Highly diastereoselective synthesis of enantioenriched *anti*-α-allyl-β-fluoroamines

Philip J. Chervis, ‡[a] Sirilak Wangngae, ‡[a,b] Thanaphat Thaima,[a] Anthony W. Carroll,[a] Anthony C. Willis,[c] Mookda Pattarawarapan[b] and Stephen G. Pyne[*]

[a.] *School of Chemistry and Molecular Biosciences, University of Wollongong, Wollongong, New South Wales, 2522, Australia*
[b.] *Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*
[c.] *Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia.*

Supplementary Information

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General Procedures

Anhydrous solvents were obtained from a John Morris solvent purifier system or commercially from Alfa Aesar or Sigma Aldrich. All flash column chromatography was performed using Chem Supply silica gel 60 230-400 mesh. Plates for TLC were aluminium backed silica gel 60 F_{254} obtained from Merck. Components were visualized under a UV lamp (254 nm), and by staining with cerium ammonium molybdate stain and development with a 2000-watt heat gun. This staining solution was prepared dissolving 48 g of ammonium molybdate and 2 g of cerium(IV) sulfate in 940 mL of distilled water, then adding 60 mL of conc. sulfuric acid. Melting point data were acquired using a Gallenkamp MF-370 capillary tube melting point apparatus and are uncorrected. FTIR data were acquired on a Bruker Vertex 70 FTIR spectrometer using neat samples. Optical rotation data were acquired using a Jasco P-2000 polarimeter equipped with a 1 dm sample cell of volume 2 mL. An average of twenty measurements were used to calculate specific rotation. NMR spectroscopy was performed on a Bruker Avance 400 MHz spectrometer, where ^{1}H NMR spectra were acquired at 400 MHz, ^{13}C spectra acquired at 100 MHz and ^{19}F NMR spectra acquired at 377 MHz. ^{1}H and ^{13}C NMR chemical shifts acquired in deuterochloroform ($CDCl_3$) are reported in ppm downfield from TMS (0.0 ppm). NMR spectra acquired in deuterated methanol (CD_3OD) were referenced to the CD_2HOD signal at 3.31 ppm in ^{1}H NMR and the CD_3OD signal at 49.0 ppm in ^{13}C NMR. All ^{19}F NMR chemical shifts were referenced externally to trifluorotoluene ($C_6H_5CF_3$) at 0.0 ppm. For camphor derivatives, the germinal dimethyl groups at C-7' are both referred to as H-8' and C-8', despite not being magnetically

equivalent. High resolution mass spectrometry data was acquired using a Micromass Waters Q-ToF Ultimate (quadrupole time-of-flight) mass spectrometer, using MeOH as the solvent. The ionization method was by electrospray ionization (ESI).

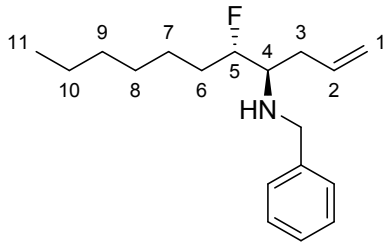
General procedure 1 for the preparation of β-fluoroamines from aldehyde:

Part A: α-Fluorination of aldehydes: To a nitrogen purged 10 mL round-bottomed flask was added (*S*)-α,α-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethylsilyl ether (Jørgensen' (*S*) catalyst) or (*R*)-α,α-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethylsilyl ether (Jørgensen' (*R*) catalyst) (1.8 mg, 0.003 mmol, 0.01 equiv or 1 mol%), anhydrous methyl *tert*-butyl ether (0.6 mL) and the aldehyde substrate (0.45 mmol, 1.5 equiv) via microlitre syringe and the mixture was stirred at room temperature for 20 min under a nitrogen atmosphere. *N*-Fluorobenzenesulfonimide (94.6 mg, 0.3 mmol, 1.0 equiv) was added to the reaction mixture, and the reaction mixture stirred at room temperature for the specified time with TLC monitoring.

Part B: Fluoro-Petasis reaction: Upon completion of Part A, to the reaction mixture was added pentane (~2 mL), the mixture stirred vigourously for 20 min and then filtered to remove insoluble material. To the filtrate was added methanol (~2 mL) and the amine component (0.6 mmol, 2.0 equiv) and the mixture was stirred for 5 min at room temperature. The organoboronic ester or potassium organotrifluoroborate component (0.6 mmol, 2.0 equiv) was then added to the mixture which was stirred vigourously at room temperature for 24 h with TLC monitoring. The crude reaction mixture was concentrated *in vacuo* and purifiled by flash column chromatography using silica gel to obtain the pure β-fluoroamine product. The yields of final products are based on the limiting reagent NFSI.

General procedure 2 for chiral derivatization of Petasis adducts using (1*S*)-(+)-10-camphorsulfonyl chloride: To a dry and nitrogen purged round-bottomed flask was added the β-fluoroamine (1.0 equiv; approx. scale ~20 mg), anhydrous CH_2Cl_2 (0.5 mL), trimethylamine (3.0 equiv), 4-(dimethylamino) pyridine (2.0 equiv) and (1*S*)-(+)-10-camphorsulfonyl chloride (2.0 equiv). The mixture was stirred for 24 hours with TLC monitoring. The crude reaction mixture was concentrated *in vacuo* and purified by flash column chromatography using silica gel to obtain the pure sulfonamide product.

(4*R*,5*S*)-*N*-Benzyl-5-fluoroundec-1-en-4-amine (2c)



The title compound was prepared according to General procedure 1, using octanal (70.4 μL, 0.45 mmol), Jørgensen (*S*)-catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.5 μL, 0.60 mmol) with 24 h reaction time for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 5% EtOAc/*n*-hexane gave the product (60.6 mg, 73%) as a pale-yellow oil.

R_f = 0.11 (5% EtOAc/*n*-hexane)

dr 97:3, ee 90%.

$[\alpha]_D^{22}$ -14.2 (*c* 1.2, $CHCl_3$).

IR (neat): ν_{max} 3064, 3028, 2925, 1640, 1495 (N-H bend), 1465, 913 (C-F str.), 733, 697cm^{-1}.

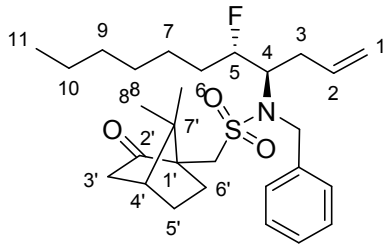
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.19 (m, 5H, Ar-*H*), 5.87 – 5.72 (m, 1H, H-2), 5.11 (ddd, *J* = 10.3, 2.0, 1.2 Hz, 1H, *cis*-H-1), 5.10 (ddd, *J* = 16.9, 1.8, 1.5 Hz, 1H, *trans*-H-1), 4.46 (dddd, *J* = 48.3, 9.4, 4.5, 3.1 Hz, 1H, H-5), 3.82 (apparent d, *J* = 1.6 Hz, 2H, CH_2Ph), 2.76 (dddd, *J* = 17.0 ($^3J_{H,F}$), 7.5, 4.6, 4.6 Hz, 1H, H-4), 2.39 – 2.18 (m, 2H, H-3), 1.78 – 1.51 (m, 2H, H-6), 1.51 – 1.21 (m, 8H, H-7, H-8, H-9, H-10), 0.89 (t, *J* = 7.0 Hz, 3H, H-11).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (*ipso*-*C*), 135.2 (C-2), 128.4 (*m*-C), 128.2 (*o*-C), 127.0 (*p*-C), 117.8 (C-1), 95.6 (d, $^1J_{C,F}$ = 171.6 Hz, C-5), 59.0 (d, $^2J_{C,F}$ = 20.7 Hz, C-4), 51.9 (*C*H_2Ph), 34.3 (d, $^3J_{C,F}$ = 6.5 Hz, C-3), 31.8 (C-9), 31.2 (d, $^2J_{C,F}$ = 21.1 Hz, C-6), 29.2 (C-10), 25.6 (d, $^3J_{C,F}$ = 3.0 Hz, C-7), 22.6 (C-8), 14.1 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.98 (major diastereomer), -129.69 (minor diastereomer). Ratio = 97:3.

HRMS (ESI): *m/z*: calculated for $C_{18}H_{29}NF$ $[M+H]^+$: 278.2284, found: 278.2296.

***N*-Benzyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*R*,5*S*)-5-fluoroundec-1-en-4-yl)methanesulfonamide (for ee of 2c)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2c** (23.1 mg, 0.0833 mmol) as starting material. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (12.2 mg, 30%) as a yellow oil.

R_f = 0.15 (10% EtOAc/*n*-hexane).

dr 95:5, ee 90%.

$[\alpha]_D^{22}$ -5.4 (*c* 1.6, $CHCl_3$).

IR (neat): ν_{max} 3067, 2924, 1746 (C=O str.), 1604, 1456, 1339 (S=O str.), 1146 (S=O str.), 918 (C-F str.), 726, 699 cm^{-1}.

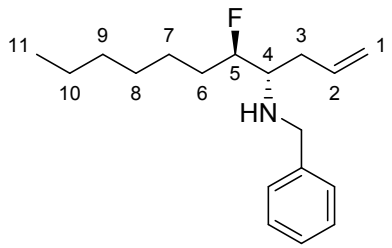
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (ddd, *J* = 6.6, 1.6, 1.6 Hz, 2H, *o*-Ar-*H*), 7.38 – 7.23 (m, 3H, *m, p*-Ar-*H*), 5.92 – 5.77 (m, 1H, H-2), 5.20 (ddd, *J* = 17.0, 1.4, 1.3 Hz, 1H, *trans*-H-1), 5.15 (ddd, *J* = 10.4, 1.5, 1.5 Hz, 1H, *cis*-H-1), 4.60 (d, *J* = 15.0 Hz, 1H, C*H*HPh), 4.35 (dddd, *J* = 49.2 ($^2J_{H,F}$), 9.0, 5.3, 3.5 Hz, 1H, H-5), 4.34 (d, *J* = 15.0 Hz, 1H, C*H*HPh), 4.09 – 3.93 (m, 1H, H-4), 3.21 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 2.58 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 2.48 (ddd, *J* = 14.3, 11.6, 4.6 Hz, 1H, H-5'), 2.32 (ddd, *J* = 18.4, 4.9, 3.2 Hz, 1H, H-3'), 2.05 (dd, *J* = 4.4, 4.4 Hz, 1H, H-4'), 2.03 – 1.94 (m, 1H, H-6'), 1.90 (d, *J* = 18.4 Hz, 1H, H-3'), 1.68 (ddd, *J* = 14.1, 9.3, 4.7 Hz, 1H, H-5'), 1.62 – 1.48 (m, 2H, H-6), 1.39 (ddd, *J* = 12.6, 9.3, 3.9 Hz, 2H, H-6'), 1.34 – 1.16 (m, 8H, H-7, H-8, H-9, H-10), 1.04 (s, 3H, H-8'), 0.87 (t, *J* = 7.1 Hz, 3H, H-11), 0.71 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 137.1 (*ipso-C*), 135.3 (C-2), 129.6 (*o*-C), 128.6 (*m*-C), 128.0 (*p*-C), 118.2 (C-1), 96.7 (d, $^1J_{C,F}$ = 174.2 Hz, C-5), 61.2 (d, $^2J_{C,F}$ = 23.4 Hz, C-4), 58.5 (C-1'), 51.0 (*C*H$_2$SO$_2$), 48.4 (*C*H$_2$Ph), 47.7 (C-7'), 42.7 (C-4'), 42.6 (C-3'), 32.7 (d, $^2J_{C,F}$ = 20.7 Hz, C-6), 31.7 (C-9), 29.7 (C-10), 28.9 (C-7), 26.9 (C-6'), 25.1 (C-5'), 22.5 (C-8), 20.0 (C-8'), 19.6 (C-8'), 14.1 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.47 (minor diastereomer), -126.05 (major diastereomer). Ratio = 3:97.

HRMS (ESI): *m/z*: calculated for $C_{28}H_{42}SO_3NFNa$ $[M+Na]^+$: 514.2767, found: 514.2784.

(4*S*,5*R*)-*N*-Benzyl-5-fluoroundec-1-en-4-amine (*ent*-2c)



The title compound was prepared according to General procedure 1, using octanal (70.4 μL, 0.45 mmol), Jørgensen (*R*)-catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (78.0 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (66.2 mg, 77%) as a yellow oil. The ^{1}H, ^{13}C and ^{19}F NMR spectra of *ent*-**2c** were identical to that of **2c**.

R$_f$ = 0.38 (10% EtOAc/*n*-hexane).

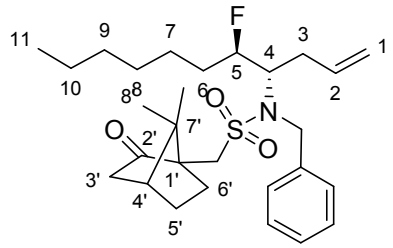
dr 98:2, ee 86%.

$[\alpha]_D^{23}$ +11.4 (*c* 11.4, $CHCl_3$).

IR (neat): ν_{max} 3064, 3028, 2924, 1640 (C=C str.), 1604, 1495 (N-H bend), 1454, 1377, 913 (C-F str.), 733, 698 cm^{-1}.

HRMS (ESI): *m/z*: calculated for $C_{18}H_{29}NF$ $[M+H]^+$: 278.2284, found: 278.2292.

***N*-Benzyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*S*,5*R*)-5-fluoroundec-1-en-4-yl)methanesulfonamide (for ee of *ent*-2c)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine *ent*-**2c** (24.3 mg, 0.0876 mmol) as starting material. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the product (5.1 mg, 12%) as a yellow oil.

R$_f$ = 0.20 (10% EtOAc/*n*-hexane).

dr 93:7, ee 86%.

$[\alpha]_D^{23}$ +25.8 (*c* 0.26, $CHCl_3$).

IR (neat): ν_{max} 3066, 2925, 1745 (C=O str.), 1642 (C=C str.), 1604, 1455, 1339 (S=O str.), 1145 (S=O str.), 917 (C-F str.), 726, 699 cm^{-1}.

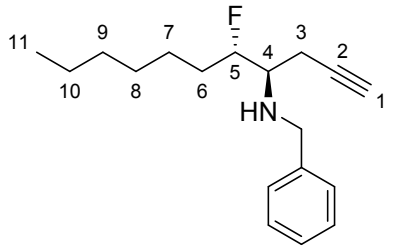
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 6.8, 1.6 Hz, 1H, *o*-Ar-*H*), 7.38 – 7.27 (m, 3H, *m, p*-Ar-*H*), 5.95 – 5.79 (m, 1H, H-2), 5.18 (ddd, *J* = 18.4, 2.8, 1.5 Hz, 1H, *trans*-H-1), 5.18 (ddd, *J* = 10.1, 2.4, 1.6 Hz, 1H, *cis*-H-1), 4.47 (q, *J* = 15.2 Hz, 2H, CH_2Ph), 4.51 – 4.31 (m, 1H, H-5), 4.00 (dddd, *J* = 19.1 ($^3J_{H,F}$), 9.6, 4.7, 4.7 Hz, 1H, H-4), 3.34 (d, *J* = 14.6 Hz, 1H, C*H*HSO_2), 2.56 (d, *J* = 14.6 Hz, 1H, C*H*HSO_2), 2.63 – 2.41 (m, 3H, H-3, H-5'), 2.34 (ddd, *J* = 18.4, 4.0, 4.0 Hz, 1H, H-3'), 2.06 (dd, *J* = 4.3, 4.3 Hz, 1H, H-4'), 2.05 – 1.95 (m, 1H, H-6'), 1.90 (d, *J* = 18.4 Hz, 1H, H-3'), 1.73 – 1.48 (m, 3H, H-5', H-6), 1.39 (ddd, *J* = 13.0, 9.2, 3.6 Hz, 1H, H-6'), 1.34 – 1.17 (m, 8H, H-8, H-9, H-10, H-11), 1.05 (s, 3H, H-8'), 0.87 (t, *J* = 7.0 Hz, 3H, H-11), 0.76 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9 (C-2'), 137.1 (*ipso*-*C*), 135.3 (C-2), 129.5 (*o*-C), 128.5 (*m*-C), 128.0 (*p*-C), 118.2 (C-1), 96.9 (d, $^1J_{C,F}$ = 174.6 Hz, C-5), 61.3 (d, $^2J_{C,F}$ = 23.5 Hz, C-4), 58.6 (C-1'), 50.9 (CH_2SO_2), 48.6 (CH_2Ph), 47.6 (C-7'), 42.8 (C-4'), 42.6 (C-3'), 32.8 (d, $^2J_{C,F}$ = 20.6 Hz, C-6), 32.2 (d, $^1J_{C,F}$ = 4.6 Hz, C-3), 31.6 (C-8), 29.7 (d, $^1J_{C,F}$ = 3.4 Hz, C-7), 28.9 (C-9), 26.9 (C-6'), 25.3 (C-5'), 22.5 (C-10), 20.0 (C-8'), 19.6 (C-8'), 14.1 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -124.49 (major diastereomer), -125.12 (minor diastereomer). Ratio = 93:7.

HRMS (ESI): m/z: calculated for $C_{28}H_{42}SO_3NFNa$ $[M+Na]^+$: 514.2767, found: 514.2782.

(4*R*,5*S*)-*N*-Benzyl-5-fluoroundec-1-yn-4-amine (2e)



The title compound was prepared according to General procedure 1, using octanal (70.4 μL, 0.45 mmol), Jørgensen (*S*)-catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (68.2 μL, 0.625 mmol) and pinacol allenylboronate (112.4 μL, 0.625 mmol) with 24 h as the reaction time for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product **2e** (18.9 mg, 33%) as an orange oil.

R$_f$ = 0.35 (10% EtOAc/*n*-hexane).

dr 97:3, ee 86%.

$[\alpha]_D^{23}$ -21.0 (*c* 1.25, $CHCl_3$).

IR (neat): ν_{max} 3309 (sp C-H str.), 3087, 2924, 2118 (C≡C str.), 1679, 1495 (N-H str.), 1454, 1431, 907 (C-F str.), 732, 698 cm^{-1}.

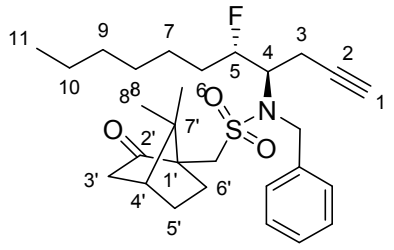
^{1}H NMR (400 MHz, $CDCl_3$,): δ 7.39 – 7.21 (m, 5H, Ar-*H*), 4.49 (dddd, *J* = 48.1 ($^2J_{H,F}$), 9.2, 6.3, 3.1 Hz, 1H, H-5), 3.95 – 3.74 (m, 2H, C*H*$_2$Ph), 2.84 (ddd, *J* = 12.2 ($^3J_{H,F}$), 6.2, 5.3 Hz, 1H, H-4), 2.52 (dddd, *J* = 5.6, 4.2, 2.7, 1.4 Hz, 2H, H-3), 2.01 (t, *J* = 2.7 Hz, 1H, H-1), 1.86 – 1.61 (m, 2H, H-6), 1.54 – 1.15 (m, 8H, H-7, H-8, H-9, H-10), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3 (*ipso*-*C*), 128.6 (*o*-C), 128.4 (*m*-C), 127.2 (*p*-C), 94.7 (d, $^1J_{C,F}$ = 171.7 Hz, C-5), 80.9 (C-2), 70.7(C-1), 58.0 (d, $^2J_{C,F}$ = 22.3 Hz, C-4), 51.5 (*C*H$_2$Ph), 31.9 (C-8, C-9 or C-10), 31.7 (d, $^2J_{C,F}$ = 20.6 Hz, C-6), 29.3 (C-8, C-9 or C-10), 25.4 (d, $^3J_{C,F}$ = 3.0 Hz, C-7), 22.7 (C-8, C-9 or C-10), 19.5 (d, $^3J_{C,F}$ = 6.5 Hz, C-3), 14.2 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -126.16 (major diastereomer), -131.67 (minor diastereomer). Ratio = 97:3.

HRMS (ESI): *m/z*: calculated for $C_{18}H_{27}NF$ $[M+H]^+$: 276.2128, found: 276.2122.

***N*-Benzyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*R*,5*S*)-5-fluoroundec-1-yn-4-yl)methanesulfonamide (3)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2e** (18.9 mg, 0.0686 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (18.6 mg, 55%) as a yellow oil. This compound produced crystals suitable for X-ray crystallography from a solution of CH_2Cl_2 and *n*-hexane.

R_f = 0.33 (20% EtOAc/*n*-hexane).

dr 93:7.

Mp = 78-80 °C.

$[\alpha]_D^{22}$ -10.4 (*c* 0.86, $CHCl_3$).

IR (neat): ν_{max} 3242 (sp C-H str.), 3064, 2930, 2117(C≡C str), 1740 (C=O str.), 1606, 1455, 1338 (S=O str.), 1147 (S=O str.), 928 (C-F str.), 726, 697 cm^{-1}.

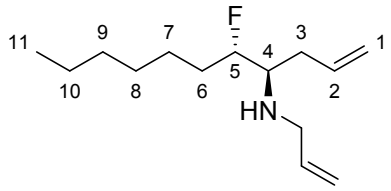
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.2 Hz, 2H, *o*-Ar-*H*), 7.39 – 7.27 (m, 3H, *m,p*-Ar-*H*), 4.77 (d, *J* = 15.2 Hz, 1H, C*H*HPh), 4.36 (d, *J* = 15.2 Hz, 1H, C*H*HPh), 4.08 – 3.88 (m, 2H, H-4, H-5), 3.49 (d, *J* = 14.7 Hz, 1H, C*H*HSO$_2$), 3.08 (d, *J* = 14.7 Hz, 1H, C*H*HSO$_2$), 2.86 – 2.67 (m, 2H, H-3), 2.53 (ddd, *J* = 11.8, 10.8, 4.1 Hz, 1H, H-5'), 2.36 (ddd, *J* = 18.4, 5.0, 3.2 Hz, 1H, H-3'), 2.14 (t, *J* = 2.7 Hz, 1H, H-1), 2.09 (dd, *J* = 3.7, 3.7 Hz, 1H, H-4'), 2.07 – 2.00 (m, 1H, H-6'), 1.93 (d, *J* = 18.4 Hz, 1H, H-3'), 1.67 (ddd, *J* = 13.7, 9.2, 4.4 Hz, 1H, H-5'), 1.70 – 1.55 (m, 2H, H-6'), 1.42 (ddd, *J* = 12.9, 9.3, 3.8 Hz, 1H, H-6'), 1.39 – 1.15 (m, 8H, H-7, H-8, H-9, H-10), 1.13 (s, 3H, H-8'), 0.86 (t, *J* = 7.1 Hz, 3H, H-11), 0.84 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.1 (C-2'), 136.8 (*ipso-C*), 129.4 (*o*-C), 128.7 (*m*-C), 128.2 (*p*-C), 95.4 (d, $^1J_{C,F}$ = 173.2 Hz, C-5), 81.5 (C-2), 71.9 (C-1), 60.1 (d, $^2J_{C,F}$ = 25.6 Hz, C-4), 58.6 (C-1'), 50.5 (*C*H$_2$SO$_2$), 49.0 (*C*H$_2$Ph), 47.8 (C-7'), 42.9 (C-4'), 42.6 (C-3'), 32.2 (d, $^2J_{C,F}$ = 20.0 Hz, C-6), 31.6 (C-8, C-9 or C-10), 28.8 (C-8, C-9 or C-10), 27.0 (C-6'), 25.2 (d, $^3J_{C,F}$ = 2.9 Hz, C-7), 25.1 (C-5'), 22.5 (C-8, C-9 or C-10), 20.1 (C-8'), 19.7 (C-8'), 18.3 (d, $^3J_{C,F}$ = 5.8 Hz, C-3), 14.0 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -124.62.

HRMS (ESI): *m/z*: calculated for $C_{28}H_{40}SO_3NFNa$ $[M+Na]^+$: 512.2611, found: 512.2614.

(4*R*,5*S*)-*N*-Allyl-5-fluoroundec-1-en-4-amine (2f)



The title compound was prepared according to General procedure 1, using octanal (70.4 μL, 0.45 mmol), Jørgensen (*S*)-catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), allylamine (44.9 μL, 0.60 mmol) and pinacol allylboronate (112.4 μL, 0.60 mmol) with 24 h as the reaction time for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 15% EtOAc/*n*-hexane gave the title product **2f** (49.6 mg, 73%) as an orange oil.

$\mathbf{R}_f$ = 0.41 (15% EtOAc/*n*-hexane).

dr 97:3, ee 92%.

$[\alpha]_D^{22}$ -7.0 (*c* 2.48, $CHCl_3$).

IR (neat): ν_{max} 3333 (N-H str.), 3077, 3005, 1641, 1464 (N-H bend), 914 (C-F str.), 724 cm^{-1}.

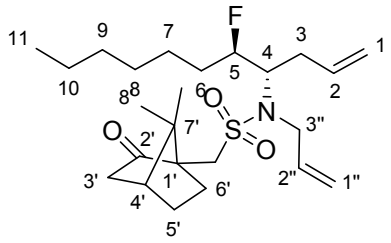
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 – 5.74 (m, 2H, H-2, H-2'), 5.21 – 5.05 (m, 2H, H-1'), 5.12 – 5.04 (m, 2H, H-1), 4.54 – 4.34 (m, 1H, H-5), 3.28 (ddd, *J* = 6.3, 1.5, 1.5 Hz, 2H, H-3'), 2.74 (dddd, *J* = 18.3 ($^2J_{H,F}$), 7.8, 4.6, 4.6 Hz, 1H, H-4), 2.36 – 2.15 (m, 2H, H-3), 1.77 – 1.58 (m, 2H, H-6), 1.52 (m, 2H, H-7), 1.41 – 1.23 (m, 6H, H-8, H-9, H-10), 0.89 (t, *J* = 7.2, Hz, 3H, H-11)

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1 (C-2'), 135.4 (C-2), 117.8 (C-1), 116.1 (C-1'), 95.6 (d, $^1J_{C,F}$ = 171.7 Hz, C-5), 59.1 (d, $^2J_{C,F}$ = 20.7 Hz, C-4), 50.6 (C-3'), 34.4 (d, $^3J_{C,F}$ = 6.0 Hz, C-3), 31.9 (C-8, C-9 or C-10), 31.3 (d, $^2J_{C,F}$ = 20.9 Hz, C-6), 29.3 (C-8, C-9 or C-10), 25.7 (d, $^3J_{C,F}$ = 3.5 Hz, C-7), 22.7 (C-8, C-9 or C-10), 14.2 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -126.68 (major diastereomer), -129.68 (minor diastereomer). Ratio = 97:3.

HRMS (ESI): *m/z*: calculated for $C_{14}H_{27}NF$ $[M+H]^+$: 228.2128, found: 228.2134.

***N*-Allyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*R*,5*S*)-5-fluoroundec-1-en-4-yl)methanesulfonamide (for ee of 2f)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2f** (20.4 mg, 0.0879 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the title product (24.9 mg, 63%) as a yellow oil.

R$_f$ = 0.46 (20% EtOAc/*n*-hexane).

dr 4:96.

$[\alpha]_D^{22}$ -12.4 (*c* 0.91, $CHCl_3$).

IR (neat): ν_{max} 3079, 2925, 1745 (C=O str.), 1456, 1336 (S=O str.), 1144 (S=O str.), 919 (C-F str.) cm^{-1}.

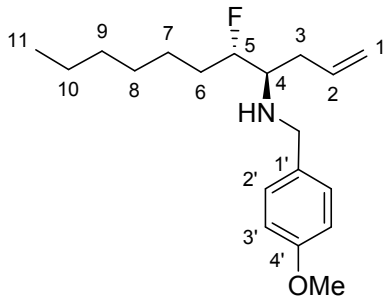
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (dddd, *J* = 17.0, 10.1, 6.8, 6.8 Hz, 1H, H-2"), 5.88 – 5.74 (m, 1H, H-2), 5.31 (ddd, *J* = 17.0, 1.5, 1.5 Hz, 1H, *trans*-H-1"), 5.21 (dd, *J* = 10.1, 1.1 Hz, 1H, *cis*-H-1"), 5.19 (dd, *J* = 17.1, 1.5 Hz, 1H, *trans*-H-1) 5.12 (d, *J* = 10.1 Hz, 1H, *cis*-H-1), 4.73 – 4.53 (m, 1H, H-5), 4.00 – 3.89 (m, 1H, H-4), 3.83 (dddd, *J* = 16.0, 6.8, 1.3, 1.3 Hz, 2H, H-3"), 3.35 (d, *J* = 14.6 Hz, 1H, C*H*HSO_2), 2.89 (d, *J* = 14.6 Hz, 1H, C*H*HSO_2), 2.59 – 2.41 (m, 3H, H-3, H-5'), 2.36 (ddd, *J* = 18.5, 4.9, 3.2 Hz, 1H, H-3'), 2.08 (dd, *J* = 4.0, 4.0 Hz, 1H, H-4'), 2.06 – 1.98 (m, 1H, H-6'), 1.92 (d, *J* = 18.4 Hz, 1H, H-3'), 1.77 – 1.46 (m, 3H, H-6, H-5'), 1.45 – 1.37 (m, 1H, H-6'), 1.36 – 1.23 (m, 8H, H-7, H-8, H-9, H-10), 1.12 (s, 3H, H-8'), 0.89 (t, *J* = 7.0 Hz, 3H, H-11), 0.85 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.1 (C-2'), 135.22 (C-2"), 135.17 (C-2), 118.8 (C-1"), 118.2 (C-1), 96.9 (d, $^1J_{C,F}$ = 175.2 Hz, C-5), 60.8 (d, $^2J_{C,F}$ = 22.7 Hz, C-4), 58.7 (C-1'), 51.1 (*C*H_2SO_2), 47.7 (C-7'), 47.3 (C-3"), 42.8 (C-4'), 42.6 (C-3'), 32.8 (d, $^2J_{C,F}$ = 21.1 Hz, C-6), 31.7 (C-8), 31.5 (d, $^3J_{C,F}$ = 4.5 Hz, C-3), 29.0 (C-9), 27.0 (C-6'), 25.4 (d, $^3J_{C,F}$ = 3.7 Hz, C-7), 25.2 (C-5'), 22.6 (C-10), 20.2 (C-8'), 19.8 (C-8'), 14.1 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -127.02 (minor diastereomer), -127.48 (major diastereomer). Ratio = 4:96.

