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$SmCp^R_2$-mediated cross-coupling of allyl and propargyl ethers with ketoesters and a telescoped approach to complex cycloheptanols

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General information

Synthesis of water- and air-sensitive organometallic compounds: All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry argon. Solvents were dried by refluxing over potassium and were degassed before use. All solvents were stored over potassium mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles, and stored under argon. KH was obtained as a suspension in mineral oil and was washed three times with hexane and dried in *vacuo*.

Synthesis of non-air- and water-sensitive compounds: All experiments were performed under an atmosphere of nitrogen. THF was distilled from sodium/benzophenone and CH_2Cl_2 was distilled from CaH_2. All other solvents and reagents were purchased from commercial sources and used as supplied.

NMR yields were determined by ^{1}H NMR spectroscopy using a 1,2,4,5-tetrachloro-3-nitrobenzene as internal standard. All NMR spectroscopic experiments were performed at 298 K. ^{1}H NMR spectra were recorded at 400 or 500 MHz, ^{13}C NMR spectra were recorded at 100 or 125 MHz.. All chemical shift values are reported in parts per million (ppm) relative to the residual solvent signal and were determined in $CDCl_3$, C_6D_6 or pyridine-d_5 with coupling constant (J) values reported in Hz. The notation of signals is: Proton: δ chemical shift in ppm (multiplicity, J value (s), number of proton, proton assignment). Carbon: δ chemical shift in ppm (carbon assignment). Silicon: δ chemical shift in ppm (silicon assignment). Paramagnetic susceptibility and magnetic moments were evaluated according to Evans method.[1-3]

Column chromatography was carried out using 35 – 70 μm, 60 Å silica gel. Routine TLC analysis was carried out on silica gel 60 Å F254 coated aluminium sheets of 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp and immersed in $KMnO_4$ in EtOH and heated.

Low resolution and high resolution mass spectra were obtained using either positive and/or negative electrospray ionisation (ES), electron impact ionisation (EI) and chemical ionisation (CI) techniques. IR spectra of non-air- and moisture-sensitive compounds were recorded on an FTIR spectrometer as evaporated films (from $CDCl_3$) or as neat liquids. For air- and

moisture-sensitive compounds FTIR spectra were recorded as Nujol mulls in KBr discs on a PerkinElmer Spectrum RX1 spectrometer.

Cyclic voltammetry

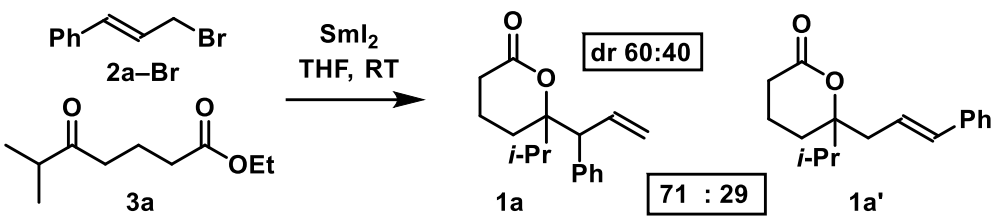
Cyclic voltammograms were collected for **5a** and **5e** at 1mM concentration in a 0.1 M $[N^nPr_4][BArF_{24}]$ THF solution. However, no data could be obtained for **5a** and **5e**, presumably because of immediate and irreversible degradation under our experimental setup, despite repeated attempts. All experiments were initially assessed at the open-circuit potential, and all voltammograms exhibited irreversible oxidation events; such peaks are very weak even at high scan rates and could be tentatively assigned as ligand-based processes.

List of known compounds and procedures

The following compounds are known and were prepared according to already published procedures. Cyclopentadiene neutral ligands: $C_5H_4(SiMePh_2)$,[4] $C_5H_4(SiPh_3)$;[5] potassium and sodium salts of cyclopentadienyl ligands: $K[C_5Me_5]$,[6] $[K\{C_5H_3(SiMe_3)_3\}]$-1,3],[7] $K[\{C_5H_2(SiMe_3)_3$-1,2,4$\}]$,[7] $Na[C_5H_5]$;[8] samarium (II) cyclopentadienyl complexes: $[Sm\{C_5Me_5\}(THF)_2]$,[9] $[Sm\{C_5H_3(SiMe_3)_3$-1,3$\}_2(THF)]$,[10] $[Sm\{C_5H_5\}]$;[11] allylic and propargylic benzyl ethers: **2b,**[12] **2b'**,[13] **2c**,[14] **2d**;[15] δ-Keto esters: **3a**,[16] **3c**,[17] **3d,**[18] **3e**.[17] The following new compounds described below were prepared according to known procedures: potassium cyclopentadienyl ligands,[7] samarium (II) cyclopentadienyl complexes,[9] δ-keto acids and δ-keto esters.[16,19]

Additional experiments

Unsuitability of SmI_2 for the Barbier step



We studied the first stage of the process and the illustrative cross-coupling of allylbromide **1a-Br** and ketoester **3a.** From the outset it was clear that Kagan's classical Sm(II) ET reagent, SmI_2, gave unsatisfactory results in the coupling-lactonization: the desired lactone **1a** was obtained with poor diastereocontrol (dr 60:40) and significant quantities of regioisomer **1a'** were also obtained.

Incompatibility of transition metal additives

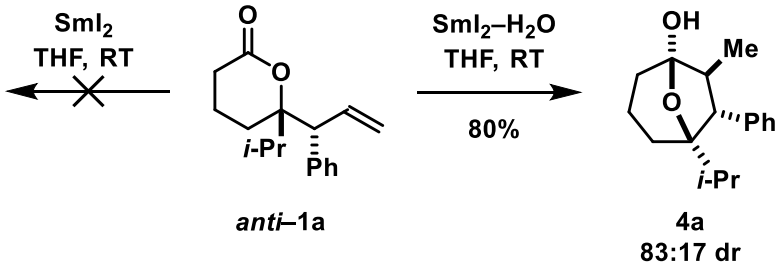
Various transition metal additives and reagents commonly used in Barbier reactions were tested for their compatibility with the SmI_2-H_2O system. In all cases the additive had a detrimental effect, causing an accelerated decay of Sm(II).

To a vial charged with the metal compound (0.014 mmol, 2 mol%) under nitrogen were added a 0.1 M solution of SmI_2 in THF (7 mL, 0.70 mmol), followed by H_2O (1.3 mL, 10.0 mmol). The resulting mixture was stirred at room temperature.

Metal source	Time to decolourization (min)	H_2 evolution
$TiCl_4$	40	Very slow
$FeBr_3$	< 1	Fast
$[IrCl(COD)_2]$	< 1	Fast
NiI_2	< 1	Fast
$HgCl_2$	180[a]	Not observed
$SnCl_2$	180[a]	Very slow

[a] The mixture turned from dark red to brown.

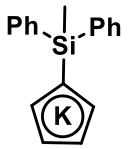
Tailoring of Sm(II) reagent for the lactone cyclization step



The requirements of the second stage of the telescoped sequence were assessed. As expected, ***anti*-1a** was unchanged after treatment with SmI_2 alone. It was required to tailor the Sm(II) reagent by adding H_2O to obtain a new reagent capable of achiving ET to the lactone carbonyl. Thus, when treated with SmI_2-H_2O, ***anti*-1a** yielded **4a** in excellent yield and with good diastereocontrol.

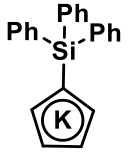
Synthesis of cyclopentadienyl ligands and $SmCp^R_2$ complexes

[K{C_5H_4($SiMePh_2$)}] ($Cp^{DPMS}K$) S1



General procedure A. Crude ($MePh_2Si)C_5H_5$ (6.45 g, 24.6 mmol) was dried overnight over 4 Å molecular sieves, dissolved in toluene (10 mL) and cooled to -78 ˚C followed by drop-wise addition of KHMDS (3.92 g, 19.7 mmol) in toluene (30 mL). The reaction mixture was allowed to warm to room temperature and stirring was continued overnight to give a pale pink precipitate which was filtered on a frit and washed with hexanes (2 × 10 mL) to give a pale pink powder (5.60 g, 18.6 mmol, 95%) which was used in the next step without further purification. Analytically pure compound was obtained by recrystallization from THF to give the monosolvated THF complex as white needles. ^{1}H NMR (400 MHz, THF-d_8) δ 0.64 (s, 3 H, SiCH_3), 1.78 (br s, 4 H, THF-C$H_2$$CH_2$O), 3.62 (br s, 4 H, THF-CH_2CH_2O), 5.82 (d, *J* = 1.8 Hz, 2 H, Cp_{Ar}C*H*), 5.98 (d, *J* = 1.5 Hz, 2 H, Cp_{Ar}C*H*), 7.14 – 7.29 (m, 6 H, ArC*H*), 7.47 – 7.63 (m, 4 H, ArC*H*) ppm. ^{13}C NMR (100 MHz, THF-d_8) δ -1.2 (Si*C*H_3), 25.9 (THF-*C*$H_2$$CH_2$O), 68.1 (THF-$CH_2$*C*$H_2$O), 105.1 ($Cp_{Ar}$*C*), 109.5 ($Cp_{Ar}$*C*H), 115.1 ($Cp_{Ar}$*C*H), 128.1 (Ar*C*H), 128.5 (Ar*C*H), 135.8 (Ar*C*H), 143.4 (Ar*C*). Anal calcd for $C_{22}H_{25}KOSi$: C, 70.91 %; H 6.76 %. Found: C, 70.73 %; H, 6.47%.[20] FTIR (Nujol,cm^{-1}): = ν 1105 (s), 1040 (s), 783 (s).

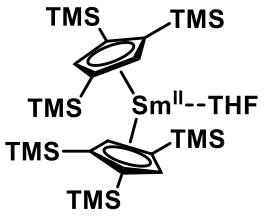
[K{C_5H_4($SiPh_3$)}] ($Cp^{TPS}K$) S2



This compound was synthesised according to general procedure A using crude ($SiPh_3)C_5H_5$ (5.00 g, 15.4 mmol) and KHMDS (2.27 g, 11.4 mmol) to give a pale yellow powder (3.84 g, yield, 10.6 mmol, 93%) which was used in the next step without further purification. Analytically pure compound was obtained by recrystallization from THF to give monosolvated THF complex as pale-yellow needles. ^{1}H NMR (500 MHz, THF-d_8) δ 1.68 – 1.84 (m, 4 H, THF-C$H_2$$CH_2$O), 3.55 – 3.68 (m, 4 H, THF-CH_2CH_2O), 5.90 (br s, 2 H,

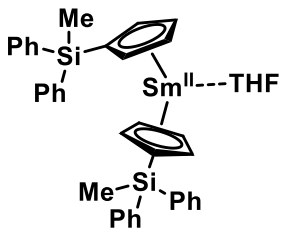
$Cp_{Ar}CH$), 6.07 (br d, *J* = 2.2 Hz, 2 H, $Cp_{Ar}CH$), 7.15 – 7.29 (m, 9 H, ArC*H*), 7.51 – 7.62 (m, 6 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, THF-d_8) δ 26.6 (THF-CH_2CH_2O), 68.4 (THF-CH_2CH_2O), 102.5 ($Cp_{Ar}C$), 109.8 ($Cp_{Ar}CH$), 116.6 ($Cp_{Ar}CH$), 128.9 (Ar*C*H), 128.74 (Ar*C*H), 137.10 (Ar*C*H), 141.55 (Ar*C*) ppm. Anal calcd for $C_{27}H_{27}KOSi$: C, 74.60 %; H 6.26 %. Found: C, 71.84 %; H, 6.27 %.[20] FTIR (Nujol,cm^{-1}): = ν 2360 (s), 2341 (s), 1259 (s), 1182 (m), 1103 (s), 1053 (s), 1033 (s), 798 (s), 733 (s).

[Sm{$C_5H_2(SiMe_3)_3$-1,2,4}$_2$(THF)] ($Cp'''_2Sm(THF)$) 5c



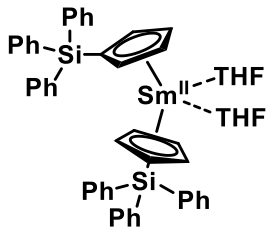
General procedure B. To a dark blue suspension of $SmI_2(THF)_2$ (2.19 g, 4.00 mmol) in THF (10 mL), K[1,2,4-$(Me_3Si)_3C_5H_2$] (2.69 g, 8.40 mmol) in THF (15 mL) was added dropwise at -78 ˚C to give a dark purple solution. The reaction mixture was allowed to warm to room temperature and stirred overnight. The white precipitate was allowed to settle over 2 h and the solution was filtered and concentrated under vacuum. The crude solid was re-dissolved in toluene (10 mL), stirred for 1 h, filtered and concentrated *in vacuo* to give a dark green foam. The product was crystallized from hexanes as dark green crystals (1.48 g, 1.99 mmol, 48 % from one crop). ^1H NMR (400 MHz, C_6D_6) δ ppm -2.16 (s, 2 H, $Cp_{Ar}CH$), -0.25 - 0.49 (m, 4 H, THF-CH_2CH_2O), 3.12 (s, 4 H, THF-CH_2CH_2O), 4.19 (s, 36 H, $Si(CH_3)_3$ × 4), 5.89 (s, 2 H, $Cp_{Ar}CH$), 13.00 (s, 18 H, $Si(CH_3)_3$ × 2) ppm. Anal calcd for $C_{32}H_{66}OSi_6Sm$: C, 48.92 %; H, 8.47 %. Found: C, 43.81 %; H, 8.08 %.[20] Magnetic susceptibility: χ_M = 5183 x 10^{-6} cgs; μ_{eff} = 3.65 μ_B. FTIR (Nujol,cm^{-1}): = ν 1259 (m), 1091 (m), 1020 (m), 833 (s), 752 (s).

[Sm{$C_5H_4(SiMePh_2)$}$_2$(THF)] ($Cp^{DPMS}{}_2Sm(THF)$) 5e



Synthesized according to a general procedure B using $SmI_2(THF)_2$ (5.48 g, 10.0 mmol) and [K{$C_5H_4(SiMePh_2)$}] (5.00 g, 21.0 mmol). The product was crystallized from toluene/THF as dark purple crystals (5.54 g, 7.43 mmol, 74% from two crops). ^{1}H NMR (400 MHz, C_6D_6/THF-d_8) δ 1.40 (s, 4 H, THF-CH_2CH$_2$O), 4.14 (s, 4 H, THF-CH$_2$CH_2O), 5.89 (s, 6 H, SiCH_3), 8.15 (s, 4 H, ArC*H*), 8.78 (s, 8 H, ArC*H*), 10.88 (s, 8 H, ArC*H*), 11.55 (s, 4 H, Cp$_{Ar}$C*H*), 16.26 (s, 4 H, Cp$_{Ar}$C*H*). Magnetic susceptibility: χ_M = 5305 x 10^{-6} cgs; μ_{eff} = 3.69 μ_B. Anal calcd for $C_{40}H_{42}OSi_2Sm$: C, 64.46 %; H, 5.68 %. Found: C, 63.16 %; H, 5.64 %.[20] FTIR (Nujol,cm^{-1}): = ν 1529 (s), 1103 (m), 1036 (m), 792 (s), 698 (s).

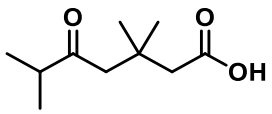
[Sm{$C_5H_4(SiPh_3)$}$_2$(THF)$_2$] (Cp$^{TPS}_2$Sm(THF)$_2$) 5f



Synthesized according to general procedure B using $SmI_2(THF)_2$ (0.92 g, 1.67 mmol) and K[($SiPh_3$)C_5H_4] (1.21 g, 3.34 mmol). The product was crystallized from THF/Hexane as dark purple crystals (0.65 g, 0.69 mmol, 41 % from two crops). ^{1}H NMR (400 MHz, C_6D_6) δ 0.22 (s, 8 H, THF-CH_2CH$_2$O), 2.12 (s, 8 H, THF-CH$_2$CH_2O), 3.38 (s, 4 H, Cp$_{Ar}$C*H*), 8.02 (s, 6 H, ArC*H*), 10.71 (s, 12 H, ArC*H*), 16.11 (s, 12 H, ArC*H*), 20.06 (s, 4 H, Cp$_{Ar}$C*H*) ppm. Magnetic susceptibility: χ_M = 4280 x 10^{-6} cgs; μ_{eff} = 3.37 μ_B. Anal calcd for $C_{54}H_{54}O_2Si_2Sm$: C, 68.89 %; H, 5.78 %. Found: C, 67.73 %; H, 5.78 %.[20] FTIR (Nujol,cm^{-1}): = ν 1529 (s), 1103 (m), 1036 (m), 792 (s), 698 (s).

Synthesis of δ-Keto acids and δ-Keto esters

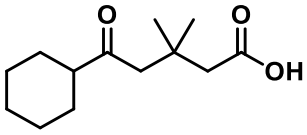
3,3-Dimethyl-5-oxo-5-isopropylpentanoic acid S3



General procedure C. 3,3-Dimethylglutaric anhydride (2.77 g, 19.5 mmol) and Fe(acac)$_3$ (0.28 g, 0.78 mmol) were dissolved in THF (20 mL) and the solution cooled to 0 ℃. A

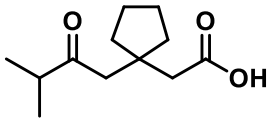
solution of isopropylmagnesium chloride (8.4 mL, 16.2 mmol, 1.93 M in Et_2O) was added by syringe pump over 45 min and the reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction was quenched at 0 ℃ with 2 M HCl (30 mL) and extracted with Et_2O (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography eluting with *i*-PrOH/petroleum ether/AcOH (10:90:0.005) to give a colorless oil (2.31 g, 12.4 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.11 (s, 6 H, C(C*H*$_3$)$_2$), 2.53 (s, 2 H, C*H*$_2$C(O)O), 2.57 (spt, *J* = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.61 (s, 2 H, C*H*$_2$C(O)) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0 (CH(*C*H$_3$)$_2$), 28.3 (C(*C*H$_3$)$_2$), 32.6 (*C*(CH$_3$)$_2$), 42.0 (*C*H(CH$_3$)$_2$), 44.4 (*C*H$_2$C(O)O), 49.3 (*C*H$_2$C(O)), 177.9 (*C*(O)O), 214.8 (*C*(O)) ppm. IR (neat)/cm^{-1} 2966, 1703 (C=O), 1466, 1383, 1366, 1243, 1048, 930. HRMS calcd for $C_{10}H_{19}O_3$ $[M + H]^+$ 187.1329, found 187.1324.

5-Cyclohexyl-3,3-dimethyl-5-oxopentanoic acid S4



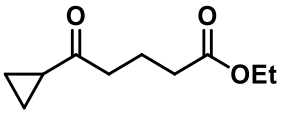
Prepared according to general procedure C using 3,3-dimethylglutaric anhydride (0.74 g, 5.20 mmol), Fe(acac)$_3$ (0.073 g, 0.20 mmol) and cyclohexylmagnesium chloride (2.42 mL, 4.72 mmol, 1.95 M in Et_2O) to give the title compound as a white solid (0.95 g, 4.20 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.11 (s, 6 H, C(C*H*$_3$)$_2$), 1.16 – 1.37 (m, 5 H, *c*-HexC*H*$_2$), 1.62 – 1.72 (m, 1 H, *c*-HexC*H*$_2$), 1.75 – 1.88 (m, 4 H, *c*-HexC*H*$_2$), 2.28 – 2.38 (m, 1 H, *c*-HexC*H*(CH$_2$)), 2.51 (s, 2 H, C*H*$_2$C(O)O), 2.59 (s, 2 H, C*H*$_2$C(O)), 10.52 (br s, 1 H, C(O)O*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 25.6 (*c*-Hex*C*H$_2$), 25.8 (*c*-Hex*C*H$_2$), 28.2 (C(*C*H$_3$)$_2$), 28.5 (*c*-Hex*C*H$_2$), 33.0 (*C*(CH$_3$)$_2$), 44.6 (*C*H$_2$C(O)O), 49.5 (*C*H$_2$C(O)), 52.4 (*c*-Hex*C*H(CH$_2$)$_2$), 175.6 (*C*(O)OH), 215.5 (*C*(O)) ppm. IR (neat)/cm^{-1} 2929, 2854, 1703 (C=O), 1449, 1368, 1239, 1144, 1065, 932. M.p ($CHCl_3$) = 61 – 63 ˚C. HRMS calcd for $C_{13}H_{23}O_3$ $[M + H]^+$ 227.1642, found 227.1635.

3,3-Tetramethylene-5-oxo-5-isopropylpentanoic acid S5



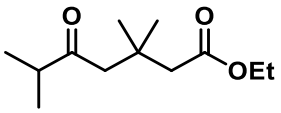
Prepared according to general procedure C using 3,3-tetramethyleneglutaric anhydride (2.0 g, 11.9 mmol), $Fe(acac)_3$ (0.13 g, 0.368 mmol) and isopropylmagnesium chloride (5.16 mL, 9.91 mmol, 1.92 M in Et_2O) to give title compound as a colorless oil (1.77 g, 8.34 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, *J* = 7.1 Hz, 6 H, $CH(CH_3)_2$), 1.44 – 1.58 (m, 2 H, *c*-PenCH_2), 1.58 – 1.74 (m, 6 H, *c*-PenCH_2), 2.57 (spt, *J* = 6.9 Hz, 1 H, $CH(CH_3)_2$), 2.61 (s, 2 H, $CH_2C(O)O$), 2.75 (s, 2 H, $CH_2C(O)$), 11.31 (br s, 1 H, C(O)O*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2 ($CH(CH_3)_2$), 23.9 (*c*-PenCH_2 × 2), 38.5 (*c*-PenCH_2 × 2), 41.4 ($CH_2C(O)O$), 41.7 ($C(CH_2)_4$), 42.8 ($CH(CH_3)_2$), 47.6 ($CH_2C(O)$), 178.1 (*C*(O)OH), 215.1 (*C*(O)) ppm. IR (neat)/cm^{-1} 2961, 2872, 1701, 1459, 1400, 1383, 1361, 1296, 1228, 1172, 1102, 1047, 929, 617. HRMS calcd for $C_{12}H_{21}O_3$ $[M + H]^+$ 213.1485, found 213.1484.

Ethyl 5-oxo-5-cyclopropylpropylpentanoate 3b



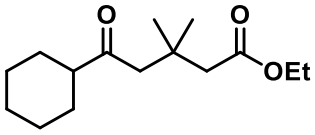
To a stirred solution of glutaric acid monomethyl ester chloride (0.55 mL, 4.40 mmol) and CuI (0.08 g, 0.42 mmol) in THF (10 mL), cyclopropylmagnesium chloride (8.5 mL, 0.47 M in Et_2O was added during 1 h at -15 ℃. After addition was complete, reaction was stirred for an additional 1 h at -15 ℃ and quenched with sat. NH_4Cl. The phases were separated and the aqueous layer washed with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give an orange oil which was purified by flash chromatography eluting with EtOAc/Hexane (3:97 to 5:95) to give a colorless oil (0.42 g, 2.27 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 – 0.91 (m, 2 H, *c*-PrCH_{2a}), 0.97 – 1.06 (m, 2 H, *c*-PrCH_{2b}), 1.26 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.88 – 1.96 (m, 3 H, 1 H from *c*-Pr$CH(CH_2)_2$, 2 H from $CH_2CH_2C(O)O$), 2.33 (t, *J* = 7.3 Hz, 2 H, $CH_2CH_2C(O)O$), 2.62 (t, *J* = 7.3 Hz, 2 H, $CH_2C(O)$), 4.13 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 10.6 (*c*-PrCH_2), 14.2 (OCH_2CH_3), 19.1 ($CH_2CH_2C(O)O$), 20.4 (*c*-Pr$CH(CH_2)_2$), 33.4 ($CH_2CH_2C(O)O$), 42.2 ($CH_2C(O)$), 60.3 (OCH_2CH_3), 173.2 (*C*(O)O), 210.0 (*C*(O)) ppm. IR (neat)/cm^{-1} 2981, 1730 (C=O), 1696, 1446, 1389, 1310, 1247, 1180, 1104, 1087, 1020, 898, 858, 817. HRMS calcd for $C_{10}H_{16}O_3Na$ $[M + Na]^+$ 207.0992, found 207.0986.

Ethyl 3,3-dimethyl-5-oxo-5-isopropylpentanoate 3g



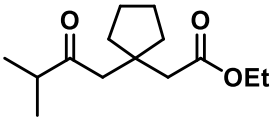
General procedure D. 3,3-Dimethyl-5-oxo-5-isopropylpentanoic acid (2.31 g, 12.4 mmol) was dissolved in EtOH (30 mL) followed by the addition of conc. H_2SO_4 (0.5 mL). The reaction mixture was stirred overnight at 78 ℃ under reflux, concentrated *in vacuo*, diluted with water (15 mL), neutralized with saturated $NaHCO_3$ and extracted with Et_2O (3 × 40 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo* to give a yellow oil which was purified by flash chromatography eluting with EtOAc/petroleum ether (5:95 to 10:95) to give a colorless oil (2.08 g, 9.71 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.09 (s, 6 H, C(C*H*$_3$)$_2$), 1.25 (t, *J* = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 2.47 (s, 2 H, C*H*$_2$C(O)O), 2.56 (spt, *J* = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.60 (s, 2 H, C*H*$_2$C(O)), 4.10 (q, *J* = 7.2 Hz, 2 H, OC*H*$_2$CH$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 14.3 (OCH$_2$*C*H$_3$), 18.1 (CH(*C*H$_3$)$_2$), 28.1 (C(*C*H$_3$)$_2$), 32.5 (*C*(CH$_3$)$_2$), 41.9 (*C*H(CH$_3$)$_2$), 44.7 (*C*H$_2$C(O)O), 49.5 (*C*H$_2$C(O)), 59.9 (O*C*H$_2$CH$_3$), 172.3 (*C*(O)O), 214.2 (*C*(O)) ppm. IR (neat)/cm^{-1} 2967, 2359, 1730 (C=O), 1467, 1229, 1150, 1035. HRMS calcd for $C_{12}H_{22}O_3Na$ [M + Na]$^+$ 237.1461, found 237.1455.

Ethyl 5-cyclohexyl-3,3-dimethyl-5-oxopentanoate 3h



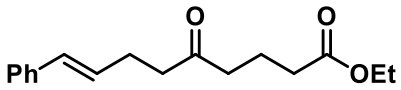
Prepared according to general procedure D using 5-cyclohexyl-3,3-dimethyl-5 oxopentanoic acid (0.93 g, 4.12 mmol), H_2SO_4 (0.3 mL) and EtOH (12 mL) to give the title compound as a colorless oil (0.89 g, 3.50 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 6 H, C(C*H*$_3$)$_2$), 1.15 – 1.36 (m, 8 H, 3 H from OCH$_2$C*H*$_3$, 5 H from *c*-HexC*H*$_2$), 1.60 – 1.70 (m, 1 H, *c*-HexC*H*$_2$), 1.73 – 1.87 (m, 4 H, *c*-HexC*H*$_2$), 2.22 – 2.36 (m, 1 H, *c*-HexC*H*(CH$_2$)), 2.46 (s, 2 H, C*H*$_2$C(O)O), 2.58 (s, 2 H, C*H*$_2$C(O)), 4.10 (q, *J* = 7.2 Hz, 2 H, OC*H*$_2$CH$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (OCH$_2$*C*H$_3$), 25.7 (*c*-Hex*C*H$_2$), 25.9 (*c*-Hex*C*H$_2$), 28.1 (C(*C*H$_3$)$_2$), 28.4 (*c*-Hex*C*H$_2$), 32.5 (*C*(CH$_3$)$_2$), 44.6 (*C*H$_2$C(O)O), 49.7 (*C*H$_2$C(O)), 52.0 (*c*-Hex*C*H(CH$_2$)$_2$), 59.9 (O*C*H$_2$CH$_3$), 172.4 (*C*(O)O), 213.6 (*C*(O)) ppm. IR (neat)/cm^{-1} 2929, 2854, 2359, 1728 (C=O), 1706, 1449, 1367, 1345, 1228, 1143, 1064, 1035. HRMS calcd for $C_{15}H_{27}O_3$ [M + H]$^+$ 255.1955, found 255.1947.

Ethyl 3,3-tetramethylene-5-oxo-5-isopropylpentanoate 3i



Prepared according to general procedure D using 3,3-tetramethylene-5-oxo-5-isopropylpentanoic acid (1.77 g, 8.34 mmol), H_2SO_4 (0.4 mL) and EtOH (20 mL) to give the title compound as a colorless oil (1.59 g, 6.61 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, *J* = 7.1 Hz, 6 H, $CH(CH_3)_2$), 1.23 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.44 – 1.55 (m, 2 H, *c*-PenCH_2), 1.56 – 1.71 (m, 6 H, *c*-PenCH_2), 2.55 (s, 2 H, $CH_2C(O)O$), 2.56 (spt, *J* = 6.9 Hz, 1 H, $CH(CH_3)_2$), 2.74 (s, 2 H, $CH_2C(O)$), 4.08 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (OCH_2CH_3), 18.2 ($CH(CH_3)_2$), 24.0 (*c*-PenCH_2), 38.5 (*c*-PenCH_2), 41.5 ($CH_2C(O)O$), 42.7 ($CH(CH_3)_2$), 47.8 ($CH_2C(O)$), 59.9 (OCH_2CH_3), 172.8 (*C*(O)O), 214.4 (*C*(O)) ppm. IR (neat)/cm^{-1} 2962, 2872, 1728 (C=O), 1711, 1465, 1382, 1367, 1344, 1218, 1160, 1096, 1035, 940. HRMS calcd for $C_{14}H_{25}O_3$ $[M + H]^+$ 241.1798, found 241.1797.

Ethyl (E)-5-oxo-9-phenylnon-8-enoate 3j

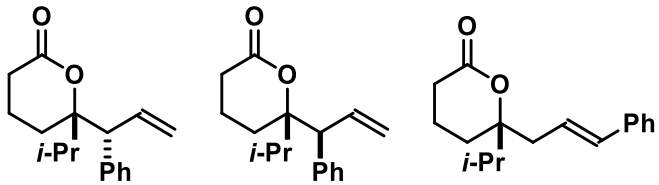


To a solution of ethyl 5-oxonon-8-enoate (430 mg, 1.57 mmol) and styrene (540 µL, 4.68 mmol) in degassed CH_2Cl_2 (10.0 mL) was added Hoveyda-Grubbs 2nd generation catalyst (10 mg, 0.016 mmol). The resulting solution was stirred at room temperature under a very slow stream of nitrogen for 16 h. Solvent was removed under vacuum and the resulting crude mixture was purified by silica gel column chromatography (pentane/Et_2O, 90:10 to 80:20) to give the title compound as a waxy solid (285 mg, 1.04 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.26 (t, *J* = 7.3 Hz, 3 H, OCH_2CH_3), 1.88 – 1.96 (m, 2 H, $C(O)CH_2CH_2$), 2.34 (t, *J* = 7.3 Hz, 2 H, $CH_2C(O)OEt$), 2.46 – 2.54 (m, 4 H, 2 H from $CH{=}CHCH_2CH_2C(O)$, 2 H from $C(O)CH_2$), 2.57 – 2.62 (m, 2 H, $CH{=}CHCH_2CH_2C(O)$), 4.13 (q, *J* = 7.3 Hz, 2 H, OCH_2CH_3), 6.19 (dt, *J* = 15.8, 6.8 Hz, 1 H, PhCH=C*H*), 6.41 (d, *J* = 15.8 Hz, 1 H, PhC*H*=CH), 7.18 – 7.23 (m, 1 H, ArC*H*), 7.27 – 7.35 (m, 4 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 14.2 (OCH_2CH_3), 18.9 ($C(O)CH_2CH_2$), 27.1 ($CH{=}CHCH_2CH_2C(O)$), 33.3 ($CH_2C(O)OEt$), 41.7 ($C(O)CH_2$), 42.3 ($CH{=}CHCH_2CH_2C(O)$), 60.4 (OCH_2CH_3), 126.0 (Ar*C*H), 127.1 (Ar*C*H), 128.5 (Ar*C*H), 128.8 (PhCH=*C*H), 130.8 (Ph*C*H=CH), 137.4 (Ar*C*), 173.2 (*C*(O)OEt), 209.2 (C(O)) ppm. IR (neat)/cm^{-1} 2979, 1730, 1713, 1492, 1447, 1412,

1374, 1248, 1176, 1098, 1028, 967, 745. HRMS calcd for $C_{17}H_{23}O_3$ $[M + H]^+$ 275.1642, found 275.1627.

Synthesis of 6-membered lactones

rac-(_R_)-6-Isopropyl-6-[(_R_)-1-phenylallyl]tetrahydro-2_H_-pyran-2-one _anti_-1a, _rac_-(_R_)-6-isopropyl-6-[(_S_)-1-phenylallyl]tetrahydro-2_H_-pyran-2-one _syn_-1a and _rac_-6-Cinnamyl-6-isopropyltetrahydro-2_H_-pyran-2-one 1a'



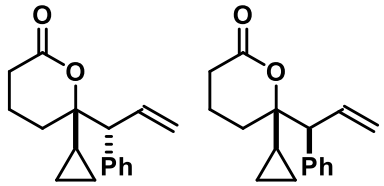
anti-**1a** _syn_-**1a** **1a'**

General procedure E. To a solution of $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) in toluene (0.5 mL), 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol) was added in toluene (0.5 mL) and the mixture stirred for 10 min to give a dark green solution which was then added dropwise to a stirred solution of ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol) in toluene (0.2 mL) and the reaction flask was sealed under argone. After 14 h at the room temperature, the reaction mixture was quenched with 1 M HCl (1.5 mL) and the phases were separated. The aqueous layer was extracted with Et_2O (3 × 1.5 mL). The combined organic layers were washed with brine (1.5 mL) and brine layer was additionally extracted with Et_2O (1.5 mL). The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography, eluting with EtOAc/Hexanes (1:99 to 2:98) to give the *anti* isomer of the title compound as a white solid (19.3 mg, 0.075 mmol, 75%), *syn*-**1a** as colorless oil (1 mg, 0.003 mmol 4 %) and isomer **1a**' as colourless oil (1 mg, 0.003 mmol, 4%). ^{1}H NMR yield from crude product mixture (88% for *anti*-**1a**+*syn*-**1a**, d.r. 92:8; (*anti*-**1a**+*syn*-**1a**):**1a'**, 91:9). ^{1}H NMR (500 MHz, $CDCl_3$) (*anti* diastereoisomer) δ 0.49 – 0.59 (m, 1 H, C$H_aH_bCH_2$C(O)O), 0.92 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_a$(CH$_3$)$_b$), 0.96 (d, J = 6.9 Hz, 3 H, CH(CH$_3$)$_a$(CH_3)$_b$), 1.33 – 1.41 (m, 1 H, CH$_a$$H_bCH_2$C(O)O), 1.62 – 1.69 (m, 1 H, CH_aH_bC-O), 1.79 (ddd, J = 14.4, 10.6, 5.2 Hz, 1 H, CH$_a$$H_b$C-O), 1.81 – 1.88 (m, 1 H, CH_aH_bC(O)O), 2.03 (ddd, J = 17.0, 10.6, 5.2 Hz, 1 H, CH$_a$$H_b$C(O)O), 2.35 (spt, J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$), 3.40 (d, J = 10.1 Hz, 1 H, CHPh), 5.10 (dd, J = 17.1, 1.6 Hz, 1 H, CH=CH_aH_b), 5.15 (dd, J = 10.1, 1.6 Hz, 1 H, CH=CH$_a$$H_b$), 6.49 (dt, J = 17.1, 10.1 Hz, 1 H, CH=CH$_2$), 7.22 – 7.26 (m, 3 H,

ArC*H*), 7.27 – 7.32 (m, 2 H, ArC*H*); (*syn* diastereoisomer) δ 0.90 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 0.94 (d, *J* = 6.8 Hz, 3 H, CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 1.65 – 1.78 (m, 2 H, C*H*$_2$CH$_2$C(O)O), 1.89 (spt, *J* = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 1.90 – 1.96 (m, 2 H, C*H*$_2$C-O), 2.04 (ddd, *J* = 17.1, 8.0, 5.7 Hz, 1 H, C*H*$_a$H$_b$C(O)O), 2.22 – 2.31 (m, 1 H, CH$_a$*H*$_b$C(O)O), 3.55 (d, *J* = 10.0 Hz, 1 H, C*H*Ph), 5.18 (dd, *J* = 10.0, 1.6 Hz, 1 H, CH=C*H*$_a$H$_b$), 5.20 (dd, *J* = 17.0, 1.6 Hz, 1 H, CH=CH$_a$*H*$_b$), 6.09 (dt, *J* = 17.0, 10.0 Hz, 1 H, C*H*=CH$_2$), 7.20 – 7.25 (m, 1 H, ArC*H*), 7.27 – 7.33 (m, 2 H, ArC*H*), 7.36 – 7.40 (m, 2 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, CDCl$_3$) δ (*anti* diastereoisomer) 16.5 (CH(*C*H$_3$)$_2$), 16.9 (CH(*C*H$_3$)$_2$), 17.6 (*C*H$_2$CH$_2$C(O)O), 24.2 (*C*H$_2$C-O), 30.2 (*C*H$_2$C(O)O), 35.4 (*C*H(CH$_3$)$_2$), 59.2 (*C*HPh), 89.4 (CH$_2$*C*-O), 117.2 (CH=*C*H$_2$), 127.3 (Ar*C*H), 128.8 (Ar*C*H), 129.6 (Ar*C*H), 137.2 (*C*H=CH$_2$), 140.7 (ArC), 172.3 (C(O)O); (*syn* diastereoisomer) 16.7 (CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 17.0 (CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 18.8 (*C*H$_2$CH$_2$C(O)O), 25.2 (*C*H$_2$C-O), 30.4 (*C*H$_2$C(O)O), 35.9 (*C*H(CH$_3$)$_2$), 59.6 (*C*HPh), 89.2 (CH$_2$*C*-O), 118.3 (CH=*C*H$_2$), 127.0 (Ar*C*H), 128.6 (Ar*C*H), 129.7 (Ar*C*H), 137.2 (*C*H=CH$_2$), 140.3 (Ar*C*), 172.5 (C(O)O) ppm. IR (neat)/cm^{-1} 2964, 1727 (C=O), 1465, 1341, 1328, 1247, 1192, 1038, 1002, 992, 766, 720, 705. M.p = 111 – 113 ˚C. HRMS calcd for C$_{17}$H$_{22}$O$_2$Na [M + Na]$^+$ 281.1512, found 281.1525.

