Copper-Catalyzed Enantioselective Allylic Alkylation with a γ-Butyrolactone-Derived Silyl Ketene Acetal.

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Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. ((4,5-dihydrofuran-2-yl)oxy)trimethylsilane (**2**) was synthesized according to a previously reported procedure.[1] Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^{1}H NMR spectra were recorded on a Bruker Avance HD 400 MHz or Varian Mercury 300 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker Avance HD 400 MHz spectrometer (101 MHz) and are reported relative to residual $CHCl_3$ (δ 77.16 ppm). ^{19}F NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer (282 MHz). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained using a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in 10 mg/1 mL, solvent). Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd.. High resolution mass spectra (HRMS) wereobtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+), or obtained from Caltech mass spectrometry laboratory. X-Band (9.4 GHz) Continuous-wave(CW) EPR spectra were obtained using a Bruker EMX spectrometer with its Bruker Win-EPR software (version 3.0). A vacuum-insulated quartz liquid nitrogen dewar was inserted into the EPR resonator to obtain all spectra at 77 K. For optimal sensitivity, all spectra were collected with 0.5 mW microwave power and averaged over four scans. UV-Vis-NIR spectra were acquired using Varian Cary 500 Scan spectrophotometer with Varian Cary WinUV software(version 4.10(464)). Samples were loaded into 1 cm Starna Cell borosilicate cuvettes enclosed with screw caps. The spectra were collected from 300 nm to 1650 nm at a 600 nm/min scan rate and corrected for THF background. IR spectra were collected using a Bruker Alpha Platinum ATR spectrometer with OPUS software (version 7.0.129) stored in a glovebox under N_2. An aliquot of sample solution was deposted onto the spectrometer to form a thin film, and the spectra were collected over 32 scans

All calculations were performed using the ORCA 4.1.2 package.[2] Unless otherwise specified, the spectroscopically calibrated Becke3-Lee-Yang-Parr density functional with 38% exact Hartree-Fock exchange (B3(38HF)LYP was employed, similar to that reported by Solomon and coworkers.[3] All atoms were described with the def2-TZVP basis set. Calculations were performed with the finest available grid (Grid7) and the chain of sphere approximation (RIJCOSX) for two-electron integrals on the corresponding finest auxiliary integration grid (GRIDX9) for the RI/J auxiliary basis set. Gas-phase geometries were optimized with tight convergence criteria ($\Delta E \leq 1*10^{-8}$ Hartree). Frequency calculations were used to confirm optimized structures represented local minima on the potential energy surfaces. To approximate solvent effects, single point energy calculations were performed on gas-phase optimized geometries using a conductor-like polarizable continuum model for THF. In all cases, counter ions were excluded from calculations.

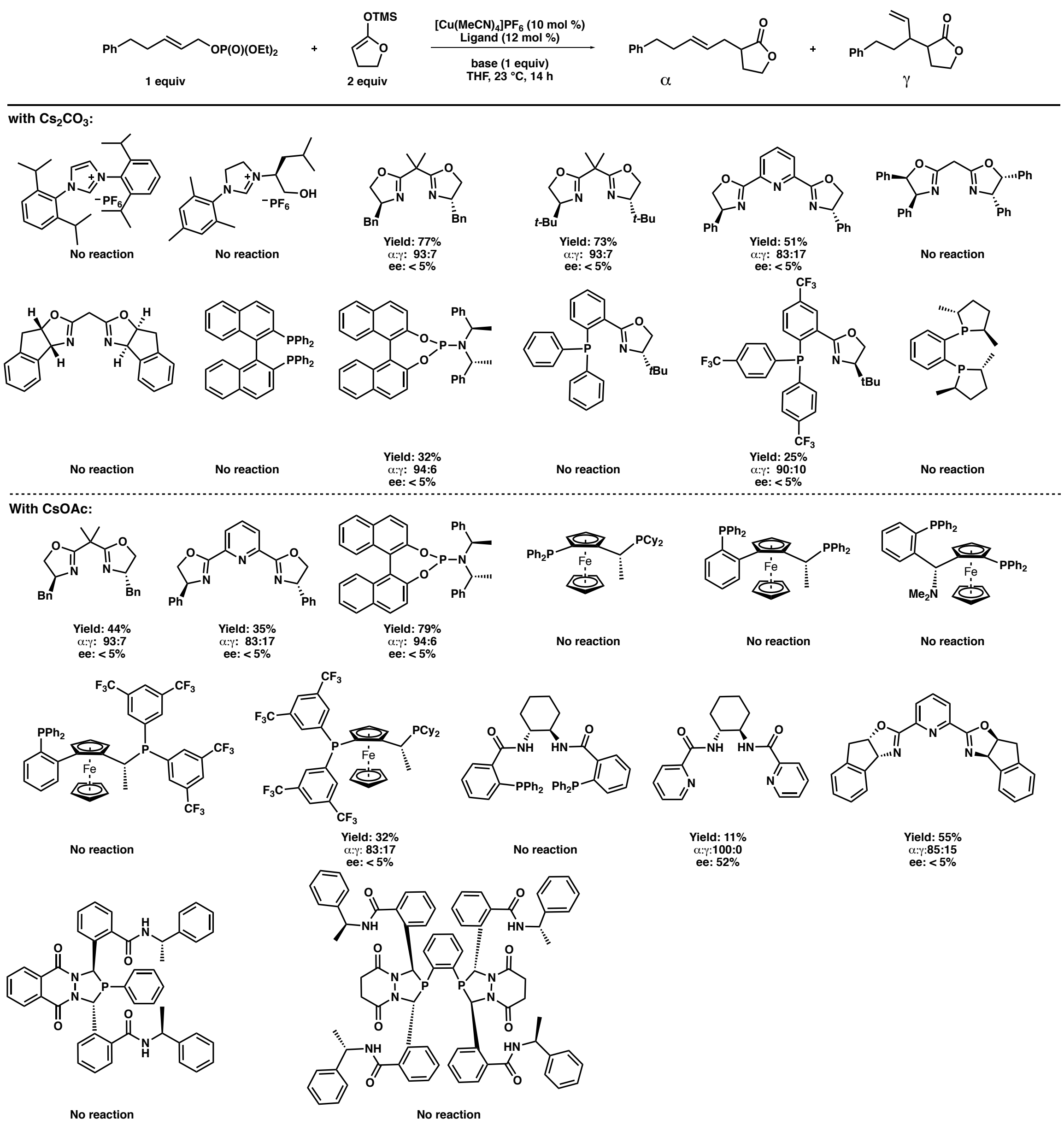
For crystal structure determination of ***3b*** A crystal was mounted on a polyimide MiTeGen loop with STP Oil Treatment and placed under a nitrogen stream. Low temperature (200K; there were crystal issues at lower temperatures) X-ray data were collected with a Bruker AXS D8 VENTURE KAPPA diffractometer running at 50 kV and 1mA (Cu K_α = 1.54178 Å; PHOTON II CPAD detector and Helios focusing multilayer mirror optics). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using TWINABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The water molecule was refined as a rigid body. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times (1.5 times for methyl groups) the U_{eq} value of the bonded atom.

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated.

List of Abbreviations

ee – enantiomeric excess, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, IPA – isopropanol, MTBE – methyl *tert*-butyl ether, PE – petroleum ether, DMAP – 4-dimethylaminopyridine, EtOAc – ethyl acetate, LiHMDS – lithium bis(trimethylsilyl)amide, NaHMDS – sodium bis(trimethylsilyl)amide, KHMDS – pottassium bis(trimethylsilyl)amide, THF – tetrahydrofuran, TMEDA – 1,2-tetramethylethylenediamine.

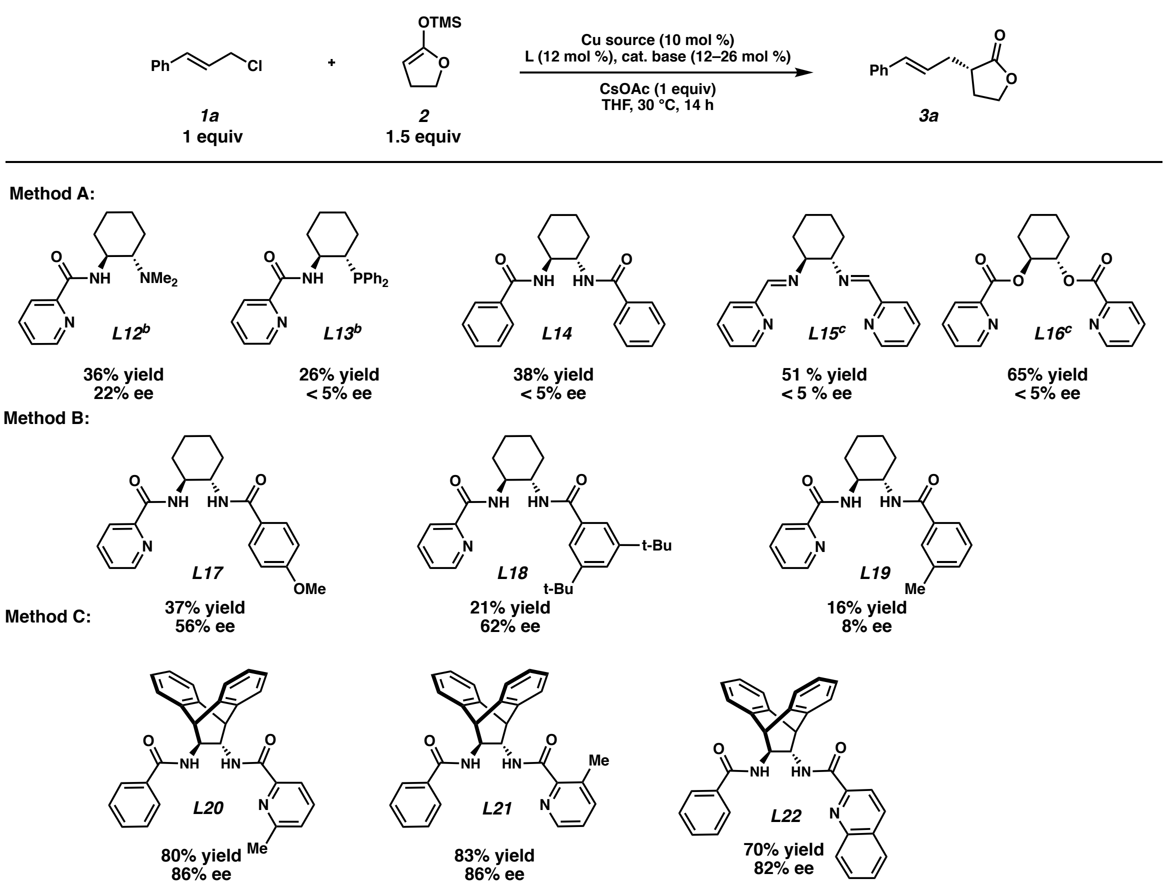
Commercial Ligand Screening:



Procedure for Evaluating Commercially Available Ligands in Cu-Catalyzed Enantioselective Allylic Alkylation:

n = the number of reactions in the screen. In the glovebox, $[Cu(MeCN)_4]PF_6$ (2.33n mg, 0.00625n mmol, 0.1 equiv), THF (0.6n mL), and a stir bar were added to a 4-mL vial A. The solution was stirred until the Cu had fully dissolved. In a separate 4-mL vial B was added the appropriate ligand (0.0075 mmol, 0.12 equiv), and Cs_2CO_3 (20 mg, 0.0625 mmol, 1.0 equiv) or CsOAc (19.2 mg, 0.1 mmol, 1 equiv) and a stir bar. The contents of vial A (0.6 mL) was then added to vial B, and allowed to stir for 20 min. ((4,5-dihydrofuran-2-yl)oxy)trimethylsilane (44 mg, 0.25 mmol, 2.0 equiv) was added to the vial, and the reaction was allowed to stir for 10 min. (*E*)-diethyl (5-phenylpent-2-en-1-yl) phosphate (18.65 mg, 0.0625 mmol, 1.0 equiv) was then added to the reaction, and the reaction was allowed to stir for 14 hours at room temperature The reaction mixture was filtered through a short silica plug eluting with ethyl acetate (5 mL). The eluate was concentrated by rotary evaporator and dissolved in CD_2Cl_2 to determine ^1H NMR yield with respect to 1,3,5-trimethoxybenzene. Then, the sample was concentrated and purified by preparative TLC (30% EtOAc/hexanes). The purified product was then dissolved in hexanes for SFC analysis on a Chiralcel AD column (12% IPA/hexanes, 2.5 mL/min).

Additional Picolinamide Ligand Screening:[a]



(a.) Conditions: 0.1 mmol scale. Yield determined by ^{1}HNMR analysis of the crude reaction mixture using 1,3,5–trimethoxybenzene as a standard. Enantiomeric Excess determined by chiral SFC analysis of isolated product. (b) only 12 mol% *n*–BuLi used. (c). no base added.

Methods for formation of Cu/L complex:

n = the number of reactions in the screen.

Method A:

To a flame-dried 4 mL vial charged with Ar and a stir bar was added the desired Ligand (0.012n mmol, 0.12 equiv) and THF (0.53n mL). The solution was cooled to –78 °C and *n*–BuLi (174n μL, 0.024n mmol, 0.138 M in THF, 0.24 equiv) was added dropwise. The reaction was stirred for 1 h at –78 °C. A solution of $[Cu(MeCN)_4]PF_6$ (3.73n mg, 0.01n mmol, 0.10 equiv) in THF was added, and the reaction was warmed to room temperature and stirred for 1 h.

Method B:

To a flame-dried 4 mL vial charged with Ar and a stir bar was added the desired Ligand (0.012n mmol, 0.12 equiv) and THF (0.63n mL). The solution was cooled to –78 °C and *n*–BuLi (174n mL, 0.024n mmol, 0.138M in THF, 0.24 equiv) was added dropwise. The reaction was stirred for 1 h at –78 °C, and then the cold solution was transferred to a flame-dried vial under Ar containing $CuCl_2$ (1.34n mg, 0.01n mmol, 0.1 equiv). The resulting mixture was then warmed to room temperature.

Method C:

To a 4 mL vial containing $CuCl_2$ (1.34n mg, 0.01n mmol, 0.1 equiv) in the glovebox was added a solution of the Ligand (0.012n mmol, 0.12 equiv) in THF (0.4n mL), followed by a solution of LiHMDS (4.35n mg, 0.026n mmol, 0.26 equiv) in THF (0.4n mL). The resulting solution was stirred for 1 h at room temperature.

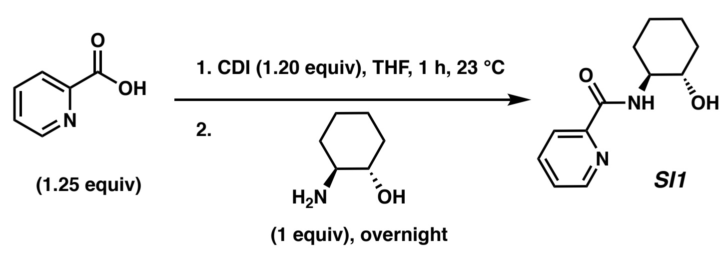
Procedure for Evaluating Picolinamide Ligands in Cu-catalyzed Enantioselective Allylic Alkylation:

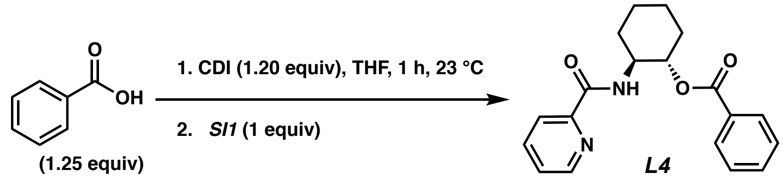
In the glovebox, CsOAc (19.2 mg, 0.1 mmol, 1.0 equiv) was added to a 4 mL vial containing a stir bar. The Cu/L complex in THF made using either Method A, B, or C (see above) was then added (0.8 mL) to the CsOAc followed immediately by the silyl ketene acetal **2** (28 mg, 0.15 mmol, 1.5 equiv) in THF (0.8 mL). The resulting solution was allowed to stir for 5 min and then cinnamyl chloride **1a** (15.3 mg, 0.1 mmol, 1.0 equiv) in THF (0.8 mL) was added, and the reaction was allowed to stir for 14 hours at room temperature. The reaction mixture was filtered through a short silica plug eluting with ethyl acetate (10 mL). The eluate was concentrated by rotary evaporator and dissolved in CD_2Cl_2 to determine ^{1}H NMR yield with respect to 1,3,5-trimethoxybenzene. Then, the sample was concentrated and purified by preparative TLC (30% EtOAc/hexanes). The purified product was then dissolved in diethyl ether for SFC analysis on a Chiralpak AD column (12% IPA/hexanes, 2.5 mL/min).

Synthesis of Chiral Picolinamide Ligands

Preparation of Known Ligands: Previously reported methods were used to prepare **L2**[4], **L5**[5], **L6**[6], **L13**[7], **L14**[8], **L15**[9].

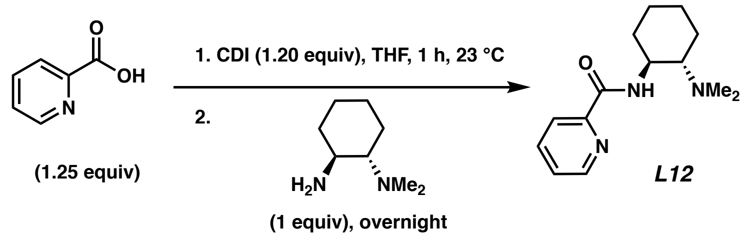
Synthesis of (1*S*,2*S*)-2-(picolinamido)cyclohexyl benzoate (L4):





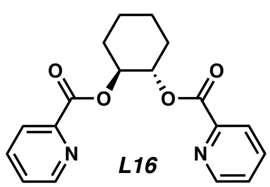
To a solution of picolinic acid (616 mg, 5.0 mmol, 1.1 equiv) in THF (12 mL) was added carbonyl diimidazole (811 mg, 5.0 mmol, 1.1 equiv). The resultant mixture was allowed to stir for 1 h at room temperature, or until the solution turned clear. The solution was then diluted with THF (84 mL) and added slowly to a solution of (1*S*,2*S*)-2-aminocyclohexan-1-ol (576 mg, 5.0 mmol, 1.0 equiv) in THF (100 mL) via a dropping funnel. The reaction was allowed to stir at room temperature overnight. The crude reaction mixture was then concentrated by rotary evaporator and purified by short silica plug (2% MeOH in EtOAc) to afford **SI1** (925 mg, 4.2 mmol, 84% yield).

To a solution of benzoic acid (269 mg, 2.2 mmol, 1.1 equiv) in THF (6.1 mL) was added carbonyl diimidazole (357 mg, 2.2 mmol, 1.1 equiv). The resultant mixture was allowed to stir for 1 h at room temperature, or until the solution turned clear. *N*-((1*S*,2*S*)-2-hydroxycyclohexyl)picolinamide (**SI1**, 414 mg, 2.0 mmol, 1.0 equiv) was added, and the reaction was allowed to stir overnight. The reaction mixture was diluted with water and allowed to stir for 1 h. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. Product **L4** was purified by column chromatography to provide a white solid (189 mg, 0.59 mmol 30% yield); $[\alpha]_D^{25}$ – 92.02 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.16 – 8.07 (m, 2H), 8.01 – 7.94 (m, 2H), 7.75 (td, *J* = 7.7, 1.7 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.39 – 7.30 (m, 3H), 5.01 (td, *J* = 10.4, 4.4 Hz, 1H), 4.31 (dddd, *J* = 13.8, 9.6, 7.4, 4.5 Hz, 1H), 2.28 – 2.13 (m, 2H), 1.90 – 1.72 (m, 2H), 1.68 – 1.57 (m, 1H), 1.55 – 1.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 164.1, 149.8, 148.1, 137.3, 132.9, 130.4, 129.8, 128.3, 126.1, 122.2, 75.7, 52.1, 32.1, 31.2, 24.5, 24.2; IR (Neat Film, NaCl) 3345, 2938, 2860, 1710, 1671, 1568, 1522, 1450, 1319, 1272, 1114, 1027, 997, 749, 713 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{19}H_{21}N_2O_3$ $[M+H]^+$: 325.1547, found 325.1553;



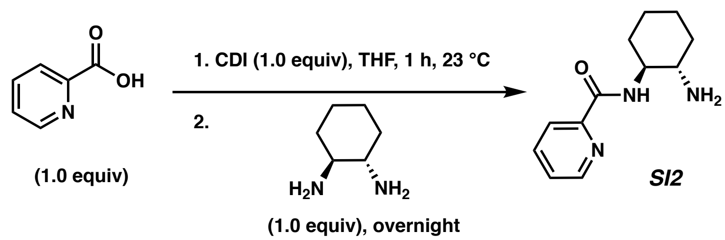
***N*-((1*S*,2*S*)-2-(dimethylamino)cyclohexyl)picolinamide (L12):** To a solution of picolinic acid (308 mg, 2.5 mmol, 1.25 equiv) in THF (3.33 mL) was added carbonyl diimidazole

(389 mg, 2.5 mmol, 1.2 equiv). The resultant mixture was allowed to stir for 1 h at room temperature, or until the solution turned clear. (1*S*,2*S*)-N^1,N^1-dimethylcyclohexane-1,2-diamine (285 mg, 2.0 mmol, 1.0 equiv) was added, and the reaction was stirred overnight. The reaction mixture was diluted with water and allowed to stir for 1 h. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. Product **L12** was purified by column chromatography to provide a white solid (247 mg, 1.0 mmol, 50% yield); $[\alpha]_D^{25}$ 74.79 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.29 (s, 1H), 8.18 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 3.80 (tdd, *J* = 10.7, 6.6, 4.0 Hz, 1H), 2.47 (dddd, *J* = 11.7, 9.8, 7.3, 3.9 Hz, 2H), 2.26 (s, 6H), 1.96 – 1.77 (m, 2H), 1.70 (dtd, *J* = 13.0, 3.3, 1.8 Hz, 1H), 1.45 – 1.12 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 150.7, 148.2, 137.3, 125.9, 122.2, 66.6, 51.0, 40.3, 33.0, 25.4, 25.0, 22.2; IR (Neat Film, NaCl) 3376, 2930, 2859, 2824, 2779, 1672, 1590, 1568, 1509, 1464, 1432, 1339, 1270, 1189, 1153, 1084, 1044, 1032, 997, 866, 844, 782, 750, 700, 671, 620 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{22}N_3O$ [M+H]$^+$: 248.1757, found 248.1753.

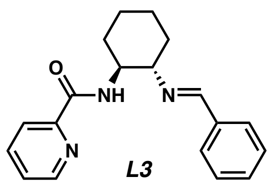


L16

(1*S*,2*S*)-cyclohexane-1,2-diyl dipicolinate (L16): To a solution of picolinic acid (345 mg, 2.8 mmol, 2.5 equiv) in THF (1.87 mL) was added carbonyl diimidazole (435 mg, 2.68 mmol, 2.4 equiv). The resultant mixture was allowed to stir for 1 h at room temperature, or until the solution turned clear. (1*S*,2*S*)-cyclohexane-1,2-diol (130 mg, 1.12 mmol, 1.0 equiv) was added, and the reaction was allowed to stir overnight. The reaction mixture was diluted with water and stirred for 1 h. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. Product **L16** was purified by column chromatography to provide a white solid (189 mg, 0.58 mmol, 52% yield); $[\alpha]_D^{25}$ –78.88 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 2H), 8.00 (dt, *J* = 7.9, 1.1 Hz, 2H), 7.74 (td, *J* = 7.8, 1.8 Hz, 2H), 7.38 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 2H), 5.45 – 5.27 (m, 2H), 2.35 – 2.25 (m, 2H), 1.93 – 1.78 (m, 2H), 1.75 – 1.56 (m, 2H), 1.58 – 1.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 150.1, 147.9, 137.1, 126.9, 125.2, 75.4, 30.5, 23.8; IR (Neat Film, NaCl) 2940, 2868, 1740, 1716, 1582, 1437, 1325, 1304, 1280, 1224, 1157, 1128, 1087, 1045, 1028, 992, 918, 845, 821, 747, 706, 674, 664, 619 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{18}H_{19}N_2O_4$ $[M+H]^+$:327.1339, found 327.1346.



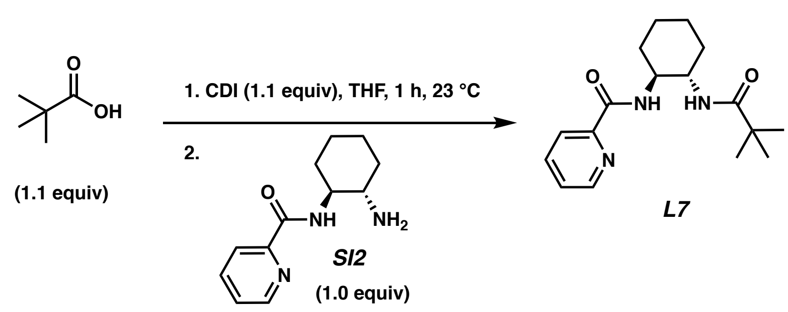
***N*-((1*S*,2*S*)-2-aminocyclohexyl)picolinamide (SI2):** To a solution of picolinic acid (1.23 g, 10.0 mmol, 1.0 equiv) in THF (25 mL) was added carbonyl diimidazole (1.62 g, 10.0 mmol, 1.0 equiv). The resultant mixture was stirred for 1 h at room temperature. The reaction was then diluted with THF (170 mL) and added slowly to a solution of (1*S*,2*S*)-cyclohexane-1,2-diamine (1.14 g, 10.0 mmol, 1.0 equiv) in THF (200 mL) via a dropping funnel. The reaction was allowed to stir at room temperature overnight. The crude reaction mixture was then concentrated by rotary evaporator and purified by column chromatography(3:1 ethyl acetate: MeOH to flush out imidazole, then 1% Et_3N to solvent mixture to elute product) to afford **SI2** (1.36 g, 6.2 mmol, 62% yield); $[\alpha]_D^{25}$ 136.06 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 8.55 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.20 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.97 (d, *J* = 9.4 Hz, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 3.72 (dtd, *J* = 11.0, 9.6, 4.0 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.04 (ddt, *J* = 12.7, 9.3, 3.1 Hz, 2H), 1.77 (dq, *J* = 9.1, 2.5 Hz, 2H), 1.66 (s, 2H), 1.47 – 1.16 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 150.0, 148.1, 137.5, 126.3, 122.5, 56.5, 55.8, 35.3, 32.6, 25.3; IR (Neat Film, NaCl) 3341, 3312, 2929, 2858, 1700, 1590, 1568, 1520, 1448, 1434, 1465, 1326, 1288, 1252, 1147, 1162, 1089, 1027, 997, 923, 906, 853, 821, 753, 692, 680, 620 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{12}H_{18}N_3O$ $[M+H]^+$: 220.1444, found 220.1434.



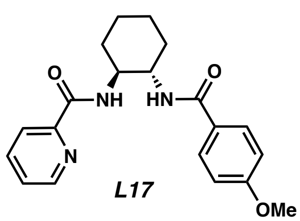
L3

***N*-((1*S*,2*S*)-2-(((*E*)-benzylidene)amino)cyclohexyl)picolinamide (L3):** To a solution of **SI2** (219 mg, 1.0 mmol, 1.0 equiv) in MeOH (5 mL) at 0°C was added benzaldehyde (112 uL, 1.1 mmoL, 1.1 equiv) in MeOH (5 mL) dropwise. The resulting mixture was warmed to room temperature, and concentrated by rotary evaporator and high-vac to afford **L3** (257 mg, 0.83 mmol, 83% yield); $[\alpha]_D^{25}$ 128.30 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.29 (s, 1H), 8.09 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.92 – 7.83 (m, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.36 – 7.28 (m, 4H), 4.19 (dtd, *J* = 10.4, 9.1, 4.1 Hz, 1H), 3.27 (td, *J* = 9.6, 5.0 Hz, 1H), 2.31 – 2.17 (m, 1H), 1.93 – 1.72 (m, 4H), 1.61 – 1.32 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 160.3, 150.2, 147.9, 137.3, 136.4, 130.5, 128.5, 128.3, 126.0, 122.3, 53.2, 33.5, 31.7, 24.9, 24.3; IR (Neat Film, NaCl) 3379, 2932, 2855, 2673, 1643, 1590, 1568, 1519, 1464, 1450, 1434, 1293, 1156, 1042, 998, 752, 695, 680 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{19}H_{22}N_3O_2$ $[M+H]^+$: 308.1757, found 308.1768.

General Procedure 1: Synthesis of Cyclohexylpicolinamide Ligands

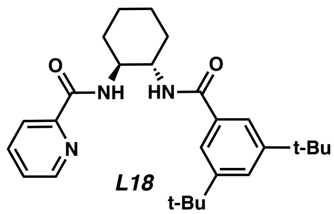


***N*-((1*S*,2*S*)-2-pivalamidocyclohexyl)picolinamide (L7):** To a solution of pivalic acid (56.2 mg, 0.55 mmol, 1.1 equiv) in THF (1.0 mL) was added carbonyl diimidazole (89.2 mg, 0.55 mmol, 1.1 equiv). The resultant mixture was stirred for 1 h at room temperature. *N*-((1*S*,2*S*)-2-aminocyclohexyl)picolinamide (**SI2**, 110 mg, 0.5 mmol, 1.0 equiv) was added, and the reaction was allowed to stir overnight. The reaction mixture was then diluted with water and allowed to stir for 1 h. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. The product was purified by column chromatography to provide a white solid (82.2 mg, 0.27 mmol, 54% yield); $[\alpha]_D^{25}$ 36.82 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.14 (dt, *J* = 7.8, 1.1 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.82 (td, *J* = 7.7, 1.7 Hz, 1H), 7.41 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 1H), 3.93 (tdd, *J* = 11.3, 9.0, 4.0 Hz, 1H), 3.73 (tdd, *J* = 11.2, 7.6, 4.0 Hz, 1H), 2.18 – 2.04 (m, 2H), 1.86 – 1.71 (m, 2H), 1.54 – 1.34 (m, 3H), 1.29 – 1.15 (m, 1H), 1.01 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 165.2, 149.5, 148.4, 137.4, 126.4, 122.2, 55.0, 52.5, 38.6, 32.7, 32.4, 27.5, 25.2, 24.7; IR (Neat Film, NaCl) 3354, 2935, 2858,1740, 1715, 1655, 1590, 1570, 1525, 1434, 1398, 1364, 1322, 1289, 1244, 1202, 1129, 1087, 1044, 997, 820, 750, 692, 620 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{17}H_{26}N_3O_2$ $[M+H]^+$: 304.2020, found 304.2008.



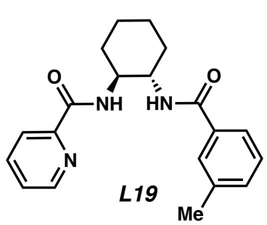
L17

***N*-((1*S*,2*S*)-2-(4-methoxybenzamido)cyclohexyl)picolinamide (L17):** Product **L17** was prepared according to the general procedure 1 and 4-methoxybenzaldehyde and **SI2**. The product was purified by column chromatography to provide a white solid (106 mg, 0.3 mmol, 60% yield); $[\alpha]_D^{25}$ 120.32 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.20 – 8.06 (m, 2H), 7.79 (td, *J* = 7.7, 1.7 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.39 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 6.90 – 6.81 (m, 2H), 4.05 (tdd, *J* = 11.5, 8.8, 4.1 Hz, 1H), 3.89 (tdd, *J* = 10.9, 7.1, 4.0 Hz, 1H), 3.80 (s, 3H), 2.37 (dq, *J* = 12.6, 2.3 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.92 – 1.74 (m, 2H), 1.57 (qd, *J* = 12.4, 3.7 Hz, 1H), 1.44 (ddt, *J* = 12.2, 9.9, 3.2 Hz, 2H), 1.37 – 1.21 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 165.8, 162.0, 149.4, 148.3, 137.5, 128.9, 126.9, 126.5, 122.3, 113.7, 56.5, 55.5, 52.4, 32.7, 32.3, 25.2, 24.6; IR (Neat Film, NaCl) 3316, 2933, 2856, 1656, 1607, 1569, 1507, 1527, 1465, 1330, 1302, 1255, 1178, 1146, 1109, 1092, 1028, 997, 843, 820, 750, 620; HRMS (MM) *m/z* calc'd for $C_{20}H_{24}N_3O_3$ $[M+H]^+$: 354.1812, found 354.1820.



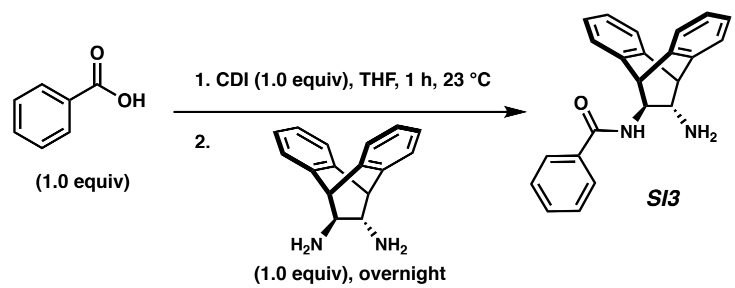
L18

***N*-((1*S*,2*S*)-2-(3,5-di-*tert*-butylbenzamido)cyclohexyl)picolinamide (L18):** Product **L18** was prepared according to General Procedure 1 from **SI2** and 3,5-di-*tert*-butylbenzoic acid. The product was purified by column chromatography to provide a white solid (66.7 mg, 0.15 mmol, 31% yield); $[\alpha]_D^{25}$ 37.12 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.23 – 8.15 (m, 2H), 7.80 (td, *J* = 7.7, 1.7 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 2H), 7.48 (t, *J* = 1.8 Hz, 1H), 7.39 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 4.07 (dddd, *J* = 11.7, 10.8, 8.8, 4.0 Hz, 1H), 3.89 (tdd, *J* = 10.9, 7.1, 4.0 Hz, 1H), 2.42 (ddt, *J* = 12.1, 4.9, 2.6 Hz, 1H), 2.12 (ddp, *J* = 12.4, 5.2, 2.6, 2.0 Hz, 1H), 1.93 – 1.73 (m, 2H), 1.59 (qd, *J* = 12.4, 3.7 Hz, 1H), 1.45 (ddt, *J* = 17.1, 11.8, 6.1 Hz, 2H), 1.32 (s, 19H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 165.6, 151.1, 149.4, 148.3, 137.3, 134.0, 126.5, 125.2, 122.4, 121.5, 56.7, 52.3, 35.1, 32.6, 32.4, 31.5, 25.3, 24.6; IR (Neat Film, NaCl) 3312, 2951, 2862, 1654, 1593, 1569, 1526, 1464, 1434, 1393, 1334, 1264, 1249, 1147, 1097, 998, 888, 820, 750, 706, 612 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{27}H_{38}N_3O_2$ $[M+H]^+$: 436.2959, found 436.2939.



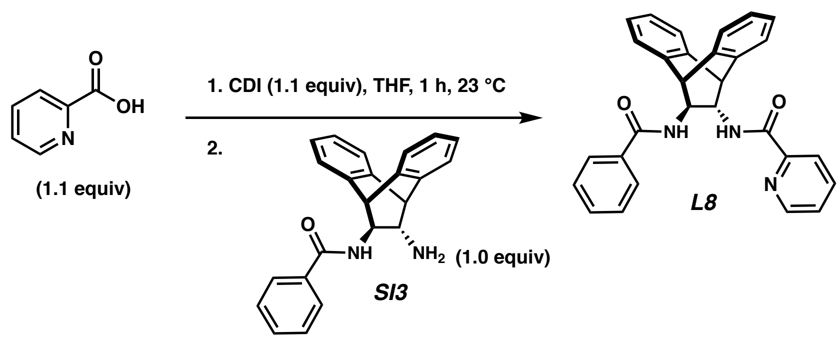
L19

N**-((1*S*,2*S*)-2-(3-methylbenzamido)cyclohexyl)picolinamide (L19):** Product **L19** was prepared according to General Procedure 1 from **SI2** and 3-methylbenzoic acid. The product was purified by column chromatography to provide a white solid (94.2 mg, 76% yield); $[\alpha]_D^{25}$ 75.30 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H), 8.13 (dt, J = 7.8, 1.1 Hz, 1H), 7.79 (td, J = 7.7, 1.7 Hz, 1H), 7.56 (dp, J = 1.6, 0.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.39 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 7.25 – 7.15 (m, 3H), 4.12 – 4.01 (m, 1H), 3.92 (tdd, J = 11.0, 7.3, 4.0 Hz, 1H), 2.40 – 2.30 (m, 4H), 2.13 (ddt, J = 12.8, 4.1, 2.7 Hz, 1H), 1.92 – 1.76 (m, 2H), 1.64 – 1.49 (m, 1H), 1.48 – 1.40 (m, 2H), 1.39 – 1.23 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 165.7, 149.4, 148.4, 138.2, 137.4, 134.5, 132.0, 128.4, 128.0, 126.5, 124.1, 122.3, 56.3, 52.5, 32.6, 32.3, 25.2, 24.6, 21.5; IR (Neat Film, NaCl) 3304, 3055, 2933, 2857, 1655, 1641, 1606, 1587, 1528, 1485, 1464, 1434, 1328, 1289, 1250, 1216, 1145, 1093, 1043, 998, 936, 816, 746, 688, 665, 620 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{23}H_{24}N_3O_2$ $[M+H]^+$: 338.1863, found 338.1851.

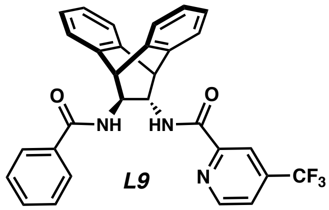


N-((11S,12S)-12-amino-9,10-dihydro-9,10-ethanoanthracen-11-yl)benzamide (SI3): To a solution of benzoic acid (1.04 g, 8.5 mmol) in THF (21 mL) was added carbonyl diimidazole (1.38 g, 8.5 mmol). The resultant mixture was allowed to stir for 1 h at room temperature, or until the solution turned clear. The solution was then diluted with THF (142 mL) and added slowly to a solution of (11*S*,12*S*)-9,10-dihydro-9,10-ethanoanthracene-11,12-diamine (1.14 g, 10.0 mmol) in THF (170 mL) via a dropping funnel. The reaction was allowed to stir at room temperature overnight. The crude reaction mixture was then concentrated by rotary evaporator and purified by column chromatography (9:1 ethyl acetate: MeOH) to afford **SI3** (1.7 g, 5.1 mmol, 60% yield, co-eluted with imidazole, used without further purification); $[\alpha]_D^{25}$ 30.33 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.49 – 7.45 (m, 1H), 7.41 – 7.34 (m, 6H), 7.23 – 7.17 (m, 4H), 5.82 (d, J = 7.7 Hz, 1H), 4.98 (s, 2H), 4.35 (s, 1H), 4.23 (s, 1H), 3.96 (d, J = 7.9 Hz, 1H), 2.97 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 142.4, 140.3, 139.2, 138.7, 134.2, 131.8, 128.8, 127.2, 126.9, 126.7, 126.4, 125.3, 124.9, 124.8, 61.1, 60.2, 52.1, 49.1; IR (Neat Film, NaCl) 3119, 2922, 2838, 2697, 2608, 1960, 1918, 1826, 1638, 1602, 1578, 1542, 1535, 1485, 1466, 1445, 1379, 1326, 1294, 1256, 1228, 1141, 1116, 1095, 1063, 1026, 1000, 931, 866, 826, 751, 720, 664 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{23}H_{21}N_2O$ $[M+H]^+$: 341.1648, found 341.1649.

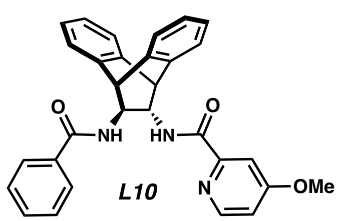
General Procedure 2: Synthesis of ANDEN Picolinyl Ligands.



***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)picolinamide (L8):** To a solution of picolinic acid (378 mg, 3.07 mmol) in THF (4.65 mL) was added carbonyl diimidazole (498 mg, 3.07 mmol). The resultant mixture was stirred for 1 h at room temperature. *N*-((11*S*,12*S*)-12-amino-9,10-dihydro-9,10-ethanoanthracen-11-yl)benzamide (**SI3**, 950 mg, 2.79 mmol) was added, and the reaction was allowed to stir overnight. The reaction mixture was then diluted with water and allowed to stir for 1 h. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. Product **L8** was purified by column chromatography to provide a white solid (747 mg, 1.68 mmol, 60% yield); $[\alpha]_D^{25}$ 174.63 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.06 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.51 – 7.39 (m, 3H), 7.39 – 7.30 (m, 5H), 7.25 – 7.14 (m, 4H), 6.10 (d, *J* = 7.7 Hz, 1H), 4.63 (d, *J* = 2.6 Hz, 1H), 4.49 (d, *J* = 2.6 Hz, 1H), 4.36 – 4.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 164.2, 149.3, 148.2, 141.2, 139.2, 138.7, 137.3, 134.3, 131.7, 128.6, 127.11, 127.07, 127.07, 127.01, 126.97, 126.91, 126.4, 126.0, 125.9, 125.1, 124.9, 122.3, 57.8, 56.9, 49.6, 49.4; IR (Neat Film, NaCl) 3360, 3006, 1652, 1569, 1517, 1489, 1465, 1434, 1327, 1293, 1146, 998, 748, 716 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{29}H_{24}N_3O_2$ $[M+H]^+$: 446.1863, found 446.1882.

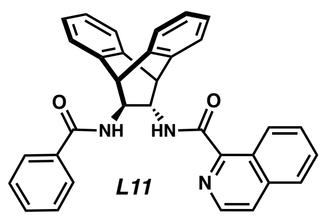


***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)-4-(trifluoromethyl)picolinamide (L9):** Product **L9** was prepared according to general procedure 2 from **SI3** and 4-(Trifluoromethyl)pyridine-2-carboxylic acid . The product was purified by column chromatography to provide a white solid (107.1 mg, 0.21 mmol, 42% yield); $[\alpha]_D^{25}$ 143.66 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dt, *J* = 5.0, 0.8 Hz, 1H), 8.28 (dt, *J* = 1.6, 0.7 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.51 – 7.40 (m, 3H), 7.38 – 7.30 (m, 4H), 7.29 – 7.15 (m, 4H), 6.13 (d, *J* = 7.9 Hz, 1H), 4.60 (d, *J* = 2.6 Hz, 1H), 4.49 (d, *J* = 2.6 Hz, 1H), 4.39 – 4.32 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 162.8, 150.8, 149.3, 141.1, 139.9 (q, *J* = 34.7 Hz), 139.1, 138.6, 134.2, 131.7, 128.6, 127.2 (d, *J* = 8.9 Hz), 125.9 (d, *J* = 10.6 Hz), 125.1 (d, *J* = 18.6 Hz), 124.0, 124.0, 121.9 (d, *J* = 3.7 Hz), 121.2, 121.2, 118.6 – 118.2 (m), 57.7, 57.1, 49.5 (d, *J* = 12.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –64.86; IR (Neat Film, NaCl) 3312, 3069, 1654, 1610, 1580, 1524, 1488, 1411, 1331, 1293, 1265, 1228, 1173, 1141, 1116, 1080, 1026, 857, 842, 797, 752, 720, 699, 665, 639 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{30}H_{23}F_3N_3O_2$ $[M+H]^+$: 514.1737, found 514.1733.

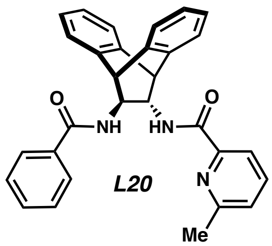


***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)-4-methoxypicolinamide (L10):** Product **L18** was prepared according to general procedure 2 from **SI3** and 4-methoxypicolinic acid (174 mg, 0.37 mmol, 70% yield); $[\alpha]_D^{25}$ 134.97 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 5.6, 0.5 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.50 – 7.40 (m, 3H), 7.39 – 7.31 (m, 4H), 7.28 – 7.14

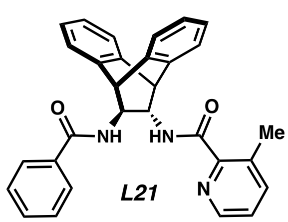
(m, 4H), 6.86 (dd, J = 5.7, 2.6 Hz, 1H), 6.12 (d, J = 7.6 Hz, 1H), 4.63 (d, J = 2.6 Hz, 1H), 4.47 (d, J = 2.5 Hz, 1H), 4.31 (dtd, J = 10.4, 6.3, 3.1 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 166.9, 164.2, 151.3, 149.4, 141.3, 141.1, 139.2, 138.7, 134.3, 131.7, 128.6, 127.12, 127.09, 127.0, 126.0, 125.1, 124.9, 113.1, 107.6, 57.9, 56.9, 55.6, 49.6, 49.4; IR (Neat Film, NaCl) 3328, 2926, 1654,1599, 1579, 1566, 1518, 1489, 1308, 1257, 1226, 1138, 1030, 994, 849, 804, 784, 761, 716, 640 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{30}H_{26}N_3O_2^+$ [M+H]: 476.1969, found 476.1950.



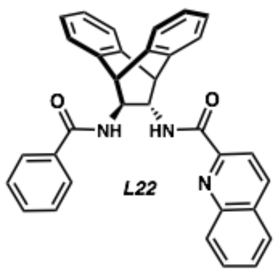
***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)isoquinoline-1-carboxamide (L11):** Product **L11** was prepared according to general procedure 2 from **SI3** and isoquinoline-1-carboxylic acid (173 mg, 69% yield); $[\alpha]_D^{25}$ 142.51 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 – 9.48 (m, 1H), 8.34 (d, J = 5.5 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.81 (dt, J = 8.4, 0.8 Hz, 1H), 7.74 (dd, J = 5.6, 1.0 Hz, 1H), 7.69 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.64 (ddt, J = 6.9, 3.7, 1.9 Hz, 3H), 7.49 (dd, J = 7.1, 1.4 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.41 – 7.32 (m, 4H), 7.28 – 7.16 (m, 4H), 6.08 (d, J = 7.7 Hz, 1H), 4.65 (d, J = 2.7 Hz, 1H), 4.58 (d, J = 2.7 Hz, 1H), 4.36 (dddd, J = 12.1, 8.6, 3.6, 2.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 166.0, 147.4, 141.4, 141.1, 140.3, 139.2, 138.9, 137.5, 134.4, 131.7, 130.6, 128.8, 128.7, 127.7, 127.10, 127.07, 127.05, 127.0, 126.9, 126.0, 125.1, 124.9, 124.6, 57.8, 57.2, 49.6, 49.5; IR (Neat Film, NaCl) 3328, 3054, 3022, 2952, 1650, 1602, 1582, 1510, 1489, 1466, 1383, 1325, 1292, 1260, 1222, 1144, 1110, 1024, 878, 834, 812, 800, 756, 715, 637, 619 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{33}H_{26}N_3O_2$ $[M+H]^+$:496.2020, found 496.2014.



***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)-6-methylpicolinamide (L20):** Product **L20** was prepared according to general procedure 2 from **SI3** and 6-methylpicolinic acid . The product was purified by column chromatography to provide a white solid (150 mg, 0.33 mmol, 65% yield); $[\alpha]_D^{25}$ 171.86 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 1H), 7.87 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.31 (m, 4H), 7.29 – 7.16 (m, 5H), 6.07 (d, *J* = 7.4 Hz, 1H), 4.64 (d, *J* = 2.6 Hz, 1H), 4.48 (d, *J* = 2.5 Hz, 1H), 4.34 – 4.27 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 164.3, 157.3, 148.6, 141.2, 139.2, 138.8, 137.5, 134.3, 131.7, 128.6, 127.1, 127.0, 126.9, 126.8, 126.1, 126.0, 125.9, 125.2, 124.9, 119.3, 57.9, 56.7, 49.7, 49.4, 24.3; IR (Neat Film, NaCl) 3328, 3022, 1654, 1595, 1578, 1521, 1489, 1455, 1376, 1312, 1328, 1292, 1258, 1227, 1116, 1084, 1026, 995, 820, 804, 757, 716, 691, 664, 638 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{30}H_{26}N_3O_2$ $[M+H]^+$: 460.2020, found 460.2039.



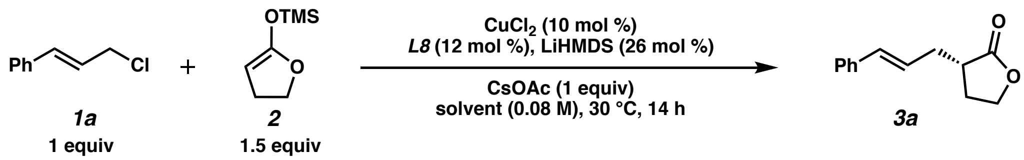
***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)-3-methylpicolinamide (L21):** Product **L21** was prepared according to general procedure 2 from **SI3** and 3-methylpicolinic acid . The product was purified by column chromatography to provide a white solid (148 mg, 0.3 mmol, 64% yield); $[\alpha]_D^{25}$ 165.82 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.53 (ddd, *J* = 7.8, 1.6, 0.8 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.40 – 7.31 (m, 4H), 7.25 – 7.14 (m, 5H), 5.98 (d, *J* = 8.0 Hz, 1H), 4.61 (d, *J* = 2.8 Hz, 1H), 4.50 (d, *J* = 2.7 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.23 (ddd, *J* = 8.8, 3.7, 2.8 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 165.8, 146.6, 145.6, 141.4, 141.1, 140.9, 139.2, 138.9, 135.5, 134.3, 131.7, 128.7, 127.1, 127.0, 126.9, 126.0, 125.0, 124.9, 57.7, 57.0, 53.6, 49.6, 49.5, 20.6; IR (Neat Film, NaCl) 3327, 3046, 2956, 1654, 1602, 1579, 1508, 1466, 1446, 1380, 1308, 1326, 1292, 1222, 1122, 1080, 1026, 1002, 900, 814, 787, 762, 751, 712, 638, 662 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{30}H_{26}N_3O_2$ $[M+H]^+$: 460.2020, found 460.2095.



***N*-((11*S*,12*S*)-12-benzamido-9,10-dihydro-9,10-ethanoanthracen-11-yl)quinoline-2-carboxamide (L22):** Product **L22** was prepared according to general procedure 2 from **SI2** and quinoline-2-carboxylic acid (174 mg, 0.35 mmol, 70% yield); $[\alpha]_D^{25}$ 221.25 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.6, 0.8 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.15 (s, 1H), 7.98 – 7.92 (m, 1H), 7.87 – 7.81 (m, 1H), 7.73 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.55 – 7.51 (m, 1H), 7.49 – 7.44 (m, 1H), 7.41 (ddd, *J* = 7.6, 6.2, 1.8 Hz, 2H), 7.39 – 7.16 (m, 7H), 6.13 (d, *J* = 7.4 Hz, 1H), 4.67 (d, *J* = 2.5 Hz, 1H), 4.54 (d, *J* = 2.5 Hz, 1H), 4.40 (ddt, *J* = 9.2, 3.5, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 164.3, 149.1, 146.5, 141.1, 139.2, 138.8, 137.5, 134.3, 131.7, 130.2, 130.0, 129.4, 128.6, 128.1, 127.7, 127.2, 127.1, 127.0, 126.02, 125.95, 125.2, 124.9, 118.8, 57.9, 56.9, 49.7, 49.4; IR (Neat Film, NaCl) 3329, 3022, 1654, 1579, 1525, 1499, 1427, 1328, 1211, 1145, 1113, 1026, 904, 844, 794, 750, 715, 674, 638 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{33}H_{26}N_3O_2$ $[M+H]^+$:496.2020, found 496.2010.

Additional Screening

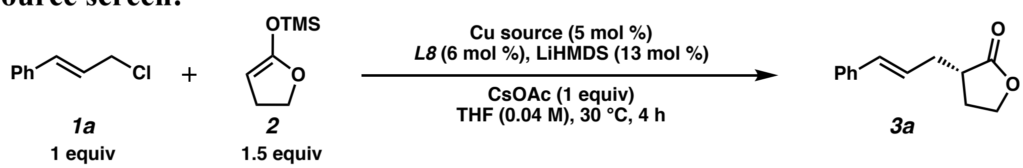
Solvent Screen:[a]



entry	solvent	conversion (%)[b]	yield (%)[b]	ee (%)[c]
1	THF	100	90	92
2	CH_2Cl_2	66	49	38
3	Et_2O	28	20	74
4	toluene	20	7	–
5	MTBE	52	< 5	–

a. Conditions: The Cu/***L8*** complex was synthesized according to Method C above. The THF was removed via vacuum, and the resulting solid was re-suspended in the appropriate solvent. The reactions were then set up and analyzed according to the procedure described above. b. determined by ^{1}H NMR of crude reaction mixture with 1,3,5-trimethoxybenzene as a standard. c. determined by chiral SFC, AD-column, 15% IPA, 2.5 mL/ min.

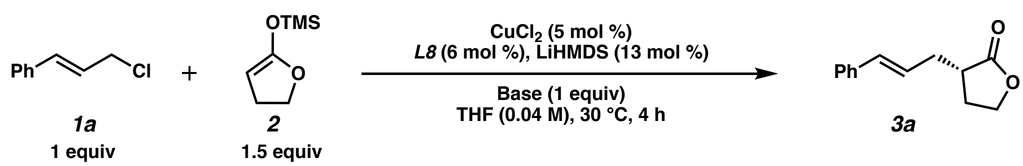
Cu source screen:[a]



entry	Cu source	conversion (%)[b]	yield (%)[b]	ee (%)[c]
1	$CuBr_2$	80	73	89
2	$Cu(OTf)_2$	94	89	92
3	CuBr	83	79	82
4	CuCN	51	34	45
5	Cu(OTf)•PhMe	65	67	90
6	$[Cu(MeCN)_4]PF_6$	45	42	84

a. Conditions: The Cu/***L8*** complex was synthesized according to Method C, but with the appropriate Cu salt. The reactions were then set up and analyzed according to the procedure described above. b. determined by ^{1}H NMR of crude reaction mixture with 1,3,5-trimethoxybenzene as a standard. c. determined by chiral SFC, AD-column, 15% IPA, 2.5 mL/ min.

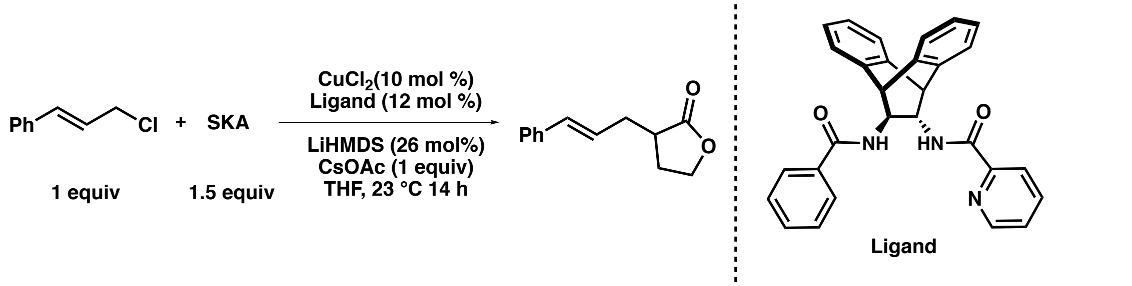
Base Screen:[a]



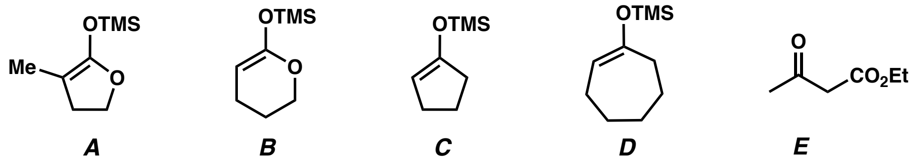
entry	Base	conversion (%)[b]	yield (%)[b]	ee (%)[c]
1	None	14	0	–
2	LiOAc	24	16	–
3	NaOAc	66	64	92
4	KOAc	67	66	89
5	CsF	100	30	–
6	Cs_2CO_3	92	0	–

a. Conditions: The Cu/***L8*** complex was synthesized according to Method C, but with the appropriate Cu salt. The reactions were then set up and analyzed according to the procedure described above. b. determined by ^{1}H NMR of crude reaction mixture with 1,3,5-trimethoxybenzene as a standard. c. determined by chiral SFC, AD-column, 15% IPA, 2.5 mL/ min.

Other Nucleophiles Tested:[a]



SKA:

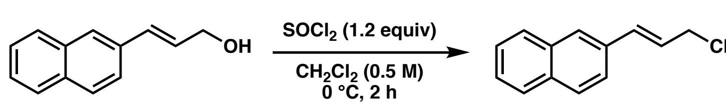


entry	Nucleophile	conversion (%)[b]	yield (linear)[b]	yield (branched)[b]
1	***A***	87	13	7
2	***B***	88	9	16
3	***C***	23	–	–
4	***D***	15	–	–
5	***E***	8	–	–

a. Conditions: The Cu/***L8*** complex was synthesized according to Method C, but with the appropriate Cu salt. The reactions were then set up and analyzed according to the procedure described above. b. determined by ^{1}H NMR of crude reaction mixture with 1,3,5-trimethoxybenzene as a standard.

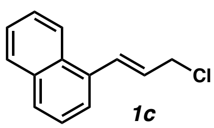
Synthesis of Allylic Chloride Electrophiles:

General Procedure 3: Synthesis of Aryl-Substituted Allylic Chlorides (**1b-1d**, **1g**, **1h**, **1j-1m**, **1p**, **1s-1u**).



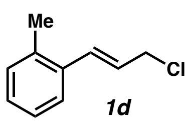
1b

(*E*)-2-(3-chloroprop-1-en-1-yl)naphthalene (1b): (*E*)-3-(naphthalen-2-yl)prop-2-en-1-ol (553 mg, 3.0 mmol, 1.0 equiv) was dissolved in methylene chloride (6 mL, 0.5 M). Then, thionyl chloride (326 μL, 4.5 mmol, 1.2 equiv) was added dropwise. The reaction was allowed to stir for 2 h at 0 °C, then quenched with saturated aqueous $NaHCO_3$ solution (6 mL) and allowed to warm to room temperature. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. The crude oil was then re-suspended in hexanes (10 mL) and washed with water 4 times. The hexanes layer was then dried with Na_2SO_4 and concentrated to afford the desired allylic chloride **1b** as a white solid (339 mg, 1.68 mmol, 56% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 3H), 7.83 – 7.79 (m, 1H), 7.65 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.57 – 7.47 (m, 2H), 6.88 (dtd, *J* = 15.6, 1.2, 0.6 Hz, 1H), 6.51 (dt, *J* = 15.6, 7.2 Hz, 1H), 4.37 (dd, *J* = 7.2, 1.2 Hz, 2H); All characterization data match those reported.[10]



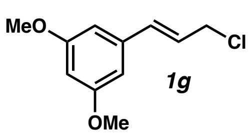
1c

(*E*)-1-(3-chloroprop-1-en-1-yl)naphthalene (1c): 994 mg, 4.9 mmol, 77% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.02 (m, 1H), 7.96 – 7.77 (m, 2H), 7.62 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.59 – 7.38 (m, 4H), 6.37 (dtd, *J* = 15.1, 7.1, 0.8 Hz, 1H), 4.36 (dt, *J* = 7.1, 1.1 Hz, 2H); All characterization data match those reported.[10]



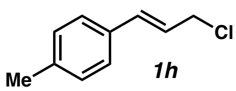
1d

(*E*)-1-(3-chloroprop-1-en-1-yl)-2-methylbenzene (1d): 274 mg, 1.64 mmol, 55% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 1H), 7.22 – 7.12 (m, 3H), 6.88 (dt, *J* = 15.5, 1.2 Hz, 1H), 6.22 (dt, *J* = 15.4, 7.2 Hz, 1H), 4.28 (dd, *J* = 7.2, 1.2 Hz, 2H), 2.37 (s, 3H); All characterization data match those reported.[11]

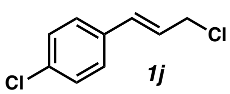


1g

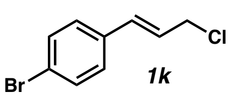
(*E*)-1-(3-chloroprop-1-en-1-yl)-3,5-dimethoxybenzene (1g): 106 mg, 0.5 mmol, 22% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (dt, *J* = 1.5, 0.8 Hz, 2H), 6.93 (tt, *J* = 1.7, 0.8 Hz, 1H), 6.66 – 6.54 (m, 1H), 6.30 (dt, J = 15.6, 7.2 Hz, 1H), 4.24 (dd, J = 7.3, 1.2 Hz, 2H), 2.31 (t, J = 0.7 Hz, 6H); All characterization data match those reported.[12]


1h

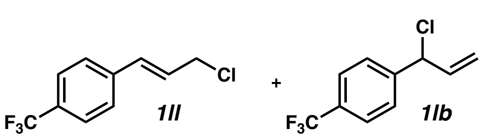
(*E*)-1-(3-chloroprop-1-en-1-yl)-4-methylbenzene (1h): 442 mg, 2.65 mmol, 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.18 – 7.11 (m, 2H), 6.63 (dd, J = 15.6, 1.1 Hz, 1H), 6.27 (dt, J = 15.6, 7.2 Hz, 1H), 4.25 (dd, J = 7.3, 1.2 Hz, 2H), 2.35 (s, 3H); All characterization data match those reported.[14]


1j

(*E*)-1-chloro-4-(3-chloroprop-1-en-1-yl)benzene (1j): 609 mg, 3.25 mmol, 81% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 1.1 Hz, 4H), 6.61 (dt, J = 15.7, 1.3 Hz, 1H), 6.30 (dt, J = 15.6, 7.1 Hz, 1H), 4.23 (dd, J = 7.1, 1.2 Hz, 2H); All characterization data match those reported.[10]

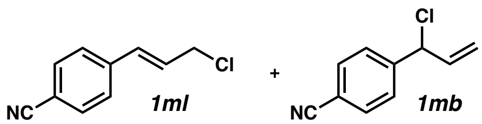

1k

(*E*)-1-bromo-4-(3-chloroprop-1-en-1-yl)benzene (1k): 579 mg, 2.5 mmol, 50% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.38 (m, 2H), 7.26 (s, 2H), 6.60 (d, J = 15.7 Hz, 1H), 6.31 (dt, J = 15.6, 7.1 Hz, 1H), 4.23 (dd, J = 7.1, 1.2 Hz, 2H); All characterization data match those reported.[10]


1ll + 1lb

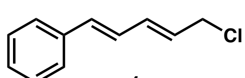
(*E*)-1-(3-chloroprop-1-en-1-yl)-4-(trifluoromethyl)benzene (1ll) and 1-(1-chloroallyl)-4-(trifluoromethyl)benzene (1lb): 405 mg, 1.8 mmol, 61% yield, **1ll**:**1lb** = 83:17 (inseparable mixture); **1ll**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.39 (m, 5H), 6.70 (d, J

= 15.7 Hz, 1H), 6.41 (dt, *J* = 15.5, 7.0 Hz, 1H), 4.25 (dd, *J* = 7.0, 1.3 Hz, 2H). **1lb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.34 (m, 4H), 6.13 (m, 1H), 5.54 – 5.26 (m, 3H); All characterization data match those reported.[15]



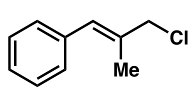
1ml *1mb*

(*E*)-4-(3-chloroprop-1-en-1-yl)benzonitrile (1ml) and 4-(1-chloroallyl)benzonitrile (1mb): Isolated as an inseparable mixture of constitutional isomers **1ml** and **1mb** (210 mg, 1.18 mmol, 56% yield, **1ml**:**1mb** = 59:42, **1m** = 86:15, E:Z); ^{1}H NMR (400 MHz, $CDCl_3$) **1ml:** δ 7.70 – 7.58 (m, 2H), 7.55 – 7.44 (m, 2H), 6.72 – 6.56 (m, 1H), 6.43 (dt, *J* = 15.7, 6.9 Hz, 1H), 4.25 (dd, *J* = 6.9, 1.2 Hz, 2H); **1mb:** δ 7.70 – 7.58 (m, 2H), 7.55 – 7.44 (m, 2H), 6.11 (ddd, *J* = 17.1, 10.1, 7.2 Hz, 1H), 5.45 (dd, *J* = 7.1, 1.1 Hz, 1H), 5.35 (dt, *J* = 16.8, 1.0 Hz, 1H), 5.30 (dt, *J* = 10.1, 0.9 Hz, 1H); **1ml** and **1mb:** ^{13}C NMR (101 MHz, $CDCl_3$) δ, 140.5, 136.6, 134.8, 132.6, 132.6, 132.2, 129.3, 128.9, 128.3, 127.3, 118.8, 118.5, 118.3, 112.3, 111.6, 77.2, 57.4, 44.7, 25.2; IR (Neat Film, NaCl) 3042, 2956, 2357, 2227, 1921, 1654, 1606, 1504, 1439, 1412, 1333, 1303, 1250, 1215, 1177, 1156, 1109, 1075, 1017, 969, 936, 834, 811, 760, 722, 688, 672 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{10}H_9ClN$ $[M+H]^+$: 178.0418, found 178.0422.



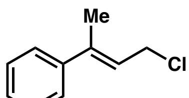
1p

((1*E*,3*E*)-5-chloropenta-1,3-dien-1-yl)benzene (1p): 1.32 g, 7.4 mmol, 92% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H), 6.78 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.46 (dd, *J* = 14.9, 10.3 Hz, 1H), 5.92 (dt, *J* = 14.8, 7.4 Hz, 1H), 4.18 (dd, *J* = 7.3, 1.1 Hz, 2H); All characterization data match those reported.[16]



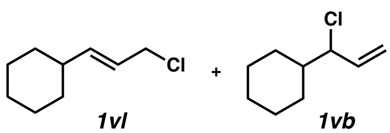
1s

(*E*)-(3-chloro-2-methylprop-1-en-1-yl)benzene (1s): 1.14 g, 6.84 mmol, 98% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 6H), 6.56 (s, 1H), 4.16 (t, *J* = 2.0 Hz, 2H), 1.96 (q, *J* = 2.2, 1.8 Hz, 3H); All characterization data match those reported.[13]



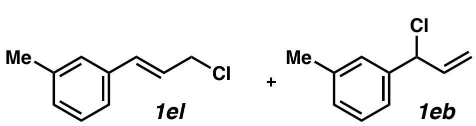
1t

(*E*)-(4-chlorobut-2-en-2-yl)benzene (1t): 883 mg, 5.29 mmol, 76% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 6H), 6.00 (tq, *J* = 8.0, 1.4 Hz, 1H), 4.29 (d, *J* = 8.0 Hz, 2H), 2.15 (d, *J* = 1.5 Hz, 3H); All characterization data match those reported.[13]



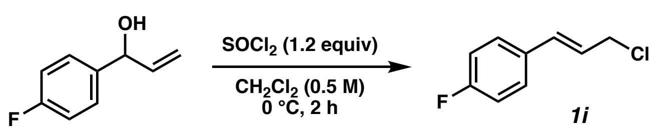
1vl ***1vb***

(*E*)-(3-chloroprop-1-en-1-yl)cyclohexane(1vl) and (1-chloroallyl)cyclohexane (1vb): Isolated as an inseparable mixture of constitutional isomers **1vl** and **1vb** (623 mg, 3.9 mmol, 78% yield, **1vl**:**1vb** = 1:2.8); ^{1}H NMR (400 MHz, $CDCl_3$) **1vl:** 5.71 (ddt, *J* = 15.3, 6.5, 1.0 Hz, 1H), 5.55 (dtd, *J* = 15.3, 7.0, 1.3 Hz, 1H), 4.03 (dt, *J* = 7.0, 0.8 Hz, 2H), 1.93 (m, 1H), 1.83 – 1.56 (m, 5H), 1.33 – 0.95 (m, 5H); **1vb:** δ 5.88 (ddd, *J* = 16.9, 10.1, 8.9 Hz, 1H), 5.31 – 5.09 (m, 2H), 4.17 (dd, *J* = 8.9, 6.4 Hz, 1H), 1.93 (ddt, *J* = 12.8, 3.6, 1.8 Hz, 1H), 1.83 – 1.56 (m, 5H), 1.33 – 0.95 (m, 5H); **1vl** and **1vb**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 137.5, 123.6, 117.2, 69.4, 46.0, 44.5, 40.3, 32.6, 29.8, 29.6, 26.4, 26.2, 26.14, 26.07, 26.05; δ IR (Neat Film, NaCl) 3084, 2926, 2853, 1641, 1450, 1419, 1300, 1249, 1197, 987, 968, 926, 891, 780, 756, 688 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_9H_{15}Cl$ $[M]^{+*}$: 158.0862, found 158.0859.



1el ***1eb***

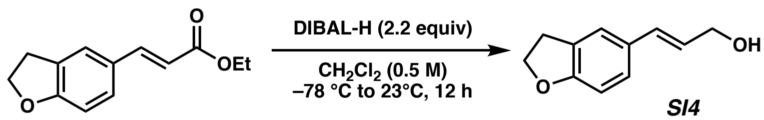
(*E*)-1-(3-chloroprop-1-en-1-yl)-3-methylbenzene (1el) and 1-(1-chloroallyl)-3-methylbenzene (1eb): 513 mg, 71% yield. To a solution of (E)-3-(*m*-tolyl)prop-2-en-1-ol (640 mg, 4.32 mmol, 1.0 equiv) in anhydrous Et_2O (4.3 mL, 1 M) at 0° C under a nitrogen atmosphere was added thionyl chloride (0.38 mL, 5.2 mmol, 1.2 equiv). Stirring was continued at 0° C for 6 hours. The reaction was then diluted with Et_2O and washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and solvent was removed in vacuo. The crude was purified by flash column chromatography (5% EtOAc/hexanes) to yield the title compound colorless oil (513 mg, 3.08 mmol, 71% yield, **1el**:**1eb**= 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) **1el**: δ 7.26 – 7.20 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 15.4 Hz, 1H), 6.32 (dt, *J* = 15.4, 7.2 Hz, 1H), 4.26 (d, *J* = 7.2 Hz, 2H), 2.37 (s, 3H); **1eb:** δ 7.28 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.21 (ddd, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.44 (d, *J* = 7.2 Hz, 1H), 5.36 (d, *J* = 16.8 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 2.39 (s, 3H); **1el** and **1eb**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.6, 138.4, 137.9, 136.0, 134.4, 129.3, 129.2, 128.7, 128.2, 127.5, 124.8, 124.6, 124.0, 116.9, 63.8, 45.7, 21.5; IR (Neat Film, NaCl) 3033, 2952, 2921, 2860, 1651, 1604, 1486, 1439, 1251, 964, 778 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{10}H_{12}$ [M–Cl$^-$]+: 131.0861, found 131.0858.



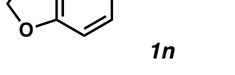
1i

(*E*)-1-(3-chloroprop-1-en-1-yl)-4-fluorobenzene (1i):): 1-(4-fluorophenyl)prop-2-en-1-ol (750 mg, 4.92 mmol, 1.0 equiv) was dissolved in methylene chloride (6 mL, 0.5 M). Then, thionyl chloride (428 μL, 5.9 mmol, 1.2 equiv) was added dropwise. The reaction was allowed to stir for 2 h at 0 °C, then quenched with saturated aqueous $NaHCO_3$ solution (6 mL) and allowed to warm to room temperature. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. The crude oil was then re-suspended in hexanes (10 mL) and washed with water 4 times. The hexanes layer was then dried with Na_2SO_4 and concentrated by rotary evaporator. The crude product was purified by column chromatography (100% hexanes) to afford the desired allylic chloride **1g** as a white solid (420 mg, 2.46 mmol, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 2H), 7.12 – 6.95 (m, 2H), 6.62 (dt, *J* = 15.6, 1.2 Hz, 1H), 6.24 (dtd, *J* = 15.6, 7.2, 0.6 Hz, 1H), 4.23 (dd, *J* = 7.2, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 161.6, 133.1, 132.2, 128.4, 124.8, 115.9, 115.7, 45.5;

^{19}F NMR (282 MHz, $CDCl_3$) δ –113.30; IR (Neat Film, NaCl) 3043, 2361, 1602, 1508, 1300, 1234, 1158, 966, 814 cm^{-1}; HRMS (MM) *m/z* calc'd for C_9H_8ClF $[M]^+$: 170.0299, found 170.0299

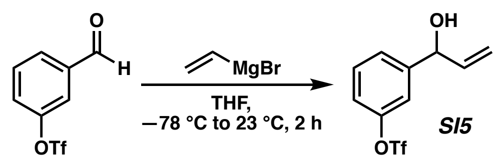


(*E*)-3-(2,3-dihydrobenzofuran-5-yl)prop-2-en-1-ol (SI4): To a solution of ethyl (*E*)-3-(2,3-dihydrobenzofuran-5-yl)acrylate (2.40 g, 11.0 mmol, 1.0 equiv) in anhydrous DCM (37 mL, 0.3 M) under nitrogen atmosphere at -78° C was dropwise added neat DIBAL-H (4.37 mL, 24.2 mmol, 2.20 equiv). The reaction was then allowed to warm to room temperature and stirring was continued for 12 hours. Upon completion, the reaction was cooled to 0° C and EtOAc (10 mL) was slowly added. The reaction was then diluted with Et_2O and a saturated aqueous solution of Rochelle's salt (*ca.* 150 mL) was added. Stirring was continued at room temperature for 1 hour. The biphasic mixture was then extracted with EtOAc (3x). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and solvent was removed in vacuo to yield the crude product as a colorless solid (1.66 g, 9.42 mmol, 86% yield). The crude alcohol was isolated in good purity and used directly in the next step. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.13 (dd, J = 8.2, 1.4 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.8, 6.0 Hz, 1H), 4.58 (t, J = 8.7 Hz, 2H), 4.29 (dd, J = 6.0, 1.4 Hz, 2H), 3.20 (t, J = 8.7 Hz, 2H), 1.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 131.6, 129.6, 127.6, 127.1, 125.7, 122.9, 109.4, 71.6, 64.2, 29.7; IR (Neat Film, NaCl) 3291, 2914, 2889, 2861, 1610, 1490, 1243, 1218, 1106, 1086, 970; HRMS (MM) *m/z* calc'd for $C_{11}H_{11}O$ $[M–OH^-]^+$: 159.0804, found 159.0804.



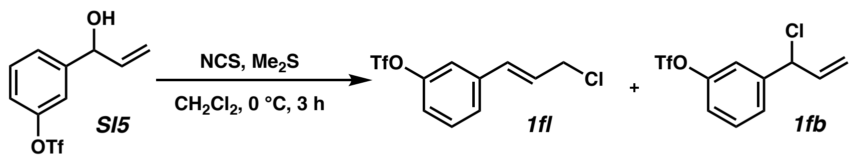
1n

(*E*)-5-(3-chloroprop-1-en-1-yl)-2,3-dihydrobenzofuran (1n): To a solution of (*E*)-3-(2,3-dihydrobenzofuran-5-yl)prop-2-en-1-ol (600 mg, 3.40 mmol, 1.0 equiv) in anhydrous Et_2O (4.3 mL, 1 M) at 0° C under a nitrogen atmosphere was added thionyl chloride (0.30 mL, 4.1 mmol, 1.2 equiv). Stirring was continued at 0° C for 12 hours. The reaction was then diluted with Et_2O and washed with saturated aqueous $NaHCO_3$, followed by brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and solvent was removed in vacuo to yield the crude product as a tan amorphous solid (350 mg, 1.80 mmol, 53% yield). The crude allyl chloride was stored cold under nitrogen and used directly in the next reaction, as it was unstable to silica and neutral alumina. (50 mg, 0.26 mmol, 51% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26 (d, J = 1.3 Hz, 1H), 7.10 (d, J = 10.0 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 6.56 (d, J = 15.6 Hz, 1H), 6.19 – 6.07 (m, 1H), 4.53 (t, J = 8.7 Hz, 3H), 4.21 (d, J = 7.4 Hz, 2H), 3.16 (t, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 134.4, 128.8, 127.7, 127.5, 123.1, 122.1, 109.4, 71.6, 46.2, 29.7; IR (Neat Film, NaCl) 2960, 2894, 1646, 1611, 1492, 1440, 1246, 1102, 982, 808 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{11}H_{12}ClO$ [M+H]$^+$: 195.0571, found 195.0571.

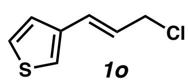


3-(1-hydroxyallyl)phenyl trifluoromethanesulfonate (SI5): To a solution of 3-formylphenyl trifluoromethanesulfonate(635 mg, 2.5 mmol, 1.0 equiv) in THF (6.6 mL, 0.38 M) at –78°C was added vinylmagnesium bromide (2.53 mL, 2.53 mmol, 1M solution in THF) slowly. The reaction was allowed to stir for 4 h at –78 °C, then quenched with saturated aqueous NH_4Cl solution (6 mL) and allowed to warm to room temperature. The aqueous layer was extracted with methylene chloride three times, and the resulting organic layers were dried over Na_2SO_4 and concentrated. The crude allylic alcohol was purified by column chromatography to afford a yellow oil (542 mg, 1.92 mmol, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.25 (s, 1H), 7.15 – 7.10 (m, 1H), 6.03 – 5.81 (m, 1H), 5.31 (d, J = 18.3 Hz, 1H), 5.19 (d, J = 11.2 Hz, 2H), 2.00 (d, J = 3.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 145.7, 139.5, 130.4, 126.3, 123.7 – 114.1 (q, J = 320.7 Hz), 120.5, 119.3, 116.7, 114.1, 74.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ –72.93; IR (Neat Film, NaCl) 3573, 3358, 3087, 2878, 1614, 1583, 1485, 1425, 1249, 1208, 1141, 1035, 990, 960, 912, 841, 96, 775, 753, 696, 657, 666 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{10}H_8F_3O_3S$ [M–OH$^-$]$^+$: 265.0141, found 265.0146.

General Procedure 4: Synthesis of Allylic Chlorides **1f**, **1n**, and **1o**.



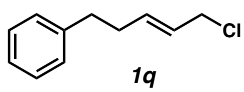
3-(1-chloroallyl)phenyl trifluoromethanesulfonate(1fl) and (*E*)-3-(3-chloroprop-1-en-1-yl)phenyl trifluoromethanesulfonate (1fb): N-chlorosuccinamide (150 mg, 1.125 mmol, 1.5 equiv) was dissolved in dicholoromethane (3.0 mL) and cooled to 0 °C. Dimethylsulfide (103 μL, 1.39 mmol, 1.85 equiv) was added slowly and the resulting suspension was cooled to –10 °C. 3-(1-hydroxyallyl)phenyl trifluoromethanesulfonate (**SI5**, 211mg, 0.75 mmol, 1.0 equiv) in dichloromethane (1.5 mL) was then added slowly. The reaction was warmed to 0 °C and allowed to stir for 3 h. Upon consumption of the starting material, the reaction was quenched with ice-cold water, and extracted with diethyl ether four times. The combined extracts were then rinsed with water and brine, and dried over Na_2SO_4. The resulting crude oil was purified by column chromatography to afford (*E*)-3-(3-chloroprop-1-en-1-yl)phenyl trifluoromethanesulfonate **(1fl)** 3-(1-chloroallyl)phenyl trifluoromethanesulfonate **(1fb)** and in an inseparable mixture (112 mg, 50% yield, **1fl**:**1fb** = 60:40, **1fl** = 86:14 E/Z); ^{1}H NMR (300 MHz, $CDCl_3$) **1fl**: δ 7.50 – 7.12 (m, 4H), 6.12 (ddd, *J* = 17.0, 10.1, 7.1 Hz, 1H), 5.46 (dt, *J* = 7.2, 1.1 Hz, 1H), 5.40 – 5.27 (m, 2H), 4.60 (s, 1H); **1fb:** δ 7.50 –7.12 (m, 4H), 6.66 (dt, *J* = 15.7, 1.2 Hz, 1H), 6.44 – 6.32 (m, 1H), 4.24 (dd, *J* = 7.0, 1.2 Hz, 2H); **1fl** and **1fb:** ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 149.7, 143.0, 138.8, 136.8, 133.7, 132.0, 130.7, 130.6, 128.5, 127.8, 127.5, 126.7, 121.6, 121.4, 120.8, 120.7, 120.4, 119.4, 118.3, 117.3, 61.9, 57.5, 44.8, 44.7, 25.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ –72.86 (m); IR (Neat Film, NaCl) 2916, 2849, 1611, 1576, 1487, 1422, 1247, 1215, 1140, 1120, 962, 908, 886, 847, 787, 680 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{10}H_8ClF_3SO_3$ [M]$^{*+}$: 299.9835, found 299.9846.



1o

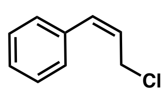
(*E*)-3-(3-chloroprop-1-en-1-yl)thiophene(1o): Synthesized from (*E*)-3-(thiophen-3-yl)prop-2-en-1-ol according to General Procedure 4, and used without further purification

(286 mg, 1.84 mmol, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (ddd, *J* = 5.0, 3.0, 0.6 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.67 (ddq, *J* = 15.6, 1.2, 0.6 Hz, 1H), 6.17 (dt, *J* = 15.5, 7.2 Hz, 1H), 4.22 (dd, *J* = 7.3, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 128.5, 126.5, 125.1, 124.9, 123.6, 45.7; IR (Neat Film, NaCl) 3736, 3103, 2952, 1650, 1417, 1293, 1247, 1150, 1074, 961, 865, 768 cm^{-1}; HRMS (MM) *m/z* calc'd for C_7H_7S $[M–Cl^-]^+$: 123.0268, found 123.0260.



1q

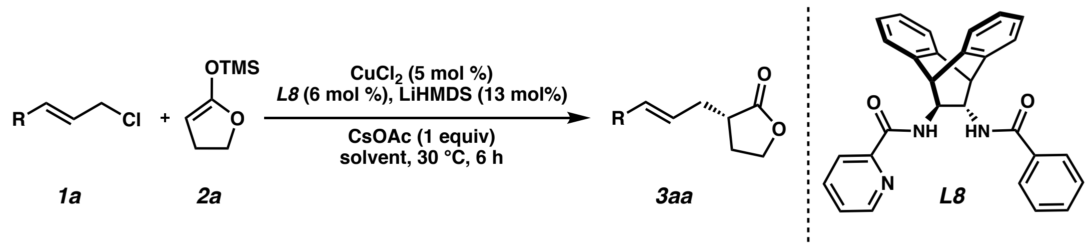
(*E*)-(5-chloropent-3-en-1-yl)benzene (1q): Compound **1q** was prepared from the corresponding allylic alcohol according to a previously reported procedure.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (td, *J* = 7.4, 1.4 Hz, 2H), 7.24 – 7.16 (m, 3H), 5.82 (dtd, *J* = 14.5, 6.6, 1.2 Hz, 1H), 5.66 (dddq, *J* = 15.4, 7.1, 6.2, 1.3 Hz, 1H), 4.04 (dt, *J* = 7.1, 1.0 Hz, 2H), 2.72 (dd, *J* = 8.7, 7.0 Hz, 2H), 2.47 – 2.33 (m, 2H); All characterization data match those reported.[12]



1u

(*Z*)-(3-chloroprop-1-en-1-yl)benzene (1u): Compound **1u** was prepared from the corresponding allylic alcohol according to a previously reported procedure (Z:E=97:3).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 6.67 (d, *J* = 11.4 Hz, 1H), 5.98 – 5.85 (m, 1H), 4.32 – 4.25 (m, 2H); All characterization data match those reported.[17]

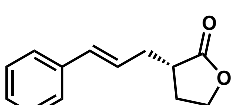
Procedure for Cu-Catalyzed Allylic Alkylation Reactions



n = number of reactions. To a 4 mL vial containing $CuCl_2$ (1.34n mg, 0.01n mmol, 0.05 equiv) in the glovebox was added a solution of the **L8** (5.2n mg, 0.012n mmol, 0.06 equiv) in THF (0.8n mL), followed by a solution of LiHMDS (4.35n mg, 0.026n mmol, 0.13 equiv) in THF (0.8n mL). The resulting solution was stirred for 1 h at room temperature. This solution (1.6 mL) was then transferred to a vial containing CsOAc, followed by silyl ketene acetal **2** (47.5 mg, 0.3 mmol, 1.5 equiv) in THF (1.6 mL). The mixture was allowed to stir for 5 min, then allyl chloride (30.4 mg, 0.2 mmol, 1 equiv) in THF (1.6 mL) was added and the reaction was allowed to stir for 6 h at 30 °C. The reaction was then quenched with sat. NH_4Cl solution and a few drops of TMEDA, and the aqueous layer was extracted five times with ethyl acetate. The combined organic extracts were dried with Na_2SO_4, and concentrated by rotary evaporator. The crude oil was then purified by column chromatography to afford the desired product.

Spectroscopic Data for Products from Catalytic Reactions

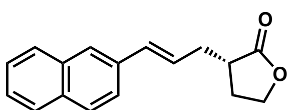
Please note that the absolute configuration was determined only for compound **3ba** *via* x-ray crystallographic analysis. The absolute configuration for all other products has been inferred by analogy.



3a

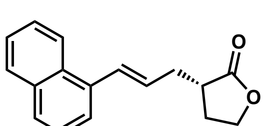
(*S*)-3-cinnamyldihydrofuran-2(3*H*)-one (3a): Product **3a** was purified by column chromatography (25% EtOAc in hexanes) to provide a white solid (36.4 mg,0.18 mmol, 90% yield); 94% *ee*; $[\alpha]_D^{25}$ 46.62 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 –

7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 6.49 (dt, *J* = 15.7, 1.4 Hz, 1H), 6.29 – 6.08 (m, 1H), 4.35 (td, *J* = 8.8, 3.1 Hz, 1H), 4.22 (td, *J* = 9.2, 6.9 Hz, 1H), 2.82 – 2.67 (m, 2H), 2.53 – 2.34 (m, 2H), 2.15 – 2.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 137.0, 133.2, 128.7, 127.6, 126.3, 125.9, 66.8, 39.4, 33.7, 27.9; IR (Neat Film, NaCl) 3057, 3027, 2988, 2936, 2906, 1770, 1480, 1436, 1378, 1314, 1294, 1251, 1208, 1190, 1164, 1074, 1021, 988, 966, 812, 798, 751, 705, 695, 681, 671, 622 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{15}O_2$ $[M+H]^+$: 203.1067, found 203.1064; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 4.70, minor = 5.02.



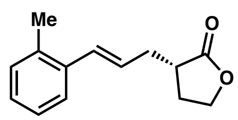
3b

(*S*,*E*)-3-(3-(naphthalen-2-yl)allyl)dihydrofuran-2(3*H*)-one (3b): Product **3b** was purified by column chromatography (25% EtOAc in hexanes) to provide a white solid (43.4 mg, 0.17 mmol, 86% yield); 91% *ee*; $[\alpha]_D^{25}$ 32.53 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 3H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.51 – 7.39 (m, 2H), 6.65 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.30 (dt, *J* = 15.7, 7.1 Hz, 1H), 4.35 (td, *J* = 8.8, 3.0 Hz, 1H), 4.22 (td, *J* = 9.3, 6.8 Hz, 1H), 2.90 – 2.68 (m, 2H), 2.62 – 2.28 (m, 2H), 2.08 (dtd, *J* = 12.7, 9.7, 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 134.5, 133.7, 133.2, 133.0, 128.3, 128.0, 127.8, 126.4, 126.3, 126.0, 125.9, 123.5, 66.7, 39.4, 33.8, 28.0; IR (Neat Film, NaCl) 2905, 1767, 1452, 1374, 1154, 1020, 964, 866, 821, 753, 668 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223, found 253.1232; SFC Conditions: 35% IPA, 3.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 3.63, minor = 3.97.



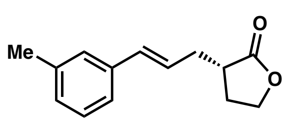
3c

(*S*,*E*)-3-(3-(naphthalen-1-yl)allyl)dihydrofuran-2(3*H*)-one (3c): Product **3c** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless solid (42.4 mg, 0.17 mmol, 84% yield); 91% *ee*; $[\alpha]_D^{25}$ 29.405 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 1H), 7.91 – 7.82 (m, 1H), 7.78 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.59 – 7.39 (m, 4H), 7.22 (s, 1H), 6.19 (dt, J = 15.5, 7.2 Hz, 1H), 4.38 (td, J = 8.8, 3.1 Hz, 1H), 4.24 (td, J = 9.3, 6.9 Hz, 1H), 2.95 – 2.74 (m, 2H), 2.58 (dddd, J = 13.9, 8.4, 7.3, 1.4 Hz, 1H), 2.45 (dddd, J = 12.7, 8.7, 6.9, 3.1 Hz, 1H), 2.14 (dtd, J = 12.7, 9.7, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 134.9, 133.7, 131.1, 130.5, 129.3, 128.7, 128.0, 126.2, 125.9, 125.7, 123.9, 123.8, 66.8, 39.5, 34.1, 28.0; IR (Neat Film, NaCl) 3746, 2909, 2358, 1769, 1508, 1374, 1153, 1023, 969, 777 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223, found 253.1221; SFC Conditions: 25% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): major = 10.39, minor = 11.48.



3d

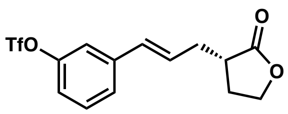
(*S*,*E*)-3-(3-(*o*-tolyl)allyl)dihydrofuran-2(3*H*)-one (3d): Product **3d** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (27.2 mg, 0.13 mmol, 63% yield); 94% *ee*; $[\alpha]_D^{25}$ 26.0 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 7.11 (s, 2H), 6.45 (d, J = 15.7 Hz, 1H), 6.17 – 6.05 (m, 1H), 4.38 – 4.30 (m, 1H), 4.26 – 4.17 (m, 1H), 2.80 – 2.67 (m, 2H), 2.51 – 2.35 (m, 2H), 2.33 (s, 3H), 2.05 (t, J = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1, 130.4, 127.5, 127.3, 126.2, 125.7, 66.7, 39.5, 34.0, 27.9, 20.0; IR (Neat Film, NaCl) 2912, 1767, 1597, 1451, 1373, 1200, 1152, 1021, 966, 863, 821, 748 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1223, found 217.1221; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 5.05, minor = 5.73.



3e

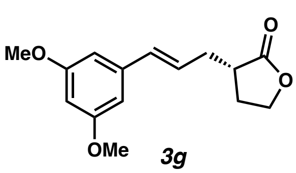
(S,E)-3-(3-(m-tolyl)allyl)dihydrofuran-2(3H)-one (**3e**): Compound **3e** was purified by column chromatography column chromatography (30% EtOAc/hexanes) to afford the title compound as a colorless oil (38.3 mg, 0.18 mmol, 88% yield); 90% *ee*; $[\alpha]_D^{23}$ 31.6 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 3H), 7.05 (d, J = 7.4 Hz, 1H), 6.46 (d, J = 15.7 Hz, 1H), 6.16 (dt, J = 15.8, 7.2 Hz, 1H), 4.34 (td, J = 8.8, 3.1 Hz, 1H), 4.21

(td, J = 9.3, 6.9 Hz, 1H), 2.78 – 2.69 (m, 2H), 2.50 – 2.36 (m, 2H), 2.34 (s, 3H), 2.11 – 2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ179.0, 137.4, 134.3, 133.0, 129.4, 126.2, 124.8, 66.8, 39.5, 33.7, 27.9, 21.3; IR (Neat Film, NaCl) 2911, 1769, 1602, 1486, 1454, 1374, 1152, 1022, 968, 775 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1223, found 217.1227; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): minor = 6.93, major = 5.48.



3f

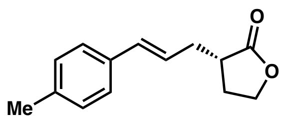
(*S*,*E*)-3-(3-(2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl)phenyl trifluoromethanesulfonate (3f): Product **3f** was purified by column chromatography (25% EtOAc in hexanes) to provide a pale yellow oil (41.8 mg, 0.12 mmol, 60% yield); 88% *ee*; $[\alpha]_D^{25}$ 16.88 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 2H), 7.24 – 7.20 (m, 1H), 7.12 (dt, J = 7.2, 2.3 Hz, 1H), 6.48 (dt, J = 15.8, 1.4 Hz, 1H), 6.25 (dt, J = 15.8, 7.1 Hz, 1H), 4.36 (td, J = 8.9, 2.8 Hz, 1H), 4.23 (td, J = 9.4, 6.8 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.54 – 2.35 (m, 2H), 2.12 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 150.0, 139.8, 131.2, 130.5, 128.9, 126.2, 120.0, 118.9, 118.8 (q, J = 320.7 Hz), 66.7, 39.2, 33.6, 28.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.94; IR (Neat Film, NaCl) 2912, 2356, 1770, 1654, 1609, 1573, 1486, 1421, 1248, 1214, 1141, 1118, 1023, 960, 904, 884, 848, 786, 736, 683, 658, 606 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{14}F_3O_2S$ $[M+H]^+$: 351.0509, found 351.0508; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 254 nm, t_R (min): minor = 6.9, major = 7.2.



3g

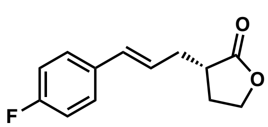
(*S*,*E*)-3-(3-(3,5-dimethoxyphenyl)allyl)dihydrofuran-2(3*H*)-one (3g): Product **3g** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (38.8 mg, 0.15 mmol, 74% yield); 80% *ee*; $[a]_D^{25}$ 30.71 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 1.5 Hz, 2H), 6.92 – 6.85 (m, 1H), 6.49 – 6.38 (m, 1H), 6.14

(dt, J = 15.7, 7.1 Hz, 1H), 4.34 (td, J = 8.8, 3.1 Hz, 1H), 4.21 (td, J = 9.3, 6.9 Hz, 1H), 2.73 (dddd, J = 12.0, 10.4, 6.7, 3.6 Hz, 2H), 2.52 – 2.24 (m, 8H), 2.16 – 2.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 138.2, 136.9, 133.3, 129.4, 129.3, 125.5, 124.2, 66.7, 39.4, 33.7, 27.9; IR (Neat Film, NaCl) 2914, 1768, 1600, 1438, 1374, 1153, 1022, 970, 844, 692 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{15}H_{19}O_4$ [M+H]$^+$: 263.1278, found 263.1268; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 5.50, minor = 6.85.



3h

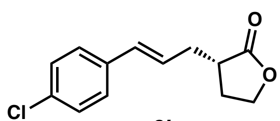
(*S*,*E*)-3-(3-(*p*-tolyl)allyl)dihydrofuran-2(3*H*)-one(3da): Product **3da** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (38.9 mg, 0.18 mmol, 90% yield); 93% *ee*; $[\alpha]_D^{25}$ 38.205 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.49 – 6.42 (m, 1H), 6.11 (dt, J = 15.7, 7.2 Hz, 1H), 4.34 (td, J = 8.8, 3.1 Hz, 1H), 4.21 (td, J = 9.2, 6.9 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.52 – 2.30 (m, 5H), 2.05 (dtd, J = 12.6, 9.6, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 137.4, 134.2, 132.9, 129.4, 126.2, 124.8, 66.7, 39.4, 33.7, 27.9, 21.3; IR (Neat Film, NaCl) 2919, 1770, 1513, 1454, 1373, 1152, 1020, 972, 823, 680 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{17}O_2$ [M+H]$^+$: 217.1223, found 217.1224; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 7.90, minor = 8.41.



3i

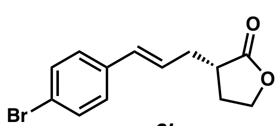
(*S*,*E*)-3-(3-(4-fluorophenyl)allyl)dihydrofuran-2(3*H*)-one (3i): Product **3i** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (37.3 mg, 0.17 mmol, 85% yield); 92% *ee*; $[\alpha]_D^{25}$ –30.42 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.05 – 6.94 (m, 2H), 6.44 (dt, J = 15.8, 1.4 Hz, 1H), 6.08 (dt, J = 15.7, 7.1 Hz, 1H), 4.35 (td, J = 8.8, 3.0 Hz, 1H), 4.22 (td, J = 9.3, 6.9 Hz, 1H), 2.79

– 2.66 (m, 2H), 2.51 – 2.33 (m, 2H), 2.05 (dtd, J = 12.7, 9.6, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 163.5, 161.1, 133.2 (d, J = 3.3 Hz), 131.9, 127.8 (d, J = 8.0 Hz), 126.0 – 125.1 (m), 115.6 (d, J = 21.6 Hz), 66.7, 39.4, 33.6, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.71 (tt, J = 8.5, 5.3 Hz); IR (Neat Film, NaCl) 3734, 2910, 2358, 1769, 1601, 1508, 1456, 1374, 1226, 1157, 1023, 970, 838 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{14}FO_2$ $[M+H]^+$: 219.0972, found 219.0974; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak OD-H column, λ = 280 nm, t_R (min): major = 5.10, minor = 5.57.



3j

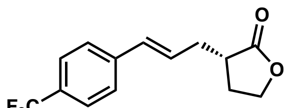
(*S*,*E*)-3-(3-(4-chlorophenyl)allyl)dihydrofuran-2(3*H*)-one (3j): Product **3j** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (44.4 mg, 0.19 mmol, 94% yield); 88% *ee*; $[\alpha]_D^{25}$ 32.55 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.43 (dt, J = 15.7, 1.4 Hz, 1H), 6.14 (dt, J = 15.8, 7.1 Hz, 1H), 4.34 (td, J = 8.8, 3.0 Hz, 1H), 4.21 (td, J = 9.3, 6.8 Hz, 1H), 2.84 – 2.67 (m, 2H), 2.53 – 2.31 (m, 2H), 2.04 (dtd, J = 12.7, 9.7, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 135.5, 133.2, 131.9, 128.8, 127.5, 126.7, 66.7, 39.3, 33.6, 28.0; IR (Neat Film, NaCl) 2910, 1770, 1490, 1454, 1405, 1375, 1326, 1154, 1091, 1023, 970, 830 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{14}ClO_2$ $[M+H]^+$: 237.0667, found 237.0682; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel aOD-H column, λ = 254 nm, t_R (min): major = 5..30, minor = 5.90.