HRMS (ESI): *m/z*: calculated for $C_{24}H_{40}SO_3NFNa$ $[M+Na]^+$: 464.2605, found: 464.2606.

(4*R*,5*S*)-5-Fluoro-*N*-(4-methoxybenzyl)undec-1-en-4-amine (2g)



The title compound was prepared according to General procedure 1, using octanal (70.4 μL, 0.45 mmol), Jørgensen (*S*)-catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), 4-methoxybenzylamine (78.0 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol), with 24 h reaction time for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product **2g** (62.6 mg, 69%) as a yellow oil.

$\mathbf{R}_f$ = 0.25 (10% EtOAc/*n*-hexane).

dr 98:2, ee 86%.

$[\alpha]_D^{22}$ -9.8 (*c* 0.89, $CHCl_3$).

IR (neat): ν_{max} 3074, 2998, 2924, 1639 (C=C str.), 1611, 1463 (N-H str.), 1441, 1300 (CH_3 bend), 914 (C-F str.), 823 cm^{-1}.

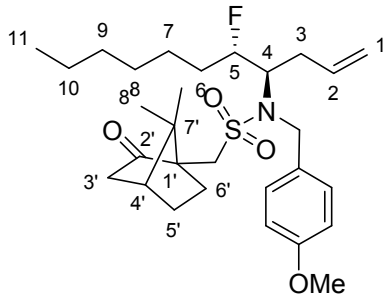
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.8 Hz, 2H, H-2'), 6.84 (d, J = 8.7 Hz, 2H, H-3'), 5.90 – 5.72 (m, 1H, H-2), 5.11 (ddd, J = 16.6, 1.5, 1.2 Hz, 1H, *trans*-H-1), 5.08 (ddd, J = 10.7, 1.2, 1.0 Hz, 1H, *cis*-H-1), 4.45 (dddd, J = 48.3 ($^2J_{H,F}$), 9.4, 4.5, 3.1 Hz, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.75 (d, J = 1.9 Hz, 2H, CH_2Ph), 2.74 (dddd, J = 17.0, 7.6, 4.6, 4.6 Hz, 1H, H-4), 2.38 – 2.14 (m, 2H, H-3), 1.76 – 1.45 (m, 2H, H-6), 1.44 – 1.22 (m, 8H, H-7, H-8, H-9, H-10), 0.88 (t, J = 7.0 Hz, 3H, H-11).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 (C-4'), 135.3 (C-2), 132.6 (C-1'), 129.4 (C-2'), 117.7 (C-11), 113.8 (C-3'), 95.6 (d, $^1J_{C,F}$ = 171.6 Hz, C-5), 58.9 (d, $^2J_{C,F}$ = 21.1 Hz, C-4), 55.3 (OCH_3), 51.3 (*C*H_2Ph), 34.3 (d, $^3J_{C,F}$ = 6.0 Hz, C-3), 31.8 (C-8, C-9 or C-10), 31.2 (d, $^2J_{C,F}$ = 21.1 Hz, C-6), 29.2 (C-8, C-9 or C-10), 25.6 (d, $^3J_{C,F}$ = 3.1 Hz, C-7), 22.6 (C-8, C-9 or C-10), 14.1 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.98 (major diastereomer), -129.64 (minor diastereomer). Ratio = 98:2.

HRMS (ESI): *m/z*: calculated for $C_{19}H_{31}ONF$ $[M+H]^+$: 308.2390, found: 308.2385.

1-(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*R*,5*S*)-5-fluoroundec-1-en-4-yl)-*N*-(4-methoxybenzyl)methanesulfonamide (for ee of 2g)



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2g** (31.0 mg, 0.101 mmol) as starting material. Upon completion of the reaction, the reaction mixture was washed with saturated $NaHCO_3$ (~2 mL), then concentrated in vacuo. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (29.0 mg, 55%) as a yellow oil.

R_f = 0.11 (10% EtOAc/*n*-hexane).

dr 7:93.

$[\alpha]_D^{23}$ -1.2 (*c* 1.3, $CHCl_3$).

IR (neat): ν_{max} 3075, 2927, 1745 (C=O str.), 1642 (C=C str.), 1611, 1456, 1375 (CH_3 bend), 1335 (S=O str.), 1145 (S=O str.), 918 (C-F str.), 846 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (ddd, *J* = 8.8, 2.8, 2.1 Hz, 2H, *m*-Ar-*H*), 6.86 (ddd, *J* = 8.8, 3.0, 2.0 Hz, 2H, *o*-Ar-*H*), 5.91 – 5.76 (m, 1H, H-2), 5.20 (ddd, *J* = 17.1, 1.5, 1.5 Hz, 1H, *trans*-H-1), 5.15 (ddd, *J* = 10.1, 1.2, 1.2 Hz, 1H, *cis*-H-1), 4.54 (d, *J* = 14.9 Hz, 1H, C*H*HPh), 4.46 – 4.24 (m, 1H, H-5), 4.29 (d, *J* = 14.9 Hz, 1H, C*H*HPh), 4.07 – 3.93 (m, 1H, H-4), 3.79 (s, 3H, OCH_3), 3.20 (d, *J* = 14.6 Hz, 1H, C*H*HSO_2), 2.57 (d, *J* = 14.6 Hz, 1H, C*H*HSO_2), 2.63 – 2.51 (m, 2H, H-3), 2.48 (ddd, *J* = 10.1, 10.1, 5.7 Hz, 1H, H-5'), 2.33 (ddd, *J* = 18.4, 4.1, 4.1 Hz, 1H, H-3'), 2.06 (dd, *J* = 4.7, 4.2 Hz, 2H, H-4'), 2.04 – 1.96 (m, 1H, H-6'), 1.90 (d, *J* = 18.4 Hz, 1H, H-3'), 1.66 (ddd, *J* = 9.3, 4.7, 4.7 Hz, 1H, H-5'), 1.61 – 1.38 (m, 2H, H-6) 1.39 (ddd, *J* = 12.6, 9.1, 3.7 Hz, 1H, H-6'), 1.32 – 1.18 (m, 8H, H-7, H-8, H-9, H-10), 1.05 (s, 3H, H-8'), 0.87 (t, *J* = 7.0 Hz, 3H, H-11), 0.72 (s, 3H, H-8').

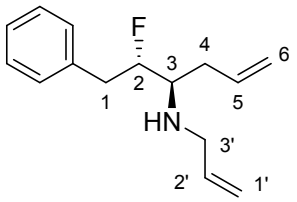
^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 159.4 (*p*-C), 135.3 (C-2), 130.9 (*m*-C), 129.1 (*ipso-C*), 118.2 (C-1), 114.0 (*o*-C), 96.7 (d, $^1J_{C,F}$ = 173.9 Hz, C-5), 61.1 (d, $^2J_{C,F}$ = 23.5 Hz, C-4), 58.5 (C-1'), 55.3 (OCH_3), 51.0 (CH_2SO_2), 47.9 (C-7'), 47.7 (CH_2Ph), 42.7 (C-4'), 42.6 (C-3'), 32.7 (d, $^2J_{C,F}$ = 20.6 Hz, C-6), 32.0 (d, $^3J_{C,F}$ = 3.6 Hz, C-3), 31.7 (C-8), 28.9 (C-9), 26.9

(C-6'), 25.4 (d, $^{3}J_{C,F}$ = 3.4 Hz, C-7), 25.1 (C-5'), 22.5 (C-10), 20.0 (C-8'), 19.6 (C-8'), 14.1 (C-11).

^{19}F NMR (377 MHz, $CDCl_3$): δ -124.27 (minor diastereomer), -124.88 (major diastereomer). Ratio = 7:93.

HRMS (ESI): *m/z*: calculated for $C_{29}H_{44}SO_4NFNa$ $[M+Na]^+$: 544.2873, found: 544.2886.

(2*S*,3*R*)-*N*-Allyl-2-fluoro-1-phenylhex-5-en-3-amine (2h)



The title compound was prepared according to General procedure 1, using hydrocinnamaldehyde (59.4 μL, 0.45 mmol), Jørgensen (*S*)-catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), allylamine (45.0 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 2.5 h as the reaction time for the fluorination reaction and 24 h reaction time for the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 15% EtOAc/*n*-hexane gave the title product (41.8 mg, 60%) as a pale-yellow oil.

R_f = 0.27 (15% EtOAc/*n*-hexane).

dr 99:1, ee 88%.

$[\alpha]_D^{22}$ -12.3 (*c* 0.43, $CHCl_3$).

IR (neat): ν_{max} 3065, 3028, 2923, 1640 (C=C str.), 1603, 1496 (N-H bend), 1454, 916 (C-F str.), 745, 699 cm^{-1}.

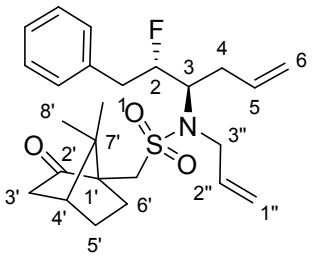
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.12 (m, 5H, Ar-*H*), 5.94 – 5.75 (m, 2H, H-5, H-2'), 5.15 (dd, *J* = 17.3, 1.5 Hz, 1H, *trans*-H-1'), 5.15 (ddd, *J* = 15.9, 1.3, 1.3 Hz, 1H, *trans*-H-6), 5.12 (dd, *J* = 11.3, 1.3, 1.3 Hz, 1H, *cis*-H-6), 5.07 (ddd, *J* = 10.2, 1.5, 1.5 Hz, 1H, *cis*-H-1'), 4.63 (dddd, *J* = 47.8 ($^{2}J_{H,F}$), 7.7, 4.7, 4.7 Hz, 1H, H-2), 3.28 (ddd, *J* = 5.9, 1.5, 1.5 Hz, 2H, H-3'), 3.10 – 2.93 (m, 2H, H-1), 2.82 (dddd, *J* = 16.1 ($^{3}J_{H,F}$), 7.3, 4.8, 4.8 Hz, 1H, H-3), 2.43 – 2.22 (m, 2H, H-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9 (d, $^{3}J_{C,F}$ = 2.3 Hz, *ipso*-*C*), 136.9 (C-1'), 134.8 (C-6), 129.3 (*m*-C), 128.5 (*o*-C), 126.5 (*p*-C), 118.1 (C-5), 116.0 (C-2'), 95.7 (d, $^{1}J_{C,F}$ = 175.3 Hz, C-2), 58.5 (d, $^{2}J_{C,F}$ = 21.1 Hz, C-3), 50.4 (C-3'), 37.7 (d, $^{2}J_{C,F}$ = 21.7 Hz, C-1), 34.2 (d, $^{3}J_{C,F}$ = 5.9 Hz, C-4).

^{19}F NMR (377 MHz, $CDCl_3$): δ -124.37 (major diastereomer), -129.29 (minor diastereomer). Ratio = 99:1.

HRMS (ESI): *m/z*: calculated for $C_{15}H_{21}NF$ $[M+H]^+$: 234.1658, found: 235.1652.

***N*-Allyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((2*S*,3*R*)-2-fluoro-1-phenylhex-5-en-3-yl)methanesulfonamide (for ee of 2h)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2h** (13.7 mg, 0.0587 mmol) as starting material. Purification by flash column chromatography eluting with 15% EtOAc/*n*-hexane gave the title product (34.4 mg, 59%) as a yellow oil.

R$_f$ = 0.21 (15% EtOAc/*n*-hexane).

dr 94:6, ee 88%.

$[\alpha]_D^{22}$ +2.8 (*c* 0.77, $CHCl_3$).

IR (neat): ν_{max} 3077, 3029, 2925, 1743 (C=O str.), 1641 (C=C str.), 1334 (S=O str.), 1150 (S=O str.), 922 (C-F str.), 747, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 2H, *m*-Ar-H), 7.27 – 7.17 (m, 3H, *o,p*-Ar-H), 5.97 (dddd, *J* = 16.9, 10.0, 6.8, 6.8 Hz, 1H, H-2''), 5.91 – 5.76 (m, 1H, H-5), 5.31 (ddd, *J* = 17.1, 1.4, 1.4 Hz, 1H, *trans*-H-1''), 5.24 (ddd, *J* = 2.1, 1.4, 1.4 Hz, 1H, *cis*-H-1''), 5.20 (ddd, *J* = 6.7, 1.3, 1.3 Hz, 1H, *cis*-H-6), 5.19 – 5.14 (m, 1H, *trans*-H-6), 4.84 (dddd, *J* = 48.7 ($^2J_{H,F}$), 9.3, 5.0, 3.5 Hz, 1H, H-2), 4.13 – 3.99 (m, 2H, H-3, H-3''), 3.83 (ddd, *J* = 15.8, 6.9, 1.2 Hz, 1H, H-3''), 3.30 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 3.09 (ddd, *J* = 35.7, 14.6, 3.5 Hz, 1H, H-1), 2.97 (ddd, *J* = 16.4, 14.7, 9.4 Hz, 1H, H-1), 2.88 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 2.67 – 2.42 (m, 3H, H-4, H-5'), 2.36 (ddd, *J* = 18.4, 3.5, 3.5 Hz, 1H, H-3'), 2.08 (dd, *J* = 4.5, 4.5 Hz, 1H, H-4'), 2.06 – 1.97 (m, 1H, H-6'), 1.92 (d, *J* = 18.4 Hz, 1H, H-3'), 1.60 (ddd, *J* = 13.9, 9.3, 4.6 Hz, 2H, H-5'), 1.41 (dddd, *J* = 12.4, 9.4, 5.1, 5.1 Hz, 1H, H-6'), 1.12 (s, 3H, H-8'), 0.85 (s, 3H, H-8').

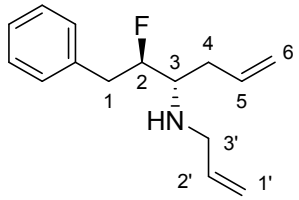
^{13}C NMR (100 MHz, $CDCl_3$): δ 215.05 (C-2'), 137.0 (d, $^3J_{C,F}$ = 2.9 Hz, *ipso-C*), 135.2 (C-2''), 135.0 (C-5), 129.2 (*m*-C), 128.6 (*o*-C), 126.8 (*p*-C), 119.1 (C-1''), 118.4 (C-6), 96.8 (d, $^1J_{C,F}$ = 178.3 Hz, C-2), 60.6 (d, $^2J_{C,F}$ = 23.3 Hz, C-3), 58.7 (C-7'), 50.9 (*C*H_2SO_2), 47.7 (C-1'),

47.4 (C-3''), 42.8 (C-4'), 42.6 (C-3'), 39.2 (d, $^{2}J_{C,F}$ = 21.2 Hz, C-1), 31.7 (d, $^{3}J_{C,F}$ = 3.9 Hz, C-4), 26.9 (C-6'), 25.2 (C-5'), 20.2 (C-8'), 19.8 (C-8').

^{19}F NMR (377 MHz, $CDCl_3$): δ -124.74 (minor diastereomer), -125.53 (major diastereomer). Ratio = 94:6.

HRMS (ESI): *m/z*: calculated for $C_{25}H_{34}SO_3NFNa$ $[M+Na]^+$: 470.2158, found: 470.2141.

(2*R*,3*S*)-*N*-Allyl-2-fluoro-1-phenylhex-5-en-3-amine (*ent*-2h)



The title compound was prepared according to General procedure 1, using phenylpropanal (59.0 μL, 0.45 mmol), Jørgensen (*R*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), allylamine (44.9 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the title product (32.5 mg, 46%) as a yellow oil. The ^{1}H, ^{13}C and ^{19}F NMR spectra of *ent*-**2h** were identical to that of **2h**.

R_f = 0.42 (20% EtOAc/*n*-hexane).

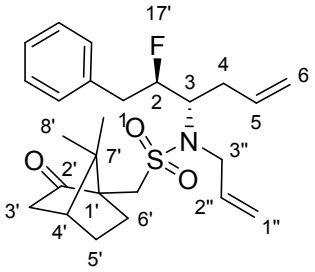
dr = 97:3, ee 88%.

$[\alpha]_D^{26}$ +27.8 (*c* 0.146, $CHCl_3$).

IR (neat): ν_{max} 3065, 3028, 2923, 1640 (C=C str.), 1496 (N-H bend), 1441, 994, 917 (C-F str.), 744, 699 cm^{-1}.

HRMS (ESI): *m/z*: calculated for $C_{15}H_{20}NF$ $[M+H]^+$: 234.1658, found: 234.1661.

***N*-Allyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((2*R*,3*S*)-2-fluoro-1-phenylhex-5-en-3-yl)methanesulfonamide (for ee of *ent*-2h)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine *ent*-**2h** (15.0 mg, 0.0600 mmol) as starting material. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the product (15.2 mg, 57%) as a yellow oil.

R$_f$ = 0.40 (20% EtOAc/*n*-hexane).

dr = 94:6.

$[\alpha]_D^{23}$ +97.0 (*c* 0.14, $CHCl_3$).

IR (neat): ν_{max} 3076, 3028, 2957, 1744 (C=O str.), 1641 (C=C str.), 1335 (S=O str.), 1145 (S=O str.), 993, 923(C-F str.), 746, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 2H, *m*-Ar-*H*), 7.26 – 7.20 (m, 3H, *o,p*-Ar-*H*), 6.02 – 5.92 (m, 1H, H-2"), 5.92 – 5.83 (m, 1H, H-5), 5.31 (dq, *J* = 17.1, 1.4 Hz, 1H, *trans*-H-1"), 5.24 (p, *J* = 1.3 Hz, 1H, *cis*-H-1"), 5.21 (dt, *J* = 3.4, 1.0 Hz, 1H, *cis*-H-1), 5.19 – 5.16 (m, 1H, *trans*-H-6), 4.84 (ddt, *J* = 48.7, 8.9, 4.3 Hz, 1H, H-2), 4.06 (ddt, J = 19.3, 10.3, 4.5 Hz, 1H, H-3), 4.00 – 3.84 (m, 2H, H-3"), 3.43 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 3.16 – 3.01 (m, 1H, H-1), 3.01 – 2.85 (m, 1H, H-1), 2.70 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 2.65 – 2.44 (m, 3H, H-4, H-5'), 2.41 – 2.31 (m, 1H, H-3'), 2.06 (dt, *J* = 7.9, 3.7 Hz, 1H. H-4'), 2.05 – 1.96 (m, 1H, H-6'), 1.92 (d, *J* = 18.4 Hz, 1H, H-3'), 1.68 – 1.54 (m, 2H, H-5'), 1.45 – 1.35 (m, 1H, H-6'), 1.09 (s, 3H, H-8'), 0.82 (s, 3H, H-8').

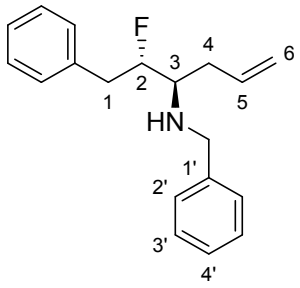
^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 136.9 (d, $J_{C,F}$ = 3.0 Hz, *ipso-C*) 135.02 (C-2"), 135.0 (C-5), 129.2 (*m-C*), 128.6 (*o-C*), 126.8 (*p-C*), 119.1 (C-1"), 118.4 (C-6), 97.2 (d, $J_{C,F}$ =

177.0 Hz, C-2), 60.4 (d, $J_{C,F}$ = 23.0 Hz, C-3), 58.7 (C-7'), 51.0 (CH_2SO_2), 47.7 (C-1'), 47.6 (C-3''), 42.9 (C-4'), 42.6 (C-3'), 39.3 (d, $J_{C,F}$ = 21.0 Hz, C-1), 32.0 (d, $J_{C,F}$ = 5.0 Hz, C-4), 26.9 (C-6'), 25.3 (C-5'), 20.1 (C-8'), 19.8 (C-7').

^{19}F NMR (377 MHz, $CDCl_3$): δ -124.53 (major diastereomer), -125.33 (minor diastereomer). Ratio = 94:6.

HRMS (ESI): *m/z*: calculated for $C_{25}H_{34}SO_3NFNa$ $[M+Na]^+$: 470.2158, found: 470.2141.

(2*S*,3*R*)-*N*-Benzyl-2-fluoro-1-phenylhex-5-en-3-amine (2i)



The title compound was prepared according to General procedure 1, however using, 3-phenylpropanal (59.0 μL, 0.45 mmol), Jørgensen (*S*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (51.2 mg, 60%) as a yellow oil.

R_f = 0.39 (10% EtOAc/*n*-hexane).

dr = 99:1 ee 92%.

$[\alpha]_D^{23}$ -11.6 (*c* 0.54, $CHCl_3$).

IR (neat): ν_{max} 3084, 3028, 2923, 1639 (C=C str.), 1603, 1495 (N-H bend), 1453, 1074, 916 (C-F str.), 843, 740, 698 cm^{-1}.

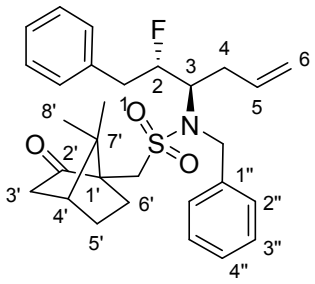
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.18 (m, 10H, Ar-*H*), 5.94 – 5.65 (m, 1H, H-5), 5.17 – 5.12 (m, 1H, *trans*-H-6), 5.13 – 5.09 (m, 1H, *cis*-H-6), 4.84 – 4.44 (m, 1H, H-2), 3.82 (s, 2H, CH_2Ph), 3.08 – 3.03 (m, 1H, H-1), 2.99 (d, *J* = 6.2 Hz, 1H, H-1), 2.85 (dddd, *J* = 15.1, 7.3, 4.9,4.9 Hz, 1H, H-3), 2.49 – 2.23 (m, 2H, H-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4 (C-1'), 138.0 (d, $^3J_{C,F}$ = 3.0 Hz, *ipso*-*C*), 134.7 (C-5), 129.3 (*o, m*-Ar-*C*H), 128.44 (*o, m*-Ar-*C*H), 128.41 (*o, m*-Ar-*C*H), 128.2 (*o, m*-Ar-*C*H), 127.0 (*p*-Ar-*C*H), 126.5 (*p*-Ar-*C*H), 118.1(C-6), 95.7 (d, $^1J_{C,F}$ = 174.0 Hz, C-2), 58.5 (d, $J_{C,F}$ = 21.0 Hz, C-3), 51.8 (CH_2Ph), 37.7 (d, $^2J_{C,F}$ = 22.0 Hz, C-1), 34.2 (d, $^3J_{C,F}$ = 6.0 Hz, C-4).

^{19}F NMR (377 MHz, $CDCl_3$): δ -123.51 (major diastereomer), -129.20 (minor diastereomer). Ratio = 99:1.

HRMS (ESI): *m/z*: calculated for $C_{19}H_{23}NF$ $[M+H]^+$: 284.1815, found: 284.1812.

_N_-Benzyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-_N_-((2_S_,3_R_)-2-fluoro-1-phenylhex-5-en-3-yl)methanesulfonamide (for ee of 2i)



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2i** (16.2 mg, 0.0572 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the title product (10.6 mg, 37%) as a dark yellow wax.

R_f = 0.30 (20% EtOAc/*n*-hexane).

dr 96:4.

$[\alpha]_D^{23}$ -18.3 (*c* 0.41, $CHCl_3$).

IR (neat): ν_{max} 3030, 2926, 1743 (C=O str.), 1641 (C=C str.), 1604, 1455, 1338 (S=O str.), 1147 (S=O str.), 920 (C-F str.), 749, 727, 699 cm^{-1}.

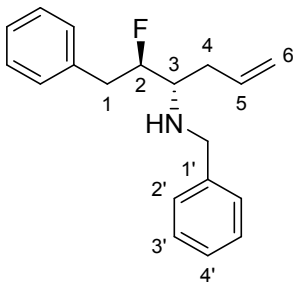
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 8.1, 1.2 Hz, 2H, *o*-Ar-*H*), 7.40 – 7.14 (m, 6H, *m,p*-Ar-*H*, H-3", H-4"), 6.97 (dd, *J* = 8.6, 1.6 Hz, 2H, H-2"), 5.93 – 5.77 (m, 1H, H-5), 5.23 (ddd, *J* = 17.1, 2.9, 1.5 Hz, 1H, *trans*-H-6), 5.18 (ddd, *J* = 9.8, 2.4, 1.3 Hz, 1H, *cis*-H-6), 4.67 (d, *J* = 15.1 Hz, 1H, C*H*HPh), 4.51 (dddd, *J* = 48.7, 9.5, 5.9, 3.0 Hz, 1H, H-2), 4.33 (d, *J* = 15.1 Hz, 1H, C*H*HPh), 4.11 (ddd, *J* = 15.5, 10.7, 5.8 Hz, 1H, H-3), 3.23 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 3.09 – 2.91 (m, 1H, H-1), 2.80 (td, *J* = 15.1, 9.9 Hz, 1H, H-1), 2.69 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 2.66 – 2.54 (m, 2H, H-4), 2.48 (ddd, *J* = 14.7, 10.8, 4.1 Hz, 1H, H-5'), 2.35 (ddd, *J* = 18.3, 4.0, 4.0 Hz, 1H, H-3'), 2.07 (dd, *J* = 4.3, 4.3 Hz, 1H, H-4'), 2.05 – 1.97 (m, 1H, H-6'), 1.92 (d, *J* = 18.4 Hz, 1H, H-3'), 1.65 (ddd, *J* = 13.7, 9.2, 4.3 Hz, 1H, H-5'), 1.46 – 1.36 (m, 1H, H-6'), 1.07 (s, 3H, H-8'), 0.77 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 137.1, 137.0 (d, $^3J_{C,F}$ = 2.1 Hz, *ipso*-*C*), 135.1 (C-5), 129.6 (*o*-C), 129.2 (C-2''), 128.8 (C-3''), 128.4 (m-C), 128.1 (*p*-C), 126.6 (C-4''), 118.5 (C-6), 96.3 (d, $^1J_{C,F}$ = 177.4 Hz., C-2), 61.1 (d, $^2J_{C,F}$ = 24.3 Hz, C-3), 58.6 (C-1'), 50.7 (CH_2SO_2), 48.5 (CH_2Ph), 47.73 (C-7'), 42.8 (C-4'), 42.6 (C-3'), 39.1 (d, $^2J_{C,F}$ = 21.1 Hz, C-1), 32.2 (d, $^3J_{C,F}$ = 4.1 Hz, C-4), 26.9 (C-6'), 25.2 (C-5'), 20.0 (C-8'), 19.7 (C-8').

^{19}F NMR (377 MHz, $CDCl_3$): δ -123.11 (minor diastereomer), -123.97 (major diastereomer). Ratio = 4:96.

HRMS (ESI): *m/z*: calculated for $C_{29}H_{37}SO_3NF$ $[M+Na]^+$: 520.2478, found: 520.2490.

(2*S*,3*R*)-*N*-Benzyl-2-fluoro-1-phenylhex-5-en-3-amine (*ent*-2i)



The title compound was prepared according to General procedure 1, using, phenylpropanal (59. μL, 0.45 mmol), Jørgensen (*R*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 5% EtOAc/*n*-hexane gave the title product (50.7 mg, 60%) as a colorless oil. The ^{1}H, ^{13}C and ^{19}F NMR spectra of *ent*-**2i** were identical to that of **2i**.

R_f = 0.30 (5% EtOAc/*n*-hexane).

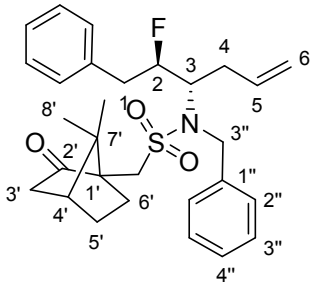
dr = 98:2, ee 92%.