Spectroscopic data for **1a'**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.98 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 0.99 (d, *J* = 6.8 Hz, 3 H, CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 1.70 – 1.92 (m, 4 H, 2 H from C*H*$_2$CH$_2$C(O)O, 2 H from C*H*$_2$C-O), 2.06 (spt, *J* = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.34 – 2.44 (m, 1 H, C*H*$_a$H$_b$C(O)O), 2.46 – 2.64 (m, 3 H, 1 H from CH$_a$*H*$_b$C(O)O, 2 H from C*H*$_2$CH=CH), 6.23 (dt, *J* = 15.9, 7.3 Hz, 1 H, CH$_2$C*H*=CH), 6.46 (d, *J* = 15.9 Hz, 1 H, CH$_2$CH=C*H*), 7.19 – 7.25 (m, 1 H, ArC*H*), 7.27 – 7.39 (m, 4 H, ArC*H*). ^{13}C NMR (100 MHz, CDCl$_3$) δ 16.7 (CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 16.9 (CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 17.0 (*C*H$_2$CH$_2$C(O)O), 26.4 (*C*H$_2$C-O), 29.9 (*C*H$_2$C(O)O), 35.6 (*C*H(CH$_3$)$_2$), 40.5 (*C*H$_2$CH=CH), 88.5 (CH$_2$*C*-O), 124.3 (CH$_2$*C*H=CH), 126.3 (Ar*C*H), 127.5 (Ar*C*H), 128.7 (Ar*C*H), 133.9 (CH$_2$CH=*C*H), 137.2 (Ar*C*), 171.9 (C(O)O). IR (neat)/cm^{-1} 2963, 1727 (C=O), 1448, 1327, 1251, 1031, 970, 924, 747, 693. HRMS calcd for C$_{17}$H$_{22}$O$_2$Na [M + Na]$^+$ 281.1512, found 281.1516.

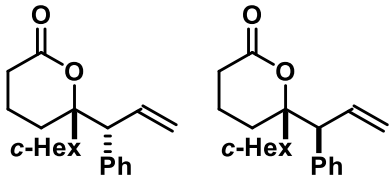
rac-(_R_)-6-Cyclopropyl-6-((_R_)-1-phenylallyl)tetrahydro-2_H_-pyran-2-one _anti_-1b and _rac_-(_R_)-6-cyclopropyl-6-((_S_)-1-phenylallyl)tetrahydro-2_H_-pyran-2-one syn-1b



anti-1b *syn*-1b

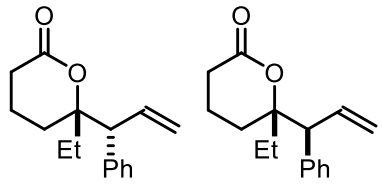
Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 5-oxo-5-cyclopropylpropylpentanoate (18.4 mg, 0.1 mmol) to give the title compound (17.0 mg, 0.072, 72%) as a mixture of diastereoisomers of which the *anti* was the major. ^{1}H NMR yield from crude product mixture (84% for *anti*-**1b**:*syn*-**1b**, d.r; 85:15; (*anti*-**1b**+*syn*-**1b**):**1b'**, 92:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 0.20 – 0.28 (m, 1 H, *c*-PrC*H*$_2$), 0.31 – 0.39 (m, 1 H, *c*-PrC*H*$_2$), 0.43 – 0.52 (m, 1 H, *c*-PrC*H*$_2$), 0.54 – 0.68 (m, 2 H, 1 H from *c*-PrC*H*$_2$, and *c*-PrC*H*(CH_2)), 1.59 – 1.69 (m, 1 H, C*H*$_a$H$_b$CH$_2$C(O)O), 1.75 – 1.82 (m, 1 H, C*H*$_a$H$_b$C-O), 1.87 – 1.98 (m, 2 H, 1 H from CH$_a$*H*$_b$CH$_2$C(O)O, 1 H from CH$_a$*H*$_b$C-O), 2.15 – 2.26 (m, 1 H, C*H*$_a$H$_b$C(O)O), 2.39 – 2.49 (m, 1 H, C*H*$_a$H$_b$C(O)O), 3.58 (d, *J* = 8.5 Hz, 1 H, C*H*Ph), 5.11 (dt, *J* = 17.3, 1.3 Hz, 1 H, CH=C*H*$_a$H$_b$), 5.16 (ddd, *J* = 10.3, 1.6, 0.9 Hz, 1 H, CH=CH$_a$*H*$_b$), 6.29 (ddd, *J* = 17.0, 10.4, 8.5 Hz, 1 H, C*H*=CH_2), 7.19 – 7.31 (m, 5 H, ArC*H*) (*syn* diastereoisomer diagnostic signals) 3.59 (br d, *J* = 9.5 Hz, 1 H, C*H*Ph), 5.16 – 5.22 (m, 2 H, CH=C*H*$_2$), 6.23 - 6.33 (m, 1 H, C*H*=CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (*anti* diastereoisomer) -0.1 (*c*-Pr*C*H$_2$), 2.1 (*c*-Pr*C*H$_2$), 16.6 (*C*H$_2$CH$_2$C(O)O), 19.8 (*c*-Pr*C*H(CH_2)), 29.4 (*C*H$_2$C-O), 29.9 (*C*H$_2$C(O)O), 60.5 (*C*HPh), 84.9 (CH$_2$*C*-O), 118.3 (CH=*C*H$_2$), 127.0 (Ar*C*H), 128.1 (ArCH), 129.6 (Ar*C*H), 136.4 (*C*H=CH_2), 139.4 (ArC), 171.4 (C(O)O) (*syn* diastereoisomer) 0.4 (*c*-Pr*C*H$_2$), 2.0 (*c*-Pr*C*H$_2$), 16.7 (*C*H$_2$CH$_2$C(O)O), 19.5 (*c*-Pr*C*H(CH_2)), 29.5 (*C*H$_2$C-O), 29.9 (*C*H$_2$C(O)O), 60.5 (*C*HPh), 84.3 (CH$_2$*C*-O), 118.7 (CH=*C*H$_2$), 126.8 (Ar*C*H), 128.8 (Ar*C*H), 129.6 (Ar*C*H), 135.8 (*C*H=CH_2), 139.7 (ArC), 171.15 (C(O)O). IR (neat)/ cm^{-1} 2929, 1728, 1493, 1452, 1417, 1328, 1238, 1190, 1116, 1090, 1024, 923, 829, 764, 703. HRMS calcd for $C_{17}H_{21}O_2$ $[M + H]^+$ 257.1536, found 257.1535.

rac-(_R_)-6-Cyclohexyl-6-[(_R_)-1-phenylallyl]tetrahydro-2_H_-pyran-2-one _anti_-1c and _rac_-(_R_)-6-Cyclohexyl-6-[(_S_)-1-phenylallyl]tetrahydro-2_H_-pyran-2-one _syn_-1c



Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 5-cyclohexyl-5-oxopentanoate (22.6 mg, 0.1 mmol) to give the *anti* isomer of the title compound as a white solid (19.1 mg, 0.064 mmol, 64%) and *syn*-**1c** as colorless oil (2 mg, 0.007 mmol, 7 %). ^{1}H NMR yield from crude product mixture (81% for *anti*-**1c**:*syn*-**1c**, d.r. 88:12; (*anti*-**1c**+*syn*-**1c**):**1c'**, 87:13). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 0.51 – 0.62 (m, 1 H, C*H*$_a$H$_b$CH$_2$C(O)O), 0.97 – 1.27 (m, 5 H, 5H from *c*-HexC*H*$_2$), 1.31 – 1.40 (m, 1 H, CH$_a$*H*$_b$CH$_2$C(O)O), 1.60 – 1.71 (m, 3 H, 1 H from C*H*$_a$H$_b$C-O, 2 H from *c*-HexC*H*$_2$), 1.74 – 1.86 (m, 5 H, 1 H from CH$_a$*H*$_b$C-O, 3 H from *c*-HexC*H*$_2$, 1 H from C*H*$_a$H$_b$C=O), 1.94 – 2.05 (m, 2 H, 1 H from *c*-HexC*H*(CH$_2$)$_2$, 1 H from CH$_a$*H*$_b$C(O)O), 3.42 (d, J = 10.0 Hz, 1 H, C*H*Ph), 5.06 (dd, J = 17.1, 1.6 Hz, 1 H, CH=C*H*$_a$H$_b$), 5.14 (dd, J = 10.0, 1.6 Hz, 1 H, CH=CH$_a$*H*$_b$), 6.46 (dt, J = 17.1, 10.0 Hz, 1 H, C*H*=CH$_2$), 7.19 – 7.30 (m, 5 H, Ar-C*H*) (*syn* diastereoisomer) 0.91 – 1.24 (m, 6 H, C*H*$_2$), 1.65 – 1.83 (m, 7 H, 4 H from C*H*$_2$, C*H*CH$_2$, 2 H from C*H*$_2$CH$_2$C(O)O), 1.91 – 1.97 (m, 2 H, C*H*$_2$C-O), 2.04 (ddd, *J* = 5.4, 8.5, 17.1 Hz, 1 H, C*H*$_a$H$_b$C(O)O), 2.21 – 2.32 (m, 1 H, CH$_a$*H*$_b$C(O)O), 3.57 (d, *J* = 9.8 Hz, 1 H, C*H*Ph), 5.15 – 5.22 (m, 2 H, CH=C*H*$_2$), 6.04 – 6.15 (m, 1 H, C*H*=CH$_2$), 7.20 – 7.25 (m, 1 H, ArC*H*), 7.27 – 7.33 (m, 2 H, ArC*H*), 7.33 – 7.39 (m, 2 H, ArC*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 17.8 (*C*H$_2$CH$_2$C(O)O), 25.6 (*C*H$_2$C-O), 26.3 (*c*-Hex*C*H$_2$), 26.4 (*c*-Hex*C*H$_2$), 26.6 (*c*-Hex*C*H$_2$), 26.6 (*c*-Hex*C*H$_2$), 26.8 (*c*-Hex*C*H$_2$), 30.3 (*C*H$_2$C(O)O), 45.8 (*c*-Hex*C*H(CH$_2$)$_2$), 58.8 (*C*HPh), 89.1 (CH$_2$*C*-O), 117.1 (CH=*C*H$_2$), 127.2 (Ar*C*H), 128.8 (Ar*C*H), 129.7 (Ar*C*H), 137.3 (*C*H=CH$_2$), 140.7 (Ar*C*), 172.4 (*C*(O)O) (*syn* diastereoisomer) 18.9 (*C*H$_2$CH$_2$C(O)O), 26.0 (*C*H$_2$C-O), 26.3 (*C*H$_2$), 26.4 (*C*H$_2$), 26.4 (*C*H$_2$), 26.4 (*C*H$_2$), 27.2 (*C*H$_2$), 30.4 (*C*H$_2$C(O)O), 46.2 (*C*HCH$_2$), 59.1 (*C*HPh), 89.1 (CH$_2$*C*-O), 118.3 (CH=*C*H$_2$), 127.0 (Ar*C*H), 128.5 (Ar*C*H), 129.7 (Ar*C*H), 137.3 (*C*H=CH$_2$), 140.2 (ArC), 172.6 (C(O)O) ppm. IR (neat)/cm^{-1} 2927, 2853, 1728 (C=O), 1452, 1331, 1033, 921, 765, 705. M.p = 124 – 127 ˚C. HRMS calcd for $C_{20}H_{26}O_2Na$ $[M + Na]^+$ 321.1830, found 321.1846.

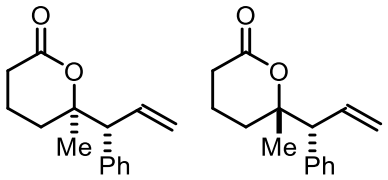
rac-(*S*)-6-Ethyl-6-((*R*)-1-phenylallyl)tetrahydro-2*H*-pyran-2-one *anti*-1d, _rac_-(*S*)-6-ethyl-6-((*S*)-1-phenylallyl)tetrahydro-2*H*-pyran-2-one *syn*-1d



***anti*-1d** ***syn*-1d**

Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 5-oxoheptanoate (17.2 mg, 0.1 to give the title compound (18.0 mg, 0.074, 74%) as a mixture of diastereoisomers of which the *anti* was the major. ^{1}H NMR yield from crude product mixture (79% for ***anti*-1d**+*syn*-**1d**, d.r. 57:43; (*anti*-**1d**+*syn*-**1d**):**1d'**, 80:20). ^{1}H NMR (500 MHz, $CDCl_3$) (*anti* diastereoisomer) δ 0.95 (t, *J* = 7.6 Hz, 3 H, CH_2CH_3), 1.43 – 1.52 (m, 1 H, $CH_aH_bCH_2C(O)O$)), 1.58 – 1.82 (m, 4 H, 1 H from $CH_aH_bCH_2C(O)O$, 2 H from CH_2C-O, 1 H from $CH_aH_bCH_3$), 1.89 – 1.98 (m, 1 H, $CH_aH_bCH_3$), 2.03 – 2.12 (m, 1 H, $CH_aH_bC(O)O$), 2.37 – 2.44 (m, 1 H, $CH_aH_bC(O)O$), 3.42 (d, *J* = 9.5 Hz, 1 H, C*H*Ph), 5.10 – 5.15 (m, 1 H, $CH=CH_aH_b$), 5.17 – 5.20 (m, 1 H, $CH=CH_aH_b$), 6.37 – 6.46 (m, 1 H, $CH=CH_2$), 7.22 – 7.27 (m, 2 H, ArC*H*), 7.29 – 7.33 (m, 2 H, ArC*H*), 7.35 – 7.39 (m, 1 H, ArC*H*); (*syn* diastereoisomer) 0.91 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.60 – 1.83 (m, 5 H, 1 H from $CH_aH_bCH_3$, 2 H from CH_2C-O, 2 H from $CH_2CH_2C(O)O$), 1.87 – 2.00 (m, 1 H, $CH_aH_bCH_3$), 2.07 – 2.19 (m, 1 H, $CH_aH_bC(O)O$), 2.44 – 2.48 (m, 1 H, $CH_aH_bC(O)O$), 3.52 (d, *J* = 9.6 Hz, 1 H, C*H*Ph), 5.16 – 5.20 (m, 1 H, $CH=CH_aH_b$), 5.20 – 5.23 (m, 1 H, $CH=CH_aH_b$), 6.17 (dt, *J* = 16.9, 9.9 Hz, 1 H, $CH=CH_2$), 7.22 – 7.33 (m, 5 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 8.0 (CH_2CH_3), 16.6 ($CH_2CH_2C(O)O$)), 27.0 (CH_2C-O), 29.7 ($CH_2C(O)O$), 30.3 (CH_2CH_3), 57.7 (*C*HPh), 87.6 (CH_2C-O), 117.6 ($CH=CH_2$), 127.0 (Ar*C*H), 128.5 (Ar*C*H), 129.4 (Ar*C*H), 136.7 ($CH=CH_2$), 140.1 (ArC), 171.3 ((C(O)O)). δ (*syn* diastereoisomer) 7.8 (CH_2CH_3), 16.9 ($CH_2CH_2C(O)O$)), 26.9 (CH_2C-O), 29.7 ($CH_2C(O)O$), 30.5 (CH_2CH_3), 57.9 (*C*HPh), 87.3 (CH_2C-O), 118.4 ($CH=CH_2$), 126.9 (Ar*C*H), 128.3 (Ar*C*H), 129.5 (Ar*C*H), 136.6 ($CH=CH_2$), 139.8 (ArC), 171.3 (C(O)O) ppm. IR (neat)/cm^{-1} 2967, 1727, 1491, 1453, 1417, 1362, 1328, 1244, 1191, 1132, 1085, 1040, 1016, 924, 834, 763, 703. HRMS calcd for $C_{16}H_{21}O_2$ $[M + H]^+$ 245.1536, found 245.1525.

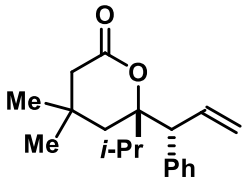
rac-(*R*)-6-Methyl-6-((*R*)-1-phenylallyl)tetrahydro-2*H*-pyran-2-one *syn*-1e, rac-(*S*)-6-methyl-6-((*R*)-1-phenylallyl)tetrahydro-2*H*-pyran-2-one *anti*-1e



***syn*-1e** ***anti*-1e**

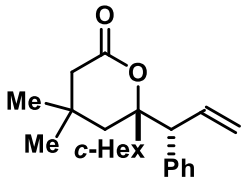
Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 5-methyl-5-oxo-pentanoate (15.8 mg, 0.1 mmol) to give title compound (12.2 mg, 0.053 mmol, 53%) as a mixture of diastereoisomers. ^{1}H NMR yield from crude (58% for *anti*-**1e**+*syn*-**1e**, d.r. 29:71, (*anti*-**1e**+*syn*-**1e**):**1e**' 81:19). ^{1}H NMR (400 MHz, $CDCl_3$) δ (*syn* diastereoisomer) 1.29 (s, 3 H, CH_3), 1.58 – 1.63 (m, 1 H, CH_aH$_b$C-O), 1.77 – 1.90 (m, 2 H, CH_2CH$_2$C(O)O), 1.96 (ddd, *J* = 13.5, 10.0, 6.3 Hz, 1 H, CH$_a$$H_b$C-O), 2.20 – 2.29 (m, 1 H, CH_aH$_b$CH$_2$C(O)O), 2.48 – 2.55 (m, 1 H, CH$_a$$H_bCH_2$C(O)O), 3.41 (d, *J* = 9.3 Hz, 1 H, C*H*Ph), 5.16 (ddd, *J* = 17.0, 1.5, 0.9 Hz, 1 H, CH=CH_aH$_b$), 5.23 (dd, *J* = 10.2, 1.5 Hz, 1 H, CH=CH$_a$$H_b$), 6.22 (ddd, *J* = 17.0, 10.2, 9.3 Hz, 1 H, C*H*=CH$_2$), 7.21 – 7.27 (m, 2 H, ArC*H*), 7.28 – 7.34 (m, 3 H, ArC*H*); (*anti* diastereoisomer) 1.39 (s, 3 H, CH_3), 1.58 – 1.65 (m, 1 H, CH_aH$_b$C-O), 1.65 – 1.74 (m, 2 H, CH_2CH$_2$C(O)O), 1.77 – 1.90 (m, 1 H, CH$_a$$H_b$C-O), 2.13 (ddd, *J* = 18.0 , 10.9, 6.9 Hz, 1 H, CH_aH$_b$CH$_2$C(O)O), 2.45 – 2.47 (m, 1 H, CH$_a$$H_bCH_2$C(O)O), 3.34 (d, *J* = 9.3 Hz, 1 H, C*H*Ph), 5.14 (ddd, *J* = 17.0, 1.6, 0.7 Hz, 1 H, CH=CH_aH$_b$), 5.20 (dd, *J* = 10.2 Hz, 1.6, 1 H, CH=CH$_a$$H_b$), 6.35 (ddd, *J* = 10.2, 9.3, 17.0 Hz, 1 H, C*H*=CH$_2$), 7.22 – 7.26 (m, 2 H, ArC*H*), 7.28 – 7.33 (m, 3 H, ArC*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ (*syn* diastereoisomer) 16.8 (*C*H$_2$CH$_2$C(O)O), 25.3 (CH_3), 29.7 (*C*H$_2$C(O)O), 30.6 (*C*H$_2$C-O), 60.8 (*C*HPh), 85.4 (CH$_2$*C*-O), 118.9 (CH=*C*H$_2$), 127.1 (Ar*C*H), 128.5 (Ar*C*H), 129.6 (Ar*C*H), 136.5 (*C*H=CH$_2$), 139.8 (Ar*C*), 171.2 (C(O)O); (*anti* diastereoisomer) 16.6 (*C*H$_2$CH$_2$C(O)O), 25.7 (CH_3), 29.7 (*C*H$_2$C(O)O), 30.6 (*C*H$_2$C-O), 61.0 (*C*HPh), 77.4 (CH$_2$*C*-O), 118.4 (CH=*C*H$_2$), 127.2 (Ar*C*H), 128.7 (Ar*C*H), 129.5 (Ar*C*H), 136.7 (*C*H=CH$_2$), 134.0 (Ar*C*), 171.3 (C(O)O) ppm. IR (neat)/ cm^{-1} 2957, 1726 (C=O), 1453, 1417, 1244, 1131, 1084, 1053, 1001, 919, 765, 703. HRMS calcd for $C_{15}H_{18}O_2K$ $[M + K]^+$ 269.0944, found 269.0948.

rac-(*R*)-6-Isopropyl-4,4-dimethyl-6-[(*R*)-1-phenylallyl]tetrahydro-2*H*-pyran-2-one *anti*-1g



Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}{}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 3,3-dimethyl-5-oxo-5-isopropylpentanoate (21.4 mg, 0.1 mmol) to give the *anti* isomer of the title compound as a white solid (24.6 mg, 0.086 mmol, 86%). ^{1}H NMR yield from crude product mixture (92% for *anti*-**1g**:*syn*-**1g**, d.r. 98:2; (*anti*-**1g**+*syn*-**1g**):**1g'**, 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (s, 3 H, $C(CH_3)_a(CH_3)_b$), 0.71 (d, *J* = 16.1 Hz, 1 H, $CH_aH_bC(O)O$)), 0.89 (s, 3 H, $C(CH_3)_a(CH_3)_b$), 0.95 (d, *J* = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.65 – 1.73 (m, 2 H, CH_2C-O), 1.74 – 1.81 (m, 1 H, $CH_aH_bC(O)O$)), 2.31 (spt, *J* = 6.8 Hz, 1 H, $CH(CH_3)_2$), 3.35 (d, *J* = 10.0 Hz, 1 H, CHPh), 5.07 (dd, *J* = 17.1, 1.0 Hz, 1 H, $CH=CH_aH_b$), 5.13 (dd, *J* = 10.2, 1.6 Hz, 1 H, $CH=CH_aH_b$), 6.53 (dt, *J* = 17.1, 10.2 Hz, 1 H, $CH=CH_2$), 7.20 - 7.34 (m, 5 H, ArCH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5 ($C(CH_3)_a(CH_3)_b$), 17.8 ($C(CH_3)_a(CH_3)_b$), 29.8 ($C(CH_3)_2$), 30.0 ($C(CH_3)_a(CH_3)_b$), 30.6 ($C(CH_3)_a(CH_3)_b$), 35.2 (CH_2C-O), 35.9 ($CH(CH_3)_2$), 42.9 ($CH_2C(O)O$), 59.9 (CHPh), 88.7 (C-O), 116.7 ($CH=CH_2$), 127.4 (ArCH), 128.6 (ArCH), 130.3 (ArCH), 137.3 ($CH=CH_2$), 140.5 (ArC), 172.8 (C(O)O) ppm. IR (neat)/cm^{-1} 2960, 1732, 1491, 1466, 1421, 1389, 1370, 1352, 1318, 1298, 1257, 1206, 1160, 1136, 1115, 1034, 1007, 970, 915, 787, 762, 709, 622, 610. M.p ($CHCl_3$) = 84 – 86 ˚C. HRMS calcd for $C_{19}H_{27}O_2$ $[M + H]^+$ 287.2006 found 287.2003.

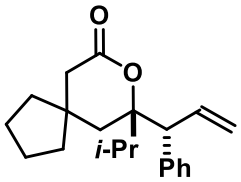
rac-(*R*)-6-Cyclohexyl-4,4-dimethyl-6-[(*R*)-1-phenylallyl]tetrahydro-2*H*-pyran-2-one *anti*-1h



Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}{}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 5-cyclohexyl-3,3-dimethyl-5-oxopentanoate (25.4 mg, 0.1 mmol) to give the *anti* isomer of the title compound as a white solid (26.4 mg, 0.081 mmol, 81%). ^{1}H NMR yield from crude product mixture (86% for *anti*-**1h**:*syn*-**1h**, d.r. 98:2; (*anti*-**1h**+*syn*-**1h**):**1h'**, 99:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.46 (s, 3 H, $C(CH_3)_a(CH_3)_b$), 0.70 (d, *J* = 16.1 Hz, 1 H, $CH_aH_bC(O)O$), 0.87 (s, 3 H,

$C(CH_3)_a(CH_3)_b$), 0.97 – 1.26 (m, 5 H, *c*-HexCH_2), 1.62 – 1.69 (m, 2 H, 1 H from *c*-HexCH_2, 1 H from CH_aH_bC-O), 1.69 – 1.82 (m, 6 H, 4 H from *c*-HexCH_2, 1 H from CH_aH_bC-O, 1 H from $CH_aH_bC(O)O$,), 1.92 (tt, *J* = 11.7, 2.6 Hz, 1 H, *c*-Hex$CH(CH_2)$), 3.37 (d, *J* = 10.1 Hz, 1 H, C*H*Ph), 5.03 (dd, *J* = 17.2, 1.4 Hz, 1 H, CH=CH_aH_b), 5.12 (dd, *J* = 10.1, 1.6 Hz, 1 H, CH=CH_aH_b), 6.49 (dt, *J* = 17.1, 10.2 Hz, 1 H, C*H*=CH_2), 7.16 – 7.33 (m, 5 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.3 (*c*-HexCH_2), 26.3 (*c*-HexCH_2), 26.4 (*c*-HexCH_2), 26.5 (*c*-HexCH_2), 27.5 (*c*-HexCH_2), 29.9 ($C(CH_3)_a(CH_3)_b$), 29.9 ($C(CH_3)_2$), 30.6 ($C(CH_3)_a(CH_3)_b$), 36.4 (CH_2C-O), 43.0 ($CH_2C(O)O$), 46.4 (*c*-Hex$CH(CH_2)_2$), 59.5 (*C*HPh), 88.3 (*C*-O), 116.6 (CH=CH_2), 127.3 (Ar*C*H), 128.6 (Ar*C*H), 130.4 (Ar*C*H), 137.3 (*C*H=CH_2), 140.5 (Ar*C*), 172.9 (*C*(O)O). IR (neat)/cm^{-1} 2927, 2853, 1732 (C=O), 1453, 1369, 1349, 1304, 1254, 1167, 1128, 1034, 1012, 914, 709. M.p ($CHCl_3$) = 104 – 105 ˚C. HRMS calcd for $C_{22}H_{31}O_2$ [M + H]$^+$ 327.2319, found 327.2312.

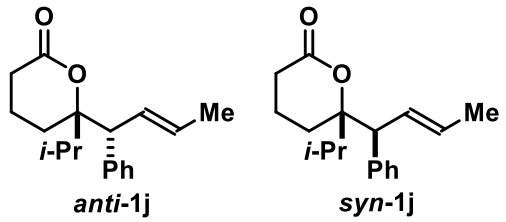
rac-(*R*)-9-Isopropyl-9-[(*R*)-1-phenylallyl]-8-oxaspiro[4.5]decan-7-one _anti_-1i



Prepared according to general procedure E using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 3,3-tetramethylene-5-oxo-5-isopropylpentanoate (24.0 mg, 0.1 mmol) to give the *anti* isomer of the title compound as a colorless oil (25.0 mg, 0.080 mmol, 80%). ^{1}H NMR yield from crude product mixture (85% for *anti*-**1i**+*syn*-**1i**, d.r. 99:1, (*anti*-**1i**+*syn*-**1i**):**1i'** 99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 – 0.88 (m, 3 H, 2 H from $CH_2CH_2CH_2CH_2$, 1 H from $CH_aH_bC(O)O$), 0.93 (d, *J* = 6.8 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 0.95 (d, *J* = 6.8 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 1.28 - 1.35 (m, 2 H, $CH_2CH_2CH_2CH_2$), 1.36 - 1.47 (m, 2 H, $CH_2CH_2CH_2CH_2$), 1.47 - 1.62 (m, 2 H, $CH_2CH_2CH_2CH_2$), 1.77 – 1.88 (m, 2 H, CH_2C-O), 1.91 (dd, *J* = 16.1, 1.0 Hz, 1 H, $CH_aH_bC(O)O$), 2.31 (spt, J = 6.9 Hz, 1 H, $CH(CH_3)_2$, 3.36 (d, *J* = 10.0 Hz, 1 H, C*H*Ph), 5.07 (dd, *J* = 17.2, 1.1 Hz, 1 H, CH=CH_aH_b), 5.12 (dd, *J* = 10.2, 1.6 Hz, 1 H, CH=CH_aH_b), 6.51 (dt, *J* = 17.1, 10.2 Hz, 1 H, C*H*=CH_2), 7.20 – 7.31 (m, 5 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5 ($C(CH_3)_a(CH_3)_b$), 17.6 ($C(CH_3)_a(CH_3)_b$), 22.5 ($CH_2CH_2CH_2CH_2$), 23.2 ($CH_2CH_2CH_2CH_2$), 34.0 (CH_2C-O), 35.9 ($CH(CH_3)_2$), 38.9 ($CH_2CH_2CH_2CH_2$), 39.8 ($CH_2C(O)O$), 39.9 ($CH_2CH_2CH_2CH_2$), 40.9 ($CCH_2C(O)O$), 59.7 (*C*HPh), 88.5 (*C*-O), 116.7 (CH=CH_2), 127.3 (Ar*C*H), 128.6 (Ar*C*H), 130.3 (Ar*C*H), 137.4 (*C*H=CH_2), 140.5 (Ar*C*),

172.8 (*C*(O)O) ppm; IR (neat)/cm^{-1} 2956, 2875, 1731, 1453, 1422, 1389, 1353, 1317, 1250, 1056, 1032, 1012, 959, 915, 790, 709. HRMS calcd for $C_{21}H_{29}O_2$ $[M + H]^+$ 312.2162, found 313.2159.

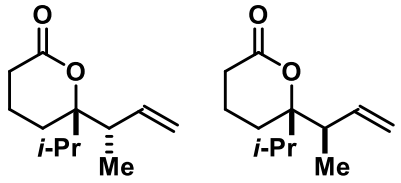
***rac*-(*R*)-6-Isopropyl-6-[(*R*,*E*)-1-phenylbut-2-en-1-yl]tetrahydro-2*H*-pyran-2-one *anti*-1j and *rac*-(*R*)-6-Isopropyl-6-[(*S*,*E*)-1-phenylbut-2-en-1-yl]tetrahydro-2*H*-pyran-2-one *syn*-1j**



Prepared according to general procedure E using (*E*)-(3-(benzyloxy)but-1-en-1-yl)benzene (31.0 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol) to give single *anti* isomer of the title compound as a white solid (16.3 mg, 60%) and mixture of diastereoisomers (2 mg, 0.007 mmol, 7%) in a ratio *syn*:*anti* (38:62). ^{1}H NMR yield from crude product mixture (86% for *anti*-**1j**:*syn*-**1j**, d.r. 75:25; (*anti*-**1j**+*syn*-**1j**):*anti*-**1j'**, 97:3). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 0.46 – 0.59 (m, 1 H, CH_aH$_b$CH$_2$C(O)O), 0.92 (d, *J* = 7.2 Hz, 3 H, CH(CH_3)$_a$(CH$_3$)$_b$), 0.95 (d, *J* = 7.0 Hz, 3 H, CH(CH$_3$)$_a$(CH_3)$_b$), 1.32 – 1.41 (m, 1 H, CH$_a$$H_bCH_2$C(O)O), 1.61 – 1.67 (m, 1 H, CH_aH$_b$C-O), 1.69 (dd, *J* = 6.5, 1.6 Hz, 3 H, CH=CHCH_3), 1.73 – 1.81 (m, 1 H, CH$_a$$H_b$C-O), 1.83 – 1.90 (m, 1 H, CH_aH$_b$C(O)O), 1.99 – 2.08 (m, 1 H, CH$_a$$H_b$C(O)O), 2.38 (spt, *J* = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.36 (d, *J* = 10.1 Hz, 1 H, C*H*Ph), 5.53 (dq, *J* = 15.2, 6.4 Hz, 1 H, CH=C*H*CH$_3$), 6.08 – 6.16 (m, 1 H, C*H*=CHCH$_3$), 7.17 – 7.36 (m, 5 H, ArC*H*); (*syn* diastereoisomer) 0.89 (d, *J* = 6.8 Hz, 3 H, CH(CH_3)$_a$(CH$_3$)$_b$), 0.92 (d, *J* = 6.8 Hz, 3 H, CH(CH$_3$)$_a$(CH_3)$_b$), 1.31 – 1.42 (m, 1 H, CH_aH$_b$CH$_2$C(O)O), 1.61 – 1.81 (m, 5 H, 1 H from CH$_a$$H_bCH_2$C(O)O, 1 H from C$H_aH_b$C-O, 3 H from CH=CHC$H_3$), 1.82 – 1.94 (m, 2 H, 1 H from C*H*(CH$_3$)$_2$, 1 H from CH$_a$$H_b$C-O), 1.98 – 2.08 (m, 1 H, CH_aH$_b$C(O)O), 2.22 – 2.32 (m, 1 H, CH$_a$$H_b$C(O)O), 3.49 (d, *J* = 9.0 Hz, 1 H, C*H*Ph), 5.58 – 5.75 (m, 2 H, C*H*=C*H*), 7.27 – 7.32 (m, 3 H, ArC*H*), 7.35 – 7.40 (m, 2 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 16.4 (CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 16.7 (CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 17.4 (*C*H$_2$CH$_2$C(O)O), 18.1 (CH=CH*C*H$_3$), 24.1 (*C*H$_2$C-O), 30.0 (*C*H$_2$C(O)O), 35.1 (*C*H(CH$_3$)$_2$), 57.8 (*C*HPh), 89.6 (CH$_2$*C*-O), 126.9 (Ar*C*H), 127.7 (CH=*C*HCH$_3$), 128.6 (Ar*C*H), 129.4 (Ar*C*H), 129.6 (*C*H=CHCH$_3$), 141.1 (Ar*C*), 172.2 (*C*(O)O); (*syn* diastereoisomer) 16.6 (CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 16.8 (CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 18.2 (*C*H$_2$CH$_2$C(O)O), 18.7 (CH=CH*C*H$_3$), 25.0 (*C*H$_2$C-O), 30.3

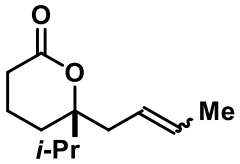
($CH_2C(O)O$), 35.7 ($CH(CH_3)_2$), 58.3 ($CHPh$), 89.5 (CH_2C-O), 126.7 (ArCH), 128.4 ($CH=CHCH_3$), 128.8 (ArCH), 129.6 (ArCH), 129.8 ($CH=CHCH_3$), 140.7 (ArC), 172.7 ($C(O)O$) ppm. IR ν_{max} (thin film)/cm^{-1} 2963, 2880, 1727, 1495, 1452, 1389, 1341, 1328, 1265, 1249, 1232, 1191, 1115, 1067, 1036, 973, 922, 902, 757, 704. M.p ($CHCl_3$) = 116 – 118 ˚C. HRMS calcd for $C_{18}H_{25}O_2$ $[M + H]^+$ 273.1849, found 273.1848.

***rac*-(*R*)-6-[(*S*)-But-3-en-2-yl]-6-isopropyltetrahydro-2*H*-pyran-2-one *anti*-1k and *rac*-(*R*)-6-[(*R*)-But-3-en-2-yl]-6-isopropyltetrahydro-2*H*-pyran-2-one *syn*-1k**



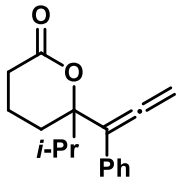
Prepared according to general procedure E using ((but-2-en-1-yloxy)methyl)benzene (21.1 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol) to give title compound (15.1 mg, 0.077 mmol, 77%) as a mixture of diastereoisomers of which the *anti* was the major. ^{1}H NMR yield from crude product mixture (87% for *anti*-**1k**:*syn*-**1k**, d.r; 90:10; (*anti*-**1k**+*syn*-**1k**):**1l**, 96:4). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 0.93 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 0.97 (d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 1.06 (d, *J* = 6.9 Hz, 3 H, $CHCH_3$), 1.73 – 1.89 (m, 4 H, 2 H from $CH_2CH_2C(O)O$, 2 H from CH_2C-O), 2.07 (spt, *J* = 6.8 Hz, 1 H, $CH(CH_3)_2$), 2.35 – 2.40 (m, 2 H, $CH_2C(O)O$), 2.56 – 2.65 (m, 1 H, $CHCH_3$), 5.06 – 5.11 (m, 2 H, $CH=CH_2$), 5.86 – 5.96 (m, 1 H, $CH=CH_2$); (*syn* diastereoisomer diagnostic signals) 1.09 (d, *J* = 6.6 Hz, 1 H, $CHCH_3$), 2.13 (spt, *J* = 6.9 Hz, 1 H, $CH(CH_3)_2$), 5.75 (ddd, *J* = 17.2, 10.3, 8.8 Hz, 1 H, $CH=CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ (*anti* diastereoisomer) 14.6 ($CHCH_3$), 16.8 ($CH(CH_3)_a(CH_3)_b$), 16.9 ($CH(CH_3)_a(CH_3)_b$), 18.6 ($CH_2CH_2C(O)O$), 24.4 (CH_2C-O), 30.4 ($CH_2C(O)O$), 35.9 ($CH(CH_3)_2$), 45.9 ($CHCH_3$), 89.4 (CH_2C-O), 116.4 ($CH=CH_2$), 139.2 ($CH=CH_2$), 172.5 ($C(O)O$) ppm. IR (neat)/cm^{-1} 2967, 1730, 1473, 1422, 1328, 1248, 1197, 1102, 1083, 1067, 1017, 919, 698, 569. HRMS calcd for $C_{12}H_{21}O_2$ $[M + H]^+$ 197.1536, found 197.1536.

***rac*-6-(But-2-en-1-yl)-6-isopropyltetrahydro-2*H*-pyran-2-one 1l**



Prepared according to general procedure E using ((but-2-en-1-yloxy)methyl)benzene (21.1 mg, 0.13 mmol), $Cp^{DPMS}{}_2Sm(THF)$ (179 mg, 0.24 mmol) and ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol) to give title compound (10.0 mg, 0.051 mmol, 51%) as a mixture of E/Z isomers 1:1 and regioisomers **1l** and **1k** (86:14). ^{1}H NMR yield from crude product mixture (63% for **1l**; **1l**:**1k,** 82:18). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.93 (d, *J* = 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.64 – 1.69 (m, 4 H, 3 H from $CH{=}CHCH_3$, 1 H from CH_aH_bC-O), 1.70 – 1.88 (m, 3 H, 1 H from CH_aH_bC-O, 2 H from $CH_2CH_2C(O)O$), 1.99 (spt, *J* = 6.8 Hz, 1 H, $CH(CH_3)_2$), 2.28 – 2.40 (m, 3 H, 2 H from $CH_2CH{=}CHCH_3$, 1 H from $CH_aH_bC(O)O$), 2.43 – 2.51 (m, 1 H, $CH_aH_bC(O)O$), 5.38 – 5.47 (m, 1 H, $CH_2CH{=}CHCH_3$), 5.47 – 5.56 (m, 1 H, $CH_2CH{=}CHCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6 ($CH(CH_3)_a(CH_3)_b$), 16.7 ($CH_2CH_2C(O)O$), 16.8 ($CH(CH_3)_a(CH_3)_b$), 18.2 ($CH{=}CHCH_3$), 26.0 (CH_2C-O), 29.8 ($CH_2C(O)O$), 35.2 ($CH(CH_3)_2$), 39.9 ($CH_2CH{=}CHCH_3$), 88.3 (CH_2C-O), 125.0 ($CH_2CH{=}CHCH_3$), 129.6 ($CH_2CH{=}CHCH_3$), 172.0 ($C(O)O$) ppm. IR (neat)/cm^{-1} 2959, 2925, 1729 (C=O), 1465, 1428, 1371, 1328, 1259, 1191, 1117, 1029, 972, 924, 877, 790, 736, 720, 700. HRMS calcd for $C_{12}H_{21}O_2$ $[M + H]^+$ 197.1536, found 197.1536.

