Synthesis of *syn*- and enantioenriched *anti*-*β*-amino alcohols by highly diastereoselective borono-Mannich allylation reactions

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Supplementary Information

Contents

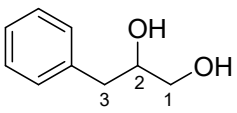
General

Anhydrous solvents were obtained from a John Morris solvent purifier system or commercially from Alfa Aesar or Sigma Aldrich. Tetrahydrofuran was purified by distillation over sodium and benzophenone.[1] All flash column chromatography was performed using Chem Supply silica gel 60 230-400 mesh. Plates for TLC were aluminium backed silica gel 60 F254 obtained from Merck or Chem-Supply. Components were visualised under a UV lamp (245 nm), and by staining with cerium ammonium molybdate stain and development with a 2000-Watt heat gun. This staining solution was prepared by dissolving 48 g of ammonium molybdate and 2 g of cerium(IV) sulfate in 940 mL of distilled water, then adding 60 mL of conc. sulfuric acid. Melting point data was acquired using a Gallenkamp MF-370 capillary tube melting point apparatus and are uncorrected. FTIR data was acquired on a Bruker Vertex 70 FTIR spectrometer using neat samples. Optical rotation data was acquired using a Jasco P-2000 polarimeter equipped with a 1 dm sample cell of volume 2 mL. An average of ten measurements were used to calculate specific rotation. NMR spectroscopy was performed on a Bruker Avance 400 MHz spectrometer, where ^{1}H NMR spectra were acquired at 400 MHz

and ^{13}C NMR spectra acquired at 100 MHz. ^{1}H and ^{13}C NMR chemical shifts acquired in deuterochloroform ($CDCl_3$) are reported in ppm downfield from tetramethylsilane (TMS) at 0.0 ppm. ^{1}H and ^{13}C NMR assignments were made from analysis of COSY, NOESY, HSQC, HMBC and H2BC 2D correlation spectra. For PMB and PMP derivatives, the assignments *o*-C, *m*-C and *p*-C refer to carbon atoms *ortho*-, *meta*-, and *para*-, with the OMe group at the *para*-position. Diastereomeric ratios (dr) were determined from ^{1}H NMR analysis of the purified compounds. High resolution mass spectrometry data was acquired using a Micromass Waters Q-ToF Ultima (quadrupole time-of-flight) mass spectrometer, using MeOH as the solvent. Ionisation method was by electrospray ionisation (ESI). Chiral High Performance Liquid Chromatography was performed on a Shimadzu 30 Series UHPLC. 2-Propanol and hexanes were used as the eluents and were either Honeywell or Reidel-de Haen brand and were filtered through a 0.45 μm Teflon or nylon membrane and ultrasonicated prior to use. Solvent ratio, flow rate, chiral HPLC column, column oven temperature and PDA wavelength are noted for each compound. Retention times and peak integrations were an average of three measurements. Peaks were assigned by comparison to the retention factors of a racemic or scalemic compound, comparison to the retention factor of an enantiomer, or inspection of the absorption spectrum of the compound to distinguish the compound from impurities.

Experimental procedures and data

3-Phenylpropane-1,2-diol (3)



To a solution of allylbenzene (0.5909 g, 5.0 mmol) in 3:1 acetone/water (24 mL) was added *N*-methylmorpholine-*N*-oxide (1.1715 g, 10.0 mmol, 2 equiv.) and potassium osmate dihydrate (18.4 mg, 0.05 mmol, 0.01 equiv.) and the solution wa stirred vigorously at room temperature for 23 h. Sat. aqueous Na_2SO_3 solution (10 mL) was added to the mixture and extracted with EtOAc (3 x 40 mL). The combined organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel eluting with 80:20 EtOAc/hexane to afford the title compound **3** as a colorless oil (0.6936 g, 91%). The spectroscopic data of this compound matched with those in the literature.[2]

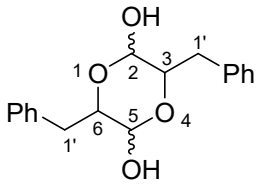
R_f = 0.3 (EtOAc:hexane = 80:20).

IR (neat): ν_{max} 3345, 3028, 2928, 2876, 1604, 1496, 1454, 1089, 1069, 1030, 745, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.29 – 7.25 (m, 2H, ArH), 7.21 – 7.16 (m, 3H, ArH), 3.85 – 3.84 (d, *J* = 5 Hz, 1H, H-2), 3.57 – 3.55 (d, *J* = 10 Hz, 1H, H-1A), 3.42 – 3.37 (br t, *J* = 7.5 Hz, 1H, H-1B), 3.33 (br s, 1H, OH), 2.69 – 2.68 (m, 2H, H-3).

^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 130.0 (*ipso*-C), 129.4 (2 x ArCH), 128.6 (2 x ArCH), 126.5 (ArCH), 73.2 (C-2), 65.9 (C-1), 39.7 (C-3).

3,6-Diphenyl-1,4-dioxane-2,5-diol or (*rac*)-2-hydroxy-3-phenylpropanal dimer (4)



A mixture of 3-phenylpropane-1,2-diol (**4**) (0.1174 g, 0.77 mmol), TEMPO (2.4 mg, 0.01 mmol, 0.02 equiv.), potassium bromide (0.1010 g, 0.85 mmol, 1.1 equiv.), anhydrous CH_2Cl_2 (7 mL) and sat. aqueous $NaHCO_3$ solution (2.8 mL) was cooled to 0 °C and added slowly dropwise commercial 0.56 M sodium hypochlorite solution (2 mL, 1.1 mmol, 1.4 equiv.) and stirred at 0 °C for 1 h. The reaction mixture was quenched by addition of sat. aqueous $Na_2S_2O_3$ (7 mL) at 0 °C and extracted with EtOAc (3 x 20 mL). The combined organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel eluting with 4:96 MeOH/CH_2Cl_2 to afford the title compound **4** as a colorless oil (0.6580 g, 68%) and as a diastereomeric mixture.

R_f = 0.4 (MeOH:CH_2Cl_2 = 4:96).

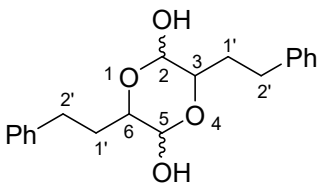
IR (neat): ν_{max} 3326, 3271, 2918, 2908, 2850, 1603, 1496, 1137, 1073, 1028, 695 cm^{-1}.

The ^{1}H and ^{13}C NMR spectroscopic data could not be determined.

ESI-MS *m/z* 323 (100%) $[M + Na]^+$.

HR-ESI-MS *m/z* calculated for $C_{20}H_{24}O_4Na$ $[M + Na]^+$: 351.1572, found: 351.1571.

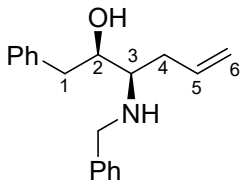
3,6-Diphenethyl-1,4-dioxane-2,5-diol or (*rac*)-2-hydroxy-3-phenylbutanal dimer (4)



The title compound was prepared according to the literature method.[3]

General procedure 1 for Petasis-Borono-Mannich (PBM) reactions with (*rac*)-2-hydroxy-3-phenylpropanal dimer

(2*S*,3*S*)-3-(Benzylamino)-1-phenylhex-5-en-2-ol (*rac*-5a)



To a solution of (*rac*)-2-hydroxy-3-phenylpropanal dimer (**4**) (50.0 mg, 0.17 mmol) in methanol (0.6640 mL) was added benzylamine (42.9 mg, 44 µL 0.4 mmol, 1.18 equiv.) and the mixture was stirred at room temperature for 1 h followed by the addition of allylboronic acid pinacol ester (67.3 mg, 75 µL, 0.4 mmol, 1.18 equiv.) and the mixture was stirred at room temperature. After the reaction had completed (20 h), the mixture was then evaporated. The crude product was dissolved in CH_2Cl_2 (2 mL) and then washed with sat. aqueous $NaHCO_3$ solution (2 x 2 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel eluting with 30:70 EtOAc/hexane to afford the title compound *rac*-**5a** as a yellow oil (63.7 mg, 67%).

R_f = 0.3 (EtOAc:hexane = 30:70).

dr 95:5.

IR (neat): ν_{max} 3576, 3391, 3027, 2919, 2850, 1638, 1603, 1495, 1453, 912, 741, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.35 – 7.19 (m, 10H, Ar*H*), 5.82 – 5.72 (m, 1H, H-5), 5.14 – 5.10 (m, 2H, H-6), 3.88 (d, *J* = 12.7 Hz, 1H, PhCH_AH_BN), 3.73 (d, *J* = 12.7 Hz, 1H, PhCH_AH_BN), 3.68 – 3.63 (m, 1H, H-2), 2.92 (dd, *J* = 13.8, 4.1 Hz, 1H, H-1_A), 2.71 (dd, *J* = 13.8, 8.2 Hz, 1H, H-1_B), 2.61 (appt. q, *J* = 6.4 Hz, 1H, H-3), 2.46 – 2.37 (m, 1H, H-4_A), 2.30 – 2.23 (m, 1H, H-4_B).

^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 140.2 (Ar*C*), 139.1 (Ar*C*), 134.6 (C-5), 129.5 (2 x Ar*C*H), 128.6 (2 x Ar*C*H), 128.5 (2 x Ar*C*H), 128.4 (2 x Ar*C*H), 127.3 (Ar*C*H), 126.4 (Ar*C*H), 118.4 (C-6), 73.0 (C-2), 60.3 (C-3), 52.1 (Ph*C*H_2N), 40.8 (C-1), 35.4 (C-4).

ESI-MS *m/z* 282 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{19}H_{24}NO$ $[M+H]^+$: 282.1858, found: 282.1860.

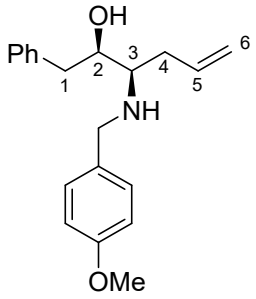
Synthesis of (2*S*,3*S*)-3-(Benzylamino)-1-phenylhex-5-en-2-ol (*rac*-5a) in EtOH

The above reaction was repeated in EtOH using 0.18 mmol of **4**. The crude product was purified by column chromatography over silica gel eluting with 30:70 EtOAc/hexane to afford the title compound *rac*-**5a** as a yellow oil (33.7 mg, 33%).

Synthesis of (2*S*,3*S*)-3-(Benzylamino)-1-phenylhex-5-en-2-ol (*rac*-5a) in DCM

The above reaction was repeated in DCM using 0.06 mmol of **4**. The reaction mixture was stirred for 5 d at rt, after which traces of the desired product (*rac*-**5a**) could be detected by TLC analysis. The crude product was purified by column chromatography over silica gel eluting with 30:70 EtOAc/hexane to afford the title compound *rac*-**5a** as a yellow oil (6.8 mg, 20%).

(2*S*,3*S*)-3-(4-Methoxybenzylamino)-1-phenylhex-5-en-2-ol (*rac*-5b)



The title compound was prepared by General method 1 using 4-methoxybenzylamine (48.4 mg, 45.8 µL 0.35 mmol, 1.18 equiv.) instead of benzylamine. The mixture was stirred at room temperature for 18 h. Purification by column chromatography over silica gel eluting with 30:70 EtOAc/hexane to give *rac*-**5b** as a yellow oil (60.3 mg, 66%).

$\mathbf{R}_f$ = 0.2 (EtOAc:hexane = 30:70).

dr 98:2.

IR (neat): $\boldsymbol{\nu_{max}}$ 3628, 3332, 2917, 2835, 1638, 1511, 1175, 1078, 914, 821, 745, 699 cm^{-1}.

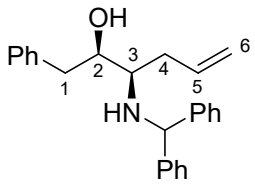
^{1}H NMR (400 MHz, $CDCl_3$): $\boldsymbol{\delta}$ 7.29 – 7.17 (m, 7H, Ar*H*), 6.84 (d, *J* = 8.6 Hz, 2H, Ar*H*), 5.80 – 5.70 (m, 1H, H-5), 5.13 – 5.08 (m, 2H, H-6), 3.81 (d, *J* = 12.6 Hz, 1H, PhCH_AH$_B$N), 3.77 (s, 1H, OCH_3), 3.67 – 3.62 (m, 1H, H-2), 3.65 (d, *J* = 15.5 Hz, 1H, PhCH$_A$$H_B$N), 2.89 (dd, *J* = 13.8, 4.1 Hz, 1H, H-1$_A$), 2.69 (dd, *J* = 13.8, 8.2 Hz, 1H, H-1$_B$), 2.58 (appt. q, *J* = 6.3 Hz, 1H, H-3), 2.42 – 2.37 (m, 1H, H-4$_A$), 2.28 – 2.21 (m, 1H, H-4$_B$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (Ar*C*), 139.1 (Ar*C*), 134.5 (C-5), 129.5 (2 x Ar*C*H), 129.4 (2 x Ar*C*H), 128.4 (2 x Ar*C*H), 126.3 (Ar*C*H), 118.3 (C-6), 114.0 (2 x Ar*C*H), 72.9 (C-2), 60.0 (C-3), 55.3 (O*C*H$_3$), 51.3 (Ph*C*H$_2$N), 40.8 (C-1), 35.3 (C-4).

ESI-MS *m/z* 312 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1964, found: 312.1974.

(2*S*,3*S*)-3-(Benzhydrylamino)-1-phenylhex-5-en-2-ol (*rac*-5c)



The title compound was prepared by General method 1 using benzhydrylamine (50.1 mg, 31.4 µL 0.27 mmol, 1.18 equiv.) instead of benzylamine. The mixture was stirred at room temperature for 16 h. Purification by column chromatography over silica gel eluting with 100% CH_2Cl_2 to give *rac*-**5c** as a yellow oil (58.7 mg, 72%).

R$_f$ = 0.2 (100% CH_2Cl_2).

dr >98:2.

IR (neat): ν_{max} 3577, 3425, 3288, 3025, 2917, 2850, 1638, 1493, 1452, 743, 696 cm^{-1}.

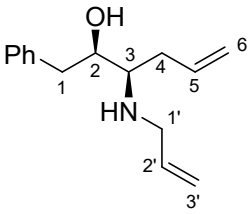
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.13 (m, 15H, Ar*H*), 5.75 – 5.64 (m, 1H, H-5), 5.09 – 5.04 (m, 2H, H-6), 5.00 (br s, 1H, $(Ph)_2CHN$), 3.71 – 3.67 (m, 1H, H-2), 2.82 (dd, *J* = 13.8, 3.9 Hz, 1H, H-1$_A$), 2.70 (dd, *J* = 13.8, 8.6 Hz, 1H, H-1$_B$), 2.60 (q, *J* = 5.5 Hz, 1H, H-3), 2.45 – 2.38 (m, 1H, H-4$_A$), 2.30 – 2.23 (m, 1H, H-4$_B$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4 (Ar*C*), 143.2 (Ar*C*), 139.2 (Ar*C*), 134.5 (C-5), 129.4 (2 x Ar*C*H), 128.7 (2 x Ar*C*H), 128.6 (2 x Ar*C*H), 128.4 (2 x Ar*C*H), 127.8 (2 x Ar*C*H), 127.3 (4 x Ar*C*H), 126.3 (Ar*C*H), 118.4 (C-6), 73.3 (C-2), 64.7 ($(Ph)_2CHN$), 57.9 (C-3), 40.6 (C-1), 35.0 (C-4).

ESI-MS *m/z* 358 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{25}H_{28}NO$ $[M+H]^+$: 358.2171, found: 358.2173.

(2*S*,3*S*)-3-(Allylamino)-1-phenylhex-5-en-2-ol (*rac*-5d)



The title compound was prepared by General method 1 using allylamine (19.7 mg, 25.9 µL 0.35 mmol, 1.18 equiv.) instead of benzylamine. The mixture was stirred at room temperature for 21 h. Purification by column chromatography over silica gel eluting with 60:40 EtOAc/hexane to give *rac*-**5d** as a yellow oil (20.9 mg, 31%).

R_f = 0.2 (EtOAc:hexane = 60:40).

dr >98:2.

IR (neat): ν_{max} 3333, 3076, 2920, 2852, 1640, 1454, 995, 914, 746, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.31 – 7.19 (m, 5H, Ar*H*), 5.91 – 5.71 (m, 2H, H-5 and H-2′), 5.19 – 5.06 (m, 4H, H-6 and H-3′), 3.63 – 3.58 (m, 1H, H-2), 3.34 (ddt, *J* = 13.9, 6.1, 1.3 Hz, 1H, H-1′$_A$), 3.20 (ddt, *J* = 13.9, 5.8, 1.4 Hz, 1H, H-1′$_B$), 2.90 (dd, *J* = 13.8, 4.0 Hz, 1H, H-1$_A$), 2.69 (dd, *J* = 13.8, 8.3 Hz, 1H, H-1$_B$), 2.54 (q, *J* = 6.4 Hz, 1H, H-3), 2.41 – 2.35 (m, 1H, H-4$_A$), 2.26 – 2.18 (m, 1H, H-4$_B$).

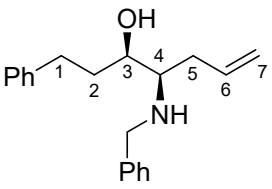
^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 139.1 (Ar*C*), 136.8 (C-2′), 134.6 (C-5), 129.5 (2 x Ar*C*H), 128.5 (2 x Ar*C*H), 126.3 (Ar*C*H), 118.3 (C-6), 116.1 (C-3′), 72.9 (C-2), 60.1 (C-3), 50.5 (C-1′), 40.8 (C-1), 35.5 (C-4).

ESI-MS *m/z* 232 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{15}H_{22}NO$ $[M+H]^+$: 232.1701, found: 232.1712.

General Procedure 2 for Petasis-Borono-Mannich (PBM) reactions with (*rac*)-2-hydroxy-3-phenylbutanal dimer

(3*S*,4*S*)-4-(Benzylamino)-1-phenylhept-6-en-3-ol (*rac*-5e)



To a solution of (*rac*)-2-hydroxy-3-phenylbutanal dimer (30.0 mg, 0.09 mmol, 1 equiv.) in methanol (0.3640 mL) was added benzylamine (23.5 mg, 24 µL 0.22 mmol, 1.18 equiv.) and the mixture was stirred at room temperature for 1 h followed by the addition of allylboronic acid pinacol ester (41.2 mg, 46 µL, 0.22 mmol, 1.18 equiv.) and the mixture was stirred at room temperature. After the reaction had completed (20 h), the mixture was then evaporated. The

crude product was dissolved in CH_2Cl_2 (2 mL) and then washed with sat. aqueous $NaHCO_3$ solution (2 x 2 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography over silica gel eluting with 30:70 EtOAc/hexane to afford the title compound *rac*-**5e** as a yellow oil (45.0 mg, 83%).

R_f = 0.2 (EtOAc:hexane = 30:70).

dr 91:9.

IR (neat): ν_{max} 3404, 3026, 2920, 2851, 1639, 1603, 1453, 913, 741, 697 cm^{-1}.

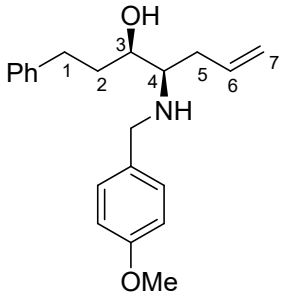
^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.33 – 7.15 (m, 10H, Ar*H*), 5.75 – 5.65 (m, 1H, H-6), 5.11 – 5.06 (m, 2H, H-7), 3.85 (d, *J* = 12.7 Hz, 1H, PhCH_AH_BN), 3.69 (d, *J* = 12.7 Hz, 1H, PhCH_AH_BN), 3.34 (td, *J* = 8.0, 3.0 Hz, 1H, H-3), 2.92 – 2.84 (m, 1H, H-1_A), 2.72 – 2.66 (m, 1H, H-1_B), 2.56 – 2.51 (m, 1H, H-4), 2.40 – 2.34 (m, 1H, H-5_A), 2.23 – 2.16 (m, 1H, H-5_B), 1.90 – 1.82 (m, 1H, H-2_A), 1.75 – 1.65 (m, 1H, H-2_B).

^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 142.5 (Ar*C*), 140.1 (Ar*C*), 134.3 (C-6), 128.6 (4 x Ar*C*H), 128.4 (2 x Ar*C*H), 128.3 (2 x Ar*C*H), 127.3 (Ar*C*H), 125.8 (Ar*C*H), 118.4 (C-7), 71.3 (C-3), 61.1 (C-4), 52.0 (Ph*C*H_2N), 36.4 (C-2), 35.1 (C-5), 32.3 (C-1).

ESI-MS *m/z* 296 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{20}H_{26}NO$ $[M+H]^+$: 296.2014, found: 296.2023.

(3*S*,4*S*)-4-(4-Methoxybenzylamino)-1-phenylhept-6-en-3-ol (*rac*-5f)



The title compound was prepared by General method 2 using 4-methoxybenzylamine (69.9 mg, 66.4 µL 0.50 mmol, 1.18 equiv.) instead of benzylamine. The mixture was stirred at room temperature for 26 h. Purification by column chromatography over silica gel eluting with 2:98 MeOH/CH_2Cl_2 to give *rac*-**5f** as a yellow oil (81.4 mg, 60%).

R_f = 0.2 (MeOH:CH_2Cl_2 = 2:98).

dr 90:10.

IR (neat): ν_{max} 3375, 2928, 1611, 1496, 1454, 1245, 1176, 1033, 916, 821, 748, 699 cm^{-1}.

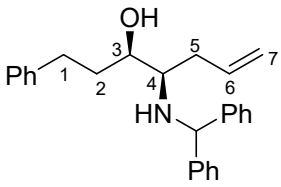
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.14 (m, 7H, Ar*H*), 6.84 (d, *J* = 8.6 Hz, 2H, Ar*H*), 5.74 – 5.64 (m, 1H, H-6), 5.10 – 5.06 (m, 2H, H-7), 3.79 (d, *J* = 12.5 Hz, 1H, PhC$H_A$$H_B$N), 3.76 (s, 1H, OC$H_3$), 3.63 (d, *J* = 12.5 Hz, 1H, PhC$H_A$$H_B$N), 3.35 (td, *J* = 8.0, 3.0 Hz, 1H, H-3), 2.91 – 2.83 (m, 1H, H-1_A), 2.70 – 2.63 (m, 1H, H-1_B), 2.52 (q, *J* = 6.6 Hz, 1H, H-4), 2.39 – 2.32 (m, 1H, H-5_A), 2.22 – 2.15 (m, 1H, H-5_B), 1.89 – 1.80 (m, 1H, H-2_A), 1.73 – 1.64 (m, 1H, H-2_B).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (Ar*C*), 142.4 (Ar*C*), 134.2 (C-6), 131.7 (Ar*C*), 129.5 (2 x Ar*C*H), 128.5 (2 x Ar*C*H), 128.4 (2 x Ar*C*H), 125.8 (Ar*C*H), 118.4 (C-7), 113.9 (2 x Ar*C*H), 71.2 (C-3), 60.8 (C-4), 55.3 (O*C*H_3), 51.2 (Ph*C*H_2N), 36.3 (C-2), 34.9 (C-5), 32.6 (C-1).

ESI-MS *m/z* 326 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{21}H_{28}NO_2$ $[M+H]^+$: 326.2120, found: 326.2130.

(3*S*,4*S*)-4-(Benzhydrylamino)-1-phenylhept-6-en-3-ol (*rac*-5g)



The title compound was prepared by General method 4 using benzhydryl amine (62.1 mg, 58.4 µL 0.34 mmol, 1.18 equiv.) instead of benzylamine. The mixture was stirred at room temperature for 28 h. Purification by column chromatography over silica gel eluting with 100% CH_2Cl_2 to give *rac*-**5g** as a yellow oil (72.0 mg, 69%).

R_f = 0.4 (100% CH_2Cl_2).

dr 95:5.

IR (neat): ν_{max} 3430, 3025, 2922, 2856, 1601, 1493, 1451, 1049, 915, 744, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.13 (m, 15H, Ar*H*), 5.67 – 5.57 (m, 1H, H-6), 5.06 – 5.02 (m, 2H, H-7), 4.98 (br s, 1H, $(Ph)_2$C*H*N), 3.41 – 3.37 (m, 1H, H-3), 2.83 – 2.76 (m, 1H, H-1_A), 2.65 – 2.58 (m, 1H, H-1_B), 2.53 (q, *J* = 5.0 Hz, 1H, H-4), 2.42 – 2.35 (m, 1H, H-5_A), 2.23 – 2.16 (m, 1H, H-5_B), 1.87 – 1.79 (m, 1H, H-2_A), 1.71 – 1.61 (m, 1H, H-2_B).

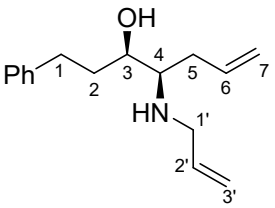
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3 (Ar*C*), 142.9 (Ar*C*), 142.4 (Ar*C*), 134.0 (C-6), 128.7 (4 x Ar*C*H), 128.6 (2 x Ar*C*H), 128.4 (2 x Ar*C*H), 127.7 (2 x Ar*C*H), 127.4 (Ar*C*H), 127.3 (3

x Ar*C*H), 125.8 (Ar*C*H), 118.7 (C-7), 71.6 (C-3), 64.5 ((Ph)$_2$*C*HN), 58.4 (C-4), 35.8 (C-2), 34.4 (C-5), 32.2 (C-1).

ESI-MS *m/z* 372 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{26}H_{29}NONa$ $[M+Na]^+$: 394.2147, found: 394.2142.

(3*S*,4*S*)-4-(Allylamino)-1-phenylhept-6-en-3-ol (*rac*-5h)



The title compound was prepared by General method 4 using allylamine (15.9 mg, 20.8 µL 0.28 mmol, 1.18 equiv.) instead of benzylamine. The mixture was stirred at room temperature for 27 h. Purification by column chromatography over silica gel eluting with 40:60 acetone/hexane to give *rac*-**5h** as a yellow oil (14.9 mg, 26%).

R$_f$ = 0.2 (acetone:hexane = 40:60).

dr 81:19.

IR (neat): ν_{max} 3387, 2923, 2856, 1640, 1496, 1454, 994, 915, 747, 699 cm^{-1}.

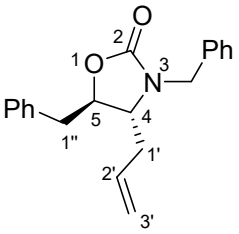
^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.30 – 7.16 (m, 5H, Ar*H*), 5.86 – 5.82 (m, 1H, H-2′), 5.71 – 5.70 (m, 1H, H-6), 5.20 – 5.06 (m, 4H, H-7 and H-3′), 3.39 – 3.32 (m, 2H, H-3 and H-1′$_A$), 3.26 – 3.18 (m, 1H, H-3 and H-1′$_B$), 2.93 – 2.86 (m, 1H, H-2$_A$), 2.73 – 2.65 (m, 1H, H-2$_B$), 2.53 – 2.46 (m, 1H, H-4), 2.37 – 2.31 (m, 1H, H-5$_A$), 2.21 – 2.14 (m, 1H, H-5$_B$), 1.88 – 1.81 (m, 1H, H-1$_A$), 1.74 – 1.66 (m, 1H, H-1$_B$).

^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 142.5 (Ar*C*), 136.2 (C-2′), 134.2 (C-6), 128.6 (2 x Ar*C*H), 128.5 (2 x Ar*C*H), 125.9 (Ar*C*H), 118.6 (C-7), 116.7 (C-3′), 71.2 (C-3), 61.0 (C-4), 50.3 (C-1′), 36.5 (C-1), 35.1 (C-5), 32.4 (C-2).

ESI-MS *m/z* 246 $[M+H]^+$

HR-ESI-MS *m/z* calculated for $C_{16}H_{24}NO$ $[M+H]^+$: 246.1858, found: 246.1866.

(4*S,5*S**)-4-Allyl-3,5-dibenzyloxazolidin-2-one (*rac*-6)**



To a solution of **5a** (11.3 mg, 0.04 mmol) and triethylamine (22.4 µL, 0.16 mmol, 4.0 equiv.) in anhydrous CH_2Cl_2 (1.3 mL) was added triphosgene

(6.3 mg, 0.02 mmol, 0.53 equiv.) at 0 °C under a nitrogen atmosphere. After being stirred for 15 min, the reaction mixture was warm to room temperature and stirred for 17 h, and then concentrated *in vacuo* to give the crude product. Purification by column chromatography over silica gel eluting with 20:80 EtOAc/hexane gave *rac*-**6** as a colorless oil (5.5 mg, 45%).

$\mathbf{R}_f$ = 0.3 (EtOAc:hexane = 20:80).

IR (neat): ν_{max} 3477, 2922, 2854, 1744, 1424, 1244, 1001, 750, 729 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.24 (m, 6H, Ar*H*), 7.10 – 7.06 (m, 4H, Ar*H*), 5.51 – 5.42 (m, 1H, H-2′), 5.12 – 5.04 (m, 2H, H-3′), 4.78 (d, *J* = 15.3 Hz, 1H, PhCH_AH_BN), 4.42 (q, *J* = 6.0 Hz, 1H, H-5), 4.49 (d, *J* = 15.3 Hz, 1H, PhCH_AH_BN), 3.30 (appt. q, *J* = 5.2 Hz, 1H, H-4), 2.86 (appt. qd, *J* = 14.0, 5.8 Hz, 1H, H-1″), 2.21 – 2.17 (m, 2H, H-1′).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7 (C-2), 135.7 (ArC), 135.0 (ArC), 131.4 (C-2′), 129.8 (2 x ArCH), 129.0 (2 x ArCH), 128.8 (2 x ArCH), 128.0 (2 x ArCH), 127.9 (ArCH), 127.2 (ArCH), 120.0 (C-3′), 78.2 (C-5), 77.4 (C-3′), 76.4 (C-5), 57.0 (C-4), 45.9 ($PhCH_2N$), 40.4 (C-1″), 36.0 (C-1′).

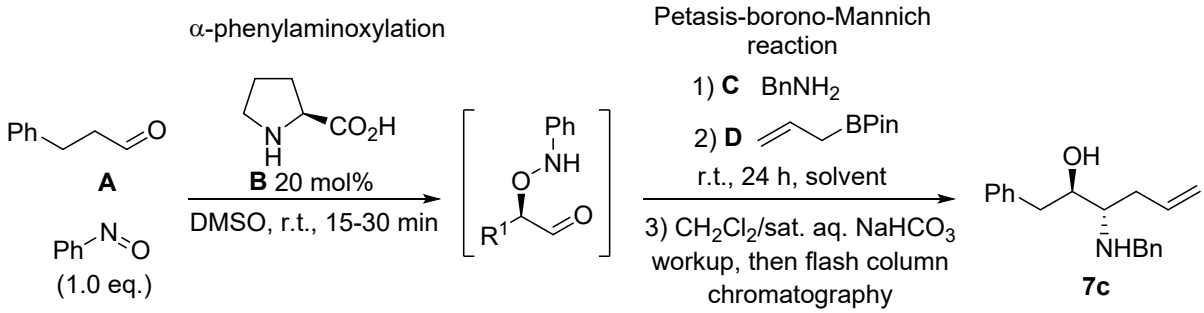
ESI-MS *m*/*z* 308 $[M+H]^+$.

HR-ESI-MS: *m*/*z* calculated for $C_{20}H_{22}NO_2$ $[M + H]^+$: 308.1651, found: 308.1659.

Optimisation studies using chiral α-phenylaminoxyaldehydes

1) Zhong DMSO method[4]

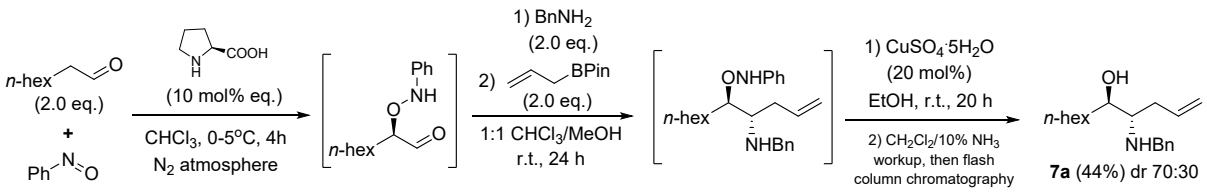
Table SI-1: Summary of PBM optimisation procedures using Zhong's method to produce chiral α-phenylaminoxyaldehydes.



Entry	Eq. of A	Solvent for PBM reaction	Eq. of C and D	Yield of 7c	Notes
1	1.2	DMSO-d_6	1.5	15	
2	1.2	1:1 DMSO/MeOH	1.5	17	
3	1.2	DMSO	1.5	31	
4	1.2	DMSO	1.5	-	Aminoxylation performed anhydrous, allyl-BF3K used. Rxn failed.
5	1.2	DMSO	2.0	31	
6	1.2	DMSO	2.0	37	N-O bond reduction after treatment with $CuSO_4$, workup with NH_3.

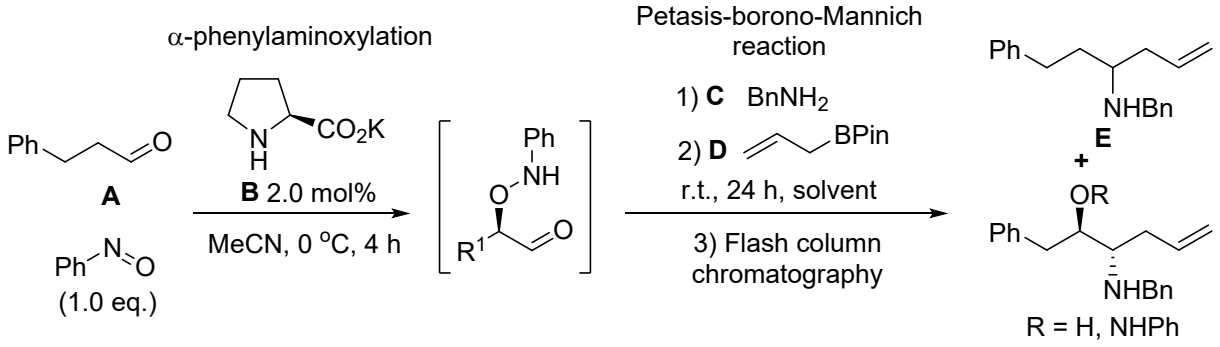
2) MacMillan $CHCl_3$ method[5]

Table SI-2: Summary of PBM optimisation procedures using Macmillan's method to produce chiral α-phenylaminoxyaldehydes. It was identified that a large excess of starting aldehyde would hinder the PBM reaction with by-products, so attempts were made to make the reaction work with less equivalents of starting material. In an attempted one-pot PBM reaction, the product **7a** was obtained in a modest yield of 44% with a poor dr of 70:30.



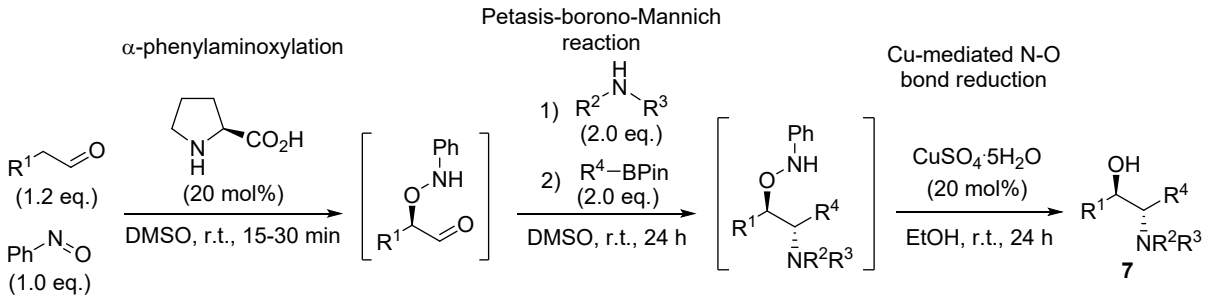
3) Hayashi MeCN method[6]

Table SI-3: Summary of PBM optimisation procedures using Hayashi's method to produce chiral α-phenylaminoxyaldehydes. As above, attempts were made to make the reaction work with less equivalents of starting materials. These reactions were unsuccessful.



Entry Book ID	Eq. of A	Solvent for PBM reaction	Eq. of C and D	Yield (%)	Notes
1 PC_3_34	1.5	MeCN	2.0	17	17% yield of Mannich adduct **E**
2 PC_3_38	1.5	-	-	-	Dry conditions. Attempted isolation of aminoxyaldehyde
3 PC_3_43	1.5	MeCN	2.0	6	White solid (boronate salt?) produced, 6% yield of Mannich adduct **E**
4 PC_3_48	1.5	1:1 MeCN/MeOH	2.0	<1	<1% yield of Mannich addict **E**
5 PC_4_58	3.0	MeCN	3.0	39	Allyl-BF_3K used. 39% yield of Mannich adduct **E**, white solid produced

General Procedure 3 for the one-pot preparation of *anti-β*-aminoalcohols from aldehydes.

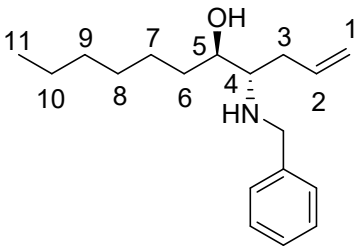


Part A: α-aminoxylation of aldehydes: To a 10 mL round-bottomed flask was added L-proline (6.9 mg, 0.06 mmol, 0.2 eq or 20 mol%) and anhydrous dimethyl sulfoxide (0.5 mL), and with stirring was added the aldehyde component (0.36 mmol, 1.2 eq). This mixture was sealed and stirred at room temperature for 5 min, after which was added nitrosobenzene (32.1 mg, 0.3 mmol, 1.0 eq), turning the reaction mixture green. The reaction mixture was then re-sealed and stirred at room temperature until completion (approx. 15-20 min), as determined by TLC and the colour change from green to yellow-orange.

Part B: Borono-Mannich reaction: Upon completion of Part A, to the reaction mixture was added the amine component (0.60 mmol, 2.0 eq) and the reaction mixture stirred at room temperature for 5 min. Pinacol allylboronate (116.0 μL, 0.60 mmol, 2.0 eq) was then added and the reaction mixture was stirred at room temperature with TLC monitoring for 24 h. Upon completion of the reaction, the mixture was added to a separating funnel with sat. $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2. (3 x 3 mL) The combined organic layers were dried over anhydrous K_2CO_3, filtered and concentrated *in vacuo* and used for Part C.

Part C: N-O bond cleavage: Upon completion of Part B, ethanol (~0.5 mL) and $CuSO_4 \cdot 5H_2O$ (15.0 mg, 0.1 mmol, 0.2 eq or 20 mol%) was added and the reaction mixture was stirred at room temperature for 24 h with TLC monitoring. The reaction mixture was then added to a separating funnel with ~10% aqueous NH_3 solution (~5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over anhydrous K_2CO_3, filtered then concentrated *in vacuo* and purified by flash column chromatography over silica gel to obtain the pure *β*-amino alcohol product **7**.

(4*S*,5*R*)-4-(Benzylamino)undec-1-en-5-ol (7a)



The title compound was prepared according to *General Procedure 3*, using octanal (56.2 μL, 0.36 mmol, 1.2 eq) as the aldehyde component and benzylamine (65.5 μL, 0.60 mmol, 2.0 eq) as the amine component. After extraction with CH_2Cl_2 in Part B the combined organic layers were washed once with sat. aq. NaCl (~5 mL) before drying and concentration. Purification by flash column chromatography eluting with a gradient of 15:85 and 1:3 EtOAc/*n*-hexane gave the title product **7a** (45.4 mg, 54%) as a pale-yellow oil.

$\mathbf{R_f}$ = 0.09 (1:3 EtOAc/*n*-hexane).

dr 97:3.

ee 92%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C PDA 207 nm. R_t (mins) 7.31 (major enantiomer), 8.31 (minor enantiomer).

$[\alpha]_D^{25}$ +1.6 (*c* 0.31, $CHCl_3$).

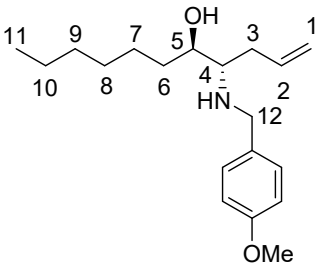
IR (neat): ν_{max} 3332 (O-H str.), 3063 (sp^2 C-H str.), 2925 (sp^3 C-H str.), 1639 (C=C str.) 1600 (Ar C=C str.), 1496 (N-H bend), 1454 (Ar C=C str.), 1075 (C-O str.), 912 (*sp^2* C-H oop), 697 (Ar C-H oop), 743 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.23 (m, 5H, Ar-*H*), 5.78 – 5.64 (m, 1H, H-2), 5.13 – 5.05 (m, 2H, H-1), 3.84 (d, *J* = 13.0 Hz, 1H, CH_AH$_B$Ph), 3.78 – 3.71 (m, 1H, H-5), 3.71 (d, *J* = 13.0 Hz, 1H, CH$_A$$H_B$Ph), 2.60 (ddd, *J* = 9.8, 3.9, 3.2 Hz, 1H, H-4), 2.28 (dddd, *J* = 12.6, 5.5, 3.9, 1.9 Hz, 1H, H-3), 2.15 – 2.03 (m, 1H, H-3), 1.57 – 1.40 (m, 2H, H-6), 1.40 – 1.21 (m, 8H, H-7, H-8, H-9, H-10), 0.89 (t, *J* = 6.8 Hz, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2 (*ipso*-C), 135.8 (C-2), 128.5 (*o*-C), 128.1 (*m*-C), 127.1 (*p*-C), 118.1 (C-1), 69.5 (C-5), 59.7 (C-4), 51.5 (*C*H$_2$Ph), 32.7 (C-3), 32.2 (C-6), 31.8 (C-9), 29.5 (C-8), 26.5 (C-7), 22.6 (C-10), 14.1 (C-11).

HRMS (ESI): *m/z* calculated for $C_{18}H_{30}NO$ $[M+H]^+$: 276.2327, found 276.2328.

(4*S*,5*R*)-4-((4-Methoxybenzyl)amino)undec-1-en-5-ol (7b)



The title compound was prepared according to *General Procedure 3*, using octanal (56.2 μL, 0.36 mmol, 1.2 eq) as the aldehyde component and *para*-methoxybenzylamine (91.5 μL, 0.60 mmol, 2.0 eq) as the amine component. After extraction with CH_2Cl_2 in Part B the combined organic layers were washed once with NaCl

brine (~5 mL) before drying and concentration. Purification by flash column chromatography eluting with 3:7 EtOAc/*n*-hexane gave the title product **7b** (35.5 mg, 37%) as a yellow-white crystal. This compound could be further purified by recrystallisation using the solvent diffusion method with CH_2Cl_2 and *n*-hexane,[7] however these crystals were unsuitable for X-ray crystallography.

R_f = 0.09 (3:7 EtOAc/*n*-hexane).

dr 99:1.

ee 99%. Chiralpak IG-3 column and guard, 20% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 °C, PDA 207 nm. R_t (mins) 8.65 (major enantiomer), minor enantiomer not observed (expected at 12.16 mins). (*ee* measured on recrystallised sample).

Mp.: 62-66 °C.

$[\alpha]_D^{25}$ +18.1 (*c* 0.73, $CHCl_3$).

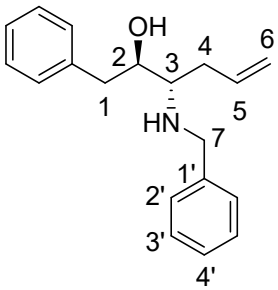
IR (neat): ν_{max} 3167 (O-H str.), 3074 (sp^2 C-H str.), 2921 (sp^3 C-H str.), 1641 (C=C str.), 1610 (Ar. C=C str.), 1513 (N-H bend), 1455 (Ar. C=C str.), 1374 (CH_3 bend), 1968 (C-O str.), 1089 (C-O str.), 907 (sp^2 C-H oop), 808 (Ar. C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.6 Hz, 2H, *m*-H), 6.86 (d, *J* = 8.6 Hz, 2H, *o*-H), 5.77 – 5.64 (m, 1H, H-2), 5.15 – 5.05 (m, 2H, H-1), 3.80 (s, 3H, OCH_3), 3.78 (d, *J* = 12.9 Hz, 1H, CH_AH$_B$ H-12), 3.73 (dt, *J* = 8.4, 3.5 Hz, 1H, H-5), 3.65 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-12), 2.59 (dt, *J* = 9.55, 3.5 Hz, 1H, H-4), 2.27 (appt. dtt, *J* = 14.3, 3.8, 1.8 Hz, 1H, H-3), 2.08 (appt. dt, *J* = 14.3, 9.55 Hz, 1H, H-3), 1.57 – 1.42 (m, 2H, H-6), 1.40 – 1.19 (m, 8H), 0.94 – 0.83 (m, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8 (*p*-C), 135.8 (C-2), 132.2 (*ipso*-C), 129.3 (*m*-C), 118.1 (C-1), 113.9 (*o*-C), 69.5 (C-5), 59.6 (C-4), 55.3 (O*C*H$_3$), 50.9 (*C*H$_2$Ar), 32.7 (C-3), 32.2 (C-6), 31.8 (C-9), 29.5 (C-8), 26.5 (C-7), 22.6 (C-10), 14.1 (C-11).

HRMS (ESI): *m/z* calculated for $C_{19}H_{32}NO_2$ $[M+H]^+$: 306.2433, found 306.2441.

(2*R*,3*S*)-3-(Benzylamino)-1-phenylhex-5-en-2-ol (7c)



The title compound was prepared according to *General Procedure 3*, using hydrocinnamaldehyde (47.5 μL, 0.36 mmol, 1.2 eq) as the aldehyde component and benzylamine as the amine component (65.5

μL, 0.6 mmol, 2.0 eq). Purification by flash column chromatography eluting with 3:7 EtOAc/*n*-hexane gave the title product **7c** (33.8 mg, 37%) as a brown crystal. This compound produced crystals suitable for X-ray crystallography, grown by the solvent diffusion method using $CHCl_3$ and *n*-hexane.[7]

R_f = 0.13 (3:7 EtOAc/*n*-hexane).

dr 94:6; 97:3 after recrystallisation.

ee 99%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 °C PDA 207 nm. R_t (mins) 9.26 (major enantiomer), minor enantiomer not detected (*ee* measured on recrystallised sample).

Mp.: 82-86 °C.

$[\alpha]_D^{25}$ +1.3 (*c* 0.61, $CHCl_3$).

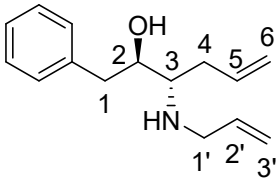
IR (neat): ν_{max} 3363 (O-H str.), 3091, 3059, 1659 (C=C str.), 1601 (Ar. C=C str.), 1484 (N-H bend), 1456 (Ar. C=C str.), 1071 (C-O str.) 687 (Ar. C-H oop), 760 (Ar. C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.21 (m, 10H, Ar-*H*), 5.79 – 5.66 (m, 1H, H-5), 5.17 – 5.08 (m, 2H, H-6), 3.99 (ddd, *J* = 8.5, 4.8, 3.4 Hz, 1H, H-2), 3.81 (d, *J* = 13.1 Hz, 1H, CH_AH$_B$Ph, H-7), 3.70 (d, *J* = 13.1 Hz, 1H, CH$_A$$H_B$Ph H-7), 2.81 (dd, *J* = 13.8, 8.5 Hz, 1H, CH_AH$_B$Ph, H-1), 2.73 (dd, *J* = 13.8, 4.8 Hz, 1H, CH$_A$$H_B$Ph H-1), 2.66 (ddd, *J* = 9.4, 4.0, 3.4 Hz, 1H, H-3), 2.42 (dddt, *J* = 14.3, 5.7, 4.1, 1.6 Hz, 1H, H-4), 2.28 – 2.16 (m, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.0 (C-1'), 139.1 (*ipso*-C), 135.5 (C-5), 129.1 (*m*-C), 128.49 (*o*-C), 128.47 (C-2'), 128.1 (C-3'), 127.1 (C-4'), 126.3 (*p*-C), 118.2 (C-6), 71.2 (C-2), 59.4 (C-3), 51.5 (C-7), 38.7 (C-1), 33.0 (C-4).