$[\alpha]_D^{27}$ +11.7 (*c* 0.086, $CHCl_3$).

IR (neat): ν_{max} 3063, 3027, 2924, 1745, 1640 (C=C str.), 1495 (N-H bend), 1453, 1145, 1028, 994, 916 (C-F str.), 729, 698 cm^{-1}.

HRMS (ESI): *m/z*: calculated for $C_{19}H_{23}NF$ $[M+H]^+$: 284.1815, found: 284.1810.

***N*-Benzyl-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((2*R*,3*S*)-2-fluoro-1-phenylhex-5-en-3-yl)methanesulfonamide (for ee of *ent*-2i)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine *ent*-**2i** (20.0 mg, 0.070 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (19.8 mg, 57%) as a colorless oil.

R$_f$ = 0.27 (30% EtOAc/*n*-hexane).

dr = 96:4.

$[\alpha]_D^{27}$ +39.8 (*c* 0.11, $CHCl_3$).

IR (neat): ν_{max} 3063, 3028, 2956, 1745 (C=O str.), 1640 (C=C str.), 1454, 1340 (S=O str.), 1146 (S=O str.), 994, 917 (C-F str.), 698 cm^{-1}.

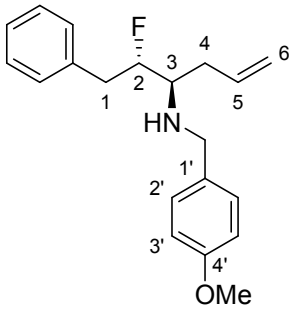
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.43 (m, 2H), 7.42 – 7.27 (m, 3H), 7.28 – 7.14 (m, 3H), 7.05 – 6.94 (m, 2H), 5.89 (dddd, *J* = 16.7, 10.3, 8.0, 6.0 Hz, 1H, H-5), 5.23 – 5.15 (m, 2H, H-6), 4.64 (ddd, *J* = 9.4, 5.6, 3.6 Hz, 1H, C*H*HPh), 4.49 (dd, *J* = 28.0, 15.2 Hz, 2H, H-2), 4.20 – 4.00 (m, 1H, C*H*HPh), 3.34 (d, *J* = 14.5 Hz, 1H, H-3), 3.00 (ddd, *J* = 36.0, 14.6, 3.6 Hz, 1H, C*H*HSO$_2$), 2.79 (td, *J* = 15.1, 9.5 Hz, 1H, H-1), 2.65 (ddq, *J* = 15.2, 6.1, 2.5, 2.1 Hz, 1H, H-1), 2.59 (s, 1H, C*H*HSO$_2$), 2.53 – 2.43 (m, 1H, H-4), 2.35 (dt, *J* = 18.4, 4.1 Hz, 1H, H-5'), 2.06 (t, *J* = 4.2 Hz, 1H, H-3'), 2.03 – 1.95 (m, 1H, H-4'), 1.91 (d, *J* = 18.4 Hz, 1H, H-6'), 1.69 – 1.53 (m, 2H, H-3', H-5'), 1.45 – 1.34 (m, 1H, H-6'), 1.06 (s, 3H, H-8'), 0.77 (s, 3H. H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 137.1 (C-1''), 137.0 (d, $^3J_{C,F}$ = 2.0 Hz, *ipso*-*C*), 135.1 (C-5), 129.6 (*o*-*C*), 129.2 (C-2''), 128.7 (C-3''), 128.4 (*m*-*C*), 128.1 (*p*-*C*), 126.6 (C-4''), 118.4 (C-6), 96.6 (d, $^1J_{C,F}$ = 176.0 Hz, C-2), 60.9 (d, $^2J_{C,F}$ = 23 Hz, C-3), 58.6 (C-1'), 50.7 (CH_2SO_2), 48.7 (CH_2Ph), 47.6 (C-7'), 42.9 (C-4'), 42.6 (C-3'), 39.2 (d, $^2J_{C,F}$ = 21.0 Hz, C-1), 32.5 (d, $^3J_{C,F}$ = 4.0 Hz, C-4), 26.9 (C-6'), 25.4 (C-5'), 20.0 (C-8'), 19.7 (C-8').

^{19}F NMR (376 MHz, $CDCl_3$): δ -123.08 (major diastereomer), -123.96 (minor diastereomer). Ratio = 96:4.

HRMS (ESI): *m/z*: calculated for $C_{29}H_{36}NO_3FNaS$ $[M+Na]^+$: 520.2478, found: 520.2476.

(2*S*,3*R*)-2-Fluoro-*N*-(4-methoxybenzyl)-1-phenylhex-5-en-3-amine (2j)



The title compound was prepared according to General procedure 1, using hydrocinnamaldehyde (59.4 μL, 0.45 mmol), Jørgensen (*S*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), 4-methoxybenzylamine (78.0 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 2.5 h as the reaction time for the fluorination reaction and 24 h as the reaction time for the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 15% EtOAc/*n*-hexane gave the title product (58.5 mg, 60%) as a pale-yellow oil.

R_f = 0.26 (15% EtOAc/*n*-hexane).

dr 98:2, ee 92%.

$[\alpha]_D^{23}$ -9.7 (*c* 1.5, $CHCl_3$).

IR (neat): ν_{max} 3063, 3028, 2928, 1639 (C=C str.), 1610, 1497 (N-H bend), 1454, 1245 (CH_3 bend), 915 (C-F str.), 699, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 2H, *m*-Ar-*H*), 7.26 – 7.22 (m, 3H, *o,p*-Ar-*H*), 7.21 (dd, *J* = 8.7, 2.1 Hz, 2H, H-3'), 6.86 (dd, *J* = 8.7, 2.1 Hz, 2H, H-2'), 5.87 – 5.72 (m, 1H, H-5), 5.13 (ddd, *J* = 11.4, 1.9, 1.1 Hz, 1H, *cis*-H-6), 5.13 (ddd, *J* = 15.7, 1.4, 1.1 Hz, 1H, *trans*-H-6), 4.72 – 4.53 (m, 1H, H-2), 3.80 (s, 3H, OCH_3), 3.75 (s, 2H, CH_2Ph), 3.11 – 3.00

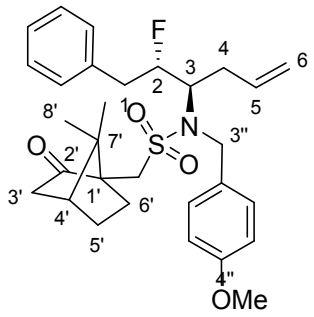
(m, 1H, H-1), 2.98 (d, J = 6.1 Hz, 1H, H-1), 2.83 (dddd, J = 15.1, 7.3, 4.9, 4.9 Hz, 1H, H-3), 2.47 – 2.34 (m, 1H, H-4), 2.29 (ddddd, J = 14.4, 7.3, 7.3, 2.4, 1.3 Hz, 1H, H-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 (C-4'), 138.0 (d, $^3J_{C,F}$ = 2.5 Hz, *ipso*-*C*), 134.8 (C-5), 132.5 (C-1'), 129.4 (C-3'), 129.3 (*m*-C), 128.4 (*o*-C), 126.5 (*p*-C), 118.1 (C-6), 113.8 (C-2'), 95.7 (d, $^1J_{C,F}$ = 175.3 Hz, C-2), 58.4 (d, $^2J_{C,F}$ = 21.0 Hz, C-3), 55.3 (OCH_3), 51.2 (CH_2Ph), 37.7 (d, $^2J_{C,F}$ = 21.2 Hz, C-1), 34.1 (d, $^3J_{C,F}$ = 6.2 Hz, C-4).

^{19}F NMR (377 MHz, $CDCl_3$): δ -122.75 (major diastereomer), -128.38 (minor diastereomer). Ratio = 98:2.

HRMS (ESI): *m/z*: calculated for $C_{20}H_{25}NOF$ $[M+H]^+$: 314.1920, found: 314.1934.

1-(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((2*S*,3*R*)-2-fluoro-1-phenylhex-5-en-3-yl)-*N*-(4-methoxybenzyl)methanesulfonamide (for ee of 2j)



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2j** (20.4 mg, 0.0651 mmol) as starting material. Upon completion of the reaction, the reaction mixture was washed with saturated $NaHCO_3$ (~2 mL), then concentrated in vacuo. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (14.3 mg, 42%) as a yellow oil.

R_f = 0.23 (20% EtOAc/*n*-hexane).

dr 4:96.

$[\alpha]_D^{23}$ -14.8 (*c* 0.66, $CHCl_3$).

IR (neat): ν_{max} 3029, 2935, 1743 (C=O str.), 1642 (C=C str.), 1611, 1455, 1374 (CH_3 bend), 1333 (S=O str.), 1147 (S=O str.), 917 (C-F str.), 844, 750, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (ddd, J = 8.7, 3.0, 2.1 Hz, 2H, H-3"), 7.27 – 7.14 (m, 3H, *m,p*-Ar-*H*), 6.97 (d, J = 6.9 Hz, 2H, *o*-Ar-*H*), 6.87 (ddd, J = 8.6, 2.9, 1.9 Hz, 2H, H-2"), 5.93 – 5.76 (m, 1H, H-5), 5.24 (ddd, J = 17.1, 1.5, 1.5 Hz, 1H, *trans*-H-6), 5.18 (ddd, J = 10.2, 1.0, 0.8 Hz, 1H, *cis*-H-6), 4.62 (d, J = 15.0 Hz, 1H, C*H*HPh), 4.48 (dddd, J = 48.7 ($^2J_{H,F}$), 9.7, 6.3, 2.8 Hz, 1H, H-2), 4.27 (d, J = 15.0 Hz, 1H, C*H*HPh), 4.10 (dddd, J = 15.0

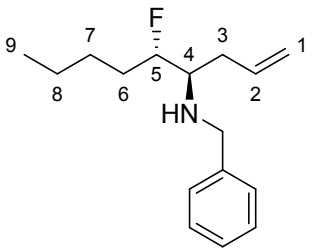
($^3J_{H,F}$), 15.0, 6.3, 4.7 Hz, 1H, H-3), 3.80 (s, 3H, OCH_3), 3.24 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 2.99 (ddd, *J* = 38.9, 14.7, 2.9 Hz, 1H, H-1), 2.79 (td, *J* = 15.2, 9.9 Hz, 1H, H-1), 2.69 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 2.69 – 2.54 (m, 2H, H-4), 2.49 (ddd, *J* = 14.9, 12.0, 3.9 Hz, 1H, H-5'), 2.35 (ddd, *J* = 18.4, 5.0, 3.3 Hz, 1H, H-3'), 2.08 (t, *J* = 4.2 Hz, 1H, H-4'), 2.02 (dddd, *J* = 12.1, 4.4, 4.4, 2.6 Hz, 1H, H-6'), 1.92 (d, *J* = 18.4 Hz, 1H, H-3'), 1.65 (ddd, *J* = 13.6, 9.2, 4.3 Hz, 1H, H-5'), 1.47 – 1.36 (m, 1H, H-6'), 1.08 (s, 3H, H-8'), 0.78 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 159.5 (C-4''), 137.2 (d, $^3J_{C,F}$ = 2.2 Hz*, ipso-C*), 135.1 (C-5), 130.9 (C-3''), 129.2 (*o*-C), 129.0 (C-1''), 128.3 (*m*-C), 126.5 (*p*-C), 118.5 (C-6), 114.2 (C-2''), 96.2 (d, $^1J_{C,F}$ = 176.7 Hz, C-2), 61.0 (d, $^2J_{C,F}$ = 24.5 Hz, C-3), 58.6 (C-1'), 55.3 (OCH_3), 50.7 (CH_2SO_2), 47.9 (C-7'), 47.7 (CH_2Ph), 42.8 (C-4'), 42.6 (C-3'), 39.1 (d, $^2J_{C,F}$ = 20.9 Hz, C-1), 32.2 (d, $^3J_{C,F}$ = 3.8 Hz, C-4), 26.9 (C-6'), 25.2 (C-5'), 20.0 (C-8'), 19.7 (C-8').

^{19}F NMR (377 MHz, $CDCl_3$): δ -121.86 (minor diastereomer), -122.69 (major diastereomer). Ratio = 4:96.

HRMS (ESI): *m/z*: calculated for $C_{30}H_{38}SO_4NFNa$ $[M+Na]^+$: 550.2403, found: 550.2424.

(4*R*,5*S*)-*N*-Benzyl-5-fluorononon-1-en-4-amine (2k)



The title compound was prepared according to General procedure 1, however hexanal (55.3 μL, 0.45 mmol), Jørgensen (*S*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (37.1 mg, 50%) as a yellow oil.

R_f = 0.39 (10% EtOAc/*n*-hexane).

dr = 98:2, ee 86%.

$[\alpha]_D^{23}$ -79.7 (*c* 0.08, $CHCl_3$).

IR (neat): ν_{max} 3065, 3027, 2956, 2860, 1641 (C=C str.), 1466 (N-H bend), 1382, 985, 916 (C-F str.), 697 cm^{-1}.

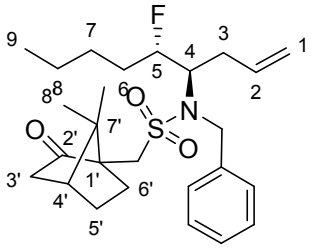
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.20 (m, 5H, Ar-*H*), 5.88 – 5.73 (m, 1H, H-2), 5.17 – 5.05 (m, 2H, H-1), 4.46 (dddd, *J* = 48.4, 9.3, 4.5, 3.2 Hz, 1H, H-5), 3.82 (d, *J* = 1.9 Hz, 2H, CH_2Ph), 2.76 (dddd, *J* = 17.0, 7.6, 4.7, 4.7 Hz, 1H, H-4), 2.41 – 2.17 (m, 2H, H-3), 1.79 – 1.61 (m, 2H, H-6), 1.56-1.52 (m, 2H, H-7), 1.41 – 1.28 (m, 2H, H-8), 0.91 (t, *J* = 7.1 Hz, 3H, H-9).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (*ipso*-*C*), 135.2 (C-2), 128.4 (*m*-*C*), 128.2 (*o*-*C*), 127.0 (*p*-*C*), 117.8 (C-1), 95.6 (d, $^1J_{C,F}$ = 170.0 Hz, C-5), 59.0 (d, $^2J_{C,F}$ = 21.0 Hz, C-4), 51.9 (CH_2Ph), 34.3 (d, $^3J_{C,F}$ = 6.0 Hz, C-3), 30.9 (d, $^2J_{C,F}$ = 21.0 Hz, C-6), 27.8 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 22.6 (C-8), 14.0 (C-9).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.83 (major diastereomer), -129.52 (minor diastereomer). Ratio = 98:2.

HRMS (ESI): *m/z*: calculated for $C_{16}H_{25}NF$ $[M+H]^+$: 250.1971, found: 250.1983.

_N_-Benzyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-_N_-((4_R_,5_S_)-5-fluoronon-1-en-4-yl)methanesulfonamide (for ee of 2k)



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2k** (20.0 mg, 0.0800 mmol) as starting material. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the product (21.6 mg, 68%) as a yellow oil.

R_f = 0.28 (10% EtOAc/*n*-hexane).

dr = 93:7.

$[\alpha]_D^{23}$ -32.8 (*c* 0.17, $CHCl_3$).

IR (neat): ν_{max} 3073, 2957, 2872, 1746 (C=O str.), 1642 (C=C str.), 1456, 1340 (S=O str.), 1147 (S=O str.), 1050, 920 (C-F str.), 875 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.42 (m, 2H, *o*-Ar-*H*), 7.32 (ddd, *J* = 12.8, 8.0, 6.2 Hz, 3H, *m, p*-Ar-*H*), 5.85 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H, H-2), 5.25 – 5.17 (m, 1H, *trans*-H-1), 5.17 – 5.13 (m, 1H, *cis*-H-1), 4.59 (d, *J* = 15.0 Hz, 1H, C*H*HPh), 4.46 – 4.25 (m, 1H, H-5), 4.35 (d, *J* = 15.1 Hz, 1H, C*H*HPh), 4.03 (ddt, *J* = 18.3, 10.2, 5.2 Hz, 1H, H-4), 3.21 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 2.55 (d, *J* = 14.5, 1H, C*H*HSO$_2$), 2.54 – 2.42 (m, 1H, H-5'), 2.38 – 2.25 (m, 1H, H-3'), 2.05 (t, *J* = 4.6 Hz, 1H, H-4'), 2.03 – 1.95 (m, 1H, H-6'), 1.90 (d, *J* = 18.4 Hz, 1H, H-3'), 1.68 (t, *J* = 5.1 Hz, 1H, H-5'), 1.63 (dt, *J* = 9.4, 4.4 Hz, 2H, H-6), 1.60 – 1.47

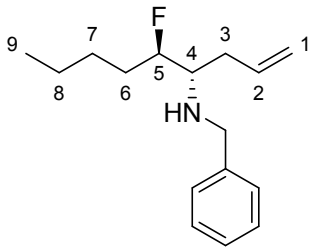
(m, 1H, H-6'), 1.43 – 1.20 (m, 4H, H-7, H-8), 1.03 (s, 3H, H-8'), 0.87 (t, J = 7.2 Hz, 3H, H-9), 0.71 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 137.1 (*ipso*-*C*), 135.3 (C-2), 129.6 (*o*-*C*), 128.6 (*m*-*C*), 128.0 (*p*-*C*), 118.2 (C-1), 97.2 (d, $J_{C,F}$ = 173.0 Hz, C-5), 61.2 (d, $J_{C,F}$ = 23.0 Hz, C-4), 58.5 (C-1'), 51.0 (CH_2SO_2), 48.5 (CH_2Ph), 47.7 (C-7'), 42.7 (C-4'), 42.6 (C-3'), 32.4 (d, $J_{C,F}$ = 20.0 Hz, C-6), 31.9 (d, $J_{C,F}$ = 4.0 Hz, C-3), 27.5 (d, $J_{C,F}$ = 4.0 Hz, C-7), 26.9 (C-6'), 25.1 (C-5'), 22.3 (C-8), 20.0 (C-8'), 19.6 (C-7'), 13.9 (C-9).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.23 (minor diastereomer), -125.84 (major diastereomer). Ratio = 93:7.

HRMS (ESI): *m/z*: calculated for $C_{26}H_{38}NO_3FNaS$ $[M+Na]^+$: 486.2454, found: 486.2456.

(4*S*,5*R*)-*N*-Benzyl-5-fluorononon-1-en-4-amine (*ent*-2k)



The title compound was prepared according to General procedure 1, using hexanal (55.3 μL, 0.45 mmol), Jørgensen (*R*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (54.1 mg, 72%) as a yellow oil. The ^{1}H, ^{13}C and ^{19}F NMR spectra of *ent*-**2k** were identical to that of **2k**.

R_f = 0.39 (10% EtOAc/*n*-hexane).

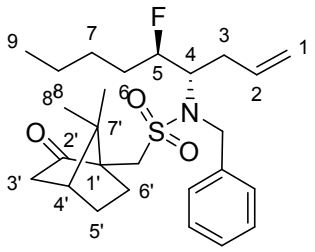
dr = 98:2, ee 88%.

$[\alpha]_D^{24}$ +18.2 (*c* 0.086, $CHCl_3$).

IR (neat): ν_{max} 3065, 3027, 2956, 2860, 1641 (C=C str.), 1466 (N-H bend), 1382, 985, 916 (C-F str.), 697 cm^{-1}.

HRMS (ESI): *m/z*: calculated for $C_{16}H_{25}NF$ $[M+H]^+$: 250.1971, found: 250.1968.

***N*-Benzyl-1-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*S*,5*R*)-5-fluoronon-1-en-4-yl)methanesulfonamide (for ee of *ent*-2k)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine *ent*-**2k** (17.0 mg, 0.0680 mmol) as starting material. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the product (20.8 mg, 66%) as a yellow oil.

R_f = 0.26 (10% EtOAc/*n*-hexane).

dr = 94:6.

$[\alpha]_D^{23}$ +26.5 (*c* 0.14, $CHCl_3$).

IR (neat): ν_{max} 3067, 2957, 2872, 1745 (C=O str.), 1641 (C=O str.), 1455, 1339 (S=O str.), 1146 (S=O str.), 1050, 918 (C-F str.), 699, 569 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.41 (m, 2H, *o*-Ar-*H*), 7.38 – 7.27 (m, 3H, *m,p*-Ar-*H*), 5.88 (dddd, *J* = 16.5, 10.4, 7.9, 5.9 Hz, 1H, H-2), 5.19 (dq, *J* = 9.3, 1.5 Hz, 1H, *trans*-H-1), 5.16 (p, *J* = 1.4 Hz, 1H, *cis*-H-1), 4.50 (d, *J* = 15.1 Hz, 1H, C*H*HPh), 4.43 (d, *J* = 15.2 Hz, 1H, H-5), 4.35 (ddd, *J* = 8.9, 4.9, 3.8 Hz, 1H, C*H*HPh), 4.01 (ddt, *J* = 19.1, 9.6, 4.6 Hz, 1H, H-4), 3.34 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 2.56 (d, *J* = 14.5 Hz, 1H, C*H*HSO$_2$), 2.47 (dddd, *J* = 13.7, 10.8, 4.3, 1.7 Hz, 1H, H-5'), 2.34 (ddd, *J* = 18.4, 4.9, 3.2 Hz, 1H, H-3'), 2.05 (t, *J* = 4.4 Hz, 1H, H-4'), 2.00 (dtd, *J* = 12.2, 4.5, 3.3 Hz, 1H, H-6'), 1.90 (d, *J* = 18.4 Hz, 1H, H-3'),

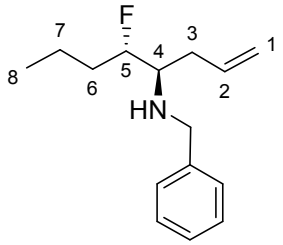
1.66 – 1.60 (m, 1H, H-5'), 1.61 – 1.55 (m, 3H, H-6, H-6'), 1.45 – 1.32 (m, 2H, H-7), 1.26 (qt, J = 8.2, 4.2 Hz, 2H, H-8), 1.05 (s, 3H, H-8'), 0.86 (t, J = 7.2 Hz, 3H, H-9), 0.75 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 137.1 (*ipso*-*C*), 135.3 (C-2), 129.5 (*o*-*C*), 128.6 (*m*-*C*), 128.0 (*p*-*C*), 118.2 (C-1), 96.9 (d, $^1J_{C,F}$ = 173.0 Hz, C-5) , 61.3 (d, $^2J_{C,F}$ = 23.0 Hz, C-4), 58.6 (C-1'), 51.0 (CH_2SO_2), 48.7 (CH_2Ph), 47.6 (C-7'), 42.8 (C-4'), 42.6 (C-3'), 32.5 (d, $^2J_{C,F}$ = 21.0 Hz, C-6), 32.2 (d, $^3J_{C,F}$ = 4.0 Hz, C-3), 27.5 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 26.9 (C-6'), 25.3 (C-5'), 22.3 (C-8), 20.0 (C-8'), 19.6 (C-7'), 13.9 (C-9).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.22 (major diastereomer), -125.83 (minor diastereomer). Ratio = 94:6.

HRMS (ESI): *m/z*: calculated for $C_{26}H_{38}NO_3FNaS$ $[M+Na]^+$: 486.2454, found: 486.2465.

(4*S*,5*R*)-*N*-Benzyl-5-fluorooct-1-en-4-amine (2l)



The title compound was prepared according to General procedure 1, however using propanal (48.0 μL, 0.45 mmol), Jørgensen (*S*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 5% EtOAc/*n*-hexane gave the title product (42.6 mg, 60%) as a colorless oil.

R_f = 0.28 (5% EtOAc/*n*-hexane).

dr = 98:2, ee 92%.

$[\alpha]_D^{26}$ -14.6 (*c* 0.09, $CHCl_3$).

IR (neat): ν_{max} 3063, 2932, 2872, 1639 (C=C str.), 1495 (N-H bend), 1447, 1369, 1279, 1136, 914 (C-F str.), 697 cm^{-1}.

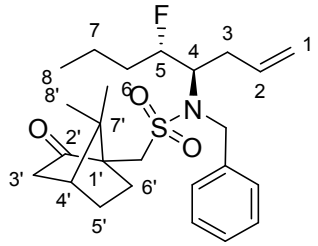
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.21 (m, 5H, Ar-*H*), 5.92 – 5.70 (m, 1H, H-2), 5.12 (ddd, J = 6.8, 1.3, 0.4 Hz, 1H, *trans*-H-1), 5.09 (t, J = 1.3 Hz, 1H, *cis*-H-1), 4.48 (dddd, J = 48.2, 9.3, 4.4, 2.6 Hz, 1H, H-5), 3.82 (d, J = 1.8 Hz, 2H, CH_2Ph), 2.76 (ddt, J = 17.0, 7.5, 4.6 Hz, 1H, H-4), 2.40 – 2.17 (m, 2H, H-3), 1.76 – 1.66 (m, 1H, H-6), 1.56 – 1.47 (m, 2H, H-7), 1.43 – 1.33 (m, 1H, H-6), 0.95 (t, J = 7.2 Hz, 3H, H-8).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (*ipso-C*), 135.2 (C-2), 128.4 (*m-C*), 128.2 (*o-C*), 127.0 (*p-C*), 117.7 (C-1), 95.3 (d, $^1J_{C,F}$ = 170.0 Hz, C-5), 59.0 (d, $^2J_{C,F}$ = 21.0 Hz, C-4), 51.9 (CH_2Ph), 34.3 (d, $^3J_{C,F}$ = 6.0 Hz, C-3), 33.3 (d, $^2J_{C,F}$ = 21.0 Hz, C-6), 18.9 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 14.0 (C-8).

^{19}F NMR (377 MHz, $CDCl_3$): δ -126.19 (major diastereomer), -129.98 (minor diastereomer). Ratio = 98:2.

HRMS (ESI): *m/z*: calculated for $C_{15}H_{23}NF$ $[M+H]^+$: 236.1815, found: 236.1821.

_N_-Benzyl-1-((1_S_,4_R_)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-_N_-((4_R_,5_S_)-5-fluorooct-1-en-4-yl)methanesulfonamide (for ee of 2l)



The title compound was prepared according to General procedure 2, using the β-fluoroamine **2l** (15.0 mg, 0.064 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (16.3 mg, 57%) as a colorless oil.

R_f = 0.36 (20% EtOAc/*n*-hexane).

dr = 4:96.

$[\alpha]_D^{26}$ +30.0 (*c* 0.08, $CHCl_3$).

IR (neat): ν_{max} 3066, 2960, 2874, 1745 (C=O str.), 1641 (C=C str.), 1339 (S=O str.), 1146 (S=O str.), 925 (C-F str.), 765, 569 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.42 (m, 2H, *o*-Ar-*H*), 7.39 – 7.27 (m, 3H, *m, p*-Ar-*H*), 5.91 – 5.78 (m, 1H, H-2), 5.26 – 5.11 (m, 2H, H-1), 4.60 (d, *J* = 15.0 Hz, 1H, CH_2Ph), 4.43 (ddd, *J* = 8.9, 5.3, 3.5 Hz, 1H, H-5), 4.35 (d, *J* = 15.0 Hz, 1H, CH_2Ph), 4.03 (ddt, *J* = 18.2, 10.1, 5.2 Hz, 1H, H-4), 3.21 (d, *J* = 14.5 Hz, 1H, C*H*HSO_2), 2.60 (d, *J* = 14.4 Hz, 1H, C*H*HSO_2), 2.56 (s, 1H, H-5'), 2.56 – 2.44 (m, 2H, H-3), 2.32 (ddd, *J* = 18.1, 4.8, 3.1 Hz, 1H,

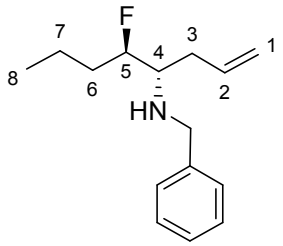
H-3'), 2.08 – 2.02 (m, 1H, H-4'), 2.02 – 1.96 (m, 1H, H-6'), 1.90 (d, J = 18.4 Hz, 1H, H-3'), 1.69 – 1.62 (m, 1H, H-5'), 1.56 (d, J = 8.3 Hz, 2H, H-6), 1.46 – 1.34 (m, 2H, H-7), 1.26 – 1.12 (m, 1H, H-6'), 1.04 (s, 3H, H-8'), 0.85 (t, J = 7.4 Hz, 3H, H-8), 0.71 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 137.1 (*ipso*-*C*), 135.3 (C-2), 129.6 (*o*-*C*), 128.6 (*m*-*C*), 128.0 (*p*-*C*), 118.2 (C-1), 96.4 (d, $^1J_{C,F}$ = 173.0 Hz, C-5), 61.2 (d, $^2J_{C,F}$ = 24.0 Hz, C-4), 58.5 (C-1'), 51.0 (CH_2SO_2), 48.4 (CH_2Ph), 47.7 (C-7'), 42.7 (C-4'), 42.6 (C-3'), 34.7, (d, $^2J_{C,F}$ = 20.0 Hz, C-6), 31.9 (d, $^3J_{C,F}$ = 4.0 Hz, C-3), 26.9 (C-6'), 25.1 (C-5'), 20.0 (C-8'), 19.6 (C-8'), 18.6 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 13.7 (C-8).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.73 (minor diastereomer), -126.25 (major diastereomer). Ratio = 4:96**.**

HRMS (ESI): *m/z*: calculated for $C_{25}H_{37}NO_3F$ $[M+H]^+$: 450.2478, found: 450.2480.

