Supporting Information for

Poly(ε-caprolactones) initiated by chiral compounds: a new protocol to support organocatalysts

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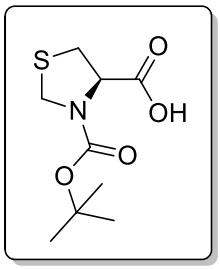
1. General procedure for the synthesis of (*R*)-3-(*tert*-butoxycarbonyl) thiazolidine-4-carboxylic acid (a)

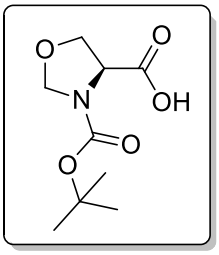
To a solution of the thiazolidine acid (3.33 g, 25 mmol) in 1,4-dioxane (50 mL),



H_2O (25 mL) and 1M aqueous NaOH solution (25 mL) at 0 °C was added Boc_2O (6.0 g, 27.5 mmol). The mixture was stirred for 12 h at room temperature, concentrated in vacuo, cooled and diluted in AcOEt (30 mL). Afterwards, it was acidified with 1M aqueous $KHSO_4$ solution until pH = 2. The aqueous phase was extracted with AcOEt (3 x 20 mL) and the organic phases were combined, dried with Na_2SO_4, filtered and evaporated. The product was obtained as a white solid in 90% yield and used without further purification. **M.p.:** 130–132 °C. **IR (KBr):** 2970, 2936 (ν C_{sp3}-H), 1746 (ν C=O Boc), 1635 (ν acid C=O), 1420 (δ_s O-H), 1390, 1370 (δ_s C-H ^{t}Bu), 1215 (ν acid C-O), 1197 (ν C_{sp3}-N), 1166 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$, conformer mixture): δ 9.41 (brs, 1H), [4.95 - 4.80 (m) and 4.77 – 4.67 (m), 1H], [4.65 (d, *J* = 7.9 Hz) and 4.57 (d, *J* = 7.9 Hz), 1H], [4.51 (d, *J* = 8.1 Hz) and 4.42 (d, *J* = 7.8 Hz), 1H], 3.45 – 3.21 (m, 2H), 1.55 – 1.40 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, conformer mixture) δ 176.3; 175.0; 154.0; 153.1; 82.0; 81.7; 61.4; 49.0; 48.4; 34.4; 32.2; 28.2.

2. General procedure for the synthesis of (*S*)-3-(*tert*-butoxycarbonyl) oxazolidine-4-carboxylic acid (b) [35]

A solution of L-serine (10.5 g, 100 mmol) and 37% aqueous formaldehyde

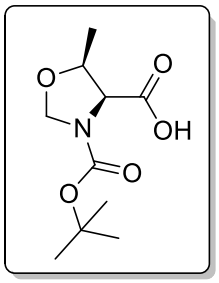


solution (10 mL) in 2M aqueous NaOH solution (50 mL) was stirred at 0 °C for 16 h. Then, a solution of hydroxylamine hydrochloride (0.67 g, 10 mmol) and sodium hydroxide (0.4 g, 10 mmol) in water (8 mL) and acetone (60 mL) was added. The solution was returned to room temperature and Boc_2O (24.0 g, 110 mmol) was added. The mixture was stirred for 3 h and then diluted with water and washed with Et_2O (3 x 50 mL). The aqueous phase was acidified with 20% aqueous citric acid solution and the product was extracted with AcOEt (3 x 50 mL). The organic phases were combined, dried over Na_2SO_4, filtered and evaporated. The product was obtained as a white solid in 30% yield and used without further purification. **M.p.:** 130–132 °C. **IR (ATR):** 3464 (ν O-H), 2975,

2937, 2871 (ν C_{sp3}-H), 1744 (ν C=O Boc), 1638 (ν acid C=O), 1424 (δ_s O-H), 1388, 1366 (δ_s C-H ^{t}Bu), 1235 (ν acid C-O), 1199 (ν C_{sp3}-N), 1166, 1143 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.95 (brs, 1H), 5.09 – 4.79 (m, 2H), 4.55 – 4.31 (m, 1H), 4.30 – 4.11 (m, 2H), 1.47 (s, 9H).

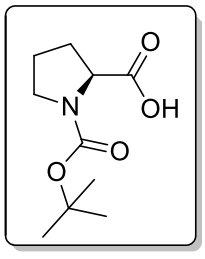
3. General procedure for the synthesis of (4*S*,5*S*)-3-(*tert*-butoxycarbonyl)-5-methyloxazolidine-4-carboxylic acid (c)

A solution of L-threonine (11.9 g, 100 mmol) and 37% aqueous formaldehyde



solution (10 mL) in 2M aqueous NaOH solution (50 mL) was stirred at 0 °C for 16 h. Then, a solution of hydroxylamine hydrochloride (0.67 g, 10 mmol), sodium hydroxide (0.4 g, 10 mmol) in water (8 mL) and acetone (60 mL) was added. The solution was returned to room temperature and Boc_2O (24.0 g, 110 mmol) was added. The mixture was stirred for 3 h and then diluted with water and washed with Et_2O (3 x 50 mL). The aqueous phase was acidified with 20% aqueous citric acid solution and the product was extracted with AcOEt (3 x 50 mL). The organic phases were combined, dried over Na_2SO_4, filtered and evaporated. The product was obtained as a white solid in 47% yield and used without further purification. **M.p.:** 130–132 °C. **IR (ATR):** 3467 (ν O-H), 2976, 2936, 2883 (ν C_{sp3}-H), 1741 (ν C=O Boc), 1634 (ν acid C=O), 1431 (δ_s O-H), 1388, 1366 (δ_s C-H ^{t}Bu), 1234 (ν acid C-O), 1197 (ν C_{sp3}-N), 1162, 1144 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.76 (brs, 1H), 5.23 – 5.05 (m, 1H), 4.90 – 4.72 (m, 1H), 4.33 – 4.20 (m, 1H), 4.05 – 3.83 (m, 1H), 1.52 – 1.41 (m, 12H).

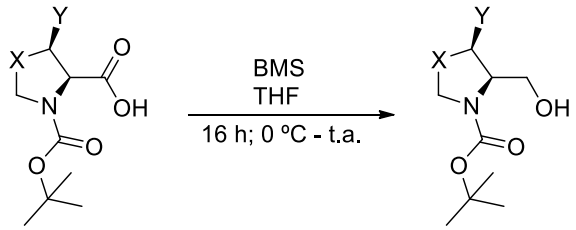
4. General procedure for the synthesis of (*S*)-1-(*tert*-butoxycarbonyl) pyrrolidine-2-carboxylic acid (d)



L-Proline (7.5 g, 65.5 mmol) was dissolved in a saturated aqueous solution of $NaHCO_3$ (85 mL). The mixture was cooled to 0°C and a solution of Boc_2O (15.7 g, 72 mmol) in THF (35 mL) was added dropwise. The reaction was returned to room temperature and stirred for 17 h. The THF was removed in vacuo and the remaining aqueous solution was acidified to pH 2 using 3M aqueous HCl solution. The aqueous phase was extracted with AcOEt (3x) and the organic phases were then combined, dried over Na_2SO_4 and evaporated.

The product was obtained as a white solid in 85% yield and was used without further purification. **M.p.:** 133–136 °C. **IR (KBr):** 3058 (ν O-H), 2924, 2853 (ν C_{sp3}-H), 1733 (ν C=O Boc), 1662 (ν acid C=O), 1432 (δ_s O-H), 1391, 1373 (δ_s C-H ^{t}Bu), 1162 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$, conformer mixture): δ 10.53 (brs, 1H), [4.36 (dd, *J* = 8.4; 3.1 Hz) e 4.24 (dd, *J* = 8.5; 4.3 Hz), 1H], 3.62 – 3.31 (m, 2H), 2.34 – 2.19 (m, 1H), 2.18 – 2.01 (m, 1H), 2.00 – 1.81 (m, 2H), [1.48 (s) and 1.42 (s), 9H]. **^{13}C NMR** (100 MHz, $CDCl_3$, conformer mixture) δ 178.9; 176.0; 155.9; 153.9; 81.1; 80.4; 59.0; 58.9; 46.9; 46.3; 30.8; 28.9; 28.4; 28.3; 24.3; 23.7.

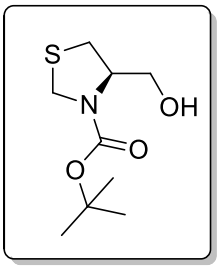
5. General procedure for the synthesis of compounds 1 to 4



a - d **1 - 4**

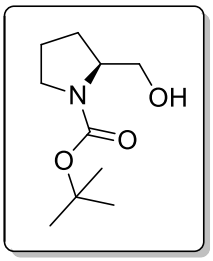
A solution of the carboxylic acid (20 mmol) in dry THF (40 mL) under an inert atmosphere was cooled to 0 °C. Then, a 2M solution of the BMS in THF (21.6 mL, 40 mmol) was added dropwise. The mixture was stirred at 0 °C for 5 h. Afterwards, the temperature was returned to room temperature and the reaction was stirred for 16 h. Then, water (80 mL) was carefully added to terminate the reaction. The mixture was diluted in AcOEt (250 mL) and the organic phase was washed with $NaCl_{(aq,sat)}$ (80 mL), $NaHCO_{3(aq,sat)}$ (80 mL), H_2O (2 x 80 mL) and more $NaCl_{(aq,sat)}$ (80 mL). The organic phase was dried with Na_2SO_4 and evaporated. The product was purified by column chromatography using a mixture of hexane and ethyl acetate (80:20) as eluent.

(*R*)-*tert*-butyl-4-(hydroxymethyl)thiazolidine-3-carboxylate (1) [16]



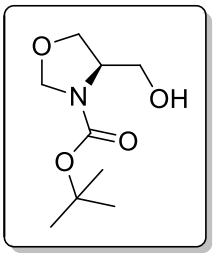
Following the general procedure, the tittle compound was obtained as white solid in 83% yield. $\boldsymbol{\alpha_D^{20}}$ = -77.033 (*c* 1, DCM). **IR (ATR):** 3418 (ν O-H), 2972, 2935, 2878 (ν C_{sp3}-H), 1670 (ν C=O Boc), 1390, 1367 (δ_s C-H ^{t}Bu), 1111 (ν C-N), 1050 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.65 – 4.51 (m, 1H), 4.37 – 4.25 (m, 1H), 4.23 (d, *J* = 9.4 Hz, 1H), 3.70 – 3.62 (m, 2H), 3.12 (dd, *J* = 11.7, 6.7 Hz, 1H), 3.00 – 2.80 (m, 1H), 1.45 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7; 81.4; 64.3; 61.8; 49.0; 33.0; 28.5. **HRMS (ESI+):** exact mass calculated for $[M+Na]^+$ ($C_9H_{17}NNaO_3S$) requires *m/z* 242.0821, found: m/z 242.0812.

(*S*)-*tert*-butyl 2-(hydroxymethyl)pyrrolidine-1-carboxylate (2) [43]



Following the general procedure, the tittle compound was obtained as colorless oil in 76% yield. $\boldsymbol{\alpha_D^{20}}$ = -63.033 (*c* 1, DCM). **IR (ATR):** 3421 (ν O-H), 2973, 2933, 2879 (ν C_{sp3}-H), 1670 (ν C=O Boc), 1405, 1367 (δ_s C-H ^{t}Bu), 1107 (ν C-N), 1040 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.76 (brs, 1H), 4.00 – 3.73 (m, 1H), 3.66 – 3.51 (m, 2H), 3.47 – 3.36 (m, 1H), 3.34 – 3.21 (m, 1H), 1.98 (td, *J* = 14.5; 7.3 Hz, 1H), 1.88 – 1.69 (m, 2H), 1.59 – 1.47 (m, 1H), 1.44 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3; 80.3; 67.7; 60.3; 47.7; 28.8; 28.6; 24.2. **HRMS (ESI+):** exact mass calculated for $[M+2H]^+$ ($C_{10}H_{21}NO_3$) requires *m/z* 203.1516, found: *m/z* 203.1513.

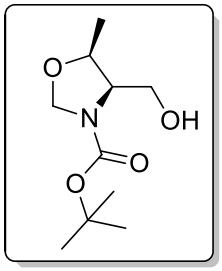
(*R*)-*tert*-butyl 4-(hydroxymethyl)oxazolidine-3-carboxylate (3)



Following the general procedure, the tittle compound was obtained as colorless oil in 77% yield. $\boldsymbol{\alpha_D^{20}}$ = -15,933 (*c* 1, DCM). **IR (ATR):** 3465 (ν O-H), 2979, 2952, 2867 (ν C_{sp3}-H), 1684 (ν C=O Boc), 1409, 1368 (δ_s C-H ^{t}Bu), 1101 (ν C-N), 1051 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.98 – 4.83 (m, 1H), 4.73 (d, *J* = 4.2 Hz, 1H), 4.09 (dd, *J* = 8.7; 6.9 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.88 – 3.74 (m, 1H), 3.71 (dd, *J* = 11.1; 5.9 Hz, 1H), 3.62 (dd, *J* = 11.1; 5.9 Hz, 1H), 1.48 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5; 81.3; 79.4; 69.4; 64.3; 57.6;

28.3. **HRMS (ESI+):** exact mass calculated for $[M+Na]^+$ ($C_9H_{17}NNaO_4$) requires *m/z* 226.1050, found: *m/z* 226.1069.

(4*R*,5*S*)-*tert*-butyl-4-(hydroxymethyl)-5-methyloxazolidine-3-carboxylate (4)

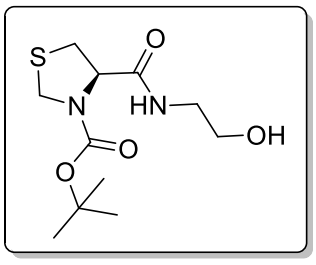


Following the general procedure, the tittle compound was obtained as colorless oil in 74% yield. $\boldsymbol{\alpha_D^{20}}$ = -78.933 (*c* 1, DCM). **IR (ATR):** 3440 (ν O-H), 2977, 2933, 2873 (ν C_{sp3}-H), 1679 (ν C=O Boc), 1403, 1367 (δ_s C-H ^{t}Bu), 1100 (ν C-N), 1041 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.15 – 4.92 (m, 1H), 4.61 (d, *J* = 4.6 Hz, 1H), 4.40 (brs, 1H), 3.85 – 3.68 (m, 1H), 3.65 (d, *J* = 5.7 Hz, 2H), 3.52 – 3.36 (m, 1H), 1.45 (s, 9H), 1.36 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7; 81.3; 78.5; 78.5; 64.7; 63.9; 28.3; 17.8. **HRMS (ESI+):** exact mass calculated for $[M+H]^+$ ($C_{10}H_{20}NO_4$) requires *m/z* 218.1387, found: *m/z* 218.1405.

6. General procedure for the synthesis of compounds 5 to 8

To a solution of the acid (10 mmol) in dry dichloromethane (30 mL) at 0 °C under an inert atmosphere was added N-methylmorpholine (3.3 mL, 30 mmol). The mixture was returned to room temperature and stirred for 15 minutes. Then, ethyl chloroformate (2.8 mL, 30 mmol) was added. After 30 minutes of stirring, ethanolamine (1.2 mL, 20 mmol) was carefully added. The reaction was stirred for 24 h. Then, the mixture was diluted in dichloromethane and washed with 1M $NaOH_{(aq)}$ solution (50 mL) and saturated $NaCl_{(aq)}$ solution (2x50 mL). The organic phase was dried with Na_2SO_4 and evaporated. The crude mixture was purified by suspension in ethyl ether followed by filtration and then by column chromatography using ethyl acetate as eluent.

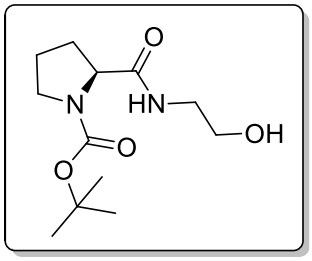
(*R*)-*tert*-butyl-4-((2-hydroxyethyl)carbamoyl)thiazolidine-3-carboxylate (5)



Following the general procedure, the tittle compound was obtained as yellow solid in 51% yield. **M.p.:** 136-138 °C. $\boldsymbol{\alpha_D^{20}}$ = -111.233 (*c* 1, DCM). **IR (ATR):** 3390 (ν O-H), 3323 (ν N-H), 2974, 2950, 2870 (ν C_{sp3}-H), 1695 (ν C=O Boc), 1663 (ν C=O), 1565 (δ_s N-H), 1394, 1366

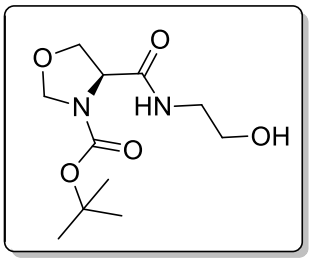
(δ_s C-H tBu), 1077 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.84 (brs, 1H), 4.72 – 4.58 (m, 2H), 4.40 (d, *J* = 8.9 Hz, 1H), 3.70 (t, *J* = 5.1 Hz, 2H), 3.50 – 3.38 (m, 2H), 3.38 – 3.30 (m, 1H), 3.30 – 3.16 (m, 1H), 3.00 – 2.77 (brs, 1H), 1.48 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3; 154.1; 82.1; 63.2; 61.6; 49.7; 42.4; 33.5; 28.3. **HRMS (ESI+):** exact mass calculated for $[M+Na]^+$ ($C_{11}H_{20}N_2NaO_4S$) requires *m/z* 299.1036, found: *m/z* 299.1025.

(*S*)-*tert*-butyl-2-((2-hydroxyethyl)carbamoyl)pyrrolidine-1-carboxylate (6) [43]



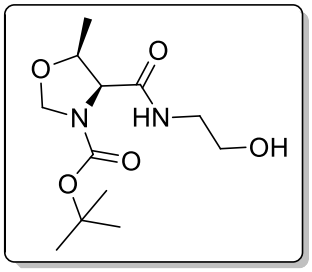
Following the general procedure, the tittle compound was obtained as white solid in 49% yield. **M.p.:** 162-164 °C. $\boldsymbol{\alpha_D^{20}}$ = -68.533 (*c* 1, DCM). **IR (ATR):** 3366 (ν O-H), 3306 (ν N-H), 2975, 2944, 2873 (ν C_{sp3}-H), 1691 (ν C=O Boc), 1658 (ν C=O), 1561 (δ_s N-H), 1404, 1361 (δ_s C-H ^{t}Bu), 1079 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25 – 6.50 (m, 1H), 4.29 – 4.16 (m, 1H), 3.70 (t, *J* = 4.9 Hz, 1H), 3.57 – 3.32 (m, 4H), 3.08 (brs, 1H), 2.38 – 1.83 (m, 4H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3; 155.8; 80.7; 61.8; 60.4; 47.2; 42.4; 28.8; 28.4; 24.6. **HRMS (ESI+):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{23}N_2O_4$) requires *m/z* 259.1652, found: *m/z* 259.1655.

(*S*)-*tert*-butyl-4-((2-hydroxyethyl)carbamoyl)oxazolidine-3-carboxylate (7)



Following the general procedure, the tittle compound was obtained as white solid in 53% yield. **M.p.:** 131-133 °C $\boldsymbol{\alpha_D^{20}}$ = -85.433 (*c* 1, DCM). **IR (ATR):** 3429 (ν O-H), 3331 (ν N-H), 2974, 2938, 2866 (ν C_{sp3}-H), 1679 (ν C=O Boc), 1660 (ν C=O), 1546 (δ_s N-H), 1409, 1363 (δ_s C-H tBu), 1077 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.96 (brs, 1H), 5.05 – 4.92 (m, 1H), 4.83 (d, *J* = 3.6 Hz, 1H), 4.37 (dd, *J* = 6.9, 4.4 Hz, 1H), 4.32 – 4.21 (m, 1H), 4.17 (t, *J* = 7.9 Hz, 1H), 3.72 (t, *J* = 5.0 Hz, 2H), 3.55 – 3.35 (m, 2H), 2.82 (brs, 1H), 1.49 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0; 153.9; 82.1; 79.7; 70.2; 61.9; 58.6; 42.3; 28;3. **HRMS (ESI+):** exact mass calculated for $[M+Na]^+$ ($C_{11}H_{20}N_2NaO_5$) requires *m/z* 283.1264, found: *m/z* 283.1281.

(4*S*,5*S*)-*tert*-butyl-4-((2-hydroxyethyl)carbamoyl)-5-methyloxazolidine-3-carboxylate (8)

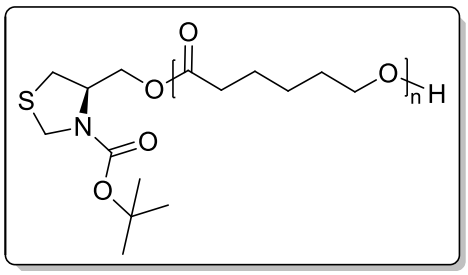


Following the general procedure, the tittle compound was obtained as white solid in 56% yield. **M.p.:** 125-127 °C. α_D^{20} = -82.333 (*c* 1, DCM). **IR (ATR):** 3368 (ν O-H), 3306 (ν N-H), 2977, 2942, 2874 (ν C_{sp3}-H), 1692 (ν C=O Boc), 1658 (ν C=O), 1562 (δ_s N-H), 1407, 1360 (δ_s C-H ^{t}Bu), 1076 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.91 (brs, 1H), 5.26 – 5.11 (m, 1H), 4.70 (d, *J* = 4.8 Hz, 1H), 4.38 – 4.17 (m, 1H), 3.83 (d, *J* = 6.9 Hz, 1H), 3.71 (t, *J* = 5.1 Hz, 2H), 3.50 – 3.38 (m, 2H), 2.97 (brs, 1H), 1.52 – 1.44 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5; 154.1; 82.0; 78.9; 78.9; 65.1; 61.7; 42.2; 28.3; 18.6. **HRMS (ESI+):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{23}N_2O_5$) requires *m/z* 275.1601, found: *m/z* 275.1620.

7. General procedure for the polymerization of caprolactone with alcohol initiators (PCL-01P to PCL-08P)

A mixture of ε-caprolactone (25 mmol) with alcohol and fumaric acid in the proportions used was stirred at 90 ºC under an inert atmosphere for 24 h. Afterwards, the mixture was quickly poured into 100 mL of hexane leading the polymer to precipitation. The solid was filtered, washed with more hexane and dried under vacuum. The resulting solid was redissolved in 10 mL of toluene and poured back into 100 mL of ice-cold diethyl ether. The mixture was cooled to 0 °C for 12 h, filtered under vacuum, washed with ice-cold diethyl ether and dried under vacuum.

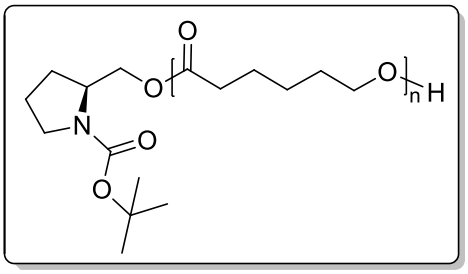
PCL-01P



Following the general procedure, the tittle compound was obtained as white solid in 85% yield. ($M_{n,NMR}$ = 2500 g/mol). **IR (ATR):** 2942, 2893, 2863 (υ C_{sp3}-H), 1720 (υ C=O), 1471 (δ_s C-H), 1238, 1175 (υ C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.65 - 4.46 (m, 2H), 4.32 – 4.15 (m, 3H), 4.04 (t, *J* = 6.6 Hz, 40H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.12 (dd, *J* =

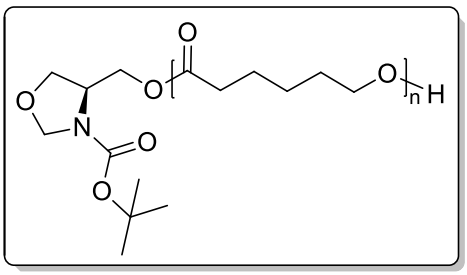
11.7, 6.6 Hz, 1H), 2.94 - 2.81 (m, 1H), 2.31 (t, *J* = 7.5 Hz, 42H), 1.75 - 1.54 (m, 84H), 1.52 - 1.27 (m, 45H).

PCL-02P



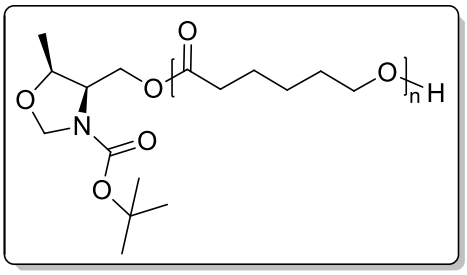
Following the general procedure, the tittle compound was obtained as white solid in 85% yield. ($M_{n,NMR}$ = 1750 g/mol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.35 - 3.83 (m, 28H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.48 - 3.28 (m, 2H), 2.31 (t, *J* = 7.1 Hz, 27H), 1.85 - 1.50 (m, 58H), 1.50 - 1.25 (m, 35H).

PCL-03P



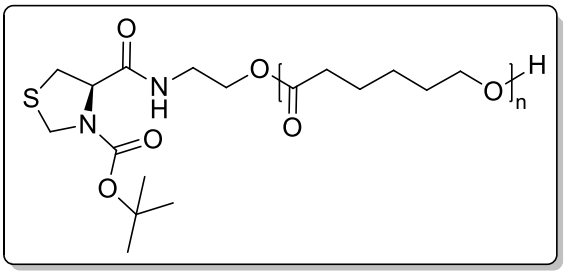
Following the general procedure, the tittle compound was obtained as white solid in 79% yield. ($M_{n,NMR}$ = 1800 g/mol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.94 - 4.75 (m, 1H), 4.74 (d, *J* = 3.9 Hz, 1H), 4.28 - 4.18 (m, 2H), 4.14 - 3.92 (m, 28H), 3.92 - 3.85 (m, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 28H), 1.73 - 1.58 (m, 56H), 1.50 - 1.26 (m, 32H).

PCL-04P



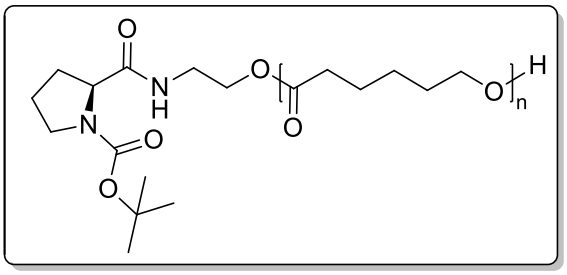
Following the general procedure, the tittle compound was obtained as white solid in 77% yield. ($M_{n,NMR}$ = 1600 g/mol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.25 - 4.95 (m, 2H), 4.62 (d, *J* = 4.6 Hz, 1H), 4.28 - 4.12 (m, 2H), 4.12 - 3.93 (m, 26H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 25H), 1.70 - 1.52 (m, 50H), 1.46 (s, 2H), 1.42 - 1.30 (m, 28H).

PCL-05P



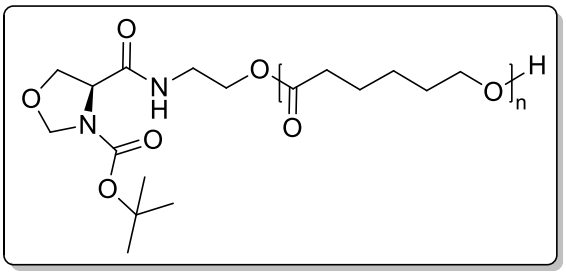
Following the general procedure, the tittle compound was obtained as white solid in 79% yield. ($M_{n,NMR}$ = 2000 g/mol). **IR (ATR):** 2942, 2895, 2863 (ν C_{sp3}-H), 1721 (ν C=O), 1471 (δ_s C-H), 1238, 1165 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): 4.75 – 4.58 (m, 1H), 4.43 – 4.28 (m, 1H), 4.26 – 4.20 (m, 1H), 4.20 – 4.12 (m, 1H), 4.12 – 3.90 (m, 29H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.54 (dd, *J* = 11.0; 5.6 Hz, 1H), 3.25 – 3.10 (m, 3H), 2.31 (t, *J* = 7.5 Hz, 30H), 1.70 – 1.53 (m, 60H), 1.48 (s, 3H), 1.40 – 1.28 (m, 30H).

PCL-06P



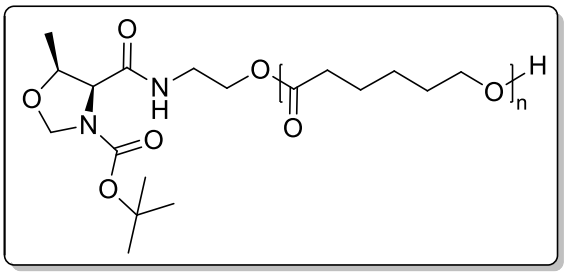
Following the general procedure, the tittle compound was obtained as white solid in 81% yield. ($M_{n,NMR}$ = 2650 g/mol). **IR (ATR):** 2943, 2895, 2864 (ν C_{sp3}-H), 1721 (ν C=O), 1470 (δ_s C-H), 1238, 1171 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): 4.17 - 3.94 (m, 41H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.55 – 3.35 (m, 4H), 2.31 (t, *J* = 7.5 Hz, 40H), 1.93 – 1.70 (m, 4H), 1.70 – 1.52 (m, 80H), 1.51 – 1.26 (m, 47H).

PCL-07P



Following the general procedure, the tittle compound was obtained as white solid in 76% yield. ($M_{n,NMR}$ = 1900 g/mol). **IR (ATR):** 2947, 2895, 2865 (ν C_{sp3}-H), 1720 (ν C=O), 1470 (δ_s C-H), 1238, 1169 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): 5.00 – 4.87 (m, 1H), 4.82 – 4.75 (m, 1H), 4.35 (dd, *J* = 7.0; 3.9 Hz, 1H), 4.27 – 3.95 (m, 30H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.58 – 3.45 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 28H), 1.71 – 1.55 (m, 56H), 1.48 (s, 4H), 1.44 – 1.28 (m, 28H).

PCL-08P



Following the general procedure, the tittle compound was obtained as white solid in 71% yield. ($M_{n,NMR}$ = 2400 g/mol). **IR (ATR):** 2943, 2894, 2864 (ν C_{sp3}-H), 1721 (ν C=O), 1469 (δ_s C-H), 1238, 1170 (ν C-O). **^{1}H NMR** (400 MHz, $CDCl_3$): 5.25 – 5.14 (m, 1H), 4.65 (d, *J* = 4.7 Hz, 1H), 4.20 – 3.95 (m, 40H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.60 – 3.45 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 38H), 1.72 - 1.57 (m, 76H), 1.47 (s, 3H), 1.46 – 1.32 (m, 41H).

8. NMR spectra of carboxylic acids (a to d)

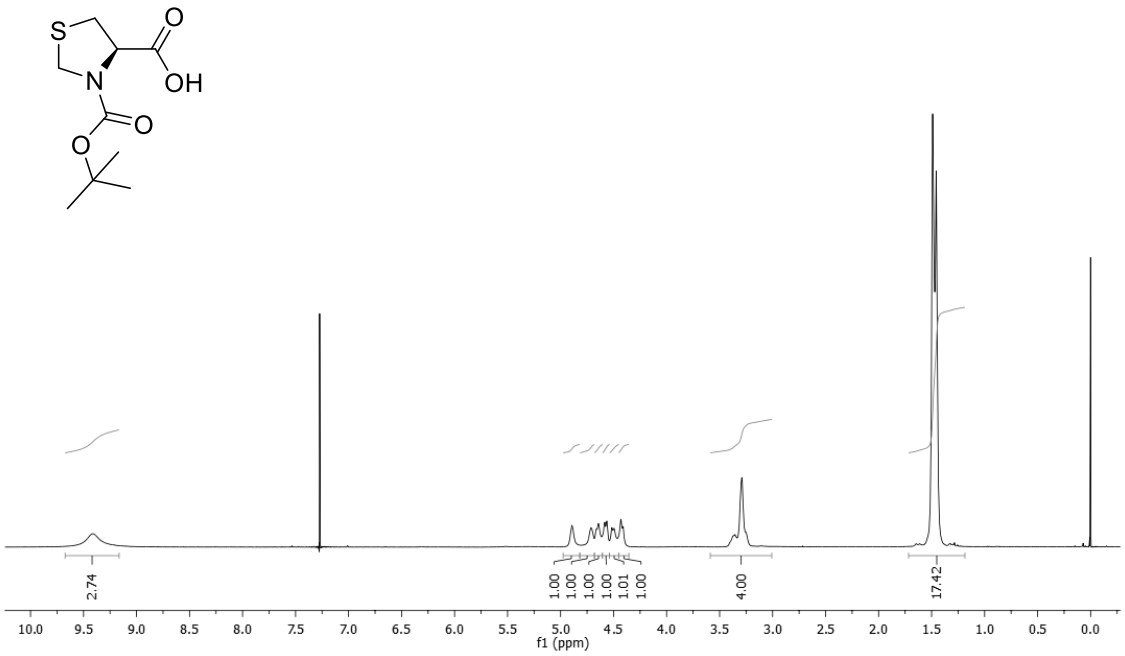


Figure S1. ^{1}H NMR spectrum for compound **a** ($CDCl_3$, 400 MHz).

