Supplementary Information

α-Sulfinyl Benzoates as Precursors to Li- and Mg Carbenoids for the Stereoselective Iterative Homologation of Boronic Esters

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Contents

1. General Information

All air- and water-sensitive reactions were carried out in oven-dried or flame-dried glassware under a N_2 atmosphere using standard Schlenk techniques. Analytical TLC was performed on aluminium backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or stained using $KMnO_4$, *p*-anisaldehyde or phosphomolybdic acid (PMA) followed by heating. Flash column chromatography was performed using Sigma Aldrich silica gel 60 (40-63 μm) or prepacked column (SNAP Ultra columns 10 g, 25 g, 100 g) with automated system (Biotage® Isolera™ One 3.0). All mixed solvent eluents are reported as v/v solutions.

^{1}H- and ^{13}C- Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated using JEOL ECS 300, JEOL ECS 400, Varian 400, Varian VNMRS500, Bruker 400 and Bruker Cryo 500 MHz spectrometers. ^{1}H and ^{13}C NMR spectra were referenced internally to the residual non-deuterated solvent signal. ^{1}H and ^{13}C NMR coupling constants are reported in Hertz (Hz). Coupling constants are reported as follows: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, dd = doublet of doublet, etc. Assignment of signals in ^{1}H- and ^{13}C-spectra was performed using ^{1}H-^{1}H COSY, DEPT, HMQC and HMBC experiments where appropriate. ^{13}C signals adjacent to boron are generally not observed due to quadrupolar relaxation.

High resolution mass spectra were recorded on Bruker Daltonics MicroTOF II by using Electronic Ionization (EI) and Electron Spray Ionization (ESI). GC-MS was perfomed on an Agilent 6890 apparatus. All IR data was obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer. Optical rotations were obtained on a Bellingham and Stanley Ltd. ADP220 polarimeter. Melting point range were determined with a Kofler hot-stage microscope apparatus and are reported uncorrected.

Chiral HPLC was performed using Daicel Chiralpak IA and IB columns (4.6 mm× 250 mm, 5 μm) fitted with the respective guard (4 mm ×10 mm) and monitored by DAD (Diode Array Detector) on an Agilent 1100 system equipped with HP Chemstation/OpenLab software using. Waters HPLC system (Waters system fluidics organizer, Waters 2545 gradient module, and Waters 2998 photodiode array detector) was used for preparative reverse phase separation. Chiral gas chromatography (Chiral GC) was performed on an Agilent 7890A using a Chiraldex β-DP 120 column (30m x 0.25mm x 0.25μm) and a Chiraldex β-DM 120 column (30m x 0.25mm x 0.25μm)

2. Materials and reagents

All reagents were used as received unless otherwise stated. Anhydrous Et_2O, THF, and CH_2Cl_2 were dried using a purification column composed of activated alumina. Anhydrous Et_2O was stored over 3 Å mol sieves. TMEDA and PMDTA were distilled over CaH_2 and stored in a Young's tube under N_2. Diisopropylamine were dried over NaOH before distillation and stored in a Young's tube under N_2. Organolithiums (*n*BuLi, *s*BuLi, and *t*BuLi) reagents were periodically titrated using *N*-benzylbenzamide.[1] *i*PrMgCl•LiCl was titrated using I_2.[2] Lithium diisopropylamide (LDA) and lithium bis(trimethylsilyl)amide (LiHMDS) solutions were freshly prepared from the corresponding distilled amines and *n*BuLi immediately before use. Basic silica gel was prepared by adding trimethylamine (2 mL) to a slurry of SiO_2 (~100 g) in Et_2O.

(1*S*,2*R*,5*S*)-(+)-Menthyl (*R*)-*p*-toluenesulfinate, (1*R*,2*S*,5*R*)-(–)-menthyl (*S*)-*p*-toluenesulfinate, benzyl bromide, 4-benzyl bromide, 1-chloro-3-iodopropane, 3-bromo-1-(trimethylsilyl)-1-propyne, and ethyl trifluoromethanesulfonate were purchased from Sigma Aldrich.

The following compounds were prepared according to literature procedures and all spectroscopic data matched those previously reported: methyl *p*-toluenesulfinate,[3] benzyl iodide,[4] 1-azido-3-iodopropane,[5] butyl trifluoromethanesulfonate,[6] 3,3,3-trifluoropropyl trifluoromethanesulfonate,[7] ethyl 6-(((trifluoromethyl)sulfonyl)oxy)hexanoate.[8]

3. General Procedures

3.1 General procedure 1 (GP1): Synthesis of *syn* and *anti* 1-(*p*-tolylsulfinyl) 2,4,6-triisopropylbenzoates by transmetalation

To a stirred solution of 2,4,6-triisopropylbenzoate (1.0 equiv) and TMEDA (1.2–1.5 equiv) in anhydrous Et_2O (0.3 M) was added *s*BuLi (1.3 M in cyclohexane/hexane, 1.2–1.5 equiv) dropwise at –78 °C. After stirring for the required time at –78 °C a solution of freshly prepared $MgBr_2$•Et_2O* (1.5 equiv in Et_2O – 0.8 M) was added at –78 °C and the reaction mixture was stirred for 2 h at that temperature. At this point a solution of (1*R*,2*S*,5*R*)-(–)-menthyl (*S*)-*p*-toluenesulfinate (1.5 equiv) in anhydrous THF (1.0 M) was added dropwise at –78 °C. The mixture was stirred for an additional hour at that temperature before being warmed to room temperature and stirred overnight. The reaction mixture was then diluted with EtOAc and sat. NH_4Cl, the phases were separated and the aqueous phase was extracted with EtOAc for 3 times. The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. In many cases separation of the desired diastereoisomers from the menthol by-product was facilitated by silylation of the menthol:[9] to a solution of the crude mixture in anhydrous DCM (0.5 M) was added Et_3N (1.5 equiv). TMSCl (1.3 equiv) was added dropwise at room temperature, the resulting mixture was stirred for 20 min, diluted with Et_2O and washed with H_2O. The organic layer was dried over $MgSO_4$ and the solvent was removed under

reduced pressure to give a crude residue, which was purified by flash column chromatography (hexane:EtOAc) to afford the *syn* (less polar) and the *anti* (more polar) diastereoisomers.
The racemates were synthesised as above but using racemic methyl 4-methylbenzenesulfinate[3] as the starting material.

* A solution of $MgBr_2 \bullet Et_2O$ was prepared as follows: Mg turnings (4.0 equiv) were put in a Schlenk tube in a N_2 atmosphere and anhydrous Et_2O (0.8 M with respect to dibromoethane) was added. The solution was cooled to 0 °C and dibromoethane (1.5 equiv) was added dropwise. The ice bath was removed and the reflux was initiated soon. After gas evolution ceased, the reaction mixture was stirred for additional 30 min.

3.2 General procedure 2 (GP2): Synthesis of *syn* and *anti* 1-(*p*-tolylsulfinyl) 2,4,6-triisopropylbenzoates by alkylation

((*R*)-*p*-Tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (1.0 equiv) and alkylating agent (1.1–2.0 equiv) in an oven dried Schlenk tube was dissolved in anhydrous THF (0.2 M) under an atmosphere of nitrogen. For substrates **14k** and **14l**, HMPA (2.0 equiv) was added at this stage. The reaction mixture was cooled to –78 °C and base (2.0 equiv) was added dropwise. The mixture was stirred at –78 °C for 30 min and then the cooling bath was removed and the solution was stirred at room temperature for 30 min. The reaction mixture was quenched with sat. NH_4Cl and diluted with EtOAc. The layers were separated and the aqueous phase was extracted with EtOAc for 3 times. The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (hexane:EtOAc) to give the *syn* (less polar) and the *anti* (more polar) diastereoisomers.
The racemates were synthesised as above but using racemic sulfoxide *rac*-**19** as the starting material.

3.3 General procedure 3 (GP3): Stereocontrolled homologation of boronic esters using α-sulfinyl benzoates: *in situ* procedure using *t*BuLi

*t*BuLi (1.7 M in pentane, 2.00 equiv) was added dropwise to a mixture of sulfoxide (1.05–1.10 equiv) and pinacol boronic ester (1.00 equiv) in anhydrous THF (0.1 M with respect to the boronic ester) at –78 °C and the resulting solution was stirred at this temperature for 1 h. After warming to room temperature, the reaction mixture was heated at 66 °C for 3 h, cooled to room temperature, diluted with Et_2O and sat. NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 times). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification of the crude reaction mixture by chromatography on silica gel (hexane:Et_2O) afforded the desired homologated boronic ester. A small portion of the boronic ester was oxidised to the corresponding alcohol following General Procedures **GP7** or **GP8** to determine the e.r.

In the presence of sensitive functional groups, after stirring the reaction mixture at –78 °C for 1 h, acetic acid (1.00 equiv) was added to quench the excess of the reactive organolithium and 1,2-metallate rearrangement was performed at room temperature for 16 h.

When the separation of the homologated boronic ester from the unreacted starting boronic ester was not possible the mixture was oxidised (see General Procedures 7 and 8 – **GP7** and **GP8**) and the corresponding alcohol was isolated clean.

The racemates were synthesised as above but using the corresponding racemic sulfoxides as the starting materials.

3.4 General procedure 4 (GP4): Stereocontrolled homologation of boronic esters using α-sulfinyl benzoates: *in situ* procedure using *i*PrMgCl•LiCl

*i*PrMgCl•LiCl (1.3 M in THF, 1.2 equiv) was added dropwise to a mixture of sulfoxide (1.3 equiv) and pinacol boronic ester (1.0 equiv) in anhydrous DCM (0.1 M with respect to the boronic ester) at –78 °C and the resulting solution was stirred at this temperature for 1 h. After warming to room temperature, the reaction mixture was heated at 40 °C for 3 h, cooled to room temperature, diluted with Et_2O and sat. NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 times). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. (Where specified the work-up procedure was modified and the crude reaction mixture was filtered through basic silica (see materials and reagents)(~10 mm depth of wetted (Et_2O) silica) and the solvent was removed under reduced pressure).The crude mixture was purified by chromatography on silica gel (hexane:Et_2O) to afford the desired homologated boronic ester. A small portion of the boronic ester was oxidised to the corresponding alcohol following General Procedures **GP7** or **GP8** to determine the e.r.

When the separation of the homologated boronic ester from the unreacted starting boronic ester was not possible the mixture was oxidised (see General Procedures 7 and 8 – **GP7** and **GP8**) and the corresponding alcohol was isolated clean.

The racemates were synthesised as above but using the corresponding racemic sulfoxides as the starting materials.

3.5 General procedure 5 (GP5): Stereocontrolled homologation of boronic esters using α-sulfinyl benzoates: *ex situ* procedure using *i*PrMgCl•LiCl

*i*PrMgCl•LiCl (1.3 M in THF, 1.2 equiv) was added dropwise to a solution of sulfoxide (1.3 equiv) in anhydrous DCM (0.13 M) at –78 °C and the resulting solution was stirred at this temperature for 30 min. A solution of the pinacol boronic ester (1.0 equiv) in DCM (0.5 M) was then added slowly and the resulting mixture was stirred at –78 °C for additional 45 min. After warming to room temperature, the reaction mixture was heated at 40 °C for 3 h, cooled to room temperature, diluted with Et_2O and sat. NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 times). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under

reduced pressure. (Where specified the work-up procedure was modified and the crude reaction mixture was filtered through basic silica (see materials and reagents)(~10 mm depth of wetted (Et_2O) silica) and the solvent was removed under reduced pressure). The crude mixture was purified by chromatography on silica gel (hexane:Et_2O) to afford the desired homologated boronic ester. A small portion of the boronic ester was oxidised to the corresponding alcohol following General Procedures **GP7** or **GP8** to determine the e.r.

When the separation of the homologated boronic ester from the unreacted starting boronic ester was not possible the mixture was oxidised (see General Procedures 7 and 8 – **GP7** and **GP8**) and the corresponding alcohol was isolated clean.

The racemates were synthesised as above but using the corresponding racemic sulfoxides as the starting materials.

3.6 General procedure 6 (GP 6): Stereocontrolled homologation of boronic esters using hindered α-sulfinyl benzoates: reverse addition procedure using *t*BuLi/PMDTA

To a solution of PMDTA (2.0–2.3 equiv) in anhydrous Et_2O (0.1 M with respect to the boronic ester) was added *t*BuLi (1.7 M in pentane, 2.0–2.3 equiv) dropwise at –78 °C. A solution of benzoate (1.05–1.3 equiv) in Et_2O (0.1 M with respect to the boronic ester) was added to the reaction mixture dropwise at –78 °C. After stirring 20 min at this temperature, a solution of boronic ester (1.0 equiv) in Et_2O (0.1 M with respect to the boronic ester) was introduced slowly. The mixture was stirred for 1 hour at –78 °C. After warming to room temperature, the reaction mixture was heated at 40 °C for 3 h, cooled to room temperature, diluted with Et_2O and sat. NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 times). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by chromatography on silica gel (hexane:EtOAc) to afford the desired homologated boronic ester. A small portion of the boronic ester was oxidised to the corresponding alcohol following General Procedures **GP7** or **GP8** to determine the e.r.

When the separation of the homologated boronic ester from the unreacted starting boronic ester was not possible the mixture was oxidised (see General Procedures 7 and 8 – **GP7** and **GP8**) and the corresponding alcohol was isolated clean.

The racemates were synthesised as above but using the corresponding racemic sulfoxides as the starting materials.

3.7 General procedure 7 (GP7): Stereospecific oxidation of boronic esters using H_2O_2/NaOH

Pinacol boronic ester (1.0 equiv) was dissolved in THF (5.0 mL) and the solution was cooled to 0 °C. An aqueous solution of 2.0 M NaOH and 30% H_2O_2 (2:1 v/v, 3.0 mL) was added dropwise. The solution was stirred vigorously for 2 h at room temperature, then it was diluted with water (10 mL) and Et_2O (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The organic

layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane:EtOAc) to afford the desired alcohol.

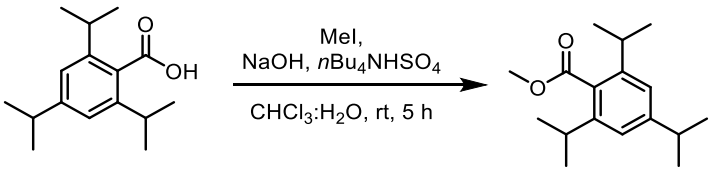
3.8 General procedure 8 (GP8): Stereospecific oxidation of boronic esters using sodium perborate tetrahydrate

To a solution of boronic ester/boronic ester mixture (0.2–0.3 mmol) in THF/water (3:2, 0.1 M) at room temperature was added $NaBO_3 \cdot 4H_2O$ (10 equiv) and the resulting suspension was stirred for 2–3 h. The mixture was filtered through silica [~10 mm depth of wetted (Et_2O) silica] and the filtrate was concentrated *in vacuo*. The crude product was purified by silica gel chromatography to afford the desired alcohol.

4. Preparation of Triisopropylbenzoates

Ethyl 2,4,6-triisopropylbenzoate,[10] propyl 2,4,6-triisopropylbenzoate,[11] isobutyl 2,4,6-triisopropylbenzoate[12] and 3-phenylpropyl 2,4,6-triisopropylbenzoate[13] were synthesised according to the literature reported procedures.

4.1 Preparation of methyl 2,4,6-triisopropylbenzoate (27)



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A biphasic mixture of 2,4,6-triisopropylbenzoic acid (7.44 g, 30.0 mmol), tetrabutylammonium hydrogen sulfate (816 mg, 2.40 mmol), sodium hydroxide (3.60 g, 90.2 mmol) and methyl iodide (9.35 mL, 150 mmol) in chloroform:water (1.22:1, v/v, 282 mL) was stirred vigorously for 5 h at room temperature. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with brine (150 mL), dried ($MgSO_4$) and the solvent was removed under reduced pressure to give **27** as a crude pink solid (7.43 g, 95%) which was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (s, 2H, ArH), 3.89 (s, 3H, CH_3), 2.89 (sept, *J* = 7.4 Hz, 1H, CH), 2.82 (sept, *J* = 7.4 Hz, 2H, CH × 2), 1.25 (d, *J* = 7.4 Hz, 18H, CH_3 × 6) ppm

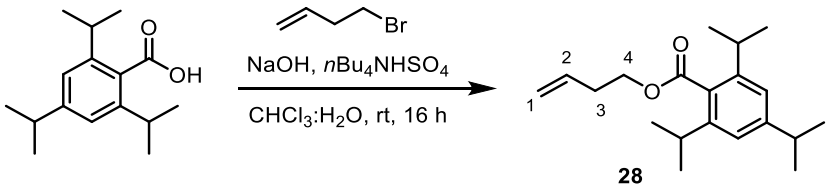
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9 (CO), 150.2 (C), 144.8 (2 × C), 130.8 (C), 120.9 (2 × CH), 60.8 (CH_3), 30.6 (CH), 31.5 (2 × CH), 24.2 (4 × CH_3), 24.0 (2 × CH_3) ppm

IR (neat): 2957, 2869, 1719, 1254, 1080, 877

HRMS (ESI): calculated for $C_{17}H_{26}ONa$ [M+Na$^+$] 285.1825, found 285.1837

M.P. 40–42 ºC

4.2 Preparation of but-3-en-1-yl 2,4,6-triisopropylbenzoate (28)[14]



To a solution of 2,4,6-triisopropylbenzoic acid (5.00 g, 20.1 mmol) in chloroform (50 mL) was added a solution of NaOH (2.42 g, 60.4 mmol) and nBu$_4$NHSO$_4$ (0.55 g, 1.61 mmol) in distilled H_2O (50 mL). 4-Bromo-1-butene (6.13 mL, 60.4 mmol) was added to the biphasic mixture under vigorous stirring and the resulting reaction mixture was stirred at room temperature for 16 h. The phases were separated, the organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting oil was dissolved in pentane:EtOAc = 90:10 and filtered through a plug of silica. The solution was concentrated under reduced pressure to afford the pure benzoate **28** (4.93 g, 81%) as a colourless oil.

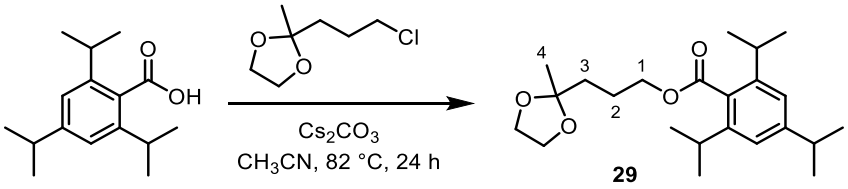
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.03 (s, 2H, Ar-H), 5.86 (m, 1H, 2-H), 5.17 (dq, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H, 1-H$_{trans}$), 5.11 (dq, J_1 = 10.3 Hz, J_2 = 1.2 Hz, 1H, 1-H$_{cis}$), 4.40 (t, J = 6.8 Hz, 2H, 4-H), 2.89 (sept, J = 6.8 Hz, 3H, C*H*(CH$_3$)$_2$ × 3), 2.52 (qt, J_1 = 6.7 Hz, J_2 = 1.4 Hz, 2H, 3-H), 1.26 (d, J = 6.9 Hz, 18H, CH$_3$ × 6) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.8 (CO), 150.1 (Ar-C), 144.7 (2C, Ar-C × 2), 134.0 (2-C), 130.5 (Ar-C), 120.8 (2C, Ar-C × 2), 117.3 (1-C), 64.0 (4-C), 34.4 (*C*H-(CH$_3$)$_2$), 33.1 (3-C), 31.4 (2C, *C*H-(CH$_3$)$_2$ × 2), 24.1 (2C, CH$_3$ × 2), 23.9 (4C, CH$_3$ × 4) ppm

HRMS (ESI) calculated for $C_{20}H_{31}O_2$: 303.2319, found: 303.2319

IR (neat): 2961, 2930, 2871, 1725, 1607, 1461, 1248, 1134, 1102, 1074, 917, 876 cm^{-1}

4.3 Preparation of 3-(2-methyl-1,3-dioxolan-2-yl)propyl 2,4,6-triisopropylbenzoate (29)

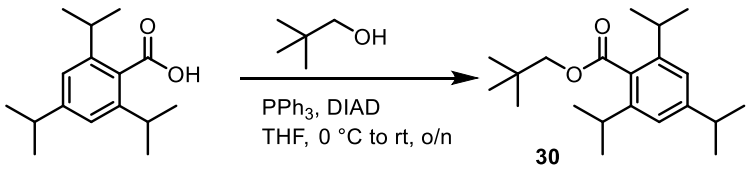


Following a modified literature reported procedure,[15] to a solution of 2,4,6-triisopropylbenzoic acid (2.20 g, 8.70 mmol) and Cs_2CO_3 (3.70 g, 11.9 mmol) in acetonitrile (90.0 mL) was added 5-chloro-2-pentanone ethylene ketal (1.30 g, 7.90 mmol) and the resulting reaction mixture was stirred at 82 °C for 24 h. After cooling to room temperature, the precipitate was filtrated off and the filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform (50 mL) and washed with 20% aq. $NaHCO_3$ solution (3 × 30 mL). The organic phases were combined, dried over $MgSO_4$,

filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, hexane:EtOAc = 80:20) afforded the pure benzoate **29** (2.51 g, 85%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.01 (s, 2H, Ar-H), 4.33 (t, *J* = 6.2 Hz, 2H, 1-H), 3.94 (m, 4H, O-CH_2 × 2), 2.87 (sept, *J* = 6.7 Hz, 3H, C*H*(CH_3)$_2$ × 3), 1.89–1.81 (m, 2H, 2-H), 1.79–1.75 (m, 2H, 3-H), 1.33 (s, 3H, 4-H), 1.25 (d, *J* = 6.8 Hz, 18H, CH_3 × 6) ppm
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 171.0 (CO), 150.0 (Ar-C), 144.7 (2C, Ar-C × 2), 130.6 (Ar-C), 120.8 (2C, Ar-C × 2), 109.6 (O-C-O), 65.0 (1-C), 64.7 (2C, O-CH_2 × 2), 35.7 (3-C), 34.4 (*C*H-(CH_3)$_2$), 31.5 (2C, *C*H-(CH_3)$_2$ × 2), 24.1 (4C, CH_3 × 4), 23.9 (2C, CH_3 × 2), 23.9 (2-C), 23.4 (4-C) ppm
IR (neat): 2961, 1722, 1462, 1250, 1137, 1068, 877, 754 cm^{-1}
HRMS (ESI) calculated for $C_{23}H_{36}NaO_4$: 399.2506, found: 399.2503

4.4 Preparation of neopentyl 2,4,6-triisopropylbenzoate (30)



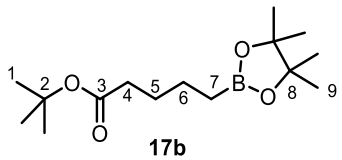
To a solution of 2,4,6-triisopropylbenzoic acid (20 g, 80.0 mmol), triphenyl phosphine (20 g, 76.0 mmol) and neopentyl alcohol (7.1 g, 80.0 mmol) in anhydrous THF (152 mL) was added diisopropyl azodicarboxylate (16 mL, 80.0 mmol) dropwise at 0 °C. The mixture was stirred for 20 min at 0 °C, then warmed to rt and stirred overnight. It was quenched with $NaHCO_3$ (120 mL) and H_2O (120 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 60 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow solid. Pentane (300 mL) was added to the solid and the resulting suspension was passed through a plug of SiO_2. The filtrate was concentrated under reduced pressure to give a pale oil. Purification by flash column chromatography (pentane:Et_2O = 98:2) gave the product benzoate **30** (23 g, 70 mmol, 93%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.01 (s, 2H, Ar-H), 3.98 (s, 2H, CH_2), 2.94–2.81 (m, 3H, CH), 1.26 (d, *J* = 7.0 Hz, 6H, CH_3 × 2), 1.25 (d, *J* = 6.8 Hz, 12H, CH_3 × 4), 0.99 (s, 9H, CH_3 × 3) ppm
^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.5 (CO), 150.0 (Ar-C), 144.8 (2C, Ar-C), 131.0 (Ar-C), 120.9 (2C, Ar-C), 74.9 (CH_2), 34.5 (CH), 31.7 (CH), 31.2 (*C*(CH_3)$_3$), 26.7 (3C, (*C*H_3)$_3$C), 24.3 (4C, CH_3 × 4), 24.1 (2C, CH_3 × 2) ppm
IR (neat): 2959, 2870, 1725, 1606 cm^{-1}
HRMS (ESI) calculated for $C_{21}H_{34}O_2Na$: 341.2451, found: 341.2452

5. Preparation of Boronic esters

Boronic esters **15**,[16] **17a**,[17] 2-(3-azidopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17c**),[18] (*E*)-*tert*-butyldimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)oxy)silane (**17d**),[19] 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17e**),[20] tert-butyl(((2*R*,4*S*)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)diphenylsilane (**17f**),[21] 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**17g**),[16] and 2-cyclohexyl-5,5-dimethyl-1,3,2-dioxaborinane (**17h**)[22] were prepared according to literature procedures and all spectroscopic data matched those previously reported.

5.1 Preparation of *tert*-butyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (17b)



17b

Boronic ester **17b** was prepared by a hydroboration of the corresponding terminal alkene using Miyaura's procedure.[23] A Schlenk flask was charged with $[Ir(cod)Cl]_2$ (58 mg, 0.086 mmol, 1.5 mol%) and dppe (68 mg, 3 mol%). *tert*-Butyl pent-4-enoate (893 mg, 5.72 mmol) in DCM (3 mL) was added to the flask. To the orange solution was added pinacolborane (1.08 mL, 7.44 mmol) dropwise at rt. The mixture was stirred overnight and quenched with H_2O (20 mL). The product was extracted with Et_2O (3 × 20 mL). Combined organic extracts were dried over $MgSO_4$ and concentrated. The crude was dissolved in pentane:Et_2O (90:10, 30 mL) and the white precipitate was removed by filtration. The product **17b** (1.13 g, 70% yield) was obtained as a yellow oil after column chromatography (pentane:Et_2O = 85:15).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.19 (t, *J* = 7.6 Hz, 2H), 1.58 (quint, *J* = 7.6 Hz, 2H), 1.46–1.38 (m, 2H), 1.43 (s, 9H), 1.23 (s, 12H), 0.78 (t, *J* = 7.8 Hz, 2H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 173.4 (3-C), 83.1 (2C, 8-C), 80.0 (2-C), 35.7, 28.3 (3C, 1-C), 27.9, 25.0 (4C, 9-C), 23.7 ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

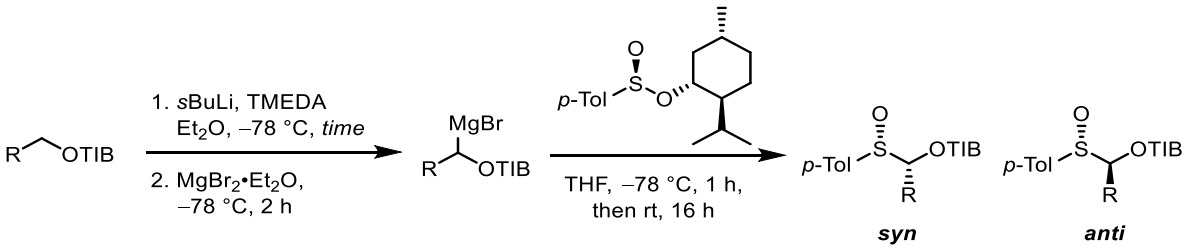
^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.4 ppm

IR (neat): 2978, 2934, 2865, 1730, 1368, 1319, 1145, 1142, 847 cm^{-1}

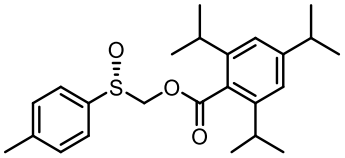
HRMS (ESI) calculated for $C_{15}H_{29}BNaO_4$: 307.2054, found: 307.2059

6. Preparation of α-Sulfinyl Benzoates

6.1 Preparation of α-sulfinyl benzoates by transmetalation

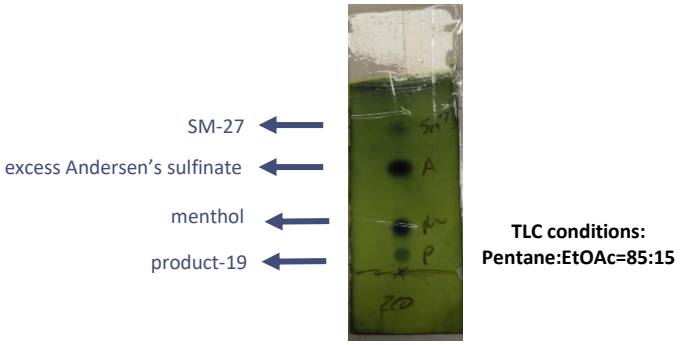


6.1.1 Preparation of (*S*)-(*p*-Tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate (19)



19

Following **GP1**, methyl benzoate **27** (5.00 g, 19.1 mmol), TMEDA (3.71 mL, 24.8 mmol), *s*BuLi (1.30 M in cyclohexane/hexane, 19.1 mL, 24.8 mmol – lithiation time = 30 min), Mg turnings (1.37 g, 57.2 mmol), dibromoethane (2.46 mL, 28.6 mmol) and (1*R*,2*S*,5*R*)-(–)-menthyl (*S*)-*p*-toluenesulfinate (8.15 g, 28.6 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 100:0→80:20) sulfoxide **19** (5.09 g, 67%) as a colourless solid.



[α]$^{24}_{D}$: +134 (*c* 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.2 Hz, 2H, ArH), 7.37 (d, *J* = 8.2 Hz, 2H, ArH), 7.02 (s, 2H, ArH), 5.28 (d, *J* = 10.4 Hz, 1H, CH*H*), 5.00 (d, *J* = 10.4 Hz, 1H, C*H*H), 2.90 (sept, *J* = 7.5 Hz, 1H, C*H*), 2.90 (sept, *J* = 6.9 Hz, 2H, CH × 2), 2.44 (s, 3H, CH_3), 1.25 (d, *J* = 6.9 Hz, 12H, CH_3 × 2), 1.23 (d, *J* = 6.9 Hz, 6H, CH_3 × 2) ppm

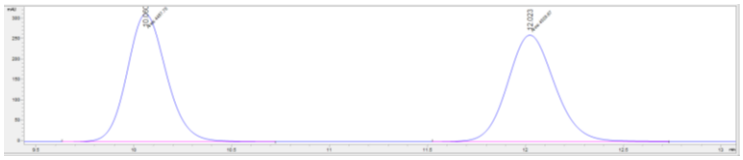
^{13}C NMR (101 MHz, $CDCl_3$): 169.8 (CO), 151.1 (C), 145.4 (2 × C), 142.5 (C), 137.4 (C), 130.3 (2 × CH), 128.6 (C), 124.8 (2 × CH), 121.1 (2 × CH), 83.4 (CH_2), 34.6 (CH), 31.8 (2 × CH), 24.4 (2 × CH_3), 24.3 (2 × CH_3), 24.1 (2 × CH_3), 21.6 (CH_3) ppm

IR (neat): 2961, 1745, 1227, 1035, 816 cm^{-1}

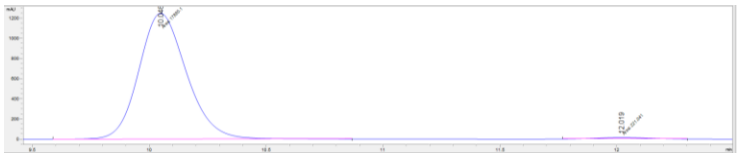
HRMS (ESI) calculated for $C_{24}H_{32}O_3SNa$: 423.1964, found 423.1974

M.P. 90–92 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm) with guard, hexane:isopropanol = 95:5, 1.0 mL/min, room temperature, 210.8 nm): tR = 10.05 minutes (major), 12.02 minutes (minor), e.r. = 99:1

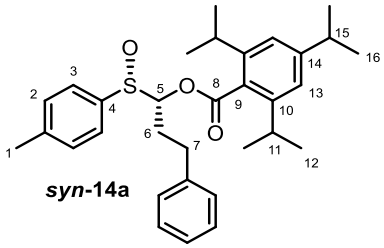


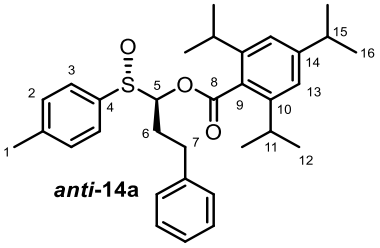
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.06	MM	4487.7	316.6	0.2363	49.768	0.863
2	12.023	MM	4529.7	264.4	0.2855	50.232	0.873



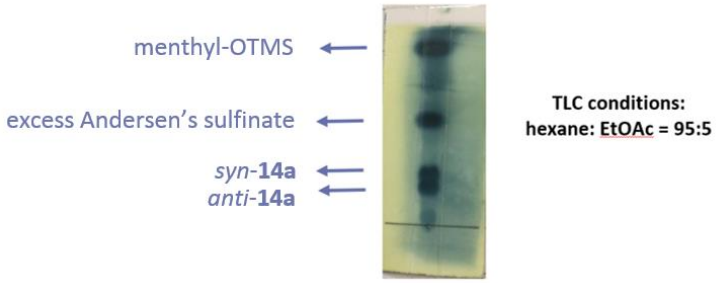
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.048	MM	17885.1	1255.6	0.2374	98.779	0.822
2	12.019	MM	221	13.5	0.273	1.221	1.051

6.1.2 Preparation of (*S*)-3-phenyl-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*syn*-14a) and (*R*)-3-phenyl-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*anti*-14a)





Following **GP1**, 3-phenylpropyl 2,4,6-triisopropylbenzoate (1.00 g, 2.70 mmol), TMEDA (485 µL, 3.24 mmol), *s*BuLi (1.30 M in cyclohexane/hexane, 2.50 mL, 3.24 mmol – lithiation time = 2 h), Mg turnings (263 mg, 10.8 mmol), dibromoethane (350 µL, 4.05 mmol), (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (1.19 g, 4.05 mmol), Et_3N (560 µL, 4.05 mmol) and TMSCl (450 µL, 3.51 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 95:5) the *syn* diastereoisomer *syn*-**14a** (less polar, 500 mg, 37%) as a colourless solid and the *anti* diastereoisomer *anti*-**14a** (more polar, 581 mg, 43%) as a colourless solid.



***syn*-14a**

[α]$^{22}_{D}$: +123 (*c* 0.9, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.60 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.21–7.15 (m, 3H, Ar-H), 7.07 (s, 2H, 14-H), 6.94 (d, *J* = 6.3 Hz, 2H, Ar-H), 5.64 (dd, J_1 = 9.7 Hz, J_2 = 2.9 Hz, 1H, 5-H), 2.96 (m, 3H, 11-H × 2 + 15-H), 2.78 (m, 1H, 7-H), 2.51 (m, 1H, 7-H), 2.45 (s, 3H, 1-H), 2.29 (m, 1H, 6-H), 1.99 (m, 1H, 6-H), 1.33–1.27 (m, 18H, CH_3 × 6) ppm

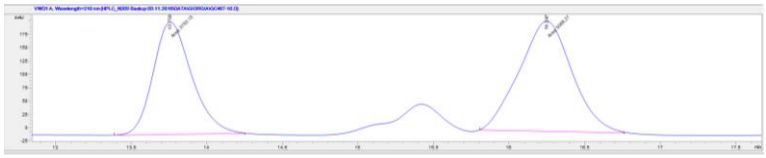
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.4 (CO), 150.9 (Ar-C), 145.2 (2C, Ar-C × 2), 141.5 (Ar-C), 139.9 (Ar-C), 137.4 (Ar-C), 130.0 (2C, Ar-C × 2), 128.8 (Ar-C), 128.4 (2C, Ar-C × 2), 128.1 (2C, Ar-C × 2), 126.2 (Ar-C), 124.2 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 92.0 (5-C), 34.5 (15-C), 31.7 (2C, 11-C), 30.8 (7-C), 24.6 (6-C), 24.4 (2C, CH-*C*H_3 × 2), 24.3 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.4 (1-C) ppm

IR (neat): 2960, 1731, 1239, 1060, 1048, 1027, 813, 756 cm^{-1}

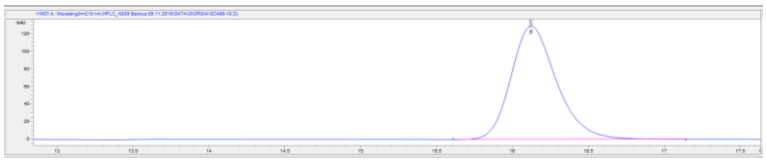
HRMS (ESI) calculated for $C_{32}H_{40}NaO_3S$: 527.2590, found: 527.2574

M.P. 99–101 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): t_R = 13.8 minutes (minor), 16.2 minutes (major), e.r. > 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.758	MM	3753.1	211.7	0.2955	42.546	0.778
2	16.247	MM	5068.3	207.9	0.4064	57.454	1.045



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.121	BB	2697.5	129.3	0.3176	100.000	0.76

***anti*-14a**

[α]$^{22}_D$: +11 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.31–7.26 (m, 4H, Ar-H), 7.21 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.09 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.07 (s, 2H, 14-H), 6.08 (dd, J_1 = 8.8 Hz, J_2 = 3.4 Hz, 1H, 5-H), 2.96 (app sept, *J* = 6.8 Hz, 3H, 11-H × 2 + 15-H), 2.78 (m, 2H, 7-H), 2.41 (s, 3H, 1-H), 2.21 (m, 1H, 6-H), 1.71 (m, 1H, 6-H), 1.30–1.25 (m, 18H, CH_3 × 6) ppm

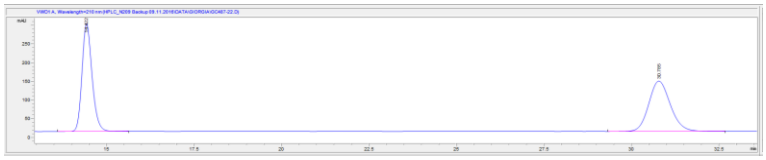
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.2 (CO), 150.8 (Ar-C), 145.2 (2C, Ar-C × 2), 142.1 (Ar-C), 139.9 (Ar-C), 136.1 (Ar-C), 129.9 (2C, Ar-C × 2), 128.9 (Ar-C), 128.6 (2C, Ar-C × 2), 128.2 (2C, Ar-C × 2), 126.4 (Ar-C), 125.5 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 87.8 (5-C), 34.4 (15-C), 31.7 (2C, 11-C × 2), 31.6 (7-C), 29.2 (6-C), 24.7 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.5 (1-C) ppm

IR (neat): 2962, 1734, 1460, 1229, 1067, 1042, 880, 815 cm^{-1}

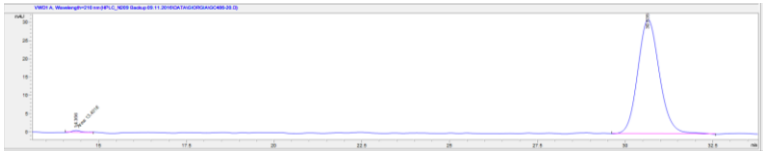
HRMS (ESI) calculated for $C_{32}H_{40}NaO_3S$: 527.2590, found: 527.2574

M.P. 91-93 ºC.

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.7 mL/min, room temperature, 210.8 nm): tR = 14.4 minutes (minor), 30.8 minutes (major), e.r. > 99:1

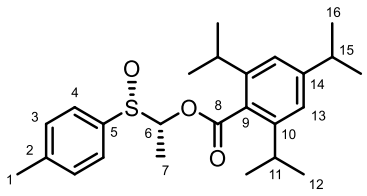


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.422	BB	5742.7	288.1	0.3039	49.932	0.781
2	30.785	BB	5758.4	134.2	0.6621	50.068	0.844

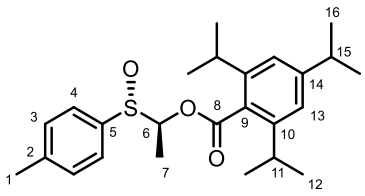


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.356	MM	13.4	6E-1	0.3722	0.990	0.585
2	30.635	BB	1340.4	31.2	0.6603	99.010	0.857

6.1.3 Preparation of (*S*)-1-((*S*)-*p*-tolylsulfinyl)ethyl 2,4,6-triisopropylbenzoate (*syn*-14b) and (*R*)-1-((*S*)-*p*-tolylsulfinyl)ethyl 2,4,6-triisopropylbenzoate (*anti*-14b)

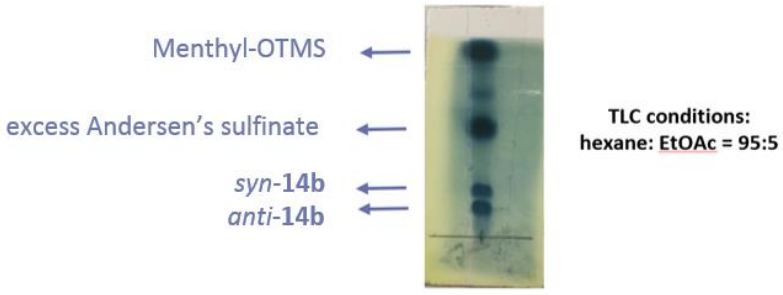


***syn*-14b**



***anti*-14b**

Following **GP1**, ethyl benzoate **1** (2.45 g, 8.86 mmol), TMEDA (1.59 mL, 10.64 mmol), *s*BuLi (1.3 M in cyclohexane/hexane, 8.18 mL, 10.6 mmol – lithiation time = 1 h), Mg turnings (869 mg, 36.2 mmol), dibromoethane (1.17 mL, 13.3 mmol), (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (3.91 g, 13.3 mmol), Et_3N (1.85 mL, 13.3 mmol) and TMSCl (1.46 mL, 11.6 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 95:5) the *syn* diastereoisomer *syn*-**14b** (less polar, 1.49 g, 41%) as a colourless solid and the *anti* diastereoisomer *anti*-**14b** (more polar, 1.48 g, 40%) as a colourless solid.



***syn*-14b**

[α]$^{24}_{D}$: +86 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.63 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.37 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.04 (s, 2H, 13-H), 5.79 (q, *J* = 6.4 Hz, 1H, 6-H), 2.90 (app sept, *J* = 6.8 Hz, 3H, 15-H + 11-H), 2.44 (s, 3H, 1-H), 1.40 (d, *J* = 6.4 Hz, 3H, 7-H), 1.29–1.24 (m, 18H, CH_3 × 6) ppm

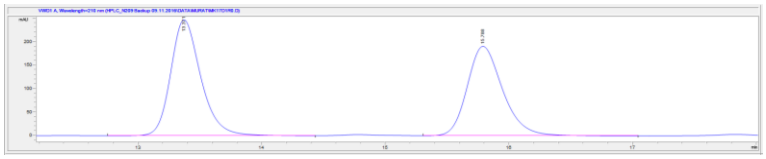
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.9 (CO), 150.9 (Ar-C), 145.2 (2C, Ar-C × 2), 141.7 (Ar-C), 137.5 (Ar-C), 130.0 (2C, Ar-C × 2), 128.7 (Ar-C), 124.4 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 89.0 (6-C), 34.5 (15-C), 31.6 (2C, 11-C), 24.2 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.4 (1-C), 9.1 (7-C) ppm

IR (neat): 2962, 1735, 1228, 1087, 1060, 1041, 874, 811 cm^{-1}

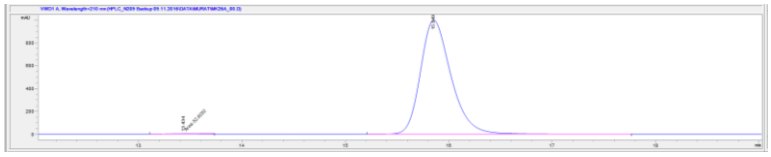
HRMS (ESI) calculated for $C_{25}H_{34}NaOS$: 437.212087, found: 437.210910

M.P. 117–119 ºC.

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 96:4, 0.5 mL/min, room temperature, 210.8 nm): tR = 13.4 minutes (minor), 15.8 minutes (major), e.r. > 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.371	BB	4170.1	246.7	0.2569	52.406	0.754
2	15.788	VB	3787.2	190.2	0.3037	47.594	0.76



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.434	MM	52.9	2.5	0.3529	0.260	1.502
2	15.849	BB	20277.3	994.3	0.3122	99.740	0.719

***anti*-14b**

[α]$^{21}_{D}$: +30 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.54 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.01 (s, 2H, 13-H), 6.07 (q, *J* = 6.4 Hz, 1H, 6-H), 2.90 (sept, *J* = 6.8 Hz, 1H, 15-H), 2.78 (sept, *J* = 6.8 Hz, 2H, 11-H), 2.41 (s, 3H, 1-H), 1.39 (d, *J* = 6.4 Hz, 3H, 7-H), 1.26–1.24 (m, 12H, 12-H), 1.19 (d, *J* = 6.0 Hz, 6H, 16-H) ppm

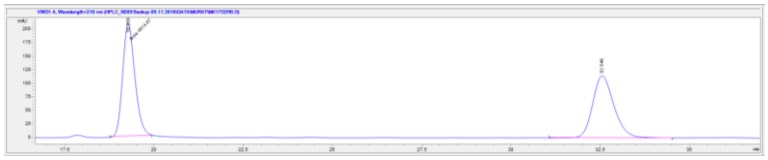
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.0 (CO), 150.7 (Ar-C), 145.1 (2C, Ar-C × 2), 142.1 (Ar-C), 136.0 (Ar-C), 129.8 (2C, Ar-C × 2), 128.8 (Ar-C), 125.6 (2C, Ar-C × 2), 120.9 (2C, Ar-C × 2), 85.0 (6-C), 34.4 (15-C), 31.5 (2C, 11-C), 24.5 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.4 (1-C), 13.1 (7-C) ppm

IR (neat): 2962, 1735, 1228, 1087, 1060, 1041, 874, 811 cm^{-1}

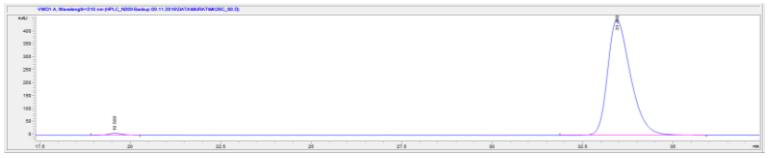
HRMS (ESI) calculated for $C_{25}H_{34}NaOS$: 437.212087, found: 437.210910

M.P. 95–97 ºC.

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 96:4, 0.5 mL/min, room temperature, 210.8 nm): tR = 19.3 minutes (minor), 32.5 minutes (major), e.r. = 99:1

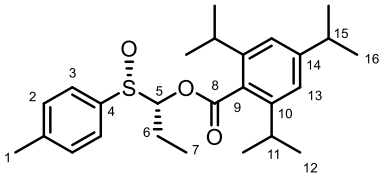


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.269	MM	4914.9	206.8	0.3961	51.009	0.802
2	32.546	BB	4720.5	114.1	0.6356	48.991	0.775

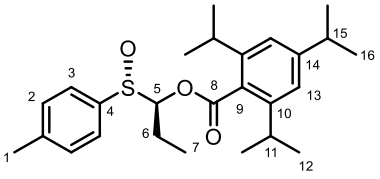


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.569	BB	184.3	7.6	0.3712	0.931	0.882
2	33.45	BB	19596.8	447.3	0.6655	99.069	0.647

6.1.4 Preparation of (*S*)-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*syn*-14c) and (*R*)-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*anti*-14c)

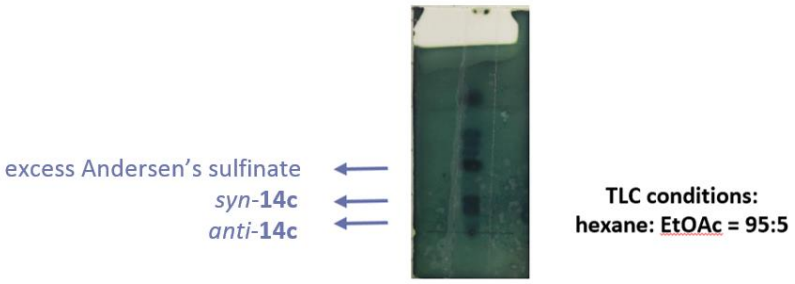


***syn*-14c**



***anti*-14c**

Following **GP1**, propyl 2,4,6-triisopropylbenzoate (2.90 g, 10.0 mmol), TMEDA (1.80 mL, 12.0 mmol), *s*BuLi (1.30 M in cyclohexane/hexane, 9.20 mL, 12.0 mmol – lithiation time = 1 h), Mg turnings (972 mg, 40.0 mmol), dibromoethane (1.30 mL, 15.0 mmol) and (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (4.40 g, 15.0 mmol), afforded after purification by flash column chromatography (hexane:EtOAc = 95:5 → 90:10) the *syn* diastereoisomer *syn*-**14c** (less polar, 1.10 g, 26%) as a colourless solid and the *anti* diastereoisomer *anti*-**14c** (more polar, 1.37 g, 32%) as a colourless oil that turned into a waxy colourless solid upon standing at room temperature.



***syn*-14c**

[α]$^{22}_{D}$: +92 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.04 (s, 2H, 13-H), 5.62 (dd, J_1 = 9.8 Hz, J_2 = 3.2 Hz, 1H, 5-H), 2.92 (app sest, *J* = 6.7 Hz, 3H, 11-H × 2 + 15-

H), 2.44 (s, 3H, 1-H), 2.01 (sept, J = 7.6 Hz, 1H, 6-H), 1.71 (m, 1H, 6-H), 1.29 (d, J = 6.8 Hz, 6H, CH_3 × 2), 1.26 (d, J = 6.9 Hz, 6H, CH_3 × 2), 1.25 (d, J = 6.6 Hz, 6H, CH_3 × 2), 0.95 (t, J = 7.4 Hz, 3H, 7-H) ppm

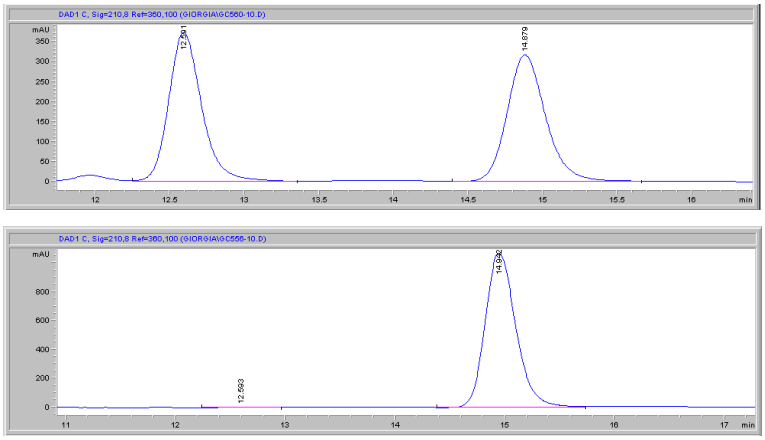
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.5 (CO), 150.8 (Ar-C), 145.2 (2C, Ar-C × 2), 141.5 (Ar-C), 137.6 (Ar-C), 130.0 (2C, Ar-C × 2), 128.9 (Ar-C), 124.4 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 93.8 (5-C), 34.4 (15-C), 31.6 (2C, 11-C × 2), 24.4 (2C, CH-*C*H_3 × 2), 24.2 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.5 (1-C), 16.7 (6-C), 9.4 (7-C) ppm

IR (neat): 3675, 2988, 2972, 2901, 1394, 1057, 892 cm^{-1}

HRMS (ESI) calculated for $C_{26}H_{36}NaO_3S$: 451.2277, found: 451.2278

M.P. 87-89 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 12.6 minutes (minor), 14.9 minutes (major), e.r. > 99:1



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.591	VB	0.2358	5728.54346	371.64734	50.3389
2	14.879	VB	0.2729	5651.41113	315.64185	49.6611

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.593	VV	0.2472	82.40370	4.08701	0.3928
2	14.942	VV	0.3018	2.08966e4	1070.01074	99.6072

***anti*-14c**

[α]$^{22}_D$: +20 (*c* 1.0, $CHCl_3$)

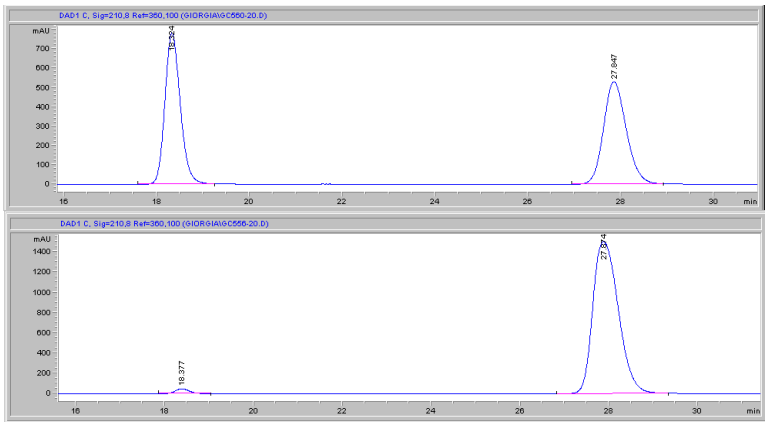
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, J = 8.1 Hz, 2H, Ar-H), 7.31 (d, J = 8.0 Hz, 2H, Ar-H), 7.02 (s, 2H, 13-H), 5.93 (dd, J_1 = 8.5 Hz, J_2 = 4.1 Hz, 1H, 5-H), 2.90 (sept, J = 6.9 Hz, 1H, 15-H), 2.84 (sept, J = 6.8 Hz, 2H, 11-H × 2), 2.41 (s, 3H, 1-H), 1.94 (m, 1H, 6-H), 1.45 (sept, J = 8.0 Hz, 1H, 6-H), 1.25 (d, J = 6.9 Hz, 6H, CH_3 × 2), 1.25 (d, J = 6.8 Hz, 6H, CH_3 × 2), 1.20 (d, J = 6.8 Hz, 6H, CH_3 × 2), 1.06 (t, J = 7.4 Hz, 3H, 7-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.4 (CO), 150.6 (Ar-C), 145.1 (2C, Ar-C × 2), 142.0 (Ar-C), 136.4 (Ar-C), 129.8 (2C, Ar-C × 2), 129.0 (Ar-C), 125.5 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 89.9 (5-C), 34.4 (15-C), 31.6 (2C, 11-C × 2), 24.6 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.5 (1-C), 21.0 (6-C), 9.8 (7-C) ppm

IR (neat): 3675, 2968, 1742, 1231, 1065, 752 cm^{-1}

HRMS (ESI) calculated for $C_{26}H_{36}NaO_3S$: 451.2277, found: 451.2278

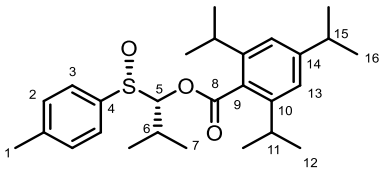
Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 18.3 minutes (minor), 27.8 minutes (major), e.r. = 98:2



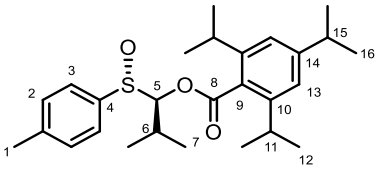
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.324	BB	0.3436	2262.10059	100.87549	50.2338
2	27.847	BB	0.5185	2241.04517	66.61805	49.7662

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.377	VV	0.3384	1096.58911	48.74957	1.8001
2	27.874	VB	0.4838	5.98218e4	1504.76941	98.1999

6.1.5 Preparation of (*S*)-2-methyl-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*syn*-14d) and (*R*)-2-methyl-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*anti*-14d)

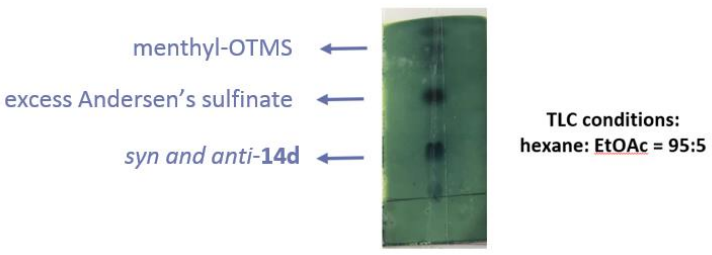


***syn*-14d**



***anti*-14d**

Following **GP1**, isobutyl 2,4,6-triisopropylbenzoate (0.51 g, 1.68 mmol), TMEDA (300 µL, 2.01 mmol), *s*BuLi (1.30 M in cyclohexane/hexane, 1.50 mL, 2.01 mmol – lithiation time = 1.5 h), Mg turnings (163 mg, 6.72 mmol), dibromoethane (220 µL, 2.52 mmol), (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (0.74 g, 2.52 mmol), Et_3N (350 µL, 2.52 mmol) and TMSCl (280 µL, 2.18 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 90:10) a 1.8:1 mixture of the *syn* diastereoisomer *syn*-**14d** and the *anti* diastereoisomer *anti*-**14d** (488 mg, 66% overall yield). A portion of the mixture (450 mg) was further purified by reverse phase HPLC (acetonitrile:water = 85:15, isocratic) to afford the *syn* diastereoisomer *syn*-**14d** (less polar, 112 mg, 15%) as a colourless solid and the *anti* diastereoisomer *anti*-**14d** (more polar, 215 mg, 29%) as a thick colourless oil.



***syn*-14d**

[α]$^{22}_{D}$: +41 (*c* 0.9, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.73 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.35 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.04 (s, 2H, 13-H), 5.72 (d, *J* = 4.9 Hz, 1H, 5-H), 2.94–2.81 (m, 3H, 11-H × 2 + 15-H), 2.54 (app sest, *J* = 6.8 Hz, 1H, 6-H), 2.43 (s, 3H, 1-H), 1.26 (d, *J* = 6.9 Hz, 12H, CH_3 × 4), 1.22 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 1.14 (d, *J* = 6.8 Hz, 3H, 7-H), 0.96 (d, *J* = 6.9 Hz, 3H, 7-H) ppm

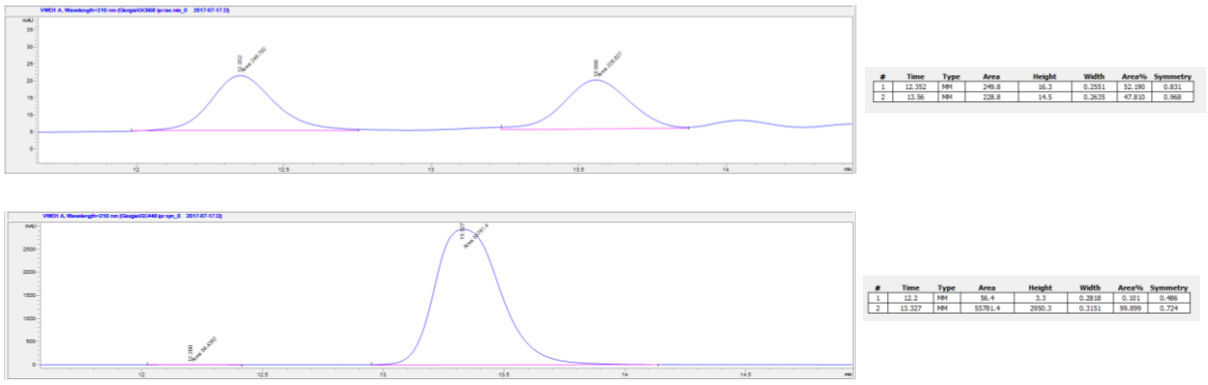
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.1 (CO), 150.7 (Ar-C), 145.2 (2C, Ar-C × 2), 141.7 (Ar-C), 138.2 (Ar-C), 129.9 (2C, Ar-C × 2), 128.7 (Ar-C), 125.3 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 95.8 (5-C), 34.4 (15-C), 31.4 (2C, 11-C × 2), 26.5 (6-C), 24.4 (2C, CH-*C*H_3 × 2), 24.3 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.4 (1-C), 20.1 (7-C), 17.5 (7-C) ppm

IR (neat): 2961, 1729, 1236, 1060, 1042, 812 cm^{-1}

HRMS (ESI) calculated for $C_{27}H_{38}NaO_3S$: 465.2434, found: 465.2439

M.P. 87–89 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 12.3 minutes (minor), 13.6 minutes (major), e.r. = >99:1



***anti*-14d**

[α]$^{22}_{D}$: +173 (*c* 1.0, $CHCl_3$)

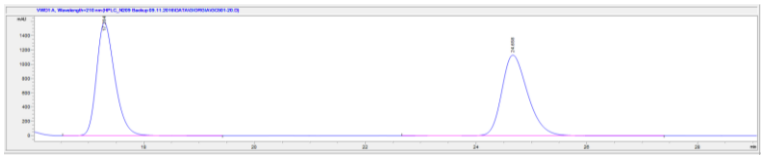
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.35 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.04 (s, 2H, 13-H), 5.89 (d, *J* = 3.5 Hz, 1H, 5-H), 3.03 (sept, *J* = 6.7 Hz, 2H, 11-H × 2), 2.90 (sept, *J* = 6.9 Hz, 1H, 15-H), 2.43 (s, 3H, 1-H), 1.95 (m, 1H, 6-H), 1.26 (d, *J* = 6.9 Hz, 12H, CH_3 × 4), 1.23 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 1.06 (app t, *J* = 6.4 Hz, 6H, 7-H × 2) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.6 (CO), 150.5 (Ar-C), 145.5 (2C, Ar-C × 2), 142.3 (Ar-C), 138.3 (Ar-C), 130.1 (2C, Ar-C × 2), 129.2 (Ar-C), 125.7 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 94.5 (5-C), 34.4 (15-C), 31.3 (2C, 11-C × 2), 28.6 (6-C), 24.5 (4C, CH-*C*H_3 × 4), 23.9 (2C, CH-*C*H_3 × 2), 21.5 (1-C), 19.5 (7-C), 17.3 (7-C) ppm

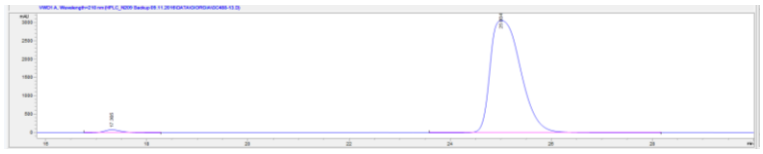
IR (neat): 2962, 1740, 1461, 1230, 1063, 1048, 877, 810 cm^{-1}

HRMS (ESI) calculated for $C_{27}H_{38}NaO_3S$: 465.2434, found: 465.2439

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 17.3 minutes (minor), 24.7 minutes (major), e.r. = 98:2

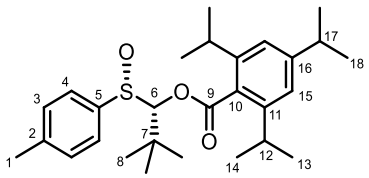


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.284	VB	36487	1588.4	0.351	49.768	0.707
2	24.658	VB R	36827.8	1131.6	0.4988	50.232	0.731

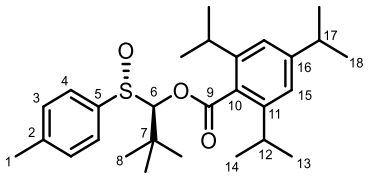


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.305	BB	1819.8	81.7	0.3414	1.396	0.763
2	25.004	BB	128499.8	3085.6	0.6577	98.604	0.532

6.1.6 Preparation of (*S*)-2,2-dimethyl-1-((*S*)-*p*-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*syn*-14e) and (*R*)-2,2-dimethyl-1-((*S*)-*p*-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*anti*-14e)

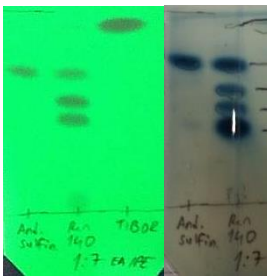


***syn*-14e**



***anti*-14e**

Following **GP1**, neopentyl benzoate **30** (1.00 g, 3.14 mmol), TMEDA (610 µL, 4.08 mmol), *s*BuLi (1.30 M in cyclohexane/hexane, 3.14 mL, 4.08 mmol – lithiation time = 2 h), Mg turnings (303 mg, 12.6 mmol), dibromoethane (410 µL, 4.71 mmol) and (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (1.39 g, 4.71 mmol), afforded after purification by flash column chromatography (hexane:EtOAc = 90:10 → 80:20) the *syn* diastereoisomer *syn*-**14e** (less polar, 557 mg, 39%) as a colourless solid and the *anti* diastereoisomer *anti*-**14e** (more polar, 654 mg, 46%) as a colourless solid.



***syn*-14e**

[α]$^{20}_{D}$: +50 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78 (d, *J* = 8.0 Hz, 2H, 4-H), 7.33 (d, *J* = 8.0 Hz, 2H, 3-H), 7.05 (s, 2H, 15-H), 5.61 (s, 1H, 6-H), 3.00–2.87 (m, 3H, 12-H + 17-H), 2.42 (s, 3H, 1-H), 1.29 (d, *J* = 7.5 Hz, 6H, 13-H), 1.28 (d, *J* = 7.3 Hz, 6H, 18-H), 1.24 (d, *J* = 6.8 Hz, 6H, 14-H), 1.12 (s, 9H, 8-H) ppm

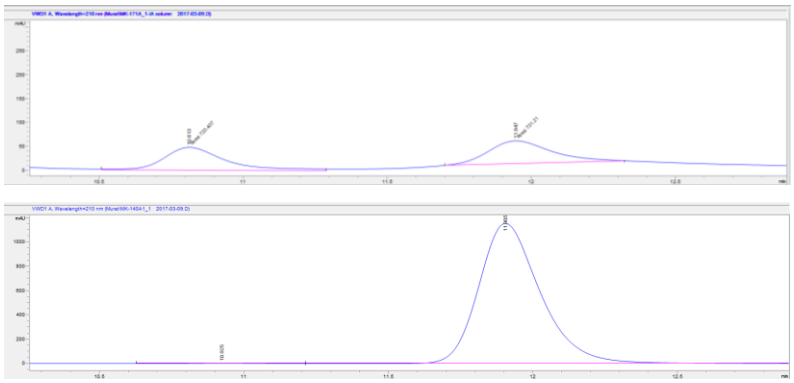
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.4 (9-C), 150.9 (16-C), 145.7 (2C, 11-C), 141.3 (2-C), 139.6 (5-C), 129.8 (2C, 3-C), 128.8 (10-C), 125.4 (2C, 4-C), 121.2 (2C, 15-C), 98.6 (6-C), 38.2 (7-C), 34.5 (17-C), 31.6 (2C, 12-C), 26.6 (3C, 8-C), 24.8 (2C, 13-C), 24.3 (2C, 14-C), 24.0 (2C, 18-C), 21.6 (1-C) ppm

IR (neat): 2962, 2929, 2871, 1730, 1606, 1461, 1235, 1058, 1040, 814 cm^{-1}

HRMS (ESI) calculated for $C_{28}H_{40}NaO_3S$: 479.2590, found: 479.2594

M.P. 90–92 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 97:3, 0.5 mL/min, room temperature, 210.8 nm): tR = 10.8 minutes (minor), 11.9 minutes (major), e.r. > 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.813	MM	720.4	48	0.2501	49.628	0.675
2	11.947	MM	731.2	47.7	0.2554	50.372	0.77

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.925	BB	31.7	2.5	0.1807	0.185	0.863
2	11.905	VB R	17117.2	1158.9	0.2229	99.815	0.728

***anti*-14e**

[α]$^{20}_{D}$: +180 (*c* 0.7, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.63 (d, *J* = 8.0 Hz, 2H, 4-H), 7.33 (d, *J* = 8.0 Hz, 2H, 3-H), 7.02 (s, 2H, 15-H), 5.66 (s, 1H, 6-H), 3.12 (sept, *J* = 6.8 Hz, 2H, 12-H), 2.89 (sept, *J* = 7.0 Hz, 1H, 17-H), 2.41 (s, 3H, 1-H), 1.25 (d, *J* = 7.0 Hz, 6H, 18-H), 1.24 (d, *J* = 6.8 Hz, 6H, 13-H), 1.21–1.19 (m, 15H, 14-H + 8-H) ppm

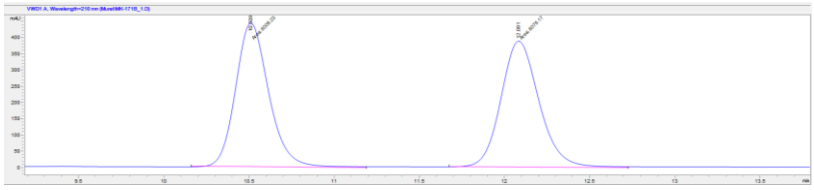
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.3 (9-C), 150.6 (16-C), 146.1 (2C, 11-C), 141.5 (2-C), 140.5 (5-C), 129.9 (2C, 3-C), 128.9 (10-C), 125.6 (2C, 4-C), 121.3 (2C, 15-C), 95.7 (6-C), 35.7 (7-C), 34.5 (17-C), 31.3 (2C, 12-C), 26.6 (3C, 8-C), 24.9 (2C, 13-C), 24.5 (2C, 14-C), 24.0 (18-C), 21.6 (1-C) ppm

IR (neat): 2962, 2870, 1738, 1607, 1461, 1230, 1066, 1036, 878, 810 cm^{-1}

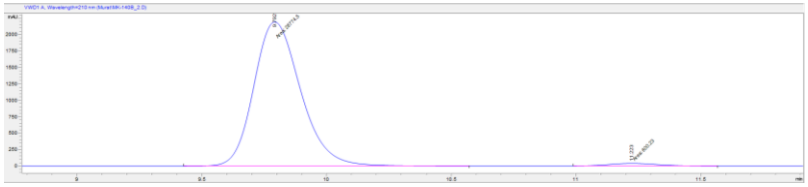
HRMS (ESI) calculated for $C_{28}H_{40}NaO_3S$: 479.2590, found: 479.2594

M.P. 84–86 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.7 mL/min, room temperature, 210.8 nm): tR = 9.8 minutes (minor), 11.2 minutes (major), e.r. = 98:2

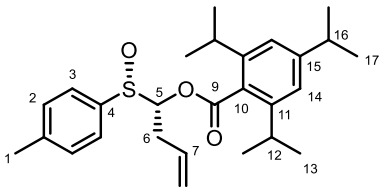


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.509	MM	6008.2	443.1	0.226	49.711	0.812
2	12.081	MM	6078.2	388.6	0.2607	50.289	0.841

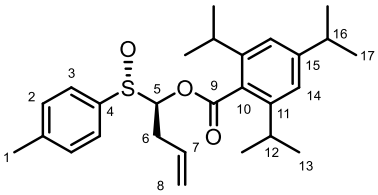


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.792	MM	28774.5	2202.4	0.2178	97.957	0.782
2	11.223	MM	600.2	41.7	0.2398	2.043	0.868

6.1.7 Preparation of (*S*)-1-((*S*)-*p*-tolylsulfinyl)but-3-en-1-yl 2,4,6-triisopropylbenzoate (*syn*-14f) and (*R*)-1-((*S*)-*p*-tolylsulfinyl)but-3-en-1-yl 2,4,6-triisopropylbenzoate (*anti*-14f)

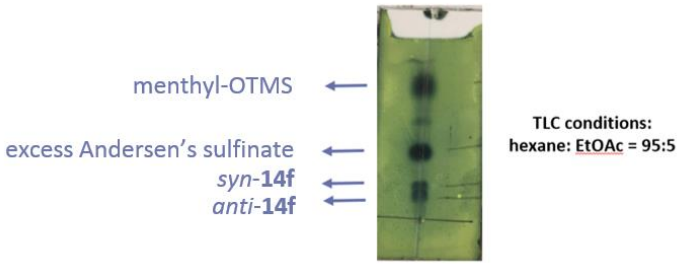


***syn*-14f**



***anti*-14f**

Following **GP1**, homoallylic benzoate **28** (700 mg, 2.31 mmol), TMEDA (417 µL, 2.78 mmol), *s*BuLi (1.35 M in cyclohexane/hexane, 2.0 mL, 2.78 mmol – lithiation time = 1 h), Mg turnings (225 mg, 9.24 mmol), dibromoethane (300 µL, 3.47 mmol), (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (1.36 g, 4.62 mmol), Et_3N (485 µL, 3.47 mmol) and TMSCl (380 µL, 3.00 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 95:5) the *syn* diastereoisomer *syn*-**14f** (less polar, 285 mg, 28%) as a colourless solid and the *anti* diastereoisomer *anti*-**14f** (more polar, 395 mg, 39%) as a dense colourless oil.



***syn*-14f**

[α]$^{22}_{D}$: +163 (*c* 0.3, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.67 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.38 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.04 (s, 2H, 14-H), 5.75 (dd, J_1 = 10.0 Hz, J_2 = 3.0 Hz, 1H, 5-H), 5.67 (m, 1H, 7-H), 5.11–5.06 (m, 2H, 7-H + 8-H), 2.91 (app sept, *J* = 6.6 Hz, 3H, 12-H + 16-H), 2.72 (m, 1H, 6-H), 2.44 (s, 3H, 1-H), 2.42 (m, 1H, 6-H), 1.28–1.23 (m, 18H, CH_3 × 6) ppm

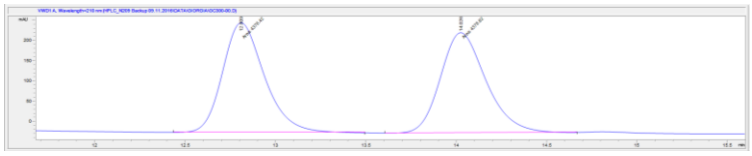
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.1 (CO), 150.7 (Ar-C), 145.1 (2C, Ar-C × 2), 141.6 (Ar-C), 137.2 (Ar-C), 131.3 (Ar-C), 130.0 (2C, Ar-C × 2), 128.7 (7-C), 124.3 (2C, Ar-C × 2), 120.9 (2C, Ar-C × 2), 119.2 (8-C), 91.3 (5-C), 34.3 (16-C), 31.4 (6-C), 27.7 (2C, 12-C), 24.3 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.8 (2C, CH-*C*H_3 × 2), 21.3 (1-C) ppm

IR (neat): 2961, 1740, 1230, 1056, 1038, 877, 809 cm^{-1}

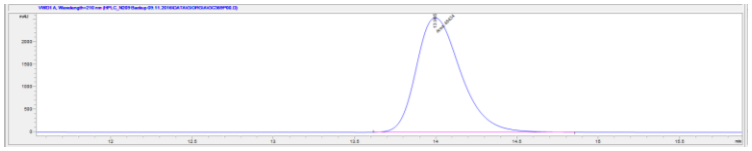
HRMS (ESI) calculated for $C_{27}H_{36}NaO_3S$: 463.2277, found: 463.2276

M.P. 85–87 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 12.8 minutes (minor), 14.0 minutes (major), e.r. > 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.809	MM	4376.4	271.8	0.2684	49.986	0.774
2	14.026	MM	4378.8	248.4	0.2938	50.014	0.785



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.995	MM	48434	2553.6	0.3161	100.000	0.715

***anti*-14f**

[α]$^{25}_D$: –8 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.02 (s, 2H, 14-H), 6.07 (dd, J_1 = 8.9 Hz, J_2 = 3.6 Hz, 1H, 5-H), 5.78 (m, 1H, 7-H), 5.15 (m, 2H, 7-H + 8-H), 2.90 (sept, *J* = 7.0 Hz, 1H, 16-H), 2.83 (sept, *J* = 6.7 Hz, 2H, 12-H × 2), 2.70 (m, 1H, 6-H), 2.42 (s, 3H, 1-H), 2.08 (m, 1H, 6-H), 1.26–1.18 (m, 18H, CH_3 × 6) ppm

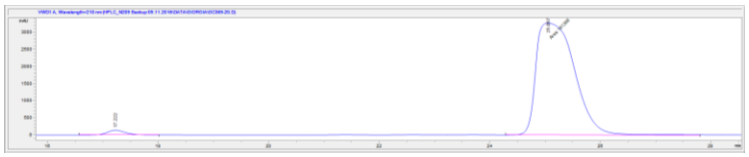
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.1 (CO), 150.6 (Ar-C), 145.2 (2C, Ar-C × 2), 142.1 (Ar-C), 136.0 (Ar-C), 131.3 (Ar-C), 129.8 (2C, Ar-C × 2), 128.8 (7-C), 125.4 (2C, Ar-C × 2), 120.9 (2C, Ar-C × 2), 119.5 (8-C), 87.2 (5-C), 34.3 (16-C), 31.8 (6-C), 31.3 (2C, 12-C), 24.4 (2C, CH-*C*H_3 × 2), 24.0 (2C, CH-*C*H_3 × 2), 23.8 (2C, CH-*C*H_3 × 2), 21.4 (1-C) ppm

IR (neat): 2961, 1740, 1230, 1056, 1038, 877, 809 cm^{-1}

HRMS (ESI) calculated for $C_{27}H_{36}NaO_3S$: 463.2277, found: 463.2276

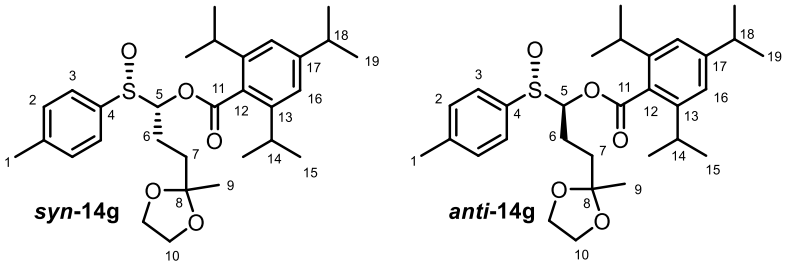
Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 16.7 minutes (minor), 24.2 minutes (major), e.r. = 98:2

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	16.723	BB	15799.6	740.3	0.3262	49.915	0.753
2	24.206	MM	15853.2	509	0.5191	50.085	0.775

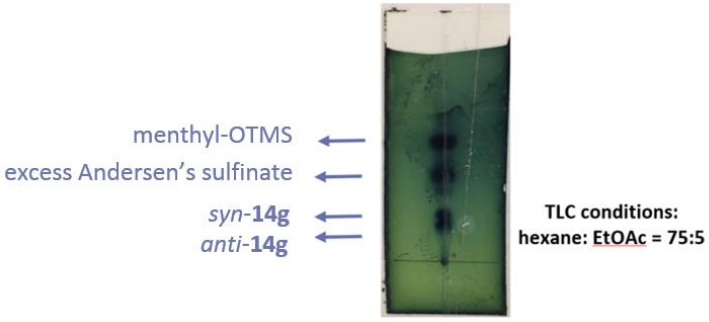


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.222	BB	3126.2	138.3	0.3452	1.901	0.798
2	25.057	MM	161368.1	3304.9	0.8138	98.099	0.46

6.1.8 Preparation of (*S*)-3-(2-methyl-1,3-dioxolan-2-yl)-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*syn*-14g) and (*R*)-3-(2-methyl-1,3-dioxolan-2-yl)-1-((*S*)-p-tolylsulfinyl)propyl 2,4,6-triisopropylbenzoate (*anti*-14g)



Following **GP1**, ketal benzoate **29** (1.45 g, 3.85 mmol), TMEDA (870 µL, 5.78 mmol), *s*BuLi (1.30 M in cyclohexane/hexane, 4.40 mL, 5.78 mmol – lithiation time = 2 h), Mg turnings (374 mg, 15.5 mmol), dibromoethane (500 µL, 5.78 mmol) and (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (1.70 g, 5.78 mmol), afforded after purification by flash column chromatography (hexane:EtOAc = 75:25 → 70:30) the *syn* diastereoisomer *syn*-**14g** (less polar, 367 mg, 19%) as a colourless solid and the *anti* diastereoisomer *anti*-**14g** (more polar, 659 mg, 33%) as a colourless oil that turned into a waxy colourless solid upon standing at room temperature.