3k

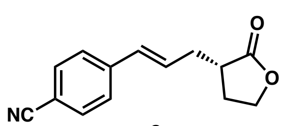
(*S*,*E*)-3-(3-(4-bromophenyl)allyl)dihydrofuran-2(3*H*)-one (3k): Product **3k** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (43.5 mg, 0.154 mmol, 77% yield); 90% *ee*; $[\alpha]_D^{25}$ 13.95 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.24 – 7.17 (m, 2H), 6.42 (dd, J = 15.7, 1.5 Hz, 1H), 6.17 (dt, J = 15.8, 7.1 Hz, 1H), 4.34 (td, J = 8.8, 3.0 Hz, 1H), 4.21 (td, J = 9.3, 6.8 Hz, 1H), 2.85 – 2.62 (m, 2H), 2.53 – 2.30 (m, 2H), 2.04 (dtd, J = 12.7, 9.7, 8.6 Hz, 1H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 178.7, 135.9, 132.0, 131.8, 127.8, 126.8, 121.3, 66.7, 39.3, 33.6, 28.0; IR (Neat Film, NaCl) 2910, 1769, 1487, 1454, 1401, 1375, 1260, 1156, 1072, 1023, 969, 799, 707 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{14}BrO_2$ $[M+H]^+$: 281.0172, found 281.0175; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 6.34, major = 7.18.



3l

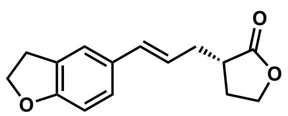
(*S*,*E*)-3-(3-(4-(trifluoromethyl)phenyl)allyl)dihydrofuran-2(3*H*)-one (3l): Product **3l** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (44.9 mg, 0.17 mmol, 83% yield); 90% *ee*; $[\alpha]_D^{25}$ 30.89 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 6.52 (dd, *J* = 15.9, 1.7 Hz, 1H), 6.29 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.36 (td, *J* = 8.8, 2.9 Hz, 1H), 4.22 (td, *J* = 9.4, 6.8 Hz, 1H), 2.84 – 2.68 (m, 2H), 2.56 – 2.34 (m, 2H), 2.05 (dtd, *J* = 12.7, 9.8, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 140.4, 131.8, 129.3 (q, *J* = 32.3 Hz), 126.4, 125.5 (q, *J* = 3.8 Hz), 122.9, 66.7, 39.2, 33.7, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.50; IR (Neat Film, NaCl) 2914, ,1770, 1614, 1414, 1376, 1326, 1157, 1119, 1067, 1018, 970, 834, 682 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{14}F_3O_2$ $[M+H]^+$: 271.0940, found 271.0945; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): major= 5.32, major = 5.86.



3m

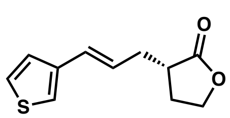
(*S*,*E*)-4-(3-(2-oxotetrahydrofuran-3-yl)prop-1-en-1-yl)benzonitrile (3m): Product **3m** was purified by column chromatography (40% EtOAc in hexanes) to provide a colorless oil (43.6 mg, 0.19 mmol, 96% yield, 98:2 E:Z); 86% *ee*; $[\alpha]_D^{25}$ 48.79 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.46 – 7.39 (m, 2H), 6.50 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.33 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.40 – 4.31 (m, 1H), 4.22 (td, *J* = 9.4, 6.7 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.56 – 2.35 (m, 2H), 2.13 – 1.96 (m, 1H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 178.5, 141.4, 132.5, 131.6, 130.2, 126.8, 119.0, 110.8, 66.7, 39.2, 33.7, 28.1; IR (Neat Film, NaCl) 3432, 2924, 2224, 1766, 1604, 1375, 1156, 1021, 970, 837 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{14}NO_2$ $[M+H]^+$: 228.1019, found 228.1020; SFC Conditions: 25% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 280 nm, t_R (min): major = 4.19, minor = 4.46.



3n

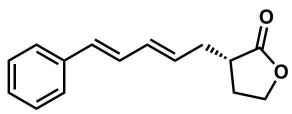
(S,E)-3-(3-(2,3-dihydrobenzofuran-5-yl)allyl)dihydrofuran-2(3H)-one (3n): Compound **3n** was purified by flash column chromatography (40% EtOAc/hexanes) to afford the title compound as a colorless amorphous solid (27.6 mg, 0.11 mmol, 56% yield); 95% *ee*; $[\alpha]_D^{23}$ 35.0 (c 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.08 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 5.98 (dt, *J* = 15.7, 7.2 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 2H), 4.33 (td, *J* = 8.8, 3.2 Hz, 1H), 4.21 (td, *J* = 9.2, 6.9 Hz, 1H), 3.19 (t, *J* = 8.6 Hz, 2H), 2.75 – 2.67 (m, 2H), 2.47 – 2.41 (m, 2H), 2.39 – 2.33 (m, 2H), 2.05 (dtd, *J* = 12.9, 9.5, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 159.9, 132.9, 129.9, 127.6, 126.7, 122.9, 122.5, 109.3, 71.5, 66.8, 39.5, 33.7, 29.7, 27.8; IR (Neat Film, NaCl) 2912, 1764, 1608, 1491, 1374, 1244, 1150, 1022, 980 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.1172, found 245.1171; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 6.93, major = 6.05.



3o

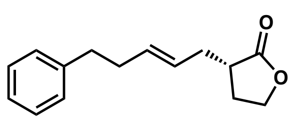
(*S*,*E*)-3-(3-(thiophen-3-yl)allyl)dihydrofuran-2(3*H*)-one (3o): Product **3o** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (29.6 mg, 0.142 mmol, 71% yield); 90% *ee*; $[\alpha]_D^{25}$ 45.11 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.18 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.10 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.49 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.09 – 5.91 (m, 1H), 4.43 – 4.28 (m, 1H), 4.25 – 4.16 (m, 1H), 2.77 – 2.63 (m, 2H), 2.49 – 2.32 (m, 2H), 2.14 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$)

δ 178.9, 139.7, 127.4, 126.2, 125.8, 125.0, 121.7, 66.7, 39.4, 33.6, 27.9; IR (Neat Film, NaCl) 3098, 2994, 2909, 1766, 1482, 1454, 1374, 1201, 1183, 1151, 1094, 1022, 967, 862, 832, 772, 696, 673, 616 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{11}H_{13}O_2S$ $[M+H]^+$: 209.0631, found 209.0637; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 4.76, major = 5.32.



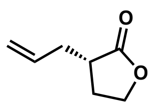
3p

(*S*)-3-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)dihydrofuran-2(3*H*)-one (3p): Product **3p** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (34.7 mg, 0.152 mmol, 76% yield); 83% *ee*; $[\alpha]_D^{25}$ 34.815 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.31 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.25 – 7.19 (m, 1H), 6.75 (ddd, *J* = 15.7, 10.4, 0.8 Hz, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.30 (ddq, *J* = 15.2, 10.4, 1.1 Hz, 1H), 5.85 – 5.69 (m, 1H), 4.35 (td, *J* = 8.8, 3.1 Hz, 1H), 4.21 (td, *J* = 9.3, 6.9 Hz, 1H), 2.75 – 2.62 (m, 2H), 2.44 – 2.33 (m, 2H), 2.03 (dtd, *J* = 12.8, 9.6, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 137.3, 133.7, 131.8, 130.2, 128.7, 128.5, 127.6, 126.4, 66.7, 39.4, 33.5, 28.0; IR (Neat Film, NaCl) 3748, 3671, 3022, 2910, 2358, 1769, 1684, 1652, 1595, 1558, 1540, 1506, 1489, 1448, 1374, 1309, 1157, 1023, 992, 749, 693, 668, 625 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{15}H_{17}O_2$ $[M+H]^+$: 229.1223, found 2229.1227; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 280 nm, t_R (min): major = 7.08, major = 7.73.

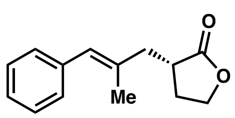


3q

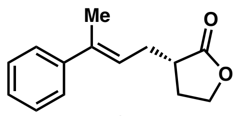
(*S*,*E*)-3-(5-phenylpent-2-en-1-yl)dihydrofuran-2(3*H*)-one (3q): Product **3q** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (44.4 mg, 0.19 mmol, 96% yield); 87% *ee*; $[\alpha]_D^{25}$ 20.90 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.55 (dtt, *J* = 14.8, 6.7, 1.3 Hz, 1H), 5.36 (dtt, *J* = 15.3, 6.9, 1.4 Hz, 1H), 4.24 (td, *J* = 8.8, 3.3 Hz, 1H), 4.15 (td, *J* = 9.1, 6.9 Hz, 1H), 2.68 (dd, *J* = 8.4, 6.9 Hz, 2H), 2.62 – 2.44 (m, 2H), 2.42 – 2.29 (m, 2H), 2.28 – 2.14 (m, 2H), 1.87 (dtd, J = 12.8, 9.5, 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 141.8, 133.1, 128.6, 128.4, 126.6, 125.9, 66.7, 39.3, 35.8, 34.3, 33.2, 27.6; IR (Neat Film, NaCl) 3520, 2918, 1770, 1602, 1496, 1454, 1374, 1297, 1251, 1209, 1171, 1149, 1084, 1024, 972, 906, 843, 748, 701, 666 cm^{-1}; HRMS (MM) m/z calc'd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1384, found 231.1384; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 5.84, major = 6.29.


3r

(*S*)-3-allyldihydrofuran-2(3*H*)-one (3r): Product **3r** was synthesized according to the General Procedure 4, but with a doubled catalyst loading (10 mol% $CuCl_2$, 12 mol% ***L8***, 26 mol% LiHMDS). The crude product was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (24.2 mg, 96% yield, 80% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (ddt, J = 16.9, 10.1, 6.9 Hz, 1H), 5.20 – 5.05 (m, 2H), 4.38 – 4.28 (m, 1H), 4.20 (td, J = 9.2, 6.9 Hz, 1H), 2.71 – 2.53 (m, 2H), 2.43 – 2.18 (m, 2H), 2.08 – 1.91 (m, 1H). All characterization data match those reported.[18] The purified product was converted to the corresponding methyl acrylate species via cross metathesis for SFC analysis (see Product Transformations).

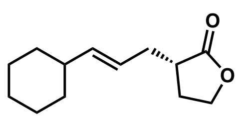

3s

(*S*,*E*)-3-(2-methyl-3-phenylallyl)dihydrofuran-2(3*H*)-one (3s): Product **3s** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (37.6 mg, 0.17 mmol, 87% yield); 89% *ee*; $[\alpha]_D^{25}$ 57.81 (c 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.26 – 7.17 (m, 3H), 6.34 (s, 1H), 4.38 (td, J = 8.8, 3.2 Hz, 1H), 4.24 (td, J = 9.2, 6.9 Hz, 1H), 2.91 – 2.74 (m, 2H), 2.38 (dddd, J = 12.8, 8.5, 6.9, 3.3 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.13 – 1.96 (m, 1H), 1.89 (d, J = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 179.10, 137.8, 135.4, 128.9, 128.3, 127.6, 126.5, 66.7, 41.5, 38.1, 28.4, 17.6; IR (Neat Film, NaCl) 2912, 1768, 1490, 1442, 1373, 1205, 1178, 1149, 1022, 958, 920, 746, 700, 668 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1223, found 217.1224; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): minor = 4.57, major = 5.37.



3t

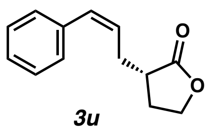
(*E*)-3-(3-phenylbut-2-en-1-yl)dihydrofuran-2(3*H*)-one (3t): Product **3t** was purified by column chromatography (20% EtOAc in hexanes) to provide a colorless oil (28.1 mg, 0.13 mmol, 65% yield, 20:1 E:Z); 5% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 7.26 (m, 1H), 5.73 (tq, *J* = 7.5, 1.5 Hz, 1H), 4.36 (td, *J* = 8.8, 3.0 Hz, 1H), 4.21 (td, *J* = 9.3, 6.8 Hz, 1H), 2.83 – 2.65 (m, 2H), 2.52 – 2.33 (m, 2H), 2.13 – 1.95 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 143.5, 138.0, 128.4, 127.2, 125.8, 123.6, 66.7, 39.6, 29.3, 28.2, 16.3; IR (Neat Film, NaCl)2922, 2855, 1760, 1597, 1494, 1456, 1374, 1311, 1203, 1182, 1149, 1068, 1022, 960, 760, 696, 676, 666; HRMS (MM) *m/z* calc'd for $C_{15}H_{17}O_2$ $[M+H]^+$: 217.1223, found 217.1223; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 5.09, major = 5.54.



3v

(*S*,*E*)-3-(3-cyclohexylallyl)dihydrofuran-2(3*H*)-one (3v): Product **3v** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (37.3 mg, 0.18 mmol, 90% yield); 87% *ee*; $[\alpha]_D^{25}$ 16.32 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (dd, *J* = 15.4, 6.7 Hz, 1H), 5.37 – 5.26 (m, 1H), 4.30 (td, *J* = 8.8, 3.5 Hz, 1H), 4.19 (td, *J* = 9.1, 7.0 Hz, 1H), 2.59 (qd, *J* = 9.0, 4.4 Hz, 1H), 2.50 (ddd, *J* = 14.2, 6.8, 4.5 Hz, 1H), 2.32 (dddd, *J* = 12.5, 8.9, 7.0, 3.5 Hz, 1H), 2.20 (dt, *J* = 14.8, 7.8 Hz, 1H), 2.05 – 1.86 (m, 2H), 1.67 (dddt, *J* = 19.5, 15.5, 8.6, 4.0 Hz, 5H), 1.31 – 0.96 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ, 179.2, 140.3, 123.0, 66.8, 40.8, 39.4, 33.4, 33.2, 27.7, 26.3, 26.1; IR (Neat Film, NaCl) 2923, 2850, 1773, 1483, 1448, 1375, 1300, 1258, 1202, 1180, 1157, 1024, 971, 894, 706, 663 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1536, found

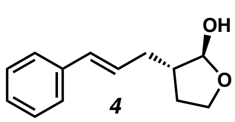
209.1537; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 3.32, minor = 3.53.



3u

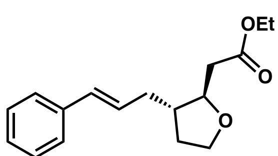
(*S*,*Z*)-3-(3-phenylallyl)dihydrofuran-2(3*H*)-one (3u): Product **3u** was purified by column chromatography (25% EtOAc in hexanes) to provide a colorless oil (34.0 mg, 0.17 mmol, 84% yield); 73% *ee*; $[\alpha]_D^{25}$ 53.19 (*c* 0.80, $CHCl_3$); **Z isomer** (for E isomer, see data for **3a**): ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 2H), 7.26 (m, 3H), 6.59 (dt, *J* = 11.7, 1.9 Hz, 1H), 5.64 (dt, *J* = 11.5, 7.2 Hz, 1H), 4.31 (td, *J* = 8.8, 3.0 Hz, 1H), 4.19 (td, *J* = 9.3, 6.8 Hz, 1H), 2.90 (dddd, *J* = 15.0, 6.8, 4.5, 1.9 Hz, 1H), 2.68 (dtd, *J* = 9.9, 8.7, 4.4 Hz, 1H), 2.57 (dddd, *J* = 14.9, 9.0, 7.3, 1.7 Hz, 1H), 2.37 (dddd, *J* = 12.8, 8.7, 6.8, 2.9 Hz, 1H), 1.94 (dtd, *J* = 12.8, 9.8, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 137.0, 131.9, 128.8, 128.5, 128.1, 127.1, 66.7, 39.6, 29.0, 28.2; IR (Neat Film, NaCl) 3016, 2912, 1766, 1598, 1494, 1448, 1374, 1308, 1208, 1150, 1074, 1023, 967, 768, 702 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{15}O_2$ $[M+H]^+$: 203.1067, found 203.1062; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 3.06, minor= 3.43.

Procedures and Spectroscopic Data for Product Transformations



4

(2*S*,3*S*)-3-cinnamyltetrahydrofuran-2-ol (4): Adapted from a previously reported procedure.[19] To a solution of lactone (12.4 mg, 0.061 mmol, 1.0 equiv) in dichloromethane (0.4 mL) at –78 °C was added diisobutylaluminium hydride (12μL, 0.067 mmol, 1.1 equiv) in dichloromethane (2.2 mL) dropwise. The reaction was allowed to stir for 30 min at –78 °C. The reaction was quenched slowly with MeOH, and then saturated aqueous potassium tartrate solution was added and the reaction was allowed to warm to room temperature. After 2 h, the layers were separated, and the aqueous layer was extracted 3 times with diethyl ether. The organic layers were combined, washed with brine, dried over sodium sulfate, and concentrated. The crude product was purified by column chromatography to afford product **4** as a white solid (11.9 mg, 0.058 mmol, 95 % yield, 68:32 anti:syn); $[\alpha]_D^{25}$ 4.20 (*c* 0.75, $CHCl_3$); **major, anti:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 4H), 7.17 – 7.11 (m, 1H), 6.39 – 6.33 (m, 1H), 6.15 – 6.07 (m, 1H), 5.19 (d, *J* = 1.5 Hz, 1H), 4.00 (td, *J* = 8.0, 6.6 Hz, 1H), 3.91 (td, *J* = 8.1, 5.5 Hz, 1H), 2.45 (dtd, *J* = 14.2, 7.1, 1.4 Hz, 1H), 2.34 – 2.18 (m, 3H), 2.18 – 2.06 (m, 1H), 1.65 – 1.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 131.8, 128.67, 128.66, 127.3, 126.2, 102.7, 67.1, 46.1, 35.8, 29.7. **minor, syn:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 4H), 7.17 – 7.11 (m, 1H), 6.43 – 6.38 (m, 1H), 6.24 – 6.16 (m, 1H), 5.30 (d, *J* = 4.4 Hz, 1H), 4.06 (ddd, *J* = 9.3, 8.2, 2.7 Hz, 1H), 3.78 (ddd, *J* = 9.4, 8.2, 7.3 Hz, 1H), 2.45 (dtd, *J* = 14.2, 7.1, 1.4 Hz, 1H), 2.18 – 2.06 (m, 1H), 1.98 (dtd, *J* = 12.0, 7.5, 2.7 Hz, 1H), 1.76 (tt, *J* = 11.8, 9.2 Hz, 1H), 1.64 – 1.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 131.1, 128.7, 128.1, 127.2, 126.1, 98.4, 67.4, 44.7, 32.2, 28.8. **major, anti** and **minor, syn**: IR (Neat Film, NaCl) 3390, 3024, 2936, 2892, 1598, 1494, 1500, 1266, 1119, 1015, 967, 912, 744, 694 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{15}O$ $[M\text{-}OH^-]^+$: 187.1117, found 187.1119.

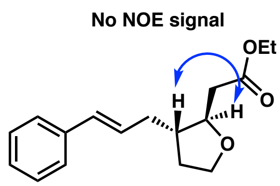


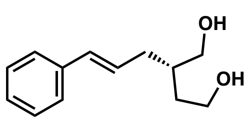
5

ethyl 2-((2*R*,3*S*)-3-cinnamyltetrahydrofuran-2-yl)acetate (5): In a flame-dried round bottom flask under argon was added NaH (3.5 mg, 0.0874 mmol, 1.5 equiv) and THF (0.3 mL). To the resulting suspension was added triethyl phosphonoacetate (17.3μL, 0.0874 mmol, 1.5 equiv) slowly. After 30 min, the reaction was cooled to 0 °C and lactol **4** (11.9 mg, 0.058 mmol, 1.0 equiv) in THF (0.6 mL) was added slowly. The reaction was allowed to warm to room temperature overnight. The reaction was subsequently quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate three times. The organic layers were then combined, dried over Na_2SO_4, and concentrated. The crude oil was purified by column chromatography to afford product **5** (13.4 mg, 0.049 mmol, 84% yield, 95:5 anti:syn); 93% ee; $[\alpha]_D^{25}$ 18.74 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38

– 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 6.47 – 6.39 (m, 1H), 6.18 (dt, J = 15.8, 7.2 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.99 (ddd, J = 7.9, 6.6, 4.8 Hz, 1H), 3.92 – 3.81 (m, 2H), 2.64 – 2.46 (m, 2H), 2.40 (dddd, J = 14.1, 7.1, 5.7, 1.4 Hz, 1H), 2.25 (dddd, J = 14.0, 8.4, 7.1, 1.4 Hz, 1H), 2.18 – 1.97 (m, 2H), 1.76 – 1.64 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 137.5, 131.7, 128.7, 128.2, 127.3, 126.1, 80.3, 67.3, 60.7, 44.4, 40.2, 36.3, 32.1, 14.3; IR (Neat Film, NaCl) 3058, 3024, 2978, 2936, 2873, 1736, 1598, 1478, 1495, 1449, 1368, 1302, 1261, 1204, 1158, 1070, 1032, 967, 843, 805, 746, 694, 670, 652 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{17}H_{23}O_3$ $[M+H]^+$: 275.1642, found 275.1649. Please note that the NMR data listed is for the major diastereomer. SFC Conditions: 15% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 254 nm, t_R (min): minor= 3.07, major= 3.39.

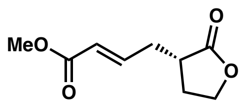
Stereochemical Assignment:





6

(*S*)-2-cinnamylbutane-1,4-diol (6): Product 6 was synthesized according to a slightly modified, previously reported procedure.[20] To a suspension of lithium aluminum hydride (3.57 mg, 0.094 mmol, 1.0 equiv) in diethyl ether (0.5 mL) was added a solution of lactone **3a** (19.0 mg, 0.094 mmol, 1.0 equiv) in diethyl ether (0.4 mL), maintaining reflux. Then, the reaction was heated to 40 °C and refluxed for 3 h. The reaction was then quenched by sequentially adding methanol, water, and 2M HCl. Then, brine was added and the aqueous layer was extracted five times with ethyl acetate. The crude diol was then purified by column chromatography to afford the desired product **6** as a clear oil (18.4 mg, 0.089 mmol, 95% yield); 94% ee $[a]_D^{25}$ –10.61 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 6.46 – 6.34 (m, 1H), 6.18 (dt, J = 15.8, 7.3 Hz, 1H), 3.78 (ddd, J = 10.8, 6.4, 4.5 Hz, 1H), 3.72 – 3.44 (m, 5H), 2.31 – 2.13 (m, 2H), 1.90 – 1.68 (m, 2H), 1.60 (dtd, J = 14.5, 8.0, 4.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 131.9, 128.6, 127.2, 126.1, 66.0, 61.1, 39.7, 35.6; IR (Neat Film, NaCl) 3322, 3080, 3058, 3024, 2921, 1754, 1598, 1494, 1448, 1053, 967, 742, 694, 661 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1380, found 207.1383. SFC Conditions: 25% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): minor = 3.64, major= 4.04.

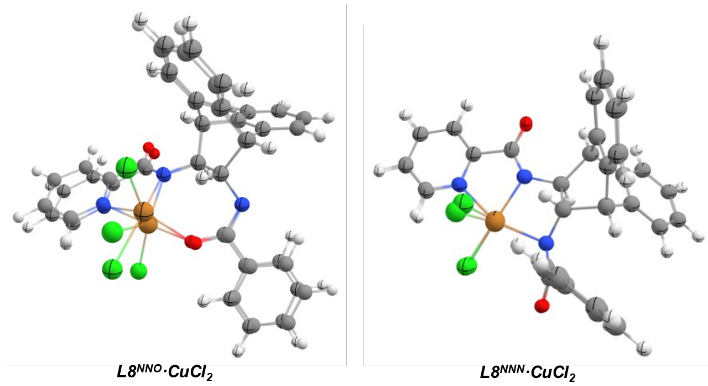


7

methyl (*S*,*E*)-4-(2-oxotetrahydrofuran-3-yl)but-2-enoate (7): Adapted from a previously reported procedure.[21] To a solution of lactone **3r** (12.1 mg, 0.096 mmol, 1.0 equiv) and methyl acrylate (86 uL, 0.96 mmol, 1.0 equiv) in dichloromethane (0.7 mL) was added Grubbs II catalyst (4.8 mg, 0.00576 mmol, 6 mol%). The reaction was sealed and heated to 40 °C for 3 h. The crude reaction mixture was filtered with a small pad of SiO_2, and concentrated. The resulting crude oil was then purified by column chromatography to afford product **7** as a yellow oil (16.8 mg, 0.091 mmol, 95% yield); 80% ee $[\alpha]_D^{25}$ 19.52 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 (dt, *J* = 15.4, 7.2 Hz, 1H), 5.93 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.37 (td, *J* = 8.9, 2.5 Hz, 1H), 4.28 – 4.17 (m, 1H), 3.74 (s, 3H), 2.85 – 2.66 (m, 2H), 2.46 – 2.34 (m, 2H), 2.06 – 1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 166.5, 144.6, 123.8, 77.2, 66.6, 51.8, 38.5, 32.9, 28.3; IR (Neat Film, NaCl) 2954, 1764, 1719, 1656, 1438, 1376, 1277, 1155, 1022, 988, 702 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{19}H_{12}O_4^+$ $[M+H]^+$: 185.0808, found 185.0812. SFC Conditions: 25% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 9.17, minor= 10.89.

Supporting Computational Results

To understand how variations in the optimized geometry affected single point energy calculations, we re-optimized the B3(38HF)LYP-optimized geometry (**geometry B**) with the B3(0HF)LYP density functional. The resulting structures (**geometry A**) show increased deviation from a trigonal bipyramidal geometry (τ_5 = 1) towards square pyramidal geometry (τ_5 = 0) (Figure S1 and Table S1).



L8^NNO·CuCl_2　　　　*L8^NNN·CuCl_2*

Figure S1. Hartree-Fock dependence on **L8^{NNO}•CuCl$_2$** (left) versus **L8^{NNN}•CuCl$_2$** (right) geometry. Geometry A (grid): B3(0HF)LYP optimized geometry; Geometry B (filled): B3(38HF)LYP optimized geometry

Table S1. Effects of Levels of Theory on the Optimized Geometry of **L8•CuCl$_2$**.

L8^{NNO}·CuCl$_2$	geometry A	geometry B
bond lengths (Å)		
Cu-N1	2.16	2.07
Cu-N2	2.06	2.16
Cu-O	2.10	1.95
Cu-Cl1	2.39	2.48
Cu-Cl2	2.37	2.54
bond angles (°)		
N1-Cu-N2	78	77
N1-Cu-O	125	174
N1-Cu-Cl1	108	89
N1-Cu-Cl2	90	86
N2-Cu-O	90	99
N2-Cu-Cl1	96	122
N2-Cu-Cl2	165	120
O-Cu-Cl1	127	97
O-Cu-Cl2	89	92
Cl1-Cu-Cl2	97	114
τ_5	0.64	0.86

L8^{NNN}·CuCl$_2$	geometry A	geometry B
bond lengths (Å)		
Cu-N1	2.10	2.20
Cu-N2	2.03	2.05
Cu-N3	2.17	2.15
Cu-Cl1	2.62	2.62
Cu-Cl2	2.31	2.36
bond angles (°)		
N1-Cu-N2	77	75
N1-Cu-N3	160	158
N1-Cu-Cl1	88	87
N1-Cu-Cl2	92	89
N2-Cu-N3	83	83
N2-Cu-Cl1	99	103
N2-Cu-Cl2	151	143
N3-Cu-Cl1	96	98
N3-Cu-Cl2	105	108
Cl1-Cu-Cl2	108	109
τ_5	0.15	0.24

Table S2. Effects of Levels of Theory on the Energy Barrier.

entry	density functional	geometry	solvent correction	E_{NNO} (Hartree)	E_{NNN} (Hartree)	ΔE (Hartree)	ΔE (kcal/mol)
1	B3(0HF)LYP	Geometry A	none	-3987.8133	-3987.7866	0.0267	16.8
2	B3(38HF)LYP	Geometry A	none	-3997.8498	-3997.8189	0.0309	19.4
3	BP86	Geometry B	none	-3994.4699	-3994.4422	0.0277	17.4
4	TPSSh	Geometry B	none	-3994.2266	-3994.1974	0.0292	18.3
5	B3LYP	Geometry B	none	-3993.0735	-3993.0411	0.0324	20.3
6	B3(0HF)LYP	Geometry B	none	-3987.8063	-3987.7774	0.0289	18.1
7	B3(10HF)LYP	Geometry B	none	-3990.4324	-3990.4018	0.0306	19.2
8	**B3(38HF)LYP**	**Geometry B**	**none**	**-3997.8647**	**-3997.8289**	**0.0358**	**22.5**
9	BP86	Geometry B	CPCM	-3994.6932	-3994.6685	0.0247	15.5
10	TPSSh	Geometry B	CPCM	-3994.4522	-3994.4265	0.0257	16.1
11	B3LYP	Geometry B	CPCM	-3993.2977	-3993.2728	0.0249	15.6
12	B3(0HF)LYP	Geometry B	CPCM	-3988.0281	-3988.0059	0.0222	13.9
13	B3(10HF)LYP	Geometry B	CPCM	-3990.6555	-3990.6321	0.0234	14.7
14	**B3(38HF)LYP**	**Geometry B**	**CPCM**	**-3998.0902**	**-3998.0591**	**0.0311**	**19.5**

Using the two optimized structures, we examined the Hartree-Fock dependence on the energy difference between **L8^{NNO}•CuCl$_2$** and **L8^{NNN}•CuCl$_2$** ($\Delta E \equiv E_{NNN} - E_{NNO}$) (Table S2). Despite **L8^{NNO}•CuCl$_2$** exhibiting a modest structural variation between different functionals, the energy difference between NNO vs. NNN coordination between the different geometries remains relatively small (entries 1 and 6, or entries 2 and 8). Additionally, within the same geometry, increasing the amount of Hartree-Fock exchange increases the energy gap between NNO/NNN coordination (entries 1 and 2; entries 3-5, or entries 5-8); this observation is maintained for calculations with solvent correction (entries 9-11, or entries 11-14). Solvent correction also reduces the energy separation between the two coordination modes. As discussed in the manuscript, similar energy differences between **L8**$^{\mathbf{NNO}}$ and **L8**$^{\mathbf{NNN}}$ are observed upon removal of $Cu^{II}Cl_2$, suggesting electronic differences between Cu-O and Cu-N bonding do not play a major role in determining the ligand binding and are likely secondary to steric contributions. Indeed, by comparing both electronic energy and Gibbs free energy, we found steric contributions enforce **L8**$^{\mathbf{NNO}}$ coordination mode for a series of possible copper intermediates (Table S3).

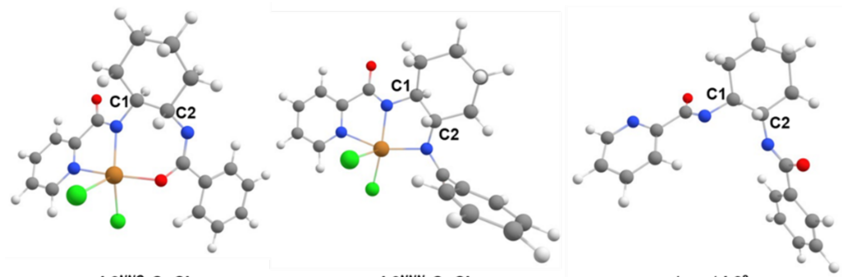
Table S3. Steric Preference for **L8**$^{\mathbf{NNO}}$ Coordination Across Different Possible Intermediates.

entry	geometry	E_{NNO} (Hartree)	E_{NNN} (Hartree)	ΔE (Hartree)	ΔE (kcal/mol)	G_{NNO} (Hartree)	G_{NNN} (Hartree)	ΔG (Hartree)	ΔG (kcal/mol)
without solvent correction									
1	***L8·Cu^{II}Cl$_2$***	**-3997.8647**	**-3997.8289**	**0.0358**	**22.5**	**-3997.4815**	**-3997.4457**	**0.0357**	**22.5**
2	***L8·Cu^{II}Cl***	-3537.3202	-3537.2842	0.0360	22.7	-3536.9324	-3536.8956	0.0368	23.2
3	***L8·Cu^{II}***	-3076.6231	-3076.6029	0.0202	12.7	-3076.2324	-3076.2123	0.0201	12.7
4	***L8·Cu^{I}Cl$_2$***[a]	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
5	***L8·Cu^{I}Cl***	-3537.2750	n.a[b]	n.a	n.a	-3536.8937	n.a	n.a	n.a
6	***L8·Cu^{I}***	**-3076.7185**	**-3076.6810**	**0.0375**	**23.6**	**-3076.3314**	**-3076.2943**	**0.0370**	**23.3**
with solvent correction									
8	***L8·Cu^{II}Cl$_2$***	**-3998.0902**	**-3998.0591**	**0.0311**	**19.5**	**-3997.7070**	**-3997.6759**	**0.0310**	**19.5**
9	***L8·Cu^{II}Cl***	-3537.3972	-3537.3682	0.0290	18.3	-3537.0094	-3536.9796	0.0298	18.8
10	***L8·Cu^{II}***	-3076.6523	-3076.6288	0.0235	14.8	-3076.2616	-3076.2382	0.0234	14.8
11	***L8·Cu^{I}Cl$_2$***[a]	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
12	***L8·Cu^{I}Cl***	-3537.4968	n.a[b]	n.a	n.a	-3537.1155	n.a	n.a	n.a
13	***L8·Cu^{I}***	**-3076.7939**	**-3076.7650**	**0.0289**	**18.2**	**-3076.4068**	**-3076.3783**	**0.0284**	**17.9**

(a) This structure failed to converge; dissociation of chloride was energetically favorable during the optimization cycles (b) The benzamide moiety dissociated in the optimized structure, resulting a T-shaped copper complex with a bidentate **L8** ligand.

The electronic effect of Cu-O vs. Cu-N coordination is hinted at, however, by comparing **L2** and **L8**. Removing $Cu^{II}Cl_2$ from **L8•CuCl$_2$** leads to a reduced energy gap (NNO vs. NNN) in both gas phase and solvent corrected calculations. In contrast, removing $Cu^{II}Cl_2$ from **L2•CuCl$_2$** increases the energy barrier (Table S4). The C-O bond appears to be favored over the C-N bond for **L8•CuCl$_2$** in THF, but the opposite holds true for **L2•CuCl$_2$**.

Table S4. DFT Calculation of **L2•CuCl$_2$** complex[a].



entry	ligand binding mode	$E_{gas\ phase}$ (kcal/mol)	$E_{solvent\ corrected}$ (kcal/mol)	τ_4' **C1**	τ_4' **C2**
with $CuCl_2$					
1	***L2***^{NNO}***·CuCl***$_2$	0	0	0.95	0.97
2	***L2***^{NNN}***·CuCl***$_2$	12.9	7.6	0.94	0.94
without $CuCl_2$[b]					
3	relaxed ***L2***$^{2-}$	0	0	0.97	0.97
4	***L2***^{NNO}	20.9	12.7	0.97	0.95
5	***L2***^{NNN}	35.8	24.6	0.94	0.93

(a) Obtained using a B3LYP density functional with 38% Hartree-Fock exchange. (b) Ligand coordination geometry was obtained by removing $CuCl_2$ from the optimized geometry of the corresponding complex.

Spin Quantification Experiment

50.0(2) mg of $CuSO_4•5H_2O$ (0.2 mmol) was added to a 20 mL scintillation vial and dissolved in ca. 3 mL of 20% glycerol 80% water mixture. The solution was then transferred to a 10 mL volumetric flask and diluted accordingly to afford a 20 mM stock solution; calibration standards were then prepared from the stock solution. Briefly, the 1 mM and the 2 mM calibration standard were prepared directly from the stock solution. The remaining standards were prepared by diluting the 1 mM or 2 mM solution once more using volumetric pipettes and volumetric flasks of varying sizes. The error associated with concentration is estimated to be ≤ 2%. Given its relatively small size compared to other sources of error, we have excluded this random error from further consideration and have assumed the concentration to be absolute.

77K X-band EPR spectra were then obtained on a variety of samples with variable Cu^{II} concentrations at 0.5 mW microwave power. A linear baseline correction was performed on the resulting EPR spectra to give a zero baseline. Double integration was performed from 260 to 340 mT. The end point of integration was chosen to minimize any higher-order baseline contribution; we found this results in a 2% definition error to the double integrated intensity of the analyte. Moreover, we collected multiple spectra for a selected number of samples by first removing the sample dewar from the EPR resonator and then collecting a new set of spectra. We estimate instrument variations and the operator errors contribute 3000 to the total integrated intensity. The calibration curve and relevant statistics have been reported in Figure S2.

Three batches of **L8•CuCl$_2$** were prepared independently using Method C and diluted to 2.1 mM in Cu. For ESI-MS (negative ion mode), this solution was further diluted with acetonitrile. HRMS (MM) *m/z* calc'd for $C_{29}H_{22}Cl_2CuN_3O_2$ $[M+H]^-$ = 577.0385, found 577.0364. An aliquot of the sample was loaded into a 4.0 mm standard quartz Norell EPR tube and immediately immersed in liquid nitrogen to avoid sample decomposition. Rapid freezing also ameliorates the adverse effect from the non-glassiness of THF, as we found preparing the complex in the glassy 2-MeTHF solvent led to a yellow solution with a different EPR spectrum (Figure S3). 2 mL of the same solution of each sample was then loaded into a 1 cm borosilicate cuvette to obtain its absorption spectrum. All three samples gave optical spectra similar to that reported herein (Figure S4) and the manuscript, albeit small variations exist. As a result, we estimate a 5% error associated with the concentrations of the analyte (± 0.1 mM).

Three **L8•CuCl$_2$** samples give double integrated intensity of 3.00 $*10^5$, 2.87$*10^5$, and 2.68$*10^5$. The averaged concentration was 1.81 mM with a standard deviation of 0.1 mM. Moreover, combing various sources of error with standard error of regression, standard error of the slope, and the standard error of the intercept resulted in a 6 % error associated with the calibration method described herein. Adding calibration error and the standard deviation in quadrature, we report the average concentration of monomeric, divalent copper in **L8•CuCl$_2$** to be 1.81 (± 0.14) mM.

Additionally, we quantified the amount of monomeric, divalent copper after the addition of 1.5 equivalents of silyl ketene acetal **2** (Figure 2, black dotted line) and found the concentration to be 0.29 (± 0.02) mM.

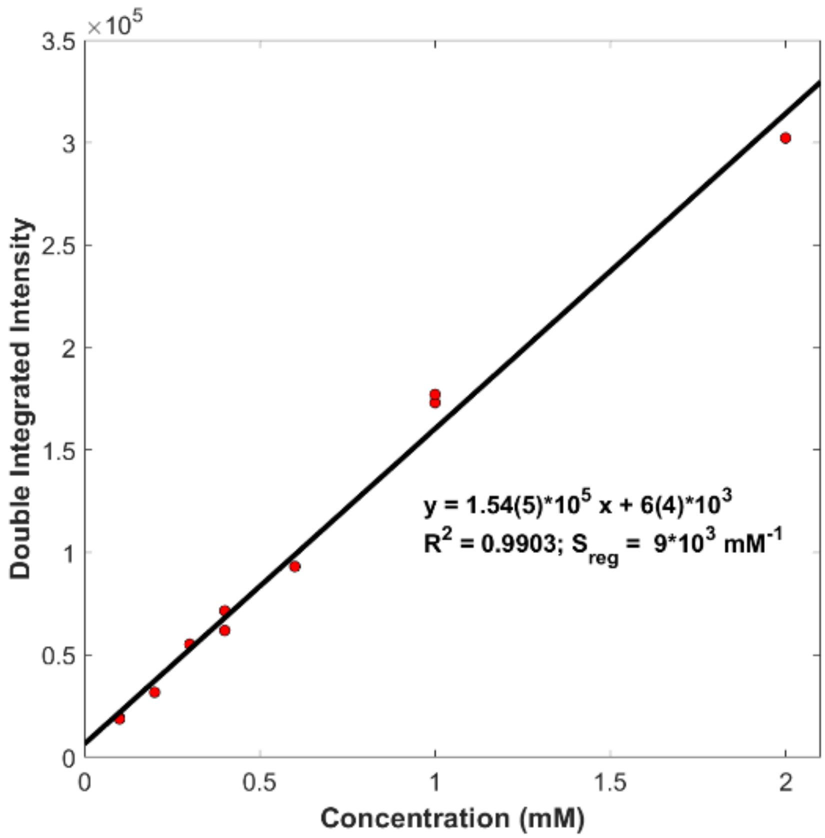


Figure S2. Calibration Curve for Spin Quantification.

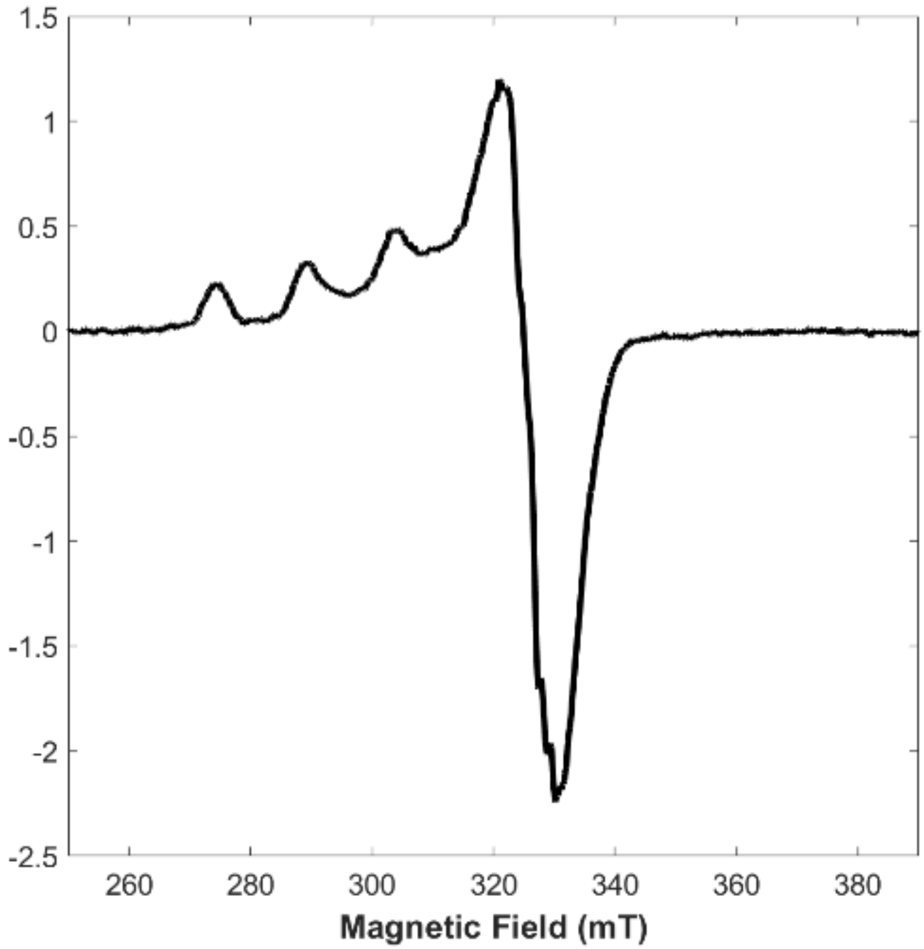


Figure S3. 77 K EPR Spectrum of **L8•$CuCl_2$** in 2-MeTHF.

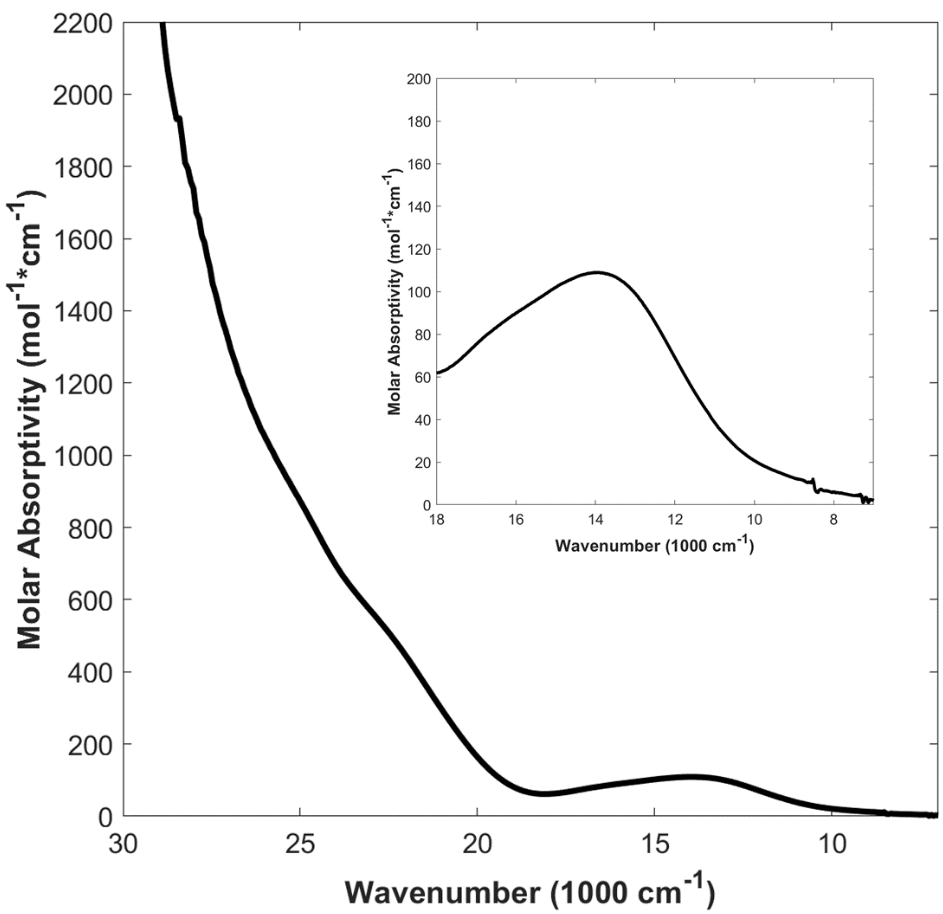
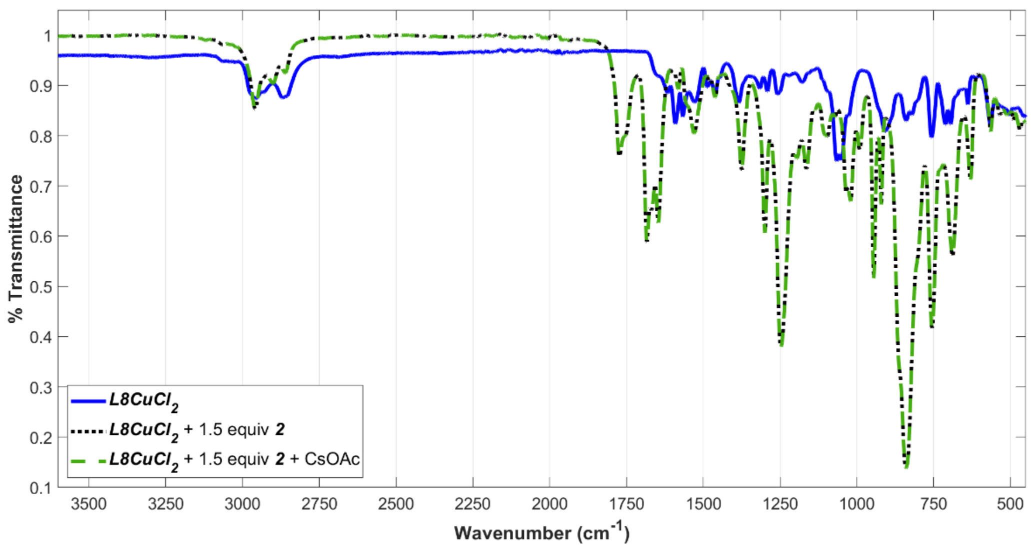


Figure S4. Absorption Spectrum of **L8•$CuCl_2$**.

Preliminary Evidence for the Dissociation of Benzamide Moiety Upon Reduction

Figure S5: IR Spectra.



Compared to that of the free ligand, the pyridine ring bending mode shifted from 748 to 756 cm^{-1}, indicating the coordination of pyridine to copper center. [22] For **L8•CuCl$_2$** (blue trace) we consistently noted high transmittance. Upon adding silyl ketene acetal **2**, we observed the reappearance of amide bands at 1683, 1669, and 1646 cm^{-1}. A ketone band was also observed at 1774 cm^{-1}. The pyridine remained bound to the copper center as the ring bending mode occurred at 755 cm^{-1}. Interestingly, we observed an intense ring C-H bend from the phenyl moiety. These results suggest that the benzamide moiety may have dissociated upon addition of silyl ketene acetal **2**.

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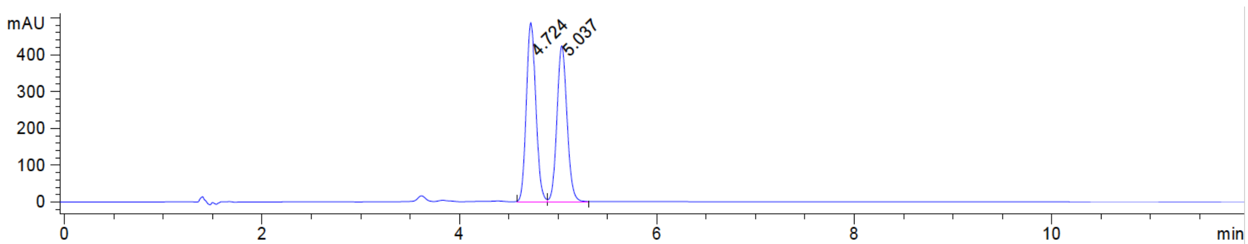
SFC traces

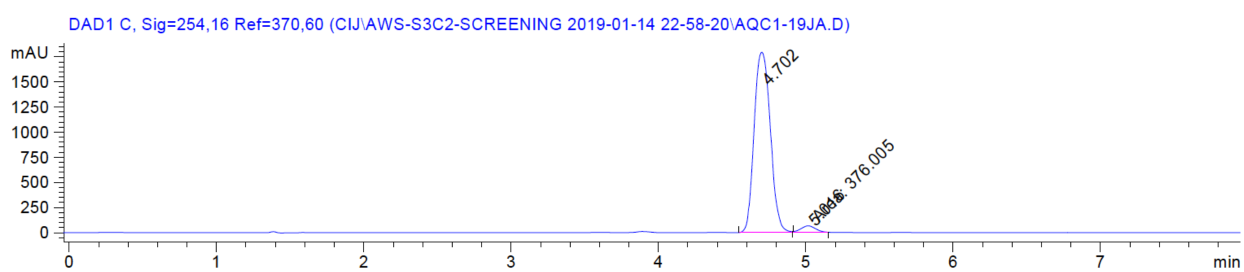
α-Allyl Lactones

Racemic **3a**



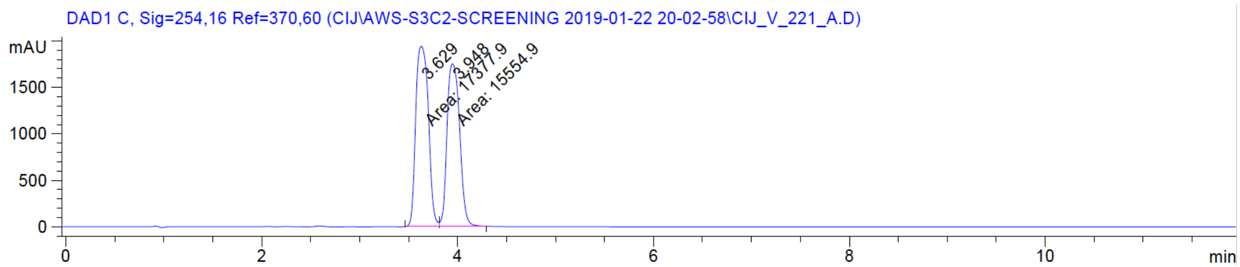
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.724	BV	0.1060	3243.59131	484.98093	51.8869
2	5.037	VB	0.1112	3007.68433	421.60733	48.1131

Enantioenriched **3a**



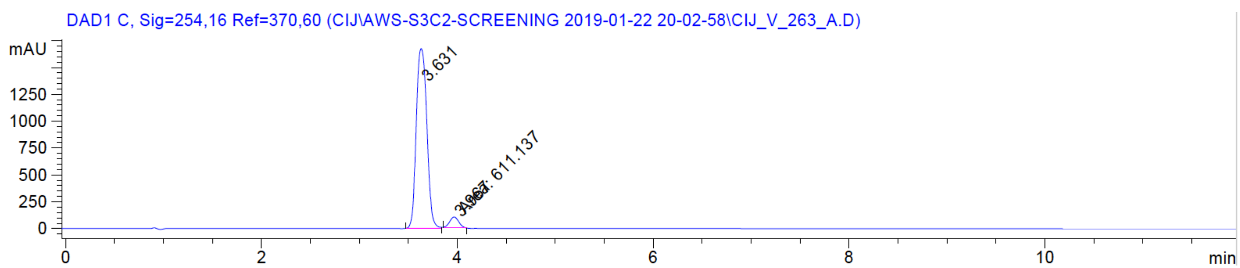
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.702	BV	0.1253	1.37143e4	1791.98560	97.3315
2	5.016	MM	0.1048	376.00534	59.78917	2.6685

Racemic **3b**



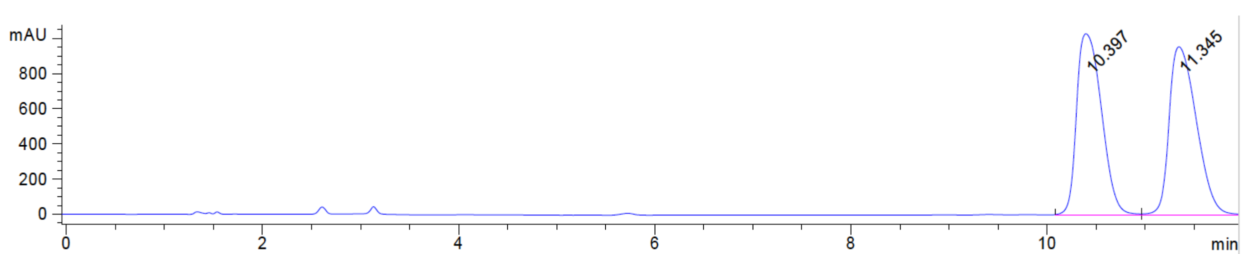
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.629	MF	0.1494	1.73779e4	1938.12292	52.7677
2	3.948	FM	0.1482	1.55549e4	1748.80554	47.2323

Enantioenriched **3b**



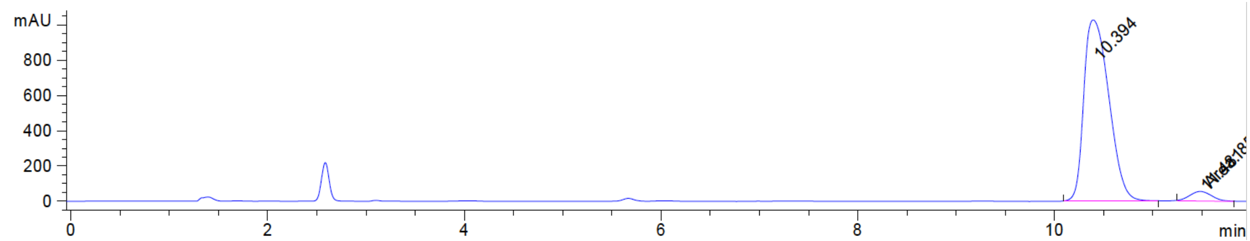
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.631	BV	0.1199	1.26312e4	1675.67847	95.3850
2	3.967	MM	0.1034	611.13721	98.48151	4.6150

Racemic **3c**



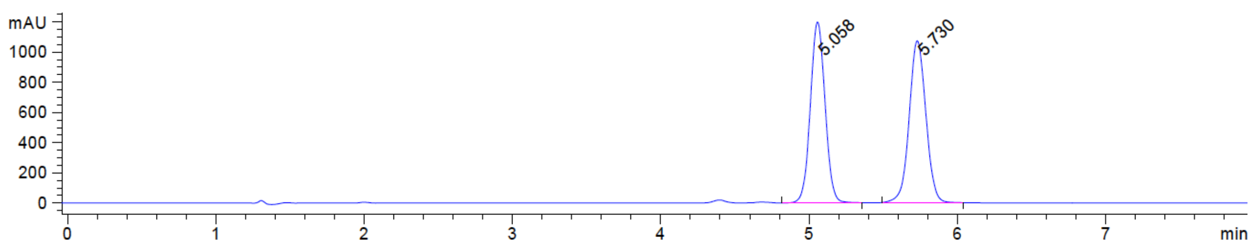
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.397	BV	0.2824	1.82289e4	1030.21924	49.6594
2	11.345	VBA	0.3054	1.84789e4	956.28119	50.3406

Enantioenriched **3c**



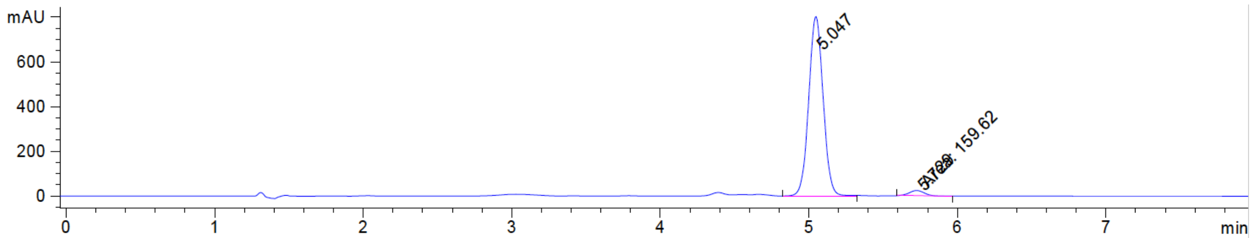
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.394	BB	0.2837	1.83262e4	1029.47913	95.5386
2	11.481	MM	0.2599	855.79230	54.87984	4.4614

Racemic **3d**



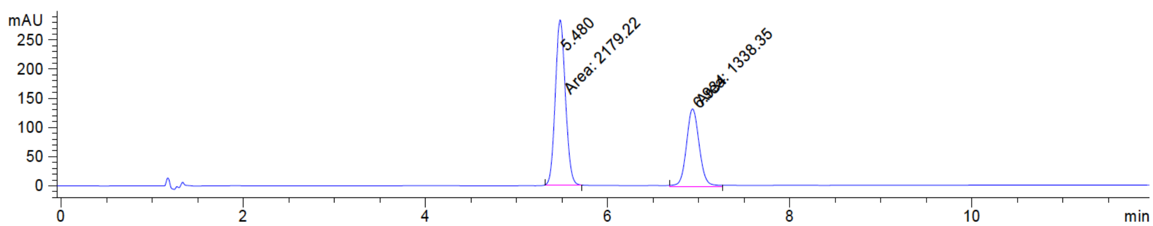
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.058	VB	0.1088	8289.11328	1196.61475	49.5072
2	5.730	BB	0.1200	8454.14746	1071.95105	50.4928

Enantioenriched **3d**



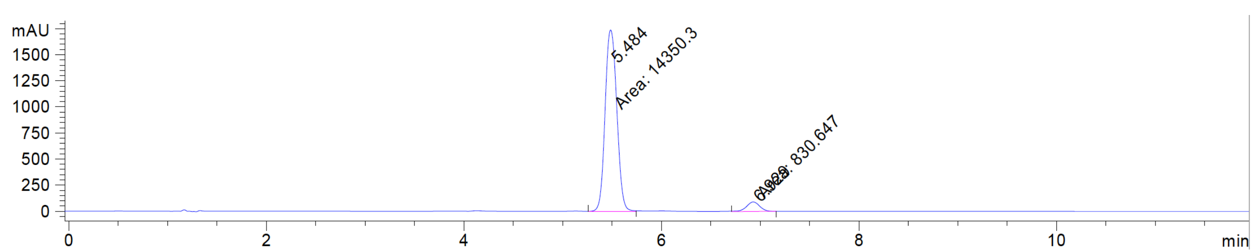
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.047	VB	0.1048	5427.30859	803.15717	97.1430
2	5.729	MM	0.1173	159.61969	22.68375	2.8570

Racemic **3e**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.480	MM	0.1280	2179.22363	283.76538	61.9526
2	6.934	MM	0.1662	1338.34521	134.24239	38.0474

Enantioenriched **3e**



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1	5.484	MM	0.1372	1.43503e4	1743.43298	94.5284
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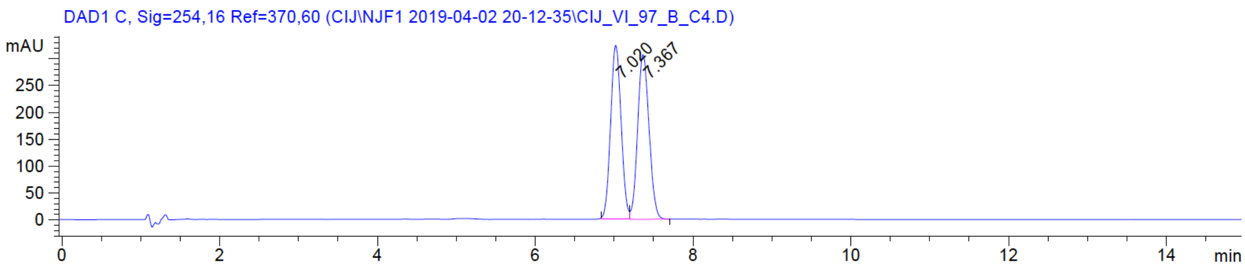
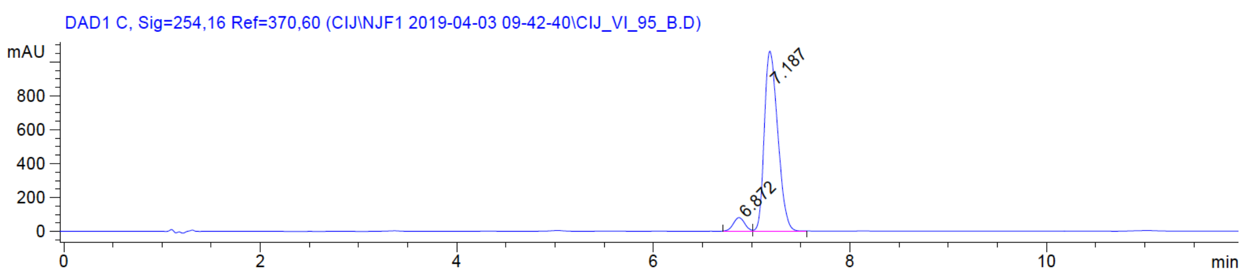
Racemic **3f**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.020	BV	0.1446	3006.54321	323.07938	49.3231
2	7.367	VB	0.1578	3089.06006	305.80429	50.6769

Enantioenriched **3f**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.872	BV	0.1265	651.71277	80.49749	6.0495
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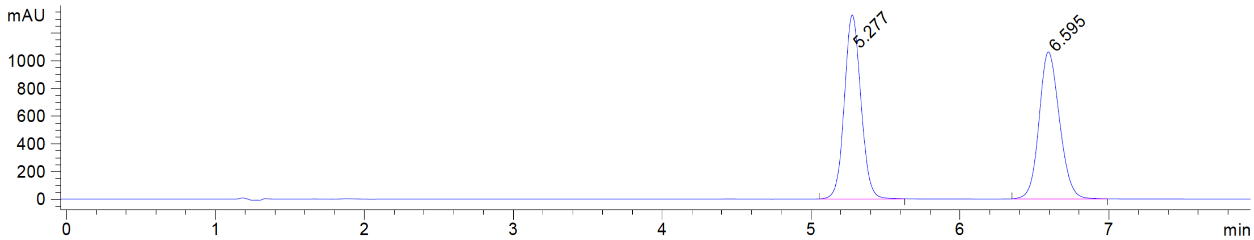
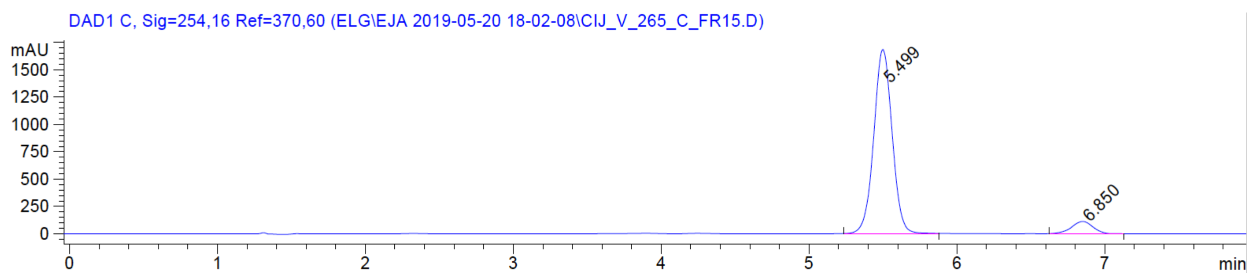
Racemic **3g**



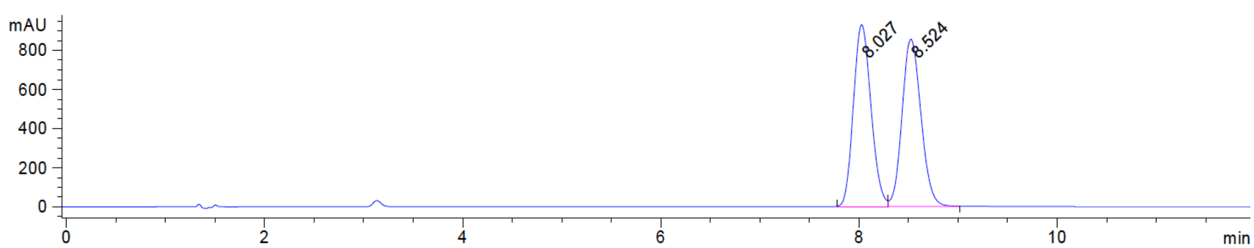
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.277	BB	0.1228	1.03162e4	1325.73035	50.3910
2	6.595	BB	0.1476	1.01561e4	1061.40625	49.6090

Enantioenriched **3g**



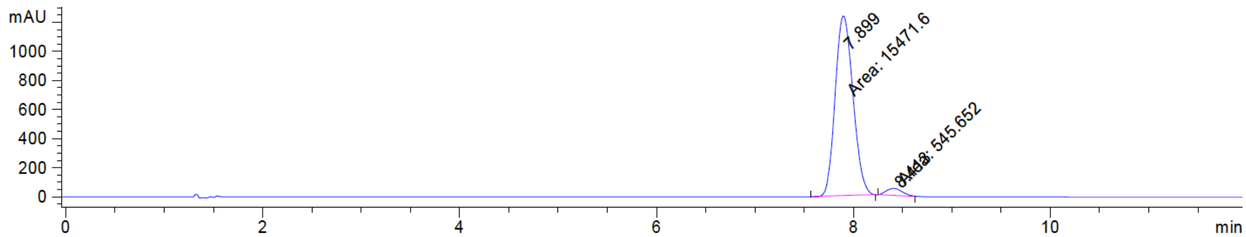
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.499	BB	0.1333	1.46081e4	1682.55164	92.8156
2	6.850	BB	0.1536	1130.74231	112.20788	7.1844

Racemic **3h**



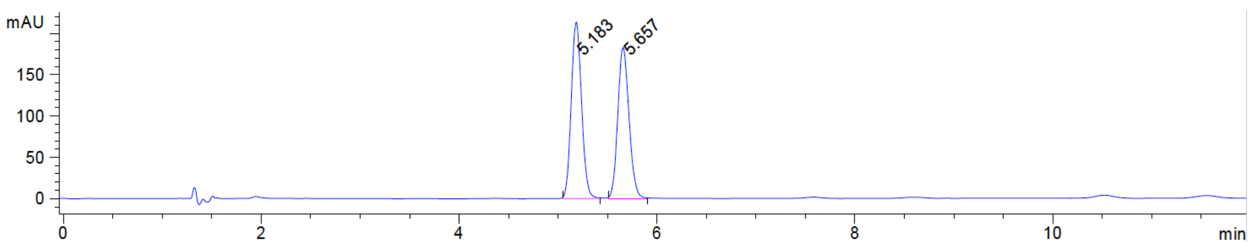
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.027	BV	0.1963	1.14860e4	928.63049	50.2484
2	8.524	VB	0.2071	1.13725e4	855.64130	49.7516

Enantioenriched **3h**



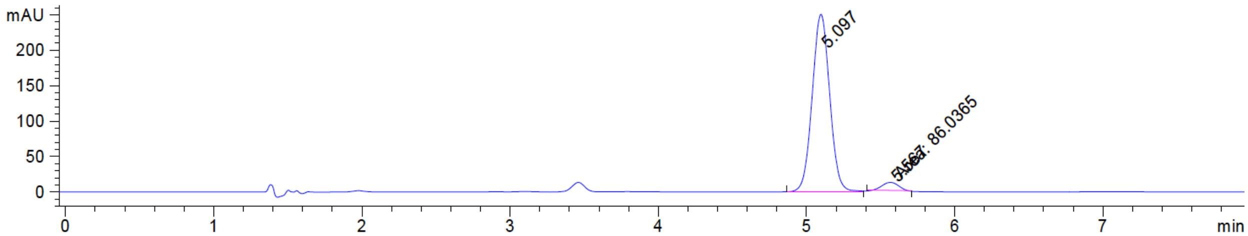
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.899	MM	0.2087	1.54716e4	1235.65808	96.5934
2	8.413	MM	0.1896	545.65204	47.97438	3.4066

Racemic **3i**



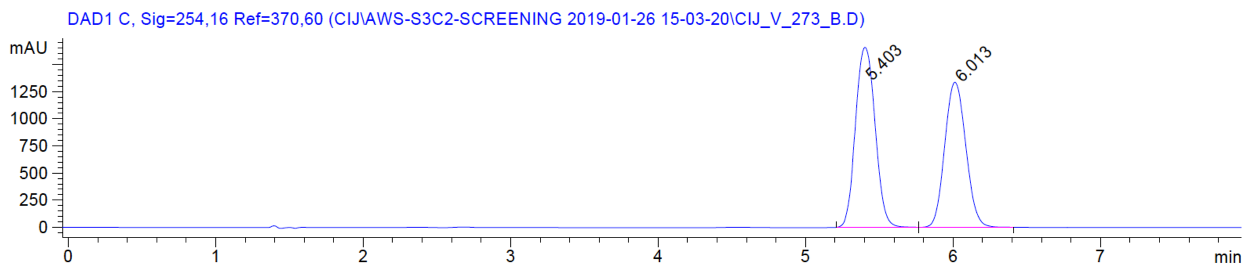
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.183	BB	0.1125	1544.36780	213.32919	51.5889
2	5.657	BB	0.1245	1449.23535	182.75525	48.4111

Enantioenriched **3i**



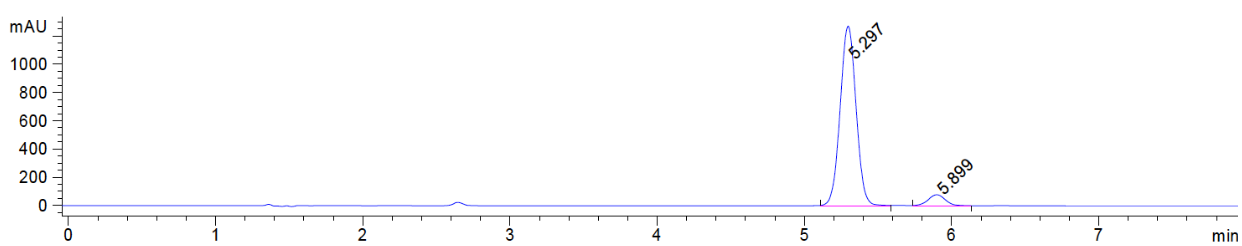
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.097	BV	0.1279	2060.14722	250.69669	95.9912
2	5.567	MM	0.1262	86.03648	11.35933	4.0088

Racemic **3j**



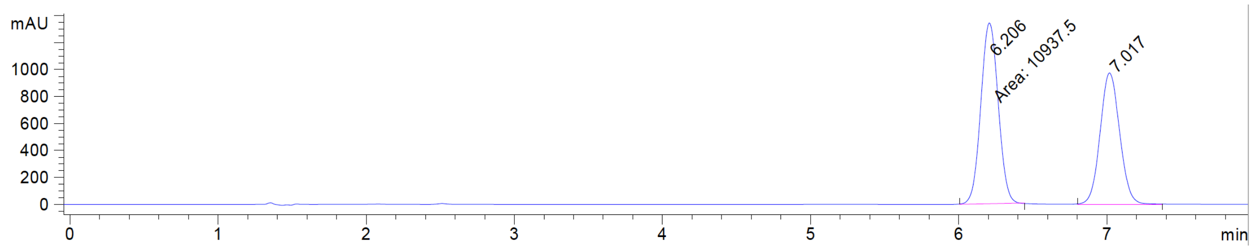
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.403	BV	0.1485	1.54266e4	1659.11975	53.5625
2	6.013	VB	0.1607	1.33745e4	1337.60620	46.4375

Enantioenriched **3j**



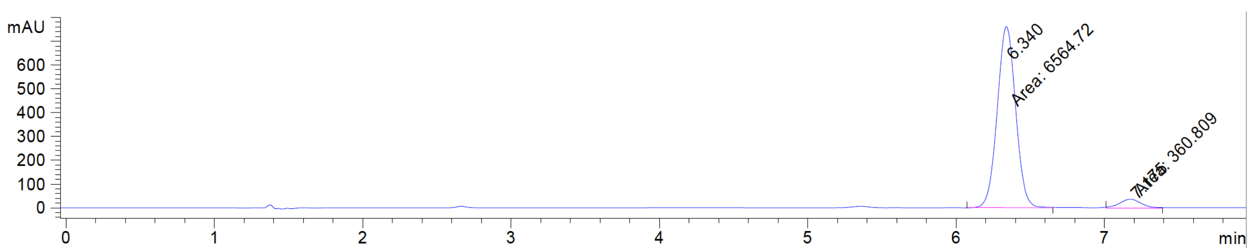
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.297	BB	0.1159	9568.44824	1269.50452	93.7769
2	5.899	BB	0.1270	634.96442	78.00102	6.2231

Racemic **3k**



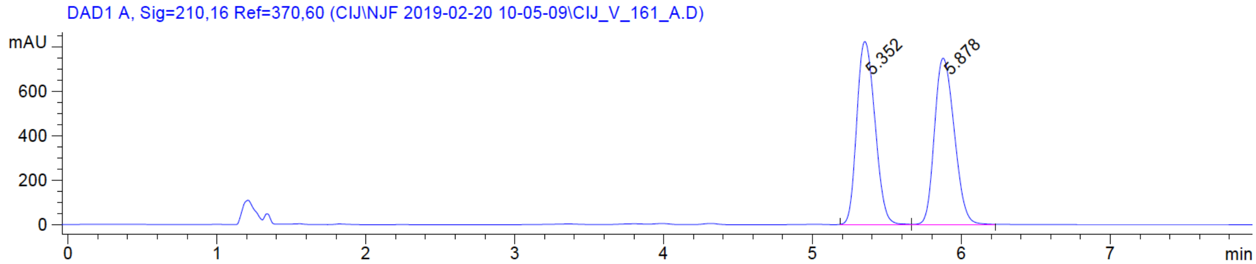
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.206	MM	0.1355	1.09375e4	1345.44360	54.9805
2	7.017	BB	0.1433	8955.94922	974.00220	45.0195

Enantioenriched **3k**



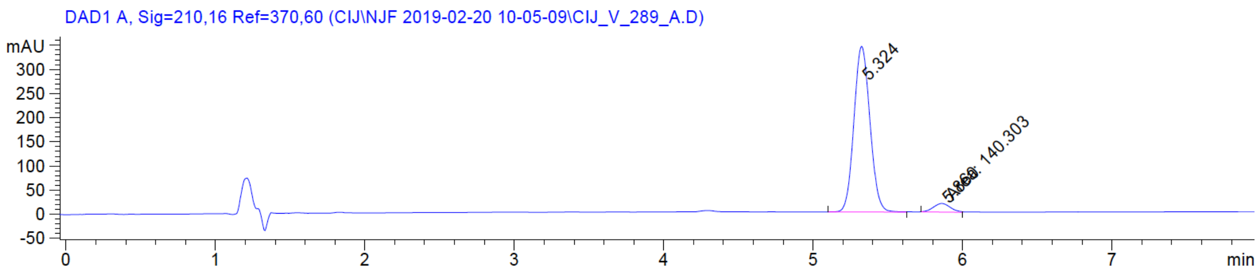
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.340	MM	0.1434	6564.71826	763.16193	94.7902
2	7.175	MM	0.1644	360.80939	36.56867	5.2098

Racemic **3l**



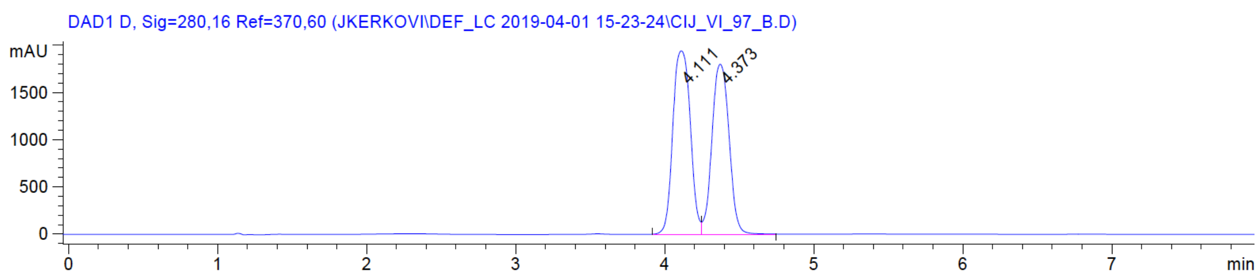
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.352	BV	0.1390	6990.80176	823.77258	50.2089
2	5.878	VB	0.1442	6932.62402	747.74805	49.7911

Enantioenriched **3l**



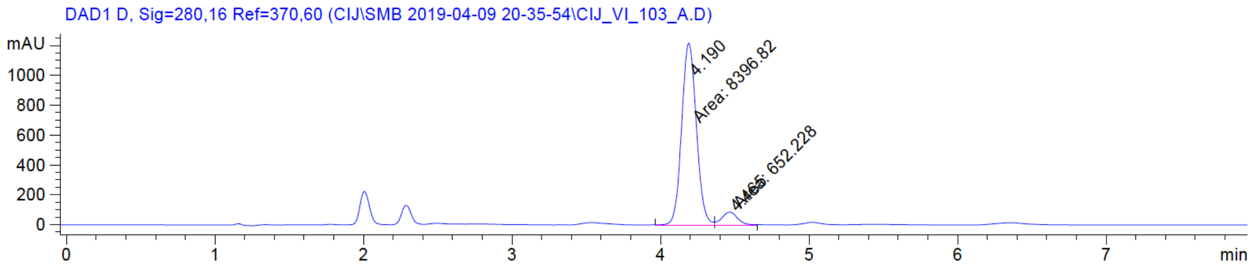
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.324	BB	0.1169	2556.22559	343.24612	94.7969
2	5.860	MM	0.1304	140.30339	17.92598	5.2031

Racemic **3m**



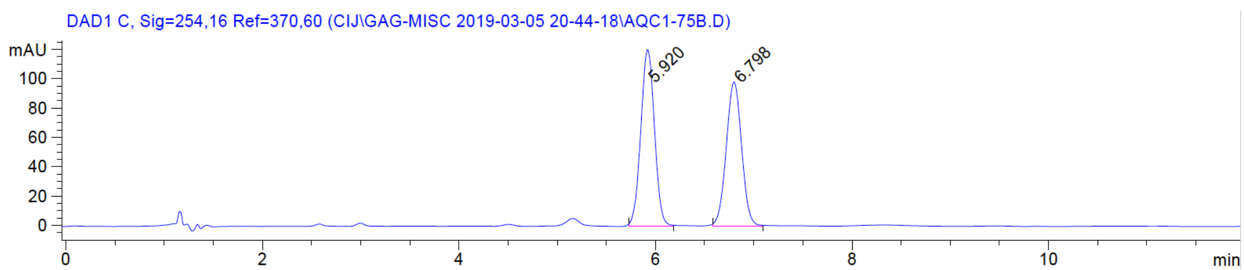
RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4.111	BV	0.1351	1.58564e4	1945.21069	52.3778
4.373	VB	0.1294	1.44167e4	1800.09290	47.6222

Enantioenriched **3m**



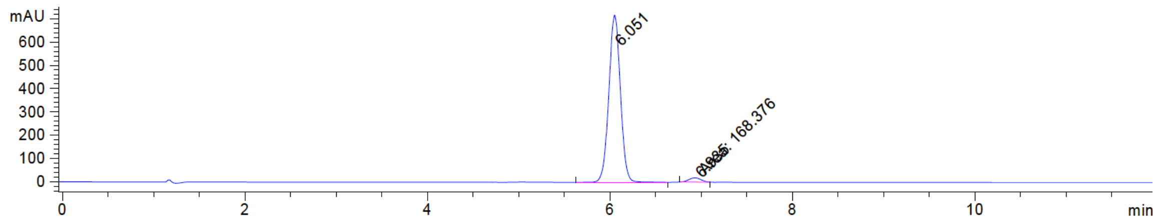
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.190	MF	0.1143	8396.82422	1224.75366	92.7923
2	4.465	FM	0.1226	652.22772	88.67475	7.2077

Racemic **3n**



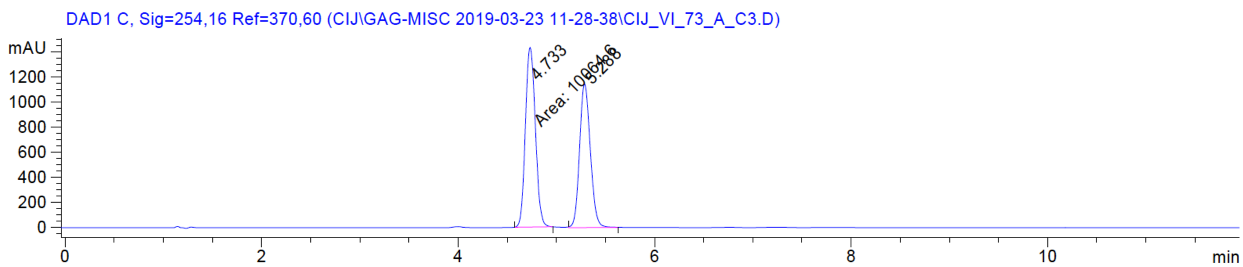
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.920	BB	0.1486	1159.30615	120.12422	52.2126
2	6.798	BB	0.1703	1061.05212	97.98095	47.7874

Enantionenriched **3n**



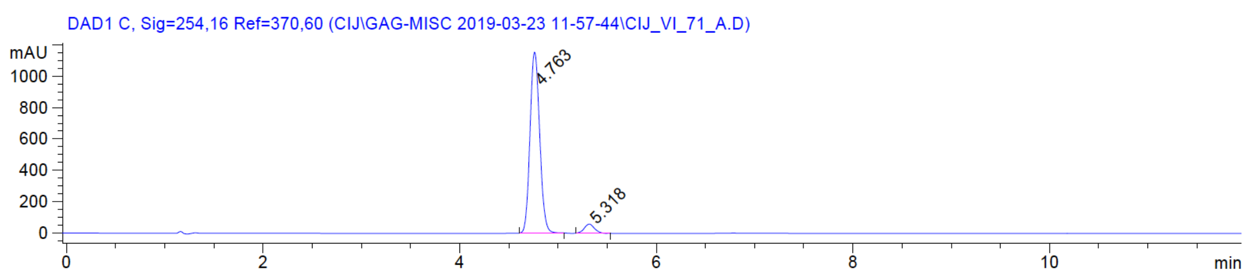
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.051	BB	0.1392	6356.37354	718.77869	97.4194
2	6.935	MM	0.1525	168.37614	18.40682	2.5806

Racemic **3o**



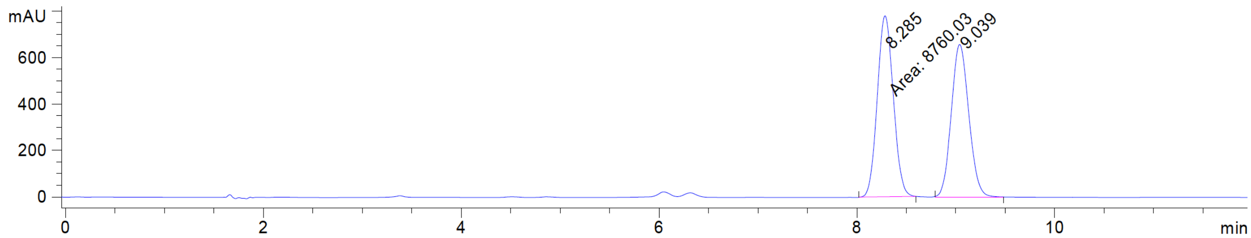
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.733	MM	0.1167	1.00646e4	1437.94543	53.4900
2	5.288	BB	0.1212	8751.25195	1144.60303	46.5100

Enantioenriched **3o**



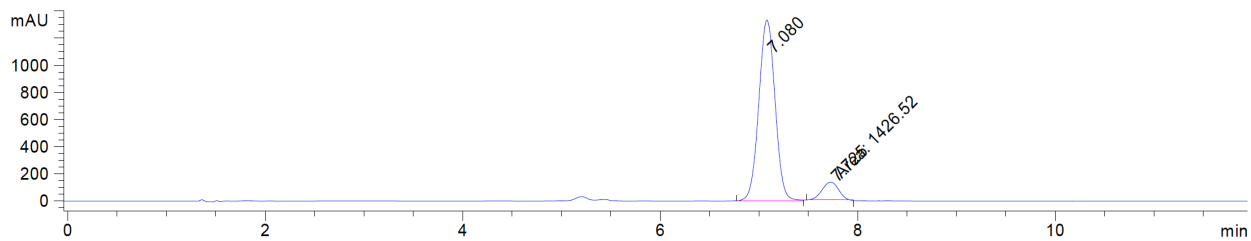
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.763	BB	0.1078	7889.89014	1153.81934	94.8321
2	5.318	BB	0.1135	429.95868	58.69624	5.1679

Racemic **3p**



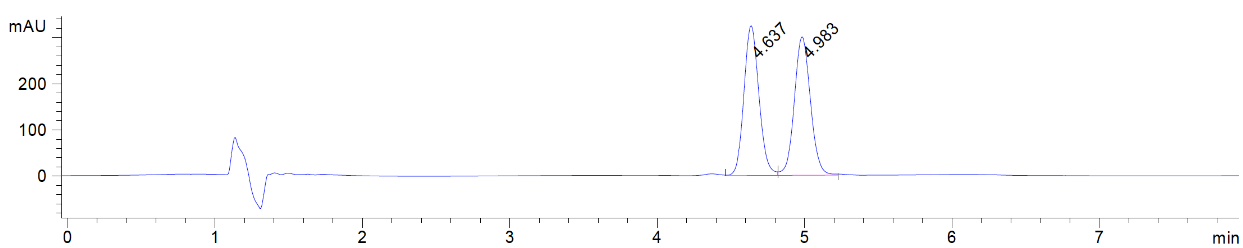
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.285	MM	0.1870	8760.02930	780.54456	51.8253
2	9.039	BB	0.1924	8142.96826	658.06299	48.1747

Enantioenriched **3p**



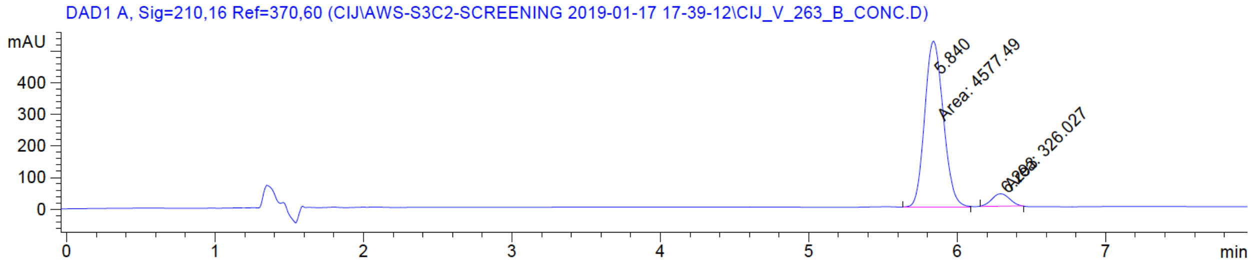
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.080	BV	0.1779	1.53011e4	1332.97339	91.4720
2	7.725	MM	0.1854	1426.52283	128.21072	8.5280

Racemic **3q**



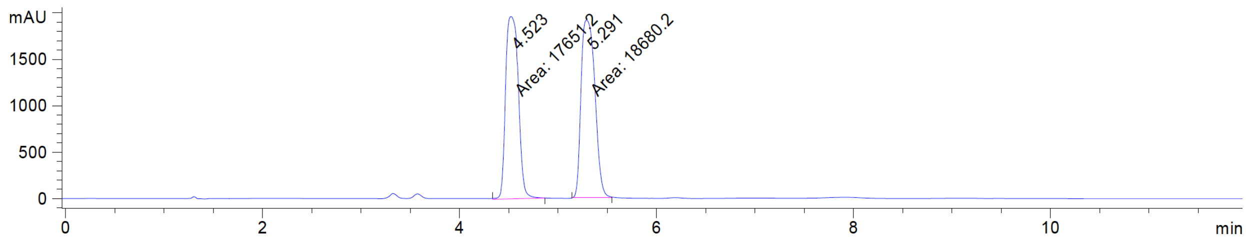
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.637	VV	0.1110	2296.77271	323.01355	50.1523
2	4.983	VB	0.1171	2282.82129	298.78006	49.8477

Enantioenriched **3q**



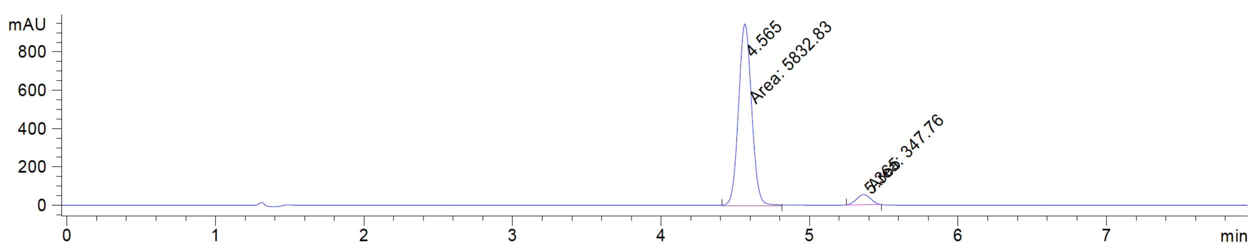
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.840	MM	0.1451	4577.49463	525.70862	93.3512
2	6.293	MM	0.1368	326.02713	39.71201	6.6488

Racemic **3s**



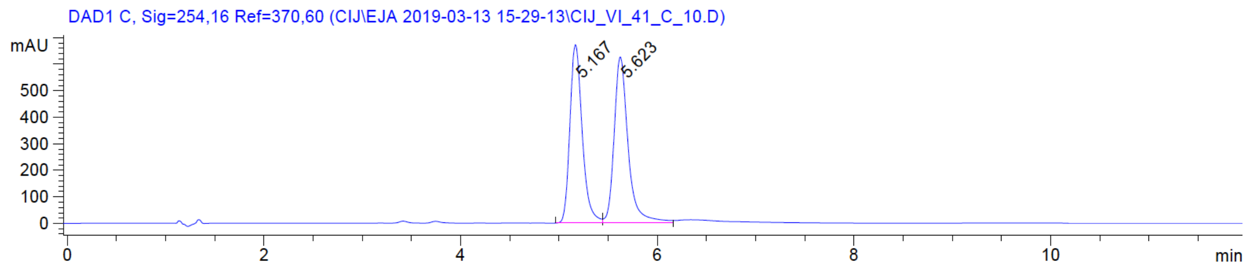
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.523	MM	0.1497	1.76512e4	1965.22815	48.5839
2	5.291	MM	0.1627	1.86802e4	1913.69226	51.4161

Enantioenriched **3s**



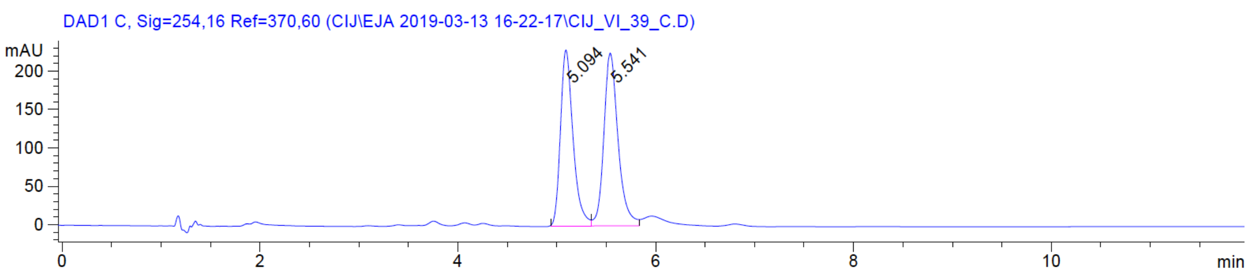
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.565	MM	0.1019	5832.82715	953.85663	94.3734
2	5.365	MM	0.1086	347.75986	53.35968	5.6266

Racemic **3t**



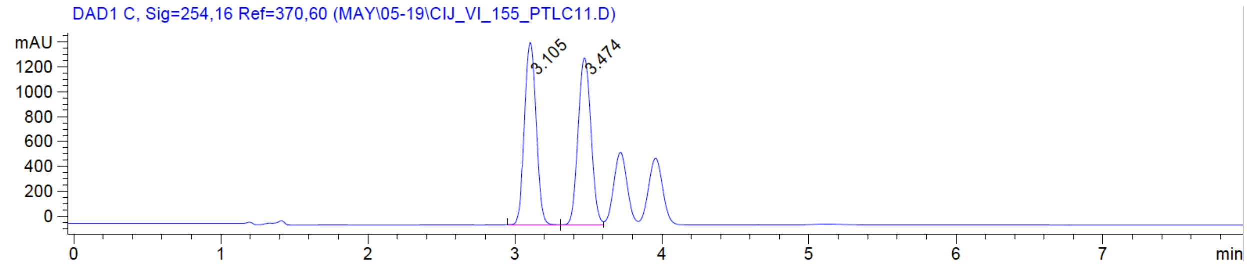
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.167	BV	0.1336	5852.95703	672.32452	48.4590
2	5.623	VV	0.1500	6225.19824	626.30823	51.5410

Enantioenriched **3t**



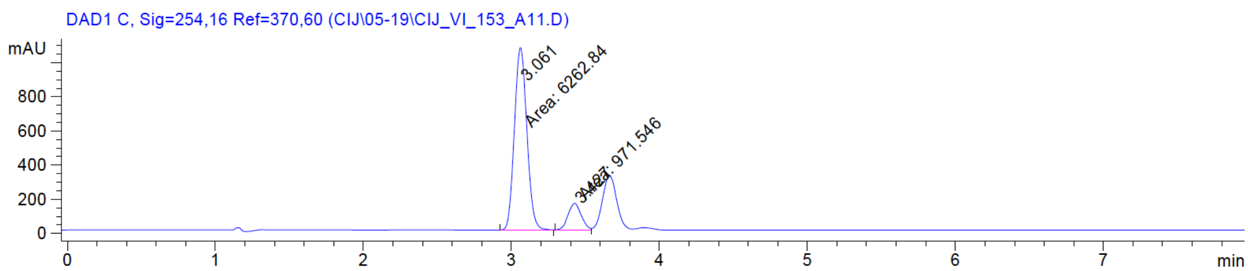
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.094	BV	0.1354	2026.62415	228.64549	47.4117
2	5.541	VV	0.1526	2247.90063	224.93742	52.5883

Racemic **3u**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.105	BV	0.0893	8159.40820	1457.32410	49.9066
2	3.474	VV	0.0955	8189.94775	1336.15613	50.0934

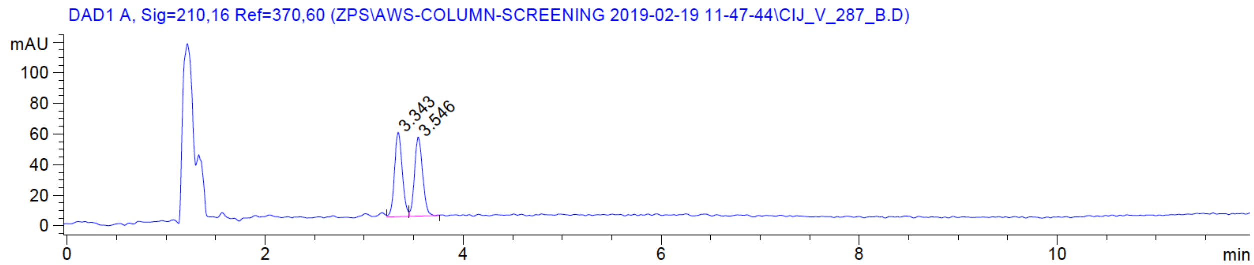
Enantioenriched **3u**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.061	MM	0.0971	6262.83984	1075.06250	86.5704
2	3.427	MM	0.1037	971.54614	156.18806	13.4296

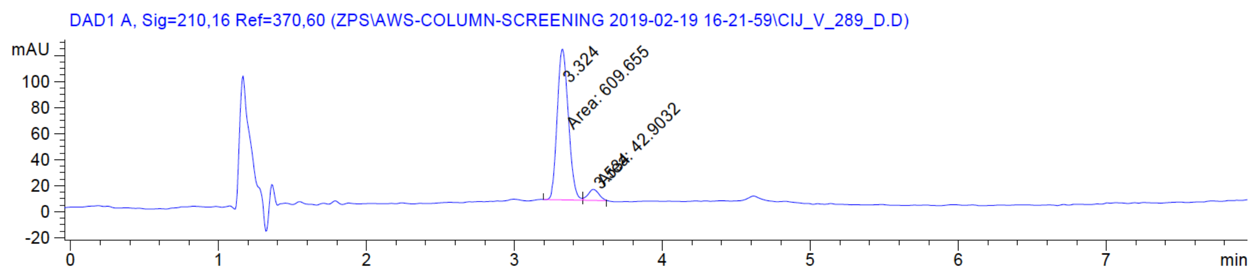
* the two additional peaks in both the racemic and chiral traces for **3v** correspond to the minor E-isomer product.