HRMS (ESI): *m/z* calculated for $C_{19}H_{25}NO$ $[M+H]^+$: 282.1858, found 282.1855.

(2*R*,3*S*)-3-(Allylamino)-1-phenylhex-5-en-2-ol (7d)



The title compound was prepared according to *General Procedure 3*, using hydrocinnamaldehyde (47.5 μL, 0.36 mmol, 1.2 eq) as the aldehyde component and allylamine (45.0 μL, 0.60 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography eluting with 2:3 EtOAc/*n*-hexane gave the title product **7d** (34.3 mg, 45%) as a dark yellow oil.

R_f = 0.07 (2:3 EtOAc/*n*-hexane).

dr 92:8.

ee could not be measured reliably.

$[\alpha]_D^{25}$ +6.34 (*c* 0.38, $CHCl_3$).

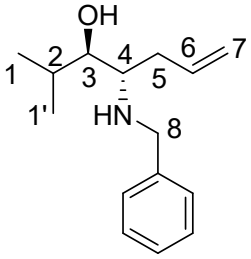
IR (neat): ν_{max} 3311 (O-H str.), 3064 (sp^2 C-H str.), 2923 (sp^3 C-H str.), 1640 (C=C str.), 1602 (Ar C=C str.), 1495 (N-H bend), 1454 (Ar C=C str.), 1030 (C-O str.) 994 (sp^2 C-H oop), 914 (sp^2 C-H oop), 745 (Ar C-H oop), 698 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.15 (m, 5H, Ar-*H*), 5.93 – 5.70 (m, 2H, H-5, H-2'), 5.23 – 5.03 (m, 4H, H-6, H-3'), 3.95 (ddd, *J* = 8.4, 4.8, 3.2 Hz, 1H, H-2), 3.27 (appt. ddt, *J* = 14.1, 5.5, 1.5 Hz, 1H, CH_AH$_B$ H-1'), 3.19 (appt. ddt, *J* = 14.1, 6.7, 1.3 Hz, 1H, CH$_A$$H_B$ H-1'), 2.80 (dd, *J* = 13.8, 8.6 Hz, 1H, CH_AH$_B$ H-1), 2.72 (dd, *J* = 13.8, 4.8 Hz, 1H, CH_AH$_B$ H-1), 2.64 (ddd, *J* = 9.1, 4.2, 3.2 Hz, 1H, H-3), 2.46 – 2.37 (m, 1H, H-4), 2.22 (dt, *J* = 14.4, 9.1 Hz, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.1 (*ipso*-C), 136.2 (C-2'), 135.5 (C-5), 129.1 (*m*-C), 128.5 (*o*-C), 126.3 (*p*-C), 118.3 (C-6), 116.5 (C-3'), 71.2 (C-2), 59.3 (C-3), 49.8 (C-1'), 38.8 (C-1), 33.0 (C-4).

HRMS (ESI): *m/z* calculated for $C_{15}H_{22}NO$ $[M+H]^+$: 232.1701, found 232.1710.

(3*R*,4*S*)-4-(Benzylamino)-2-methylhept-6-en-3-ol (7e)



The title compound was prepared according to *General Procedure 3*, using isovaleraldehyde (39.5 μL, 0.36 mmol, 1.2 eq) as the aldehyde component and benzaldehyde (65.5 μL, 0.60 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography eluting with 3:7 EtOAc/*n*-hexane gave the title product **7e** (30.1 mg, 42%) as a yellow oil.

$\mathbf{R}_f$ = 0.10 (3:7 EtOAc/*n*-hexane).

dr 90:10.

ee 98%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 7.46 (major enantiomer), minor enantiomer not detected.

$[\alpha]_D^{25}$ +58.7 (*c* 1.17, $CHCl_3$).

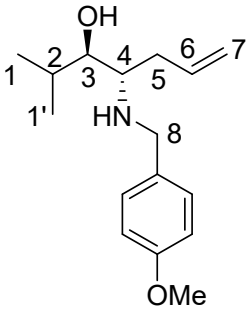
IR (neat): ν_{max} 3330 (O-H str.), 3063 (sp^2 C-H str.), 2924 (sp^3 C-H str.), 1639 (C=C str.), 1600 (Ar C=C str.), 1495 (N-H bend) 1454 (Ar C=C str.), 1364 (CH_3 bend), 1072 (C-O str.), 743 (Ar C-H oop), 697 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.21 (m, 5H, Ar-*H*), 5.75 – 5.63 (m, 1H, H-6), 5.14 – 5.04 (m, 2H, H-7), 3.85 (d, *J* = 13.0 Hz, 1H, CH_AH$_B$ H-8), 3.64 (d, *J* = 13.0 Hz, 1H, CH$_A$$H_B$ H-8), 3.31 (dd, *J* = 9.2, 3.1 Hz, 1H, H-3), 2.74 (dt, *J* = 10.5, 3.1 Hz, 1H, H-4), 2.31 (appt. dddt, *J* = 14.45, 4.9, 3.3, 1.7 Hz, 1H, H-5), 2.03 (dt, *J* = 14.45, 9.9 Hz, 1H, H-5), 1.70 (dp, *J* = 9.2, 6.6 Hz, 1H, H-2), 1.09 (d, *J* = 6.5 Hz, 3H, H-1), 0.84 (d, *J* = 6.7 Hz, 3H, H-1').

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.0 (*ipso*-C), 135.8 (C-6), 128.5 (*o*-C), 128.2 (*m*-C), 127.1 (*p*-C), 118.3 (C-7), 74.5 (C-3), 57.4 (C-4), 51.3 (C-8), 31.9 (C-5), 29.8 (C-2), 20.6 (C-1), 18.1 (C-1).

HRMS (ESI): *m/z* calculated for $C_{15}H_{24}NO$ $[M+H]^+$: 234.1858, found 234.1862.

(3*R*,4*S*)-4-((4-Methoxybenzyl)amino)-2-methylhept-6-en-3-ol (7f)



The title compound was prepared according to *General Procedure 5*, using isovaleraldehyde (39.5 μL, 0.36 mmol, 1.2 eq) as the aldehyde component and *para*-methoxybenzaldehyde (91.5 μL, 0.60 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography eluting with 2:3 EtOAc/*n*-hexane gave the title product **7f** (30.1 mg, 42%) as a yellow oil.

$\mathbf{R}_f$ = 0.17 (2:3 EtOAc/*n*-hexane).

dr 88:12.

ee 98%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 9.62 (major enantiomer), 11.15 (minor enantiomer), 14.2 (minor diastereomer).

$[\alpha]_D^{25}$ −12.8 (*c* 0.44, $CHCl_3$).

IR (neat): ν_{max} 3432 (O-H str.), 3074 (sp^2 C-H str.), 2928 (sp^3 C-H str.), 1639 (C=C str.), 1611 (Ar C=C str.), 1512 (N-H bend), 1441 (Ar C=C str.), 1091 (C-O str.), 1034 (C-O str), 821 (Ar C-H oop) cm^{-1}.

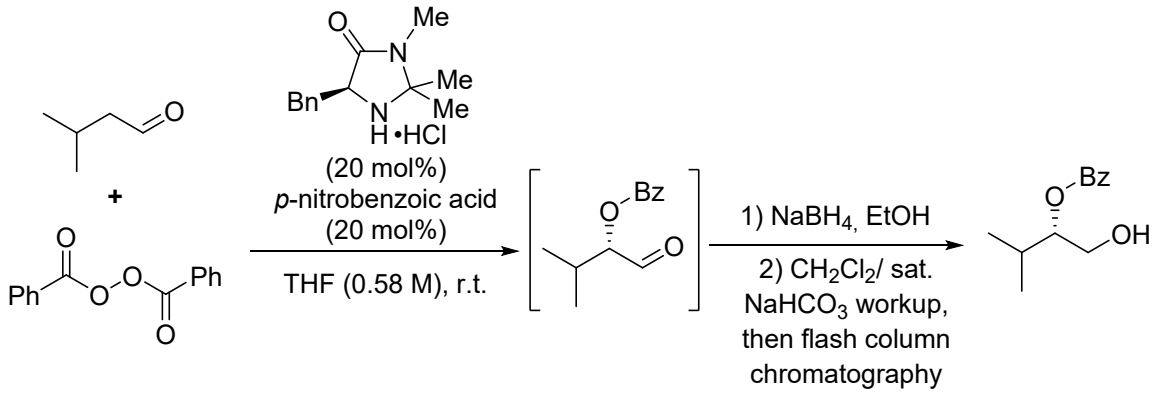
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.6 Hz, 2H, *m*-H), 6.86 (d, *J* = 8.6 Hz, 2H, *o*-H), 5.75 – 5.62 (m, 1H, H-6), 5.13 – 5.04 (m, 2H, H-7), 3.80 (s, 3H, OCH_3), 3.76 (d, *J* = 12.8 Hz, 1H, CH_AH$_B$ H-8), 3.57 (d, *J* = 12.8 Hz, 1H CH$_A$$H_B$ H-8), 3.30 (dd, *J* = 9.2, 3.1 Hz, 1H, H-3), 2.72 (dt, *J* = 10.5, 3.1 Hz, 1H, H-4), 2.30 (dddt, *J* = 14.5, 4.9, 3.3, 1.7 Hz, 1H, H-5), 2.01 (dt, *J* = 14.5, 10.0 Hz, 1H, H-5), 1.69 (dp, *J* = 9.2, 6.6 Hz, 1H, H-2), 1.09 (d, *J* = 6.5 Hz, 3H, H-1), 0.83 (d, *J* = 6.7 Hz, 3H, H-1').

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7 (*p*-C), 135.8 (C-6), 132.2 (*ipso*-C), 129.3 (*m*-C), 118.2 (C-7), 113.9 (*o*-C), 74.49 (C-3), 57.3 (C-4), 55.3 (O*C*H$_3$), 50.6 (C-8), 31.9 (C-5), 29.8 (C-2), 20.7 (C-1), 18.0 (C-1').

HRMS (ESI): *m/z* calculated for $C_{16}H_{26}NO_2$ $[M+H]^+$: 264.1964, found 264.1970.

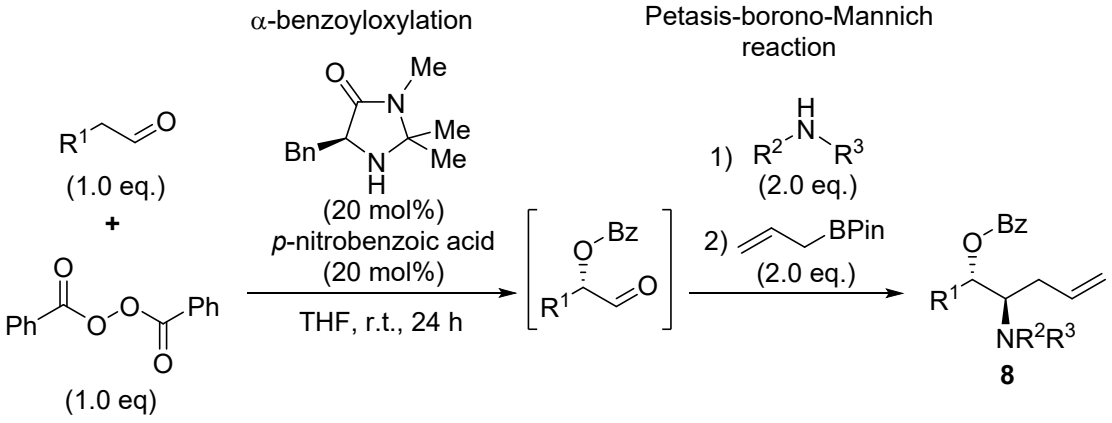
Investigations in the synthesis of chiral α-benzoyloxyaldehydes[8]

Table SI-4: Investigations in the synthesis of chiral α-benzoyloxyaldehydes. From the literature it was not immediately clear what form the catalyst was used in (i.e. free amine or commercially available hydrochloride salt) nor if this would make a difference. The authors were also interested in if any excess of BPO or aldehyde or strict anhydrous conditions would change the yield. Although entry 6 produced the highest yield, this was with the hydrochloride salt of the catalyst, and therefore the effect on ee was (as yet) unknown. For this reason the reported literature conditions in entry 7 were followed.



Entry	Eq. of aldehyde	Eq. of BPO	Additive	Time	Yield (%)	Notes
1	1.0	1.0	-	48 h	23	
2	1.0	1.0	-	24 h	22	
3	1.0	1.0	H_2O (50 μL)	24 h	16	
4	1.0	2.0	-	24 h	22	
5	1.0	1.0	-	24 h	25	Anhydrous
6	1.0	2.0	-	24 h	45	Anhydrous
7	1.0	1.0	-	24 h	32	Free amine catalyst
8	1.0	2.0	-	24 h	24	Free amine catalyst, NMR yield
9	1.5	1.0	-	24 h	30	Free amine catalyst

General Procedure 4 for the preparation of *anti*-β-amino esters from aldehydes.



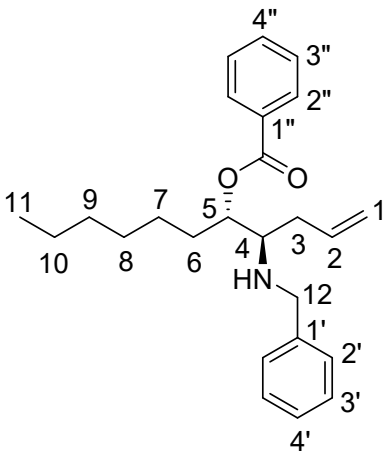
Preparation of (5*S*)-(−)-2,2,3-Trimethyl-5-benzyl-4-imidazolidinone free base catalyst

(5*S*)-(−)-2,2,3-Trimethyl-5-benzyl-4-imidazolidinone monohydrochloride (30.6 mg, 0.12 mmol, 0.20 eq. or 20 mol%) was added to a separating funnel with sat. aq. $NaHCO_3$ (~2 mL) and extracted with CH_2Cl_2 (3 x ~2 mL). The combined organic layers were dried over anhydrous K_2CO_3, filtered and concentrated *in vacuo*. The pale-yellow residue was used immediately in chemical reactions.

Part A: α-benzoyloxylation of aldehydes: To a 10 mL oven-dried round bottomed flask was added (5*S*)-(−)-2,2,3-trimethyl-5-benzyl-4-imidazolidinone free base catalyst (30.6 mg, 0.12 mmol, 0.20 eq. or 20 mol%) and distilled THF (1.0 mL) and stirred until dissolved. *Para*-nitrobenzoic acid (20.1 mg, 0.12 mmol, 0.20 eq. or 20 mol%) was then added and the mixture stirred until dissolved. The aldehyde component (0.58 mmol, 1.0 eq.) was then added, followed by benzoyl peroxide (Luperox® 75%, 187.3 mg, 0.58 mmol, 1.0 eq). The flask was then covered with aluminium foil and stirred with TLC monitoring for 24 h.

Part B: Petasis-Borono-Mannich reaction: Upon completion of Part A, the reaction mixture was added to a separating funnel with 1 M aq. HCl (~4 mL) and extracted with CH_2Cl_2 (3 x ~3 mL). The combined organic layers were washed with brine (~4 mL), then sat. aq. $NaHCO_3$ (~4 mL), then dried over anhydrous K_2CO_3, filtered and concentrated *in vacuo*. To the residue was added DMSO (0.5 mL) and the amine component (1.16 mmol, 2.0 eq.) and the mixture stirred for 5 min. Pinacol allylboronate (224.4 μL, 1.16 mmol, 2.0 eq.) was then added and the reaction mixture stirred for 24 h with TLC monitoring. Once complete, the crude reaction mixture was added to a separating funnel with sat. aq. $NaHCO_3$ (~5 mL) and extracted with CH_2Cl_2 (3 x ~3 mL). The combined organic layers were dried over anhydrous K_2CO_3, filtered and concentrated *in vacuo* and purified by flash column chromatography over silica gel to obtain the aminoester product **8**.

(4*R*,5*S*)-4-(Benzylamino)undec-1-en-5-yl benzoate (8a)



The title compound was prepared according to *General Procedure 4*, using octanal (90.5 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and benzylamine (126.8 μL, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 3:17 EtOAc/*n*-hexane gave the title product **8a** (132.9 mg, 60%) as a pale-yellow oil.

$\mathbf{R}_f$ = 0.48 (1:4 EtOAc/*n*-hexane).

dr 97:3.

$[\alpha]_D^{25}$ +14.0 (c 0.23, $CHCl_3$).

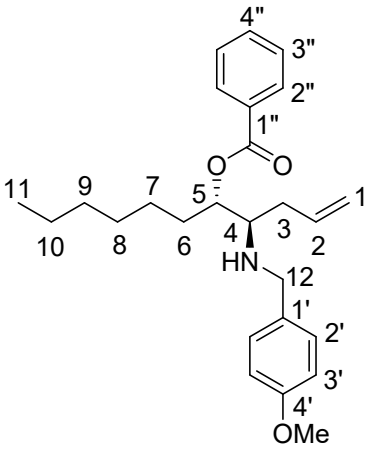
IR (neat): ν_{max} 3064 (sp^2 C-H str.), 2926 (sp^3 C-H str.), 1714 (C=O str.), 1640 (C=C str.), 1602 (Ar C=C str.), 1494 (N-H bend), 1451 (Ar C=C str.), 1269 (C-O str.), 1176 (C-O str.), 996 (sp^2 C-H oop), 913 (sp^2 C-H oop), 734 (Ar C-H oop), 699 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.02 (m, 2H, H-2"), 7.56 (ddt, J = 8.0, 6.8, 1.3 Hz, 1H, H-4"), 7.45 (ddd, J = 8.2, 6.7, 1.2 Hz, 2H, H-3"), 7.33 – 7.17 (m, 5H, H-2', H-3', H-4'), 5.83 (dddd, J = 17.0, 10.3, 7.5, 6.7 Hz, 1H, H-2), 5.31 (dt, J = 9.0, 3.8 Hz, 1H, H-5), 5.15 – 5.07 (m, 2H, H-1), 3.91 (d, J = 13.1 Hz, 1H, CH_AH$_B$ H-12), 3.79 (d, J = 13.1 Hz, 1H, CH$_A$$H_B$ H-12), 2.88 (ddd, J = 8.3, 4.6, 3.8 Hz, 1H, H-4), 2.40 (dddt, J = 14.2, 6.2, 4.6, 1.4 Hz, 1H, H-3), 2.30 – 2.19 (m, 1H, H-3), 1.87 – 1.64 (m, 2H, H-6), 1.44 – 1.18 (m, 8H, H-7, H-8, H-9, H-10), 0.86 (t, J = 7.1 Hz, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3 (*C*=O), 140.6 (C-1'), 135.6 (C-2), 132.8 (C-4"), 130.6 (C-1"), 129.7 (C-2"), 128.37 (C-3"), 128.32 (C-2'), 128.2 (C-3'), 126.9 (C-4'), 117.6 (C-1), 75.7 (C-5), 58.8 (C-4), 51.8 (C-12), 35.1 (C-3), 31.7 (C-9), 30.3 (C-6), 29.2 (C-8), 25.8 (C-7), 24.8 (C-9), 22.6 (C-10), 14.0 (C-11).

HRMS (ESI): *m/z* calculated for $C_{25}H_{34}NO_2$ $[M+H]^+$: 380.2590, found 380.2596.

(4*R*,5*S*)-4-((4-Methoxybenzyl)amino)undec-1-en-5-yl benzoate (8b)



The title compound was prepared according to *General Procedure 4*, using octanal (90.5 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and *para*-methoxybenzylamine (151.6 μL, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 1:9 EtOAc/*n*-hexane gave the title product **8b** (132.9 mg, 60%) as a pale-yellow oil.

$\mathbf{R}_f$ = 0.40 (1:4 EtOAc/*n*-hexane).

dr 99:1.

$[\alpha]_D^{25}$ +5.90 (*c* 0.68, $CHCl_3$).

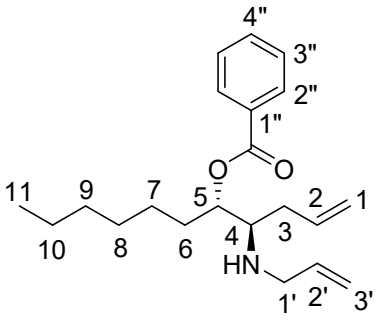
IR (neat): ν_{max} 3071 (sp^2 C-H str.), 2998 (sp^3 C-H str.), 1714 (C=O str.), 1640 (C=C str.), 1611 (Ar C=C str.), 1511 (N-H bend), 1463 (Ar C=C str.), 1270 (C-O str.), 1174 (C-O str.), 997 (sp^2 C-H oop), 915 (sp^2 C-H oop), 809 (Ar C-H oop), 756 Ar C-H oop), 688 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.02 (m, 2H, H-2"), 7.59 – 7.53 (m, 1H, H-4"), 7.48 – 7.41 (m, 2H, H-3"), 7.23 – 7.17 (m, 2H, H-3'), 6.82 – 6.77 (m, 2H, H-2'), 5.90 – 5.76 (m, 1H, H-2), 5.29 (dt, *J* = 9.0, 3.8 Hz, 1H, H-5), 5.15 – 5.06 (m, 2H, H-1), 3.84 (d, *J* = 12.9 Hz, 1H, CH_AH$_B$ H-12), 3.77 (s, 3H, OCH_3), 3.73 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-12), 2.91 – 2.83 (m, 1H, H-4), 2.44 – 2.34 (m, 1H, H-3), 2.30 – 2.18 (m, 1H, H-3), 1.88 – 1.63 (m, 2H, H-6), 1.44 – 1.18 (m, 8H, H-7, H-8, H-9, H-10), 0.86 (t, *J* = 7.0 Hz, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3 (*C*=O), 158.6 (C-4'), 135.6 (C-2), 132.8 (C-4"), 132.7 (C-1'), 130.6 (C-1"), 129.7 (C-2"), 129.4 (C-3'), 128.4 (C-3"), 117.5 (C-1), 113.7 (C-2'), 75.7 (C-5), 58.6 (C-4), 55.3 (O*C*H$_3$), 51.1 (C-12), 35.1 (C-3), 31.7 (C-9), 30.3 (C-6), 29.2 (C-7), 25.8 (C-8), 22.6 (C-10), 14.0 (C-11).

HRMS (ESI): *m/z* calculated for $C_{26}H_{36}NO_3$ $[M+H]^+$: 410.2695, found 410.2690.

(4*R*,5*S*)-4-(Allylamino)undec-1-en-5-yl benzoate (8c)



The title compound was prepared according to *General Procedure 4*, using octanal (90.5 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and allylamine (87.0 μL, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 1:4 EtOAc/*n*-hexane gave the title product **8c** (97.9 mg, 51%) as a pale-yellow oil.

R_f = 0.51 (1:4 EtOAc/*n*-hexane).

dr 97:3.

$[\alpha]_D^{25}$ +6.6 (*c* 0.59, $CHCl_3$).

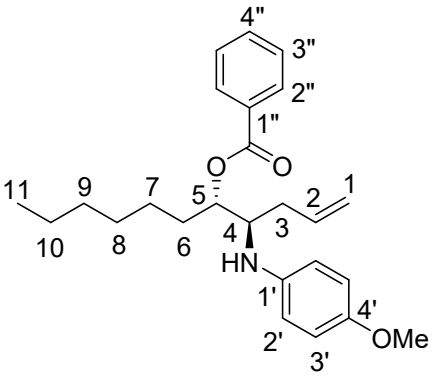
IR (neat): ν_{max} 3074 (sp^2 C-H str.), 2926 (sp^3 C-H str.), 1715 (C=O str.), 1641 (C=C str.), 1602 (Ar C=C str.), 1465 (N-H bend), 1451 (Ar C=C str.), 1268 (C-O str.), 1176 (C-O str.), 994 (sp^2 C-H oop), 914 (sp^2 C-H oop), 709 (Ar C-H oop), 688 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.01 (m, 2H, H-2"), 7.56 (ddt, *J* = 8.0, 6.9, 1.3 Hz, 1H, H-4"), 7.49 – 7.41 (m, 2H, H-3"), 5.93 – 5.78 (m, 2H, H-2, H-2'), 5.24 (dt, *J* = 9.1, 3.8 Hz, 1H, H-5), 5.18 – 5.08 (m, 3H, H-1, H-3'), 5.04 (ddt, *J* = 10.2, 2.1, 1.3 Hz, 1H, H-3'), 3.35 (ddt, *J* = 14.0, 5.8, 1.5 Hz, 1H, CH_AH$_B$ H-1'), 3.27 (ddt, *J* = 14.0, 6.3, 1.4 Hz, 1H CH$_A$$H_B$ H-1'), 2.89 (ddd, *J* = 8.3, 4.8, 3.8 Hz, 1H, H-4), 2.38 (dddt, *J* = 14.4, 6.3, 4.8, 1.4 Hz, 1H, H-3), 2.29 – 2.17 (m, 1H, H-3), 1.86 – 1.62 (m, 2H, H-6), 1.51 – 1.18 (m, 8H, H-7, H-8, H-9, H-10), 0.86 (t, *J* = 7.0 Hz, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3 (*C*=O), 137.1 (C-2'), 135.6 (C-2), 132.8 (C-4"), 130.6 (C-1"), 129.6 (C-2"), 128.4 (C-3"), 117.5 (C-1), 115.9 (C-3'), 75.9 (C-5), 58.6 (C-4), 50.4 (C-1'), 35.2 (C-3), 31.7 (C-9), 30.3 (C-6), 29.2 (C-8), 25.8 (C-7), 22.6 (C-10), 14.0 (C-11).

HRMS (ESI): *m/z* calculated for $C_{21}H_{32}NO_2$ $[M+H]^+$: 330.2433, found 330.2426.

(4*R*,5*S*)-4-((4-Methoxyphenyl)amino)undec-1-en-5-yl benzoate (8d)



The title compound was prepared according to *General Procedure 4*, using octanal (90.5 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and *para*-anisidine (147.6 mg, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 1:19 EtOAc/*n*-hexane gave the title product **8d** (61.5 mg, 27%) as a brown oil.

R_f = 0.36 (1:9 EtOAc/*n*-hexane).

dr 97:3.

$[\alpha]_D^{25}$ +26.3 (*c* 0.60, $CHCl_3$).

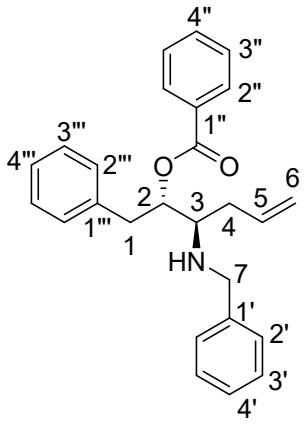
IR (neat): ν_{max} 3395 (N-H str.), 3071 (sp^2 C-H str.), 2927 (sp^3 C-H str.), 1712 (C=O str.), 1641 (C=C str.), 1601 (Ar C=C str.), 1510 (N-H bend), 1451 (Ar C=C str.), 1268 (C-O str.), 1176 (C-O str.), 1000 (sp^2 C-H oop), 914 (sp^2 C-H oop), 817 (Ar C-H oop), 757 (Ar C-H oop), 687 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.98 (m, 2H, H-2"), 7.56 (ddt, *J* = 8.0, 6.9, 1.3 Hz, 1H, H-4"), 7.48 – 7.41 (m, 2H, H-3"), 6.76 – 6.70 (m, 2H, H-3'), 6.60 – 6.54 (m, 2H, H-2'), 5.88 (dddd, *J* = 16.4, 10.6, 7.4, 6.6 Hz, 1H, H-2), 5.23 (dt, *J* = 8.0, 4.7 Hz, 1H, H-5), 5.14 – 5.03 (m, 2H, H-1), 3.72 (s, 3H, OCH_3), 3.64 (dt, *J* = 8.9, 4.7 Hz, 1H, H-4), 2.51 – 2.42 (m, 1H, H-3), 2.38 – 2.27 (m, 1H, H-3), 1.78 (ddd, *J* = 14.0, 9.6, 5.4 Hz, 2H, H-6), 1.44 – 1.18 (m, 8H, H-7, H-8, H-9, H-10), 0.88 – 0.80 (m, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.2 (*C*=O), 152.3 (C-4'), 141.7 (C-1'), 134.9 (C-2), 132.9 (C-4"), 130.3 (C-1"), 129.7 (C-2"), 128.4 (C-3"), 117.8 (C-1), 115.3 (C-2'), 114.9 (C-3'), 76.3 (C-5), 56.9 (C-4), 55.8 (O*C*H_3), 35.4 (C-3), 31.7 (C-9), 31.1 (C-6), 29.2 (C-8), 25.6 (C-7), 22.6 (C-10), 14.0 (C-11).

HRMS (ESI): *m/z* calculated for $C_{25}H_{34}NO_3$ $[M+H]^+$: 396.2539, found 396.2538.

(2*S*,3*R*)-3-(Benzylamino)-1-phenylhex-5-en-2-yl benzoate (8e, Method 1)



The title compound was prepared according to *General Procedure 4*, using hydrocinnamaldehyde (76.5 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and benzylamine (126.8 μL, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 3:17 EtOAc/*n*-hexane gave the title product **8e** (100.8 mg, 45%) as a pale-yellow oil.

R$_f$ = 0.36 (3:17 EtOAc/*n*-hexane).

dr 97:3.

$[\alpha]_D^{25}$ –34.4 (*c* 0.62, $CHCl_3$).

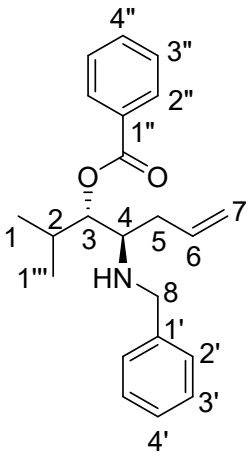
IR (neat): ν_{max} 3062 (sp^2 C-H str.), 2923 (sp^3 C-H str.), 1713 (C=O str.), 1639 (C=C str.), 1601 (Ar C=C str.), 1495 (N-H bend), 1451 (Ar C=C str.), 1268 (C-O str.), 1176 (C-O str.), 994 (sp^2 C-H oop), 914 (sp^2 C-H oop), 697 (Ar C-H oop), 743 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.96 (m, 2H, H-2''), 7.58 – 7.52 (m, 1H, H-4''), 7.46 – 7.39 (m, 2H, H-3''), 7.29 – 7.14 (m, 10H, Ar-*H*), 5.81 (ddt, *J* = 17.7, 9.5, 7.1 Hz, 1H, H-5), 5.48 (ddd, *J* = 7.8, 5.2, 4.0 Hz, 1H, H-2), 5.16 – 5.07 (m, 2H, H-6), 3.87 (d, *J* = 13.1 Hz, 1H, CH_AH$_B$ H-7), 3.76 (d, *J* = 13.1 Hz, 1H, CH$_A$$H_B$ H-7), 3.14 (dd, *J* = 14.1, 7.8 Hz, 1H, CH_AH$_B$ H-1), 3.06 (dd, *J* = 14.1, 5.2 Hz, 1H, CH$_A$$H_B$ H-1), 2.93 (dt, *J* = 7.9, 4.4 Hz, 1H, H-3), 2.52 – 2.42 (m, 1H, H-4), 2.36 – 2.25 (m, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9 (*C*=O), 140.4 (C-1'), 137.8 (C-1'''), 135.2 (C-5), 132.9 (C-4''), 130.4 (C-1''), 129.6 (C-2''), 129.4 (C-3'''), 128.39 (C-3''), 128.35 (C-2'), 128.33 (C-2'''), 128.24 (C-3'), 126.9 (C-4'), 126.4 (C-4'''), 117.9 (C-6), 76.3 (C-2), 57.9 (C-3), 51.7 (C-7), 36.7 (C-1), 34.9 (C-4).

HRMS (ESI): *m/z* calculated for $C_{26}H_{28}NO_2$ $[M+H]^+$: 386.2120, found 386.2121.

(3*S*,4*R*)-4-(Benzylamino)-2-methylhept-6-en-3-yl benzoate (8g)



The title compound was prepared according to *General Procedure 4*, using isovaleraldehyde (63.8 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and benzylamine (126.8 μL, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 1:9 EtOAc/*n*-hexane gave the title product **8g** (58.4 mg, 30%) as a pale-yellow oil.

R$_f$ = 0.57 (1:4 EtOAc/*n*-hexane).

dr 97:3.

$[\alpha]_D^{25}$ +27.1 (*c* 0.74, $CHCl_3$).

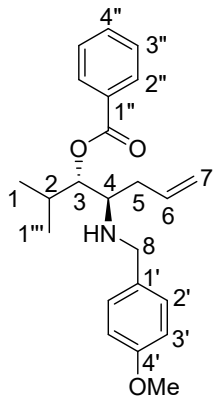
IR (neat): ν_{max} 3063 (sp^2 C-H str.), 2963 (sp^3 C-H str.), 1714 (C=O str.), 1639 (C=C str.), 1602 (Ar C=C str.), 1494 (N-H bend), 1451 (Ar C=C str.), 1267 (C-O str.), 1176 (C-O str.), 698 (Ar C-H oop), 735 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.02 (m, 2H, H-2"), 7.56 (ddt, *J* = 7.9, 6.8, 1.4 Hz, 1H, H-4"), 7.49 – 7.41 (m, 2H, H-3"), 7.37 – 7.18 (m, 5H, H-2', H-3', H-4'), 5.85 (dddd, *J* = 16.5, 10.6, 7.4, 6.8 Hz, 1H, H-6), 5.16 (dd, *J* = 6.7, 5.0 Hz, 1H, H-3), 5.12 – 5.04 (m, 2H, H-7), 3.90 (d, *J* = 13.0 Hz, 1H, CH_AH$_B$ H-8), 3.79 (d, *J* = 13.0 Hz, 1H, CH$_A$$H_B$ H-8), 2.92 (ddd, *J* = 8.5, 5.0, 3.7 Hz, 1H, H-4), 2.49 – 2.39 (m, 1H, H-5), 2.27 – 2.12 (m, 2H, H-5, H-2), 0.97 (d, *J* = 6.7 Hz, 3H, H-1), 0.94 (d, *J* = 6.9 Hz, 3H, H-1''').

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4 (*C*=O), 140.6 (C-4'), 135.7 (C-6), 132.8 (C-4"), 130.5 (C-1"), 129.7 (C-2"), 128.39 (C-3"), 128.35 (C-2'), 128.29 (C-3'), 126.9 (C-4'), 117.5 (C-7), 78.8 (C-3), 56.8 (C-4), 51.2 (C-8), 34.1 (C-5), 29.3 (H-2), 19.6 (C-1), 18.2 (C-1''').

HRMS (ESI): *m/z* calculated for $C_{22}H_{28}NO_2$ $[M+H]^+$: 338.2120, found 338.2129.

(3*S*,4*R*)-4-((4-Methoxybenzyl)amino)-2-methylhept-6-en-3-yl benzoate (8h)



The title compound was prepared according to *General Procedure 4*, using isovaleraldehyde (63.8 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and *para*-methoxybenzylamine (151.6 μL, 1.16 mmol, 2.0 eq) as the amine component. Purification by flash column chromatography over silica gel eluting with 3:17 EtOAc/*n*-hexane gave the title product **8h** (62.8 mg, 29%) as a pale-yellow oil.

$\mathbf{R}_f$ = 0.44 (1:4 EtOAc/*n*-hexane).

dr 99:1.

$[\alpha]_D^{25}$ +27.9 (*c* 0.59, $CHCl_3$).

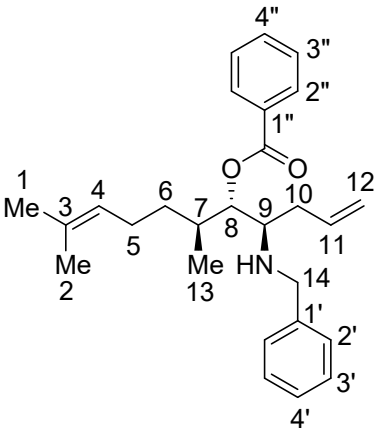
IR (neat): ν_{max} 3071 (sp^2 C-H str.), 2933 (sp^3 C-H str.), 1713 (C=O str.), 1640 (C=C str.), 1611 (Ar C=C str.), 1511 (N-H str.) 1464 (Ar C=C str.), 1268, (C-O str.) 1174 (C-O str.), 998 (sp^2 C-H oop), 917 (sp^2 C-H oop), 827 (Ar C-H oop), 757 (Ar C-H oop), 672 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.04 (m, 2H, H-2''), 7.59 – 7.53 (m, 1H, H-4''), 7.49 – 7.42 (m, 2H, H-3''), 7.25 – 7.20 (m, 2H, H-3'), 6.86 – 6.80 (m, 2H, H-2'), 5.90 – 5.78 (m, 1H, H-6), 5.15 (dd, *J* = 6.7, 5.0 Hz, 1H, H-3), 5.12 – 5.03 (m, 2H, H-7), 3.84 (d, *J* = 12.7 Hz, 1H, CH_AH_B H-8), 3.79 (s, 3H, OCH_3), 3.72 (d, *J* = 12.7 Hz, 1H, CH_AH_B H-8), 2.91 (ddd, *J* = 8.5, 5.0, 3.7 Hz, 1H, H-4), 2.47 – 2.39 (m, 1H, H-5), 2.18 (m, 2H, H-5, H-2), 0.97 (d, *J* = 6.7 Hz, 3H, H-1), 0.94 (d, *J* = 6.9 Hz, 3H, H-1''').

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4 (*C*=O), 158.6 (C-4'), 135.8 (C-6), 132.8 (C-4''), 132.7 (C-1'), 130.5 (C-1''), 129.7 (C-2''), 129.5 (C-3'), 128.4 (C-3''), 117.5 (C-7), 113.7 (C-2'), 78.8 (C-3), 56.6 (C-4), 55.3 (OCH_3), 50.6 (C-8), 34.1 (C-5), 29.3 (C-2), 19.6 (C-1), 18.2 (C-1''').

HRMS (ESI): *m/z* calculated for $C_{23}H_{30}NO_3$ $[M+H]^+$: 368.2226, found 368.2236.

(4*R*,5*S*,6*S*)-4-(Benzylamino)-6,10-dimethylundeca-1,9-dien-5-yl benzoate (8i)



The title compound was prepared according to *General Procedure 4*, using (*S*)-citronellal (105.2 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and benzylamine (126.7 μL, 1.16 mmol, 2.0 eq) as the amine component. CH_2Cl_2 was used as the solvent for the PBM reaction. The crude reaction mixture was triturated with Et_2O (1 mL) to remove solid material and the organic rinsings concentrated *in vacuo*. Purification by flash column chromatography over silica gel eluting with 1:19 EtOAc/*n*-hexane gave the title product **8i** (76.3 mg, 32%) as a pale-yellow oil.

R_f = 0.25 (1:19 EtOAc/*n*-hexane 2x elutions).

dr 93:7.

$[\alpha]_D^{23}$ +23.7 (*c* 0.87, $CHCl_3$).

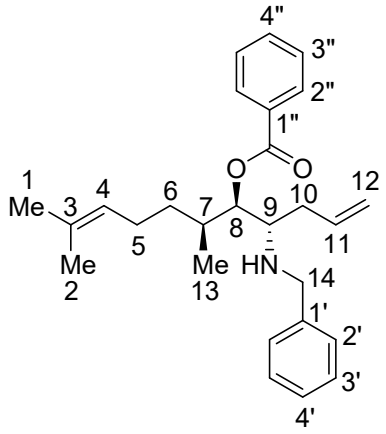
IR (neat): ν_{max} 3063 (sp^2 C-H str.), 3029 (sp^3 C-H str.), 1715 (C=O str.), 1640 (C=C str.), 1602 (Ar C=C str.), 1494 (N-H bend), 1451 (Ar C=C str.), 1378 (CH_3 bend), 1268 (C-O str.), 1176 (C-O str.), 995 (sp^2 C-H oop), 916 (sp^2 C-H oop), 736 (Ar C-H oop), 699 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.04 (m, 2H, H-2"), 7.59 – 7.53 (m, 1H, H-4"), 7.48 – 7.42 (m, 2H, H-3"), 7.38 – 7.19 (m, 5H, H-2', H-3', H-4'), 5.84 (dddd, *J* = 16.4, 10.7, 7.4, 6.7 Hz, 1H, H-11), 5.21 (dd, *J* = 6.6, 5.1 Hz, 1H, H-8), 5.13 – 5.02 (m, 3H, H-12, H-4), 3.90 (d, *J* = 13.0 Hz, 1H, CH_AH$_B$ H-14), 3.78 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-14), 2.95 (ddd, *J* = 8.4, 5.1, 3.55 Hz, 1H, H-9), 2.43 (dddt, *J* = 14.4, 6.7, 3.55, 1.3 Hz, 1H, H-10), 2.19 (dddd, *J* = 15.7, 8.4, 4.8, 1.3 Hz, 1H, H-10), 2.14 – 1.98 (m, 2H, H-7, H-5), 1.93 (appt. hept., *J* = 7.7 Hz, 1H, H-5), 1.65 (appt. q, *J* = 1.3 Hz, 3H, H-1), 1.63 – 1.50 (m, 1H, H-6), 1.57 (appt. d, *J* = 1.2 Hz, 3H, H-2), 1.29 – 1.18 (m, 1H, H-6), 0.94 (d, *J* = 6.8 Hz, 3H, H-13).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4 (*C*=O), 140.6 (C-1'), 135.7 (C-11), 132.8 (C-4"), 130.6 (C-1"), 129.7 (C-2"), 128.38 (C-3"), 128.36 (C-2'), 128.29 (C-3'), 126.9 (C-4'), 124.5 (C-4), 117.5 (C-12), 78.3 (C-8), 56.7 (C-9), 51.2 (C-14), 34.1 (C-10), 33.8 (C-7), 31.8 (C-6), 25.7 (C-1), 25.4 (C-5), 17.7 (C-2), 16.3 (C-13).

HRMS (ESI): *m/z* calculated for $C_{27}H_{36}NO_2$ $[M+H]^+$: 406.2746, found 406.2749.

(4*S*,5*R*,6*S*)-4-(Benzylamino)-6,10-dimethylundeca-1,9-dien-5-yl benzoate (8j)



The title compound was prepared according to *General Procedure 4*, using (5*R*)-(−)-2,2,3-trimethyl-5-benzyl-4-imidazolidinone (26.2 mg, 0.12 mmol, 0.20 eq or 20 mol%) as the organocatalyst, (*S*)-citronellal (105.2 μL, 0.58 mmol, 1.0 eq) as the aldehyde component and benzylamine (126.7 μL, 1.16 mmol, 2.0 eq) as the amine component. CH_2Cl_2 was used as the solvent for the PBM reaction. The crude reaction mixture was triturated with Et_2O (1 mL) to remove solid material and the organic rinsings concentrated *in vacuo*. Purification by flash column chromatography over silica gel eluting with 1:9 EtOAc/*n*-hexane gave the title product **8j** (61.8 mg, 26%) as a pale-yellow oil.

R_f = 0.46 (1:9 EtOAc/*n*-hexane).

dr 90:10; 92:8 (isolated).

$[\alpha]_D^{23}$ –11.5 (*c* 0.95, $CHCl_3$).

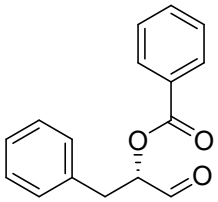
IR (neat): ν_{max} 3063 (sp^2 C-H str.), 3029 (sp^3 C-H str.), 1715 (C=O str.), 1640 (C=C str.), 1602 (Ar C=C str.), 1494 (N-H bend), 1451 (Ar C=C str.), 1378 (CH_3 bend), 1268 (C-O str.), 1176 (C-O str.), 996 (sp^2 C-H oop), 916 (sp^2 C-H oop), 735 (Ar C-H oop), 699 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.03 (m, 2H, H-2"), 7.60 – 7.53 (m, 1H, H-4"), 7.49 – 7.42 (m, 2H, H-3"), 7.39 – 7.20 (m, 5H, H-2', H3', H-4'), 5.91 – 5.79 (m, 1H, H-11), 5.22 (dd, *J* = 6.5, 4.9 Hz, 1H, H-8), 5.13 – 5.03 (m, 3H, H-12, H-4), 3.86 (d, *J* = 12.9 Hz, 1H CH_AH$_B$ H-14), 3.80 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-14), 2.96 (ddd, *J* = 7.6, 6.5, 3.9 Hz, 1H, H-9), 2.46 – 2.37 (m, 1H, H-10), 2.25 – 2.09 (m, 2H, H-10, H-7), 2.08 – 1.98 (m, 2H, H-5), 1.67 (appt. d, *J* = 0.9 Hz, 3H, H-1), 1.59 (appt. d, *J* = 1.3 Hz, 3H, H-2), 1.47 – 1.33 (m, 1H, H-6), 1.27 – 1.15 (m, 1H, H-6), 0.98 (d, *J* = 6.8 Hz, 3H, H-13).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3 (*C*=O), 140.6 (C-1'), 135.5 (C-11), 132.9 (C-4"), 131.7 (C-3), 130.5 (C-1"), 129.7 (C-2"), 128.4 (C-3"), 128.33 (C-2'), 128.30 (C-3'), 126.9 (C-4'), 124.3 (C-12), 117.7 (C-4), 77.6 (C-8), 56.7 (C-9), 51.2 (C-14), 34.4 (C-10), 33.9 (C-6), 33.5 (C-7), 25.7 (C-1), 25.4 (C-5), 17.7 (C-2), 14.5 (C-13).

HRMS (ESI): *m/z* calculated for $C_{27}H_{36}NO_2$ $[M+H]^+$: 406.2746, found 406.2734.

(*S*)-1-Oxo-3-phenylpropan-2-yl benzoate (2, R^1 = Bn)



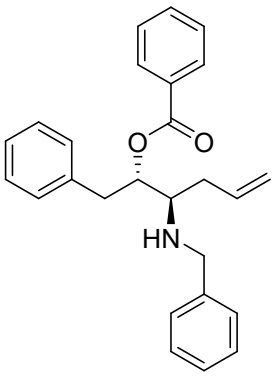
The title compound was prepared according to that described in Vaismaa *et al.* 2009 (1.0 mmol scale),[8] with the following modifications from Kano *et al.* 2009.[9] At the conclusion of the reaction, the reaction mixture was added to a separating funnel with 1 M aq. HCl (~4 mL) and extracted with CH_2Cl_2 (3 x ~3 mL). The combined organic layers were washed with NaCl brine (~4 mL), then sat. aq. $NaHCO_3$ (~4 mL), then dried over anhydrous K_2CO_3, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography eluting with 3:17 EtOAc/*n*-hexane, obtaining the title product **2** (140.5 mg, 55%). The spectroscopic data for **2** was identical to that previously reported.[5]

$\mathbf{R}_f$ = 0.23 (1:4 EtOAc/*n*-hexane).

General Procedure 5 for the preparation of amino esters from aldehyde 2 (R^1 = Bn)

To a 10 mL round-bottomed flask was added **2** (R^1 = Bn) (~30-60 mg, 1.0 eq.) and anhydrous CH_2Cl_2 (0.5 mL), and the mixture stirred until the substrate was dissolved. To the reaction mixture was added an amine component (1.2 eq.) and the mixture stirred for 5 mins. Pinacol allylboronate (1.2 eq.) was then added and the reaction vessel flushed with nitrogen, sealed and stirred for 12 h with TLC monitoring. Upon completion of the reaction, the reaction mixture was added to a separating funnel with sat. aq. $NaHCO_3$ (~2 mL) and extracted with CH_2Cl_2 (3 x ~2 mL). The combined organic layers were dried over K_2CO_3, filtered, concentrated *in vacuo* and purified by flash column chromatography over silica gel to obtain the pure *β*-amino ester product.

(2*S*,3*R*)-3-(Benzylamino)-1-phenylhex-5-en-2-yl benzoate (8e, Method 2)



The title compound was prepared according to *General Procedure 5,* using **2** (R^1 = Bn) (30.7 mg, 0.121 mmol, 1.0 eq.) and benzylamine (15.9 μL, 0.145 mmol, 1.2 eq.) as the amine component. The compound was purified by flash column chromatography over silica gel eluting with 3:17 EtOAc/*n*-hexane, obtaining the title product **8e** (25.2 mg, 54%) as a pale-yellow oil. The spectroscopic data was identical to those previously obtained for **8e**.