***syn*-14g**

[α]$^{22}_{D}$: +64 (*c* 0.7, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.36 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.04 (s, 2H, 13-H), 5.78 (dd, J_1 = 10.2 Hz, J_2 = 2.1 Hz, 1H, 5-H), 3.83 (m, 2H, 10-H), 3.72–3.60 (m, 2H, 10-H), 2.99–2.88 (m, 3H, 14-H × 2 and 18-H), 2.43 (s, 3H, 1-H), 2.05 (m, 1H, 6-H), 1.83–1.73 (m, 2H, 7-H), 1.64 (m, 1H, 6-H), 1.29 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 1.26 (d, *J* = 6.9 Hz, 12H, CH_3 × 4), 1.16 (s, 3H, 9-H) ppm

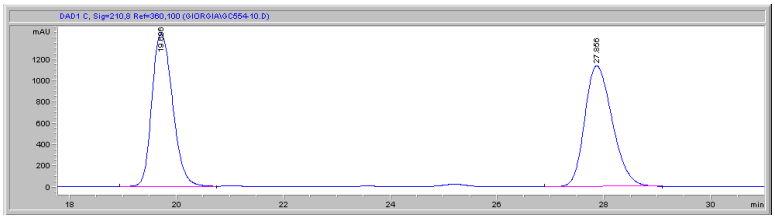
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.4 (CO), 150.8 (Ar-C), 145.2 (2C, Ar-C × 2), 141.4 (Ar-C), 137.6 (Ar-C), 129.9 (2C, Ar-C × 2), 128.9 (Ar-C), 124.3 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 109.3 (8-C), 92.5 (5-C), 64.7 (10-C), 64.4 (10-C), 34.4 (18-C), 33.6 (7-C), 31.5 (2C, 14-C × 2), 24.4 (2C, CH-*C*H_3 × 2), 24.2 (2C, CH-*C*H_3 × 2), 23.9 (9-C), 23.9 (CH-*C*H_3), 23.9 (CH-*C*H_3), 21.4 (1-C), 17.6 (6-C) ppm

IR (neat): 3675, 2988, 2901, 1394, 1250, 1066, 1057, 892 cm^{-1}

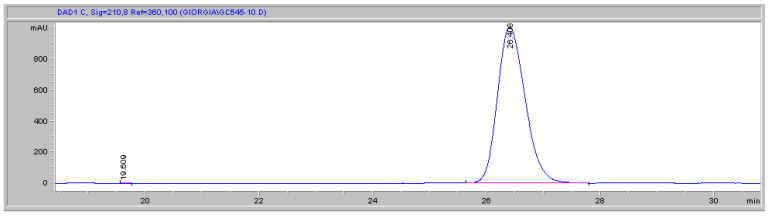
HRMS (ESI) calculated for $C_{30}H_{42}NaO_5S$: 537.2645, found: 537.2641

M.P. 71–73 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 19.7 minutes (minor), 27.8 minutes (major), e.r. > 99:1



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.696	VB	0.4219	3.92311e4	1439.80762	48.9997
2	27.856	BB	0.5563	4.08329e4	1133.42981	51.0003



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.860	VV	0.3266	115.64310	4.28786	0.3392
2	26.408	BB	0.5242	3.39788e4	1005.62115	99.6608

***anti*-14g**

[α]$^{22}_D$: +47 (*c* 1.0, $CHCl_3$)

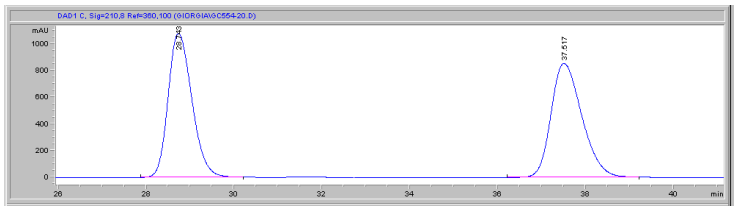
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.56 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.31 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.01 (s, 2H, 13-H), 6.09 (dd, J_1 = 8.2 Hz, J_2 = 4.2 Hz, 1H, 5-H), 3.92 (m, 2H, 10-H), 3.84 (m, 2H, 10-H), 2.90 (sept, *J* = 6.9 Hz, 1H, 18-H), 2.82 (sept, *J* = 6.8 Hz, 2H, 14-H × 2), 2.41 (s, 3H, 1-H), 2.04 (m, 1H, 6-H), 1.84 (m, 2H, 7-H), 1.58 (m, 1H, 6-H), 1.26–1.20 (m, 21H, CH_3 × 6 + 9-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.20 (CO), 150.6 (Ar-C), 145.1 (2C, Ar-C × 2), 142.0 (Ar-C), 136.4 (Ar-C), 129.8 (2C, Ar-C × 2), 128.9 (Ar-C), 125.5 (2C, Ar-C × 2), 120.9 (2C, Ar-C × 2), 109.2 (8-C), 88.4 (5-C), 64.7 (10-C), 64.7 (10-C), 34.4 (14-C), 34.3 (7-C), 31.5 (2C, 18-C × 2), 24.6 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (CH_3), 23.9 (CH_3), 23.9 (CH_3), 22.5 (6-C), 21.4 (1-C) ppm

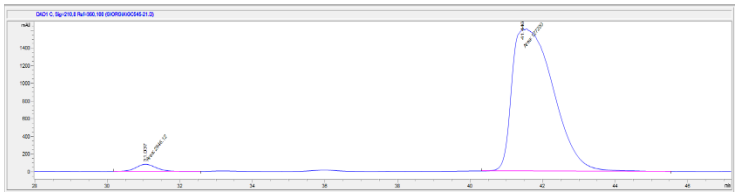
IR (neat): 3675, 2962, 1736, 1230, 1040, 812 cm^{-1}

HRMS (ESI) calculated for $C_{30}H_{42}NaO_5S$: 537.2645, found: 537.2641

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 28.7 minutes (minor), 37.5 minutes (major), e.r. = 98:2

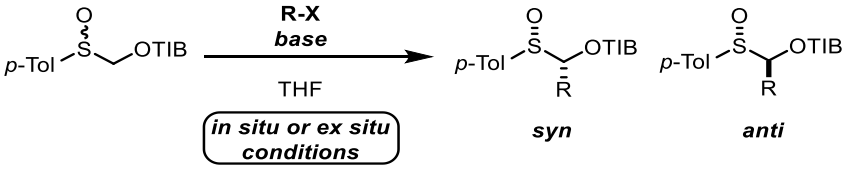


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.743	PB	0.5717	4.04683e4	1078.54944	49.3256
2	37.517	VB	0.7090	4.15750e4	852.47467	50.6744

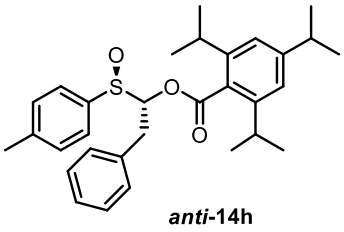


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	31.037	MM	2946.1	78.9	0.6226	2.264	0.842
2	41.446	MM	127199.8	1604.6	1.3212	97.736	0.364

6.2 Preparation of α-sulfinyl benzoates by alkylation



6.2.1 Preparation of (*S*)-2-phenyl-1-((*R*)-*p*-tolylsulfinyl)ethyl 2,4,6-triisopropylbenzoate (*anti*-14h)



According to **GP 2** using ((*R*)-*p*-tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (400 mg, 1.00 mmol), LiHMDS (1.0 M in THF, 2.00 mL, 2.00 mmol) and benzyl bromide (140 µL, 1.10 mmol). The crude residue (d.r. = 10:1) was purified by silica gel chromatography (pentane:EtOAc = 100:0 → 91:9) which gave *anti*-**14h** (311 mg, 63%) as a colourless oil.

[α]$^{22}_{D}$: +45 (*c* 1.0, $CHCl_3$)

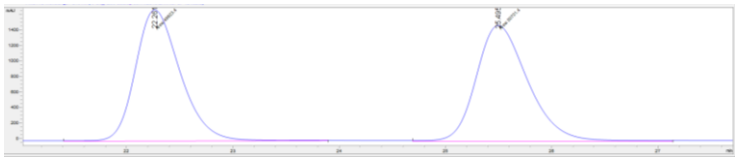
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H, ArH), 7.36–7.20 (m, 7H, ArH), 6.97 (s, 2H, ArH), 6.37 (dd, J_1 = 10.0 Hz, J_2 = 4.0 Hz, 1H, CH), 3.32 (d, *J* = 14.6 Hz, 1H, C*H*H), 2.88 (sept, *J* = 6.8 Hz, 1H, CH), 2.59 (dd, J_1 = 14.8 Hz, J_2 =10.0 Hz, 1H, CH*H*), 2.47 (sept, *J* = 6.8 Hz, 2H, CH × 2), 2.43 (s, 3H, CH_3), 1.24 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 1.08 (app. t, *J* = 6.8 Hz, 12H, CH_3 × 4) ppm

^{13}C NMR (101 MHz, $CDCl_3$): 169.2 (CO), 150.8 (C), 145.3 (2 × C), 142.3 (C), 136.2 (C), 135.1 (C), 130.1 (2 × CH), 129.3 (2 × CH), 128.9 (C), 128.8 (2 × CH), 127.3 (CH), 125.6 (2 × CH), 121.0 (2 × CH), 88.3 (CH), 34.5 (CH), 33.4 (CH_2), 31.4 (2 × CH), 24.5 (2 × CH_3), 24.3 (2 × CH_3), 24.0 (2 × CH_3), 21.6 (CH_3) ppm

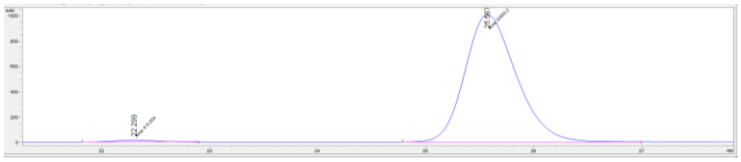
IR (neat): 2965, 2233, 1734, 1233, 1031, 730 cm^{-1}

HRMS (ESI) calculated for $C_{31}H_{38}O_3SNa$: 513.2434, found 513.2442

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm) with guard, hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 22.30 minutes (minor), 25.57 minutes (major), e.r. = 99:1

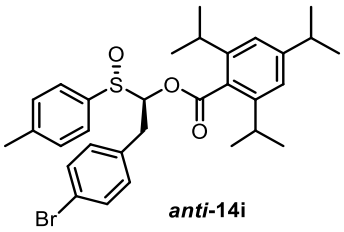


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.261	MM	49923.4	1687.2	0.4932	49.613	0.733
2	25.495	MM	50701.4	1488.9	0.5676	50.387	0.723



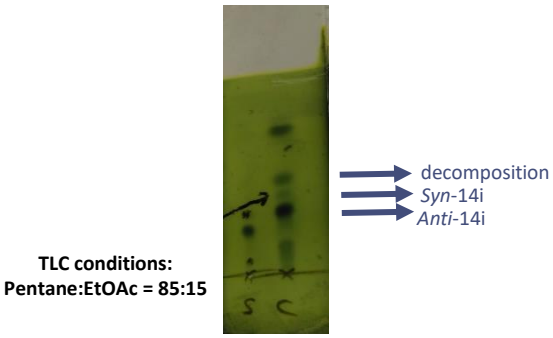
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.299	MM	415.9	14.8	0.4674	1.224	0.981
2	25.567	MM	33553.2	1007.7	0.555	98.776	0.761

6.2.2 Preparation of (*R*)-2-(4-bromophenyl)-1-((*S*)-*p*-tolylsulfinyl)ethyl 2,4,6-triisopropylbenzoate (*anti*-14i)



anti-14i

According to **GP 2** using ((*S*)-*p*-tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (1.00 g, 2.50 mmol), LiHMDS (1.0 M in THF, 5.00 mL, 5.00 mmol) and 4-bromobenzyl bromide (929 mg, 3.75 mmol). The crude residue (d.r. = 15:1) was purified by silica gel chromatography (pentane:EtOAc = 100:0 → 91:9) which gave *anti*-**14i** (568 mg, 40%) as a colourless crystalline solid.



[α]$^{22}_D$: –82 (*c* 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.1 Hz, 2H, ArH), 7.42 (d, *J* = 8.3 Hz, 2H, ArH), 7.34 (d, *J* = 8.1 Hz, 2H, ArH), 7.08 (d, *J* = 8.3 Hz, 2H, ArH), 6.96 (s, 2H, ArH), 6.31 (dd, J_1 = 10.2 Hz, J_2 =3.8 Hz, 1H, CH), 3.25 (dd, J_1 = 14.4 Hz, J_2 = 3.8 Hz, 1H, C*H*H), 2.87 (sept, *J* = 6.8 Hz, 1H, CH), 2.50 (dd, J_1 = 14.4 Hz, J_2 =10.2 Hz, 1H, CH*H*), 2.43 (s, 3H, CH_3), 2.41 (sept, *J* = 6.8 Hz, 2H, CH × 2), 1.23 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 1.10 (d, *J* = 6.8 Hz, 6H, CH_3 × 2) 1.08 (d, *J* = 6.8 Hz, 6H, CH_3 × 2) ppm

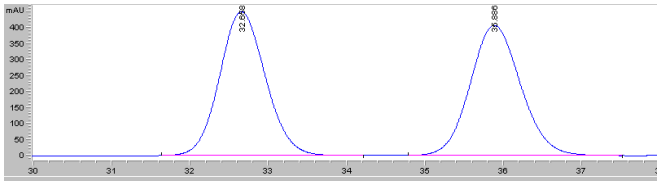
^{13}C NMR (101 MHz, $CDCl_3$): 169.1 (CO), 150.9 (C), 145.3 (C), 142.4 (C), 136.0 (C), 134.2 (C), 131.9 (2 × CH), 131.1 (2 × CH), 130.2 (2 × CH), 128.7 (C), 125.6 (2 × CH), 127.3 (CH), 121.3 (C), 121.0 (2 × CH), 87.9 (CH), 34.5 (CH), 32.8 (CH_2), 31.5 (2 × CH), 24.4 (2 × CH_3), 24.3 (2 × CH_3), 24.0 (2 × CH_3), 21.6 (CH_3) ppm

IR (neat): 2962, 1736, 1229, 1039, 810 cm^{-1}

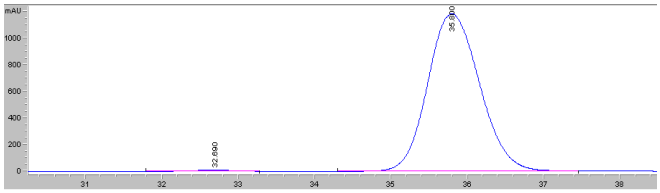
HRMS (ESI) calculated for $C_{31}H_{37}BrO_3SNa$: 591.1539, found 591.1541

M.P. 114–116 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm) with guard, hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 32.70 minutes (minor), 35.80 minutes (major), e.r. >99:1

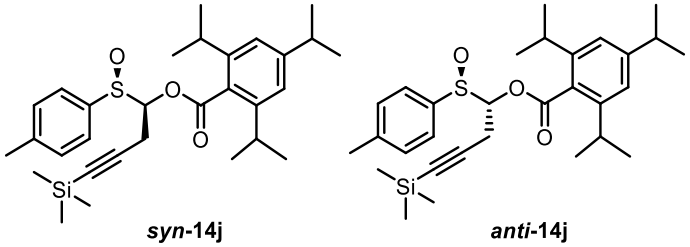


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	A
1	32.658	BB	0.6374	1.84946e4	451.94720	50
2	35.886	BP	0.6962	1.83782e4	408.99823	49



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.690	BV	0.4772	398.13724	9.98506	0.7056
2	35.800	VB	0.6425	5.60285e4	1183.17224	99.2944

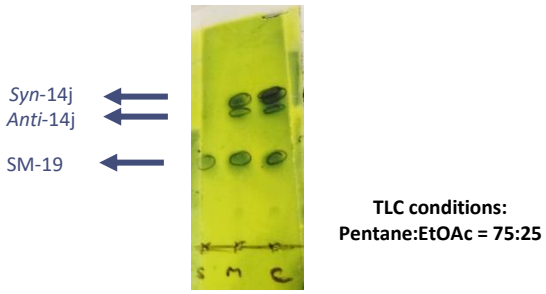
6.2.3 Preparation of (*R*)-1-((*R*)-*p*-tolylsulfinyl)-4-(trimethylsilyl)but-3-yn-1-yl 2,4,6-triisopropylbenzoate (*syn*-14j) and (*S*)-1-((*R*)-*p*-tolylsulfinyl)-4-(trimethylsilyl)but-3-yn-1-yl 2,4,6-triisopropylbenzoate (*anti*-14j)



***syn*-14j** ***anti*-14j**

((*R*)-*p*-Tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (400 mg, 1.00 mmol) in an oven dried Schlenk tube was dissolved in anhydrous THF (4.00 mL). The solution was cooled to –78 °C and 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex (1.0 M in THF/toluene, 1.05 mL, 1.05 mmol) was added dropwise. The solution was stirred for 20 min, at which point a solution

of 3-bromo-1-(trimethylsilyl)-1-propyne (495 µL, 3.00 mmol) in THF (1.0 mL) was added dropwise. The reaction mixture was stirred at –78 °C for a further 2 h and then the cooling bath was removed and the solution was stirred at room temperature for 30 min. The reaction mixture was quenched with sat. NH_4Cl solution (5 mL) and diluted with EtOAc (5 mL). The layers were separated and the aqueous phase was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure. The crude residue (d.r. = 2.5:1) was purified by silica gel chromatography (pentane:EtOAc = 100:0 → 93:7) which gave *syn*-**14j** (*less polar*,160 mg, 31%) and *anti*-**14j** (*more polar*, 70.0 mg, 14%) as colourless amorphous solids. Further elution (pentane:EtOAc = 93:7 → 75:25) gave recovered starting material (154 mg, 39%) as a colourless crystalline solid.



***syn*-14j**

[α]$^{22}_{D}$: –40 (*c* 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.8 Hz, 2H, ArH), 7.37 (d, *J* = 8.8 Hz, 2H, ArH), 7.05 (s, 2H, ArH), 5.84 (dd, J_1 = 8.7 Hz, J_2 =3.8 Hz, 1H, CH), 3.02-2.82 (m, 4H, C*H*H and CH × 3), 2.72 (dd, J_1 = 18.0 Hz, J_2 = 3.8 Hz, 1H, CH*H*), 2.45 (s, 3H, CH_3), 1.30–1.25 (m, 18H, CH_3 × 6), 0.08 (s, 9H, $Si(CH_3)_3$) ppm

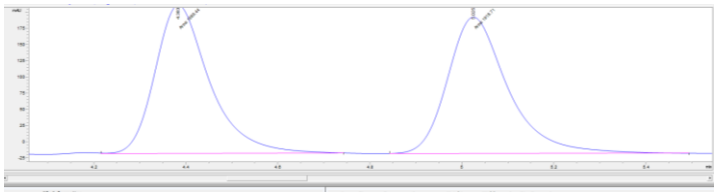
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1 (CO), 151.2 (C), 145.6 (2 × C), 142.1 (C), 137.0 (C), 130.3 (2 × CH), 128.6 (C), 124.7 (2 × CH), 121.2 (2 × CH), 100.0 (C), 90.3 (CH), 88.1 (C), 34.6 (CH), 31.6 (2 × CH), 24.6 (2 × CH_3), 24.4 (2 × CH_3), 24.0 (2 × CH_3), 21.6 (CH_3), 16.4 (CH_2), 0.0 (3 × CH_3) ppm

IR (neat): 2961, 2182, 1736, 1041, 837 cm^{-1}

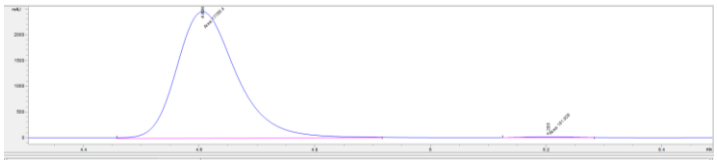
HRMS (ESI) calculated for $C_{30}H_{42}O_3SSiNa$: 533.2516, found 533.2504

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm) with guard, hexane:isopropanol = 95:5, 1.0 mL/min, room temperature, 210.8 nm): tR = 4.60 minutes (major), 5.20 minutes (minor), e.r. > 99:1

Note: *Syn* Diastereomer **14j** decomposes in its neat form at room temperature and should be stored in a freezer where it is stable for over several months.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.383	MM T	1889.4	229.1	0.1374	49.616	0.716
2	5.025	MM T	1918.7	210.7	0.1518	50.384	0.724



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.606	MM T	17788.4	2455.8	0.1207	99.098	0.739
2	5.203	MM T	161.9	22.3	0.1209	0.902	0.901

***anti*-14j**

[α]$^{22}_{D}$: +29 (*c* 1.0, $CHCl_3$)

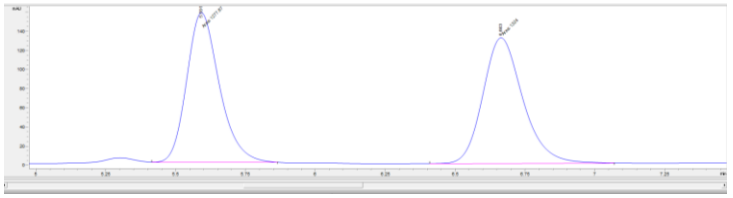
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 (d, *J* = 8.4 Hz, 2H, ArH), 7.02 (s, 2H, ArH), 6.06 (dd, J_1 = 7.4 Hz, J_2 = 4.4 Hz, 1H, CH), 2.96 (dd, J_1 = 17.5 Hz, J_2 = 4.4 Hz, 1H, CH*H*), 2.92–2.78 (m, 3H, CH × 3), 2.41 (s, 3H, CH_3), 2.31 (dd, J_1 = 17.5 Hz, J_2 = 7.4 Hz, 1H, CH*H*), 1.27–1.18 (m, 18H, CH_3 × 6), 0.15 (s, 9H, $Si(CH_3)_3$) ppm

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0 (CO), 151.0 (C), 145.5 (2 × C), 142.4 (C), 136.0 (C), 130.1 (2 × CH), 128.6 (C), 125.5 (2 × CH), 121.1 (2 × CH), 99.5 (C), 89.0 (C), 86.5 (CH), 34.6 (CH), 31.7 (2 × CH), 25.0 (2 × CH_3), 24.0 (4 × CH_3), 21.6 (CH_3), 20.2 (CH_2), 0.0 (3 × CH_3) ppm

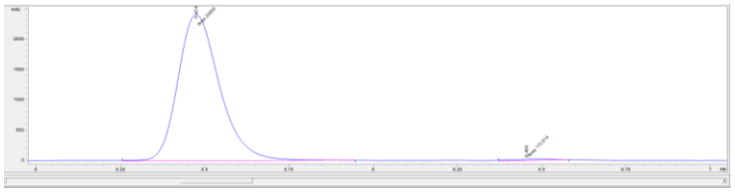
IR (neat): 2967, 2181, 1746, 1054, 839 cm^{-1}

HRMS (ESI) calculated for $C_{30}H_{42}O_3SSiNa$: 533.2516, found 533.2510

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm) with guard, hexane:isopropanol = 95:5, 1.0 mL/min, room temperature, 210.8 nm): tR = 5.47 minutes (major), 6.46 minutes (minor), e.r. > 99:1

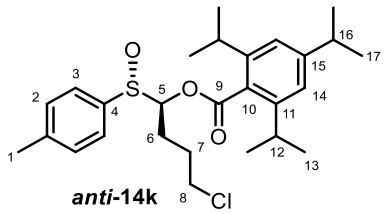


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.591	MM T	1277.9	156.6	0.136	49.113	0.79
2	6.663	MM T	1324	131.6	0.1676	50.887	0.802



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.474	MM T	20800	2416.8	0.1434	99.176	0.75
2	6.455	MM T	172.8	19.8	0.1523	0.824	0

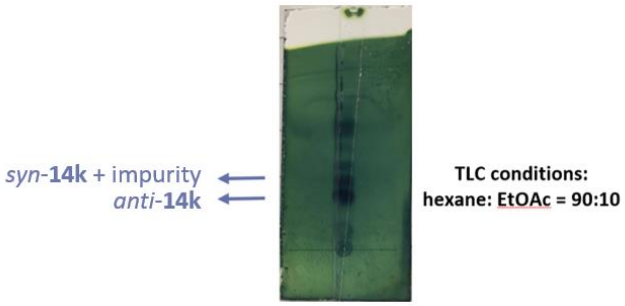
6.2.4 Preparation of (*R*)-4-chloro-((*S*)-p-tolylsulfinyl)butyl 2,4,6-triisopropylbenzoate (*anti*-14k)



***anti*-14k**

Following **GP2**, ((*S*)-*p*-tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (1.00 g, 2.50 mmol), 1-chloro-3-iodopropane (1.00 g, 5.00 mmol), *i*Pr_2NH (700 µL, 5.00 mmol), *n*BuLi (1.6 M in hexane, 3.10

mL, 5.00 mmol) and HMPA (870 µL, 5.00 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 90:10) the *syn* diastereoisomer *syn*-**14k** (less polar, mixed with impurity) and the *anti* diastereoisomer *anti*-**14k** (more polar, 482 mg, 40%) as a colourless solid.



[α]$^{22}_{D}$: –15 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.56 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.03 (s, 2H, 14-H), 6.02 (dd, J_1 = 8.4 Hz, J_2 = 3.4 Hz, 1H, 5-H), 3.49 (m, 2H, 8-H), 2.91 (sept, *J* = 6.9 Hz, 1H, 16-H), 2.84 (sept, *J* = 6.8 Hz, 2H, 12-H × 2), 2.42 (s, 3H, 1-H), 2.06–1.90 (m, 3H, 7-H × 2 + 6-H), 1.60 (m, 1H, 6-H), 1.26 (d, *J* = 6.8 Hz, 12H, CH_3 × 4), 1.21 (d, *J* = 6.8 Hz, 6H, CH_3 × 2) ppm

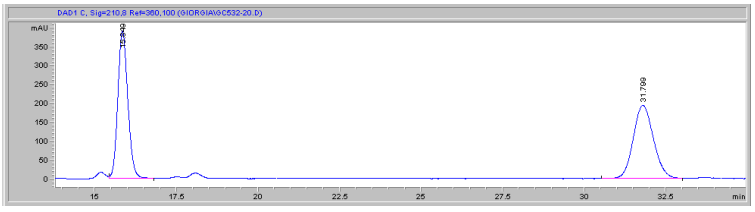
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.2 (CO), 150.8 (Ar-C), 145.2 (2C, Ar-C × 2), 142.3 (Ar-C), 136.1 (Ar-C), 130.0 (2C, Ar-C × 2), 128.7 (Ar-C), 125.5 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 87.6 (5-C), 43.8 (8-C), 34.4 (16-C), 31.6 (2C, 12-C × 2), 28.3 (7-C), 25.2 (6-C), 24.5 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.5 (1-C) ppm

IR (neat): 3675, 2965, 1741, 1229, 1073, 1040 cm^{-1}

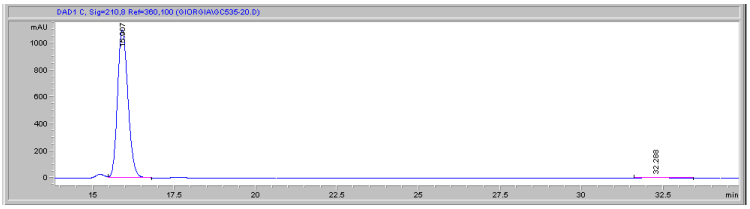
HRMS (ESI) calculated for $C_{27}H_{37}ClNaO_3S$: 499.2044, found: 499.2044

M.P. 95–97 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.7 mL/min, room temperature, 210.8 nm): tR = 15.8 minutes (major), 31.8 minutes (minor), e.r. = 99:1

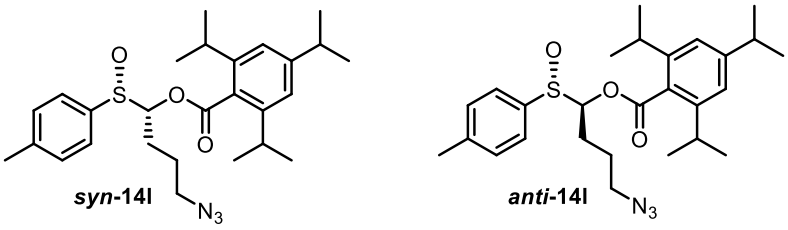


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.849	VB	0.3323	8411.31055	392.06799	50.1070
2	31.799	VV	0.6194	8375.37891	194.12285	49.8930



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.907	VB	0.3548	2.45615e4	1098.77454	98.7785
2	32.288	VV	0.5321	303.72989	6.89234	1.2215

6.2.5 Preparation of (*S*)-4-azido-1-((*S*)-*p*-tolylsulfinyl)butyl 2,4,6-triisopropylbenzoate (*syn*-14l) and (*R*)-4-azido-1-((*S*)-*p*-tolylsulfinyl)butyl 2,4,6-triisopropylbenzoate (*anti*-14l)



Following **GP2**, ((*S*)-*p*-tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (400 mg, 1.00 mmol), 1-azido-3-iodopropane (421 mg, 2.00 mmol), *i*Pr_2NH (280 µL, 2.00 mmol), *n*BuLi (1.6 M in hexane, 1.25 mL, 2.00 mmol) and HMPA (350 µL, 2.00 mmol) afforded after purification by flash column chromatography (petroleum ether:EtOAc = 10:1) the *syn* diastereoisomer *syn*-**14l** (less polar, 54 mg, 11%) as a colourless oil and the *anti* diastereoisomer *anti*-**14l** (more polar, 122 mg, 25%) as a colourless solid.

***syn*-14l**

$[\alpha]^{24}_D$: –47 (*c* 1.0, $CHCl_3$)

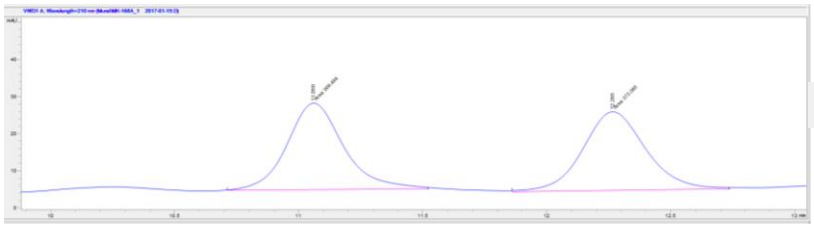
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.38 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.05 (s, 2H, Ar-H), 5.67 (dd, J_1 = 9.8 Hz, J_2 = 2.8 Hz, 1H, CH), 3.25–3.18 (m, 2H, CH_2), 2.91 (sept, *J* = 6.9 Hz, 3H, CH × 3), 2.45 (s, 3H,CH_3), 2.10–2.01 (m, 1H), 1.77–1.68 (m, 2H, CH_2), 1.55–1.50 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H, CH_3 × 2), 1.26 (d, *J* = 6.9 Hz, 12H, CH_3 × 4) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.5 (CO), 151.2 (Ar-C), 145.4 (2C, Ar-C), 142.0 (Ar-C), 137.4 (Ar-C), 130.3 (2C, Ar-C), 128.7 (Ar-C), 124.4 (2C, Ar-C), 121.2 (2C, Ar-C), 92.1 (CH), 50.9 (CH_2), 34.6 (CH), 31.9 (2C, CH × 2), 24.5 (3C, CH_3 × 2 + CH_2), 24.3 (2C, CH_3 × 2), 24.0 (2C, CH_3 × 2), 21.6 (CH_3), 20.7 (CH_2) ppm

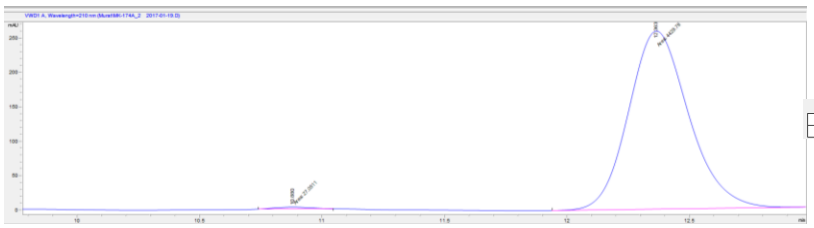
IR (neat): 2962, 2871, 2097, 1732, 1606, 1234, 1045, 845, 812 cm^{-1}

HRMS (ESI) calculated for $C_{27}H_{37}N_3NaO_3S$: 506.2448, found: 506.2445

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 96:4, 0.8 mL/min, room temperature, 210.8 nm): tR = 10.9 minutes (minor), 12.4 minutes (major), e.r. = 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.88	MM	27.1	2.7	0.1673	0.607	0.947
2	12.363	MM	4429.8	258.4	0.2857	99.393	0.841



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.059	MM	369.5	23.2	0.2651	49.760	0.861
2	12.265	MM	373.1	21.1	0.2945	50.240	0.905

***anti*-14l**

[α]$^{23}_{D}$: +46 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.33 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.03 (s, 2H, Ar-H), 6.01 (dd, J_1 = 8.7 Hz, J_2 = 3.8 Hz, 1H, CH), 3.39–3.16 (m, 2H, CH_2), 2.97–2.73 (m, 3H, CH × 3), 2.42 (s, 3H, CH_3), 1.99–1.89 (m, 1H), 1.78–1.69 (m, 2H, CH_2), 1.54–1.43 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 12H, CH_3 × 4), 1.21 (d, *J* = 6.8 Hz, 6H, CH_3 × 2) ppm

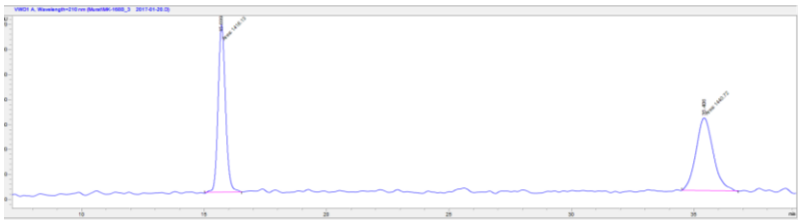
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.4 (CO), 151.0 (Ar-C), 145.3 (2C, Ar-C), 142.5 (Ar-C), 136.2 (Ar-C), 130.1 (2C, Ar-C), 128.8 (Ar-C), 125.6 (2C, Ar-C), 121.2 (2C, Ar-C), 87.8 (CH), 50.9 (CH_2), 34.6 (CH), 31.8 (2C, CH × 2), 25.1 (CH_2), 25.0 (CH_2), 24.7 (2C, CH_3 × 2), 24.2 (2C, CH_3 × 2), 24.1 (2C, CH_3 × 2), 21.7 (CH_3) ppm

IR (neat): 2962, 2099, 1041 cm^{-1}

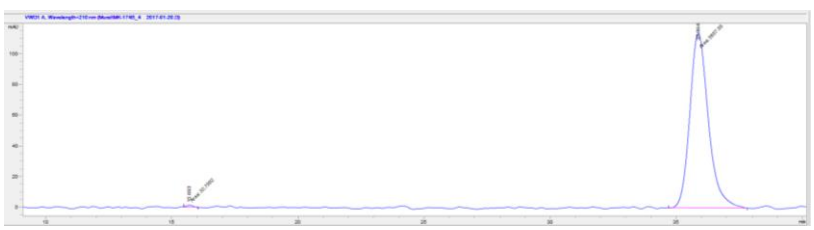
HRMS (ESI) calculated for $C_{27}H_{37}N_3NaO_3S$: 506.2448, found: 506.2445

M.P. 120–122 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 96:4, 0.8 mL/min, room temperature, 210.8 nm): tR = 15.7 minutes (minor), 35.9 minutes (major), e.r. > 99:1

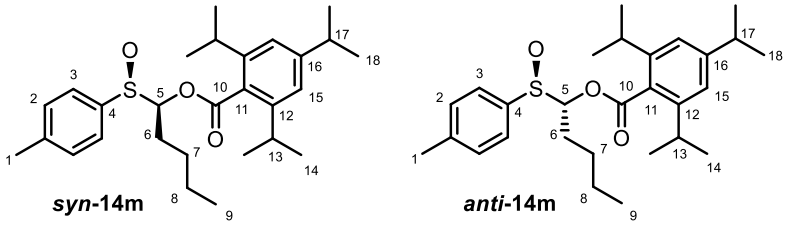


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.699	MM	1416.1	66.8	0.3531	49.570	0.872
2	35.406	MM	1440.7	29.2	0.8234	50.430	0.866

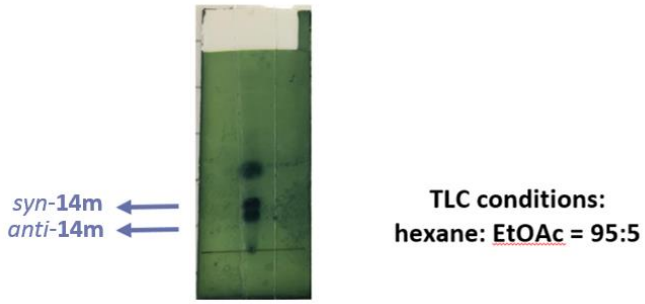


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.693	MM	30.8	1.6	0.3247	0.523	0.994
2	35.864	MM	5857.6	114	0.8567	99.477	0.804

6.2.6 Preparation of (*R*)-1-((*R*)-*p*-tolylsulfinyl)pentyl 2,4,6-triisopropylbenzoate (*syn*-14m) and (*S*)-1-((*R*)-*p*-tolylsulfinyl)pentyl 2,4,6-triisopropylbenzoate (*anti*-14m)



Following **GP2**, ((*S*)-*p*-tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (601 mg, 1.50 mmol), butyl trifluoromethanesulfonate (260 µL, 1.65 mmol), NaHMDS (1.0 M in THF, 1.60 mL, 1.58 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 95:5) the *syn* diastereoisomer *syn*-**14m** (less polar, 290 mg, 42%) as a colourless solid and the *anti* diastereoisomer *anti*-**14m** (more polar, 246 mg, 36%) as a colourless solid.



***syn*-14m**

[α]$^{22}_{D}$: –126 (*c* 1.3, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.65 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.37 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.05 (s, 2H, 13-H), 5.67 (dd, J_1 = 10.2 Hz, J_2 = 2.8 Hz, 1H, 5-H), 2.93 (app sept, *J* = 7.0 Hz, 3H, 13-H × 2 + 17-H), 2.44 (s, 3H, 1-H), 2.00 (m, 1H, 6-H), 1.61 (m, 1H, 6-H), 1.41 (m, 1H, 7-H), 1.34–1.16 (m, 3H, 7-H + 8-H), 1.29 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 1.26 (d, *J* = 6.7 Hz, 12H, CH_3 × 4), 0.80 (t, *J* = 7.4 Hz, 3H, 9-H) ppm

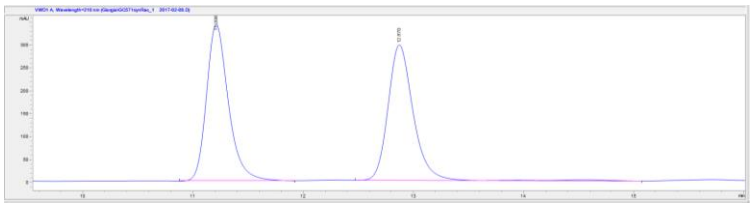
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.5 (CO), 150.8 (Ar-C), 145.2 (2C, Ar-C × 2), 141.5 (Ar-C), 137.5 (Ar-C), 130.0 (2C, Ar-C × 2), 128.9 (Ar-C), 124.4 (2C, Ar-C × 2), 120.9 (2C, Ar-C × 2), 92.5 (5-C), 34.4 (17-C), 31.6 (2C, 13-C × 2), 26.9 (7-C), 24.4 (2C, CH-*C*H_3 × 2), 24.2 (2C, CH-*C*H_3 × 2), 23.9 (CH-*C*H_3), 23.9 (CH-*C*H_3), 22.6 (6-C), 22.2 (8-C), 21.4 (1-C), 13.7 (9-C) ppm

IR (neat): 2960, 1735, 1461, 1232, 1046, 753 cm^{-1}

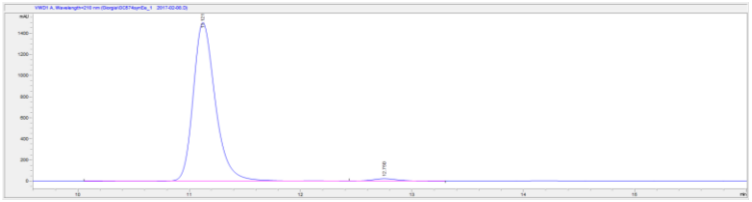
HRMS (ESI) calculated for $C_{28}H_{40}NaO_3S$: 479.259037, found: 479.258003

M.P. 104–106 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 11.2 minutes (major), 12.9 minutes (minor), e.r. = 98:2



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.208	BB	4710	341.9	0.2084	49.954	0.746
2	12.87	BV R	4718.6	295	0.2397	50.046	0.769



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.121	VV R	20929.9	1507.5	0.2112	98.281	0.74
2	12.75	VB E	366.1	22.8	0.2386	1.719	0.88

***anti*-14m**

[α]$^{22}_{D}$: –14 (*c* 1.3, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.31 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.03 (s, 2H, 13-H), 6.00 (m, 1H, 5-H), 2.94–2.82 (m, 3H, 13-H × 2 + 17-H), 2.42 (s, 3H, 1-H), 1.85 (m, 1H, 6-H), 1.47–1.39 (m, 3H, 6-H + 7-H), 1.35–1.29 (m, 2H, 8-H), 1.25 (d, *J* = 6.9 Hz, 12H, CH_3 × 4), 1.21 (d, *J* = 6.8 Hz, 6H, CH_3 × 2), 0.85 (t, *J* = 7.4 Hz, 3H, 9-H) ppm

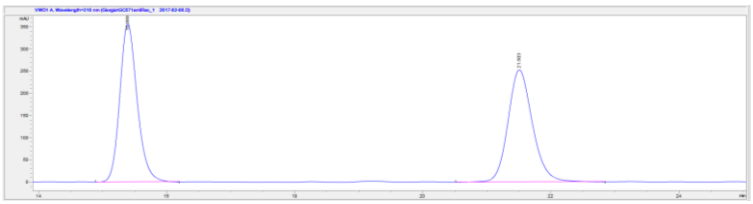
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.3 (CO), 150.6 (Ar-C), 145.1 (2C, Ar-C × 2), 142.0 (Ar-C), 136.5 (Ar-C), 129.8 (2C, Ar-C × 2), 129.0 (Ar-C), 125.5 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 88.5 (5-C), 34.4 (17-C), 31.5 (2C, 13-C × 2), 27.3 (7-C), 27.1 (6-C), 24.6 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (CH-*C*H_3), 23.9 (CH-*C*H_3), 22.2 (8-C), 21.5 (1-C), 13.7 (9-C) ppm

IR (neat): 3675, 2968, 2901, 1736, 1394, 1230, 1066, 1044, 879 cm^{-1}

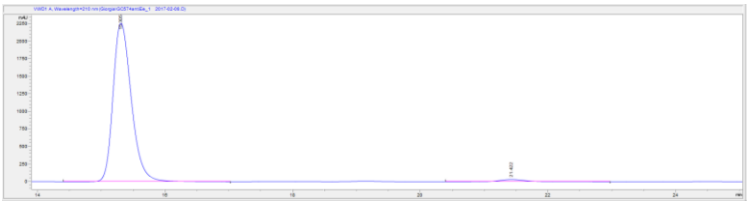
HRMS (ESI) calculated for $C_{28}H_{40}NaO_3S$: 479.259037, found: 479.258003

M.P. 112–114 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 15.4 minutes (major), 21.5 minutes (minor), e.r. = 98:2

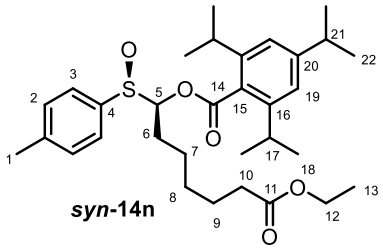


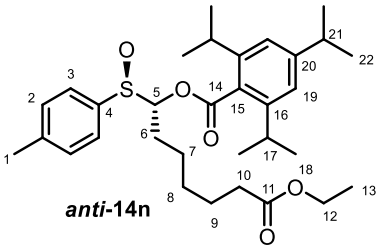
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.389	BB	6718.7	356.7	0.2867	50.042	0.801
2	21.503	BB	6707.5	252.4	0.4062	49.958	0.823



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.305	VV R	44930.7	2259.3	0.3074	98.105	0.717
2	21.422	BV R	867.8	30.9	0.4038	1.895	0.774

6.2.7 Preparation of (*R*)-7-ethoxy-7-oxo-1-((*R*)-*p*-tolylsulfinyl)heptyl 2,4,6-triisopropylbenzoate (*syn*-14n) and (*S*)-7-ethoxy-7-oxo-1-((*R*)-*p*-tolylsulfinyl)heptyl 2,4,6-triisopropylbenzoate (*anti*-14n)





Following **GP2**, ((*S*)-*p*-tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (600 mg, 1.50 mmol), ethyl hexanoate trifluoromethanesulfonate (575 mg, 1.95 mmol), NaHMDS (1.0 M in THF, 2.25 mL, 2.25 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 85:15) the *syn* diastereoisomer *syn*-**14n** (less polar, 239 mg, 29%) as a thick colourless oil and the *anti* diastereoisomer *anti*-**14n** (more polar, 217 mg, 27%) as a thick colourless oil which was found to contain 5% of *syn*-**14n**. Further subsequent purification by reverse phase HPLC (acetonitrile:water = 30:70 → 85:15) afforded pure *anti*-**14n**.

***syn*-14n**

[α]$^{22}_{D}$: –93 (*c* 0.7, $CHCl_3$)

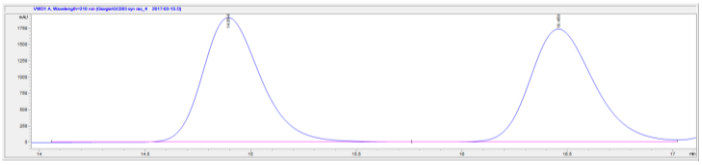
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.64 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.37 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.04 (s, 2H, Ar-H), 5.66 (dd, J_1 = 9.6 Hz, J_2 = 2.2 Hz, 1H, 5-H), 4.09 (q, *J* = 7.0 Hz, 2H, 12-H), 2.92 (quint, *J* = 6.4 Hz, 3H, 17-H × 2 + 21-H), 2.44 (s, 3H, 1-H), 2.20 (t, *J* = 7.4 Hz, 2H, 10-H), 1.99 (m, 1H, 6-H), 1.64–1.41 (m, 5H, 6-H + 7-H × 2 + 9-H × 2), 1.30–1.21 (m, 23H, CH_3 × 7 + 8-H × 2) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 173.4 (11-C), 170.4 (14-C), 150.8 (Ar-C), 145.1 (2C, Ar-C × 2), 141.6 (Ar-C), 137.5 (Ar-C), 130.0 (2C, Ar-C × 2), 128.8 (Ar-C), 124.3 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 92.5 (5-C), 60.2 (12-C), 34.4 (21-C), 34.0 (10-C), 31.6 (2C, 17-C × 2), 28.6 (8-C), 24.6 (9-C), 24.5 (7-C), 24.4 (2C, CH-*C*H_3 × 2), 24.2 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 22.8 (6-C), 21.4 (1-C), 14.2 (13-C) ppm

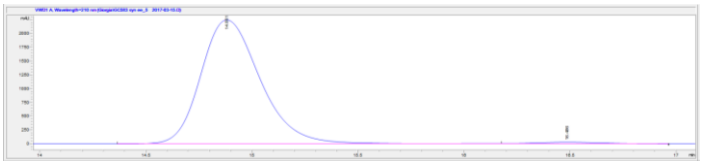
IR (neat): 2960, 1731, 1461, 1233, 1044, 811 cm^{-1}

HRMS (ESI) calculated for $C_{32}H_{46}NaO_5S$: 565.295816, found: 565.295522

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 90:10, 0.5 mL/min, room temperature, 210.8 nm): tR = 14.9 minutes (major), 16.5 minutes (minor), e.r. = 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.894	VV R	36853.7	1923.7	0.2964	49.880	0.753
2	16.459	VV	37031.4	1747.2	0.3266	50.120	0.77



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.881	BV R	43441.2	2235.5	0.2995	98.746	0.74
2	16.486	VB E	551.9	27.1	0.3079	1.254	0.924

***anti*-14n**

[α]$^{22}_{D}$: –9 (*c* 0.8, $CHCl_3$)

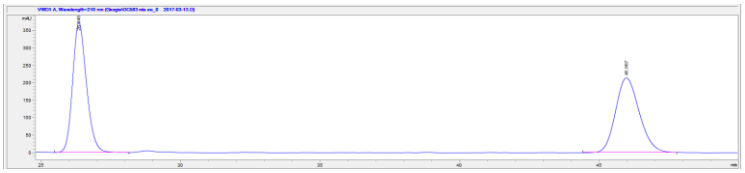
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.31 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.02 (s, 2H, Ar-H), 5.99 (dd, J_1 = 8.5 Hz, J_2 = 4.1 Hz, 1H, 5-H), 4.11 (q, *J* = 7.2 Hz, 2H, 12-H), 2.90 (sept, *J* = 6.9 Hz, 1H, 21-H), 2.84 (sept, *J* = 6.8 Hz, 2H, 17-H × 2), 2.42 (s, 3H, 1-H), 2.25 (t, *J* = 7.5 Hz, 2H, 10-H), 1.85 (m, 1H, 6-H), 1.56 (quint, *J* = 7.5 Hz, 2H, 9-H), 1.50–1.31 (m, 5H, 6-H + 7-H × 2 + 8-H × 2), 1.26–1.20 (m, 21H, CH_3 × 7) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 173.4 (11-C), 169.3 (14-C), 150.7 (Ar-C), 145.1 (2C, Ar-C × 2), 142.1 (Ar-C), 136.3 (Ar-C), 129.9 (2C, Ar-C × 2), 128.9 (Ar-C), 125.5 (2C, Ar-C × 2), 121.0 (2C, Ar-C × 2), 88.7 (5-C), 60.2 (12-C), 34.4 (21-C), 34.1 (10-C), 31.6 (2C, 17-C × 2), 28.7 (8-C), 27.2 (6-C), 25.1 (7-C), 24.6 (9-C), 24.6 (2C, CH-*C*H_3 × 2), 24.1 (2C, CH-*C*H_3 × 2), 23.9 (2C, CH-*C*H_3 × 2), 21.5 (1-C), 14.2 (13-C) ppm

IR (neat): 2961, 1733, 1230, 1088, 1038, 810 cm^{-1}

HRMS (ESI) calculated for $C_{32}H_{46}NaO_5S$: 565.295816, found: 565.295522

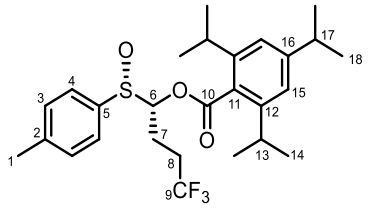
Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 26.3 minutes (major), 46.0 minutes (minor), e.r. = 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	26.345	BV R	12879.4	372.5	0.5147	50.479	0.784
2	45.987	BB	12634.9	214.2	0.8556	49.521	0.816

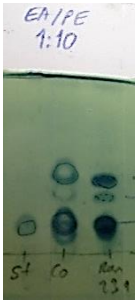
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	26.224	VV R	46882.7	1324.3	0.5379	98.654	0.664
2	46.139	VV R	639.8	10.2	0.734	1.346	0.903

6.2.8 Preparation of (*S*)4,4,4-trifluoro-1-((*S*)-*p*-tolylsulfinyl)butyl 2,4,6-triisopropylbenzoate (*syn*-14o)



***syn*-14o**

((*S*)-*p*-Tolylsulfinyl)methyl 2,4,6-triisopropylbenzoate **19** (240 mg, 0.60 mmol) in an oven dried Schlenk tube was dissolved in anhydrous THF (3.00 mL). The solution was cooled to –78 °C and 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex (1.0 M in THF/toluene, 0.66 mL, 0.66 mmol) was added dropwise. The solution was stirred for 20 min, at which point a solution of 3,3,3-trifluoropropyl trifluoromethanesulfonate (442 mg, 1.80 mmol) in THF (1 mL) was added dropwise. The reaction mixture was stirred at –78 °C for a further 2 h and then the cooling bath was removed and the solution was stirred at room temperature overnight. The reaction mixture was quenched with sat. NH_4Cl solution (5 mL) and diluted with Et_2O (5 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (petroleum ether:EtOAc = 98:2 → 85:15) which gave *syn*-**14o** (84 mg, 28%) as a colourless solid. *Anti*-**14o** (17 mg, 6%) could not be separated from impurities. Further elution (petroleum ether:EtOAc = 85:15 → 75:25) gave recovered starting material **19** (146 mg, 61%) as a colourless solid.



***syn*-14o**

$[\alpha]^{24}_D$: +69 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68–7.66 (m, 2H, 4-H), 7.41–7.39 (m, 2H, 3-H), 7.06 (s, 2H, 15-H), 5.68 (dd, J_1 = 9.1 Hz, J_2 = 3.6 Hz, 1H, 6-H), 2.97–2.84 (m, 3H, 17-H + 13-H × 2), 2.45 (s, 3H, 1-H), 2.36–2.21 (m, 2H, 7-H_a, 8-H_a), 2.18–2.06 (m, 1H, 8-H_b), 1.93–1.85 (m, 1H, 7-H_b), 1.30 (d, *J* = 6.8 Hz, 6H, 18-H), 1.28–1.26 (m, 12H, 14-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 170.2 (10-C), 151.3 (16-C), 145.4 (2C, 12-C), 142.2 (2-C), 137.1 (5-C), 130.4 (2C, 3-C), 128.4 (11-C), 126.6 (q, $^1J_{CF}$ = 276.4 Hz, 9-C), 124.3 (2C, 4-C), 121.3 (2C, 15-C), 90.7 (6-C), 34.6 (17-C), 31.9 (2C, 13-C), 29.3 (q, $^2J_{CF}$ = 29.6 Hz, 8-C), 24.5 (2C, CH_3), 24.3 (2C, CH_3), 24.1 (CH_3), 24.0 (CH_3), 21.6 (1-C), 16.6 (q, $^3J_{CF}$ = 3.1 Hz, 7-C) ppm

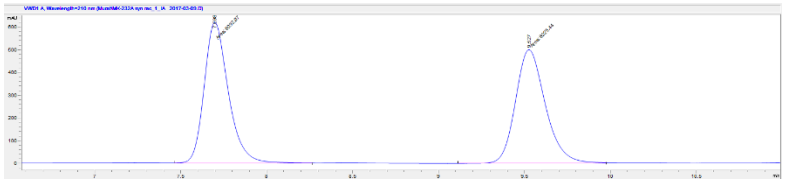
^{19}F NMR ($CDCl_3$, 377 MHz) δ: –66.5 (t, *J* = 10.4 Hz, CF_3) ppm

IR (neat): 2963, 2929, 2871, 1736, 1232, 1141, 1039, 1013, 812 cm^{-1}

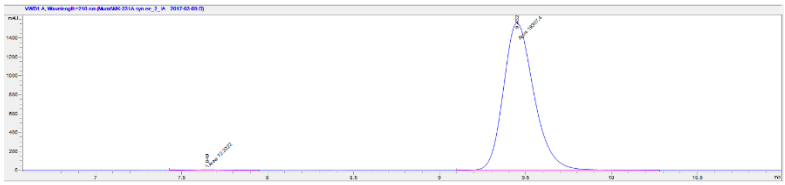
HRMS (ESI) calculated for $C_{27}H_{35}F_3NaO_3S$: 519.2151, found: 519.2146

M.P. 143–144 ºC

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 96:4, 0.7 mL/min, room temperature, 210.8 nm): tR = 7.7 minutes (minor), 9.5 minutes (major), e.r. > 99:1

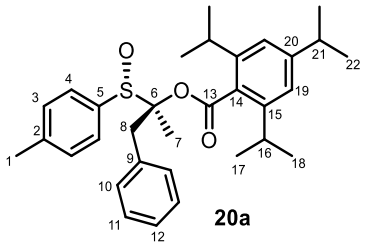


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.698	MM	6093	619.6	0.1639	50.279	0.75
2	9.527	MM	6025.4	498.9	0.2013	49.721	0.789



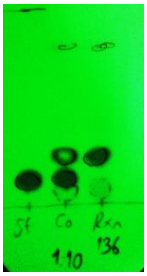
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.649	MM	72.3	6.9	0.1734	0.373	0.759
2	9.452	MM	19307.4	1561.3	0.2061	99.627	0.777

6.2.9 Preparation of (*R*)-1-phenyl-2-((*S*)-*p*-tolylsulfinyl)propan-2-yl 2,4,6-triisopropylbenzoate (20a)



20a

Following **GP2**, sulfoxide *anti*-**14b** (800 mg, 1.93 mmol), benzyl iodide (505 mg, 2.32 mmol), *i*Pr_2NH (490 µL, 3.47 mmol), *n*BuLi (1.6 M in hexane, 2.17 mL, 3.47 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 90:10) sulfoxide **20a** (736 mg, 76%, *dr* >95:5) as a colourless oil.



[α]$^{25}_{D}$: +27 (*c* 1.0, $CHCl_3$)

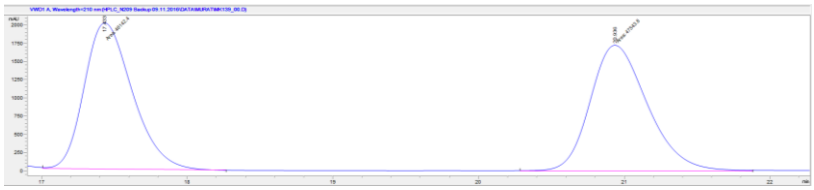
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J* = 7.9 Hz, 2H, 4-H), 7.34–7.33 (m, 2H, 10-H), 7.32–7.27 (m, 3H, 11-H + 12H), 7.22 (d, *J* = 7.9 Hz, 2H, 3-H), 6.96 (s, 2H, 19-H), 3.62 (d, ^{2}J = 13.9 Hz, 1H, 8-H_a), 3.40 (d, ^{2}J = 13.9 Hz, 1H, 8-H_b), 2.88 (sept, *J* = 6.9 Hz, 1H, 21-H), 2.67 (sept, *J* = 6.8 Hz, 2H, 16-H × 2), 2.38 (s, 3H, 1-H), 1.68 (s, 3H, 7-H), 1.25 (d, *J* = 6.9 Hz, 6H, 22-H), 1.16 (d, *J* = 6.8 Hz, 6H, 17-H), 1.05 (d, *J* = 6.8 Hz, 6H, 18-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.6 (13-C), 150.5 (20-C), 145.2 (2C, 15-C), 142.3 (2-C), 136.3 (5-C), 134.7 (9-C), 131.2 (2C, 10-C), 129.6 (14-C), 129.5 (2C, 3-C), 128.5 (2C, 11-C), 127.3 (12-C), 127.2 (2C, 4-C), 120.9 (2C, 19-C), 99.0 (6-C), 38.1 (8-C), 34.5 (21-C), 31.1 (2C, 16-C), 24.4 (2C, 17-C), 24.2 (2C, 18-C), 24.1 (2C, 22-C), 21.6 (1-C), 18.3 (7-C) ppm

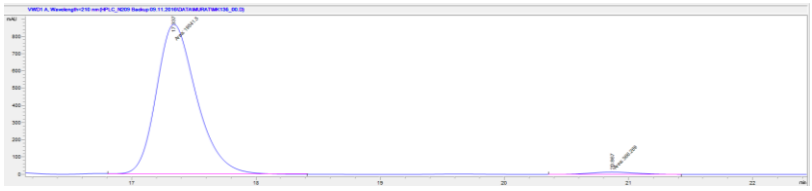
IR (neat): 2961, 2870, 1730, 1458, 1236, 1042, 811, 738, 703 cm^{-1}

HRMS (ESI) calculated for $C_{32}H_{40}NaO_3S$: 527.2590, found: 527.2592

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 17.3 minutes (major), 20.9 minutes (minor), e.r. = 98:2

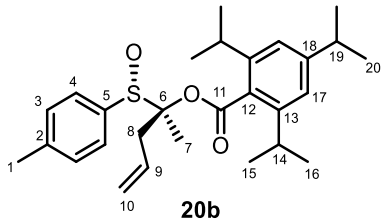


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.433	MM	46142.4	2003.2	0.3839	49.252	0.727
2	20.936	MM	47543.8	1725.1	0.4593	50.748	0.743



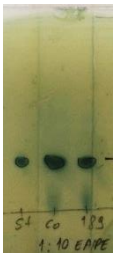
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.337	MM	19541.5	870.6	0.3741	98.160	0.753
2	20.867	MM	366.3	13.8	0.4435	1.840	0.887

6.2.10 Preparation of (*R*)-2-((*S*)-*p*-tolylsulfinyl)pent-4-en-2-yl 2,4,6-triisopropylbenzoate (20b)



20b

Following **GP2**, sulfoxide *anti*-**14a** (414 mg, 1.00 mmol), allyl iodide (140 µL, 1.50 mmol), *i*Pr_2NH (250 µL, 1.80 mmol), *n*BuLi (1.6 M in hexane, 1.12 mL, 1.80 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 90:10) sulfoxide **20b** (348 mg, 77%, *dr* >95:5) as a colourless oil.



$[\alpha]^{23}_D$: +49 (*c* 1.0, $CHCl_3$)

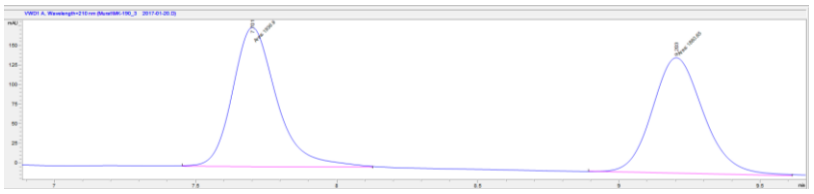
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.54 (d, *J* = 7.9 Hz, 2H, 4-H), 7.25 (d, *J* = 7.9 Hz, 2H, 3-H), 7.00 (s, 2H, 17-H), 5.83 (ddt, J_{trans} = 17.1 Hz, J_{cis} = 10.1 Hz, *J* = 7.1 Hz, 1H, 9-H), 5.24–5.17 (m, 2H, 10-H), 3.03 (dd, ^2J = 14.6 Hz, ^3J = 6.9 Hz, 1H, 8-H_a), 2.94–2.86 (m, 3H, 14-H + 19-H), 2.68 (dd, ^2J = 14.6 Hz, ^3J = 7.3 Hz, 1H, 8-H_b), 2.40 (s, 3H, 1-H), 1.74 (s, 3H, 7-H), 1.26 (d, *J* = 6.9 Hz, 6H, 20-H), 1.22 (d, *J* = 6.8 Hz, 6H, 15-H), 1.17 (d, *J* = 6.8 Hz, 6H, 16-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 169.3 (11-C), 150.6 (18-C), 145.3 (2C, 13-C), 142.3 (2-C), 136.4 (5-C), 131.1 (9-C), 129.7 (12-C), 129.5 (2C, 3-C), 126.8 (2C, 4-C), 121.0 (2C, 17-C), 120.4 (10-C), 98.9 (6-C), 37.3 (8-C), 34.6 (19-C), 31.2 (2C, 14-C), 24.4 (2C, CH_3 × 2), 24.3 (2C, CH_3 × 2), 24.1 (2C, 20-C), 21.6 (1-C), 17.7 (7-C) ppm

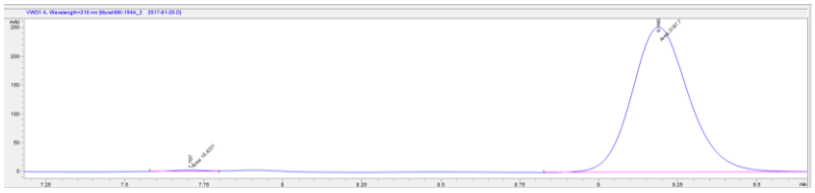
IR (neat): 2962, 1733, 1607, 1460, 1236, 1047, 810 cm^{-1}

HRMS (ESI) calculated for $C_{28}H_{38}NaO_3S$: 477.2434, found: 477.2425

Chiral HPLC: (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 96:4, 1.0 mL/min, room temperature, 210.8 nm): tR = 7.7 minutes (minor), 9.2 minutes (major), e.r. = 99:1



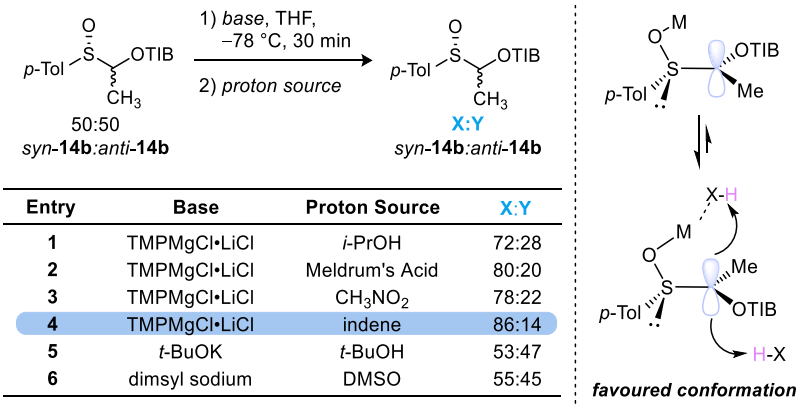
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.701	MM	1936.9	177.5	0.1819	51.004	0.786
2	9.203	MM	1860.6	147	0.211	48.996	0.853



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.707	MM	18.4	2.2	0.137	0.575	0.879
2	9.19	MM	3187.7	253.1	0.2099	99.425	0.855

7. Epimerization of *anti*-14a to *syn*-14b (Figure S1)

In many cases, standard flash chromatography was sufficient for separating mixtures of *syn*- and *anti* diastereomers. Diastereomeric pairs showed differences in retention factors (R_f values) of up to 0.2, the *anti* diastereomer always proving to be the more polar. However, in some cases, separation was more challenging; for example, the isopropyl-substituted benzoates, *syn*- and *anti*-**14d**, could only be separated using preparative HPLC. Therefore, we investigated the base-mediated epimerization of a diastereomeric mixture of the α-sulfinyl benzoates, *syn* and *anti*-**14b**, under both kinetic and thermodynamic conditions, hoping to enrich the mixture heavily towards one diastereomer, thus facilitating chromatographic separation. The Knochel–Hauser base, TMPMgCl·LiCl, was found to be the optimal reagent to affect the deprotonation, LiHMDS and NaHMDS being ineffective and LDA leading to complete decomposition. A 50:50 mixture of *syn* and *anti*-**14b** in THF was exposed to TMPMgCl·LiCl at –78 °C for 30 minutes followed by a quench with excess *i*-PrOH at the same temperature; the process resulted in a mixture more enriched in the *syn* diastereomer (*syn*-**14b**/*anti*-**14b** 72:28; Figure 1, entry 1). The origin of the selectivity for the *syn* diastereomer presumably is the favored approach of the proton source from the less hindered *Re* face of the carbanion center presented by the more thermodynamically stable conformer, that is, the one that places the large OTIB group gauche to the small substituent (the lone pair) of the vicinal sulfur center (Figure S1). Surmising that the minor *anti* isomer was formed through approach of the proton source from the *Si* face of this conformer, the increased steric hindrance of this face being mitigated by a favorable interaction between the magnesium ion and the oxygen atom of the proton source, we explored other proton sources where such an interaction might be diminished or absent. Indeed, the use of less coordinating proton sources proved to be beneficial, with the use of indene exhibiting the highest d.r. value (*syn*-14b/*anti*-14b 86:14; Figure 1, entry 4). We also explored epimerization under conditions that would be expected to permit equilibration of the mixture, namely, KO*t*Bu/*t*BuOH and dimsyl sodium/DMSO; however, resulting mixtures were only very slightly enriched in favor of the *syn* diastereomer. Unfortunately, when we subjected a mixture of the isopropyl-substituted benzoates, *syn*- and *anti*-**14d**, to the optimized conditions (TMPMgCl·LiCl, THF, –78 °C; indene), the d.r. value did not change, suggesting that deprotonation did not occur, presumably owing to steric hindrance.



Entry	Base	Proton Source	X:Y
1	TMPMgCl•LiCl	*i*-PrOH	72:28
2	TMPMgCl•LiCl	Meldrum's Acid	80:20
3	TMPMgCl•LiCl	CH_3NO_2	78:22
4	TMPMgCl•LiCl	indene	86:14
5	*t*-BuOK	*t*-BuOH	53:47
6	dimsyl sodium	DMSO	55:45

Figure S1: Optimization of reaction conditions for the epimerization of methyl-substituted α-sulfinyl benzoate. Reactions performed on 0.05 mmol scale; d.r. values were measured by ^{1}H NMR analysis of the crude reaction mixture.

7.1 Representative Procedure Using TMPMgCl•LiCl

A stirred solution of a 50:50 mixture of *syn*- and *anti*-**14b** (20.70 mg, 0.050 mmol) in dry THF (0.500 mL) under nitrogen was treated with TMPMgCl•LiCl (1.0 M in THF/toluene, 0.750 mL, 0.075 mmol) at −78 °C. The resulting mixture was stirred for 30 min at that temperature before the proton source (0.500 mmol, 10 equiv) was added. The quenched reaction mixture was warmed to room temperature, H_2O (5 mL) and Et_2O (5 mL) were added, the phases were separated and the aqueous phase was extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The d.r. and the yield of each diastereoisomer were determined by ^{1}H NMR using 1,4-dimethoxybenzene as internal standard.

7.2 Procedure Using *t*-BuOK/*t*-BuOH

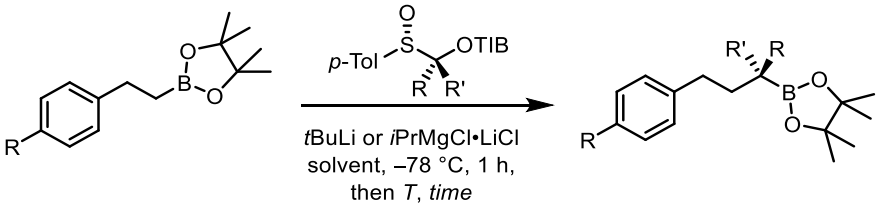
A stirred solution of a 50:50 mixture of *syn*- and *anti*-**14b** (20.70 mg, 0.050 mmol) in dry THF (0.500 mL) under nitrogen was treated with *t*-BuOK (1.0 M in *t*-BuOH, 0.750 mL, 0.075 mmol) at −78 °C. The resulting mixture was stirred for 30 min at that temperature before it was warmed to room temperature. H_2O (5 mL) and Et_2O (5 mL) were added, the phases were separated and the aqueous phase was extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The d.r. and the yield of each diastereoisomer were determined by ^{1}H NMR using 1,4-dimethoxybenzene as internal standard.

7.3 Procedure Using NaDMSO/DMSO

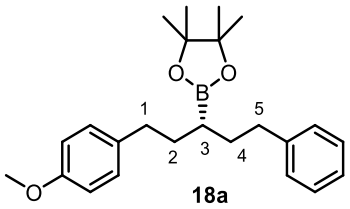
NaDMSO was freshly prepared according to a modified literature procedure.[24] A dry schlenk tube was charged with NaH (60% dispersion in mineral oil, 8.0 mg, 0.2 mmol). Pentane (1.0 mL) was added, the suspension was swirled for few minutes, decanted and the solvent was removed with a syringe. The

procedure was repeated for three times to remove all the mineral oil, then NaH was dried in high vacuum before suspending in dry DMSO (1.0 mL). The resulting suspension was heated at 60 °C for 40 minutes. Completion of the reaction was shown by disappearance of solid NaH and cessation of gas evolution to give a pale yellow solution. The flask was cooled to room temperature and a 50:50 mixture of *syn*- and *anti*-**14b** (42 mg, 0.1 mmol) in DMSO:THF (2:1 v/v, 1.0 mL in total) under nitrogen was added slowly. The resulting mixture was stirred for 1 hour at room temperature before H_2O (5 mL) and Et_2O (5 mL) were added. The phases were separated and the aqueous phase was extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The d.r. and the yield of each diastereoisomer were determined by ^1H NMR using 1,4-dimethoxybenzene as internal standard.

8. Homologation of Boronic Esters



8.1 Preparation of (*R*)-2-(1-(4-methoxyphenyl)-5-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18a)



Following **GP3**, phenyl ethyl sulfoxide *syn*-**14a** (106 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18a** (61.7 mg, 81%) as a colourless oil.

Following **GP4**, phenyl ethyl sulfoxide *syn*-**14a** (131 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18a** (61.7 mg, 71%) as a colourless oil.

$[\alpha]^{23}_D$: –6 (*c* 0.5, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.26 (m, 2H, Ar-H), 7.21–7.17 (m, 3H, Ar-H), 7.11 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.83 (d, *J* = 8.6 Hz, 2H, Ar-H), 3.80 (s, 3H, O-CH_3), 2.70–2.51 (m, 4H, 1-H + 5-H), 1.86–1.64 (m, 4H, 2-H + 4-H), 1.30 (s, 12H, C-CH_3 × 4), 1.14 (m, 1H, 3-H) ppm

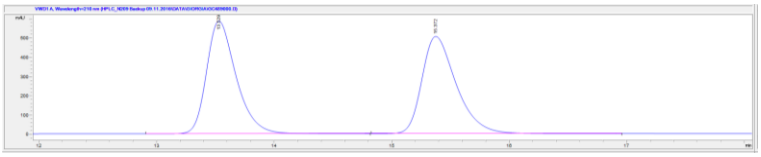
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.6 (Ar-C), 143.0 (Ar-C), 135.0 (Ar-C), 129.2 (2C, Ar-C × 2), 128.4 (2C, Ar-C × 2), 128.2 (2C, Ar-C × 2), 125.5 (Ar-C), 113.6 (2C, Ar-C × 2), 83.0 (2C, B-O-C × 2), 55.2 (O-CH_3), 35.6 (5-C), 34.6 (1-C), 33.6 (2-C), 33.4 (4-C), 24.9 (4C, C-CH_3 × 4) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.5 ppm

IR (neat): 2977, 2926, 1511, 1379, 1316, 1243, 1142, 1037, 821 cm^{-1}

HRMS (ESI) calculated for $C_{24}H_{33}BNaO_3$: 403.2419, found: 403.2412

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 90:10, 0.7 mL/min, room temperature, 210.8 nm): tR = 13.5 minutes (major), 15.3 minutes (minor), e.r. = 98:2 (Li), e.r. > 99:1 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
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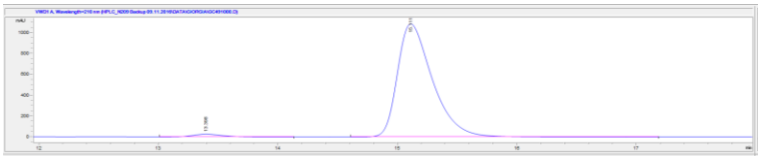
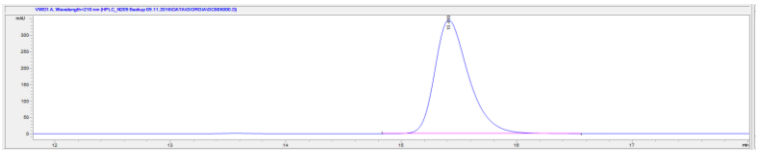
2	15.372	BB	10237.6	505.4	0.3077	50.024	0.637

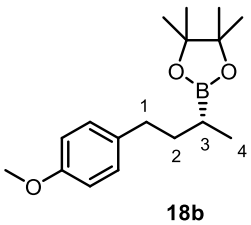


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.398	BB	426.3	26	0.2497	1.897	0.775
2	15.111	BB	22040.9	1085.9	0.3067	98.103	0.577



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.41	BB	6947.7	343.1	0.309	100.000	0.668

8.2 Preparation of (*R*)-2-(4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)



18b

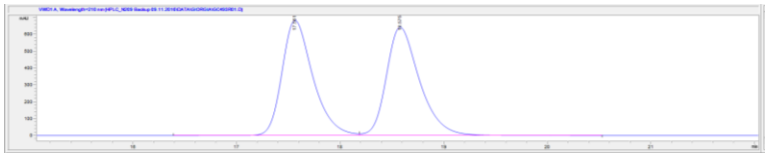
Following **GP3**, methyl sulfoxide *syn*-**14b** (87.1 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column

chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18b** (45.4 mg, 78%) as a colourless oil.

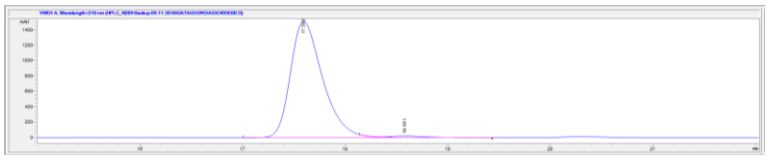
Following **GP4**, methyl sulfoxide *syn*-**14b** (108 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18b** (33.6 mg, 58%) as a colourless oil.

Spectral data matched that previously reported.[25]

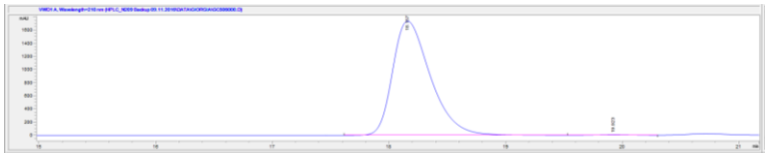
[α]$^{23}_D$: –19 (*c* 0.7, $CHCl_3$). Lit. for (*R*):[26] –8.2 (*c* 0.98, $CHCl_3$); for (*S*):[25] +7.6 (*c* 1.7, $CHCl_3$)
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.10 (dt, J_1 = 8.7 Hz, J_2 = 2.9 Hz, 2H, Ar-H), 6.81 (dt, J_1 = 8.6 Hz, J_2 = 3.0 Hz, 2H, Ar-H), 3.78 (s, 3H, O-CH_3), 2.60–2.53 (m, 2H, 1-H), 1.75 (m, 1H, 2-H), 1.56 (m, 1H, 2-H), 1.25 (s, 12H, C-CH_3 × 4), 1.10–1.00 (m, 4H, 3-H + 4-H) ppm
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.5 (Ar-C), 135.2 (Ar-C), 129.3 (2C, Ar-C × 2), 113.6 (2C, Ar-C × 2), 82.8 (2C, B-O-C × 2), 55.2 (O-CH_3), 35.5 (1-C), 34.4 (2-C), 24.8 (2C, C-*C*H_3 × 2), 24.8 (2C, C-*C*H_3 × 2), 15.4 (4-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)
^{11}B NMR ($CDCl_3$, 128 MHz) δ: 34.3 ppm
IR (neat): 2977, 2931, 1612, 1512, 1463, 1380, 1370, 1314, 1243, 1142, 1112, 1038, 967, 863, 848, 822, 687, 670, 561 cm^{-1}
HRMS (ESI) calculated for $C_{17}H_{27}BO_3$: 291.2132, found: 291.2123
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 95:5, 0.5 mL/min, room temperature, 210.8 nm): tR = 17.6 minutes (major), 18.6 minutes (minor), e.r. = 99:1 (Li), >99:1 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.561	VV R	14130.3	681.3	0.3133	49.783	0.695
2	18.575	VB	14253.7	640.7	0.3352	50.217	0.668

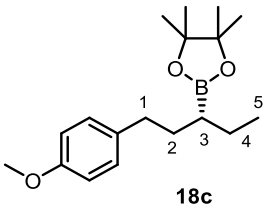


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.593	BV R	32696.8	1506.2	0.3304	98.566	0.658
2	18.581	VB E	475.7	20.4	0.3442	1.434	0.702



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.157	BV R	39056.7	1736.5	0.3439	99.666	0.617
2	19.923	VV E	131	6.6	0.3132	0.334	0.901

8.3 Preparation of (*R*)-2-(1-(4-methoxyphenyl)pentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 18c



18c

Following **GP3**, ethyl sulfoxide *syn*-**14c** (90.0 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18c** (37.1 mg, 61%) as a colourless oil.

Following **GP4**, ethyl sulfoxide *syn*-**14c** (111 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.3 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18c** (29.8 mg, 49%) as a colourless oil.

Spectral data matched that previously reported.[25]

[α]$^{23}_D$: –9 (*c* 0.7, $CHCl_3$)). Lit. for (*R*):[26] –9.6 (*c* 1.05, $CHCl_3$); for (*S*):[25] +9.4 (*c* 1.6, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.10 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.78 (s, 3H, O-CH_3), 2.61–2.48 (m, 2H, 1-H), 1.72 (m, 1H, 2-H), 1.62 (m, 1H, 2-H), 1.51–1.43 (m, 2H, 4-H), 1.27 (s, 12H, C-CH_3 × 4), 0.98 (m, 1H, 3-H), 0.22 (t, *J* = 7.4 Hz, 3H, 5-H) ppm

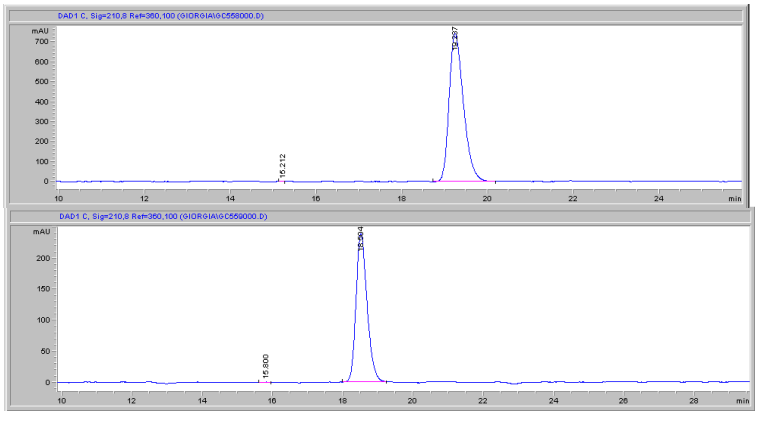
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.6 (Ar-C), 135.2 (Ar-C), 129.2 (2C, Ar-C × 2), 113.6 (2C, Ar-C × 2), 82.9 (2C, B-O-C × 2), 55.2 (O-CH_3), 34.7 (1-C), 33.4 (2-C), 24.8 (2C, C-*C*H_3 × 2), 24.8 (2C, C-*C*H_3 × 2), 24.1 (4-C), 13.6 (5-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.6 ppm

IR (neat): 2976, 2927, 1511, 1371, 1313, 1244, 1142, 1038, 966, 852, 824 cm^{-1}

HRMS (ESI) calculated for $C_{18}H_{29}BNaO_3$: 327.2105, found: 327.2099

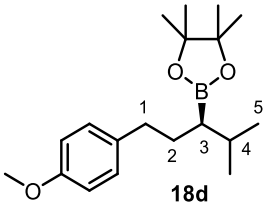
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 97:3, 0.7 mL/min, room temperature, 210.8 nm): the racemate was previously analysed (see reference 16) with retention times tR = 16.0 minutes, 19.1 minutes, e.r. > 99:1 (Li), e.r. > 99:1 (Mg)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.212	VV	0.0972	8.73743	1.11776	0.0506
2	19.237	VV	0.3579	1.72745e4	741.09216	99.9494

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.800	VV	0.1758	15.85568	1.12918	0.3029
2	18.504	VB	0.3288	5218.14941	238.96301	99.6971

8.4 Preparation of (*R*)-2-(1-(4-methoxyphenyl)-4-methylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18d)



18d

Following **GP3**, isopropyl sulfoxide *anti*-**14d** (93.0 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 97:3) the homologated boronic ester **18d** (34.1 mg, 54%) as a colourless solid.

Following **GP4**, isopropyl sulfoxide *syn*-**14d** (95.0 mg, 0.22 mmol), boronic ester **17a** (43.3 mg, 0.17 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 170 µL, 0.20 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 97:3) the homologated boronic ester **18d** (4.00 mg, 8%) as a colourless solid.

