Supporting Information for

A mild and efficient approach to enantioenriched α-hydroxyethyl α,β-unsaturated δ-lactams

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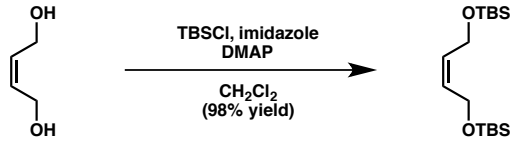
Materials and Methods.

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. THF, Et_2O, CH_2Cl_2, toluene, benzene, CH_3CN, and dioxane were dried by passage through an activated alumina column under argon. Purified water was obtained using a Barnstead NANOpure Infinity UV/UF system. Brine solutions are saturated aqueous solutions of sodium chloride. Commercially available reagents were purchased from Sigma-Aldrich, Acros Organics, TCI, Oakwood chemicals, Strem, or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag temperature modulator unless otherwise indicated. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, $KMnO_4$ or PMA (phosphomolybdic acid) staining. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.064 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz, a Bruker AV III HD 400 MHz spectrometer equipped with a Prodigy liquid nitrogen temperature cryoprobe, Varian Inova 500 MHz, and 600 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm), $CHDCl_2$ (δ 5.32) or C_6HD_6 (δ 7.16 ppm). ^{13}C NMR spectra are recorded on a Varian Mercury 300 MHz, a Bruker AV III HD 400 MHz spectrometer equipped with a Prodigy liquid nitrogen temperature cryoprobe, Varian Inova 500 MHz, and 600 MHz spectrometers (75 MHz, 126 MHz, and 151 MHz, respectively) and are reported relative to $CHCl_3$ (δ 77.16 ppm), $CHDCl_2$ (δ 53.84) or C_6HD_5 (δ 128.06 ppm). Data for ^{1}H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m

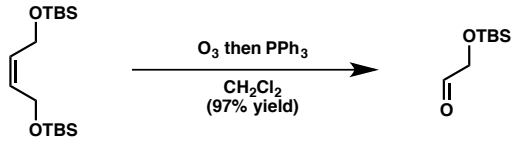
= multiplet, br s = broad singlet, br d= broad doublet, app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained using a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) or electron ionization (EI+) mode, or 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+).

Experimental Procedures and Spectroscopic Data



4 *5*

To a solution of diol **4** (0.930 mL, 11.3 mmol, 1.00 equiv) in CH_2Cl_2 (28.3 mL) were added imidazole (7.69 g, 113 mmol, 10.0 equiv) and TBSCl (5.11 g, 33.9 mmol, 3.00 equiv) at 23 °C. The reaction mixture was stirred for 12 h and quenched with water. The aqueous phase was extracted with CH_2Cl_2 (3 x 10.0 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:8 EtOAc:hexanes) to afford bis-silyl ether **5** (3.51 g, 98% yield). The spectroscopic data were identical to those previously reported.[1]



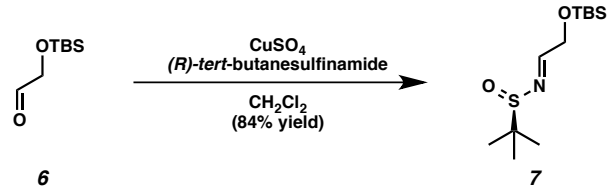
5 *6*

A solution of bis-silyl ether **5** (1.00 g, 3.16 mmol, 1.00 equiv) in CH_2Cl_2 (21.1 mL) was cooled to –78 °C and ozone was bubbled through until the solution turned blue. N_2 gas was then bubbled through the solution until the reaction mixture turned colorless. PPh_3 (0.99 g, 3.79 mmol, 1.20 equiv) was then added and the mixture was warmed to 23 °C slowly. The reaction mixture was stirred under N_2 for 1.5 h and the solvent was evaporated *in vacuo*. The residue was purified by silica gel chromatography (1:8 EtOAc:hexanes) to afford aldehyde **6** (1.07 g, 97% yield).

R_f = 0.25 (1:8 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (t, J = 0.8 Hz, 1H), 4.22 (d, J = 0.8 Hz, 2H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$)

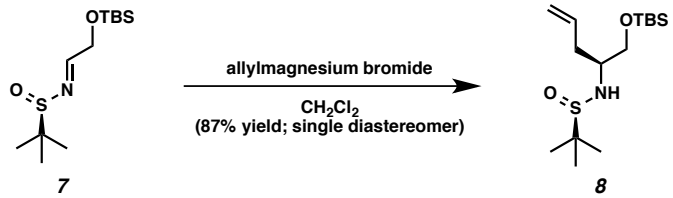
[1] Tran, V. T.; Woerpel, K. A. *J. Org. Chem.* **2013**, *78*, 6609–6621.

δ 202.5, 69.8, 25.9, 18.5, -5.3; IR (Neat Film NaCl) 2955, 2931, 2858, 1740, 1473, 1256, 1128, 838, 779 cm^{-1}; HRMS (MM: FAB+) *m/z* calc'd for $C_8H_{19}O_2Si$ $[M+H]^+$: 175.1154; found: 175.1067.



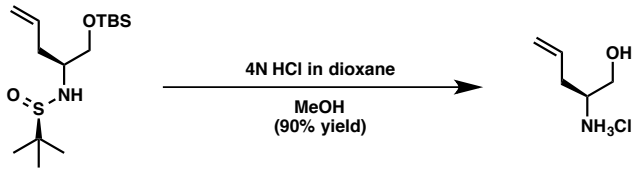
To a solution of aldehyde **6** (100 mg, 0.574 mmol, 1.00 equiv) in CH_2Cl_2 (1.91 mL) was added $CuSO_4$ (275 mg, 1.72 mmol, 3.00 equiv) followed by the addition of *tert*-butanesulfinamide (104 mg, 0.861 mmol, 1.50 equiv). The reaction mixture was stirred at 23 °C for 12 h. Solids were removed via a filtration through a celite plug and the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (1:8 EtOAc:hexanes) to furnish the *tert*-butylsulfinyl imine **7** (133 mg, 84% yield).

$[a]_D^{25}$ –127.8 (*c* 0.19, $CHCl_3$); R_f = 0.20 (1:8 EtOAc:hexanes); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.99 (t, J = 3.1 Hz, 1H), 4.53 (d, J = 3.1 Hz, 2H), 1.17 (s, 9H), 0.92 (s, 9H), 0.10 (d, J = 0.6 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.1, 66.1, 57.1, 26.1, 22.6, 18.8, -5.1; IR (Neat Film NaCl) 2956, 2930, 2858, 1628, 1473, 1364, 1255, 1089, 838, 779 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{12}H_{28}NO_2SSi$ $[M+H]^+$: 278.1605; found: 278.1606.



To a solution of *tert*-butylsulfinyl imine **7** (800 mg, 2.88 mmol, 1.00 equiv) in CH_2Cl_2 (14.4 mL) was added allylmagnesium bromide (1M in diethyl ether; 6.05 mL, 6.05 mmol, 2.10 equiv) dropwise at –78 °C. The reaction mixture was stirred for 5 h at –78 °C and slowly warmed to 23 °C. The reaction was quenched with sat. aq NH_4Cl. The aqueous phase was extracted with CH_2Cl_2 (3 x 10.0 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:4 EtOAc:hexanes) to afford silyl ether **8** (797 mg, 87% yield).

$[a]_D^{25}$ –53.7 (*c* 0.26, $CHCl_3$); R_f = 0.25 (1:4 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 5.18 – 5.11 (m, 2H), 3.66 (dd, J = 9.9, 4.2 Hz, 1H), 3.54 – 3.51 (m, 1H), 3.48 (s, 1H), 3.34 (t, J = 5.8 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.39 (dtt, J = 13.9, 6.7, 1.3 Hz, 1H), 1.19 (s, 9H), 0.89 (s, 9H), 0.05 (d, J = 0.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.5, 118.6, 77.2, 65.1, 56.5, 56.0, 37.2, 26.0, 22.7, 18.4, -5.3, -5.3; IR (Neat Film NaCl) 2955, 2929, 2858, 1472, 1253, 1113, 1072, 836, 777 cm^{-1}; HRMS (MM: FAB+) *m/z* calc'd for $C_{15}H_{34}NO_2SSi$ $[M+H]^+$: 320.2001; found: 320.2084.

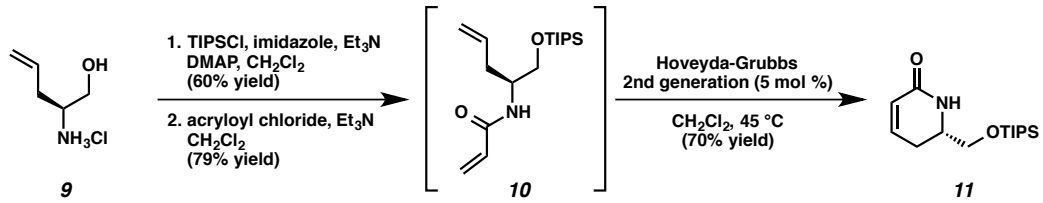


8 *9*

To a solution of silyl ether **8** (126 mg, 0.394 mmol, 1.00 equiv) in MeOH (1.97 mL) was added 4N HCl in dioxane (1.97 mL, 1.97 mmol, 5.00 equiv) at 0 °C. The reaction mixture was warmed to 23 °C and stirred for 2 h. The volatile was evaporated under reduced pressure. The resulting oil was washed with ether revealing

a yellow solid. The solid was filtered to give amine hydrochloride **9** (49.0 mg, 90% yield).

$[a]_D^{25}$ +9.52 (*c* 0.06, MeOH); R_f = 0.10 (2:1 EtOAc:hexane); ^{1}H NMR (500 MHz, CD_3OD) δ 5.81 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 5.29 – 5.19 (m, 2H), 3.76 (dd, J = 11.6, 3.7 Hz, 1H), 3.55 (dd, J = 11.6, 6.7 Hz, 1H), 3.29 – 3.20 (m, 1H), 2.47 – 2.32 (m, 2H); ^{13}C NMR (126 MHz, CD_3OD) δ 133.28, 120.24, 61.92, 53.96, 34.90; IR (Neat Film NaCl) 3369, 2929, 1618, 1508, 1053, 928 cm^{-1}.



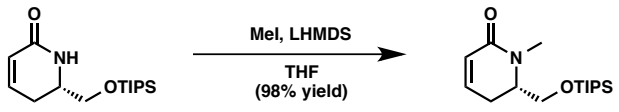
To a solution of amine hydrochloride **9** (188 mg, 1.37 mmol, 1.00 equiv) in CH_2Cl_2 (7.00 mL) were added Et_3N (0.38 mL, 2.74 mmol, 2.00 equiv), imidazole (930 mg, 13.7 mmol, 10.0 equiv), DMAP (8.40 mg, 0.0685 mmol, 0.05 equiv), and TIPSCl (0.59 mL, 2.74 mmol, 2.00 equiv). The reaction mixture was stirred for 12 h at 23 °C and quenched with water. The aqueous phase was extracted with CH_2Cl_2 (3 x 8.00 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (2:1 EtOAc:hexane) to afford the silyl ether (212 mg, 60% yield).

To a solution of the resultant silyl ether (100 mg, 0.388 mmol, 1.00 equiv) and Et_3N (0.160 mL, 1.16 mmol, 3.00 equiv) in CH_2Cl_2 (1.94 mL) was added acryloyl chloride (35.0 μL, 0.427 mmol, 1.10 equiv) at 23 °C. The reaction was stirred for 12 h at 23 °C and quenched with water. The aqueous phase was extracted with CH_2Cl_2 (3 x 2.00 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and

concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:4 EtOAc:hexanes) to afford amide **10** (95.0 mg, 79% yield).

To a stirred solution of amide **10** (1.08 g, 3.47 mmol, 1.00 equiv) in CH_2Cl_2 (116 mL) was added Hoveyda-Grubbs 2nd generation catalyst (0.109 g, 0.173 mmol, 0.05 equiv) at 23 °C. Then, the solution was stirred at 45 °C for 12 h. After the reaction was done, the solution was cooled to 23 °C and water was added. The aqueous phase was extracted with CH_2Cl_2 (3 x 30.0 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:2 EtOAc:hexanes) to afford lactam **11** (688 mg, 70% yield).

$[a]_D^{25}$ –15.6 (*c* 0.22, $CHCl_3$); R_f = 0.20 (1:2 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (ddd, *J* = 9.9, 5.4, 3.0 Hz, 1H), 5.92 (dtd, *J* = 9.9, 2.4, 1.3 Hz, 1H), 5.87 (s, br, 1H), 3.80 – 3.72 (m, 2H), 3.66 – 3.58 (m, 1H), 2.31 (dtt, *J* = 17.6, 5.4, 1.2 Hz, 1H), 2.16 (ddt, *J* = 17.7, 10.9, 2.8 Hz, 1H), 1.21 – 1.00 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 140.0, 124.8, 66.0, 52.6, 26.0, 18.1, 12.0; IR (Neat Film NaCl) 2943, 2866, 1682, 1615, 1463, 1114, 813 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{30}NO_2Si$ $[M+H]^+$: 284.2040; found: 284.2045.

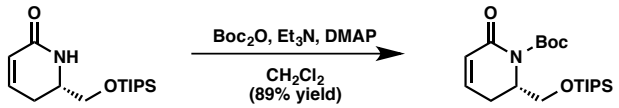


11 *2a*

To a solution of lactam **11** (100 mg, 0.353 mmol, 1.00 equiv) in THF (1.80 mL) was added LHMDS (89.0 mg, 0.530 mmol, 1.50 equiv) at 0 °C. The reaction was stirred for 1 h and then MeI (66.0 μL, 1.06 mmol, 3.00 equiv) was added. The solution was stirred for 4 h at 23 °C and quenched with sat. aq NH_4Cl. The aqueous phase was

extracted with EtOAc (3 x 2.00 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:2 EtOAc:hexanes) to afford amide **2a** (103 mg, 98% yield).

$[a]_D^{25}$ +46.9 (*c* 0.12, $CHCl_3$); R_f = 0.27 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 6.42 – 6.35 (m, 1H), 5.91 (ddd, J = 9.8, 2.7, 1.1 Hz, 1H), 3.74 (dd, J = 9.6, 5.2 Hz, 1H), 3.66 (dd, J = 9.6, 8.6 Hz, 1H), 3.55 – 3.48 (m, 1H), 3.05 (s, 3H), 2.58 (ddt, J = 6.8, 5.0, 2.0 Hz, 2H), 1.15 – 1.00 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 137.3, 125.0, 61.6, 59.2, 34.3, 25.0, 18.1, 12.0; IR (Neat Film NaCl) 2942, 2866, 1670, 1618, 1464, 1111, 882 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{32}NO_2Si$ $[M+H]^+$: 298.2197; found: 298.2199.

