di-*o*-tolylphosphanyl)benzoate (S9)

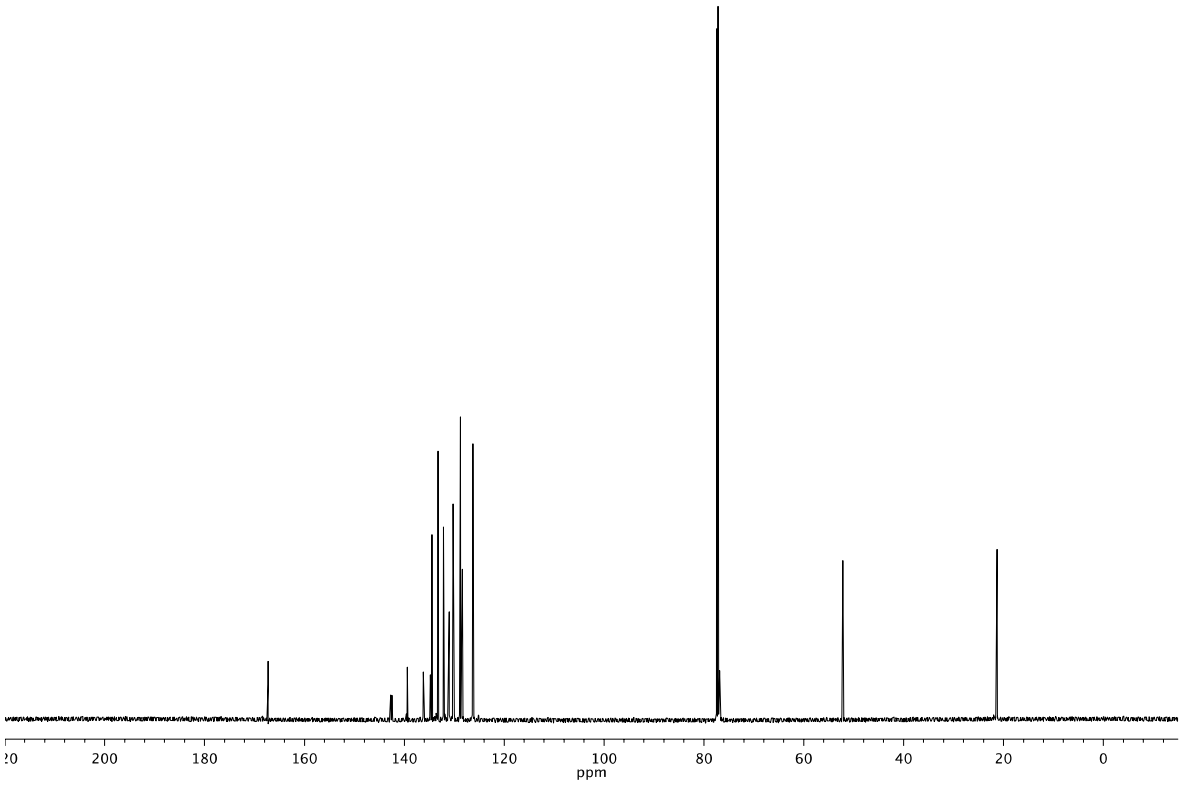




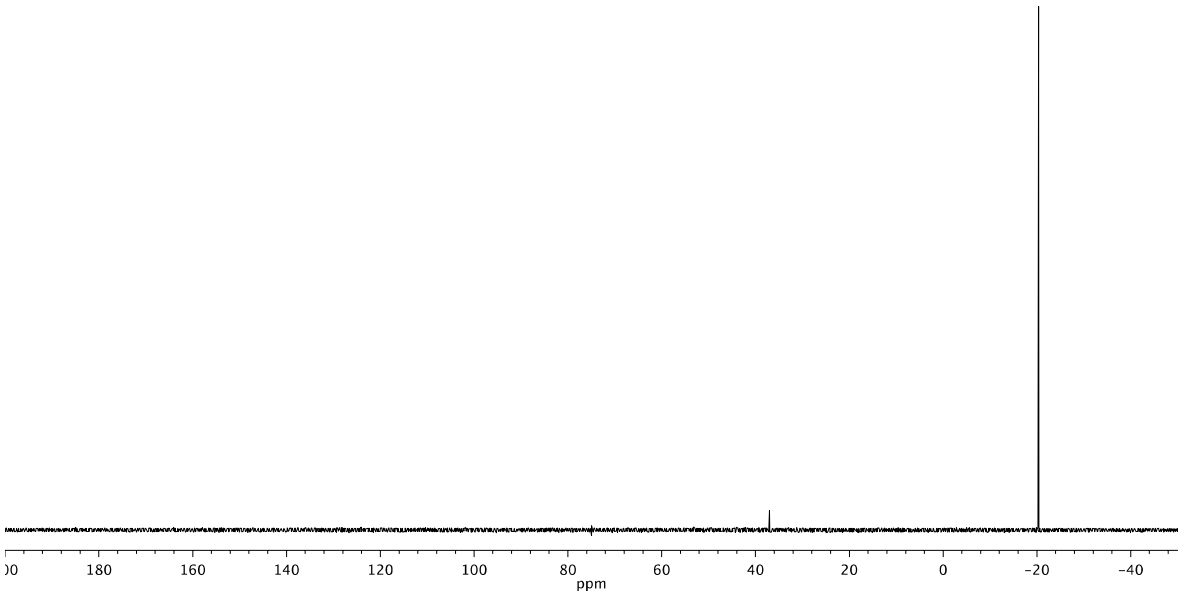
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S9**.



Infrared spectrum (Thin Film, NaCl) of compound **S9**.

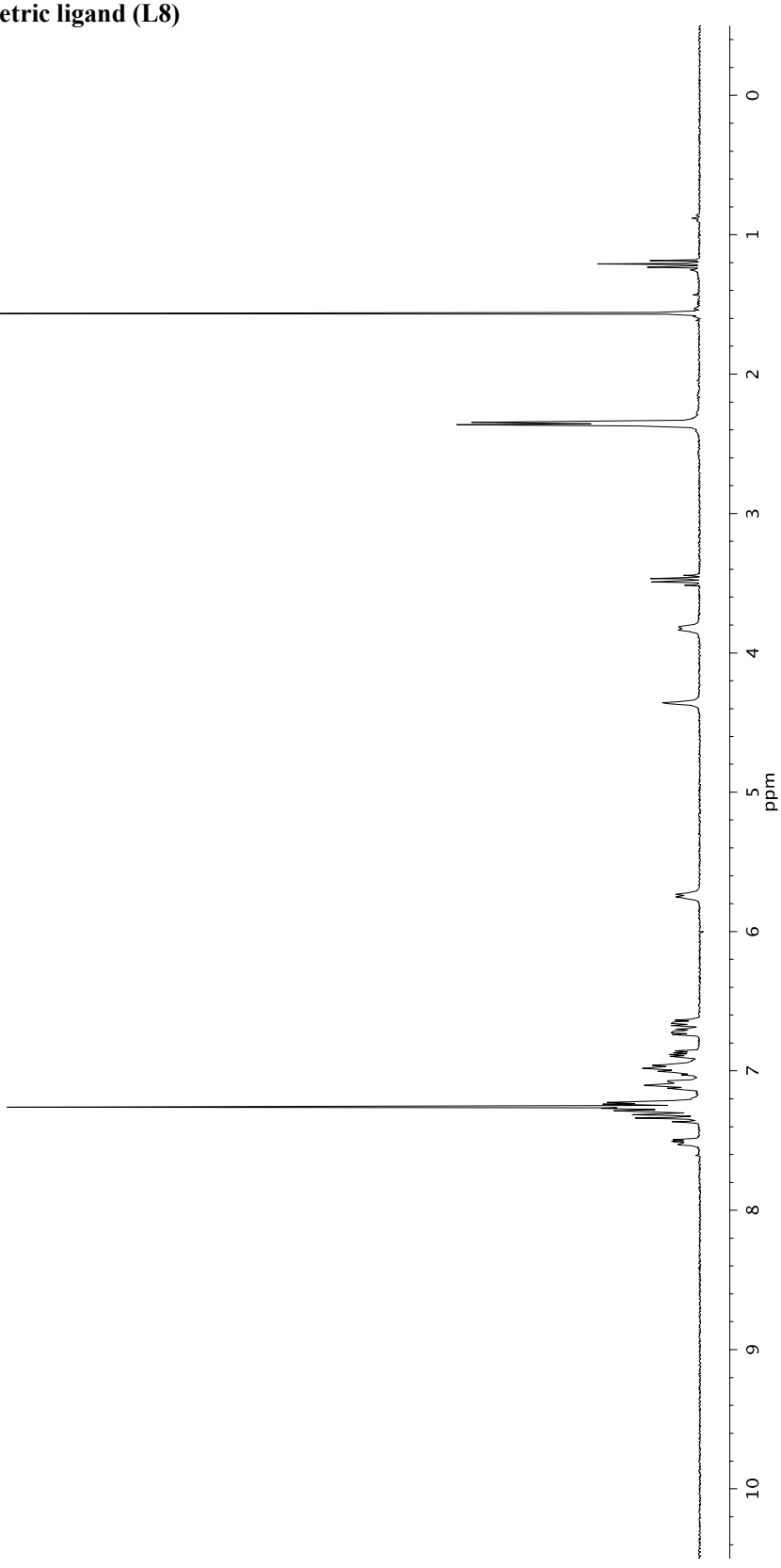


^{13}C NMR (126 MHz, $CDCl_3$) of compound **S9**.

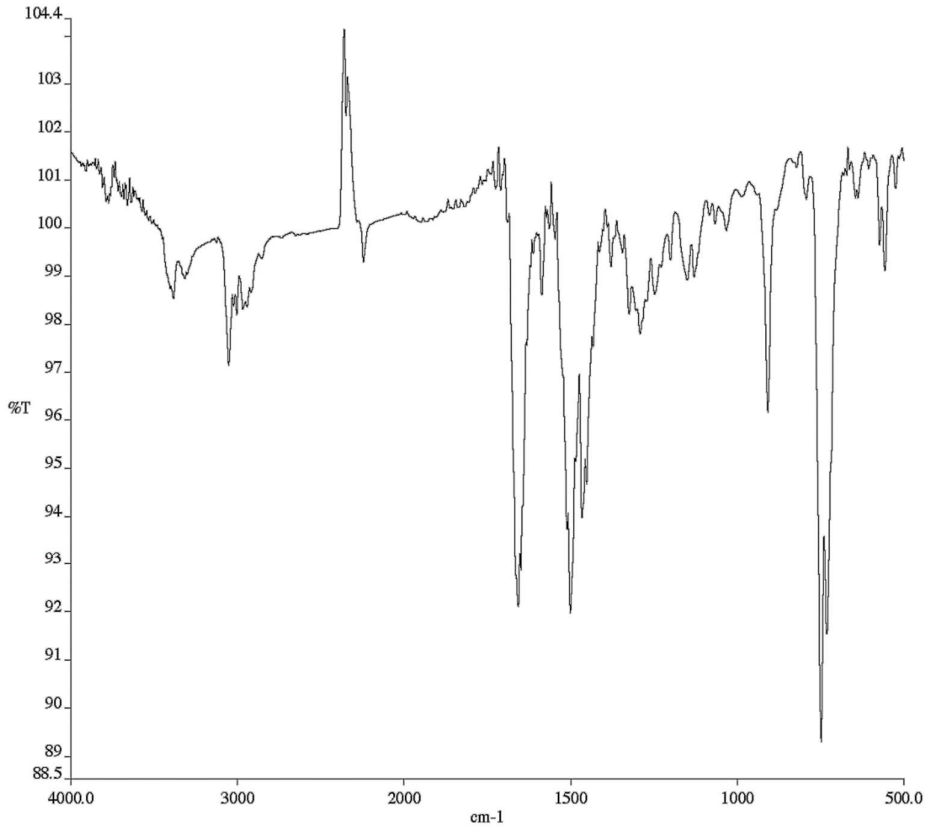


^{31}P NMR (121 MHz, $CDCl_3$) of compound **S9**.

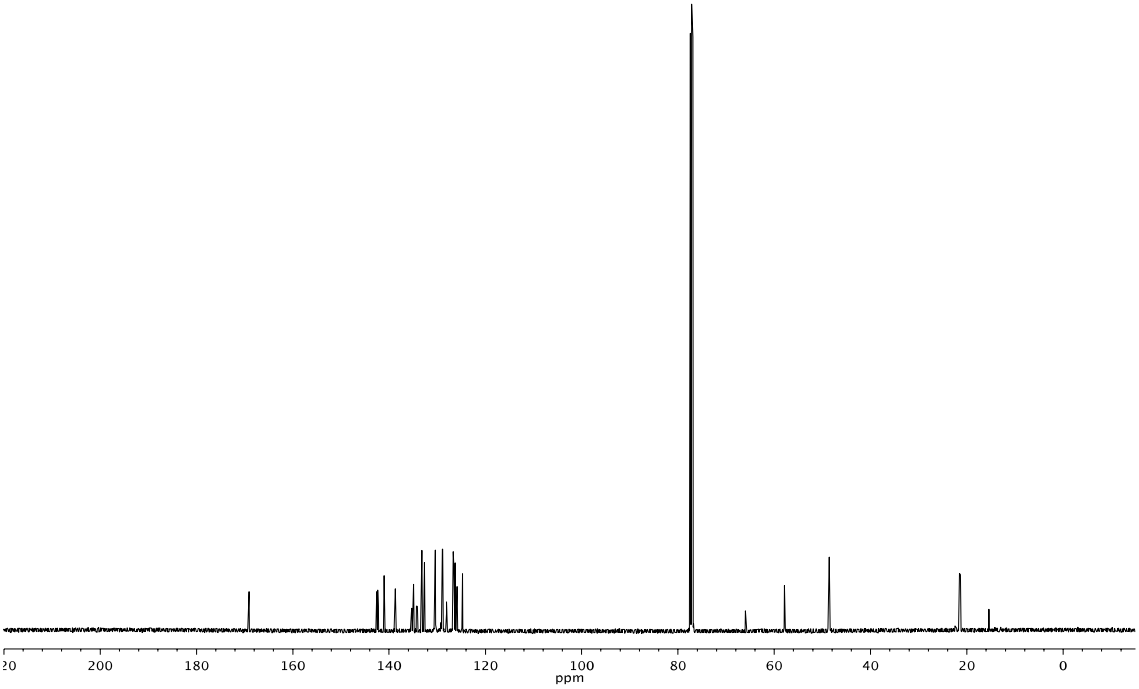
Sterically hindered C_2-symmetric ligand (L8)



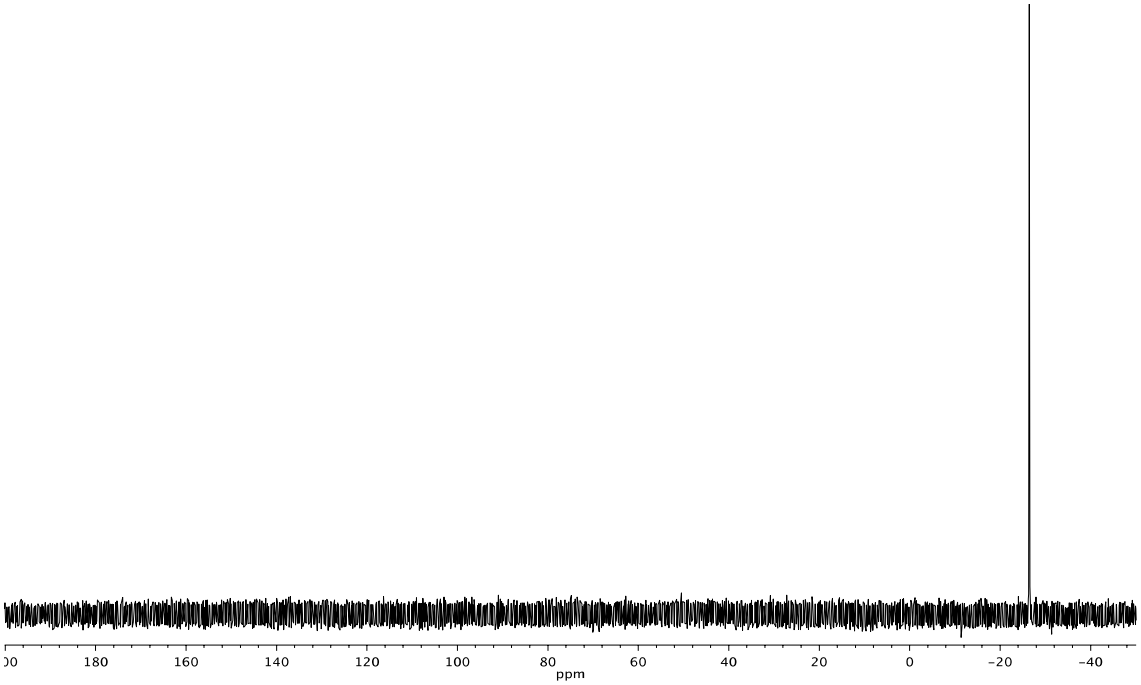
^{1}H NMR (500 MHz, $CDCl_3$) of compound **L8**.



Infrared spectrum (Thin Film, NaCl) of compound **L8**.

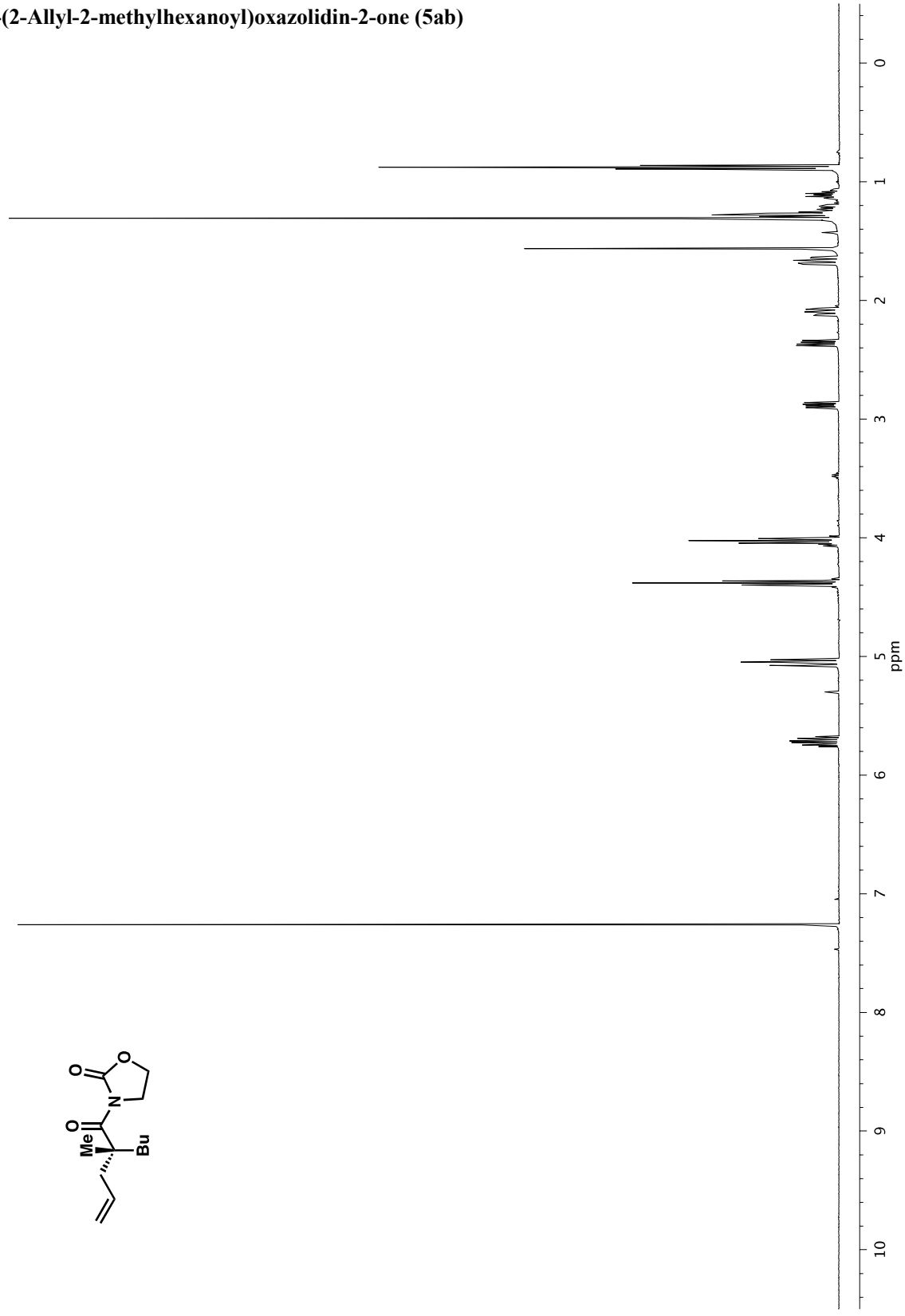


^{13}C NMR (126 MHz, $CDCl_3$) of compound **L8**.

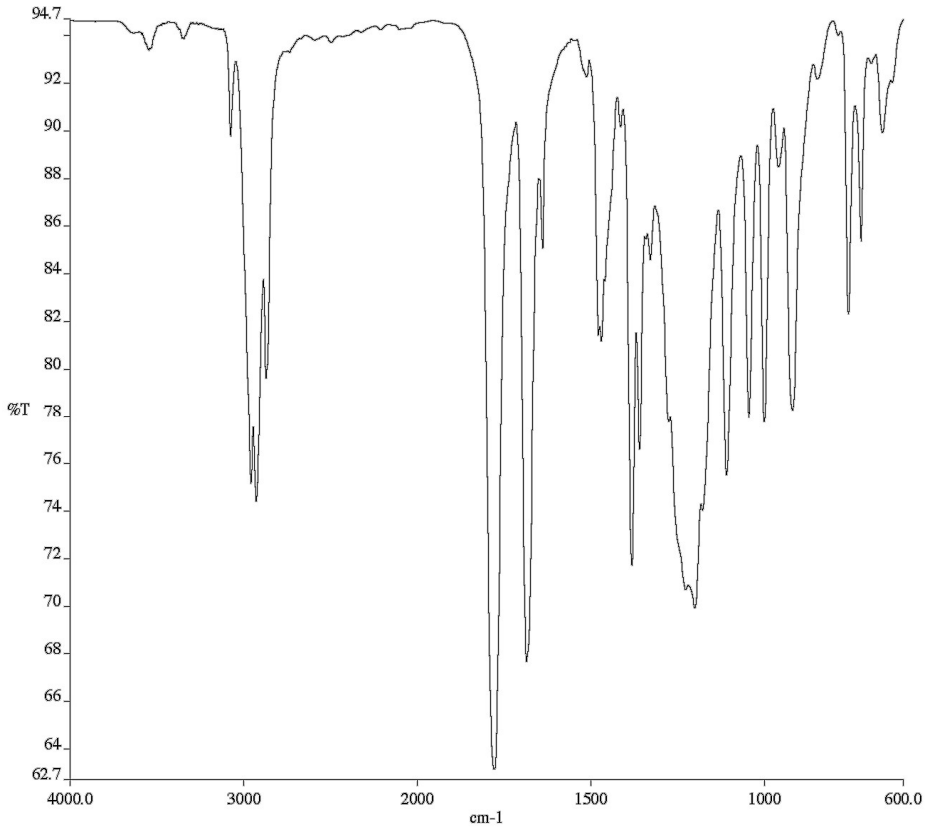


^{31}P NMR (121 MHz, $CDCl_3$) of compound **L8**.

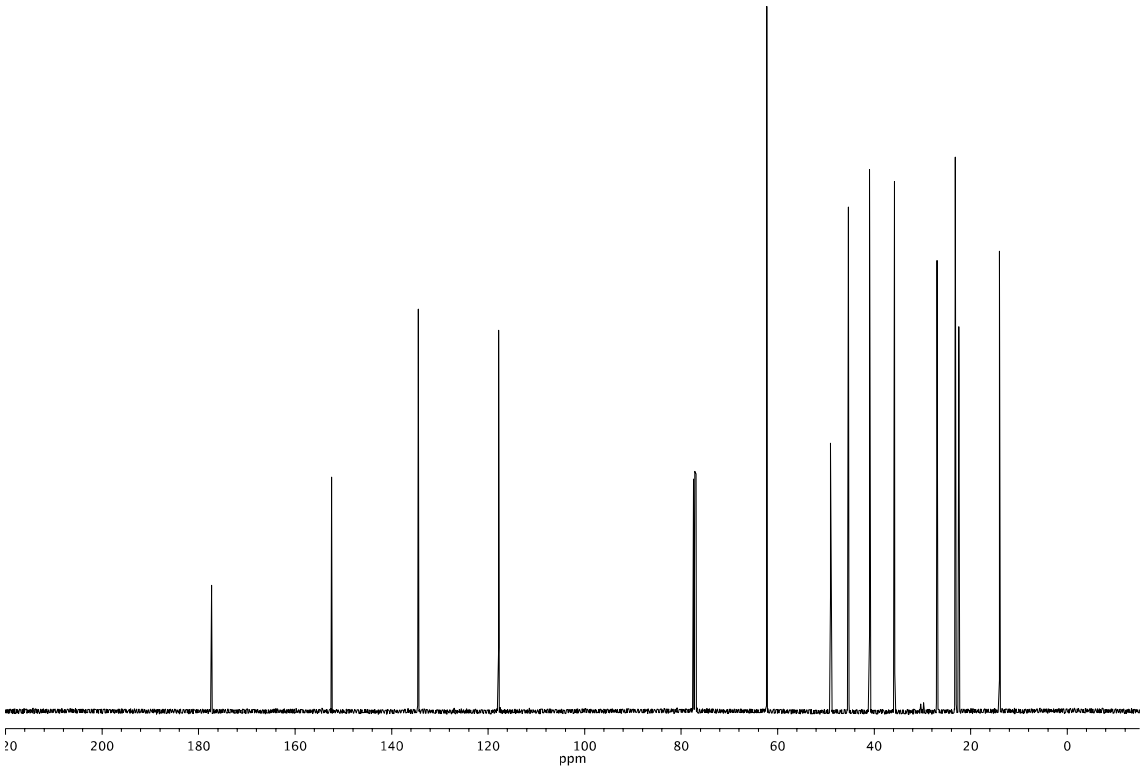
3-(2-Allyl-2-methylhexanoyl)oxazolidin-2-one (5ab)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5ab**.

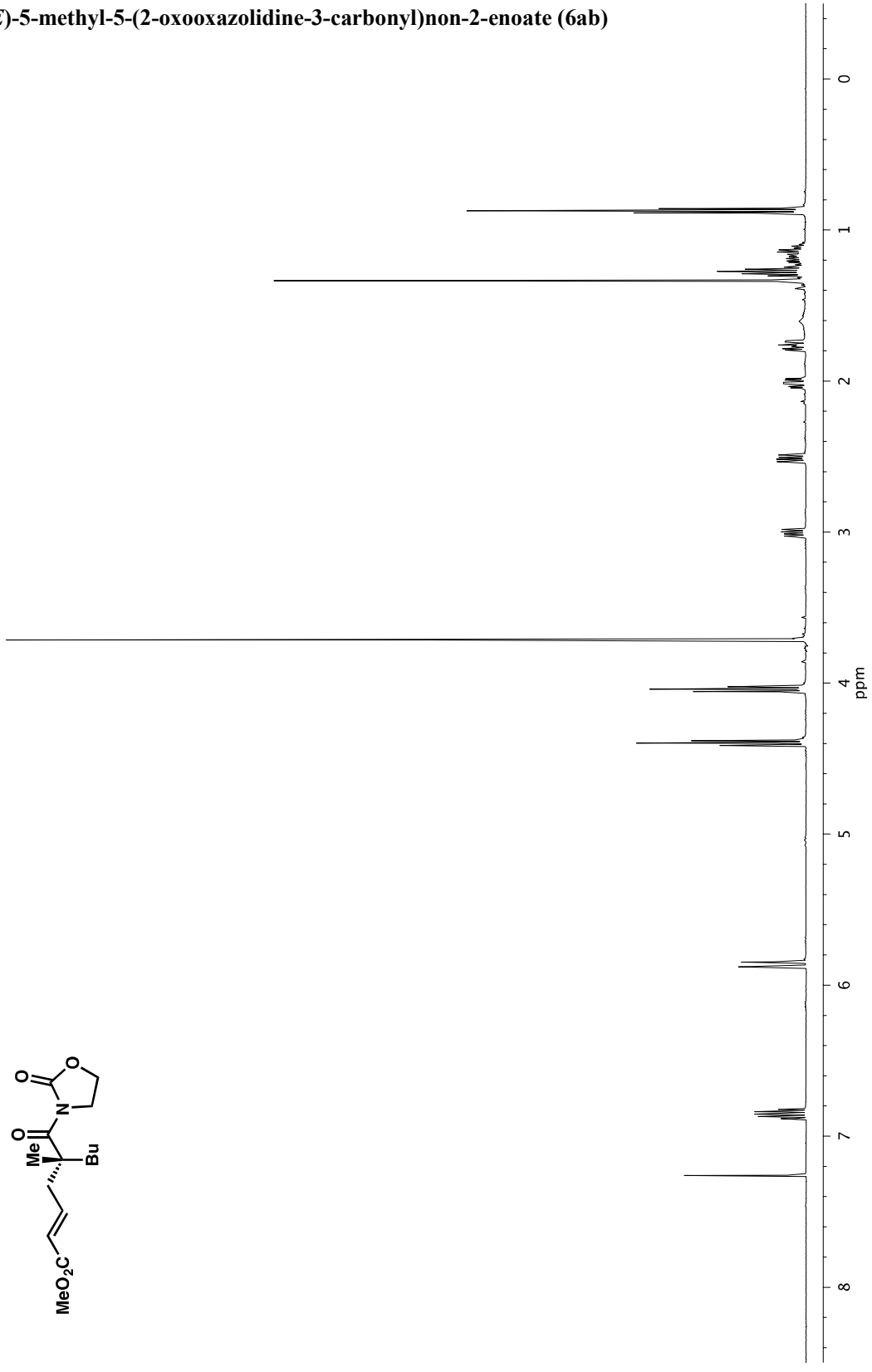


Infrared spectrum (Thin Film, NaCl) of compound **5ab**.

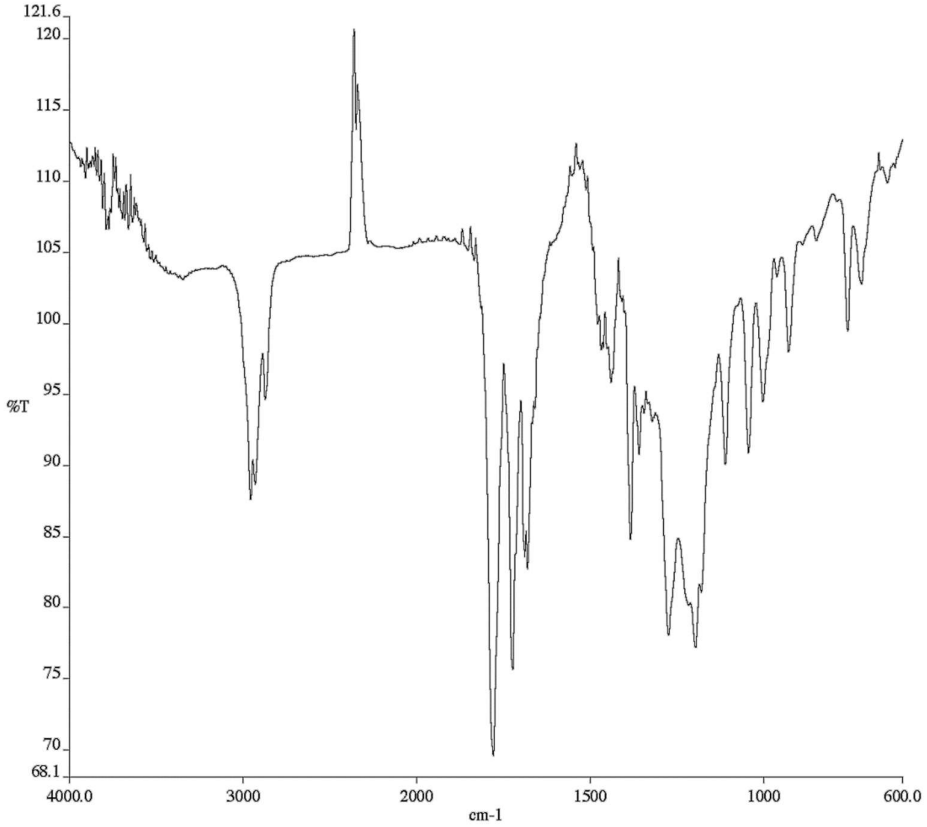


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5ab**.

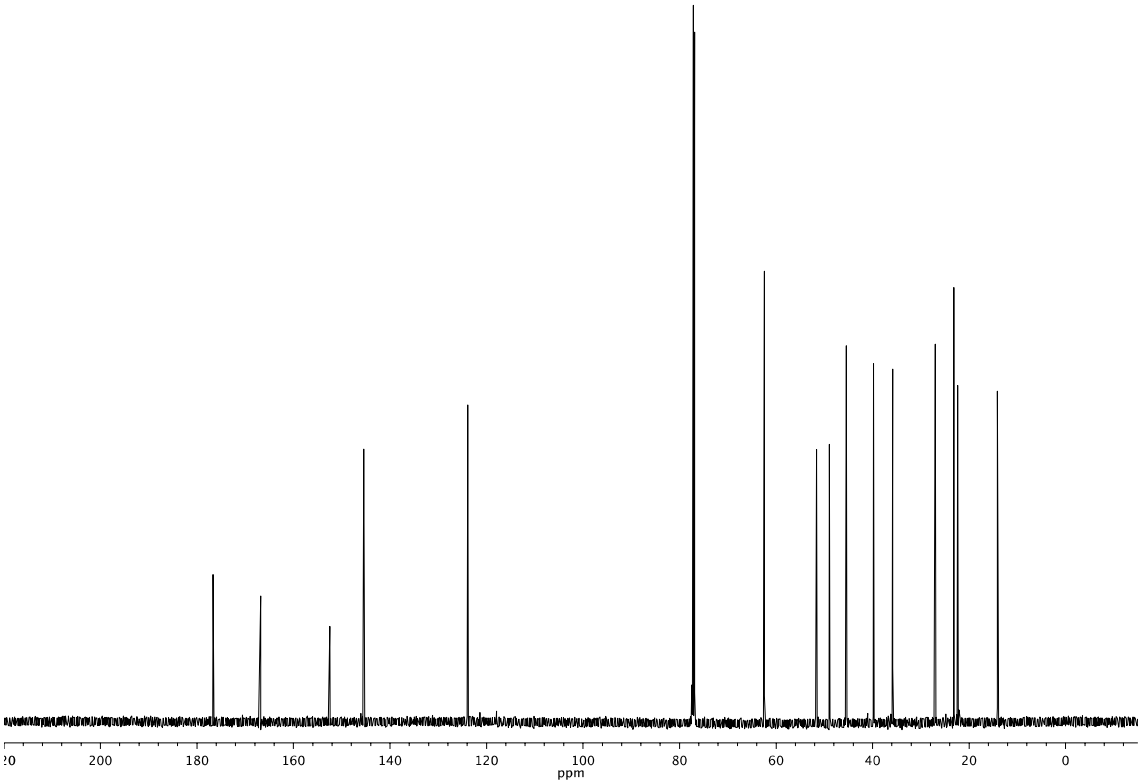
Methyl (*E*)-5-methyl-5-(2-oxooxazolidine-3-carbonyl)non-2-enoate (6ab)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6ab**.

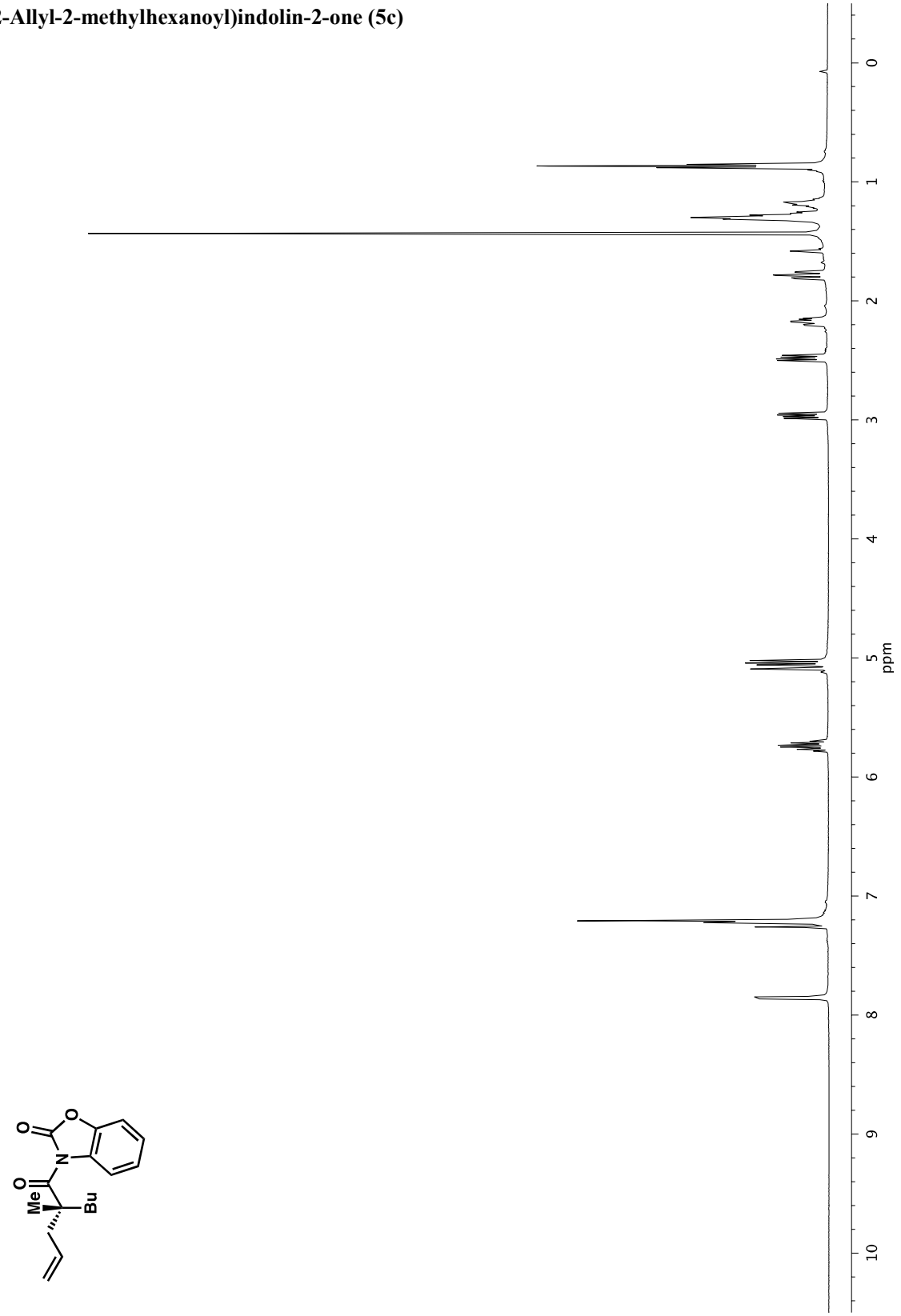


Infrared spectrum (Thin Film, NaCl) of compound **6ab**.

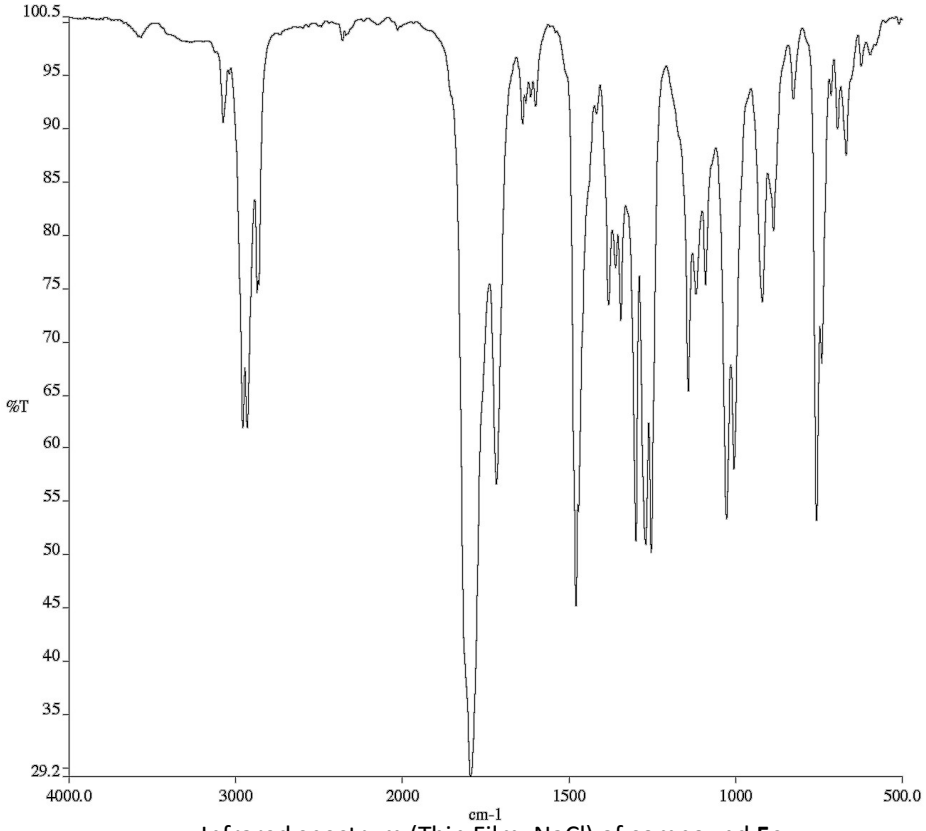


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6ab**.