$[\alpha]^{23}_D$: +3 (*c* 1.1, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.12 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.79 (s, 3H, O-CH_3), 2.58 (m, 1H, 1-H), 2.46 (m, 1H, 1-H), 1.80–1.59 (m, 3H, 2-H + 4-H), 1.28 (s, 12H, C-CH_3 × 4), 0.93 (d, *J* = 6.8 Hz, 6H, 5-H × 2), 0.91 (m, 1H, 3-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.68 (Ar-C), 135.4 (Ar-C), 129.3 (2C, Ar-C × 2), 113.8 (2C, Ar-C × 2), 83.0 (2C, B-O-C × 2), 55.3 (O-CH_3), 35.2 (1-C), 31.8 (2-C), 29.7 (4-C), 25.2 (2C, C-*C*H_3 × 2), 25.0 (2C, C-*C*H_3 × 2), 22.4 (5-C), 21.8 (5-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

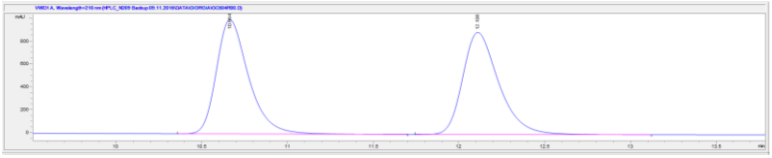
^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.7 ppm

IR (neat): 2952, 2857, 1512, 1312, 1297, 1235, 1141, 1041, 874, 824, 515 cm^{-1}

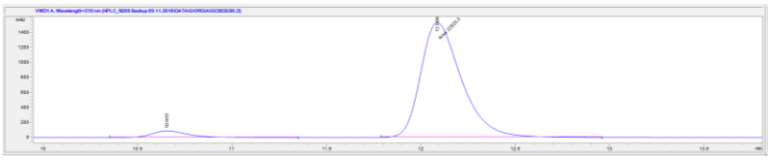
HRMS (ESI) calculated for $C_{19}H_{31}BNaO_3$: 341.2262, found: 341.2261

M.P. 35–37 ºC

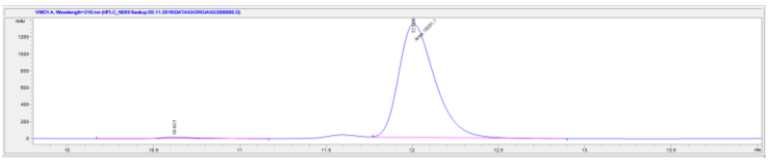
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 90:10, 0.5 mL/min, room temperature, 210.8 nm): tR = 10.7 minutes (minor), 12.1 minutes (major), e.r. = 95:5 (Li), e.r. = 98:2 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.664	BB	13086.7	1001.5	0.1976	49.961	0.675
2	12.108	BB	13107.1	894	0.222	50.039	0.677

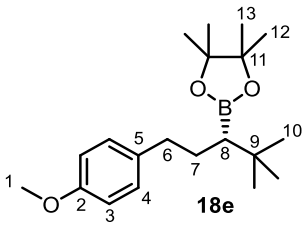


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.655	BB	1130.7	87.1	0.1967	4.720	0.689
2	12.086	MM	22825.5	1535.5	0.2478	95.280	0.668



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.621	BV	298.9	18.4	0.2313	1.526	0.497
2	12.006	MM	19291.1	1336.4	0.2406	98.474	0.687

8.5 Preparation of (*S*)-2-(1-(4-methoxyphenyl)-4,4-dimethylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18e)



18e

Following **GP6**, sulfoxide *syn*-**14e** (177 mg, 0.39 mmol), boronic ester **17a** (78.0 mg, 0.30 mmol), *t*BuLi (1.6 M in pentane, 370 µL, 0.60 mmol) and PMDTA (120 µL, 0.60 mmol) afforded after purification by flash column chromatography (petroleum ether:EtOAc = 98:2 → 90:10) the homologated boronic ester **18e** (53.0 mg, 54%) as a colourless oil.

$[\alpha]^{24}_D$: +12 (*c* 0.25, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.11 (d, *J* = 8.5 Hz, 2H, 4-H), 6.82 (d, *J* = 8.5 Hz, 2H, 3-H), 3.78 (s, 3H, 1-H), 2.57 (ddd, $^2J_1$ = 13.6 Hz, J_2 = 9.9 Hz, J_3 = 5.7 Hz 1H, 6-H_a), 2.36 (ddd, $^2J_1$ = 13.6 Hz, J_2 = 9.8 Hz, J_3 = 7.1 Hz, 1H, 6-H_b), 1.76–1.61 (m, 2H, 7-H), 1.29 (s, 12H, 12-H + 13-H), 0.93 (s, 9H, 10-H), 0.87 (dd, J_1 = 11.2 Hz, J_2 = 4.6 Hz, 1H, 8-H_b) ppm

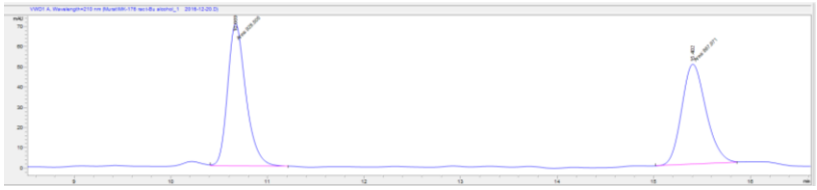
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.8 (2-C), 135.5 (5-C), 129.4 (2C, 4-C), 113.8 (2C, 3-C), 83.1 (2C, 11-C), 55.4 (1-C), 36.0 (6-C), 32.2 (9-C), 29.9 (7-C), 29.7 (3C, 10-C), 25.3 (2C, 12-C), 25.2 (2C, 13-C) ppm (*carbon attached to boron (8-C) not observed due to quadrupolar relaxation) in ^{13}C NMR but it correlates with 10-H at 37.0 ppm in HMBC*)

^{11}B NMR ($CDCl_3$, 96 MHz) δ: 32.4 ppm

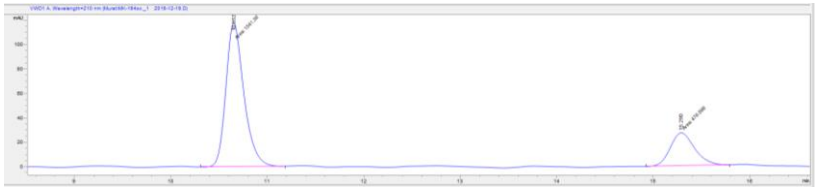
IR (neat): 2953, 2866, 1512, 1371, 1245, 1144, 1040, 826 cm^{-1}

HRMS (ESI) calculated for $C_{20}H_{33}BNaO_3$: 355.2419, found: 355.2420

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 97:3, 0.8 mL/min, room temperature, 210.8 nm): tR = 10.7 minutes (major), 15.3 minutes (minor), e.r. = 76:24

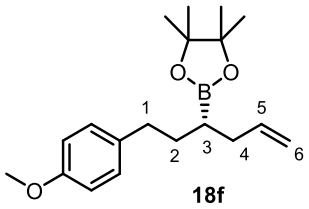


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.669	MM	928.5	70.6	0.2191	51.685	0.745
2	15.402	MM	868	49.5	0.2921	48.315	0.816



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.652	MM	1541.4	118.2	0.2173	76.382	0.745
2	15.29	MM	476.6	27.1	0.2936	23.618	0.799

8.6 Preparation of (*S*)-2-(1-(4-methoxyphenyl)hex-5-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18f)



18f

Following **GP3**, allylic sulfoxide *syn*-**14f** (92.5 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18f** (53.6 mg, 85%) as a colourless oil.

Following **GP4**, allylic sulfoxide *syn*-**14f** (115 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18f** (43.9 mg, 69%) as a colourless oil.

Spectral data matched that previously reported.[25]

[α]$^{23}_D$: –16 (*c* 0.8, $CHCl_3$). Lit. for (*R*):[25] +0.12 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.09 (dt, J_1 = 8.6 Hz, J_2 = 2.9 Hz, 2H, Ar-H), 6.81 (dt, J_1 = 8.6 Hz, J_2 = 2.9 Hz, 2H, Ar-H), 5.80 (m, 1H, 5-H), 5.03 (dq, J_1 = 17.1 Hz, J_2 = 2.0 Hz, 1H, 6-H_{trans}), 4.95 (dq, J_1 = 10.1 Hz, J_2 = 1.0 Hz, 1H, 6-H_{cis}), 3.78 (s, 3H, O-CH_3), 2.55 (m, 2H, 1-H), 2.19 (m, 2H, 4-H), 1.68 (m, 2H, 2-H), 1.25 (s, 12H, C-CH_3 × 4), 1.13 (m, 1H, 3-H) ppm

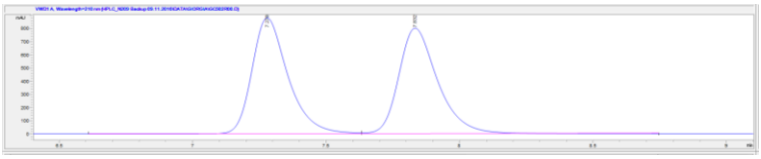
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.6 (Ar-C), 138.4 (5-C), 135.0 (Ar-C), 129.2 (2C, Ar-C × 2), 114.9 (6-C), 113.7 (2C, Ar-C × 2), 83.0 (2C, B-O-C × 2), 55.2 (O-CH_3), 35.4 (1-C), 34.5 (3-C), 33.2 (2-C), 24.9 (2C, C-*C*H_3 × 2), 24.8 (2C, C-*C*H_3 × 2) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.3 ppm

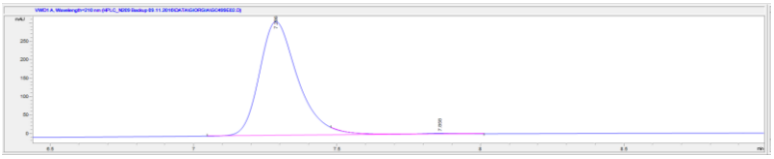
IR (neat): 2977, 2924, 1511, 1318, 1142, 1038, 823 cm^{-1}

HRMS (ESI) calculated for $C_{19}H_{29}BNaO_3$: 339.2105, found: 339.2109

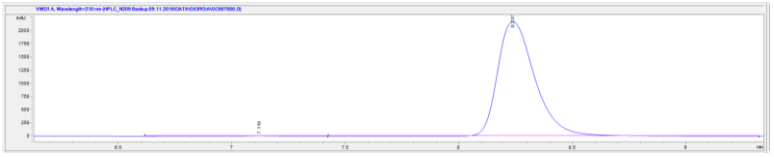
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 90:10, 0.8 mL/min, room temperature, 210.8 nm): tR = 7.3 minutes, 7.8, e.r. = 99:1 (Li), e.r. >99:1 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.278	BV	8222.7	878.2	0.1413	50.349	0.685
2	7.832	VB	8108.8	799.8	0.1532	49.651	0.679

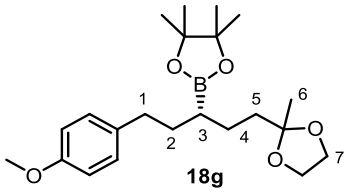


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.286	BV R	2887.9	310.3	0.1392	99.000	0.701
2	7.858	VB E	29.2	1.8	0.2201	1.000	2.73



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.119	VB R	54.6	4.8	0.1639	0.219	1.068
2	8.237	VBAR	24854.8	2182.2	0.1751	99.781	0.64

8.7 Preparation of (*S*)-2-(1-(4-methoxyphenyl)-5-(2-methyl-1,3-dioxolan-2-yl)pentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18g)



18g

Following **GP3**, ketal sulfoxide *syn*-**14g** (108 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 75:25) the homologated boronic ester **18g** (54.3 mg, 70%) as a colourless oil.

Following **GP4**, ketal sulfoxide *syn*-**14g** (134 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 75:25) the homologated boronic ester **18g** (48.9 mg, 63%) as a colourless oil.

$[\alpha]^{23}_D$: –3 (*c* 0.6, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.09 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.81 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.95–3.87 (m, 4H, 7-H × 2), 3.77 (s, 3H, O-CH_3), 2.61–2.47 (m, 2H, 1-H), 1.77–1.46 (m, 6H, 2-H + 4-H + 5-H), 1.31 (s, 3H, 6-H), 1.25 (s, 12H, C-CH_3 × 4), 1.00 (m, 1H, 3-H) ppm

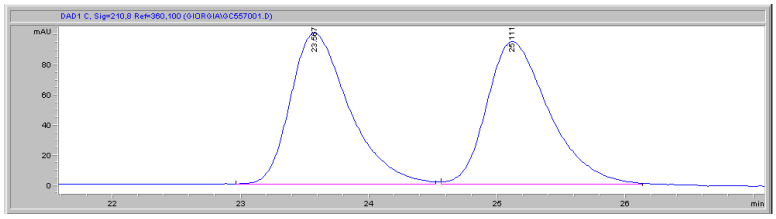
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.6 (Ar-C), 135.1 (Ar-C), 129.2 (2C, Ar-C × 2), 113.6 (2C, Ar-C × 2), 110.1 (O-C-O), 82.9 (2C, B-O-C × 2), 64.5 (2C, 7-C × 2), 55.2 (O-CH_3), 38.3 (5-C), 34.6 (1-C), 33.6 (2-C), 25.5 (4-C), 24.8 (2C, C-CH_3 × 2), 24.8 (2C, C-CH_3 × 2), 23.6 (6-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.7 ppm

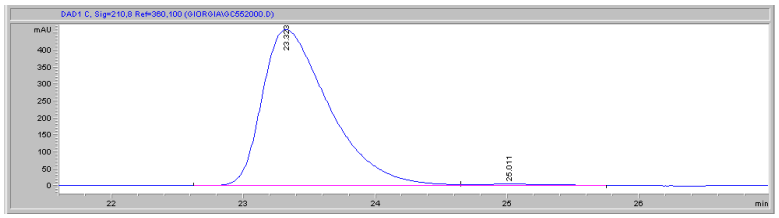
IR (neat): 2978, 2932, 1511, 1372, 1316, 1244, 1142, 1037, 848, 825 cm^{-1}

HRMS (ESI) calculated for $C_{22}H_{35}BNaO_5$: 413.2474, found: 413.2475

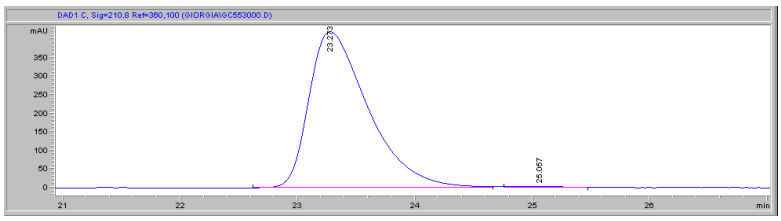
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 95:5, 0.7 mL/min, room temperature, 210.8 nm): tR = 23.6 minutes (major), 25.1 minutes (minor), e.r. = 99:1 (Li), e.r. = 99:1 (Mg)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.567	VB	0.4792	3218.14966	100.58985	50.0394
2	25.111	BV	0.4994	3213.07983	94.80626	49.9606

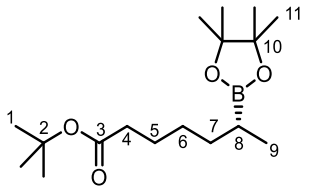


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.323	VB	0.5300	1.61917e4	460.73987	98.6724
2	25.011	BV	0.5090	217.85738	5.19751	1.3276



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.273	VB	0.5233	1.47985e4	421.79361	99.1386
2	25.057	BV	0.3655	128.57690	4.24386	0.8614

8.8 Preparation of (*R*)-tert-butyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (18h)



18h

Following **GP4**, sulfoxide *ent-anti*-**14b** (108 mg, 0.26 mmol), boronic ester **17b** (57 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.3 M in THF, 170 µL, 0.22 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 95:5) the homologated boronic ester **18h** (43 mg, 69%) as a colourless oil.

[α]$^{23}_{D}$: –4 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.19 (t, *J* = 7.4 Hz, 2H, 4-H), 1.63–1.52 (m, 2H, 5-H), 1.48–1.41 (m, 1H), 1.43 (s, 9H, 1-H), 1.36–1.25 (m, 3H), 1.22 (s, 12H, 11-H), 1.03–0.92 (m, 4H, 8-H + 9-H) ppm

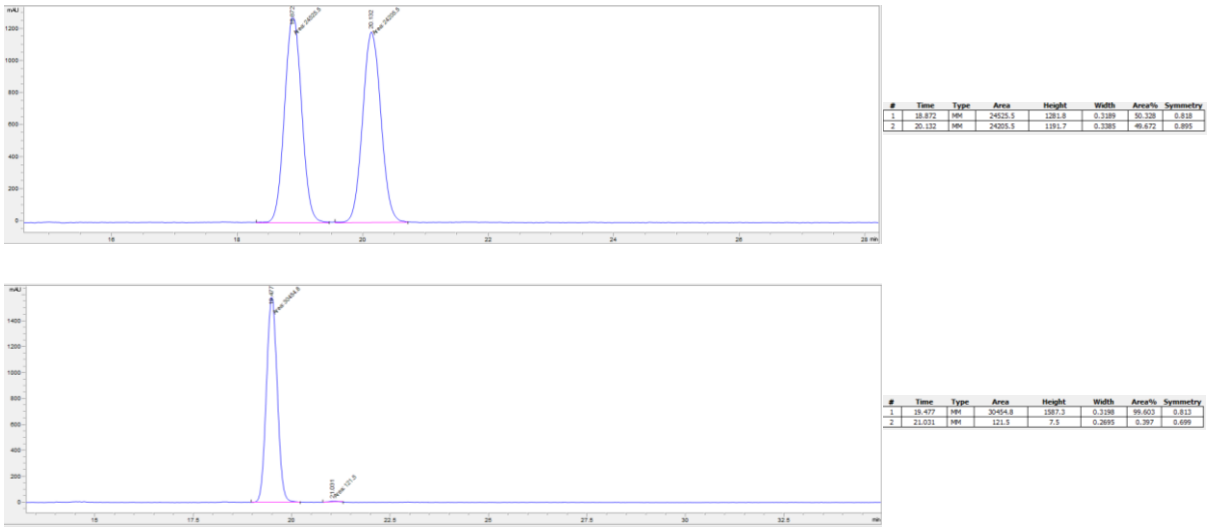
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 173.4 (3-C), 83.0 (2C, 10-C), 80.0 (2-C), 35.8 (4-C), 33.0 (CH_2), 28.6 (CH_2), 28.3 (3C, 1-C), 25.5 (5-C), 24.9 (4C, 11-C), 15.6 (9-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.8 ppm

IR (neat): 2977, 2930, 1730, 1462, 1367, 1314, 1142, 859 cm^{-1}

HRMS (ESI) calculated for $C_{17}H_{33}BNaO_4$: 335.2367, found: 335.2382

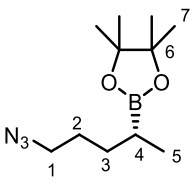
Chiral HPLC: A small portion of the product was oxidized and the corresponding alcohol was converted to the benzoate using benzoyl chloride[27] for HPLC analysis. (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 98:2, 0.3 mL/min, room temperature, 230 nm): tR = 18.9 minutes (major), 20.1 minutes (minor), e.r. > 99:1 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.872	MM	24525.5	1281.8	0.3189	50.328	0.818
2	20.132	MM	24205.5	1191.7	0.3385	49.672	0.895

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.477	MM	30454.8	1587.3	0.3198	99.603	0.813
2	21.031	MM	121.5	7.5	0.2695	0.397	0.699

8.9 Preparation of (*R*)-2-(5-azidopentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18i)



18i

Following **GP4**, sulfoxide *syn*-**14b** (135.3 mg, 0.33 mmol), boronic ester **17c** (53 mg, 0.25 mmol) and *i*PrMgCl•LiCl (1.30 M in THF, 230 µL, 0.30 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 95:5) the homologated boronic ester **18i** (46 mg, 77%) as a colourless oil.

[α]$^{24}_{D}$: –9 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.24 (t, 2H, 1-H), 1.68–1.56 (m, 2H, 2-H), 1.56–1.45 (m, 1H, 3-H_a), 1.40–1.29 (m, 1H, 3-H_b), 1.24 (s, 12H, 7-H), 1.09–0.94 (m, 4H, 4-H + 5-H) ppm

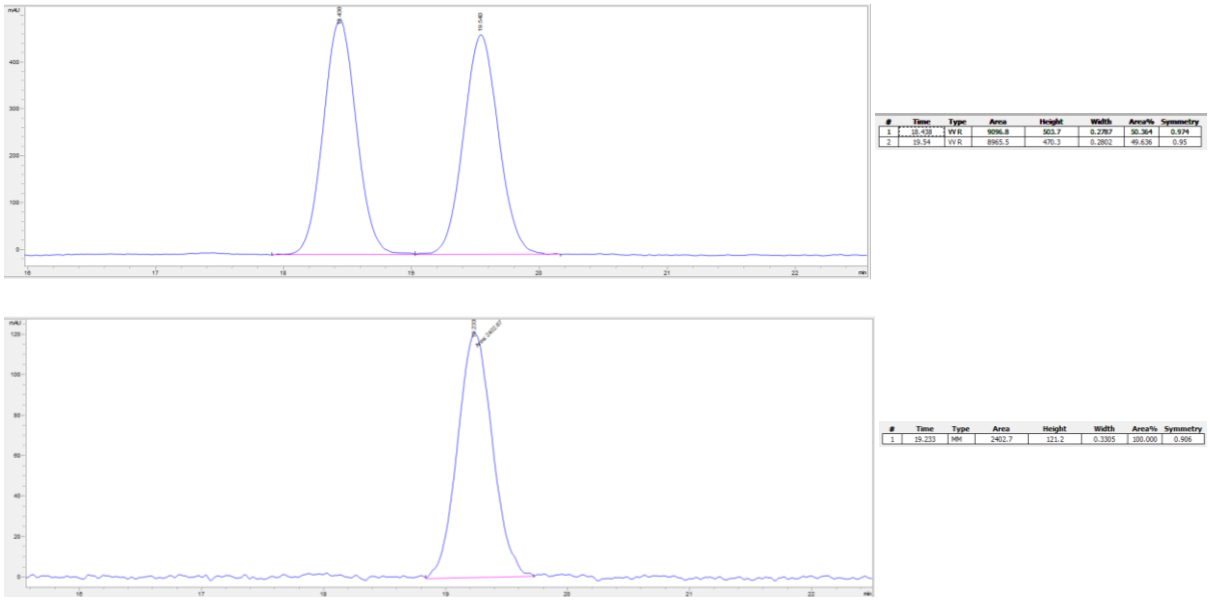
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 83.1 (2C, 6-C), 51.8 (1-C), 30.4 (3-C), 28.3 (2-C), 24.9 (4C, 7-C), 15.6 (5-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 34.0 ppm

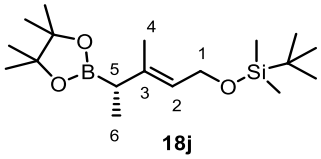
IR (neat): 2978, 2934, 2869, 2093, 1464, 1372, 1257, 1144, 967 cm^{-1}

HRMS (ESI) calculated for $C_{11}H_{22}BN_3NaO_2$: 262.1699, found: 262.1696

Chiral HPLC: A small portion of the product was oxidized and the corresponding alcohol was converted to the benzoate using benzoyl chloride[27] for HPLC analysis. (Daicel Chiralcel-IA column (25 cm), hexane:isopropanol = 98:2, 0.3 mL/min, room temperature, 230 nm): tR = 18.4 minutes (minor), 19.5 minutes (major), e.r. > 99:1 (Mg)



8.10 Preparation of (*S*,*E*)-*tert*-butyldimethyl((3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-yl)oxy)silane (18j)



18j

Following **GP3**, methyl sulfoxide *anti*-**14b** (87 mg, 0.21 mmol), boronic ester **17d** (63 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 97:3) the homologated boronic ester **18j** (20.8 mg, 31%) as a colourless oil.

Following **GP4**, methyl sulfoxide *anti*-**14b** (108 mg, 0.26 mmol), boronic ester **17d** (63 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.25 M in THF, 190 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 97:3) the homologated boronic ester **18j** (49 mg, 73%) as a colourless oil.

[α]$^{23}_D$: –95 (*c* 0.8, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.27 (t, *J* = 6.4 Hz, 1H, 2-H), 4.21 (d, *J* = 6.3 Hz, 2H, 1-H), 1.80 (q, *J* = 7.3 Hz, 1H, 5-H), 1.65 (s, 3H, CH_3), 1.22 (s, 12H, C-CH_3 x 4), 1.09 (d, *J* = 7.4 Hz, 3H, 6-H), 0.89 (s, 9H, Si-C-$(CH_3)_3$), 0.06 (s, 6H, Si-$(CH_3)_2$) ppm

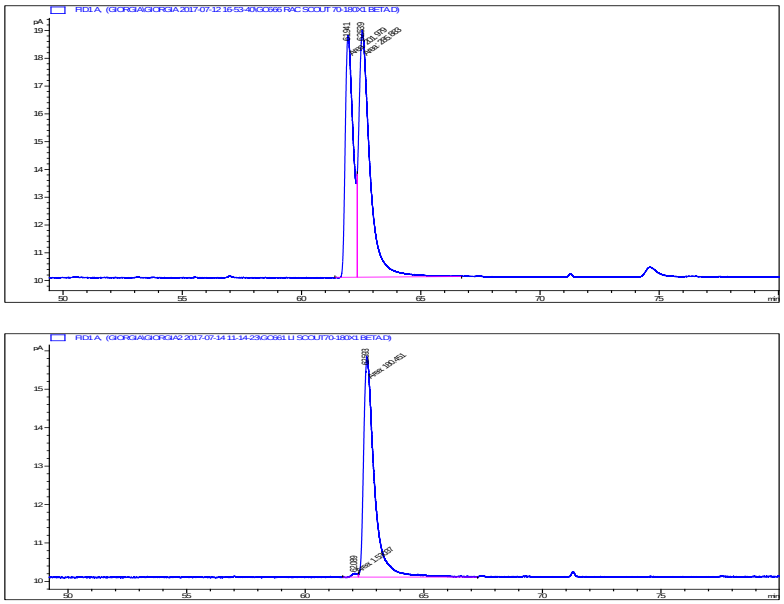
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 139.2 (2-C), 122.7 (3-C), 83.1 (2C, B-O-C × 2), 60.6 (1-C), 26.0 (Si-C-*C*H_3)$_3$), 24.7 (2C, C-*C*H_3 × 2), 24.6 (2C, C-*C*H_3 × 2), 18.4 (Si-C), 16.7 (4-C), 14.1 (6-C), –5.0 (Si-$CH_3)_2$) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

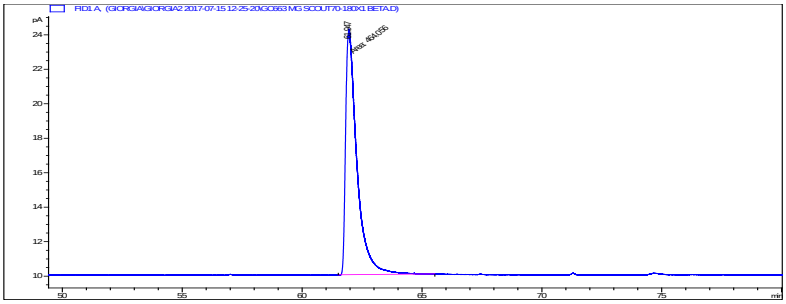
^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.8 ppm

IR (neat): 2956, 2929, 1462, 1347, 1317, 1253, 1144, 834, 774 cm^{-1}

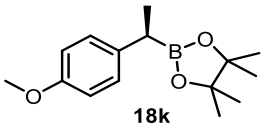
HRMS (ESI) calculated for $C_{18}H_{37}BNaO_3Si$: 363.2501, found: 363.2512

Chiral GC: (Chiraldex β-DM column, injector T = 250 °C, detector T = 300 °C. Oven conditions: Inject at T = 70 °C for 3 min then ramp (1 °C min^{-1}) until 180 °C then hold for 5 min. He carrier gas at 1.0 mL min^{-1}. tR (minor) = 61.9 min, tR (major) = 62.5 min, total analysis time 120 min; e.r. = 99:1 (Li), e.r. >99:1 (Mg).





8.11 Preparation of (*R*)-2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18k)



18k

Following **GP3**, methyl sulfoxide *ent-anti*-**14b** (87 mg, 0.21 mmol), 4-methoxyphenyl pinacol boronic ester (**17e**, 47 mg, 0.20 mmol), and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18k** (23.1 mg, 44%) as a colourless oil. A solution of $MgBr_2$•MeOH* (1.0 M, 300 µL, 0.3 mmol) was added prior to warm the reaction mixture to 66 °C.

* 1.0 M $MgBr_2$•MeOH solution was prepared in advance by adding anhydrous MeOH to $MgBr_2$ solid. Reaction without addition of $MgBr_2$•MeOH gave the desired homologated alcohol in 56% yield but only 85:15 er due to reversible "ate" complex formation.[28]

Following **GP4**, methyl sulfoxide *ent-anti*-**14b** (108 mg, 0.26 mmol), boronic ester **17e** (47 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.25 M in THF, 190 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) the homologated boronic ester **18k** (37 mg, 71%) as a colourless oil.

Spectral data matched that previously reported.[29]

[α]$^{23}_D$: –10 (*c* 0.1, $CHCl_3$). Lit. for (*R*)[30]: –120.3 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.14 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.6 Hz, 2H, Ar-H), 3.78 (s, 3H, O-CH_3), 2.38 (q, *J* = 7.6 Hz, 1H, C*H*-CH_3), 1.30 (d, *J* = 7.5 Hz, 3H, CH-C*H*$_3$), 1.22 (s, 6H, C-CH_3 x 2), 1.20 (s, 6H, C-CH_3 x 2) ppm

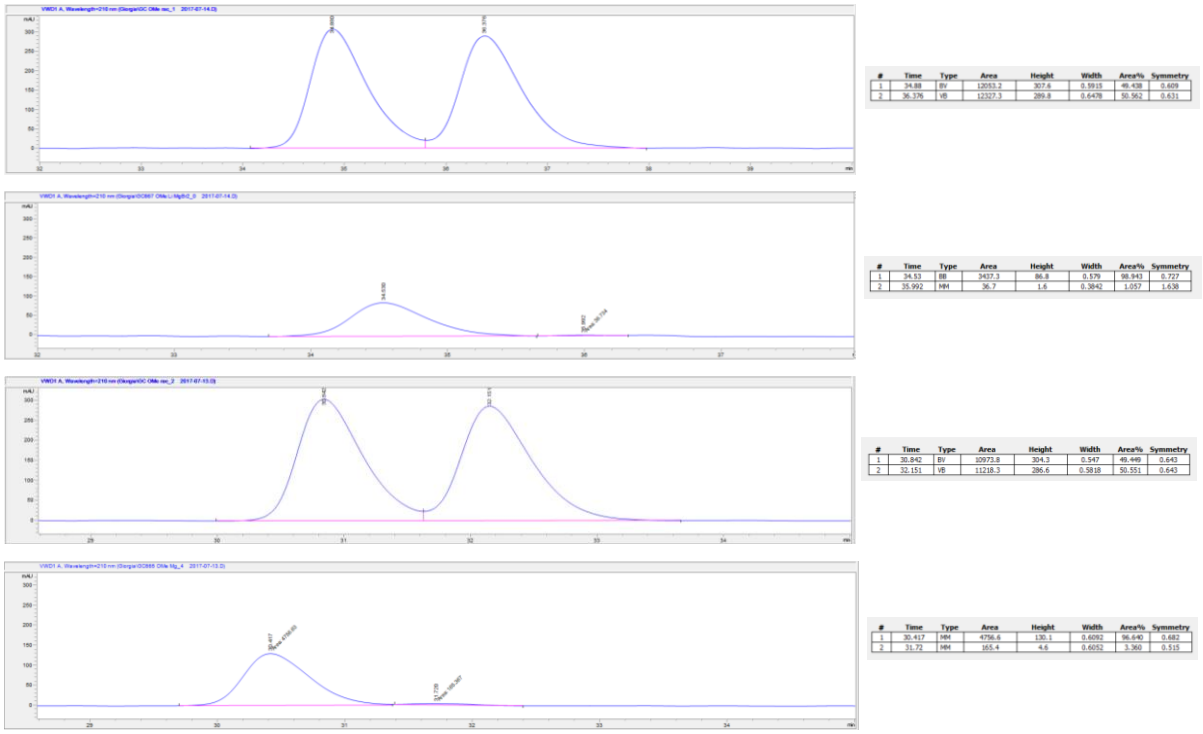
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.2 (Ar-C), 137.0 (Ar-C), 128.6 (Ar-C x 2), 113.7 (Ar-C x 2), 83.2 (2C, B-O-C × 2), 55.2 (O-CH_3), 24.6 (2C, C-*C*H_3 × 2), 24.6 (2C, C-*C*H_3 × 2), 17.3 (CH-*C*H_3) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.8 ppm

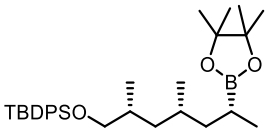
IR (neat): 2977, 1509, 1353, 1318, 1242, 1141, 1038, 845, 828 cm^{-1}

HRMS (ESI) calculated for $C_{15}H_{24}BO_3$: 263.1816, found: 263.1822

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 99:1, 0.7 mL/min, room temperature, 210.8 nm): tR = 34.5 minutes (major), 36.0 minutes (minor), e.r. = 99:1 (Li), e.r. = 97:3 (Mg)



8.12 Preparation of (*tert*-butyl(((2*R*,4*R*,6*R*)-2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)diphenylsilane (18l)



18l

Following **GP3**, methyl sulfoxide *syn*-**14b** (87.1 mg, 0.21 mmol), boronic ester **17f** (96 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:dichloromethane = 100:0→80:20) the homologated boronic ester **18l** (86 mg, 85%, >95:5 d.r.) as a colourless oil.

Following **GP4**, methyl sulfoxide *syn*-**14b** (108 mg, 0.26 mmol), boronic ester **17f** (96 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:dichloromethane = 100:0→80:20) the homologated boronic ester **18l** (34 mg, 33%, >95:5 d.r.) as a colourless oil.

[α]$^{23}_{D}$: +10 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66 (d, *J* = 7.8 Hz, 4H, Ar-H), 7.44–7.34 (m, 6 H, Ar-H), 3.53 (dd, J_1 = 9.6 Hz, J_2 = 5.1 Hz, 1H, CH*H*) 3.36 (dd, J_1 = 9.6 Hz, J_2 = 7.0 Hz, 1H. C*H*H), 1.77 (dq, J_1 = 7.0 Hz, J_2 = 6.7 Hz, 1H, CH), 1.56–1.45 (m, 1H, CH), 1.33-1.12 (m, 15H, CH*H*, CH_2 and 4 × CH_3), 1.08 (m, 1H, CH), 1.05 (s, 9H, 3 × CH_3), 0.93 (d, *J* = 6.7 Hz, 3H, CH_3), 0.92 (m, 1H, C*H*H), 0.90 (d, *J* = 7.5 Hz, 3H, CH_3), 0.78 (d, *J* = 6.6 Hz, 3H, CH_3) ppm

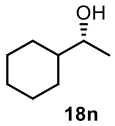
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 135.8 (4 × CH), 134.3 (2 × C), 129.6 (2 × CH), 127.7 (4 × CH), 82.9 (2 × C), 69.2 (CH_2), 41.9 (CH_2), 40.0 (CH_2), 33.3 (CH), 28.5 (CH), 27.0 (3 × CH_3), 24.9 (4 × CH_3), 20.0 (CH_3), 19.5 (CH), 18.0 (CH_3), 15.2 (CH_3) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 35.9 ppm

IR (neat): 2955, 2929, 1427, 1378, 1143, 1110, 823, 739 cm^{-1}

HRMS (ESI) calculated for $C_{31}H_{49}BNaO_3Si$: 531.3442, found: 531.3442

8.13 Preparation (*R*)-1-cyclohexylethanol (18n)



18n

Following **GP3**, methyl sulfoxide *ent-anti*-**14b** (87.1 mg, 0.21 mmol), pinacol boronic ester **17g** (42 mg, 0.20 mmol), *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol), afforded a crude mixture. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol) afforded after purification by flash column chromatography (pentane:dichloromethane = 100:0 → 30:70) a mixture of the alcohol **18n** and 2,4,6-triisopropylbenzoic acid. The residue was dissolved in Et_2O (ca. 5 mL) and filtered through a pad of basic silica (~20 mm depth, contents of flask washed with Et_2O ca. 30 mL) and the solvent was removed under reduced pressure to give alcohol **18n** (15.2 mg, 59%) as a colourless oil.

Following **GP4**, methyl sulfoxide *ent-anti*-**14b** (108 mg, 0.26 mmol), pinacol boronic ester **17g** (42 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded a crude mixture. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol) afforded after purification by flash column chromatography (pentane:dichloromethane = 100:0 → 30:70) a mixture of the alcohol **18n** and 2,4,6-triisopropylbenzoic acid. The residue was dissolved in Et_2O (ca. 5 mL) and filtered through a pad of basic silica (~20 mm depth, contents of flask washed with Et_2O ca. 30 mL) and the solvent was removed under reduced pressure to give alcohol **18n** (9.3 mg, 36%) as a colourless oil.

Following **GP3**, methyl sulfoxide *ent-anti*-**14b** (87.1 mg, 0.21 mmol), neopentyl boronic ester **17h** (38 mg, 0.20 mmol), *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol), afforded a crude mixture. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol) afforded after purification by flash column chromatography (pentane:dichloromethane = 100:0 → 30:70) a mixture of the alcohol **18n** and 2,4,6-triisopropylbenzoic acid. The residue was dissolved in Et_2O (ca. 5 mL) and filtered through a pad of basic silica (~20 mm depth, contents of flask washed with Et_2O ca. 30 mL) and the solvent was removed under reduced pressure to give alcohol **18n** (9.2 mg, 36%) as a colourless oil.

Following **GP4**, methyl sulfoxide *ent-anti*-**14b** (108 mg, 0.26 mmol), neopentyl boronic ester **17h** (38 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded a crude mixture. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol) afforded after purification by flash column chromatography (pentane:dichloromethane = 100:0 → 30:70) a mixture of the alcohol **18n** and 2,4,6-triisopropylbenzoic acid. The residue was dissolved in Et_2O (ca. 5 mL) and filtered through a pad of basic silica (~20 mm depth, contents of flask washed with Et_2O ca. 30 mL) and the solvent was removed under reduced pressure to give alcohol **18n** (12.4 mg, 48%) as a colourless oil.

Spectral data matched that previously reported.[31]

$[\alpha]^{24}_D$: –1.8 (*c* 0.4, $CHCl_3$). Lit.:[31] –3.8 (*c* 1.2, $CHCl_3$, 87% ee)

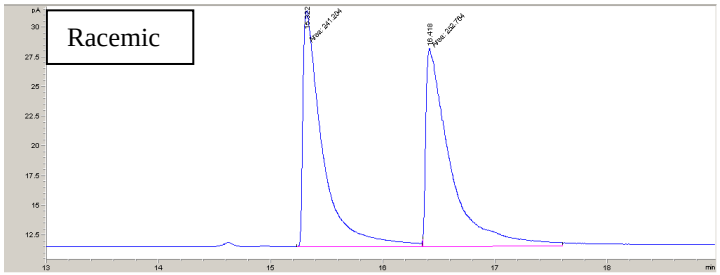
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.55 (p, *J* = 6.2 Hz, 1H, CH), 1.85 (app. br. d, *J* = 13.0 Hz, 1H, CH*H*), 1.80–1.72 (m, 2H, CH_2), 1.67 (app. br. d, *J* = 13.0 Hz, 2H, 2 × CH*H*), 1.48 (br. s, 1H, OH), 1.33–1.17 (m, 4H, CH, CH_2 and C*H*H), 1.16 (d, *J* = 6.2, 3H, CH_3), 1.07–0.90 (m, 2H, C*H*H) ppm

^{13}C NMR (101 MHz, $CDCl_3$): 72.4 (CH), 45.3 (CH), 28.9 (CH_2), 28.5 (CH_2), 26.7 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 20.6 (CH_3) ppm

IR (neat): 3362 (br.), 2922, 2852, 1702, 1448, 1062, 938 cm^{-1}

GC-MS (EI) calculated for $C_8H_{16}O$: 128.1, found 128.0

Chiral GC: Chiraldex β-DP, injector T = 250 °C, detector T = 300 °C. Oven conditions: Inject at T = 70 °C then ramp (10 °C min^{-1}) until 87 °C, then ramp (1 °C min^{-1}) until 102 °C, and ramp (10 °C min^{-1}) until 180 °C. He carrier gas at 3.0 mL min^{-1}. tR (minor) = 15.3 min, tR (major) = 16.4 min, total analysis time 28 min; e.r. = 99:1 (Bpin, Li), e.r. >99:1 (Bpin, Mg), e.r. = 98:2 (Bneo, Li), e.r. >99:1 (Bneo, Mg) .



#	Time	Area	Height	Width	Symmetry
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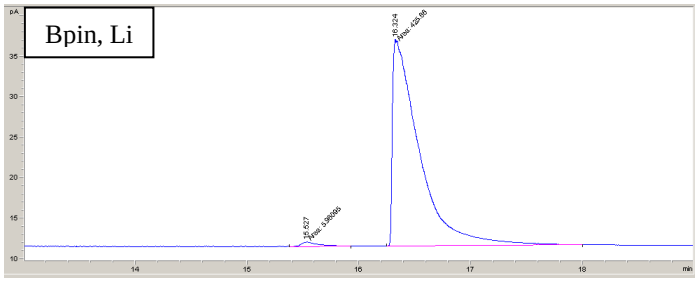
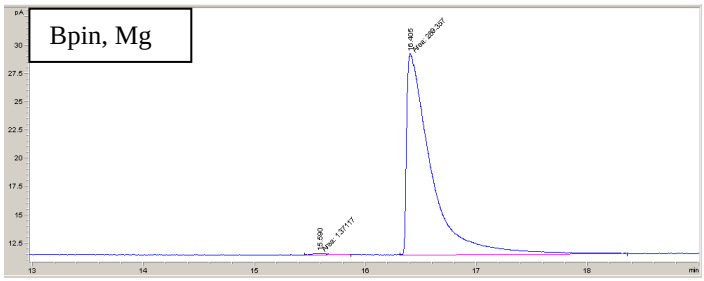
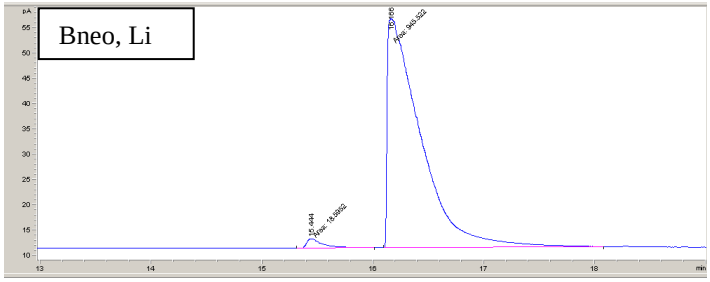
2	16.418	252.8	16.7	0.2525	0.172



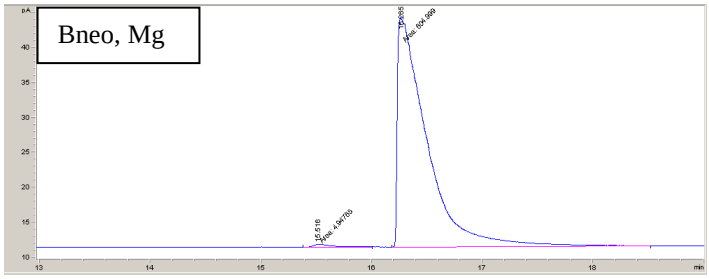
#	Time	Area	Height	Width	Symmetry
1	15.527	6	5.3E-1	0.1881	0.35
2	16.324	425.7	25.5	0.2782	0.114



#	Time	Area	Height	Width	Symmetry
1	15.59	1.4	1.4E-1	0.1655	0.671
2	16.405	269.4	17.8	0.2526	0.162

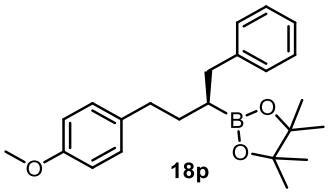


#	Time	Area	Height	Width	Symmetry
1	15.444	18.6	1.9	0.1671	0.318
2	16.166	945.5	45.3	0.3482	0.115



#	Time	Area	Height	Width	Symmetry
1	15.516	4.9	4.2E-1	0.1969	0.274
2	16.265	605	32.8	0.3077	0.117

8.14 Preparation of (*S*)-2-(4-(4-methoxyphenyl)-1-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18p) and (*S*)-4-(4-methoxyphenyl)-1-phenylbutan-2-ol (31)



Following **GP3**, benzyl sulfoxide *anti*-**14h** (108 mg, 0.22 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol), filtered through basic silica, afforded after purification by flash column chromatography (pentane:Et_2O = 95:5) the homologated boronic ester **18p** (58 mg, 79%) as a colourless oil.

Following **GP4**, benzyl sulfoxide *anti*-**14h** (128 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.2 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol), filtered through basic silica, afforded after purification by flash column chromatography (pentane:Et_2O = 95:5) a mixture of the homologated boronic ester **18p** and starting boronic ester **17a**. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol), afforded after purification by flash column chromatography (pentane:EtOAc = 80:20) the corresponding alcohol **31** (33 mg, 58%) as a colourless oil.

[α]$^{24}_D$: –31 (*c* 0.9, $CHCl_3$)

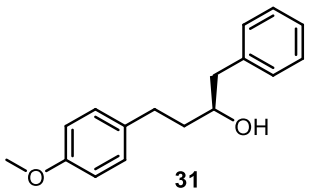
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.17 (m, 4H, Ar-H), 7.14 (app. tt, 1H, J_1 = 6.9 Hz, J_1 = 2.6 Hz, ArH), 7.07 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.78 (s, 3H, OCH_3), 2.78–2.68 (m, 2H, CH_2), 2.65–2.50 (m, 2H, CH_2), 1.78–1.61 (m, 2H, CH_2), 1.44 (quint, *J* = 6.0 Hz, 1H, CH), 1.18 (s, 6H, CH_3 × 2), 1.15 (s, 6H, CH_3 × 2) ppm

^{13}C NMR (101 MHz, $CDCl_3$): 157.5 (C) 141.9 (C), 134.7 (C), 129.1 (2 × CH), 128.7 (2 × CH), 127.9 (2 × CH), 125.4 (CH), 113.5 (2 × CH), 82.9 (2 × C), 55.1 (CH_3), 37.0 (CH_2), 34.4 (CH_2), 33.2 (CH_2), 25.4 (CH), 24.7 (2 × CH_3), 24.6 (2 × CH_3) ppm

^{11}B NMR (96 MHz, $CDCl_3$): 32.9 ppm

IR (neat): 2977, 2924, 1511, 1370, 1244, 1143, 1037 cm^{-1}

HRMS (ESI) calculated for $C_{23}H_{31}BO_3Na$: 389.2263, found 389.2264



31

[α]$^{24}_D$: –17 (*c* 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.29 (m, 2H, Ar-H), 7.27–7.18 (m, 3H, Ar-H), 7.12 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.3 Hz, 2H, Ar-H), 3.84 (app. sept, *J* = 4.2 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 2.85 (dd, J_1 = 13.8 Hz, J_2 =4.2 Hz, 1H, CH*H*), 2.82–2.75 (m, 1H, CH*H*), 2.73–2.62 (m, 2H, 2 × C*H*H), 1.85–1.78 (m, 2H, CH_2), 1.57 (br. s, 1H, O*H*) ppm

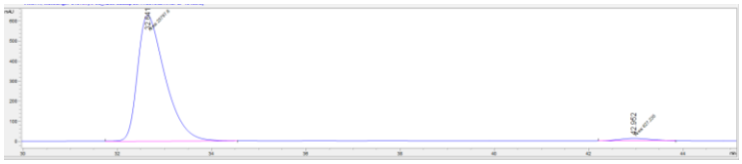
^{13}C NMR (101 MHz, $CDCl_3$): 157.9 (C), 138.5 (C), 134.2 (C), 129.6 (2 × CH), 129.5 (2 × CH), 128.7 (2 × CH), 126.6 (CH), 114.0 (2 × CH), 72.1 (CH), 55.4 (CH_3), 44.3 (CH_2), 38.8 (CH_2), 31.3 (CH_2) ppm

IR (neat): 3407 (br), 2933, 1511, 1243, 1034, 823 cm^{-1}

HRMS (ESI) calculated for $C_{17}H_{20}O_2Na$: 279.1356, found 279.1351

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm) with guard, hexane:isopropanol = 98:2, 0.5 mL/min, room temperature, 210.8 nm): tR = 32.7 minutes (major), 42.4 minutes (minor), e.r. = 98:2 (Li), e.r. = 98:2 (Mg)

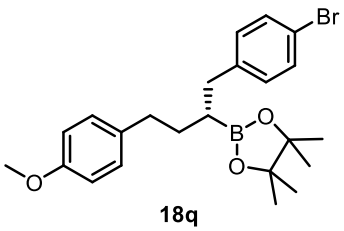
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	32.749	MM	10556.5	265	0.6638	49.814	0.666
2	42.424	MM	10635.3	209.5	0.8462	50.186	0.644



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	32.641	MM	25797.6	629.7	0.6828	97.626	0.561
2	42.952	MM	627.2	13	0.8014	2.374	0.849

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	33.247	MM	19965.9	468.4	0.7104	98.055	0.589
2	43.757	MM	396.1	7.1	0.9349	1.945	0.884

8.15 Preparation of (*R*)-2-(1-(4-bromophenyl)-4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18q) and (*R*)-1-(4-bromophenyl)-4-(4-methoxyphenyl)butan-2-ol (32)



18q

Following modified **GP3**, *p*-bromobenzyl sulfoxide *anti*-**14i** (125 mg, 0.22 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol), and *t*BuLi (1.7 M in pentane, 142 µL, 0.24 mmol), filtered through basic silica, afforded after purification by flash column chromatography (pentane:Et_2O = 95:5) a mixture of the homologated boronic ester **18q** and starting boronic ester **17a**. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol), afforded after purification by flash column chromatography (pentane:EtOAc = 80:20) the alcohol **32** (24.0 mg, 36%) as a colourless solid.

Following **GP4**, *p*-bromobenzyl sulfoxide *anti*-**14i** (148 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol), filtered through basic silica, afforded after purification by flash column chromatography (pentane:Et_2O = 95: 5) the homologated boronic ester **18q** (72.0 mg, 81%) as a colourless oil.

$[\alpha]^{24}_D$: +15 (*c* 1.0, $CHCl_3$)

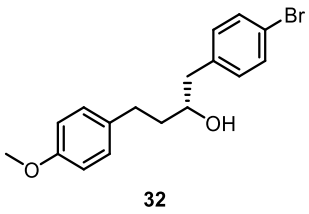
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.3 Hz, 2H, ArH), 7.09–7.04 (m, 4H, ArH), 6.81 (d, *J* = 8.0 Hz, 2H, ArH), 3.78 (s, 3H, OCH_3), 2.74–2.47 (m, 4H, H), 1.78–1.58 (m, 2H, CH_2), 1.37 (quint, 1H, *J* = 7.5 Hz, CH), 1.19 (s, 6H, CH_3 × 2), 1.17 (s, 6H, CH_3 × 2) ppm

^{13}C NMR (101 MHz, $CDCl_3$): 157.9 (C) 141.2 (C), 134.8 (C), 131.2 (2 × CH), 130.8 (2 × CH), 129.4 (2 × CH), 119.5 (C), 113.8 (2 × CH), 83.3 (2 × C), 55.4 (CH_3), 36.7 (CH_2), 34.6 (CH_2), 33.4 (CH_2), 25.5 (CH), 25.0 (2 × CH_3), 24.9 (2 × CH_3) ppm

^{11}B NMR (96 MHz, $CDCl_3$): 33.5 ppm

IR (neat): 2982, 2935, 1511, 1379, 1244, 1142, 824 cm^{-1}

HRMS (ESI) calculated for $C_{23}H_{30}BBrO_3Na$: 467.1368, found 467.1381



32

[α]$^{24}_D$: +20 (*c* 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.10 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.08 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.83 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.83–3.76 (m, 1H, C*H*), 3.79 (s, 3H, OCH_3), 2.81–2.76 (m, 2H, 2 × CH*H*), 2.69–2.61 (m, 2H, 2 × C*H*H), 1.84–1.74 (m, 2H, CH_2), 1.46 (br. d, *J* = 3.6 Hz, 1H, O*H*)

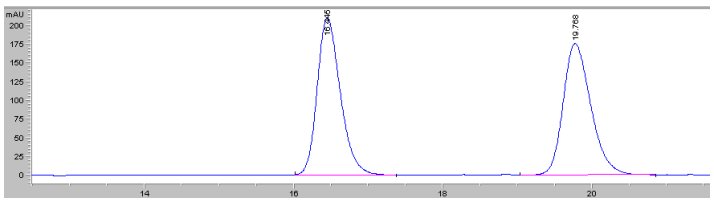
^{13}C NMR (101 MHz, $CDCl_3$): 158.0 (C), 137.6 (C), 133.9 (C), 129.6 (2 × CH), 131.7 (2 × CH), 131.3 (2 × CH), 129.4 (2 × CH), 120.5 (C) 114.0 (2 × CH), 71.9 (CH), 55.4 (CH_3), 43.6 (CH_2), 38.8 (CH_2), 31.3 (CH_2)

IR (neat): 3320, 2945, 1512, 1247, 1012, 802 cm^{-1}

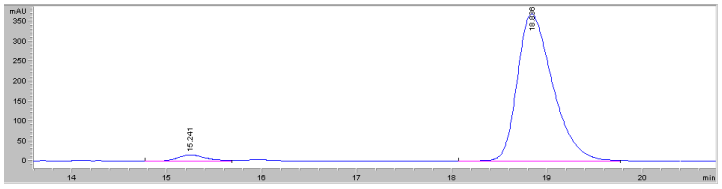
HRMS (ESI) calculated for $C_{17}H_{19}BrO_2Na$: 357.0461, found 357.0456

M.P. 72–74 ºC

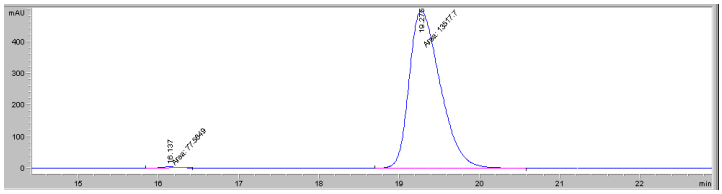
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm) with guard, hexane:isopropanol = 96:4, 1.0 mL/min, room temperature, 210.8 nm): tR = 16.4 minutes (minor), 19.8 minutes (major), e.r. = 97:3 (Li), e.r. > 99:1 (Mg)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.445	BB	0.3317	4534.43652	210.19647	49.9442
2	19.768	VB	0.4021	4544.57178	175.48772	50.0558

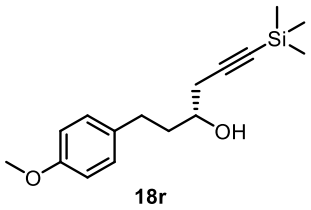


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.241	VV	0.2975	320.99515	15.76789	3.2428
2	18.836	VV	0.3924	9577.67090	369.48154	96.7572



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.137	MM	0.2931	77.56490	4.41115	0.5705
2	19.275	MM	0.4509	1.35177e4	499.63275	99.4295

8.16 Preparation (*R*)-1-(4-methoxyphenyl)-6-(trimethylsilyl)hex-5-yn-3-ol (18r)



18r

Following **GP3**, alkynyl sulfoxide *syn*-**14j** (112 mg, 0.22 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol), *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol), afforded after purification by flash column chromatography (pentane:Et_2O = 95:5) a mixture of the homologated boronic ester and starting boronic ester **17a**. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol) afforded after purification by flash column chromatography (pentane:EtOAc = 85:15) the alcohol **18r** (30.0 mg, 54%) as a colourless oil.

Following **GP4**, alkynyl sulfoxide *syn*-**14j** (133 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (pentane:Et_2O = 95:5) a mixture of the desired homologated boronic ester and starting boronic ester **17a**. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (308 mg, 2.00 mmol) afforded after purification by flash column chromatography (pentane:EtOAc = 85:15) the alcohol **18r** (33.0 mg, 60%) as a colourless oil.

[α]$^{24}_D$: +7 (*c* 1.0, $CHCl_3$)

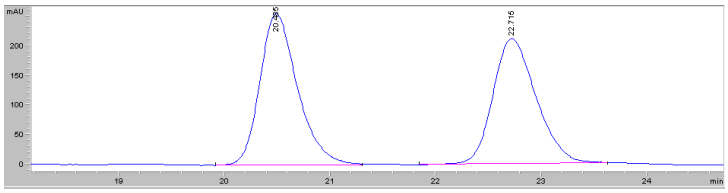
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.6 Hz, 2H, ArH), 6.84 (d, *J* = 8.6 Hz, 2H, ArH), 3.79 (s, 3H, OCH_3), 3.74 (app. br. quint, *J* = 6.0 Hz, 1H, CH), 2.74 (quint., *J* = 6.8 Hz, 1H, CH*H*), 2.64 (quint., *J* = 6.8 Hz, 1H, C*H*H), 2.47 (dd, J_1 = 17.1 Hz, J_2 =4.8 Hz, 1H, CH*H*), 2.38 (dd, J_1 = 17.1 Hz, J_2 =4.8 Hz, 1H, *CH*H), 2.00 (s, 1H, OH), 1.82 (dt, J_1 = 8.1 Hz, J_2 =6.0 Hz, 2H, CH_2), 0.16 (s, 9H, $Si(CH_3)_3$) ppm

^{13}C NMR (101 MHz, $CDCl_3$): 158.0 (C), 133.9 (C), 129.4 (2 × CH), 114.0 (2 × CH), 103.2 (C), 87.9 (C), 69.2 (CH), 55.4 (CH_3), 38.1 (CH_2), 31.1 (CH_2), 29.1 (CH_2), 0.2 (3 × CH_3) ppm

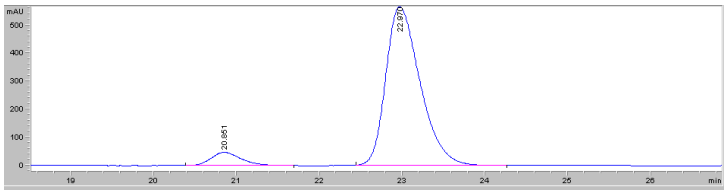
IR (neat): 3389, 2954, 2173, 1512, 1246, 841 cm^{-1}

HRMS (ESI) calculated for $C_{16}H_{24}O_2SiNa$: 299.1546, found 299.1534

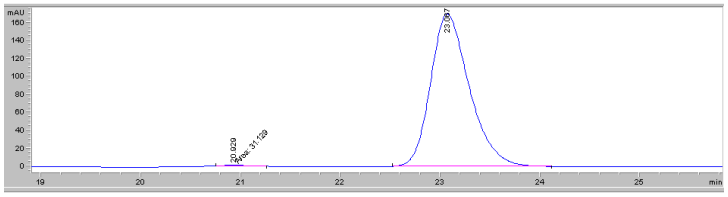
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm) with guard, hexane:isopropanol = 98:2, 0.5 mL/min, room temperature, 210.8 nm): tR = 20.5 minutes (minor), 22.7 minutes (major), e.r. = 93:7 (Li), e.r. > 99:1 (Mg)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.485	BV	0.3725	6348.99463	254.99316	51.4036
2	22.715	VB	0.4419	6002.26514	211.01735	48.5964

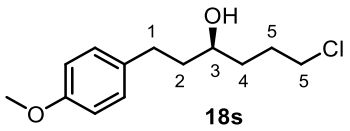


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.851	BB	0.3851	1203.91187	47.28028	6.8658
2	22.970	BB	0.4402	1.63309e4	566.62854	93.1342



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.929	MM	0.3508	31.12901	1.47888	0.6718
2	23.067	BB	0.4082	4602.38721	169.80510	99.3282

8.17 Preparation of (*R*)-6-chloro-1-(4-methoxyphenyl)hexan-3-ol (18s)



18s

Following **GP3**, chloropropyl sulfoxide *anti*-**14k** (100 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol), *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) and acetic acid (11 µL), afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) a mixture of the desired homologated boronic ester and starting boronic ester **17a**. Following **GP7**, oxidation of the mixture using H_2O_2 (1 mL) afforded after purification by flash column chromatography (hexane:EtOAc = 80:20) the alcohol **18s** (20.3 mg, 42%) as a colourless solid.

Following **GP4**, chloropropyl sulfoxide *syn*-**14k** (124 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) a mixture of the desired homologated boronic ester and starting boronic ester **17a**. Following **GP7**, oxidation of the mixture using H_2O_2 (1 mL) afforded after purification by flash column chromatography (hexane:EtOAc = 80:20) the alcohol **18s** (27.0 mg, 56%) as a colourless solid.

$[\alpha]^{23}_D$: –8 (*c* 0.5, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.12 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.6 Hz, 2H, Ar-H), 3.79 (s, 3H, O-CH_3), 3.65 (m, 1H, 3-H), 3.57 (t, *J* = 6.0 Hz, 2H, 6-H), 2.73 (m, 1H, 1-H), 2.63 (m, 1H, 1-H), 1.96 (m, 1H, 5-H), 1.89–1.64 (m, 4H, 5-H + 2-H × 2 + 4-H), 1.56 (m, 1H, 4-H), 1.48 (bs, 1H, OH) ppm

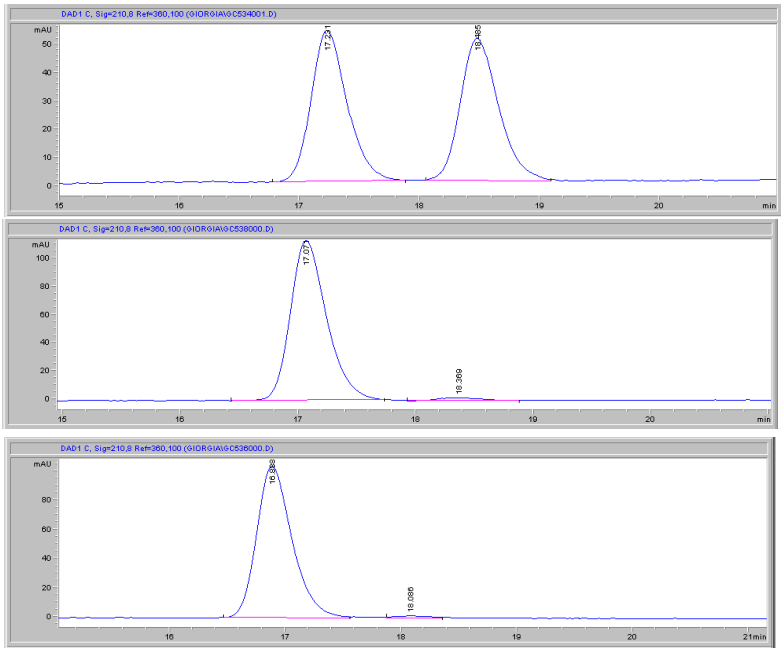
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.8 (Ar-C), 133.8 (Ar-C), 129.3 (2C, Ar-C × 2), 113.9 (2C, Ar-C × 2), 70.7 (3-C), 55.3 (O-CH_3), 45.2 (6-C), 39.4 (2-C), 34.6 (4-C), 31.1 (1-C), 28.8 (5-C) ppm

IR (neat): 3675, 2988, 2972, 2901, 1394, 1074, 1066, 1057, 892, 879 cm^{-1}

HRMS (ESI) calculated for $C_{13}H_{19}ClNaO_2$: 265.0966, found: 265.0976

M.P. 37–39 ºC

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 95:5, 0.7 mL/min, room temperature, 210.8 nm): tR = 17.2 minutes (major), 18.5 minutes (minor), e.r. = 98:2 (Li), e.r. = 99:1 (Mg)

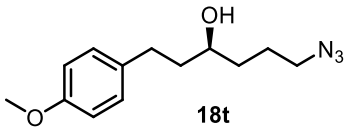


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.231	PB	0.3161	1110.17432	53.05347	50.0516
2	18.485	BB	0.3226	1107.88672	49.98637	49.9484

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.071	VB	0.3207	2444.90698	113.78085	97.9217
2	18.369	PV	0.2860	51.89127	2.16219	2.0783

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.888	BB	0.3186	2201.40137	104.13776	98.5457
2	18.086	BV	0.2309	32.48722	1.76329	1.4543

8.18 Preparation of (*R*)-6-azido-1-(4-methoxyphenyl)hexan-3-ol (18t)



18t

Following **GP4**, sulfoxide *anti*-**14l** (59.6 mg, 0.120 mmol), boronic ester **17a** (22.0 mg, 0.084 mmol) and *i*PrMgCl•LiCl (1.2 M in THF, 90 µL, 0.110 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) a mixture of the desired homologated boronic ester and starting boronic ester **17a**. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (146 mg, 0.950 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 80:20) the alcohol **18t** (11.7 mg, 56%) as a colourless oil.

[α]$^{22}_{D}$: +16 (*c* 0.5, $CHCl_3$)

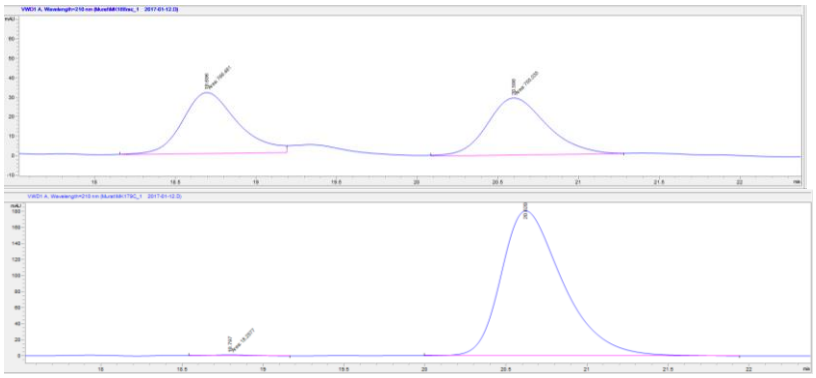
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.12 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.79 (s, 3H, OCH_3), 3.64 (tt, J_1 = 8.9 Hz, J_2 = 4.8 Hz, 1H, CH), 3.31 (t, *J* = 6.7 Hz, 2H, CH_2), 2.73 (ddd, $^2J_1$ = 14.0 Hz, J_2 = 8.8 Hz, J_3 = 6.4 Hz, 1H, CH_{2a}), 2.63 (ddd, $^2J_1$ = 14.0 Hz, J_2 = 9.0 Hz, J_3 = 7.1 Hz, 1H, CH_{2b}), 1.83–1.46 (m, 6H, CH_2 × 3), 1.42 (br. s, 1H, OH) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 158.0 (Ar-C), 133.9 (Ar-C), 129.4 (2C, Ar-C), 114.0 (2C, Ar-C), 70.9 (CH), 55.4 (OCH_3), 51.7 (CH_2), 39.6 (CH_2), 34.7 (CH_2), 31.3 (CH_2), 25.3 (CH_2) ppm

IR (neat): 3446, 2918, 2097, 1512, 1246, 1036, 736 cm^{-1}

HRMS (ESI) calculated for $C_{13}H_{19}N_3NaO_2$: 272.1369, found: 272.1368

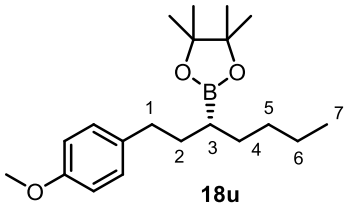
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 96:4, 0.8 mL/min, room temperature, 210.8 nm): tR = 18.8 minutes (minor), 20.6 minutes (major), e.r. > 99:1



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.696	MM	766.5	31.7	0.4027	50.376	0.777
2	20.598	MM	755	29.4	0.4278	49.624	0.8

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.797	MM	18.3	1.1	0.2894	0.381	0.751
2	20.62	BB	4775.6	180.6	0.3987	99.619	0.633

8.19 Preparation of (*R*)-2-(1-(4-methoxyphenyl)pentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18u)



18u

Following **GP3**, butyl sulfoxide *syn*-**14m** (95.5 mg, 0.21 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *t*BuLi (1.7 M in pentane, 235 µL, 0.40 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 98:2) the homologated boronic ester **18u** (43.2 mg, 65%) as a colourless oil.

Following **GP4**, ethyl sulfoxide *syn*-**14m** (119 mg, 0.26 mmol), boronic ester **17a** (52.4 mg, 0.20 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 210 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 98:2) the homologated boronic ester **18u** (46.2 mg, 70%) as a colourless oil.

[α]$^{23}_{D}$: +6 (*c* 0.5, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.10 (dt, J_1 = 8.6 Hz, J_2 = 2.9 Hz, 2H, Ar-H), 6.81 (dt, J_1 = 8.6 Hz, J_2 = 2.9 Hz, 2H, Ar-H), 3.78 (s, 3H, O-CH_3), 2.61–2.48 (m, 2H, 1-H), 1.70 (m, 1H, 2-H), 1.62 (m, 1H, 2-H), 1.49–1.36 (m, 2H, 4-H), 1.32–1.23 (m, 4H, 5-H + 6-H), 1.26 (s, 12H, C-CH_3 × 4), 1.03 (m, 1H, 3-H), 0.88 (t, *J* = 7.0 Hz, 3H, 7-H) ppm

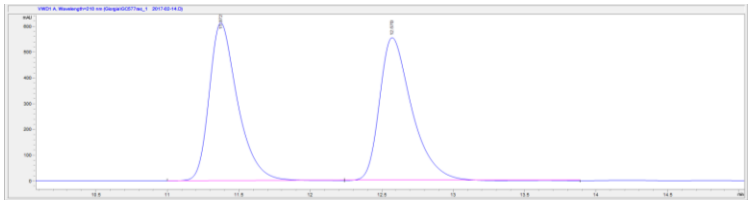
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.6 (Ar-C), 135.3 (Ar-C), 129.2 (2C, Ar-C × 2), 113.6 (2C, Ar-C × 2), 82.9 (2C, B-O-C × 2), 55.2 (O-CH_3), 34.7 (1-C), 33.8 (2-C), 31.5 (4-C), 30.9 (5-C), 24.9 (2C, C-*C*H_3 × 2), 24.8 (2C, C-*C*H_3 × 2), 23.0 (6-C), 14.1 (7-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 33.8 ppm

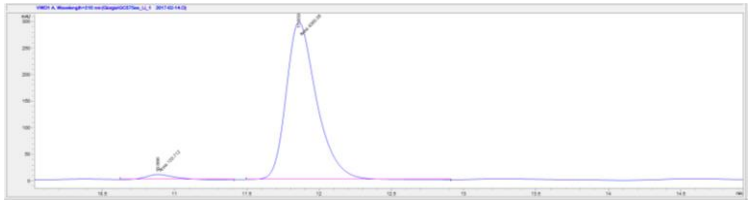
IR (neat): 2923, 2856, 1512, 1379, 1314, 1244, 1143, 1039, 967, 824 cm^{-1}

HRMS (ESI) calculated for $C_{20}H_{33}BNaO_3$: 355.241863, found: 355.242160

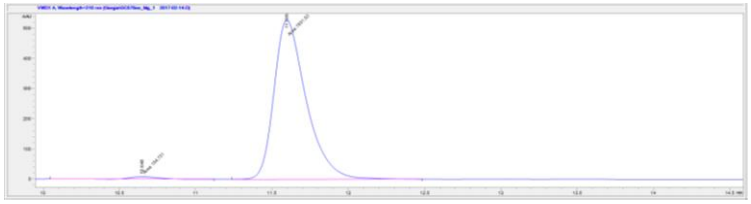
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 95:5, 0.7 mL/min, room temperature, 210.8 nm): tR = 11.4 minutes (minor), 12.6 minutes (major), e.r. = 97:3 (Li), e.r. = 98:2 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.372	BB	8426.9	611	0.2075	49.199	0.651
2	12.57	BV R	8701.2	553.2	0.2392	50.801	0.599

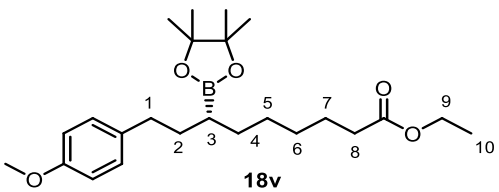


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.886	MM	133.7	9.7	0.2297	2.975	0.731
2	11.859	MM	4360.4	296.8	0.2448	97.025	0.697



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.648	MM	154.7	8.9	0.2906	1.937	1.111
2	11.595	MM	7831.5	531.7	0.2455	98.063	0.645

8.20 Preparation of ethyl (*S*)-9-(4-methoxyphenyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanate (18v)



18v

Following **GP4**, ethyl sulfoxide *anti*-**14n** (70.6 mg, 0.13 mmol), boronic ester **17a** (26.2 mg, 0.10 mmol) and *i*PrMgCl•LiCl (1.14 M in THF, 105 µL, 0.12 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 85:15) the homologated boronic ester **18v** (25.4 mg, 61%) as a colourless oil.

[α]$^{23}_D$: –6 (*c* 0.8, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.08 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.10 (q, *J* = 7.1 Hz, 2H, 10-H), 3.77 (s, 3H, O-CH_3), 2.59–2.57 (m, 2H, 1-H), 2.26 (t, *J* = 7.5 Hz, 2H, 8-H), 1.74–1.66 (m, 1H, 2-H), 1.64–1.56 (m, 3H, 2-H + 7-H), 1.47–1.36 (m, 2H, 4-H), 1.31–1.21 (m, 19H, C-CH_3 × 4, 5-H, 6-H, 11-H), 1.03 (m, 1H, 3-H) ppm

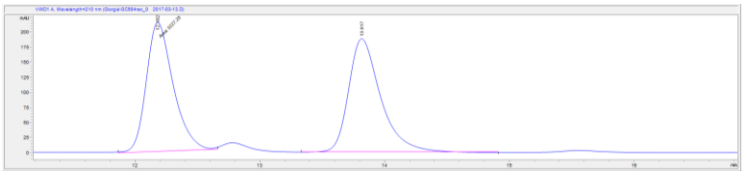
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 173.9 (CO), 157.6 (Ar-C), 135.1 (Ar-C), 129.2 (2C, Ar-C × 2), 113.6 (2C, Ar-C × 2), 82.9 (2C, B-O-C × 2), 60.1 (10-C), 55.2 (O-CH_3), 34.7 (1-C), 34.3 (8-C), 33.7 (2-C), 31.0 (4-C), 29.4 (6-C), 28.8 (5-C), 24.9 (7-C), 24.8 (2C, C-*C*H_3 × 2), 24.8 (2C, C-*C*H_3 × 2), 14.2 (11-C) ppm (*carbon attached to boron not observed due to quadrupolar relaxation*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 34.2 ppm

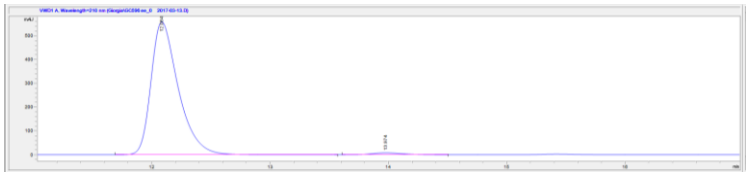
IR (neat): 2927, 1733, 1512, 1379, 1314, 1244, 1143, 1036, 967, 824 cm^{-1}

HRMS (ESI) calculated for $C_{24}H_{39}BNaO_5$: 441.278712, found: 441.279249

Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 90:10, 0.7 mL/min, room temperature, 210.8 nm): tR = 12.2 minutes (major), 13.8 minutes (minor), e.r. = 99:1

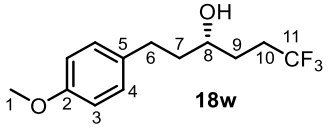


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.182	MM	3227.3	214.5	0.2508	48.898	0.722
2	13.817	BB	3372.8	188.2	0.2699	51.102	0.65



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.084	BV R	8893.1	557.3	0.2412	98.544	0.611
2	13.974	BB	131.4	7.7	0.2415	1.456	0.769

8.21 Preparation of (*S*)-6,6,6-trifluoro-1-(4-methoxyphenyl)hexan-3-ol (18w)



18w

Following **GP3**, sulfoxide *syn*-**14o** (62 mg, 0.12 mmol), boronic ester **17a** (31 mg, 0.12 mmol) and *t*BuLi (1.7 M in pentane, 141 µL, 0.24 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) a mixture of the desired homologated boronic ester and starting boronic ester **17a**. Following **GP7**, oxidation of the mixture using H_2O_2 (1 mL) afforded after

purification by flash column chromatography (hexane:EtOAc = 80:20) the alcohol **18w** (11 mg, 35%) as a colourless solid.

Following **GP4**, sulfoxide *syn*-**14o** (79 mg, 0.16 mmol), boronic ester **17a** (32 mg, 0.12 mmol) and *i*PrMgCl•LiCl (1.3 M in THF, 100 µL, 0.13 mmol) afforded after purification by flash column chromatography (hexane:Et_2O = 95:5) a mixture of the desired homologated boronic ester and starting boronic ester **17a**. Following **GP8**, oxidation of the mixture using $NaBO_3$•$4H_2O$ (189 mg, 1.22 mmol) afforded after purification by flash column chromatography (hexane:EtOAc = 80:20) the alcohol **18w** (17 mg, 52%) as a colourless solid

[α]$^{24}_D$: –11 (*c* 0.5, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.11 (d, J = 8.5 Hz, 2H, 4-H), 6.84 (d, J = 8.6 Hz, 2H, 3-H), 3.79 (s, 3H, 1-H), 3.66 (tt, J_1 = 8.4 Hz, J_2 = 4.3 Hz, 1H, 8-H), 2.73 (dt, J_1 = 15.0 Hz, J_2 = 7.6 Hz, 1H, 6-H_a), 2.64 (dt, J_1 = 13.8 Hz, J_2 = 7.9 Hz, 1H, 6-H_b), 2.40–2.24 (m, 1H, 10-H_a), 2.23–2.05 (m, 1H, 10-H_b), 1.82–1.71 (m, 3H, 7-H, 9-H_a), 1.65 (dddd, J_1 = 13.9 Hz, J_2 = 10.8 Hz, J_3 = 8.7 Hz, J_4 = 5.2 Hz, 1H, 9-H_b), 1.43 (br. s, 1H, OH) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 158.1 (2-C), 133.5 (5-C), 129.4 (2C, 4-C), 127.5 (q, $^1J_{CF}$ = 275.9 Hz, 11-C), 114.1 (2C, 4-C), 70.0 (8-C), 55.4 (1-C), 39.5 (7-C), 31.2 (6-C), 30.3 (q, $^2J_{CF}$ = 29.1 Hz, 10-C), 29.7 (q, $^1J_{CF}$ = 2.5 Hz, 9-C) ppm

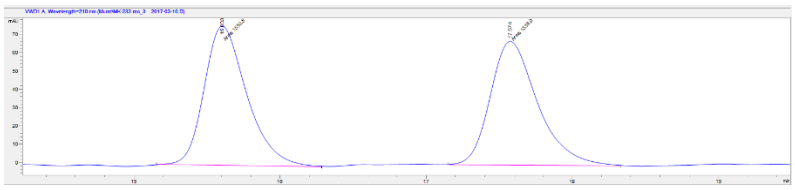
^{19}F NMR ($CDCl_3$, 377 MHz) δ: –66.4 (t, J = 10.9 Hz, CF_3) ppm

IR (neat): 3415, 2936, 2846, 1512, 1246, 1135, 1034, 830 cm^{-1}

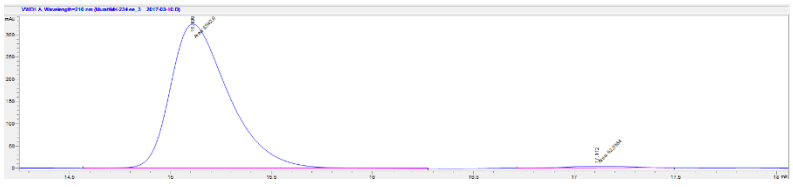
HRMS (EI) calculated for $C_{13}H_{17}O_2F_3$: 262.1175, found: 262.1184

M.P. 43–45 ºC

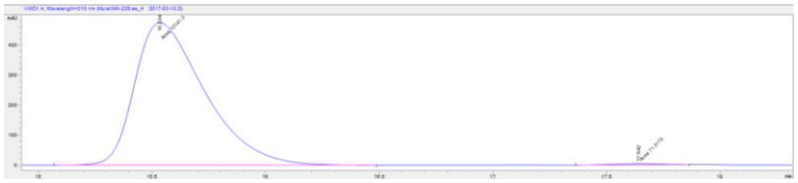
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 98:2, 1.0 mL/min, room temperature, 210.8 nm): tR = 15.6 minutes (major), 17.7 minutes (minor), e.r. = 99:1 (Li), e.r. > 99:1 (Mg)



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.603	MM	1550.8	76.3	0.3388	50.241	0.714
2	17.574	MM	1535.9	67.8	0.3777	49.759	0.709

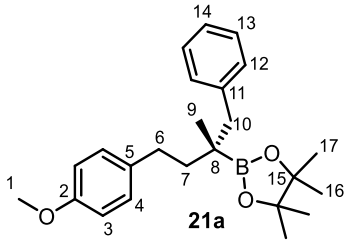


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.109	MM	6540.6	325.7	0.3347	98.612	0.609
2	17.112	MM	92	4.5	0.3409	1.388	0.886



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	15.534	MM	10141.3	474.5	0.3562	99.302	0.55
2	17.642	MM	71.3	4.2	0.285	0.698	0.871

8.22 Preparation of (*S*)-2-(4-(4-methoxyphenyl)-2-methyl-1-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21a)



Following **GP6**, sulfoxide **20a** (195 mg, 0.39 mmol), boronic ester **17a** (78 mg, 0.30 mmol), *t*BuLi (1.6 M in pentane, 370 µL, 0.60 mmol) and PMDTA (120 µL, 0.60 mmol) afforded after purification by flash column chromatography (petroleum ether:EtOAc = 98:2 to 90:10) the desired homologated boronic ester **21a** (65 mg, 57%) as a colourless oil.