Racemic **3v**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.343	VV	0.0858	301.82306	55.20087	50.4772
2	3.546	VB	0.0867	296.11688	51.81462	49.5228

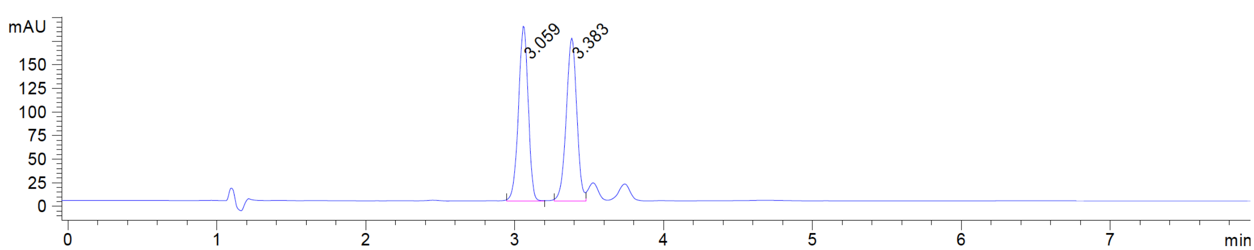
Enantioenriched **3v**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.324	MF	0.0874	609.65472	116.29012	93.4254
2	3.534	FM	0.0842	42.90318	8.48838	6.5746

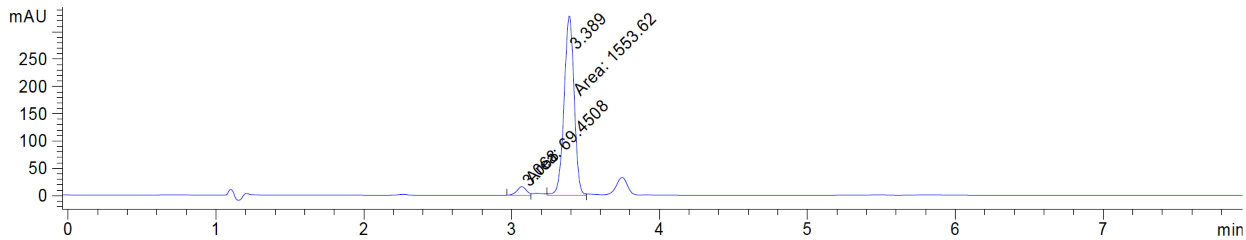
Product Transformations

Racemic **5**



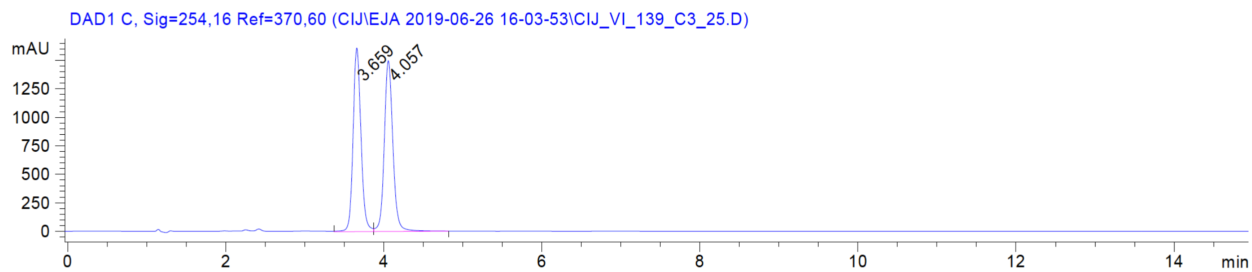
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.059	BB	0.0695	841.17938	183.38898	49.9066
2	3.383	BV	0.0775	844.32831	171.27727	50.0934

Enantioenriched **5**



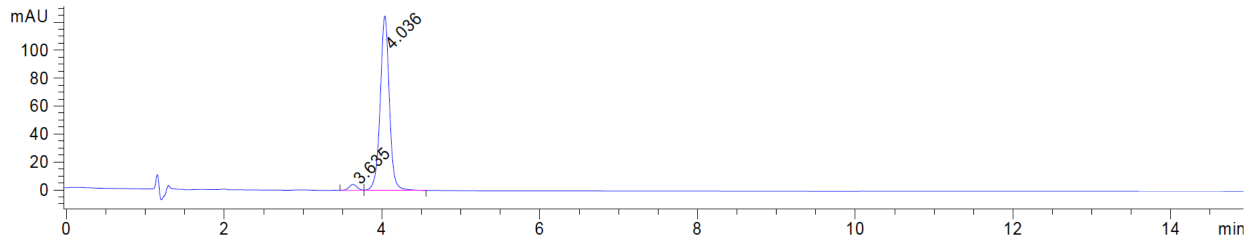
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.068	MF	0.0739	69.45084	15.67137	4.2790
2	3.389	MF	0.0785	1553.61877	329.98630	95.7210

Racemic **6**



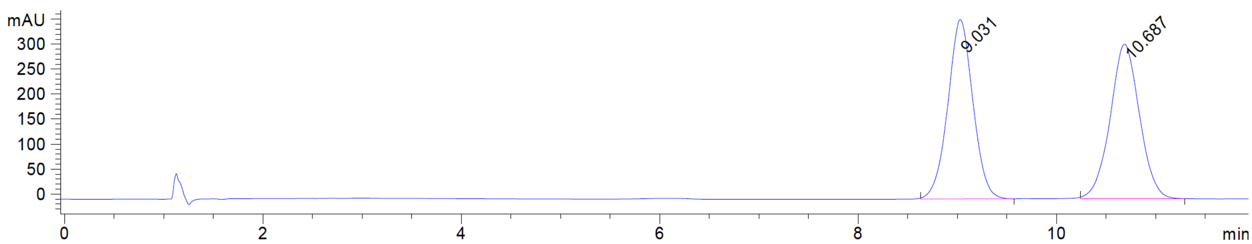
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.659	BV	0.1088	1.11784e4	1614.33826	49.4426
2	4.057	VB	0.1169	1.14305e4	1500.47424	50.5574

Enantioenriched **6**



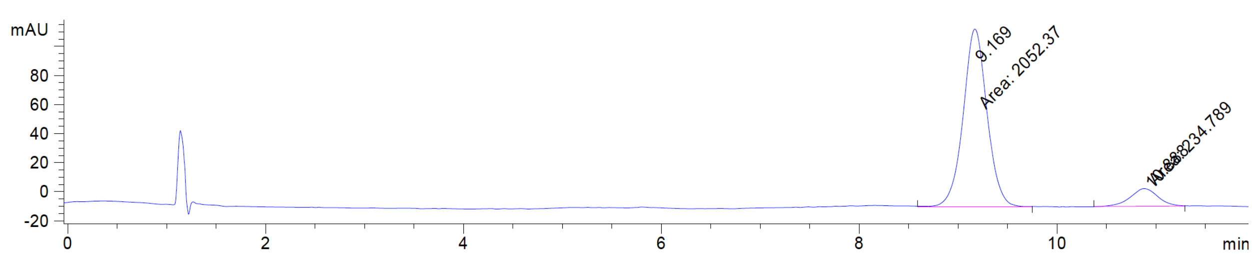
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.635	BV	0.1094	30.99894	4.33705	2.9666
2	4.036	VB	0.1247	1013.91583	124.89724	97.0334

Racemic **7**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.031	BB	0.2696	6322.48828	358.84088	49.8706
2	10.687	BB	0.3118	6355.31055	309.21637	50.1294

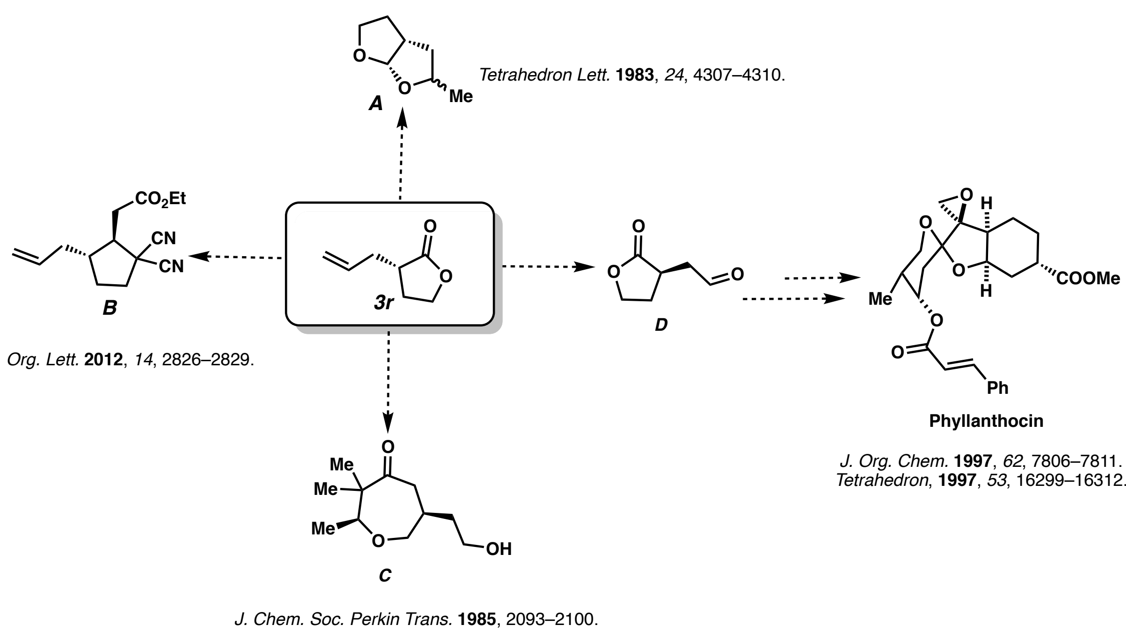
Enantioenriched **7**



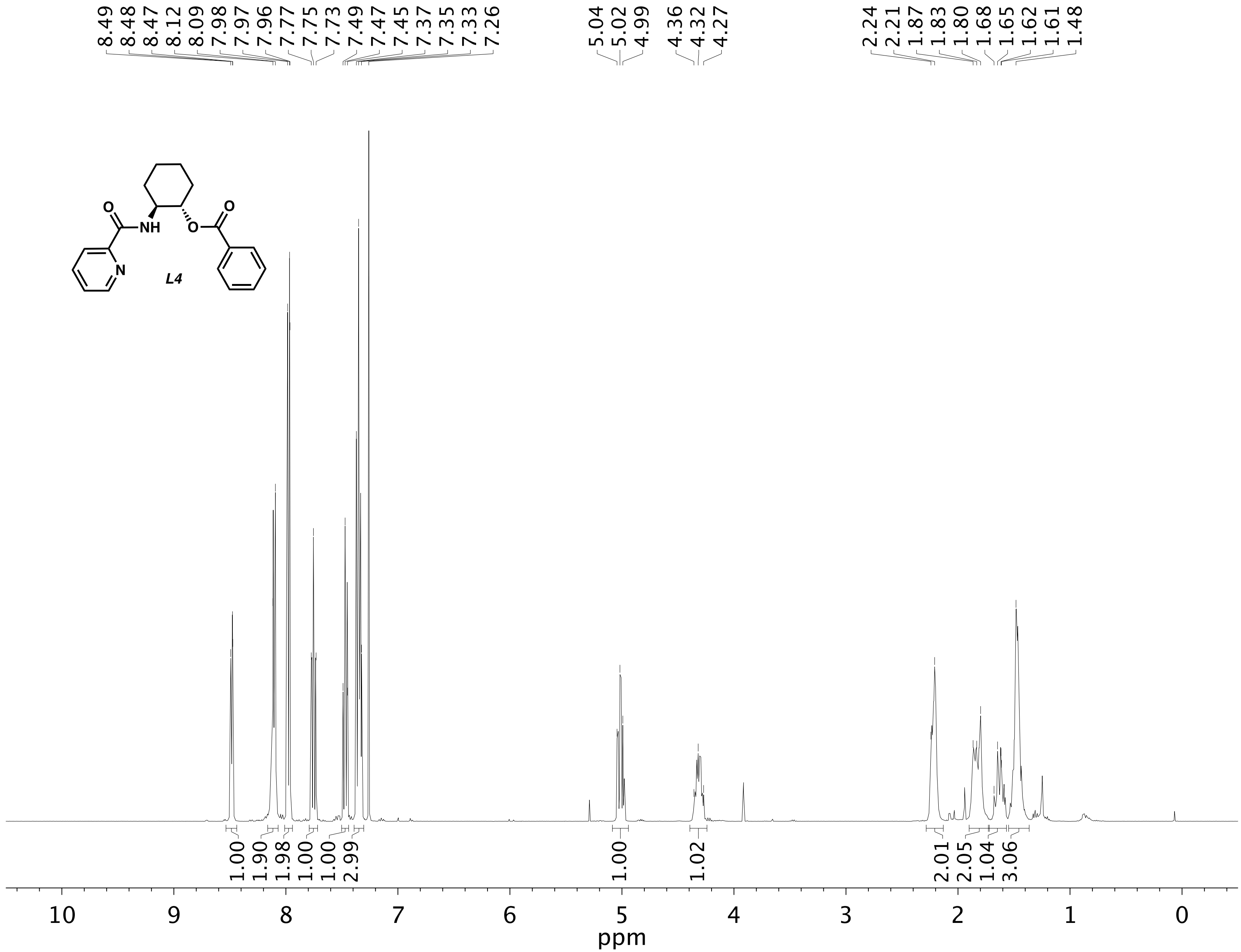
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.169	MM	0.2799	2052.36890	122.21217	89.7345
2	10.888	MM	0.3218	234.78865	12.15906	10.2655

Synthetic Utility of α-allyl γ-butyrolactones

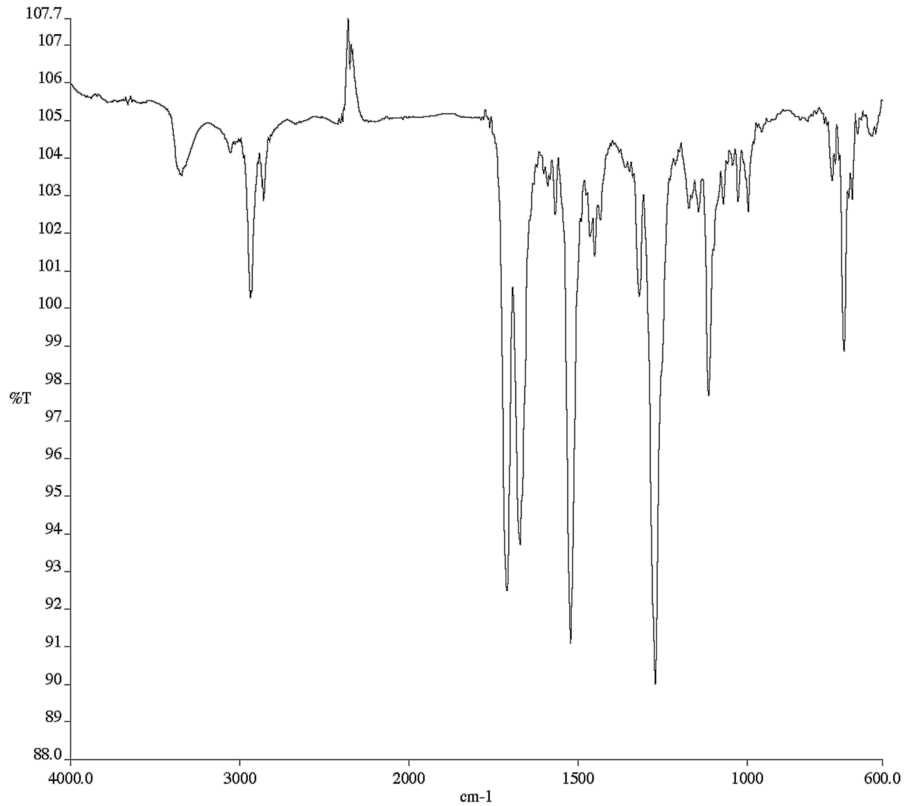
In addition to the product transformations reported in the paper, there are a number of other transformations reported in the literature that lead to very useful products. Below are some examples:



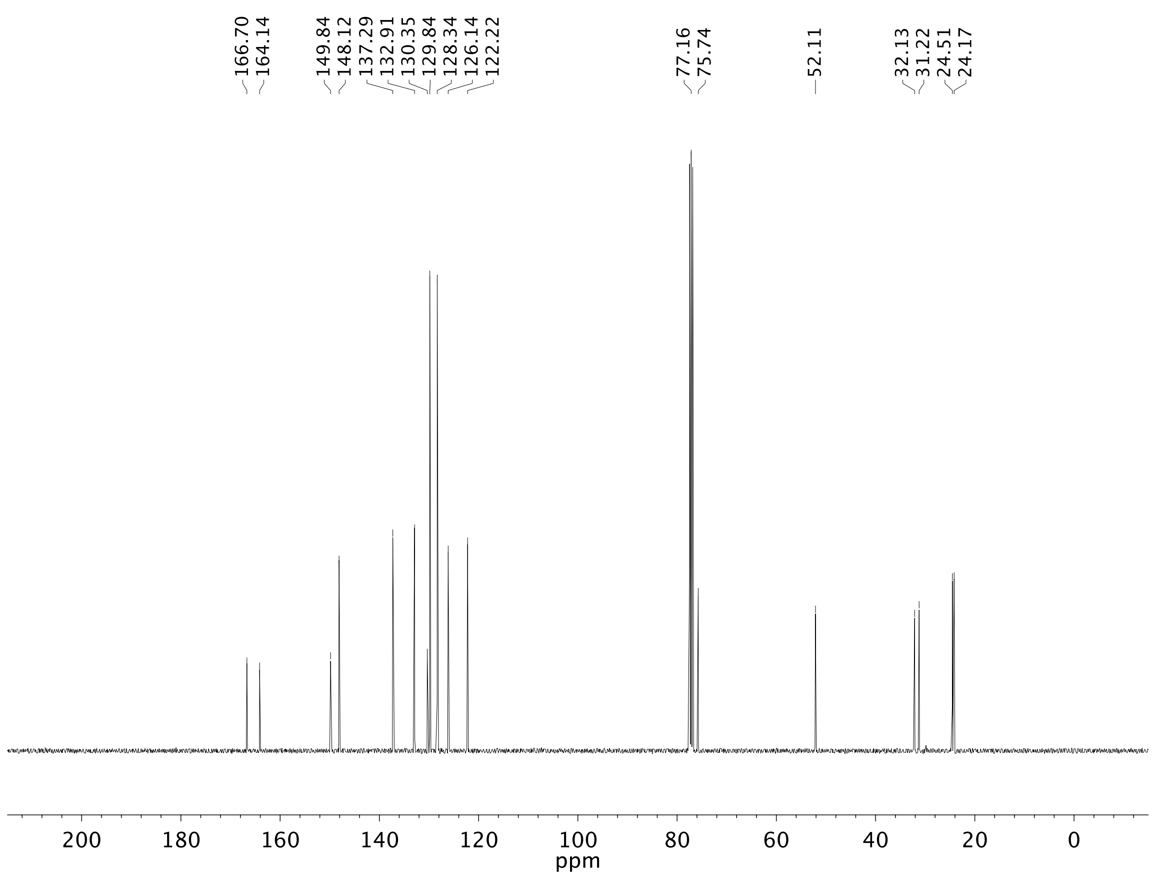
Chiral lactols such as **4** can also be converted to acyclic molecules possessing propargylic stereocenters (*Org. Lett.* **2012**, *14*, 3648–3651) or allylic stereocenters (*J. Am. Chem. Soc.* **2017**, *139*, 13272–13275) without loss of enantiomeric excess. In addition, the high levels of enantiomeric excess can also be retained under mild lactone ring-opening reactions. Zhang and coworkers (ACIE, **2013**, *52*, 5807–5812) reported a ring opening with a Weinreb amide and subsequent addition of ethylmagnesium bromide to form α-chiral ketones with full retention of enantiomeric excess. Koert and coworkers also demonstrated that an α-chiral γ-butyrolactone can undergo ring opening of the lactone with HBr without loss of stereochemistry: *Chem. Eur. J.* **2013**, *19*, 7423–7436. For an example with HCl see: *Helv. Chim. Acta*, **1979**, *62*, 474–480.



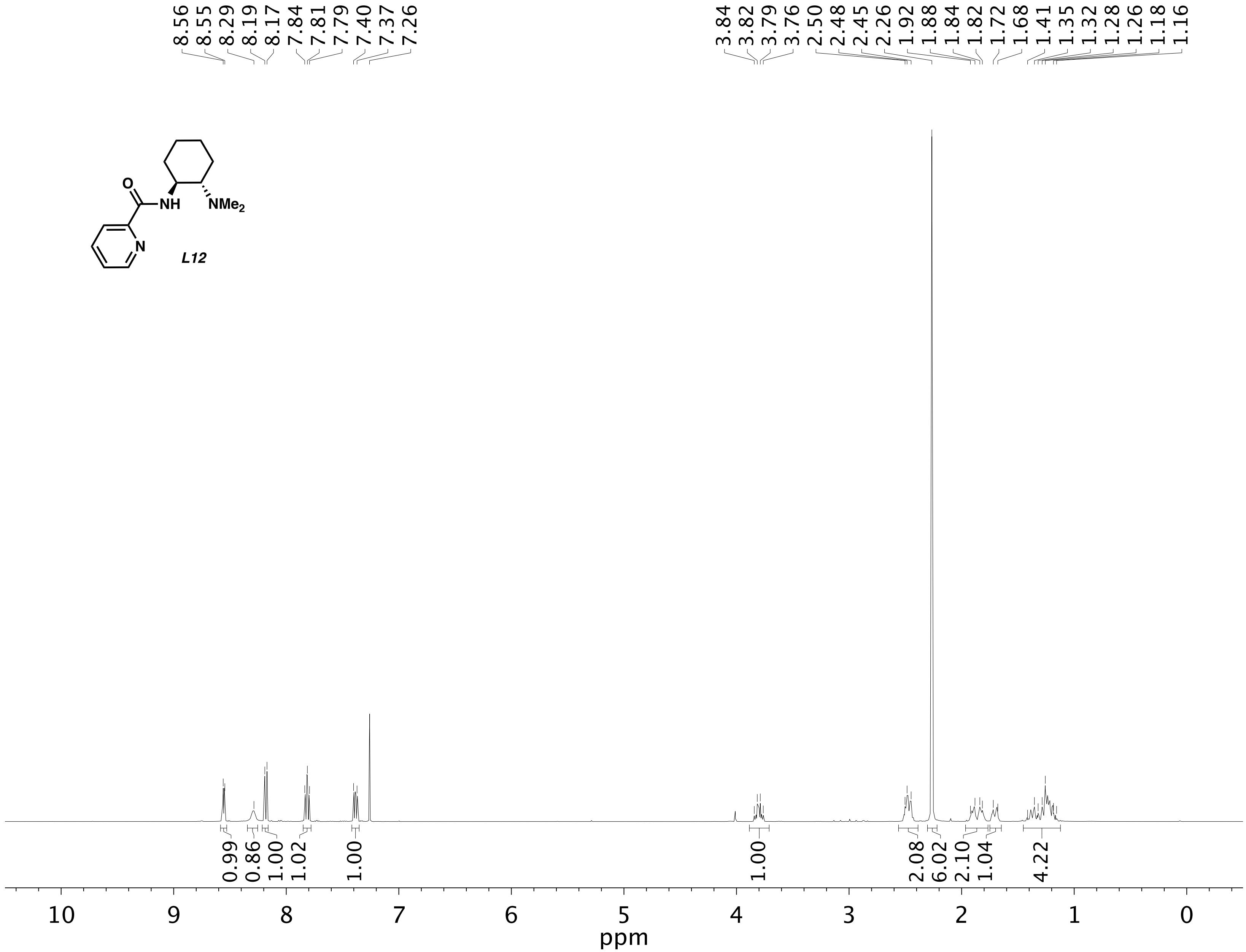
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L4**



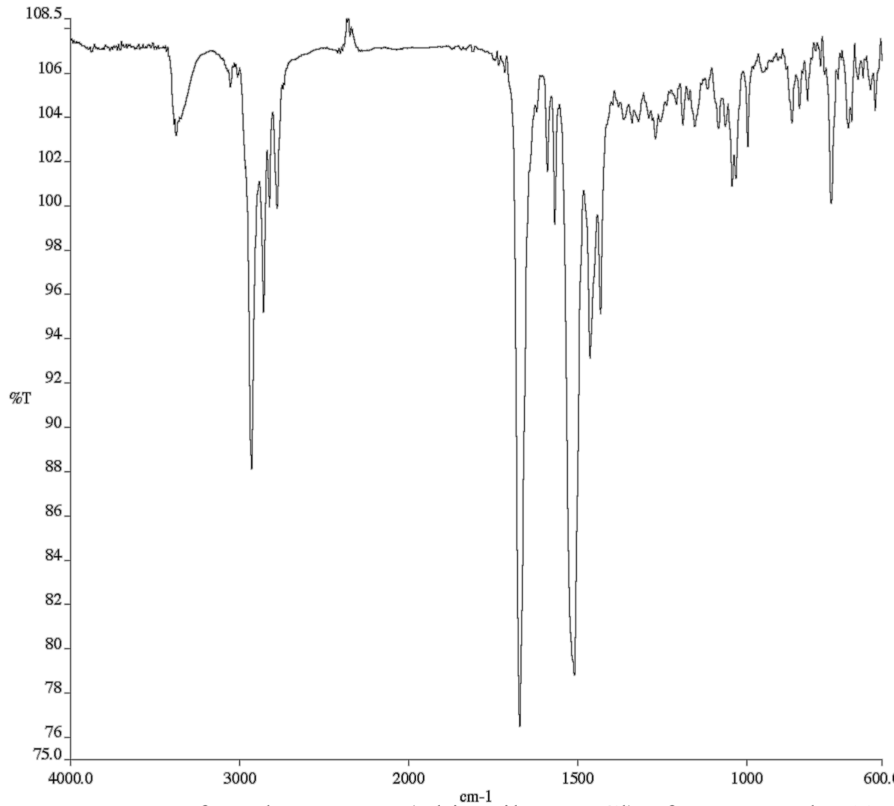
Infrared spectrum (Thin Film, NaCl) of compound **L4**



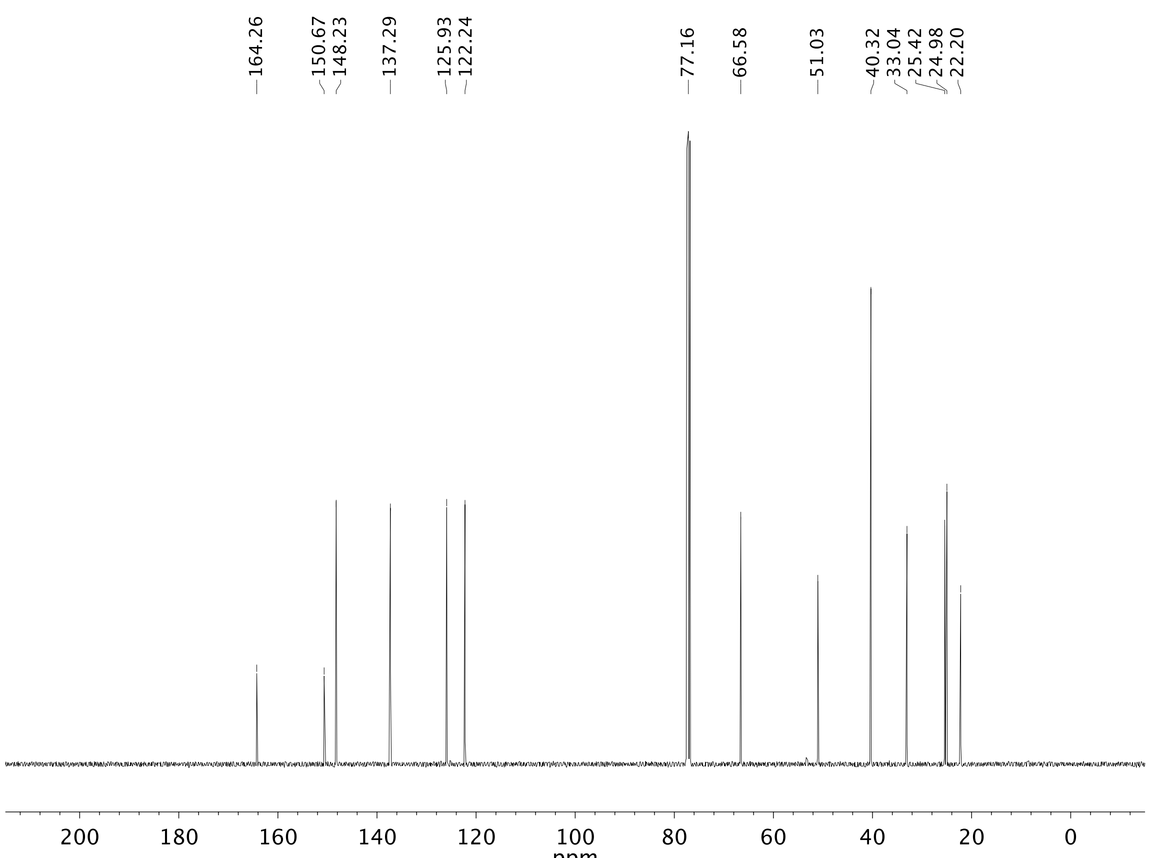
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L4**



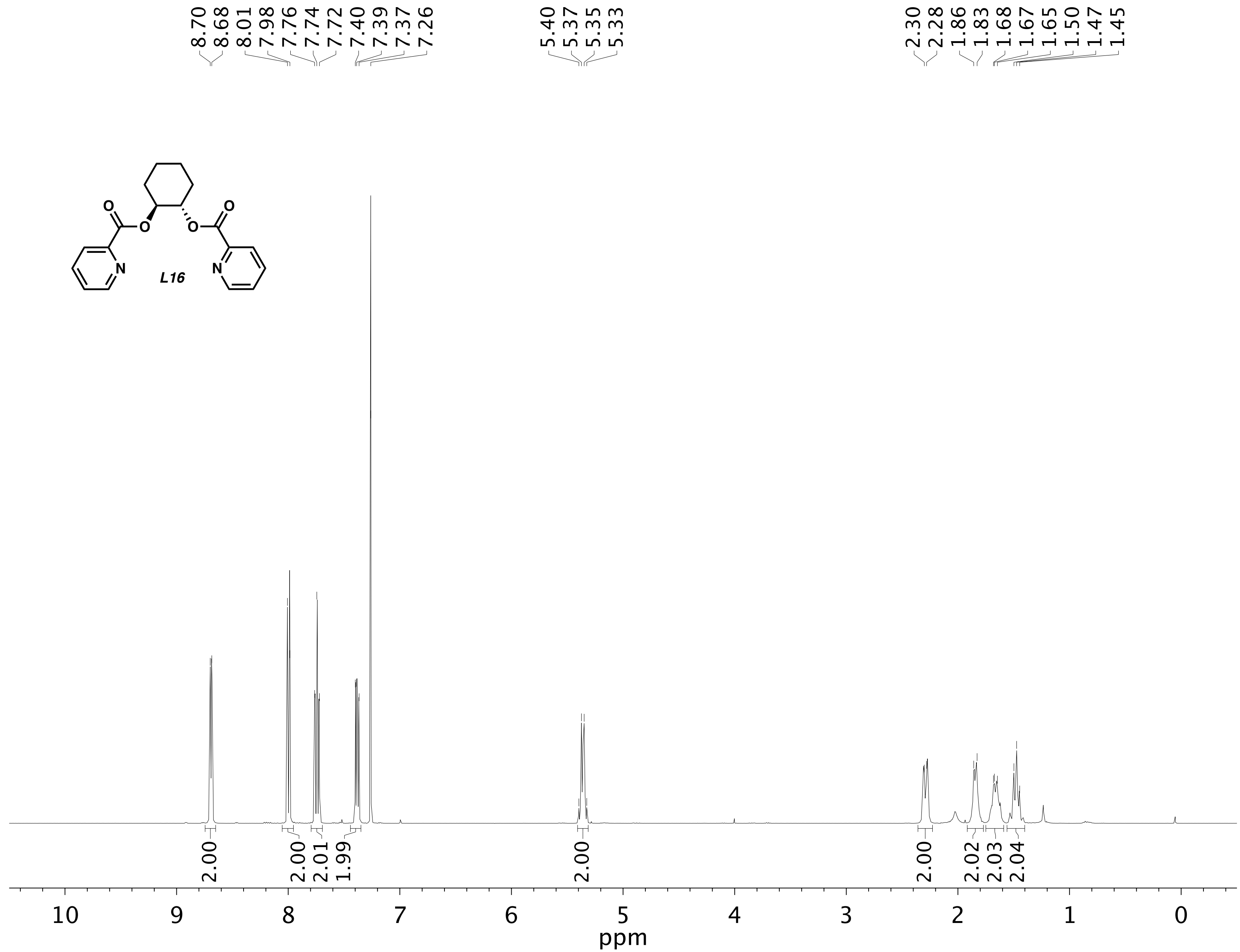
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L12**



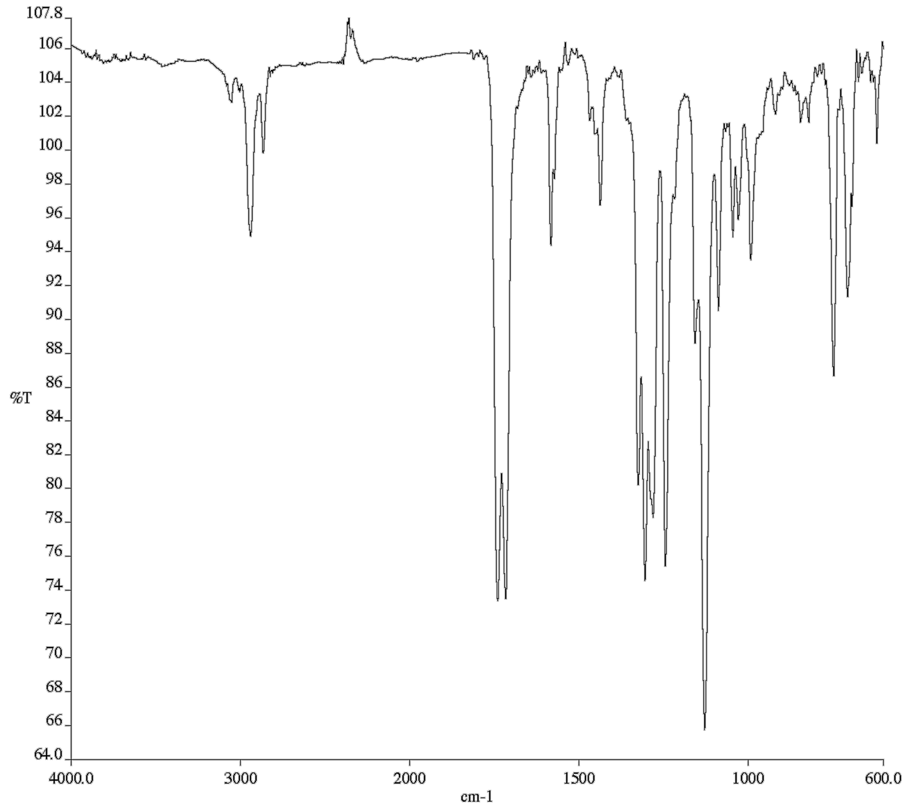
Infrared spectrum (Thin Film, NaCl) of compound **L12**



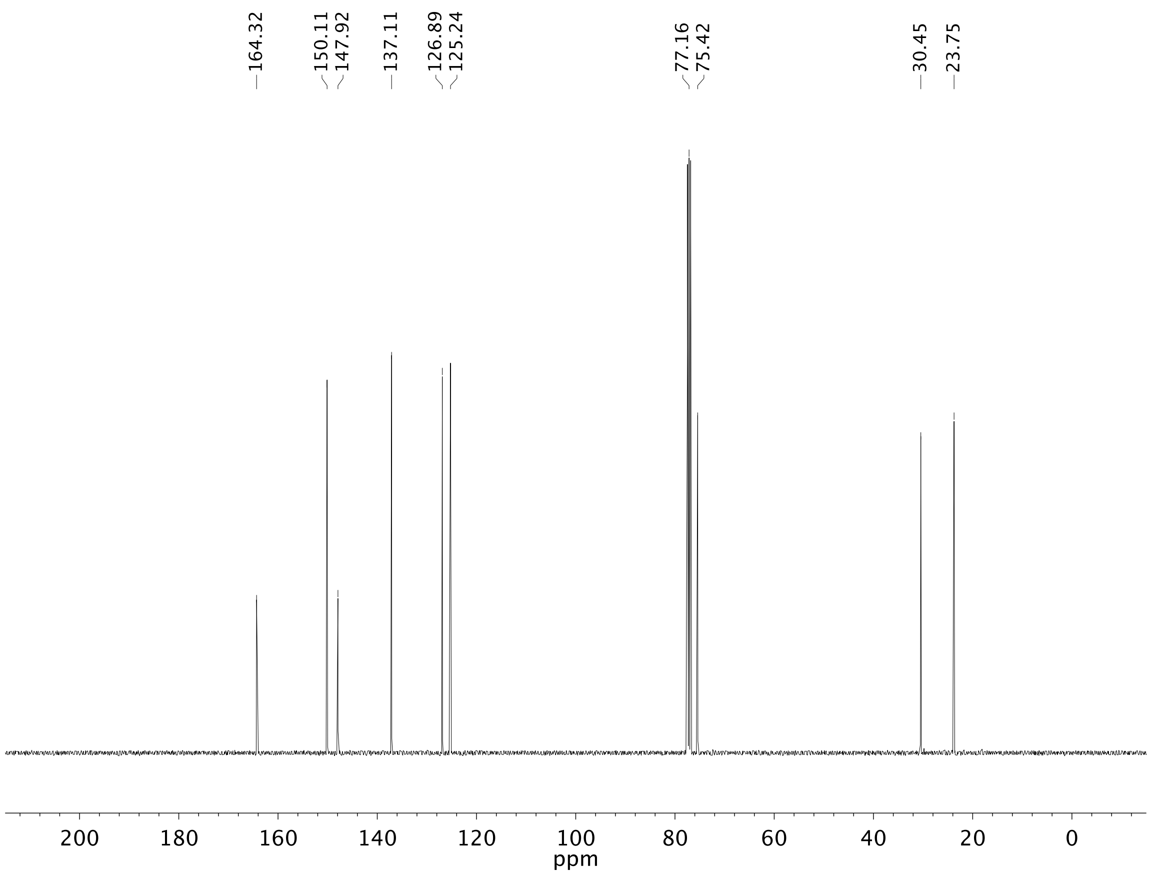
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L12**



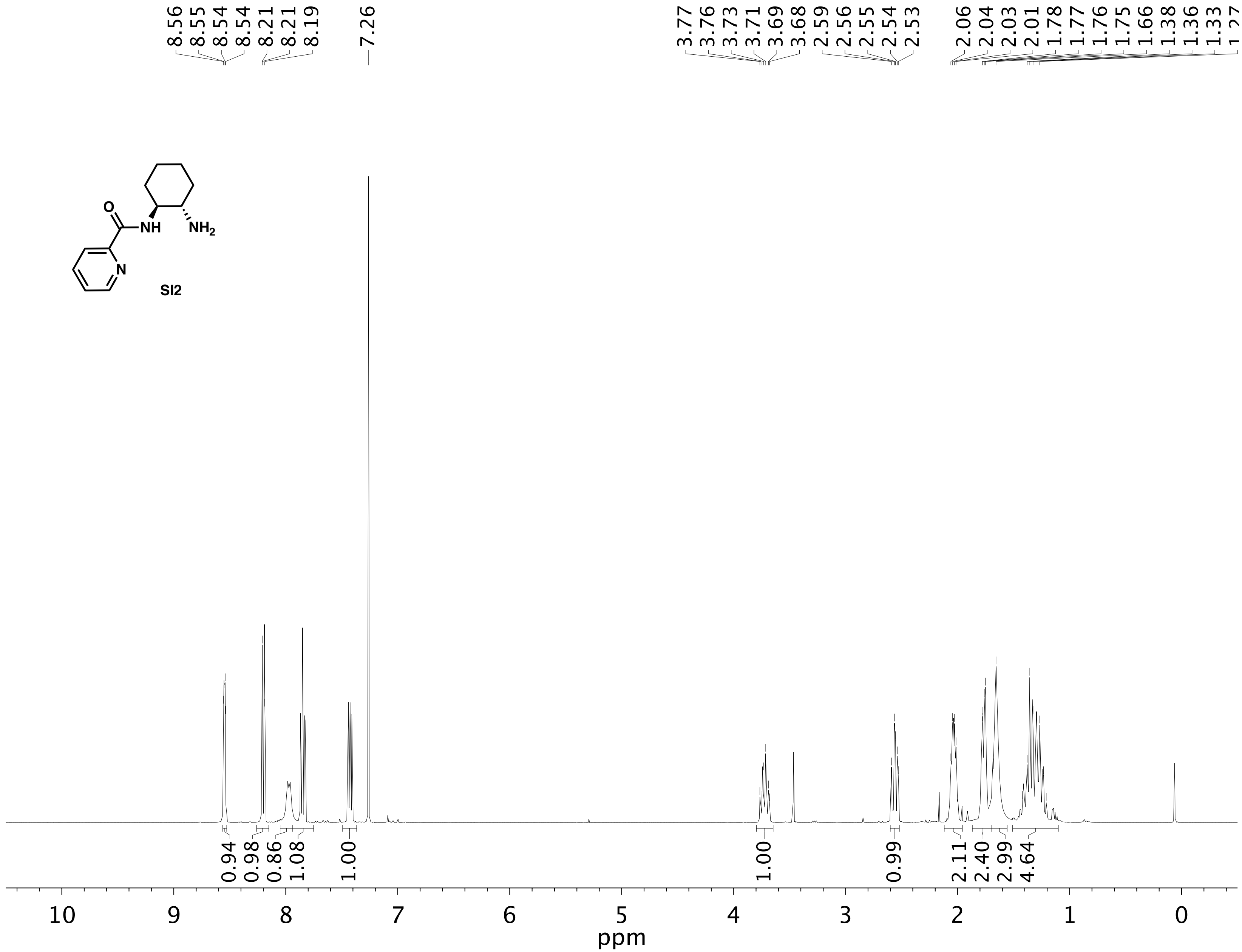
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L16**



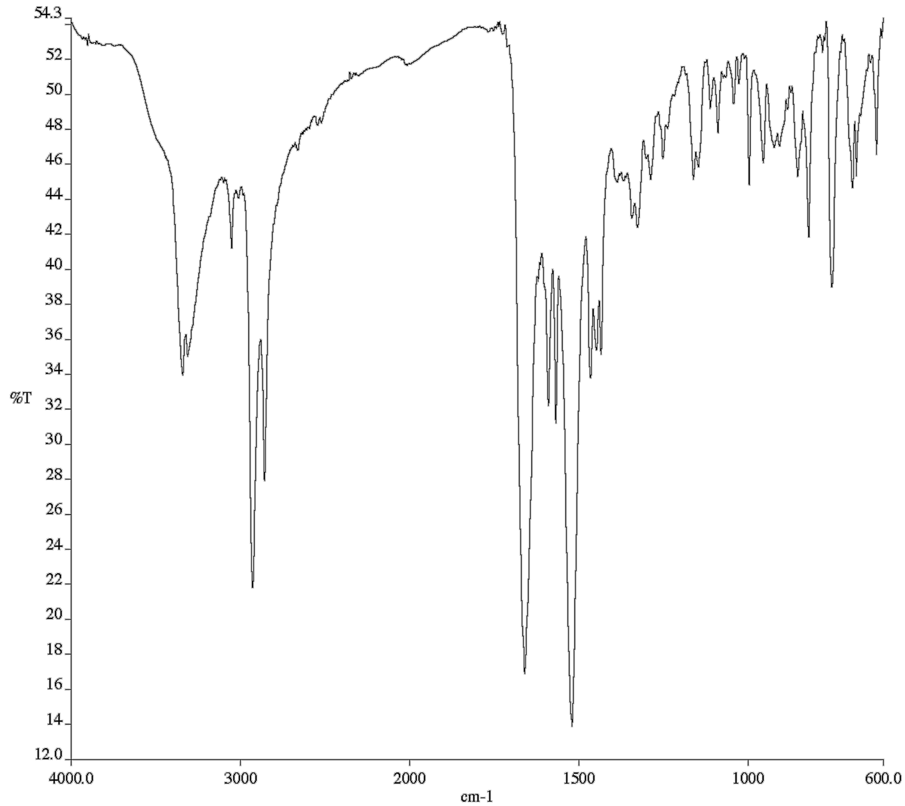
Infrared spectrum (Thin Film, NaCl) of compound **L16**



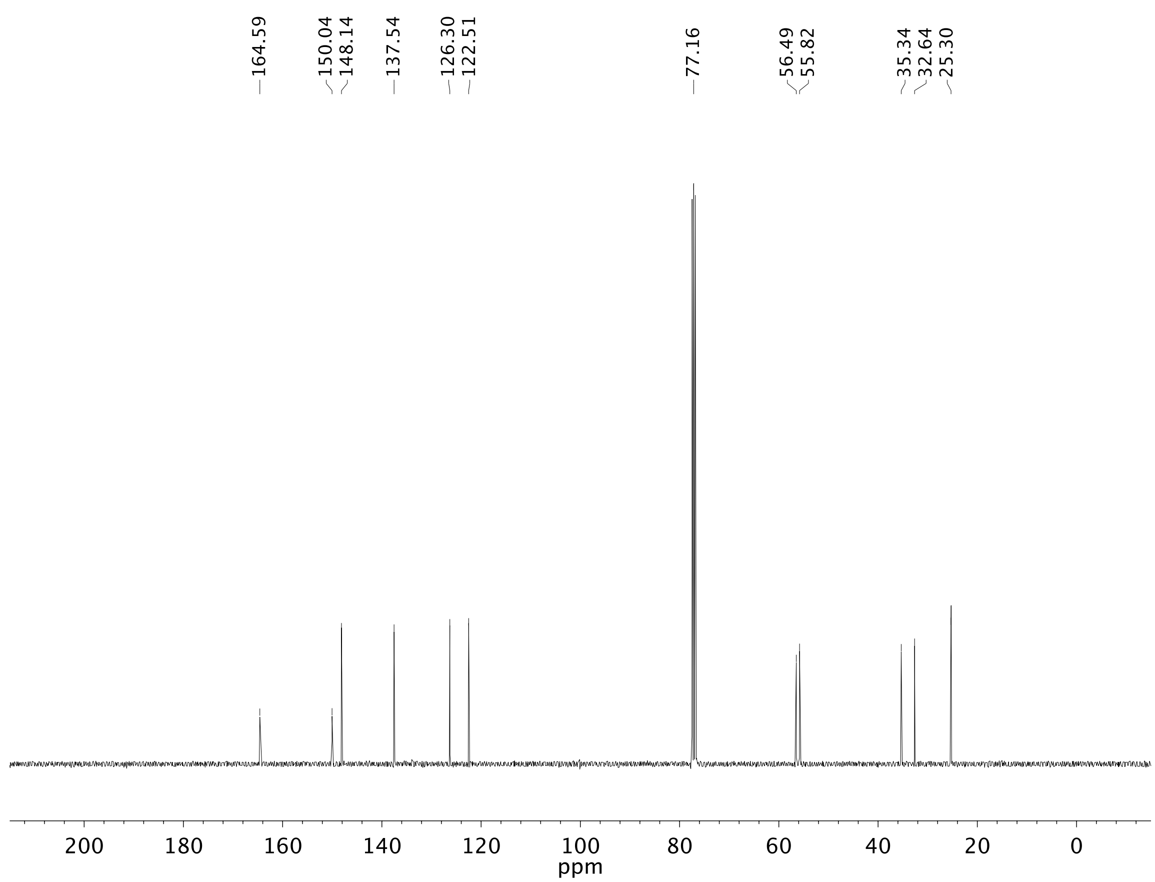
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L16**



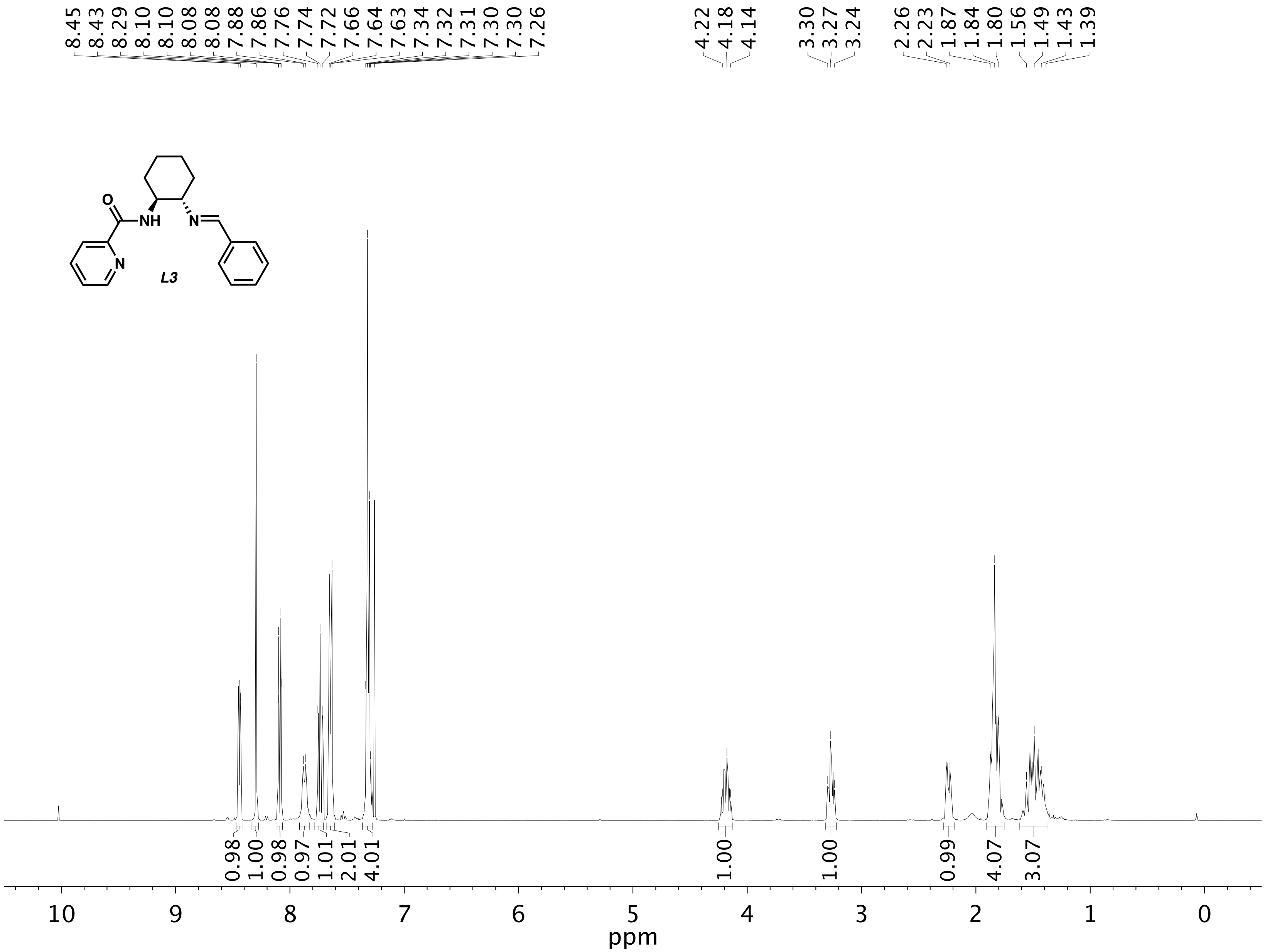
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI2**



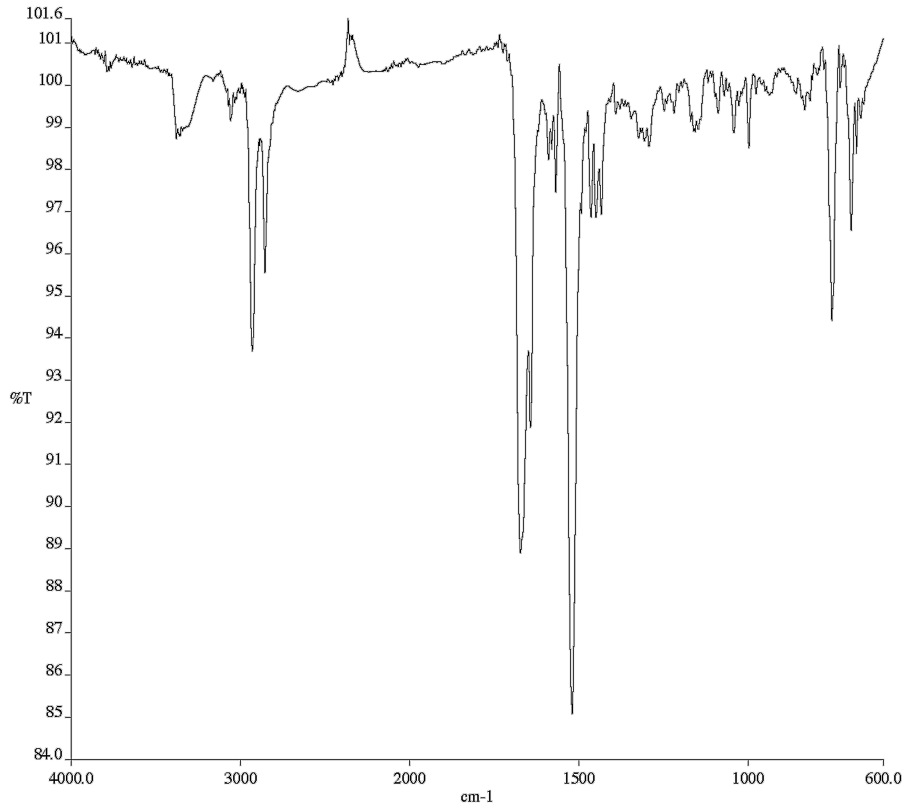
Infrared spectrum (Thin Film, NaCl) of compound **SI2**



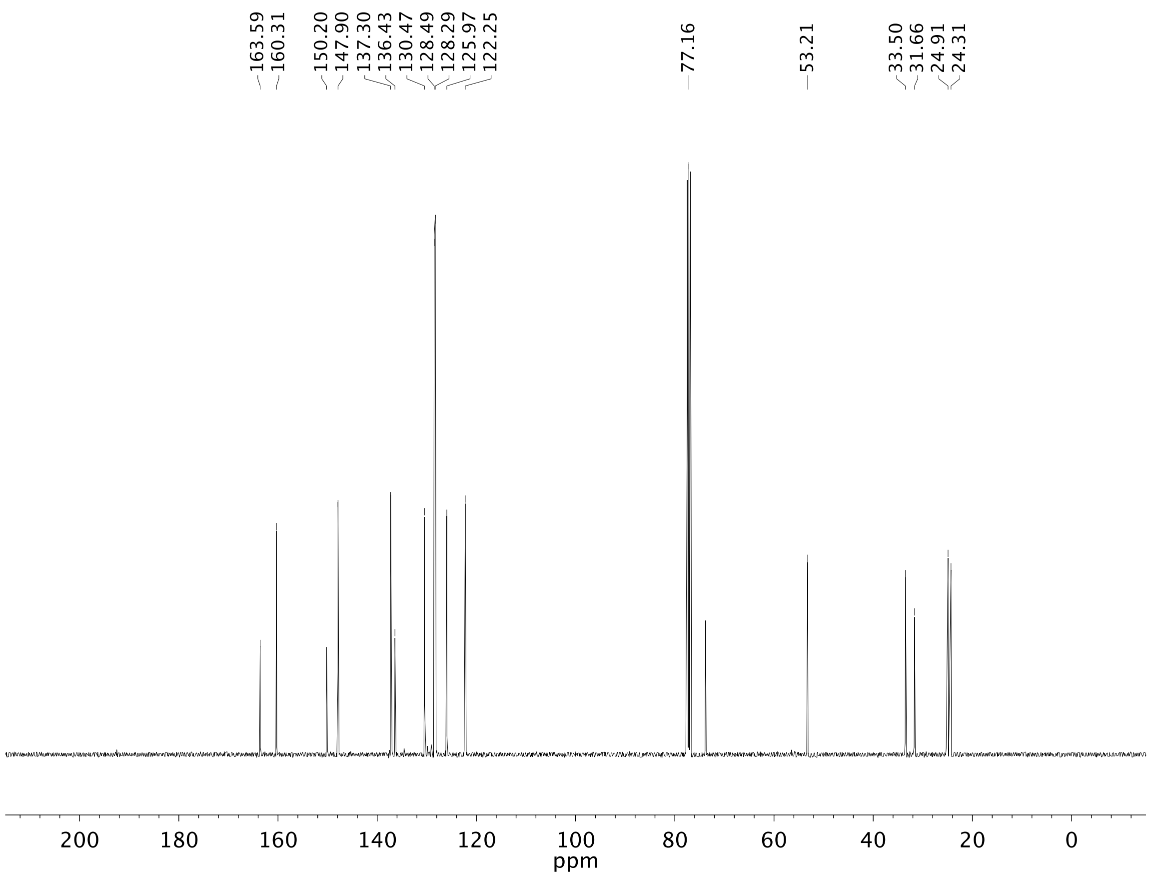
^{13}C NMR (101 MHz, $CDCl_3$) of compound **SI2**



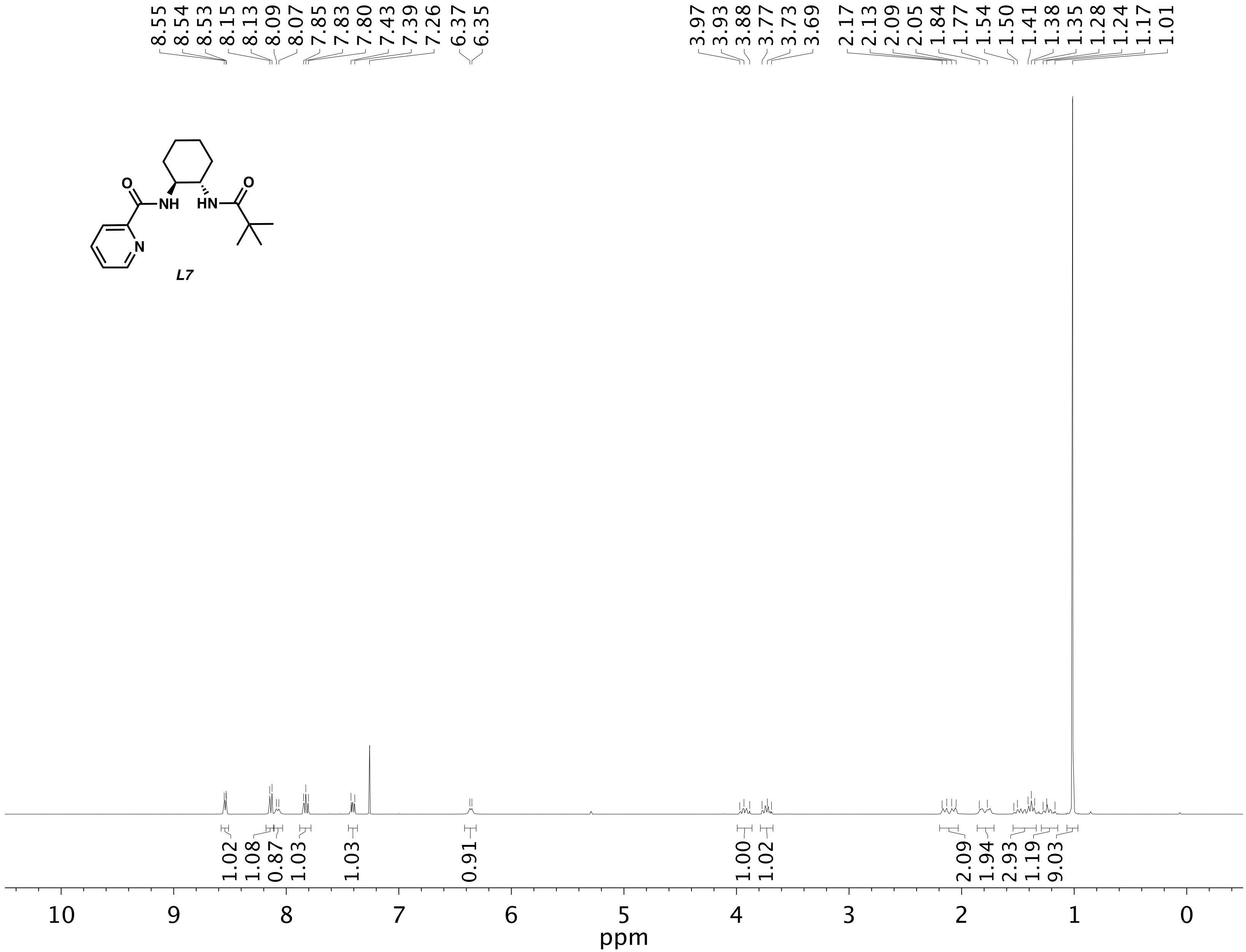
[1]H NMR (400 MHz, $CDCl_3$) of compound **L3**



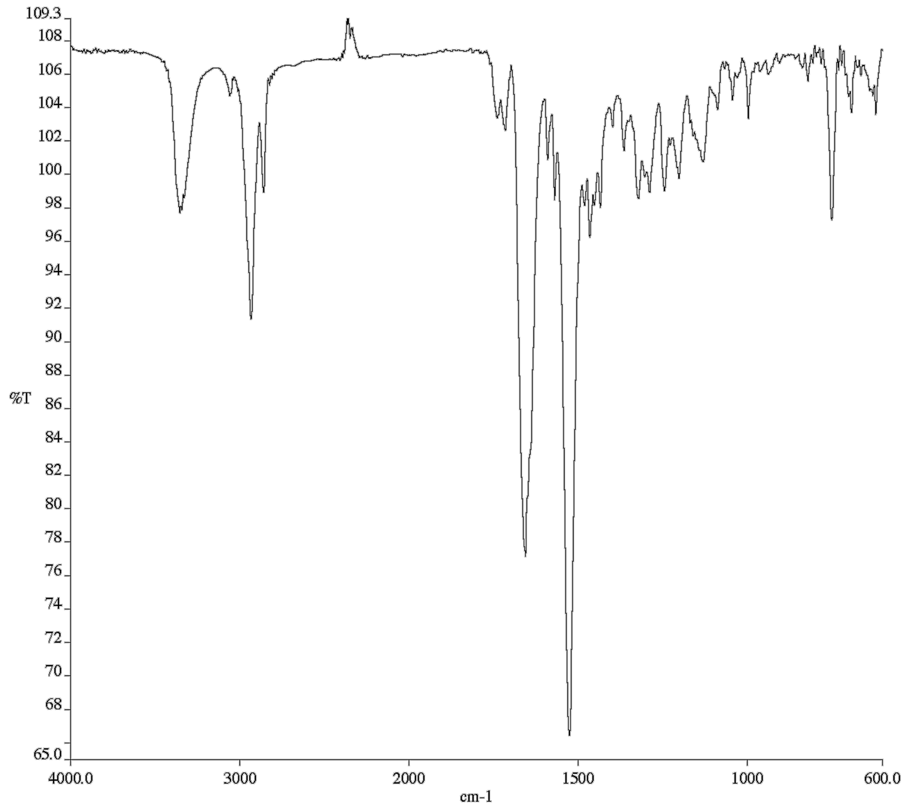
Infrared spectrum (Thin Film, NaCl) of compound **L3**



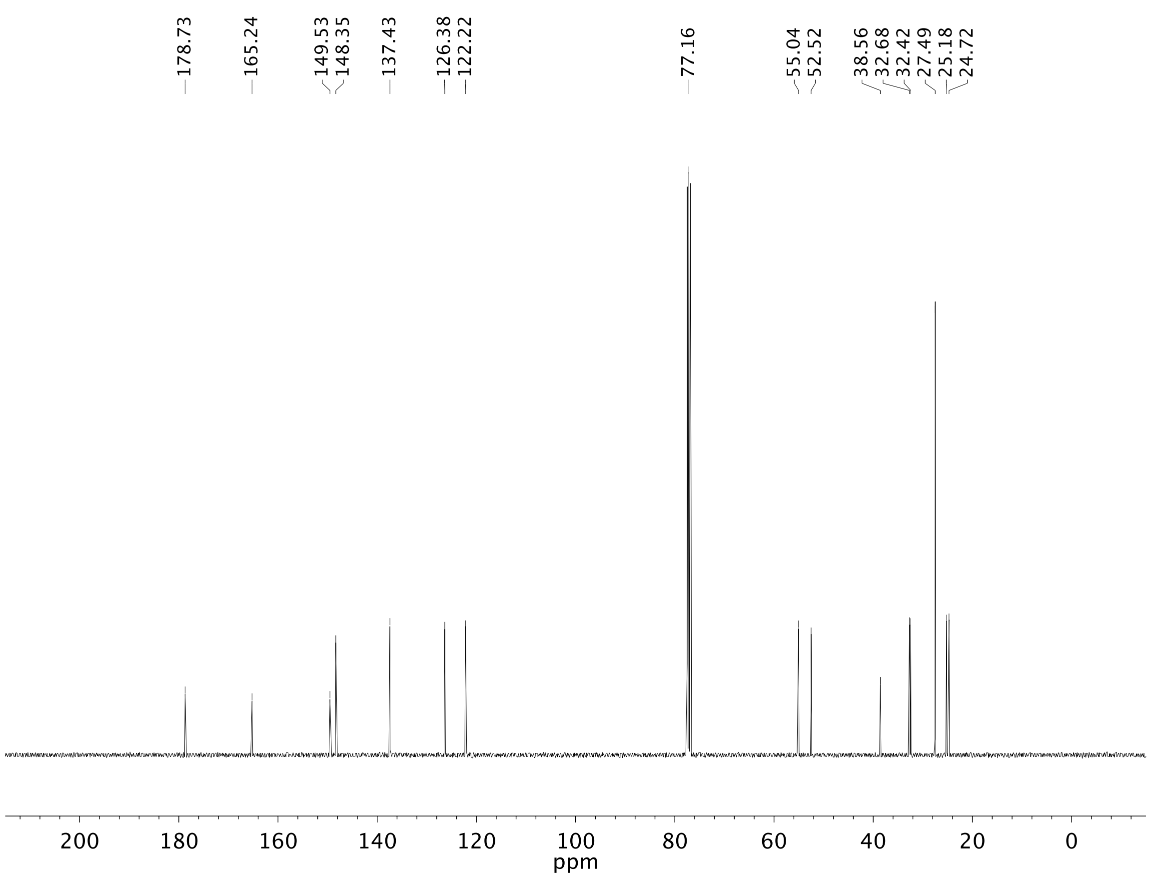
^{13}C NMR (100 MHz, $CDCl_3$) of compound **L3**



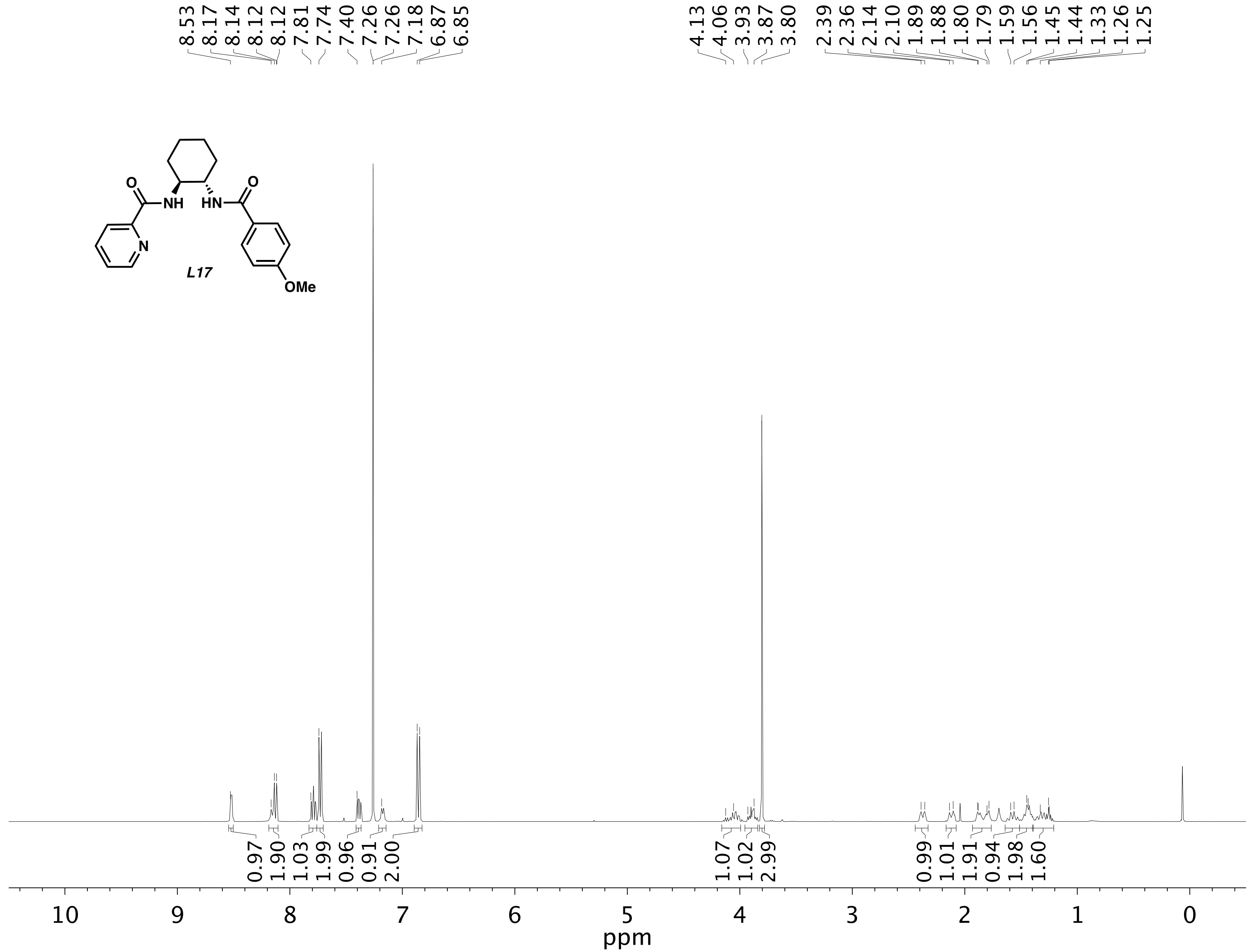
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L7**



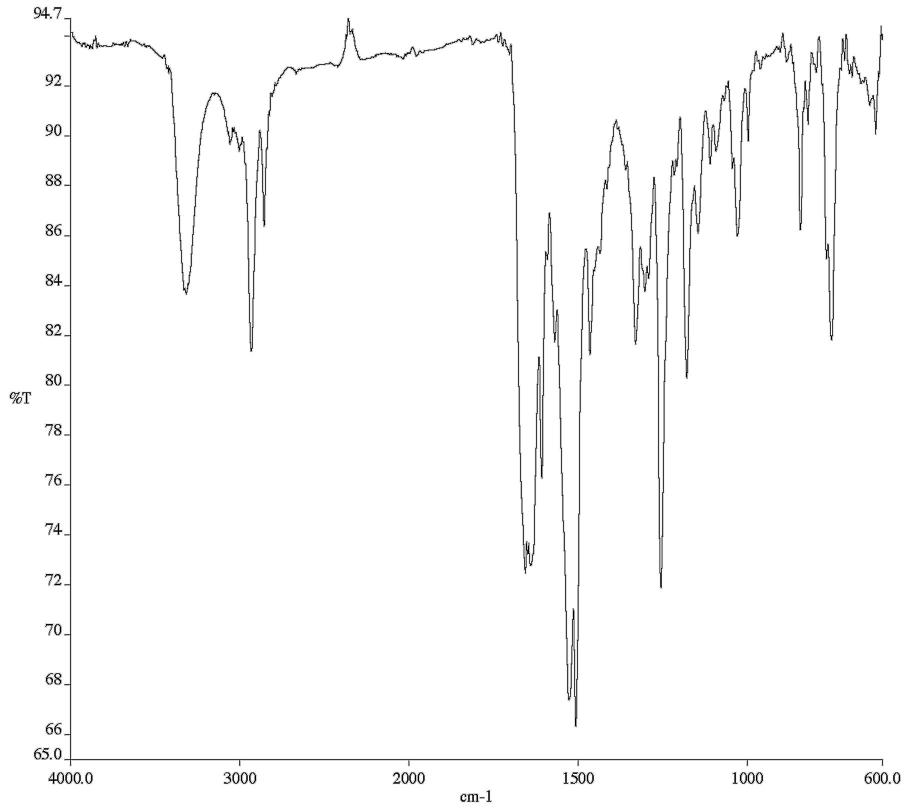
Infrared spectrum (Thin Film, NaCl) of compound **L7**



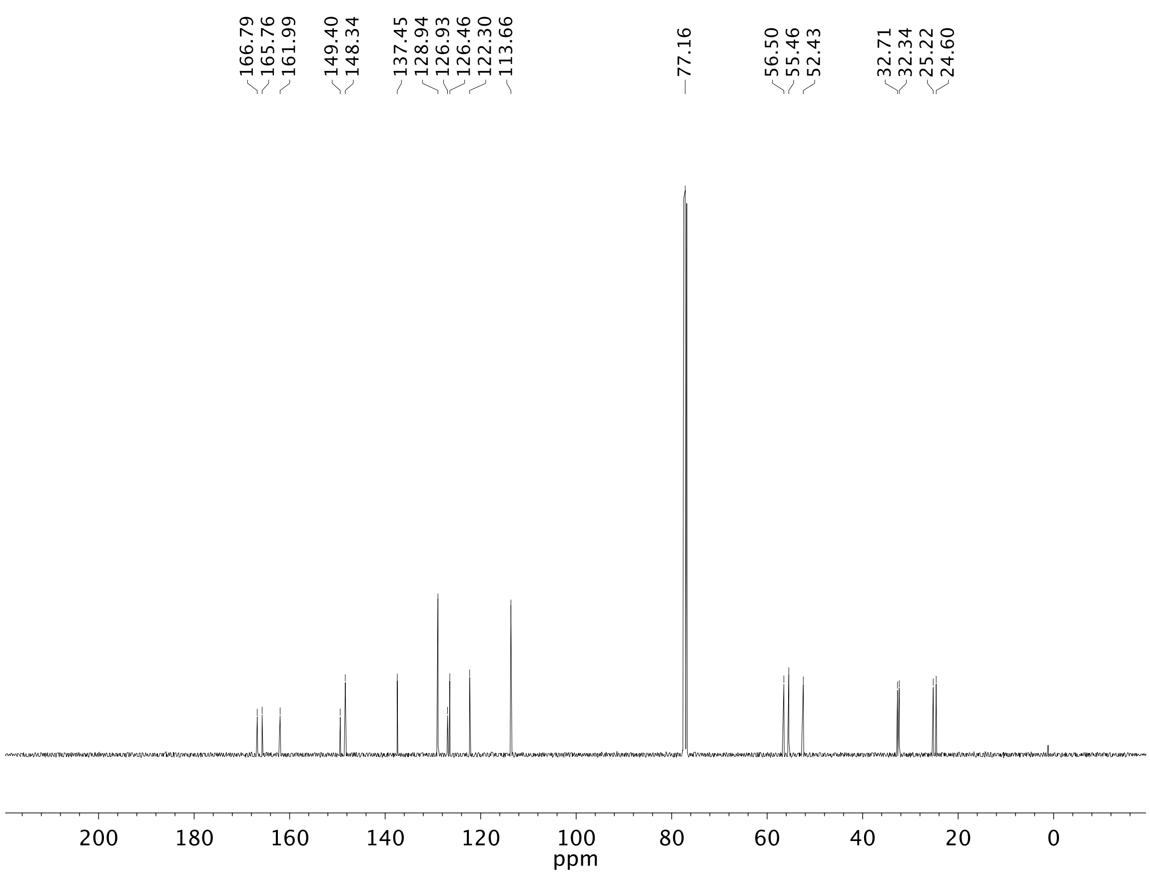
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L7**



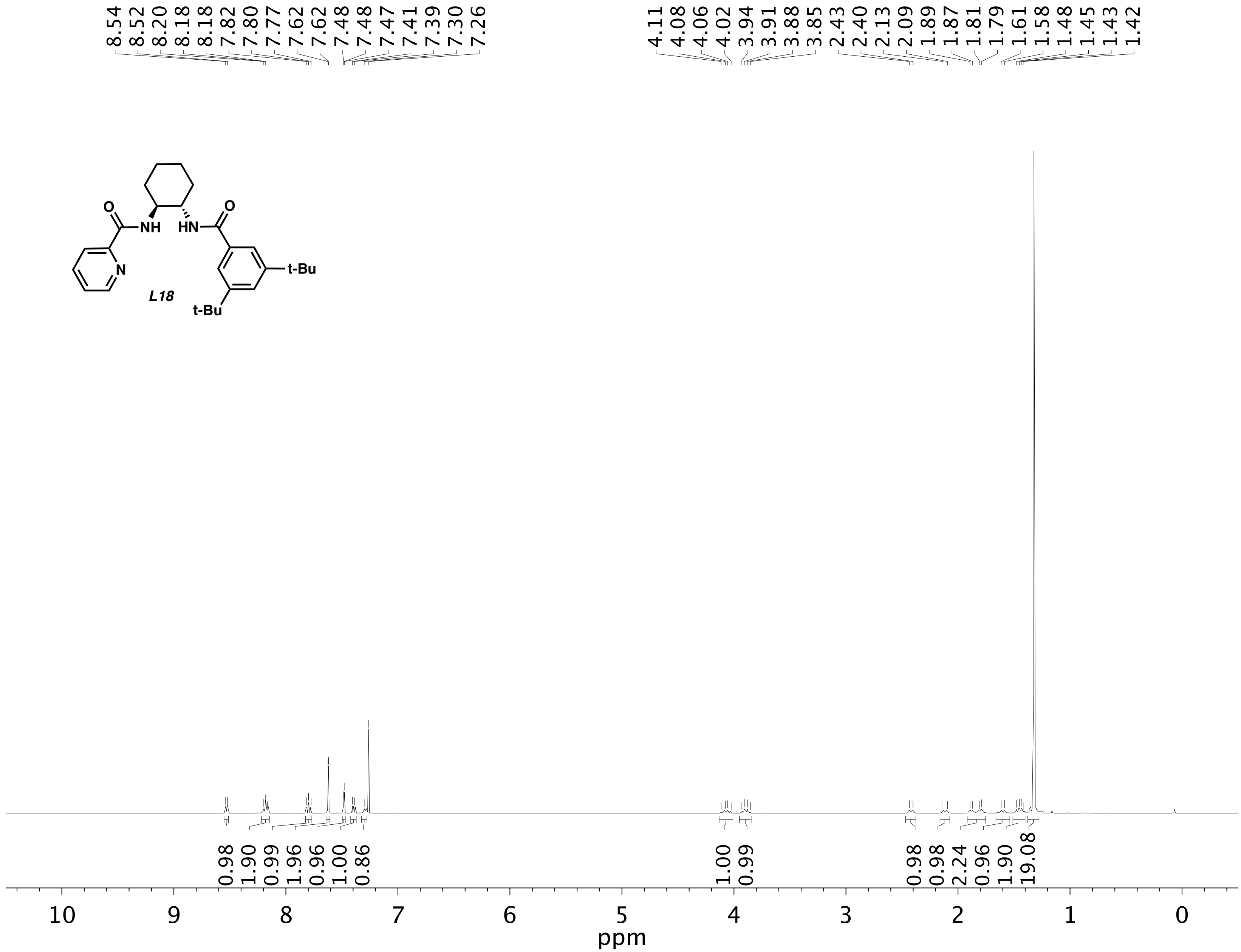
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L17**



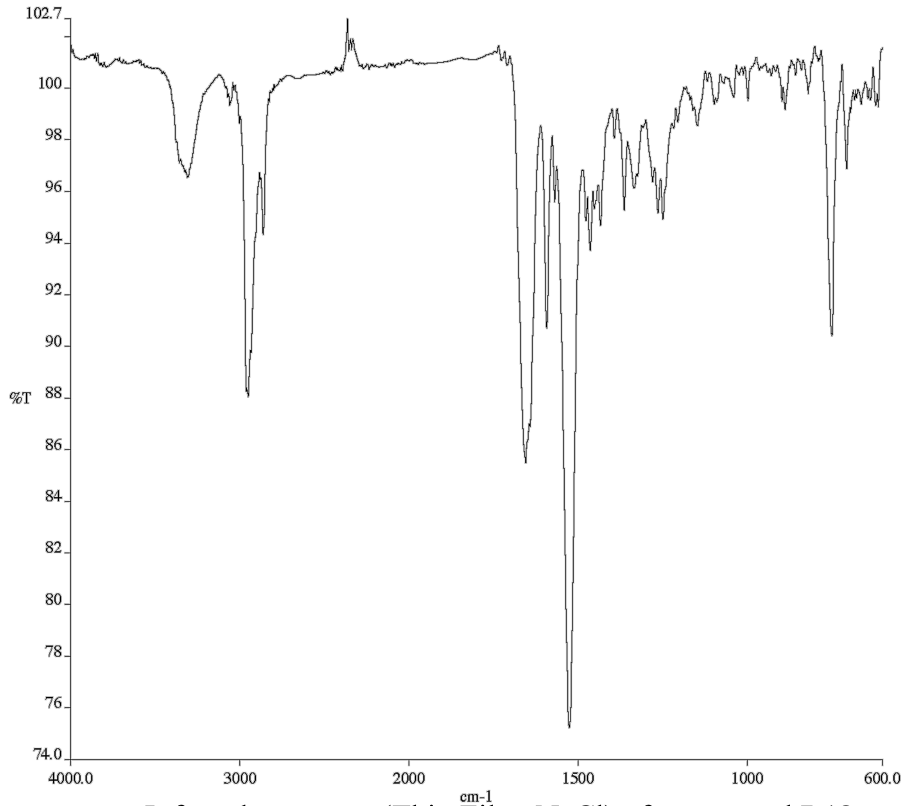
Infrared spectrum (Thin Film, NaCl) of compound **L17**.



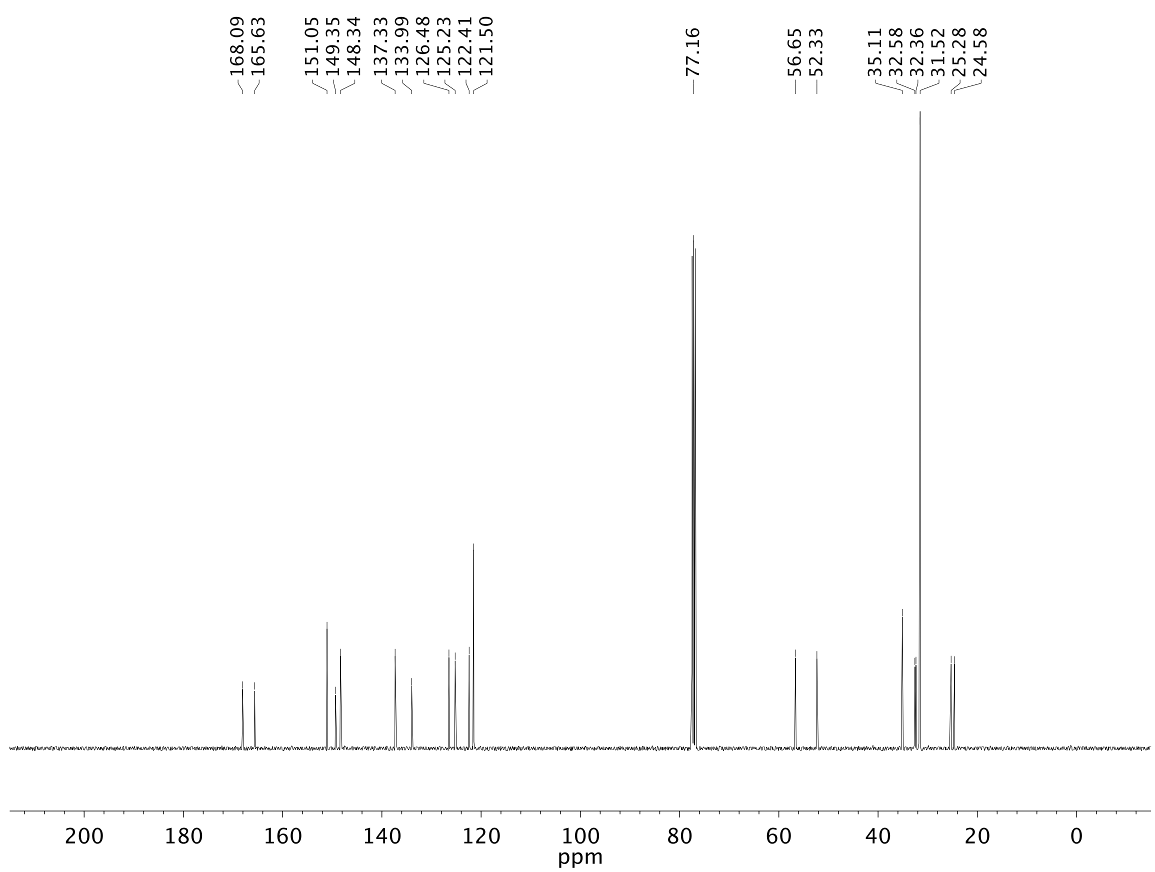
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L17**



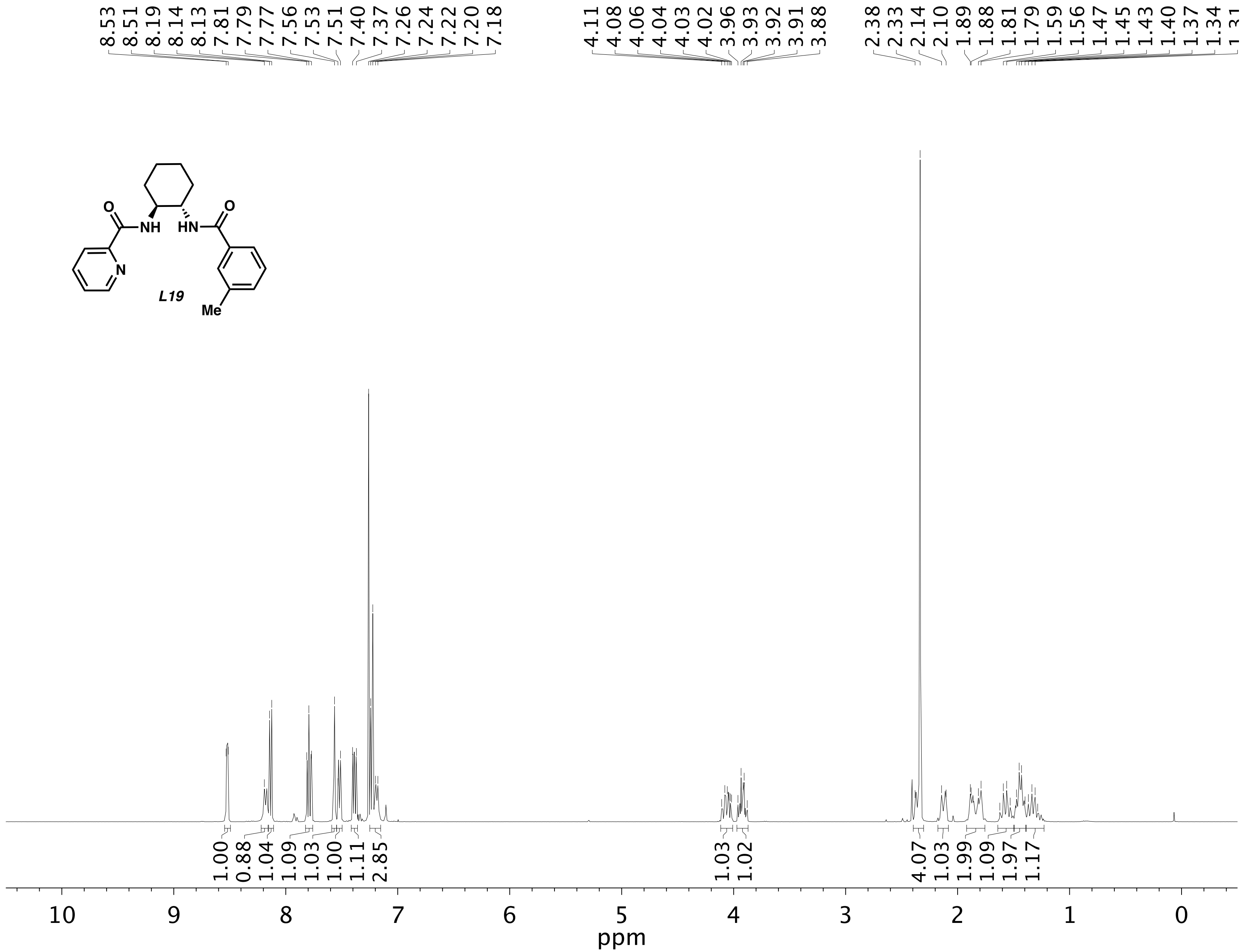
[1]H NMR (400 MHz, $CDCl_3$) of compound **L18**



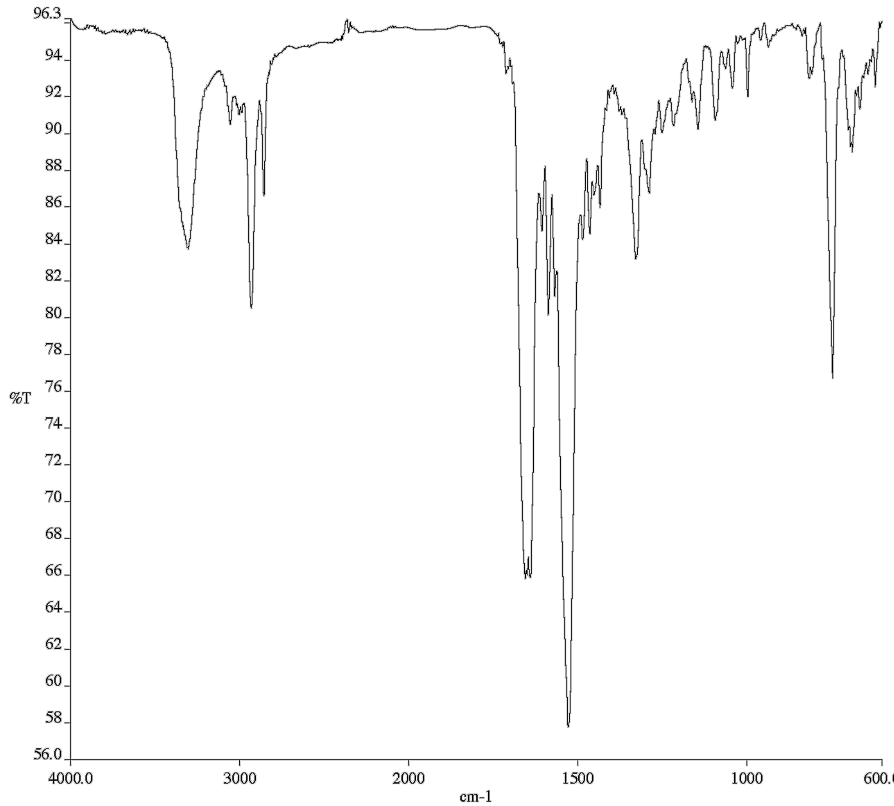
Infrared spectrum (Thin Film, NaCl) of compound **L18**.