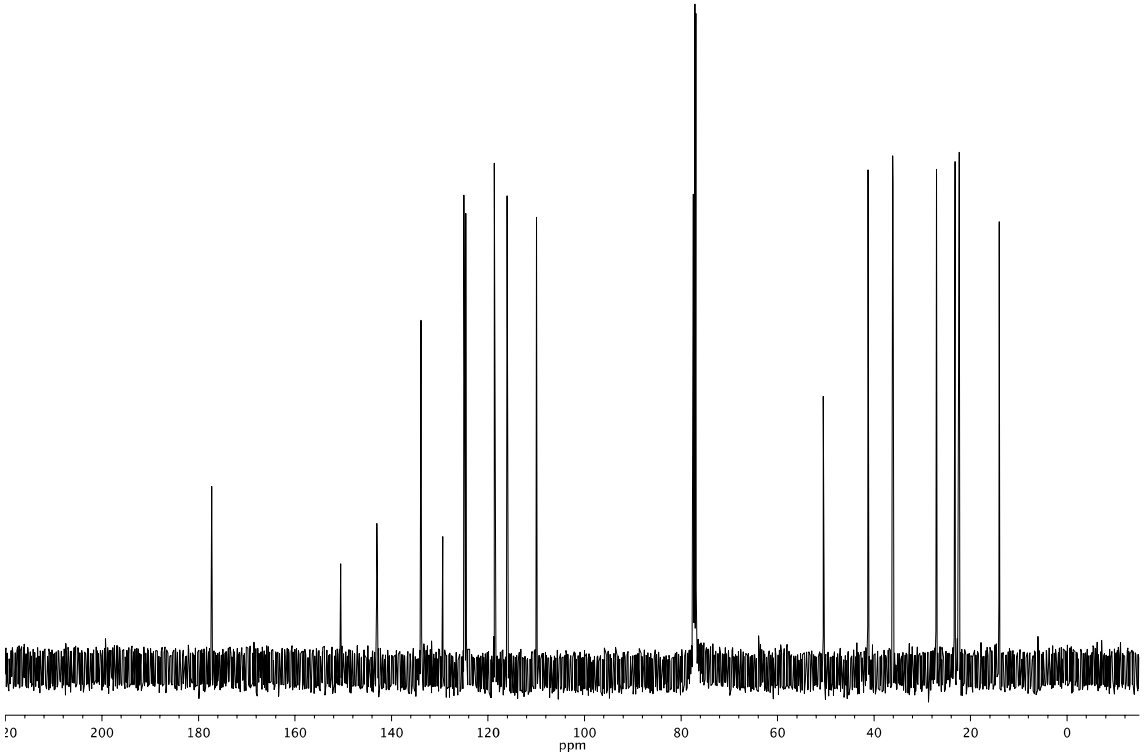
1-(2-Allyl-2-methylhexanoyl)indolin-2-one (5c)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5c**.

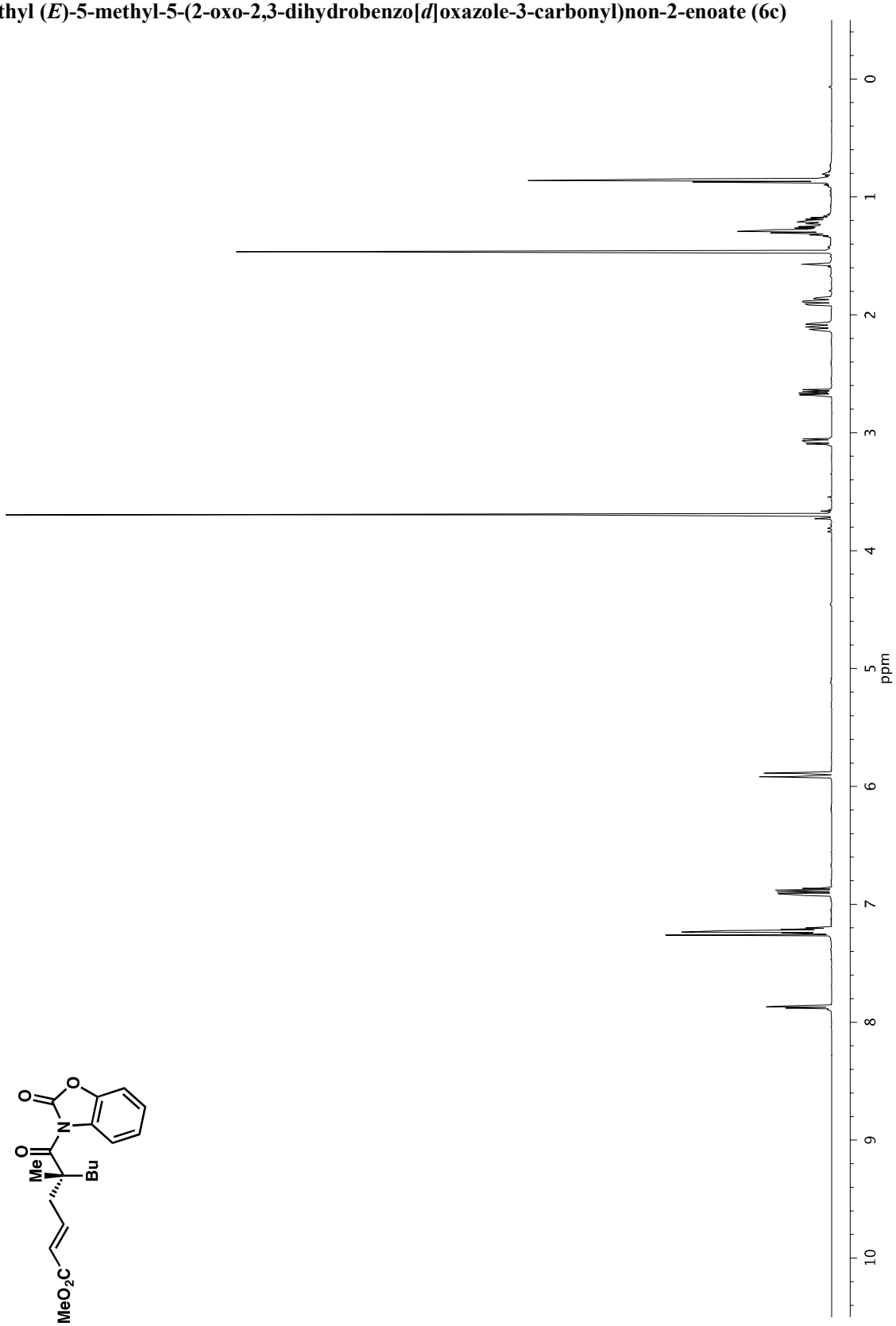


Infrared spectrum (Thin Film, NaCl) of compound **5c**.

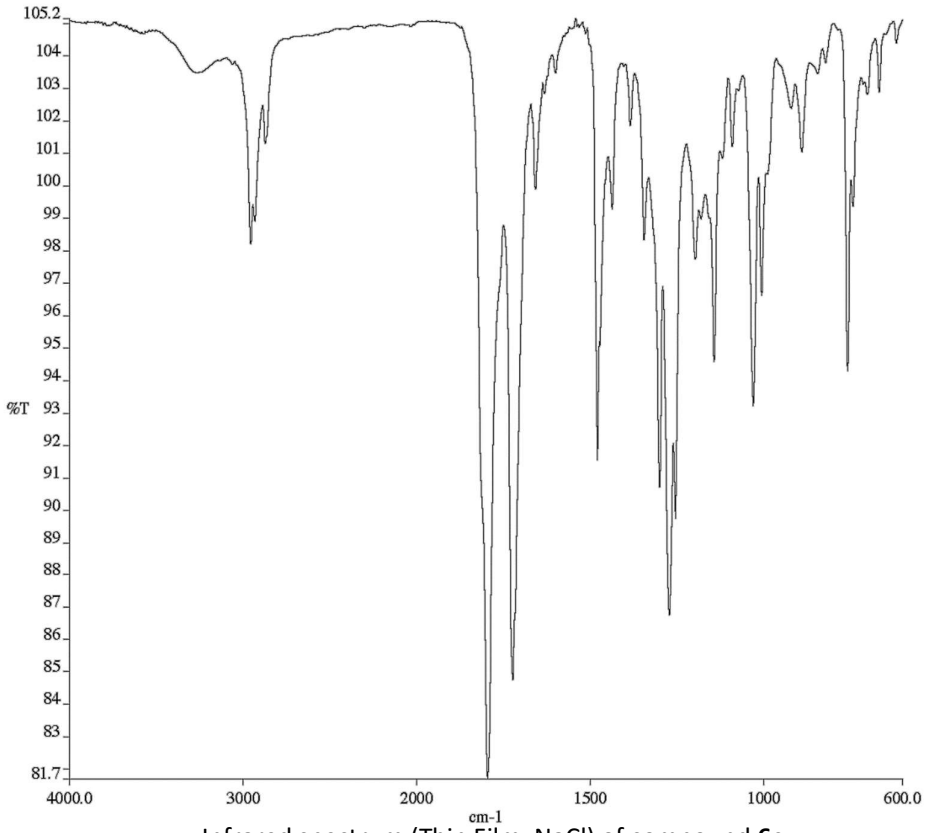


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5c**.

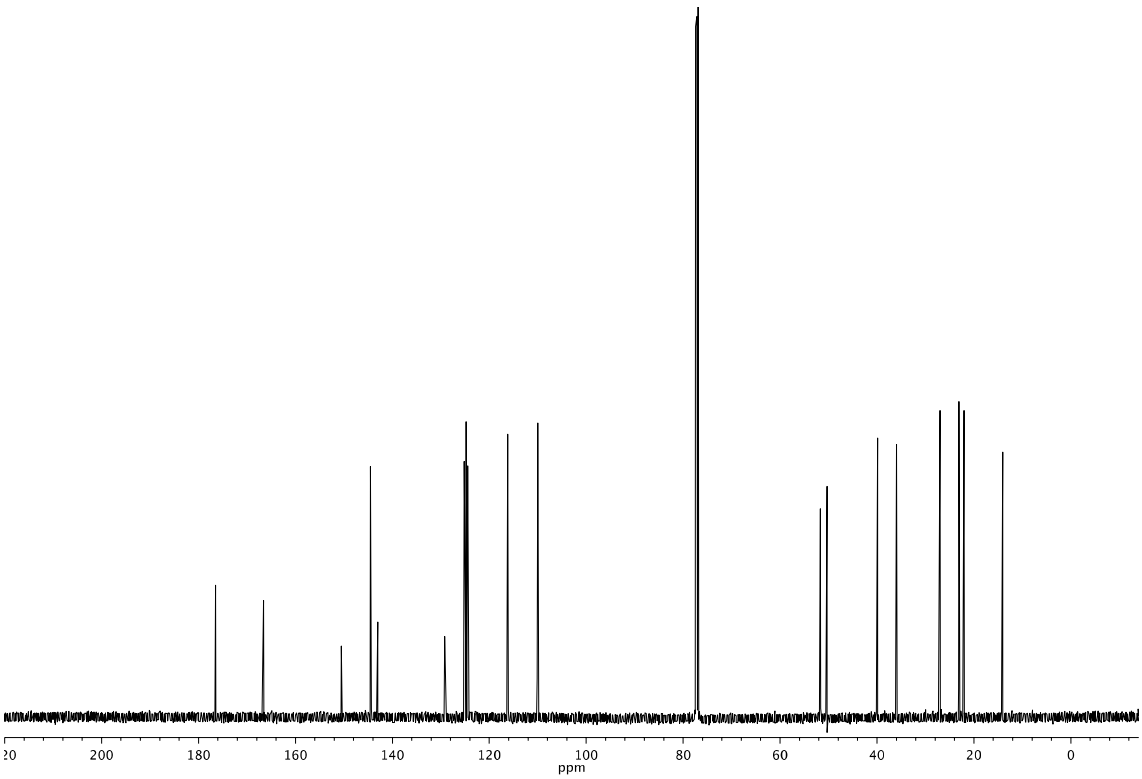
Methyl (*E*)-5-methyl-5-(2-oxo-2,3-dihydrobenzo[*d*]oxazole-3-carbonyl)non-2-enoate (6c)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6c**.

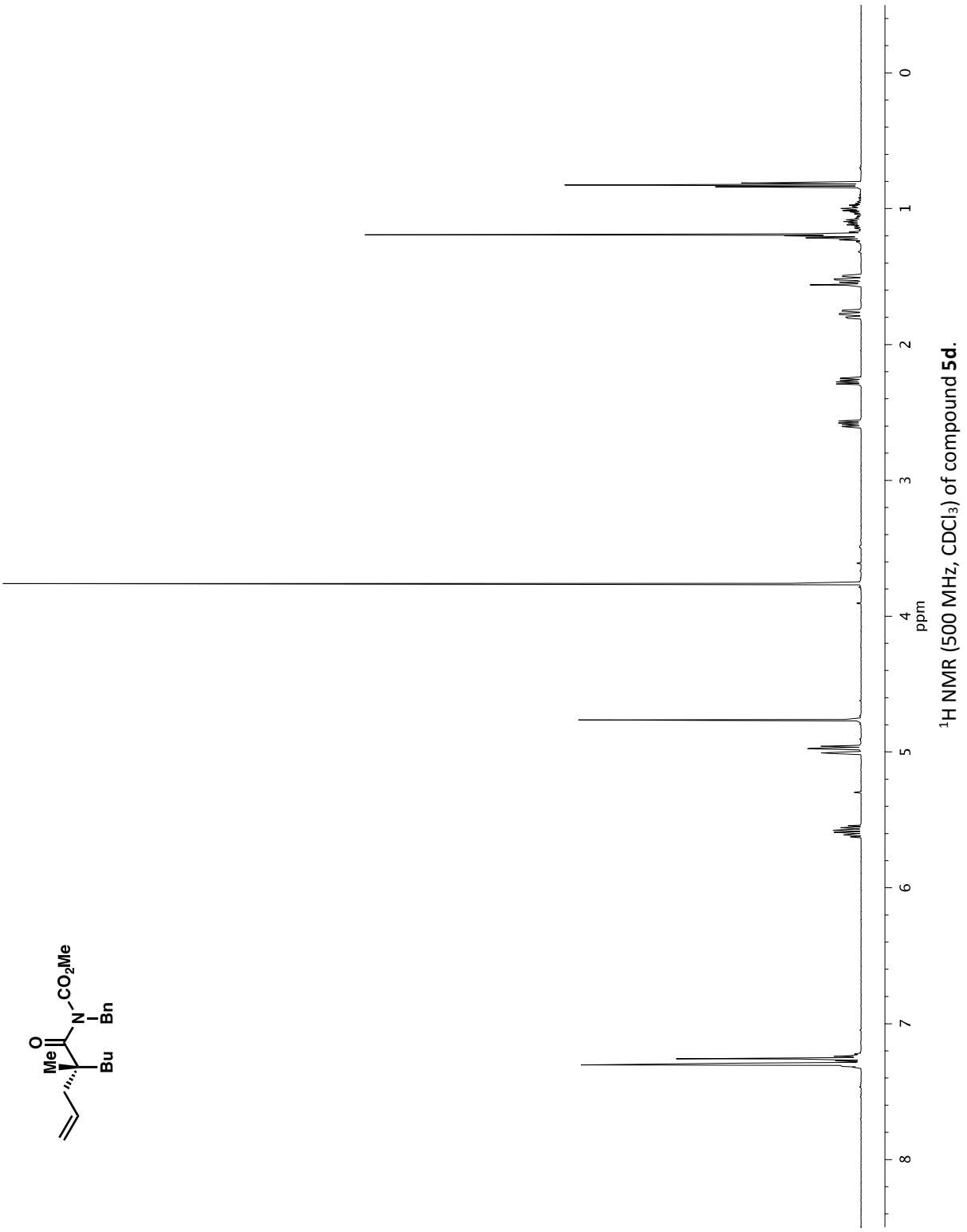


Infrared spectrum (Thin Film, NaCl) of compound **6c**.

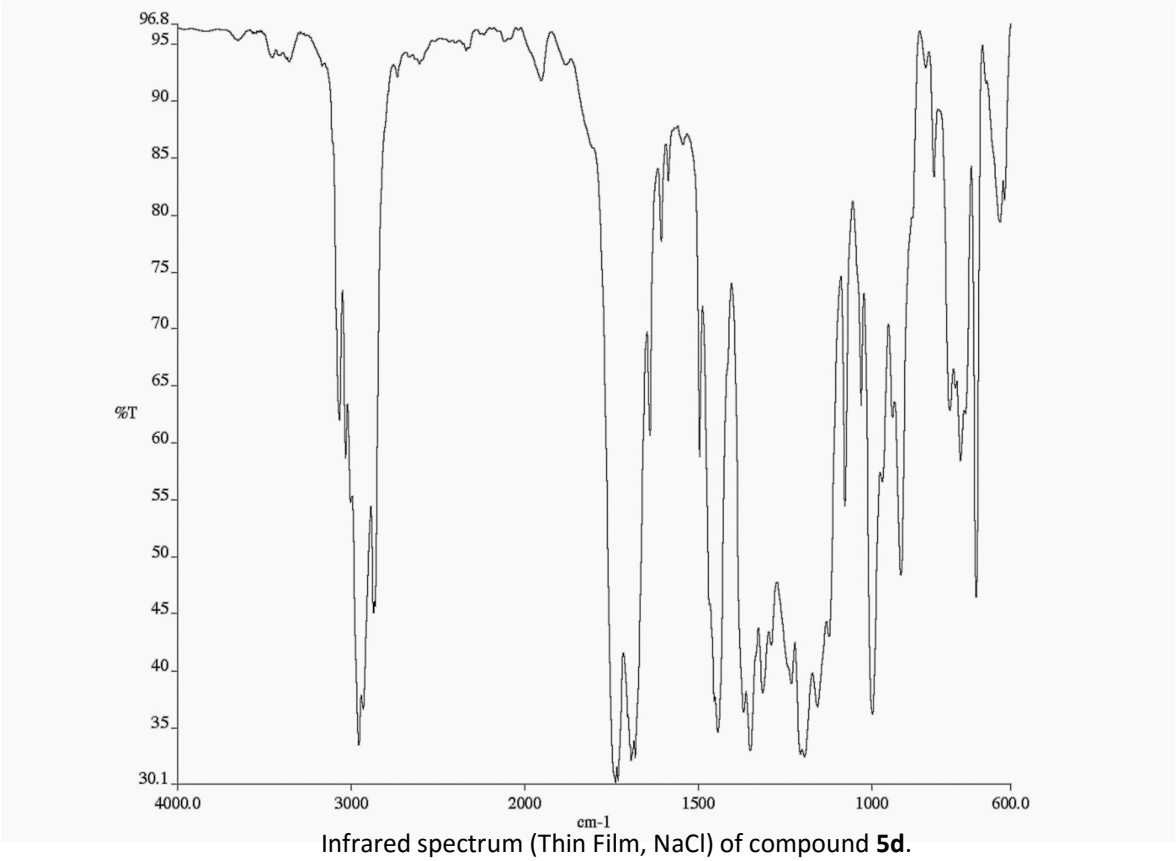


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6c**.

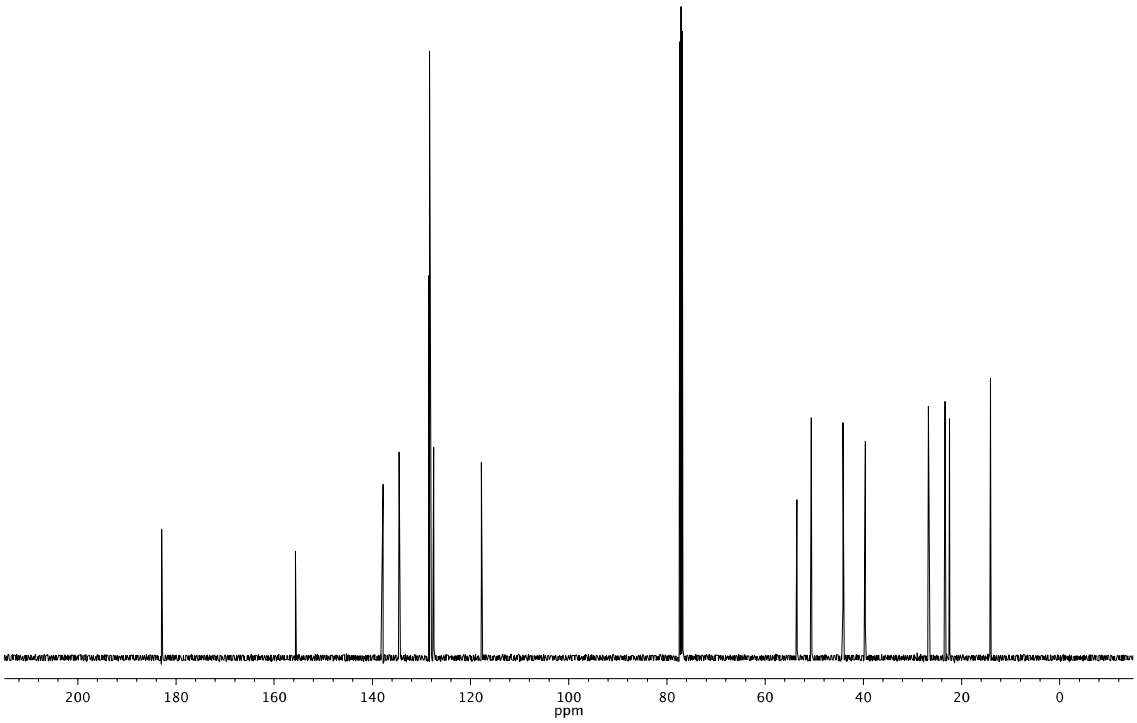
Methyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5d)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5d**.

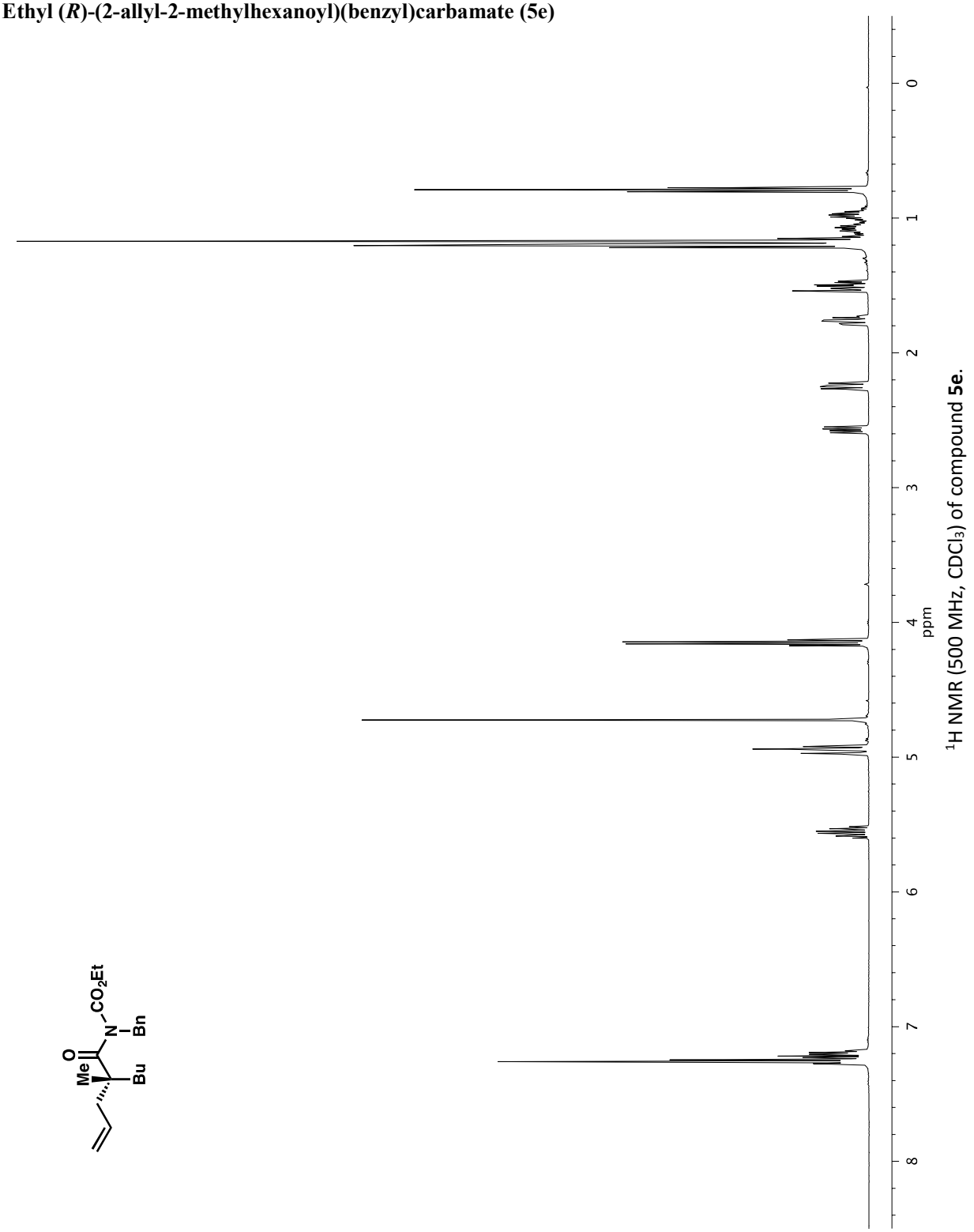


Infrared spectrum (Thin Film, NaCl) of compound **5d**.

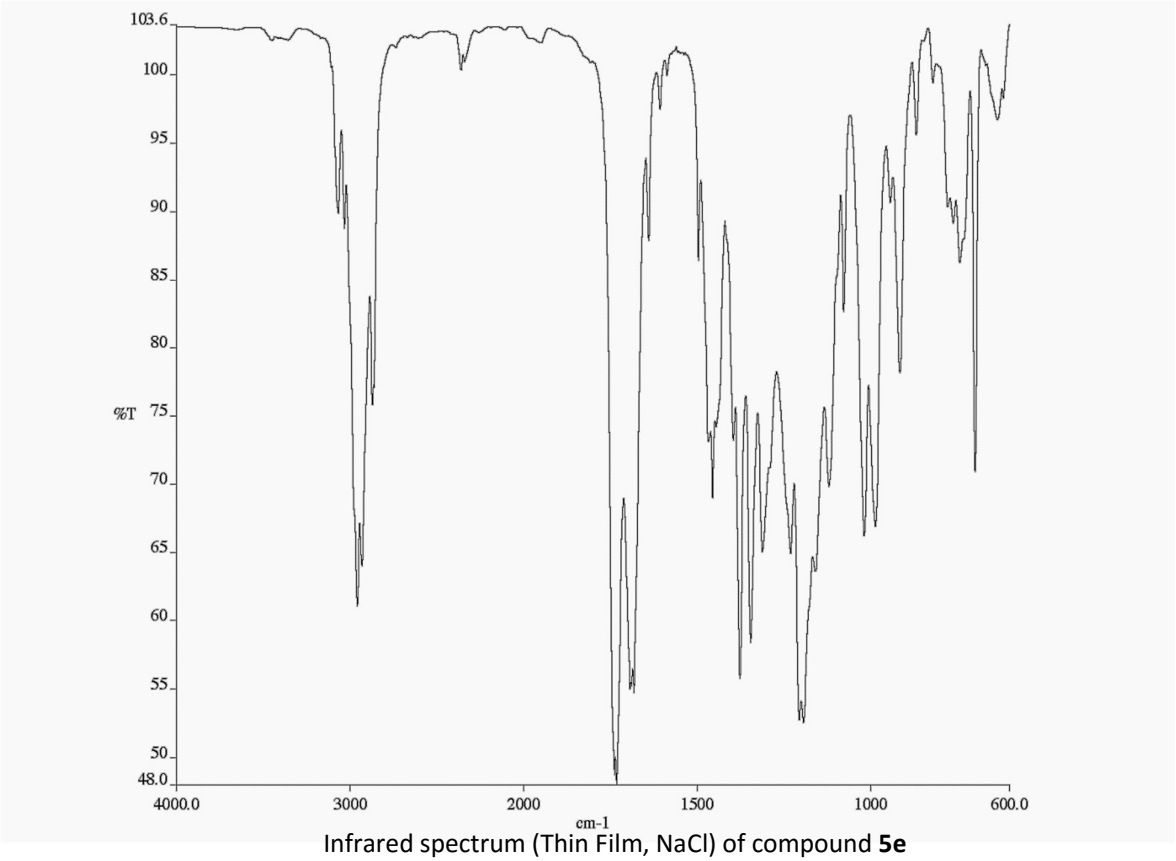


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5d**.

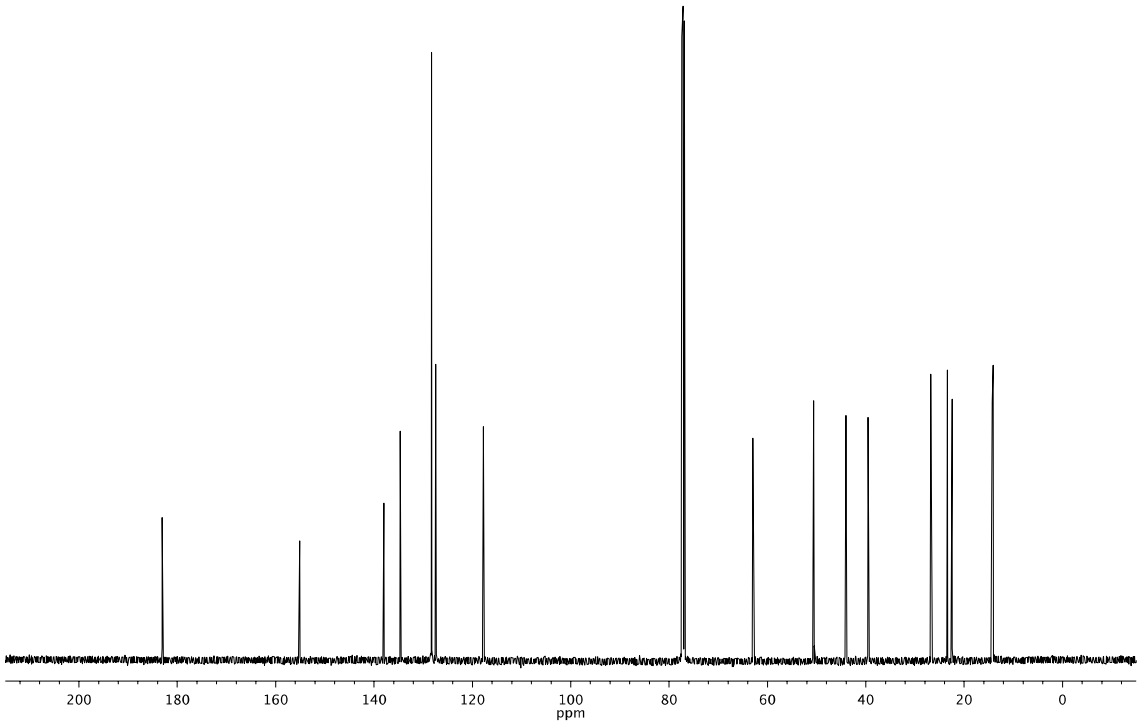
Ethyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5e)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5e**.

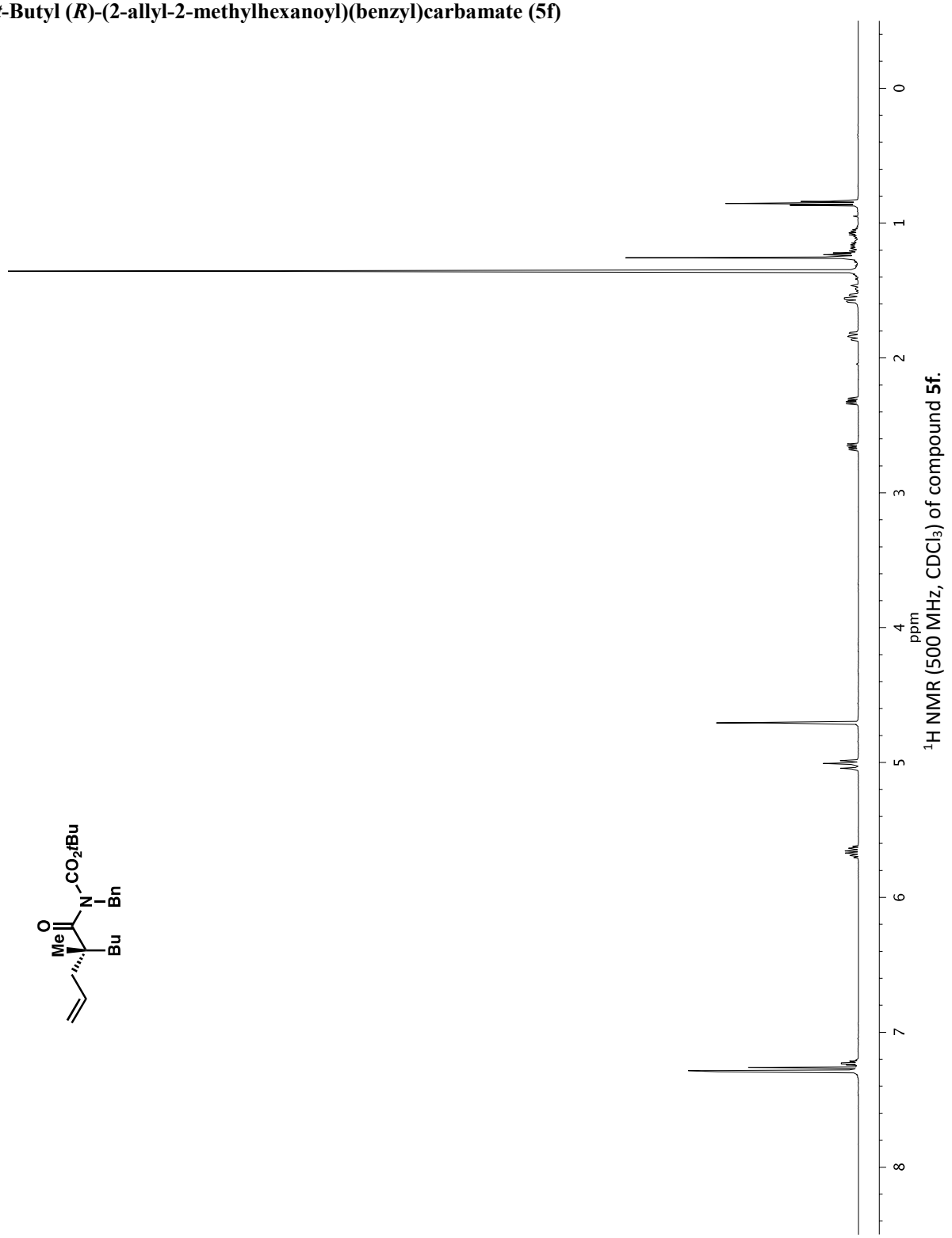


Infrared spectrum (Thin Film, NaCl) of compound **5e**

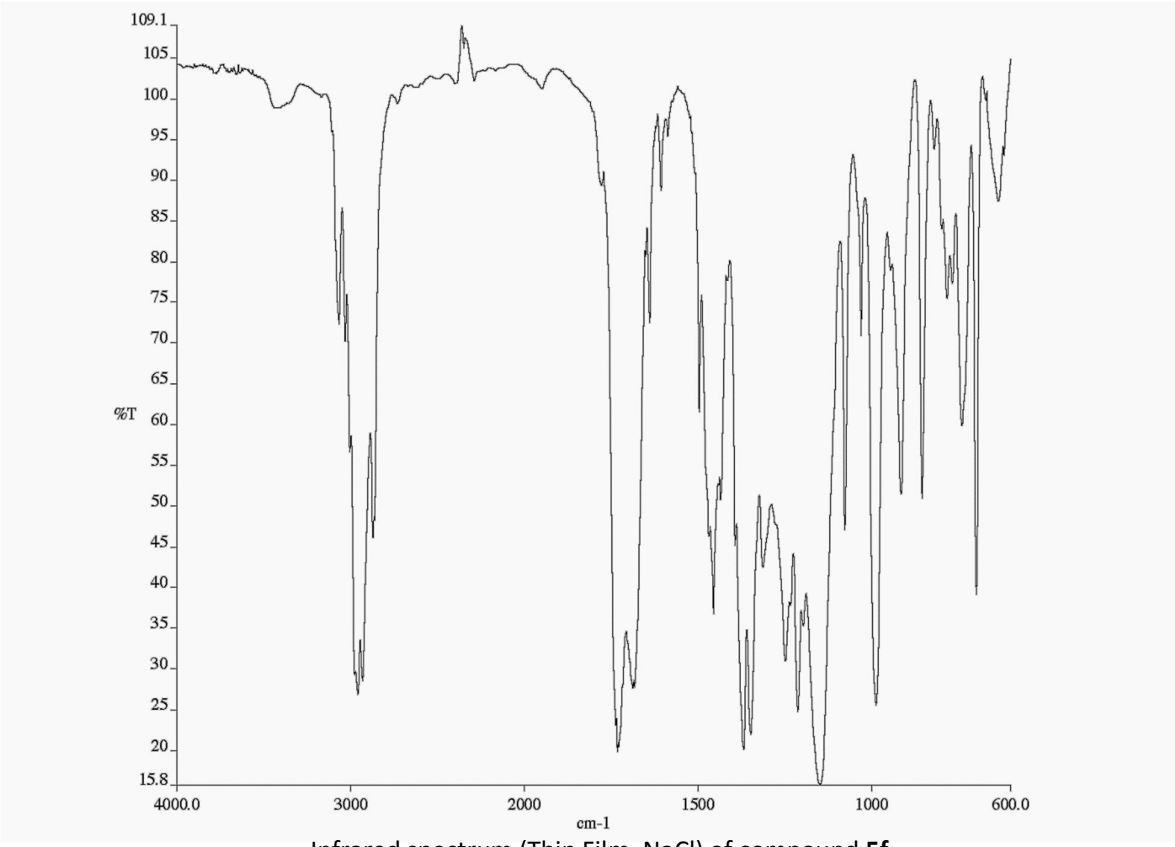


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5e**.

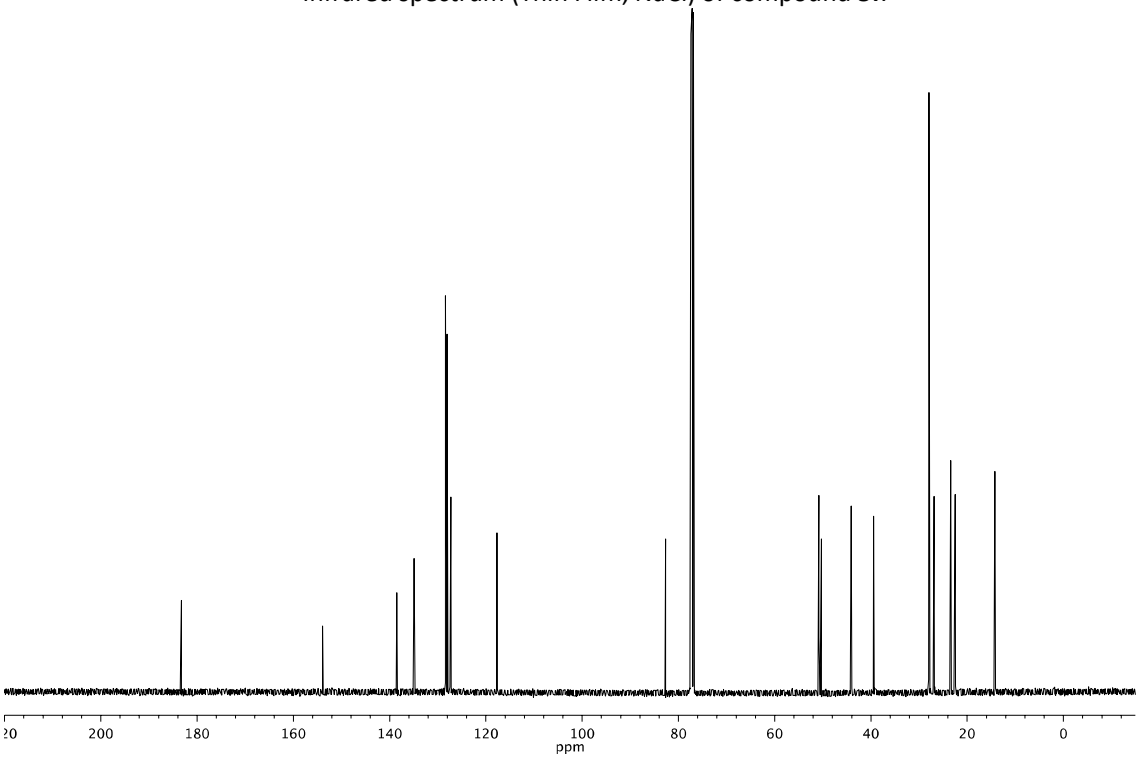
***tert*-Butyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5f)**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5f**.

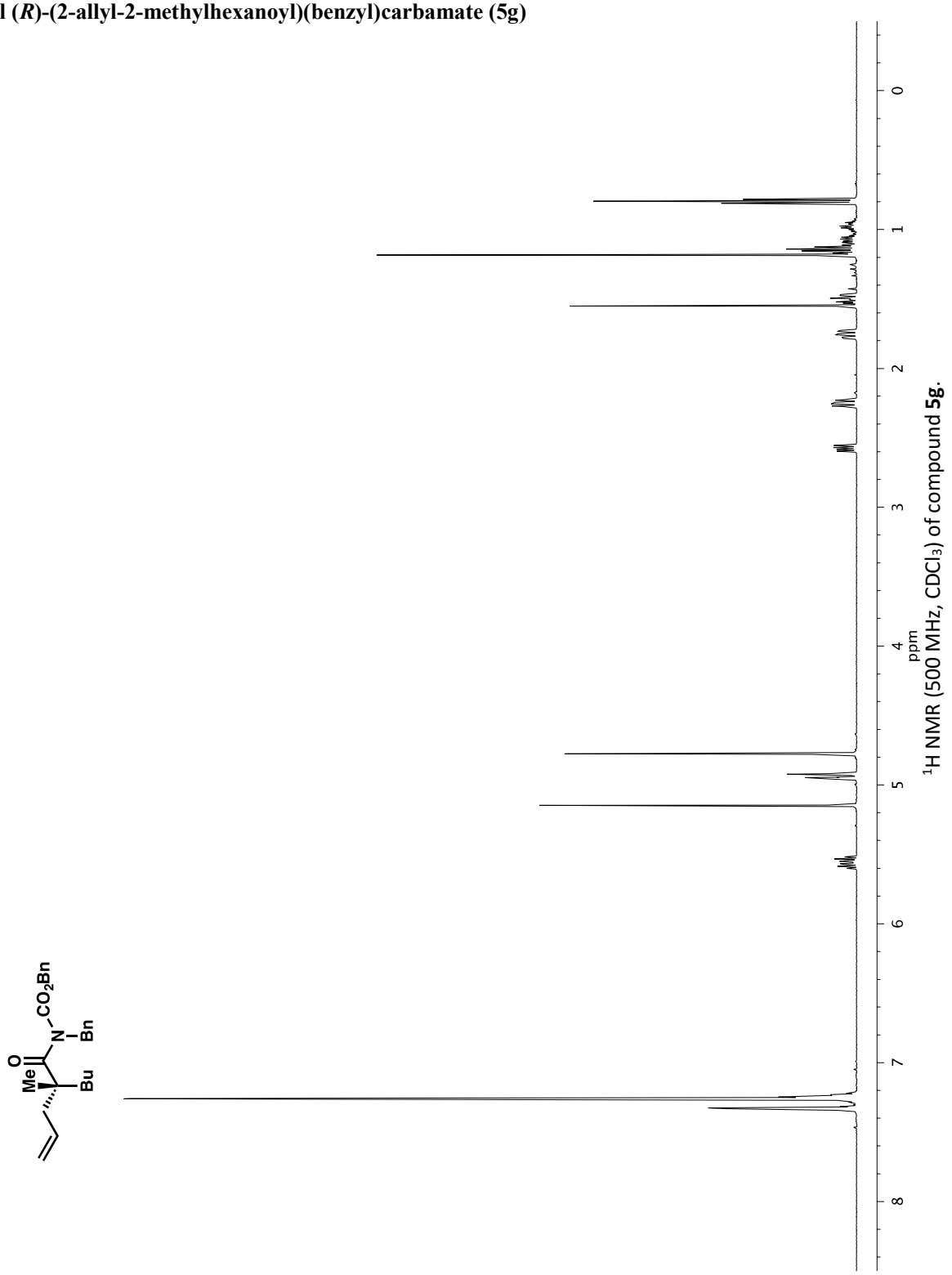


Infrared spectrum (Thin Film, NaCl) of compound **5f**.