$[\alpha]^{22}_{D}$: +7 (*c* 1.0, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.23–7.20 (m, 4H, 12-H and 13H), 7.18–7.14 (m, 1H, 14-H), 7.10 (d, *J* = 8.3 Hz, 2H, 4-H), 6.82 (d, *J* = 8.3 Hz, 2H, 3-H), 3.78 (s, 3H, 1-H), 2.84 (d, ^{2}J = 13.1 Hz, 1H, 10-H_a), 2.63–2.53 (m, 3H, 10-H_b + 6-H), 1.75 (td, J_t = 12.5 Hz, J_d = 5.4 Hz, 1H, 7-H_a), 1.49 (td, J_1 = 12.5 Hz, J_2 = 5.7 Hz, 1H, 7-H_b), 1.26 (s, 6H, 16-H), 1.22 (s, 6H, 17-H), 0.98 (s, 3H, 9-H) ppm

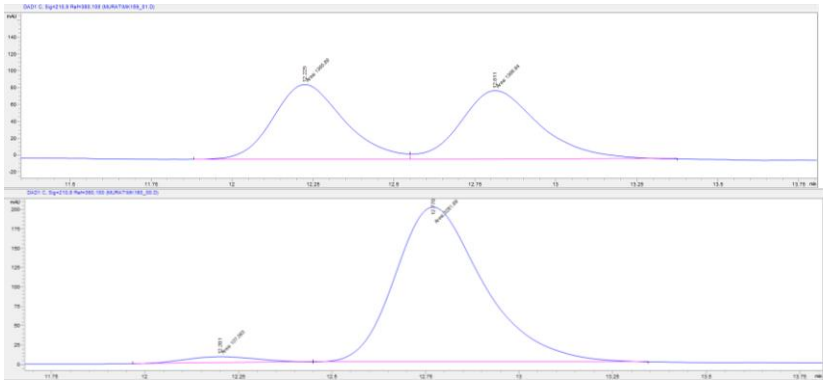
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 157.7 (2-C), 140.1(11-C), 135.7 (5-C), 130.5 (2C, 12-C), 129.3 (2C, 4-C), 127.8 (2C, 13-C), 125.9 (14-C), 113.9 (2C, 3-C), 83.4 (2C, 15-C), 55.4 (1-C), 44.9 (10-C), 42.1 (7-C), 31.8 (6-C), 25.3 (2C, 17-C), 25.0 (2C, 16-C), 21.4 (9-C) ppm (*carbon attached to boron (8-C) was not observed due to quadrupolar relaxation in ^{13}C NMR but it correlates with 9-H at 26.9 ppm in HMBC*)

^{11}B NMR ($CDCl_3$, 128 MHz) δ: 32.1 ppm

IR (neat): 2976, 2929, 1511, 1310, 1244, 1038, 821, 703 cm^{-1}

HRMS (ESI) calculated for $C_{24}H_{33}BNaO_3$: 403.2419, found: 403.2414

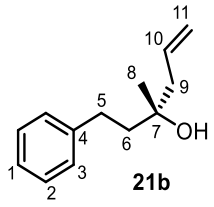
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 96:4, 0.9 mL/min, room temperature, 210.8 nm): tR = 12.2 minutes (minor), 12.8 minutes (major), e.r. = 97:3



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.225	MF	1365.9	88.7	0.2565	49.944	0.801
2	12.811	FM	1368.9	81.1	0.2814	50.056	0.759

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.201	MM	107.1	7.9	0.2247	3.159	0.958
2	12.77	MM	3281.9	199.5	0.2741	96.841	0.729

8.23 Preparation of (*R*)-3-methyl-1-phenylhex-5-en-3-ol (21b)



21b

Following **GP6**, sulfoxide **20b** (153 mg, 0.34 mmol), phenyl ethyl pinacol boronic ester **15** (60 mg, 0.26 mmol), *t*BuLi (1.6 M in pentane, 350 µL, 0.59 mmol) and PMDTA (120 µL, 0.59 mmol) afforded after purification by flash column chromatography (petroleum ether:EtOAc = 98:2 to 90:10) a mixture of the desired homologated boronic ester and the starting boronic ester **15**. Following **GP7**, oxidation of the mixture using H_2O_2 (1 mL) afforded after purification by flash column chromatography (hexane:EtOAc = 90:10 to 70:30) the alcohol **21b** (29 mg, 59%) as a colourless oil.

Spectral data matched that previously reported.[32]

[α]$^{22}_{D}$: +18 (*c* 0.8, $CHCl_3$) Lit. for (*R*):[32a] +57 (*c* 1.0, $CHCl_3$, *er* 99:1): for (*S*):[32b] –58 (*c* 1.0, $CHCl_3$, *er* 91:9)

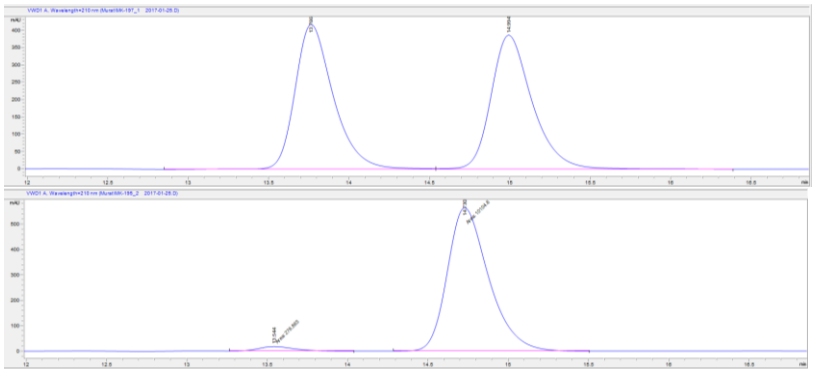
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.27 (m, 2H, 2-H), 7.21–7.16 (m, 3H, 1-H + 3-H), 5.89 (ddt, J_{trans} = 16.8 Hz, J_{cis} = 10.4 Hz, *J* = 7.5 Hz, 1H, 10-H), 5.19–5.13 (m, 2H, 11-H), 2.73–2.69 (m, 2H, 5-H), 2.30 (d, *J* = 7.5 Hz, 2H, 9-H), 1.80–1.76 (m, 2H, 6-H), 1.48 (br. s, 1H, OH), 1.26 (s, 3H, 8-H) ppm

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 142.7 (4-C), 133.9 (10-C), 128.6 (2C, 2-C), 128.5 (2C, 3-C), 125.9 (1-C), 119.1 (11-C), 72.2 (7-C), 46.6 (9-C), 43.9 (6-C), 30.4 (5-C), 26.9 (8-C) ppm

IR (neat): 3402, 2975, 2931, 1640, 1455, 915, 744 cm^{-1}

HRMS (ESI) calculated for $C_{13}H_{18}NaO$: 213.1250, found: 213.1255

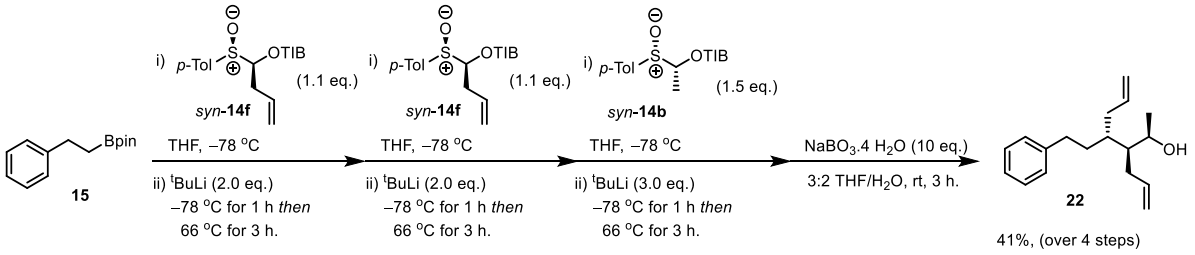
Chiral HPLC: (Daicel Chiralcel-IB column (25 cm), hexane:isopropanol = 98:2, 0.7 mL/min, room temperature, 210.8 nm): tR = 13.6 minutes (minor), 14.7 minutes (major), e.r. = 97:3



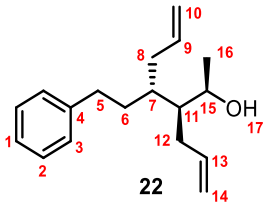
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.766	VV R	6942	417.8	0.2507	50.133	0.69
2	14.994	VB	6905.3	386.5	0.271	49.867	0.706

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.544	MM	276.9	17.9	0.2573	2.667	0.74
2	14.73	MM	10104.8	566.1	0.2975	97.333	0.703

8.24 Iterative homologation sequence



(2*S*, 3*R*, 4*S*)-3-Allyl-4-phenethylhept-6-en-2-ol (22)

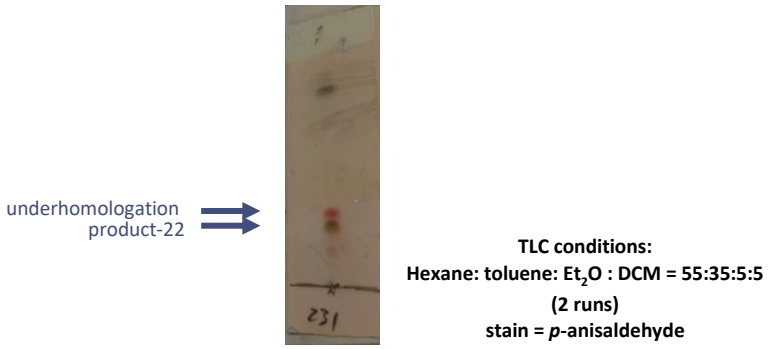


1st homologation: According to **GP3** using allylic sulfoxide *syn*-**14f** (485 mg, 1.10 mmol), phenyl ethyl pinacol boronic ester **15** (233 mg, 1.00 mmol) and *t*-BuLi (1.7 M in pentane, 1.18 mL, 2.00 mmol). The resulting mixture was concentrated *in vacuo* and the residue was suspended in pentane:Et_2O = 95:5 (ca. 20 mL). The suspension was filtered (~ 6 cm depth of wetted silica), the silica was washed (180 mL, pentane:Et_2O = 95:5) and the filtrate was concentrated *in vacuo* to give the crude homologated boronic ester.

2nd homologation: The crude product from the first homologation was dissolved in toluene (4 mL) and transferred to an oven dried Schlenk tube. The solvent was removed *in vacuo* and the compound was dried on high vacuum for 1 h with stirring. The reaction was performed according to **GP3** using allylic sulfoxide *syn*-**14f** (485 mg, 1.10 mmol), the crude boronic ester obtained from the firs homologation (assumed 1.00 mmol) and *t*-BuLi (1.7 M in pentane, 1.18 mL, 2.00 mmol). The resulting mixture was concentrated *in vacuo* and the residue was suspended in pentane:Et_2O = 95:5 (ca. 20 mL). The

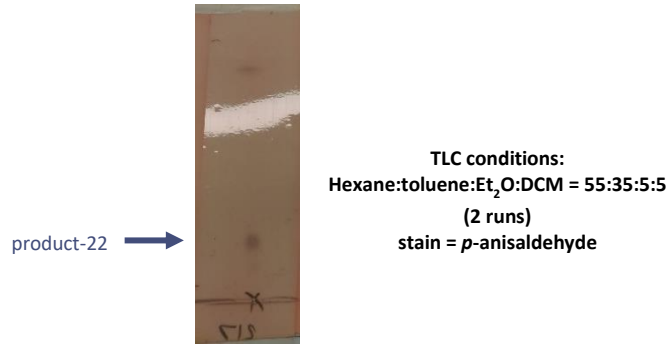
suspension was filtered (~ 6 cm depth of wetted silica), the silica was washed (180 mL, pentane:Et_2O = 95:5) and the filtrate was concentrated *in vacuo* to give the crude homologated boronic ester.

3rd homologation (with sulfoxide): The crude product from the second homologation was divided into three batches (3 mL of a 9 mL solution in toluene was transferred to an oven dried Schlenk tube). The solvent was removed *in vacuo* and the compound was dried on high vacuum for 1 h with stirring. The reaction was performed according to modified **GP3** using methyl sulfoxide *syn*-**14b** (207 mg, 0.50 mmol), the crude boronic ester obtained from the second homologation (assumed 0.33 mmol), and *t*-BuLi (1.7 M in pentane, 583 µL, 0.99 mmol). The resulting mixture was concentrated *in vacuo* and the residue was suspended in pentane:Et_2O = 95:5 (ca. 20 mL). The suspension was filtered (~ 6 cm depth of wetted silica), the silica was washed (180 mL, pentane:Et_2O = 95:5) and the filtrate was concentrated *in vacuo* to give crude boronic ester. Oxidation of the crude boronic ester was performed according to **GP8** using $NaBO_3$•$4H_2O$ (508 mg, 3.30 mmol) for 3 h.



Purification by silica gel chromatography (58:35:5:2 hexane/toluene/diethyl ether/dichloromethane) gave **22** as a colourless oil (35.0 mg, 41% over 4 steps, d.r. >95:5).

3rd homologation (with stannane): The crude product from the second homologation was divided into three batches (3 mL of a 9 mL solution in toluene was transferred to an oven dried Schlenk tube). The solvent was removed *in vacuo* and the compound was dried on high vacuum for 1 h with stirring. The reaction was performed according to S. Balieu *et al.*[30] using (*S*)-stannane (*S*)-**3** (198 mg, 0.45 mmol), the crude boronic ester obtained from the second homologation (assumed 0.33 mmol), and *n*-BuLi (1.6 M in hexanes, 269 µL, 0.43 mmol) in Et_2O (2.5 mL). The reaction mixture was filtered through silica (~10 mm depth of wetted (Et_2O) silica, using a filter frit connected directly to an oven dried receiving vessel) to give a pale yellow solution. The silica was washed with Et_2O (reagent grade, 20 mL) and the solvent was removed under reduced pressure to give the crude boronic ester. Oxidation of the crude boronic ester was performed according to **GP8** using $NaBO_3$•$4H_2O$ (508 mg, 3.30 mmol) for 3 h.



Purification by silica gel chromatography (58:35:5:2 hexane/toluene/diethyl ether/dichloromethane) gave **22** as a colourless oil (44.0 mg, 52% over 4 steps, d.r. >95:5).

[α]$^{22}_{D}$: –12 (*c* 1.0, $CHCl_3$)

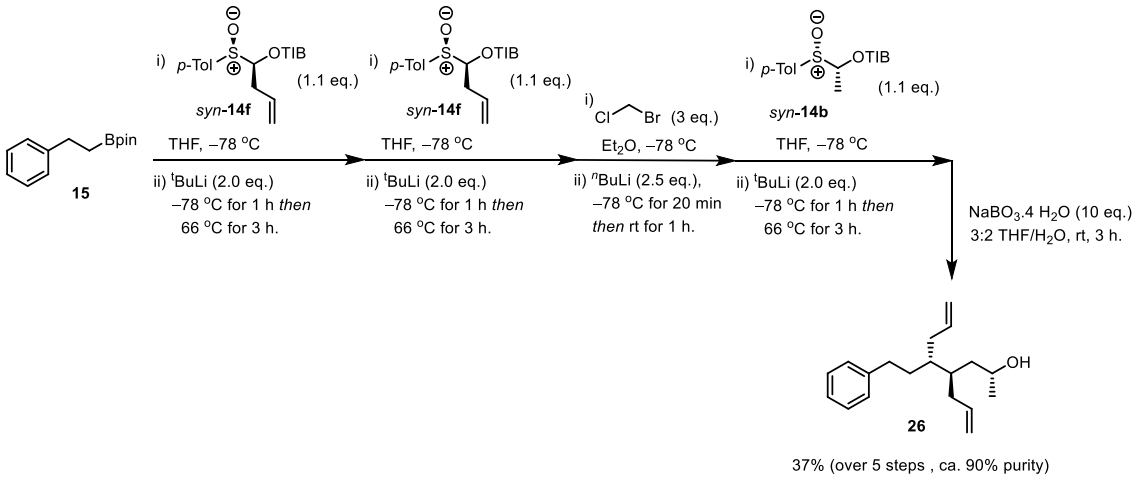
R_f = 0.18 (55:35:5:5 hexane/toluene/diethyl ether/dichloromethane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.25 (m, 2H, H-2), 7.21–7.15 (m, 3H, H-1 and H-3), 5.83–5.71 (m, 2H, H-9 and H-13), 5.08–4.95 (m, 4H, H-10 and H-14), 3.80 (app. sext, J = 6.2 Hz,1H, H-15), 2.73 (ddd, J_1 = 13.8 Hz, J_2 = 10.0 Hz, J_3 = 4.9 Hz, 1H, H-5$_a$), 2.55 (ddd, J_1 = 13.8 Hz, J_2 = 9.4 Hz, J_3 = 7.2 Hz, 1H, H-5$_b$), 2.29–2.22 (m, 1H, H-8$_a$), 2.14–2.00 (3H, m, H-8$_b$ and H-12), 1.86 (ddt, J_1 = 13.8 Hz, J_2 = 6.4 Hz, J_3 = 3.3 Hz, 1H, H-6$_a$), 1.81–1.73 (m, 1H, H-7), 1.58–1.52 (m, 1H, H-11), 1.48 (ddt, J_1 = 13.8 Hz, J_2 = 9.3 Hz, J_3 = 5.0 Hz, 1H, H-6$_b$), 1.14 (dd, J_1 = 6.2 Hz, J_2 = 0.8 Hz, 3H, H-16), 1.07 (d, J = 5.2 Hz, 1H, H-17) ppm

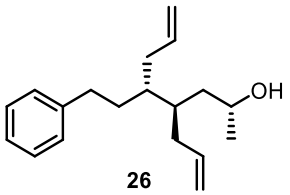
^{13}C NMR (101 MHz, $CDCl_3$): 142.9 (C-4), 139.1 (C-13), 138.0 (C-9), 128.6 (2C, C-3 × 2), 128.5 (2C, C-2 × 2), 125.9 (C-1), 116.3 (C-10), 115.7 (C-14), 69.2 (C-15), 49.4 (C-11), 37.0 (C-7), 36.7 (C-8), 34.4 (C-5), 32.8 (C-6), 31.4 (C-12), 21.8 (C-16) ppm

IR (neat): 3397, 2920, 2851, 1455, 909 cm^{-1}

HRMS (ESI) calculated for $C_{18}H_{26}ONa$: 281.1876, found: 281.1865



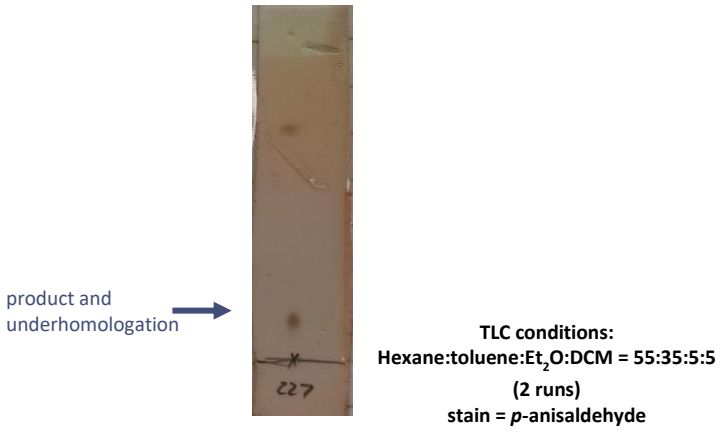
(*2R,4R,5R*)-4-allyl-5-phenethyloct-7-en-2-ol 26



26

3rd and 4th homologation (with bromochloromethane and then *syn*-sulfoxide 14b): The crude product from the second homologation was divided into three batches (3 mL of a 9 mL solution in toluene was transferred to an oven dried Schlenk tube). The solvent was removed *in vacuo* and the compound was dried on high vacuum for 1 h with stirring. The reaction was performed according to S. Balieu *et al.*[30] using bromochloromethane (67 μL, 0.99 mmol), crude boronic ester obtained from the second homologation (assumed 0.33 mmol), and *n*-BuLi (1.6 M in hexanes, 519 μL, 0.83 mmol) in Et_2O (1.3 mL). The reaction mixture was filtered through silica (~10 mm depth of wetted (Et_2O) silica, using a filter frit connected directly to an oven dried receiving vessel) to give a pale yellow solution. The silica was washed with Et_2O (reagent grade, 20 mL) and the solvent was removed under reduced pressure to give the crude boronic ester.

The crude product from the homologation with bromochloromethane was dissolved in toluene (2 mL) and transferred to an oven dried Schlenk tube. The solvent was removed *in vacuo* and the compound was dried on high vacuum for 1 h with stirring. The reaction was performed according to **GP3** using methyl sulfoxide *syn*-**14b** (151 mg, 0.36 mmol), crude boronic ester obtained from the homologation with bromochloromethane (assumed 0.33 mmol) and *t*-BuLi (1.7 M in pentane, 389 μL, 0.66 mmol). The resulting mixture was concentrated *in vacuo* and the residue was suspended in pentane:Et_2O = 95:5 (ca. 20 mL). The suspension was filtered (~ 6 cm depth of wetted silica), the silica was washed (180 mL, pentane:Et_2O = 95:5) and the filtrate was concentrated *in vacuo* to give crude boronic ester. Oxidation of the crude boronic ester was performed according to **GP8** using $NaBO_3 \cdot 4H_2O$ (508 mg, 3.30 mmol) for 3 h.



Purification by silica gel chromatography (pentane/EtOAc 100:0 → 75:25) gave **26** as the major component of a mixture with under-homologation product (37 mg, 41% over 5 steps, ca. 90% purity). Further purification using reverse phase HPLC (acetonitrile:water = 60:40 → 85:15) gave **26** as a colourless oil (25 mg, 24% over 5 steps, d.r. >95:5).

$[\alpha]^{22}_D$: –9 (*c* 0.5, $CHCl_3$)

R_f = 0.13 (55:35:5:5 hexane/toluene/diethyl ether/dichloromethane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.25 (m, 2H, ArH), 7.21–7.14 (m, 3H, ArH), 5.83–5.66 (m, 2H, CH_2=C*H*), 5.07–4.96 (m, 4H, CH=CH_2), 3.71 (app. sext, *J* = 6.1 Hz,1H, CH), 2.72-2.63 (m, 1H, C*H*H), 2.60-2.50 (m, 1H, CH*H*), 2.19–2.06 (m, 3H, CH_2 and C*H*H), 1.90 (dt, J_1 = 14.0 Hz, J_2 = 8.0 Hz, 1H, CH*H*), 1.70 (app. br. p, *J* = 6.6 Hz, 1H, CH), 1.63–1.47 (m, 3H, CH_2 and CH), 1.42-1.26 (m, 2H, CH_2), 1.13 (d, *J* = 6.7 Hz, 1H, CH_3) ppm *(OH not observed)*

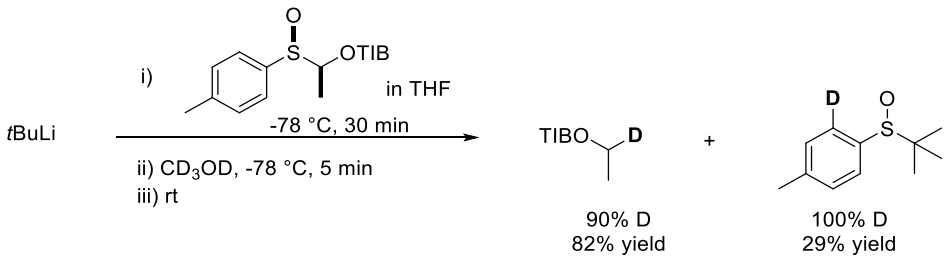
^{13}C NMR (101 MHz, $CDCl_3$): 142.7 (C), 138.2 (2 × CH), 128.5 (4 × CH), 125.9 (CH), 116.1 (2 × CH_2), 66.4 (CH), 40.5 (CH_2), 39.1 (CH), 36.1 (CH), 35.5 (CH_2), 35.4 (CH_2), 34.4 (CH_2), 32.2 (CH_2), 24.0 (CH_3) ppm

IR (neat): 3351, 2923, 2858, 1453, 908 cm^{-1}

HRMS (ESI) calculated for $C_{19}H_{28}ONa$: 295.2032, found: 295.2034

9. Trapping Experiments

To a solution of *t*BuLi (2 equiv) in THF were added a solution of sulfoxide **14b** (1 equiv) in THF at –78 °C dropwise. After 30 min, the reaction was quenched with CD_3OD (2 equiv) and it was stirred 5 min at the same temperature. The mixture was warmed to rt and diluted with EtOAc. H_2O was added and the layers were separated. The organic layer was dried over $MgSO_4$ and all volatiles were removed under reduced pressure. After adding 1,3,5-trimethoxybenzene as an internal standard, the mixture was analyzed by ^{1}H NMR measurements. By ^{1}H NMR spectrum of the crude mixture, it is clear that the deuteriated *p*-tolyl *tert*-buytl sulfoxide is one of the by-products of the reaction (Figure S2).



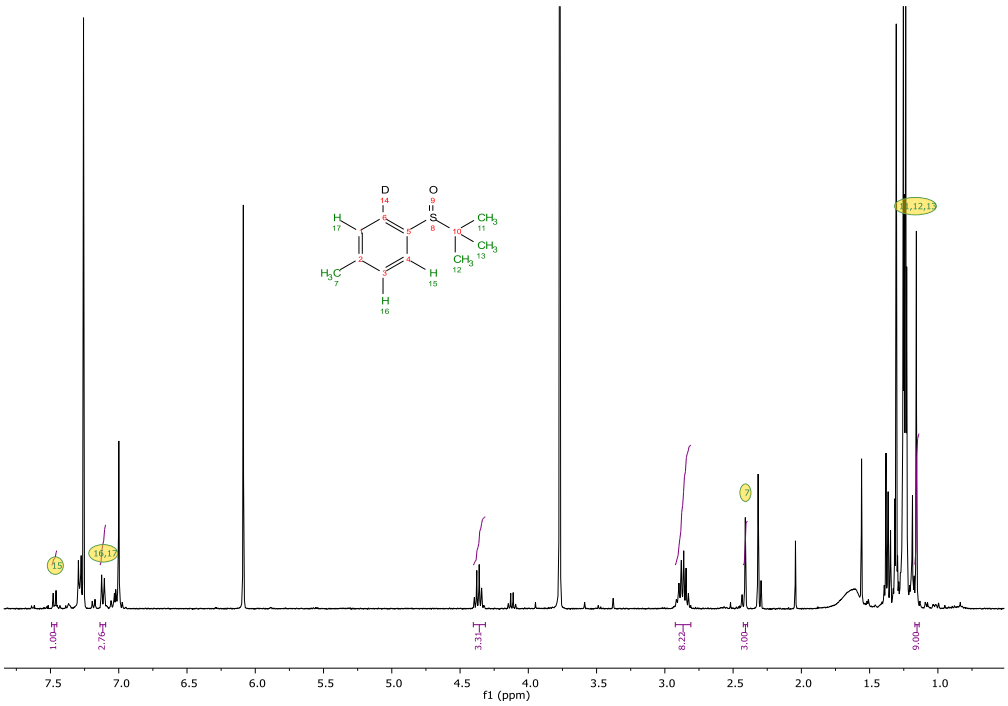
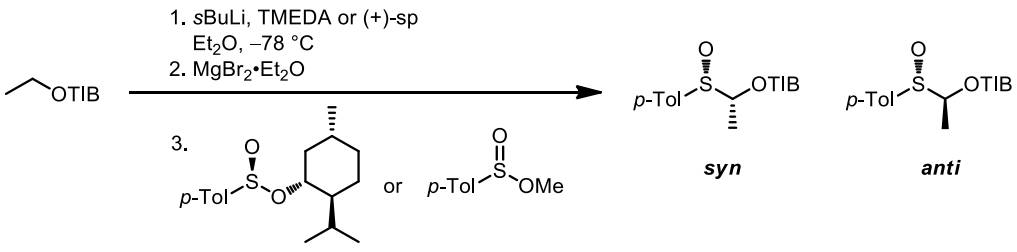


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$)

10. Determination of Absolute Configuration of Benzoates

The stereochemistry of sulfoxide–ligand exchange is well established in literature.[33] While inversion of configuration at sulfur occurs with sulfoxide–ligand exchange,[34] generated metal carbenoids reacts with boronic esters with retention of configuration. When ethyl TIB ester **1** was lithiated with *s*BuLi in the presence of TMEDA and trapped with racemic methyl tolylsulfinate after lithium-magnesium exchange, all four stereoisomers were obtained (Figure S3, A). Replacing racemic methyl tolylsulfinate with enantiopure Andersen's sulfinate gave two major stereoisomers of benzoate **14b** with *S*-configuration at the sulfur atom (B). On the other hand, enantioselective lithiation of ethyl TIB ester using (+)-sparteine and trapping with racemic methyl tolylsulfinate after lithium-magnesium exchange gave two major stereoisomers of benzoate **14b** with *R*-configuration at the carbon centre (C). The less polar compound on TLC was therefore identified as the *syn* diastereomer *syn*-**14b**, while the more polar compound was revealed to be the *anti* diastereomer *anti*-**14b**.



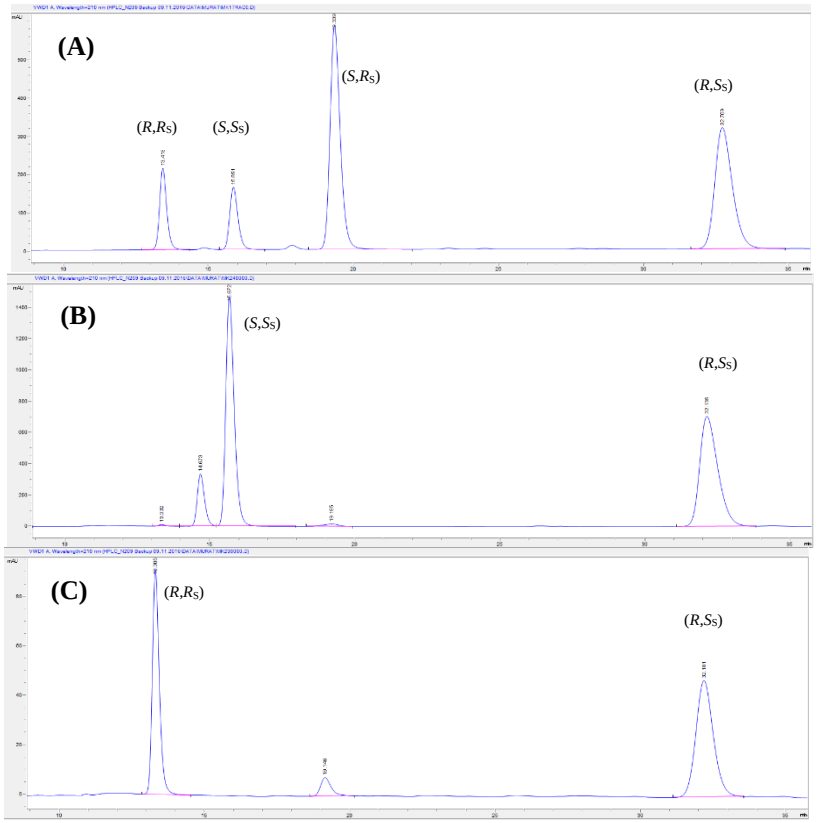


Figure S3. (A): Reaction using TMEDA and methyl sulfinate; (**B**) reaction using TMEDA and Andersen's sulfinate (*S*)-**9**; (**C**): reaction using (+)-sparteine and methyl sulfinate.

The same experiment using (+)-sparteine was done starting from homoallylic benzoate **28** and the opposite enantiomer of Andersen's sulfinate *ent*-**9** to generate *syn*-**14f** as the major diastereomer (less polar) with only minor amount of *anti*-**14f** (more polar).

After comparison of the chemical shifts for the α-sulfinyl proton (^{1}H NMR) and α-sulfinyl carbon (^{13}C NMR), the trends, as highlighted in Figure **S4**, have been used to assign the stereochemistry of sulfoxides **14a-o** as *syn* or *anti*.

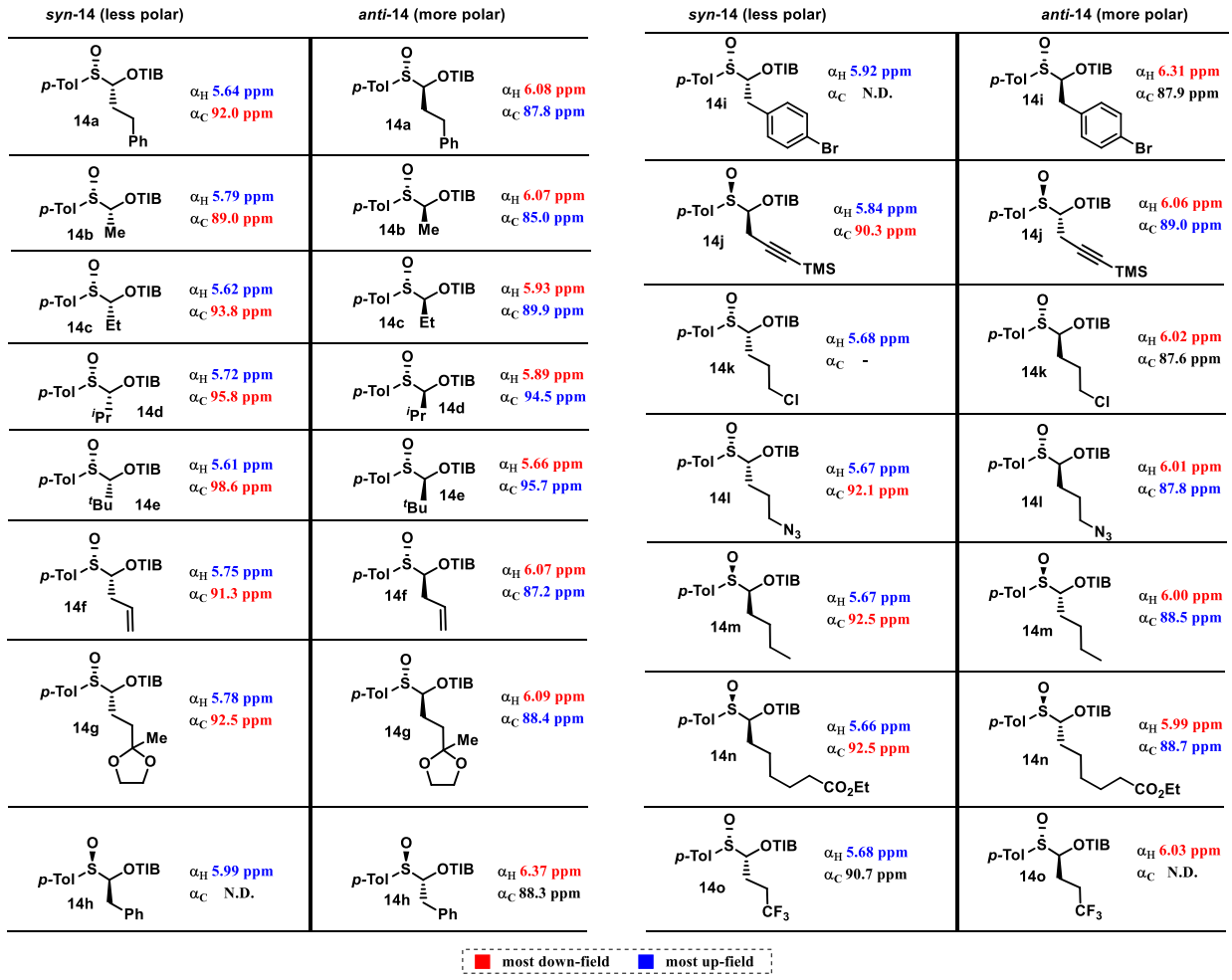
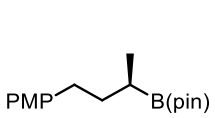


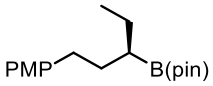
Figure S4. Correlation between the chemical shifts α–proton and carbon of sulfinyl benzoates and the relative configuration of compounds **14**

Furthermore, four known compounds have been synthesized and optical rotation of each compound was compared with the literature values.



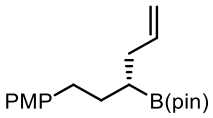
(*R*)-**18b**

$[a]^{23}_{D}$: –19 (c 0.7, $CHCl_3$)
for (*R*): –8.2 (c 0.98, $CHCl_3$)[17]
for (*S*): +7.6 (c 1.7, $CHCl_3$)[16]



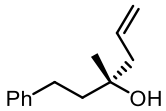
(*R*)-**18c**

$[a]^{23}_{D}$: –9 (c 0.7, $CHCl_3$)
for (*R*): –9.6 (c 1.05, $CHCl_3$)[17]
for (*S*): +9.4 (c 1.6, $CHCl_3$)[16]



(*S*)-**18f**

$[a]^{23}_{D}$: –16 (c 0.8, $CHCl_3$)
for (*R*): +0.12 (c 1.05, $CHCl_3$)[16]



(*R*)-**21b**

$[a]^{22}_{D}$: +18 (c 0.8, $CHCl_3$)
for (*R*): +57 (c 1, $CHCl_3$)[18a]
for (*S*): -58 (c 1, $CHCl_3$)[18b]

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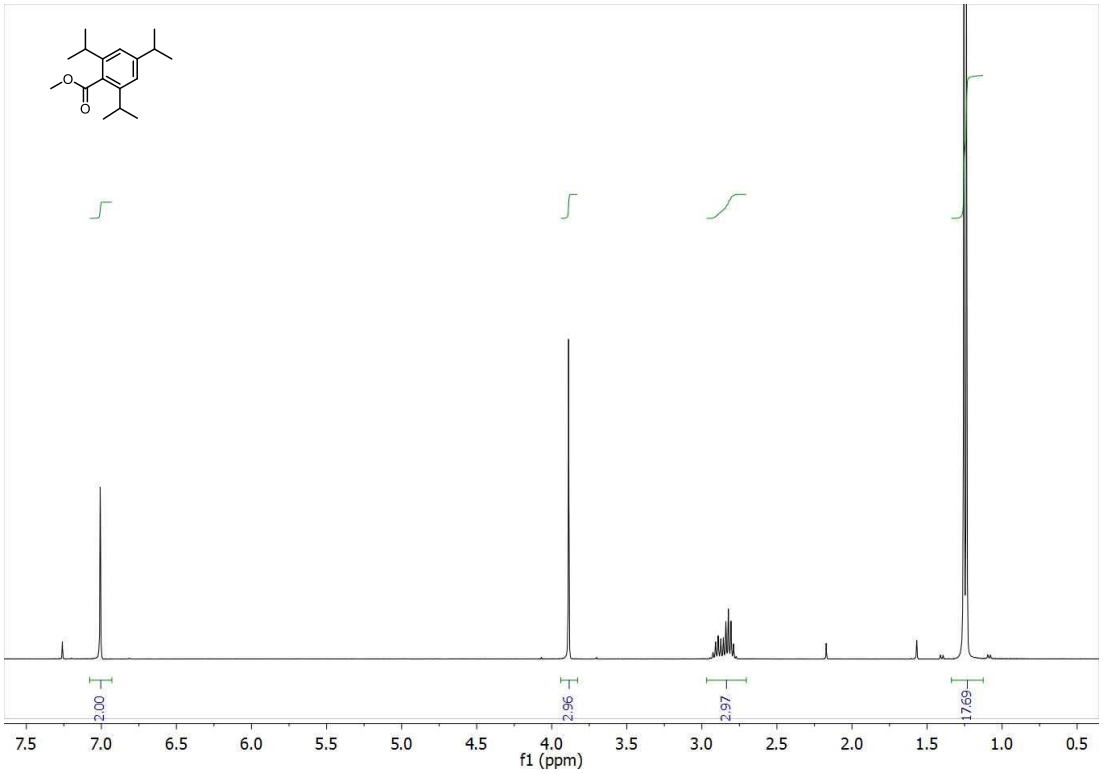
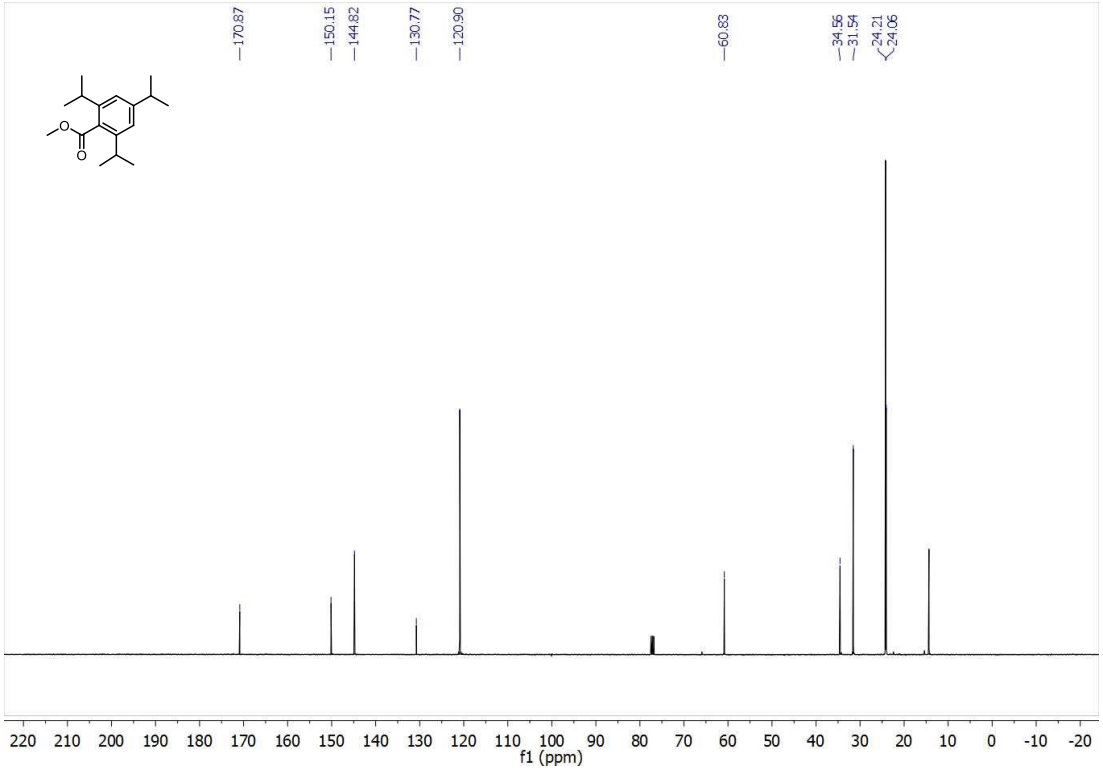
12. NMR Spectra

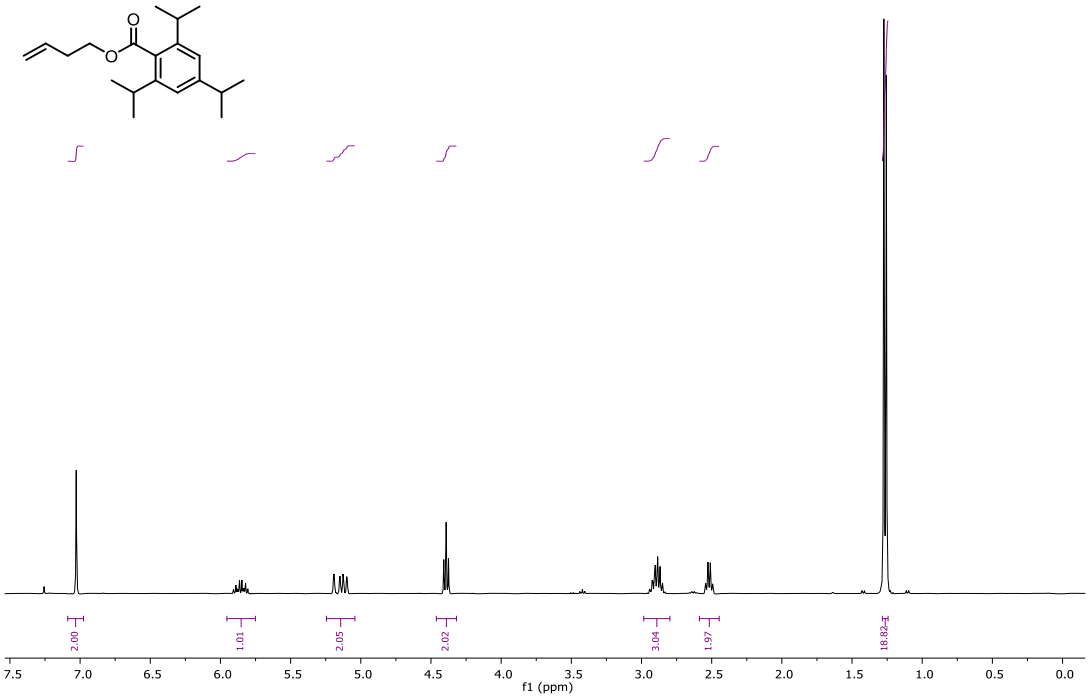
^{1}H NMR of **27** (400 MHz, $CDCl_3$)



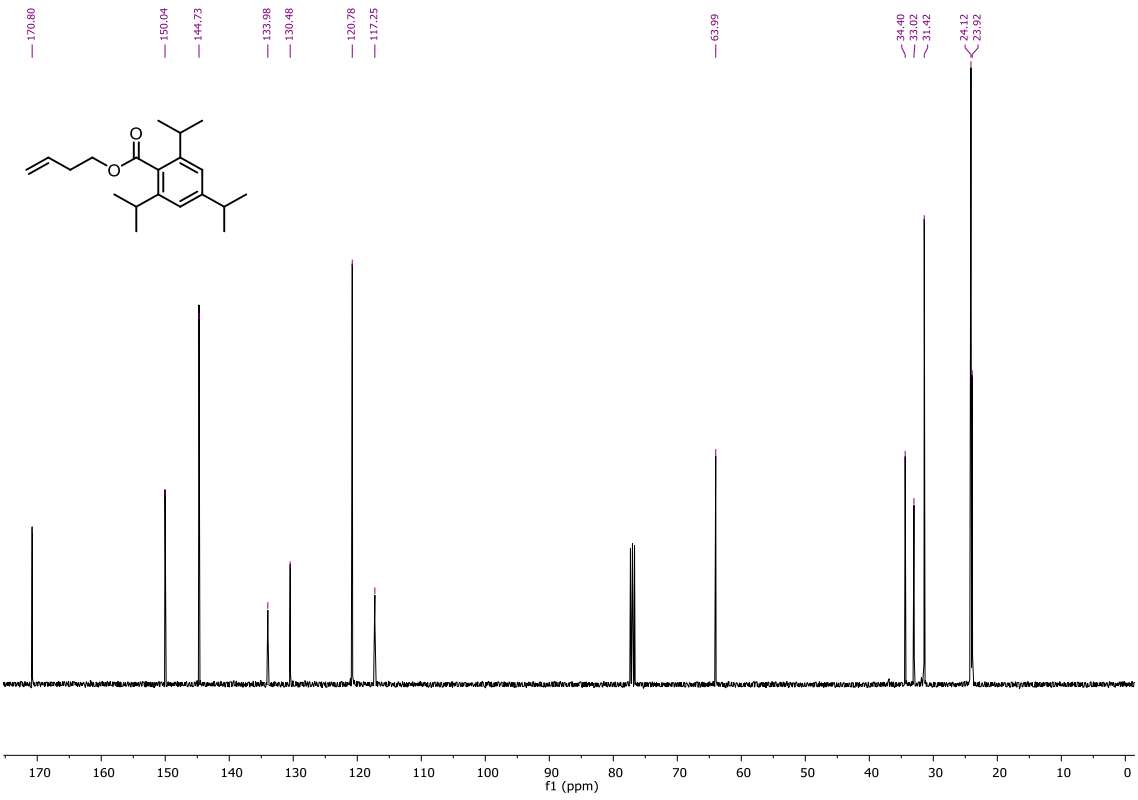
^{13}C NMR of **27** (101 MHz, $CDCl_3$)



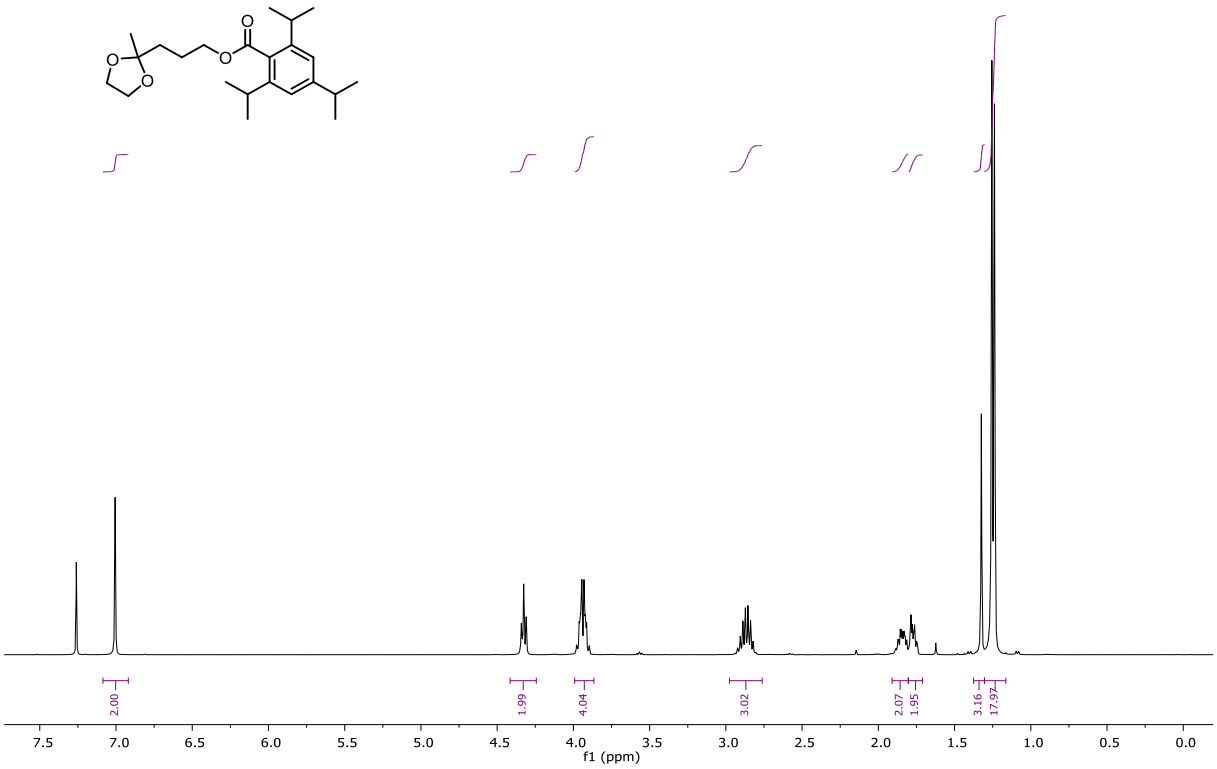
^{1}H NMR of **28** (400 MHz, $CDCl_3$)



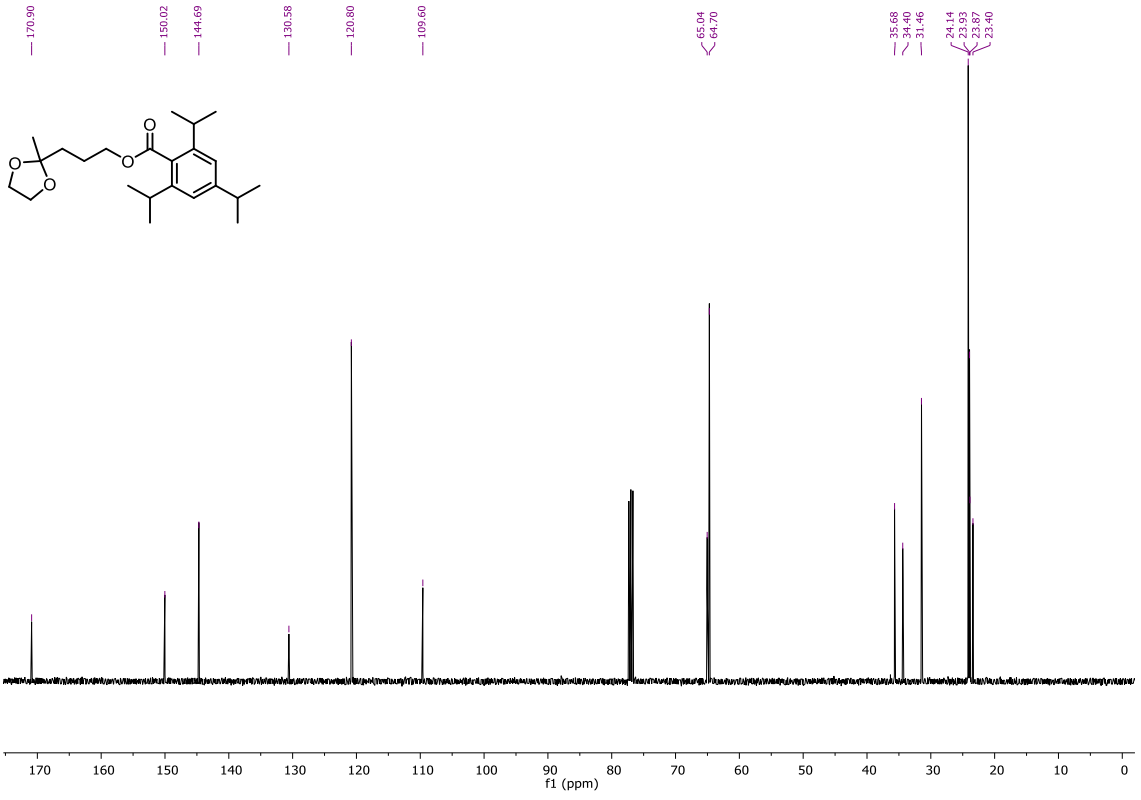
^{13}C NMR of **28** (101 MHz, $CDCl_3$)



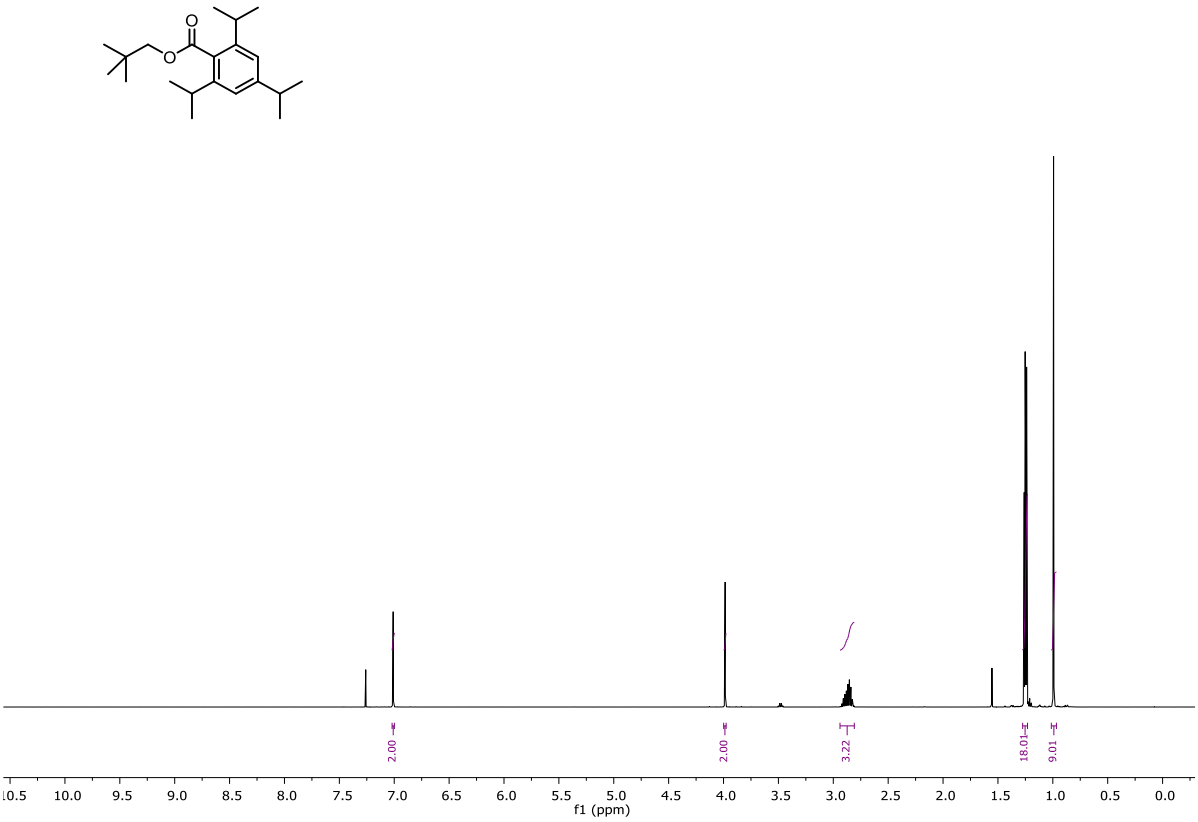
^{1}H NMR of **29** (400 MHz, $CDCl_3$)



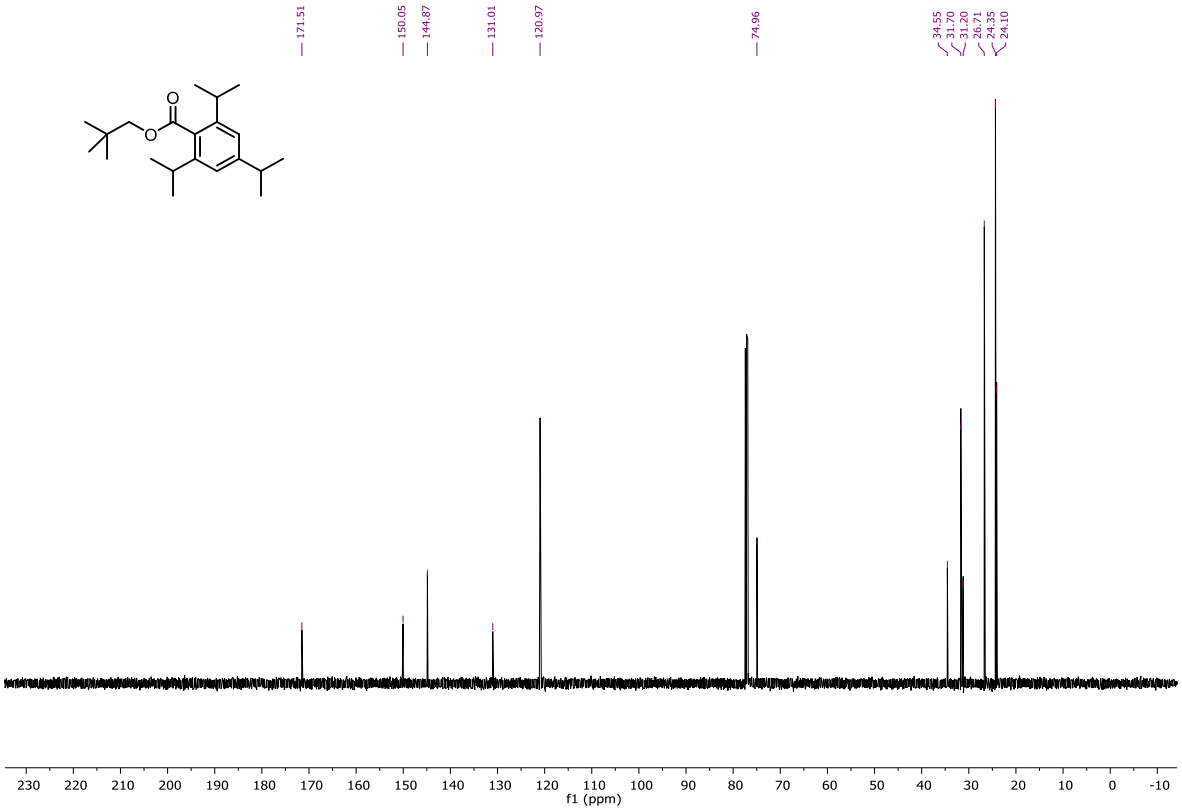
^{13}C NMR of **29** (101 MHz, $CDCl_3$)



^{1}H NMR of **30** (400 MHz, $CDCl_3$)

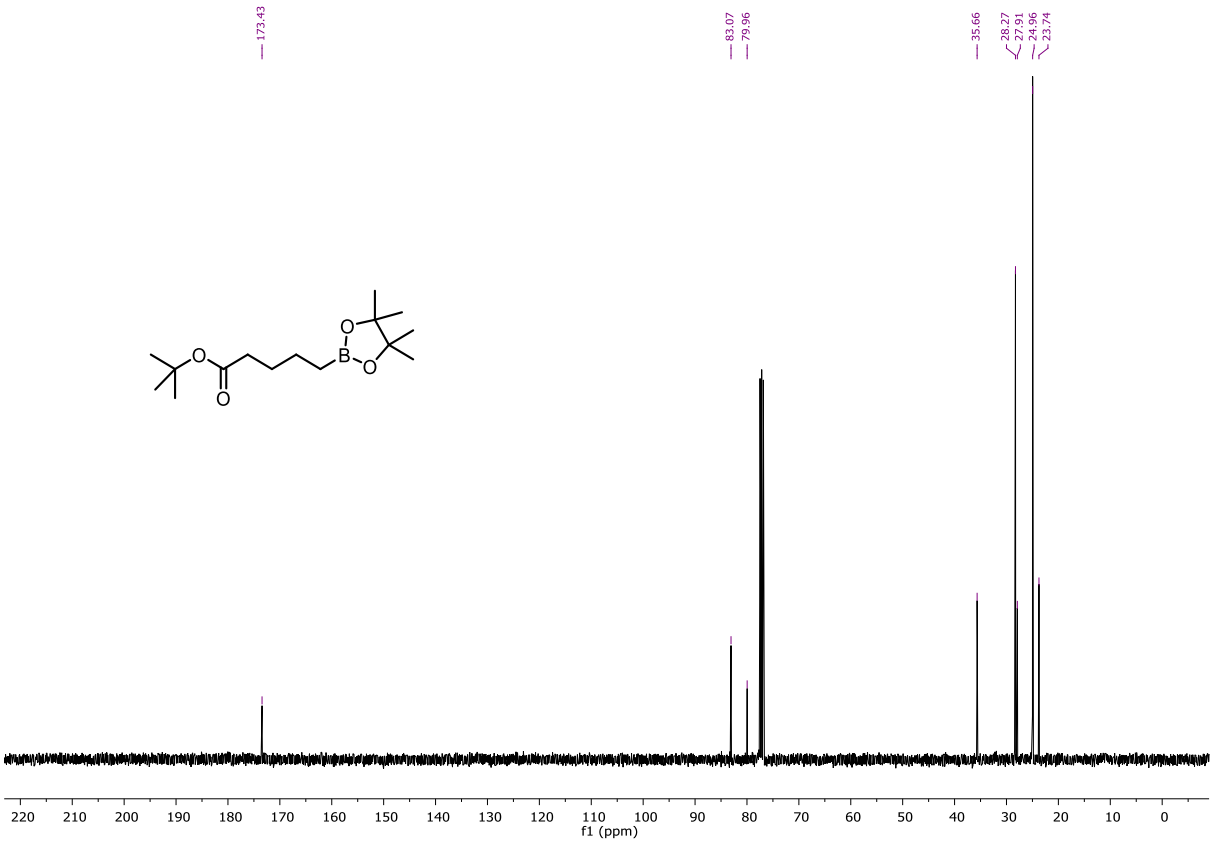


^{13}C NMR of **30** (101 MHz, $CDCl_3$)

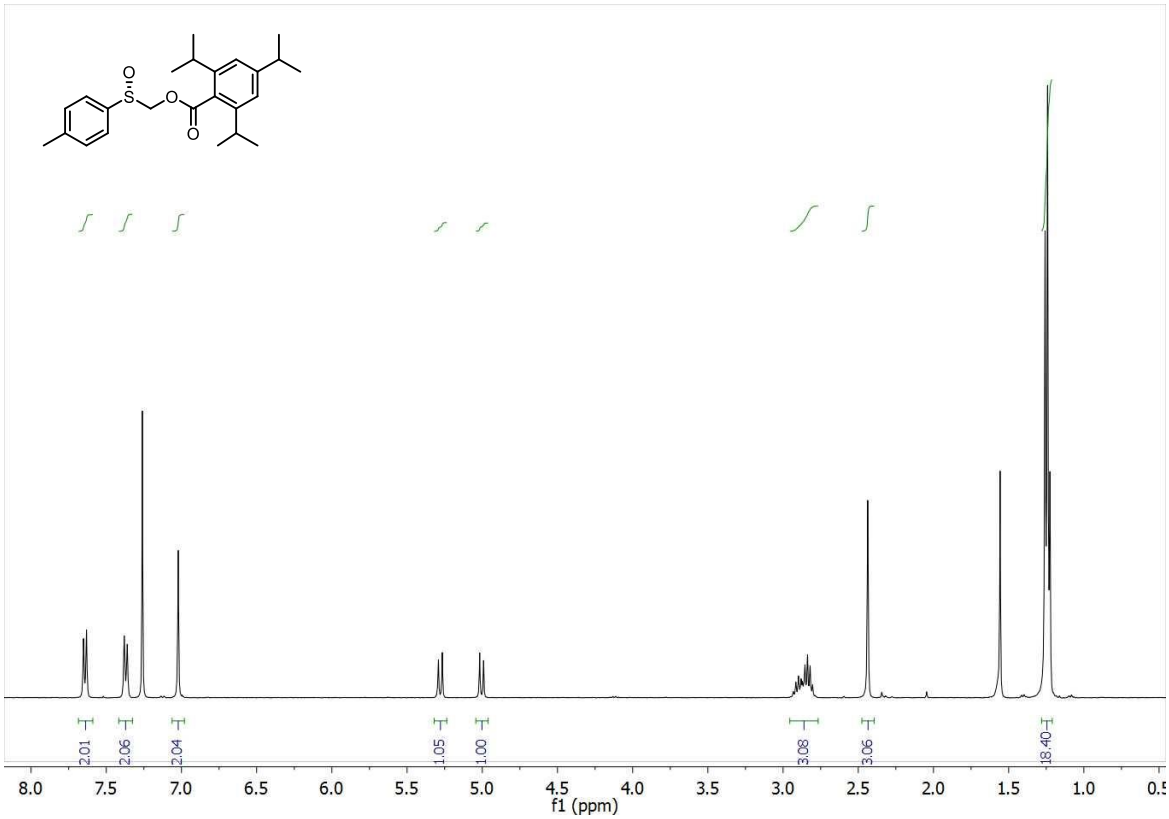


^{1}H NMR of **17b** (400 MHz, $CDCl_3$)

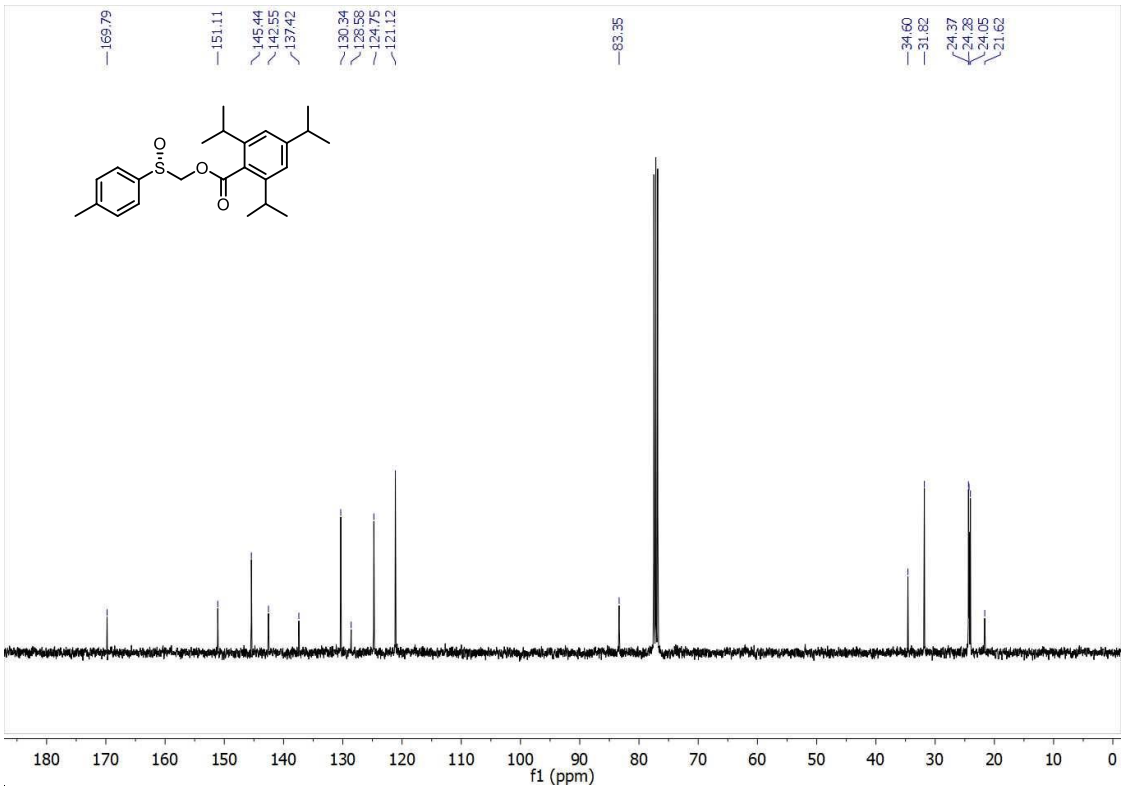
^{13}C NMR of **17b** (101 MHz, $CDCl_3$)



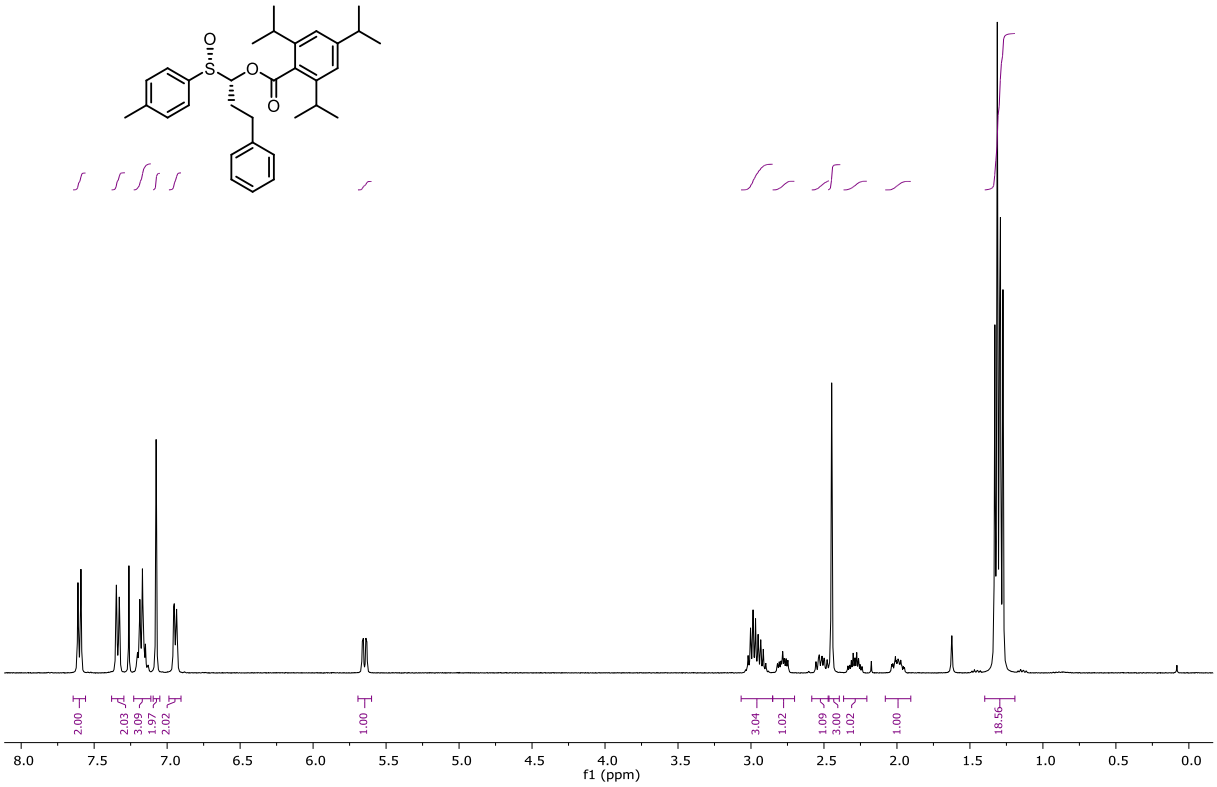
^{1}H NMR of **19** (400 MHz, $CDCl_3$)



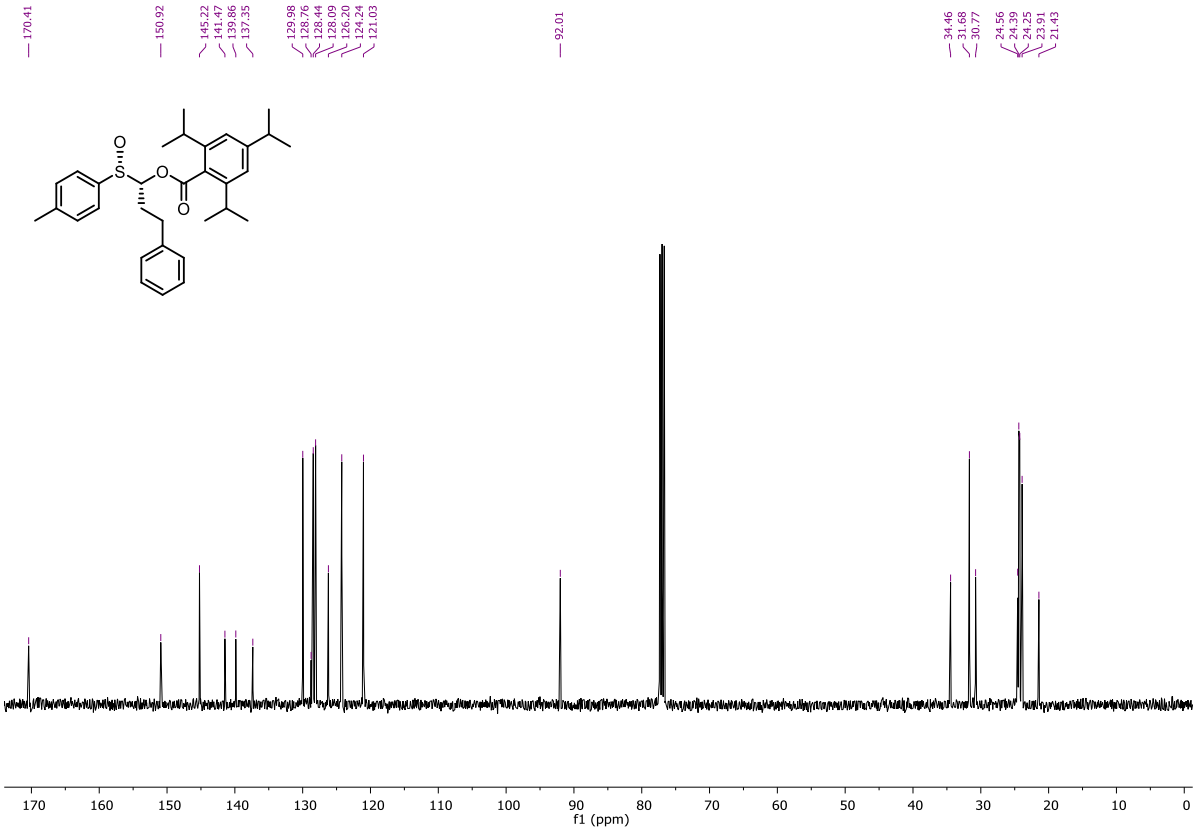
^{13}C NMR of **19** (101 MHz, $CDCl_3$)



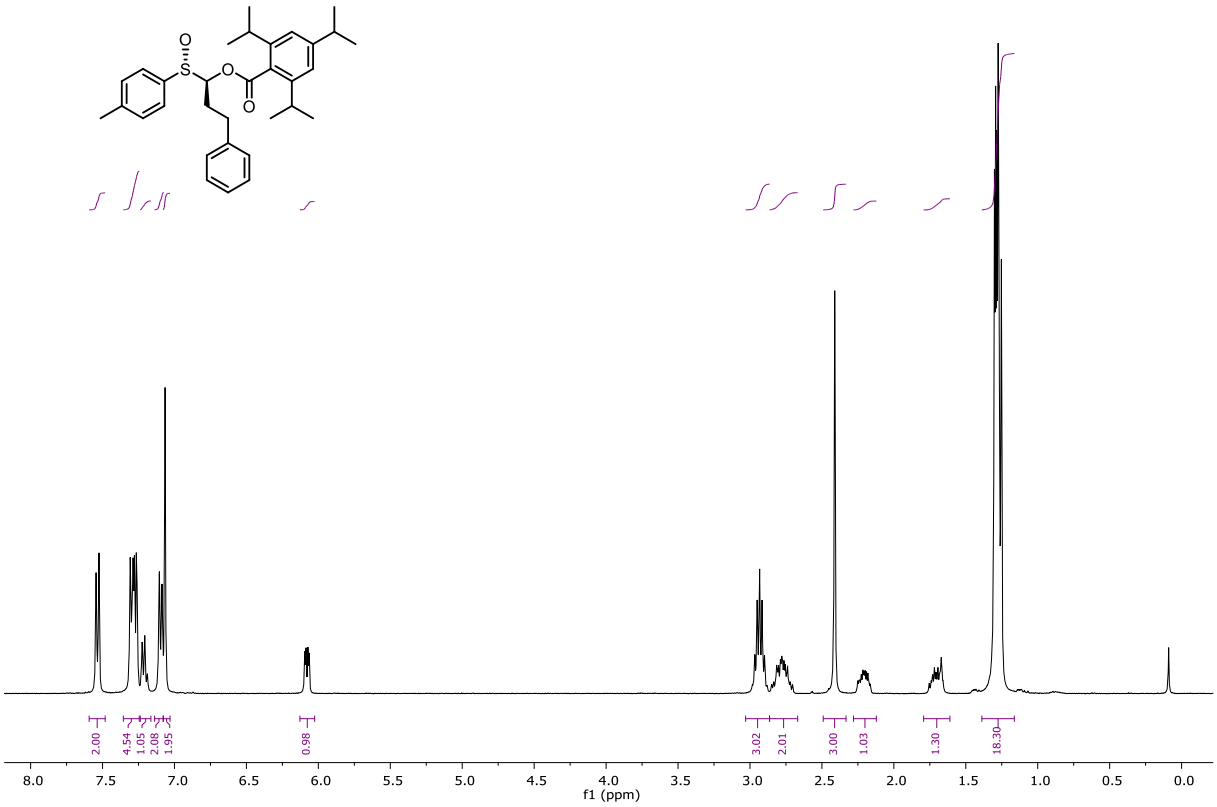
^{1}H NMR of *syn*-**14a** (400 MHz, $CDCl_3$)



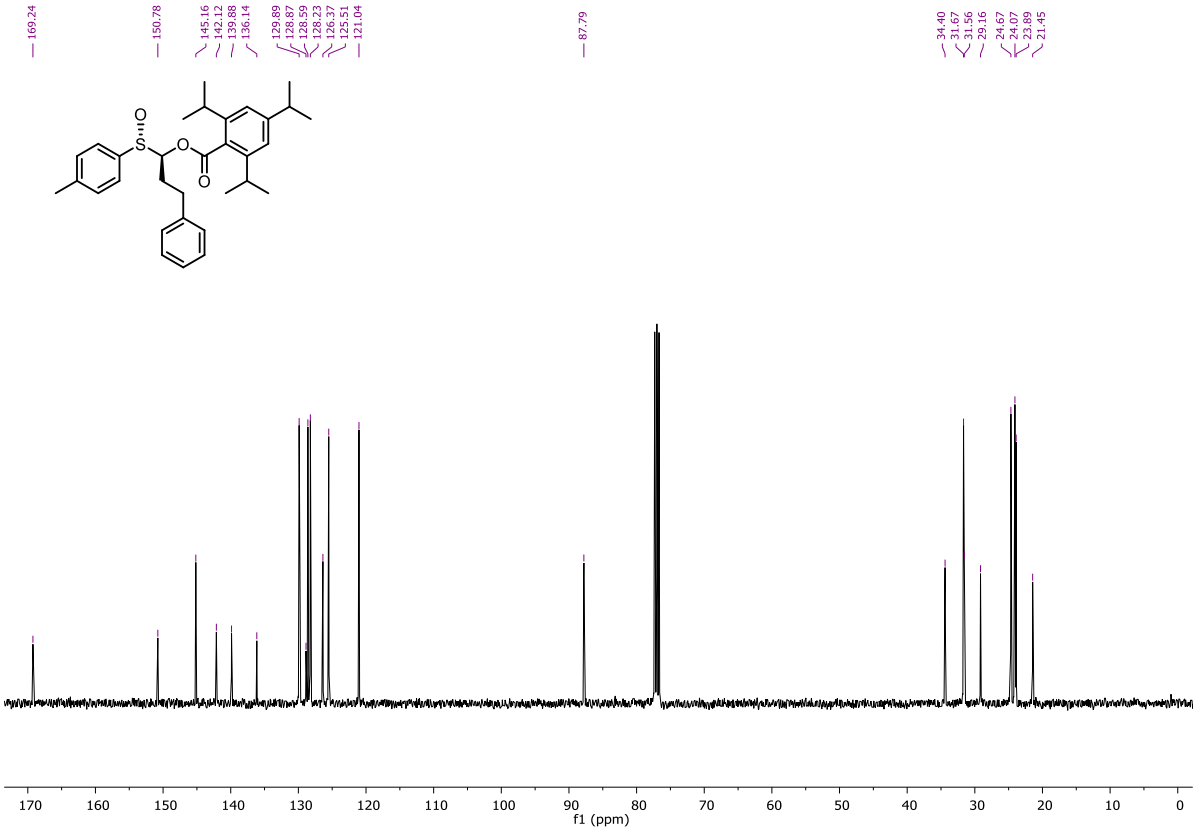
^{13}C NMR of *syn*-**14a** (101 MHz, $CDCl_3$)