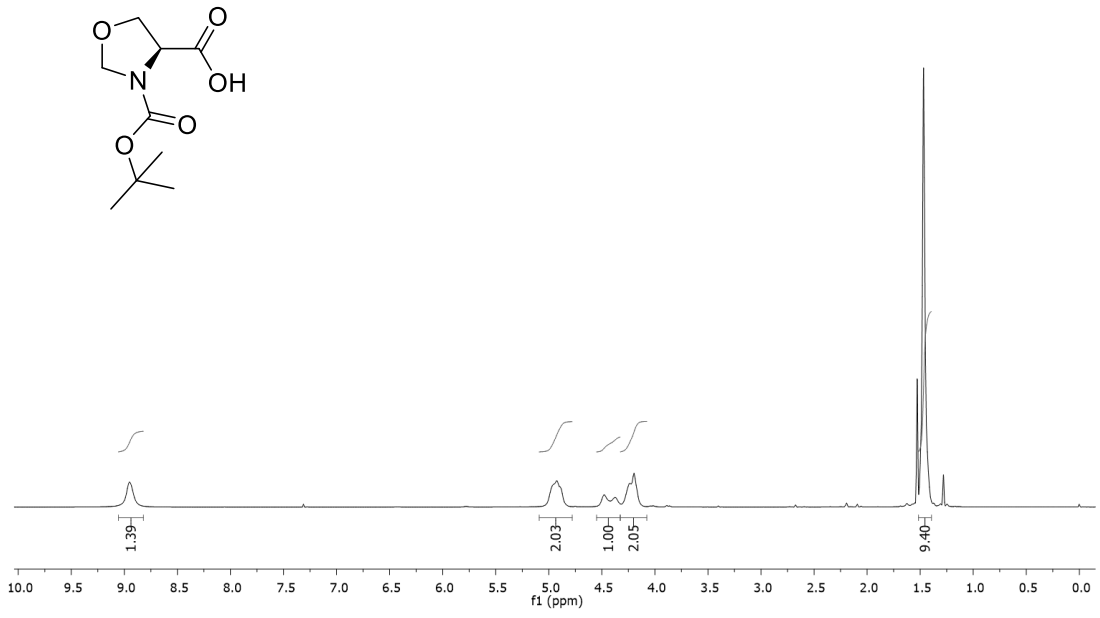


Figure S2. ^{1}H NMR spectrum for compound **b** ($CDCl_3$, 400 MHz).

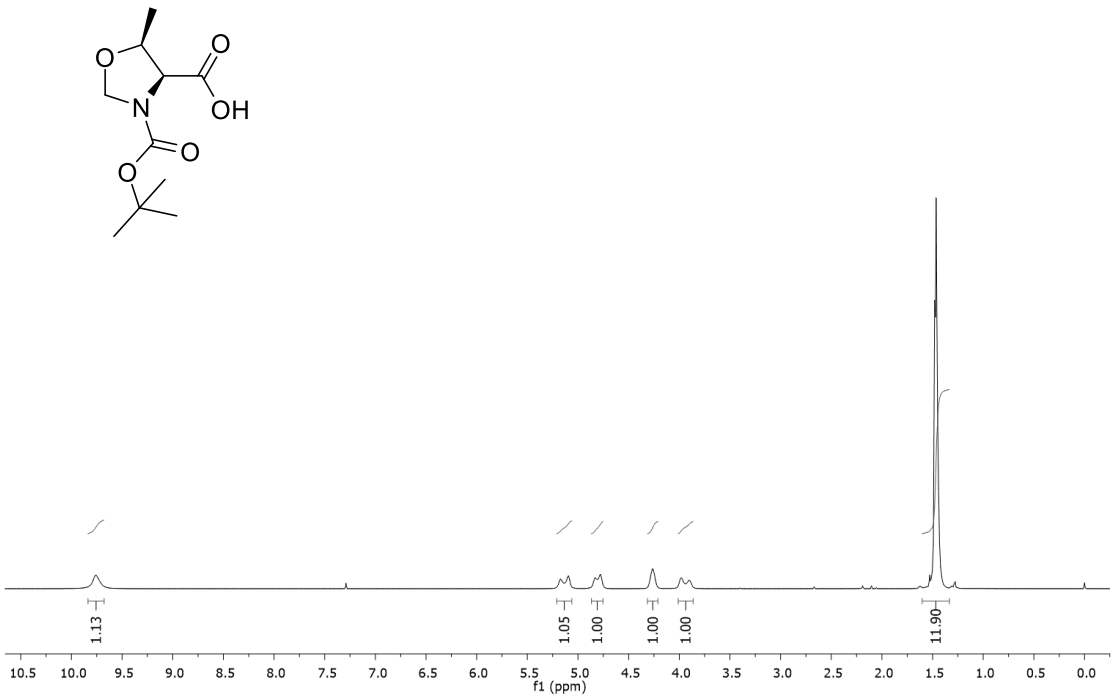


Figure S3. ^{1}H NMR spectrum for compound **c** ($CDCl_3$, 400 MHz).

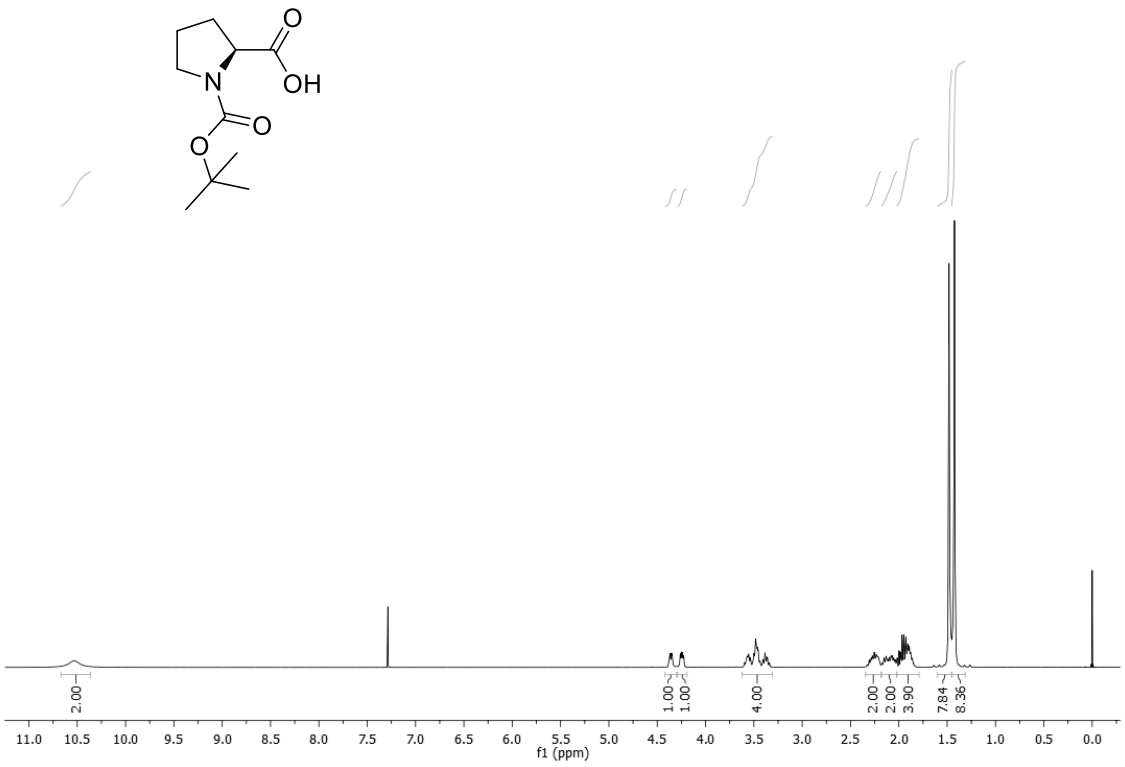


Figure S4. ^{1}H NMR spectrum for compound **d** ($CDCl_3$, 400 MHz).

9. NMR and IR-ATR spectra of compounds 1 to 4

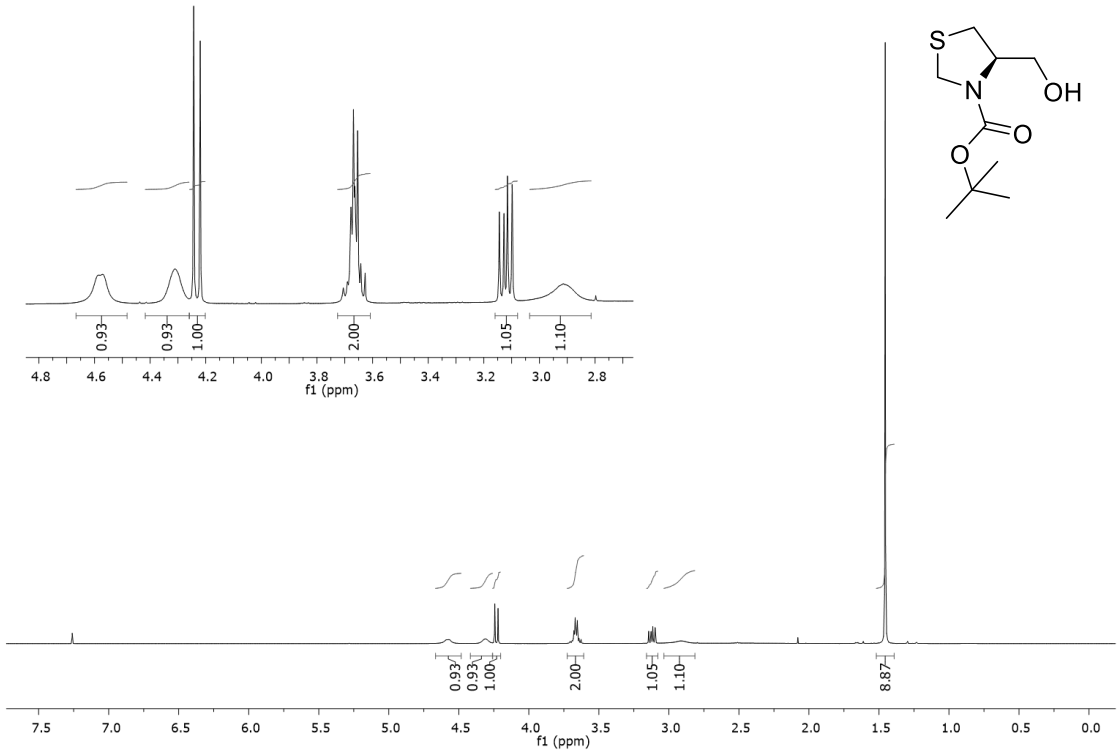


Figure S5. ^{1}H NMR spectrum for compound **1** ($CDCl_3$, 400 MHz).

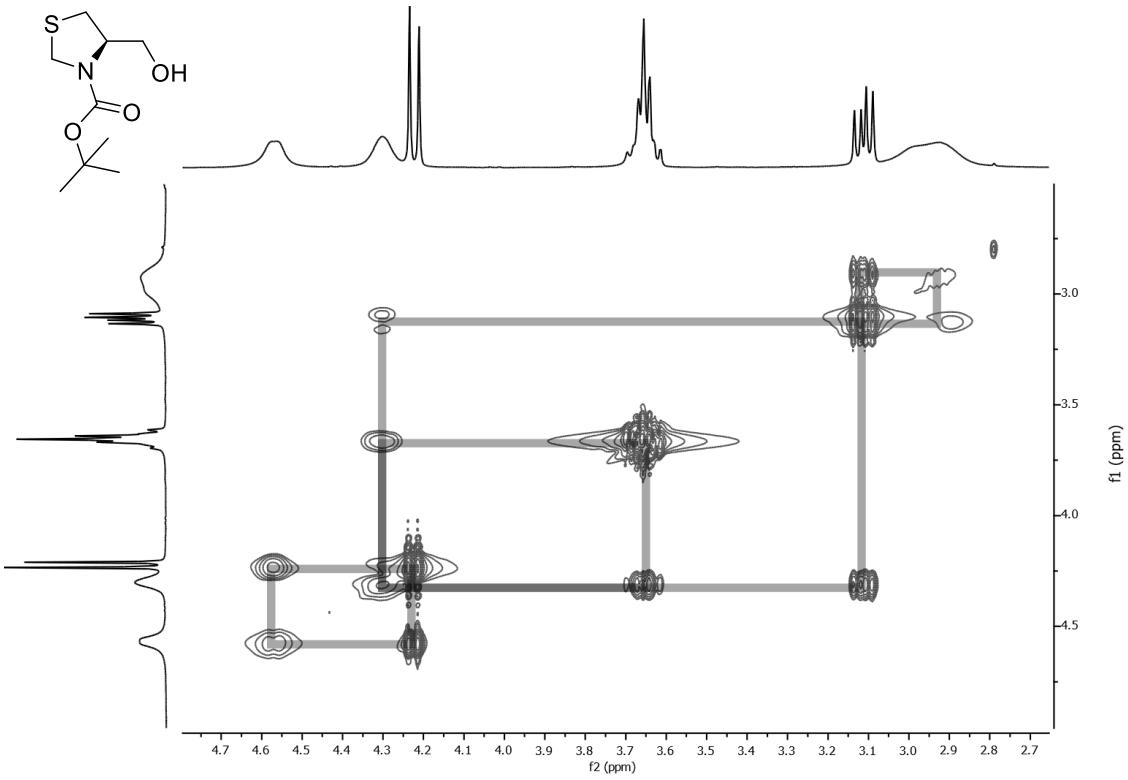


Figure S6. ^{1}H-^{1}H COSY spectrum for compound **1** ($CDCl_3$, 400 MHz).

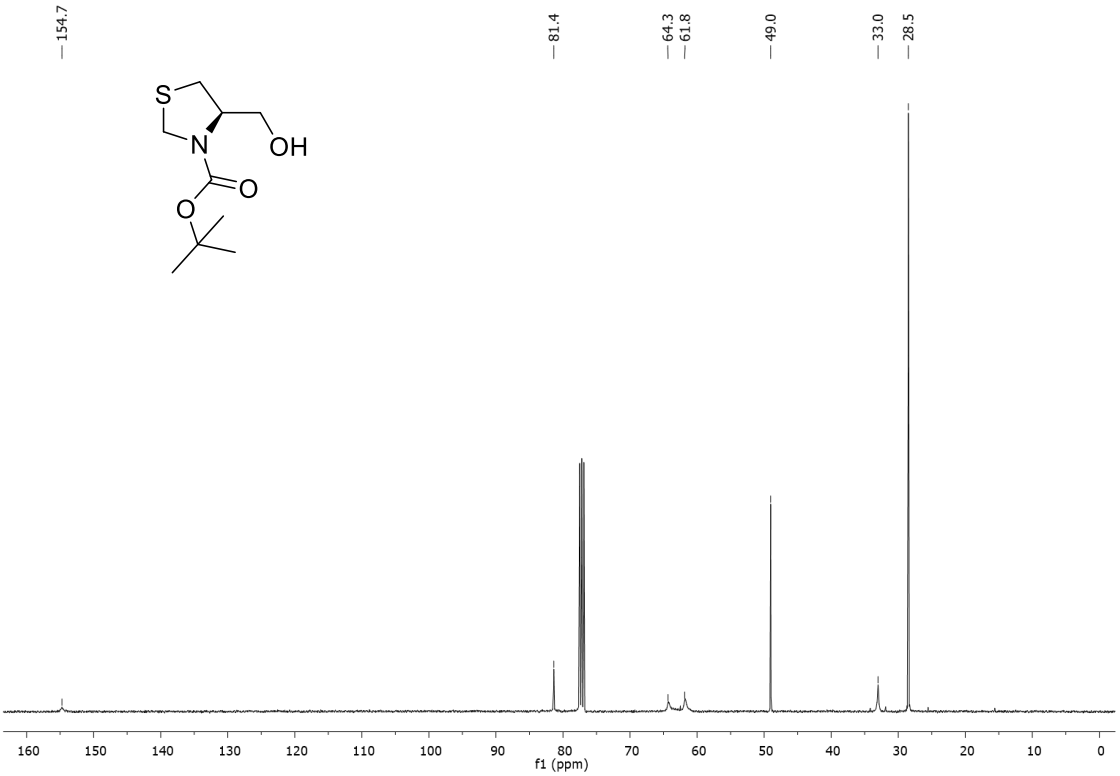


Figure S7. ^{13}C NMR spectrum for compound **1** ($CDCl_3$, 100 MHz).

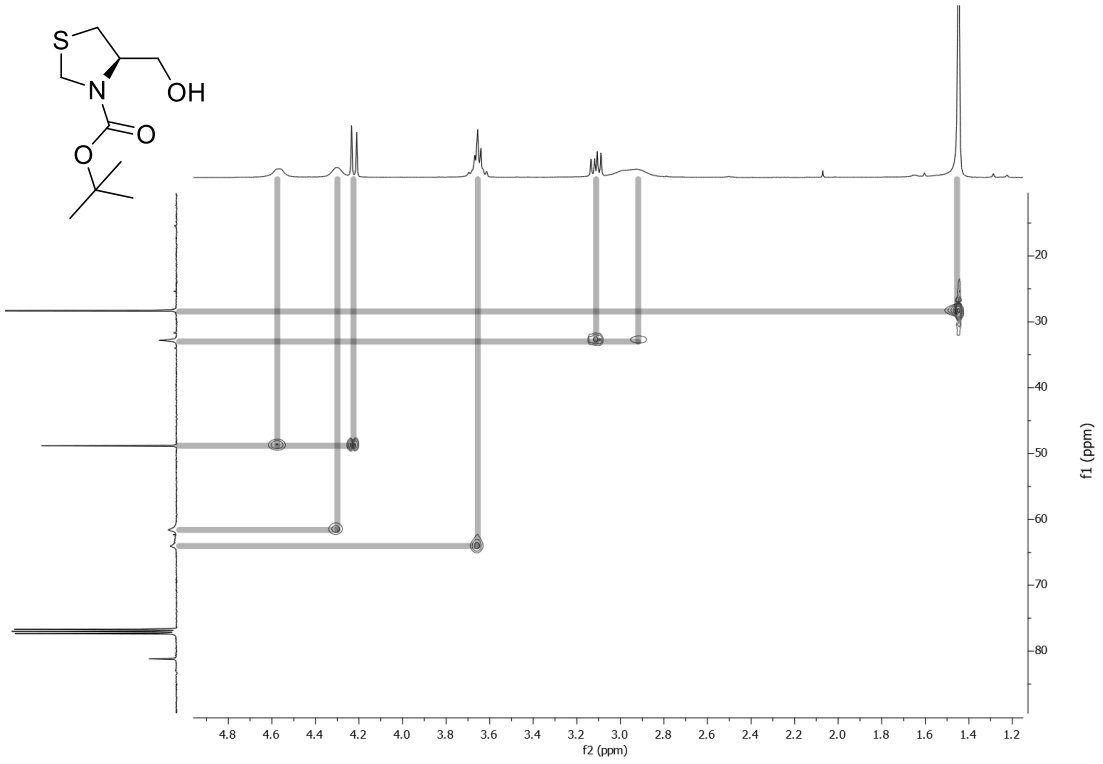


Figure S8. ^{1}H-^{13}C HSQC spectrum for compound **1** ($CDCl_3$, 400 MHz).

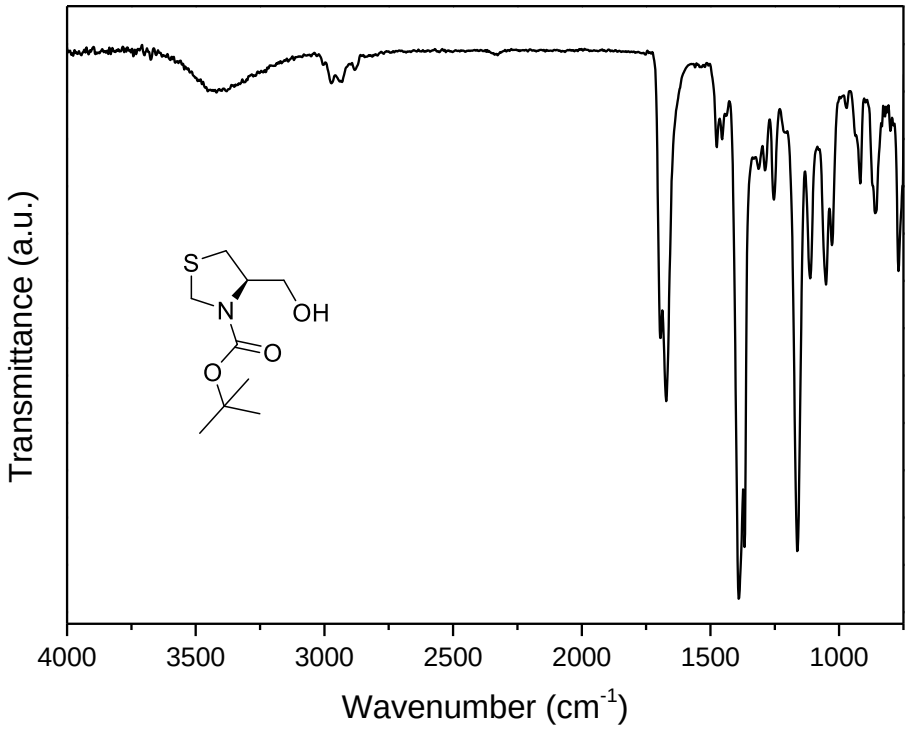


Figure S9. IR-ATR spectrum for compound **1**.

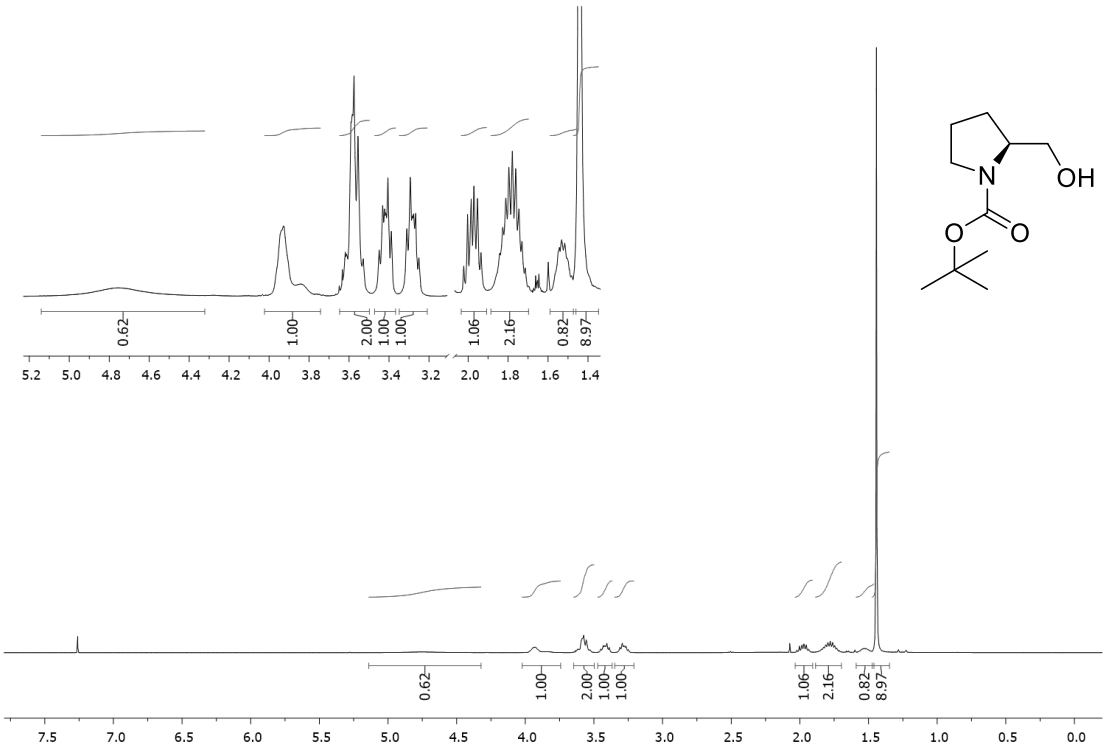


Figure S10. ^{1}H NMR spectrum for compound **2** ($CDCl_3$, 400 MHz).

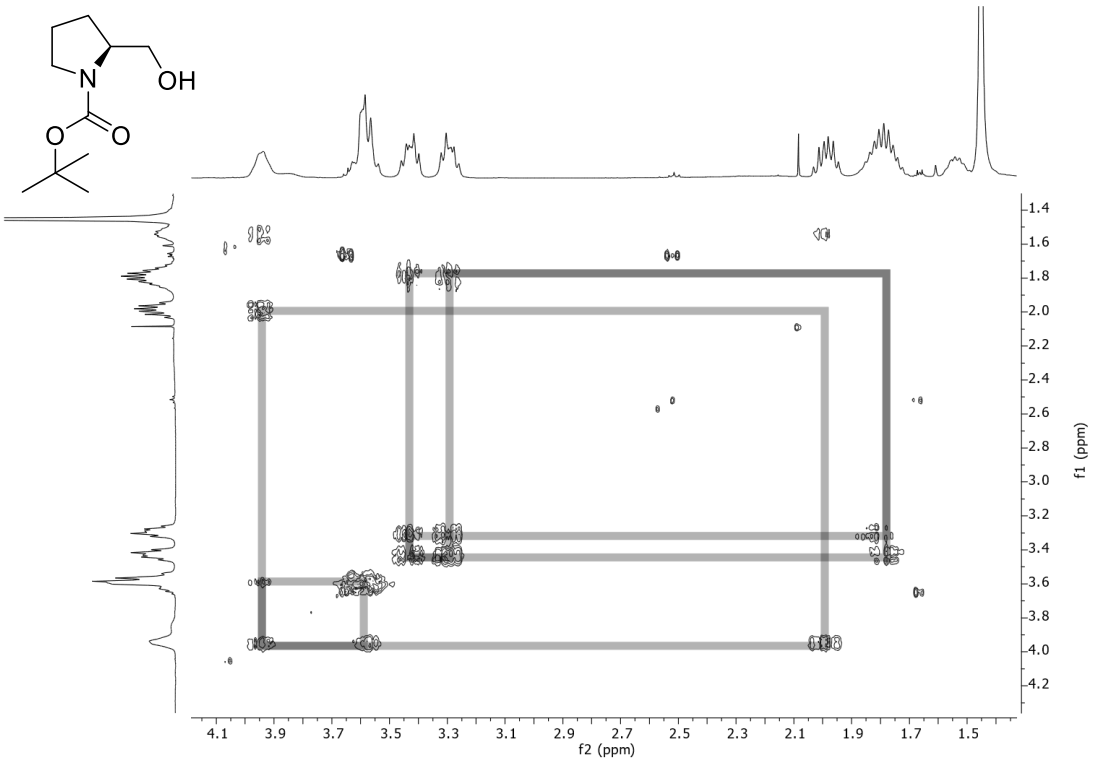


Figure S11. ^{1}H-^{1}H COSY spectrum for compound **2** ($CDCl_3$, 400 MHz).

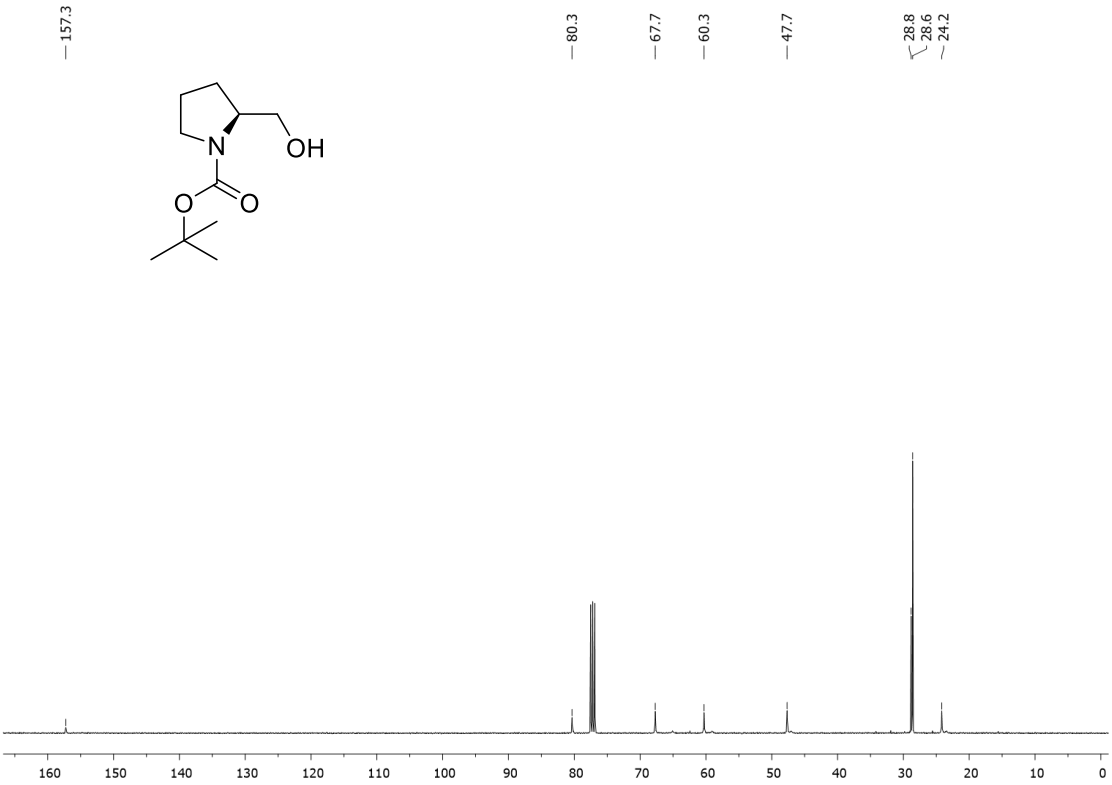


Figure S12. ^{13}C NMR spectrum for compound **2** ($CDCl_3$, 100 MHz).