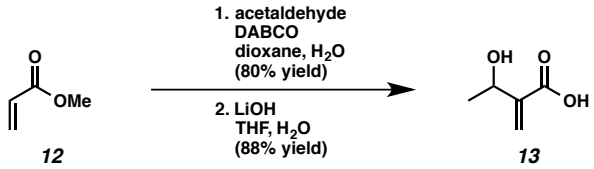


11 *2b*

To a solution of amide **11** (50.0 mg, 0.176 mmol, 1.00 equiv) and DMAP (32.2 mg, 0.264 mmol, 1.50 equiv) in CH_2Cl_2 (0.90 mL) at 0 °C were added Et_3N (49.1 μL, 0.352 mmol, 2.00 equiv) and Boc anhydride (77.0 mg, 0.353 mmol, 2.00 equiv). The reaction mixture was warmed to 23 °C and stirred for 12 h. The reaction was quenched with sat. aq NH_4Cl. The aqueous phase was extracted with CH_2Cl_2 (3 x 1.00 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:8 EtOAc:hexanes) to afford carbamate **2b** (60.0 mg, 89% yield).

$[a]_D^{25}$ +11.5 (*c* 0.07, $CHCl_3$); R_f = 0.85 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 6.59 (ddt, J = 9.8, 6.3, 1.9 Hz, 1H), 5.94 (ddd, J = 9.8, 3.1, 0.8 Hz, 1H), 4.45

(ddt, J = 9.6, 4.8, 3.1 Hz, 1H), 3.74 (dd, J = 9.3, 4.8 Hz, 1H), 3.67 (t, J = 9.5 Hz, 1H), 2.76 (dd, J = 18.8, 6.3 Hz, 1H), 2.62 – 2.54 (m, 1H), 1.53 (s, 9H), 1.20 – 0.96 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 152.3, 140.9, 126.0, 83.1, 77.2, 61.8, 54.6, 28.2, 24.8, 18.1, 12.0; IR (Neat Film NaCl) 2944, 2867, 1717, 1368, 1297, 1239, 1160, 1114, 810 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{30}NO_2Si$ [M+H–Boc]$^+$: 284.2040; found: 284.2046.



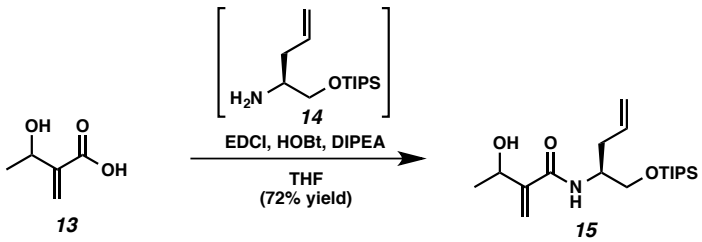
To a solution of acetaldehyde (1.27 mL, 22.7 mmol, 1.00 equiv) in dioxane/water (1.10 mL/1.10 mL) was added methyl acrylate **12** (6.13 mL, 68.1 mmol, 3.00 equiv) and DABCO (2.55 g, 22.7 mmol, 1.00 equiv). The reaction was stirred at 23 °C for 48 h. After the reaction was done, water was added. The aqueous phase was extracted with EtOAc (3 x 10.0 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:4 EtOAc:hexanes) to afford the ester (2.36 g, 80% yield). The spectroscopic data were identical to those previously reported.[2]

To a solution of the resultant ester (300 mg, 2.31 mmol, 1.00 equiv) in THF (12.0 mL) and H_2O (5.00 mL) at 23 °C was added LiOH (88.0 mg, 3.69 mmol, 1.60 equiv). The reaction was stirred at 23 °C for 1 h and then water was added. The aqueous phase was separated and acidified until pH = 1 with 1N HCl. Then, the aqueous phase was extracted with EtOAc (3 x 10.0 mL). The combined organic phases were

[2] Latorre, A.; Sáez, J. A.; Rodríguez, S.; González, F. V. *Tetrahedron* **2014**, *70*, 97–102.

washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford acid **13** (236 mg, 88% yield).

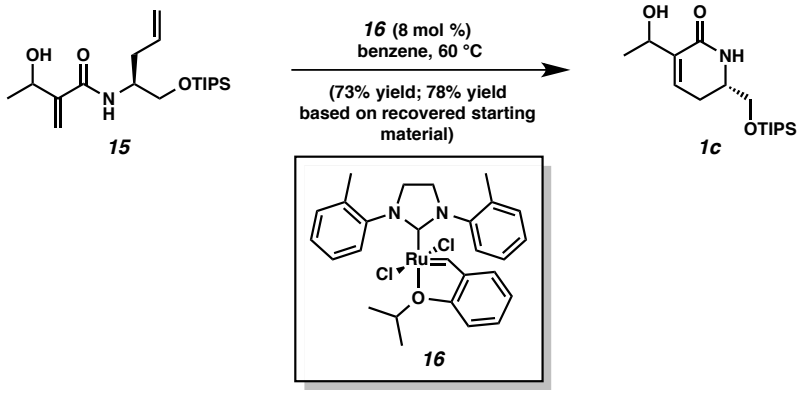
R_f = 0.15 (1:1 EtOAc:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (t, *J* = 0.8 Hz, 1H), 5.96 (t, *J* = 1.1 Hz, 1H), 4.65 (q, J = 6.5 Hz, 1H), 1.42 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 142.8, 127.0, 67.1, 22.2; IR (Neat Film NaCl) 3390, 1694, 1633, 1416, 1277, 1176, 1093, 962, 928 cm^{-1}; HRMS (MM: FAB+) *m/z* calc'd for $C_5H_9O_3$ $[M+H]^+$: 117.0552; found: 117.0521.



To a solution of amine **14** (50.0 mg, 0.194 mmol, 1.00 equiv) in THF (1.00 mL) were added acid **13** (24.0 mg, 0.204 mmol, 1.05 equiv), HOBt (39.3 mg, 0.291 mmol, 1.50 equiv), EDCI (45.2 mg, 0.291 mmol, 1.50 equiv), and DIPEA (41.0 μL. 0.233 mmol, 1.2 equiv). The reaction was stirred for 12 h at 23 °C and then quenched with sat. aq NH_4Cl. The aqueous phase was extracted with EtOAc (3 x 1.50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (1:4 → 1:2 EtOAc:hexanes) to afford amide **15** (49.7 mg, 72% yield).

$[a]_D^{25}$ –29.5 (*c* 0.07, $CHCl_3$); R_f = 0.35 (1:2 EtOAc:hexanes); (Due to the distinct presence of rotameric isomers, the ^{13}C NMR contained extra peaks. See the attached spectrum), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (dd, *J* = 18.7, 8.7 Hz, 1H), 5.81 (ddtd, *J* = 17.2, 10.2, 7.1, 1.5 Hz, 1H), 5.65 (d, *J* = 6.5 Hz, 1H), 5.45 (s, br, 1H), 5.19 – 5.00 (m, 2H), 4.57 (qt, *J* = 6.5, 1.2 Hz, 1H), 4.10 (dddddd, *J* = 8.2, 6.9, 5.1, 3.9, 2.8, 1.2

Hz, 1H), 3.85 – 3.68 (m, 2H), 2.48 – 2.29 (m, 2H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.16 – 1.02 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 167.6, 147.24, 147.17, 134.80, 134.77, 118.0, 117.9, 117.9, 117.7, 69.2, 69.1, 64.12, 64.11, 50.13, 50.12, 36.09, 36.07, 21.94, 21.86, 18.1, 12.0; IR (Neat Film NaCl) 3305, 2943, 2866, 1655, 1618, 1542, 1534, 1460, 1118, 882, 788, 682 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{38}NO_3Si$ $[M+H]^+$: 356.2615; found: 356.2624.



To a solution of amide **15** (740 mg, 2.08 mmol, 1.00 equiv) in benzene (104 mL) was added Ru catalyst **16** (95.0 mg, 0.17 mmol, 0.08 equiv). The solution was stirred at 60 °C for 12 h. The solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography (1:2 EtOAc:hexanes) to furnish two diastereomers of lactam **1c** (499 mg, 73% yield; 2:3 **1ca**:**1cb**; 78% yield based on recovered starting material).

Diastereomer **1ca**: $[a]_D^{25}$ –1.54 (*c* 0.78, $CHCl_3$); R_f = 0.35 (1:1 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (ddd, *J* = 5.7, 3.0, 1.2 Hz, 1H), 5.93 (s, br, 1H), 4.62 – 4.55 (m, 1H), 3.75 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.61 (dd, *J* = 9.2, 8.5 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.22 – 2.15 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.13 – 1.03 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 137.0, 132.9, 66.7, 66.0, 52.3, 25.8, 21.1, 18.1, 12.0; IR (Neat Film NaCl) 3408, 2943, 2866, 1678, 1627, 1461, 1117, 1070, 882, 789,

683 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{34}NO_3Si$ $[M+H]^+$: 328.2302; found: 328.2306.

Diastereomer **1cb**: $[a]_D^{25}$ –1.77 (*c* 0.43, $CHCl_3$); R_f = 0.30 (1:1 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 6.40 (dd, J = 5.8, 3.0 Hz, 1H), 5.92 (s, br, 1H), 4.54 (q, J = 6.5 Hz, 1H), 3.78 – 3.74 (m, 1H), 3.74 – 3.69 (m, 1H), 3.60 (t, J = 8.8 Hz, 1H), 2.31 (dt, J = 17.5, 5.5 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.40 (d, J = 6.4 Hz, 3H), 1.13 – 1.04 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 137.1, 133.2, 67.7, 66.0, 52.2, 25.8, 21.7, 18.1, 12.0; IR (Neat Film NaCl) 3294, 2943, 2866, 1678, 1627, 1463, 1115, 882 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{34}NO_3Si$ $[M+H]^+$: 328.2302; found: 328.2303.

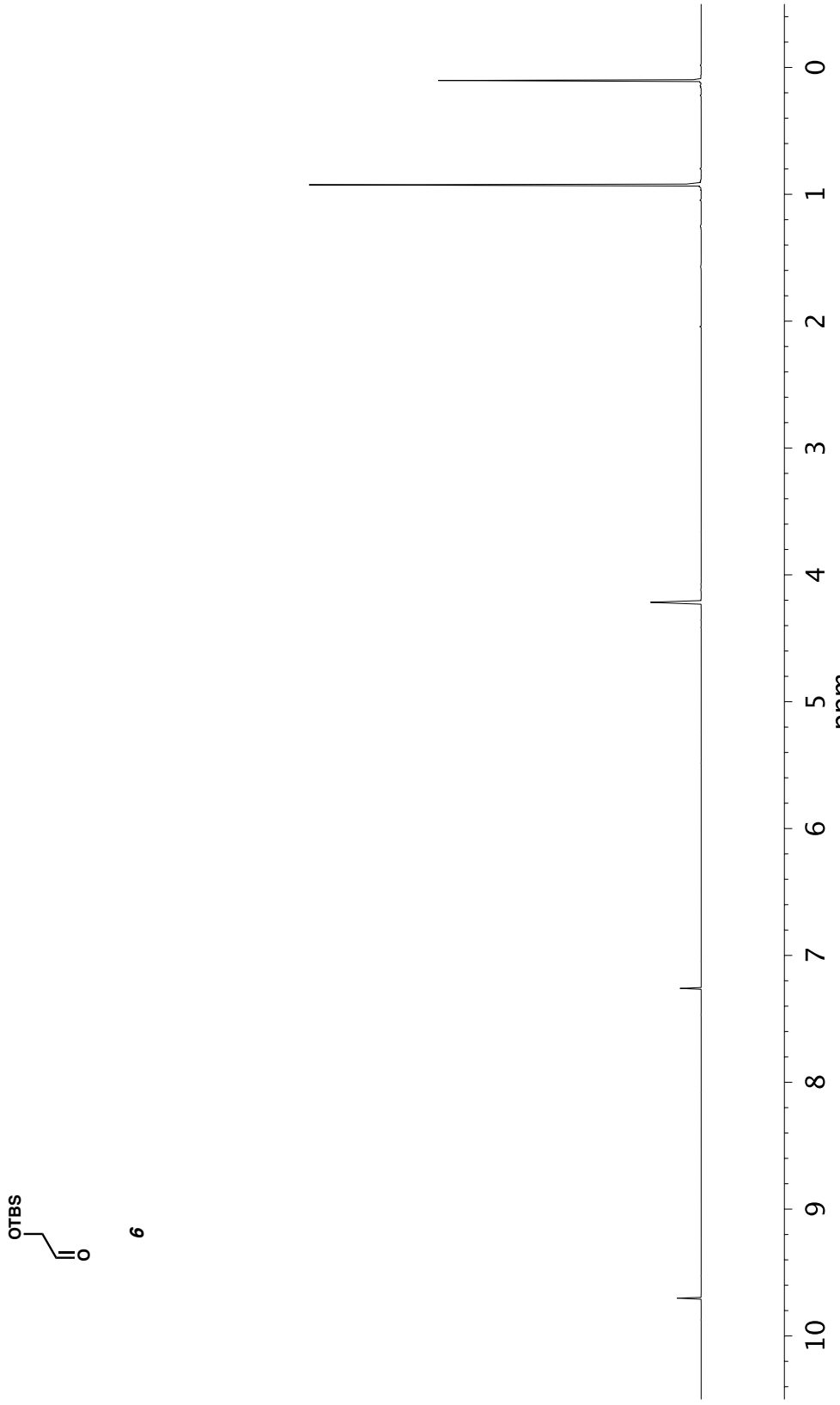


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound ***6***.

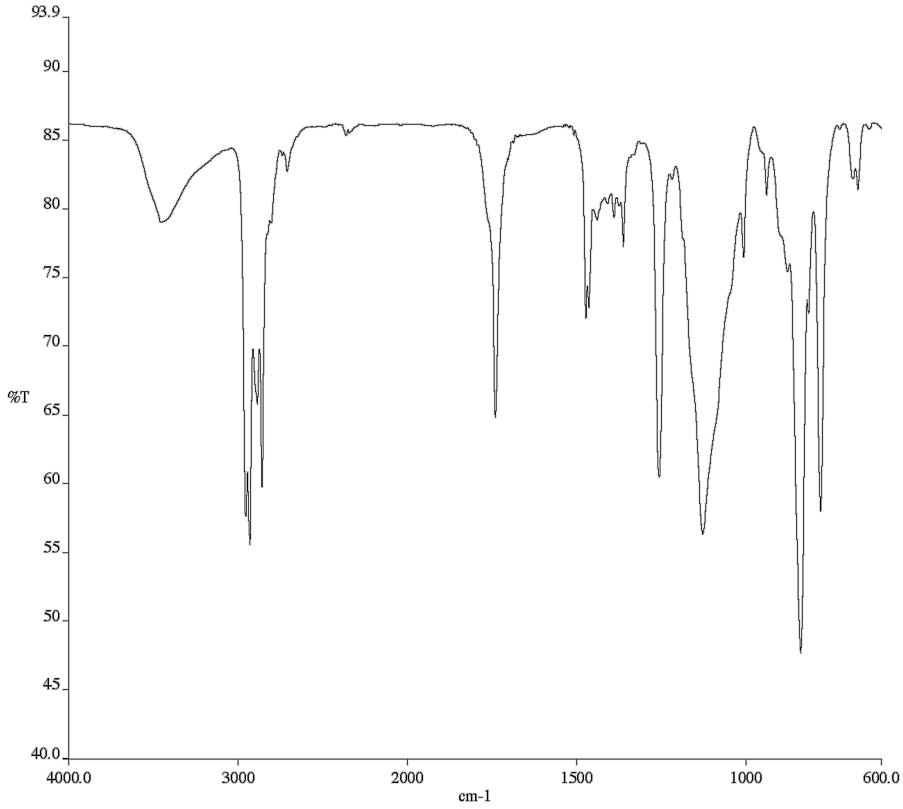


Figure S2. Infrared spectrum (Thin Film, NaCl) of compound **6**.

