Electronic Supplementary Information (ESI)

Effective 1,5-stereocontrol in Pd(0)/InI promoted reactions of chiral *N*-Ts-4-vinylazetidin-2-ones with aldehydes. An efficient entry to nonracemic semi-protected (3*Z*)-2,6-*anti*-enediols.

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1. General Remarks.

The reagents were purchased from Sigma Aldrich, Alfa Aesar or ABCR and used without further purification. All reactions involving air- and moisture-sensitive materials were carried out under argon atmosphere in oven-dried glassware with magnetic stirring. THF was distilled from Na and benzophenone and CH_2Cl_2 from CaH_2. Column chromatography was performed with Kiesel gel (230-400 mesh). Analytical TLC was performed with Silica gel 60 F254 aluminum plates (Merck) with visualization by UV light and charring with aqueous $KMnO_4$ or Pancaldi reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O). NMR analyses were performed with Bruker 400 MHz Avance III or Bruker DRX 500 Avance spectrometers. Chemical shifts are calibrated using residual solvents signals (CDCl3: δ (H)= 7.26, δ (C)= 77.16) or TMS and are reported in ppm. Infrared spectra (IR) were recorded on a FT-IR-1600-Perkin Elmer spectrophotometer and are reported in frequency of absorption (cm^{-1}). HRMS spectra were recorded on ESI-TOF Mariner spectrometer (Perspective Biosystem) and are given in m/z. Melting points were measured on Melting Point Meter MPM-H2 apparatus and are uncorrected. Optical rotations [α] were measured on Jasco P-2000 Polarymeter for concentration [c] given in g/100 mL. HPLC analysis were performed on Hitachi/Merck HPLC system equipped with Hitachi L-2130 pump and Diode Array L2450 detector.

β-Lactams (±)-**1**,[1] (-)-**1**,[1] (±)-cis-3-isopropyl-4-vinylazetidin-2-one[2] and 4-hydroksybutyric aldehyde[3] were prepared according to literature procedures and their properties were consistent with the published data.

2. Experimental details and characterization data for β-lactams (±)-2, (-)-2, (±)-12; (3*Z*)-2,6-*anti*-enediols (±)-3a - (±)-11a, (+)-5a, (+)-7a; (3*E*)-2,6-*anti*-enediols (±)-3b - (±)-11b, homoallylic alcohols (±)-13a and (±)-13b; caprolactams (±)-15 and (±)-16; caprolactone (±)-17; 2,6- diols (±)-22 - (±)-23 and Mosher's esters 20, 21, 20/20' and 21/21'.

2.1. Syntheses of *N*-Ts-azetidin-2-ones (±)-2 and (-)-2.

To a solution of *N*-PMP-azetidin-2-one (±)-**1**, (-)-**1** (1.878 g, 5 mmol) in acetonitrile (200 mL) and water (40 mL) cooled to -10°C a solution of CAN (9.594 g, 17.5 mmol) in water (160 mL) was added dropwise within 15 min. The reaction was stirred at the same temperature for 3.5 h, quenched with saturated aqueous $Na_2S_2O_3$ solution (50 mL) and poured into water (500 mL). Aqueous layer was extracted with ethyl acetate (3 x 100 mL). Combined extracts were washed with water (300 mL) and brine (300 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Filtration of the residue through silica gel with CH_2Cl_2 (to remove quinone formed as the byproduct) afforded crude product which was then dissolved in toluene (25 mL) and added in one portion to a vigorously stirred mixture of TsCl (2.860 g, 15 mmol), TBAB (161.2 mg, 0.5 mmol) and solid NaOH (15g) in toluene (225 mL) at 25°C. After 30 min at the same temperature, excess of NaOH was filtered off and washed with a portion of toluene (50 mL). Combined filtrates were then washed with water (300 mL), dried over $MgSO_4$ and concentrated. Purification

of the crude product by column chromatography on silica gel using an ethyl acetate/hexane mixture as an eluant afforded *N*-Ts-azetidin-2-ones (±)-**2** and (-)-**2** as colorless crystals.

2.1.1 (3R,4S*)-1-Tosyl-3-(triisopropylsilyloxy)-4-vinylazetidin-2-one ((±)-**2**).* Yield: 1.631 g (77%); Yield: 1.631 g (77%); colorless crystals; mp = 73.0-73.9 ^{o}C; R*f* (10% ethyl acetate/hexane) 0.50; ^{1}H NMR (400 MHz, $CDCl_3$) *δ:* 7.88 – 7.81 (m, 2H), 7.38 – 7.29 (m, 2H), 5.78 – 5.62 (m, 1H), 5.48 (d, *J* = 16.9 Hz, 1H), 5.40 (d, *J* = 10.3 Hz, 1H), 5.05 (d, *J* = 5.7 Hz, 1H), 4.65 (dd, *J* = 8.8, 5.7 Hz, 1H), 2.44 (s, 3H), 1.13 – 0.96 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 164.6, 145.2, 136.2, 130.9, 129.9, 127.6, 122.9, 77.7, 64.6, 21.7, 17.5, 17.5, 11.7. IR (film) $\tilde{\nu}$: 3578, 2945, 2868, 1804, 1366, 1171, 1138, 884, 712 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{33}NO_4SiSNa$ [M + Na^{+}] 446.1797. Found. 446.1796.

*2.1.2 (3S,4R)-1-Tosyl-3-(triisopropylsilyloxy)-4-vinylazetidin-2-one ((-)-**2**).* Yield: 1.313 g (62%); colorless crystals; mp = 76.1-76.9 ^{o}C; R*f* (10% ethyl acetate/hexane) 0.50; $[\alpha]_D^{22}$ = -56.8 (*c* = 1.01 in $CHCl_3$); NMR and IR data are consistent with (±)-**2;** HRMS (ESI-TOF) m/z calcd for $C_{21}H_{33}NO_4SiSNa$ [M + Na^{+}] 446.1797. Found. 446.1793.

2.2. Synthesis of *N*-Ts-3-*i*Pr-azetidin-2-one (±)-12

To a vigorously stirred mixture of TsCl (191 mg, 3mmol), TBAB (32 mg, 0.1 mmol) and solid NaOH (4 g) in toluene (45 mL), (±)-cis-3-isopropyl-4-vinylazetidin-2-one (139 mg, 1 mmol) in toluene (5 mL) was added in one portion at 25^{o}C. After 30 min at the same temperature excess of NaOH was filtered off and washed with a portion of toluene (10 mL). Combined filtrates were then washed with water (100 mL), dried over $MgSO_4$ and concentrated. Purification of the crude product by column chromatography on silica gel using an ethyl acetate/hexane mixture as an eluant afforded β-lactam (±)-**12** as colorless crystals.

