Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Aminoalcohol derivatives by nickel-catalyzed enantioselective coupling of imines and dienol ethers

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Supporting Crystallographic Information

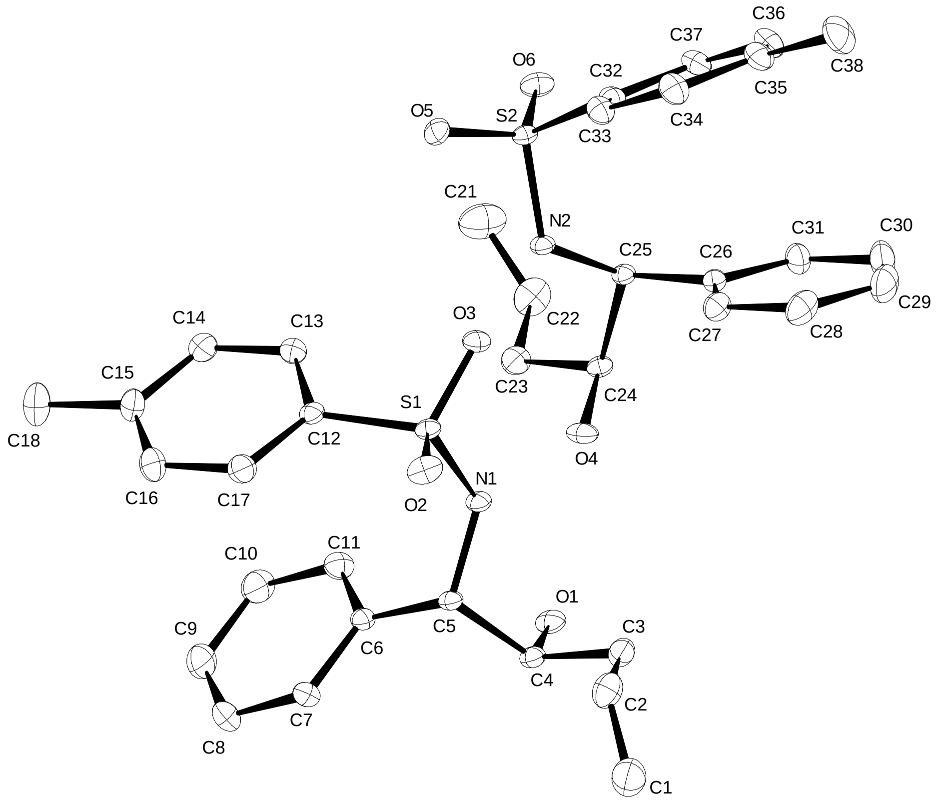
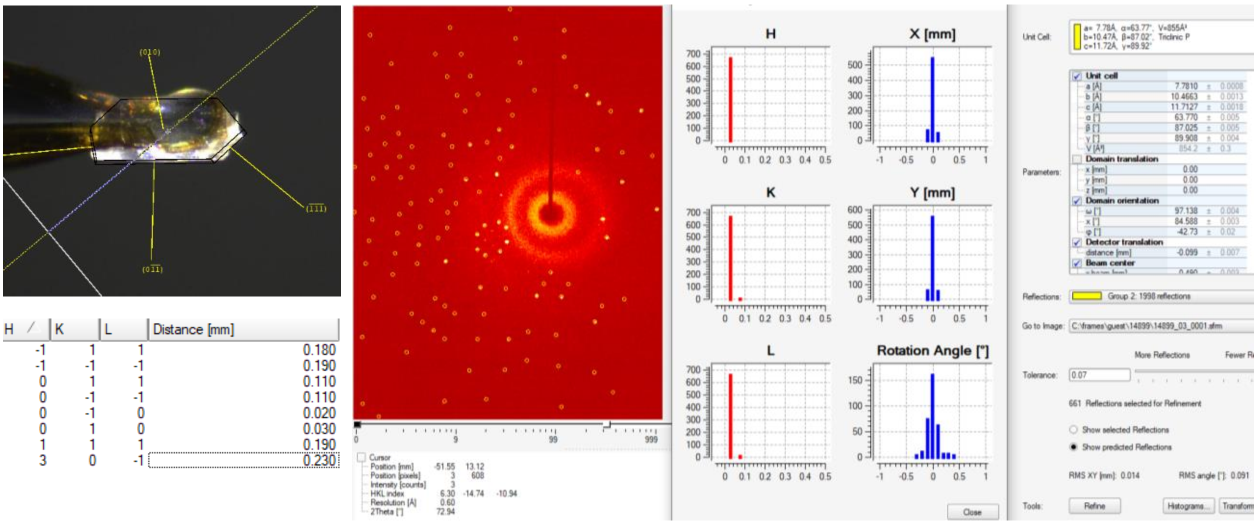


Figure S1. Structure of compound **12** in the solid state; H-atoms are removed for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

X-ray Crystal Structure Analysis of Compound 12: $C_{18} H_{21} N O_3 S$, M_r = 331.42 g mol^{-1}, colourless plate, crystal size 0.493 x 0.321 x 0.06 mm^3, triclinic, space group *P*1 [1], a = 7.7766(4) Å, b = 10.4591(5) Å, c = 11.6939(6) Å, α = 63.794(2)°, β = 86.998(2)°, γ = 89.877(2)°, V = 851.97(8) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.292 g·cm^3, λ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.204 mm^{-1}, numerical absorption correction ($T_{\min}$ = 0.9363, $T_{\max}$ = 0.9974), Bruker AXS D8-Venture diffractometer with IµS Diamond Mo-anode X-ray source and PHOTON III detector, 1.944 < θ < 34.202°, 145574 measured reflections, 14138 independent reflections, 13864 reflections with $I > 2\sigma(I)$, R_{int} = 0.0379.

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.0261 [$I > 2\sigma(I)$], wR_2 = 0.0708 [all data], 433 parameters, 3 restraints and an absolute structure parameter Flack x = 0.008(8).

Full .cif data for the compound are available under the number **CCDC-2294750**



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-1	-1	-1	0.190
0	1	1	0.110
0	-1	-1	0.110
0	-1	0	0.020
0	1	0	0.030
1	1	1	0.190
3	0	-1	0.230

☐ Cursor
Position [mm] -51.55 13.12
Position [pixels] 3 608
Intensity [counts] 3
HKL index 6.30 -14.74 -10.94
Resolution [A] 0.60
2Theta [°] 72.94

Unit Cell: a= 7.78A, α=63.77°, V=855A³ b=10.47A, β=87.02°, Triclinic P c=11.72A, γ=89.92°

Parameters:
☑ Unit cell
a [Å] 7.7810 ± 0.0008
b [Å] 10.4663 ± 0.0013
c [Å] 11.7127 ± 0.0018
α [°] 63.770 ± 0.005
β [°] 87.025 ± 0.005
γ [°] 89.908 ± 0.004
V [Å³] 854.2 ± 0.3
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y [mm] 0.00
z [mm] 0.00
☑ Domain orientation
ω [°] 97.138 ± 0.004
χ [°] 84.588 ± 0.003
φ [°] -42.73 ± 0.02
☑ Detector translation
distance [mm] -0.099 ± 0.007
☑ Beam center

Reflections: Group 2: 1998 reflections

Go to Image: C:\frames\guest\14899\14899_03_0001.sfrm

Tolerance: 0.07

661 Reflections selected for Refinement

○ Show selected Reflections
● Show predicted Reflections

RMS XY [mm]: 0.014 RMS angle [°]: 0.091

Tools:

Figure S1. Crystal faces and unit cell determination/refinement of compound **12**

```
INTENSITY STATISTICS FOR DATASET
-----------------------------------------------------------------------------
Resolution    #Data #Theory %Complete Redundancy Mean I Mean I/s Rmerge  Rsigma
-----------------------------------------------------------------------------
  Inf - 2.53     213    218     97.7     14.61     90.26  103.41  0.0247  0.0204
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 1.70 - 1.36     712    712    100.0     17.53     18.05   89.15  0.0271  0.0095
 1.36 - 1.18     738    738    100.0     15.03     19.66   79.25  0.0289  0.0105
 1.18 - 1.08     678    678    100.0     12.81     15.24   65.96  0.0316  0.0123
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 0.77 - 0.74    1002   1002    100.0      8.49      4.44   26.68  0.0655  0.0309
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 0.66 - 0.65     518    518    100.0      7.48      2.62   16.51  0.1059  0.0527
 0.65 - 0.64     698    698    100.0      7.42      2.63   16.16  0.1094  0.0545
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  Inf - 0.63   14138  14170     99.8     10.27      9.05   40.43  0.0378  0.0196
-----------------------------------------------------------------------------
```

Table S1. Crystal data and structure refinement of compound **12**

Identification code	14899	
Empirical formula	$C_{18} H_{21} N O_3 S$	
Color	colourless	
Formula weight	331.42 g · mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*1, (no. 1)	
Unit cell dimensions	a = 7.7766(4) Å	α= 63.794(2)°.
	b = 10.4591(5) Å	β= 86.998(2)°.
	c = 11.6939(6) Å	γ = 89.877(2)°.
Volume	851.97(8) Å^3	
Z	2	
Density (calculated)	1.292 Mg · m^{-3}	
Absorption coefficient	0.204 mm^{-1}	
F(000)	352 e	
Crystal size	0.493 x 0.321 x 0.06 mm^3	
θ range for data collection	1.944 to 34.202°.	
Index ranges	$-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$	
Reflections collected	145574	
Independent reflections	14138 [R_{int} = 0.0379]	
Reflections with $I>2\sigma(I)$	13864	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.94	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14138 / 3 / 433	
Goodness-of-fit on F^2	1.083	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0261	wR^2 = 0.0704
R indices (all data)	R_1 = 0.0268	wR^2 = 0.0708
Absolute structure parameter	0.008(8)	
Largest diff. peak and hole	0.5 and -0.2 e · Å^{-3}	

Table S2. Bond lengths [Å] and angles [°] of compound **12**

S(1)-O(2)	1.4367(9)	S(1)-O(3)	1.4528(9)
S(1)-N(1)	1.6098(10)	S(1)-C(12)	1.7588(12)
O(1)-H(1)	0.76(3)	O(1)-C(4)	1.4263(14)
N(1)-H(1A)	0.83(2)	N(1)-C(5)	1.4719(14)
C(1)-C(2)	1.326(2)	C(2)-C(3)	1.4960(19)
C(3)-C(4)	1.5315(17)	C(4)-C(5)	1.5358(16)
C(5)-C(6)	1.5199(15)	C(6)-C(7)	1.3940(16)
C(6)-C(11)	1.3926(16)	C(7)-C(8)	1.3898(19)
C(8)-C(9)	1.383(2)	C(9)-C(10)	1.393(2)
C(10)-C(11)	1.3943(18)	C(12)-C(13)	1.3932(16)
C(12)-C(17)	1.3907(16)	C(13)-C(14)	1.3895(17)
C(14)-C(15)	1.3933(19)	C(15)-C(16)	1.396(2)
C(15)-C(18)	1.503(2)	C(16)-C(17)	1.3858(19)
S(2)-O(5)	1.4388(9)	S(2)-O(6)	1.4360(10)
S(2)-N(2)	1.6254(10)	S(2)-C(32)	1.7604(11)
O(4)-H(4A)	0.73(3)	O(4)-C(24)	1.4222(14)
N(2)-H(2A)	0.82(3)	N(2)-C(25)	1.4694(14)
C(21)-C(22)	1.326(2)	C(22)-C(23)	1.497(2)
C(23)-C(24)	1.5258(17)	C(24)-C(25)	1.5284(16)
C(25)-C(26)	1.5166(15)	C(26)-C(27)	1.3938(16)
C(26)-C(31)	1.3932(16)	C(27)-C(28)	1.3942(17)
C(28)-C(29)	1.390(2)	C(29)-C(30)	1.387(2)
C(30)-C(31)	1.3887(19)	C(32)-C(33)	1.3907(16)
C(32)-C(37)	1.3958(17)	C(33)-C(34)	1.3924(17)
C(34)-C(35)	1.3938(18)	C(35)-C(36)	1.3964(19)
C(35)-C(38)	1.5056(18)	C(36)-C(37)	1.3888(17)
O(2)-S(1)-O(3)	119.27(6)	O(2)-S(1)-N(1)	108.57(5)
O(2)-S(1)-C(12)	107.68(6)	O(3)-S(1)-N(1)	105.09(5)
O(3)-S(1)-C(12)	107.27(5)	N(1)-S(1)-C(12)	108.59(5)
C(4)-O(1)-H(1)	107.4(18)	S(1)-N(1)-H(1A)	114.9(15)
C(5)-N(1)-S(1)	121.98(7)	C(5)-N(1)-H(1A)	117.7(15)
C(1)-C(2)-C(3)	123.47(14)	C(2)-C(3)-C(4)	112.69(10)
O(1)-C(4)-C(3)	110.18(10)	O(1)-C(4)-C(5)	106.63(9)
C(3)-C(4)-C(5)	114.26(9)	N(1)-C(5)-C(4)	108.56(9)
N(1)-C(5)-C(6)	114.99(9)	C(6)-C(5)-C(4)	110.24(9)
C(7)-C(6)-C(5)	118.58(10)	C(11)-C(6)-C(5)	122.29(10)

C(11)-C(6)-C(7)	119.08(11)	C(8)-C(7)-C(6)	121.03(13)
C(9)-C(8)-C(7)	119.65(13)	C(8)-C(9)-C(10)	119.94(13)
C(9)-C(10)-C(11)	120.33(13)	C(6)-C(11)-C(10)	119.93(12)
C(13)-C(12)-S(1)	119.63(9)	C(17)-C(12)-S(1)	119.15(9)
C(17)-C(12)-C(13)	120.99(11)	C(14)-C(13)-C(12)	118.69(11)
C(13)-C(14)-C(15)	121.37(12)	C(14)-C(15)-C(16)	118.63(12)
C(14)-C(15)-C(18)	120.73(14)	C(16)-C(15)-C(18)	120.63(13)
C(17)-C(16)-C(15)	120.94(12)	C(16)-C(17)-C(12)	119.29(12)
O(5)-S(2)-N(2)	105.13(5)	O(5)-S(2)-C(32)	108.12(5)
O(6)-S(2)-O(5)	120.04(6)	O(6)-S(2)-N(2)	107.49(5)
O(6)-S(2)-C(32)	107.74(6)	N(2)-S(2)-C(32)	107.79(5)
C(24)-O(4)-H(4A)	109.8(18)	S(2)-N(2)-H(2A)	111.0(18)
C(25)-N(2)-S(2)	120.32(7)	C(25)-N(2)-H(2A)	116.9(18)
C(21)-C(22)-C(23)	124.63(16)	C(22)-C(23)-C(24)	112.87(11)
O(4)-C(24)-C(23)	110.04(10)	O(4)-C(24)-C(25)	107.11(9)
C(23)-C(24)-C(25)	113.73(10)	N(2)-C(25)-C(24)	108.42(9)
N(2)-C(25)-C(26)	114.48(9)	C(26)-C(25)-C(24)	111.87(9)
C(27)-C(26)-C(25)	122.16(10)	C(31)-C(26)-C(25)	118.91(10)
C(31)-C(26)-C(27)	118.93(10)	C(26)-C(27)-C(28)	120.06(12)
C(29)-C(28)-C(27)	120.46(13)	C(30)-C(29)-C(28)	119.65(12)
C(29)-C(30)-C(31)	119.89(13)	C(30)-C(31)-C(26)	120.98(12)
C(33)-C(32)-S(2)	119.69(9)	C(33)-C(32)-C(37)	120.74(11)
C(37)-C(32)-S(2)	119.32(9)	C(32)-C(33)-C(34)	119.13(11)
C(33)-C(34)-C(35)	121.11(11)	C(34)-C(35)-C(36)	118.77(11)
C(34)-C(35)-C(38)	120.99(12)	C(36)-C(35)-C(38)	120.24(12)
C(37)-C(36)-C(35)	120.97(11)	C(36)-C(37)-C(32)	119.27(11)

Reaction Optimization

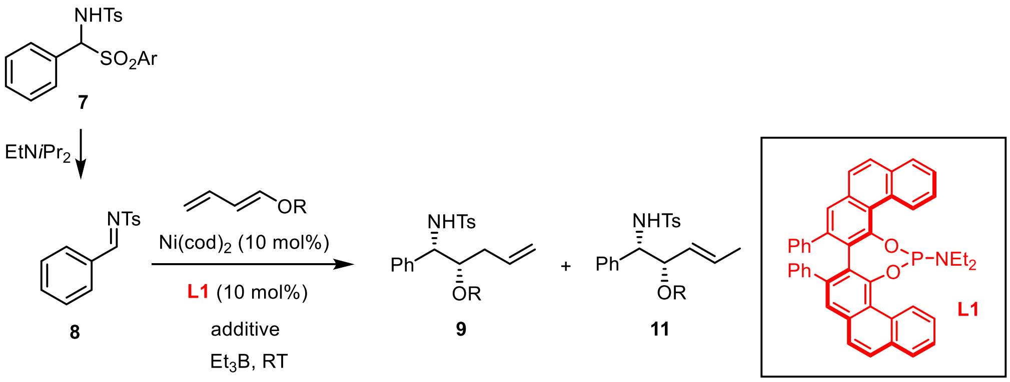


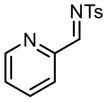
Table S3. Screening Results

##	Substrate	R (diene)	Solvent	Additive	Yield	9:11	ee (major)
1	**7** (Ar = Ph)	TES	THF	---	40%	3.9:1	94%
2		TBS	THF	---	53%	4.7:1	94%
3			toluene	---	52%	4.0:1	92%
4			DMF	---	trace	n.d.	
5			Et_2O	---	8%	n.d.	91%
6	**7** (Ar = *p*-tol)	MOM	THF	---	40%	9.0:1	92%
7	**7** (Ar = *p*-tol)	TES	THF	H_2O (1 equiv.)	70%	5.2:1	92%
8				H_2O (2 equiv.)	85%	7.3:1	93%
9				H_2O (3 equiv.)	91%	8.7:1	93%
10	**7** (Ar = *p*-tol)	TBS	THF	H_2O (3 equiv.)	75%	7.6:1	94%
11	**7** (Ar = *p*-tol)	TIPS	THF	H_2O (3 equiv.)	70%	>20:1	92%
12	**8**			MeOH (3 equiv.)	47%	>20:1	79%
13	**8**			HFIP (3 equiv.)	28%	>20:1	85%
14	**8**			$(EtO)_3B$ (1.5 equiv.)	<5%	n.d.	n.d.
15	**8**	TIPS	THF	H_2O (3 equiv.)	93%	>20:1	90%
16	**8**	MOM	THF	H_2O (3 equiv.)	87%	>20:1	90%
17	**8**	Bn	THF	H_2O (3 equiv.)	81%	4.0:1	89%

n. d. = not determined; HFIP = hexafluoroisopropanol

Limitations

unsuccessful substrates:



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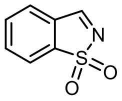

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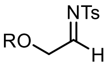


R = TBS, TBDPS, TIPS, tBu
unstable

General Considerations

Unless stated otherwise, all reactions were carried out under argon atmosphere in flame-dried Schlenk glassware. Solvents were purified by distillation over the indicated drying agents under argon: toluene (CaH_2), THF (Mg/anthracene), Et_2O (Mg/anthacene), pentane (Na/K), CH_2Cl_2 (CaH_2). MeCN and Et_3N were dried by an absorption solvent purification system based on molecular sieves. Flash chromatography: VWR Chemicals silica gel 40 – 63 µm.

NMR spectra were recorded on Bruker DPX 300 or AV 400 spectrometers in the solvents indicated; chemical shifts are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C = 77.16$ ppm; $\delta_H = 7.26$ ppm; C_6D_6: $\delta_C = 128.06$ ppm; $\delta_H = 7.16$ ppm; CD_2Cl_2: $\delta_C = 54.0$ ppm; $\delta_H = 5.32$ ppm). Proton and carbon assignments were established using HSQC, HMBC and NOESY experiments, where necessary.

IR: Alpha Platinum ATR (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}.

MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), Thermo Scientific LTQ-FT, or Thermo Scientific Exactive. HRMS: Bruker APEX III FT-MS (7T magnet), MAT 95 (Finnigan), Thermo Scientific LTQ-FT, or Thermo Scientific Exactive. GC-MS: Shimadzu GCMS-QP2010 Ultra instrument.

HPLC analyses for the determination of enantiomeric excesses were conducted on a Shimadzu LC 2020 instrument equipped with a Shimadzu SPD-M20A UV/VIS detector. Solvents (HPLC grade) were purchased and used as received. The exact conditions are stated separately for each compound.

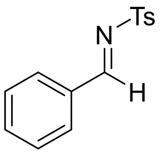
Optical rotations were measured with an A-Krüss Otronic Model P8000-t polarimeter at a wavelength of 589 nm. The values are given as specific optical rotation with exact temperature, concentration (*c* (10 mg/mL)) and solvent.

Aldehydes were purchased from commercial suppliers and used as received. Unless stated otherwise, all other commercially available compounds (abcr, Acros, TCI, Aldrich, Alfa Aesar, Fluorochem) were used as received.

The phosphoramidite ligand **L1**,[1] the aromatic imines,[2] and the aliphatic imine derivatives[3] were prepared according to literature procedures. Silyl dienol ether compounds were prepared according to literature procedures; the recorded characterization data matched the literature.[4]

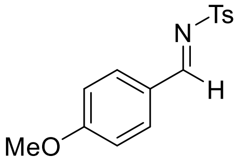
Characterization Data of the Substrates

N-Tosyl Imines

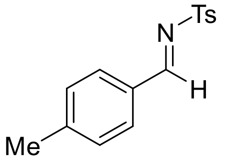


(*E*)-*N*-Benzylidene-4-methylbenzenesulfonamide (8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.97 – 7.85 (m, 4H), 7.66 – 7.57 (m, 1H), 7.54 – 7.45 (m, 2H), 7.39 – 7.31 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 144.8, 135.3, 135.1, 132.6, 131.5, 130.0, 129.3, 128.3, 21.8. Matches known data.[6]

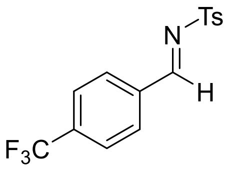
(*E*)-*N*-(4-methoxybenzylidene)-4-methylbenzenesulfonamide (S1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.92 – 7.85 (m, 4H), 7.36 – 7.31 (m, 2H), 7.01 – 6.93 (m, 2H), 3.88 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 165.4, 144.4, 135.9, 133.9, 129.9, 128.1, 125.4, 114.8, 55.8, 21.8. Matches known data.[6]



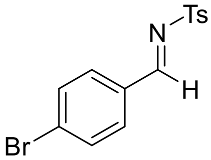
(***E***)**-4-Methyl-*N*-(4-methylbenzylidene)benzenesulfonamide (S2).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.91 – 7.85 (m, 2H), 7.84 – 7.79 (m, 2H), 7.39 – 7.32 (m, 2H), 7.30 – 7.27 (m, 2H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 146.5, 144.6, 135.5, 131.6, 130.1, 129.9, 128.2, 126.6, 22.1, 21.8. Matches known data.[7]



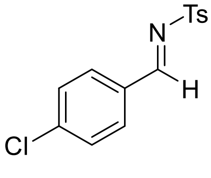
(*E*)-4-Methyl-*N*-(4-(trifluoromethyl)benzylidene)benzenesulfonamide (**S3).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.08 – 8.01 (m, 2H), 7.94 – 7.86 (m, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.40 – 7.35 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 145.2, 135.9 (q, $^2J_{CF}$ = 32.8 Hz), 135.5, 134.6, 131.5, 129.8, 128.4, 126.2 (q, $^3J_{CF}$ = 3.8 Hz), 123.4 (q, $^1J_{CF}$ = 272.8 Hz), 21.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.3. Matches known data.[8]



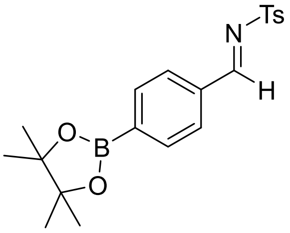
(*E*)-*N*-(4-Bromobenzylidene)-4-methylbenzenesulfonamide (S4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.92 – 7.84 (m, 2H), 7.82 – 7.74 (m, 2H), 7.67 – 7.60 (m, 2H), 7.39 – 7.31 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 145.0, 135.0, 132.8, 132.5, 131.4, 130.4, 130.0, 128.3, 21.8. Matches known data.[6]



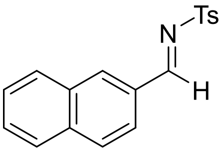
(*E*)-*N*-(4-Chlorobenzylidene)-4-methylbenzenesulfonamide (S5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.94 – 7.80 (m, 4H), 7.51 – 7.43 (m, 2H), 7.39 – 7.31 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 144.9, 141.6, 135.1, 132.5, 131.0, 130.0, 129.8, 128.3, 21.8. Matches known data.[6]



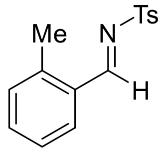
(*E*)-4-methyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)benzenesulfonamide (S6). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.03 (s, 1H), 7.92 – 7.87 (m, 6H), 7.37 – 7.33 (m, 2H), 2.44 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 170.3, 144.8, 135.4, 134.5, 130.4, 130.0, 129.9, 128.3, 126.6, 84.5, 25.0, 21.8; IR (ATR): ṽ =2977, 1597, 1549, 1512, 1389, 1352, 1317, 1303, 1271, 1221, 1157, 1085, 1017, 964, 903, 868, 811, 784, 679; HRMS (ESI$^+$, *m/z*) calculated for [C$_{20}$H$_{24}$NO$_4$SB+Na]$^+$ ([M+Na]$^+$) 408.1411, found 408.1414.



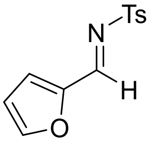
(*E*)-4-Methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide (S7). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.18 (s, 1H), 8.37 – 8.32 (m, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 – 7.85 (m, 5H), 7.64 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.40 – 7.32 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 170.2, 144.7, 136.7, 136.3, 135.4, 132.8, 130.3, 130.0, 129.7, 129.6, 129.3, 128.3, 128.2, 127.4, 124.3, 21.8. Matches known data.[8]



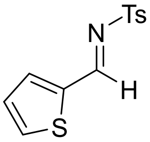
(*E*)-4-Methyl-*N*-(2-methylbenzylidene)benzenesulfonamide (S8). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.35 (s, 1H), 8.01 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.47 (app. td, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.29 – 7.27 (m, 2H), 2.61 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.8, 144.6, 142.4, 135.6, 134.7, 131.7, 130.8, 129.9, 129.9, 128.2, 126.8, 21.8, 19.8. Matches known data.[8]



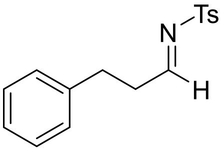
(*E*)-*N*-(Furan-2-ylmethylene)-4-methylbenzenesulfonamide (S9). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.82 (d, *J* = 0.5 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.74 (app. dt, *J* = 1.3, 0.6 Hz, 1H), 7.34 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.33 – 7.32 (m, 2H), 6.65 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.8, 149.9, 149.3, 144.7, 135.4, 129.9, 128.2, 124.7, 113.8, 21.8. Matches known data.[7]



(*E*)-4-Methyl-*N*-(thiophen-2-ylmethylene)benzenesulfonamide (S10). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.11 (d, *J* = 0.7 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.38 – 7.29 (m, 2H), 7.24 – 7.17 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.3, 144.6, 139.1, 138.3, 136.8, 135.6, 129.9, 129.0, 128.1, 21.8. Matches known data.[6]

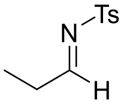


(*E*)-4-Methyl-*N*-(3-phenylpropylidene)benzenesulfonamide (S11). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.63 (t, *J* = 4.1 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.20 (m, 2H), 7.21 – 7.16 (m, 1H), 7.15 – 7.11 (m, 2H), 3.01 – 2.91 (m, 2H), 2.89 – 2.81 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ

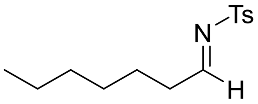


177.5, 144.9, 139.7, 134.6, 129.9, 128.8, 128.5, 128.3, 126.6, 37.5, 30.8, 21.8. Matches known data.[9]

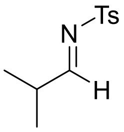
(*E*)-4-Methyl-*N*-propylidenebenzenesulfonamide (S12). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.62 (t, *J* = 4.0 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.38 – 7.28 (m, 2H), 2.55 (qd, *J* = 7.3, 4.0 Hz, 2H), 2.44 (s, 3H), 1.16 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 179.1, 144.8, 134.8, 129.9, 128.3, 29.6, 21.8, 8.8; IR (ATR): ṽ =2982, 2939, 2896, 1631, 1595, 1493, 1452, 1403, 1381, 1314, 1302, 1288, 1185, 1153, 1089, 1017, 900, 812, 800, 704, 669; HRMS (ESI$^+$, *m*/*z*) calculated for [C$_{10}$H$_{13}$NO$_2$S]$^+$ ([M+H]$^+$) 212.0740, found 212.0742.



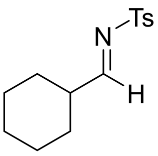
(*E*)-*N*-Heptylidene-4-methylbenzenesulfonamide (S13). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.60 (t, *J* = 4.6 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.42 – 7.30 (m, 2H), 2.50 (td, *J* = 7.5, 4.6 Hz, 2H), 2.44 (s, 3H), 1.66 – 1.57 (m, 2H), 1.37 – 1.24 (m, 6H), 0.90 – 0.80 (m, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.7, 144.8, 134.9, 129.9, 128.3, 36.1, 31.5, 28.9, 24.8, 22.5, 21.8, 14.1; IR (ATR): ṽ =2955, 2927, 2858, 1626, 1597, 1456, 1402, 1321, 1291, 1157, 1091, 1019, 813, 741, 670; HRMS (ESI$^+$, *m*/*z*) calculated for [C$_{14}$H$_{21}$NO$_2$S]$^+$ ([M+H]$^+$) 268.1366, found 268.1368.



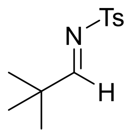
(*E*)-4-Methyl-*N*-(2-methylpropylidene)benzenesulfonamide (S14). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.51 (d, *J* = 4.2 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.38 – 7.28 (m, 2H), 2.69 (app. pd, *J* = 6.9, 4.2 Hz, 1H), 2.44 (s, 3H), 1.16 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 182.0, 144.8, 134.9, 129.9, 128.3, 34.8, 21.8, 18.2. Matches known data.[10]



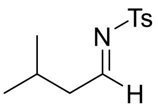
(*E*)-*N*-(Cyclohexylmethylene)-4-methylbenzenesulfonamide (S15). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.48 (d, *J* = 4.4 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.37 – 7.29 (m, 2H), 2.44 (s, 3H), 2.43 – 2.38 (m, 1H), 1.91 – 1.80 (m, 2H), 1.79 – 1.72 (m, 2H), 1.70 – 1.64 (m, 1H), 1.38 – 1.16 (m, 5H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 181.2, 144.7, 135.0, 129.9, 128.2, 43.8, 28.5, 25.8, 25.2, 21.8. Matches known data.[10]



(*E*)-*N*-(2,2-Dimethylpropylidene)-4-methylbenzenesulfonamide (S16). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.44 (s, 1H), 7.85 – 7.78 (m, 2H), 7.37 – 7.32 (m, 2H), 2.44 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 184.0, 144.7, 135.0, 129.9, 128.2, 38.0, 26.0, 21.8. Matches known data.[7]



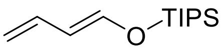
(*E*)-4-Methyl-*N*-(3-methylbutylidene)benzenesulfonamide (27). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.59 (t, *J* = 5.1 Hz, 1H), 7.86 – 7.75 (m, 2H), 7.38 – 7.28 (m, 2H), 2.44 (s, 3H), 2.39 (dd, *J* = 6.9, 5.1 Hz, 2H), 2.07 (app. dp, *J* = 13.5, 6.7 Hz, 1H), 0.96 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.3, 144.8, 134.9, 130.0, 128.2, 44.6, 26.1, 22.6, 21.8; IR (ATR): ṽ =2958, 2872, 1624, 1597, 1465, 1319, 1291, 1156, 1090,



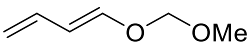
1019, 855, 814, 741, 670; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{12}H_{17}NO_2S]^+$ ($[M+H]^+$) 240.1053, found 240.1052.

Dienol Ethers

(*E*)-(Buta-1,3-dien-1-yloxy)triisopropylsilane (1, R = TIPS). ^{1}H NMR (400 MHz, C_6D_6) δ 6.64 (app. dq, *J* = 11.6, 0.6 Hz, 1H), 6.27 (dddd, *J* = 16.9, 10.9, 10.2, 0.6 Hz, 1H), 5.98 (app. ddt, *J* = 11.6, 10.8, 0.7 Hz, 1H), 5.04 (app. ddt, *J* = 16.9, 1.8, 0.8 Hz, 1H), 4.87 (app. ddt, *J* = 10.3, 1.8, 0.7 Hz, 1H), 1.03 (s, 21H); ^{13}C NMR (101 MHz, C_6D_6) δ 145.9, 133.8, 114.9, 112.0, 17.8, 12.2. Matches known data.[4]

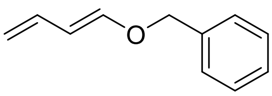


(*E*)-1-(Methoxymethoxy)buta-1,3-diene (1, R = MOM). Chloromethyl methyl ether (1.5 mL, 20 mmol) was added dropwise to a stirred solution of *cis*-2-butene-1,4-diol (0.82 mL, 10 mmol) and *N*,*N*-diisopropylethylamine (5.2 mL, 30 mmol) in dichloromethane (10 mL) at 0 ºC. After stirring for 19 h at room temperature, aqueous HCl (1 M, 15 mL) was slowly added at 0 ºC and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a colorless oil, which was used in the next step without purification.



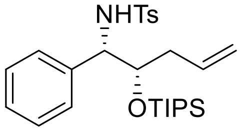
n-BuLi (1.6 M in hexanes, 12.5 mL, 20 mmol) was added dropwise to a stirred solution of *i*-Pr_2NH (2.8 mL, 20 mmol) in degassed THF (40 mL) at 0 °C, and the resulting solution was stirred for 20 min. (*Z*)-2,4,9,11-Tetraoxadodec-6-ene (1.76 g, 10 mmol) was added dropwise to the resulting solution of lithium diisopropylamide at –78 °C. After stirring for 2 h at 0 °C, a saturated aqueous solution of $NaHCO_3$ (30 mL) was added and the aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford pale yellow oil. The residue was purified by flash chromatography (SiO_2; methyl *tert*-butyl ether/pentane, 1:20) to afford title compound as a colorless oil (554 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (dd, *J* = 12.4, 0.7 Hz, 1H), 6.21 (dddd, *J* = 16.9, 10.8, 10.2, 0.6 Hz, 1H), 5.79 (app. ddt, *J* = 12.4, 10.9, 0.8 Hz, 1H), 5.04 (app. ddt, *J* = 16.9, 1.6, 0.7 Hz, 1H), 4.87 (app. ddt, *J* = 10.3, 1.5, 0.6 Hz, 1H), 4.85 (s, 2H), 3.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 133.1, 113.1, 111.1, 96.0, 56.1; IR (ATR): $\tilde{\nu}$ =2957, 2899, 1656, 1642, 1466, 1443, 1420, 1403, 1305, 1250, 1219, 1191, 1153, 1137, 1105, 1052, 994, 973, 942, 914, 885, 837, 783, 659; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_6H_{11}O_2]^+$ ($[M+H]^+$) 115.0754, found 115.0753.

(*E*)-((Buta-1,3-dien-1-yloxy)methyl)benzene (1, R = Bn). Sodium hydride (0.96 g, 40 mmol) was suspended in anhydrous dimethyl sulfoxide (45 mL) and benzyl alcohol (2.6 mL, 25 mmol) was added dropwise to this mixture at room temperature. After stirring for 1 h at room temperature, *cis*-1,4-dichloro-2-butene (1.2 mL, 11 mmol) was added and stirring was continued at 50 °C overnight. The reaction was cooled to 0 °C, the mixture diluted with diethyl ether (20 mL) and saturated NH_4Cl solution (60 mL). The aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with distilled water (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a brown oil. The residue was purified by flash chromatography (SiO_2; diethyl ether/pentane, 2:98) to afford the title compound as a yellow liquid as a mixture of diastereomers (1.5 g, 84%; *E:Z* = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 5H), 6.72 (d, *J* = 12.5 Hz, 1H), 6.35 – 6.21 (m, 1H), 5.79 – 5.72 (m, 1H), 5.12 – 5.05 (m, 1H), 4.93 – 4.88 (m, 1H), 4.86 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 136.7, 133.4, 128.7, 128.2, 127.7, 112.1, 108.2, 71.8. Matches known data.**[11]**



Ni-catalyzed Reductive Coupling of Dienol Ethers and Imines

Representative Procedure A



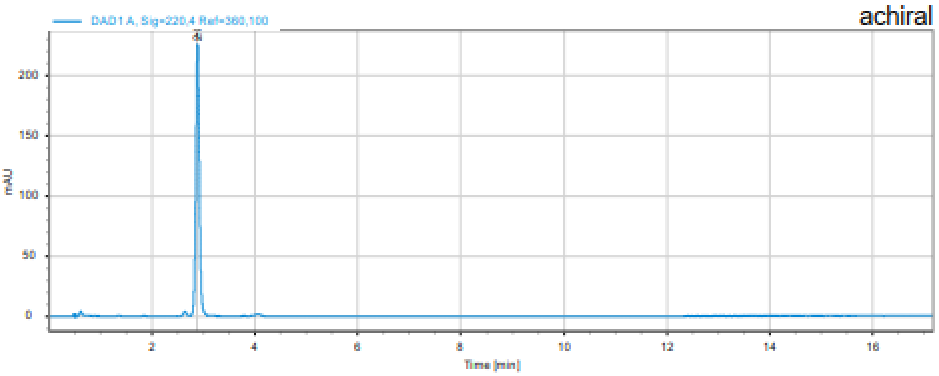
4-Methyl-*N*-((1*S*,2*S*)-1-phenyl-2-((triisopropylsilyl)oxy)-pent-4-en-1-yl)benzenesulfonamide (9c). A flame-dried Schlenk flask was charged under argon with bis(cyclooctadiene)nickel(0) (8.0 mg, 0.029 mmol, 10 mol%), phosphoramidite **L1** (19 mg, 0.029 mmol, 10 mol%) and THF (0.60 mL). Dienol ether **1** (R = TIPS) (0.23 mL, 0.87 mmol) and triethylborane (1.0 M in THF, 0.44 mL, 0.44 mmol) were added. N-Tosyl imine **8** (75 mg, 0.29 mmol) and distilled and degassed water (16 µL, 0.87 mmol, 3.0 equiv) were introduced, the flask was sealed under argon, and the mixture was stirred at room temperature overnight. The reaction was quenched with sat. $NaHCO_3$ solution (3.0 mL) and stirring was continued for 10 min. The mixture was diluted with methyl *tert*-butyl ether (3.0 mL) and the aqueous layer was extracted with methyl *tert*-butyl ether (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a pale yellow oil. Purification by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) afforded the title compound as a white solid (132 mg, 93%, >20:1 dr, 90% ee). $[\alpha]_D^{20}$ = +44.6 (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.14 – 7.06 (m, 5H), 7.05 – 7.00 (m, 2H), 5.73 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.41 (d, *J* = 7.7 Hz, 1H), 5.13 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.03 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.49 (dd, *J* = 7.7, 2.5 Hz, 1H), 3.92 (dt, *J* = 9.5, 3.0 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.33 (s, 3H), 2.22 (dddd, *J* = 11.6, 6.8, 3.4, 1.7 Hz, 1H), 0.96 – 0.87 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.6, 138.2, 133.2, 129.3, 128.0, 127.18, 127.16, 127.1, 119.2, 77.4, 58.8, 39.0, 21.5, 18.2, 18.0, 12.8; IR (ATR): ṽ = 3313, 2938, 2889, 2863, 1600, 1497, 1455, 1395, 1327, 1261, 1159, 1088, 1064, 1015, 997, 953, 885, 849, 813, 765, 750; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{27}H_{41}NO_3SSi+Na]^+$ ($[M+Na]^+$) 510.2469, found 510.2472.

Note: Two methyl groups of isopropyl substituents of the TIPS ether are split in ^{13}C NMR spectrum.

When the reaction was carried out on larger scale (259 mg of **8**, 1 mmol), product **9c** was obtained in 91% yield (444 mg, dr >20:1, 90% ee)

The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. D., methanol/water = 90:10, v = 1.0 mL/min, λ = 220 nm, t(major) = 2.90 min, 308 K.

^{1}D chromatogram(s)



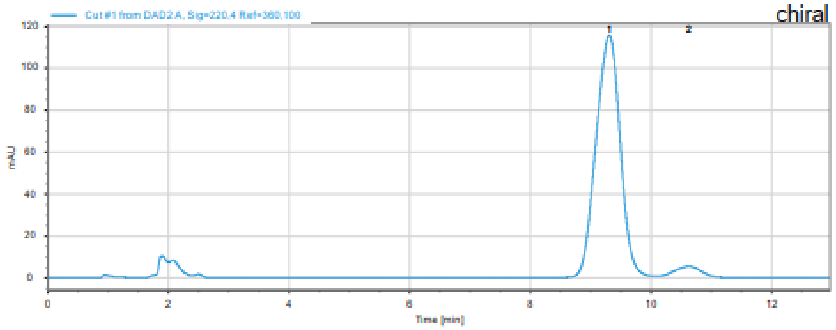
Sampling table (^{1}D)

Cut group	Cut #	^{1}D Cut start [min]	^{1}D Ret. time [min]	^{1}D Duration [min]	Trigger	^{2}D Run start [min]	
	1	2.87	2.897	0.04	Peak	2.91	product

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralcel OZ-3R, ∅ 4.6 mm i. d., acetonitrile/water = 75:25, v = 1.0 mL/min, λ = 220 nm, t(major) = 9.31 min, t(minor) = 10.64 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry		
1	1	9.313	3207.776 **3207.776**	0.395	115.498	1.143	1st enantiomer	ee = 90.0 %
2	1	10.636	168.670 **168.670**	0.369	5.341	1.209	2nd enantiomer	

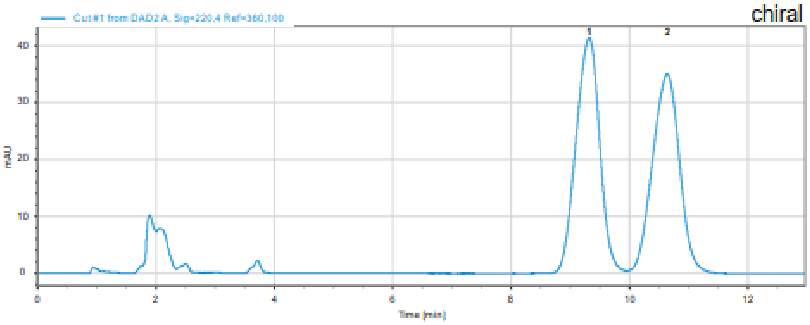
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%
1	2.87 - 2.91	9.313	3207.776	95.005
2	2.87 - 2.91	10.636	168.670	4.995

Determination of the ee of compound **9c**

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	9.321	1153.121 **1153.121**	0.329	41.469	1.151	1st enantiomer
2	1	10.647	1116.394 **1116.394**	0.377	35.092	1.190	2nd enantiomer

Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%
1	2.88 - 2.92	9.321	1153.121	50.809
2	2.88 - 2.92	10.647	1116.394	49.191

Separation of the enantiomers of *rac*-**9c**

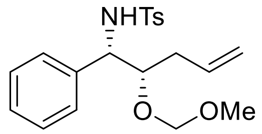
Notes:

1. $Ni(cod)_2$ was purchased from Strem Chemicals and transferred into a flame-dried Schlenk flask under argon immediately after opening. The complex was stored in a freezer at –20 °C under an over-pressure of argon. The color should be bright yellow. When taken out of the freezer, the Schlenk flask was allowed to warm to room temperature under Ar before weighing the solid out directly into the reaction flask using “Argon pants” as shown in Figure S3 below. Under these conditions, the $Ni(cod)_2$ sample can be used numerous times for over a year without any sign of decomposition.
2. Solid imines were used after recrystallization, liquid imines were used without purification after checking their purity by ^{1}H NMR spectroscopy. These compounds were stored in the freezer in a vial or round-bottom flask under air (–20 °C).
3. All dienol ether used in this study are liquids that were stored in the freezer (–20 °C) under argon in a crimp-capped vial. These compounds are stable for extended periods of time when stored at –20 °C.
4. Triethylborane (1.0 M in THF) was stored in the freezer at –20 °C under argon. Although triethylborane itself is highly pyrophoric and any solution of it must be handled with great care under oxygen-free conditions, no issues whatsoever where encountered when transfering the THF solutions using syringe techniques.
5. $Ni(cod)_2$ is relatively stable in the solid state but extremely O_2-sensitive in solution. Therefore the ligand should always be added ***before*** the solvent, because it coordinates to the Ni(0) species and helps to stabilize the catalyst in case traces of inadvertent oxygen are present in solution. The dienol ether also seems to help stabilize the nickel species, while triethylborane will react with any excess oxygen. These two components should therefore be added immediately after the solvent to minimize potential catalyst decomposition.
6. The reactions were carried out in a sealed Schlenk flask rather than under a flow of argon due to the volatility of triethylborane (bp 95 °C). However, ethylene gas is generated by reduction of the nickel catalyst with triethylborane and given off over time; care must therefore be taken to use reaction vessels that withstand the increase in pressure caused by the gas evolution, especially upon scale-up.
7. In all cases investigated herein, the racemic samples needed for accurate ee determination were prepared analogously using a racemic sample of ligand **L1**
8. In most cases, the minor diastereomer could not be detected by ^{1}H NMR spectroscopy but it was usually observed by HPLC in a ≈1:50 ratio relative to the major diastereomer. In all such cases, the dr is noted as >20:1.
9. In many cases, 2D HPLC analysis was employed for accurate ee determination. To this end, the product was first purified on an achiral column to separate the

diastereomers, followed by separation of the enantiomers of the major diastereomer on a column with a chiral stationary phase.