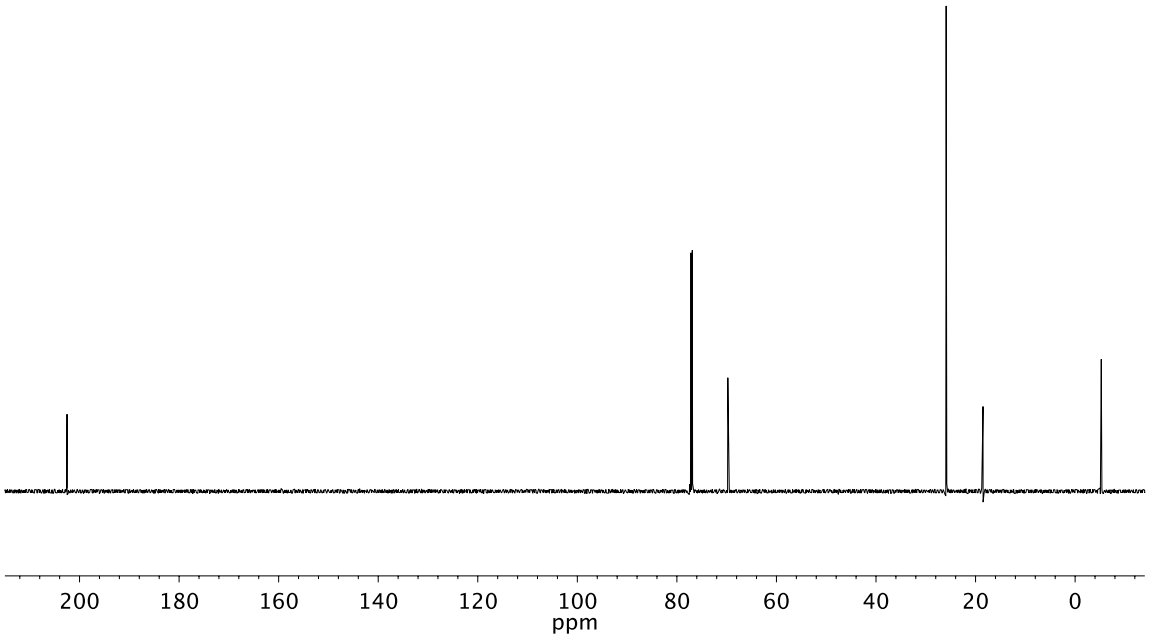


Figure S3. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **6**.

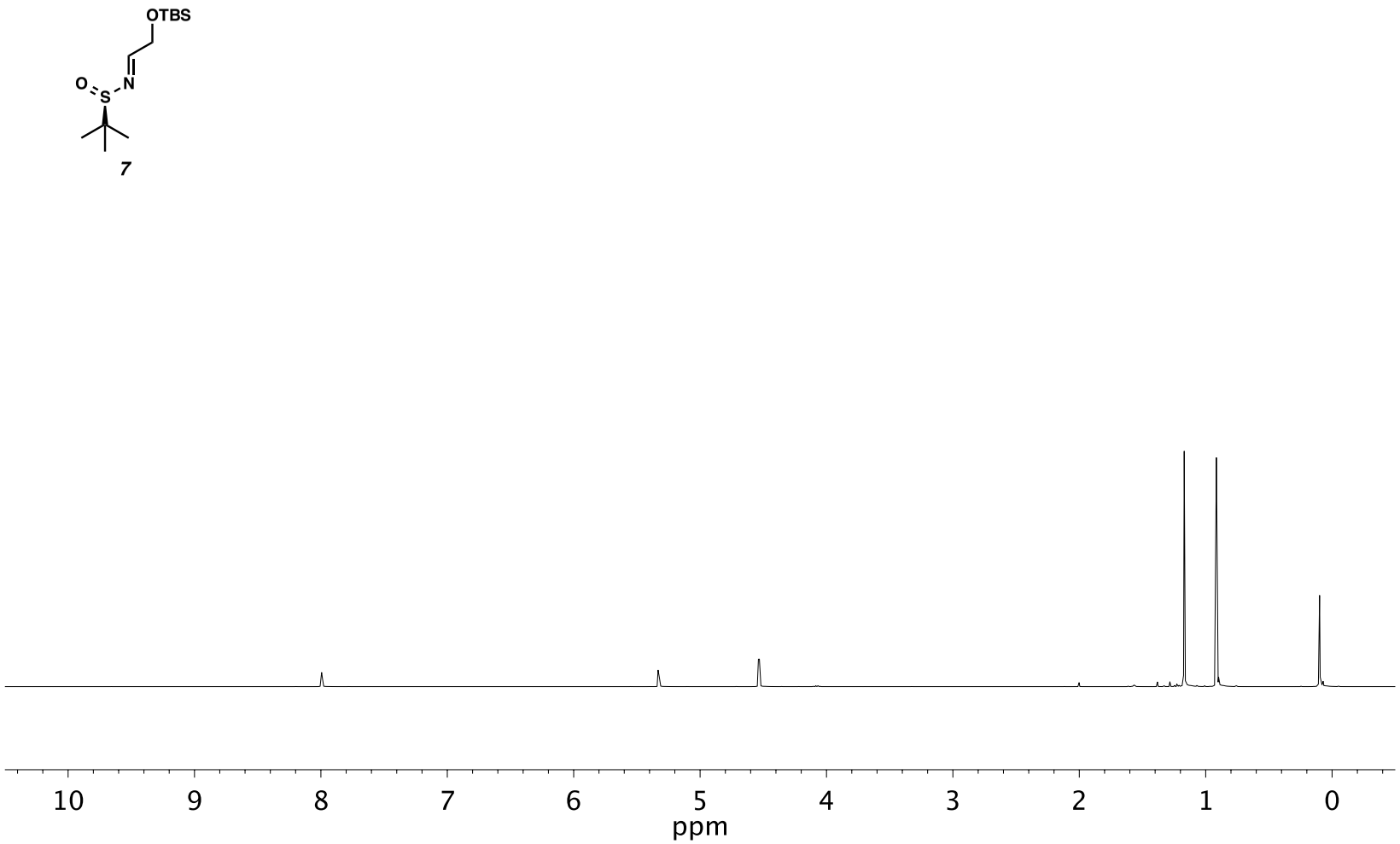


Figure S4. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **7**.

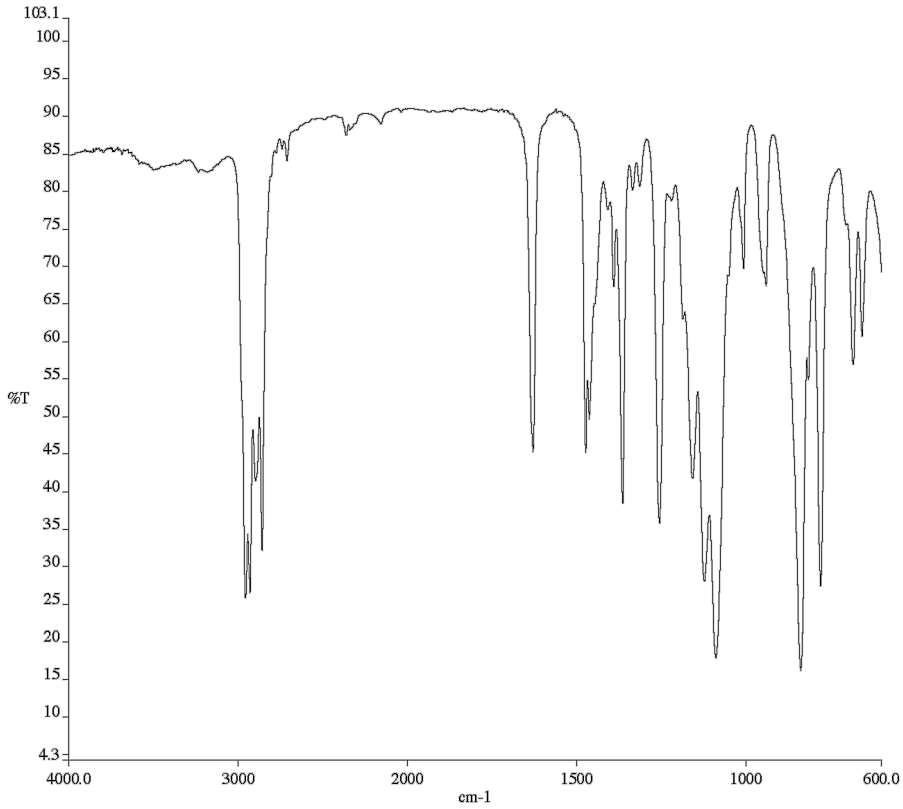


Figure S5. Infrared spectrum (Thin Film, NaCl) of compound **7**.

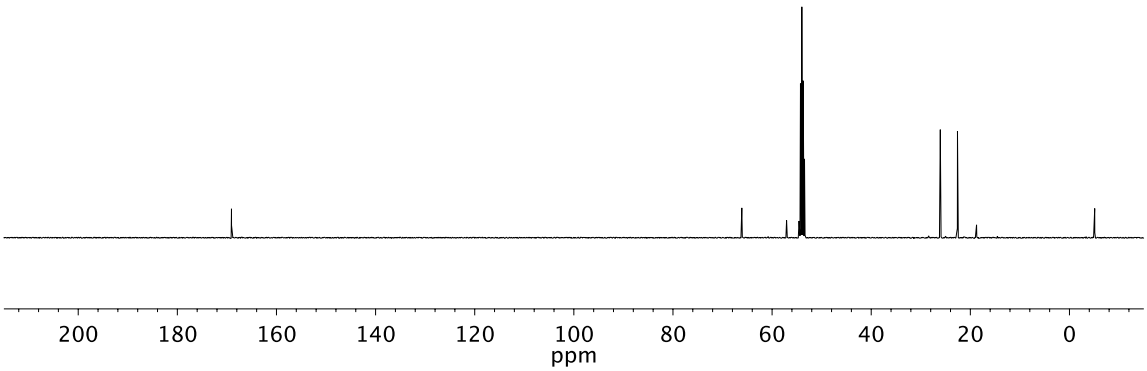


Figure S6. ^{13}C NMR (101 MHz, CD_2Cl_2) of compound **7**.

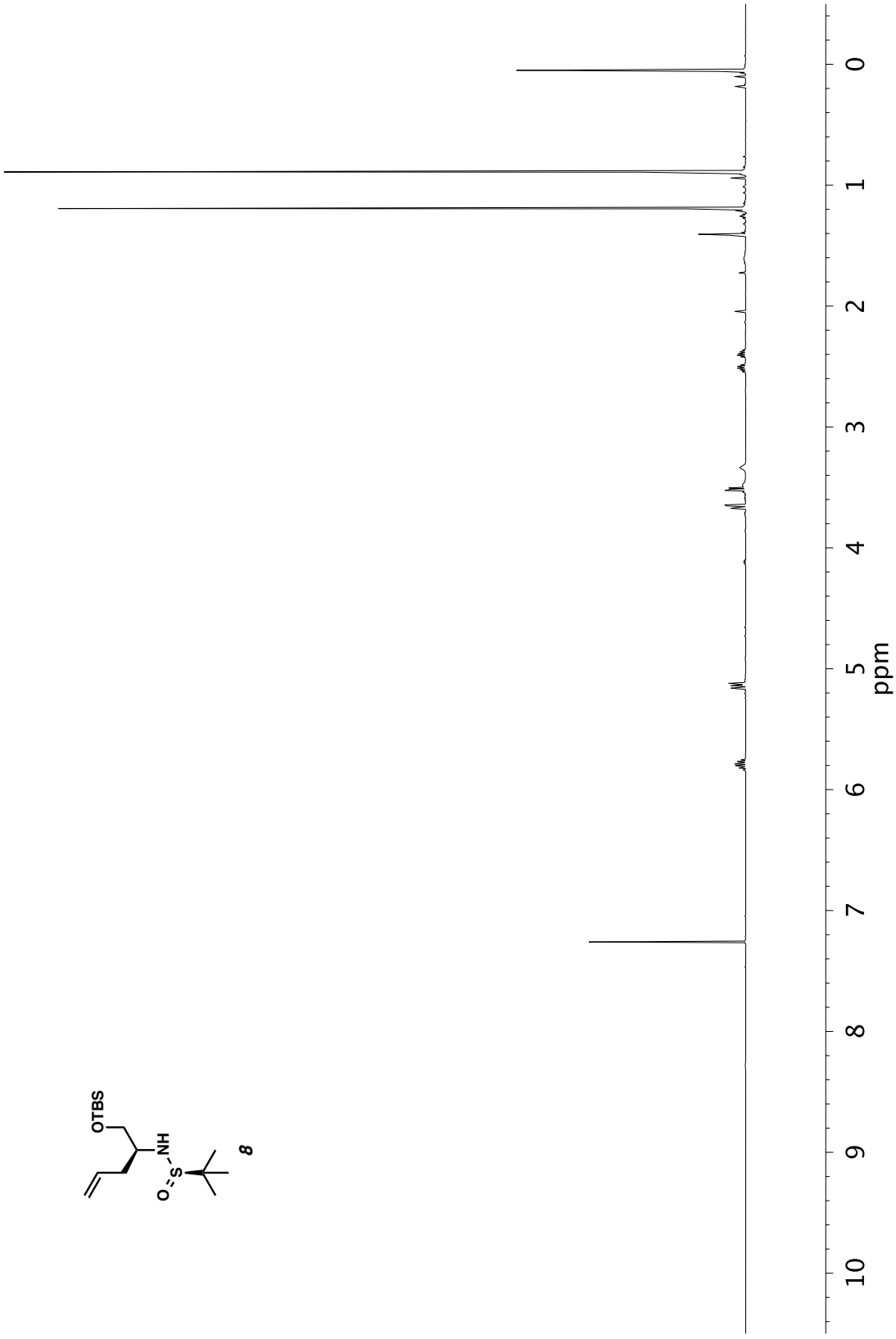


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.