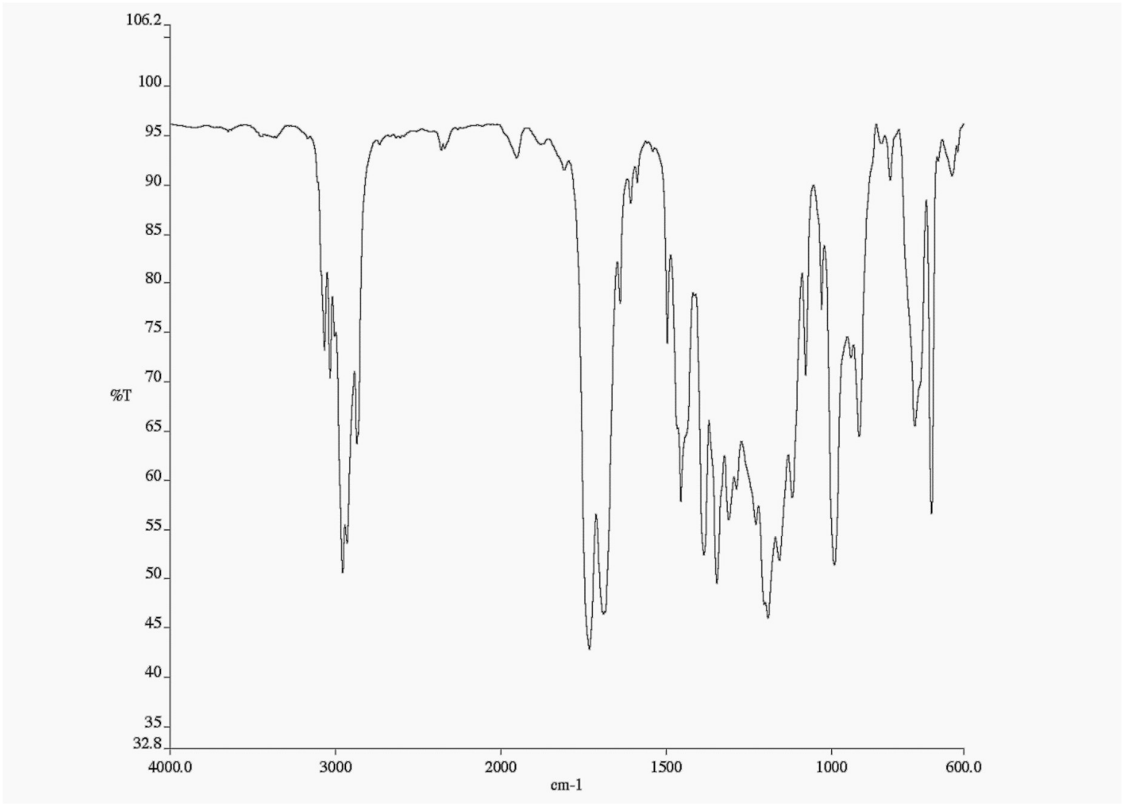


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5f**.

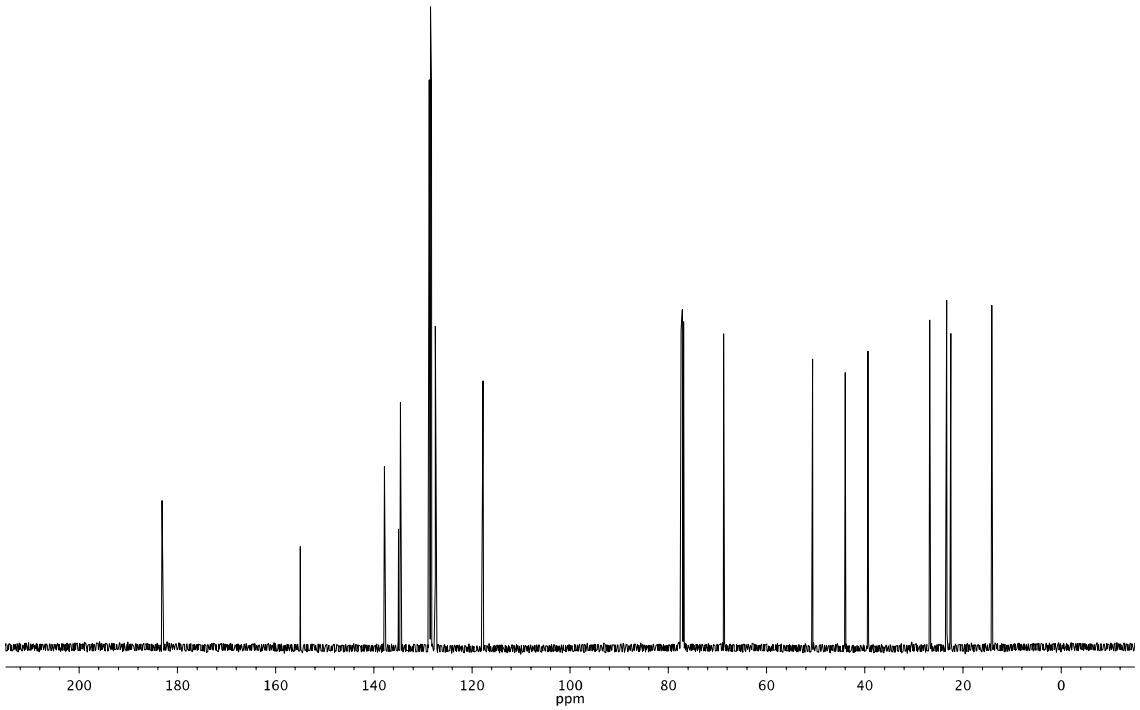
Benzyl (*R*)-(2-allyl-2-methylhexanoyl)(benzyl)carbamate (5g)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5g**.

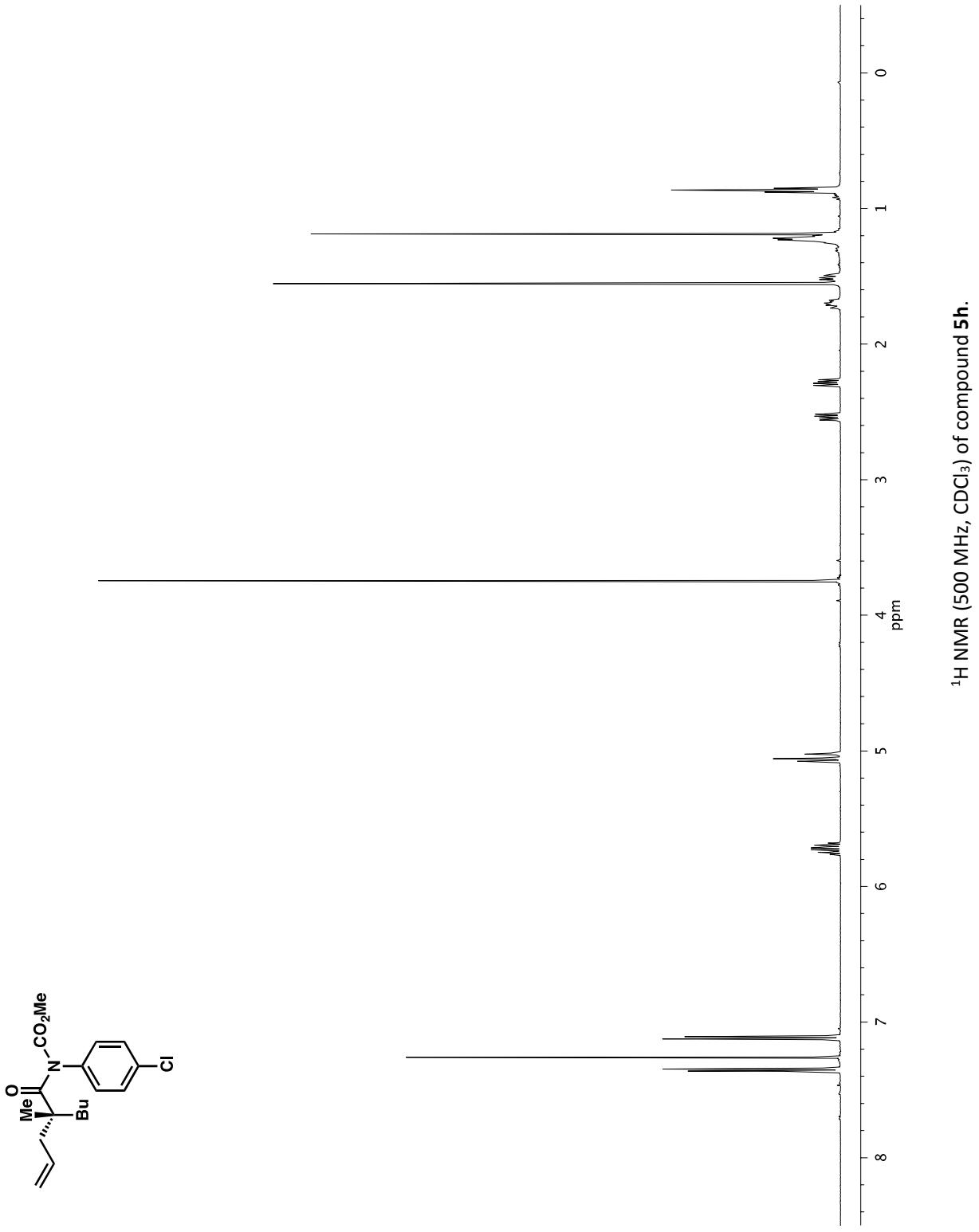


Infrared spectrum (Thin Film, NaCl) of compound **5g**.

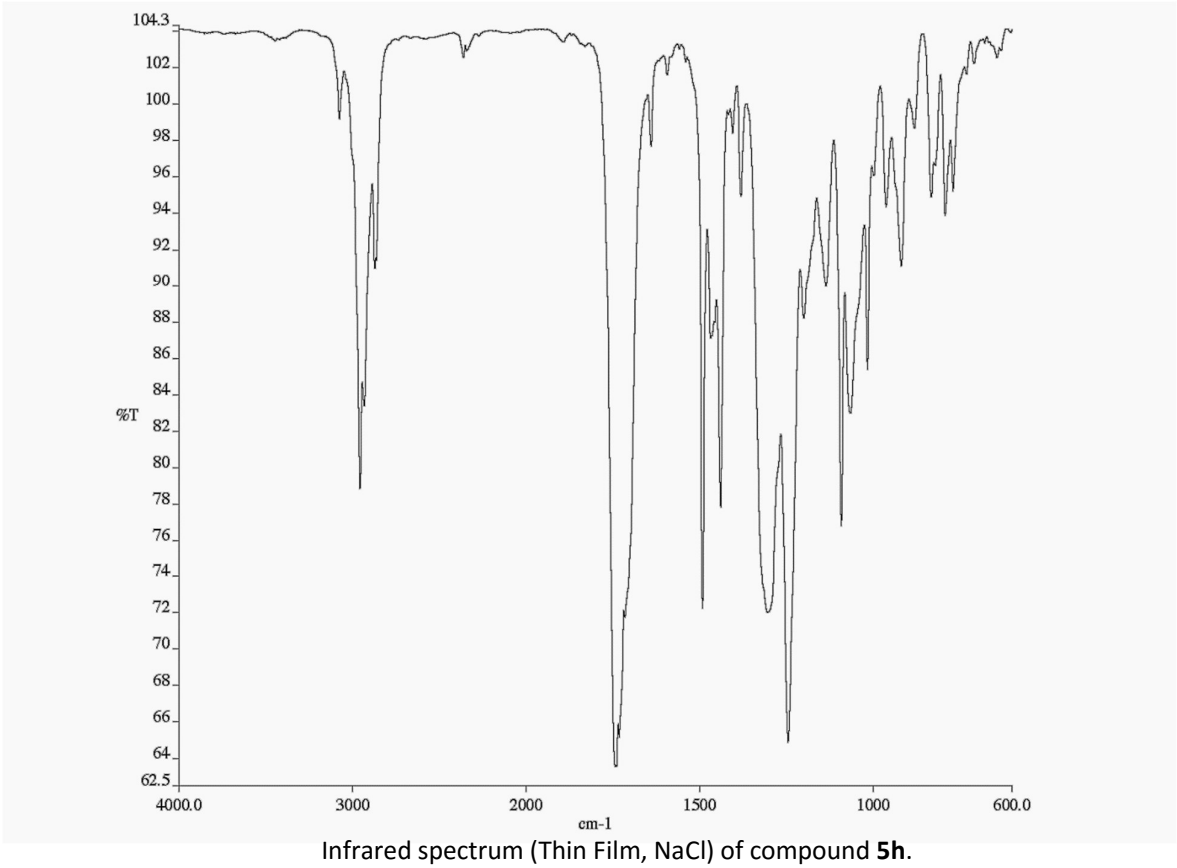


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5g**.

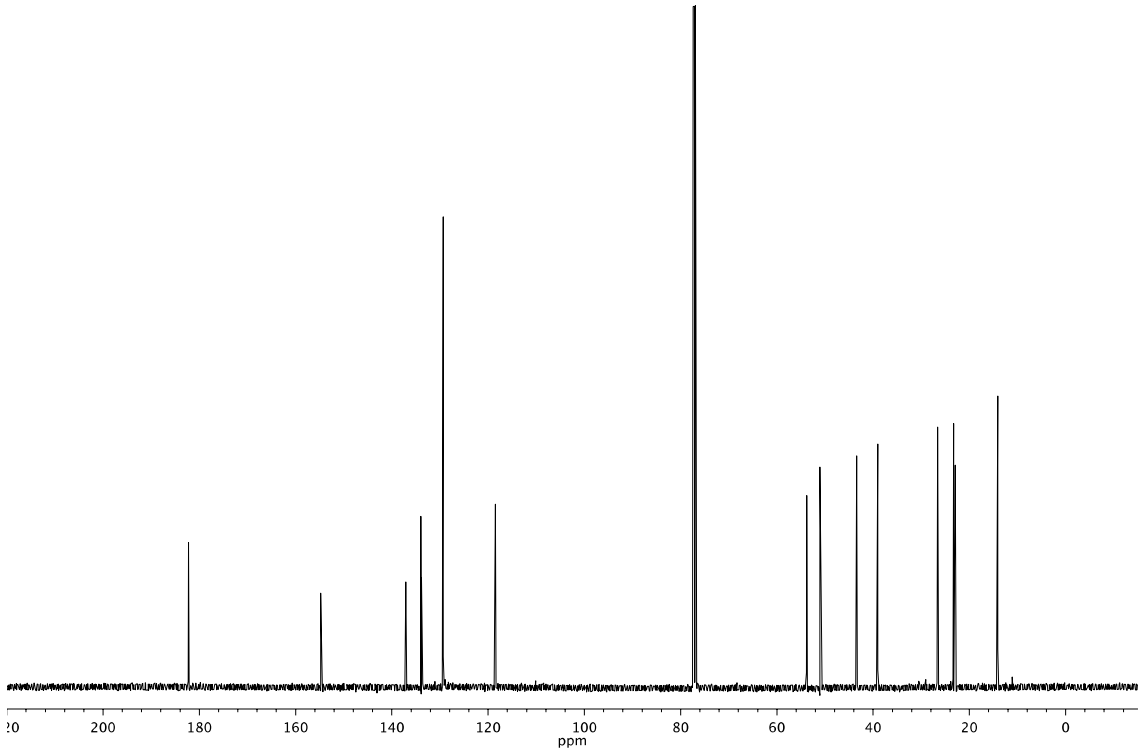
Methyl (*R*)-(2-allyl-2-methylhexanoyl)(4-chlorophenyl)carbamate (5h)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5h**.

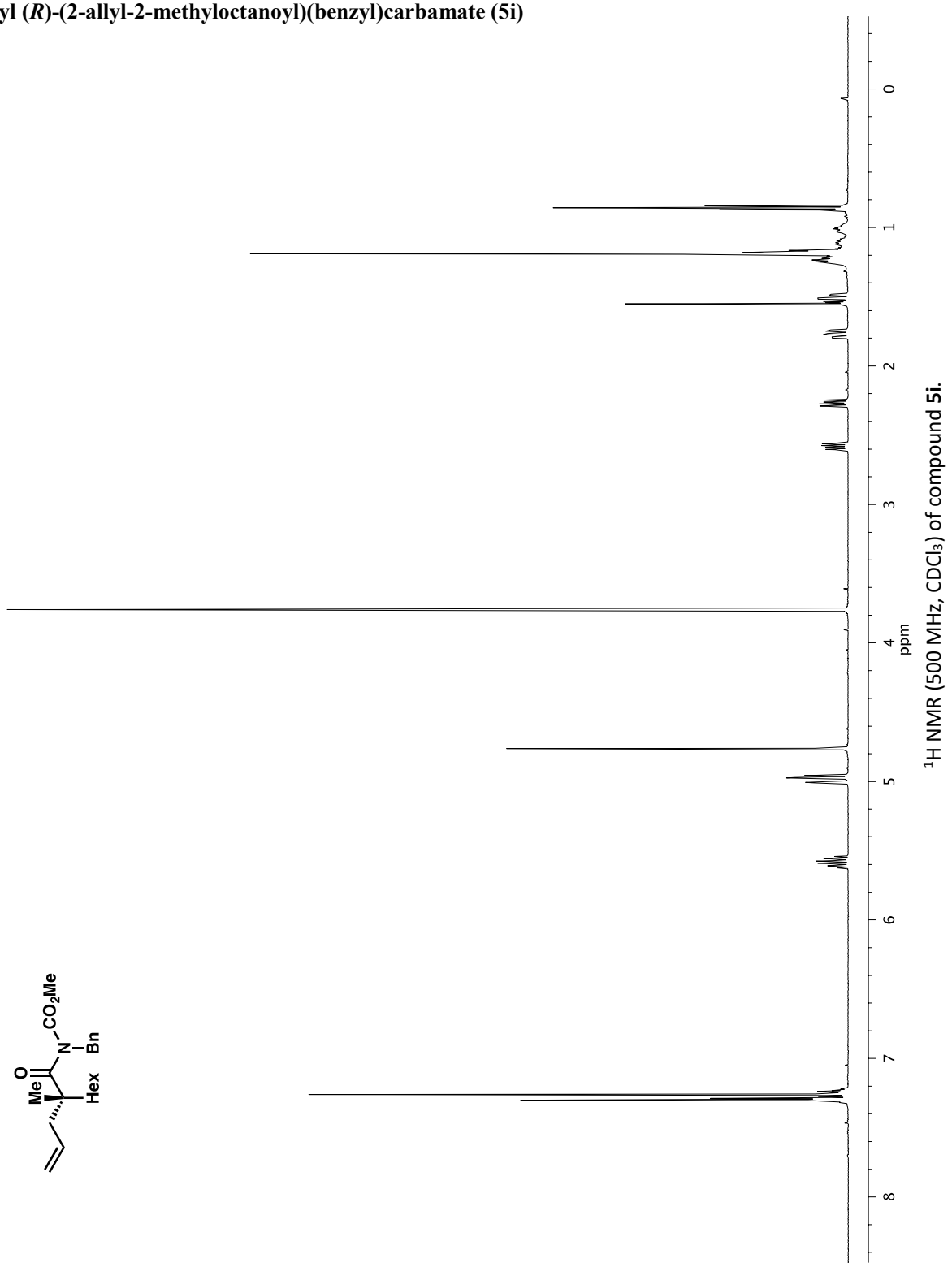


Infrared spectrum (Thin Film, NaCl) of compound **5h**.

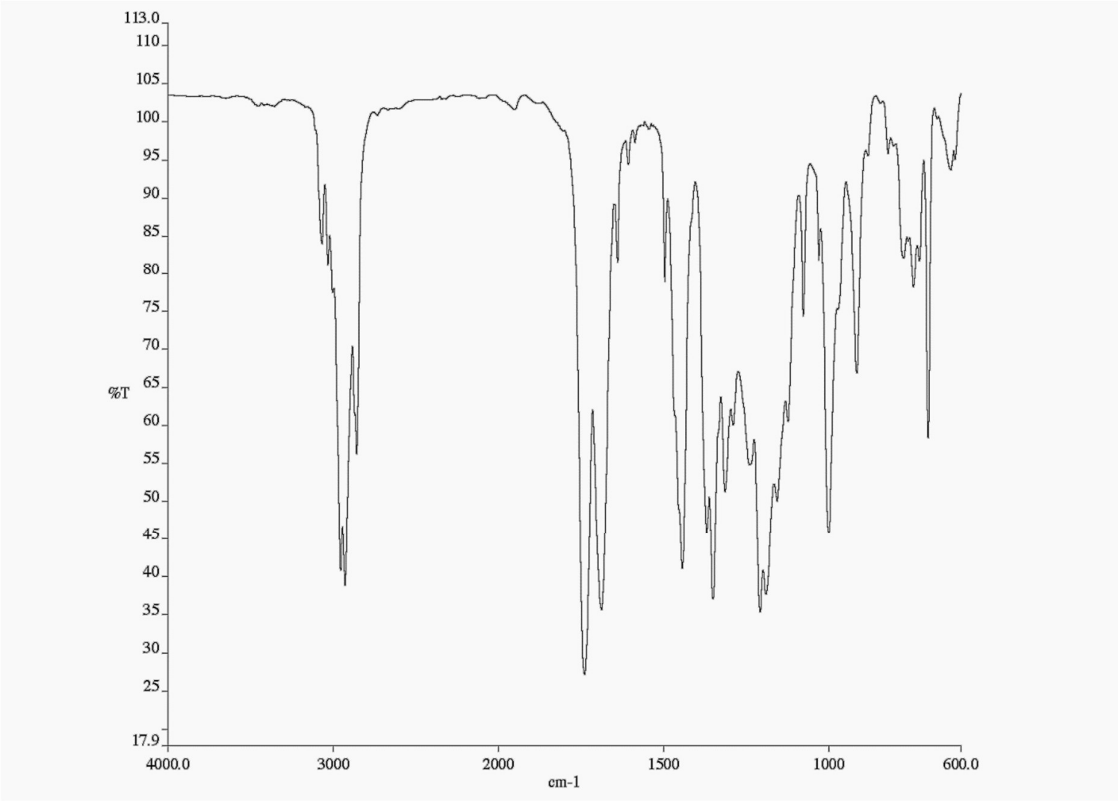


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5h**.

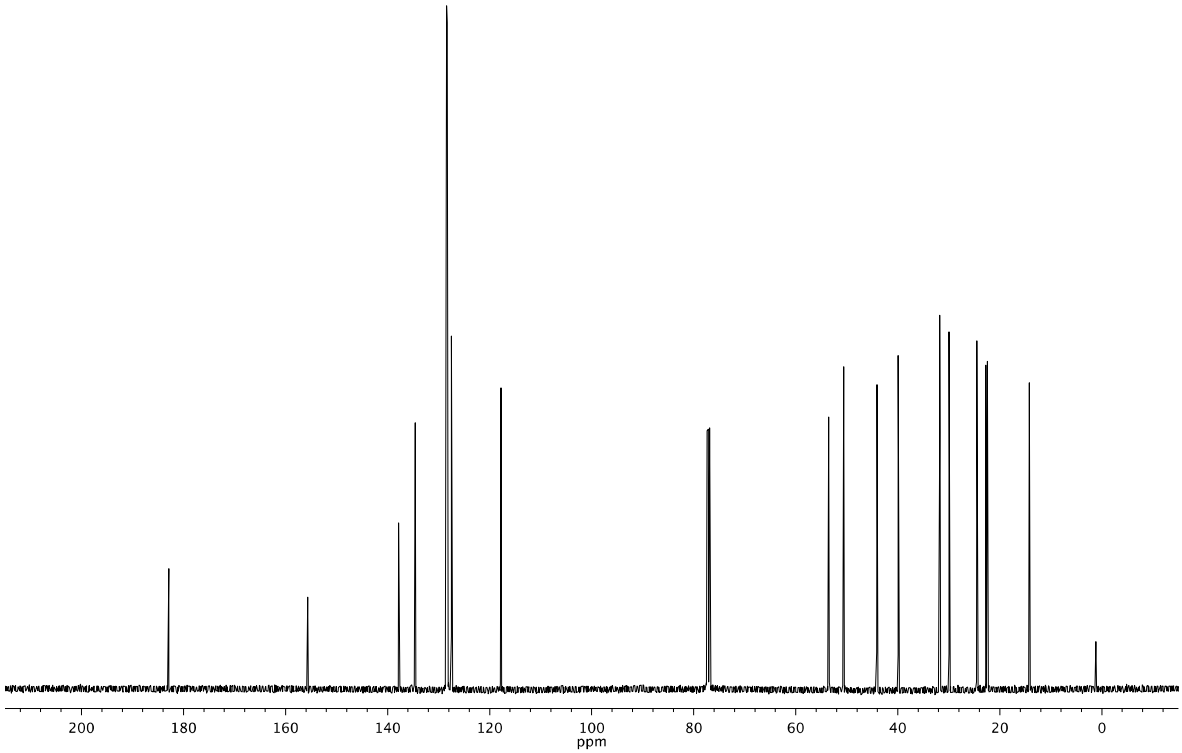
Methyl (*R*)-(2-allyl-2-methyloctanoyl)(benzyl)carbamate (5i)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5i**.

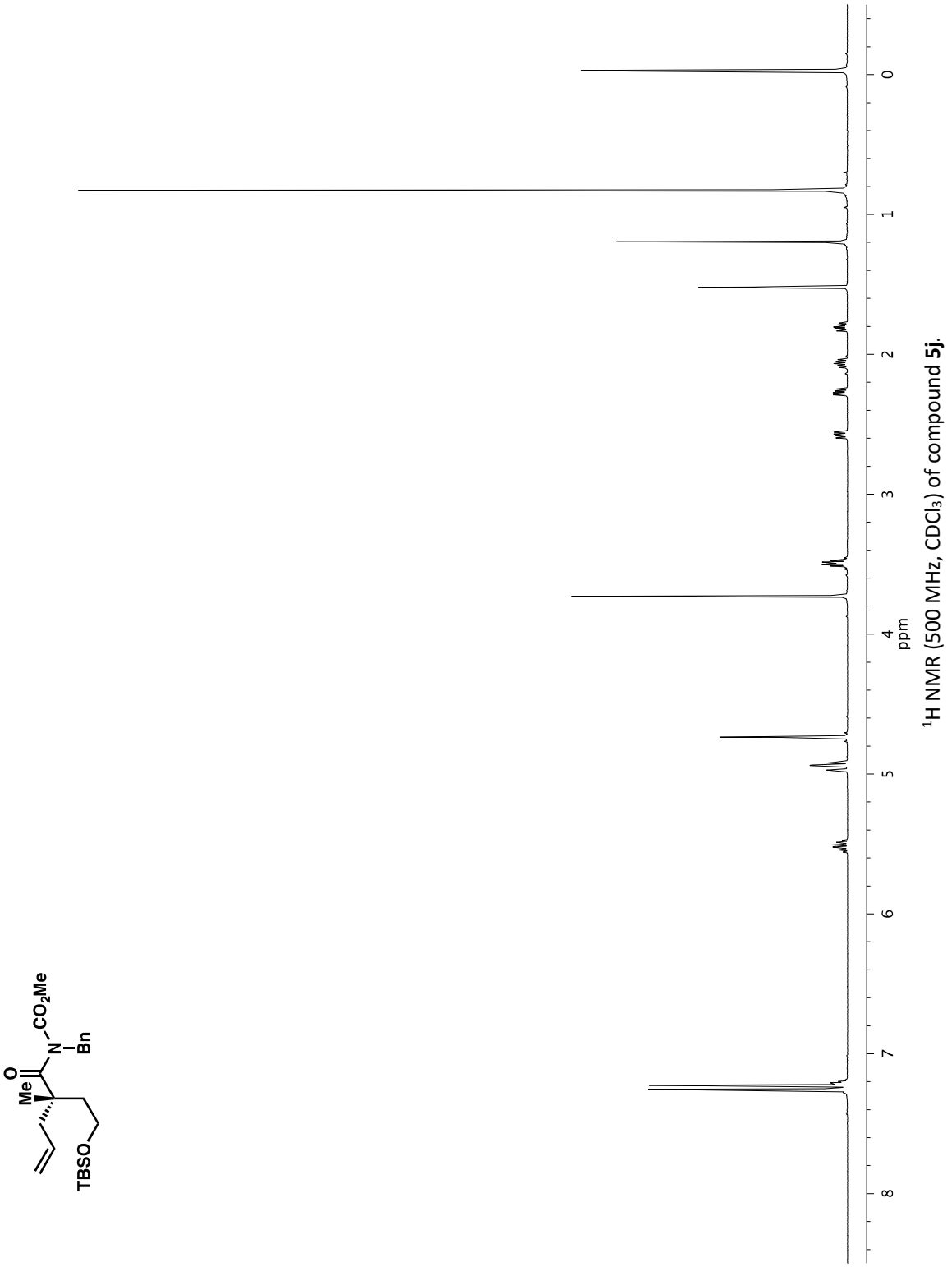


Infrared spectrum (Thin Film, NaCl) of compound **5i**.

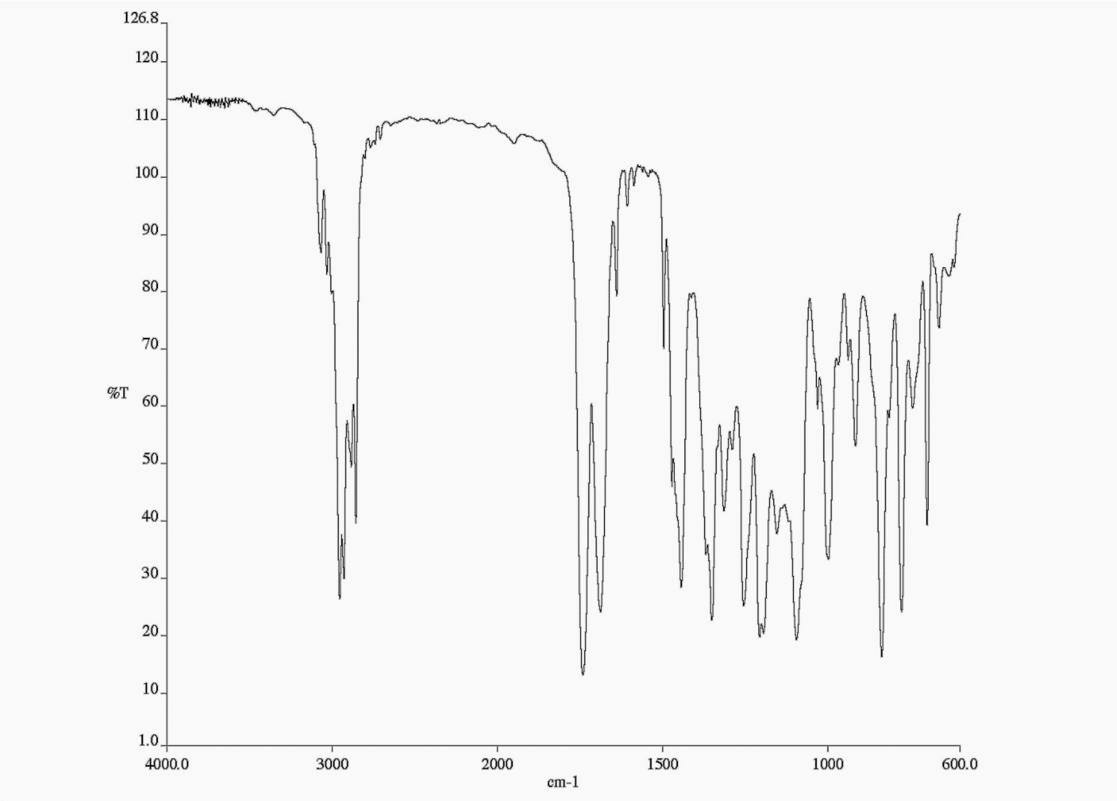


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5i**.

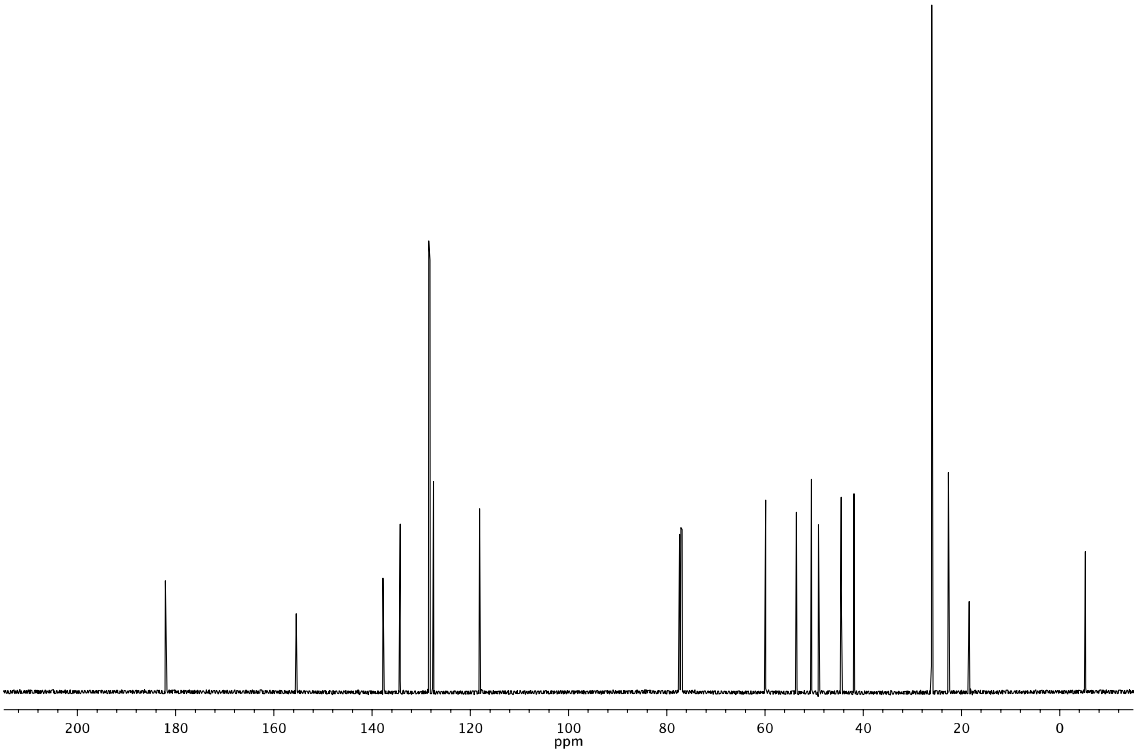
Methyl (*S*)-benzyl(2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-methylpent-4-enoyl)carbamate (5j)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5j**.

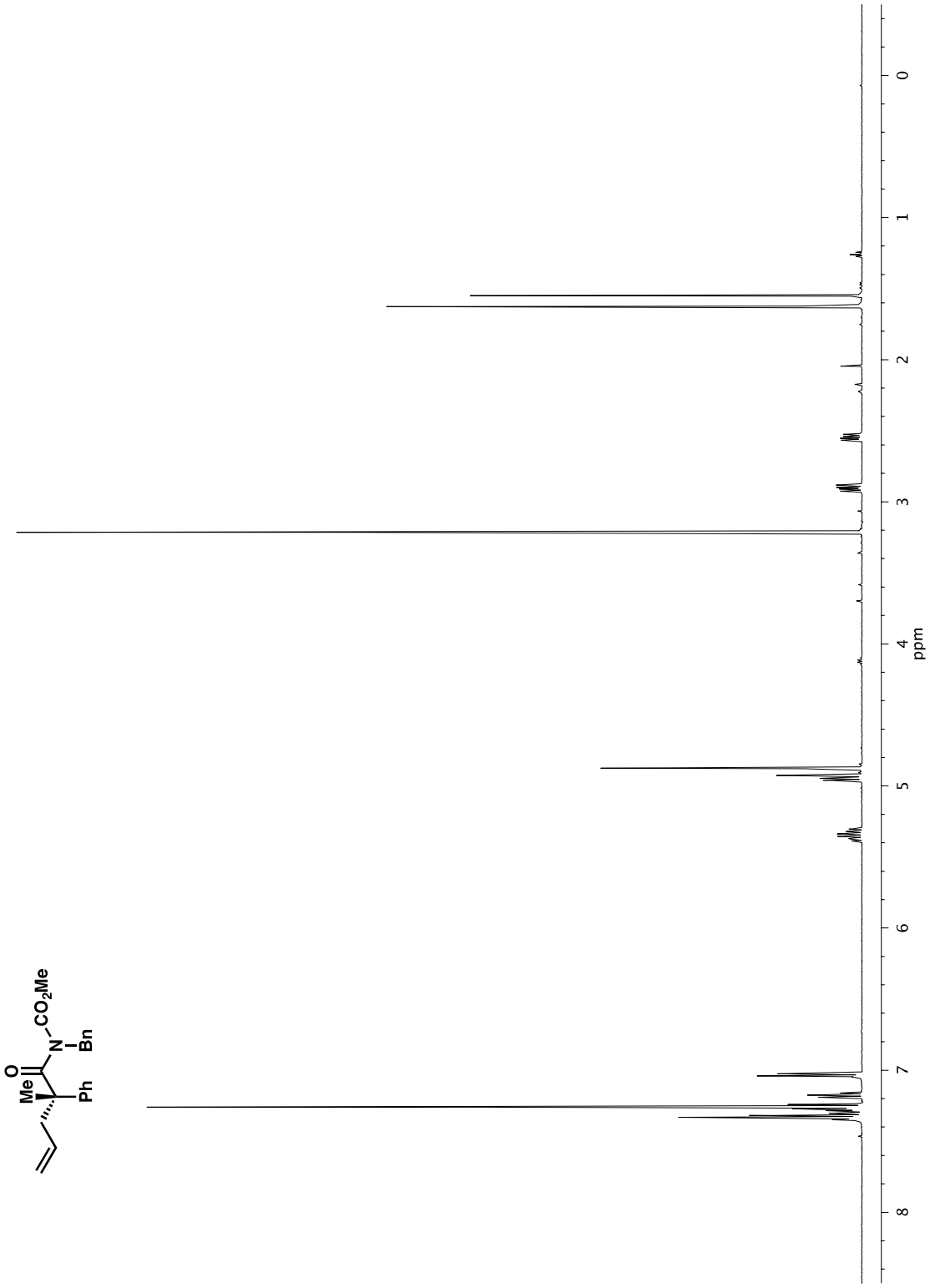


Infrared spectrum (Thin Film, NaCl) of compound **5j**.

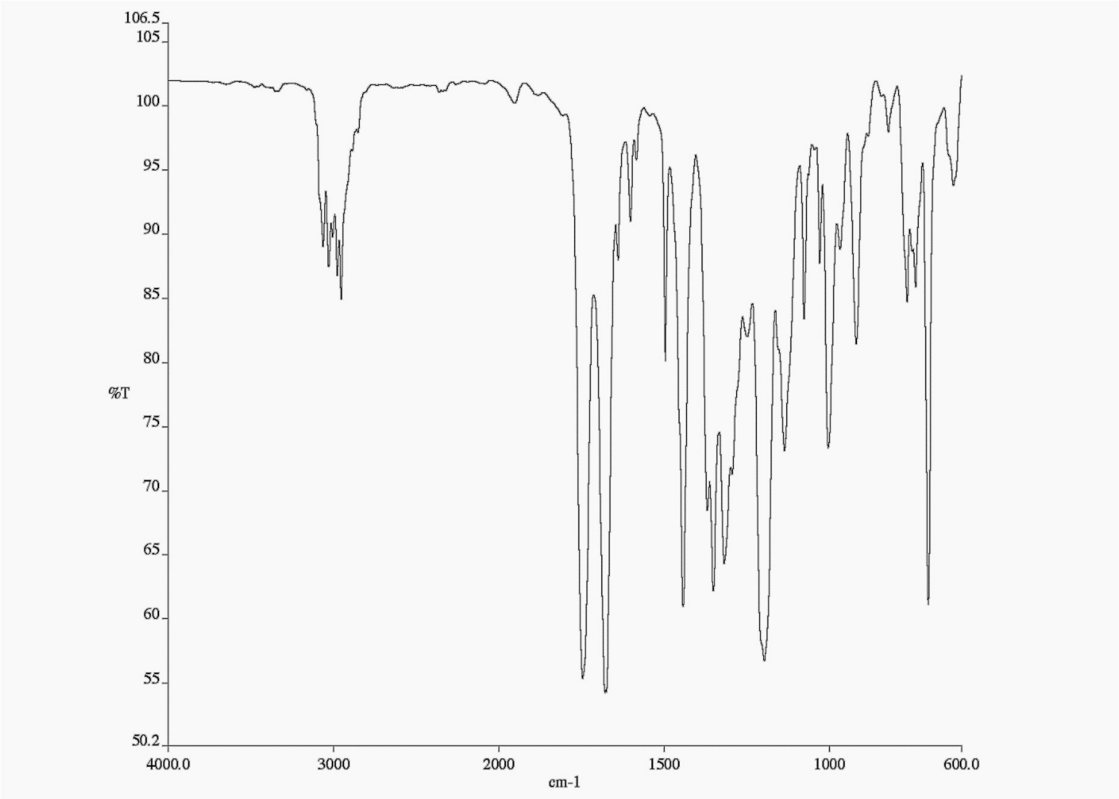


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5j**.

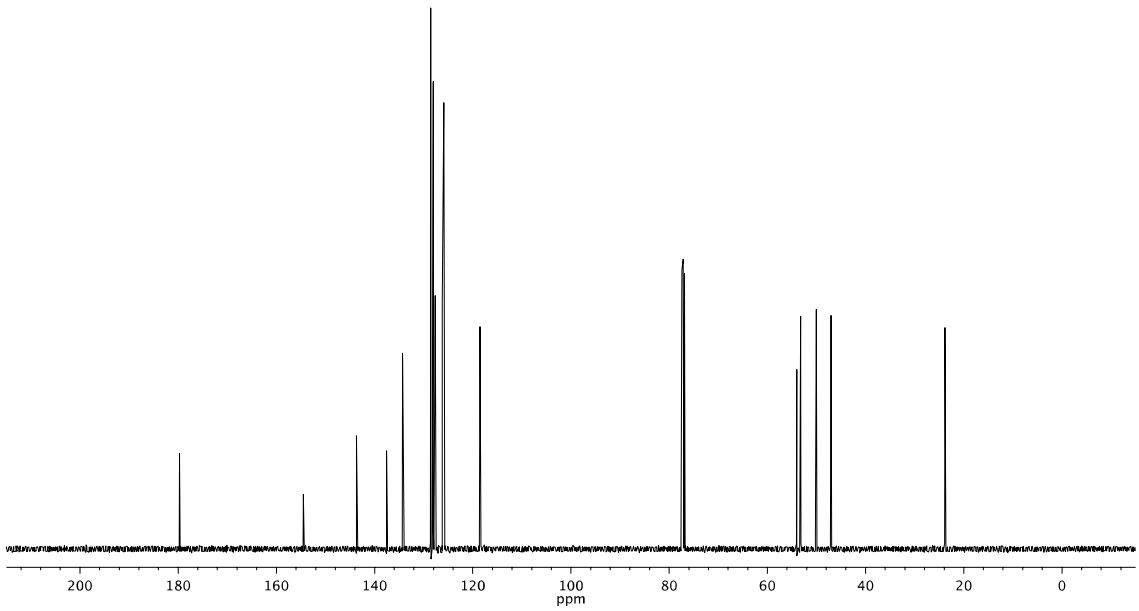
Methyl (*S*)-benzyl(2-methyl-2-phenylpent-4-enoyl)carbamate (5k)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5k**.