(4*R*,5*S*)-*N*-Benzyl-5-fluorooct-1-en-4-amine (*ent*-2l)



The title compound was prepared according to General procedure 1, however using propanal (48.0 μL, 0.45 mmol), Jørgensen (*R*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 5% EtOAc/*n*-hexane gave the title product (28.7 mg, 41%) as a colorless oil.

R_f = 0.25 (5% EtOAc/*n*-hexane).

dr = 98:2, ee 86%.

$[\alpha]_D^{26}$ +17.2 (*c* 0.12, $CHCl_3$).

IR (neat): ν_{max} 3027, 2933, 2846, 1640 (C=C str.), 1495 (N-H bend), 1441, 1367, 994, 914 (C-F str.), 740, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.21 (m, 5H, Ar-*H*), 5.91 – 5.72 (m, 1H, H-2), 5.12 (dd, J = 6.8, 1.2 Hz, 1H, *trans*-H-1), 5.09 (t, J = 1.3 Hz, 1H, *cis*-H-1), 4.48 (dddd, J = 48.3,

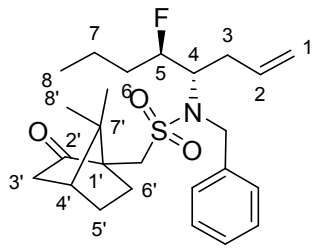
9.3, 4.5, 2.7 Hz, 1H, H-5), 3.82 (d, J = 1.8 Hz, 2H, CH_2Ph), 2.76 (ddt, J = 17.0, 7.6, 4.6 Hz, 1H, H-4), 2.40 – 2.16 (m, 2H, H-3), 1.78 –1.31 (m, 4H, H-6, H-7), 0.95 (t, J = 7.2 Hz, 3H, H-8).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (*ipso-C*), 135.2 (C-2), 128.4 (*m-C*), 128.2 (*o-C*), 127.0, (*p-C*), 117.7 (C-1), 95.3 (d, $^1J_{C,F}$ = 170.0 Hz, C-5), 59.1 (d, $^2J_{C,F}$ = 22.0 Hz, C-4), 51.9 (*C*H_2Ph), 34.3 (d, $^3J_{C,F}$ = 6.0 Hz, C-3), 33.3 (d, $^2J_{C,F}$ = 21.0 Hz, C-6), 18.9 (d, $^3J_{C,F}$ = 3.0 Hz, C-7), 14.0 (C-8).

^{19}F NMR (377 MHz, $CDCl_3$): δ -126.16 (major diastereomer), -129.95 (minor diastereomer). Ratio = 98:2.

HRMS (ESI): *m/z*: calculated for $C_{15}H_{23}NF$ $[M+H]^+$: 236.1815, found: 236.1811.

***N*-Benzyl-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*S*,5*R*)-5-fluorooct-1-en-4-yl)methanesulfonamide (for ee of *ent*-2l)**



The title compound was prepared according to General procedure 2, using the β-fluoroamine *ent*-**2l** (15.0 mg, 0.064 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (12.5 mg, 43%) as a colorless oil.

R_f = 0.37 (20% EtOAc/*n*-hexane).

dr = 93:7.

$[\alpha]_D^{26}$ +30.2 (*c* 0.08, $CHCl_3$).

IR (neat): ν_{max} 3065, 2938, 2874, 1745 (C=O str.), 1641 (C=C str.), 1391 (S=O str.), 1146 (S=O str.), 1047, 918 (C-F str.), 765, 569 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.8 Hz, 2H, *o*-Ar-*H*), 7.38 – 7.24 (m, 3H, *m, p*-Ar-*H),* 5.97 – 5.78 (m, 1H, H-2), 5.23 – 5.13 (m, 2H, H-1), 4.47 (q, J = 15.1 Hz, 2H, CH_2Ph),

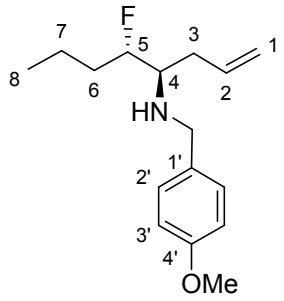
4.36 (dt, J = 9.2, 4.8 Hz, 1H, H-5), 4.01 (ddt, J = 19.1, 9.7, 4.7 Hz, 1H, H-4), 3.34 (d, J = 14.6 Hz, 1H, C*H*HSO$_2$), 2.61 (ddt, J = 4.5, 3.0, 1.7 Hz, 1H, H-5'), 2.56 (d, J = 14.7 Hz, 1H, C*H*HSO$_2$), 2.53 – 2.43 (m, 2H, H-3), 2.33 (dt, J = 18.4, 4.1 Hz, 1H, H-3'), 2.05 (t, J = 4.5 Hz, 1H, H-4'), 1.99 (dt, J = 12.0, 3.8 Hz, 1H, H-6'), 1.90 (d, J = 18.4 Hz, 1H, H-3'), 1.68 – 1.51 (m, 3H, H-5', H-6), 1.46 – 1.34 (m, 2H, H-7), 1.21 (ddd, J = 15.9, 13.3, 7.0 Hz, 1H, H-6'), 1.05 (s, 3H, H-8'), 0.86 (t, J = 7.3 Hz, 3H, H-8), 0.75 (s, 3H, H-8').

^{13}C NMR (100 MHz, CDCl$_3$): δ 214.9 (C-2'), 137.1 (*ipso-C*), 135.3 (C-2), 129.5 (*o-C*), 128.5 (*m-C*), 128.0 (*p-C*), 118.2 (C-1), 96.6 (d, $^1J_{C,F}$ = 173.0 Hz, C-5), 61.2 (d, $^2J_{C,F}$ = 23.0 Hz, C-4), 58.6 (C-1'), 51.0 (*C*H$_2$SO$_2$), 48.6 (*C*H$_2$SO$_2$), 47.6 (C-7'), 42.8 (C-4'), 42.6 (C-3'), 34.8 (d, $^2J_{C,F}$ = 21.0 Hz, C-6), 32.2 (d,$^1J_{C,F}$ = 4.0 Hz, C-3), 26.9 (C-6'), 25.3 (C-5'), 20.0 (C-8'), 19.6 (C-8), 18.6 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 13.7 (C-8).

^{19}F NMR (377 MHz, CDCl$_3$): δ -125.72 (major diastereomer), -126.20 (minor diastereomer). Ratio = 93:7.

HRMS (ESI): *m/z*: calculated for $C_{25}H_{37}NO_3FS$ $[M+H]^+$: 450.2478, found: 450.2490.

(4*S*,5*R*)-5-Fluoro-*N*-(4-methoxybenzyl)oct-1-en-4-amine (2m)



The title compound was prepared according to General procedure 1, using propanal (48.0 μL, 0.45 mmol), Jørgensen (*S*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), 4-methoxybenzylamine (78.0 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol), with 24 h reaction time for both the fluornation reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10 % EtOAc/*n*-hexane gave the title product (39.7 mg, 50%) as a colorless oil.

R$_f$ = 0.32 (10% EtOAc/*n*-hexane).

dr = 98:2, ee 92%.

$[\alpha]_D^{26}$ -14.3 (c 0.09, CHCl$_3$).

IR (neat): ν_{max} 3072, 2998, 2935, 1640 (C=C str.), 1612, 1463 (N-H bend), 1441, 1299 (CH$_3$ bend), 917 (C-F str.), 829 cm^{-1}.

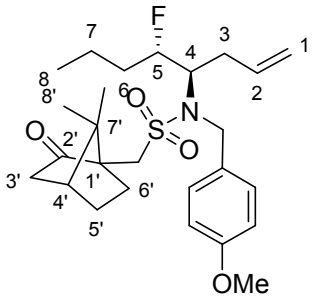
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.6 Hz, 2H, H-2'), 6.85 (d, J = 8.6 Hz, 2H, H-3'), 5.91 – 5.69 (m, 1H, H-2), 5.12 (ddd, J = 6.0, 4.8, 1.6 Hz, 1H, *trans*-H-1), 5.08 (t, J = 1.2 Hz, 1H, *cis*-H-1), 4.47 (dddd, J = 48.3, 9.3, 4.5, 2.6 Hz, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.76 (d, J = 2.4 Hz, 2H, CH_2Ph), 2.75 (ddt, J = 17.0, 7.5, 4.6 Hz, 1H, H-4), 2.42 – 2.13 (m, 2H, H-3), 1.81 –1.34 (m, 4H, H-6, H-7), 0.95 (t, J = 7.2 Hz, 3H, H-8).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 (C-4'), 135.3 (C-2), 132.6 (C-1'), 129.3 (C-2'), 117.7 (C-2), 113.8 (C-3'), 95.3 (d, $^1J_{C,F}$ = 171.0 Hz, C-5), 58.9 (d, $^2J_{C,F}$ = 21.0 Hz, C-4), 55.3 (O*C*H$_3$), 51.3 (*C*H$_2$Ph), 34.3 (d, $^3J_{C,F}$ = 6.0 Hz, C-3), 33.3 (d, $^2J_{C,F}$ = 20.0 Hz, C-6), 18.9 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 14.0 (C-8).

^{19}F NMR (377 MHz, $CDCl_3$): δ -126.19 (major diastereomer), -129.89 (minor diastereomer). Ratio = 98:2.

HRMS (ESI): *m/z*: calculated for $C_{16}H_{25}NOF$ $[M+H]^+$: 266.1920, found: 266.1922.

1-((1*S*,4*R*)-7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*R*,5*S*)-5-fluorooct-1-en-4-yl)-*N*-(4-methoxybenzyl)methanesulfonamide (for ee of 2m)



The title compound was prepared according to General procedure 2, using β-fluoroamine **2m** (15.0 mg, 0.06 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (16.7 mg, 61%) as a colorless oil.

R$_f$= 0.20 (20% EtOAc/*n*-hexane).

dr = 96:4.

$[\alpha]_D^{25}$ +9.0 (*c* 0.07, $CHCl_3$).

IR (neat): ν_{max} 3076, 2960, 1746 (C=O str.), 1641 (C=C str.), 1391 (CH_3 bend), 1329 (S=O str.), 1146 (S=O str.), 918 (C-F str.), 840 cm^{-1}.

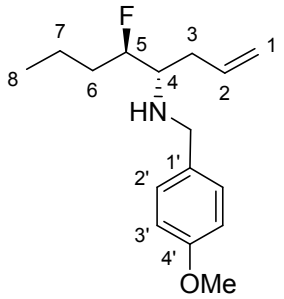
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.7 Hz, *m*-Ar-*H*), 6.86 (d, J = 8.7 Hz, *o*-Ar-*H*), 5.95 – 5.79 (m, 1H, H-2), 5.23 – 5.17 (d, J = 16.8, 1.6 Hz, 1H, *trans*-H-1), 5.17 – 5.13 (d, J = 10.0, 1.2 Hz, 1H, *cis*-H-1), 4.45 (d, J = 15.4 Hz, 1H, C*H*HPh), 4.37 (d, J = 15.1 Hz, 1H, C*H*HPh), 4.05 – 3.93 (m, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.33 (d, J = 14.6 Hz, 1H, C*H*HSO_2), 2.64 – 2.57 (m, 2H, H-3), 2.55 (d, J = 14.5 Hz, 1H, C*H*HSO_2), 2.51 – 2.42 (m, 1H, H-5'), 2.34 (ddd, J = 18.4, 5.0, 3.2 Hz, 1H, H-3'), 2.09 – 2.02 (m, 2H, H-4'), 2.01 – 1.96 (m, 1H, H-6'), 1.90 (d, J = 18.4 Hz, 1H, H-3'), 1.65 (dd, J = 9.4, 4.6 Hz, 1H, H-5'), 1.61 (d, J = 3.3 Hz, 2H, H-6), 1.57 – 1.50 (m, 1H, H-6'), 1.41 (dddd, J = 16.3, 12.5, 6.9, 3.0 Hz, 2H, H-7), 1.06 (s, 3H, H-8'), 0.86 (t, J = 7.2 Hz, 3H, H-8), 0.76 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9 (C-2'), 159.4 (*p*-*C*), 135.4 (C-2), 130.9 (*m*-*C*), 129.0 (*ipso*-*C*), 118.2 (C-1), 113.9 (*o*-*C*), 96.5 (d, $^1J_{C,F}$ = 173.0 Hz, C-5), 61.2 (d, $^2J_{C,F}$ = 24.0 Hz, C-4), 58.6 (C-1') 55.3 (O*C*H_3), 51.0 (*C*H_2SO_2), 48.1 (C-7'), 47.6 (*C*H_2Ph), 42.8 (C-4'), 42.6 (C-3'), 34.8 (d, $^2J_{C,F}$ = 21.0 Hz, C-6), 32.3 (d, $^1J_{C,F}$ = 5.0 Hz, C-3), 26.9 (C-6'), 25.3 (C-5'), 20.0 (C-8'), 19.6 (C-8'), 18.6 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 13.7 (C-8).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.52 (major diastereomer), -126.08 (minor diastereomer). Ratio = 96:4.

HRMS (ESI): *m/z*: calculated for $C_{26}H_{38}NO_4FNaS$ $[M+Na]^+$: 502.2403, found: 502.2395.

(4*R*,5*S*)-5-Fluoro-*N*-(4-methoxybenzyl)oct-1-en-4-amine (*ent*-2m)



The title compound was prepared according to General procedure 1, using propanal (48.0 μL, 0.45 mmol), Jørgensen (*R*) catalyst (1.8 mg, 0.003 mmol), NFSI (94.6 mg, 0.3 mol), 4-methoxybenzylamine (78.0 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol), with 24 h reaction time for both the fluornation reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10 % EtOAc/*n*-hexane gave the title product (42.2 mg, 53%) as a colorless oil. The ^{1}H, ^{13}C and ^{19}F NMR spectra of *ent*-**2m** were identical to that of **2m**.

R_f = 0.32 (10% EtOAc/*n*-hexane).

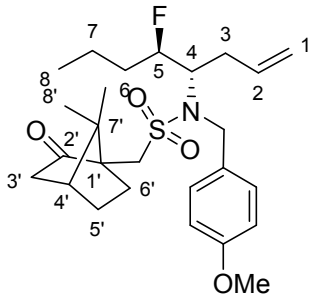
dr = 99:1, ee 92%.

$[\alpha]_D^{25}$ +11.7 (c 0.11, $CHCl_3$).

IR (neat): ν_{max} 3074, 2933, 2915, 1640 (C=C str.), 1612, 1463 (N-H bend), 1441, 1300 (CH_3 bend), 915 (C-F str.), 829 cm^{-1}.

HRMS (ESI): *m/z*: calculated for $C_{16}H_{25}NOF$ $[M+H]^+$: 266.1920, found: 266.1929.

1-((1*S*,4*R*)-7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-((4*S*,5*R*)-5-fluorooct-1-en-4-yl)-*N*-(4-methoxybenzyl)methanesulfonamide (for ee of *ent*-2m)



The title compound was prepared according to General procedure 2, using β-fluoroamine *ent*-**2m** (15.0 mg, 0.06 mmol) as starting material. Purification by flash column chromatography eluting with 20% EtOAc/*n*-hexane gave the product (12.4 mg, 46%) as a colorless oil.

$\mathbf{R}_f$= 0.28 (20% EtOAc/*n*-hexane).

dr = 4:96.

$[\alpha]_D^{26}$ +21.8 (*c* 0.11, $CHCl_3$).

IR (neat): ν_{max} 3074, 2952, 1745 (C=O str.), 1641 (C=C str.), 1611, 1459, 1376 (CH_3 bend), 1335 (S=O str.), 1146 (S=O str.), 918 (C-F str.), 836 cm^{-1}.

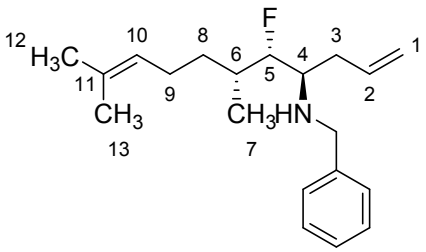
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.7 Hz, 2H, *m*-Ar-*H*), 6.87 (d, J = 8.7 Hz, 2H, *o*-Ar-*H*), 5.92 – 5.74 (m, 1H, H-2), 5.20 (dd, J = 17.1, 1.6 Hz, 1H, *trans*-H-1), 5.15 (dd, J = 10.4, 1.6 Hz, 1H, *cis*-H-1), 4.54 (d, J = 14.9 Hz, 1H, C*H*HPh), 4.48 – 4.31 (m, 1H, H-5), 4.28 (d, J = 14.9 Hz, 1H, C*H*HPh), 4.00 (ddt, J = 18.0, 9.3, 5.3 Hz, 1H, H-4), 3.79 (s, 3H, OCH_3), 3.20 (d, J = 14.5 Hz, 1H, C*H*HSO$_2$), 2.58 (d, J = 14.5 Hz, 1H, C*H*HSO$_2$), 2.56 (d, J = 4.9 Hz, 2H, H-3), 2.53 – 2.43 (m, 1H, H-5'), 2.33 (ddd, J = 18.4, 4.9, 3.2 Hz, 1H, H-3'), 2.08 – 2.03 (m, 2H, H-4'), 2.02 – 1.97 (m, 1H, H-6'), 1.90 (d, J = 18.4 Hz, 1H, H-3'), 1.69 – 1.63 (m, 1H, H-5'), 1.62 – 1.57 (m, 2H, H-6), 1.44 – 1.38 (m, 1H, H-6'), 1.28 – 1.13 (m, 2H, H-7), 1.05 (s, 3H, H-8'), 0.86 (t, J = 7.3 Hz, 3H, H-8), 0.72 (s, 3H, H-8').

^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0 (C-2'), 159.4 (*p*-*C*), 135.3 (C-2), 130.9 (*m*-*C*), 129.1 (*ipso*-*C*), 118.2 (C-1), 114.0 (*o*-*C*), 96.4 (d, $^1J_{C,F}$ = 172.0 Hz, C-5), 61.1 (d, $^2J_{C,F}$ = 24.0 Hz, C-4), 58.5 (C-1'), 55.3 (O*C*H$_3$), 51.0 (*C*H$_2$SO$_2$), 47.9 (C-7'), 47.7 (*C*H$_2$Ph), 42.7 (C-4'), 42.6 (C-3'), 34.7 (d, $^2J_{C,F}$ = 20.0 Hz, C-6), 31.9 (d, $^3J_{C,F}$ = 5.0 Hz, C-3), 26.9 (C-6'), 25.1 (C-5'), 20.0 (C-8'), 19.6 (C-8'), 18.6 (d, $^3J_{C,F}$ = 4.0 Hz, C-7), 13.7 (C-8).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.52 (minor diastereomer), -126.08 (major diastereomer). Ratio = 4:96**.**

HRMS (ESI): *m/z*: calculated for $C_{26}H_{38}FNO_4NaS$ $[M+Na]^+$: 502.2403, found: 502.2395.

(4*S*,5*R*,6*S*)-*N*-Benzyl-5-fluoro-6,10-dimethylundeca-1,9-dien-4-amine (2n)



The title compound was prepared according to General procedure 1, however using (*S*)-(-)-citronellal (36.0 μL, 0.20 mmol), Jørgensen (*S*) catalyst (18.0 mg, 0.03 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (44.0 μL, 0.40 mmol) and pinacol allylboronate (75.0 μL, 0.40 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (34.1 mg, 51%) as a colorless oil.

R$_f$= 0.35 (10% EtOAc/*n*-hexane).

dr = 93:7.

$[\alpha]_D^{26}$ +4.4 (*c* 0.11, $CHCl_3$).

IR (neat): ν_{max} 3063, 3026, 2963, 2919, 1640 (C=C str.), 1452 (N-H bend), 1380 (CH_3 bend), 915 (C-F str.), 697 cm^{-1}.

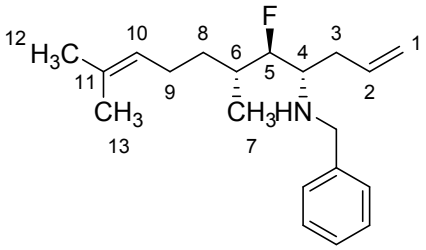
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.18 (m, 5H, Ar-*H*), 5.85 (ddtd, *J* = 17.3, 10.2, 7.2, 1.2 Hz, 1H, H-2), 5.25 – 5.13 (m, 1H, H-10), 5.12 (d, *J* = 1.8 Hz, 1H, *trans*-H-1), 5.11 – 5.07 (dd, *J* = 2.8, 1.6 Hz, 1H, *cis*-H-1), 4.24 (ddd, *J* = 47.8, 6.6, 4.9 Hz, 1H, H-5), 3.80 (s, 2H, CH_2Ph), 2.80 (dddd, *J* = 19.9, 7.6, 4.9, 3.8 Hz, 1H, H-4), 2.57 – 2.35 (m, 1H, H-3), 2.30 – 2.19 (m, 1H, H-3), 1.90 (dddd, *J* = 15.9, 12.7, 9.4, 5.0 Hz, 2H, H-9), 1.68 (d, *J* = 1.4 Hz, 3H, H-12), 1.61 (d, *J* = 1.6 Hz, 3H, H-13), 1.50 (d, *J* = 13.6 Hz, 1H, H-8), 1.28 – 1.14 (m, 1H, H-8), 1.03 (d, *J* = 6.8 Hz, 1H, H-6), 0.90 (d, *J* = 6.9 Hz, 2H, H-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4 (*ipso*-*C*), 135.5 (C-2), 131.6 (C-11), 128.4 (*m*-*C*), 128.2 (*o*-*C*), 127.0 (*p*-*C*), 124.5 (C-10), 117.6 (C-1), 98.4 (d, $^1J_{C,F}$ = 174.0 Hz, C-5), 56.3 (d, $^2J_{C,F}$ = 21.0 Hz, C-4), 51.4 (*C*H_2Ph), 33.6 (d, $^3J_{C,F}$ = 19.0 Hz, C-3), 33.4(d, $J_{C,F}$ = 5.0 Hz, C-6), 31.4 (d, $^3J_{C,F}$ = 5.0 Hz, C-8), 25.7 (C-12), 25.3 (C-9), 17.7 (C-13), 15.8 (d, $J_{C,F}$ = 6.0 Hz, C-7).

^{19}F NMR (377 MHz, $CDCl_3$): δ -135.25 (major diastereomer), -137.92 (minor diastereomer). Ratio = 93:7.

HRMS (ESI): *m/z*: calculated for $C_{20}H_{31}NF$ $[M+H]^+$: 304.2441, found: 304.2428.

(4*R*,5*S*,6*S*)-*N*-Benzyl-5-fluoro-6,10-dimethylundeca-1,9-dien-4-amine (2p)



The title compound was prepared according to General procedure 1, however using (*S*)-(-)-citronellal (36.0 μL, 0.20 mmol), Jørgensen (*R*) catalyst (18.0 mg, 0.03 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (44.0 μL, 0.40 mmol) and pinacol allylboronate (75.0 μL, 0.40 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 10% EtOAc/*n*-hexane gave the title product (35.7 mg, 53%) as a colorless oil.

R_f = 0.35 (10% EtOAc/*n*-hexane).

dr = 2:98.

$[\alpha]_D^{26}$ +23.6 (c 0.11, $CHCl_3$).

IR (neat): ν_{max} 3064, 2921, 1639 (C=C str.), 1496, 1452 (N-H bend), 1379 (CH_3 bend), 1279, 915 (C-F str.), 739, 698 cm^{-1}.

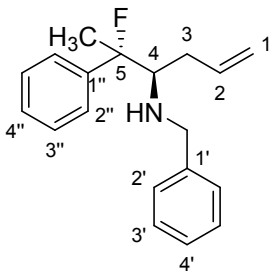
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.20 (m, 5H, Ar-*H*), 5.93 – 5.78 (m, 1H, H-2), 5.15 (dt, J = 4.0, 1.6 Hz, 1H, H-10), 5.11 (t, J = 1.3 Hz, 1H, *trans*-H-1), 5.08 (dp, J = 6.9, 1.4 Hz, 1H, *cis*-H-1), 4.23 (ddd, J = 47.8, 6.7, 4.4 Hz, 1H, H-5), 3.79 (dd, J = 12.8, 8.0 Hz, 2H, CH_2Ph), 2.82 (dtd, J = 13.8, 6.9, 3.9 Hz, 1H, H-4), 2.46 (dddd, J = 14.2, 7.1, 3.8, 1.7 Hz, 1H, H-3), 2.26 (dtq, J = 14.5, 7.2, 1.3 Hz, 1H, H-3), 2.00 (dq, J = 15.0, 7.6 Hz, 2H, H-9), 1.69 (d, J = 1.4 Hz, 3H, H-12), 1.60 (d, J = 1.3 Hz, 3H, H-13), 1.41 (dddd, J = 14.3, 9.1, 6.9, 5.4 Hz, 2H, H-8), 1.33 – 1.20 (m, 1H, H-6), 0.93 (dd, J = 6.8, 1.1 Hz, 3H, H-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (*ipso-C*), 135.1 (C-2), 131.7 (C-11), 128.4 (*m-C*), 128.2 (*o-C*), 127.0 (*p-C*), 124.3 (C-10), 117.9 (C-1), 97.4 (d, $^1J_{C,F}$ = 174.0 Hz, C-5), 56.3 (d, $^2J_{C,F}$ = 23.0 Hz, C-4), 51.5 (*C*H_2Ph), 33.9 (d, $^3J_{C,F}$ = 4.0 Hz, C-3), 33.6 (d, $^2J_{C,F}$ = 4.0 Hz, C-6), 33.3 (d, $^3J_{C,F}$ = 19.0 Hz, C-8), 25.7 (C-12), 25.3 (C-9), 17.7 (C-13), 13.5 (d, $^3J_{C,F}$ = 6.0 Hz, C-7).

^{19}F NMR (377 MHz, $CDCl_3$): δ -135.25 (minor diastereomer), -137.92 (major diastereomer). Ratio = 2:98.

HRMS (ESI): *m/z*: calculated for $C_{20}H_{31}NF$ $[M+H]^+$: 304.2441 found: 304.2433.

(3*R*)-*N*-Benzyl-2-fluoro-2-phenylhex-5-en-3-amine (2o)



The title compound was prepared according to General procedure 1, however using 2-phenylpropanal (60.0 μL, 0.45 mmol), Jørgensen (*S*) catalyst (18.0 mg, 0.03 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 5% EtOAc/*n*-hexane gave the title product (14.8 mg, 17%) as a colorless oil.

R_f = 0.31 (5% EtOAc/*n*-hexane).

dr = 37:63.

$[\alpha]_D^{27}$ -26.6 (*c* 0.11, $CHCl_3$).

IR (neat): ν_{max} 3063, 2921, 1639 (C=C str.), 1495 (N-H bend), 1446, 1377 (CH_3 bend), 1279, 1175, 914 (C-F str.), 697 cm^{-1}.

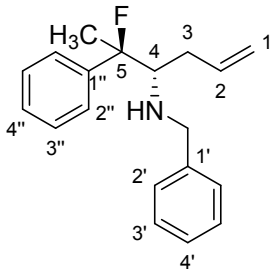
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.02 (m, 10H, Ar-*H*), 5.97 – 5.46 (m, 1H, H-2), 5.02 (dt, *J* = 16.3, 7.1 Hz, 2H, H-1), 3.79 (dt, *J* = 14.0, 3.6, 2.4 Hz, 1H, C*H*$_2$Ph), 3.59 (ddd, *J* = 73.8, 12.6, 2.5 Hz, 1H, C*H*$_2$Ph), 2.89 (dddt, *J* = 25.0, 18.9, 9.1, 3.1 Hz, 1H, H-4), 2.51 – 2.21 (m, 1H, H-3), 2.02 (tt, *J* = 11.2, 5.6 Hz, 1H, H-3), 1.75 (dd, *J* = 23.2, 2.7 Hz, 3H, C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9 (d, $J_{C,F}$ = 22.0 Hz, C-1", major), 142.9 (d, $J_{C,F}$ = 21.0 Hz, C-1", minor), 140.7 (C-2), 136.0 (C-1'), 128.3 (d, $J_{C,F}$ = 5.0 Hz, C-3", minor), 128.27, 128.1 (C-3'), 128.0 (C-4"), 127.4 (C-4', minor), 127.3 (C-4', major), 126.9 (C-2'), 125.3 (d, $J_{C,F}$ = 9.0 Hz, C-2", minor), 124.9 (d, $J_{C,F}$ = 9.0 Hz, C-2", major), 117.2 (C-1), 101.2 (d, $J_{C,F}$ = 7.0 Hz, C-5, major), 99.5 (d, $J_{C,F}$ = 10.0 Hz, C-5, minor), 64.4 (d, $J_{C,F}$ = 9.0 Hz, C-4, major), 64.1 (d, $J_{C,F}$ = 8.0 Hz, C-4, minor), 53.8 (*C*H$_2$Ph, minor), 53.3 (*C*H$_2$Ph, major), 35.5 (d, $J_{C,F}$ = 5.0 Hz, C-3, minor), 34.9 (d, $J_{C,F}$ = 3.0 Hz, C-3, major), 24.6 (d, $J_{C,F}$ = 28.0 Hz, *C*H$_3$, major), 23.7 (d, $J_{C,F}$ = 8.0 Hz, *C*H$_3$, minor) 23.5 (d, $J_{C,F}$ = 9.0 Hz, *C*H$_3$, minor).