(3R,4S*)-3-Isopropyl-1-tosyl-4-vinylazetidin-2-one ((±)-**12**).* Yield: 217 mg (74%); colorless crystals; mp = 91.4-91.8 ^{o}C; R*f* (15% ethyl acetate/hexane) 0.60; ^{1}H NMR (400 MHz, $CDCl_3$) *δ:* 7.85 – 7.78 (m, 1H), 7.35 – 7.27 (m, 1H), 5.76 (ddd, *J* = 17.0, 10.2, 8.6 Hz, 1H), 5.48 (d, *J* = 17.0 Hz, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 4.53 (dd, *J* = 8.6, 6.6 Hz, 1H), 2.98 (dd, *J* = 11.0, 6.6 Hz, 1H), 2.42 (s, 3H), 2.00 – 1.84 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ:* 166.1, 145.1, 136.2, 131.6, 129.9, 127.5, 122.3, 61.2, 60.2, 25.4, 21.6, 21.1, 20.3. IR (film) $\tilde{\nu}$: 2963, 1787, 1364, 1169, 1090, 816, 664 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{29}H_{45}NO_6SSiNa$ [M + Na^{+}] 586.2635. Found 586.2639.

2.3. Pd/InI promoted additions of *N*-Ts-β-lactams (±)-2, and (-)-2 to aldehydes. Syntheses of (3*Z*)- and (3*E*)-2,6-*anti*-enediols (±)-3a - (±)-11a, (+)-5a, (+)-7a, (±)-3b - (±)-11b. General procedure.

To an a vigorously stirred solution of β-lactam (±)-**2**, (-)-**2** (50 mg, 0.118 mmol) and aldehyde (0.236 mmol) in anhydrous 25% THF/HMPA mixture (2 mL), InI (57mg, 0.236 mmol) was added in one portion followed by $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol) at 25^{o}C under argon atmosphere. After 30 min at the same temperature reaction was quenched with 1M aqueous HCl solution (2 mL), poured into water and extracted with CH_2Cl_2 (3 x 10 mL). Combined extracts were then washed with water (2 x 25 mL), dried over $MgSO_4$ and concentrated.

Purification of the crude product by column chromatography on silica gel using an acetone/hexane mixture as an eluant afforded 2,6-*anti*-enediols (±)-**3a** - (±)-**11a,** (±)-**3b** - **(±)-11b**, (+)-**5a**, (+)-**7a**.

2.3.1 (2R,6S*,Z)-6-Hydroxy-6-phenyl-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((±)-**3a**)*. Yield: 50.2 mg (80%); d.r. = 95:5; colorless crystals; mp = 79.5-81.5 ^{o}C; R*f* (20% acetone/hexane) 0.45; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.51 (s, 1H), 7.94 (m, 2H), 7.40 – 7.27 (m, 7H), 5.79 – 5.71 (m, 1H), 5.42 (dd, *J* = 10.1, 9.4 Hz, 1H), 4.95 (d, *J* = 9.4 Hz, 1H), 4.74 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.59 (m, 1H), 2.50 – 2.45 (m, 1H), 2.44 (s, 3H), 1.07 – 0.94 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.3, 145.1, 144.2, 135.4, 131.6, 129.6, 129.5, 128.5, 128.4, 127.6, 125.6, 73.0, 70.6, 39.2, 21.7, 17.8, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3486, 3350, 2944, 1737, 1409, 1122, 1088, 880 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{41}NO_5SiSNa$ [M + Na^+] 554.2372. Found 554.2364.

2.3.2. (2R,6R*,E)-6-Hydroxy-6-phenyl-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((±)-**3b**)*. Yield: 9.4 mg (15%); colorless oil; d.r. = 92:8; R*f* (20% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (s, 1H), 7.93 (m, 2H), 7.37 – 7.24 (m, 7H), 5.84 – 5.76 (m, 1H), 5.50 (dd, *J* = 15.4, 5.8 Hz, 1H), 4.67 (t, *J* = 6.5 Hz, 1H), 4.54 (d, *J* = 5.8 Hz, 1H), 2.50-2.46 (m, 2H), 2.43 (s, 3H), 1.12 – 0.88 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.6, 145.1, 143.5, 135.4, 130.5, 129.5, 129.5, 128.5, 128.4, 127.7, 125.8, 74.9, 73.4, 41.8, 21.6, 17.8, 11.9; IR (film) $\tilde{\nu}$: 3356, 2944, 1731, 1408, 1176, 1089, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{41}NO_5SiSNa$ [M + Na^+] 554.2372. Found 554.2363.

2.3.3. (2R,6S*,Z)-6-(4-Cyanophenyl)-6-hydroxy-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide((±)-**4a**)*.Yield: 52.2 mg (81%); d.r. = 95:5; colorless crystals; mp = 103.0-103.8 ^{o}C; R*f* (20% acetone/hexane) 0.30; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.33 (s, 1H), 7.95 (m, 2H), 7.63 (m, 2H), 7.49 (m, 2H), 7.34 (m, 2H), 5.75 (td, *J* = 10.7, 6.0 Hz, 1H)., 5.46 (dd, *J* = 10.7, 8.6 Hz, 1H), 4.93 (d, *J* = 8.6 Hz, 1H), 4.78 (dd, *J* = 9.1, 3.6 Hz, 1H), 2.56 – 2.46 (m, 2H), 2.45 (s, 3H), 1.04 – 0.98 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.8, 149.7, 145.4, 135.1, 132.3, 131.0, 130.2, 129.6, 128.4, 126.3, 118.8, 111.2, 72.1, 70.7, 39.4, 21.7, 17.8, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3475, 3348, 2944, 2228, 1735, 1410, 1176, 1087, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{40}N_2O_5SSiNa$ [M + Na^+] 579.2325. Found 579.2311.

2.3.4. (2R,6R*,E)-6-(4-Cyanophenyl)-6-hydroxy-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide((±)-**4b**)*. Yield: 11.2 mg (17%); d.r. = 94:6; colorless oil; R*f* (20% acetone/hexane) 0.25; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.92 (s, 1H), 7.93 (m, 2H), 7.63 (m, 2H), 7.43 (m, 2H), 7.33 (m, 2H), 5.82 – 5.74 (m, 1H), 5.52 (dd, *J* = 15.4, 5.7 Hz, 1H), 4.76 (dd, *J* = 7.4, 5.1 Hz, 1H), 4.53 (d, *J* = 5.7 Hz, 1H), 2.53 – 2.39 (m, 5H), 1.99 (br s,1H), 1.10 – 0.90 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.5, 148.7, 145.3, 135.3, 132.3, 130.6, 129.5, 129.4, 128.4, 126.5, 118.7, 111.4, 74.8, 72.5, 41.8, 21.7, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3491, 3353, 2944, 2228, 1731, 1408, 1176, 1089, 880 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{40}N_2O_5SSiNa$ [M + Na^+] 579.2325. Found 579.2322.