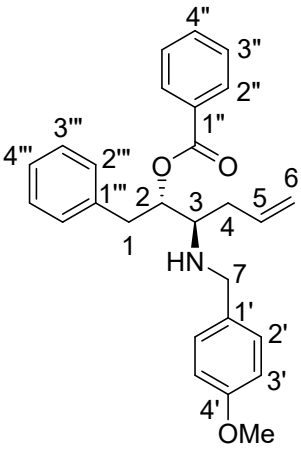
$\mathbf{R}_f$ = 0.34 (3:17 EtOAc/*n*-hexane).

dr 99:1.

$[\alpha]_D^{23}$ –36.1 (*c* 1.26, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{16}H_{28}NO_2$ $[M+H]^+$: 386, found 386 (100%).

(2*S*,3*R*)-3-((4-Methoxybenzyl)amino)-1-phenylhex-5-en-2-yl benzoate (8f)



The title compound was prepared according to *General Procedure 5,* using **2** (R^1 = Bn) (34.0 mg, 0.134 mmol, 1.0 eq.) and *para*-methoxybenzylamine (21.0 μL, 0.160 mmol, 1.2 eq.) as the amine component. The compound was purified by flash column chromatography over silica gel eluting with 1:3 EtOAc/*n*-hexane, obtaining the title product **8f** (33.2 mg, 60%) as a pale-yellow oil.

$\mathbf{R}_f$ = 0.43 (1:3 EtOAc/*n*-hexane).

dr 99:1

$[\alpha]_D^{23}$ –35.1 (*c* 0.59, $CHCl_3$).

IR (neat): ν_{max} 3063 (sp^2 C-H str.), 3028 (sp^3 C-H str.), 1639 (C=C str.), 1610 (Ar C=C str.), 1452 (Ar C=C str.), 1713 (C=O str.), 1496 (N-H bend), 1269 (C-O str.), 1174 (C-O str.), 995 (sp^2 C-H oop), 751 (Ar C-H oop), 700 (Ar C-H oop), 822 (Ar C-H oop) cm^{-1}.

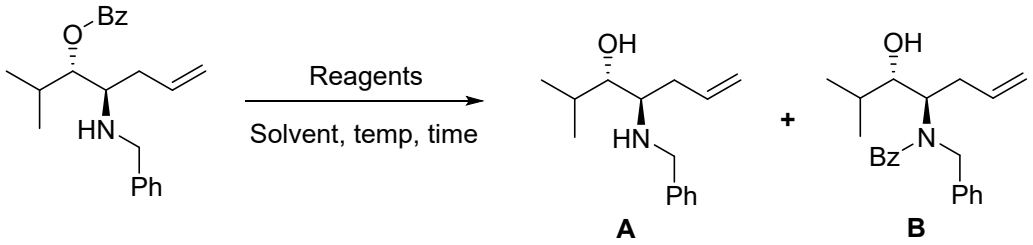
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.95 (m, 2H, H-2"), 7.54 (m, 1H, H-4"), 7.46 – 7.39 (m, 2H, H-3"), 7.28 – 7.17 (m, 5H, H-2"', H-3"', H-4"'), 7.15 (m, 2H, H-3'), 6.78 (m, 2H, H-2'), 5.81 (ddt, *J* = 18.8, 9.5, 7.1 Hz, 1H, H-5), 5.47 (ddd, *J* = 7.8, 5.3, 4.1 Hz, 1H, H-2), 5.15 – 5.08 (m, 2H, H-6), 3.80 (d, *J* = 12.9 Hz, 1H, CH_AH$_B$ H-7), 3.77 (s, 3H, OCH_3), 3.69 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-7), 3.13 (dd, *J* = 14.1, 7.8 Hz, 1H, CH_AH$_B$ H-1), 3.06 (dd, *J* = 14.1, 5.3 Hz, 1H CH$_A$$H_B$ H-1), 2.91 (dt, *J* = 7.8, 4.4 Hz, 1H, H-3), 2.51 – 2.41 (m, 1H, H-4), 2.34 – 2.24 (m, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9 (*C*=O), 158.6 (C-4'), 137.9 (C-1"'), 135.3 (C-5), 132.9 (C-4"), 132.6 (C-1'), 130.4 (C-1"), 129.6 (C-2"), 129.42 (C-3"'), 129.39 (C-3'), 128.4 (C-3"), 128.3 (C-2"'), 126.4 (C-4"'), 117.8 (C-6), 113.7 (C-2'), 76.3 (C-2), 57.7 (C-3), 55.3 (O*C*H$_3$), 51.0 (C-7), 36.7 (C-1), 34.9 (C-4).

HRMS (ESI): *m/z* calculated for $C_{27}H_{30}NO_3$ $[M+H]^+$: 416.2226, found 416.2245.

Optimisation of the ester deprotection

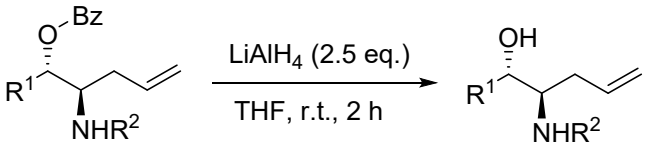
Table SI-6: Optimisation of the ester deprotection of *O*-protected PBM products. It was discovered that basic hydrolysis procedures resulted in a mixture of the starting material, the target product, and a more stable amide product where the *O*-protecting ester had migrated to the secondary amine. Therefore, a variety of methods were attempted with variations on reagents, solvent and concentration. The ester was found to be stable to acidic hydrolysis methods, however reduction with $LiAlH_4$ resulted in complete reduction of the ester and simple purification by silica gel plug (Entry 10).



Entry	Reagents	Solvent	Temp. (°C)	Time	Yield A (%)	Yield B (%)	Notes
1	K_2CO_3 (5.5. eq.)	MeOH (0.019M)	r.t.	2 d	-	36	Isolated yield
2	$LiOH{\cdot}H_2O$ (2.7 eq.)	MeOH (0.02M)	r.t.	18 h	25	61	NMR yield
3	$LiOH{\cdot}H_2O$ (5.0 eq.)	THF:H_2O 3:1 (0.066M)	r.t.	24 h	-	8	"
4	$LiBH_4$ (1.2 eq.)	THF (10 drops MeOH) (0.15M)	r.t.	2 h	-	trace	37% yield of hydrogenated product. Insep. from SM by FCC.
5	$LiAlH_4$ (2.8 eq.)	THF (0.048M)	r.t.	2 h	-	-	Apparent quant. yield (ESI-MS and ^{1}H NMR). Product could not be isolated.
6	$LiOH{\cdot}H_2O$ (3.1 eq.)	MeOH (0.1067M)	r.t.	20 h	25	64	
7	15% ethanolic HCl (0.0876M)		r.t.-80 °C	22 h	7	-	r.t. 18 h, 50 °C 2h, 80 °C 2 h
8	1:1 MeOH/4.73 M methanolic NH_3 (0.0493M)		r.t.	42 h	19	30	

9	AcOH (0.104M)		r.t.-80 °C	24 h	-	-	No reaction. r.t. 18 h, 80 °C 6 h
10	$LiAlH_4$ (13.4 eq.)	THF (0.0138M)	r.t.	2 h	38	-	Small scale, measuring error
11	$LiAlH_4$ (2.6 eq.)	THF (0.116)	r.t.	2 h	60	-	Larger 50 mg scale

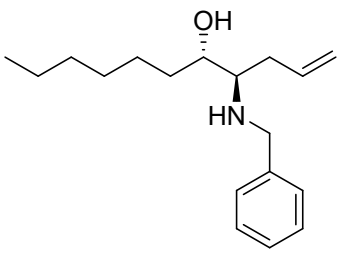
General Procedure 6 for the reduction of benzoyl amino esters



To a 10 mL oven-dried nitrogen purged round bottomed flask was added crushed lithium aluminium hydride (2.5 eq.) and distilled anhydrous THF (0.3 mL) and the mixture was gently stirred under nitrogen for 2 mins. The benzoyl amino ester substrate (1.0 eq.) was then dissolved under nitrogen in distilled THF (0.3 mL) and transferred by syringe into the reaction vessel, with continuous stirring. The flask containing the substrate was then rinsed under nitrogen with aliquots of distilled THF (3 x 0.2 mL) and the rinsings transferred by syringe to the reaction vessel. The reaction mixture was then stirred under nitrogen for 2 h with TLC monitoring.

At the conclusion of the reaction, the reaction mixture was transferred to a separating funnel with sat. aq. Rochelle's salt solution (~2 mL) and extracted with CH_2Cl_2 (3 x ~3 mL). The combined organic layers were dried over K_2CO_3, filtered and concentrated *in vacuo* and the residue dissolved in EtOAc (~4 mL). This organic phase was washed with sat. aq. NaCl brine (6 x ~3 mL), then concentrated *in vacuo* to afford the free amino alcohol product.

(4*R*,5*S*)-4-(Benzylamino)undec-1-en-5-ol (*ent*-7a)



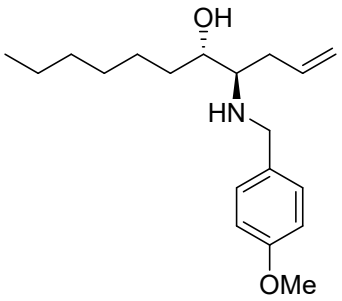
The title compound was prepared according to *General Procedure 6*, using **8a** as the benzoyl amino ester substrate and obtaining ***ent*-7a** (24.9 mg, 73%) as a pale-yellow oil. The spectroscopic data obtained was identical to those for **7a**.

ee 98%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 6.92 (minor enantiomer), 7.84 (major enantiomer).

$[\alpha]_D^{25}$ −5.82 (*c* 0.50, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{18}H_{30}NO$ $[M+H]^+$: 276, found 276 (100%).

(4*R*,5*S*)-4-((4-Methoxybenzyl)amino)undec-1-en-5-ol (*ent*-7b)



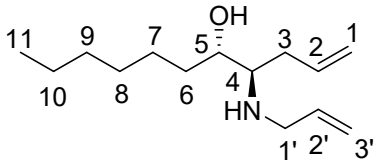
The title compound was prepared according to *General Procedure 6*, using **8b** as the benzoyl amino ester substrate and obtaining ***ent*-7b** (22.8 mg, 94%) as a pale-yellow oil. The spectroscopic data obtained was identical to those for **7b**.

ee >99%. Chiralpak IG-3 column and guard, 20% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 9.39 (major enantiomer), minor enantiomer not observed.

$[\alpha]_D^{25}$ −3.68 (*c* 1.14, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{19}H_{32}NO_2$ $[M+H]^+$: 306, found 306 (100%).

(4*R*,5*S*)-4-(Allylamino)undec-1-en-5-ol (SI-10)



The title compound was prepared according to *General Procedure 6*, using **8c** as the benzoyl amino ester substrate. Excess benzyl alcohol by-product was removed by high vacuum (6 h). **SI-10** (24.1 mg, 78%) was obtained as a pale-yellow oil, which solidified to an amorphous solid under high vacuum.

R_f = 0.29 (3:7 EtOAc/*n*-hexane).

dr 97:3.

ee 96%. Chiralpak IG-3 column and guard, 20% 2-propanol/hexane, flow rate 0.4 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 8.69 (minor enantiomer), 9.54 (major enantiomer).

$[\alpha]_D^{25}$ −18.2 (*c* 1.21, $CHCl_3$).

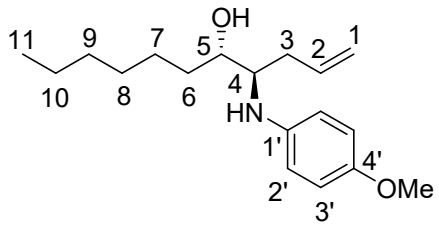
IR (neat): ν_{max} 3281 (N-H str.), 3081 (sp^2 C-H str.), 2919 (sp^3 C-H str.), 1640 (C=C str.), 1464 (N-H bend) 1074 (C-O str.), 996 (sp^2 C-H oop), 912 (sp^2 C-H oop), 723 (CH_2 chain bend) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 – 5.68 (m, 2H, H-2, H-2'), 5.21 – 5.05 (m, 4H, H-1, H-3'), 3.66 (dt, *J* = 8.3, 3.3 Hz, 1H, H-5), 3.28 (ddt, *J* = 14.2, 5.3, 1.6 Hz, 1H, CH_AH$_B$ H-1'), 3.19 (ddt, *J* = 14.2, 6.6, 1.3 Hz, 1H, CH$_A$$H_B$ H-1'), 2.56 (ddd, *J* = 9.7, 4.0, 3.3 Hz, 1H, H-4), 2.32 – 2.22 (m, 1H, H-3), 2.12 – 2.01 (m, 1H, H-3), 1.62 – 1.21 (m, 10H, H-6, H-7, H-8, H-9, H-10), 1.00 – 0.77 (m, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 136.8 (C-2'), 135.9 (C-2), 118.0 (C-1), 115.9 (C-3'), 69.6 (C-5), 59.5 (C-4), 49.9 (C-1'), 32.8 (C-3), 32.2 (C-6), 31.8 (C-9), 29.5 (C-8), 26.5 (C-7), 22.6 (C-10), 14.1 (C-11).

HRMS (ESI): *m/z* calculated for $C_{14}H_{28}NO$ $[M+H]^+$: 226.2171, found 226.2161.

(4*R*,5*S*)-4-((4-Methoxyphenyl)amino)undec-1-en-5-ol (SI-11)



The title compound was prepared according to *General Procedure 6*, using **8d** as the benzoyl amino ester substrate. Excess benzyl alcohol by-product was removed by high vacuum (6 h) and the crude purified by flash column chromatography over silica gel eluting with 1% MeOH/CH_2Cl_2, obtaining the title product **SI-11** (16.8 mg, 73%) as a brown oil.

R_f = 0.52 (3:7 EtOAc/*n*-hexane); 0.65 (1% MeOH/CH_2Cl_2).

dr 97:3

ee 86%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.5 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 12.34 (minor enantiomer), 12.77 (major enantiomer).

$[\alpha]_D^{25}$ −18.5 (*c* 0.80, $CHCl_3$).

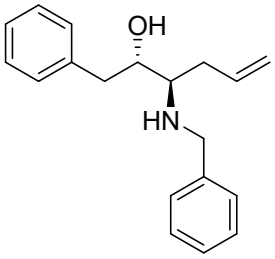
IR (neat): ν_{max} 3387 (O-H str.), 3073 (sp^2 C-H str.), 2927 (sp^3 C-H str.), 1640 (C=C str.), 1618 (Ar C=C str.), 1509 (N-H bend) 1464 (Ar C=C str.), 1038 (C-O str.), 995 (sp^2 C-H oop), 911 (sp^2 C-H oop), 817 (Ar C-H oop), 725 (CH_2 chain bend) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 – 6.74 (m, 2H, H-3'), 6.66 – 6.58 (m, 2H, H-2'), 5.83 (dddd, *J* = 16.8, 10.1, 7.7, 6.4 Hz, 1H, H-2), 5.18 – 5.05 (m, 2H, H-1), 3.83 – 3.72 (m, 1H, H-5), 3.75 (s, 3H, OCH_3), 3.33 (dt, *J* = 8.4, 4.3 Hz, 1H, H-4), 2.44 – 2.23 (m, 2H, H-3), 1.61 – 1.43 (m, 2H, H-6), 1.41 – 1.23 (m, 8H, H-7, H-8, H-9, H-10), 0.95 – 0.84 (m, 3H, H-11).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6 (C-4'), 141.7 (C-1'), 135.6 (C-2), 117.6 (C-1), 115.5 (C-2'), 114.9 (C-3'), 72.1 (C-5), 58.3 (C-4), 55.8 (OCH_3), 33.7 (C-3), 32.9 (C-6), 31.8 (C-9), 29.4 (C-8), 26.3 (C-7), 22.6 (C-10), 14.1 (C-11).

HRMS (ESI): *m/z* calculated for $C_{18}H_{30}NO_2$ $[M+H]^+$: 292.2277, found 292.2282.

(2*S*,3*R*)-3-(Benzylamino)-1-phenylhex-5-en-2-ol (*ent*-7c)



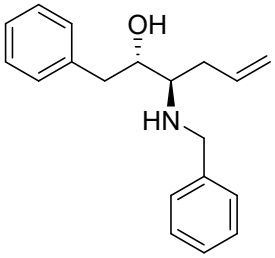
The title compound was prepared according to *General Procedure 6*, using **8e** (Method 1) as the benzoyl amino ester substrate. Excess benzyl alcohol by-product was removed by high vacuum (6 h). ***Ent*-7c** (35.9 mg, 95%) was obtained as a pale-yellow oil, which crystallised under high vacuum. The spectroscopic data obtained was identical to those for **7c**.

ee 88%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 9.28 (minor enantiomer), 11.19 (major enantiomer).

$[\alpha]_D^{25}$ –2.89 (*c* 1.80, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{19}H_{24}NO$ $[M+H]^+$: 282, found 282 (100%).

(2*S*,3*R*)-3-(Benzylamino)-1-phenylhex-5-en-2-ol (*ent*-7c).



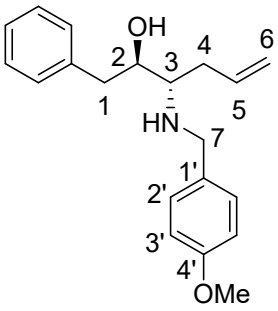
The title compound was prepared according to *General Procedure 6*, not including the brine washes, using **8e** (Method 2) as the benzoyl amino ester substrate. The crude material was purified by silica plug eluting with 1:4 and 1:1 EtOAc/*n*-hexane and excess benzyl alcohol by-product was removed by high vacuum (6 h), obtaining ***ent*-7c** (10.8 mg, 70%) as a pale-yellow oil, which crystallised under high vacuum. The spectroscopic data obtained was identical to those for **7c**.

ee 94%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 9.65 (minor enantiomer), 11.68 (major enantiomer).

$[\alpha]_D^{24}$ –0.63 (*c* 0.54, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{19}H_{24}NO$ $[M+H]^+$: 282, found 282 (100%).

(2*S*,3*R*)-3-((4-Methoxybenzyl)amino)-1-phenylhex-5-en-2-ol (SI-12).



The title compound was prepared according to *General Procedure 6*, not including the brine washes, using **8f** as the benzoyl amino ester substrate. The crude material was purified by silica plug eluting with 1:4 and 1:1 EtOAc/*n*-hexane and excess benzyl alcohol by-product was removed by high vacuum (6 h), obtaining **SI-12** (4.3 mg, 27%) as a pale-yellow oil.

ee 96%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 1.0 mL.min^{-1}, column oven 30 ^{o}C, PDA 207 nm. R_t (mins) 8.57 (minor enantiomer), 11.61 (major enantiomer).

$[\alpha]_D^{25}$ –2.19 (*c* 0.28, $CHCl_3$).

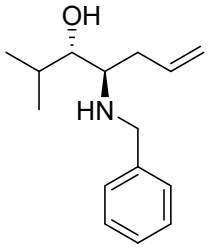
IR (neat): ν_{max} 3329 (O-H str.), 3062 (sp^2 C-H str.), 2922 (sp^3 C-H str.), 1639 (C=C str.), 1610 Ar C=C str.), 1496 (N-H bend) 1454 (Ar C=C str.), 1077 (C-O str.), 699 (Ar C-H oop), 749 (Ar C-H oop), 821 (Ar C-H oop) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.19 (m, 5H, Ar-*H*), 7.16 (d, *J* = 8.6 Hz, 2H, H-3'), 6.84 (d, *J* = 8.6 Hz, 2H, H-2'), 5.72 (dtd, *J* = 18.1, 9.0, 5.5 Hz, 1H, H-5), 5.16 – 5.06 (m, 2H, H-6), 3.97 (ddd, *J* = 8.4, 4.75, 3.4 Hz, 1H, H-2), 3.79 (s, 3H, OCH_3), 3.74 (d, *J* = 12.9 Hz, 1H, CH_AH$_B$ H-7), 3.63 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-7), 2.80 (dd, *J* = 13.8, 8.5 Hz, 1H, CH_AH$_B$ H-1), 2.72 (dd, *J* = 13.8, 4.75 Hz, 1H, CH$_A$$H_B$ H-1), 2.64 (dt, *J* = 9.5, 3.8 Hz, 1H, H-3), 2.45 – 2.37 (m, 1H, H-4), 2.20 (dt, *J* = 14.3, 9.1 Hz, 1H, H-4).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7 (C-4'), 139.2 (*ipso*-C), 135.6 (C-5), 132.3 (C-1'), 129.3 (C-3'), 129.1 (*m*-C), 128.5 (*o*-C), 126.3 (*p*-C), 118.2 (C-6), 113.9 (C-2'), 71.2 (C-2), 59.3 (C-3), 55.3 (OCH_3), 50.9 (C-7), 38.7 (C-1), 33.0 (C-4).

HRMS (ESI): *m/z* calculated for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1964, found 312.1974.

(3*S*,4*R*)-4-(Benzylamino)-2-methylhept-6-en-3-ol (*ent*-7e)



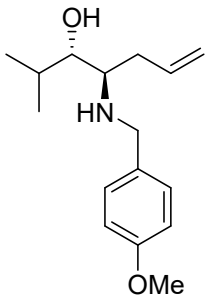
The title compound was prepared according to *General Procedure 6*, using **8g** as the benzoyl amino ester substrate and obtaining ***ent*-7e** (19.5 mg, 60%) as a pale-yellow oil. The spectroscopic data obtained was identical to those for **7e**.

ee 90%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 °C, PDA 207 nm. R_t (mins) 7.46 (minor enantiomer), 7.74 (major enantiomer).

$[\alpha]_D^{25}$ +12.5 (*c* 0.87, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{15}H_{24}NO$ $[M+H]^+$: 234, found 234 (100%).

(3*S*,4*R*)-4-((4-Methoxybenzyl)amino)-2-methylhept-6-en-3-ol (*ent*-7f)



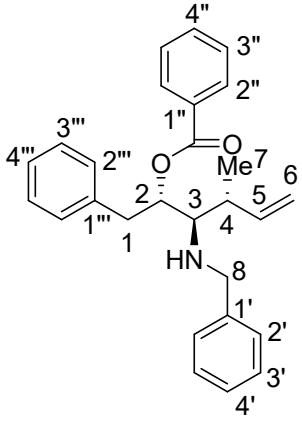
The title compound was prepared according to *General Procedure 8*, using **8h** as the benzoyl amino ester substrate. Excess benzyl alcohol by-product was removed by high vacuum (6 h) and the crude purified by silica plug eluting with 1:4 and 1:1 EtOAc/*n*-hexane, obtaining ***ent*-7f** (16.4 mg, 72%) as a pale-yellow oil. The spectroscopic data obtained was identical to those for **7f**.

ee 94%. Chiralpak IG-3 column and guard, 15% 2-propanol/hexane, flow rate 0.6 mL.min^{-1}, column oven 30 °C, PDA 207 nm. R_t (mins) 10.36 (minor enantiomer), 11.06 (major enantiomer).

$[\alpha]_D^{25}$ +12.0 (*c* 0.73, $CHCl_3$).

LRMS (ESI): *m/z* calculated for $C_{16}H_{26}NO_2$ $[M+H]^+$: 264, found 264 (100%).

(2*S*,3*R*)-3-(Benzylamino)-4-methyl-1-phenylhex-5-en-2-yl benzoate (9a)



To an NMR tube was added **2** (R^1 = Bn) (20.4 mg, 0.0802 mmol, 1.0 eq.), 1,2,3-trimethoxybenzene (4.4 mg, 0.0265 mmol, 0.33 eq.) as an internal standard and CD_2Cl_2 (~500 μL). A 500 MHz ^{1}H NMR spectrum was then acquired. Benzylamine (10.5 μL, 0.0962 mmol, 1.2 eq.) was then added and mixed by shaking and another 500 MHz ^{1}H NMR spectrum was acquired to confirm the formation of the imine reactive intermediate. Pinacol (*E*)-crotylboronate (19.7 μL, 0.0962 mmol, 1.2. eq.) was then added and mixed by shaking. 500 MHz ^{1}H NMR spectra were acquired at t = 0, 5, 21, 30 and 44 h, then at 4, 8 11 and 14 d. The solvent was topped up periodically as the reaction progressed. Upon completion of the reaction, the reaction mixture was added to a separating funnel with sat. aq. $NaHCO_3$ (~2 mL) and extracted with CH_2Cl_2 (3

x ~2 mL). The combined organic layers were dried over K_2CO_3, filtered, concentrated *in vacuo* and purified by flash column chromatography over silica gel eluting with 3:17 EtOAc/*n*-hexane, obtaining the title product **9a** (10.2 mg, 32%) as a yellow oil. Enantiomeric excess was determined by diastereomeric salt formation according to the literature procedure using (*R*)- and (*S*)-1,1'-binaphthyl-2,2'-diylphosphoric acid[10] and analysis of their respective ^{1}H, COSY, TOCSY and HSQC spectra.

R_f = 0.40 (3:17 EtOAc/*n*-hexane).

dr 95:5.

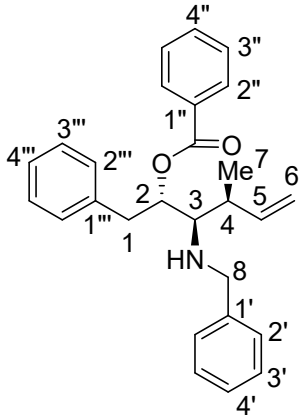
ee 78%.

$[\alpha]_D^{23}$ –53.9 (*c* 0.51, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.93 (m, 2H, H-2"), 7.53 (ddt, *J* = 8.7, 6.9, 1.3 Hz, 1H, H-4"), 7.45 – 7.38 (m, 2H, H-3"), 7.34 – 7.24 (m, 5H, H-2', H-3', H-4'), 7.24 – 7.11 (m, 5H, H-2'", H-3'", H-4'"), 5.93 (ddd, *J* = 17.5, 9.7, 7.9 Hz, 1H, H-5), 5.51 (ddd, *J* = 7.45, 5.6, 4.1 Hz, 1H, H-2), 5.13 – 5.06 (m, 2H, H-6), 3.96 (d, *J* = 12.9 Hz, 1H, CH_AH$_B$ H-8), 3.81 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-8), 3.11 (appt. dd, *J* = 7.45, 5.8 Hz, 2H, H-1), 2.89 (dd, *J* = 6.5, 4.1 Hz, 1H, H-3), 2.47 (appt. h, *J* = 6.8 Hz, 1H, H-4), 1.16 (d, *J* = 6.8 Hz, 3H, H-7).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8 (*C*=O), 141.9, (C-5) 140.7 (C-1'), 138.2 (C-1'"), 132.8 (C-4"), 130.4 (C-1"), 129.5 (C-2"), 129.4 (C-3'"), 128.34 (C-2'), 128.33 (C-3"), 128.29 (C-2'"), 128.24 (C-3'), 127.0 (C-4'), 126.3 (C-4'"), 114.6 (C-6), 77.4 (C-2), 63.1 (C-3), 53.8 (C-8), 40.4 (C-4), 36.0 (C-1), 16.7 (C-7).

HRMS (ESI): *m/z* calculated for $C_{27}H_{30}NO_2$ $[M+H]^+$: 400.2277, found 400.2280.



(2*S*,3*R*)-3-(Benzylamino)-4-methyl-1-phenylhex-5-en-2-yl benzoate (9b)

The title compound was prepared as per **9a**, however using pinacol (*Z*)-crotylboronate. 500 MHz ^{1}H NMR spectra were acquired at t = 0, 5 and 22 h, then at 2, 4, 7, 9, 11, 14, 16, 18, 21, 23, 25 and 28 d. The compound was purified by flash column chromatography over silica gel eluting with 1:9 EtOAc/*n*-hexane, obtaining the title product **9b** (13.9 mg, 46%) as a yellow oil. Enantiomeric excess was again determined by diastereomeric salt formation according to the

literature procedure using (*R*)- and (*S*)-1,1'-binaphthyl-2,2'-diylphosphoric acid[10] and analysis of their respective ^{1}H, COSY, TOCSY and HSQC spectra.

R_f = 0.40 (3:17 EtOAc/*n*-hexane).

dr 99:1.

ee 88%.

$[\alpha]_D^{23}$ –60.1 (*c* 0.70, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.94 (m, 2H, H-2''), 7.56 – 7.50 (m, 1H, H-4''), 7.44 – 7.38 (m, 2H, H-3''), 7.30 – 7.12 (m, 10H, Ar-*H*), 5.88 – 5.77 (m, 1H, H-5), 5.54 (dt, *J* = 8.6, 4.2 Hz, 1H, H-2), 5.12 – 5.04 (m, 2H, H-6), 3.97 (d, *J* = 12.9 Hz, 1H, CH_AH$_B$ H-8), 3.77 (d, *J* = 12.9 Hz, 1H, CH$_A$$H_B$ H-8), 3.20 (dd, *J* = 14.3, 8.8 Hz, 1H, CH_AH$_B$ H-1), 3.12 (dd, *J* = 14.3, 4.4 Hz, 1H, CH_AH$_B$ H-1), 2.80 (dd, *J* = 6.2, 3.9 Hz, 1H, H-3), 2.53 – 2.42 (m, 1H, H-4), 1.17 (d, *J* = 6.8 Hz, 3H, H-7).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9 (*C*=O), 141.0 (C-5), 140.7 (C-1'), 138.3 (C-1'''), 132.8 (C-4''), 130.4 (C-1''), 129.6 (C-2''), 129.3 (C-3'''), 128.34 (C-2'), 128.33 (C-3''), 128.31 (C-2'''), 128.2 (C-3'), 126.9 (C-4'), 126.3 (C-4'''), 115.7 (C-6), 77.2 (C-2), 63.2 (C-3), 53.9 (C-8), 40.1 (C-4), 36.3 (C-1), 18.0 (C-7).

HRMS (ESI): *m/z* calculated for $C_{27}H_{30}NO_2$ $[M+H]^+$: 400.2277, found 400.2291.

NMR spectra and Chiral HPLC traces

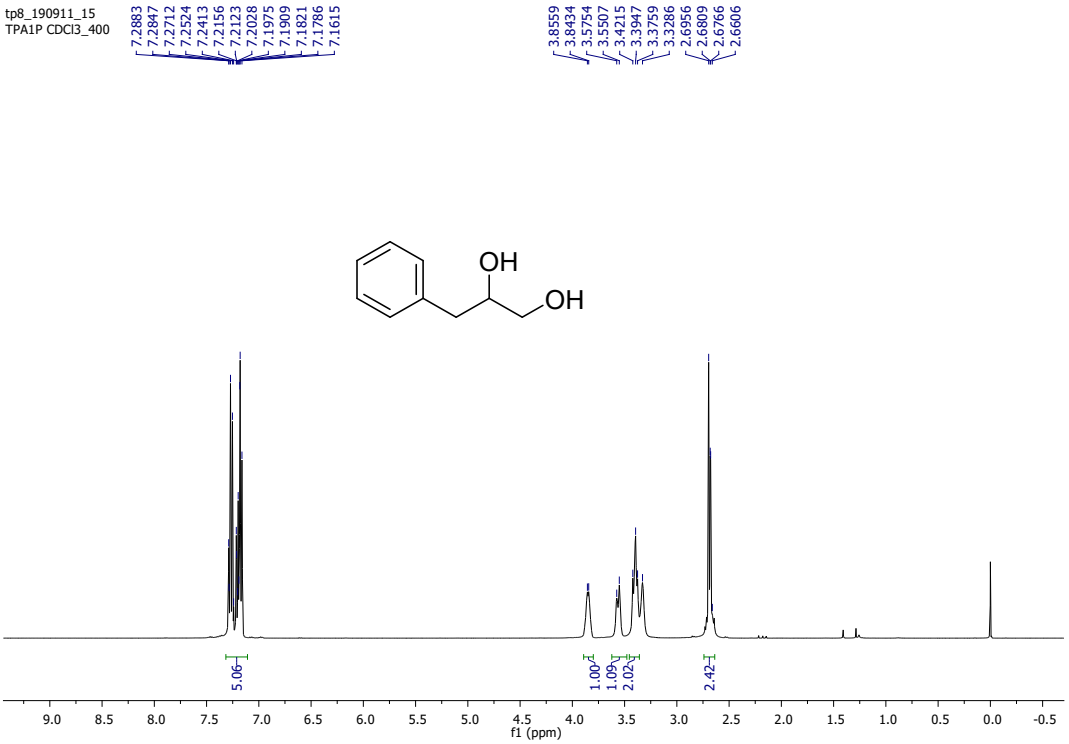


Figure 1. ^{1}H NMR spectrum of **3** (R^1 = Bn) (400 MHz, $CDCl_3$)

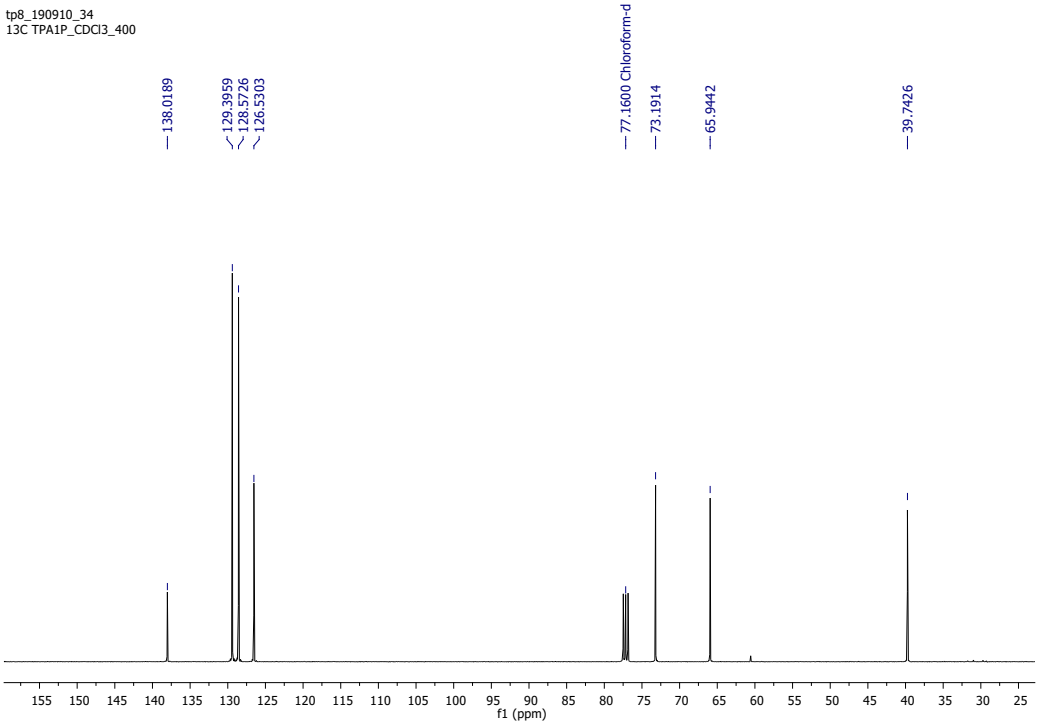


Figure 2. ^{13}C NMR spectrum of **3** (R^1 = Bn) (100 MHz, $CDCl_3$)

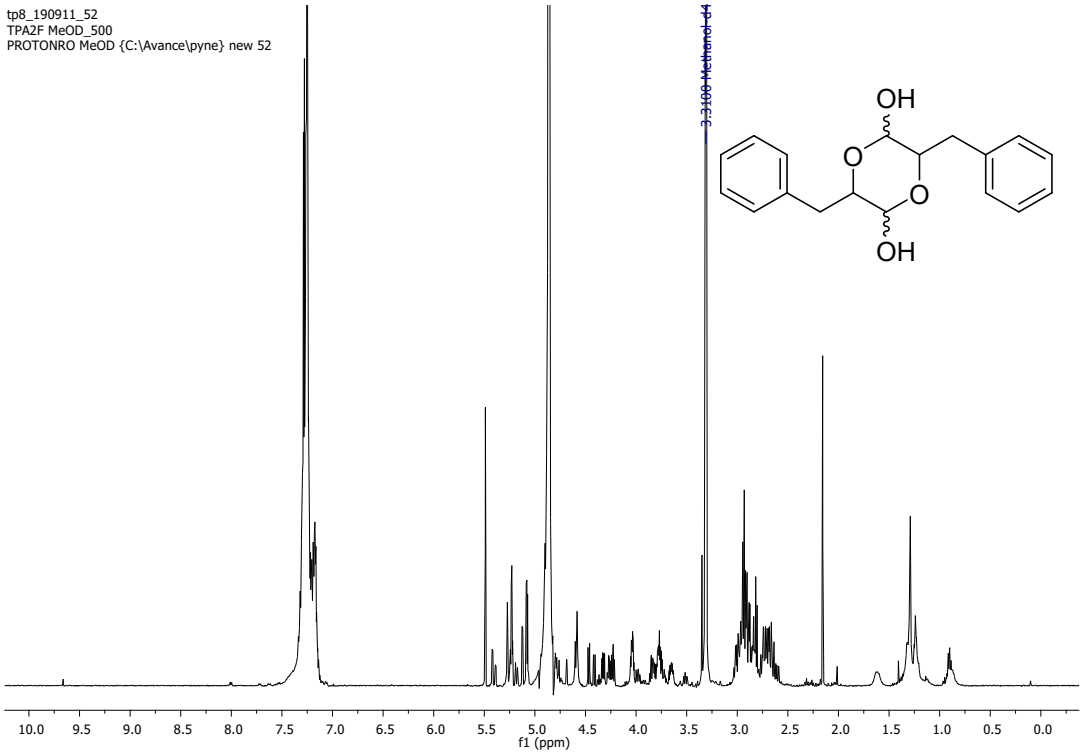


Figure 3. ^{1}H NMR spectrum of **4** (R^1 = Bn) (500 MHz, MeOH-d_4), mixture of diastereomers and possibly oligomers.

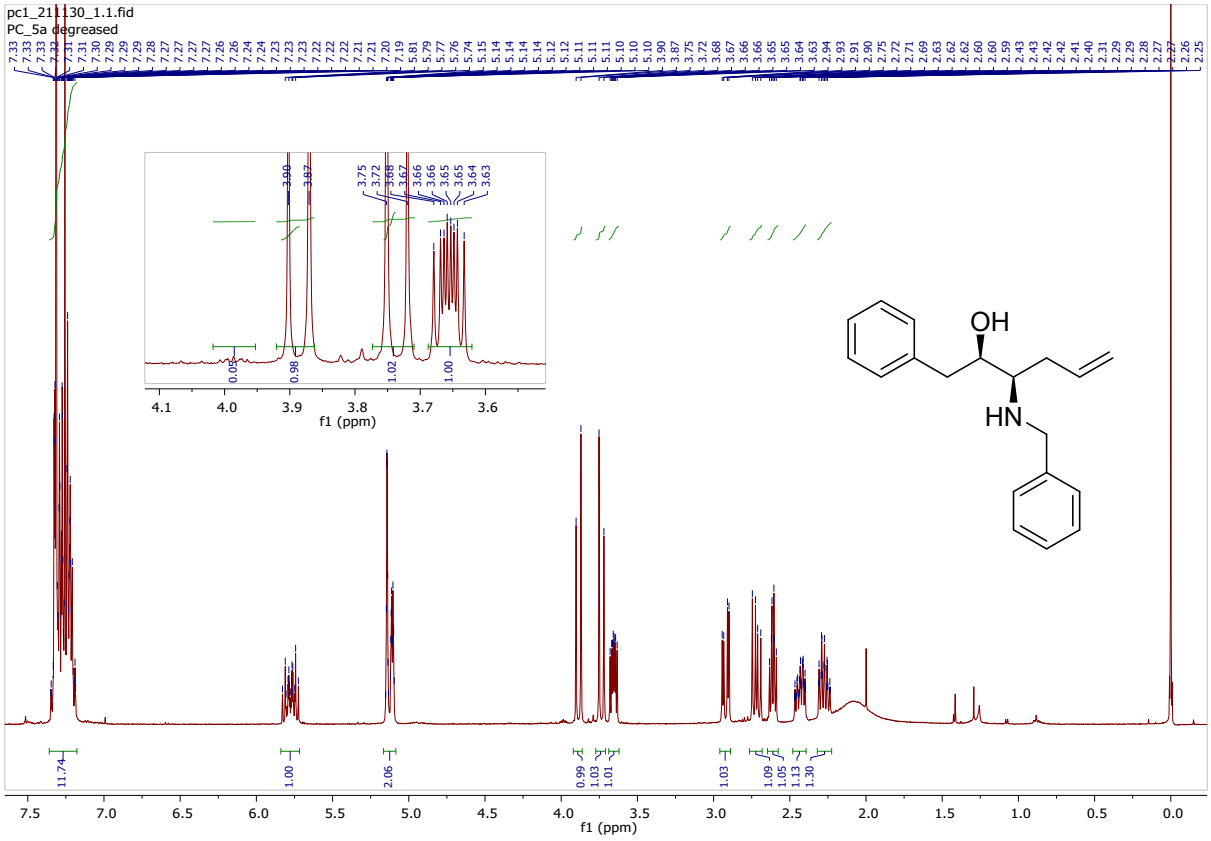


Figure 4. ^{1}H NMR spectrum of *rac*-**5a** (400 MHz, $CDCl_3$, dr 95:5)

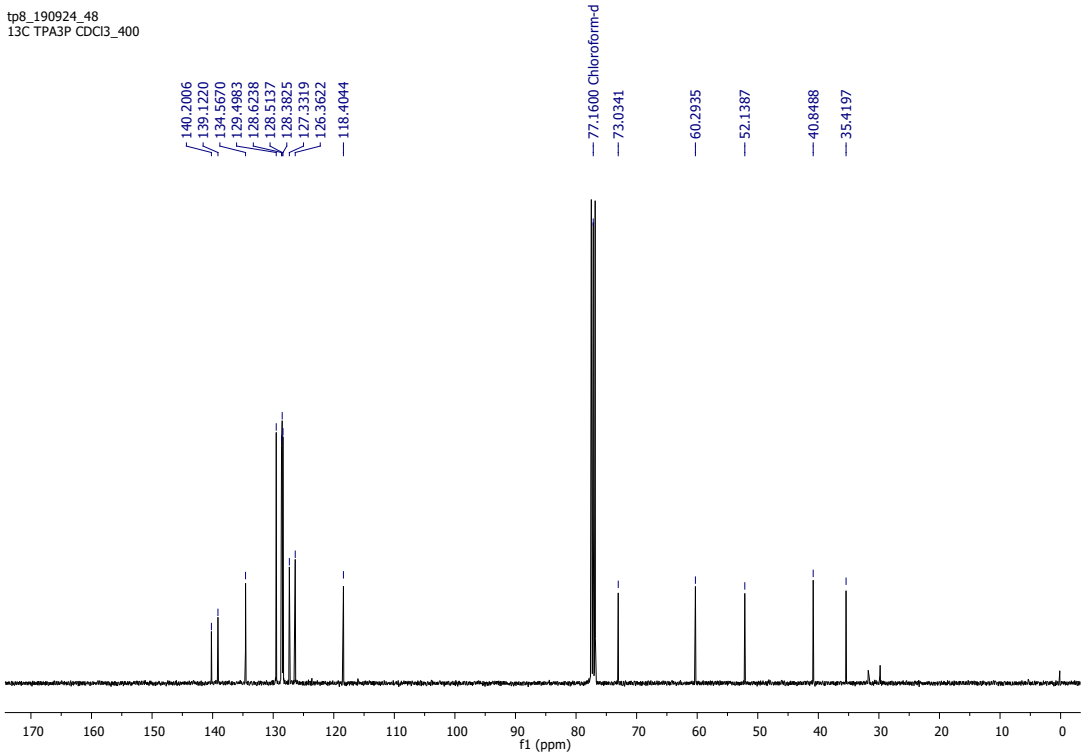


Figure 5. ^{13}C NMR spectrum of *rac*-**5a** (101 MHz, $CDCl_3$)

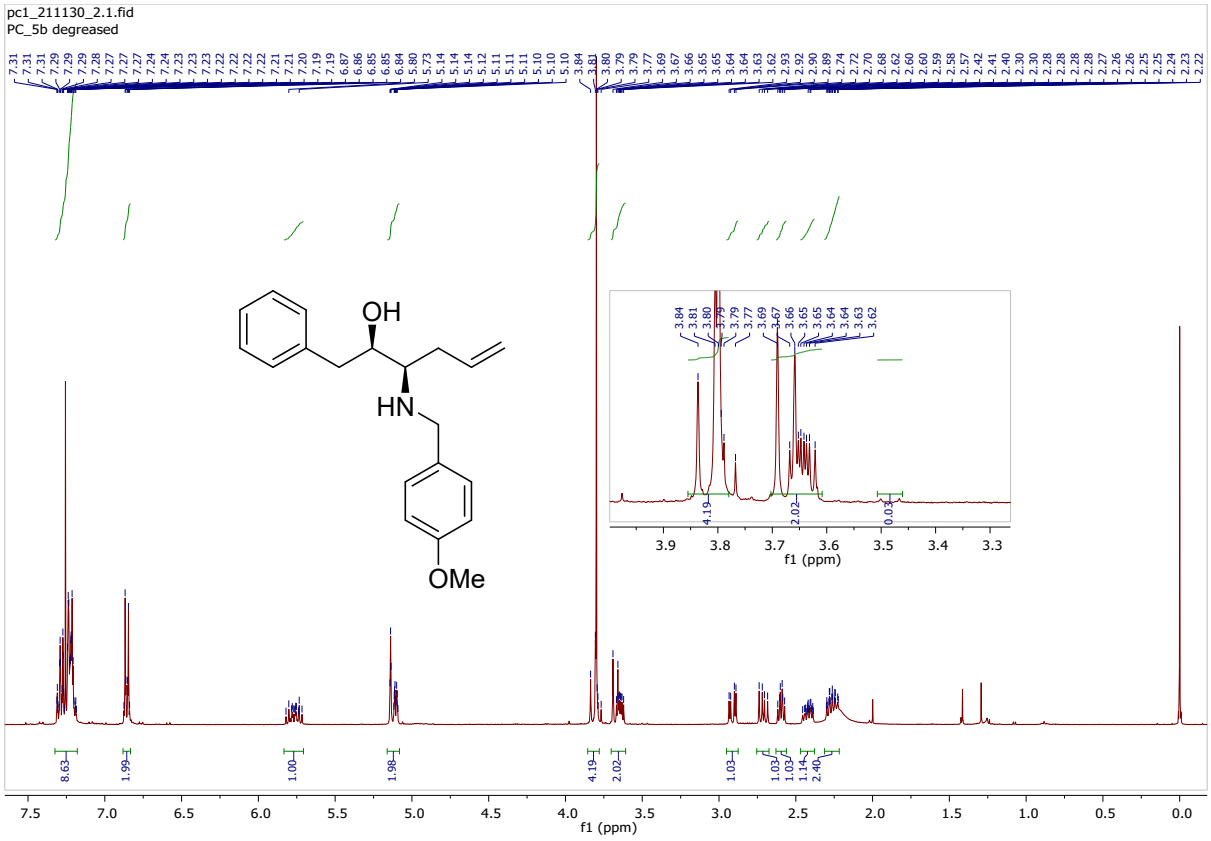


Figure 6. ^{1}H NMR spectrum of *rac*-**5b** (400 MHz, $CDCl_3$, dr = 98:2)