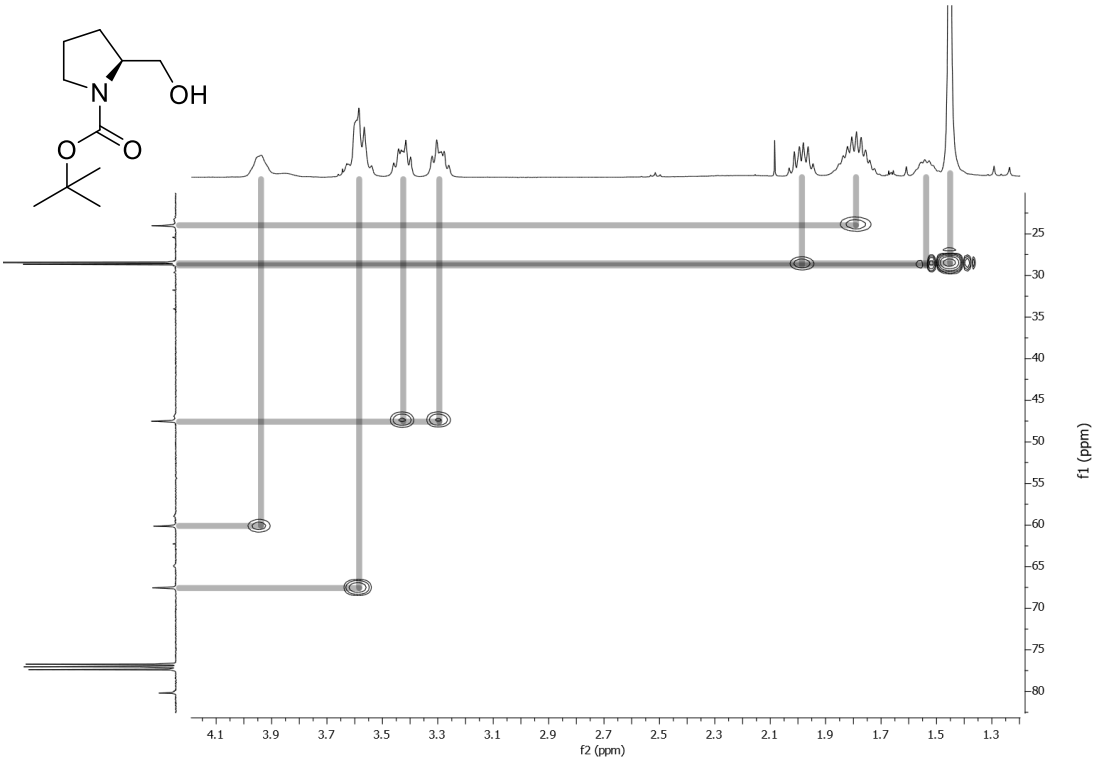


Figure S13. ^{1}H-^{13}C HSQC spectrum for compound **2** ($CDCl_3$, 400 MHz).

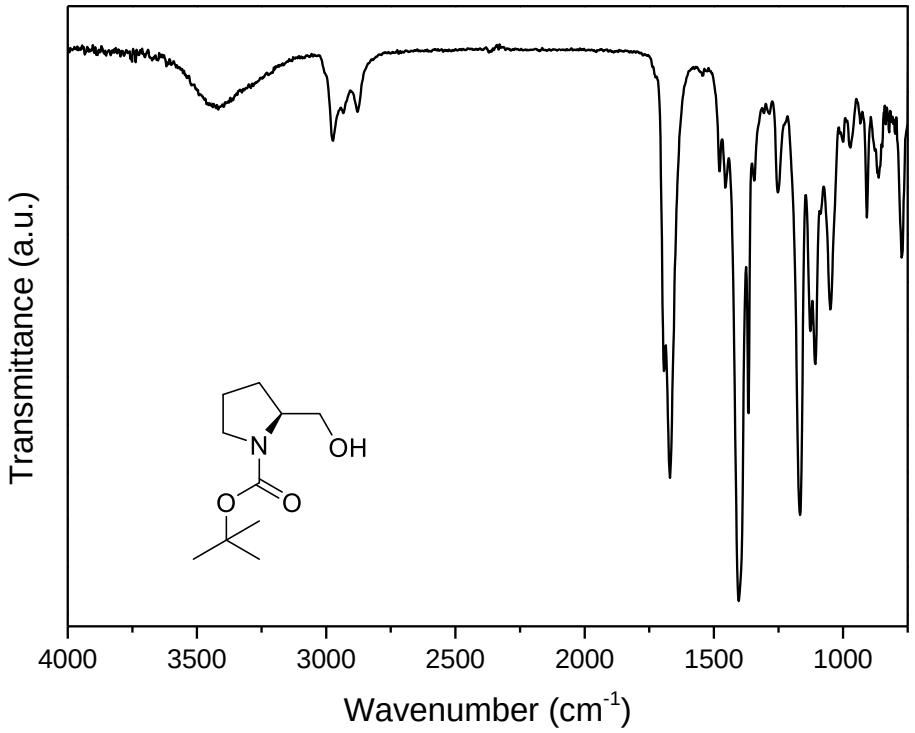


Figure S14. IR-ATR spectrum for compound **2**.

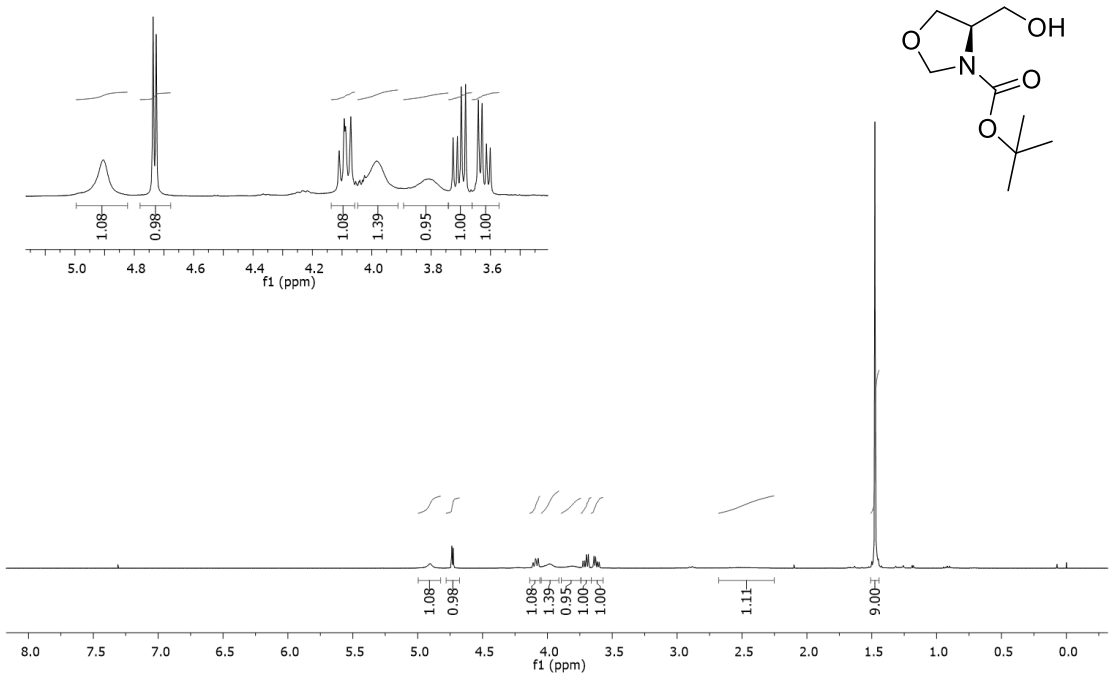


Figure S15. ^{1}H NMR spectrum for compound **3** ($CDCl_3$, 400 MHz).

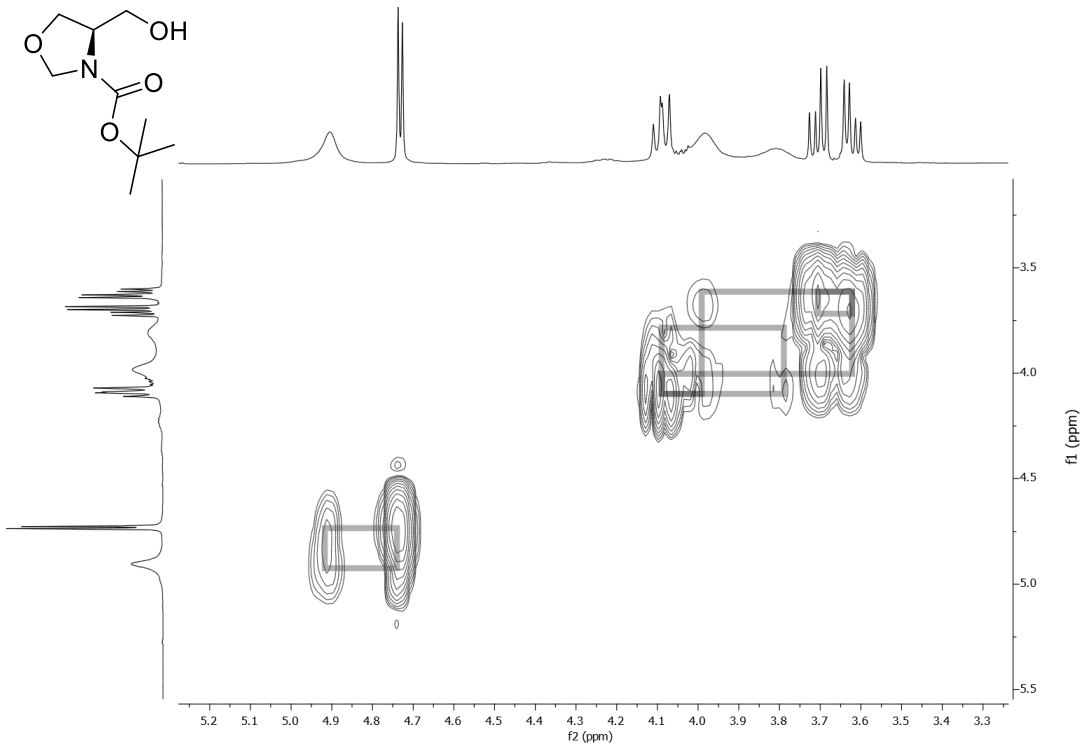


Figure S16. ^{1}H-^{1}H COSY spectrum for compound **3** ($CDCl_3$, 400 MHz).

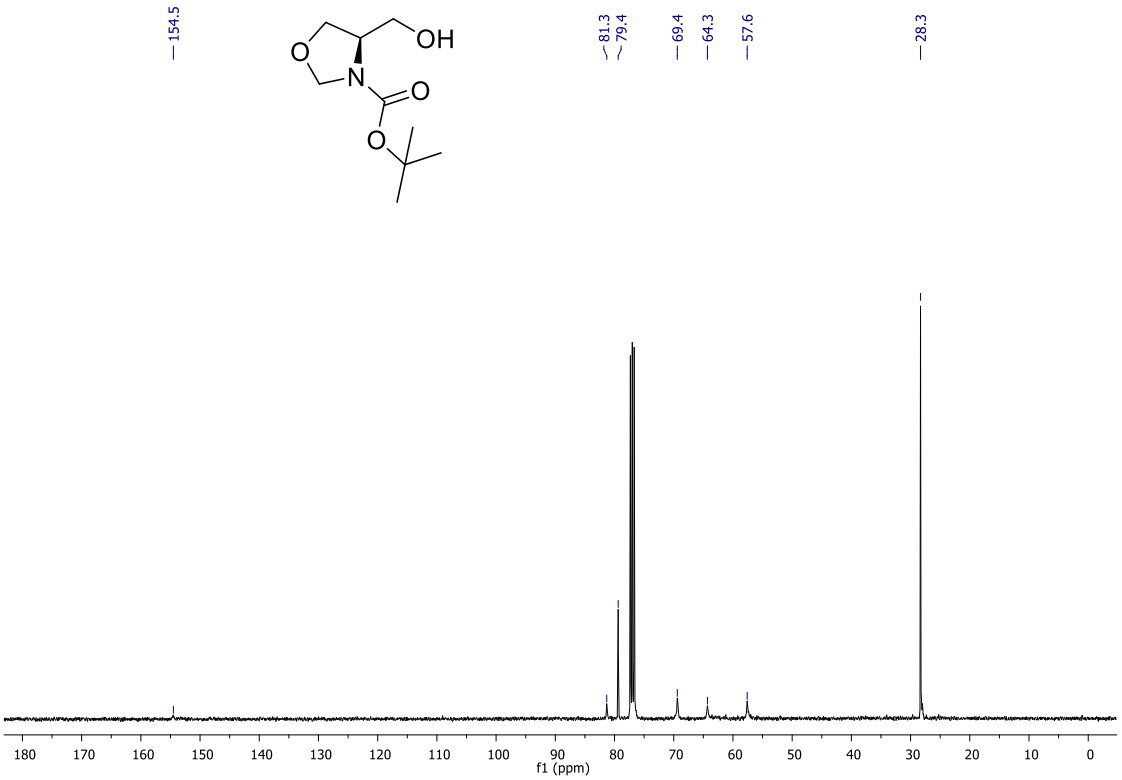


Figure S17. ^{13}C NMR spectrum for compound **3** ($CDCl_3$, 100 MHz).

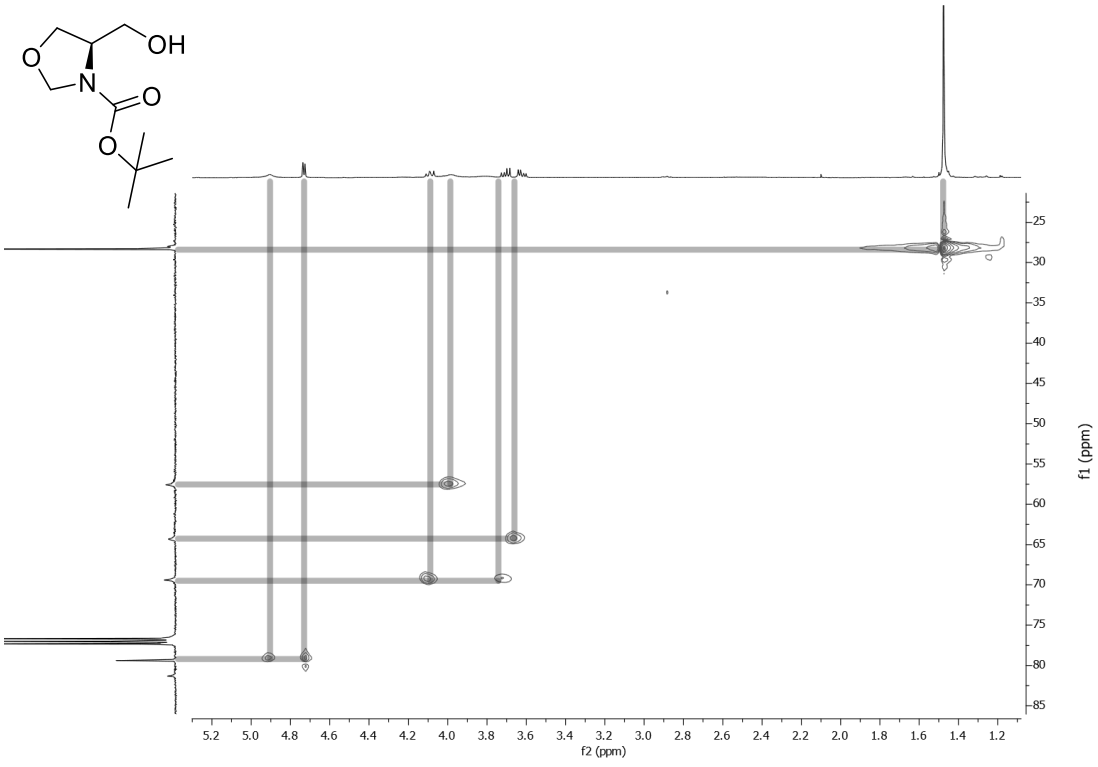


Figure S18. ^{1}H-^{13}C HSQC spectrum for compound **3** ($CDCl_3$, 400 MHz).

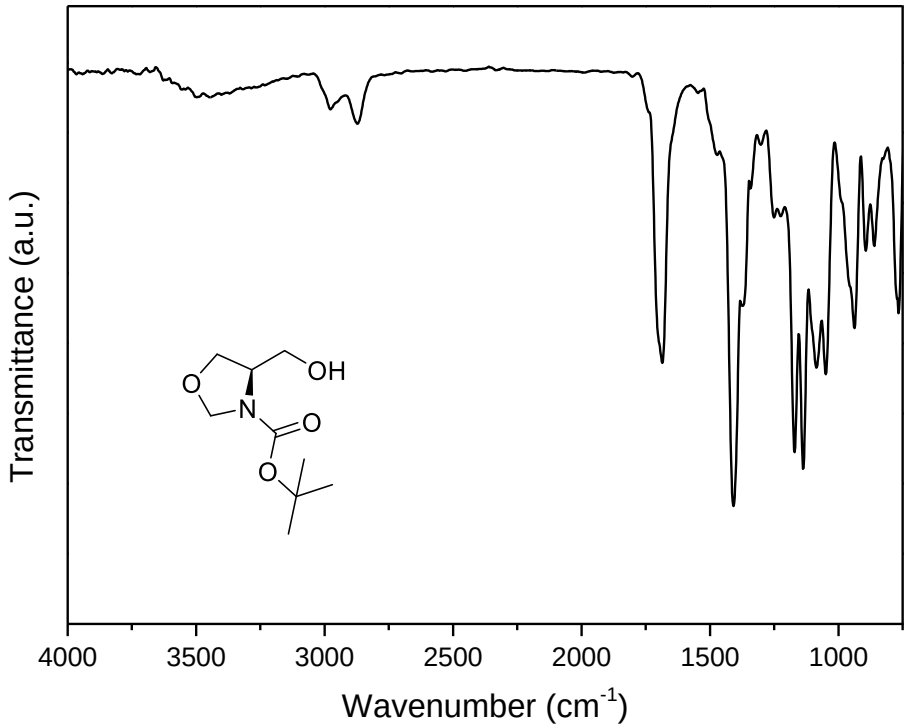


Figure S19. IR-ATR spectrum for compound **3**.

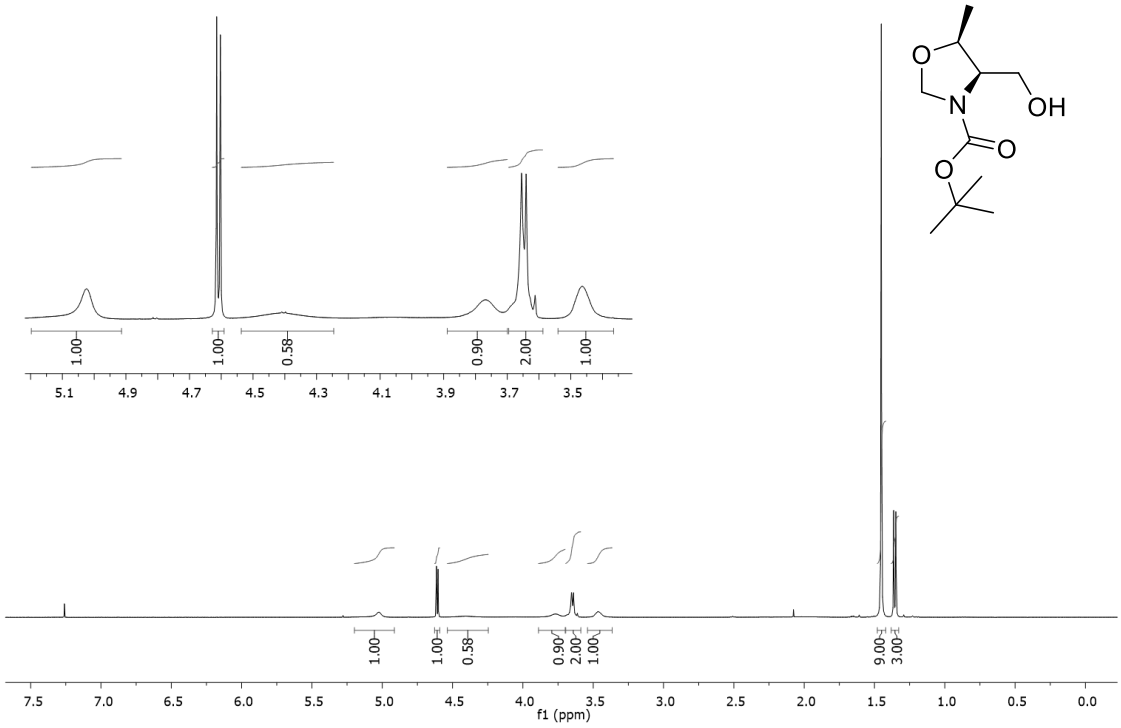


Figure S20. ^{1}H NMR spectrum for compound **4** ($CDCl_3$, 400 MHz).

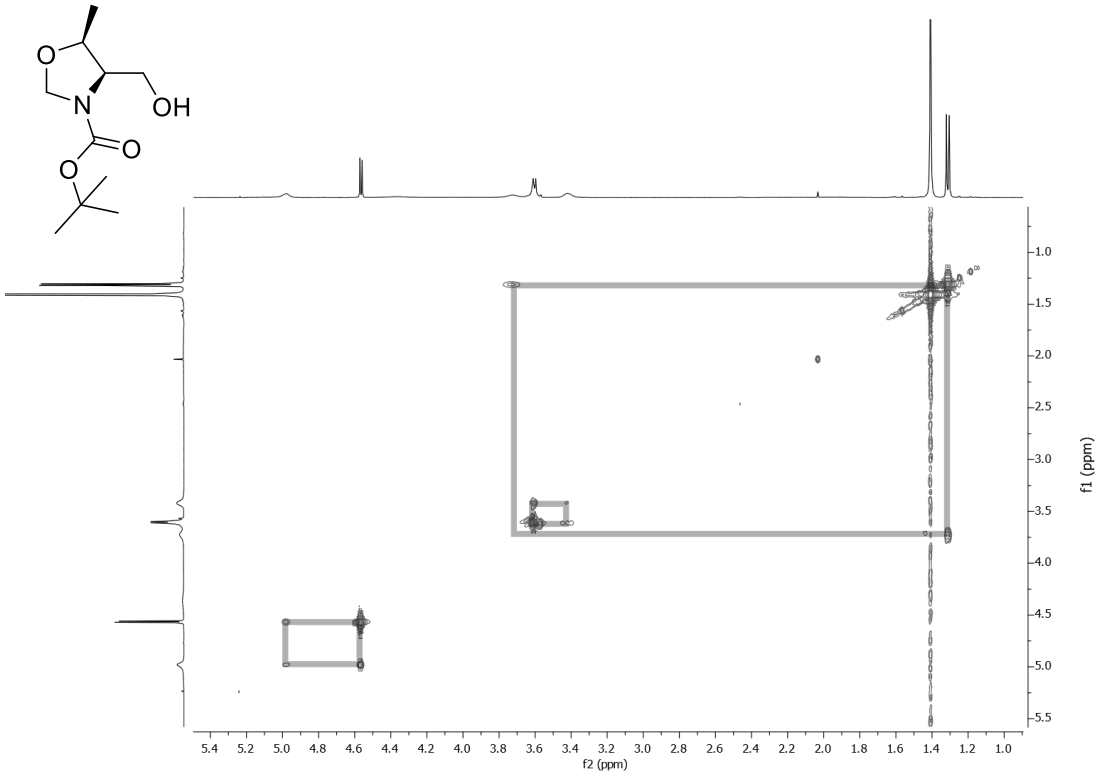


Figure S21. ^{1}H-^{1}H COSY spectrum for compound **4** ($CDCl_3$, 400 MHz).

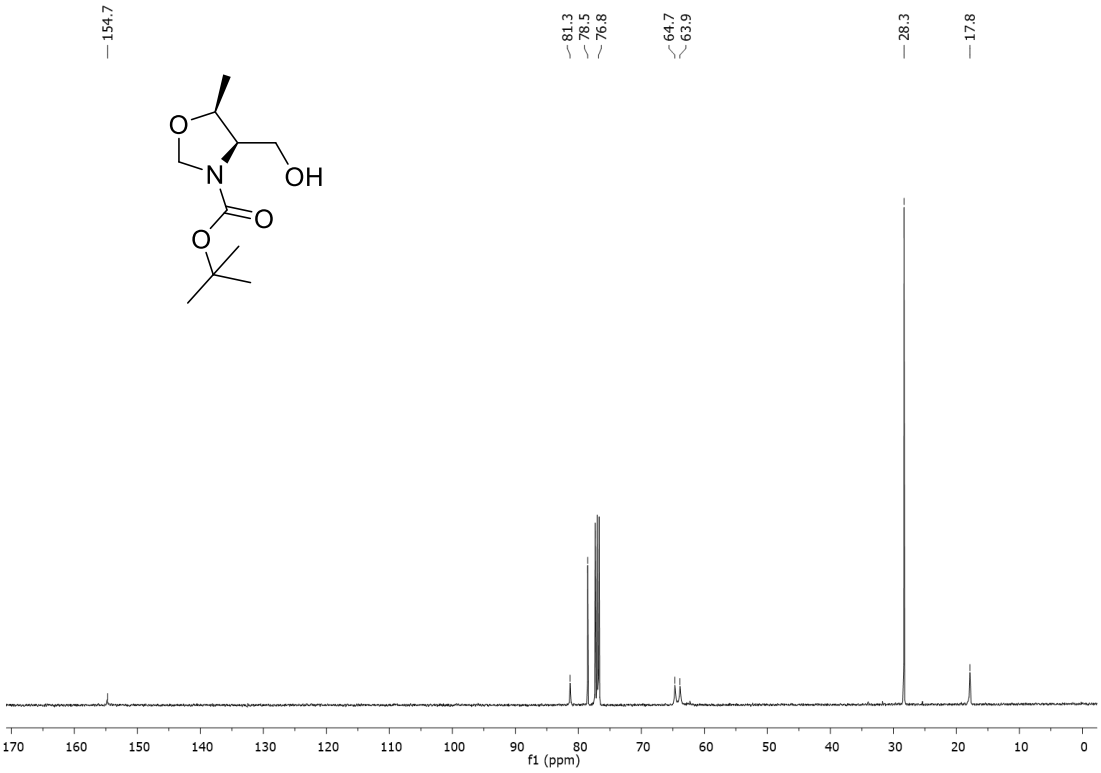


Figure S22. ^{13}C NMR spectrum for compound **4** ($CDCl_3$, 100 MHz).

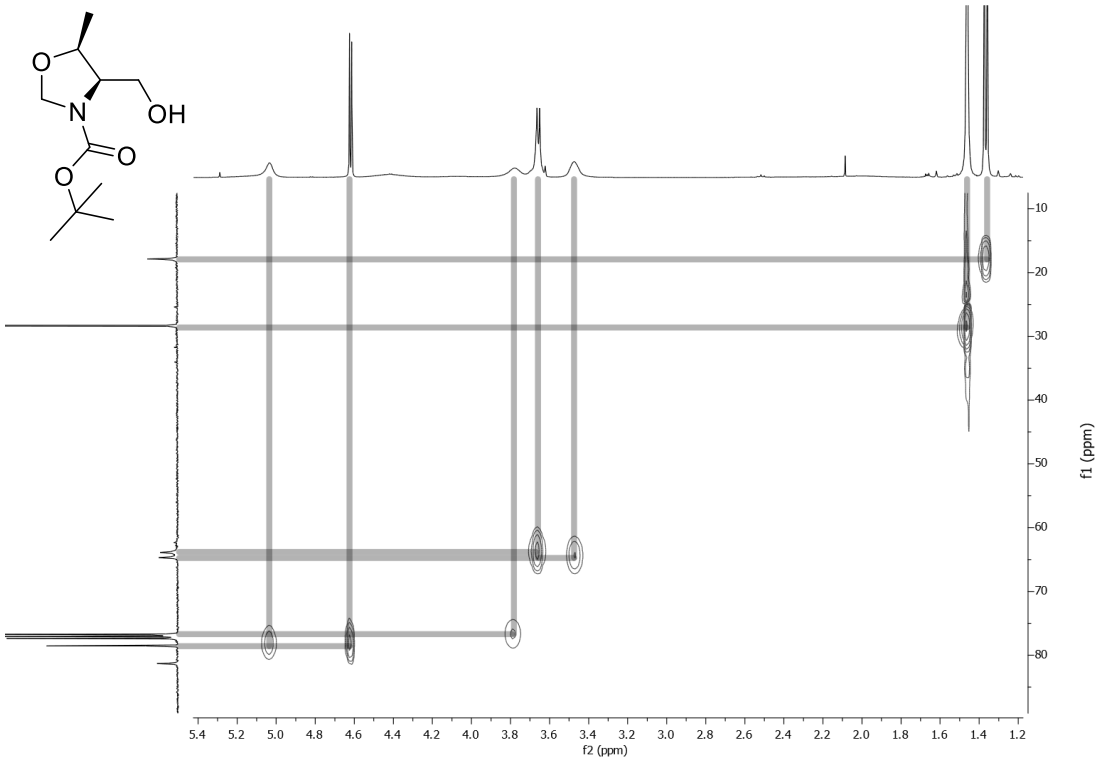


Figure S23. ^{1}H-^{13}C HSQC spectrum for compound **4** ($CDCl_3$, 400 MHz).

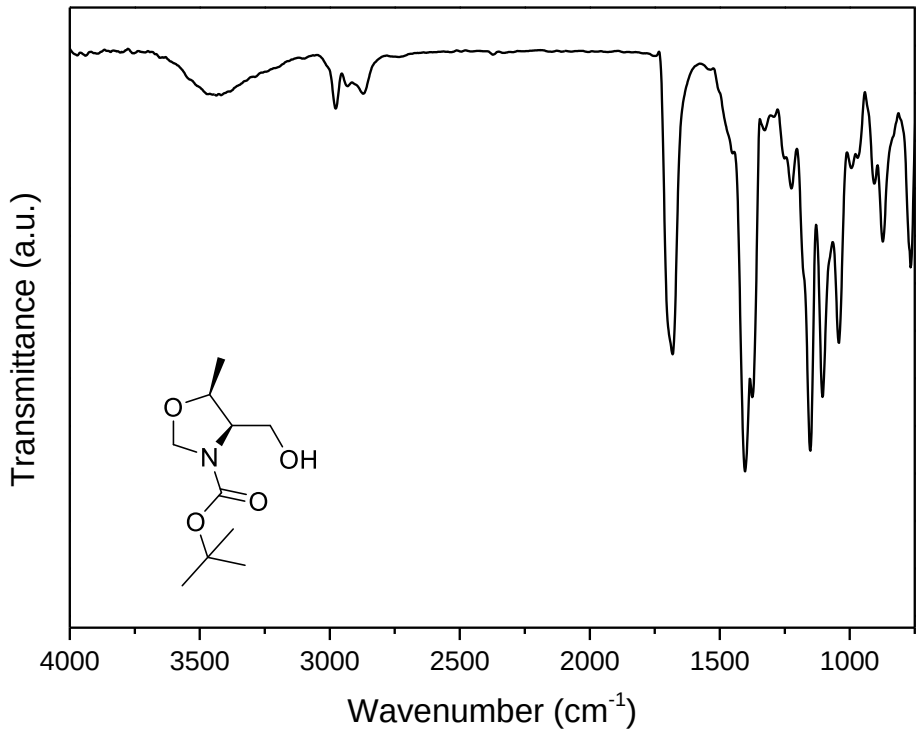


Figure S24. IR-ATR spectrum for compound **4**.

10. NMR and IR-ATR spectra of compounds 5 to 8

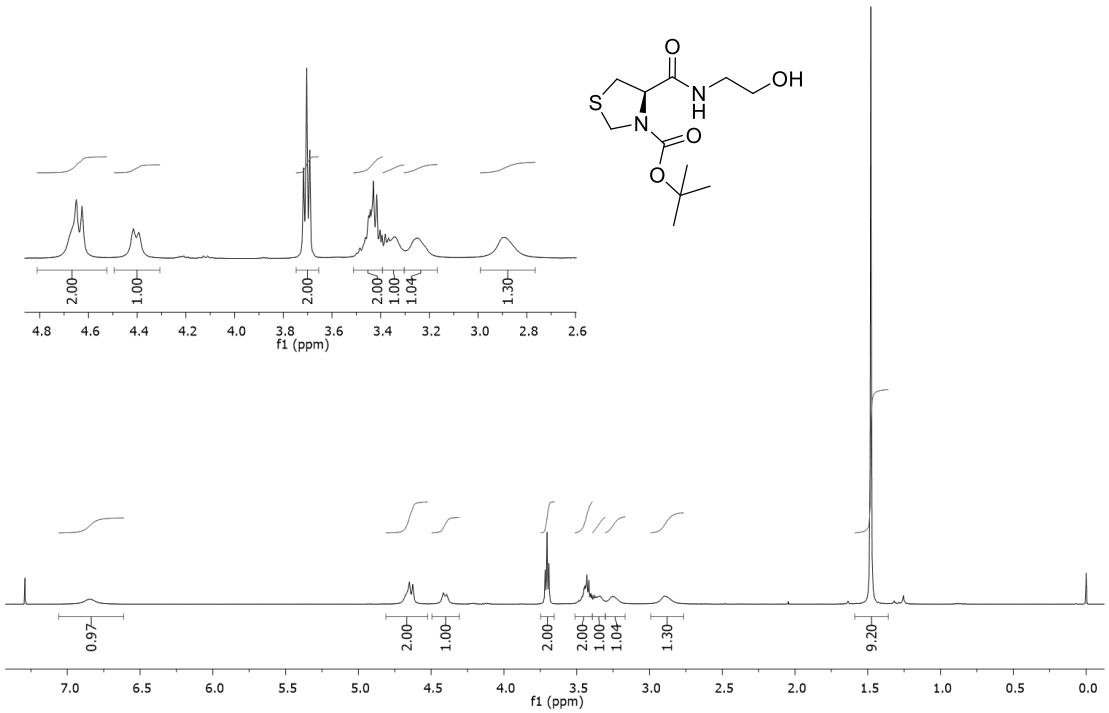


Figure S25. ^{1}H NMR spectrum for compound **5** ($CDCl_3$, 400 MHz).