^{19}F NMR (377 MHz, $CDCl_3$): δ -85.90 (minor diastereomer), -91.97 (major diastereomer). Ratio = 37:63.

HRMS (ESI): *m/z*: calculated for $C_{19}H_{23}NF$ $[M+H]^+$: 284.1815, found: 284.1810.

(3*S*)-*N*-Benzyl-2-fluoro-2-phenylhex-5-en-3-amine (*ent*-2o)



The title compound was prepared according to General procedure 1, however using 2-phenylpropanal (60.0 μL, 0.45 mmol), Jørgensen (*R*) catalyst (18.0 mg, 0.03 mmol), NFSI (94.6 mg, 0.3 mol), benzylamine (65.5 μL, 0.60 mmol) and pinacol allylboronate (112.6 μL, 0.60 mmol) with 24 h as the reaction times for both the fluorination reaction and the fluoro-Petasis reaction. Purification by flash column chromatography eluting with 5% EtOAc/*n*-hexane gave the title product (9.1 mg, 11%) as a colorless oil.

R$_f$ = 0.31 (5% EtOAc/*n*-hexane).

dr = 30:70.

$[\alpha]_D^{26}$ +34.1 (*c* 0.08, $CHCl_3$).

IR (neat): ν_{max} 3062, 2929, 2854, 1639 (C=C str.), 1611, 1495 (N-H bend), 1446, 1371 (CH_3 bend), 1279, 1175, 1137, 913 (C-F str.), 698 cm^{-1}.

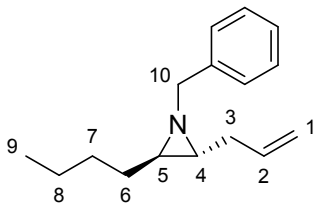
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 6.94 (m, 10H, Ar-*H*), 5.95 – 5.48 (m, 1H, H-2), 5.13 – 4.84 (m, 2H, H-1), 3.79 (dd, *J* = 12.8, 3.6 Hz, 1H, CH_2Ph), 3.59 (dd, *J* = 74.2, 12.7 Hz, 1H, CH_2Ph), 2.89 (dddd, *J* = 30.1, 18.8, 9.0, 3.7 Hz, 1H, H-4), 2.46 – 2.22 (m, 1H, H-3), 2.07 – 1.80 (m, 1H, H-3), 1.75 (dd, *J* = 23.4, 4.7 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9 (d, $J_{C,F}$ = 21.0 Hz, C-1", major), 142.9 (d, $J_{C,F}$ = 22.0 Hz, C-1", minor), 140.7 (C-2), 136.0 (C-1', major), 135.9 (C-1', minor), 128.3 (d, $J_{C,F}$ = 6.0 Hz, C-3"), 128.1 (C-3'), 128.0 (C-4"), 127.4 (C-4', minor), 127.3 (C-4', major), 126.9 (C-2'), 125.2 (d, $J_{C,F}$ = 9.0 Hz, C-2", minor), 124.9 (d, $J_{C,F}$ = 9.0 Hz, C-2", major), 117.2 (C-1), 101.2 (d, $J_{C,F}$ = 7.0 Hz, C-5, major), 99.5 (d, $J_{C,F}$ = 9.0 Hz, C-5, minor), 64.4 (d, $J_{C,F}$ = 9.0 Hz, C-4, major), 64.1 (d, $J_{C,F}$ = 8.0 Hz, C-4, minor), 53.8 (*C*H_2Ph, minor), 53.3 (*C*H_2Ph, major), 35.5 (d, $J_{C,F}$ = 4.0 Hz, C-3, minor), 34.9 (d, $J_{C,F}$ = 3.0 Hz, C-3, major), 24.7 (d, $J_{C,F}$ = 28.0 Hz, *C*H_3, major), 23.7 (d, $J_{C,F}$ = 9.0 Hz, *C*H_3, minor), 23.5 (d, $J_{C,F}$ = 9.0 Hz, *C*H_3, minor).

^{19}F NMR (377 MHz, $CDCl_3$): δ -85.93 (minor diastereomer), -92.01 (major diastereomer). Ratio = 30:70.

HRMS (ESI): *m/z*: calculated for $C_{19}H_{23}NF$ $[M+H]^+$: 284.1815, found: 284.1809.

(2*R*, 3*R*)2-Allyl-1-benzyl-3-butylaziridine (4)



Compound **2k** (0.010 g, 0.040 mmol) in EtOH (0.7 mL) was added to a flask containing KOH (0.015 g, 0.260 mmol). The reaction mixture was stirred and heated at reflux for 24 h, and then extracted into EtOAc (0.5 mL x 3). The EtOAc layer was dried and evaporated to afford a thick liquid that was purified by column chromatography to afford **4** (0.0044 g, 44%) as a colorless oil.

Rf = 0.28 (10% EtOAc/*n*-hexane).

***N*-invertomer** = 1:1.

$[\alpha]_D^{25}$ -76.1 (*c* 0.11, $CHCl_3$).

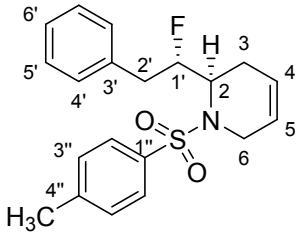
IR (neat): ν_{max} 3045, 2954, 1690, 1641 (C=C str.), 1503, 1009, 982, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$ (*for other invertomer)): δ 7.46 – 7.13 (m, 10H, Ar-*H*), 5.90 (ddt, *J* = 16.7, 10.1, 6.3 Hz, 1H, H-2), 5.71 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-2*), 5.17 (dd, *J* = 17.2, 1.7 Hz, 1H, H-1), 5.07 (dd, *J* = 10.3, 1.6 Hz, 1H, H-1), 5.03 (dd, *J* = 17.0, 1.5 Hz, 1H, H-1*), 4.95 (dd, *J* = 9.7, 1.6 Hz, 1H, H-2*), 3.85 (dd, *J* = 13.7, 7.4 Hz, 2H, H-10), 3.47 (dd, *J* = 13.7, 7.3 Hz, 2H, H-10*), 2.51 – 2.39 (m, 1H, H-3), 2.36 – 2.28 (m, 1H, H-3), 2.27 – 2.19 (m, 1H, H-3*), 2.15 – 2.05 (m, 1H, H-3*), 1.92 (td, *J* = 6.9, 2.9 Hz, 1H, H-4), 1.84 (dd, *J* = 7.4, 3.4 Hz, 1H, H-4*), 1.80 – 1.68 (m, 1H, H-5), 1.51 (q, *J* = 7.6 Hz, 1H, H-5*), 1.48 – 1.40 (m, 4H, H-6), 1.37 (dp, *J* = 8.1, 2.4 Hz, 4H, H-7), 1.24 (td, *J* = 8.0, 7.2, 3.7 Hz, 4H, H-8), 0.92 (t, *J* = 7.1 Hz, 3H, H-9), 0.82 (t, *J* = 6.8 Hz, 3H, H-9*).

^{13}C NMR (100 MHz, $CDCl_3$ (*for other invertomer)): δ 136.0 (*ipso-C*), 135.8 (*ipso-C**), 134.5 (C-2), 134.2 (C-2*), 128.3 (*m-C*), 128.1 (*o-C*), 126.7 (*p-C*), 116.0 (C-1), 115.7 (C-1*), 56.1 (C-10), 55.8 (C-10*), 45.8 (C-5), 45.3 (C-5*), 43.3 (C-4), 42.4 (C-4*), 37.6 (C-3), 35.5 (C-3*), 30.8 (C-7), 30.7 (C-7*), 26.8 (C-6), 25.9 (C-6*), 22.6 (C-8), 22.5 (C-8*), 16.4 (C-9), 14.0 (C-9*).

HRMS (ESI): *m/z:* calculated for $C_{16}H_{24}N$ $[M+H]^+$: 230.1909, found: 230.1905.

(*R*)-2-((*S*)-1-Fluoro-2-phenylethyl)-1-tosyl-1,2,3,6-tetrahydropyridine (5)



The title product was prepared by adding the tosylate (16.3 mg, 0.0421 mmol, 1.0 eq) to an oven dried 25 mL round-bottomed flask fitted with an oven dried condenser and flushing the apparatus with nitrogen for 10 min. To the flask was added anhydrous CH_2Cl_2 (4 mL) and Grubbs second generation catalyst (3.5 mg, 0.00421 mmol, 0.1 eq or 10 mol%) and the mixture was stirred and heated at reflux for 2 h with TLC monitoring. The resultant mixture was concentrated in vacuo and separated by flash column chromatography to obtain the pure product (10.9 mg, 72%) as a brown oil. This oil later crystallised into brown crystals after the removal of residual solvent under high vacuum.

R_f = 0.33 (20% EtOAc/*n*-hexane).

dr >99:1.

Mp.: 123-126 °C.

$[\alpha]_D^{22}$ +23.9 (*c* 0.52, $CHCl_3$).

IR (neat): ν_{max} 3029, 2927, 1662 (C=C str.), 1596, 1494, 1343 (S=O str.), 1164 (S=O str.), 923 (C-F str.), 817, 750, 701 cm^{-1}.

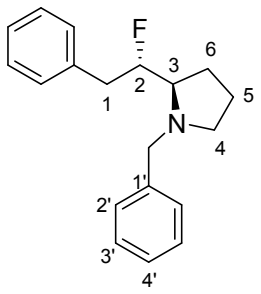
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.3, 1.5 Hz, 2H, H-2''), 7.36 – 7.19 (m, 7H, Ar-H, H-3''), 5.66 – 5.53 (m, 2H, H-4, H-5), 4.64 (dddd, *J* = 48.1 ($^2J_{H,F}$), 9.2, 2.1 Hz, 1H, H-1'), 4.23 – 4.12 (m, 2H, H-2, H-6), 3.68 – 3.56 (m, 1H, H-6), 3.16 (ddd, *J* = 37.1 ($^3J_{H,F}$), 15.0, 3.0 Hz, 1H, H-2'), 2.98 (ddd, *J* = 18.7, 15.0, 9.3 Hz, 1H, H-2'), 2.42 (s, 3H, CH_3Ph), 2.23 (ddd, *J* = 20.2 ($^3J_{H,F}$), 3.8, 3.4 Hz, 1H, H-3), 1.98 – 1.85 (m, 1H, H-3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5 (C-1''), 137.5 (C-4''), 137.4 (d, $^3J_{C,F}$ = 2.0 Hz, C-3'), 129.8 (C-2''), 129.3 (C-5'), 128.5 (C-4'), 126.9 (C-3''), 126.6 (C-6'), 123.5 (C-4), 122.3 (C-5), 92.7 (d, $^1J_{C,F}$ = 177.4 Hz, C-1'), 52.8 (d, $^2J_{C,F}$ = 27.4 Hz, C-2), 41.4 (C-6), 39.0 (d, $^2J_{C,F}$ = 20.5 Hz, C-2'), 22.8 (d, $^3J_{C,F}$ = 3.0 Hz, C-3), 21.6 (CH_3Ph).

^{19}F NMR (377 MHz, $CDCl_3$): δ -125.22.

HRMS (ESI): *m/z*: calculated for $C_{20}H_{22}SO_2NFNa$ $[M+Na]^+$: 382.1253, found: 382.1250.

2*R*-((1*S*)-Fluoro-2-phenylethyl)-1-benzylpyrrolidine (6)



Compound **2i** (0.015 g, 0.053 mmol) in THF (0.5 mL) was added to a stirred solution of mercury acetate (0.034 g, 0.106 mmol) in THF-water (1:1, 0.5 mL). The reaction mixture was stirred at rt for 24 h, quenched by sodium borohydride (0.008 g, 0.212 mmol) and then extracted into $CHCl_3$ (0.5 mL x 3). The $CHCl_3$ layer was dried and evaporated to afford a

thick liquid that was purified by column chromatography to afford **6** (0.0034 g, 23%) as a colorless oil.

R_f = 0.33 (10% EtOAc/*n*-hexane).

dr = 6:94.

$[\alpha]_D^{23}$ +16.8 (*c* 0.20, $CHCl_3$).

IR (neat): ν_{max} 3028, 2922, 2793, 1495, 1072, 996, 822, 737 (C-F str.), 698 cm^{-1}.

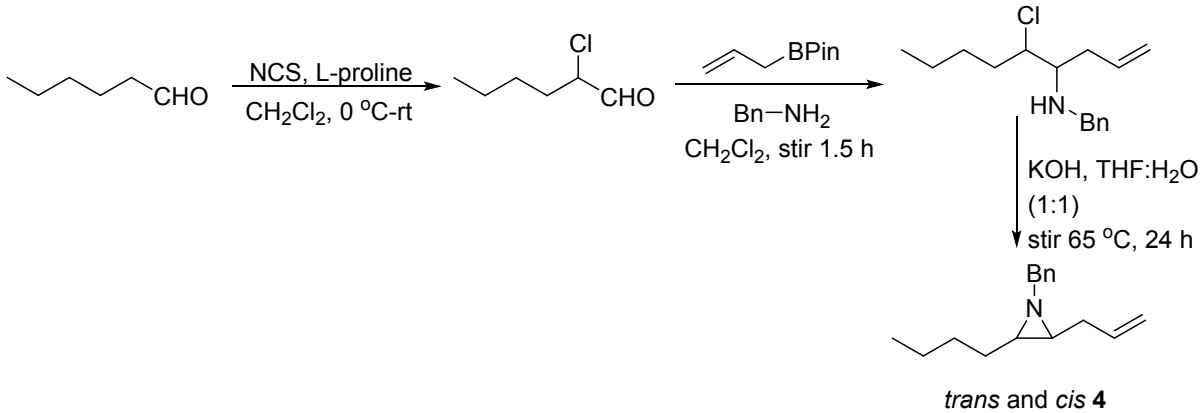
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 6.83 (m, 10H, Ar-*H*), 4.77 – 4.48 (m, 1H, H-2), 4.02 (dd, *J* = 13.2, 1.7 Hz, 1H, CH_2Ph), 3.44 (dd, *J* = 13.3, 1.7 Hz, 1H, CH_2Ph), 3.09 – 2.93 (m, 2H, H-1), 2.93 – 2.72 (m, 2H, H-3, H-4), 2.26 (q, *J* = 8.5, 8.1 Hz, 1H, H-4), 1.87 (td, *J* = 7.4, 2.2 Hz, 2H, H-6), 1.81 – 1.66 (m, 2H, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3 (C-1'), 137.9 (*ipso*-*C*), 129.2 (*o, m*-Ar-*C*H), 128.9 (*o, m*-Ar-*C*H), 128.5 (*o, m*-Ar-*C*H), 128.2 (*o, m*-Ar-*C*H), 126.9 (*p*-Ar-*C*H), 126.5 (*p*-Ar-*C*H), 95.1 (d, $^1J_{C,F}$ = 175.0 Hz, C-2), 65.5 (d, $^2J_{C,F}$ = 65.5 Hz, C-3), 59.6 (*C*H_2Ph), 54.6 (C-4), 38.4 (d, $^2J_{C,F}$ = 22.0 Hz, C-1), 25.6 (d, $^3J_{C,F}$ = 6.0 Hz, C-6), 23.42 (C-5).

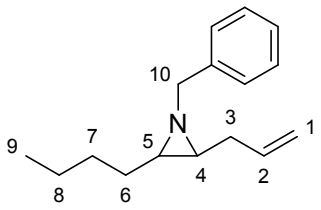
^{19}F NMR (377 MHz, $CDCl_3$): δ -123.52 (minor diastereomer), -124.50 (major diastereomer). Ratio = 6:94.

HRMS (ESI): *m/z*: calculated for $C_{19}H_{23}NF$ $[M+H]^+$: 284.1815, found: 284.1826.

***Trans* and *cis*-2-Allyl-1-benzyl-3-butylaziridine (4)**



Scheme 2 Synthesis of *trans* and *cis* aziridine **4** from α-chloroaldehyde.



The title compounds were prepared by adding NCS (0.060 g, 0.45mmol) to a mixture of hexanal (55.0 μL, 0.45 mmol) and L-proline (0.010 g, 0.09 mmol) at 0 °C and the reaction mixture was allowed to warm to rt and stirred for 1 h. Pentane (2 mL) was added and the mixture was stirred vigourously for 20 min and then filtered through a pad of celite eluting with CH_2Cl_2. Benzylamine (74.0 μL, 0.675 mmol) and pinacol allylboronate (126.0 μL, 0.675mmol) were then added to the mixture and the mixture stirred vigourously at room temperature for 1.5 h with TLC monitoring. The crude reaction mixture was concentrated in vacuo then dissolved in 1:1 THF/H_2O along with KOH (6.5 equiv) and stirred overnight at 65 ^oC. The reaction mixture was extracted with EtOAc, dried over $NaSO_4$, and concentrated under vacuum to give the crude product. Purification by flash column chromatography eluting with 30 % EtOAc/*n*-hexane gave the *trans*-aziridine (33.6 mg, 32%) and the *cis*-aziridine (10.7 mg, 10%) as colorless oils.

R_f = *trans*-aziridine, 0.45 (30% EtOAc/*n*-hexane) and *cis*-aziridine 0.38 (30% EtOAc/*n*-hexane).

IR (neat): ν_{max} 3045, 2954, 1690, 1641 (C=C str.), 1503, 1009, 982, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): *trans* (1:1 mixture of invertomers, *other invertomer) δ 7.46 – 7.13 (m, 10H, Ar-*H*), 5.90 (ddt, *J* = 16.7, 10.1, 6.3 Hz, 1H, H-2), 5.71 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-2*), 5.17 (dd, *J* = 17.2, 1.7 Hz, 1H, H-1), 5.07 (dd, *J* = 10.3, 1.6 Hz, 1H, H-1), 5.03 (dd, *J* = 17.0, 1.5 Hz, 1H, H-1*), 4.95 (dd, *J* = 9.7, 1.6 Hz, 1H, H-2*), 3.85 (dd, *J* = 13.7, 7.4 Hz, 2H, H-10), 3.47 (dd, *J* = 13.7, 7.3 Hz, 2H, H-10*), 2.51 – 2.39 (m, 1H, H-3), 2.36 – 2.28 (m, 1H, H-3), 2.27 – 2.19 (m, 1H, H-3*), 2.15 – 2.05 (m, 1H, H-3*), 1.92 (td, *J* = 6.9, 2.9 Hz, 1H, H-4), 1.84 (dd, *J* = 7.4, 3.4 Hz, 1H, H-4*), 1.80 – 1.68 (m, 1H, H-5), 1.51 (q, *J* = 7.6 Hz, 1H, H-5*), 1.48 – 1.40 (m, 4H, H-6), 1.37 (dp, *J* = 8.1, 2.4 Hz, 4H, H-7), 1.24 (td, *J* = 8.0, 7.2, 3.7 Hz, 4H, H-8), 0.92 (t, *J* = 7.1 Hz, 3H, H-9), 0.82 (t, *J* = 6.8 Hz, 3H, H-9*).

^{1}H NMR (400 MHz, $CDCl_3$): c*is* (1:1 mixture of invertomers, *other invertomer) δ 7.40 – 7.21 (m, 15H, Ar-*H*), 5.96 – 5.85 (m, 1H, H-2), 5.86 – 5.76 (m, 1H, H-2), 5.76 – 5.65 (m, 1H, H-2*), 5.21 – 5.14 (m, 2H, H-1), 5.07 (dd, *J* = 10.3, 1.6 Hz, 1H, H-1), 5.05 – 4.99 (m, 1H, H-1), 4.98 – 4.91 (m, 1H, H-1*), 4.74 (dd, *J* = 7.7, 5.3 Hz, 1H, H-1*), 3.85 (dd, *J* = 13.7, 7.6 Hz, 2H, H-10), 3.47 (dd, *J* = 13.7, 7.5 Hz, 2H, H-10), 2.58 – 2.49 (m, 2H, H-3), 2.50 – 2.40 (m, 1H, H-3*), 2.37 – 2.20 (m, 1H, H-3*), 2.15 – 2.02 (m, 1H, H-4), 1.92 (td, *J* = 7.0, 3.0 Hz, 1H, H-4*), 1.84 (dd, *J* = 7.4, 3.4 Hz, 1H, H-5), 1.79 – 1.69 (m, 1H, H-5*), 1.50 – 1.41 (m, 4H, H-6), 1.42 – 1.32 (m, 4H, H-7), 1.24 (td, *J* = 8.1, 7.1, 3.8 Hz, 4H, H-8), 0.92 (t, *J* = 7.1 Hz, 3H, H-9), 0.82 (t, *J* = 6.8 Hz, 3H, H-9*).

^{13}C NMR (100 MHz, $CDCl_3$): *trans* (1:1 mixture of invertomers, *other invertomer) δ 136.0 (*ipso-C*), 135.8 (*ipso-C**), 134.5 (C-2), 134.2 (C-2*), 128.3 (*m-C*), 128.1 (*o-C*), 126.7 (*p-C*),

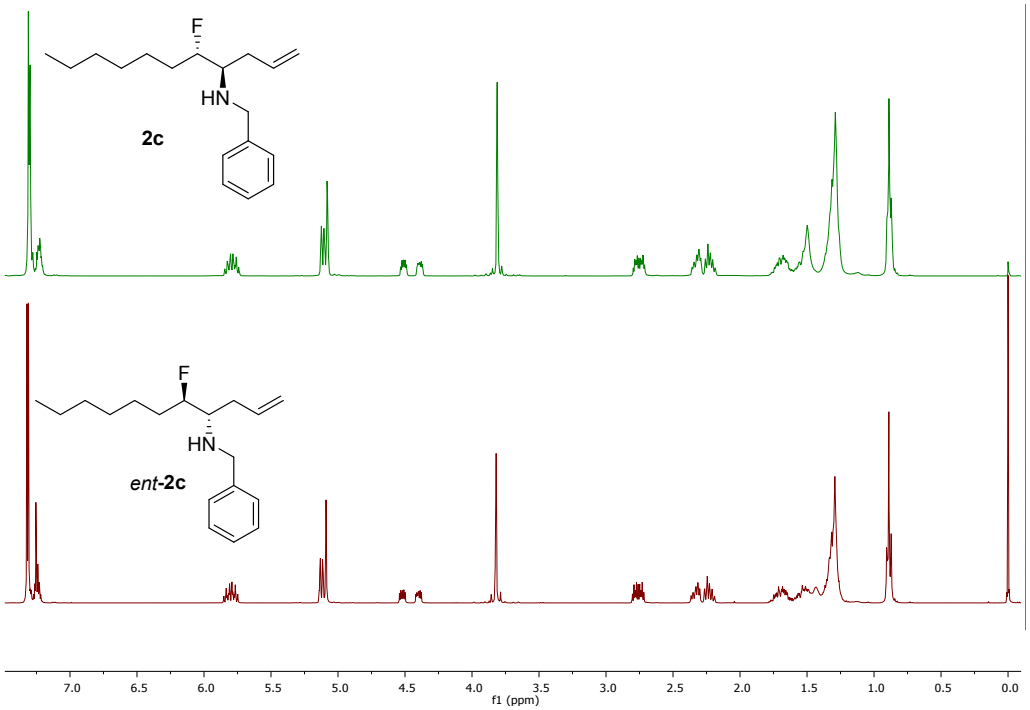
116.0 (C-1), 115.7 (C-1*), 56.1 (C-10), 55.8 (C-10*), 45.8 (C-5), 45.3 (C-5*), 43.3 (C-4), 42.4 (C-4*), 37.6 (C-3), 35.5 (C-3*), 30.8 (C-7), 30.7 (C-7*), 26.8 (C-6), 25.9 (C-6*), 22.6 (C-8), 22.5 (C-8*), 16.4 (C-9), 14.0 (C-9*).

^{13}C NMR (100 MHz, $CDCl_3$): *cis* (1:1 mixture of invertomers, *other invertomer) δ 136.0 (*ipso-C*), 135.8 (*ipso-C**), 134.5 (C-2), 128.4 (*m-C*), 128.3 (*m-C**), 128.1 (*o-C*), 128.0 (*o-C**), 127.6 (*p-C*), 126.8 (*p-C**), 118.4 (C-1), 116.1 (C-1*) , 73.32, 56.1 (C-10), 55.8 (C-10*), 45.8 (C-5), 45.3 (C-5*), 43.9 (C-4), 43.3 (C-4*), 42.46, 37.6 (C-3), 32.8 (C-3*), 30.8 (C-7), 30.7 (C-7*), 29.6 (C-8), 25.9 (C-8*), 22.6 (C-9), 14.0 (C-9*).

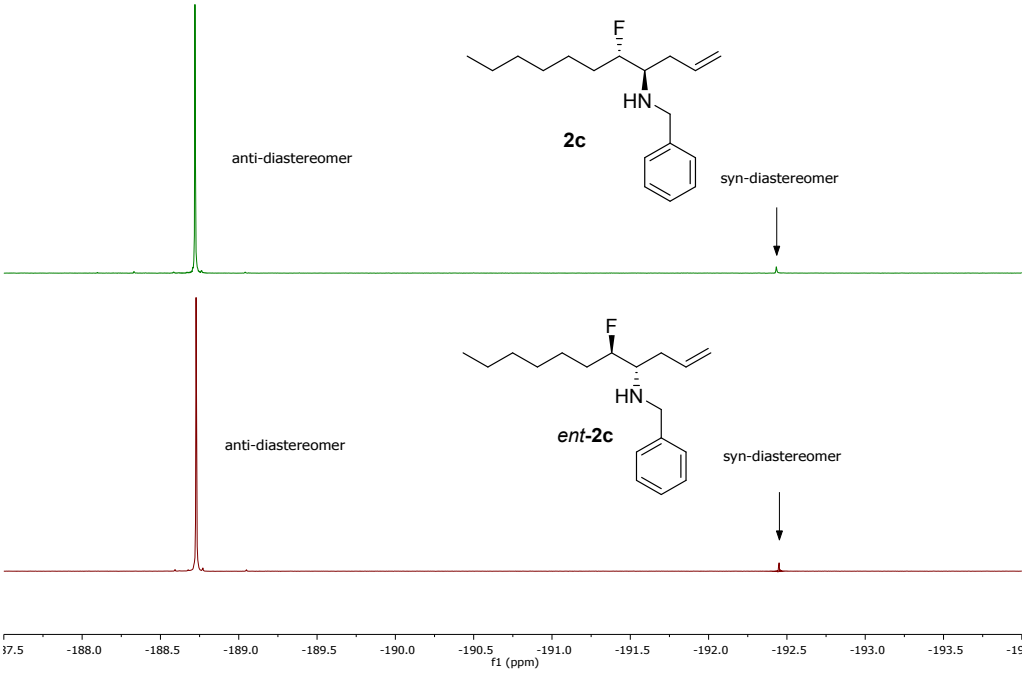
HRMS (ESI): *m/z:* calculated for $C_{16}H_{24}N$ $[M+H]^+$: 230.1909, found: 230.1905.