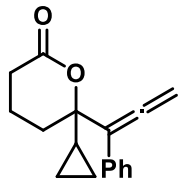
***rac*-6-Isopropyl-6-(1-phenylpropa-1,2-dien-1-yl)tetrahydro-2H-pyran-2-one 1m**



Prepared according to general procedure E using (3-(benzyloxy)prop-1-yn-1-yl)benzene (28.9 mg, 0.13 mmol), $Cp^*{}_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol) to give the title compound as a colorless oil (21.0 mg, 0.082 mmol, 82%). ^{1}H NMR yield from crude product mixture (92% for **1m**; **1m**:**1m'**, 99:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 1.03 (d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 1.81 – 1.90 (m, 2 H, 1 H from $CH_aH_bCH_2C(O)O$, 1 H from CH_aH_bC-O), 2.02 – 2.14 (m, 2 H, 1 H from $CH_aH_bCH_2C(O)O$, 1 H from CH_aH_bC-O), 2.16 (spt, J = 6.8 Hz, 1 H, $CH(CH_3)_2$), 2.38 – 2.46 (m, 1 H, $CH_aH_bC(O)O$), 2.56 – 2.63 (m, 1 H, $CH_aH_bC(O)O$), 5.07 (s, 2 H, $C{=}C{=}CH_2$), 7.23 – 7.29 (m, 1 H, ArC*H*), 7.29 – 7.34 (m, 2 H,

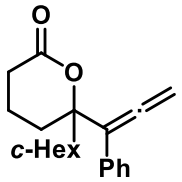
ArC*H*), 7.40 – 7.45 (m, 2 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6 (CH(*C*H_3)$_a$(CH_3)$_b$), 16.7 (*C*$H_2$$CH_2$C(O)O), 16.9 (CH($CH_3$)$_a$(*C*$H_3$)$_b$), 25.1 (*C*$H_2$C-O), 29.4 (*C*$H_2$C(O)O), 35.2 (*C*H($CH_3$)$_2$), 78.0 (C=C=*C*$H_2$), 88.8 ($CH_2$*C*-O), 108.9 (*C*=C=$CH_2$), 127.5 (Ar*C*H), 128.4 (Ar*C*H), 129.2 (Ar*C*H), 134.4 (Ar*C*), 171.6 (*C*(O)O), 208.5 (C=*C*=CH_2) ppm. IR (neat)/cm^{-1} 2967, 1943, 1731 (C=O), 1492, 1462, 1444, 1386, 1368, 1328, 1244, 1192, 1158, 1115, 1073, 1026, 988, 925, 850, 762, 699. HRMS calcd for $C_{17}H_{21}O_2$ $[M + H]^+$ 257.1536, found 257.1531.

***rac*-6-Cyclopropyl-6-(1-phenylpropa-1,2-dien-1-yl)tetrahydro-2H-pyran-2-one 1n**



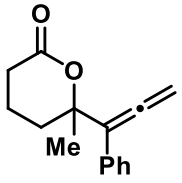
Prepared according to general procedure E using (3-(benzyloxy)prop-1-yn-1-yl)benzene (28.9 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-oxo-5-cyclopropylpropylpentanoate (18.4 mg, 0.1 mmol) dissolved in THF (rather than toluene) to give the title compound as a colorless oil (19.6 mg, 0.077 mmol, 77%). ^{1}H NMR yield from crude product mixture (90% for **1n**; **1n**:**1n'**, 99:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.42 – 0.56 (m, 3 H, *c*-PrC*H*$_2$), 0.63 – 0.71 (m, 1 H, *c*-PrC*H*$_2$), 1.15 – 1.23 (m, 1 H, *c*-PrC*H*(CH_2)$_2$), 1.74 – 1.82 (m, 1 H, C*H*$_a$H$_b$C-O), 1.85 – 1.93 (m, 1 H, C*H*$_a$H$_b$$CH_2$C(O)O), 1.94 – 2.04 (m, 1 H, CH_a*H*$_b$$CH_2$C(O)O), 2.09 – 2.17 (m, 1 H, CH_a*H*$_b$C-O), 2.38 – 2.47 (m, 1 H, C*H*$_a$H$_b$C(O)O), 2.47 – 2.55 (m, 1 H, CH_a*H*$_b$C(O)O), 5.03 (d, *J* = 11.5 Hz, 1 H, C=C=C*H*$_a$H$_b$), 5.06 (d, *J* = 11.5 Hz, 1 H, C=C=CH_a*H*$_b$), 7.24 - 7.29 (m, 1 H, ArC*H*$_{(o)}$), 7.29 - 7.34 (m, 2 H, ArC*H*$_{(m)}$), 7.37 - 7.42 (m, 2 H, ArC*H*$_{(p)}$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.3 (*c*-Pr*C*H_2), 2.4 (*c*-Pr*C*H_2), 16.5 (*C*$H_2$$CH_2$C(O)O), 20.8 (*c*-Pr*C*H(CH_2)$_2$), 29.4 (*C*H_2C(O)O), 30.9 (*C*H_2C-O), 78.3 (C=C=*C*H_2), 83.7 (CH_2*C*-O), 110.0 (*C*=C=CH_2), 127.5 (Ar*C*H), 128.2 (Ar*C*H), 129.2 (Ar*C*H), 134.7 (Ar*C*), 171.0 (*C*(O)O), 207.4 (C=*C*=CH_2) ppm. IR (neat)/cm^{-1} 2922, 2854, 1950, 1736 (C=O), 1491, 1459, 1443, 1374, 1327, 1239, 1125, 1080, 1031, 990, 921, 850, 760, 700, 668, 658, 644. HRMS calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380, found 255.1373.

***rac*-6-Cyclohexyl-6-(1-phenylpropa-1,2-dien-1-yl)tetrahydro-2H-pyran-2-one 1o**



Prepared according to general procedure E using (3-(benzyloxy)prop-1-yn-1-yl)benzene (28.9 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-cyclohexyl-5-oxopentanoate (22.6 mg, 0.10 mmol) to give single isomer of the title compound as a colorless oil (24.9 mg, 0.084 mmol, 84%). ^{1}H NMR yield from crude product mixture (93% for **1o**; **1o**:**1o'**, 99:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 – 1.27 (m, 5 H, *c*-HexC*H*$_2$), 1.62 (br d, *J* = 5.7 Hz, 1 H, *c*-HexC*H*$_2$), 1.70 – 1.85 (m, 5 H, 1 H from C*H*$_a$H$_b$CH$_2$C(O)O, 1 H from *c*-HexC*H*(CH$_2$)$_2$, 3 H from *c*-HexC*H*$_2$), 1.85 – 1.92 (m, 2 H, 1 H from *c*-HexC*H*$_2$, 1 H from C*H*$_a$H$_b$C-O), 1.97 – 2.09 (m, 2 H, 1 H from CH$_a$*H*$_b$CH$_2$C(O)O, 1 H from CH$_a$*H*$_b$C-O), 2.34 – 2.43 (m, 1 H, C*H*$_a$H$_b$C(O)O), 2.52 – 2.59 (m, 1 H, CH$_a$*H*$_b$C(O)O), 5.03 (s, 2 H, C=C=C*H*$_2$), 7.22 – 7.26 (m, 1 H, ArC*H*), 7.27 – 7.32 (m, 2 H, ArC*H*), 7.35 – 7.40 (m, 2 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8 (*C*H$_2$CH$_2$C(O)O), 25.8 (*C*H$_2$C-O), 26.3 (*c*-Hex*C*H$_2$), 26.4 (*c*-Hex*C*H$_2$), 26.5 (*c*-Hex*C*H$_2$), 26.6 (*c*-Hex*C*H$_2$), 27.2 (*c*-Hex*C*H$_2$), 29.5 (*C*H$_2$C(O)O), 45.4 (*c*-Hex*C*H(CH$_2$)$_2$), 78.0 (C=C=*C*H$_2$), 88.6 (CH$_2$*C*-O), 108.6 (*C*=C=CH$_2$), 127.4 (Ar*C*H), 128.4 (Ar*C*H), 129.1 (Ar*C*H), 134.4 (Ar*C*), 171.6 (*C*(O)O), 208.5 (C=*C*=CH$_2$) ppm. IR (neat)/cm^{-1} 2928, 2852, 1943, 1731 (C=O), 1492, 1445, 1328, 1254, 1234, 1197, 1179, 1077, 1026, 1003, 993, 924, 895, 847, 802, 762, 698, 647. HRMS calcd for $C_{20}H_{25}O_2$ $[M + H]^+$ 297.1843, found 297.1849.

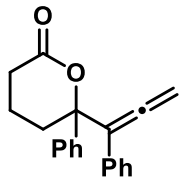
***rac*-6-Methyl-6-(1-phenylpropa-1,2-dien-1-yl)tetrahydro-2H-pyran-2-one 1p**



Prepared according to general procedure E using (3-(benzyloxy)prop-1-yn-1-yl)benzene (28.9 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-methyl-5-oxo-pentanoate (15.8 mg, 0.1 mmol) to give the title compound as a colorless oil (13.4 mg, 0.059 mmol, 59%). ^{1}H NMR yield from crude product mixture (70% for **1p**; **1p**:**1p'**, 99:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (s, 3 H, C*H*$_3$), 1.69 (ddd, *J* = 14.1, 9.5, 4.7 Hz, 1 H, C*H*$_a$H$_b$C-O), 1.76 – 1.85 (m, 1 H, C*H*$_a$H$_b$CH$_2$C(O)O), 1.88 – 1.99 (m, 1 H, CH$_a$*H*$_b$CH$_2$C(O)O), 2.10 (ddd, *J* = 14.2, 6.6, 4.7 Hz, 1 H, CH$_a$*H*$_b$C-O), 2.42 (t, *J* = 7.1 Hz, 2 H, C*H*$_2$C(O)O), 4.99 (d, *J*

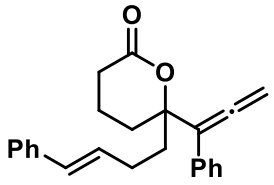
= 11.7 Hz, 1H, C=C=CH_aH_b), 5.01 (d, *J* = 11.7 Hz, 1H, C=C=CH_aH_b), 7.17 – 7.34 (m, 5 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8 (*C*H_2CH_2C(O)O), 28.1 (*C*H_3), 29.0 (*C*H_2C(O)O), 32.1 (*C*H_2C-O), 78.6 (C=C=*C*H_2), 83.4 (CH_2*C*-O), 110.3 (*C*=C=CH_2), 127.5 (Ar*C*H), 128.4 (Ar*C*H), 129.0 (Ar*C*H), 134.4 (Ar*C*), 170.9 (*C*(O)O), 207.3 (C=*C*=CH_2) ppm. IR (neat)/cm^{-1} 2979, 1947, 1731 (C=O), 1447, 1376, 1354, 1327, 1249, 1169, 1113, 1071, 1052, 986, 930, 855, 768, 700. HRMS calcd for $C_{15}H_{17}O_2$ $[M + H]^+$ 229.1223, found 229.1219.

***rac*-6-Phenyl-6-(1-phenylpropa-1,2-dien-1-yl)tetrahydro-2*H*-pyran-2-one 1q**



Prepared according to general procedure E using (3-(benzyloxy)prop-1-yn-1-yl)benzene (14.5 mg, 0.07 mmol), $Cp^*_2Sm(THF)_2$ (68 mg, 0.12 mmol) and ethyl 5-oxo-5-phenyl-pentanoate (11.0 mg, 0.05 mmol) to give the title compound as a pale-yellow oil (7.0 mg, 0.048 mmol, 48%). ^{1}H NMR yield from crude product mixture (52% for **1q**; **1q**:**1q'**, 99:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.66 – 1.79 (m, 1 H, CH_aH_bCH_2C(O)O), 1.95 – 2.05 (m, 1 H, CH_aH_bCH_2C(O)O), 2.12 – 2.21 (m, 1 H, CH_aH_bC-O), 2.43 – 2.52 (m, 1 H, CH_aH_bC-O), 2.52 – 2.66 (m, 2 H, CH_2C(O)O), 5.28 (d, *J* = 12.2 Hz, 1 H, C=C=CH_aH_b), 5.29 (d, *J* = 12.2 Hz, 1 H, C=C=CH_aH_b), 7.11 – 7.23 (m, 5 H, ArC*H*), 7.26 – 7.32 (m, 1 H, ArC*H*), 7.36 (t, *J* = 7.6 Hz, 2 H, ArC*H*), 7.45 (d, *J* = 7.8 Hz, 2 H, ArC*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.5 (*C*H_2CH_2C(O)O), 28.1 (*C*H_2C(O)O), 33.0 (*C*H_2C-O), 78.6 (C=C=*C*H_2), 85.7 (CH_2*C*-O), 109.2 (*C*=C=CH_2), 124.5 (Ar*C*H), 126.2 (Ar*C*H), 126.7 (Ar*C*H), 127.0 (Ar*C*H), 127.5 (Ar*C*H), 127.7 (Ar*C*H), 132.2 (Ar*C*), 141.9 (Ar*C*), 169.9 (*C*(O)O), 207.4 (C=*C*=CH_2) ppm. IR (neat)/cm^{-1} 2922, 1941, 1737, 1493, 1446, 1328, 1238, 1238, 1206, 1182, 1114, 1036, 999, 932, 857, 757, 697. HRMS calcd for $C_{20}H_{18}O_2Na$ $[M + Na]^+$ 313.1199, found 313.1193.

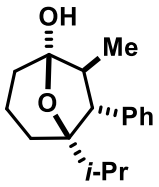
***rac*-(*E*)-6-(4-Phenylbut-3-en-1-yl)-6-(1-phenylpropa-1,2-dien-1-yl)tetrahydro-2H-pyran-2-one 1r**



Prepared according to general procedure E using (3-(benzyloxy)prop-1-yn-1-yl)benzene (23.1 mg, 0.10 mmol), $Cp^*_2Sm(THF)_2$ (109 mg, 0.19 mmol) and ethyl (E)-5-oxo-9-phenylnon-8-enoate (21.9 mg, 0.08 mmol) to give title product as a white wax (21 mg, 0.061 mmol, 76%). ^{1}H NMR yield from crude product mixture (80% for **1r**; **1r**:**1r'**, 99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.89 (m, 2 H, C*H*$_a$H$_b$CH$_2$CH$_2$C(O)O + CH$_2$C*H*$_a$H$_b$CH$_2$C(O)O), 1.94 – 2.09 (m, 3H, CH$_2$CH$_a$*H*$_b$CH$_2$C(O)O + CH$_2$C*H*$_2$CH=CHAr), 2.11 – 2.21 (m, 1 H, CH$_a$*H*$_b$CH$_2$CH$_2$C(O)O), 2.25 – 2.61 (m, 4 H, C*H*$_2$CH$_2$CH=CHAr + CH$_2$CH$_2$C*H*$_2$C(O)O), 5.06 (d, *J* = 12.0 Hz, 1 H, ArC=C=C*H*$_a$H$_b$), 5.09 (d, *J* = 12.0 Hz, 1 H, ArC=C=CH$_a$*H*$_b$), 6.11 (dt, *J* = 15.8, 6.8 Hz, 1 H, CH$_2$CH$_2$C*H*=CHAr), 6.34 (d, *J* = 15.8 Hz, 1 H, CH$_2$CH$_2$CH=C*H*Ar), 7.12 – 7.19 (m, 1 H, Ar*H*), 7.21 – 7.41 (m, 9 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6 (CH$_2$*C*H$_2$CH$_2$C(O)O), 27.2 (*C*H$_2$CH$_2$CH=CHAr), 29.1 (CH$_2$CH$_2$*C*H$_2$C(O)O), 30.2 (*C*H$_2$CH$_2$CH$_2$C(O)O), 39.7 (CH$_2$*C*H$_2$CH=CHAr), 78.6 (ArC=C=*C*H$_2$), 85.6 (*C*O), 108.8 (Ar*C*=C=CH$_2$), 125.9 (Ar*C*H), 127.0 (Ar*C*H), 127.6 (Ar*C*H), 128.5 (Ar*C*H), 128.5 (Ar*C*H), 128.8 (Ar*C*H), 129.4 (CH$_2$CH$_2$*C*H=CHAr), 130.4 (CH$_2$CH$_2$CH=*C*HAr), 134.2 (Ar*C*), 137.4 (Ar*C*), 171.0 (CH$_2$CH$_2$CH$_2$*C*(O)O), 208.2 (ArC=*C*=CH$_2$) ppm; IR ν_{max} (neat/cm^{-1}): 3024, 2953, 1943, 1731 (C=O), 1492, 1447, 1240, 1043; HRMS calcd for $C_{24}H_{24}O_2Na$ [M+Na]$^+$: 367.1669, found 367.1658.

One-pot approach to cycloheptanols

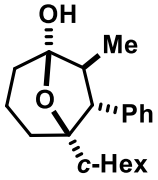
rac-Hemiketal 4a



General procedure F. To a solution of $Cp^{DPMS}_2Sm(THF)$ (179 mg, 0.24 mmol) in toluene (0.5 mL), 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol) was added in toluene (0.5 mL) and stirred for 10 min to give a dark green solution which was then added dropwise to a stirred solution of ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol) in THF (0.2 mL) in a Schlenk flask under argon. After 16 h at the room temperature, a mixture of 0.1 M SmI_2

in THF (10 mL, 1.00 mmol) and degassed distilled H_2O (1.8 mL, 100 mmol) was added and the resulting solution was stirred for 4 days. Saturated solution of Rochelle's salt was then added, the mixture was extracted with Et_2O (3 × 15 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The resulting crude product mixture was purified by silica gel column chromatography (hexane/EtOAc, 98:2 to 95:5) to obtain the title product as white crystals (14 mg, 0.053 mmol, 53%), mp (CH_2Cl_2) 92−95 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (d, *J* = 7.0 Hz, 3 H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 0.94 (d, *J* = 7.0 Hz, 3 H, CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 1.06 (d, *J* = 7.0 Hz, 3 H, CHC*H*$_3$), 1.46–1.53 (m, 1 H, C*H*$_a$H$_b$CH$_2$CH$_2$COH), 1.54–1.64 (m, 1 H, CH$_a$*H*$_b$CH$_2$CH$_2$COH), 1.72–1.88 (m, 3 H, CH$_2$C*H*$_a$H$_b$CH$_2$COH + CH$_2$CH$_2$C*H*$_2$COH), 1.93 (hept, *J* = 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$), 1.98–2.14 (m, 1 H, CH$_2$CH$_a$*H*$_b$CH$_2$COH), 2.50 (quint, *J* = 7.0 Hz, 1 H, C*H*CH$_3$), 2.63 (s, 1 H, O*H*), 2.92 (d, *J* = 7.0 Hz, 1 H, C*H*Ph), 7.21–7.27 (m, 1 H, Ar*H*), 7.29–7.39 (m, 4 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0 (CH*C*H$_3$), 17.6 (CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 17.7 (CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 19.0 (CH$_2$*C*H$_2$CH$_2$COH), 25.6 (*C*H$_2$CH$_2$CH$_2$COH), 35.8 (*C*H(CH$_3$)$_2$), 35.9 (CH$_2$CH$_2$*C*H$_2$COH), 44.7 (*C*HCH$_3$), 60.2 (*C*HPh), 86.0 (*i*-Pr*C*O), 102.3 (O*C*OH), 126.5 (Ar*C*H), 128.5 (Ar*C*H), 128.6 (Ar*C*H), 140.1 (Ar*C*) ppm; IR ν_{max} (neat/cm^{-1}): 3400, 2961, 2879, 1732, 1465, 1228, 1036, 953; HRMS calcd for $C_{17}H_{24}O_2Na$ [M+Na]$^+$: 283.1669, found 283.1667.

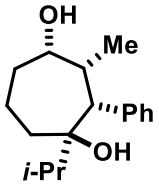
***rac*-Hemiketal 4b**



Prepared according to general procedure F using 1-[(cinnamyl-oxy)methyl]benzene (29.2 mg, 0.13 mmol), Cp$^{DPMS}_2$Sm(THF) (179 mg, 0.24 mmol) and ethyl 5-cyclohexyl-5-oxopentanoate (22.6 mg, 0.1 mmol), followed by 0.1 M SmI_2 in THF (10 mL, 1.00 mmol) and H_2O (1.8 mL, 100 mmol). The resulting crude product mixture was purified by silica gel column chromatography (hexane/EtOAc, 99:1 to 95:5) to give the title product as a colourless oil (14 mg, 0.047 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99–1.29 (m, 8 H, CHC*H*$_3$ + *c*-HexC*H*$_a$H$_b$ × 5), 1.50–1.88 (m, 11 H, CH$_2$C*H*$_a$H$_b$CH$_2$COH + C*H*$_2$CH$_2$CH$_2$COH + *c*-HexCH$_a$*H*$_b$ × 5 + CH$_2$CH$_2$C*H*$_2$COH + *c*-HexC*H*), 1.96–2.12 (m, 1 H, CH$_2$CH$_a$*H*$_b$CH$_2$COH), 2.45 (quint, *J* = 7.6 Hz, 1 H, C*H*CH$_3$), 2.63 (s, 1 H, O*H*), 2.93 (d, *J* = 7.6, 1 H, C*H*Ph),

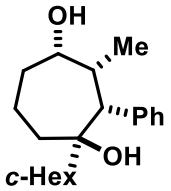
7.22–7.27 (m, 1 H, Ar*H*), 7.29–7.37 (m, 4 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0 (CH*C*H_3), 19.1 (CH_2*C*H_2CH_2COH), 26.1 (*C*$H_2CH_2CH_2COH$), 26.5 (*c*-Hex*C*H_2), 26.8 (*c*-Hex*C*H_2), 26.9 (*c*-Hex*C*H_2), 27.4 (*c*-Hex*C*H_2), 27.6 (*c*-Hex*C*H_2), 36.0 (CH_2CH_2*C*H_2COH), 44.9 (*C*HCH$_3$), 46.7 (*c*-Hex*C*H), 60.4 (*C*HPh), 85.9 (*c*-Hex*C*O), 102.3 (O*C*OH), 126.5 (Ar*C*H), 128.5 (Ar*C*H), 128.6 (Ar*C*H), 140.3 (Ar*C*) ppm; IR ν_{max} (thin film/cm^{-1}): 3395, 2925, 2851, 1451, 1227; HRMS calcd for $C_{20}H_{28}O_2Na$ $[M+Na]^+$: 323.1982, found 323.1979.

***rac*-Diol 4c**



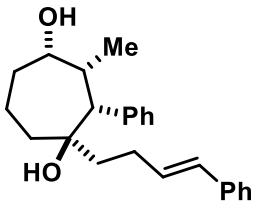
Prepared according to general procedure F using (3-(benzyloxy)prop-1-yn-1-yl)benzene (28.9 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-oxo-5-isopropylpentanoate (18.6 mg, 0.1 mmol), followed by 0.1 M SmI_2 in THF (10 mL, 1.00 mmol) and H_2O (9.0 mL, 500 mmol). The resulting crude product mixture was purified by silica gel column chromatography (hexane/EtOAc, 99:1 to 80:20) to give the title product as a colourless oil (19 mg, 0.072 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_a$(CH$_3$)$_b$), 0.87 (d, *J* = 7.2 Hz, 3 H, CH(CH$_3$)$_a$(C*H*$_3$)$_b$), 1.19 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$), 1.64–1.90 (m, 4 H, C*H*(CH$_3$)$_2$ + $CH_2CH_2CH_aH_bCHOH$ + $CH_2CH_2CH_2CHOH$), 1.99–2.09 (m, 1 H, $CH_aH_bCH_2CH_2CHOH$), 2.15–2.25 (m, 1 H, $CH_aH_bCH_2CH_2CHOH$), 2.39–2.50 (m, 1 H, $CH_2CH_2CH_aH_bCHOH$), 2.81–2.91 (m, 2 H, C*H*Ph + C*H*CH$_3$), 3.76 (td, *J* = 8.8, 4.3 Hz, 1 H, C*H*OH), 7.25 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 7.33 (t, *J* = 7.4 Hz, 2 H, Ar*H*), 7.43 (d, *J* = 7.4 Hz, 2 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5 (CH(*C*H$_3$)$_a$(CH$_3$)$_b$), 17.1 (CH(CH$_3$)$_a$(*C*H$_3$)$_b$), 19.2 (CH_2*C*H_2CH_2CHOH), 19.6 (CH*C*H$_3$), 34.7 (*C*H(CH$_3$)$_2$), 35.2 (*C*HCH$_3$), 36.6 (CH_2CH_2*C*H_2CHOH), 40.9 (*C*$H_2CH_2CH_2CHOH$), 58.9 (*C*HPh), 75.6 (*C*HOH), 76.7 (*i*-Pr*C*OH), 126.6 (Ar*C*H), 128.4 (Ar*C*H), 130.7 (Ar*C*H), 139.9 (Ar*C*) ppm; IR ν_{max} (thin film/cm^{-1}): 3563, 3457, 2934, 2871, 1452, 964; HRMS calcd for $C_{17}H_{26}O_2Na$ $[M+Na]^+$: 285.1825, found 285.1816.

***rac*-Diol 4d**



Prepared according to general procedure F using (3-(benzyloxy)prop-1-yn-1-yl)benzene (28.9 mg, 0.13 mmol), $Cp^*_2Sm(THF)_2$ (136 mg, 0.24 mmol) and ethyl 5-cyclohexyl-5-oxopentanoate (22.6 mg, 0.10 mmol), followed by 0.1 M SmI_2 in THF (10 mL, 1.00 mmol) and H_2O (9.0 mL, 500 mmol). The resulting crude product mixture was purified by silica gel column chromatography (hexane/EtOAc, 99:1 to 80:20) to give the title product as a pale solid (21 mg, 0.068 mmol, 68%), mp (CH_2Cl_2) 47−50 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67–0.81 (m, 1H, *c*-HexC*H*$_a$H$_b$), 0.87–1.10 (m, 4 H, *c*-HexC*H*$_a$H$_b$ × 4), 1.19 (d, *J* = 7.2 Hz, 3 H, C*H*$_3$), 1.24–1.34 (m, 1 H, C*H*-*c*-Hex), 1.45–1.60 (m, 3 H, *c*-HexCH$_a$*H*$_b$ × 3), 1.64–1.89 (m, 5 H, CH$_2$C*H*$_2$CH$_2$CHOH + *c*-HexCH$_a$*H*$_b$ × 2 + CH$_2$CH$_2$C*H*$_a$H$_b$CHOH), 1.96–2.06 (m, 1 H, C*H*$_a$H$_b$CH$_2$CH$_2$CHOH), 2.17–2.26 (m, 1 H, CH$_a$*H*$_b$CH$_2$CH$_2$CHOH), 2.38–2.48 (m, 1 H, CH$_2$CH$_2$CH$_a$*H*$_b$CHOH), 2.79–2.91 (m, 2 H, C*H*Ph + C*H*CH$_3$), 3.75 (td, *J* = 8.8, 4.1 Hz, 1 H, C*H*OH), 7.24 (t, *J* = 7.6 Hz, 1 H, Ar*H*), 7.32 (t, *J* = 7.6 Hz, 2 H, Ar*H*), 7.41 (d, *J* = 7.6 Hz, 2 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2 (CH$_2$*C*H$_2$CH$_2$CHOH), 19.5 (*C*H$_3$), 25.9 (*c*-Hex*C*H$_2$), 26.1 (*c*-Hex*C*H$_2$), 26.4 (*c*-Hex*C*H$_2$), 26.4 (*c*-Hex*C*H$_2$), 26.7 (*c*-Hex*C*H$_2$), 35.3 (*C*HCH$_3$), 36.6 (CH$_2$CH$_2$*C*H$_2$CHOH), 40.6 (*C*H$_2$CH$_2$CH$_2$CHOH), 44.8 (*c*-Hex*C*H), 58.4 (*C*HPh), 75.7 (*C*HOH), 76.9 (*c*-Hex*C*OH), 126.6 (Ar*C*H), 128.4 (Ar*C*H), 130.7 (Ar*C*H), 139.9 (Ar*C*) ppm; IR ν_{max} (neat/cm^{-1}): 3445, 2924, 2850, 1450, 965; HRMS calcd for $C_{20}H_{30}O_2Na$ $[M+Na]^+$: 325.2138, found 325.2124.

***rac*-Diol 4e**

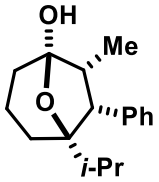


Prepared according to general procedure F using (3-(benzyloxy)prop-1-yn-1-yl)benzene (43.4 mg, 0.19 mmol), $Cp^*_2Sm(THF)_2$ (204 mg, 0.36 mmol) and **3j** (41.1 mg, 0.15 mmol), followed by 0.1 M SmI_2 in THF (15 mL, 1.50 mmol) and H_2O (13.5 mL, 750 mmol) to give the title product as a colourless oil (16 mg, 45.6×10^{-3} mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23–1.39 (m, 4 H, CHC*H*$_3$ + C*H*$_a$H$_b$CH$_2$CH=CHAr), 1.45 (bs, 1 H, O*H*), 1.52 –

1.89 (m, 5 H, $CH_2CH_2CH_2CHOH$ + $CH_2CH_2CH_aH_bCHOH$ + $CH_aH_bCH_2CH_2CHOH$ + $CH_aH_bCH_2CH$=CHAr), 2.02 – 2.31 (m, 4H, CH_2CH_2CH=CHAr + $CH_2CH_2CH_aH_bCHOH$ + $CH_aH_bCH_2CH_2CHOH$), 2.40 – 2.51 (m, 1 H, $CHCH_3$), 3.01 (s, 1 H, CHAr), 3.83 – 3.95 (m, 1 H, $CH_2CH_2CH_2CHOH$), 6.08 (dt, *J* = 15.8, 6.8 Hz, 1 H, CH_2CH_2CH=CHAr), 6.30 (d, *J* = 15.8 Hz, 1 H, CH_2CH_2CH=CHAr), 7.14 – 7.22 (m, 1 H, ArH), 7.23 – 7.41 (m, 9 H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3 ($CHCH_3$), 18.5 ($CH_2CH_2CH_2CHOH$), 26.7 (CH_2CH_2CH=CHAr), 34.5 ($CH_2CH_2CH_2CHOH$), 39.8 ($CH_2CH_2CH_2CHOH$), 40.4 (CH_2CH_2CH=CHAr), 41.6 ($CHCH_3$), 56.3 (CHAr), 76.0 (COH), 77.0 ($CH_2CH_2CH_2CHOH$), 125.8 (ArCH), 126.6 (ArCH), 126.9 (ArCH), 128.4 (ArCH), 128.4 (ArCH), 129.7 (ArCH), 129.8 (CH_2CH_2CH=CHAr), 131.0 (CH_2CH_2CH=CHAr), 137.6 (ArC), 143.0 (ArC) ppm; IR ν_{max} (neat/cm^{-1}): 3413 (O-H), 3024, 2932, 2861, 1598, 1493, 1447, 1295, 1034; HRMS calcd for $C_{24}H_{30}O_2Na$ $[M+Na]^+$: 373.2138, found 373.2138.

Oxidation of allene cyclisation product

***rac*-Hemiketal 4c'**



Dess-Martin periodinane (39 mg, 0.092 mmol) was added in one portion to a solution of diol **4c** (16 mg, 0.061 mmol) in CH_2Cl_2 (0.9 mL) at 0 ºC and the resulting mixture was stirred allowing it to slowly warm up to room temperature. After 3 h the reaction was quenched with a mixture of saturated aqueous solutions $Na_2S_2O_3$/$NaHCO_3$ (1:1.5 mL). Layers were separated and the aqueous fraction was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum. The resulting crude mixture was purified by silica gel column chromatography (hexane/EtOAc, 90:10 to 80:20) to obtain the title product as a pale solid (12 mg, 0.046, 76%), mp (CH_2Cl_2) 98−100 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75 (d, *J* = 8.0 Hz, 3 H, $CHCH_3$), 0.77 (d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 0.88 (d, *J* = 7.0 Hz, 3 H, $CH(CH_3)_a(CH_3)_b$), 1.63–1.74 (m, 2 H, $CH_2CH_2CH_aH_bCOH$ + $CH_aH_bCH_2CH_2COH$), 1.86–2.02 (m, 4 H, $CH_2CH_aH_bCH_2COH$ + $CH_2CH_2CH_aH_bCOH$ + $CH_aH_bCH_2CH_2COH$ + $CH(CH_3)_2$), 2.04–2.19 (m, 1 H, $CH_2CH_aH_bCH_2COH$), 2.47–2.56 (m, 1 H, $CHCH_3$), 3.69 (d, *J* = 13.5 Hz, 1 H, CHPh),

7.19–7.25 (m, 3 H, Ar*H*), 7.27–7.31 (m, 2 H, Ar*H*) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3 (CH*C*H_3), 17.4 (CH(*C*H_3)$_a$(CH_3)$_b$), 18.4 (CH(CH_3)$_a$(*C*H_3)$_b$), 19.2 (CH_2*C*$H_2$$CH_2$COH), 25.7 (*C*$H_2$$CH_2$$CH_2$COH), 31.5 ($CH_2$$CH_2$*C*$H_2$COH), 38.9 (*C*H($CH_3$)$_2$), 46.8 (*C*H$CH_3$), 54.4 (*C*HPh), 88.5 (*i*-Pr*C*O), 104.8 (O*C*OH), 126.2 (Ar*C*H), 128.3 (Ar*C*H), 130.2 (Ar*C*H), 139.6 (Ar*C*) ppm; IR ν_{max} (neat/cm^{-1}): 3358, 3261, 2958, 2873, 1732, 1453, 1366, 1356, 940; HRMS calcd for $C_{17}H_{24}O_2Na$ $[M+Na]^+$: 283.1669, found 283.1656.