2.3.5. (2R,6S*,Z)-6-Hydroxy-6-(4-methoxyphenyl)-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((±)-**5a**)*.Yield: 49.1 mg (74%); d.r. = 93:7; colorless crystals; mp = 122.9-123.9 ^{o}C; R*f* (20% acetone/hexane) 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.54 (s, 1H), 7.94 (m, 2H), 7.37 – 7.25 (m, 4H), 6.88 (m, 2H), 5.73 (td, J = 10.6, 6.1 Hz, 1H), 5.41 (dd, J = 10.6, 8.8 Hz,

1H), 4.95 (d, *J* = 8.8 Hz, 1H), 4.70 (dd, *J* = 9.1, 3.8 Hz, 1H), 3.80 (s, 3H), 2.60 (dt, *J* = 14.0, 9.6 Hz, 1H). 2.47 – 2.39 (m, 4H), 1.08 – 0.97 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.2, 159.1, 145.1, 136.3, 135.5, 131.6, 129.6, 129.4, 128.4, 126.8, 113.9, 72.7, 70.6, 55.3, 39.1, 21.7, 17.8, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3485, 3349, 2944, 1737, 1513, 1409, 1176, 1088, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{43}NO_6SSiNa$ [M + Na^+] 584.2478. Found 584.2466.

*2.3.6. (2S,6R,Z)-6-Hydroxy-6-(4-methoxyphenyl)-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((+)-**5a**).* Yield: 49.8 mg (75%); d.r. = 93:7; colorless oil; R*f* (20% acetone/hexane) 0.35; $[\alpha]_D^{22}$ = +98.6 (*c* = 0.83 in $CHCl_3$); NMR and IR data are consistent with (±)-**5a**; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{43}NO_6SSiNa$ [M + Na^+] 584.2478. Found 584.2471.

2.3.7. (2R,6R*,E)-6-Hydroxy-6-(4-methoxyphenyl)-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((±)-**5b**).* Yield: 11.3 mg (17%); d.r. = 88:12; colorless oil; R*f* (20% acetone/hexane) 0.30; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (s, 1H), 7.92 (m, 2H), 7.31 (m, 2H), 7.22 (m, 2H), 6.87 (m, 2H), 5.82 – 5.73 (m, 1H), 5.48 (dd, *J* = 15.2, 5.7 Hz, 1H), 4.61 (t, *J* = 6.6 Hz, 1H), 4.53 (d, *J* = 5.7 Hz, 1H), 3.80 (s, 3H), 2.52 – 2.39 (m, 5H), 1.08 – 0.91 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.6, 159.2, 145.1, 135.6, 135.4, 130.7, 129.5, 129.3, 128.3, 127.1, 113.9, 75.0, 73.1, 55.3, 41.7, 21.6, 17.7, 11.9; IR (film) 3355, 2944, 1731, 1407, 1176, 1089, 880 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{43}NO_6SSiNa$ [M + Na^+] 584.2478. Found 584.2491.

2.3.8. (2R,6R*,Z)-6-Hydroxy-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide ((±)-**6a**).* Yield: 37.1 mg (65%); d.r. = 91:9; colorless oil; R*f* (20% acetone/hexane) 0.50; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.54 (s, 1H), 7.92 (m, 2H), 7.30 (m, 2H), 5.76 – 5.68 (m, 1H), 5.40 (dd, *J* = 10.5, 9.3 Hz, 1H), 4.93 – 4.91 (m, 1H), 3.60 – 3.53 (m, 1H), 2.50 (br s,1H), 2.42 (s, 3H), 2.27 – 2.22 (m, 2H), 1.59 – 1.45 (m, 2H), 1.11 – 0.99 (m, 21H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.4, 145.1, 135.4, 132.1, 129.5, 129.0, 128.4, 71.9, 70.4, 36.2, 30.6, 21.6, 17.8, 17.7, 11.9, 9.9; IR (film) $\tilde{\nu}$: 3508, 3351, 2943, 2867, 1738, 1464, 1176, 1122, 1088, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{41}NO_5SSiNa$ [M + Na^+] 506.2372. Found 506.2361.

2.3.9. (2R,6S*,E)-6-Hydroxy-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide ((±)-**6b**).* Yield: 18.8 mg (33%); d.r. = 79:21; colorless oil; R*f* (20% acetone/hexane) 0.45; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.96 (s, 1H), 7.93 (m, 2H), 7.32 (m, 2H), 5.89 – 5.80 (m, 1H), 5.49 (dd, *J* = 15.4, 5.9 Hz, 1H), 4.57 (d, *J* = 5.9 Hz, 1H), 3.56 – 3.48 (m, 1H), 2.43 (s, 3H), 2.24 (td, *J* = 14.1, 7.5 Hz, 1H), 2.12 (tt, *J* = 14.8, 7.5 Hz, 1H), 1.50 – 1.37 (m, 2H), 1.14 – 0.97 (m, 21H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.7, 145.1, 135.4, 131.3, 129.5, 129.2, 128.3, 75.0, 72.0, 39.6, 29.6, 21.6, 17.7, 11.9, 9.8; IR (film) $\tilde{\nu}$: 3356, 2943, 2868, 1732, 1408, 1177, 1089, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{41}NO_5SSiNa$ [M + Na^+] 506.2372. Found 506.2362.

2.3.10. (2R,6S*,Z)-6-Hydroxy-7-methyl-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide ((±)-**7a**).* Yield: 41.1 mg (70%); d.r. = 94:6; colorless oil; R*f* (30% acetone/hexane) 0.60; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.59 (s, 1H), 7.92 (m, 2H), 7.30 (m, 2H), 5.77 – 5.68 (m, 1H), 5.39 (dd, *J* = 10.6, 9.0 Hz, 1H), 4.92 (dd, *J* = 9.0, 0.9 Hz, 1H), 3.40 (dd, *J* = 11.9, 5.4 Hz, 1H), 2.58 (br s, 1H), 2.42 (s, 3H), 2.27 – 2.21 (m, 2H), 1.75 – 1.66 (m, 1H), 1.12 – 0.98 (m, 21H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.4, 145.0, 135.5, 132.6, 129.5, 128.8, 128.3, 75.3, 70.4, 34.0, 33.3, 21.6, 18.5, 17.8, 17.7, 17.5, 12.0; IR (film)

$\tilde{\nu}$: 3504, 3352, 2945, 1738, 1465, 1122, 1088, 876 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{43}NO_5SiNa$ [M + Na^+] 520.2529. Found 520.2523.

*2.3.11. (2S,6R,Z)-6-Hydroxy-7-methyl-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide ((+)-**7a**).* Yield: 39.9 mg (68%); d.r. = 94:6; colorless oil; R*f* (30% acetone/hexane) 0.60; $[\alpha]_D^{22}$ = +40.3 (*c* = 0.94 in $CHCl_3$); NMR and IR data consistent with (±)-**7a**; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{43}NO_5SiNa$ [M + Na^+] 520.2529. Found 520.2526.

2.3.12. (2R,6R*,E)-6-Hydroxy-7-methyl-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide ((±)-**7b**).* Yield: 15.9 mg (27%); d.r. = 85:15; colorless oil; R*f* (30% acetone/hexane) 0.55; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.95 (s, 1H), 7.93 (m, 2H), 7.32 (m, 2H), 5.85 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.50 (dd, *J* = 15.4, 5.5 Hz, 1H), 4.57 (d, *J* = 5.5 Hz, 1H), 3.37 – 3.31 (m, 1H), 2.43 (s, 3H), 2.28 – 2.20 (m, 1H), 2.15 – 2.05 (m, 1H), 1.67 – 1.58 (m, 1H), 1.13 – 0.98 (m, 21H), 0.91 (d, *J* = 4.2 Hz, 3H), 0.89 (d, *J* = 4.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.7, 145.1, 135.4, 131.8, 129.5, 129.1, 128.4, 75.4, 75.0, 37.1, 33.2, 21.6, 18.7, 17.8, 17.3, 11.9; IR (film) $\tilde{\nu}$: 3538, 3356, 2945, 1732, 1408, 1177, 1090, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{43}NO_5SiNa$ [M + Na^+] 520.2529. Found 520.2523.