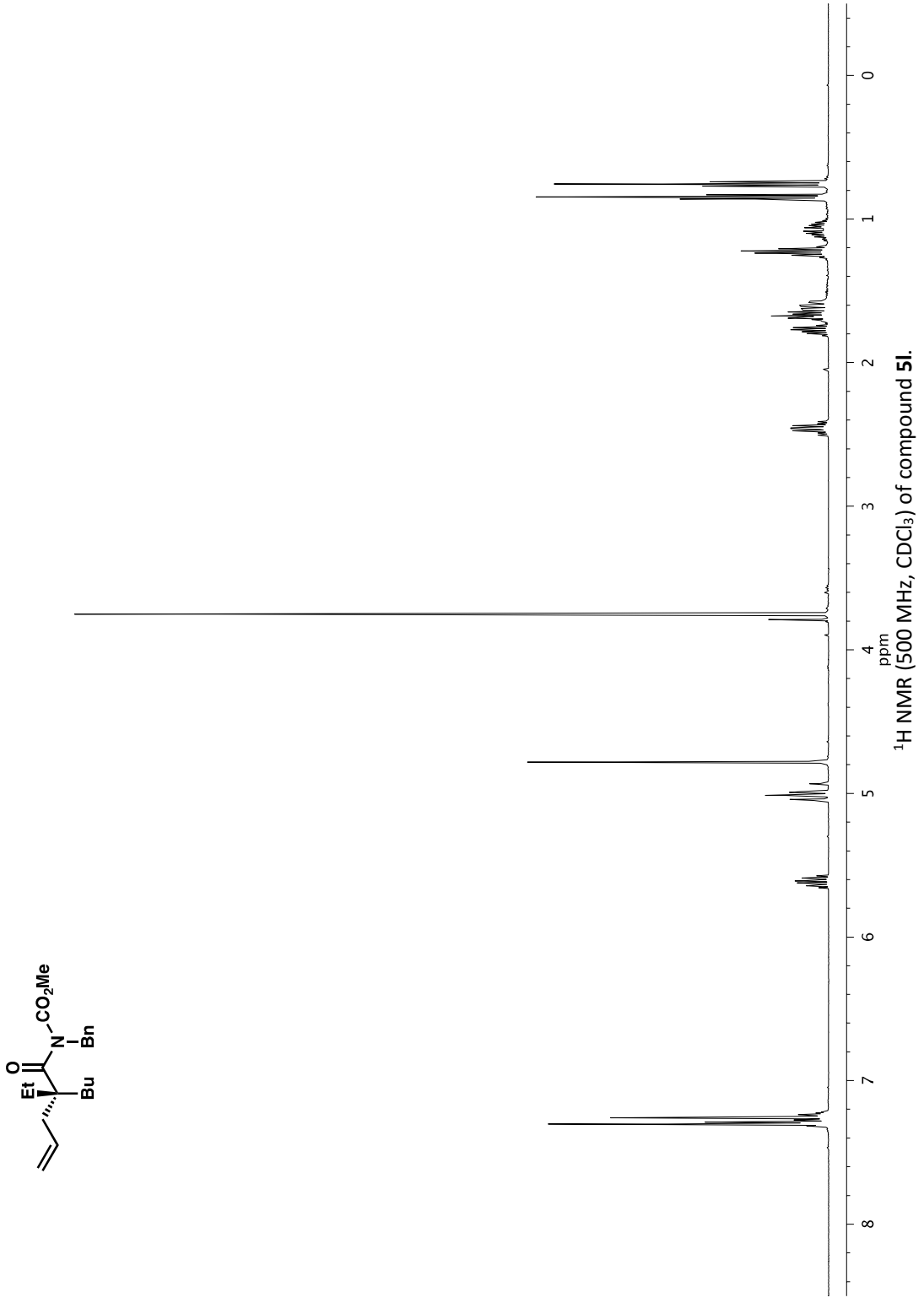


Infrared spectrum (Thin Film, NaCl) of compound **5k**.

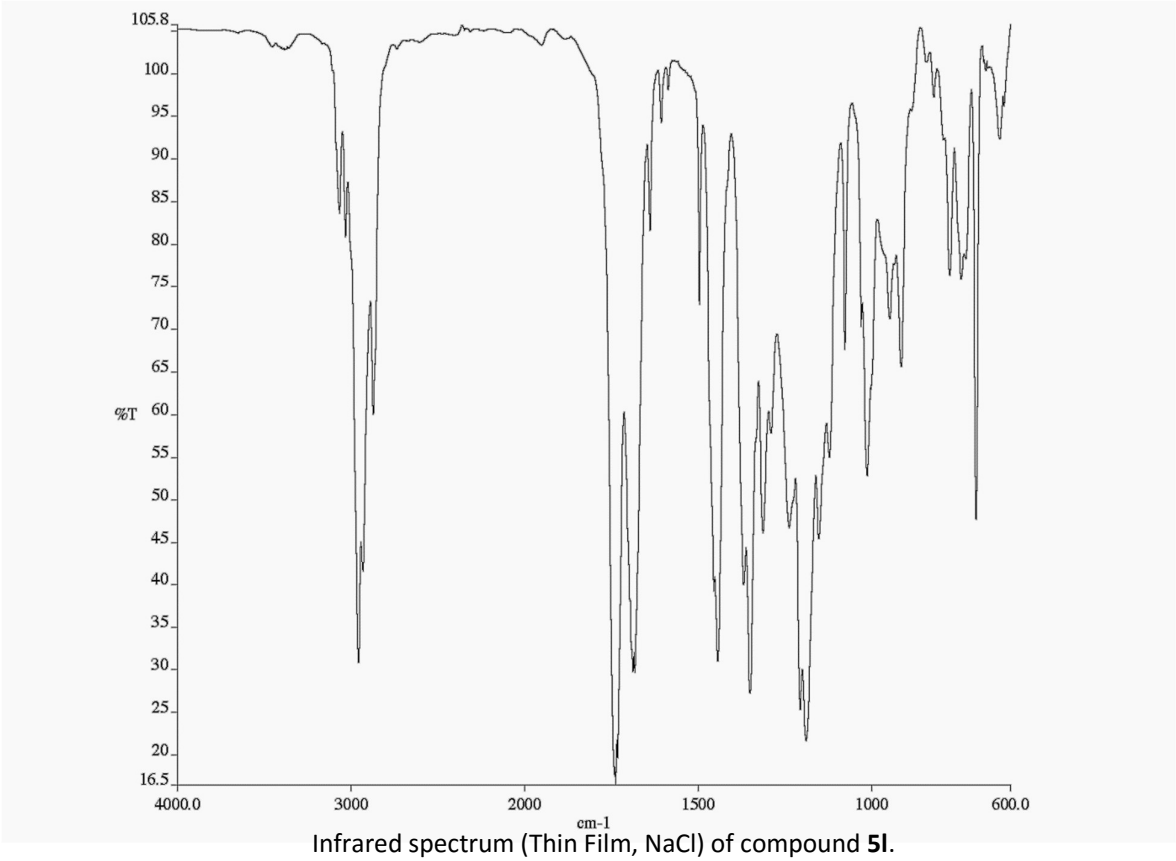


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5k**.

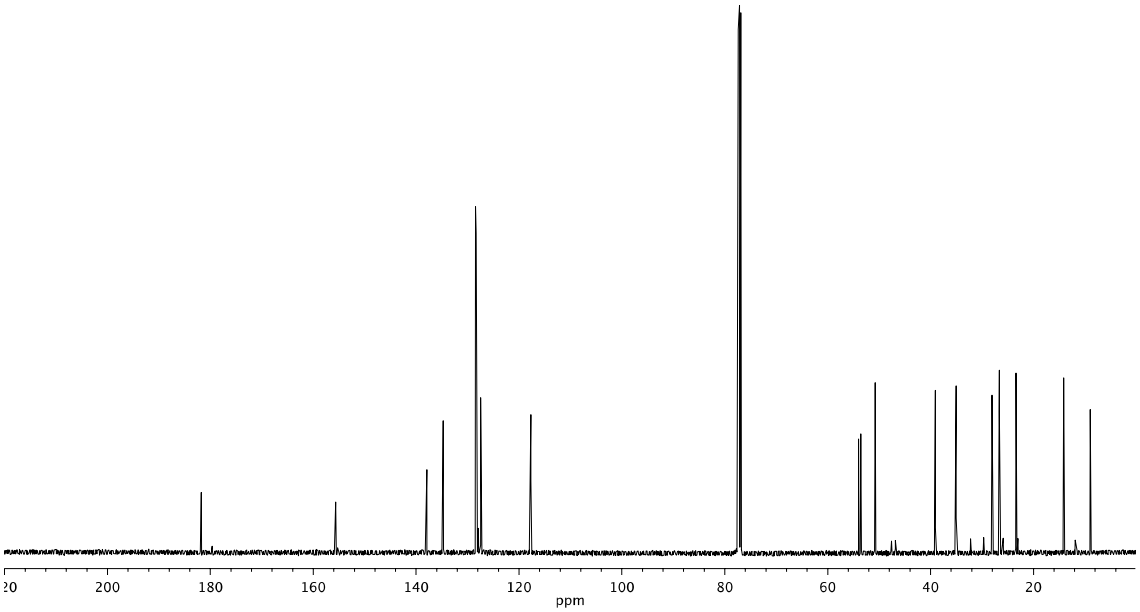
Methyl (*R*)-(2-allyl-2-ethylhexanoyl)(benzyl)carbamate (5l)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5l**.

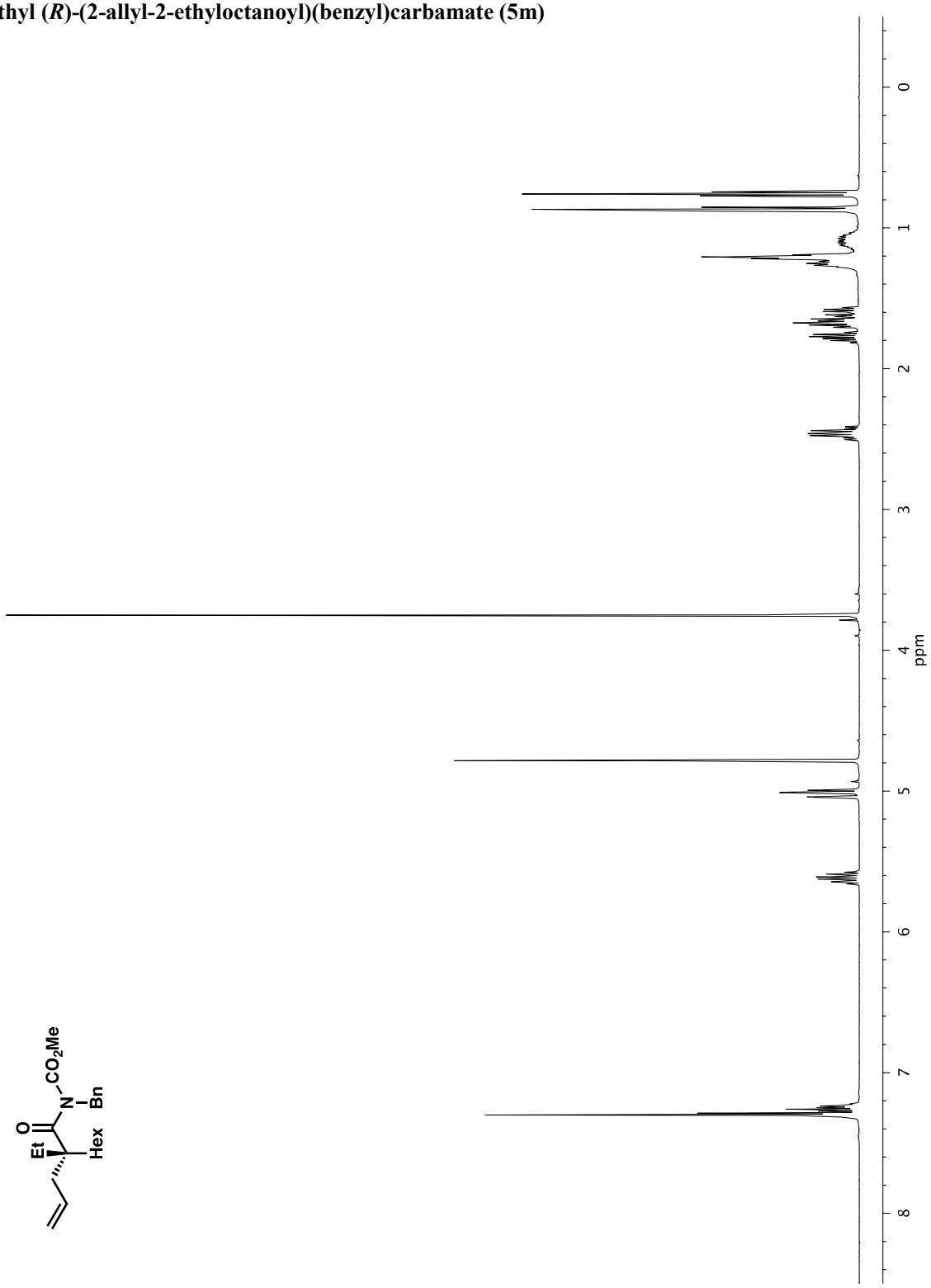


Infrared spectrum (Thin Film, NaCl) of compound **5l**.

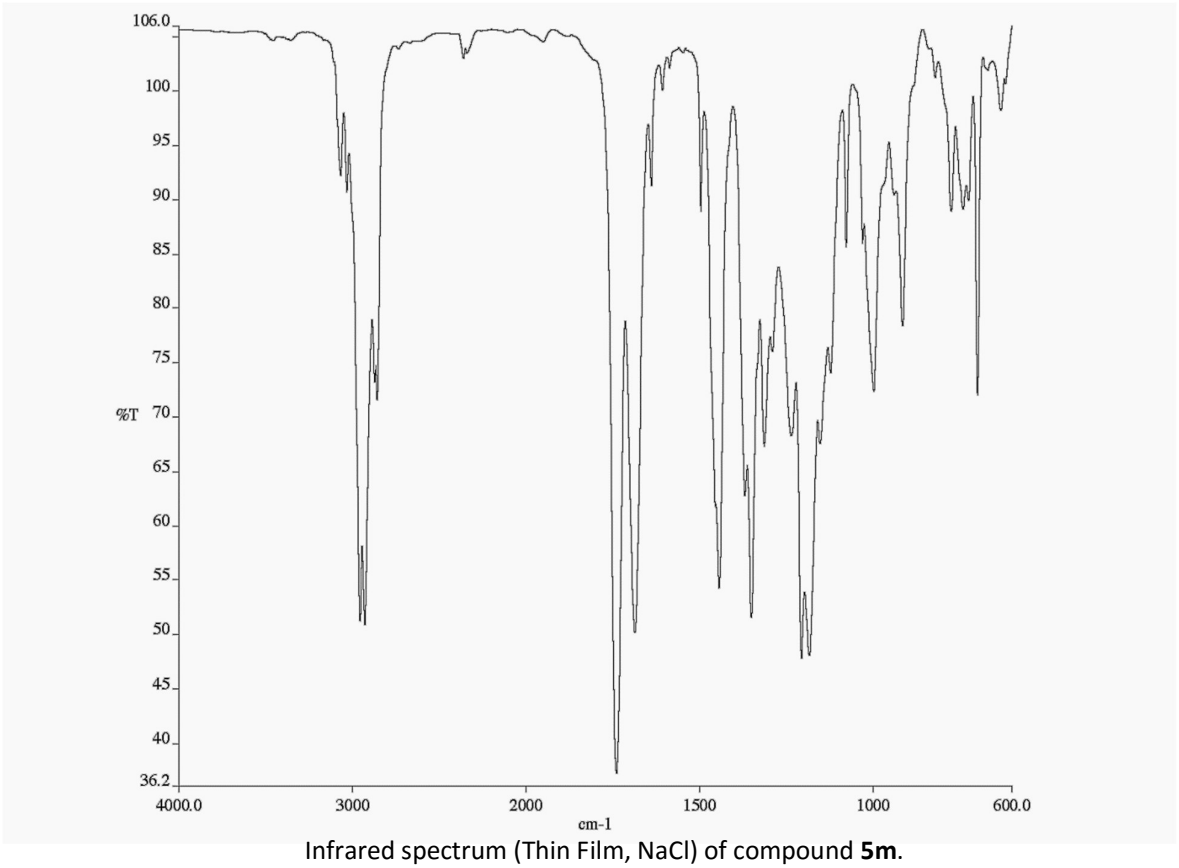


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5l**.

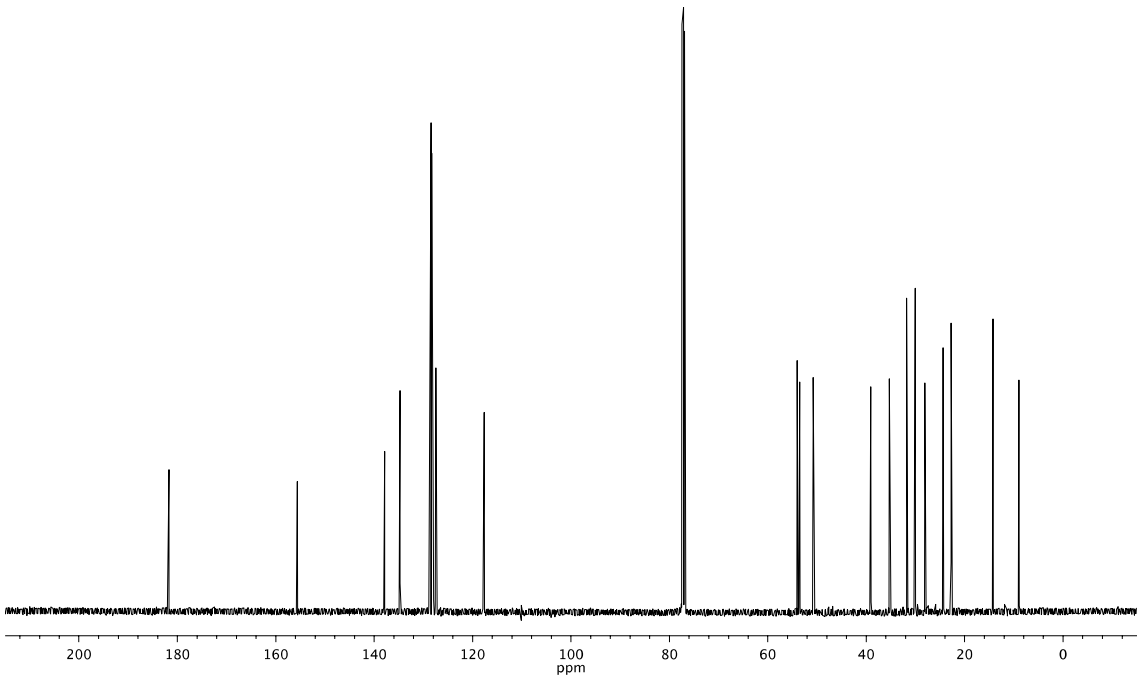
Methyl (*R*)-(2-allyl-2-ethyloctanoyl)(benzyl)carbamate (5m)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5m**.

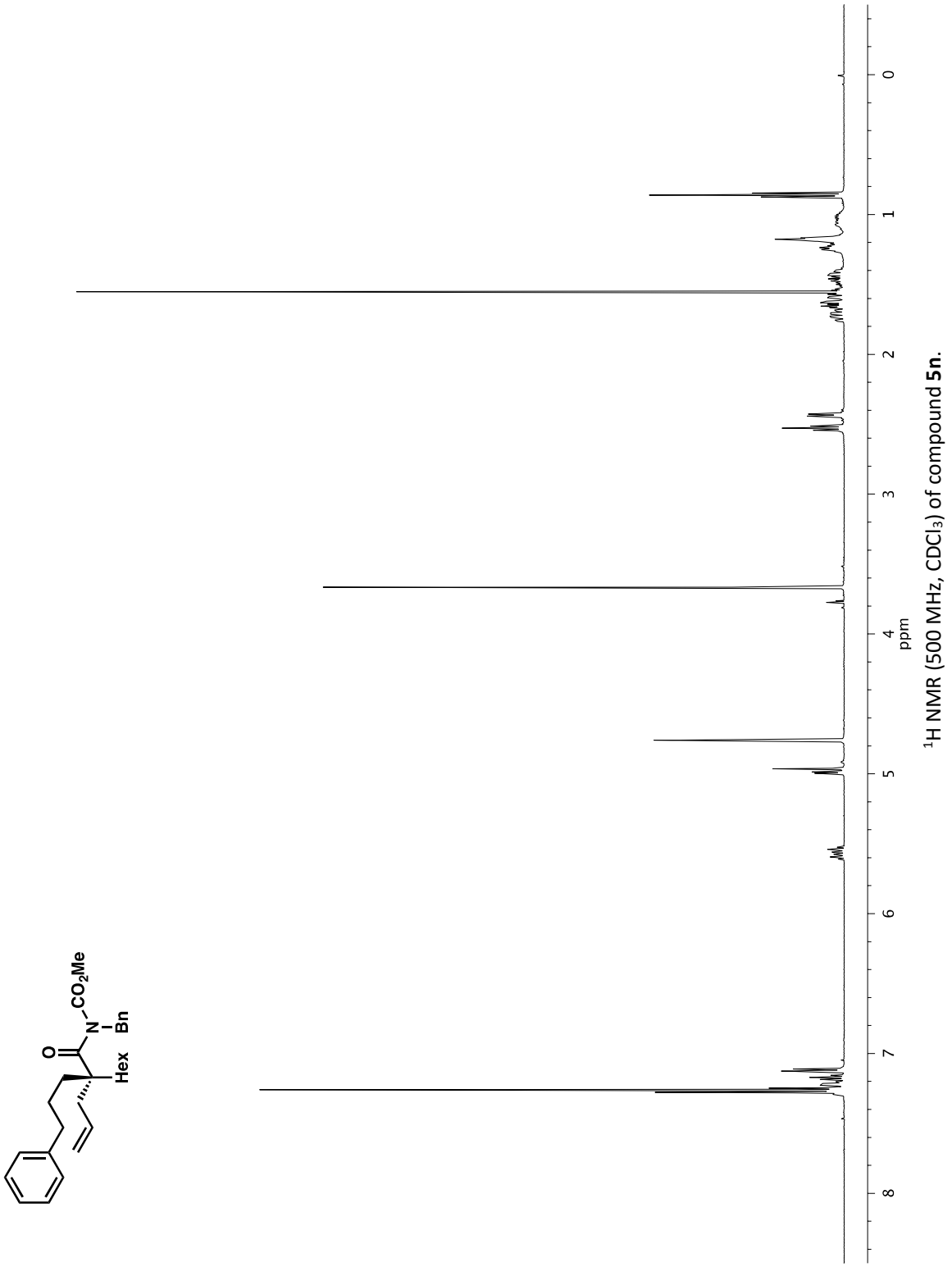


Infrared spectrum (Thin Film, NaCl) of compound **5m**.

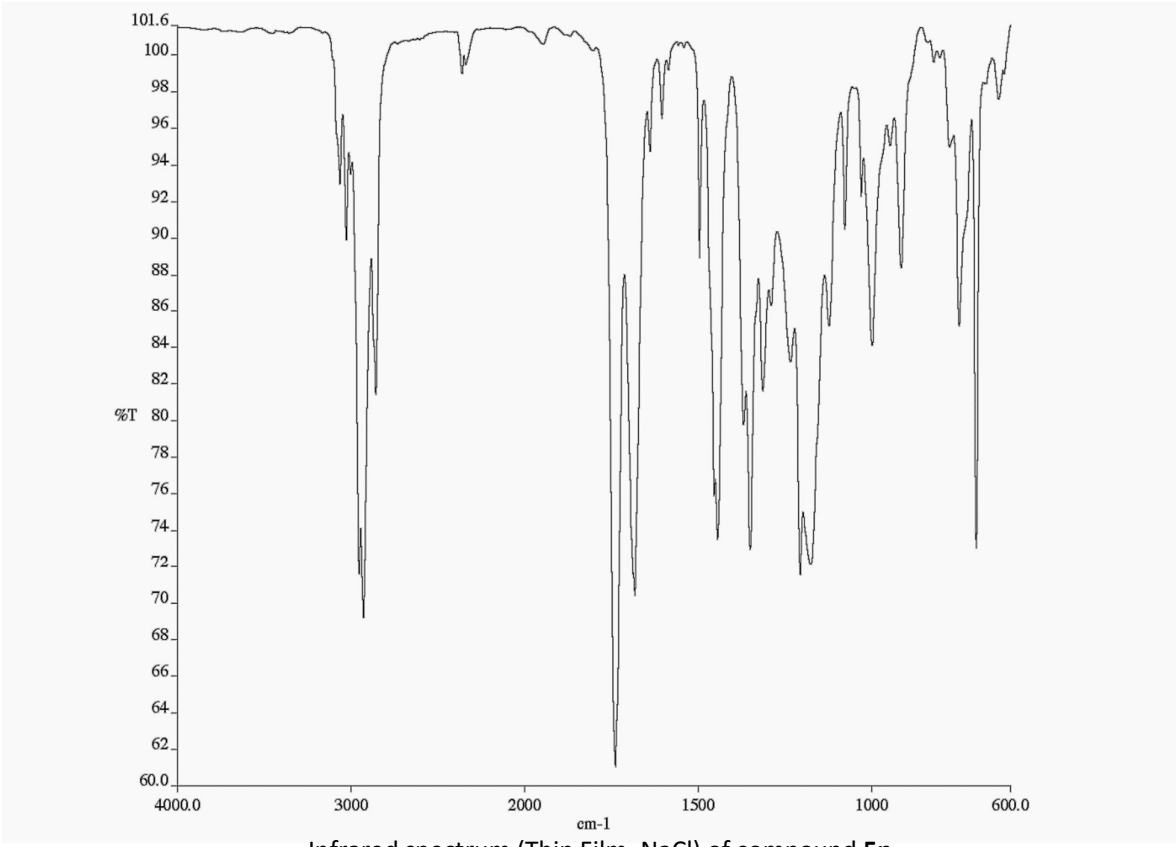


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5m**.

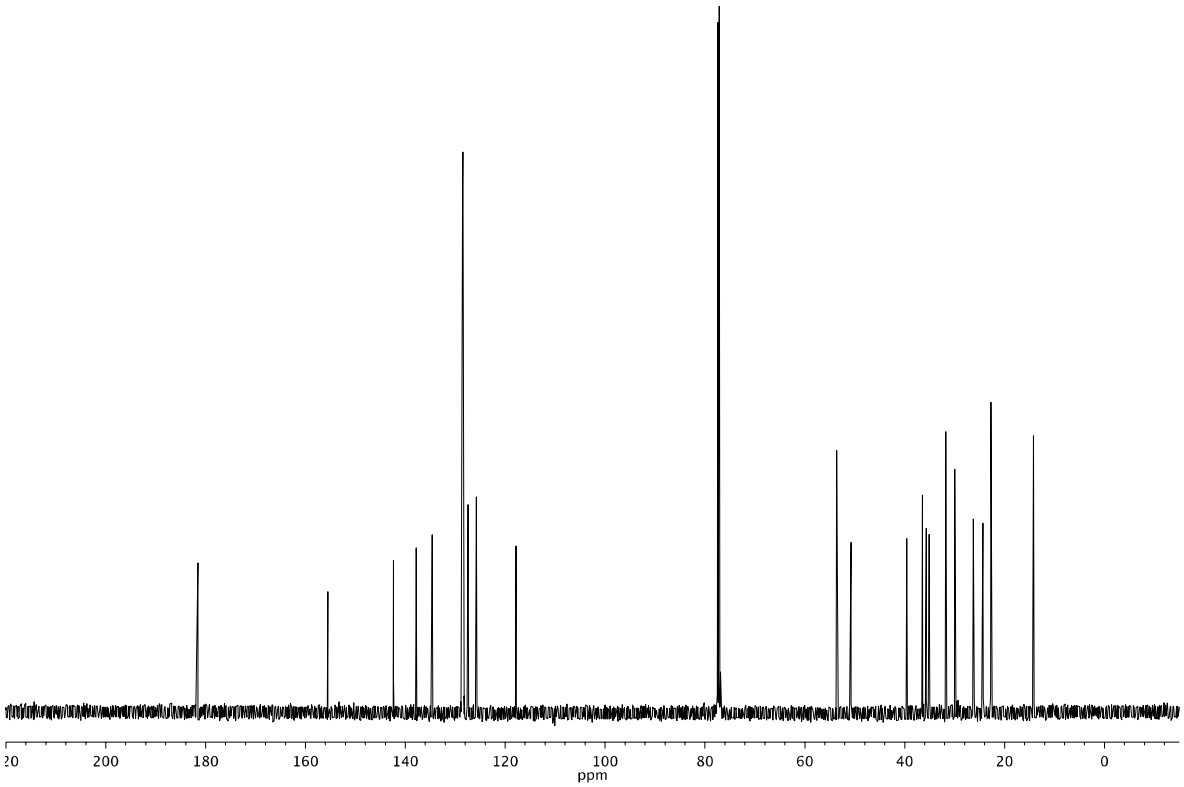
Methyl (*S*)-(2-allyl-2-(3-phenylpropyl)octanoyl)(benzyl)carbamate (5n)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5n**.

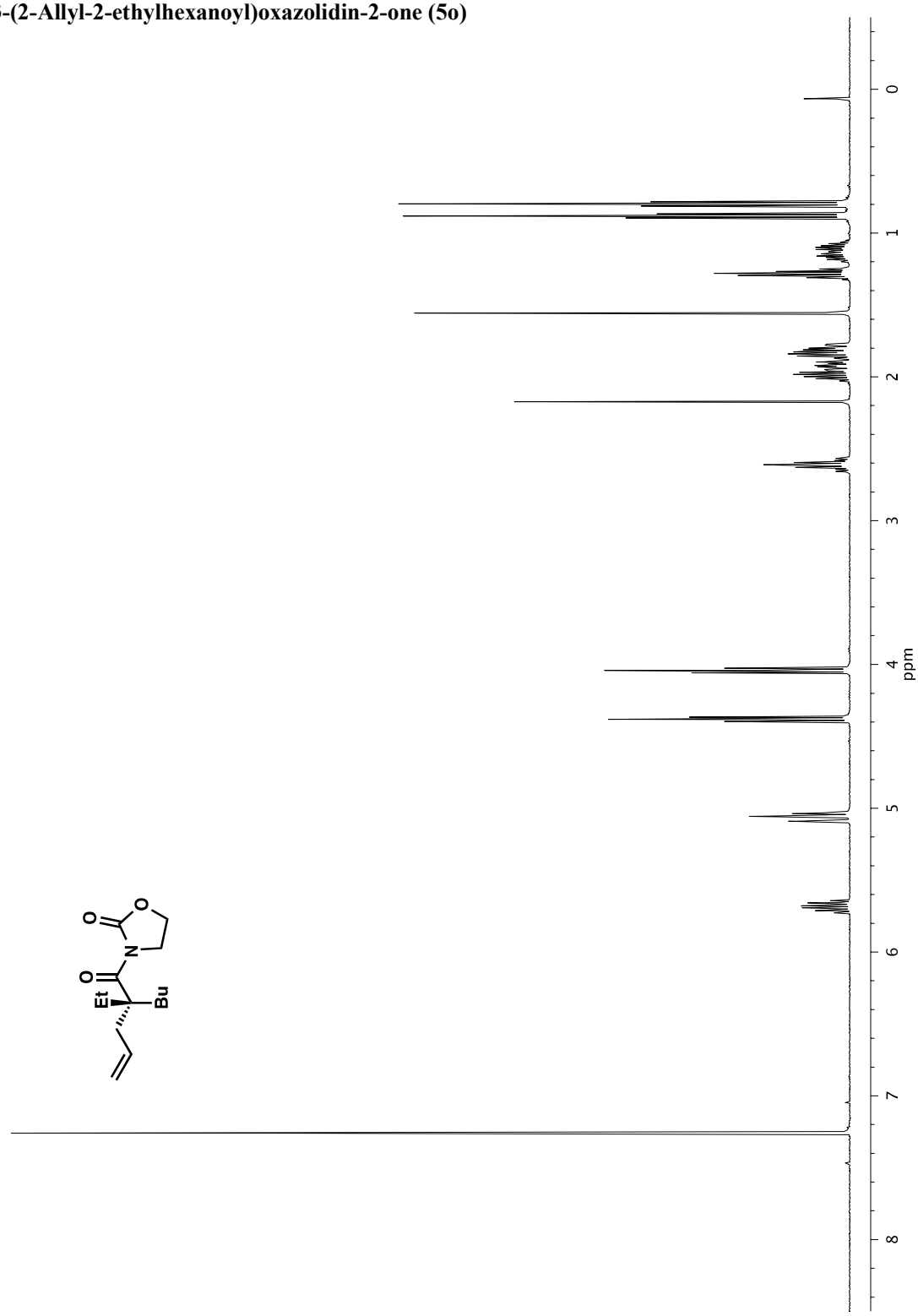


Infrared spectrum (Thin Film, NaCl) of compound **5n**.

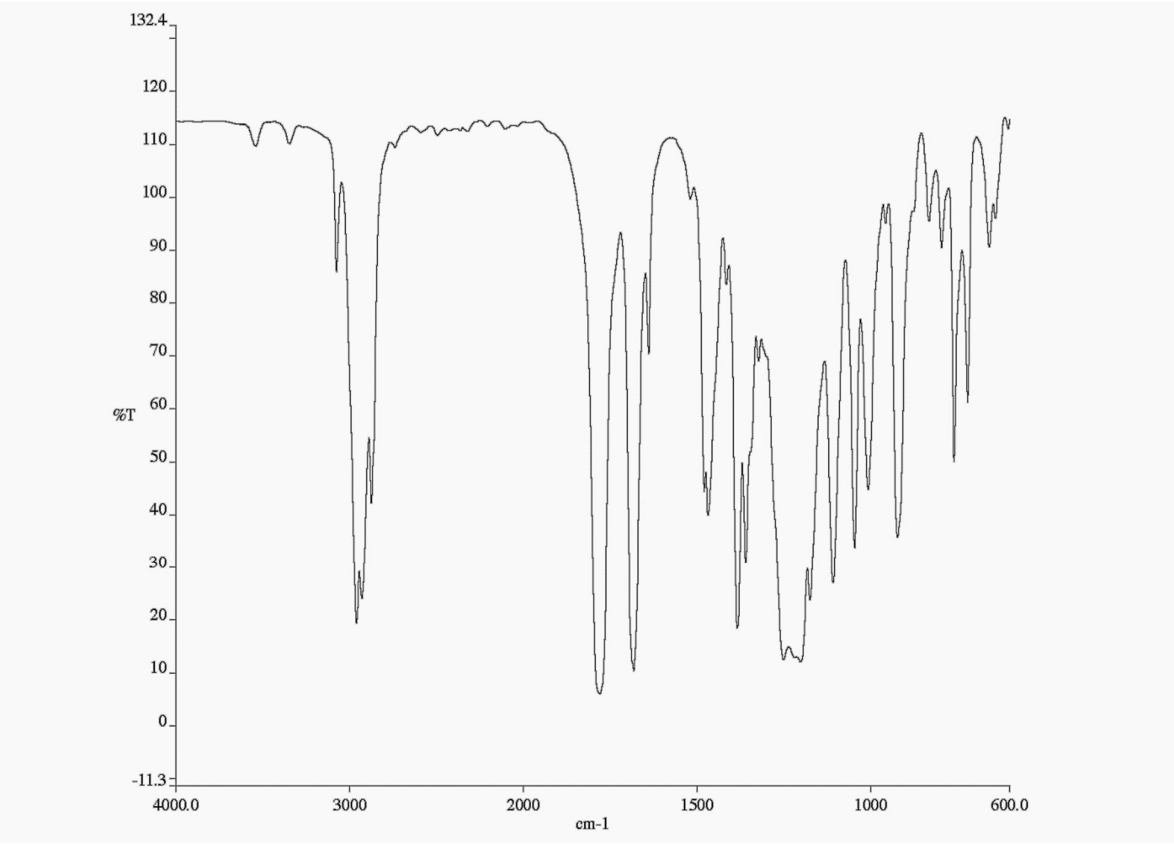


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5n**.

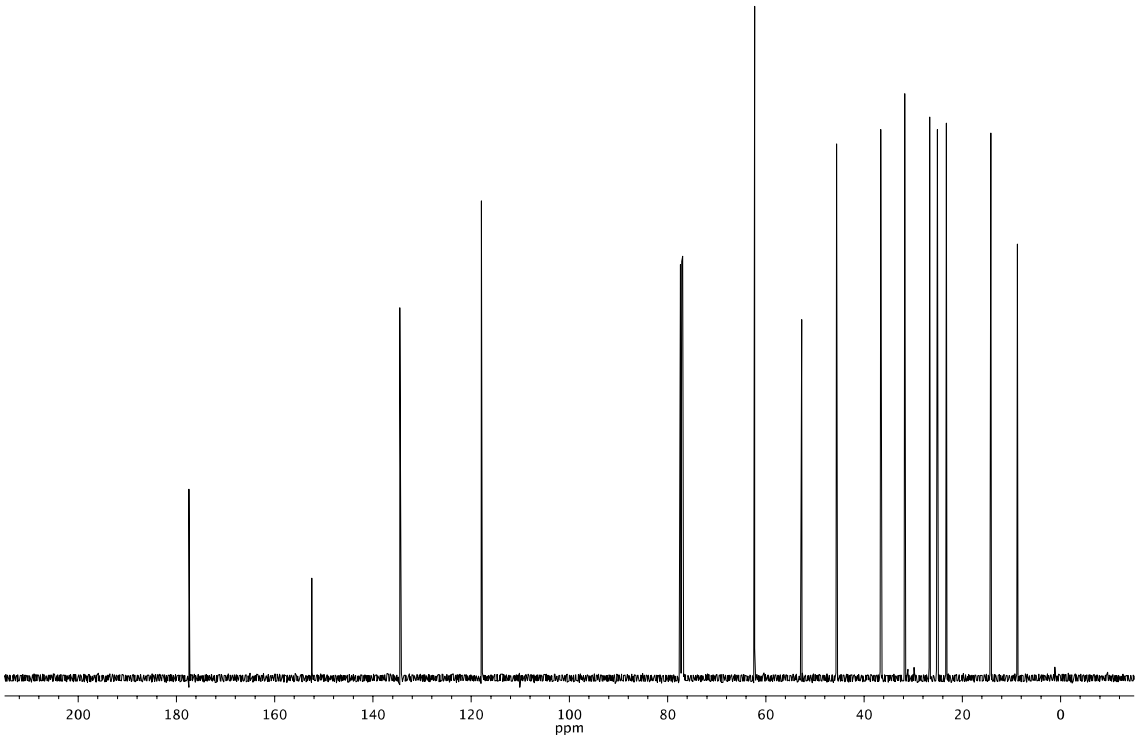
(*R*)-3-(2-Allyl-2-ethylhexanoyl)oxazolidin-2-one (5o)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5o**.

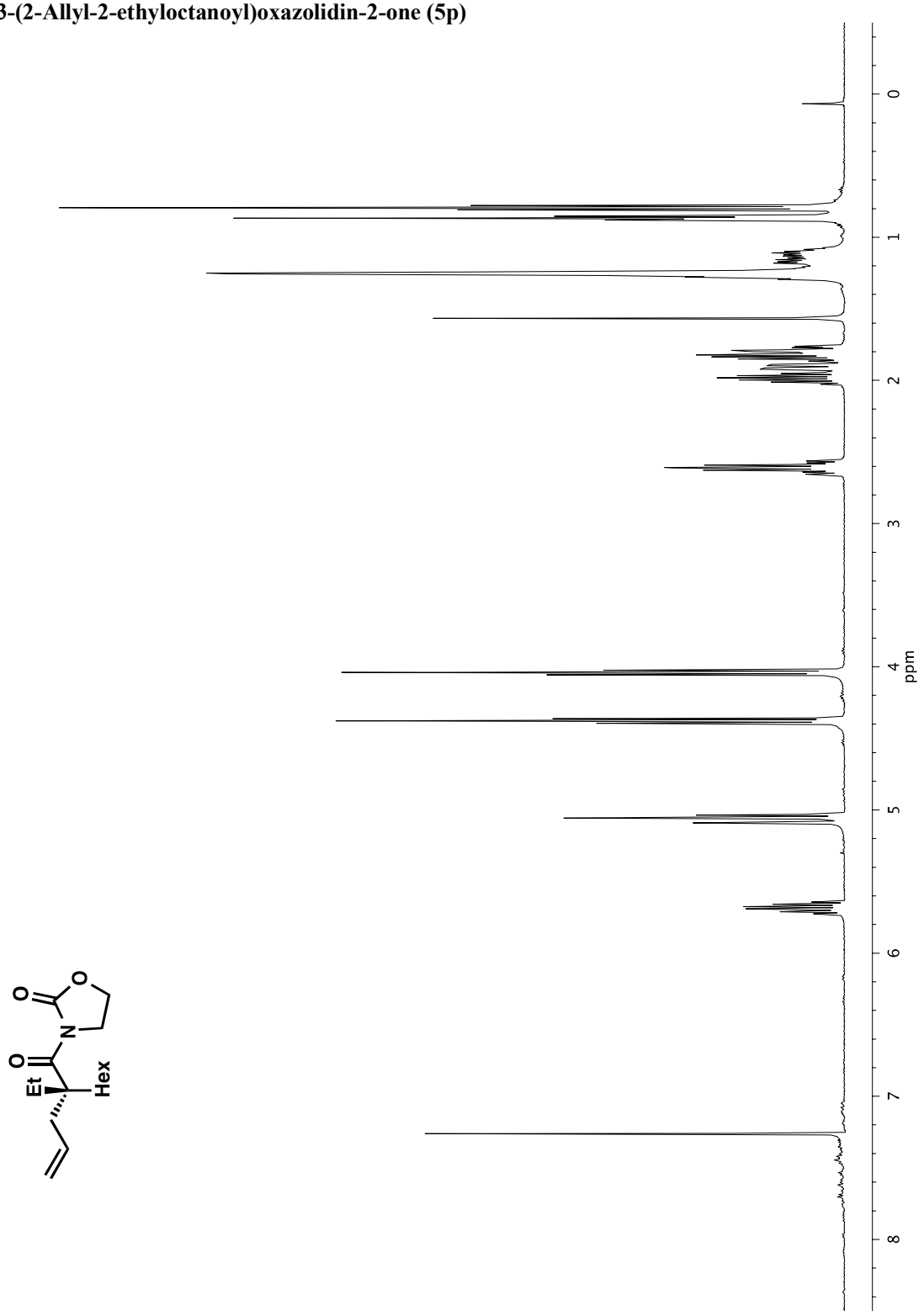


Infrared spectrum (Thin Film, NaCl) of compound **5o**.