X-Ray structure of *anti*-1a

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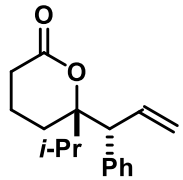
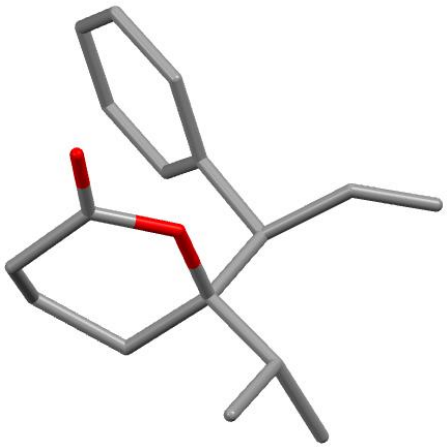


1a



X-Ray structure of 4a

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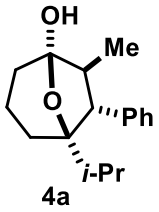
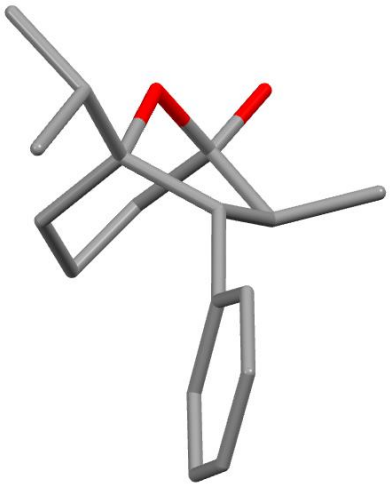


4a



X-Ray structure of 5b

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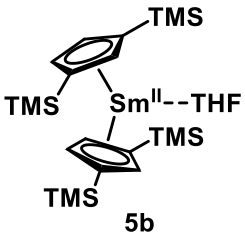
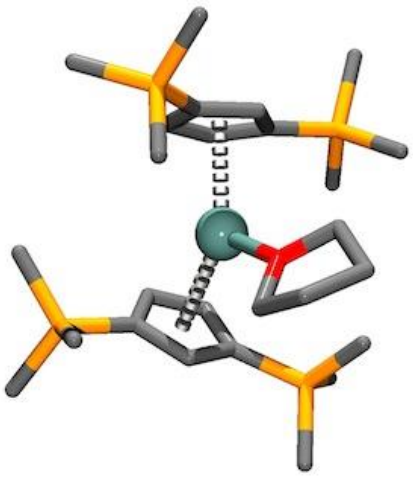


5b



X-Ray structure of 5c

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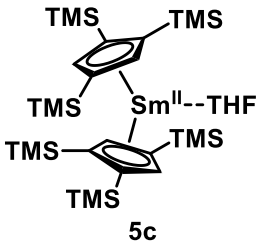
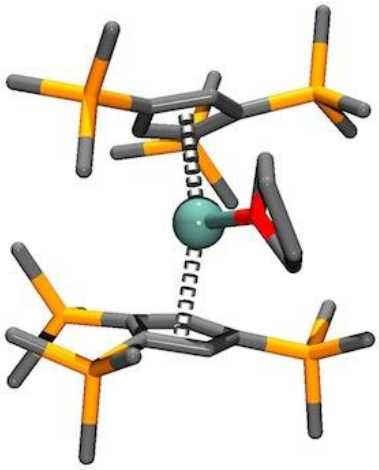
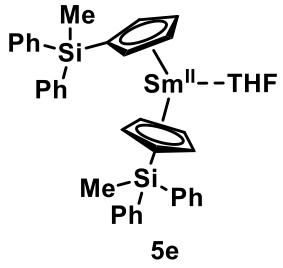


5c

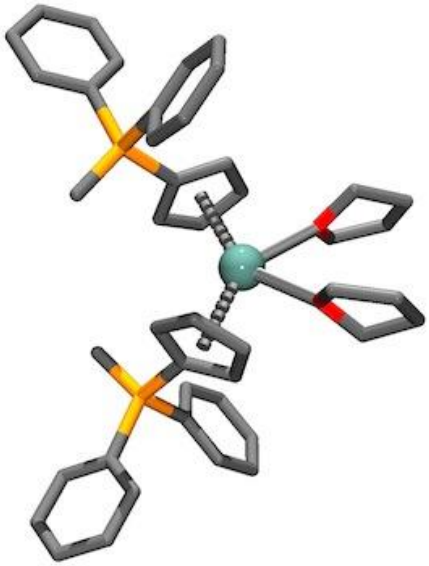


X-Ray structure of 5e

CCDC = 1472304

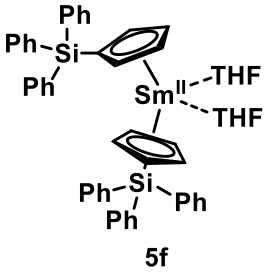


5e

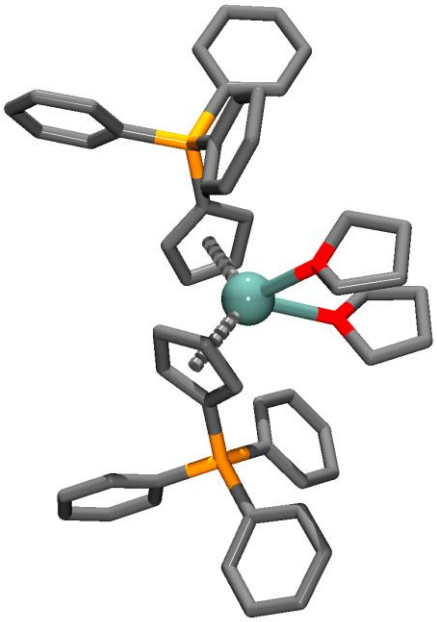


X-Ray structure of 5f

CCDC = 1472305



5f



Crystallographic method

The crystal data for compounds *anti*-**1a**, **4a**, **5b**, **5c**, **5e** and **5f** are compiled in Tables S2 and S3; relevant bond lengths and angles are listed in Table S1. Crystals were examined using Supernova Agilent (*anti*-**1a**, **4a**, **5b**, **5c**, **5e**) and Xcalibur Oxford Diffraction (**5f**) diffractometers, both equipped with CCD area detector and mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on 1° frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed (**4a**, **5b**, **5c**), analytical (**5f**) or multi-scan (anti-**1a**, **5e**) absorption correction with a beam profile correction was applied.[1] The structures were solved variously by direct and heavy atom methods using SHELXS[2a] or SIR2004,[3] and were refined by full-matrix least-squares on all unique F^2 values,[2b] with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; U_{iso}(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlis^{Pro} was used for control and integration;[1] SHELX[2] and SIR2004[3] were employed through OLEX2[4] for structure solution and refinement. ORTEP-3[5] and POV-Ray[6] were employed for molecular graphics. CCDC (anti-**1a**, **4a**, **5b**, **5c**, **5e**, **5f**) contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Table S1: Selected bond lengths (Å) and angles (º) for **5b**, **5c**, **5e**, **5f**

	5b	**5c**	**5e**	**5f**
M–$Cent_{Cp}$	2.5347(14)	2.5737(2)	2.5178(2)	2.561(2)
		2.5810(2)		2.5955(5)
M–O	2.470(7)	2.566(3)	2.78(3)	2.574(9)
				2.564(10)
Cp–M–Cp	137.24(2)	144.979(8)	135.294(2)	124.52(2)

Table S2: Crystallographic data for **5b**, **5c**, **5e**, **5f**

	5b	**5c**	**5e**	**5f**
Formula	$C_{27}H_{51}OSi_4Sm$	$C_{32}H_{66}OSi_6Sm$	$C_{44}H_{50}O_2Si_2Sm$	$C_{54}H_{54}O_2Si_2Sm$
Fw	654.39	785.73	817.37	941.50
cryst size, mm	0.05 x 0.20 x 0.37	0.08 x 0.13 x 0.23	0.10 x 0.10 x 0.17	0.16 x 0.23 x 0.41
crystal syst	orthorhombic	monoclinic	tetragonal	monoclinic
space group	*Cmc*2_1	*P*2_1/*n*	*I*−4	*Cc*
a, Å	11.6326(6)	11.2870(3)	13.1871(2)	17.1230(6)
b, Å	13.7770(7)	22.3415(7)	13.1871(2)	9.6421(3)
c, Å	21.1559(14)	16.9210(5)	11.4268(4)	27.6291(11)
α, °	90	90	90	90
β, °	90	97.974(3)	90	99.283(4)
γ, °	90	90	90	90
V, Å^3	3390.5(3)	4225.7(2)	1987.12(9)	4501.9(3)
Z	4	4	2	4
ρ_{calcd}, g cm^3	1.282	1.235	1.366	1.389
μ, mm^{-1}	1.889	1.581	1.572	1.398
F(*000*)	1356	11648	840	1936
no. of reflections (unique)	6444(2876)	17017(7723)	7156(1808)	8182(31392)
S[a]	1.06	1.04	1.10	1.08
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0530(0.1050)	0.0438(0.0918)	0.0729(0.1842)	0.0624(0.1586)
R_{int}	0.058	0.039	0.049	0.123
min., max. diff map, e Å^{-3}	−0.67, 1.40	−0.51, 1.20	−1.42, 1.74	−1.48, 1.98

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

Table S3: Crystallographic data for *anti*-**1a** and **4a**

	anti-**1a**	**4a**
Formula	$C_{17}H_{22}O_2$	$C_{17}H_{24}O_2$
Fw	258.34	260.36
cryst size, mm	0.05 x 0.07 x 0.30	0.28 x 0.31 x 0.52
crystal syst	triclinic	monoclinic
space group	*P*−1	$P2_1/n$
a, Å	8.9679(13)	12.7728(5)
b, Å	11.9038(16)	8.2427(3)
c, Å	14.801(2)	14.1842(6)
α, °	91.758(11)	90
β, °	94.311(12)	103.024(4)
γ, °	110.931(13)	90
V, Å^3	1468.8(4)	1454.93(10)
Z	4	4
ρ_{calcd}, g cm^3	1.168	1.189
μ, mm^{-1}	0.075	0.076
F(*000*)	560	568
no. of reflections (unique)	9199(5365)	9115(2658)
S[a]	1.03	1.04
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0816(0.2048)	0.0473(0.1220)
R_{int}	0.060	0.037
min., max. diff map, e Å^{-3}	−0.24, 0.38	−0.20, 0.21

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

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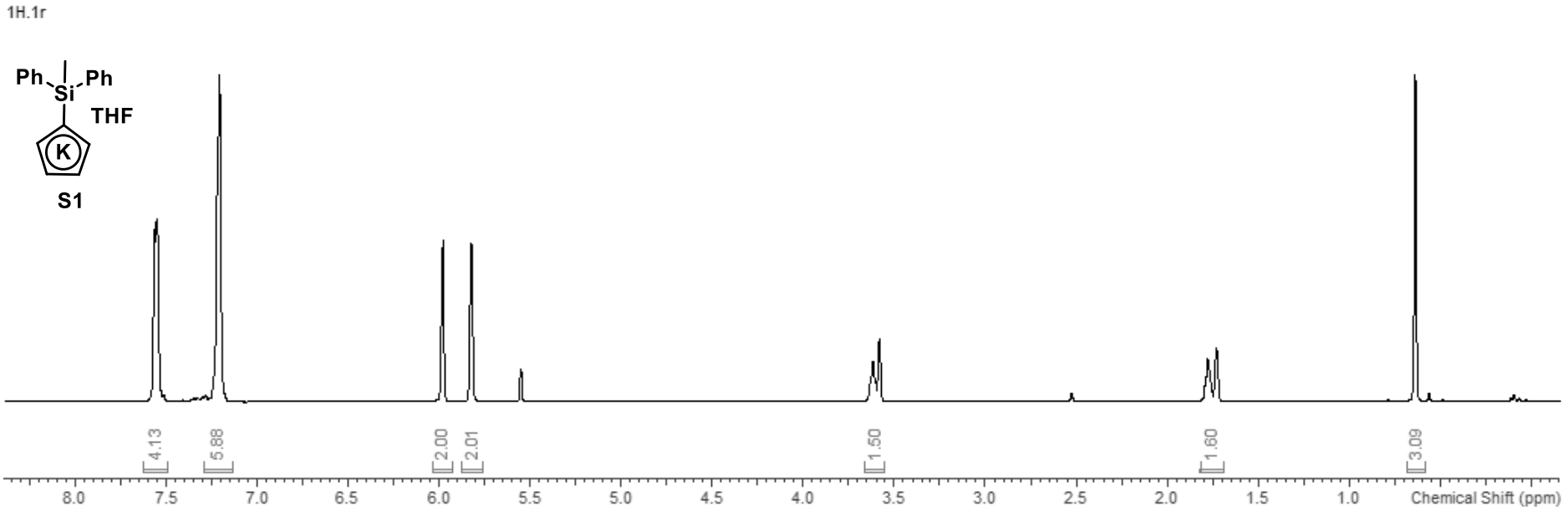
400 MHz, THF-d_8



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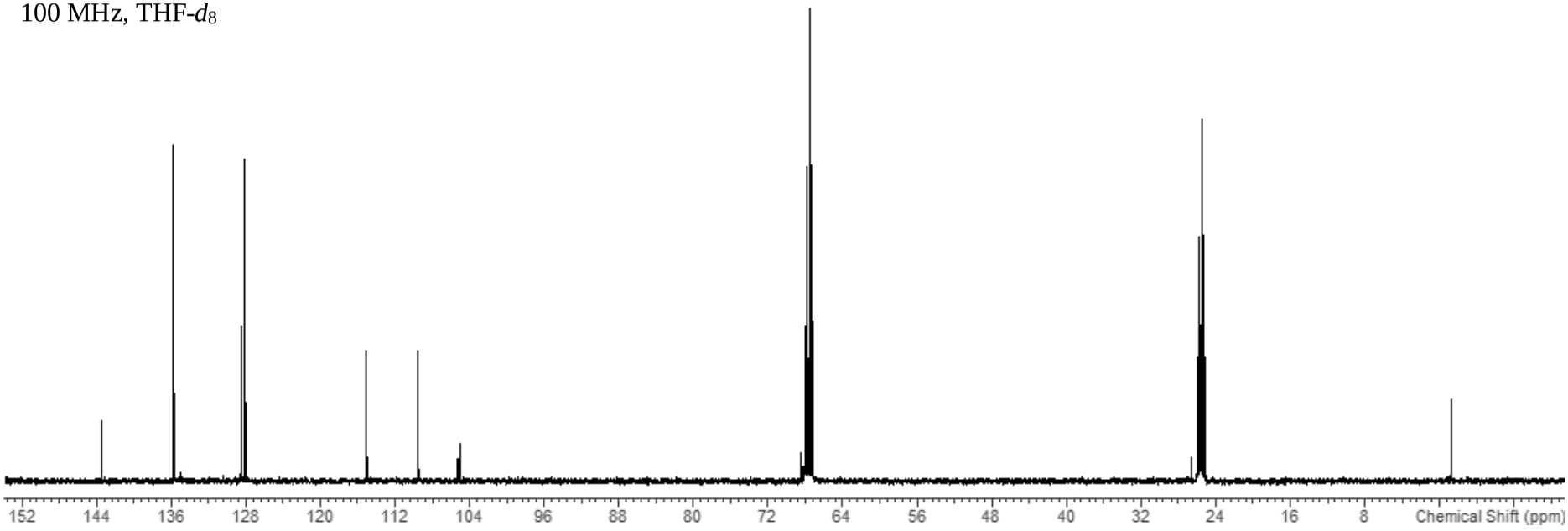

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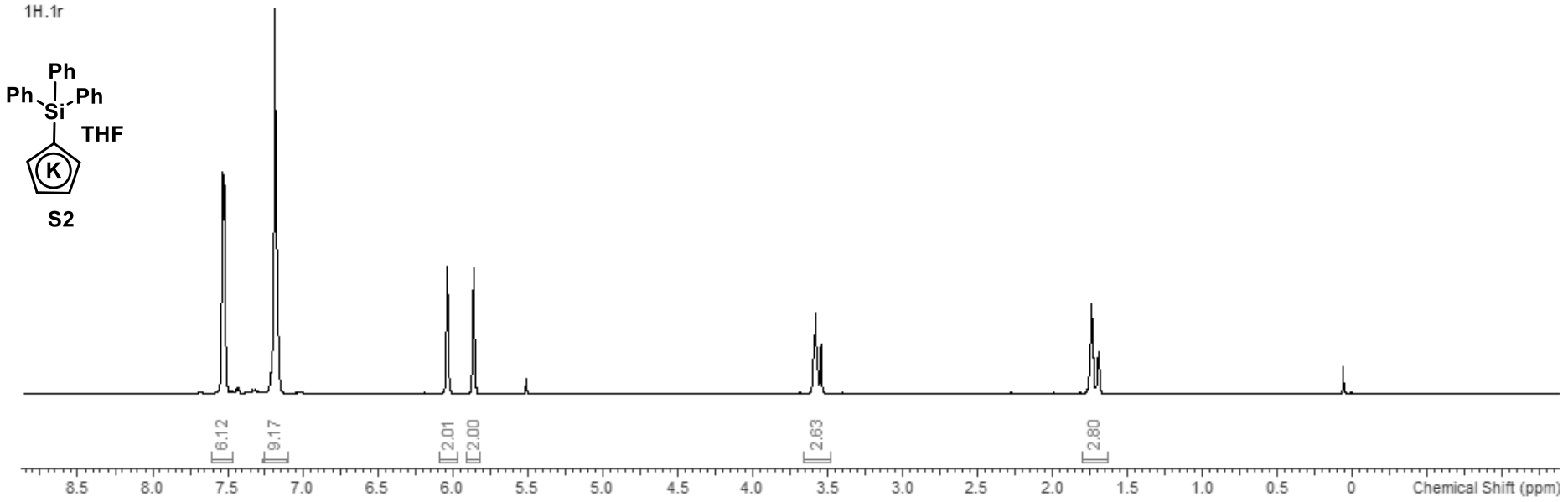

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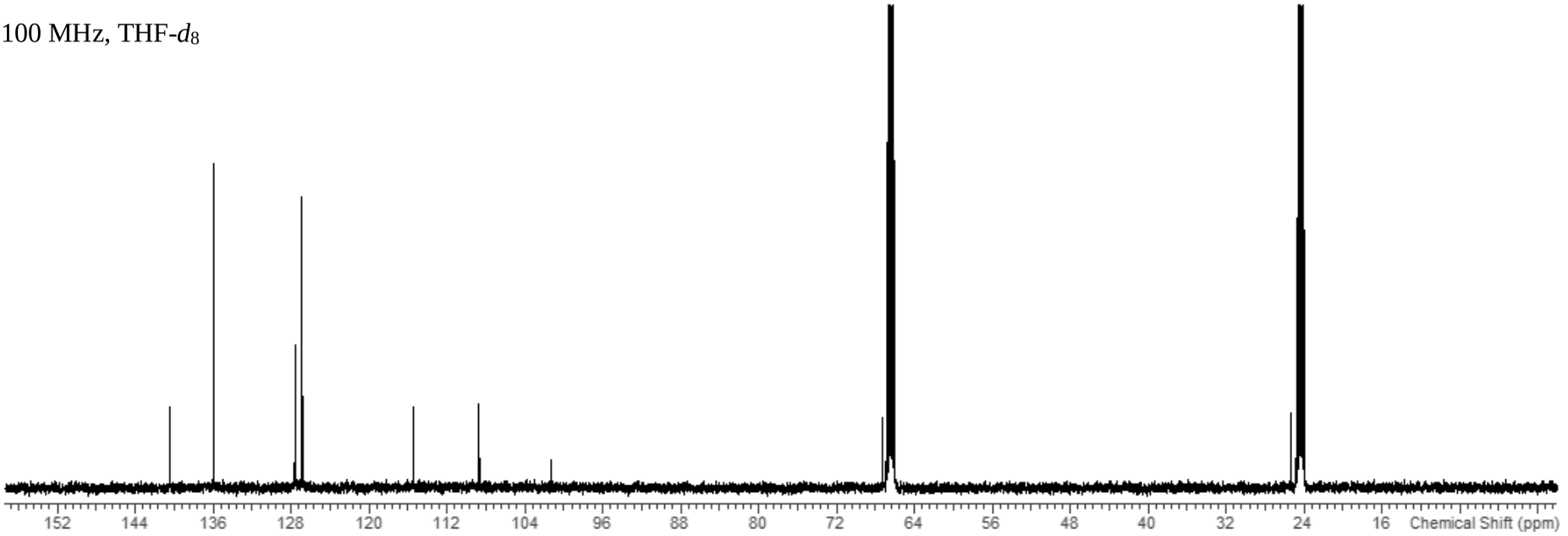

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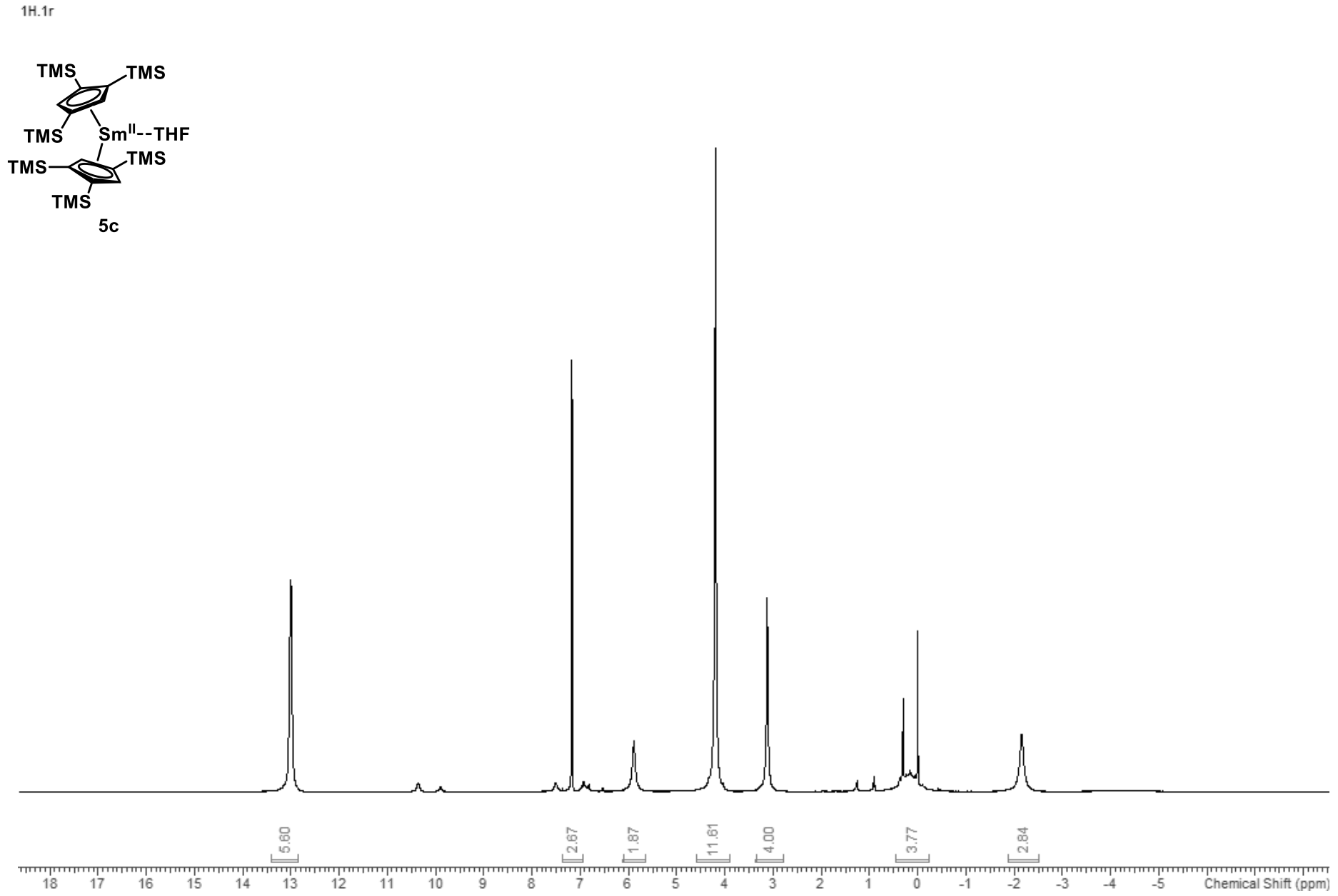
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5c
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11.61
4.00
3.77
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Chemical Shift (ppm)

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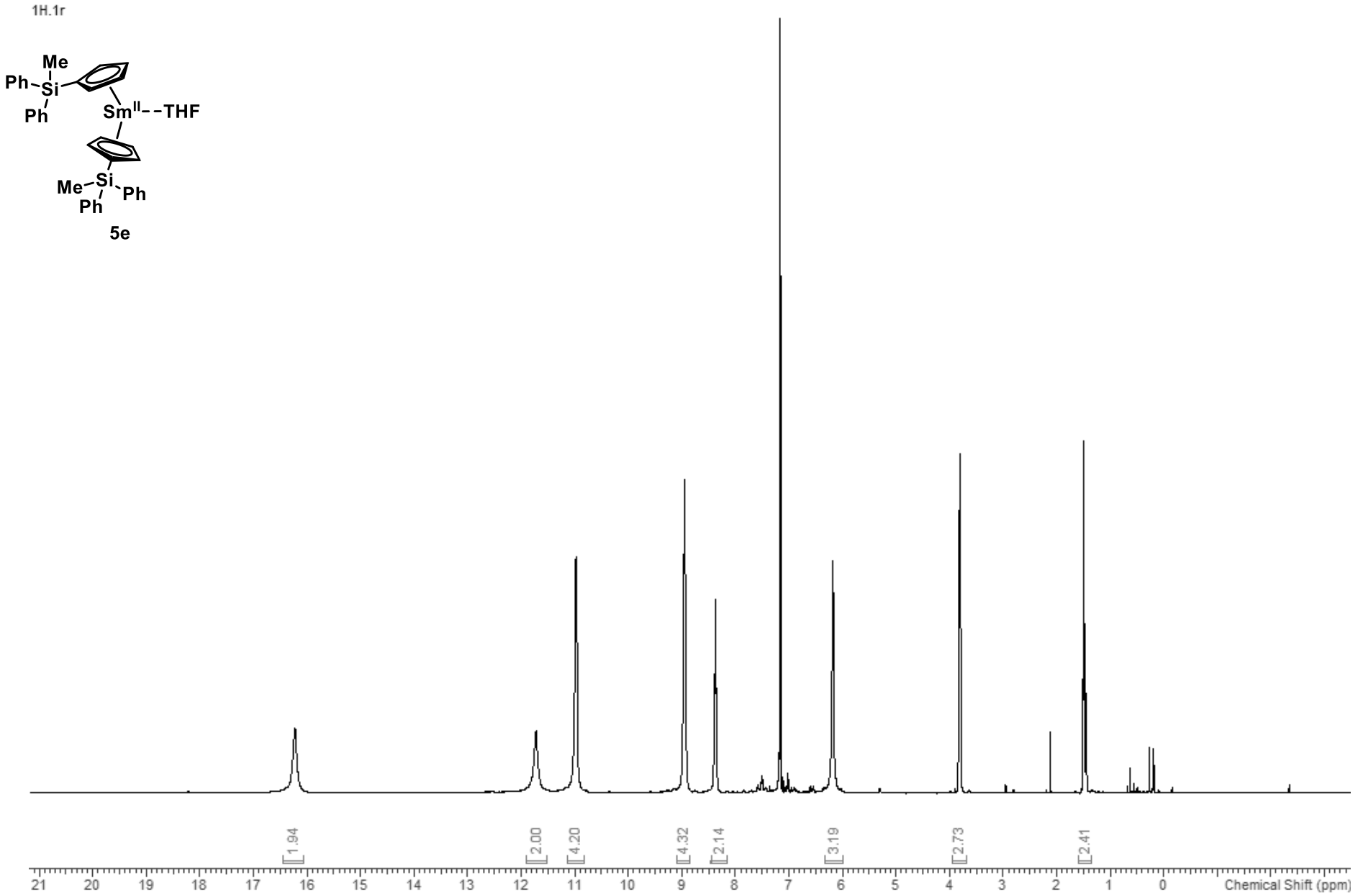
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Si
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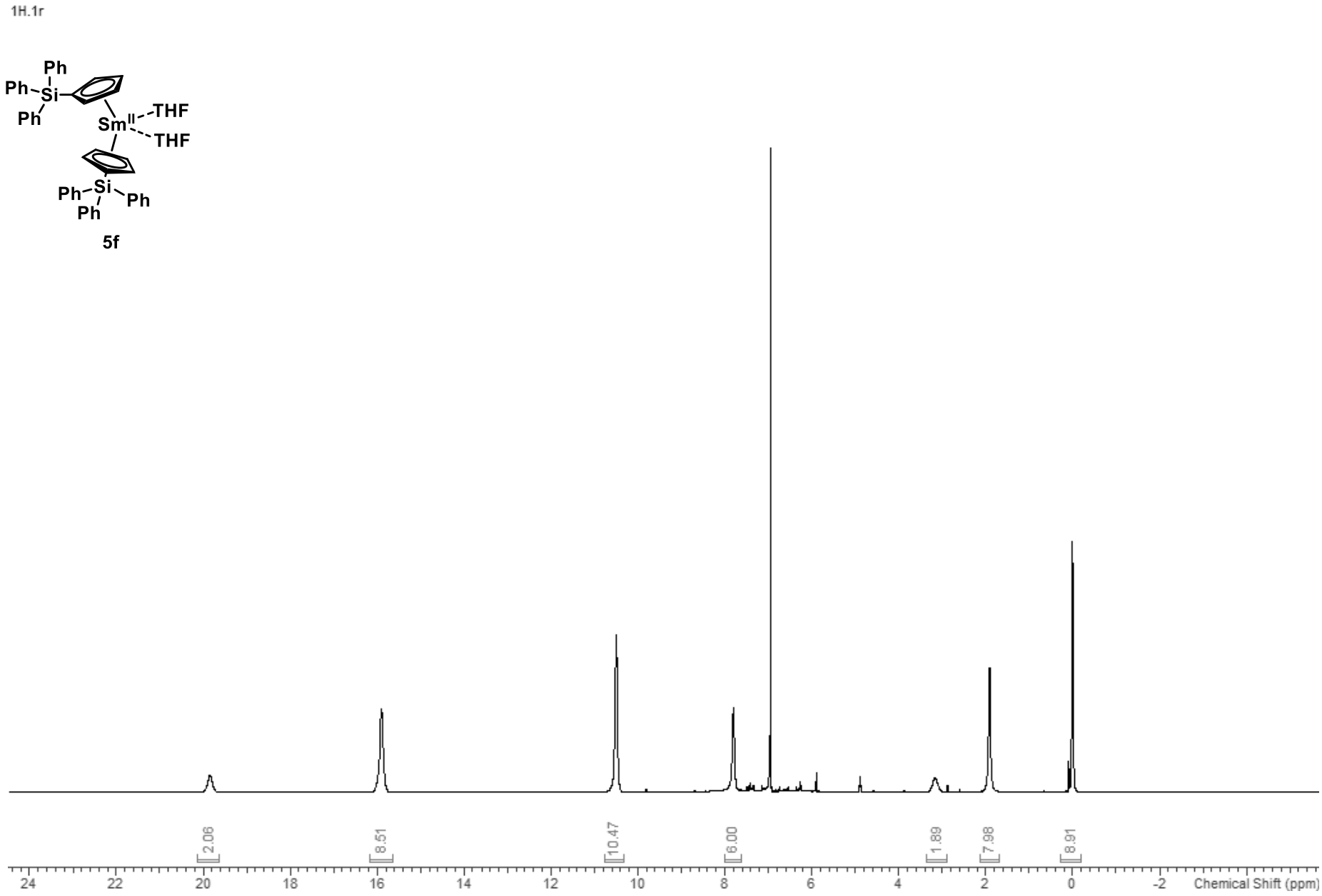
Chemical Shift (ppm)

400 MHz, C_6D_6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10.47
6.00
1.89
7.98
8.91
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2
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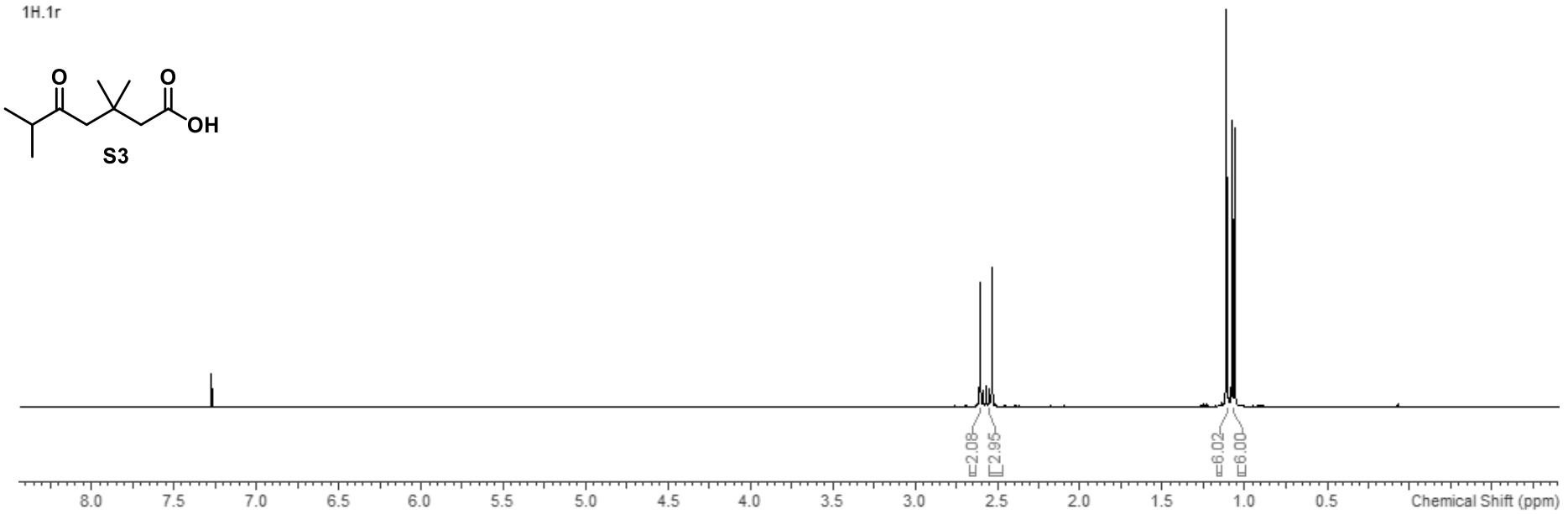
Chemical Shift (ppm)

400 MHz, $CDCl_3$



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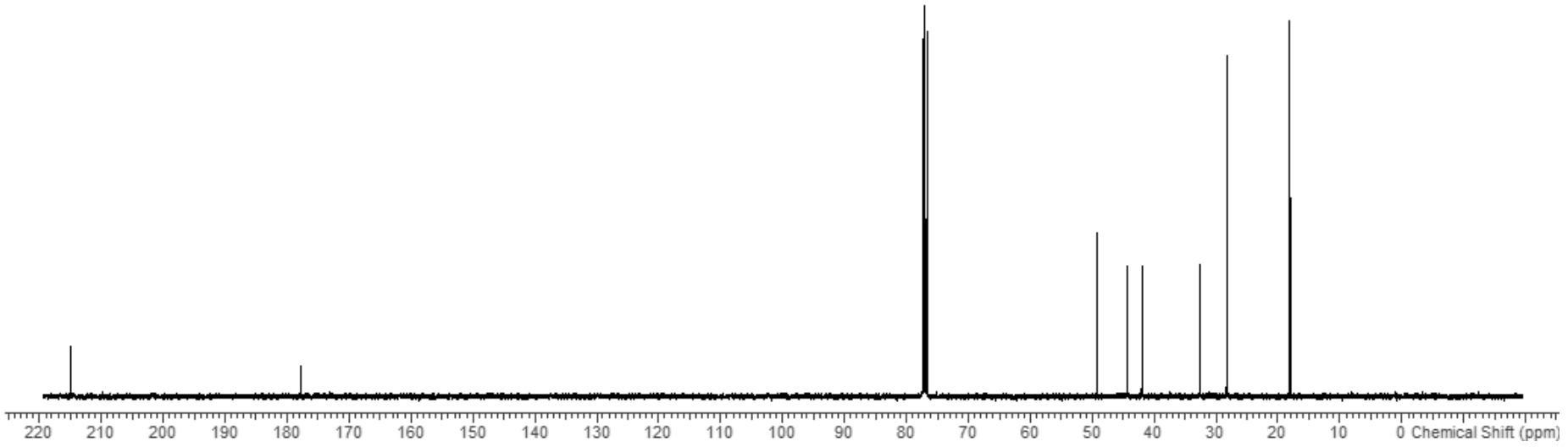

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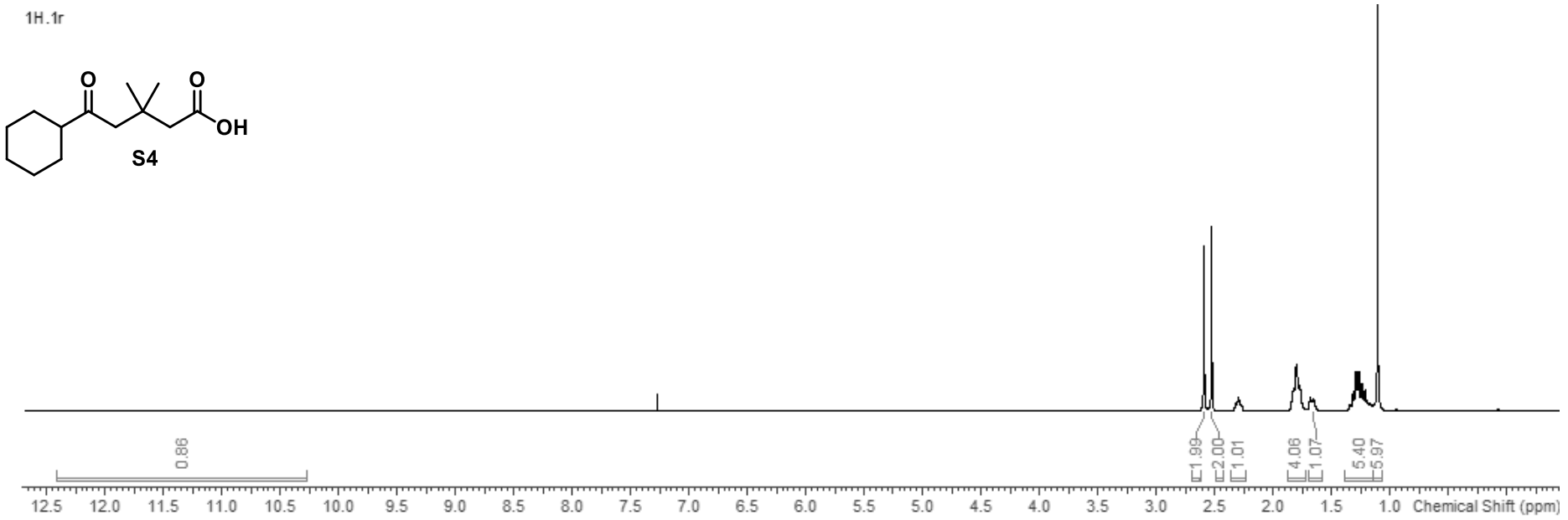

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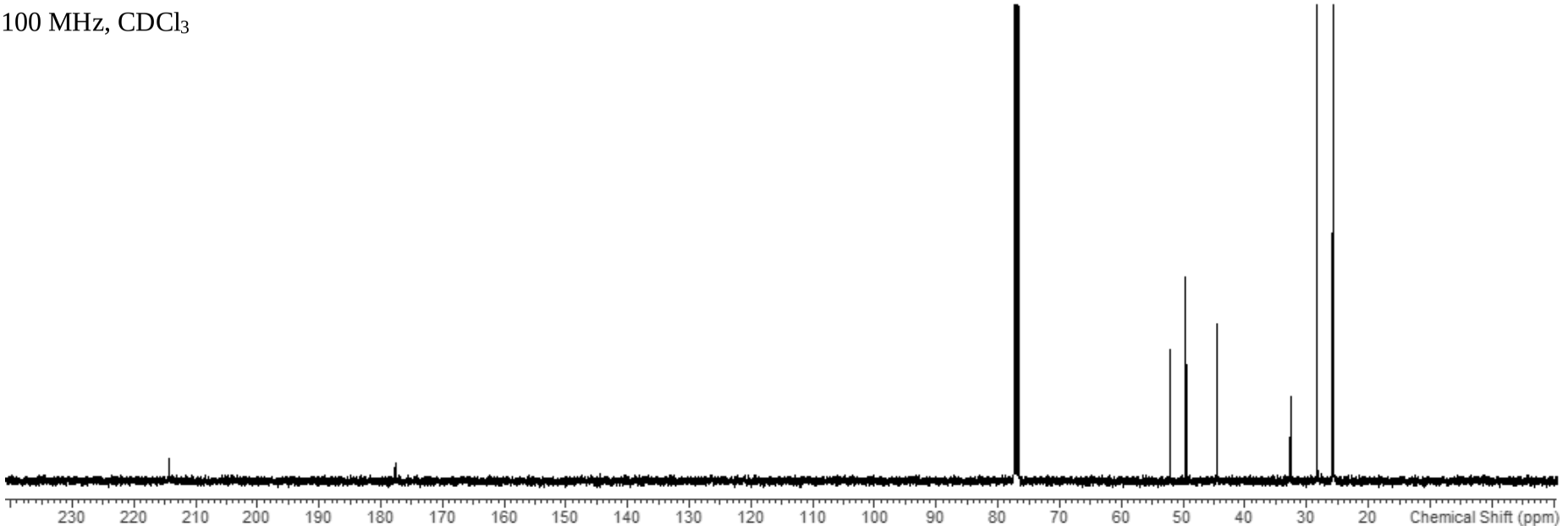
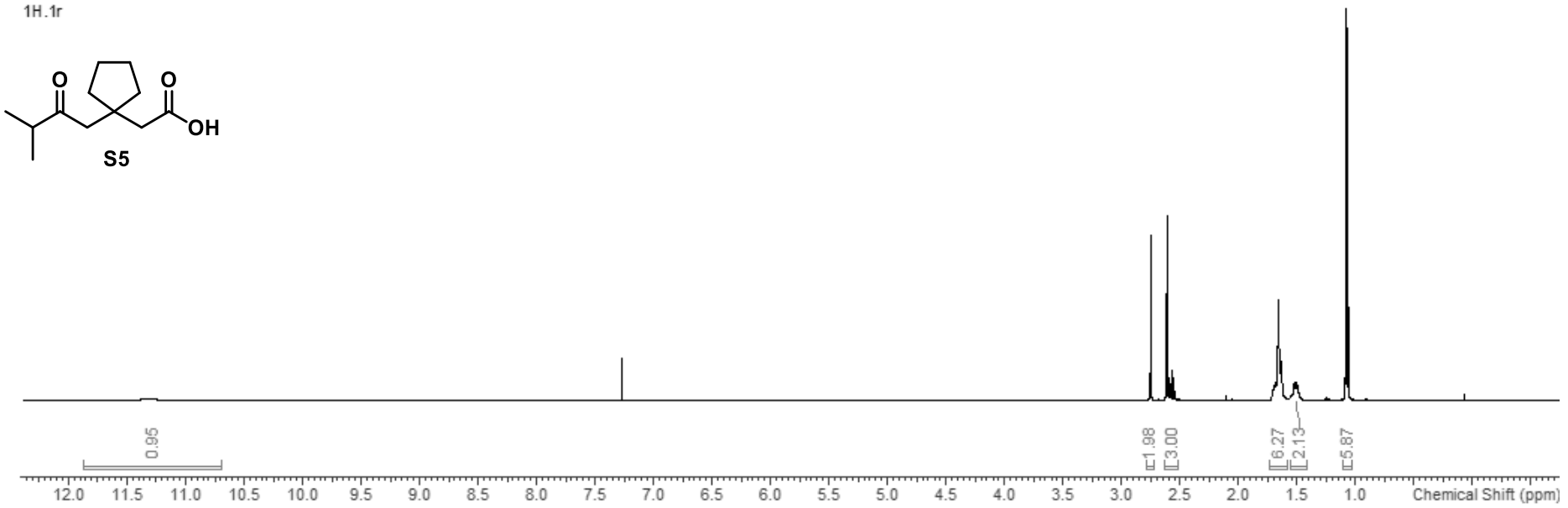
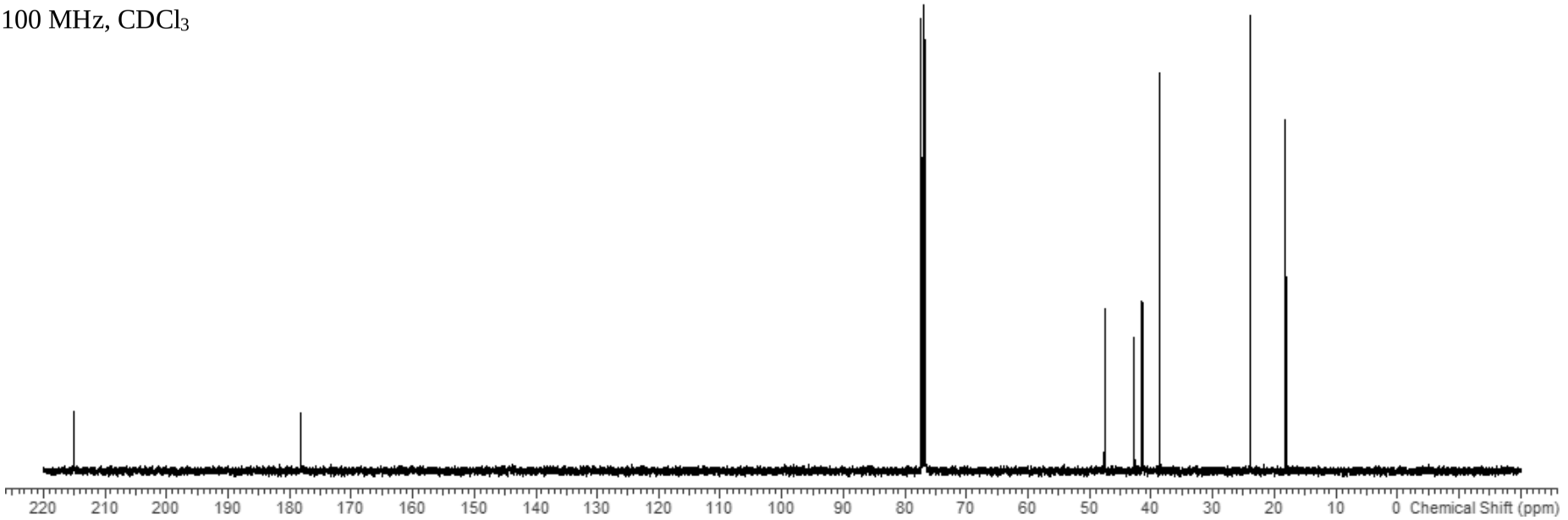