NMR Spectra

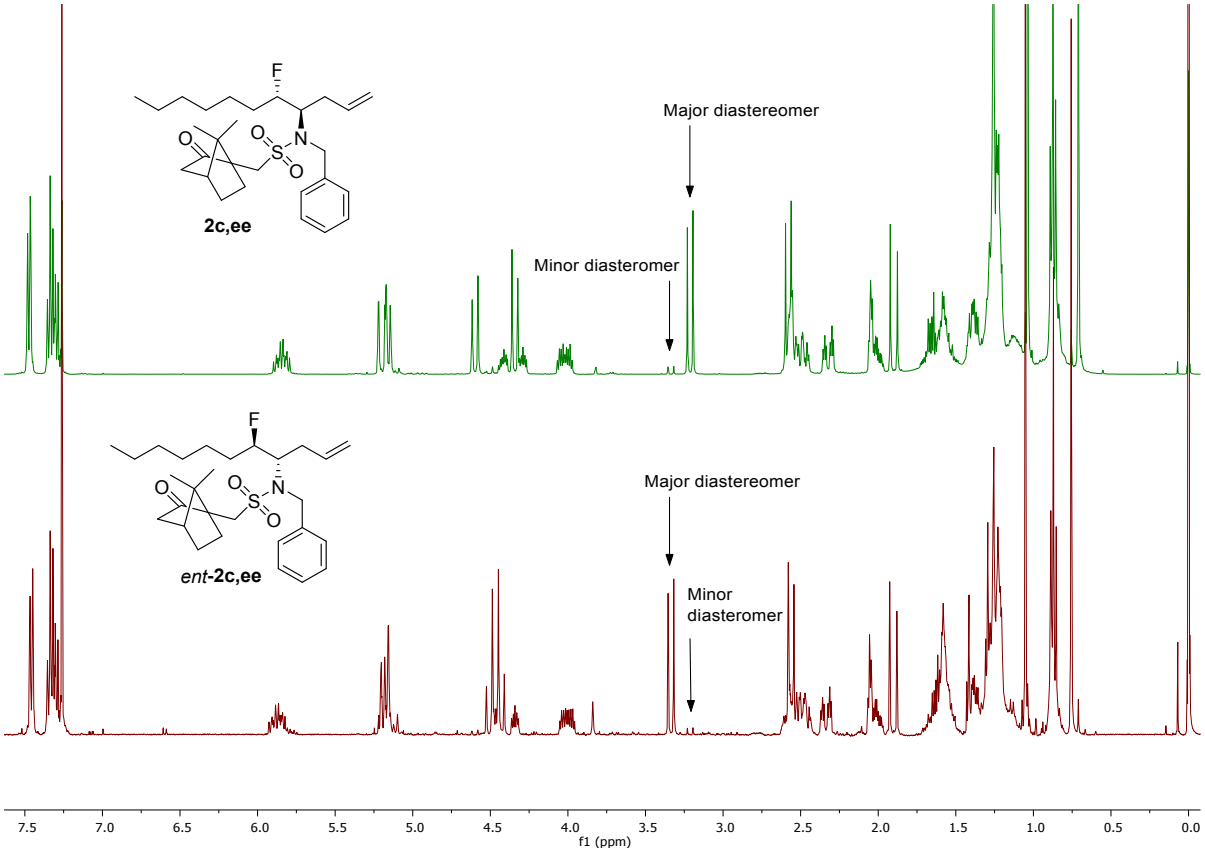
.



^{1}H NMR spectra ($CDCl_3$, 400 MHz) of the enantiomeric compounds **2c** (top) and *ent*-**2c** (bottom), which produce identical spectra.



^{19}F NMR spectra ($CDCl_3$, 377 MHz) of the enantiomeric compounds **2c** (top) and *ent*-**2c** (bottom), which produce identical spectra.



^{1}H NMR spectra ($CDCl_3$, 400 MHz) of the (S)-camphorsulfonamide derivatives of compounds **2c** (top) and *ent*-**2c** (bottom).

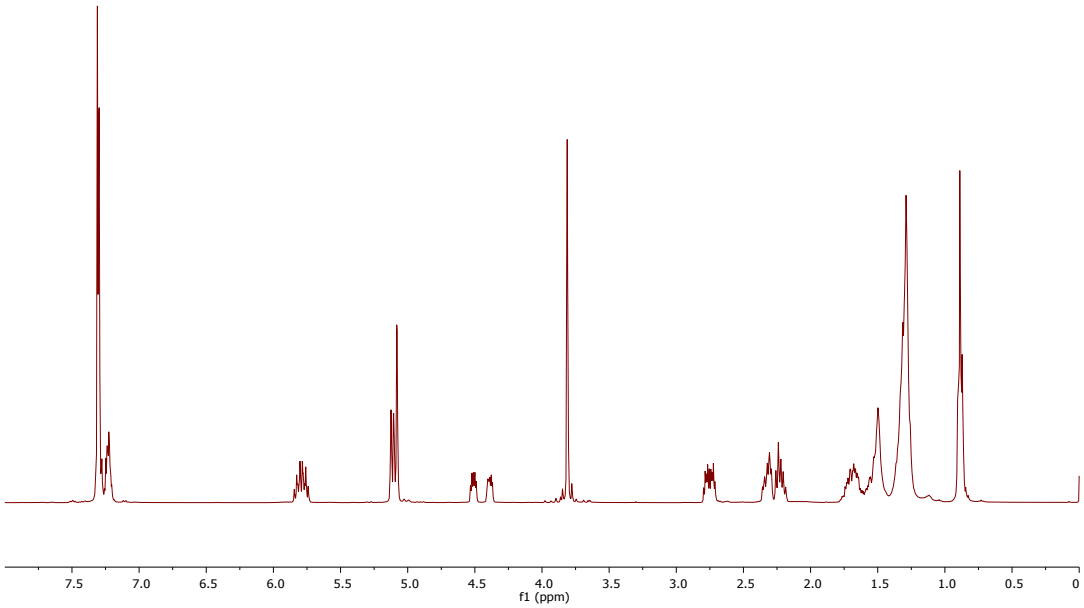


Figure 2.1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**.

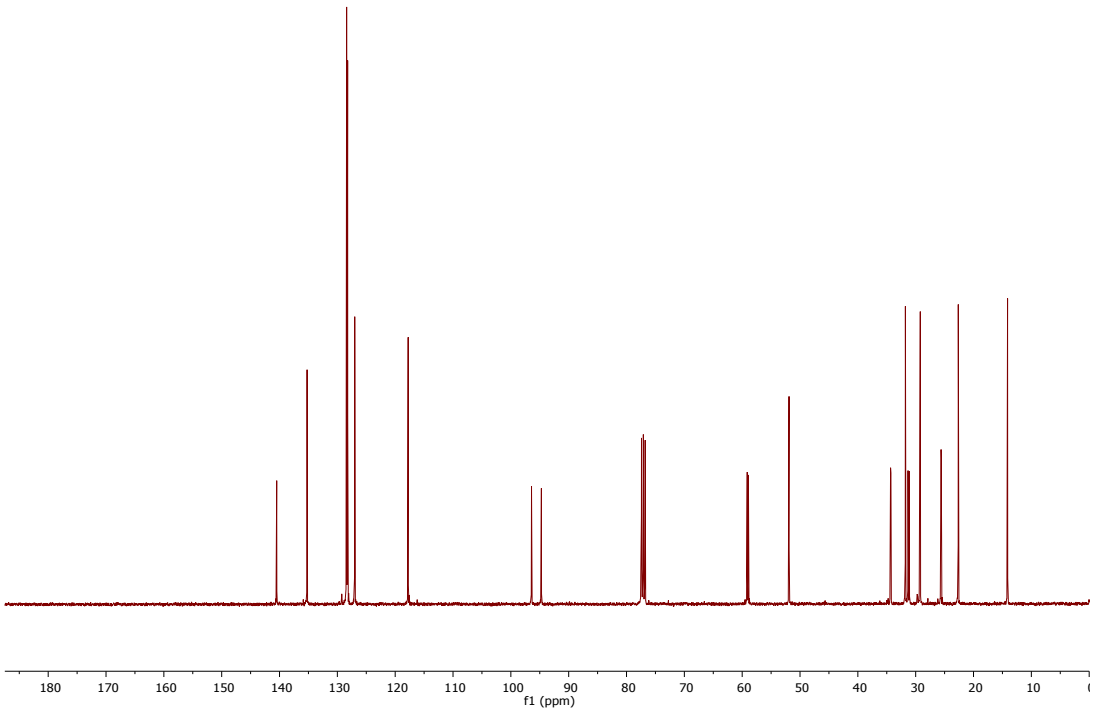


Figure 2.2: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2c**.

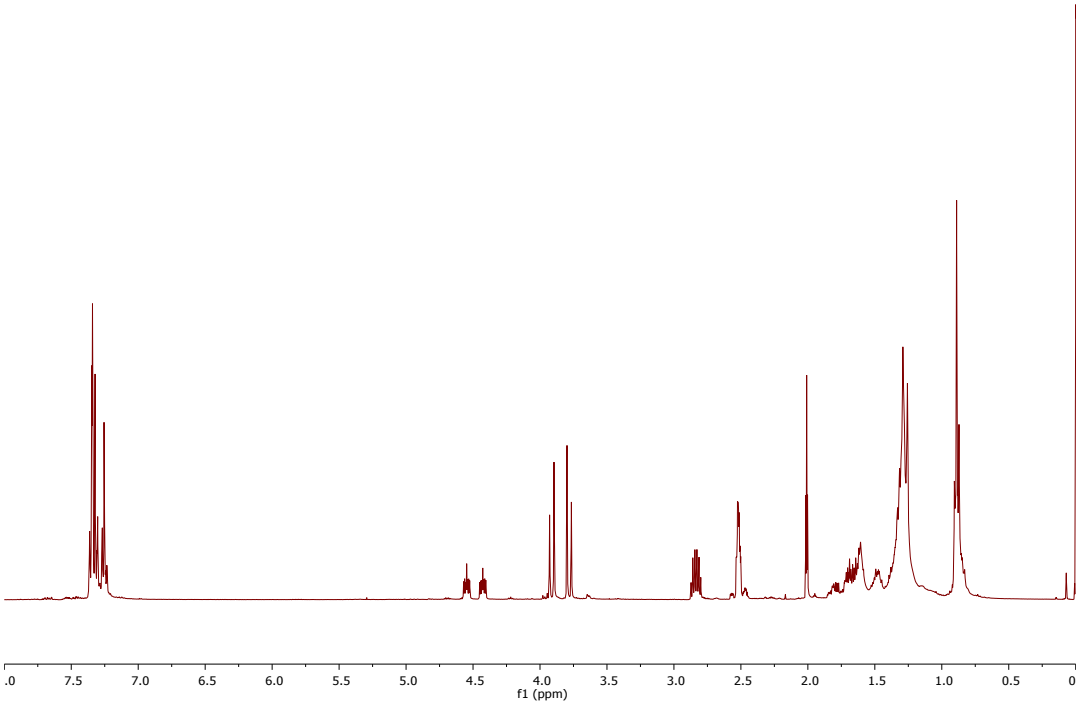


Figure 2.5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2e**.

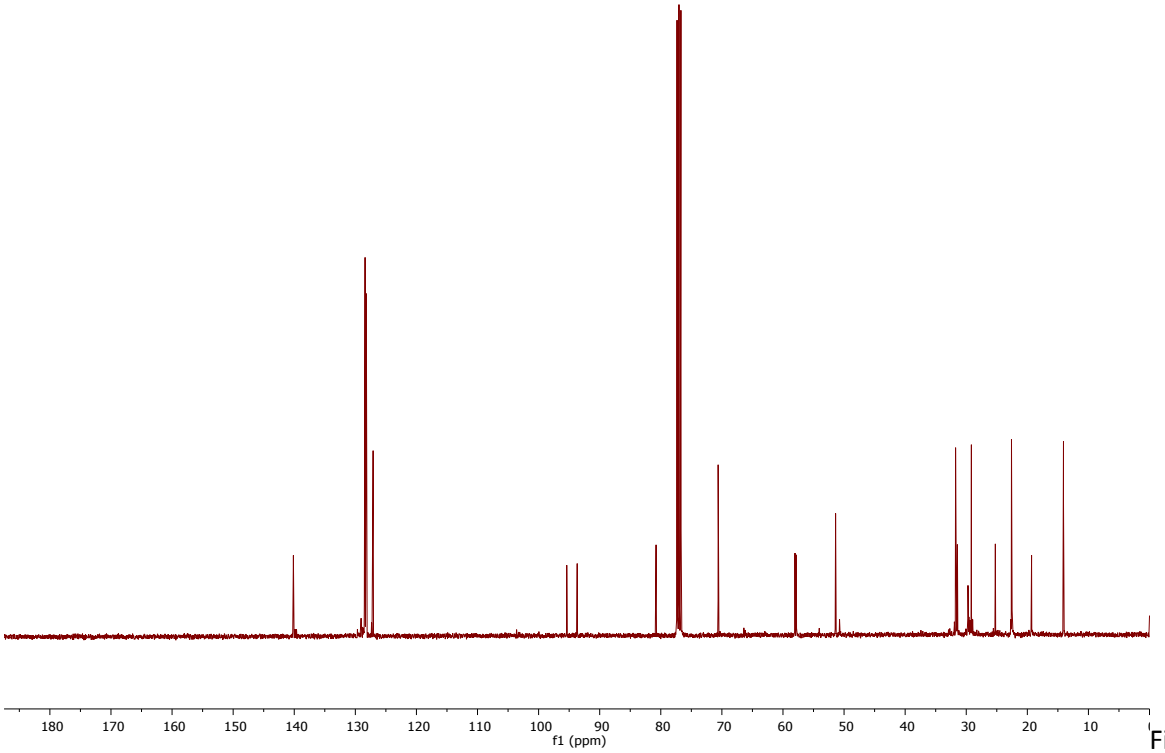


Figure 2.6: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2e**.

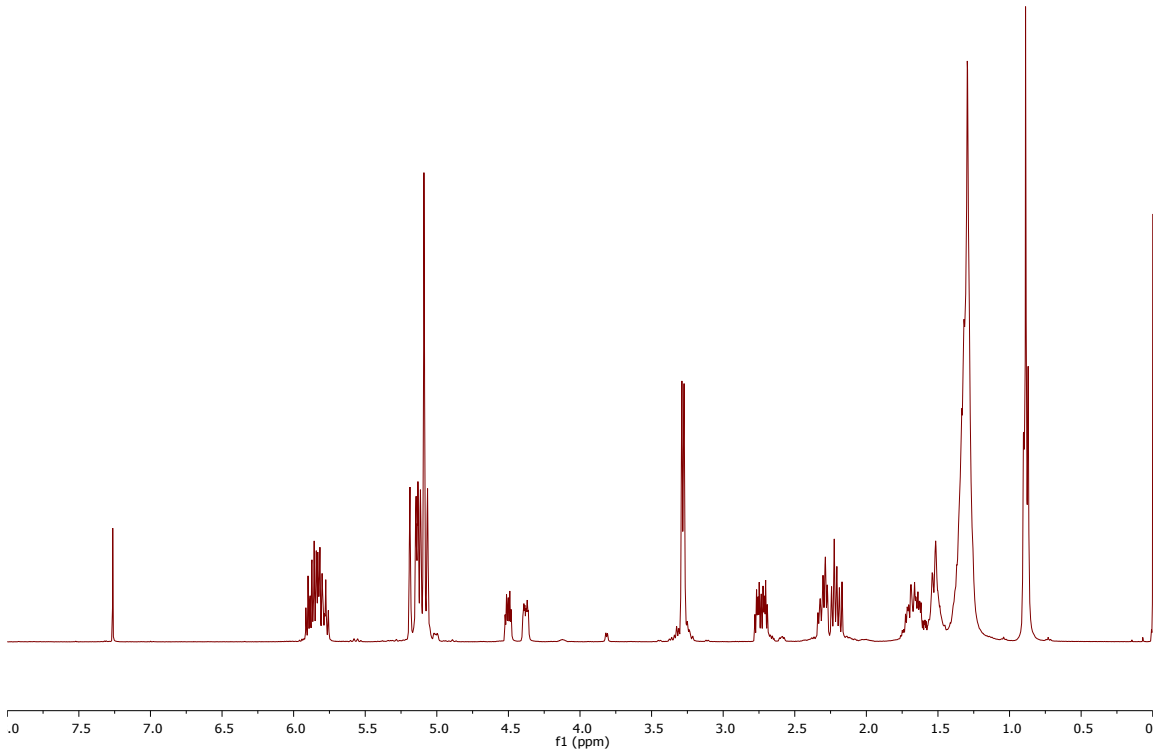


Figure 2.7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2f**.

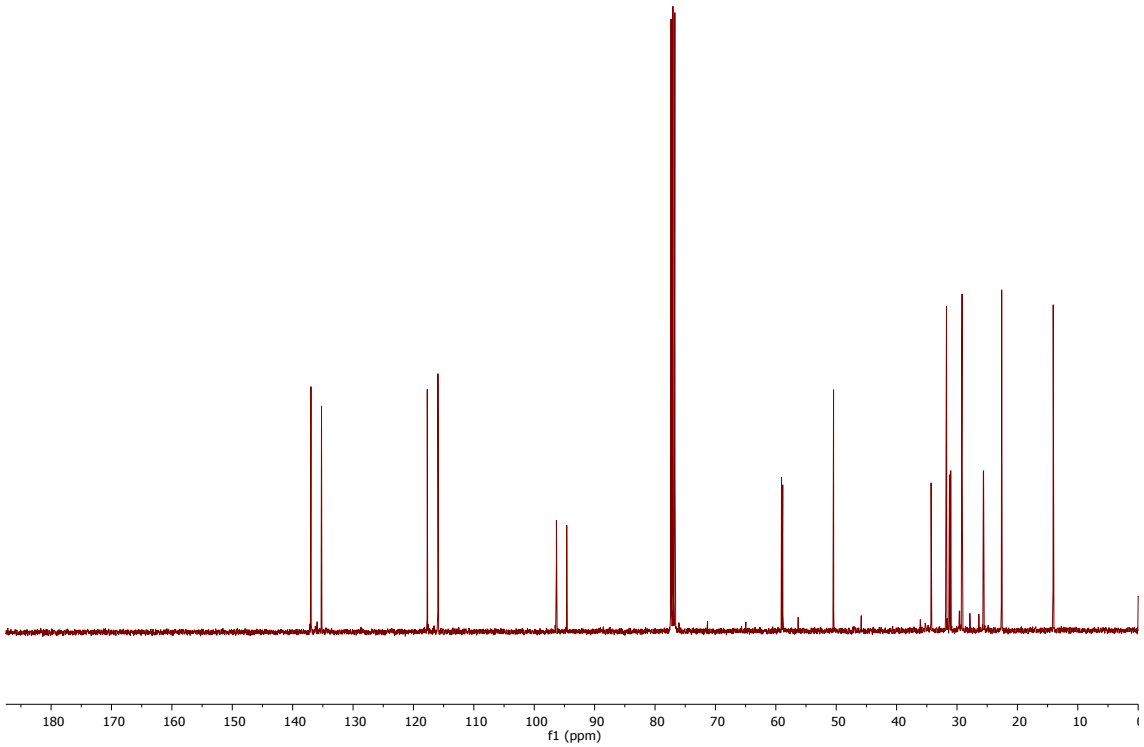


Figure 2.8: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2f**.

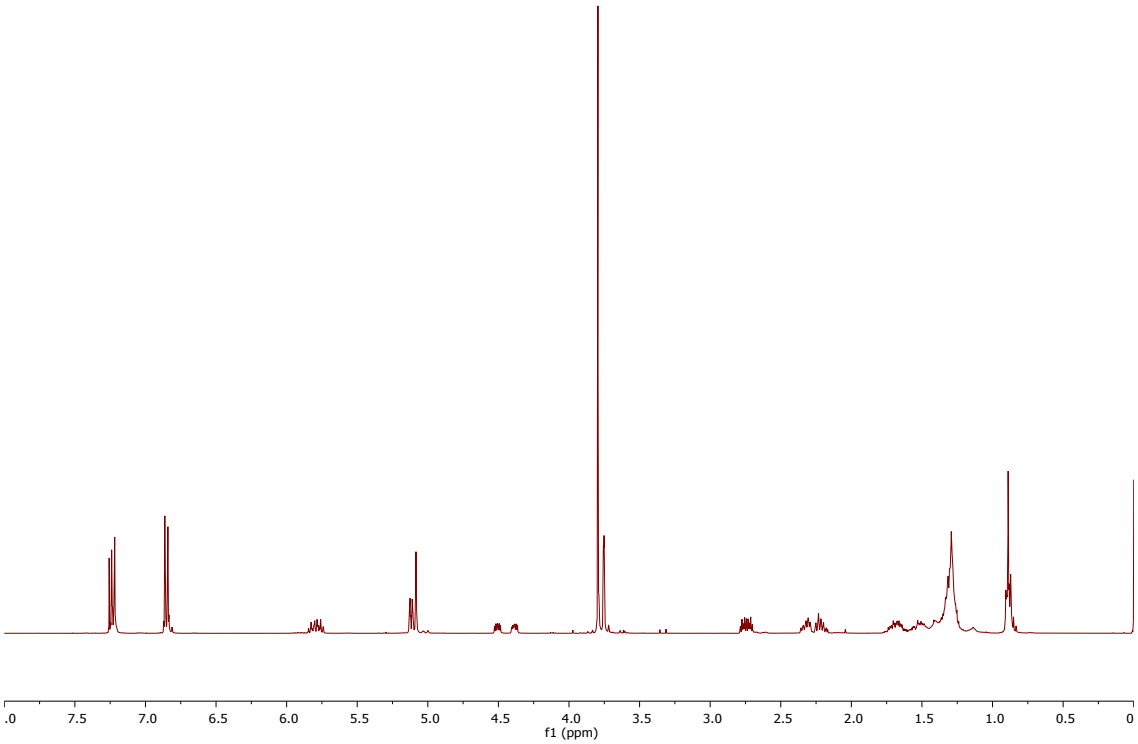


Figure 2.9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2g**.

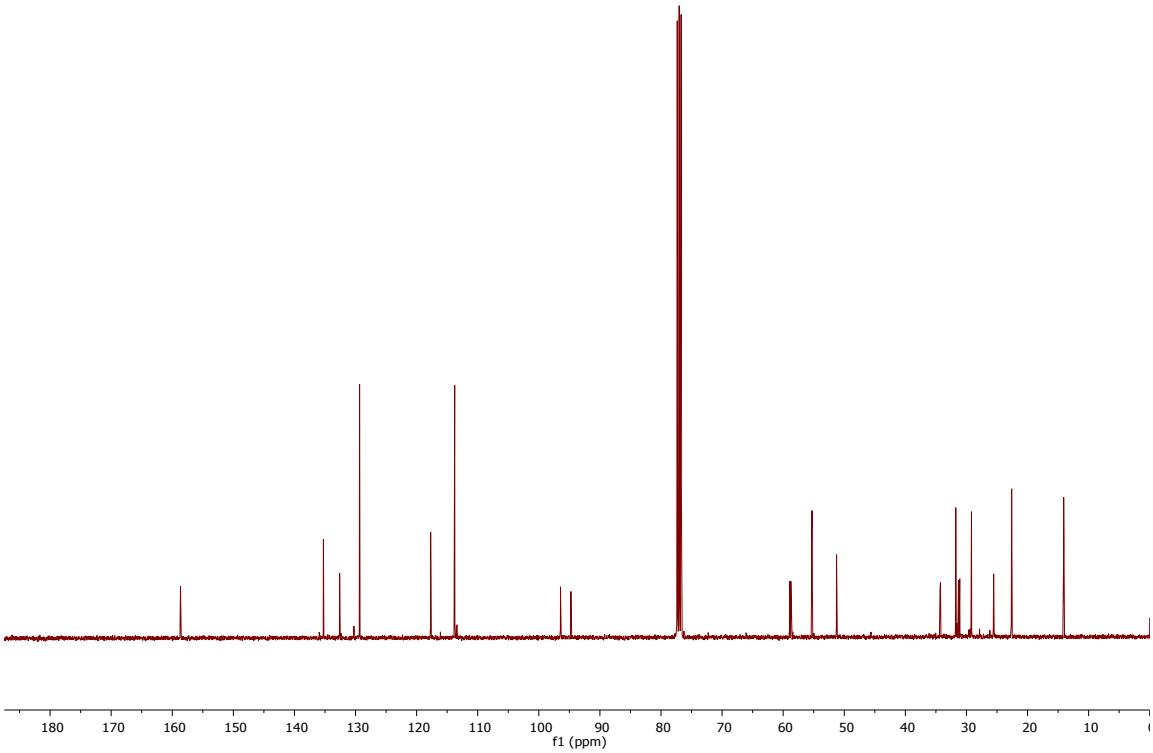


Figure 2.10: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2g**.

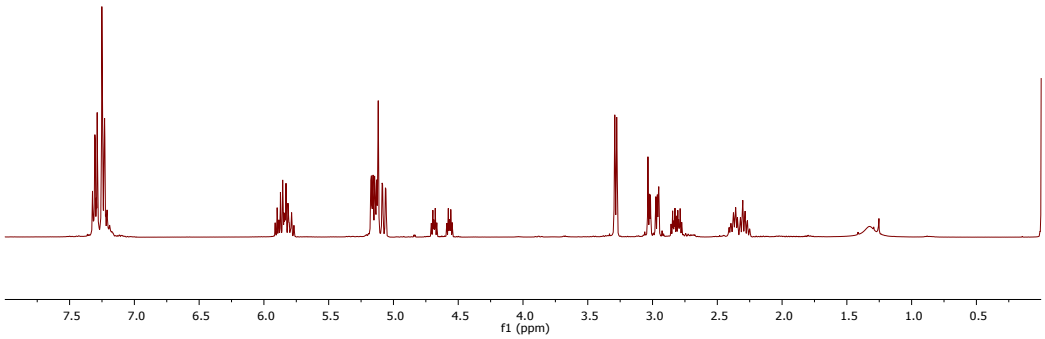


Figure 2.11: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2h**.

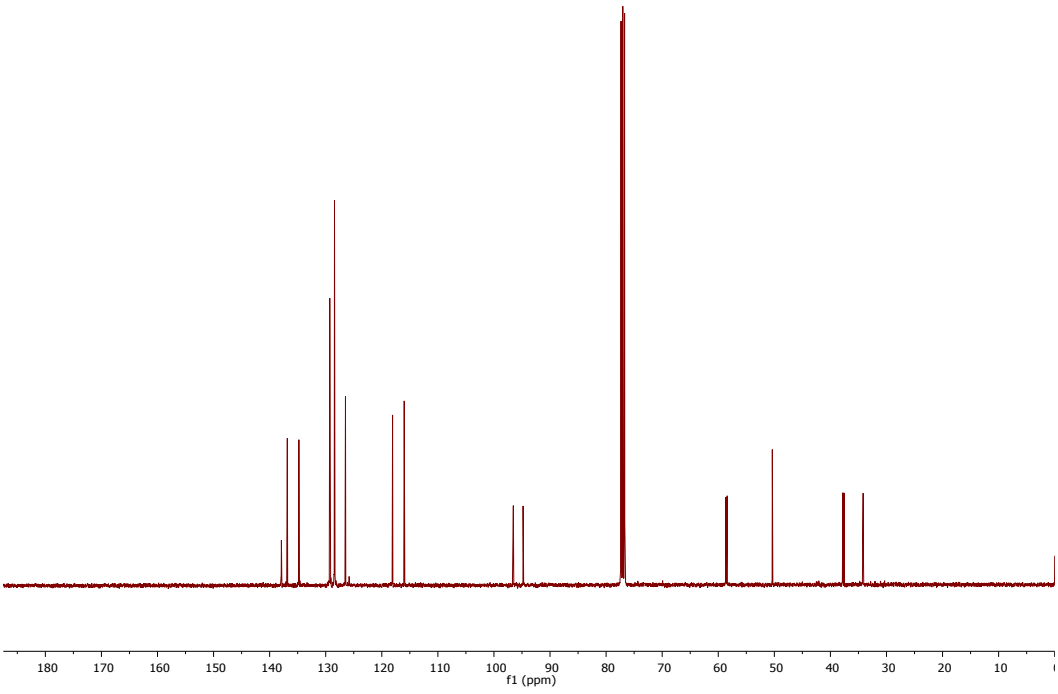


Figure 2.12: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2h**.

Figure 2.13: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2i**.

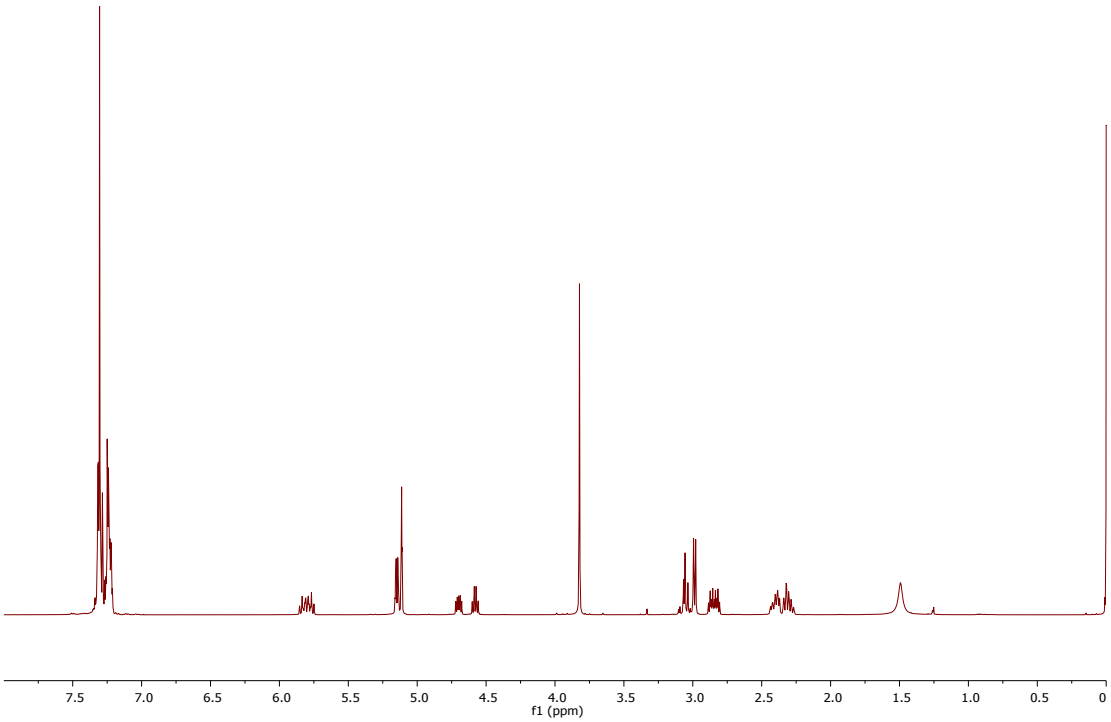


Figure 2.3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2i**.