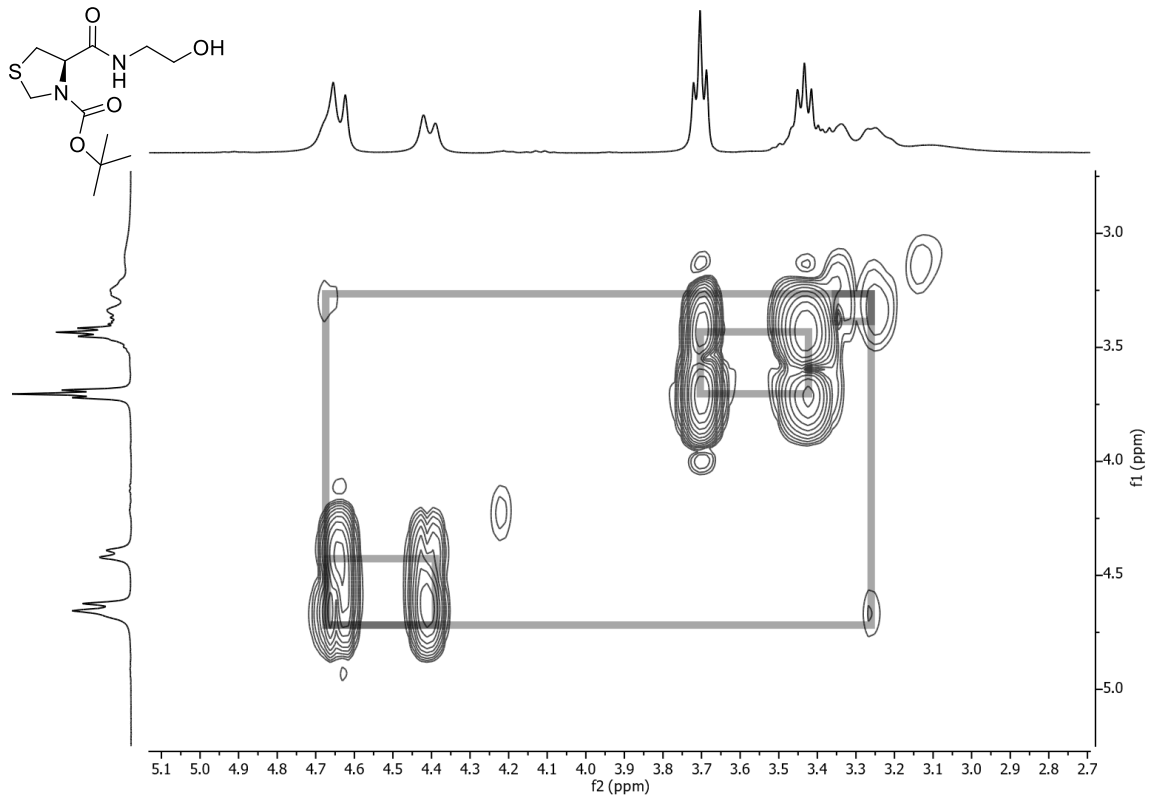


Figure S26. ^{1}H-^{1}H COSY spectrum for compound **5** ($CDCl_3$, 400 MHz).

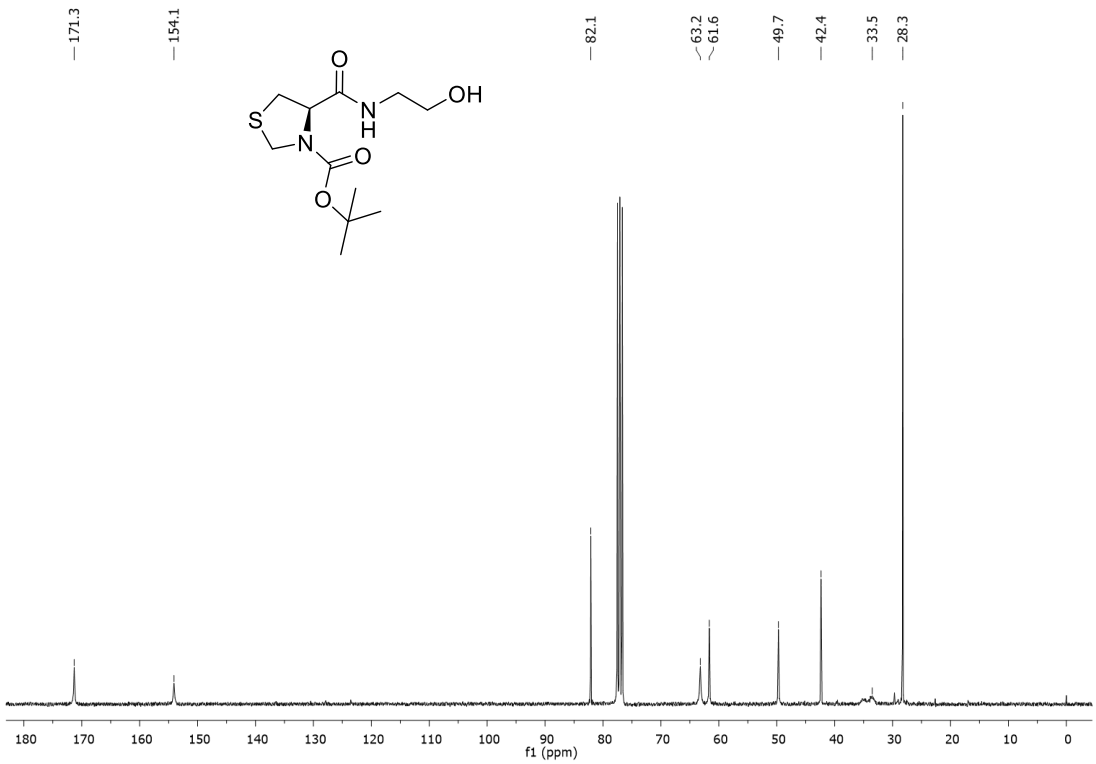


Figure S27. ^{13}C NMR spectrum for compound **5** ($CDCl_3$, 100 MHz).

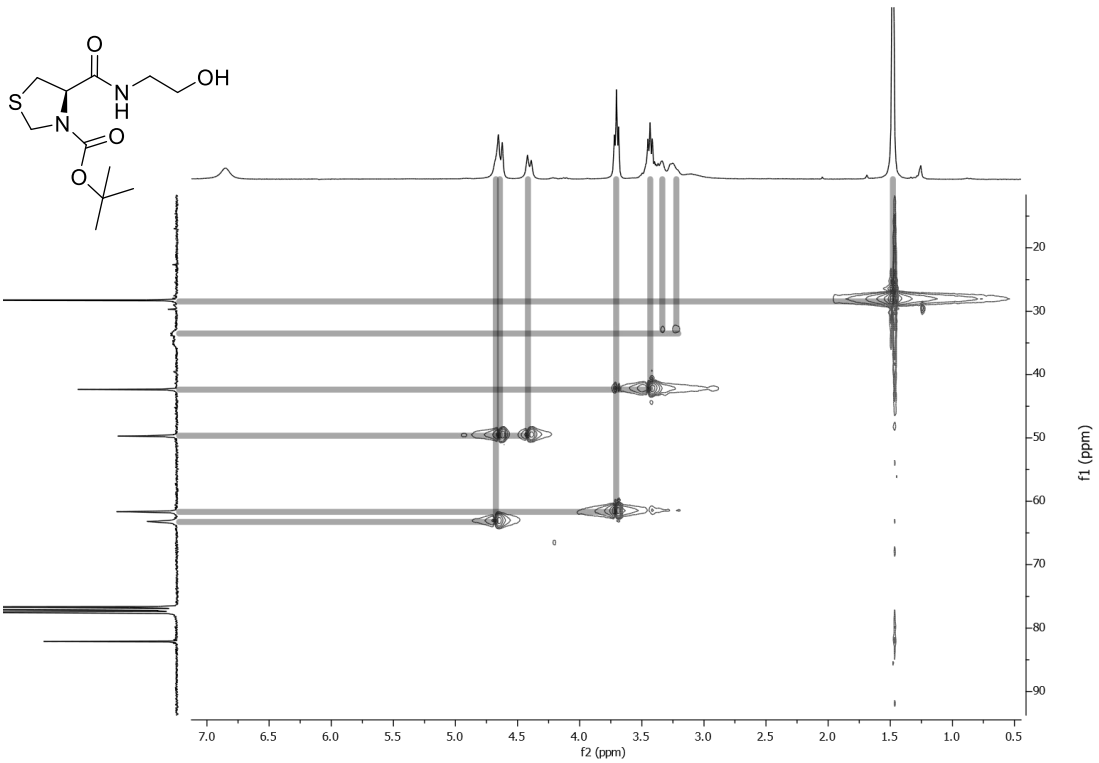


Figure S28. ^{1}H-^{13}C HSQC spectrum for compound **5** ($CDCl_3$, 400 MHz).

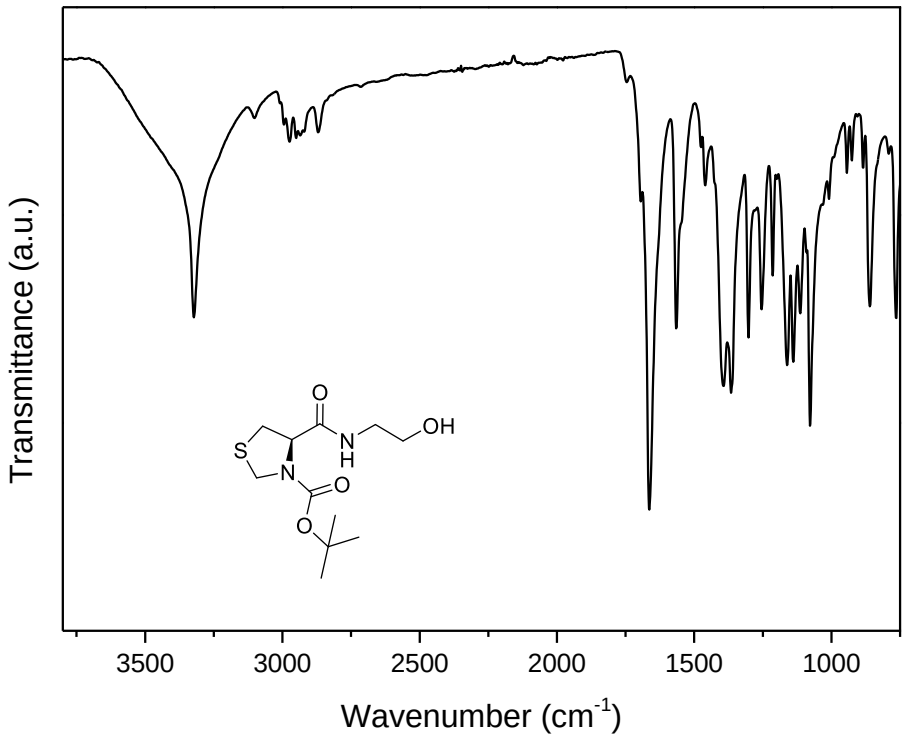


Figure S29. IR-ATR spectrum for compound **5**.

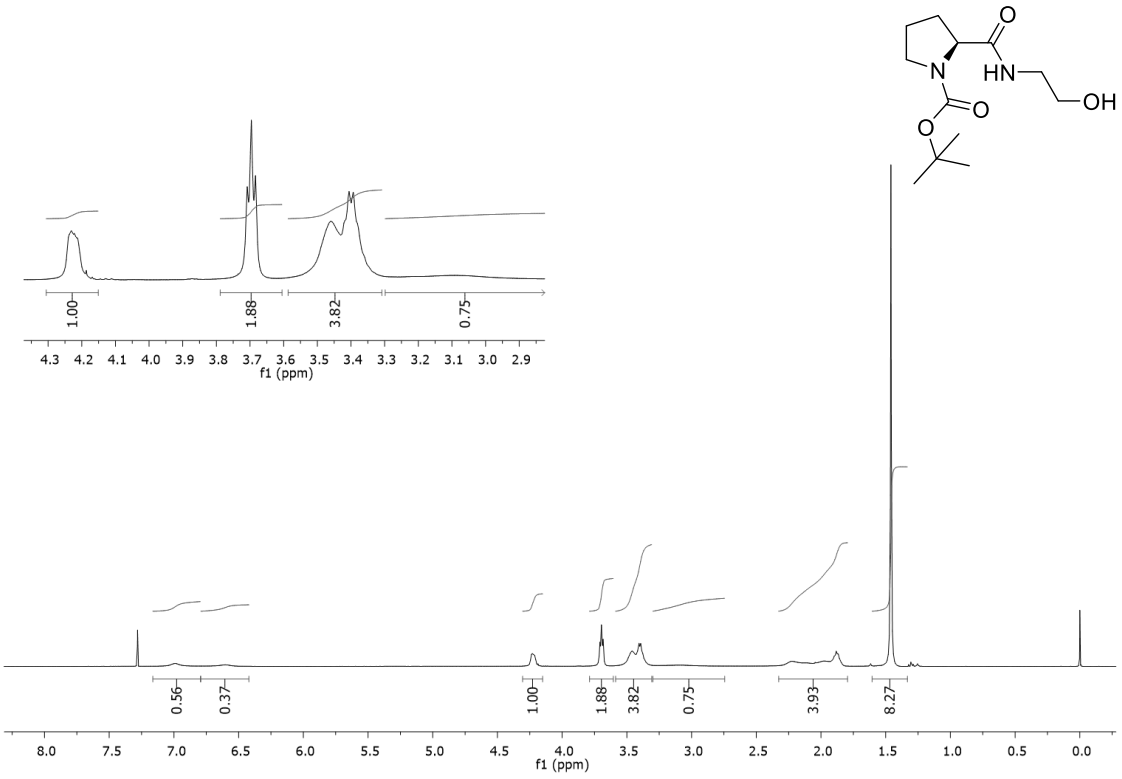


Figure S30. ^{1}H NMR spectrum for compound **6** ($CDCl_3$, 400 MHz).

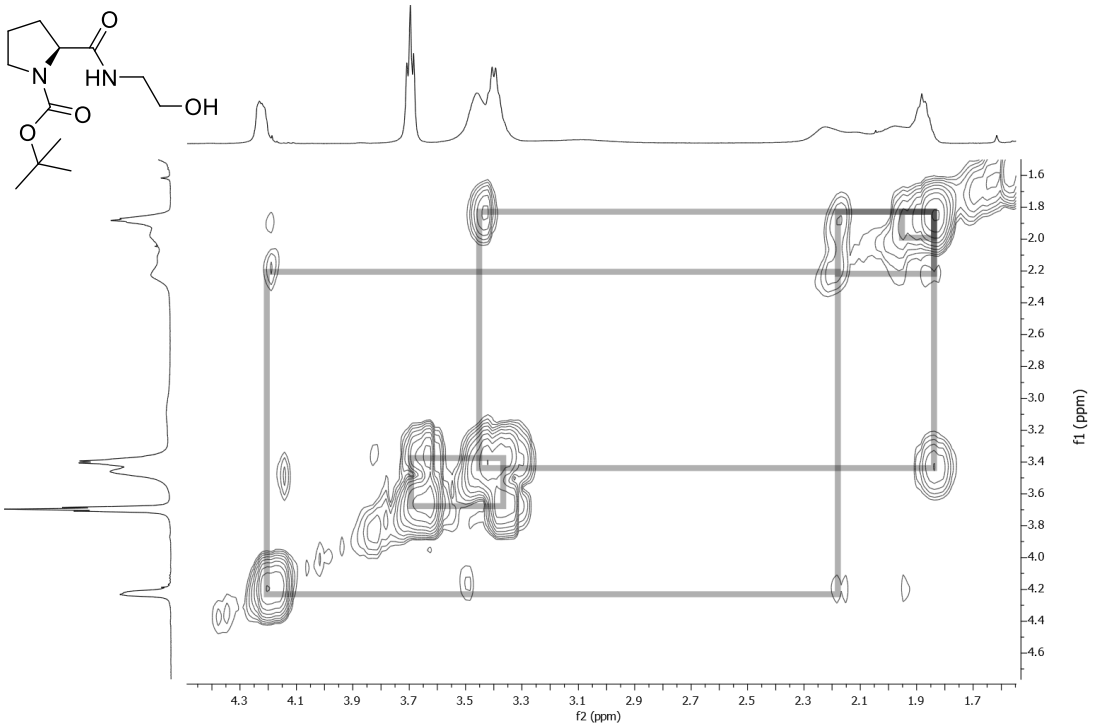


Figure S31. ^{1}H-^{1}H COSY spectrum for compound **6** ($CDCl_3$, 400 MHz).

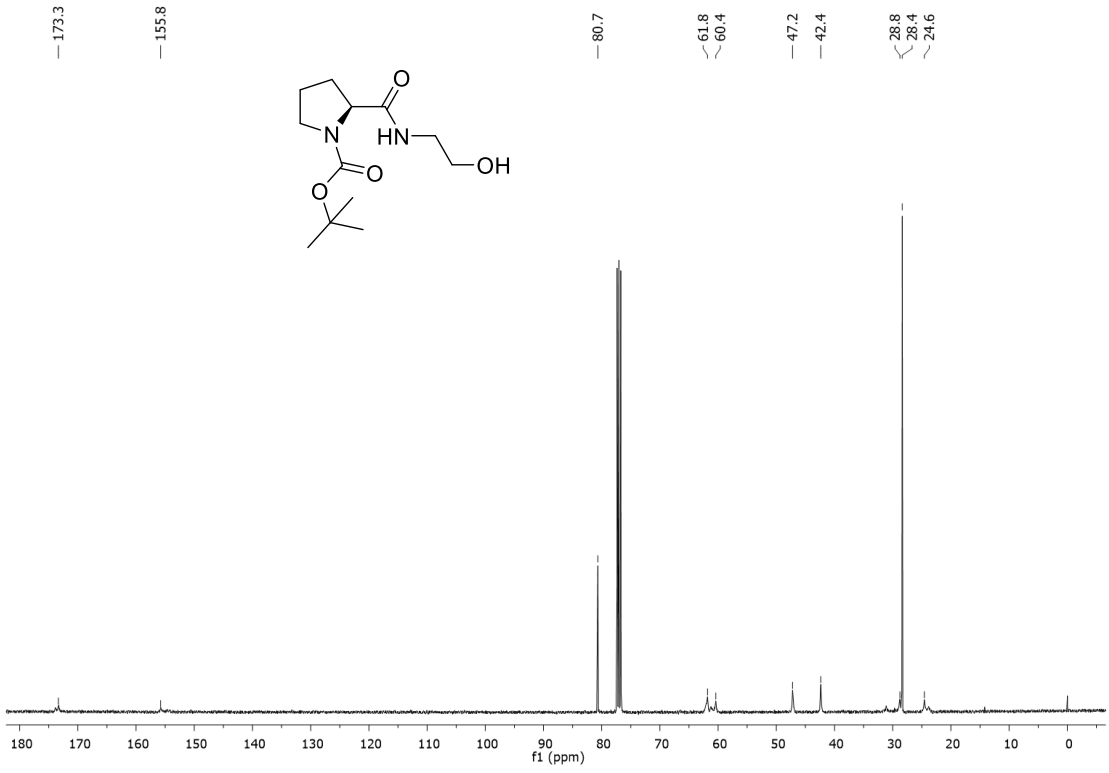


Figure S32. ^{13}C NMR spectrum for compound **6** ($CDCl_3$, 100 MHz).

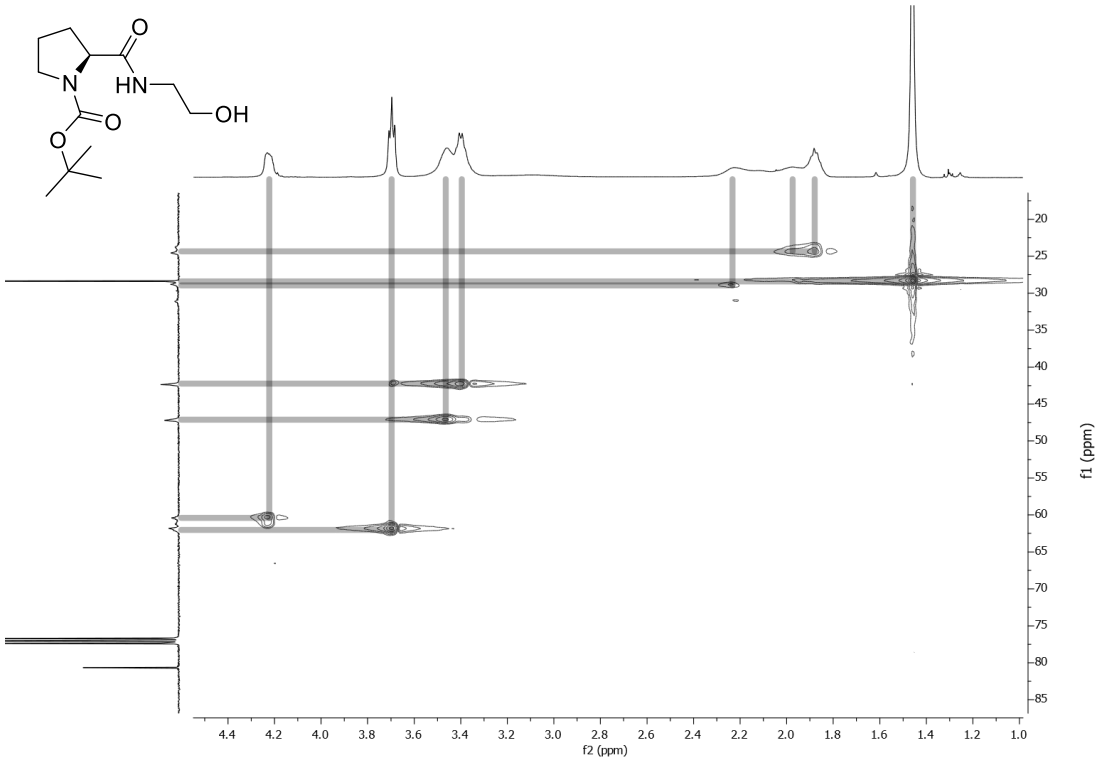


Figure S33. ^{1}H-^{13}C HSQC spectrum for compound **6** ($CDCl_3$, 400 MHz).

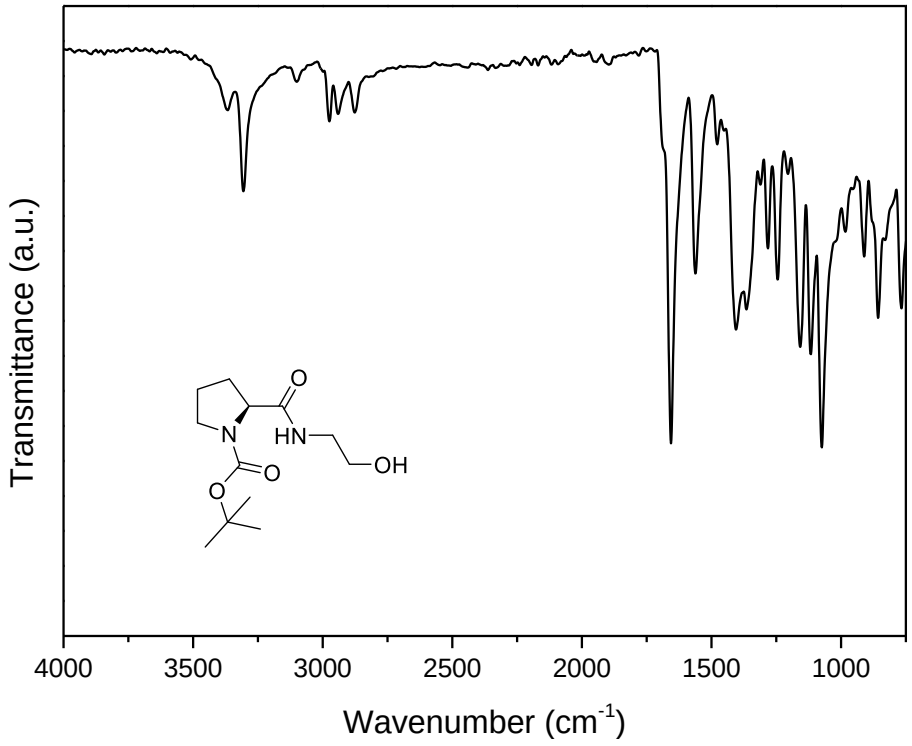


Figure S34. IR-ATR spectrum for compound **6**.

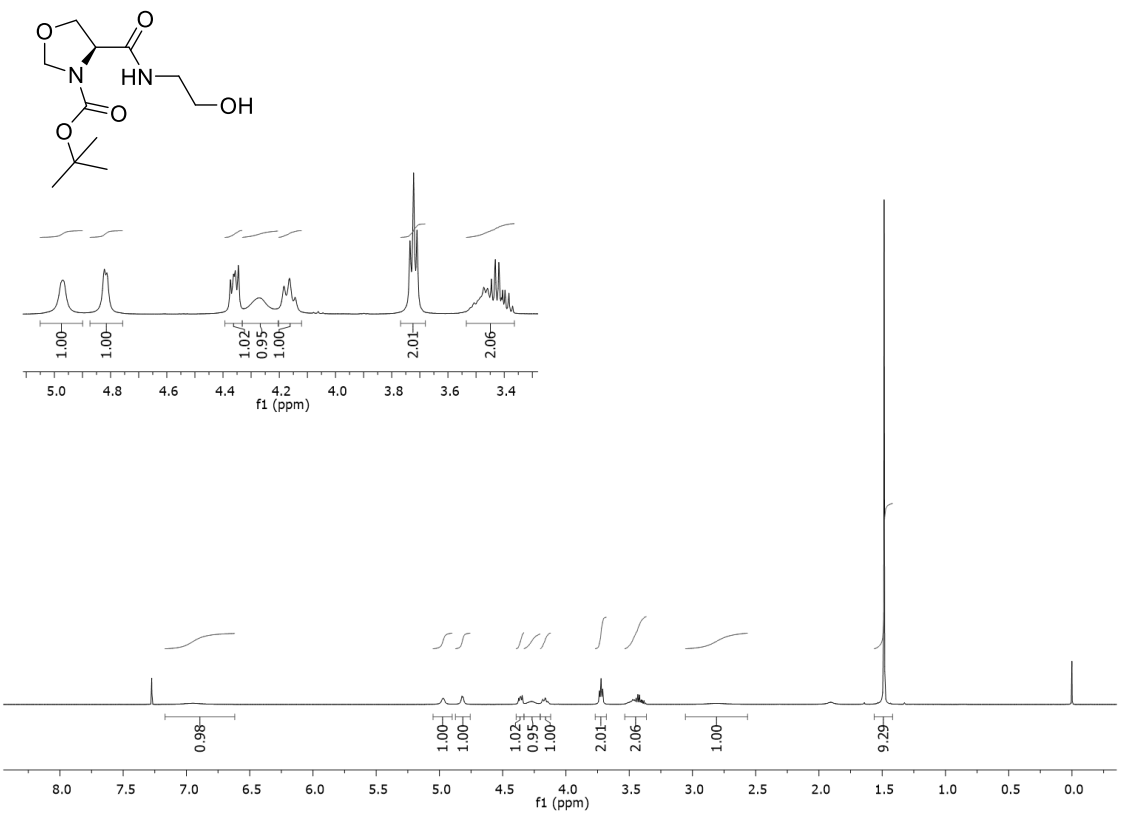


Figure S35. ^{1}H NMR spectrum for compound **7** ($CDCl_3$, 400 MHz).

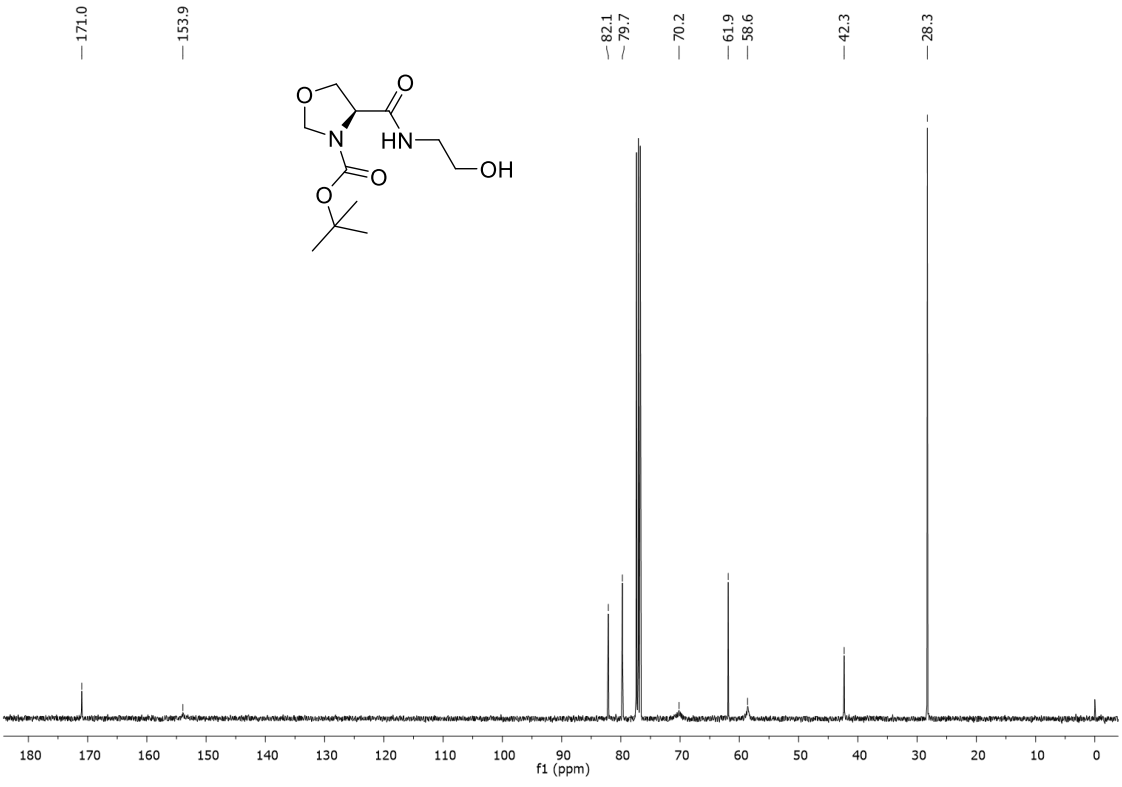


Figure S36. ^{13}C NMR spectrum for compound **7** ($CDCl_3$, 100 MHz).