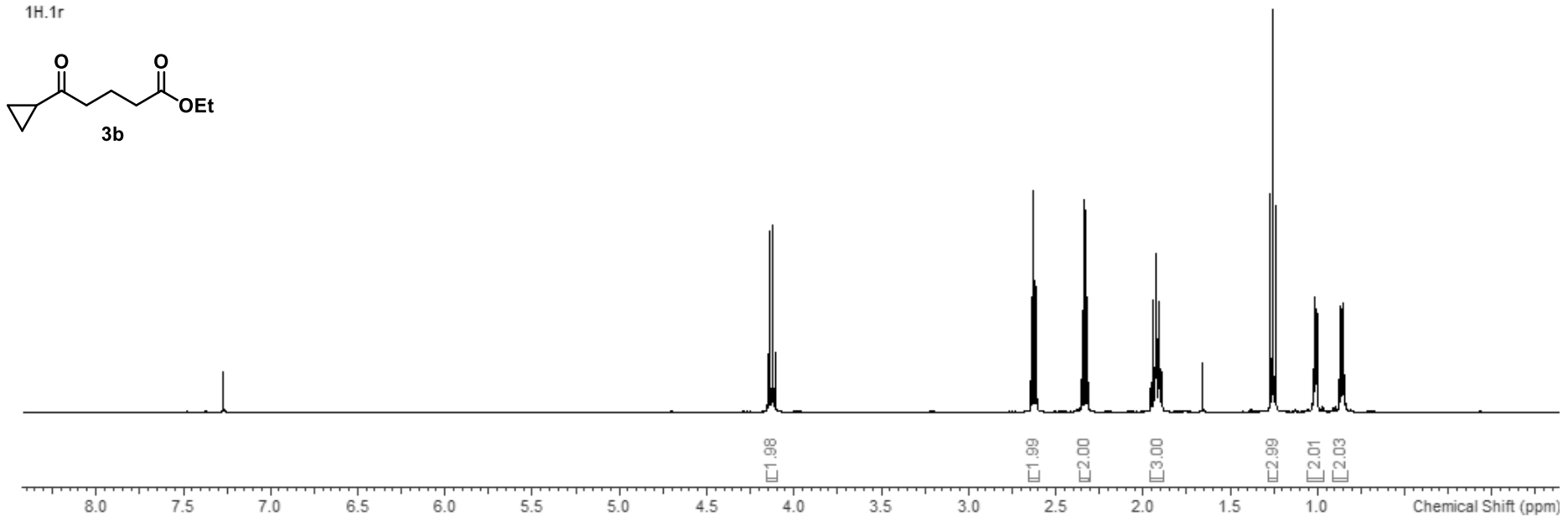
400 MHz, $CDCl_3$



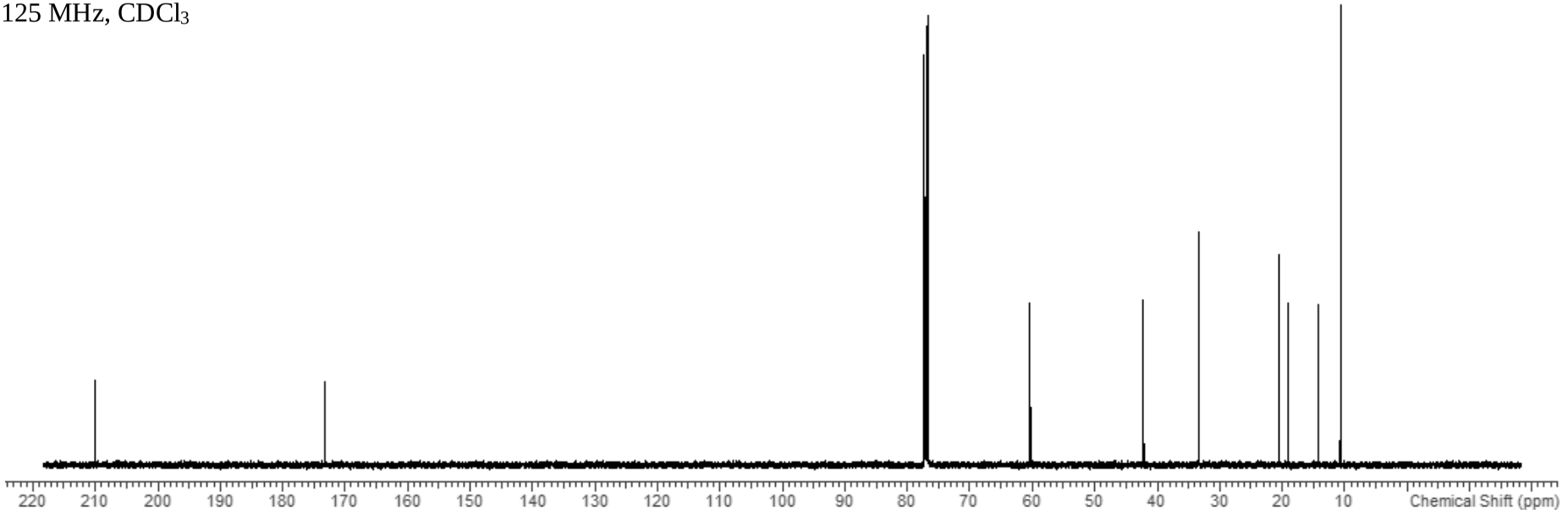
100 MHz, $CDCl_3$



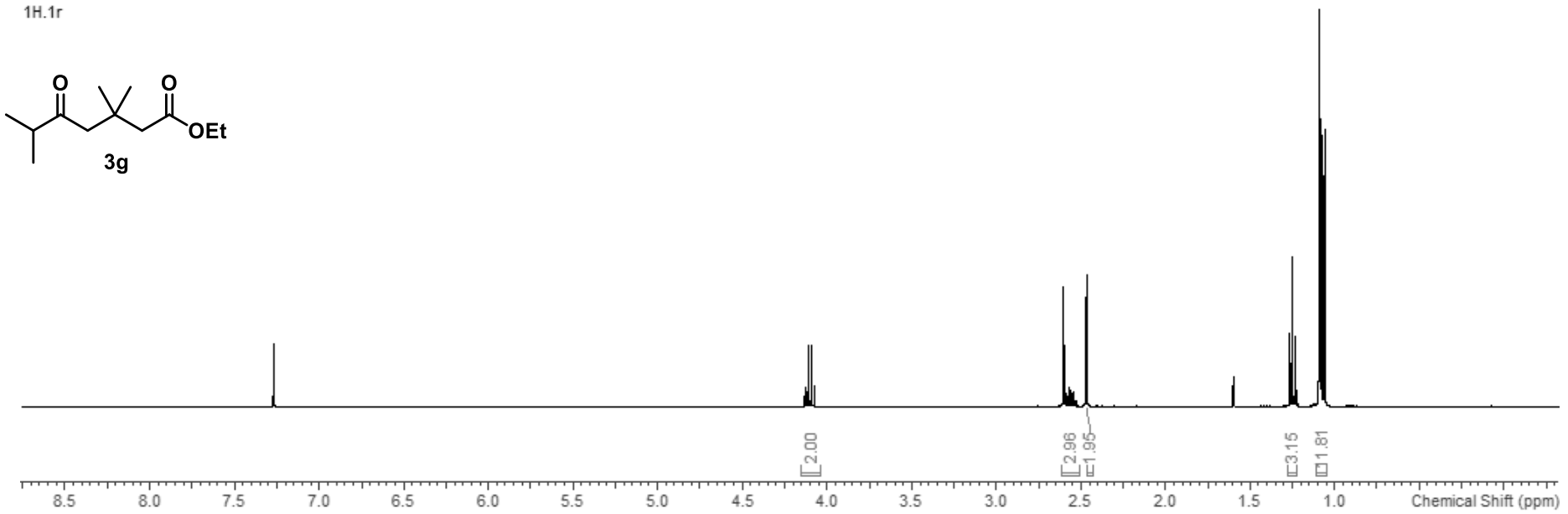
500 MHz, $CDCl_3$



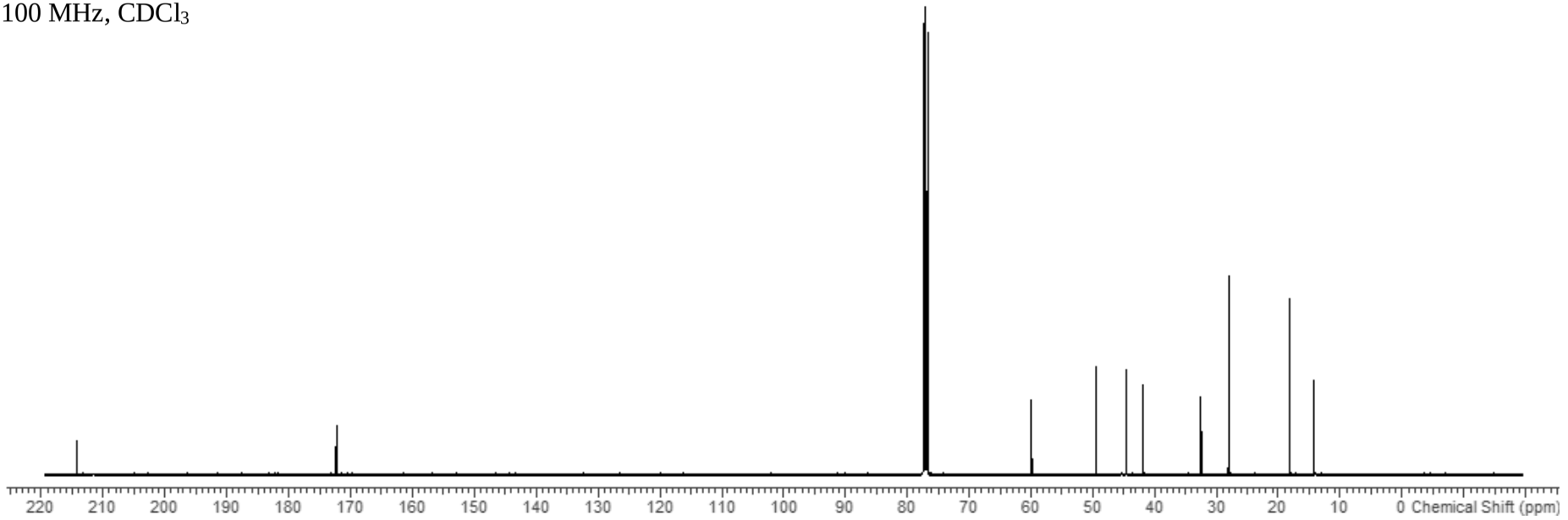
125 MHz, $CDCl_3$



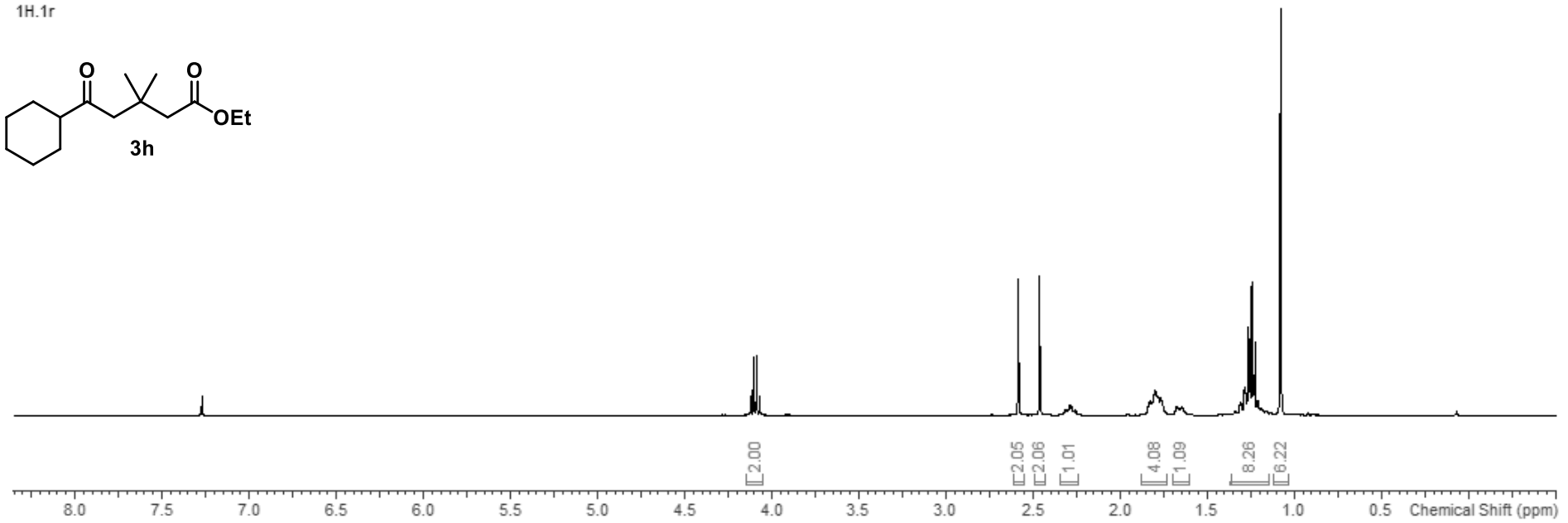
400 MHz, $CDCl_3$



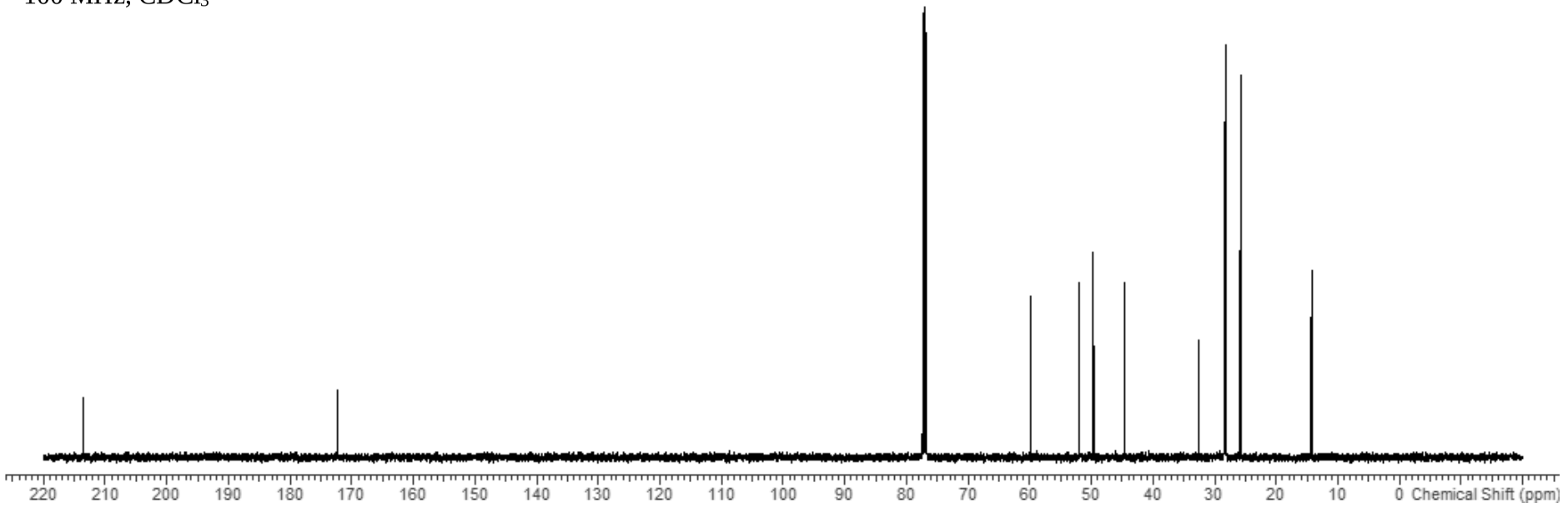
100 MHz, $CDCl_3$



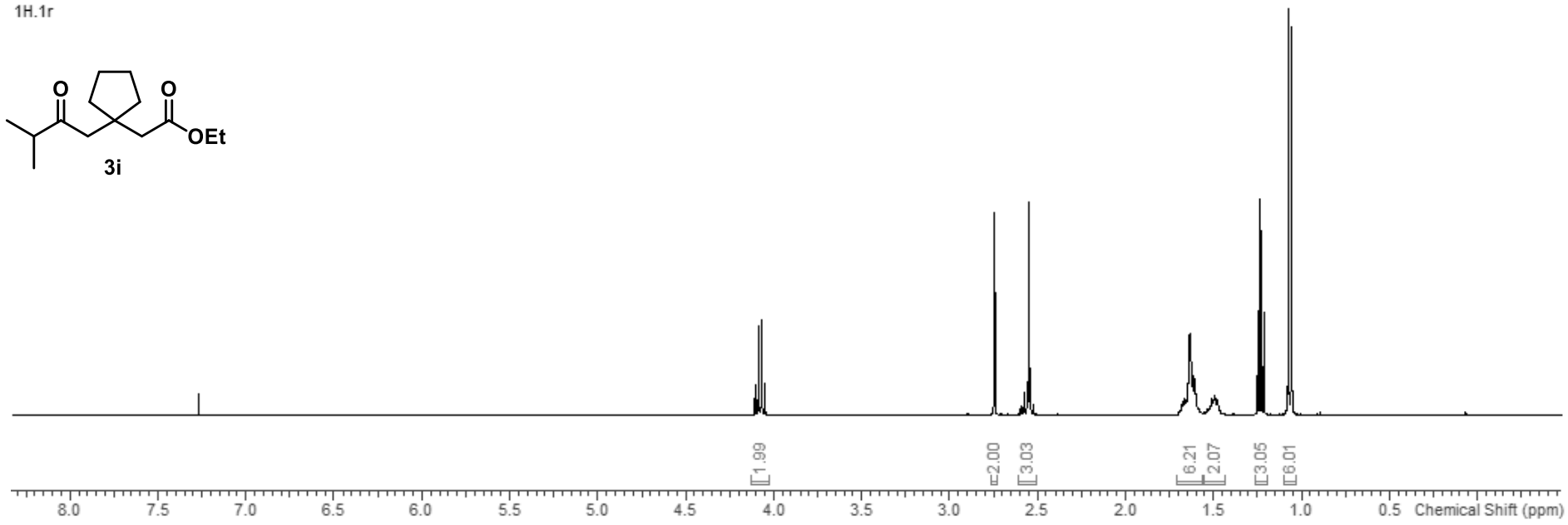
400 MHz, $CDCl_3$



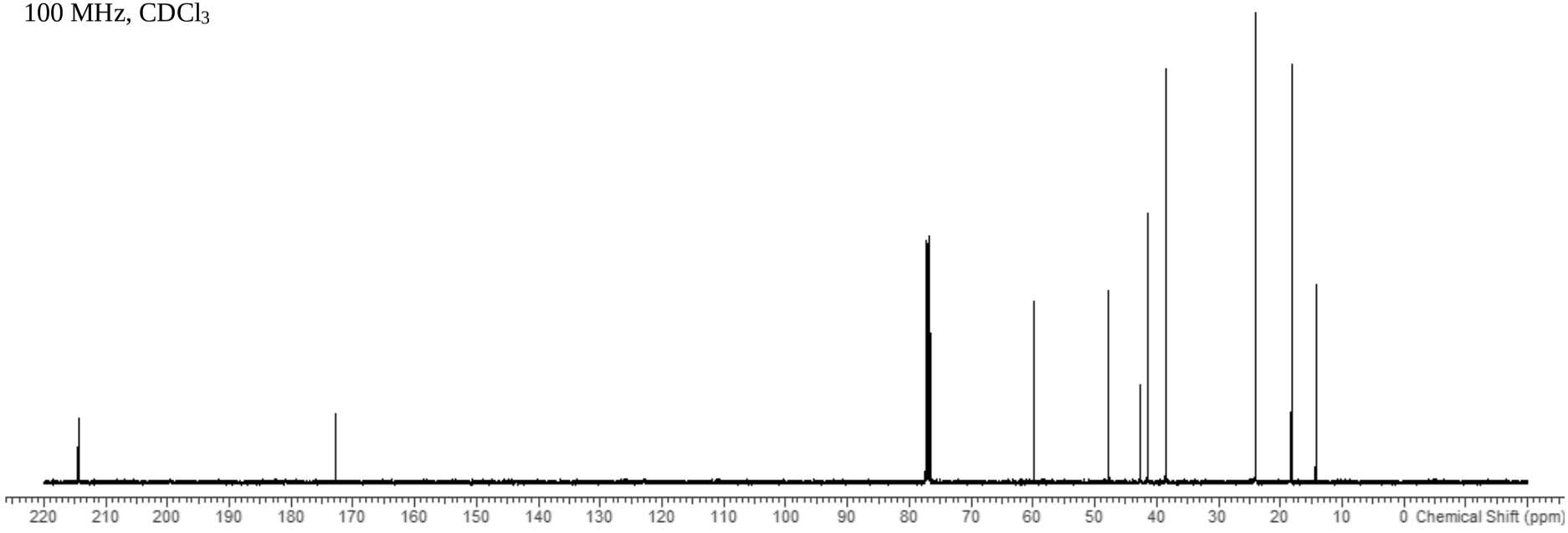
100 MHz, $CDCl_3$



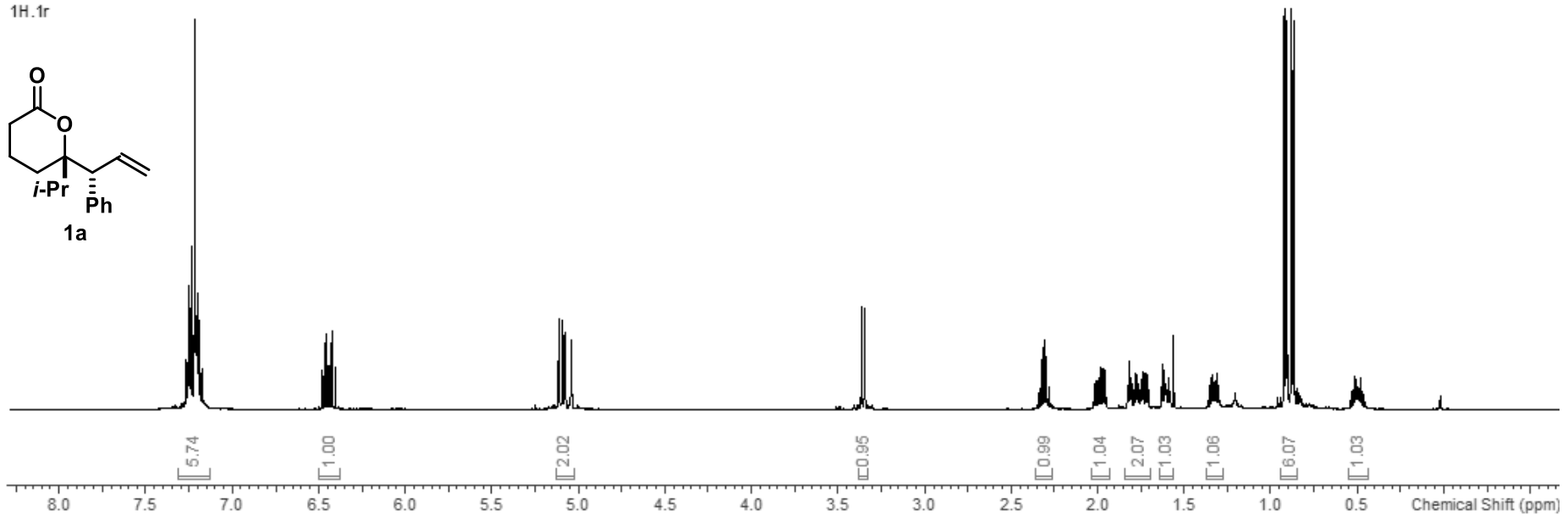
400 MHz, $CDCl_3$



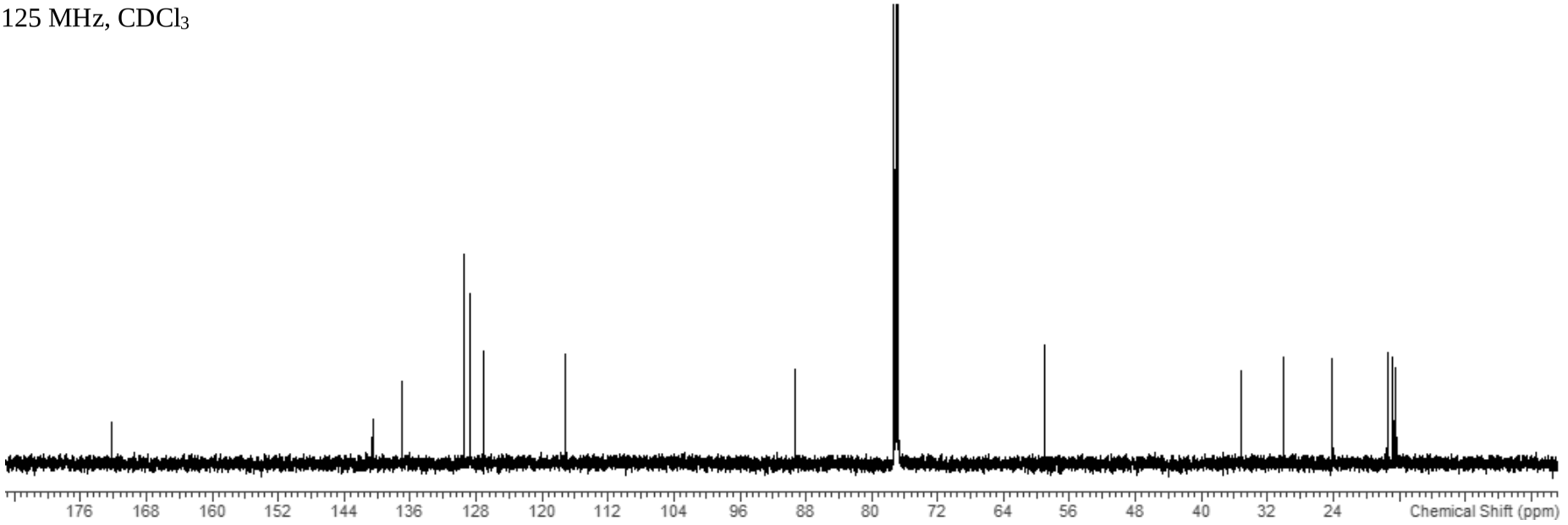
100 MHz, $CDCl_3$



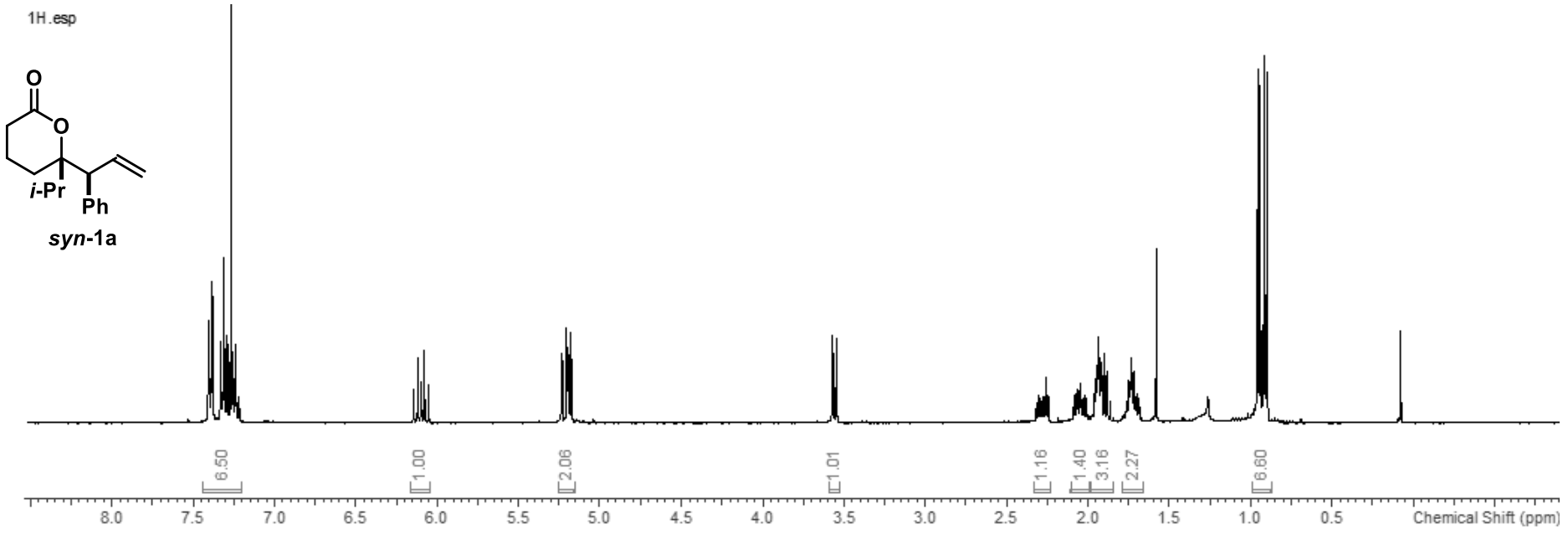
500 MHz, $CDCl_3$



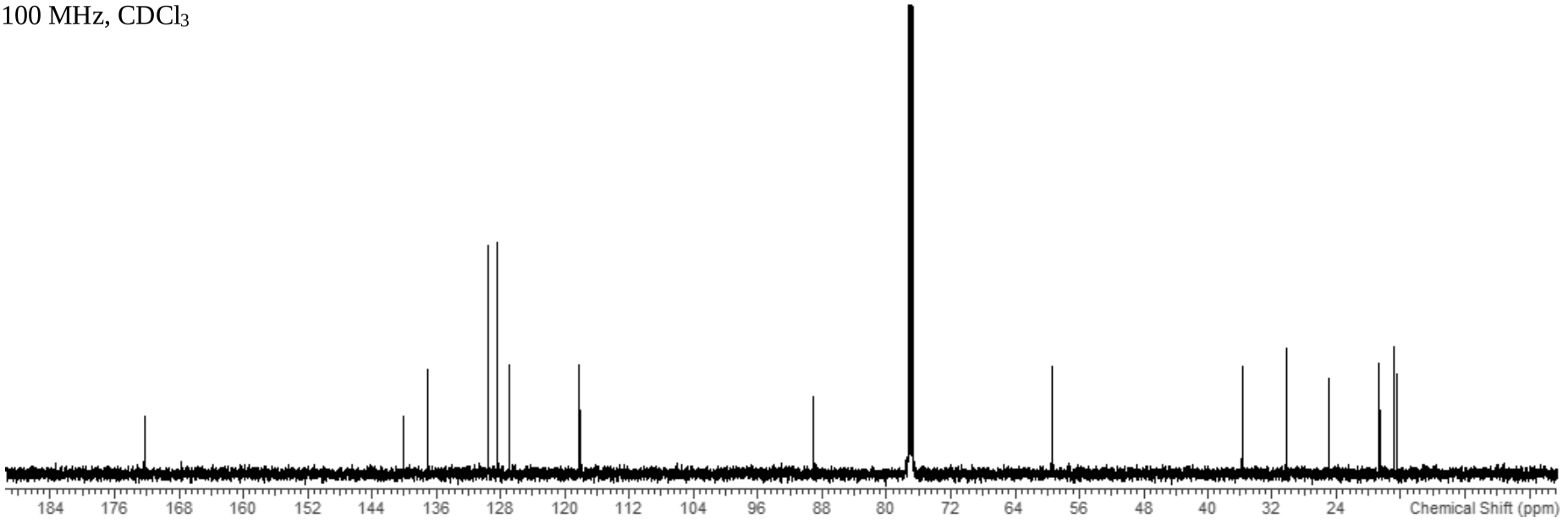