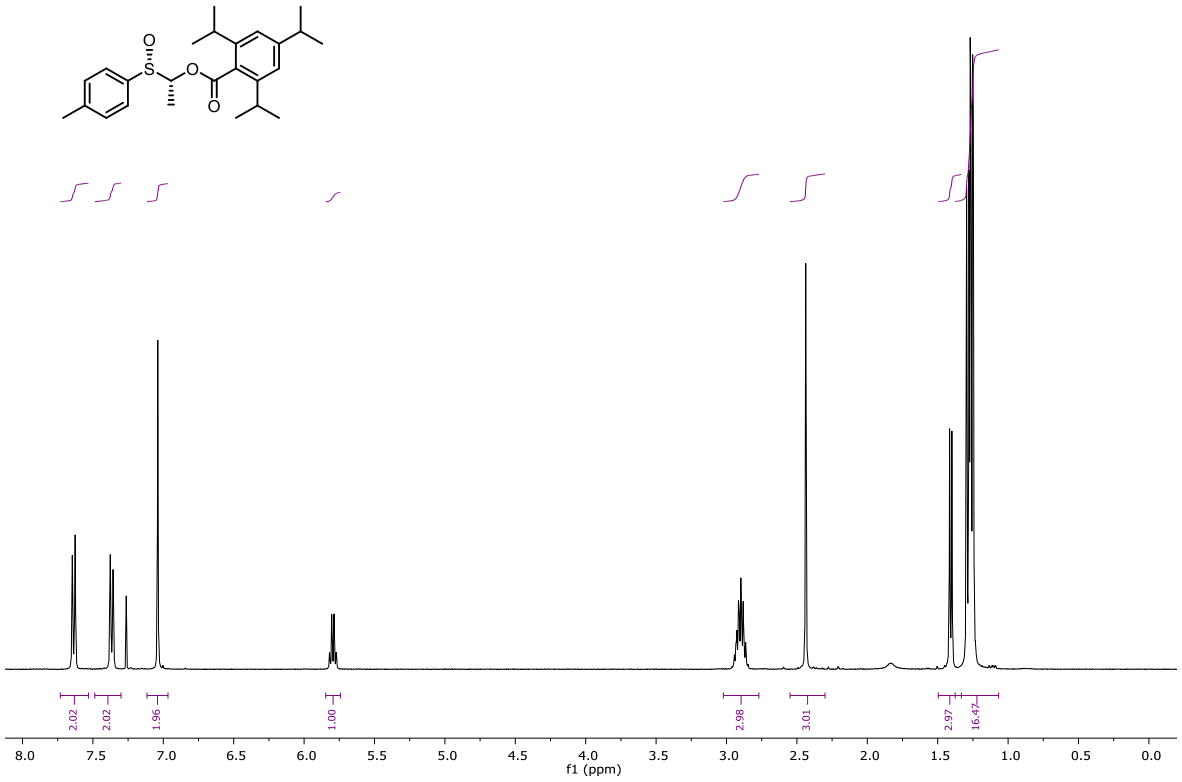
^{1}H NMR of *anti*-**14a** (400 MHz, $CDCl_3$)



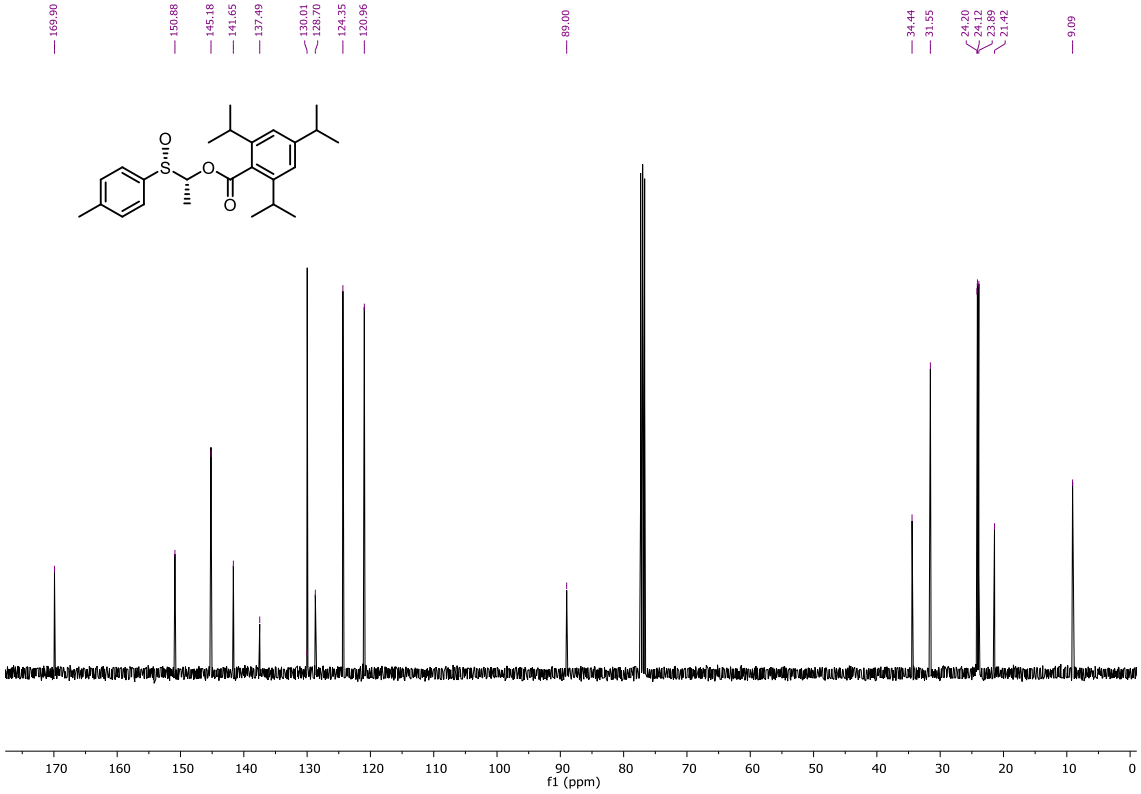
^{13}C NMR of *anti*-**14a** (101 MHz, $CDCl_3$)



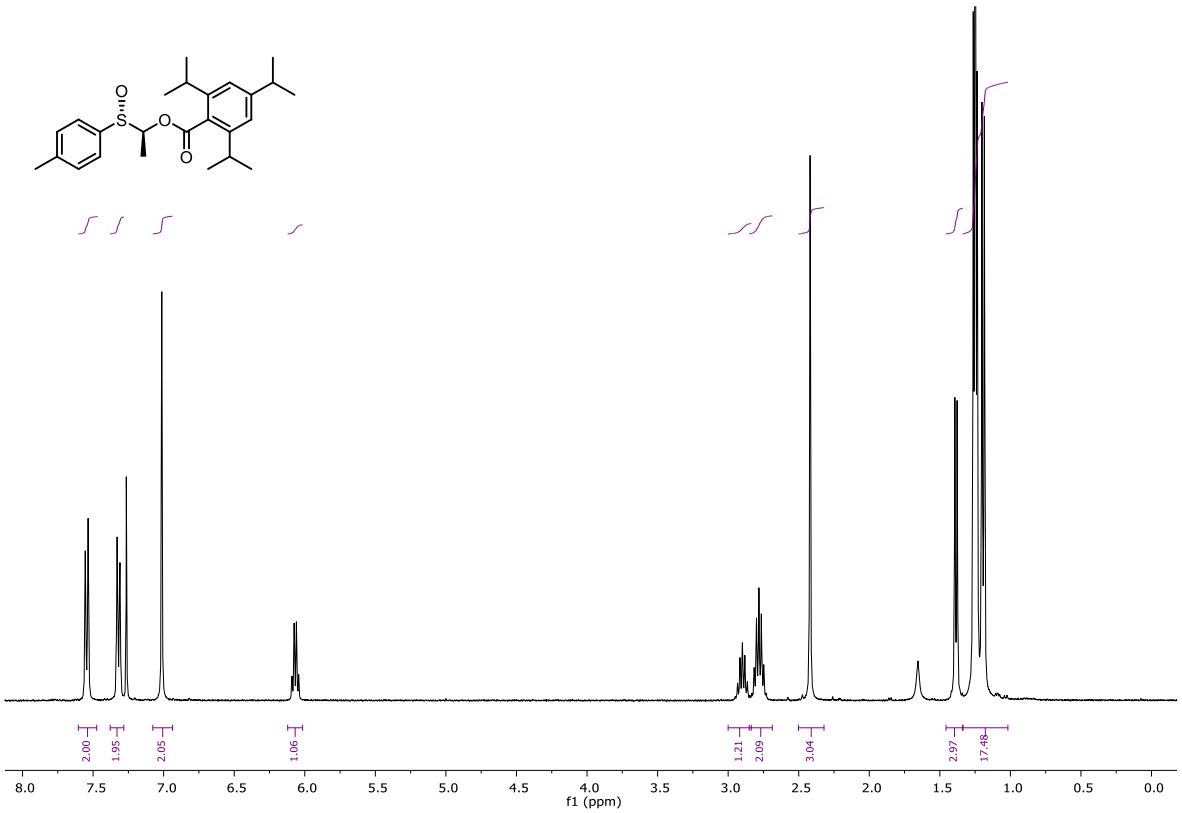
^{1}H NMR of *syn*-**14b** (400 MHz, $CDCl_3$)



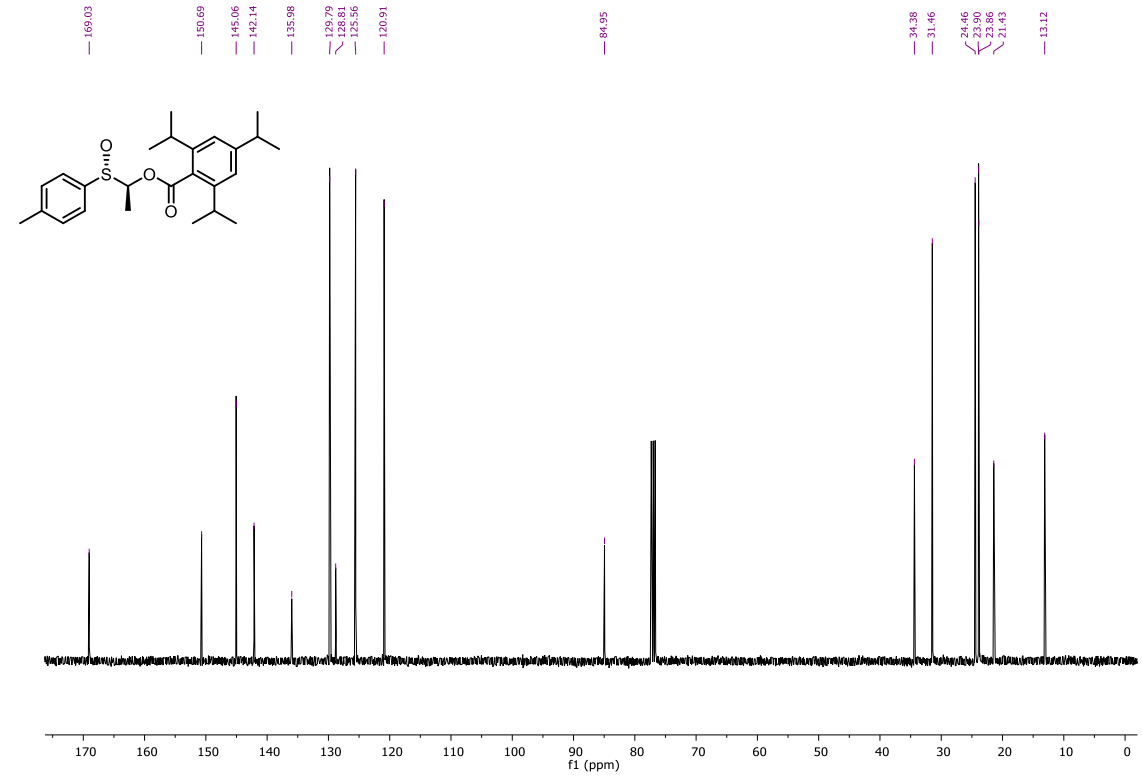
^{13}C NMR of *syn*-**14b** (101 MHz, $CDCl_3$)



^{1}H NMR of *anti*-**14b** (400 MHz, $CDCl_3$)



^{13}C NMR of *anti*-**14b** (101 MHz, $CDCl_3$)



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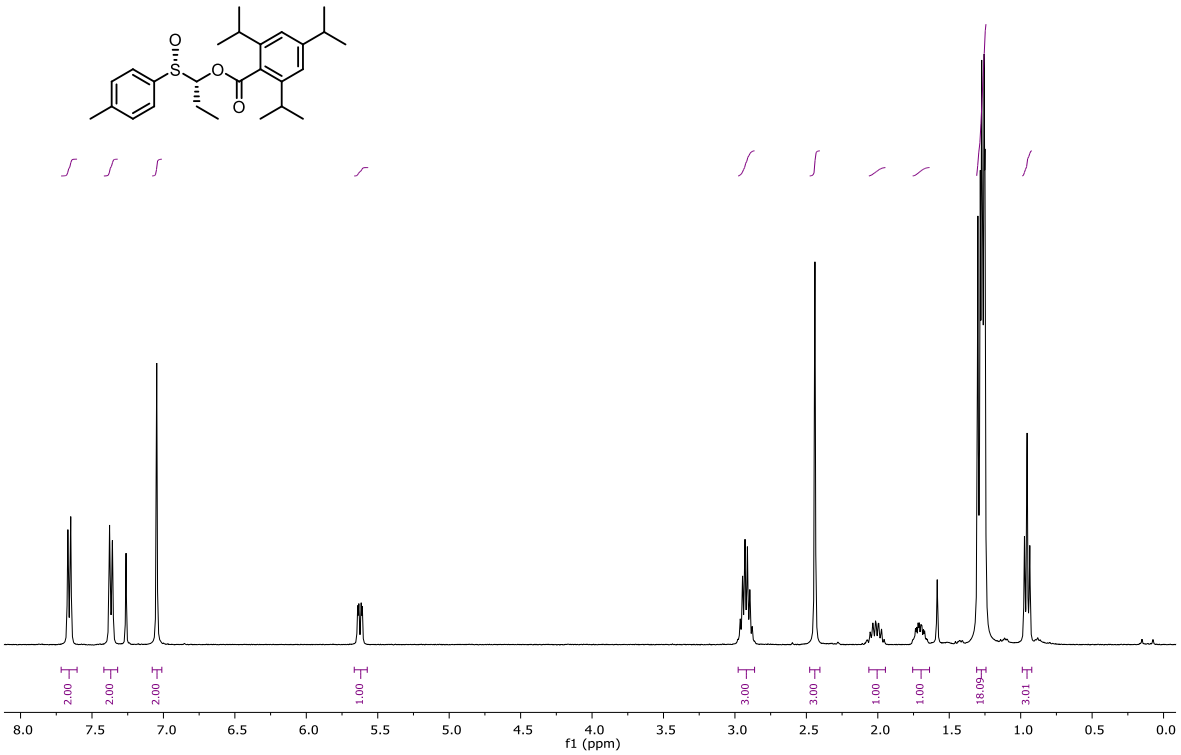
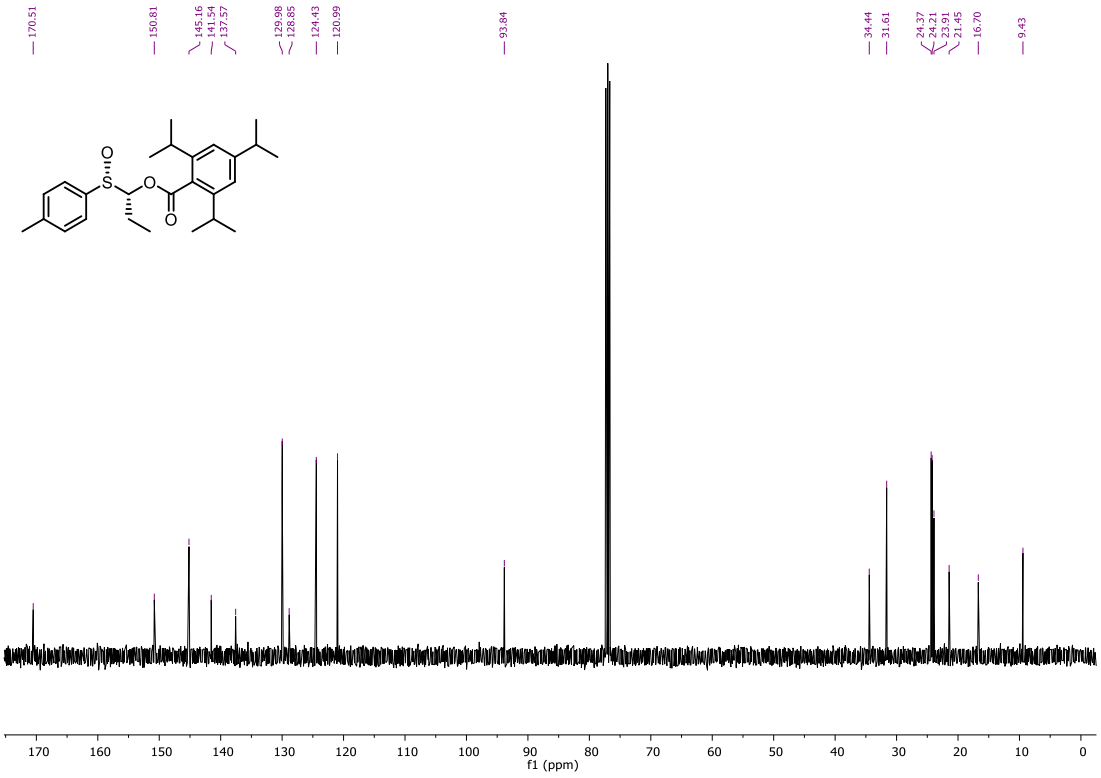
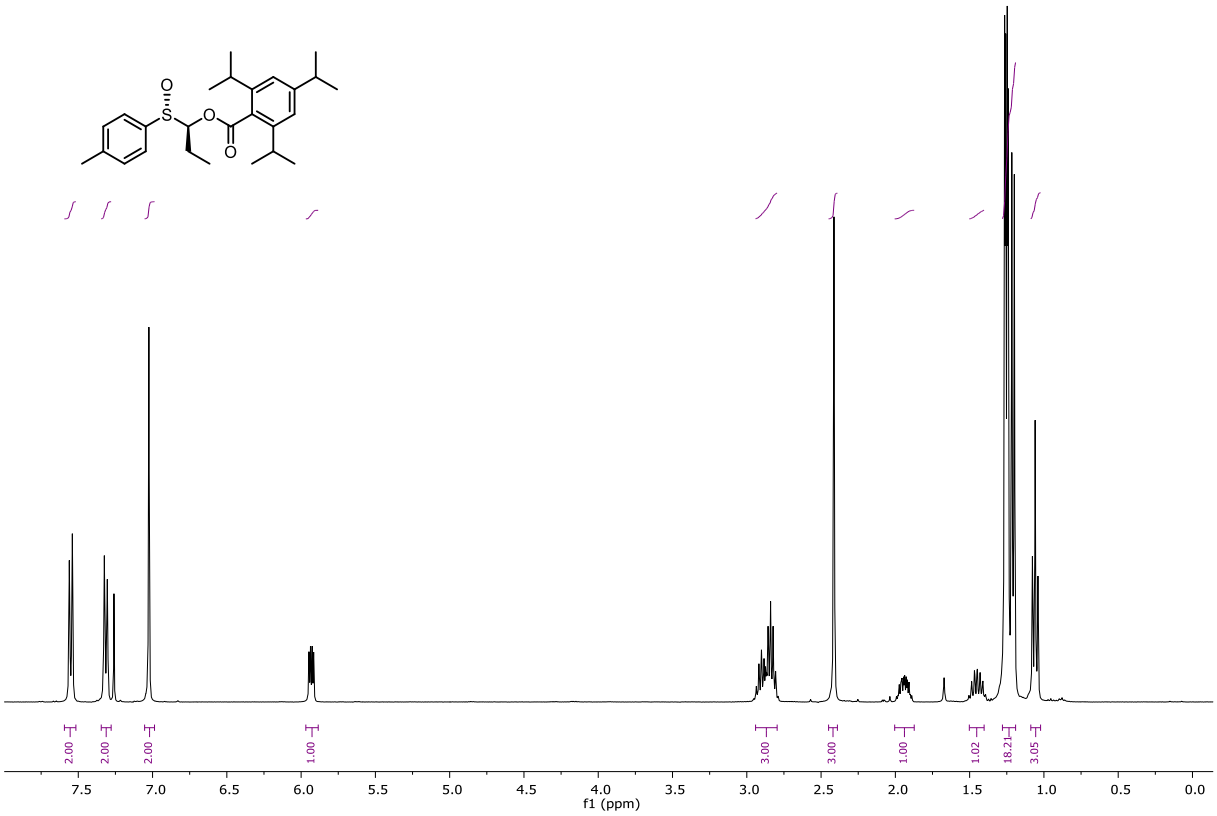


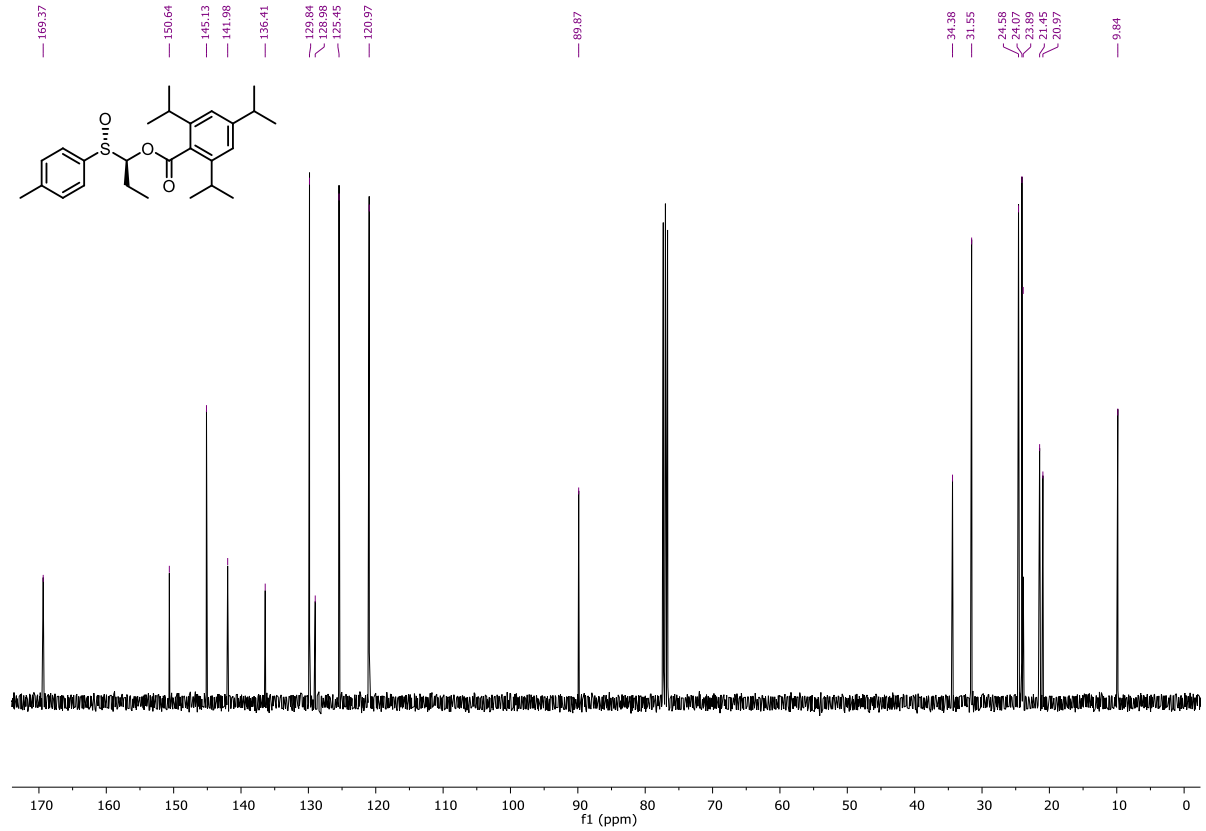
^{13}C NMR of *syn*-**14c** (101 MHz, $CDCl_3$)



^{1}H NMR of *anti*-**14c** (400 MHz, $CDCl_3$)



^{13}C NMR of *anti*-**14c** (101 MHz, $CDCl_3$)



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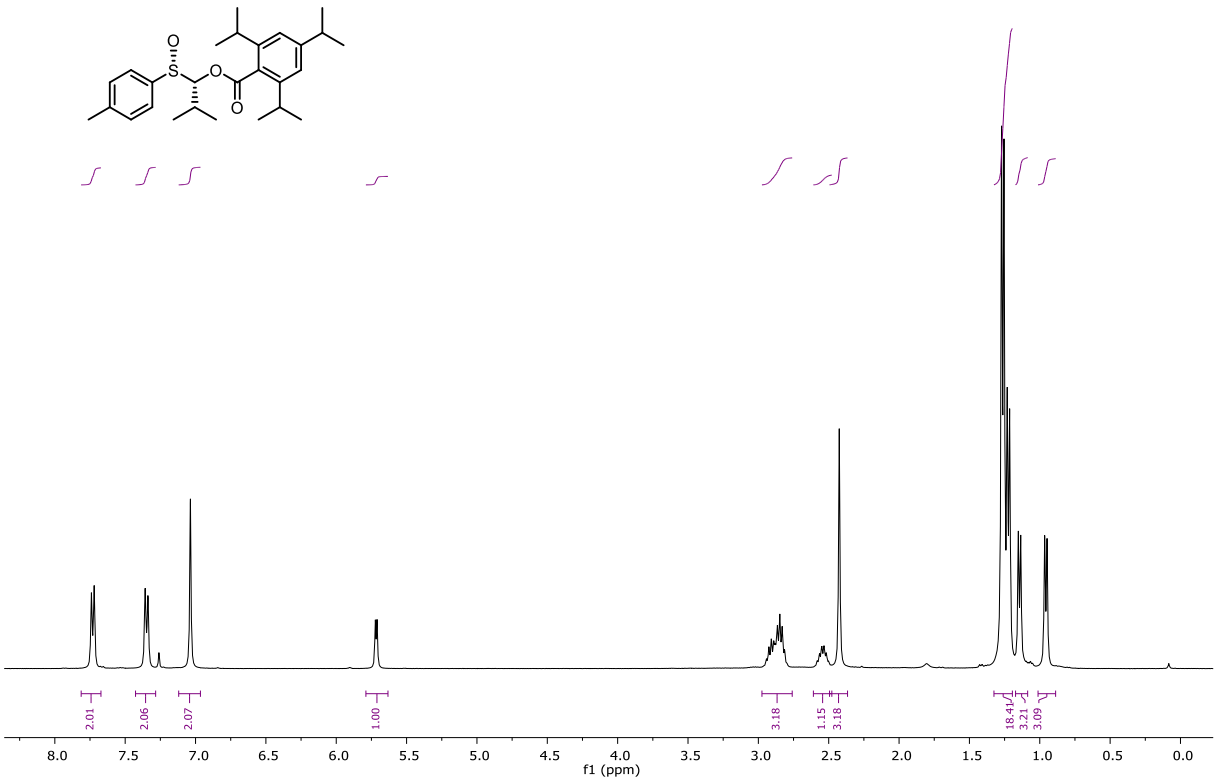
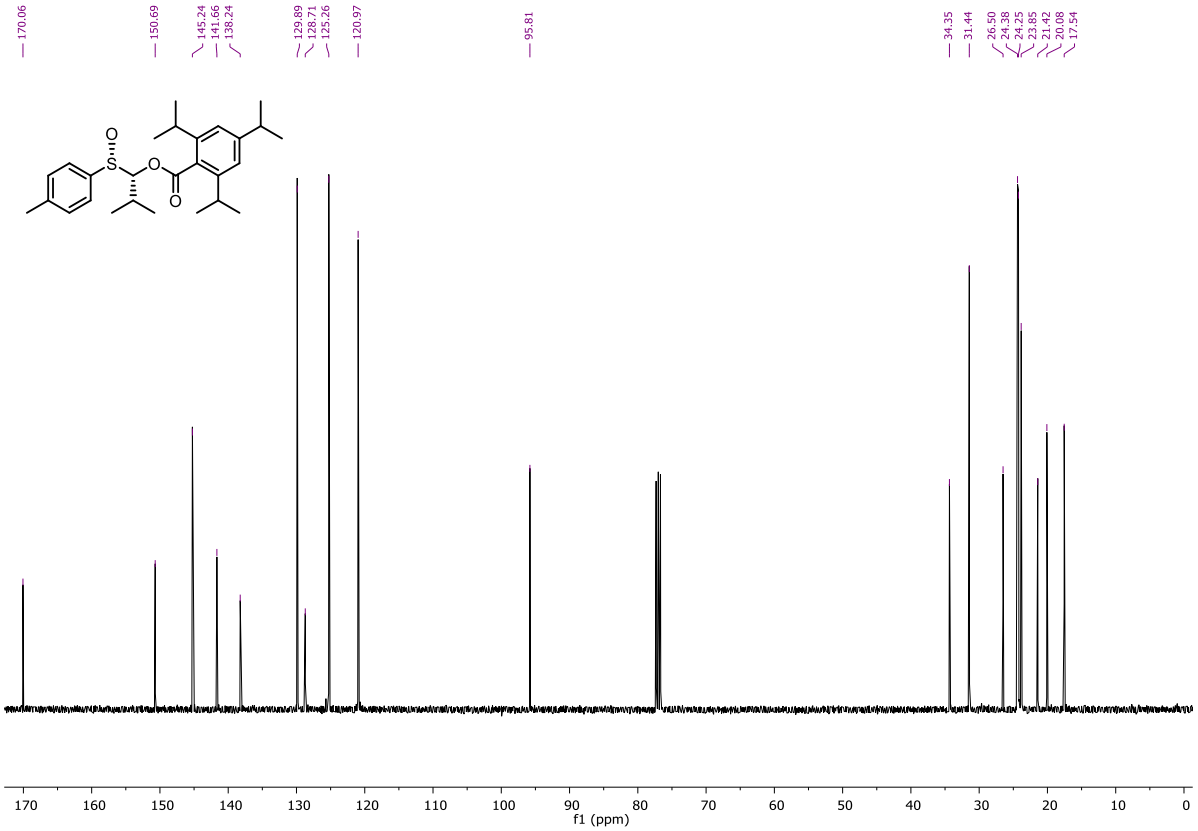


^{13}C NMR of *syn*-**14d** (101 MHz, $CDCl_3$)



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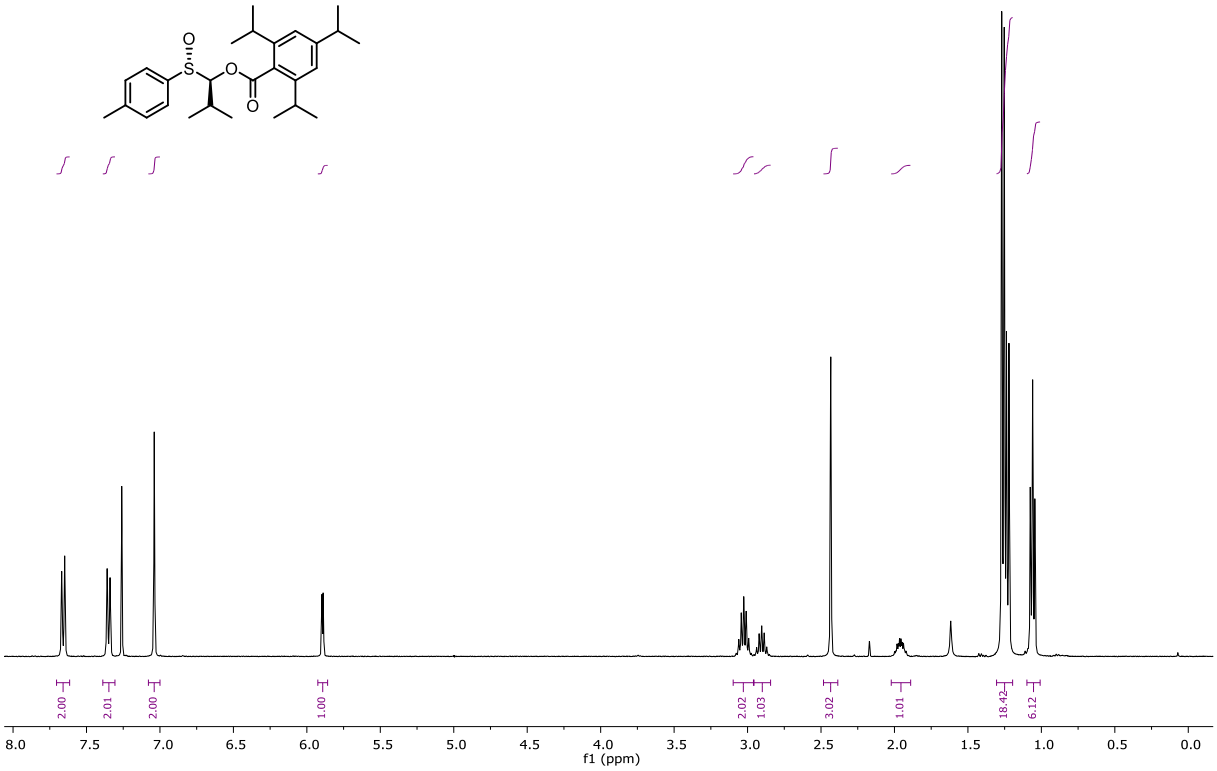
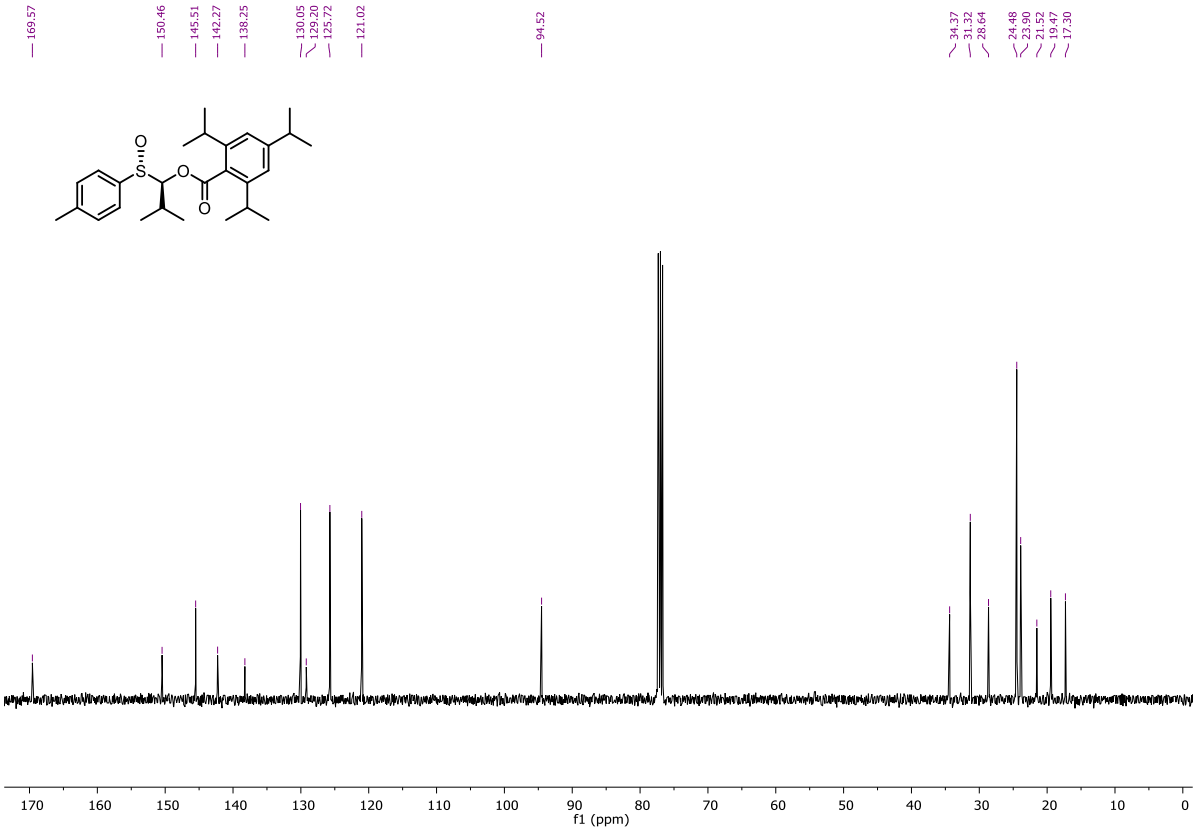


^{13}C NMR of *anti*-**14d** (101 MHz, $CDCl_3$)



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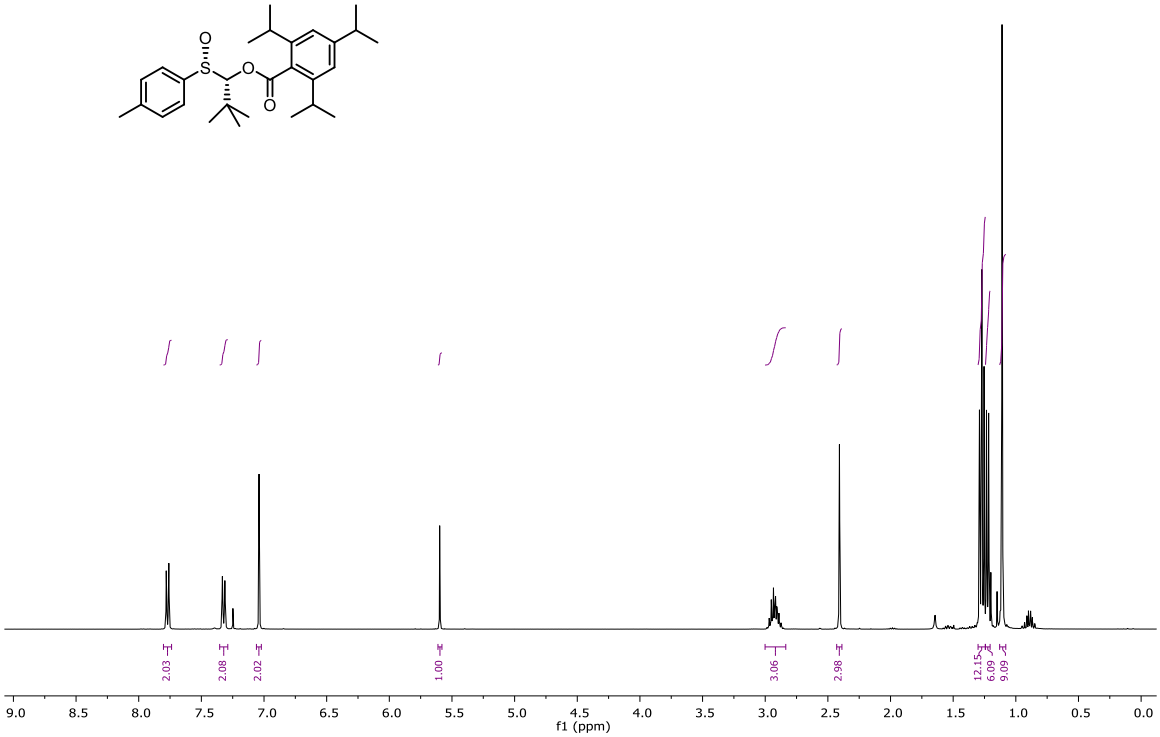
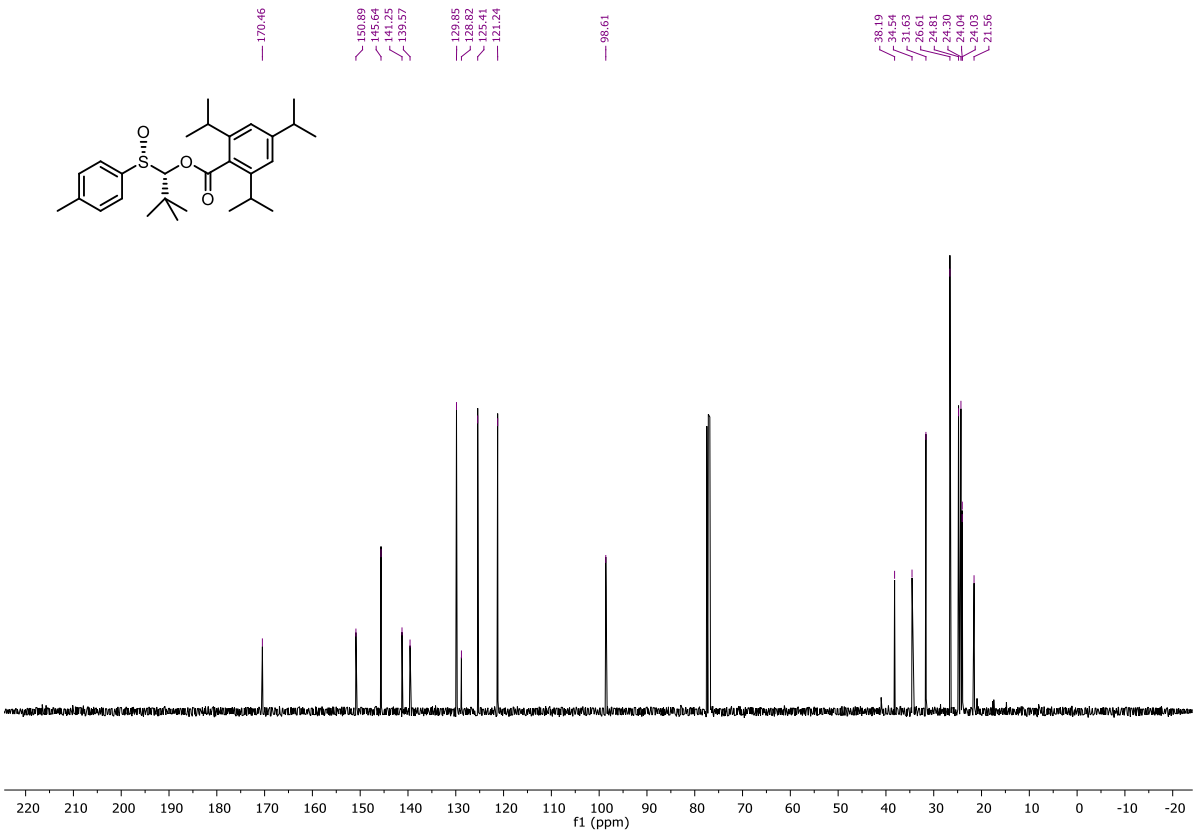


^{13}C NMR of *syn*-**14e** (101 MHz, $CDCl_3$)



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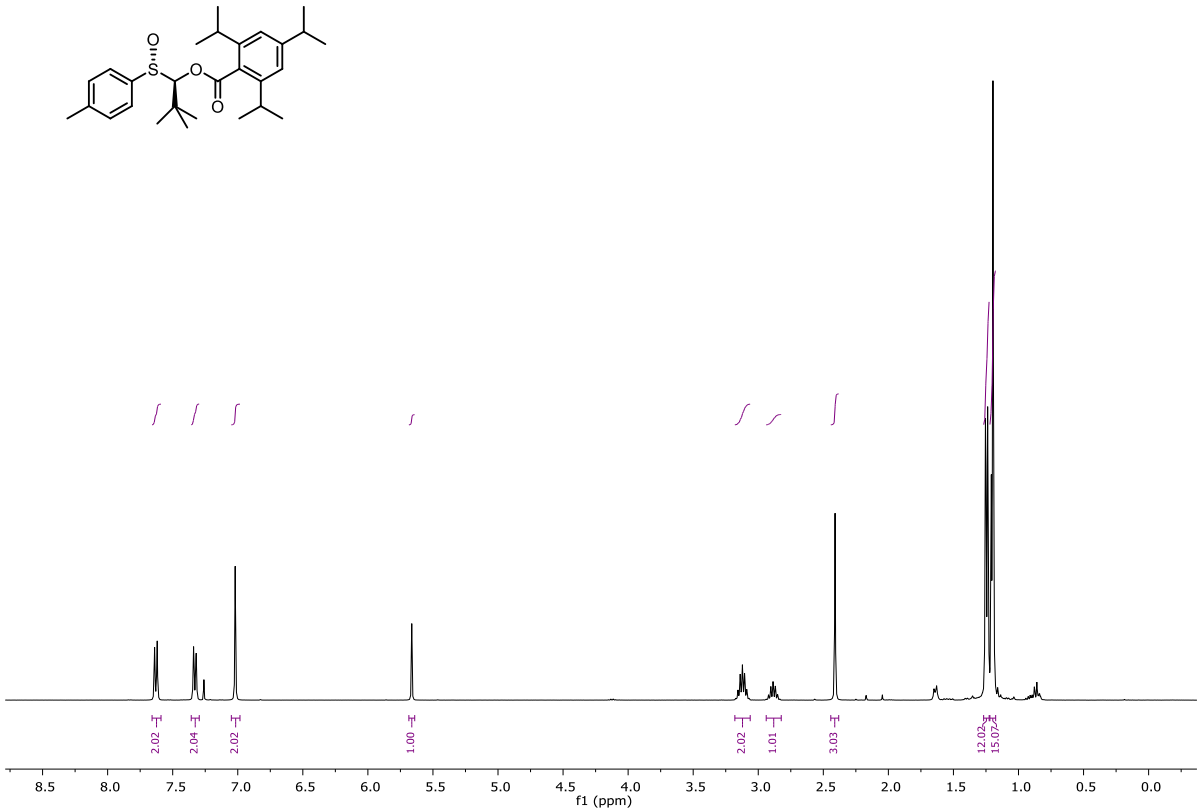
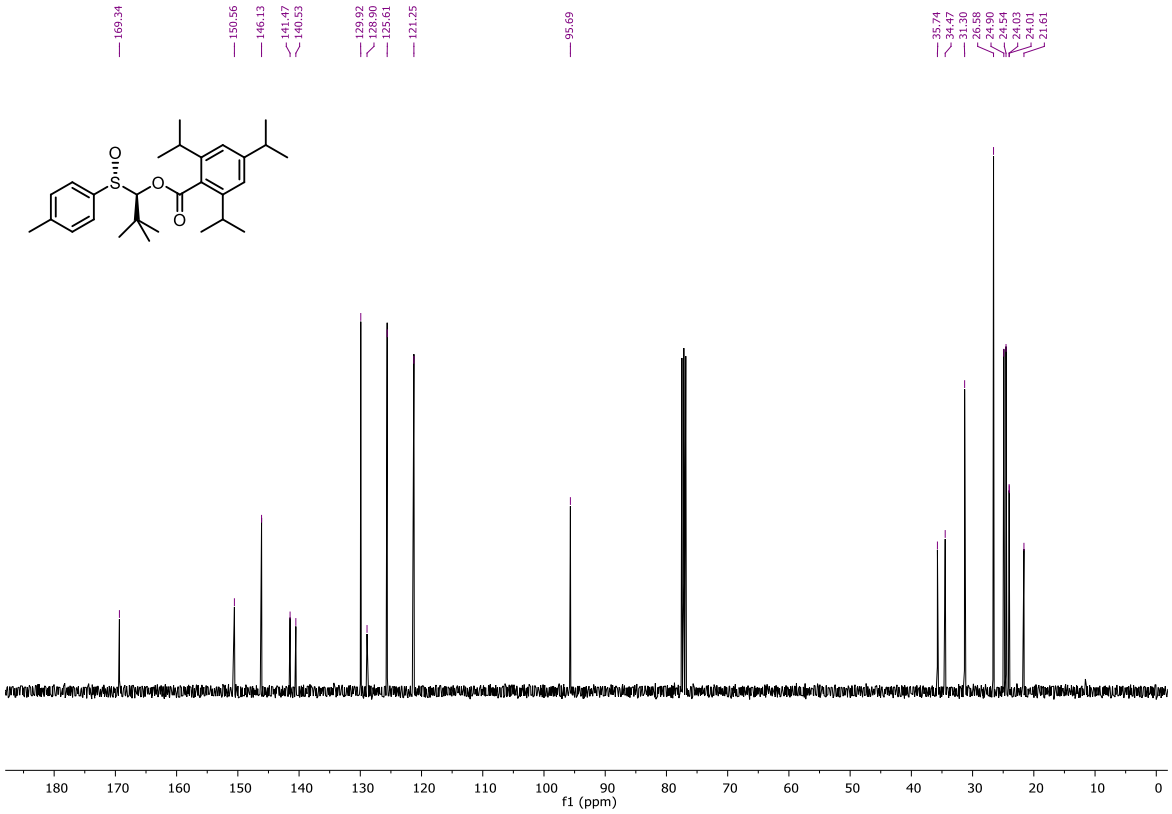
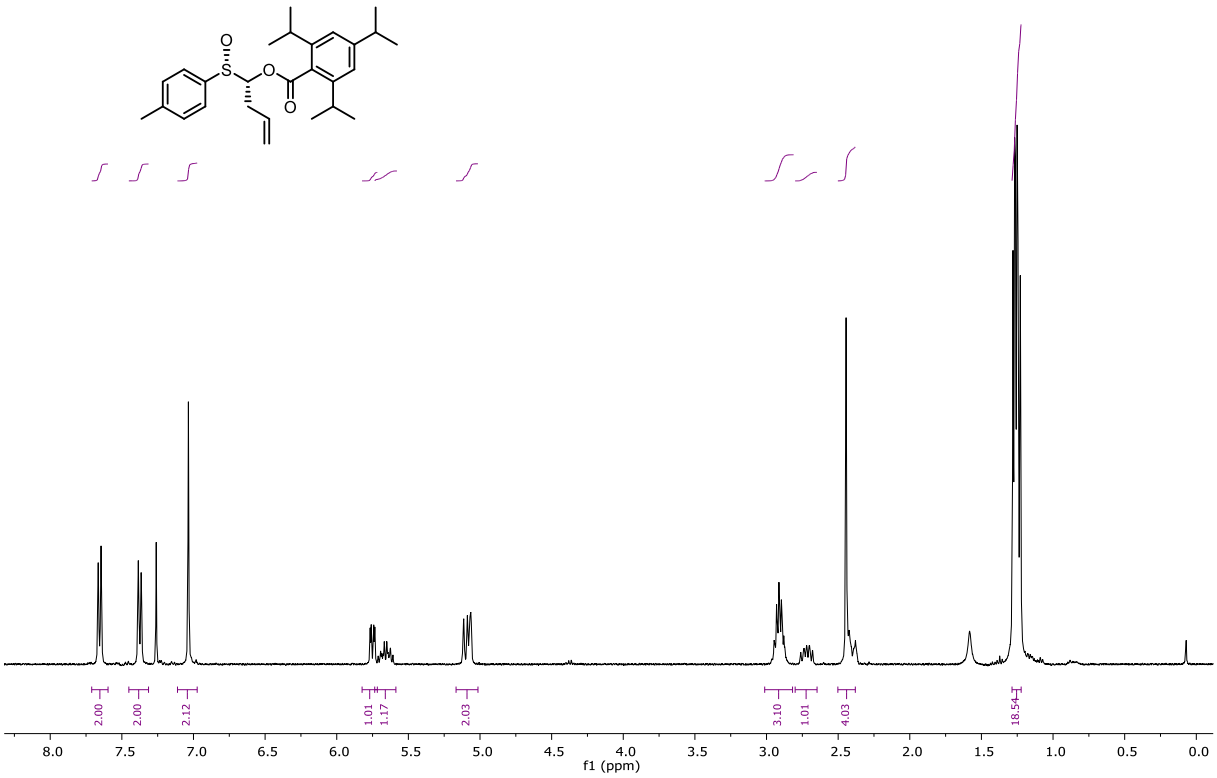


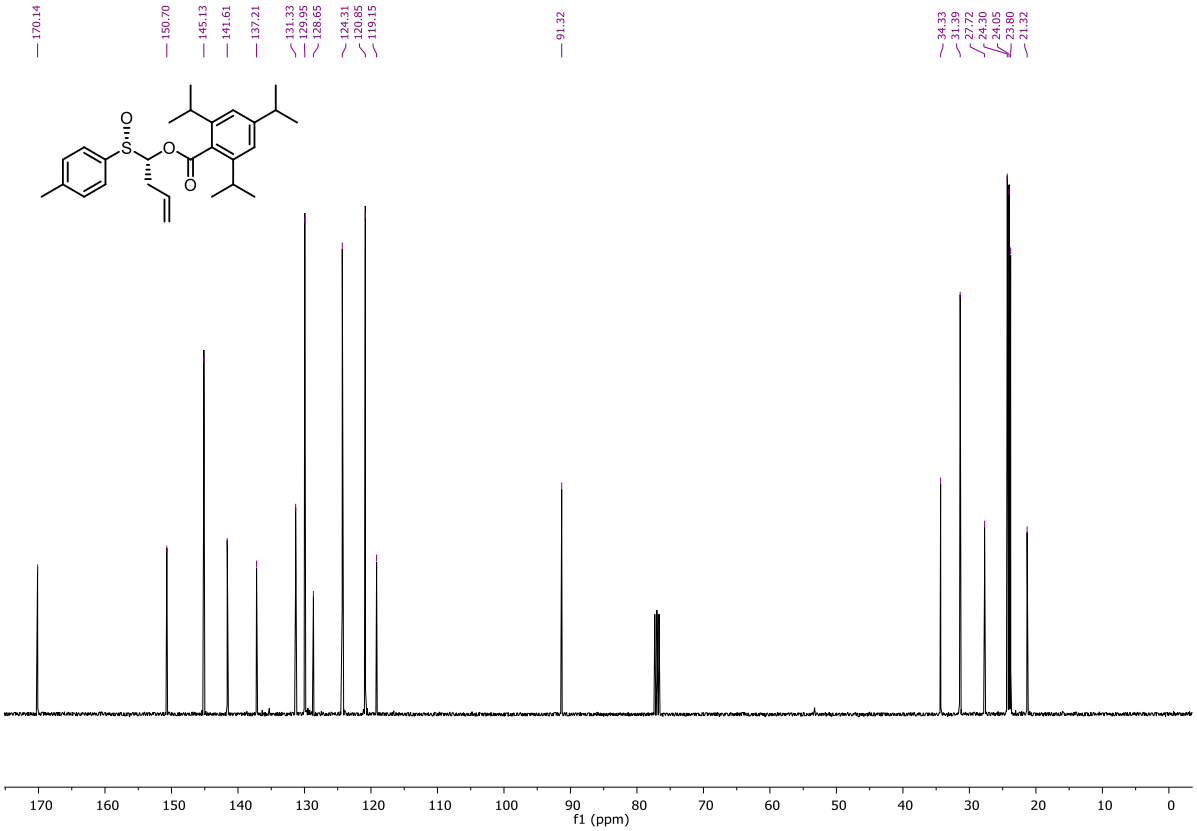
^{13}C NMR of *anti*-**14e** (101 MHz, $CDCl_3$)



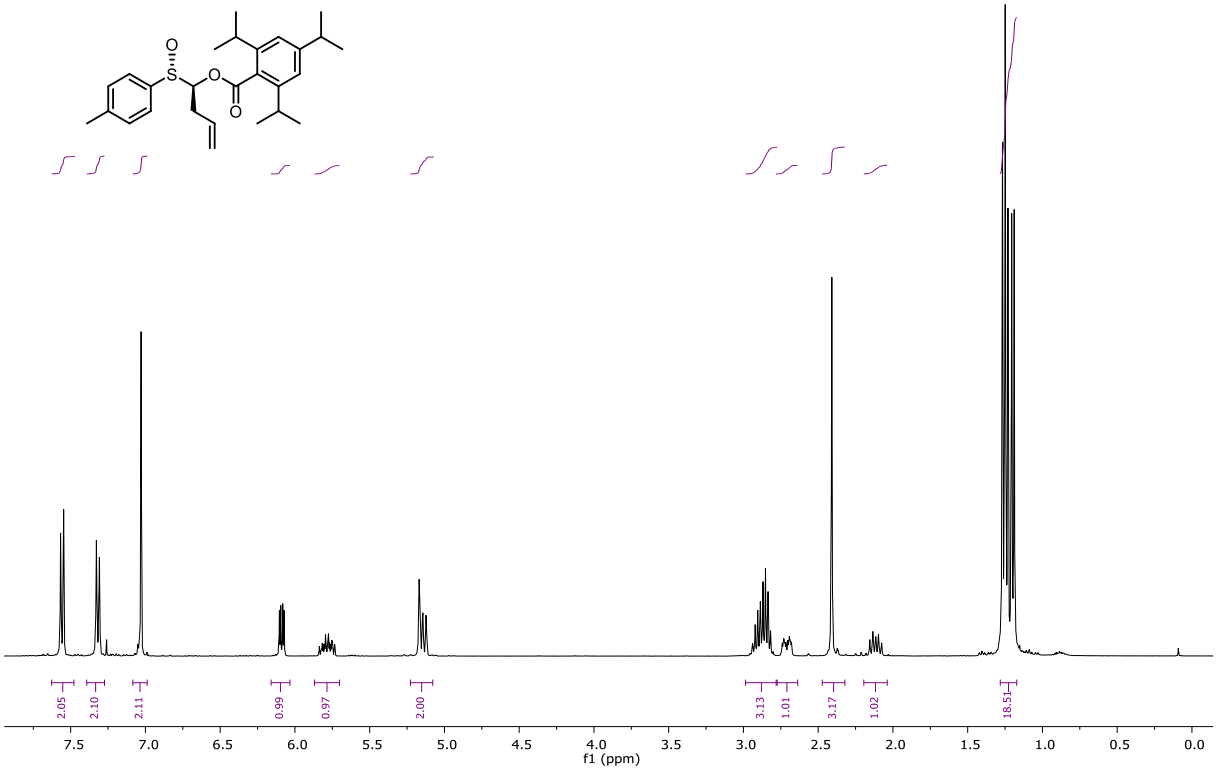
^{1}H NMR of *syn*-**14f** (400 MHz, $CDCl_3$)



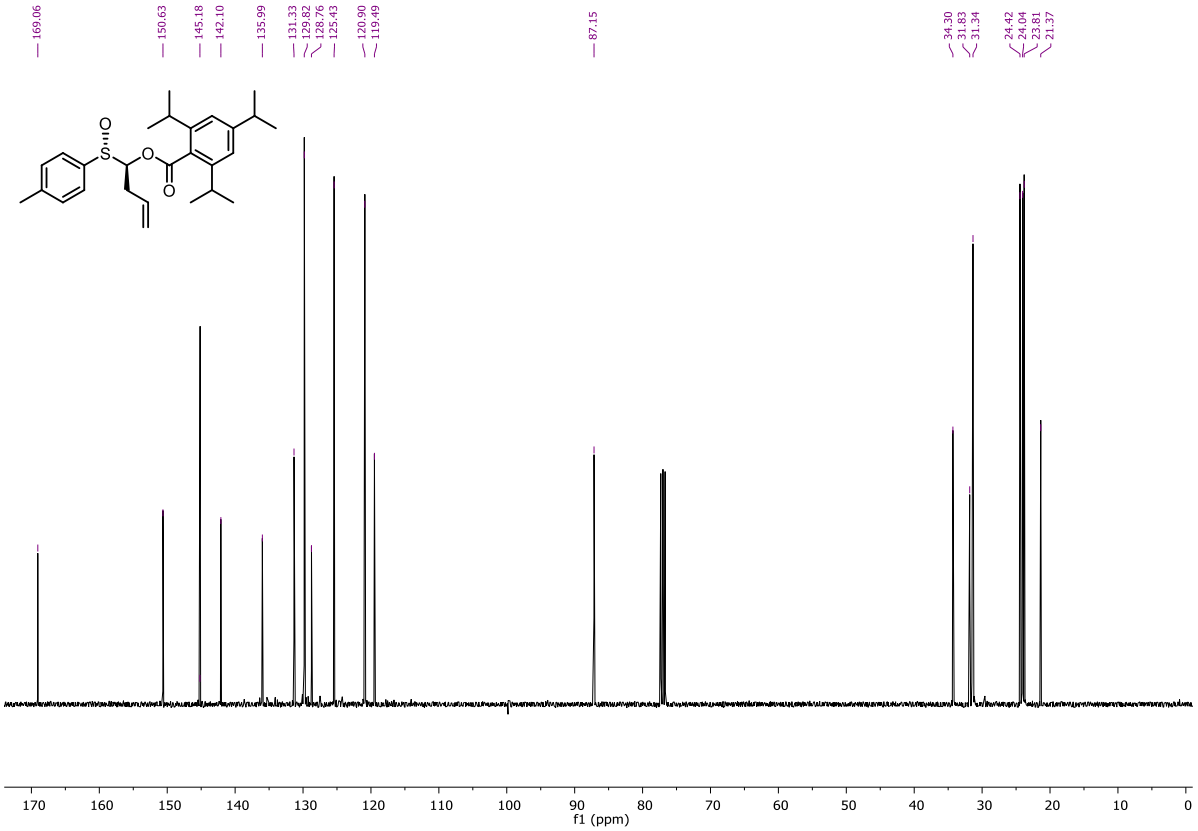
^{13}C NMR of *syn*-**14f** (101 MHz, $CDCl_3$)



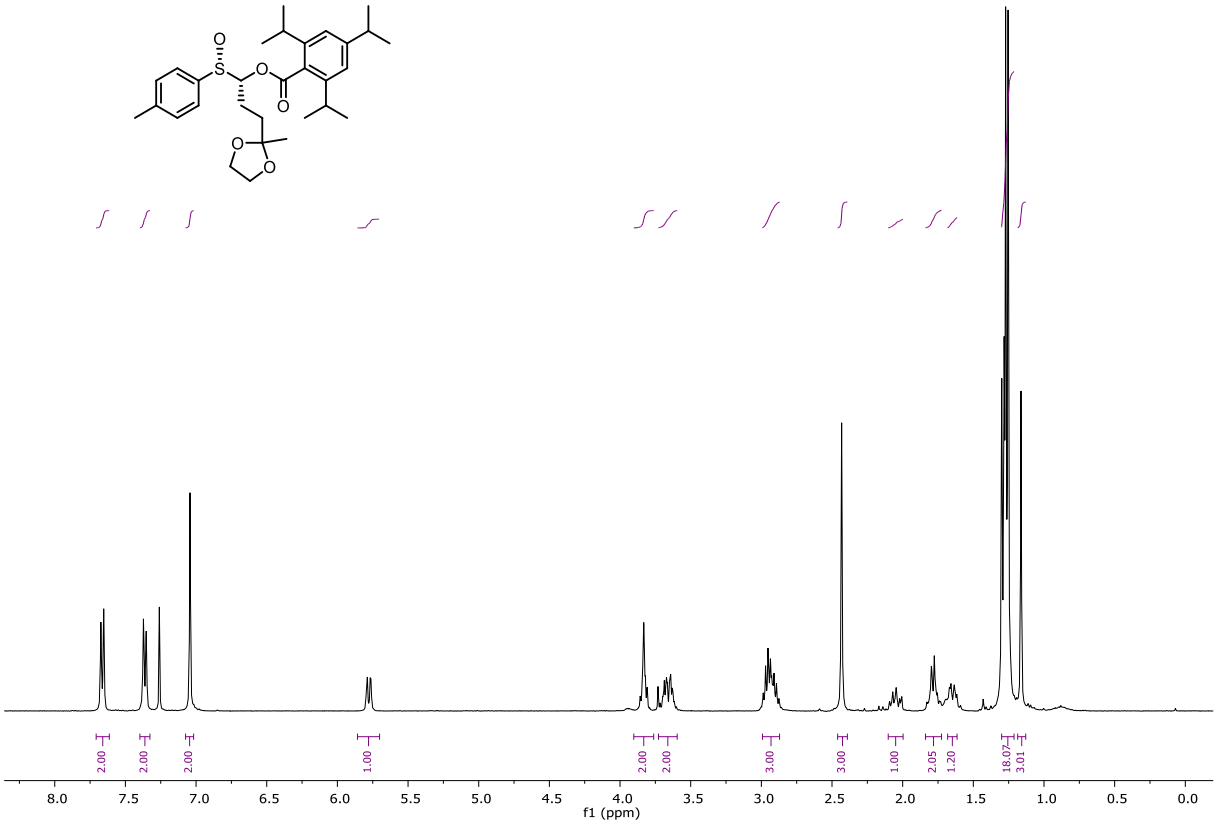
^{1}H NMR of *anti*-**14f** (400 MHz, $CDCl_3$)



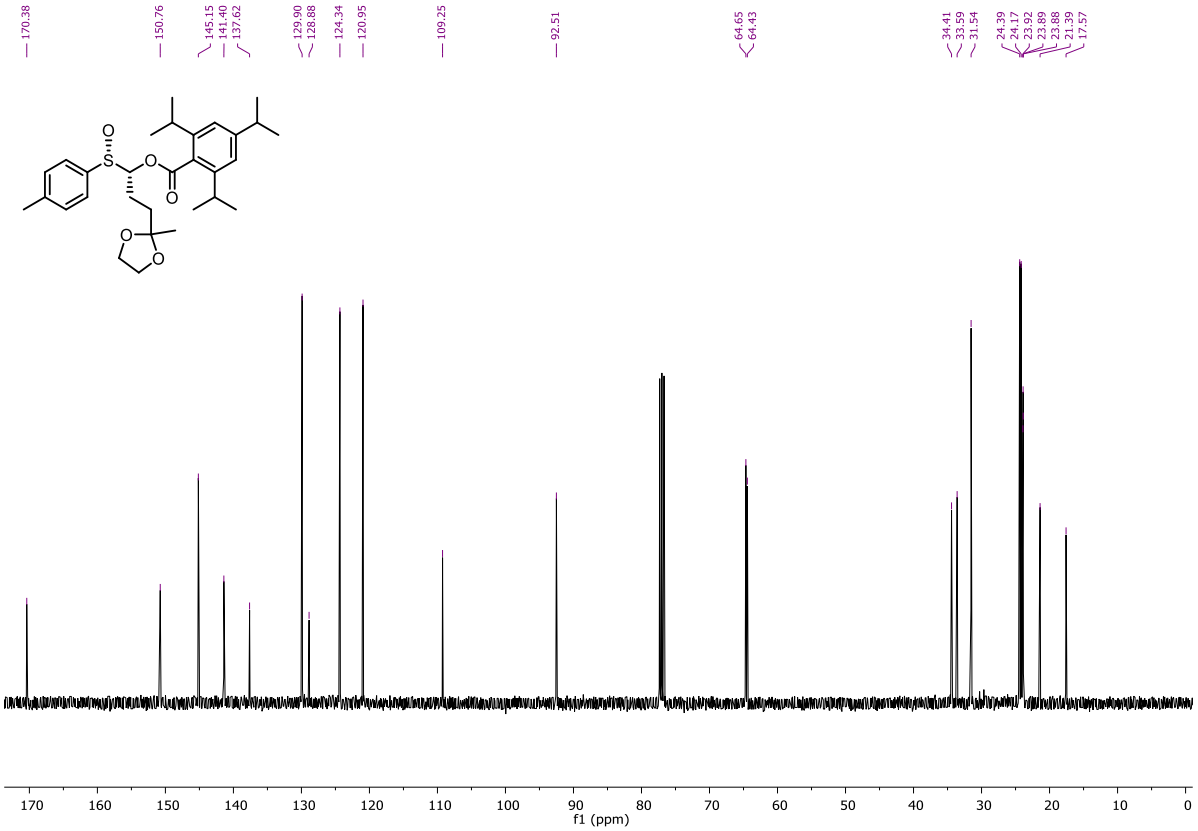
^{13}C NMR of *anti*-**14f** (101 MHz, $CDCl_3$)



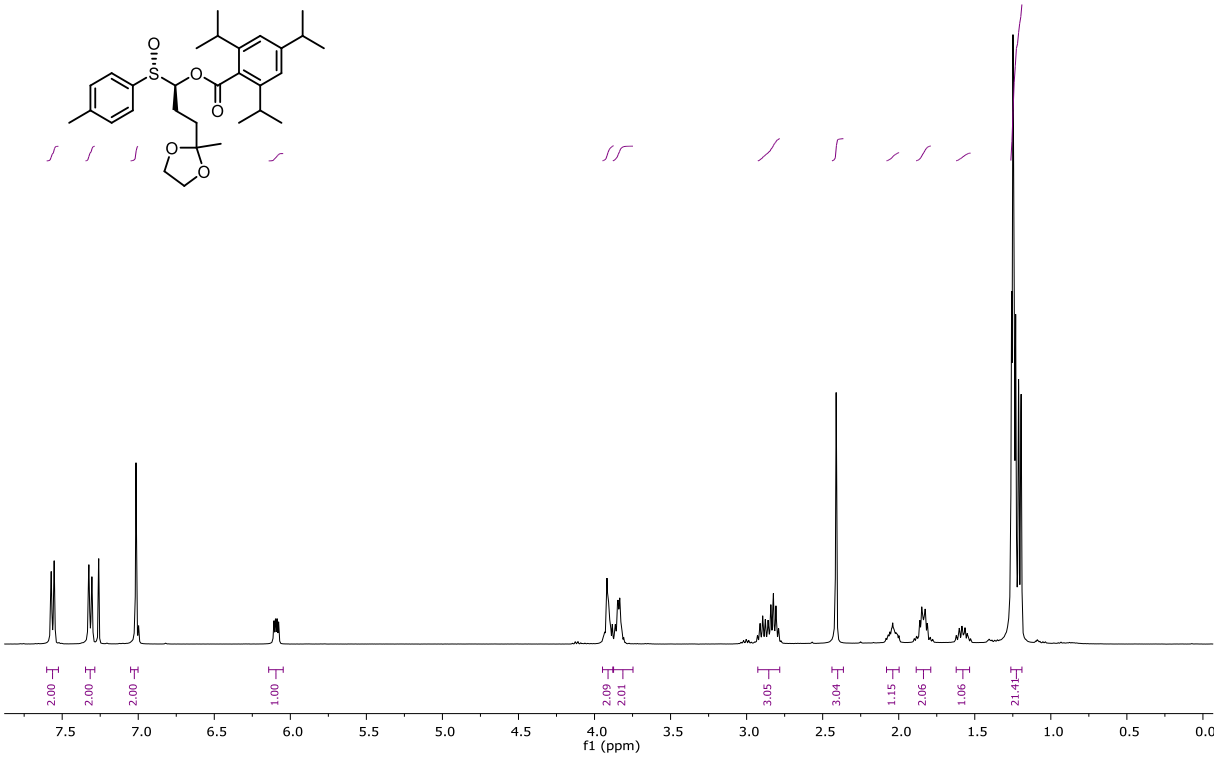
^{1}H NMR of *syn*-**14g** (400 MHz, $CDCl_3$)



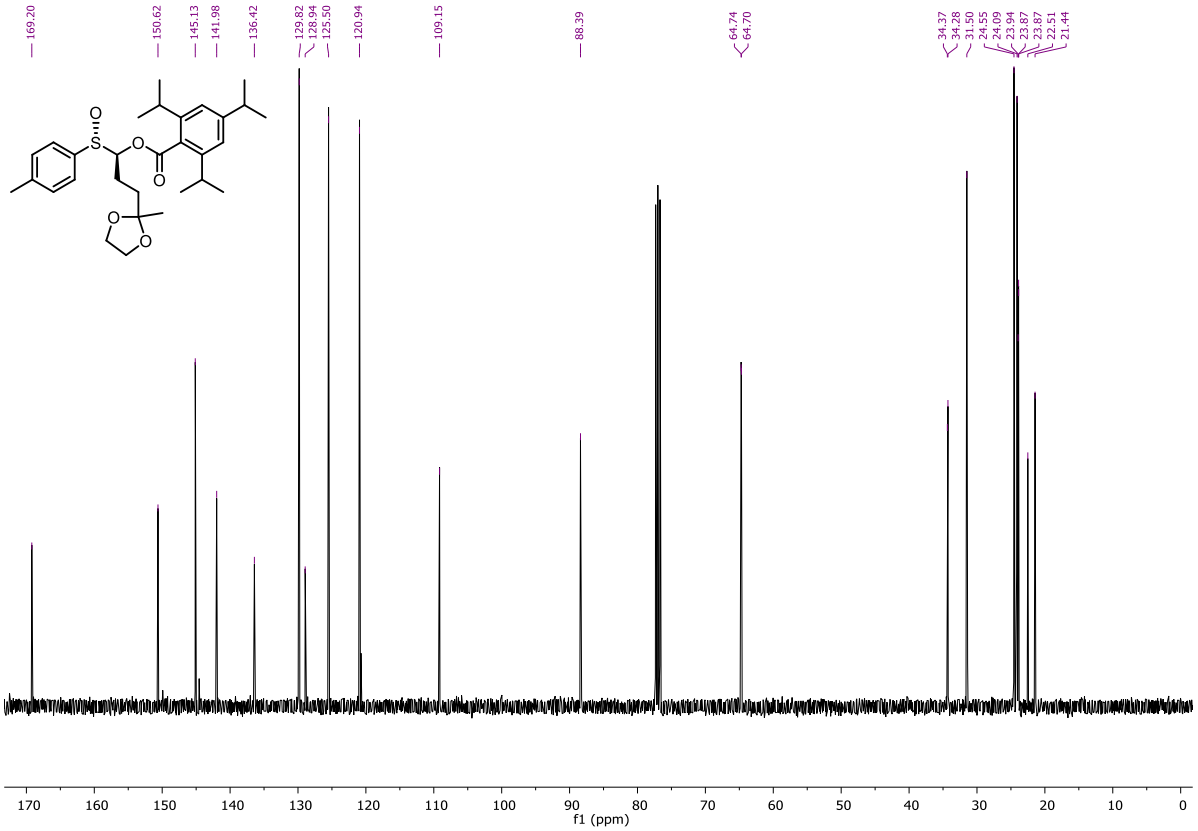
^{13}C NMR of *syn*-**14g** (101 MHz, $CDCl_3$)



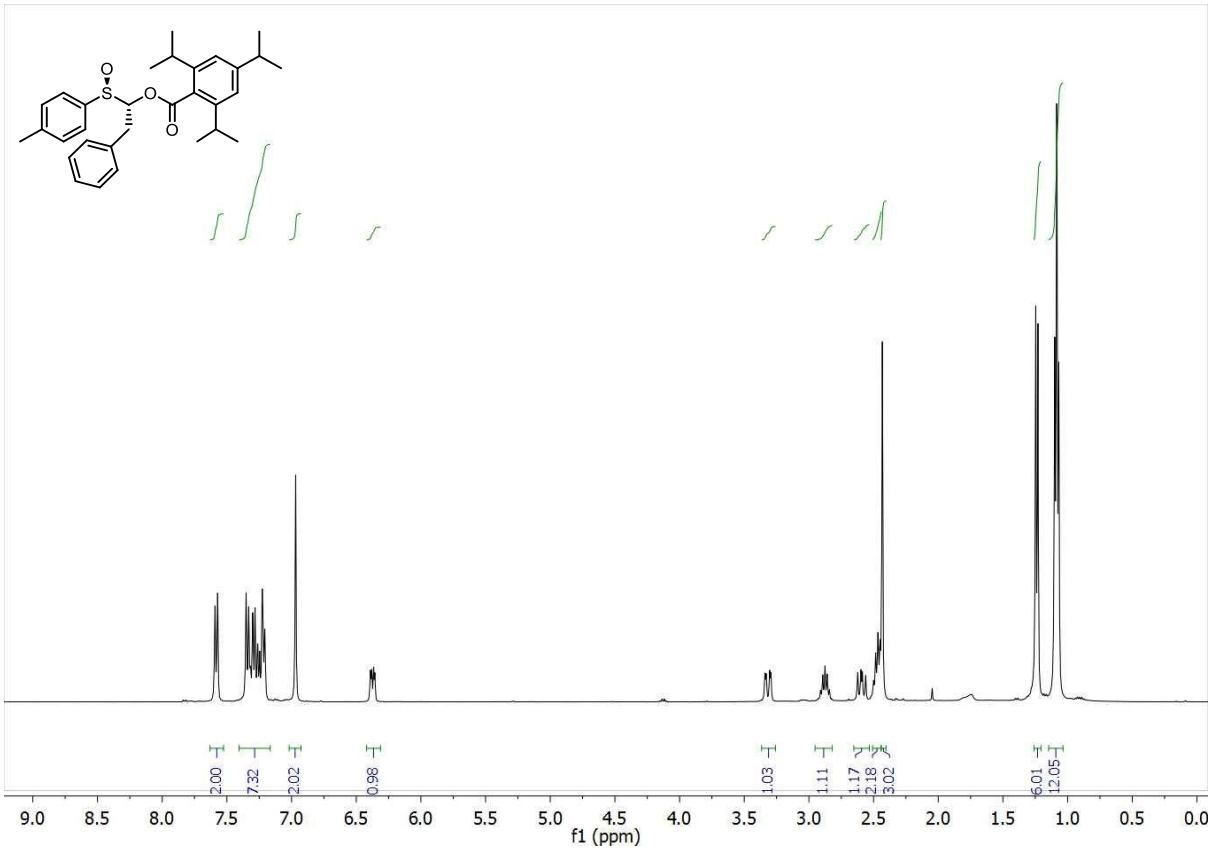
^{1}H NMR of *anti*-**14g** (400 MHz, $CDCl_3$)



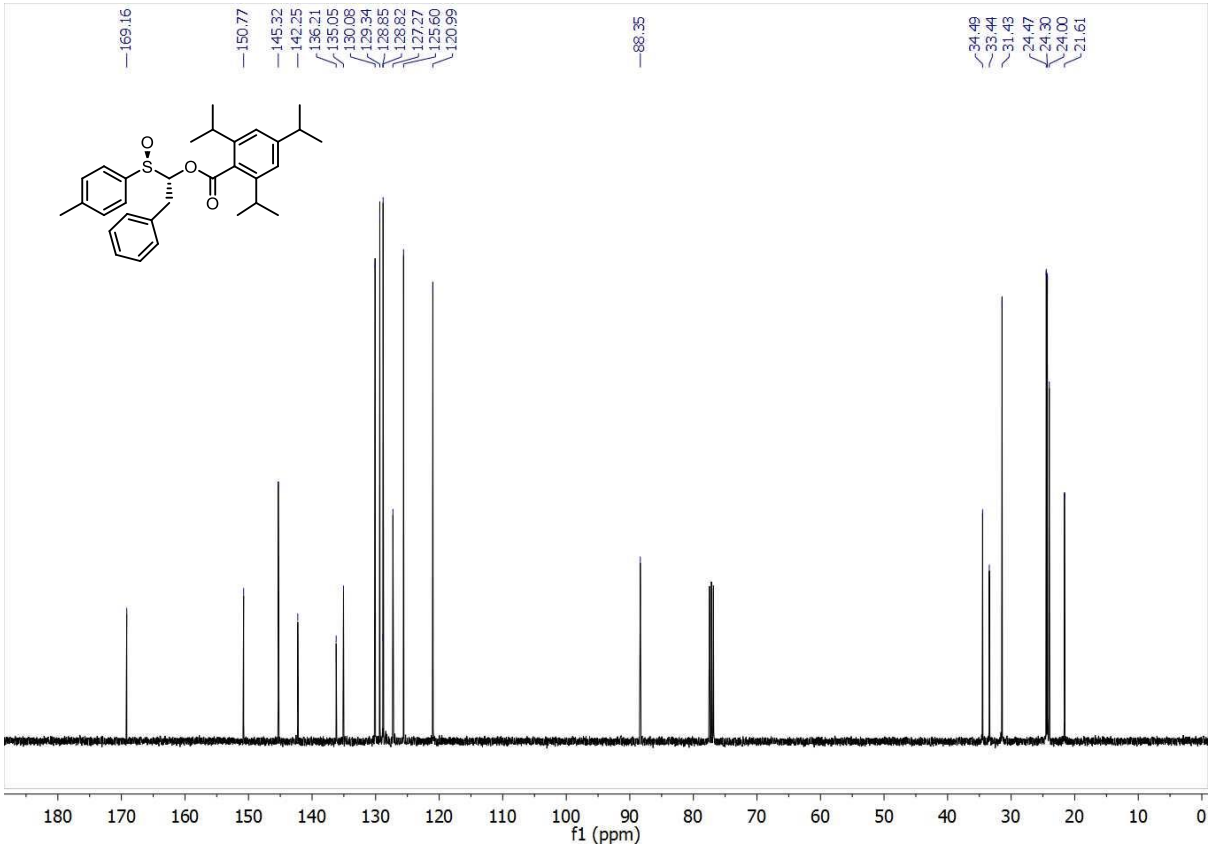
^{13}C NMR of *syn*-**14g** (101 MHz, $CDCl_3$)



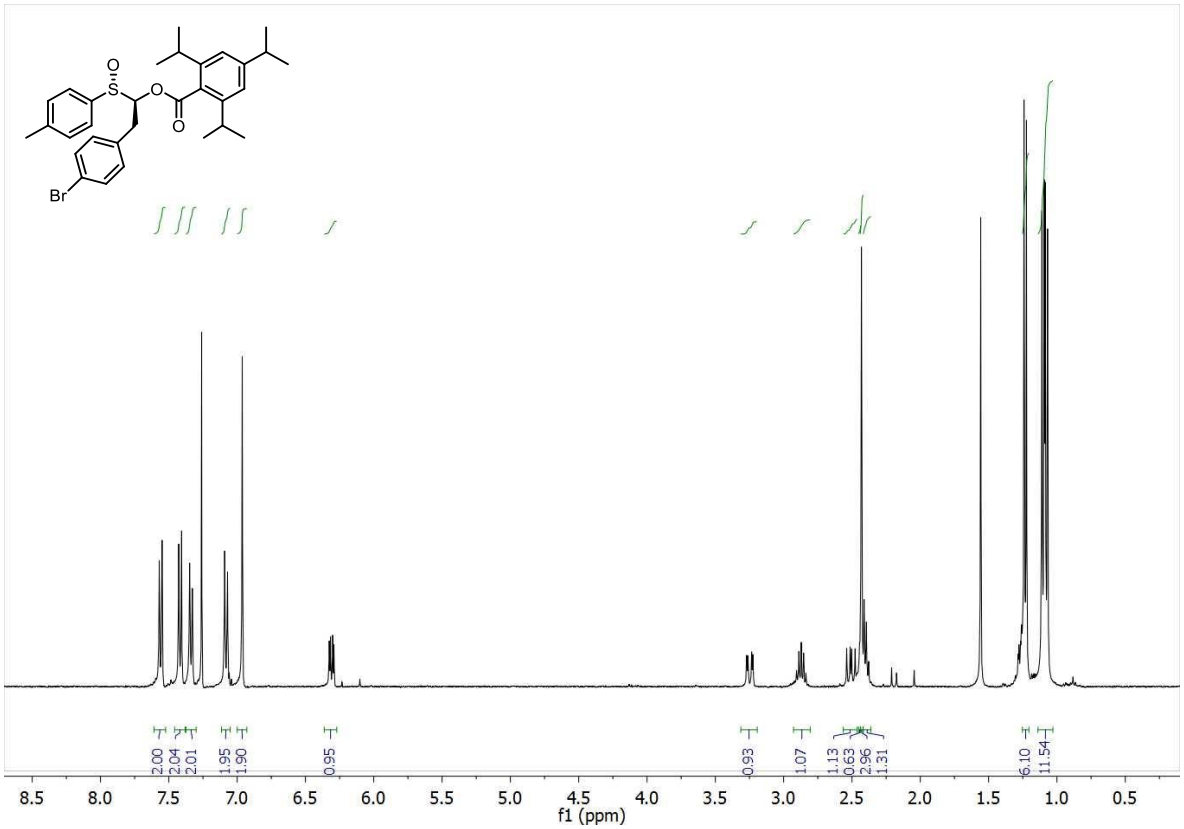
^{1}H NMR of *anti*-**14h** (400 MHz, $CDCl_3$)