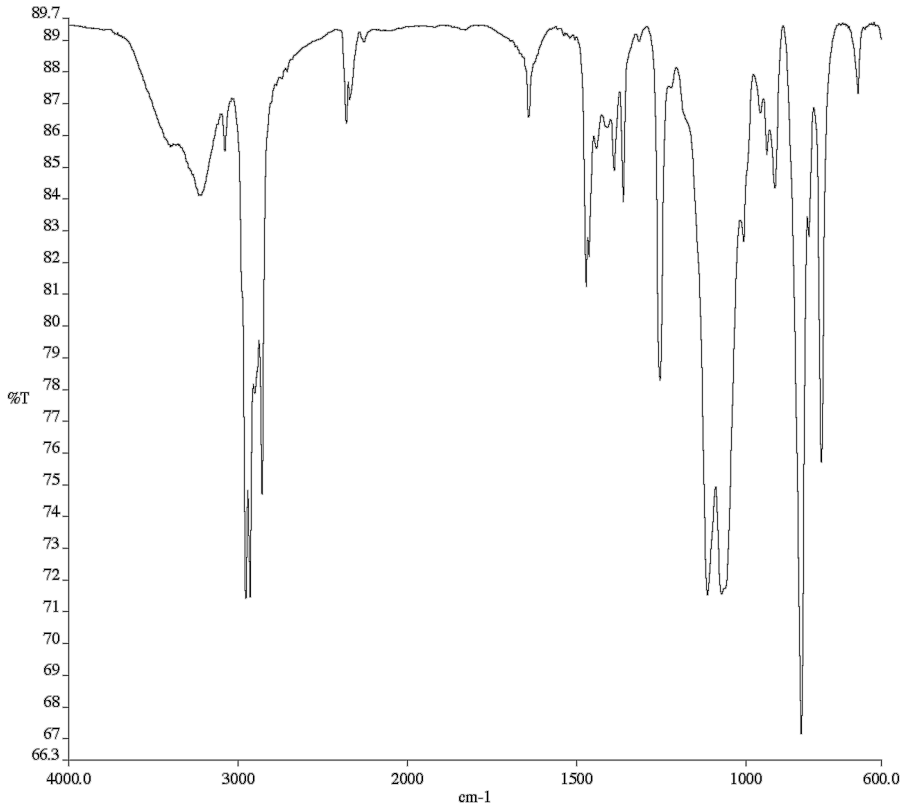


Figure S8. Infrared spectrum (Thin Film, NaCl) of compound **8**.

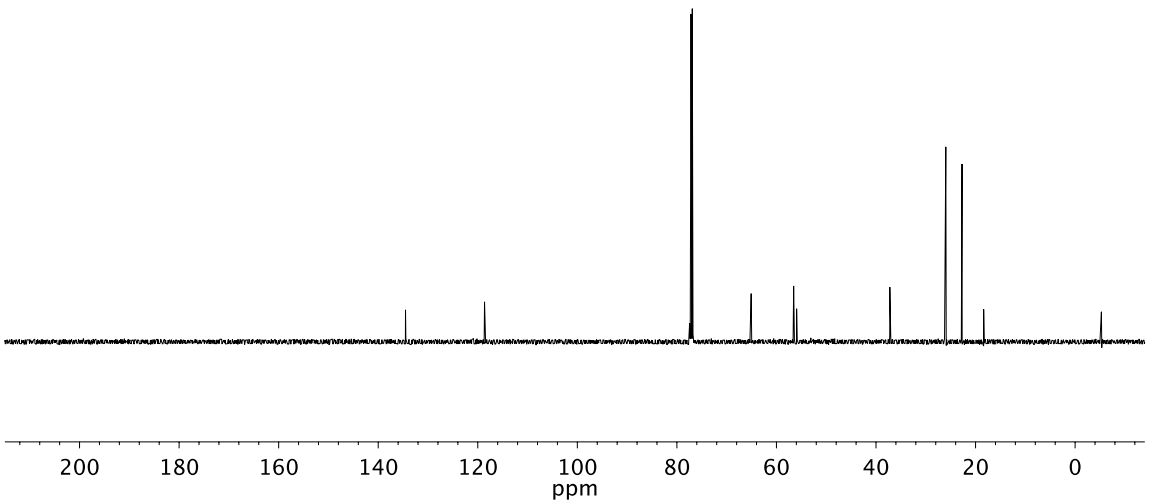


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **8**.

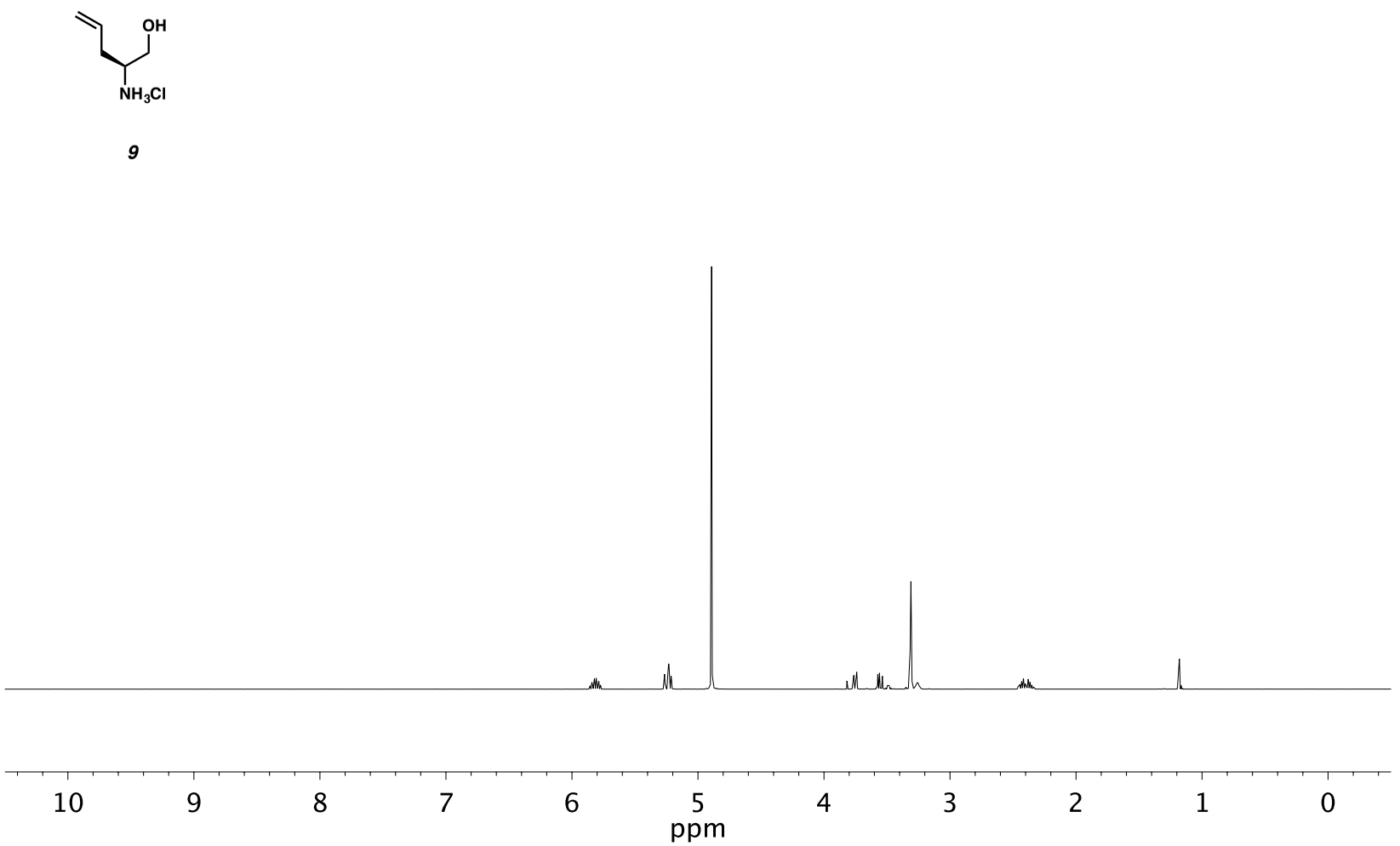


Figure S10. ^{1}H NMR (500 MHz, CD_3OD) of compound **9**.

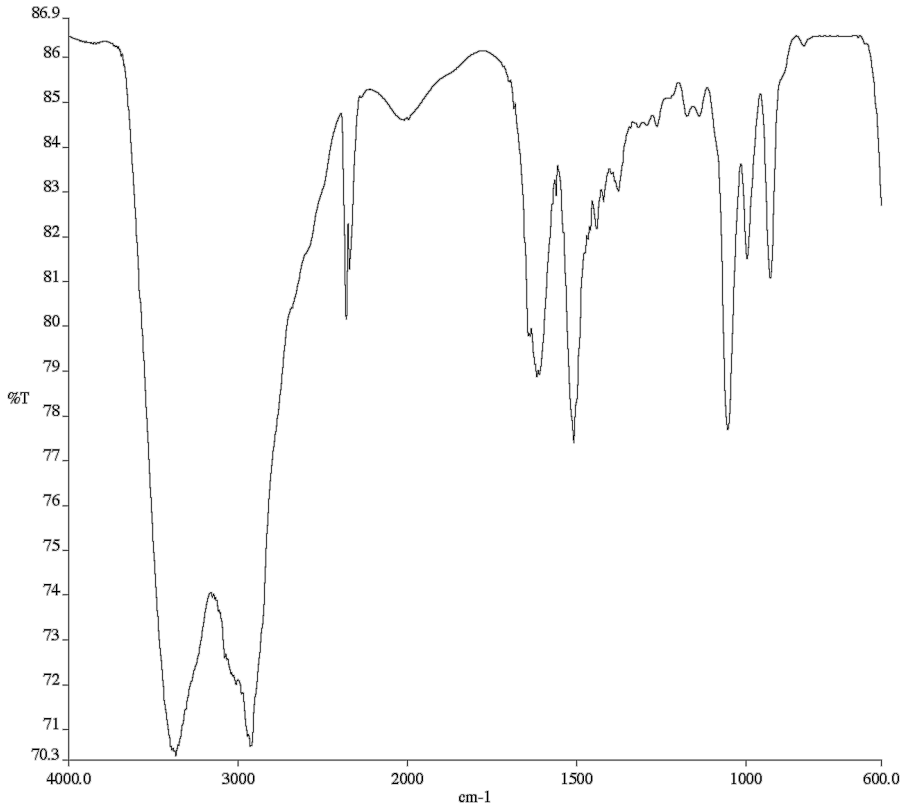


Figure S11. Infrared spectrum (Thin Film, NaCl) of compound **9**.

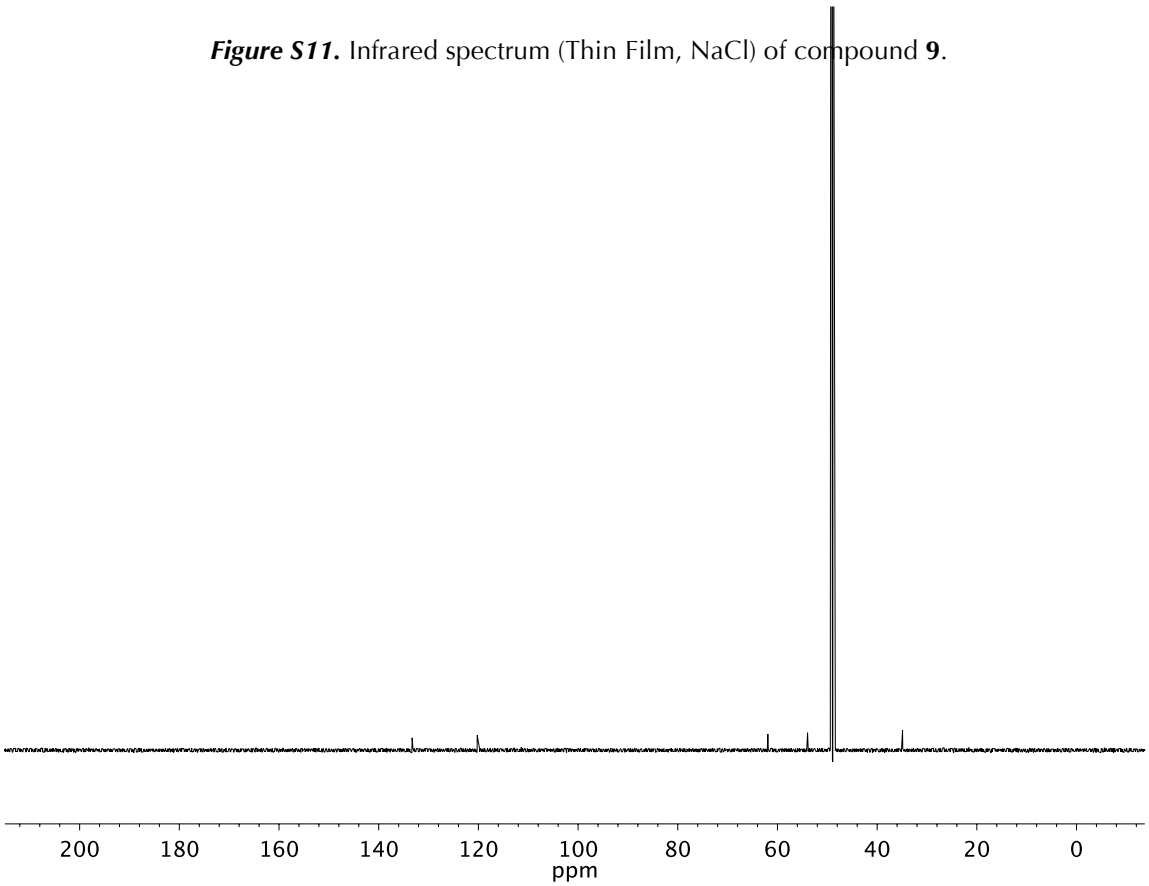
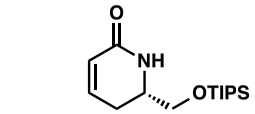


Figure S12. ^{13}C NMR (126 MHz, CD_3OD) of compound **9**.