125 MHz, $CDCl_3$



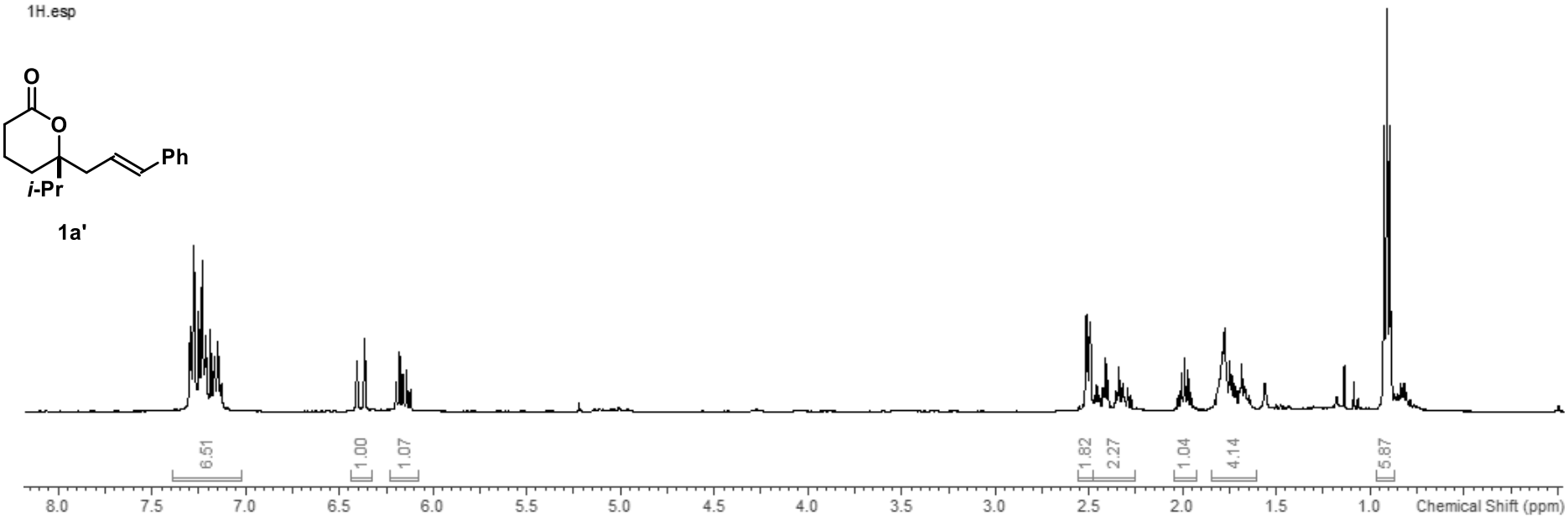
400 MHz, $CDCl_3$



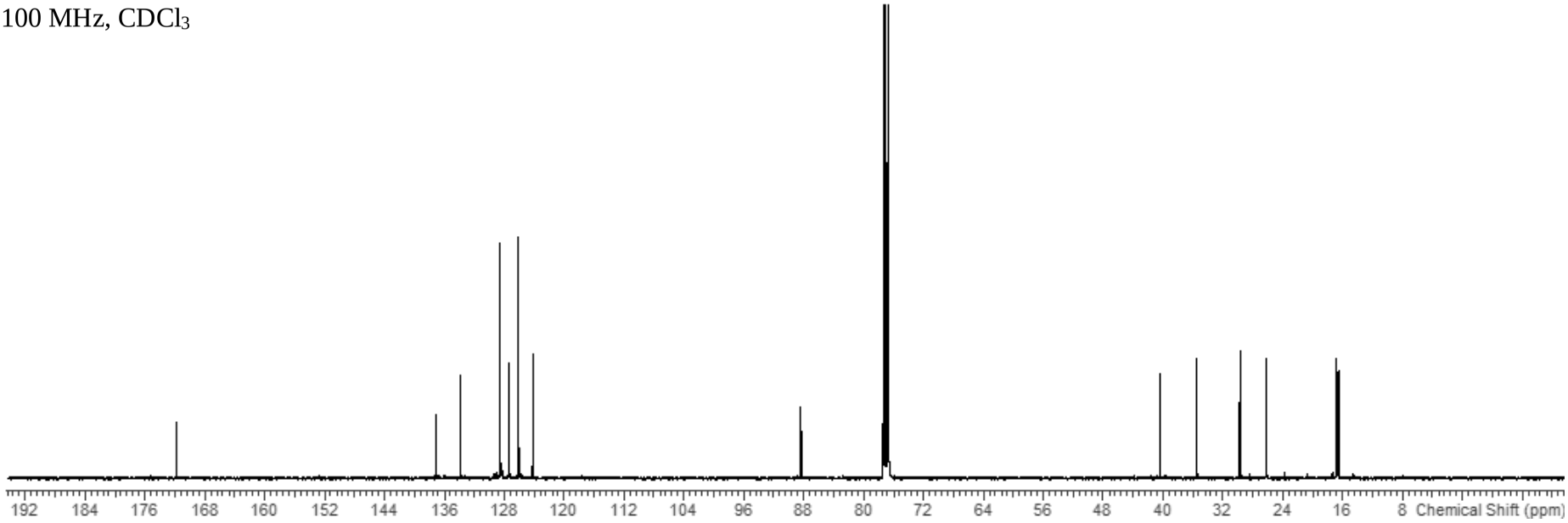
100 MHz, $CDCl_3$



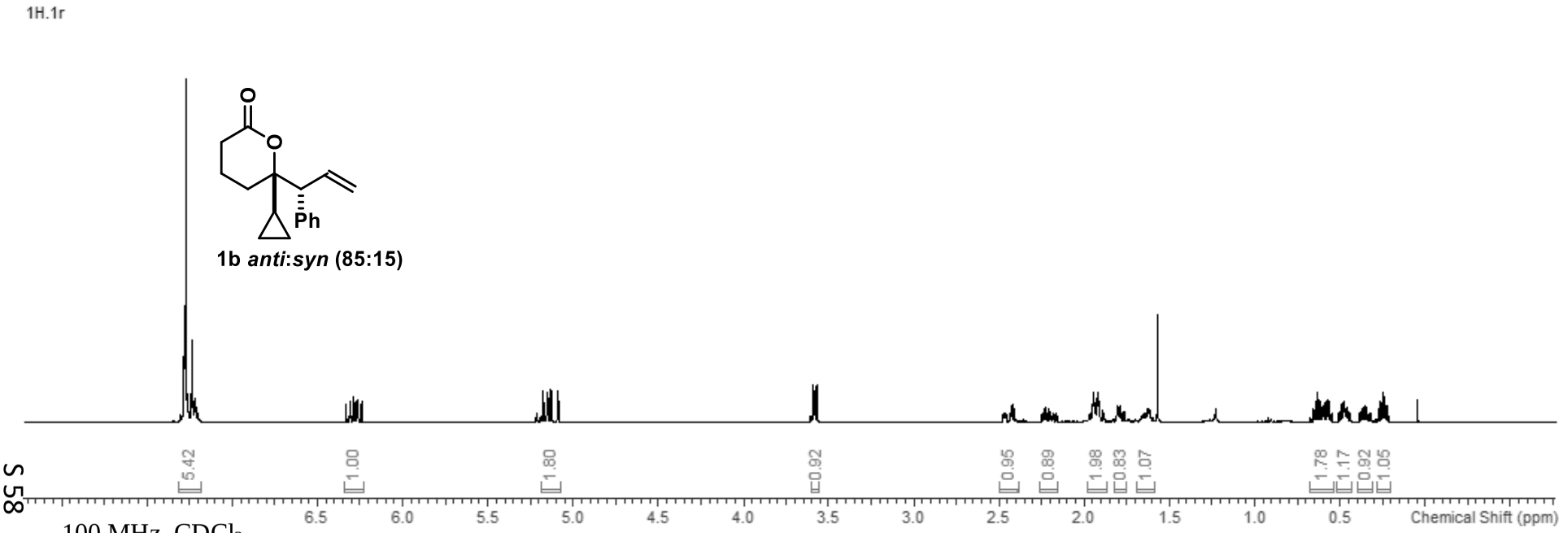
400 MHz, $CDCl_3$



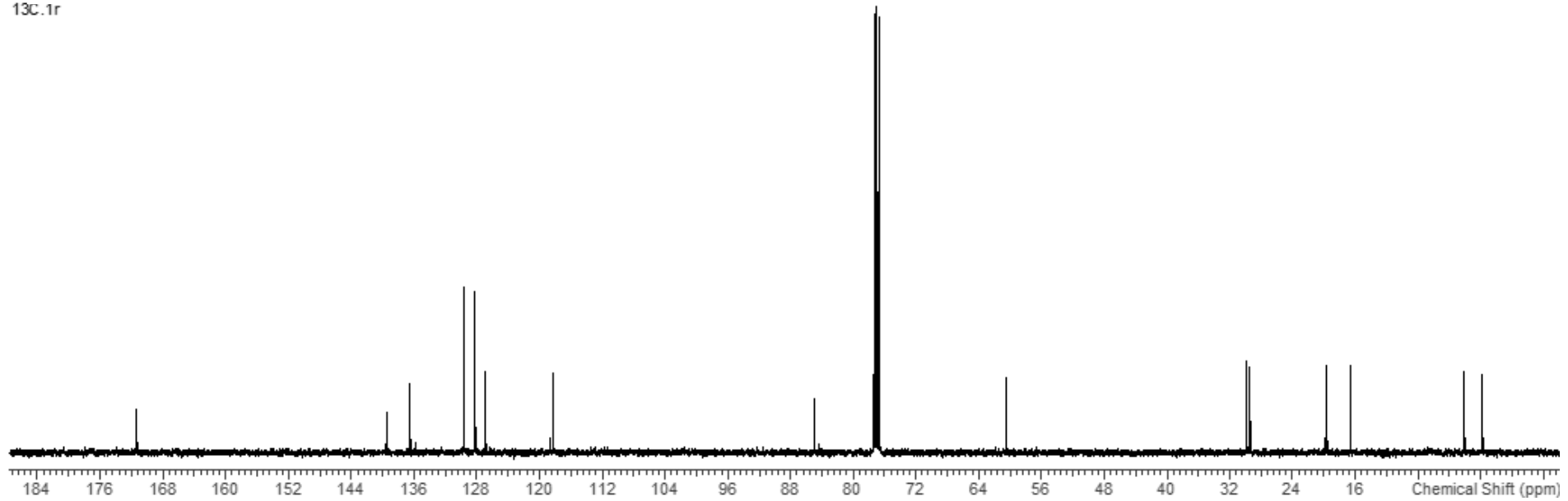
100 MHz, $CDCl_3$



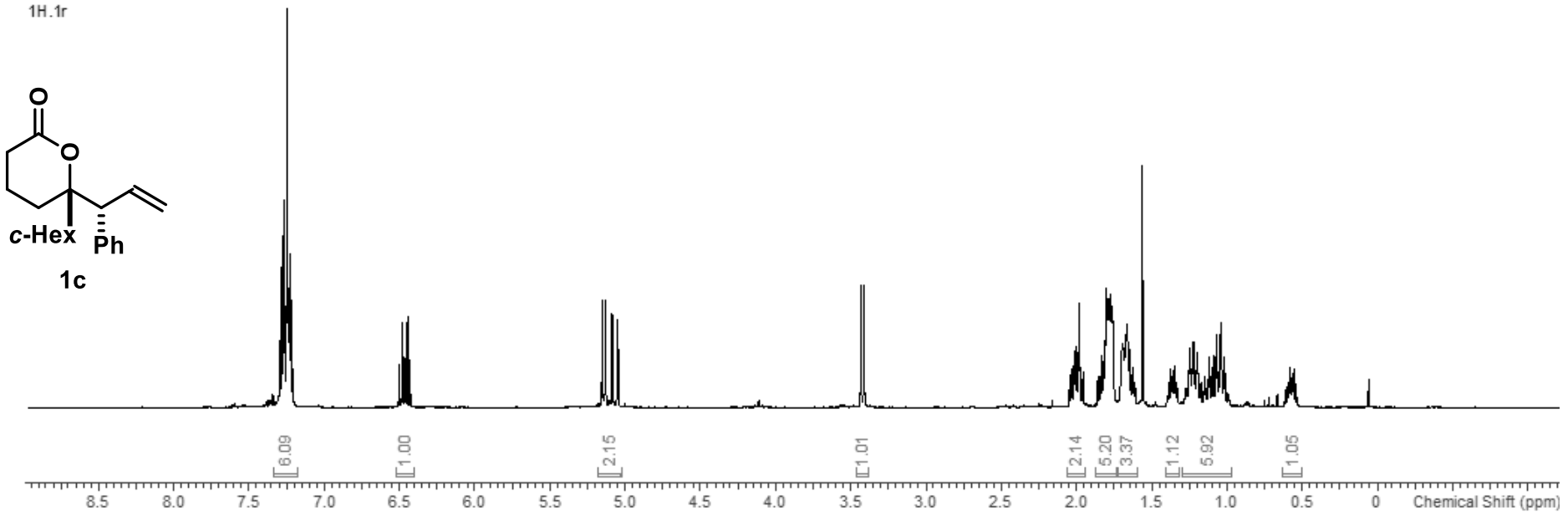
400 MHz, $CDCl_3$



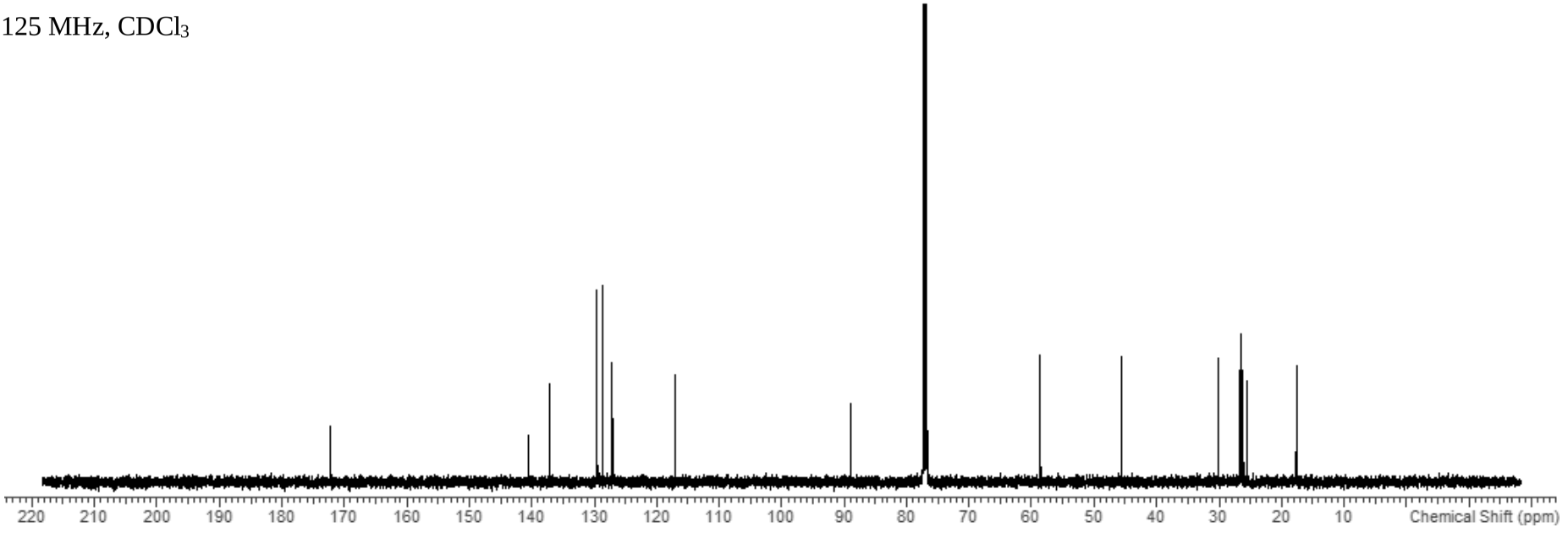
100 MHz, $CDCl_3$



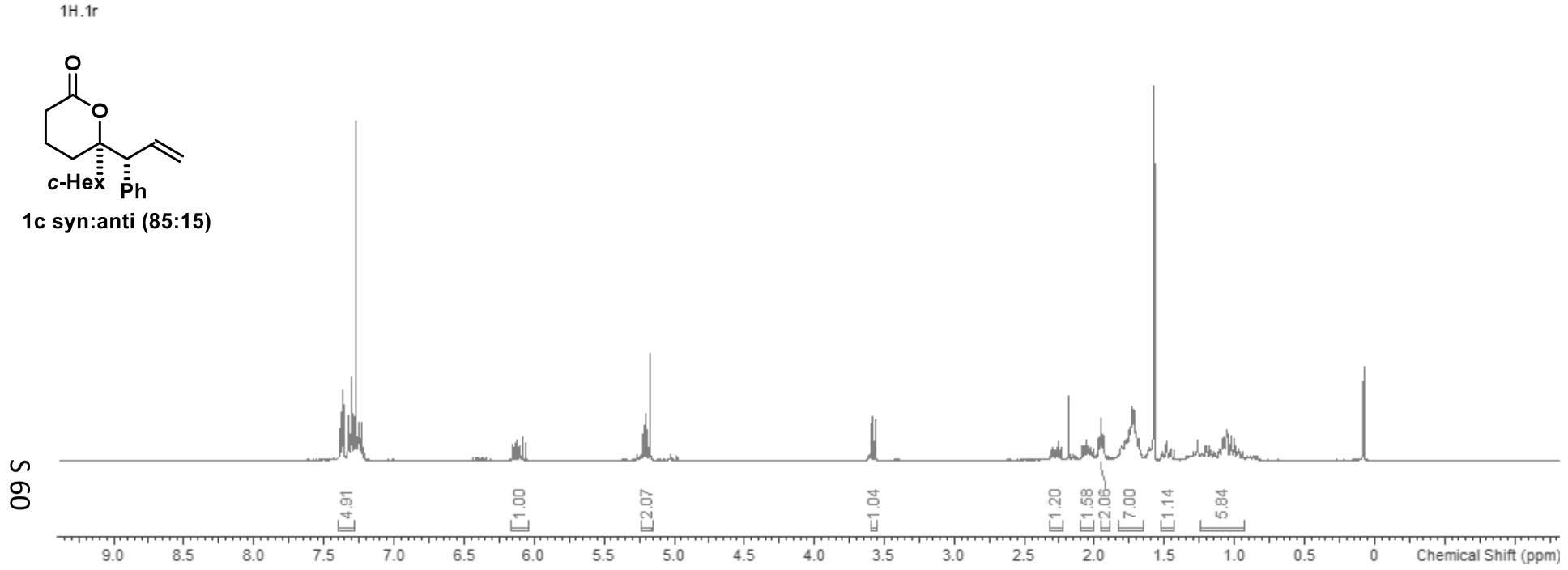
500 MHz, $CDCl_3$

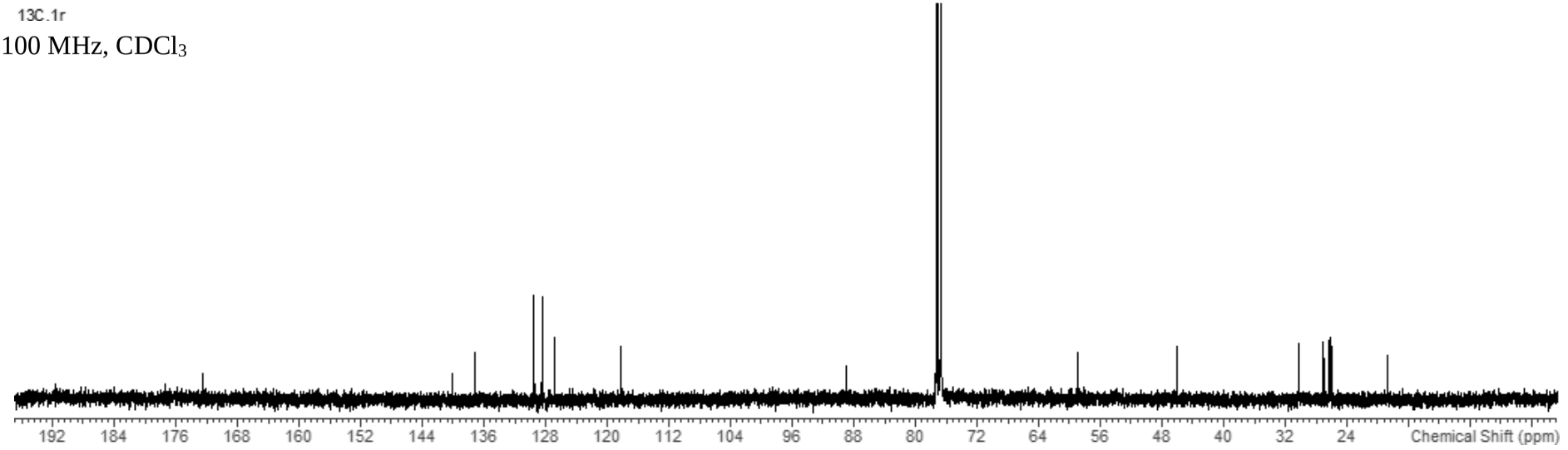


125 MHz, $CDCl_3$



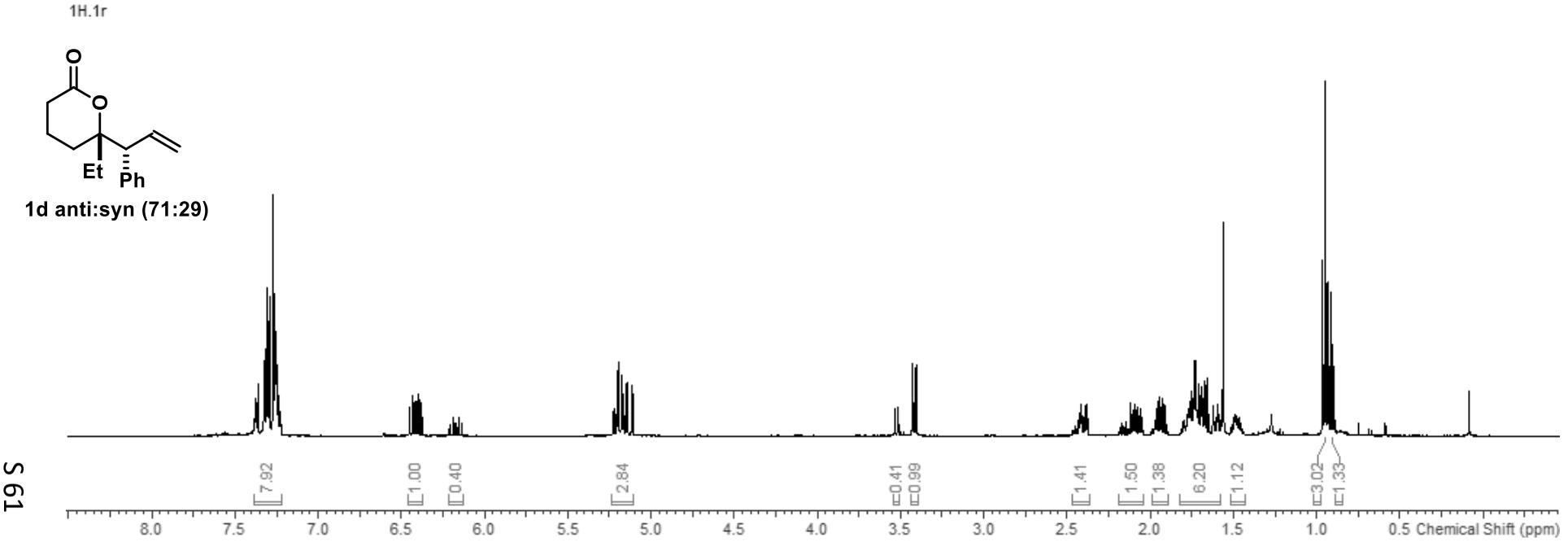
400 MHz, $CDCl_3$





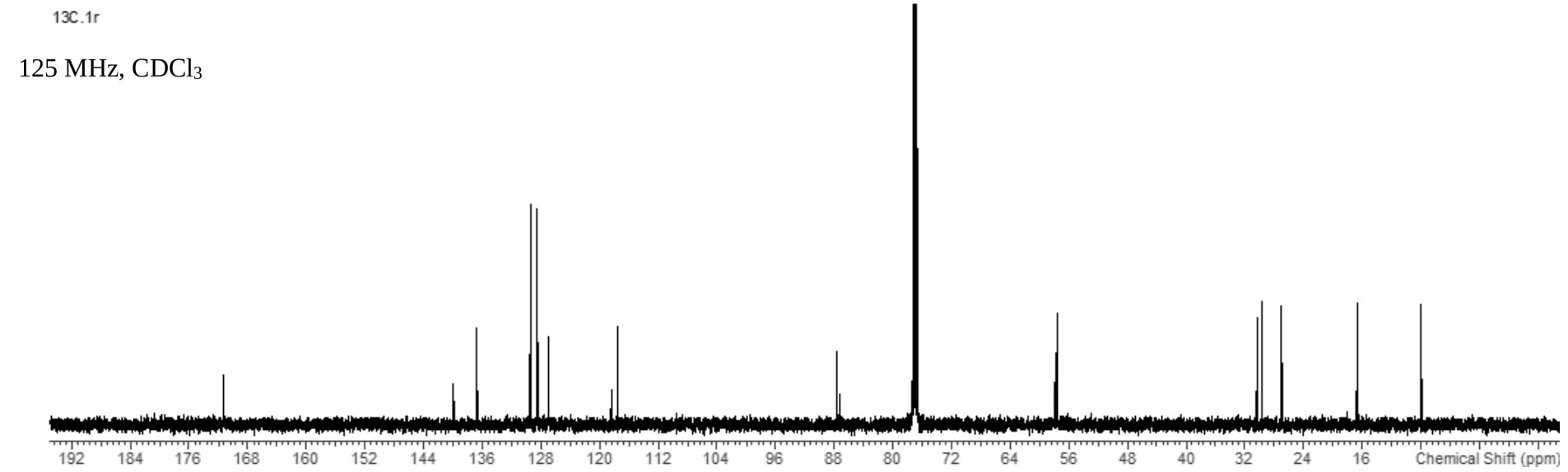
100 MHz, $CDCl_3$

500 MHz, $CDCl_3$

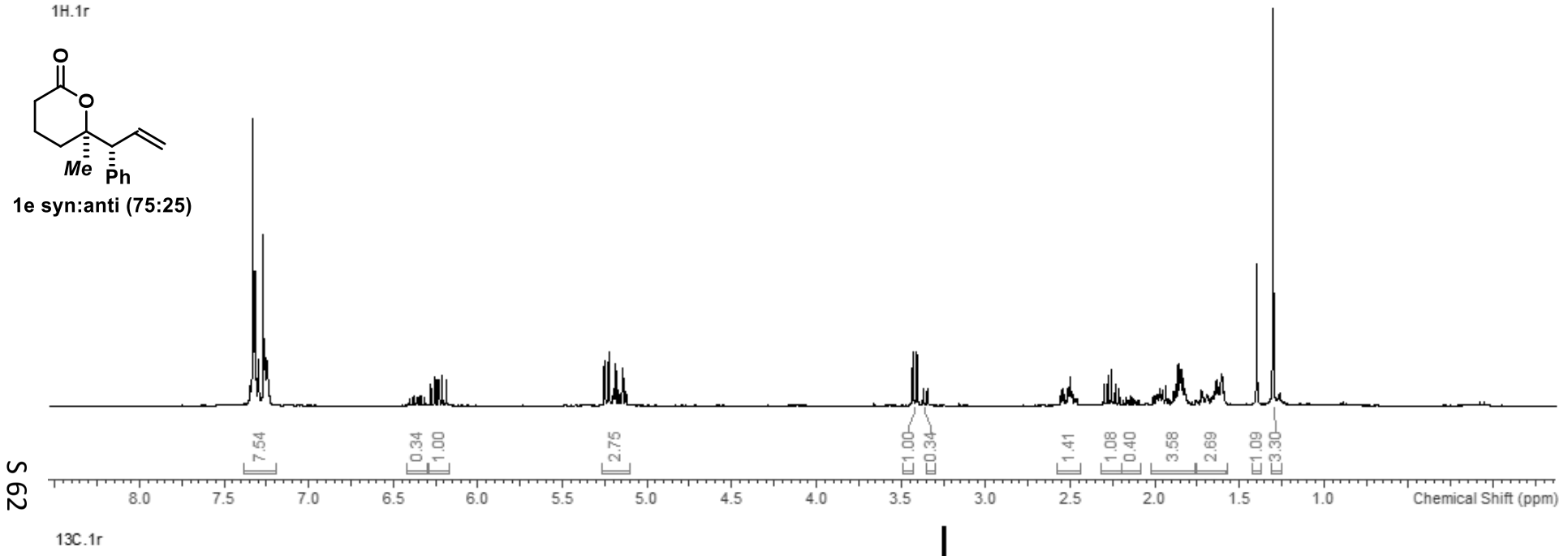


1d anti:syn (71:29)