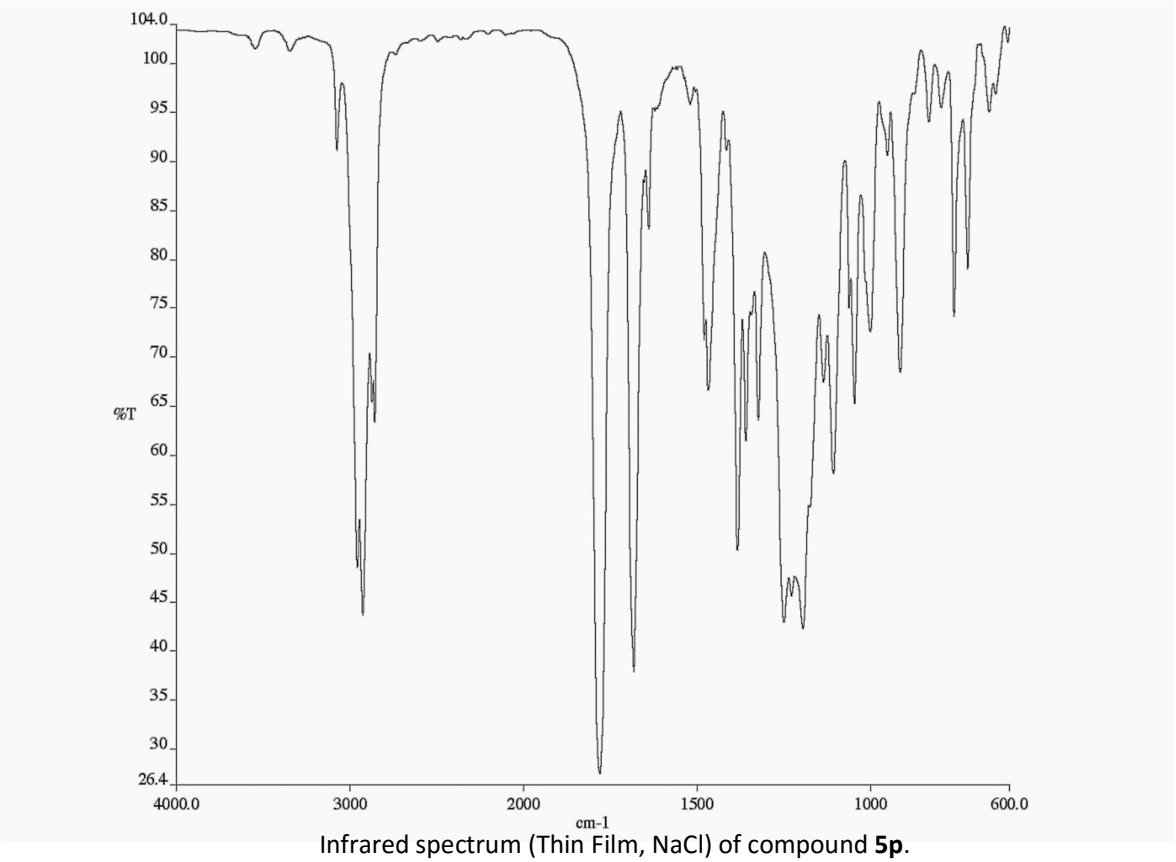


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5o**.

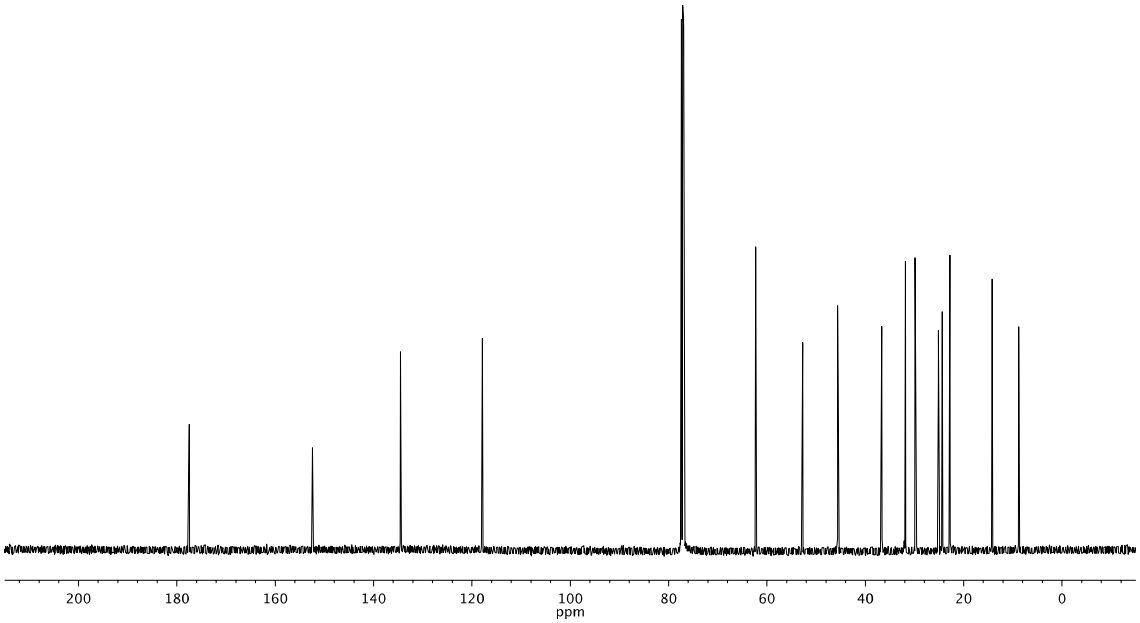
(*R*)-3-(2-Allyl-2-ethyloctanoyl)oxazolidin-2-one (5p)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5p**.

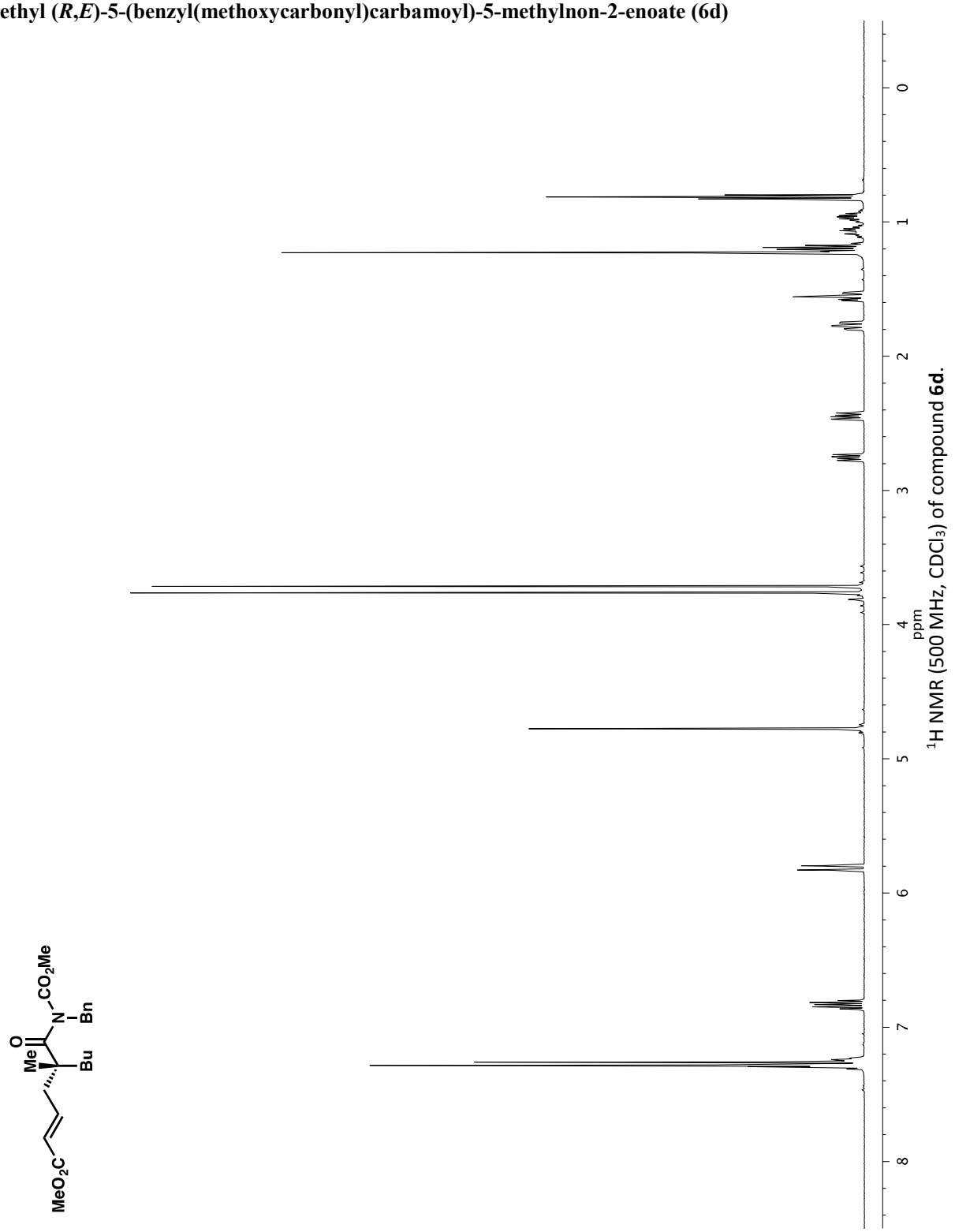


Infrared spectrum (Thin Film, NaCl) of compound **5p**.

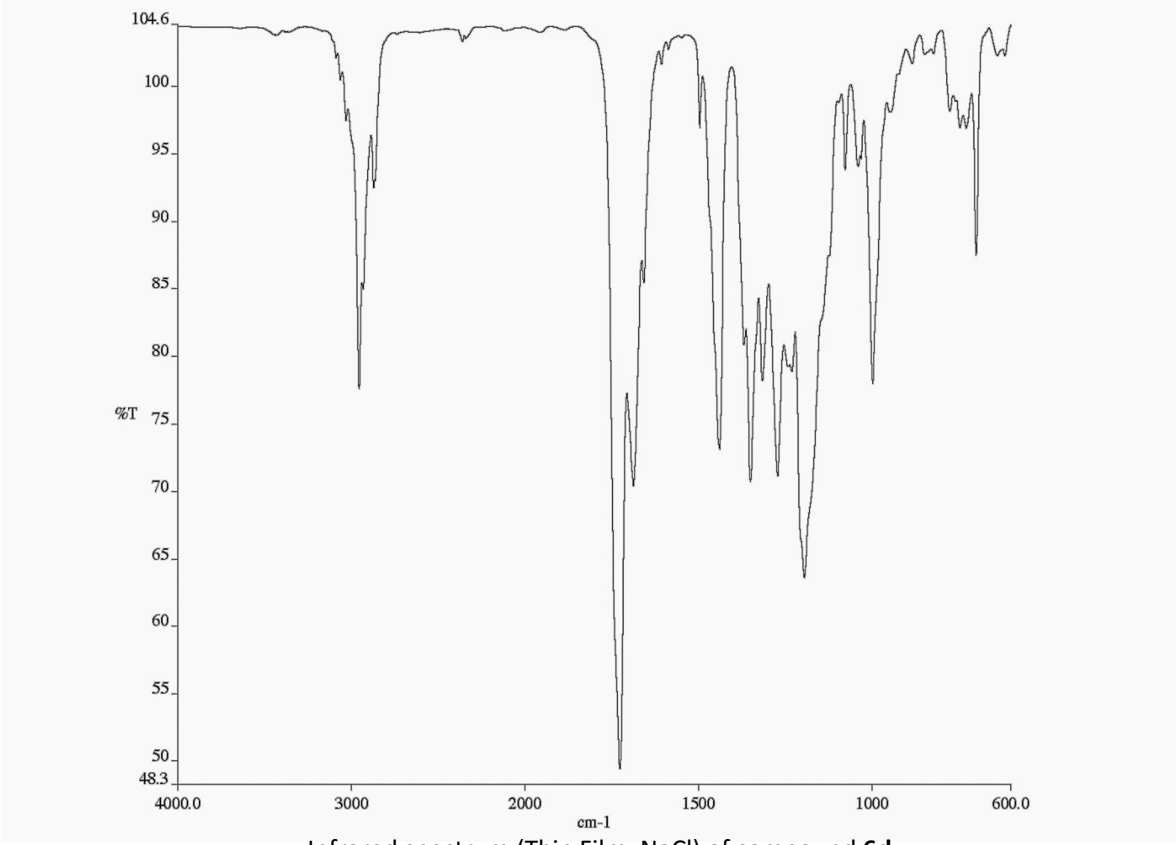


^{13}C NMR (126 MHz, $CDCl_3$) of compound **5p**.

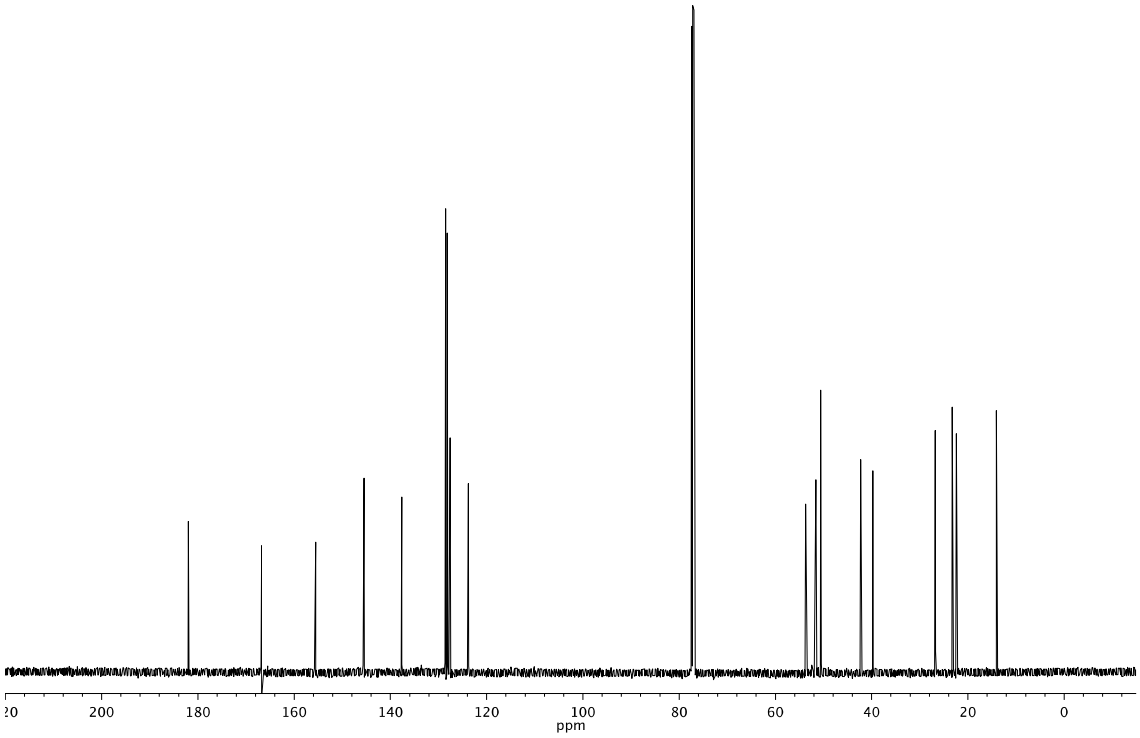
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6d)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6d**.

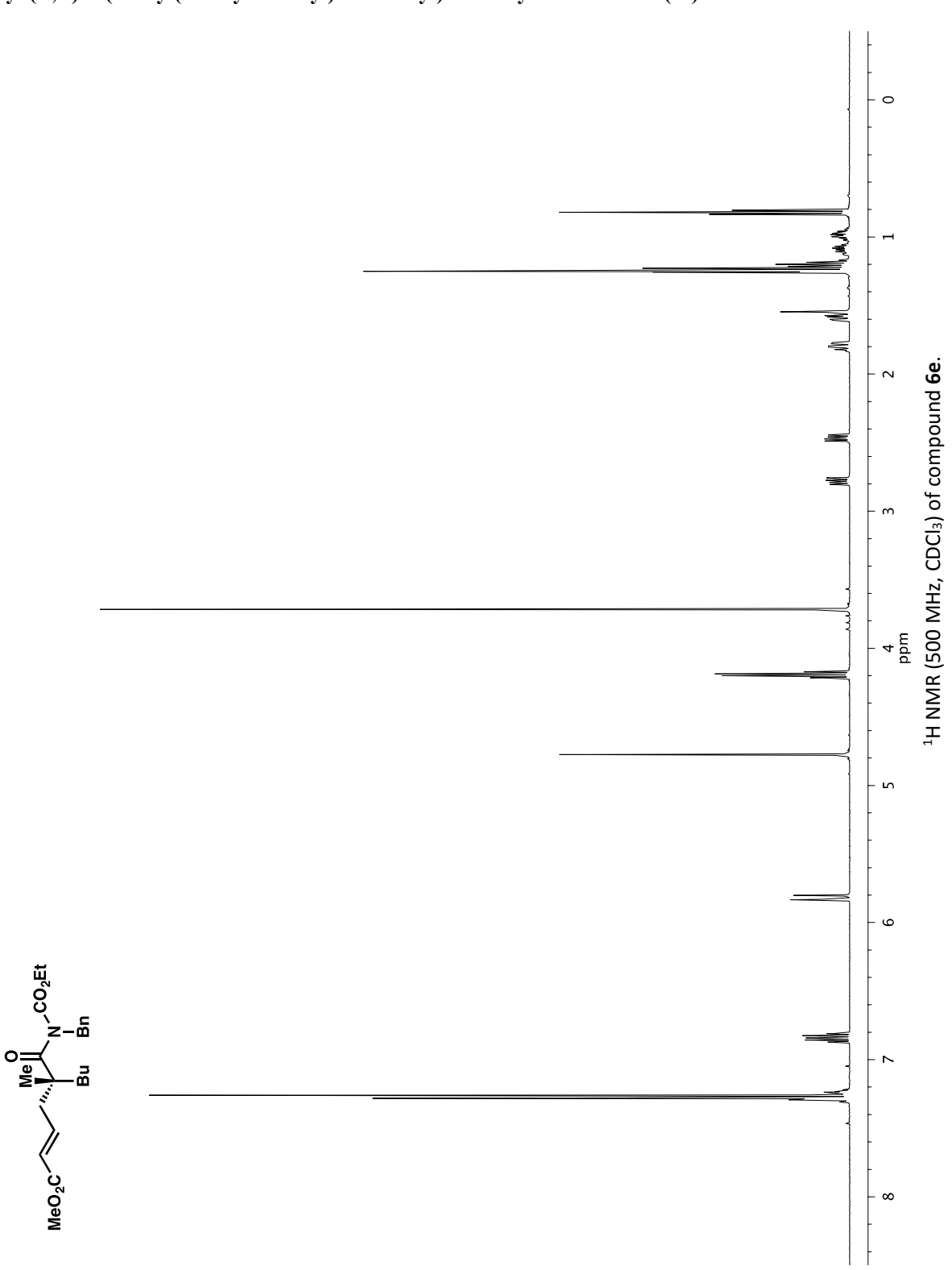


Infrared spectrum (Thin Film, NaCl) of compound **6d**.

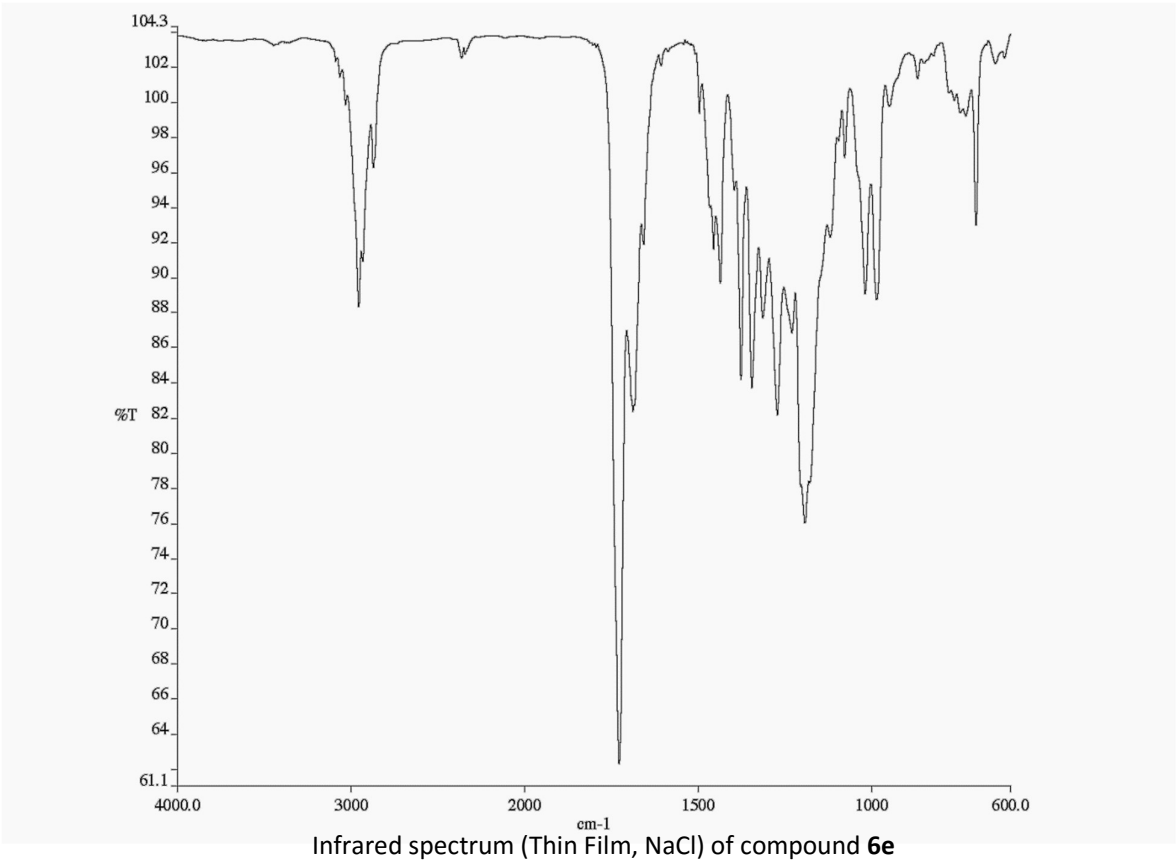


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6d**.

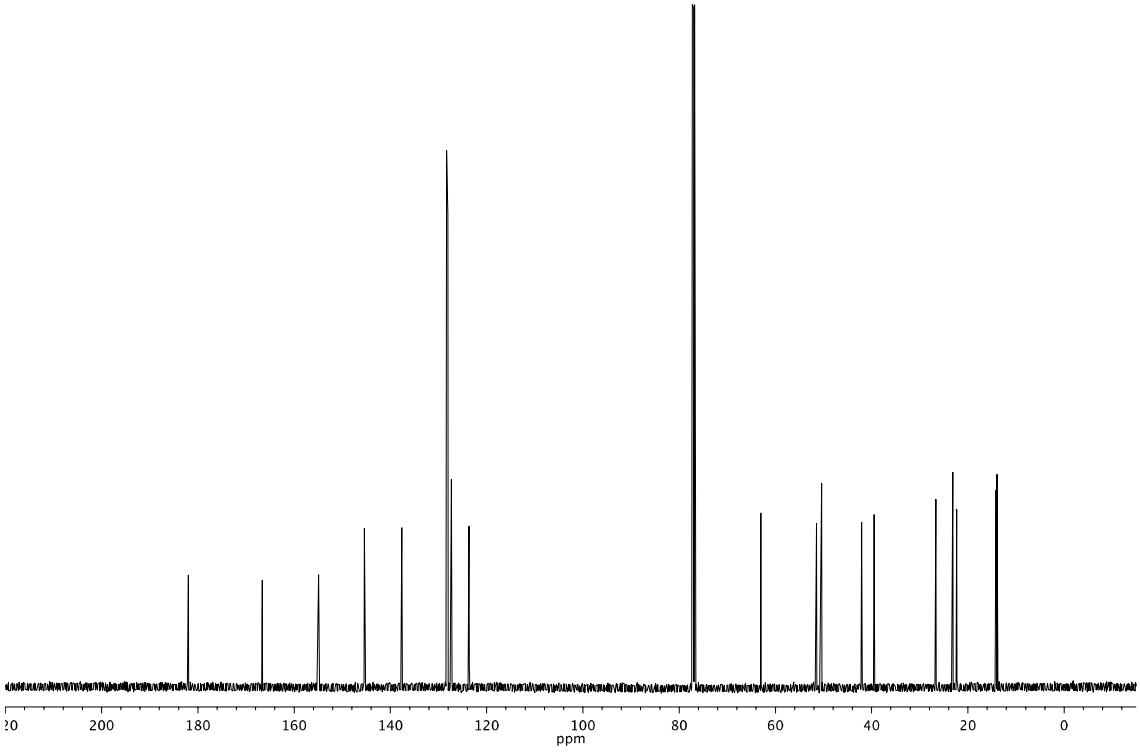
Methyl (*R*,*E*)-5-(benzyl(ethoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6e)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6e**.

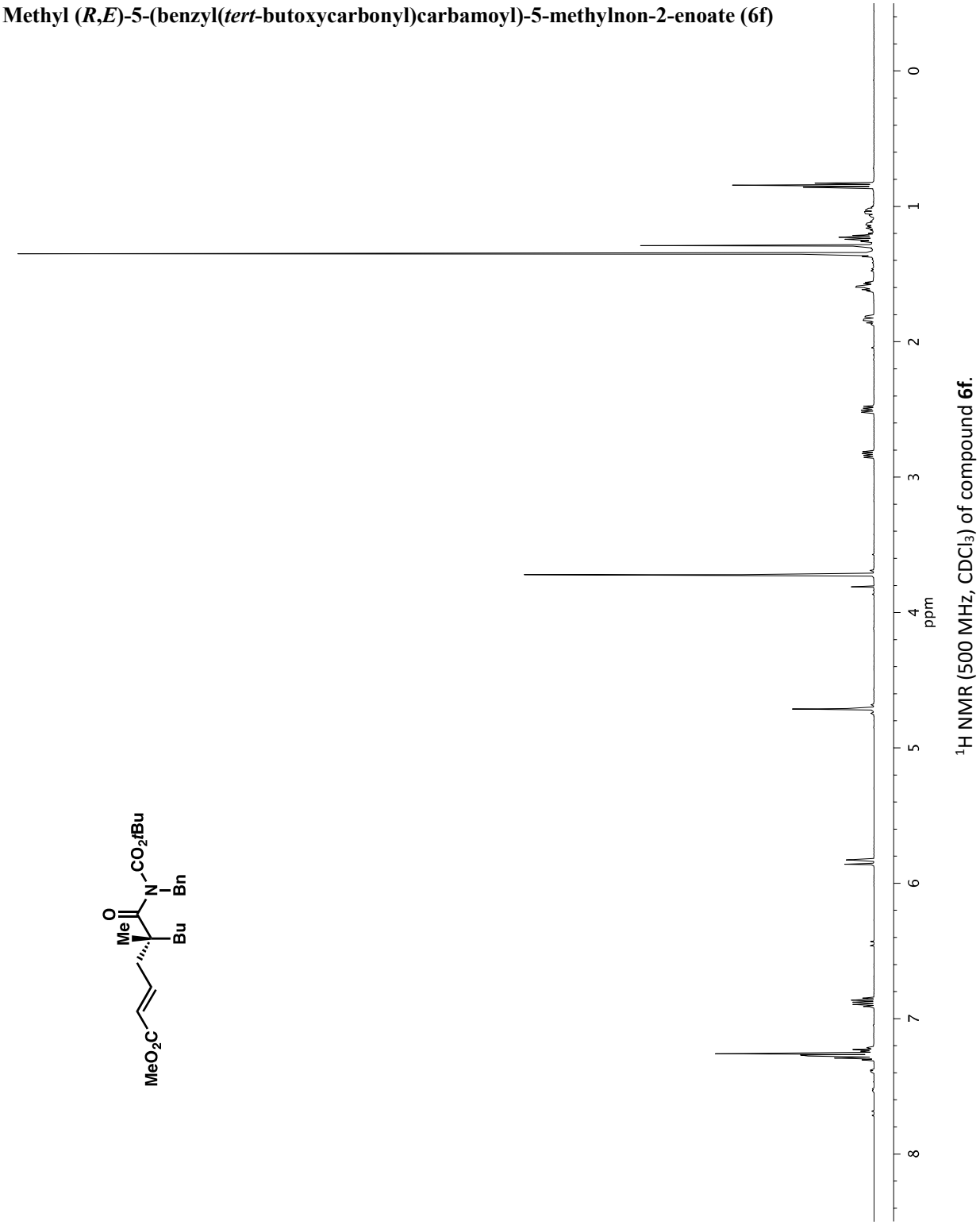


Infrared spectrum (Thin Film, NaCl) of compound **6e**

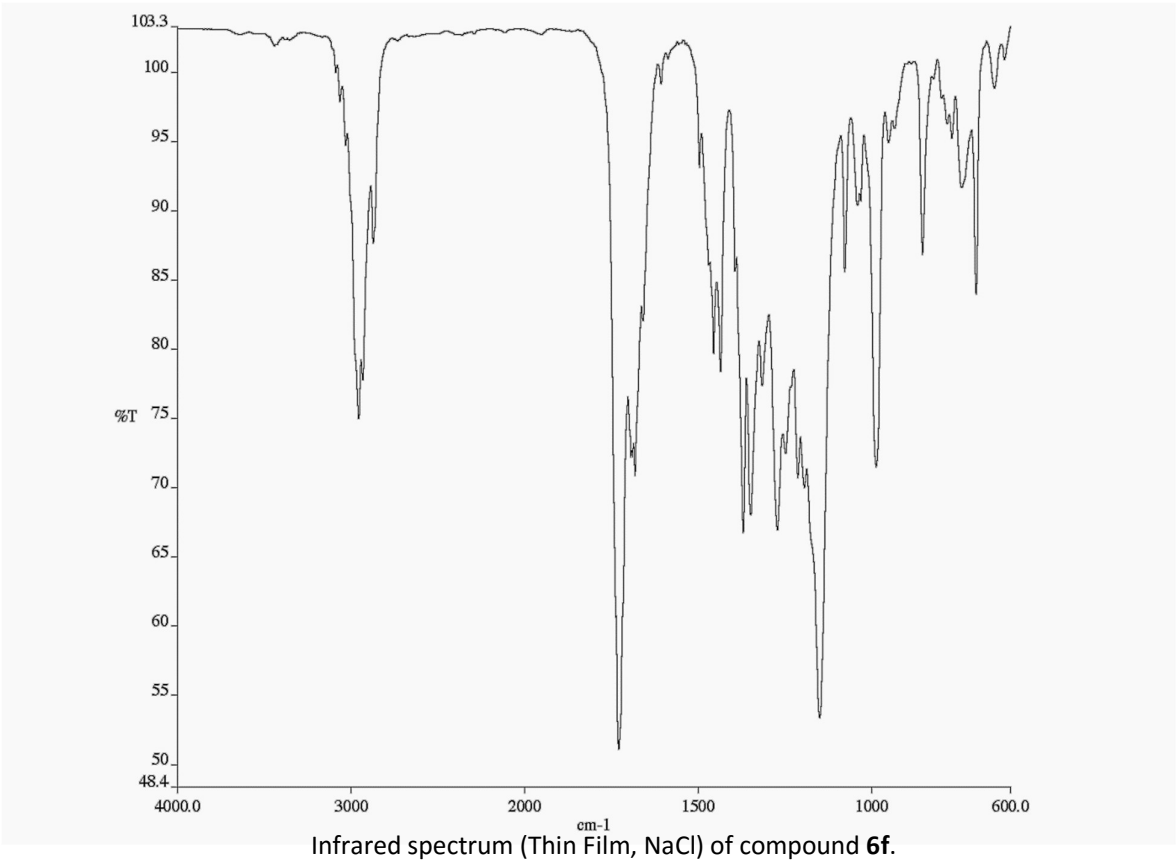


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6e**.

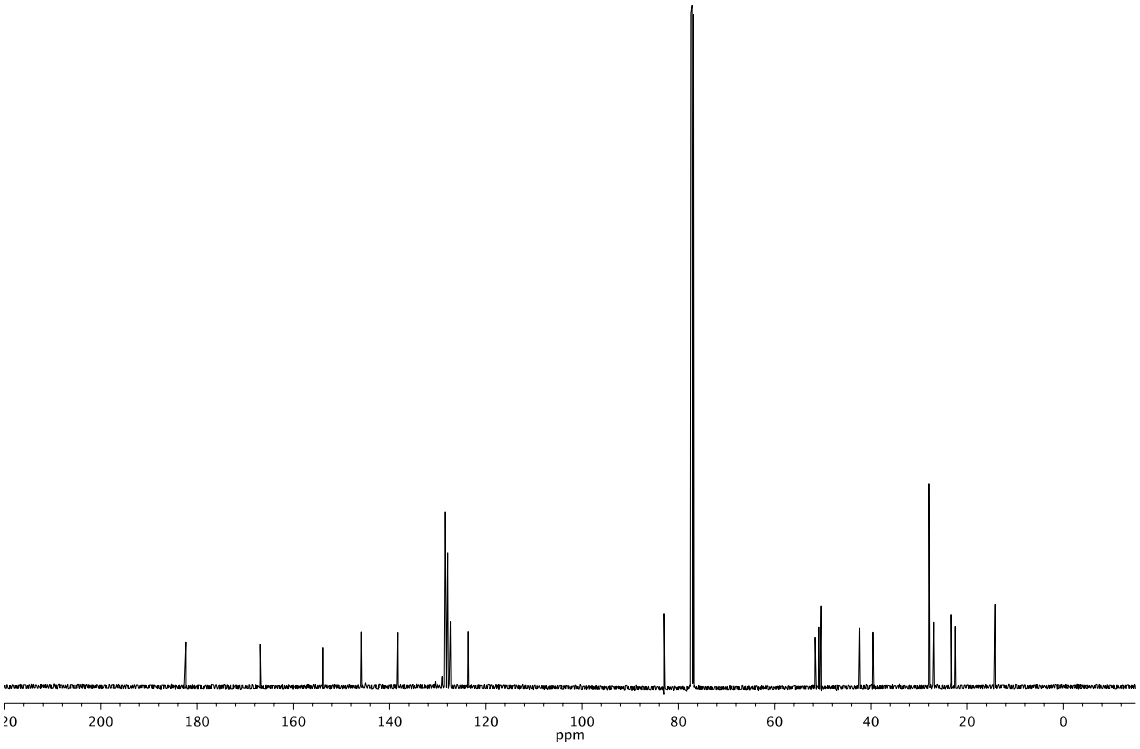
Methyl (*R*,*E*)-5-(benzyl(*tert*-butoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6f)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6f**.

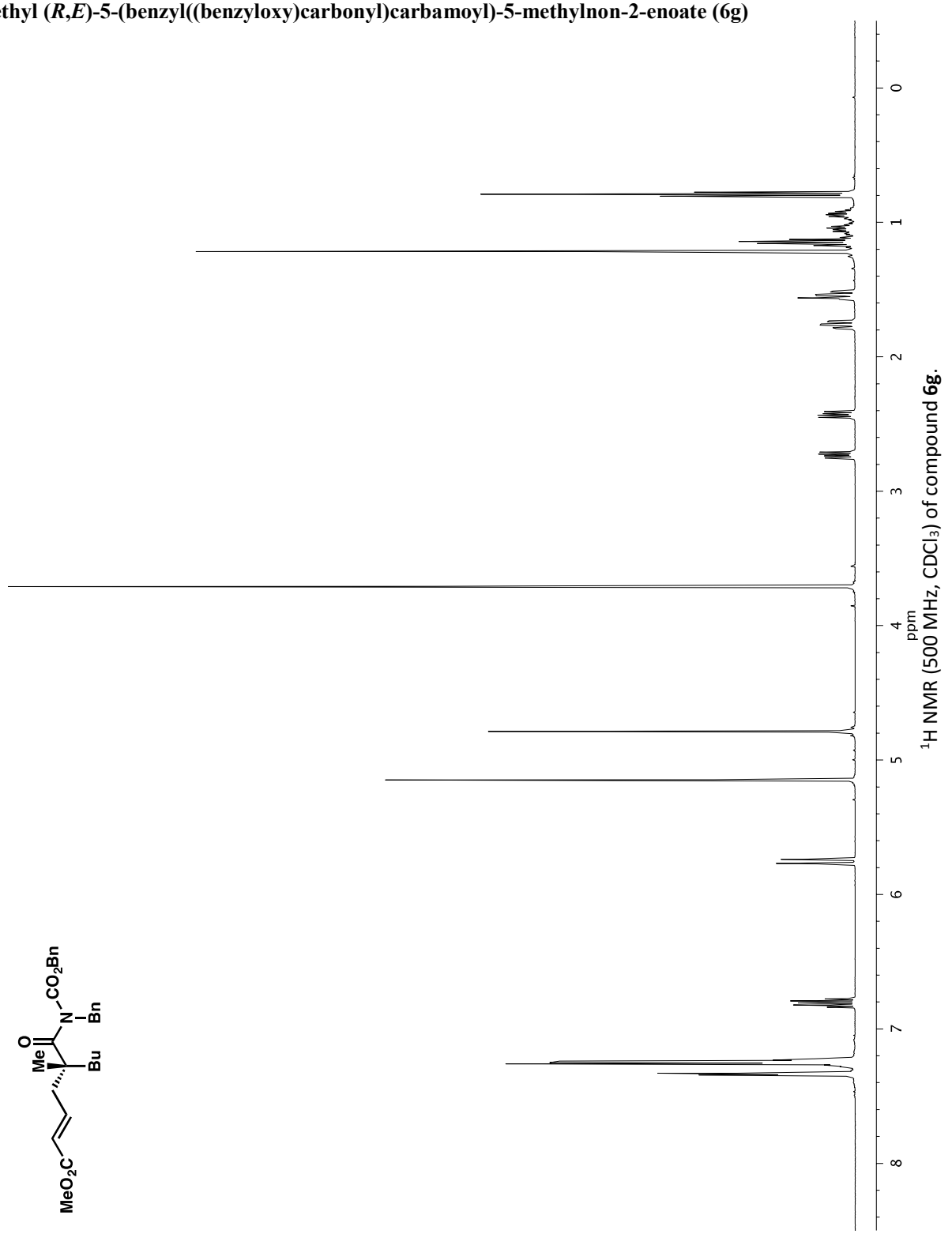


Infrared spectrum (Thin Film, NaCl) of compound **6f**.

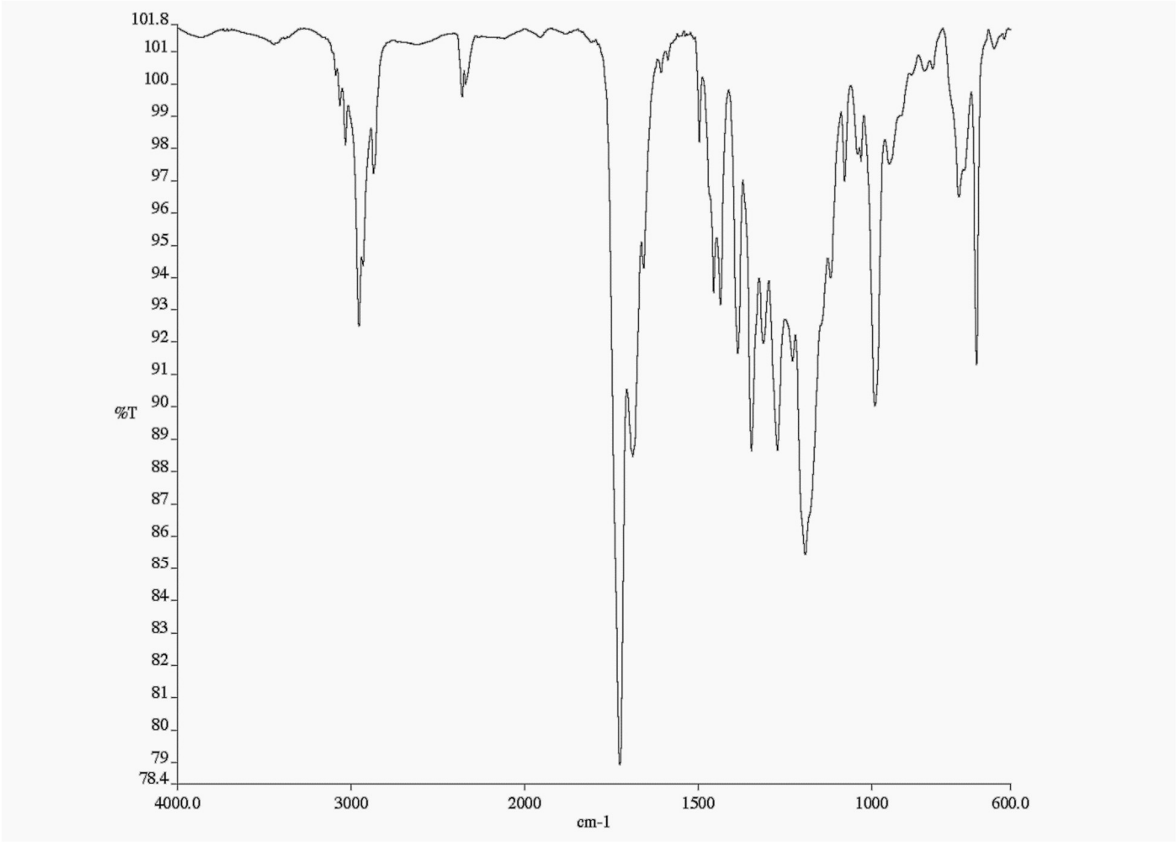


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6f**.