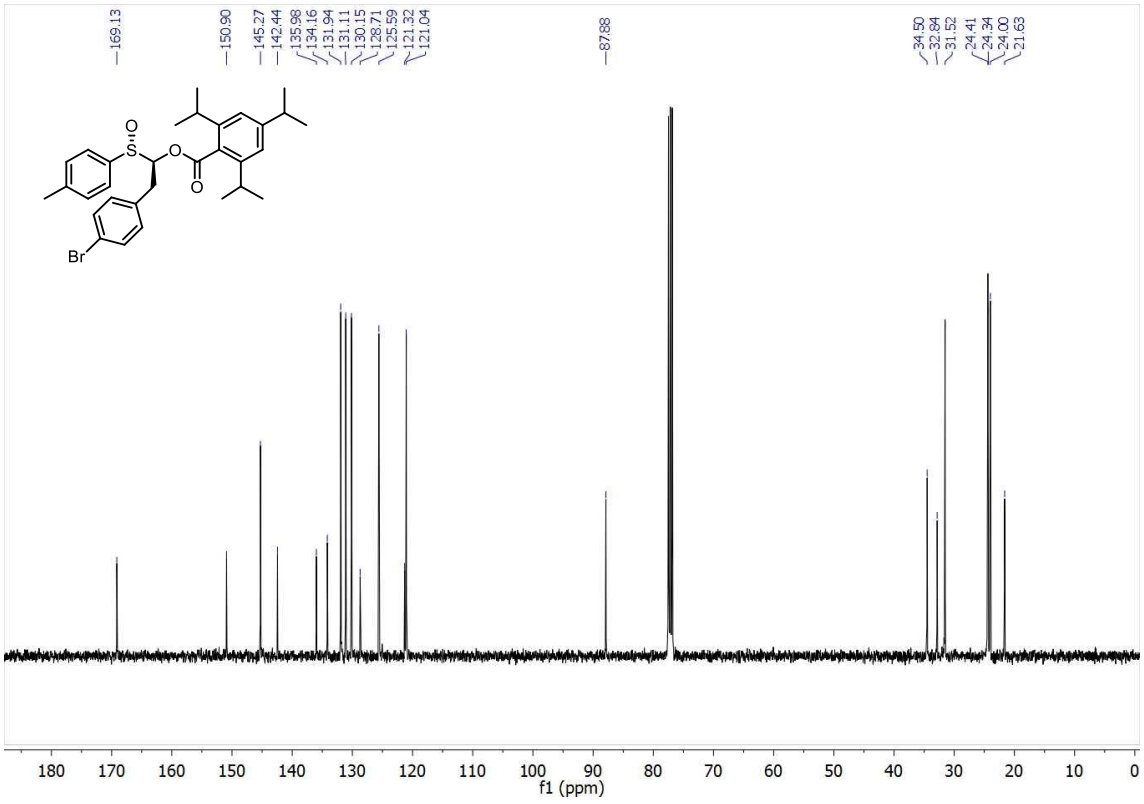
^{13}C NMR of *anti*-**14h** (101 MHz, $CDCl_3$)



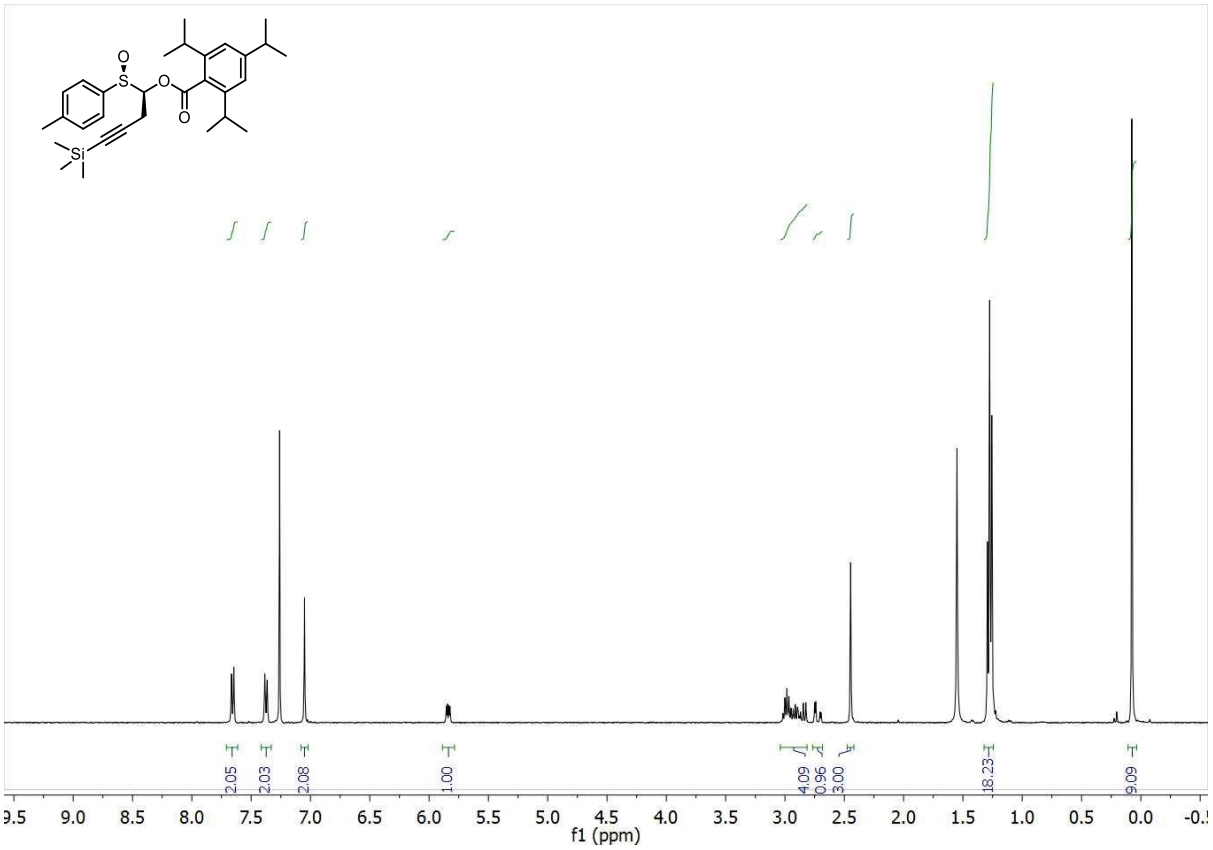
^{1}H NMR of *anti*-**14i** (400 MHz, $CDCl_3$)



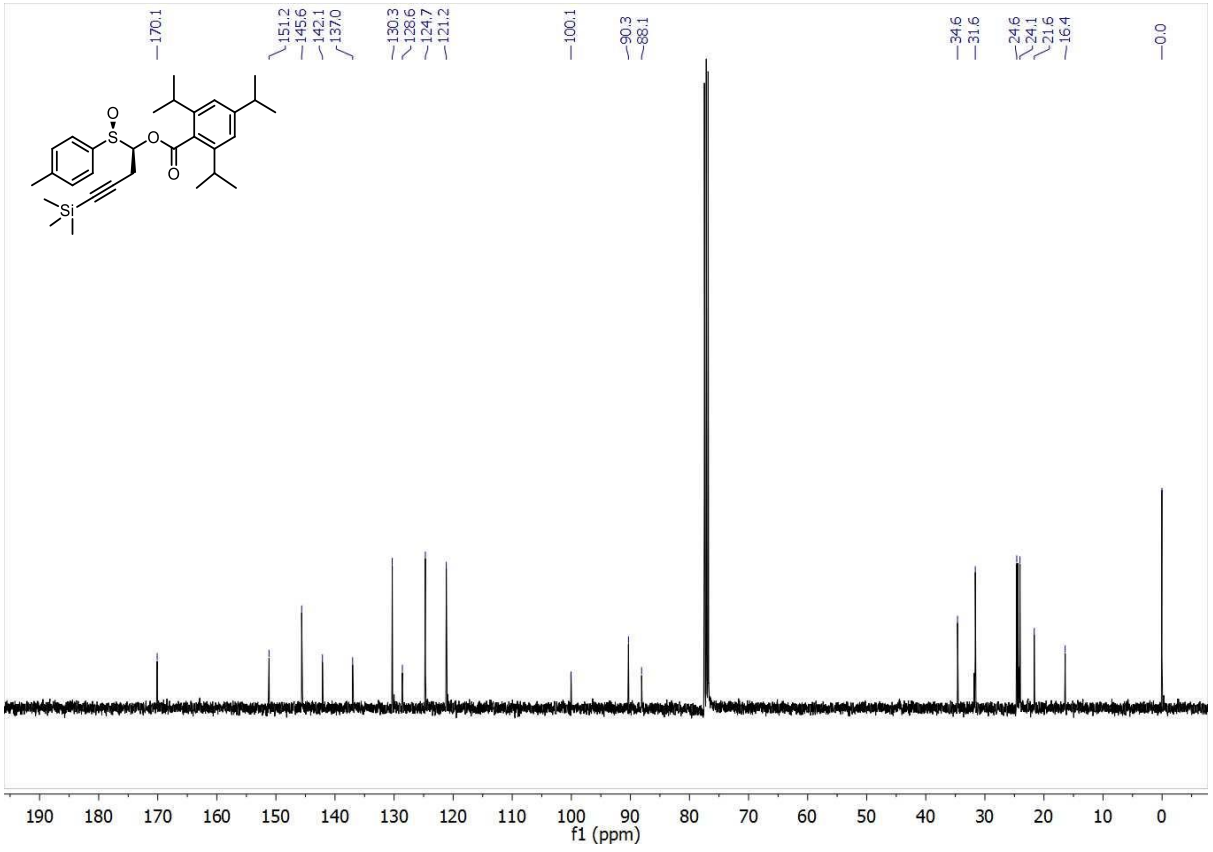
^{13}C NMR of *anti*-**14i** (101 MHz, $CDCl_3$)



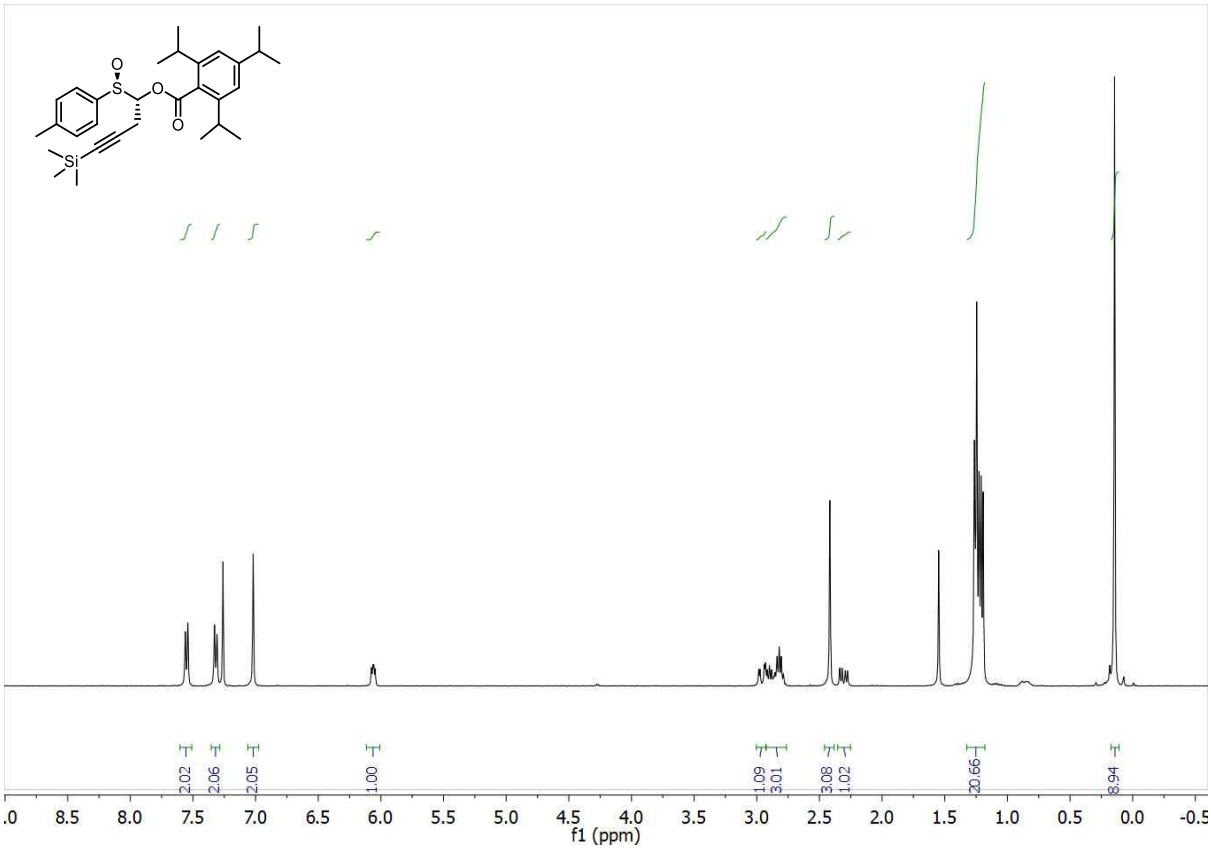
^{1}H NMR of *syn*-**14j** (400 MHz, $CDCl_3$)



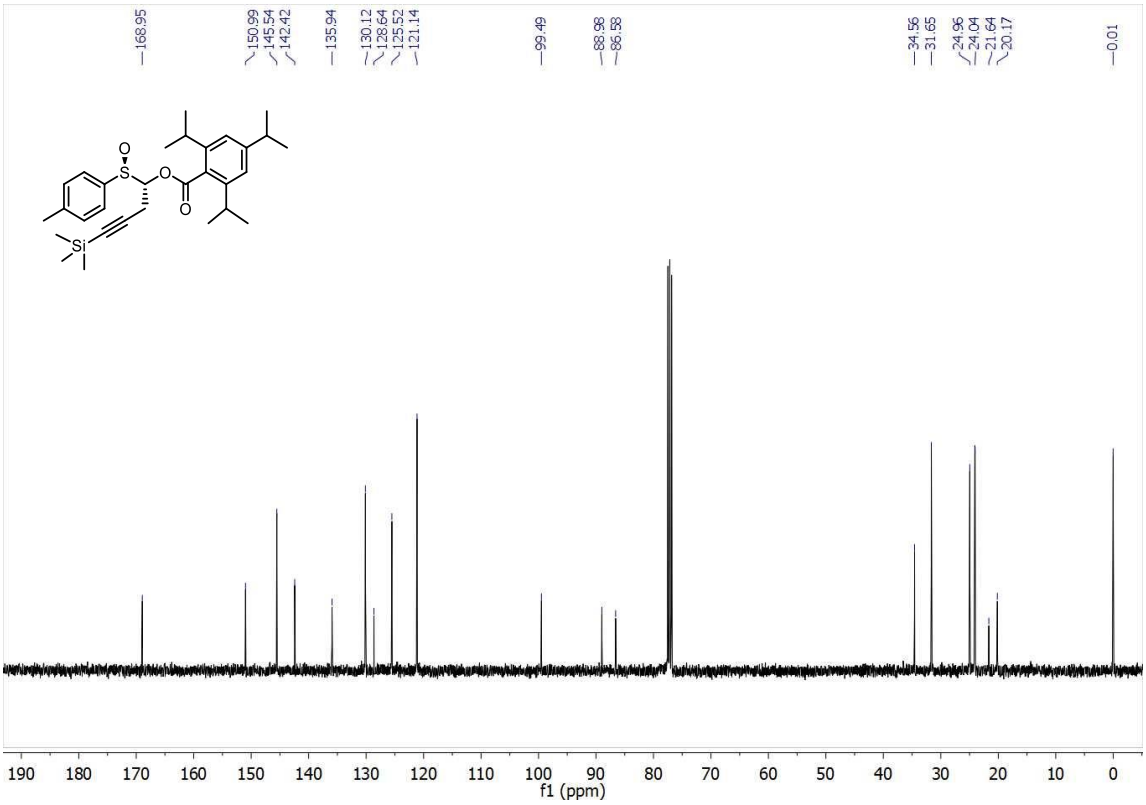
^{13}C NMR of *syn*-**14j** (101 MHz, $CDCl_3$)



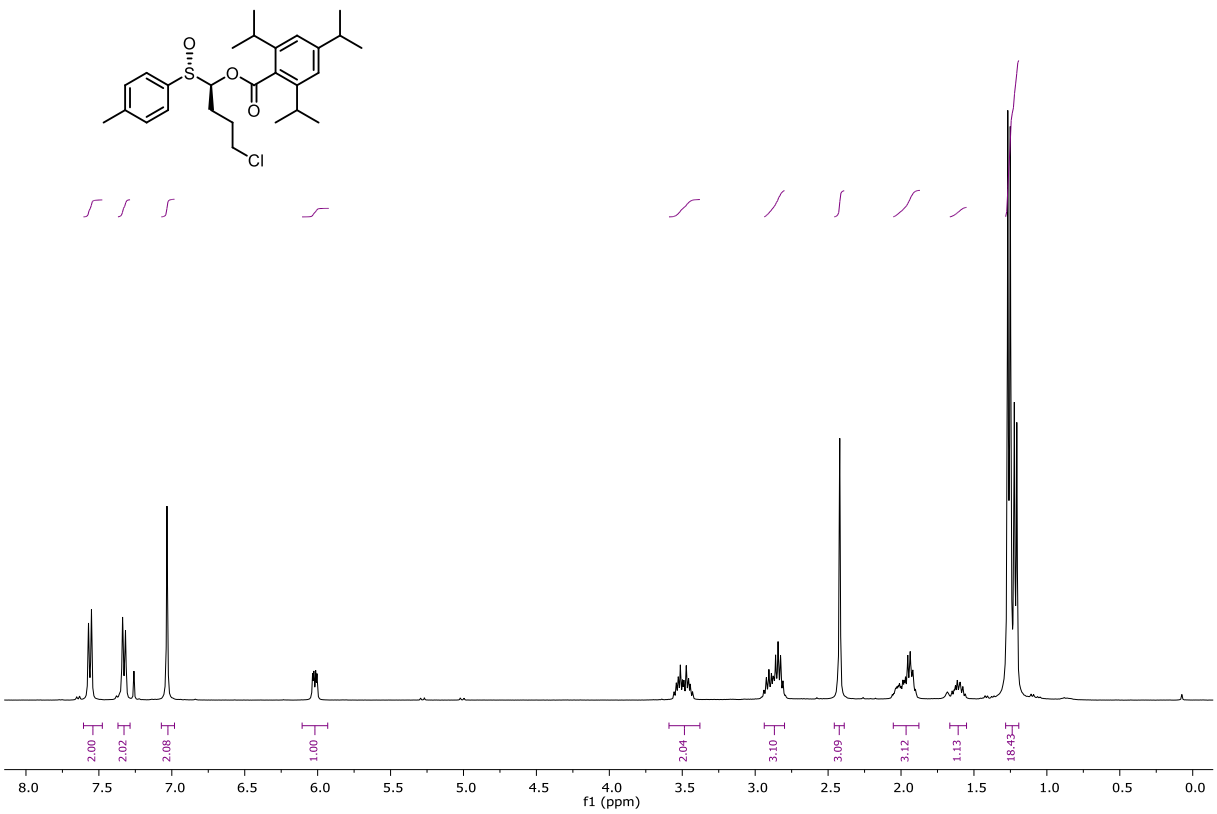
^{1}H NMR of *anti*-**14j** (400 MHz, $CDCl_3$)



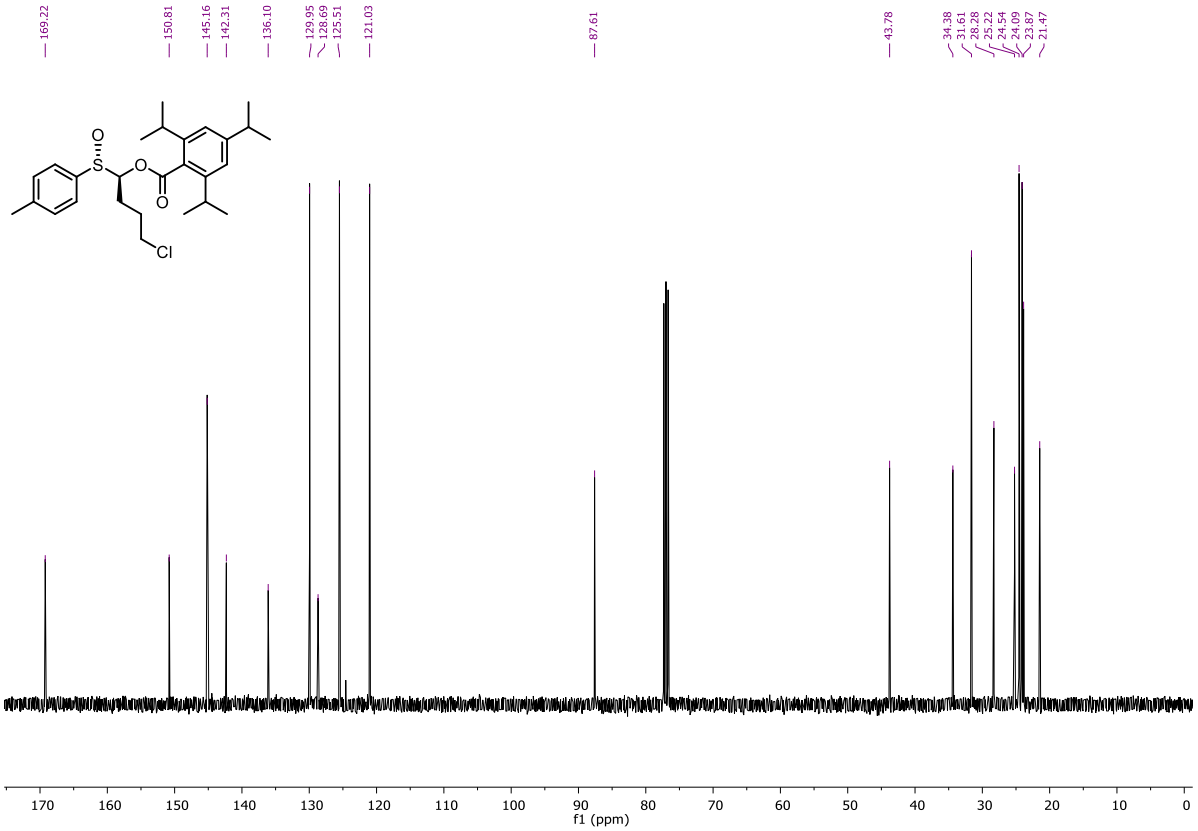
^{13}C NMR of *anti*-**14j** (101 MHz, $CDCl_3$)



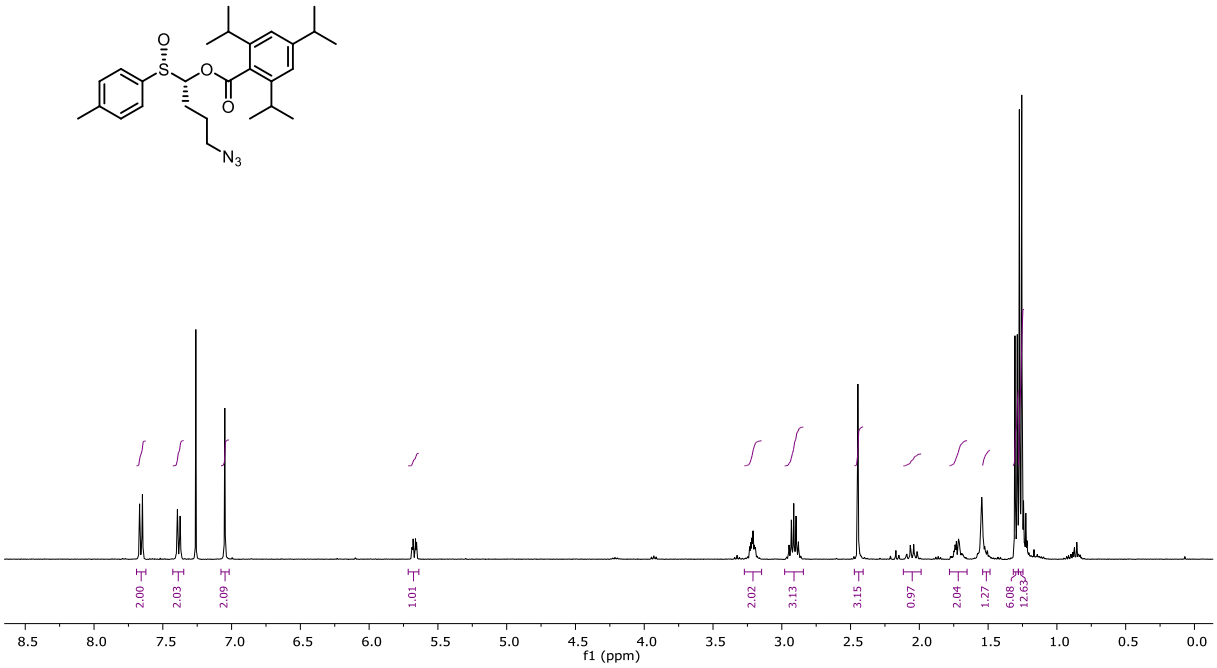
^{1}H NMR of *anti*-**14k** (400 MHz, $CDCl_3$)



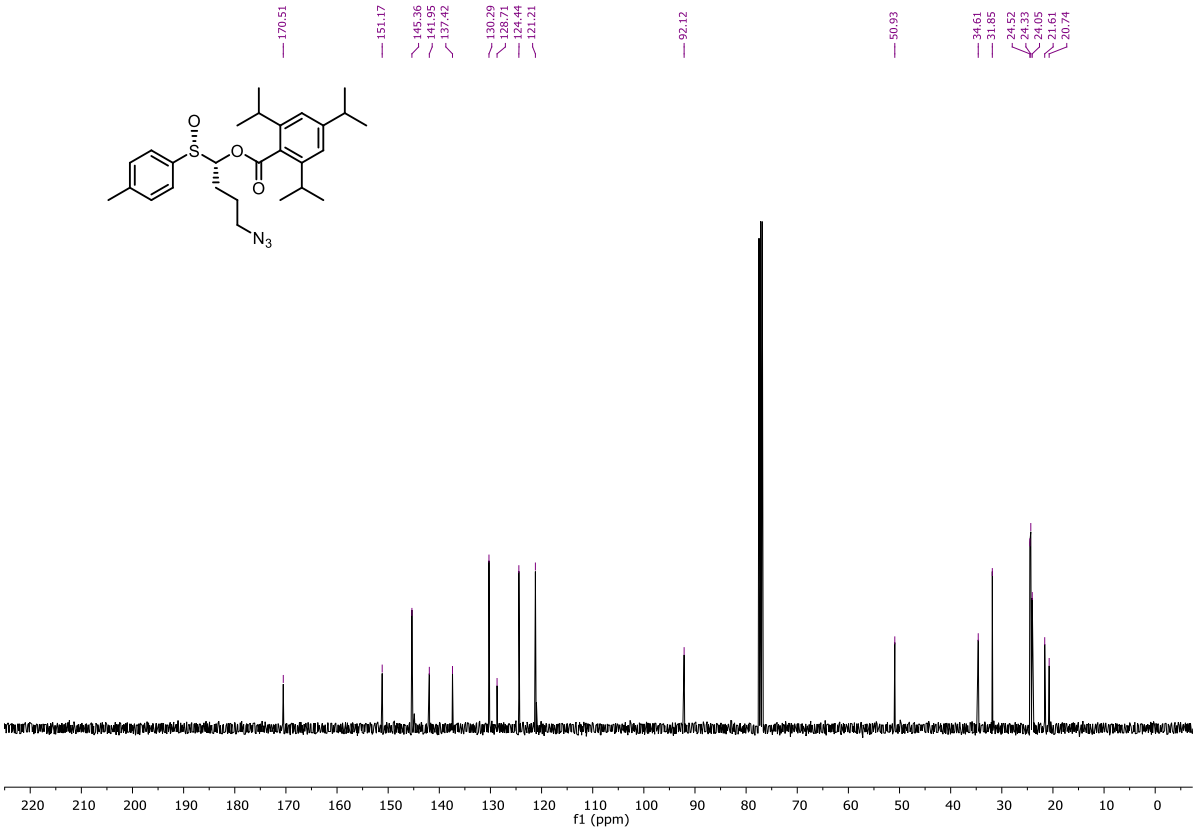
^{13}C NMR of *anti*-**14k** (101 MHz, $CDCl_3$)



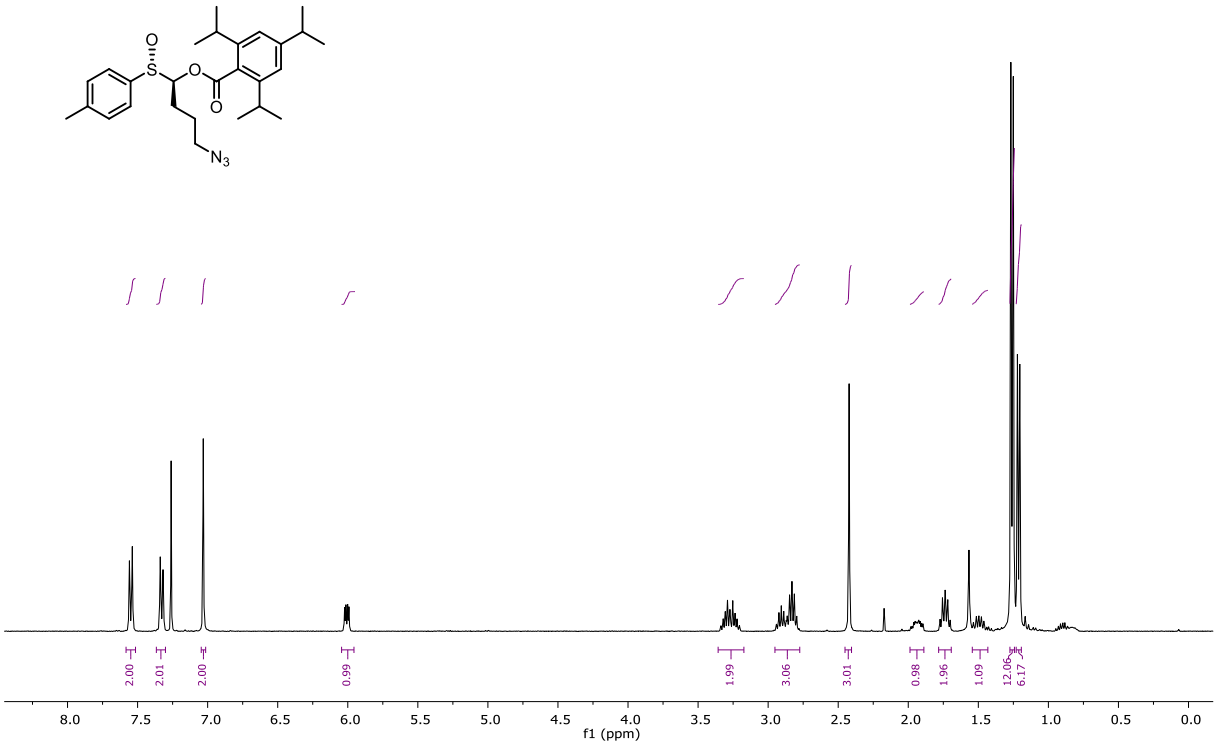
^{1}H NMR of *syn*-**14l** (400 MHz, $CDCl_3$)



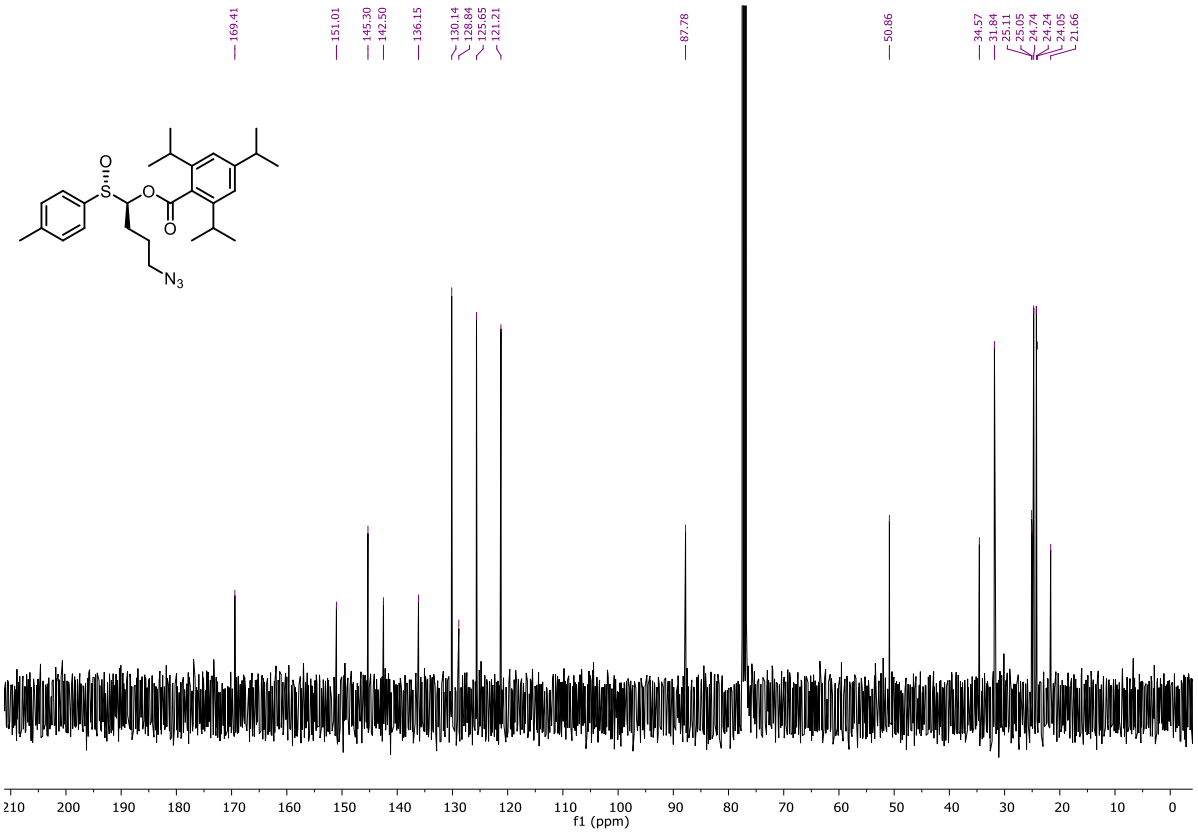
^{13}C NMR of *syn*-**14l** (101 MHz, $CDCl_3$)



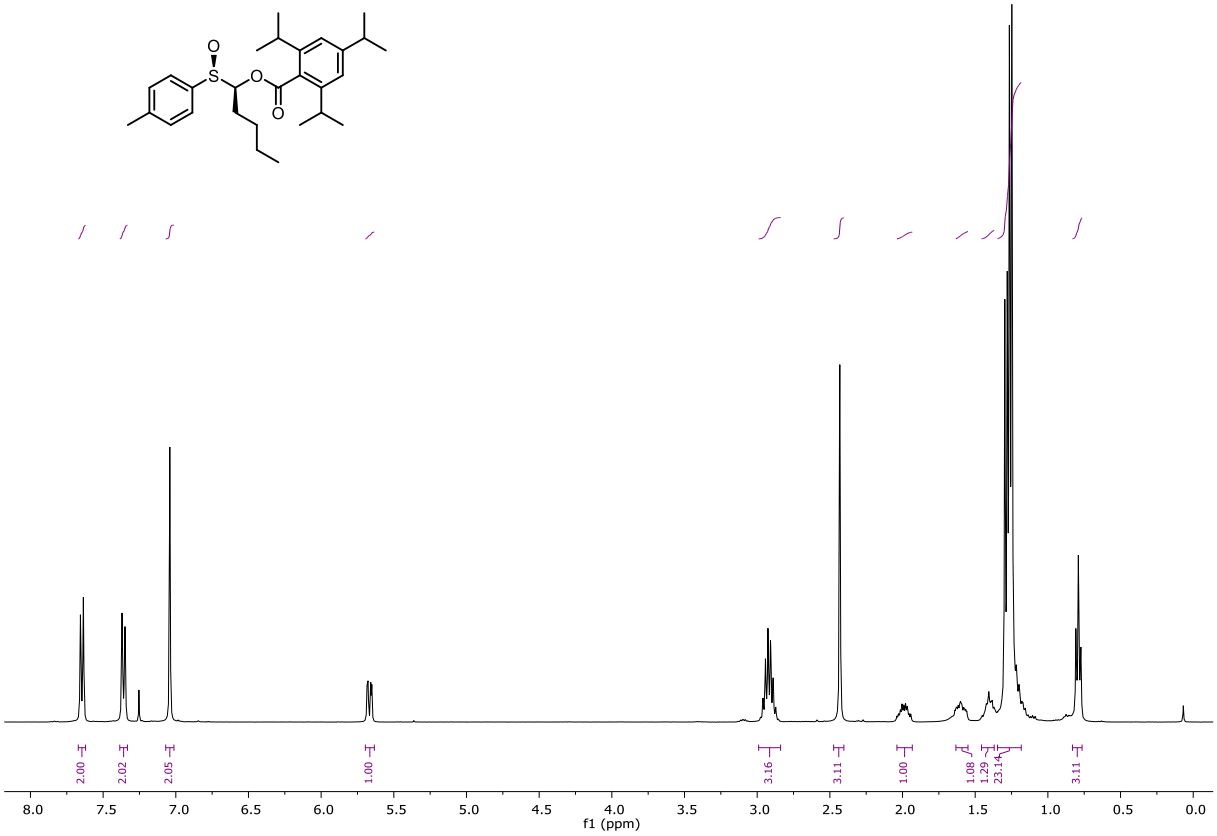
^{1}H NMR of *anti*-**14l** (400 MHz, $CDCl_3$)



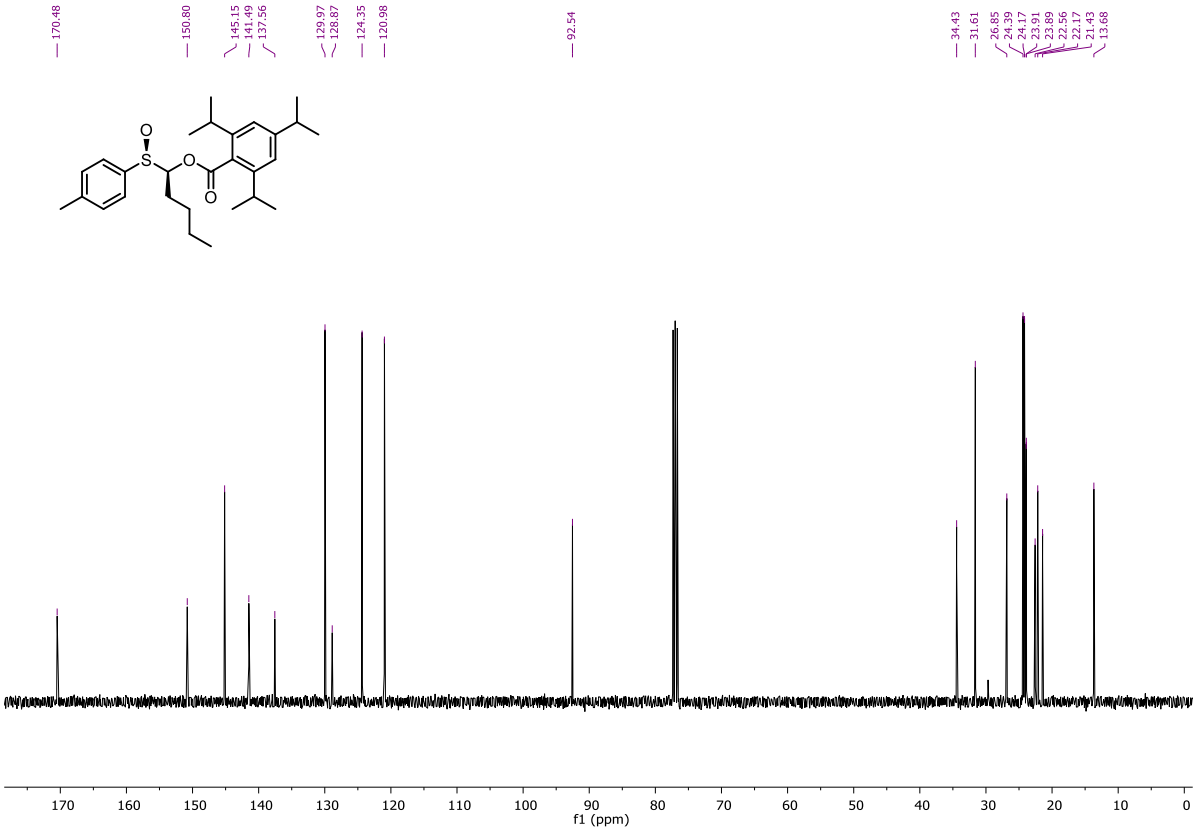
^{13}C NMR of *anti*-**14l** (101 MHz, $CDCl_3$)



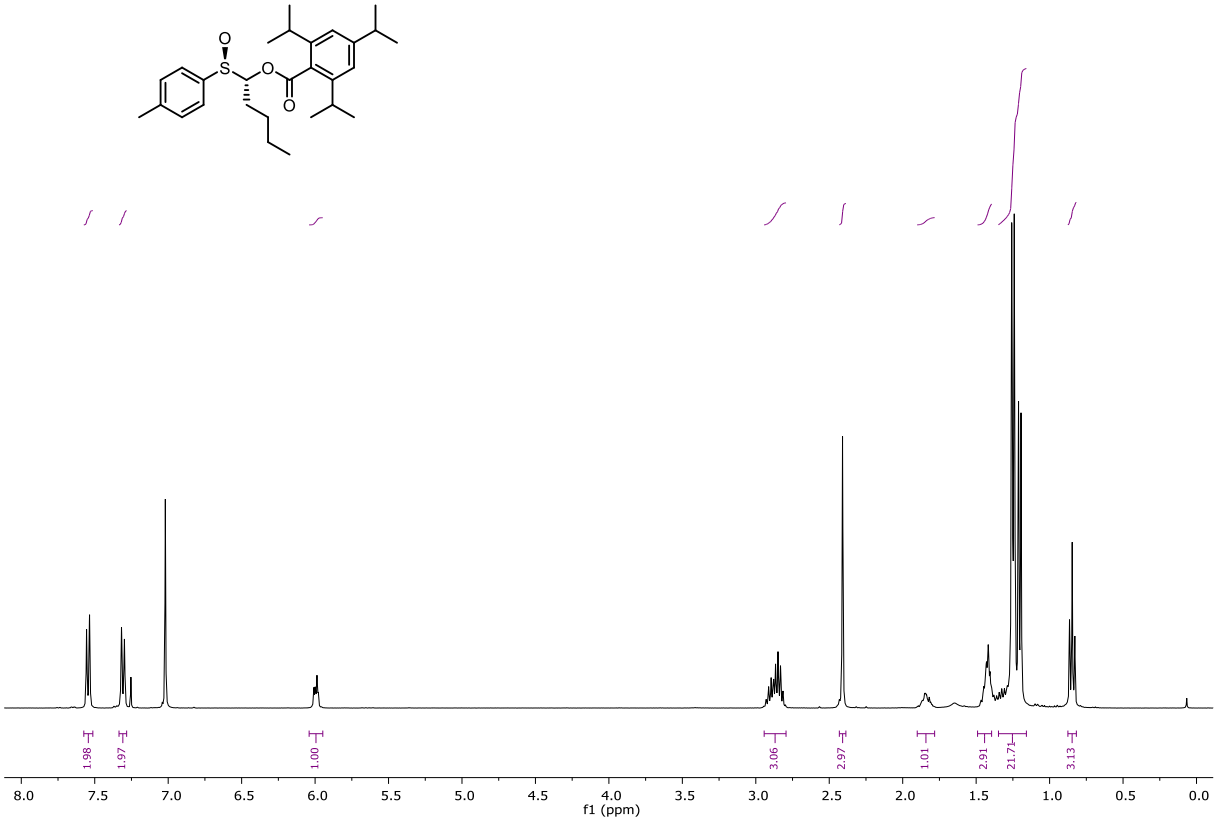
^{1}H NMR of *syn*-**14m** (400 MHz, $CDCl_3$)



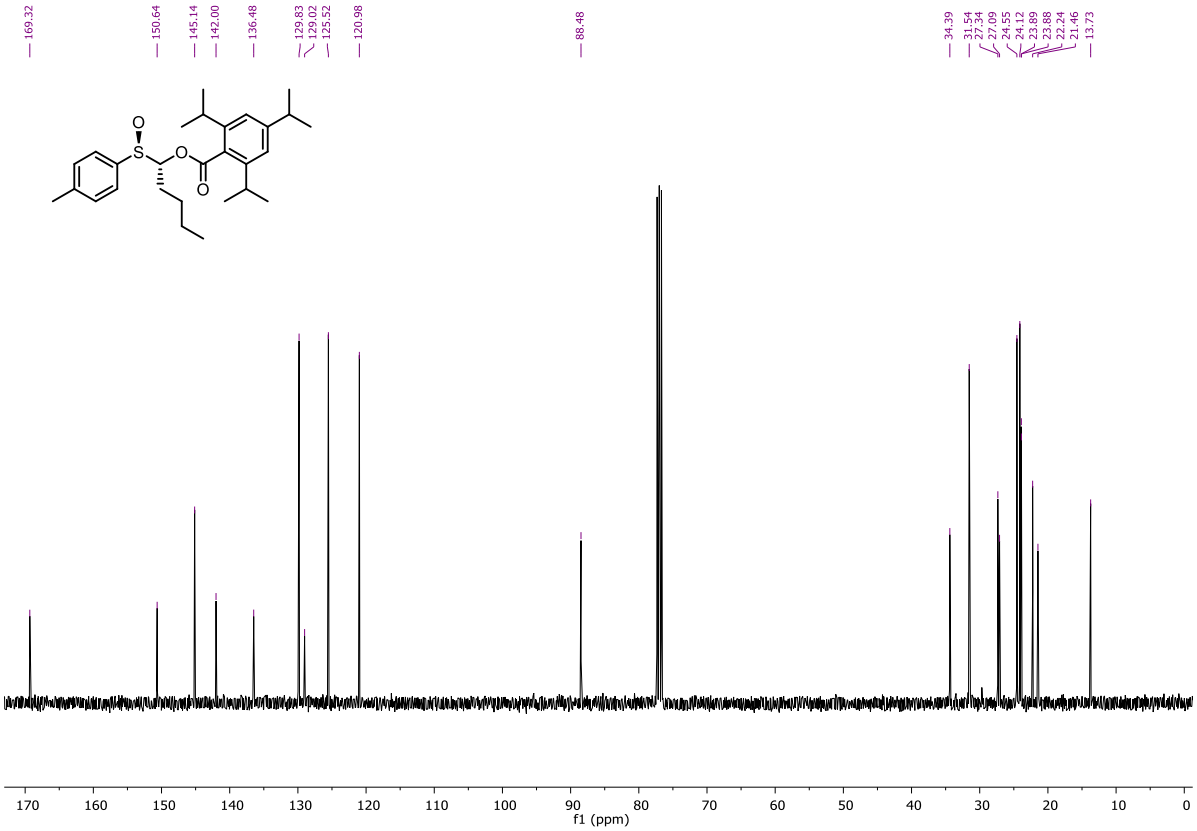
^{13}C NMR of *syn*-**14m** (101 MHz, $CDCl_3$)



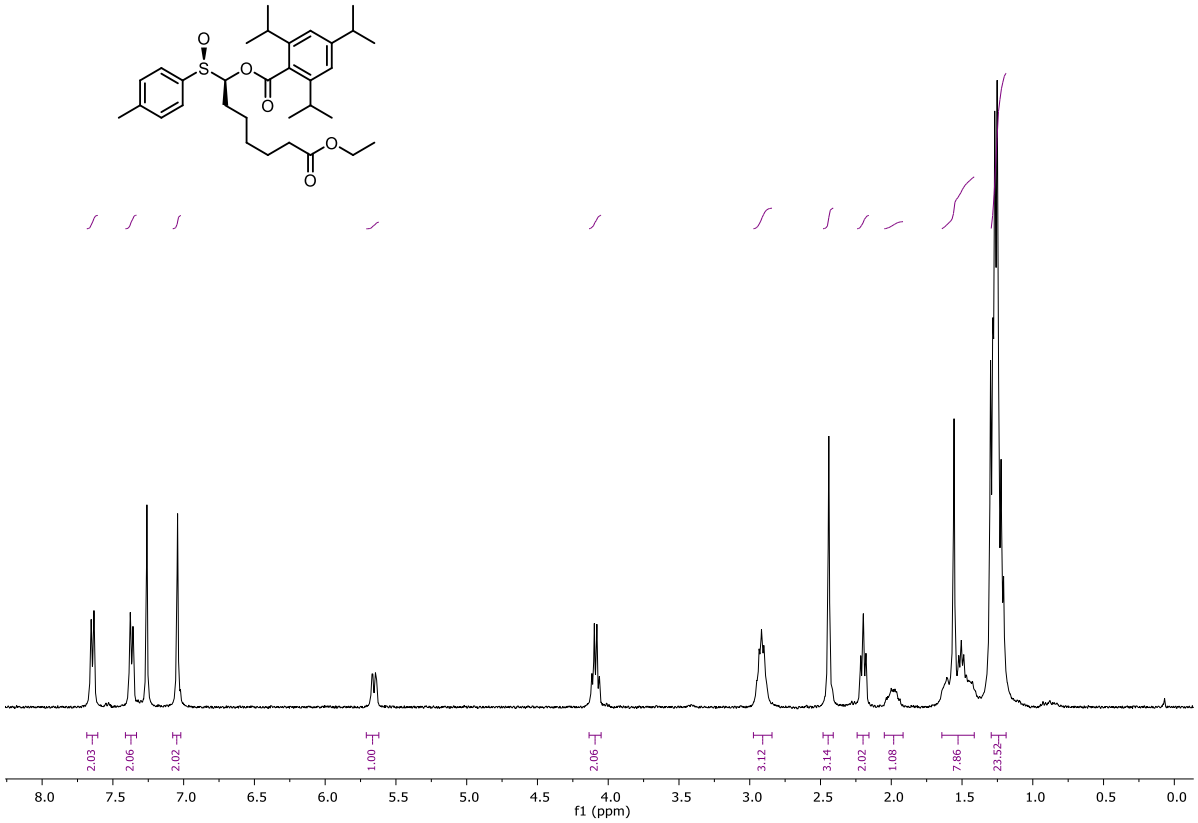
^{1}H NMR of *anti*-**14m** (400 MHz, $CDCl_3$)



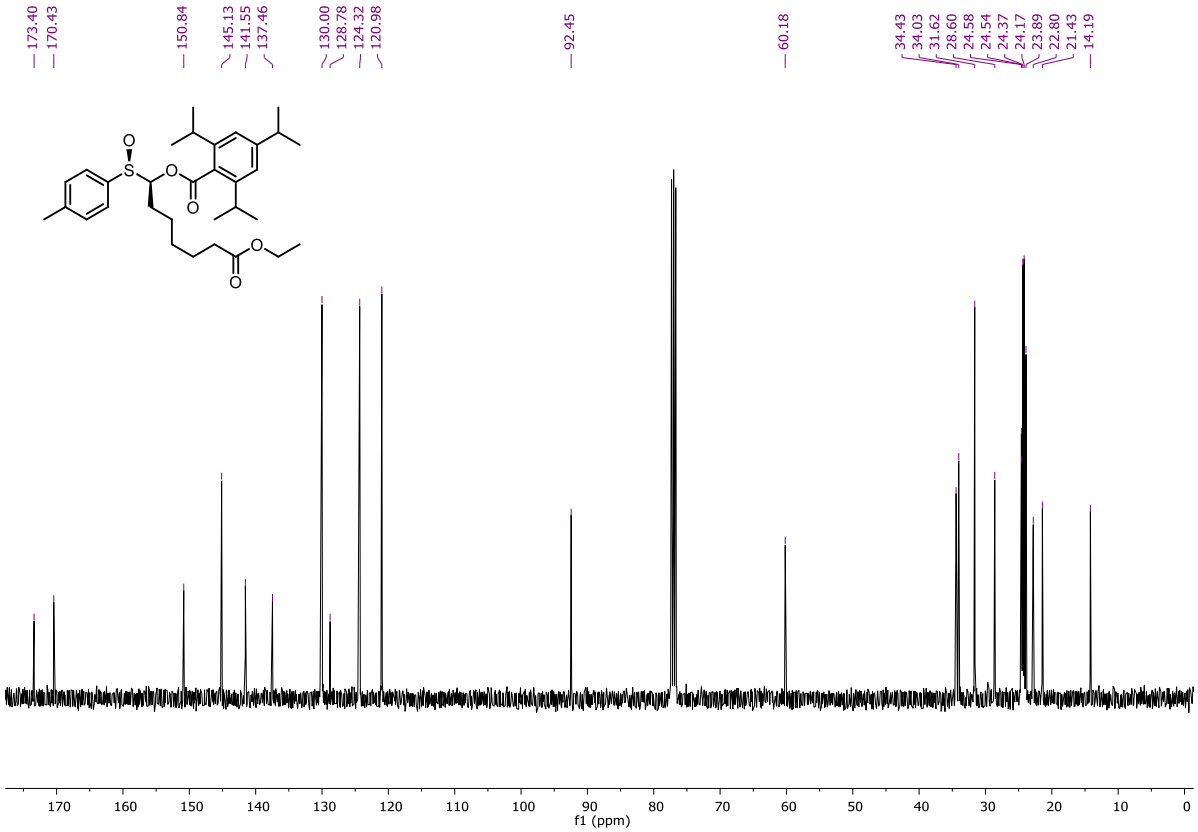
^{13}C NMR of *anti*-**14m** (101 MHz, $CDCl_3$)



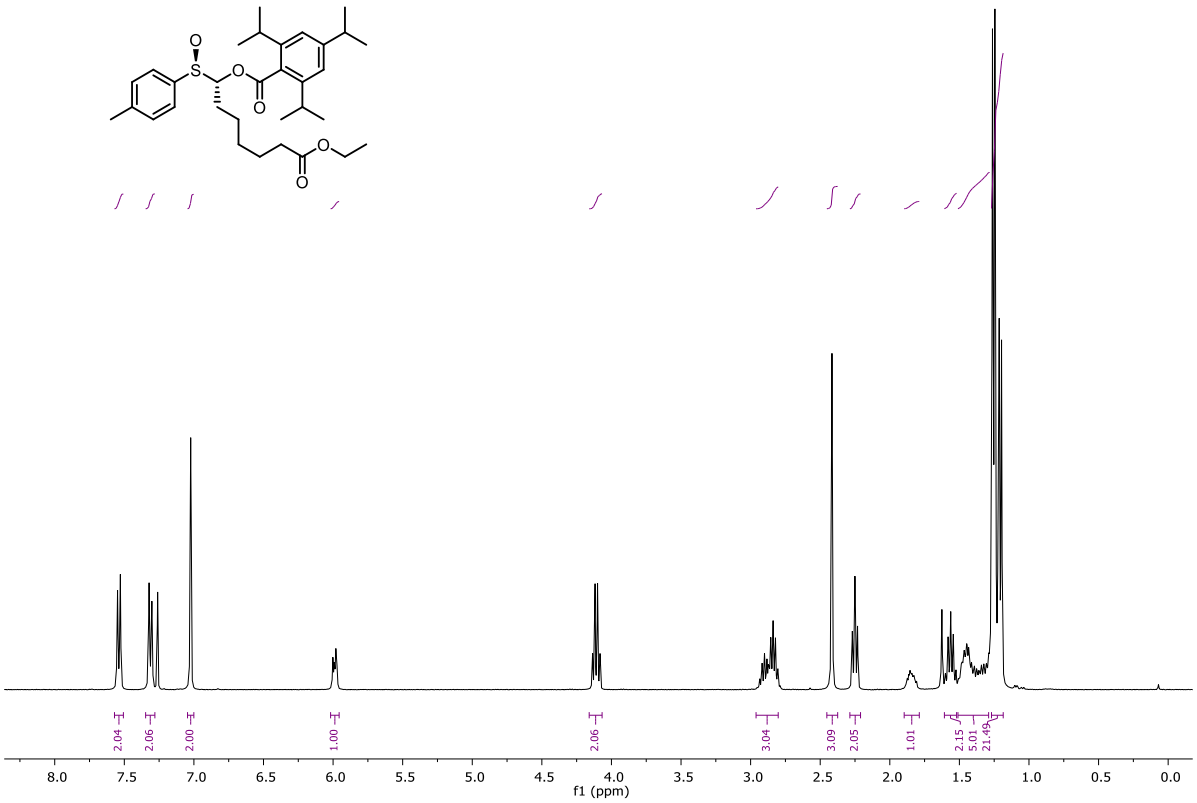
^{1}H NMR of *syn*-**14n** (400 MHz, $CDCl_3$)



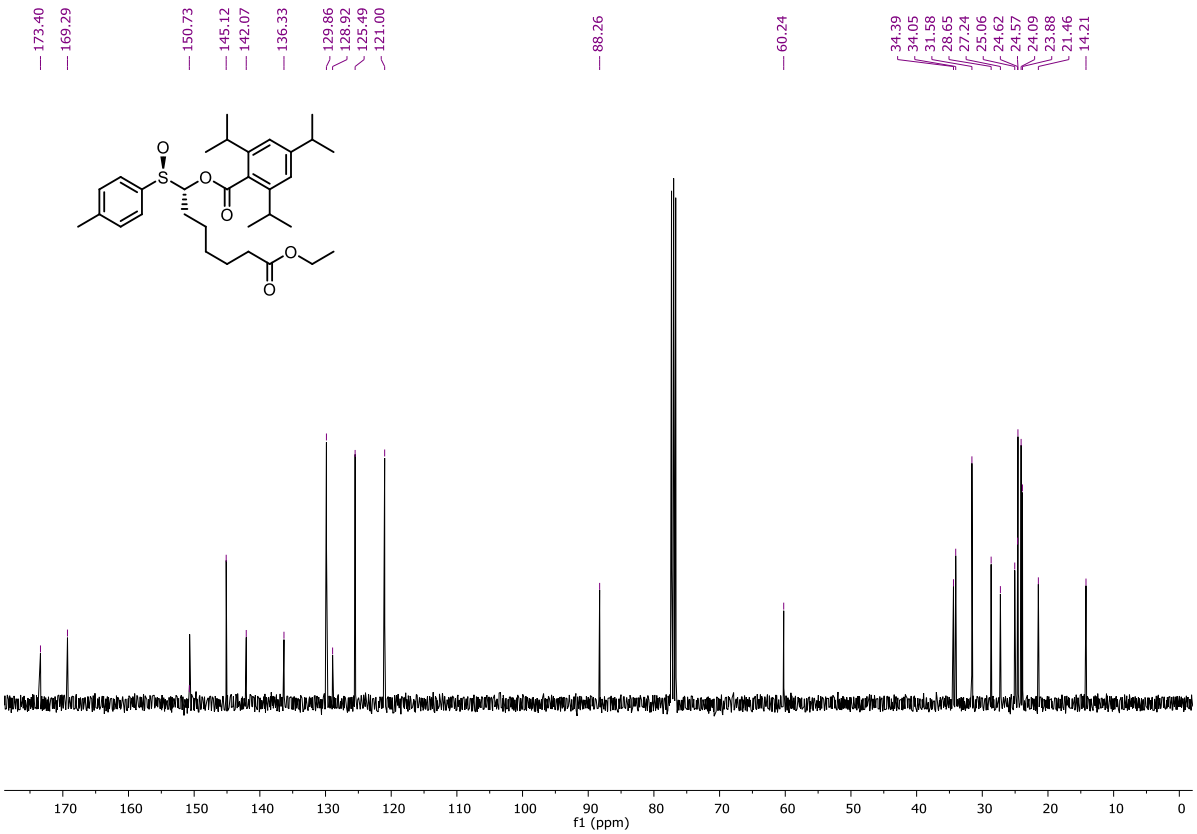
^{13}C NMR of *syn*-**14n** (101 MHz, $CDCl_3$)



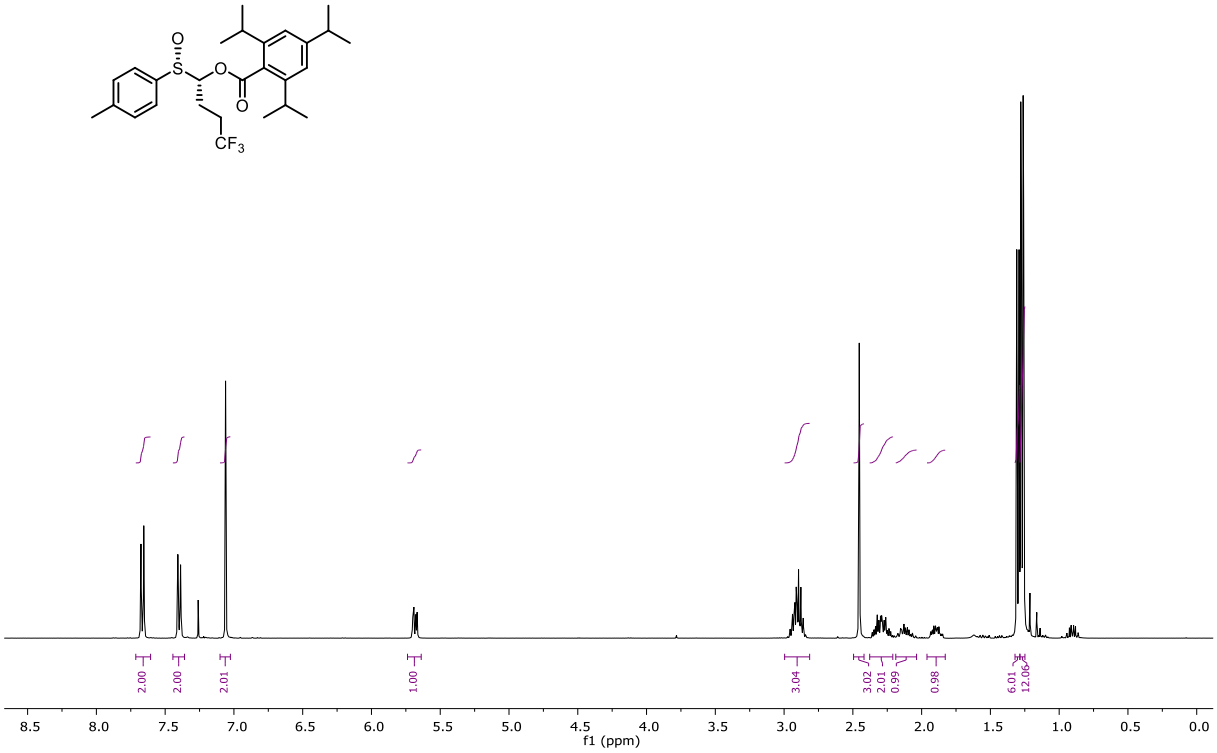
^{1}H NMR of *anti*-**14n** (400 MHz, $CDCl_3$)



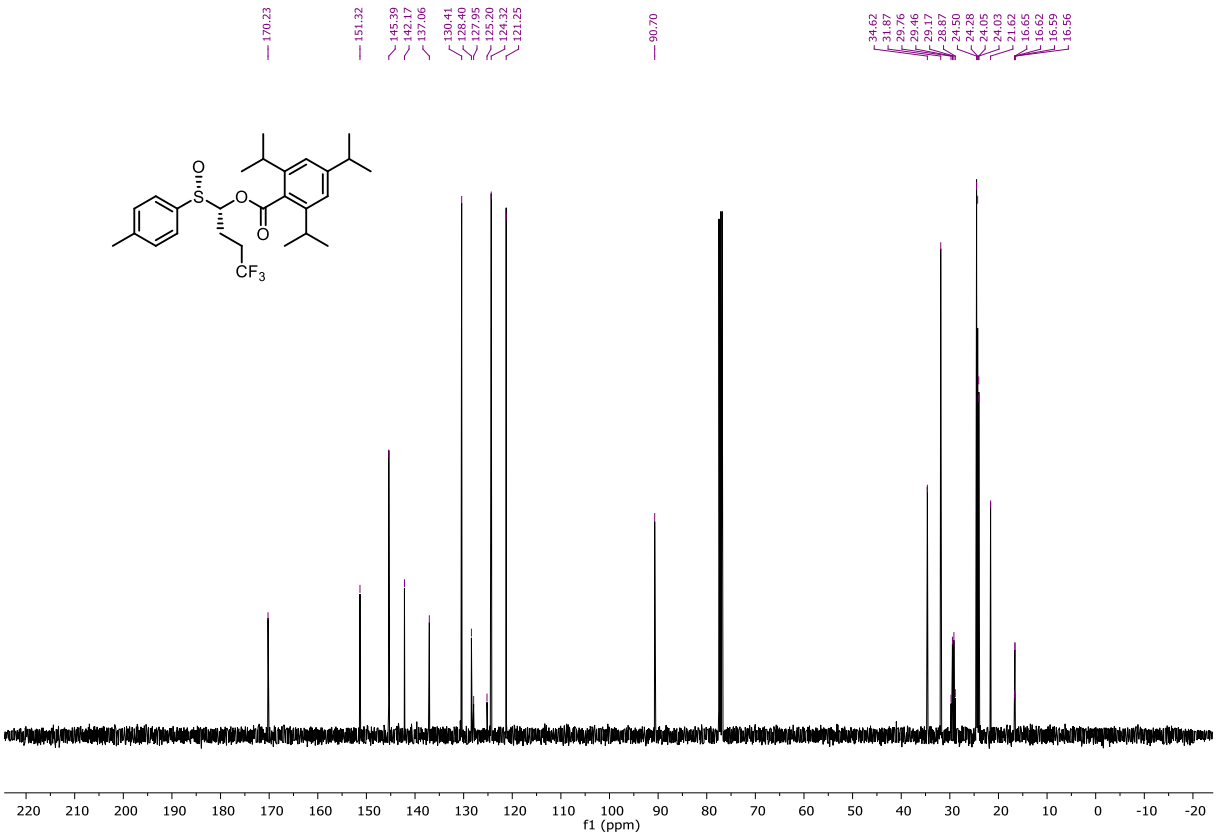
^{13}C NMR of *anti*-**14n** (101 MHz, $CDCl_3$)



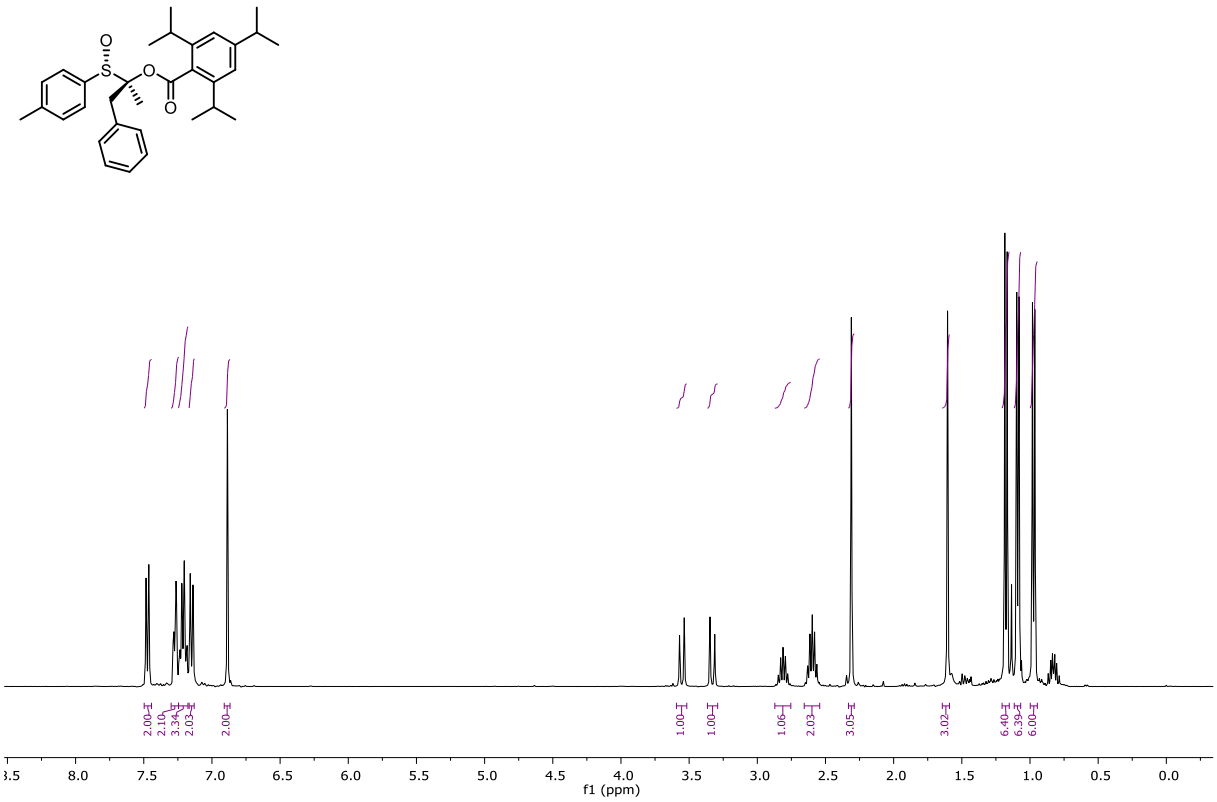
^{1}H NMR of *syn*-**14o** (400 MHz, $CDCl_3$)



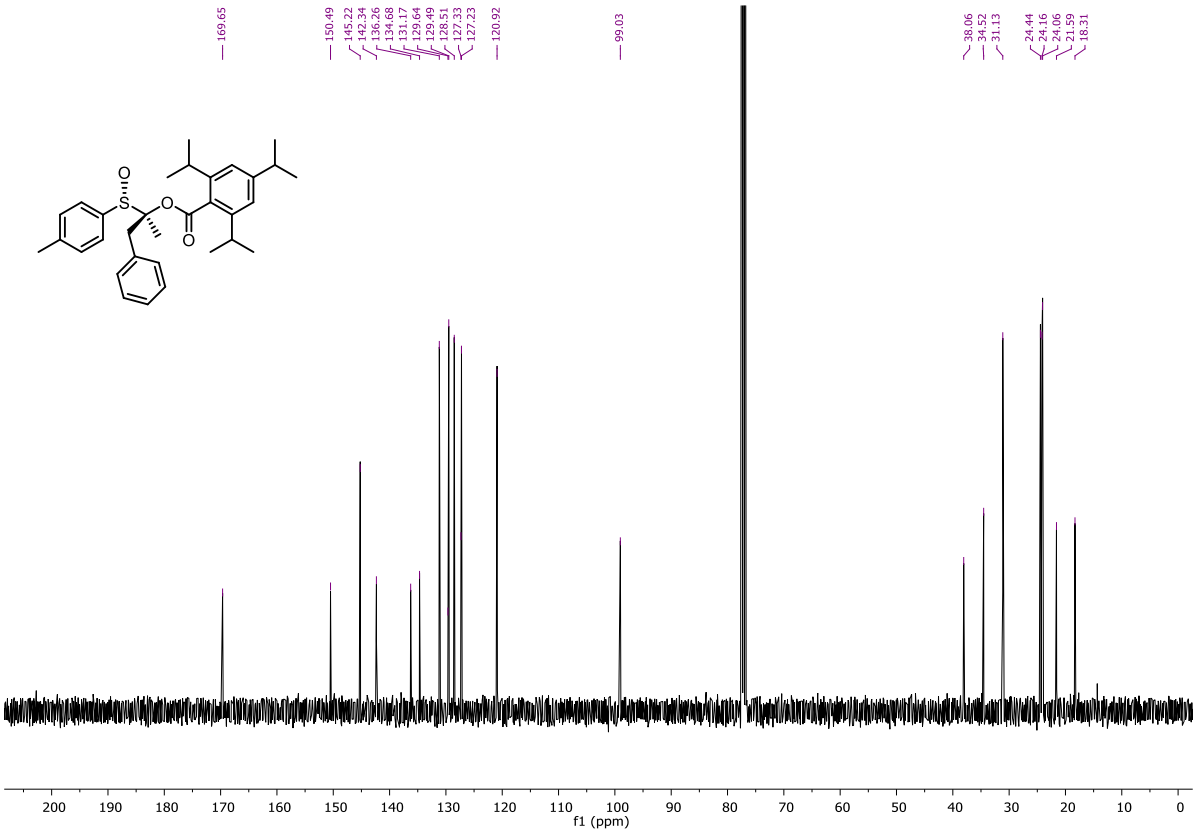
^{13}C NMR of *syn*-**14o** (101 MHz, $CDCl_3$)



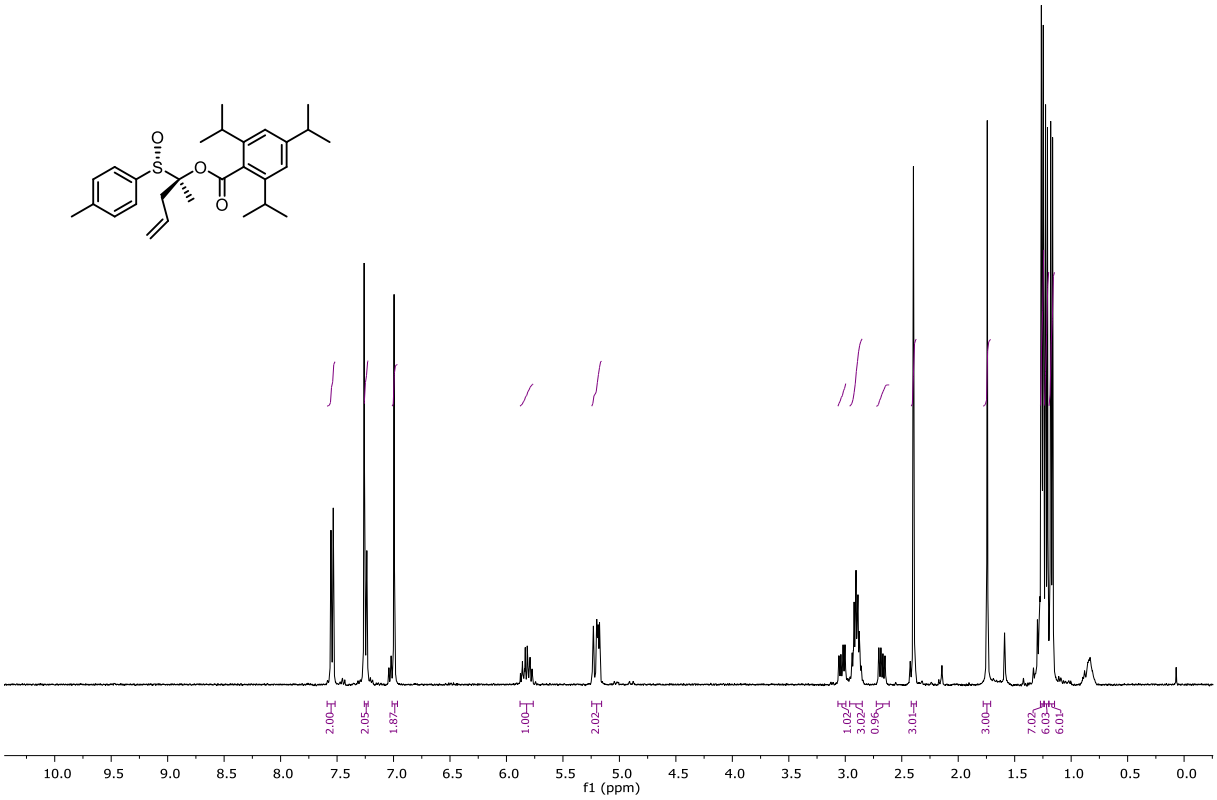
^{1}H NMR of **20a** (400 MHz, $CDCl_3$)



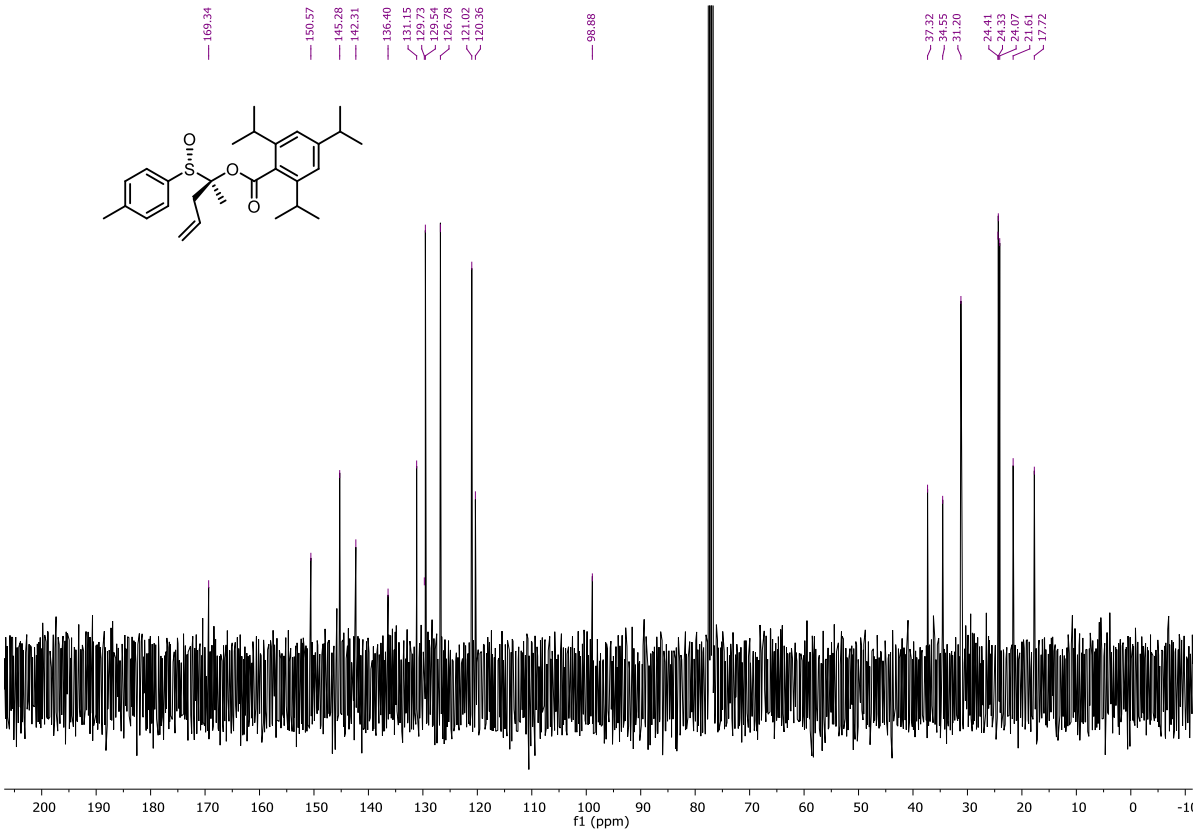
^{13}C NMR of **20a** (101 MHz, $CDCl_3$)



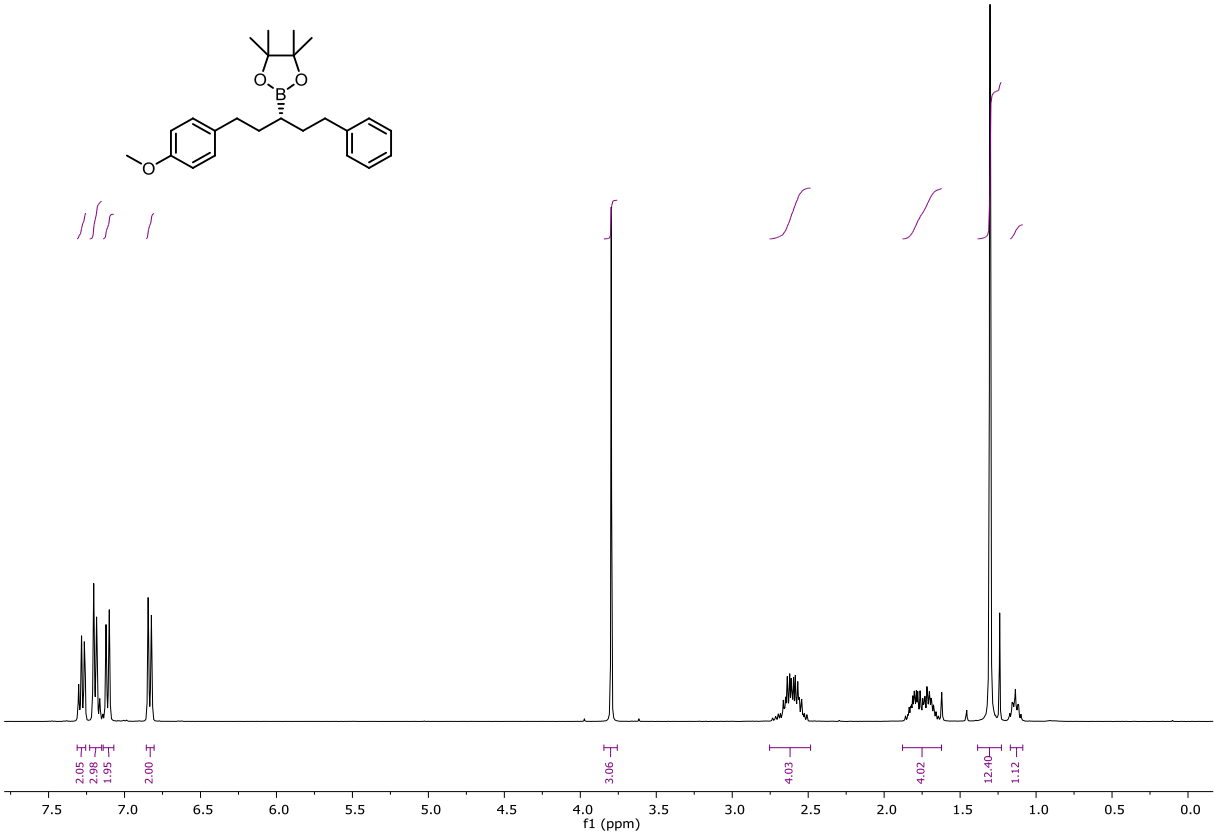
^{1}H NMR of **20b** (400 MHz, $CDCl_3$)