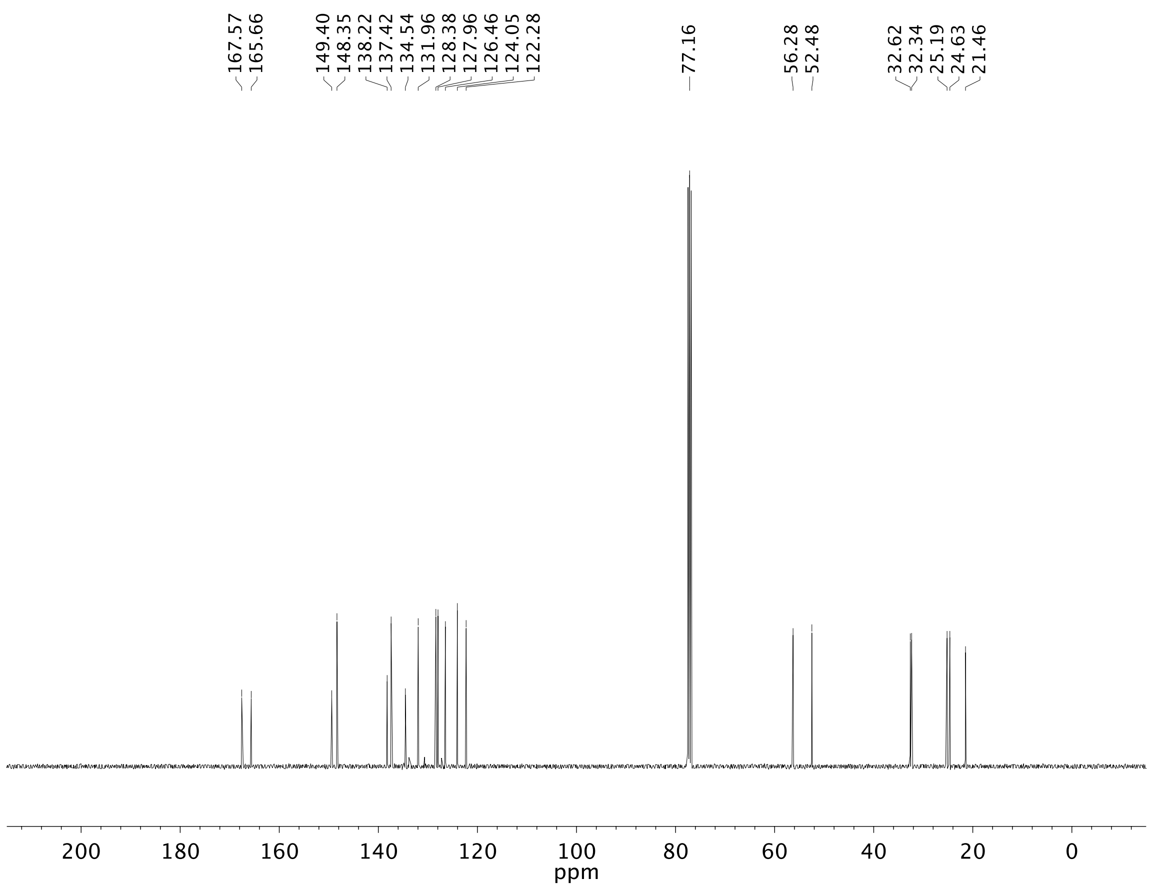
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L18**



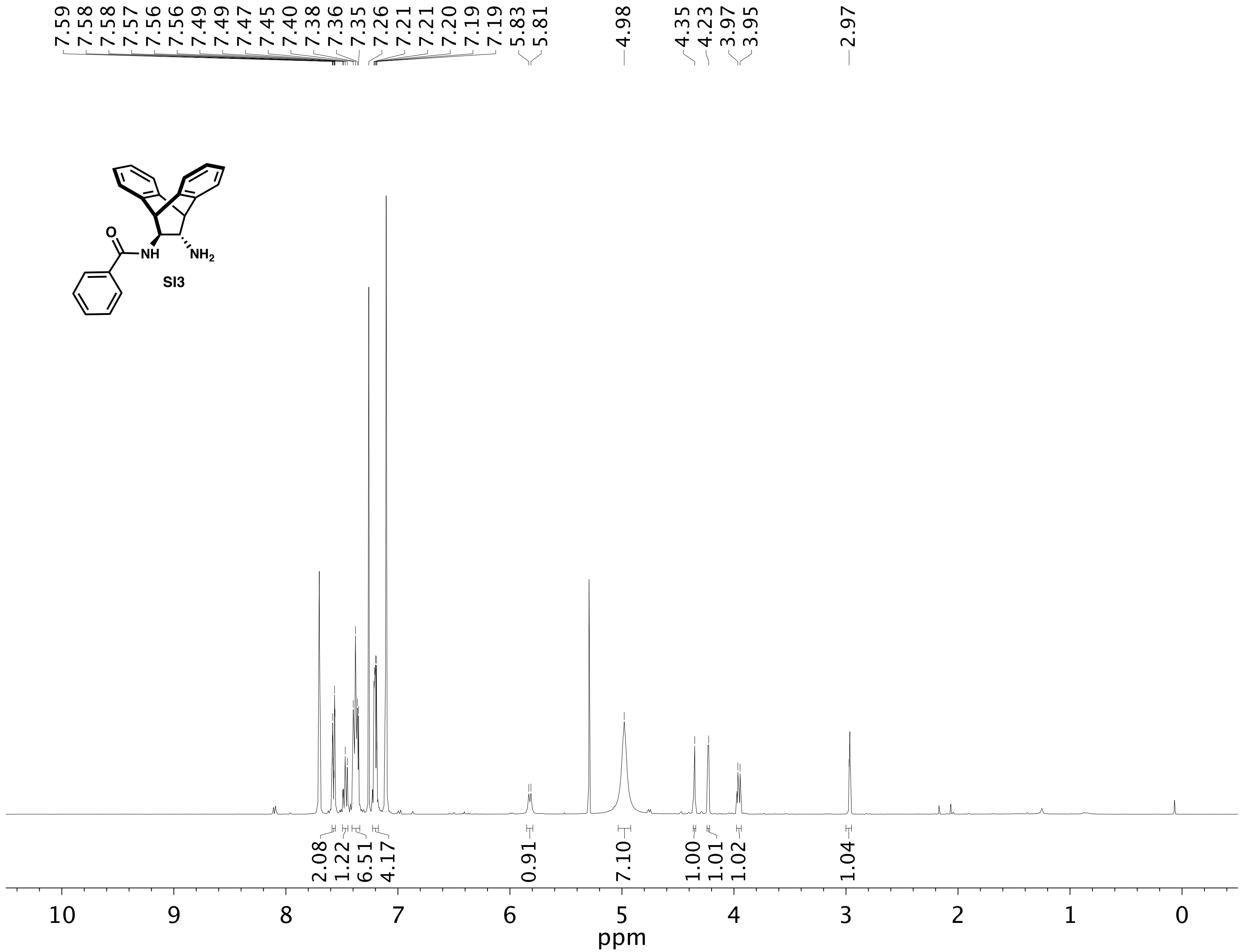
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L19**



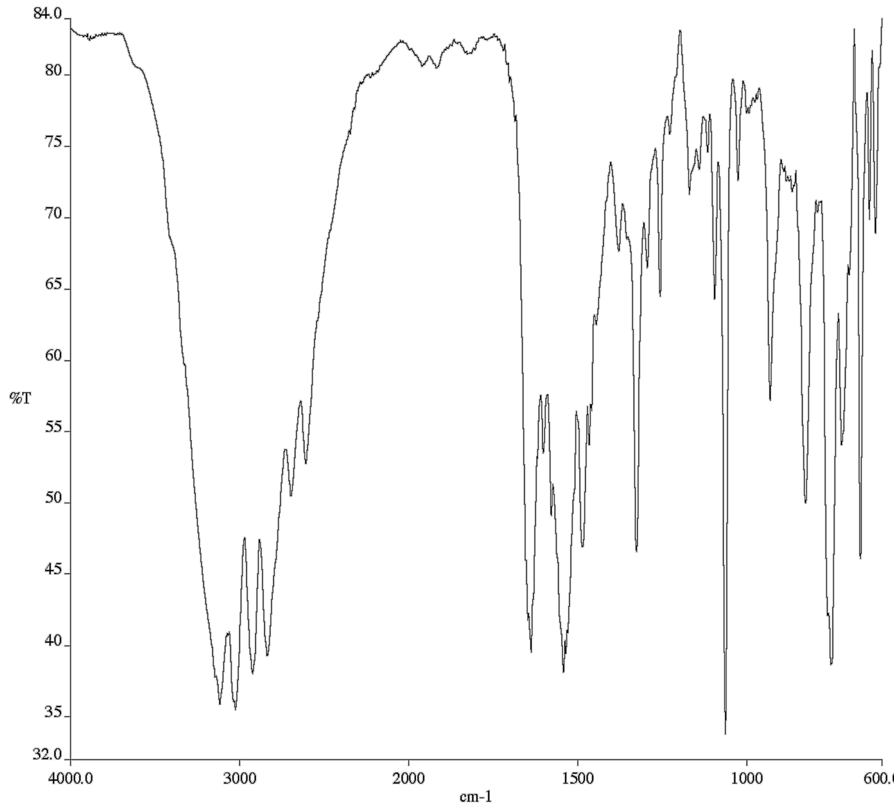
Infrared spectrum (Thin Film, NaCl) of compound **L19**



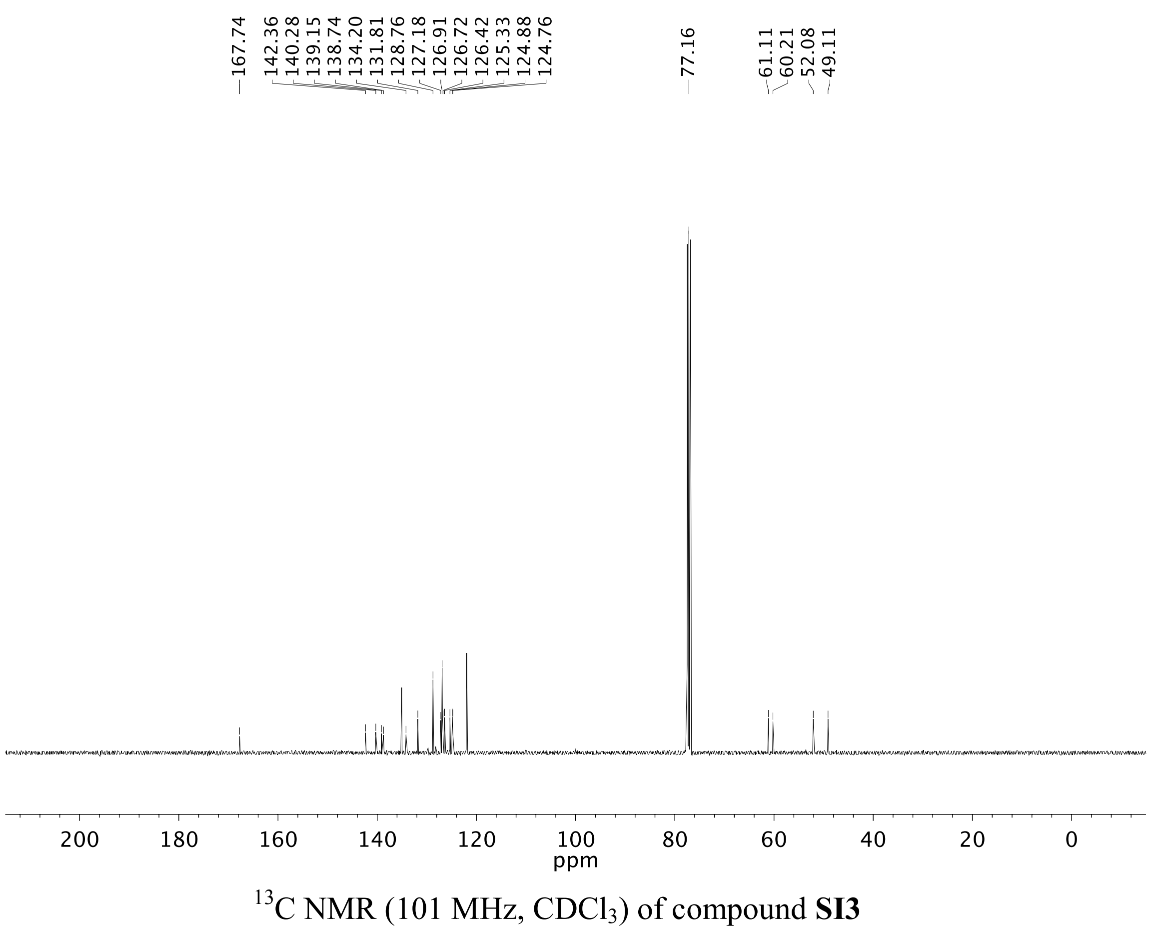
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L19**



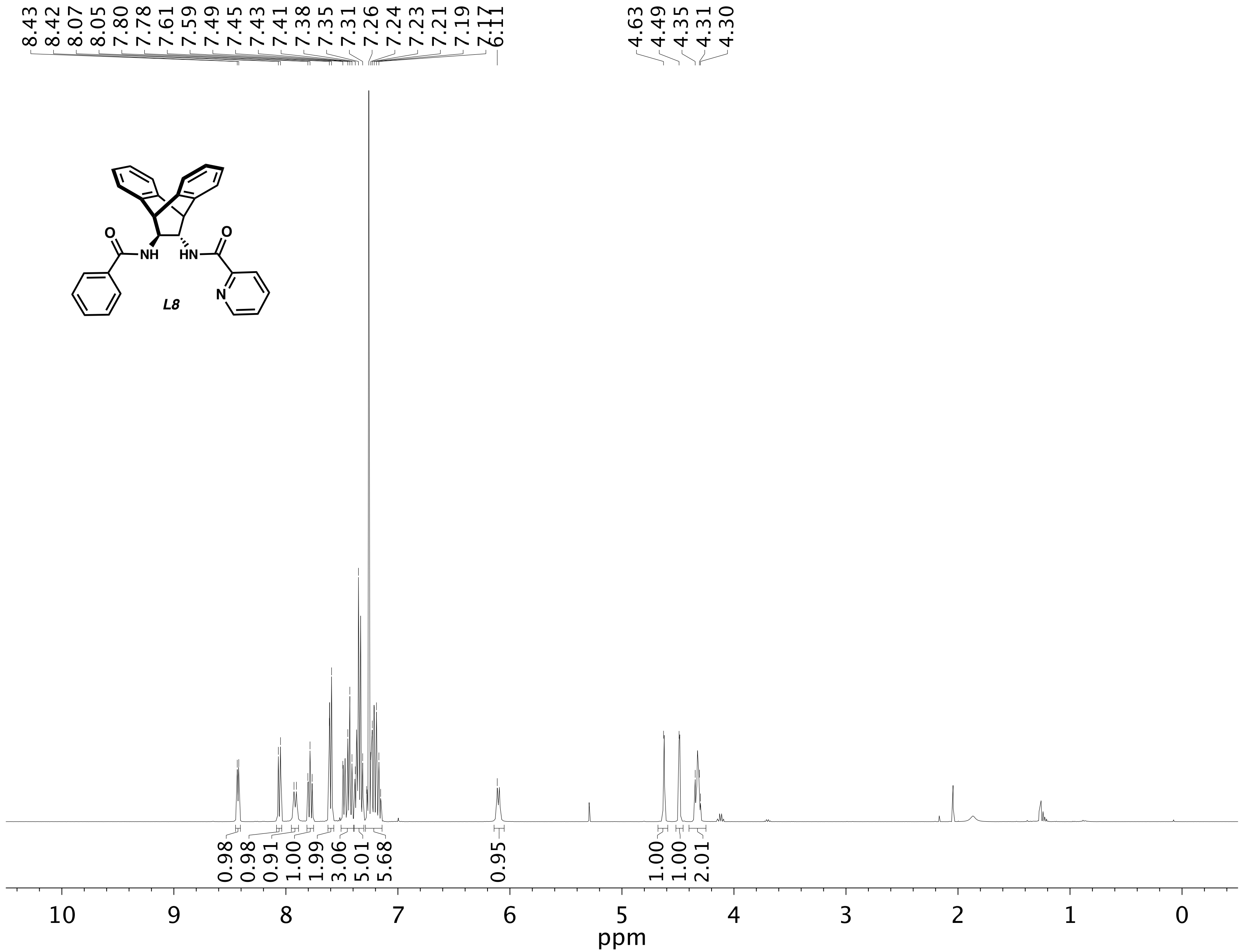
^{1}H NMR (300 MHz, $CDCl_3$) of compound **SI3**



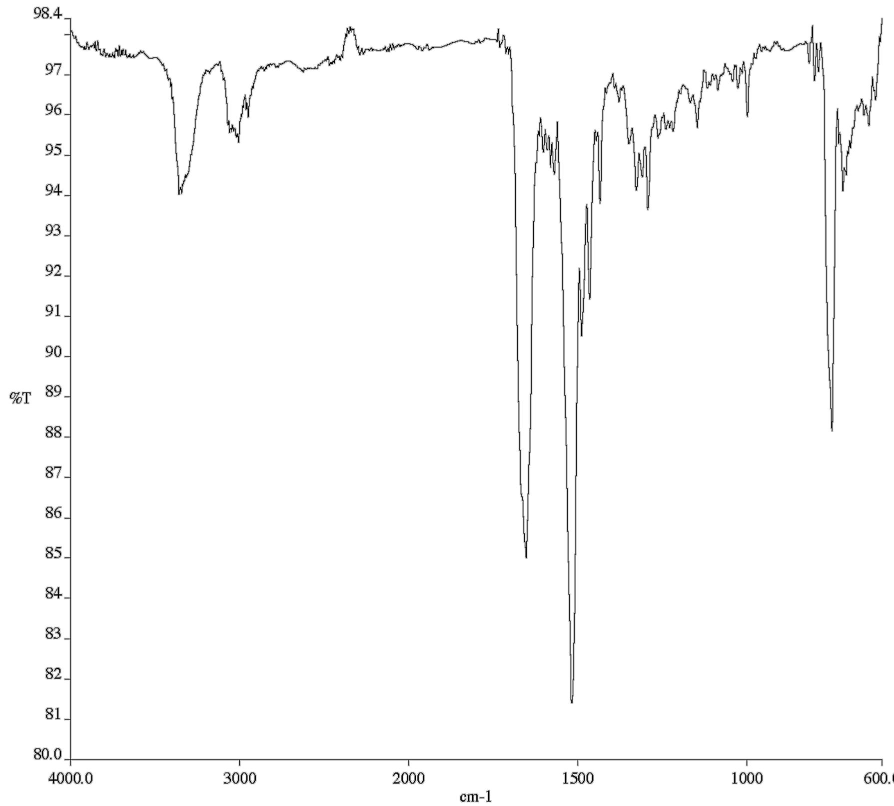
Infrared spectrum (Thin Film, NaCl) of compound **SI3**.



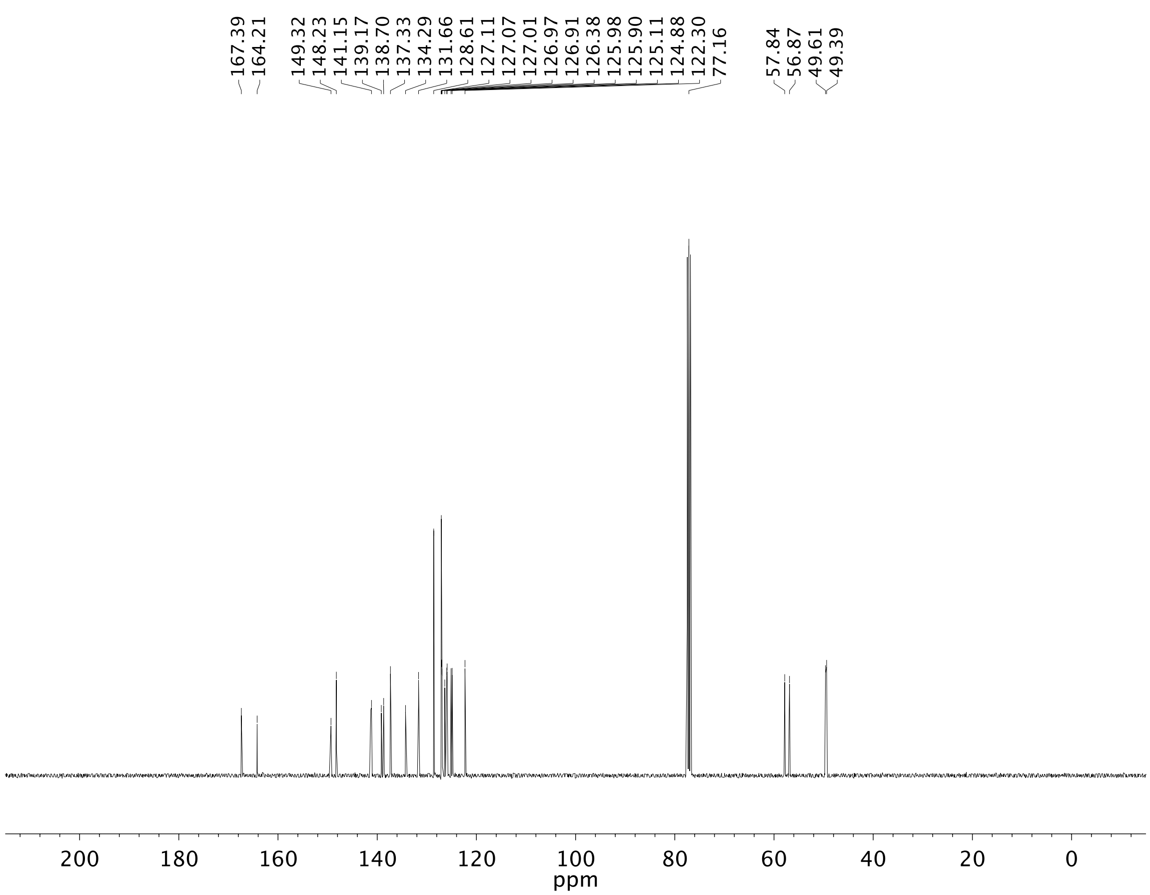
^{13}C NMR (101 MHz, $CDCl_3$) of compound **SI3**



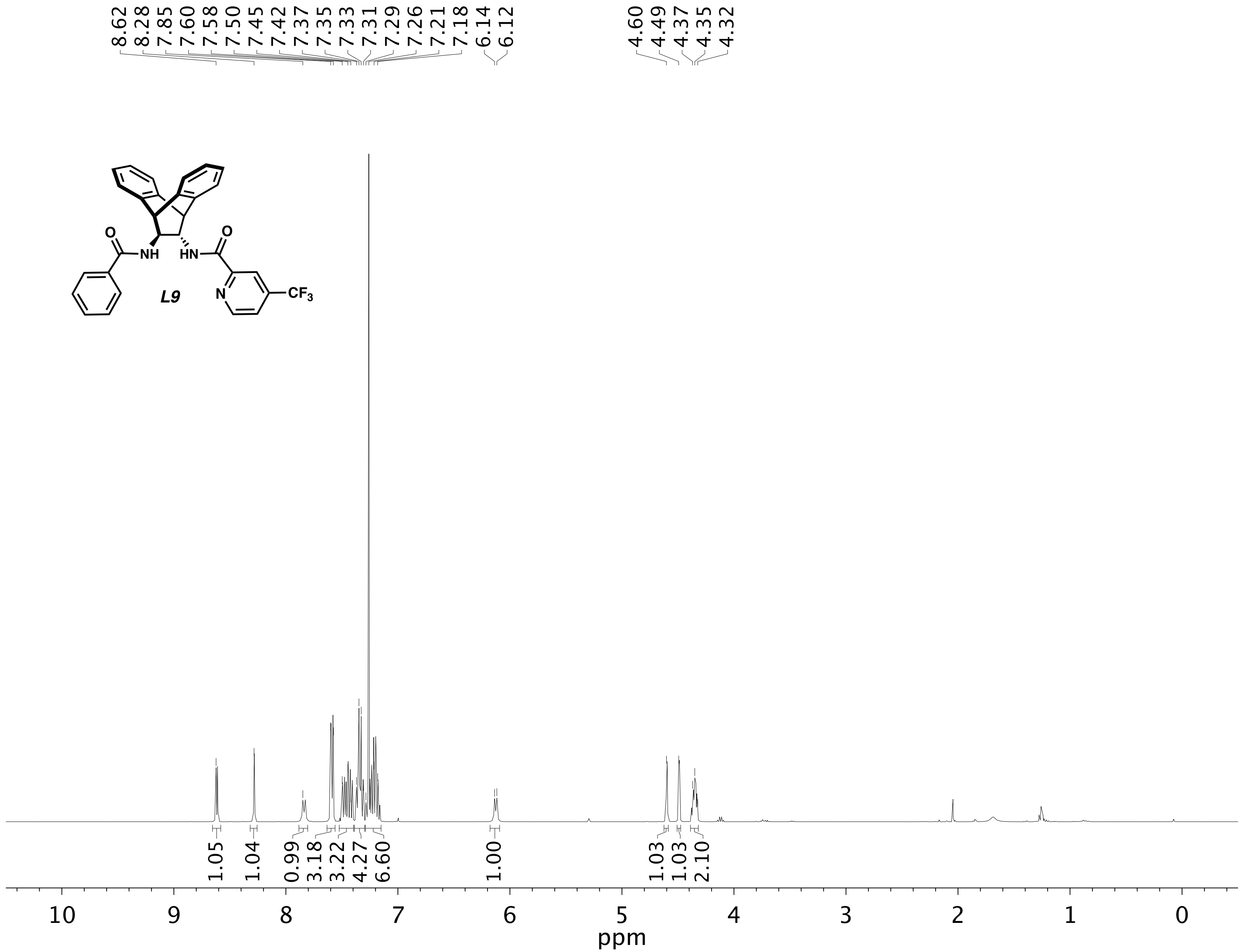
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L8**



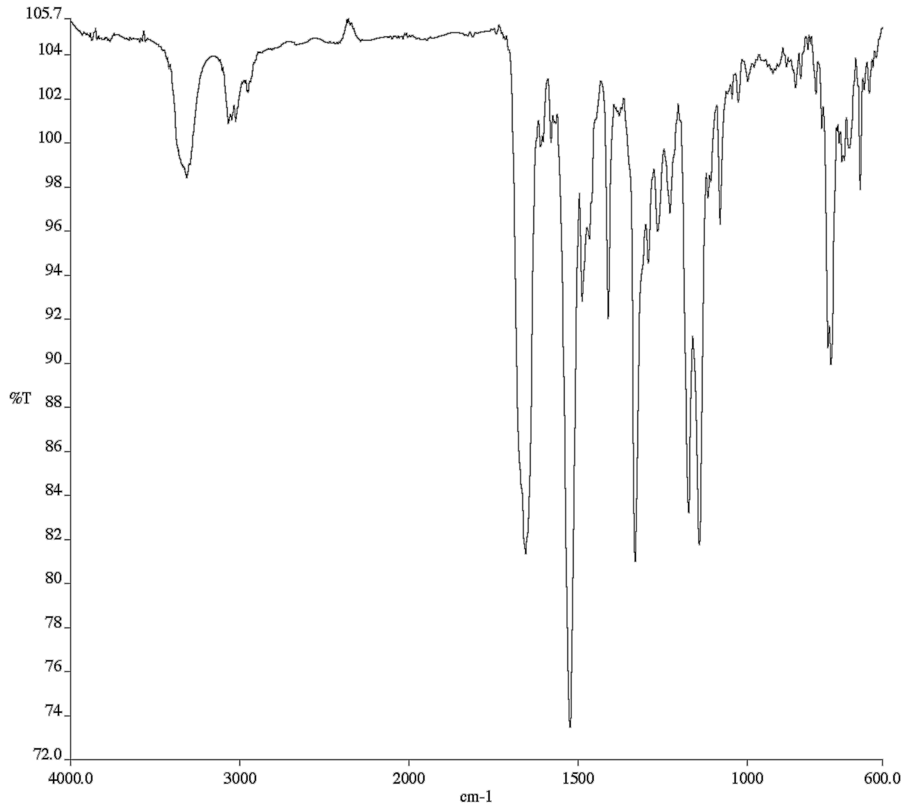
Infrared spectrum (Thin Film, NaCl) of compound **L8**.



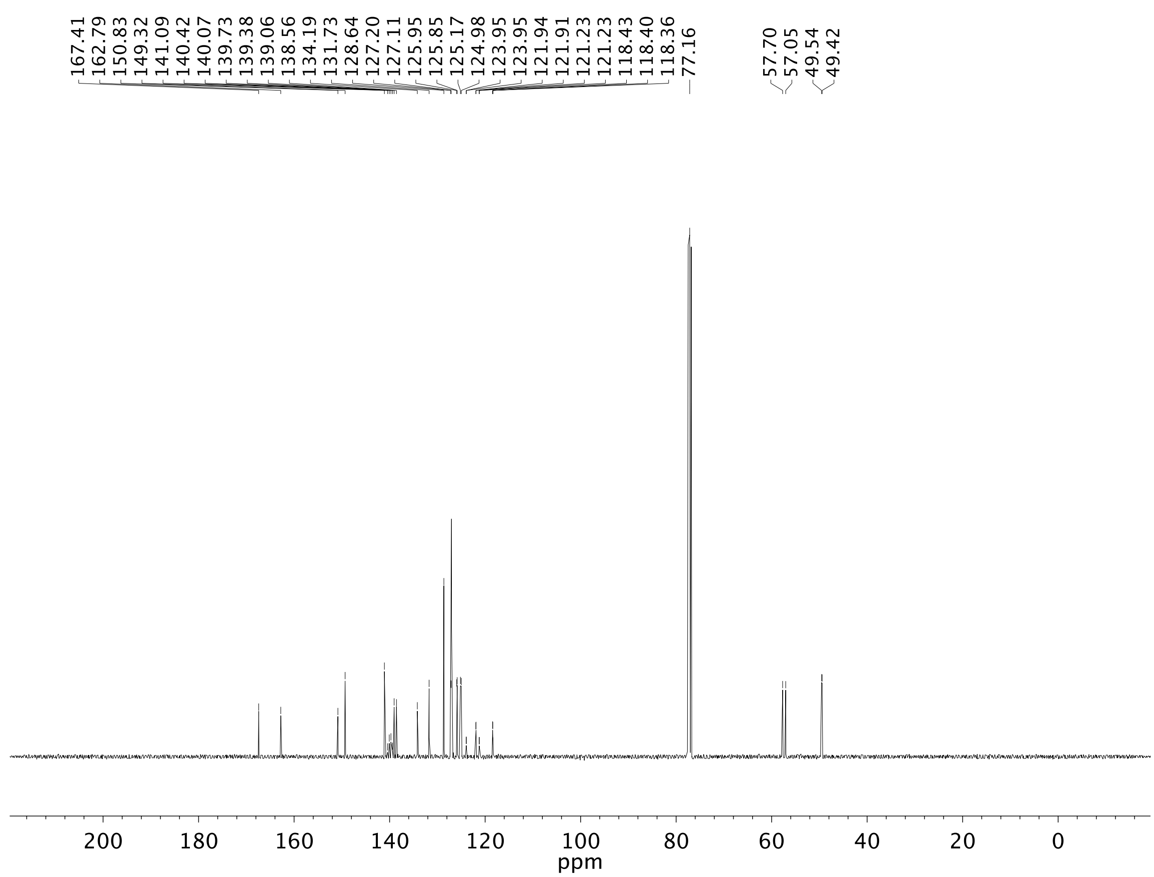
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L8**



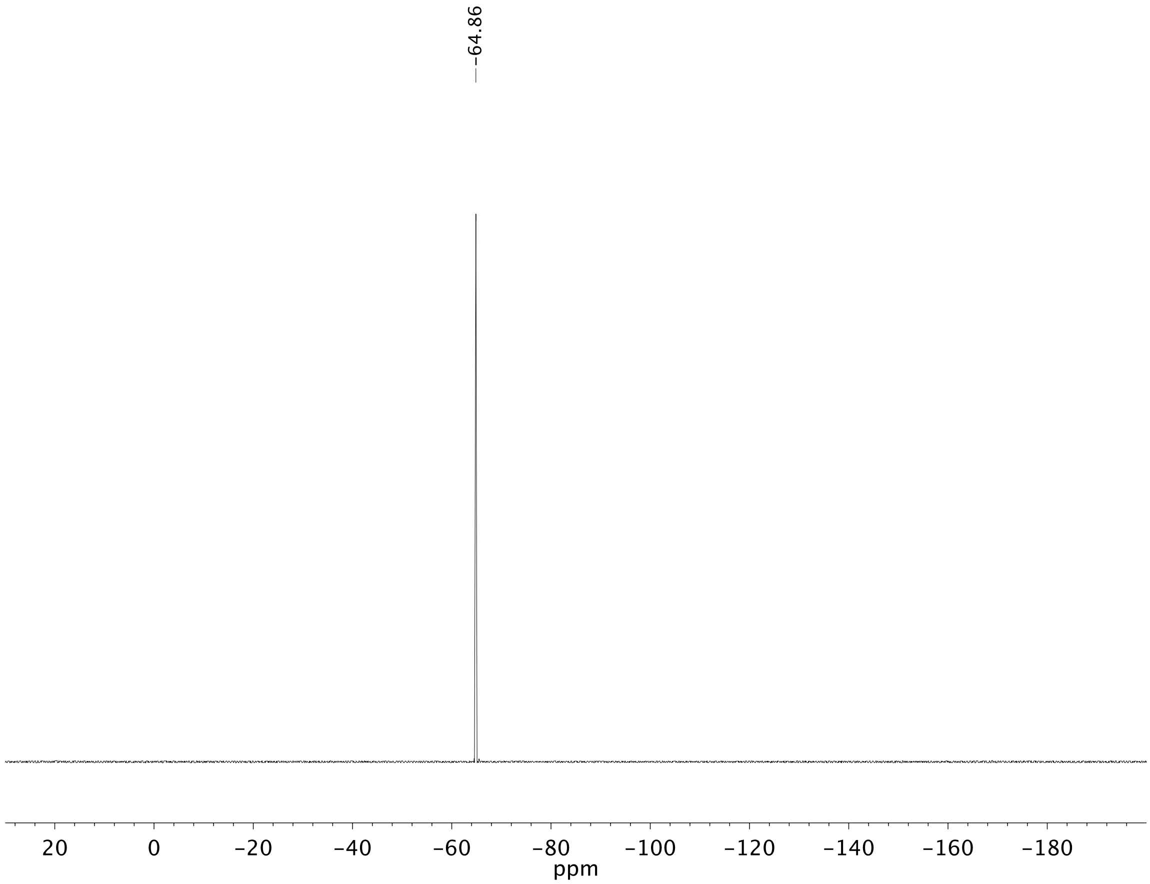
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L9**



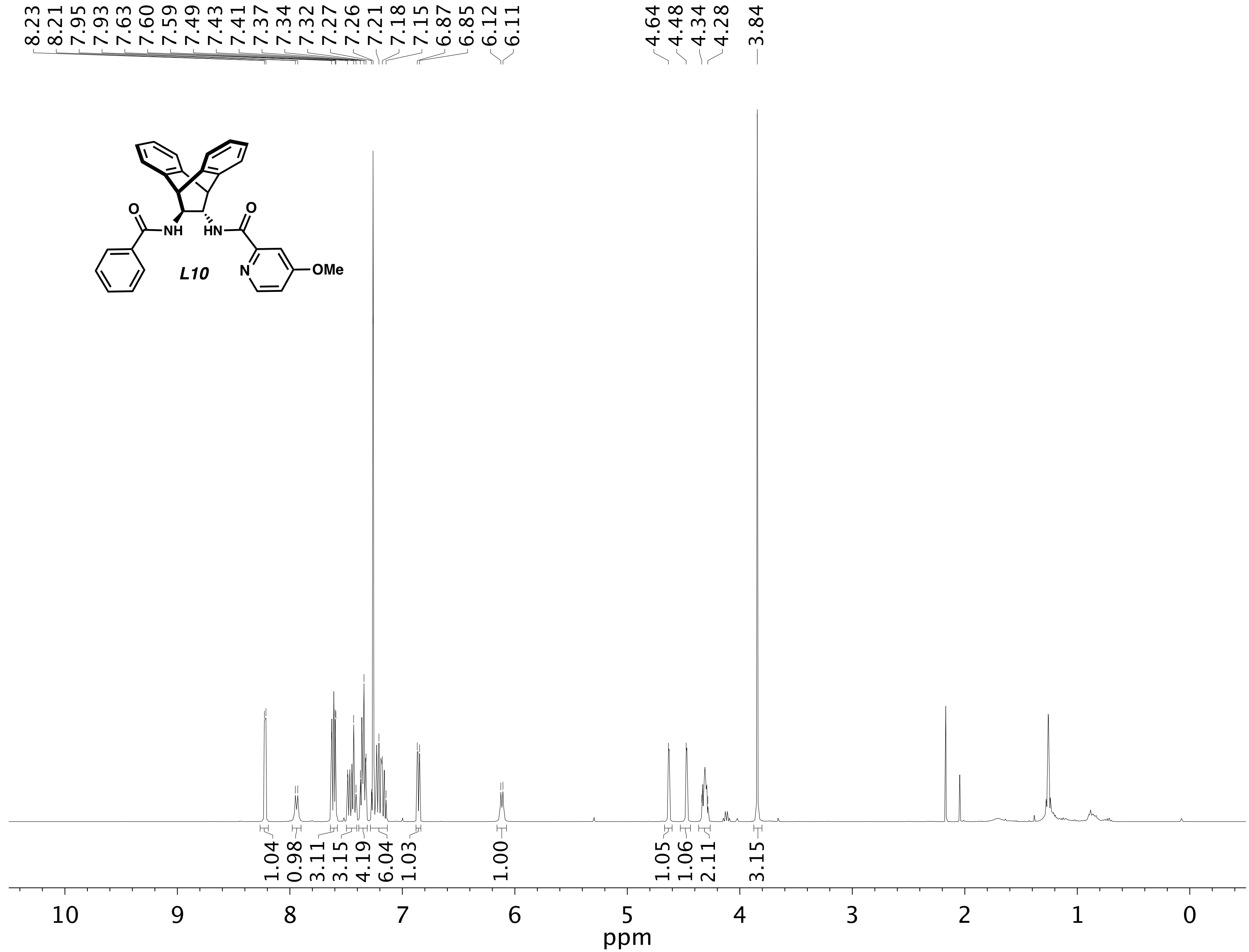
Infrared spectrum (Thin Film, NaCl) of compound **L9**



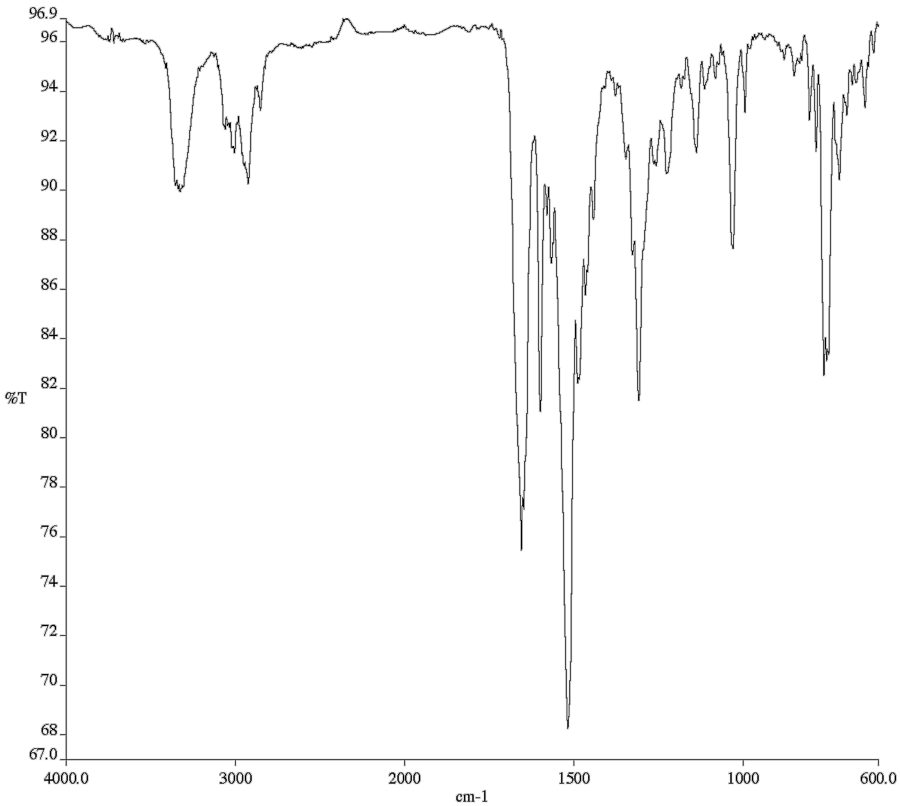
^{13}C NMR (101 MHz, CDCl$_3$) of compound **L9**



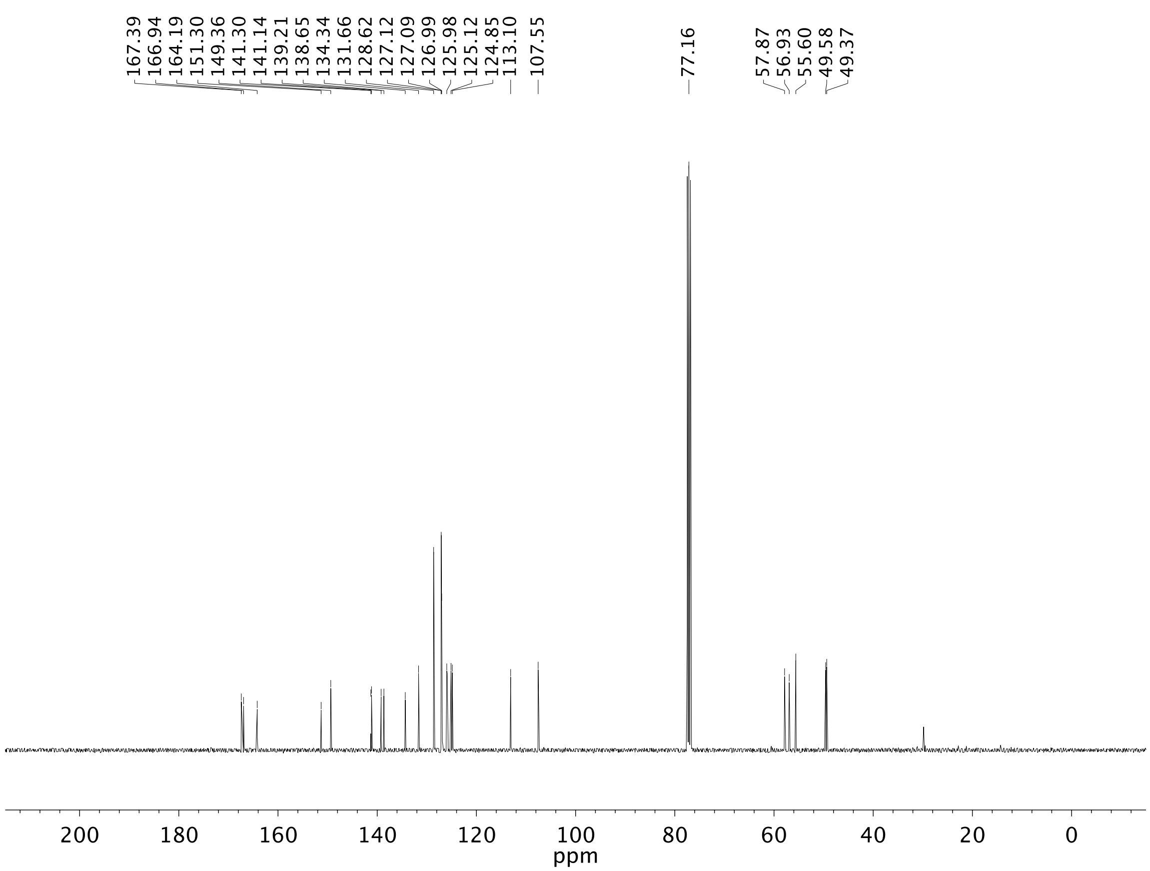
^{19}F NMR (282 MHz, $CDCl_3$) of compound **L9**



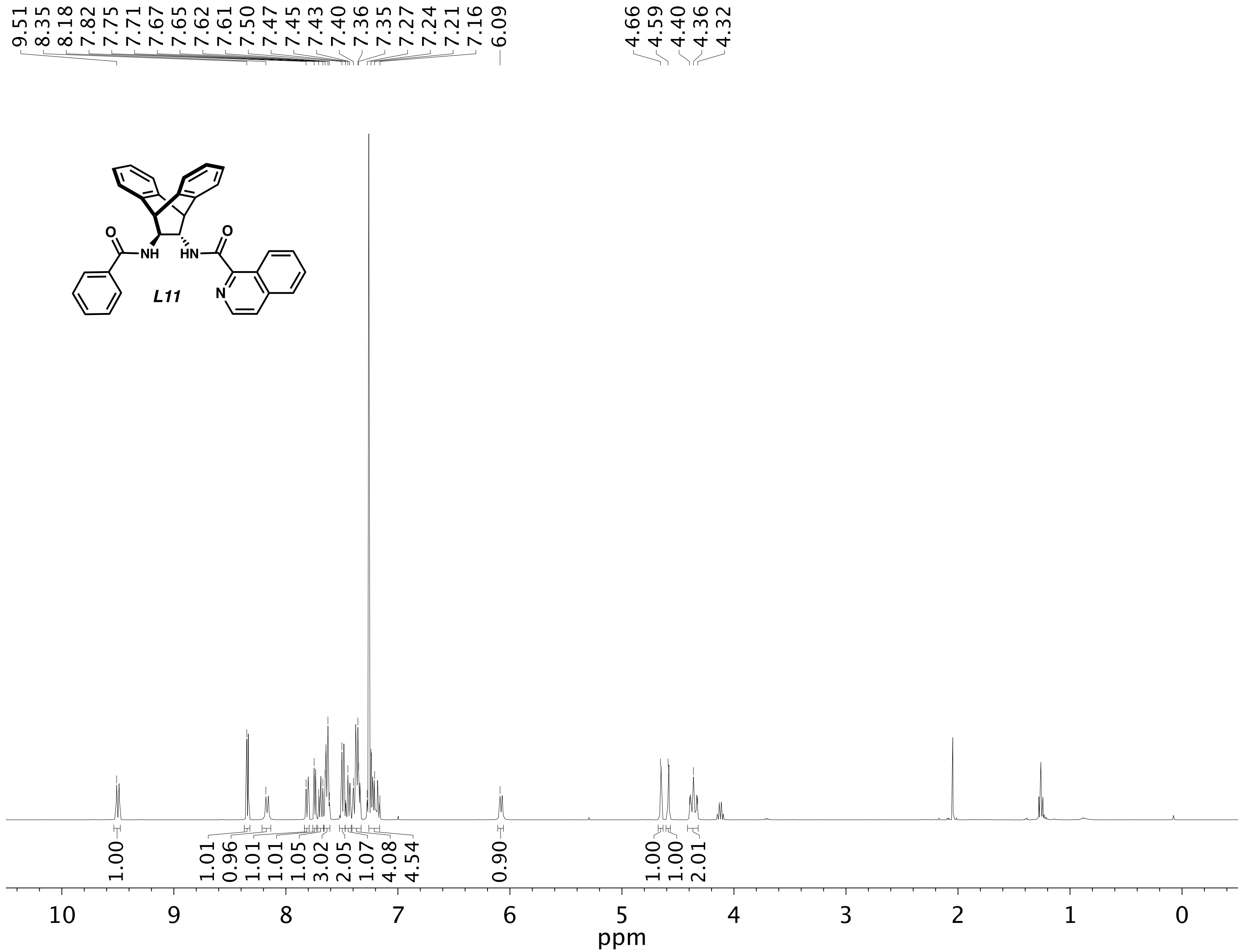
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L10**



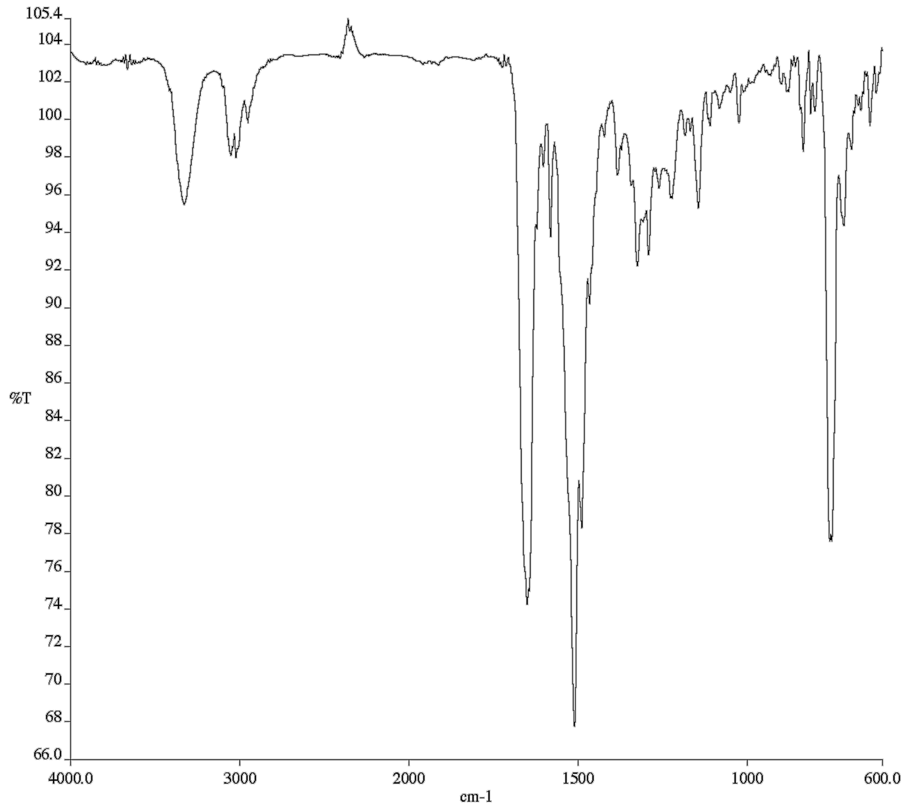
Infrared spectrum (Thin Film, NaCl) of compound **L10**.



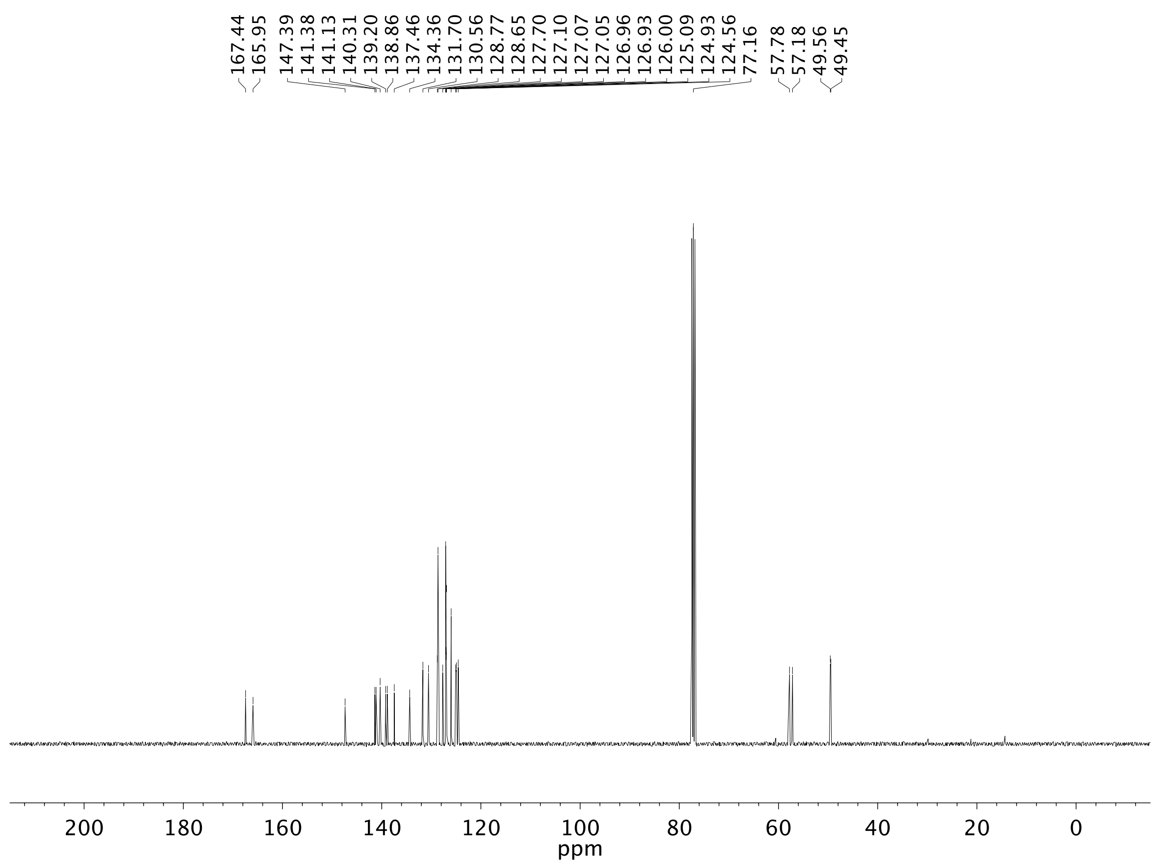
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L10**



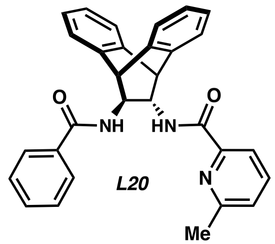
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L11**



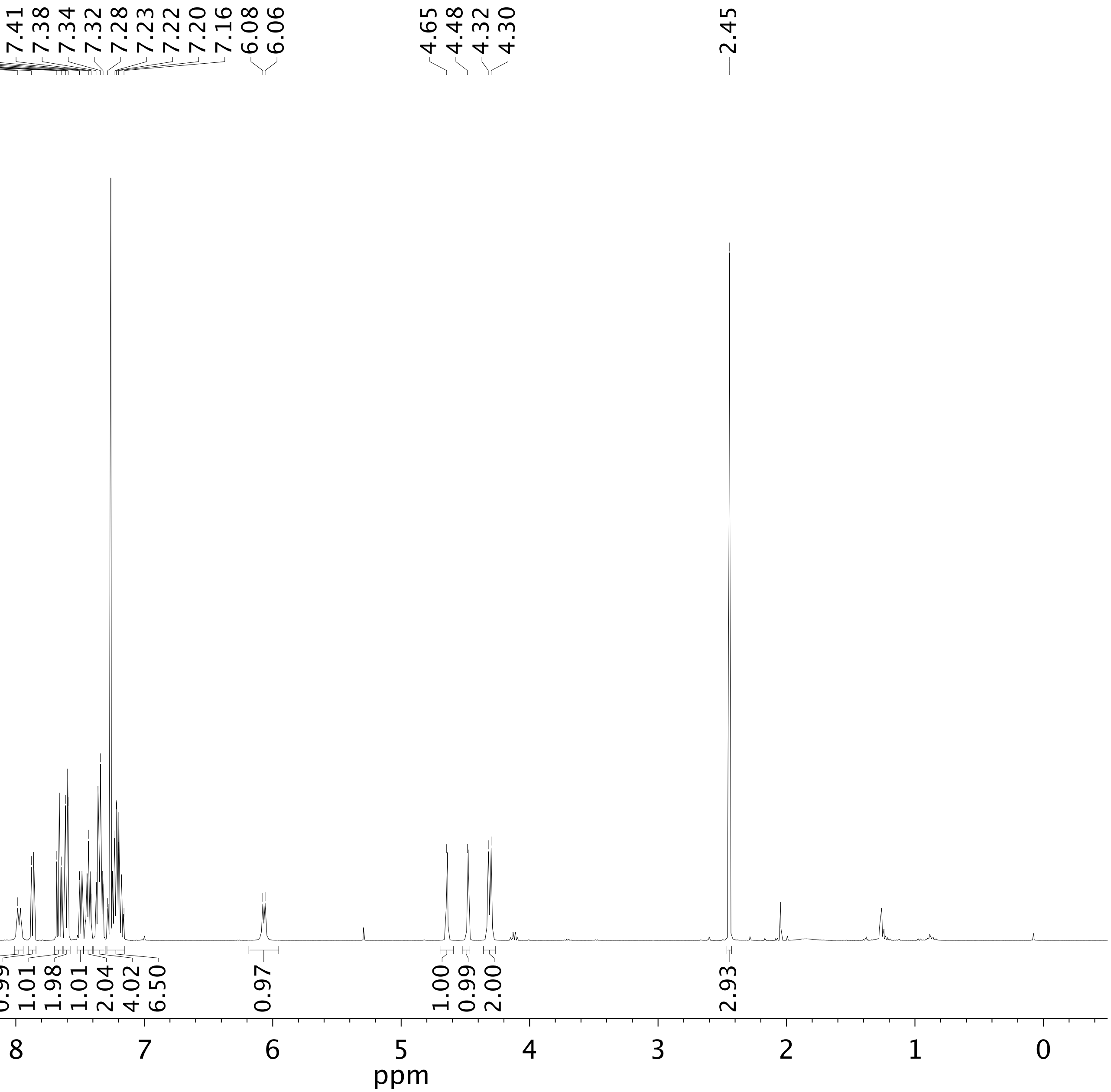
Infrared spectrum (Thin Film, NaCl) of compound **L11**



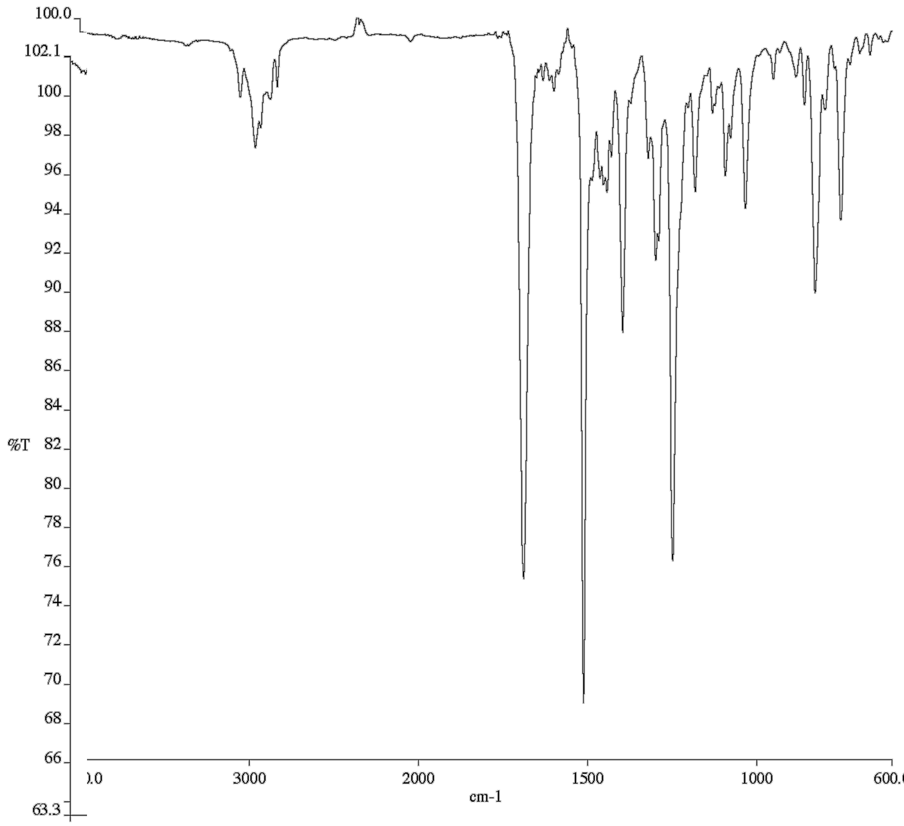
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L11**



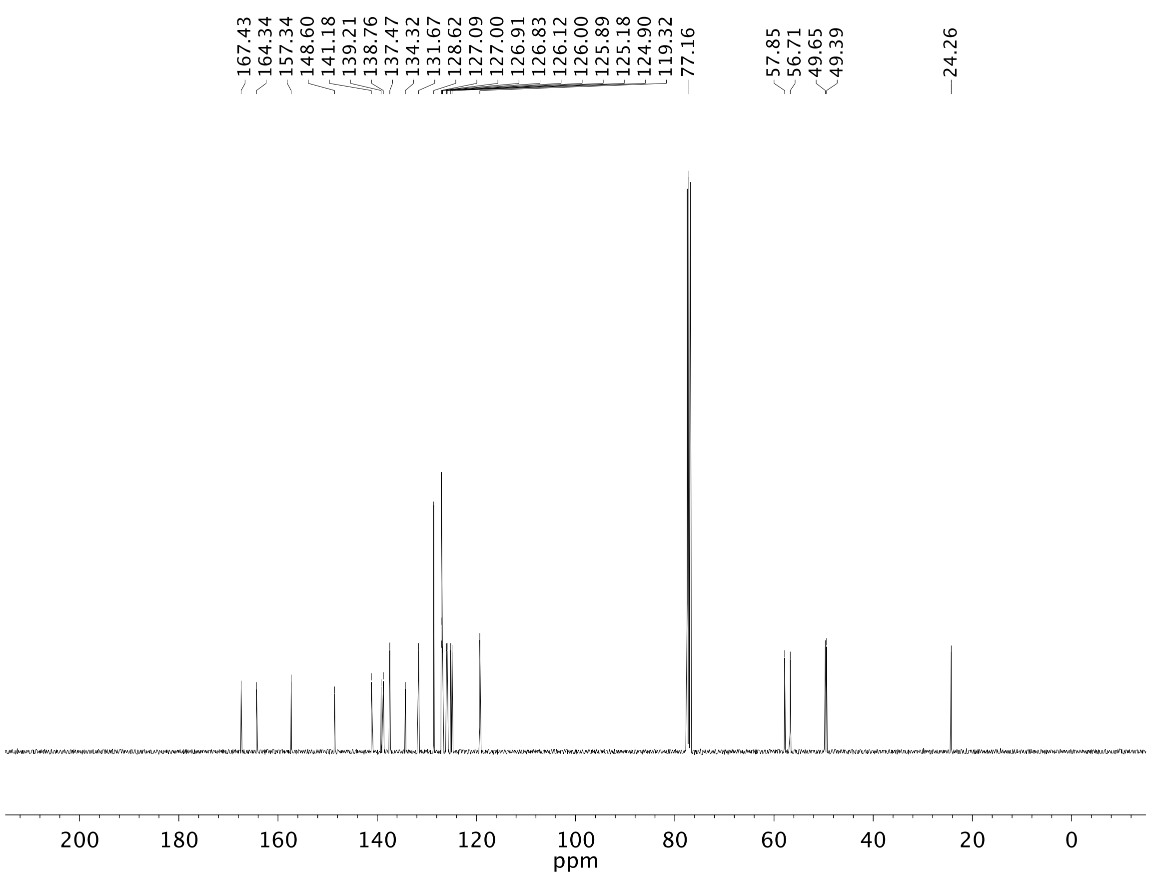
L20



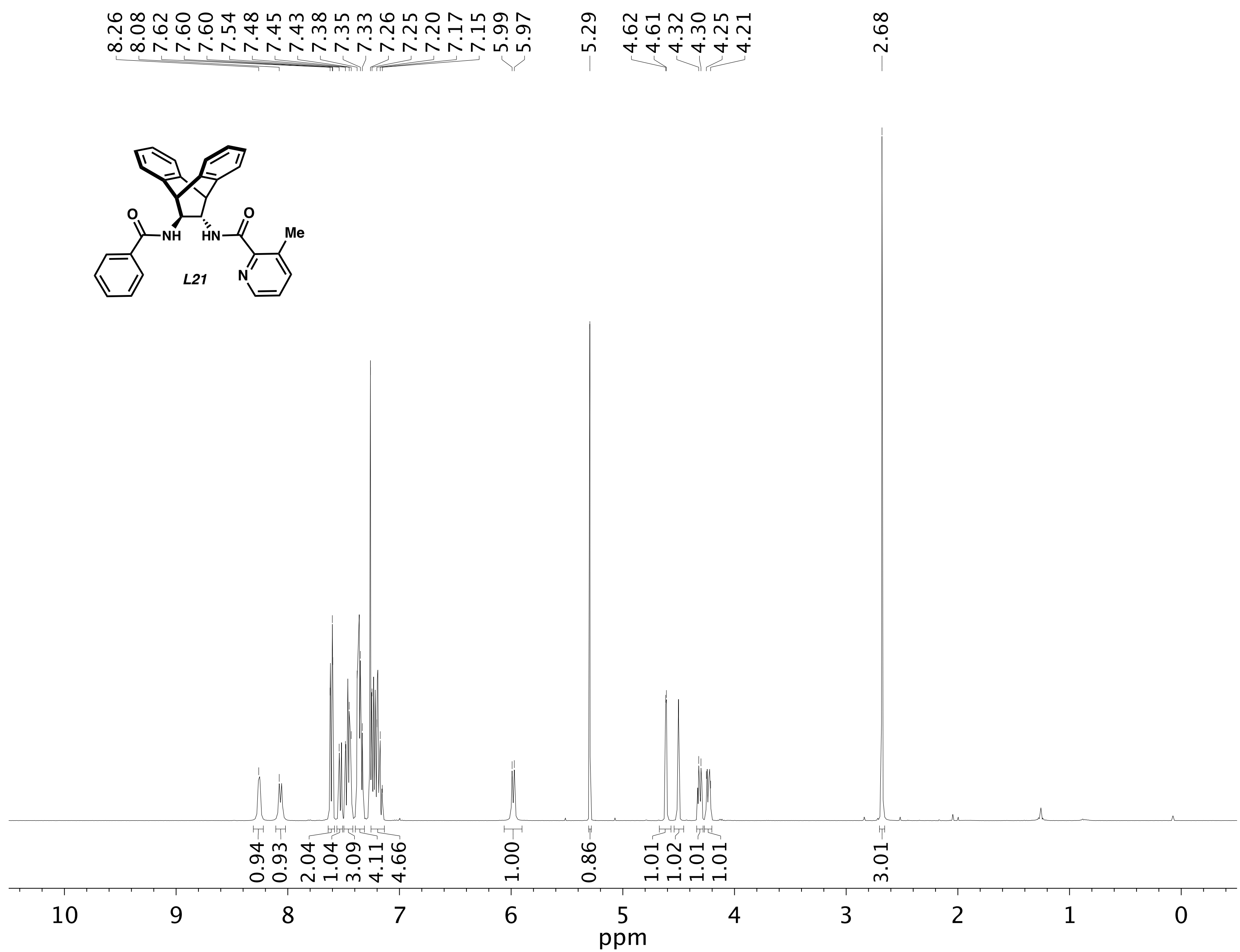
[1]H NMR (400 MHz, $CDCl_3$) of compound **L20**



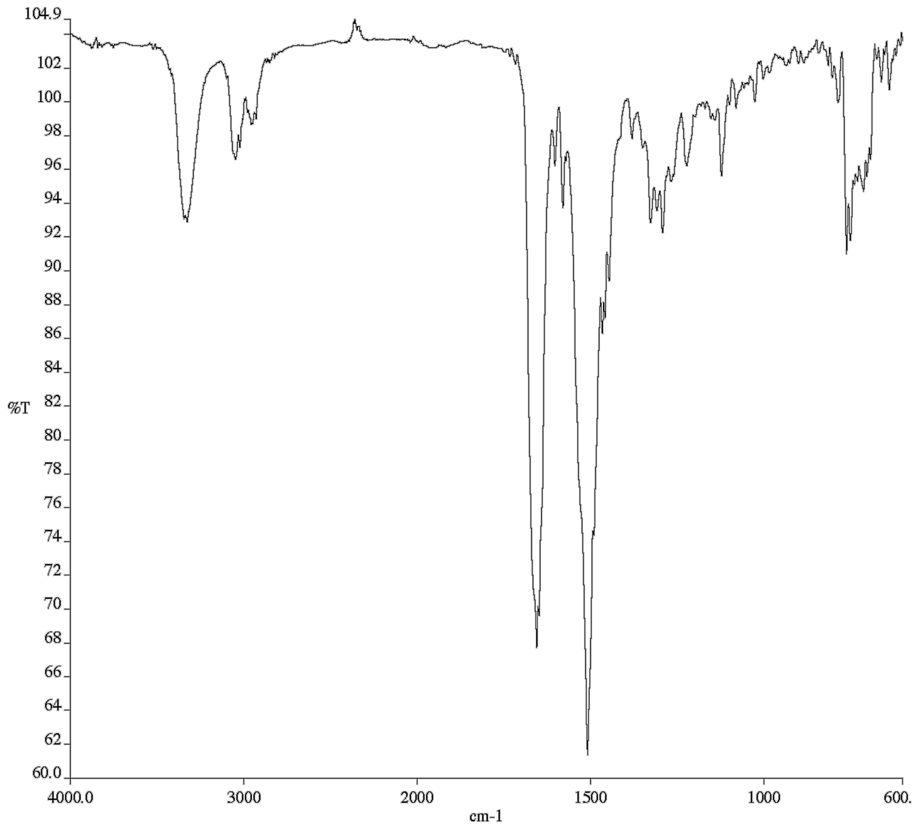
Infrared spectrum (Thin Film, NaCl) of compound **L20**



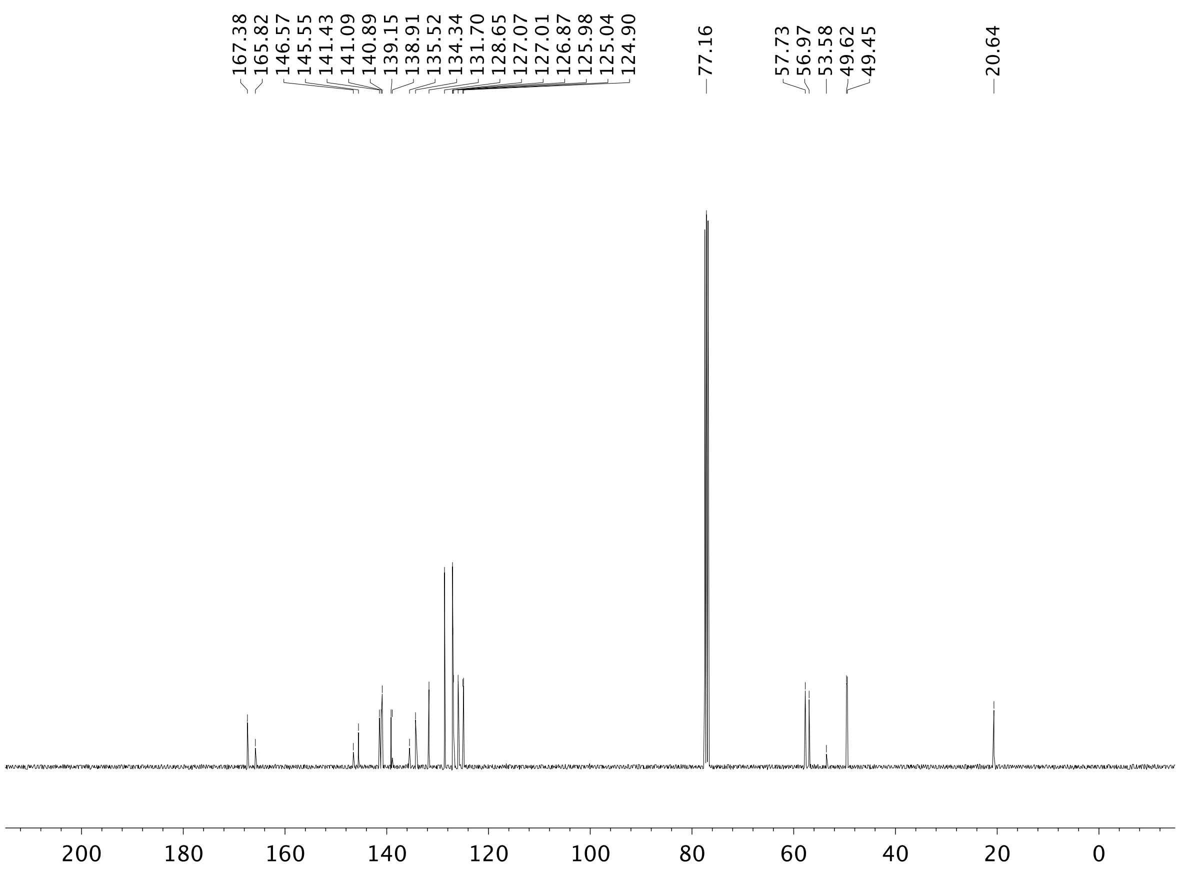
^{13}C NMR (101 MHz, CDCl$_3$) of compound **L20**.



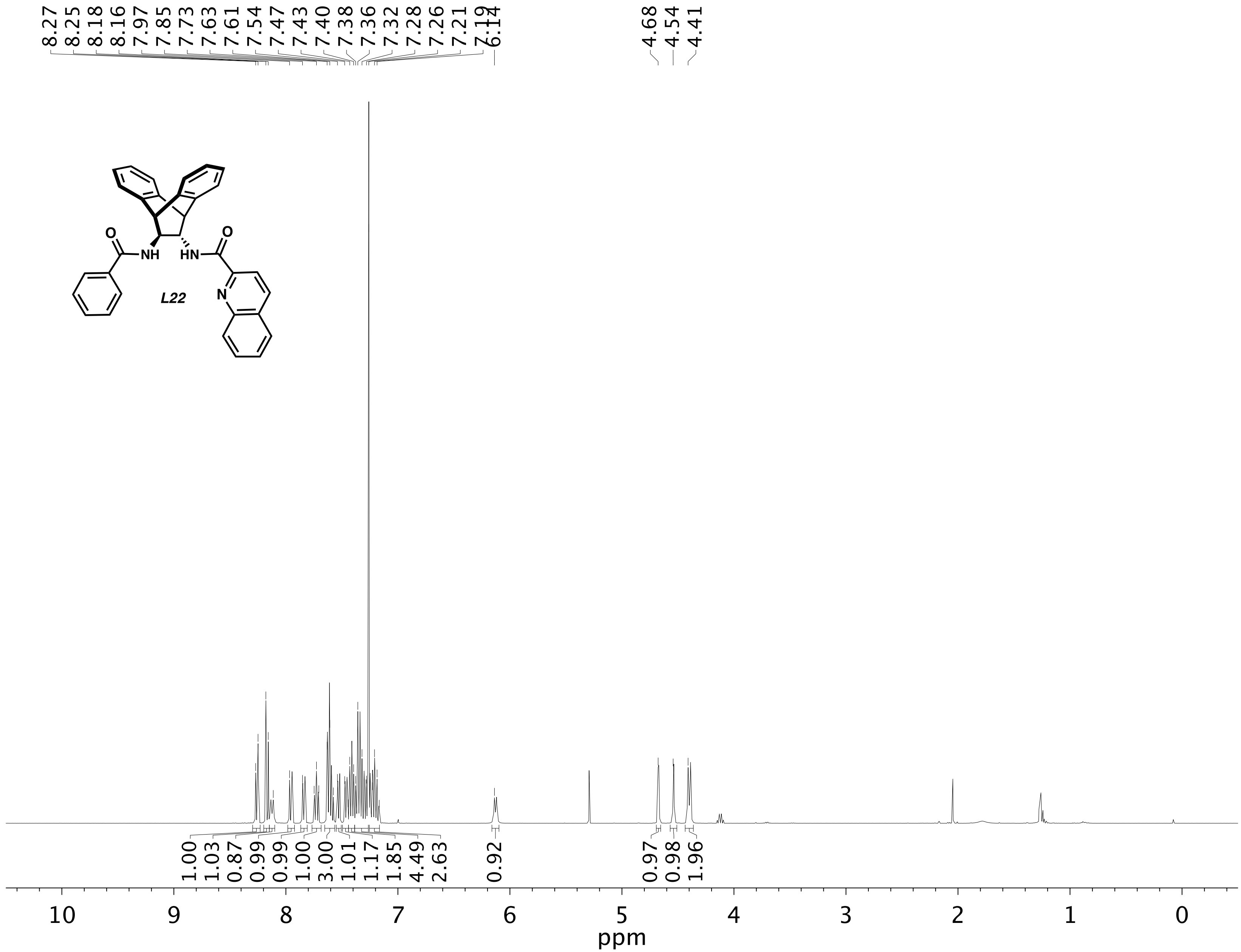
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L21**



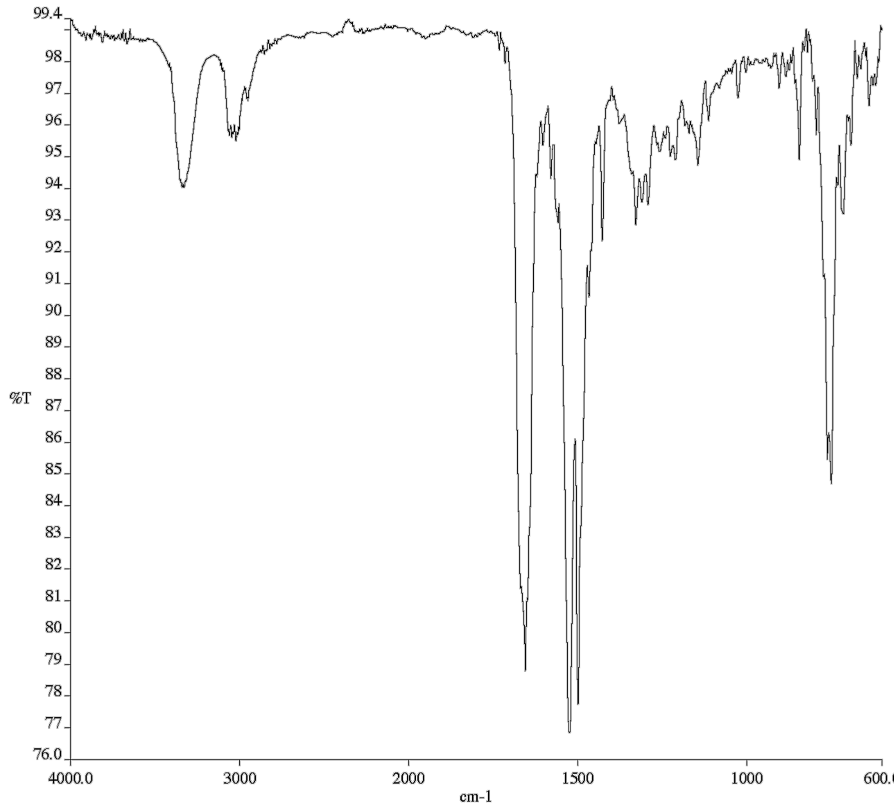
Infrared spectrum (Thin Film, NaCl) of compound **L21**



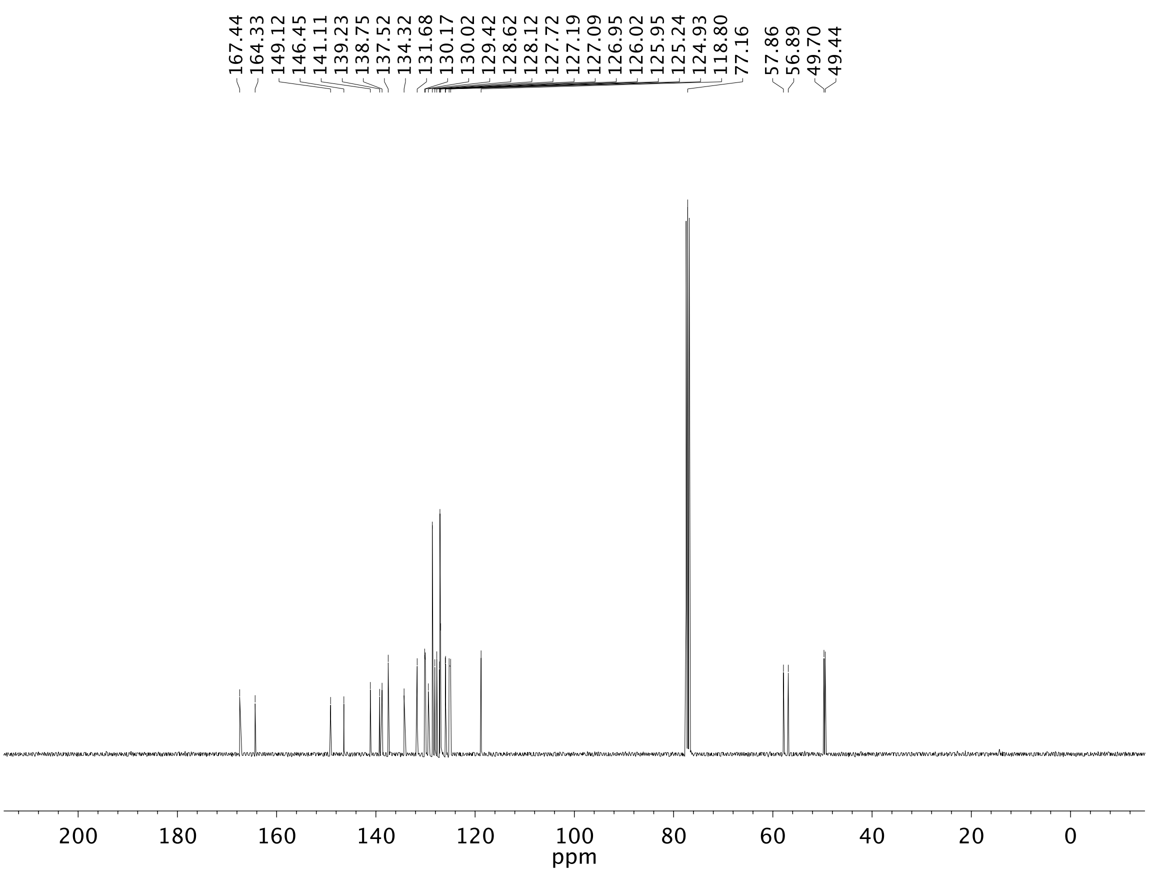
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L22**



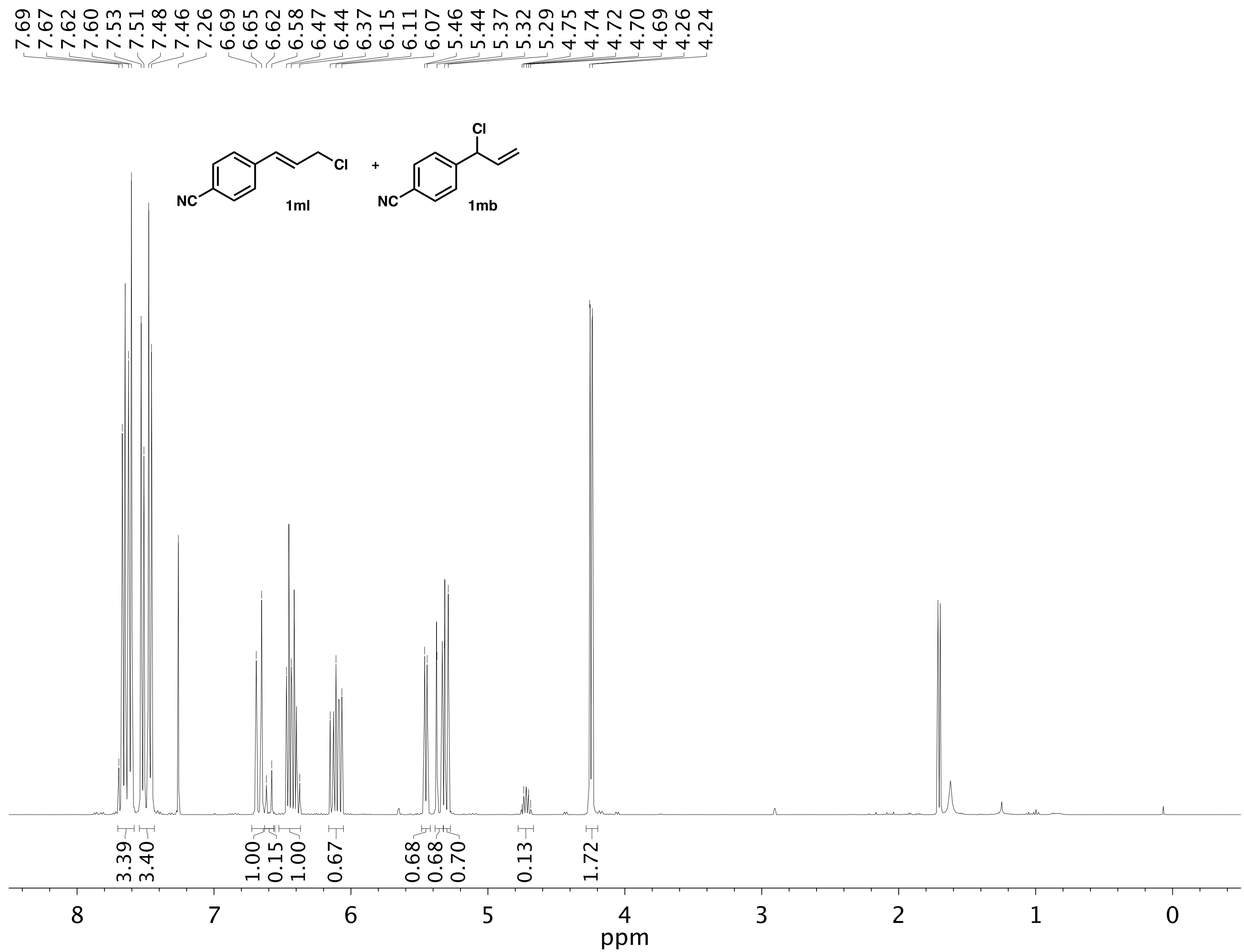
^{1}H NMR (400 MHz, $CDCl_3$) of compound **L22**



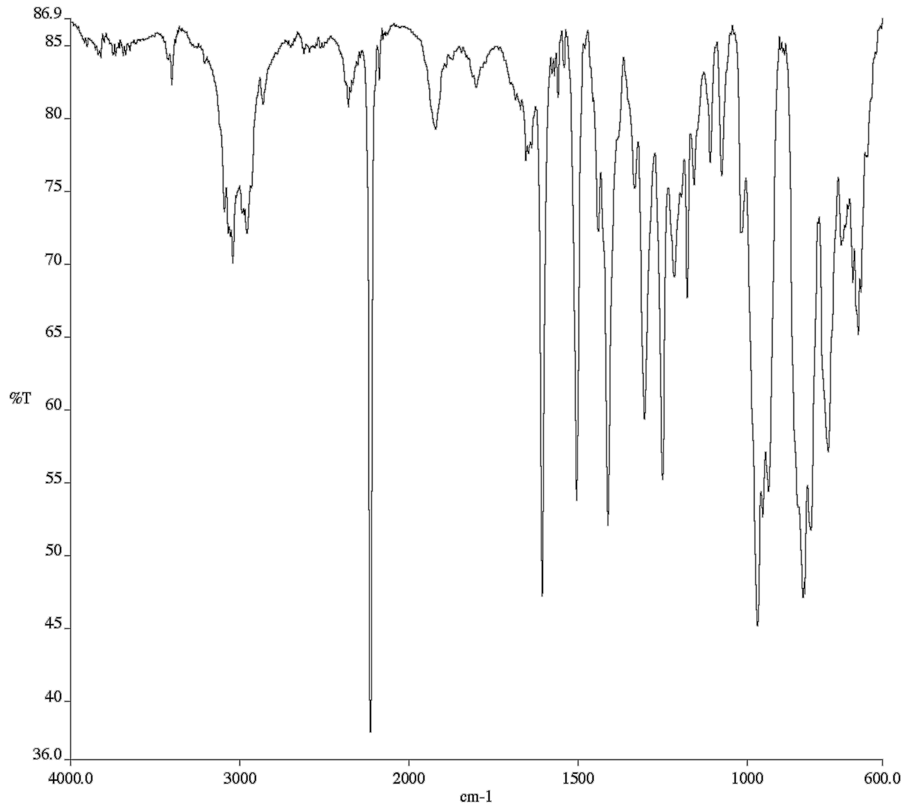
Infrared spectrum (Thin Film, NaCl) of compound **L22**



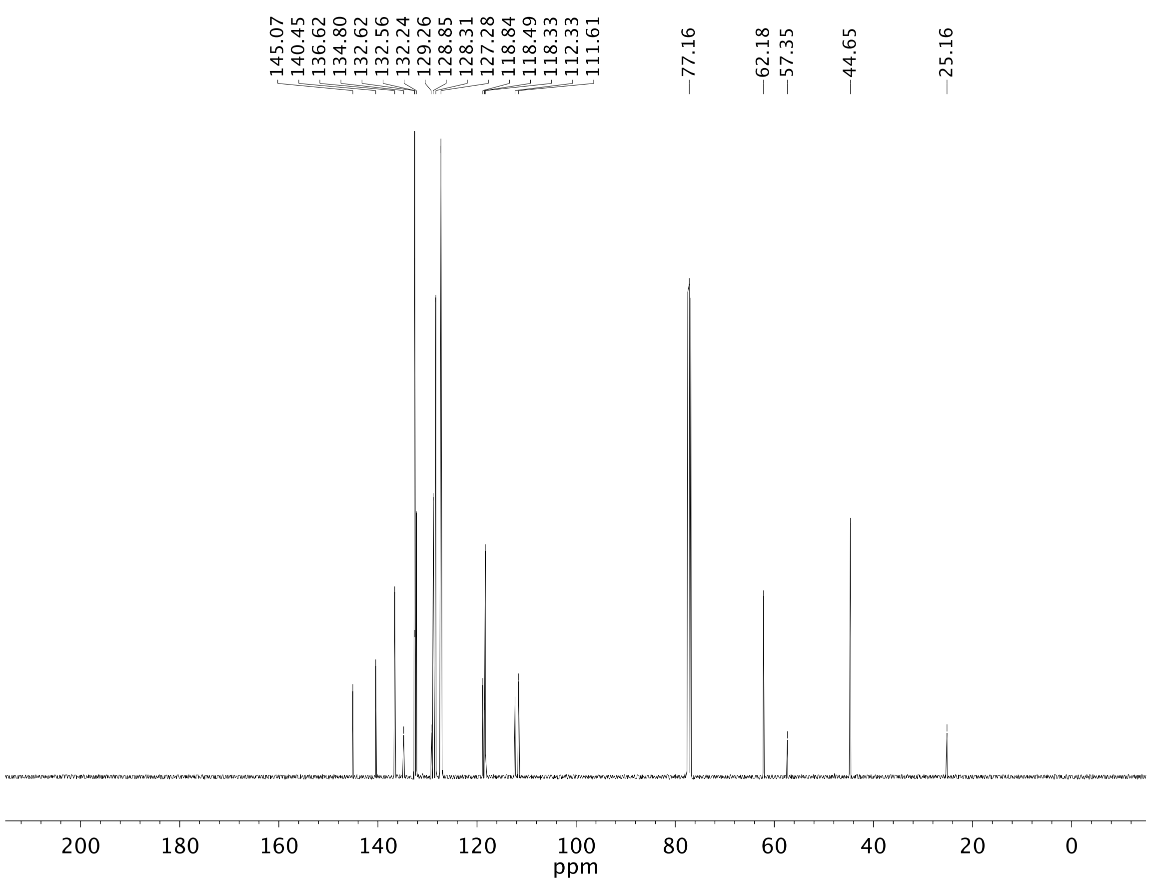
^{13}C NMR (101 MHz, $CDCl_3$) of compound **L22**



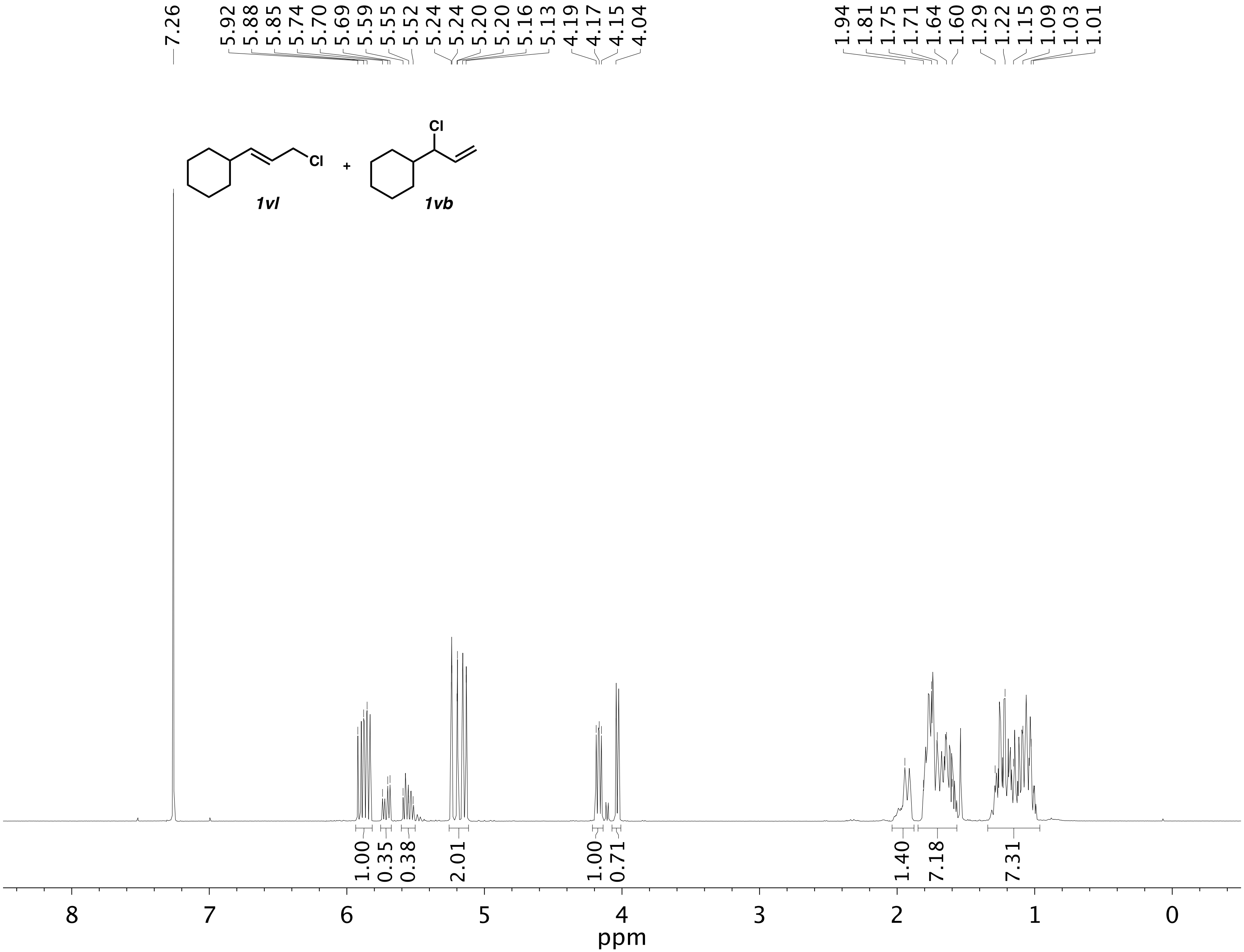
^1H NMR (400 MHz, $CDCl_3$) of compound **1m**



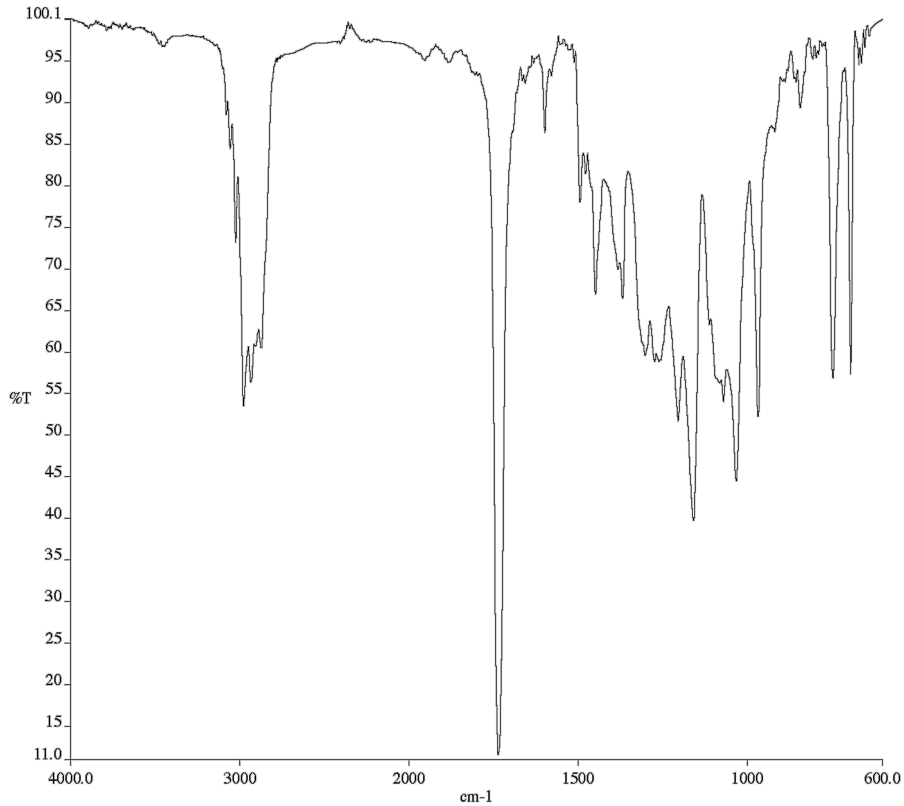
Infrared spectrum (Thin Film, NaCl) of compound **1m**



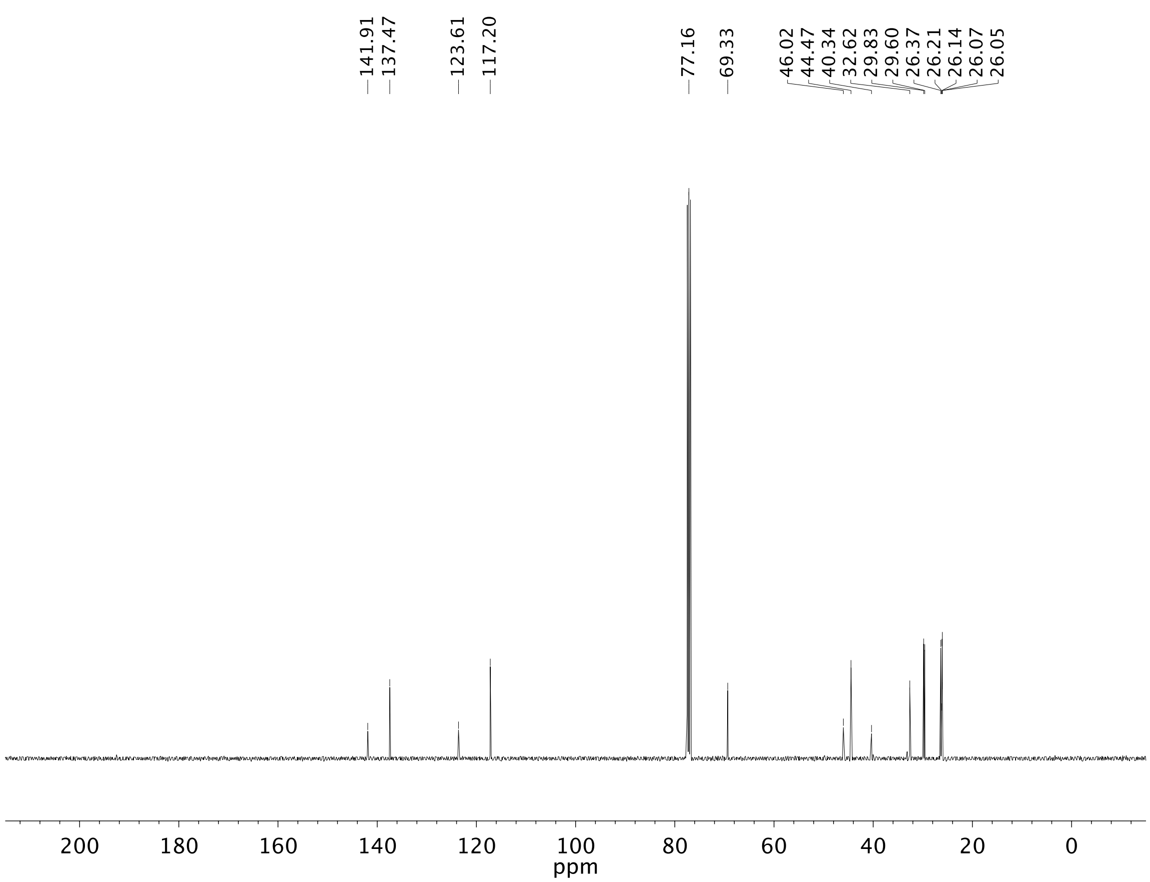
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1m**



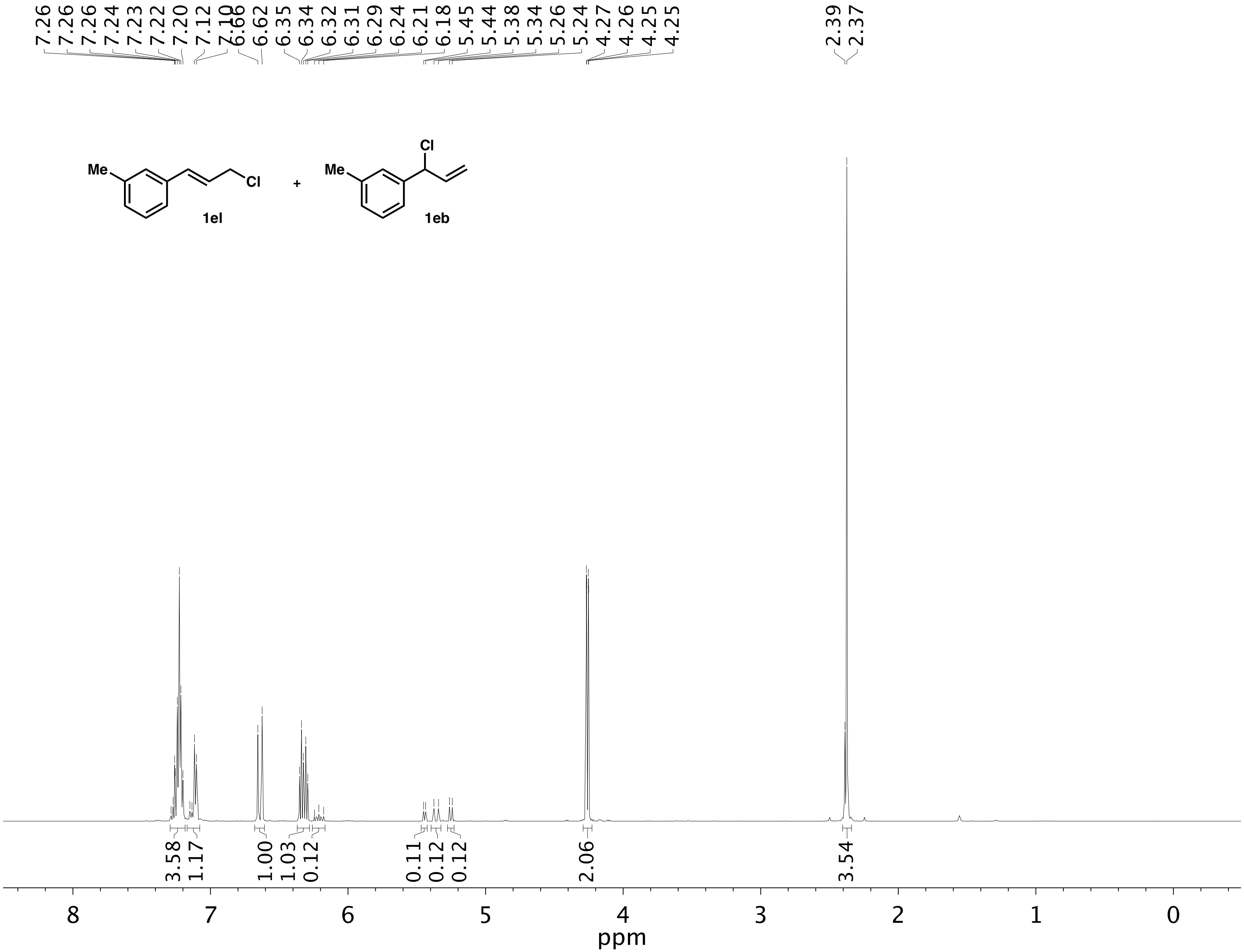
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1v**



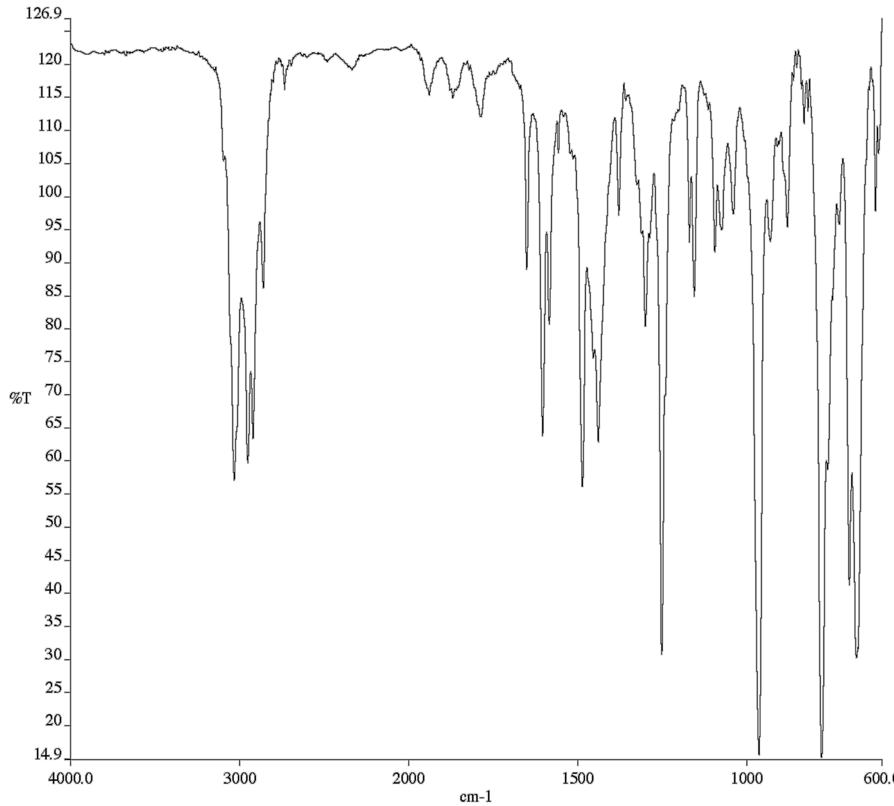
Infrared spectrum (Thin Film, NaCl) of compound **1v**