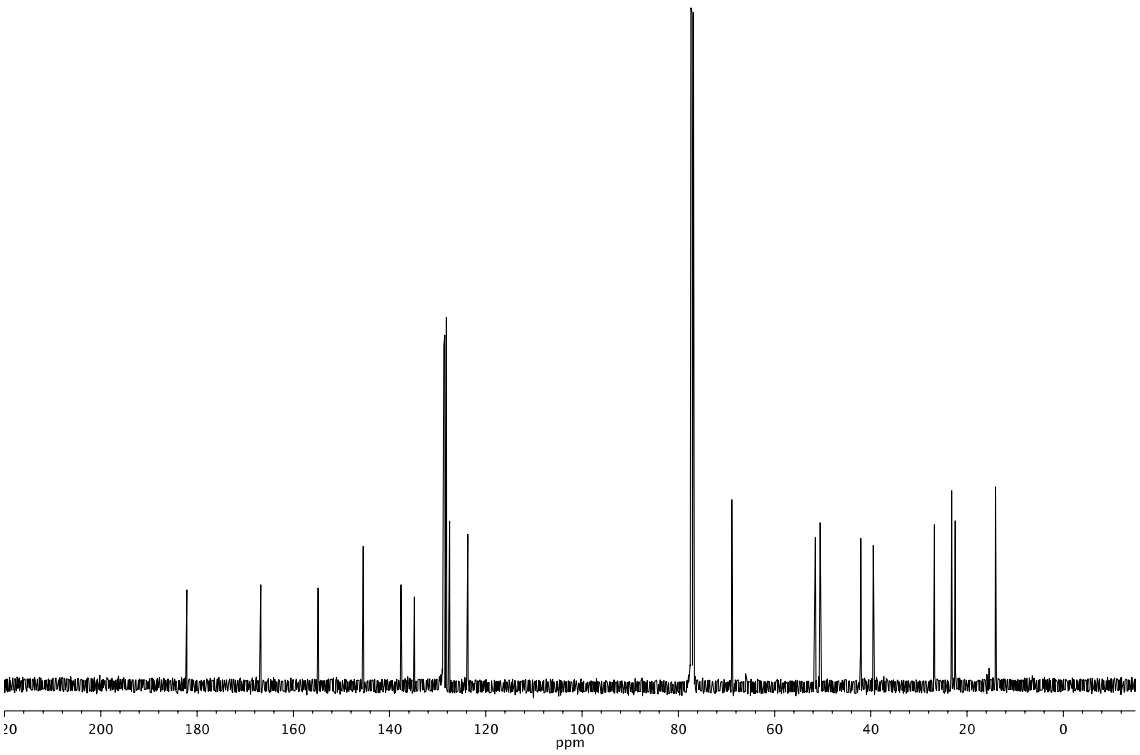
Methyl (*R*,*E*)-5-(benzyl((benzyloxy)carbonyl)carbamoyl)-5-methylnon-2-enoate (6g)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6g**.

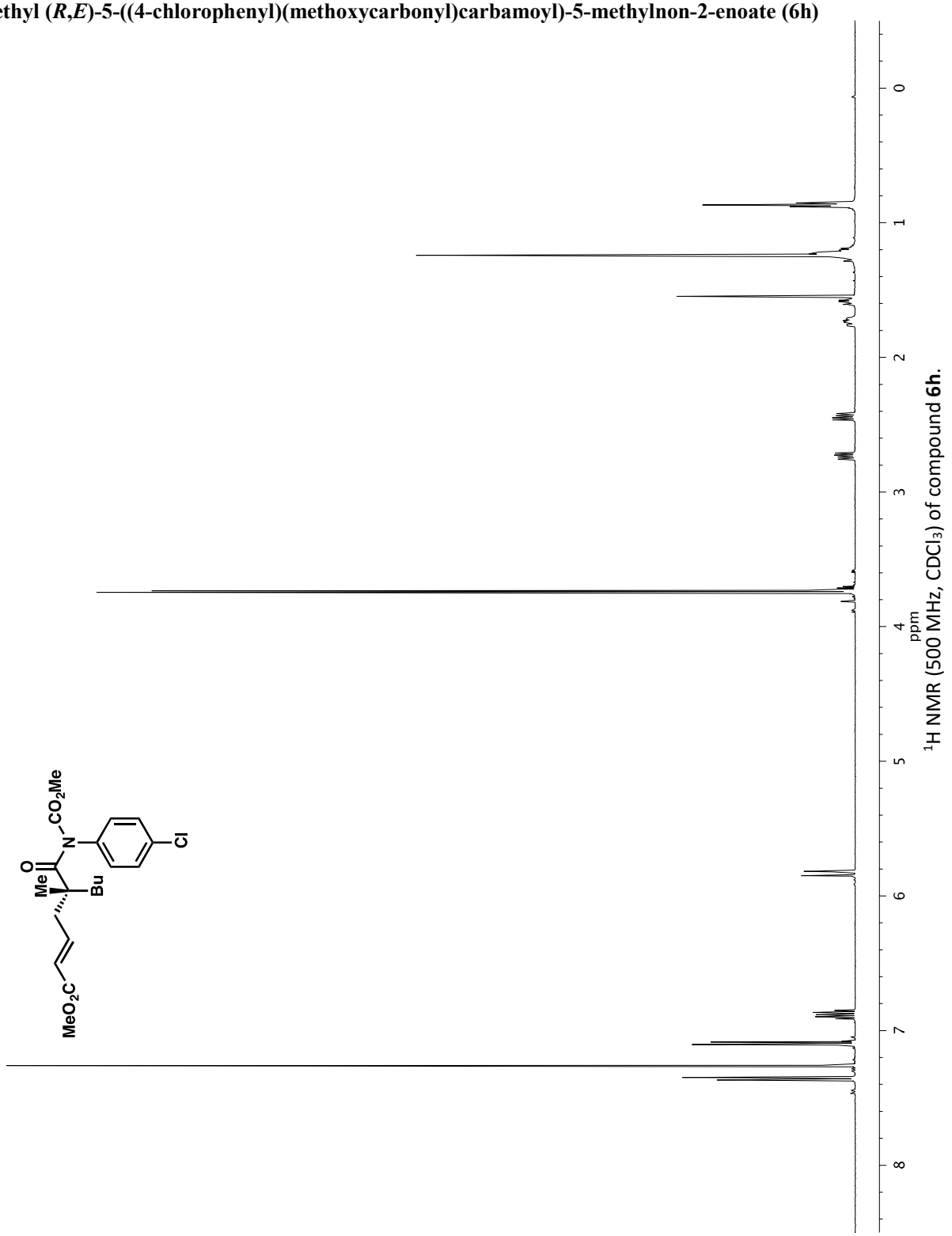


Infrared spectrum (Thin Film, NaCl) of compound **6g**.

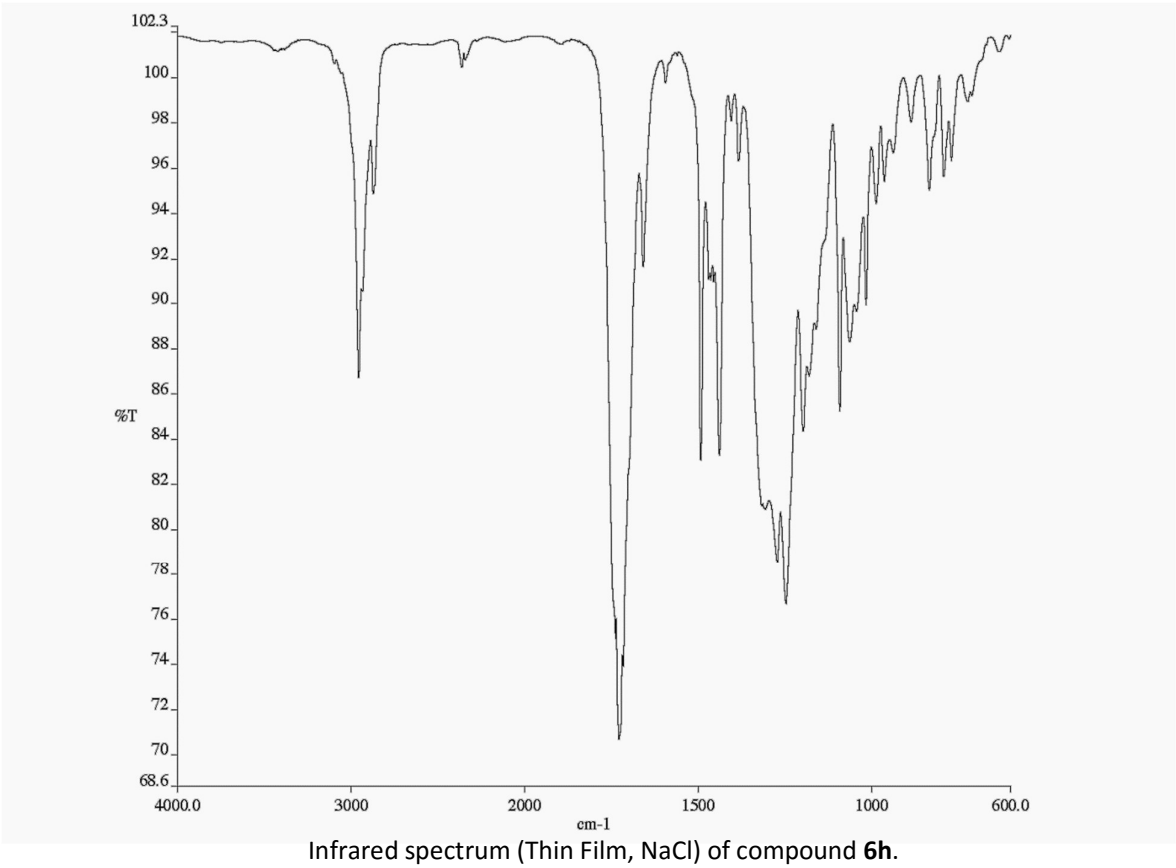


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6g**.

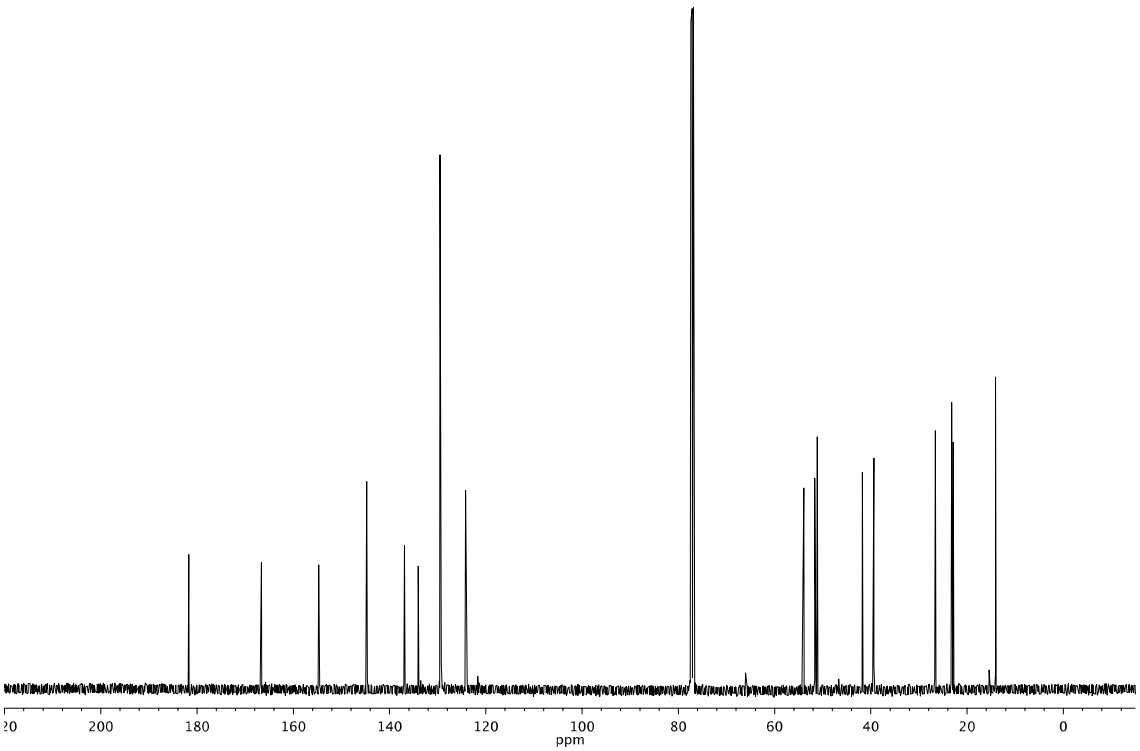
Methyl (*R*,*E*)-5-((4-chlorophenyl)(methoxycarbonyl)carbamoyl)-5-methylnon-2-enoate (6h)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6h**.

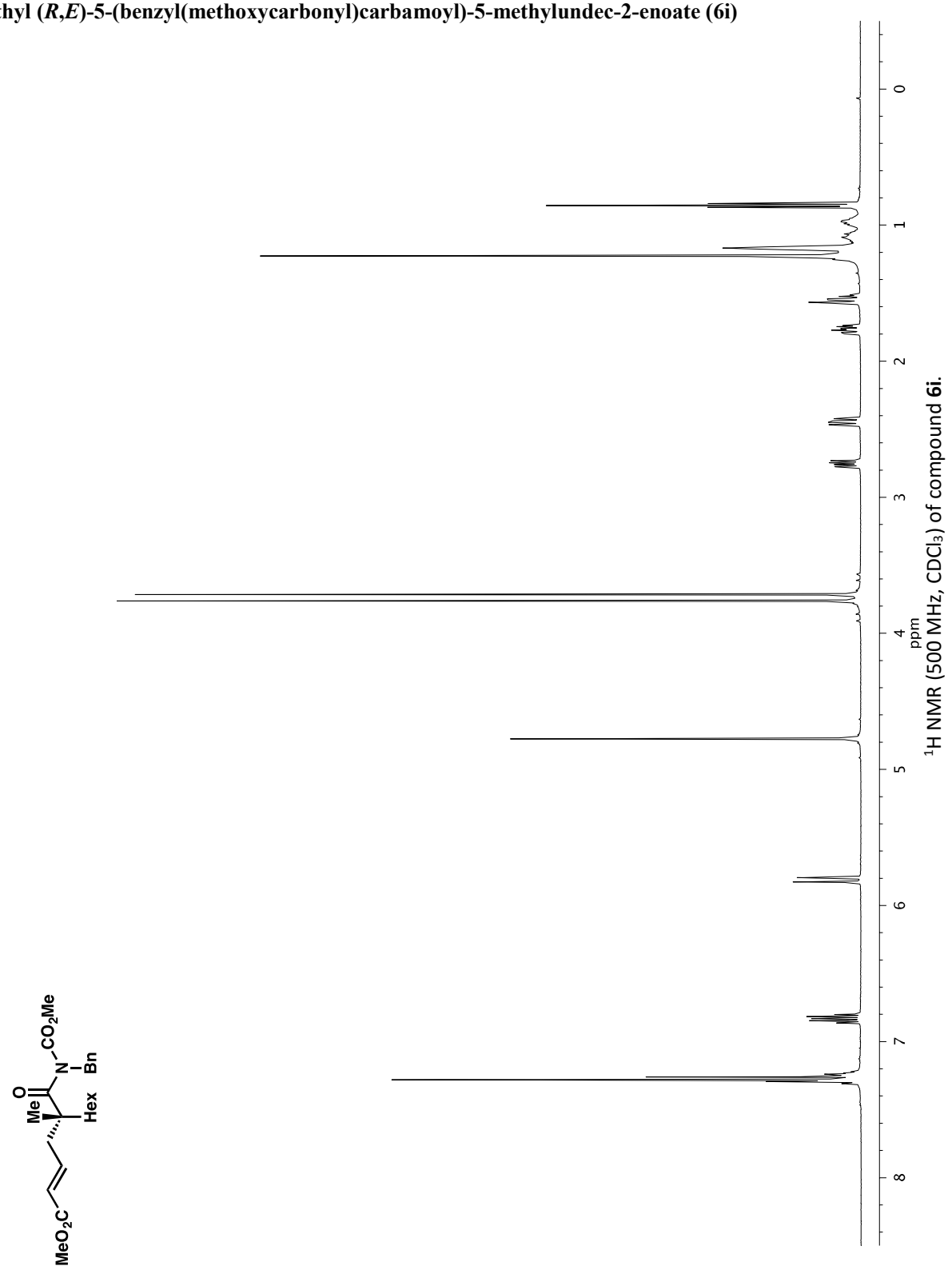


Infrared spectrum (Thin Film, NaCl) of compound **6h**.

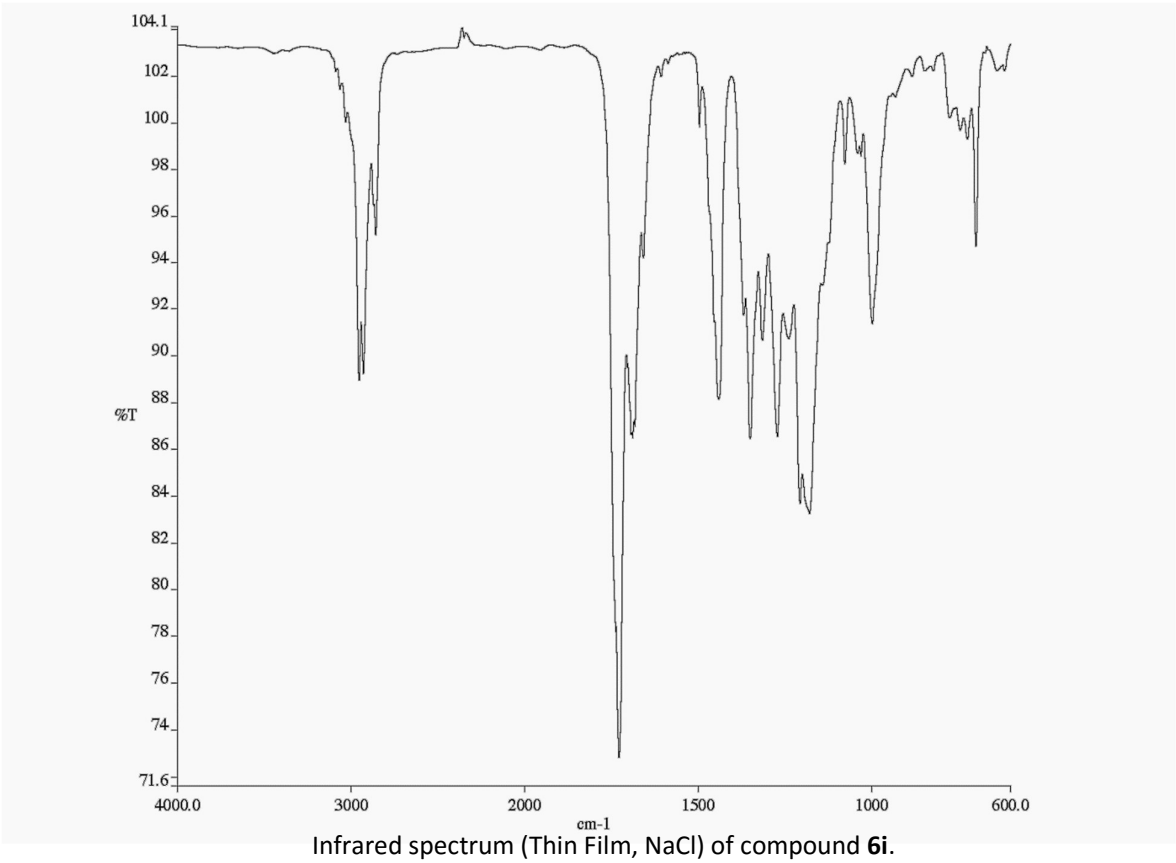


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6h**.

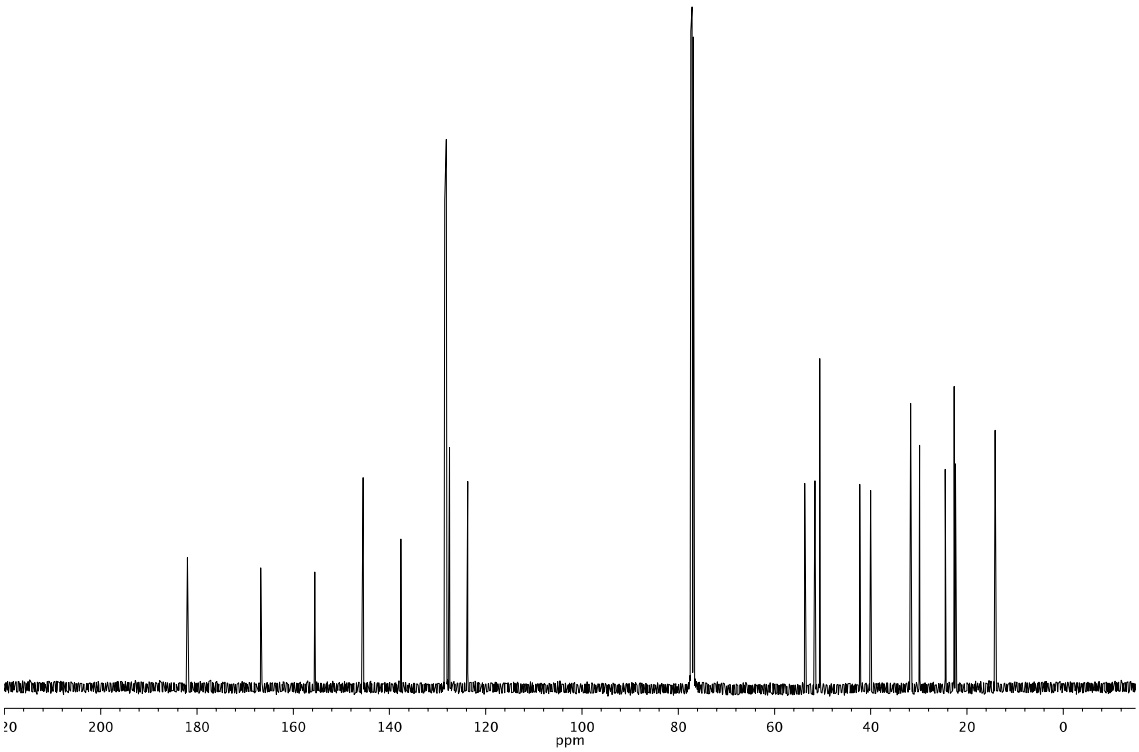
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-methylundec-2-enoate (6i)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6i**.

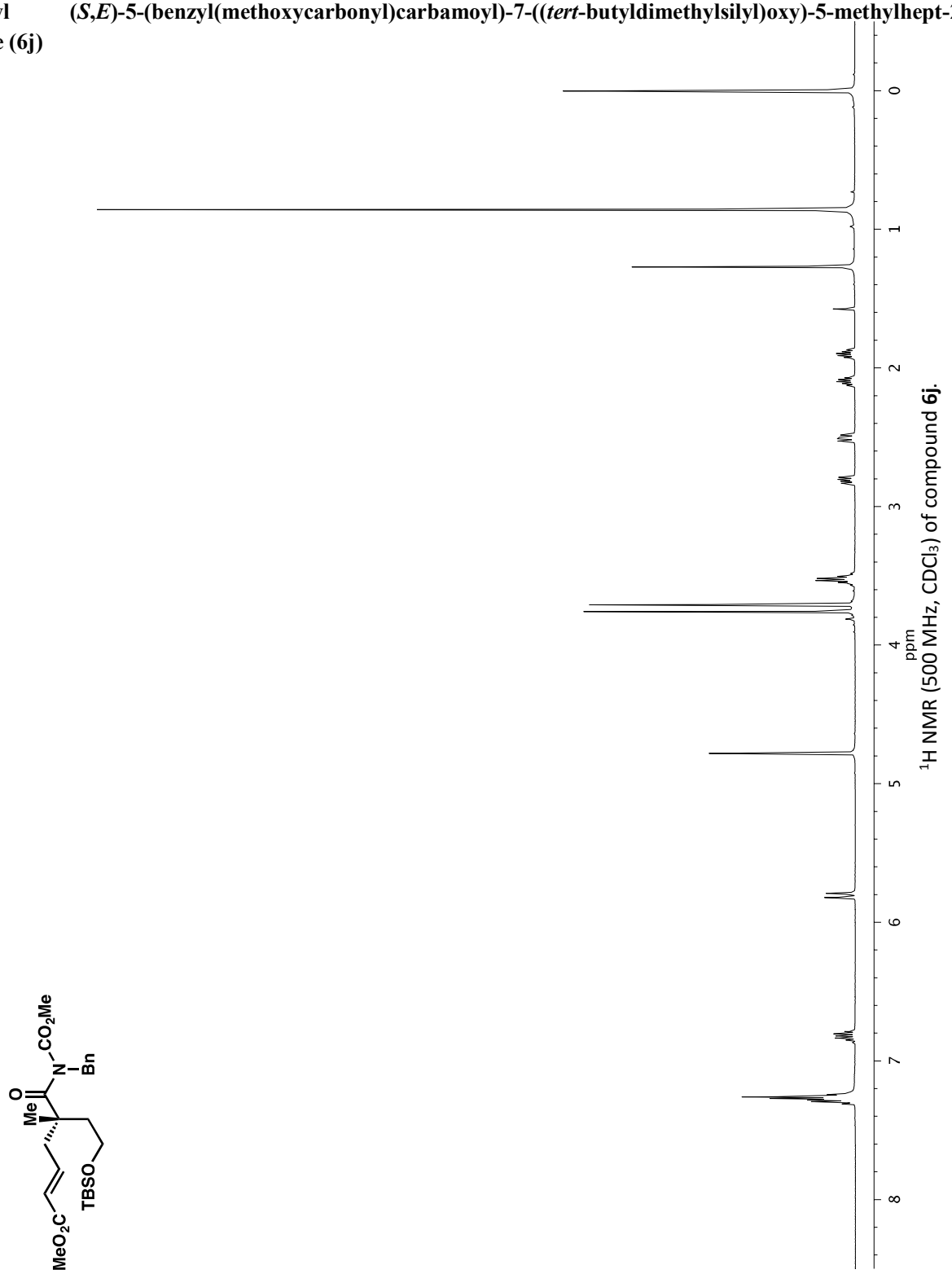


Infrared spectrum (Thin Film, NaCl) of compound **6i**.

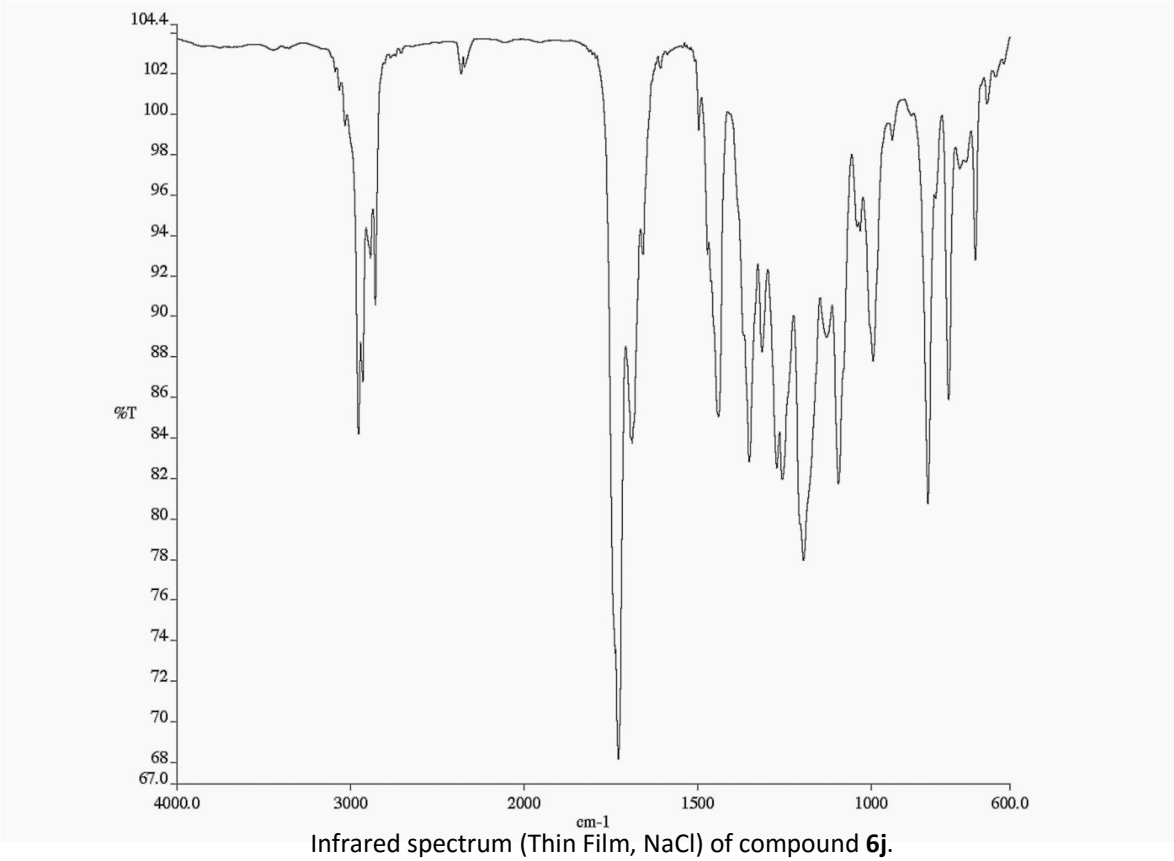


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6i**.

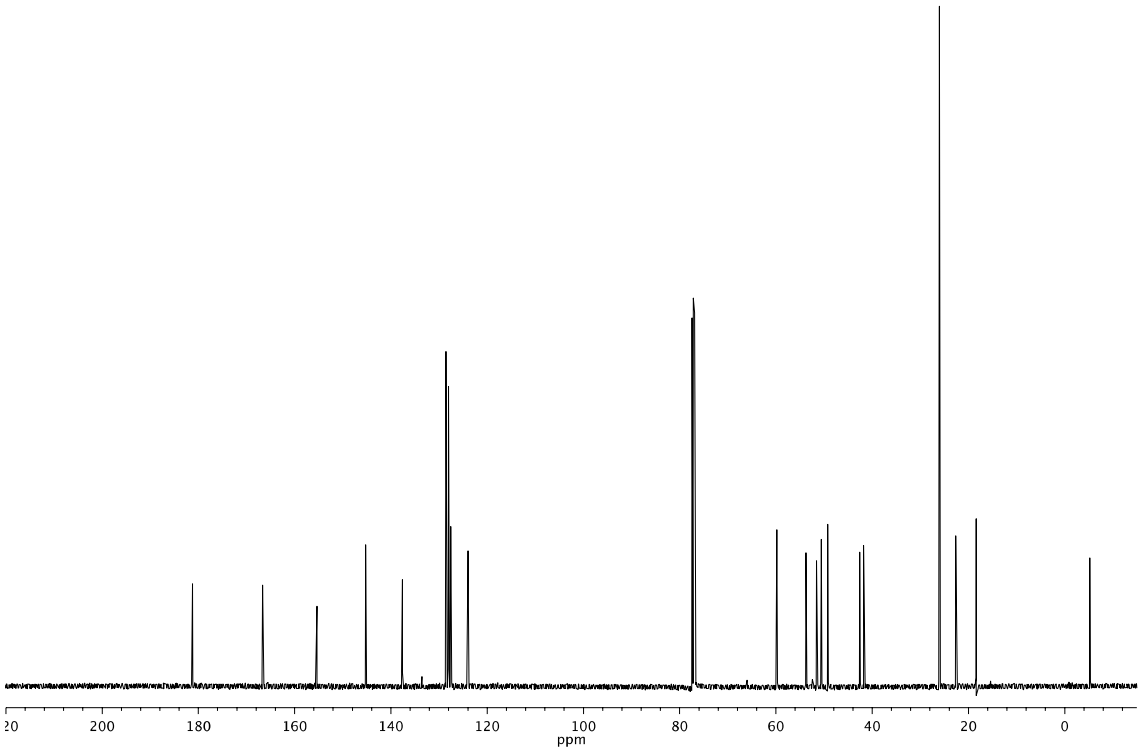
Methyl (*S*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-7-((*tert*-butyldimethylsilyl)oxy)-5-methylhept-2-enoate (6j)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6j**.

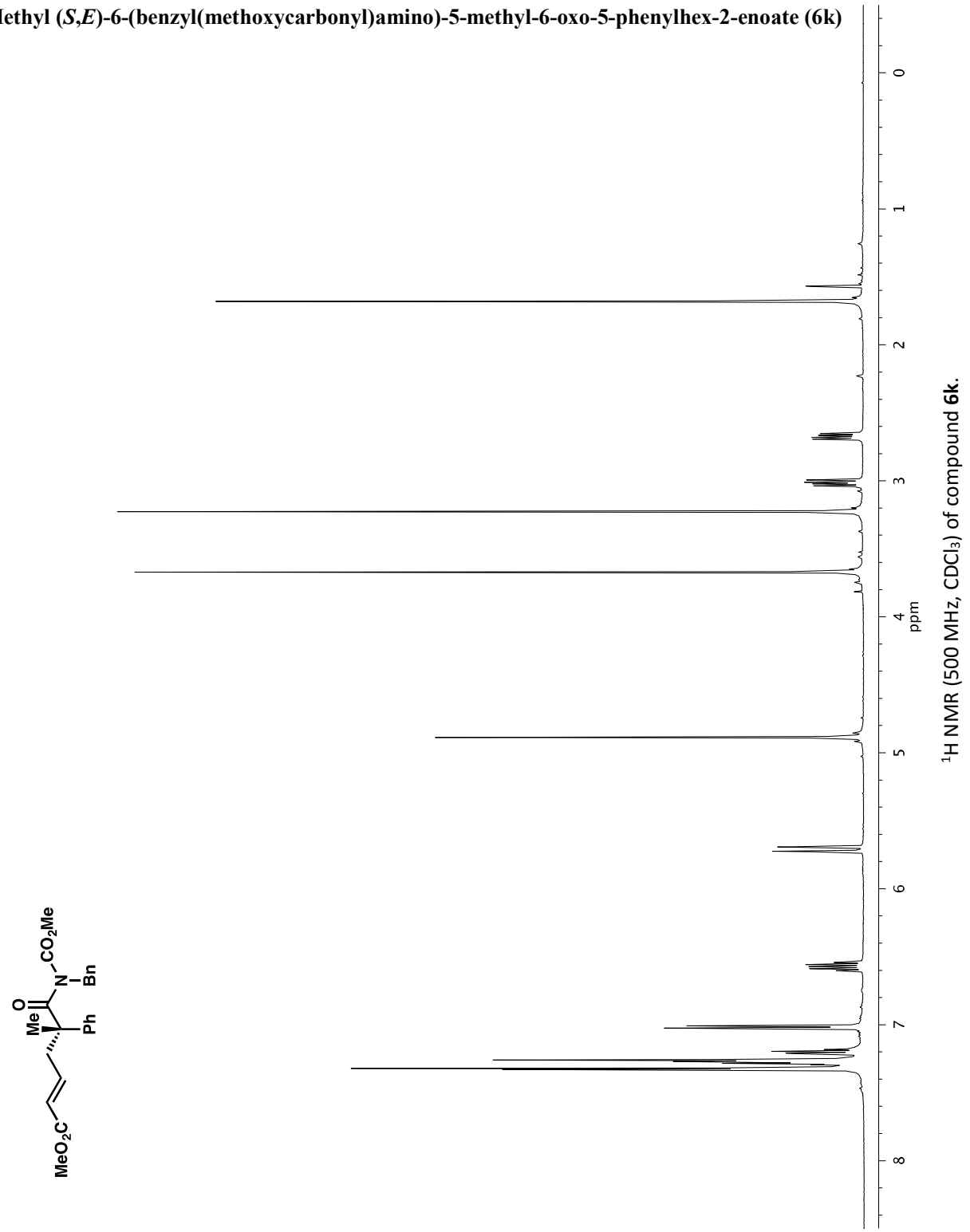


Infrared spectrum (Thin Film, NaCl) of compound **6j**.

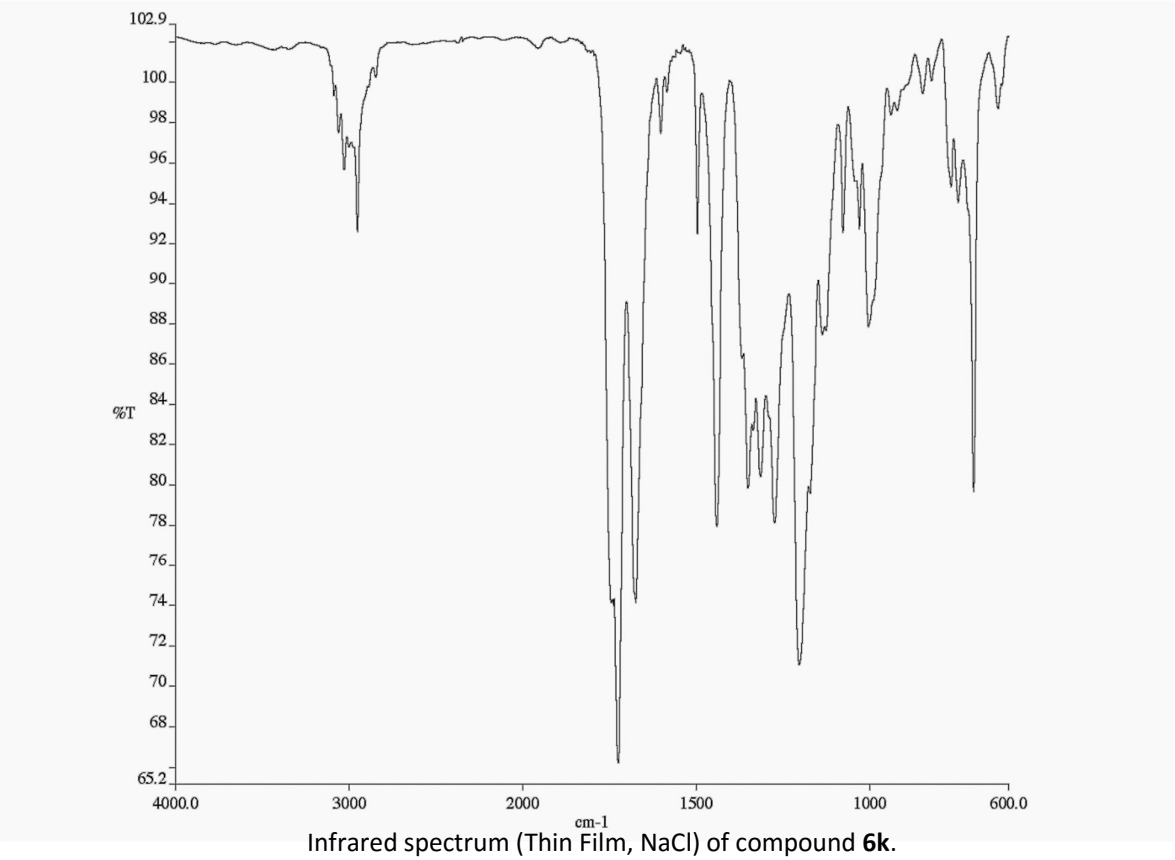


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6j**.

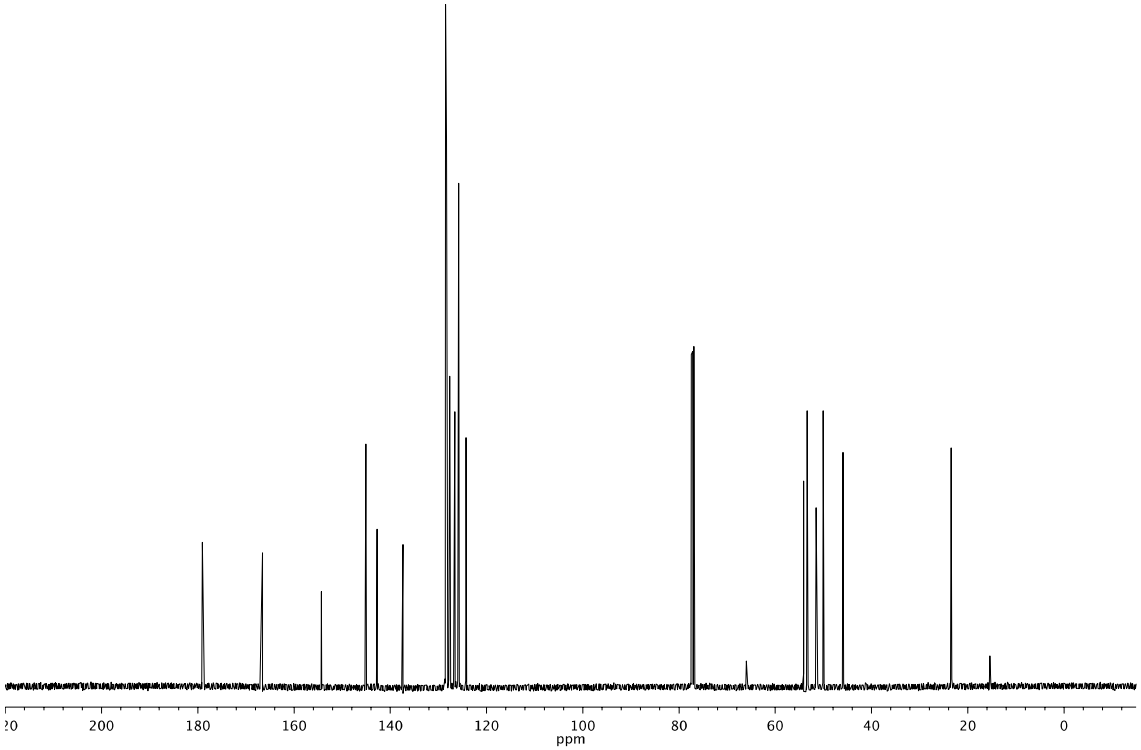
Methyl (*S*,*E*)-6-(benzyl(methoxycarbonyl)amino)-5-methyl-6-oxo-5-phenylhex-2-enoate (6k)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6k**.