2.3.13. (2R,6S*,Z)-6-Hydroxy-7,7-dimethyl-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide((±)-**8a**) and (2R*,6R*,E)-6-hydroxy-7,7-dimethyl-N-tosyl-2-(triisopropylsilyloxy)oct-3-enamide ((±)-**8b**), inseparable mixture.* Yield: 58.0 mg (96%, (±)-**8a**:(±)-**8b** = 82:18); d.r. = 97:3 ((±)-**8a)**, 92:8 ((±)-**8b)**; colorless oil; R*f* (30% acetone/hexane) 0.65; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.58 (s, $1H_a$), 8.96 (s, $1H_b$), 7.95 – 7.89 (m, 2H), 7.34 – 7.28 (m, 2H), 5.93 – 5.83 (m, $1H_b$), 5.73 (td, *J* = 10.7, 6.3 Hz, $1H_a$), 5.50 (dd, *J* = 15.5, 5.9 Hz, $1H_b$), 5.39 (dd, J = 10.7, 9.0 Hz, $1H_a$), 4.93 (dd, *J* = 9.0 Hz, $1H_a$), 4.57 (d, *J* = 5.9 Hz, $1H_b$), 3.26 (dd, *J* = 10.0, 1.8 Hz, $1H_a$), 3.18 (dd, *J* = 10.5, 2.0 Hz, $1H_b$), 2.43 (s, 3H), 2.35 – 2.10 (m, 2H), 1.15 – 0.99 (m, 21H), 0.93 (s, $9H_a$), 0.89 (s, $9H_b$); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.4, 169.7, 145.0, 135.5, 135.4, 133.2, 132.9, 129.5, 129.5, 128.9, 128.7, 128.4, 128.3,78.4, 78.3, 75.0, 70.3, 35.0, 34.8, 31.2, 25.7, 25.6, 21.6, 17.8, 17.7, 12.0, 11.9; IR (film) $\tilde{\nu}$: 3519, 3352, 2947, 2868, 1738, 1410, 1176, 1088, 880 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{45}NO_5SSiNa$ [M + Na^+] 534.2685. Found 534.2683.

2.3.14. (2R,6R*,Z)-6,9-Dihydroxy-N-tosyl-2-(triisopropylsilyloxy)non-3-enamide ((±)-**9a**).* Yield: 39.4 mg (65%); d.r. = 94:6; colorless oil; R*f* (40% acetone/hexane) 0.55; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.91 (m, 2H), 7.30 (m, 2H), 5.72 (dd, *J* = 10.6, 6.1 Hz, 1H), 5.39 (dd, *J* = 10.6, 9.0 Hz, 1H), 4.92 (d, *J* = 9.0 Hz, 1H), 3.82 – 3.61 (m, 3H), 2.83 (br s, 2H), 2.43 (s, 3H), 2.36 – 2.26 (m, 1H), 2.26 – 2.17 (m, 1H), 1.80 – 1.64 (m, 3H), 1.64 – 1.49 (m, 1H), 1.15 – 0.93 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.5, 145.0, 135.5, 131.8, 129.5, 129.1, 128.3, 70.5, 70.3, 62.9, 37.0, 35.4, 29.3, 21.6, 17.8, 17.7, 12.0; IR (film) $\tilde{\nu}$: 3509, 3349, 2943, 1737, 1464, 1122, 1088, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{43}NO_6SSiNa$ [M + Na^+] 536.2478. Found 536.2485.

2.3.15. (2R,6S*,E)-6,9-Dihydroxy-N-tosyl-2-(triisopropylsilyloxy)non-3-enamide ((±)-**9b**).* Yield: 12.1 mg (20%); d.r. = 82:18; colorless oil; R*f* (40% acetone/hexane) 0.50; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.04 (s, 1H), 7.92 (m, 2H), 7.32 (m, 2H), 5.90 – 5.80 (m, 1H), 5.49 (dd, *J* = 15.4, 5.9 Hz, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 3.73 – 3.60 (m, 3H), 2.64 (br s, 2H), 2.43 (s, 3H), 2.30 – 2.13 (m, 2H), 1.71 – 1.58 (m, 3H), 1.51 – 1.42 (m, 1H), 1.15 – 0.94 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.8, 145.2, 135.3, 131.3, 129.5, 129.3, 128.3, 75.1, 70.7, 62.8,

40.2, 33.8, 28.9, 21.6, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3356, 2925, 1730, 1176, 1089, 881 cm-1; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{43}NO_6SSiNa$ [M + Na^+] 536.2478. Found 536.2490.

2.3.16. (2R,6S*,Z)-6-(Furan-3-yl)-6-hydroxy-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((±)-**10a**)*. Yield: 43.1 mg (70%); d.r. = 95:5; colorless oil; R*f* (20% acetone/hexane) 0.45; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.40 (s, 1H), 7.92 (m, 2H), 7.37 – 7.35 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.34 – 6.29 (m, 1H), 6.27 – 6.24 (m, 1H), 5.77 – 5.69 (m, 1H), 5.44 (dd, *J* = 10.7, 8.7 Hz, 1H), 4.95 (d, *J* = 8.7 Hz, 1H), 4.73 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.32 (br s, 1H), 2.77 – 2.57 (m, 2H), 2.43 (s, 3H), 1.17 – 0.93 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.3, 156.0, 145.2, 141.9, 135.3, 130.8, 129.8, 129.5, 128.4, 110.1, 105.9, 70.7, 66.7, 35.4, 21.6, 17.8, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3351, 2944, 1733, 1408, 1177, 1087, 870 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{39}NO_6SSiNa$ [M + Na^+] 544.2165. Found 544.2175.

2.3.17. (2R,6R*,E)-6-(Furan-3-yl)-6-hydroxy-N-tosyl-2-(triisopropylsilyloxy)hex-3- enamide ((±)-**10b**)*. Yield: 11.1 mg (18%); d.r. = 94:6; colorless oil; R*f* (20% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.89 (s, 1H), 7.93 (m, 2H), 7.36 – 7.35 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.33 – 6.30 (m, 1H), 6.23 – 6.19 (m, 1H), 5.85 – 5.78 (m, 1H), 5.53 (dd, *J* = 15.5, 5.5 Hz, 1H), 4.67 (t, *J* = 6.6 Hz, 1H), 4.55 (d, *J* = 5.5 Hz, 1H), 2.64 – 2.53 (m, 2H), 2.43 (s, 3H), 1.13 – 0.91 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.5, 155.6, 155.3, 145.2, 142.1, 135.4, 129.7, 129.5, 128.4, 110.2, 106.3, 74.9, 67.0, 38.3, 21.7, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3357, 2944, 1731, 1407, 1177, 1089, 882 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{39}NO_6SSiNa$ [M + Na^+] 544.2165. Found 544.2172.