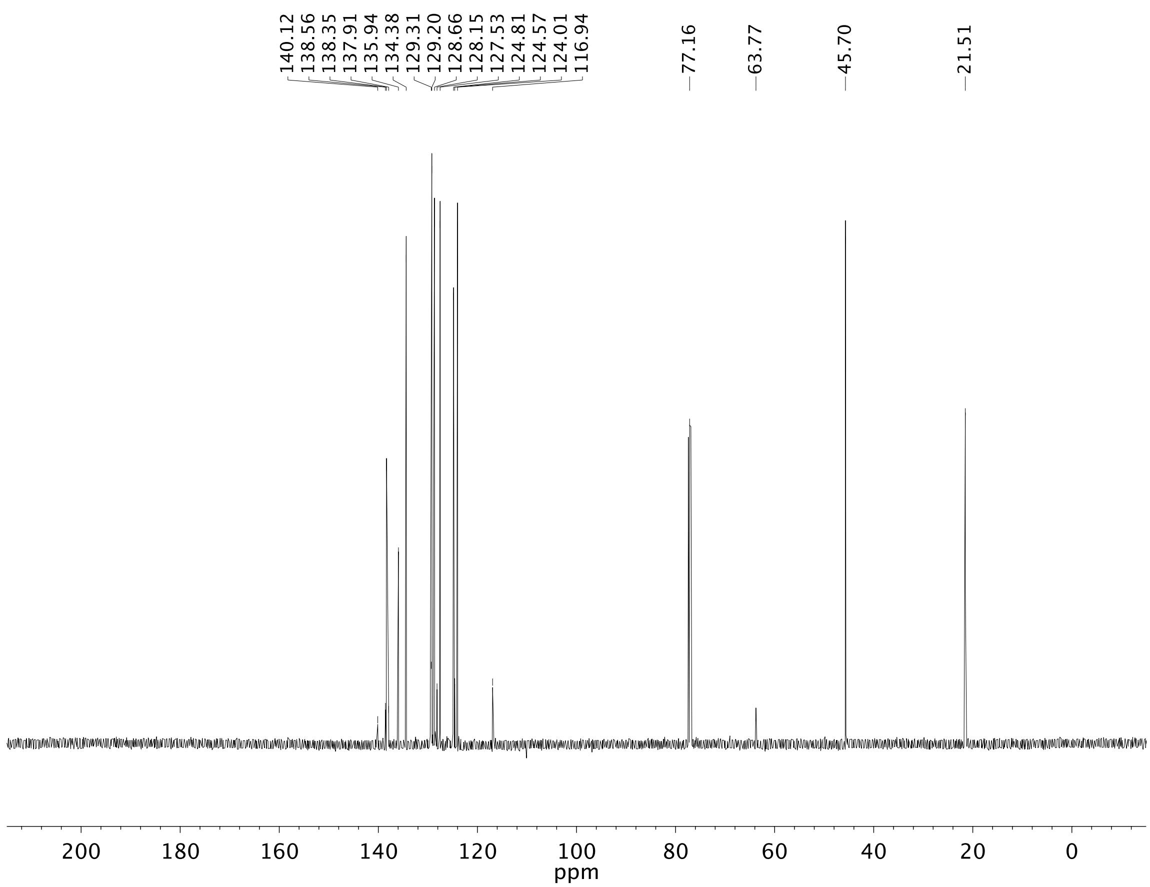
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1v**



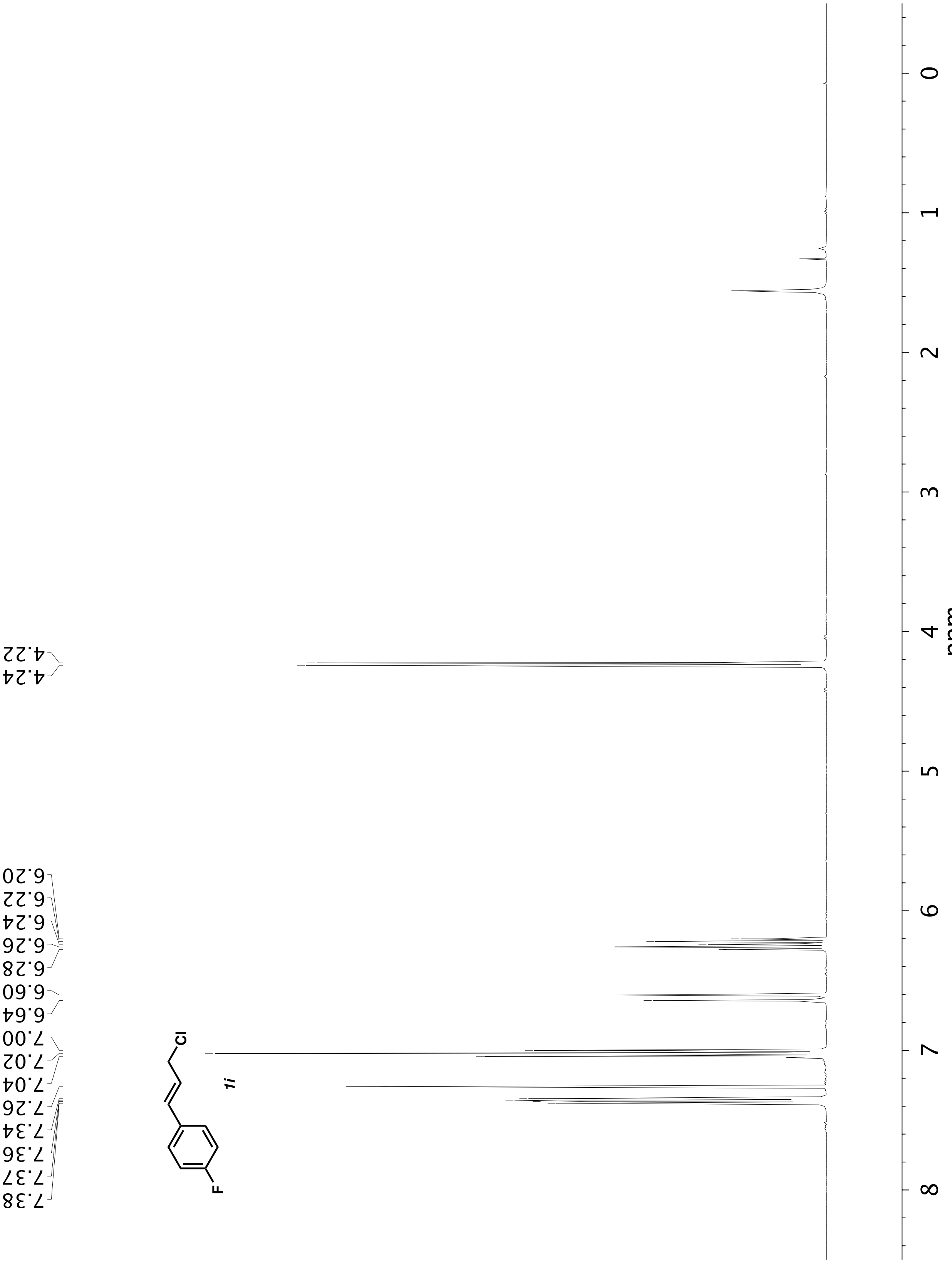
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1e**



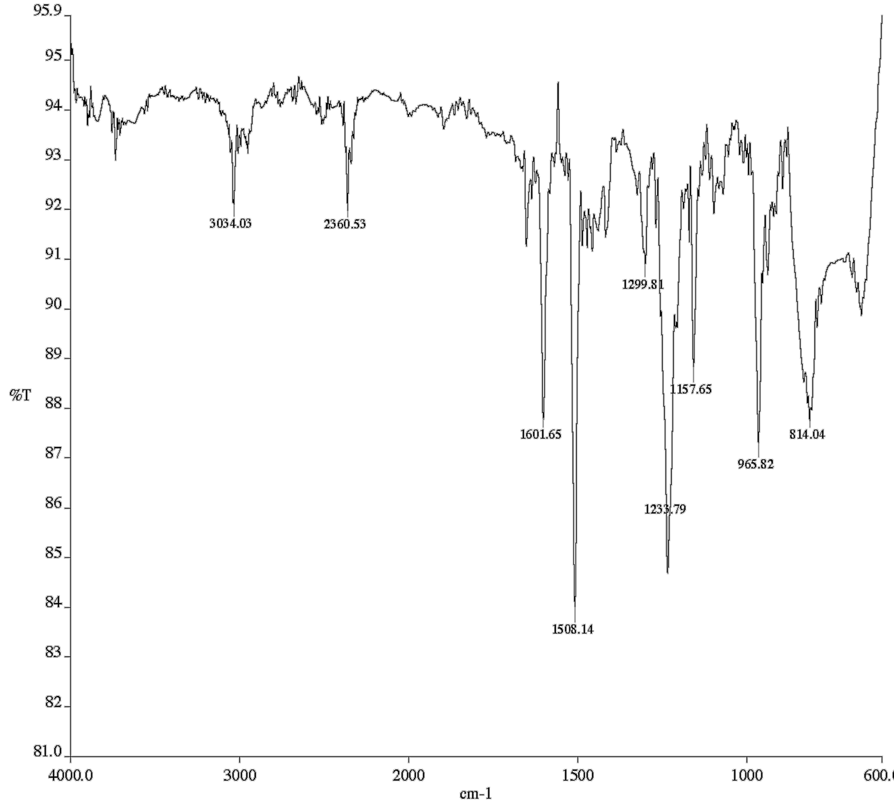
Infrared spectrum (Thin Film, NaCl) of compound **1e**



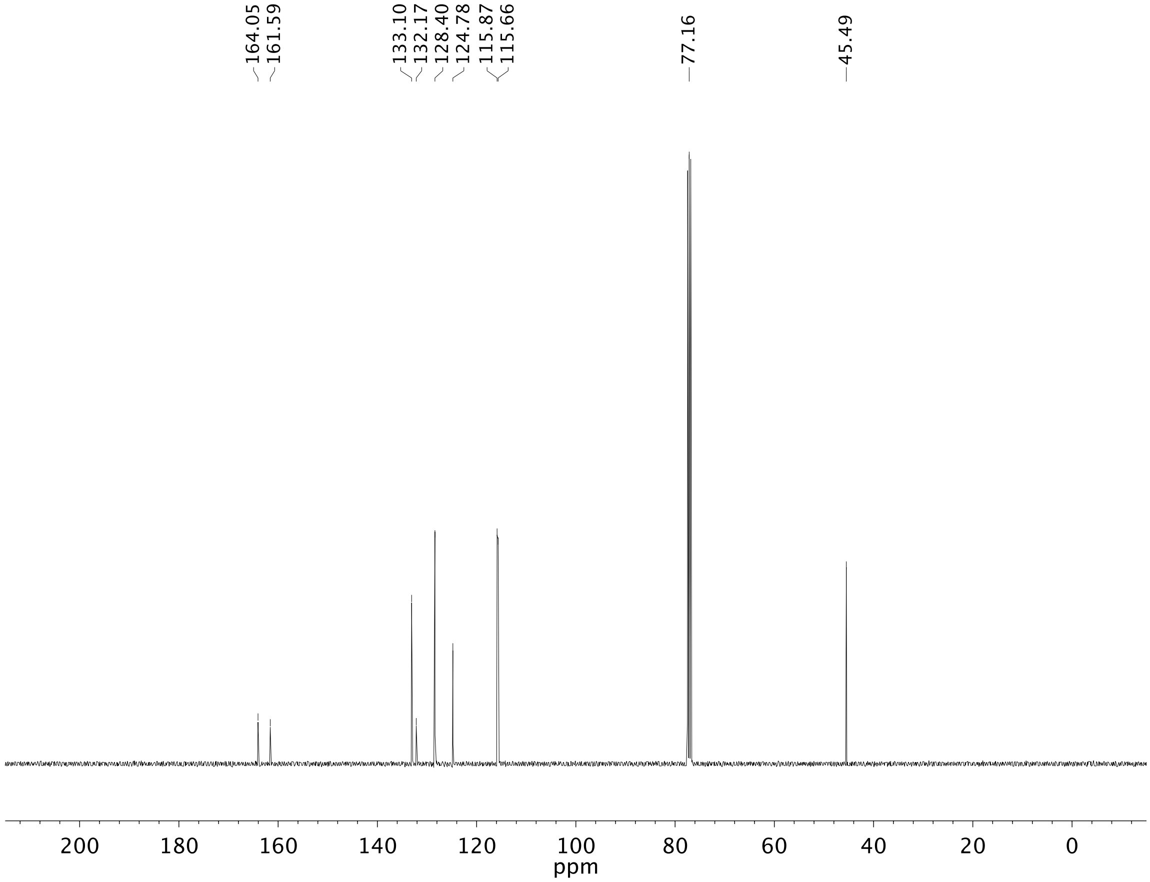
^{13}C NMR (126 MHz, $CDCl_3$) of compound **1e**



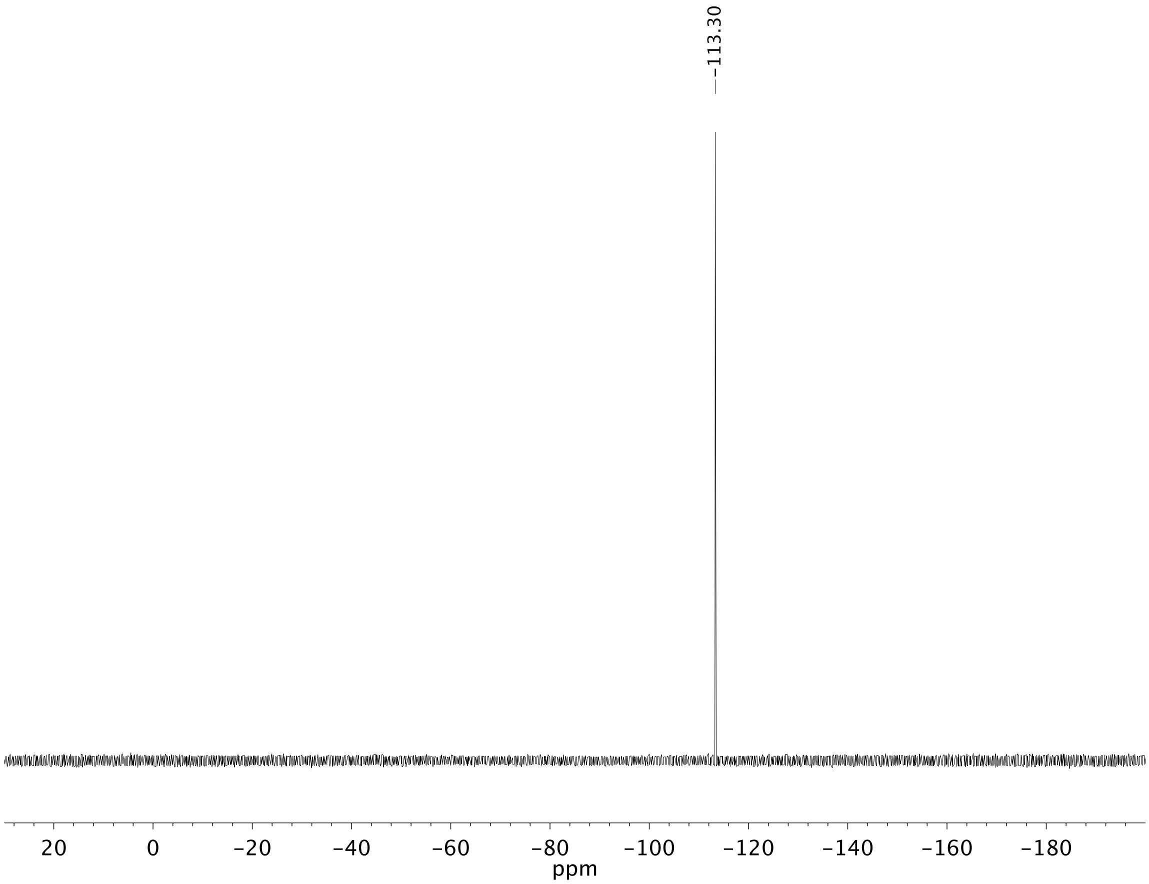
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1i**



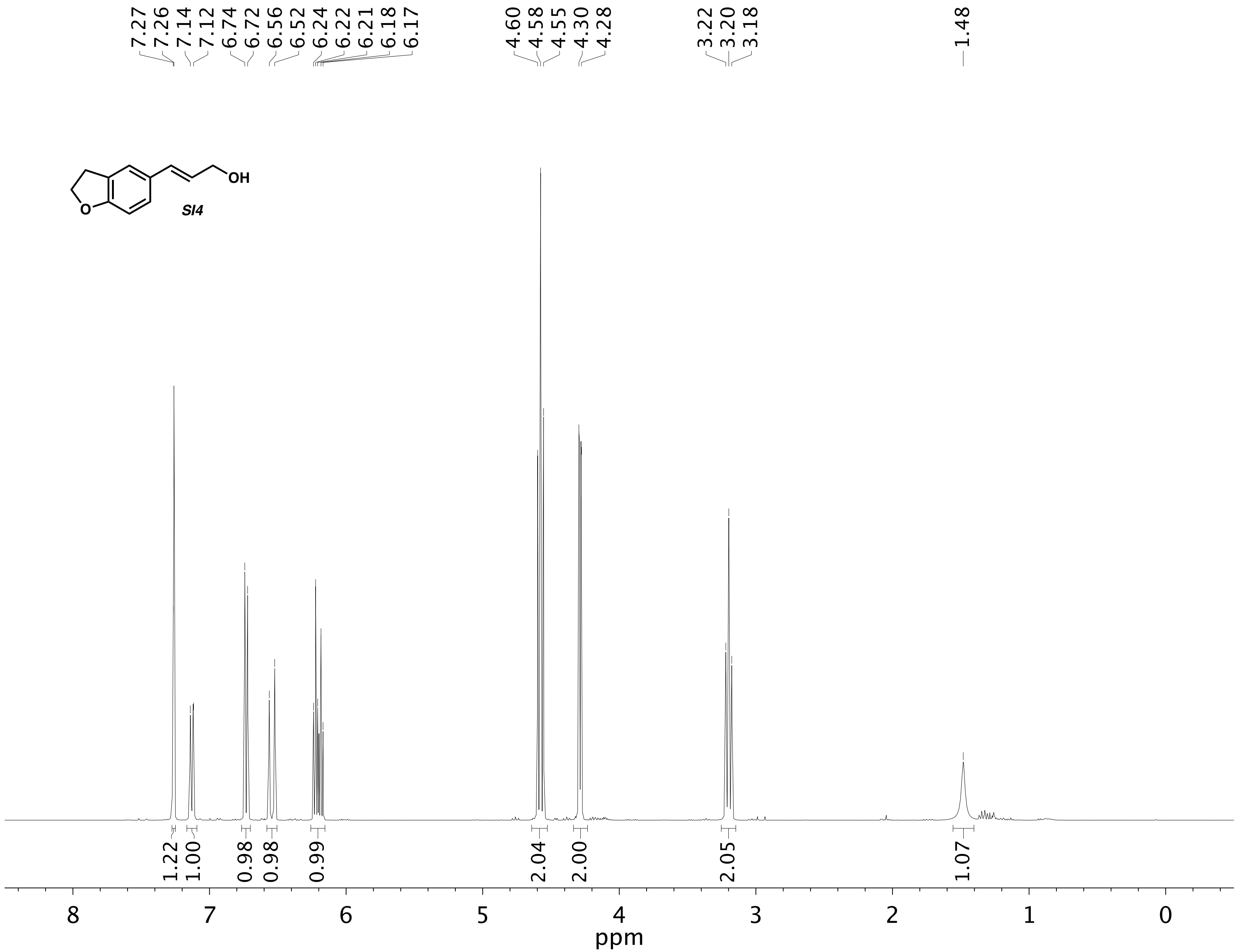
Infrared spectrum (Thin Film, NaCl) of compound **1i**



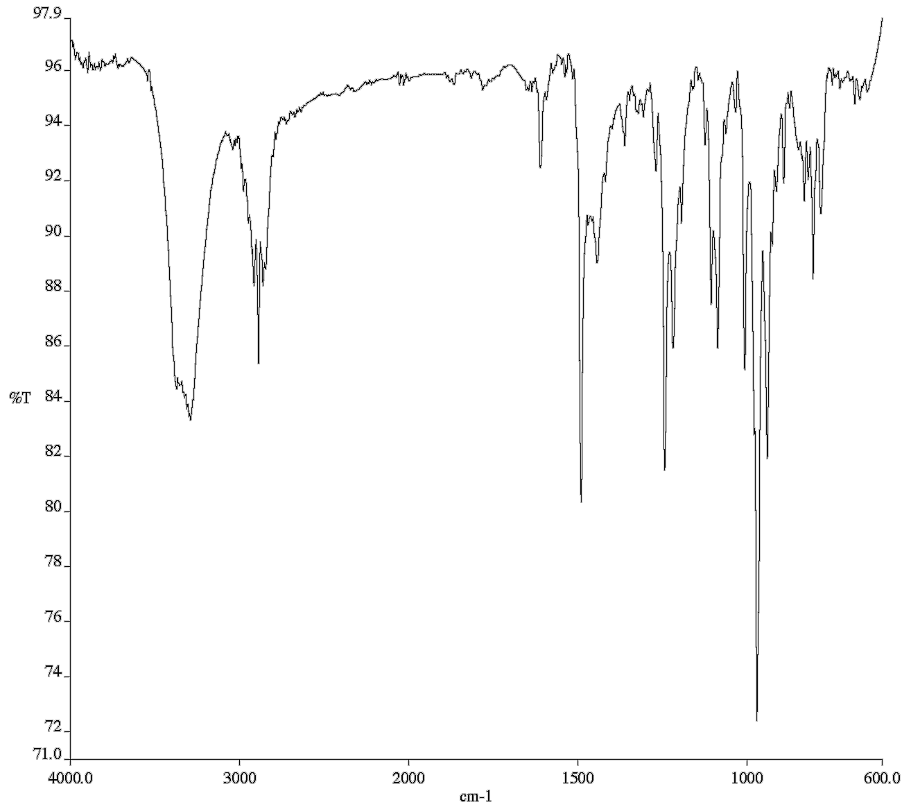
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1i**



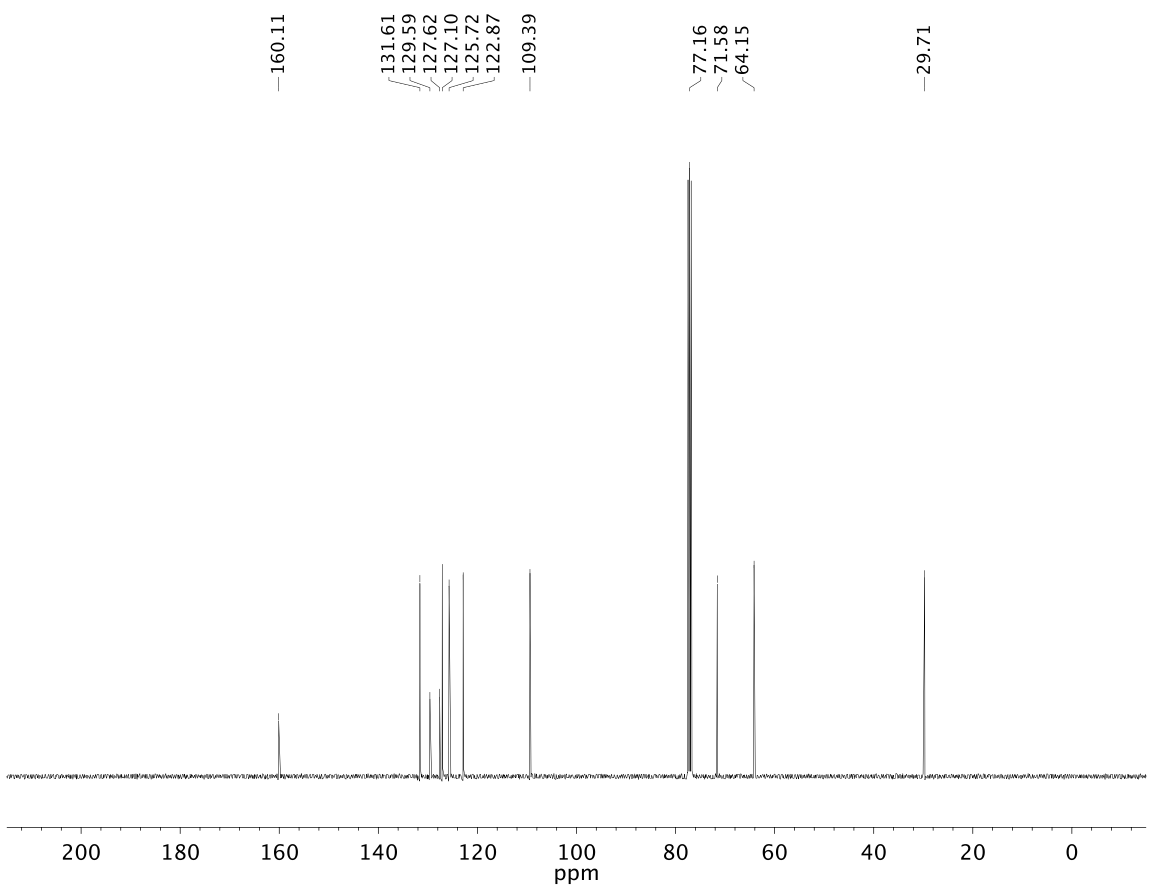
^{19}F NMR (282 MHz, $CDCl_3$) of compound **1i**



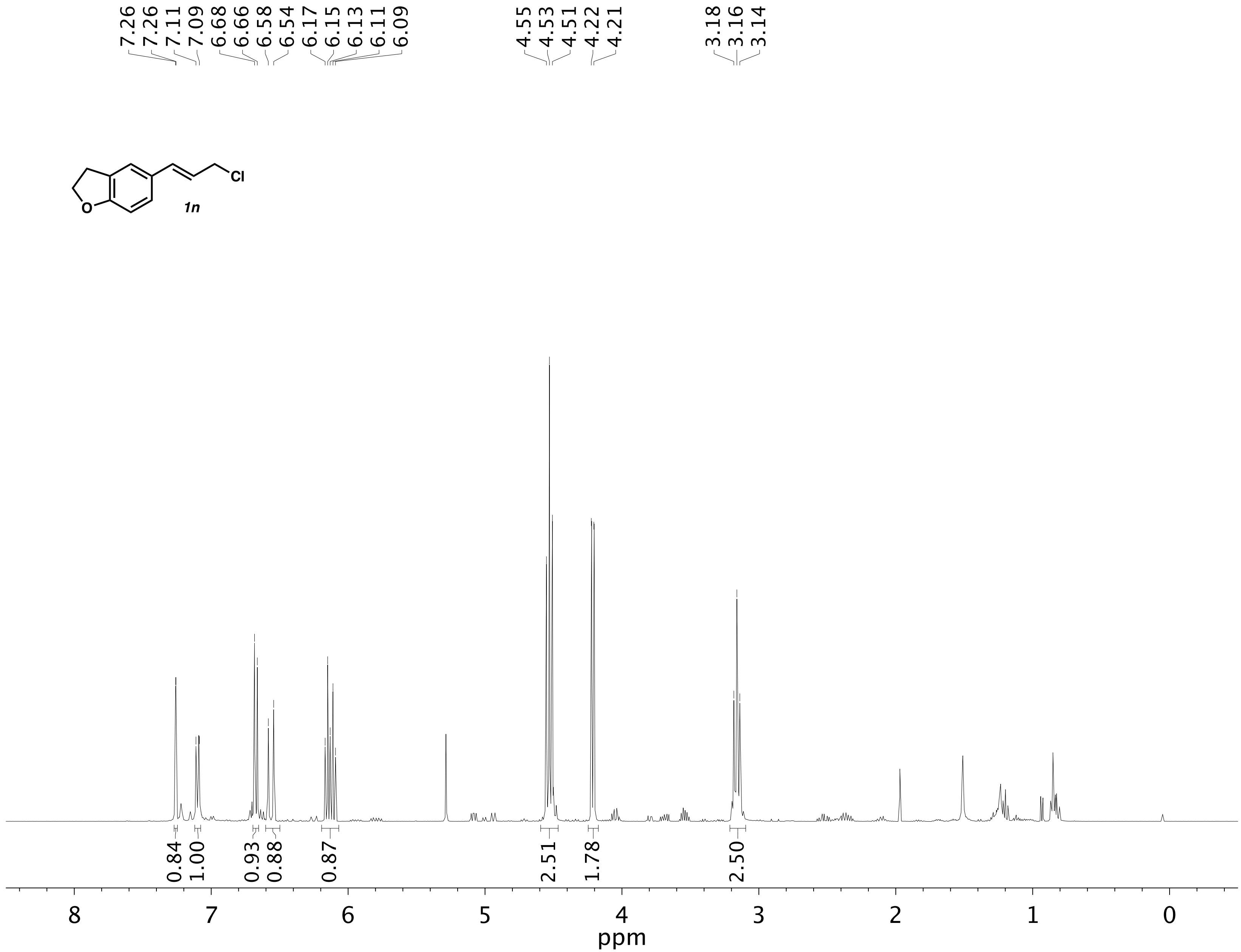
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI4**



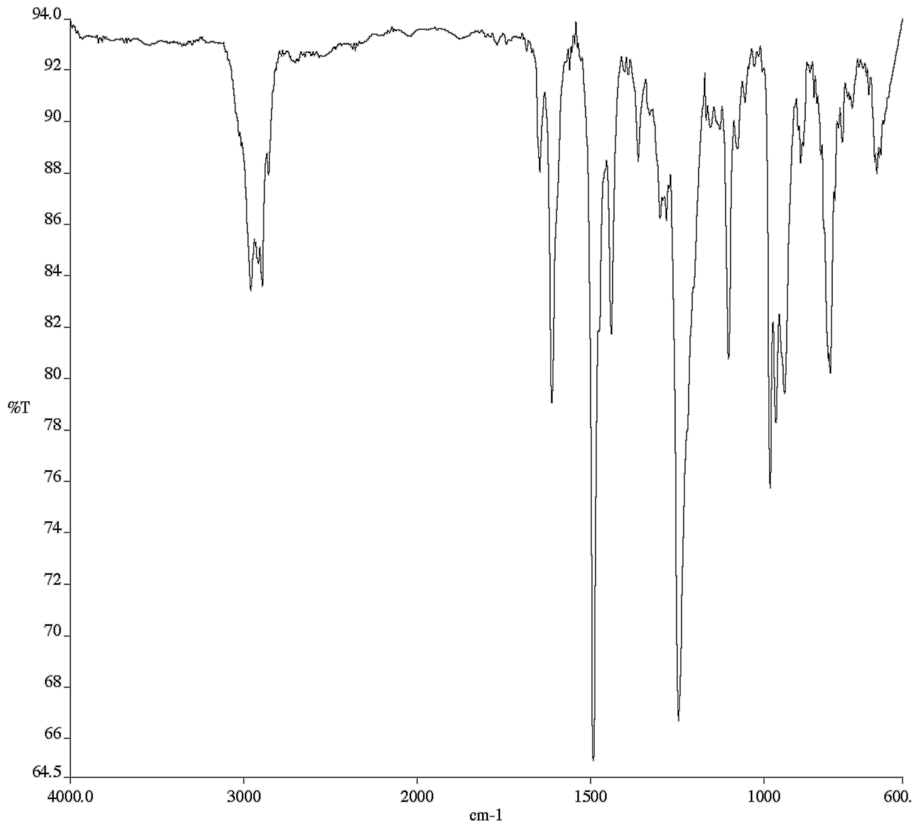
Infrared spectrum (Thin Film, NaCl) of compound **SI4**



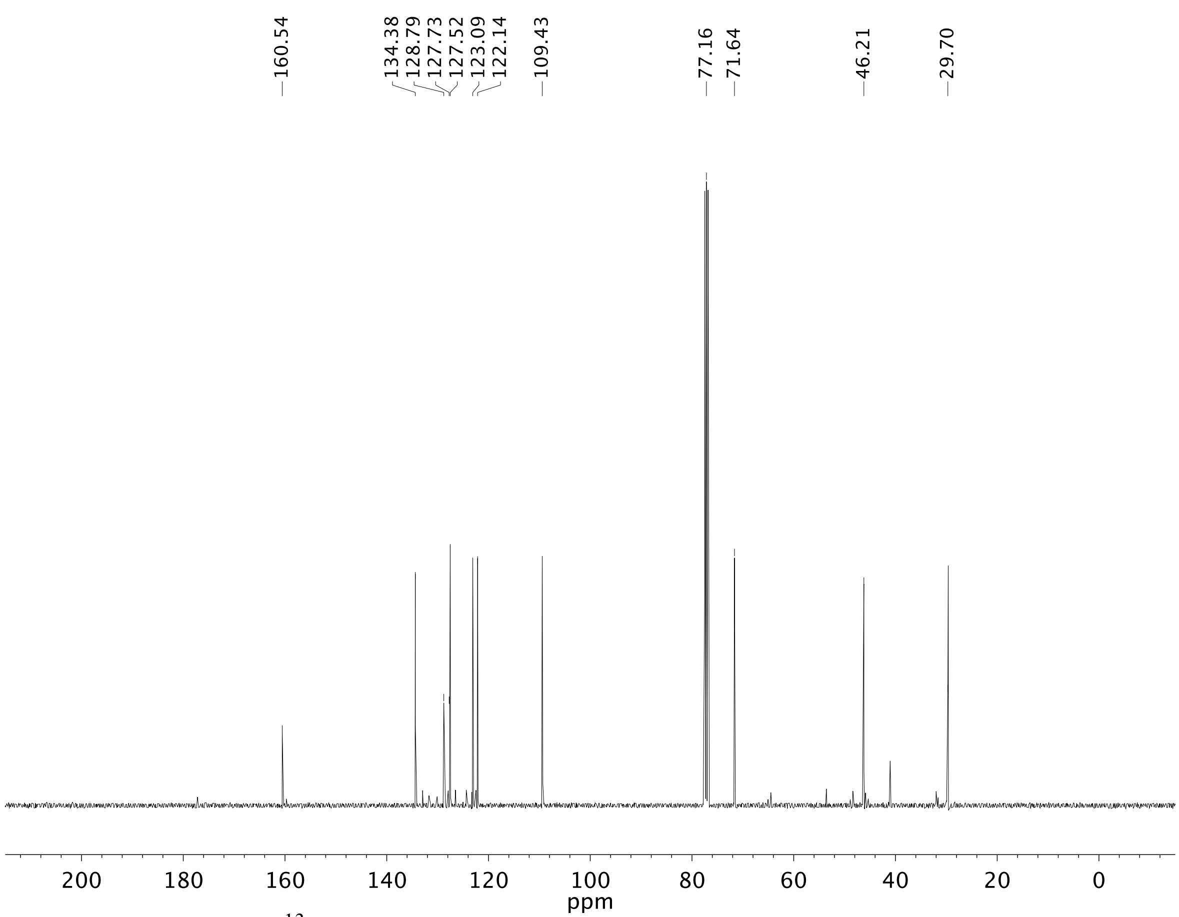
^{13}C NMR (101 MHz, $CDCl_3$) of compound **SI4**



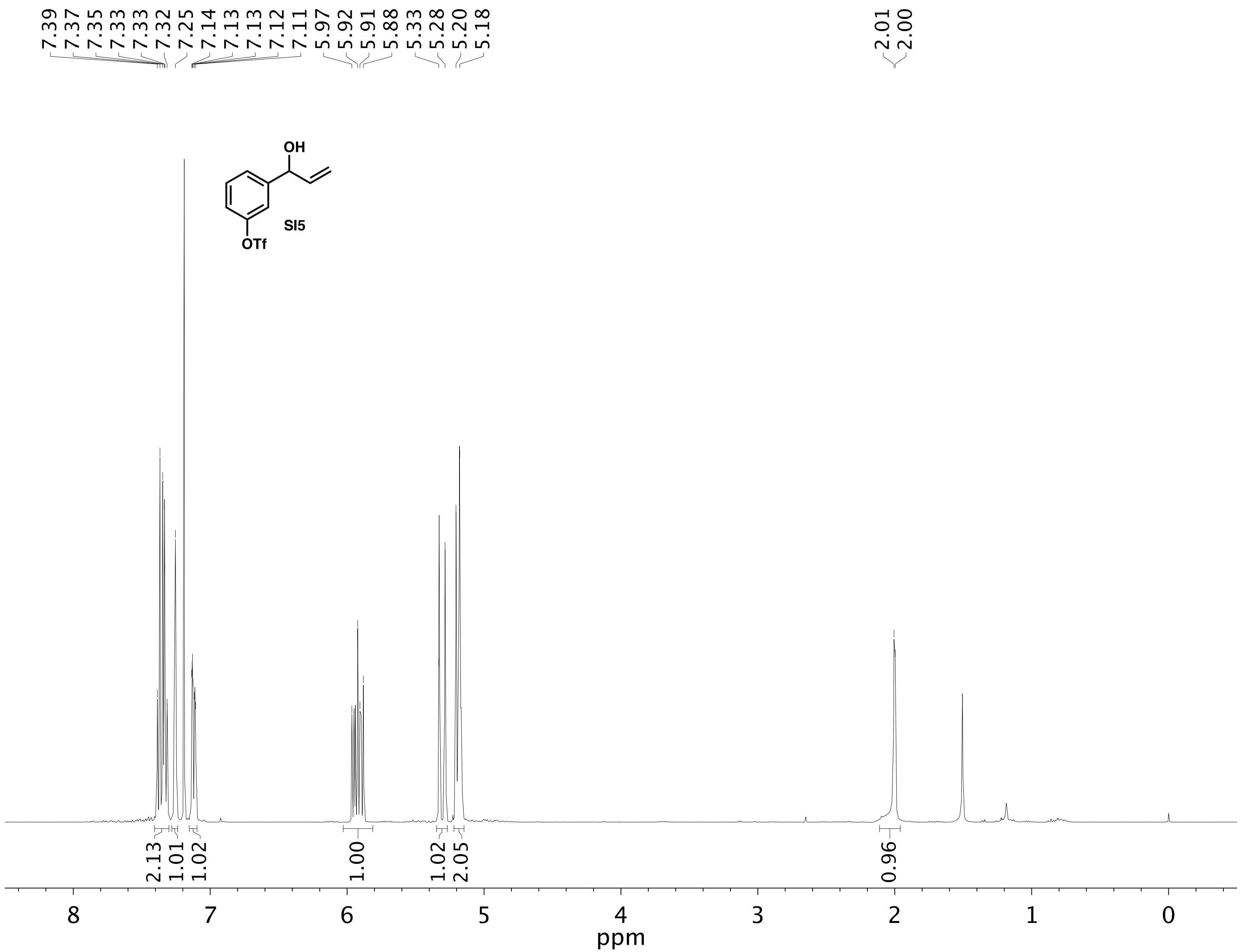
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1n**



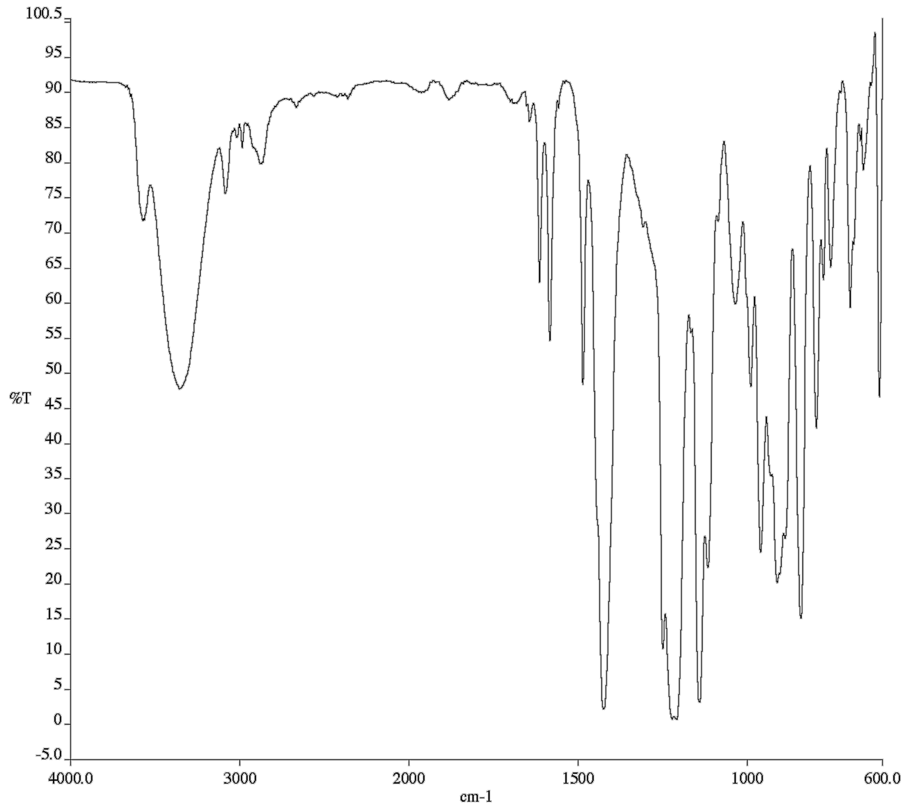
Infrared spectrum (Thin Film, NaCl) of compound **1n**



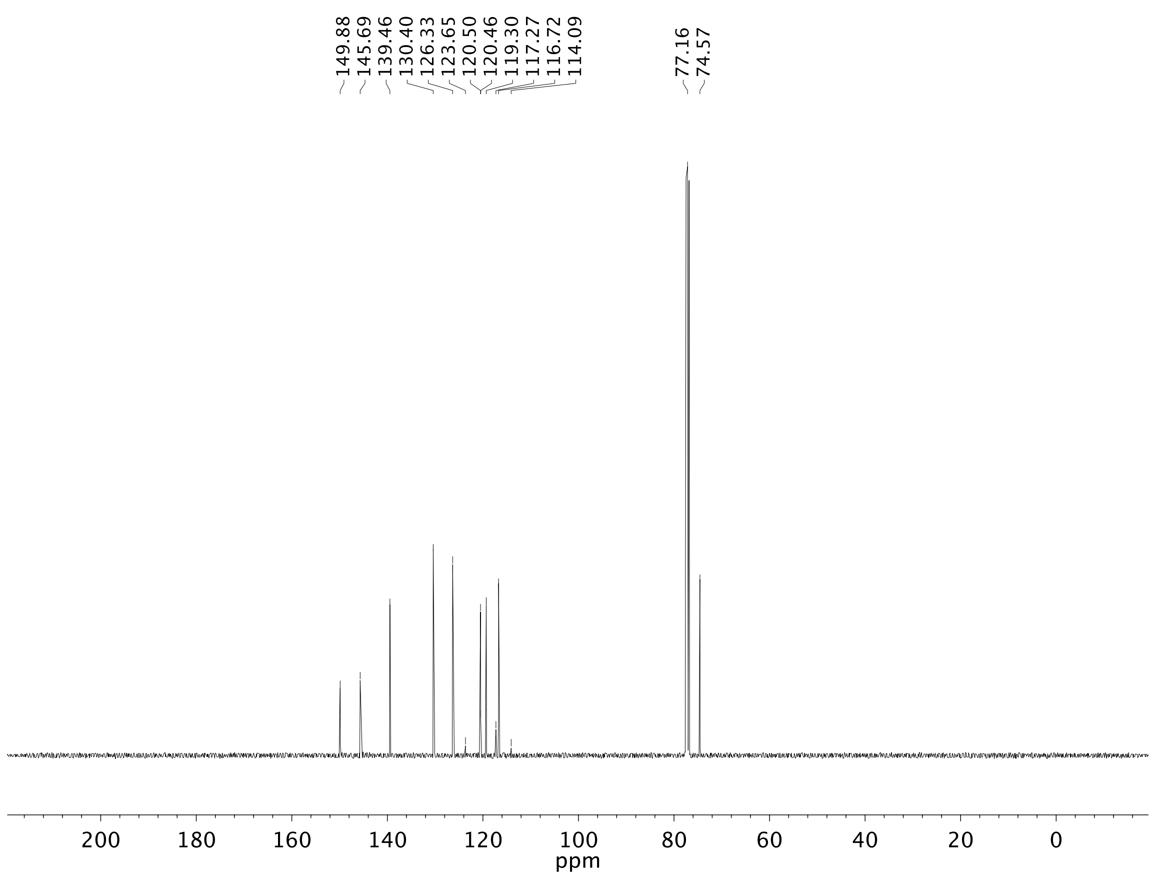
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1n**



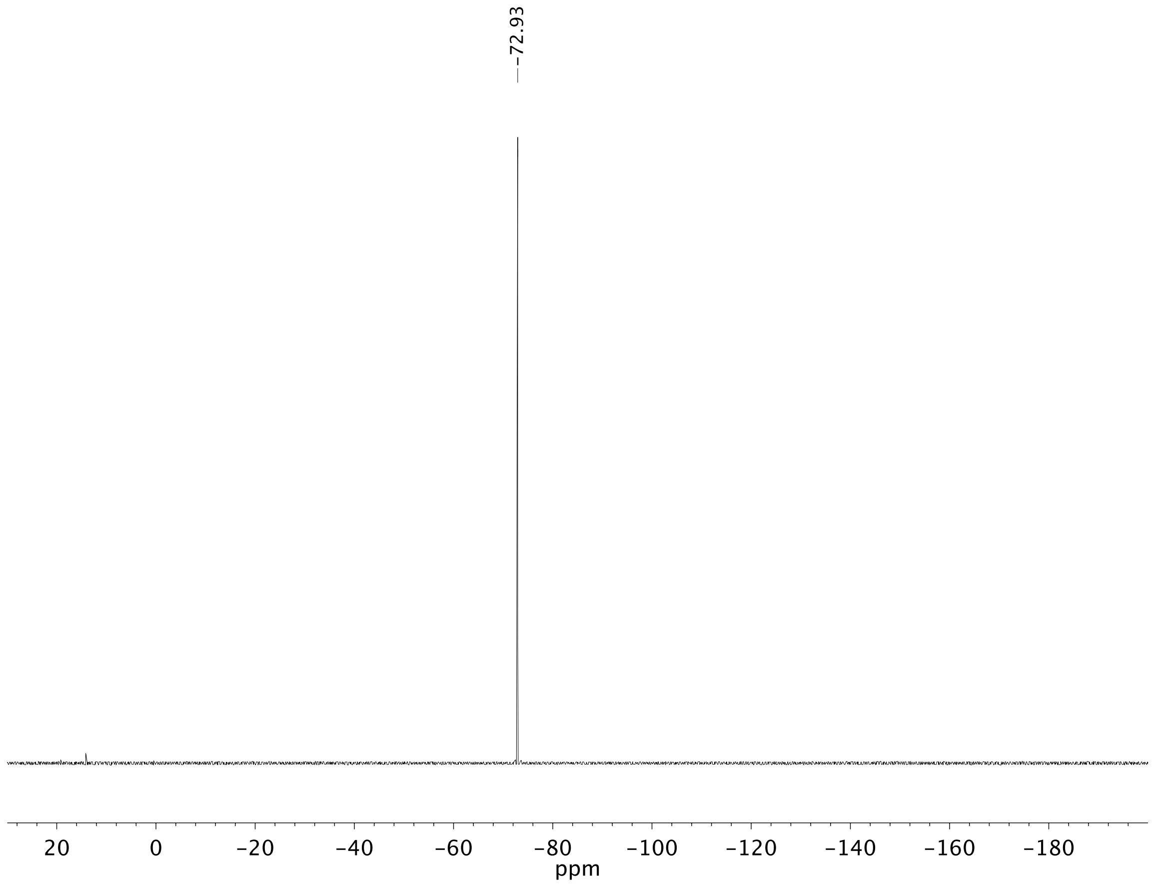
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI5**



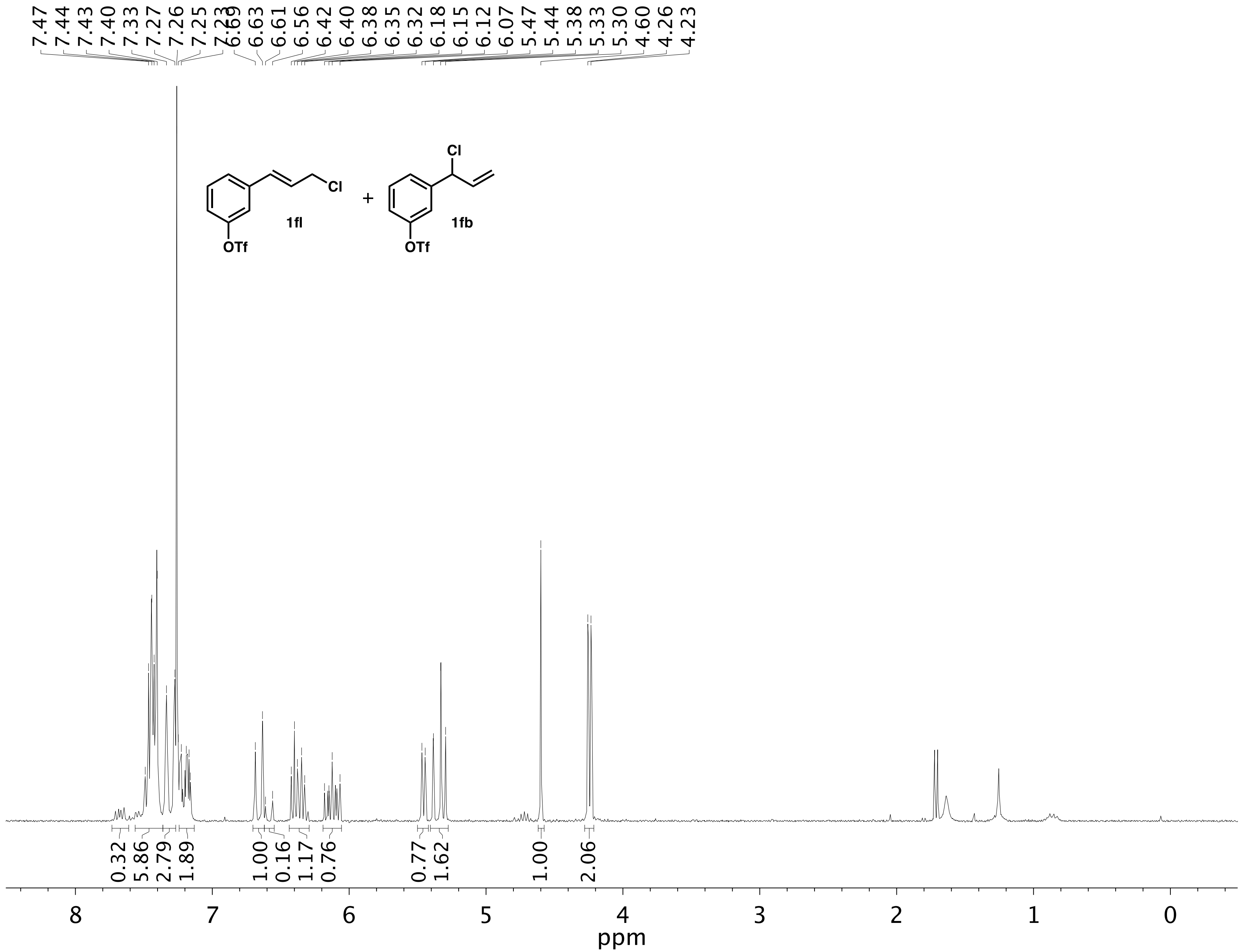
Infrared spectrum (Thin Film, NaCl) of compound **SI5**



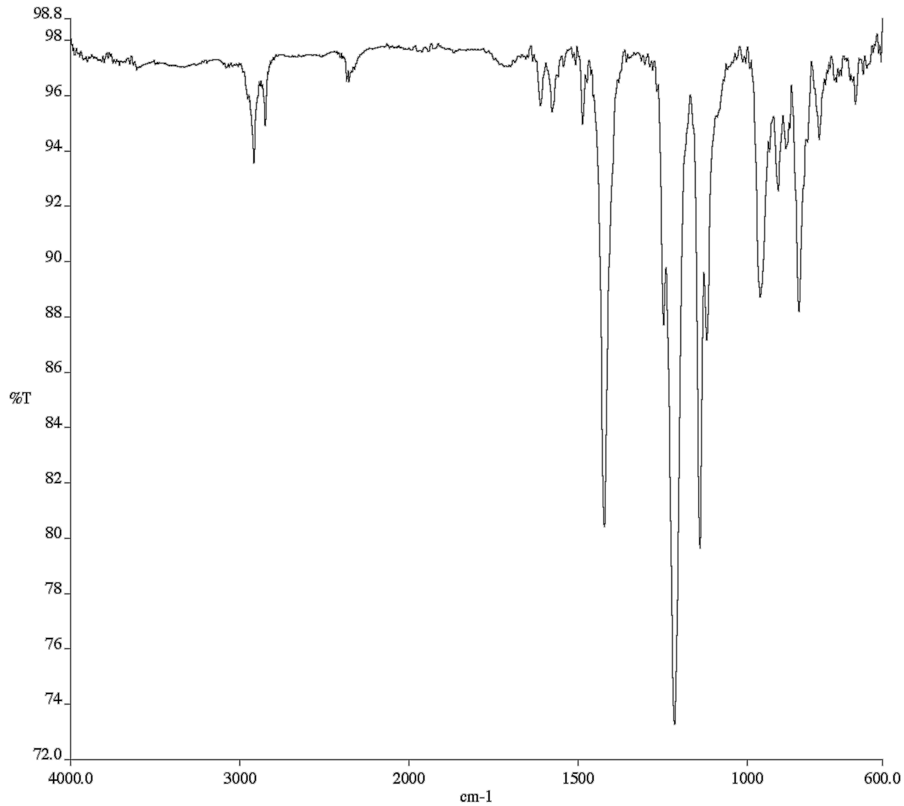
^{13}C NMR (101 MHz, $CDCl_3$) of compound **SI5**



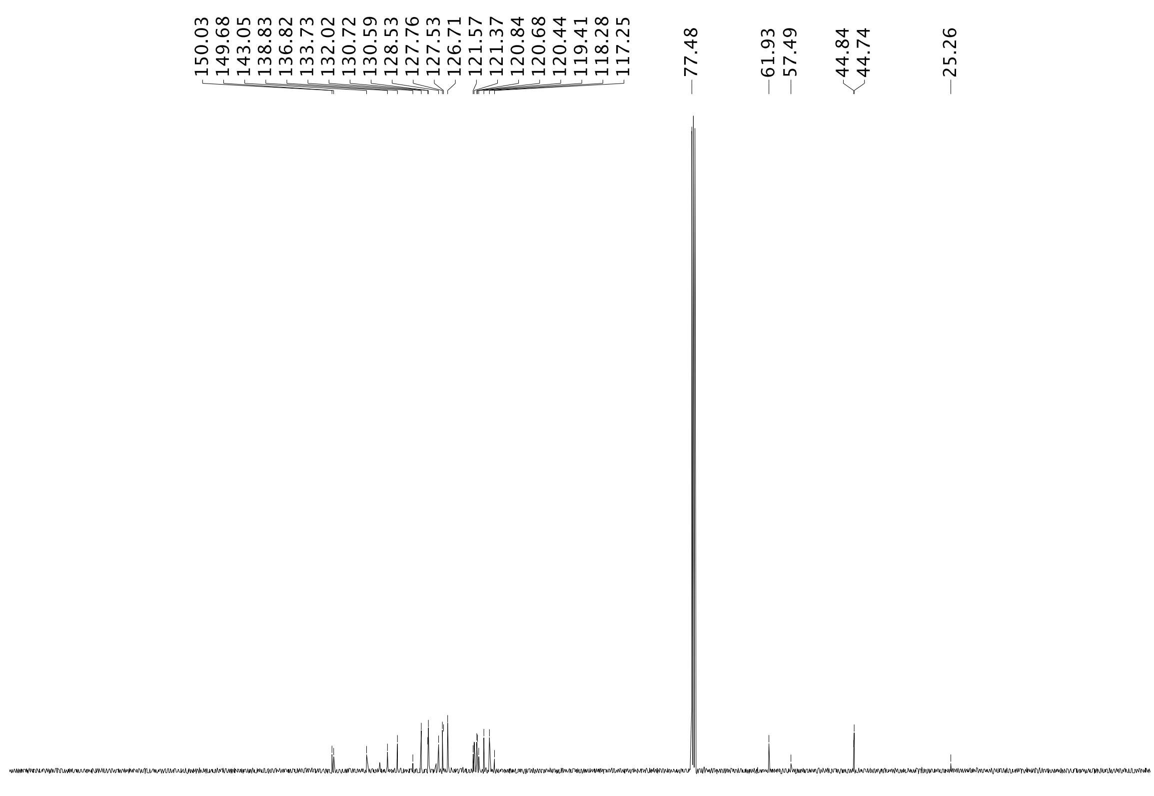
^{19}F NMR (282 MHz, $CDCl_3$) of compound **SI5**



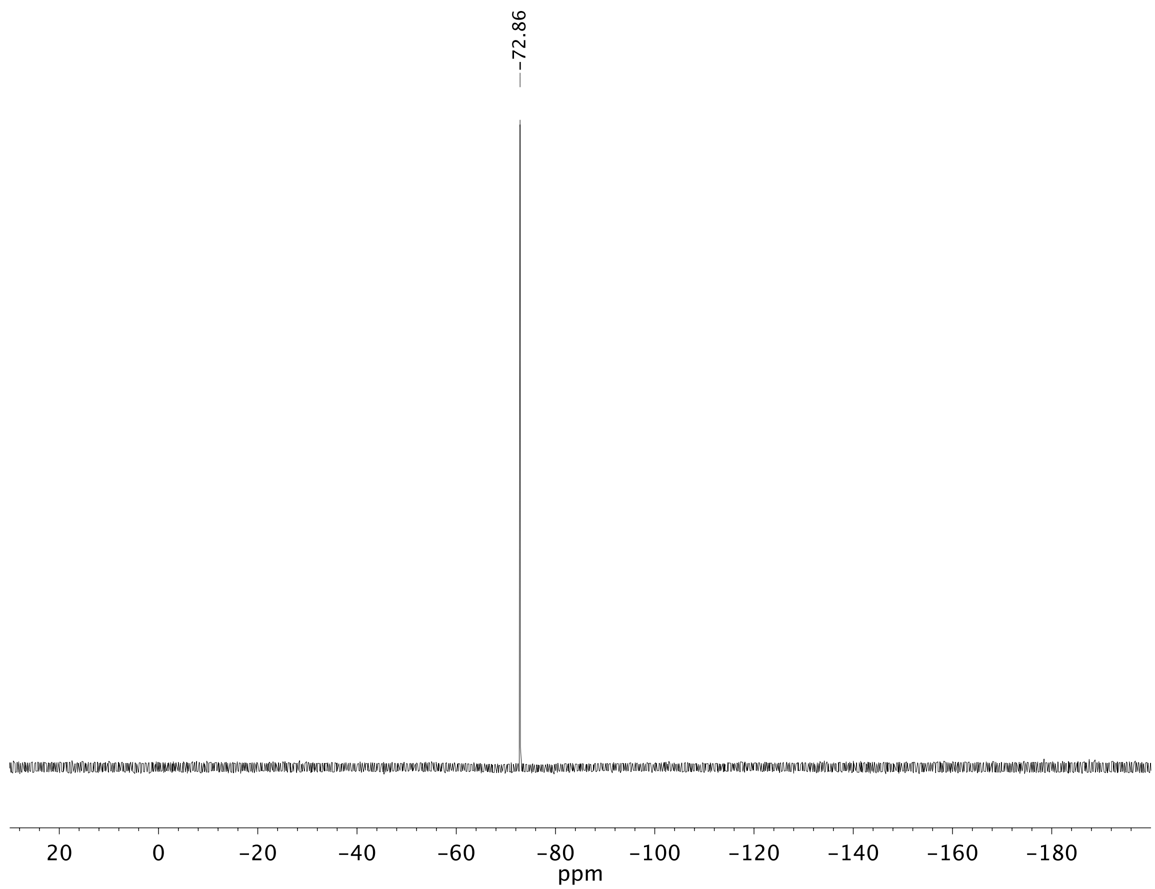
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1f**



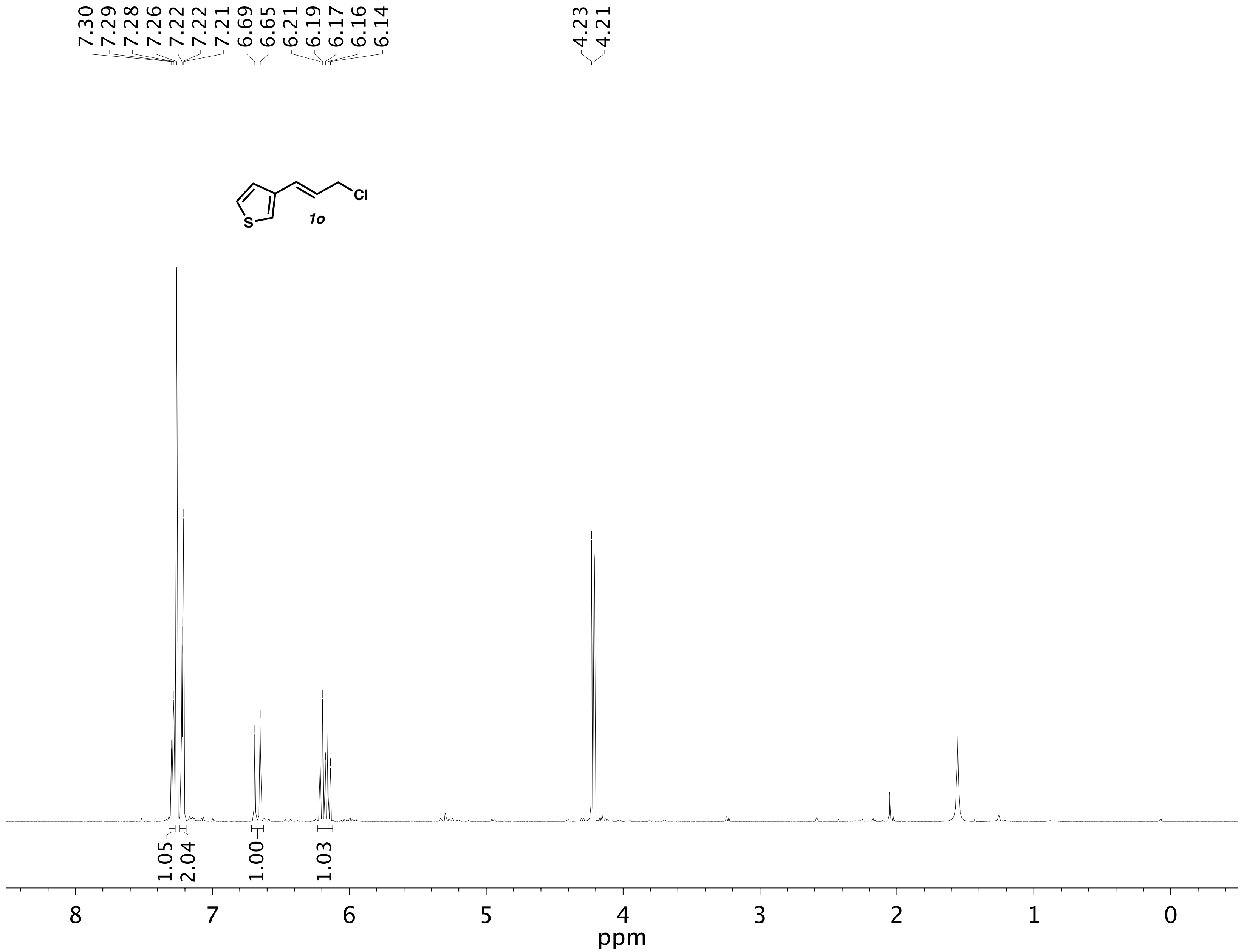
Infrared spectrum (Thin Film, NaCl) of compound **1f**



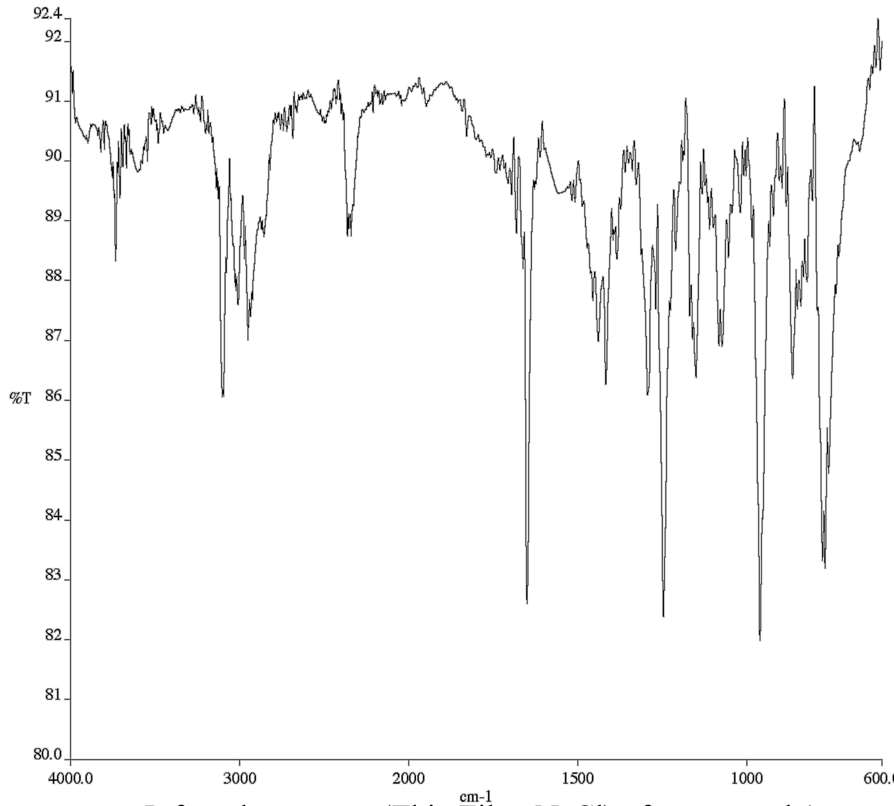
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1f**



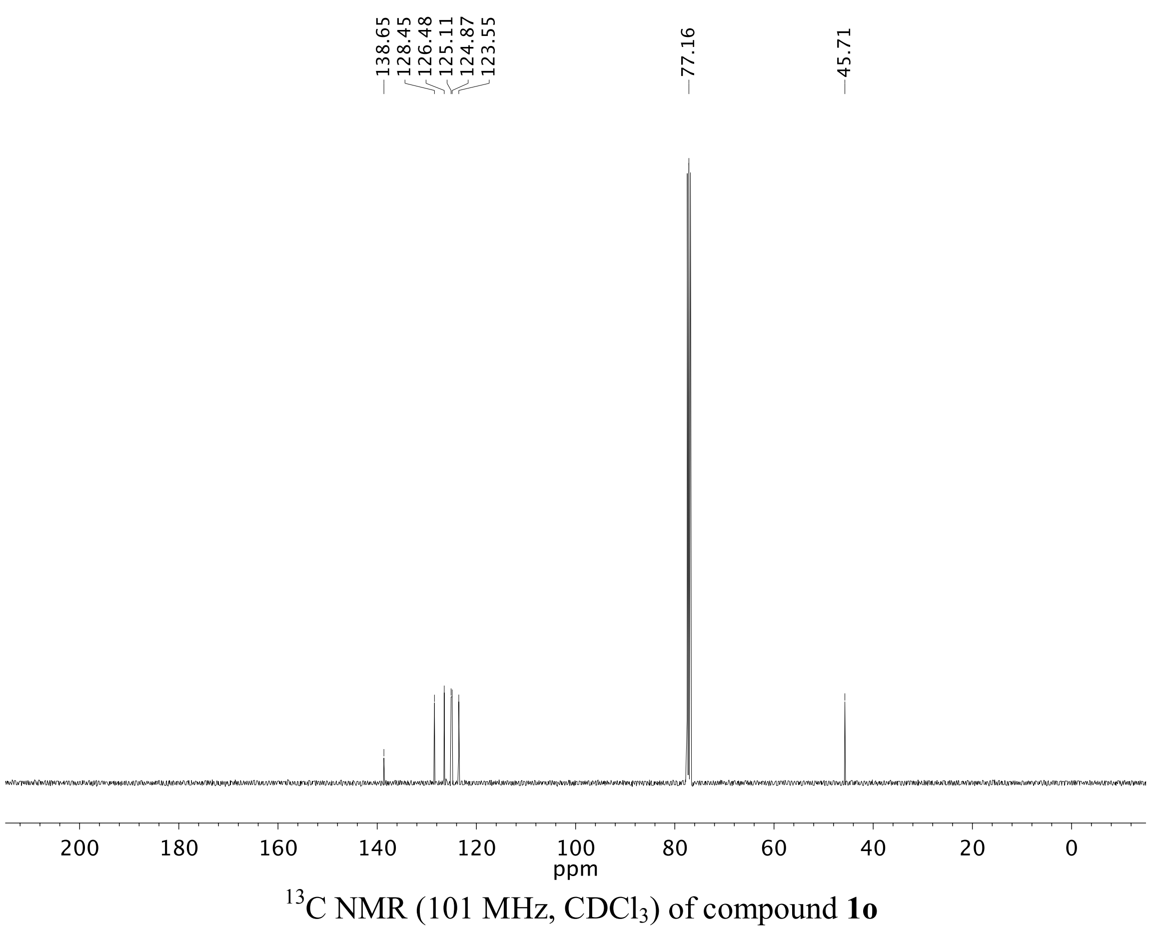
^{19}F NMR (282 MHz, $CDCl_3$) of compound **1f**



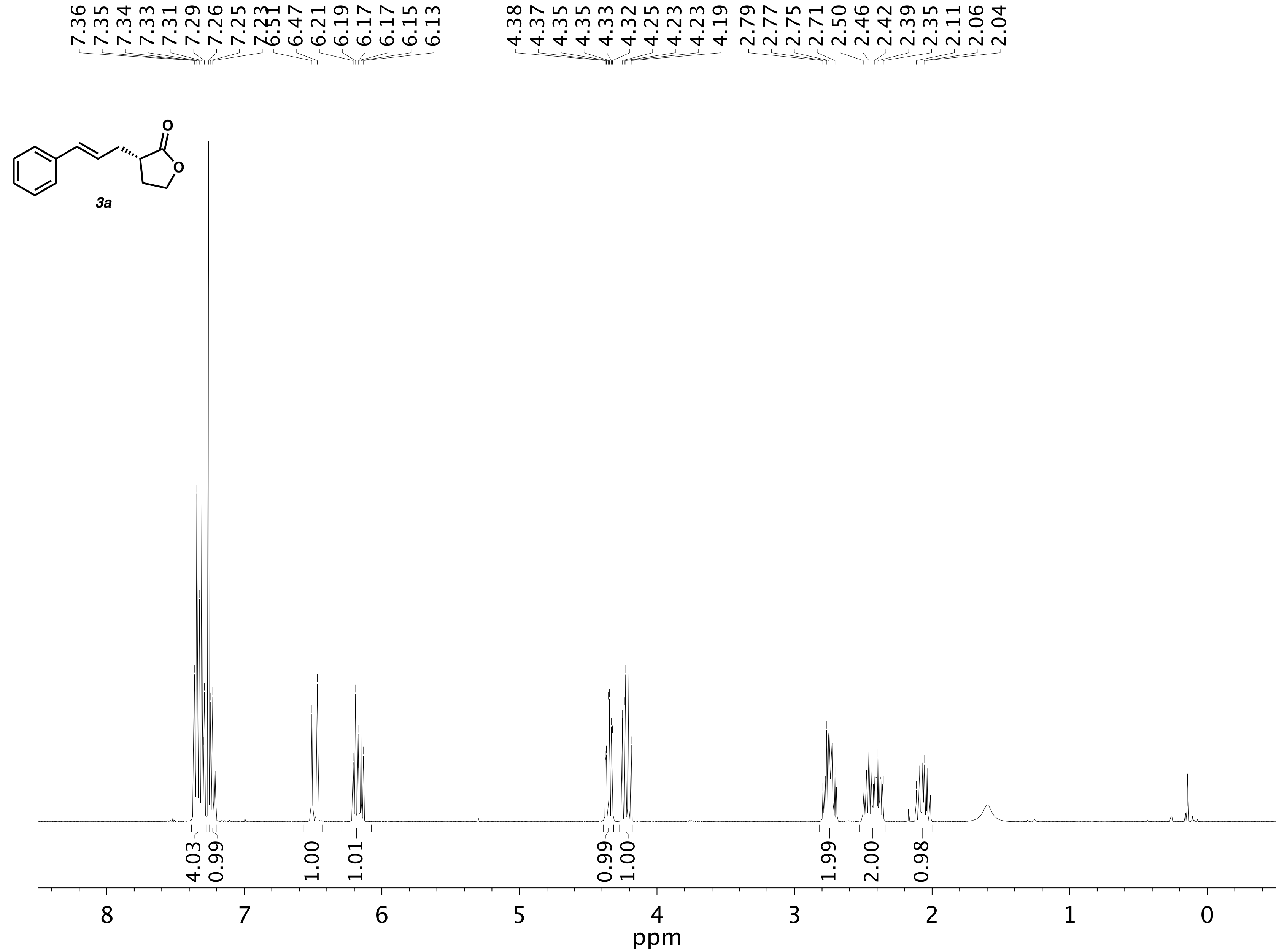
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1o**



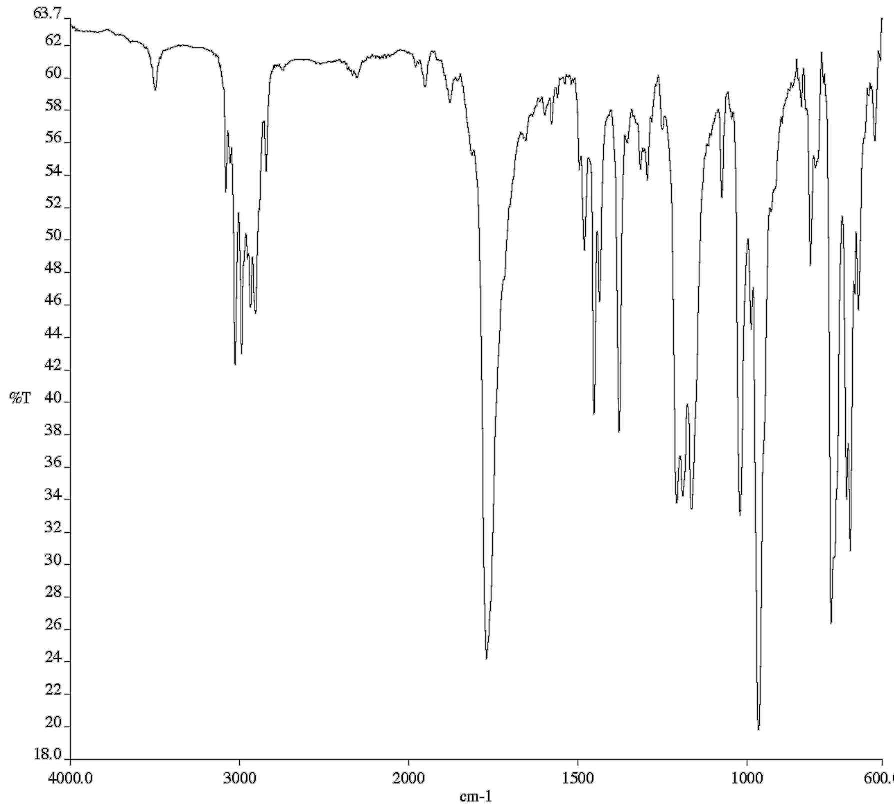
Infrared spectrum (Thin Film, NaCl) of compound **1o**



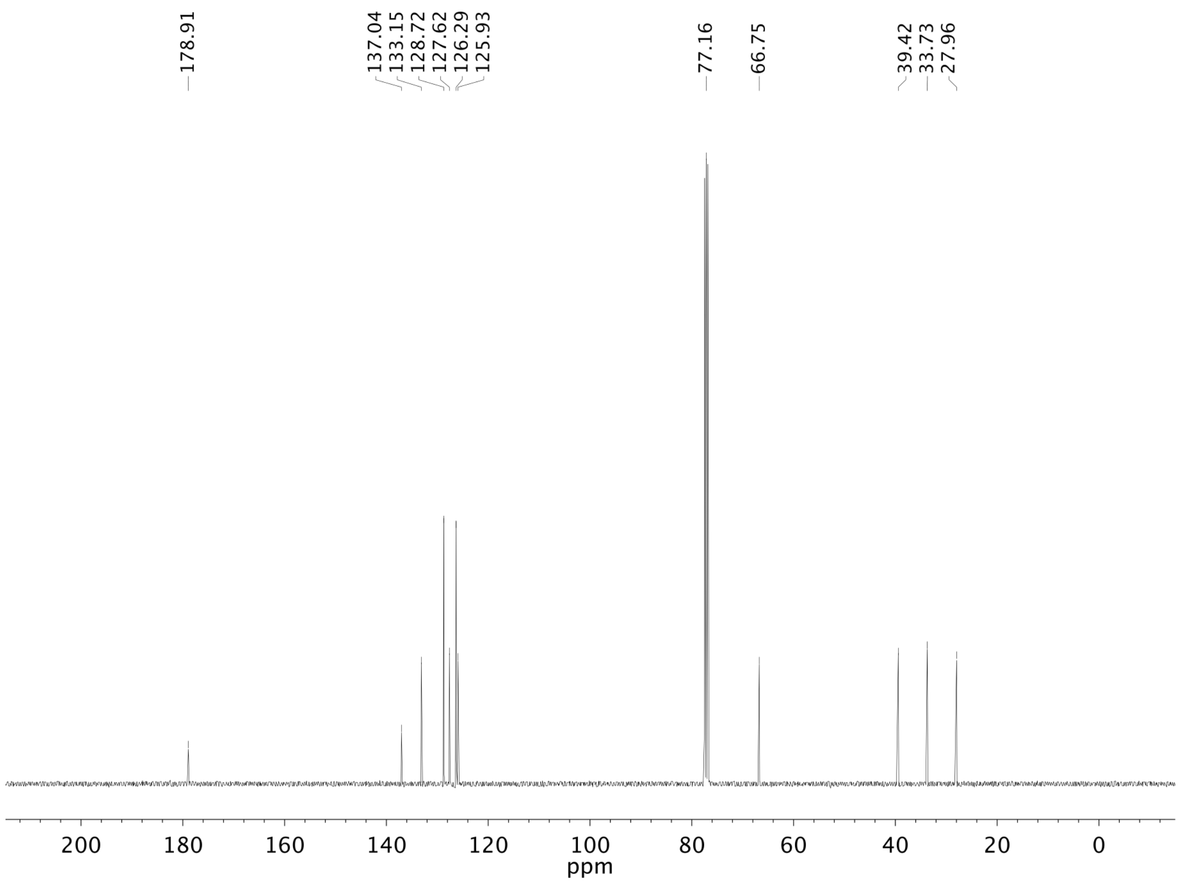
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1o**



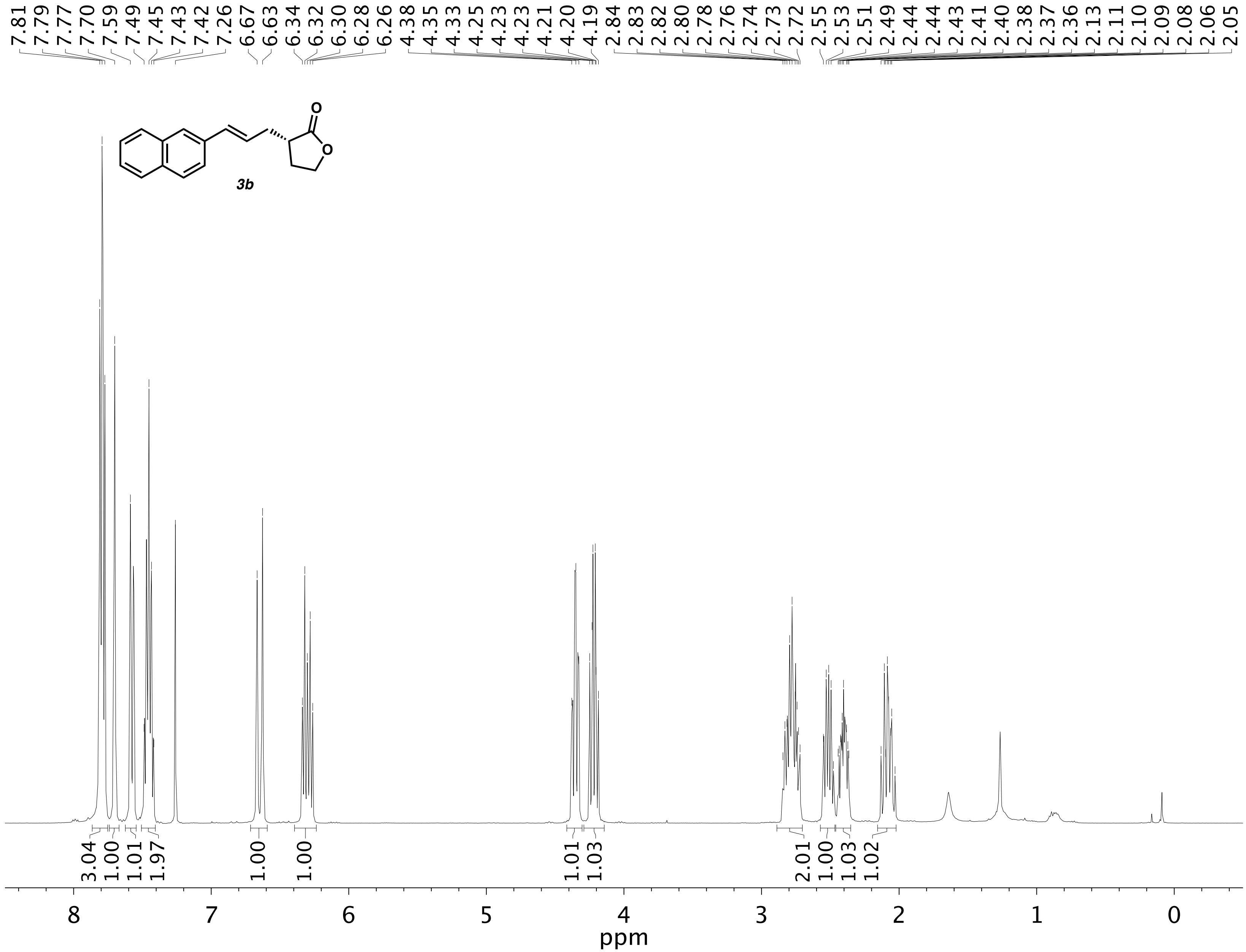
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**



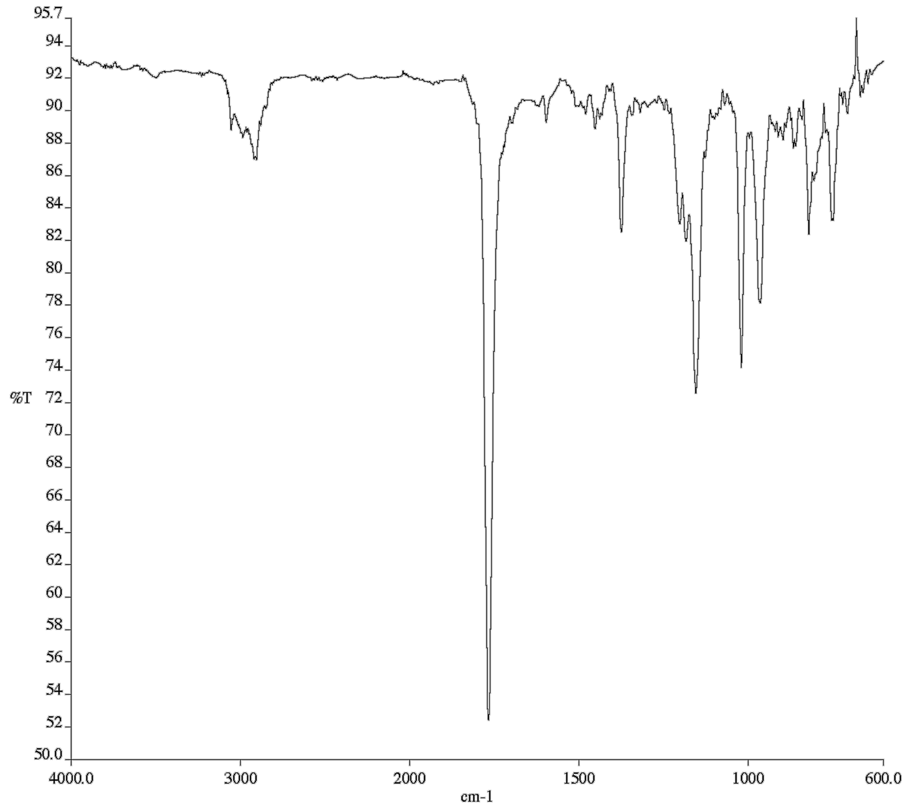
Infrared spectrum (Thin Film, NaCl) of compound **3a**



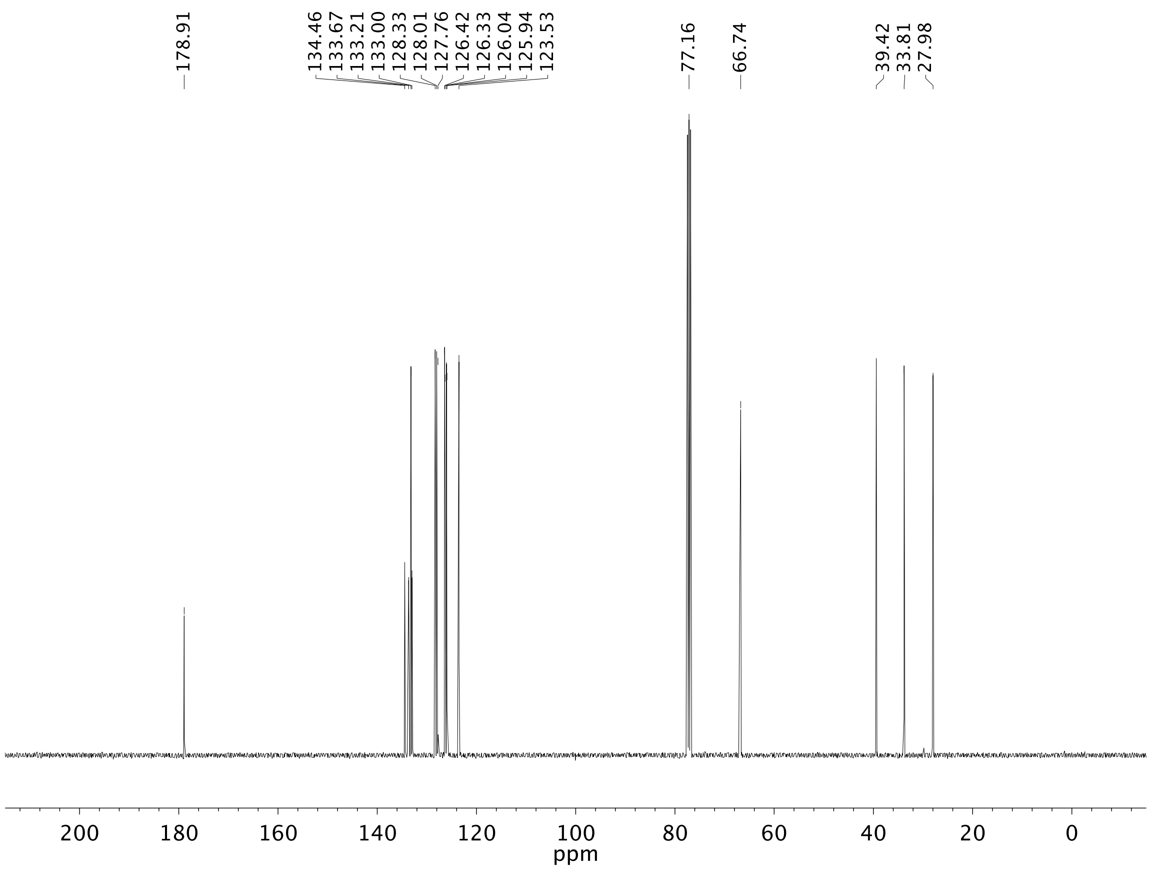
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3a**



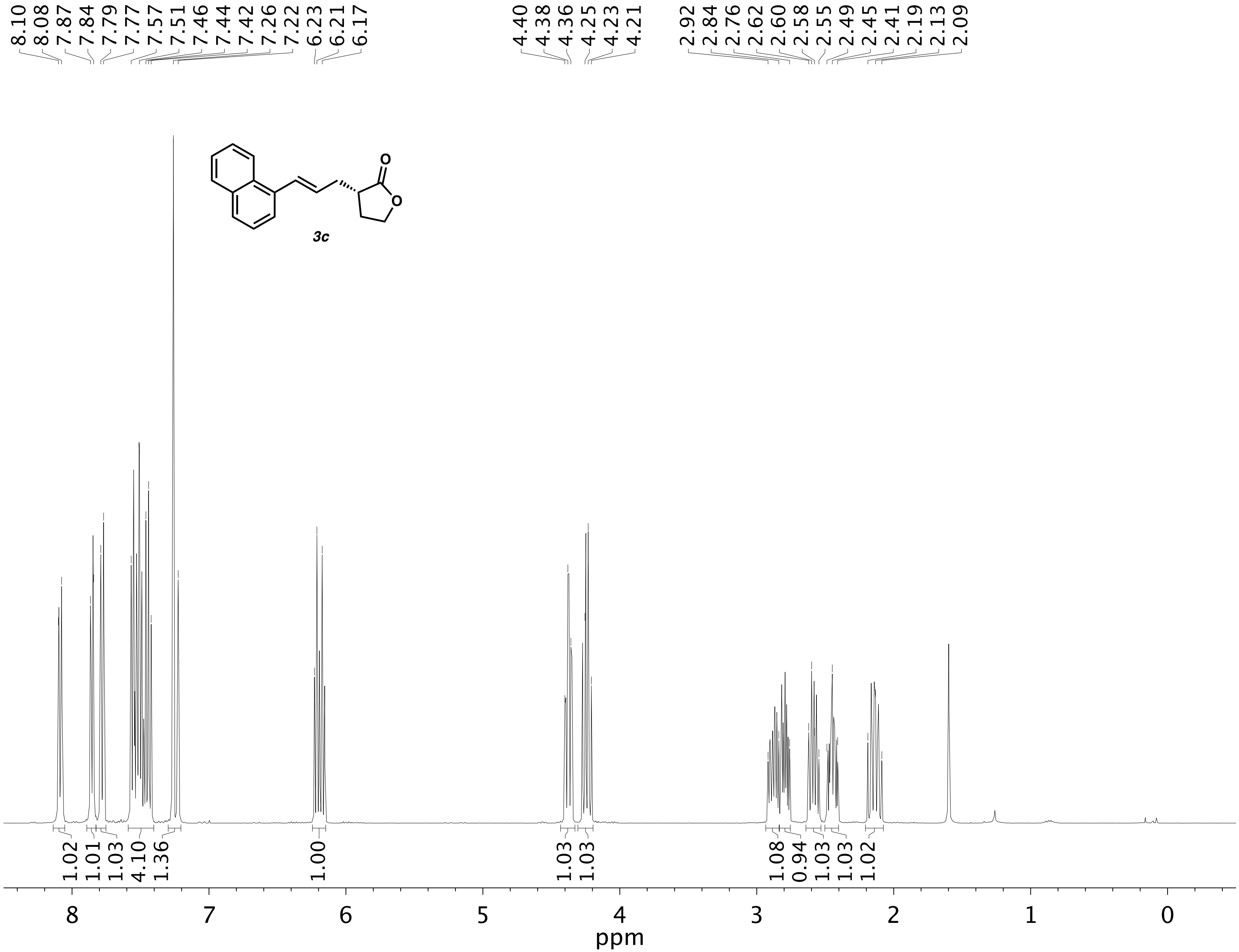
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**



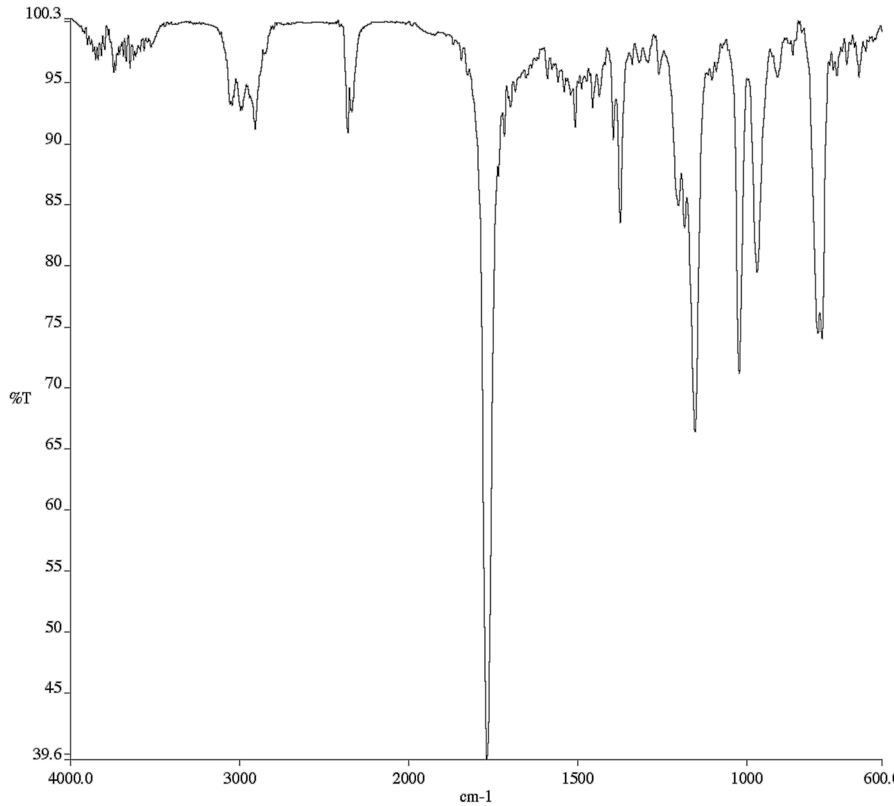
Infrared spectrum (Thin Film, NaCl) of compound **3b**



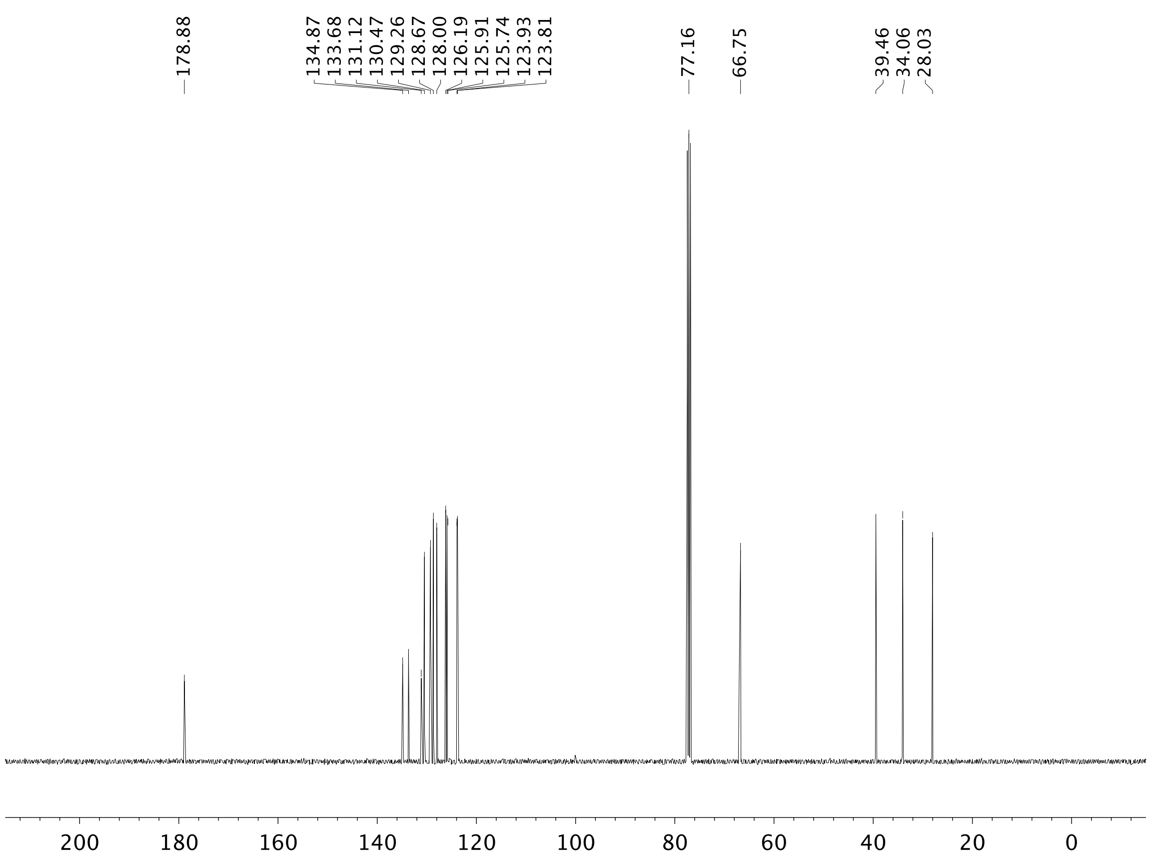
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3b**