11

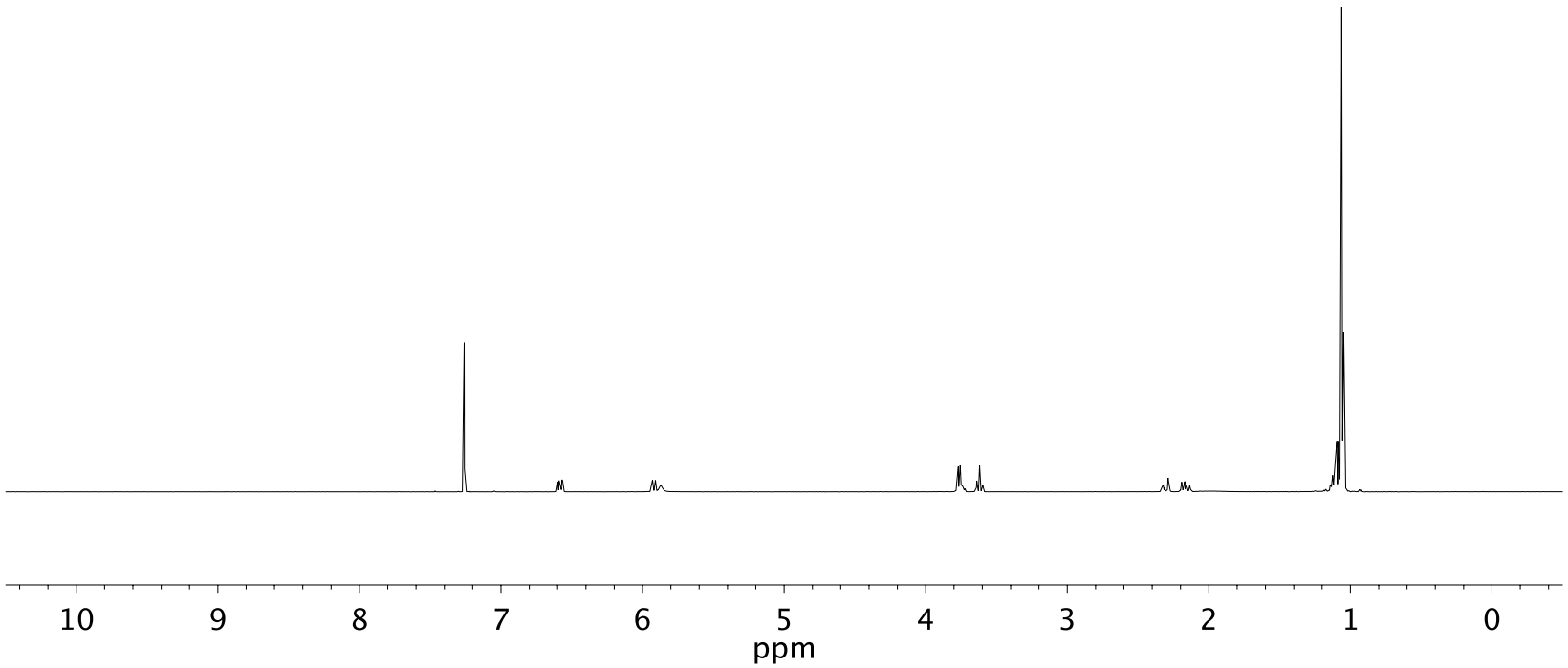


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.

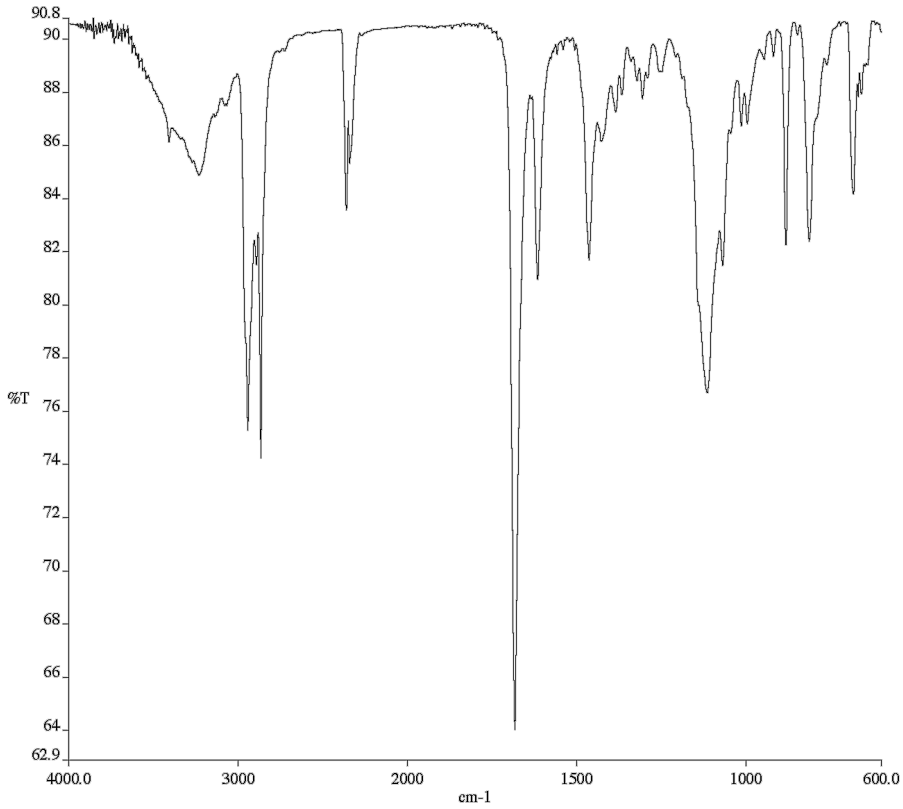


Figure S14. Infrared spectrum (Thin Film, NaCl) of compound **11**.

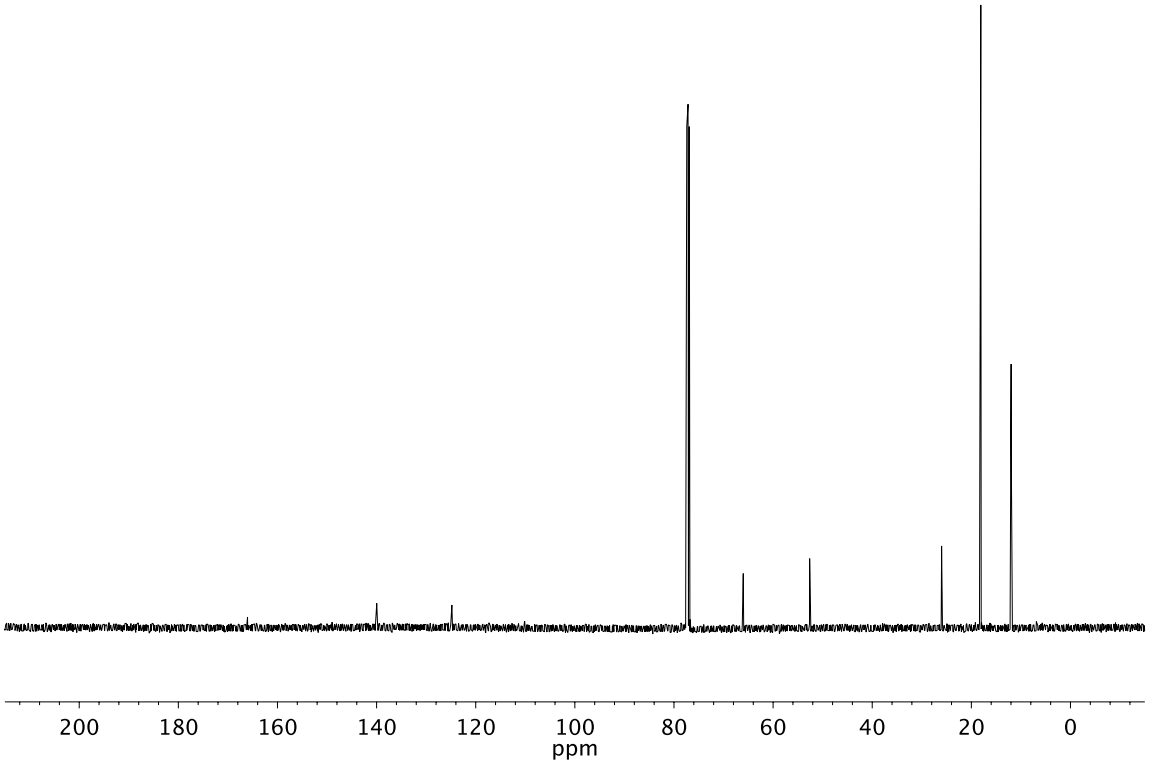
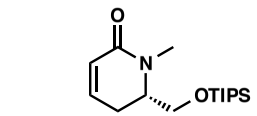


Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **11**.



2a

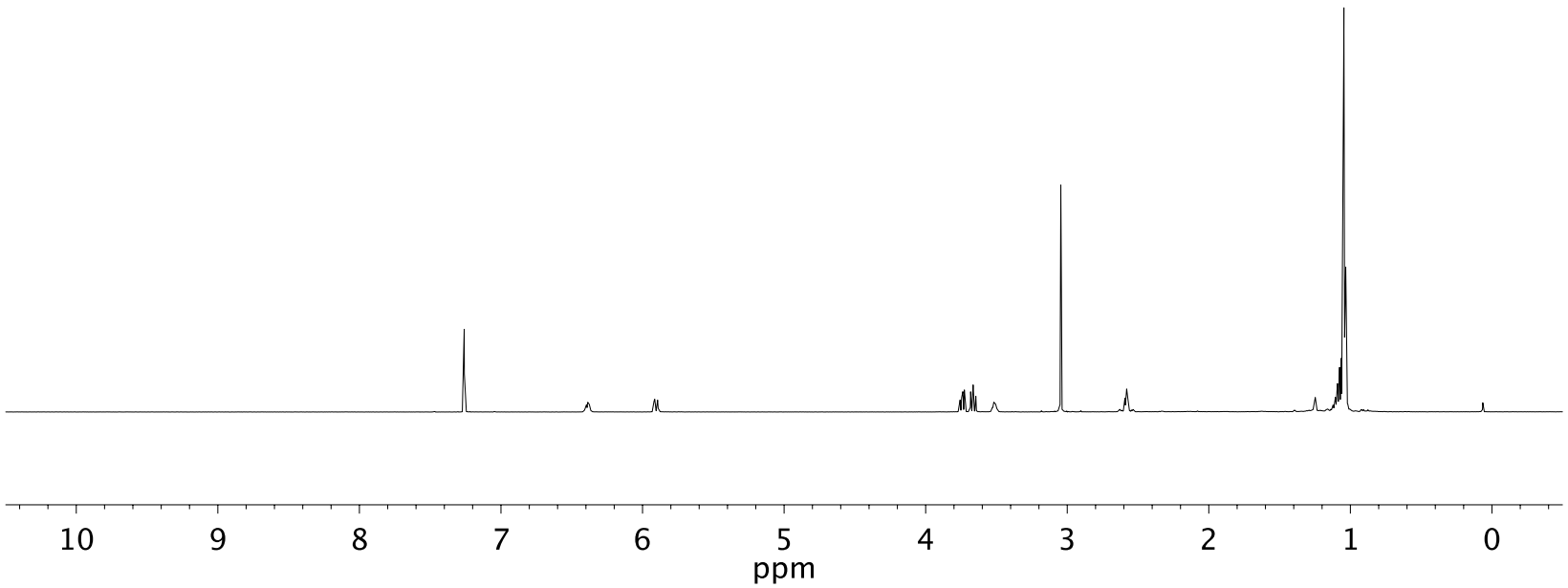


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**.

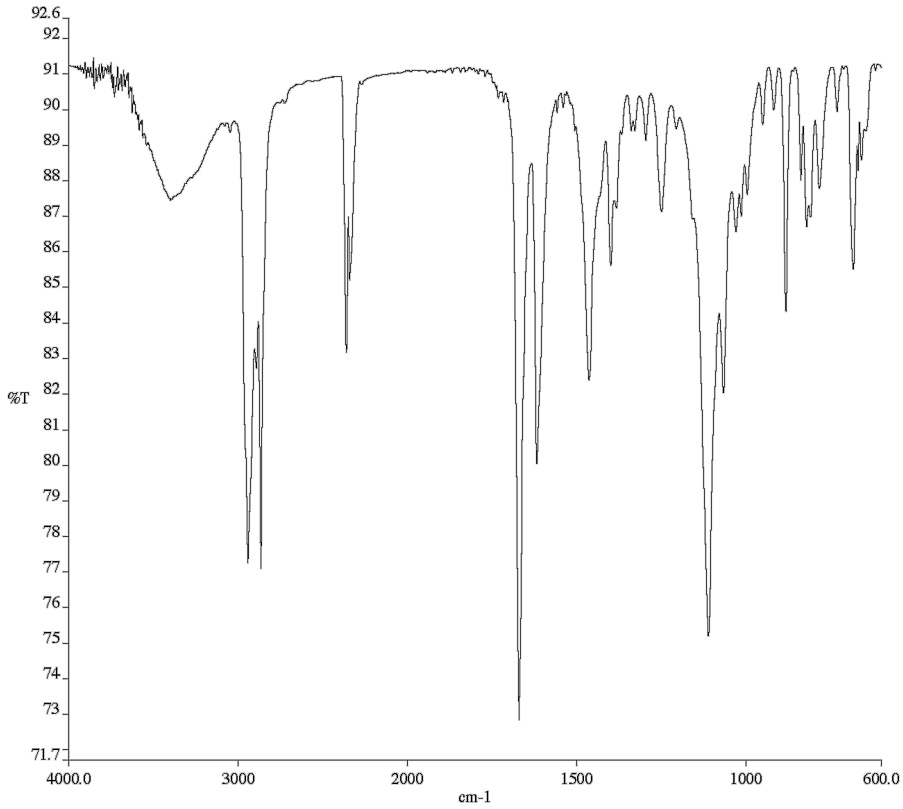


Figure S17. Infrared spectrum (Thin Film, NaCl) of compound **2a**.

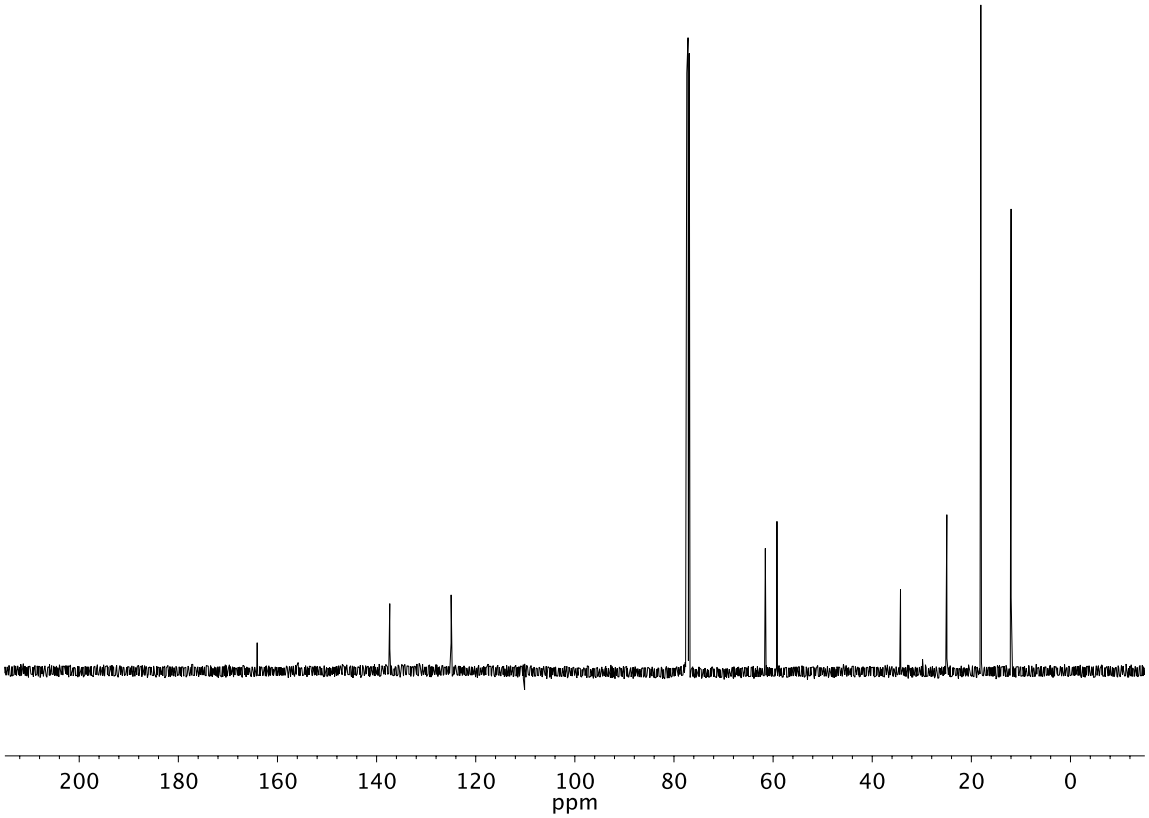


Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2a**.