2.3.18. (2R,6S*,Z)-6-Hydroxy-8-methyl-N-tosyl-2-(triisopropylsilyloxy)nona-3,7-dienamide((±)-**11a**)*. Yield: 21.1 mg (35%); d.r. = 83:17; colorless oil; R*f* (20% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.69 (s, 1H), 7.91 (m, 2H), 7.30 (m, 2H), 5.74 – 5.67 (m, 1H), 5.42 – 5.37 (m, 1H), 5.22 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 8.9 Hz, 1H), 4.42 (td, *J* = 8.7, 3.9 Hz, 1H), 2.46-2.37 (m, 4 H), 2.25 – 2.17 (m, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 1.10 – 0.98 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.9, 144.9, 135.6, 135.6, 131.3, 129.5, 129.2, 128.3, 127.3, 70.4, 67.7, 36.9, 25.7, 21.6, 18.2, 17.8, 17.7, 12.0; IR (film) $\tilde{\nu}$: 3476, 3355, 2944, 1730, 1409, 1176, 1088, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{43}NO_5SSiNa$ [M + Na^+] 532.2529. Found. 532.2524.

2.3.19. (2R,6R*,E)-6-Hydroxy-8-methyl-N-tosyl-2-(triisopropylsilyloxy)nona-3,7-dienamide ((±)-**11b**)*. Yield: 36.1 mg (60%); d.r. = 76:24; colorless oil; R*f* (20% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.93 (s, 1H), 7.93 (m, 2H), 7.31 (m, 2H), 5.86 – 5.77 (m, 1H), 5.49 (dd, *J* = 15.4, 5.7 Hz, 1H), 5.14 (d, *J* = 8.6 Hz, 1H), 4.55 (d, *J* = 5.7 Hz, 1H), 4.38 – 4.30 (m, 1H), 2.43 (s, 3H), 2.34 – 2.15 (m, 2H), 1.71 (s, 3H), 1.66 (s, 3H), 1.14 – 0.93 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.6, 145.1, 136.0, 135.4, 130.7, 129.5, 128.9, 128.3, 127.0, 75.0, 67.7, 40.3, 25.7, 21.6, 18.2, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3357, 2944, 1733, 1408, 1176, 1089, 881 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{43}NO_5SSiNa$ [M + Na^+] 532.2529. Found. 532.2529.

2.4. Pd/InI promoted addition of *N*-Ts-3-*i*Pr-β-lactam (±)-12 to benzaldehyde. Syntheses of homoallylic alcohols (±)-13a and (±)-13b.

(±)-**13a** and (±)-**13b** were prepared according to general procedure **2.3** using *N*-Ts-β-lactam (±)-**12** (50 mg, 0.17 mmol), benzaldehyde (36 mg, 0.34 mmol), InI (82 mg, 0.34 mmol)

and $Pd(PPh_3)_4$ (9.8 mg, 0.0085 mmol) in anhydrous 25% THF/HMPA mixture (2.8 mL). The crude product was purified by column chromatography on silica gel using an acetone/hexane mixture as an eluant to give homoallylic alcohols (±)-**13a** and (±)-**13b** as colorless oils.

2.4.1. (2R,6S*,Z)-6-Hydroxy-2-isopropyl-6-phenyl-N-tosylhex-3-enamide ((±)-**13a**).* Yield: 52 mg (76%); colorless oil; R*f* (30% acetone/hexane) 0.45; ^{1}H NMR (500 MHz, $CDCl_3$) *δ:* 10.62 (s, 1H), 7.91 – 7.86 (m, 2H), 7.41 – 7.27 (m, 7H), 5.85 (td, *J* = 11.0, 5.5 Hz, 1H), 5.35 (t, *J* = 11.0 Hz, 1H), 4.82 (dd, *J* = 10.6, 2.0 Hz, 1H), 3.07 (dd, *J* = 11.2, 7.4 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.43 (s, 3H), 2.27 – 2.21 (m, 1H), 2.09 (dq, *J* = 13.6, 6.8 Hz, 1H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ:* 170.8, 144.3, 143.7, 136.3, 131.0, 129.4, 128.8, 128.4, 128.2, 128.1, 125.5, 74.1, 51.8, 37.5, 27.5, 21.6, 21.1, 19.0; IR (film) $\tilde{\nu}$: 3488, 3250, 3030, 2960, 1720, 1452, 1173, 1086, 877, 660 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{27}NO_4SNa$ [M + Na^+] 424.1558. Found. 424.1552.

2.4.2. (2R,6R*,E)-6-Hydroxy-2-isopropyl-6-phenyl-N-tosylhex-3-enamide ((±)-**13b**).* Yield: 15 mg (22%); colorless oil; R*f* (30% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) *δ:* 9.58 (s, 1H), 7.94 – 7.88 (m, 2H), 7.40 – 7.27 (m, 7H), 5.70 – 5.62 (m, 1H), 5.49 (dd, *J* = 15.3, 9.7 Hz, 1H), 4.73 (dd, *J* = 8.8, 4.8 Hz, 1H), 2.73 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.49 – 2.40 (m, 6H), 2.17 (dq, *J* = 13.4, 6.8 Hz, 1H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ:* 171.5, 144.7, 143.7, 135.9, 134.2, 129.4, 128.6, 128.3, 128.0, 127.9, 125.7, 73.5, 57.2, 42.4, 28.7, 21.6, 20.7, 18.3; IR (film) $\tilde{\nu}$: 3501, 3245, 2961, 1714, 1451, 1172, 1086, 873, 660 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{27}NO_4SNa$ [M + Na^+] 424.1558. Found. 424.1554.

2.5. Synthesis of (2R*,6S*,Z)-6-hydroxy-N-methyl-6-phenyl-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide (±)-14

To a vigorously stirred solution of (*Z*)-2,6-*anti*-enediol (±)-**3a** (532 mg, 1 mmol) and TBAB (32 mg, 0.1 mmol) in MeI (5 mL), K_2CO_3 (2 g) was added in one portion at 25^{o}C. After 12 h at the same temperature excess of K_2CO_3 was filtered off and washed with CH_2Cl_2 (20 ml). Combined filtrates were then concentrated under reduced pressure. Purification of the crude product by column chromatography on silica gel using an ethyl acetate/hexane mixture as an eluant afforded (2R*,6S*,Z)-6-hydroxy-N-methyl-6-phenyl-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide **(±)-14** as colorless oil.