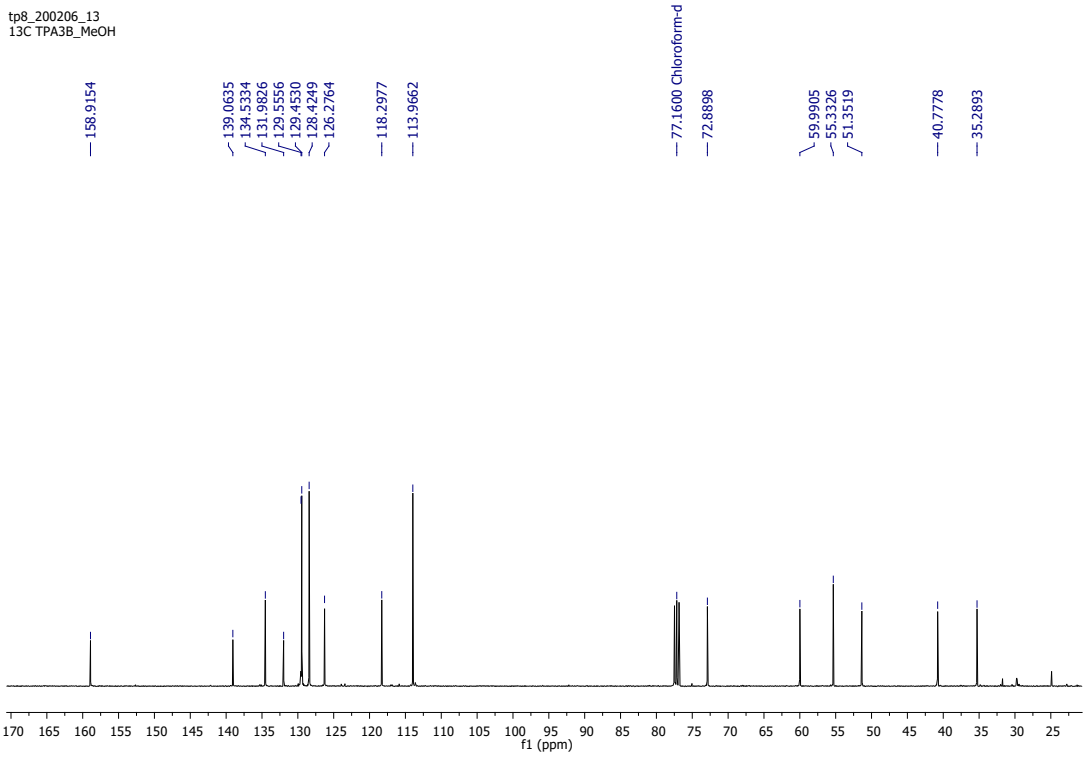


Figure 7. ^{13}C NMR spectrum of *rac*-**5b** (101 MHz, $CDCl_3$)

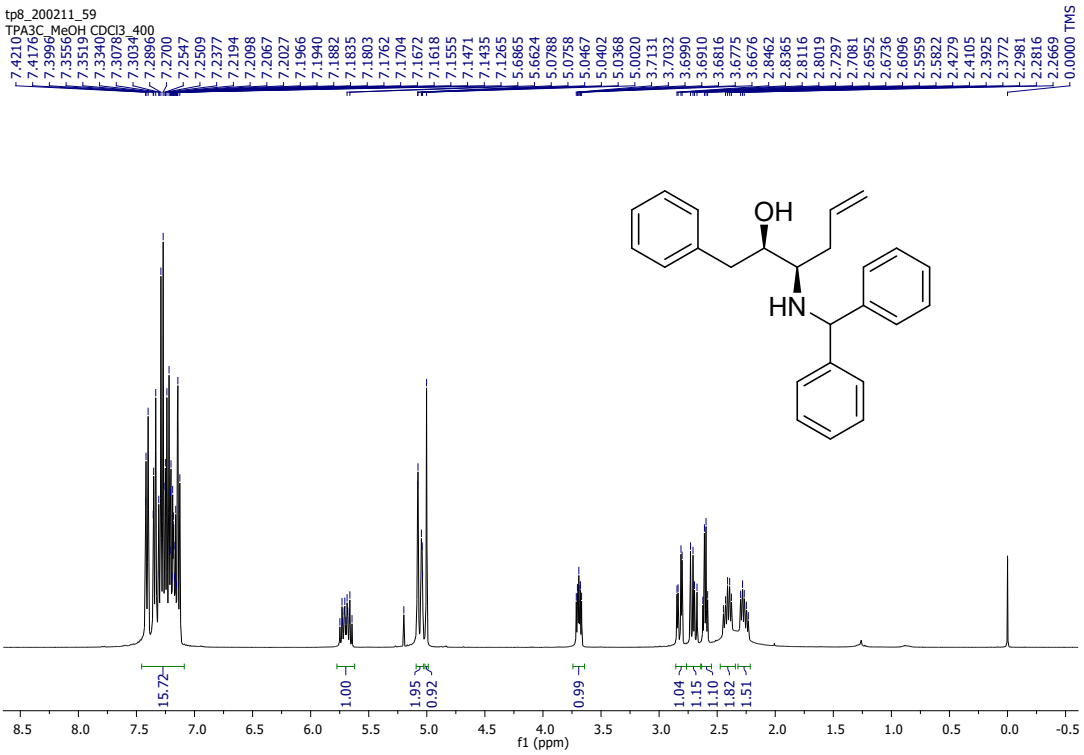


Figure 8. ^{1}H NMR spectrum of *rac*-**5c** (400 MHz, $CDCl_3$, dr = >98:2)

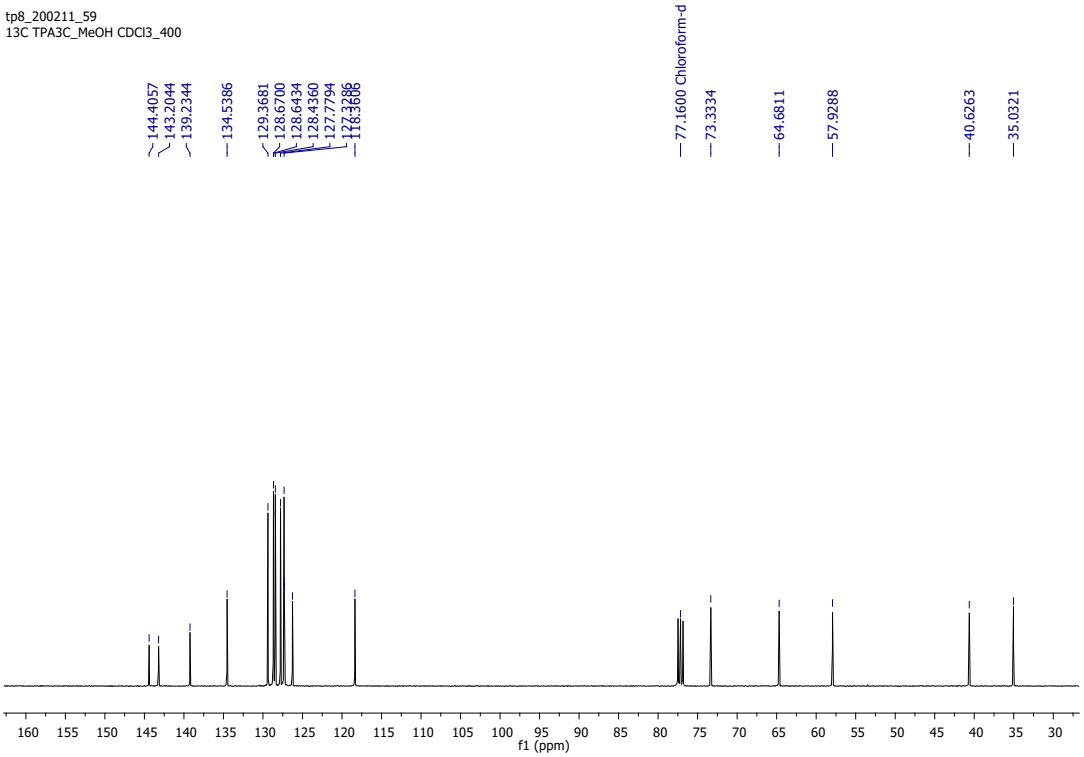


Figure 9. ^{13}C NMR spectrum of *rac*-**5c** (101 MHz, $CDCl_3$)

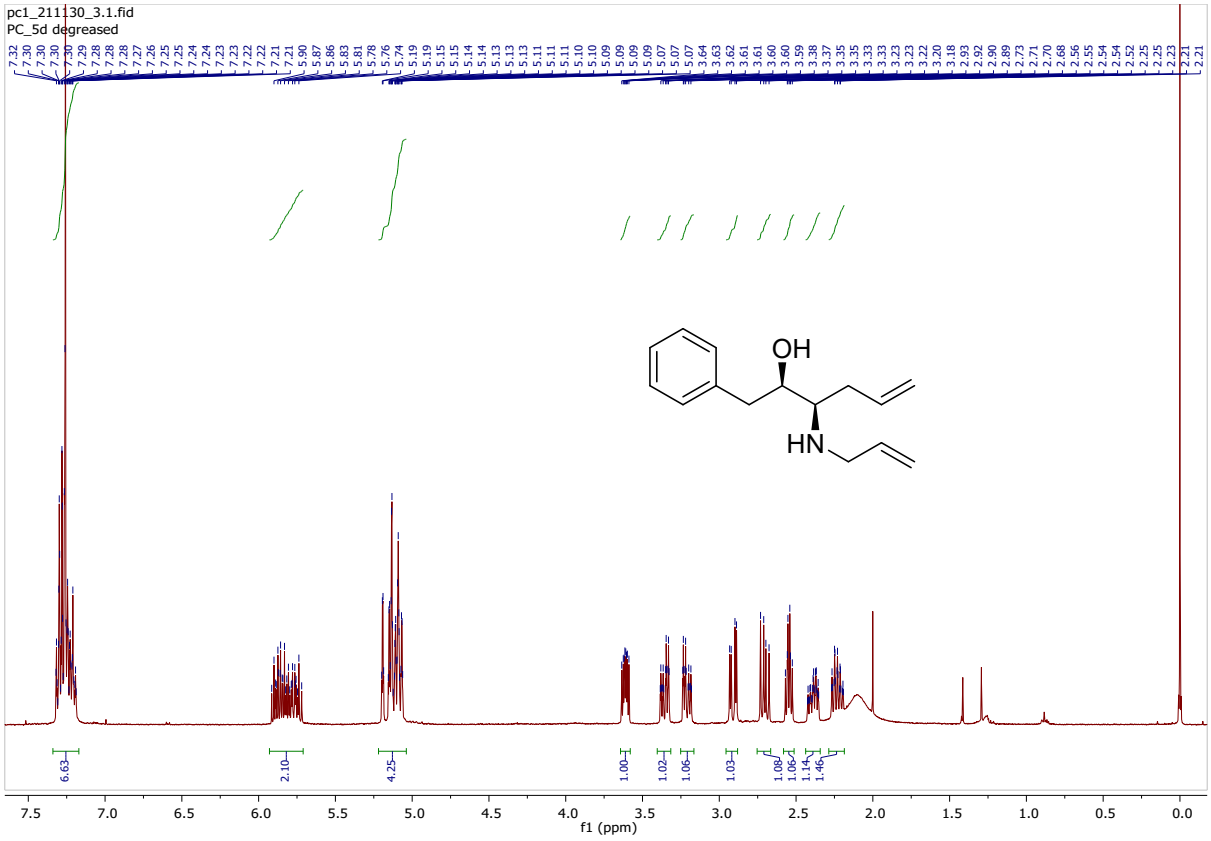


Figure 10. ^{1}H NMR spectrum of *rac*-**5d** (400 MHz, $CDCl_3$, dr = >98:2)

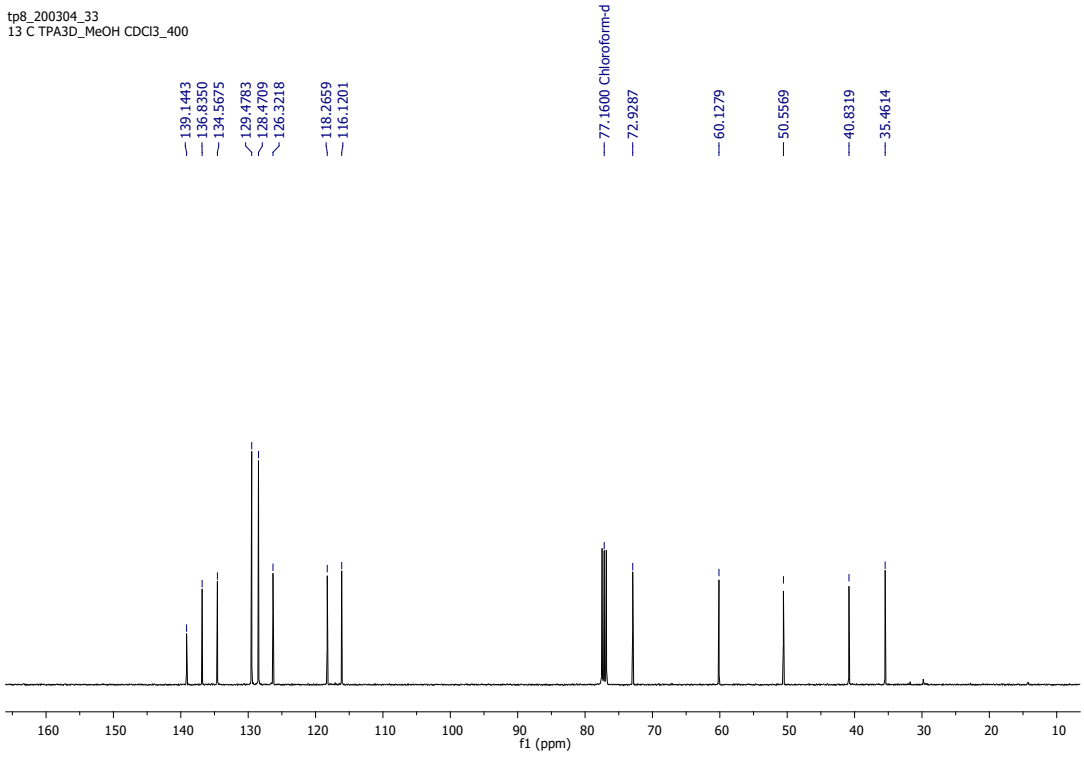


Figure 11. ^{13}C NMR spectrum of *rac*-**5d** (100 MHz, $CDCl_3$)

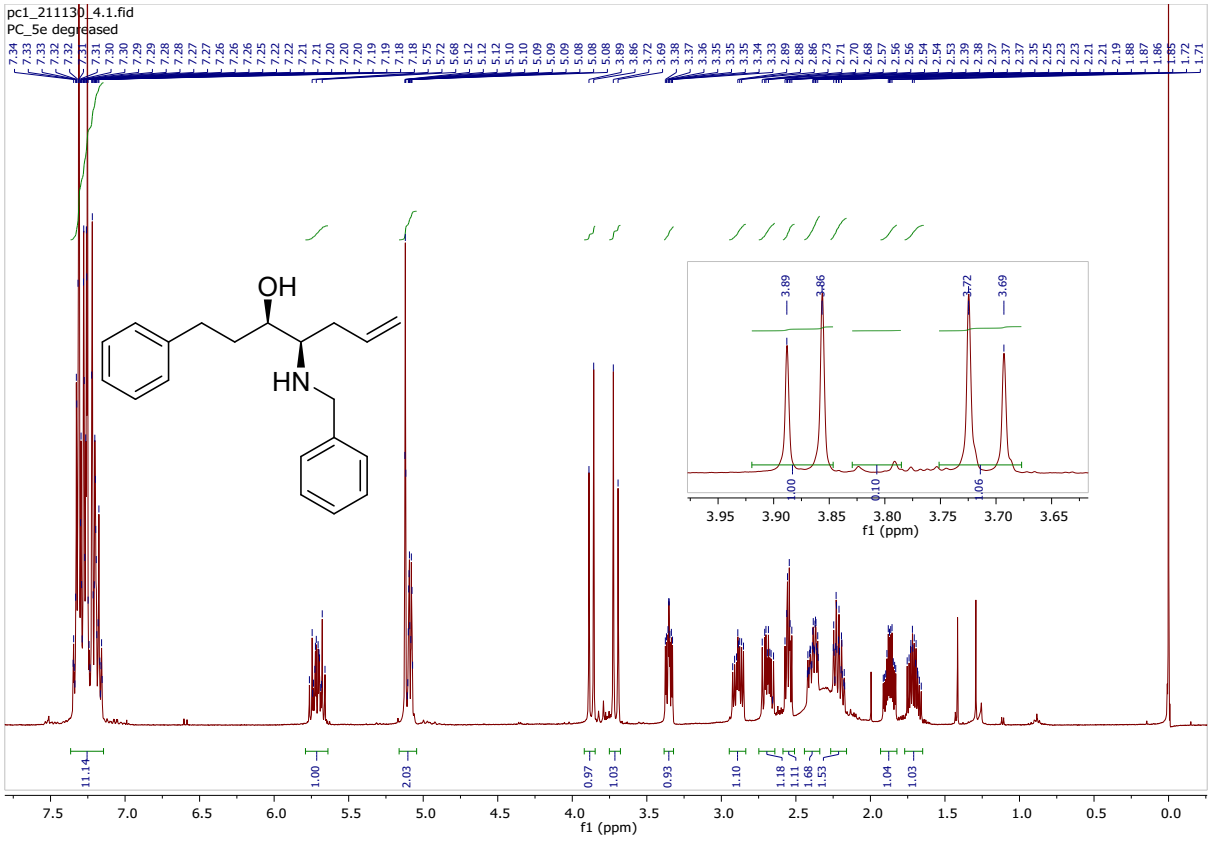


Figure 12. ^{1}H NMR spectrum of *rac*-**5e** (400 MHz, $CDCl_3$, dr = 91:9)

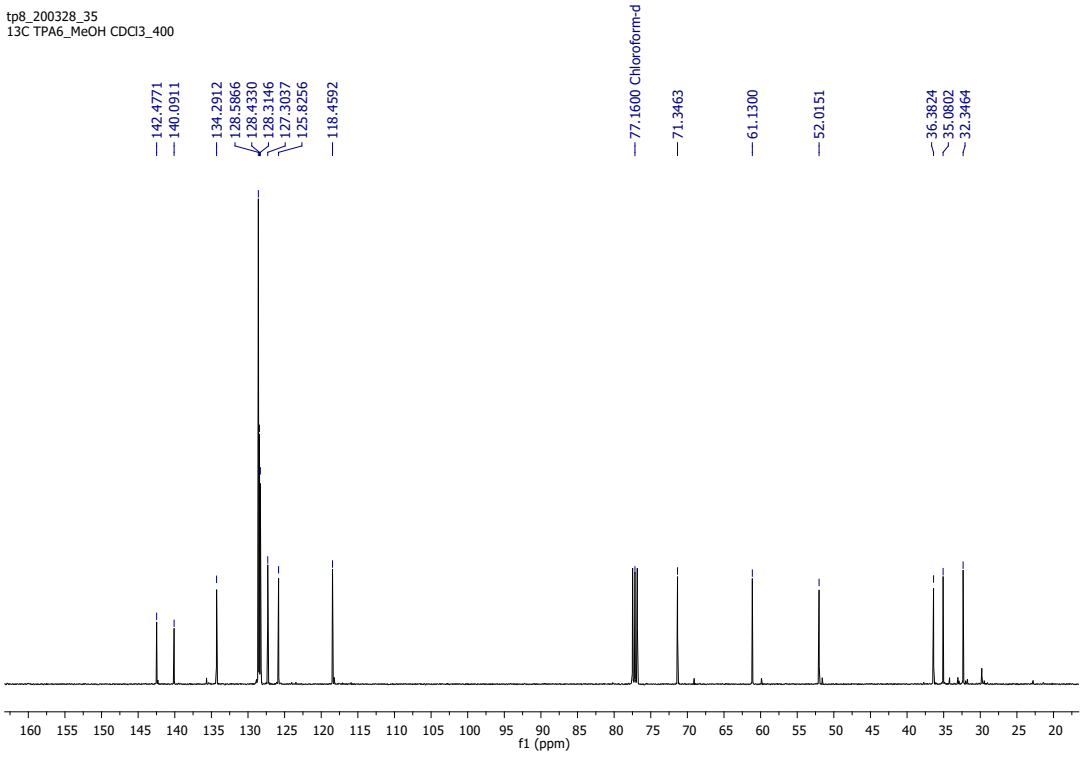


Figure 13. ^{13}C NMR spectrum of *rac*-**5e** (101 MHz, $CDCl_3$)

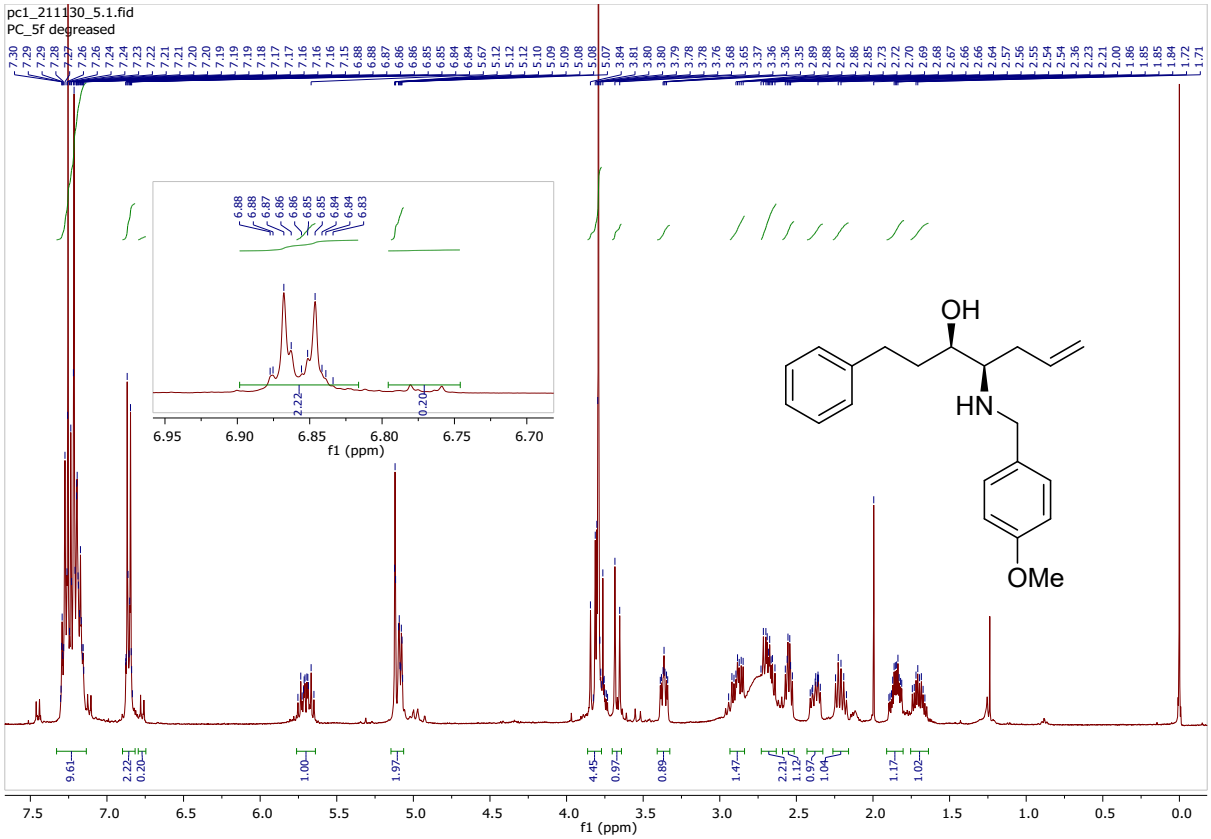


Figure 14. ^{1}H NMR spectrum of *rac*-**5f** (400 MHz, $CDCl_3$, dr = 90:10, trace of acetone)

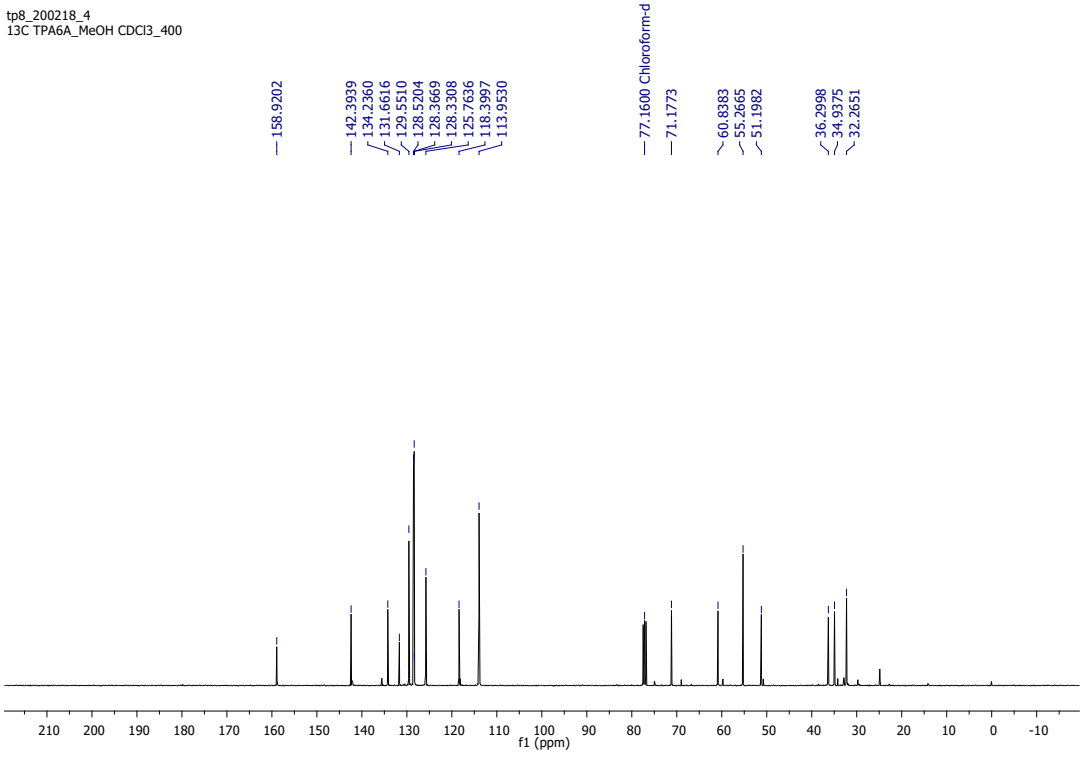


Figure 15. ^{13}C NMR spectrum of *rac*-**5f** (101 MHz, $CDCl_3$)

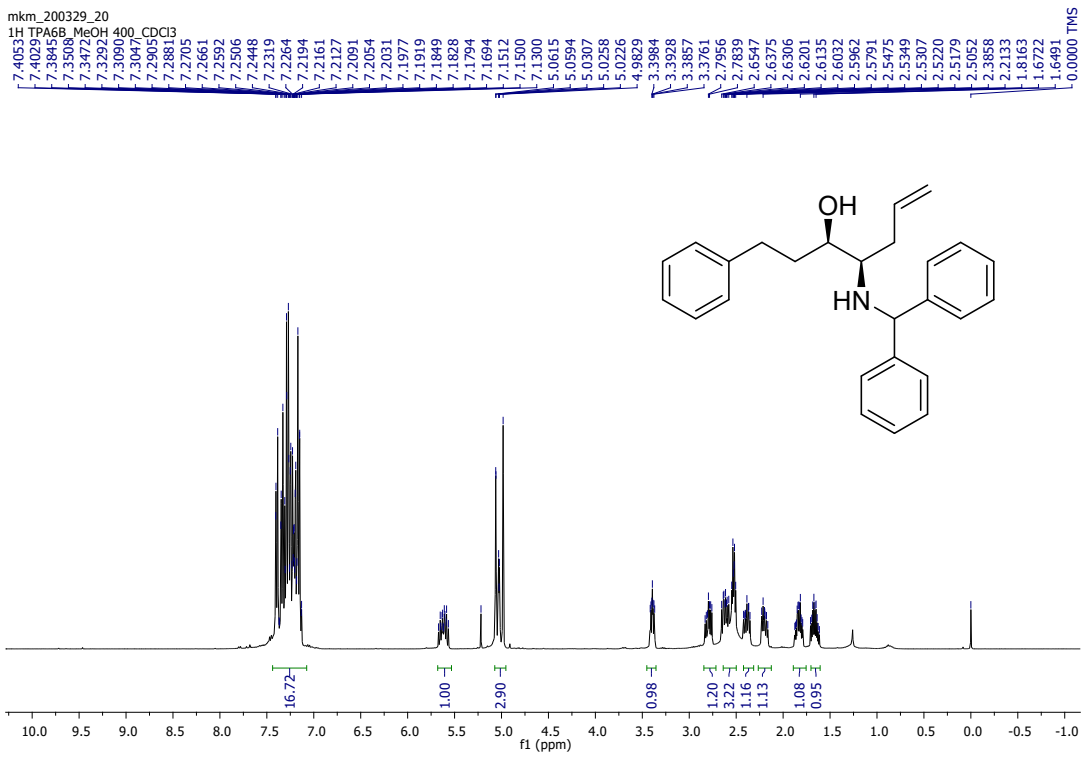


Figure 16. ^{1}H NMR spectrum of *rac*-**5g** (400 MHz, $CDCl_3$, dr = 95:5)

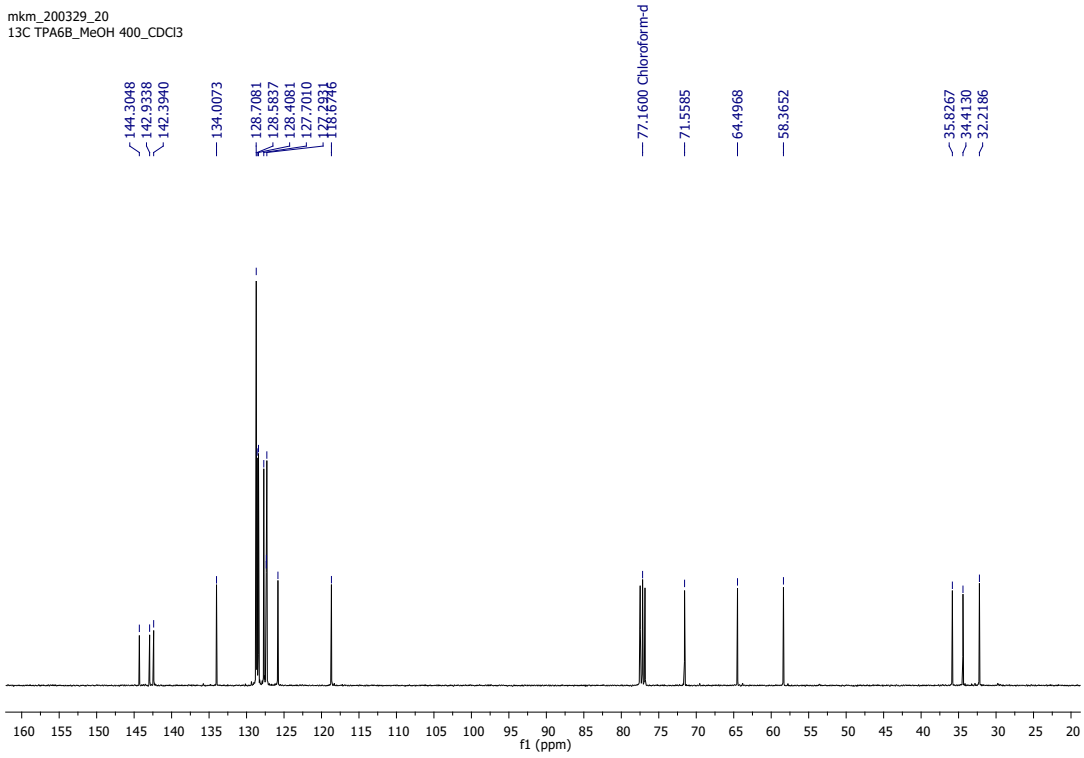


Figure 17. ^{13}C NMR spectrum of *rac*-**5g** (101 MHz, $CDCl_3$)

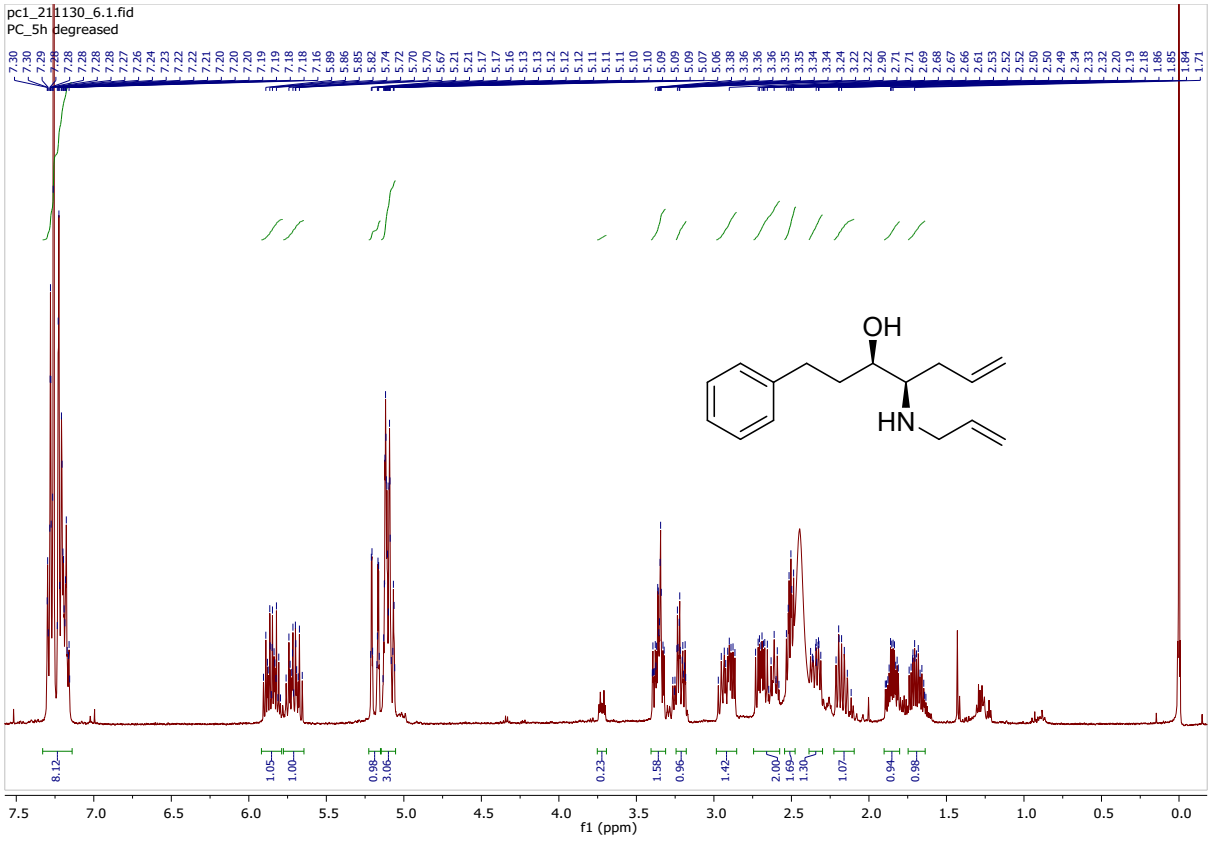


Figure 18. ^{1}H NMR spectrum of *rac*-**5h** (400 MHz, $CDCl_3$, dr = 81:19)

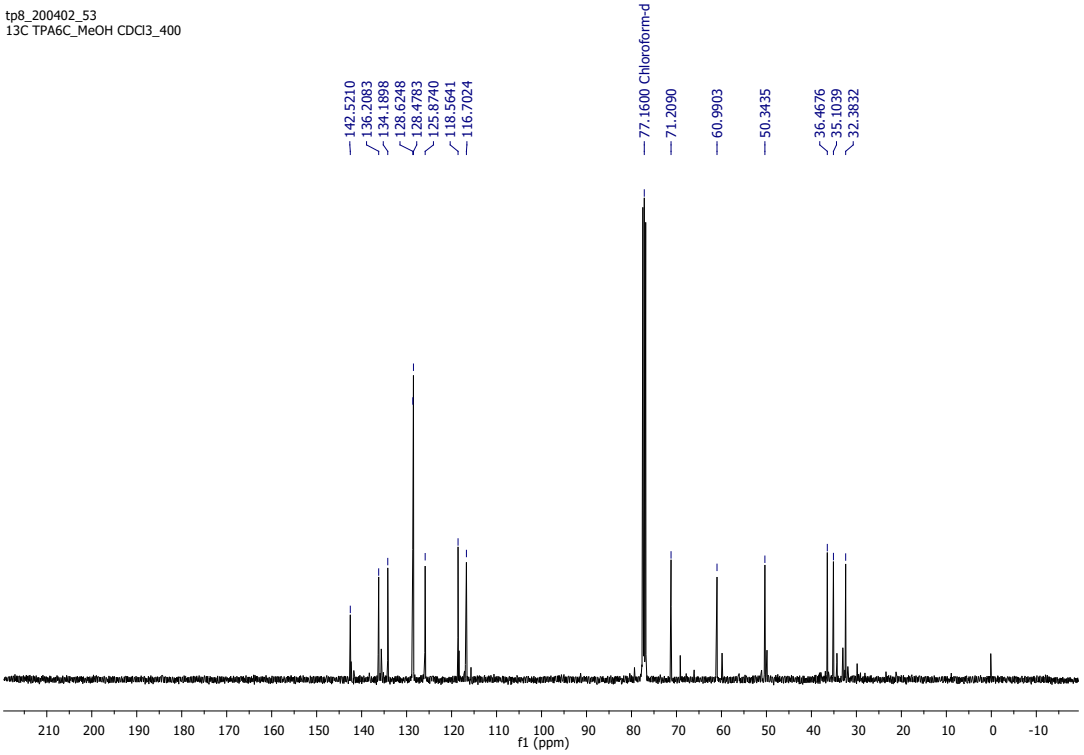


Figure 19. ^{13}C NMR spectrum of *rac*-**5h** (101 MHz, $CDCl_3$)

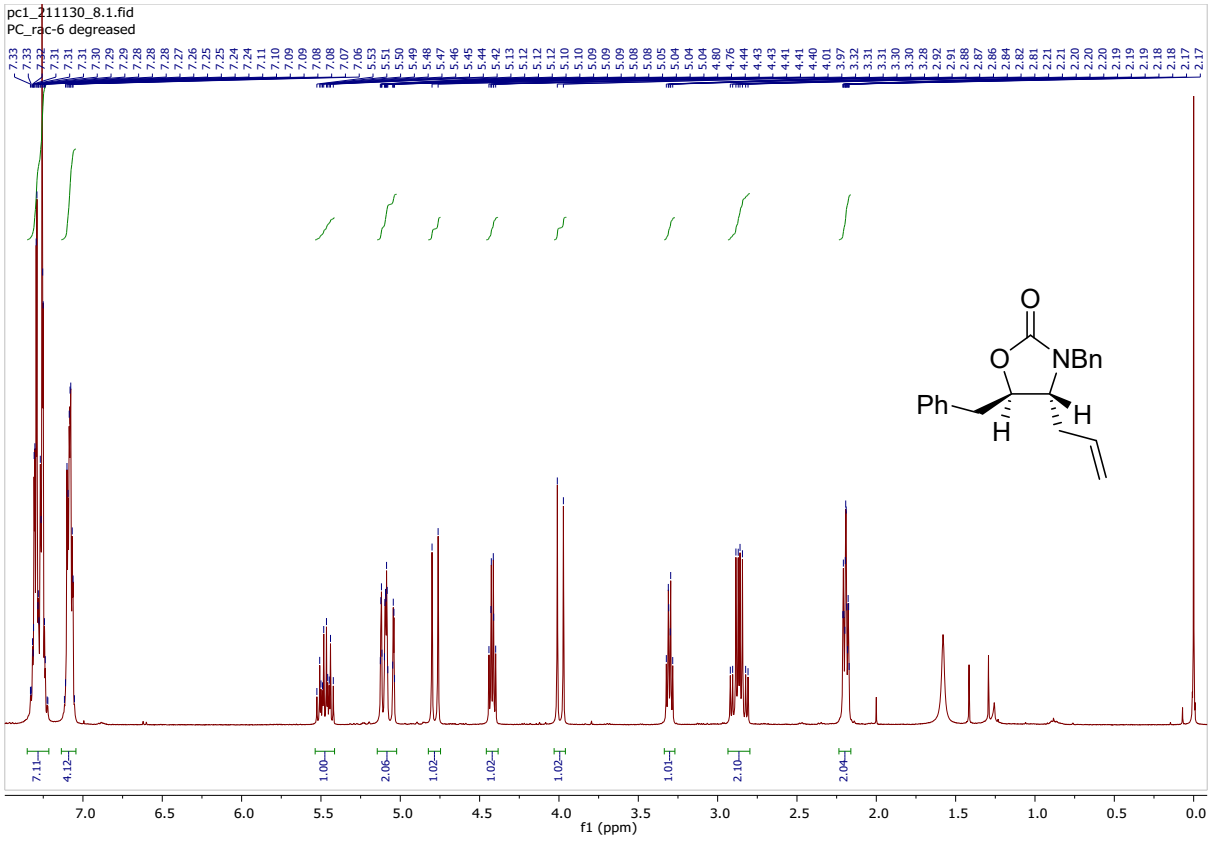


Figure 20. ^{1}H NMR spectrum of *rac*-**6** (400 MHz, $CDCl_3$)

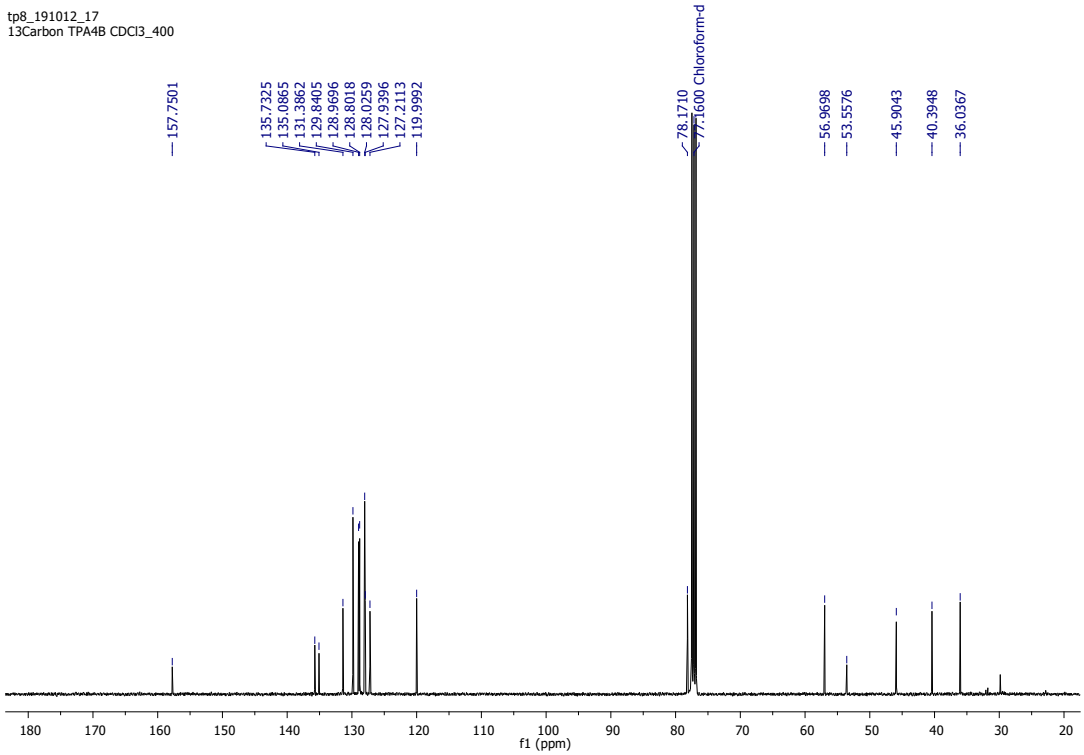


Figure 21. ^{13}C NMR spectrum of *rac*-**6** (101 MHz, $CDCl_3$)

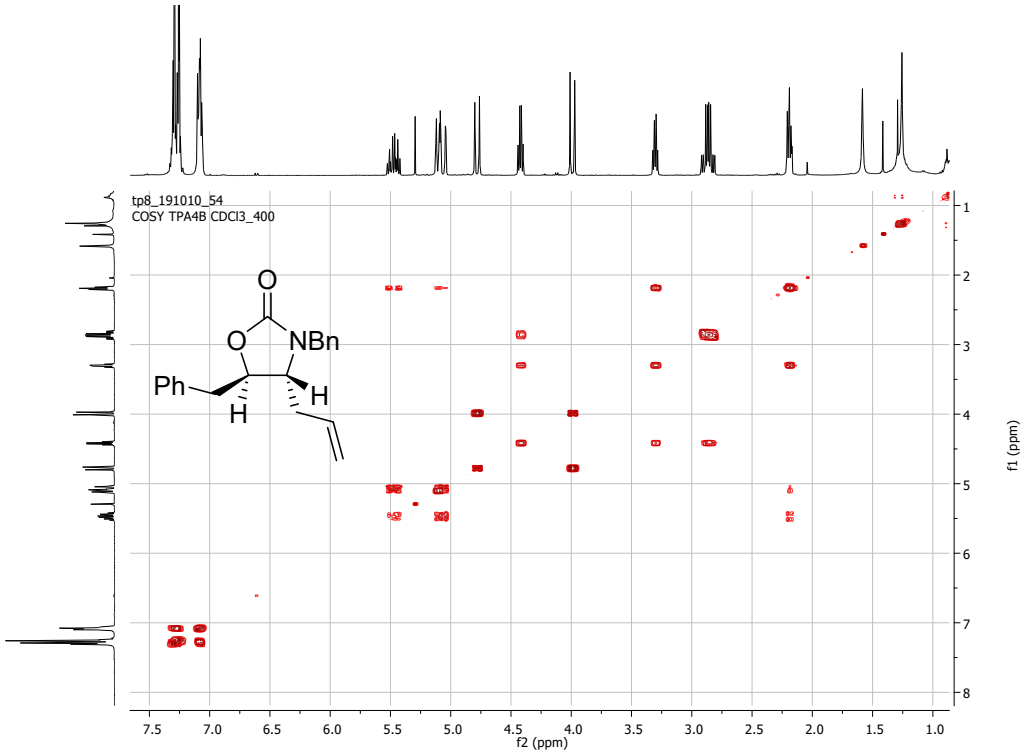


Figure 22. COSY spectrum of *rac*-**6**

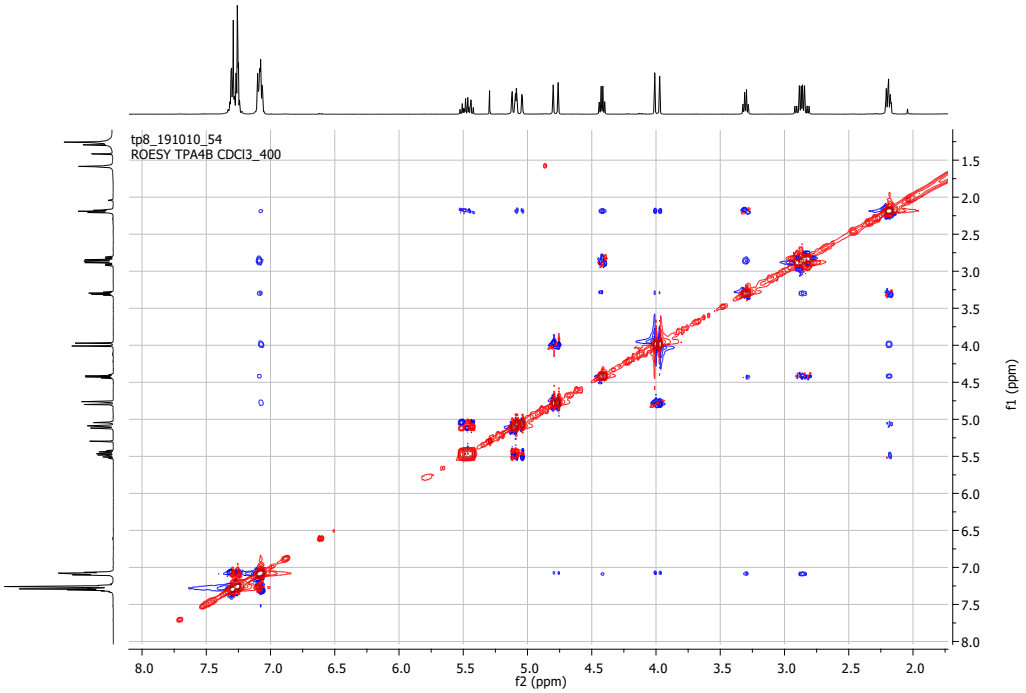


Figure 23. ROESY spectrum of *rac*-**6**

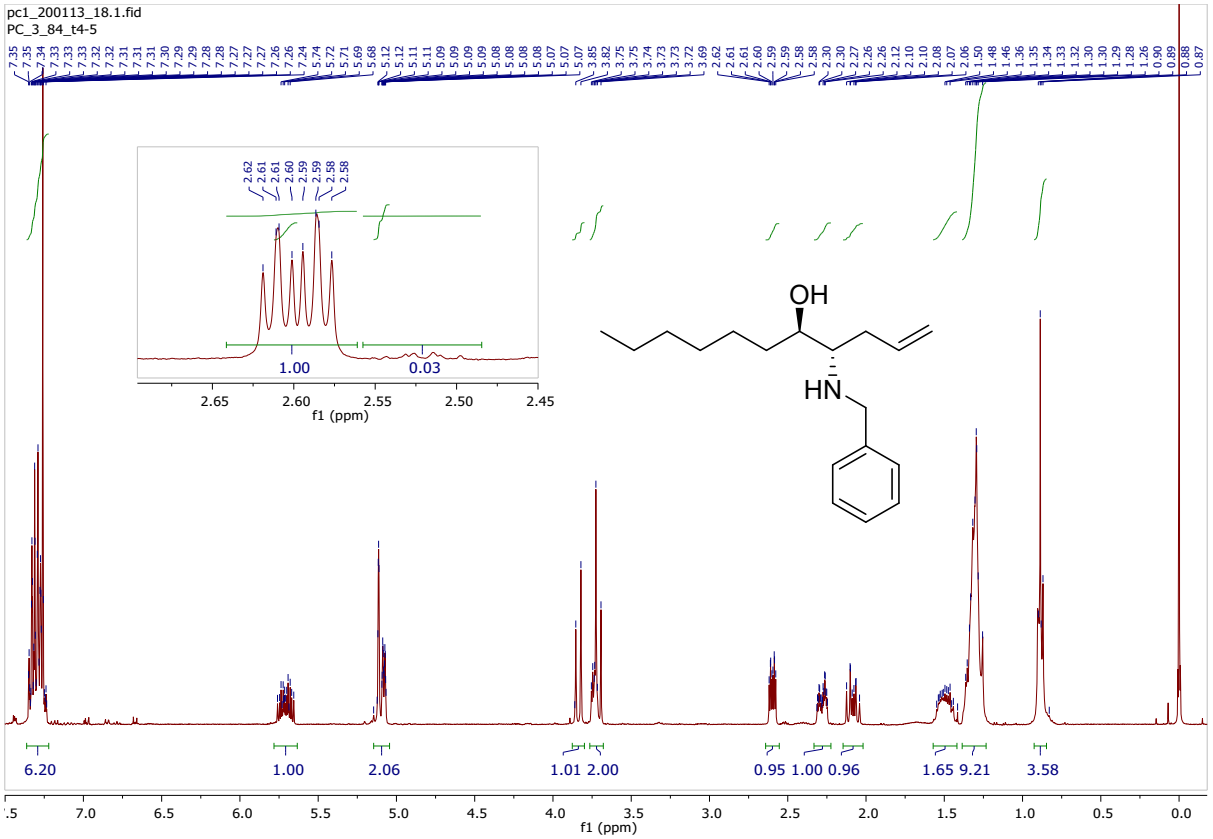


Figure 24: ^{1}H NMR spectrum of **7a** (400 MHz, $CDCl_3$, dr = 97:3).