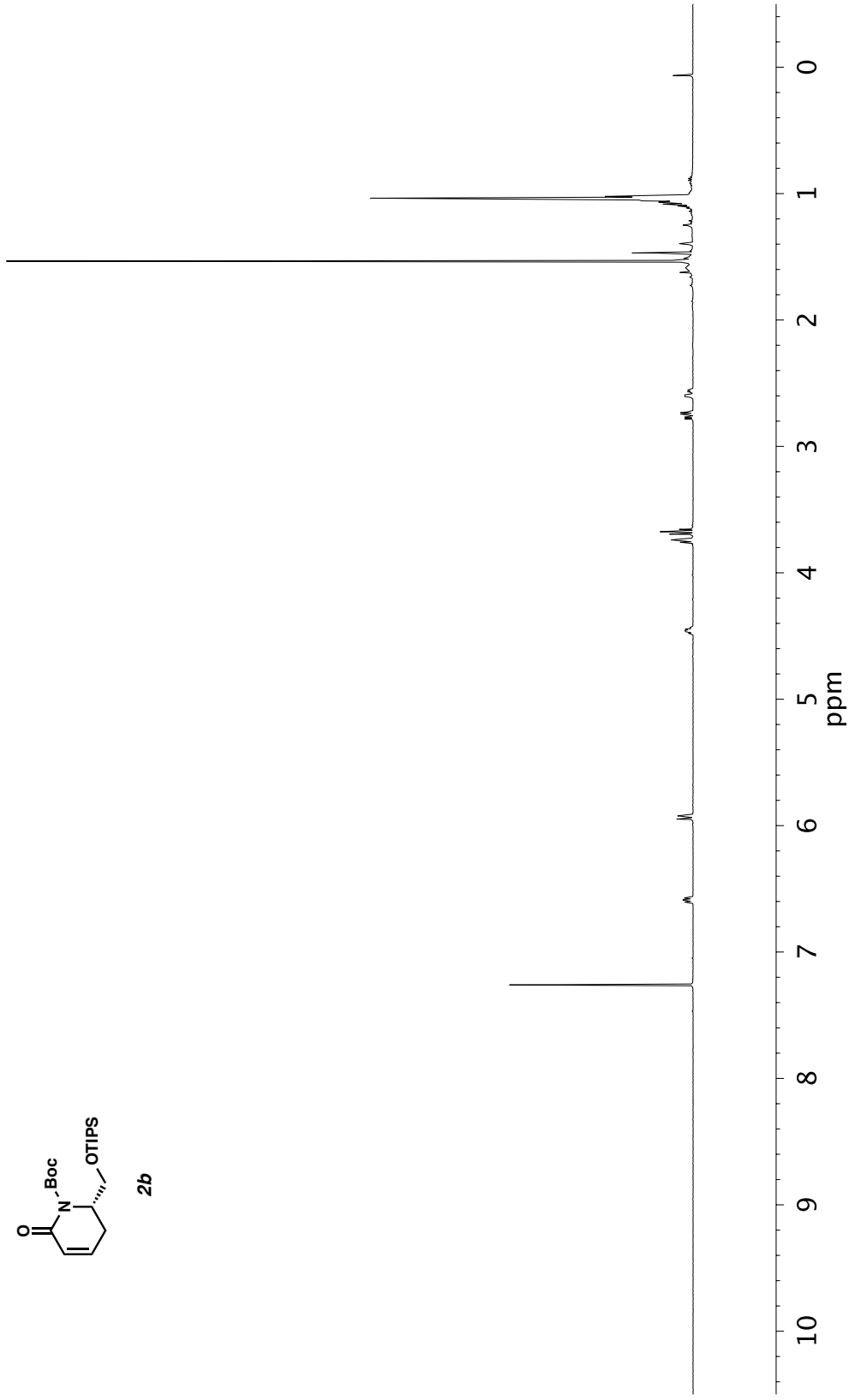


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**.

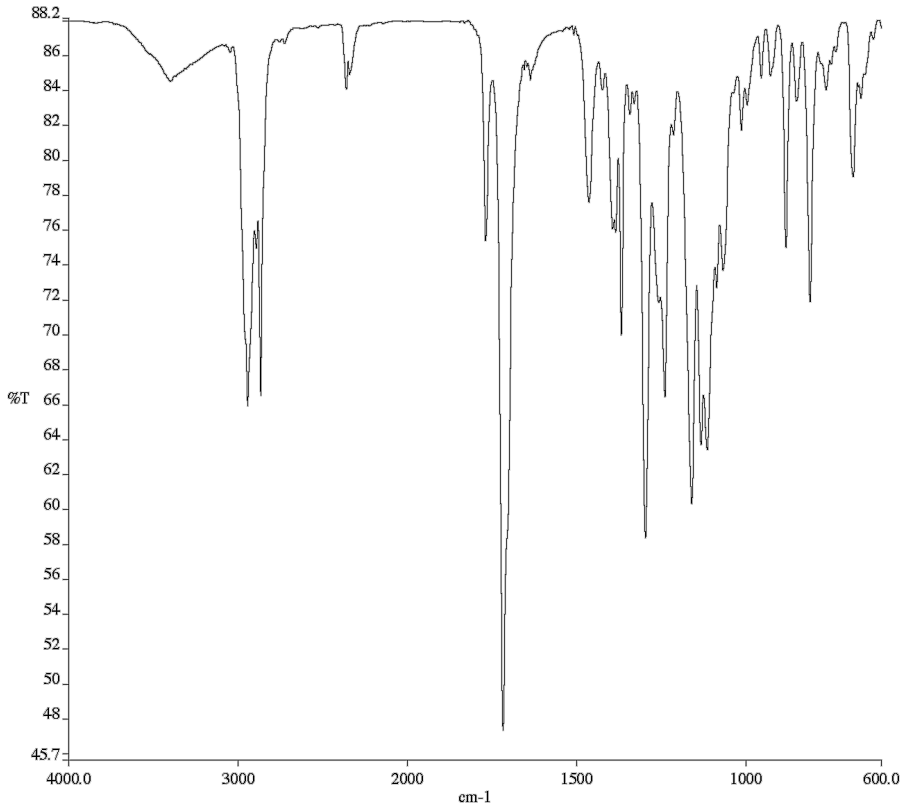


Figure S20. Infrared spectrum (Thin Film, NaCl) of compound **2b**.

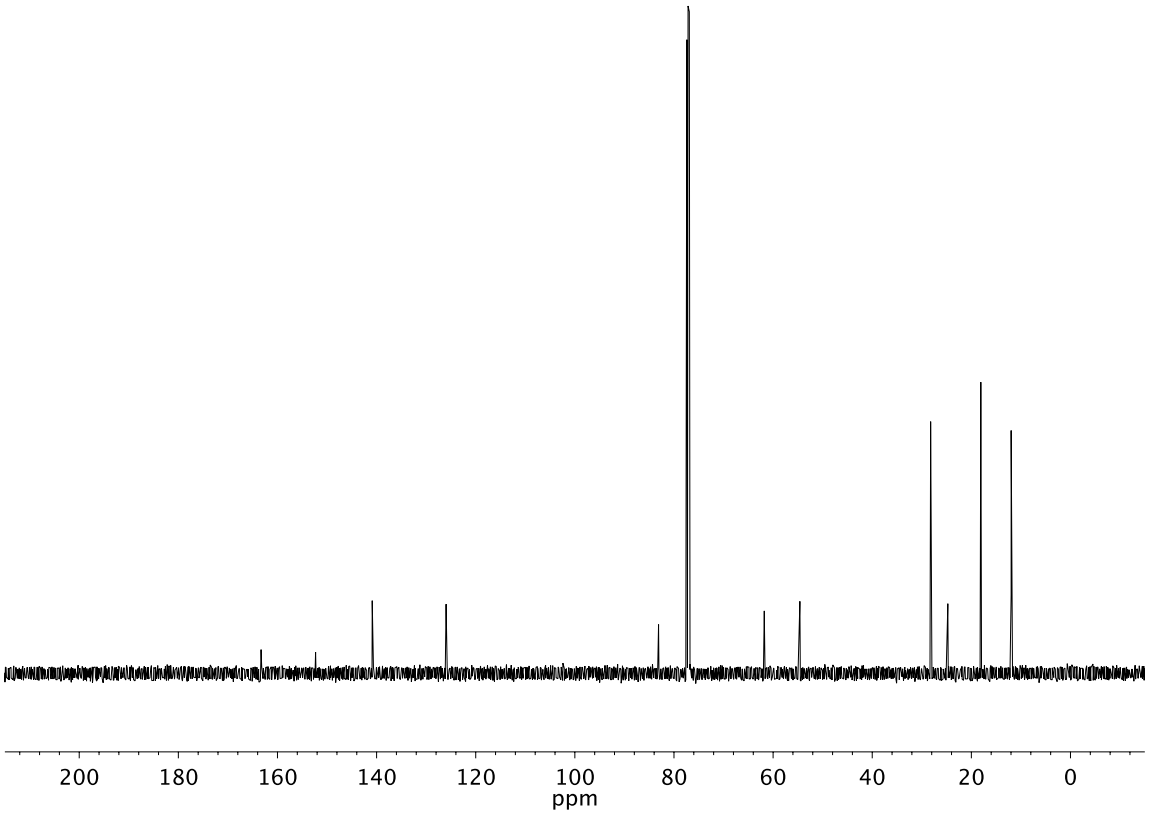
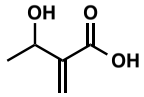


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2b**.



13

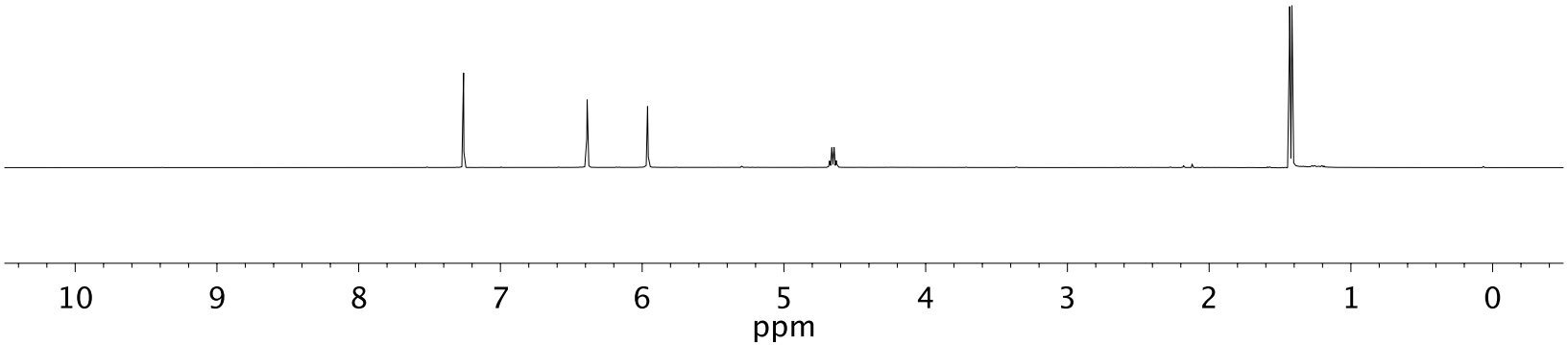


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **13**.

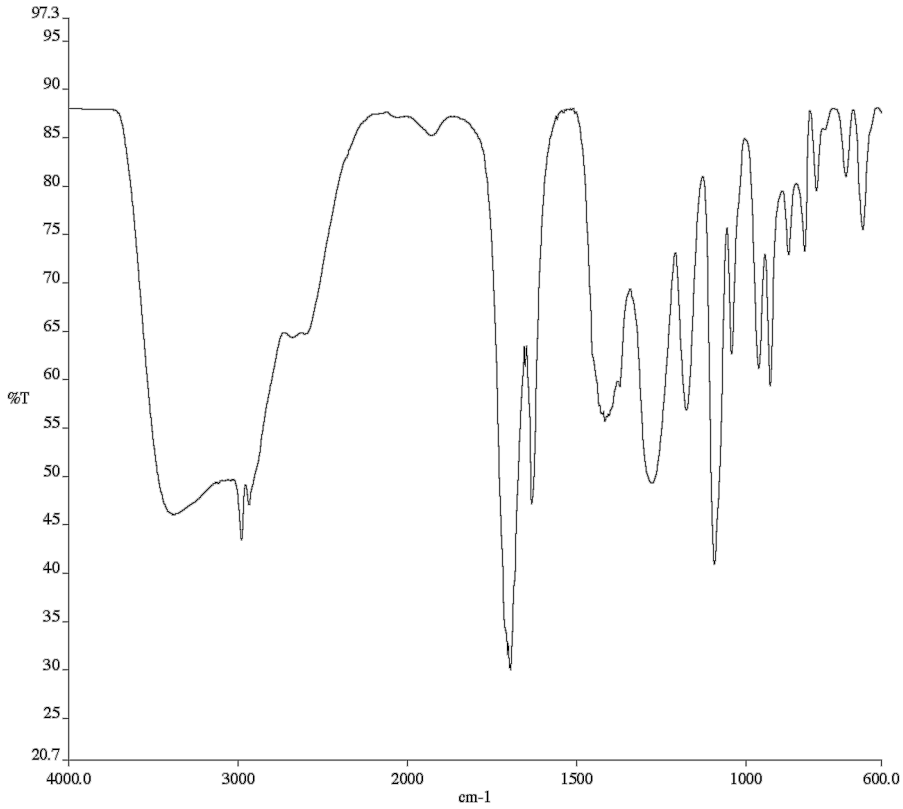


Figure S23. Infrared spectrum (Thin Film, NaCl) of compound **13**.