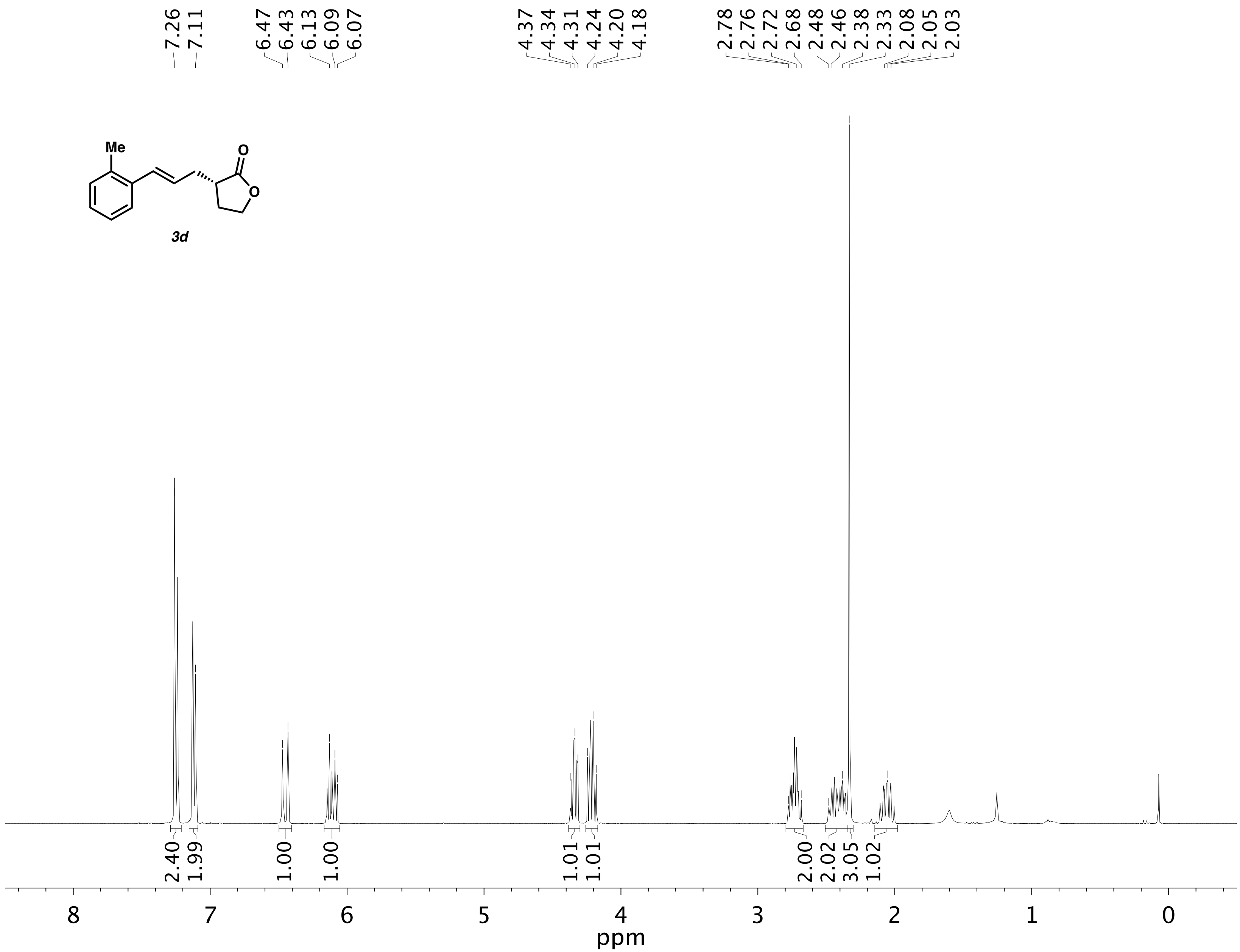
[1]H NMR (400 MHz, $CDCl_3$) of compound **3c**



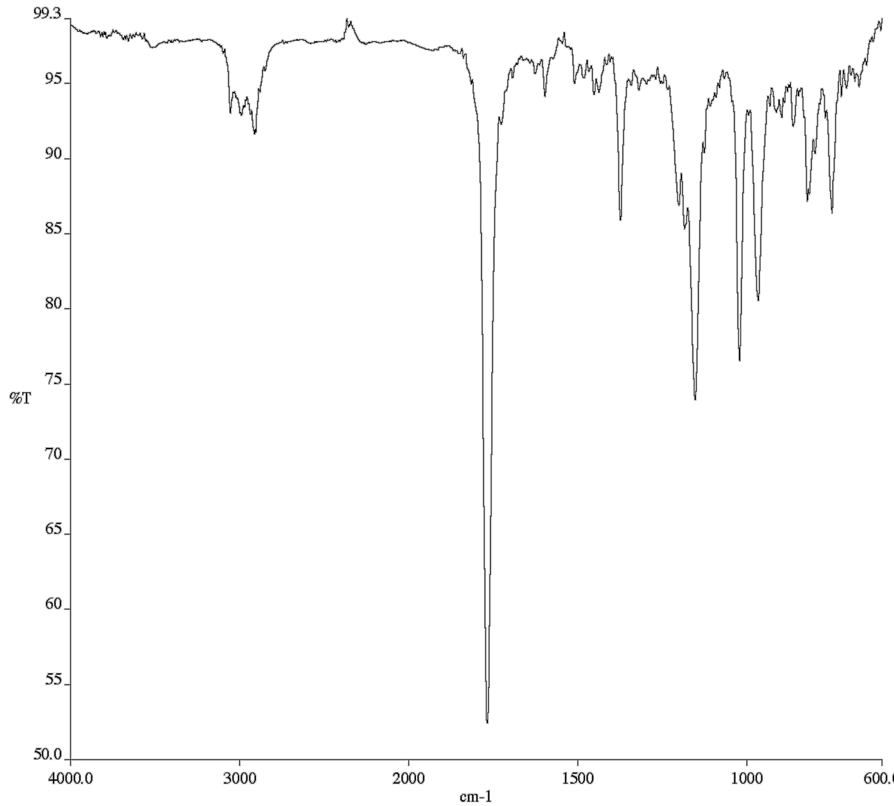
Infrared spectrum (Thin Film, NaCl) of compound **3c**



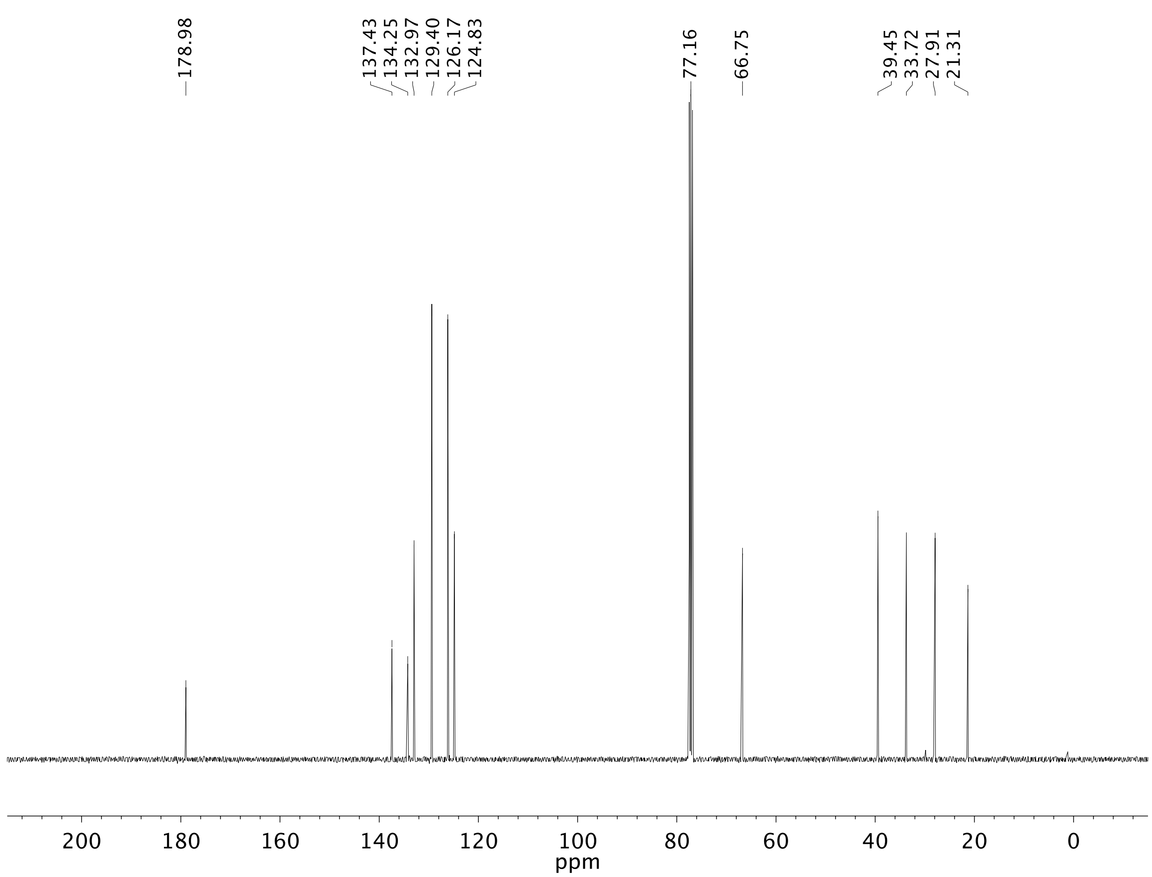
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3c**



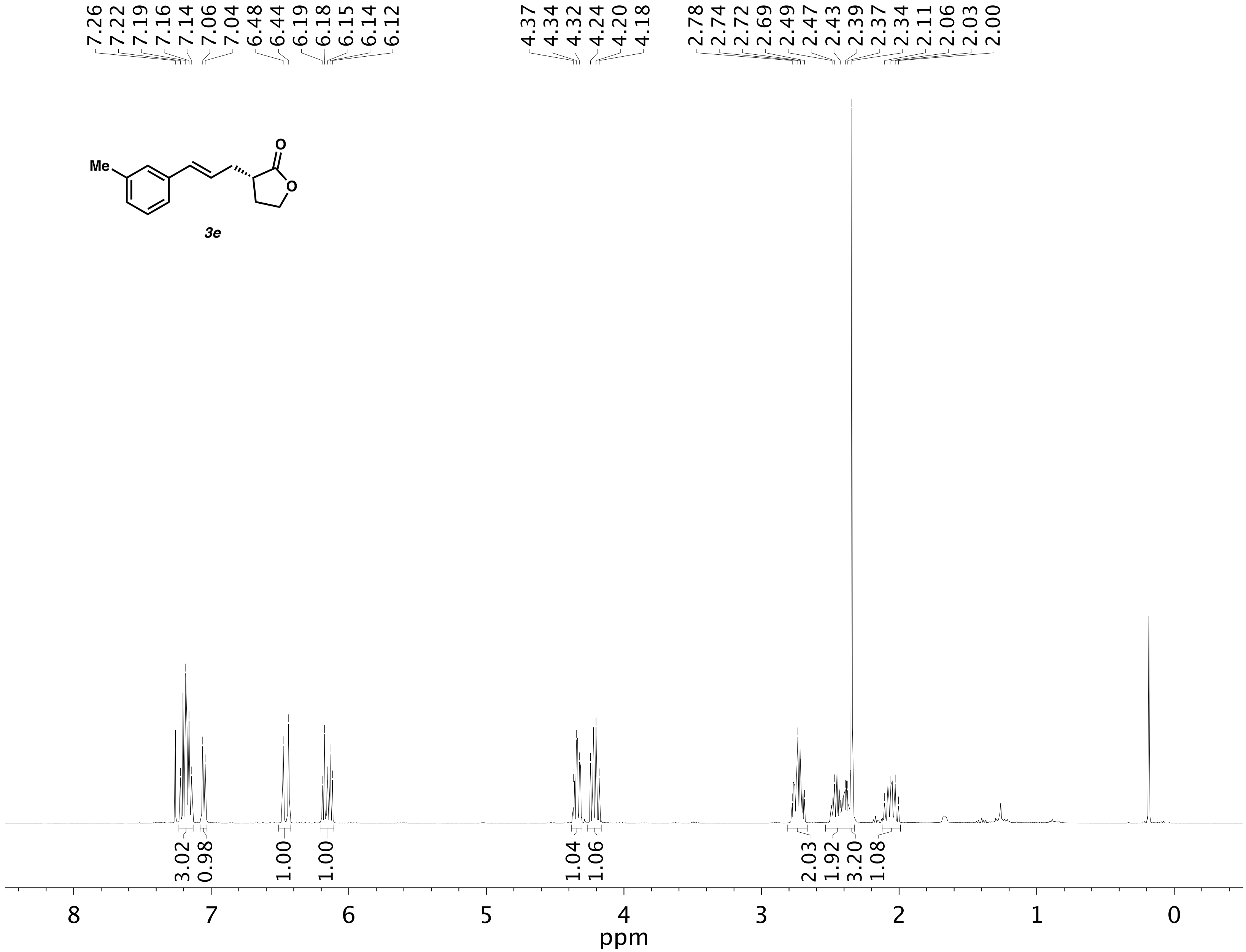
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**



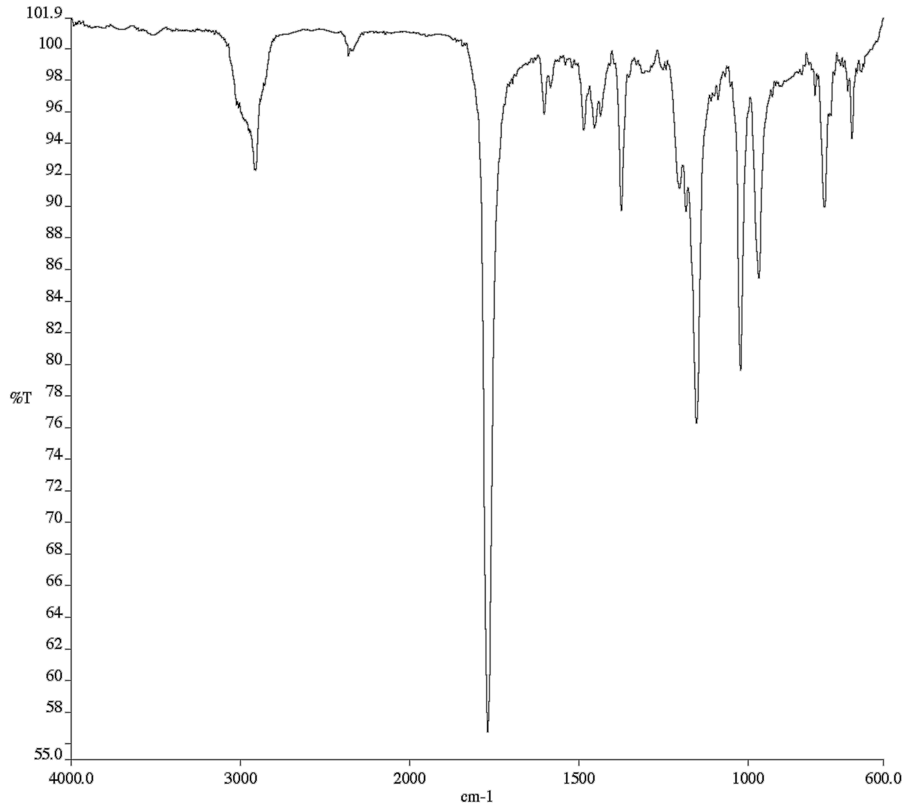
Infrared spectrum (Thin Film, NaCl) of compound **3d**



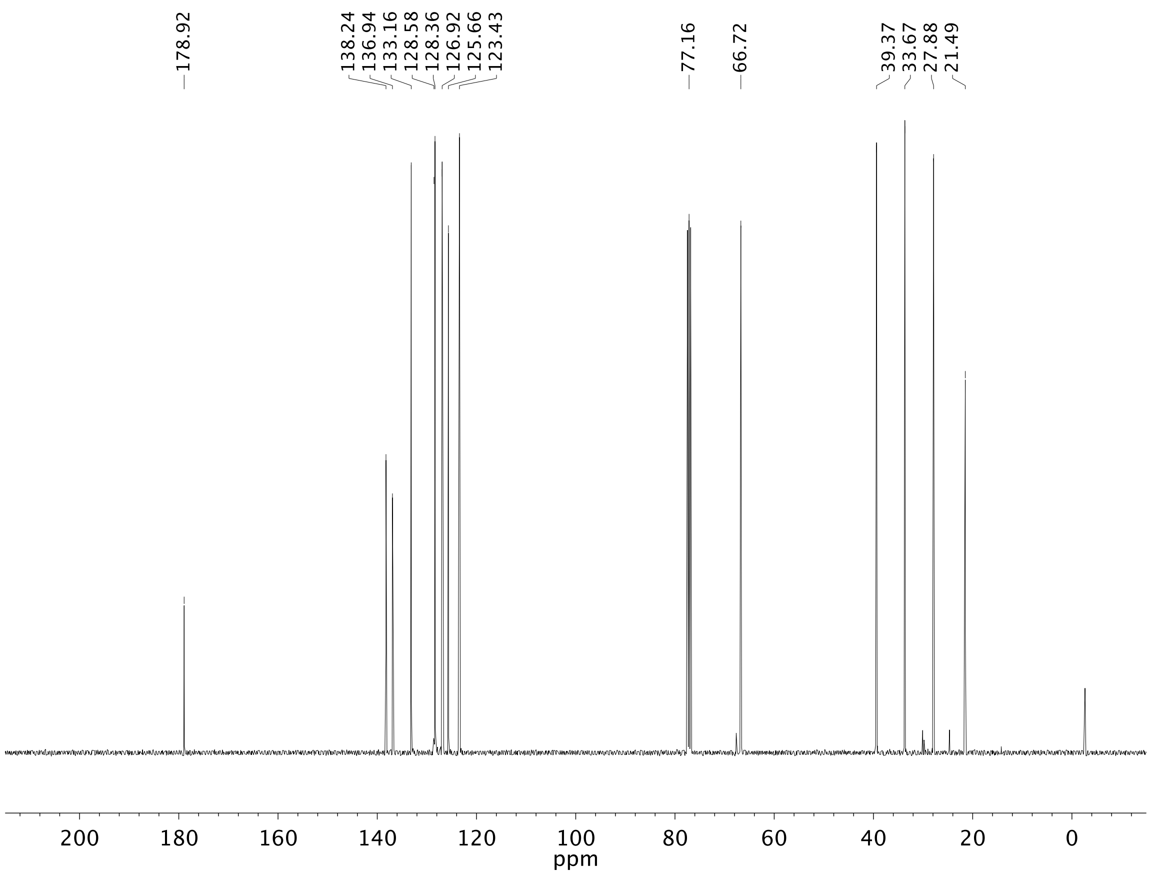
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3d**



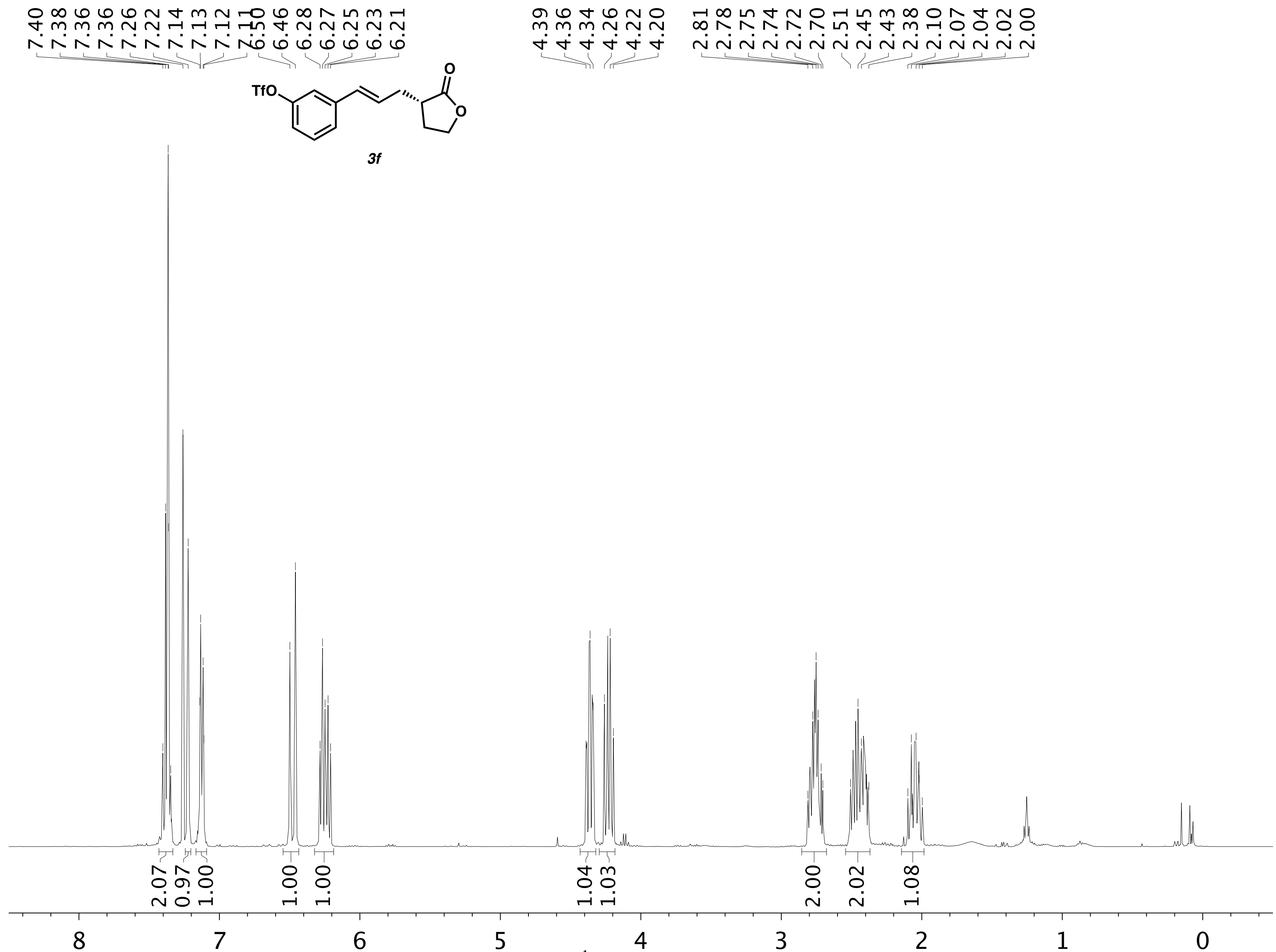
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**



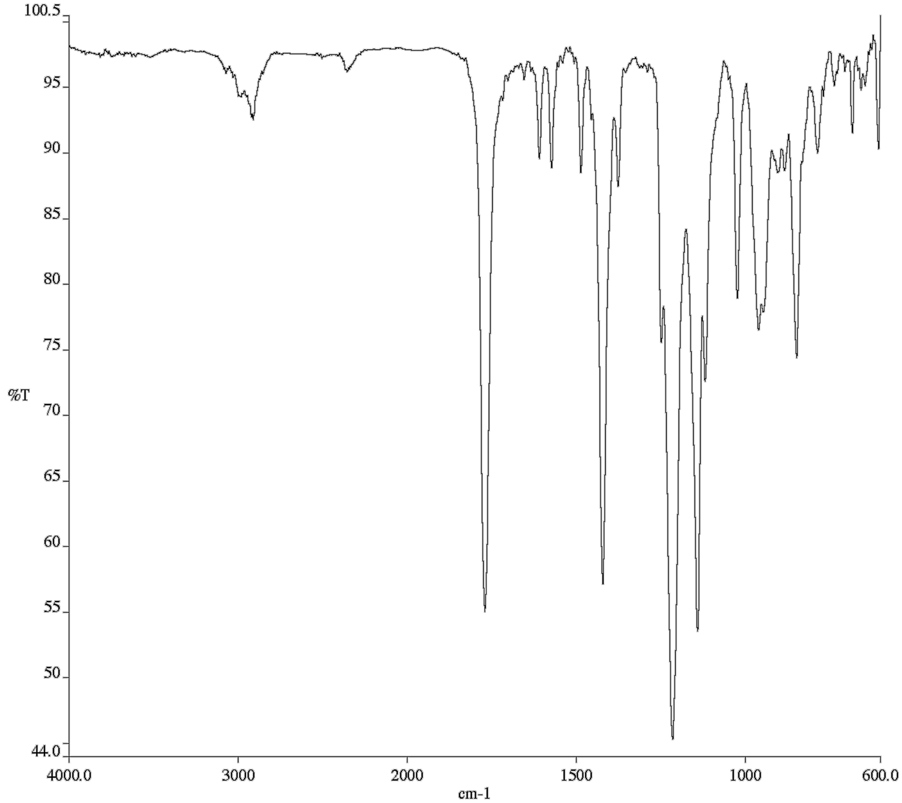
Infrared spectrum (Thin Film, NaCl) of compound **3e**



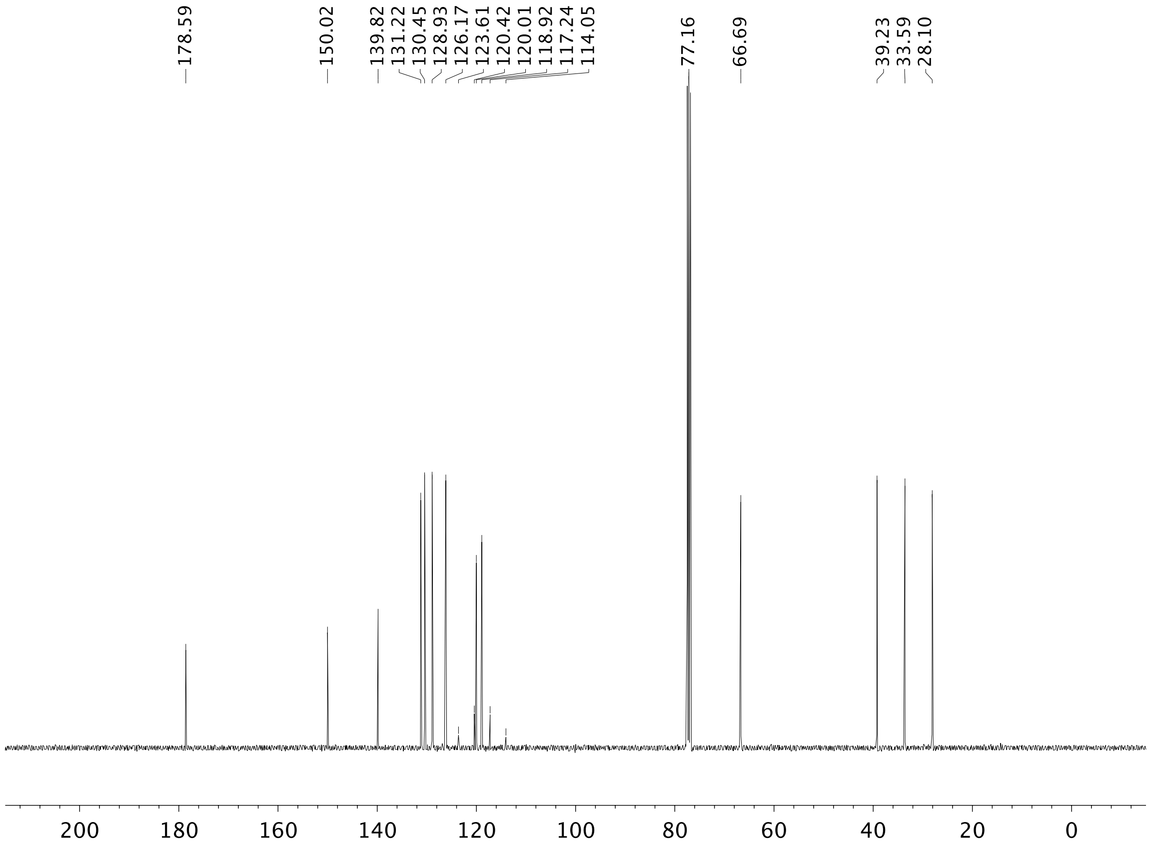
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3e**



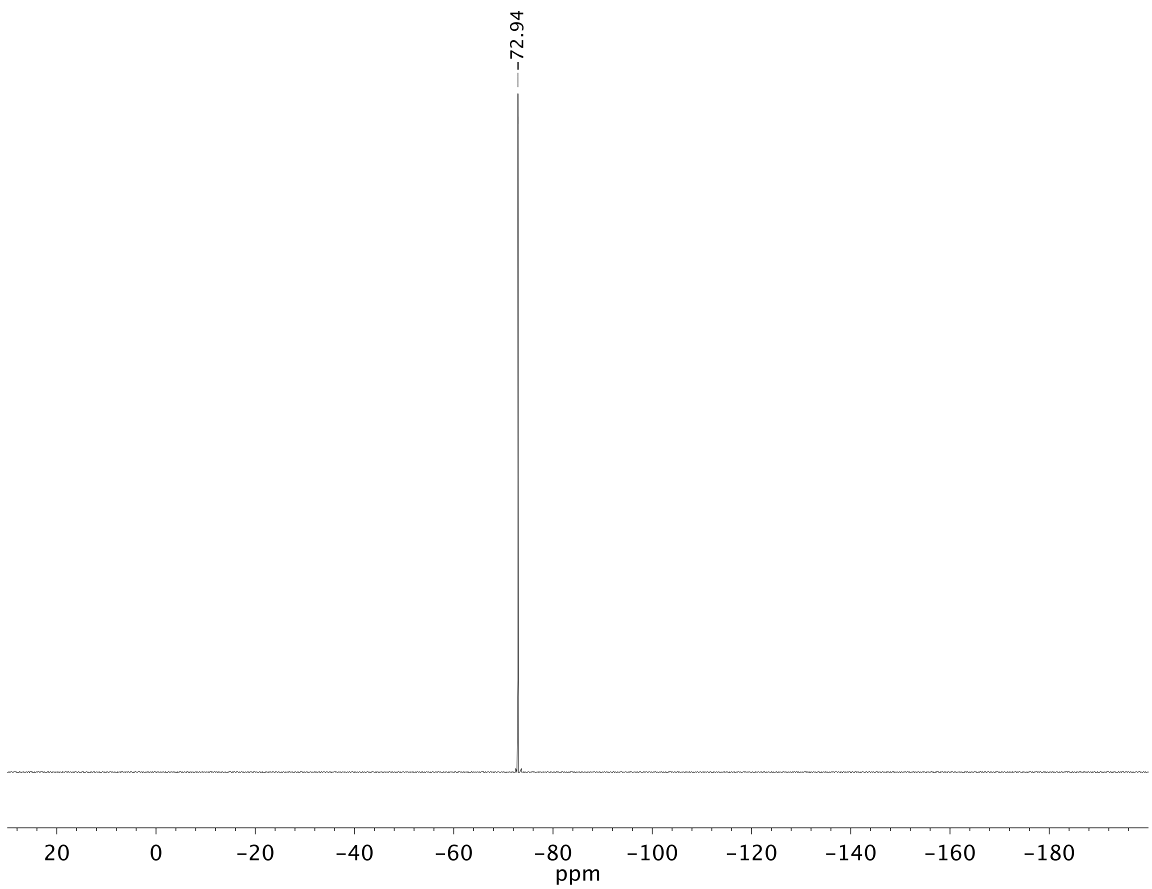
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**



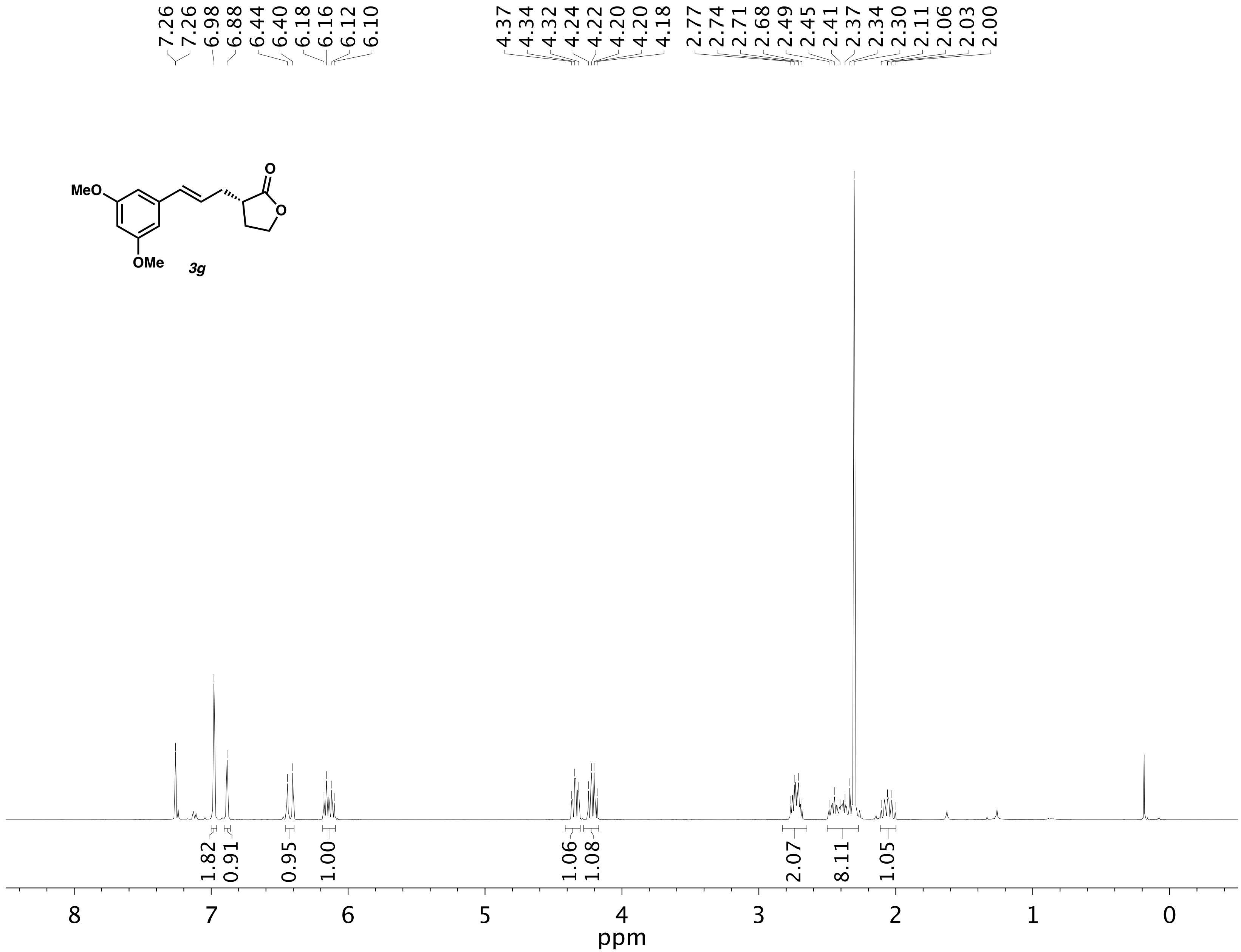
Infrared spectrum (Thin Film, NaCl) of compound **3f**



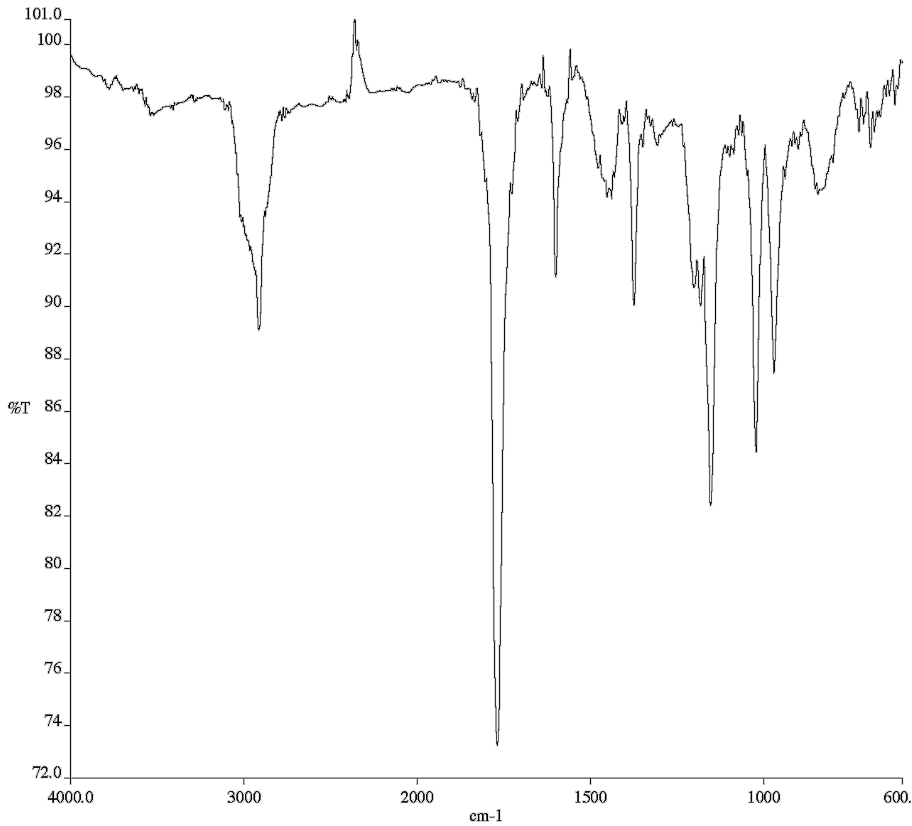
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3f**



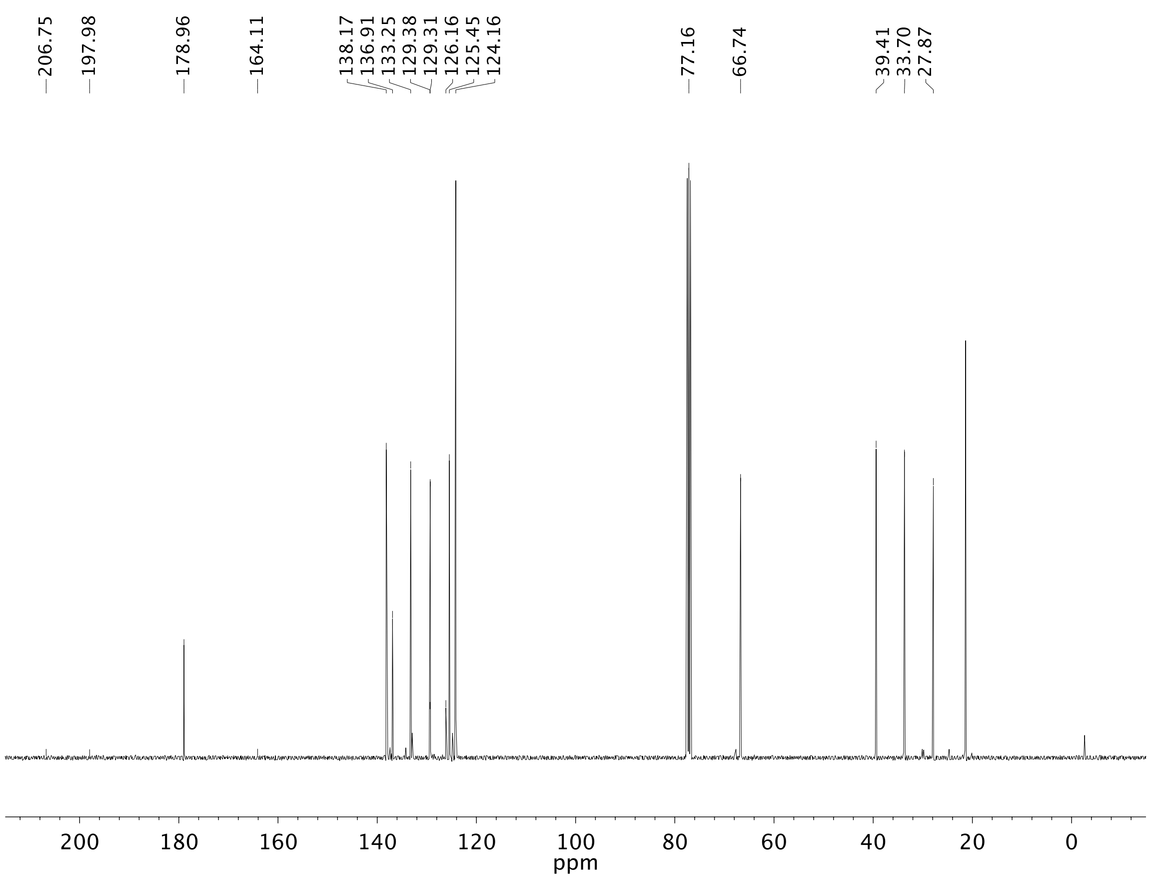
[19]F NMR (282 MHz, $CDCl_3$) of compound **3f**



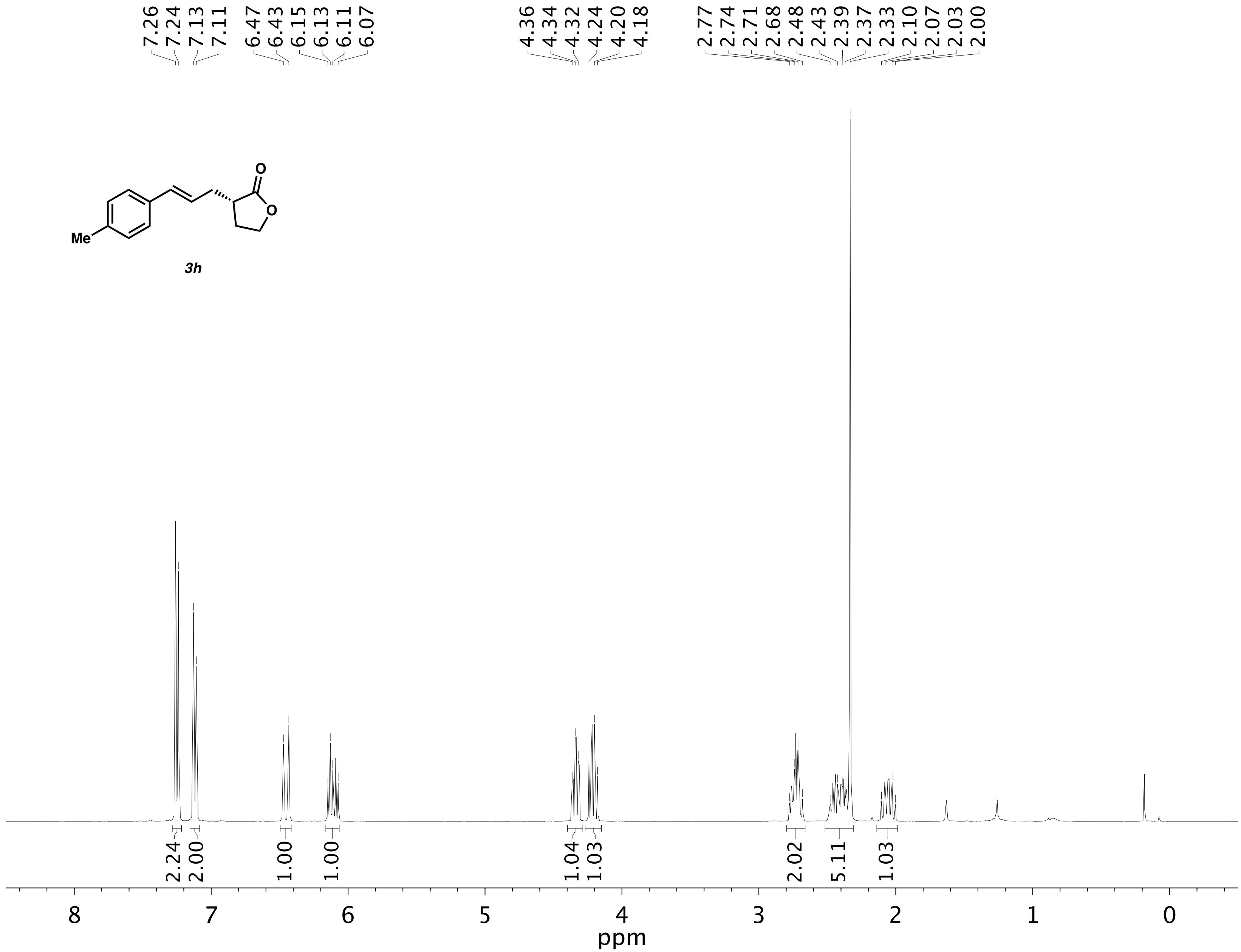
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**



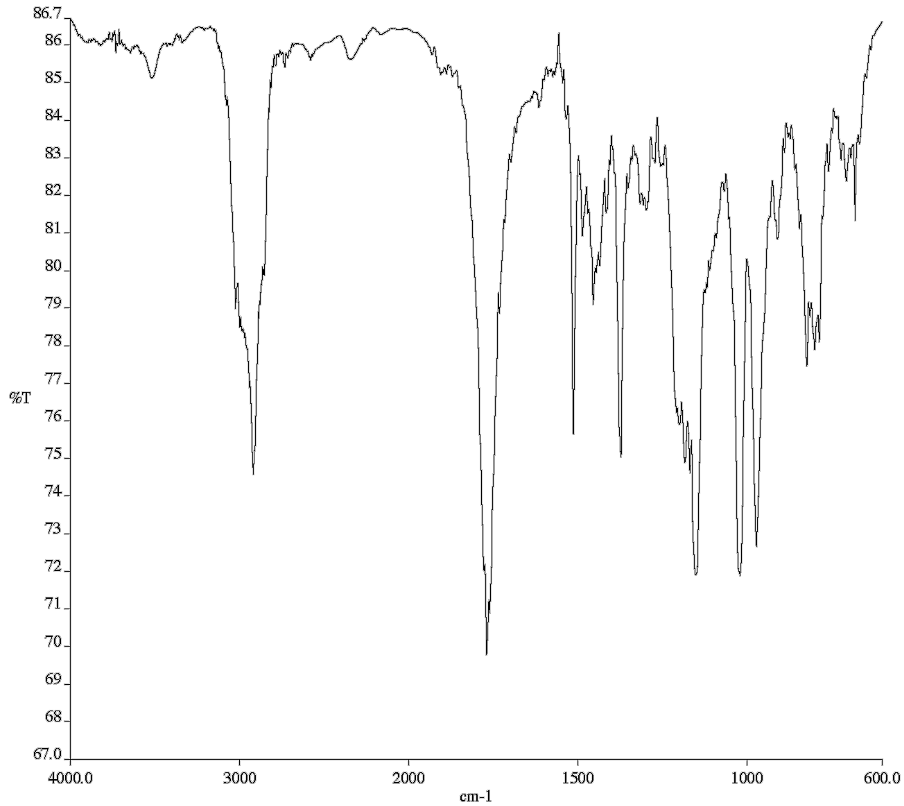
Infrared spectrum (Thin Film, NaCl) of compound **3g**.



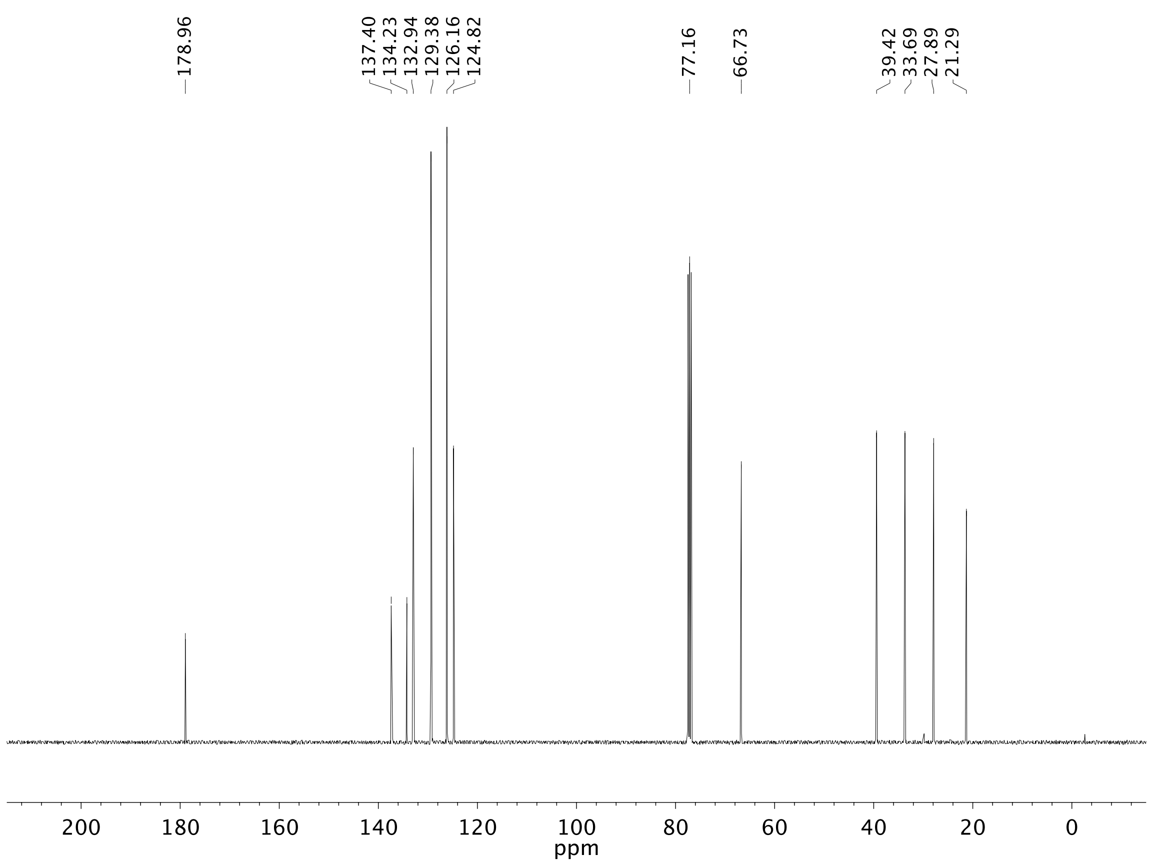
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3g**.



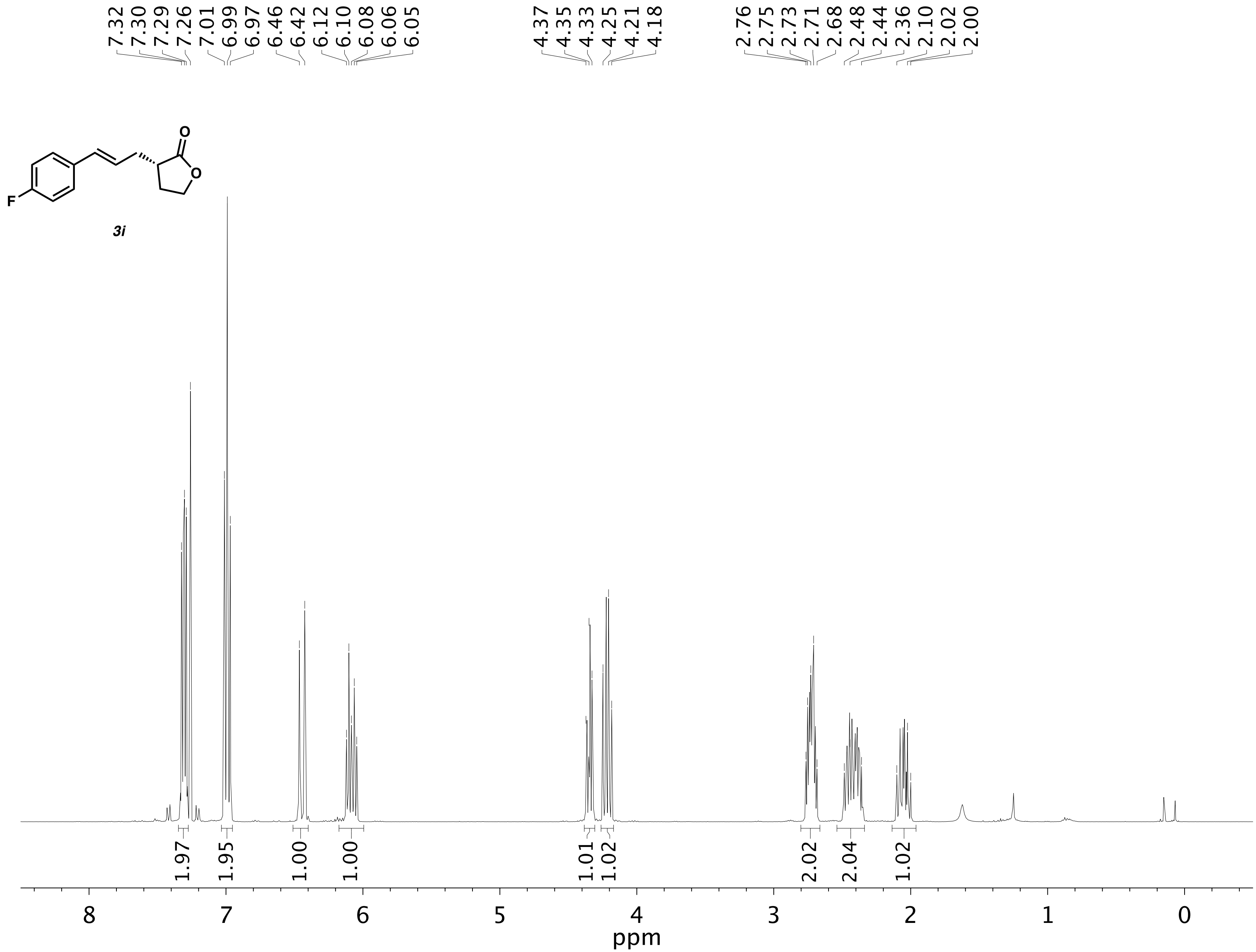
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**



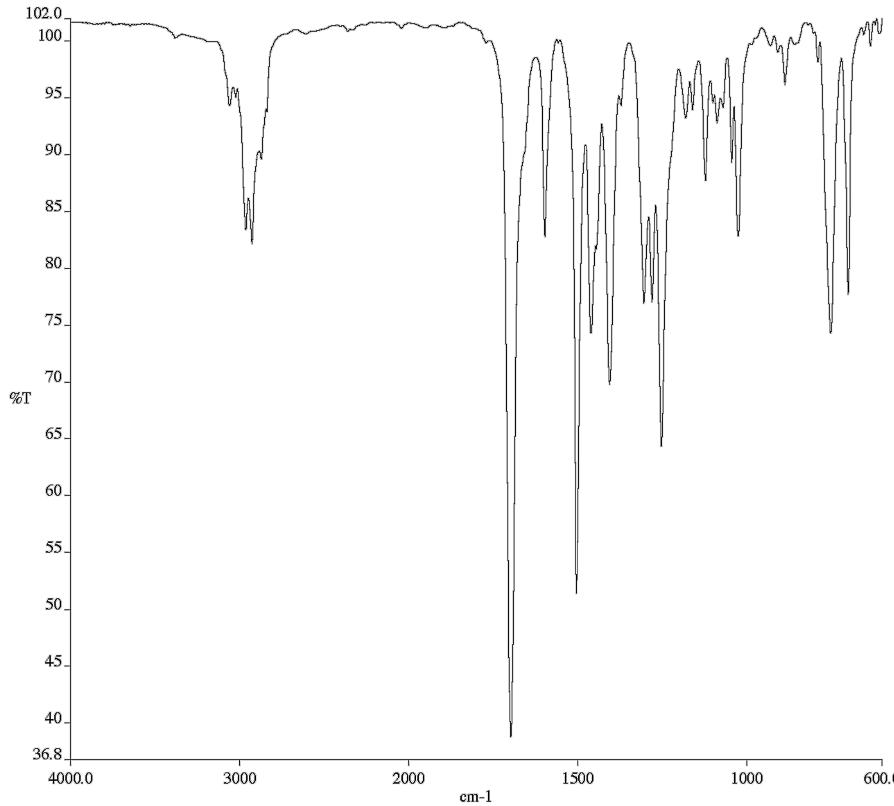
Infrared spectrum (Thin Film, NaCl) of compound **3h**.



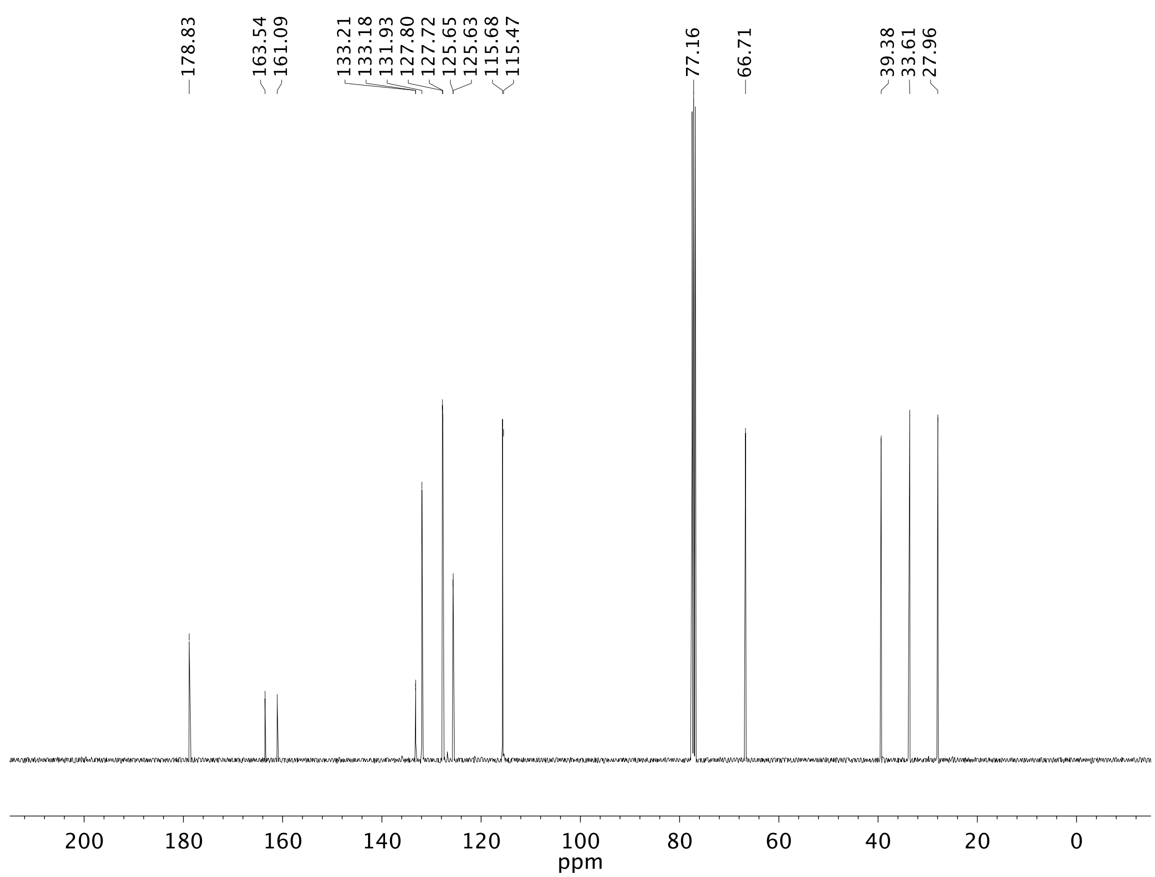
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3h**



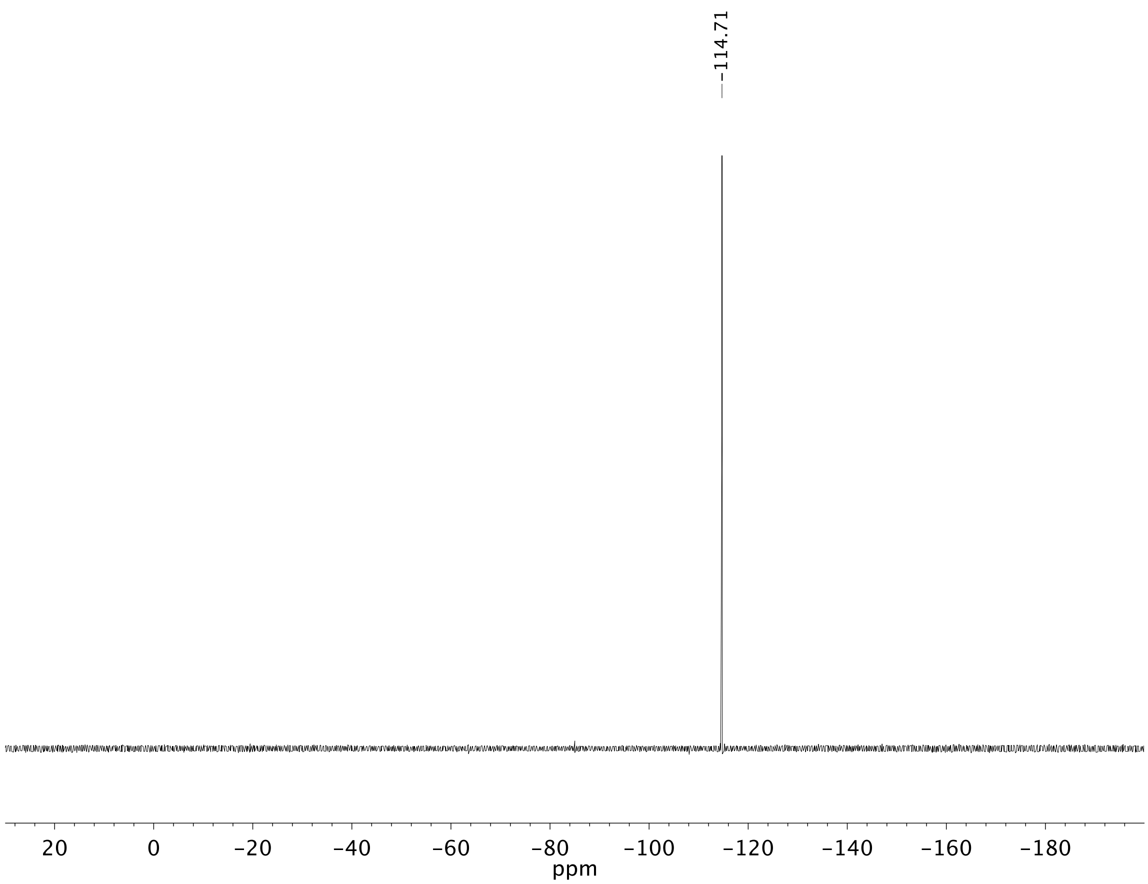
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**



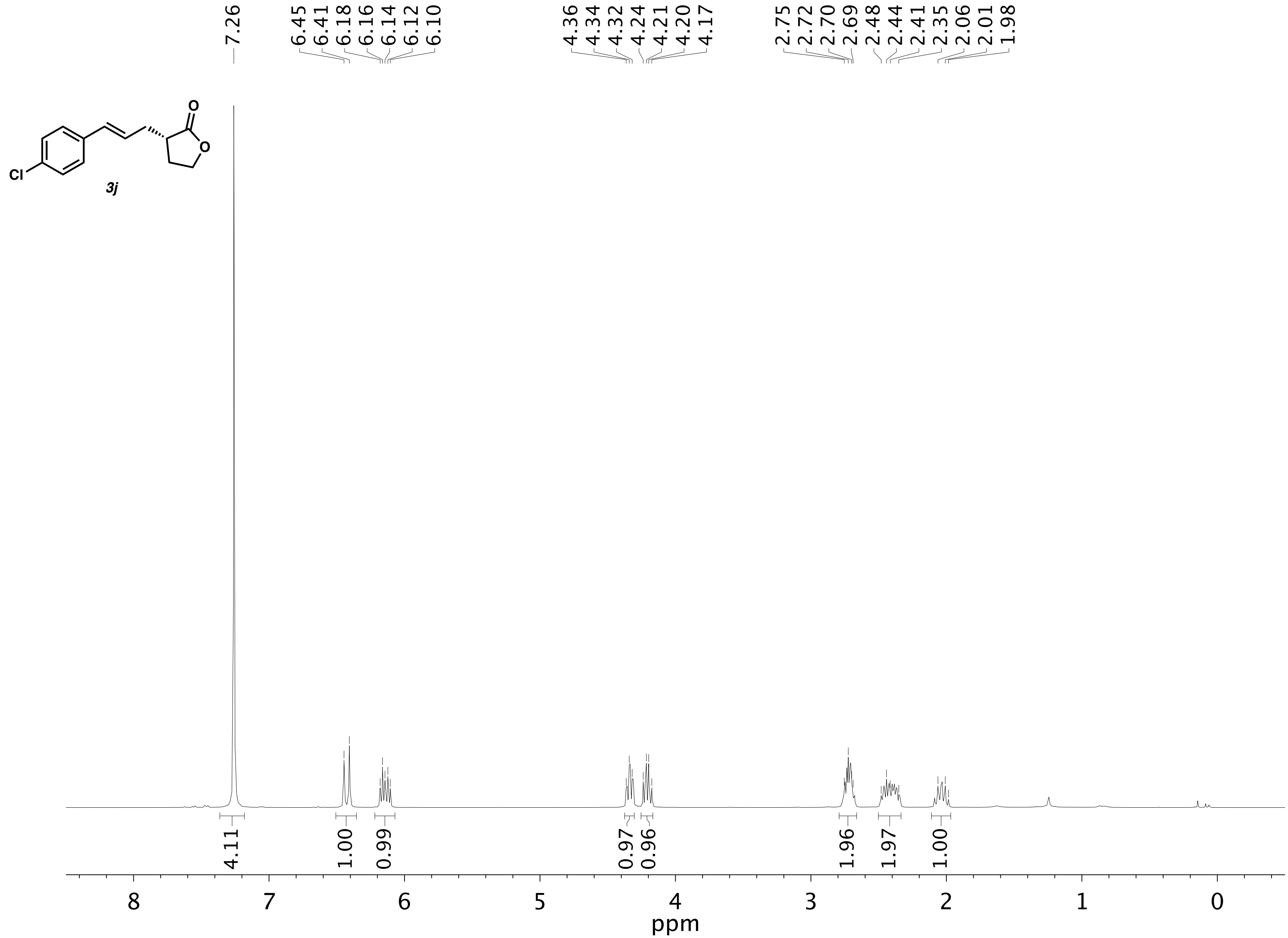
Infrared spectrum (Thin Film, NaCl) of compound **3i**.



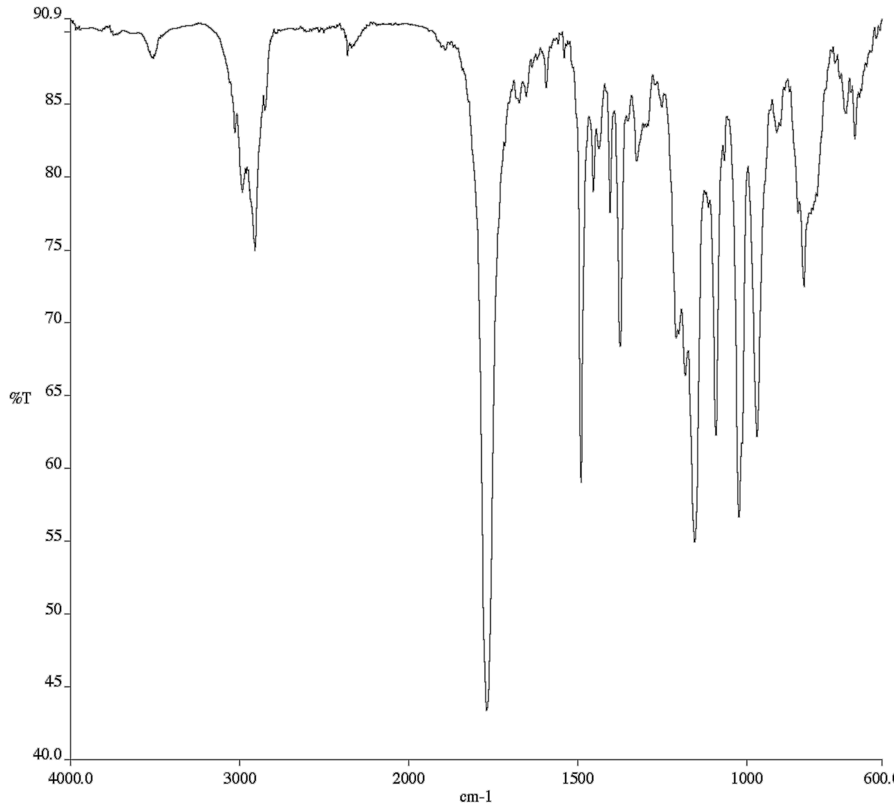
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3i**



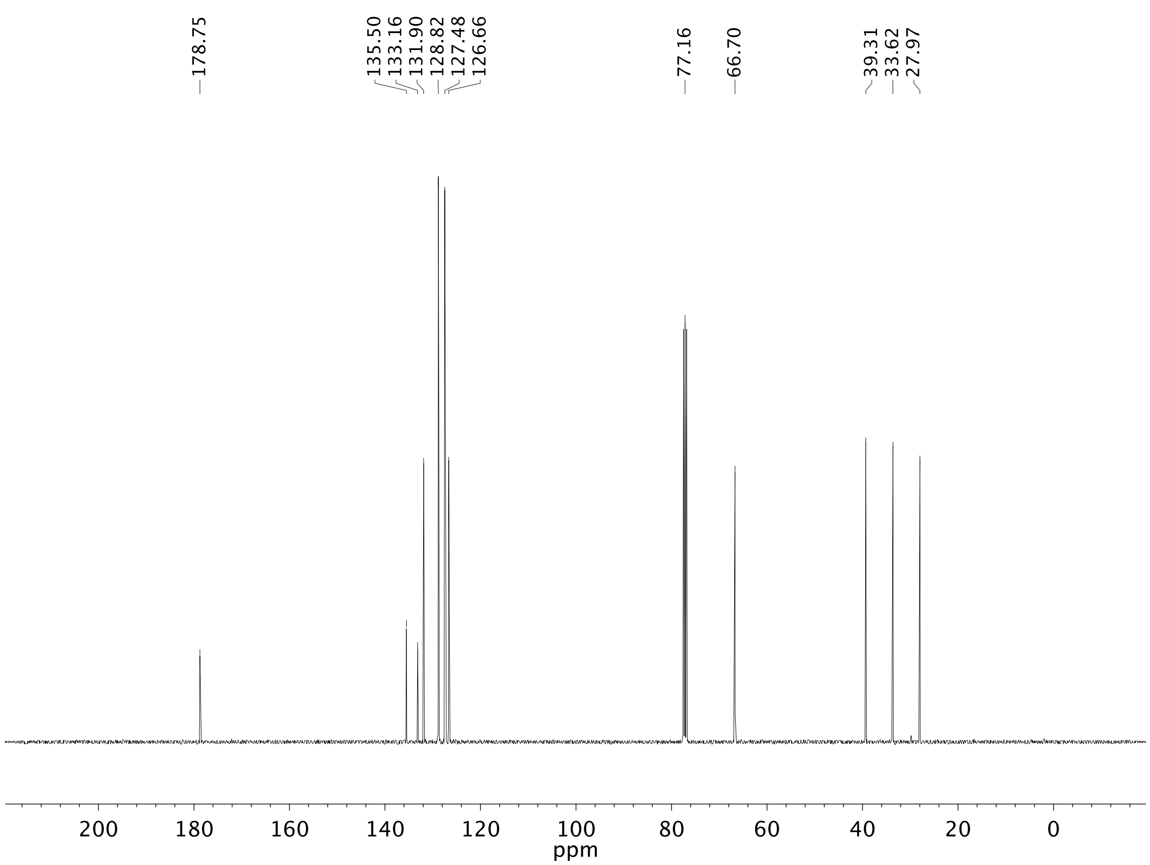
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3i**



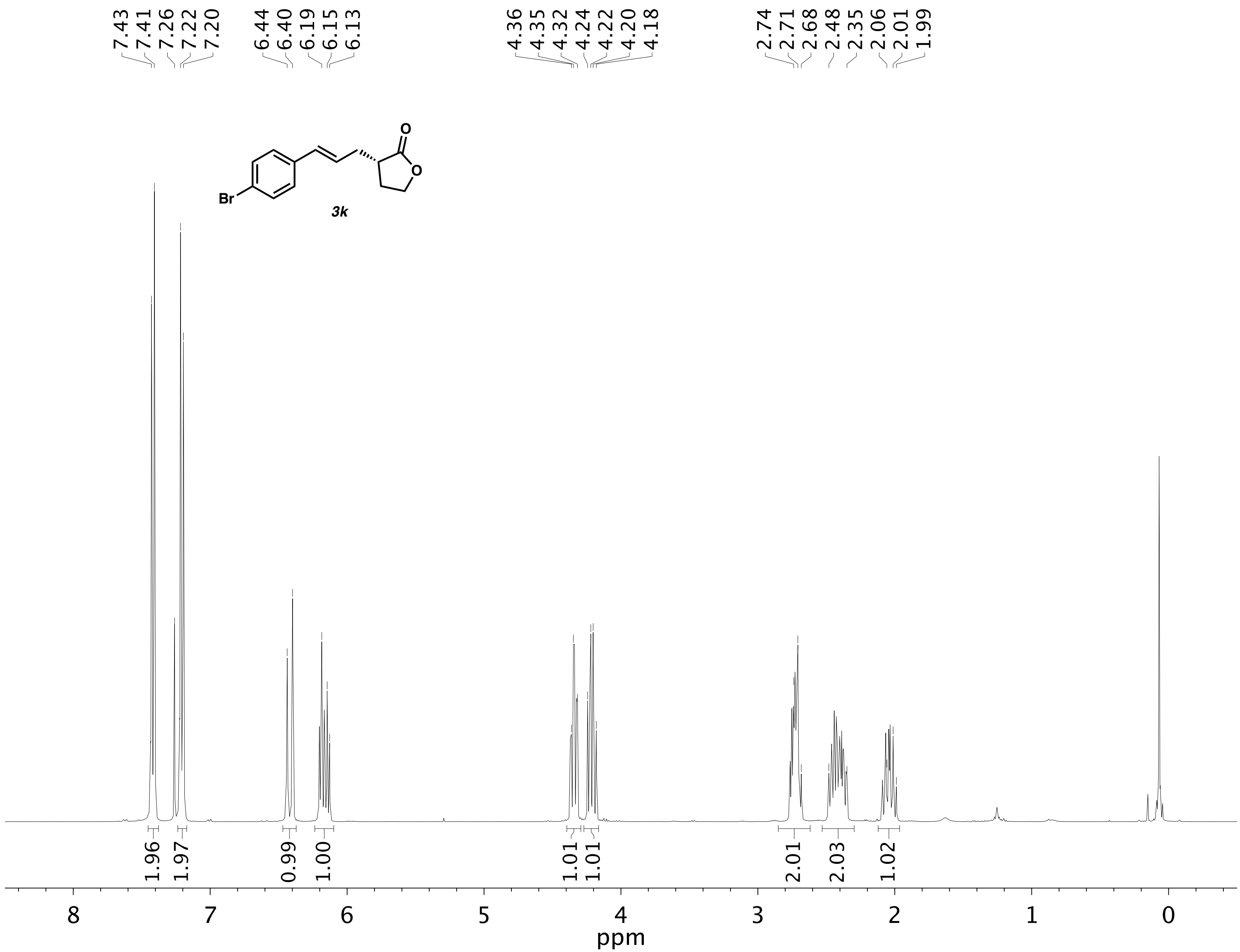
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**



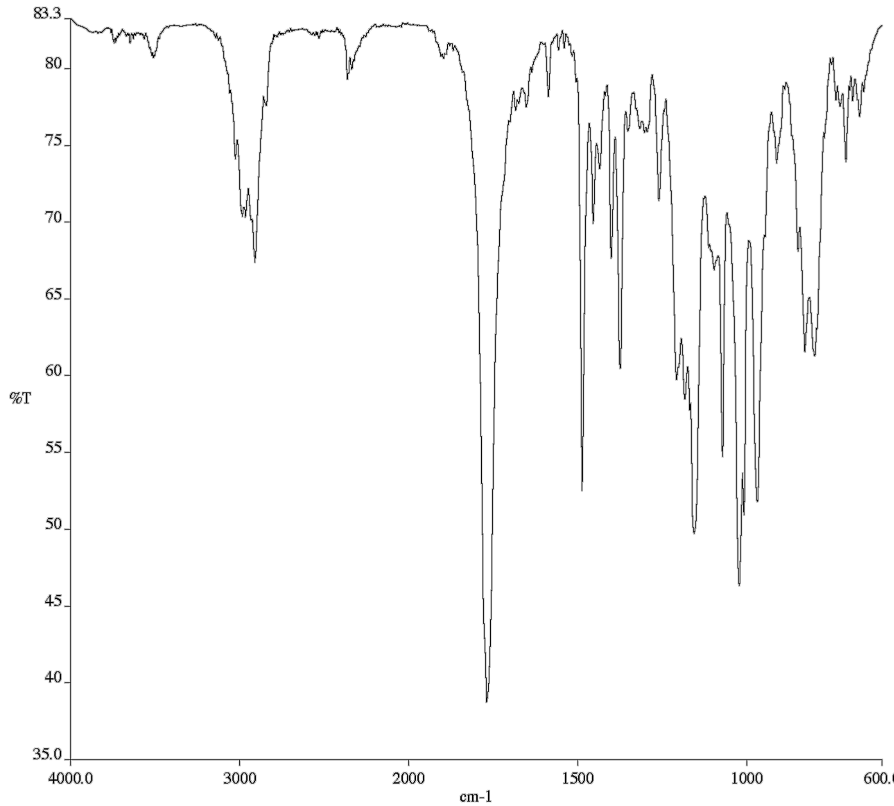
Infrared spectrum (Thin Film, NaCl) of compound **3j**.



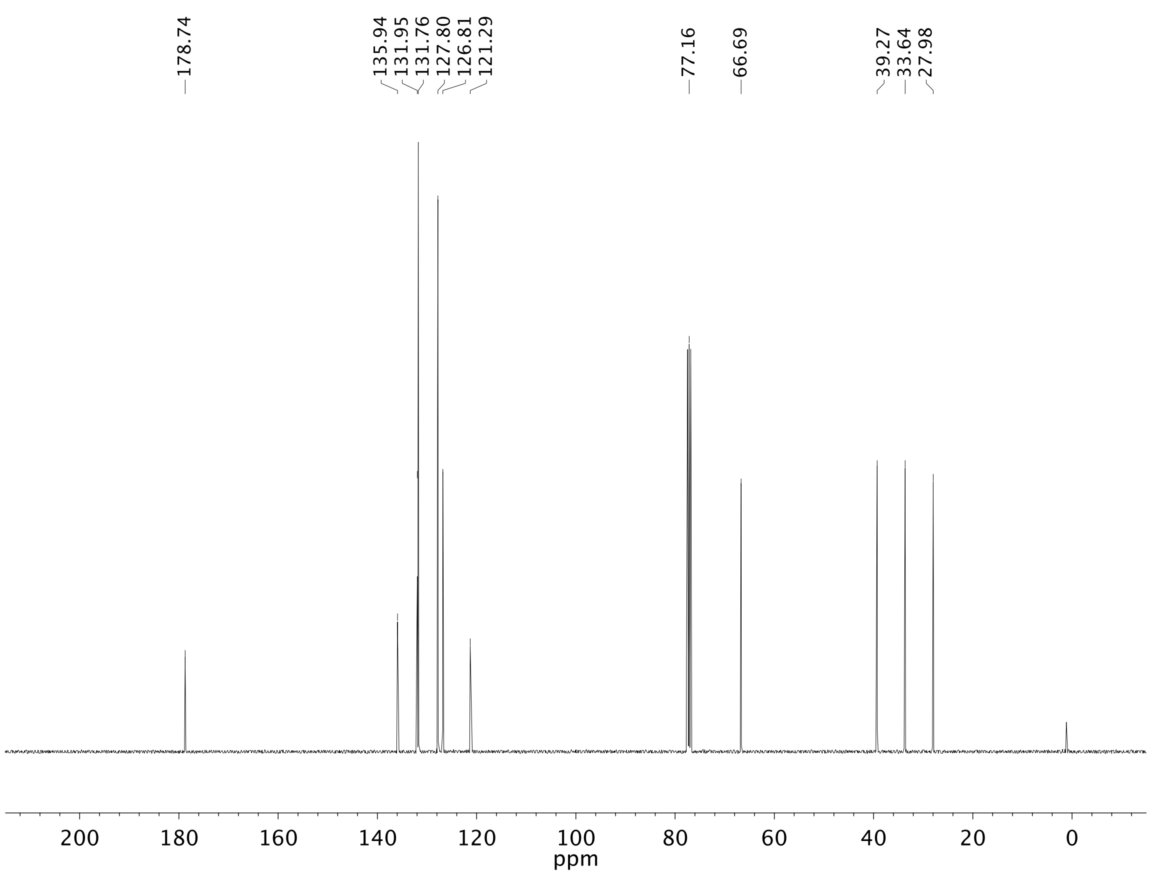
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3j**



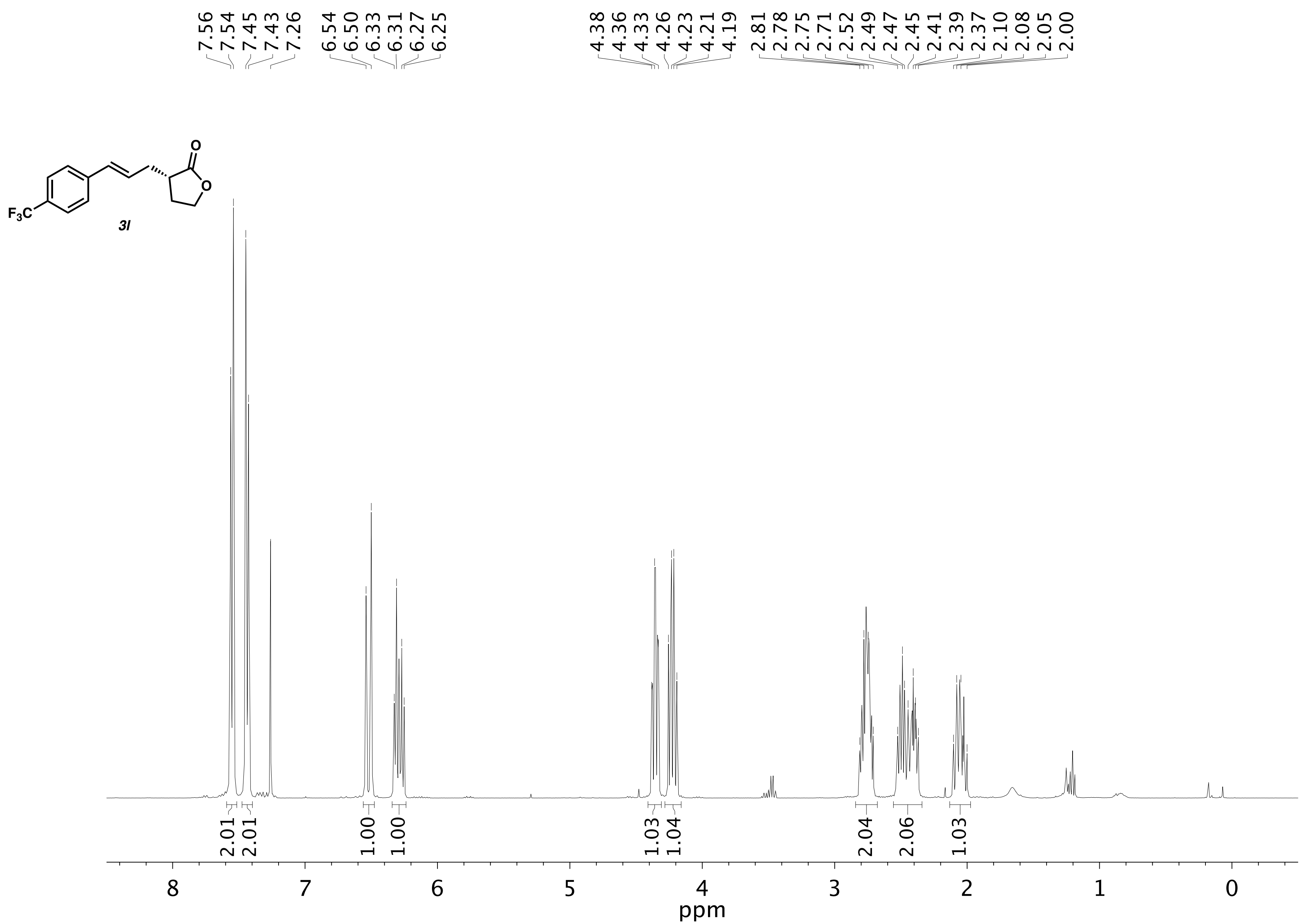
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**



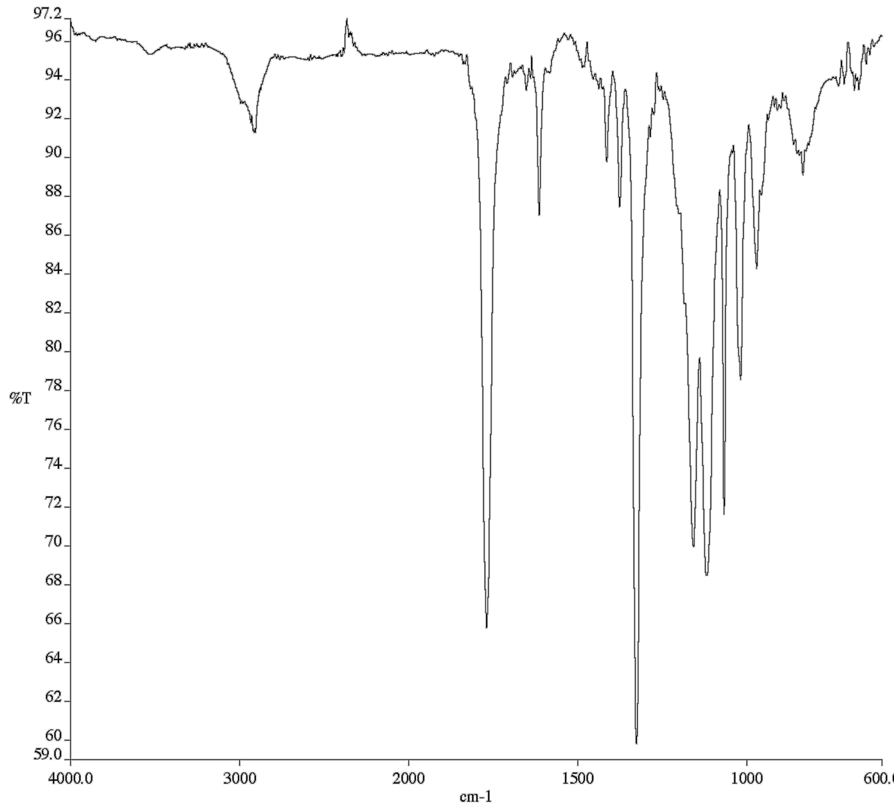
Infrared spectrum (Thin Film, NaCl) of compound **3k**



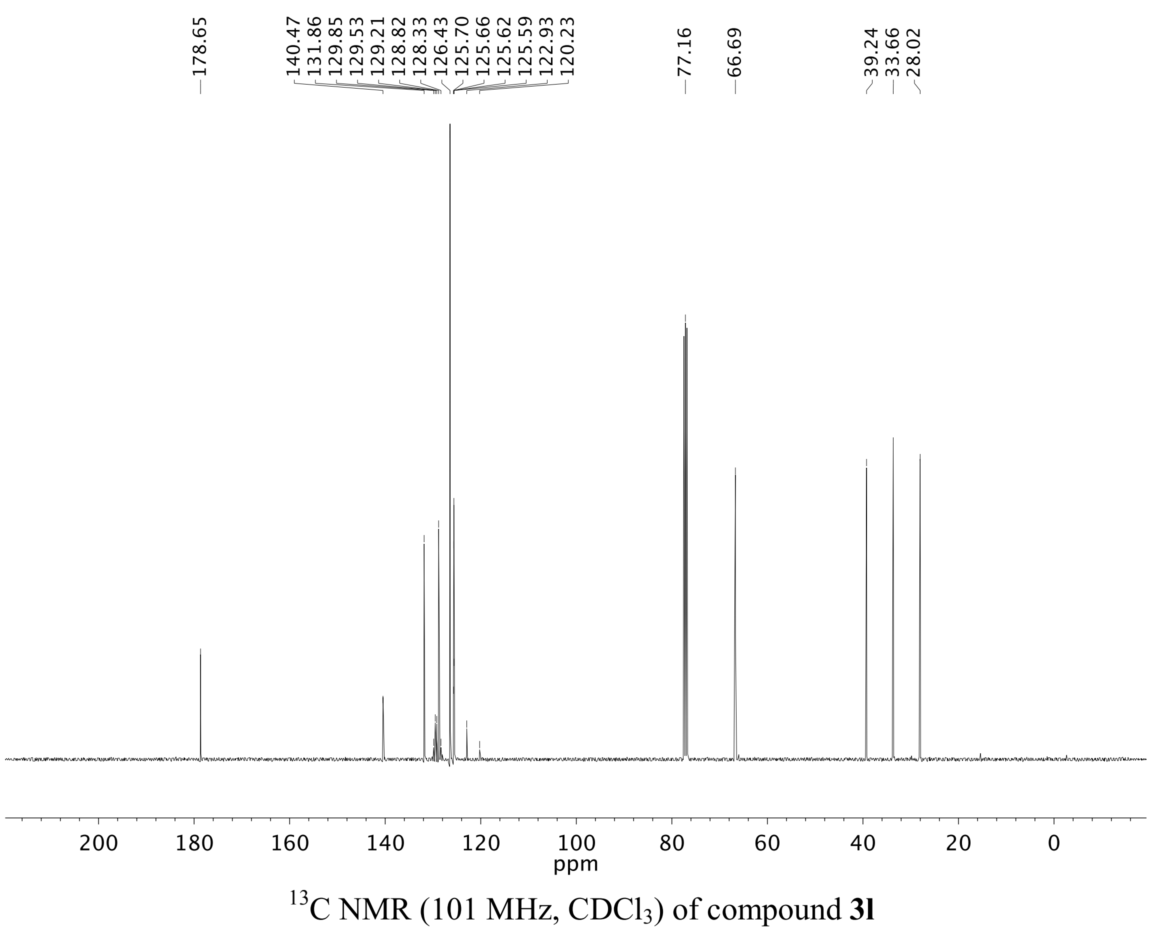
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3k**



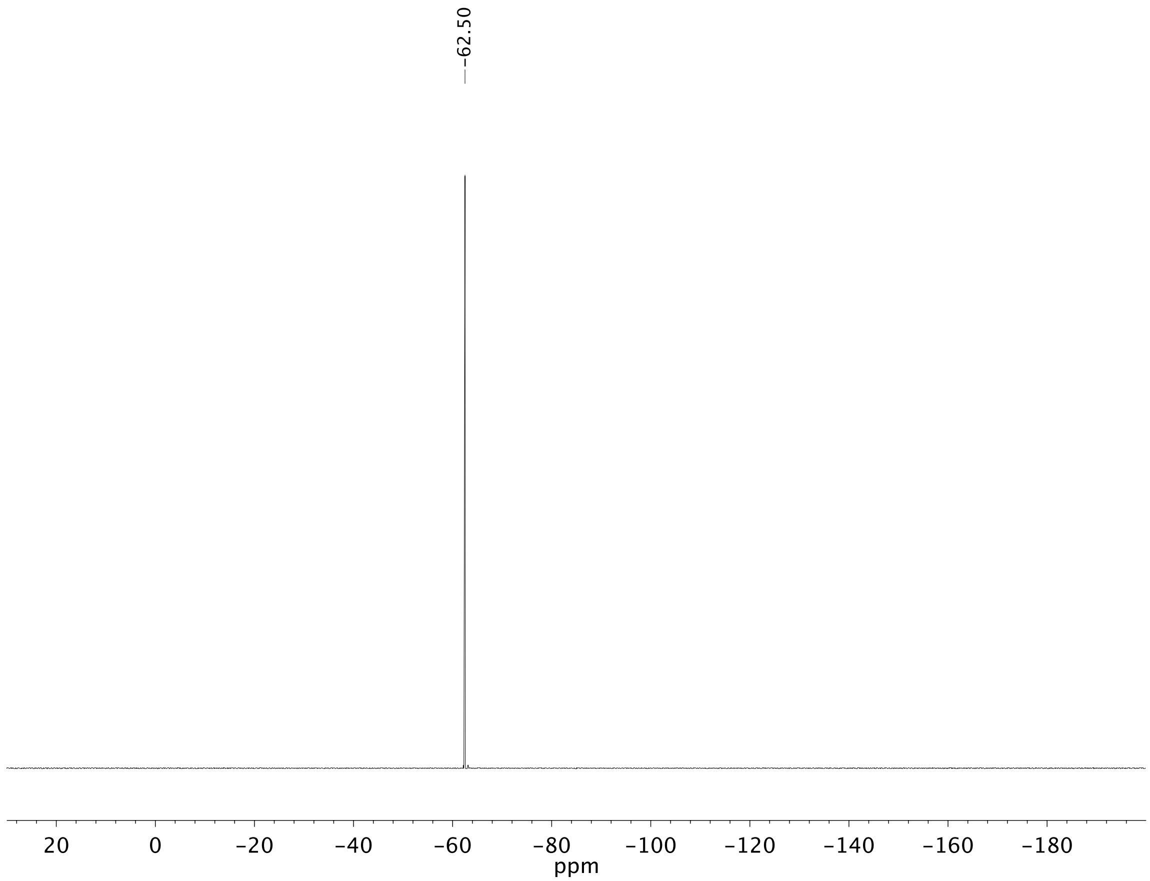
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**



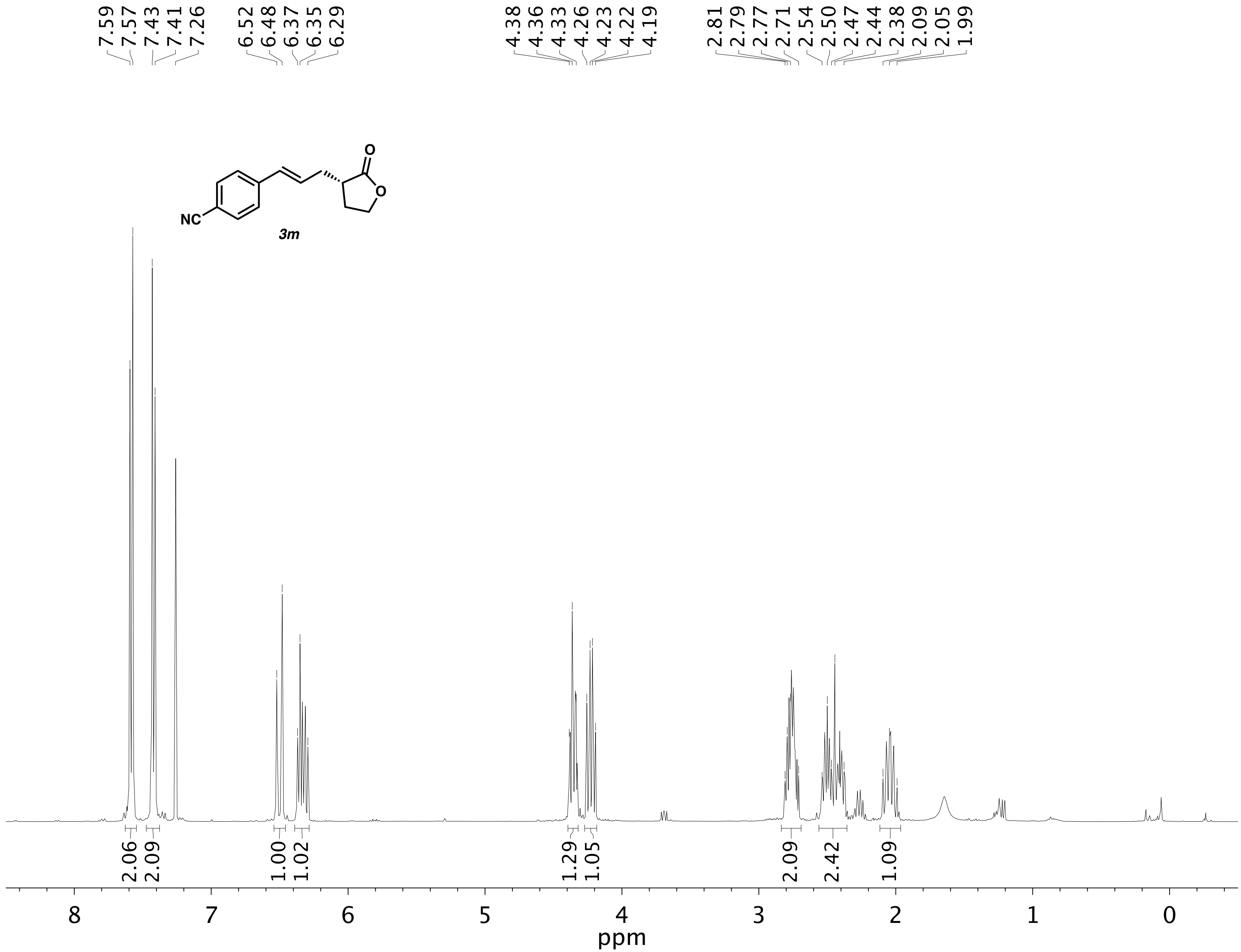
Infrared spectrum (Thin Film, NaCl) of compound **3l**.