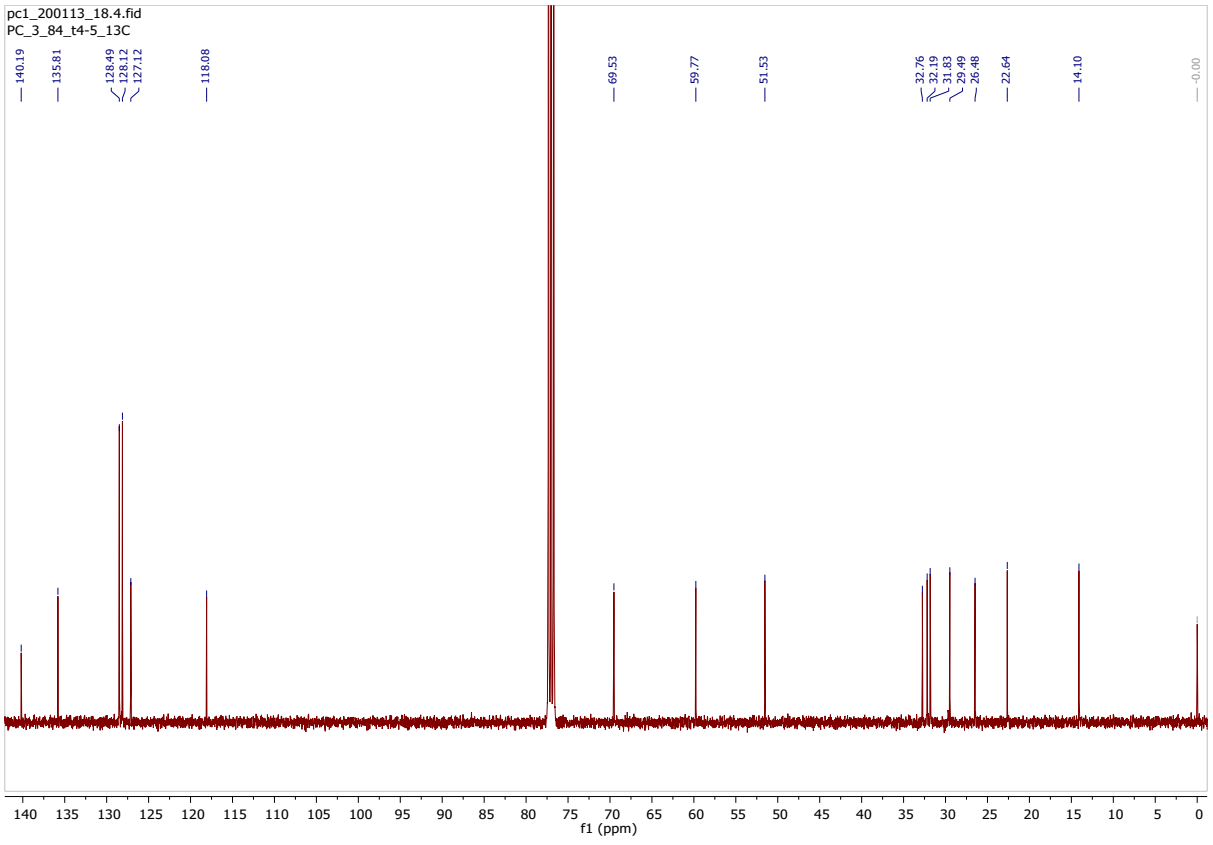
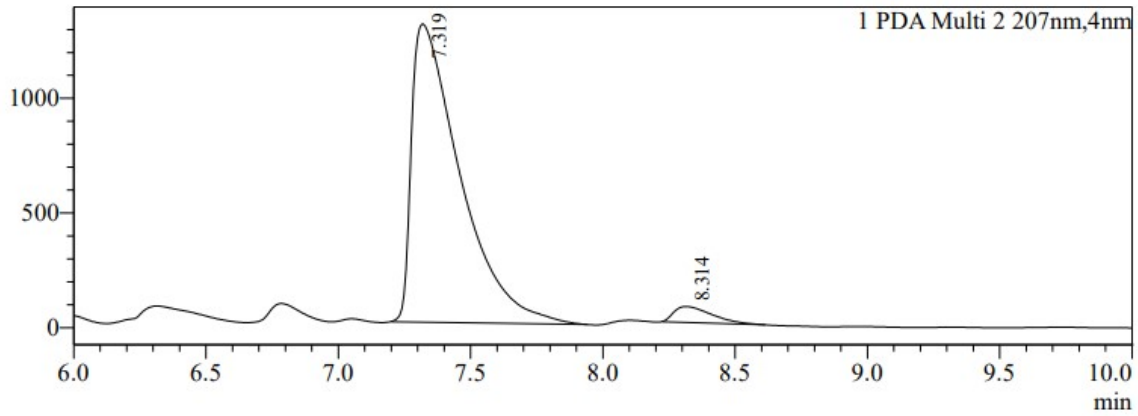


Figure 25: ^{13}C NMR spectrum of **7a** (101 MHz, $CDCl_3$).

Chromatogram
PC_4_62_2.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	7.319	96.017	
2	8.314	3.983	
Total		100.000	

Figure 26: Chiral HPLC trace of **7a**.

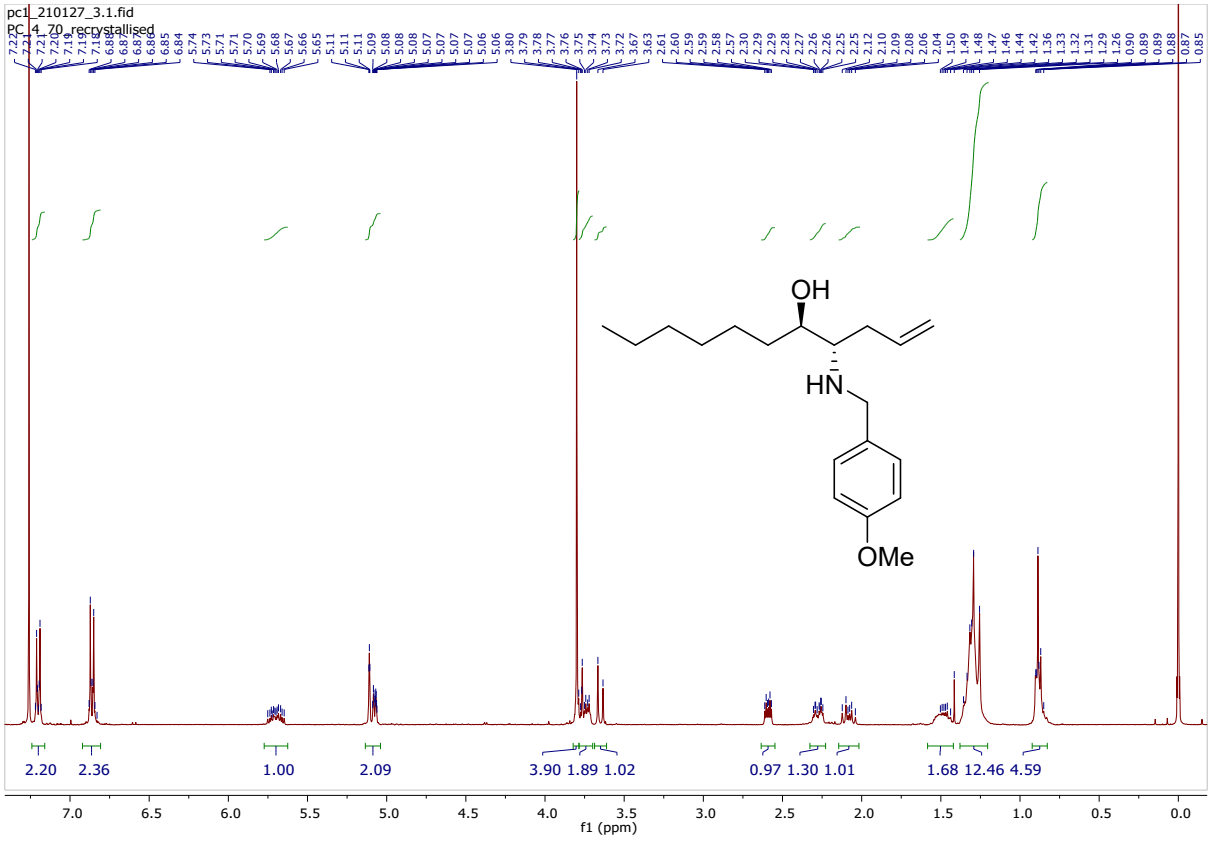


Figure 27: ^{1}H NMR spectrum of **7b** (400 MHz, $CDCl_3$).

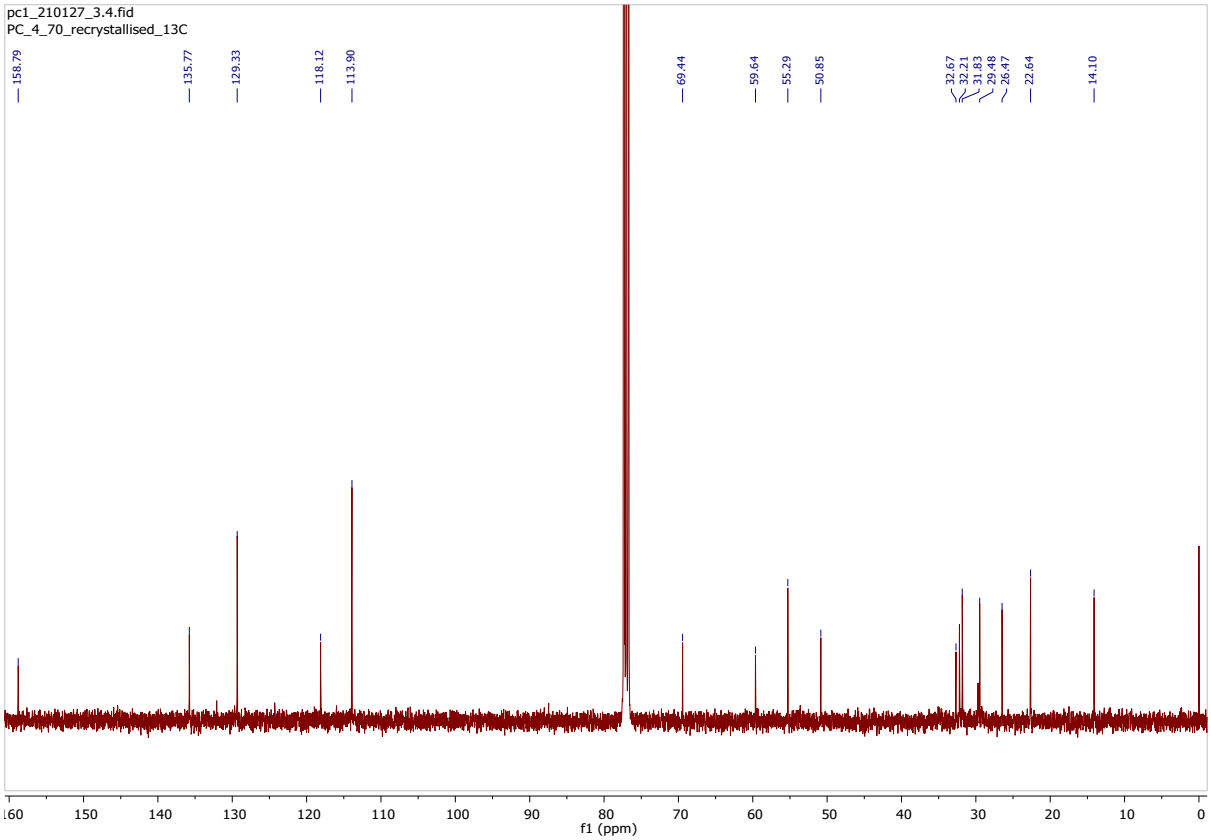
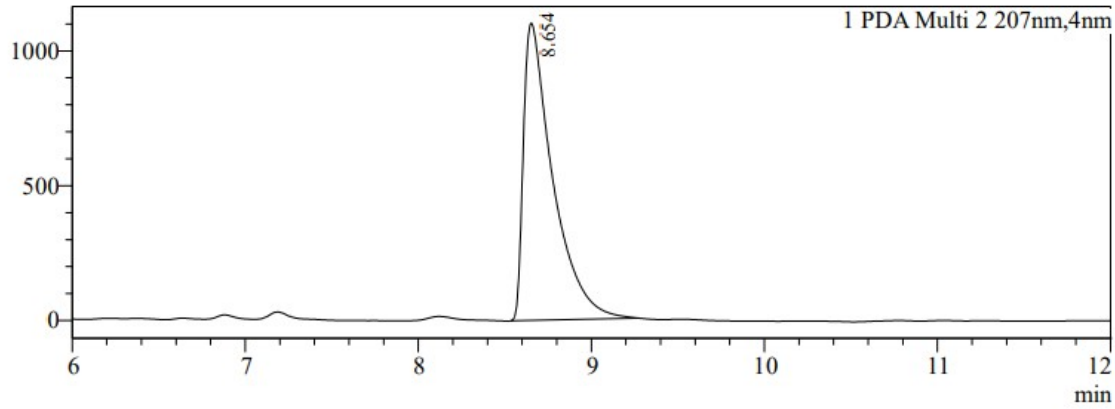


Figure 28: ^{13}C NMR spectrum of **7b** (101 MHz, $CDCl_3$).

Chromatogram
PC_4_70_4.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	8.654	100.000	
Total		100.000	

Figure 29: Chiral HPLC trace of **7b**.

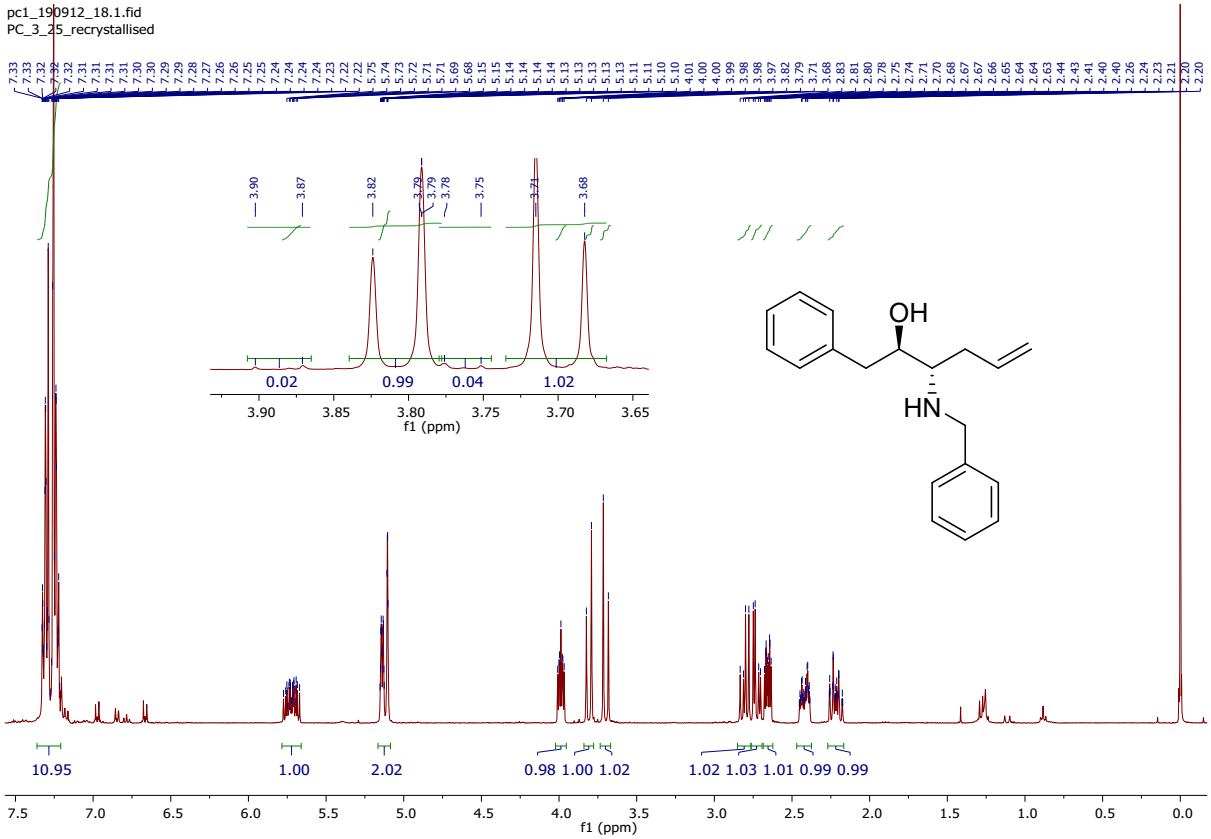


Figure 30: ^{1}H NMR spectrum of **7c** (400 MHz, $CDCl_3$, recrystallised dr = 97:3).

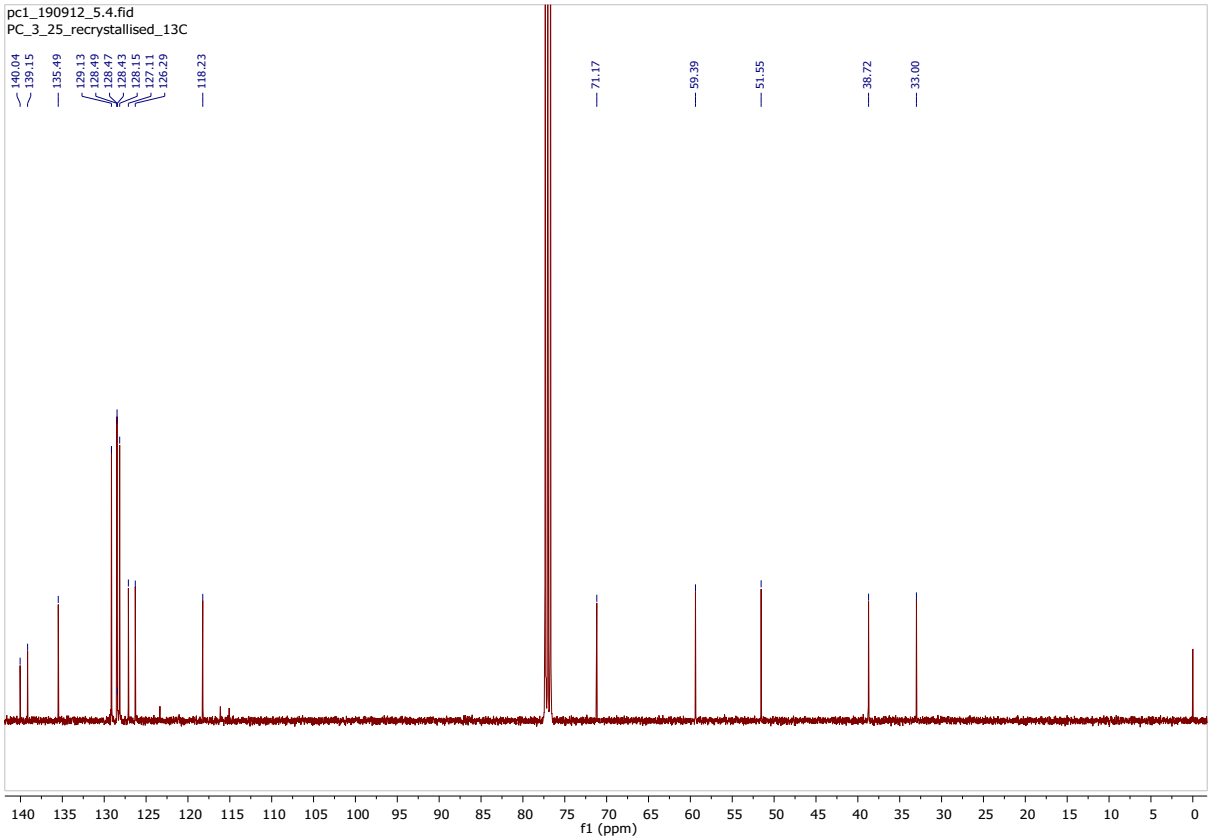
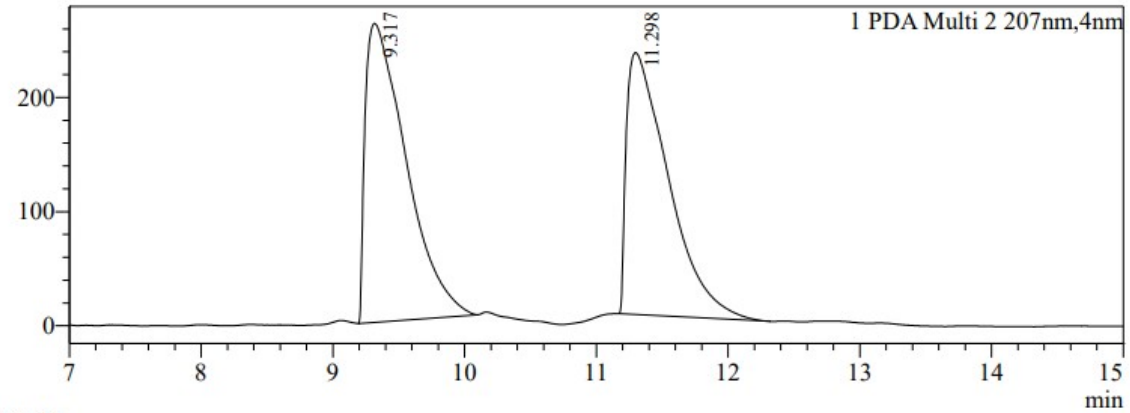


Figure 31: ^{13}C NMR spectrum of **7c** (101 MHz, $CDCl_3$).

Chromatogram
Racemic sample 46.lcd
mAU

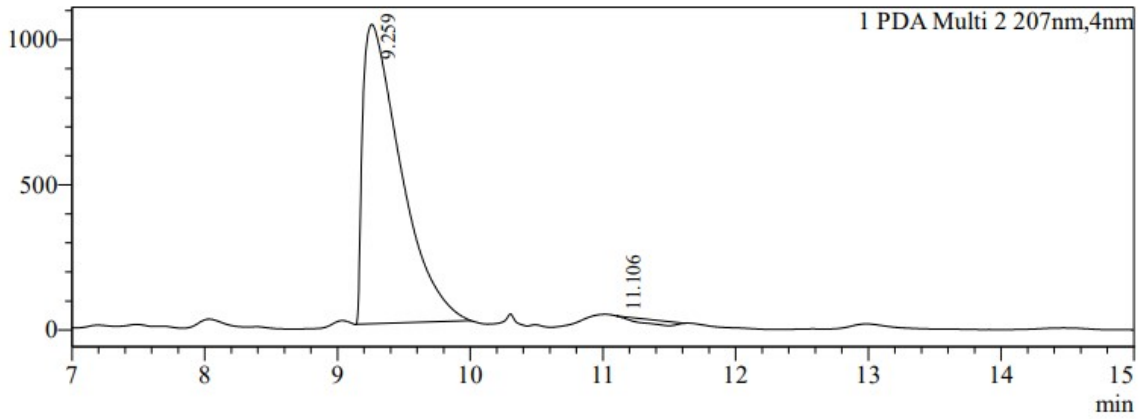


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	9.317	52.606	
2	11.298	47.394	
Total		100.000	

Figure 32: Chiral HPLC trace of nearly racemic **7c** (made by mixing D- and L-proline)

Chromatogram
PC_4_90_2.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	9.259	101.612	
2	11.106	-1.612	
Total		100.000	

Figure 33: Chiral HPLC trace of **7c**.

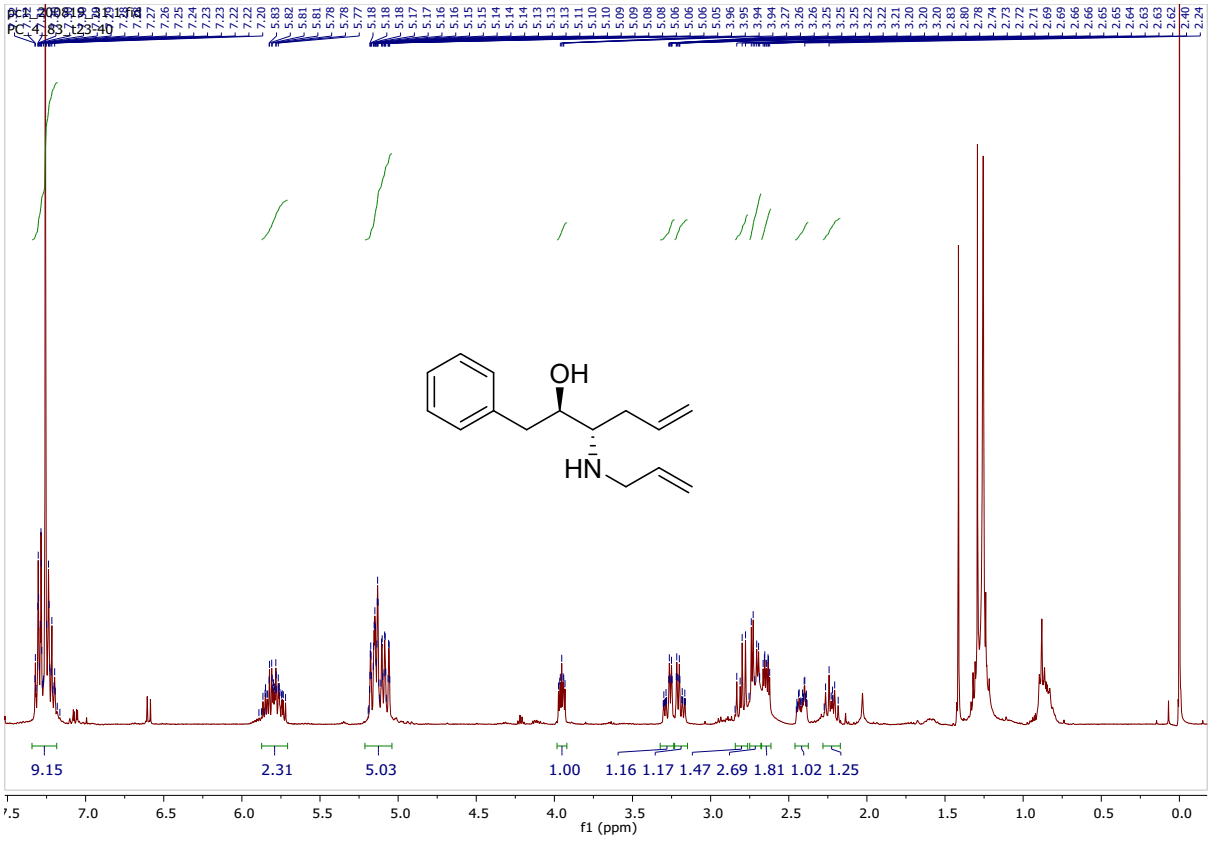


Figure 34: ^{1}H NMR spectrum of **7d** (400 MHz, $CDCl_3$, dr = 92:8 with impurities (grease)).

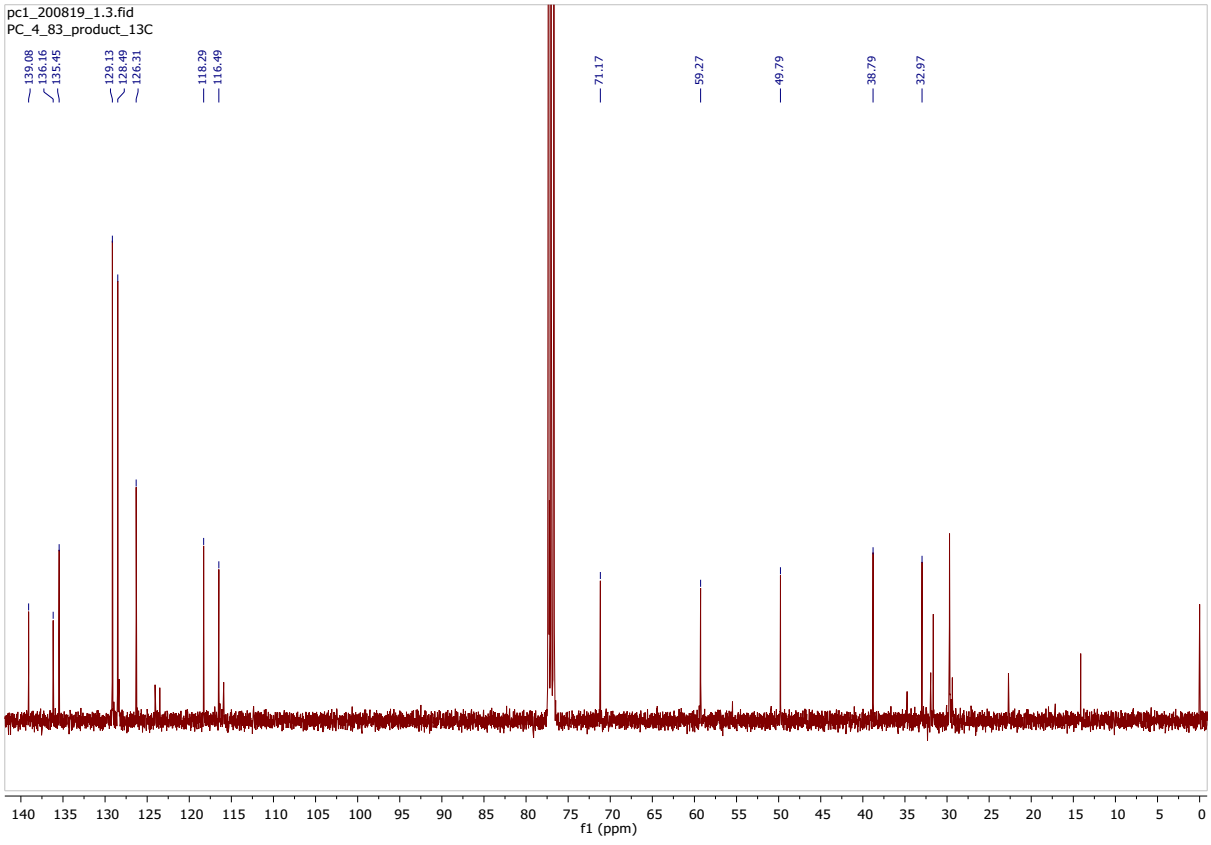


Figure 35: ^{13}C NMR spectrum of **7d** (101 MHz, $CDCl_3$).

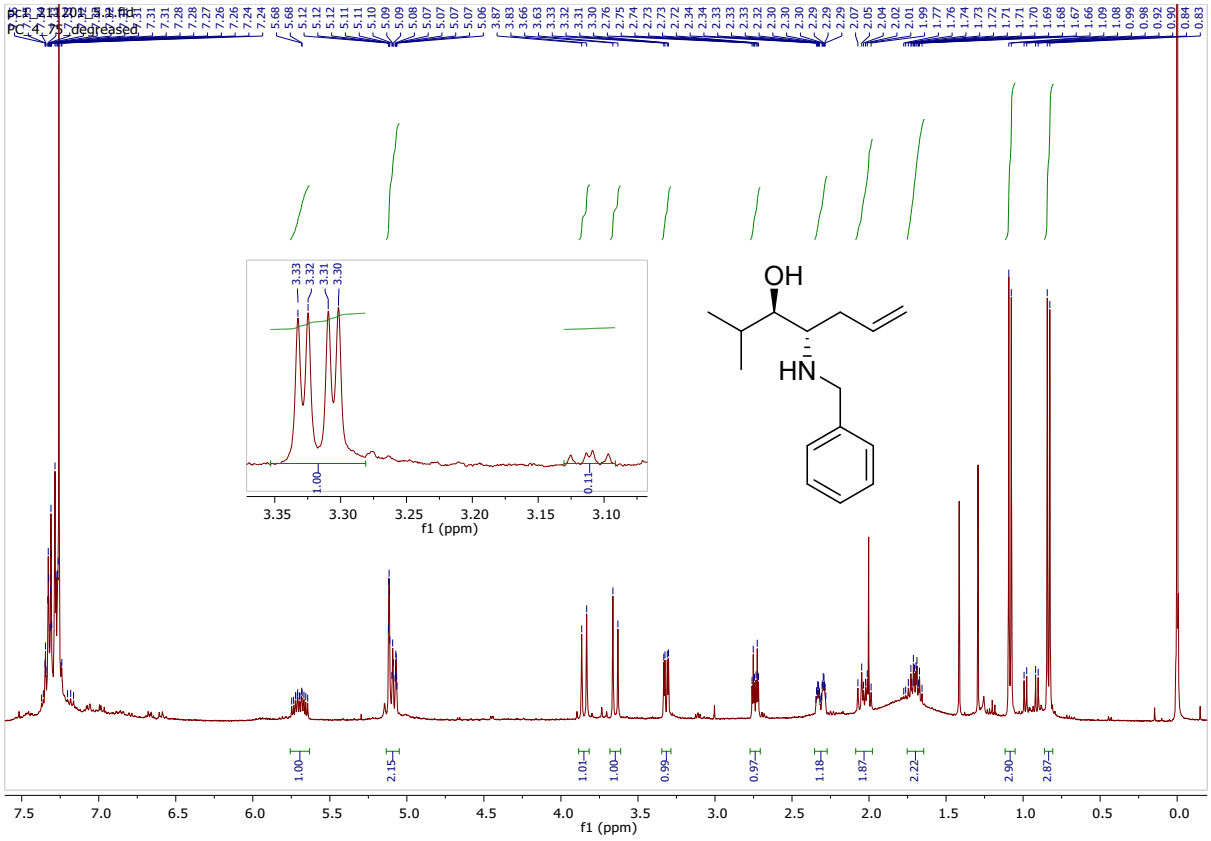


Figure 36: ^{1}H NMR spectrum of **7e** (400 MHz, $CDCl_3$, dr = 90:10).

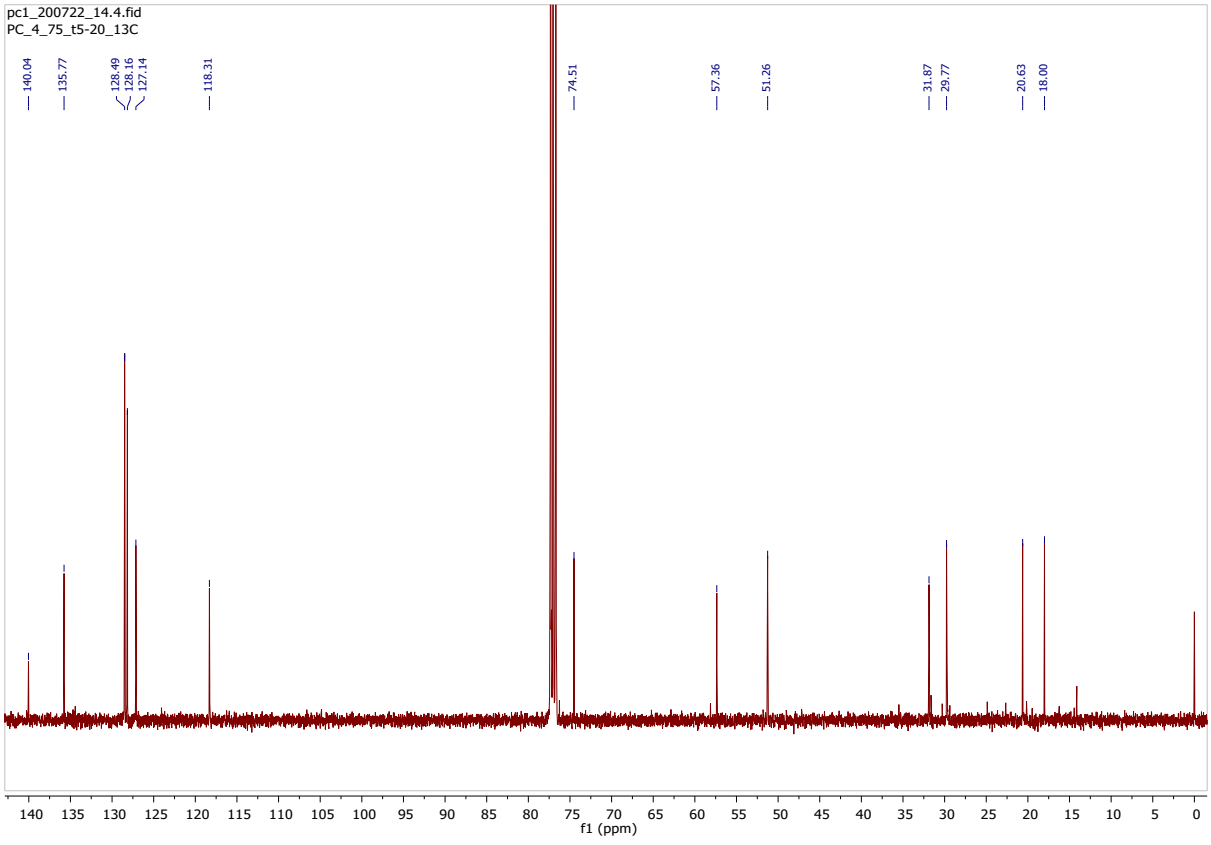
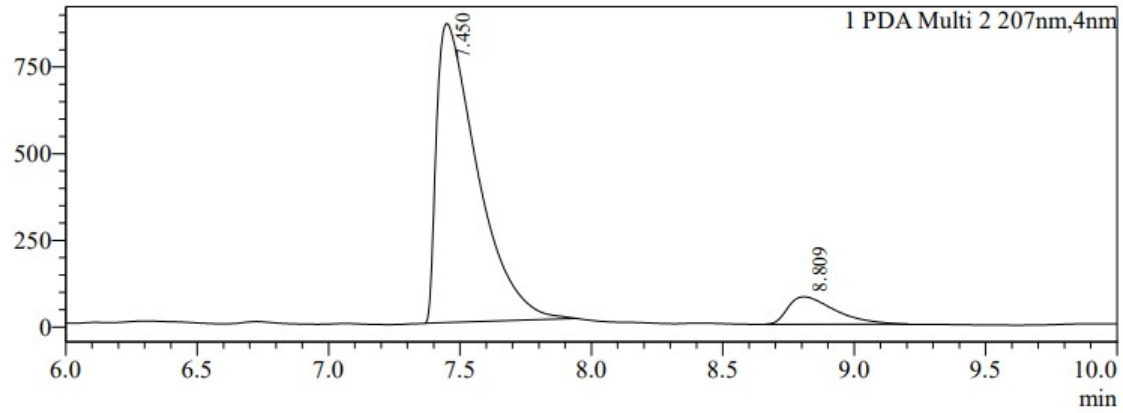


Figure 37: ^{13}C NMR spectrum of **7e** (101 MHz, $CDCl_3$).

Chromatogram
PC_4_75_2.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	7.450	90.474	
2	8.809	9.526	
Total		100.000	

Figure 38: Chiral HPLC trace of **7e**.

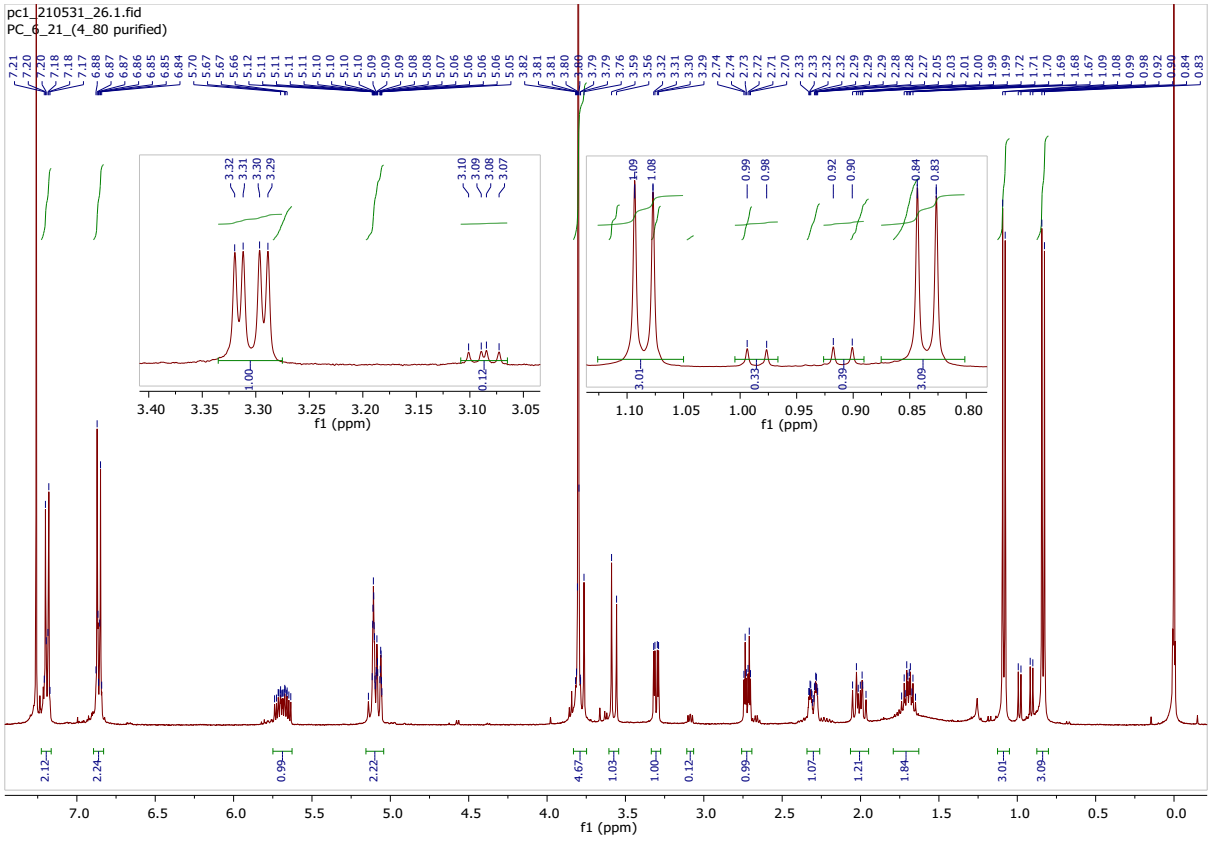


Figure 39: ^{1}H NMR spectrum of **7f** (400 MHz, $CDCl_3$, dr = 88:12).

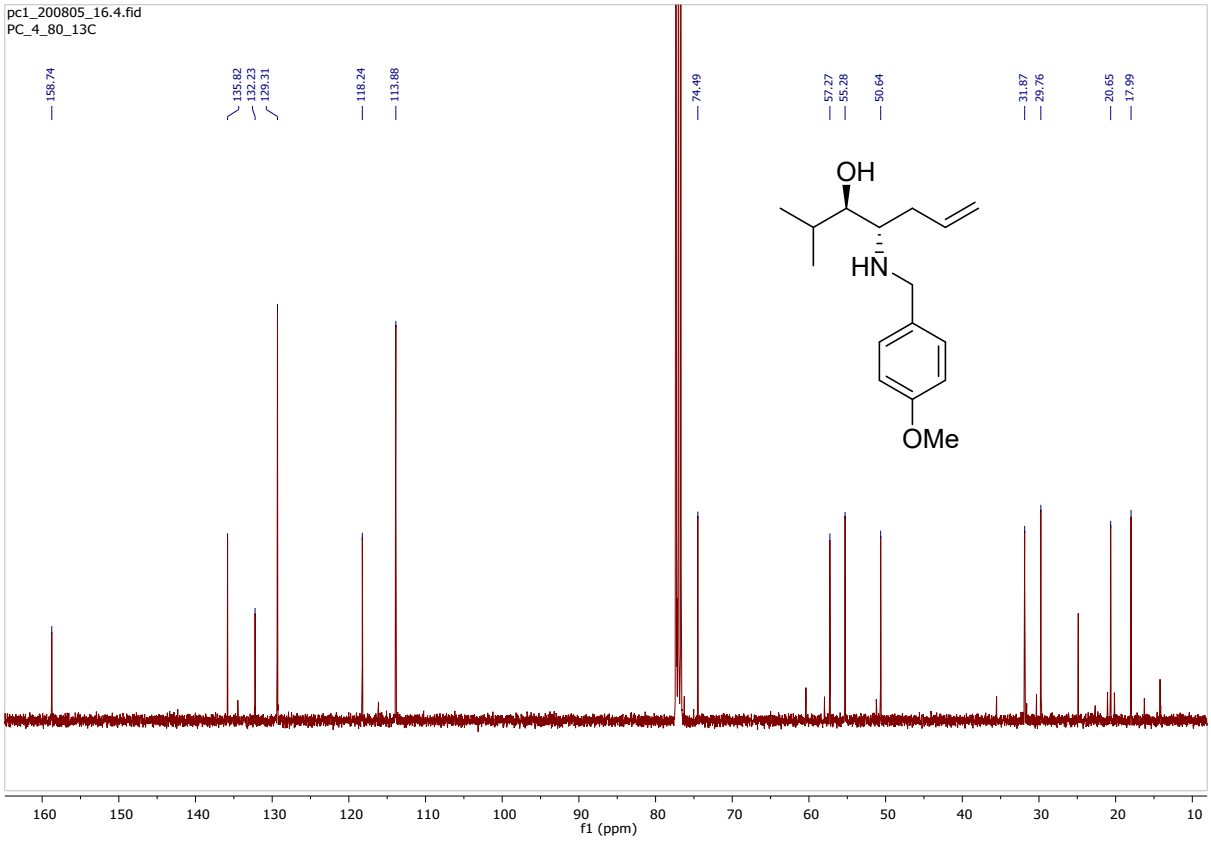
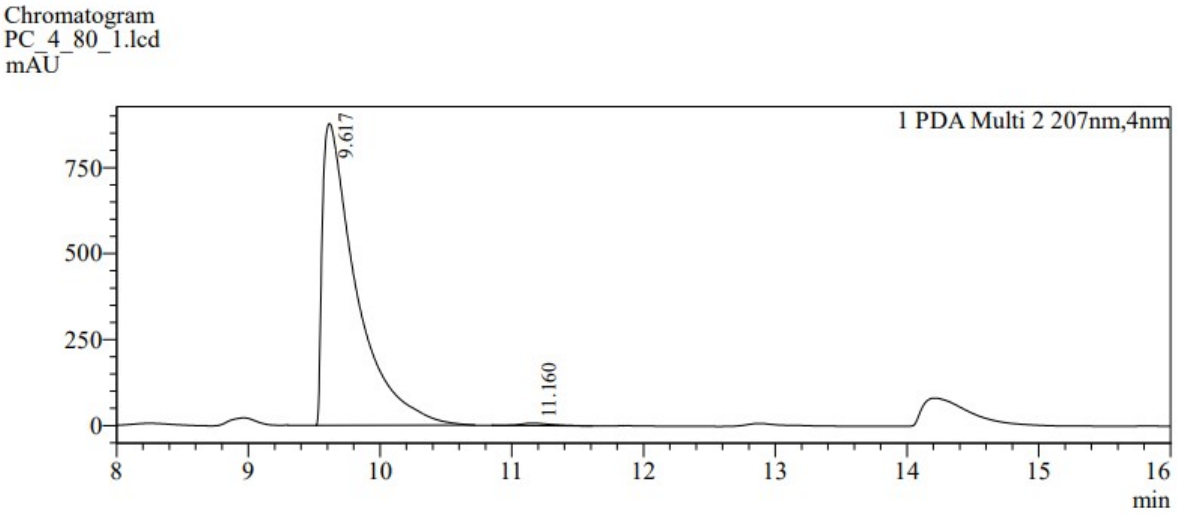


Figure 40: ^{13}C NMR spectrum of **7f** (101 MHz, $CDCl_3$).