Figure S3. Use of “argon pants” for the transfer of air-sensitive compounds such as Ni(cod)$_2$. The reaction and reagent flasks are connected *via* a glassware with two legs and an open top. Argon is run through both Schlenk flasks continuously to ensure an inert atmosphere. This technique allows weighing of air-sensitive compounds without use of a glovebox.

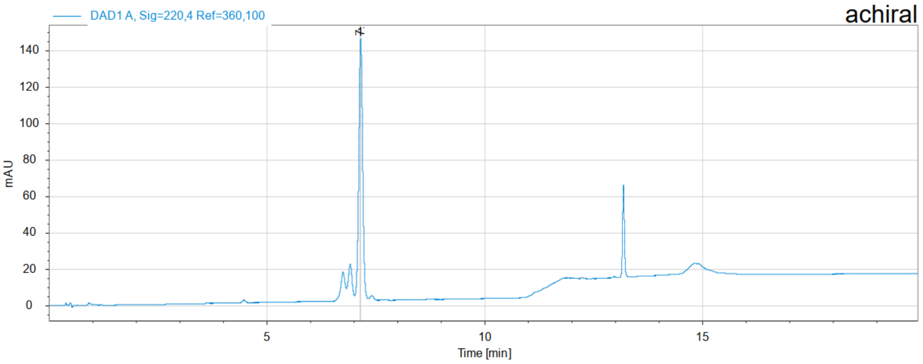
_N_-((1_S_,2_S_)-2-(Methoxymethoxy)-1-phenylpent-4-en-1-yl)-4-methylbenzenesulfonamide



(9d). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO$_2$; hexane/ethyl acetate, 25:1 to 5:1) to give the title compound as a colorless oil (95 mg, 87%, >20:1 dr, 90% ee). $[\alpha]_D^{20}$ = +33.9 (*c* = 0.59, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.45 (m, 2H), 7.17 – 7.08 (m, 3H), 7.08 – 7.02 (m, 4H), 5.73 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.63 (d, *J* = 6.6 Hz, 1H), 5.09 (ddt, *J* = 10.3, 2.1, 1.1 Hz, 1H), 5.02 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.53 (d, *J* = 6.9 Hz, 1H), 4.44 (dd, *J* = 6.7, 4.6 Hz, 1H), 4.34 (d, *J* = 6.9 Hz, 1H), 3.65 (ddd, *J* = 6.8, 5.9, 4.6 Hz, 1H), 3.18 (s, 3H), 2.32 (s, 3H), 2.29 – 2.15 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.9, 138.9, 138.0, 133.4, 129.2, 128.3, 127.5, 127.3, 127.2, 118.9, 96.6, 81.5, 59.6, 56.0, 36.3, 21.5; IR (ATR): ṽ = 3236, 3064, 3030, 2975, 2897, 1641, 1599, 1495, 1455, 1433, 1328, 1288, 1212, 1151, 1089, 1025, 964, 922, 907, 864, 847, 812, 756, 734, 699, 691, 661; HRMS (ESI$^+$, *m*/*z*) calculated for [C$_{20}$H$_{25}$O$_4$S+Na]$^+$ ([M+Na]$^+$) 398.1397, found 398.1396.

The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. d., methanol/water gradient 55% to 70% over 10 min and 95% over 1 min, v = 1.0 mL/min, λ = 220 nm, t(major) = 7.16 min, 308 K.

^{1}D chromatogram(s)



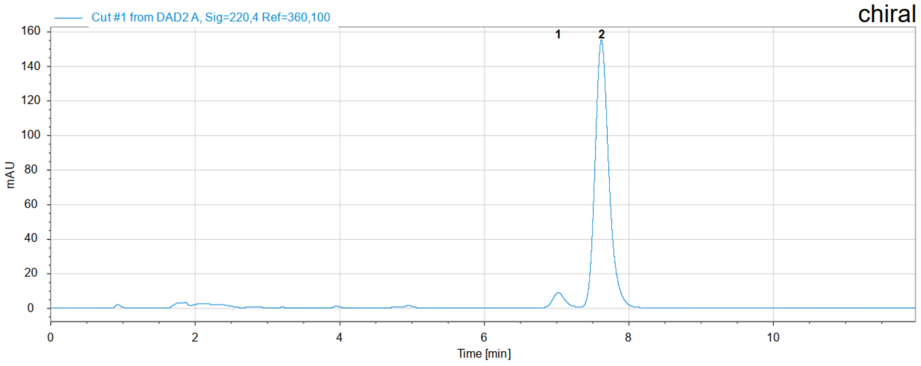
Sampling table (^{1}D)

Cut group	Cut #	^{1}D Cut start [min]	^{1}D Ret. time [min]	^{1}D Duration [min]	Trigger	^{2}D Run start [min]	
	1	7.13	7.160	0.04	Peak	7.17	desired product

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralpak IC-3, ∅ 4.6 mm i. d., acetonitrile/water = 50:50, v = 1.0 mL/min, λ = 220 nm, t(minor) = 7.03 min, t(major) = 7.63 min.

Cut# : 1

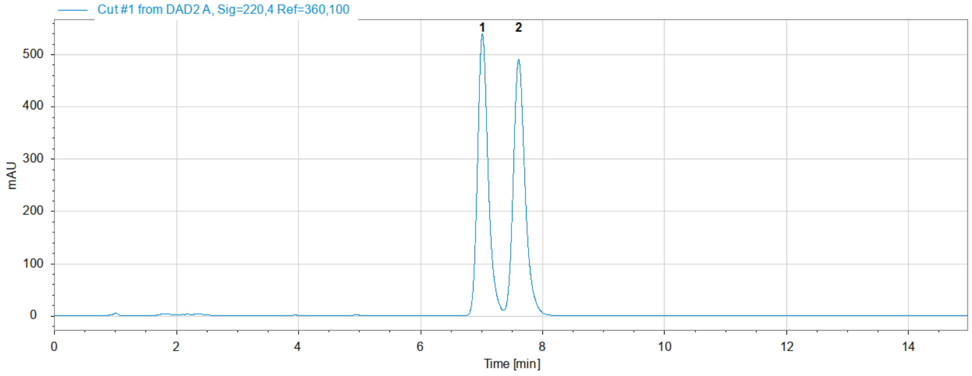


Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry		
1	1	7.029	103.392 **103.392**	0.149	8.686	0.820	1st enantiomer	ee = 90.4 %
2	1	7.626	2048.981 **2048.981**	0.200	154.952	0.795	2nd enantiomer	

Determination of the ee of **9d**

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	7.020	6520.659 **6520.659**	0.184	540.382	0.776
2	1	7.614	6569.238 **6569.238**	0.203	490.607	0.778

Component table

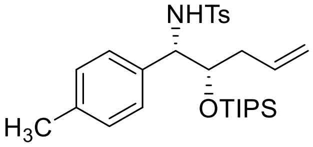
Signal: DAD2 A, Sig=220,4 Ref=360,100

chiral

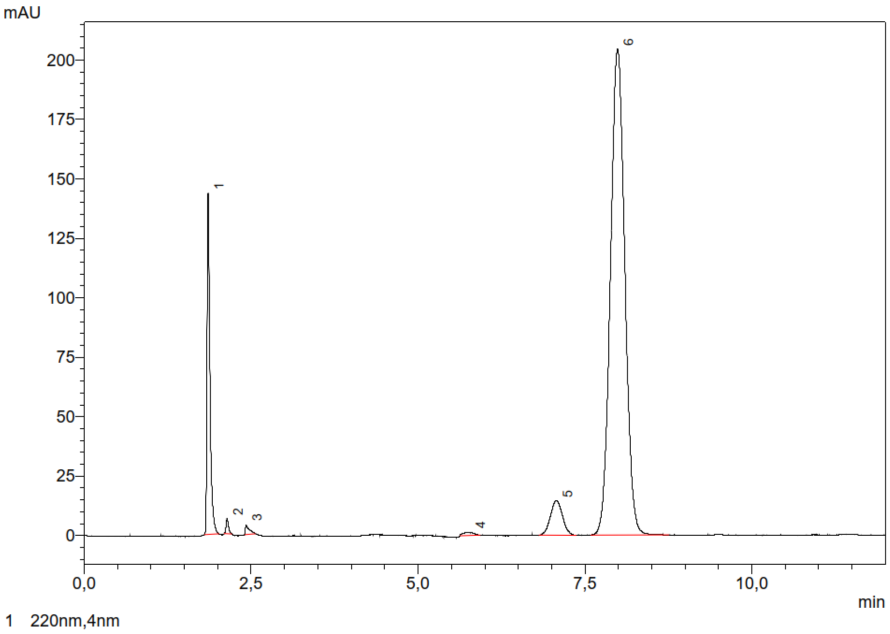
Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	
1	7.16 - 7.20	7.020	6520.659	49.814	1st enantiomer
2	7.16 - 7.20	7.614	6569.238	50.186	2nd enantiomer

Separation of the enantiomers of *rac*-**9d**

4-Methyl-*N*-((1*S*,2*S*)-1-(*p*-tolyl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)benzenesulfonamide (13a). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 25:1) to give the title compound as a white solid (141 mg, 97%, >20:1 dr, 89% ee). $[\alpha]_D^{20}$ = +58.6 (*c* = 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.11 – 7.07 (m, 2H), 6.92 (app. s, 4H), 5.71 (ddt, *J* = 17.4, 10.3, 7.1 Hz, 1H), 5.38 (d, *J* = 7.4 Hz, 1H), 5.10 (ddt, *J* = 10.4, 2.0, 1.0 Hz, 1H), 5.00 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.41 (dd, *J* = 7.3, 3.0 Hz, 1H), 3.91 (dt, *J* = 9.4, 3.2 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 2.19 (dddd, *J* = 12.6, 7.0, 3.2, 1.5 Hz, 1H), 0.96 – 0.88 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 138.1, 136.8, 136.5, 133.3, 129.3, 128.7, 127.2, 127.1, 119.0, 77.2, 58.8, 38.9, 21.5, 21.1, 18.2, 18.1, 12.8; IR (ATR): ṽ = 3288, 2944, 2865, 1599, 1516, 1463, 1422, 1404, 1327, 1159, 1094, 1066, 1015, 995, 921, 881, 804, 755; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{28}H_{43}NO_3SSi+Na]^+$ ($[M+Na]^+$) 524.2625, found 524.2630.



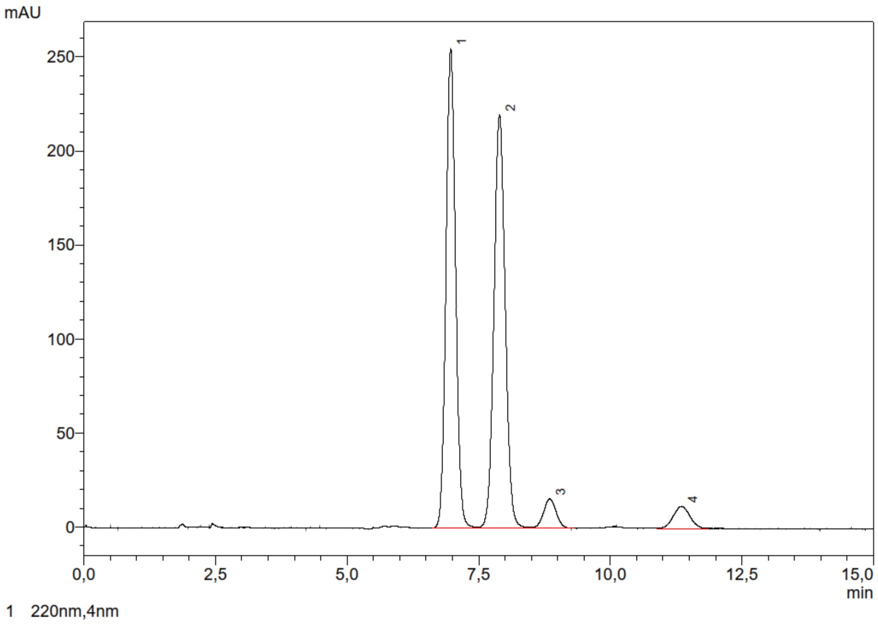
The ee was determined by HPLC analysis: Chiralpak 150 mm IC-3, ∅ 4.6 mm i. d., *n*-heptane/ethanol = 98:2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 7.08 min, t(major) = 7.99 min.



PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	1,86	11,41	
2	2,14	0,45	
3	2,42	0,44	
4	5,77	0,39	
5	7,08	4,91	1. Enantiomer
6	7,99	82,40	2. Enantiomer 88.7 % ee
Total		100,00	

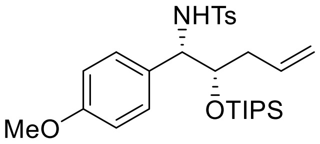
Determination of the ee of **13a**



PDA Ch1 220nm

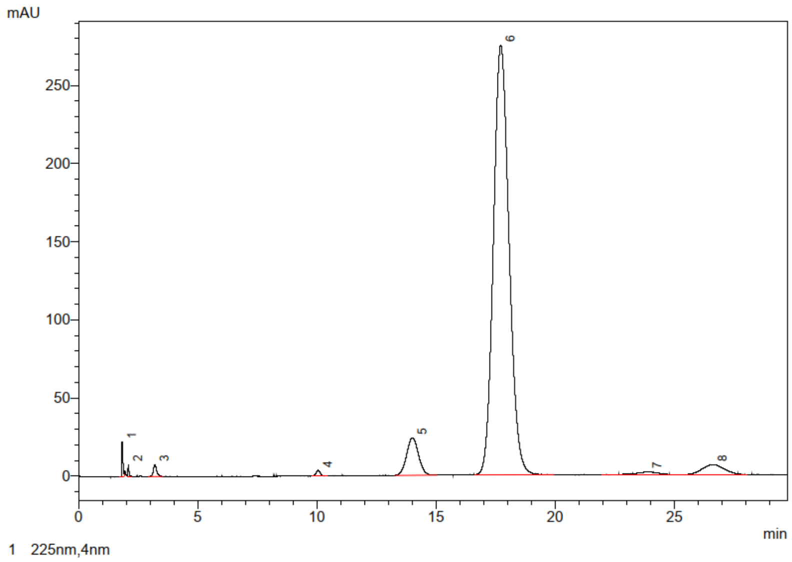
Peak #	Ret. Time	Area %		Name
1	6,97	46,12	1. Enantiomer	
2	7,90	46,50	2. Enantiomer	
3	8,85	3,66		
4	11,36	3,72		
Total		100,00		

Separation of enantiomers of *rac*-**13a**



_N_-((1_S_,2_S_)-1-(4-Methoxyphenyl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)-4-methylbenzenesulfonamide (13b). Prepared according to the representative procedure **A** but at 0 °C. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (120 mg, 80%, >20:1 dr, 87% ee). $[\alpha]_D^{20}$ = +33.1 (*c* = 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.14 – 7.06 (m, 2H), 6.99 – 6.91 (m, 2H), 6.69 – 6.61 (m, 2H), 5.71 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.37 (d, *J* = 7.1 Hz, 1H), 5.10 (ddt, *J* = 10.2, 2.0, 1.0 Hz, 1H), 5.00 (app. dq, *J* = 17.2, 1.5 Hz, 1H), 4.40 (dd, *J* = 7.1, 3.1 Hz, 1H), 3.89 (dt, *J* = 9.3, 3.3 Hz, 1H), 3.74 (s, 3H), 2.46 – 2.36 (m, 1H), 2.34 (s, 3H), 2.19 (dddd, *J* = 12.6, 6.9, 3.2, 1.6 Hz, 1H), 0.98 – 0.91 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 142.9, 138.2, 133.3, 131.6, 129.3, 128.4, 127.2, 119.0, 113.5, 77.2, 58.6, 55.4, 38.9, 21.6, 18.2, 18.1, 12.8; IR (ATR): ṽ = 3307, 2943, 2867, 1613, 1518, 1464, 1429, 1413, 1322, 1288, 1270, 1246, 1185, 1157, 1109, 1077, 1028, 1014, 961, 918, 881, 858, 813, 748; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{28}H_{43}NO_4SSi+Na]^+$ ($[M+Na]^+$) 540.2574, found 540.2579.

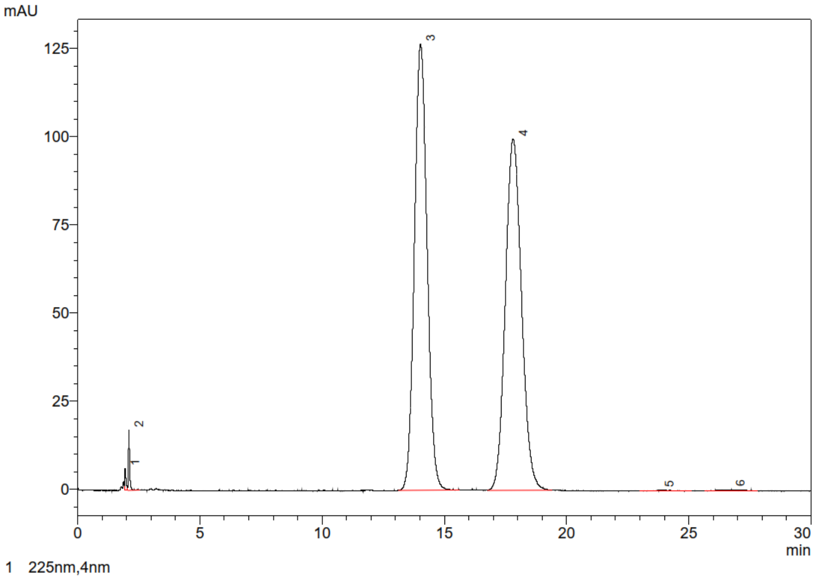
The ee was determined by HPLC analysis: Chiralpak 150 mm IC-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 95:5, v = 1.0 mL/min, λ = 225 nm, t(minor) = 14.02 min, t(major) = 17.72 min.



PDA Ch1 225nm

Peak #	Ret. Time	Area %	Name
1	1,83	0,54	
2	2,10	0,19	
3	3,21	0,53	
4	10,06	0,31	
5	14,02	5,90	1. Enantiomer
6	17,72	88,34	2. Enantiomer 87.5 % ee
7	23,88	0,99	
8	26,62	3,20	
Total		100,00	

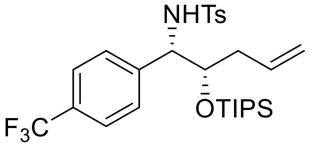
Determination of the ee of **13b**



PDA Ch1 225nm

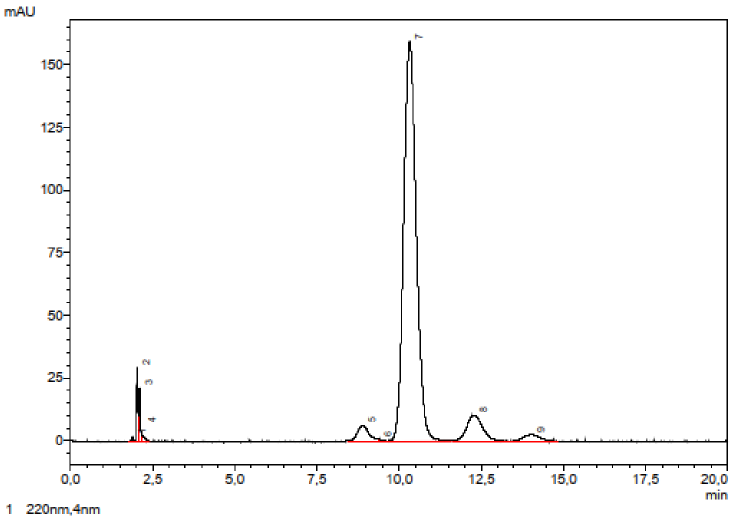
Peak #	Ret. Time	Area %	Name
1	1,94	0,22	
2	2,10	0,62	
3	14,03	49,28	1. Enantiomer
4	17,82	49,51	2. Enantiomer
5	23,80	0,11	
6	26,70	0,26	
Total		100,00	

Separation of the enantiomers of *rac*-**13b**



4-Methyl-*N*-((1*S*,2*S*)-1-(4-(trifluoromethyl)phenyl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)benzenesulfonamide (13c). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO$_2$; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (100 mg, 62%, >20:1 dr, 93% ee). $[\alpha]_D^{20}$ = +32.4 (*c* = 0.51, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.47 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 5.72 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.45 (dd, *J* = 7.2, 2.1 Hz, 1H), 5.16 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.04 (app. dq, *J* = 17.2, 1.5 Hz, 1H), 4.54 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.91 (dt, *J* = 9.7, 3.2 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.32 (s, 3H), 2.25 (dddd, *J* = 13.9, 6.5, 3.3, 1.6 Hz, 1H), 0.96 – 0.84 (m, 21H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.8, 143.4, 137.8, 132.8, 129.6 (q, $^2J_{CF}$ = 32.3 Hz), 129.4, 127.6, 127.1, 125.0 (q, $^3J_{CF}$ = 3.8 Hz), 124.2 (q, $^1J_{CF}$ = 272.1 Hz), 119.6, 77.1, 58.5, 39.0, 21.4, 18.1, 17.9, 12.8; ^{19}F NMR (282 MHz, CDCl$_3$) δ –62.6; IR (ATR): ṽ = 3286, 2943, 2867, 1621, 1599, 1466, 1426, 1403, 1324, 1273, 1160, 1112, 1067, 1017, 992, 974, 922, 882, 850, 824, 809, 782, 756, 746; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{28}H_{40}NO_3SF_3Si+Na]^+$ ($[M+Na]^+$) 578.2342, found 578.2346.

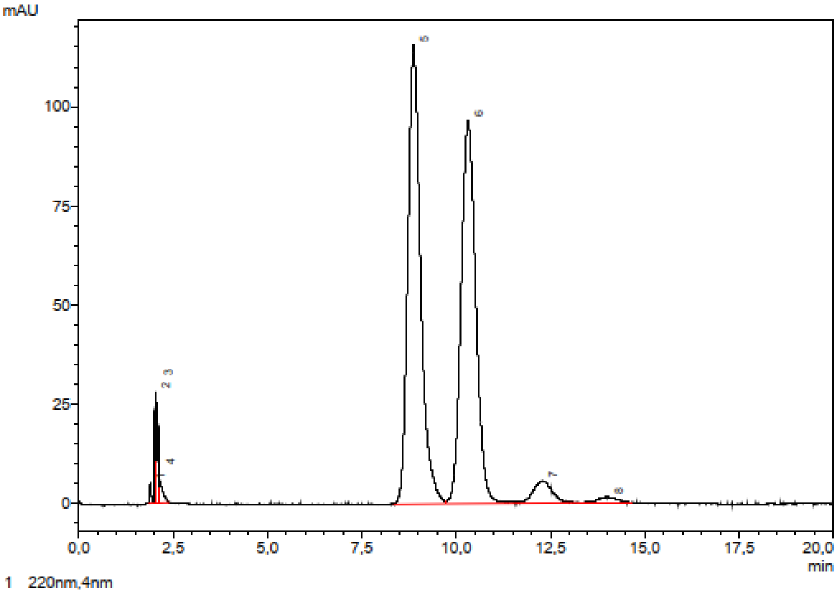
The ee was determined by HPLC analysis: Chiralpak 150 mm IC-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 98:2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 8.89 min, t(major) = 10.32 min.



PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	1,89	0,18	
2	2,03	1,65	
3	2,10	1,28	
4	2,20	0,32	
5	8,89	3,19	1. Enantiomer
6	9,38	0,20	
7	10,32	84,05	2. Enantiomer 92.7 % ee
8	12,28	7,21	
9	14,03	1,92	
Total		100,00	

Determination of the ee of **13c**

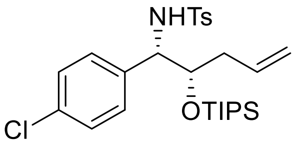


PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	1,89	0,30	
2	2,02	1,21	
3	2,09	1,13	
4	2,15	0,62	
5	8,87	47,27	1. Enantiomer
6	10,32	45,23	2. Enantiomer
7	12,28	3,37	
8	14,03	0,88	
Total		100,00	

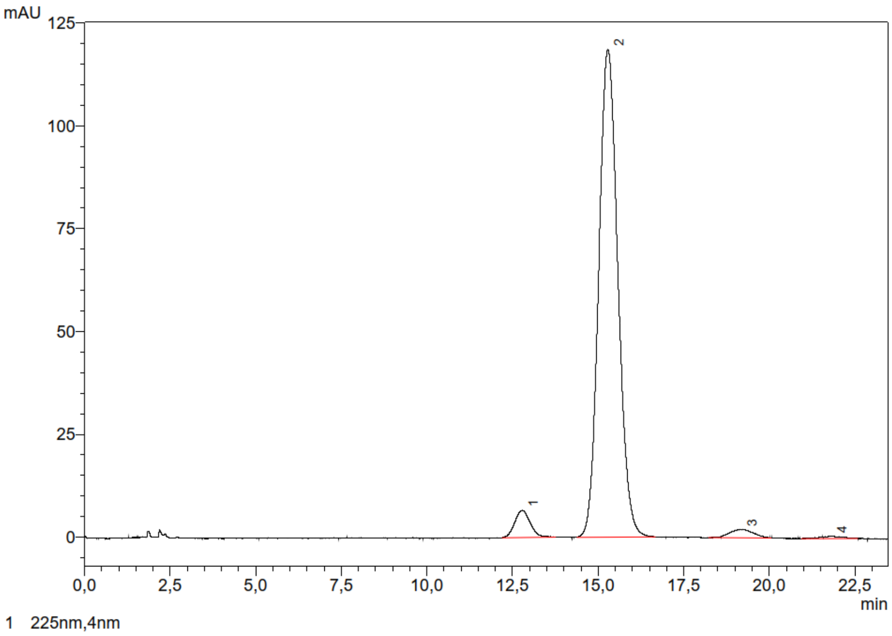
Separation of enantiomers of *rac*-**13c**

***N*-((1*S*,2*S*)-1-(4-Chlorophenyl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)-4-methyl-**



benzenesulfonamide (13d). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (129 mg, 85%, >20:1 dr, 91% ee). $[\alpha]_D^{20}$ = +41.5 (*c* = 0.48, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.17 – 7.13 (m, 2H), 7.13 – 7.08 (m, 2H), 7.02 – 6.97 (m, 2H), 5.72 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.42 (d, *J* = 7.5 Hz, 1H), 5.15 (ddt, *J* = 10.2, 2.0, 0.9 Hz, 1H), 5.04 (app. dq, *J* = 17.2, 1.5 Hz, 1H), 4.47 (dd, *J* = 7.5, 2.6 Hz, 1H), 3.91 (dt, *J* = 9.6, 3.1 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.39 (s, 3H), 2.25 (dddd, *J* = 12.5, 6.8, 3.2, 1.6 Hz, 1H), 0.99 – 0.89 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 138.3, 138.0, 133.1, 133.0, 129.4, 128.6, 128.2, 127.1, 119.4, 77.1, 58.3, 38.9, 21.6, 18.2, 18.0, 12.8; IR (ATR): ṽ = 3290, 2963, 2946, 2865, 1493, 1464, 1422, 1400, 1330, 1292, 1278, 1257, 1161, 1091, 1067, 1013, 996, 937, 921, 881, 847, 810, 758, 709, 669, 607; HRMS (ESI^+, *m*/*z*) calculated for $[C_{27}H_{40}NO_3SClSi+Na]^+$ ($[M+Na]^+$) 544.2079, found 544.2085.

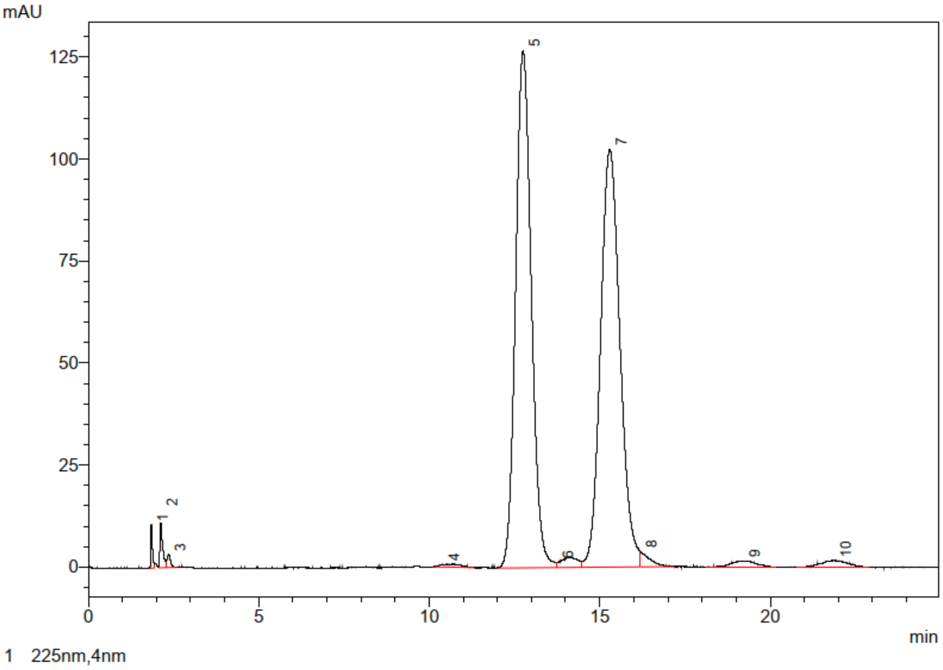
The ee was determined by HPLC analysis: Chiralpak 150 mm IC-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 98:2, v = 1.0 mL/min, λ = 225 nm, t(minor) = 12.78 min, t(major) = 15.29 min.



PDA Ch1 225nm

Peak #	Ret. Time	Area %	Name
1	12,78	4,26	1. Enantiomer
2	15,29	93,19	2. Enantiomer 91.3 % ee
3	19,18	2,01	
4	21,80	0,53	
Total		100,00	

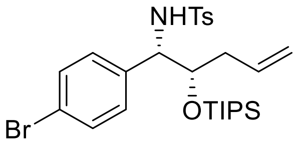
Determination of the ee of **13d**



PDA Ch1 225nm

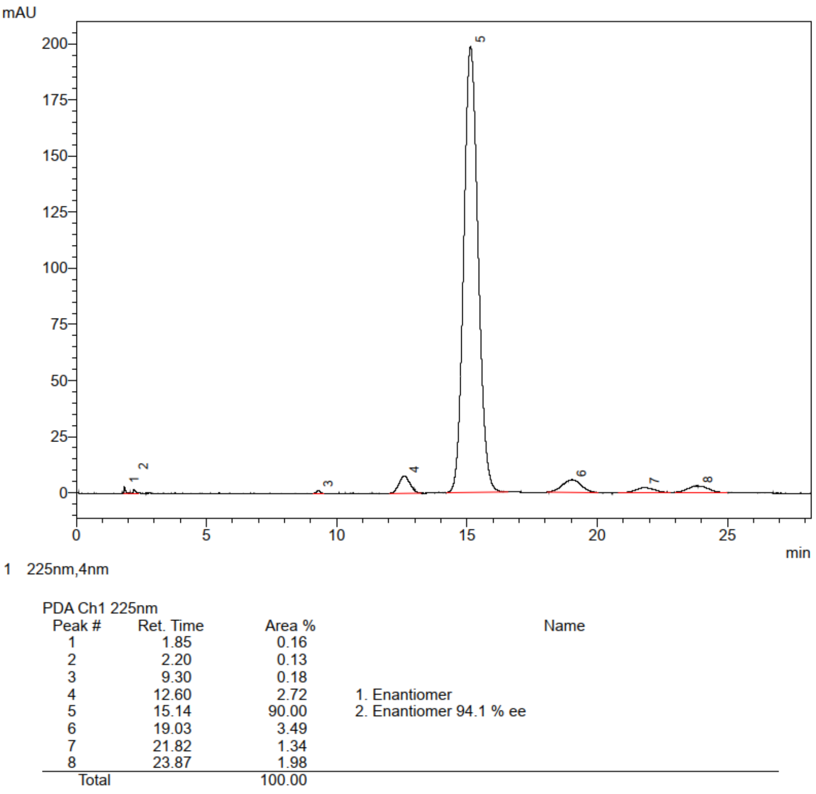
Peak #	Ret. Time	Area %	Name
1	1,85	0,41	
2	2,13	0,71	
3	2,36	0,28	
4	10,39	0,38	
5	12,75	47,23	1. Enantiomer
6	13,74	0,97	
7	15,30	47,22	2. Enantiomer
8	16,18	0,85	
9	19,22	0,92	
10	21,88	1,04	
Total		100,00	

Separation of enantiomers of *rac*-**13d**



***N*-((1*S*,2*S*)-1-(4-Bromophenyl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)-4-methylbenzenesulfonamide (13e)**. Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (146 mg, 89%, >20:1 dr, 94% ee). $[\alpha]_D^{20}$ = +35.3 (*c* = 0.49, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.26 – 7.22 (m, 2H), 7.14 – 7.10 (m, 2H), 6.94 – 6.88 (m, 2H), 5.70 (ddt, *J* = 17.4, 10.3, 6.9 Hz, 1H), 5.38 (d, *J* = 7.5 Hz, 1H), 5.13 (ddt, *J* = 10.3, 2.0, 1.0 Hz, 1H), 5.01 (app. dq, *J* = 17.2, 1.5 Hz, 1H), 4.42 (dd, *J* = 7.5, 2.7 Hz, 1H), 3.88 (dt, *J* = 9.6, 3.1 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.37 (s, 3H), 2.22 (dddd, *J* = 13.9, 6.4, 3.3, 1.5 Hz, 1H), 0.96 – 0.88 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 138.8, 137.9, 132.9, 131.1, 129.4, 129.0, 127.1, 121.2, 119.4, 77.0, 58.4, 38.9, 21.6, 18.2, 18.0, 12.8; IR (ATR): $\tilde{\nu}$ = 3287, 2945, 2865, 1463, 1421, 1398, 1330, 1291, 1278, 1161, 1131, 1094, 1071, 1010, 995, 937, 921, 881, 846, 808, 774, 709, 674, 661, 607; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{27}H_{40}NO_3SSiBr+Na]^+$ ($[M+Na]^+$) 588.1574, found 588.1581.

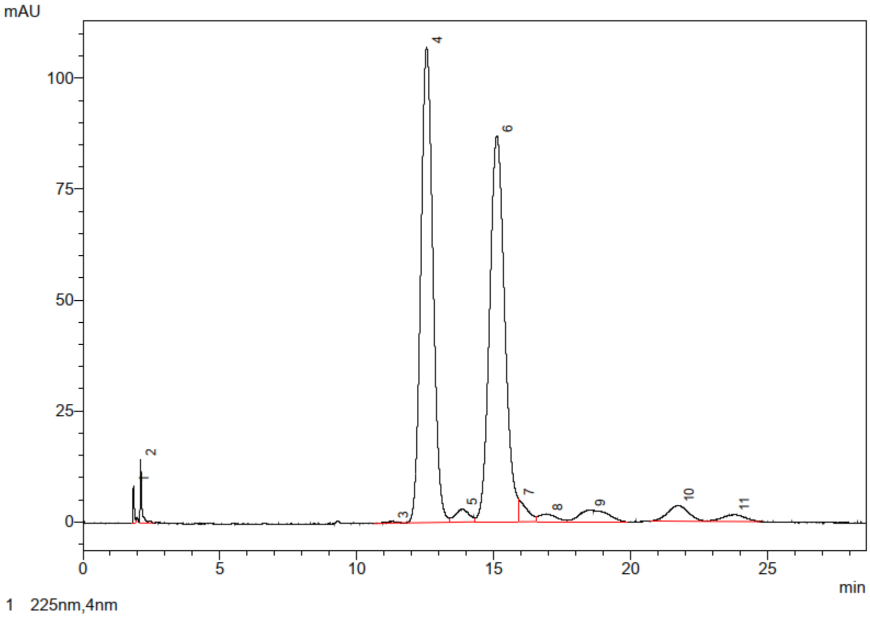
The ee was determined by HPLC analysis: Chiralpak 150 mm IC-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 98:2, v = 1.0 mL/min, λ = 225 nm, t(minor) = 12.60 min, t(major) = 15.14 min.



PDA Ch1 225nm

Peak #	Ret. Time	Area %	Name
1	1.85	0.16	
2	2.20	0.13	
3	9.30	0.18	
4	12.60	2.72	1. Enantiomer
5	15.14	90.00	2. Enantiomer 94.1 % ee
6	19.03	3.49	
7	21.82	1.34	
8	23.87	1.98	
Total		100.00	

Determination of the ee of **13e**

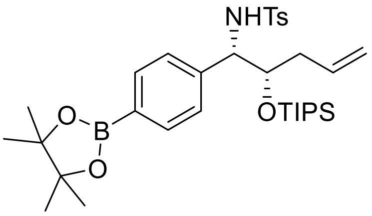


PDA Ch1 225nm

Peak #	Ret. Time	Area %	Name
1	1,85	0,34	
2	2,11	0,80	
3	11,31	0,15	
4	12,56	43,93	1. Enantiomer
5	13,82	1,37	
6	15,12	44,68	2. Enantiomer
7	15,91	1,45	
8	16,95	1,03	
9	18,50	2,53	
10	21,75	2,50	
11	23,77	1,21	
Total		100,00	

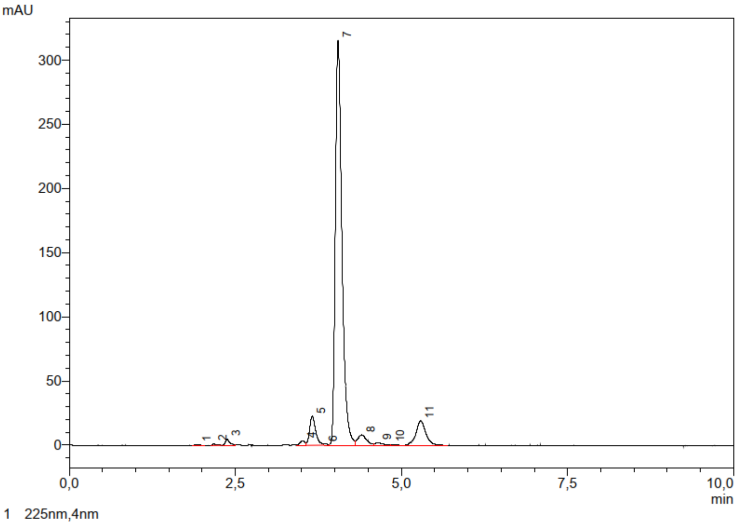
Separation of the enantiomers of *rac*-**13e**

4-Methyl-*N*-((1*S*,2*S*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2-((tri-iso-propylsilyl)oxy)pent-4-en-1-yl)benzenesulfonamide (13f).



Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 50:1 to 10:1) to give the title compound as a white solid (132 mg, 74%, >20:1 dr, 88% ee). $[\alpha]_D^{20}$ = +33.3 (*c* = 0.62, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 7.06 – 7.03 (m, 2H), 7.02 – 6.99 (m, 2H), 5.74 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.40 (d, *J* = 7.7 Hz, 1H), 5.13 (ddt, *J* = 10.2, 1.8, 0.9 Hz, 1H), 5.05 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.46 (dd, *J* = 7.7, 2.6 Hz, 1H), 3.93 (dt, *J* = 9.5, 3.1 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.32 (s, 3H), 2.22 (dddd, *J* = 13.9, 6.8, 3.2, 1.6 Hz, 1H), 1.34 (app. d, *J* = 1.9 Hz, 12H), 0.97 – 0.87 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.6, 138.0, 134.6, 133.2, 129.3, 127.1, 126.6, 119.3, 83.9, 77.4, 59.0, 39.0, 25.0, 24.9, 21.5, 18.2, 18.1, 12.8; IR (ATR): ṽ = 3293, 2943, 2866, 1612, 1463, 1391, 1356, 1329, 1214, 1163, 1144, 1088, 1067, 1019, 995, 961, 922, 882, 858, 811, 745; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{33}H_{52}BNO_5SSi+Na]^+$ ($[M+Na]^+$) 636.3321, found 636.3324.

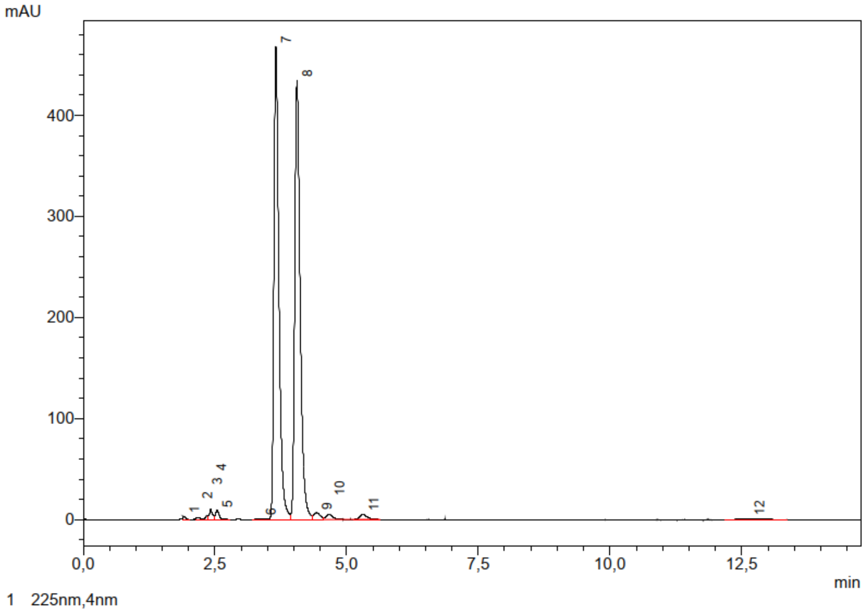
The ee was determined by HPLC analysis: Chiralpak 150 mm IB-N-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 98:2, v = 1.0 mL/min, λ = 225 nm, t(minor) = 3.66 min, t(major) = 4.05 min.



PDA Ch1 225nm

Peak #	Ret. Time	Area %	Name
1	1,93	0,15	
2	2,18	0,21	
3	2,38	0,83	
4	3,51	0,73	
5	3,66	5,45	1. Enantiomer
6	3,84	0,14	
7	4,05	81,48	2. Enantiomer 87.5 % ee
8	4,40	2,84	
9	4,65	0,65	
10	4,85	0,11	
11	5,29	7,40	
Total		100,00	

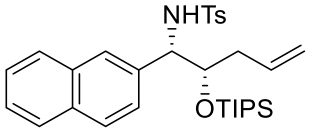
Determination of the ee of **13f**



PDA Ch1 225nm

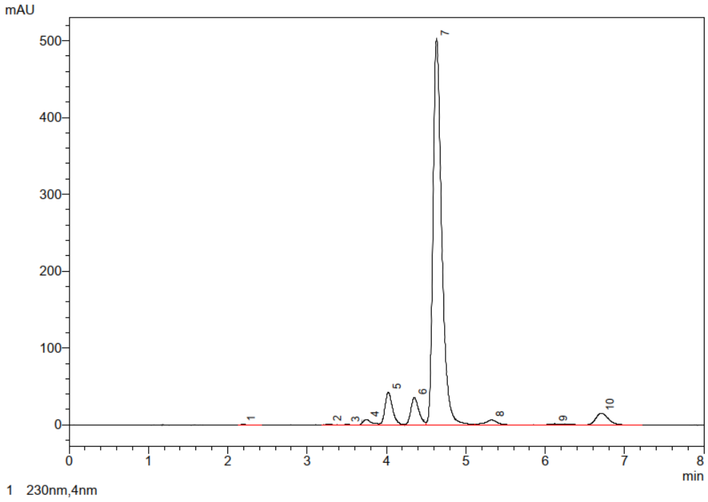
Peak #	Ret. Time	Area %	Name
1	1,91	0,21	
2	2,16	0,23	
3	2,35	0,21	
4	2,42	0,69	
5	2,54	0,78	
6	3,37	0,14	
7	3,66	46,98	1. Enantiomer
8	4,06	47,59	2. Enantiomer
9	4,43	0,93	
10	4,67	0,75	
11	5,32	0,77	
12	12,64	0,73	
Total		100,00	

Separation of the enantiomers of *rac*-**13f**



4-Methyl-*N*-((1*S*,2*S*)-1-(naphthalen-2-yl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)-benzenesulfonamide (14). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether 100:1 to 20:1) to give the title compound as a white solid (145 mg, 93%, >20:1 dr, 88% ee). $[\alpha]_D^{20}$ = +56.5 (*c* = 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.58 (dt, *J* = 8.4, 3.3 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.45 – 7.42 (m, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.17 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.97 – 6.90 (m, 2H), 5.83 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.53 (d, *J* = 7.6 Hz, 1H), 5.20 (ddt, *J* = 10.2, 1.8, 0.9 Hz, 1H), 5.12 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.66 (dd, *J* = 7.6, 2.7 Hz, 1H), 4.05 (dt, *J* = 9.6, 3.1 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.30 (dddd, *J* = 13.8, 6.7, 3.2, 1.5 Hz, 1H), 2.17 (s, 3H), 0.96 – 0.87 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 138.1, 136.6, 133.2, 133.0, 132.7, 129.2, 127.9, 127.8, 127.6, 127.1, 126.5, 126.0, 125.8, 125.1, 119.3, 77.0, 59.1, 39.1, 21.3, 18.2, 18.0, 12.8; IR (ATR): ṽ = 3286, 2942, 2889, 2865, 1599, 1508, 1464, 1411, 1328, 1289, 1272, 1164, 1067, 1015, 996, 951, 915, 882, 857, 810, 744; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{31}H_{43}NO_3SSi+Na]^+$ ($[M+Na]^+$) 560.2625, found 560.2631.