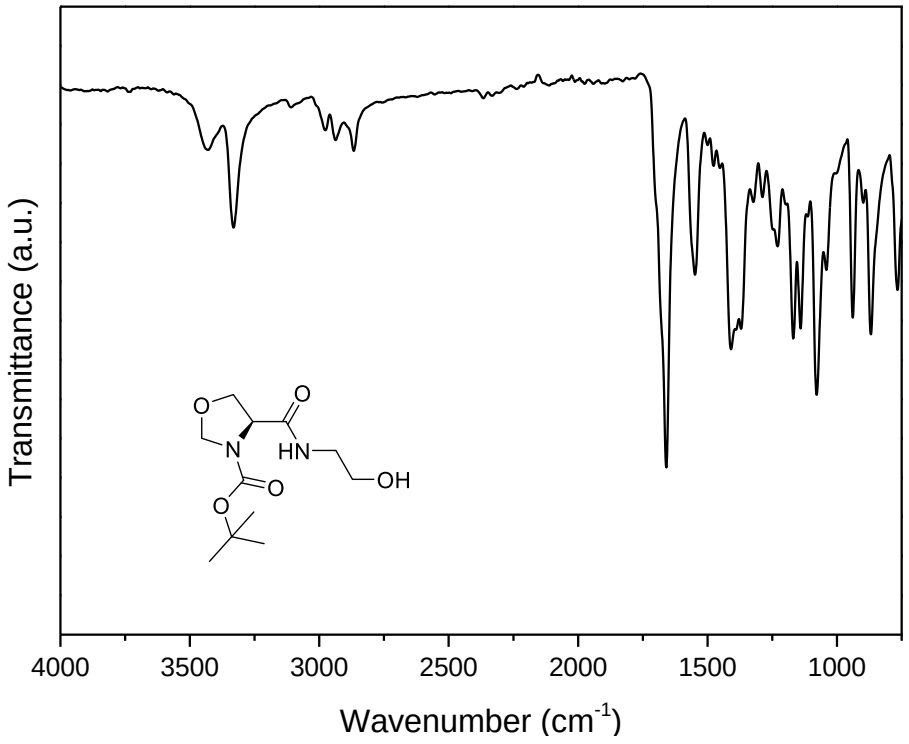


Figure S37. IR-ATR spectrum for compound **7**.

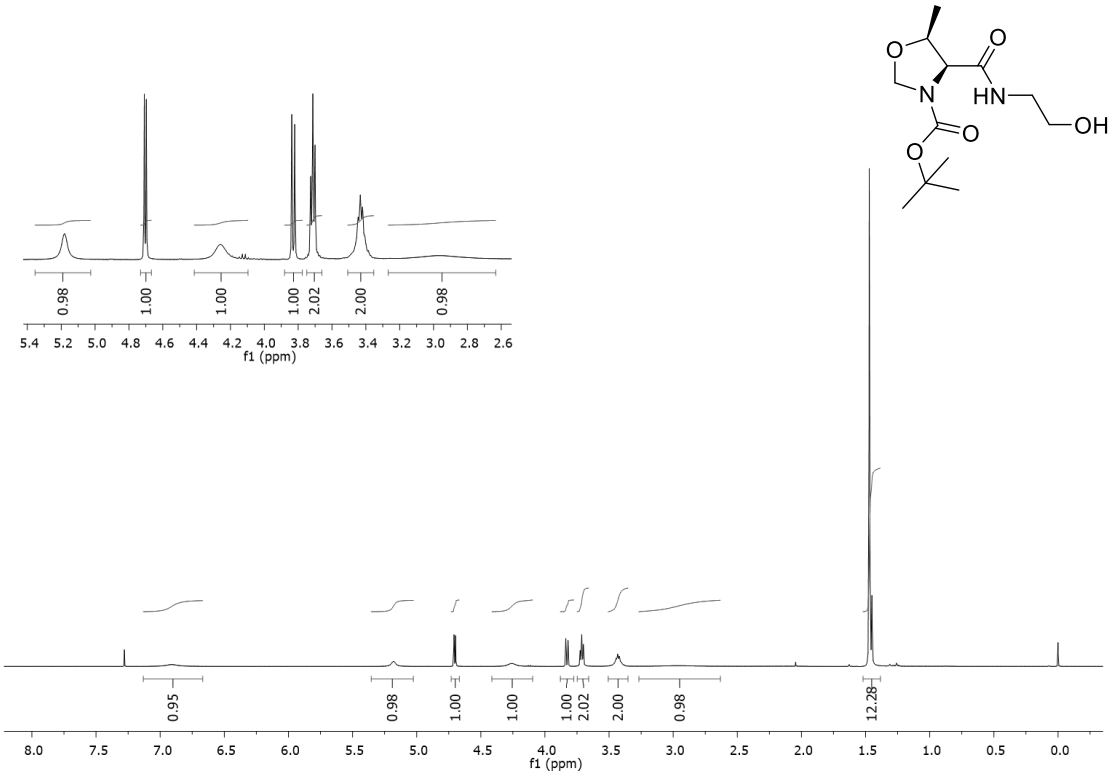


Figure S38. ^{1}H NMR spectrum for compound **8** ($CDCl_3$, 400 MHz).

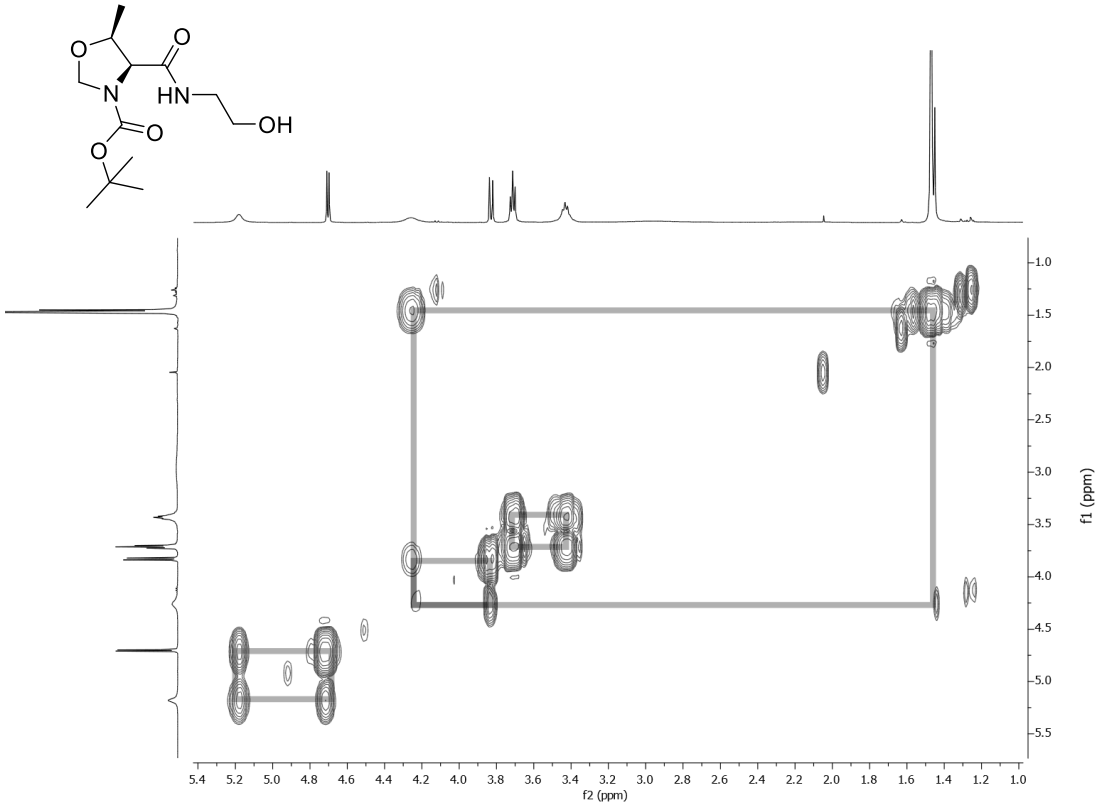


Figure S39. ^{1}H-^{1}H COSY spectrum for compound **8** ($CDCl_3$, 400 MHz).

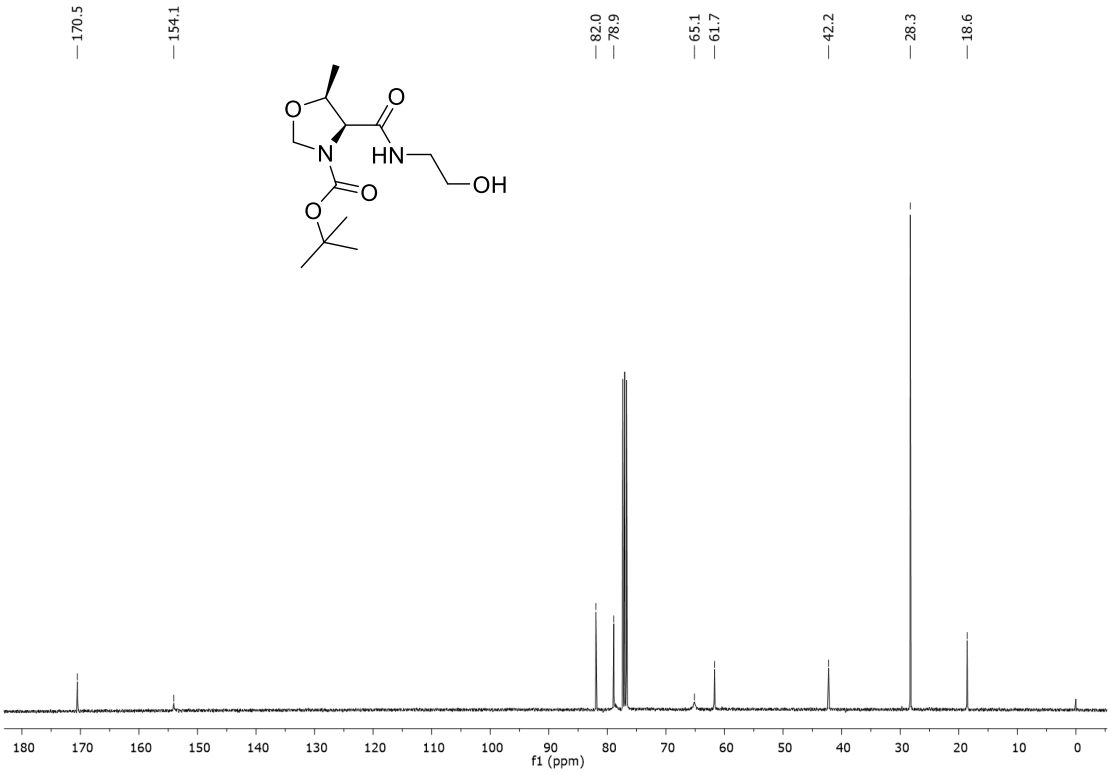


Figure S40. ^{13}C NMR spectrum for compound **8** ($CDCl_3$, 100 MHz).

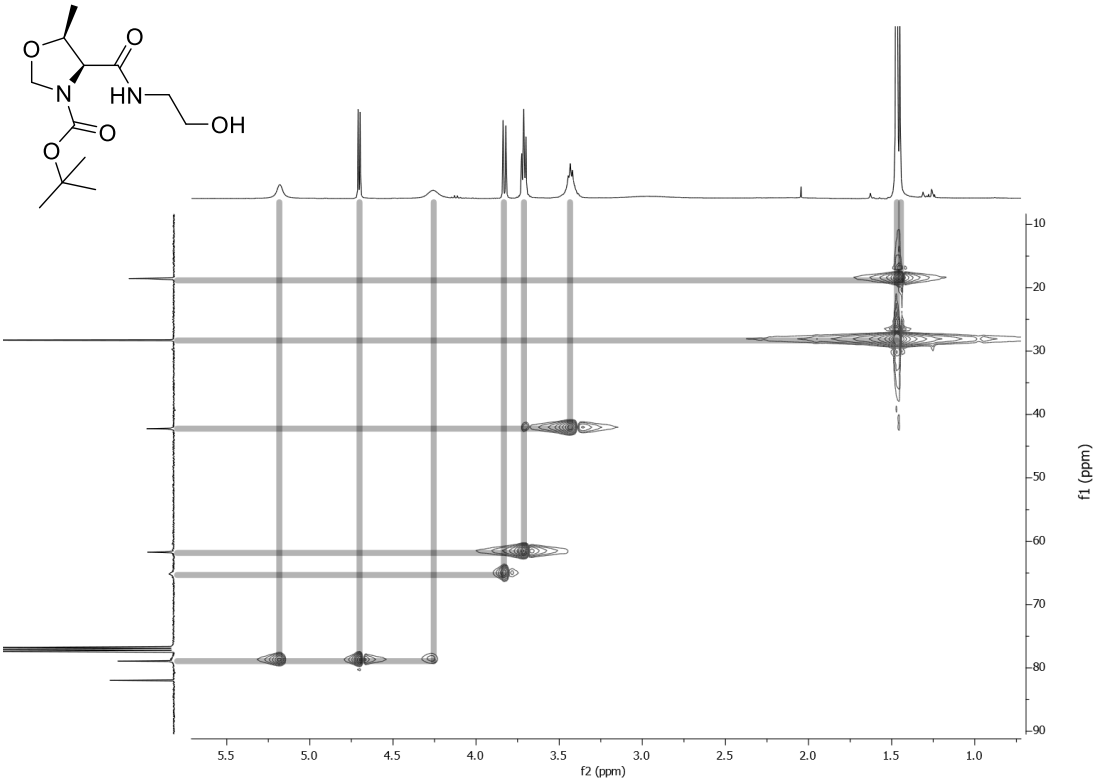


Figure S41. ^{1}H-^{13}C HSQC spectrum for compound **8** ($CDCl_3$, 400 MHz).

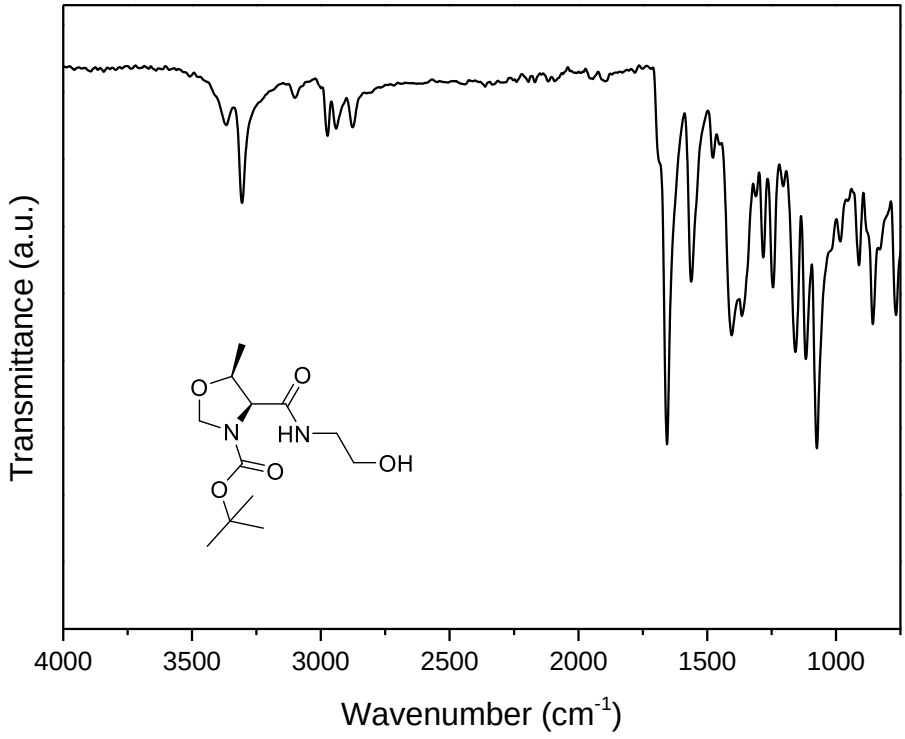


Figure S42. IR-ATR spectrum for compound **8**.

11. NMR spectra of compounds PCL-01P to PCL-08P

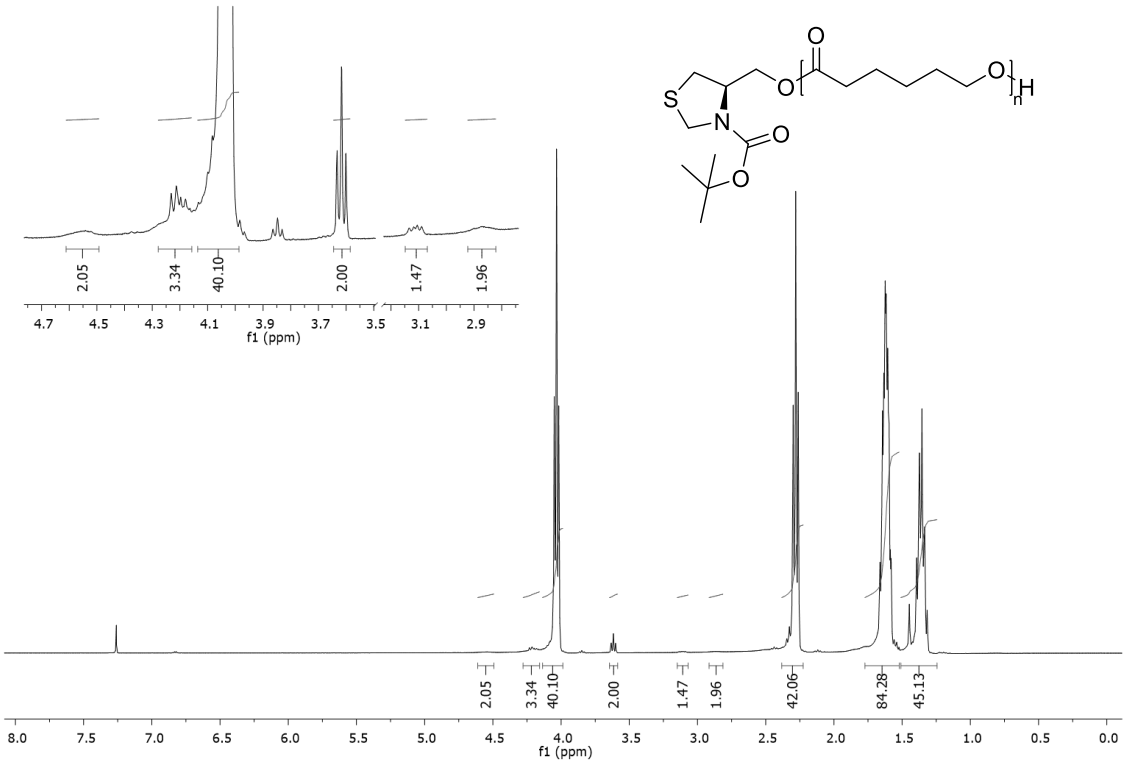


Figure S43. ^{1}H NMR spectrum for compound **PCL-01P** ($CDCl_3$, 400 MHz).

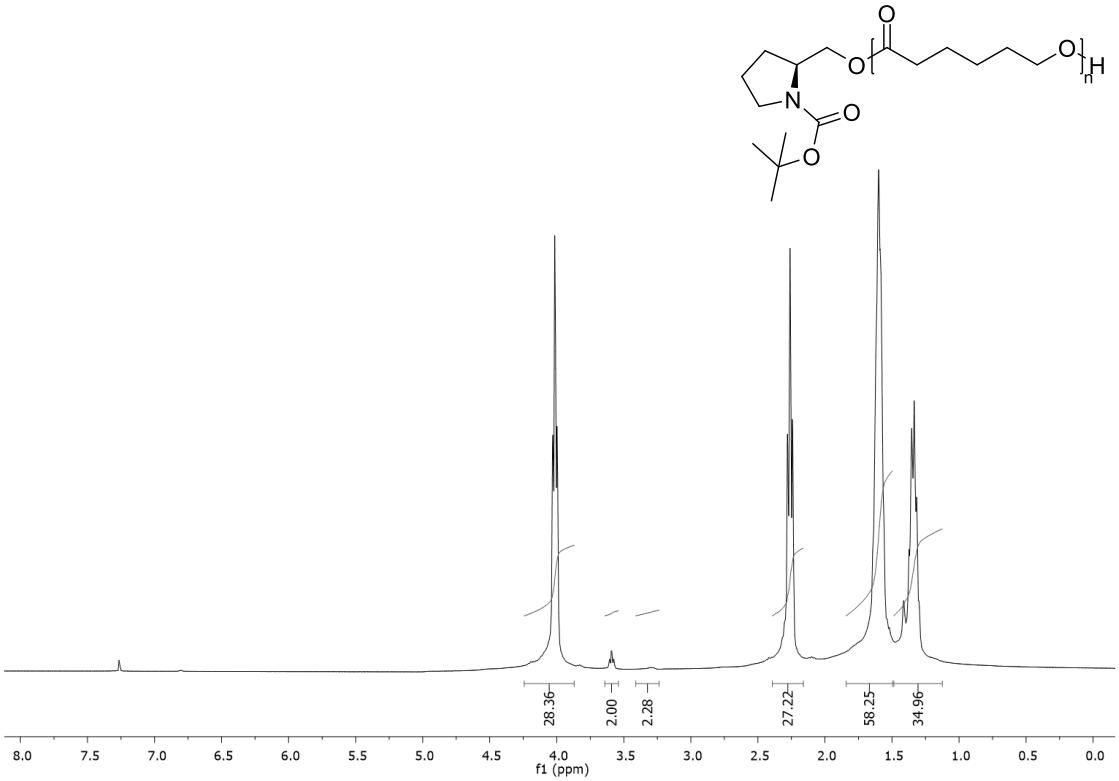


Figure S44. ^{1}H NMR spectrum for compound **PCL-02P** ($CDCl_3$, 400 MHz).

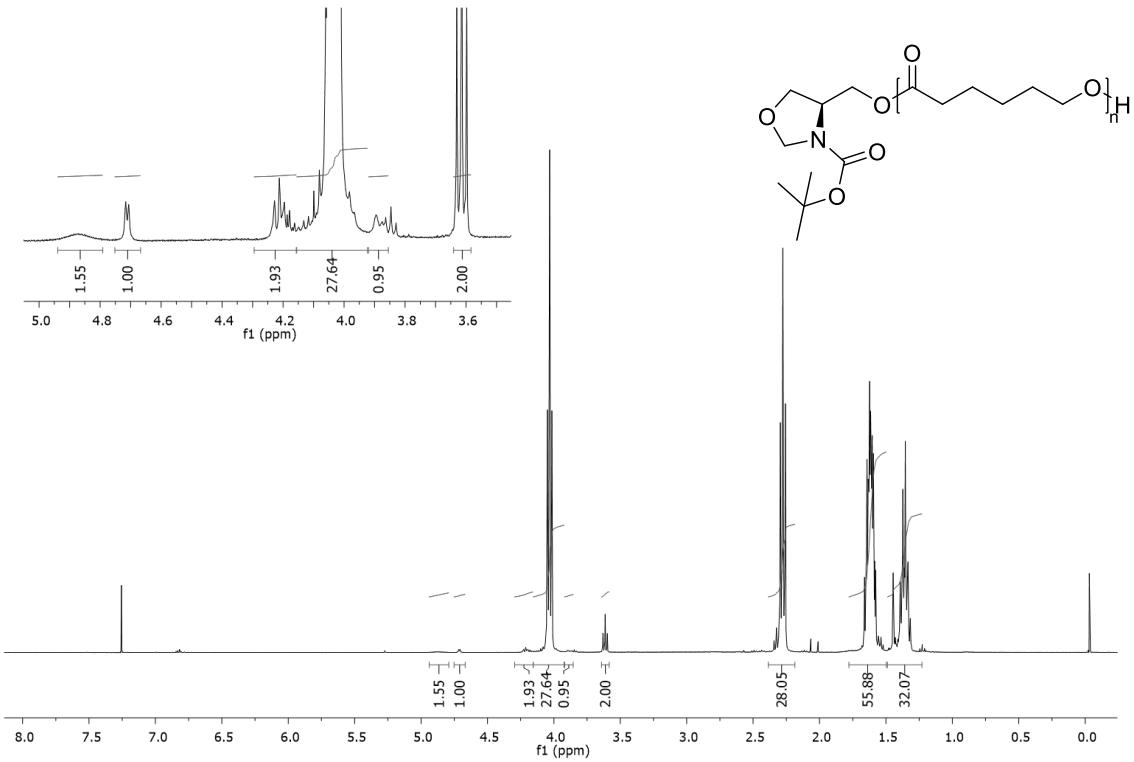


Figure S45. ^{1}H NMR spectrum for compound **PCL-03P** ($CDCl_3$, 400 MHz).

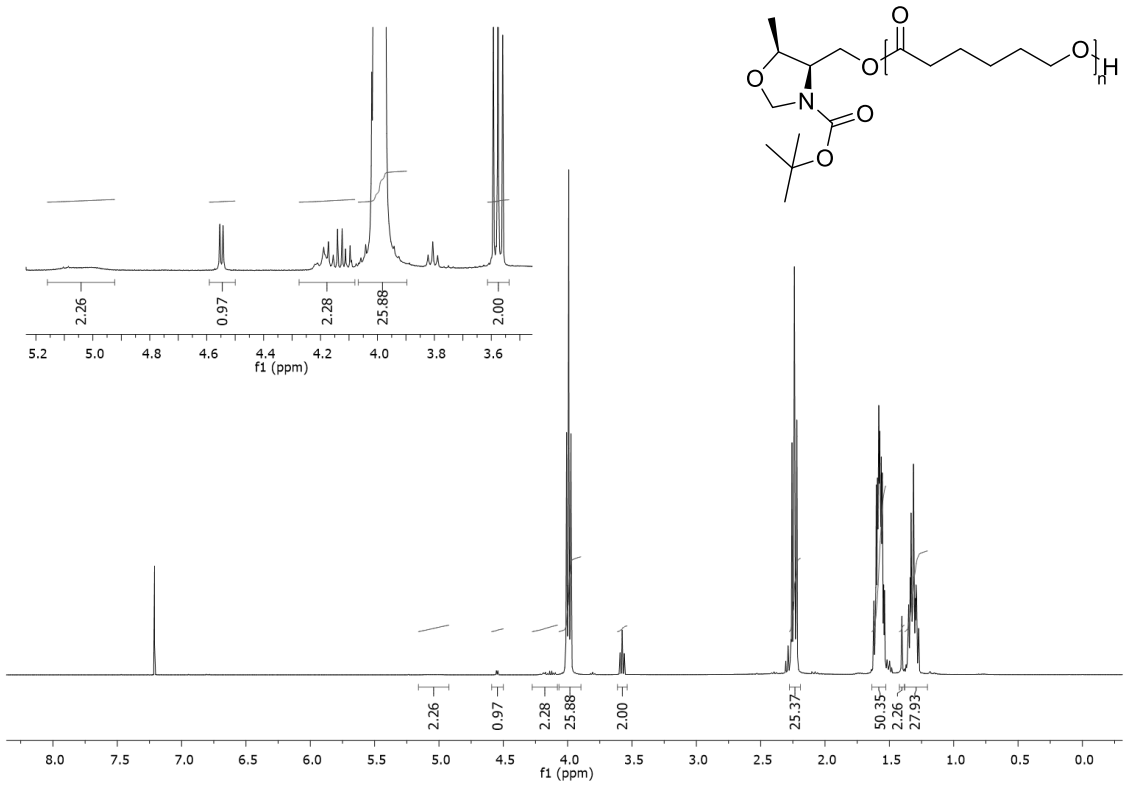


Figure S46. ^{1}H NMR spectrum for compound **PCL-04P** ($CDCl_3$, 400 MHz).

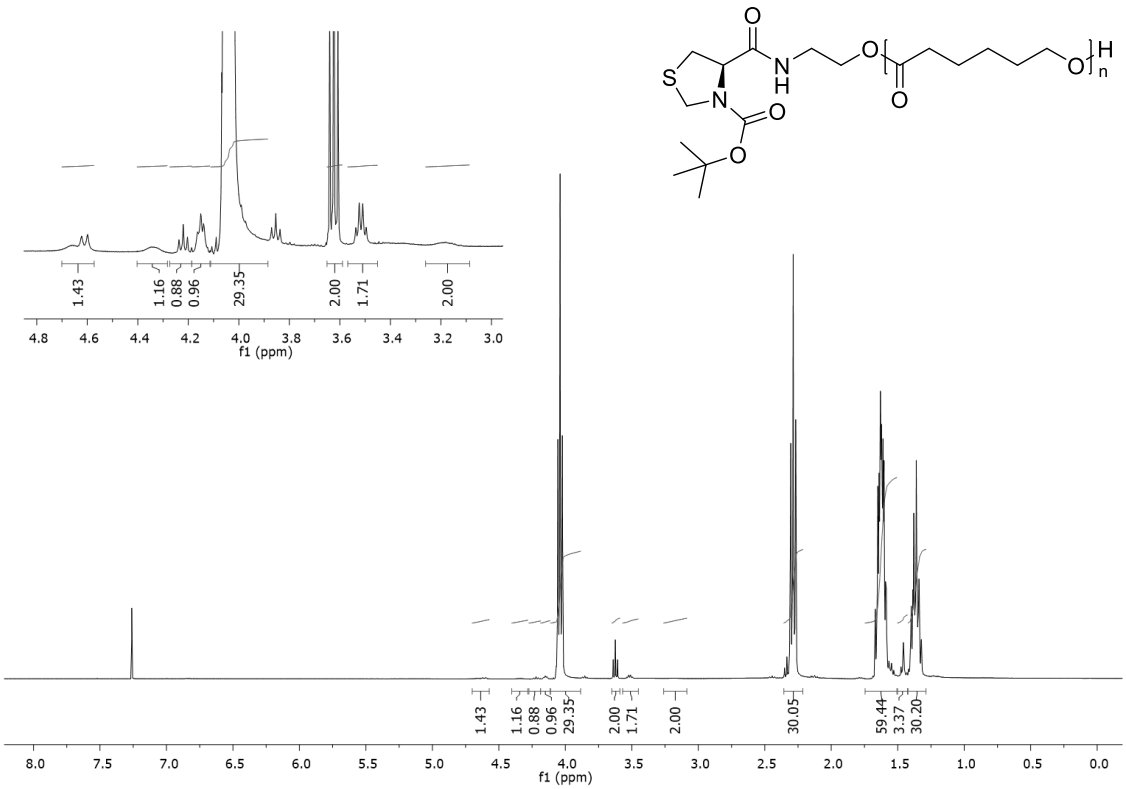


Figure S47. ^{1}H NMR spectrum for compound **PCL-05P** ($CDCl_3$, 400 MHz).

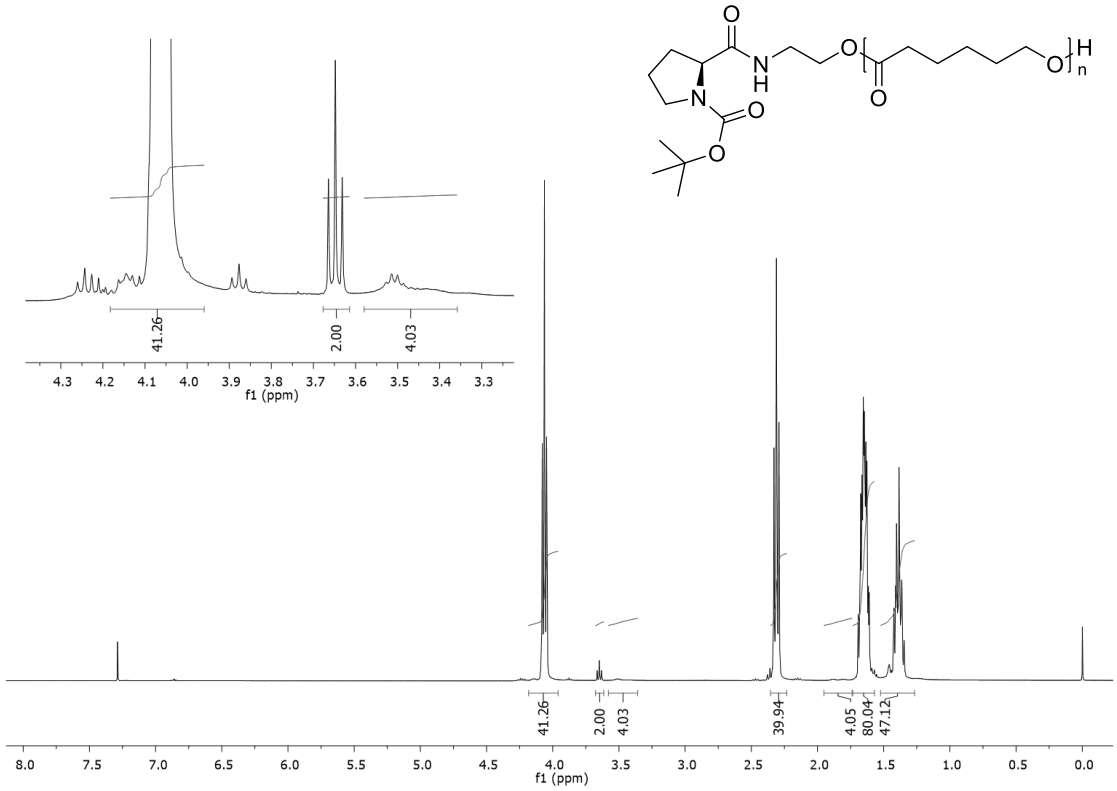


Figure S48. ^{1}H NMR spectrum for compound **PCL-06P** ($CDCl_3$, 400 MHz).