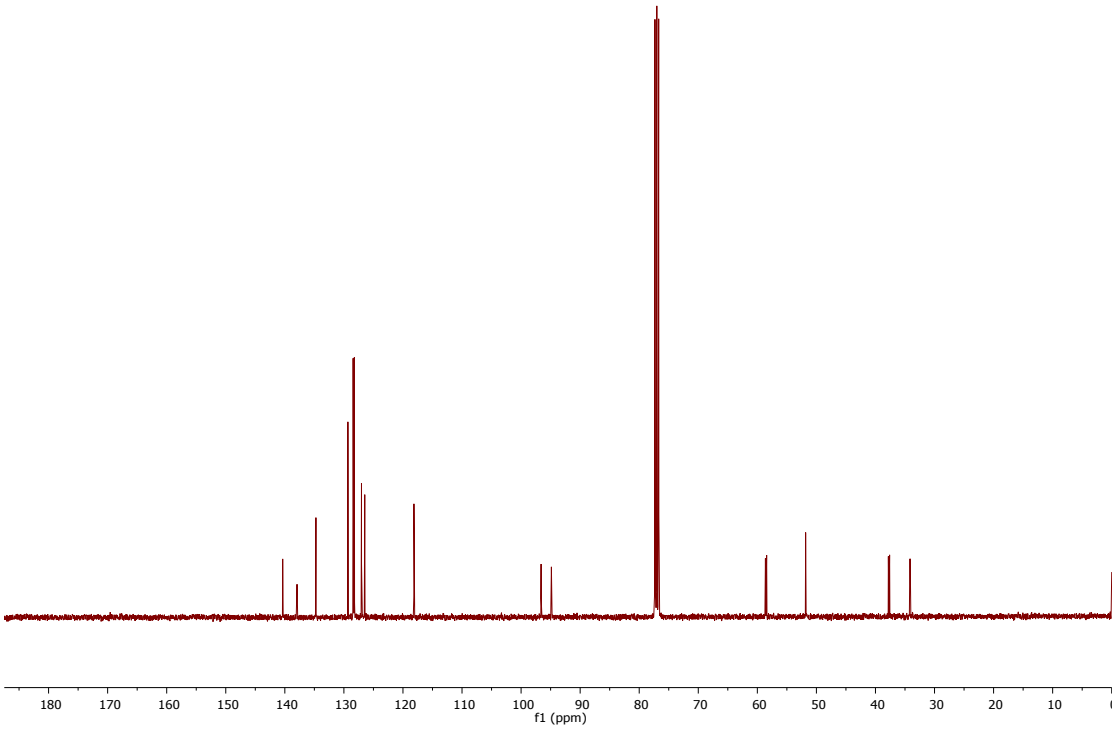


Figure 2.4: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2i**.

^{1}H and ^{13}C NMR spectra of compound 2j.

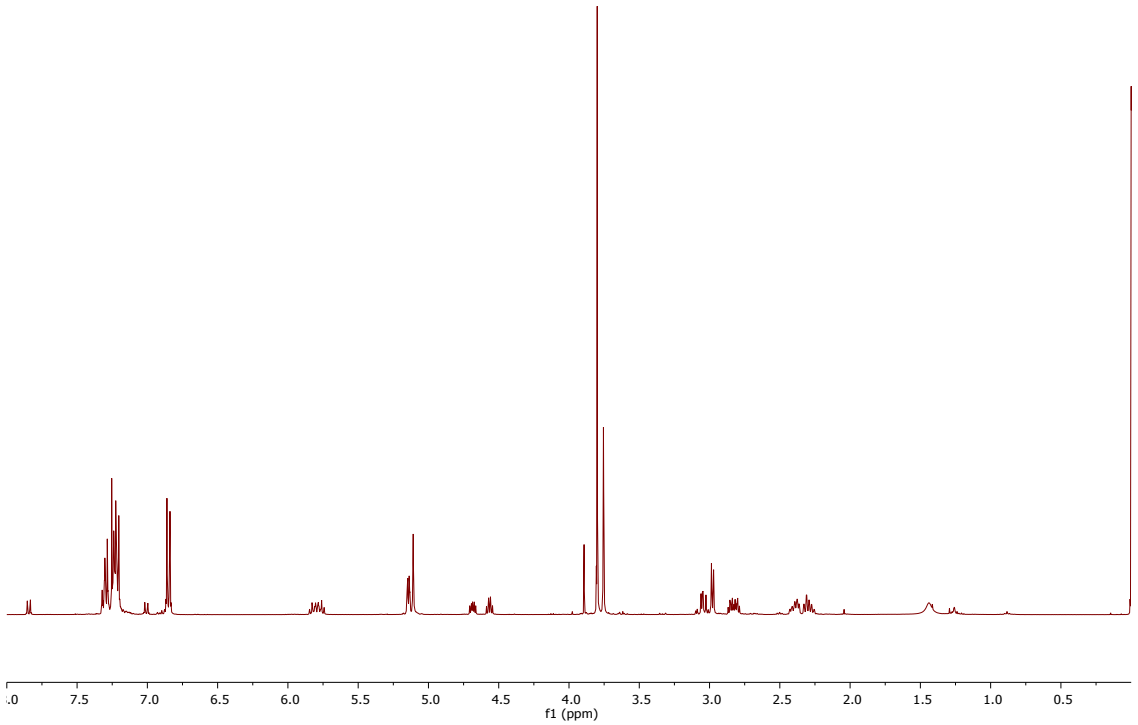


Figure 2.15: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2j**.

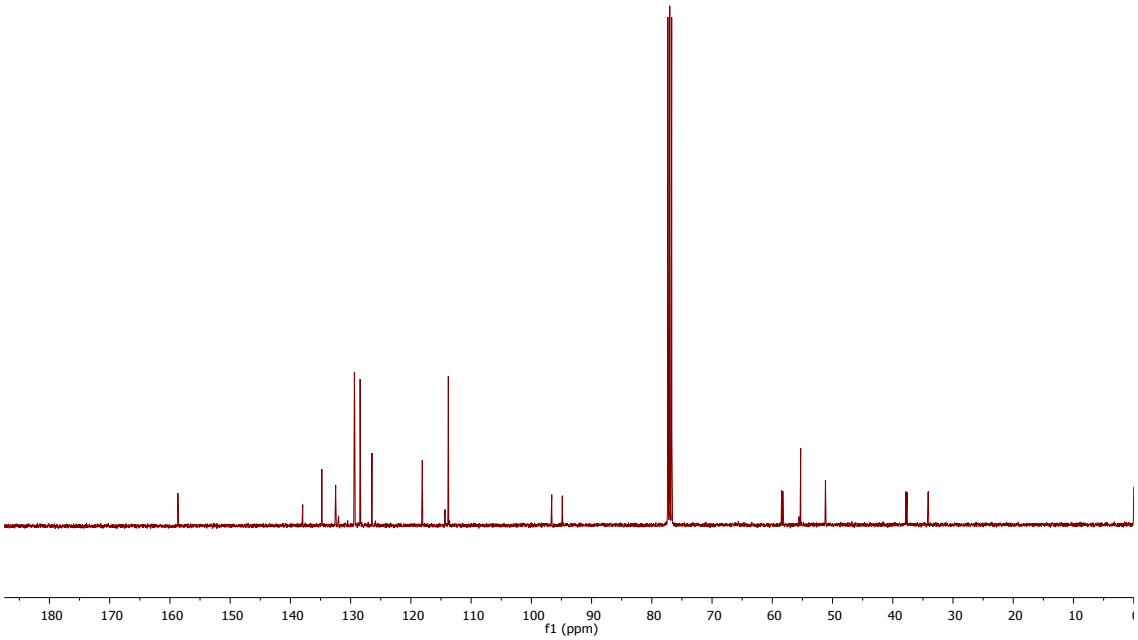


Figure 2.16: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2j**.

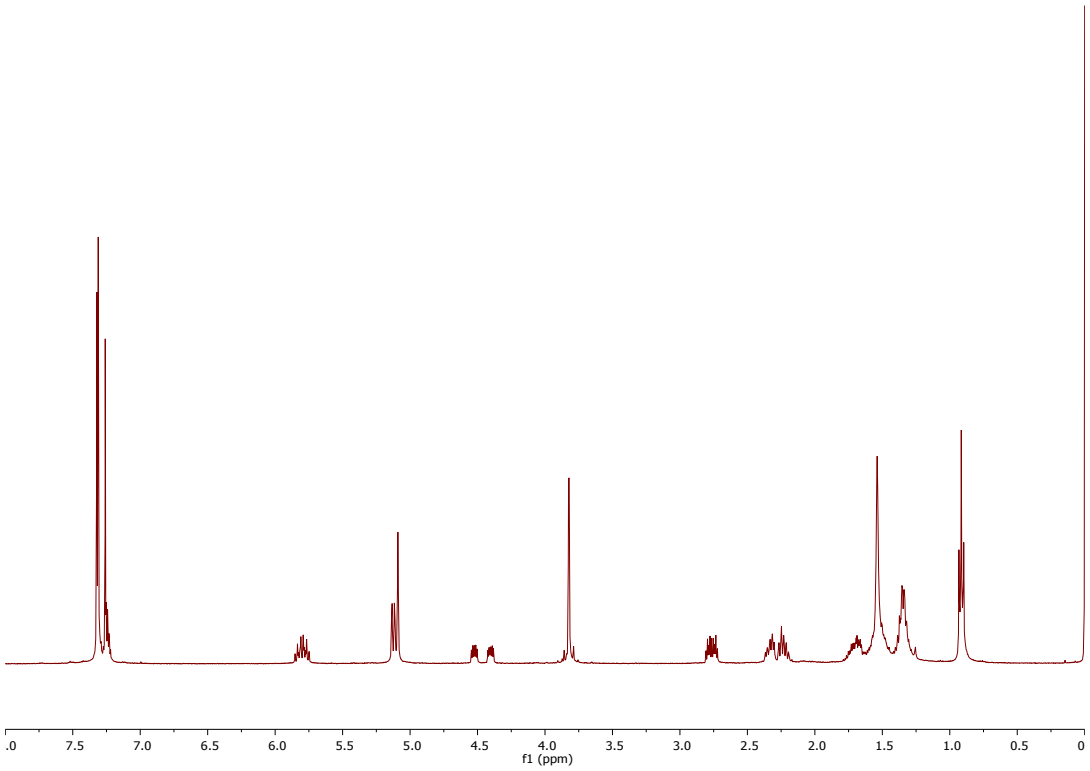


Figure 2.7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2k**.

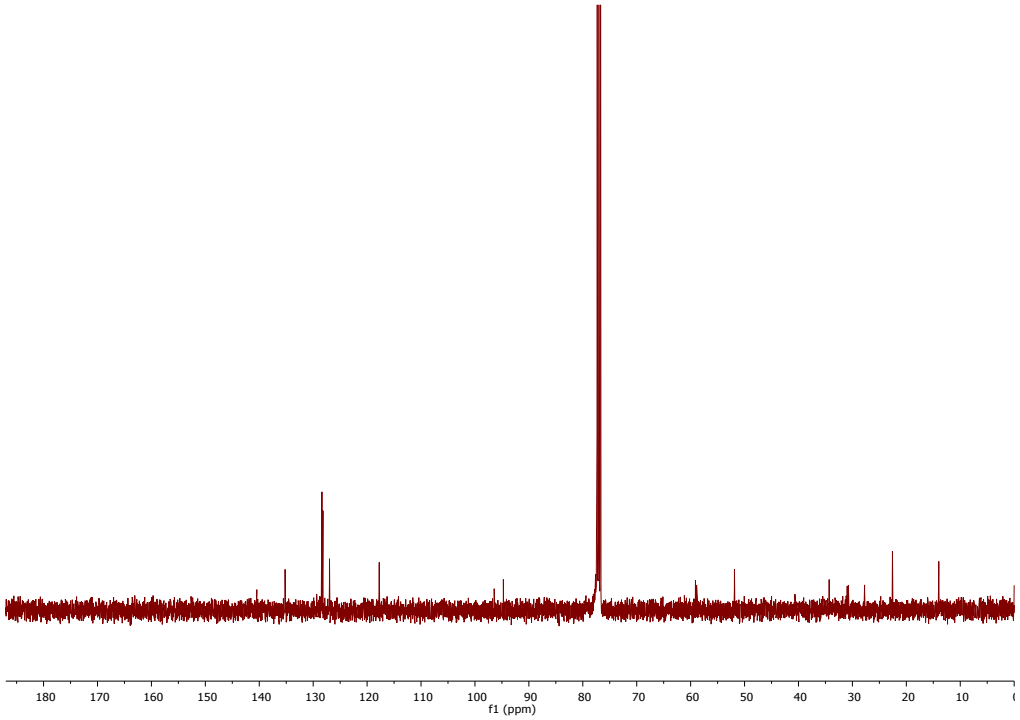


Figure 2.8: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2k**.

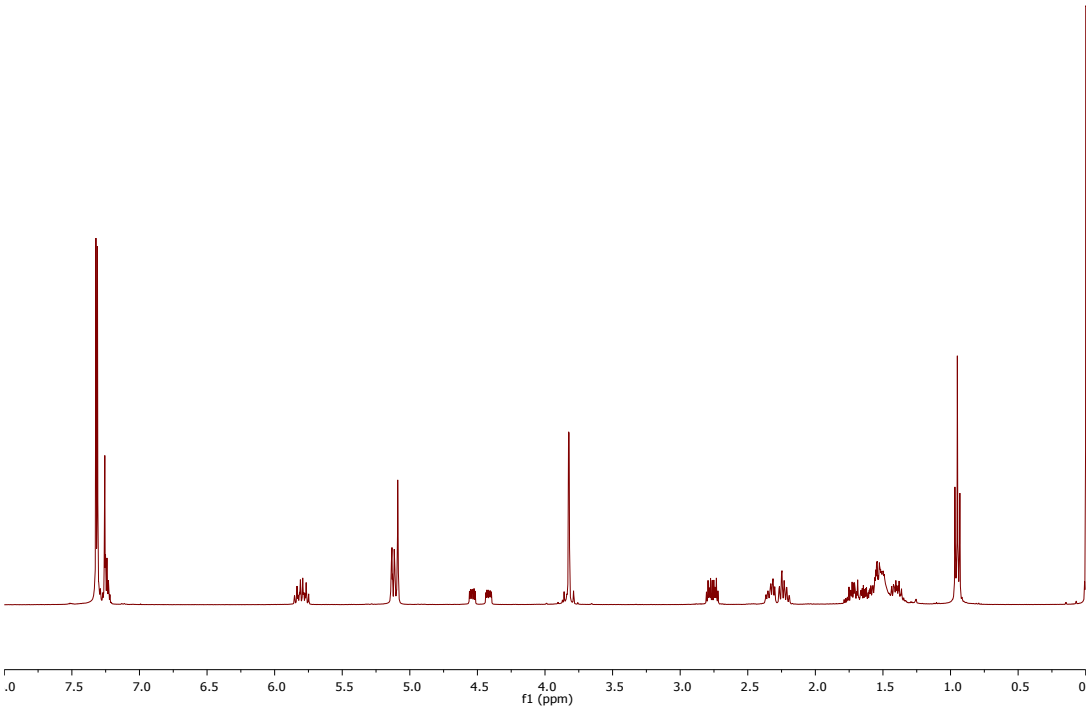


Figure 2.11: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2l**.

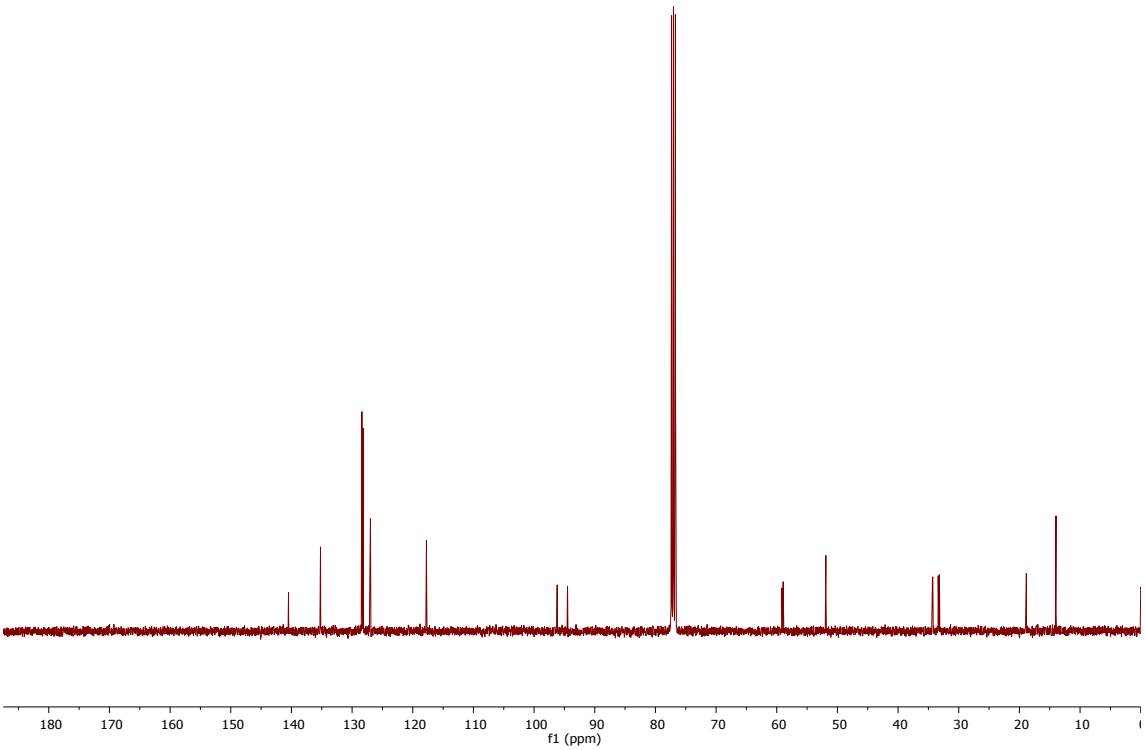


Figure 2.12: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2l.**

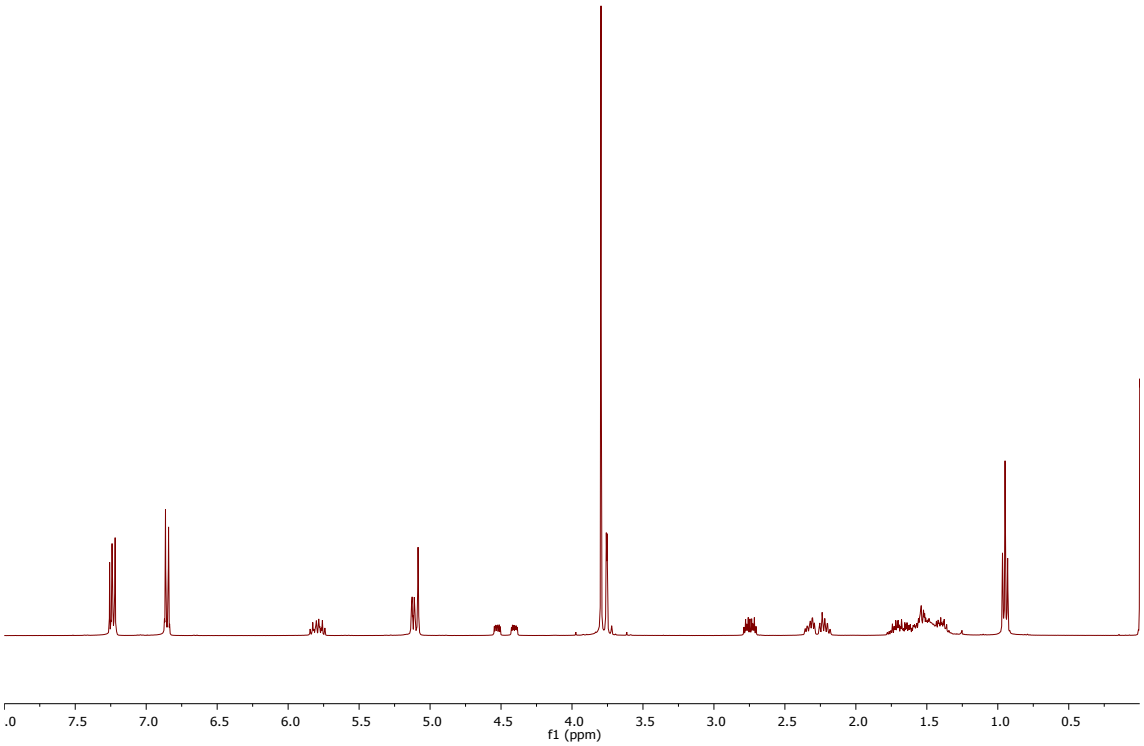


Figure 2.15: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2m**.

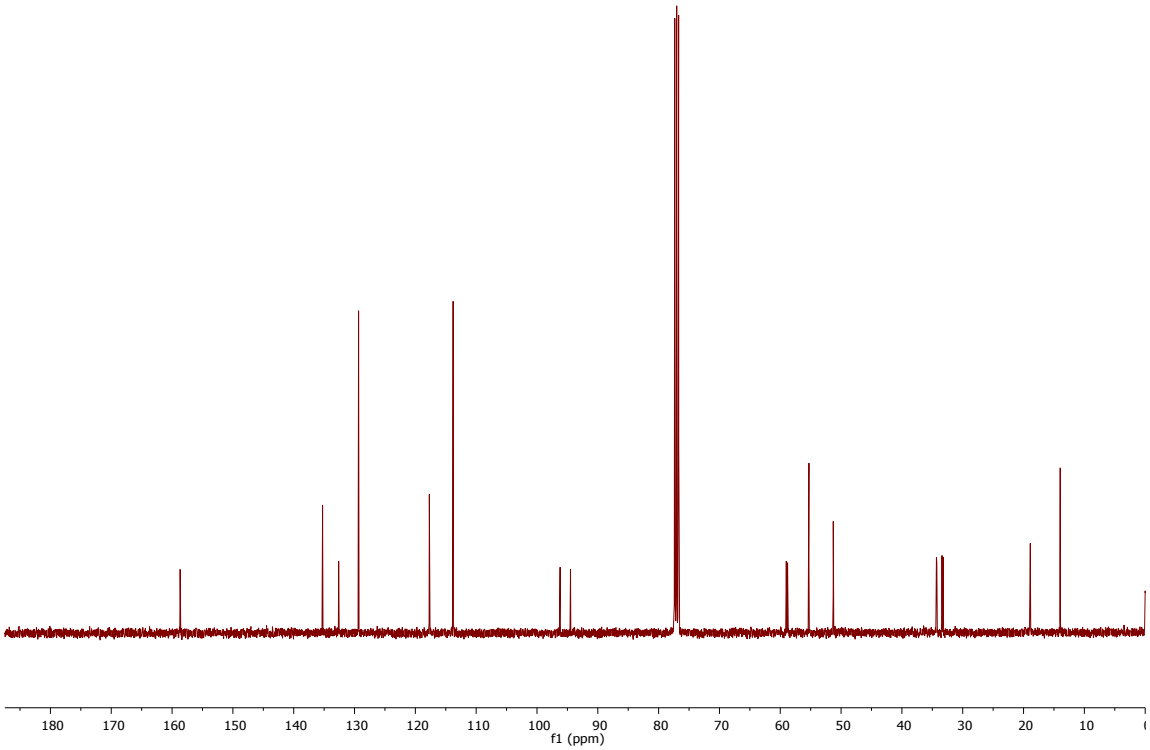


Figure 2.16: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2m.**

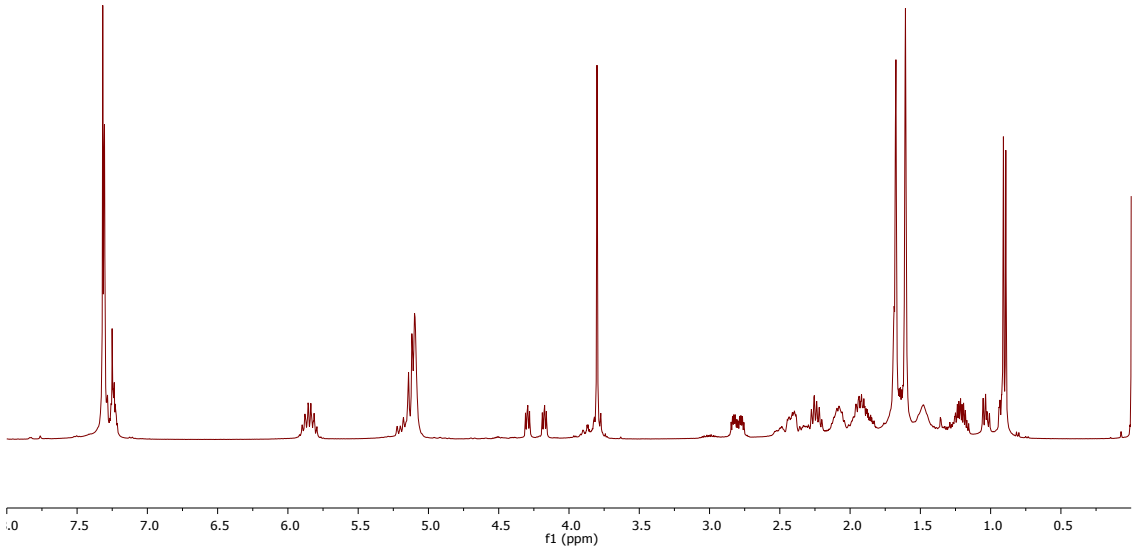


Figure 2.19: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2n**.

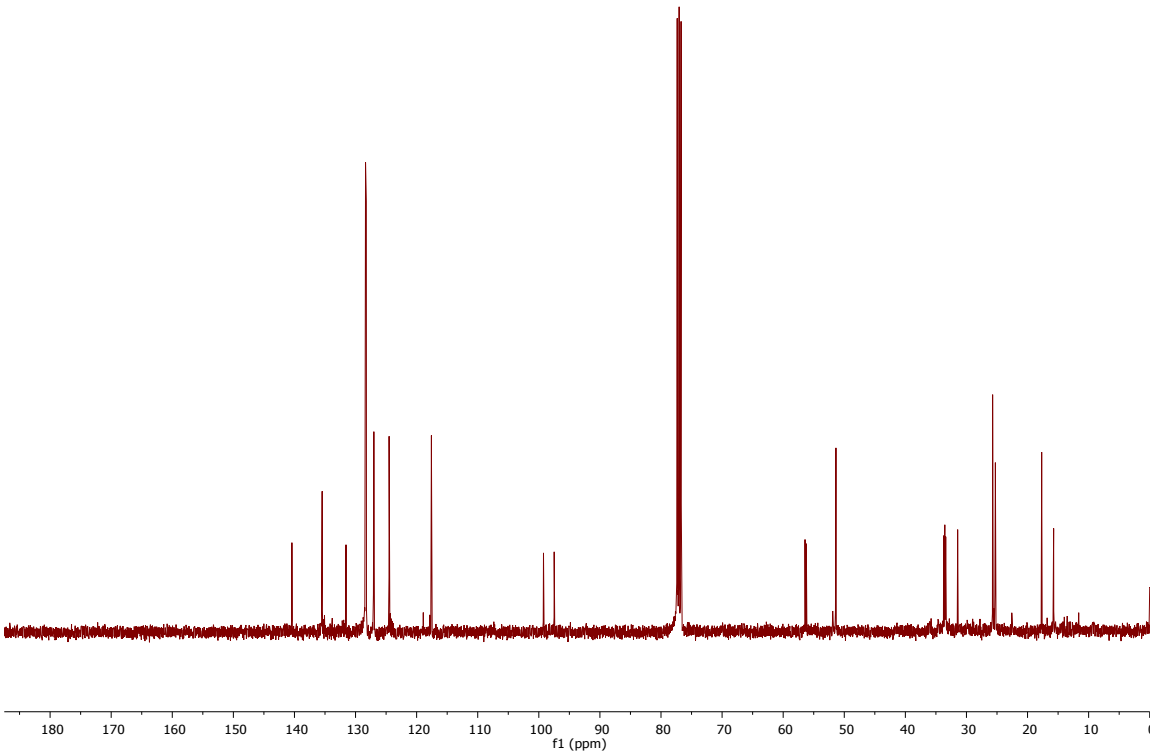


Figure 2.20: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2n**.