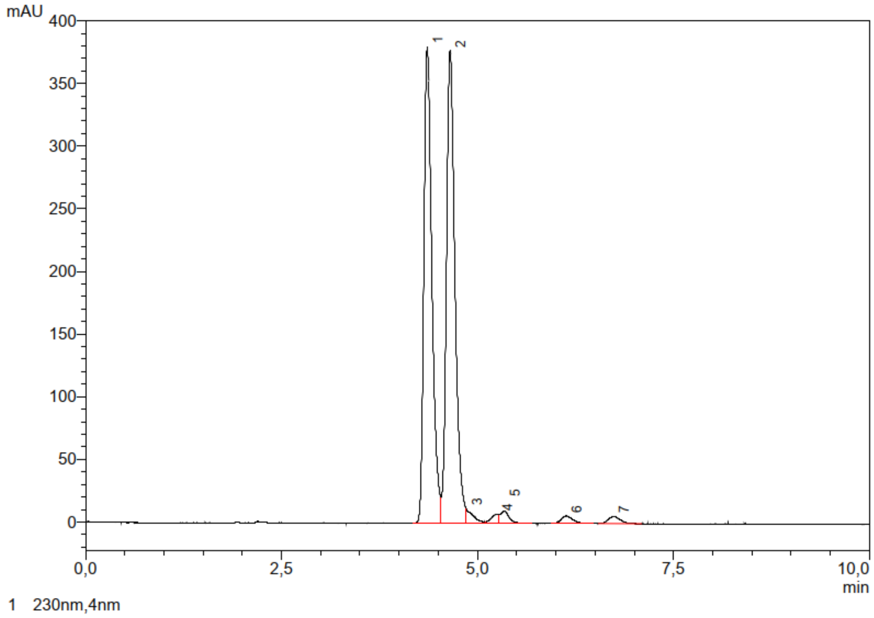
The ee was determined by HPLC analysis: Chiralpak 150 mm IB-N-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 98:2, v = 1.0 mL/min, λ = 230 nm, t(minor) = 4.35 min, t(major) = 4.63 min.



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	2,19	0,11	
2	3,27	0,13	
3	3,50	0,11	
4	3,74	1,16	
5	4,02	6,04	
6	4,35	5,32	1. Enantiomer
7	4,63	81,22	2. Enantiomer 87.7 % ee
8	5,32	1,66	
9	6,12	0,63	
10	6,71	3,63	
Total		100,00	

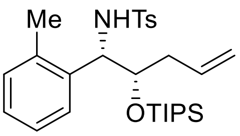
Determination of the ee of **14**



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	4,36	45,98	1. Enantiomer
2	4,65	48,46	2. Enantiomer
3	4,86	1,24	
4	5,25	0,78	
5	5,35	1,35	
6	6,13	1,10	
7	6,73	1,09	
Total		100,00	

Separation of enantiomers of *rac*-**14**

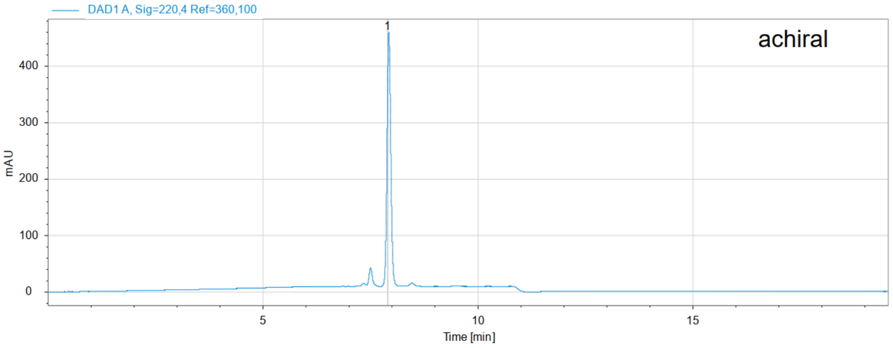


4-Methyl-*N*-((1*S*,2*S*)-1-(*o*-tolyl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)benzenesulfonamide (15). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (116 mg, 80%, >20:1 dr, 83% ee). $[\alpha]_D^{20}$ = +18.4 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.05 – 7.00 (m, 2H), 6.99 – 6.95 (m, 2H), 6.93 – 6.91 (m, 1H), 6.84 – 6.78 (m, 1H), 5.79 (dddd, *J* = 17.0, 10.3, 7.9, 6.7 Hz, 1H), 5.43 (d, *J* = 8.4 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.77 (dd, *J* = 8.4, 1.9 Hz, 1H), 3.81 (ddd, *J* = 10.2, 3.4, 1.8 Hz, 1H), 2.58 (ddd, *J* = 13.6, 9.9, 7.6 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.29 (s, 3H), 2.20 (s, 3H), 0.96 – 0.84 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.2, 137.2, 134.3, 133.1, 130.2, 129.2, 127.4, 126.9 (2C), 125.4, 119.5, 75.5, 54.8, 39.5, 21.5, 19.5, 18.2, 18.0, 12.9; IR (ATR): ṽ = 3276, 2942, 2889, 2866, 1463, 1411, 1327, 1290, 1162, 1094, 1065, 1014, 920, 882, 851, 814, 762, 707, 662; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{28}H_{43}NO_3SSi+Na]^+$ ($[M+Na]^+$) 524.2625, found 524.2631.

94 mg of the product were recrystallized from methyl *tert*-butyl ether/*n*-hexane. The mother liquor was decanted and concentrated to give the enantioenriched product in 86% ee (65 mg).

The ee was determined by 2D HPLC analysis; Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. d., methanol/water gradient 70% to 90% over 5 minutes, v = 1.0 mL/min, λ = 220 nm, t(major) = 7.88 min, 308 K.

^{1}D chromatogram(s)



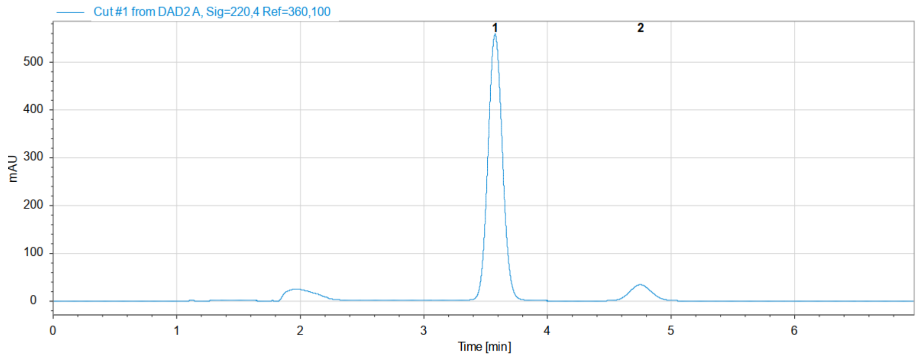
Sampling table (^{1}D)

Cut group	Cut #	^{1}D Cut start [min]	^{1}D Ret. time [min]	^{1}D Duration [min]	Trigger	^{2}D Run start [min]	
	1	7.88	***	0.04	Peak	7.92	product

Separation of impurities on an achiral column

Step 2: Resolution of the enantiomers: Daicel 150 mm Chiralcel OZ-3R, ∅ 4.6 mm i. d., acetonitrile/water = 90:10, v = 1.0 mL/min, λ = 220 nm, t(major) = 3.58 min, t(minor) = 4.75 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	3.578	4555.609 **4555.609**	0.127	557.298	0.904
2	1	4.754	416.534 **416.534**	0.192	33.487	0.933

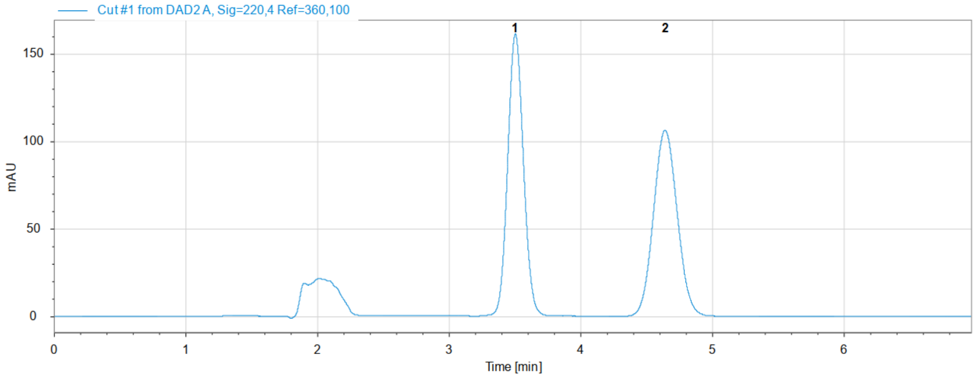
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	chiral
1	7.90 - 7.94	3.578	4555.609	91.623	1st enantiomer
2	7.90 - 7.94	4.754	416.534	8.377	2nd enantiomer

Determination of the ee of **15**

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

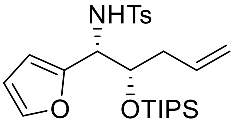
Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	3.505	1337.411 **1337.411**	0.128	161.245	0.912
2	1	4.642	1334.009 **1334.009**	0.195	106.426	0.914

Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%
1	7.85 - 7.89	3.505	1337.411	50.064
2	7.85 - 7.89	4.642	1334.009	49.936

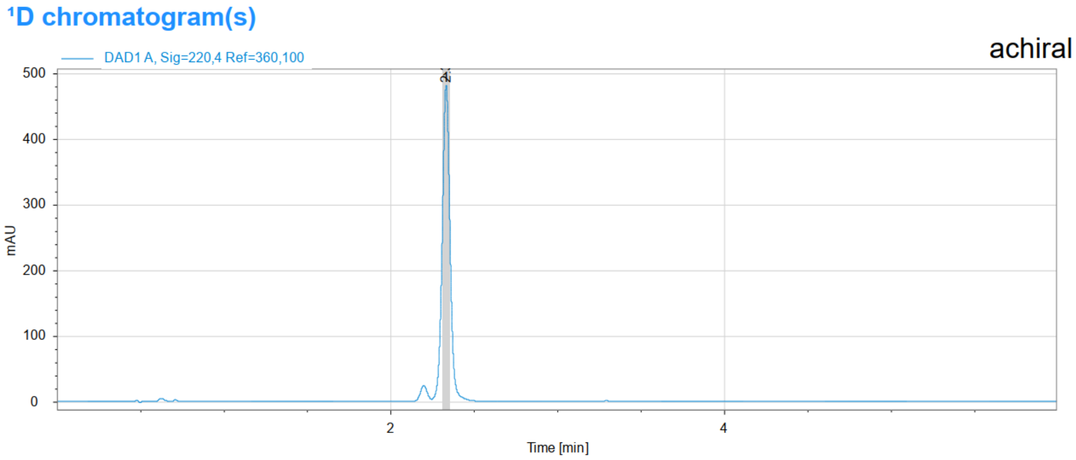
Separation of the enantiomers of *rac*-**15**



***N*-((1*R*,2*S*)-1-(Furan-2-yl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)-4-methylbenzenesulfonamide (16)**. Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (102 mg, 74%, >20:1 dr, 86% ee). $[\alpha]_D^{20}$ = +23.9 (*c* = 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.22 – 7.17 (m, 2H), 7.12 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.11 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.91 (app. dt, *J* = 3.3, 0.9 Hz, 1H), 5.70 (dddd, *J* = 16.9, 10.3, 7.8, 6.5 Hz, 1H), 5.27 (d, *J* = 8.9 Hz, 1H), 5.09 (dtd, *J* = 10.3, 1.7, 0.8 Hz, 1H), 5.04 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.53 (ddd, *J* = 8.8, 2.2, 0.9 Hz, 1H), 4.15 (ddd, *J* = 9.8, 3.8, 2.1 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.38 (s, 3H), 2.24 (dddd, *J* = 14.0, 6.5, 3.7, 1.7 Hz, 1H), 0.97 – 0.94 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 143.1, 141.4, 138.1, 133.2, 129.5, 127.1, 119.0, 110.4, 107.8, 74.4, 53.9, 38.8, 21.6, 18.1(2), 18.0(6), 12.7; IR (ATR): ṽ = 3312, 2943, 2864, 1598, 1499, 1464, 1421, 1382, 1326, 1289, 1255, 1160, 1141, 1085, 1065, 1012, 994, 919, 883, 810, 758; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{25}H_{39}NO_4SSi+Na]^+$ ($[M+Na]^+$) 500.2261, found 500.2266.

70 mg of the product were recrystallized from methyl *tert*-butyl ether/*n*-hexane to give a sample of 90% ee (55 mg).

The ee was determined by 2D HPLC analysis; Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. d., methanol/water 90:10, v = 1.0 mL/min, λ = 220 nm, t(major) = 2.33 min, 308 K.



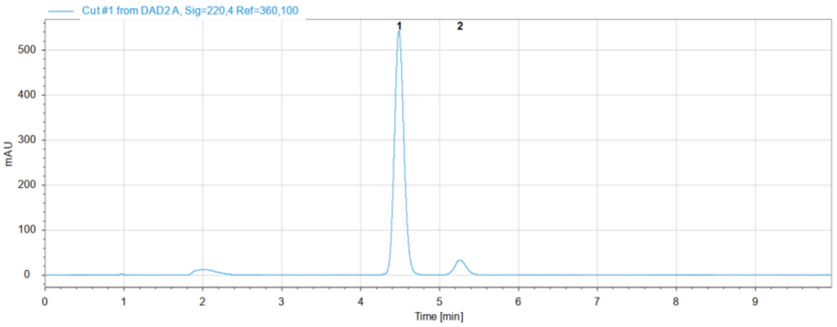
Sampling table (¹D)

Cut group	Cut #	¹D Cut start [min]	¹D Ret. time [min]	¹D Duration [min]	Trigger	²D Run start [min]
	1	2.31	2.333	0.04	Peak	2.36

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralcel OZ-3R, ∅ 4.6 mm i. d., acetonitrile/water = 80:20, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.49 min, t(minor) = 5.27 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	4.490	4532.446 **4532.446**	0.130	541.465	0.883
2	1	5.266	336.409 **336.409**	0.155	32.709	0.900

Component table

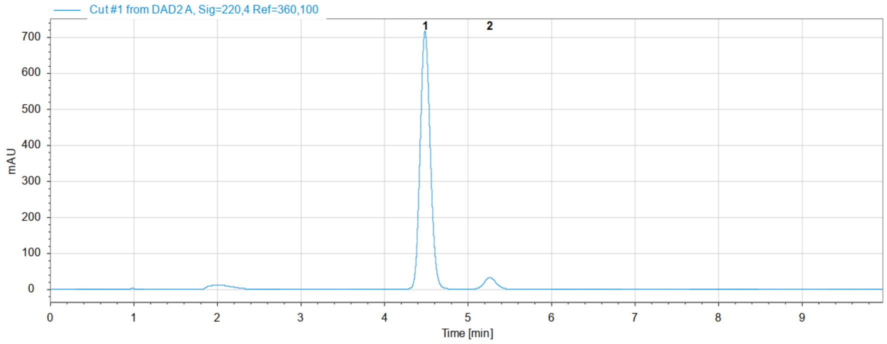
Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	chiral
1	2.33 - 2.37	4.490	4532.446	93.091	1st enantiomer
2	2.33 - 2.37	5.266	336.409	6.909	2nd enantiomer

= 86.2 % ee

Determination of the ee of **16** before recrystallization

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	4.490	6016.581 **6016.581**	0.131	715.768	0.881
2	1	5.266	325.642 **325.642**	0.156	31.825	0.906

Component table

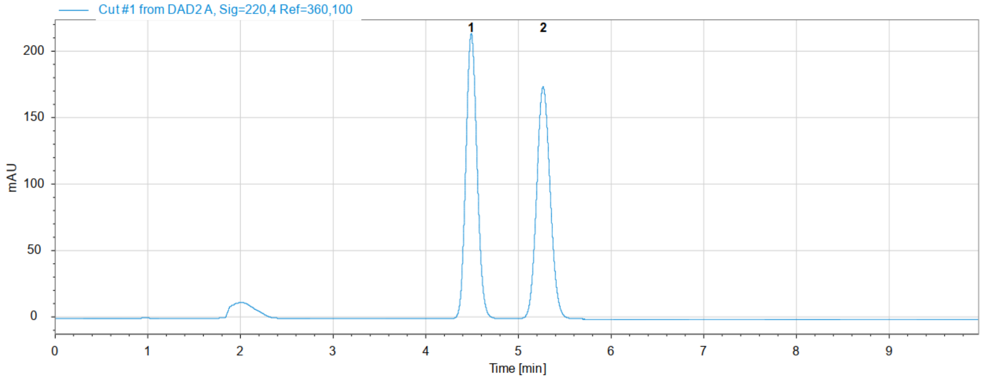
Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	chiral
1	2.31 - 2.35	4.490	6016.581	94.865	1st enantiomer
2	2.31 - 2.35	5.266	325.642	5.135	2nd enantiomer

= 89.7 % ee

Determination of the ee of **16** after recrystallization

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	4.497	1802.352 **1802.352**	0.130	214.646	0.892
2	1	5.272	1793.188 **1793.188**	0.159	174.745	0.903

Component table

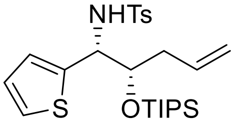
Signal: DAD2 A, Sig=220,4 Ref=360,100

chiral

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%	
1	2.34 - 2.38	4.497	1802.352	50.127	1st enantiomer
2	2.34 - 2.38	5.272	1793.188	49.873	2nd enantiomer

Separation of the enantiomers of *rac*-**16**

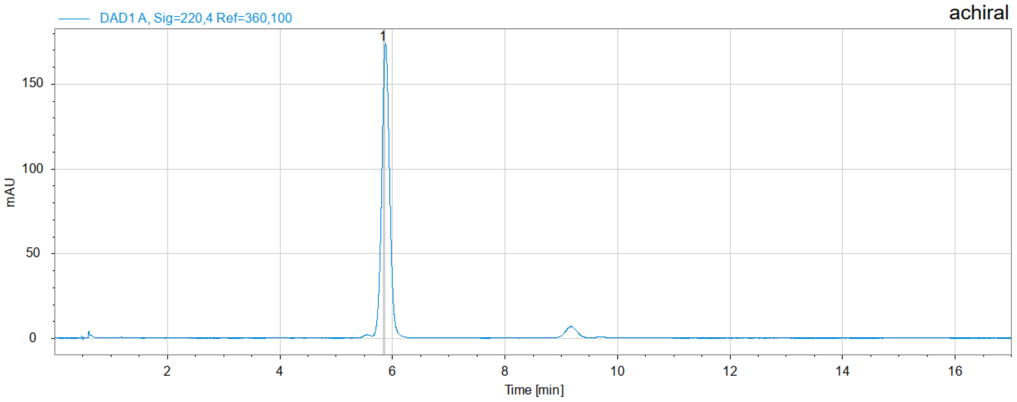
4-Methyl-*N*-((1*R*,2*S*)-1-(thiophen-2-yl)-2-((triisopropylsilyl)oxy)pent-4-en-1-yl)benzenesulfonamide (17). Prepared according to the representative procedure **A**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (127 mg, 89%, >20:1 dr, 73% ee). $[\alpha]_D^{20}$ = +17.1 (*c* = 0.49, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.17 – 7.12 (m, 2H), 7.05 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.75 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.70 (app. dt, *J* = 3.5, 1.1 Hz, 1H), 5.74 (dddd, *J* = 16.9, 10.3, 7.7, 6.5 Hz, 1H), 5.34 (d, *J* = 8.1 Hz, 1H), 5.13 (app. dq, *J* = 10.4, 1.1 Hz, 1H), 5.07 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.77 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 4.02 (ddd, *J* = 9.6, 3.6, 2.6 Hz, 1H), 2.45 (app. dddt, *J* = 14.0, 9.7, 7.7, 1.0 Hz, 1H), 2.36 (s, 3H), 2.27 (dddd, *J* = 14.0, 6.6, 3.4, 1.7 Hz, 1H), 1.02 – 0.95 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 143.1, 138.1, 133.2, 129.4, 127.2, 126.3, 125.3, 124.7, 119.3, 77.0, 55.8, 38.7, 21.6, 18.2, 18.1, 12.9; IR (ATR): ṽ = 3275, 2943, 2889, 2866, 1462, 1433, 1361, 1326, 1290, 1163, 1081, 1033, 1005, 970, 919, 882, 852, 836, 816, 765, 711, 688, 661, 631; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{25}H_{39}NO_3S_2Si+Na]^+$ ($[M+Na]^+$) 516.2033, found 516.2038.



96 mg of product were recrystallized from methyl *tert*-butyl ether/*n*-hexane. The mother liquor was decanted and concentrated to give a sample of 89% ee (81 mg).

The ee was determined by 2D HPLC analysis; Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. d., methanol/water 85:15, v = 1.0 mL/min, λ = 220 nm, t(major) = 5.83 min, 308 K.

¹D chromatogram(s)



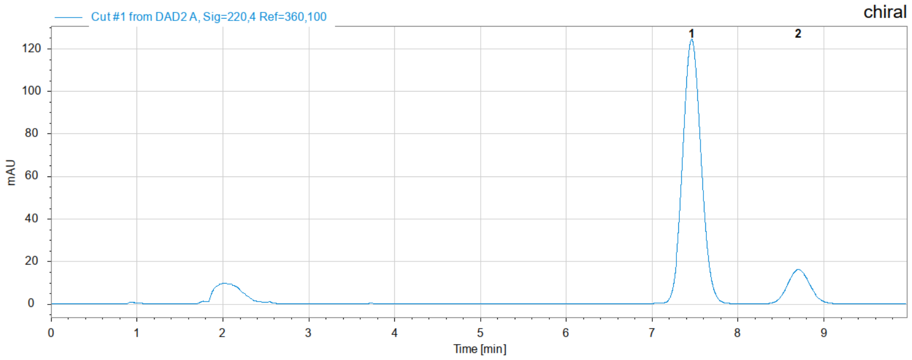
Sampling table (¹D)

Cut group	Cut #	¹D Cut start [min]	¹D Ret. time [min]	¹D Duration [min]	Trigger	²D Run start [min]
	1	5.83	***	0.04	Peak	5.87

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralcel OZ-3R, ∅ 4.6 mm i. d., acetonitrile/water = 75:25, v = 1.0 mL/min, λ = 220 nm, t(major) = 7.67 min, t(minor) = 8.93 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	7.467	1864.184 **1864.184**	0.228	124.442	0.922
2	1	8.708	293.978 **293.978**	0.223	16.201	0.955

Component table

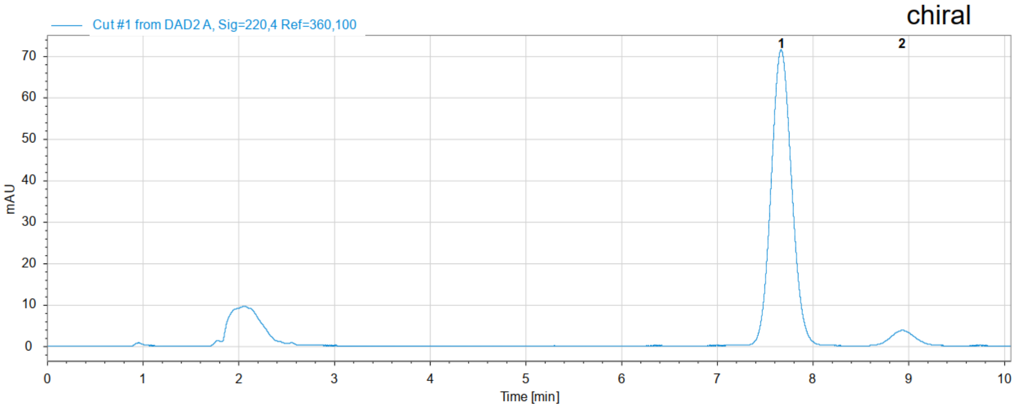
Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%
1	5.83 - 5.87	7.467	1864.184	86.378
2	5.83 - 5.87	8.708	293.978	13.622

ee = 72.8%

Determination of the ee of **17** before recrystallization

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	7.670	1061.059 **1061.059**	0.226	71.300	0.905
2	1	8.933	64.634 **64.634**	0.208	3.656	0.865

Component table

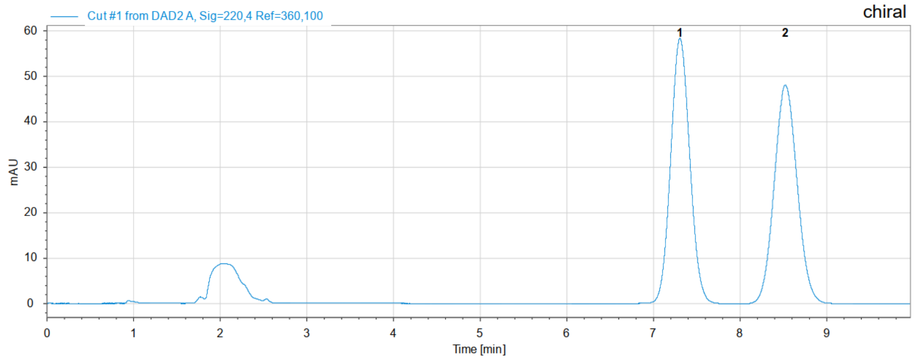
Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	
1	5.94 - 5.98	7.670	1061.059	94.258	1. enantiomer
2	5.94 - 5.98	8.933	64.634	5.742	2. enantiomer

ee = 88.5%

Determination of the ee of **17** after recrystallization

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	7.310	891.810 **891.810**	0.226	58.370	0.905
2	1	8.528	891.110 **891.110**	0.253	48.112	0.931

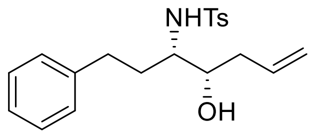
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%	
1	5.89 - 5.93	7.310	891.810	50.020	1st enantiomer
2	5.89 - 5.93	8.528	891.110	49.980	2nd enantiomer

Separation of enantiomers of *rac*-**17**

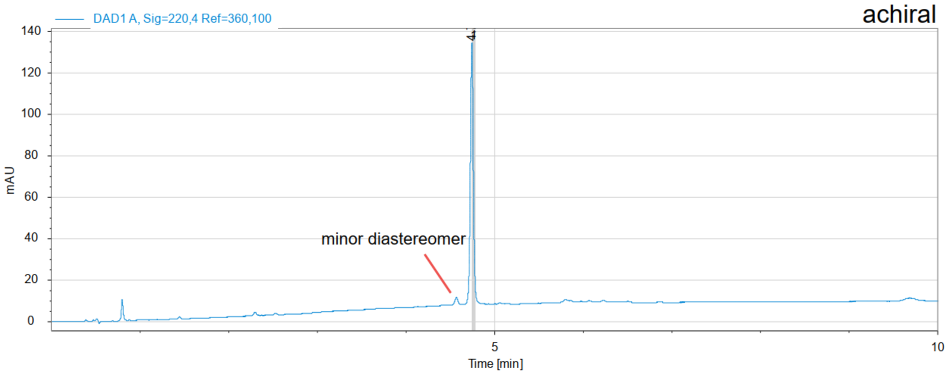
Representative Procedure B



***N*-((3*S*,4*S*)-4-Hydroxy-1-phenylhept-6-en-3-yl)-4-methyl-benzenesulfonamide (19)**. Bis(cyclooctadiene)nickel(0) (8.0 mg, 0.029 mmol, 10 mol%), phosphoramidite **L1** (19 mg, 0.029 mmol, 10 mol%) and THF (0.60 mL) were added to a flame-dried Schlenk flask under argon. Dienol ether **1** (R = TIPS) (0.23 mL, 0.87 mmol) and triethylborane (1.0 M in THF, 0.44 mL, 0.44 mmol) were added. Next, dihydrocinnamaldehyde N-tosylimine (**S11**) (75 mg, 0.29 mmol) and distilled and degassed water (5.2 µL, 0.29 mmol) were added, the flask was sealed under argon, and the mixture was stirred at room temperature overnight. The reaction was quenched with sat. $NaHCO_3$ solution (3.0 mL) and stirring was continued for 10 min. The mixture was diluted with methyl *tert*-butyl ether (3.0 mL) and the aqueous layer was extracted with methyl *tert*-butyl ether (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a pale yellow oil. The residue was dissolved in THF (1 mL) and tetrabutylammonium fluoride (1 M in THF, 0.87 mL, 0.87 mmol) was added. After stirring for 1 h at room temperature, distilled water (2.0 mL) was added and the aqueous phase was extracted by methyl *tert*-butyl ether (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a yellow oil. Purification by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 5:1 to 3:2) afforded the title compound as a pale yellow oil (77 mg, 74%, >20:1 dr, 81% ee). $[\alpha]_D^{20}$ = −6.5 (*c* = 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.35 – 7.27 (m, 2H), 7.24 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 7.08 – 6.96 (m, 2H), 5.72 (dddd, *J* = 17.1, 10.2, 8.2, 6.1 Hz, 1H), 5.13 (ddt, *J* = 10.3, 2.0, 1.0 Hz, 1H), 5.08 (app. dq, *J* = 16.9, 1.5 Hz, 1H), 4.75 (d, *J* = 9.0 Hz, 1H), 3.70 – 3.64 (m, 1H), 3.28 (dtd, *J* = 9.3, 6.8, 2.6 Hz, 1H), 2.51 – 2.43 (m, 2H), 2.43 (s, 3H), 2.27 – 2.07 (m, 2H), 1.88 (ddt, *J* = 13.8, 8.8, 6.9 Hz, 1H), 1.77 (br s, 1H), 1.68 – 1.57 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 141.3, 138.5, 134.1, 129.8, 128.6, 128.4, 127.2, 126.2, 119.2, 71.0, 56.9, 38.9, 34.5, 32.1, 21.7; IR (ATR): $\tilde{\nu}$ = 3493, 3275, 3064, 3026, 2926, 2866, 1641, 1599, 1495, 1430, 1325, 1289. 1217, 1154, 1091, 1062, 980, 917, 883, 814, 750, 700, 663; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{20}H_{25}NO_3S+Na]^+$ ($[M+Na]^+$) 382.1447, found 382.1448.

The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. d., methanol/water gradient 50% to 80% over 5 min, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.74 min, 308 K.

^{1}D chromatogram(s)



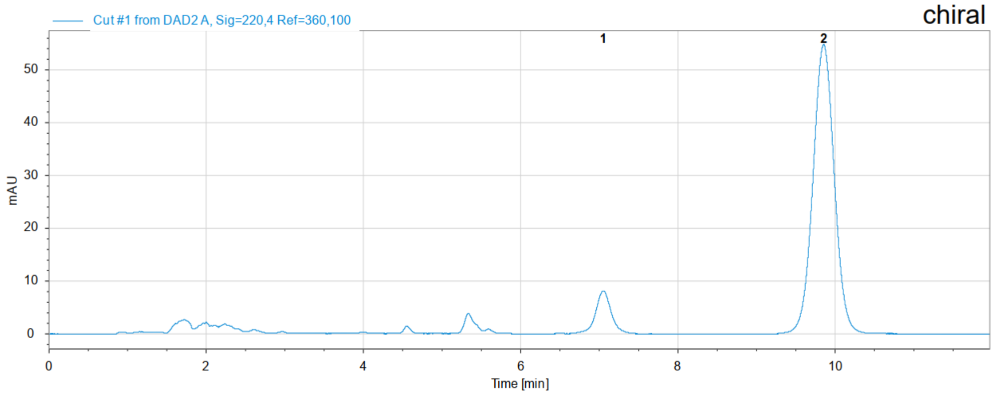
Sampling table (^{1}D)

Cut group	Cut #	^{1}D Cut start [min]	^{1}D Ret. time [min]	^{1}D Duration [min]	Trigger	^{2}D Run start [min]	
	1	4.74	4.748	0.04	Peak	4.79	major diastereomer

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralpak AS-3R, ∅ 4.6 mm i. d., acetonitrile/water = 50:50, v = 1.0 mL/min, λ = 220 nm, t(minor) = 7.06 min, t(major) = 9.86 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry		
1	1	7.056	110.603 **110.603**	0.162	8.083	0.962	1st enantiomer	ee = 80.6 %
2	1	9.857	1031.690 **1031.690**	0.274	54.757	0.979	2nd enantiomer	

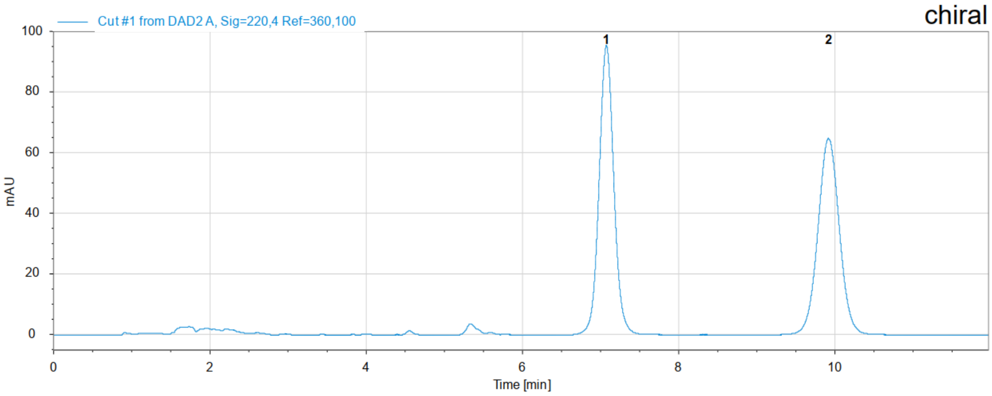
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%	
1	4.74 - 4.78	7.056	110.603	9.683	1st enantiomer
2	4.74 - 4.78	9.857	1031.690	90.317	2nd enantiomer

Determination of the ee of **19**

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	7.080	1247.914 **1247.914**	0.201	95.372	0.945	1st enantiomer
2	1	9.922	1230.976 **1230.976**	0.276	64.817	0.956	2nd enantiomer

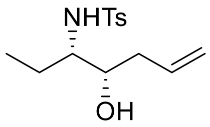
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

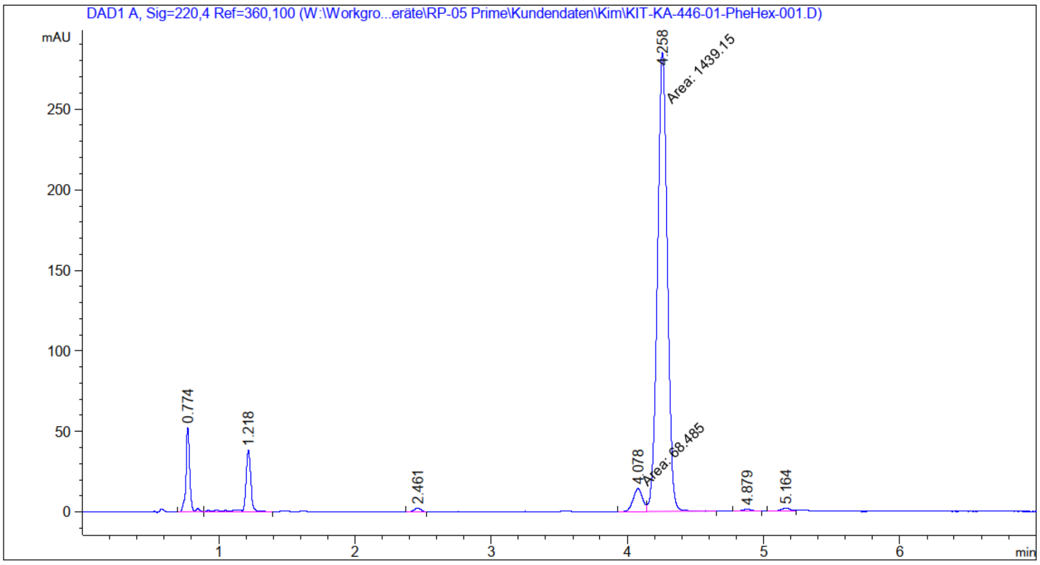
Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%	
1	4.74 - 4.78	7.080	1247.914	50.342	1st enantiomer
2	4.74 - 4.78	9.922	1230.976	49.658	2nd enantiomer

Separation of the enantiomers of *rac*-**19**

_N_-((3_S_,4_S_)-4-Hydroxyhept-6-en-3-yl)-4-methylbenzenesulfonamide (18). Prepared according to the representative procedure **B**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 5:1 to 3:2) to give the title compound as a yellow oil (65 mg, 79%, >20:1 dr, 83% ee). $[\alpha]_D^{20}$ = −20.0 (*c* = 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.32 – 7.27 (m, 2H), 5.75 (dddd, *J* = 17.1, 10.3, 8.2, 6.1 Hz, 1H), 5.16 – 5.05 (m, 2H), 4.65 (d, *J* = 8.8 Hz, 1H), 3.64 (app. dq, *J* = 7.3, 3.4 Hz, 1H), 3.15 (dtd, *J* = 9.6, 6.9, 2.8 Hz, 1H), 2.42 (s, 3H), 2.26 – 2.08 (m, 2H), 1.75 (br s, 1H), 1.65 – 1.50 (m, 1H), 1.37 (ddd, *J* = 14.1, 7.6, 6.9 Hz, 1H), 0.74 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 138.7, 134.2, 129.8, 127.1, 119.0, 70.7, 58.9, 38.9, 25.8, 21.7, 10.4; IR (ATR): ṽ = 3500, 3250, 2970, 2927, 2895, 1643, 1597, 1434, 1327, 1283, 1215, 1155, 1088, 1007, 991, 937, 916, 900, 869, 815, 755, 709, 653; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{14}H_{21}NO_3S+Na]^+$ ($[M+Na]^+$) 306.1134, found 306.1134.



The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Phenyl Hexyl, ∅ 4.6 mm i. d., acetonitrile/water gradient 30% to 40% over 5 minutes, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.26 min, 308 K.

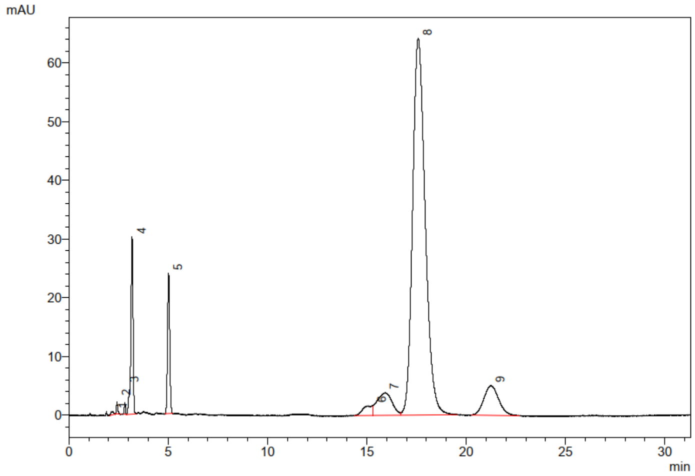


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   0.774 BV R  0.0297  103.55791   52.09127   5.9746
   2   1.218 VB R  0.0388   98.81053   38.02311   5.7007
   3   2.461 BB    0.0495    7.59845    2.21849   0.4384
   4   4.078 MF    0.0801   68.48502   14.25222   3.9511 minor diastereomer
   5   4.258 FM    0.0843 1439.14685  284.65808  83.0291 major diastereomer   dr = 21:1
   6   4.879 BB    0.0725    5.83014    1.15332   0.3364
   7   5.164 BV    0.0847    9.87532    1.79466   0.5697

Totals :                  1733.30423  394.19115
```

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralpak OJ-3R, ∅ 4.6 mm i. d., methanol/water = 55:45, v = 1.0 mL/min, λ = 220 nm, t(major) = 17.59 min, t(minor) = 21.25 min.



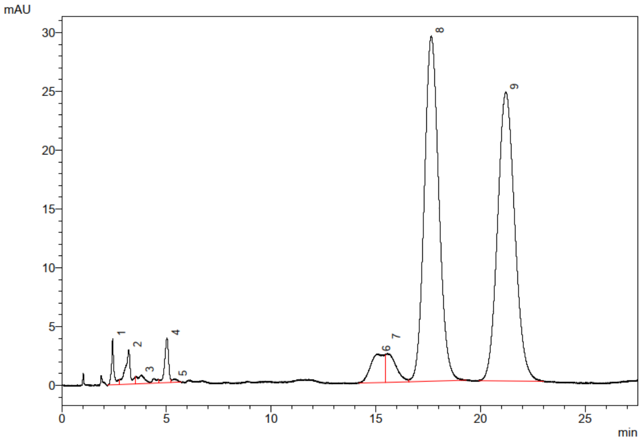
1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	2.24	0.13	
2	2.42	0.23	
3	2.82	0.21	
4	3.18	6.15	
5	5.02	4.85	
6	15.28	1.44	enantiomers of minor diastereomer
7	15.91	5.33	
8	17.59	74.70	1. enantiomer
9	21.25	6.96	2. enantiomer
Total		100.00	

ee = 83.0 %

Determination of the ee of **18**



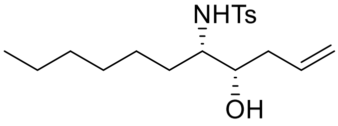
1 220nm,4nm

PDA Ch1 220nm

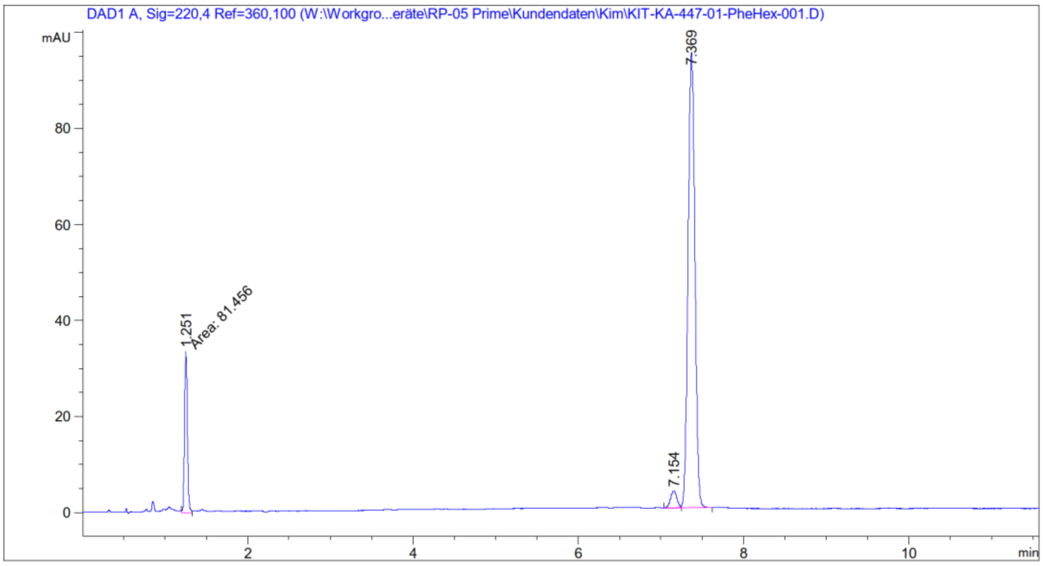
Peak #	Ret. Time	Area %	Name
1	2.43	0.95	
2	3.20	1.54	
3	3.79	0.78	
4	5.03	1.51	
5	5.37	0.16	
6	15.09	3.50	enantiomers of minor diastereomer
7	15.57	2.68	
8	17.65	44.64	1. enantiomer
9	21.21	44.24	2. enantiomer
Total		100.00	

Separation of the enantiomers of *rac*-**18**

***N*-((4*S*,5*S*)-4-Hydroxyundec-1-en-5-yl)-4-methylbenzenesulfonamide (20)**. Prepared according to the representative procedure **B**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 15:1 to 3:1) to give the title compound as a yellow oil (79 mg, 80%, >20:1 dr, 82% ee). $[\alpha]_D^{20}$ = −19.8 (*c* = 0.59, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.32 – 7.27 (m, 2H), 5.76 (dddd, *J* = 16.3, 10.3, 8.2, 6.0 Hz, 1H), 5.16 – 5.07 (m, 2H), 4.60 (d, *J* = 8.9 Hz, 1H), 3.62 (ddd, *J* = 8.7, 4.3, 2.7 Hz, 1H), 3.21 (dtd, *J* = 9.5, 6.9, 2.7 Hz, 1H), 2.42 (s, 3H), 2.29 – 2.10 (m, 2H), 1.50 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.36 – 1.23 (m, 1H), 1.23 – 1.12 (m, 2H), 1.11 – 1.01 (m, 6H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 138.6, 134.3, 129.7, 127.2, 119.0, 71.2, 57.5, 38.8, 32.8, 31.7, 29.1, 25.8, 22.6, 21.6, 14.2; IR (ATR): ṽ = 3493, 3275, 2953, 2926, 2857, 1641, 1598, 1495, 1428, 1323, 1289, 1215, 1155, 1093, 1065, 989, 959, 913, 814, 755, 707, 663; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{18}H_{29}NO_3S+Na]^+$ ($[M+Na]^+$) 362.1760, found 362.1762.



The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Phenyl Hexyl, ∅ 4.6 mm i. d., acetonitrile/water gradient 30% to 50% over 5 minutes, v = 1.0 mL/min, λ = 220 nm, t(major) = 7.37 min, 308 K.



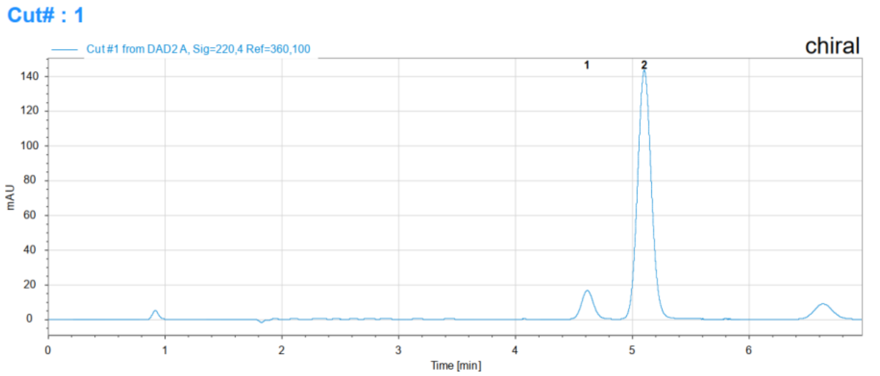
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   1.251 MM    0.0404   81.45597   33.63570  12.6625
   2   7.154 BV E  0.0687   18.43841    3.51350   2.8663 minor diastereomer
   3   7.369 VB R  0.0904  543.38928   94.77242  84.4712 major diastereomer

Totals :                   643.28366  131.92161
```

dr = 29.5:1

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralpak IC-3, ∅ 4.6 mm i. d., acetonitrile/water = 60:40, v = 1.0 mL/min, λ = 220 nm, t(minor) = 4.62 min, t(major) = 5.10 min.