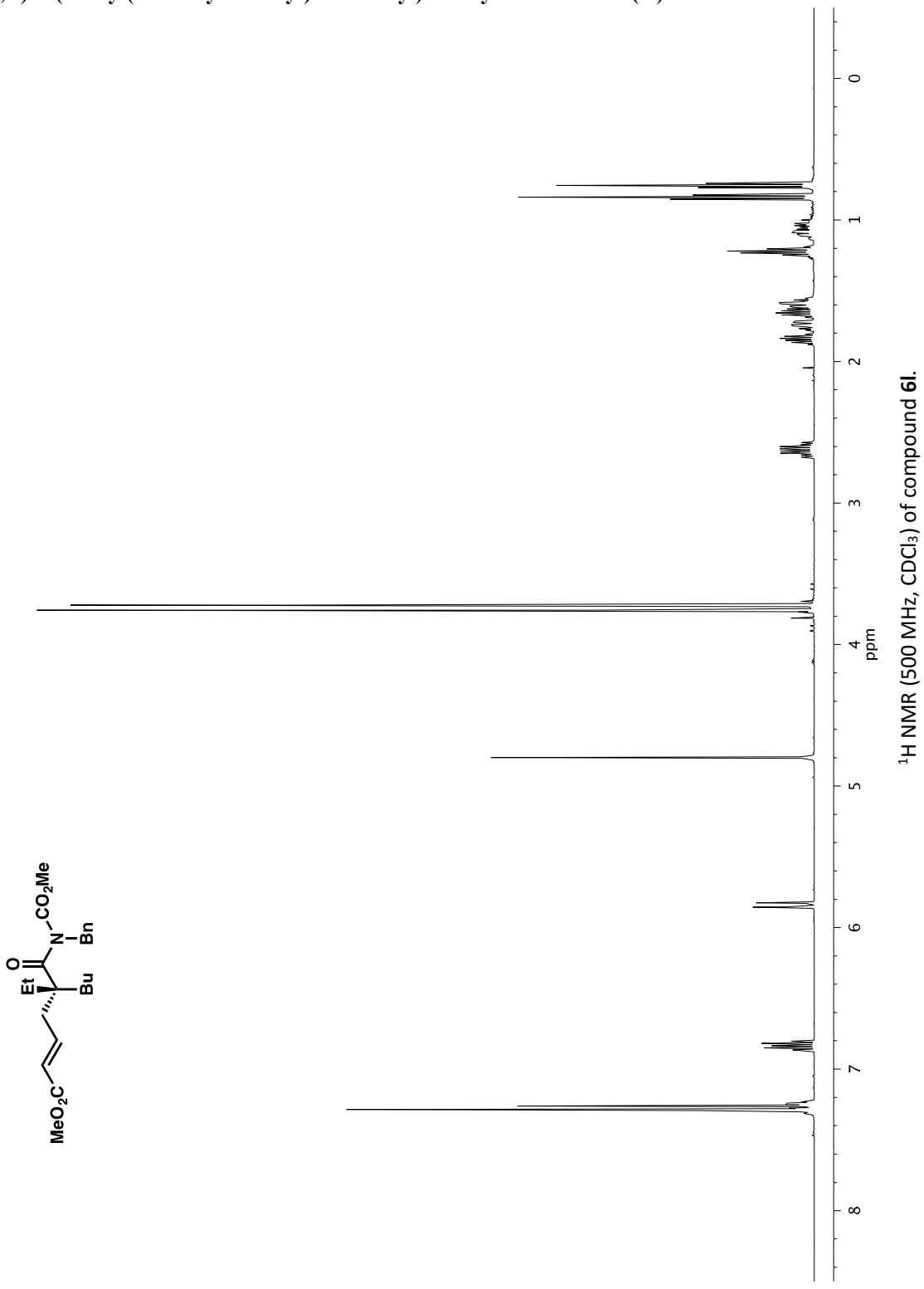


Infrared spectrum (Thin Film, NaCl) of compound **6k**.

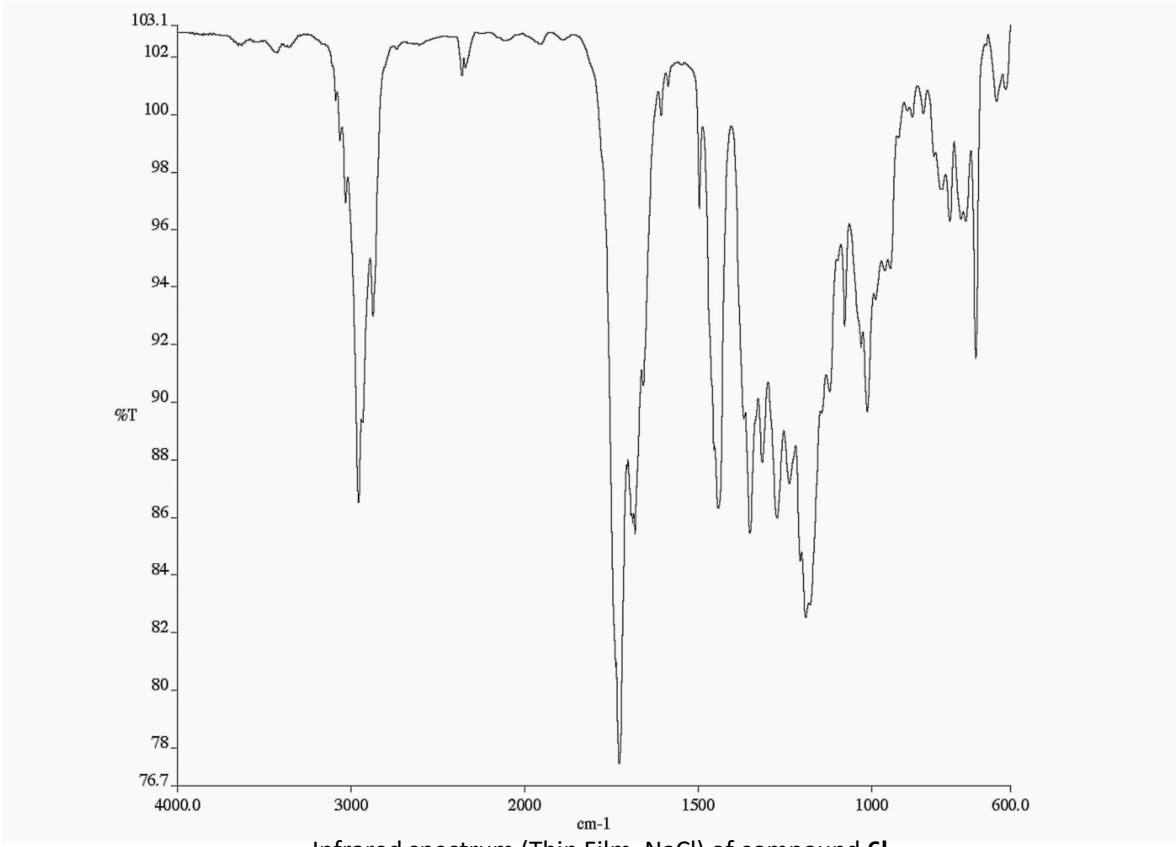


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6k**.

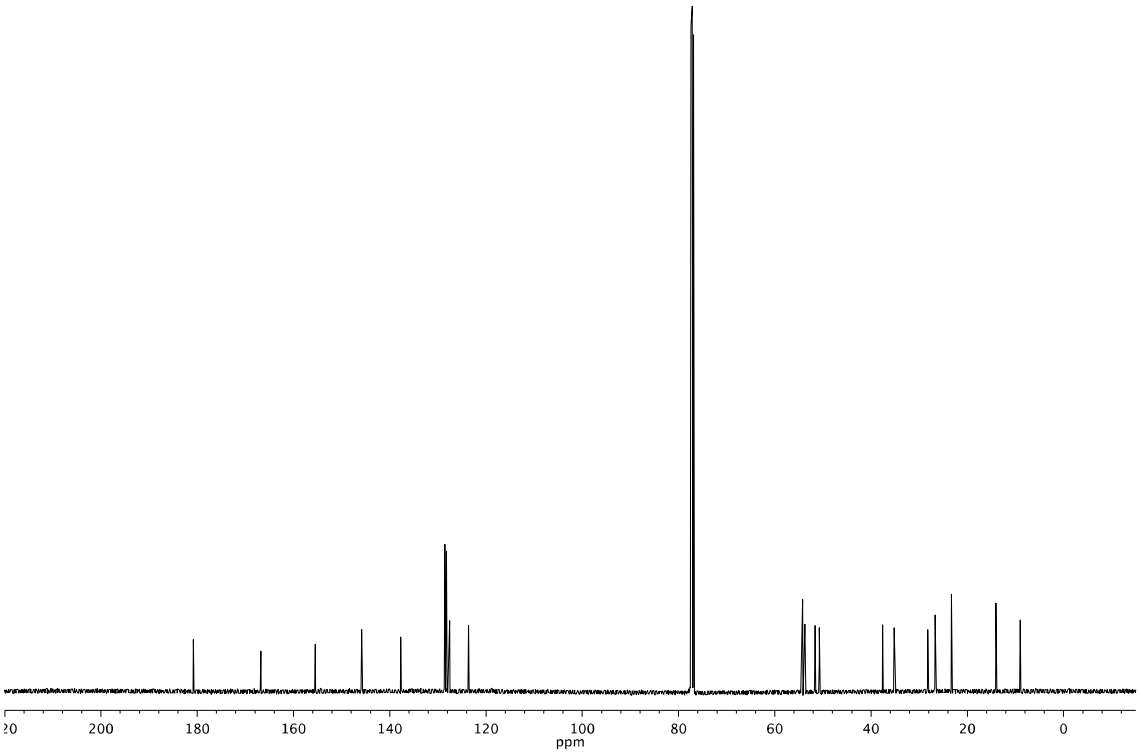
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-ethylnon-2-enoate (6l)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6l**.

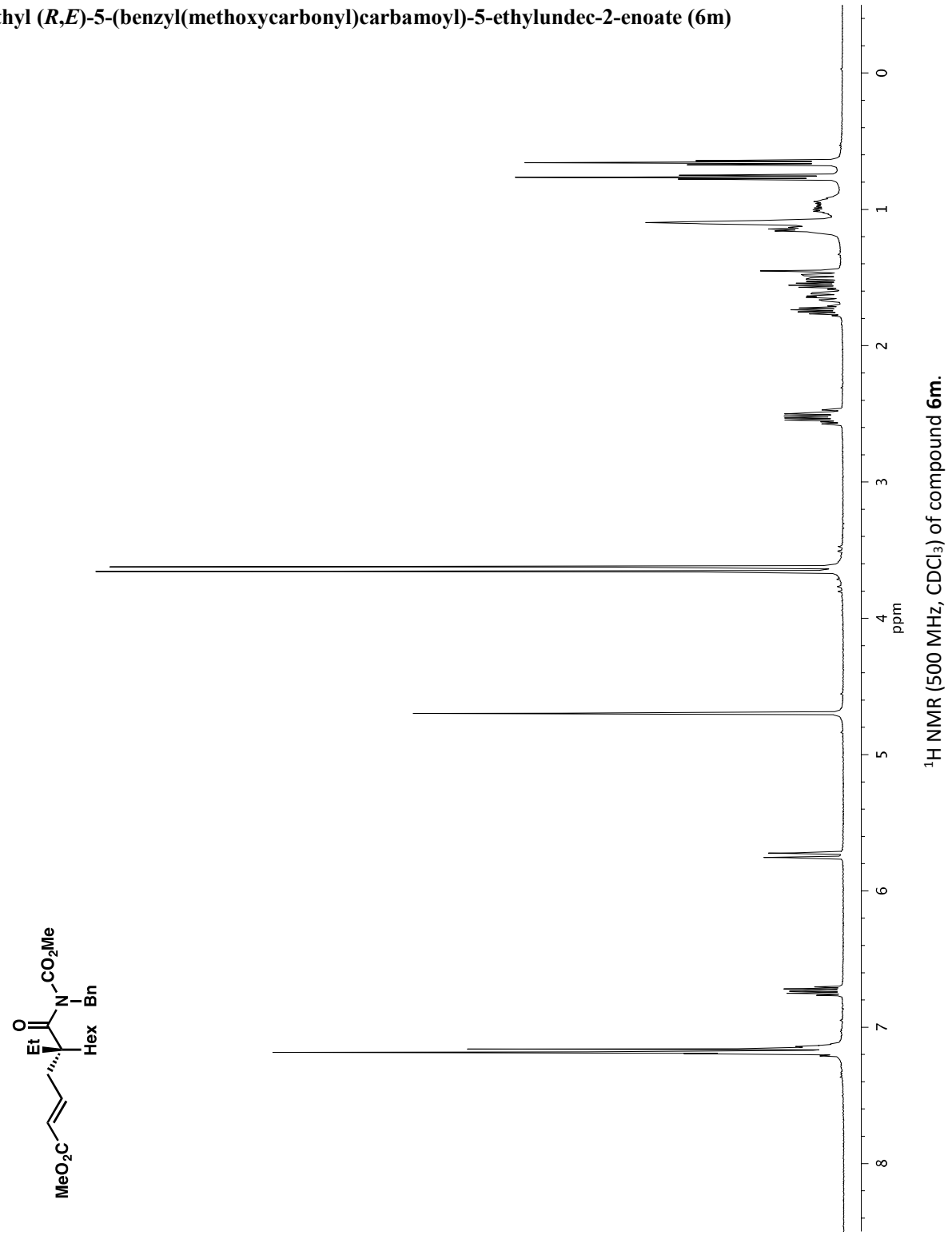


Infrared spectrum (Thin Film, NaCl) of compound **6l**.

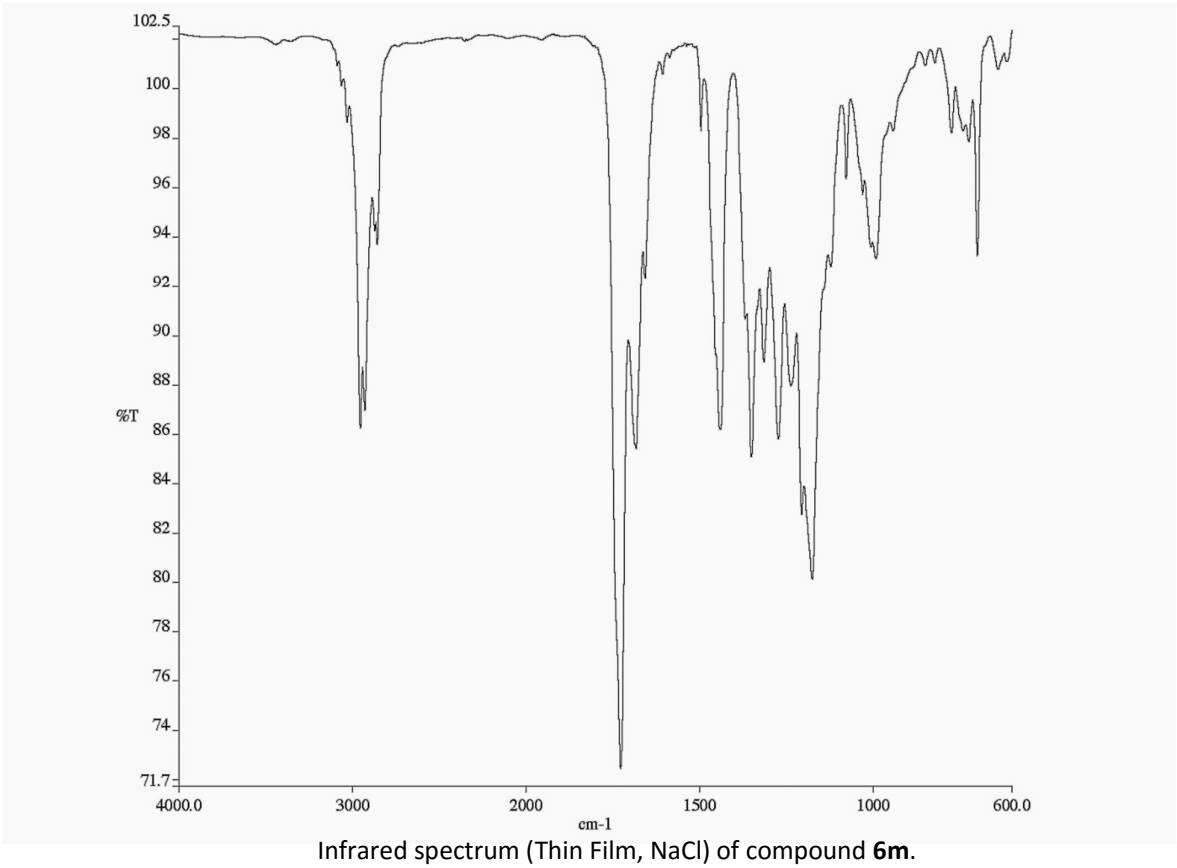


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6l**.

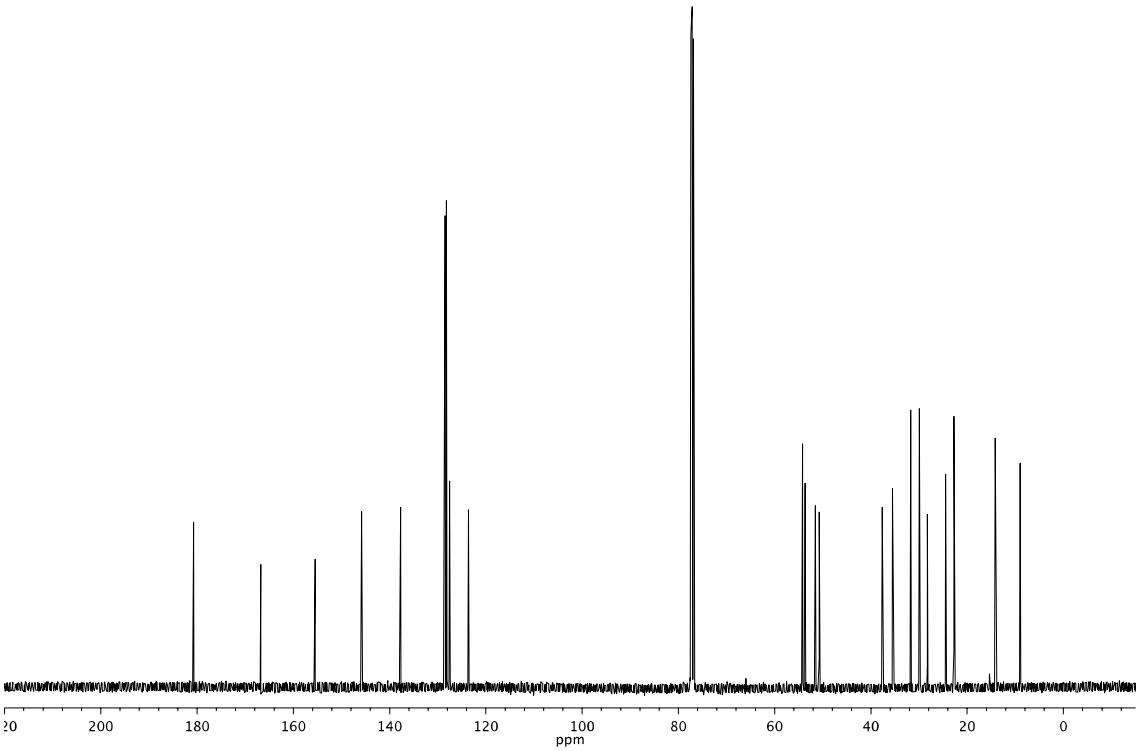
Methyl (*R*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-ethylundec-2-enoate (6m)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6m**.

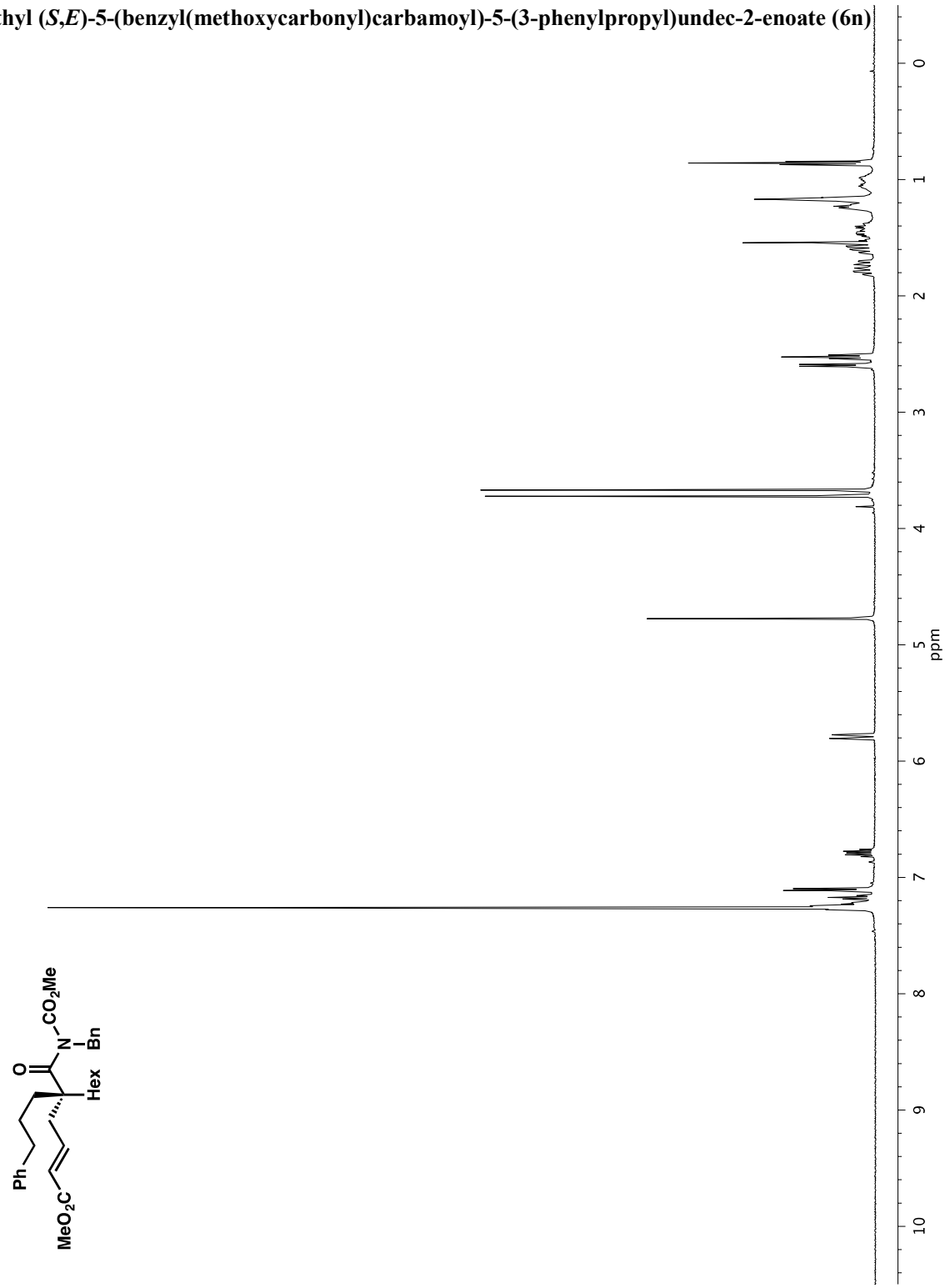


Infrared spectrum (Thin Film, NaCl) of compound **6m**.

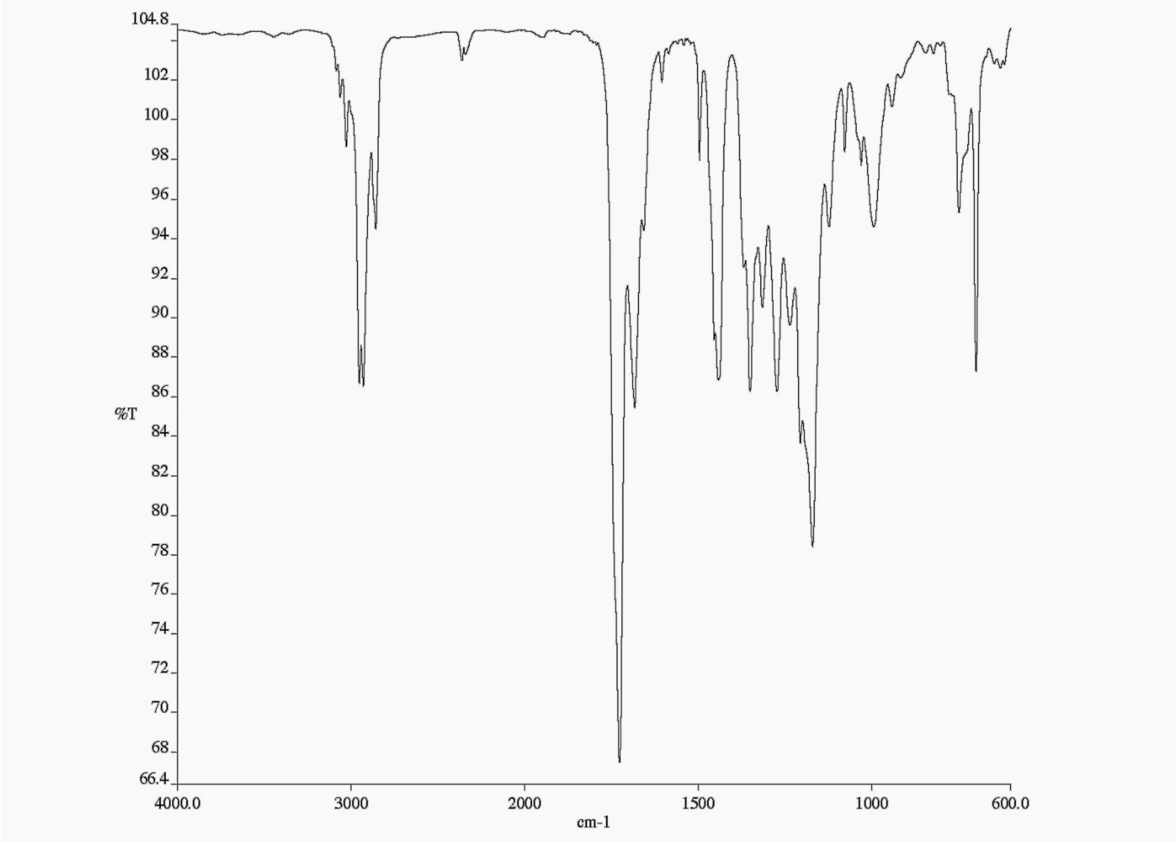


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6m**.

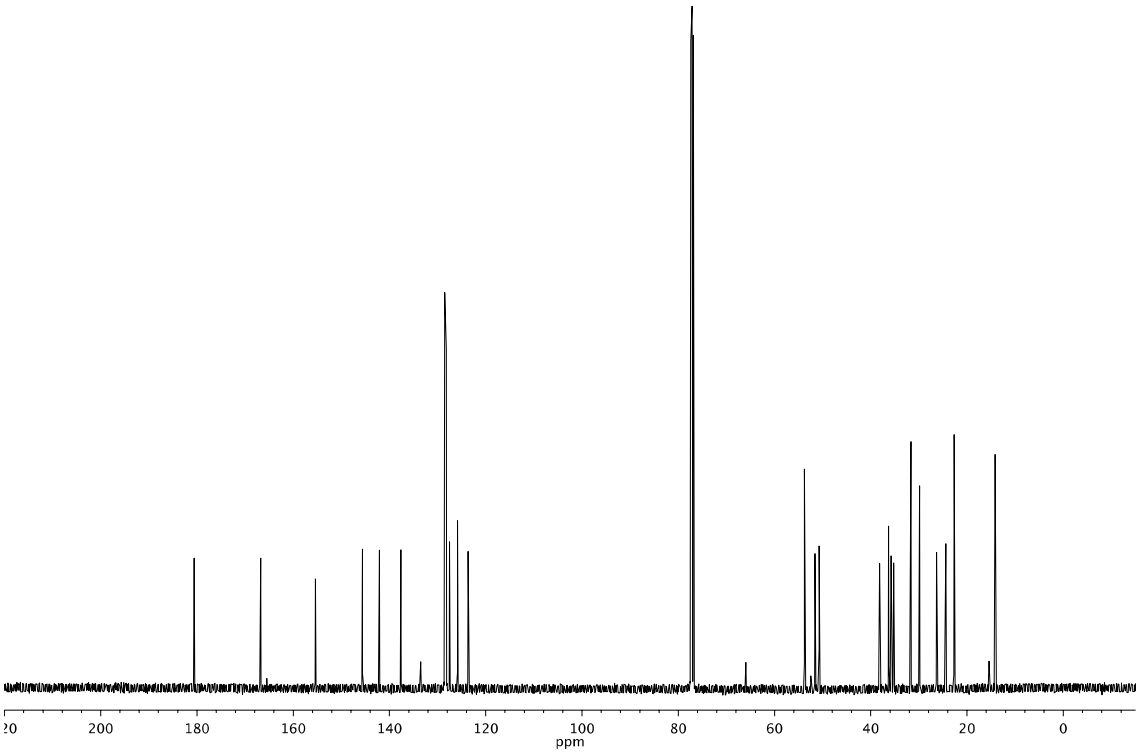
Methyl (*S*,*E*)-5-(benzyl(methoxycarbonyl)carbamoyl)-5-(3-phenylpropyl)undec-2-enoate (6n)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6n**.

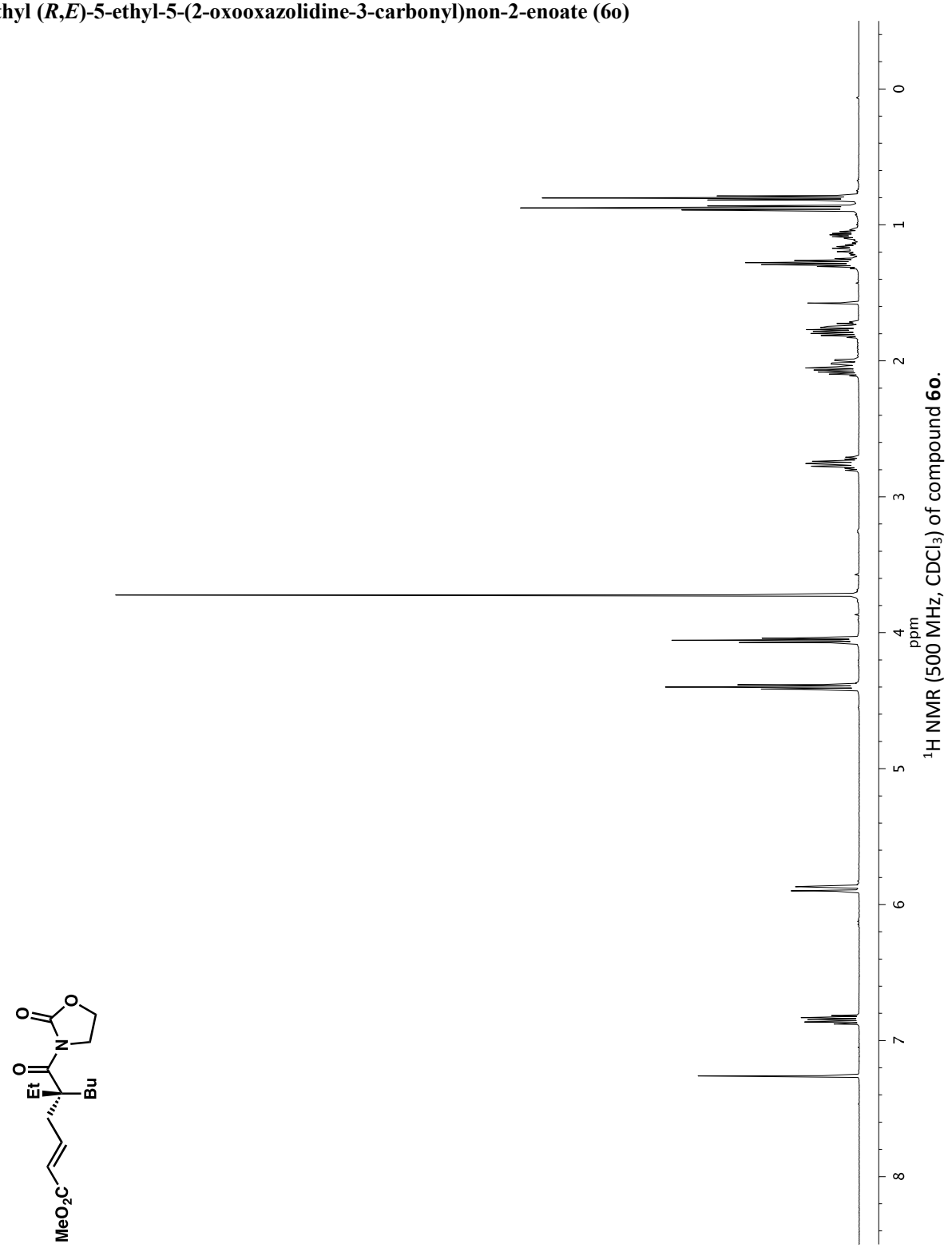


Infrared spectrum (Thin Film, NaCl) of compound **6n**.

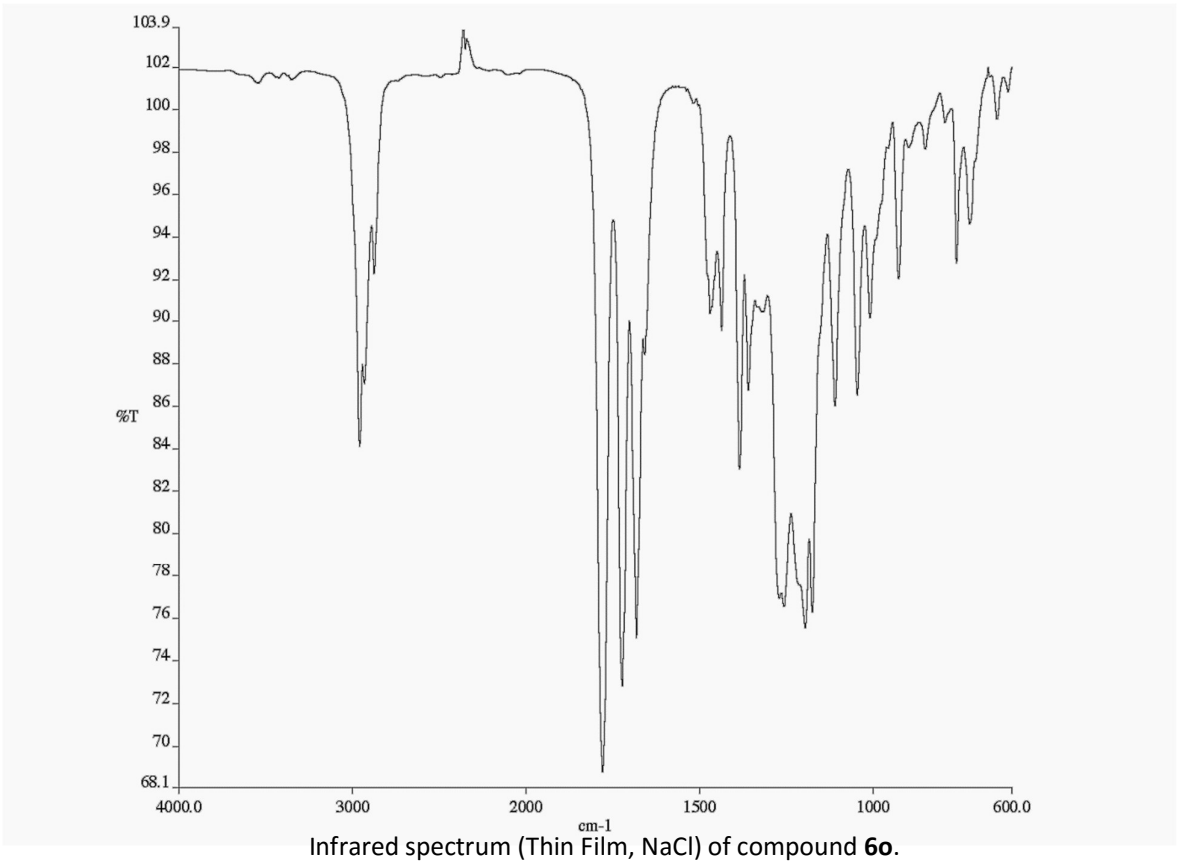


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6n**.

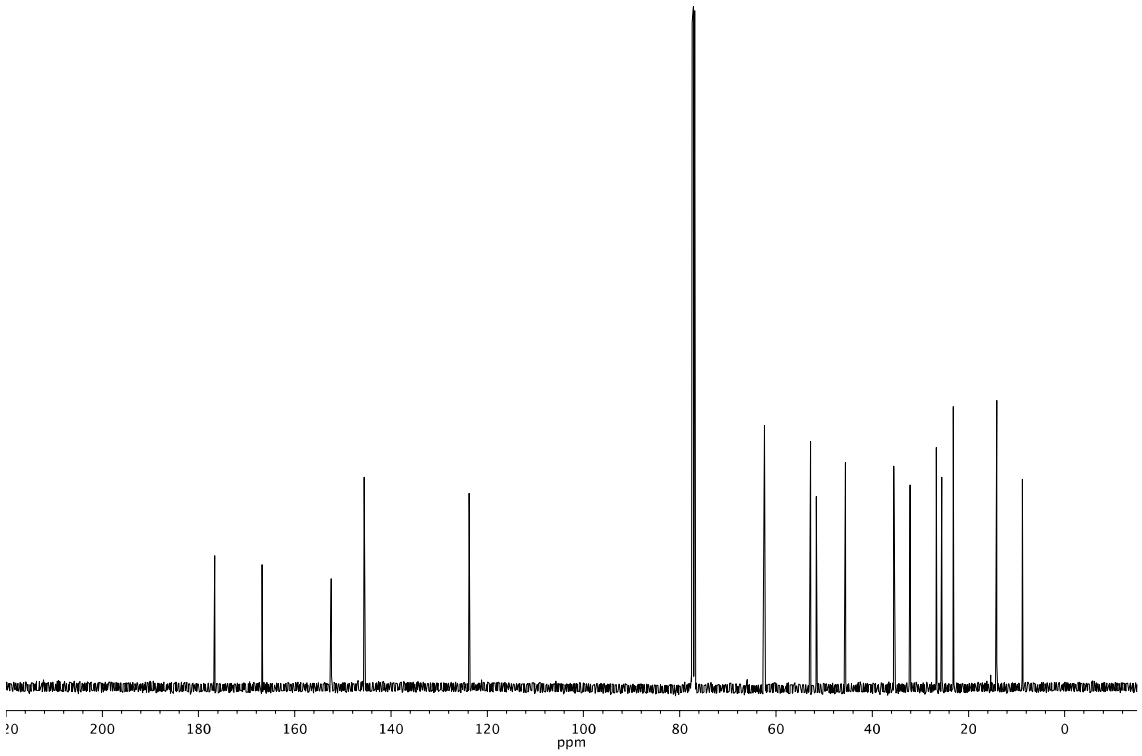
Methyl (*R*,*E*)-5-ethyl-5-(2-oxooxazolidine-3-carbonyl)non-2-enoate (6o)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6o**.

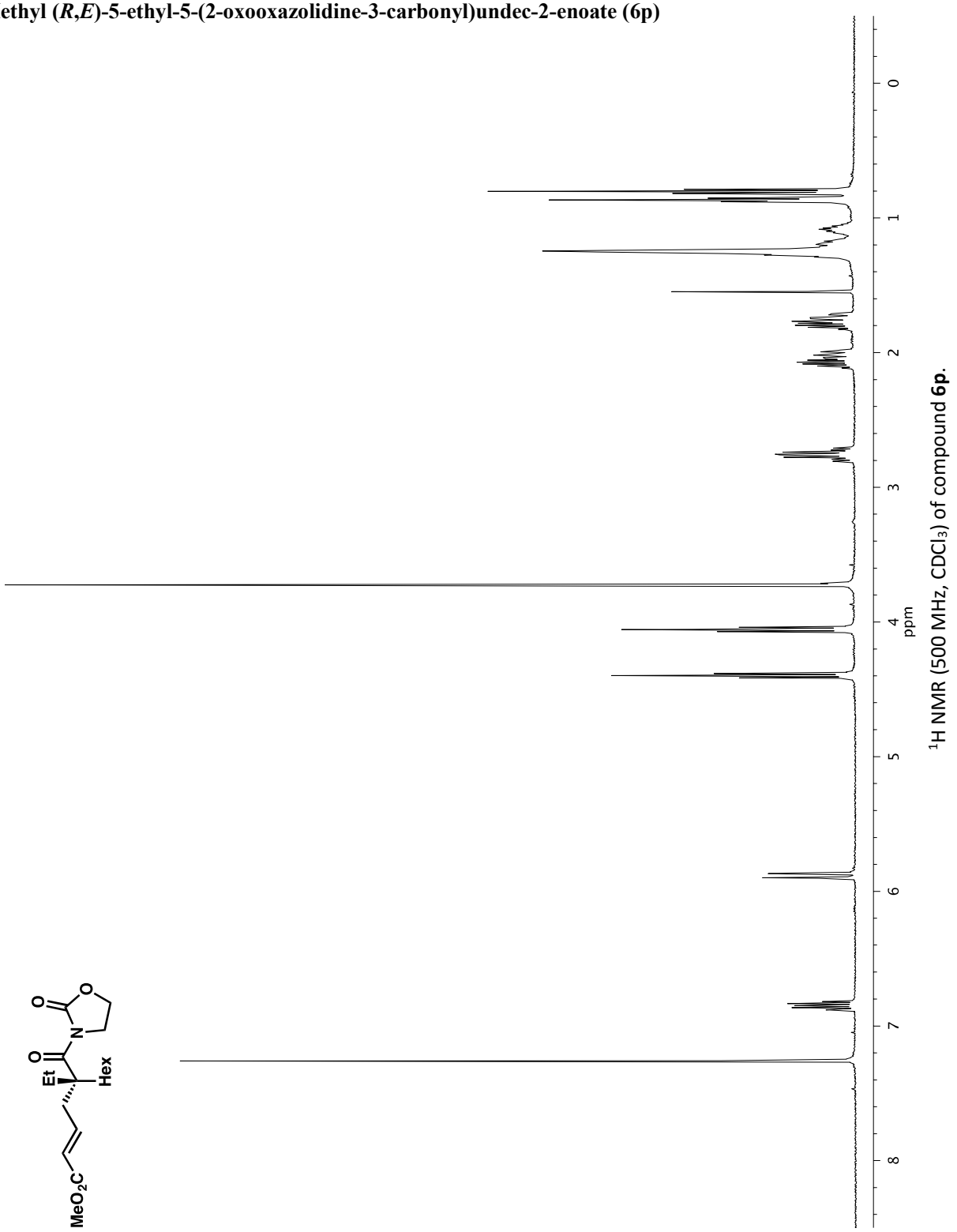


Infrared spectrum (Thin Film, NaCl) of compound **6o**.

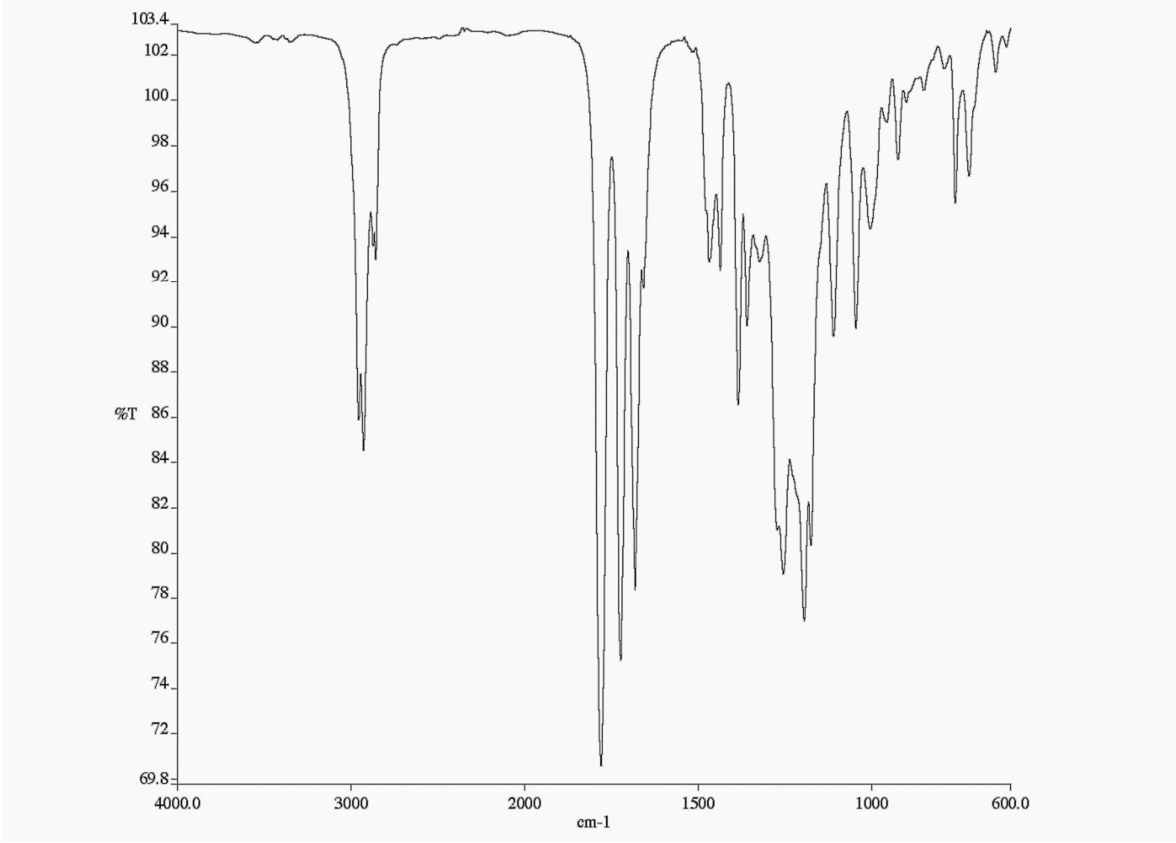


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6o**.