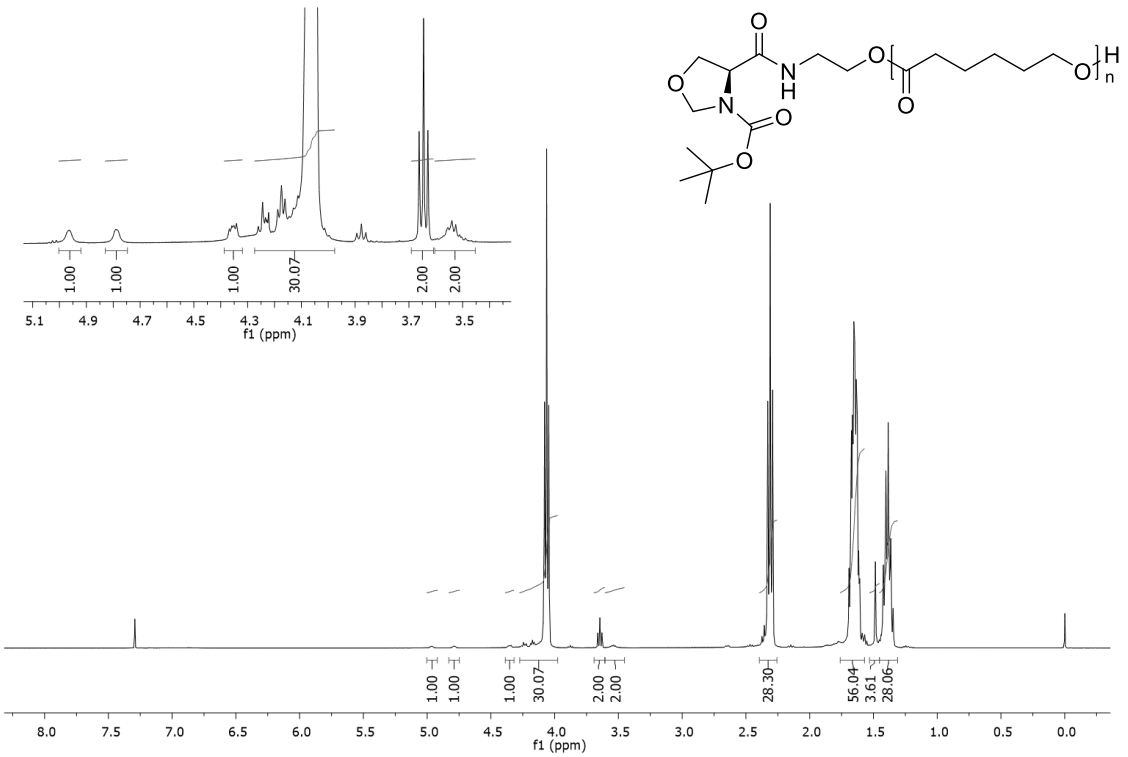


Figure S49. ^{1}H NMR spectrum for compound **PCL-07P** ($CDCl_3$, 400 MHz).

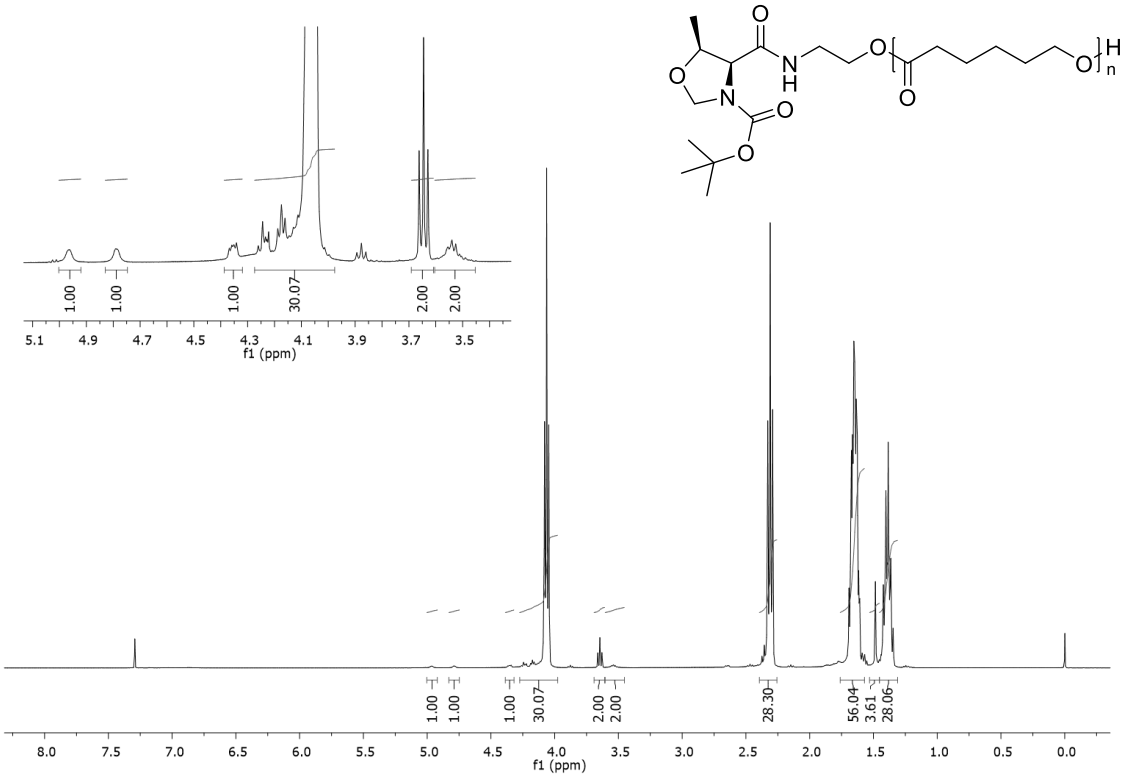


Figure S50. ^{1}H NMR spectrum for compound **PCL-08P** ($CDCl_3$, 400 MHz).

12. NMR and IR-ATR spectra of compounds PCL-01 to PCL-08

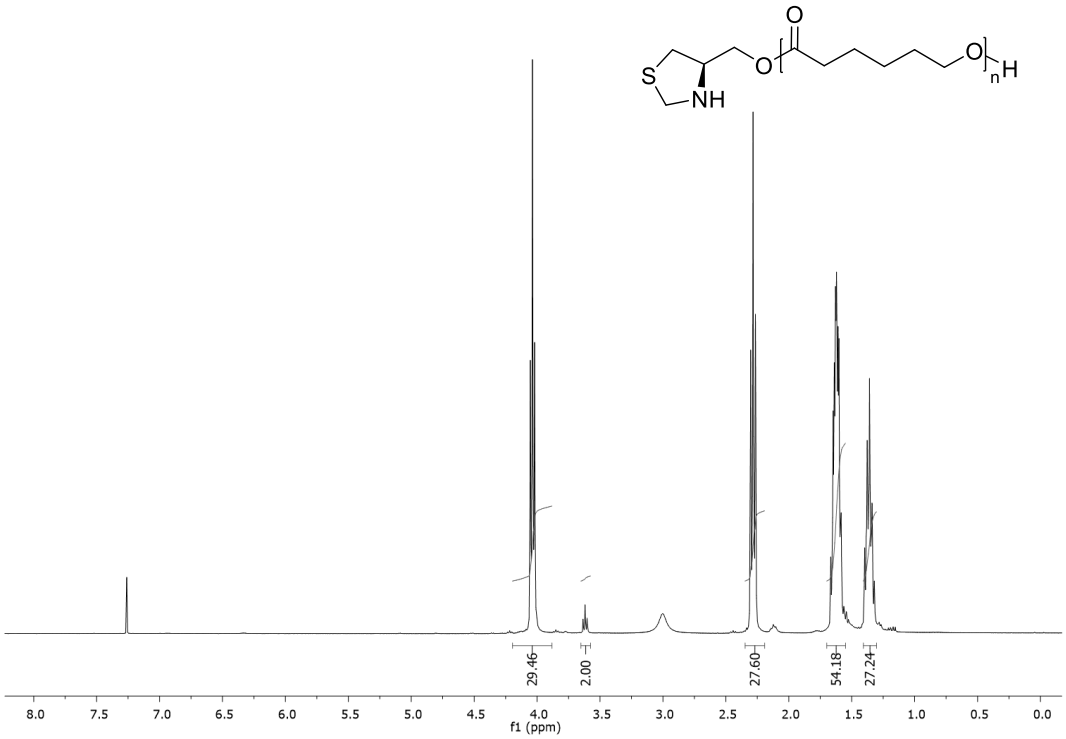


Figure S51. ^{1}H NMR spectrum for compound **PCL-01** ($CDCl_3$, 400 MHz).

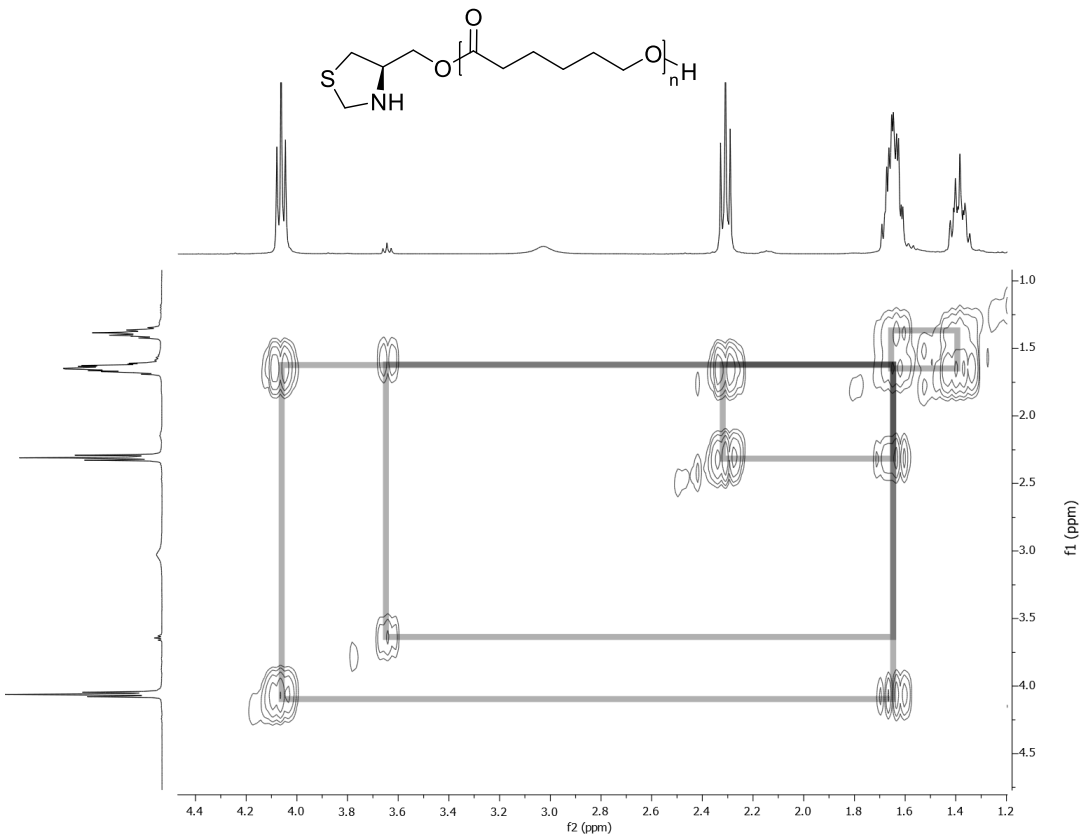


Figure S52. ^{1}H-^{1}H COSY spectrum for compound **PCL-01** ($CDCl_3$, 400 MHz).

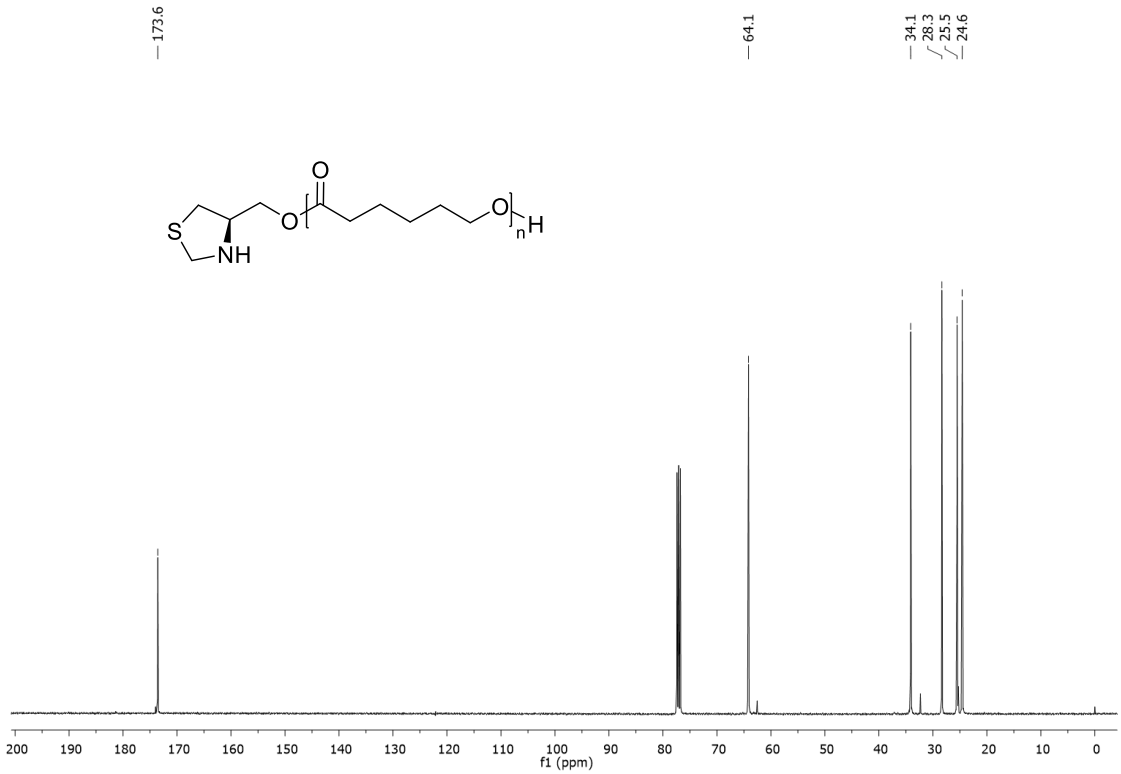


Figure S53. ^{13}C NMR spectrum for compound **PCL-01** ($CDCl_3$, 100 MHz).

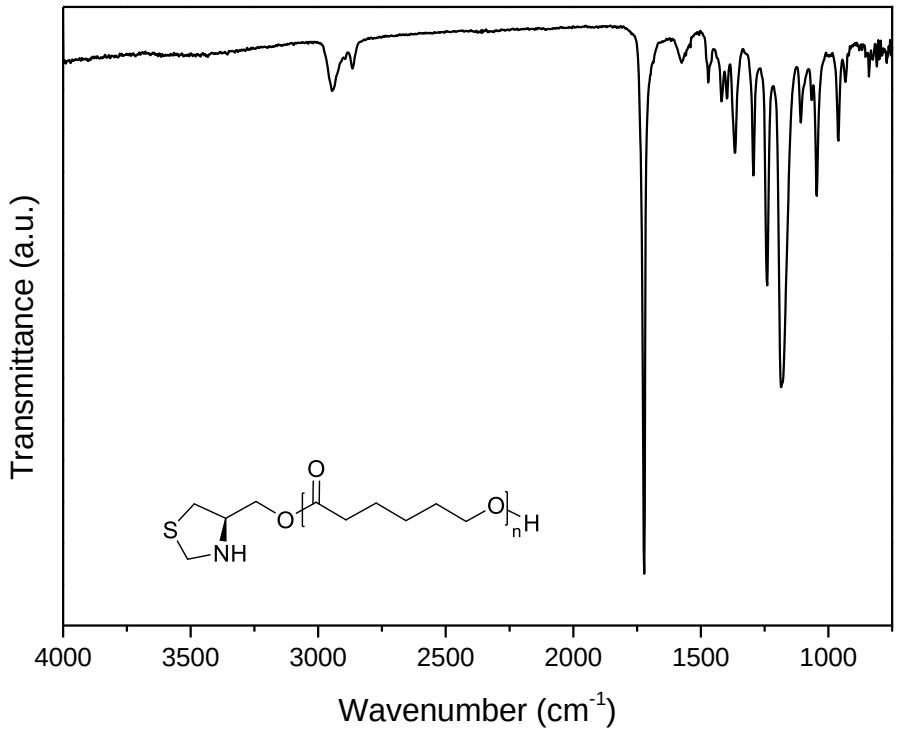


Figure S54. IR-ATR spectrum for compound **PCL-01**.

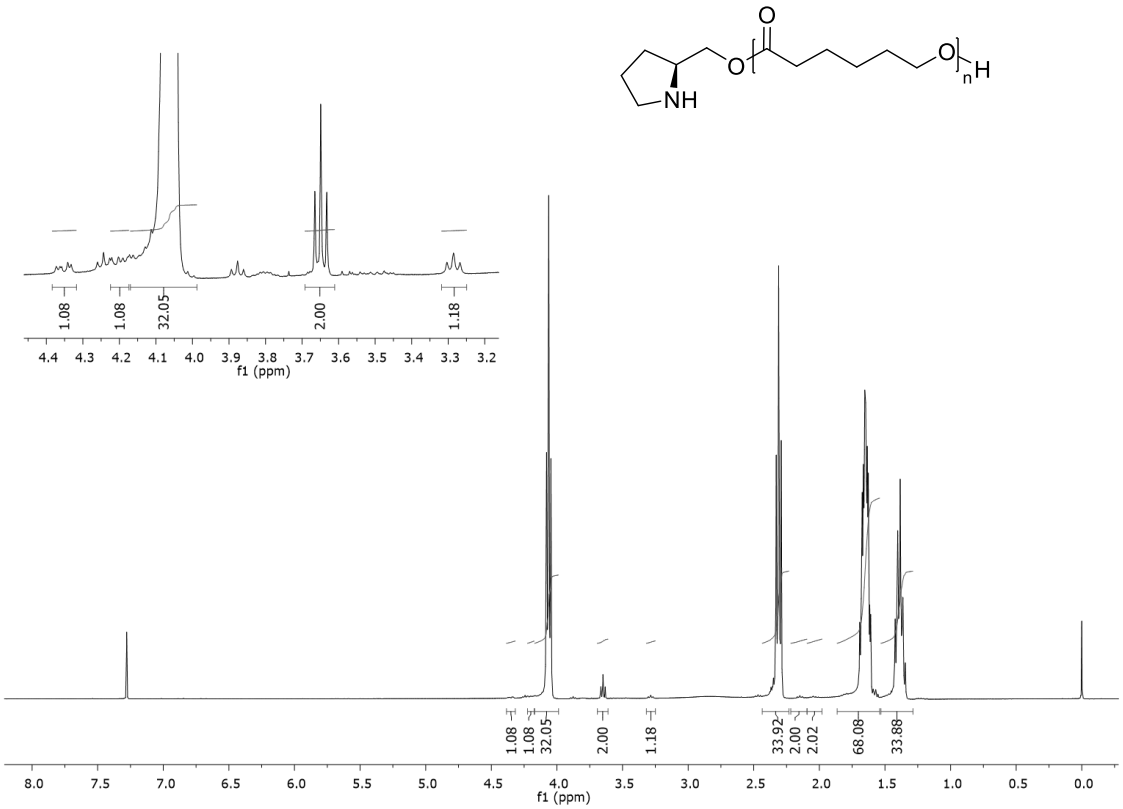


Figure S55. ^{1}H NMR spectrum for compound **PCL-02** ($CDCl_3$, 400 MHz).

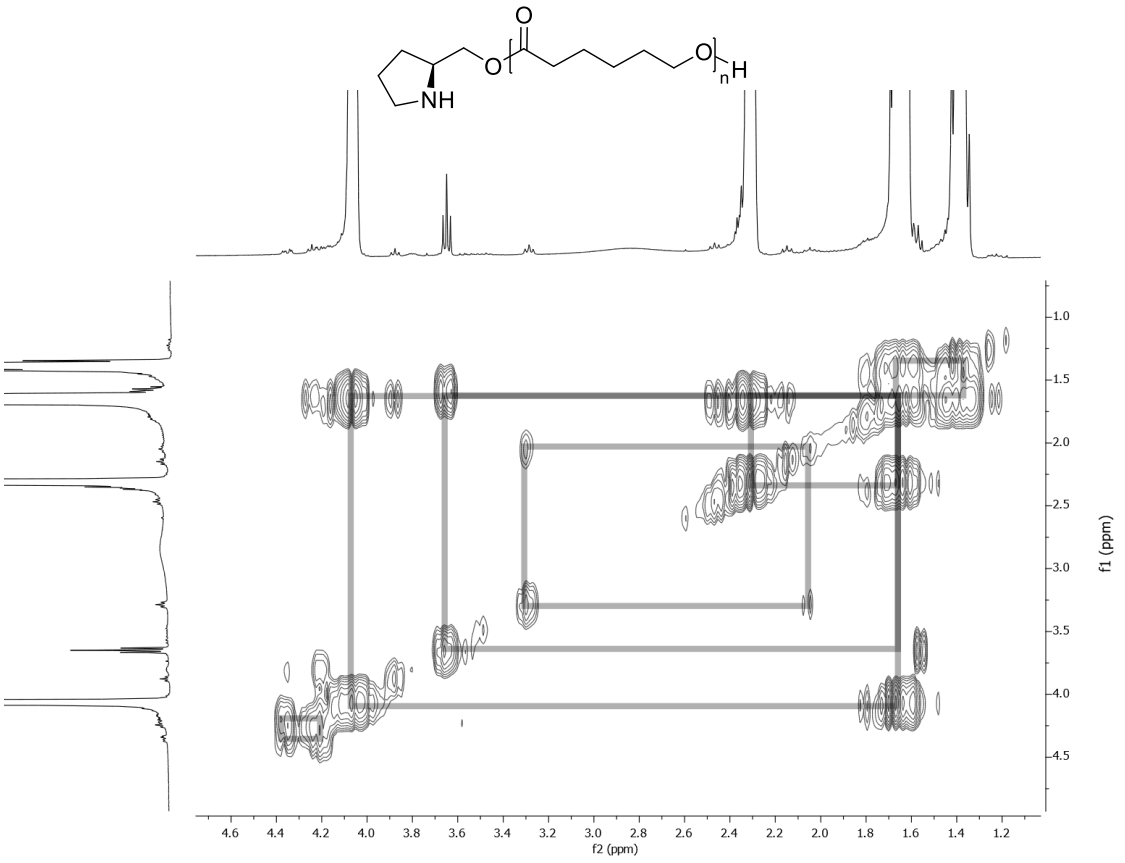


Figure S56. ^{1}H-^{1}H COSY spectrum for compound **PCL-02** ($CDCl_3$, 400 MHz).

Figure S57. ^{13}C NMR spectrum for compound **PCL-02** ($CDCl_3$, 100 MHz).

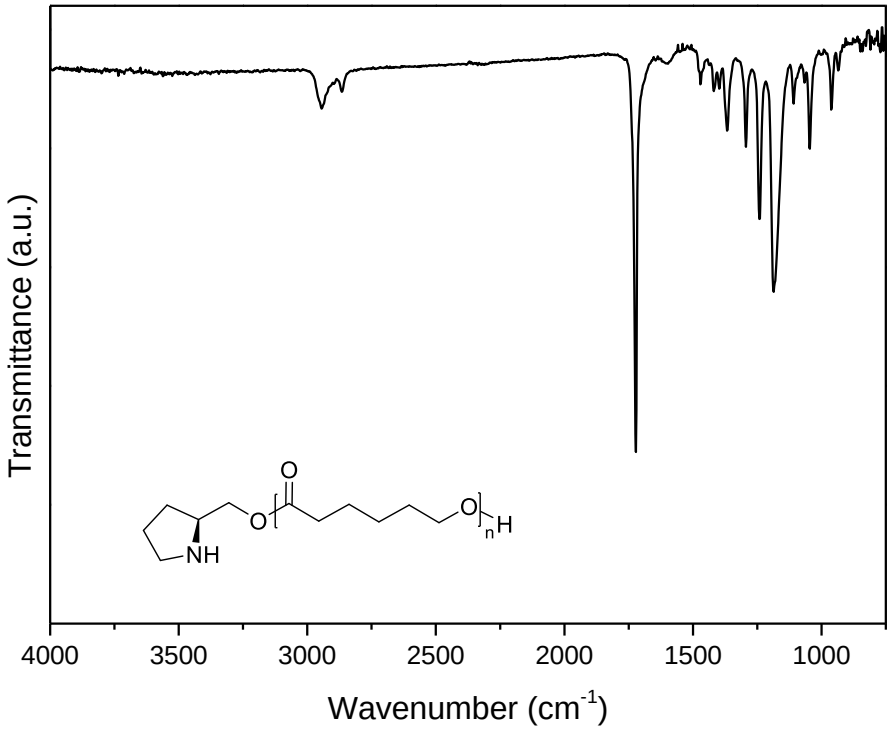


Figure S58. IR-ATR spectrum for compound **PCL-02**.

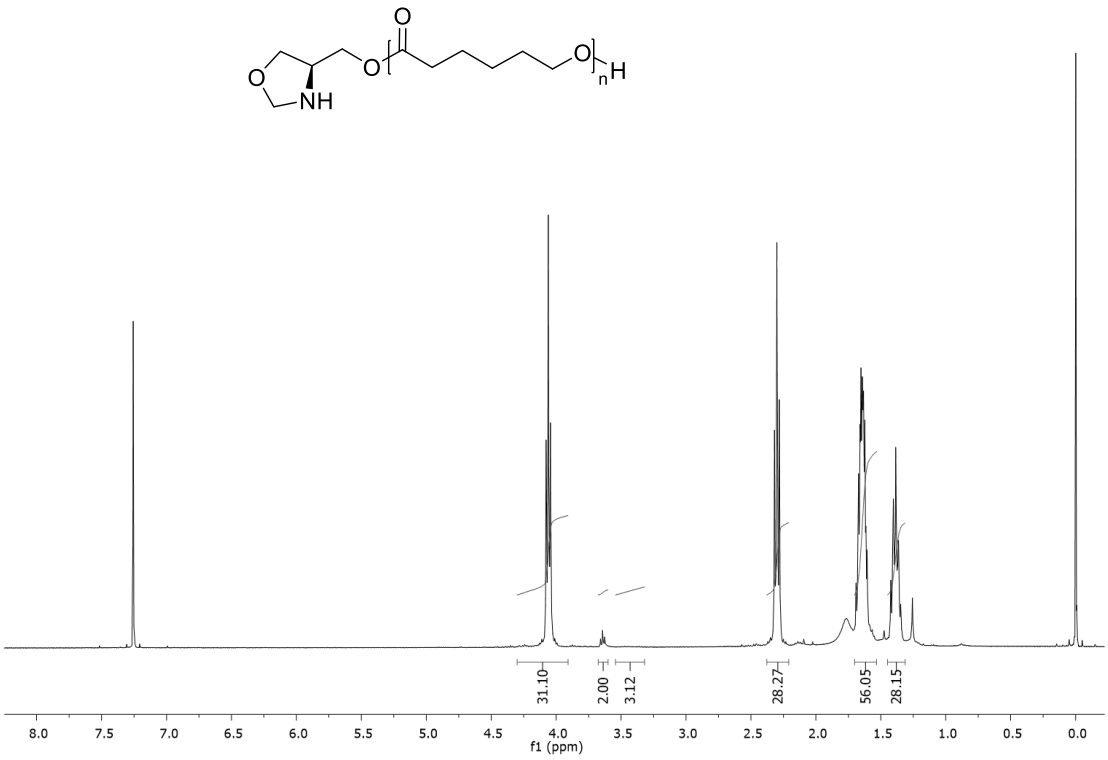


Figure S59. ^{1}H NMR spectrum for compound **PCL-03** ($CDCl_3$, 400 MHz).

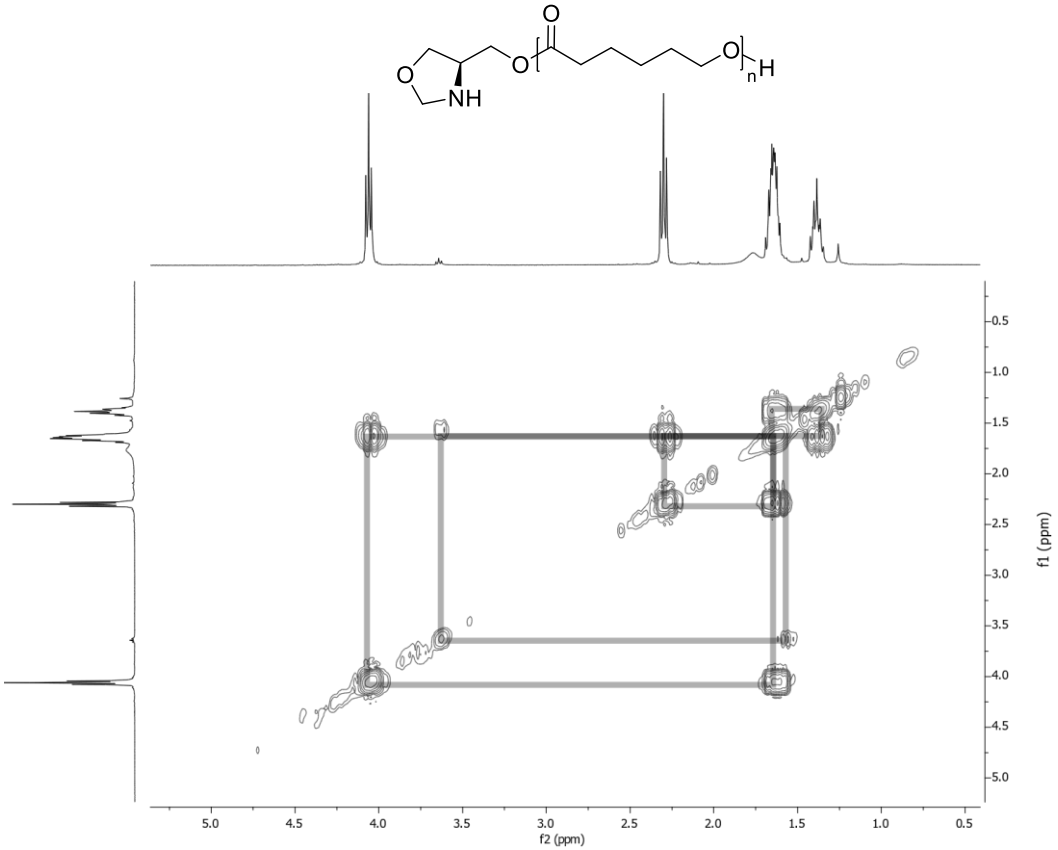


Figure S60. ^{1}H-^{1}H COSY spectrum for compound **PCL-03** ($CDCl_3$, 400 MHz).