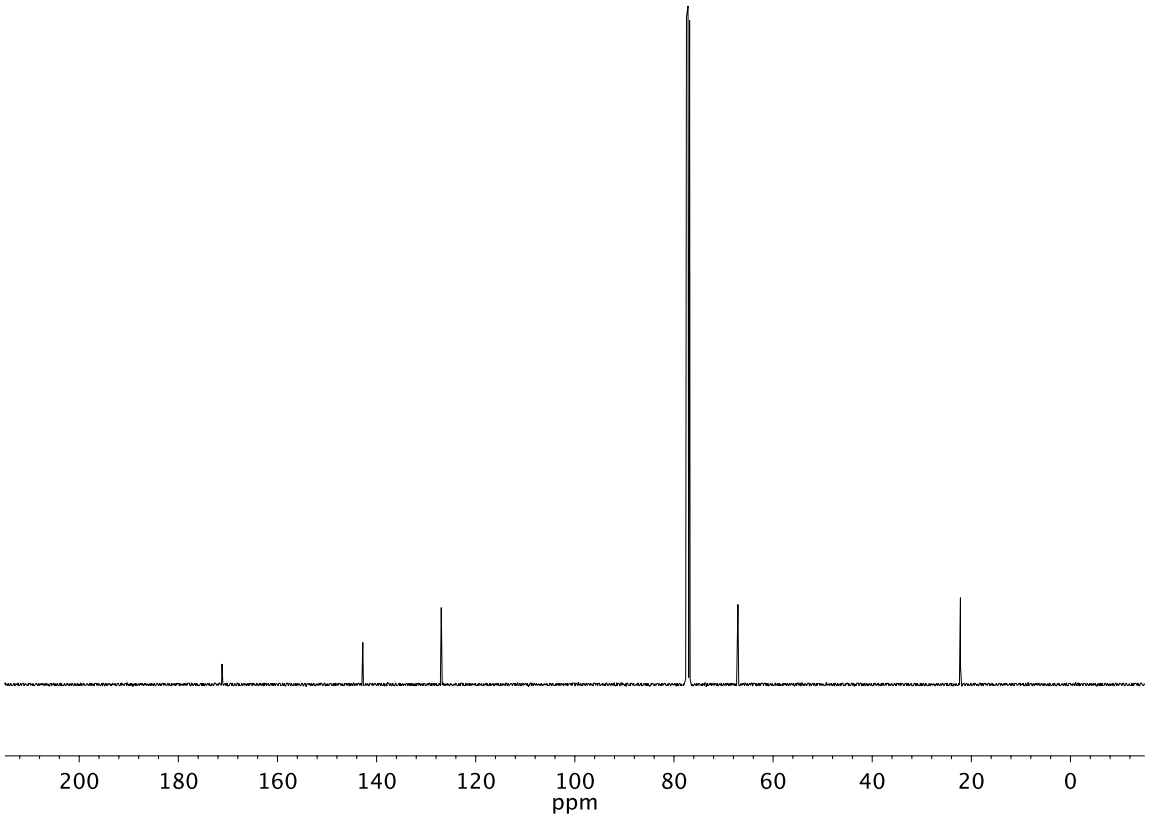


Figure S24. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **13**.

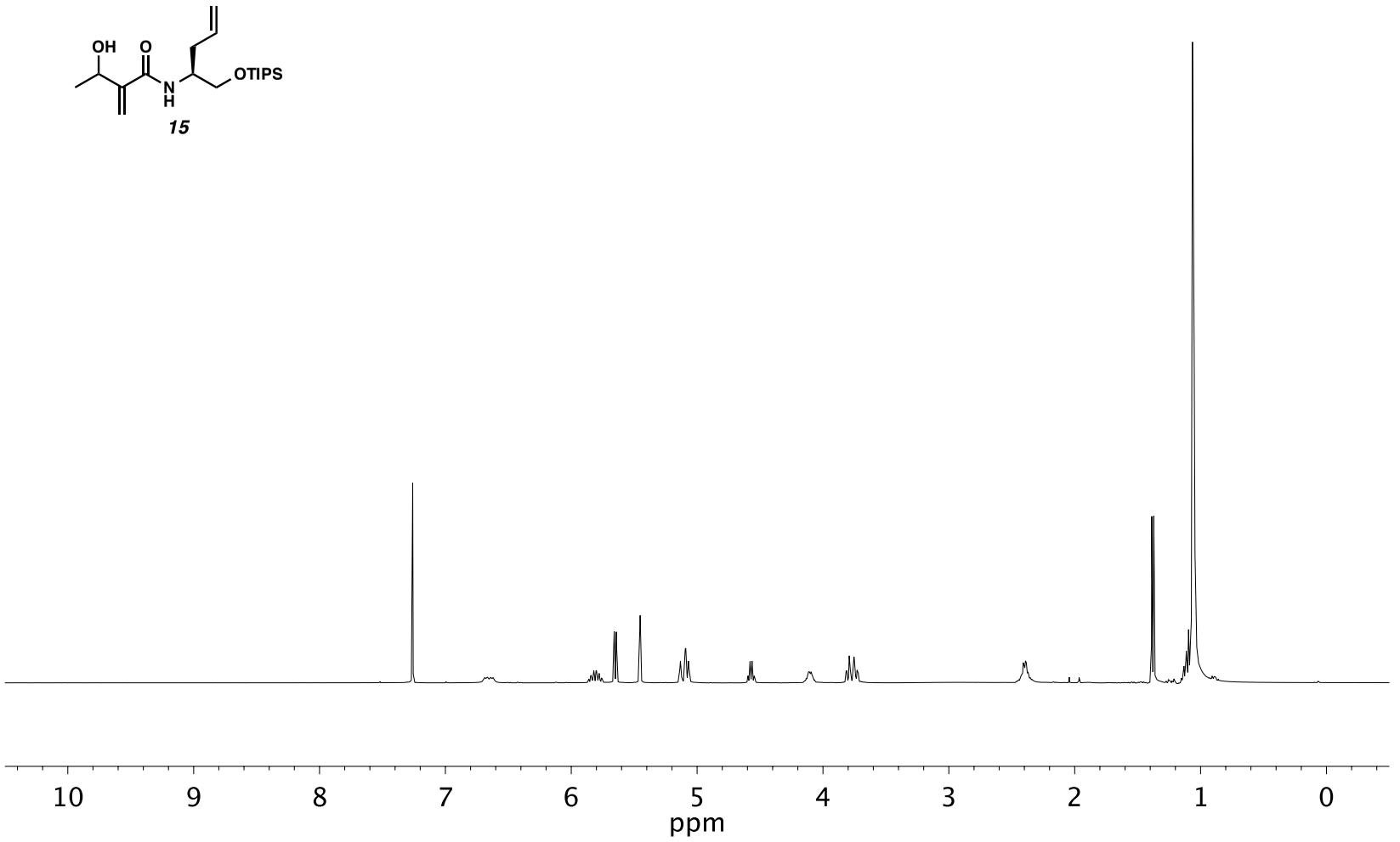


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **15**.

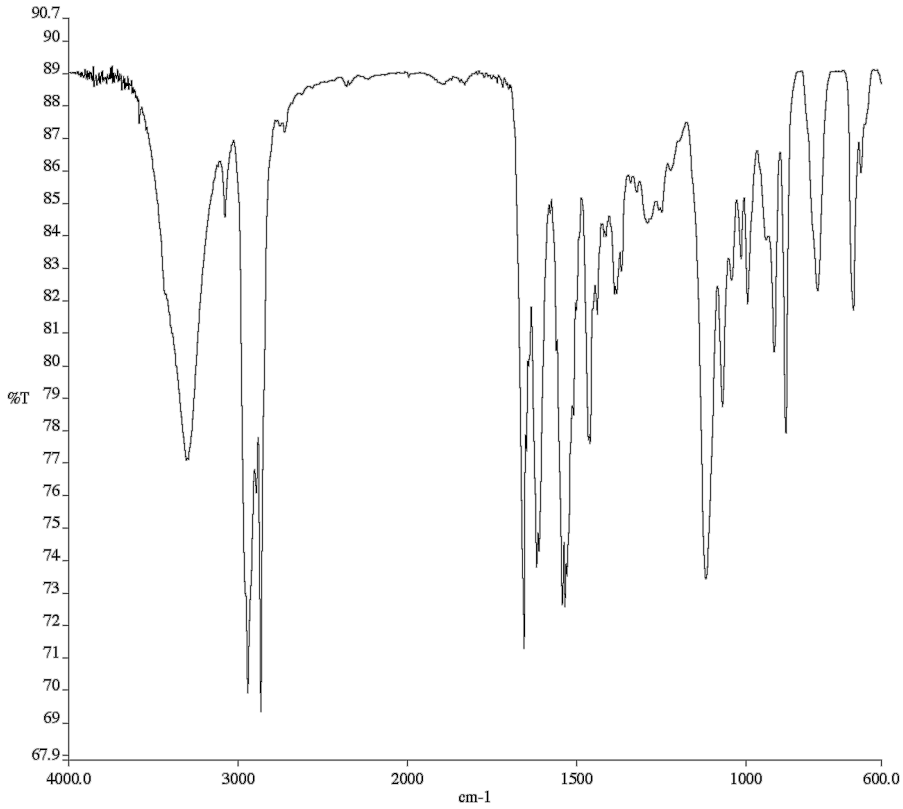


Figure S26. Infrared spectrum (Thin Film, NaCl) of compound **15**.

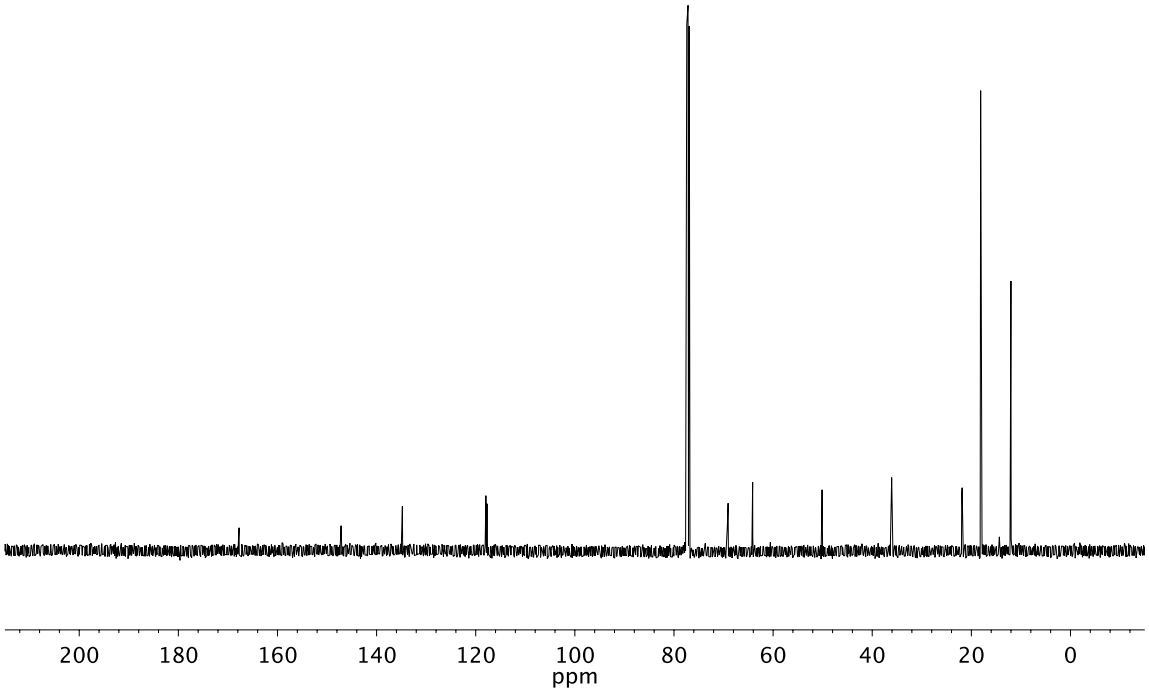


Figure S27. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **15**.

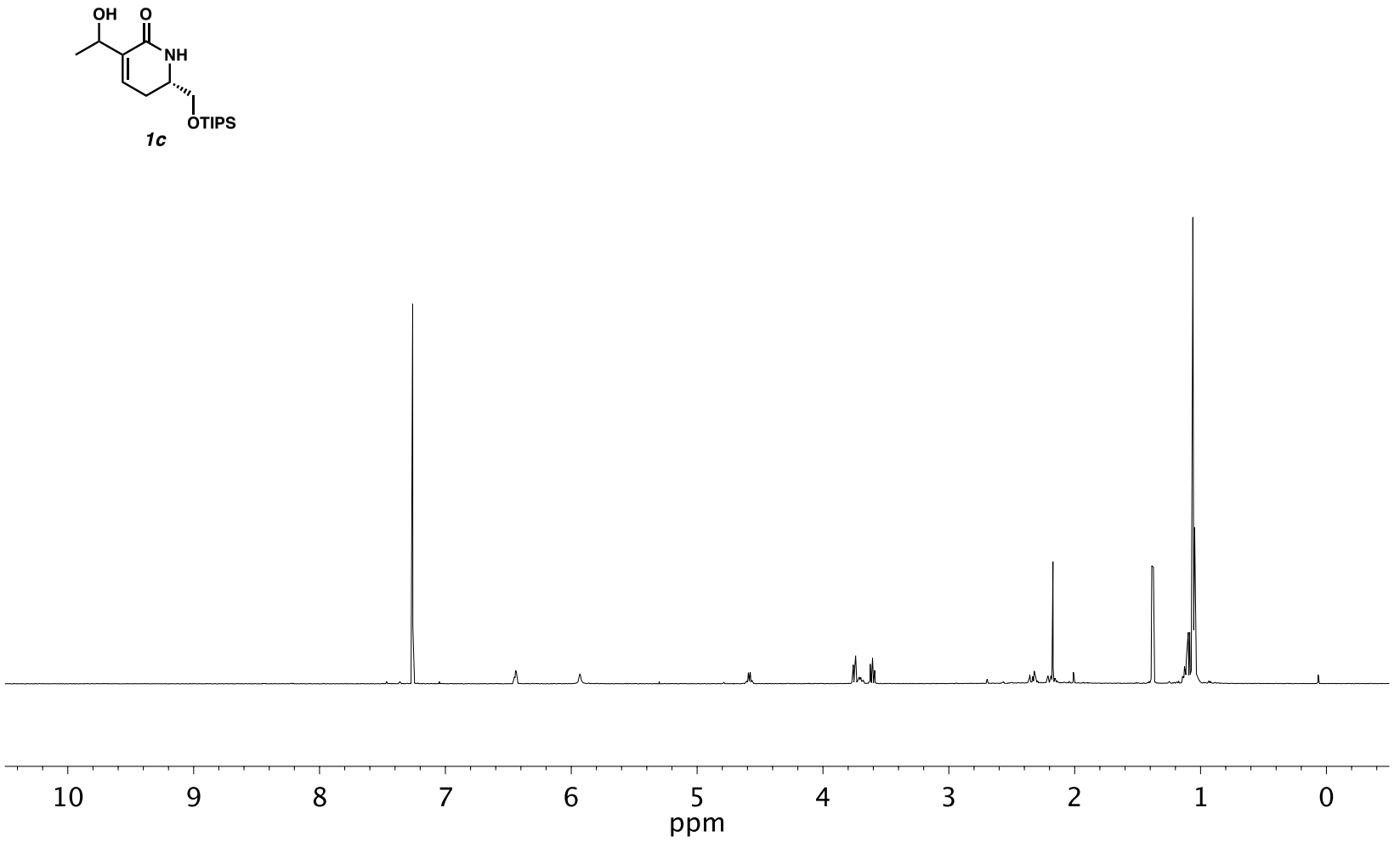


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1ca**.