Signal: DAD2 A, Sig=220,4 Ref=360,100

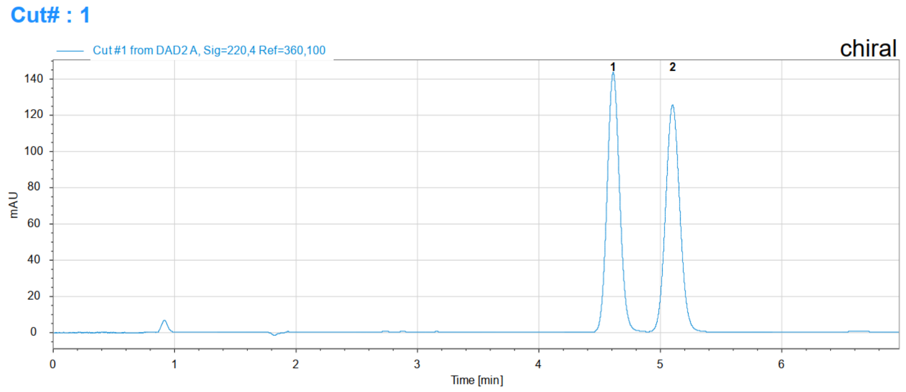
Compound	Cut	Ret.Time	Area	Width	Height	Symmetry		
1	1	4.617	118.484 **118.484**	0.109	16.682	0.910	1st enantiomer	ee = 81.6 %
2	1	5.104	1169.016 **1169.016**	0.128	143.320	0.916	2nd enantiomer	

Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	
1	7.01 - 7.05	4.617	118.484	9.203	1st enantiomer
2	7.01 - 7.05	5.104	1169.016	90.797	2nd enantiomer

Determination of the ee of **20**



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	4.614	1020.607 **1020.607**	0.111	143.437	0.904	1st enantiomer
2	1	5.103	1019.935 **1019.935**	0.126	125.554	0.926	2nd enantiomer

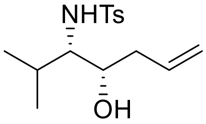
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	
1	7.01 - 7.05	4.614	1020.607	50.016	1st enantiomer
2	7.01 - 7.05	5.103	1019.935	49.984	2nd enantiomer

Separation of the enantiomers of *rac*-**20**

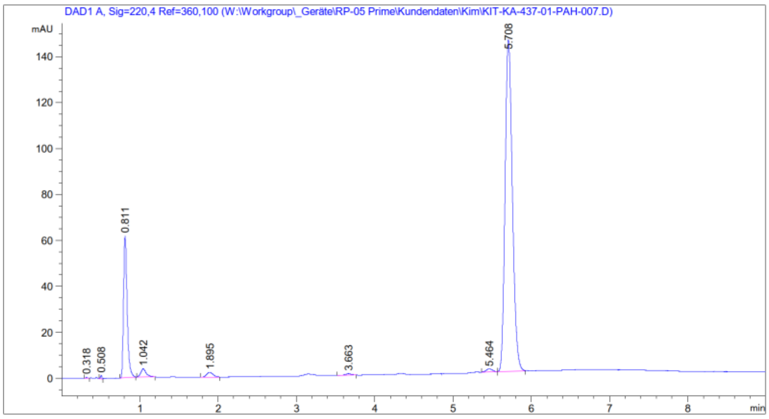
N-((3S,4S)-4-Hydroxy-2-methylhept-6-en-3-yl)-4-methylbenzenesulfonamide (21).



Prepared according to the representative procedure **B**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 10:1 to 2:1) to give the title compound as a white solid (70 mg, 81%, >20:1 dr, 86% ee). $[\alpha]_D^{20}$ = −21.9 (*c* = 0.48, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.31 – 7.27 (m, 2H), 5.73 (dddd, *J* = 17.1, 10.2, 8.2, 6.0 Hz, 1H), 5.12 (ddt, *J* = 10.2, 2.0, 1.0 Hz, 1H), 5.08 – 5.01 (m, 1H), 4.87 (d, *J* = 9.1 Hz, 1H), 3.73 (ddd, *J* = 8.7, 4.3, 2.4 Hz, 1H), 3.06 (ddd, *J* = 8.9, 6.1, 2.4 Hz, 1H), 2.42 (s, 3H), 2.14 (app. dddt, *J* = 14.1, 5.9, 4.6, 1.4 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.83 – 1.75 (m, 2H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.0, 134.2, 129.7, 127.1, 119.1, 69.5, 62.4, 40.0, 31.4, 21.7, 19.6, 19.0; IR (ATR): ṽ = 3531, 3498, 3316, 3219, 2969, 2901, 2874, 1598, 1497, 1437, 1326, 1317, 1230, 1157, 1145, 1094, 1048, 1003, 969, 868, 816, 685; HRMS (ESI⁺, *m*/*z*) calculated for $[C_{15}H_{23}NO_3S+Na]^+$ ($[M+Na]^+$) 320.1291, found 320.1290.

41 mg of product were recrystallized from methyl *tert*-butyl ether/*n*-hexane to give a sample with >99% ee (23 mg).

The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Eclipse PAH, ∅ 4.6 mm i. d., methanol/water gradient 40% to 60% over 5 min, v = 1.0 mL/min, λ = 220 nm, t(major) = 5.71 min, 308 K.

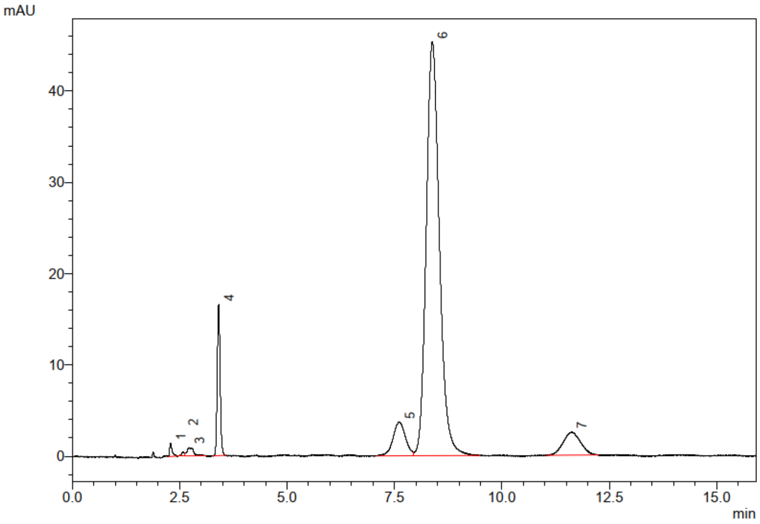


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   0.318 VV R  0.0154 6.49249e-1 5.48255e-1   0.0555
   2   0.508 BV    0.0185    1.78815    1.39206   0.1527
   3   0.811 BB    0.0483  198.46944   61.72309  16.9532
   4   1.042 BB    0.0559   16.99746    3.59871   1.4519
   5   1.895 VV R  0.0668   12.05885    2.12144   1.0301
   6   3.663 VV R  0.0725    4.10784 6.72282e-1   0.3509
   7   5.464 VV R  0.0681    7.38580    1.28177   0.6309 minor diastereomer   dr = 125:1
   8   5.708 VB    0.0980  929.23523  144.21286  79.3749 major diastereomer