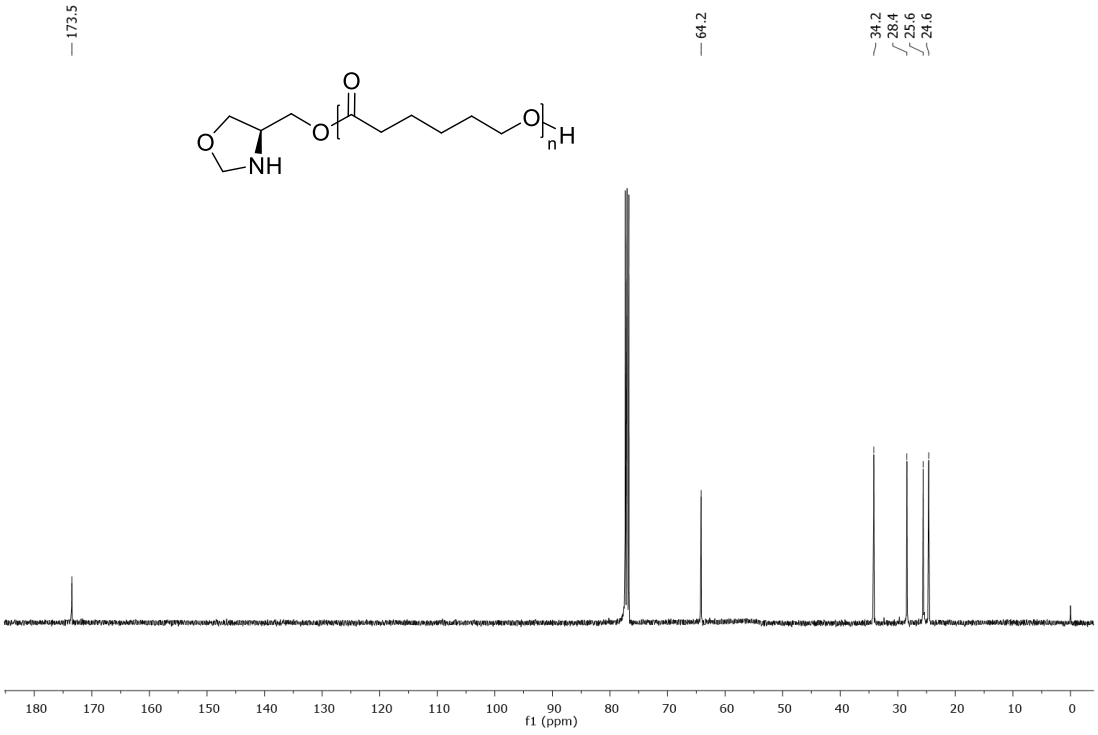


Figure S61. ^{13}C NMR spectrum for compound **PCL-03** ($CDCl_3$, 100 MHz).

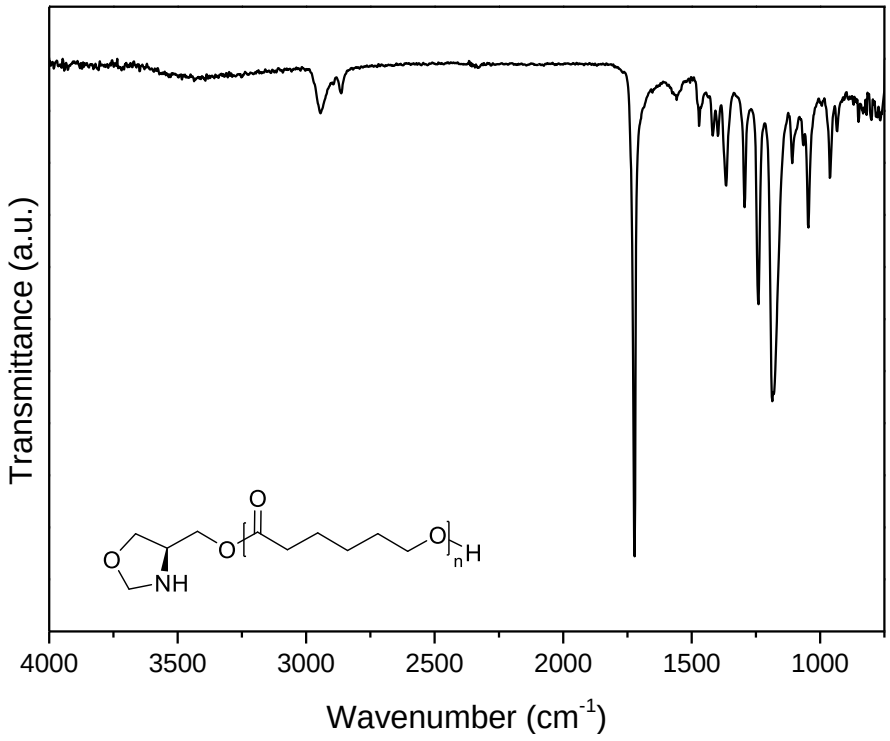


Figure S62. IR-ATR spectrum for compound **PCL-03**.

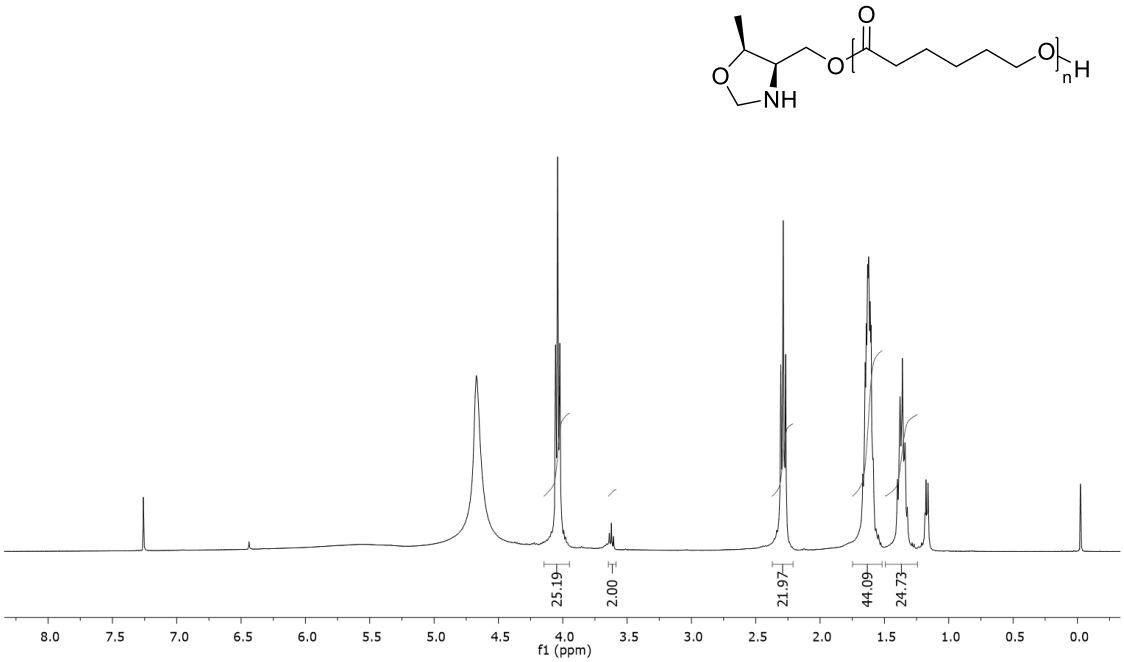


Figure S63. ^{1}H NMR spectrum for compound **PCL-04** ($CDCl_3$, 400 MHz).

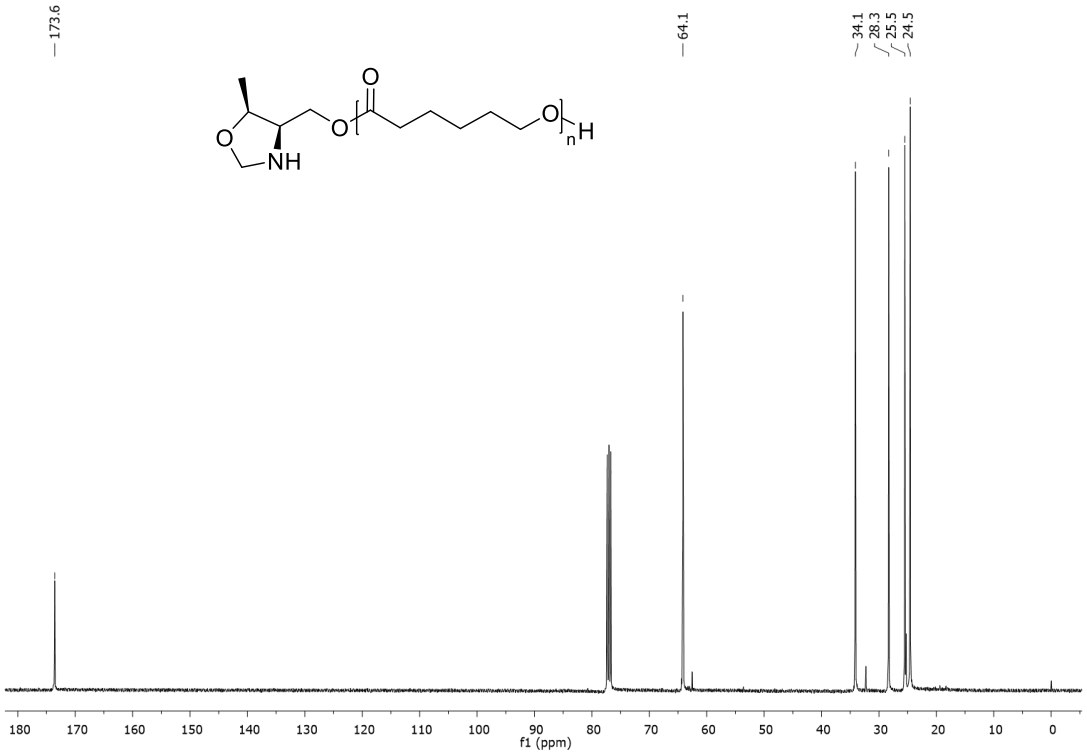


Figure S64. ^{13}C NMR spectrum for compound **PCL-04** ($CDCl_3$, 100 MHz).

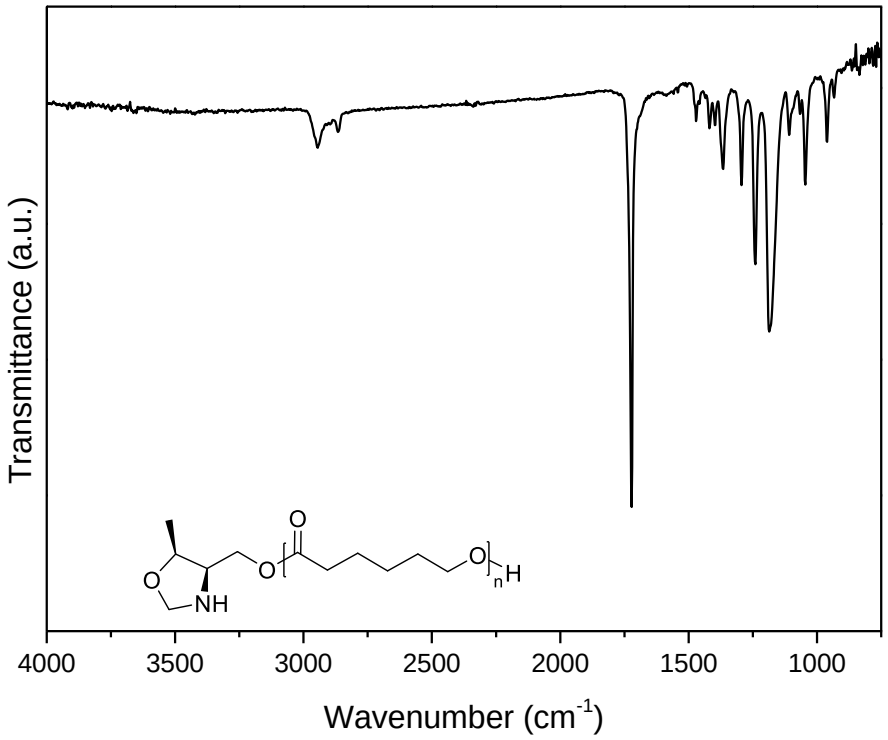


Figure S65. IR-ATR spectrum for compound **PCL-04**.

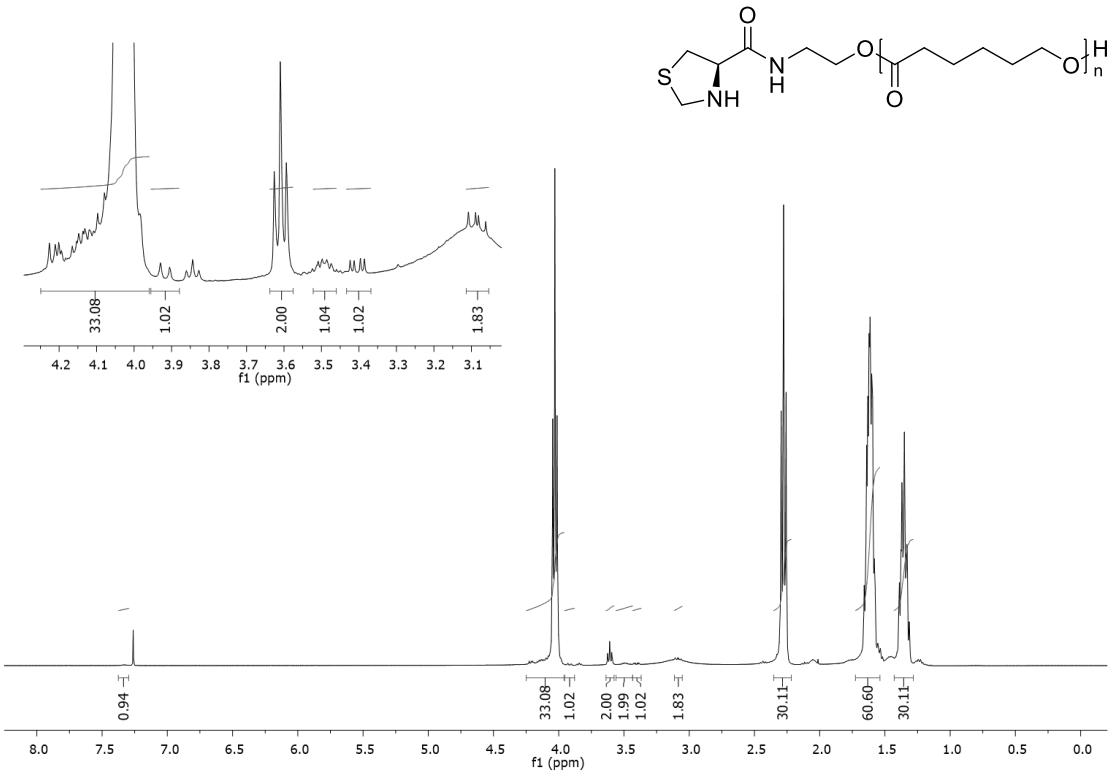


Figure S66. ^{1}H NMR spectrum for compound **PCL-05** ($CDCl_3$, 400 MHz).

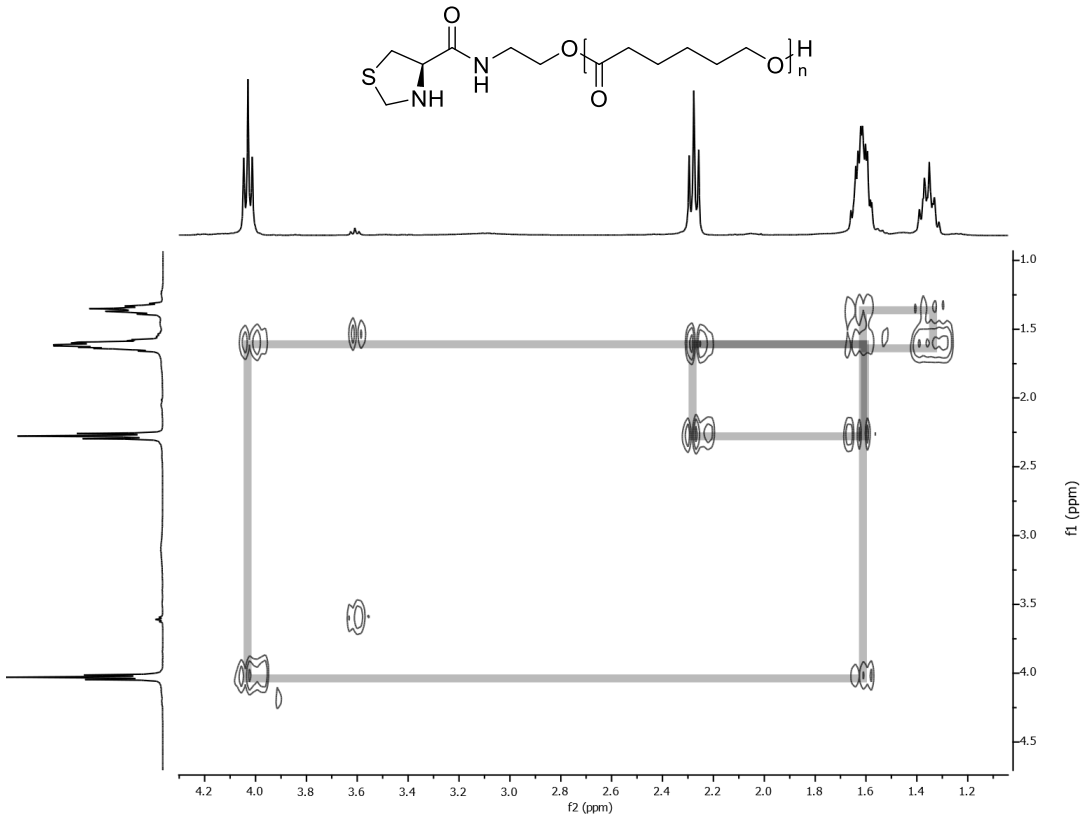


Figure S67. ^{1}H-^{1}H COSY spectrum for compound **PCL-05** ($CDCl_3$, 400 MHz).

Figure S68. ^{13}C NMR spectrum for compound **PCL-05** ($CDCl_3$, 100 MHz).

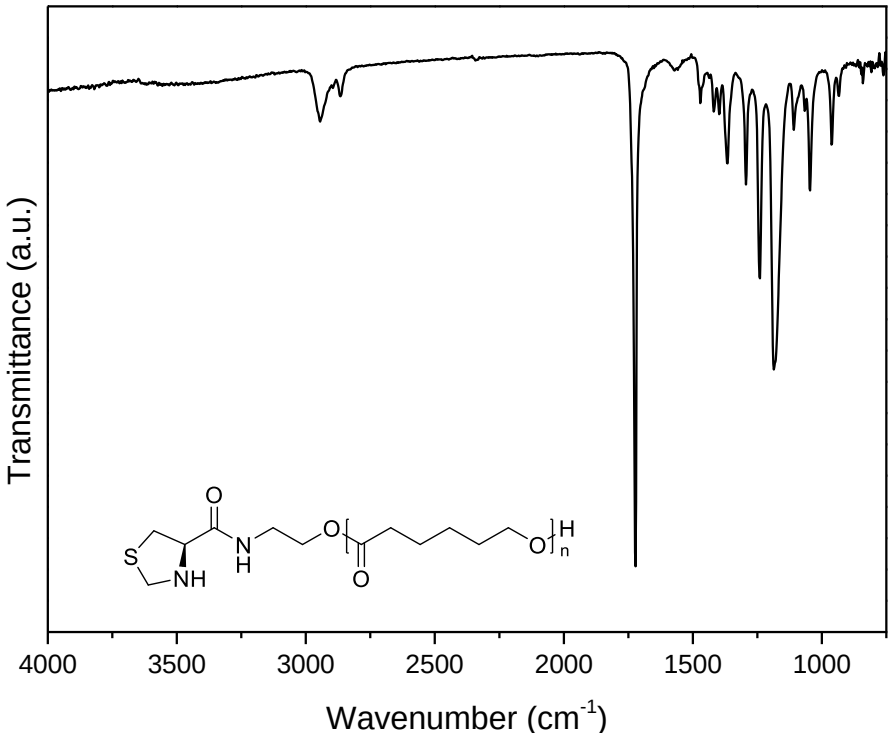


Figure S69. IR-ATR spectrum for compound **PCL-05**.

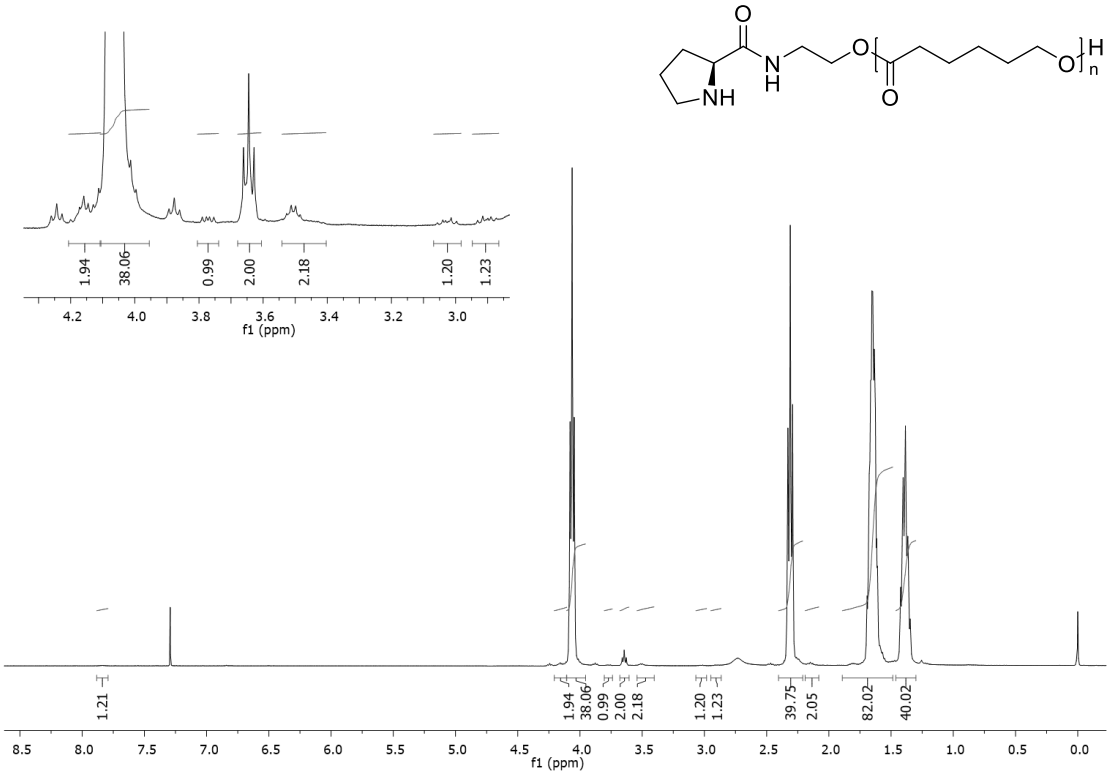


Figure S70. ^{1}H NMR spectrum for compound **PCL-06** ($CDCl_3$, 400 MHz).

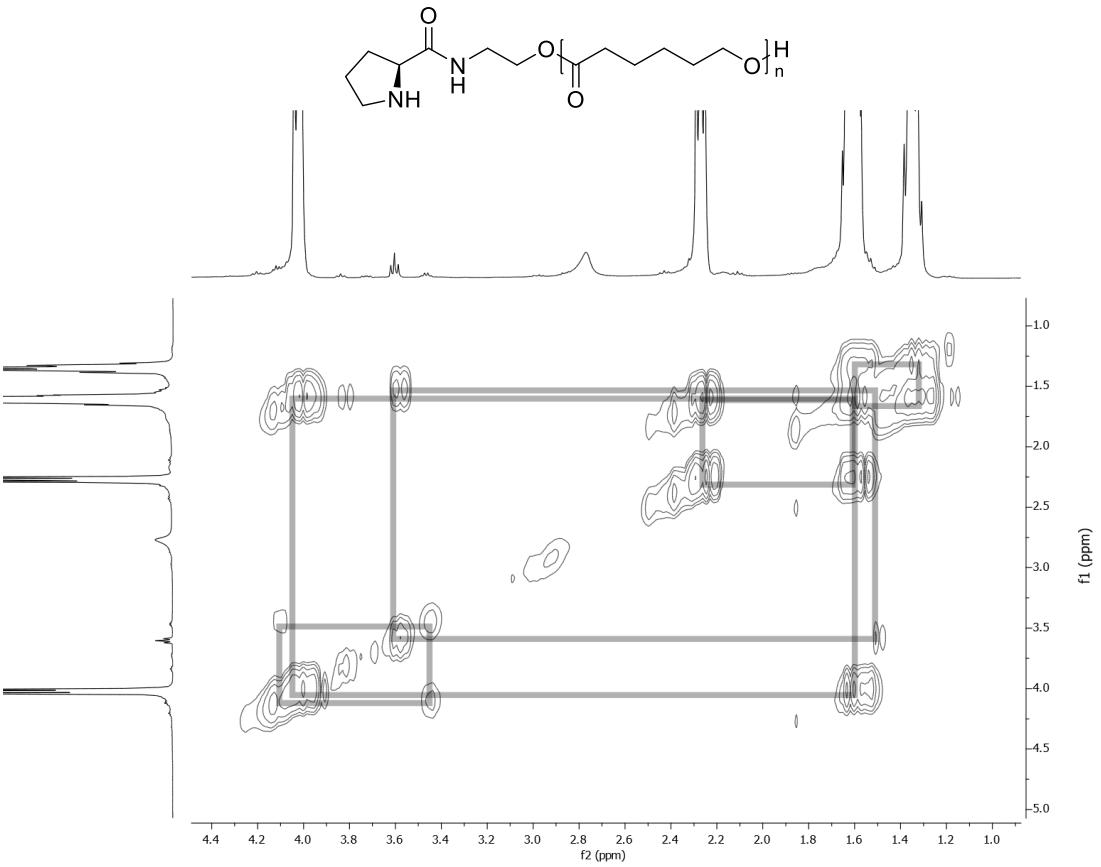


Figure S71. ^{1}H-^{1}H COSY spectrum for compound **PCL-06** ($CDCl_3$, 400 MHz).

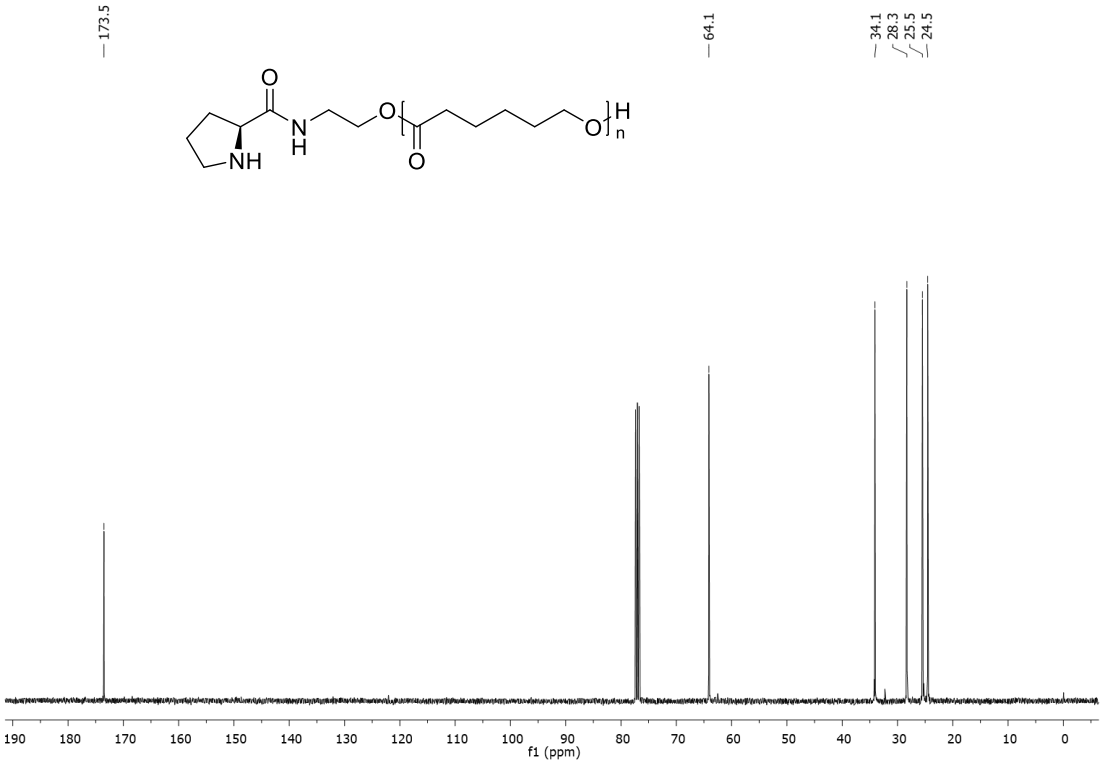


Figure S72. ^{13}C NMR spectrum for compound **PCL-06** ($CDCl_3$, 100 MHz).

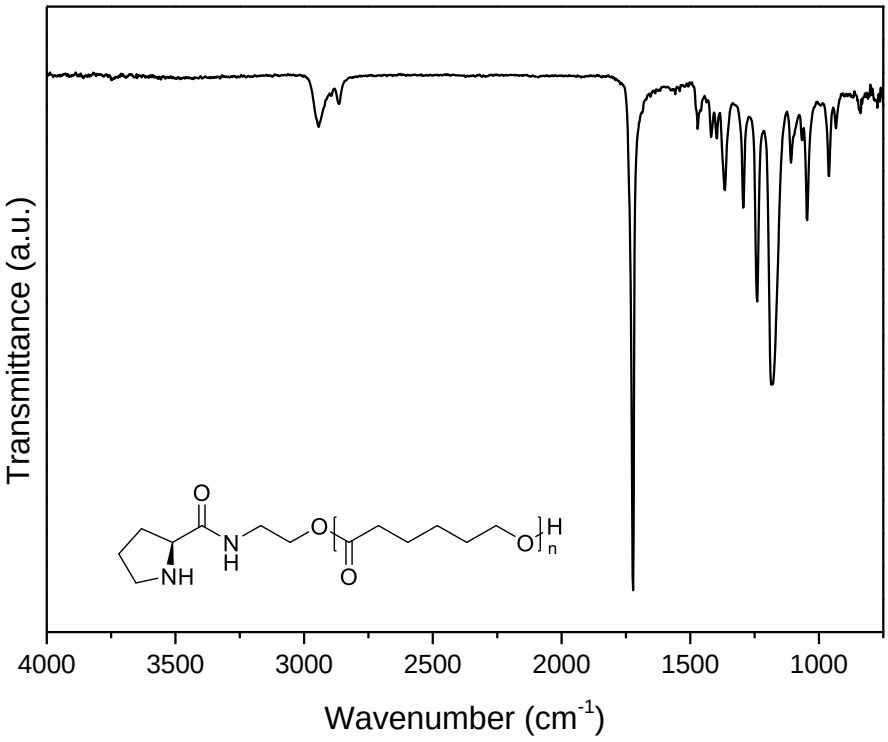


Figure S73. IR-ATR spectrum for compound **PCL-06**.