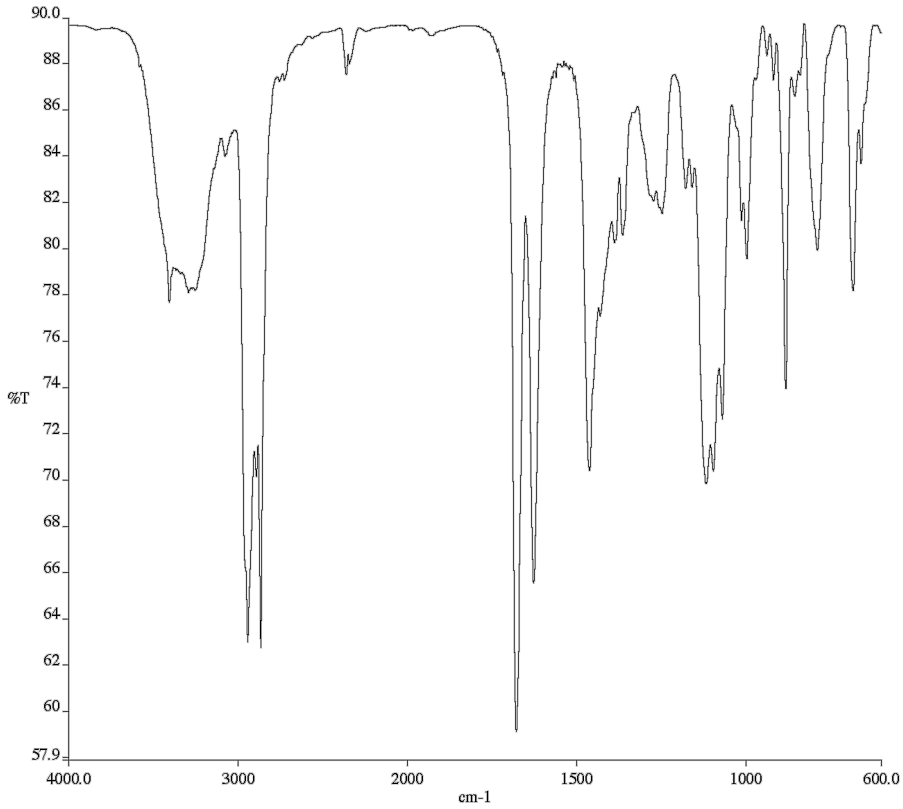


Figure S29. Infrared spectrum (Thin Film, NaCl) of compound **1ca**.

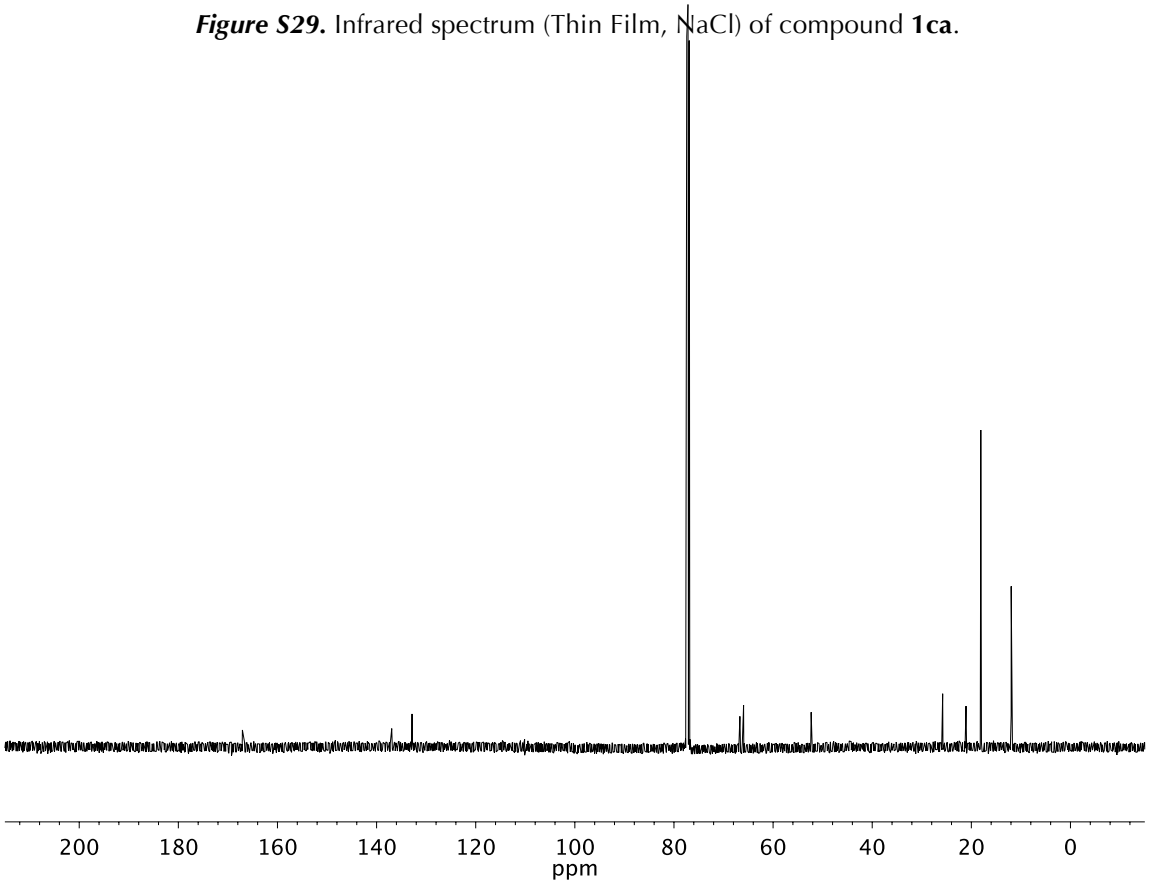


Figure S30. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **1ca**.

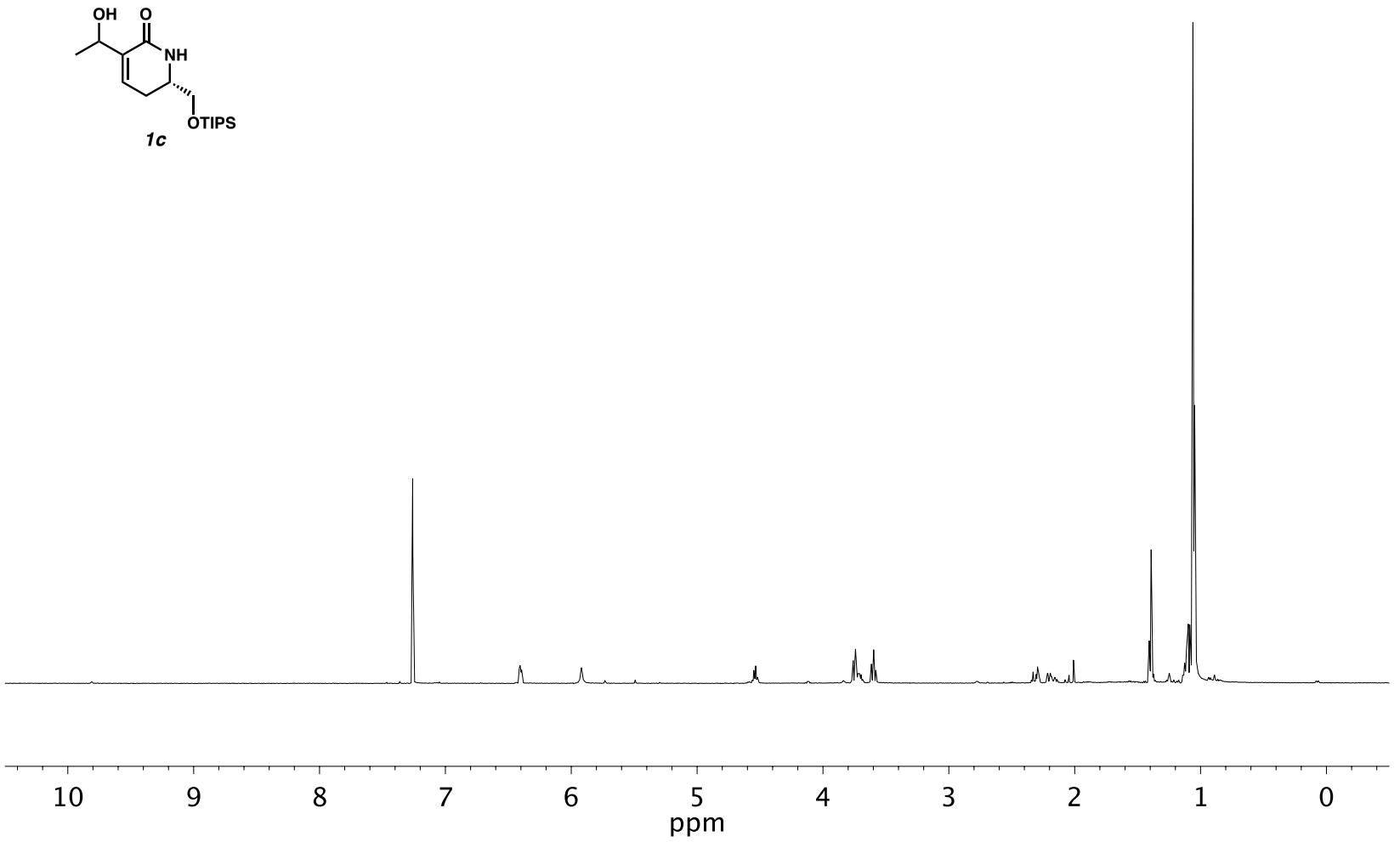


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1cb**.

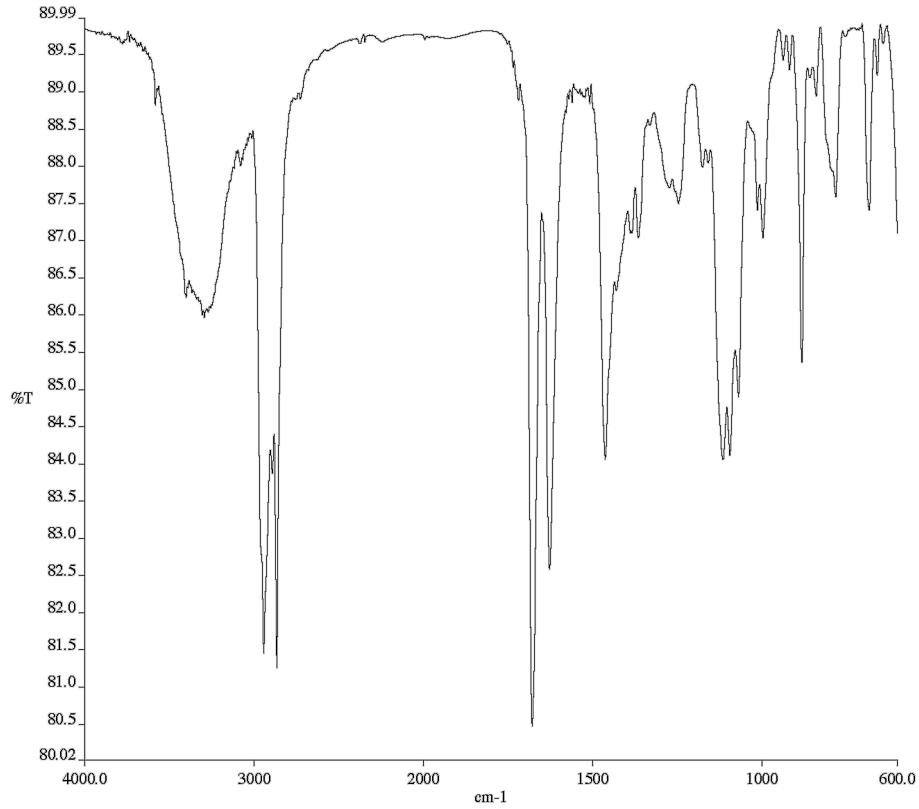


Figure S32. Infrared spectrum (Thin Film, NaCl) of compound **1cb**.

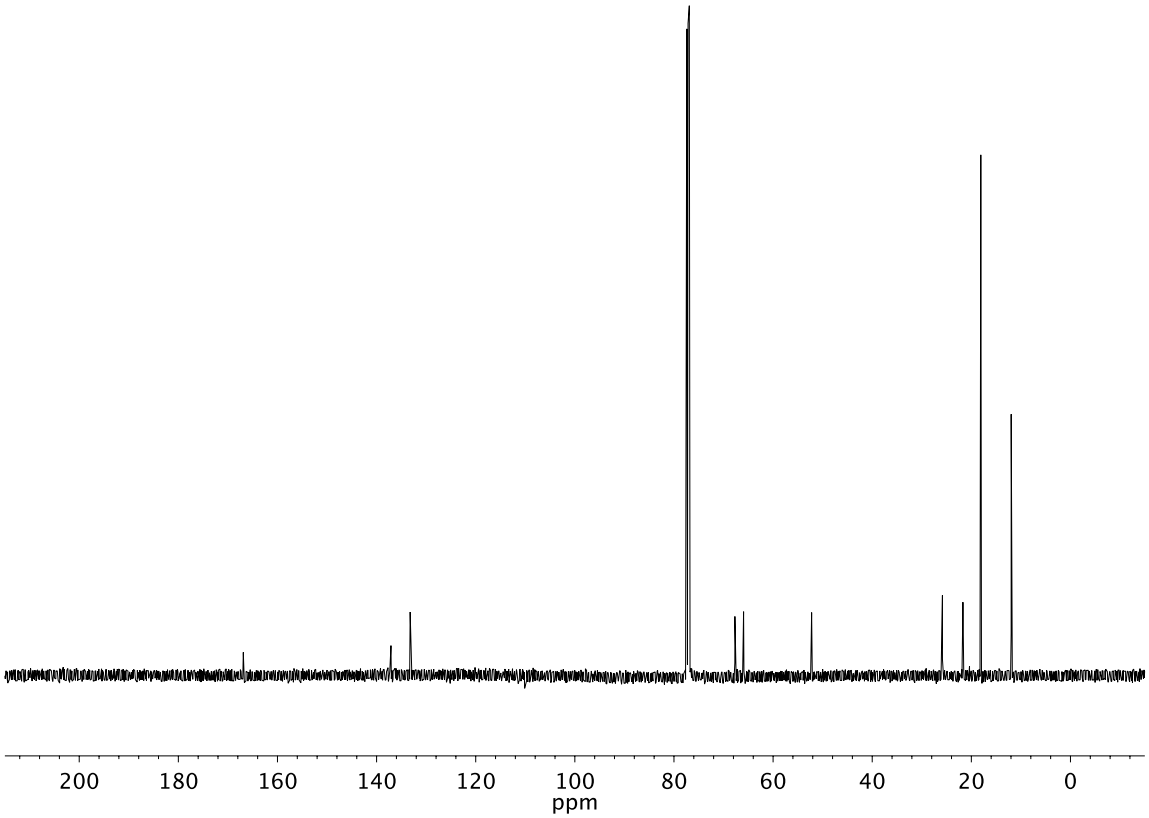


Figure S33. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **1cb**.