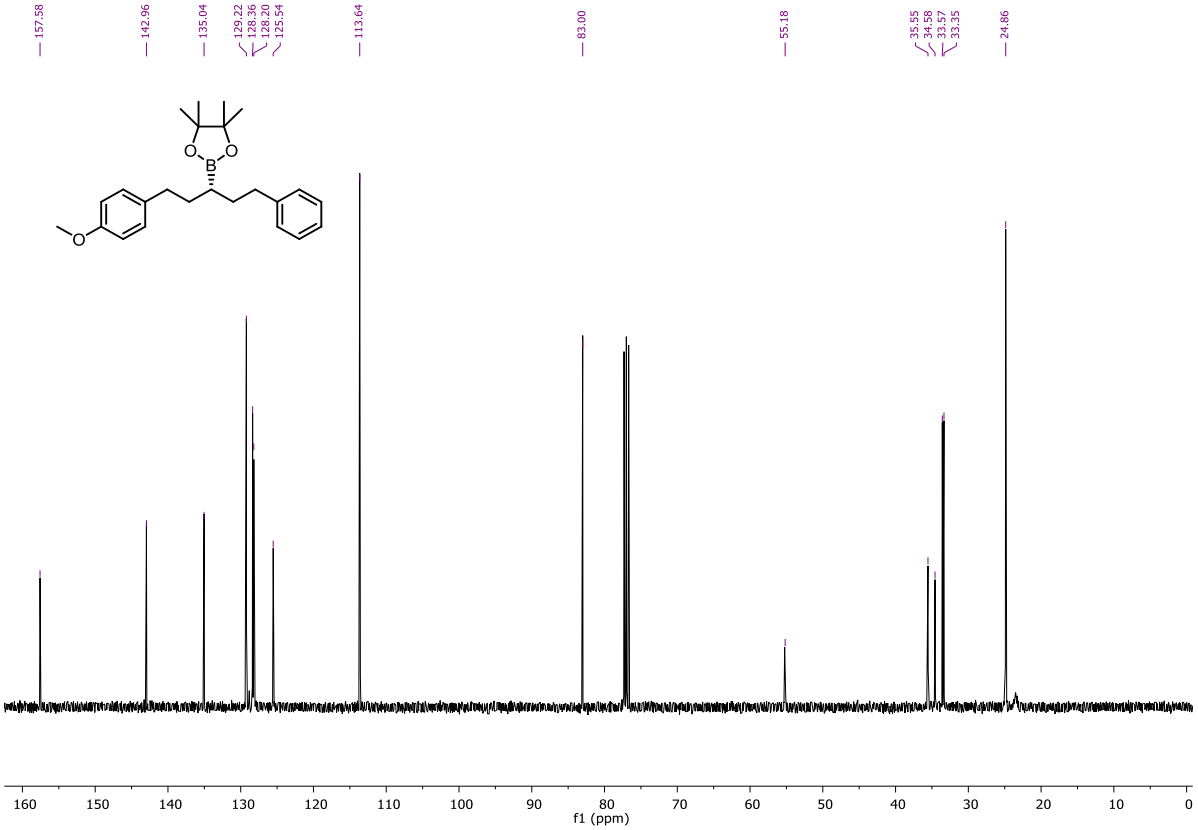
^{13}C NMR of **20b** (101 MHz, $CDCl_3$)



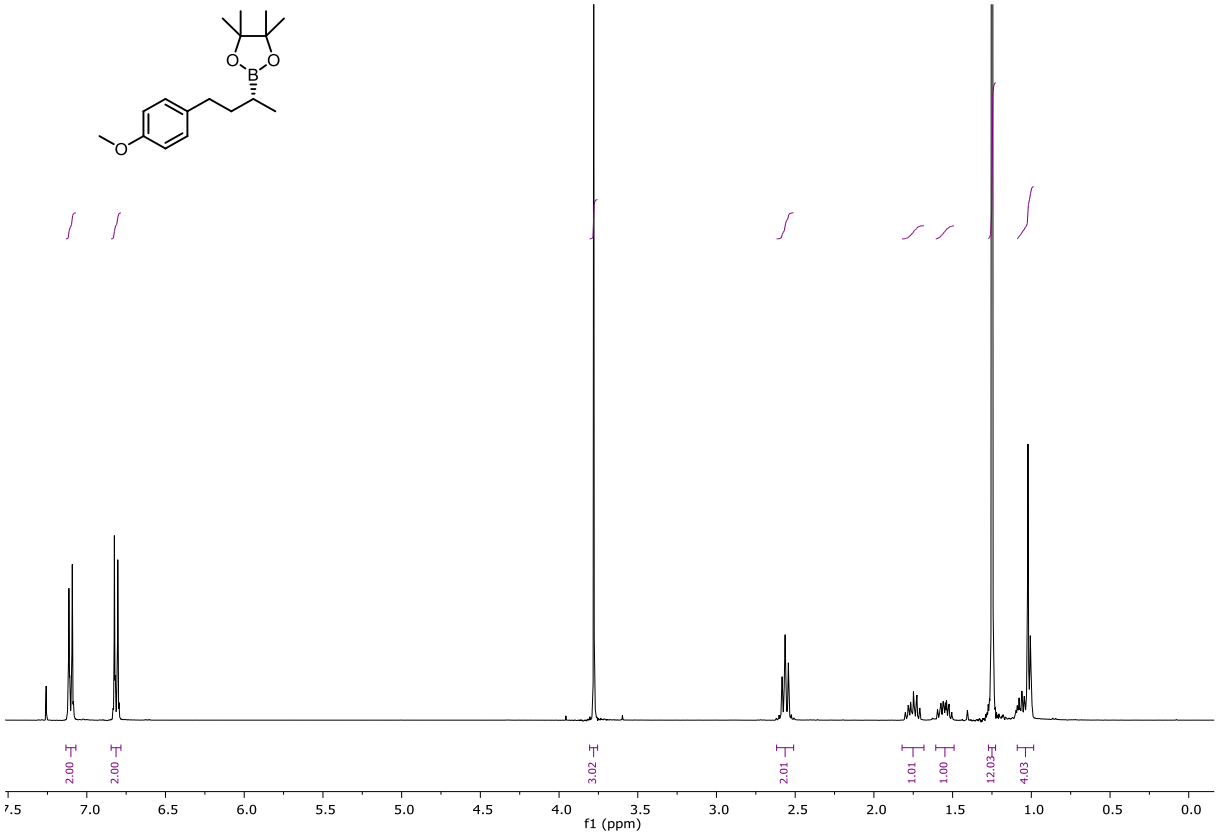
^{1}H NMR of **18a** (400 MHz, $CDCl_3$)



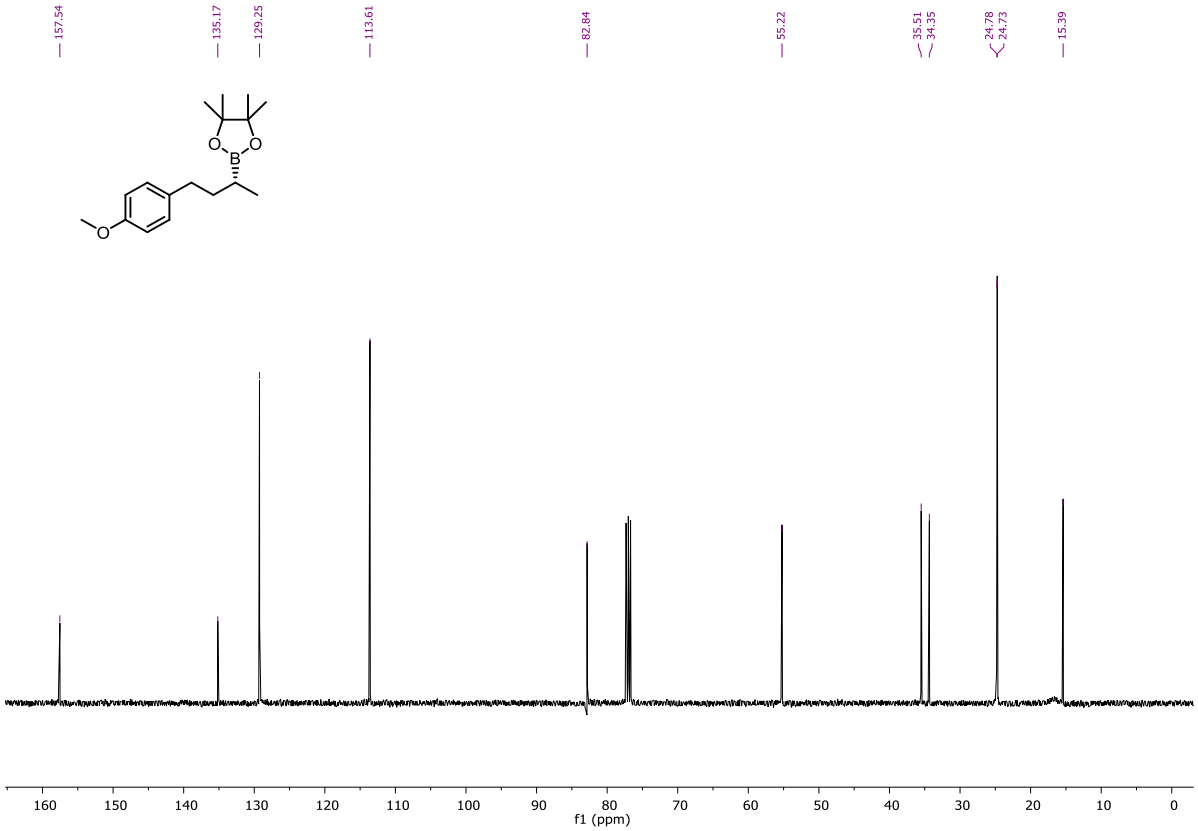
^{13}C NMR of **18a** (101 MHz, $CDCl_3$)



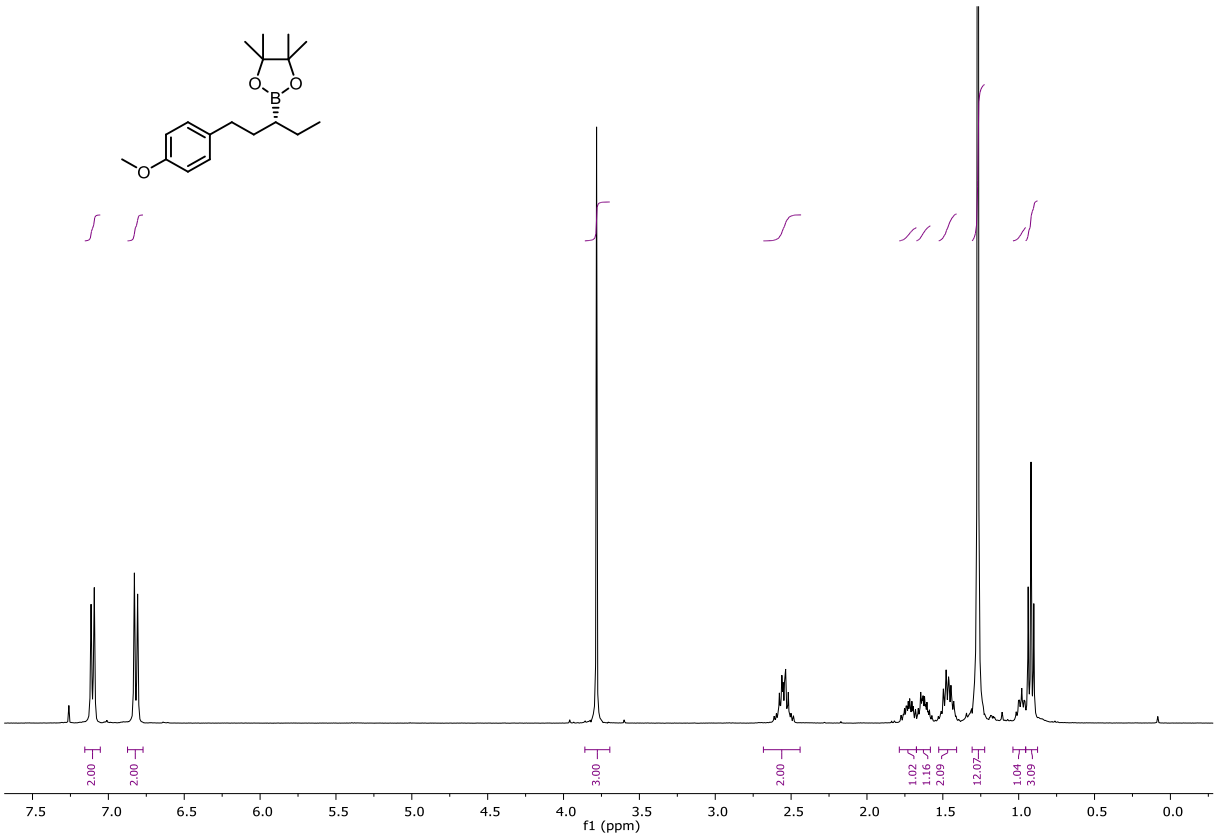
^{1}H NMR of **18b** (400 MHz, $CDCl_3$)



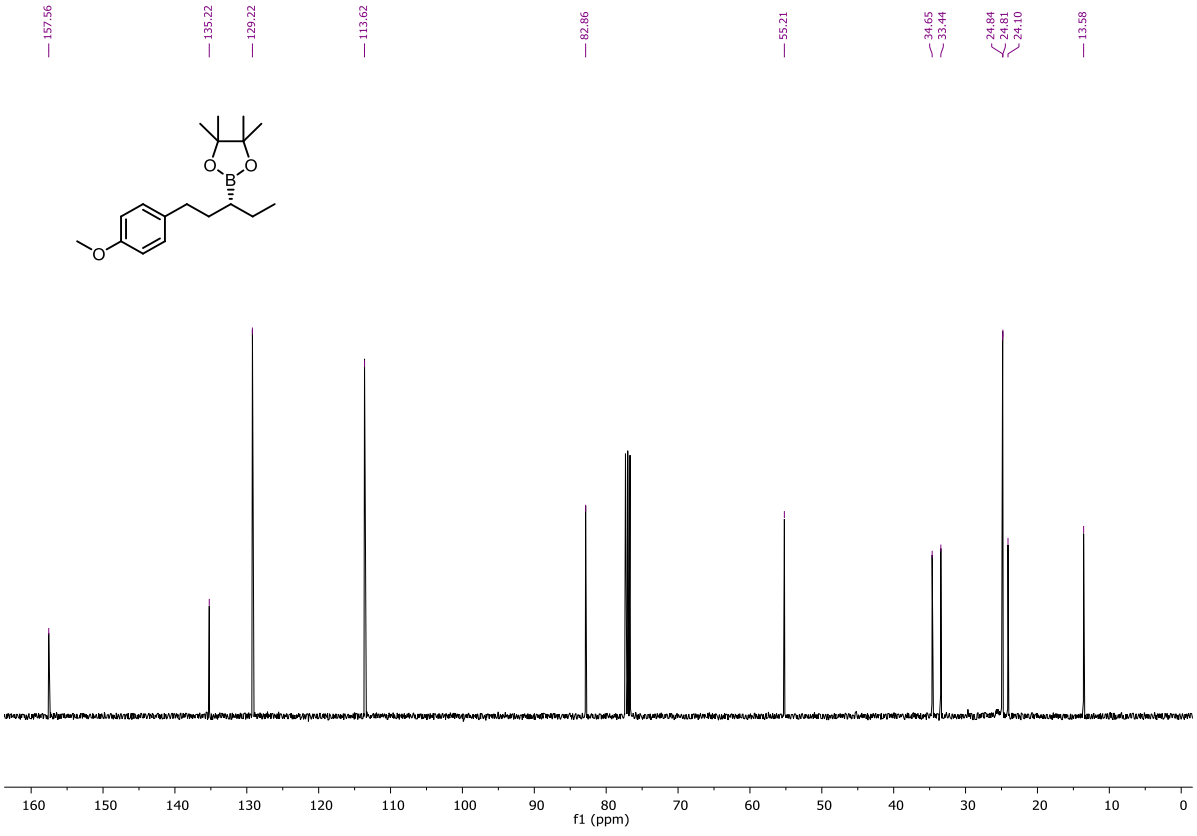
^{13}C NMR of **18b** (101 MHz, $CDCl_3$)



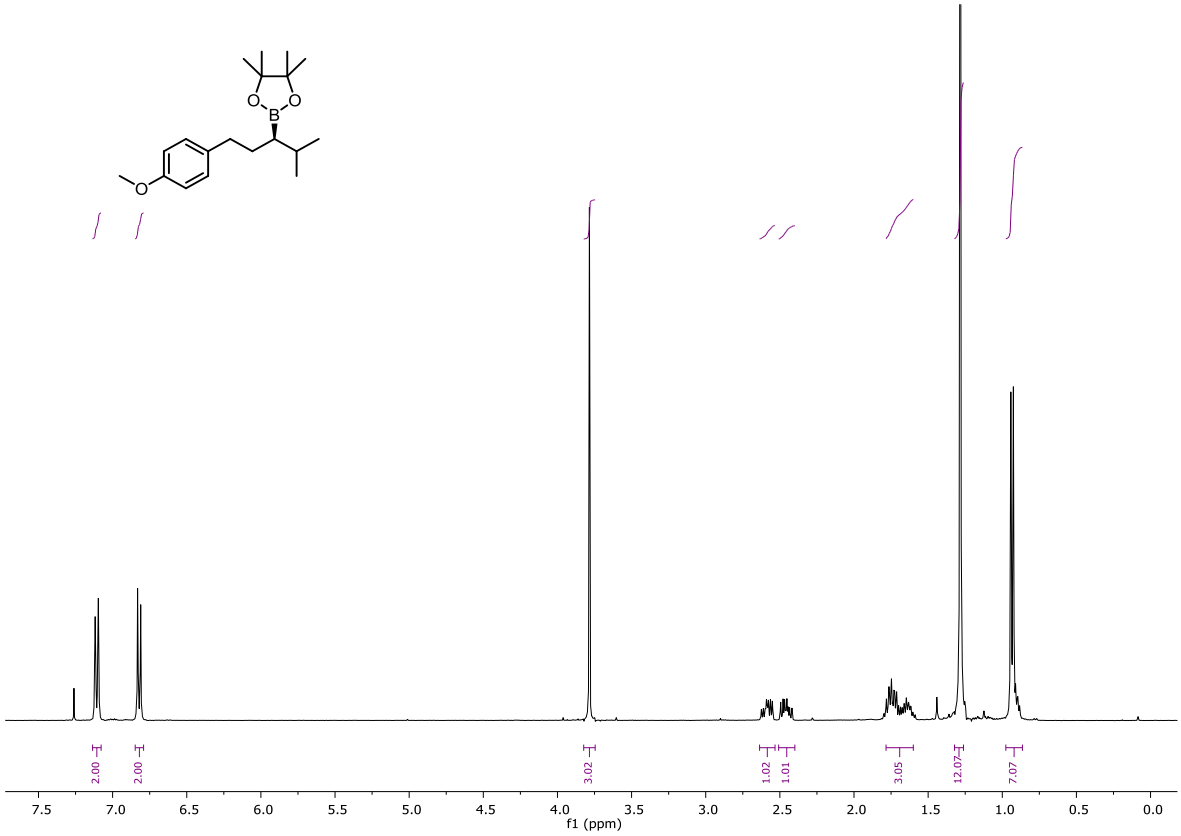
^{1}H NMR of **18c** (400 MHz, $CDCl_3$)



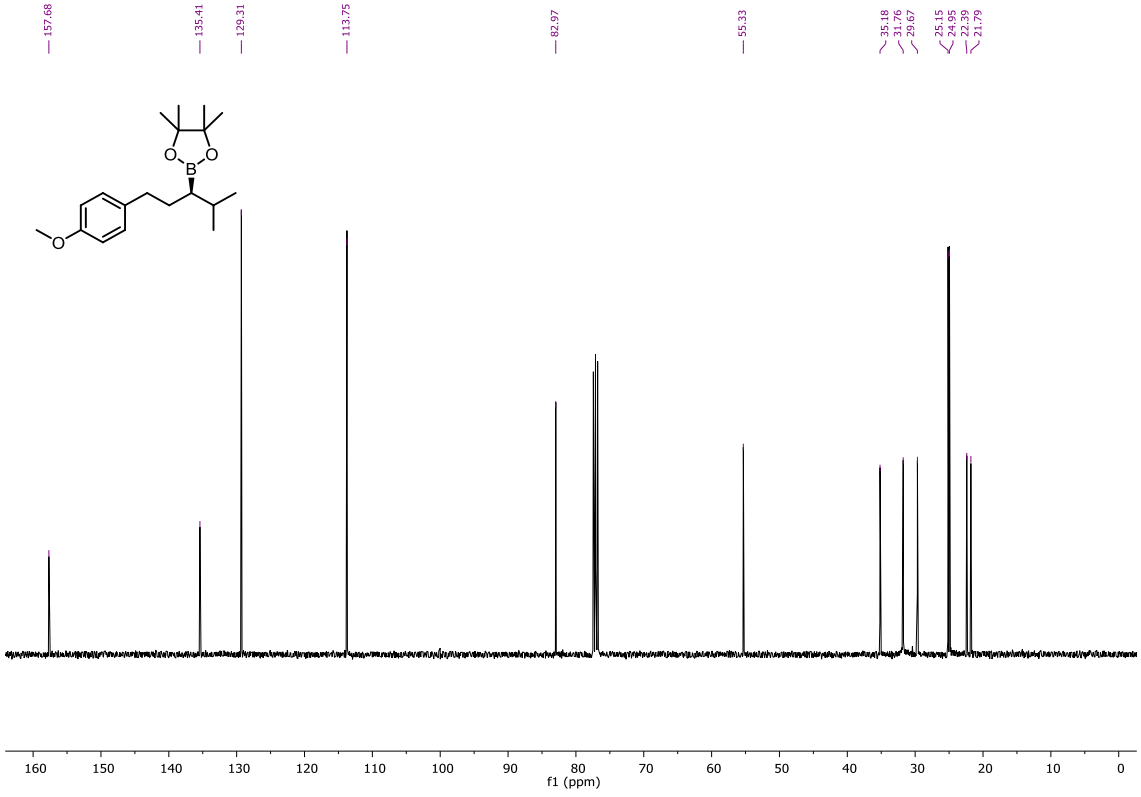
^{13}C NMR of **18c** (101 MHz, $CDCl_3$)



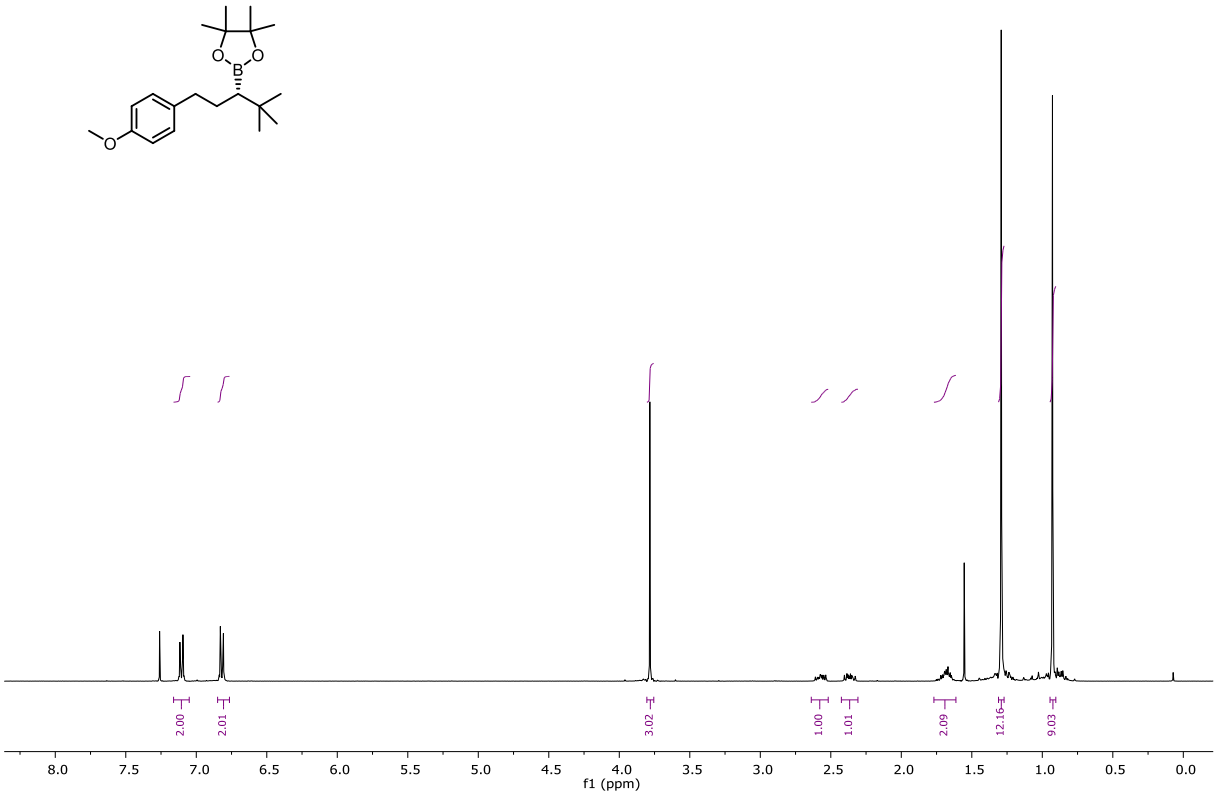
^{1}H NMR of **18d** (400 MHz, $CDCl_3$)



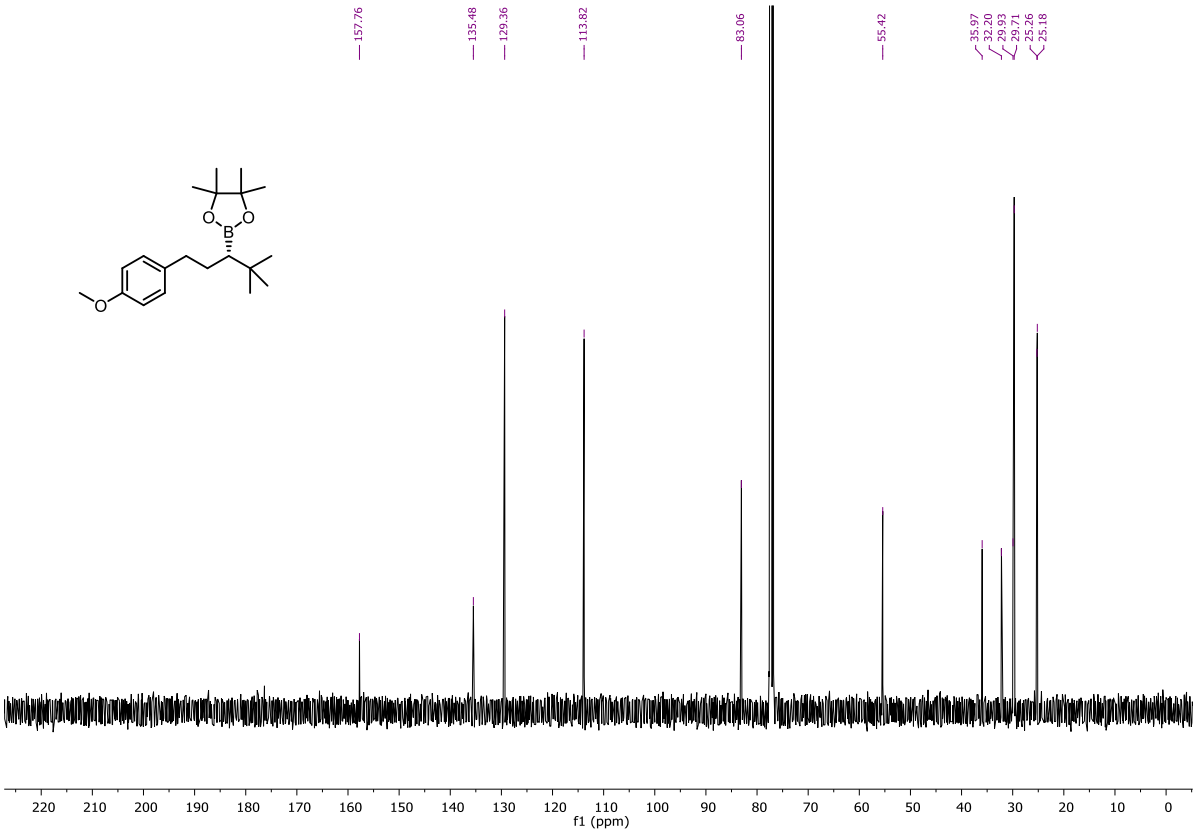
^{13}C NMR of **18d** (101 MHz, $CDCl_3$)



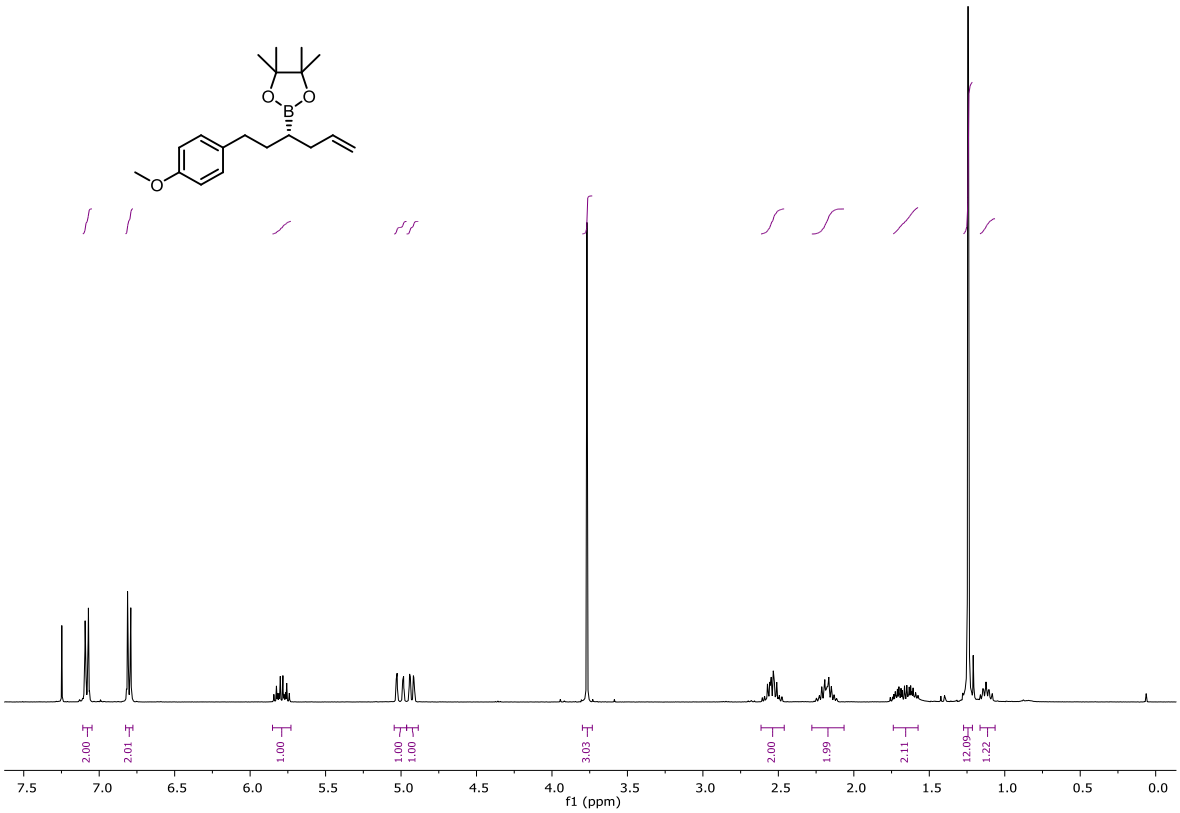
^{1}H NMR of **18e** (400 MHz, $CDCl_3$)



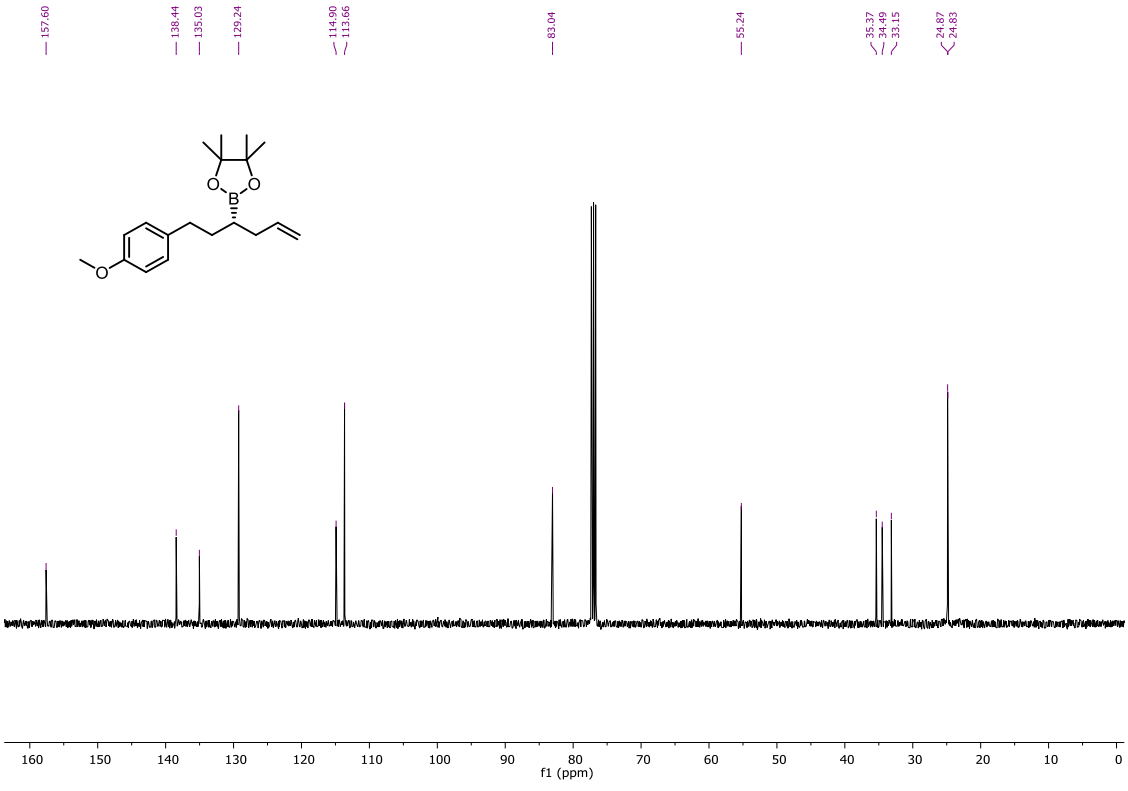
^{13}C NMR of **18e** (101 MHz, $CDCl_3$)



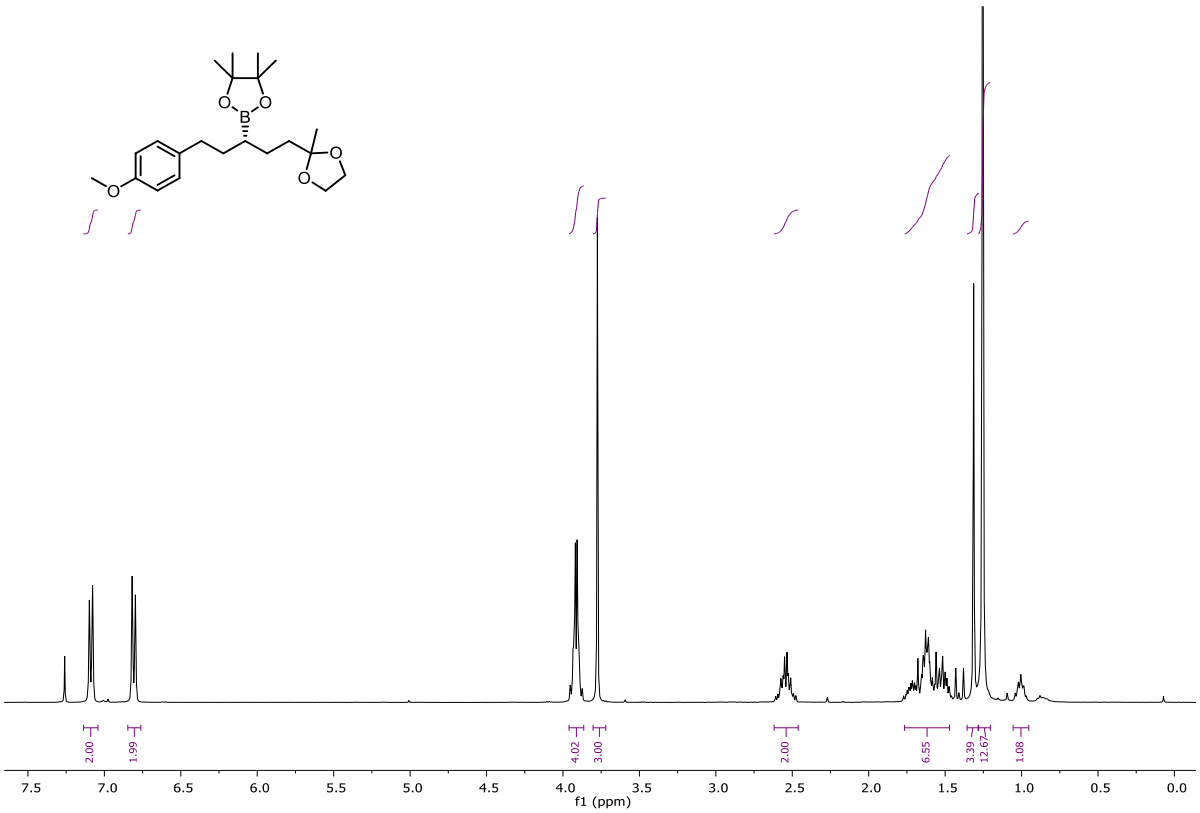
^{1}H NMR of **18f** (400 MHz, $CDCl_3$)



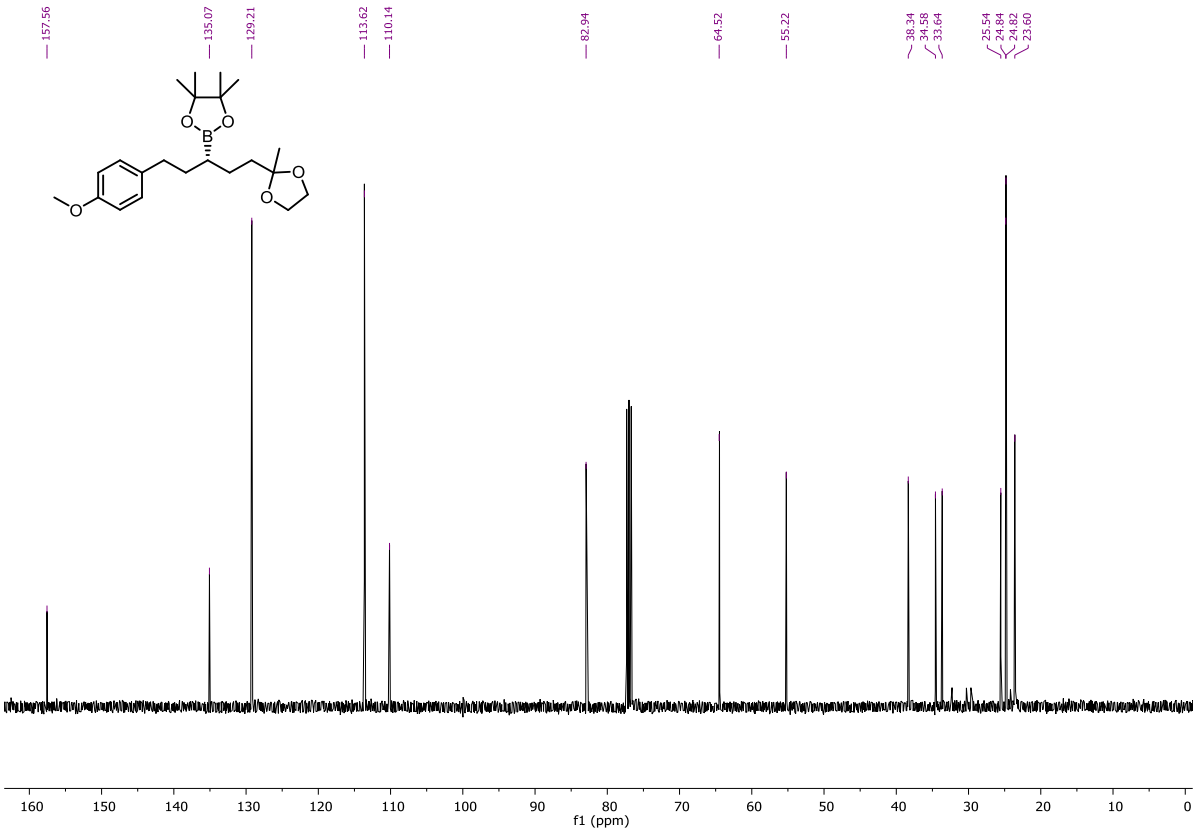
^{13}C NMR of **18f** (101 MHz, $CDCl_3$)



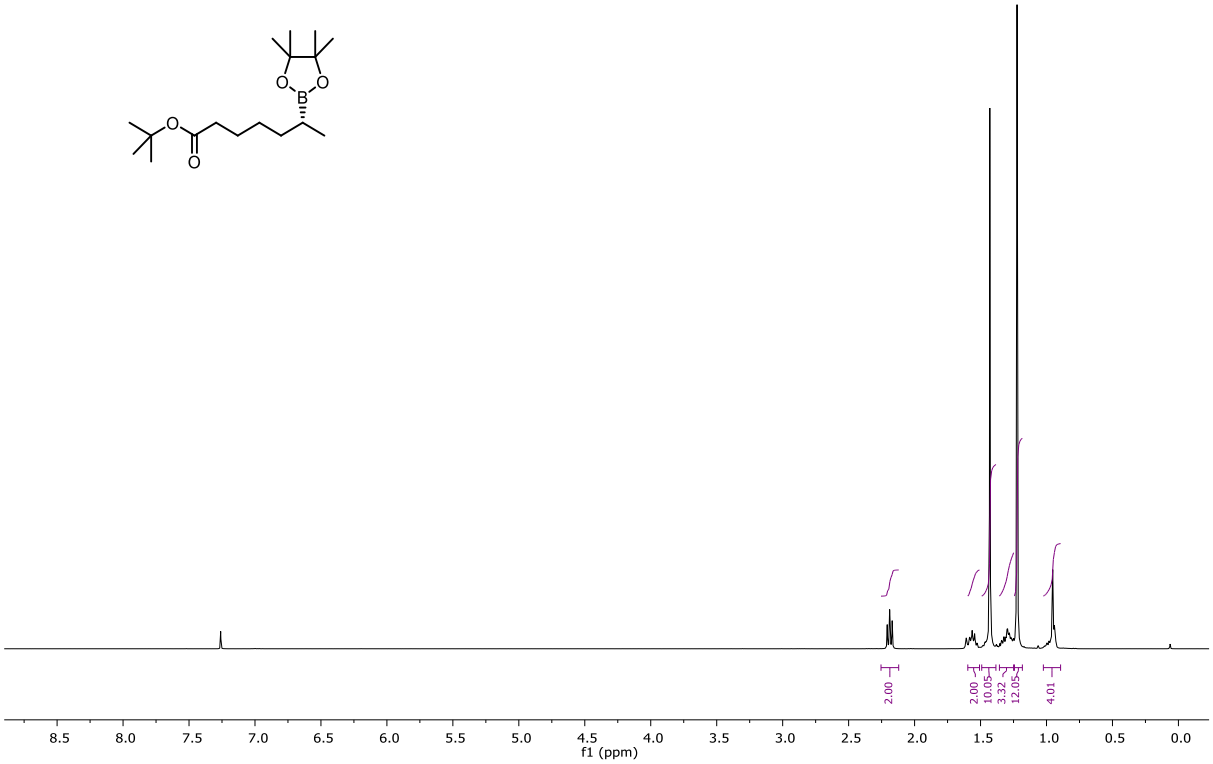
^{1}H NMR of **18g** (400 MHz, $CDCl_3$)



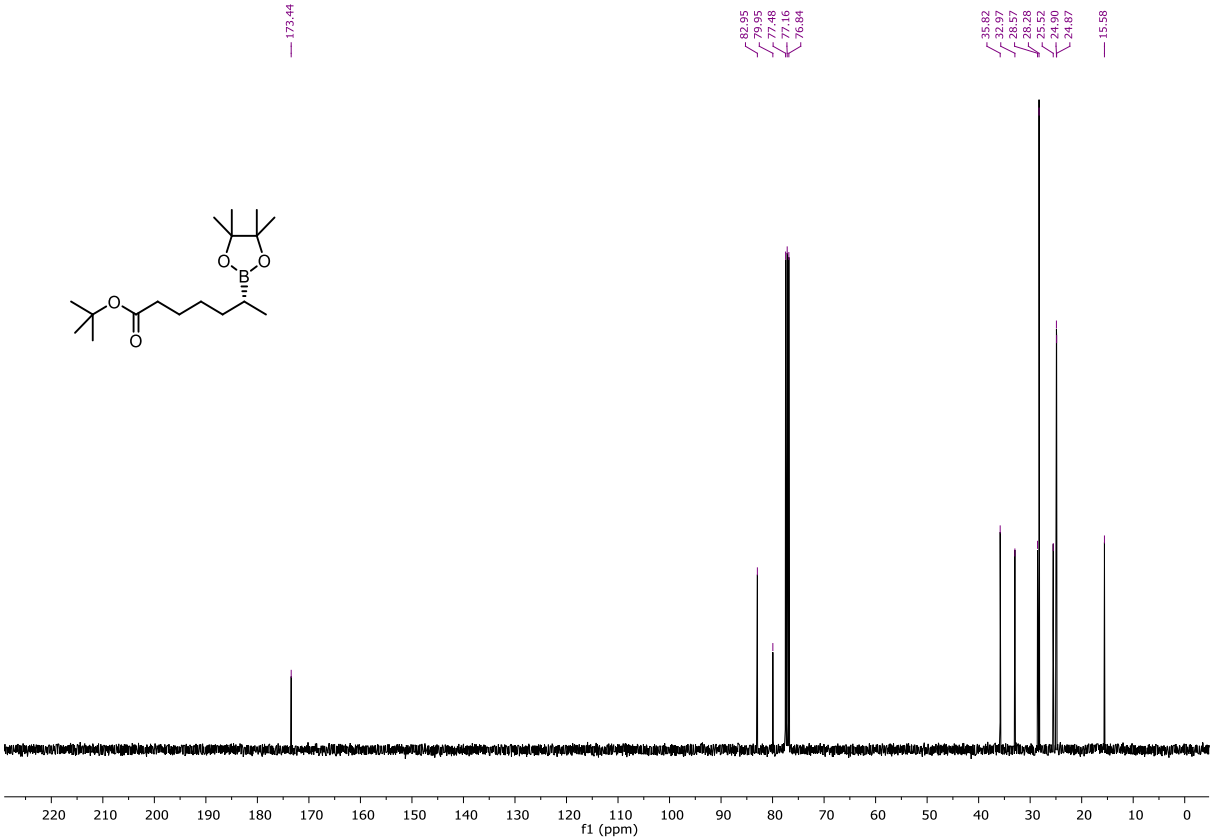
^{13}C NMR of **18g** (101 MHz, $CDCl_3$)



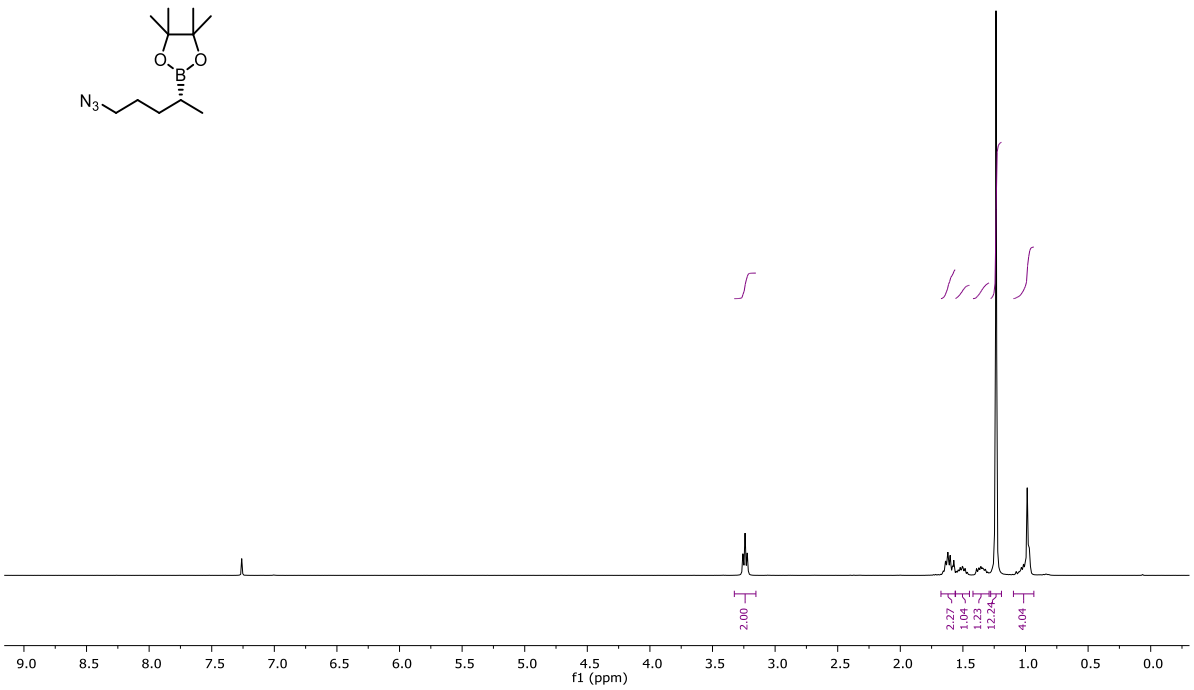
^{1}H NMR of **18h** (400 MHz, $CDCl_3$)



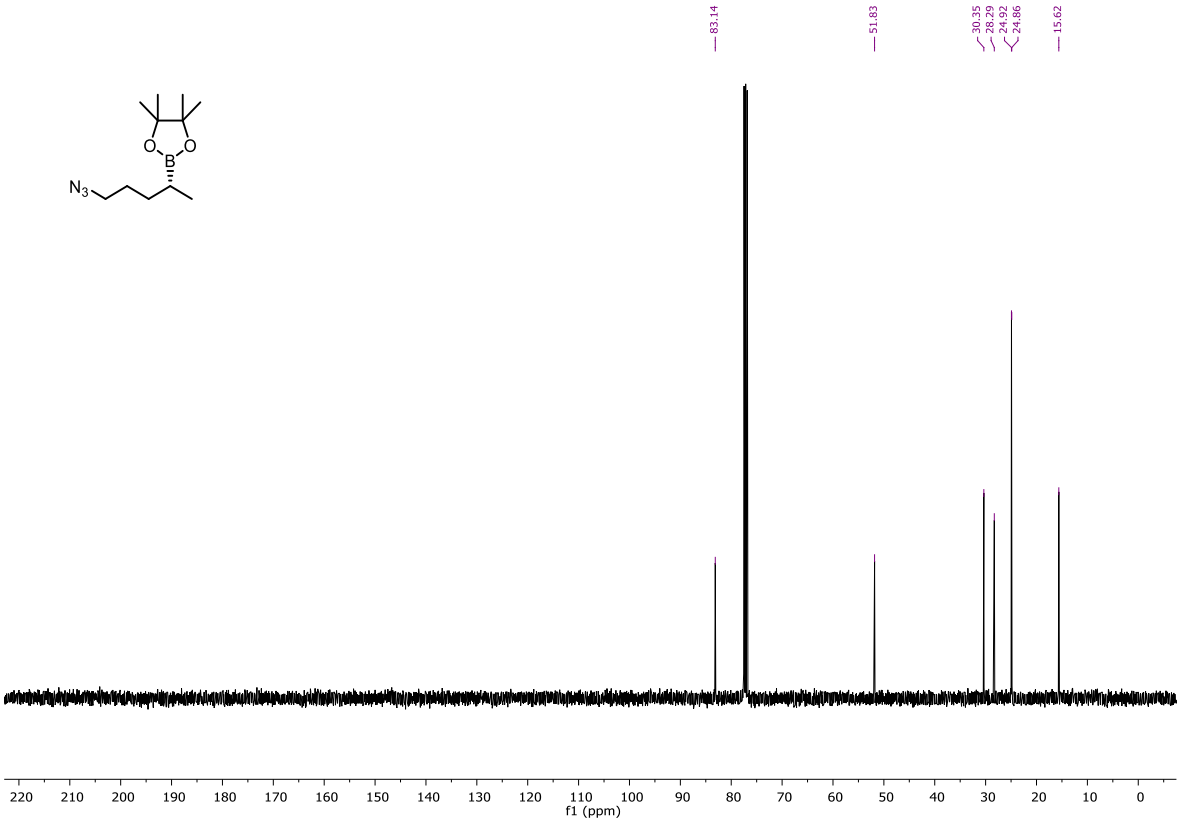
^{13}C NMR of **18h** (101 MHz, $CDCl_3$)



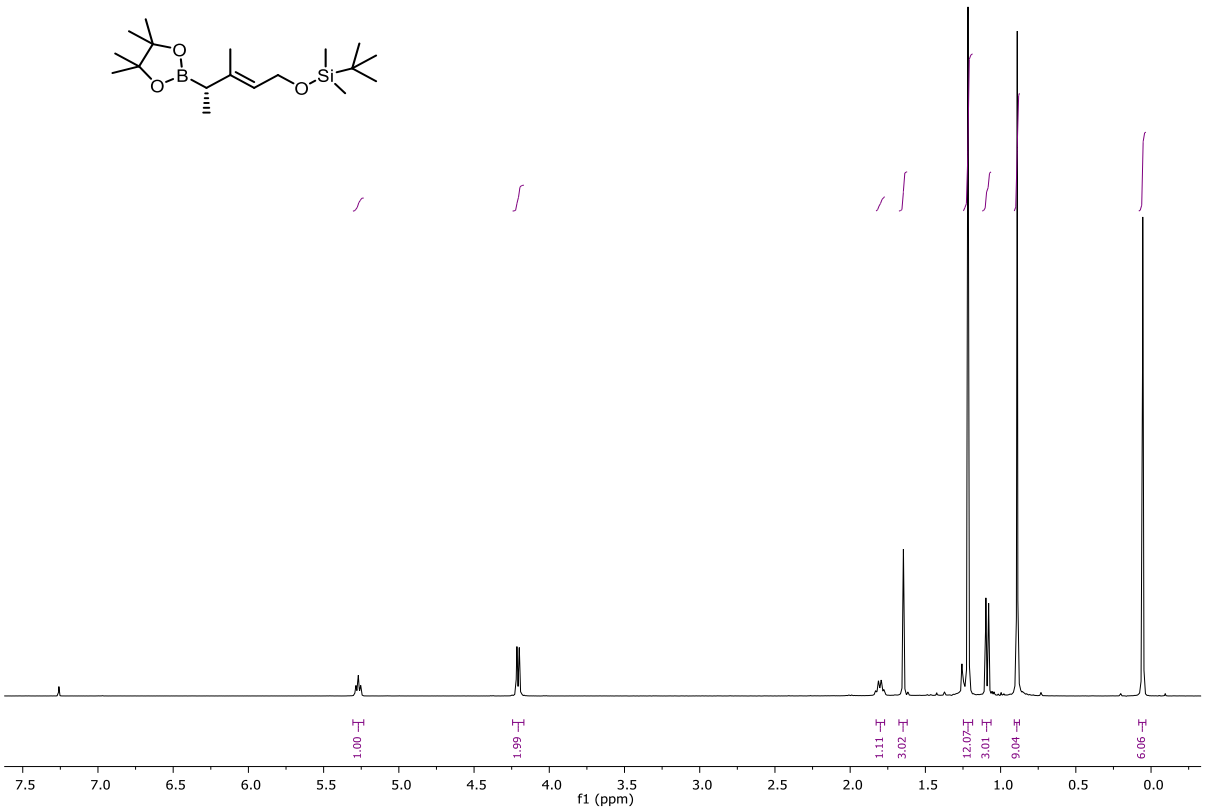
^{1}H NMR of **18i** (400 MHz, $CDCl_3$)



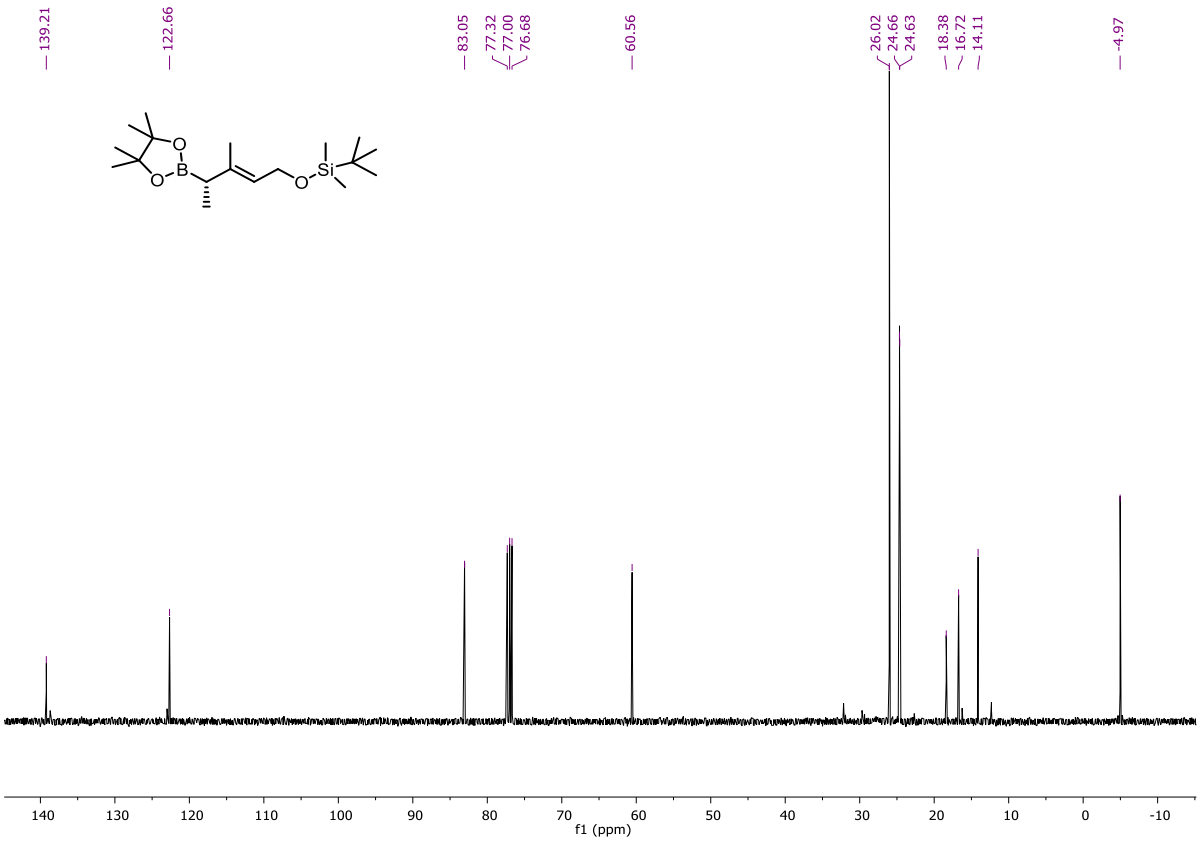
^{13}C NMR of **18i** (101 MHz, $CDCl_3$)



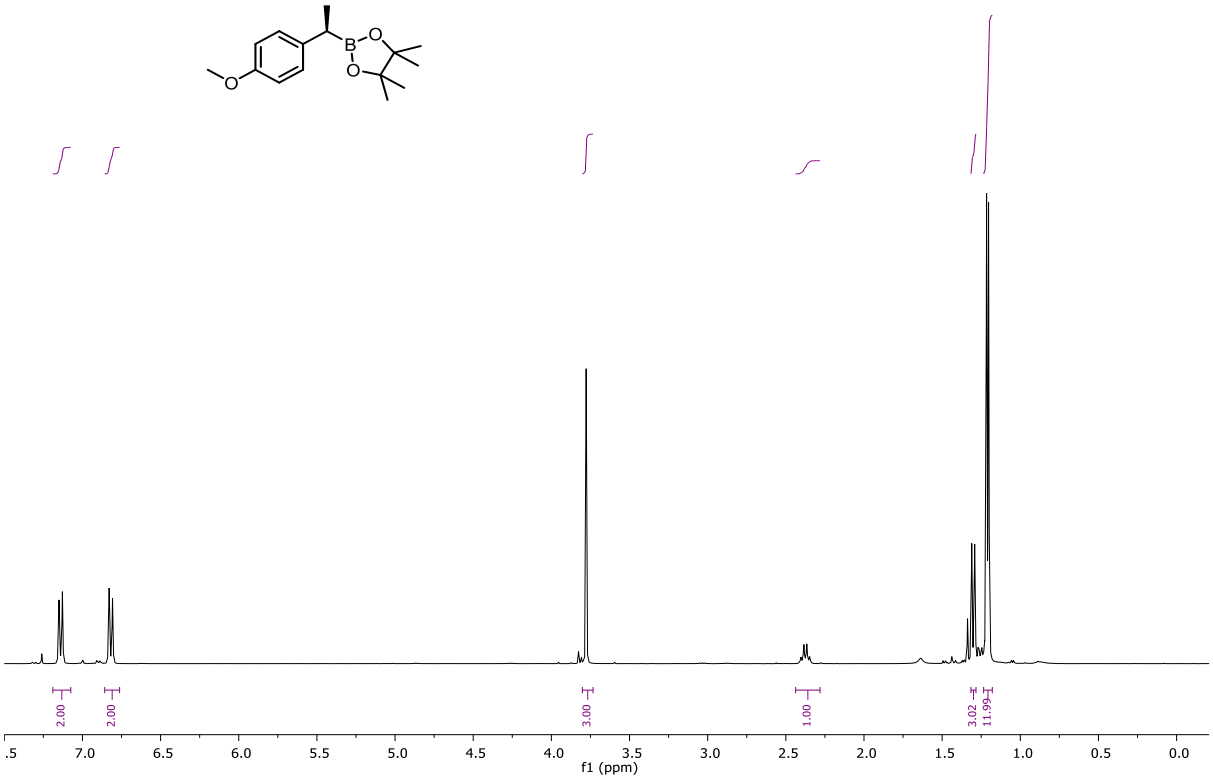
^{1}H NMR of **18j** (400 MHz, $CDCl_3$)



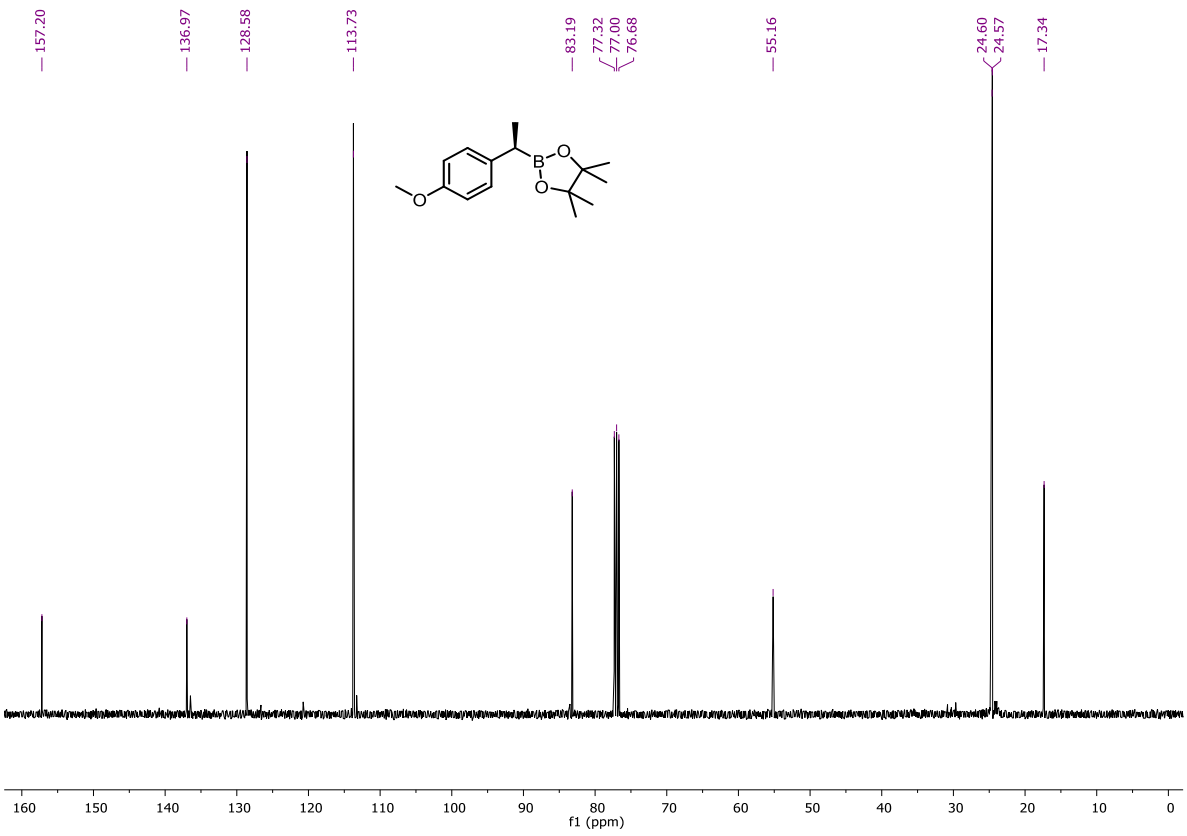
^{13}C NMR of **18j** (101 MHz, $CDCl_3$)



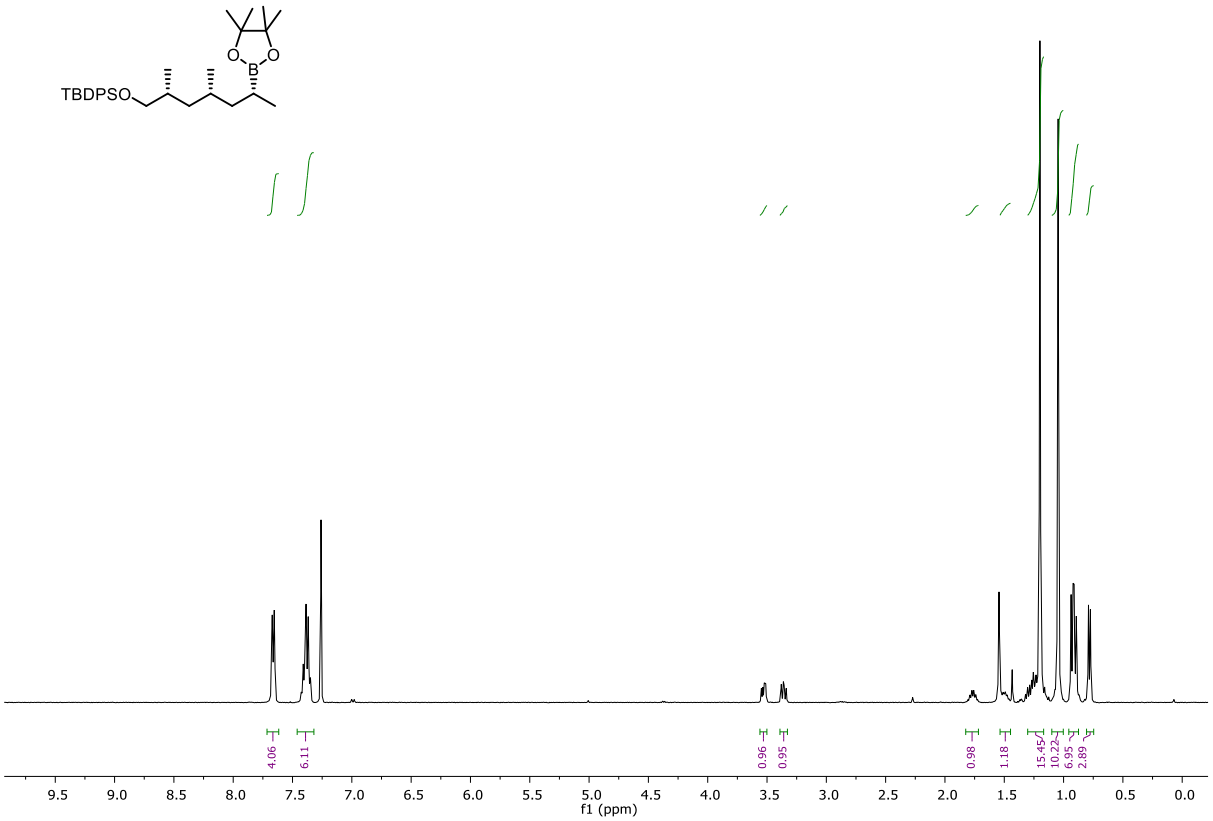
^{1}H NMR of **18k** (400 MHz, $CDCl_3$)



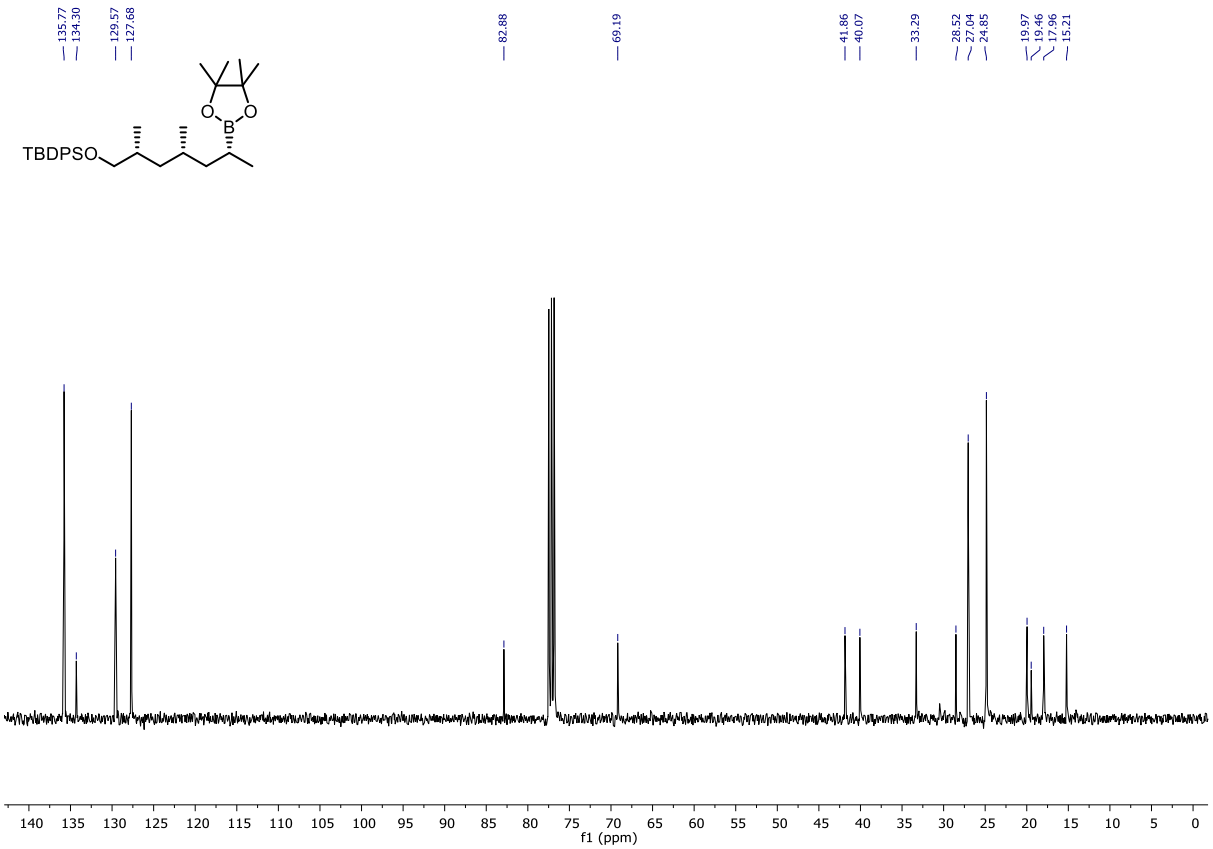
^{13}C NMR of **18k** (101 MHz, $CDCl_3$)



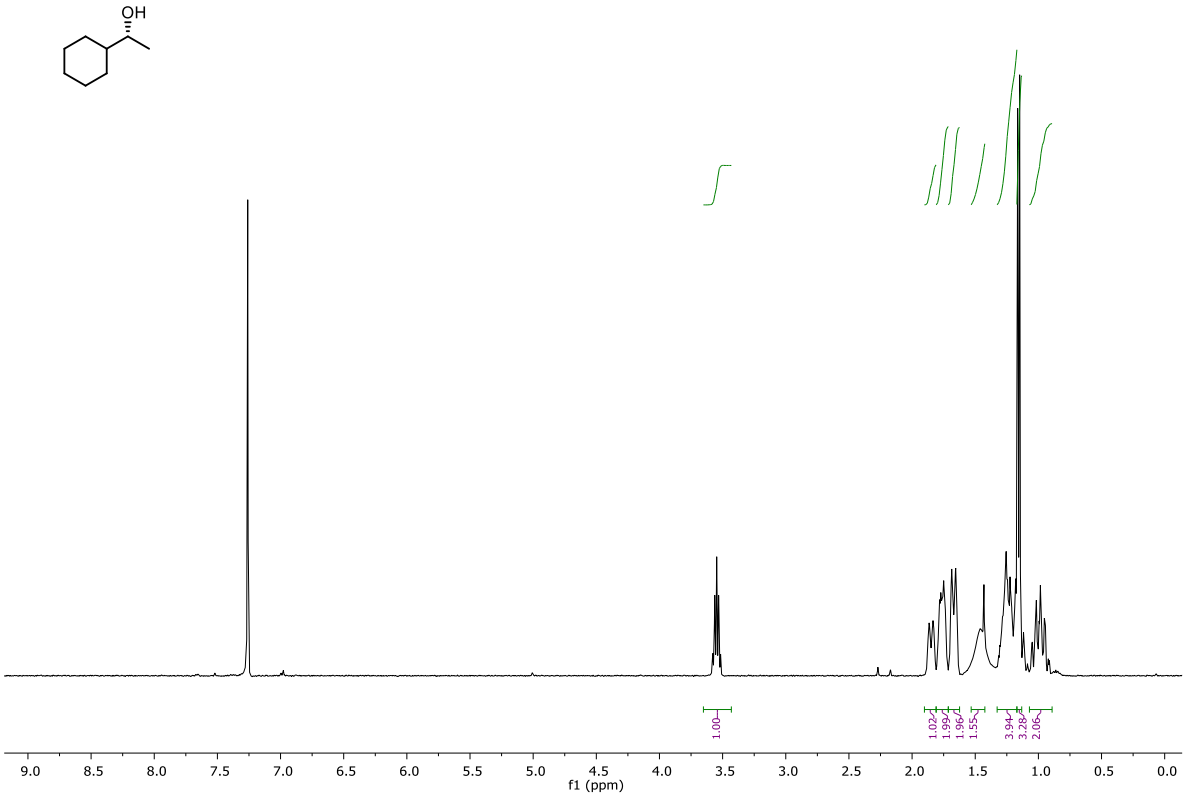
^{1}H NMR of **18l** (400 MHz, $CDCl_3$)



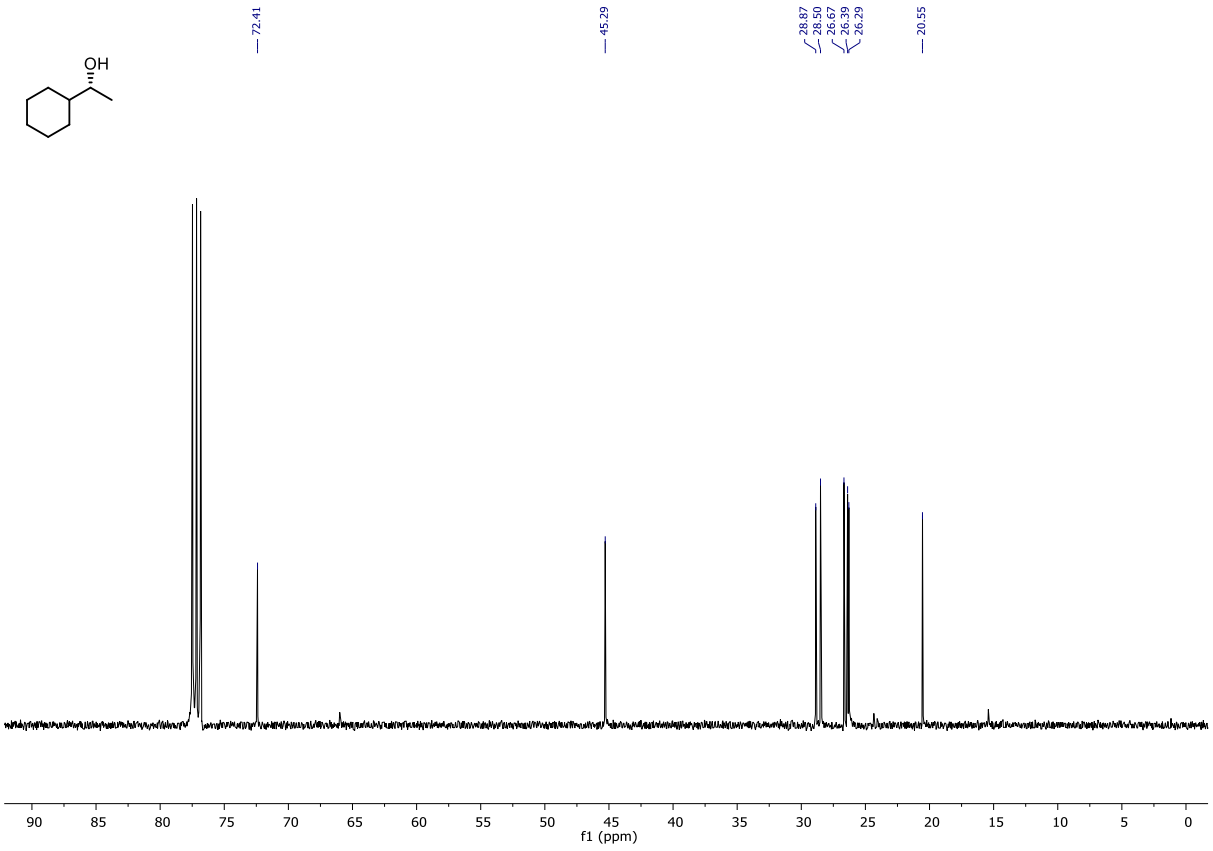
^{13}C NMR of **18l** (101 MHz, $CDCl_3$)



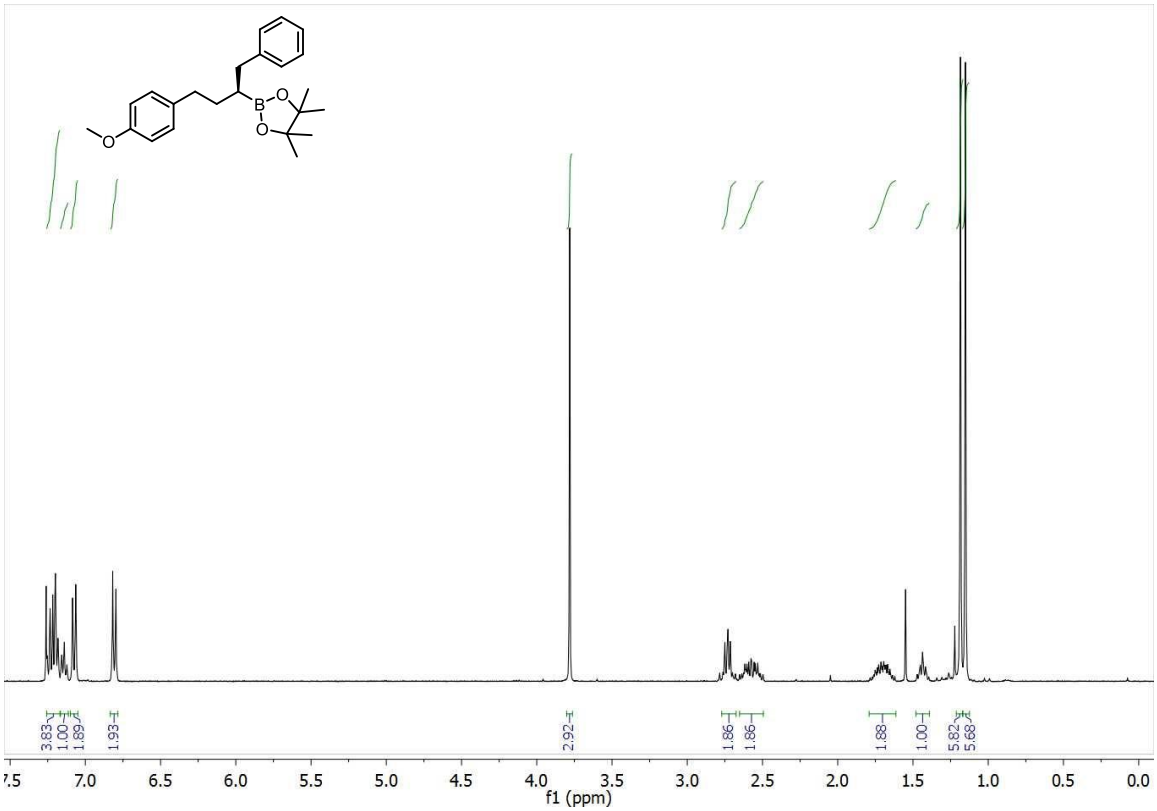
^{1}H NMR of **18n** (400 MHz, $CDCl_3$)