(2R,6S*,Z)-6-Hydroxy-N-methyl-6-phenyl-N-tosyl-2-(triisopropylsilyloxy)hex-3-enamide ((±)-**14**).* Yield: 464 mg (85%); colorless oil; R*f* (30% ethyl acetate/hexane) 0.70; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.86 (m, 2H), 7.39 – 7.21 (m, 7H), 5.67 – 5.53 (m, 2H), 5.25 (d, *J* = 6.2 Hz, 1H), 4.53 (dd, *J* = 7.9, 5.5 Hz, 1H), 3.48 (s, 3H), 2.54 (dt, *J* = 15.6, 7.9 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.38 (s, 3H), 1.82 (br s, 1H), 1.07 – 0.90 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ*: 171.8, 144.7, 143.9, 135.6, 131.2, 129.3, 129.3, 128.6, 128.4, 127.6, 125.7, 74.3, 73.4, 38.0, 32.6, 21.6, 17.7, 17.7, 11.9; IR (film) $\tilde{\nu}$: 3540, 2944, 1690, 1359, 1172, 1088, 864 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{43}NO_5SSiNa$ [M + Na^+] 568.2529. Found 568.2524.

2.6. Synthesis of (±)-7-phenyl-1-tosyl-3-(triisopropylsilyloxy)-6,7-dihydro-1H-azepin-2(5H)-one ((±)-15).

To a solution of (*Z*)-2,6-*anti*-enediol (±)-**3a** (53.2 mg, 0.1 mmol) and PPh_3 (79 mg, 0.3 mmol) in anhydrous THF (3mL), DIAD (neat, 49 μL, 0.25 mmol) was added dropwise under argon atmosphere at 25°C and reaction mixture was then refluxed for 1h. After cooled to 25°C and evaporation of solvent under reduced pressure, crude product was purified by column chromatography on silica gel using an ethyl acetate/hexane mixture as an eluant to afford (±)-7-phenyl-1-tosyl-3-(triisopropylsilyloxy)-6,7-dihydro-1H-azepin-2(5H)-one ((±)-**15**) as colorless oil.

*(±)-7-Phenyl-1-tosyl-3-(triisopropylsilyloxy)-6,7-dihydro-1H-azepin-2(5H)-one ((±)-**15**)*. Yield: 23.6 mg (46%); colorless oil; R*f* (30% ethyl acetate/hexane) 0.50; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (m, 2H), 7.47 – 7.34 (m, 5H), 7.06 (m, 2H), 5.82 (dd, J = 8.1, 5.5 Hz, 1H), 5.38 (dd, J = 10.8, 4.1 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.38 – 2.28 (m, 5H), 2.27 – 2.18 (m, 1H), 1.21 – 0.95 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 164.9, 143.4, 142.6, 138.8, 138.1, 128.7, 128.6, 128.4, 127.2, 126.3, 117.8, 84.1, 36.1, 21.4, 21.1, 17.9, 12.5; IR (film) $\tilde{\nu}$: 2945, 1730, 1597, 1459, 1160, 1089, 883 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{39}NO_4SSiNa$ [M + Na^+] 536.2267. Found 536.2263.

2.7. Synthesis of (±)-cis-7-phenyl-3-(triisopropylsilyloxy)-6,7-dihydro-1H-azepin-2(3H)-one ((±)-16).

To a solution of *N*-Me-(*Z*)-2,6-*anti*-enediol (±)-**14** (109 mg, 0.2 mmol), diphenylphosphoryl azide (65 μL, 0.3 mmol) and PPh_3 (157 mg, 0.6 mmol) in anhydrous THF (15 mL), DIAD (neat, 99 μL, 0.5 mmol) was added dropwise at 0°C under argon atmosphere. After 15 min reaction mixture was warmed to 25°C and stirred for additional 24 h. Removal of solvent under reduced pressure and filtration of the residue through a pad of silica gel with CH_2Cl_2 afforded crude azide which was then dissolved in THF (1 mL) and added in one portion to a vigorously stirred suspension of Zn dust (131 mg, 2 mmol) in THF (1 mL) at 25°C. To the so obtained reaction mixture AcOH (92 μL,1.6 mmol) was added dropwise at the same temperature and after 15 min reaction mixture was refluxed for 2 h. After cooled to 25°C, Zn dust excess was filtered off and washed with CH_2Cl_2 (5 mL). Solvents were then removed under reduced pressure and crude product was purified by column chromatography on silica gel using an ethyl acetate/hexane mixture as an eluant to afford (±)-cis-7-phenyl-3-(triisopropylsilyloxy)-6,7-dihydro-1H-azepin-2(3H)-one ((±)-**16**) as colorless crystals.

*(±)-cis-7-Phenyl-3-(triisopropylsilyloxy)-6,7-dihydro-1H-azepin-2(3H)-one ((±)-**16**)*. Yield: 29.5 mg (41%); colorless crystals; mp = 99.5-100.6 °C; R*f* (30% ethyl acetate/hexane) 0.60; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 – 7.31 (m, 5H), 5.71 – 5.57 (m, 4H), 4.90 – 4.82 (m, 1H), 2.68 – 2.43 (m, 2H), 1.26 – 1.04 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.1, 140.2, 131.6, 129.2, 128.5, 126.3, 126.0, 68.8, 53.9, 36.9, 17.9, 12.2; IR (film) $\tilde{\nu}$: 3236, 3030, 2942, 2865, 1691, 1146, 884 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{33}NO_2SiNa$ [M + Na^+] 382.2178. Found 382.2189.

2.8. Synthesis of (±)-trans-7-phenyl-3-(triisopropylsilyloxy)-6,7-dihydrooxepin-2(3H)-one ((±)-17).

To a solution of *N*-Me-(*Z*)-2,6-*anti*-enediol (±)-**14** (55 mg, 0.1 mmol) in anhydrous THF (5 mL), 1M solution of NaHMDS in THF (110 uL, 0.11 mmol) was added dropwise at -30°C. After 15 min at the same temperature, reaction was quenched with saturated aqueous solution of NH_4Cl (5 mL), poured into water and extracted with Et_2O (3 x 10 mL). Combined extracts were then washed with brine (30 mL), dried over $MgSO_4$ and concentrated. Purification

of the crude product by column chromatography on silica gel using an ethyl acetate/hexane mixture as an eluant afforded (±)-trans-7-phenyl-3-(triisopropylsilyloxy)-6,7-dihydrooxepin-2(3H)-one ((±)-**17**) as colorless oil.

*(±)-trans-7-Phenyl-3-(triisopropylsilyloxy)-6,7-dihydrooxepin-2(3H)-one ((±)-**17**).* Yield: 22.7 mg (63%); colorless oil; R*f* (20% ethyl acetate/hexane) 0.80; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 – 7.30 (m, 5H), 6.71 (br d, J = 11.3 Hz, 1H), 6.08 – 5.95 (m, 2H), 4.93 (d, J = 7.3 Hz, 1H), 2.81 (ddt, J = 19.6, 11.3, 2.2 Hz, 1H), 2.62 (dd, J = 19.6, 5.1 Hz, 1H), 1.36 – 1.00 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.5, 139.6, 134.8, 128.6, 128.3, 126.2, 125.0, 76.6, 71.7, 38.5, 17.8, 17.8, 12.0; IR (film) $\tilde{\nu}$: 3032, 2944, 1741, 1463, 1274, 1060, 882 cm^{-1}: HRMS (ESI-TOF) m/z calcd for $C_{21}H_{32}O_3SiNa$ [M + Na^+] 383.2018. Found 383.2016.