Totals :                 1170.69201  215.55047
```

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralpak OJ-3R, ∅ 4.6 mm i. d., methanol/water = 65:35, v = 1.0 mL/min, λ = 220 nm, t(major) = 8.08 min, t(minor) = 11.21 min.



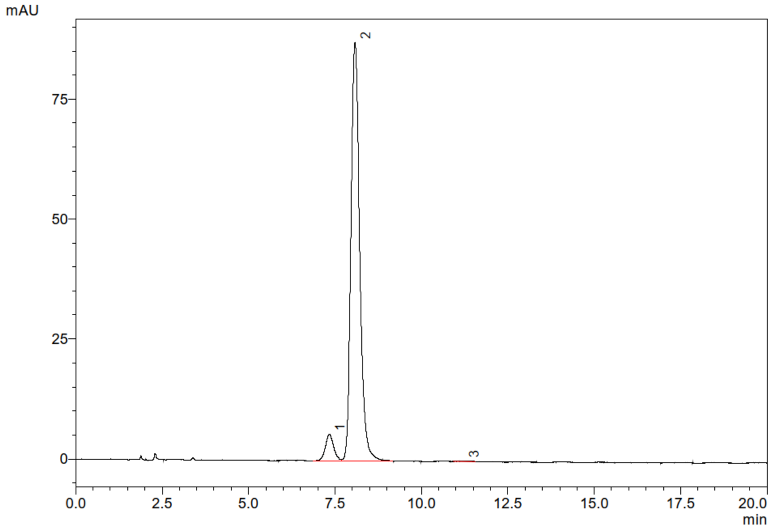
1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	2.29	0.48	
2	2.58	0.17	
3	2.72	0.81	
4	3.41	6.38	
5	7.62	6.17	one or both enantiomer(s) of minor diastereomer
6	8.38	80.10	1. enantiomer
7	11.62	5.89	2. enantiomer
Total		100.00	

ee = 86 %

Determination of the ee of **21** before recrystallization



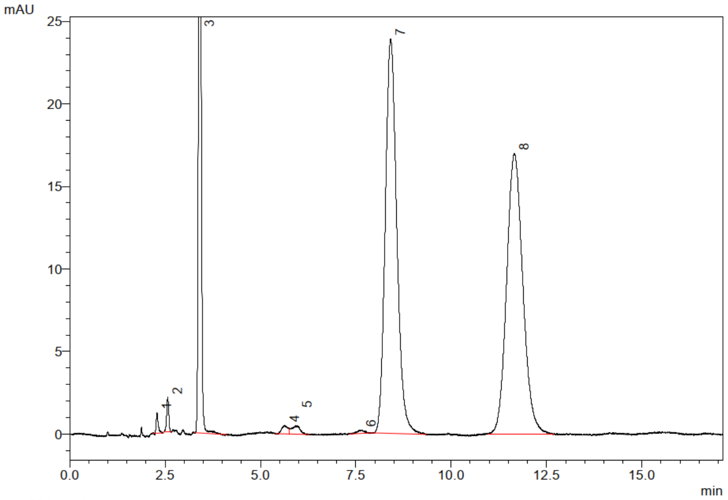
1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	7.33	5.76	minor diastereomer
2	8.08	94.06	1. enantiomer
3	11.21	0.17	2. enantiomer
Total		100.00	

= 99.6 % ee

Determination of the ee of **21** after recrystallization



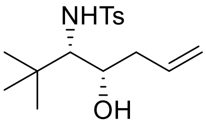
1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	2.29	0.37	
2	2.57	0.65	
3	3.41	17.47	
4	5.64	0.45	
5	5.97	0.62	
6	7.65	0.21	one or both enantiomer(s) of minor diastereomer
7	8.41	40.12	1. enantiomer
8	11.66	40.11	2. enantiomer
Total		100.00	

Separation of the enantiomers of *rac*-**21**

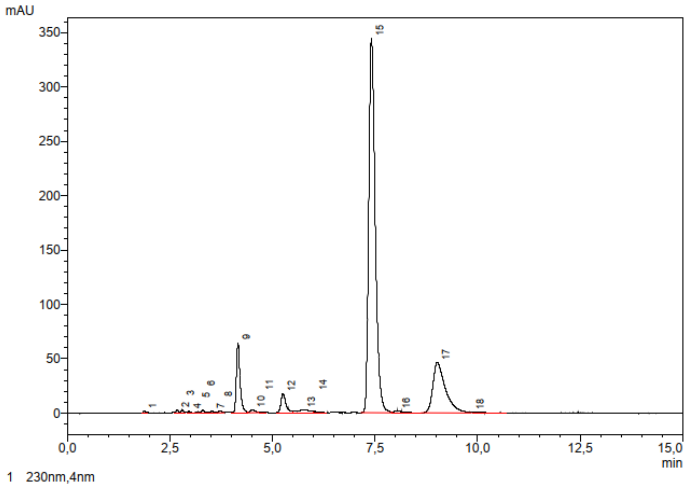
N-((3S,4S)-4-Hydroxy-2,2-dimethylhept-6-en-3-yl)-4-methylbenzenesulfonamide (22).



Prepared according to the representative procedure **B**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 10:1 to 2:1) to give the title compound as a pale yellow solid (46 mg, 51%, >20:1 dr, 81% ee). $[\alpha]_D^{20}$ = −32.3 (*c* = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.30 – 7.27 (m, 2H), 5.69 (dddd, *J* = 17.1, 10.2, 8.5, 5.8 Hz, 1H), 5.16 – 5.09 (m, 2H), 5.06 – 4.96 (m, 1H), 3.85 (ddd, *J* = 9.4, 4.6, 0.9 Hz, 1H), 3.05 (dd, *J* = 9.1, 0.9 Hz, 1H), 2.42 (s, 3H), 2.09 (app. dddt, *J* = 13.3, 5.9, 4.6, 1.5 Hz, 1H), 1.92 (app. dddt, *J* = 13.9, 9.4, 8.4, 1.0 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.5, 134.2, 129.6, 127.1, 119.6, 67.7, 64.7, 41.3, 35.5, 27.3, 21.6; IR (ATR): ṽ = 3510, 3329, 2962, 2926, 2870, 1598, 1418, 1369, 1330, 1289, 1236, 1204, 1148, 1090, 1072, 1031, 1019, 1008, 962, 915, 816, 707, 680, 653; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{16}H_{25}NO_3S+Na]^+$ ($[M+Na]^+$) 334.1447, found 334.1449.

35 mg of product were recrystallized from methyl *tert*-butyl ether/*n*-hexane to give a sample of 93% ee (25 mg).

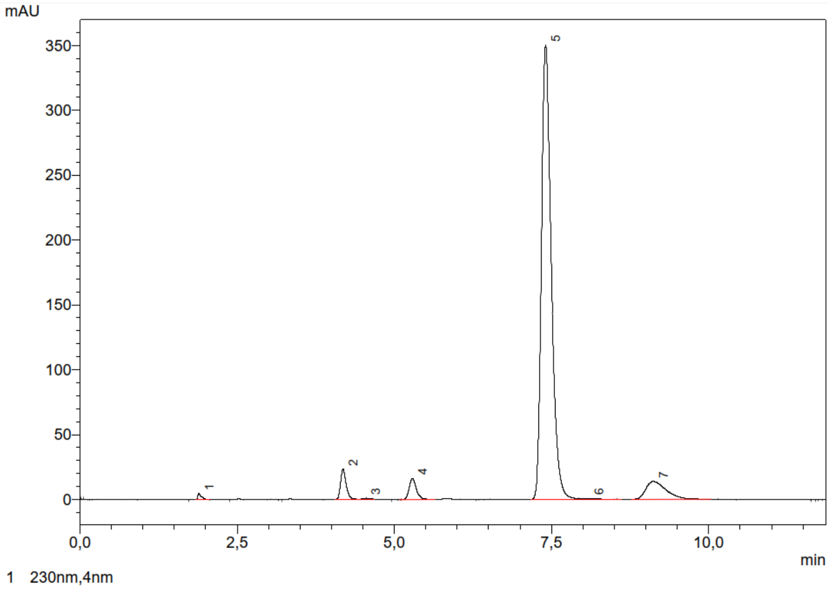
The ee was determined by HPLC analysis: Chiralpak 150 mm IB-N-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 90:10, v = 1.0 mL/min, λ = 230 nm, t(minor) = 4.18 min, t(major) = 7.41 min.



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	1,87	0,17	
2	2,67	0,25	
3	2,80	0,23	
4	2,96	0,14	
5	3,18	0,13	
6	3,30	0,28	
7	3,53	0,18	
8	3,72	0,20	
9	4,16	7,26	1. Enantiomer
10	4,52	0,45	
11	4,72	0,10	
12	5,26	2,65	
13	5,74	0,99	
14	6,03	0,21	
15	7,41	68,18	2. Enantiomer 80:7 % ee
16	8,06	0,51	
17	9,02	17,79	
18	9,86	0,28	
Total		100,00	

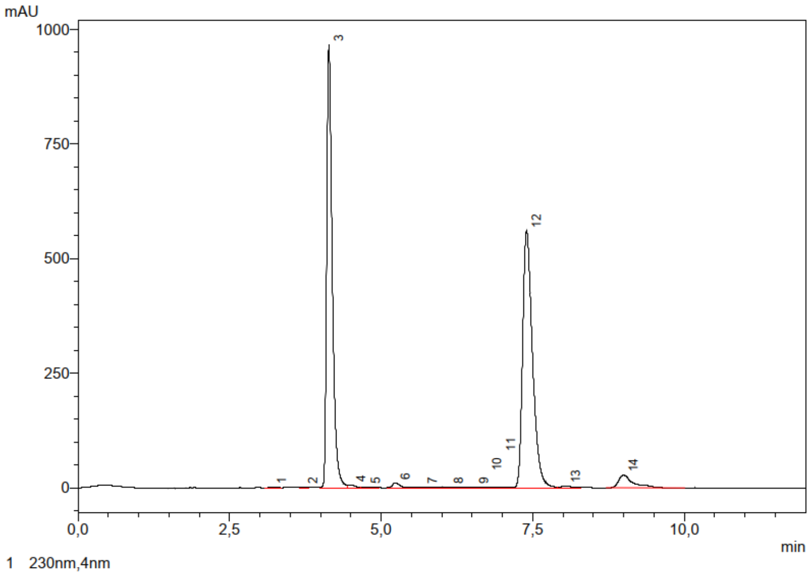
Determination of the ee of **22** before recrystallization



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	1,89	0,45	
2	4,18	3,29	1. Enantiomer
3	4,54	0,18	
4	5,29	2,90	
5	7,41	85,75	2. Enantiomer 92.6 % ee
6	8,09	0,25	
7	9,12	7,18	
Total		100,00	

Determination of the ee of **22** after recrystallization

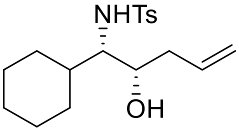


PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	3,20	0,13	
2	3,71	0,10	
3	4,14	46,17	1. Enantiomer
4	4,51	0,46	
5	4,75	0,21	
6	5,24	0,84	
7	5,69	0,11	
8	6,12	0,35	
9	6,53	0,20	
10	6,75	0,11	
11	6,98	0,15	
12	7,40	47,09	2. Enantiomer
13	8,05	0,41	
14	9,00	3,66	
Total		100,00	

Separation of the enantiomers of *rac*-**22**

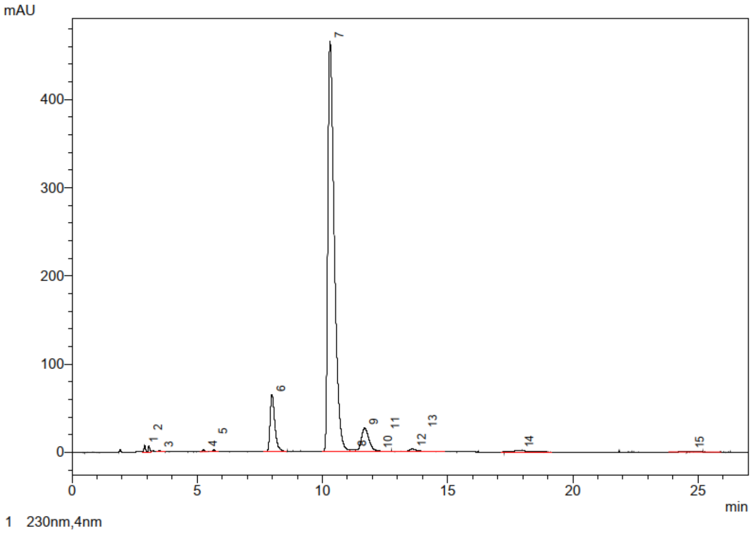
***N*-((1*S*,2*S*)-1-Cyclohexyl-2-hydroxypent-4-en-1-yl)-4-methylbenzenesulfonamide (23)**.



Prepared according to the representative procedure **B**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 10:1 to 2:1) to give the title compound as a pale yellow solid (66 mg, 67%, >20:1 dr, 82% ee). $[\alpha]_D^{20}$ = −1.0 (*c* = 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.30 – 7.27 (m, 2H), 5.70 (dddd, *J* = 17.1, 10.2, 8.1, 6.0 Hz, 1H), 5.11 (ddt, *J* = 10.2, 2.0, 1.0 Hz, 1H), 5.05 – 4.98 (m, 1H), 4.86 (d, *J* = 9.1 Hz, 1H), 3.75 (ddd, *J* = 8.7, 4.5, 2.2 Hz, 1H), 3.07 (ddd, *J* = 8.9, 6.4, 2.2 Hz, 1H), 2.42 (s, 3H), 2.09 (app. dddt, *J* = 14.1, 6.0, 4.5, 1.4 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.72 – 1.55 (m, 6H), 1.43 (tdt, *J* = 11.9, 6.2, 3.2 Hz, 1H), 1.16 – 1.00 (m, 3H), 1.02 – 0.76 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.1, 134.2, 129.6, 127.1, 119.0, 69.2, 61.9, 41.2, 39.9, 30.0, 29.5, 26.4 (2C), 26.3, 21.6; IR (ATR): ṽ = 3531, 3293, 2918, 2850, 1433, 1324, 1283, 1157, 1094, 1071, 1052, 1039, 996, 969, 908, 864, 813, 712; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{18}H_{27}NO_3S+Na]^+$ ($[M+Na]^+$) 360.1604, found 360.1604.

32 mg of product were recrystallized from methyl *tert*-butyl ether/*n*-hexane to give a sample of 88% ee (21 mg, 66% yield).

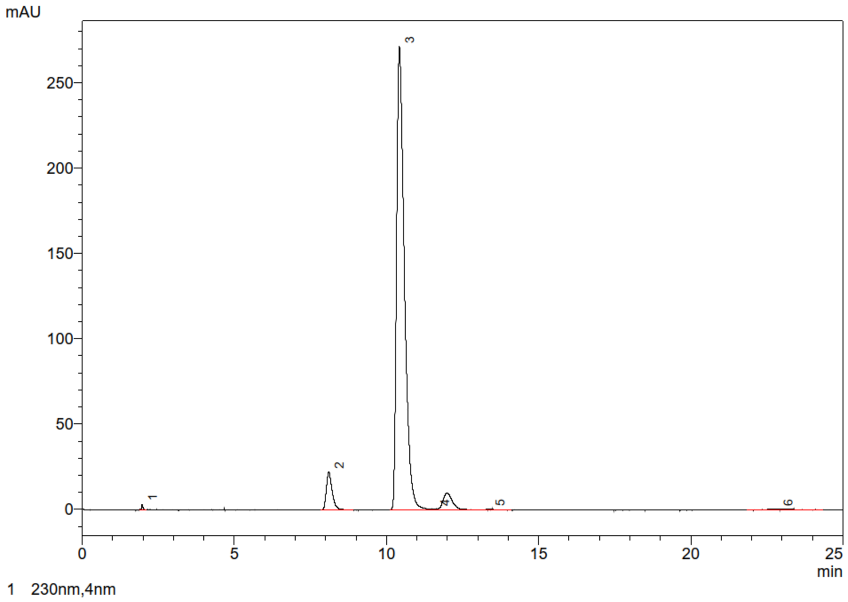
The ee was determined by HPLC analysis: Chiralpak 150 mm IB-N-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 95:5, v = 1.0 mL/min, λ = 230 nm, t(minor) = 8.11 min, t(major) = 10.43 min.



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	2,90	0,33	
2	3,07	0,30	
3	3,51	0,13	
4	5,26	0,14	
5	5,67	0,14	
6	7,99	8,40	1. Ennatiomer
7	10,31	82,31	2. Enantiomer 81.5 % ee
8	11,22	0,33	
9	11,69	5,77	
10	12,26	0,15	
11	12,54	0,13	
12	13,60	0,80	
13	14,04	0,17	
14	17,90	0,68	
15	24,70	0,24	
Total		100,00	

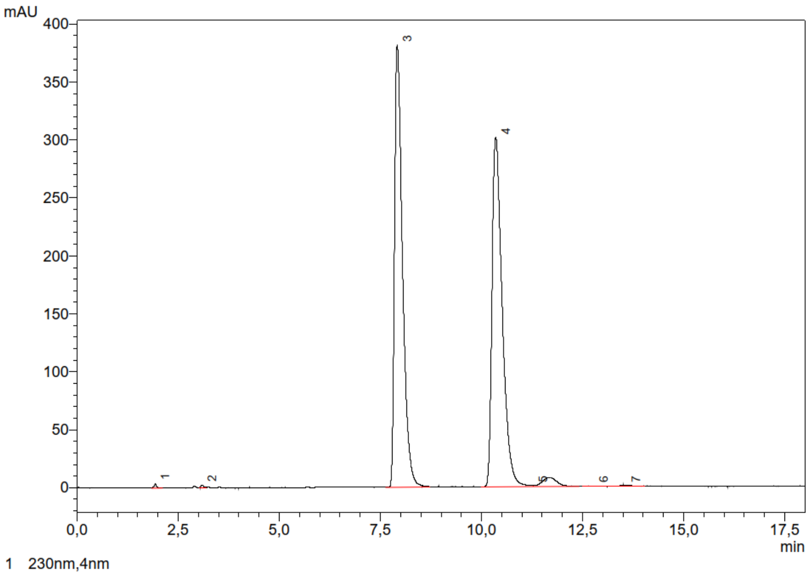
Determination of the ee of **23** before recrystallization



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	1,97	0,20	
2	8,11	5,51	1. Enantiomer
3	10,43	89,37	2. Enantiomer 88.4 % ee
4	11,58	4,17	
5	13,40	0,18	
6	22,86	0,57	
Total		100,00	

Determination of the ee of **23** after recrystallization

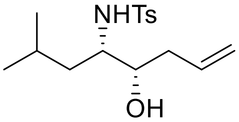


PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	1,93	0,14	
2	3,09	0,13	
3	7,92	48,55	1. Enantiomer
4	10,35	48,96	2. Enantiomer
5	11,28	1,87	
6	12,77	0,10	
7	13,57	0,25	
Total		100,00	

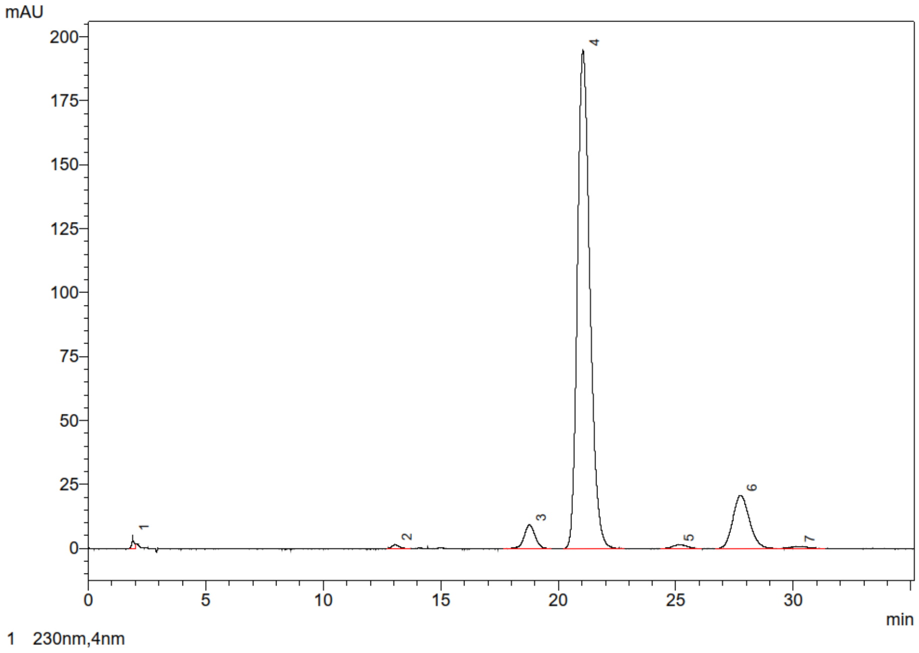
Separation of the enantiomers of *rac*-**23**

Larger Scale Reaction. ***N*-((4*S*,5*S*)-5-Hydroxy-2-methyloct-7-en-4-yl)-4-methylbenzenesulfonamide (28).** Bis(cyclooctadiene)nickel(0) (28 mg, 0.10 mmol, 10 mol%), phosphoramidite **L1** (64 mg, 0.10 mmol, 10 mol%) and THF (3.0 mL) were added to a flame-dried Schlenk flask under argon. Dienol ether **1** (R = TIPS) (0.80 mL, 3.0 mmol) and triethylborane (1.0 M in THF, 1.5 mL, 1.5 mmol) were added before the N-tosyl imine **27** (240 mg, 1.0 mmol) and distilled and degassed water (18 µL, 1.0 mmol) were introduced. The flask was sealed under argon and the mixture was stirred at room temperature overnight. The reaction was quenched by sat. $NaHCO_3$ solution (5 mL) and stirring was continued for 1 h. The mixture was diluted with methyl *tert*-butyl ether (10 mL) and the aqueous phase was extracted with methyl *tert*-butyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a pale yellow oil.



The residue was dissoved in THF (3 mL) and tetrabutylammonium fluoride (1 M in THF, 3.0 mL, 3.0 mmol) was added. After stirring for 1 h at room temperature, distilled water (5 mL) was added and the aqueous phase was extracted by methyl *tert*-butyl ether (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a yellow oil. Purification of the residue by flash chromatography (SiO_2; toluene/methyl *tert*-butyl ether, 25:1 to 5:1) afforded the title compound as a yellow oil (278 mg, 89%, >20:1 dr, 75% ee). $[\alpha]_D^{20}$ = −14.2 (*c* = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.35 – 7.30 (m, 2H), 5.77 (dddd, *J* = 17.1, 10.3, 8.2, 6.1 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.57 (d, *J* = 9.0 Hz, 1H), 3.62 (ddd, *J* = 8.4, 6.7, 4.1 Hz, 1H), 3.33 (dtd, *J* = 9.4, 7.1, 2.4 Hz, 1H), 2.45 (s, 3H), 2.27 (app. dddt, *J* = 13.4, 6.0, 4.7, 1.4 Hz, 1H), 2.23 – 2.14 (m, 1H), 1.77 (d, *J* = 3.7 Hz, 1H), 1.51 – 1.39 (m, 2H), 1.18 – 1.11 (m, 1H), 0.78 (d, *J* = 6.5 Hz, 3H), 0.74 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 138.6, 134.3, 129.7, 127.2, 119.0, 71.2, 55.4, 42.0, 38.9, 24.5, 22.6, 21.7; IR (ATR): ṽ = 3525, 3279, 2957, 2926, 2870, 1429, 1326, 1305, 1289, 1158, 1094, 1057, 967, 913, 815, 669; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{16}H_{25}NO_3S+Na]^+$ ($[M+Na]^+$) 334.1447, found 334.1449.