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	9.617	99.204	
2	11.160	0.796	
Total		100.000	

Figure 41: Chiral HPLC trace of **7f**. The peak at R_t ~14.2 min is the *syn*-diastereomer.

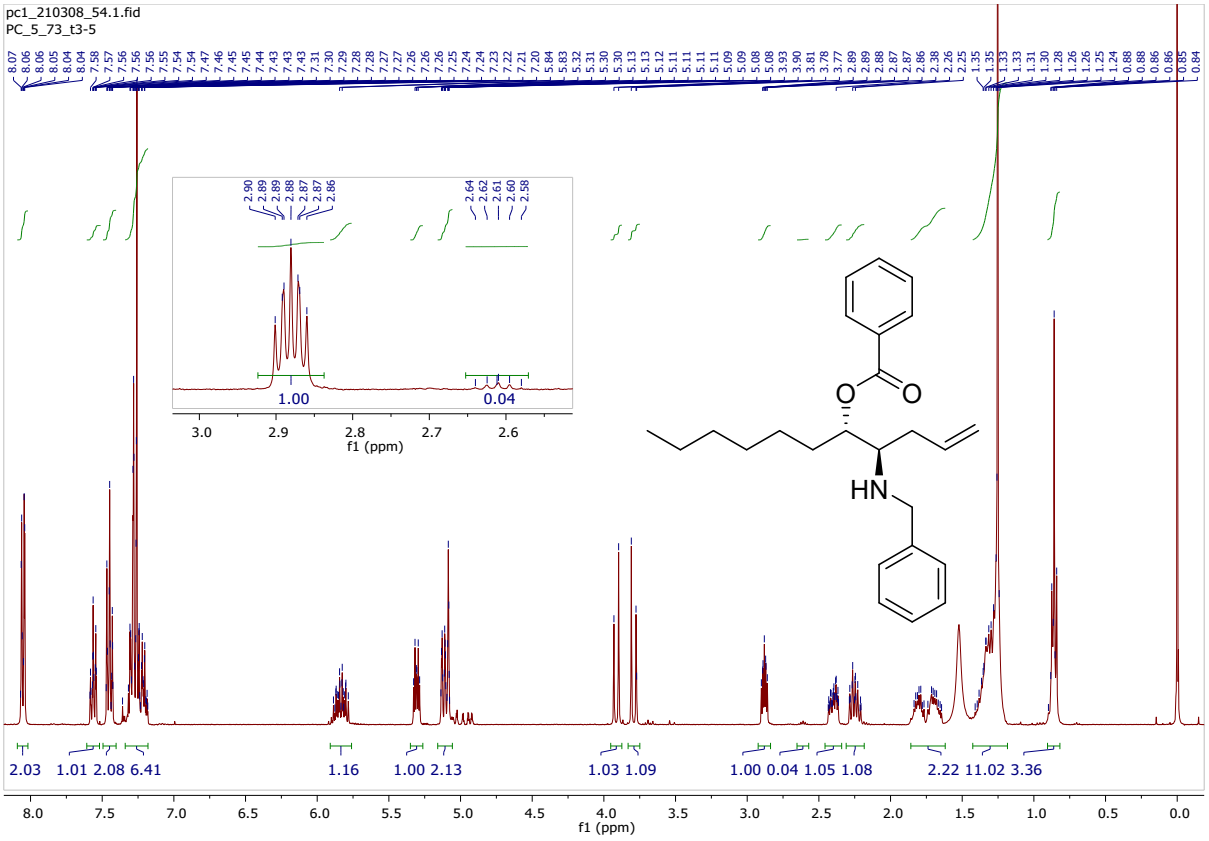


Figure 42: ^{1}H NMR spectrum of **8a** (400 MHz, $CDCl_3$, dr = 97:3).

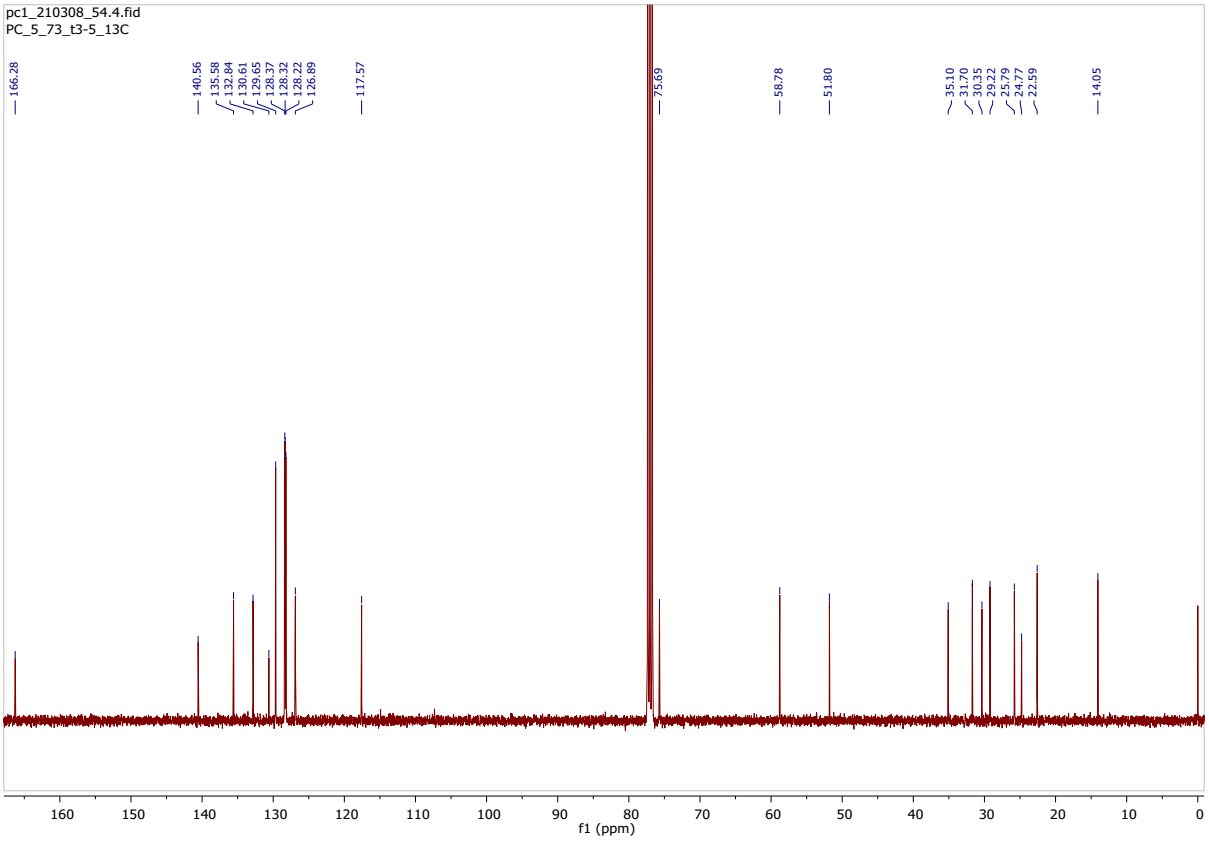


Figure 43: ^{13}C NMR spectrum of **8a** (101 MHz, $CDCl_3$).

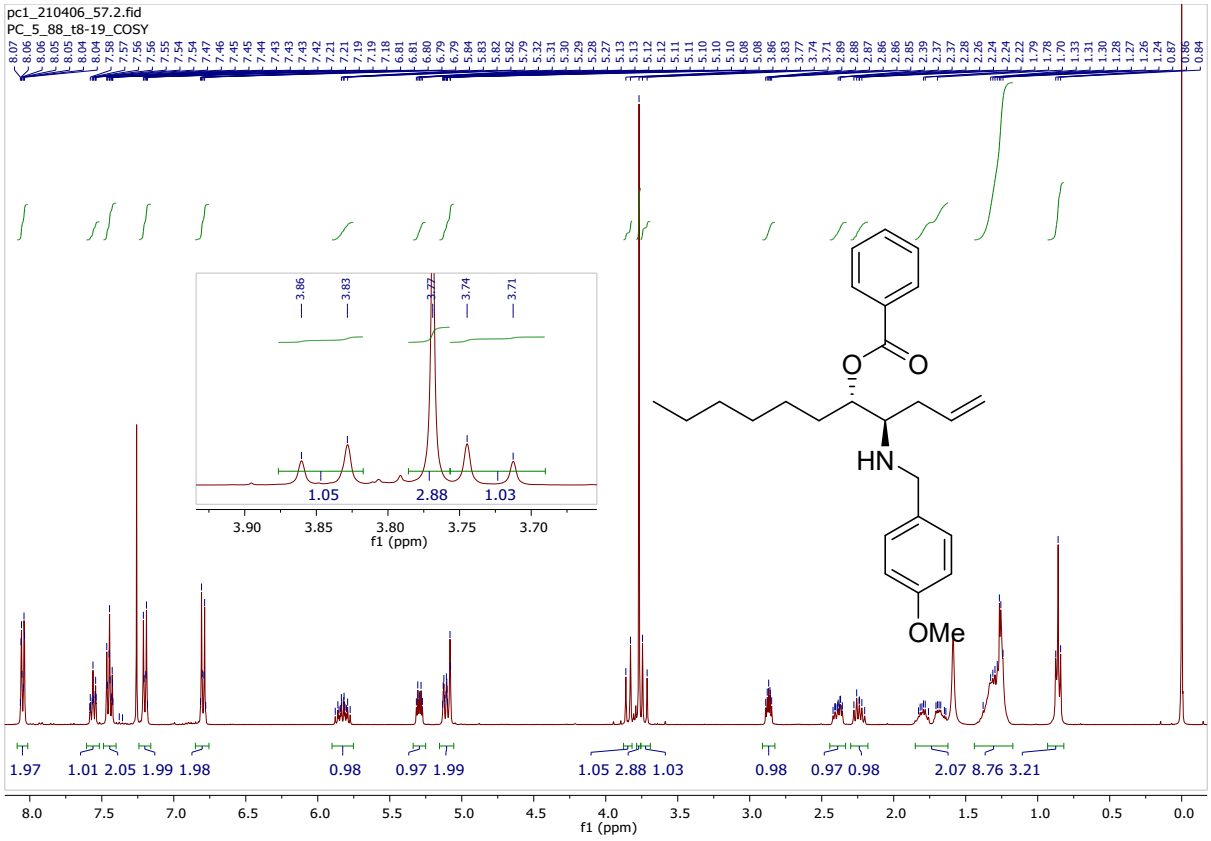


Figure 44: ^{1}H NMR spectrum of **8b** (400 MHz, $CDCl_3$, dr = 99:1).

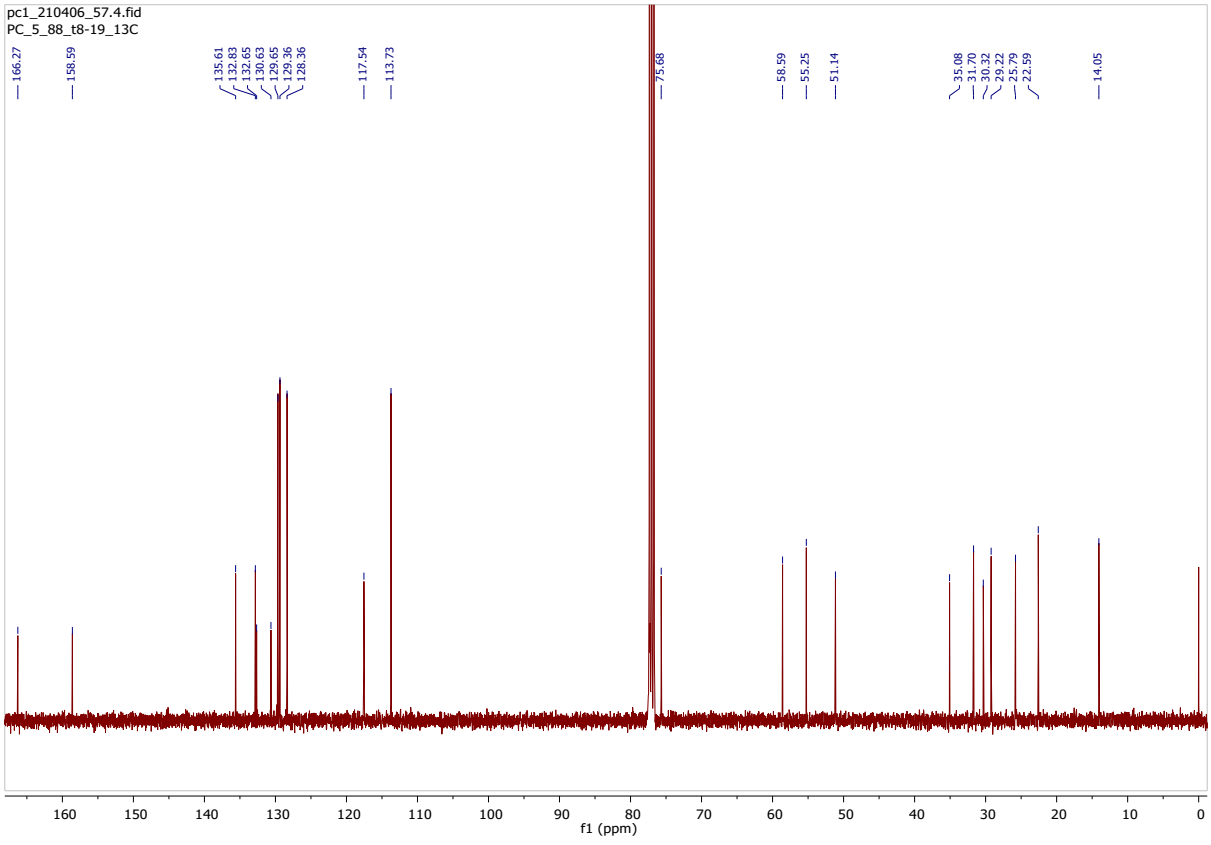


Figure 45: ^{13}C NMR spectrum of **8b** (101 MHz, $CDCl_3$).

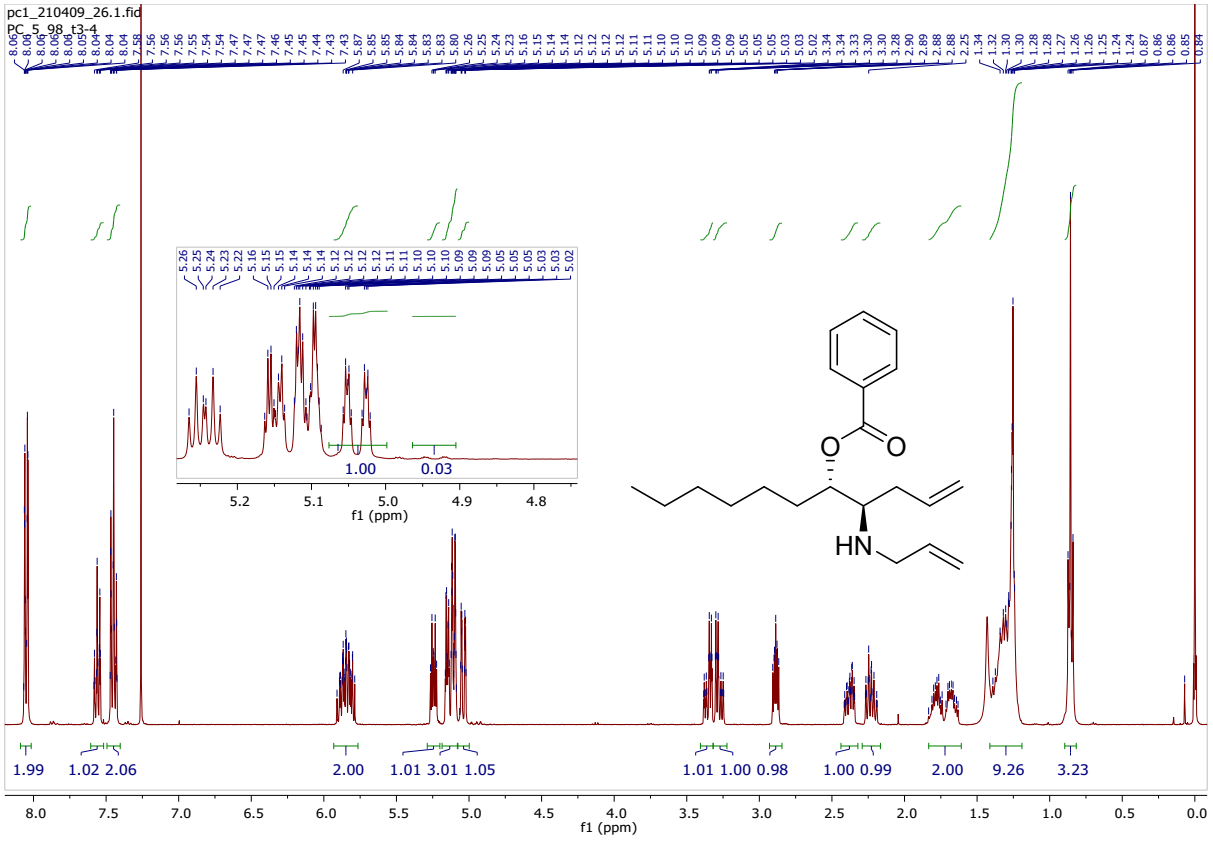


Figure 46: ^{1}H NMR spectrum of **8c** (400 MHz, $CDCl_3$, dr = 97:3).

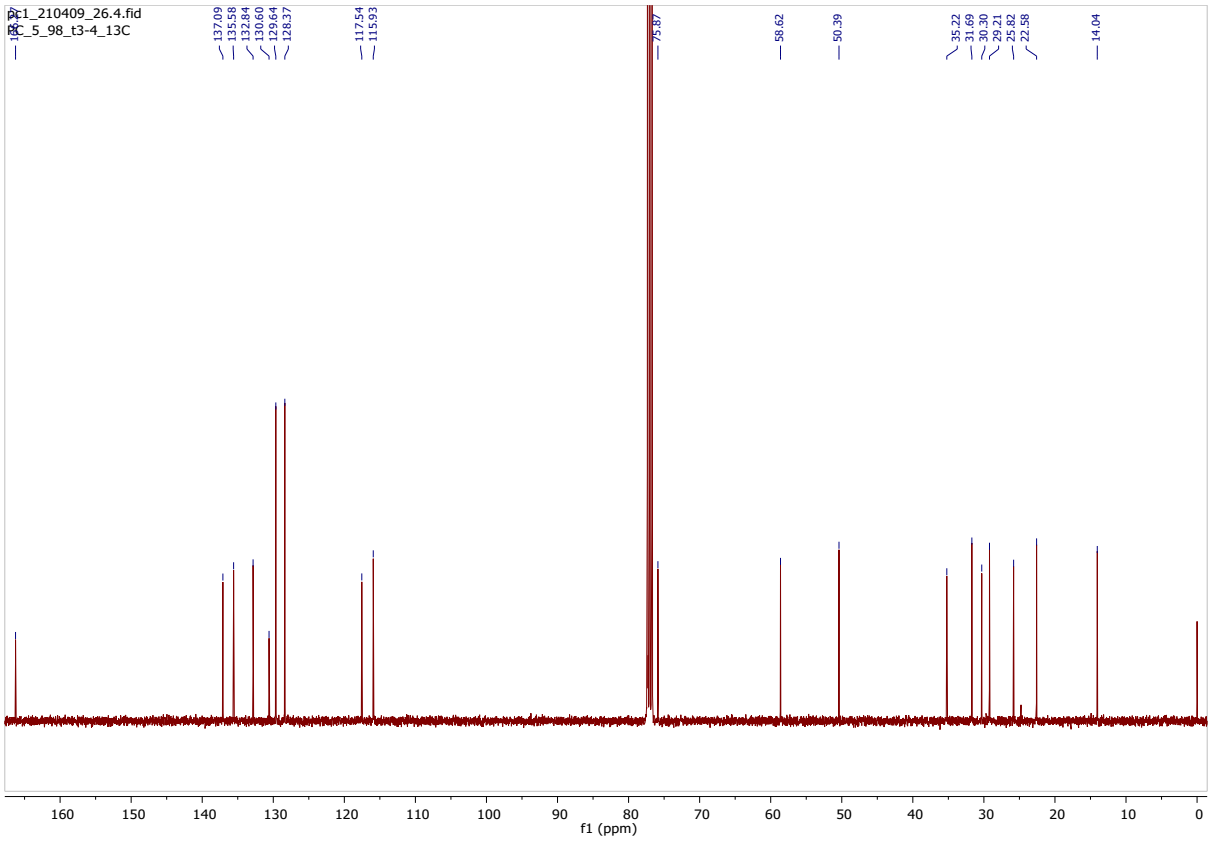


Figure 47: ^{13}C NMR spectrum of **8c** (101 MHz, $CDCl_3$).

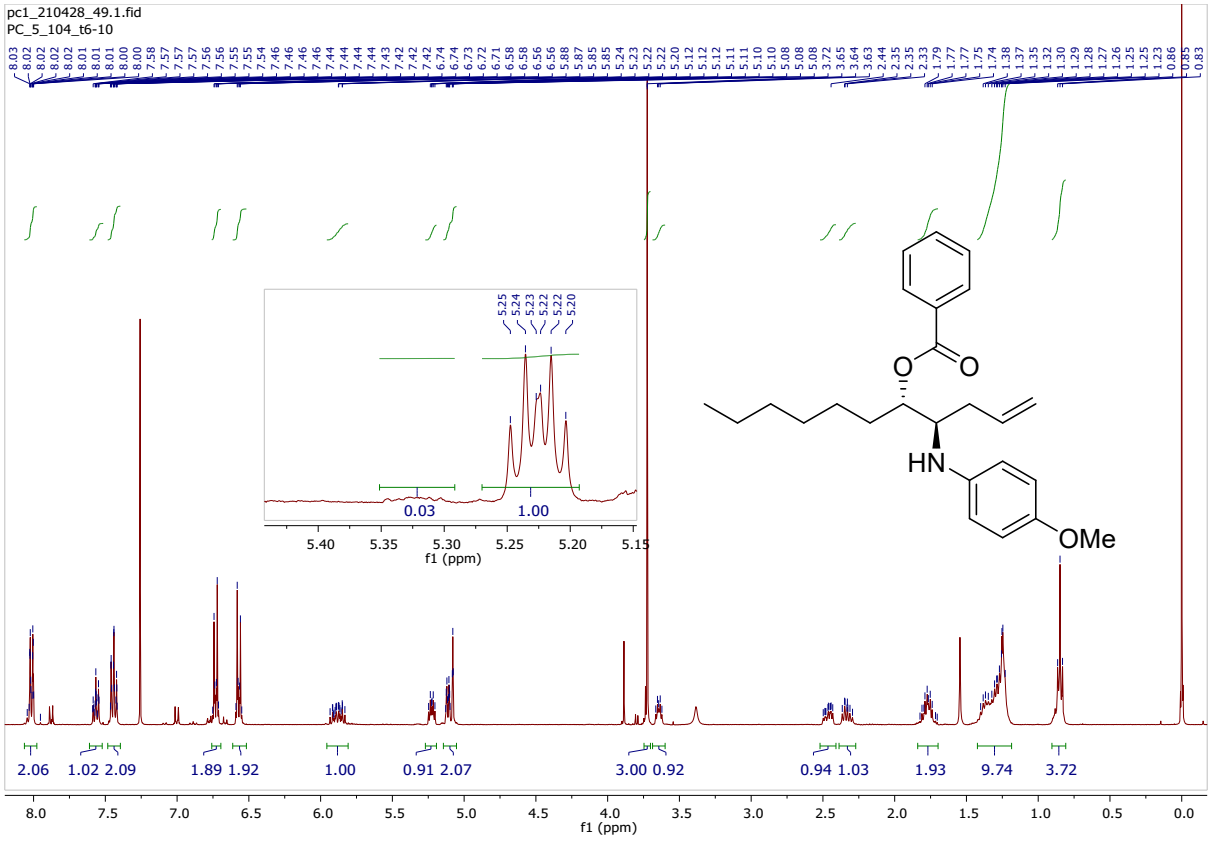


Figure 48: ^{1}H NMR spectrum of **8d** (400 MHz, $CDCl_3$, dr = 97:3).

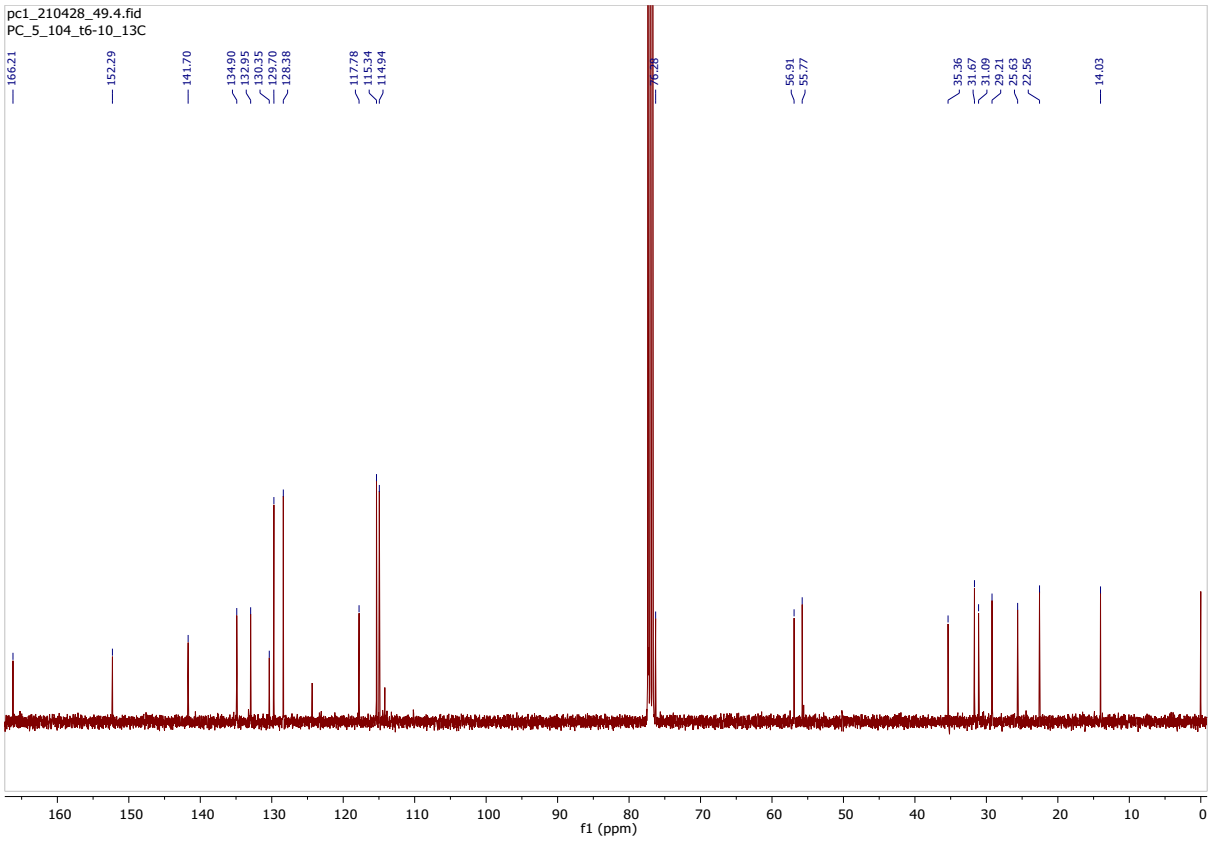


Figure 49: ^{13}C NMR spectrum of **8d** (101 MHz, $CDCl_3$).

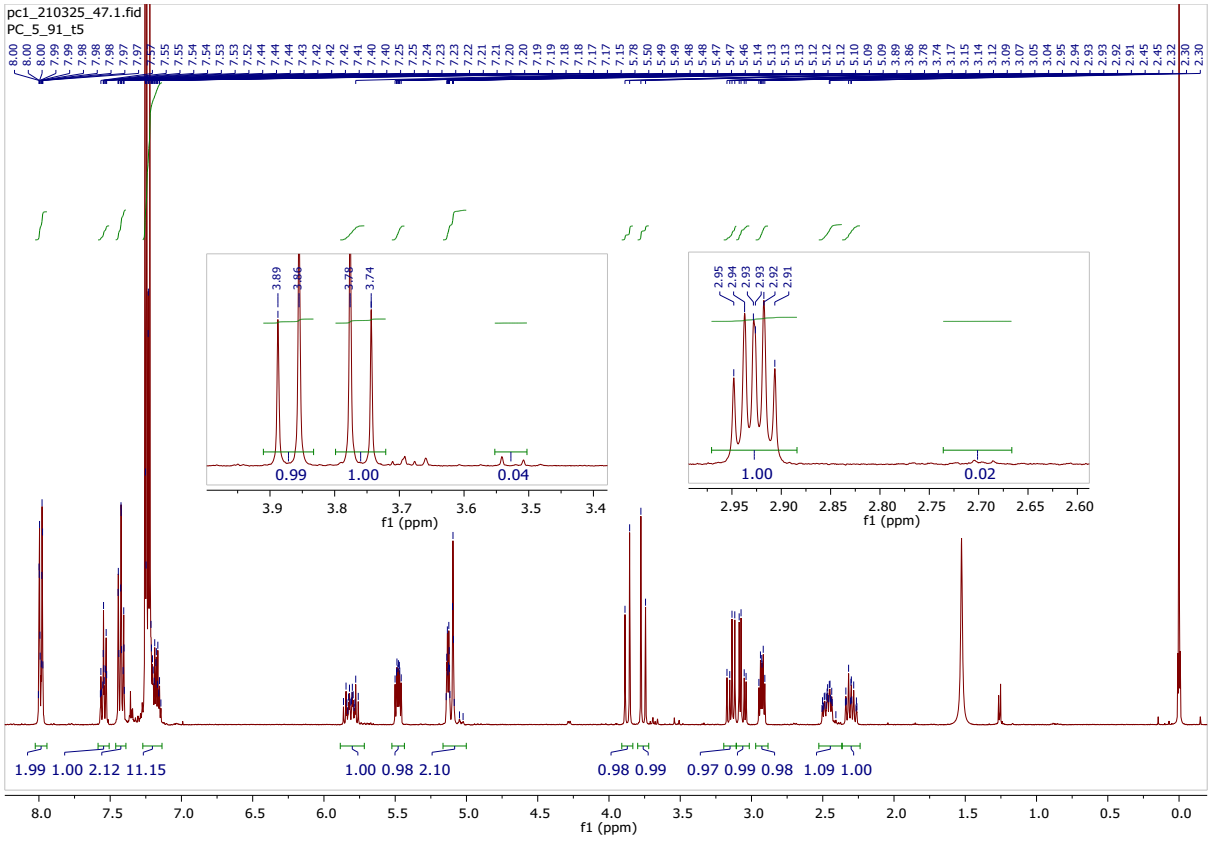


Figure 50: ^{1}H NMR spectrum of **8e** (400 MHz, $CDCl_3$, dr = 97:3).

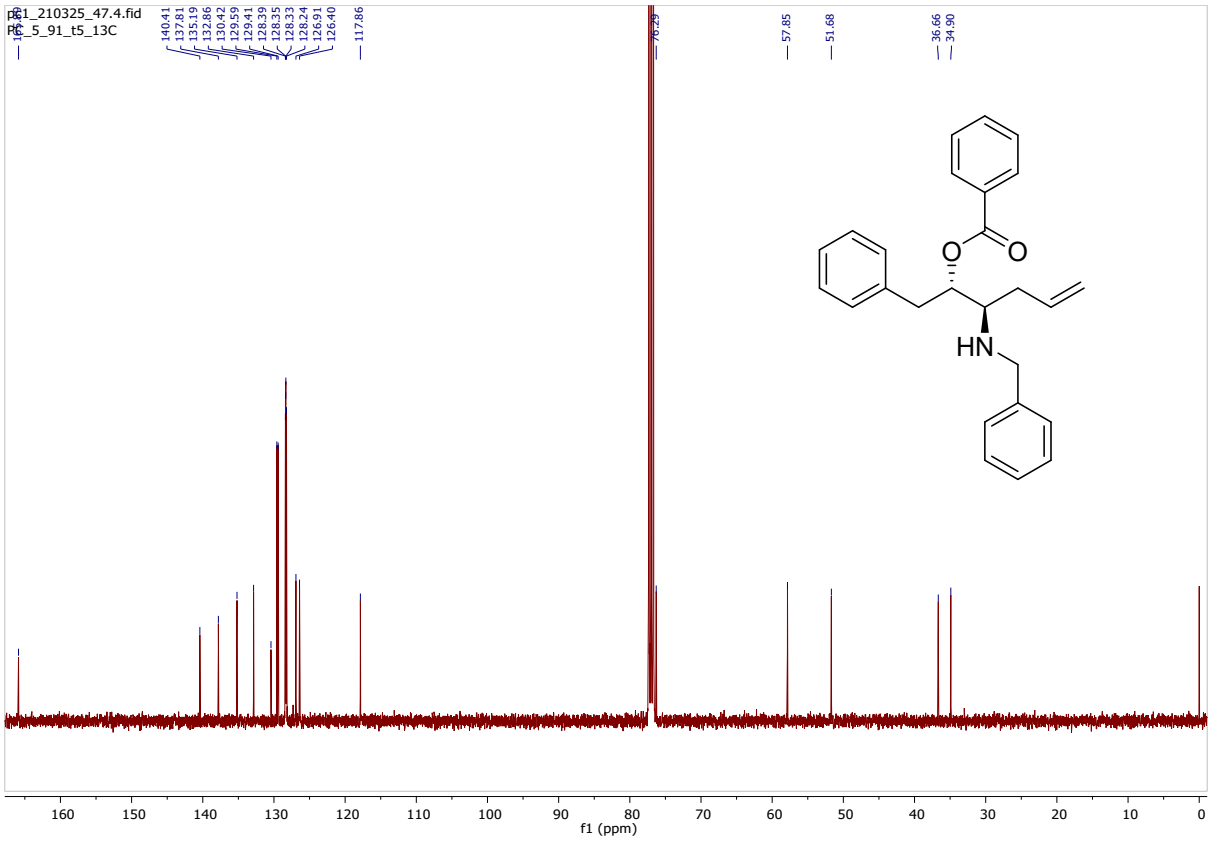


Figure 51: ^{13}C NMR spectrum of **8e** (101 MHz, $CDCl_3$).

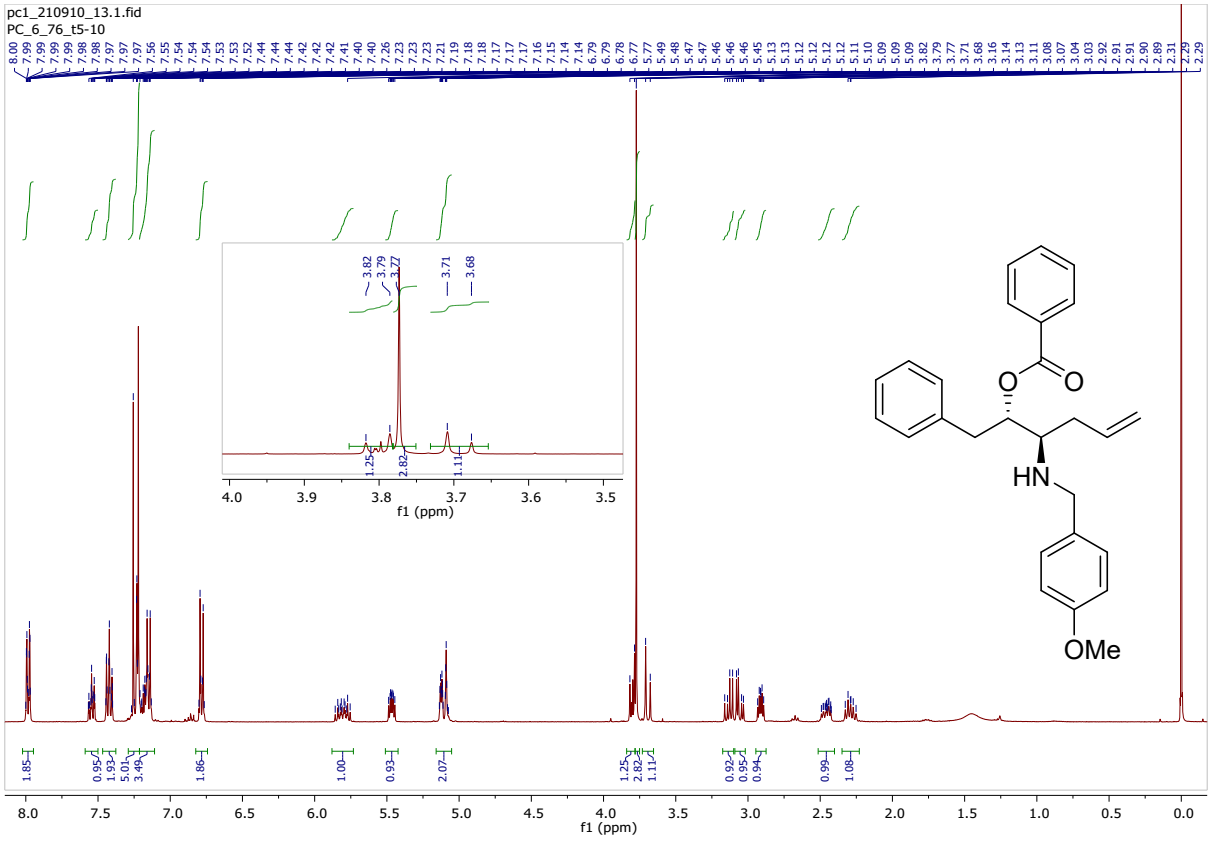


Figure 52: ^{1}H NMR spectrum of **8f** (400 MHz, $CDCl_3$, dr = 99:1).

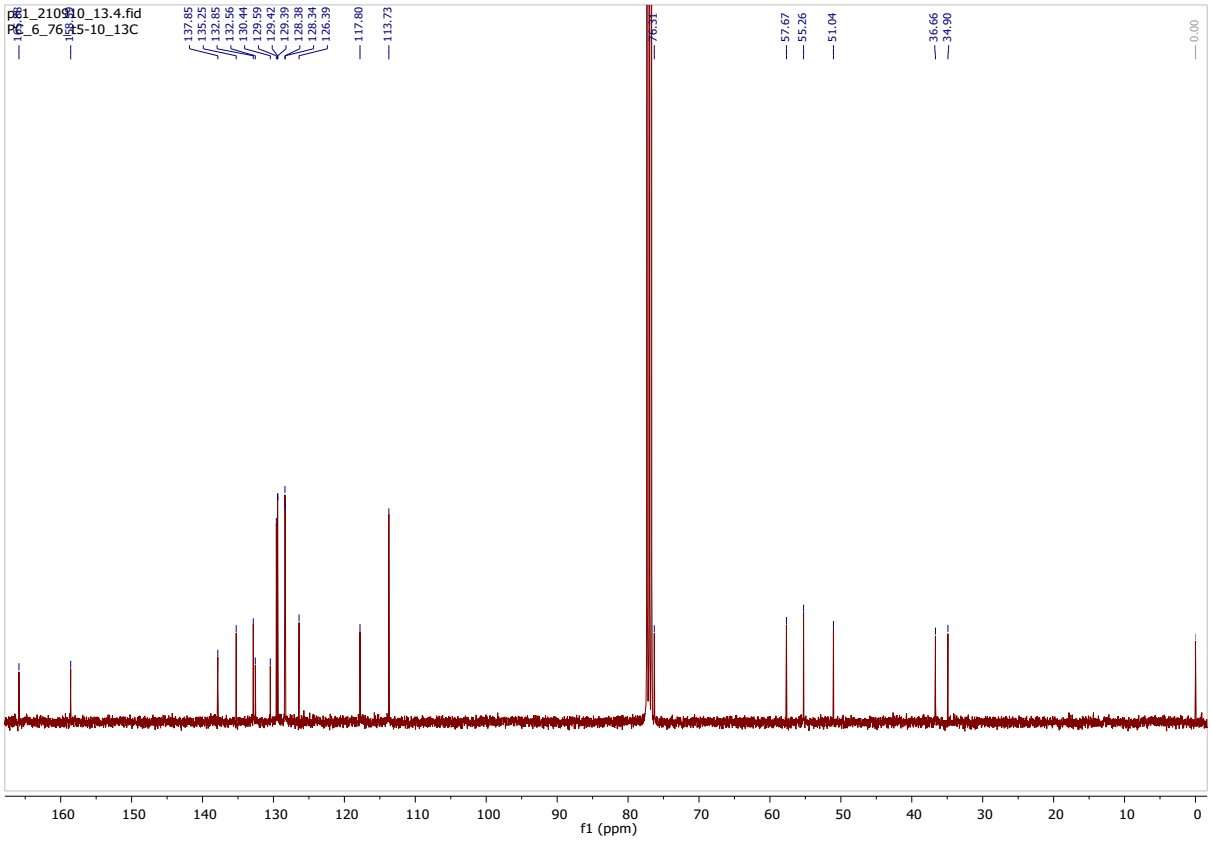


Figure 53: ^{13}C NMR spectrum of **8f** (101 MHz, $CDCl_3$).

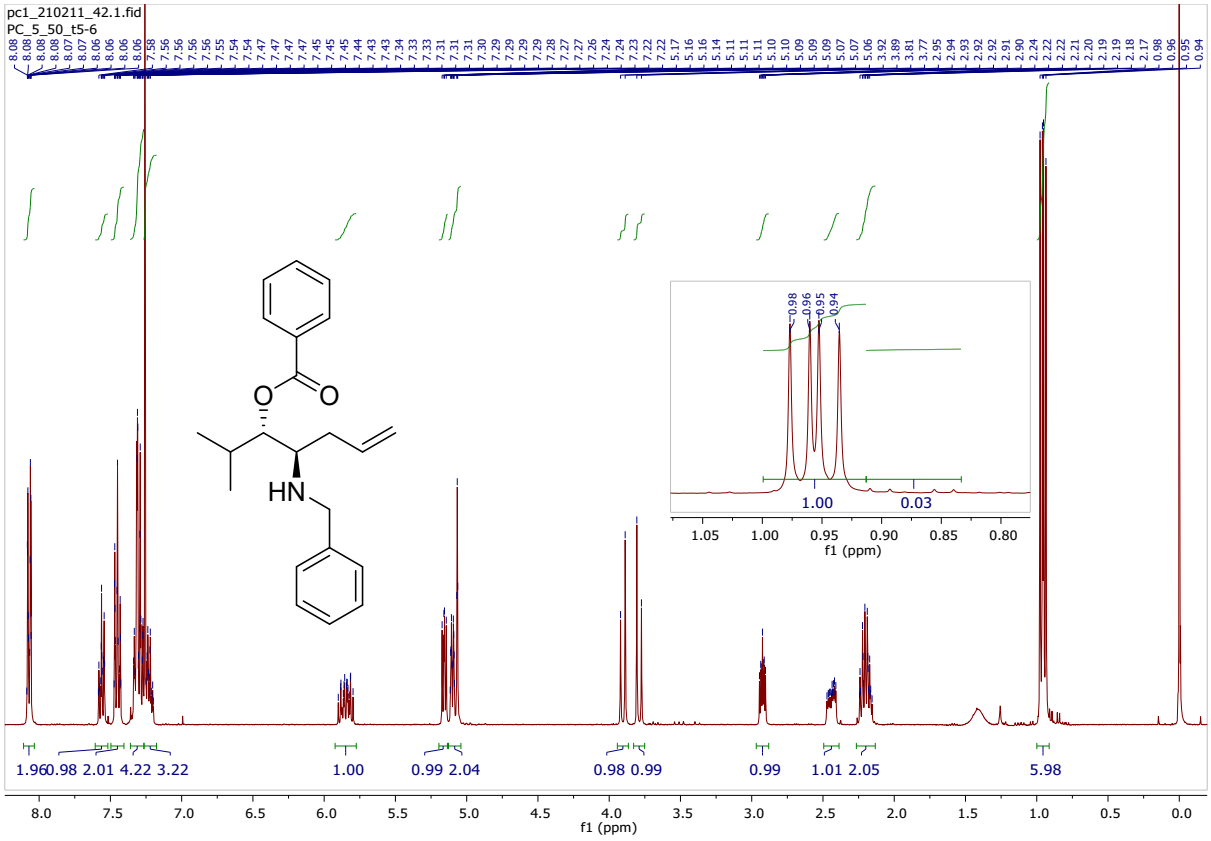


Figure 54: ^{1}H NMR spectrum of **8g** (400 MHz, $CDCl_3$, dr = 97:3).