2.9. Syntheses of 2,6-diols (±)-22 and (±)-23

To a solution of 2,6-*anti*-enediol (±)-**5a**, (±)-**5b** (28.1 mg, 0.05 mmol) in toluene (2 mL), PtO_2 (1.1 mg, 0.005 mmol) was added in one portion at 25 ^{o}C and the resulting suspension was saturated with H_2. After 24 h at the same temperature reaction mixture was diluted with toluene (5 mL) and filtered through the pad of Celite. Removal of solvent under reduced pressure and purification of the crude product by column chromatography on silica gel using an acetone/hexane mixture as an eluant afforded saturated 1,5-diols (±)-**23** - (±)-**24** as colorless oils.

2.9.1. (2R,6S*)-6-Hydroxy-6-(4-methoxyphenyl)-N-tosyl-2-(triisopropylsilyloxy)hexanamide ((±)-**22**).* Yield: 27.1 mg (96%); d.r. = 92:8; colorless oil; R*f* (25% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.93 (s, 1H), 7.97-7.89 (m, 2H), 7.35-7.28 (m, 2H), 7.24-7.16 (m, 2H), 6.90-6.83 (m, 2H), 4.50 (t, J = 6.7 Hz, 1H), 4.18 (dd, J = 5.9, 4.0 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 1.86 – 1.67 (m, 3H), 1.63 – 1.48 (m, 2H), 1.39 – 1.27 (m, 1H), 1.24 – 1.12 (m, 1H). 1.09 – 0.90 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 159.1, 145.1, 136.6, 135.5, 129.5, 128.3, 127.0, 113.9, 73.8, 73.6, 55.3, 38.6, 35.0, 21.6, 19.7, 17.8, 17.8, 12.0; IR (film) $\tilde{\nu}$: 3529, 3356, 2944, 2867, 1730, 1513, 1406, 1170, 881 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{29}H_{45}NO_6SSiNa$ [M + Na^+] 586.2635. Found 586.2635.

2.9.2. (2R,6R*)-6-Hydroxy-6-(4-methoxyphenyl)-N-tosyl-2-(triisopropylsilyloxy)hexanamide ((±)-**23**).* Yield: 26.2 mg (93%); d.r. = 91:9; colorless oil; R*f* (25% acetone/hexane) 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.94 (s, 1H), 7.93 (m, 2H), 7.31 (m, 2H), 7.21 (m, 2H), 6.87 (m, 2H), 4.51 (dd, J = 7.3, 5.6 Hz, 1H), 4.18 (dd, J = 5.9, 4.1 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 1.81 – 1.66 (m, 3H), 1.61 – 1.47 (m, 2H), 1.34 – 1.20 (m, 2H), 1.09 – 0.95 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 171.4, 159.1, 145.1, 136.7, 135.5, 129.5, 128.4, 127.0, 113.9, 73.8, 73.7, 55.3, 38.6, 35.1, 21.6, 19.8, 17.8, 17.8, 12.0; IR (film) $\tilde{\nu}$: 3533, 3357, 2944, 2867, 1730, 1513, 1406, 1171, 881 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{29}H_{45}NO_6SSiNa$ [M + Na^+] 586.2635. Found 586.2639.

2.7. Syntheses of Mosher's esters 20 and 21. General procedure.

To a solution of (*Z*)-2,6-*anti*-enediol (+)-**5a**, (+)-**7a**, (±)-**5a**, (±)-**7a,** (0.01 mmol), DMAP (0.3 mg; 0.0025 mmol) and Et_3N (5.6 μL, 0.04 mmol) in anhydrous CH_2Cl_2 (0.6 mL), 1M solution of (+)-MTPACl in CH_2Cl_2 (11 μL, 0.011 mmol) was added dropwise at 25^{o}C. After 1h at the same temperature, reaction was quenched with saturated aqueous solution of NH_4Cl (0.5 mL), poured into water (10 mL) and extracted with CH_2Cl_2 (3 x 5 mL). Combined extracts were then washed with brine (15 mL), dried over $MgSO_4$ and concentrated. Filtration of the crude product through pad of silica gel with

an acetone/hexane mixture afforded Mosher's esters **20**, **21** and inseparable mixtures of diastereoisomers **20**/**20'** and **21**/**21'** as colorless oils.

*2.7.1. (R)-((1R,5S,Z)-1-(4-Methoxyphenyl)-6-(4-methylphenylsulfonamido)-6-oxo-5-(triisopropylsilyloxy)hex-3-enyl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**20**).* Yield: 5.6 mg (72%); d.r. = 92:8; ee > 99%; colorless oil; R*f* (30% acetone/hexane) 0.55; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.40 (anti-**20**), -71.60 (syn-**20**), -71.68 (anti-**20'**); HRMS (ESI-TOF) m/z calcd for $C_{39}H_{50}NO_8F_3SSiNa$ [M + Na^+] 800.2876. Found 800.2859.

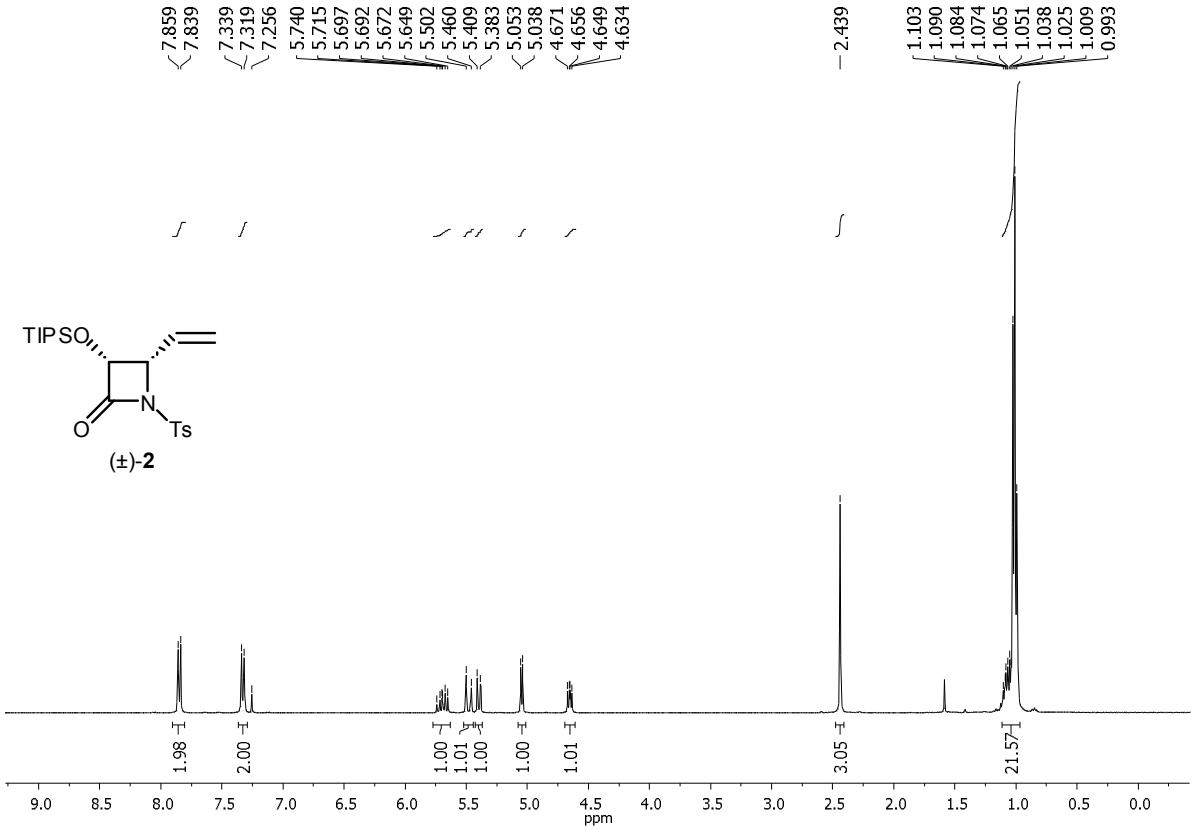
*2.7.2. (R)-((1R,5S,Z)-1-(4-Methoxyphenyl)-6-(4-methylphenylsulfonamido)-6-oxo-5-(triisopropylsilyloxy)hex-3-enyl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**20**) and (R)-((1S,5R,Z)-1-(4-methoxyphenyl)-6-(4-methylphenylsulfonamido)-6-oxo-5-(triisopropylsilyloxy)hex-3-enyl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**20'**), inseparable mixture.* Yield: 5.2 mg (67%, **20**:**20'** = 1:1); d.r.(**20**) = 92:8, d.r. (**20'**) = 92:8; colorless oil; R*f* (30% acetone/hexane) 0.55; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.38 (syn-**20'**), -71.41 (anti-**20**), -71.60 (syn-**20**), -71.68 (anti-**20'**); HRMS (ESI-TOF) m/z calcd for $C_{39}H_{50}NO_8F_3SSiNa$ [M + Na^+] 800.2876. Found 800.2856.