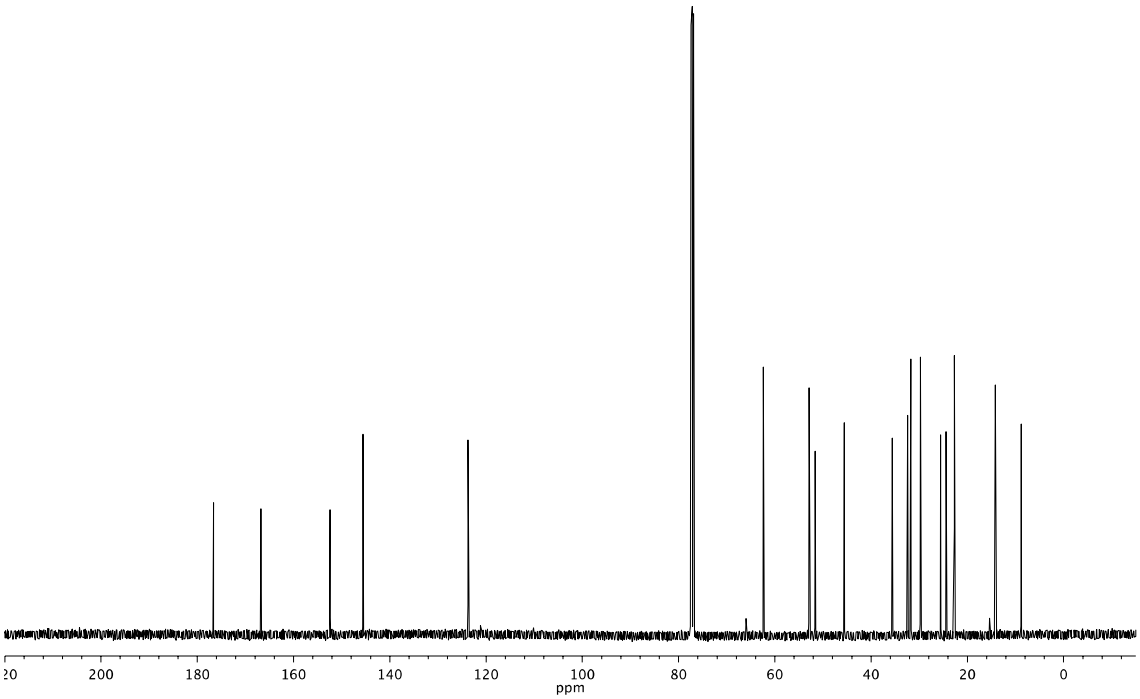
Methyl (*R*,*E*)-5-ethyl-5-(2-oxooxazolidine-3-carbonyl)undec-2-enoate (6p)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **6p**.

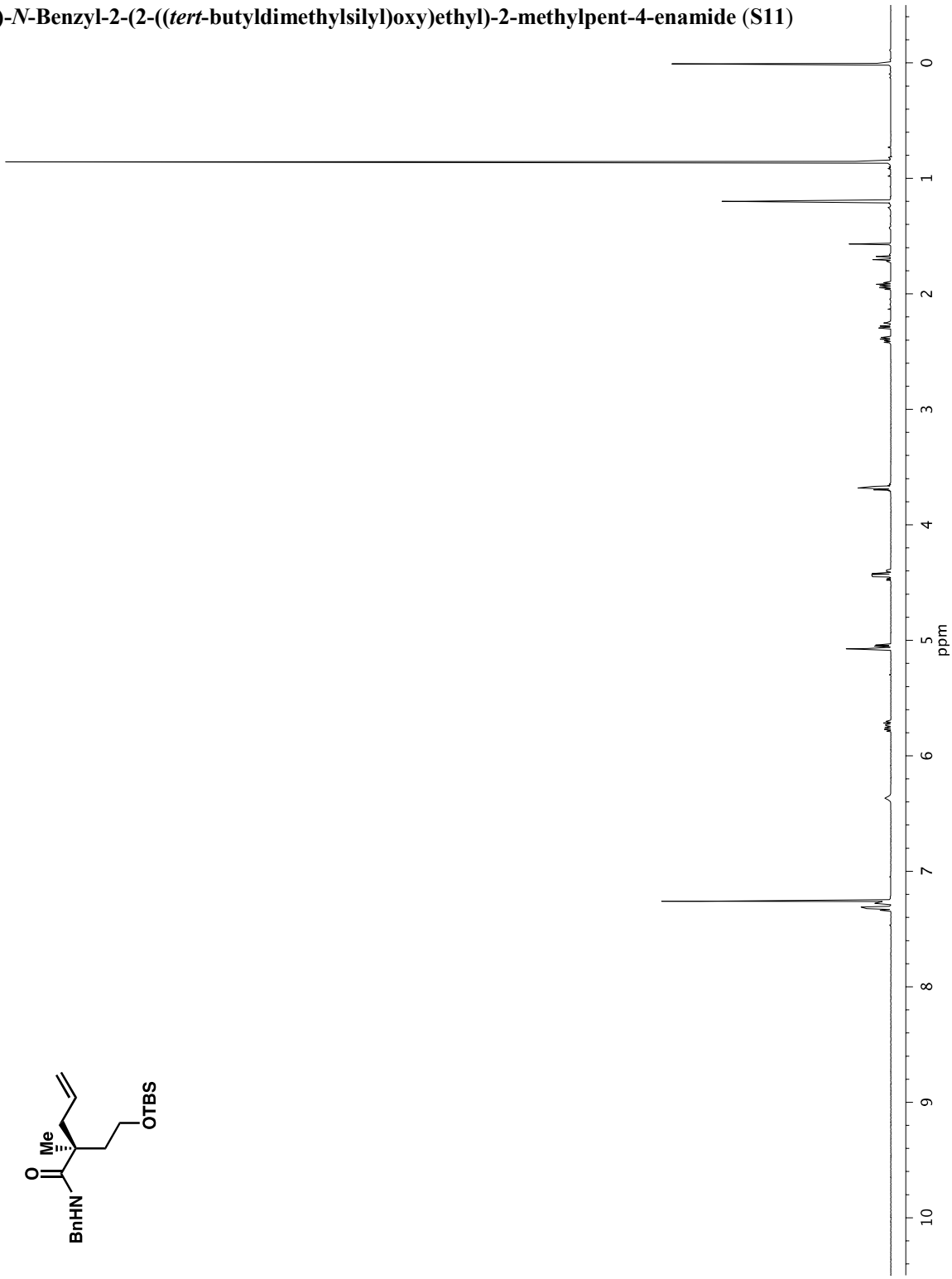


Infrared spectrum (Thin Film, NaCl) of compound **6p**

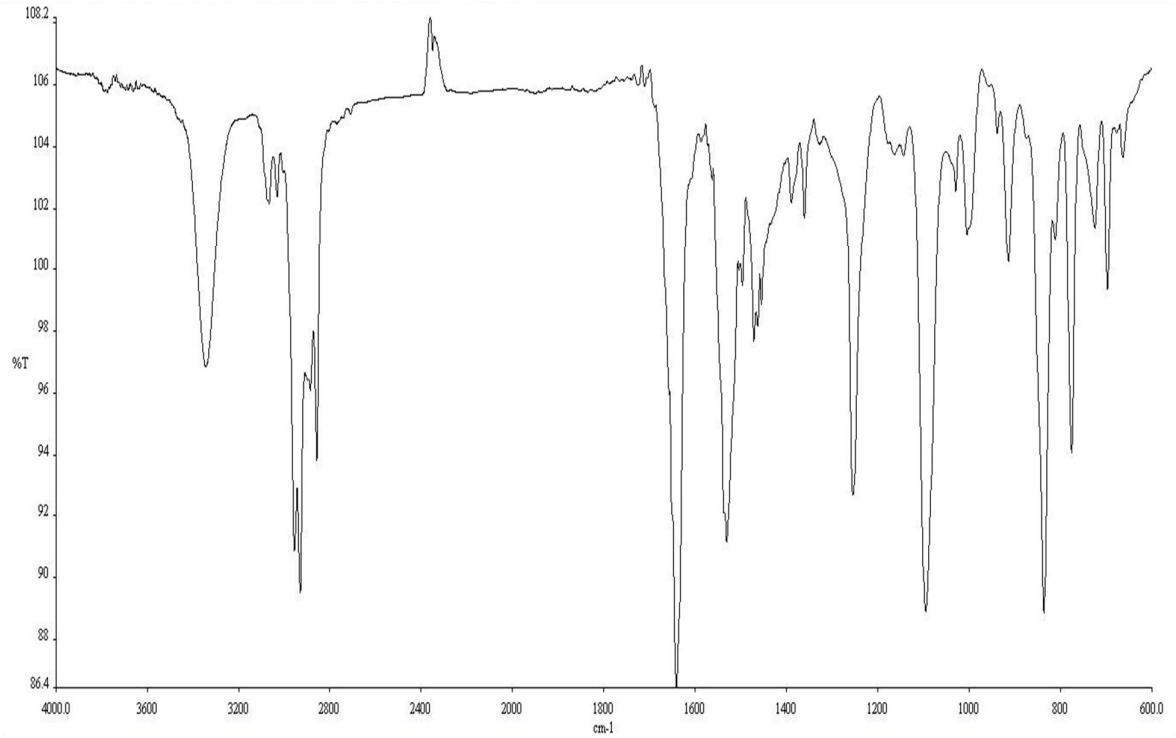


^{13}C NMR (126 MHz, $CDCl_3$) of compound **6p**.

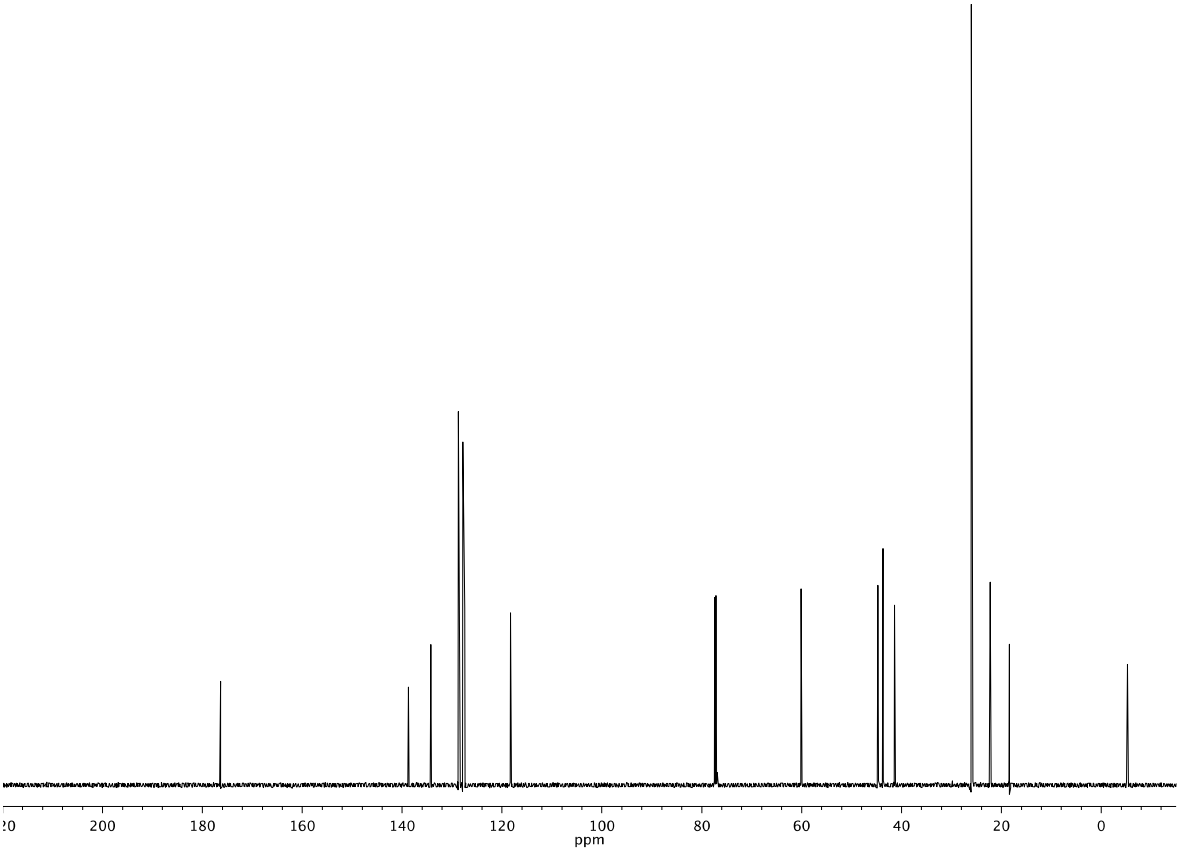
(*S*)-*N*-Benzyl-2-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-methylpent-4-enamide (S11)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **S11**.

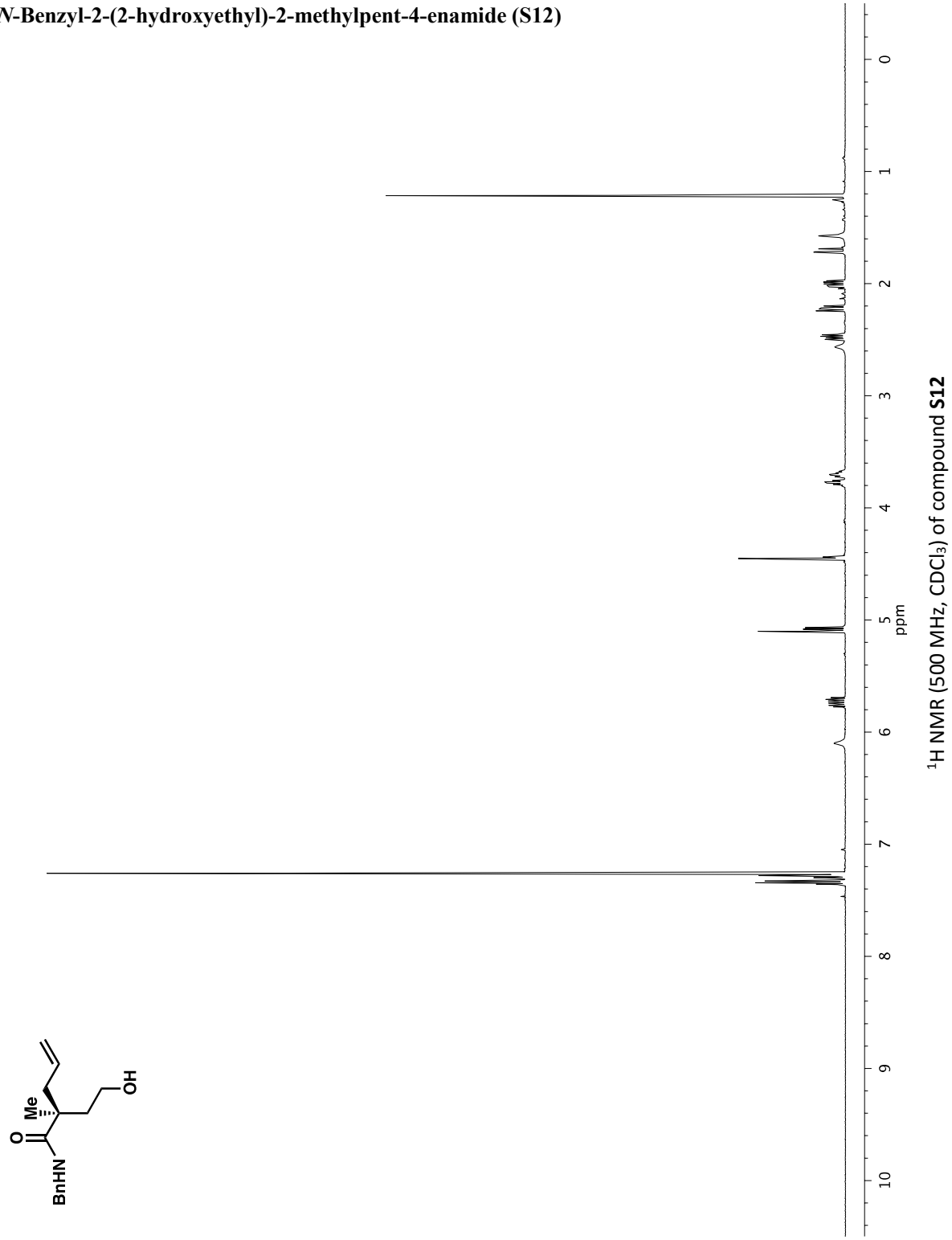


Infrared spectrum (Thin Film, NaCl) of compound **S11**.

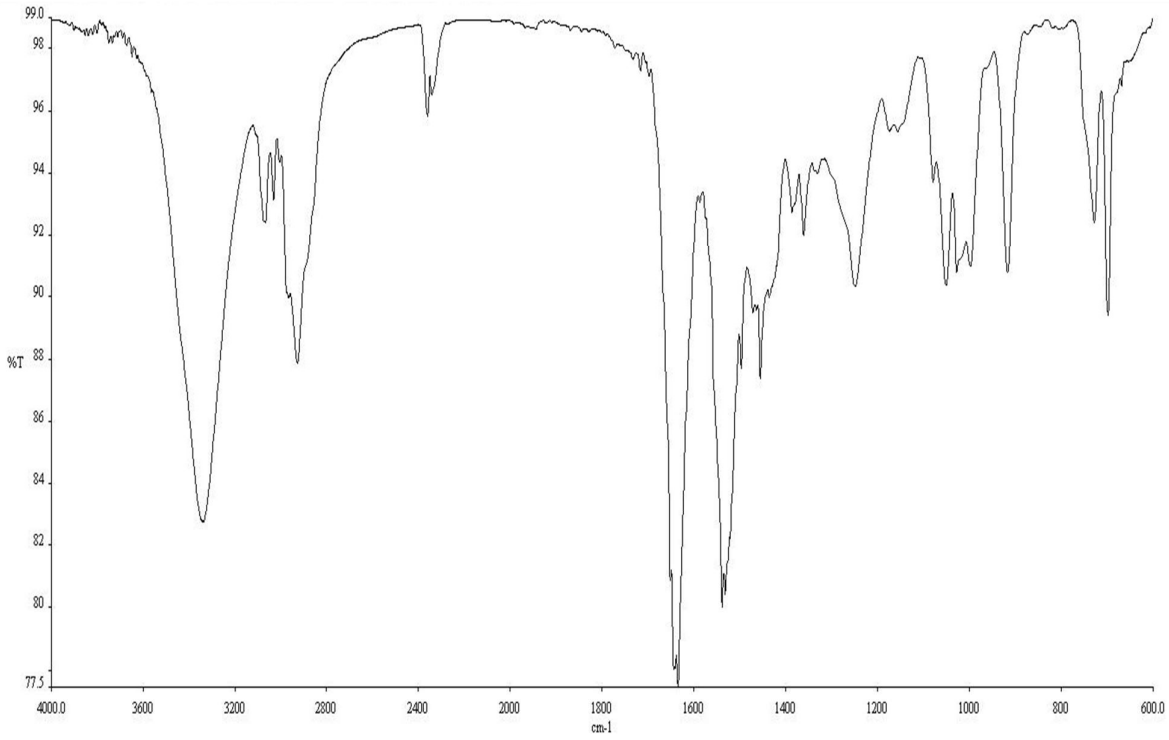


^{13}C NMR (126 MHz, $CDCl_3$) of compound **S11**.

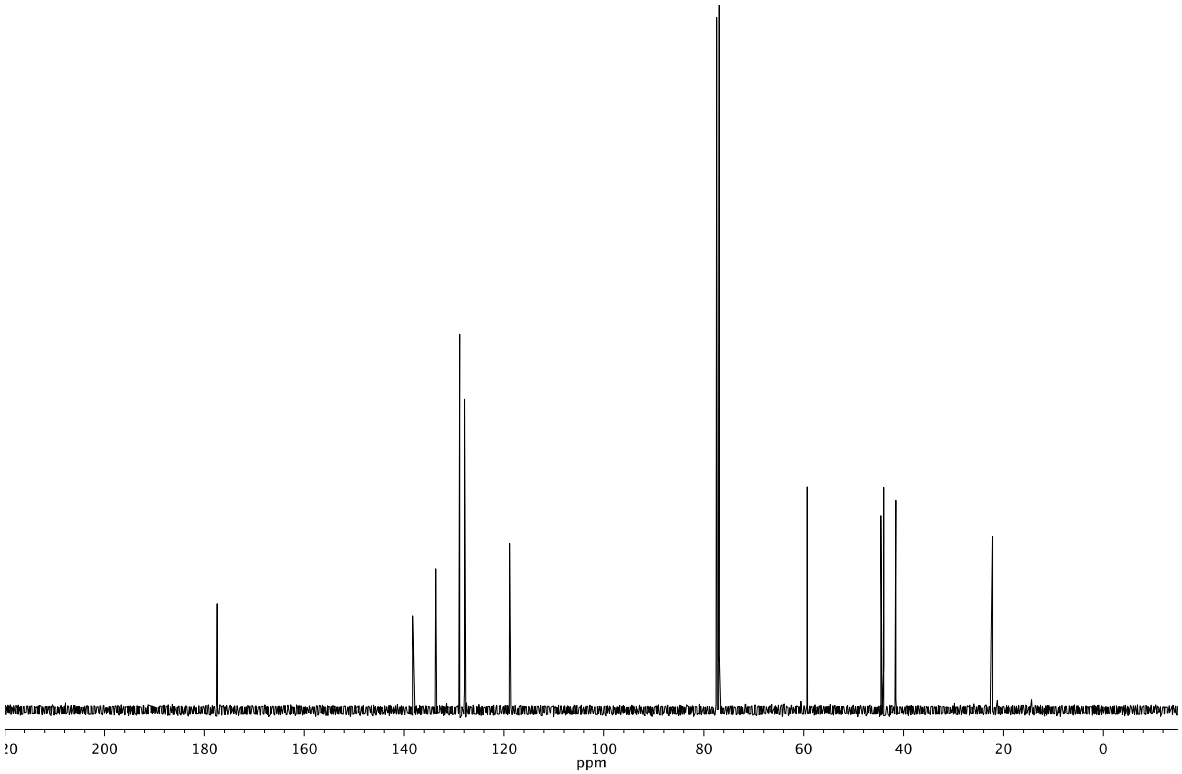
(*S*)-*N*-Benzyl-2-(2-hydroxyethyl)-2-methylpent-4-enamide (S12)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **S12**

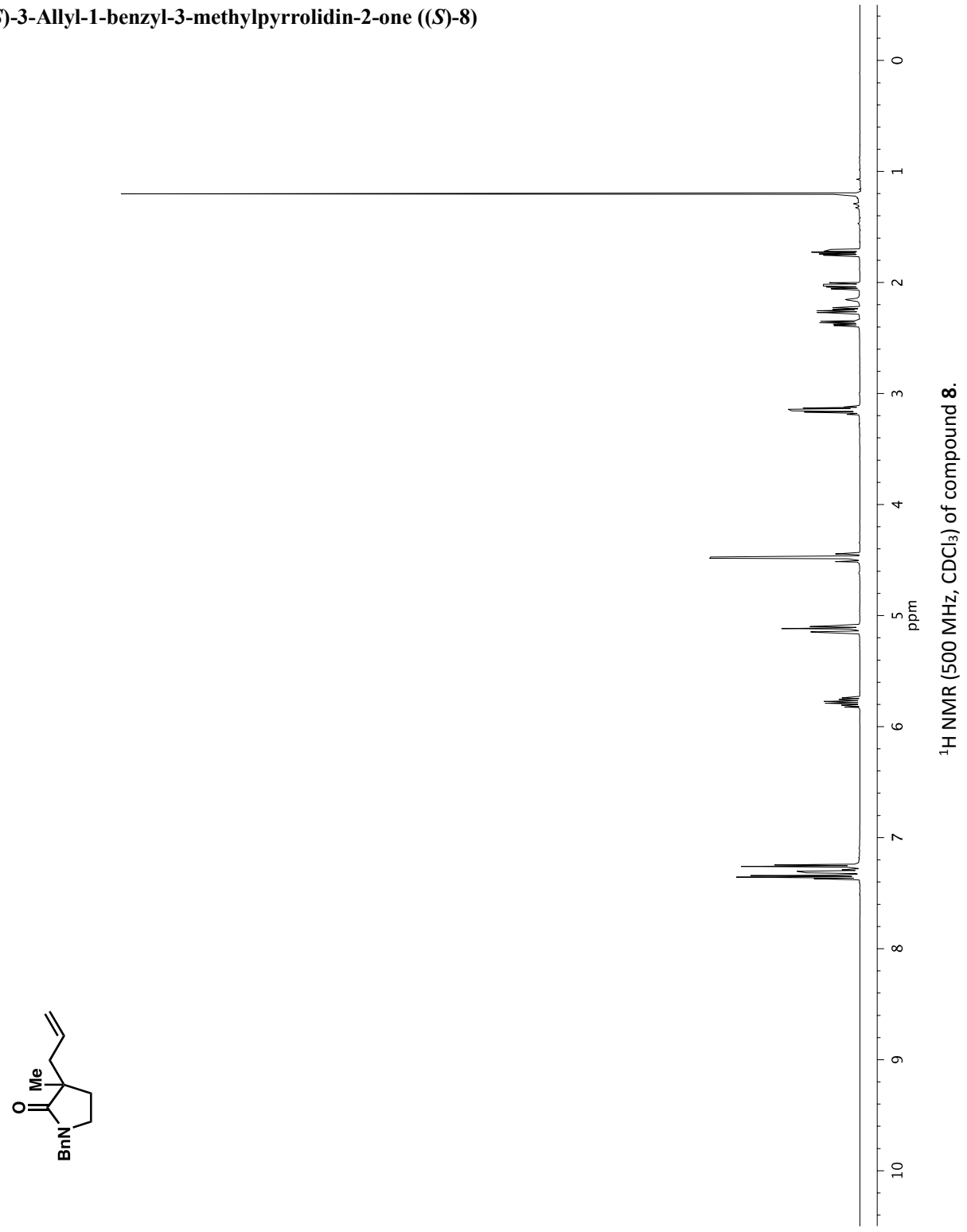


Infrared spectrum (Thin Film, NaCl) of compound **S12**.

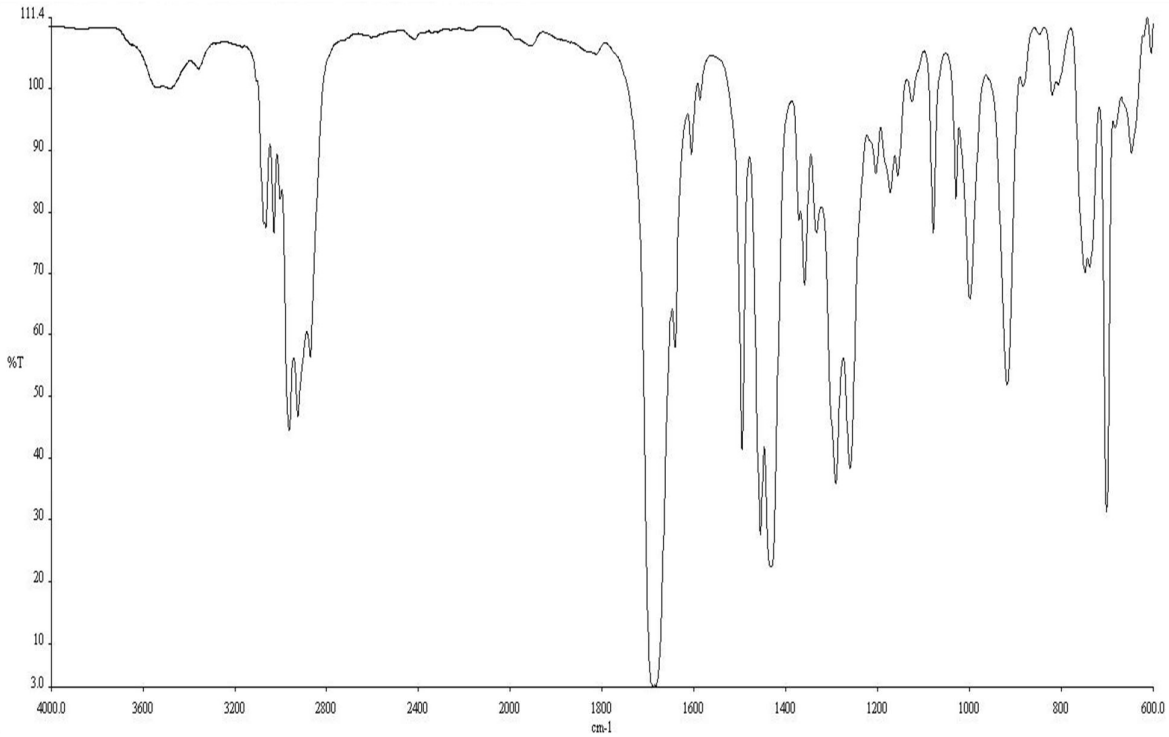


^{13}C NMR (126 MHz, $CDCl_3$) of compound **S12**.

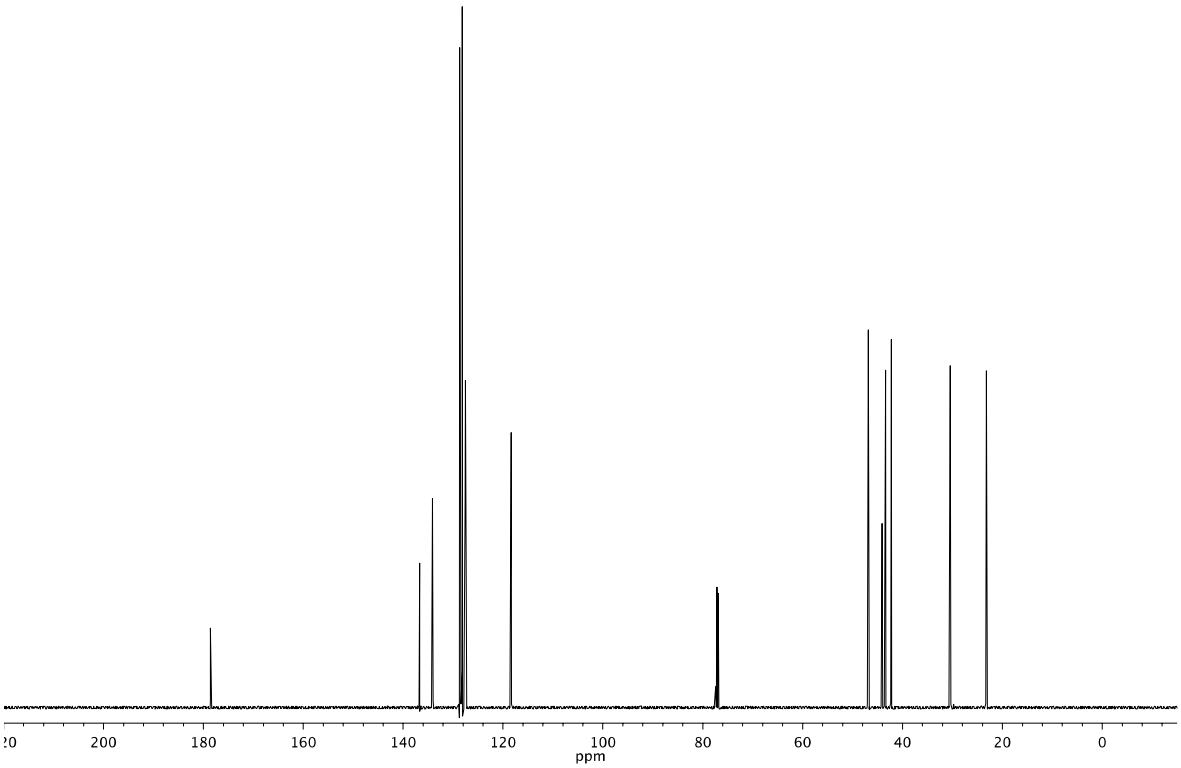
(*S*)-3-Allyl-1-benzyl-3-methylpyrrolidin-2-one ((*S*)-8)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.

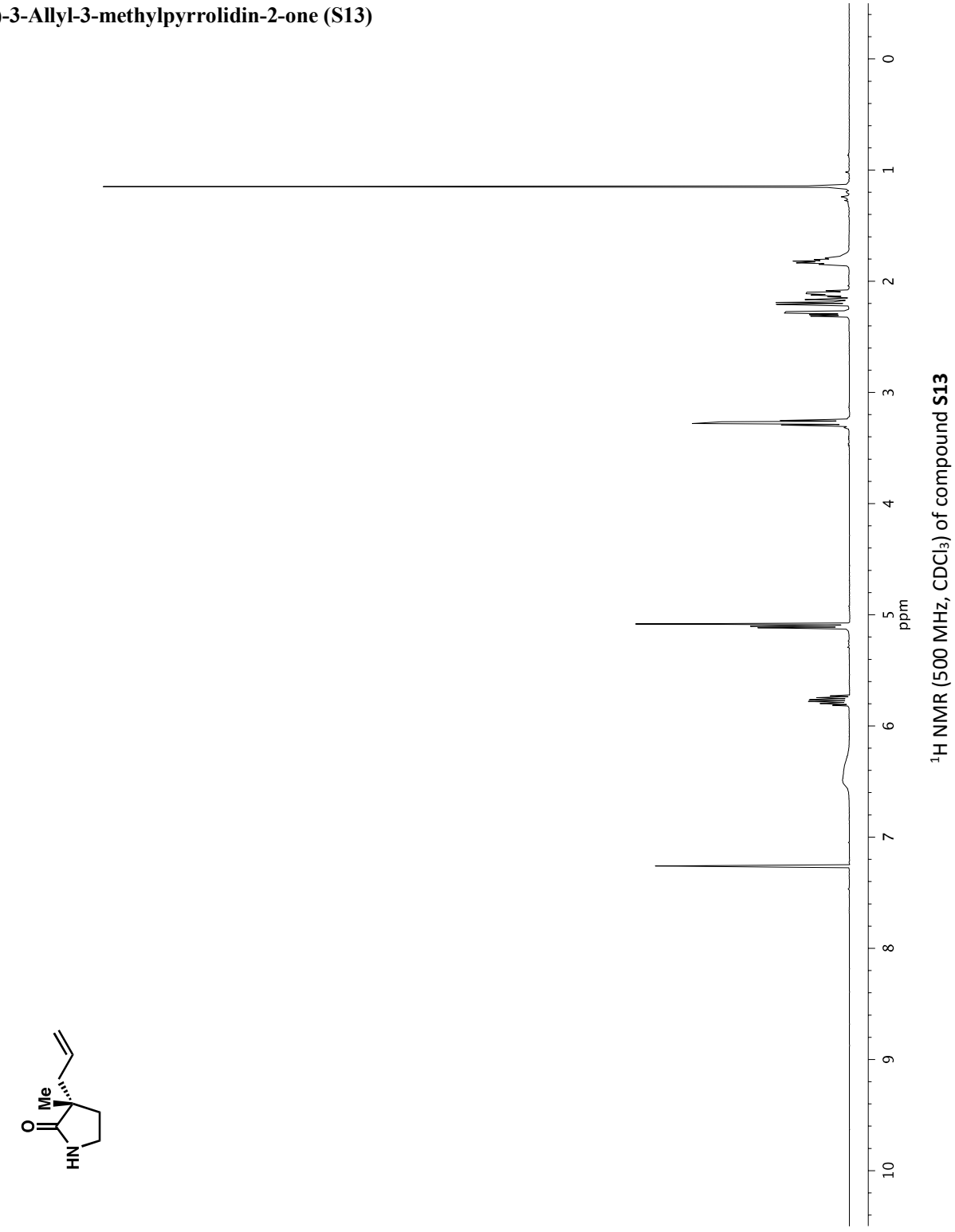


Infrared spectrum (Thin Film, NaCl) of compound **8**.

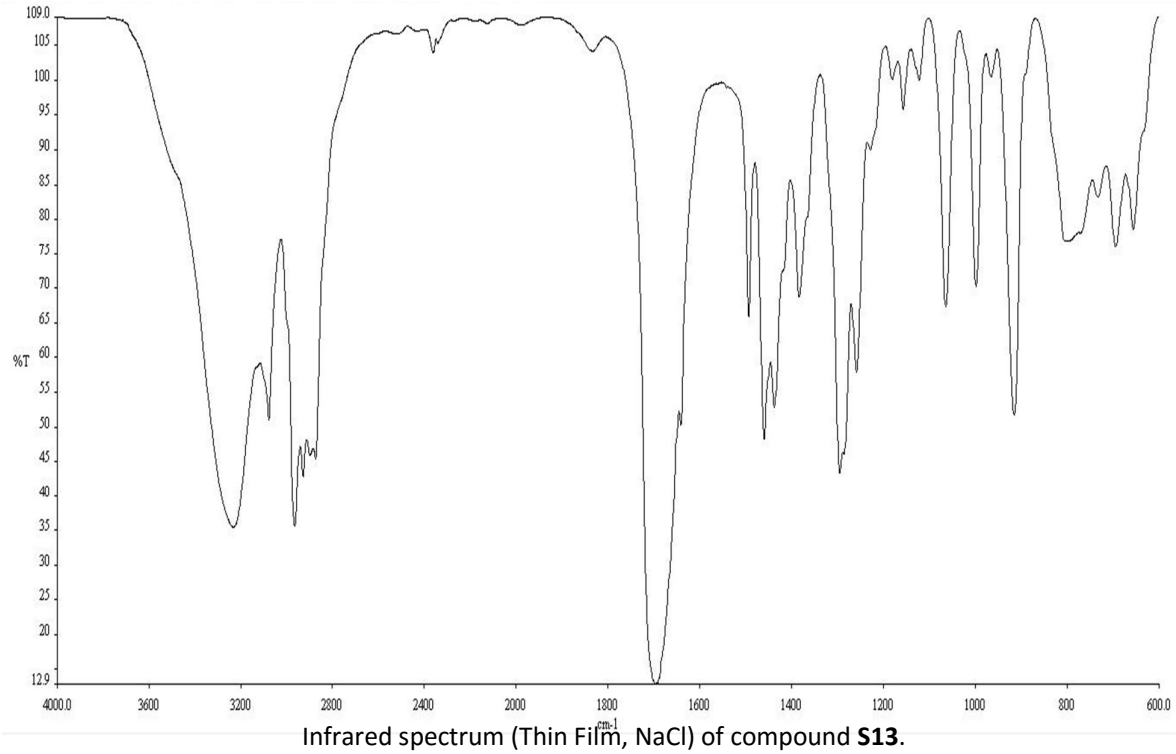


^{13}C NMR (126 MHz, $CDCl_3$) of compound **8**.

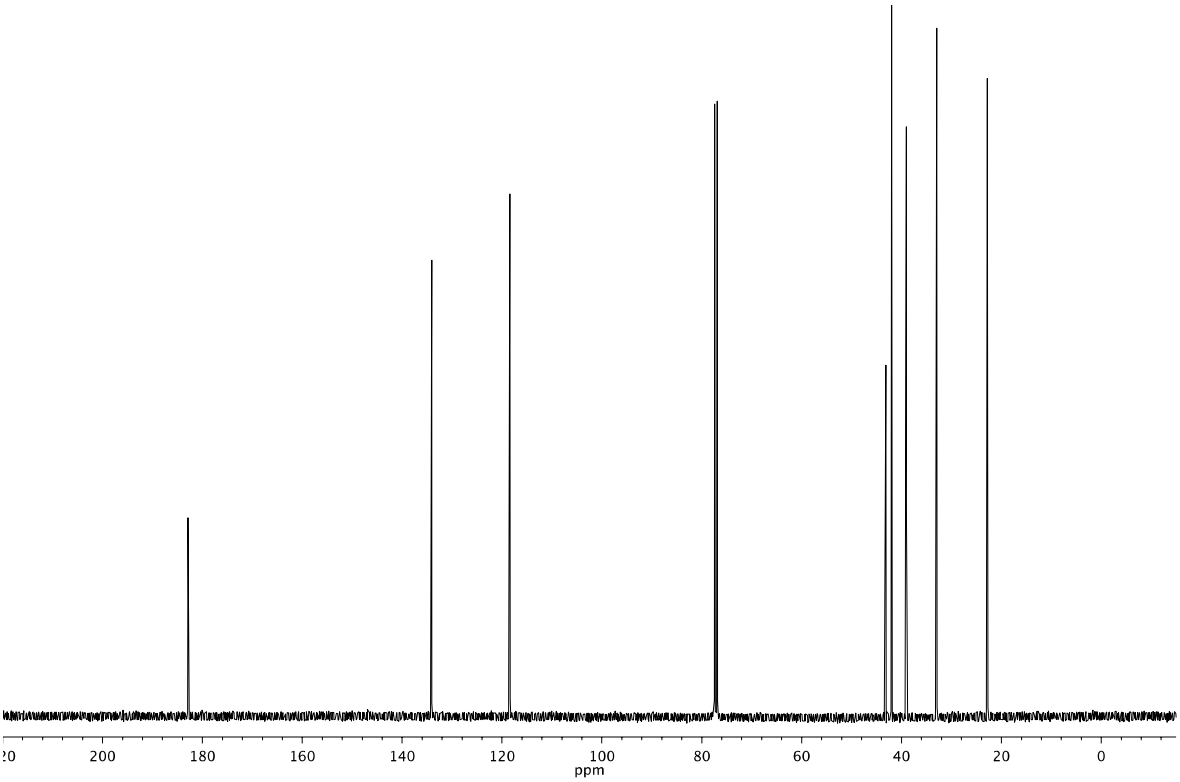
(*R*)-3-Allyl-3-methylpyrrolidin-2-one (S13)



^{1}H NMR (500 MHz, $CDCl_3$) of compound **S13**



Infrared spectrum (Thin Film, NaCl) of compound **S13**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **S13**.