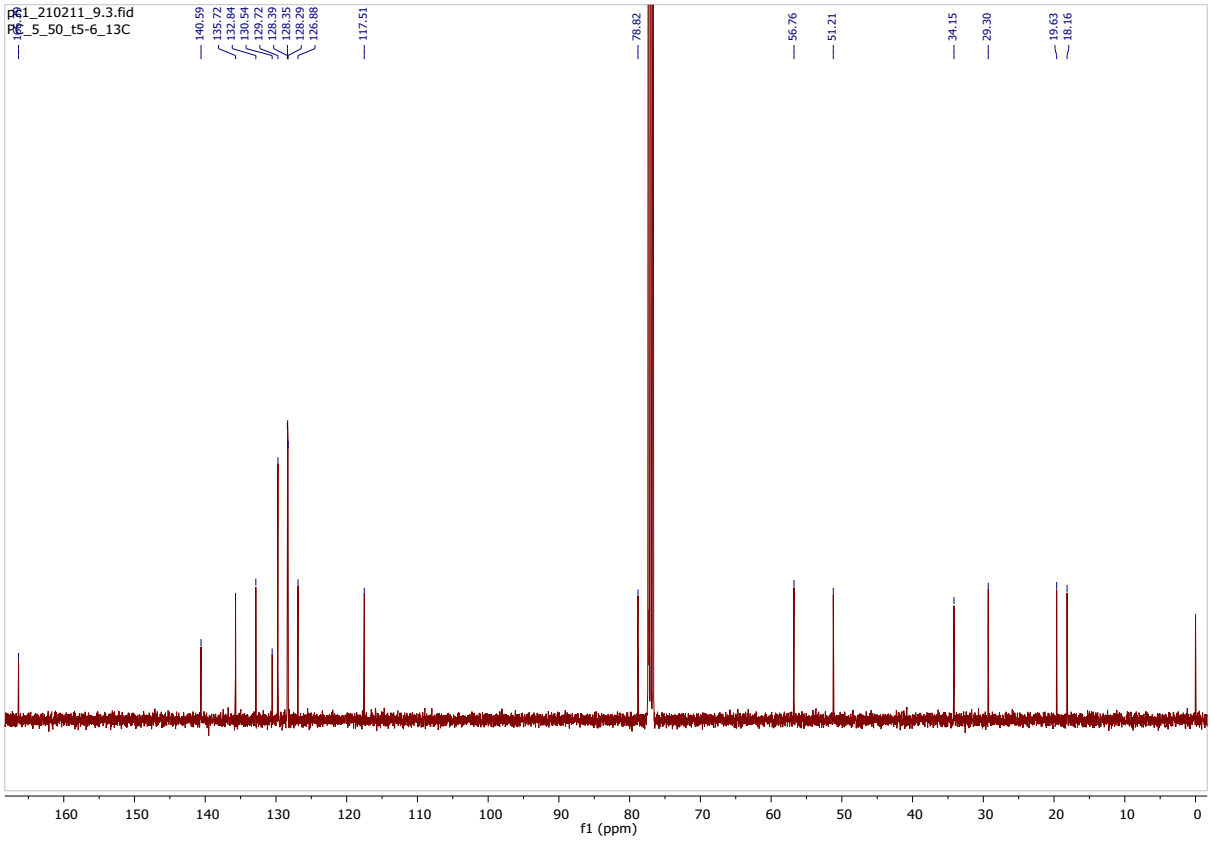


Figure 55: ^{13}C NMR spectrum of **8g** (400 MHz, $CDCl_3$).

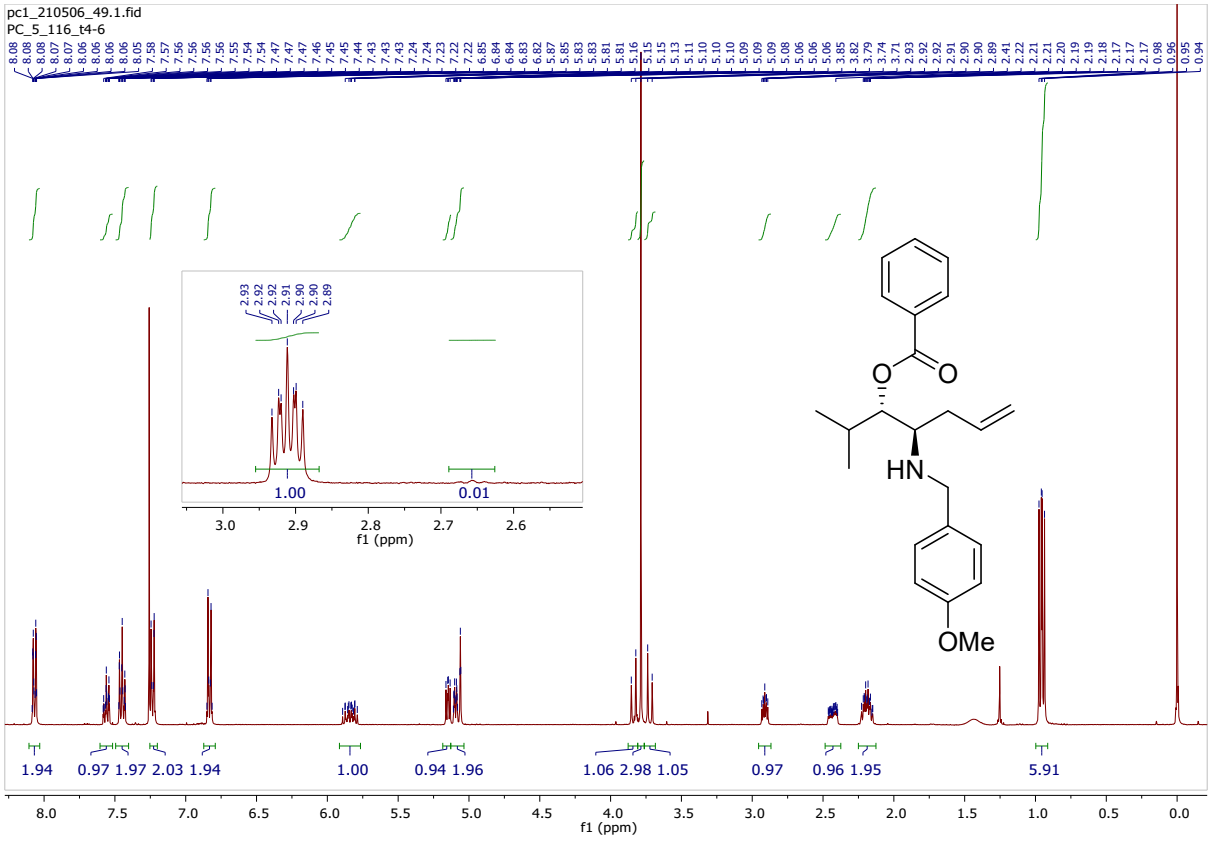


Figure 56: ^{1}H NMR spectrum of **8h** (400 MHz, $CDCl_3$, dr = 99:1).

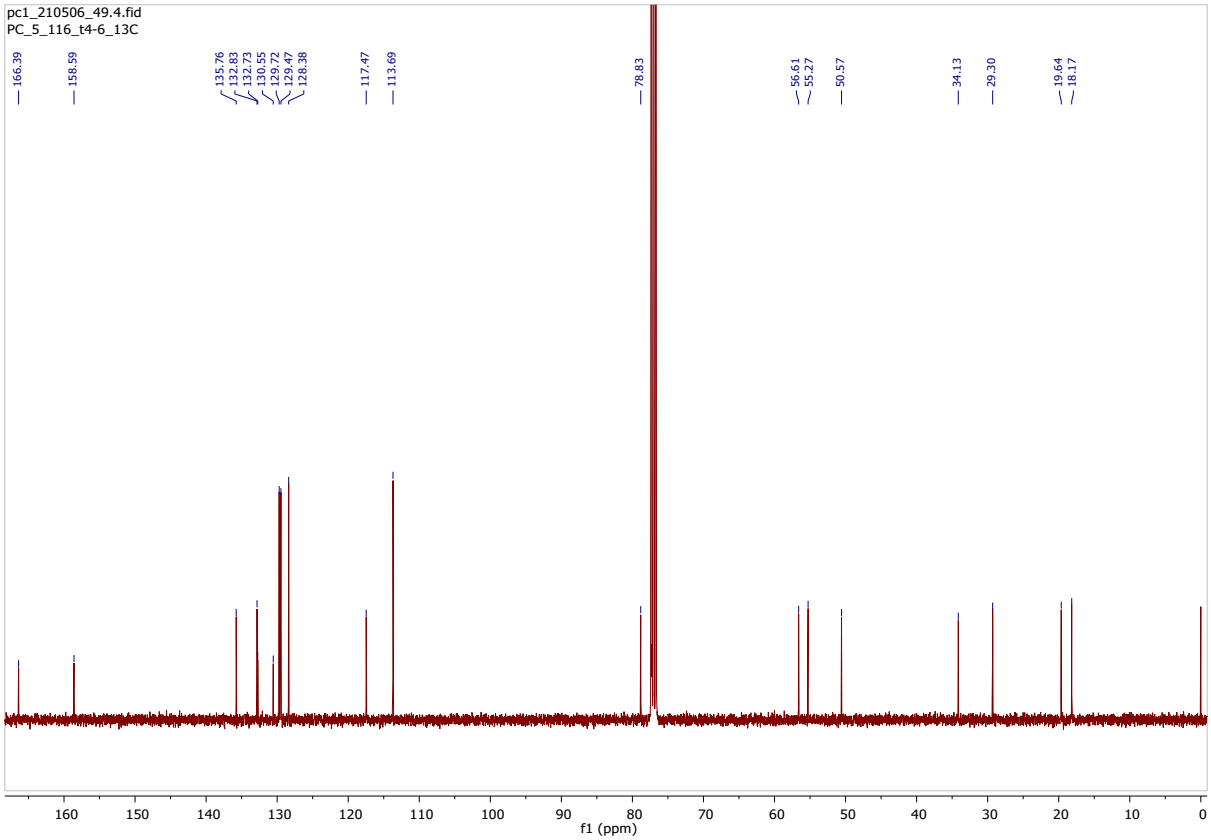


Figure 57: ^{13}C NMR spectrum of **8h** (101 MHz, $CDCl_3$).

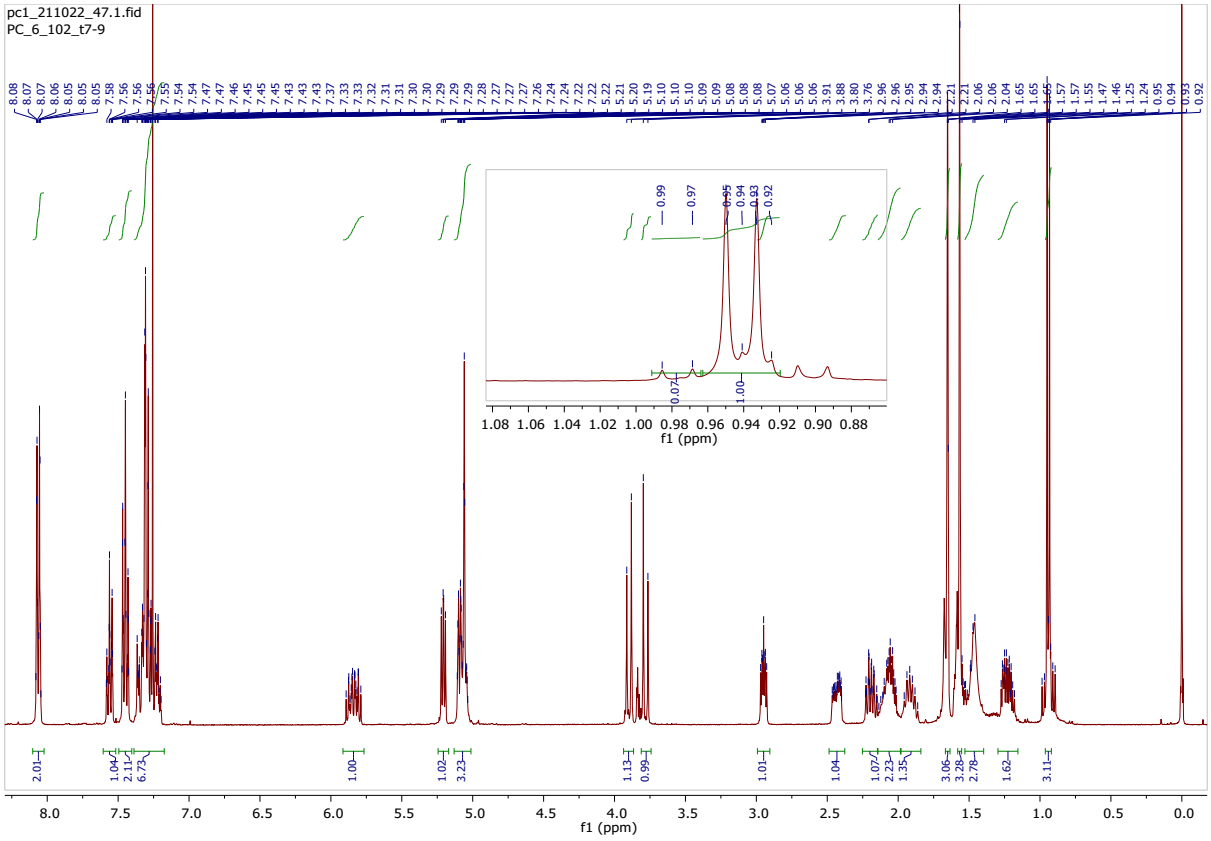


Figure 58: ^{1}H NMR spectrum of **8i** (400 MHz, $CDCl_3$, dr [**8i**:**8j**] = 93:7). The other doublets at 0.88-0.94 ppm are likely to be *syn*-aminoester diastereomers, but could not be unequivocally identified as such.

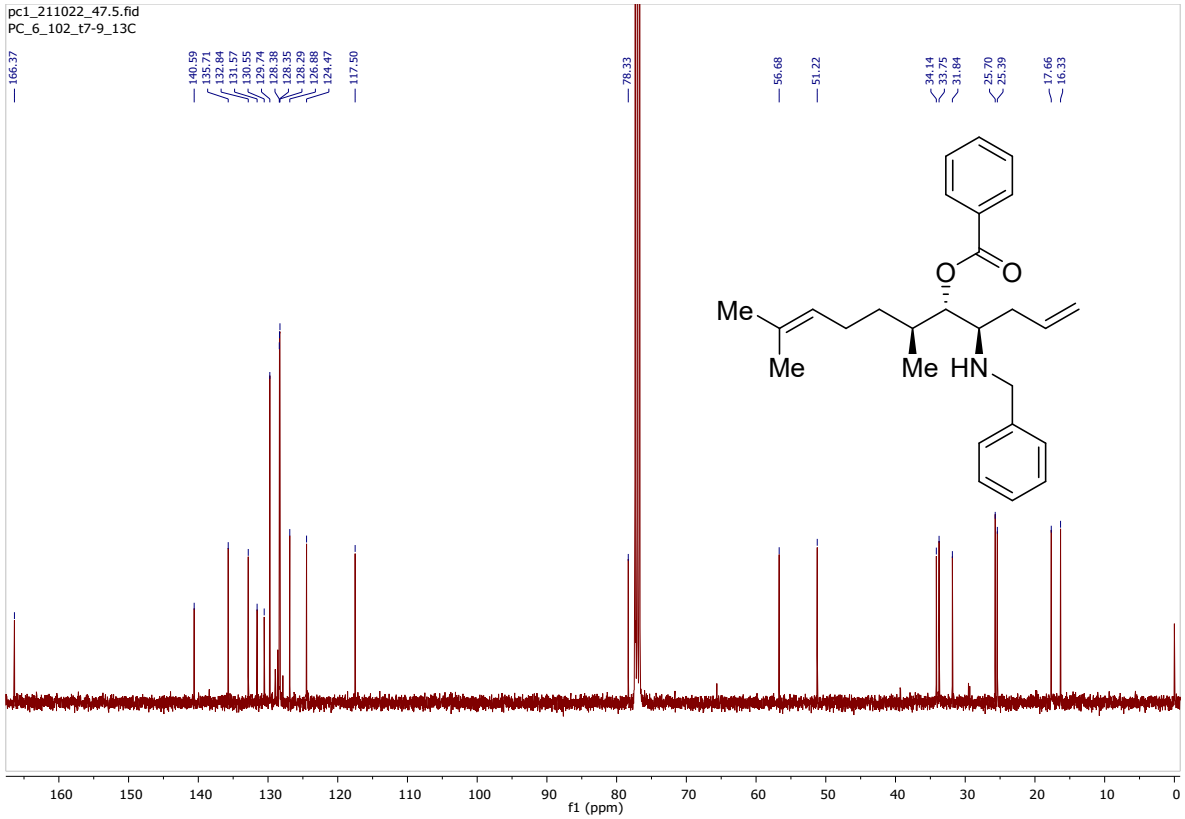


Figure 59: ^{13}C NMR spectrum of **8i** (101 MHz, $CDCl_3$).

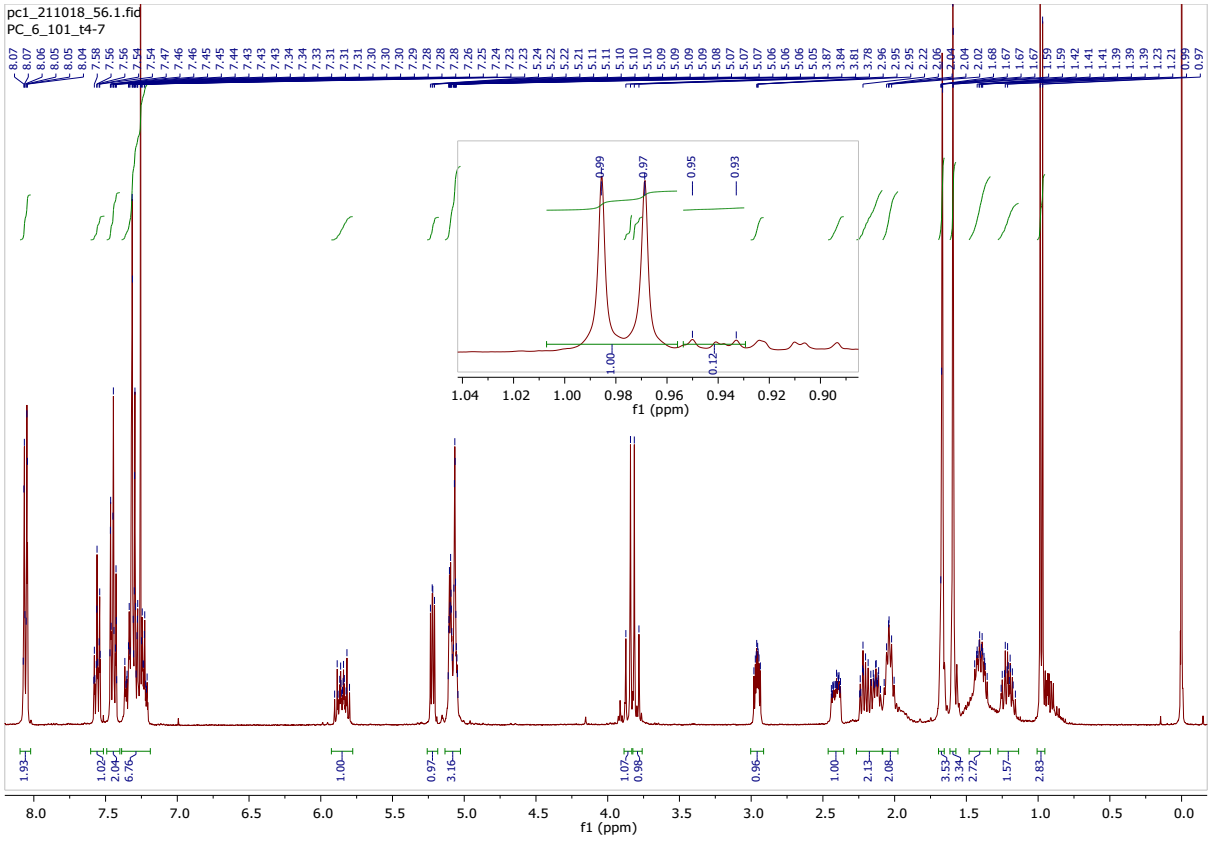


Figure 60: ^{1}H NMR spectrum of **8j** (400 MHz, $CDCl_3$, dr [**8i**:**8j**] = 10:90). The other doublets at 0.89-0.94 ppm are likely to be *syn*-aminoester diastereomers, but could not be unequivocally identified as such.

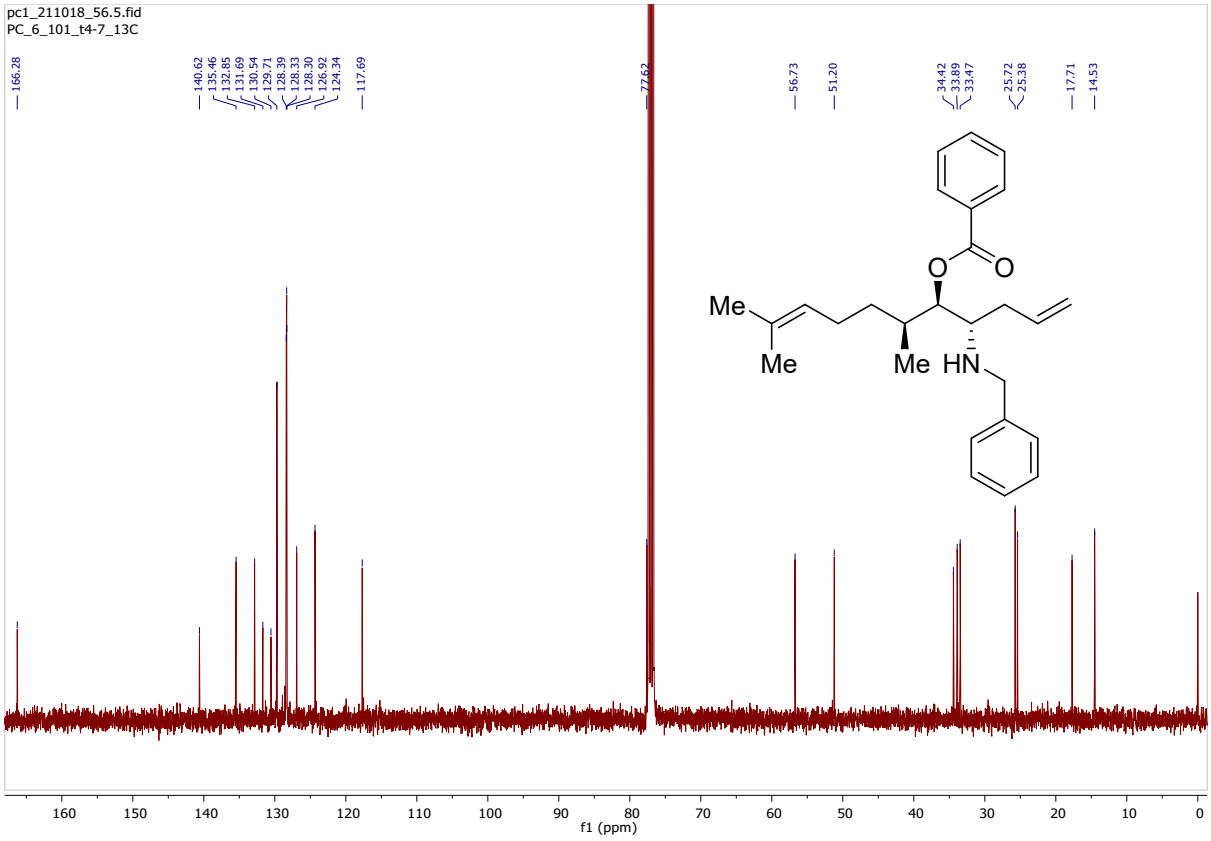
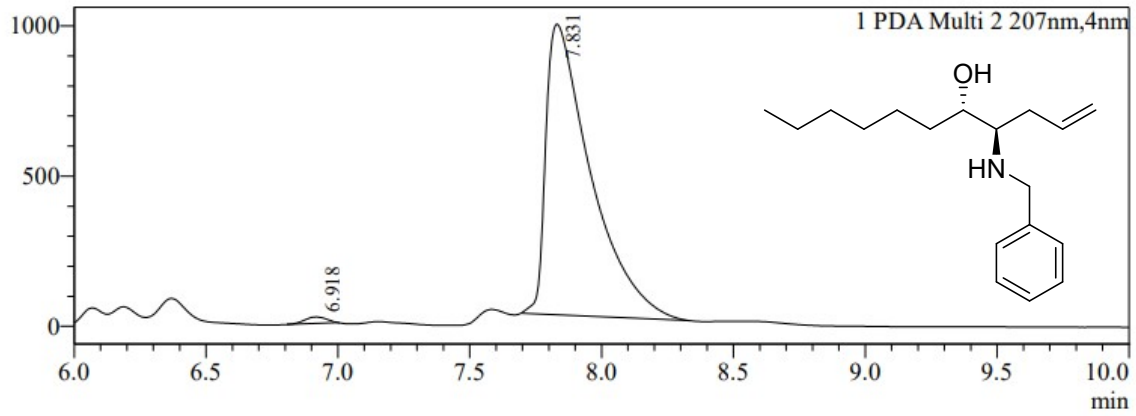


Figure 61: ^{13}C NMR spectrum of **8j** (101 MHz, $CDCl_3$).

Chromatogram
PC_6_18_3.lcd
mAU

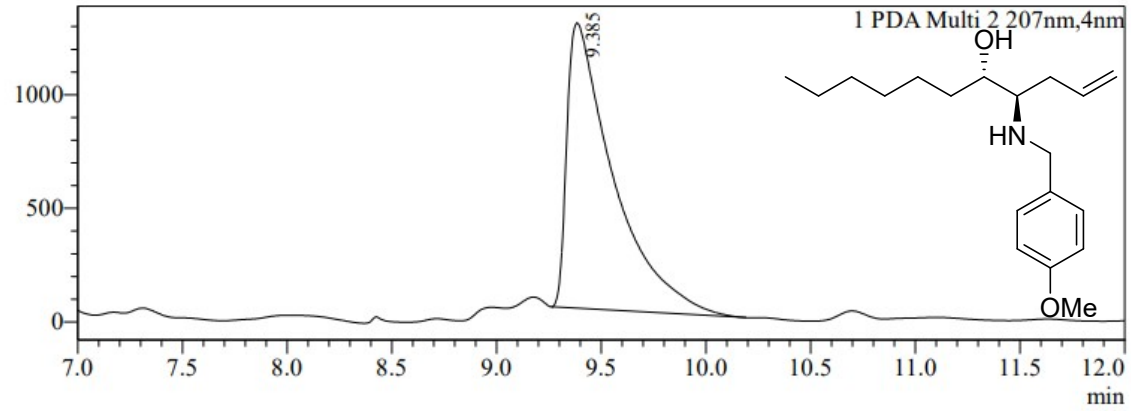


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	6.918	1.056	
2	7.831	98.944	
Total		100.000	

Figure 62: Chiral HPLC trace of ***ent*-7a**.

Chromatogram
PC_6_22_3.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	9.385	100.000	
Total		100.000	

Figure 63: Chiral HPLC trace of ***ent*-7b**.

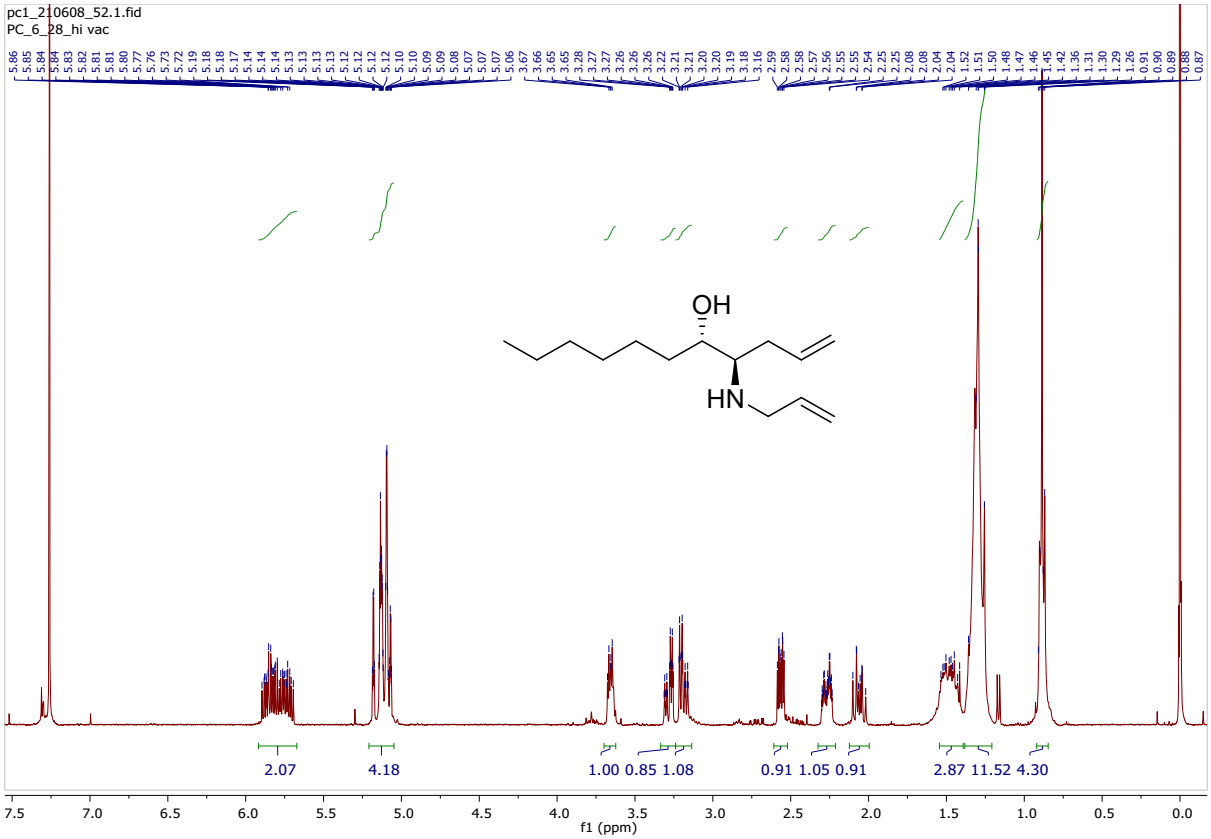


Figure 64: ^{1}H NMR spectrum of **SI-10** (400 MHz, $CDCl_3$).

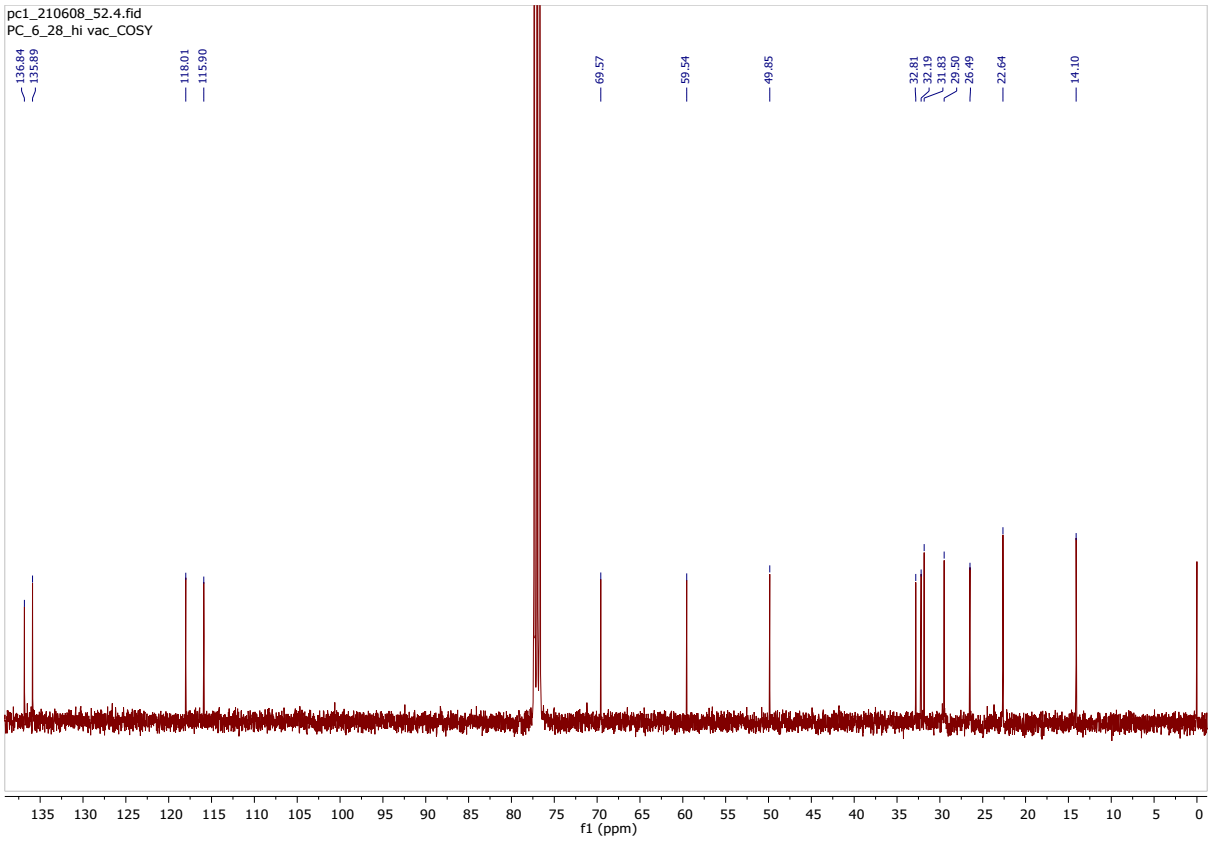
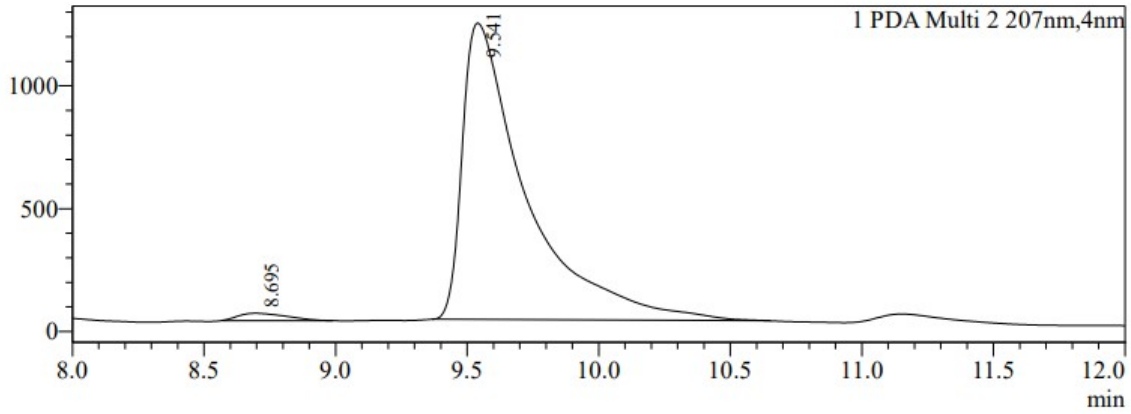


Figure 65: ^{13}C NMR spectrum of **SI-10** (101 MHz, $CDCl_3$).

Chromatogram
PC_6_29_9.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	8.695	1.839	
2	9.541	98.161	
Total		100.000	

Figure 66: Chiral HPLC trace of **SI-10**.

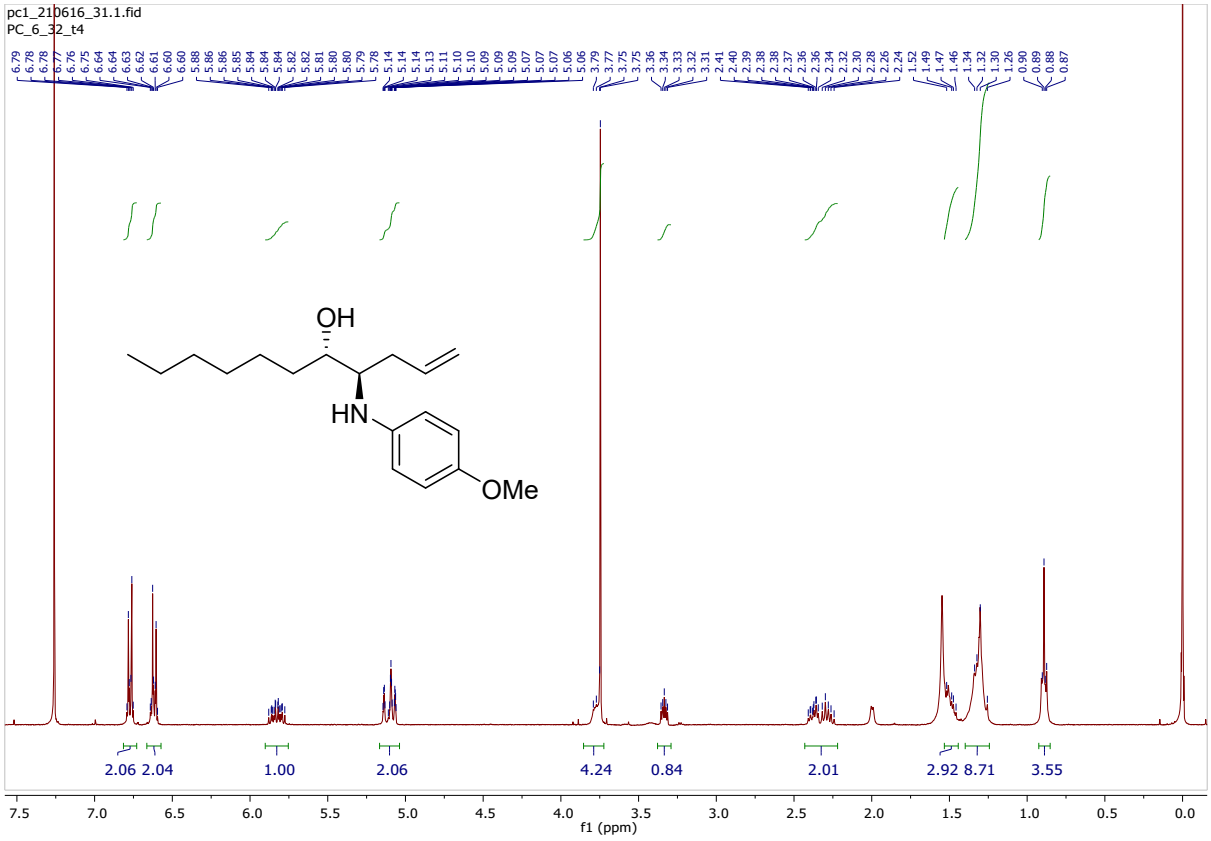


Figure 67: ^{1}H NMR spectrum of **SI-11** (400 MHz, $CDCl_3$).

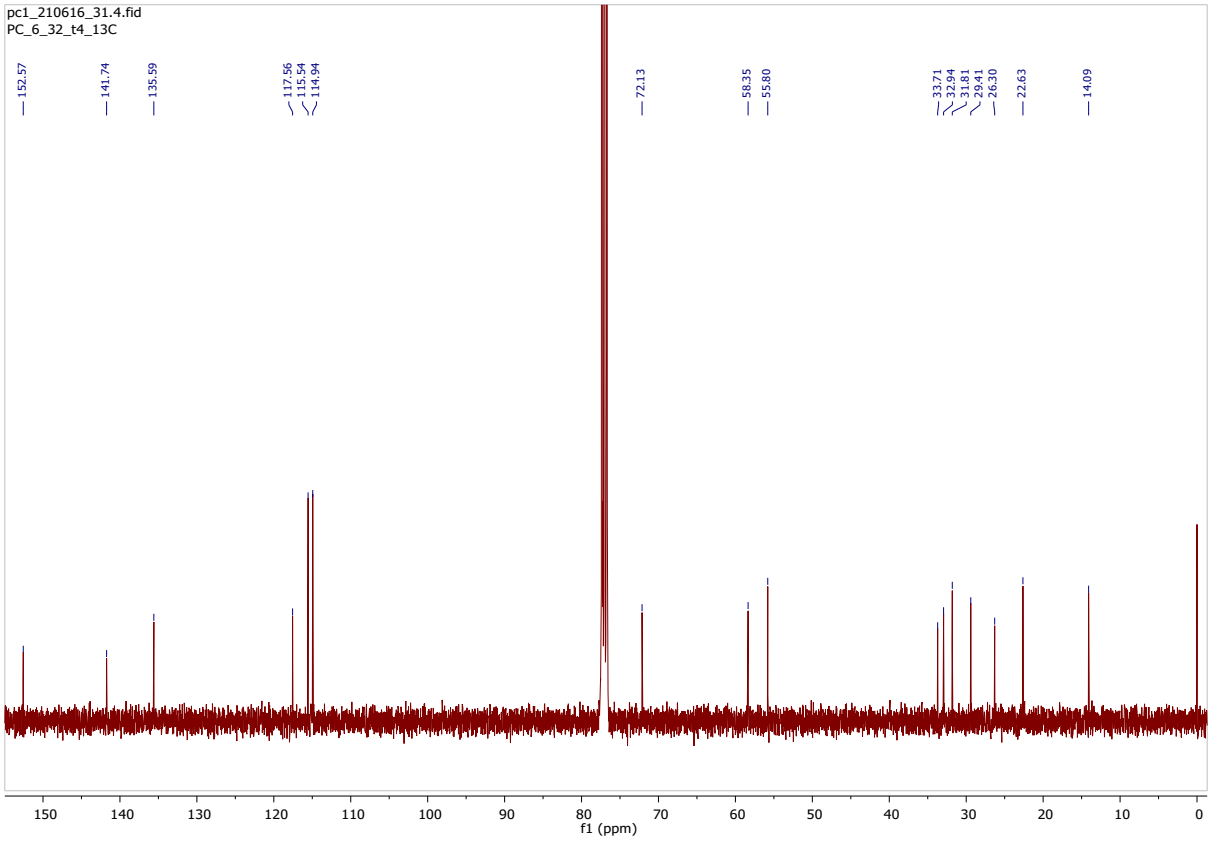
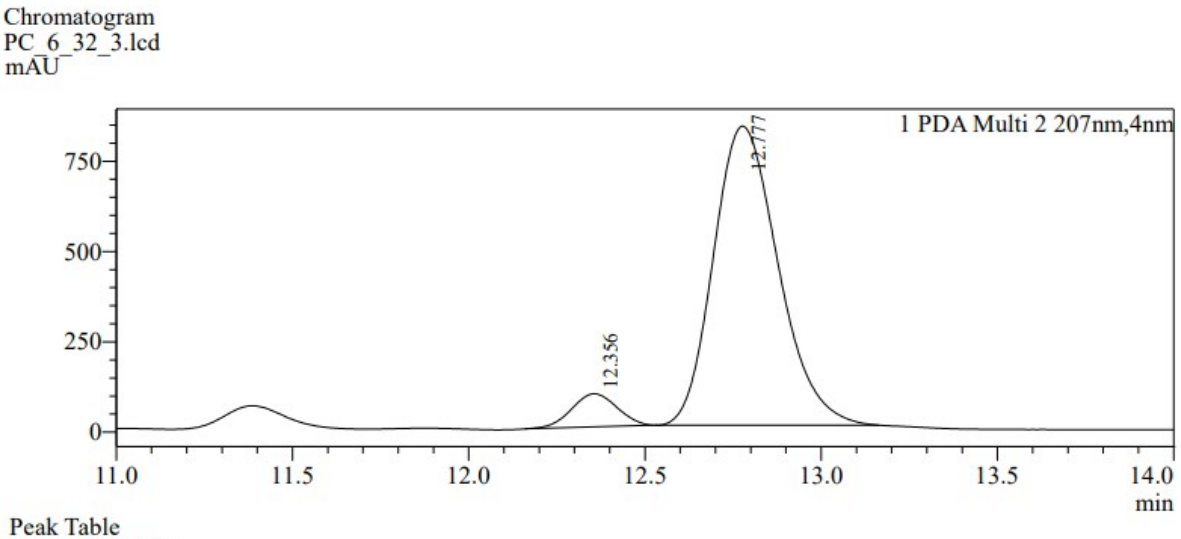


Figure 68: ^{13}C NMR spectrum of **SI-11** (101 MHz, $CDCl_3$).

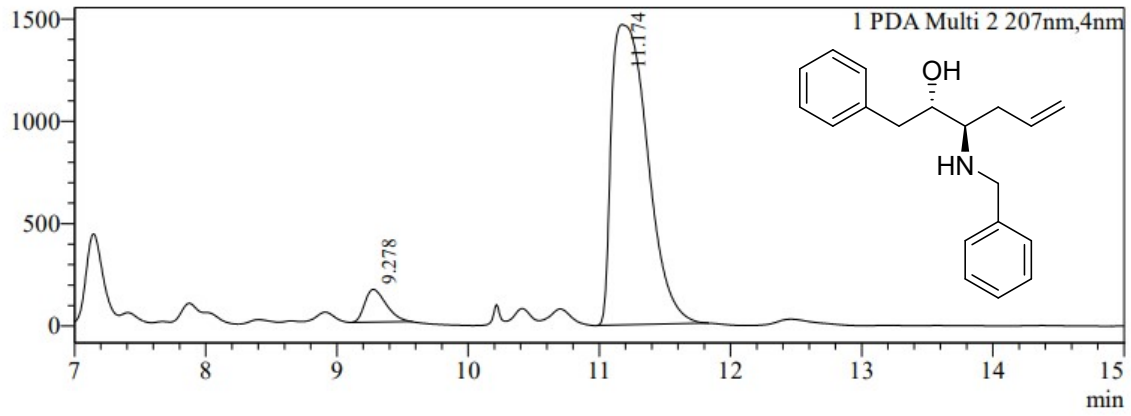


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	12.356	7.167	
2	12.777	92.833	
Total		100.000	

Figure 69: Chiral HPLC trace of **SI-11**. The peak at R_t ~11.4 min likely corresponds to the *syn*-diastereomer.

Chromatogram
PC_6_25_1.lcd
mAU

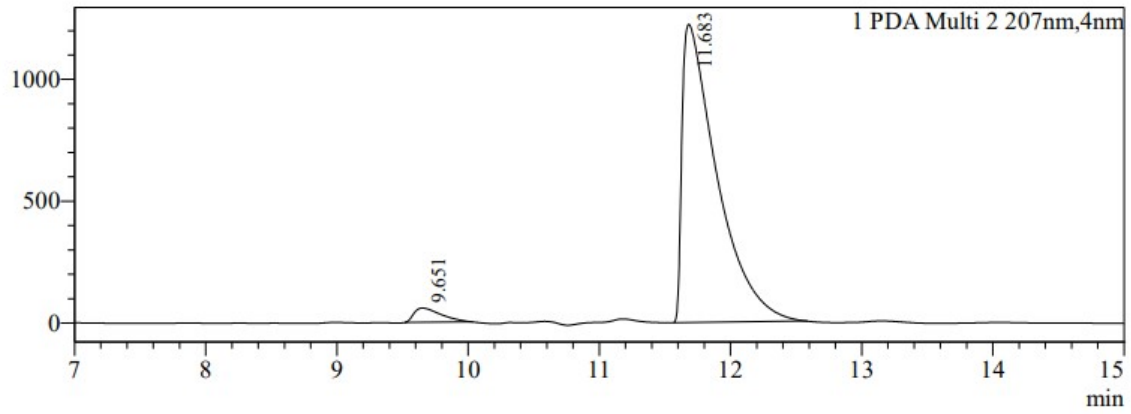


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	9.278	6.001	
2	11.174	93.999	
Total		100.000	

Figure 70: Chiral HPLC trace of ***ent*-7c** (Method 1 derivative).

Chromatogram
batch1_8112021_PC_6_110_2_005.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	9.651	3.575	
2	11.683	96.425	
Total		100.000	

Figure 71: Chiral HPLC trace of ***ent*-7c** (Method 2 derivative).

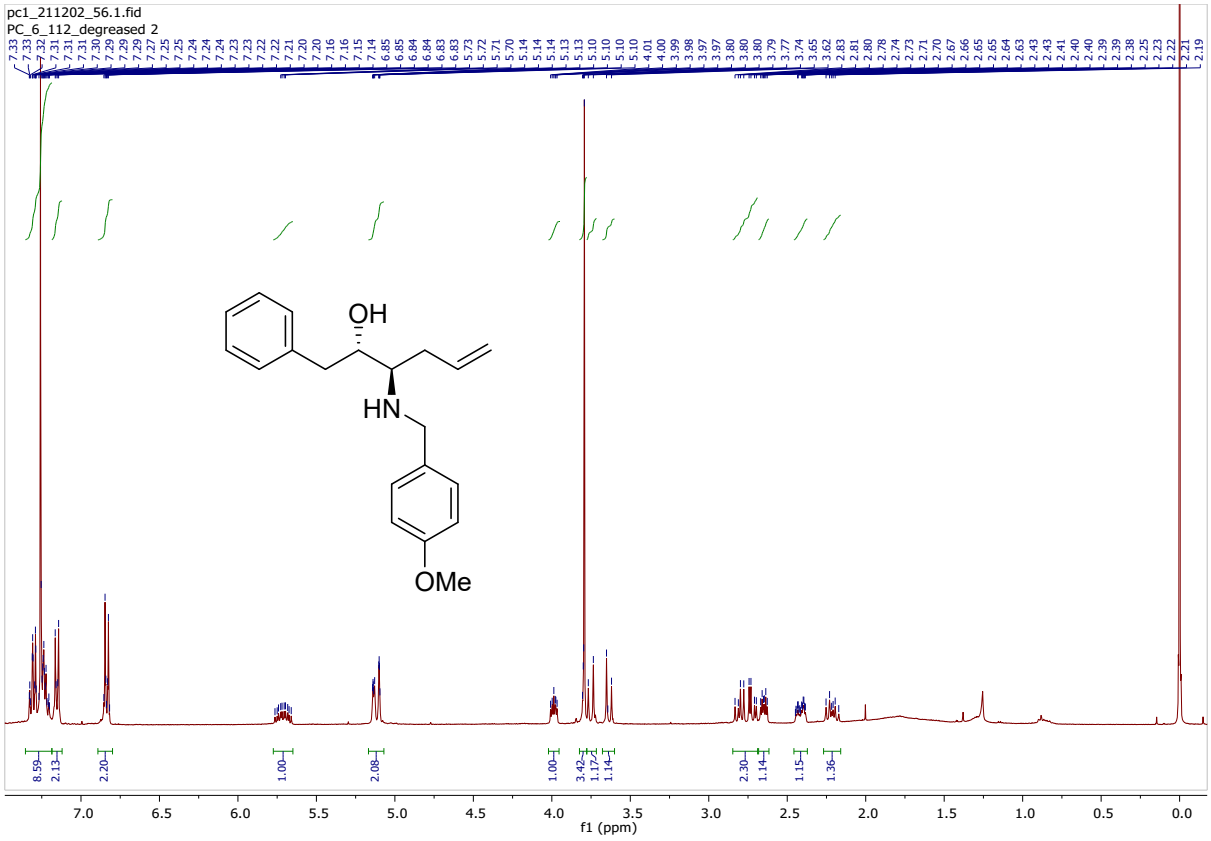


Figure 72: ^{1}H NMR spectrum of **SI-12** (400 MHz, $CDCl_3$).