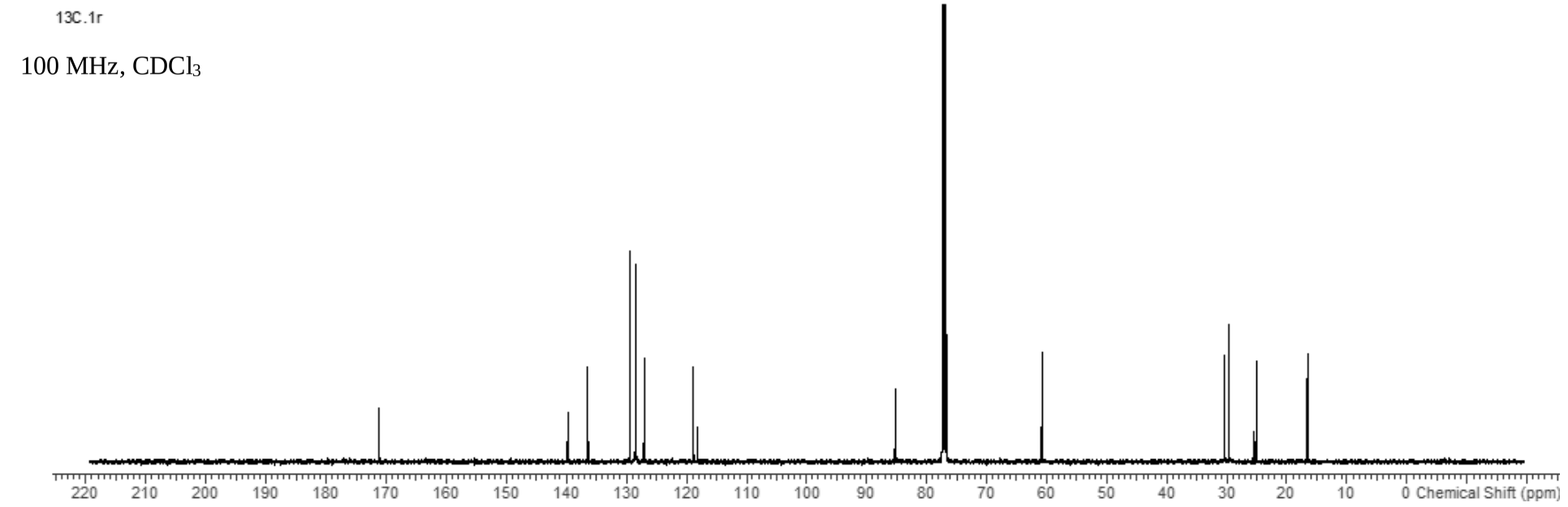
125 MHz, $CDCl_3$



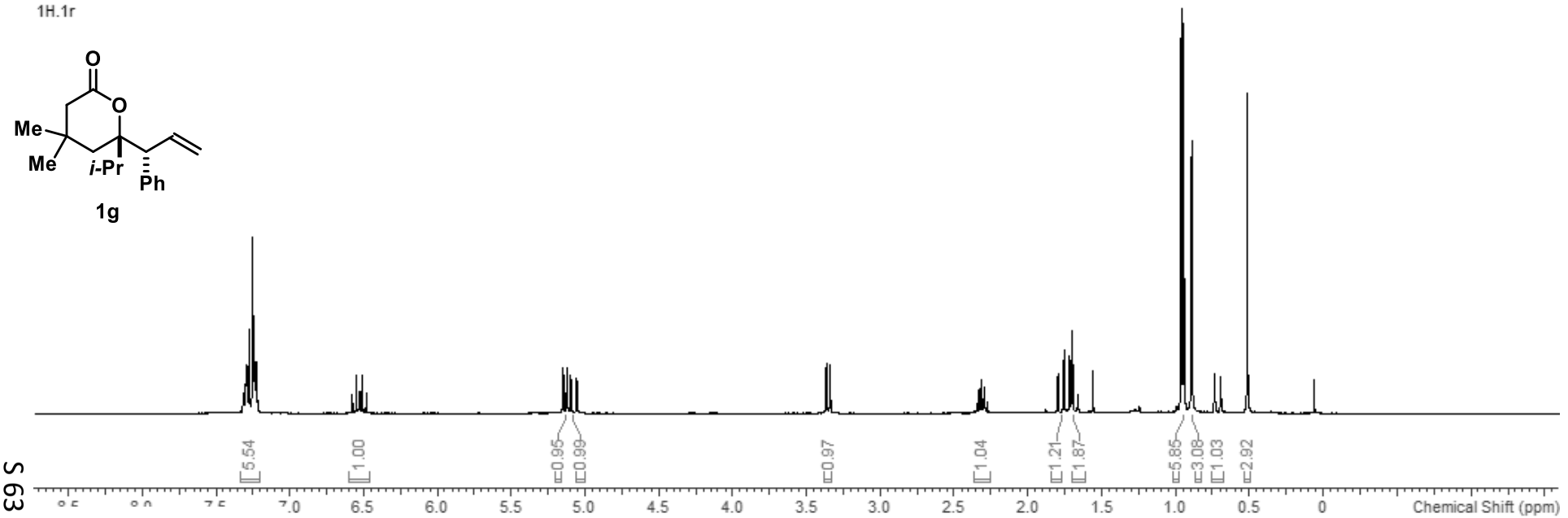
400 MHz, $CDCl_3$



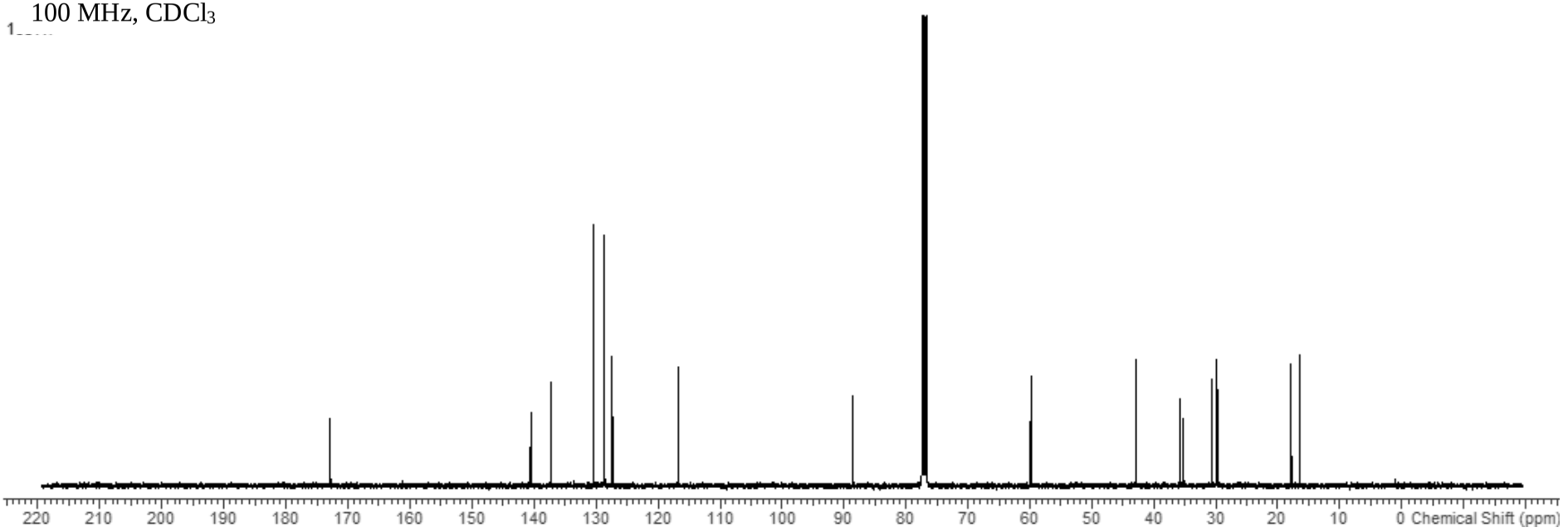
100 MHz, $CDCl_3$



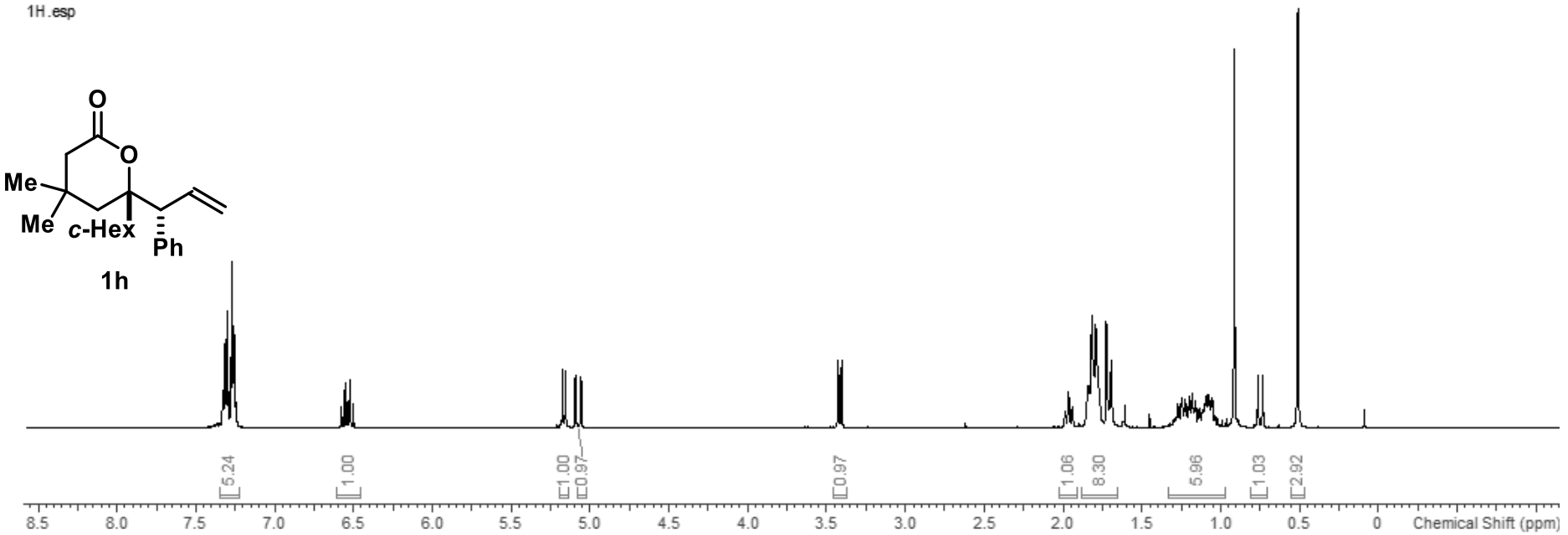
400 MHz, $CDCl_3$



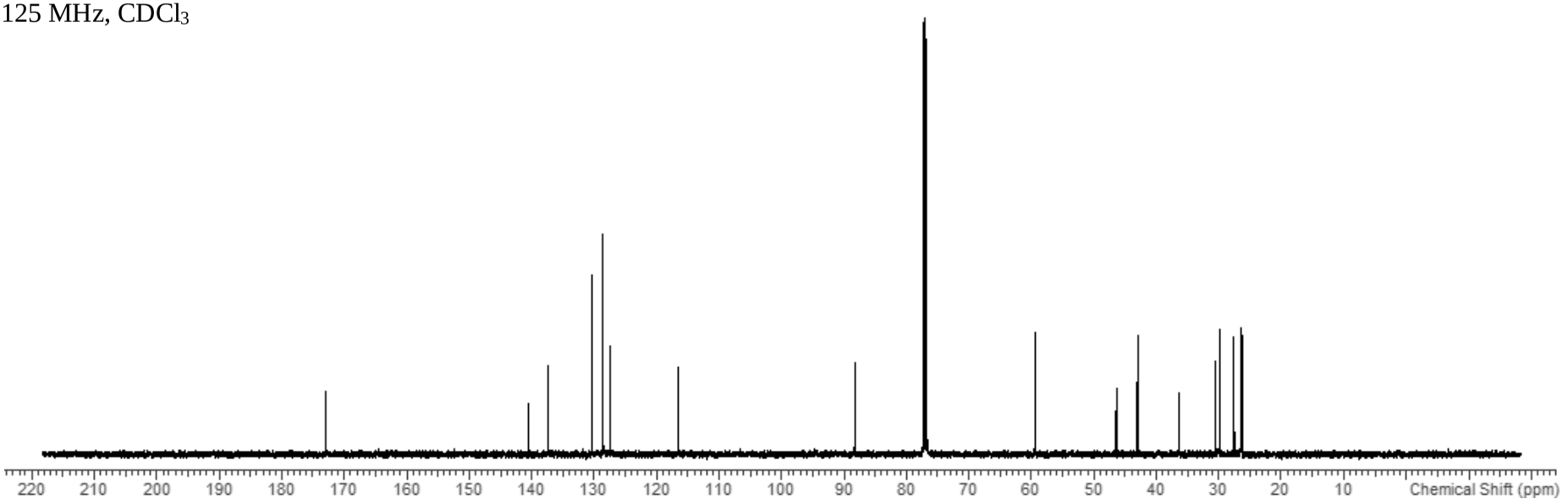
100 MHz, $CDCl_3$



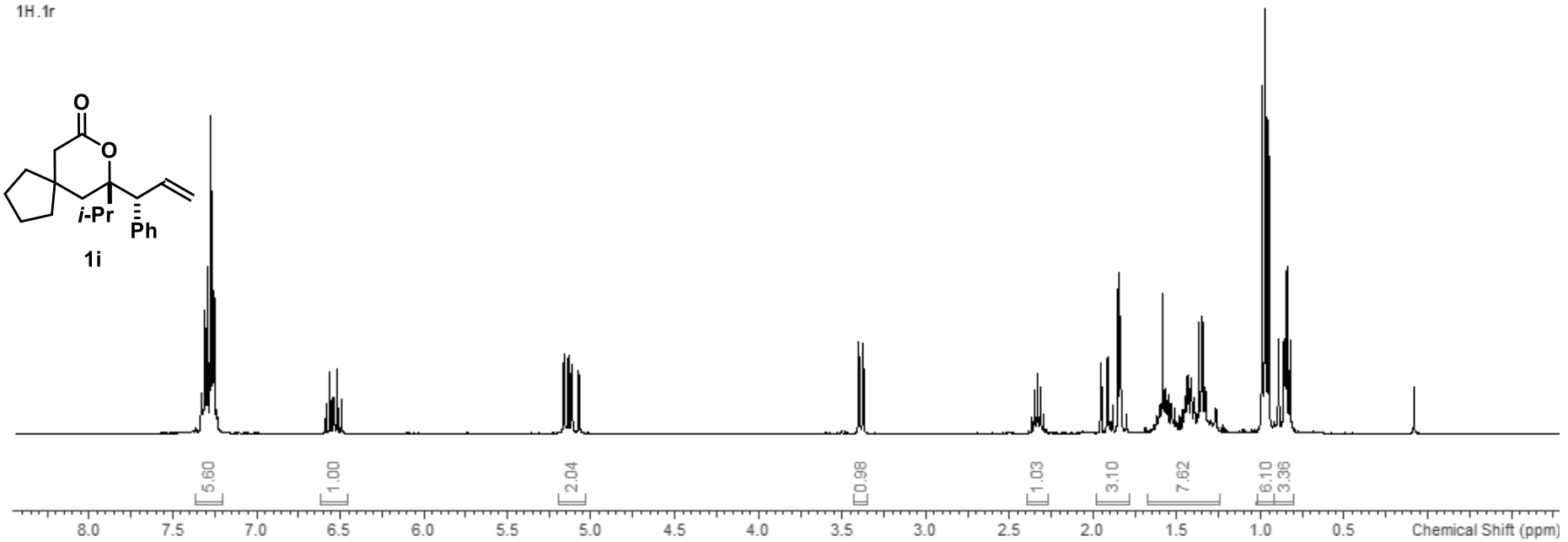
500 MHz, $CDCl_3$



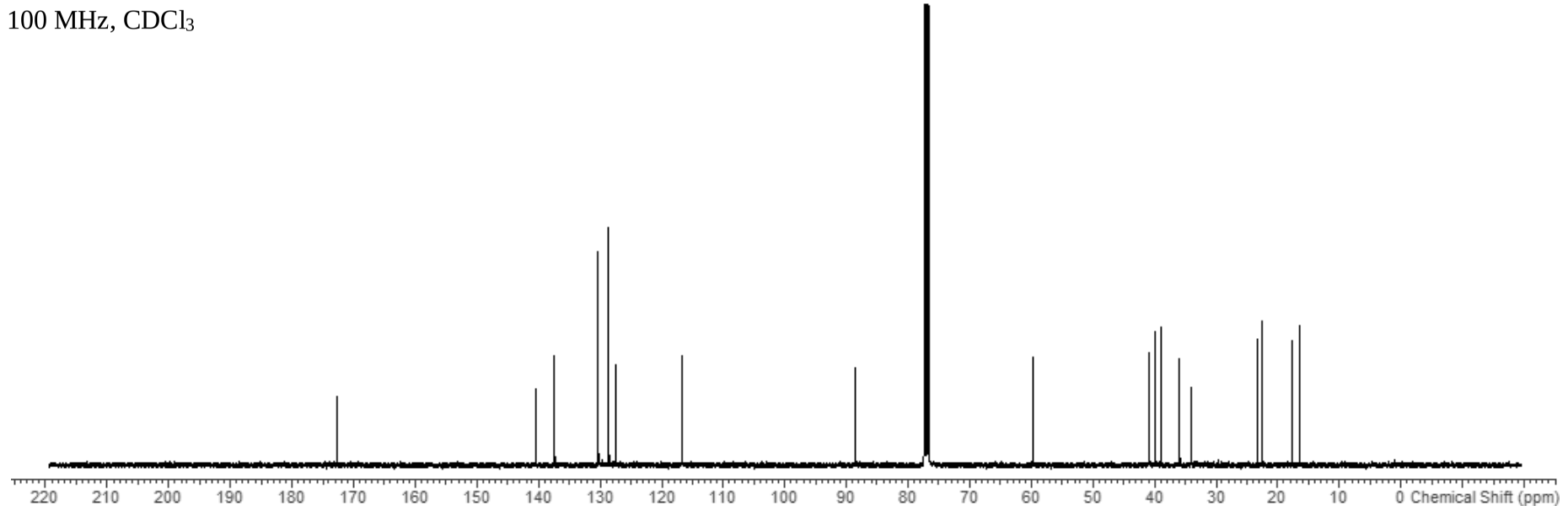
125 MHz, $CDCl_3$



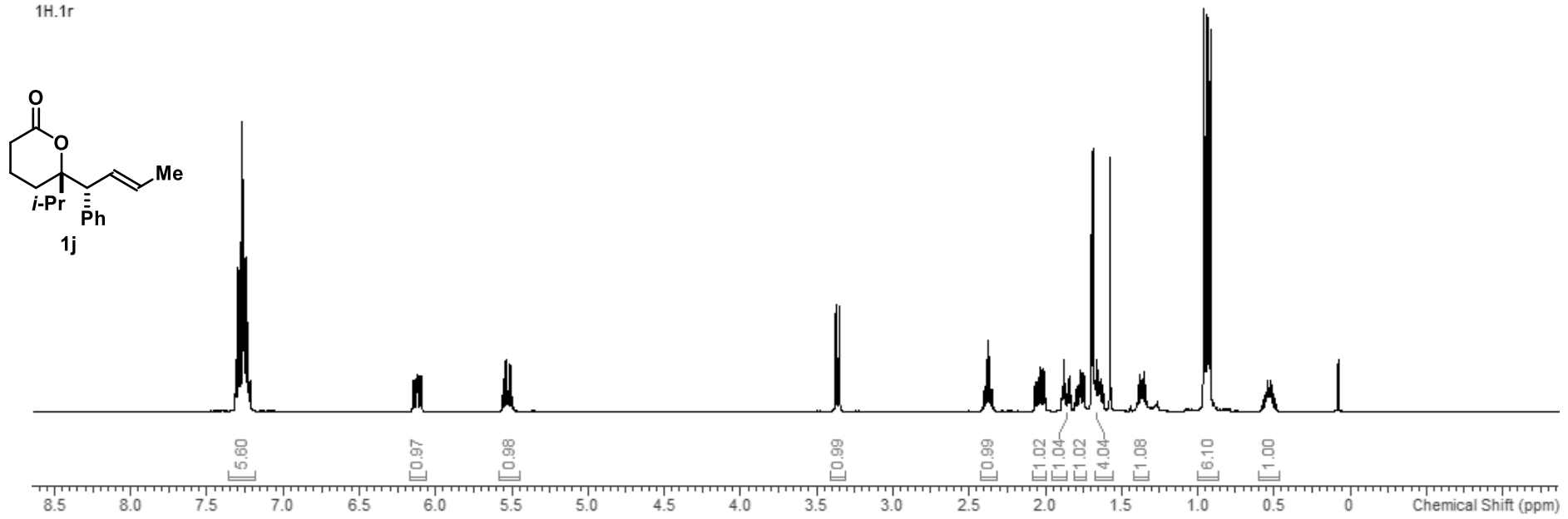
400 MHz, $CDCl_3$



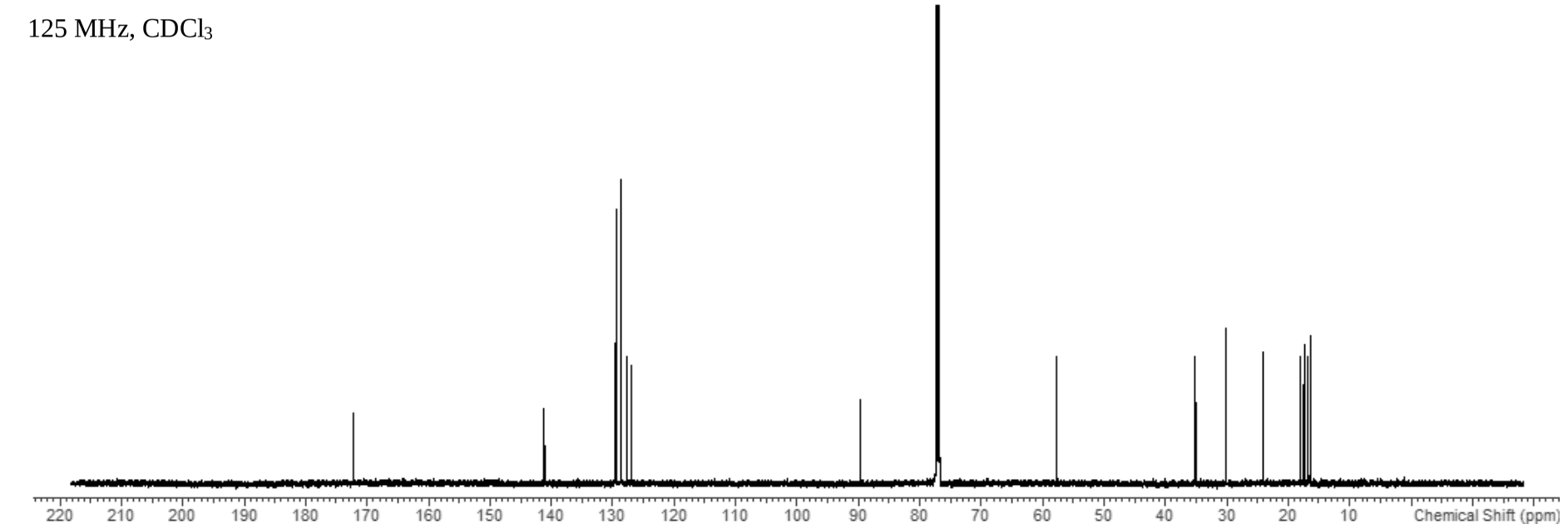
100 MHz, $CDCl_3$



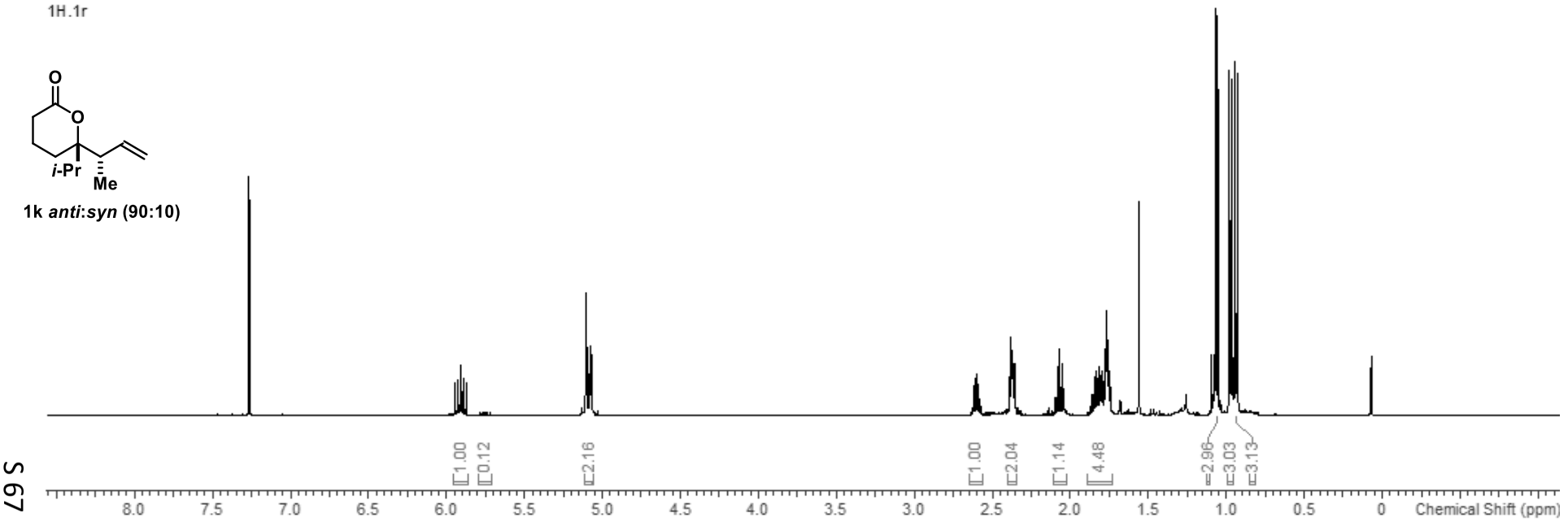
500 MHz, $CDCl_3$



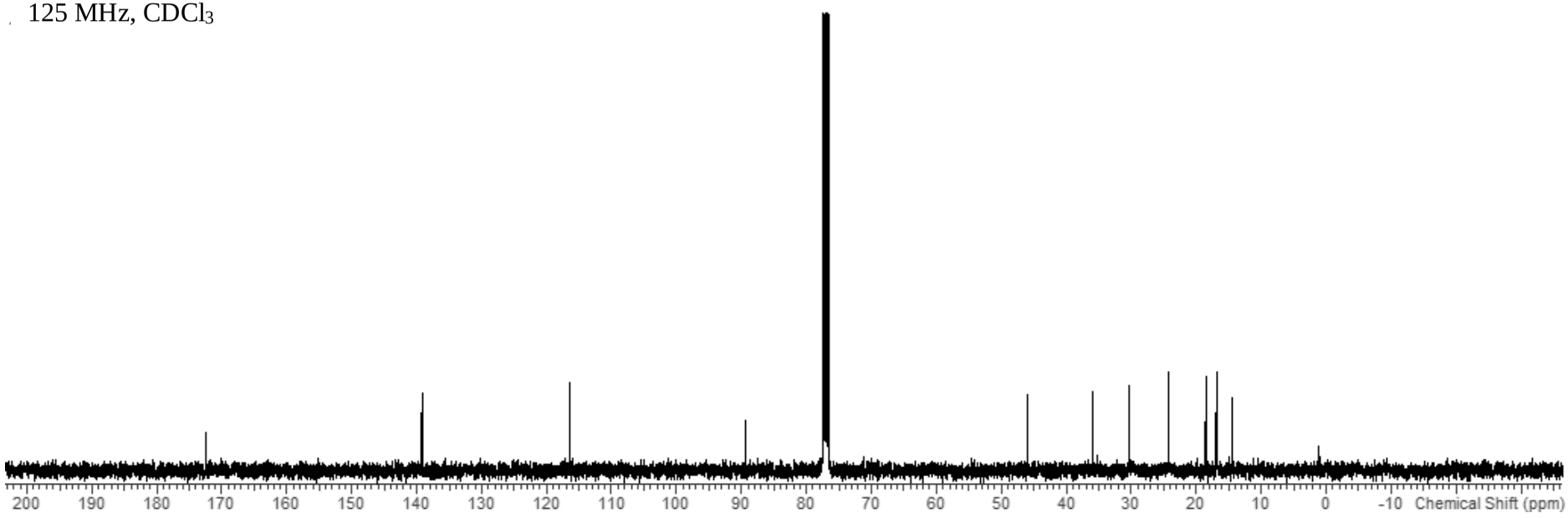
125 MHz, $CDCl_3$



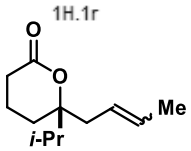
500 MHz, $CDCl_3$



125 MHz, $CDCl_3$

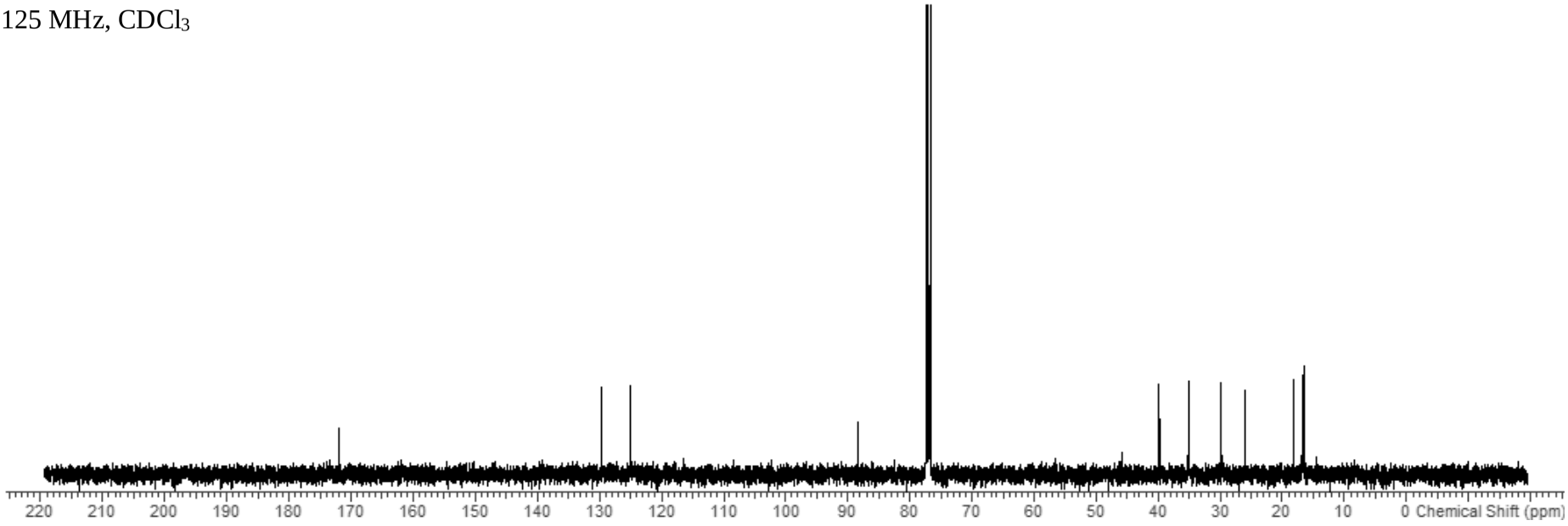


500 MHz, $CDCl_3$

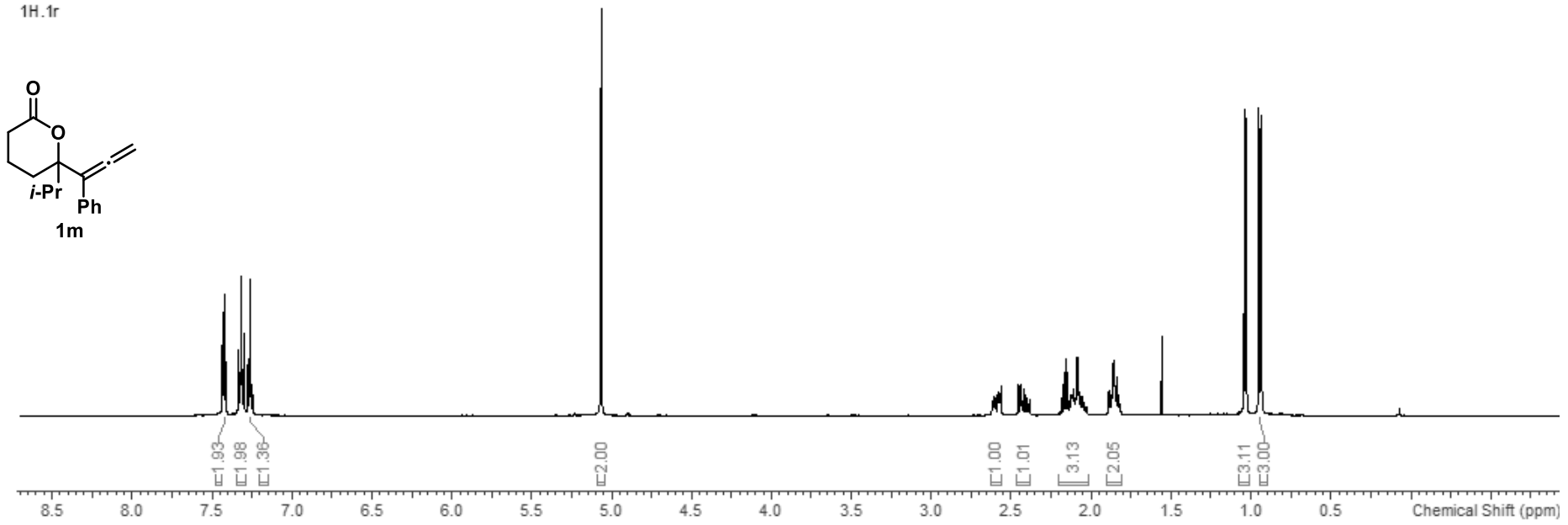


1l E/Z (1:1):4e (86:14)