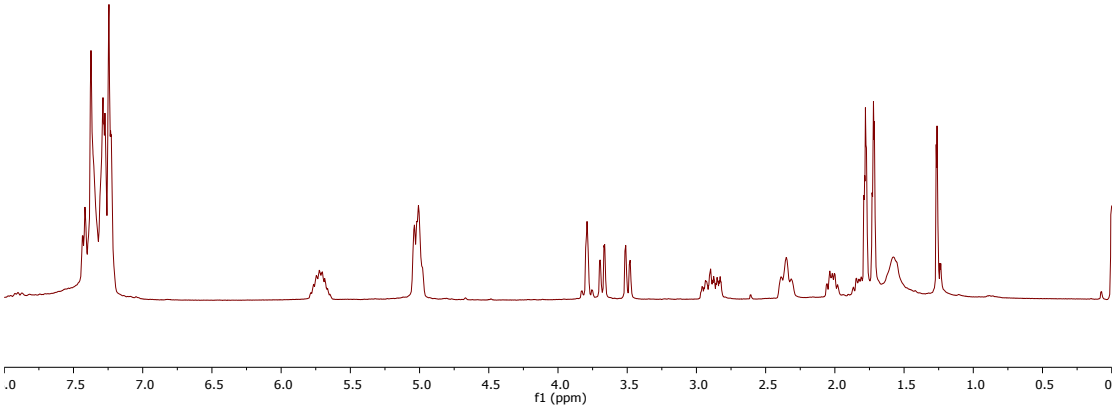


Figure 2.23: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2o**.

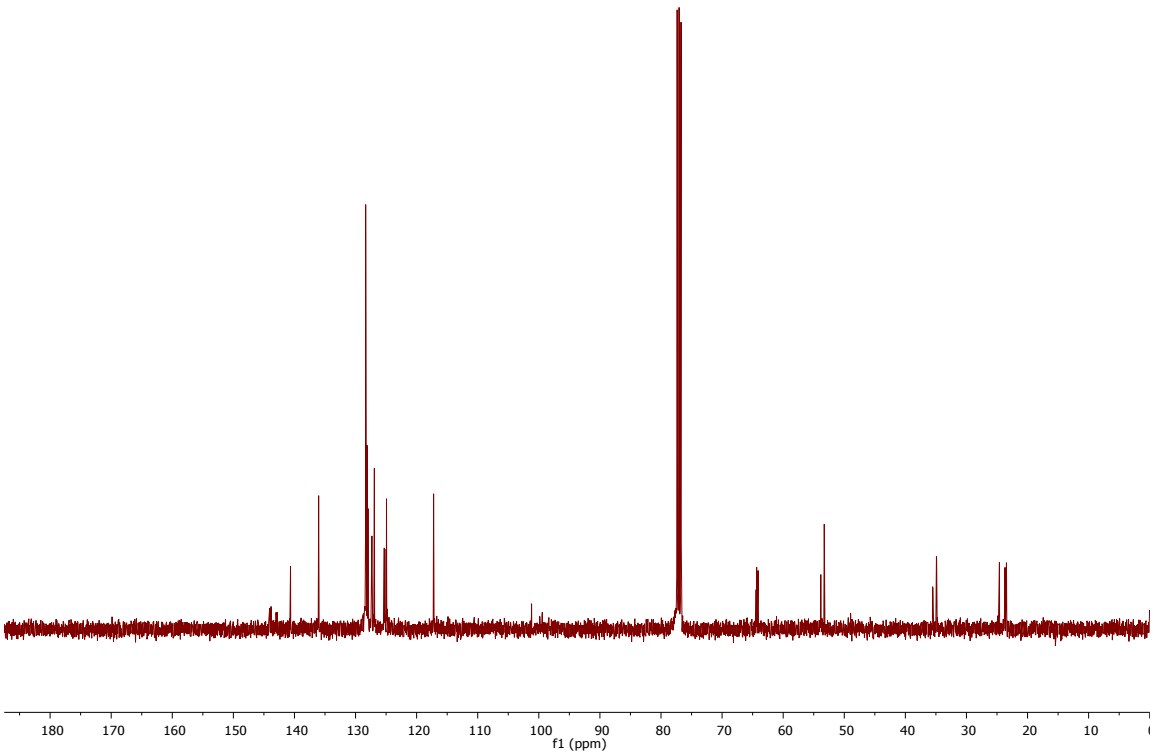


Figure 2.24: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2o**

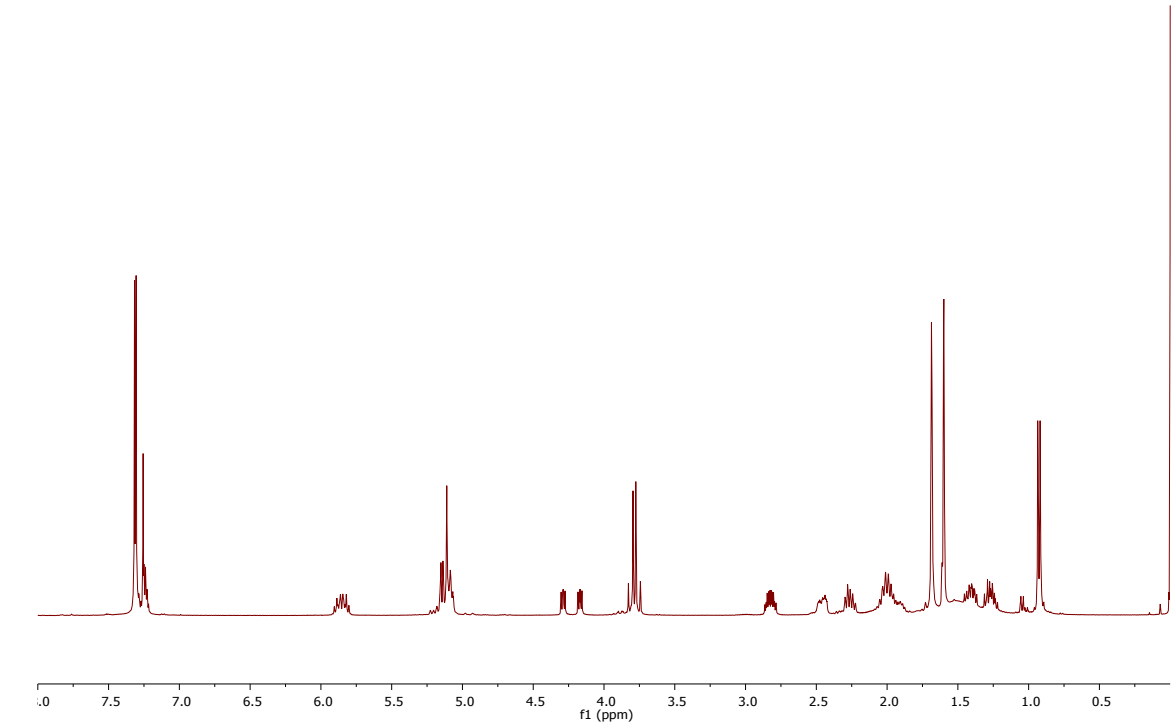


Figure 2.21: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2p**.

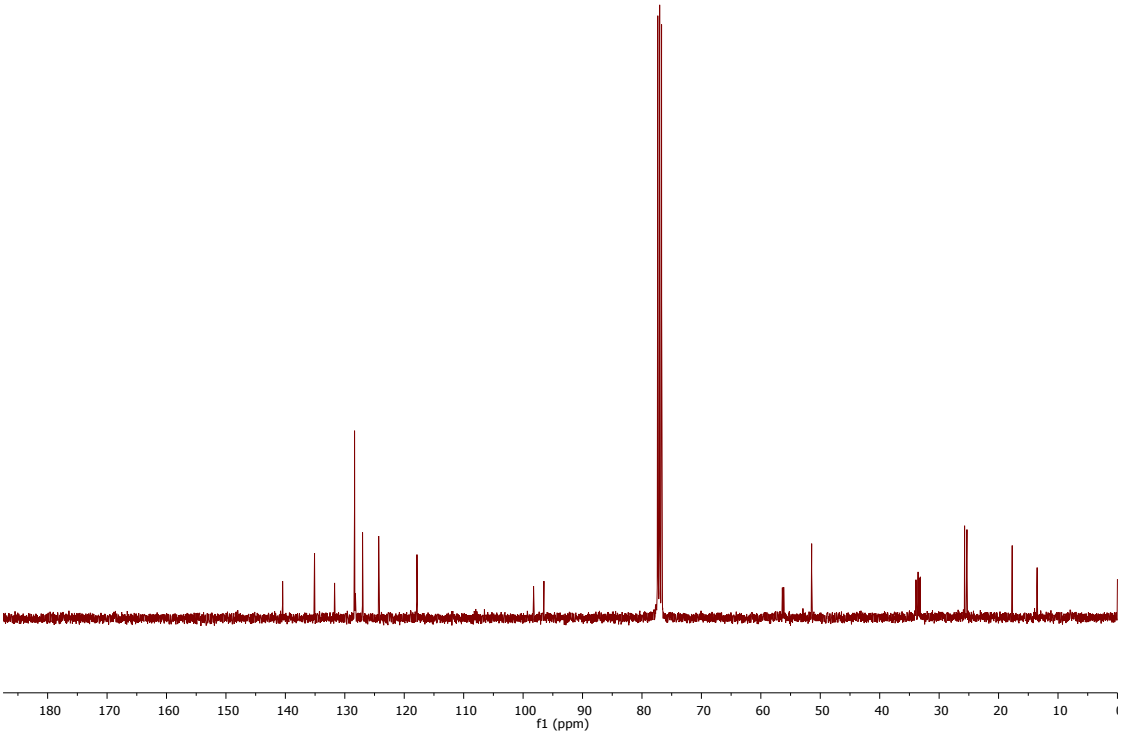


Figure 2.22: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2p**.

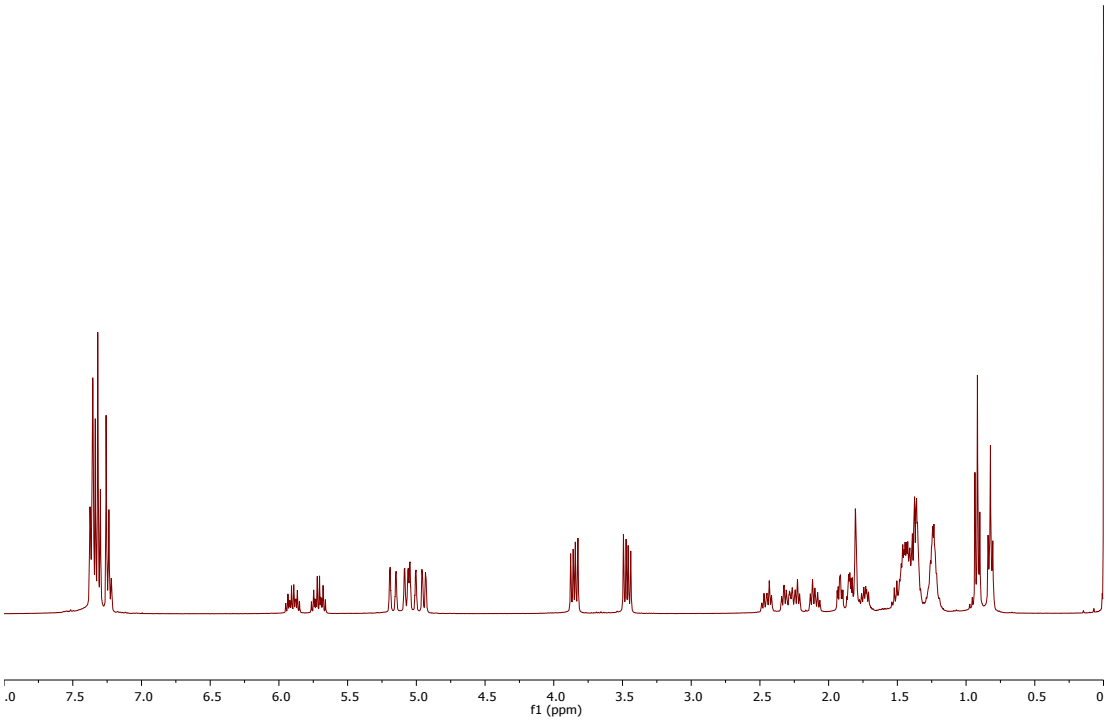


Figure 2.27: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

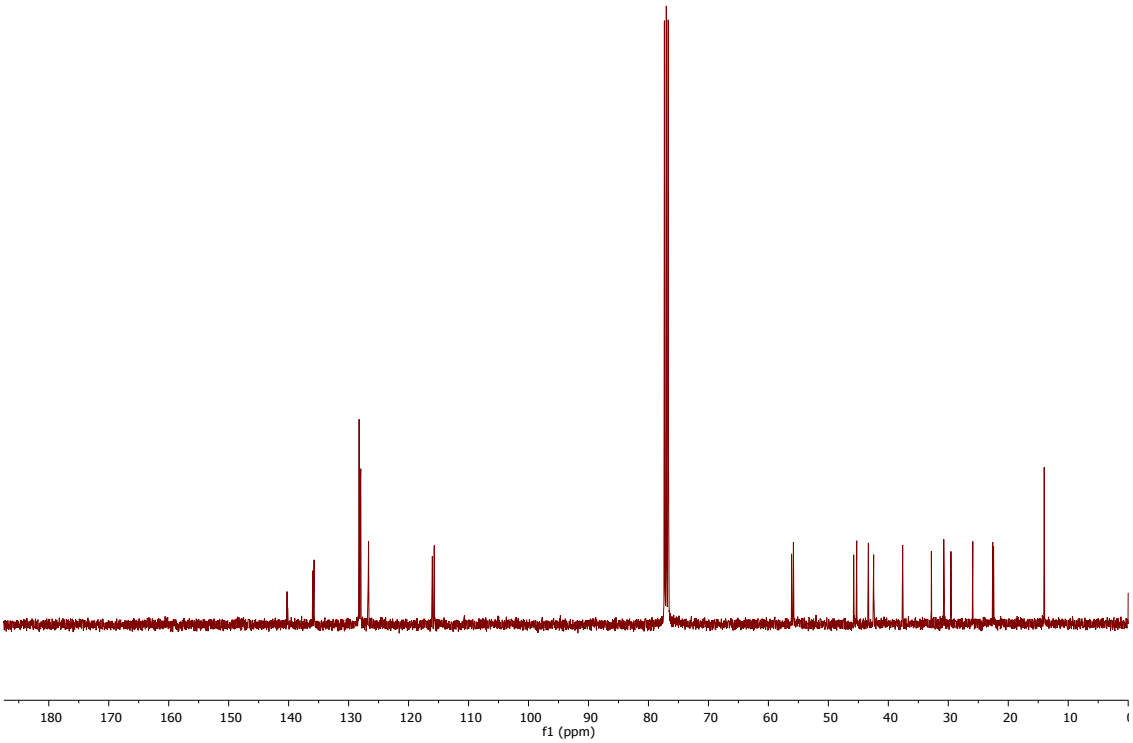


Figure 2.28: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4**.

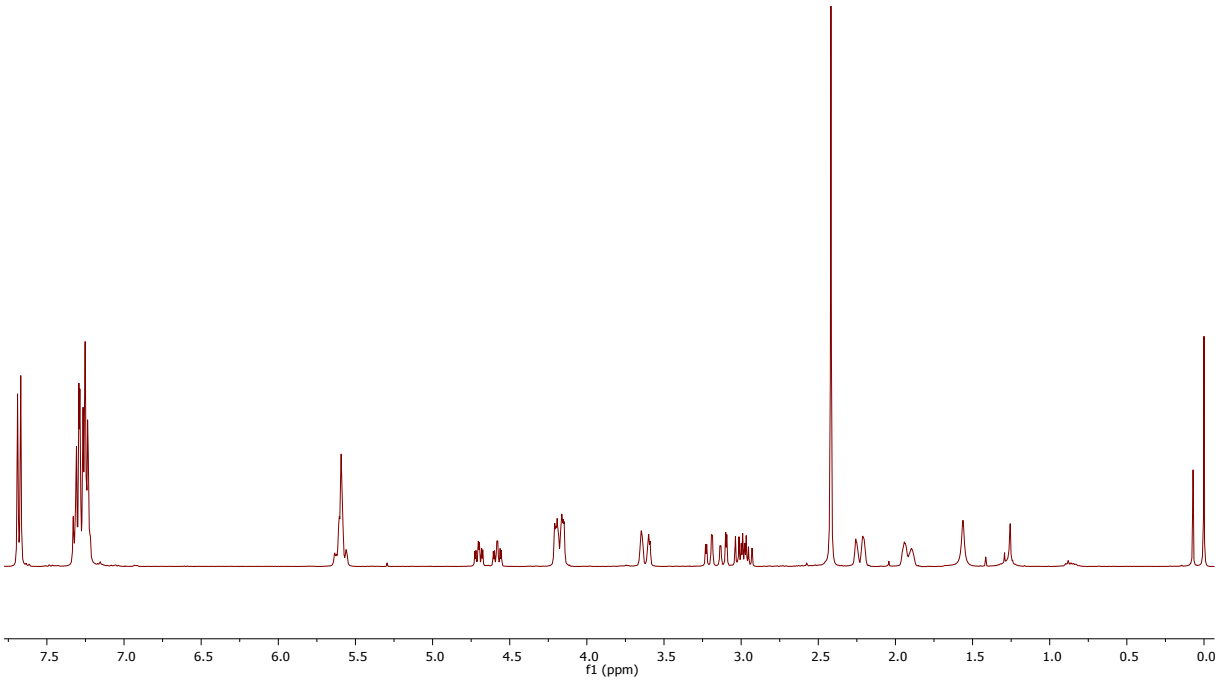


Figure 2.29: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5.**

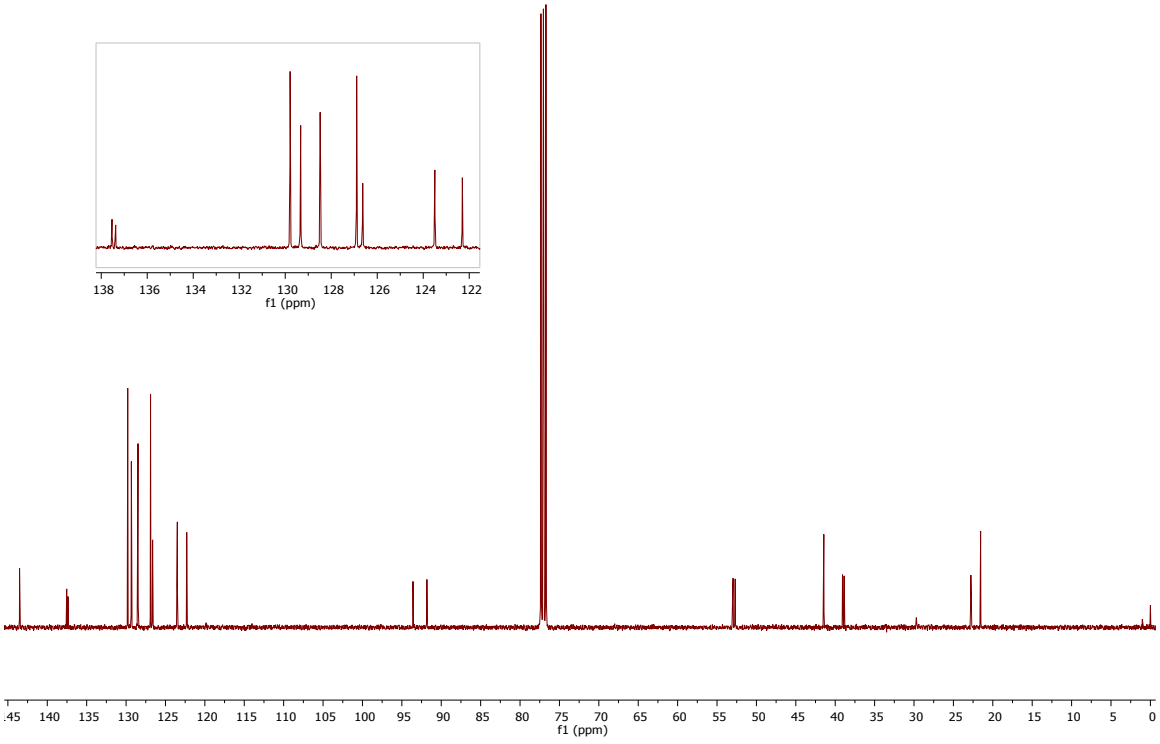


Figure 2.30: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **5**.

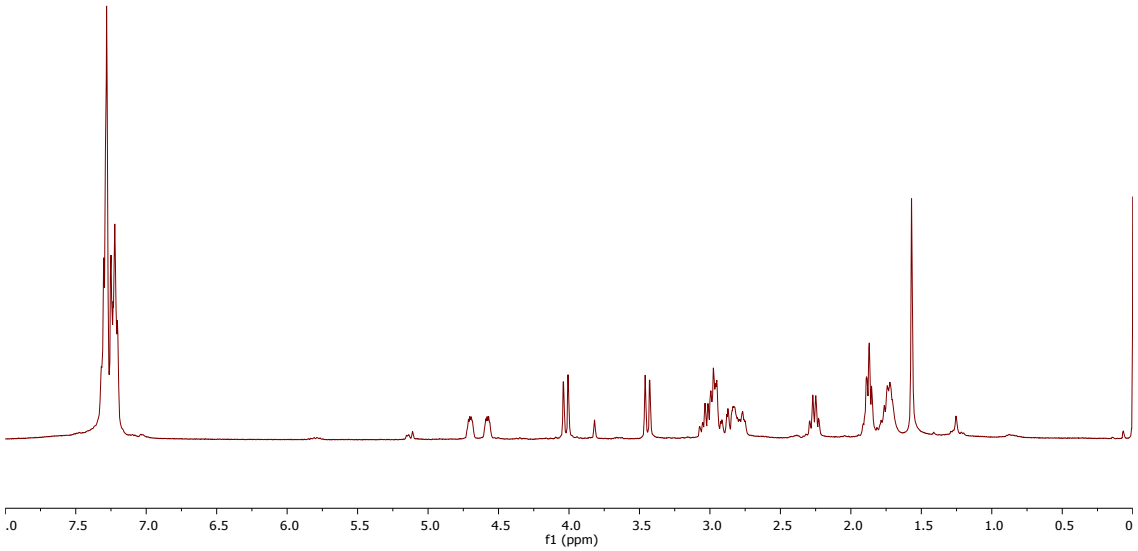


Figure 2.31: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6.**

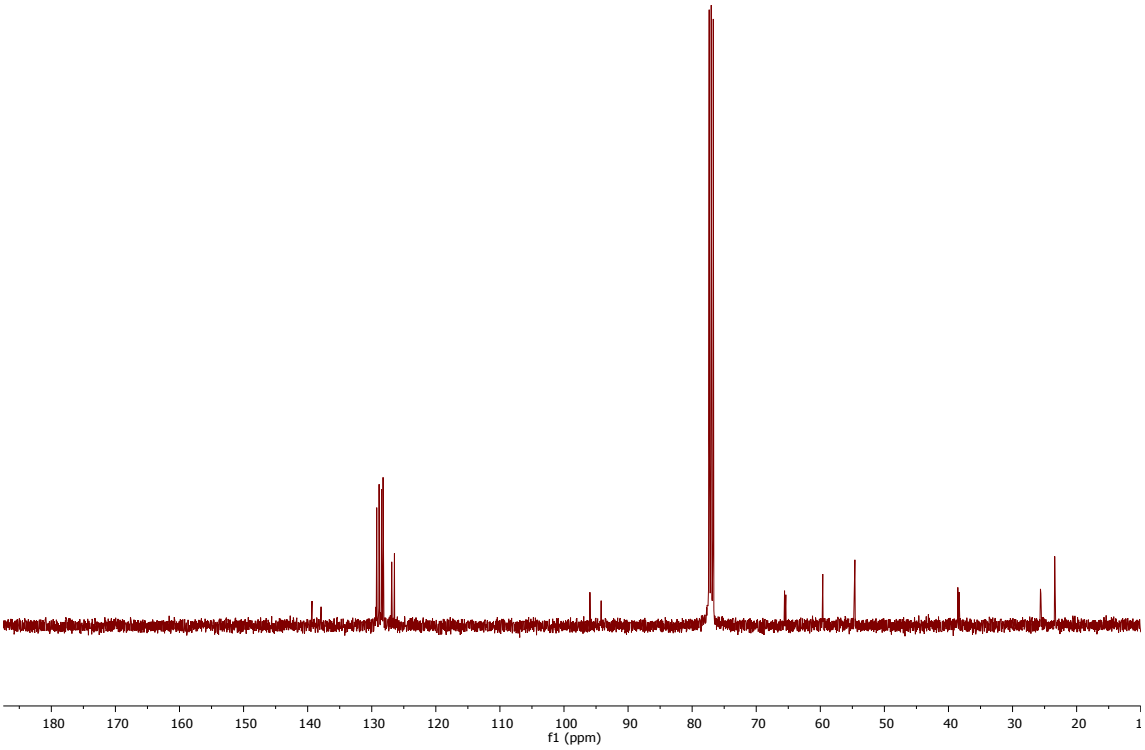
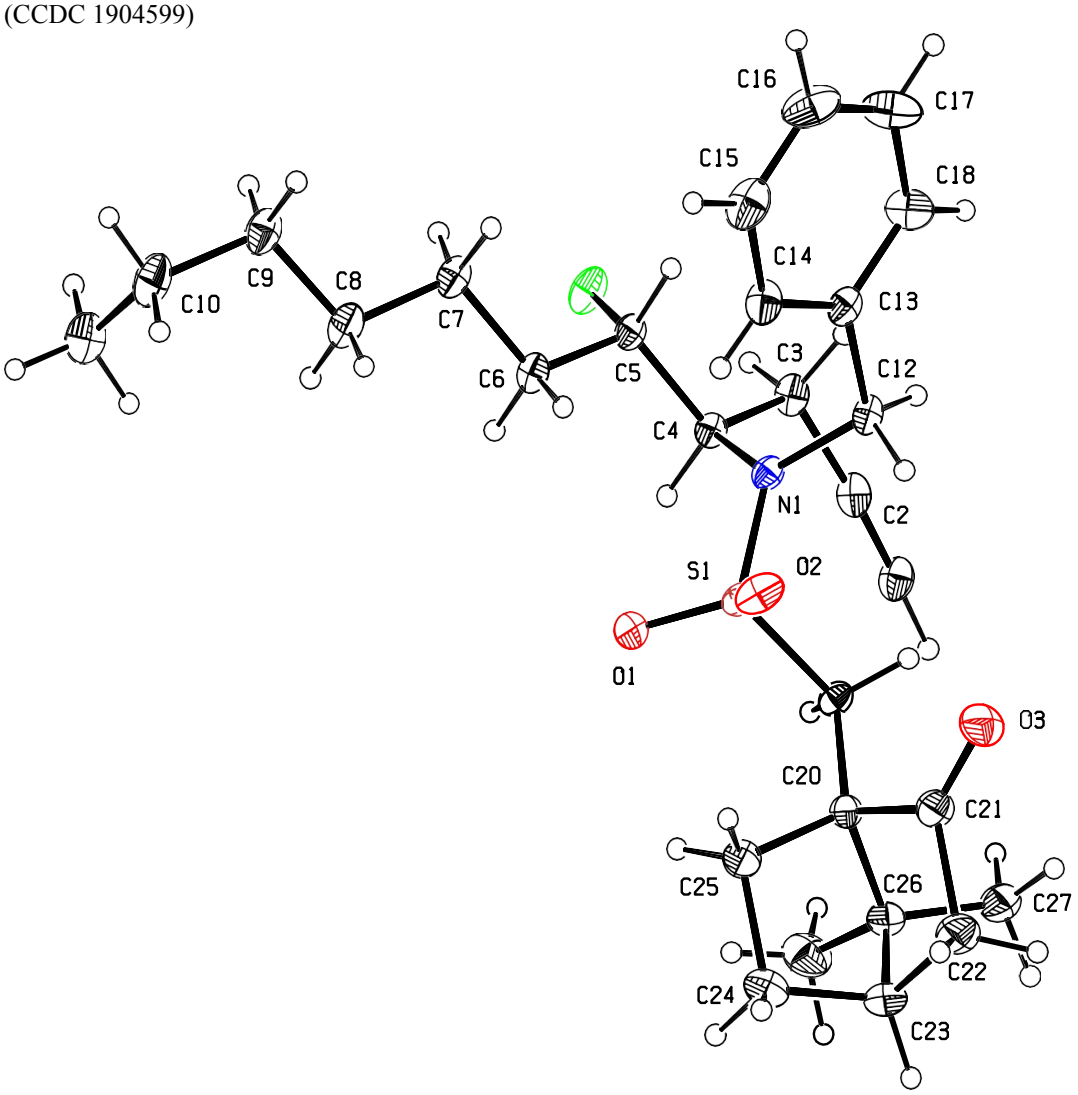


Figure 2.32: ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **6**.

Structure of the C28H40FNO3S (compound **2e**) molecule with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii. (CCDC 1904599)



Structure of the $C_{20}H_{22}FNO_2S$ molecule (compound **5**) with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii. (CCDC 1904600)