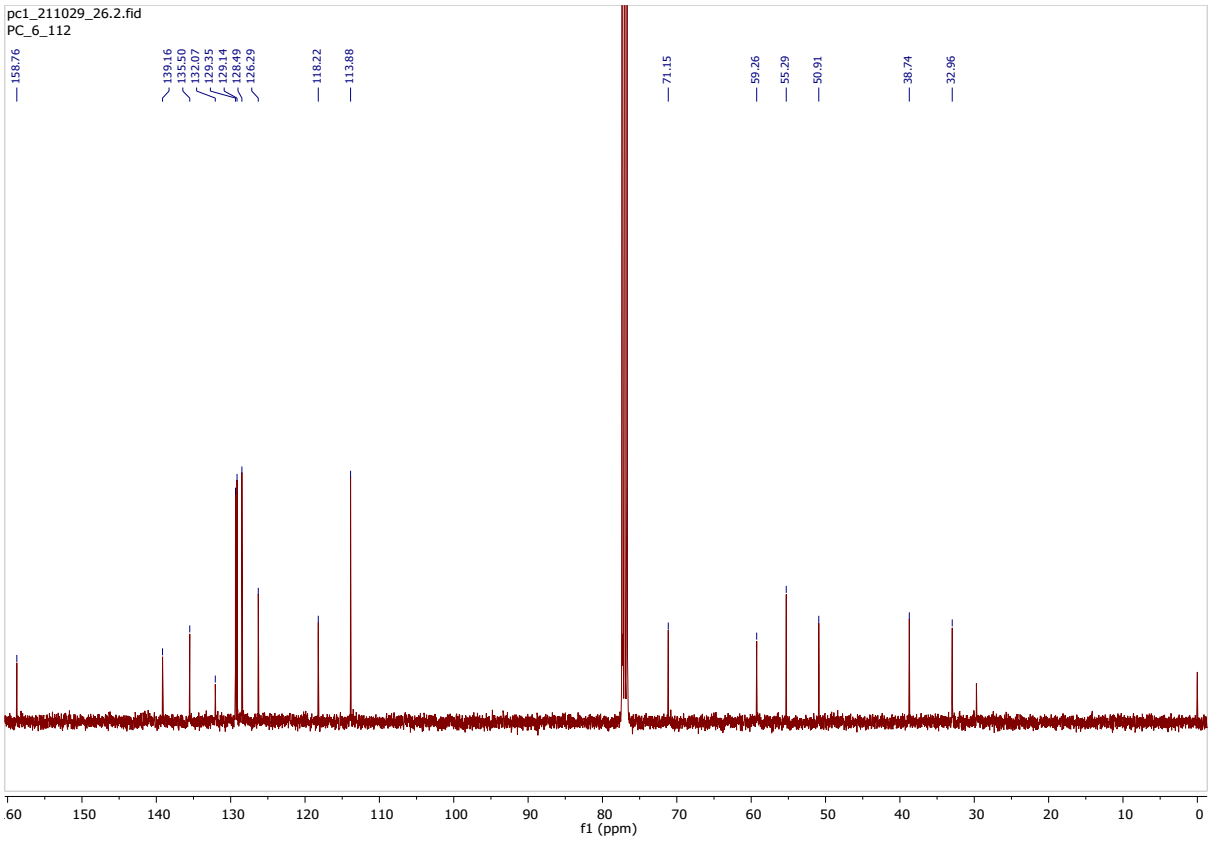
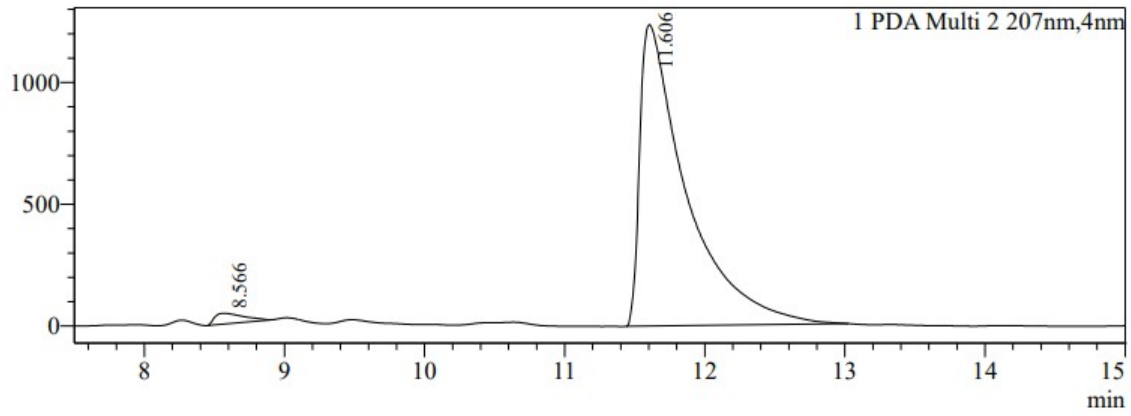


Figure 73: ^{13}C NMR spectrum of **SI-12** (101 MHz, $CDCl_3$).

Chromatogram
PC_6_112_3.lcd
mAU

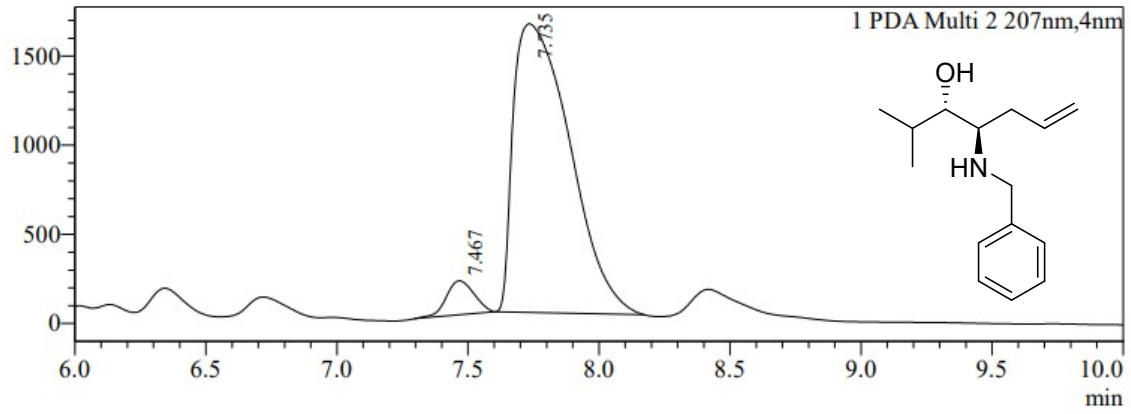


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	8.566	2.162	
2	11.606	97.838	
Total		100.000	

Figure 74: Chiral HPLC trace of **SI-12**.

Chromatogram
PC_6_12_1.lcd
mAU

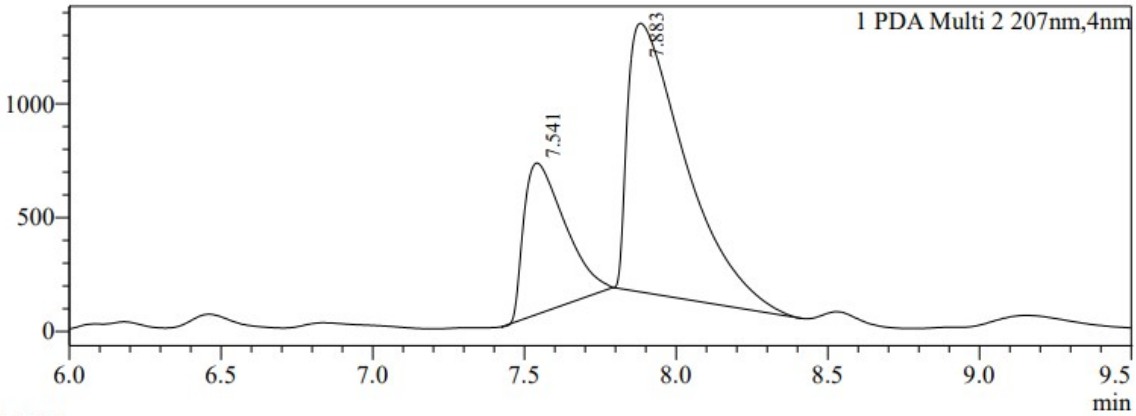


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	7.467	5.448	
2	7.735	94.552	
Total		100.000	

Figure 75: Chiral HPLC trace of ***ent*-7e**.

Chromatogram
PC_4_75 6_12 scal_1.lcd
mAU

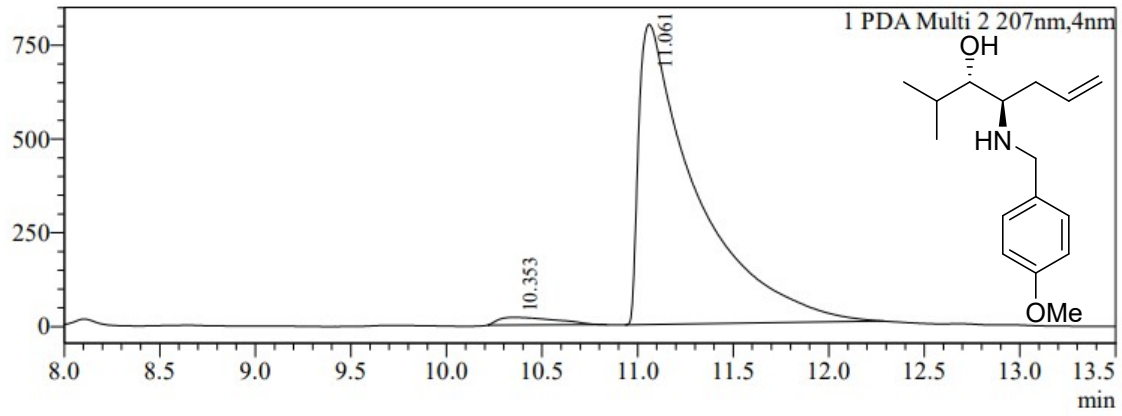


Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	7.541	28.424	
2	7.883	71.576	
Total		100.000	

Figure 76: Chiral HPLC trace of a premade scalemic mixture of **7e** and ***ent*-7e**.

Chromatogram
PC_6_36_10.lcd
mAU



Peak Table
PDA Ch2 207nm

Peak#	Ret. Time	Area%	Name
1	10.353	2.516	
2	11.061	97.484	
Total		100.000	

Figure 77: Chiral HPLC trace of ***ent*-7f**.

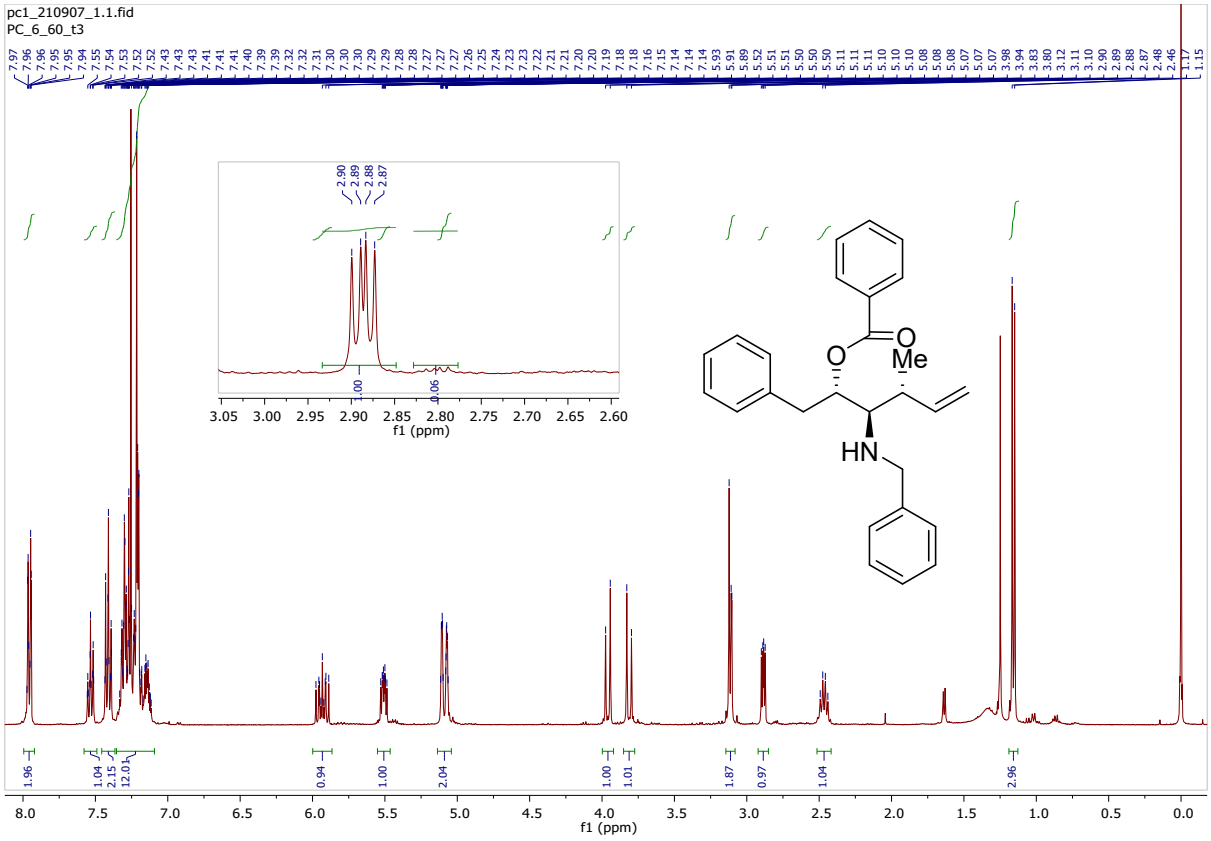


Figure 78: ^{1}H NMR spectrum of **9a** (400 MHz, $CDCl_3$, dr [**9a**:**9b**] = 95:5. No other diastereomers were detected). Note this spectrum contains a trace of pinacol (*E*)-crotylboronate, which was inseparable from **9a**.

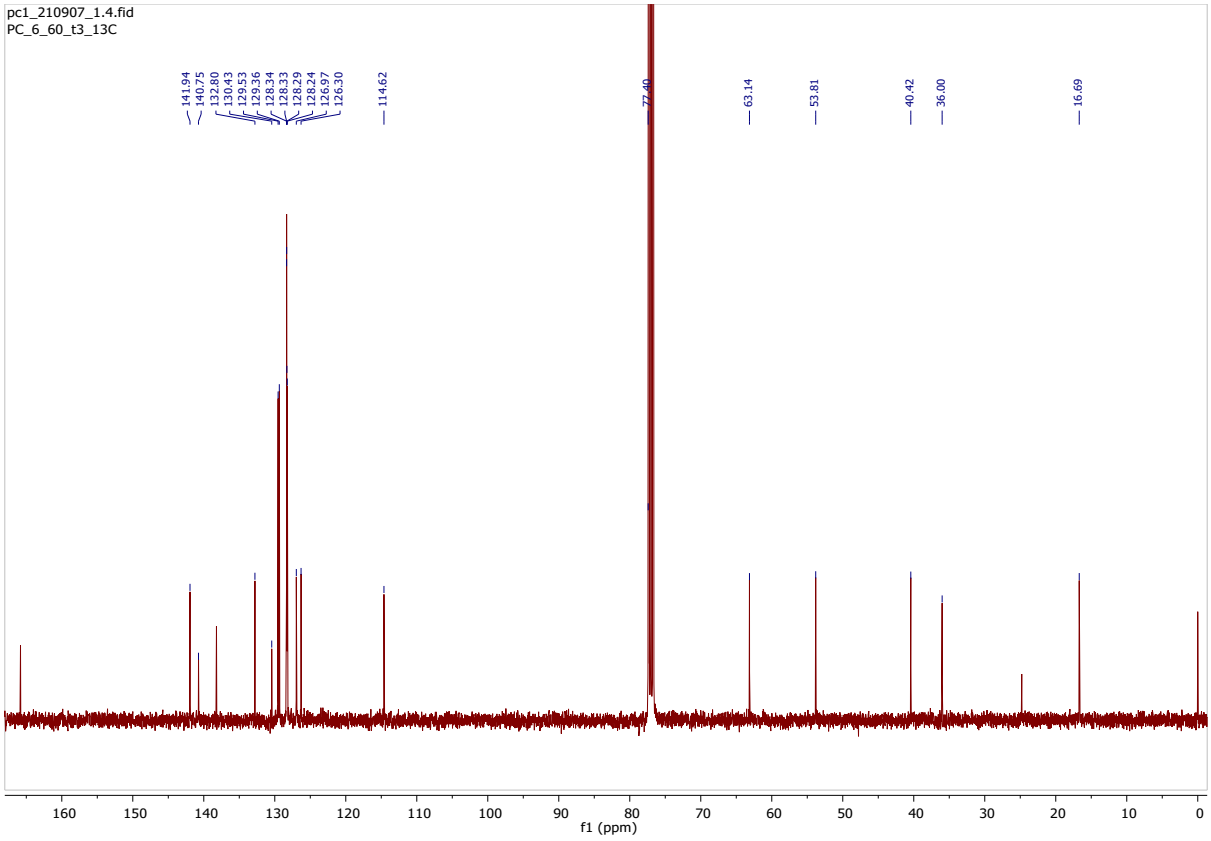


Figure 79: ^{13}C NMR spectrum of **9a** (101 MHz, $CDCl_3$).

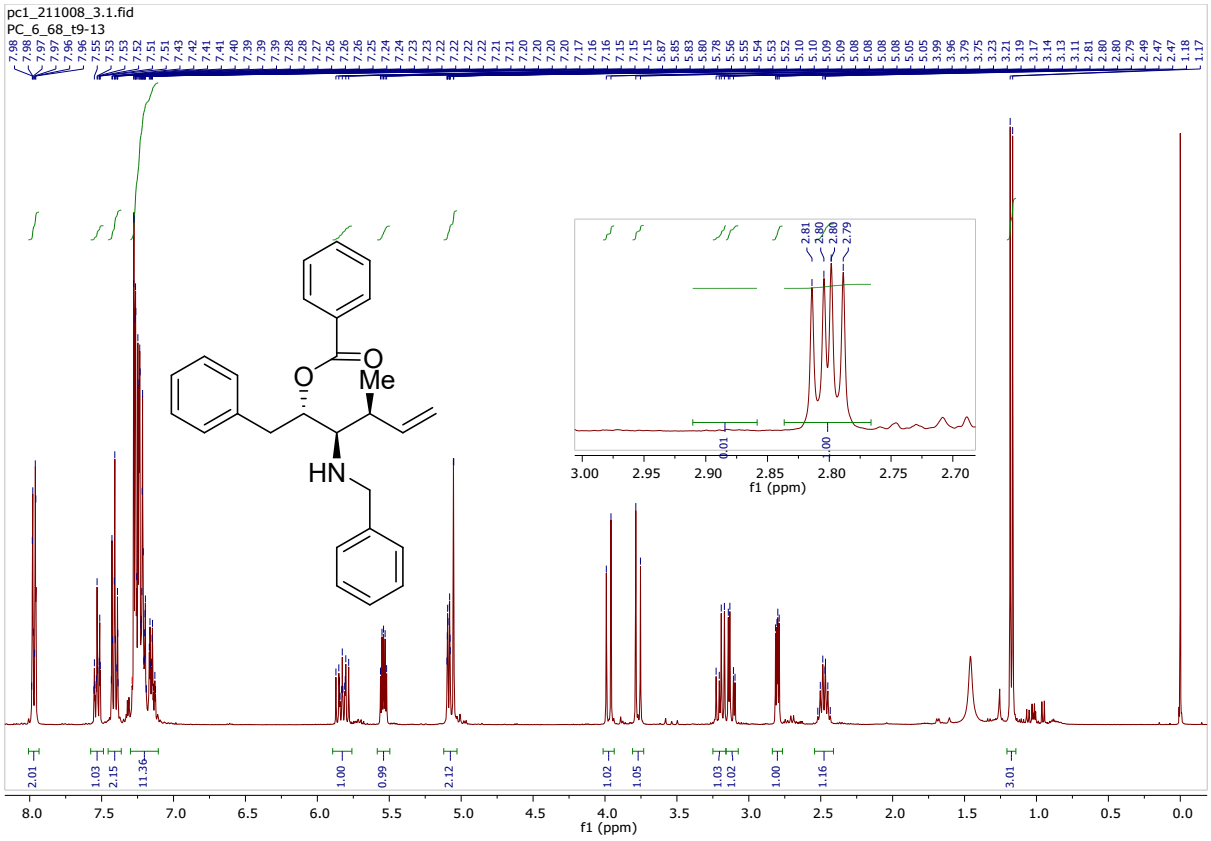


Figure 80: ^{1}H NMR spectrum of **9b** (400 MHz, $CDCl_3$, dr [**9a**:**9b**] = 1:99. No other diastereomers were detected).

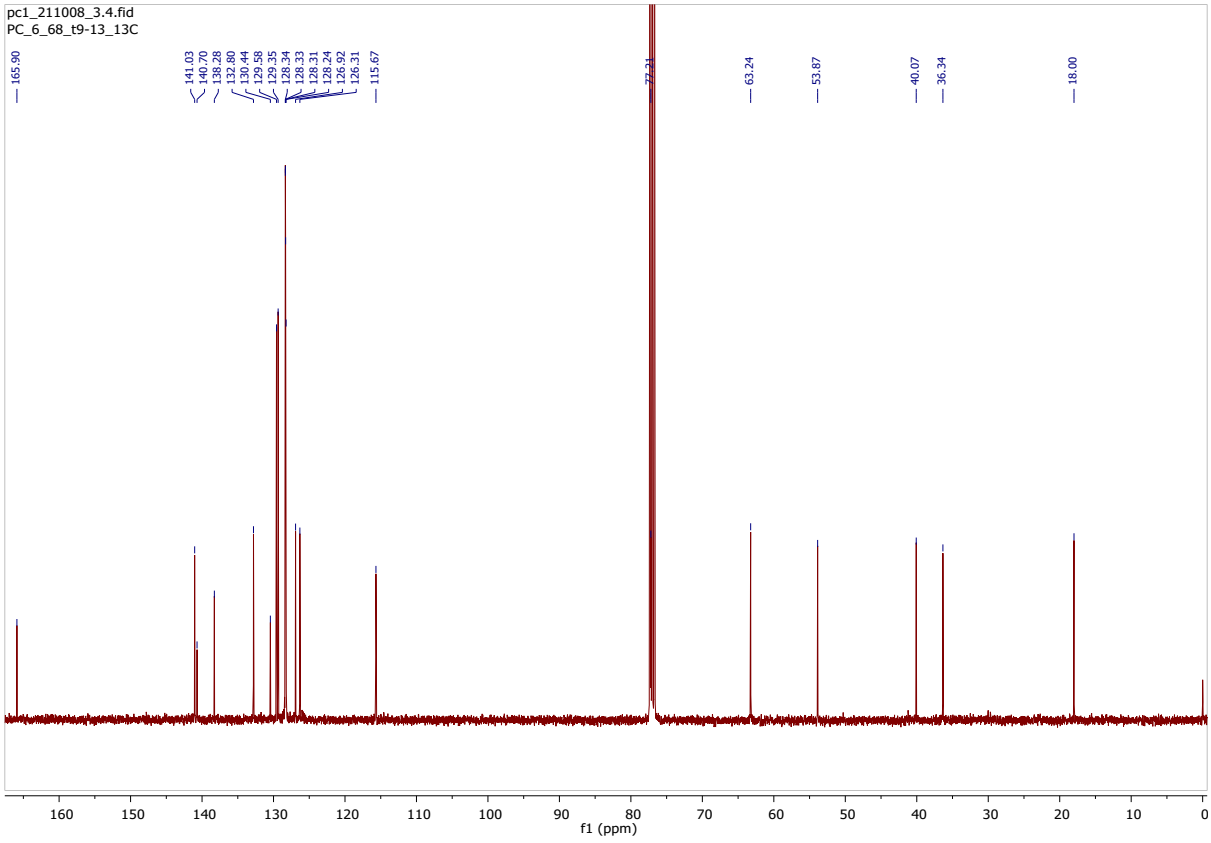


Figure 81: ^{13}C NMR spectrum of **9b** (101 MHz, $CDCl_3$).

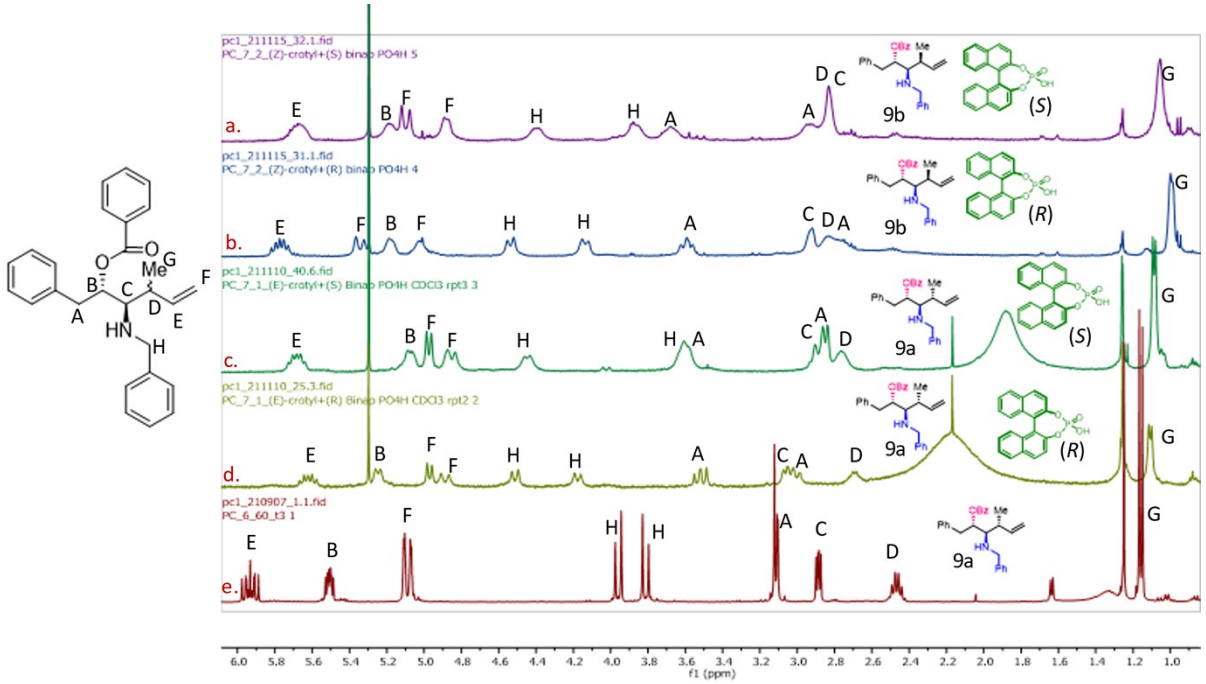


Figure 82: Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the derivatisation experiments (diastereotomeric salt formation) using (*R*) and (*S*)-1,1'-binaphthyl-2,2'-diylphosphoric acids and **9a** (spectrum e.), with assignments, determined by analysis of respective COSY, TOCSY and HSQC 2D spectra.

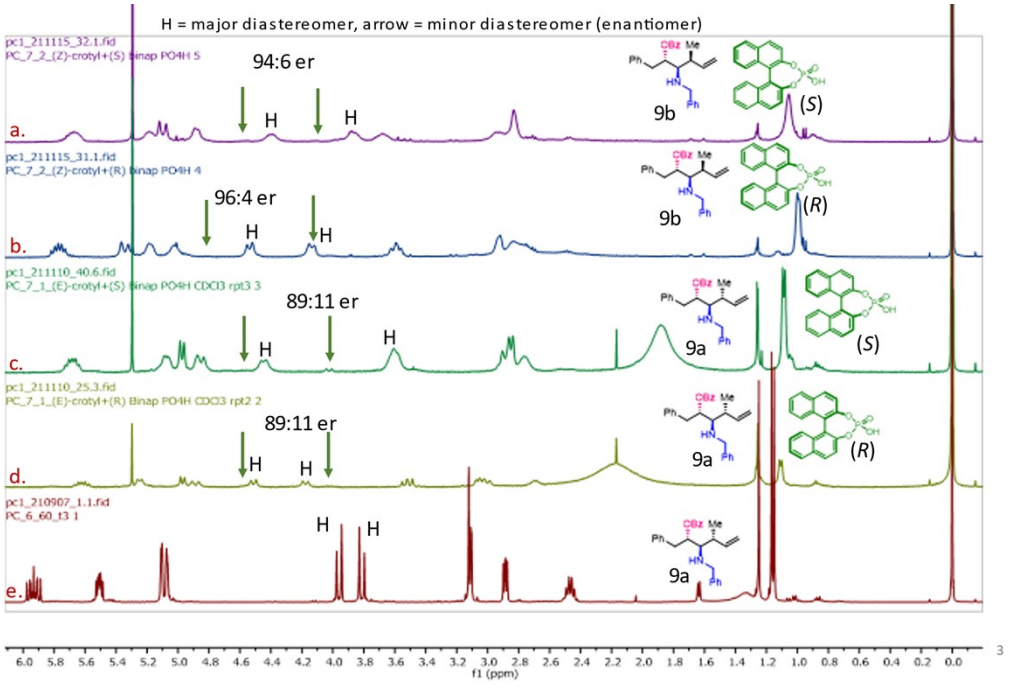


Figure 83: Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the derivatisation experiments, with labelling of the chemical shifts for protons H of the major and minor diastereomeric salts, therefore corresponding to enantiomers of **9a** and **9b**.

X-ray crystal structure report for **7c**

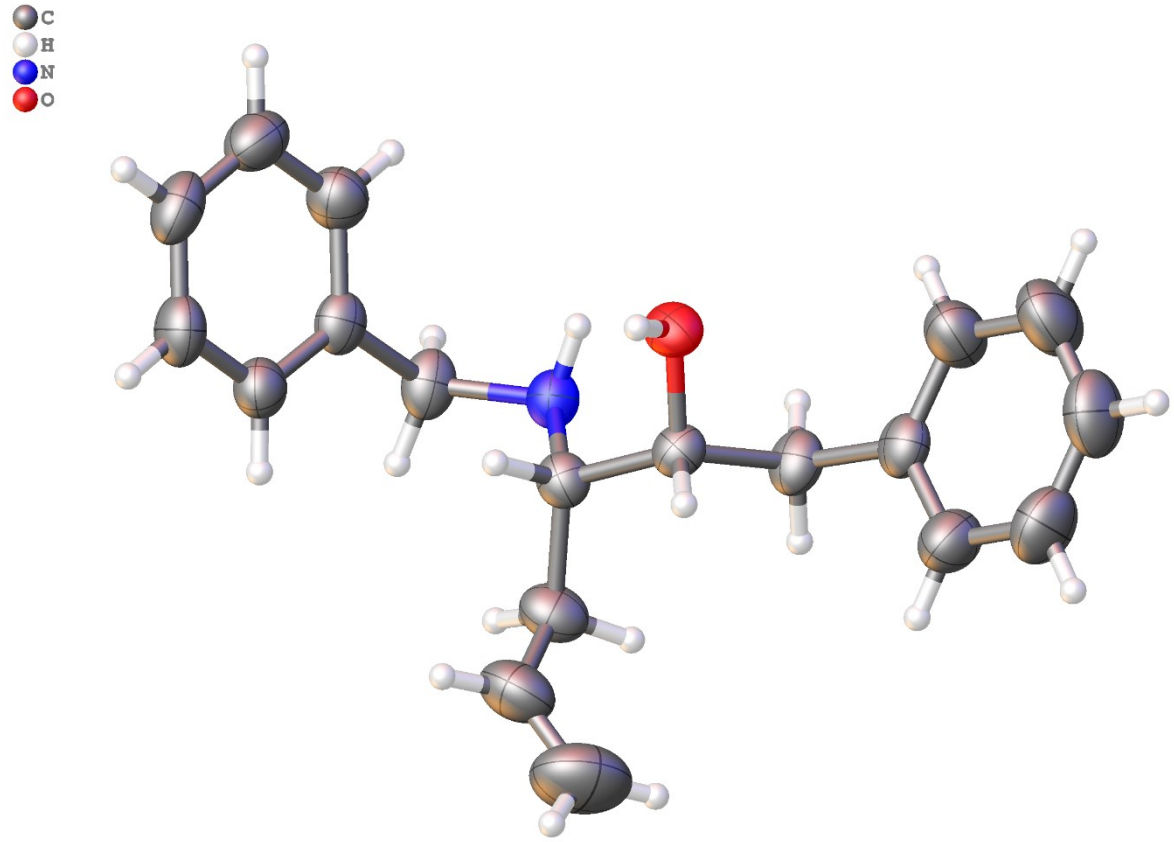


Figure 84: ORTEP plot of **7c**.

exp_198_PC

Table 1 Crystal data and structure refinement for exp_198_PC.

Identification code	exp_198_PC
Empirical formula	$C_{19}H_{23}NO$
Formula weight	281.38
Temperature/K	294(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.89740(10)
b/Å	10.1935(3)
c/Å	32.6734(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1631.11(8)
Z	4
ρ_{calc}g/cm^3	1.146
μ/mm^{-1}	0.070
F(000)	608.0
Crystal size/mm^3	0.5 × 0.31 × 0.23
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.186 to 60.064
Index ranges	-6 ≤ h ≤ 6, -14 ≤ k ≤ 14, -45 ≤ l ≤ 45
Reflections collected	39780
Independent reflections	4750 [R_{int} = 0.0289, R_{sigma} = 0.0212]
Data/restraints/parameters	4750/4/215
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0852
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.0910
Largest diff. peak/hole / e Å^{-3}	0.14/-0.11
Flack parameter	0.1(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_198_PC. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	4256(3)	4723.3(16)	3959.8(5)	45.9(4)
O2	1056(2)	3925.4(10)	3475.5(3)	42.1(3)
C2	2550(3)	3536.6(14)	3828.7(4)	35.7(3)
C3	4166(3)	2291.5(14)	3730.1(4)	37.6(3)

N3	6103(3)	2566.2(12)	3396.7(4)	38.6(3)
C4	5615(4)	1703.7(19)	4104.1(5)	52.7(4)
C5	3683(7)	958(4)	4370.6(11)	65.8(10)
C6	3160(13)	1240(7)	4747.3(12)	104.4(18)
C5A	3910(30)	1626(16)	4480(4)	64(4)
C6A	2590(40)	583(16)	4603(7)	92(5)
C1B	7031(3)	1395.1(16)	3166.3(5)	47.2(4)
C2B	4849(3)	687.2(16)	2925.6(5)	40.8(3)
C3B	3572(4)	-425.0(15)	3074.4(5)	46.2(4)
C4B	1568(4)	-1056.6(17)	2850.5(6)	53.1(4)
C5B	834(4)	-606.8(18)	2473.3(6)	55.7(4)
C6B	2098(4)	494(2)	2315.9(5)	57.8(5)
C7B	4068(4)	1136.1(17)	2542.2(5)	52.8(4)
C1P	2433(3)	5833.0(16)	4095.3(5)	44.5(4)
C2P	1568(5)	6780.8(18)	3824.3(6)	62.0(5)
C3P	-246(5)	7749(2)	3943.6(7)	77.9(7)
C4P	-1237(5)	7778(2)	4338.1(7)	73.6(6)
C5P	-382(5)	6849(2)	4610.8(7)	70.9(6)
C6P	1434(4)	5888(2)	4490.4(5)	59.1(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_198_PC. The Anisotropic displacement factor exponent takes the form: -$2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	35.6(8)	47.6(9)	54.3(9)	-11.3(7)	-6.0(7)	-3.4(7)
O2	34.2(5)	45.7(6)	46.3(6)	2.4(4)	-9.6(5)	-2.2(5)
C2	28.5(6)	41.1(7)	37.5(7)	-2.4(6)	-1.3(6)	-2.1(6)
C3	29.4(7)	38.4(7)	44.9(8)	-0.2(6)	-1.9(6)	-2.1(6)
N3	31.7(6)	39.2(6)	45.1(7)	-3.8(5)	0.2(6)	-0.9(5)
C4	45.1(9)	55.6(10)	57.6(10)	11.8(8)	-4.6(8)	5.9(8)
C5	66.5(19)	61(2)	70(2)	21.6(17)	-5.3(16)	-3.4(18)
C6	116(4)	124(5)	74(3)	30(2)	14(3)	8(3)
C5A	77(7)	66(8)	48(7)	22(6)	-10(6)	-15(7)
C6A	93(10)	101(13)	81(13)	10(9)	20(9)	-20(10)
C1B	32.9(8)	48.0(9)	60.7(10)	-13.5(7)	2.3(7)	1.2(7)
C2B	32.8(7)	41.1(8)	48.7(8)	-9.0(7)	3.2(6)	4.0(6)
C3B	49.2(9)	40.1(8)	49.4(8)	-4.7(7)	-1.9(8)	2.7(7)
C4B	52.2(10)	41.7(9)	65.5(11)	-11.3(8)	0.7(9)	-6.8(8)
C5B	49.7(10)	56.2(10)	61.1(10)	-23.9(9)	-7.5(9)	3.4(9)
C6B	63.4(11)	64.1(11)	45.8(9)	-7.9(8)	-7.5(8)	10.6(10)
C7B	55.1(10)	50.7(9)	52.7(9)	0.7(7)	4.7(9)	-2.8(9)
C1P	39.4(8)	42.7(8)	51.3(9)	-10.6(7)	-4.5(7)	-5.8(7)
C2P	74.9(13)	49.2(10)	62.0(11)	3.7(8)	9.0(10)	5.2(10)

C3P	95.4(17)	50.2(11)	88.2(15)	5.8(10)	5.4(14)	15.5(12)
C4P	69.2(13)	54.3(11)	97.5(16)	-17.0(11)	8.7(13)	12.0(11)
C5P	75.6(15)	75.1(14)	62.1(12)	-20.3(11)	10.1(11)	5.1(12)
C6P	65.7(12)	61.6(11)	49.9(9)	-7.4(8)	-3.9(9)	8.0(10)

Table 4 Bond Lengths for exp_198_PC.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.531(2)	C2B	C3B	1.383(2)
C1	C1P	1.508(2)	C2B	C7B	1.387(2)
O2	C2	1.4229(17)	C3B	C4B	1.383(2)
C2	C3	1.530(2)	C4B	C5B	1.363(3)
C3	N3	1.4711(19)	C5B	C6B	1.381(3)
C3	C4	1.535(2)	C6B	C7B	1.381(3)
N3	C1B	1.4827(19)	C1P	C2P	1.377(3)
C4	C5	1.493(4)	C1P	C6P	1.382(2)
C4	C5A	1.487(10)	C2P	C3P	1.383(3)
C5	C6	1.290(6)	C3P	C4P	1.378(3)
C5A	C6A	1.307(12)	C4P	C5P	1.366(3)
C1B	C2B	1.510(2)	C5P	C6P	1.381(3)

Table 5 Bond Angles for exp_198_PC.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1P	C1	C2	110.59(12)	C7B	C2B	C1B	120.50(15)
O2	C2	C1	106.70(12)	C2B	C3B	C4B	121.10(16)
O2	C2	C3	109.03(11)	C5B	C4B	C3B	120.58(17)
C3	C2	C1	115.59(12)	C4B	C5B	C6B	119.45(17)
C2	C3	C4	113.28(13)	C7B	C6B	C5B	119.93(17)
N3	C3	C2	109.36(11)	C6B	C7B	C2B	121.32(17)
N3	C3	C4	111.46(13)	C2P	C1P	C1	121.33(16)
C3	N3	C1B	114.85(12)	C2P	C1P	C6P	117.60(16)
C5	C4	C3	111.72(18)	C6P	C1P	C1	120.95(17)
C5A	C4	C3	114.7(5)	C1P	C2P	C3P	121.12(19)
C6	C5	C4	124.7(6)	C4P	C3P	C2P	120.3(2)
C6A	C5A	C4	125.2(19)	C5P	C4P	C3P	119.2(2)
N3	C1B	C2B	115.61(13)	C4P	C5P	C6P	120.2(2)
C3B	C2B	C1B	121.90(15)	C5P	C6P	C1P	121.52(19)
C3B	C2B	C7B	117.60(15)				

Table 6 Hydrogen Bonds for exp_198_PC.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°

O2 H2 N3[1]	0.82	1.99	2.8055(16)	175.1	

[1]-1+X,+Y,+Z

Table 7 Torsion Angles for exp_198_PC.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	N3	-59.00(17)	C4	C3	N3	C1B	75.91(17)
C1	C2	C3	C4	65.99(17)	C1B	C2B	C3B	C4B	179.67(14)
C1	C1P	C2P	C3P	175.77(18)	C1B	C2B	C7B	C6B	179.33(15)
C1	C1P	C6P	C5P	−175.60(17)	C2B	C3B	C4B	C5B	1.1(3)
O2	C2	C3	N3	61.16(14)	C3B	C2B	C7B	C6B	-0.3(2)
O2	C2	C3	C4	−173.86(12)	C3B	C4B	C5B	C6B	-0.4(3)
C2	C1	C1P	C2P	-91.7(2)	C4B	C5B	C6B	C7B	-0.6(3)
C2	C1	C1P	C6P	84.22(19)	C5B	C6B	C7B	C2B	1.0(3)
C2	C3	N3	C1B	−158.05(12)	C7B	C2B	C3B	C4B	-0.7(2)
C2	C3	C4	C5	78.2(3)	C1P	C1	C2	O2	65.18(17)
C2	C3	C4	C5A	45.5(7)	C1P	C1	C2	C3	−173.41(13)
C3	N3	C1B	C2B	65.21(18)	C1P	C2P	C3P	C4P	-0.3(3)
C3	C4	C5	C6	-119.0(4)	C2P	C1P	C6P	C5P	0.5(3)
C3	C4	C5A	C6A	97.3(15)	C2P	C3P	C4P	C5P	0.7(4)
N3	C3	C4	C5	-158.0(2)	C3P	C4P	C5P	C6P	-0.6(4)
N3	C3	C4	C5A	169.3(7)	C4P	C5P	C6P	C1P	0.0(3)
N3	C1B	C2B	C3B	-98.61(18)	C6P	C1P	C2P	C3P	-0.3(3)
N3	C1B	C2B	C7B	81.78(19)					

Table 8 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for exp_198_PC.

Atom	*x*	*y*	*z*	U(eq)
H1A	5456.27	4474.64	4182.88	55
H1B	5380.61	5010.87	3732.45	55
H2	-396.98	3526.59	3467.69	63
H2A	1248.89	3335.03	4047.73	43
H3	2866.29	1635.45	3629.58	45
H3A	5250(40)	3087(16)	3219(5)	42(5)
H4A	7057.77	1121.7	4012.56	63
H4B	6445.86	2403.74	4261.93	63
H4BC	6234.59	827.5	4034.98	63
H4BD	7217.45	2228.88	4163.85	63
H5	2794.08	239.7	4256.63	79

H6A	4011.3	1951.53	4871.32	125
H6B	1930.09	730.24	4895.03	125
H5A	3762.76	2378.13	4639.09	76
H6AA	2680.31	-188.78	4452.04	110
H6AB	1559.82	613.16	4842.24	110
H1BA	7832.9	780.71	3358.55	57
H1BB	8458.98	1663.44	2978.46	57
H3B	4069.65	-753.61	3329.21	55
H4BA	714.38	-1794.72	2958.25	64
H5B	-507.12	-1037.85	2323.17	67
H6BA	1622.07	802.82	2057.68	69
H7B	4888.71	1884.44	2435.48	63
H2P	2213.26	6770	3556.67	74
H3P	-799.05	8382.7	3756.44	93
H4P	-2471.94	8421.92	4417.72	88
H5P	-1025.26	6864.18	4878.51	85
H6P	1998.15	5262.23	4679.64	71

Table 9 Atomic Occupancy for exp_198_PC.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H4A	0.796(9)	H4B	0.796(9)	H4BC	0.204(9)
H4BD	0.204(9)	C5	0.796(9)	H5	0.796(9)
C6	0.796(9)	H6A	0.796(9)	H6B	0.796(9)
C5A	0.204(9)	H5A	0.204(9)	C6A	0.204(9)
H6AA	0.204(9)	H6AB	0.204(9)		

Experimental

Single crystals of $C_{19}H_{23}NO$ **[exp_198_PC]** were **[]**. A suitable crystal was selected and **[Mitegen mount + Paratone]** on a **XtaLAB Mini II** diffractometer. The crystal was kept at 294(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

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Crystal structure determination of [exp_198_PC]

Crystal Data for $C_{19}H_{23}NO$ (M =281.38 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 4.89740(10) Å, b = 10.1935(3) Å, c = 32.6734(11) Å, V = 1631.11(8) Å^3, Z = 4, T = 294(2) K, μ(Mo Kα) = 0.070 mm^{-1}, *Dcalc* = 1.146 g/cm^3, 39780 reflections measured (4.186° ≤ 2Θ ≤ 60.064°), 4750 unique (R_{int} = 0.0289, R_{sigma} = 0.0212) which were used in all calculations. The final R_1 was 0.0387 (I > 2σ(I)) and wR_2 was 0.0910 (all data).

Refinement model description

Number of restraints - 4, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups
```

```
 At 1.5 times of:
  All O(H) groups
2. Restrained distances
 C5-C4
 1.46 with sigma of 0.01
 C5A-C4
 1.46 with sigma of 0.01
 C6A-C5A = C6-C5
 1.33 with sigma of 0.01
3. Others
 Sof(H4BC)=Sof(H4BD)=Sof(C5A)=Sof(H5A)=Sof(C6A)=Sof(H6AA)=Sof(H6AB)=1-FVAR(1)
 Sof(H4A)=Sof(H4B)=Sof(C5)=Sof(H5)=Sof(C6)=Sof(H6A)=Sof(H6B)=FVAR(1)
4.a Ternary CH refined with riding coordinates:
 C2(H2A), C3(H3)
4.b Secondary CH2 refined with riding coordinates:
 C1(H1A,H1B), C4(H4A,H4B), C4(H4BC,H4BD), C1B(H1BA,H1BB)
4.c Aromatic/amide H refined with riding coordinates:
 C5(H5), C5A(H5A), C3B(H3B), C4B(H4BA), C5B(H5B), C6B(H6BA), C7B(H7B),
 C2P(H2P), C3P(H3P), C4P(H4P), C5P(H5P), C6P(H6P)
4.d X=CH2 refined with riding coordinates:
 C6(H6A,H6B), C6A(H6AA,H6AB)
4.e Idealised tetrahedral OH refined as rotating group:
 O2(H2)
```

This report has been created with Olex2, compiled on 2019.04.23 svn.r3594 for Rigaku Oxford Diffraction. Please let us know if there are any errors or if you would like to have additional features.

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