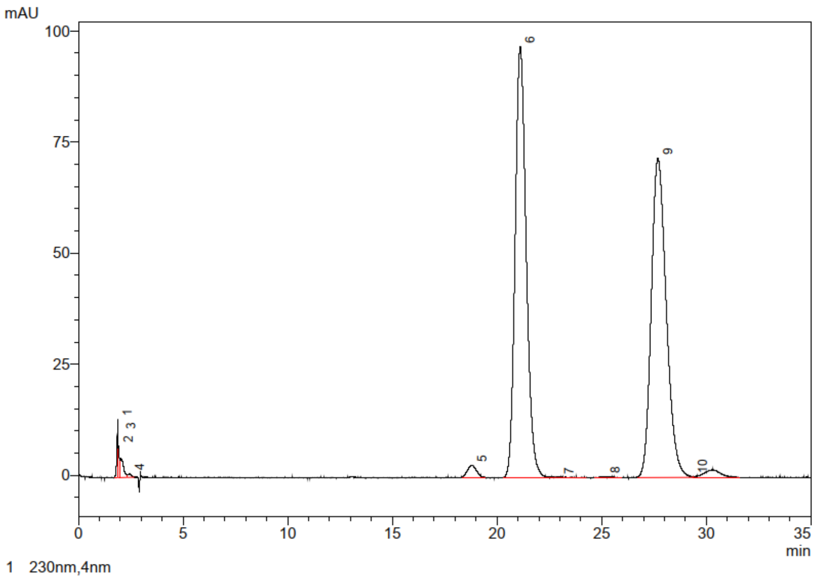
The ee was determined by HPLC analysis: Chiralpak 150 mm IG-3, ∅ 4.6 mm i. d., *n*-heptane/ethanol = 90:10, v = 1.0 mL/min, λ = 230 nm, t(major) = 21.05 min, t(minor) = 27.76 min.



PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	1,89	0,38	
2	13,07	0,48	
3	18,79	3,55	
4	21,05	82,49	1. Enantiomer 74.9 % ee
5	25,08	0,75	
6	27,76	11,83	2. Enantiomer
7	30,21	0,51	
Total		100,00	

Determination of the ee of **28**



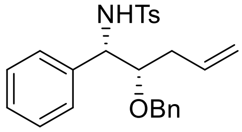
PDA Ch1 230nm

Peak #	Ret. Time	Area %	Name
1	1,87	0,51	
2	1,92	0,47	
3	2,04	0,59	
4	2,45	0,13	
5	18,81	1,15	
6	21,12	47,76	1. Enantiomer
7	22,98	0,12	
8	25,18	0,11	
9	27,70	47,87	2. Enantiomer
10	29,36	1,29	
Total		100,00	

Separation of enantiomers of **28**

Representative Procedure C

N-((1S,2S)-2-(Benzyloxy)-1-phenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (9e).

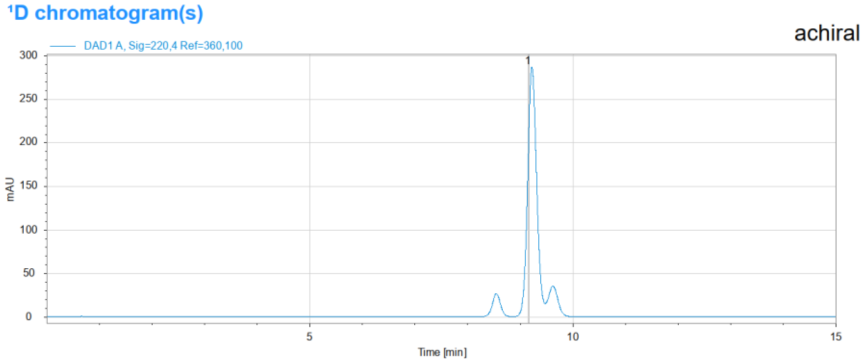


Bis(cyclooctadiene)nickel(0) (8.0 mg, 0.029 mmol, 10 mol%), phosphoramidite **L1** (19 mg, 0.029 mmol, 10 mol%) and THF (0.60 mL) were added to a flame-dried Schlenk flask under argon. (*E*)-((Buta-1,3-dien-1-yloxy)methyl)benzene (**1**, R = Bn) (0.15 mL, 0.87 mmol) and triethylborane (1.0 M in THF, 0.44 mL, 0.44 mmol) were added before 4-methyl-*N*-(phenyl(phenylsulfonyl)methyl)benzenesulfonamide (**7**, Ar = *p*-tolyl) (120 mg, 0.29 mmol),[3] distilled and degassed water (16 µL, 0.87 mmol), and *N*,*N*-diisopropylethylamine (61 µL, 0.35 mmol) were introduced. The flask was sealed under argon and the mixture was stirred at room temperature overnight. The reaction was quenched with sat. $NaHCO_3$ solution (3 mL) and stirring was continued for 10 min. The mixture was diluted with ethyl acetate (3 mL) and the aqueous phase was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a pale yellow oil. Purification of the residue by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 30:1 to 6:1) afforded the title compound as a white solid (103 mg, 84%, >20:1 dr, 89% ee). $[\alpha]_D^{20}$ = +60.4 (*c* = 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.30 – 7.27 (m, 2H), 7.17 – 7.10 (m, 6H), 7.10 – 7.03 (m, 4H), 5.75 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.43 (d, *J* = 7.3 Hz, 1H), 5.13 – 5.03 (m, 2H), 4.47 – 4.44 (m, 1H), 4.43 (d, *J* = 11.1 Hz, 1H), 4.14 (d, *J* = 11.1 Hz, 1H), 3.54 (ddd, *J* = 6.8, 5.7, 3.7 Hz, 1H), 2.37 – 2.31 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.3, 137.9, 137.6, 133.6, 129.3, 128.5, 128.3, 128.1, 128.0, 127.4, 127.3, 127.2, 118.8, 82.4, 72.5, 59.3, 35.5, 21.5; IR (ATR): ṽ = 3292, 3064, 3029, 2939, 1641, 1600, 1497, 1455, 1431, 1320, 1290, 1161, 1086, 1059, 1025, 967, 923, 902, 832, 811, 776, 734, 694, 669; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{25}H_{27}NO_3S+Na]^+$ ($[M+Na]^+$) 444.1604, found 444.1603.

Note: Internal alkene isomer **11e** (rr = 7.5:1, NMR) was not separable by flash chromatography.

The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Zorbax Eclipse Plus C18, ∅ 4.6 mm i. d., acetonitrile/water gradient 50% to 60% over 5 minutes, v = 1.0 mL/min, λ = 220 nm, t(major) = 9.14 min, 308 K.

^{1}D chromatogram(s)



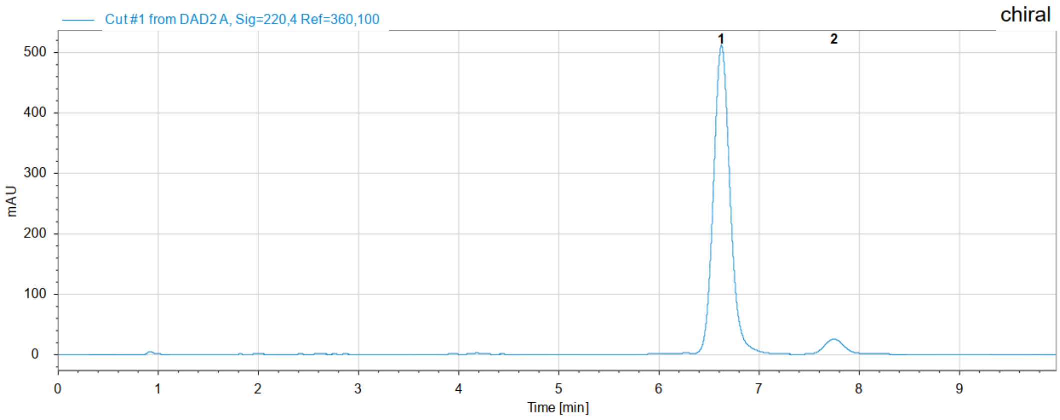
Sampling table (^{1}D)

Cut group	Cut #	^{1}D Cut start [min]	^{1}D Ret. time [min]	^{1}D Duration [min]	Trigger	^{2}D Run start [min]
	1	9.14	***	0.04	Peak	9.19

Separation of impurities on an achiral column

Step 2: Chiral resolution of major diastereomer: Daicel 150 mm Chiralcel OZ-3R, ∅ 4.6 mm i. d., acetonitrile/water = 65:35, v = 1.0 mL/min, λ = 220 nm, t(major) = 6.63 min, t(minor) = 7.75 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	6.628	5896.156 **5896.156**	0.178	510.956	0.868
2	1	7.751	352.259 **352.259**	0.203	25.211	0.849

Component table

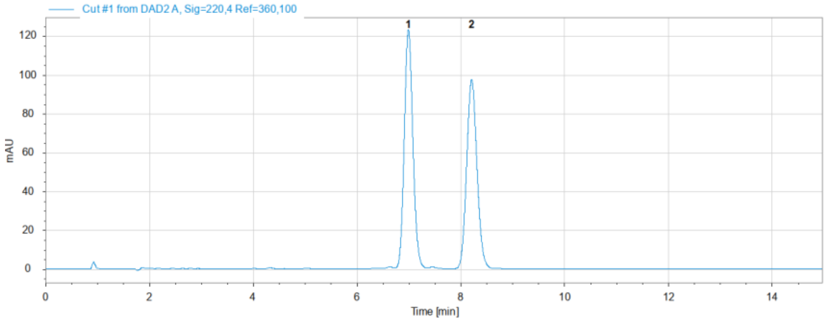
Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%
1	8.97 - 9.01	6.628	5896.156	94.362
2	8.97 - 9.01	7.751	352.259	5.638

ee = 88.7%

Determination of the ee of **9e**

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	6.996	1425.809 **1425.809**	0.176	123.430	0.883
2	1	8.213	1346.945 **1346.945**	0.208	97.494	0.896

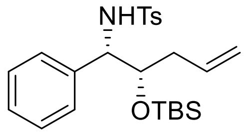
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

chiral

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%
1	9.19 - 9.23	6.996	1425.809	51.422
2	9.19 - 9.23	8.213	1346.945	48.578

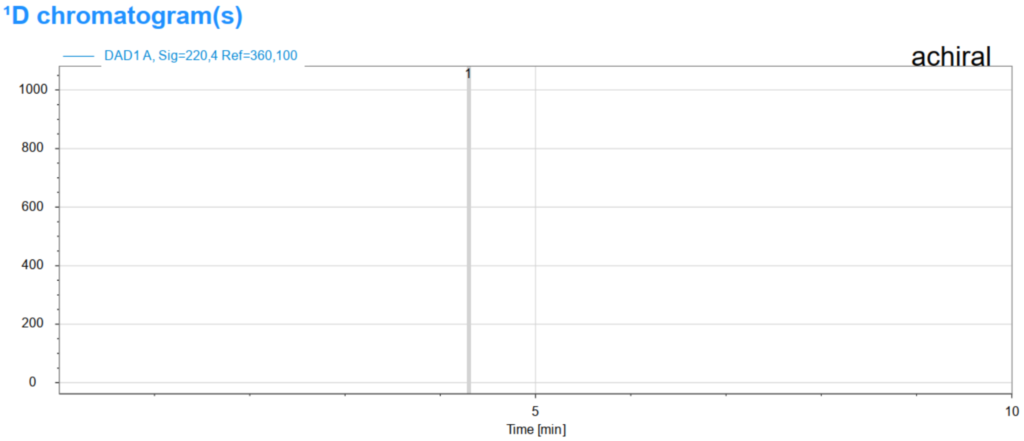
Separation of the enantiomers of *rac*-**9e**



***N*-((1*S*,2*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (9a)**. Prepared according to the representative procedure **C**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a white solid (97 mg, 75%, >20:1 dr, 94% ee). $[\alpha]_D^{20}$ = +29.8 (*c* = 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.15 – 7.04 (m, 5H), 7.02 – 6.98 (m, 2H), 5.72 (ddt, *J* = 17.3, 10.3, 7.2 Hz, 1H), 5.35 (d, *J* = 8.0 Hz, 1H), 5.11 (ddt, *J* = 10.2, 1.9, 1.0 Hz, 1H), 5.02 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.48 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.71 (ddd, *J* = 9.0, 4.0, 2.5 Hz, 1H), 2.41 (app. dddt, *J* = 14.0, 8.8, 7.7, 1.1 Hz, 1H), 2.33 (s, 3H), 2.16 (dddd, *J* = 13.8, 6.8, 4.0, 1.4 Hz, 1H), 0.80 (s, 9H), -0.17 (s, 3H), -0.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.6, 138.1, 133.4, 129.3, 128.1, 127.1(8), 127.1(5), 127.0(9), 119.0, 77.1, 59.0, 49.6, 39.1, 27.1, 25.9, -4.7, -5.4; IR (ATR): ṽ = 3285, 2951, 2926, 2884, 2854, 1597, 1495, 1453, 1404, 1361, 1326, 1251, 1159, 1084, 1067, 1004, 954, 907, 882, 834, 809, 777, 748, 600. 671; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{24}H_{35}NO_3SSi+Na]^+$ ($[M+Na]^+$) 468.1999, found 468.1997.

Note: Internal alkene isomer **11a** (rr = 7.6:1, NMR) was not separable by flash chromatography.

The ee was determined by 2D HPLC analysis. Step 1: Purification: 100 mm Zorbax RX-SiL, ∅ 4.6 mm i. d., *n*-heptane/methyl *tert*-butyl ether = 95:5, v = 1.0 mL/min, λ = 220 nm, t(major) = 4.31 min, 308 K.



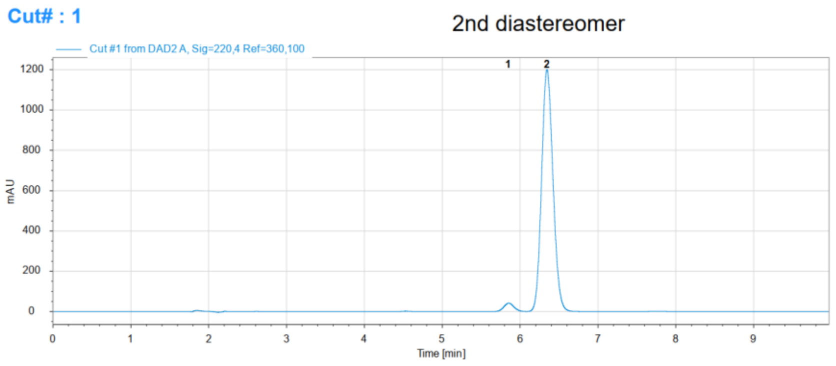

Sampling table (¹D)

achiral

Cut group	Cut #	¹D Cut start [min]	¹D Ret. time [min]	¹D Duration [min]	Trigger	²D Run start [min]	
	1	4.28	4.311	0.04	Peak	4.33	2nd diastereomer

Separation of impurities on an achiral column

Step 2: Chiral resolution of the major diastereomer: Daicel 150 mm Chiralpak IG-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 95:5, v = 1.0 mL/min, λ = 220 nm, t(minor) = 5.85 min, t(major) = 6.34 min.



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	5.854	381.070 **381.070**	0.153	41.521	0.934	1st enantiomer
2	1	6.345	12200.356 **12200.356**	0.169	1203.131	0.816	2nd enantiomer

Component table

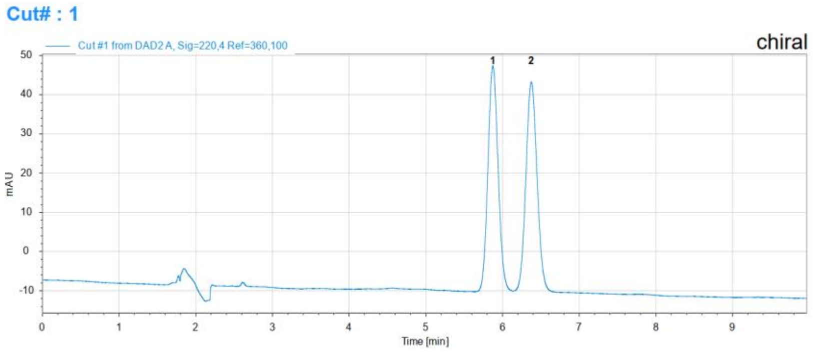
Signal: DAD2 A, Sig=220,4 Ref=360,100

chiral

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%	
1	4.28 - 4.32	5.854	381.070	3.029	1st enantiomer
2	4.28 - 4.32	6.345	12200.356	96.971	2nd enantiomer

= 93.9 % ee

Determination of the ee of **9a**



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry	
1	1	5.874	532.045 **532.045**	0.154	57.727	0.897	1st enantiomer
2	1	6.376	543.938 **543.938**	0.169	53.661	1.016	2nd enantiomer

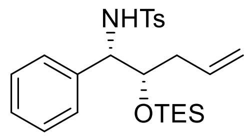
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	^{1}D Sampling range [min]	Ret.Time ^{2}D [min]	Area	Area%
1	5.14 - 5.18	5.874	532.045	49.447
2	5.14 - 5.18	6.376	543.938	50.553

Separation of the enantiomers of *rac*-**9a**

4-Methyl-*N*-((1*S*,2*S*)-1-phenyl-2-((triethylsilyl)oxy)pent-4-en-1-yl)benzenesulfonamide

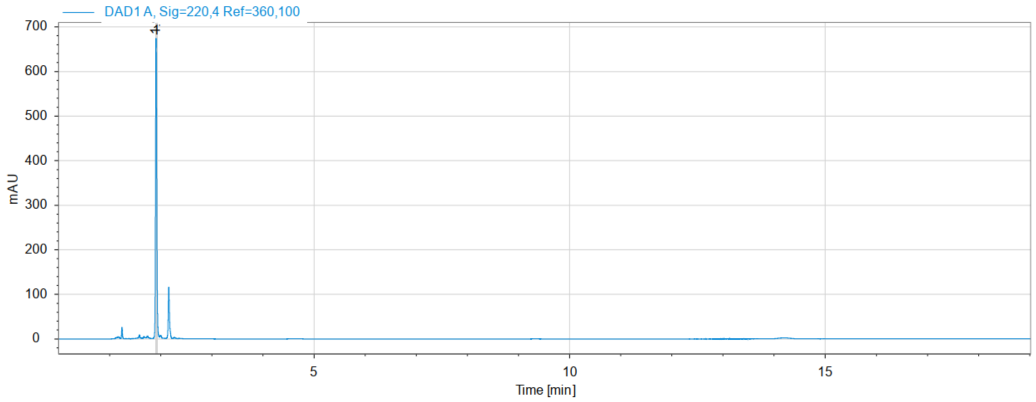


(9b). Prepared analogously according to the representative procedure **C**. Purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a colorless oil (117 mg, 91%, >20:1 dr, 93% ee). $[\alpha]_D^{20}$ = +27.9 (*c* = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.14 – 7.10 (m, 3H), 7.09 – 7.05 (m, 2H), 7.02 – 6.98 (m, 2H), 5.72 (ddt, *J* = 17.3, 10.3, 7.3 Hz, 1H), 5.43 (d, *J* = 8.1 Hz, 1H), 5.11 (ddt, *J* = 10.3, 2.0, 1.0 Hz, 1H), 5.03 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 4.44 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.73 (ddd, *J* = 8.8, 4.3, 2.5 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.32 (s, 3H), 2.16 (app. dddt, *J* = 13.9, 7.0, 4.3, 1.4 Hz, 1H), 0.77 (t, *J* = 7.9 Hz, 9H), 0.42 – 0.25 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.7, 138.2, 133.5, 129.3, 128.1, 127.2, 127.1, 127.0, 118.9, 77.0, 59.1, 39.3, 21.5, 6.8, 4.8; IR (ATR): ṽ = 3308, 2956, 2913, 2877, 1600, 1495, 1455, 1408, 1328, 1215, 1159, 1086, 1066, 1005, 951, 929, 813, 700, 667; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{24}H_{35}NO_3SSi+Na]^+$ ($[M+Na]^+$) 468.1999, found 468.2000.