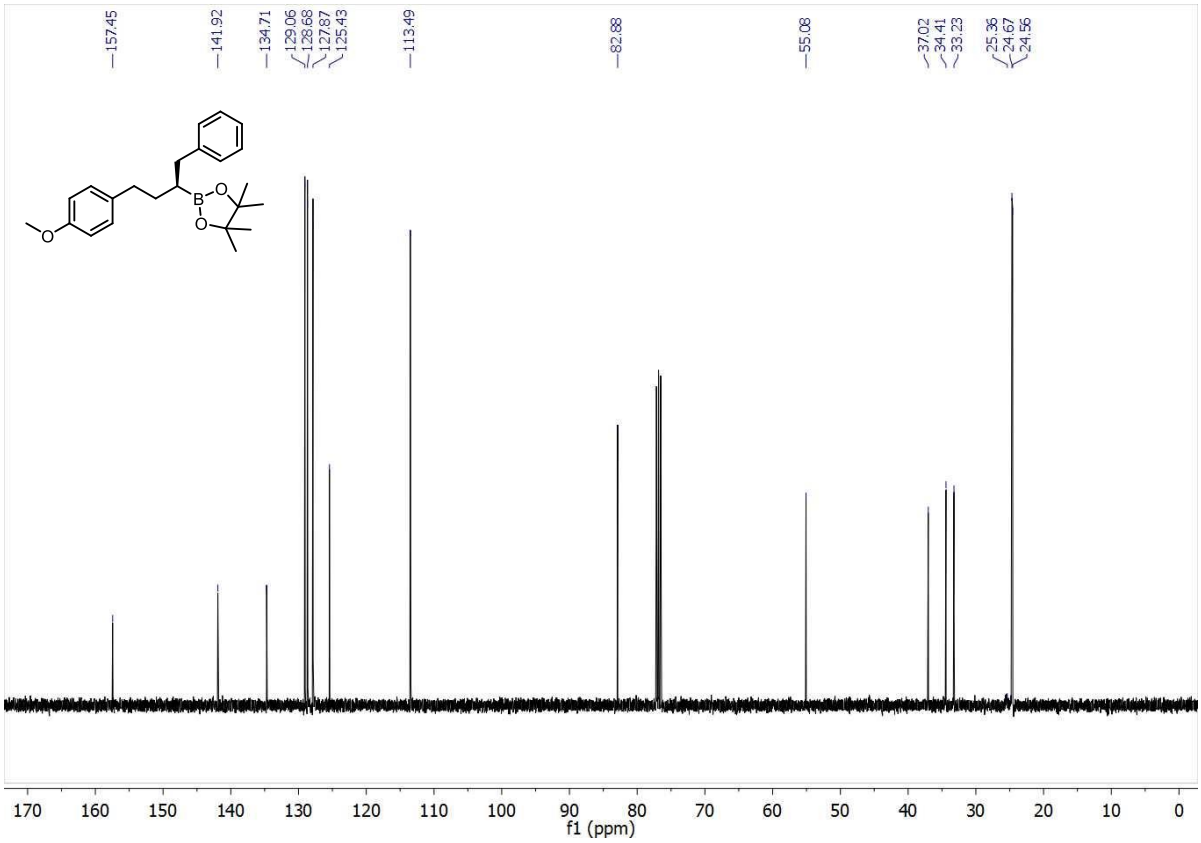
^{13}C NMR of **18n** (101 MHz, $CDCl_3$)



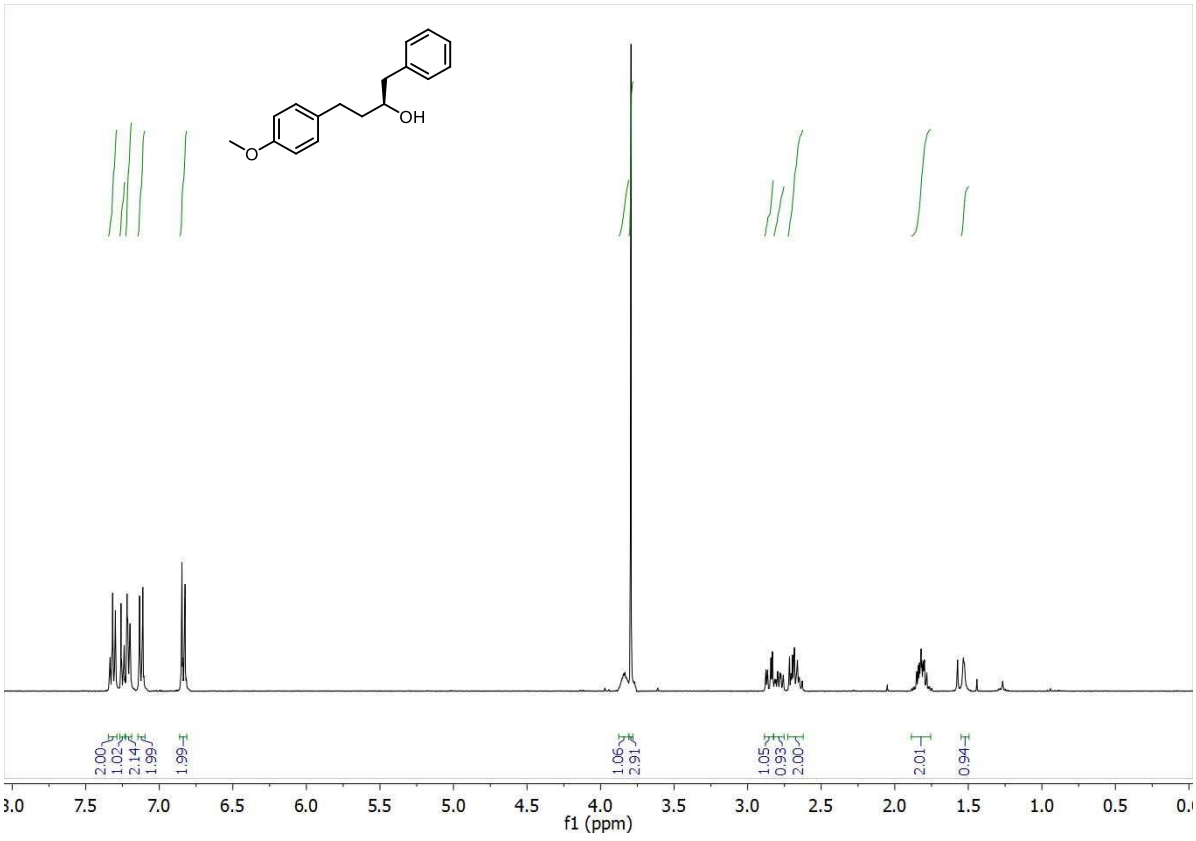
^{1}H NMR of **18p** (400 MHz, $CDCl_3$)



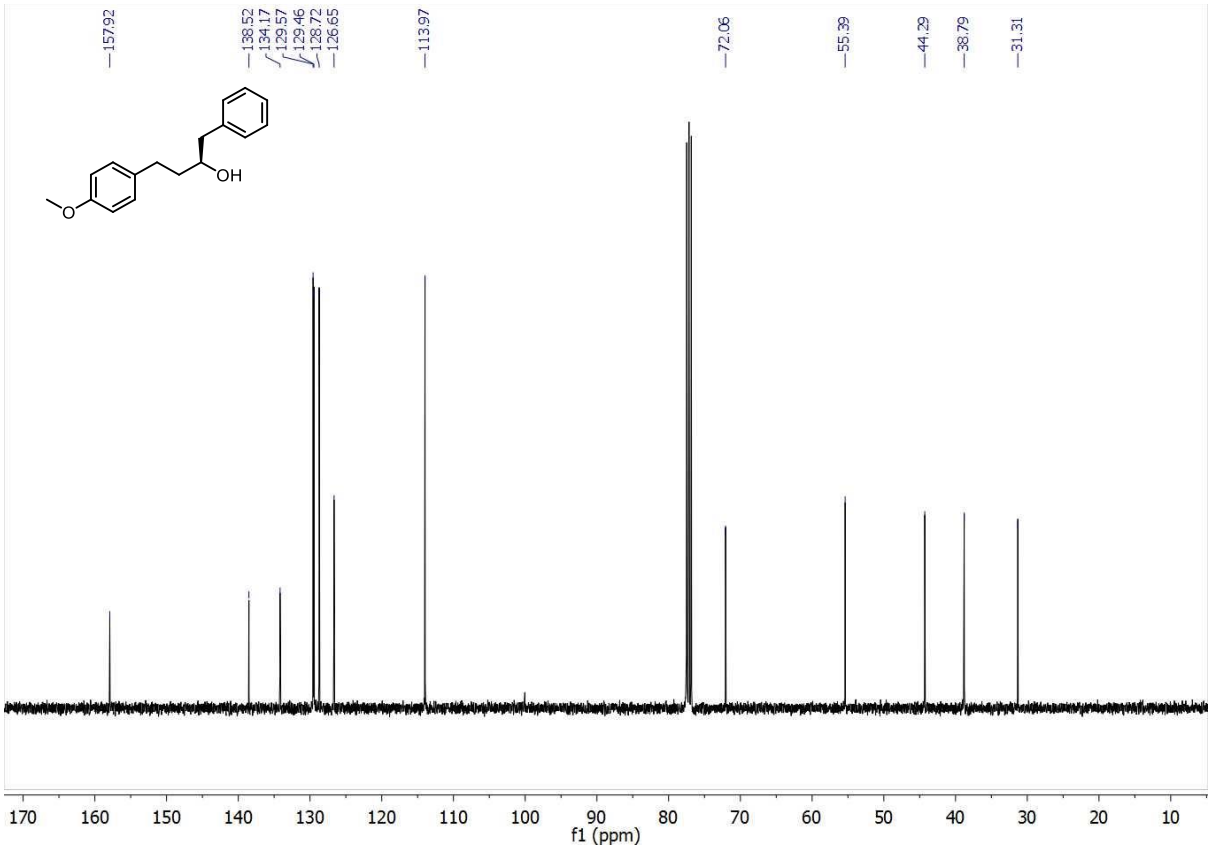
^{13}C NMR of **18p** (101 MHz, $CDCl_3$)



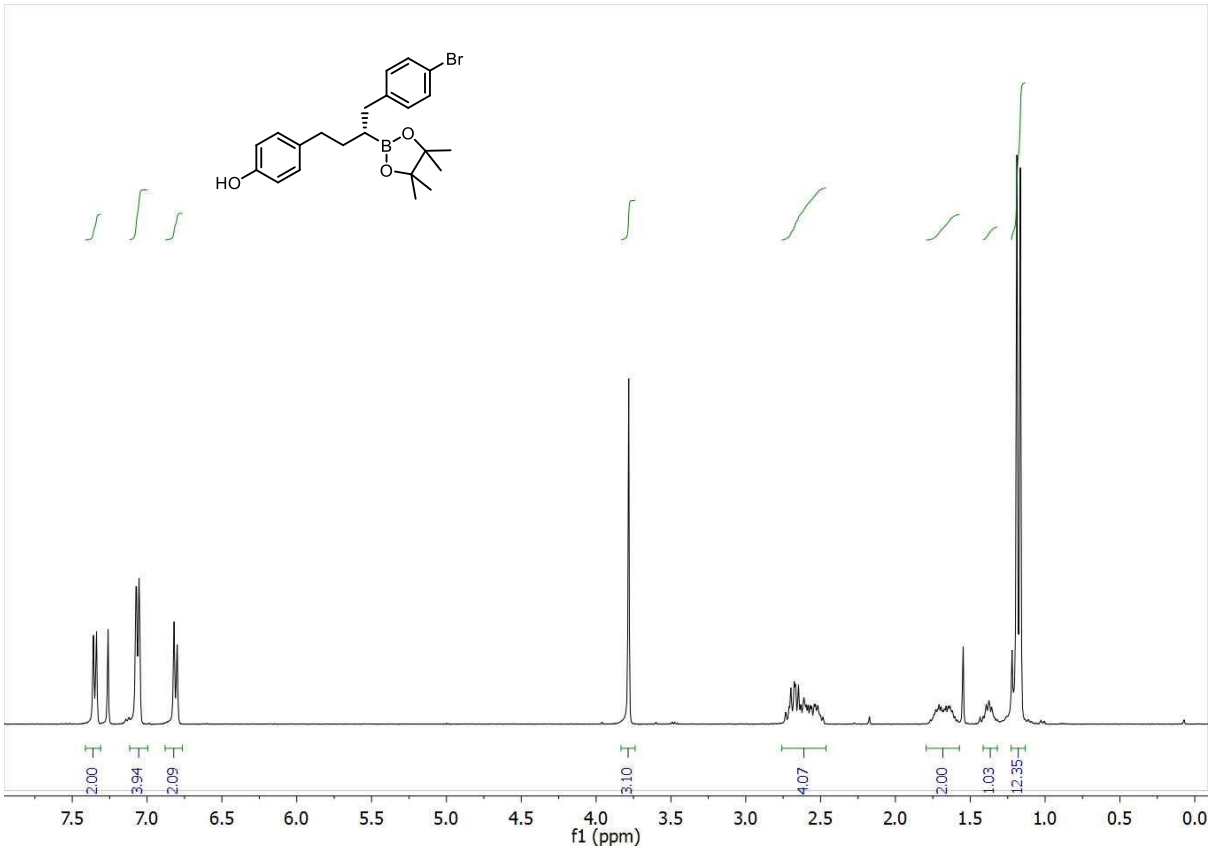
^{1}H NMR of **31** (400 MHz, $CDCl_3$)



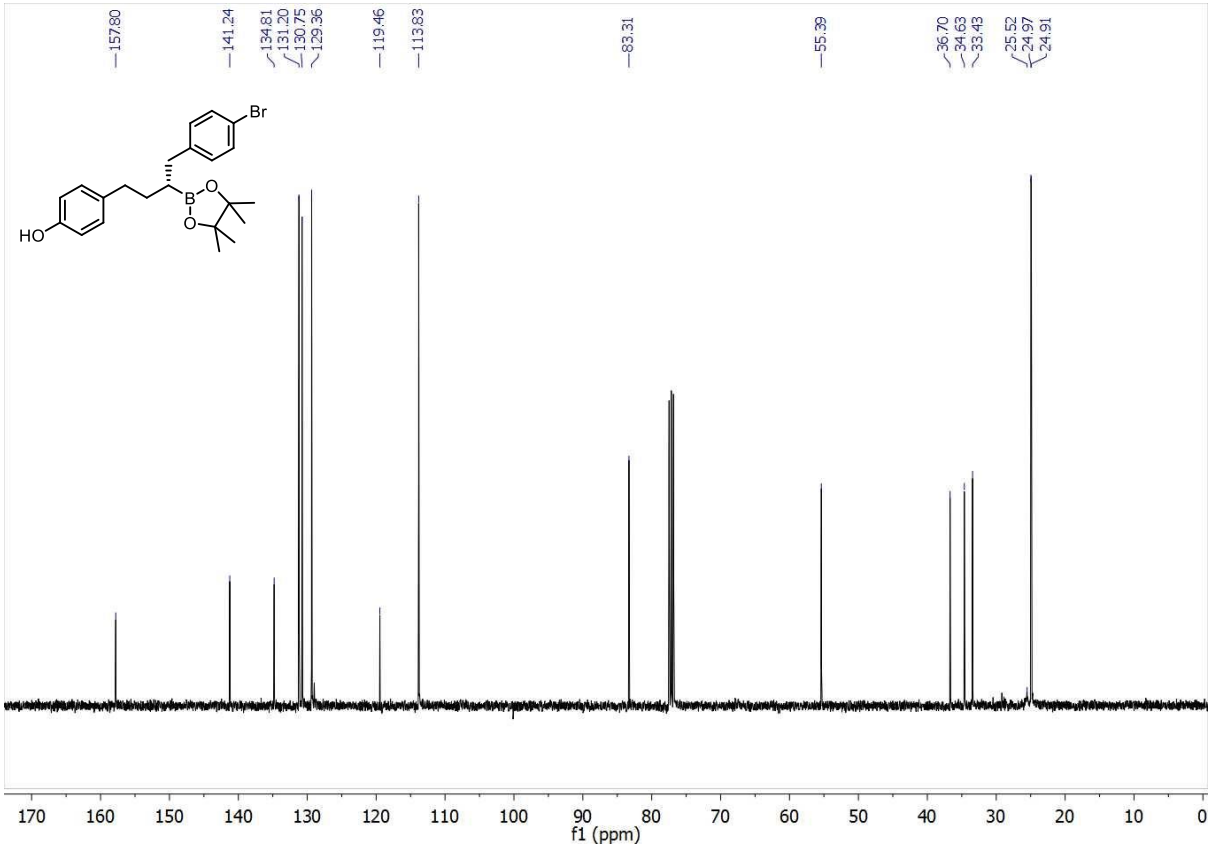
^{13}C NMR of **31** (101 MHz, $CDCl_3$)



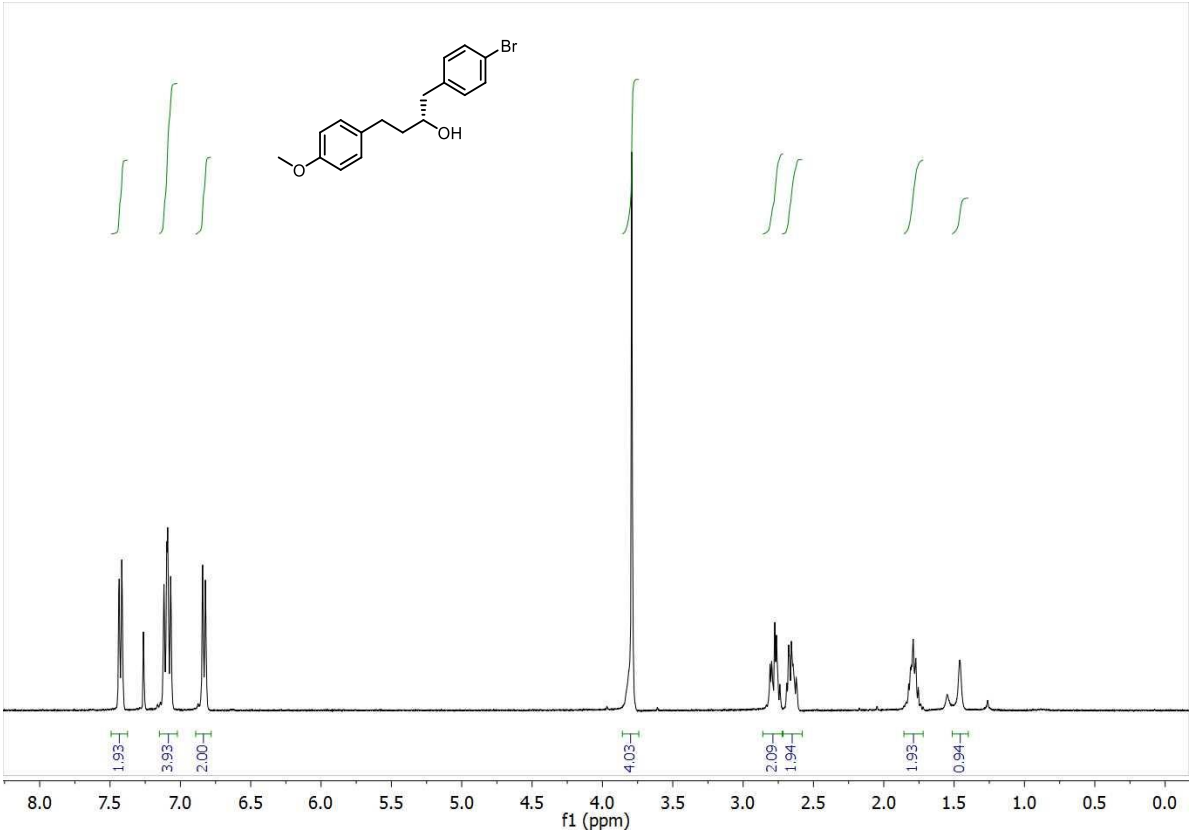
^{1}H NMR of **18q** (400 MHz, $CDCl_3$)



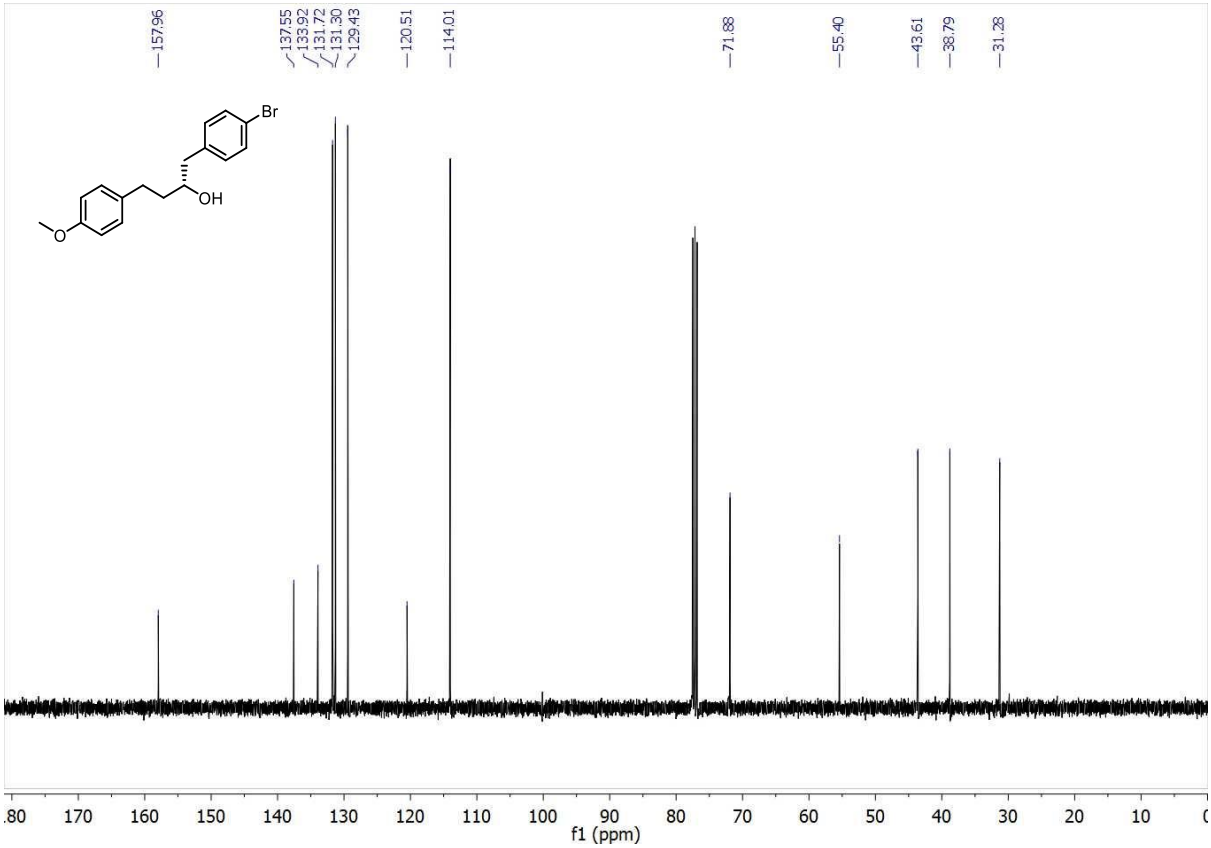
^{13}C NMR of **18q** (101 MHz, $CDCl_3$)



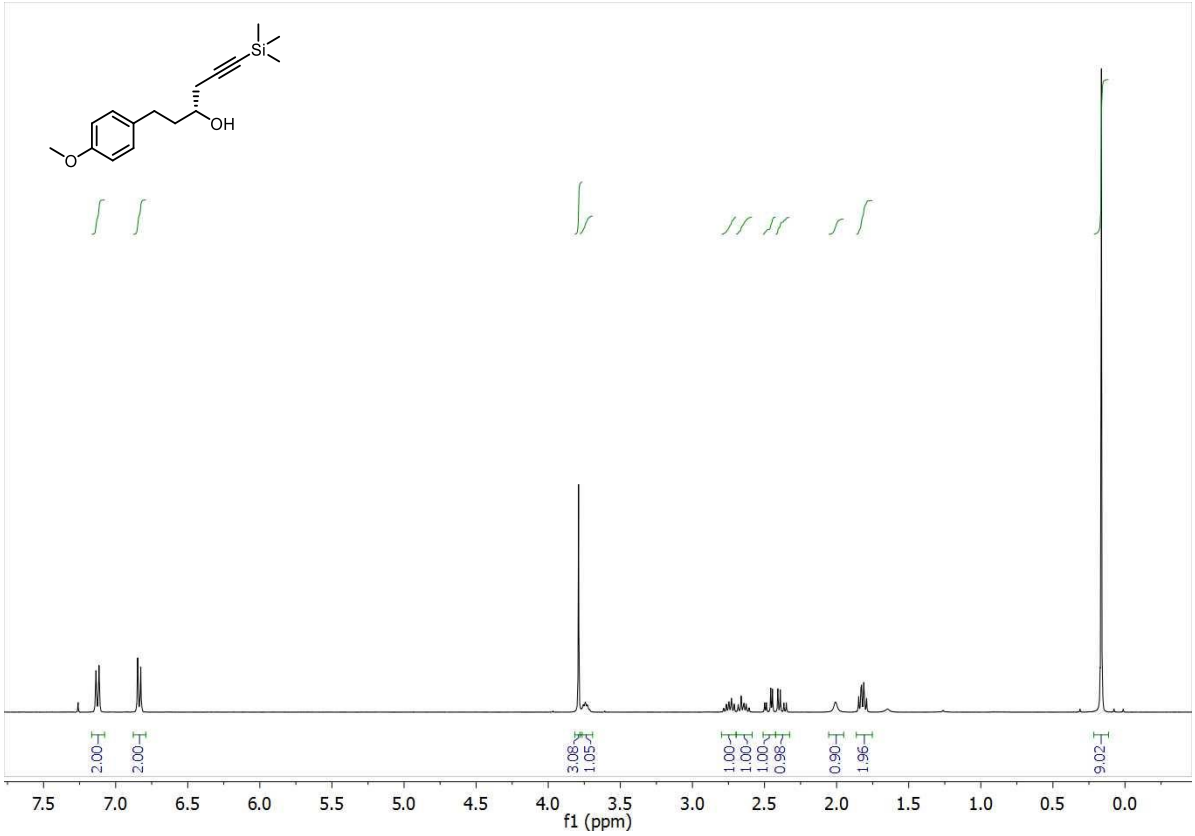
^{1}H NMR of **32** (400 MHz, $CDCl_3$)



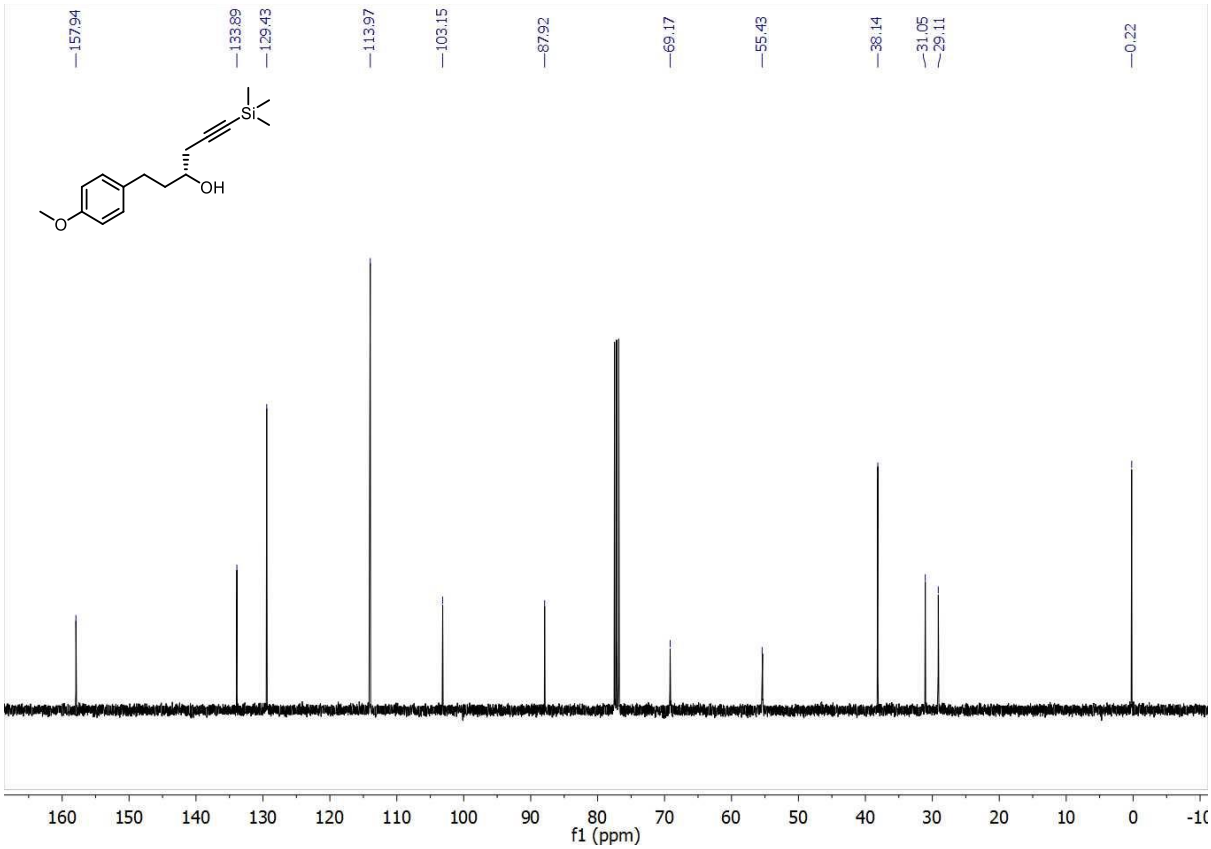
^{13}C NMR of **32** (101 MHz, $CDCl_3$)



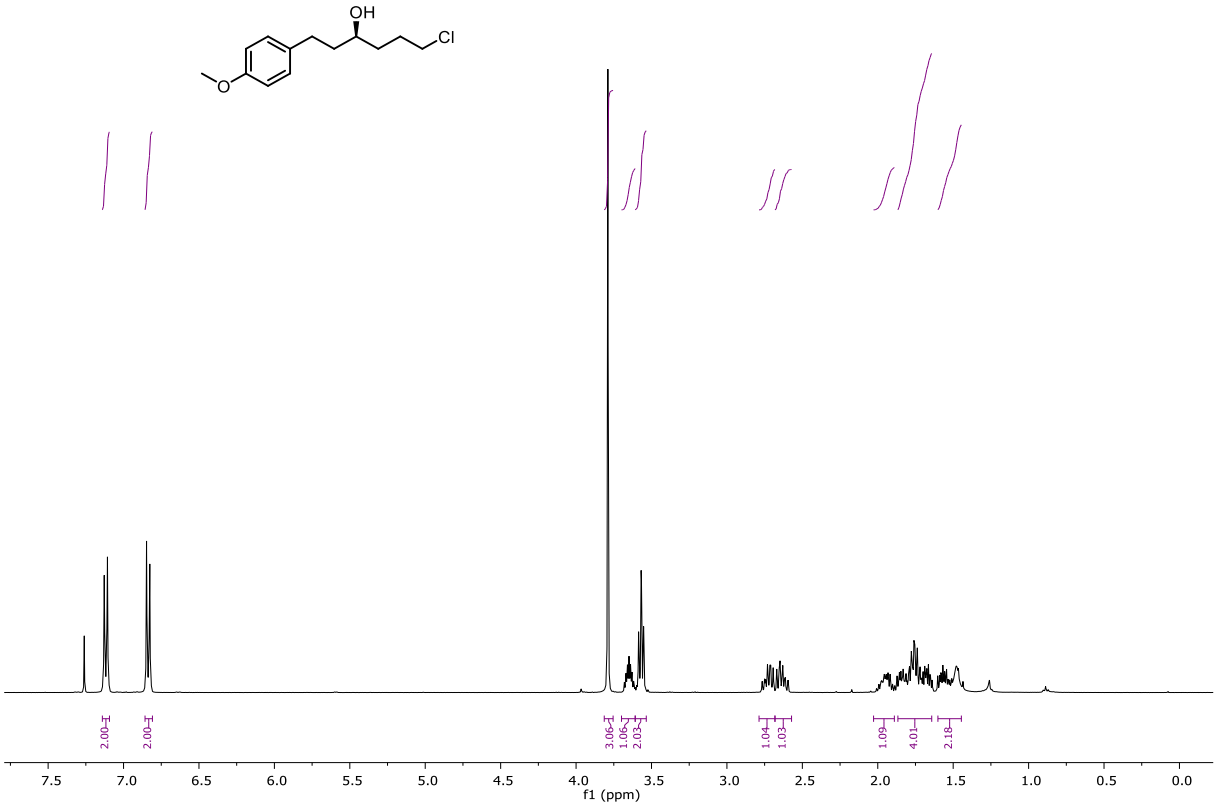
^{1}H NMR of **18r** (400 MHz, $CDCl_3$)



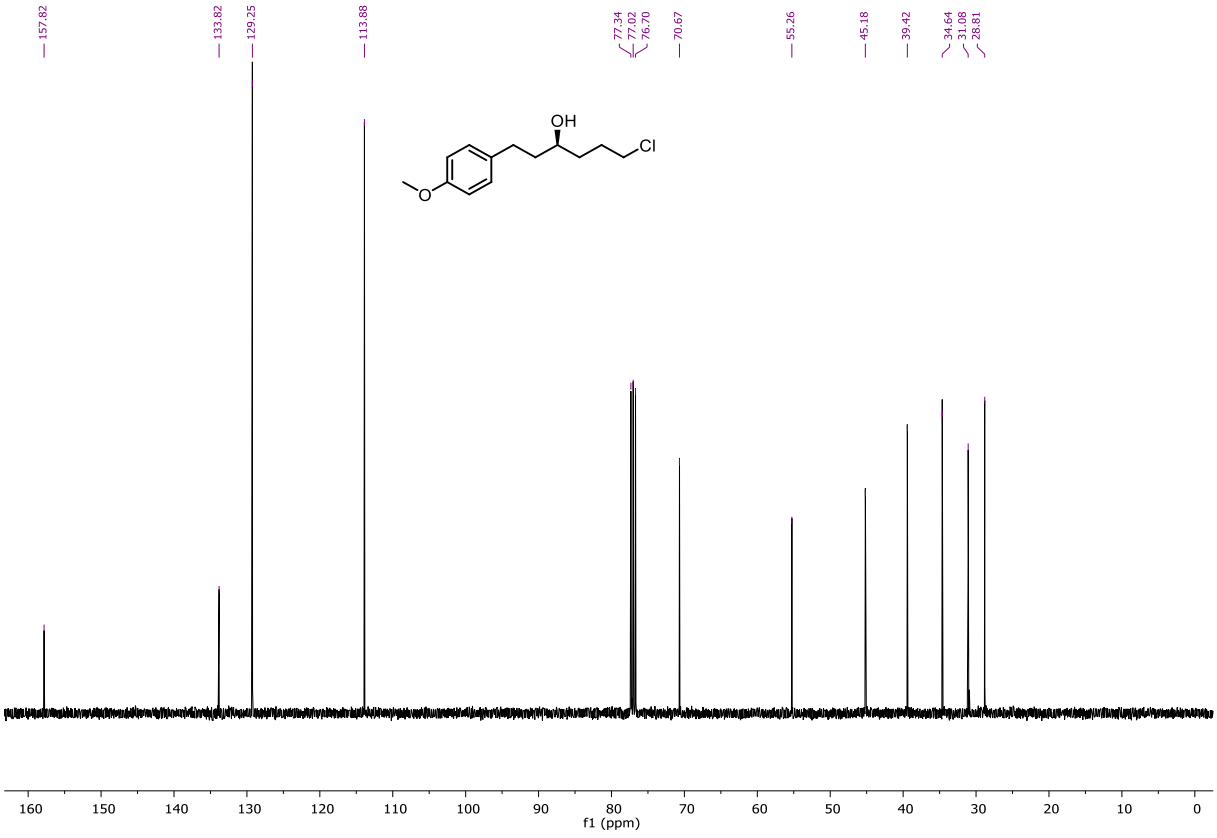
^{13}C NMR of **18r** (101 MHz, $CDCl_3$)



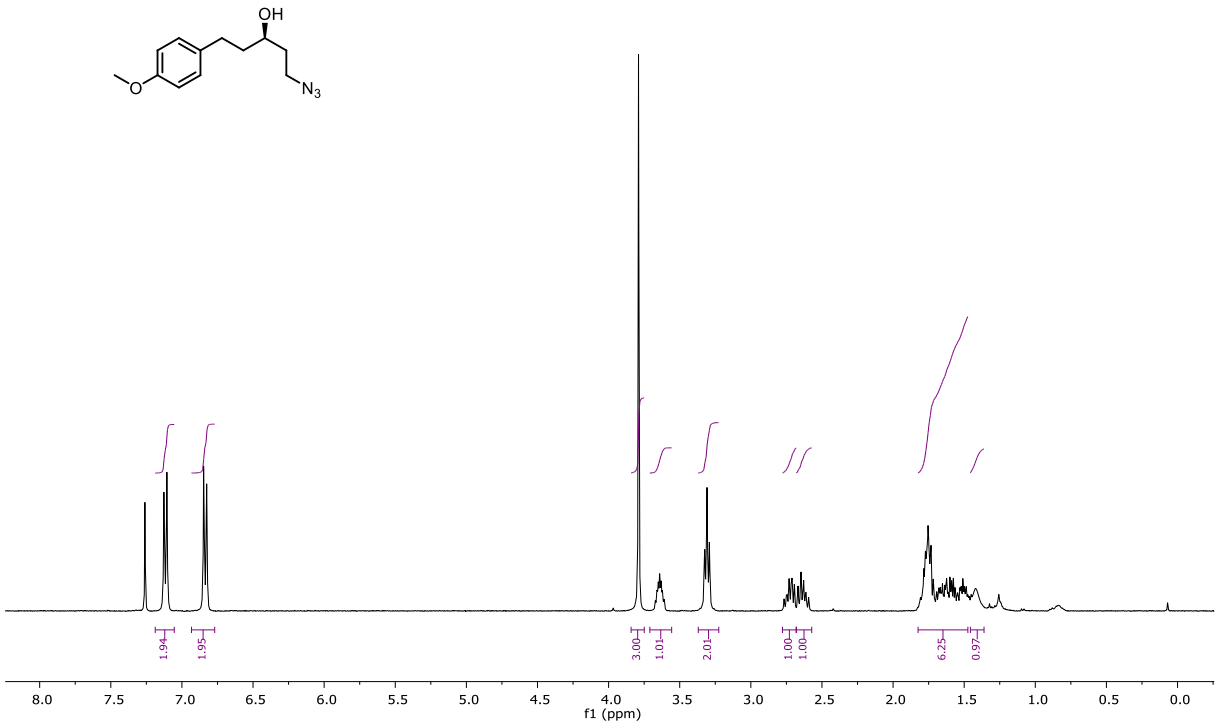
^{1}H NMR of **18s** (400 MHz, $CDCl_3$)



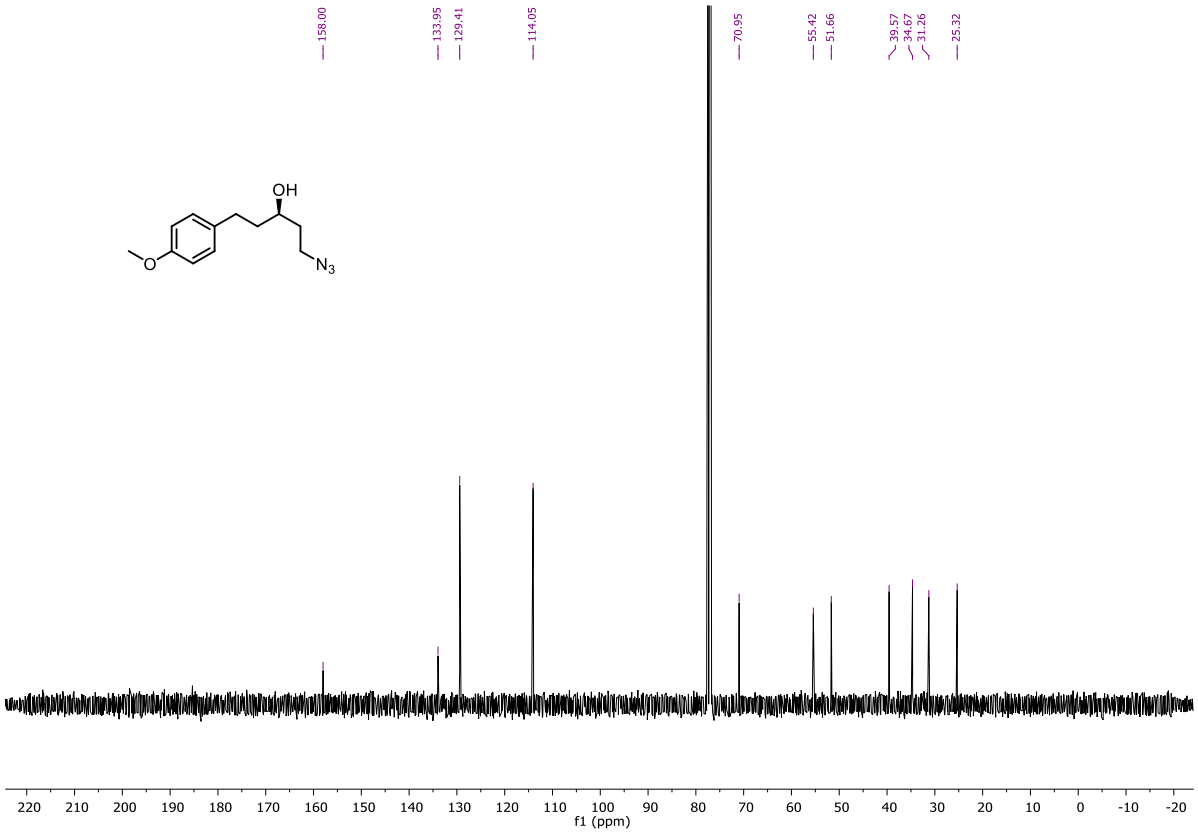
^{13}C NMR of **18s** (101 MHz, $CDCl_3$)



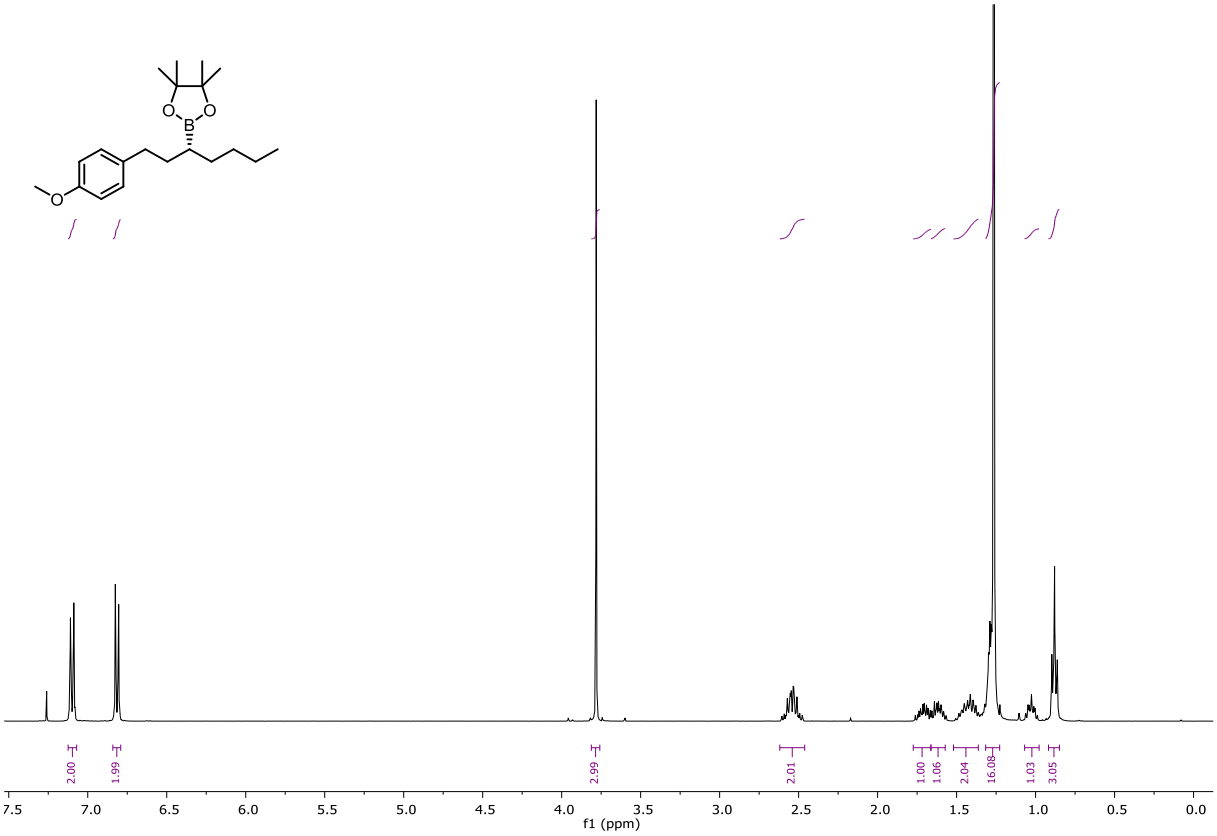
^{1}H NMR of **18t** (400 MHz, $CDCl_3$)



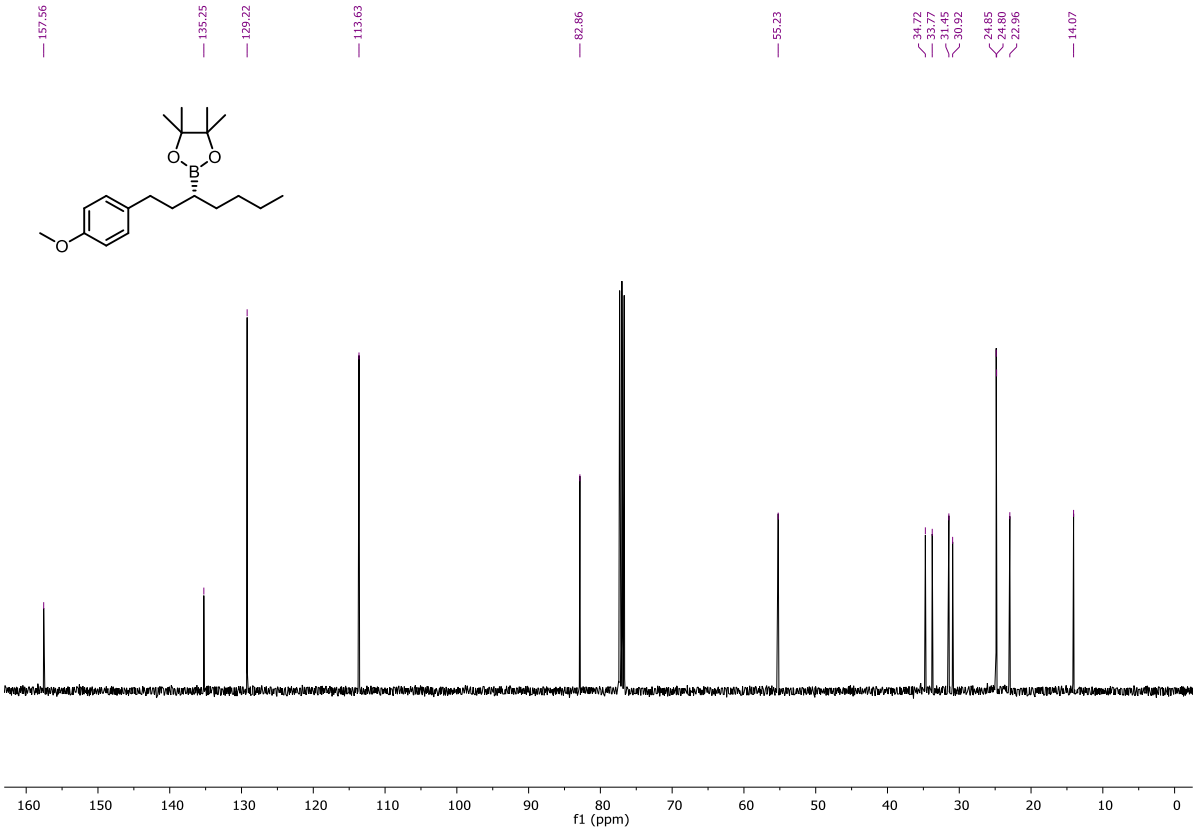
^{13}C NMR of **18t** (101 MHz, $CDCl_3$)



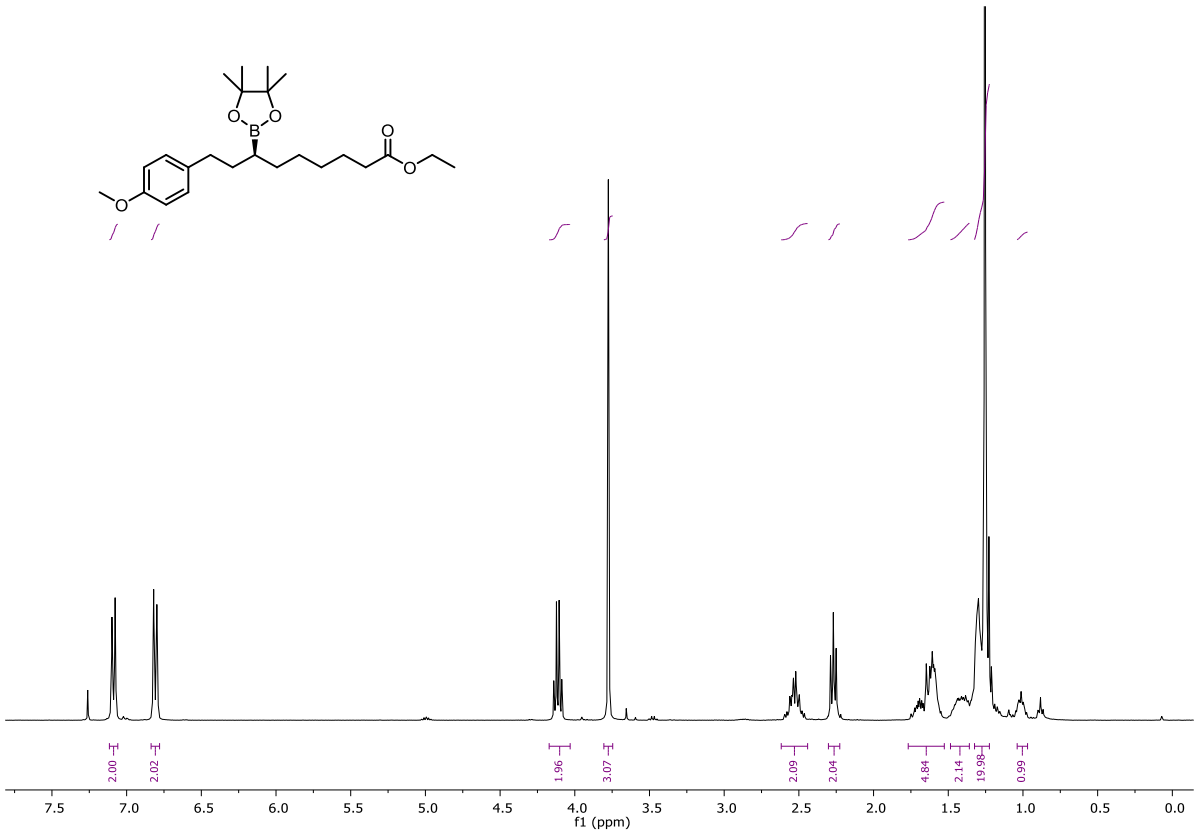
^{1}H NMR of **18u** (400 MHz, $CDCl_3$)



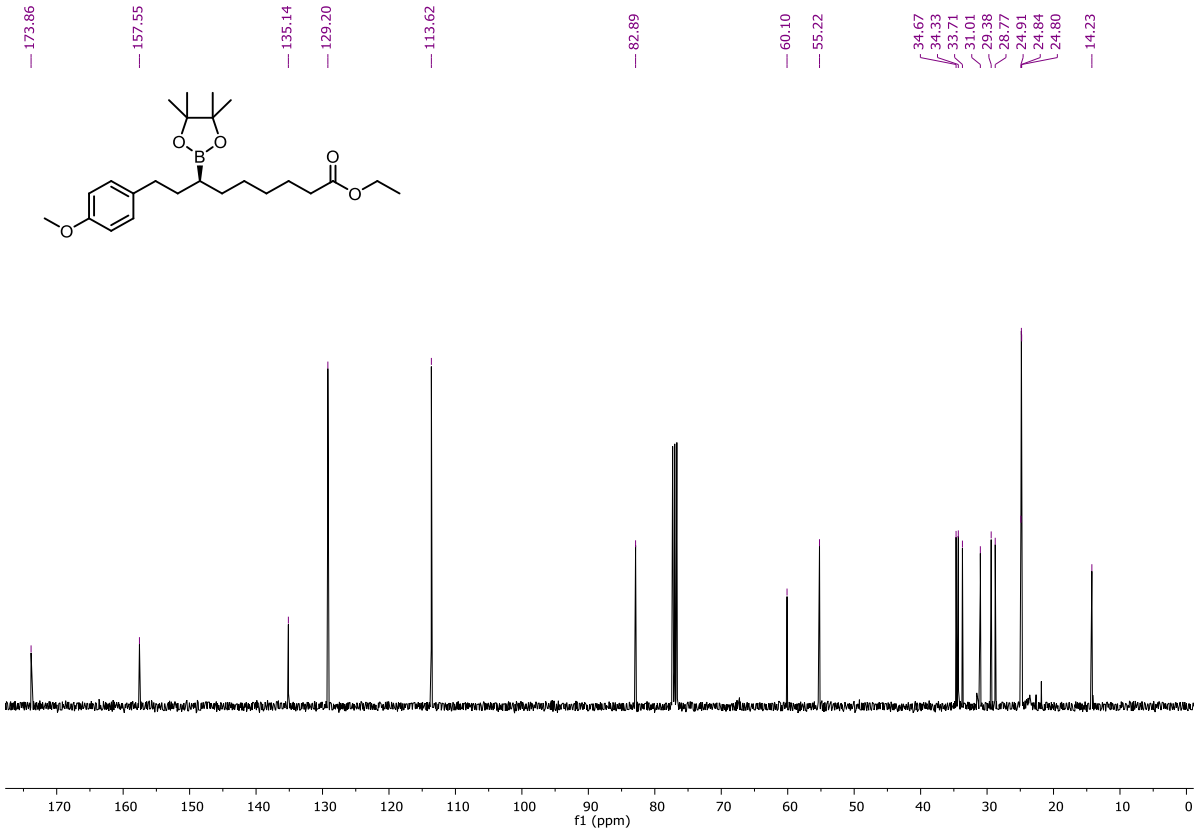
^{13}C NMR of **18u** (101 MHz, $CDCl_3$)



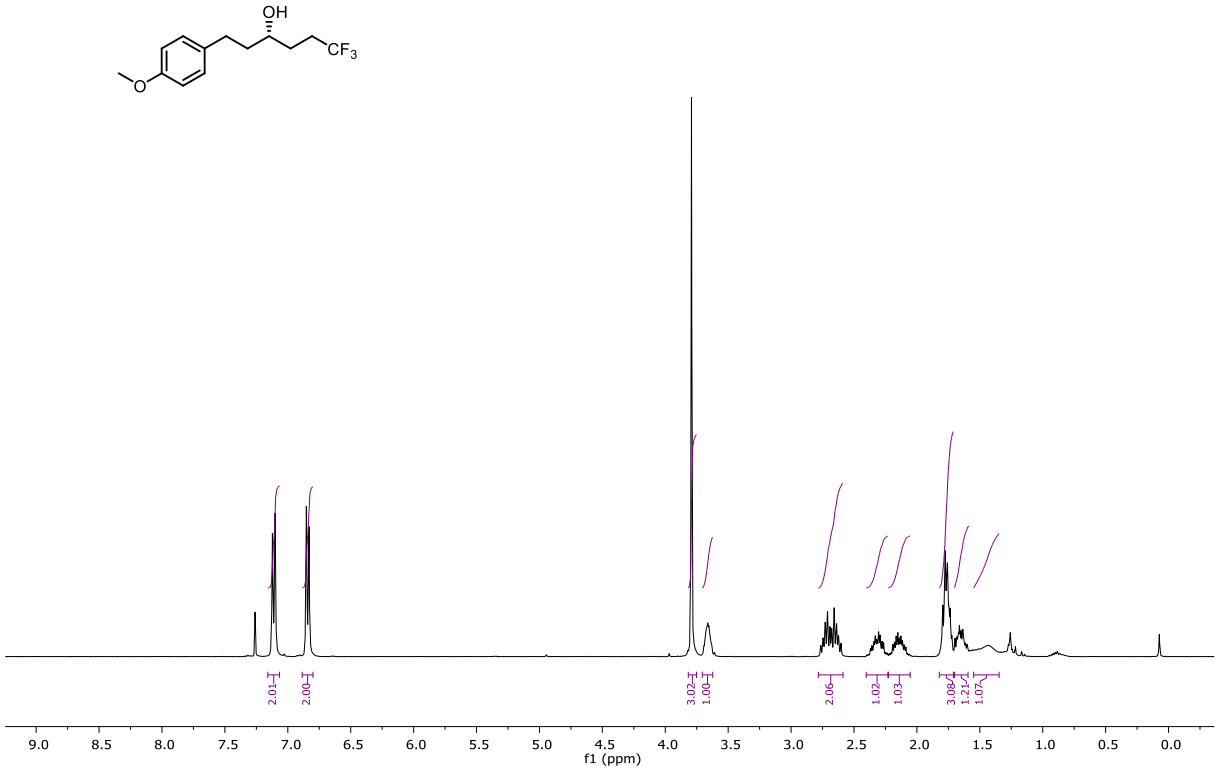
^{1}H NMR of **18v** (400 MHz, $CDCl_3$)



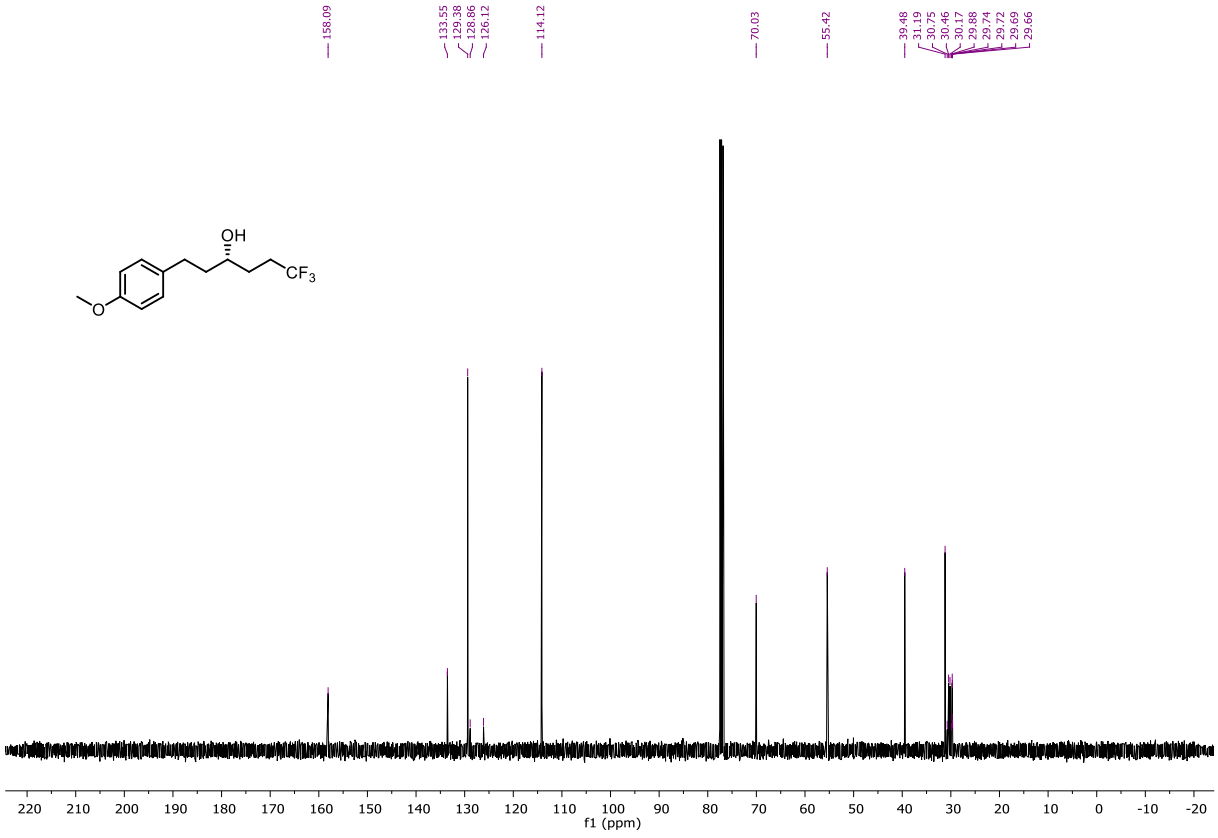
^{13}C NMR of **18v** (101 MHz, $CDCl_3$)



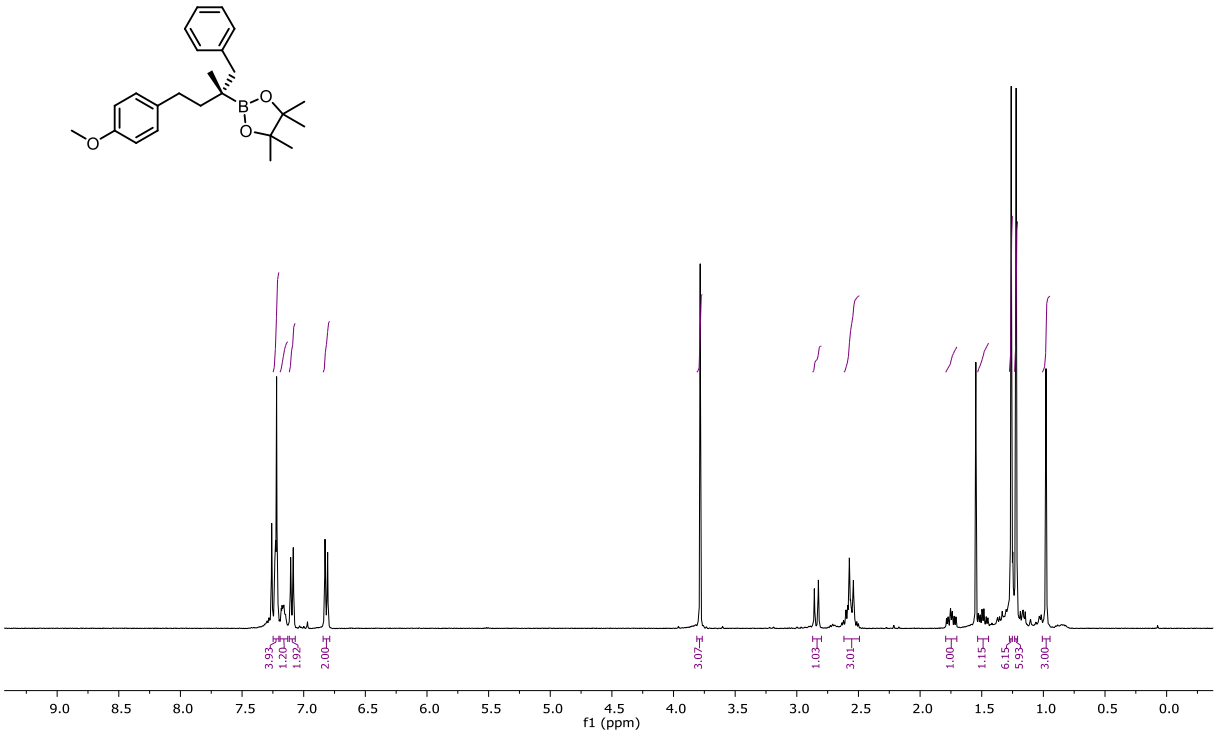
^{1}H NMR of **18w** (400 MHz, $CDCl_3$)



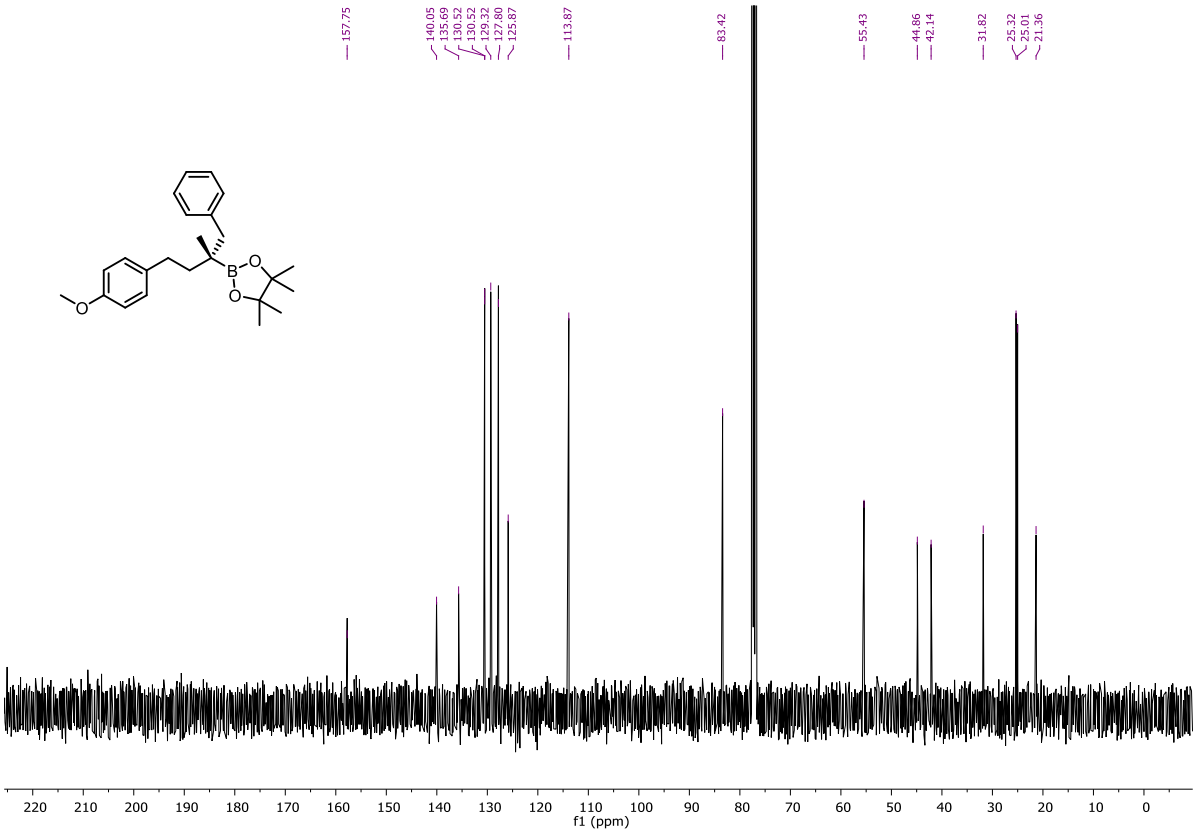
^{13}C NMR of **18w** (101 MHz, $CDCl_3$)



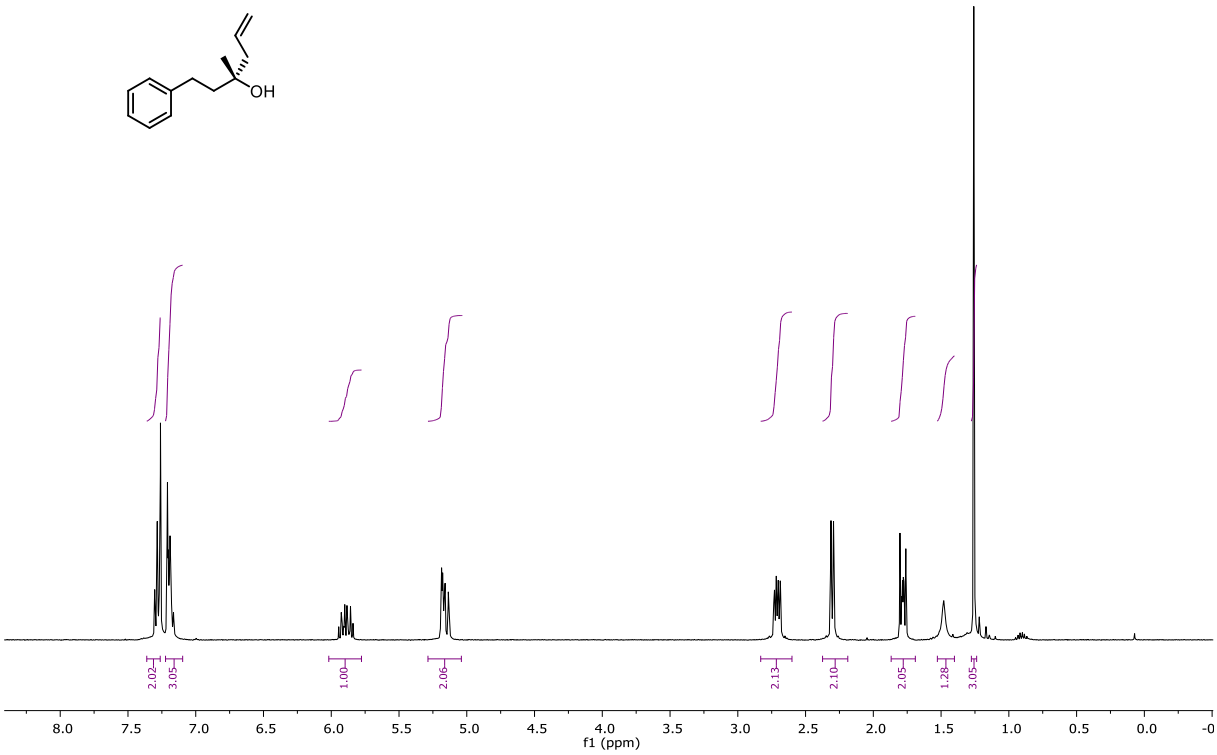
^{1}H NMR of **21a** (400 MHz, $CDCl_3$)



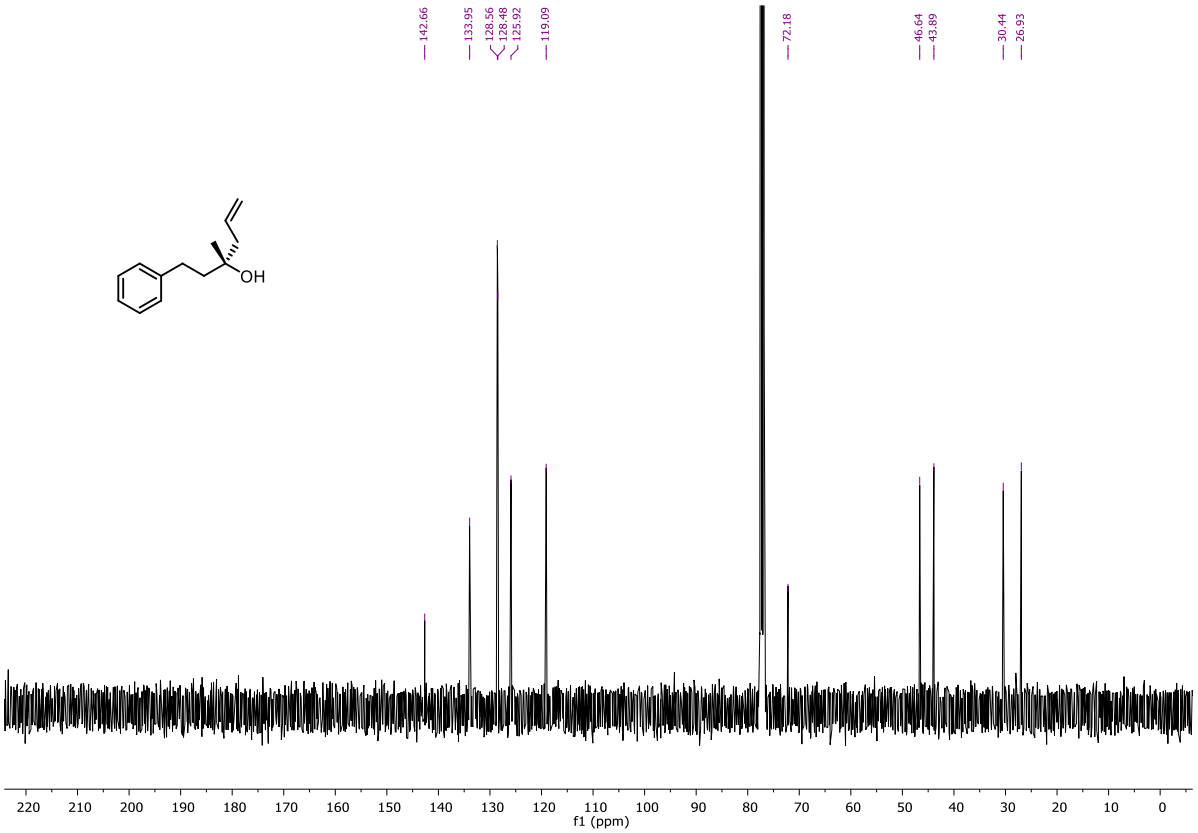
^{13}C NMR of **21a** (101 MHz, $CDCl_3$)



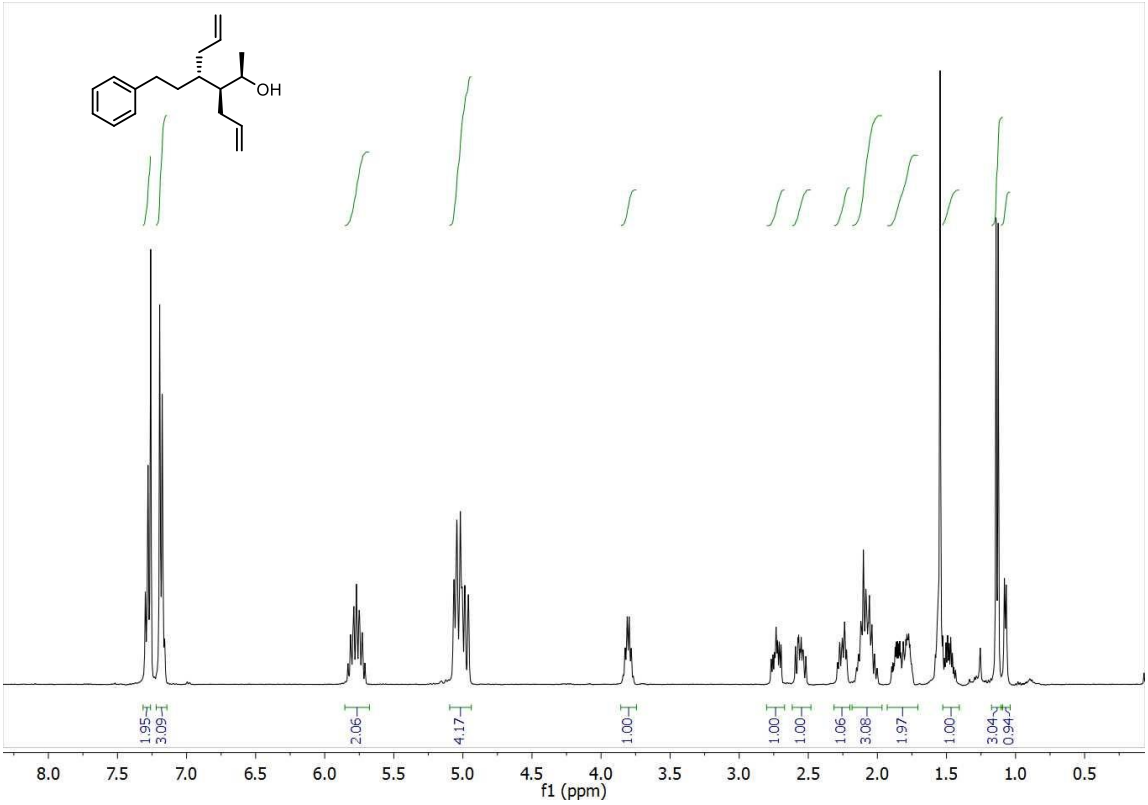
^{1}H NMR of **21b** (400 MHz, $CDCl_3$)



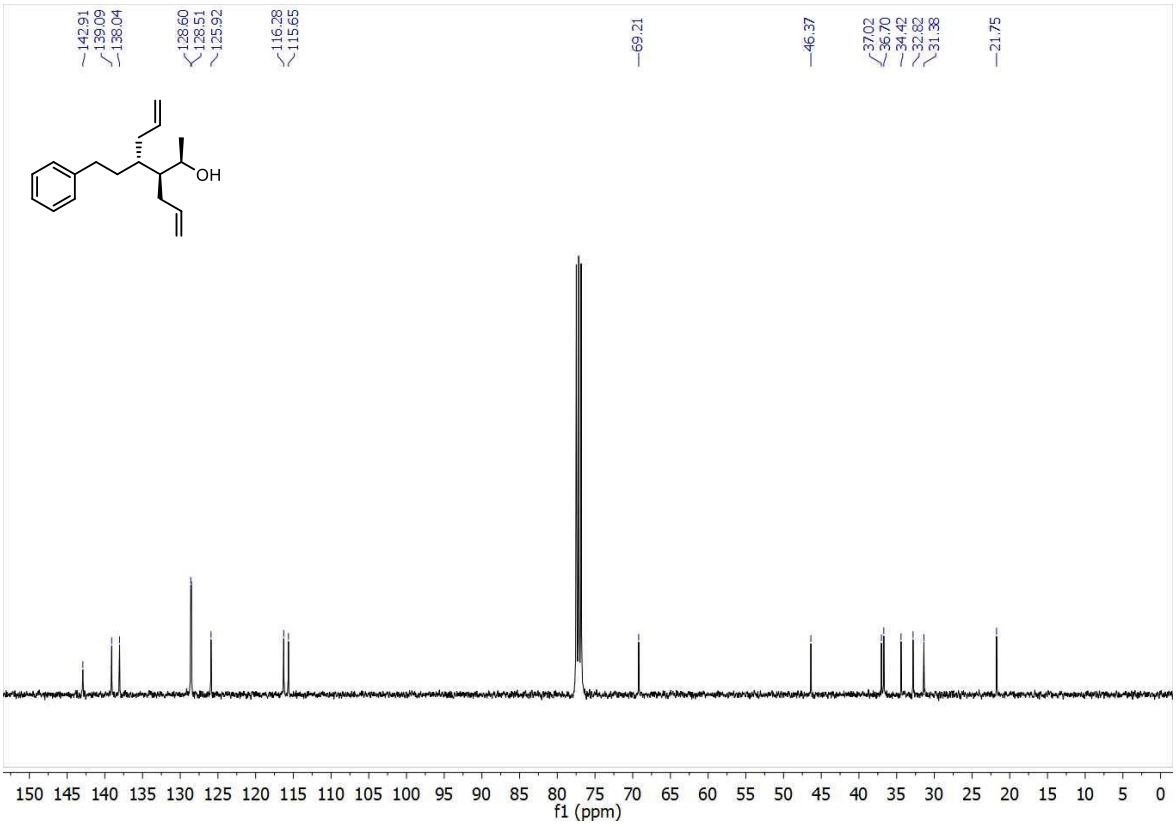
^{13}C NMR of **21b** (101 MHz, $CDCl_3$)



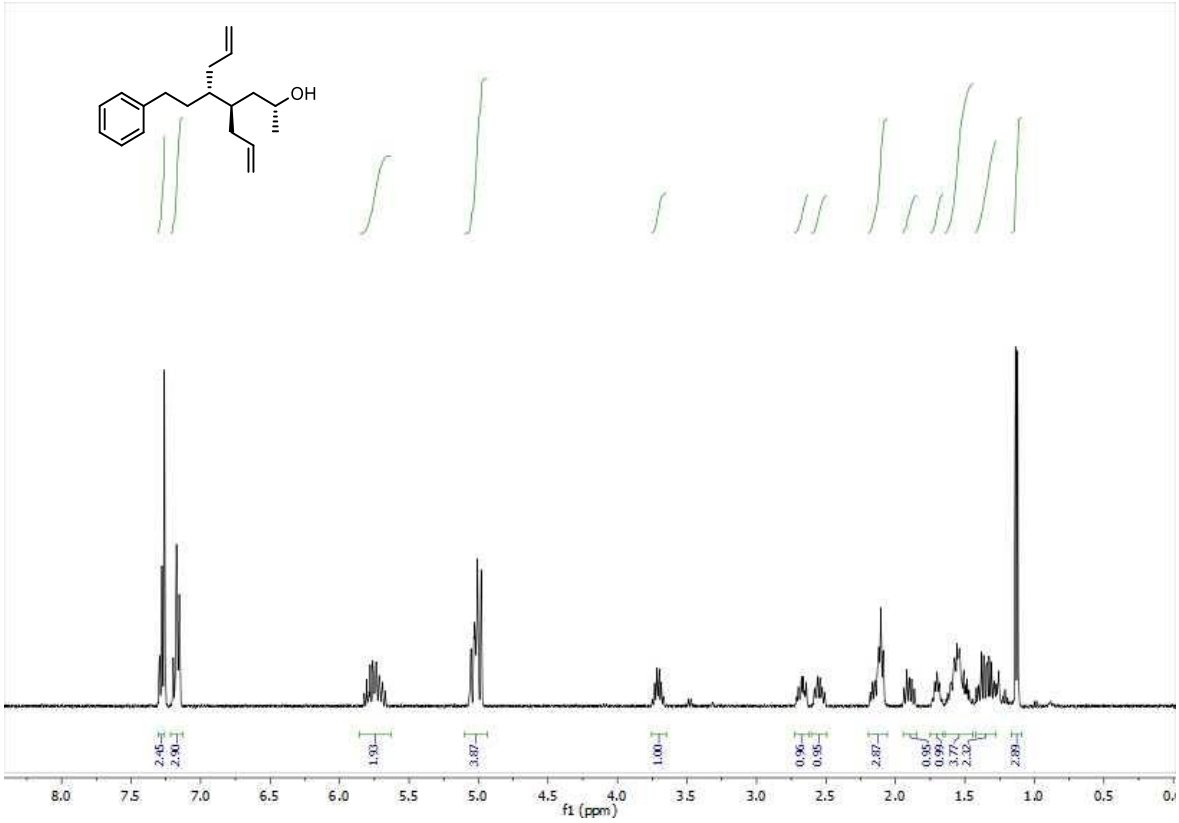
^{1}H NMR of **22** (400 MHz, $CDCl_3$)



^{13}C NMR of **22** (101 MHz, $CDCl_3$)



^{1}H NMR of **26** (400 MHz, $CDCl_3$)



^{13}C NMR of **26** (101 MHz, $CDCl_3$)