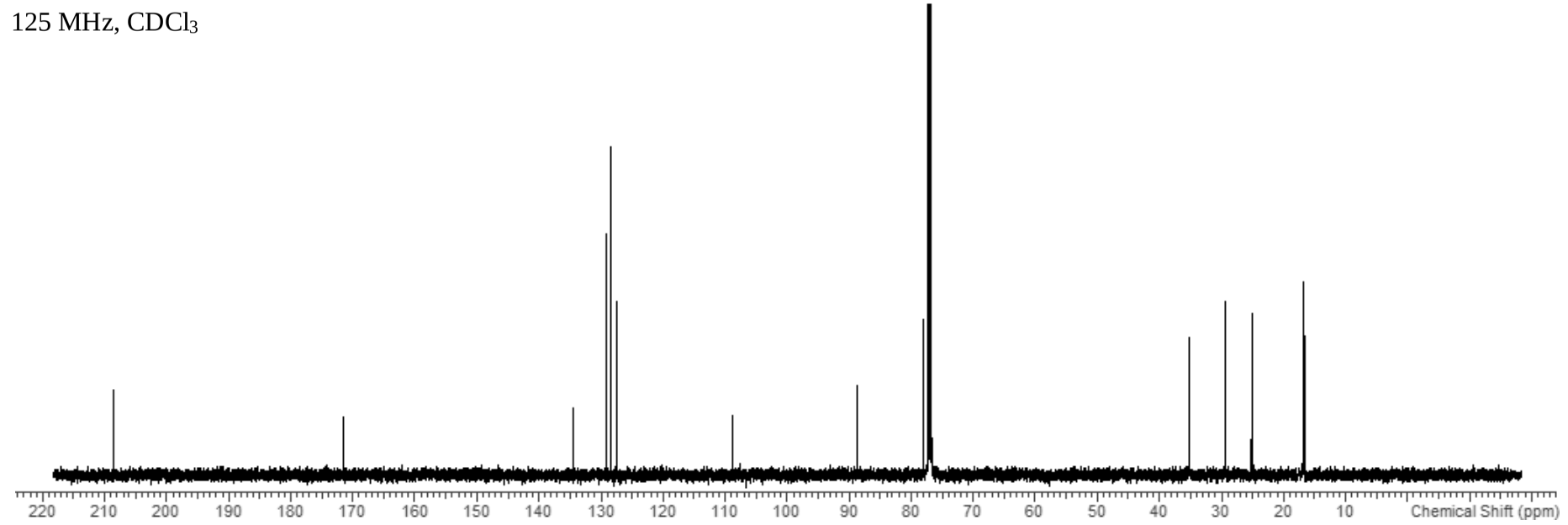
125 MHz, $CDCl_3$



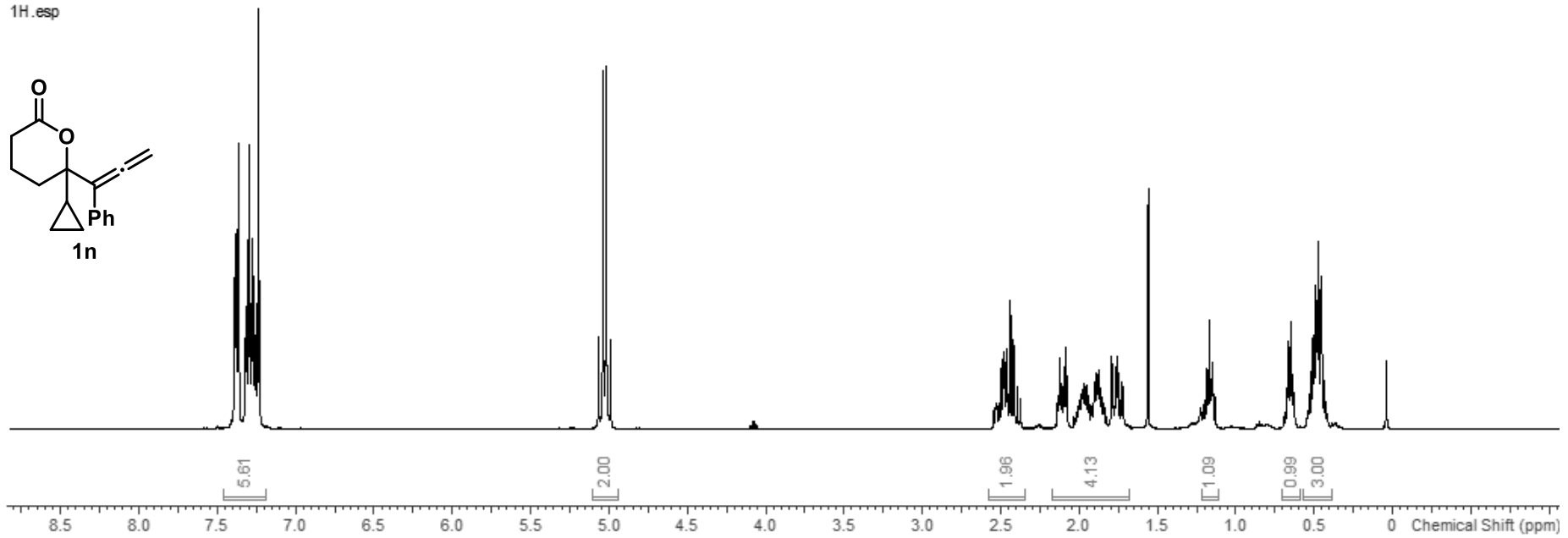
500 MHz, $CDCl_3$



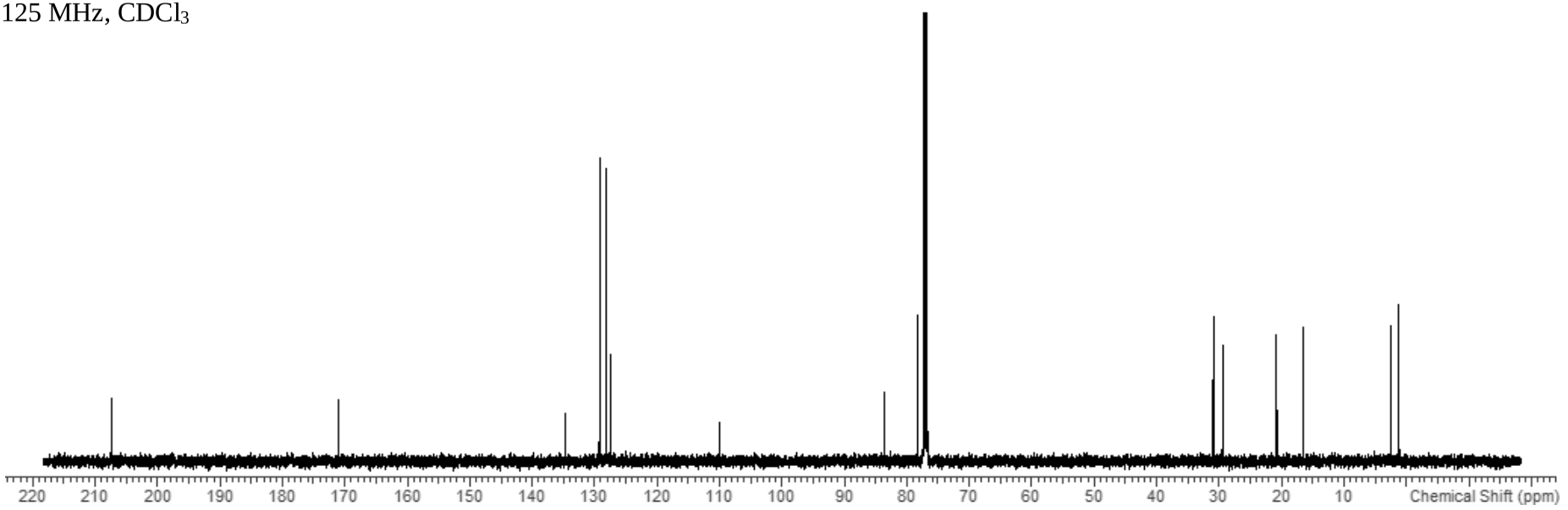
125 MHz, $CDCl_3$



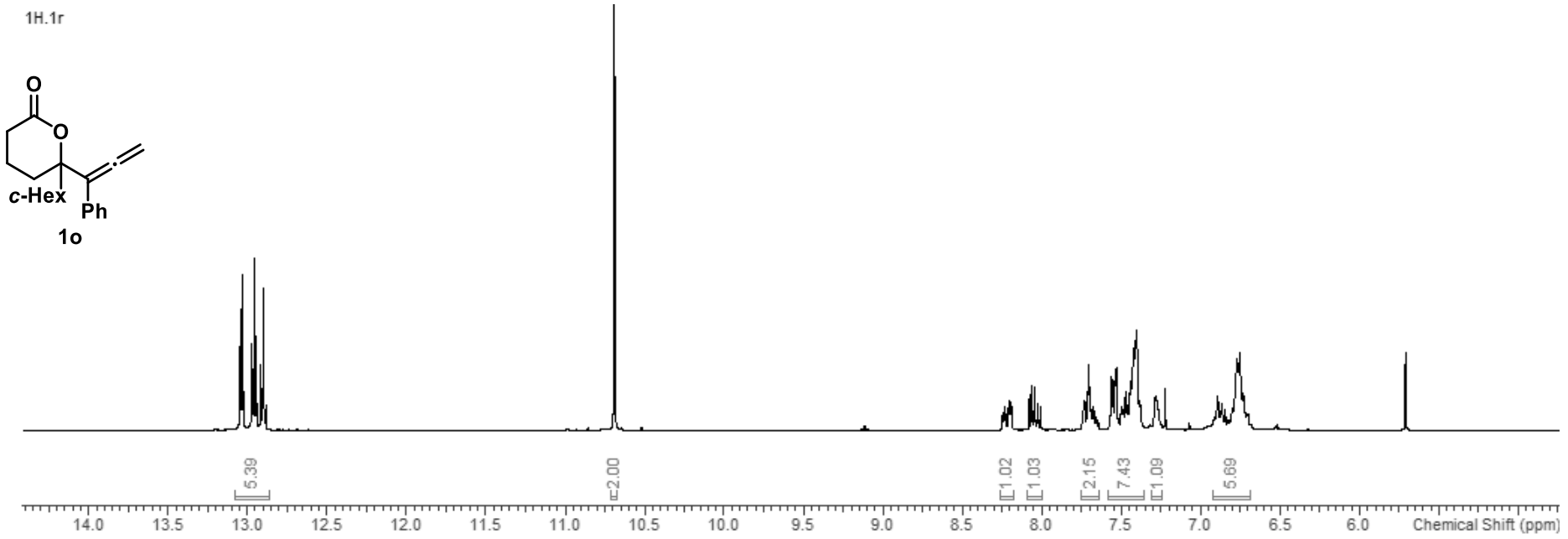
500 MHz, $CDCl_3$



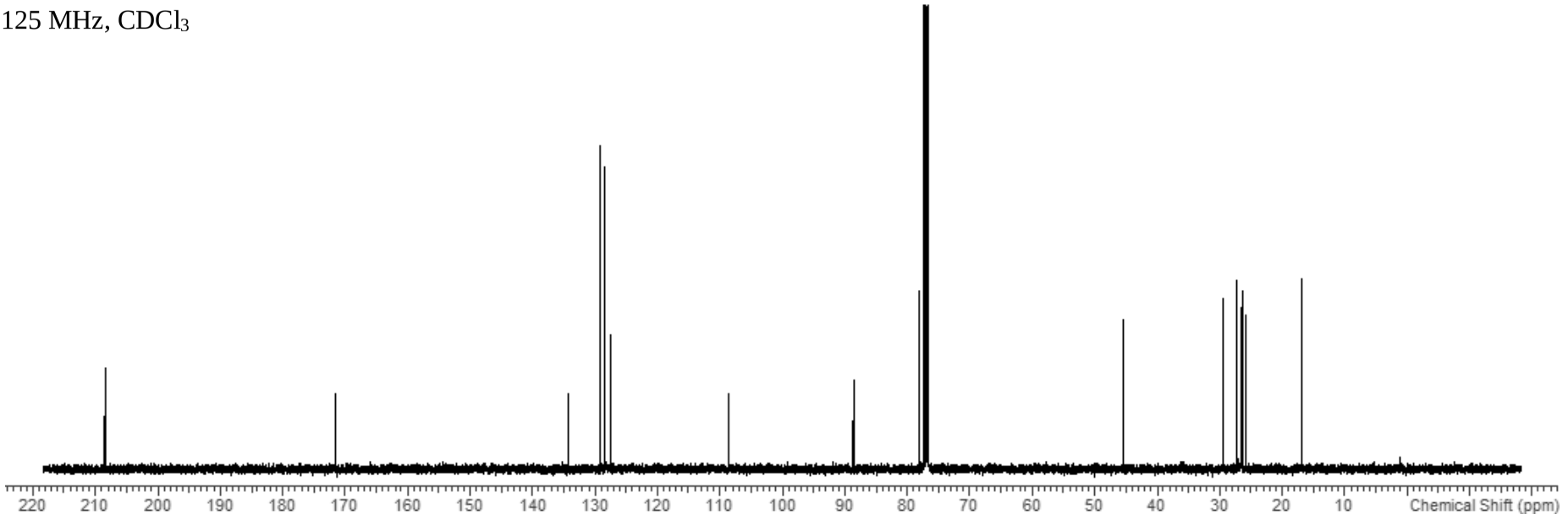
125 MHz, $CDCl_3$



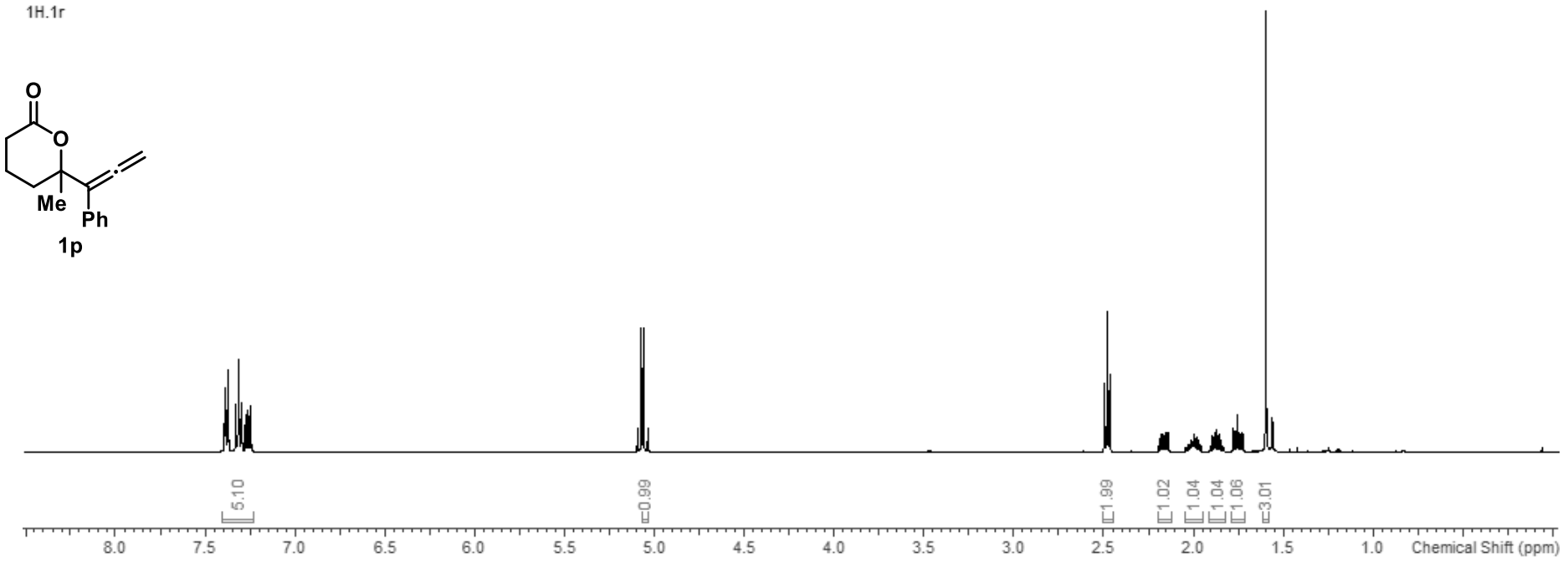
500 MHz, $CDCl_3$

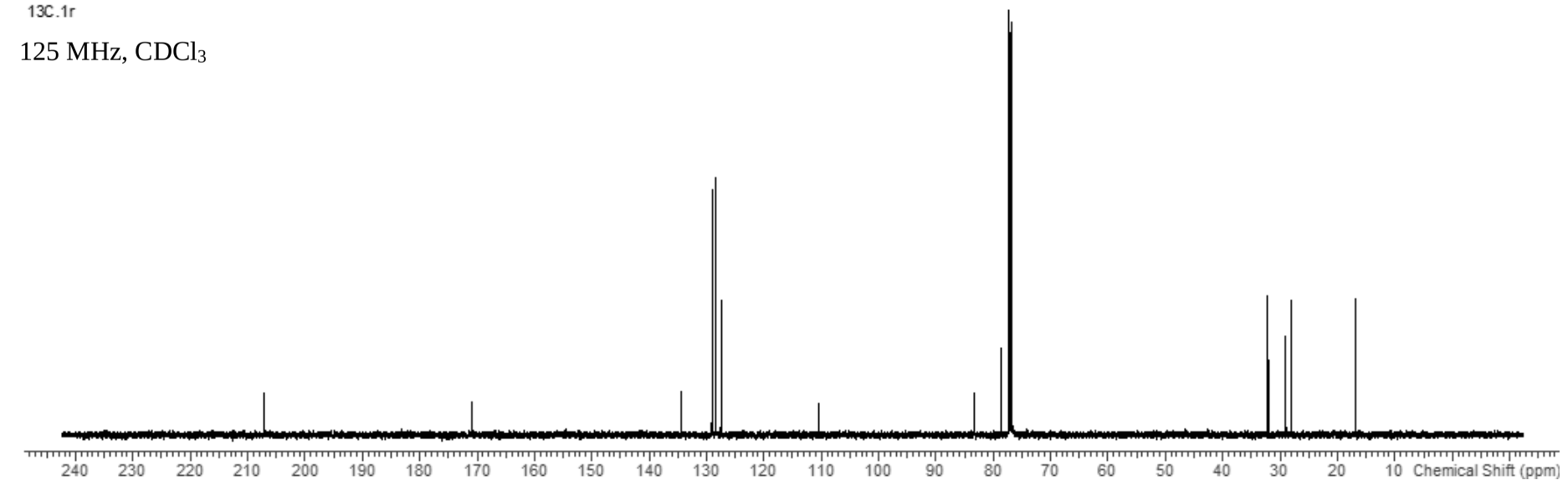


125 MHz, $CDCl_3$



500 MHz, $CDCl_3$

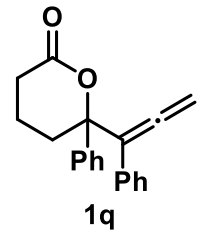




125 MHz, $CDCl_3$

400 MHz, $CDCl_3$

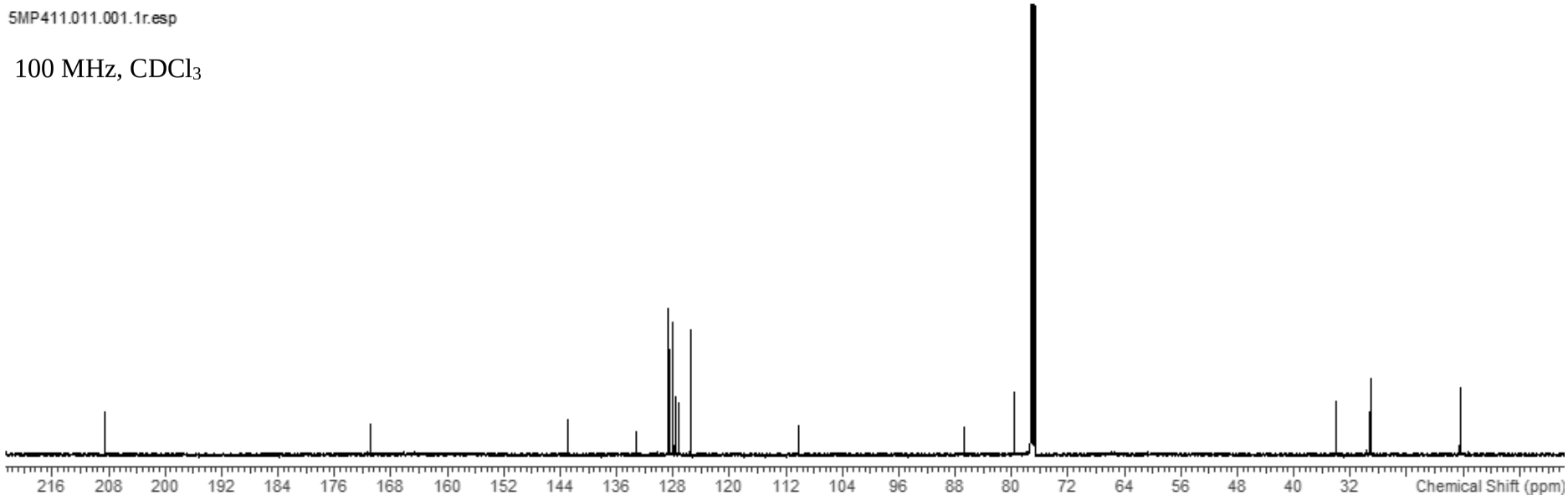
Ch3CN 2nd wash HV.010.001.1r.esp



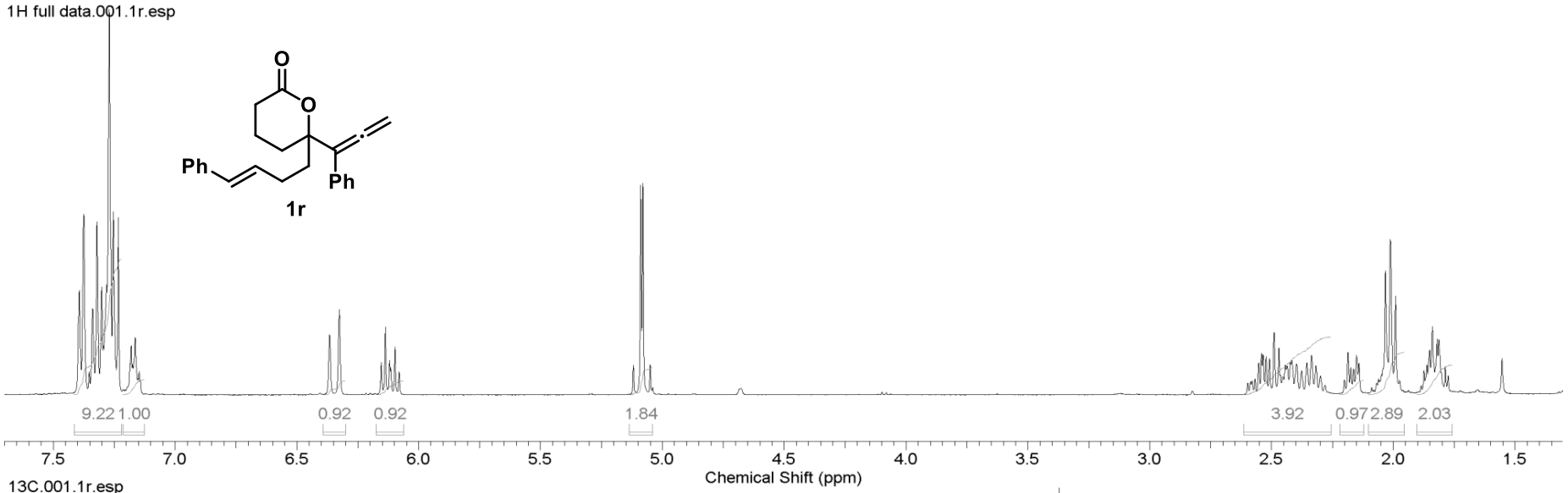
1q

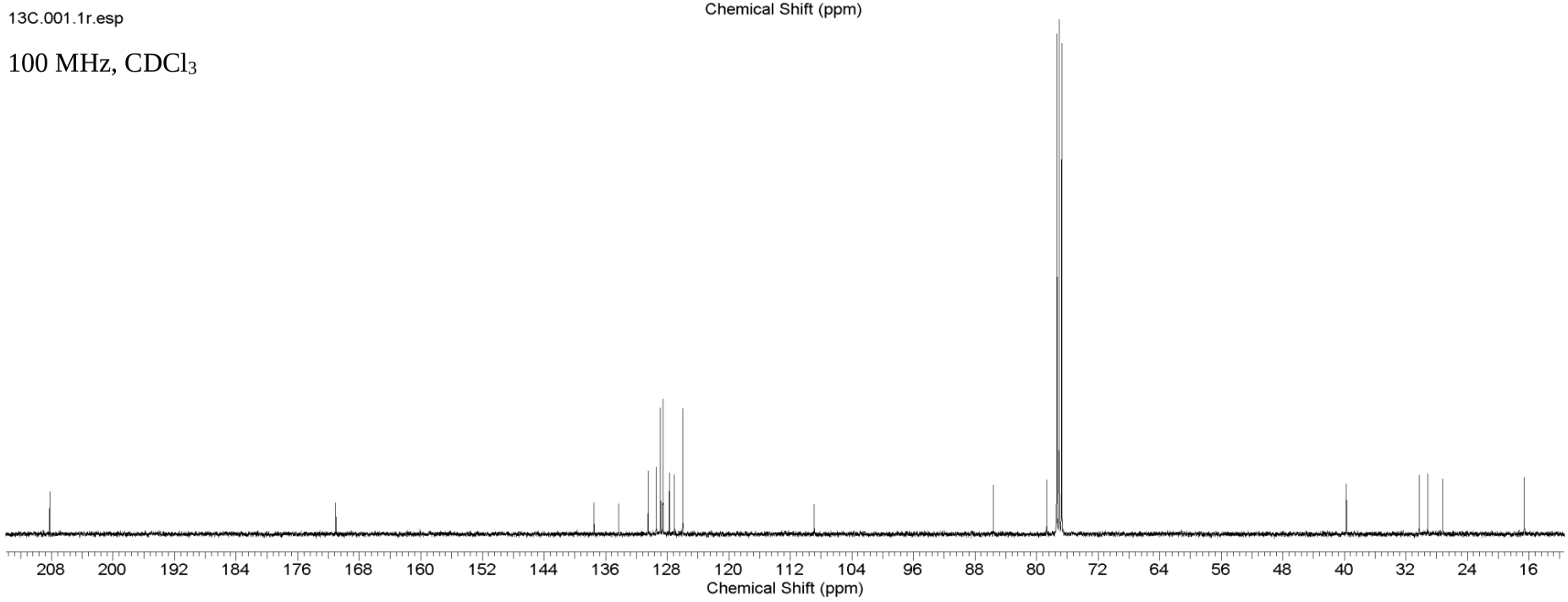
5MP411.011.001.1r.esp

100 MHz, $CDCl_3$



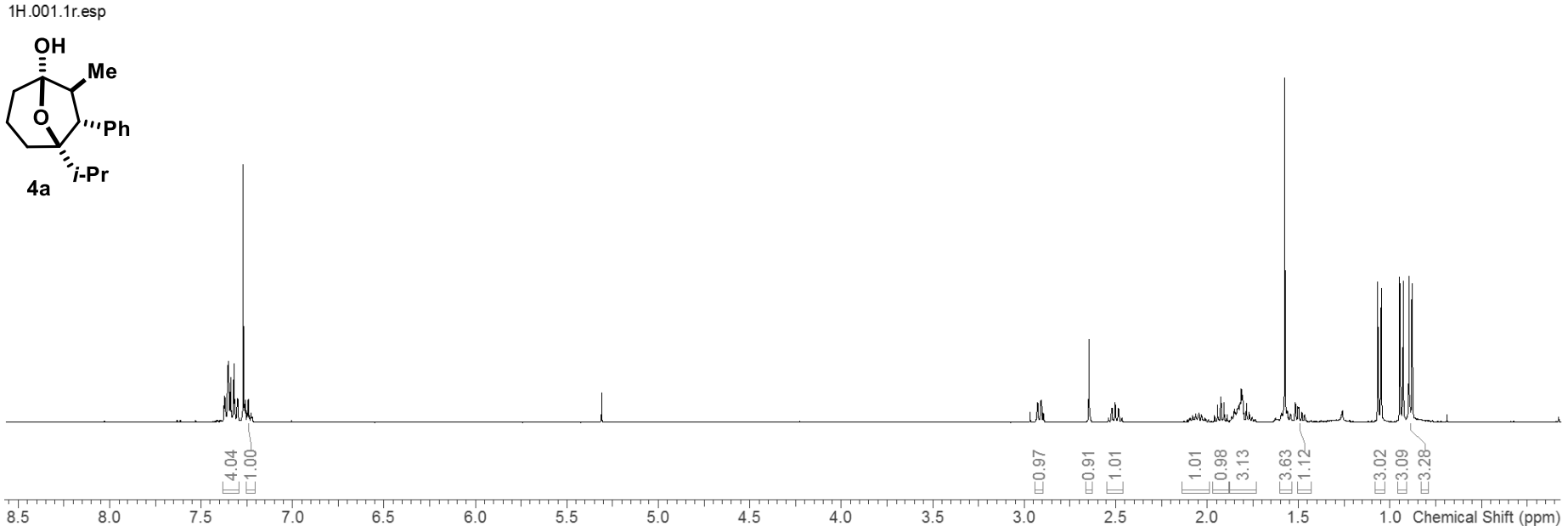
400 MHz, $CDCl_3$



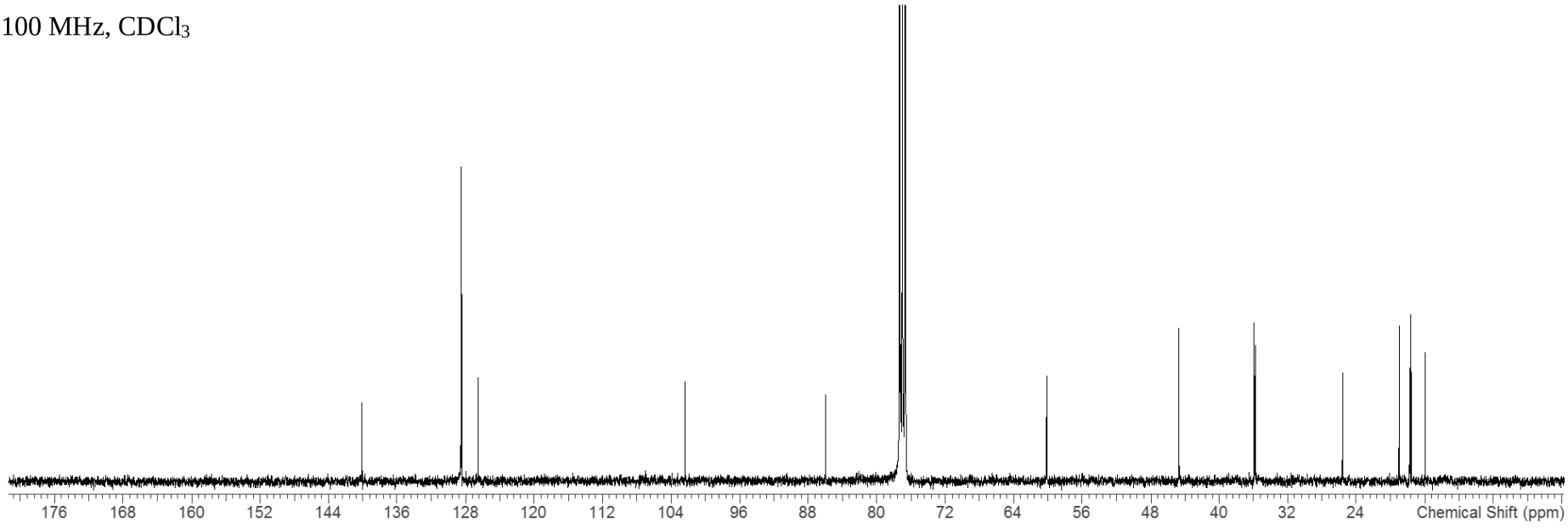


100 MHz, $CDCl_3$

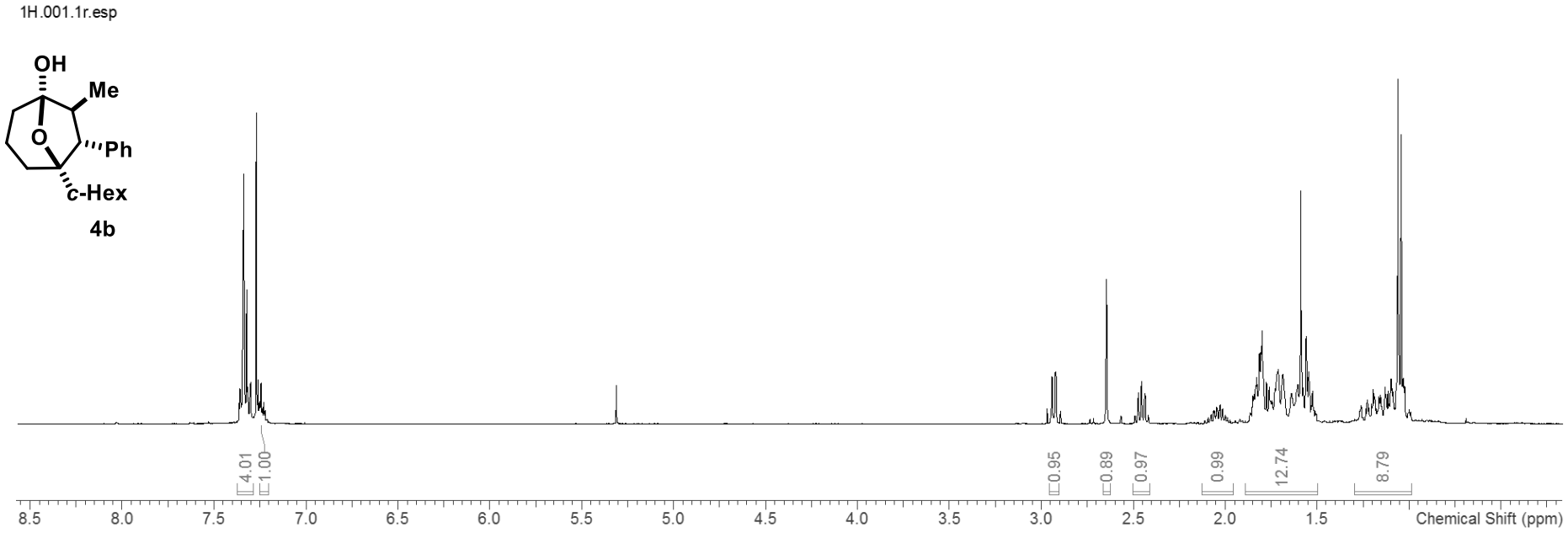
400 MHz, $CDCl_3$



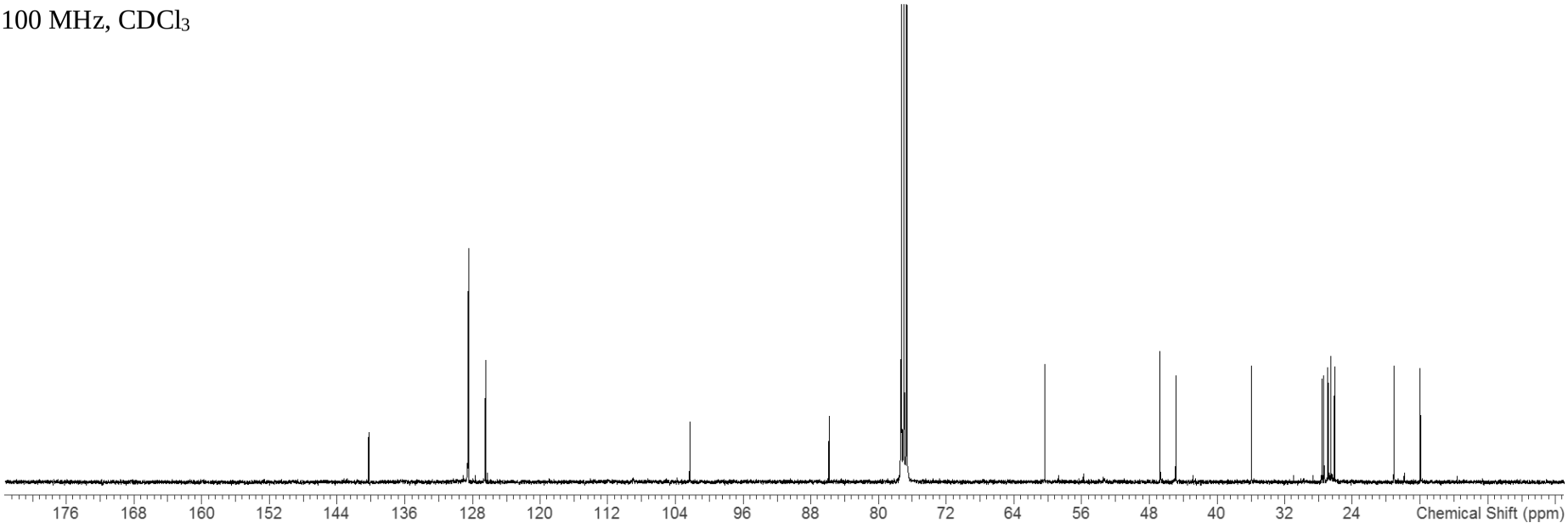
100 MHz, $CDCl_3$



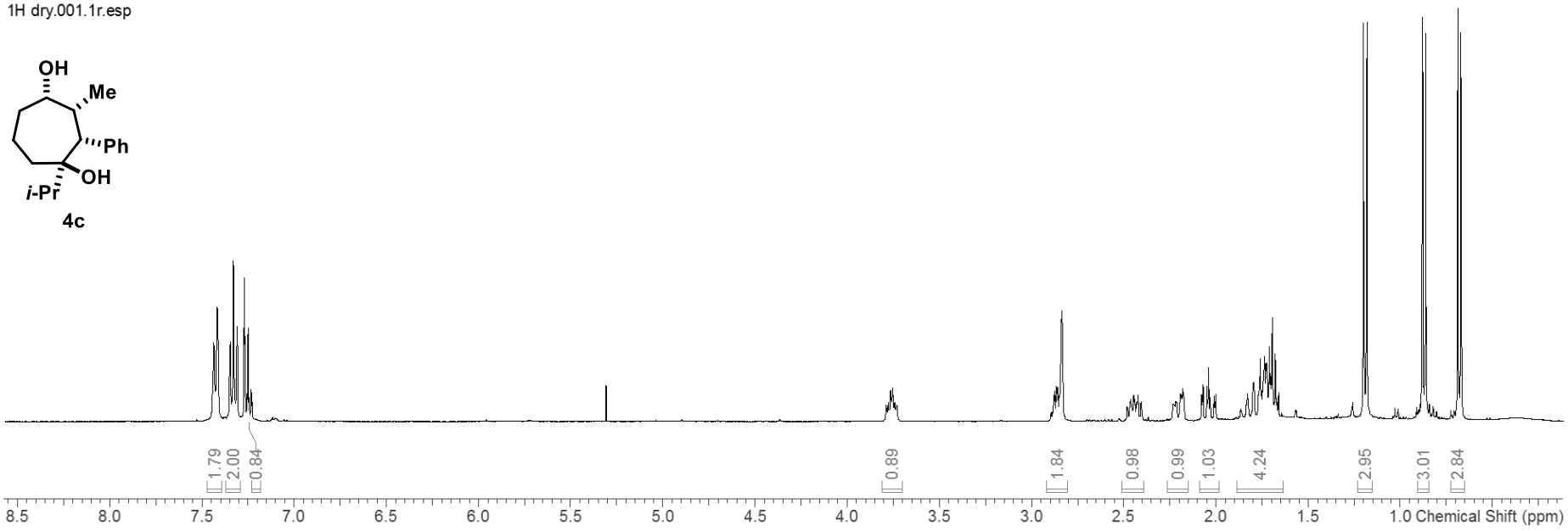
400 MHz, $CDCl_3$



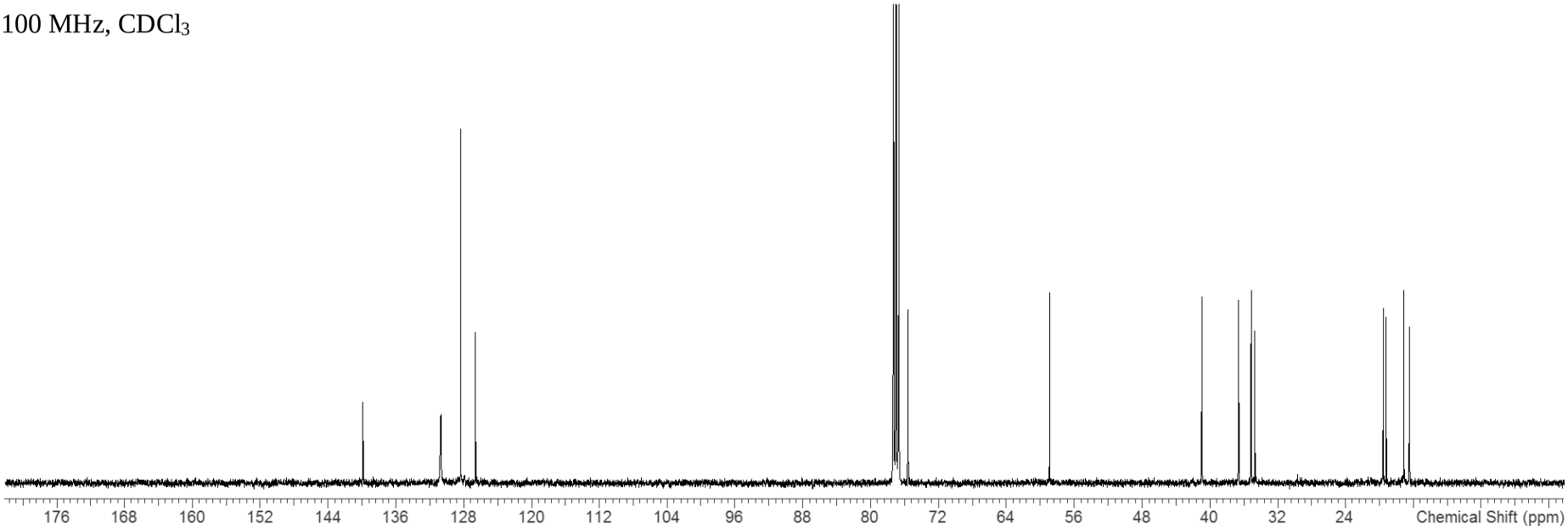
100 MHz, $CDCl_3$



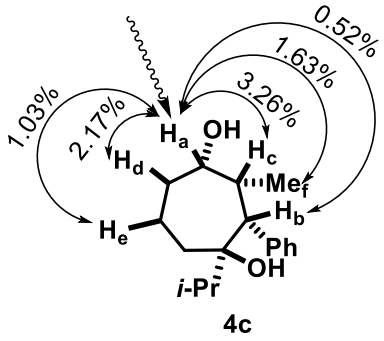
400 MHz, $CDCl_3$



100 MHz, $CDCl_3$

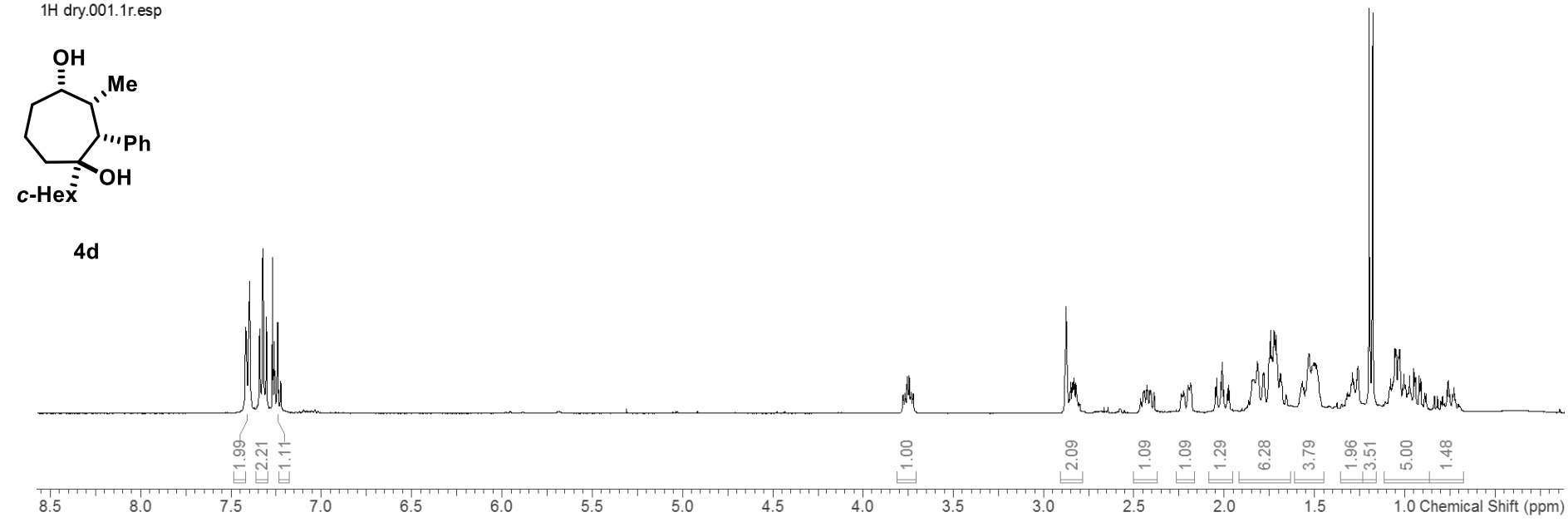


Relative stereochemistry elucidation of **4c** by NOE in CD_3OD (500 MHz)

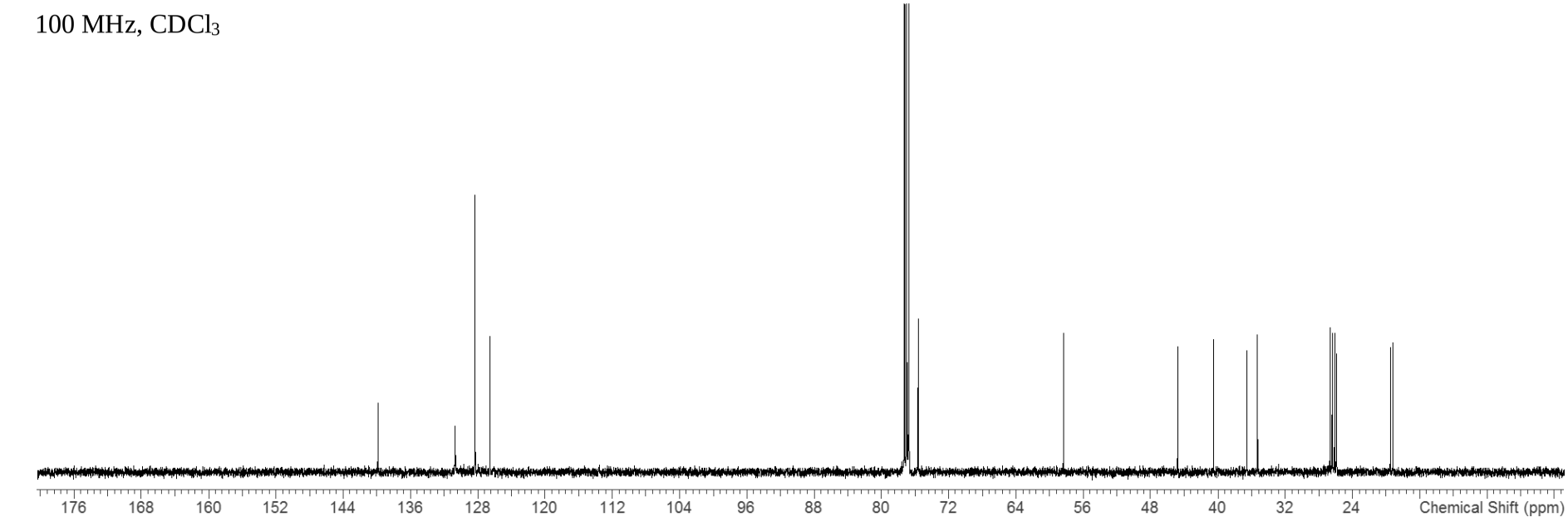


4c

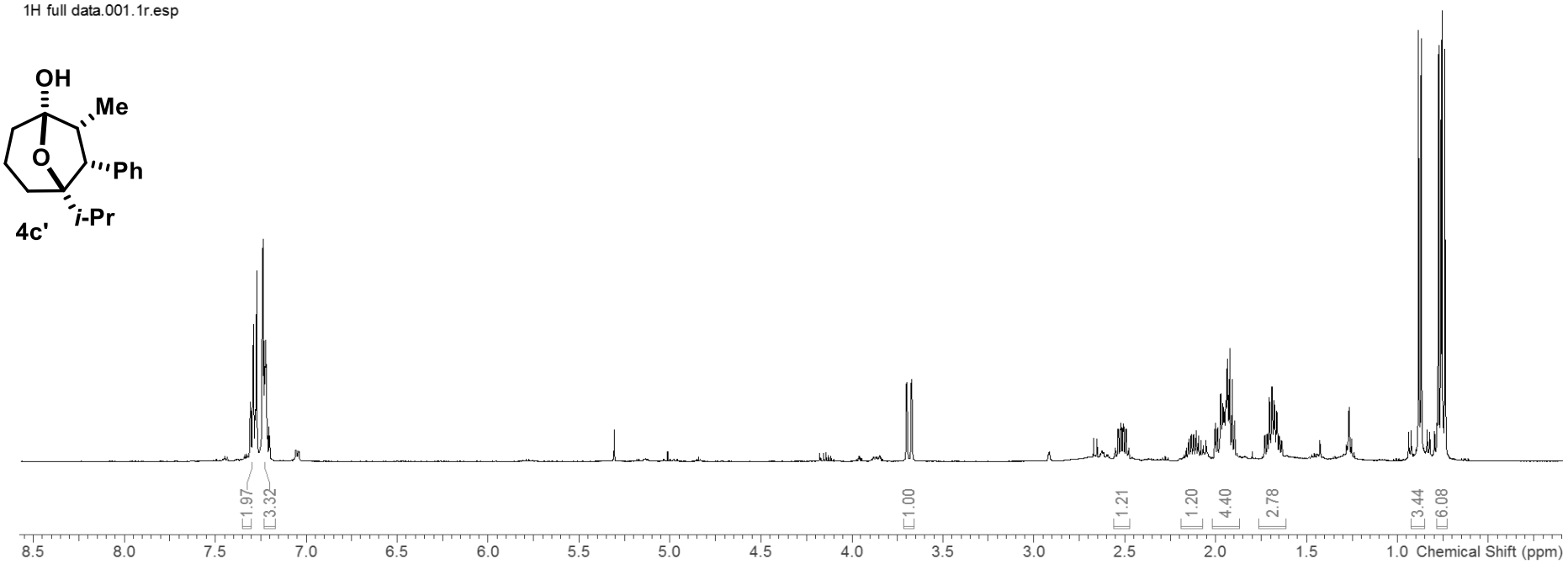
400 MHz, $CDCl_3$



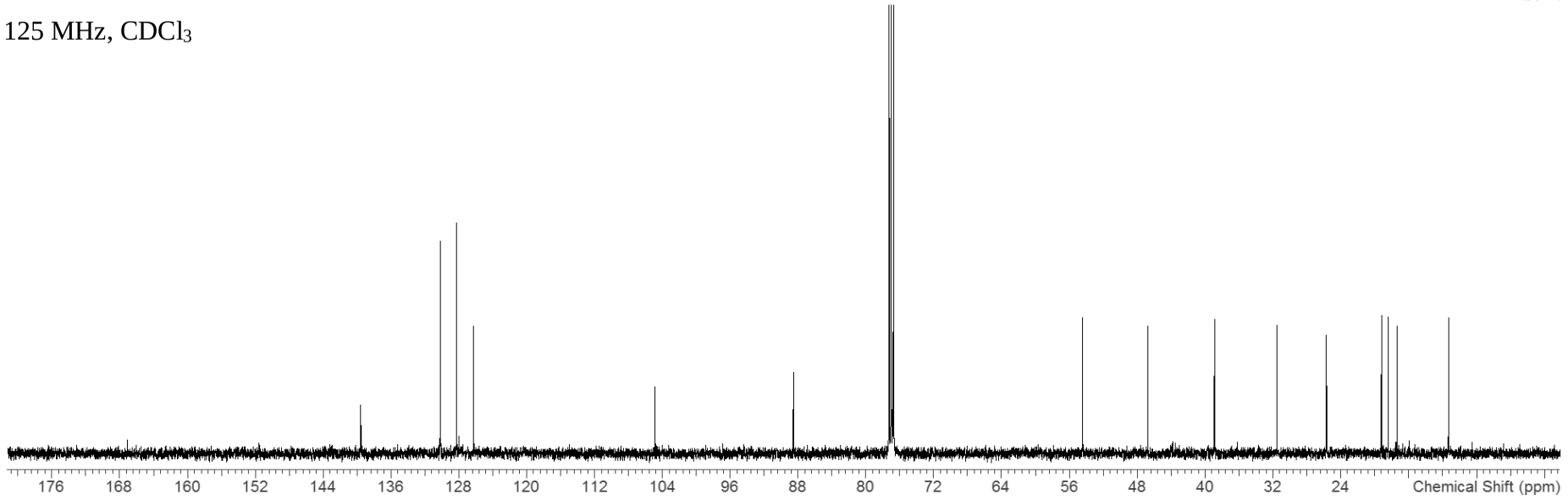
100 MHz, $CDCl_3$



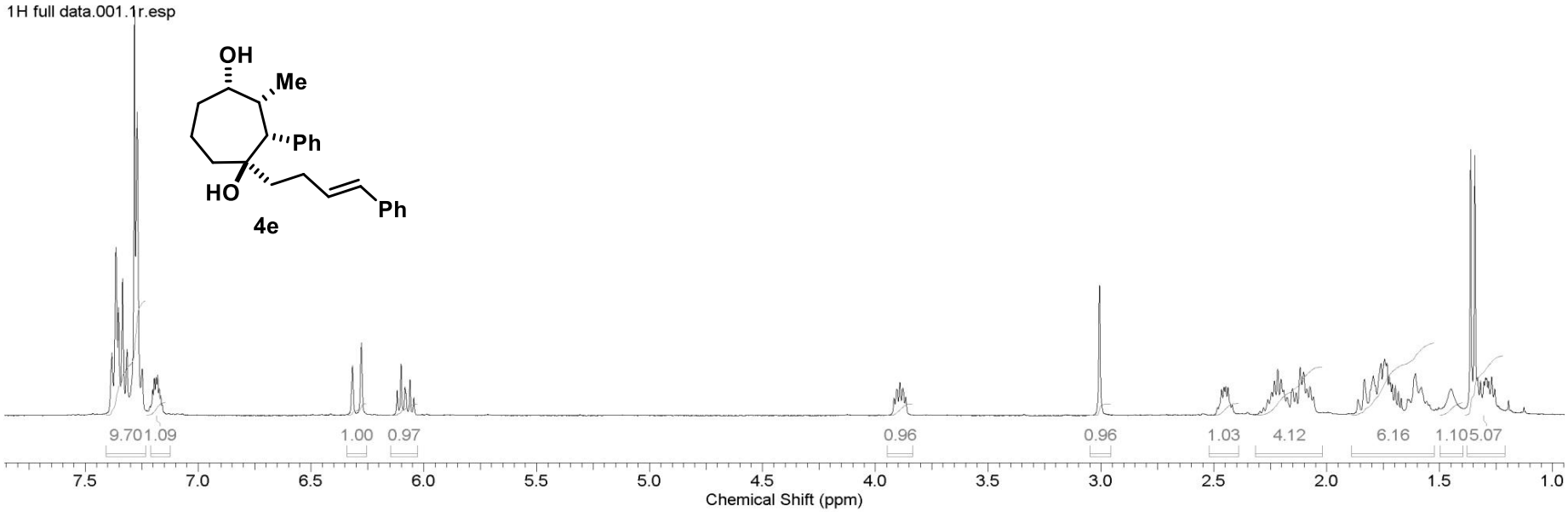
500 MHz, $CDCl_3$

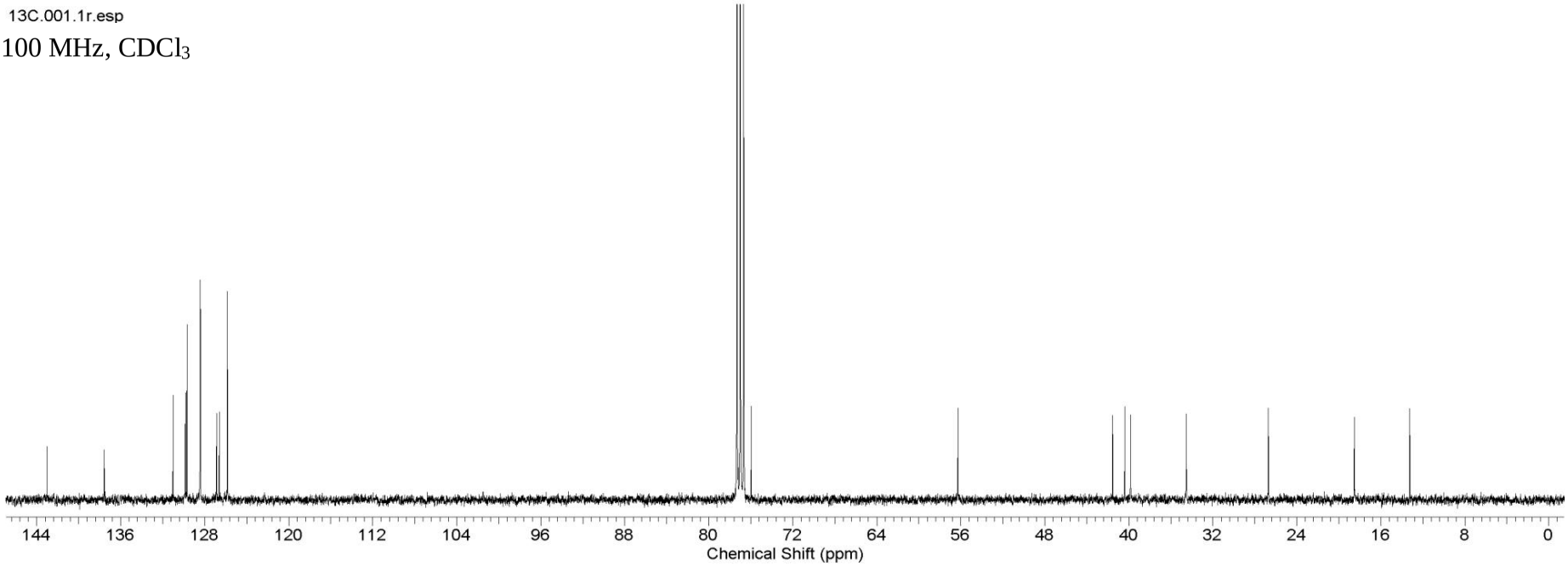


125 MHz, $CDCl_3$



400 MHz, $CDCl_3$





Comparison of diagnostic peaks for *syn* and *anti* lactones (500 MHz, $CDCl_3$)