Note: The corresponding internal alkene isomer **11b** (rr = 8.8:1, NMR) was not separable by flash chromatography.

The ee was determined by 2D HPLC analysis. Step 1: Purification: 50 mm Zorbax RX-SiL, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 99.5:0.5, v = 1.0 mL/min, λ = 220 nm, t(major) = 1.91 min, 308 K.

¹D chromatogram(s)



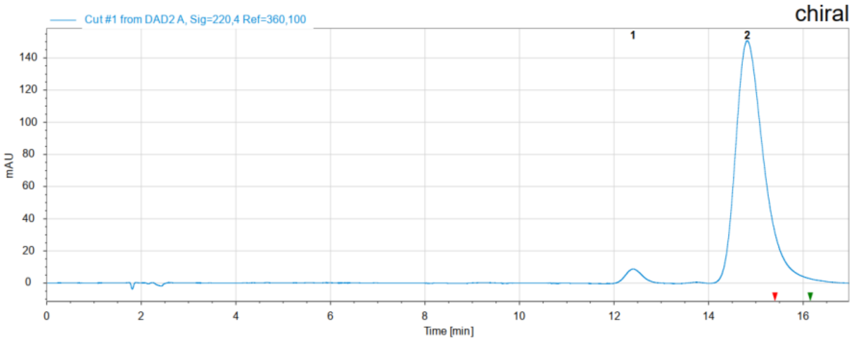
Sampling table (¹D)

Cut group	Cut #	¹D Cut start [min]	¹D Ret. time [min]	¹D Duration [min]	Trigger	²D Run start [min]	
	1	1.90	1.906	0.04	Peak	1.95	product

Separation of impurities on an achiral column

Step 2: Chiral resolution of major diastereomer: Daicel 150 mm Chiralpak IG-3, ∅ 4.6 mm i. d., *n*-heptane/*i*-propanol = 98:2, v = 1.0 mL/min, λ = 220 nm, t(minor) = 12.41 min, t(major) = 14.82 min.

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry		
1	1	12.410	210.220 **210.220**	0.401	8.728	0.835	1st enantiomer	ee = 93.4 %
2	1	14.820	6207.033 **6207.033**	0.685	150.994	0.702	2nd enantiomer	

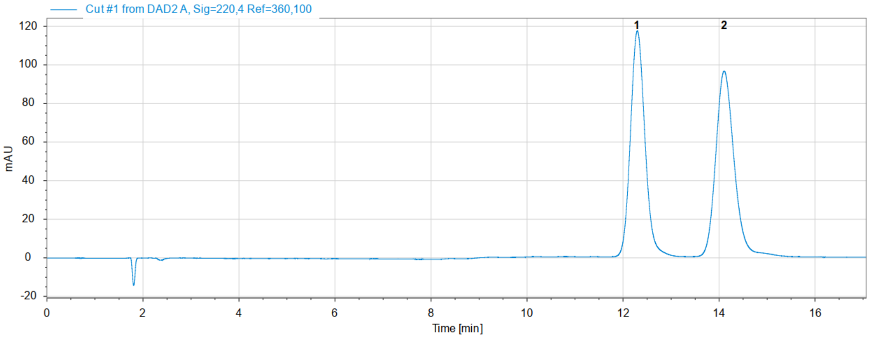
Component table

Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%
1	1.89 - 1.93	12.410	210.220	3.276
2	1.89 - 1.93	14.820	6207.033	96.724

Determination of the ee of **9b**

Cut# : 1



Signal: DAD2 A, Sig=220,4 Ref=360,100

Compound	Cut	Ret.Time	Area	Width	Height	Symmetry
1	1	12.297	2454.624 **2454.624**	0.246	117.089	0.873
2	1	14.106	2542.107 **2542.107**	0.313	96.084	0.806

Component table

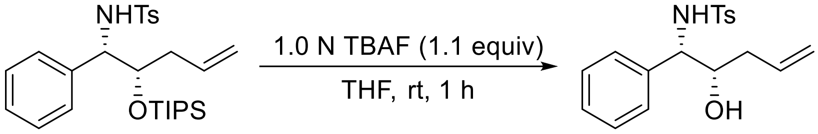
Signal: DAD2 A, Sig=220,4 Ref=360,100

Component	¹D Sampling range [min]	Ret.Time ²D [min]	Area	Area%	
1	1.90 - 1.94	12.297	2454.624	49.125	1. enantiomer
2	1.90 - 1.94	14.106	2542.107	50.875	2. enantiomer

Separation of the enantiomers of *rac*-**9b**

Assignment of the Absolute and Relative Configuration

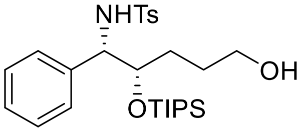
The absolute and relative configuration of product **9c** was determined by X-ray crystallography after deprotection of TIPS group to give the corresponding aminoalcohol **12**.



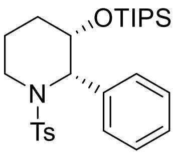
A solution of tetrabutylammonium fluoride (0.1 M in THF, 0.27 mL, 0.27 mmol) was added to a stirred solution of compound **9c** (122 mg, 0.25 mmol) in tetrahydrofuran (1.0 mL) and stirring was continued for 1 h at room temperature. Distilled water (2.0 mL) was added and the aqueous phase was extracted with methyl *tert*-butyl ether (3 x 2 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a white solid. The residue was purified by flash chromatography (SiO_2; ethyl acetate/hexane, 1:10 to 1:3) to give the title compound as a white solid (80 mg, 97% yield). Single crystals suitable for X-ray diffraction analysis were obtained by diffusing *n*-hexane into a saturated solution of the compound in methyl *tert*-butyl ether at room temperature.

$[\alpha]_D^{20}$ = +35.1 (*c* = 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.20 – 7.12 (m, 3H), 7.10 – 7.06 (m, 2H), 7.05 – 7.01 (m, 2H), 5.74 (dddd, *J* = 16.9, 10.3, 7.7, 6.5 Hz, 1H), 5.44 (br s, 1H), 5.13 (ddt, *J* = 10.2, 2.0, 1.1 Hz, 1H), 5.08 (app. dq, *J* = 17.0, 1.5 Hz, 1H), 4.26 (dd, *J* = 6.9, 5.1 Hz, 1H), 3.75 (dt, *J* = 7.9, 4.9 Hz, 1H), 2.33 (s, 3H), 2.27 – 2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.5, 137.6, 133.6, 129.4, 128.6, 127.8, 127.3, 127.2, 119.3, 74.0, 61.8, 38.2, 21.6; IR (ATR): ṽ = 3475, 3289, 3199, 2920, 1597, 1494, 1455, 1430, 1317, 1288, 1231, 1205, 1186, 1156, 1089, 1052, 1002, 958, 925, 828, 810, 752, 700, 685, 660; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{18}H_{20}NO_3S]^-$ ($[M–H]^-$) 330.1169, found 330.1173.

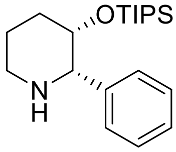
Synthetic Applications



***N*-((1*S*,2*S*)-5-Hydroxy-1-phenyl-2-((triisopropylsilyl)oxy)pentyl)-4-methylbenzene-sulfonamide (24).** Borane dimethylsulfide complex (55 *µ*L, 0.62 mmol) was added to a solution of compound **9c** (100 mg, 0.21 mmol) in tetrahydrofuran (8 mL) at 0 °C. After stirring for 1.5 h at room temperature, the reaction was carefully quenched with distilled water (0.20 mL). Aqueous NaOH solution (3 M, 2 mL) and aqueous H_2O_2 (35% *w/w*, 1.0 mL) were added to the mixture and stirring continued for 3 h at room temperature. The aqueous phase was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a white solid. The residue was purified by flash chromatography (SiO_2; hexane/ethyl acetate, 15:1 to 3:1) to give the title compound as a colorless oil (90 mg, 87% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.18 – 7.00 (m, 7H), 5.42 (d, *J* = 7.8 Hz, 1H), 4.47 (dd, *J* = 7.7, 2.5 Hz, 1H), 3.95 (dt, *J* = 9.3, 2.7 Hz, 1H), 3.64 – 3.52 (m, 2H), 2.33 (s, 3H), 1.62 – 1.47 (m, 4H), 0.92 – 0.86 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.6, 138.1, 129.4, 128.1, 127.2, 127.1, 127.0, 77.5, 62.8, 59.1, 31.1, 28.5, 21.5, 18.2, 18.0, 12.9; IR (ATR): ṽ = 3023, 2944, 2867, 1600, 1495, 1454, 1402, 1326, 1215, 1157, 1088, 1063, 943, 883, 813, 770; HRMS (ESI$^+$, *m/z*) calculated for $[C_{27}H_{43}NO_4SSi+Na]^+$ ($[M+Na]^+$) 528.2574, found 528.2574.

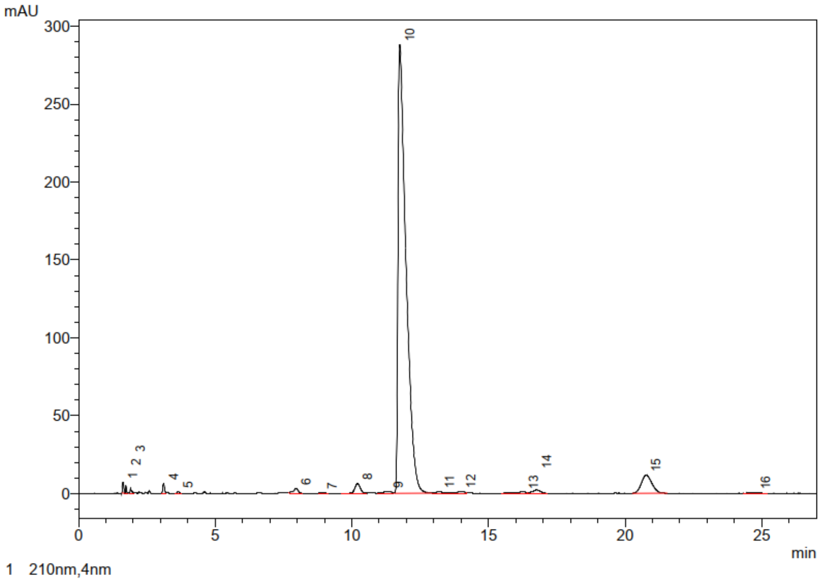


(2*S*,3*S*)-2-Phenyl-1-tosyl-3-((triisopropylsilyl)oxy)piperidine (25). Methanesulfonyl chloride (25 *µ*L, 0.32 mmol) and triethylamine (88 *µ*L, 0.63 mmol) were added to a solution of alcohol **24** (80 mg, 0.16 mmol) in dichloromethane (3 mL) at −78 °C. After stirring for 2 h at this temperature, the reaction was quenched with saturated NH_4Cl solution (1 mL) and the mixture was allowed to reach room temperature. The aqueous phase was extracted with dichloromethane (3 × 2 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a colorless oil. The oil was dissolved in tetrahydrofuran (3 mL) and potassium *tert*-butoxide (27 mg, 0.24 mmol) was added to the solution at 0 °C. After stirring for 1 h at room temperature, the reaction was quenched with saturated NH_4Cl solution (1 mL). The aqueous phase was extracted with dichloromethane (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; hexane/methyl *tert*-butyl ether, 100:1 to 20:1) to give the title compound as a pale yellow oil (71 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.70 – 7.62 (m, 2H), 7.30 – 7.18 (m, 5H), 5.28 (d, *J* = 5.4 Hz, 1H), 3.98 (ddd, *J* = 11.7, 5.5, 4.1 Hz, 1H), 3.85 – 3.74 (m, 1H), 2.85 (ddd, *J* = 14.2, 12.1, 4.1 Hz, 1H), 2.44 (s, 3H), 1.93 (app. qd, *J* = 12.1, 5.0 Hz, 1H), 1.83 – 1.74 (m, 1H), 1.61 – 1.56 (m, 2H), 1.05 – 0.99 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.6, 136.9, 129.8, 129.5, 128.1, 127.2, 127.1, 71.7, 59.9, 40.8, 29.0, 24.7, 21.6, 18.2, 18.1, 12.3; IR (ATR): ṽ = 2943, 2891, 2866, 1599, 1495, 1461, 1343, 1278, 1216, 1182, 1158, 1116, 1040, 1008, 954, 882, 861, 817, 727, 698; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{27}H_{41}NO_3SSi+Na]^+$ ($[M+Na]^+$) 510.2469, found 510.2468.



(2*S*,3*S*)-2-Phenyl-3-((triisopropylsilyl)oxy)piperidine (26). Magnesium powder (60 mg, 2.5 mmol) was added to a solution of compound **25** (60 mg, 0.12 mmol) in methanol (1.0 mL). The suspension was sonicated for 6 h at room temperature before the reaction was quenched with saturated NH_4Cl solution (2 mL). Then the residue was basified with aqueous NaOH (3 M) until pH ≈ 10 was reached. The aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. This residue was purified by flash chromatography (SiO_2; hexane/ethyl acetate, 2:1 to 1:2) on activated silica gel (0.50 % *v*/*v* Et_3N in hexane) to give the title compound as a colorless oil (31 mg, 76%, 90% ee). $[\alpha]_D^{20}$ = +36.9 (*c* = 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 4H), 7.18 (app. ddd, *J* = 8.6, 5.5, 2.3 Hz, 1H), 4.16 (dt, *J* = 3.6, 1.8 Hz, 1H), 3.76 (d, *J* = 1.5 Hz, 1H), 3.28 (ddt, *J* = 13.2, 4.2, 2.0 Hz, 1H), 2.79 (td, *J* = 12.8, 3.1 Hz, 1H), 2.57 (br s, 1H), 2.07 – 2.00 (m, 1H), 1.99 – 1.86 (m, 1H), 1.80 (tdd, *J* = 13.1, 3.9, 2.1 Hz, 1H), 1.49 – 1.38 (m, 1H), 0.94 – 0.82 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.0, 126.9, 126.6, 70.0, 64.8, 47.4, 33.3, 21.0, 18.1, 18.1, 12.8; IR (ATR): ṽ = 3024, 2942, 2892, 2865, 1460, 1384, 1363, 1247, 1216, 1127, 1098, 1082, 1066, 1025, 924, 881, 698, 678, 640; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{20}H_{36}NOSi]^+$ ($[M+H]^+$) 334.2561, found 334.2561.