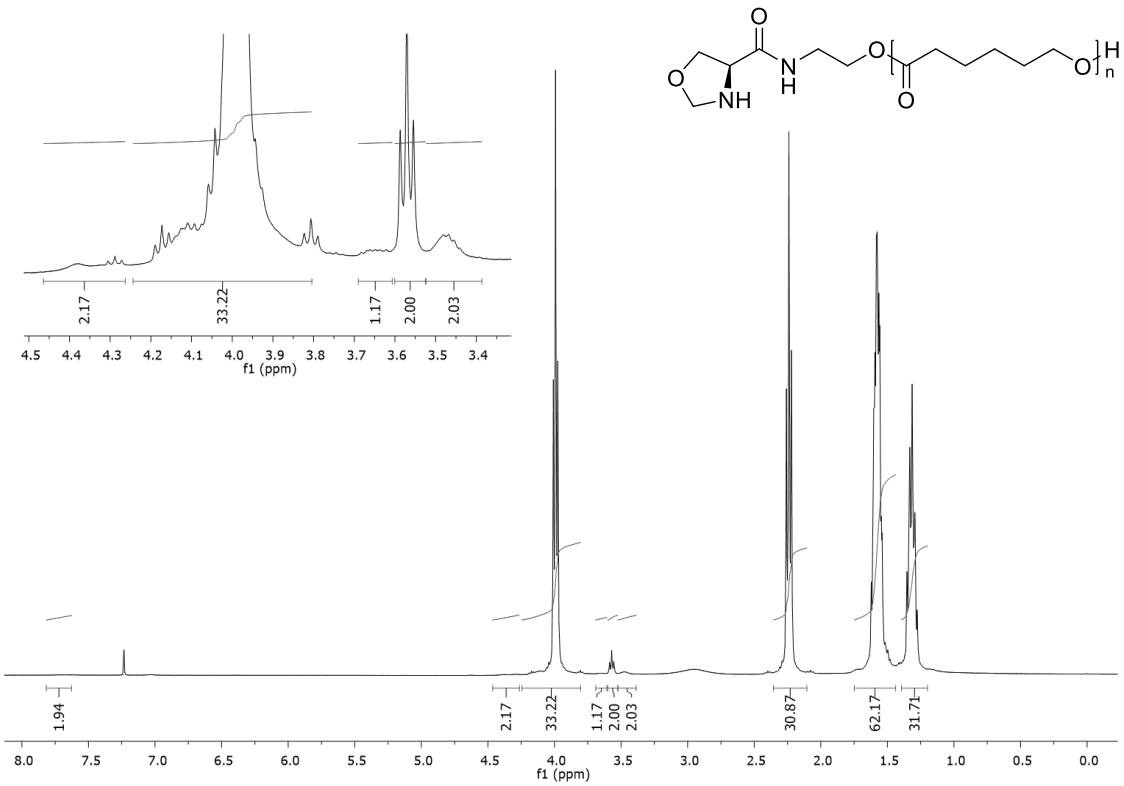


Figure S74. ^{1}H NMR spectrum for compound **PCL-07** ($CDCl_3$, 400 MHz).

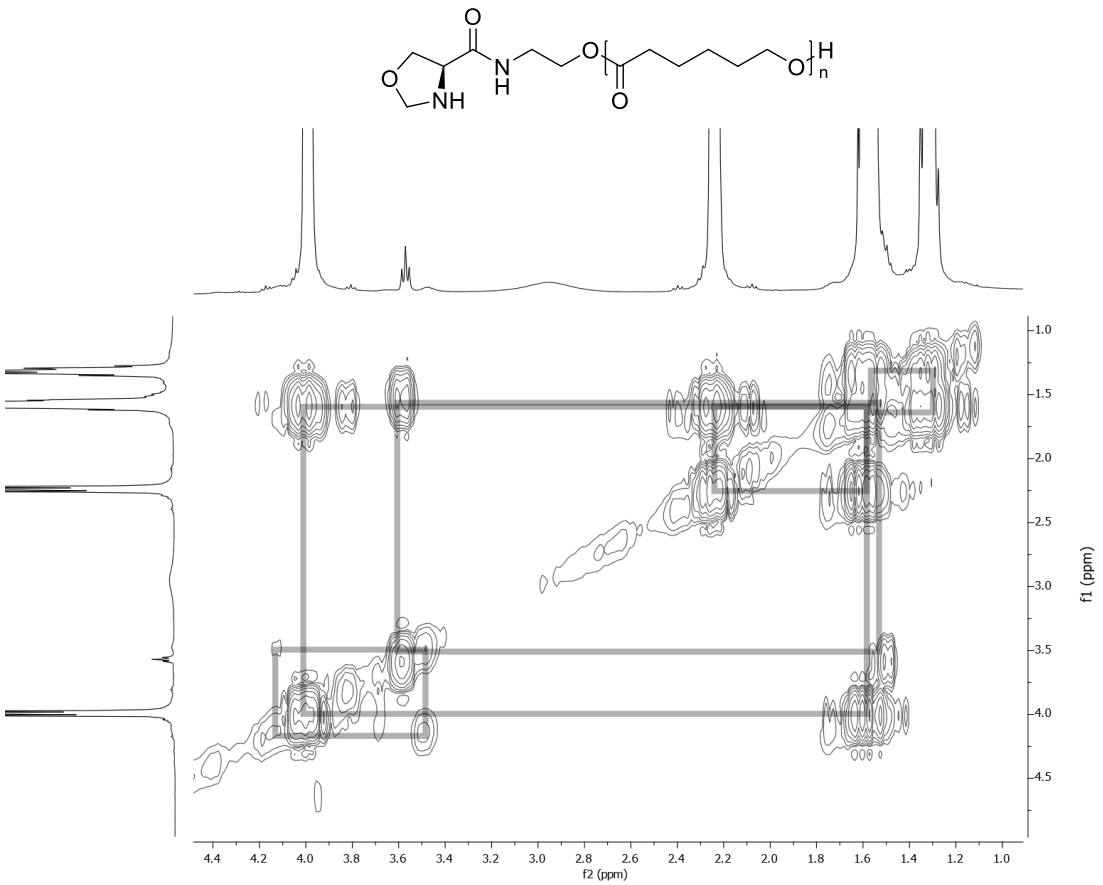


Figure S75. ^{1}H-^{1}H COSY spectrum for compound **PCL-07** ($CDCl_3$, 400 MHz).

Figure S76. ^{13}C NMR spectrum for compound **PCL-07** ($CDCl_3$, 100 MHz).

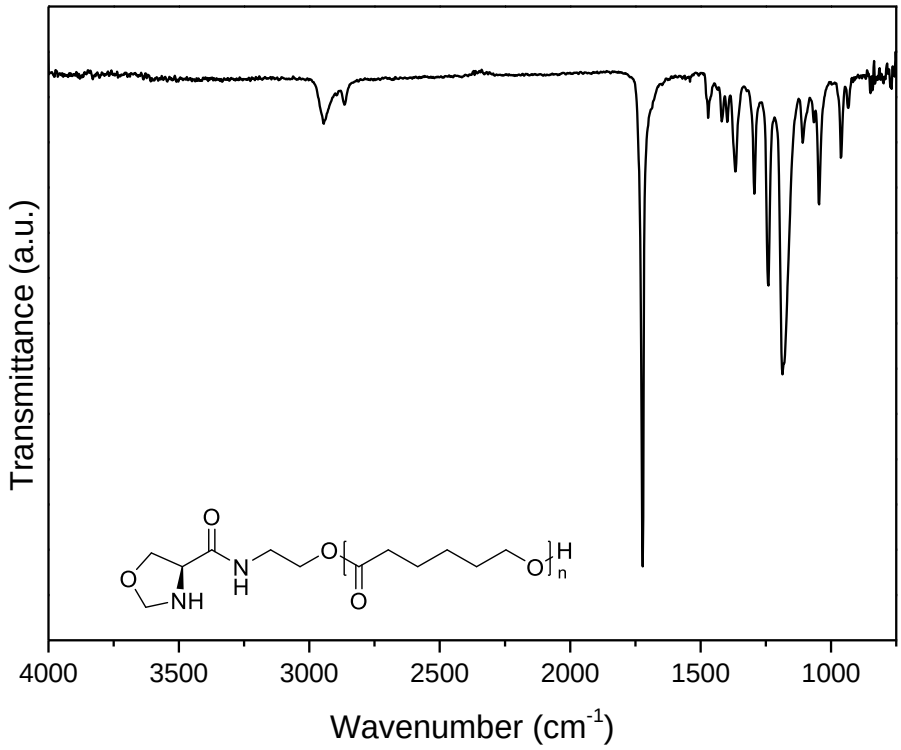


Figure S77. IR-ATR spectrum for compound **PCL-07**

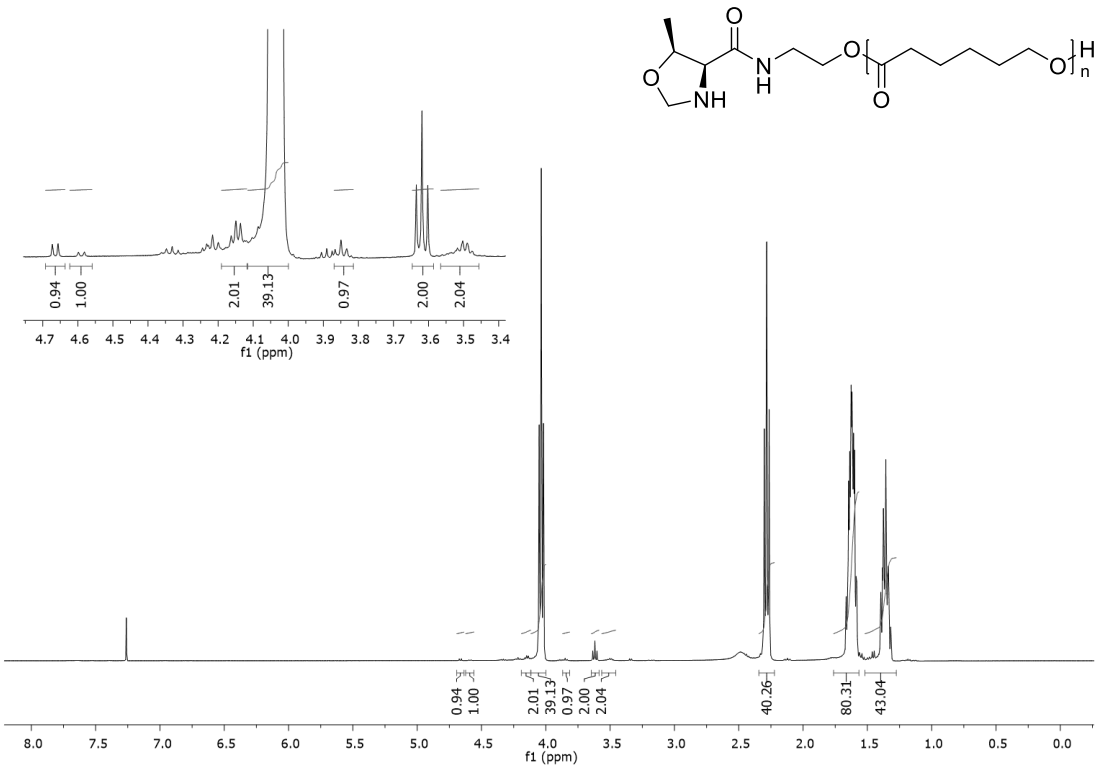


Figure S78. ^{1}H NMR spectrum for compound **PCL-08** ($CDCl_3$, 400 MHz).

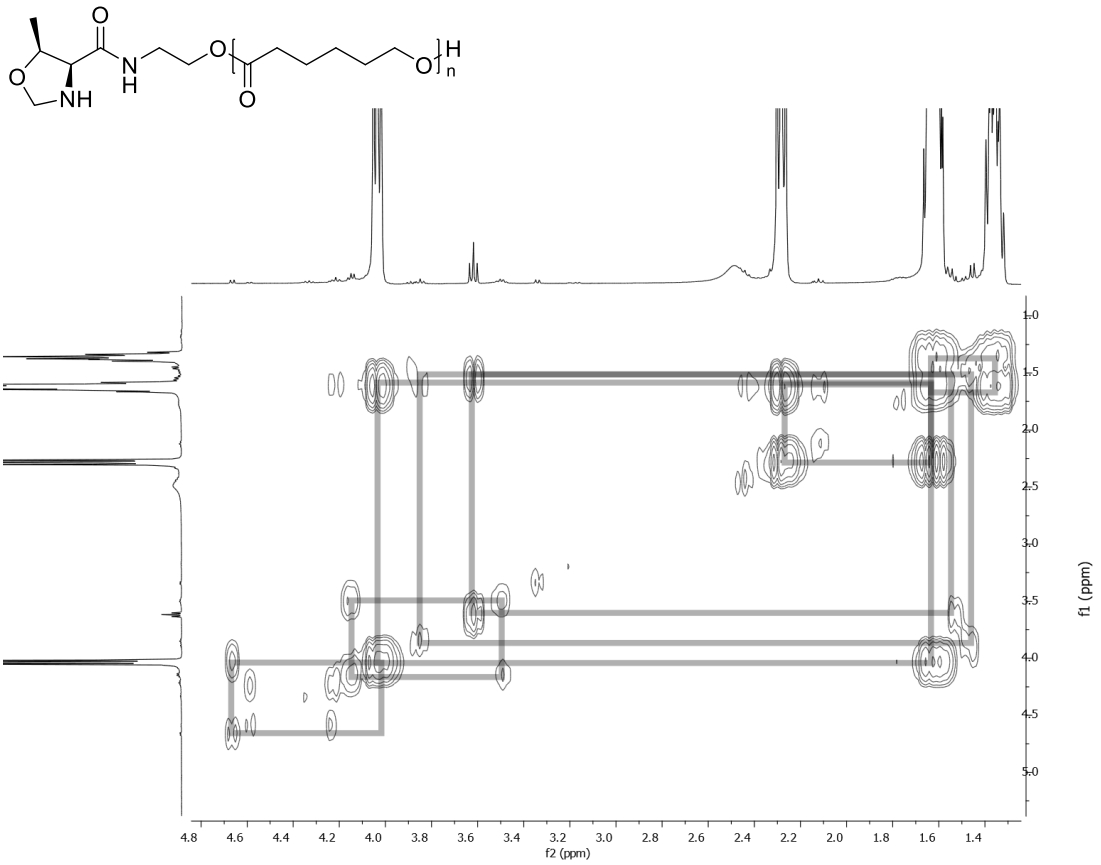


Figure S79. ^{1}H-^{1}H COSY spectrum for compound **PCL-08** ($CDCl_3$, 400 MHz).

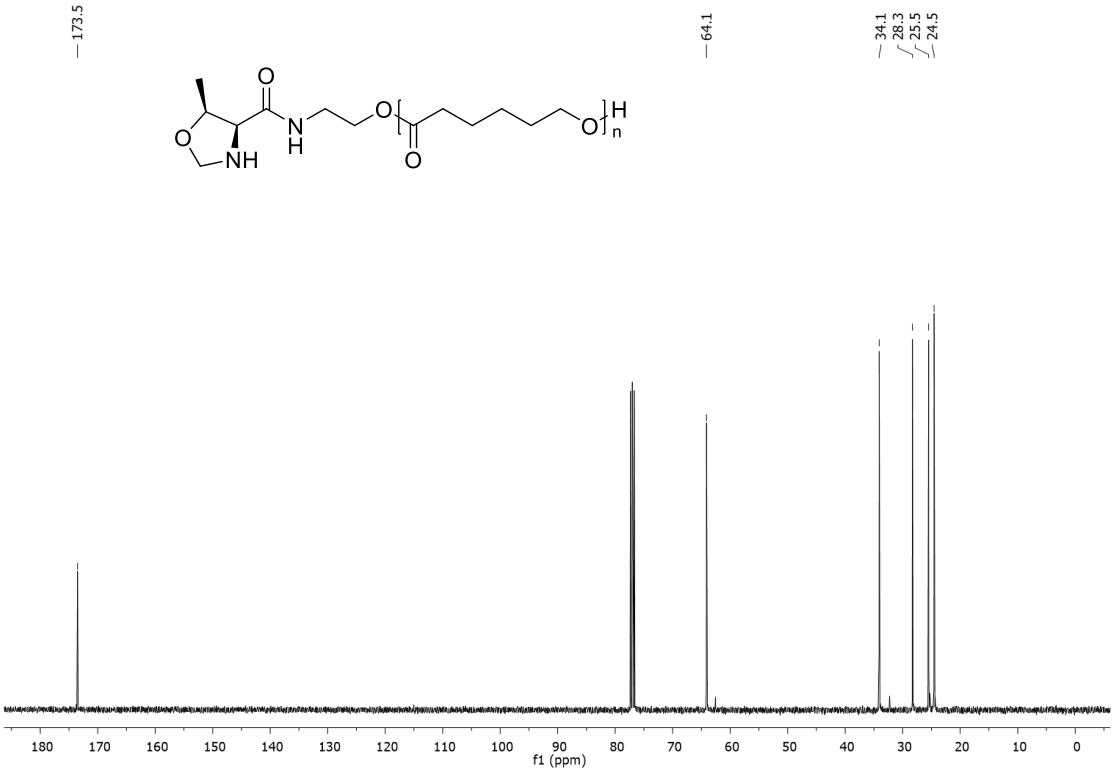


Figure S80. ^{13}C NMR spectrum for compound **PCL-08** ($CDCl_3$, 100 MHz).

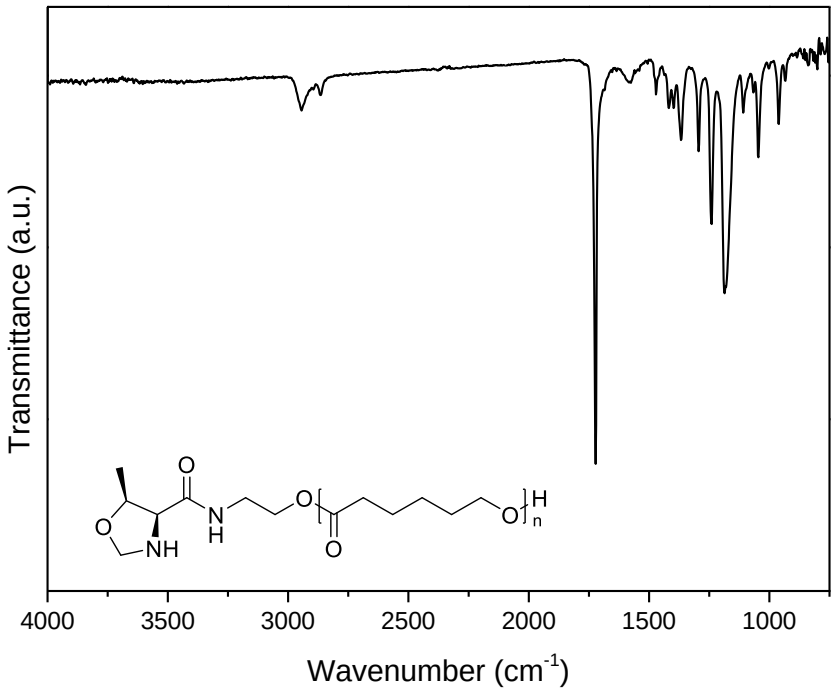


Figure S81. IR-ATR spectrum for compound **PCL-08**

13. ESI-QTOF mass spectra of the model reaction

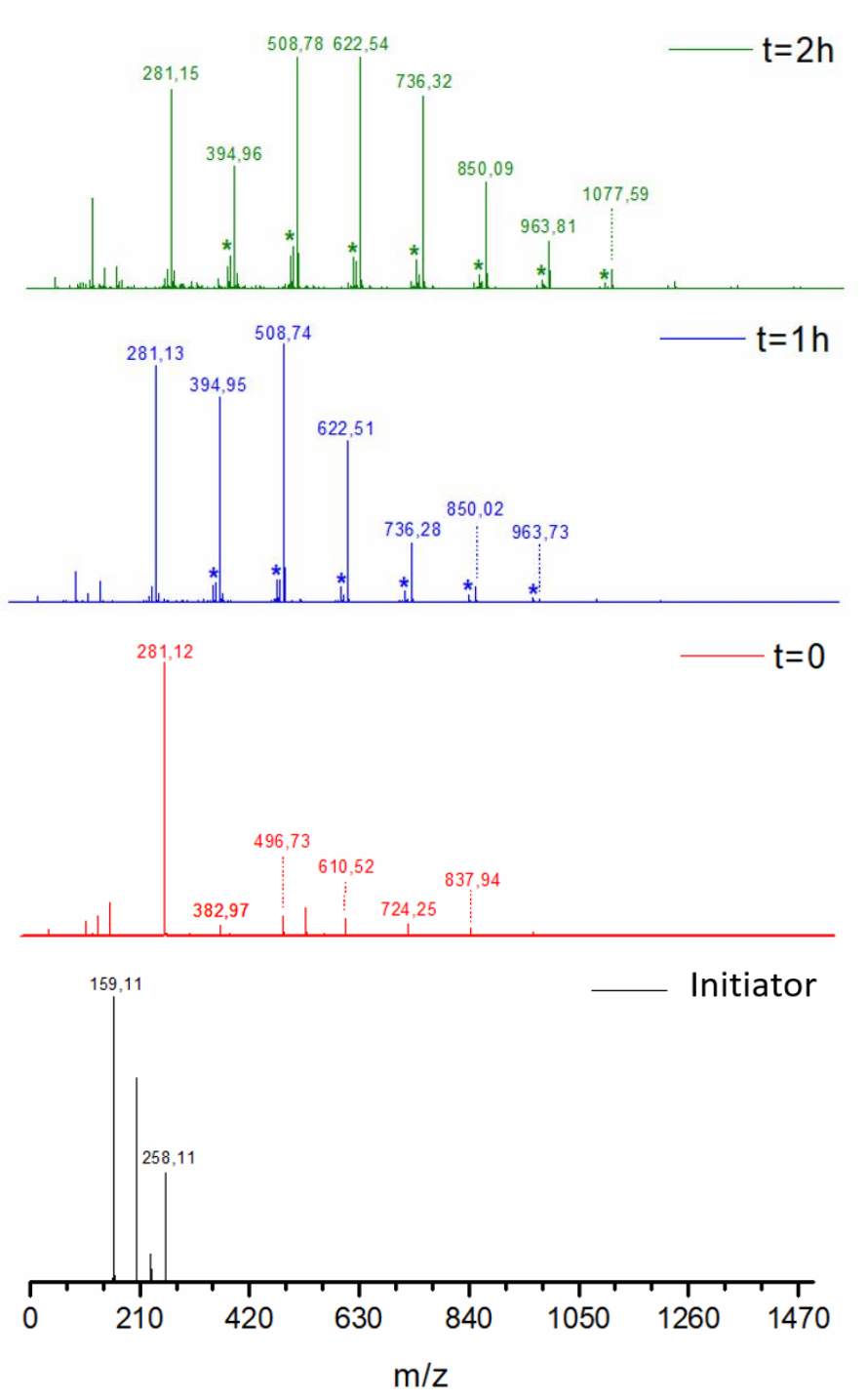


Figure S82. ESI-QTOF of first hours of the model reaction. The symbol (*) indicates hydrogen-terminated chains.

14. TGA and DSC thermograms of compounds PCL-01 to PCL-08

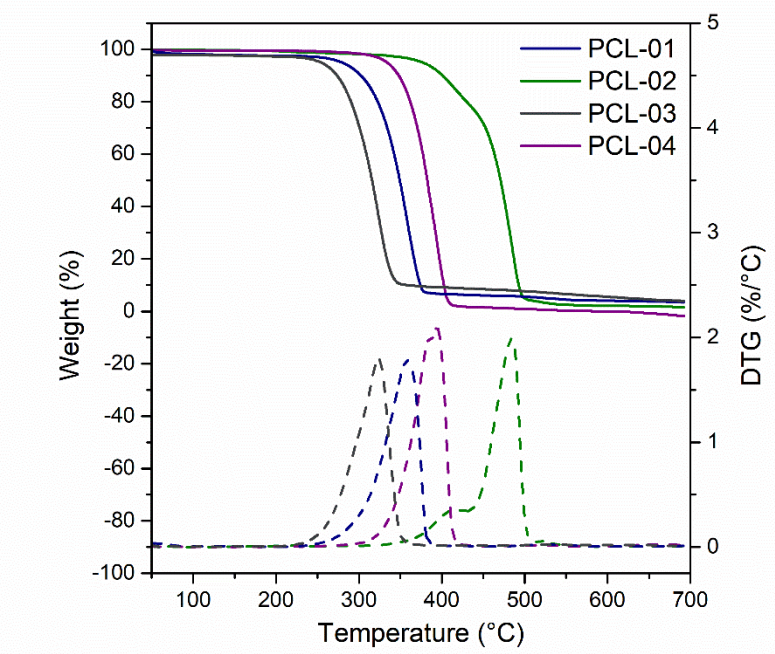


Figure S83. TGA thermograms for compounds **PCL-01** to **PCL-04**.

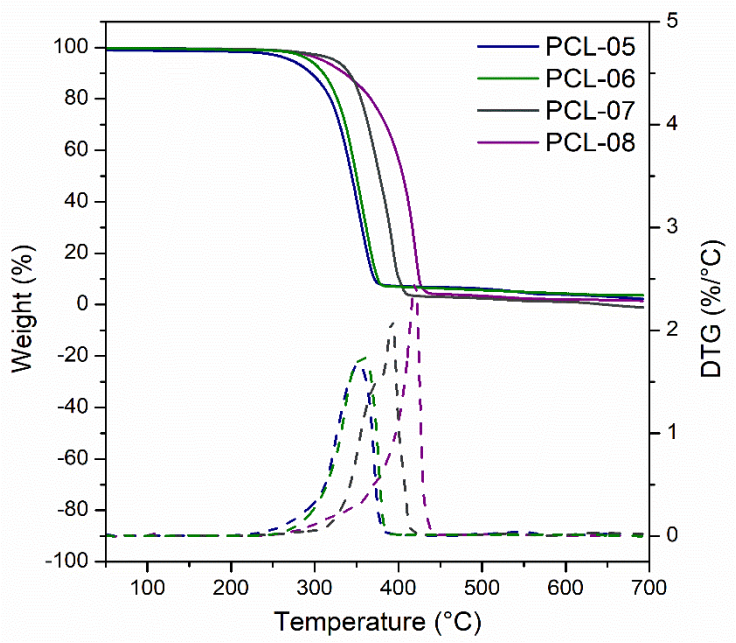


Figure S84. TGA thermograms for compounds **PCL-05** to **PCL-08**.

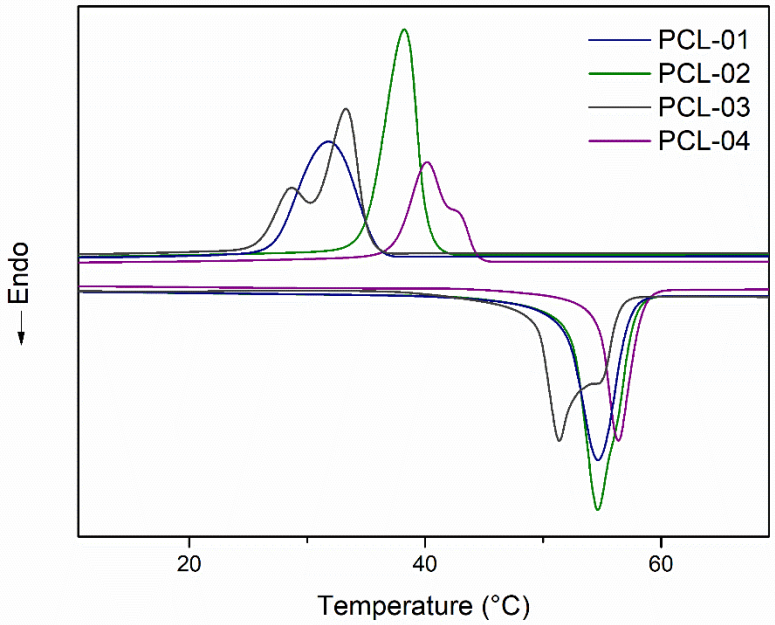


Figure S85. DSC thermograms for compounds **PCL-01** to **PCL-04**.

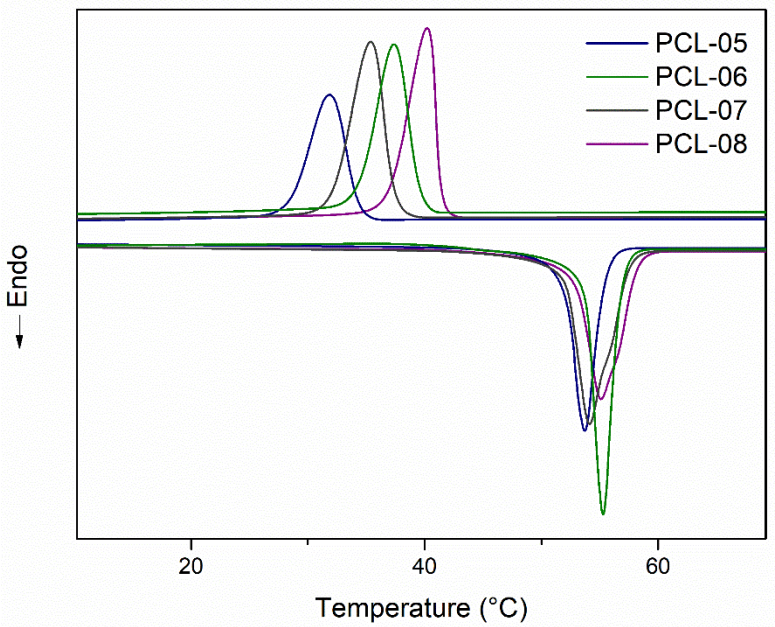


Figure S86. DSC thermograms for compounds **PCL-05** to **PCL-08**.

15. HPLC chromatogram and NMR spectra of (*S*)-2-((*R*)-hydroxy(4-nitro phenyl)methyl)cyclohexanone (11)

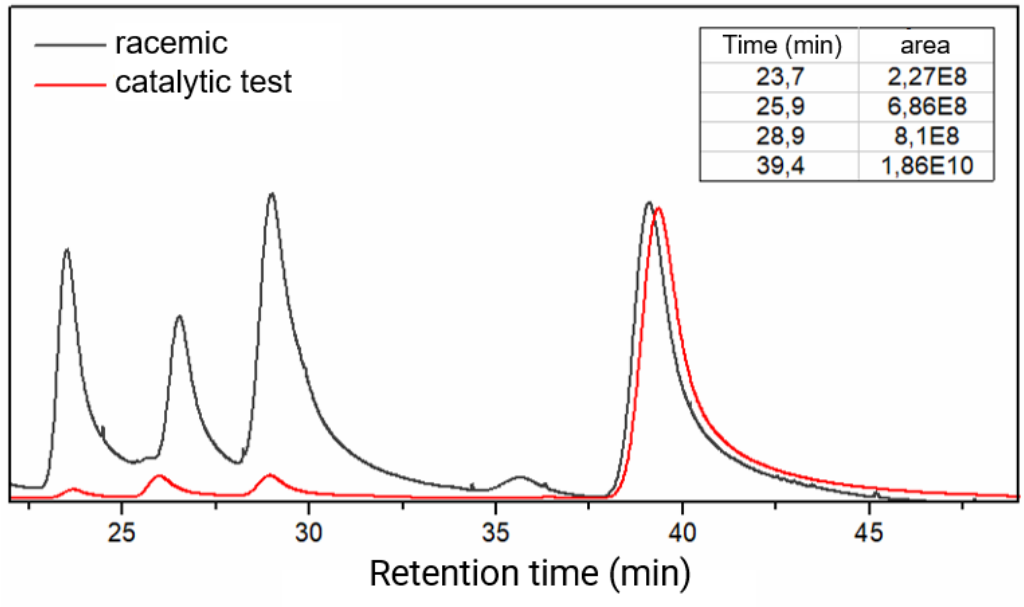


Figure S87. HPLC chromatogram of compound **11** (racemic mixture and catalytic test product).

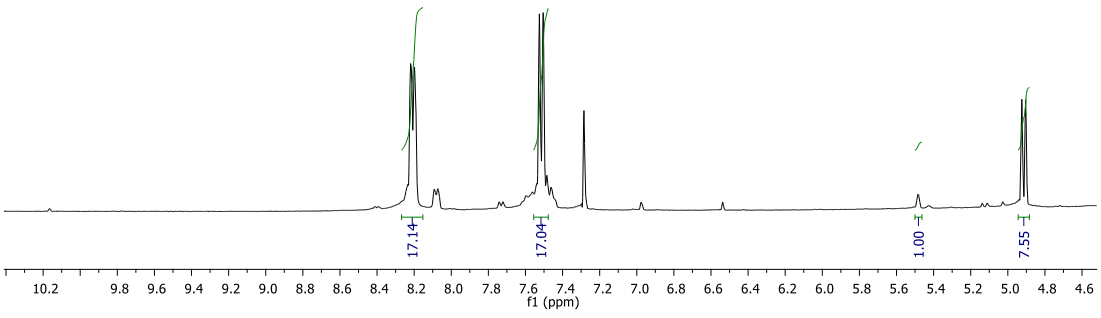


Figure S88. Magnification of the ^{1}H NMR spectrum for compound **11** of the ether phase after termination of the catalytic test ($CDCl_3$, 400 MHz).