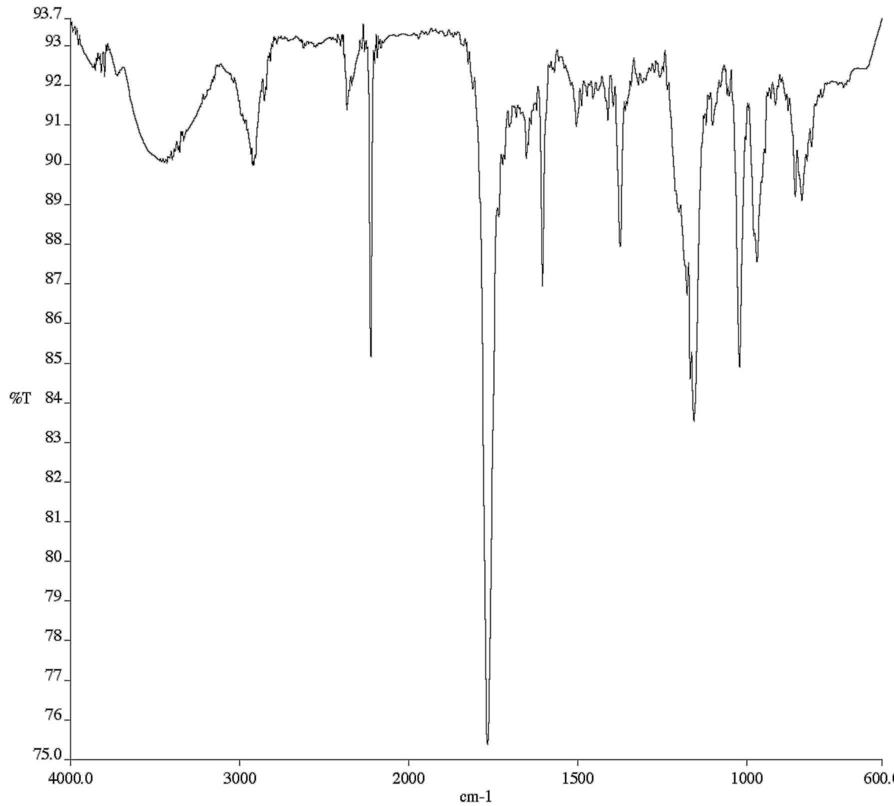
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3l**



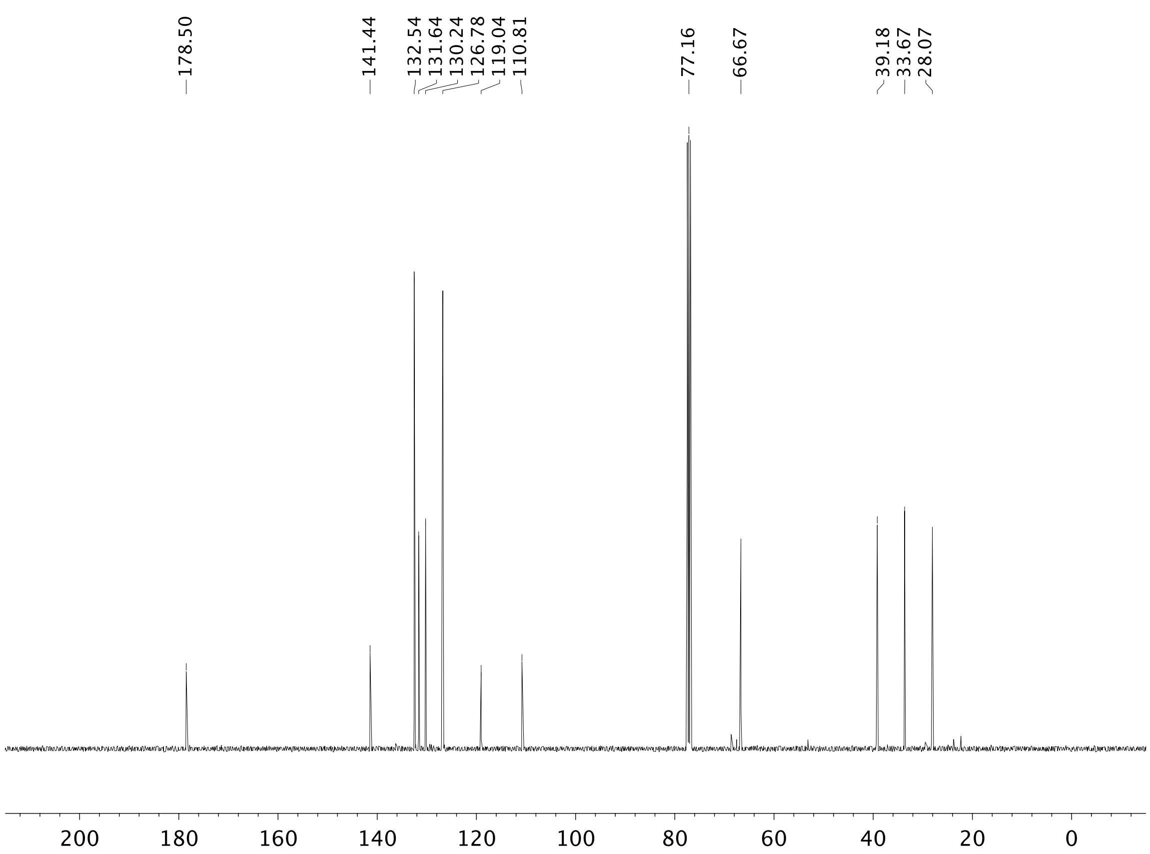
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3l**



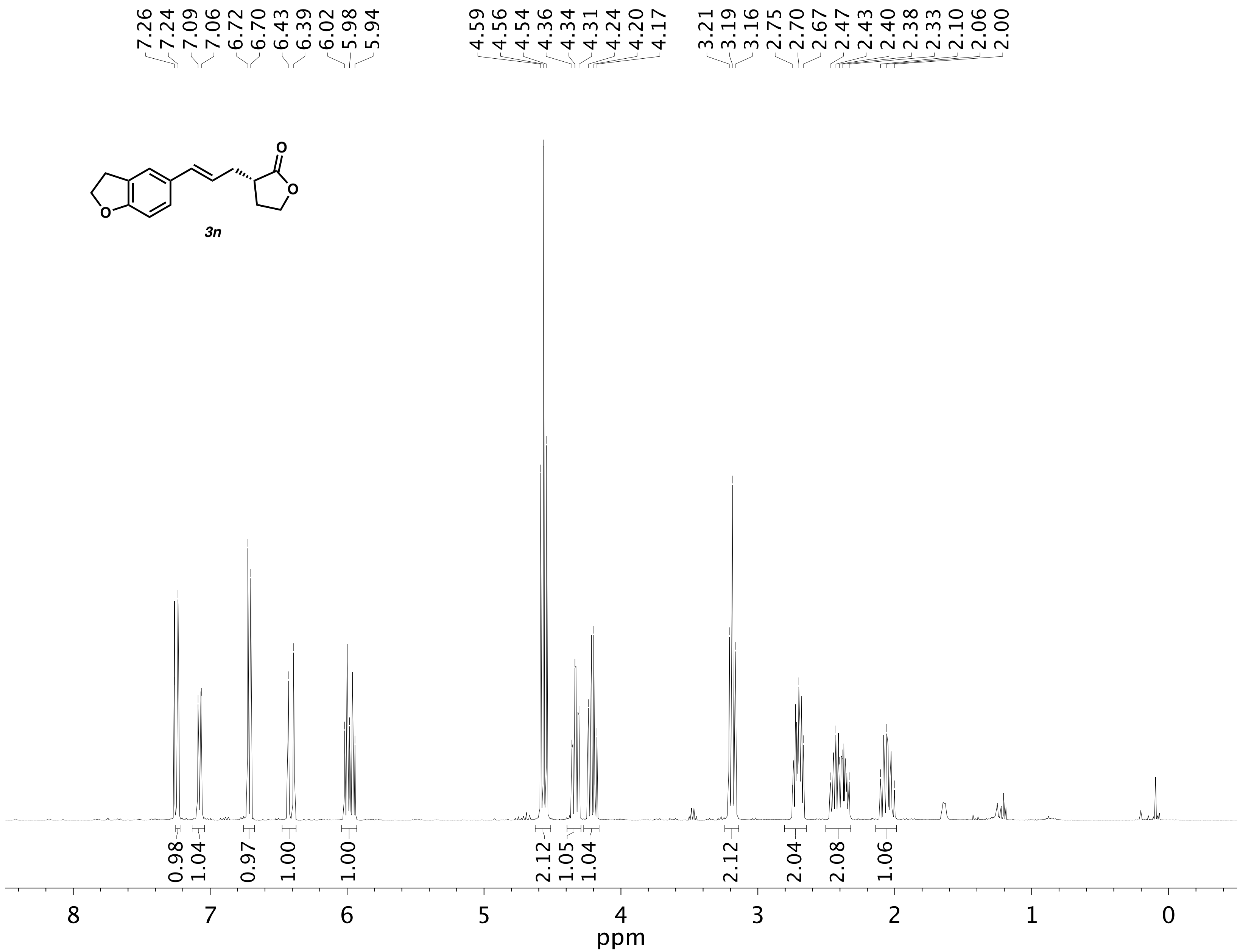
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**



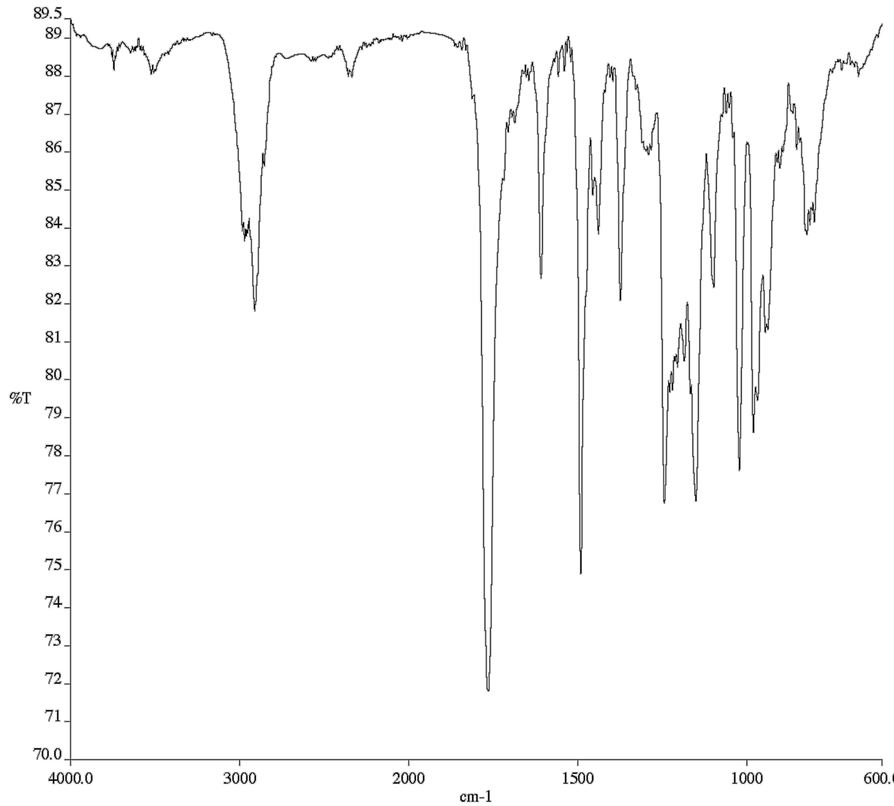
Infrared spectrum (Thin Film, NaCl) of compound **3m**



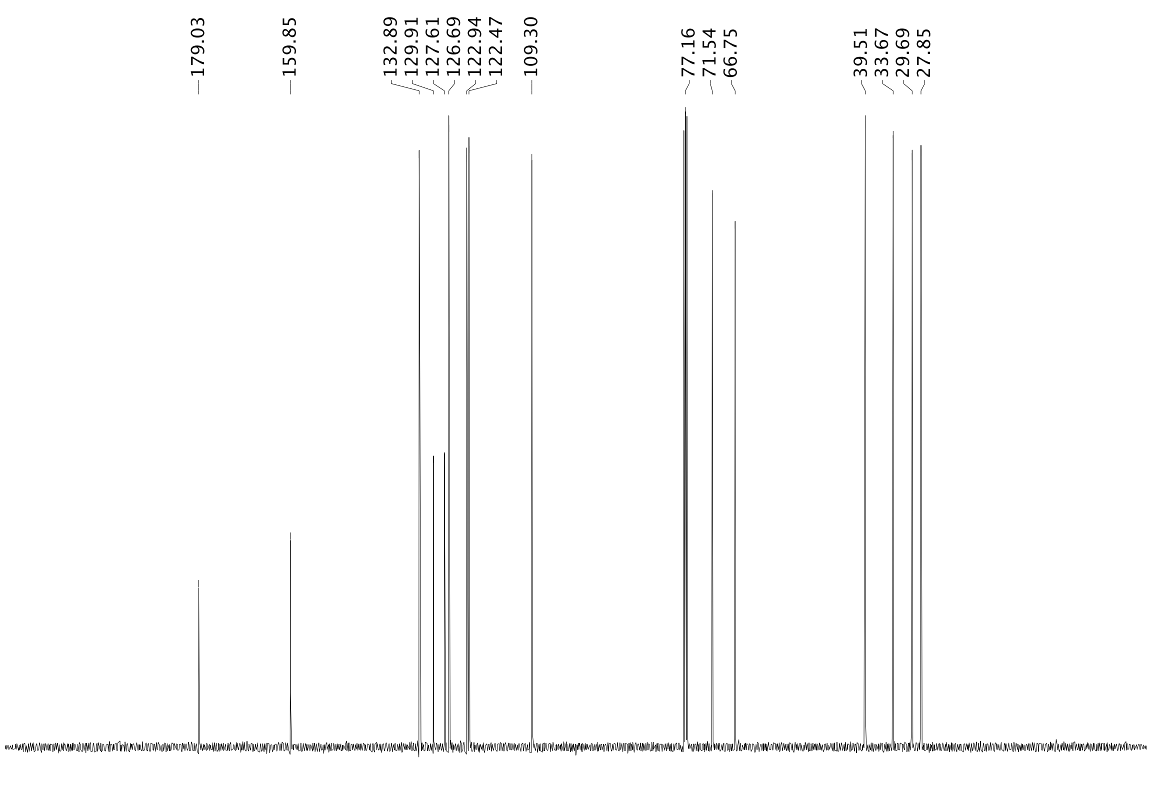
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3m**



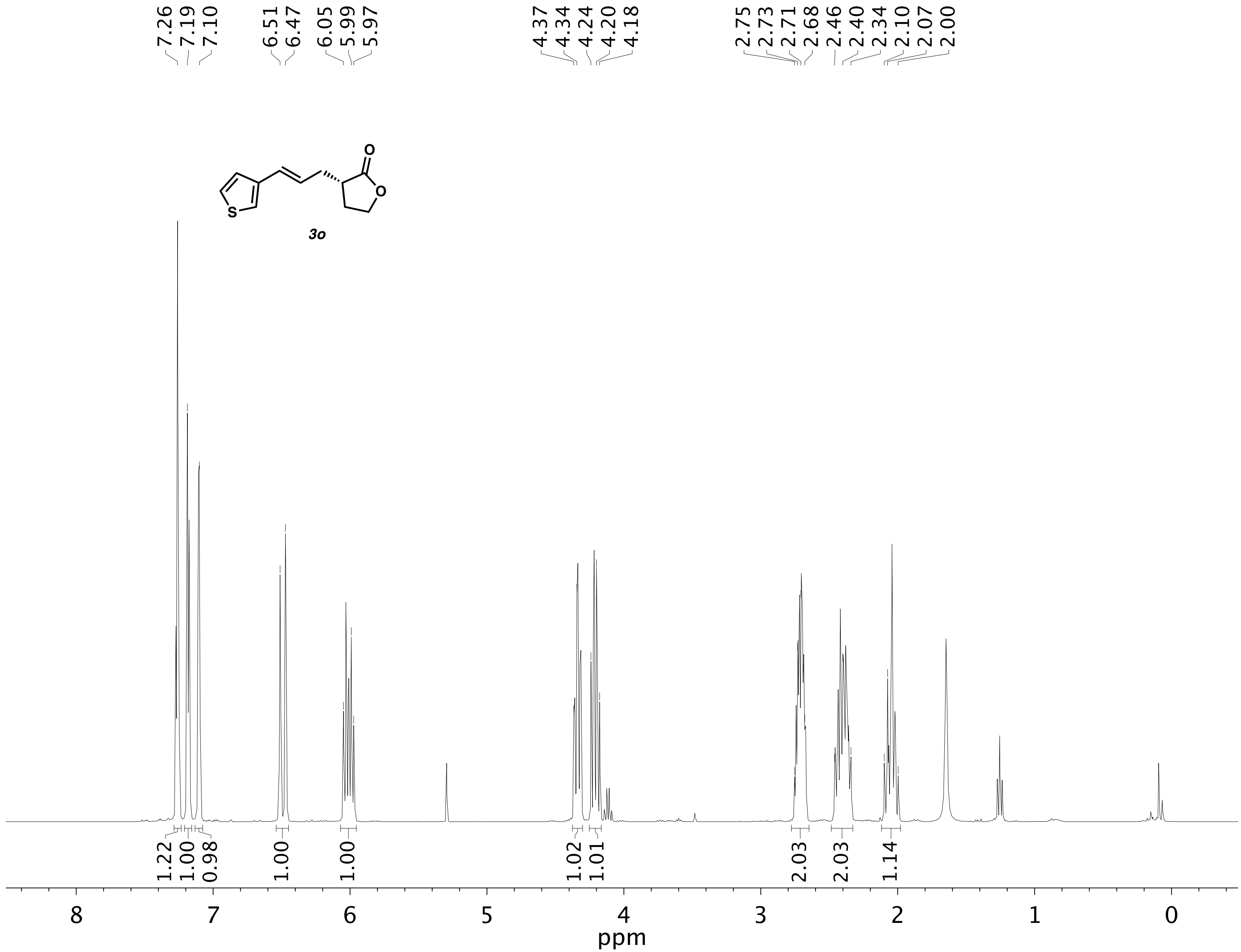
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**



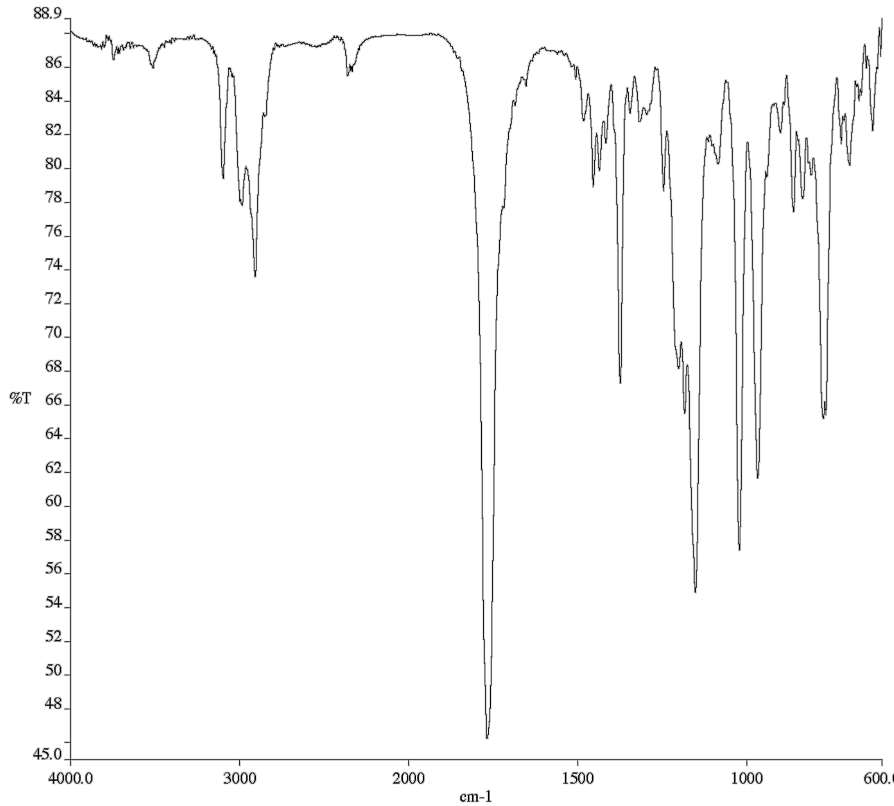
Infrared spectrum (Thin Film, NaCl) of compound **3n**



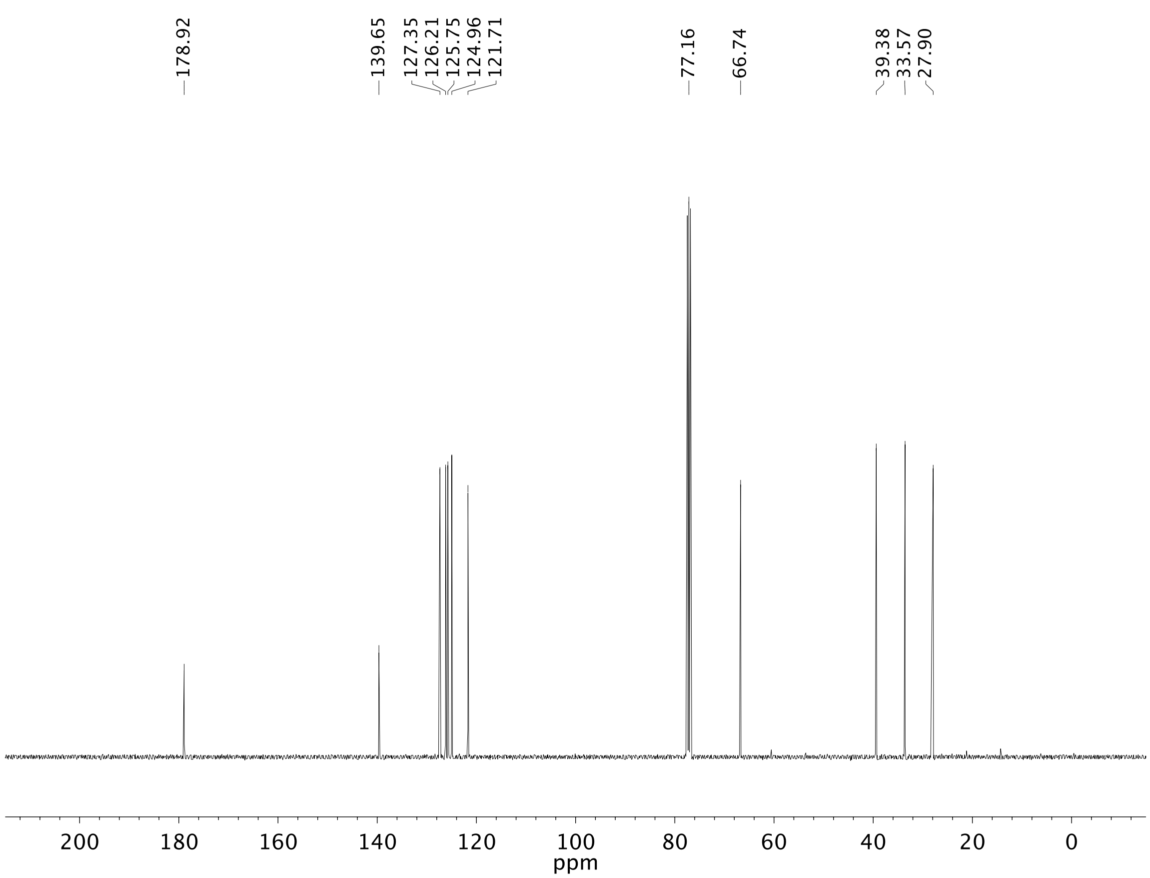
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3n**



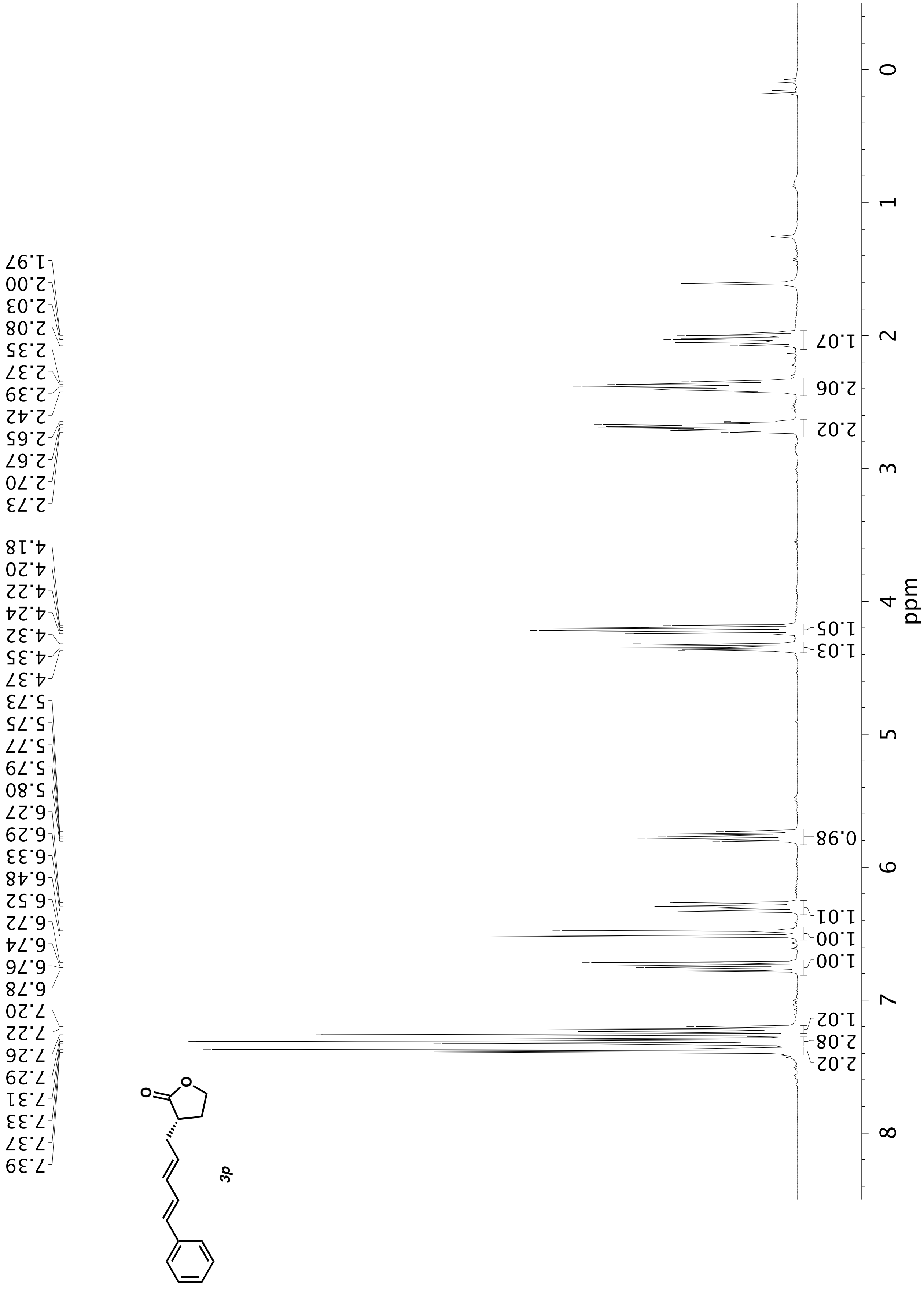
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**



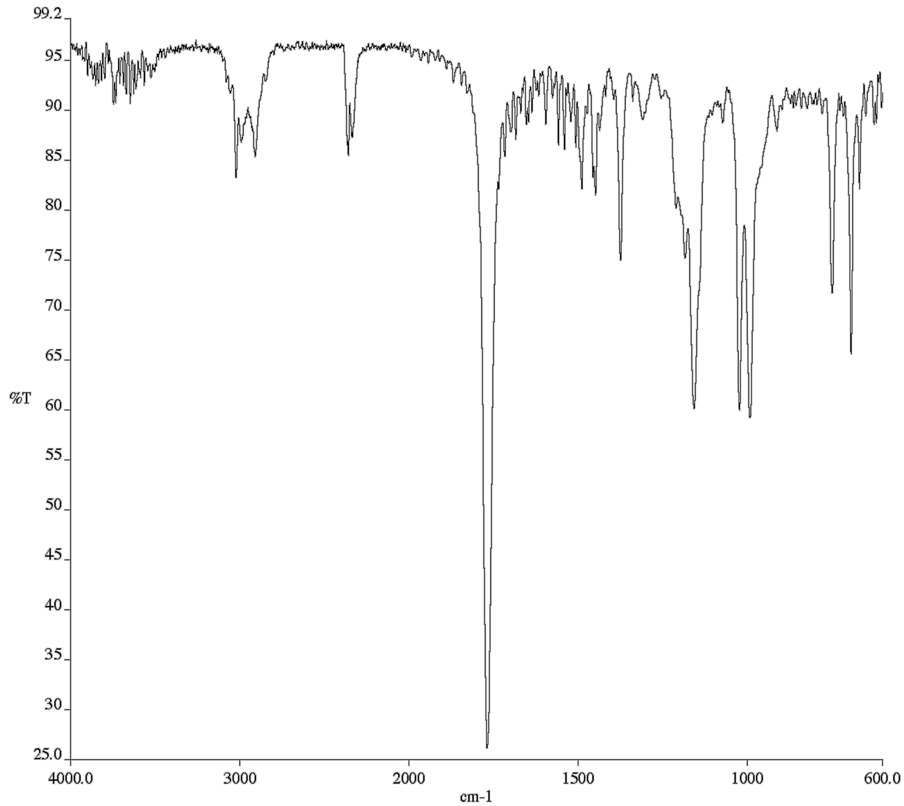
Infrared spectrum (Thin Film, NaCl) of compound **3o**



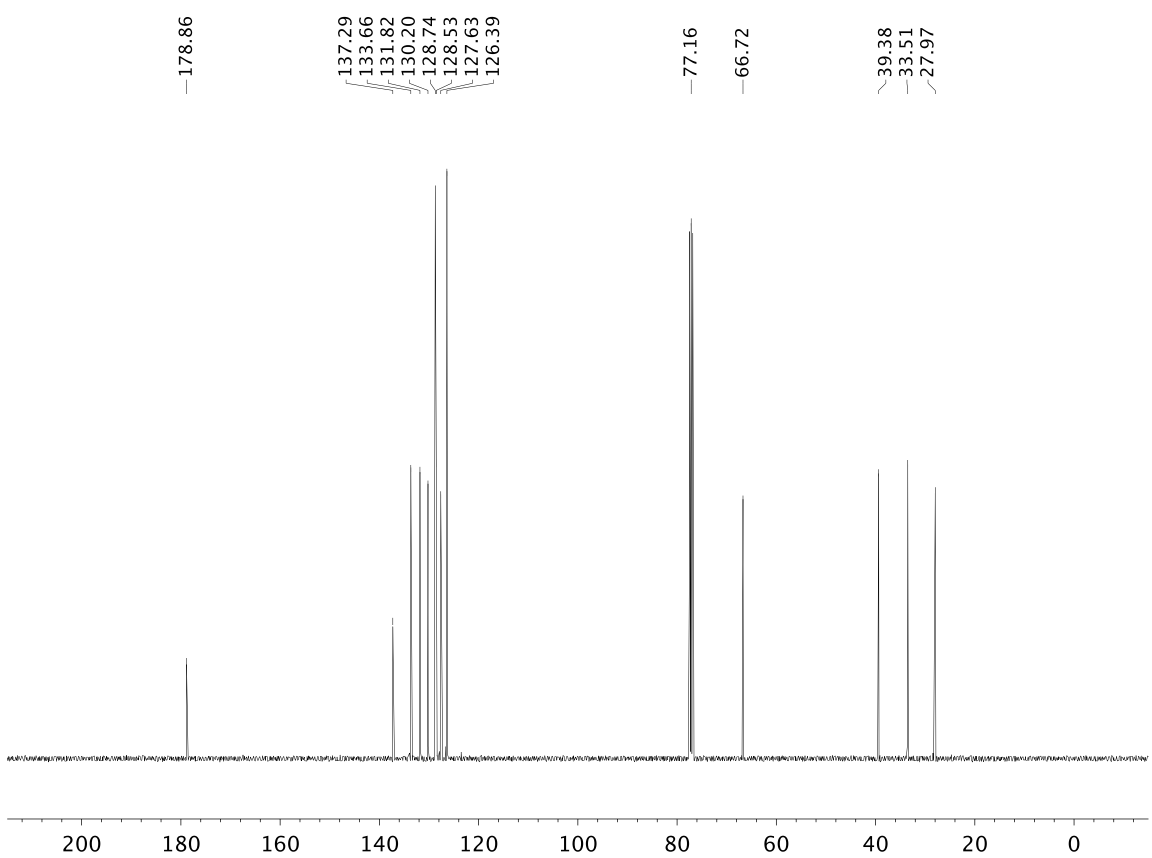
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3o**



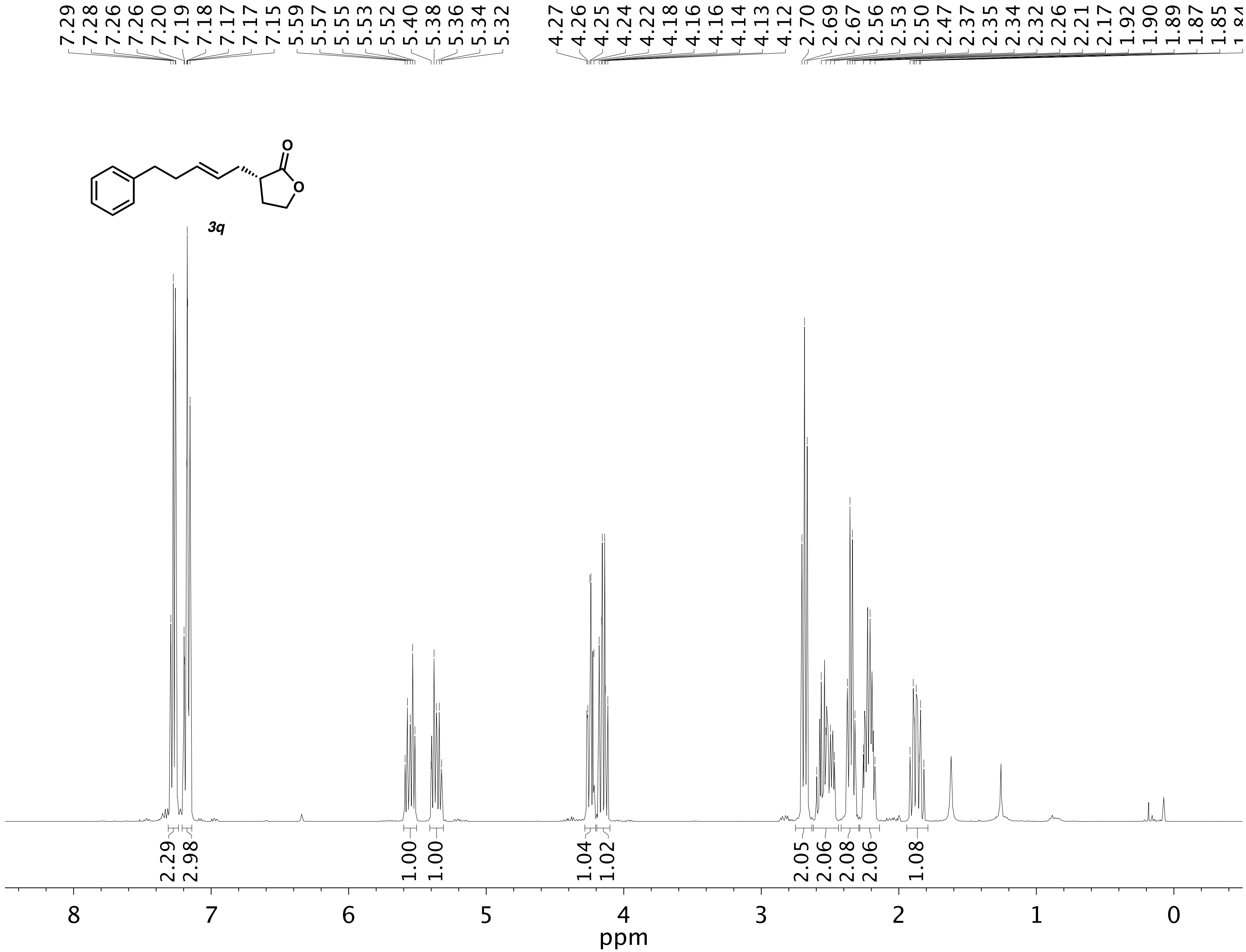
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**



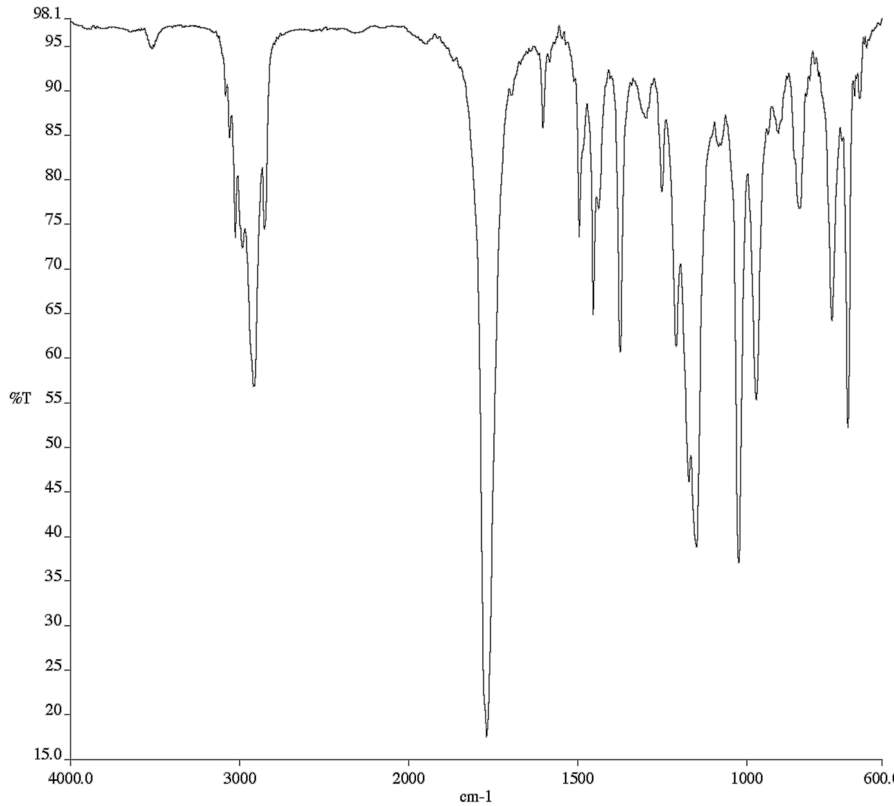
Infrared spectrum (Thin Film, NaCl) of compound **3p**.



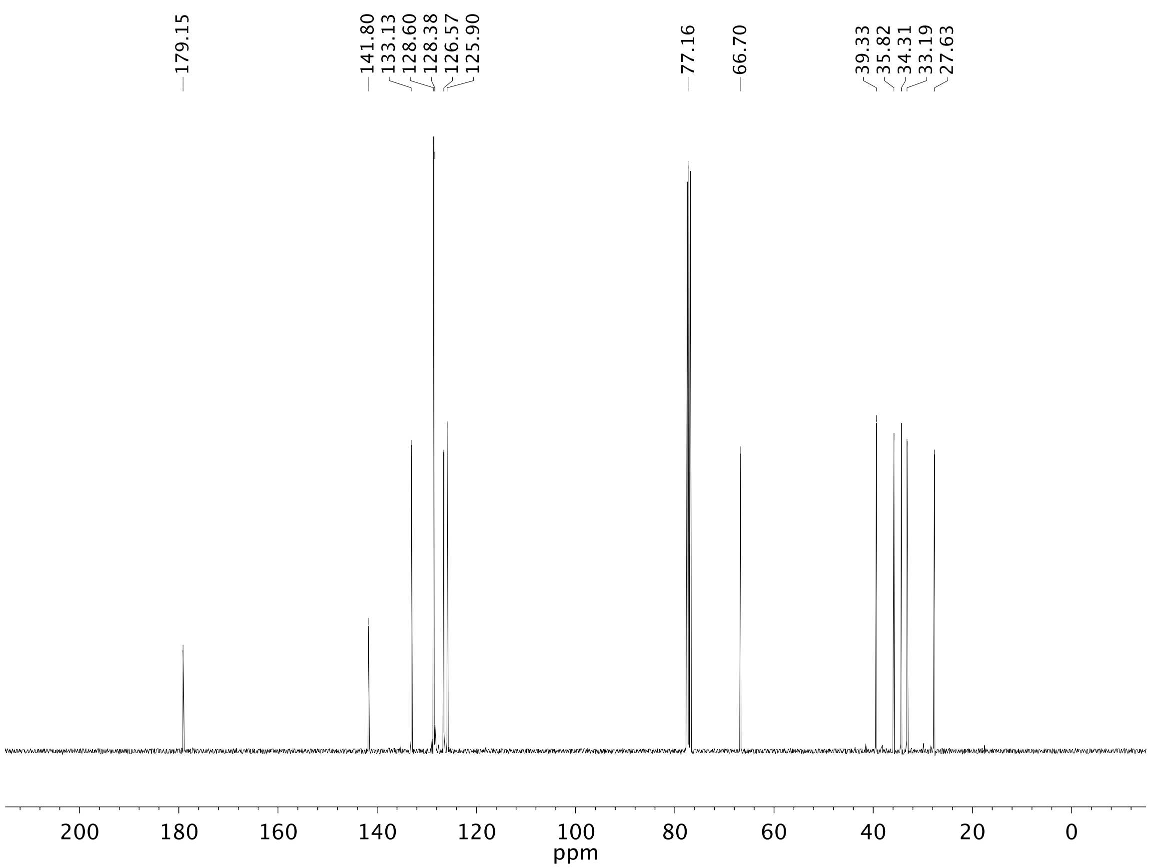
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3p**



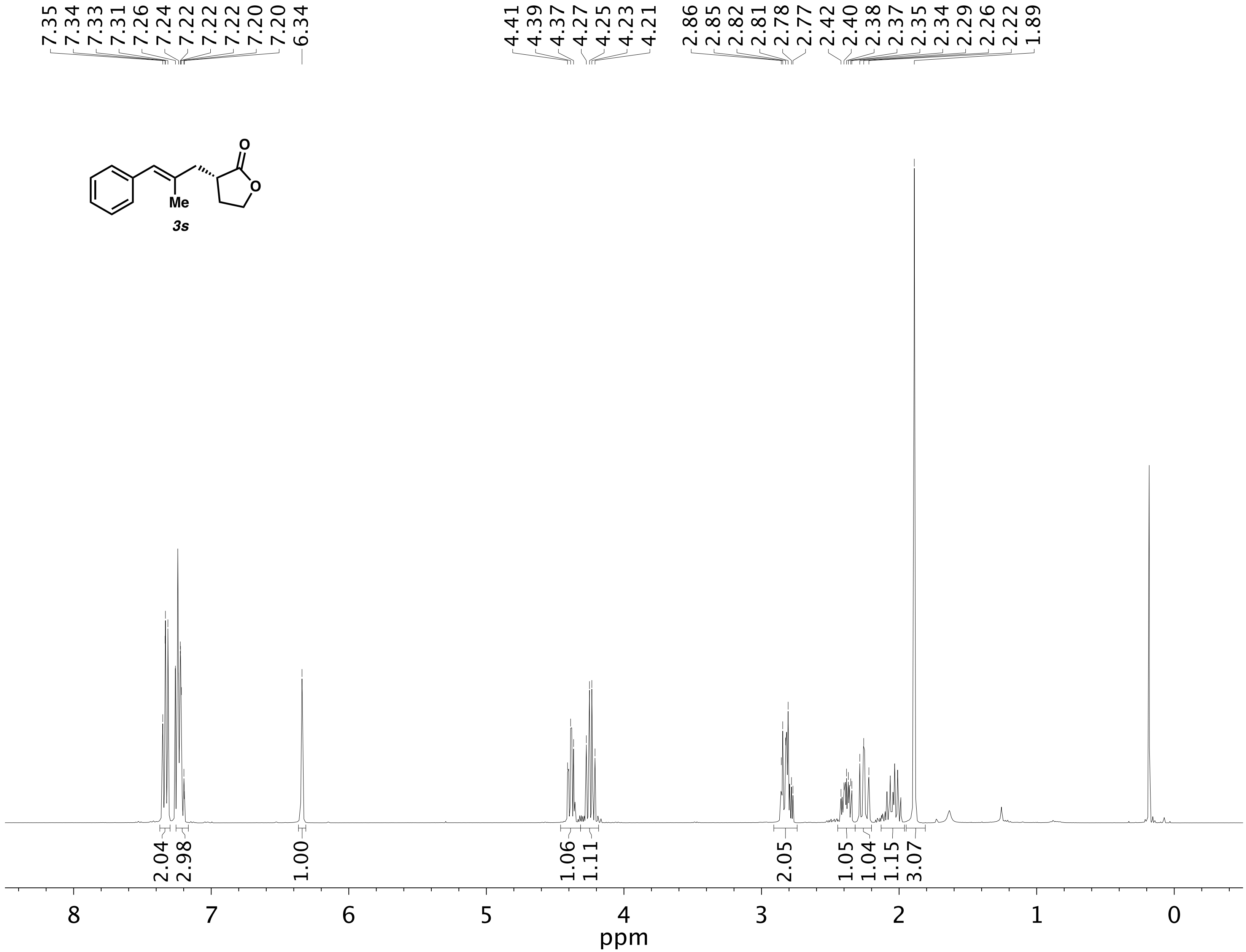
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**



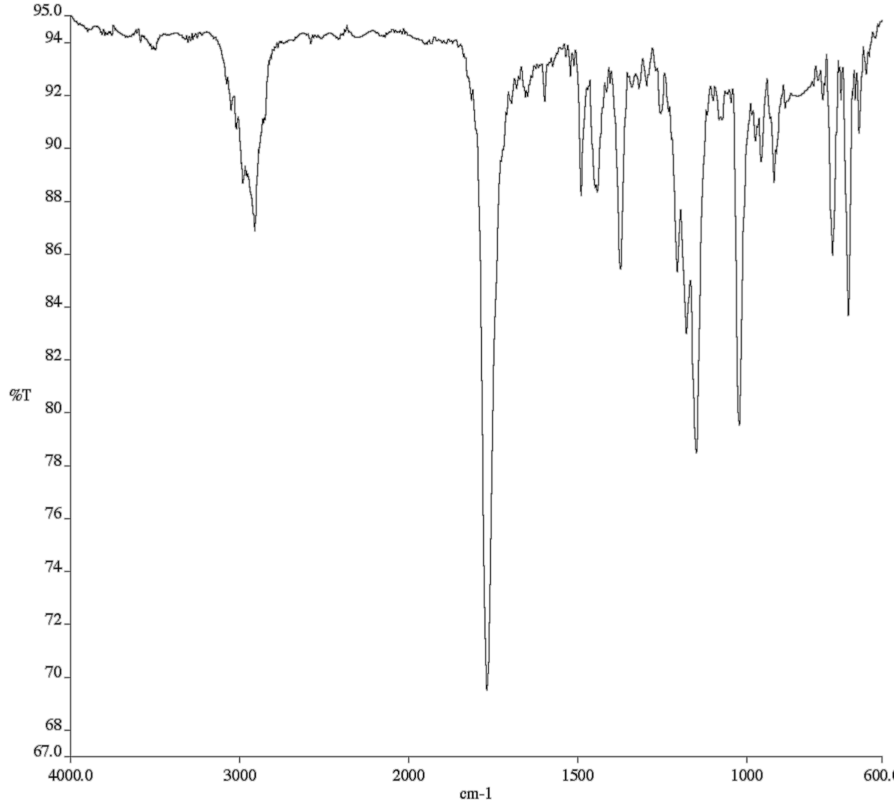
Infrared spectrum (Thin Film, NaCl) of compound **3q**



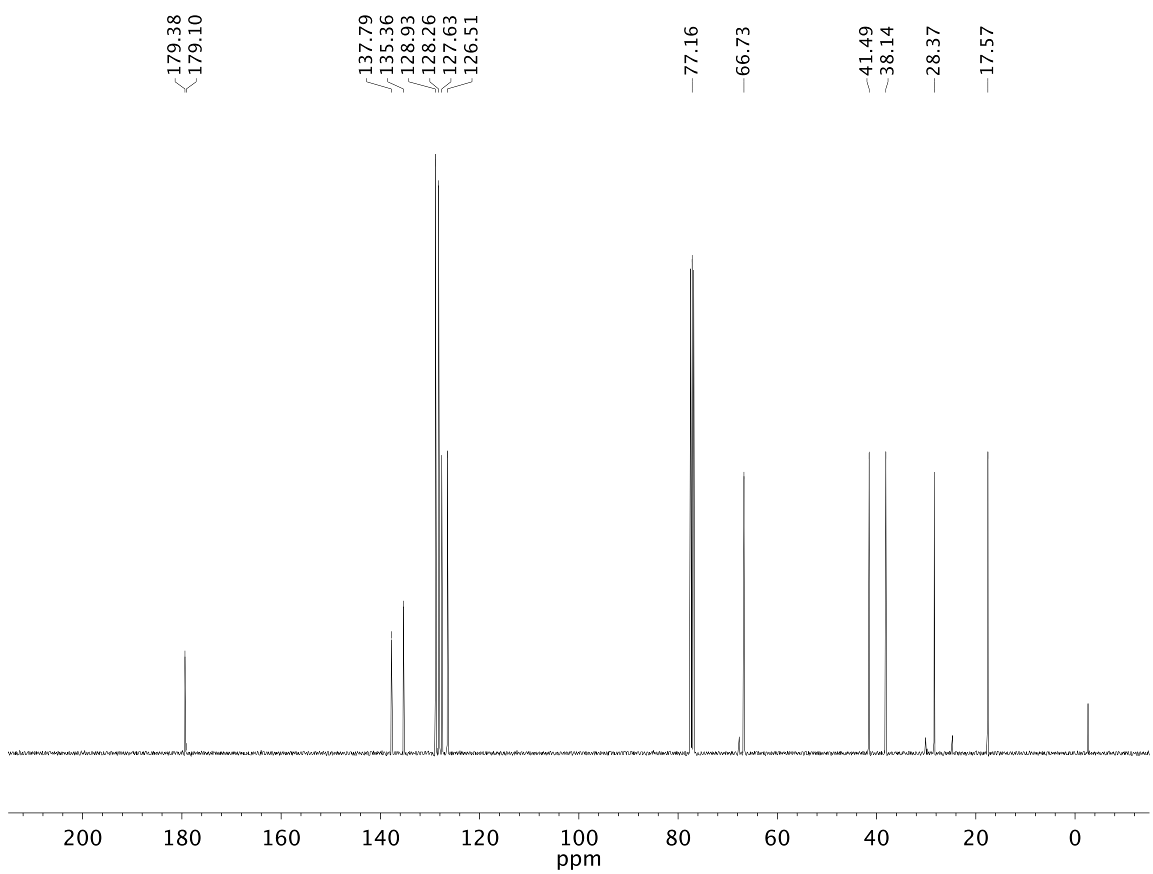
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3q**



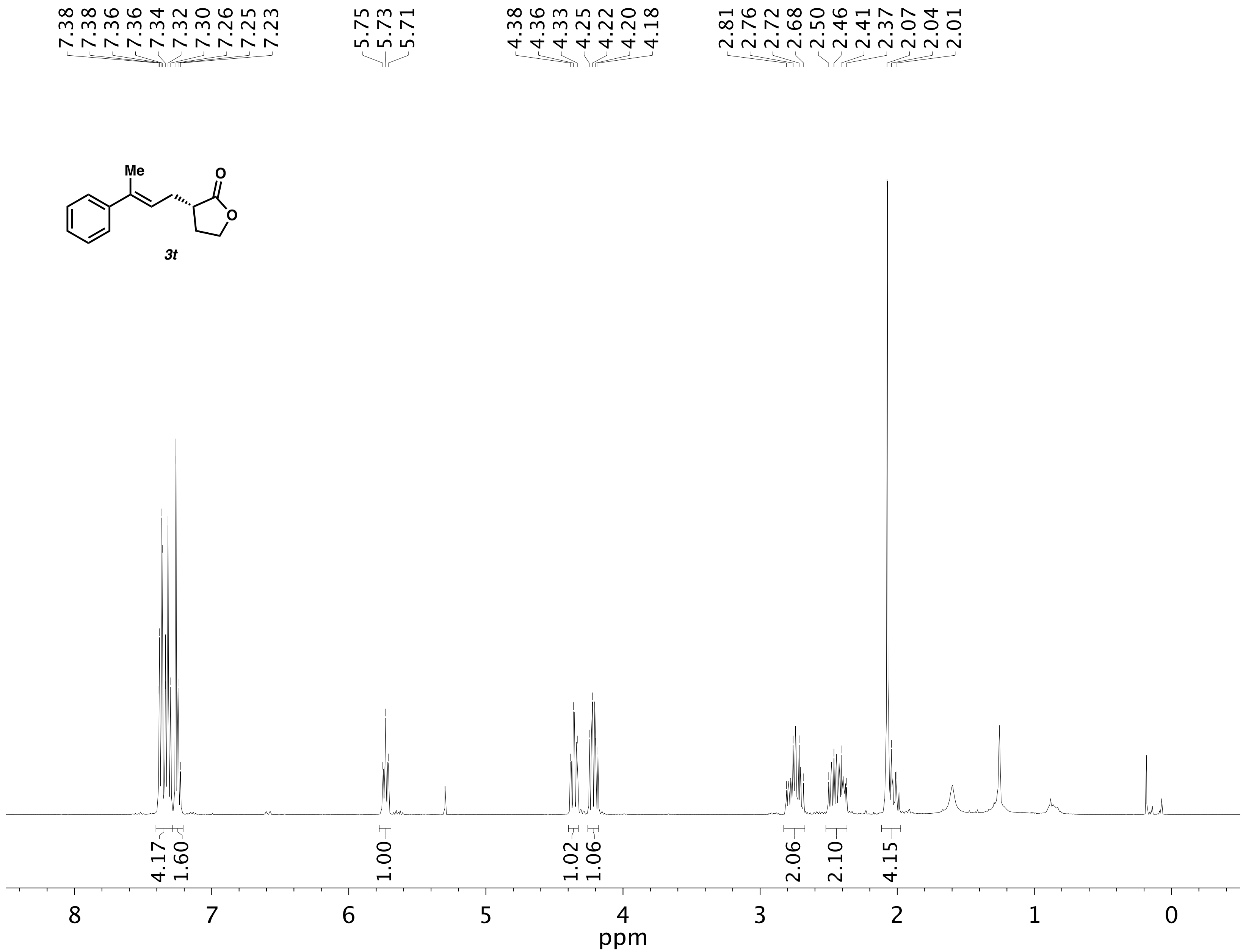
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**



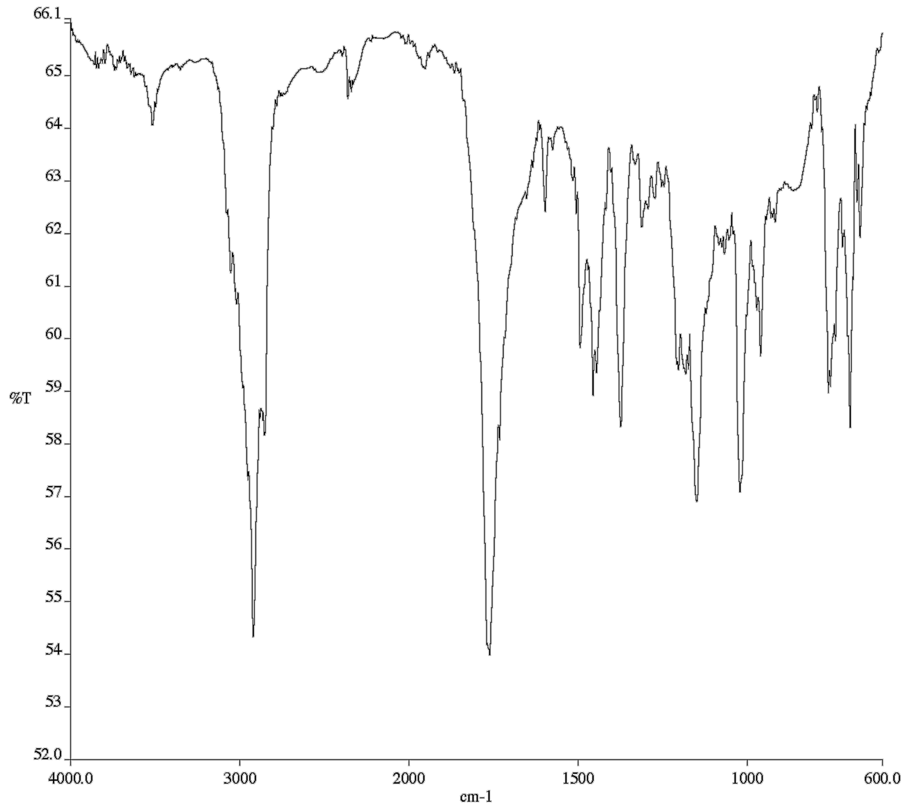
Infrared spectrum (Thin Film, NaCl) of compound **3s**.



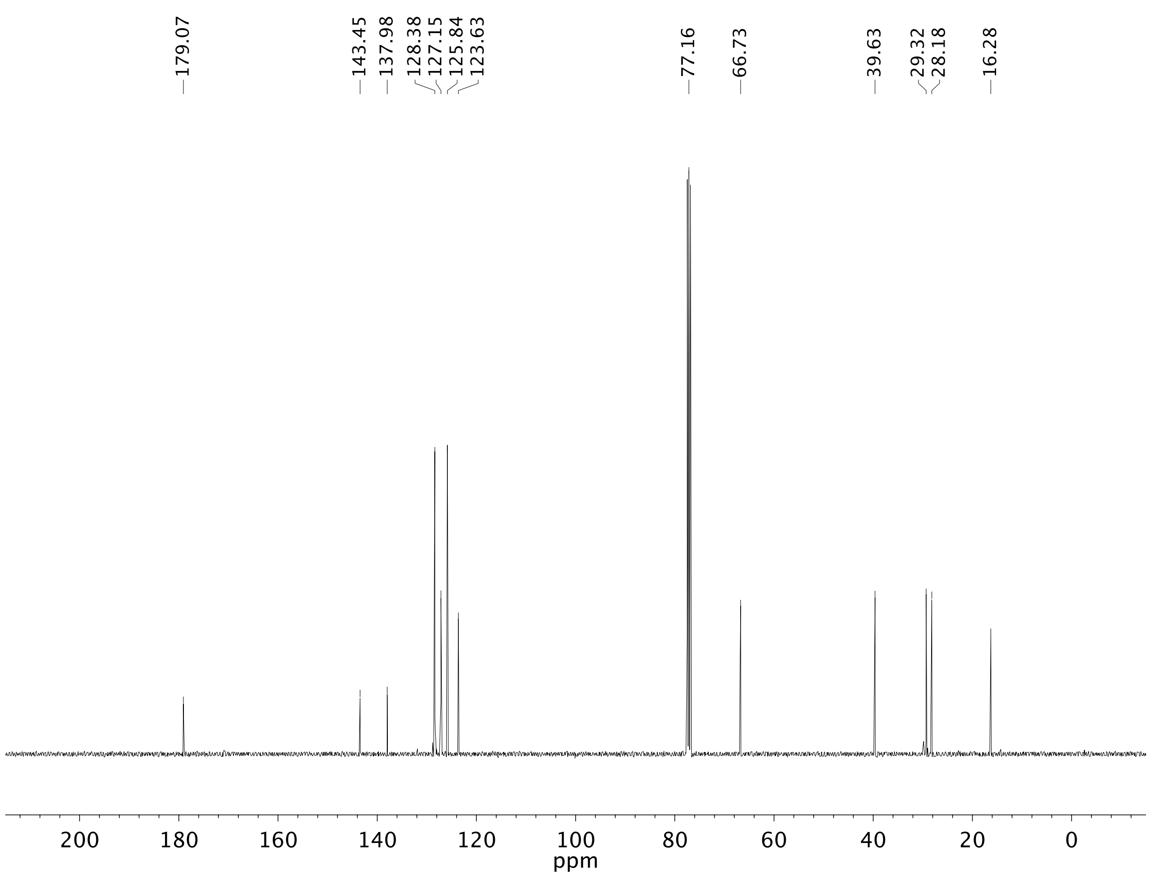
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3s**



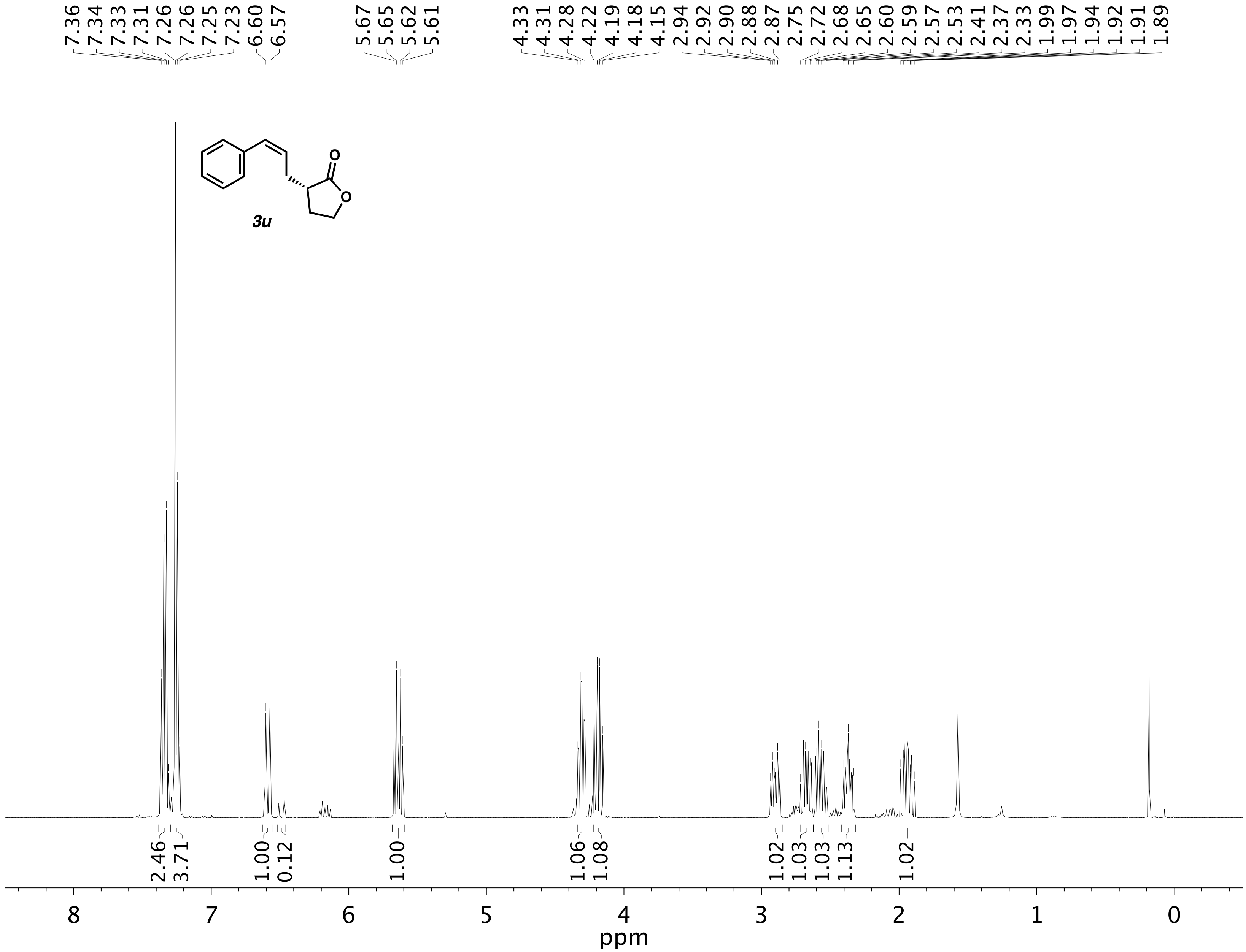
[1]H NMR (400 MHz, $CDCl_3$) of compound **3t**



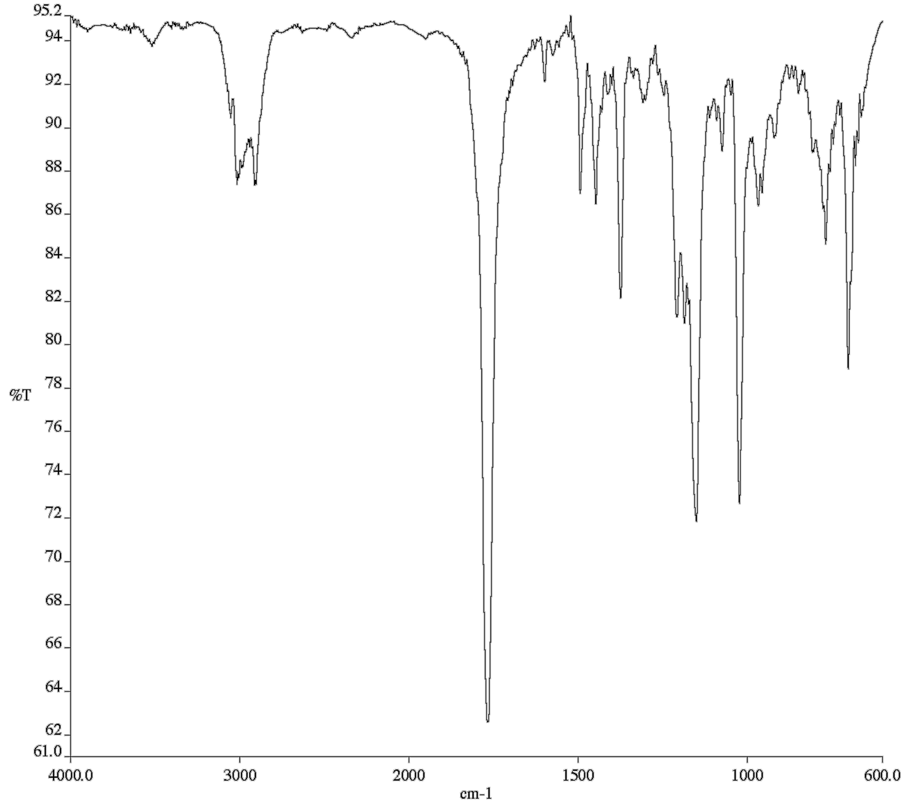
Infrared spectrum (Thin Film, NaCl) of compound **3t**



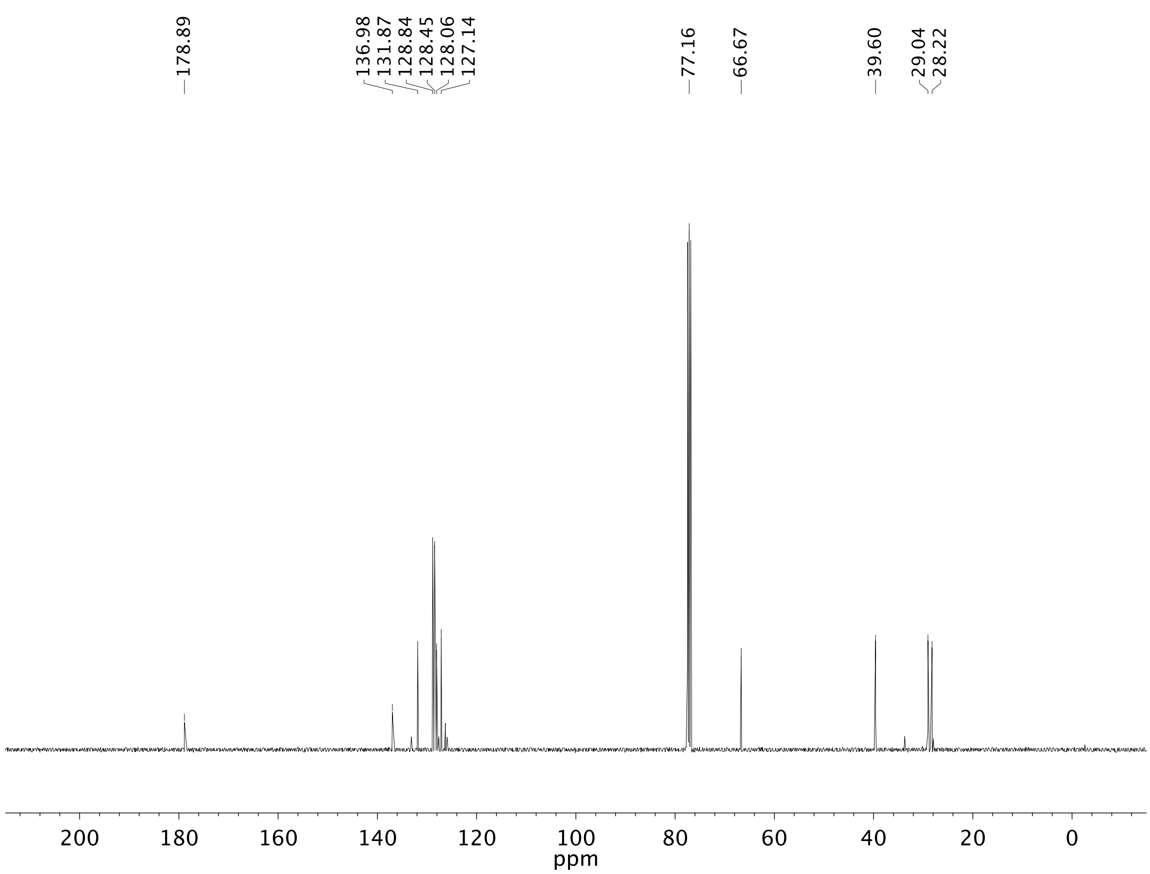
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3t**



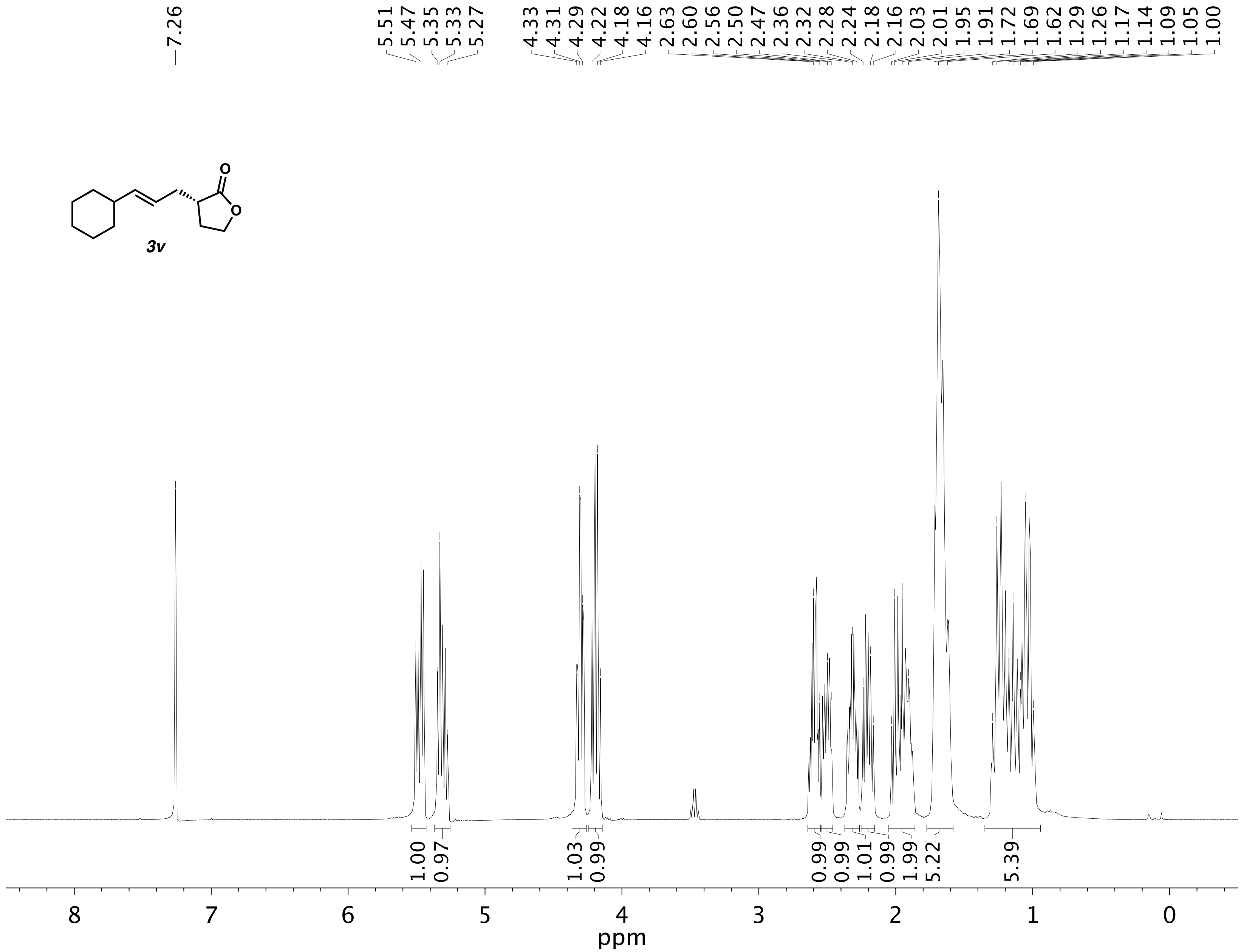
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**



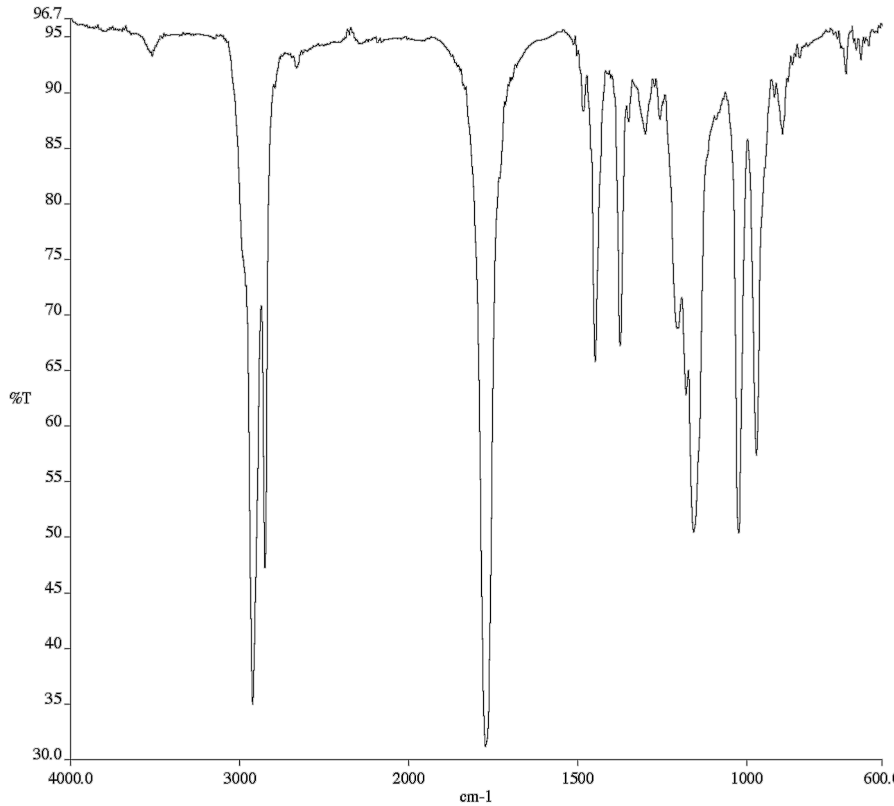
Infrared spectrum (Thin Film, NaCl) of compound **3u**



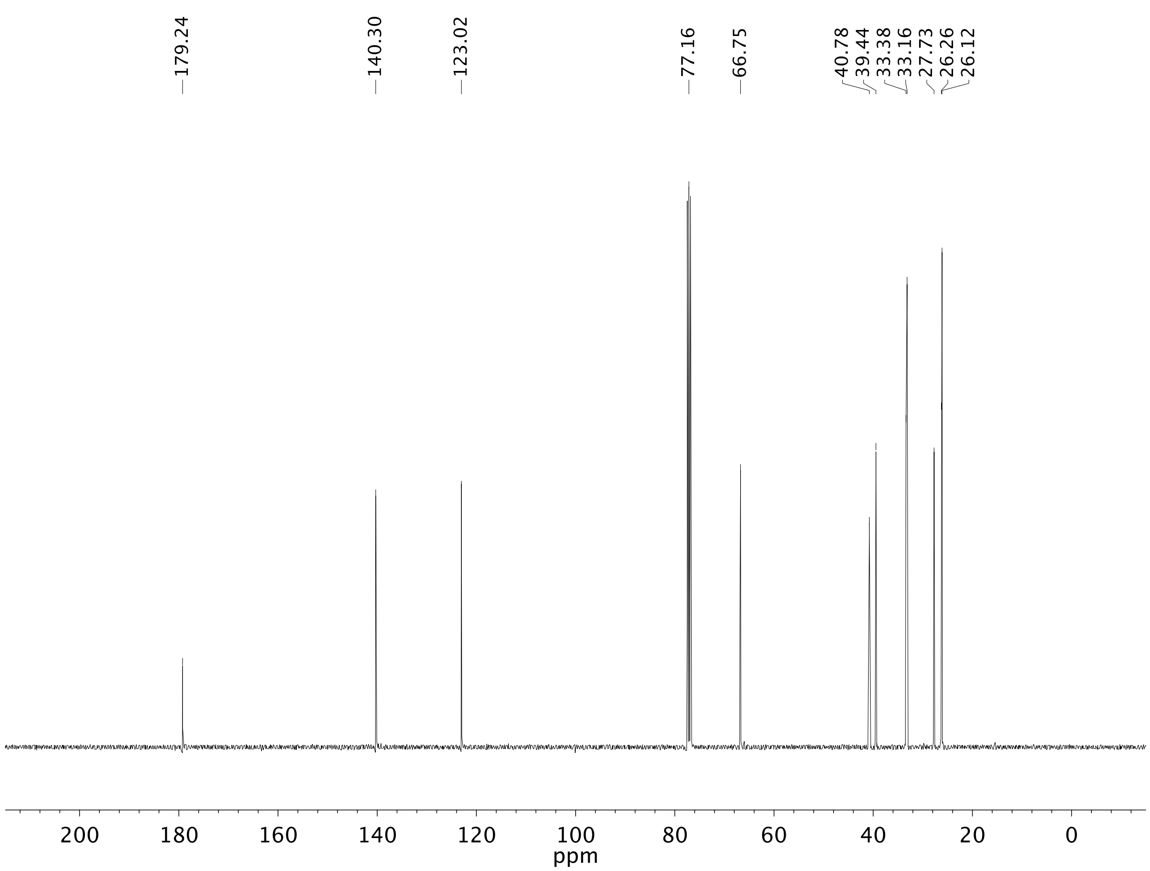
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3u**



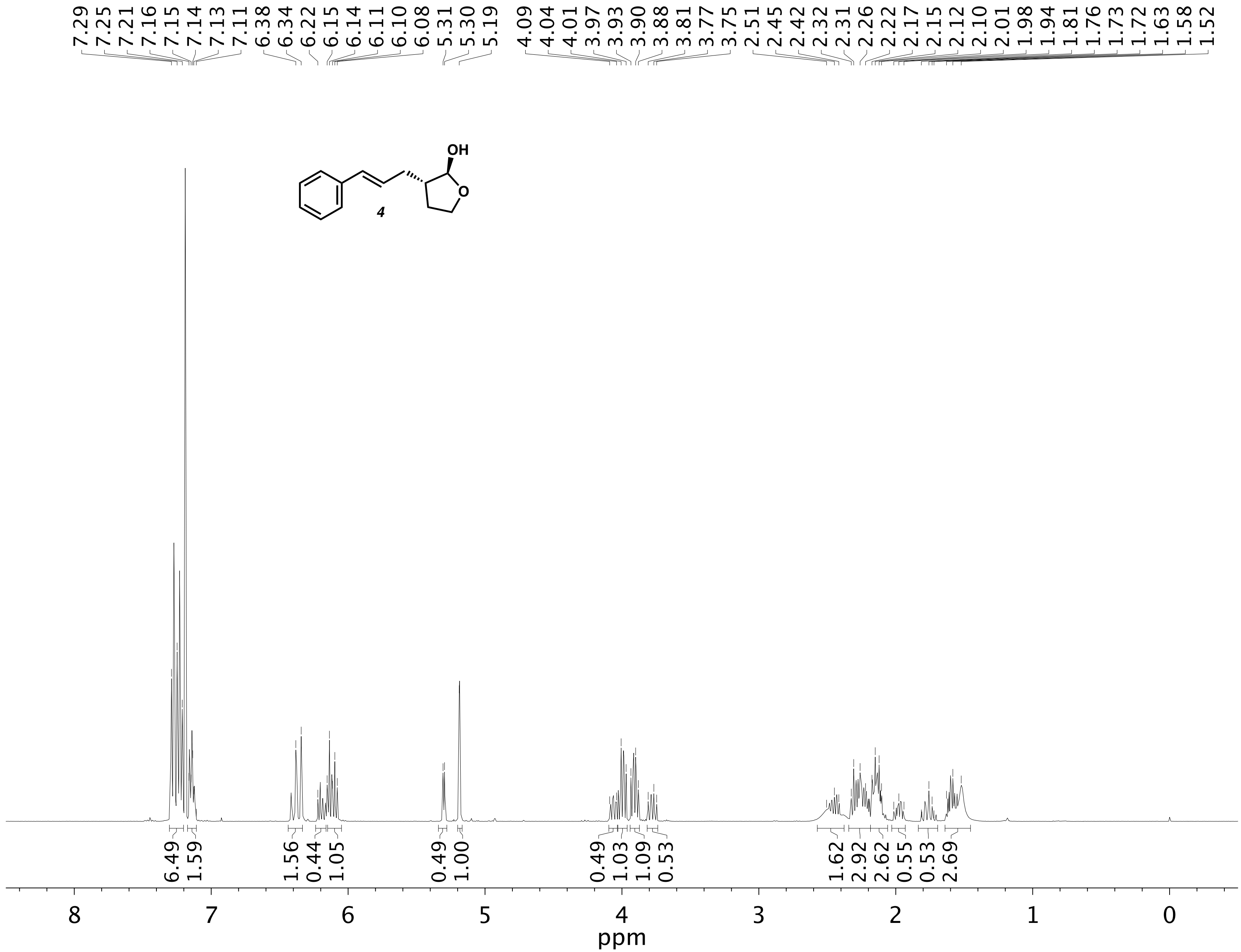
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3v**



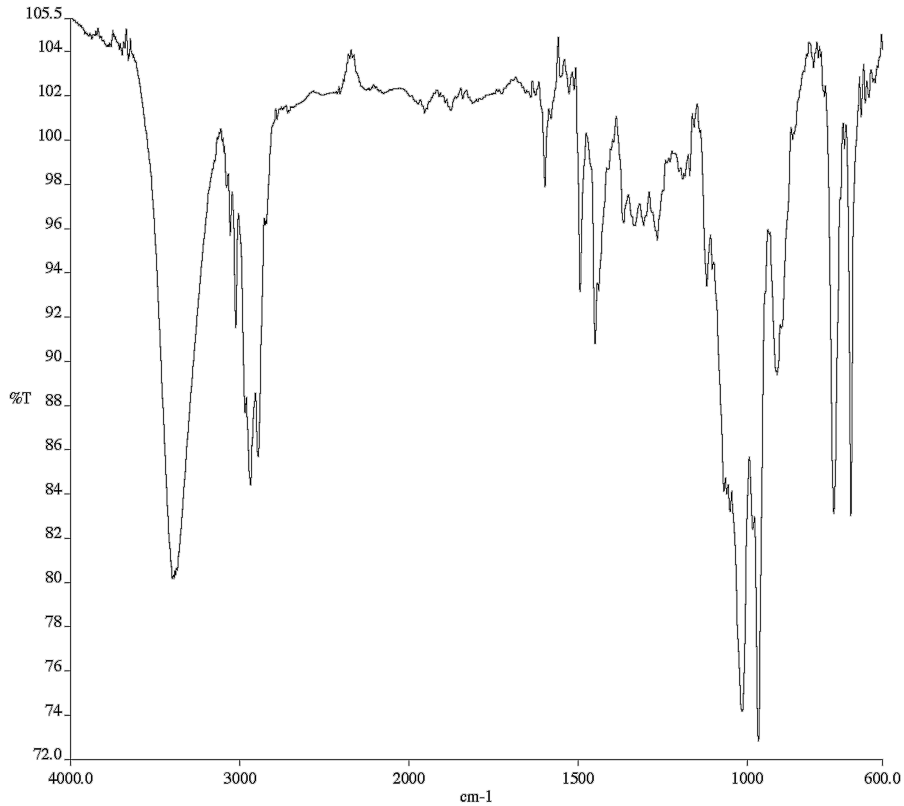
Infrared spectrum (Thin Film, NaCl) of compound **3v**



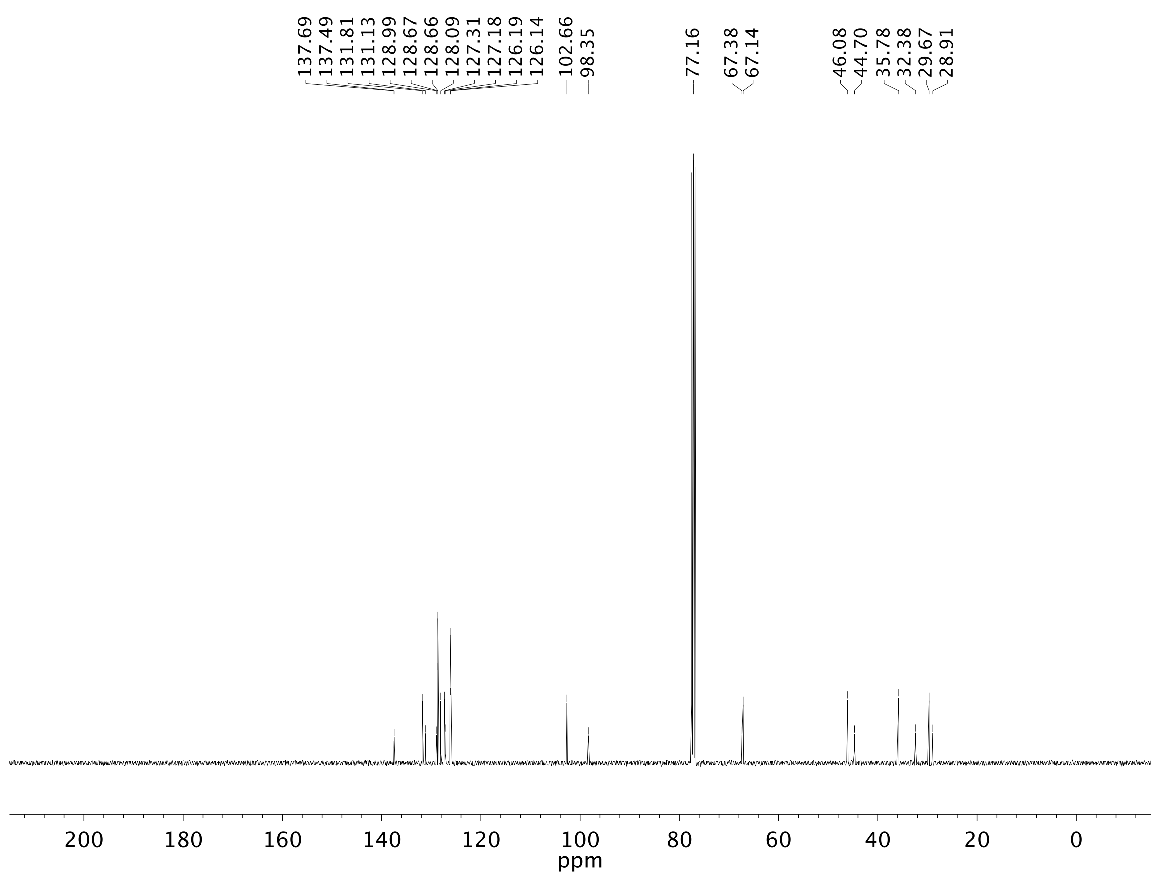
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3v**



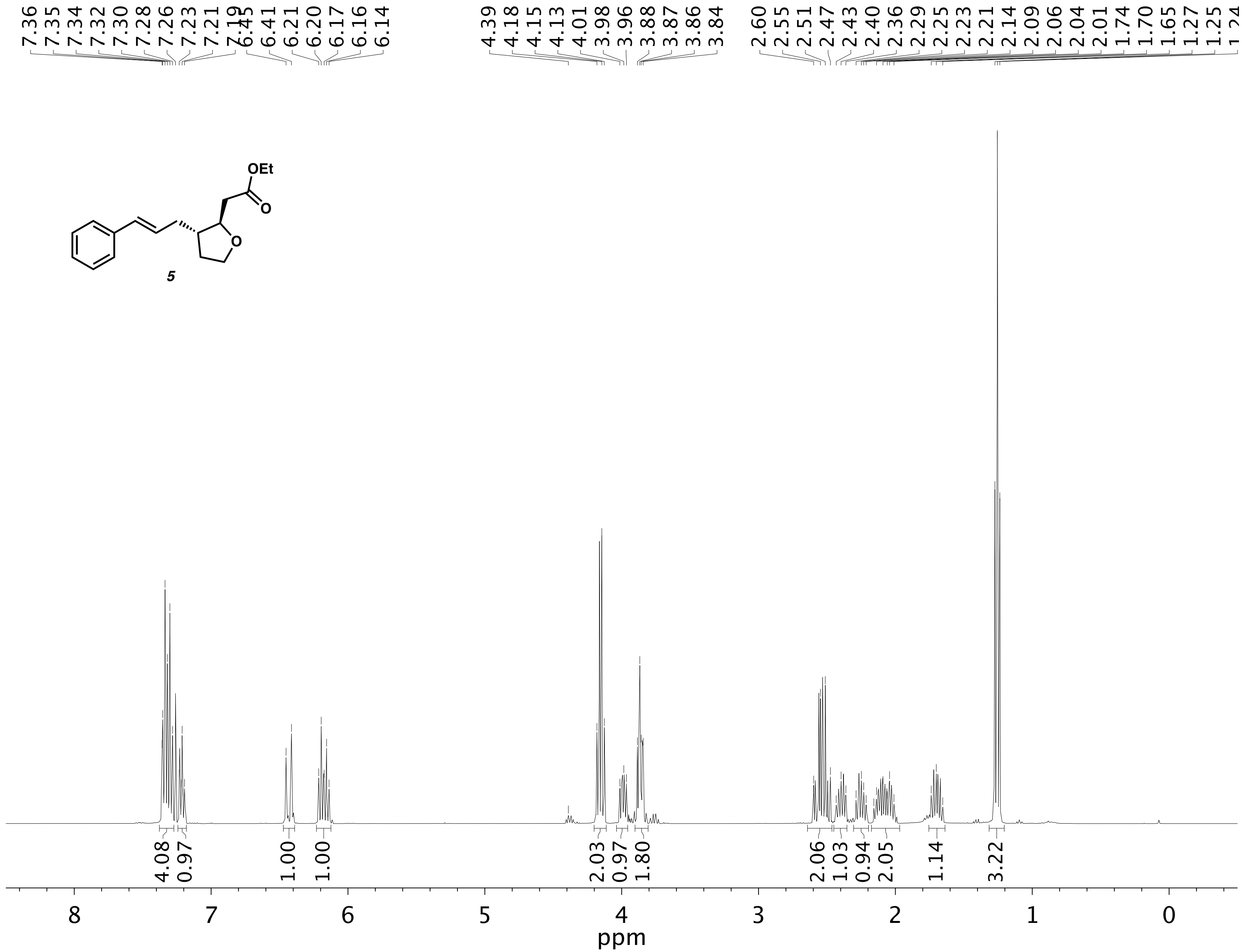
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**



Infrared spectrum (Thin Film, NaCl) of compound **4**

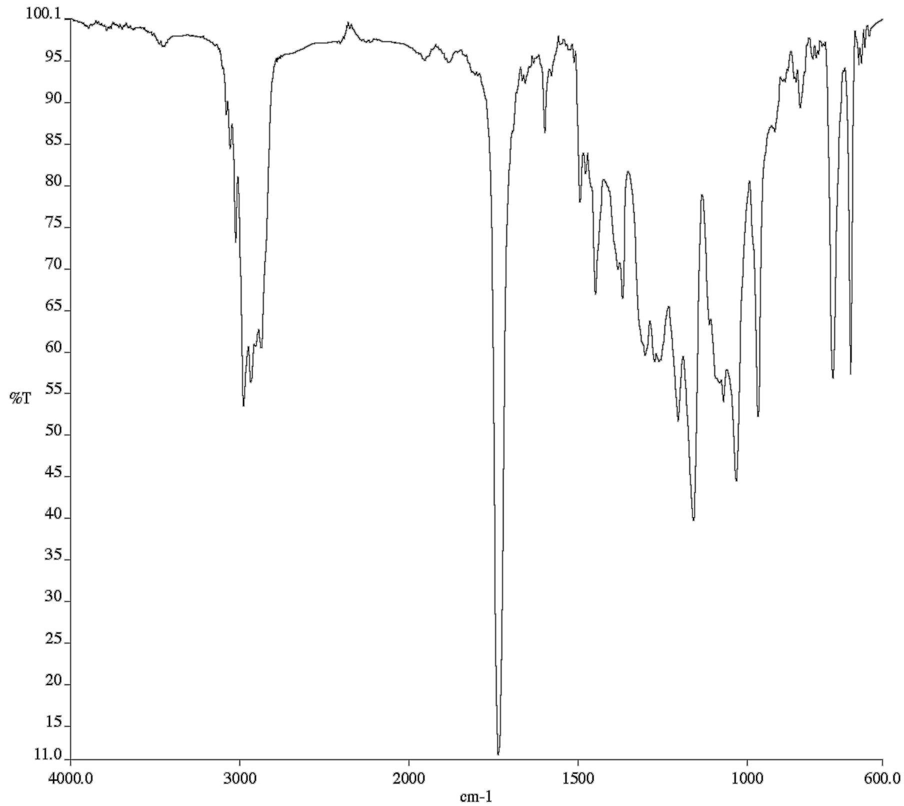


^{13}C NMR (101 MHz, $CDCl_3$) of compound **4**

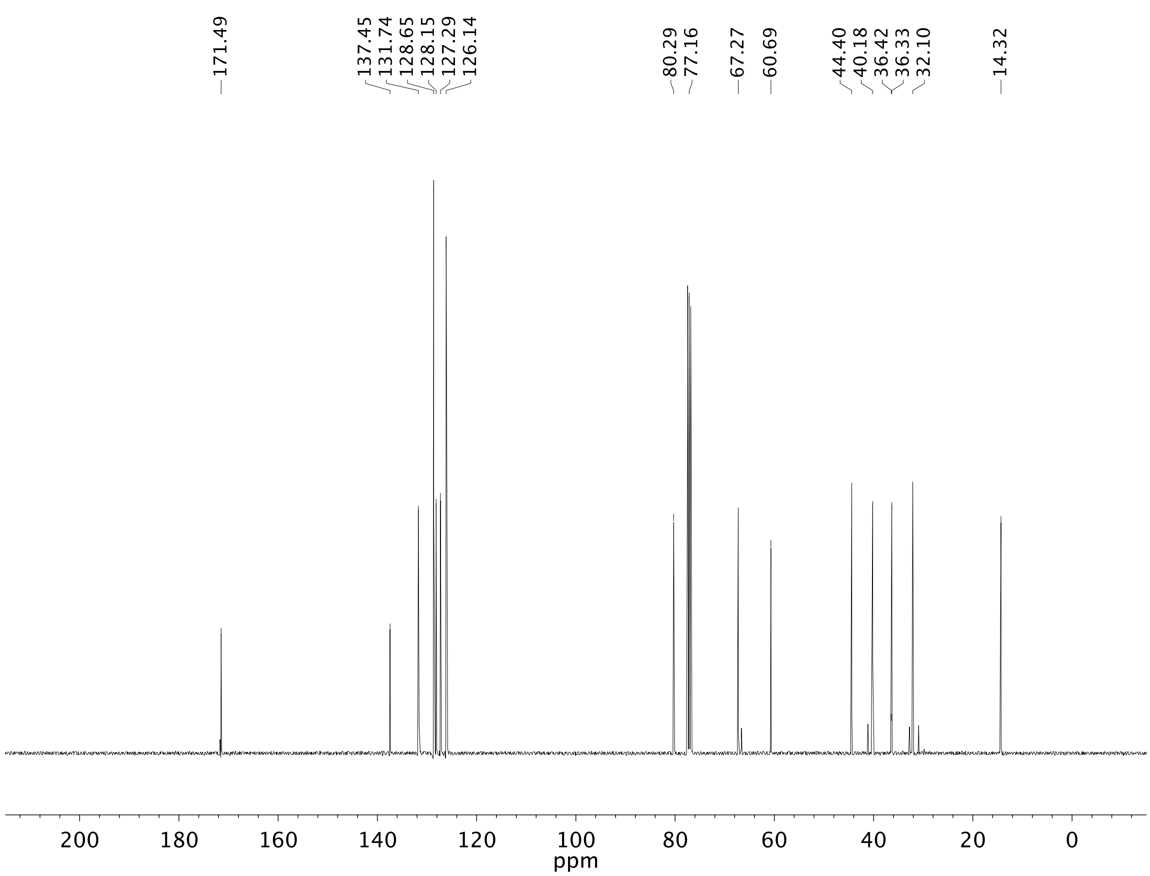


5

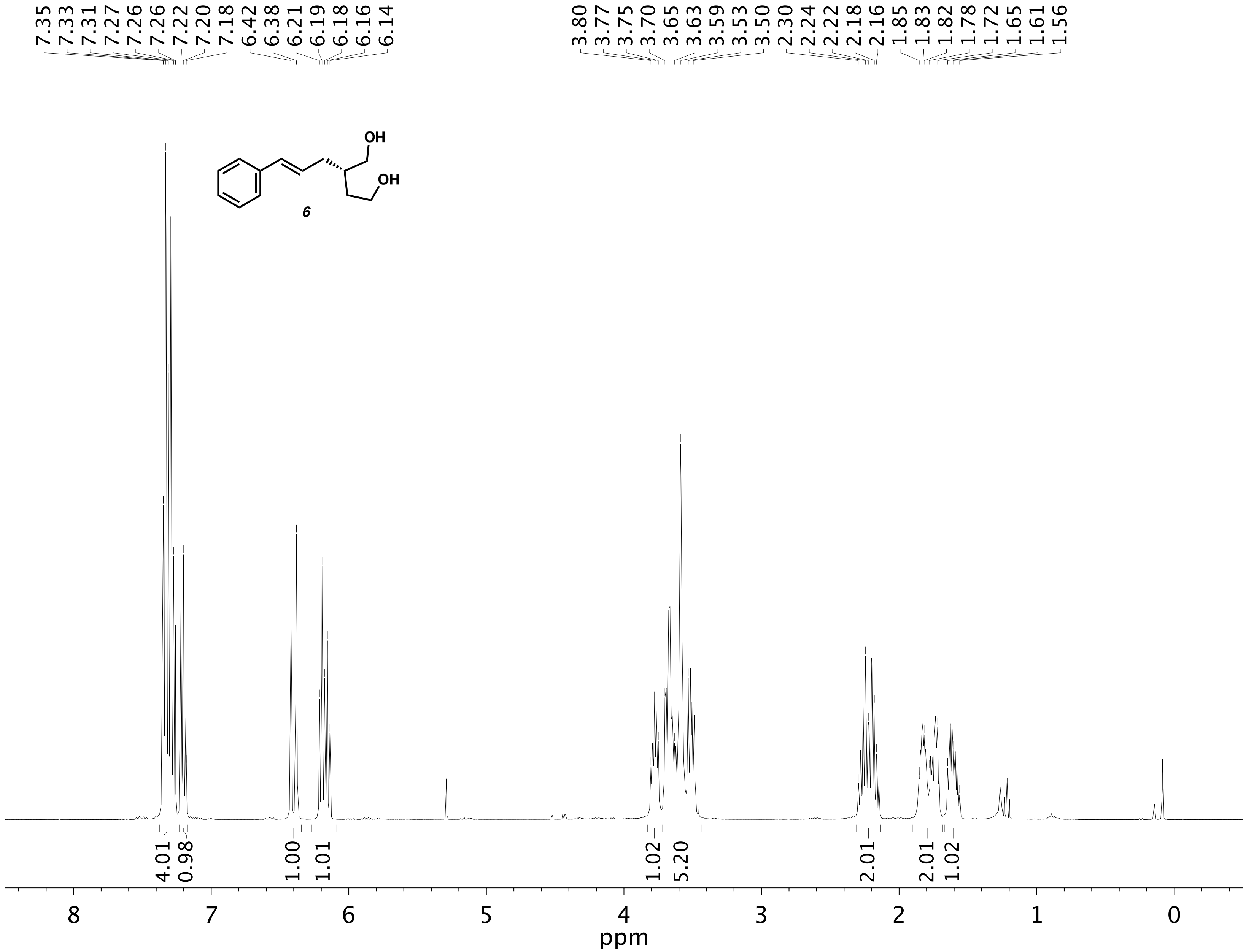
[1]H NMR (400 MHz, $CDCl_3$) of compound **5**