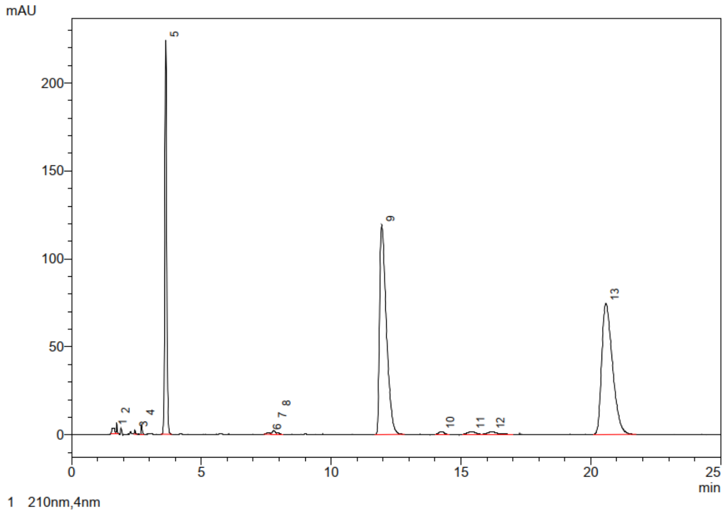
The ee was determined by HPLC analysis: Chiralpak 150 mm IB-N-3, ∅ 4.6 mm i. d., acetonitrile/20 mmol NH_4HCO_3 pH 9 = 60:40, v = 1.0 mL/min, λ = 210 nm, t(major) = 11.76 min, t(minor) = 20.77 min.



PDA Ch1 210nm

Peak #	Ret. Time	Area %	Name
1	1,62	0,38	
2	1,74	0,17	
3	1,90	0,22	
4	3,12	0,43	
5	3,65	0,11	
6	7,97	0,60	
7	8,92	0,10	
8	10,21	1,36	
9	11,34	0,38	
10	11,76	89,57	1. Enantiomer 89.8 % ee
11	13,22	0,37	
12	14,00	0,35	
13	16,29	0,36	
14	16,77	0,67	
15	20,77	4,80	2. Enantiomer
16	24,78	0,14	
Total		100,00	

Determination of the ee of **26**

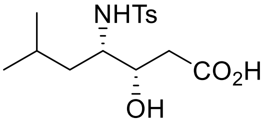


PDA Ch1 210nm

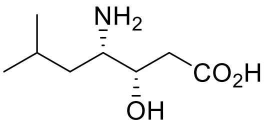
Peak #	Ret. Time	Area %	Name
1	1,63	0,50	
2	1,74	0,26	
3	2,44	0,13	
4	2,70	0,32	
5	3,63	19,63	
6	7,59	0,17	
7	7,79	0,33	
8	7,94	0,11	
9	11,95	38,25	1. Enantiomer
10	14,25	0,47	
11	15,42	0,73	
12	16,19	0,85	
13	20,58	38,27	2. Enantiomer
Total		100,00	

Separation of enantiomers of *rac*-**26**

(3*S*,4*S*)-3-Hydroxy-6-methyl-4-((4-methylphenyl)sulfonamido)heptanoic acid (29). A solution of aqueous H_2SO_4 (1.5 M, 1.5 mL, 2.3 mmol) and potassium permanganate (730 mg, 4.6 mmol) in distilled water (15 mL) was added dropwise to a stirred solution of compound **28** (240 mg, 0.77 mmol) in acetone (15 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min before the reaction was slowly quenched with neat $Na_2S_2O_5$ until the solution was colorless. The mixture was acidified to pH ≈ 3 by dropwise addition of aqueous H_2SO_4 (1.5 M). The layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a colorless oil. The residue was purified by flash chromatography (dichloromethane/methanol, 100:1 to 25:1) on activated silica gel (0.5 % *v*/*v* acetic acid in dichloromethane) to give the title compound as a white foam (131 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.32 – 7.27 (m, 2H), 5.29 (d, *J* = 9.1 Hz, 1H), 4.08 (d, *J* = 9.2 Hz, 1H), 3.28 (app. q, *J* = 8.3 Hz, 1H), 2.72 (dd, *J* = 16.7, 9.4 Hz, 1H), 2.53 (dd, *J* = 16.9, 3.1 Hz, 1H), 2.42 (s, 3H), 1.48 – 1.31 (m, 2H), 1.10 – 0.96 (m, 1H), 0.70 (d, *J* = 6.5 Hz, 3H), 0.66 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 143.6, 138.3, 129.8, 127.1, 68.6, 55.6, 41.2, 38.7, 24.4, 22.7, 22.3, 21.7; IR (ATR): ṽ = 3490, 3257, 2957, 2871, 1712, 1422, 1325, 1305, 1289, 1264, 1158, 1093, 1059, 971, 909, 815, 730, 704; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_{15}H_{23}NO_5S+Na]^+$ ($[M+Na]^+$) 352.1189, found 352.1189.



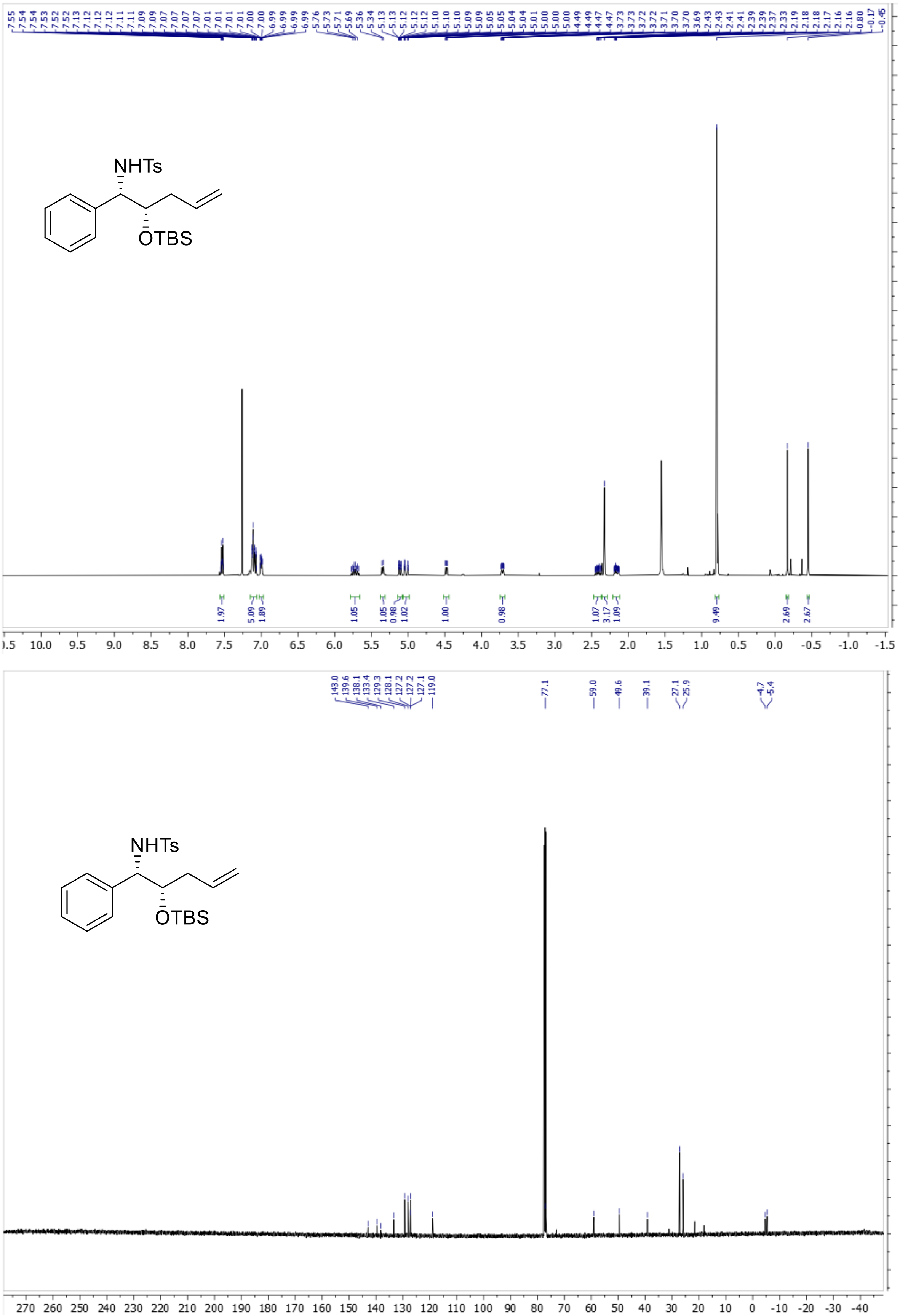
Statine (30). Naphthalene (486 mg, 3.79 mmol) was added to a suspension of lithium (26 mg, 3.79 mmol) in tetrahydrofuran (3.0 mL) at 0 °C. The mixture was stirred at room temperature overnight before a solution of compound **29** (125 mg, 0.379 mmol) in tetrahydrofuran (1 mL) was added at 0 °C. The mixture was stirred at 0 °C for 10 min before the reaction was carefully quenched with a solution of aqueous HCl (1 M) until the pH ≈ 3 was reached. The layers were separated and the aqueous phase was extracted with methyl *tert*-butyl ether (3 × 5 mL). The aqueous phase was concentrated under reduced pressure to give a white solid. The residue was purified by ion exchange chromatography (Amberlite® IR-120, H$^+$ form), eluting first with water and then with a NH_4OH solution (1 M) to give the title compound as a white solid (34 mg, 51%). An aliquot of this material (17 mg) was further purified with preparative HPLC (column: 50 mm Eclipse Plus C18, 1.8 µm, ∅ 4.6 mm i. d., methanol/0.1% TFA in H_2O = 30:70, 0.5 mL/min) to give an analytically pure sample of the title compound as a white amorphous solid (11 mg, 65%). $[\alpha]_D^{20}$ = –7.8 (*c* = 0.50, H_2O) (lit.: –20 (*c* = 0.50, H_2O));**[5]** ^{1}H NMR (400 MHz, D_2O) δ 4.13 (ddd, *J* = 8.6, 6.1, 3.8 Hz, 1H), 3.35 (app. q, *J* = 6.7 Hz, 1H), 2.78 (dd, *J* = 16.1, 3.8 Hz, 1H), 2.60 (dd, *J* = 16.1, 8.9 Hz, 1H), 1.73 (app. dp, *J* = 13.5, 6.7 Hz, 1H), 1.53 (dd, *J* = 7.7, 6.0 Hz, 2H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, D_2O) δ 178.0, 70.2, 56.6, 41.6, 41.1, 26.8, 25.0, 23.7; IR (ATR): ṽ = 3257, 2961, 2933, 2876, 1729, 1665, 1600,



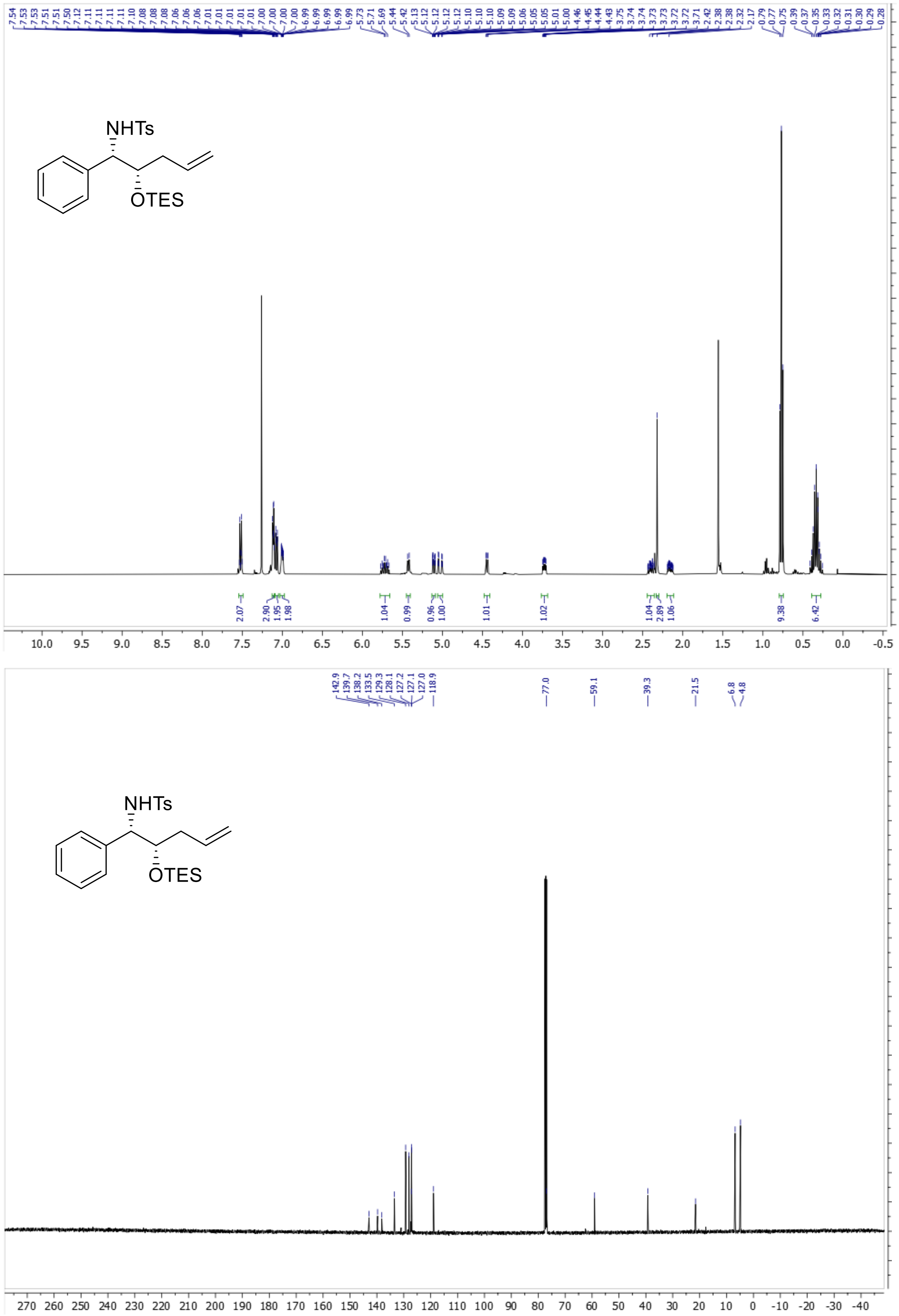
1519, 1426, 1405, 1281, 1197, 1170, 1139, 1097, 1035, 987, 921, 878, 842, 798, 723, 700, 669; HRMS (ESI$^+$, *m*/*z*) calculated for $[C_8H_{18}NO_3]^+$ ($[M+H]^+$) 176.1281, found 176.1284. Matches known data.**[5]**

NMR Spectra

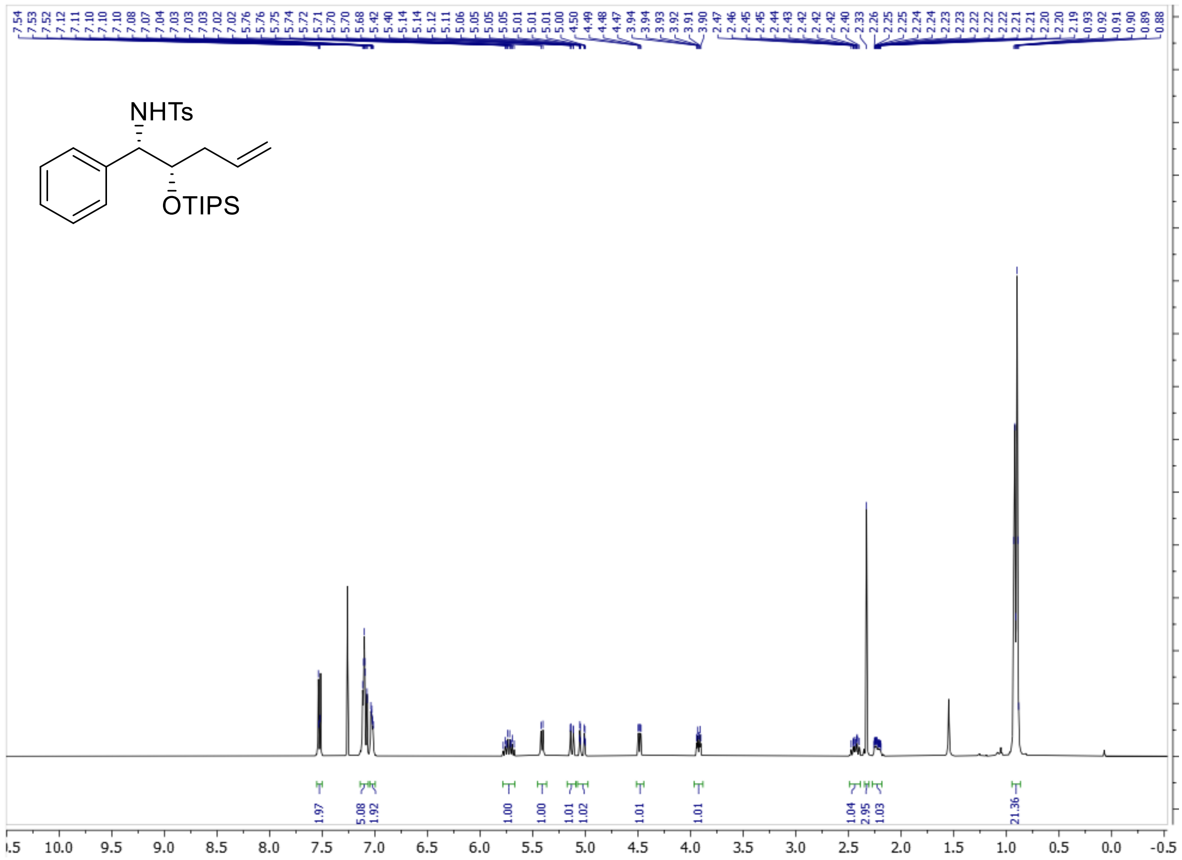
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **9a** *(*NOTE*: the minor internal alkene isomer* **11a** *was not separable by flash chromatography)*

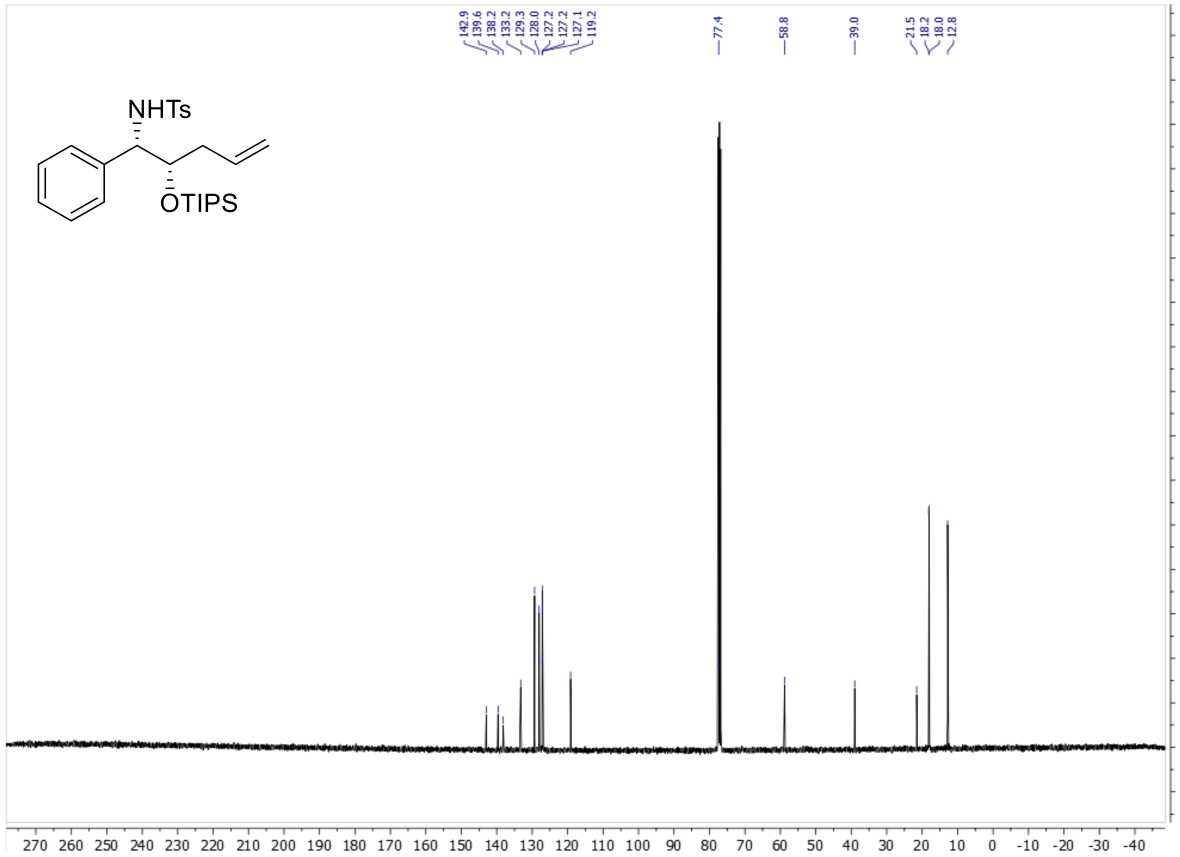


^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **9b** (NOTE*: the minor internal alkene isomer* ***11b*** *was not separable by flash chromatography)*

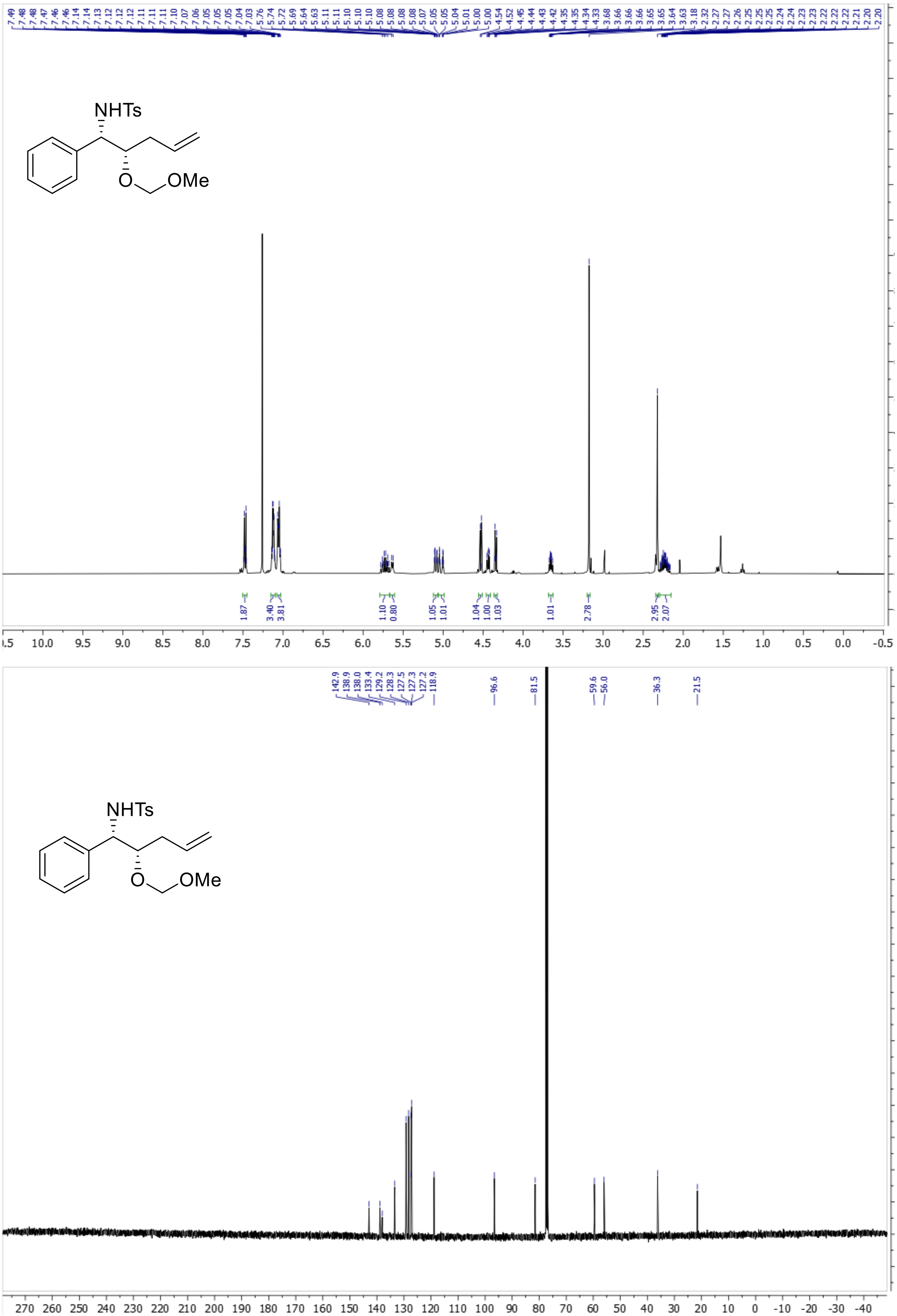


^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **9c**



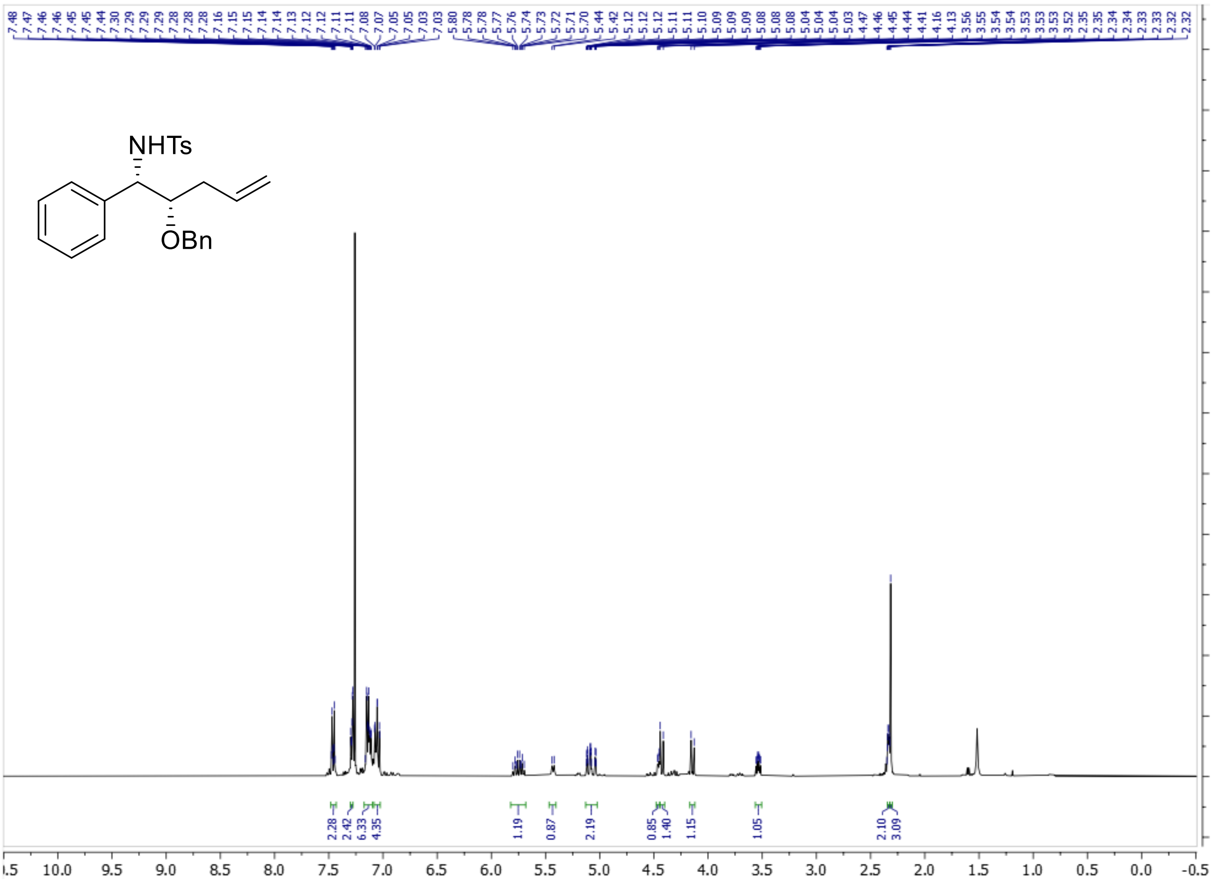


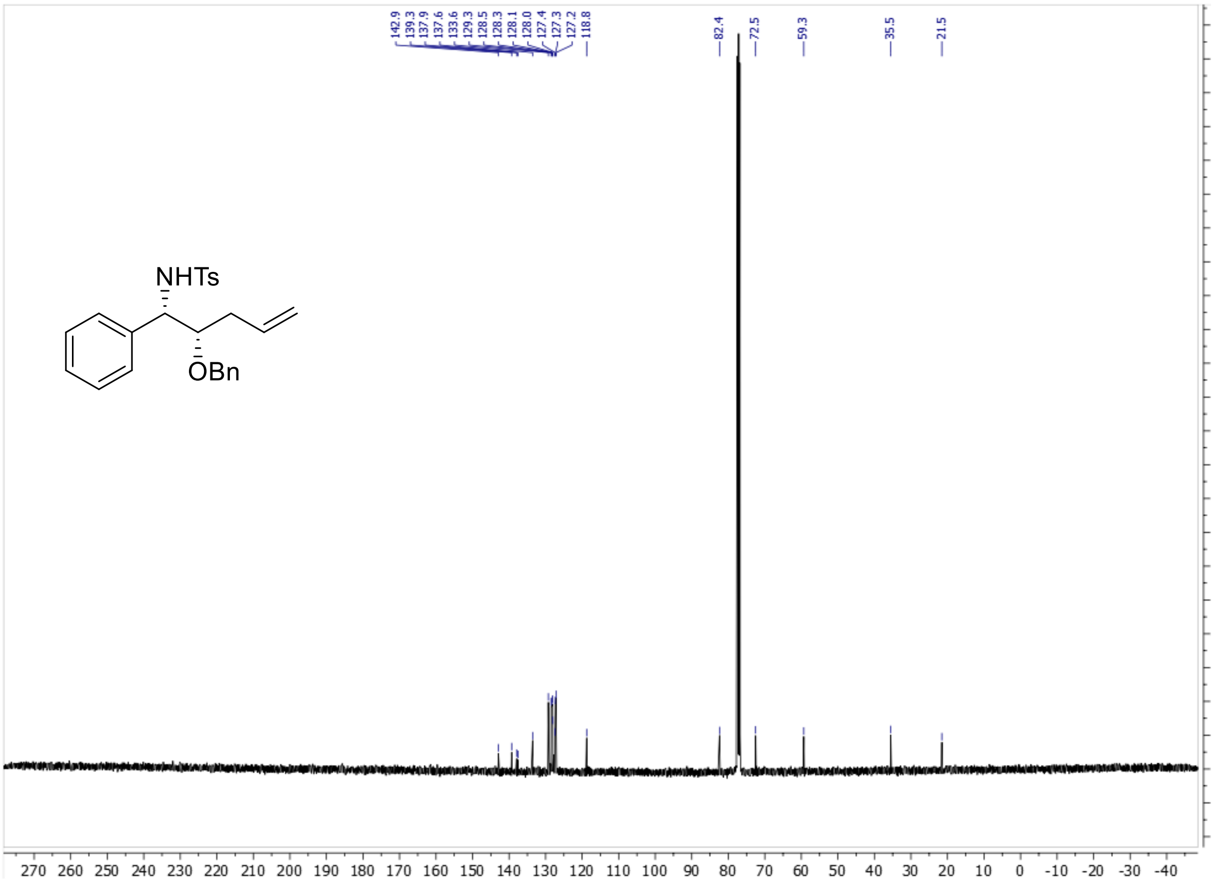
^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **9d**



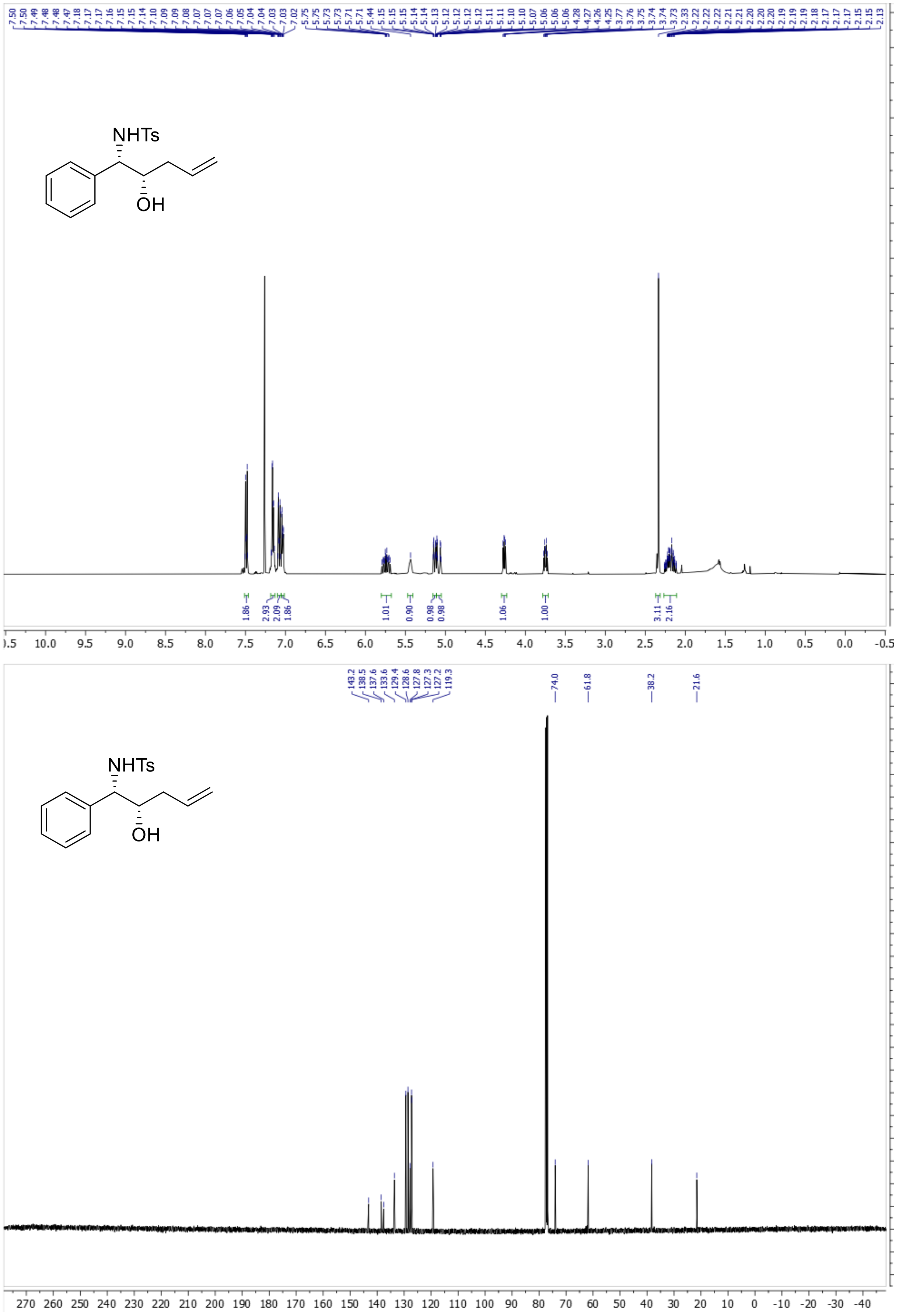
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **9e**

(NOTE: *the minor internal alkene isomer* **11e** *was not separable by flash chromatography*)

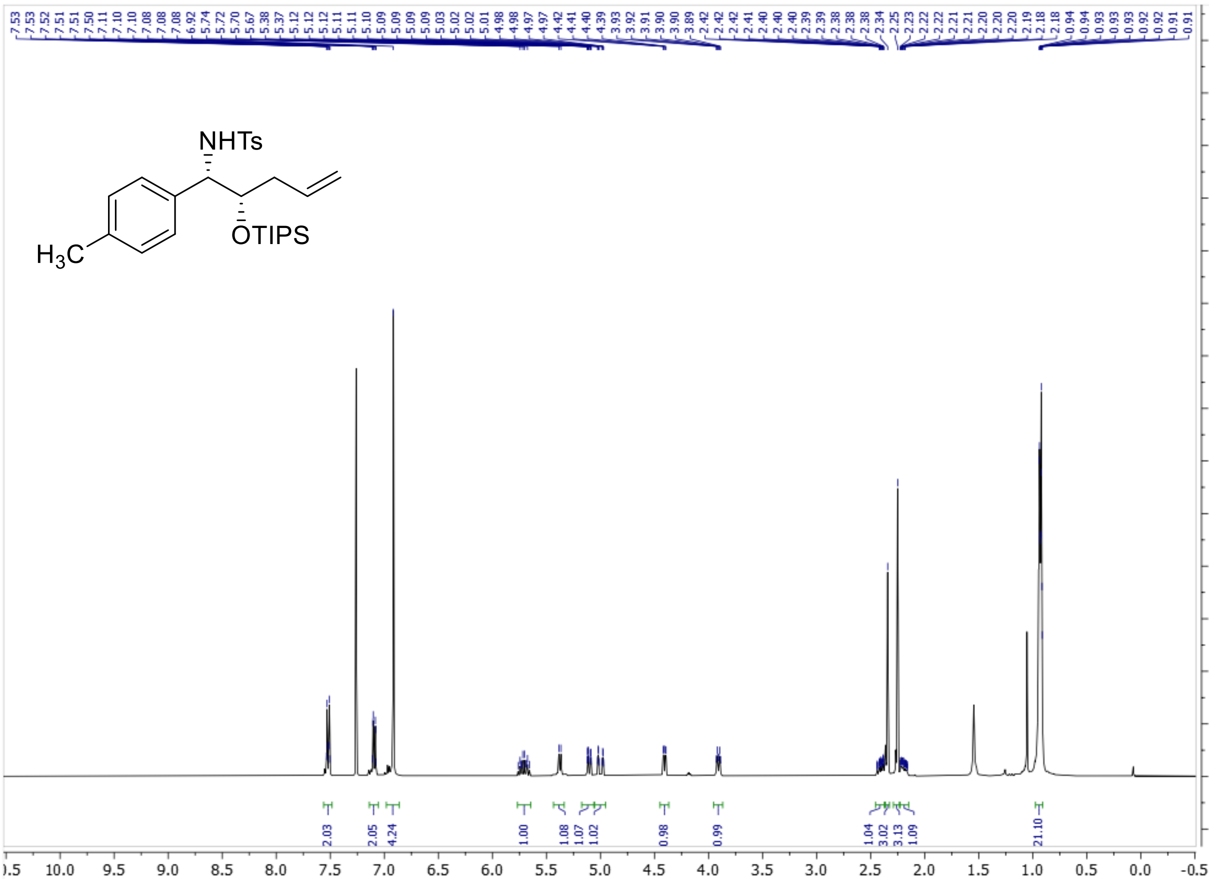


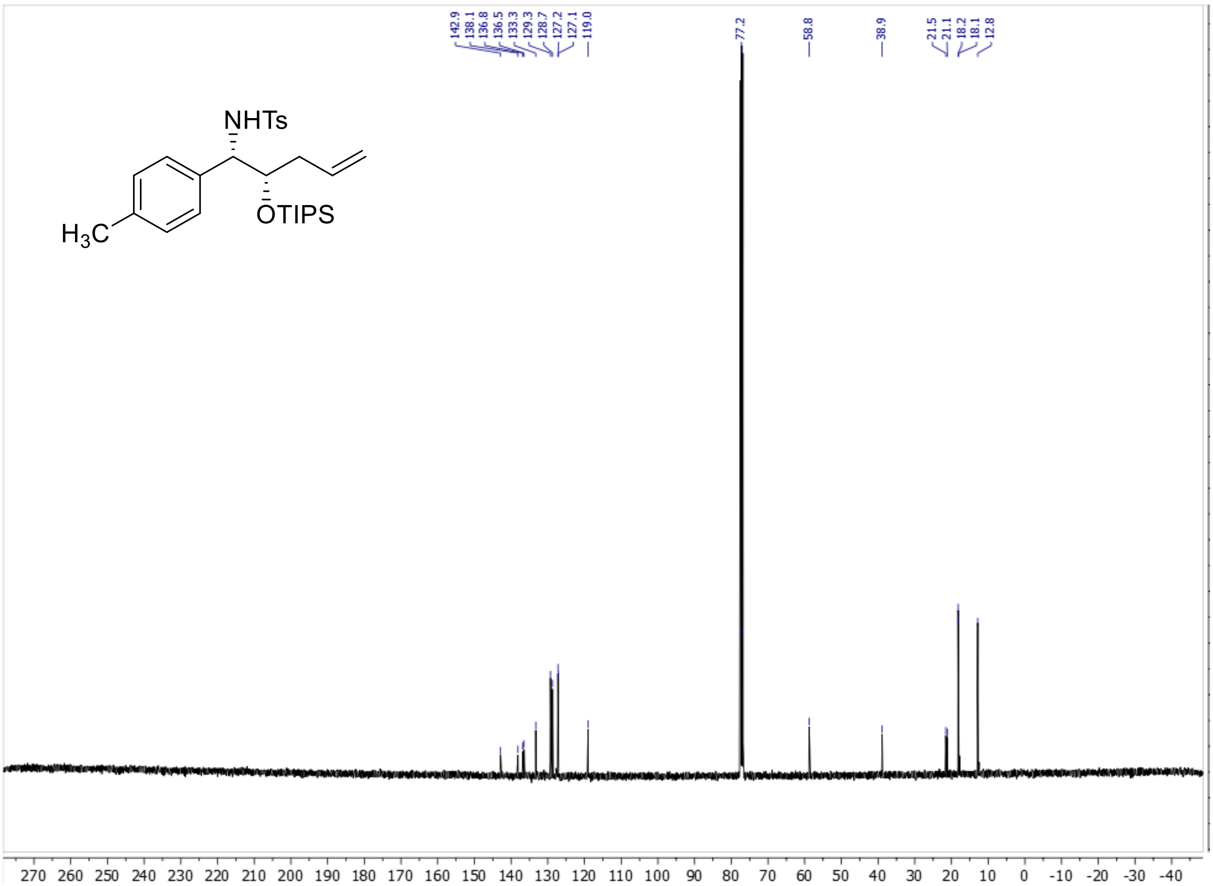


^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **12**

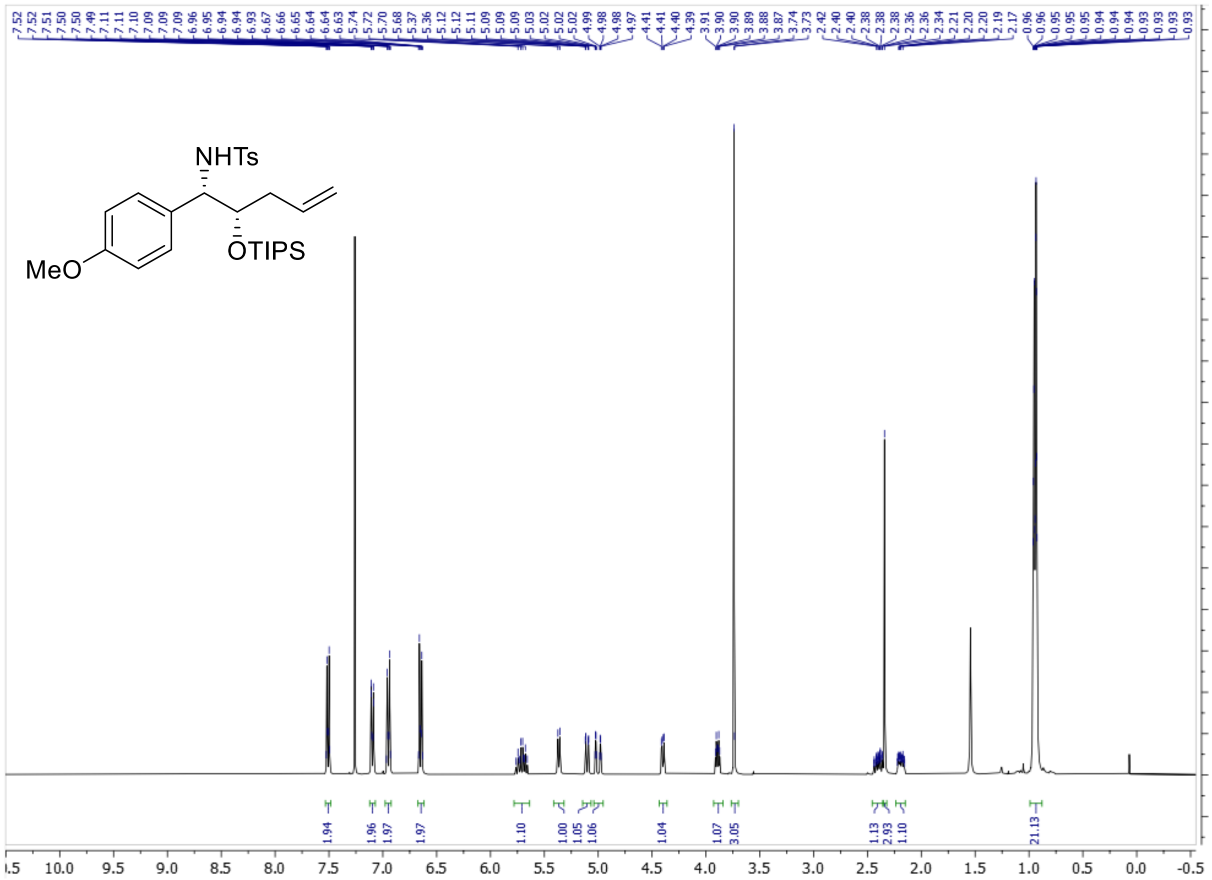


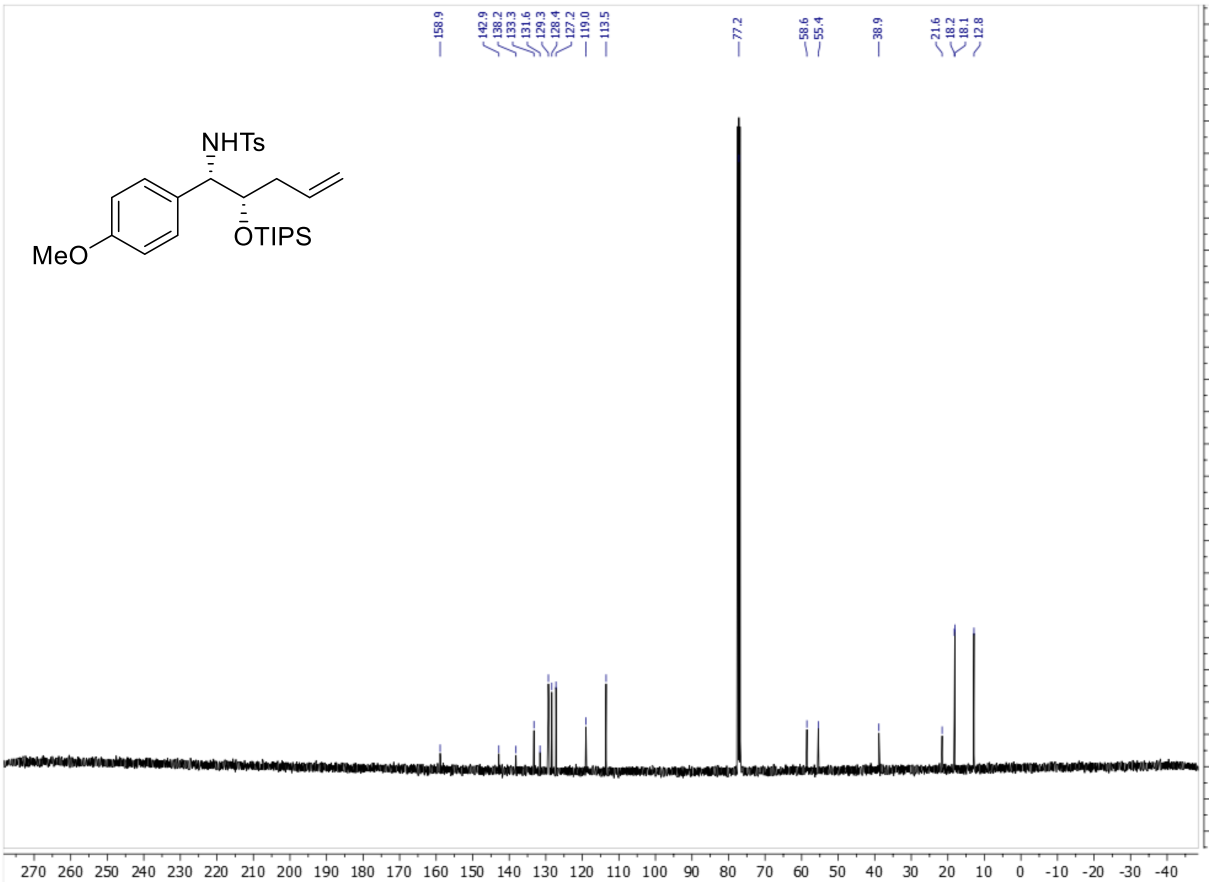
^1H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **13a**



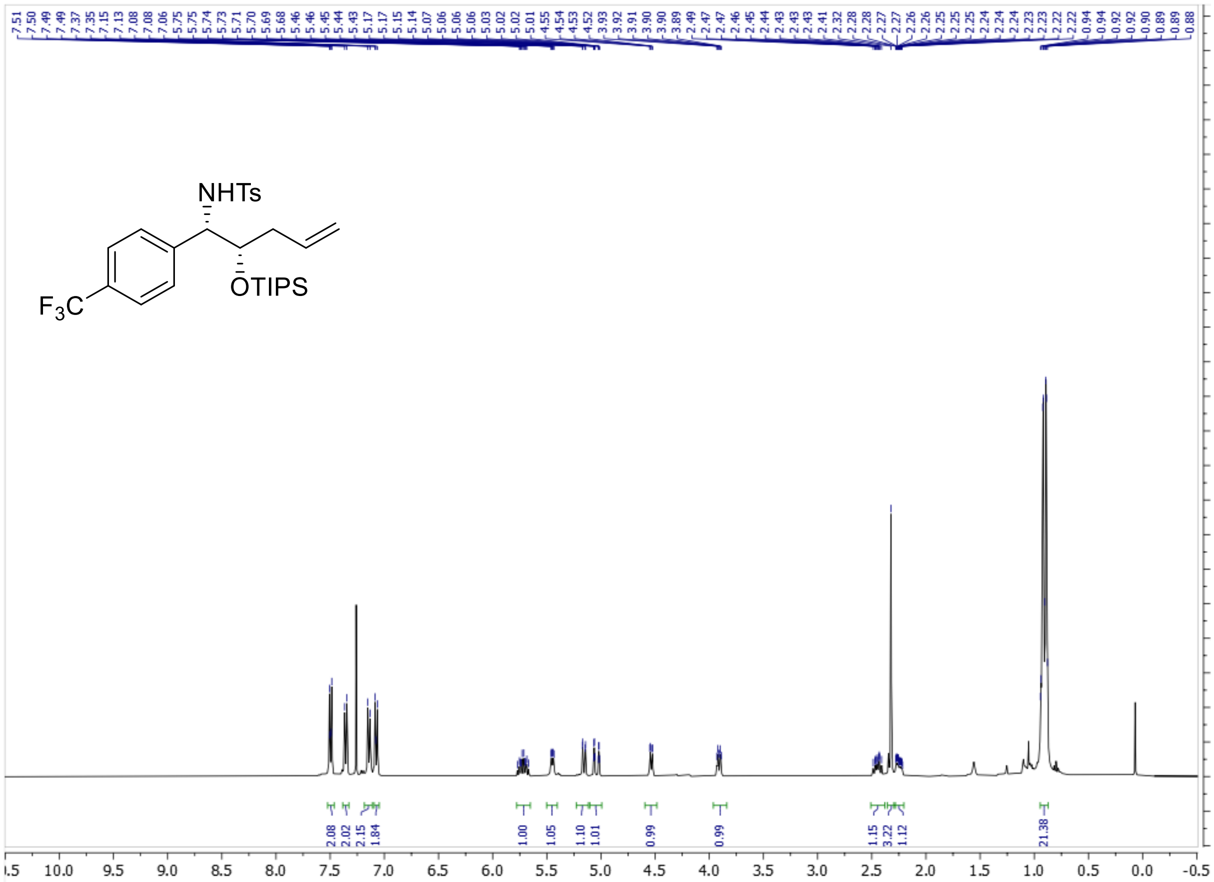


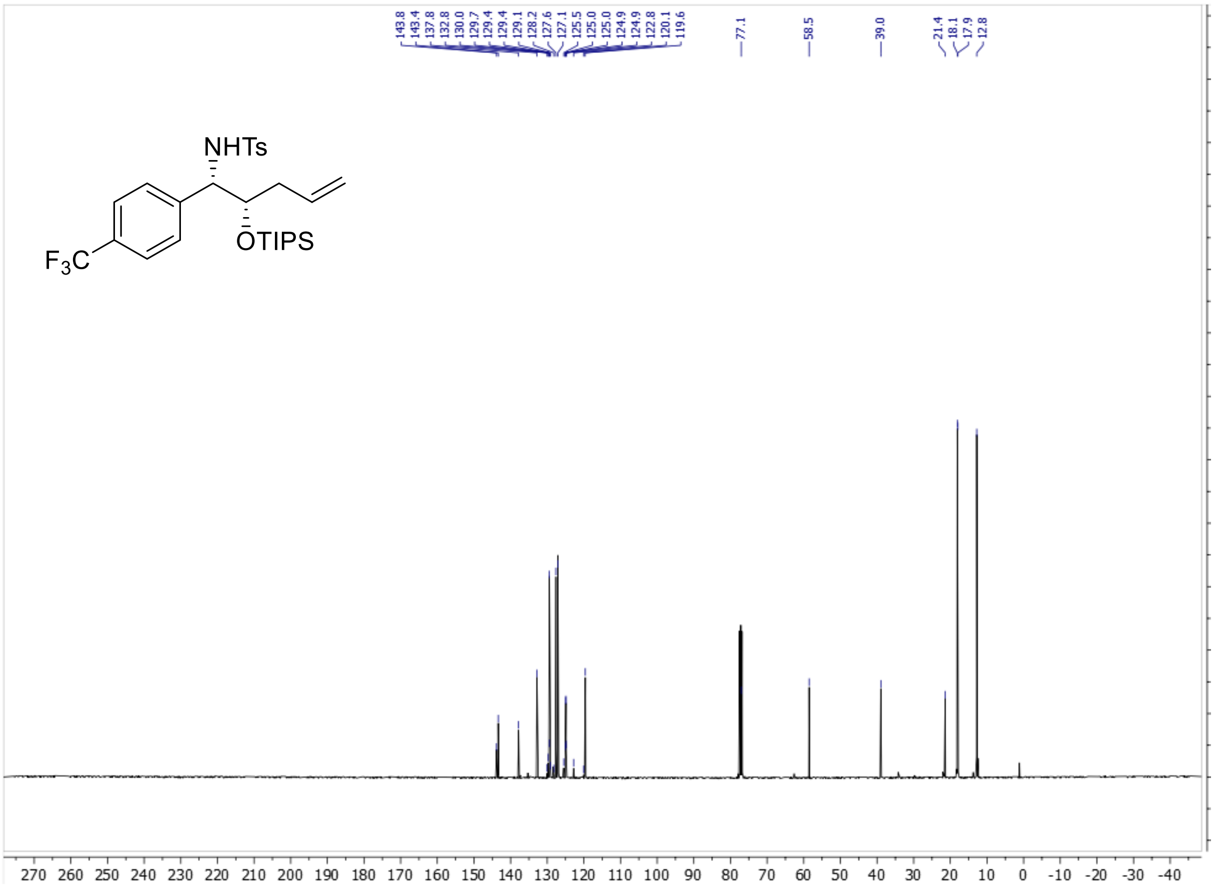
^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **13b**



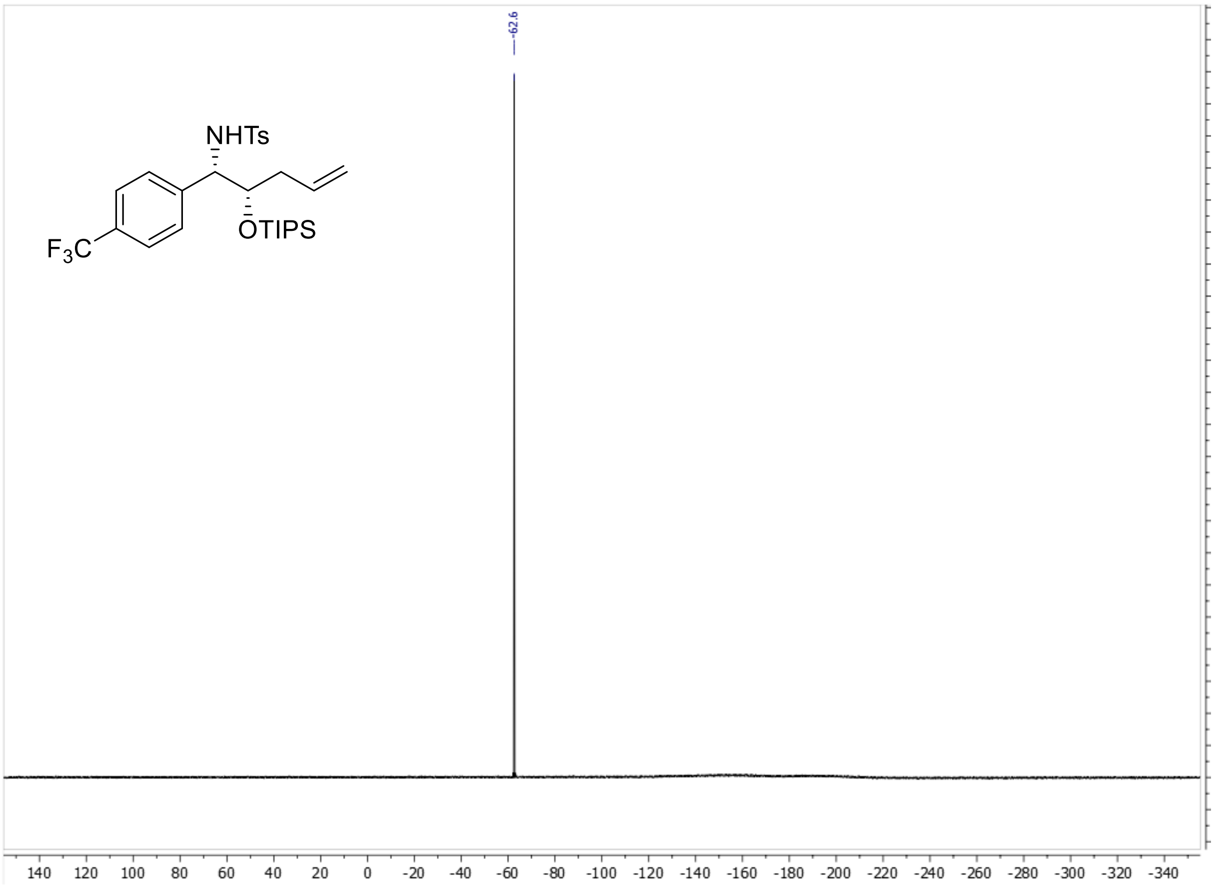


^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **13c**

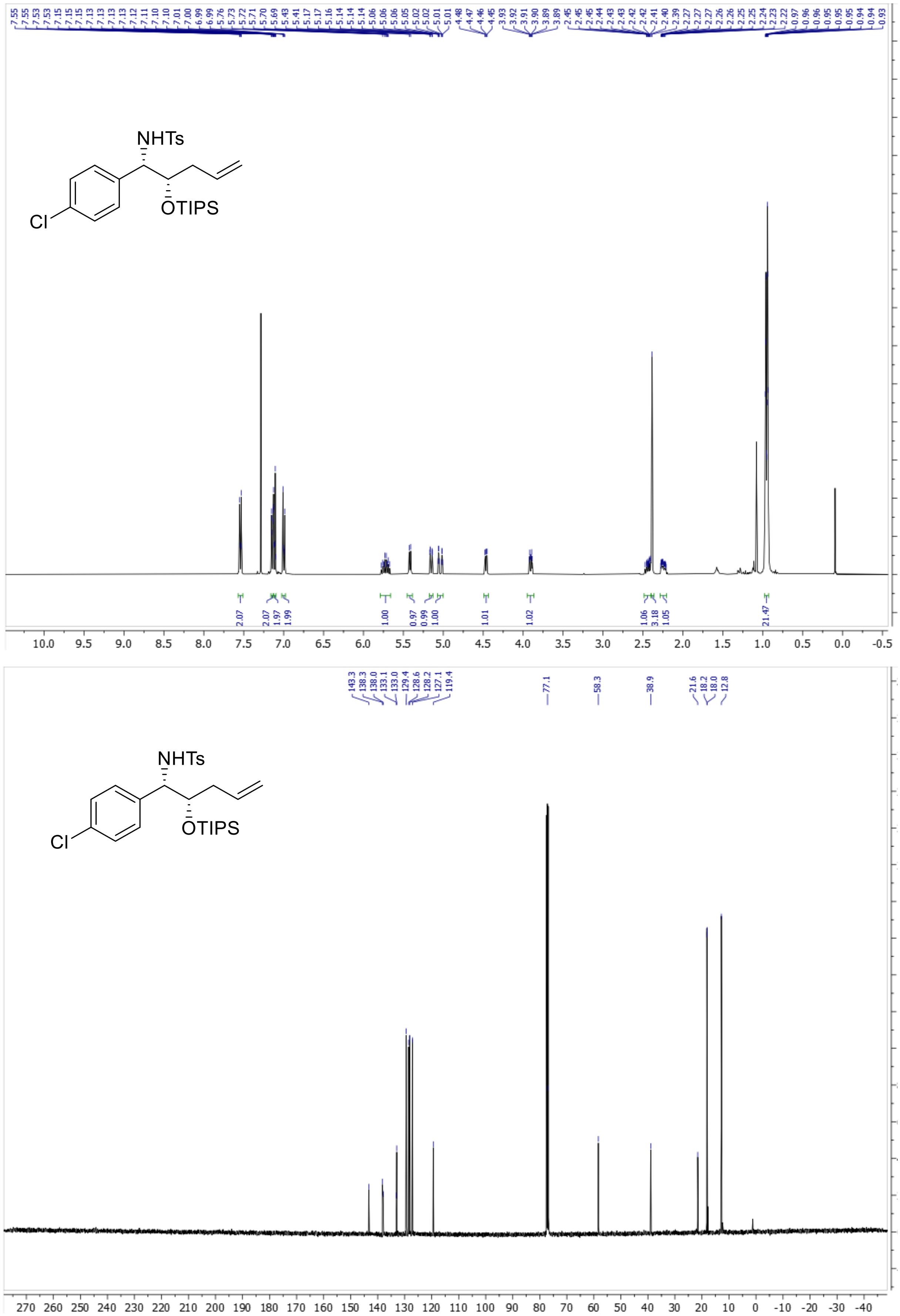




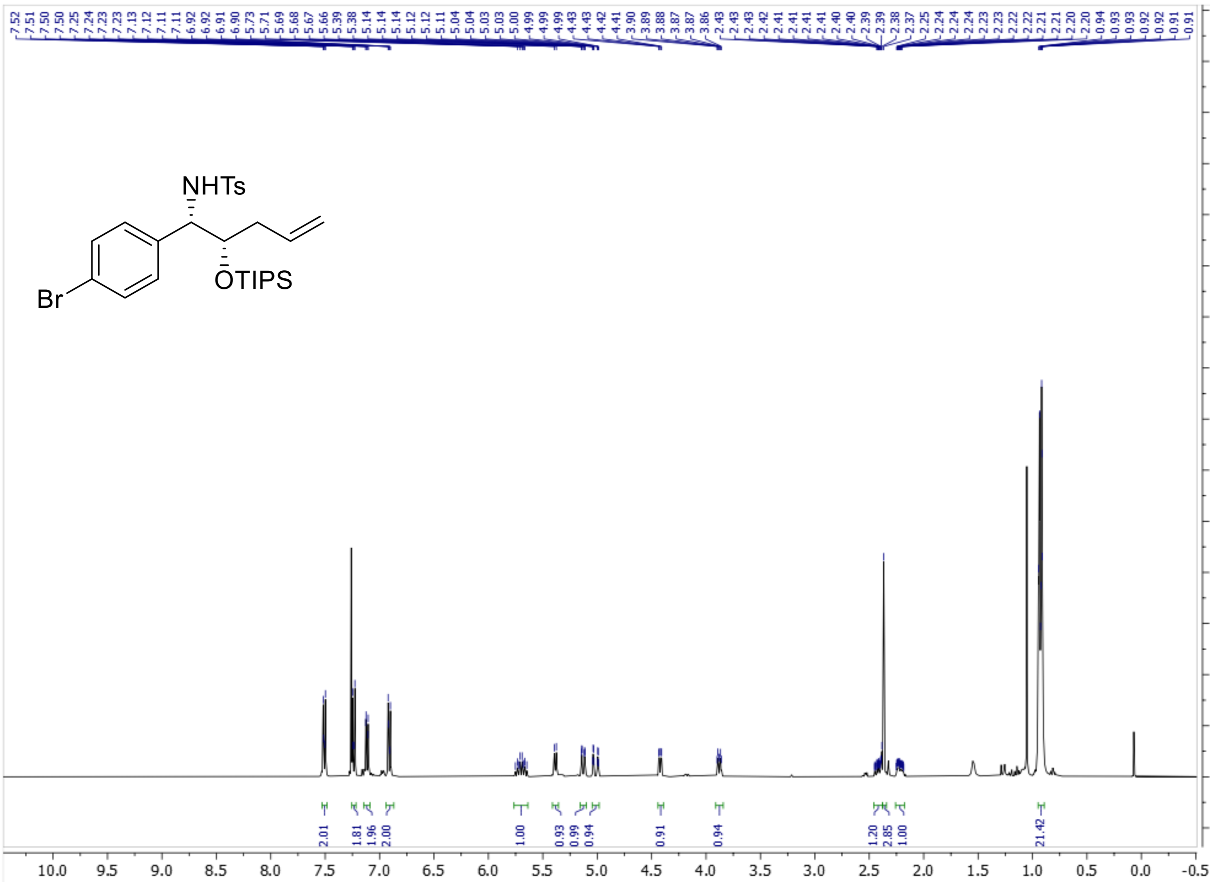
^{19}F NMR (282 MHz, CDCl$_3$) of compound **13c**

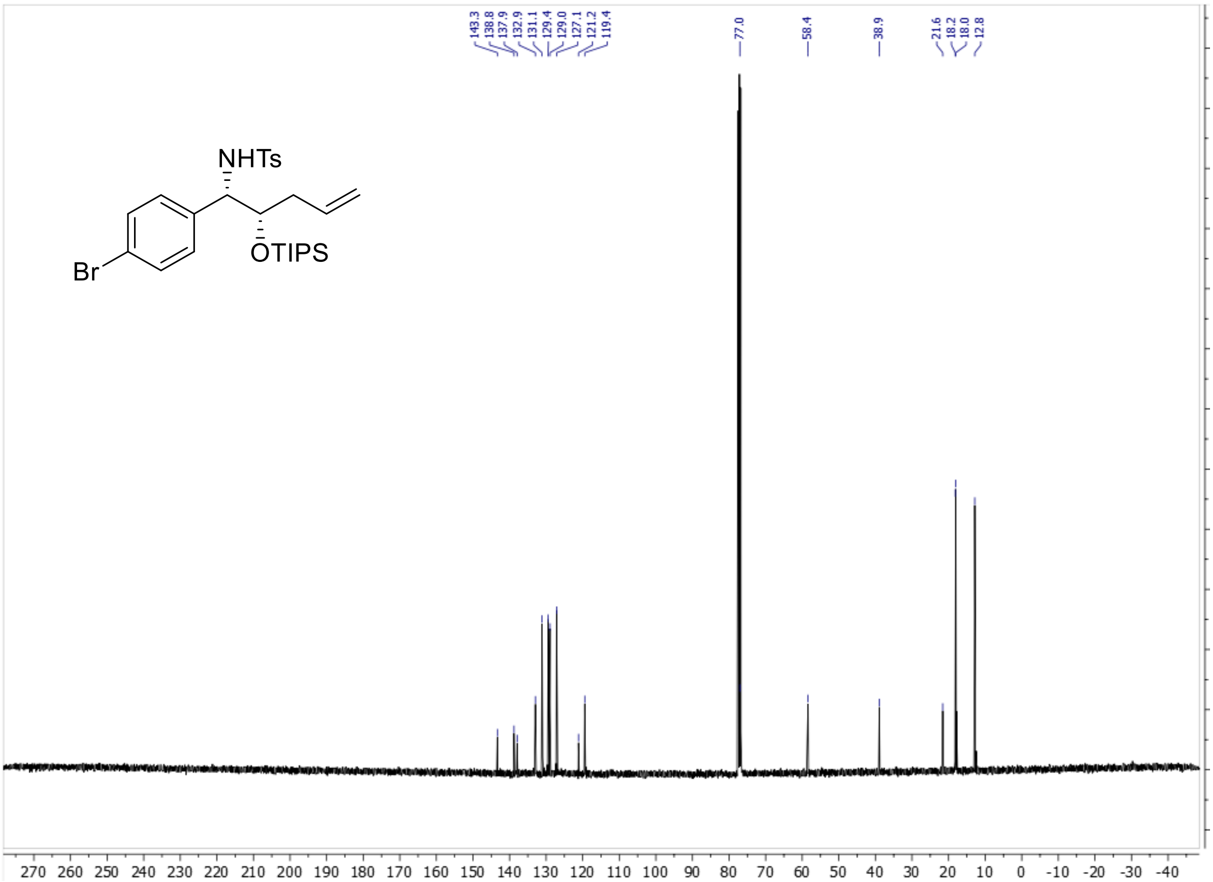


^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **13d**

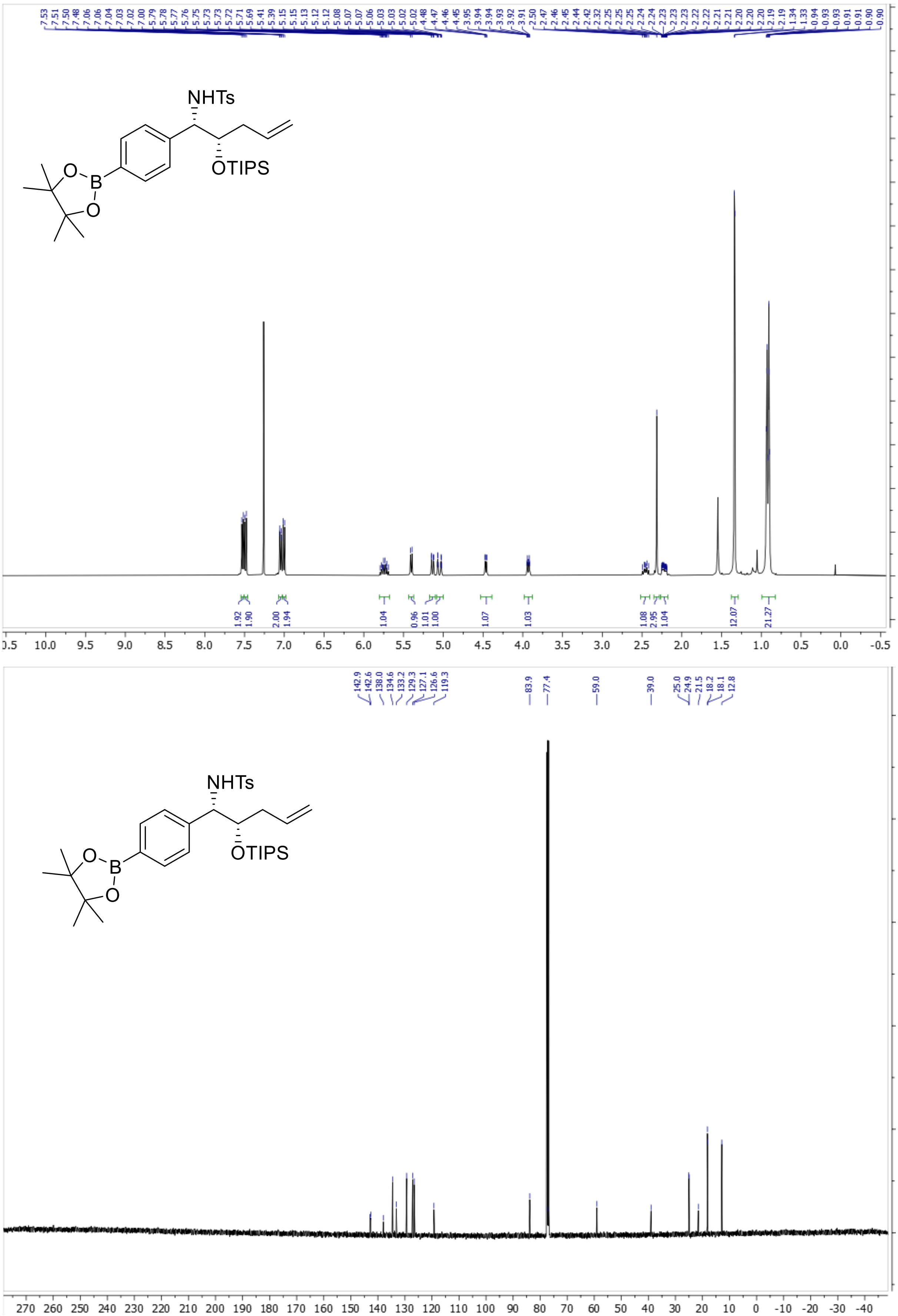


^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **13e**

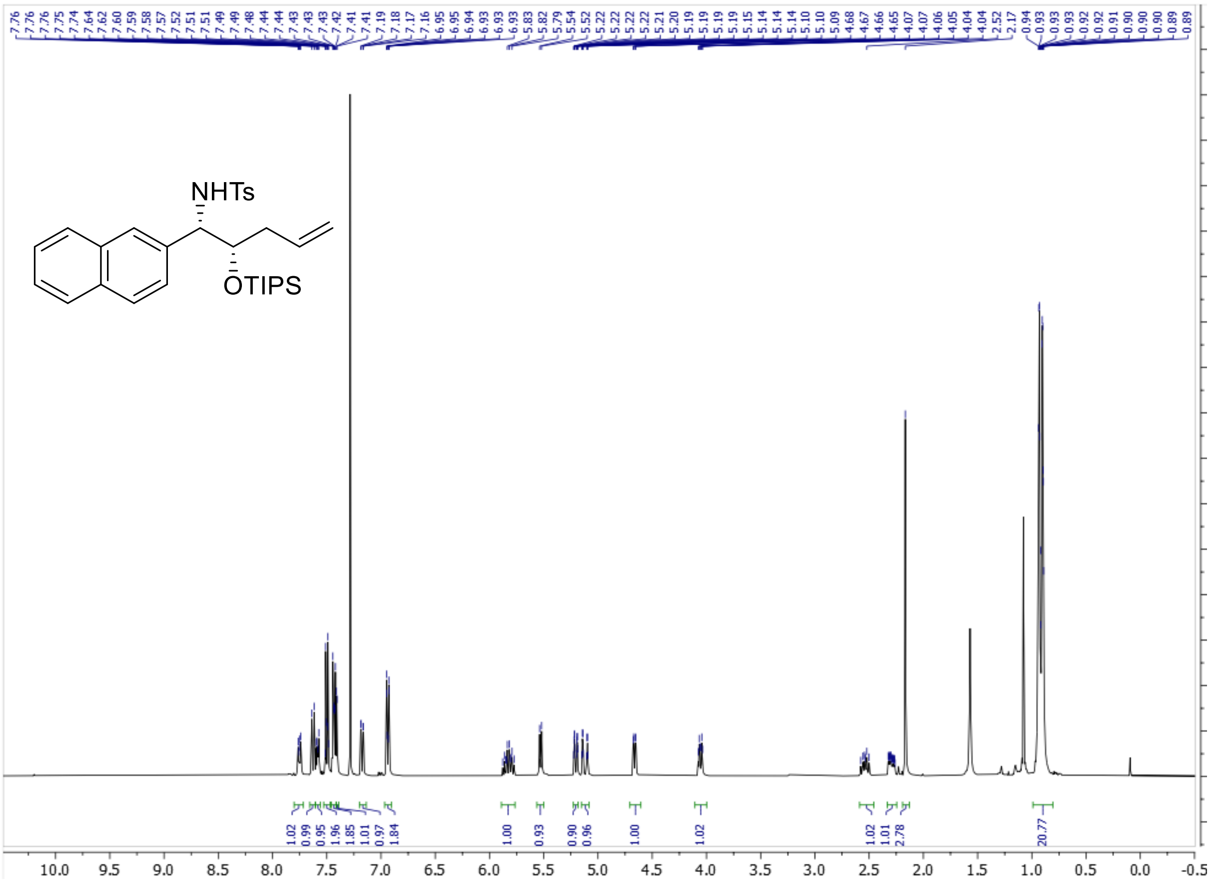


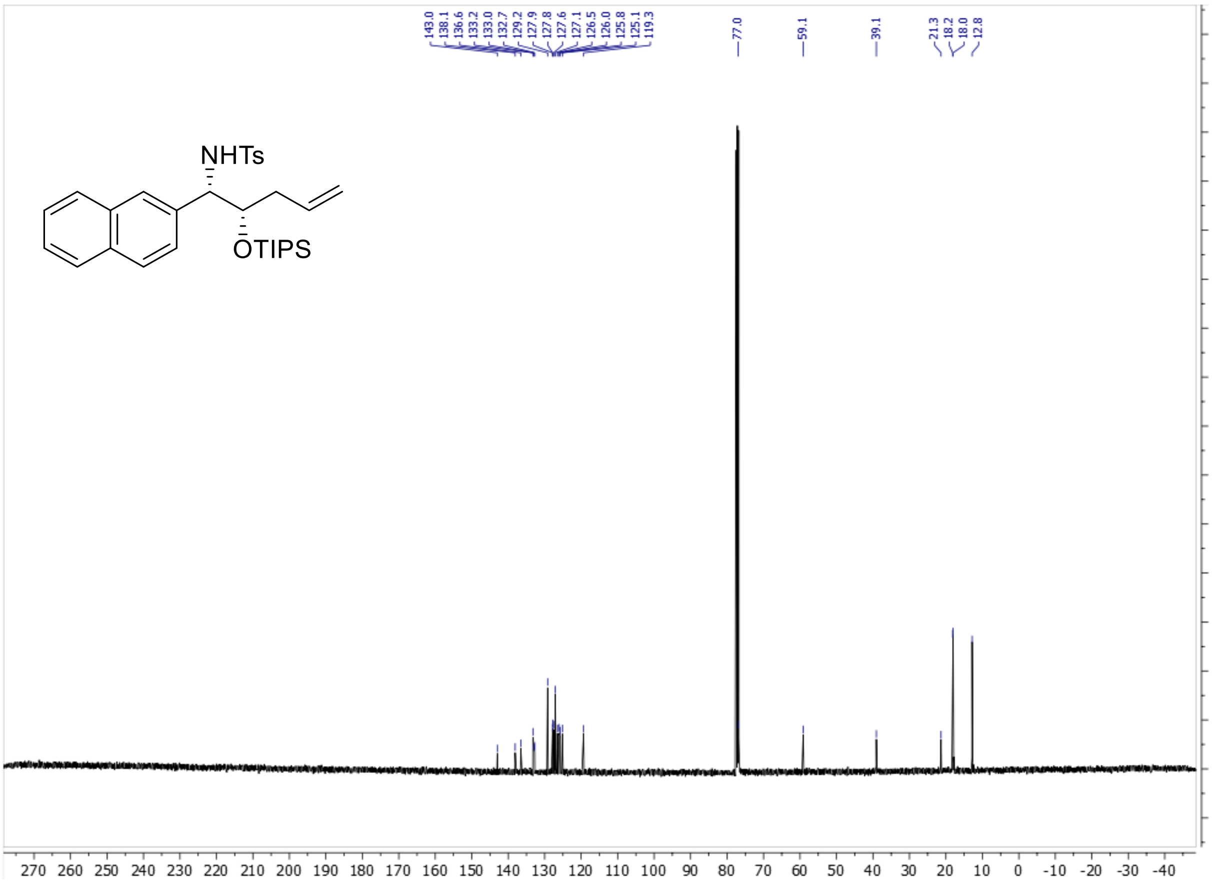


^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **13f**

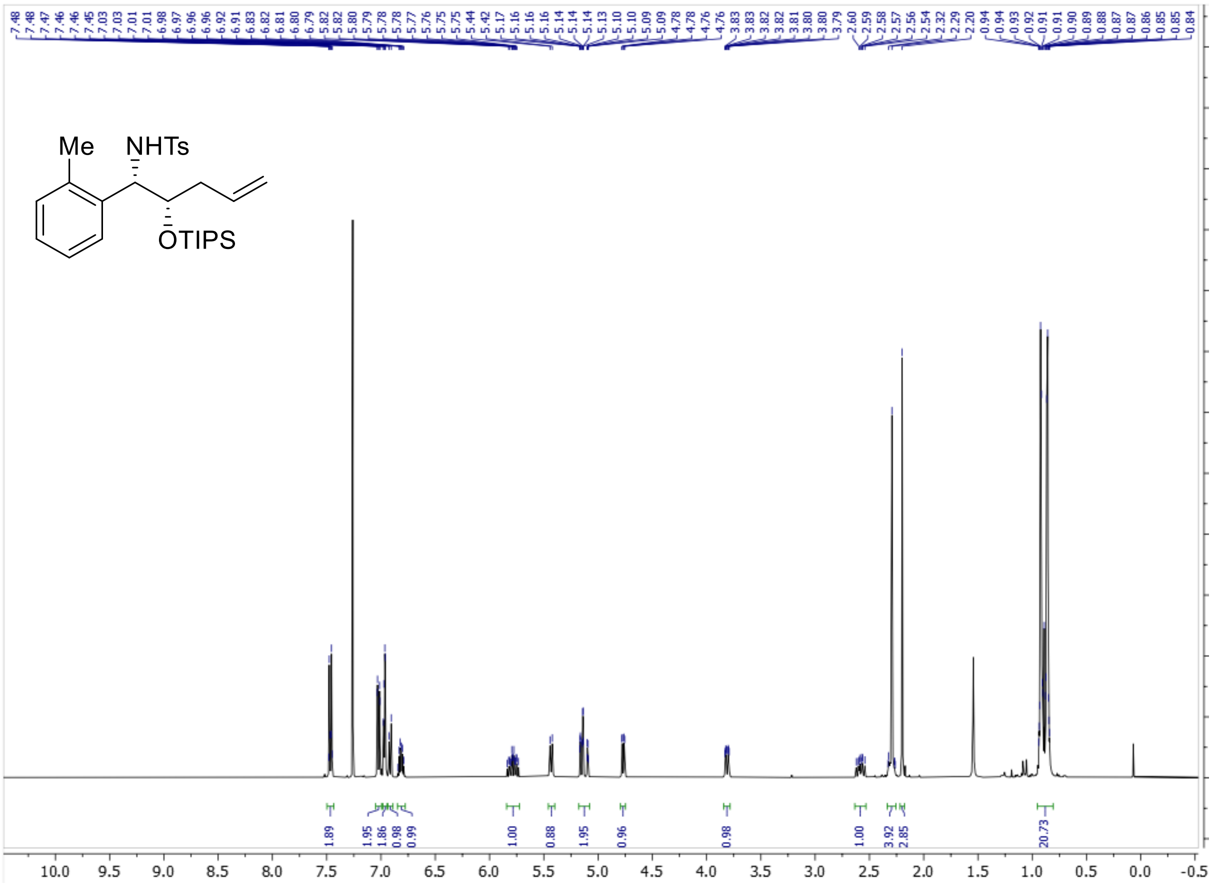


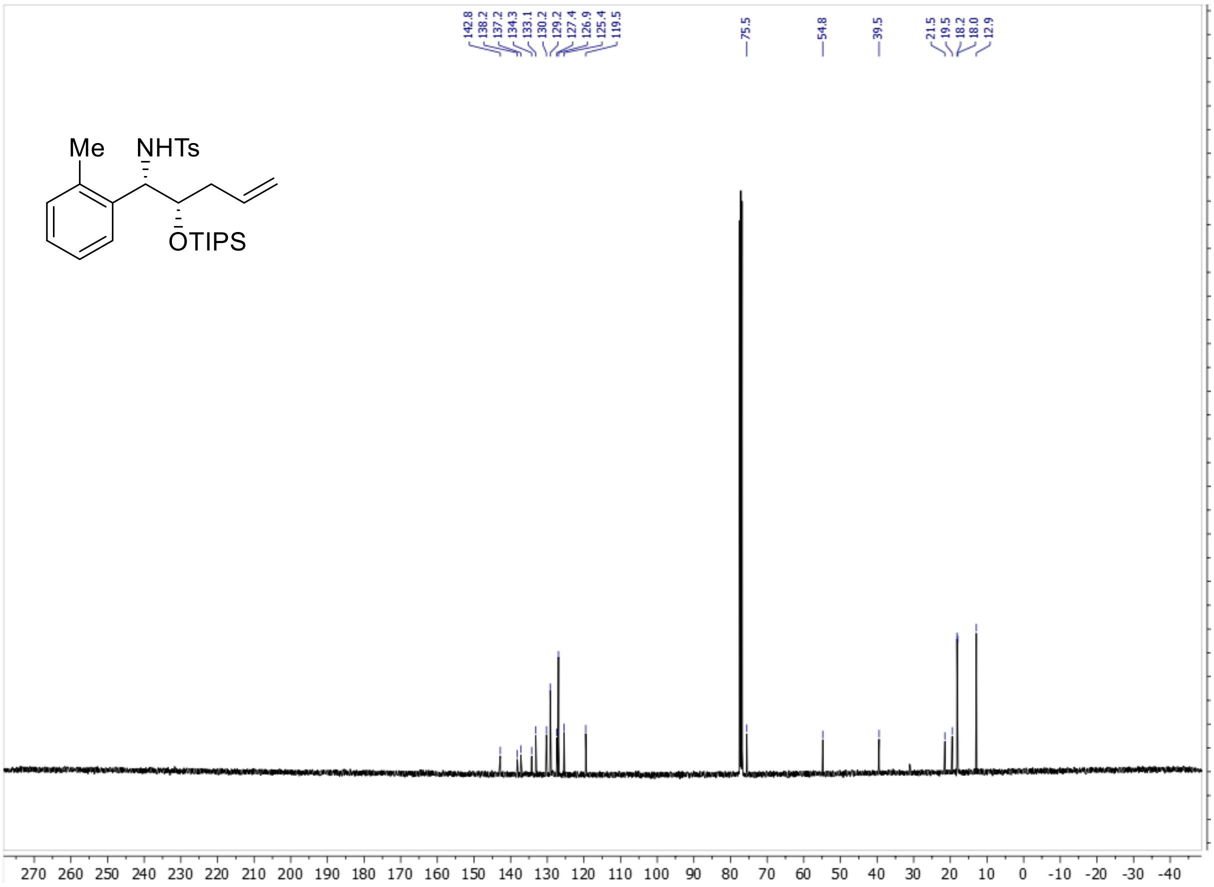
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **14**



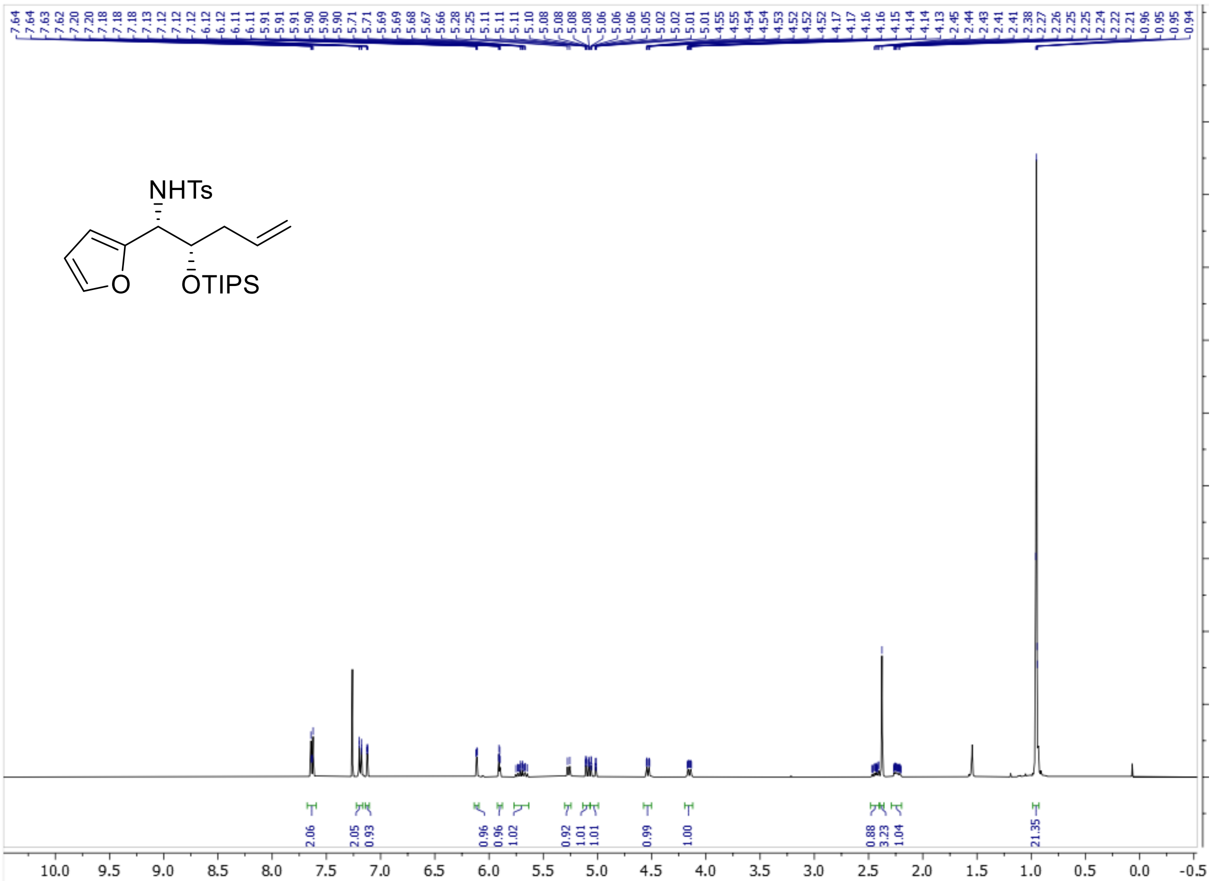


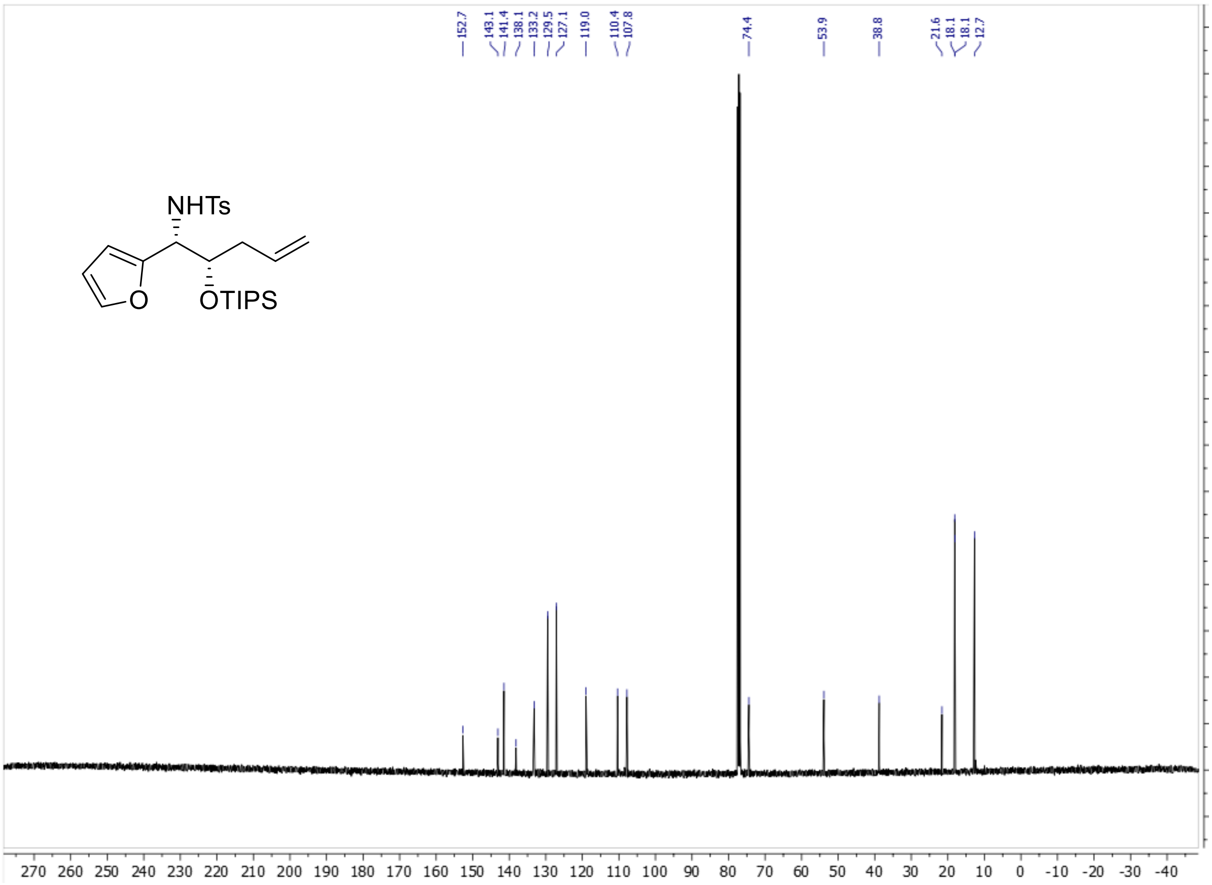
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **15**





^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **16**





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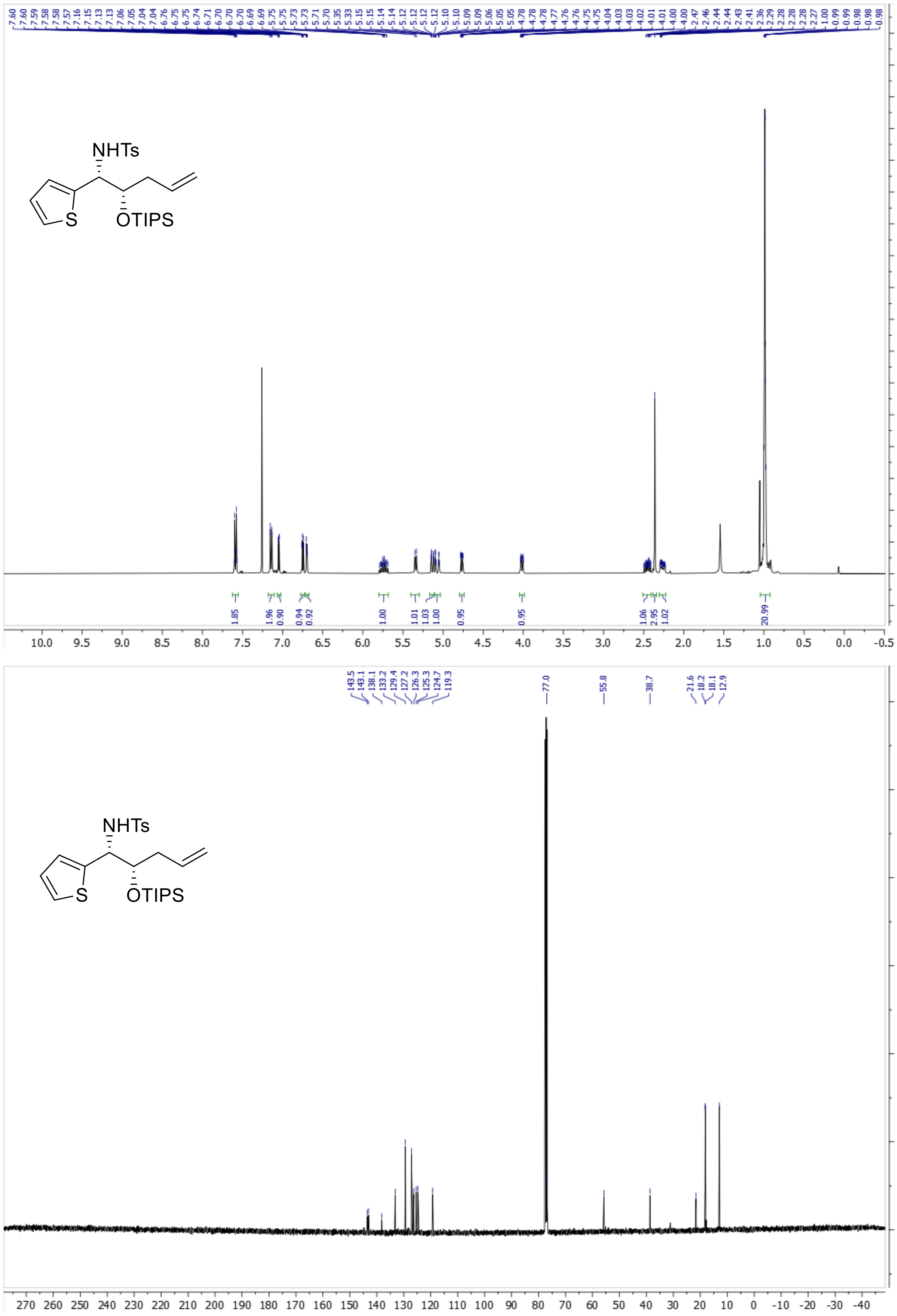
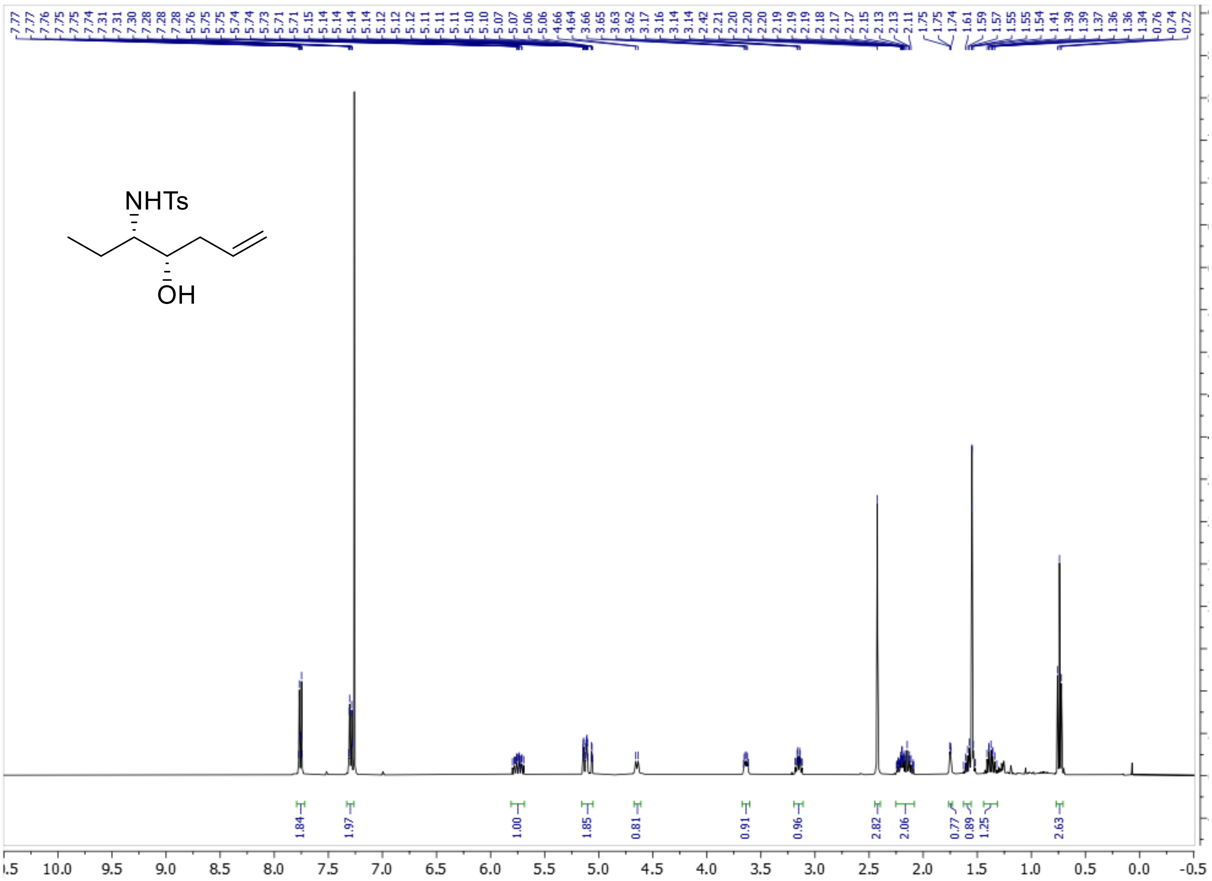
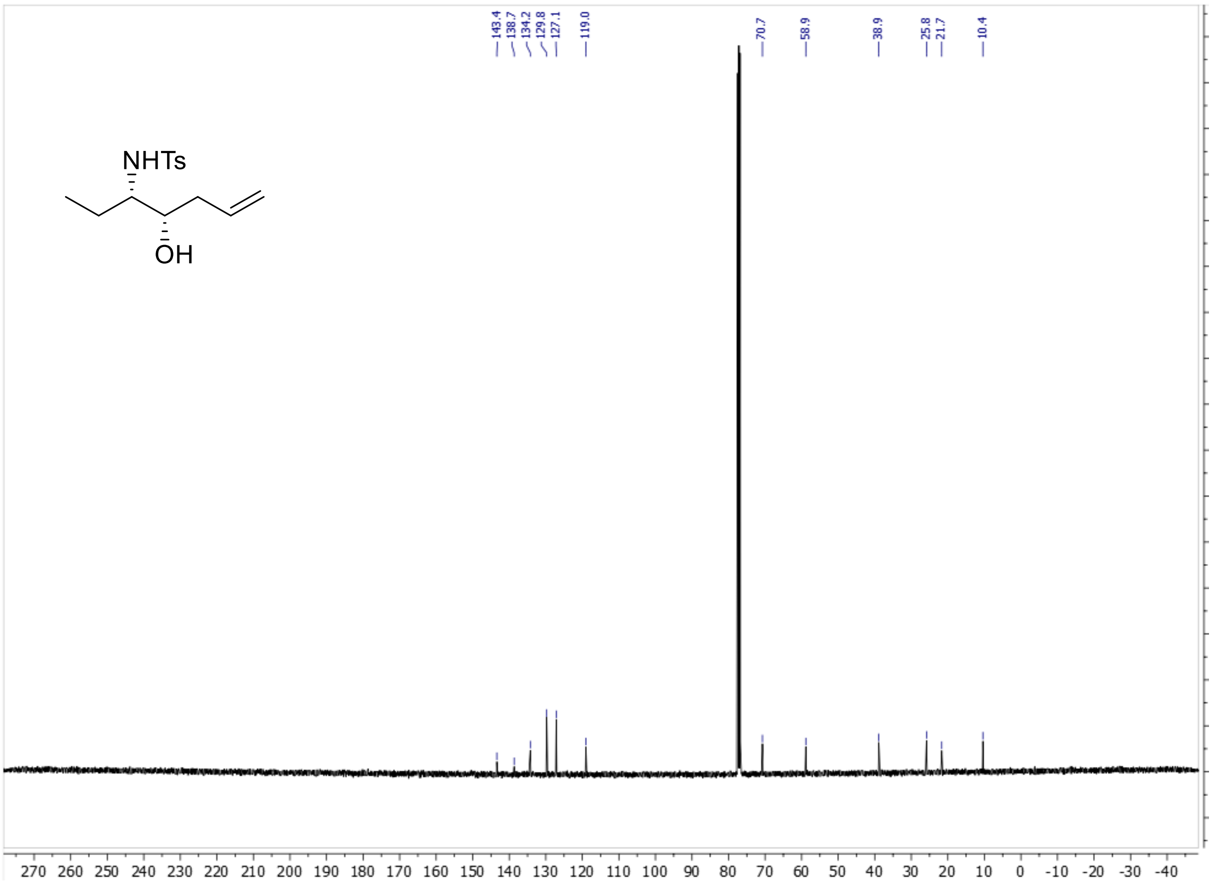
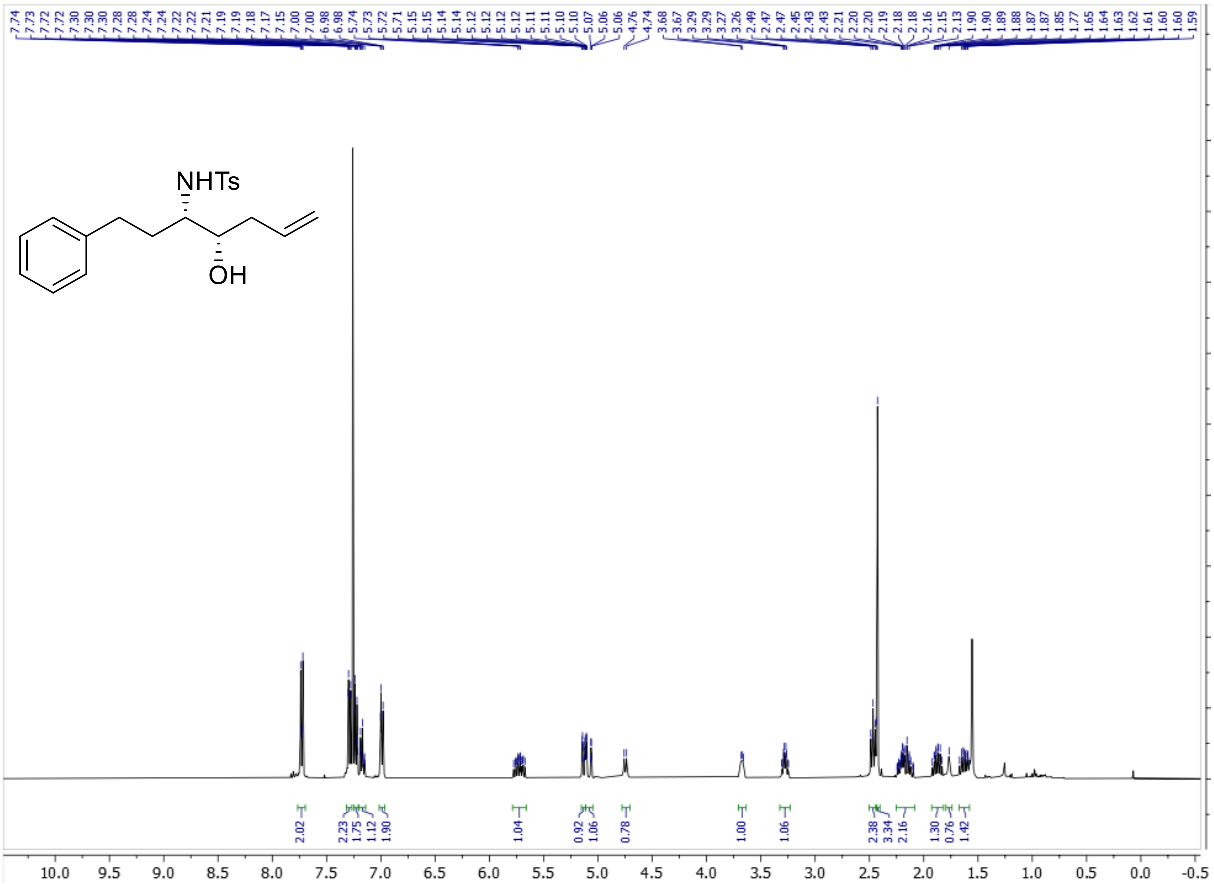


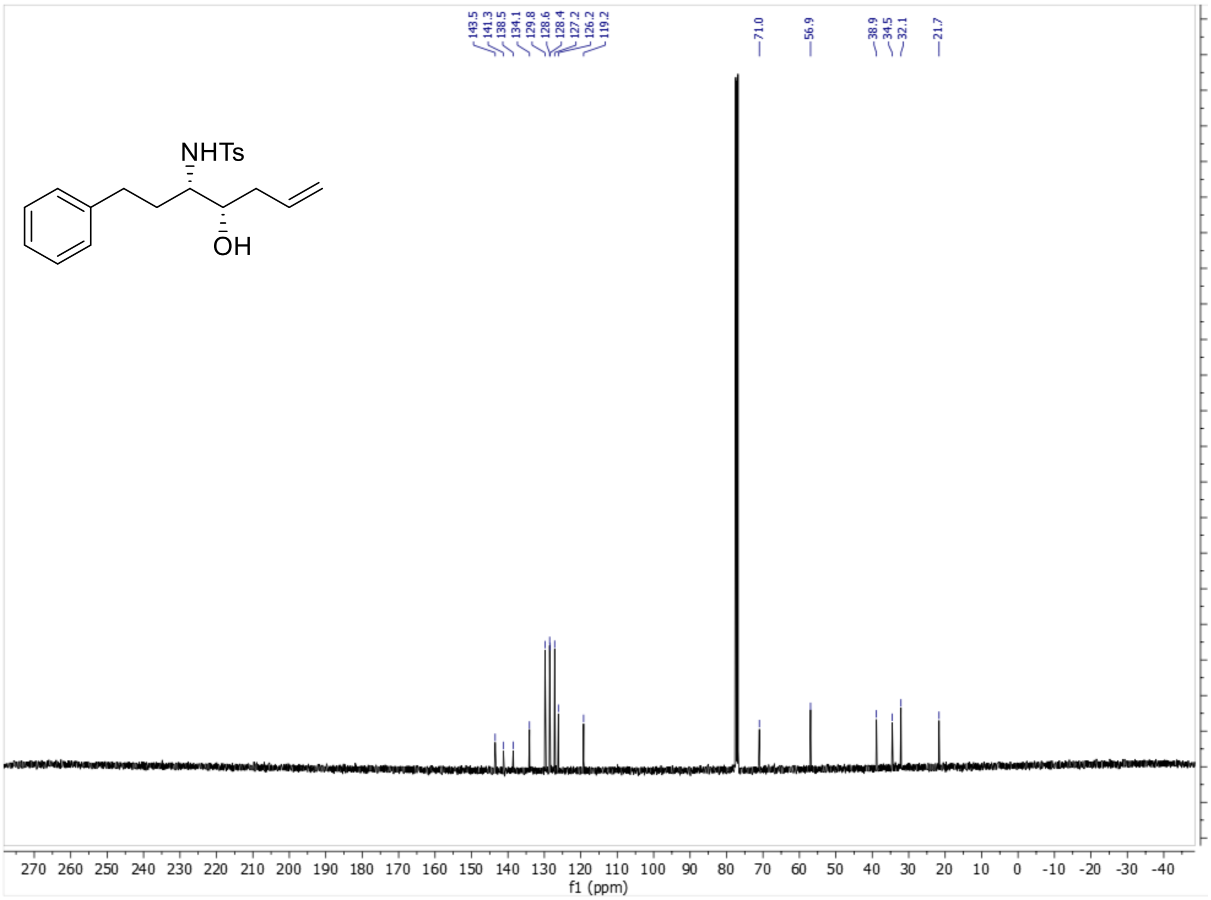
^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **18**



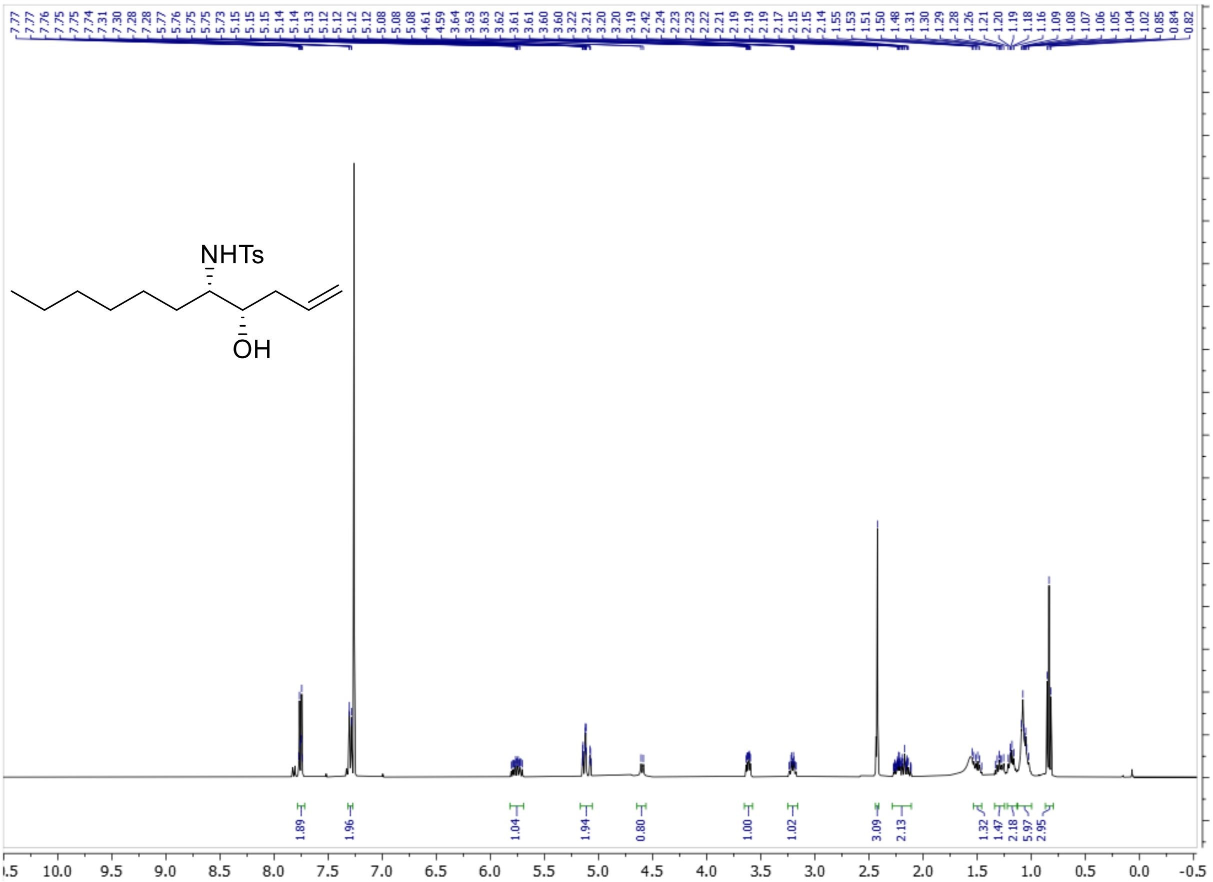


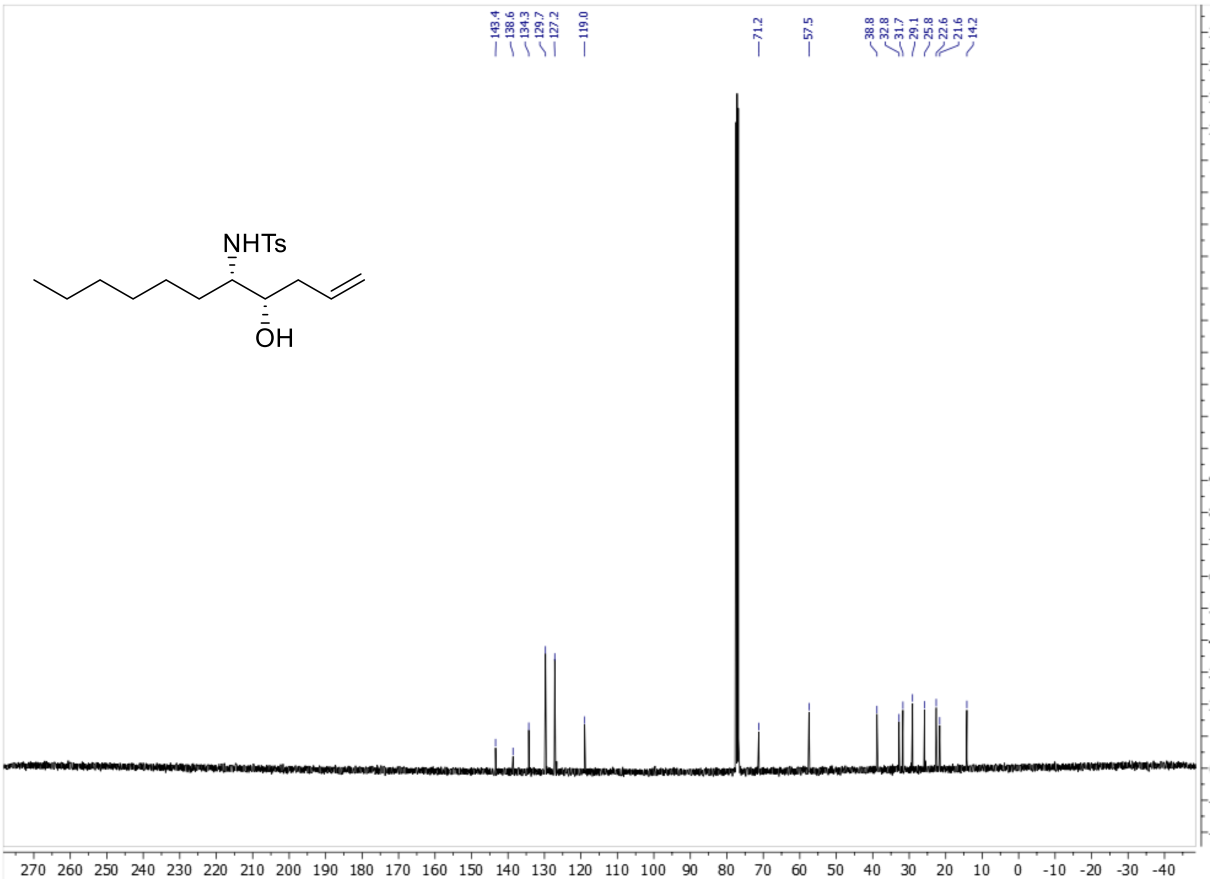
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **19**



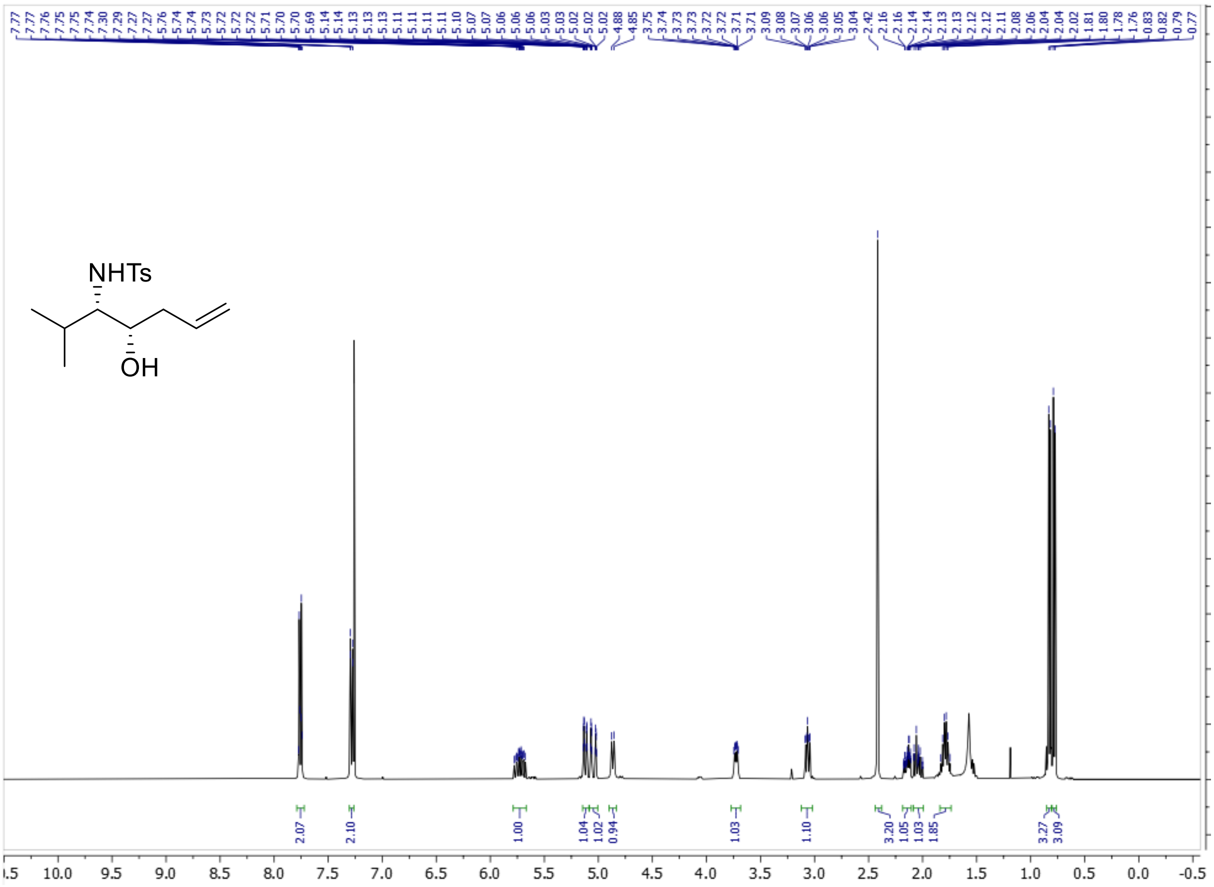


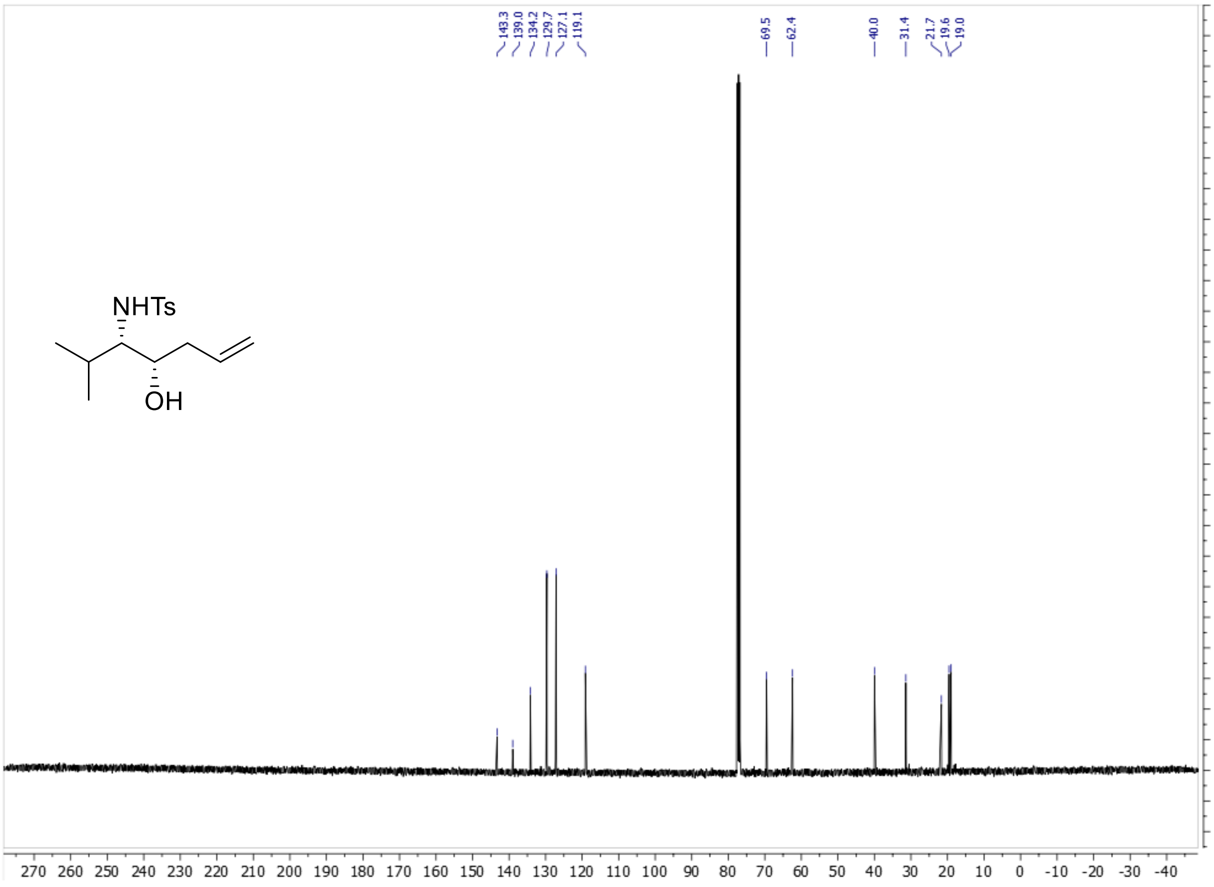
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **20**



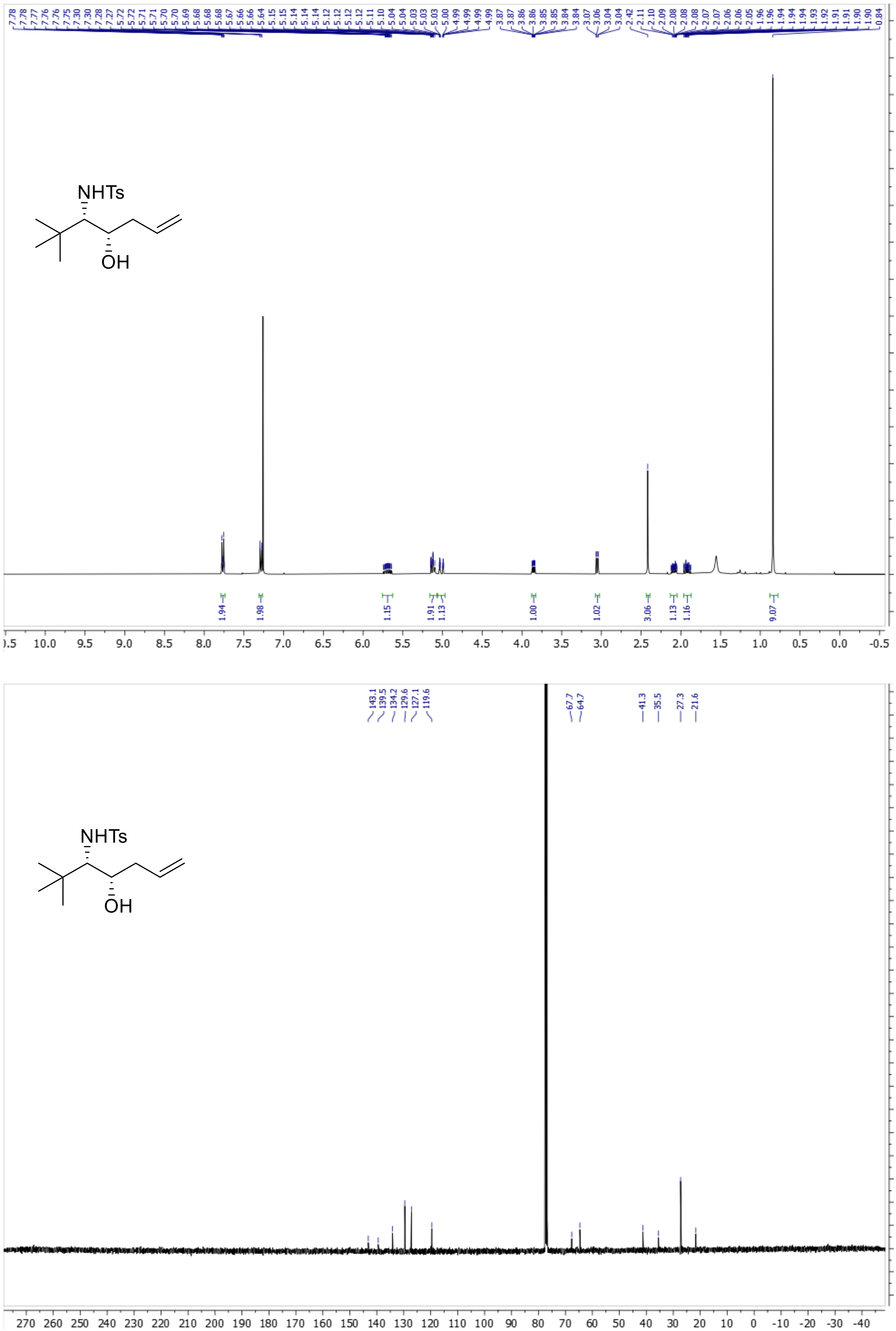


^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **21**





^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **22**



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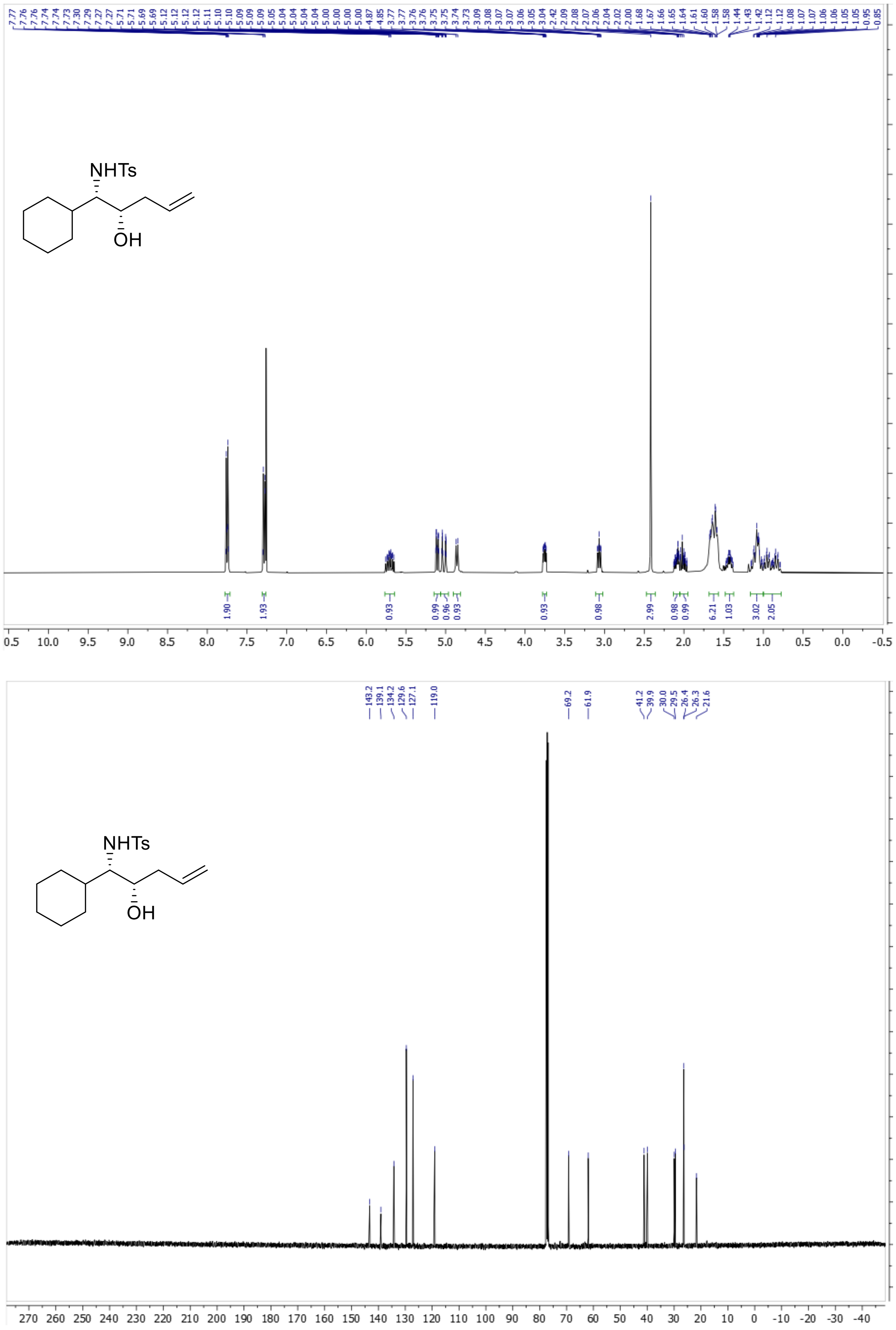
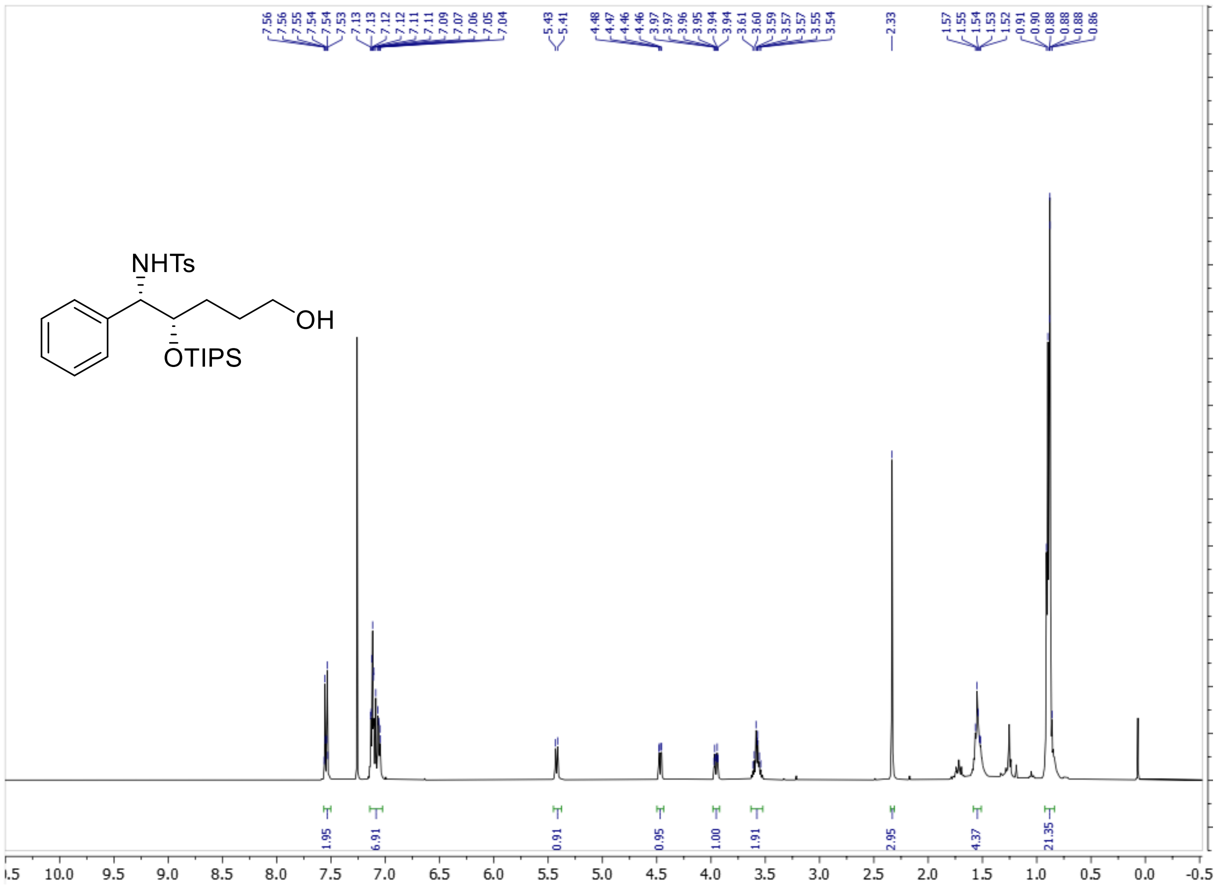
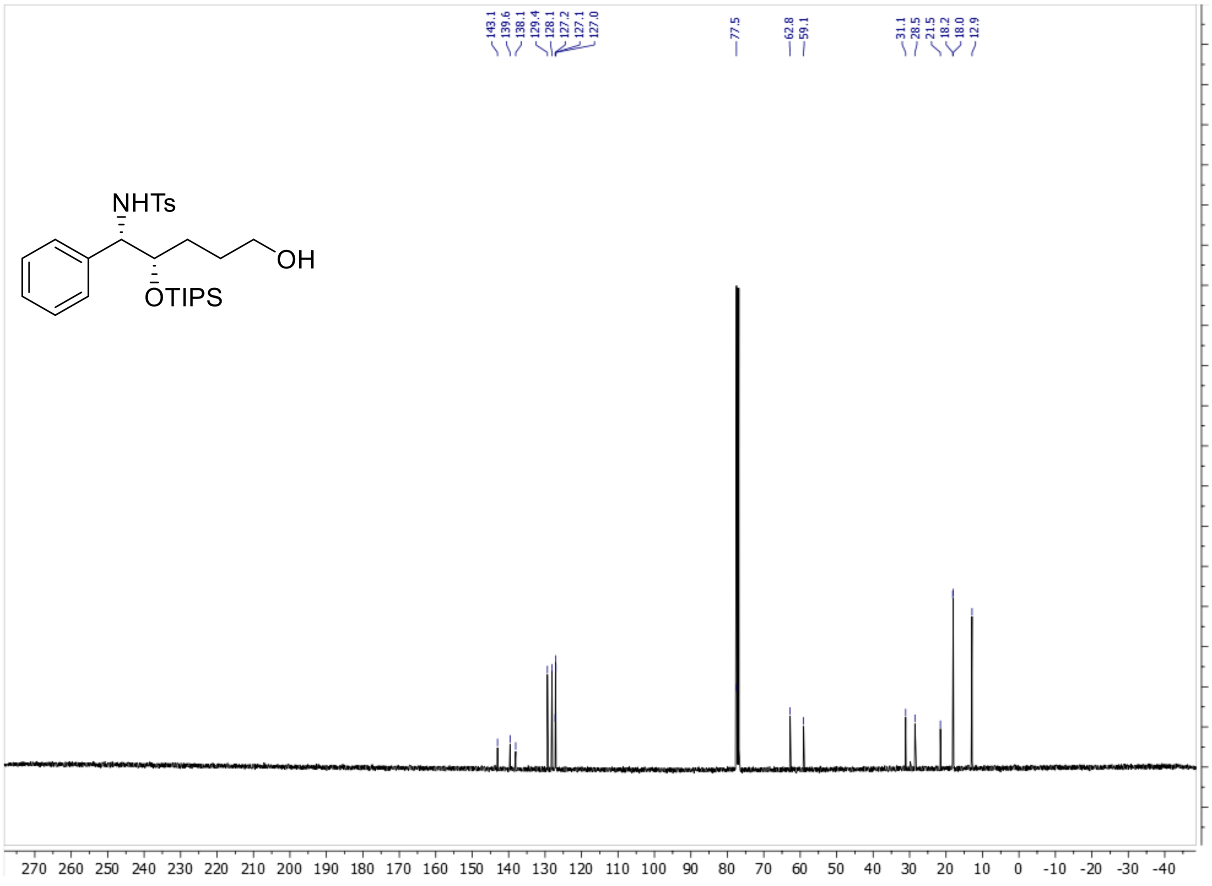
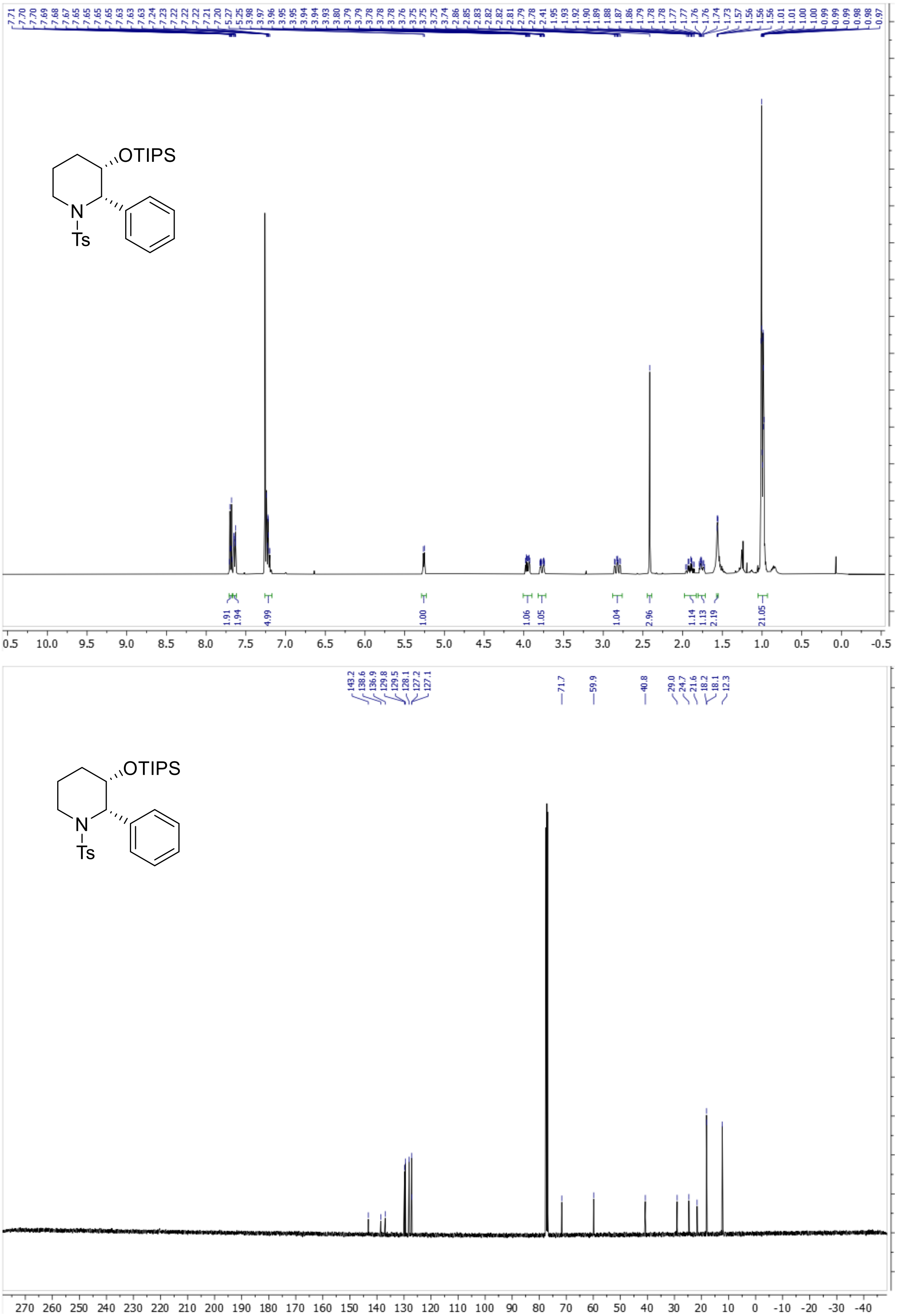


^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **24**

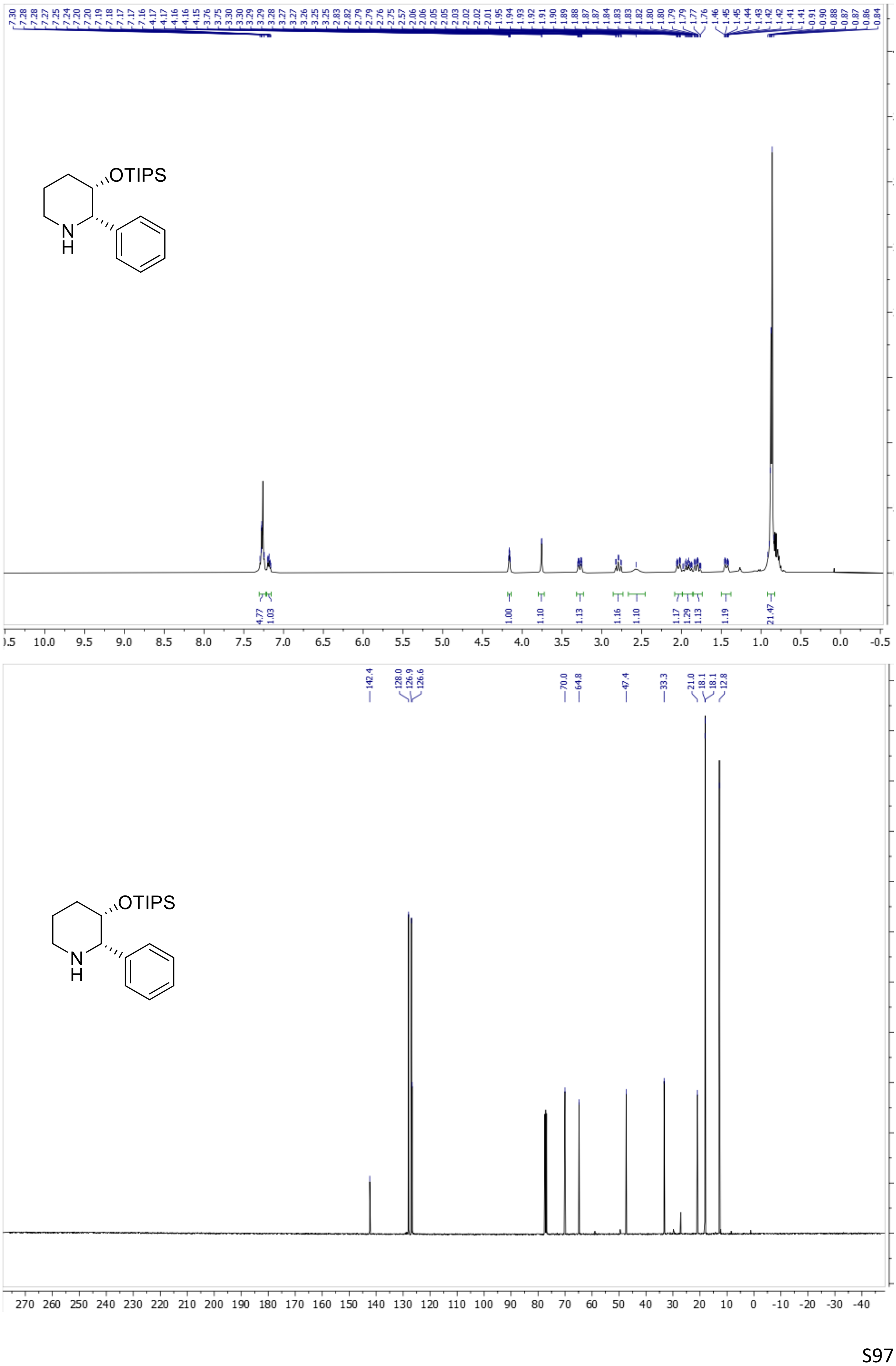




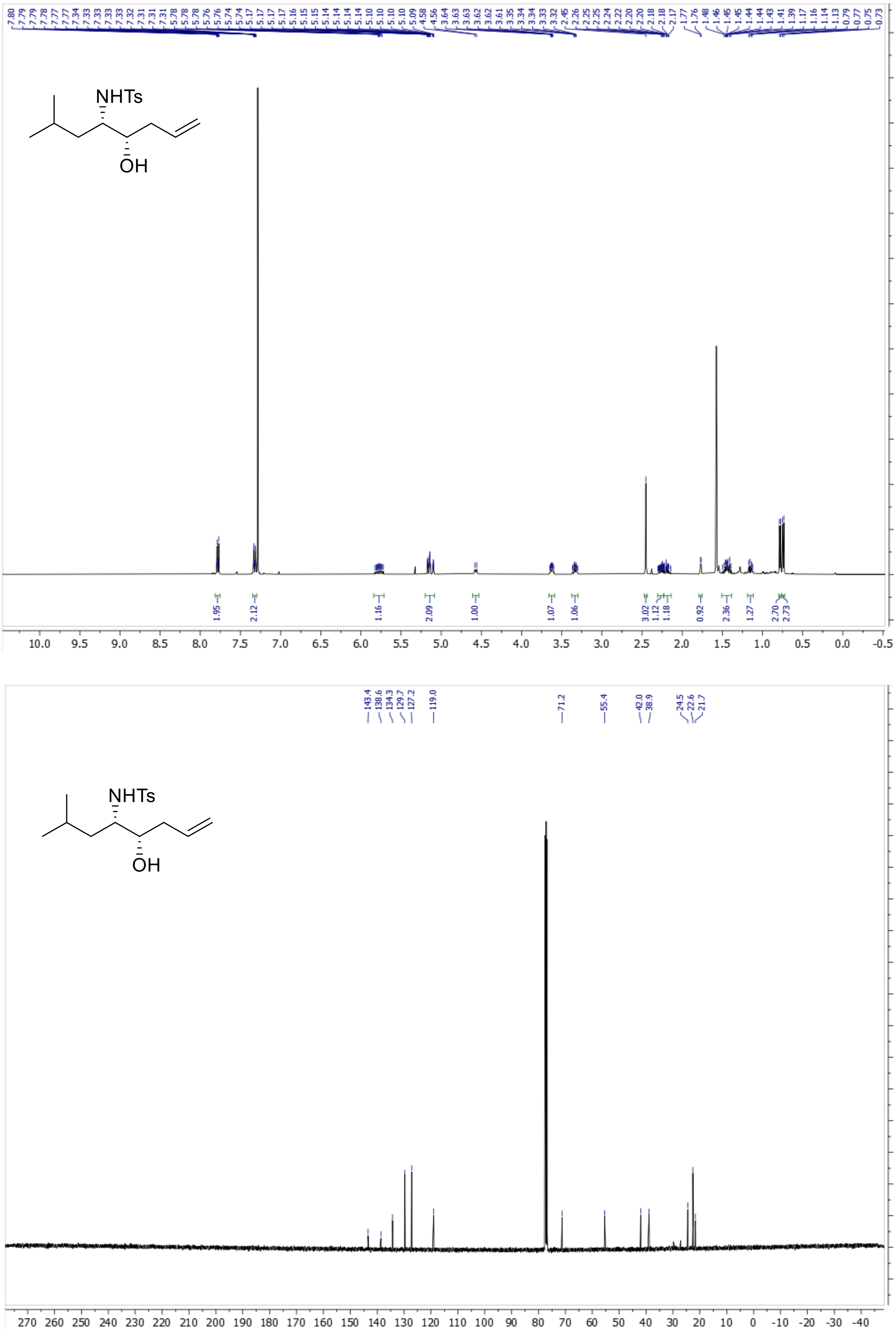
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **25**



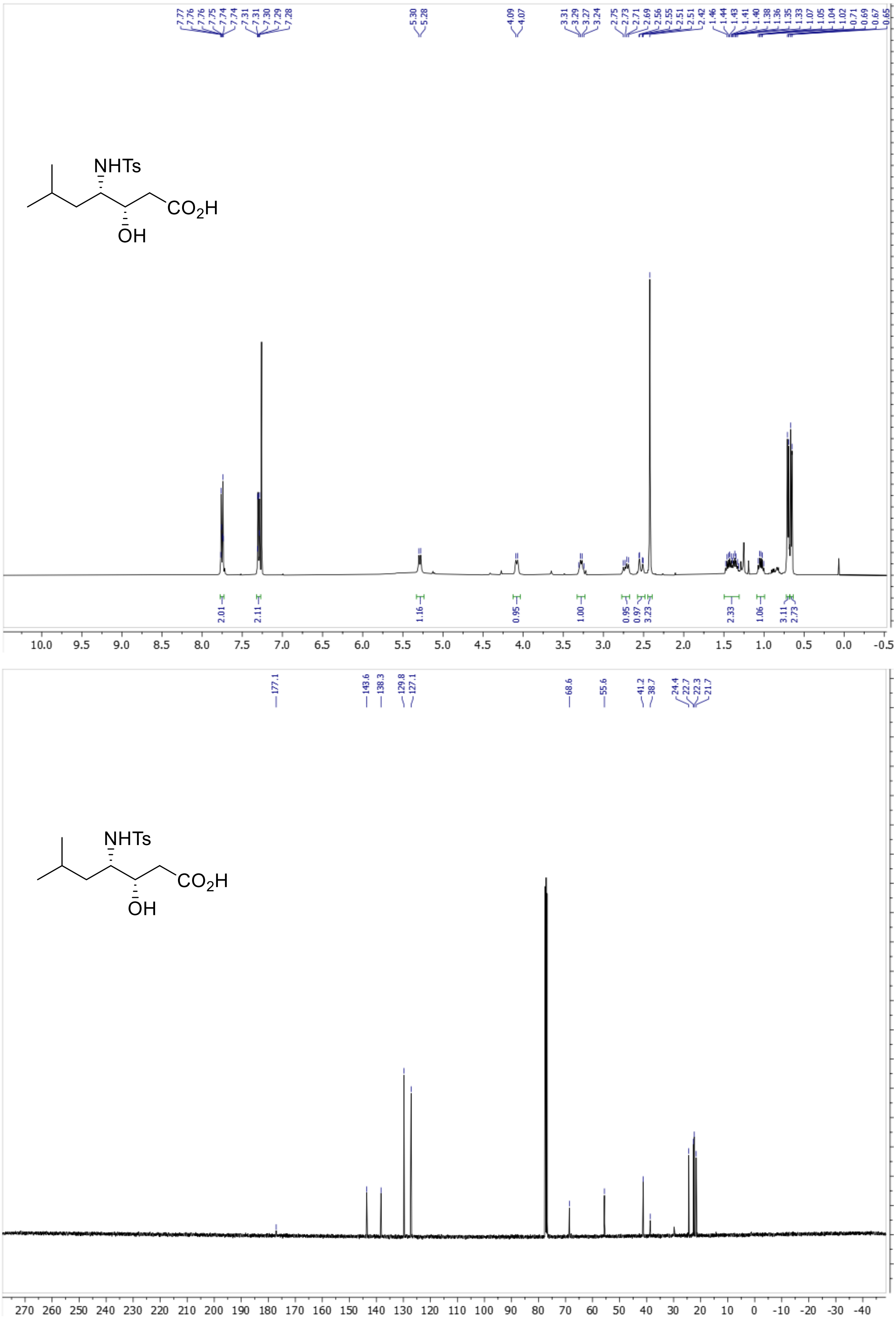
^{1}H NMR (400 MHz, $CDCl_3$; top) and ^{13}C NMR (101 MHz, $CDCl_3$; bottom) of compound **26**



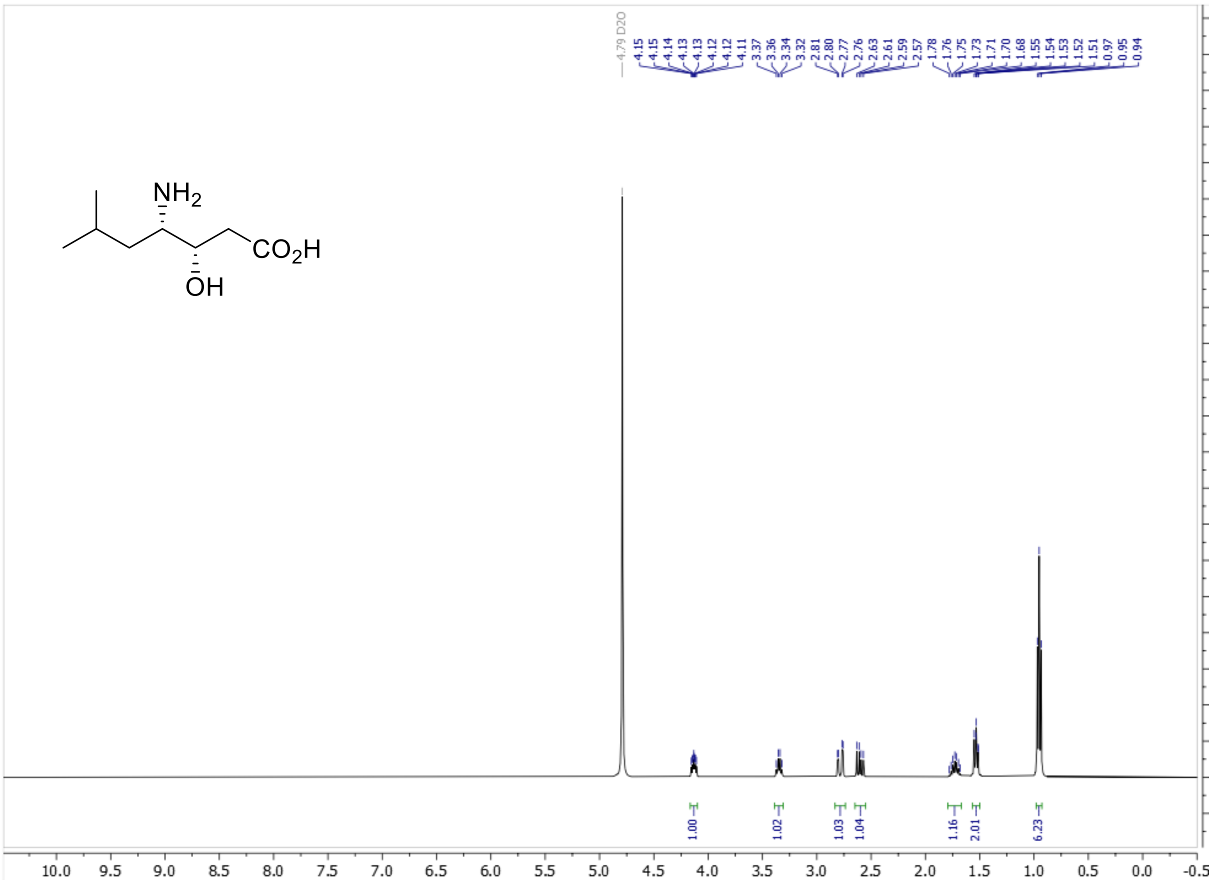
^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **28**

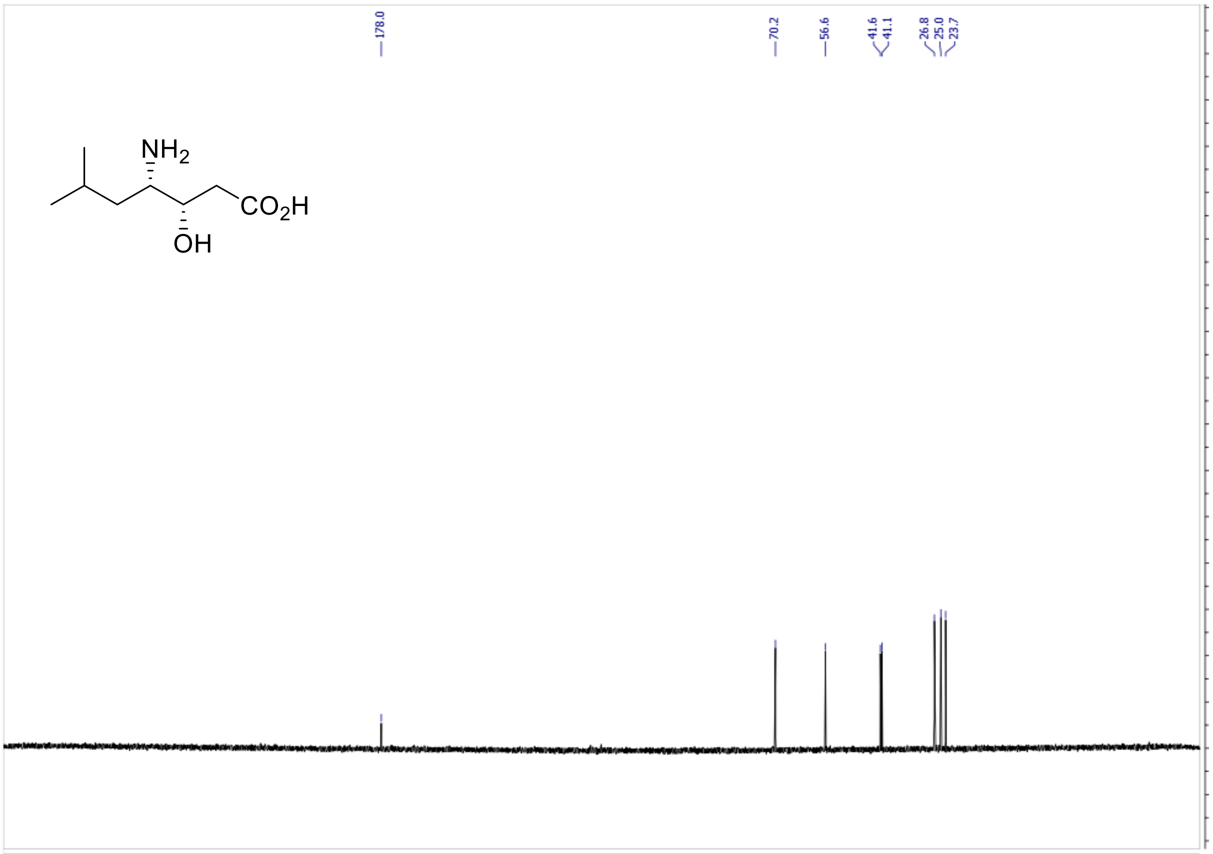


^{1}H NMR (400 MHz, CDCl$_3$; top) and ^{13}C NMR (101 MHz, CDCl$_3$; bottom) of compound **29**



^{1}H NMR (400 MHz, D_2O; top) and ^{13}C NMR (101 MHz, D_2O; bottom) of compound **30**





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