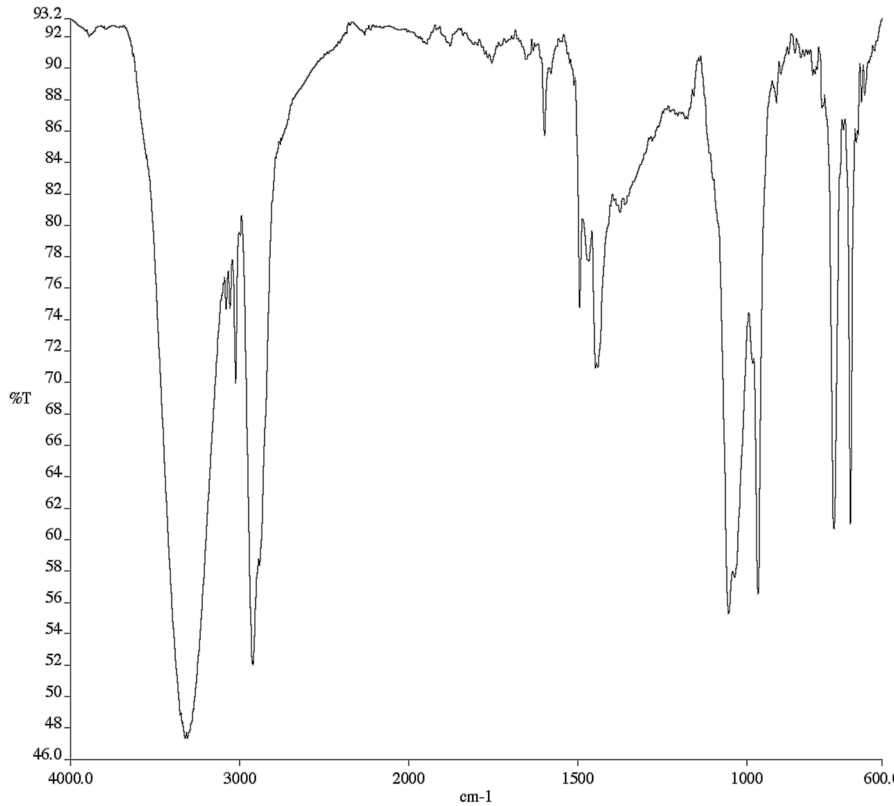
Infrared spectrum (Thin Film, NaCl) of compound **5**



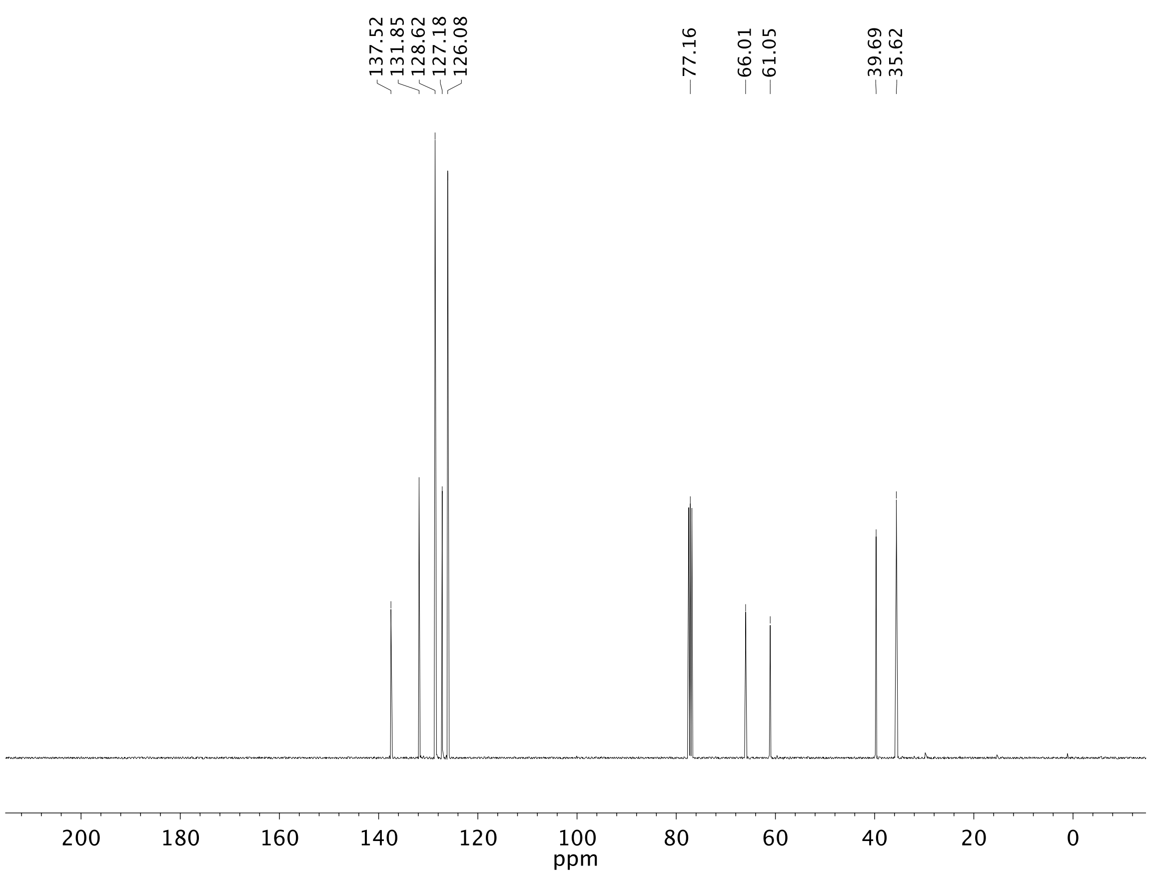
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5**



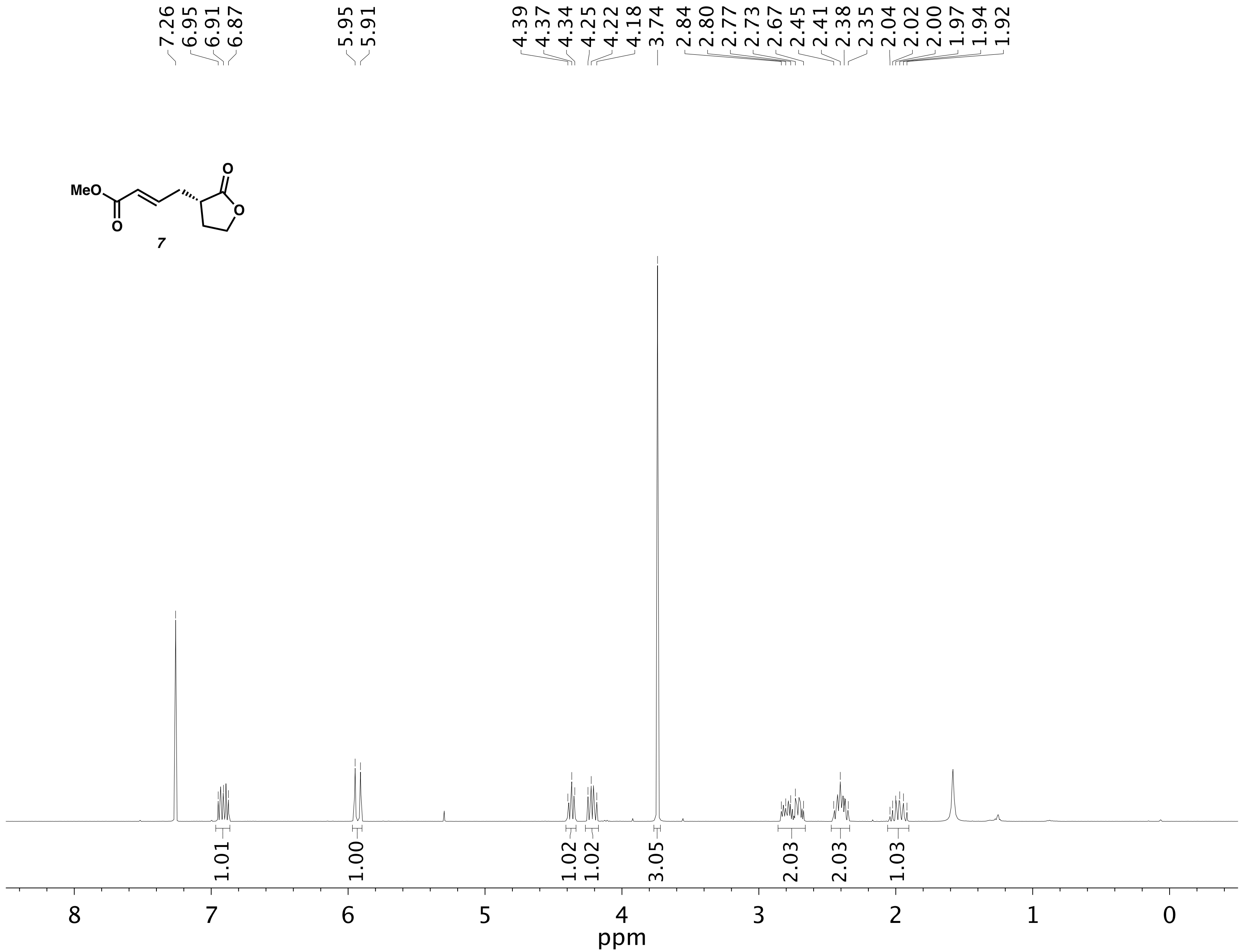
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6**



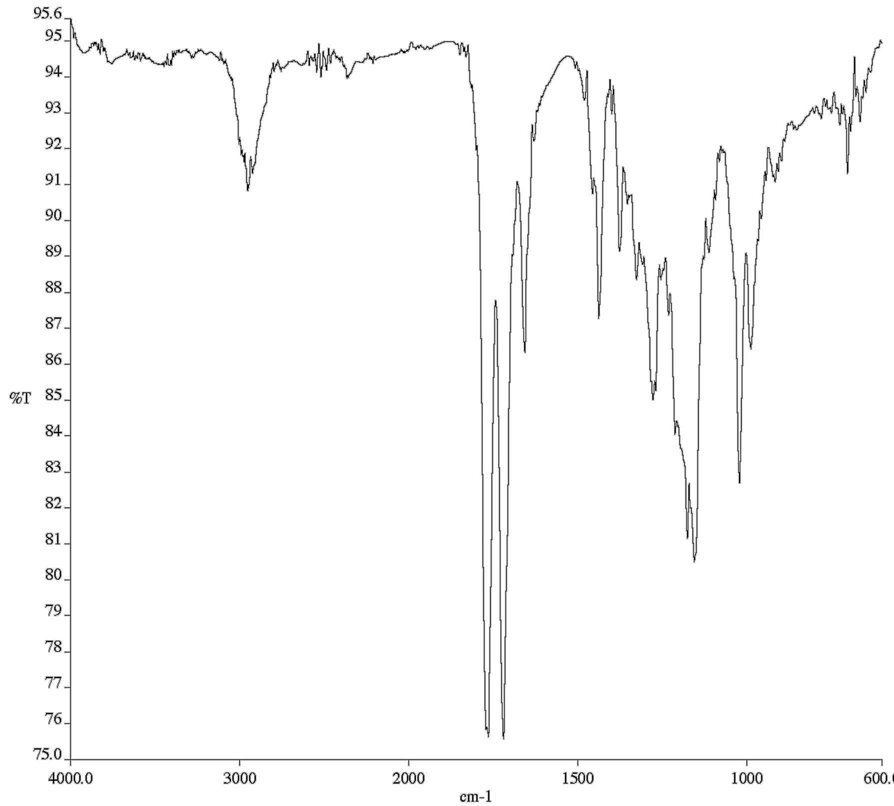
Infrared spectrum (Thin Film, NaCl) of compound **6**



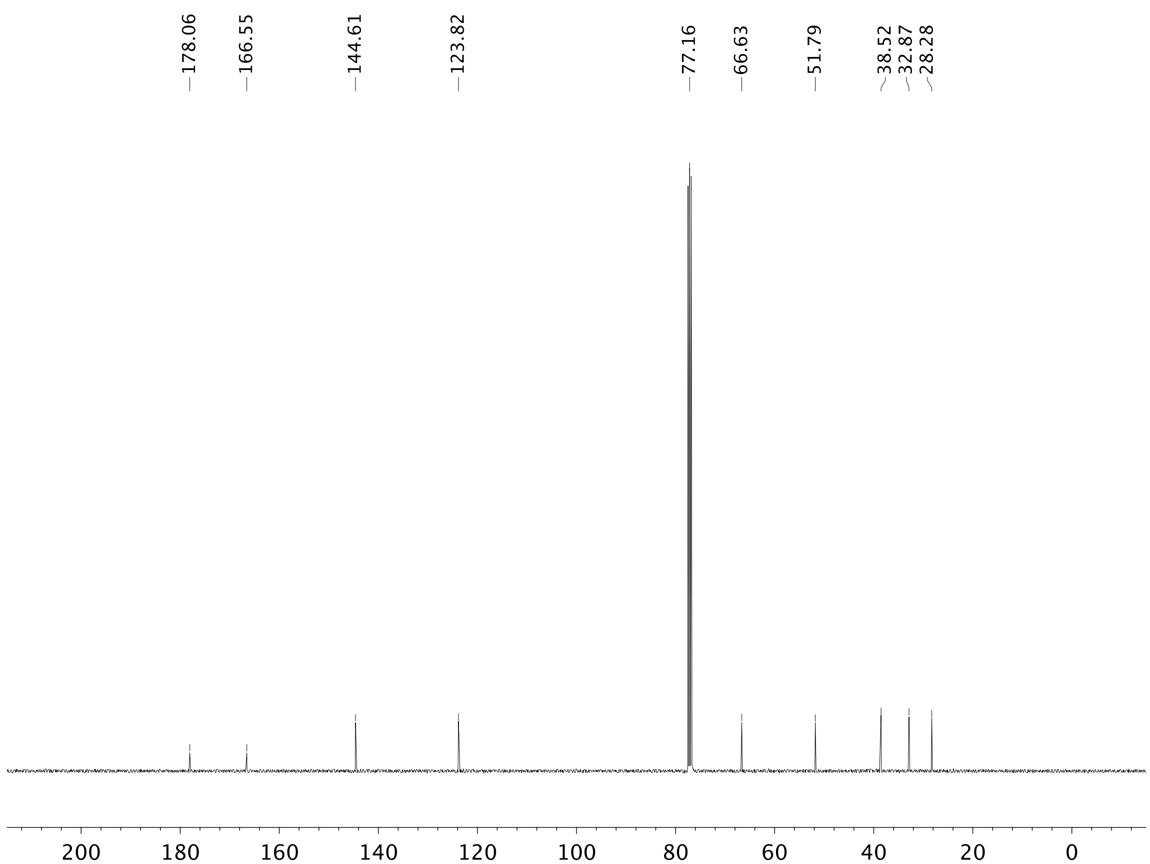
^{13}C NMR (101 MHz, $CDCl_3$) of compound **6**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**

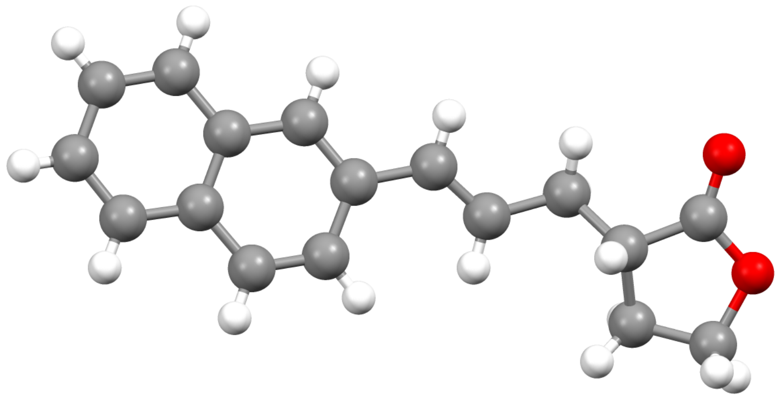


Infrared spectrum (Thin Film, NaCl) of compound **7**



^{13}C NMR (101 MHz, $CDCl_3$) of compound **7**

Crystal Structure for 3b:



Crystal data and structure refinement for v19036.

Identification code	v19036	
Empirical formula	C17 H16 O2	
Formula weight	252.30	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.9377(5) Å	a= 90°
	b = 7.1431(5) Å	b= 98.260(5)°
	c = 13.2770(10) Å	g = 90°
Volume	651.14(8) $Å^3$	
Z	2	
Density (calculated)	1.287 g/cm^3	
Absorption coefficient	0.659 mm^{-1}	
F(000)	268	
Crystal size	0.32 x 0.17 x 0.05 mm^3	
Theta range for data collection	3.364 to 80.143°.	
Index ranges	-8 £ h £ 8, -9 £ k £ 9, -16 £ l £ 16	
Reflections collected	2467	

Independent reflections	2467 [R(int) = ?]
Completeness to theta = 67.679°	97.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2467 / 1 / 173
Goodness-of-fit on F^2	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0996
R indices (all data)	R1 = 0.0349, wR2 = 0.1006
Absolute structure parameter [Flack]	-0.13(13)
Extinction coefficient	n/a
Largest diff. peak and hole	0.163 and -0.178 e.Å^{-3}

Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters ($Å^2$x 10^4) for v19036. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-94170(30)	-49190(30)	-37017(12)	254(4)
O(2)	-113080(30)	-46280(30)	-51927(13)	277(5)
C(1)	-27370(40)	-55580(30)	-77985(18)	207(5)
C(2)	-13460(40)	-59970(40)	-83901(18)	206(5)
C(3)	-16470(40)	-56390(30)	-94593(18)	200(5)
C(4)	-2330(50)	-60820(40)	-100900(20)	242(6)
C(5)	-5780(50)	-57100(40)	-111190(20)	274(6)
C(6)	-23470(50)	-48680(40)	-115498(17)	280(6)
C(7)	-37520(40)	-44350(40)	-109595(18)	245(6)
C(8)	-34350(40)	-48180(40)	-98950(17)	211(5)
C(9)	-48730(40)	-44210(40)	-92670(17)	206(5)
C(10)	-45640(40)	-47770(40)	-82329(17)	207(5)
C(11)	-61220(40)	-43810(40)	-76283(19)	220(5)
C(12)	-59920(40)	-43400(40)	-66160(20)	235(6)
C(13)	-76880(40)	-38650(40)	-60750(20)	255(6)
C(14)	-78040(40)	-50900(40)	-51425(18)	219(5)
C(15)	-63020(40)	-47120(50)	-42066(19)	296(6)
C(16)	-73710(50)	-53270(40)	-33449(19)	308(7)
C(17)	-97060(40)	-48510(40)	-47252(18)	216(5)

Bond lengths [Å] and angles [°] for v19036.

O(1)-C(16)	1.459(3)
O(1)-C(17)	1.346(3)
O(2)-C(17)	1.203(3)
C(1)-H(1)	0.9500
C(1)-C(2)	1.366(4)
C(1)-C(10)	1.428(4)
C(2)-H(2)	0.9500
C(2)-C(3)	1.428(3)
C(3)-C(4)	1.415(4)
C(3)-C(8)	1.418(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.378(4)
C(5)-H(5)	0.9500
C(5)-C(6)	1.412(5)
C(6)-H(6)	0.9500
C(6)-C(7)	1.371(4)
C(7)-H(7)	0.9500
C(7)-C(8)	1.425(3)
C(8)-C(9)	1.418(4)
C(9)-H(9)	0.9500
C(9)-C(10)	1.383(3)
C(10)-C(11)	1.463(4)
C(11)-H(11)	0.9500
C(11)-C(12)	1.334(4)
C(12)-H(12)	0.9500
C(12)-C(13)	1.503(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(13)-C(14)	1.527(4)
C(14)-H(14)	1.0000
C(14)-C(15)	1.527(3)
C(14)-C(17)	1.512(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900

C(15)-C(16)	1.515(4)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(17)-O(1)-C(16)	109.4(2)
C(2)-C(1)-H(1)	119.4
C(2)-C(1)-C(10)	121.1(2)
C(10)-C(1)-H(1)	119.4
C(1)-C(2)-H(2)	119.5
C(1)-C(2)-C(3)	121.1(2)
C(3)-C(2)-H(2)	119.5
C(4)-C(3)-C(2)	122.3(3)
C(4)-C(3)-C(8)	119.4(2)
C(8)-C(3)-C(2)	118.3(2)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-C(3)	120.5(3)
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-H(5)	120.0
C(4)-C(5)-C(6)	120.1(3)
C(6)-C(5)-H(5)	120.0
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-C(5)	120.8(2)
C(7)-C(6)-H(6)	119.6
C(6)-C(7)-H(7)	119.9
C(6)-C(7)-C(8)	120.1(3)
C(8)-C(7)-H(7)	119.9
C(3)-C(8)-C(7)	119.0(2)
C(9)-C(8)-C(3)	119.4(2)
C(9)-C(8)-C(7)	121.5(2)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-C(8)	121.7(3)
C(10)-C(9)-H(9)	119.1
C(1)-C(10)-C(11)	122.4(2)
C(9)-C(10)-C(1)	118.3(2)
C(9)-C(10)-C(11)	119.2(3)
C(10)-C(11)-H(11)	116.3

C(12)-C(11)-C(10)	127.5(3)
C(12)-C(11)-H(11)	116.3
C(11)-C(12)-H(12)	118.6
C(11)-C(12)-C(13)	122.9(3)
C(13)-C(12)-H(12)	118.6
C(12)-C(13)-H(13A)	108.9
C(12)-C(13)-H(13B)	108.9
C(12)-C(13)-C(14)	113.3(2)
H(13A)-C(13)-H(13B)	107.7
C(14)-C(13)-H(13A)	108.9
C(14)-C(13)-H(13B)	108.9
C(13)-C(14)-H(14)	108.4
C(15)-C(14)-C(13)	116.7(3)
C(15)-C(14)-H(14)	108.4
C(17)-C(14)-C(13)	112.5(2)
C(17)-C(14)-H(14)	108.4
C(17)-C(14)-C(15)	102.19(19)
C(14)-C(15)-H(15A)	111.3
C(14)-C(15)-H(15B)	111.3
H(15A)-C(15)-H(15B)	109.2
C(16)-C(15)-C(14)	102.3(2)
C(16)-C(15)-H(15A)	111.3
C(16)-C(15)-H(15B)	111.3
O(1)-C(16)-C(15)	104.8(2)
O(1)-C(16)-H(16A)	110.8
O(1)-C(16)-H(16B)	110.8
C(15)-C(16)-H(16A)	110.8
C(15)-C(16)-H(16B)	110.8
H(16A)-C(16)-H(16B)	108.9
O(1)-C(17)-C(14)	110.8(2)
O(2)-C(17)-O(1)	121.2(2)
O(2)-C(17)-C(14)	128.0(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^4) for v19036. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	237(10)	304(10)	222(7)	-1(7)	39(7)	23(10)
O(2)	185(9)	358(12)	291(8)	41(8)	43(7)	-7(9)
C(1)	218(14)	191(12)	202(9)	1(9)	-1(10)	-17(11)
C(2)	193(13)	173(11)	240(10)	12(9)	-9(9)	10(11)
C(3)	229(13)	149(11)	220(10)	-11(9)	27(10)	-30(11)
C(4)	271(15)	187(11)	273(11)	-19(9)	56(11)	1(13)
C(5)	354(17)	215(13)	270(11)	-49(10)	101(11)	-33(13)
C(6)	407(17)	224(12)	207(10)	-11(10)	33(10)	-57(15)
C(7)	302(15)	186(12)	229(10)	10(9)	-28(10)	-25(12)
C(8)	257(14)	146(10)	221(10)	-9(9)	10(10)	-37(12)
C(9)	192(11)	151(11)	259(11)	14(9)	-21(10)	7(10)
C(10)	206(12)	166(11)	247(10)	-1(10)	29(10)	-30(13)
C(11)	167(12)	195(12)	297(11)	39(9)	25(9)	6(11)
C(12)	187(13)	232(13)	296(11)	27(10)	66(10)	13(12)
C(13)	207(12)	264(14)	305(12)	25(10)	71(11)	18(12)
C(14)	161(13)	227(12)	276(11)	-4(10)	50(10)	18(12)
C(15)	200(13)	356(16)	318(11)	4(13)	-11(10)	18(13)
C(16)	293(16)	357(16)	254(11)	12(10)	-30(11)	67(13)
C(17)	234(13)	191(11)	225(10)	2(10)	41(9)	-32(14)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for v19036.

	x	y	z	U(eq)
H(1)	-2486	-5777	-7086	25
H(2)	-158	-6549	-8085	25
H(4)	964	-6640	-9803	29
H(5)	375	-6021	-11538	33
H(6)	-2566	-4599	-12258	34
H(7)	-4940	-3878	-11261	29
H(9)	-6080	-3897	-9565	25
H(11)	-7369	-4124	-7999	26
H(12)	-4775	-4622	-6220	28
H(13A)	-8909	-4007	-6556	31
H(13B)	-7583	-2538	-5859	31
H(14)	-7687	-6429	-5344	26
H(15A)	-5105	-5459	-4223	36
H(15B)	-5956	-3368	-4150	36
H(16A)	-7178	-6681	-3207	37
H(16B)	-6908	-4620	-2715	37

Coordinates for Optimized Geometries

B3(0HF)LYP Optimized **L8^{NNO}•$CuCl_2$**

C	5.84649546244608	3.80009699351144	0.35677478540613
C	5.20628526966995	3.54427414304280	-0.85151136053620
H	4.43843795031227	2.76843330873990	-0.90835413876220
C	5.57245233271477	4.26132049922000	-1.99597840840474
H	5.08426380468348	4.04912827253866	-2.95002940226531
C	6.58444927880399	5.21979523225337	-1.92845268989370
H	6.88761810191443	5.75689867271473	-2.83024296532060
C	7.23429840965186	5.47277190941920	-0.71554445088301
H	8.04419813809433	6.20414098150249	-0.66273787952742
C	6.86219041994545	4.77025442858758	0.42717089475257
C	5.30496521823870	4.16228481163829	2.70241434681085
C	4.20464883302810	4.21555948924984	3.55410647567852
H	3.45746943449329	3.41864977965394	3.52367912547705
C	4.06813515504421	5.28043398840012	4.45448458800090
H	3.20513152189289	5.32041239151633	5.12396366085001
C	5.04030065361813	6.28168666930179	4.50798361184927
H	4.93656590251965	7.10682345399245	5.21717236619432
C	6.15553774358018	6.22433546221199	3.66163260937201
H	6.93145199137887	6.99208727144098	3.71326637429685
C	6.28537861380839	5.17385945461384	2.75570481662866
C	5.61451361883679	3.09732596931170	1.67624322562103
H	4.83689219573620	2.32362262990335	1.62166420560046
C	7.44128734641475	4.93417225745630	1.81153173151597
H	8.21660734850250	5.70542260472605	1.87895308012207
C	6.99020539493881	2.42161896893882	2.05109037797509

C	8.04681470655706	3.54298665525527	2.30301787644251
N	9.34198340358532	3.20559310556420	1.74624823044713
N	6.81198664777545	1.53718192569435	3.18054367626867
H	7.31744573425189	1.87555501800638	1.14618124200731
H	8.15806025707222	3.65619677241761	3.39720925522048
C	10.35608981540664	4.04107966120902	1.98321306435662
O	10.32879068814233	5.15956749600066	2.57251240964311
C	11.67870186598739	3.53497846343068	1.46931752768328
C	12.81219652818755	4.35577804506283	1.45892617339345
C	12.88123982953077	1.75127822478929	0.59599020617176
C	14.01311177792603	3.83665616689550	0.98446690292745
H	12.70289569921495	5.37436890327597	1.83253919876009
C	14.05101744738914	2.50967213035211	0.54380980371241
H	12.81813121858895	0.70170982238844	0.28734594617472
H	14.91375003066435	4.45627132189672	0.95763838319354
H	14.97379228418060	2.06315202979394	0.16745155915373
N	11.72791642775386	2.25967329706688	1.04816085785147
C	7.76953333849433	0.65613759361462	3.36999766425075
O	8.85789374960608	0.46005013518106	2.71217330596226
C	7.56202451529443	-0.29073674850832	4.53447474624347
C	6.49076757713324	-0.14352330098897	5.42867366583204
C	8.46271336951653	-1.34796709344498	4.73296718314431
C	6.32332472641905	-1.02850528256569	6.49414479241306
H	5.80337216894331	0.68535771923953	5.25350485451498
C	8.29242956768574	-2.23803661039940	5.79595166187977
H	9.28675271813469	-1.44242311159463	4.02310413232512
C	7.22426313412840	-2.08342462544594	6.68408353157662
H	5.48512663311003	-0.89645921870251	7.18457801423826

H	9.00045801111915	-3.06021158385933	5.93278558227576
H	7.09364084620980	-2.77780189712960	7.51863447158090
Cu	9.78120858103308	1.32888903607831	1.03240081285816
Cl	8.81554460742632	1.66004498732765	-1.12698476570414
Cl	10.77685195326325	-0.77597868178764	0.56658305264232

B3(0HF)LYP Optimized **L8^{NNN}•CuCl$_2$**

C	-2.86181484528682	-3.58940008954456	1.95054375745875
C	-3.31349561668561	-3.69892806317600	3.26250890510869
H	-4.13201981424364	-3.06402295850537	3.60957023087454
C	-2.69166078877141	-4.59997873554681	4.13703540534236
H	-3.03977202382283	-4.68112858726659	5.16951055772232
C	-1.61450006587853	-5.37333267302338	3.70063026890984
H	-1.11918665003785	-6.05923485469390	4.39211883046056
C	-1.15401417694491	-5.25930197698310	2.38244463344789
H	-0.29497713299160	-5.84023114359128	2.03926924108307
C	-1.78033160369459	-4.37729609827755	1.50634650947363
C	-3.75173736489797	-3.46521827440768	-0.30282559372406
C	-4.97750369229859	-3.45829869736675	-0.96435677423204
H	-5.75890544455049	-2.76349384916088	-0.64721581442237
C	-5.20152493383831	-4.33602636614491	-2.03381041432141
H	-6.16297769083989	-4.32618806709272	-2.55283331174731
C	-4.19794824599778	-5.21690234943456	-2.44008383027092
H	-4.37365180775356	-5.89846280196543	-3.27601398450806
C	-2.95831455020654	-5.21994771719559	-1.78496612231822
H	-2.16174467701921	-5.89328943504955	-2.11177768958318
C	-2.73457961553729	-4.35083735592329	-0.72127916470769
C	-3.37331706245782	-2.62165160380954	0.89614157692924

H	-4.20993714530172	-2.01936063426353	1.26309702517890
C	-1.43861634905272	-4.16617112198962	0.04697374420373
H	-0.61530612865887	-4.80049980067353	-0.29977462931757
C	-2.06870834057739	-1.74653729845357	0.60823164693850
C	-1.12654857996390	-2.64169144200025	-0.23329153273700
N	0.17807677174764	-2.07369500144812	-0.07939931260257
N	-2.09369454295182	-0.46650754392405	-0.09469085132616
H	-1.58270398413108	-1.62011890928101	1.59414633634100
H	-1.42476319348728	-2.47473829499704	-1.28631421994704
C	1.35017636433688	-2.68913092021165	-0.13436395652539
O	1.62217792878584	-3.91633192589262	-0.26140901416013
C	2.46882463684969	-1.67935675525097	-0.01466482661331
C	3.80702569585218	-2.06782406847755	0.08881457473474
C	3.04753423417500	0.57234335209120	0.08034955842634
C	4.78601910284615	-1.08485112427463	0.20200902682291
H	4.02479659050468	-3.13652980921024	0.07731692490857
C	4.40177120154489	0.25960948036649	0.19958080239680
H	2.65834052547137	1.59364133141025	0.04256709356220
H	5.84049892387173	-1.35945818433587	0.29304536329919
H	5.13794677710420	1.06064536626853	0.28872484545744
N	2.11506484582269	-0.38003878037524	-0.02380140843529
C	-3.02514947327033	0.48548434128828	0.13683851027035
O	-3.21524042877017	1.48258008233778	-0.58726858437059
C	-3.93226547087433	0.42024079169482	1.36293991576418
C	-5.32290435103615	0.52628181281700	1.21086131984595
C	-3.39013801733346	0.38169637034138	2.65723336046604
C	-6.16566520360415	0.54758700487333	2.32232049749550
C	-4.23537416878162	0.43692714636742	3.76952438980982

H	-2.29879871680153	0.32988609081922	2.78194031834153
C	-5.62265894532815	0.50431892619841	3.61216165872487
H	-7.24940273261483	0.60899672948706	2.18616275181731
H	-3.79882607853386	0.42200923800630	4.77175867899157
H	-6.27834421558201	0.53067053223428	4.48680812861745
Cu	0.03617643535316	-0.05242231160071	-0.01913595566441
Cl	0.18202321645312	0.27002263103041	2.57231415549656
Cl	0.29325881017386	2.02731557064579	-0.99523340875897
H	-5.72956104448254	0.60579524254171	0.20004752957136

B3(38HF)LYP Optimized **L8^{NNO}•CuCl$_2$**

C	5.996110782131	3.901206403957	0.452079601878
C	5.423486805078	3.679827078564	-0.786061411137
H	4.667520217538	2.920436572539	-0.904396692789
C	5.839428879551	4.428986077828	-1.882956965284
H	5.399476923526	4.253036574871	-2.851016388804
C	6.831735664453	5.384431642849	-1.735752036232
H	7.163768223835	5.951501965469	-2.590124163908
C	7.414576303946	5.602299341489	-0.490743626918
H	8.200673516229	6.330040744673	-0.376741521911
C	6.993777917947	4.867261840308	0.602015616610
C	5.332116417736	4.195442603273	2.771842483688
C	4.189952214415	4.228420058479	3.549276556945
H	3.452856064764	3.447771617348	3.456712372216
C	4.003114019401	5.262696013321	4.461957736775
H	3.114280724597	5.286917391230	5.071525355996
C	4.963659331499	6.252329528748	4.597542301981
H	4.821097874227	7.048346639473	5.310476614833

C	6.118926140900	6.214766956788	3.821485434612
H	6.875332932452	6.974013361780	3.935563307494
C	6.300724842810	5.192942761987	2.907440975164
C	5.701703622593	3.161820372109	1.736566102369
H	4.938984917382	2.402224595939	1.617074970074
C	7.504965252742	4.987214850609	2.017555170105
H	8.243515277002	5.763153761470	2.130243426082
C	7.051091178732	2.487207621378	2.159542821071
C	8.108184864734	3.596027330405	2.468159587946
N	9.388220838187	3.236459144108	1.885942503798
N	6.821977544490	1.589070334148	3.263889240509
H	7.405838448457	1.949687548234	1.284158346282
H	8.208910724937	3.659528248118	3.549920834187
C	10.361555359048	4.121037817158	1.850408640231
O	10.399565897214	5.302062669248	2.245415300616
C	11.608868581047	3.583798199216	1.172962636089
C	12.662071242279	4.426011550783	0.835823368586
C	12.700918451362	1.759832401351	0.284878185249
C	13.758218129810	3.891235217255	0.188377419153
H	12.584116608080	5.465348971456	1.092656241391
C	13.780532506528	2.533894554776	-0.098888455296
H	12.647574982173	0.703386050431	0.099431046553
H	14.587726990705	4.521367067434	-0.090838439002
H	14.616384137745	2.079333196417	-0.601273669208
N	11.651231278595	2.285805536168	0.900400206884
C	7.627405417897	0.581479742613	3.340901878820
O	8.605258220891	0.274703870437	2.579248858236
C	7.379616572659	-0.398956292953	4.463387474823

C	6.188345145551	-0.405767353400	5.184974754904
C	8.369197171738	-1.322048044660	4.791669699835
C	5.982790318877	-1.321928298980	6.204409970181
H	5.438004240614	0.320923913183	4.931620045610
C	8.166026280491	-2.233333149044	5.818485765358
H	9.293690860245	-1.295770003667	4.242240757041
C	6.972684656387	-2.242128143675	6.525988503078
H	5.052373773028	-1.317837679978	6.750566413328
H	8.945645435044	-2.935109870487	6.066962597461
H	6.815759858662	-2.953772317392	7.321352582794
Cu	10.066149178894	1.192064170598	1.672139645038
Cl	9.898255811504	-0.030829863250	-0.484324121440
Cl	11.773634426644	0.232647107470	3.284474140053

B3(38HF)LYP Optimized **L8^{NNN}•CuCl$_2$**

C	5.945807246296	3.107202192485	1.502335399784
C	5.047563103218	2.379285222991	0.746343080120
H	4.570427748968	1.509381540430	1.165978116224
C	4.782768893749	2.760492505325	-0.566855568440
H	4.086869742328	2.189559730583	-1.159765933959
C	5.427200654394	3.855577495917	-1.117654468486
H	5.233426104196	4.137075308720	-2.139949337469
C	6.336557647805	4.587245397077	-0.357878209749
H	6.854912142272	5.428320936185	-0.787303785004
C	6.589595534335	4.219687578302	0.949683852854
C	6.131121302581	4.048341019032	3.724889537997
C	5.400164393550	4.130523241191	4.894877378511
H	4.996481378647	3.236411831315	5.340407106897

C	5.191444046219	5.368653903605	5.498534273740
H	4.623686673517	5.430533231572	6.412629514348
C	5.716271662029	6.516700127011	4.929825554562
H	5.556653039856	7.473481866126	5.400121563219
C	6.462717046995	6.436264224317	3.755789016043
H	6.889172175177	7.325900480823	3.321613355388
C	6.667487660645	5.209672483760	3.155039839766
C	6.399315341173	2.796223001674	2.917976233572
H	5.886576934930	1.938280165358	3.320996928774
C	7.505536128462	4.928401115723	1.922440944151
H	7.964320073348	5.810445406169	1.504147969042
C	7.954403720473	2.549268354511	2.717750668989
C	8.585918378494	3.940571494812	2.491939698213
N	9.839124011004	3.694359168249	1.839109493965
N	8.807338169448	1.905572387920	3.705421189512
H	8.024697362767	2.020819248718	1.769417397151
H	8.820775248370	4.324926197443	3.483186188373
C	10.503389077773	4.531301676875	1.086118307732
O	10.198189428818	5.659984750505	0.656210430818
C	11.861068479588	3.961185481642	0.711618004369
C	12.675513079510	4.584082690324	-0.225750385992
C	13.412394622472	2.298779074916	1.057406317120
C	13.898658859848	4.013502710789	-0.523691904981
H	12.324679512827	5.488339757776	-0.686782941406
C	14.278308649264	2.848471185087	0.126380041060
H	13.646137485181	1.408922428976	1.614059182886
H	14.550361235383	4.468644478482	-1.252684116163
H	15.221910040494	2.373013912293	-0.078326749282

N	12.240182639866	2.848804009728	1.332770866814
C	8.440267134508	0.839528182969	4.427295430888
O	9.018245504531	0.445770563139	5.437324187872
C	7.248873356043	-0.027316676101	4.019906417854
C	6.262057443613	-0.328586452190	4.955173371299
C	7.192197665405	-0.629234895493	2.765958784198
C	5.213160011470	-1.176432268797	4.636283690487
C	6.155472554838	-1.500582048909	2.456242301259
H	7.973801751575	-0.434211589525	2.048418465465
C	5.156086357629	-1.768394043887	3.380474480416
H	4.447866698088	-1.386497338331	5.367167713507
H	6.133377765647	-1.970328285775	1.486261451803
H	4.347359112124	-2.437036387966	3.131266526377
Cu	10.699039502479	2.038456173134	2.682684332339
Cl	10.285273616349	0.175760174498	0.885400531079
Cl	12.394853006098	1.330995784988	4.155710819502
H	6.336071843333	0.102080093511	5.939177444591

L8^{NNO}•Cu^{II}Cl

C	-2.29864477597556	-3.58731153675347	1.77943236012319
C	-2.82269583769079	-3.37374726294824	3.03998455660984
H	-3.82701029132694	-2.99987819926119	3.15365994361713
C	-2.04382217012108	-3.63643097880283	4.16309273863349
H	-2.44938709680332	-3.47113707563367	5.14708218916788
C	-0.74692298206639	-4.10027993433679	4.01747265080046
H	-0.14471943208168	-4.29563690410795	4.88889274827863
C	-0.21644932181507	-4.30882108586799	2.74781533841623
H	0.79471489534926	-4.66283531029266	2.63394162469672

C	-0.99152935467057	-4.05639183543934	1.63151164098629
C	-2.92616304079229	-4.59253312440871	-0.34787032253630
C	-3.99252998395378	-5.24887761103317	-0.93220535133589
H	-4.98690011244504	-4.84233849291993	-0.85200224855454
C	-3.77399110614694	-6.43152970026845	-1.63192819871353
H	-4.60366358941286	-6.94577359969880	-2.08758384224271
C	-2.49249588495234	-6.94476882736923	-1.75022120629525
H	-2.32665399997289	-7.85839849088098	-2.29624914443834
C	-1.41639760879049	-6.27895395106108	-1.17106628532963
H	-0.41716709085784	-6.66816822521432	-1.27472182824629
C	-1.63499603747155	-5.10971688084549	-0.46705376849506
C	-2.97568433355135	-3.31376200277411	0.45453102760618
H	-3.98244513790593	-2.93275597138695	0.56820717352760
C	-0.58203704396480	-4.24267793578932	0.18890515346645
H	0.41133384563383	-4.64878477147106	0.08119199247920
C	-2.08213664190885	-2.23680469153504	-0.24391464833591
C	-0.69289486801510	-2.86368139642553	-0.56354513184782
N	0.36692221042153	-1.91060487263126	-0.27209249000565
N	-2.74488671788774	-1.68898054010092	-1.39664796206734
H	-1.92507385203720	-1.46753634974589	0.51266858341727
H	-0.67044085044108	-3.10180276561733	-1.62326886176089
C	1.61955311932614	-2.25366741023266	-0.53235408887348
O	2.06711077336694	-3.31925298554036	-0.96323800365650
C	2.60760856798099	-1.14397787826392	-0.22228376371913
C	3.97615308261379	-1.35609408712208	-0.28371544611937
C	2.90837451973131	1.05351522885967	0.41418631597412
C	4.82331858165214	-0.30769085546144	0.02477240521091
H	4.33110696729582	-2.32767490524341	-0.57037334143926

C	4.28461501589137	0.91909299177955	0.38289724643908
H	2.41814557422152	1.97082534856068	0.68889633040352
H	5.89124760642107	-0.44269173167419	-0.01149432966664
H	4.91174677501937	1.75596858370341	0.63248208332725
N	2.10277170126038	0.04132210337837	0.11467101328793
C	-2.37582879730922	-0.52053814375877	-1.78782641323640
O	-1.46101898064543	0.24497554741815	-1.29610585003924
C	-3.11450898600925	0.06644339211880	-2.96387258960770
C	-4.02929985388284	-0.69122830042472	-3.69234886863277
C	-2.89323795160488	1.38779504640400	-3.33956362463047
C	-4.70476365630797	-0.14058928061053	-4.76836571349237
H	-4.19563938467940	-1.71056298780792	-3.39723873440266
C	-3.57487013768014	1.94217056885130	-4.41367458322156
H	-2.18860338374280	1.96971076043692	-2.77500200180587
C	-4.48177831719301	1.18070328920468	-5.13378625825837
H	-5.40618613494452	-0.74153548567637	-5.32354383684020
H	-3.39621849738451	2.96901671045815	-4.68697043539714
H	-5.00942180853932	1.60952082777139	-5.96974728801084
Cu	0.00545942313146	0.03655931315095	-0.03965192972256
Cl	-0.28504383133412	1.95596010134205	1.17118492250833

L8^{NNN}•Cu^{II}Cl

C	-2.67185294410575	-3.74581222287031	2.27453108077461
C	-3.06931575738793	-4.00680042709489	3.57075494299466
H	-3.85283283661694	-3.42301690421306	4.02475060338536
C	-2.44696427070843	-5.02422576005257	4.29087815398733
H	-2.75709711908311	-5.23194717409296	5.30120386403083
C	-1.42813430987645	-5.76236113702235	3.71373496104396

H	-0.94449163867816	-6.54376649568084	4.27550935977981
C	-1.02642601628321	-5.49888791856164	2.40634789512476
H	-0.23330135470357	-6.07244219795091	1.95630174673321
C	-1.64935923084263	-4.49834593975350	1.68629527124923
C	-3.67620047050665	-3.32978927002081	0.11029168476090
C	-4.93438904848705	-3.22853467283452	-0.45162681167076
H	-5.66770831297295	-2.57033422044106	-0.01772958358513
C	-5.24879805049901	-3.97862314473308	-1.58212535973805
H	-6.22918838658975	-3.89903972405887	-2.02092519099521
C	-4.30597925933208	-4.82308220599138	-2.14256666248858
H	-4.55227533313058	-5.40063297156872	-3.01777090162448
C	-3.03510616038500	-4.92350226480484	-1.58163903098343
H	-2.29517931073666	-5.56889437375397	-2.02497590232605
C	-2.72405800242955	-4.18318233648698	-0.45871876215824
C	-3.19733433828898	-2.63765330556285	1.37296965781113
H	-3.98105212788972	-2.07504395579334	1.85200522688830
C	-1.37881342875729	-4.12312322347919	0.24477697211078
H	-0.62792313081405	-4.74000932181240	-0.22437534130799
C	-1.88435689353236	-1.79458326295217	1.12280910524273
C	-1.03118645221682	-2.60090085502976	0.11739951231122
N	0.30838694415626	-2.08461968010786	0.25108598639121
N	-1.78029546455593	-0.41340313864540	0.67150373471262
H	-1.36075712172097	-1.85292610834637	2.07517741854809
H	-1.37890988953541	-2.31732238050960	-0.87382880519817
C	1.36228541049567	-2.59636894857824	-0.35229231815807
O	1.50853957696851	-3.68260724759085	-0.91832485949395
C	2.53962646111336	-1.63387775496380	-0.30910533605580
C	3.81354985730786	-2.03008832926891	-0.68427614359350

C	3.26036113364100	0.51485504577369	0.11645395624669
C	4.83704758674355	-1.10073859128611	-0.64404672622021
H	3.96189719260342	-3.04571688746704	-0.99932859282961
C	4.55970985896924	0.19511287882489	-0.23732534069413
H	2.97425539484856	1.49598298558185	0.45250357309007
H	5.83823789261706	-1.38071008537193	-0.92593362169702
H	5.32816923871985	0.94588790427340	-0.19266721377797
N	2.28240123289376	-0.38212605980402	0.07595832739248
C	-2.71847730778715	0.51898098152497	0.50689799815197
O	-2.56871367798798	1.51898702453799	-0.19044973788906
C	-4.03443593177107	0.44742844671305	1.26041577357980
C	-5.24136554653843	0.55181179946546	0.57772811326328
C	-4.05237383008002	0.41938367955050	2.65065822638565
C	-6.44299044229318	0.58749772257501	1.26718321993916
C	-5.25219109321234	0.48092815102599	3.34480420258158
H	-3.12023946706383	0.36316250169373	3.18617000573214
C	-6.45308284645493	0.55366168059024	2.65513333200770
H	-7.37120452041003	0.65398758736066	0.72400953807077
H	-5.24837804999414	0.47341100328718	4.42210527636135
H	-7.38594719995050	0.59301863852258	3.19223464585292
Cu	0.21651555259459	-0.12009121619230	0.61690785022554
Cl	0.57798473507685	1.85486886433973	1.68666971388371
H	-5.22714264053895	0.61480449310846	-0.49617888216012

L8^{NNO}•Cu^{II}

C	-2.20003181308295	-3.58141656281122	1.72980578537622
C	-2.67251170659025	-3.32934361995174	3.00377026270975
H	-3.65591359556593	-2.91314199726360	3.14714153117363

C	-1.87098971763960	-3.62252535064683	4.10300206477360
H	-2.23843218764835	-3.43739157413717	5.09778572469613
C	-0.60472885349447	-4.15426671431079	3.92095403156063
H	0.01014429537774	-4.38120756723473	4.77502647253295
C	-0.12555478797295	-4.40083663195002	2.63802094037041
H	0.85921862355543	-4.81268939171241	2.49498406884499
C	-0.92463819970519	-4.11743024259730	1.54629262543712
C	-2.94843043643592	-4.57526577975780	-0.37245965740370
C	-4.06470273752915	-5.18299709654796	-0.91404887189210
H	-5.03702631259909	-4.73460921049958	-0.79845355355437
C	-3.92333181310996	-6.37800899044153	-1.61145150210578
H	-4.79034393207008	-6.85805299664567	-2.03173251753519
C	-2.67177324850753	-6.95136003451505	-1.76889581398402
H	-2.56837538446065	-7.87653817592666	-2.30931737160675
C	-1.54664585676470	-6.33459504332720	-1.23180905092176
H	-0.57266114891930	-6.77667149151174	-1.35935545109566
C	-1.68930246370151	-5.15184006919893	-0.53090993496102
C	-2.90990145117784	-3.29237928857963	0.42404050890372
H	-3.89223274381092	-2.86194530566553	0.56900861377191
C	-0.57288230085670	-4.34005592152370	0.09276203433866
H	0.39279395308010	-4.80035695194838	-0.03644132355909
C	-1.99116872518845	-2.26654016195671	-0.31114534129391
C	-0.63105525125306	-2.96525398377875	-0.66173371988612
N	0.45743031916393	-2.03320732958847	-0.39268444586219
N	-2.65985303741974	-1.70343671898111	-1.45599565401705
H	-1.77193108833925	-1.49552044742968	0.42502180056979
H	-0.63676619703201	-3.19458136098921	-1.72334536542498
C	1.73964875486623	-2.37516859188164	-0.30482491546319

O	2.26931544120965	-3.47421997074102	-0.37510151615855
C	2.63921675571763	-1.16737232385632	-0.06047826351092
C	3.98549359402577	-1.32291769224592	0.21520771533571
C	2.82458726791228	1.13839920818660	0.07415845626445
C	4.75829236692057	-0.19740682099372	0.43401954533157
H	4.38533721484551	-2.31849452626147	0.24810355662654
C	4.17026196068306	1.05707520385749	0.36420599559831
H	2.32462731462718	2.08817264814794	0.00175098668223
H	5.80691102448398	-0.29282059461052	0.65509180478838
H	4.73792988943775	1.95444641929036	0.52676516329813
N	2.08197747370914	0.04895001015435	-0.12963616758980
C	-2.38026237370951	-0.51969701087638	-1.83089173672265
O	-1.45887734719449	0.27194819262574	-1.29910429532263
C	-3.14223687384816	0.08706140518041	-2.96493622302119
C	-4.10197125440388	-0.65855221916302	-3.64773822626402
C	-2.90811808646545	1.40123975467590	-3.35825987913847
C	-4.80645494248210	-0.10082703218331	-4.69919236048530
H	-4.27923478681439	-1.67272432397950	-3.34256440711676
C	-3.61883922526160	1.96110733073748	-4.40929938514995
H	-2.17228141772684	1.98245601859803	-2.83508662686981
C	-4.56854236773557	1.21205950384504	-5.08402657095423
H	-5.54198295941802	-0.68935272415562	-5.22020137225018
H	-3.42922109092542	2.98029966851652	-4.69969007390780
H	-5.11895823834202	1.64476885602404	-5.90174351264737
Cu	0.17604730958700	-0.14376904246234	-0.62959785630831

L8^{NNN}•Cu^{II}

C	-2.90318100304892	-4.04187347603220	2.19279641678500

C	-3.43224597195278	-4.21500019194389	3.45547496775815
H	-4.33047239074837	-3.69585626757540	3.74635026585597
C	-2.80050152735493	-5.07225340945572	4.35371756449165
H	-3.21387802184112	-5.21561855231104	5.33712409383720
C	-1.64459487311139	-5.73714474850710	3.98487905118704
H	-1.15773145023167	-6.39620176274622	4.68274479983594
C	-1.11101586726088	-5.56349403496826	2.71018792596241
H	-0.21492486551599	-6.08700092463947	2.42261744005074
C	-1.73976663101980	-4.72237149031189	1.81376322258851
C	-3.66783794025881	-3.96824659412816	-0.10932323330323
C	-4.85066999411354	-4.05839146980725	-0.81560233252799
H	-5.69268093792478	-3.44268697291398	-0.54638598721093
C	-4.95294883793043	-4.95566383313711	-1.87561062147900
H	-5.87494413320613	-5.03078410799399	-2.42577521292581
C	-3.87499669398461	-5.75218373650055	-2.21956779631602
H	-3.95906603840380	-6.44660912599990	-3.03764224164616
C	-2.67773412637193	-5.65736455624890	-1.51402774648951
H	-1.83532892866394	-6.26826261087565	-1.79137604796745
C	-2.57726148631347	-4.77116309201715	-0.46135775574593
C	-3.41731083907104	-3.10064990339184	1.11016042281603
H	-4.30212046811460	-2.56017773124244	1.41502948388522
C	-1.33511692554216	-4.48224757634928	0.37126910851063
H	-0.47650928065942	-5.06131454805896	0.06678262997375
C	-2.16838673712002	-2.16765167506992	0.91485047812034
C	-1.13548443761153	-2.95786258611577	0.08145676006216
N	0.11995411109486	-2.23676257039328	0.21655665056979
N	-2.17161671907831	-0.84510807693456	0.30499775616023
H	-1.74230760277207	-2.05447263764764	1.90822936158648

H	-1.43469032156489	-2.83867945125013	-0.95722037027923
C	1.30645248003891	-2.61868450782261	-0.22937550736211
O	1.72481266768451	-3.72826392233376	-0.52904493366089
C	2.24389625581416	-1.41375432032406	-0.36970737814576
C	3.60280590063494	-1.58662884526604	-0.56153422258532
C	2.46830251578818	0.88739894169005	-0.50034493605655
C	4.40784362560222	-0.47182062664978	-0.71226648727216
H	3.98923080997298	-2.58783529342751	-0.59284793896670
C	3.83374457711137	0.78951945906383	-0.68142874387569
H	1.97303513488029	1.84229239152896	-0.47701023952611
H	5.46862260681872	-0.58239008953801	-0.85547390655256
H	4.42438410191922	1.67936605971361	-0.79856615456059
N	1.69588131192471	-0.18648062121858	-0.34647240344066
C	-2.46551583024016	0.37461579828894	0.71092455436005
O	-1.64509702377751	1.26904750227492	0.32015253843435
C	-3.63949027180550	0.80332462945583	1.51922278543182
C	-4.24460638875893	2.02169045903534	1.21638377685715
C	-4.12070145052607	0.05395995676199	2.58754968631844
C	-5.33248012092667	2.46313910631366	1.94820962829467
C	-5.19359008117886	0.51114862682058	3.33656885915325
H	-3.64610175919175	-0.86991844350673	2.85876148343815
C	-5.80839268776599	1.70969518715661	3.01187870375128
H	-5.80297358826453	3.39752926907079	1.69617701802922
H	-5.54643989461316	-0.06796325241184	4.17204157937704
H	-6.64799805141629	2.05833567634167	3.58782336868797
Cu	-0.31170000498584	-0.35176161313300	-0.03318021507640
H	-3.85339977604248	2.61130699768284	0.40774012180214

L8^{NNO}•Cu^{I}Cl

C	-2.28511132202420	3.73106744047687	-2.57793739170622
C	-2.39692691199541	3.66956531834250	-3.95412848911881
H	-3.24045965866246	3.17254451525446	-4.40571339663531
C	-1.40898721629852	4.23588797086717	-4.75494130483988
H	-1.49100725985927	4.18172274331999	-5.82837663154526
C	-0.31180894655980	4.84954839097590	-4.17322248951257
H	0.46103117168344	5.27208352875719	-4.79463299835095
C	-0.19516284237603	4.90578496221842	-2.78728505753373
H	0.66652382536033	5.36718290382750	-2.33373700537810
C	-1.18072705865316	4.35409621774475	-1.98997316704677
C	-3.64181048810671	4.25668757882339	-0.63363748124919
C	-4.92884619416002	4.64443446107470	-0.31192066909744
H	-5.76966693672577	4.11839391695666	-0.73355170857326
C	-5.13525635856397	5.70053981303235	0.57183479645403
H	-6.13946180915865	5.99967616047978	0.82643029490338
C	-4.05269867748719	6.35618381183642	1.13635467082542
H	-4.21394358381062	7.16697410881638	1.82871961929167
C	-2.75528380363397	5.96148103241855	0.82020028897557
H	-1.91079228883584	6.45426827078866	1.27347160847765
C	-2.54947094691458	4.92097937610948	-0.06716610830456
C	-3.23185645117395	3.13865241610797	-1.56168527552451
H	-4.08230398263132	2.64656539081825	-2.01729226841549
C	-1.21941910157753	4.33904710162747	-0.48211065865156
H	-0.38322307078077	4.84857203936841	-0.02799636658566
C	-2.39370870058853	2.08821872551069	-0.74641813212193
C	-1.25945112942135	2.83767818776711	0.01872406193722
N	0.01500638741678	2.15065459183480	-0.08090034336732

N	-3.27681420874644	1.32783691980640	0.10086755185853
H	-1.91027542744034	1.45109961033817	-1.48582206058455
H	-1.55328518483392	2.89618175828730	1.06339200362918
C	0.95392335767021	2.58855299680780	0.72636464783328
O	0.93395899351823	3.57120729499236	1.50449865728361
C	2.25115138398183	1.79396718571410	0.69061630121334
C	3.42404954900810	2.35948179761651	1.19388496325031
C	3.36438276901313	-0.13171730250597	0.12405218221461
C	4.59574584885197	1.63047914461443	1.14054027045911
H	3.37457880233114	3.34742162456042	1.61168644211115
C	4.57448939446976	0.35523835994555	0.59030640829246
H	3.28078382634560	-1.10503614531384	-0.33291432186937
H	5.51682508050836	2.04839035382704	1.51620780394193
H	5.46674700972483	-0.24455596503711	0.52253403092397
N	2.24025391919386	0.56636459832514	0.18551794967972
C	-2.89965438935129	0.10702992770664	0.36895968012663
O	-1.86032909766683	-0.51206883511571	0.02163431313980
C	-3.88911486631854	-0.68208902430769	1.22013658562349
C	-5.04574157311707	-0.11013407031261	1.74807891120075
C	-3.63828064635801	-2.02527801700893	1.48725876501040
C	-5.92441037403382	-0.85859555559479	2.51626235739870
H	-5.22975544939440	0.92817094607774	1.54057159359127
C	-4.51826705324332	-2.77937030975318	2.25169333677175
H	-2.74011544158371	-2.45206456926334	1.07822263013634
C	-5.66682038853332	-2.20031734969847	2.77177835993231
H	-6.81234921532667	-0.39590496061548	2.91885286465497
H	-4.30593203390408	-3.81966999387641	2.44360443499005
H	-6.35070177591196	-2.78320671101246	3.36880078122371

Cu	0.15965166358524	0.21642433159637	-0.97694695047009
Cl	0.98588480910045	-1.29740452595581	-2.55736746487380

L8^{NNN}•Cu^{I}Cl

C	-2.89027943273917	-3.65764678352983	1.86190462355790
C	-3.27799145774849	-3.79508533198864	3.18229823475140
H	-4.18892765309442	-3.33391757112034	3.52722822055543
C	-2.47922933921401	-4.51290739052547	4.06731572347038
H	-2.77566837429579	-4.61014886407740	5.09896586236411
C	-1.29386290465066	-5.08112637001851	3.63074741711613
H	-0.66809950980957	-5.62135632777768	4.32240954914178
C	-0.89612628217139	-4.93316689910695	2.30510643008433
H	0.03652196405351	-5.35616916874674	1.96884037372430
C	-1.69097200752835	-4.22545802379161	1.42308754192795
C	-3.81022994367113	-3.83763329000184	-0.37885132925086
C	-4.99902928356614	-4.13285956396533	-1.01925791707625
H	-5.91200969855846	-3.65487059521556	-0.70537109975801
C	-5.00898163291902	-5.02880964726112	-2.08416723669392
H	-5.93583381105901	-5.25312413734126	-2.58733670427332
C	-3.82906712296715	-5.61709318072916	-2.51102589133925
H	-3.83750389662130	-6.30220927411718	-3.34368262503297
C	-2.62868375229376	-5.31105125883293	-1.87561282341467
H	-1.70470917277514	-5.74726456355136	-2.21912653798744
C	-2.62099725731705	-4.42976441581986	-0.81062234060020
C	-3.61185708091566	-2.89388339286628	0.78047801500128
H	-4.54183101686132	-2.46375684996518	1.12852882632215
C	-1.41308490146772	-3.96032160785722	-0.03628412132904
H	-0.49848736153647	-4.41963188369138	-0.38422830753224

C	-2.63581868694982	-1.72947842923079	0.30408612608387
C	-1.34219897894930	-2.39970077274101	-0.25663709032529
N	-0.09460776849807	-1.84535694560422	0.27225071593212
N	-3.24618054035965	-0.90693751227617	-0.70247647194598
H	-2.36150731329199	-1.20618482306832	1.21824228043870
H	-1.36165049698173	-2.24684781703526	-1.32715678262604
C	0.95515494757272	-2.06133282952991	-0.50095010669386
O	1.01148991021516	-2.70111273589372	-1.56807031228103
C	2.27609101672677	-1.45164069034885	-0.03806577092779
C	3.39993616919129	-1.55894733184259	-0.85890534632165
C	3.48243905794942	-0.30062999858052	1.54149810766304
C	4.59175172552359	-1.00228643659773	-0.43857192786997
H	3.29648376656803	-2.07281685289083	-1.79536544590811
C	4.64389635975096	-0.35669229489746	0.78985332017502
H	3.45367230949712	0.18522951235672	2.50444874215599
H	5.47219298006359	-1.06826029927680	-1.05793358217433
H	5.55363709267580	0.08975021709485	1.15419207052752
N	2.34033124073953	-0.83179571972908	1.13285904999391
C	-4.03969376216117	0.09568561176922	-0.42166943647970
O	-4.66125077508372	0.77815621611317	-1.26881390648136
C	-4.32477978188978	0.54931625757369	1.01615222449665
C	-5.64284735665062	0.53466072663341	1.47582660641364
C	-3.34796307349947	1.05601382518796	1.86835494687795
C	-5.96918496128681	0.98782207033849	2.74342785091478
C	-3.66819670620413	1.51942779827209	3.13813199129166
H	-2.32230035133471	1.08391454719673	1.54646263703077
C	-4.97983929504762	1.48435425494733	3.58446425606429
H	-6.99553593821708	0.95773863527934	3.07680179545669

H	-2.88079243365650	1.87759776263851	3.77943421089528
H	-5.22842341816728	1.83215998899678	4.57454334160896
Cu	0.13942063367543	-0.92049698419207	2.03744876013629
Cl	0.25952373276251	0.08526378649440	4.03135416966742
H	-6.41316952095481	0.18132332874144	0.81138889848157

L8^{NNO}•Cu^{I}

C	-2.26607830177772	3.84840594541677	-2.51485661046162
C	-2.35205781243868	3.77737367032772	-3.89245368058958
H	-3.16580365084757	3.24482179143088	-4.35743927888943
C	-1.38021203258064	4.39160823379520	-4.67756412355062
H	-1.44681000296832	4.34015970097817	-5.75166342357540
C	-0.32617337505139	5.06285475590569	-4.07969657086398
H	0.42803400581208	5.53207527104171	-4.68944294251359
C	-0.23587257876524	5.12995228593644	-2.69230663346010
H	0.58834896324131	5.64310773149735	-2.22560605543039
C	-1.20572248530227	4.52947860672319	-1.91148172155414
C	-3.68091073040540	4.29309588898663	-0.58435777470112
C	-4.99284712777604	4.60585405260877	-0.28370168613419
H	-5.79683446376194	4.03672048001798	-0.72021023158543
C	-5.27047122295612	5.65062621111583	0.59282130640122
H	-6.29277697263455	5.89526378309787	0.82902799480762
C	-4.23560851288812	6.37018792114708	1.16809115644150
H	-4.45328777718457	7.17548387183302	1.84990113366513
C	-2.91354145351555	6.05120896371530	0.87200449559254
H	-2.10698099735127	6.60097713072602	1.32833313514942
C	-2.63743225585573	5.01952760656335	-0.00595586106725
C	-3.19728963456280	3.20367888432414	-1.51221406466061

H	-4.01212219548290	2.66852646577478	-1.98375751929999
C	-1.26754121740357	4.51634986531738	-0.40238827657162
H	-0.46600209460068	5.07418616947586	0.05764624026166
C	-2.30041911825567	2.20360602870315	-0.70417328808121
C	-1.23242543768345	3.02278213725117	0.09445617918861
N	0.04022974983659	2.34760549116649	-0.00726197661616
N	-3.12197020020294	1.34345598913872	0.11114655201166
H	-1.75235914247502	1.63163591052737	-1.44879713389807
H	-1.54446531272270	3.05227777366298	1.13683401322458
C	1.11809359878266	2.81716523192603	0.56340325437011
O	1.33880662777686	3.88624888477986	1.15922931277800
C	2.29582952822734	1.84163422447313	0.44744082857580
C	3.58328406048176	2.28273521302633	0.73376585089207
C	3.08570843499959	-0.27738258591983	0.00457186225753
C	4.64248234669974	1.40374266856188	0.63054743459315
H	3.70422466693801	3.30619642717129	1.03414899225863
C	4.39315394301642	0.09166455890008	0.25559529931168
H	2.84247619421291	-1.28812695787111	-0.27530316677604
H	5.64728659000912	1.73025702188774	0.84088658041859
H	5.18486100411556	-0.63089110587110	0.16624604778192
N	2.06222525216131	0.56976329430659	0.09491174681475
C	-2.79190302280291	0.10656241240133	0.26427112424038
O	-1.75470917442183	-0.53404229036675	-0.16543830676096
C	-3.77068589427325	-0.74239704346286	1.04663017742525
C	-4.92337851112514	-0.19695462211894	1.60965526410857
C	-3.52927991845903	-2.10210054851298	1.22029102021348
C	-5.80722351112708	-0.98896337186852	2.32325014992627
H	-5.10336987405111	0.85354944365655	1.47629211212505

C	-4.41660151748437	-2.89874916330598	1.93068945899396
H	-2.63788279175477	-2.51872836832637	0.78950683064733
C	-5.55949843413810	-2.34613742420694	2.48652335685437
H	-6.69122562807580	-0.54802276682174	2.75424585232823
H	-4.21265846673506	-3.95021323666061	2.05200525238463
H	-6.24802818782155	-2.96214805315068	3.04130775846618
Cu	0.02558085140960	0.25081057916660	-0.18507209546837

L8^{NNN}•Cu^{I}

C	-2.90781129124592	-3.68046865675812	2.13164834635104
C	-3.46035747886549	-3.82065378319546	3.38984152479710
H	-4.27745436770137	-3.18815854855292	3.69462714512012
C	-2.94985087797712	-4.77635431742260	4.26541256348064
H	-3.38141027011127	-4.88916859673130	5.24608626475853
C	-1.88718271262363	-5.57582522469807	3.87980291619148
H	-1.49039839919948	-6.30989656857782	4.56124261548890
C	-1.32982625116660	-5.43476800885337	2.61144811426673
H	-0.50264613123690	-6.05638808194214	2.31085060144345
C	-1.84070588466859	-4.49472782702951	1.73686569660659
C	-3.62631387091864	-3.43629787997717	-0.17193905515669
C	-4.79552260478670	-3.35342687986923	-0.90377195027406
H	-5.56363751274495	-2.65449244304425	-0.61693963154380
C	-4.97700358320674	-4.17489637845732	-2.01355959189677
H	-5.88815317801540	-4.11058089052533	-2.58461685225351
C	-3.98832493733641	-5.07033753415306	-2.38490531219769
H	-4.12970406139996	-5.70238114862981	-3.24579905701514
C	-2.80588653768993	-5.15120968815544	-1.65352534211520
H	-2.02750420447906	-5.83301311067909	-1.95315690561643

C	-2.62851631577805	-4.34129599935583	-0.54908949140439
C	-3.29501325645231	-2.65334646886807	1.08142256983360
H	-4.12447084248195	-2.04688873137428	1.40600722094273
C	-1.38967270098707	-4.24064621559159	0.31770897504466
H	-0.59479146686010	-4.89690781516964	-0.00621144266850
C	-1.95371407971483	-1.82710957778720	0.91605120623941
C	-0.97195483384726	-2.73600791447806	0.12600287452467
N	0.36195944831228	-2.28574355522053	0.41584244325957
N	-1.89407443279824	-0.49498034100695	0.31203484701908
H	-1.54716107908181	-1.76324214929581	1.92346562280588
H	-1.16030606218252	-2.54403857936095	-0.92956458229663
C	1.36407780174846	-2.63751474885840	-0.34690762686901
O	1.53840160926782	-3.60217243784438	-1.10945226856254
C	2.47815693927773	-1.58459803152473	-0.31865720008314
C	3.81536017185770	-1.94177274375556	-0.44468708212917
C	3.04494803615624	0.65242577966787	-0.30517768723389
C	4.78385163386447	-0.95928812732132	-0.46415229144450
H	4.05532762476149	-2.98497944611403	-0.53309425981839
C	4.39375112772911	0.37099922389786	-0.39307014220096
H	2.69401822844662	1.66957514012908	-0.27208312200388
H	5.82652302714565	-1.21902459896298	-0.54060853851793
H	5.11169272791813	1.17139319063058	-0.41632018437782
N	2.10748555917640	-0.29438288993679	-0.26031436273015
C	-2.69938534261749	0.53290964760177	0.54081627432254
O	-2.54787429567852	1.64877670388144	0.02462768426344
C	-3.88363870891324	0.45147874366222	1.48884965059238
C	-5.17238068873012	0.66827855644842	1.00893602975712
C	-3.70460995718364	0.28538872333586	2.85770078614459

C	-6.25705324149071	0.68531391095161	1.87011196431455
C	-4.78673272079972	0.32465593510361	3.72604441478805
H	-2.71414431579864	0.12571355352052	3.24753035146751
C	-6.06897331945761	0.51560378304089	3.23562744782018
H	-7.24907500265285	0.84062753581404	1.47899902234991
H	-4.62669551863065	0.20225096264092	4.78448593509709
H	-6.91068593675811	0.53681644206987	3.90731135536042
Cu	0.05382852343182	-0.14354025469507	-0.01337905713486
H	-5.31361006582430	0.83208917237764	-0.04513933590688

Relaxed **L8**$^{2-}$

C	-1.50980226084915	-3.62116911105623	2.72615860314258
C	-1.68340799356656	-3.35860169562684	4.07323134827566
H	-2.59483981702770	-2.89582078173036	4.41589570582876
C	-0.67460272951149	-3.67842775539011	4.97826380108572
H	-0.80887890248065	-3.47176667409105	6.02843777746346
C	0.50615731833735	-4.24796831889832	4.52847145142283
H	1.29320272857669	-4.48162267860238	5.22792426735532
C	0.68669722033739	-4.50121342513615	3.17134393436695
H	1.61434478656440	-4.91963513040380	2.81674460300411
C	-0.31759423511593	-4.19425697240955	2.27206048157501
C	-2.70156566335182	-4.58789816231023	0.84738635268309
C	-3.91766838169115	-5.17282443811878	0.54584575846410
H	-4.83244588091537	-4.70326056560895	0.86848478893298
C	-3.95820982278705	-6.35366684773445	-0.19122442266858
H	-4.90795562694109	-6.80556946444191	-0.43014987186307
C	-2.78148982925926	-6.93835136380692	-0.63216536929142
H	-2.81433403966444	-7.84727986952626	-1.21215658252973

C	-1.55577679165536	-6.34613404076767	-0.33785773842845
H	-0.63938107398957	-6.78643853051787	-0.69659752740514
C	-1.51383810284546	-5.17956003763884	0.40443987255748
C	-2.47781918369340	-3.30887238560186	1.61442782916270
H	-3.39401883773722	-2.85918950452032	1.96935068259883
C	-0.28538345053009	-4.38980303622759	0.77679664141039
H	0.62898944866872	-4.84780259174546	0.42676330454808
C	-1.73914522626712	-2.28860317440128	0.64874203888385
C	-0.44890857328055	-2.96687850633627	0.09548401043282
N	0.72920556642948	-2.15321921208103	0.29823579186393
N	-2.61190882184876	-1.84170064435282	-0.41271153494271
H	-1.43091139768558	-1.45903658966913	1.27942782633752
H	-0.60922271938651	-3.16705888891441	-0.96086661376087
C	1.75959584368178	-2.46914083420471	-0.42755916220803
O	1.92057331092540	-3.39500780489706	-1.27345384596586
C	2.97079546861827	-1.54876963249551	-0.26513410139782
C	3.86403878420004	-1.45870114093756	-1.34356549190996
C	4.27070786604539	-0.10161446457716	0.94302848545016
C	4.96893118827598	-0.63980154186559	-1.25597108824262
H	3.65092338169721	-2.05001610006941	-2.21395593853973
C	5.19008931231989	0.06455297620416	-0.07864517959414
H	4.41027948854706	0.41788458259362	1.88207479459363
H	5.65275565563666	-0.55037331279288	-2.08629436119444
H	6.04202779533599	0.71281006179979	0.04598876149418
N	3.19357471421462	-0.87111089682644	0.86235775416589
C	-3.56813982398621	-1.02036339169791	-0.07138394523836
O	-3.88291616298300	-0.56480491561861	1.06007486553971
C	-4.43227795829112	-0.56017595905553	-1.24635941704756

C	-4.20528533029771	-0.98435972663075	-2.55558137309629
C	-5.48918755058185	0.31696887307395	-1.01666631786900
C	-5.00829167357217	-0.54539041526907	-3.59691360457047
H	-3.38646937086661	-1.66017318741823	-2.72330818578493
C	-6.29587989103031	0.76037098089488	-2.05670395926556
H	-5.65164591230094	0.63674086353243	-0.00258438488795
C	-6.06052465872253	0.33105903039748	-3.35482759008372
H	-4.81384611131610	-0.88559736658161	-4.60243093631265
H	-7.10852515135652	1.44178532949650	-1.85442854067287
H	-6.68425261702601	0.67323531461210	-4.16612444786781

L2^{NNO}•CuCl$_2$

C	-1.88649399072427	-4.53976587870486	2.72782702458312
C	-0.48502919218565	-4.96273143383004	2.29651665997950
C	-2.60957767751661	-3.83892335299510	1.58055982065353
H	-3.58686011847290	-3.48675161120067	1.90305806781028
C	0.28976427158957	-3.77235621100259	1.73538735644610
H	1.26968359034699	-4.08962189454434	1.39906726459391
C	-1.84233868045315	-2.64064507693845	0.99367500047383
C	-0.42922470969714	-3.07470977893471	0.55858215990898
N	0.38526453982909	-1.95020106834930	0.10681484430566
N	-2.65520472354931	-2.11624193856780	-0.08479163398959
H	-1.71582830179127	-1.89204001542938	1.77830956690188
H	-0.53451455147409	-3.79687133952208	-0.25273293351979
C	1.51524845379303	-2.26617867092129	-0.49021403928215
O	1.93239589309772	-3.37945538892417	-0.86185988470177
C	2.45570217672732	-1.08760735333184	-0.65005818896021
C	3.73530007896181	-1.25254046842614	-1.16927483846763

C	2.84654520408443	1.14245305295259	-0.22293690936261
C	4.58521739725218	-0.16464431524358	-1.19375216366386
H	4.01813164360290	-2.22644198901454	-1.52131203435920
C	4.14105189590896	1.05483861916263	-0.70169472022958
H	2.42627709034077	2.05689723007802	0.15012019239676
H	5.58531039457651	-0.26229344136905	-1.58609690994936
H	4.77492842567471	1.92433018057947	-0.69857243628480
N	2.03970466333009	0.09065491166226	-0.20401763430390
C	-2.63949209190348	-0.84368653704707	-0.27413716383796
O	-1.92762930555714	0.04377885271604	0.32629898886650
C	-3.62396557968075	-0.30519946887745	-1.28944853028947
C	-4.66017203078304	-1.09359718917730	-1.78784907790013
C	-3.51437470703289	1.01109161178586	-1.72939339011029
C	-5.57120124940920	-0.57933678354885	-2.69656113473524
H	-4.72813359538719	-2.11105213764763	-1.44794437447946
C	-4.42406966182256	1.52388305977081	-2.64482815089316
H	-2.69487219185000	1.60709594915265	-1.36959751293908
C	-5.45847652661991	0.73680000423998	-3.12857076686367
H	-6.36918996640720	-1.20323485507527	-3.06893287170665
H	-4.31490741111953	2.54130716570057	-2.98448676374390
H	-6.16488115798038	1.13909367321711	-3.83820252523004
Cu	0.01909162342559	0.13210409542787	0.29598271739894
Cl	0.53003247806746	1.12867232642933	2.53340096521830
Cl	-0.02448529228963	2.04531022952820	-1.48380698797233
H	-2.79105969100433	-4.54963642477851	0.77417492347649
H	-1.80747696782295	-3.86155059313215	3.57779979579056
H	-2.46355384808443	-5.40171293652907	3.06841272461078
H	0.05822973811298	-5.40233740540651	3.13442247193106

H	-0.56184481854012	-5.73958788732545	1.53407610626102
H	0.43746562043702	-3.03186067960819	2.51976273816863

L2^{NNN}•CuCl$_2$

C	-3.76732416474454	-3.71903771504974	0.26022618571144
C	-2.61658187688120	-4.60644859180410	-0.21469754664906
C	-3.60694782979964	-2.26678821888084	-0.20264441539727
H	-3.68277482667684	-2.20866762798681	-1.28895220465478
C	-1.25178465110627	-3.99904447860014	0.11835164743162
H	-0.45521570109036	-4.59890565448462	-0.30195208161755
C	-2.24629530223693	-1.68543165988688	0.22370912199325
C	-1.15022211164922	-2.56431298082626	-0.42163233272824
N	0.12440223323475	-1.92014578193149	-0.21116236530148
N	-2.00785683649429	-0.29943004248951	-0.17598668695174
H	-2.14736952632392	-1.81768815136154	1.30398632767587
H	-1.35072310877546	-2.59844951674723	-1.49810335255874
C	1.25843510044054	-2.45977826095302	-0.58182027903736
O	1.49655260402214	-3.55353998939383	-1.12906104098198
C	2.43565505057576	-1.55751825805794	-0.25857075520056
C	3.74568142010302	-2.00890648370203	-0.36671023945065
C	3.13638402600041	0.51626879222276	0.44952541240640
C	4.77312179065858	-1.14665601501045	-0.03423661219095
H	3.91210916797015	-3.01476357909475	-0.70409995785489
C	4.46800484807159	0.14010710363604	0.38526213113985
H	2.82148223420132	1.50254831046559	0.74113575364067
H	5.80011290818702	-1.47022894561147	-0.09977294786994
H	5.23938764713039	0.84061850816170	0.65512144005093
N	2.15802636391888	-0.31856077442172	0.13407174997778

C	-2.93457666107770	0.65516082596400	0.03051920320034
O	-3.05064817024354	1.67270765378880	-0.64519364060163
C	-3.91311500159120	0.56516838045517	1.20506844334957
C	-5.25526814690576	0.88225535682735	1.00759587024009
C	-3.47209468875868	0.29096002472273	2.49647125204633
C	-6.15091949888211	0.88833498947134	2.06444857576535
C	-4.36595059422270	0.32208866027987	3.56034788757997
H	-2.42833930157959	0.08359970908513	2.67648919329414
C	-5.70678210522904	0.60731598007666	3.35111906140889
H	-7.18958757288823	1.12373624523693	1.89010999598464
H	-4.00294410746271	0.12442947695904	4.55588016078229
H	-6.39750745430310	0.62123993196946	4.17977189907866
Cu	0.00288195582255	0.04525948537972	0.20110302065726
Cl	0.14067032411241	-0.22517690517628	2.97018365237010
Cl	0.38576165541683	2.33076864844883	-0.18709649686925
H	-5.58112081369467	1.13616600092855	0.01343965998913
H	-2.68994898598036	-4.73757389770071	-1.29547683260359
H	-4.72164391333099	-4.11899551253384	-0.08651717263661
H	-1.10631027618951	-3.97387418479918	1.19735172142107
H	-2.70362062989036	-5.60241578674092	0.22224302342695
H	-4.42149746723664	-1.67783298496365	0.19921720503885
H	-3.80357728962073	-3.73597501287071	1.34936787149486

Relaxed **L2**$^{2-}$

C	-2.11942368754348	-4.10181777716059	2.97232764094247
C	-0.74852421774391	-4.73050323902847	2.73302571073285
C	-2.64118704423382	-3.43798642008050	1.69816767957203
H	-3.58965309053429	-2.94474970972249	1.88594047636575

C	0.22386609028330	-3.70282651324206	2.15516812587944
H	1.18104355002130	-4.16377565064258	1.93351260253401
C	-1.67545107737990	-2.39343105914858	1.09371278915413
C	-0.28018163589558	-3.01822347989316	0.86445835295087
N	0.68859003475880	-2.02919198477091	0.43925359225072
N	-2.24624893563330	-1.87543570275463	-0.13453405788327
H	-1.55974498862873	-1.59151347528928	1.82852032754322
H	-0.38713078626750	-3.79685391164601	0.10311184180388
C	1.75947809839109	-2.47510898730045	-0.16209140409977
O	2.11593669714755	-3.63868573335568	-0.46331436266206
C	2.70102393890283	-1.32533433739327	-0.54664008630035
C	2.19164844656635	-0.02576384209568	-0.70634794718484
C	4.80142827927421	-0.57725131995713	-1.08210373979240
C	3.03299157783785	0.99965603514199	-1.07477420874864
H	1.14345511191054	0.11899920594728	-0.52551230087302
C	4.38498504570658	0.72687963858220	-1.26837128398772
H	5.84524852904395	-0.83319498365570	-1.21757375267816
H	2.64884447224830	1.99876672615698	-1.21165407410167
H	5.08602067295123	1.49462911220388	-1.55424058174140
N	3.99711415217590	-1.57988157227936	-0.74358184087312
C	-3.18468338691377	-0.98115797638708	-0.01427063839803
O	-3.70055327994146	-0.46178340355012	1.01565204892988
C	-3.74725050149363	-0.50188723018333	-1.35456135919812
C	-3.23661067599276	-0.93303830425190	-2.57961963172051
C	-4.81025489931369	0.39827184314429	-1.37129614455200
C	-3.77267592086220	-0.48127995953872	-3.77558988512652
H	-2.41200603981135	-1.62242932068253	-2.55544339901168
C	-5.35271294920758	0.85201482864701	-2.56715347352036

H	-5.18909713707961	0.72662969655381	-0.41945658359616
C	-4.83745038133042	0.41428536361355	-3.77874327765415
H	-3.35806076477142	-0.82469481700686	-4.71113177835410
H	-6.17727920687639	1.54944558349343	-2.55395726334996
H	-5.25335929947521	0.76634949290858	-4.71034832465323
H	-2.81980281862190	-4.20482208645314	0.94259275766568
H	-2.03542052573185	-3.35303980015276	3.76191812155484
H	-2.83024663558391	-4.85130200135398	3.33094521318823
H	-0.35157463342283	-5.15364654916379	3.65974748862277
H	-0.85376542586803	-5.56211634277176	2.03412652362455
H	0.40452124893872	-2.92378703548049	2.89772810674593

L8^{NNO}Cu (S)-C-Enolate

C	6.23138593724797	2.96196078822824	0.48237789687364
C	5.68267254403445	2.41170270274685	-0.66196916138826
H	5.08944414379719	1.51446154276804	-0.59499725682078
C	5.91200909402029	3.01136897645679	-1.89726983191344
H	5.48971390631961	2.57983998298752	-2.79027078264113
C	6.69674368810879	4.15011593679467	-1.98318988546934
H	6.88687931738758	4.60277062008411	-2.94269437470466
C	7.25736433160519	4.69935723147744	-0.83340528381160
H	7.88355081142589	5.57399989915845	-0.90078470218938
C	7.02321823865359	4.11054994737616	0.39524359322318
C	5.58999607103294	3.55804207401050	2.74481164900830
C	4.48833869713904	3.52535853340400	3.57973410410531
H	3.91017486736351	2.62068128987170	3.66949772467876
C	4.14173660564787	4.65534378919622	4.31518203885417
H	3.28488087110543	4.62786787241845	4.96913796926374

C	4.90417431461776	5.80881728361554	4.22041185855776
H	4.63961582631854	6.67988670808733	4.79837221150177
C	6.02081148027886	5.84026387521291	3.38901870314886
H	6.62952824274030	6.72787663564954	3.32957017956280
C	6.35799614105652	4.72164122063747	2.64970682325925
C	6.11076704925245	2.43138628601081	1.88810817392602
H	5.51208419826368	1.53481225053958	1.94969333848465
C	7.54861455314569	4.56881626989617	1.73382244328124
H	8.13802635671131	5.47209338270831	1.67152280849130
C	7.58442120364501	2.09370917465075	2.36950381571651
C	8.41829158762314	3.40649313266543	2.35669273965202
N	9.71444382567642	3.28945385800712	1.68827976986568
N	7.60401208841442	1.47783751553811	3.67252392998379
H	7.98261954942518	1.41901862596722	1.61272289419353
H	8.58539399438363	3.68490544414209	3.38985368733510
C	10.56787194278682	4.24946087768450	1.99684962382321
O	10.39016105592918	5.22814150669685	2.74814564853353
C	11.94711568525629	4.16014101229111	1.34922997010394
C	12.90994190340793	5.11793715179770	1.66701530121187
C	13.40183272338183	3.09748107599107	-0.08117330912680
C	14.15582233367549	5.03529838589071	1.07587476121315
H	12.64718601984582	5.89040085033288	2.36423247982483
C	14.41429328870955	4.00690914513698	0.18077195577845
H	13.53208124320067	2.27653831831397	-0.76806672500869
H	14.91769476085926	5.76306330300878	1.30717929449225
H	15.37087000229080	3.90855808584072	-0.30381266968040
N	12.20773898222695	3.17994312940101	0.49283861252694
C	7.14010296320940	0.25632831560436	3.73870937198228

O	6.64655277508278	-0.46491243031521	2.83495330169411
C	7.21148397789433	-0.35870773935019	5.13517930738592
C	7.72406199695065	0.33109578096545	6.23310739650596
C	6.74970804040382	-1.65704124585808	5.33322393369461
C	7.77132071526837	-0.25913301967631	7.48663509943403
H	8.08074320587613	1.33183747478098	6.07138080575170
C	6.79598249668222	-2.25268772079195	6.58662921928115
H	6.35955849559413	-2.17854048327869	4.47740700148599
C	7.30685022967873	-1.55614103646031	7.67215378246229
H	8.17310651261168	0.29195912048143	8.32269036567091
H	6.43449753915807	-3.26132729740667	6.71621283005958
H	7.34557394811480	-2.01559399115571	8.64744331746310
Cu	10.27610805242375	1.77359694839308	0.47994354470838
H	8.56324330048843	-0.72675776121907	-3.01881070034895
O	10.37781535252626	0.19646627708095	-2.81918564888737
C	11.27374166556948	0.27075130367659	-1.76198212838787
C	10.58223475300523	0.00451090643053	-0.51684851721195
C	9.30657033522834	-0.72368564457775	-0.93816145369407
C	9.07198909454216	-0.08636367121458	-2.30372543201604
H	8.46004129402521	-0.58890030450431	-0.27624075377657
H	9.46244133517130	-1.80174842868064	-1.05659161046759
H	8.52237189479143	0.84740477470941	-2.20843774444964
O	12.43485204733239	0.52209419085496	-2.01438179739486
H	11.21455454735805	-0.51282281818208	0.19502045733385

L8^{NNO}Cu O-Enolate

C	6.09322652833337	3.50421025231355	0.34246207781556
C	5.55021766510462	3.13424132260723	-0.87347655432101

H	4.82961321649832	2.33390680067478	-0.92221078601585
C	5.95092619296987	3.78521564669939	-2.03692007996189
H	5.53487545712919	3.49162235056164	-2.98684855463401
C	6.89897869434046	4.79340147123227	-1.97695314713401
H	7.22046574997618	5.28474508916950	-2.88091906036769
C	7.45213782649295	5.16109359410153	-0.75372421881460
H	8.20312257038623	5.93249402732695	-0.70752272817270
C	7.04767723067114	4.52307009423411	0.40410528854708
C	5.38880135322856	4.00155625824176	2.61379123380903
C	4.23767136942012	4.06383558728334	3.37608726115348
H	3.53444464081275	3.24749885484014	3.35502715614754
C	3.99887362299216	5.17321424255335	4.18276810343471
H	3.10275662733930	5.21970995580782	4.78057366179997
C	4.91791053143664	6.20936699246096	4.22938096410659
H	4.73612434535522	7.06373806386966	4.86153269295425
C	6.08252537447417	6.14427052463029	3.46883531090381
H	6.80883388671690	6.93900842595115	3.51732395584493
C	6.31495853934417	5.04801511504637	2.65843221572668
C	5.81001648001692	2.88417496497894	1.69053772136359
H	5.07574819377443	2.08976940404423	1.64026940969594
C	7.53551891933459	4.79966251651814	1.80444478458866
H	8.25041535983980	5.60665139778081	1.85589555018213
C	7.17786747946795	2.30264885067738	2.19911159241183
C	8.18517667828321	3.48025081167612	2.38780013732094
N	9.48708807916564	3.16725466002625	1.82701607110720
N	6.95293367145486	1.51816837356444	3.38674007941789
H	7.56023737997291	1.68725852756104	1.38582876624539
H	8.28595281758308	3.66025440490769	3.45502458180513

C	10.45264135540876	4.00892860427367	2.11781294009436
O	10.39802925382369	5.09216152496426	2.74467917247928
C	11.82532811979805	3.60988416475288	1.59458701595358
C	12.82877588670171	4.57353954281980	1.48351181447189
C	13.22874000637443	1.98523280368338	0.78149385063138
C	14.06380851008091	4.20168901271583	0.98997484199789
H	12.60683951226080	5.57830244326478	1.79036639049308
C	14.27555033531394	2.87877872576144	0.62401569127427
H	13.32305145005856	0.94643880949590	0.50861101115244
H	14.85255921460111	4.93040451824925	0.88633466540636
H	15.22163071834627	2.54765973422411	0.22985835088542
N	12.04587902229019	2.34355783303319	1.25984093244623
C	7.78653639120910	0.53903884469127	3.59976668503117
O	8.79766402720539	0.17645493054400	2.93742588863185
C	7.47229219629328	-0.29984006794312	4.83214202469537
C	6.43695841615077	0.02079071201520	5.70891920696298
C	8.23846675312142	-1.43020156040557	5.10325489490873
C	6.17456168073814	-0.76610574320410	6.81962590848115
H	5.85272835433408	0.89692509012474	5.49467956876579
C	7.97564402268555	-2.22325281758037	6.21203512731964
H	9.03698622359387	-1.66455901395326	4.42265115344068
C	6.94208102113765	-1.89577990897106	7.07746046992556
H	5.37042518698155	-0.49876715514318	7.48762747847345
H	8.57967637143779	-3.09694665729407	6.40088370470716
H	6.73743189597732	-2.50915256328498	7.94092226178023
Cu	9.93501045646071	1.17622807010139	1.24874609874757
H	9.04739198280949	-0.83469159692127	-3.44919294972644
O	9.07930790656605	-0.79009740655898	-1.40023613803039

C	10.40058061097480	-0.97505431998636	-0.94051133307120
C	11.02410059774683	-1.94133707851705	-1.68701381714986
C	10.04383333627783	-2.57985307081058	-2.62535187759146
C	8.93003722381986	-1.51888335683946	-2.60534639250755
H	11.99155869369515	-2.33521647906333	-1.44121668731970
H	9.66326870008506	-3.55488317700264	-2.28514062788806
H	10.40399417751459	-2.73449444126803	-3.64602358479373
H	7.92531308985570	-1.93390217257068	-2.63714800186997
O	10.76686481835389	-0.26977177373785	0.02013120983030

L8^{NNO}Cu (R)-C-Enolate

C	6.22448802795410	3.32700636267636	0.41780447404632
C	5.65005098656497	2.91434340826566	-0.77073097231448
H	5.02739459294637	2.03497891289679	-0.78917414698947
C	5.89283328629005	3.62743194983595	-1.94125271344459
H	5.44992289325574	3.30294693331660	-2.86897492254997
C	6.71595368202547	4.74179621363067	-1.91932464761228
H	6.91451893718348	5.28364211675035	-2.82980809993021
C	7.30453637802892	5.15107635750716	-0.72597600605518
H	7.96174563333541	6.00523345631588	-0.71105784905568
C	7.05822872677582	4.44874881651333	0.43895344429357
C	5.62429438345502	3.71385998669105	2.73674067410715
C	4.52724917995733	3.64063690052572	3.57514240916516
H	3.91323952810754	2.75530948830736	3.57914833506642
C	4.23044217163379	4.70356599850317	4.42372623365845
H	3.37680958518041	4.64409052887078	5.07976880933534
C	5.03790327294161	5.82981976333825	4.43801503927410
H	4.81156236069467	6.64808873638871	5.10282818126791

C	6.15003405664394	5.90081469950665	3.60307085368734
H	6.79290621893212	6.76577880151563	3.62640021557503
C	6.43805335632884	4.84995573556098	2.75191991091243
C	6.09368657838901	2.66092366188231	1.76411497847958
H	5.45951968340723	1.78680168827157	1.74068766287298
C	7.61400232424845	4.74596714017407	1.81060796499241
H	8.23892997057193	5.62731134469418	1.83349505570794
C	7.55541980383860	2.21999525763662	2.19179014907947
C	8.44324523089543	3.49208095145309	2.29531681781835
N	9.71646526779650	3.38468519217442	1.58449520441629
N	7.55510766595042	1.47828149903059	3.42743551269343
H	7.91880591655863	1.60860153459789	1.36771136738055
H	8.64335960540710	3.65805797213048	3.34659346546070
C	10.63019025004062	4.25508814617120	1.97257516737959
O	10.52696345642532	5.15309111847369	2.83096973705453
C	11.98651966654538	4.15693098153754	1.27970868089851
C	13.00926480648650	5.02410314240066	1.66301406480777
C	13.34631328540899	3.16297675013403	-0.28659090734815
C	14.23520386909631	4.93251519547508	1.03284023301916
H	12.80644680379303	5.73610417283209	2.44009143725154
C	14.41509216860515	3.98435578238534	0.03589859758174
H	13.41836226539191	2.40473883420824	-1.04979304514989
H	15.04259175042017	5.59036465663131	1.31384806104304
H	15.35470221780452	3.87940906201692	-0.47939367095844
N	12.17094879844240	3.25398391089516	0.32377827172595
C	7.08519475639624	0.25914963461680	3.36128008798931
O	6.60901185519204	-0.36411055769185	2.37827570140726
C	7.12346736471935	-0.49348390617908	4.68982236796984

C	7.63085926554274	0.07365344452080	5.85819149712853
C	6.63481835692457	-1.79559740769223	4.75079603043712
C	7.64714575740926	-0.63895343937342	7.04716610378764
H	8.00777052364639	1.07848930603556	5.80231144110681
C	6.64931922190678	-2.51330458982980	5.93936129643269
H	6.24985369363055	-2.22207658638895	3.84168568684473
C	7.15547260100384	-1.93831836353329	7.09593062807023
H	8.04576448598913	-0.18180513231600	7.93947872229532
H	6.26713053617726	-3.52231920983420	5.96275380457916
H	7.16986677622190	-2.49296281808332	8.02108773270724
Cu	10.11823343976920	2.03780849899201	0.13357202896680
H	10.44097453792311	-1.19470985823924	0.80026417634661
O	11.55650623904605	-1.13222827611906	-0.93147807777776
C	11.39572302411117	0.09547648039636	-1.55431972709673
C	10.05314521613578	0.59067578507900	-1.32197445130512
C	9.25260807757006	-0.65115292722180	-0.92566345409902
C	10.34431966594540	-1.47155454110112	-0.24715830639226
H	8.87154560765937	-1.19447683443839	-1.79799370503516
H	8.41984553798189	-0.47739978153940	-0.25562048877748
H	10.21040243873803	-2.54666343194338	-0.31780406038963
O	12.33808862680528	0.55106026163936	-2.17166258502072
H	9.67841834879530	1.15308904412108	-2.16881816681983

[1]HNMR (400 MHz, THF-d8) Spectrum of $CuCl_2$/L8 + 30 equivalents of *2*