*2.7.3. (R)-((3R,7S,Z)-2-Methyl-8-(4-methylphenylsulfonamido)-8-oxo-7-(triisopropylsilyloxy)oct-5-en-3-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**21**).* Yield: 4.6 mg (65%); d.r. = 95:5; ee> 99% colorless oil; R*f* (30% acetone/hexane) 0.60; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.17 (anti-**21'**), -71.25 (syn-**21**), -71.27 (anti-**21**); HRMS (ESI-TOF) m/z calcd for $C_{35}H_{50}NO_7F_3SSiNa$ [M + Na^+] 736.2927. Found 736.2917

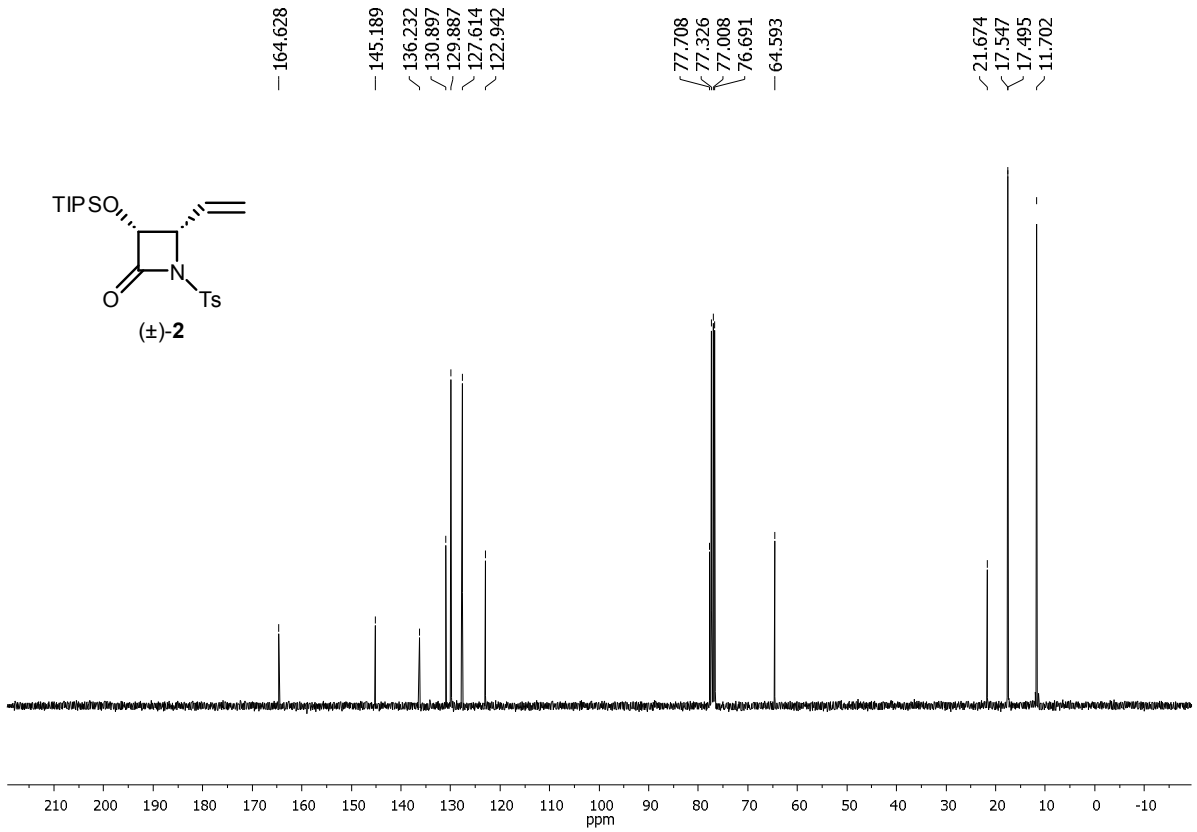
*2.7.4. (R)-((3R,7S,Z)-2-Methyl-8-(4-methylphenylsulfonamido)-8-oxo-7-(triisopropylsilyloxy)oct-5-en-3-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**21**) and (R)-((3S,7R,Z)-2-methyl-8-(4-methylphenylsulfonamido)-8-oxo-7-(triisopropylsilyloxy)oct-5-en-3-yl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (**21'**), inseparable mixture.* Yield: 4.8 mg (67%, **21**:**21'** = 1:1); d.r. = 95:5 (**21**), 95:5 (**21'**); colorless oil; R*f* (30% acetone/hexane) 0.60; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.17 (anti-**21'**), -71.25 (syn-**21**), -71.27 (anti-**21**), -71.29 (syn-**21'**); HRMS (ESI-TOF) m/z calcd for $C_{35}H_{50}NO_7F_3SSiNa$ [M + Na^+] 736.2927. Found 736.2917.

3. ^{1}H and ^{13}C NMR spectra for β-lactams (±)-2, (-)-2, (±)-12; (3*Z*)-2,6-*anti*-enediols (±)-3a - (±)-11a, (+)-5a, (+)-7a; (3*E*)-2,6-*anti*-enediols (±)-3b - (±)-11b, homoallylic alcohols (±)-13a and (±)-13b; caprolactams (±)-15 and (±)-16; caprolactone (±)-17 and 2,6- diols (±)-22 - (±)-23.

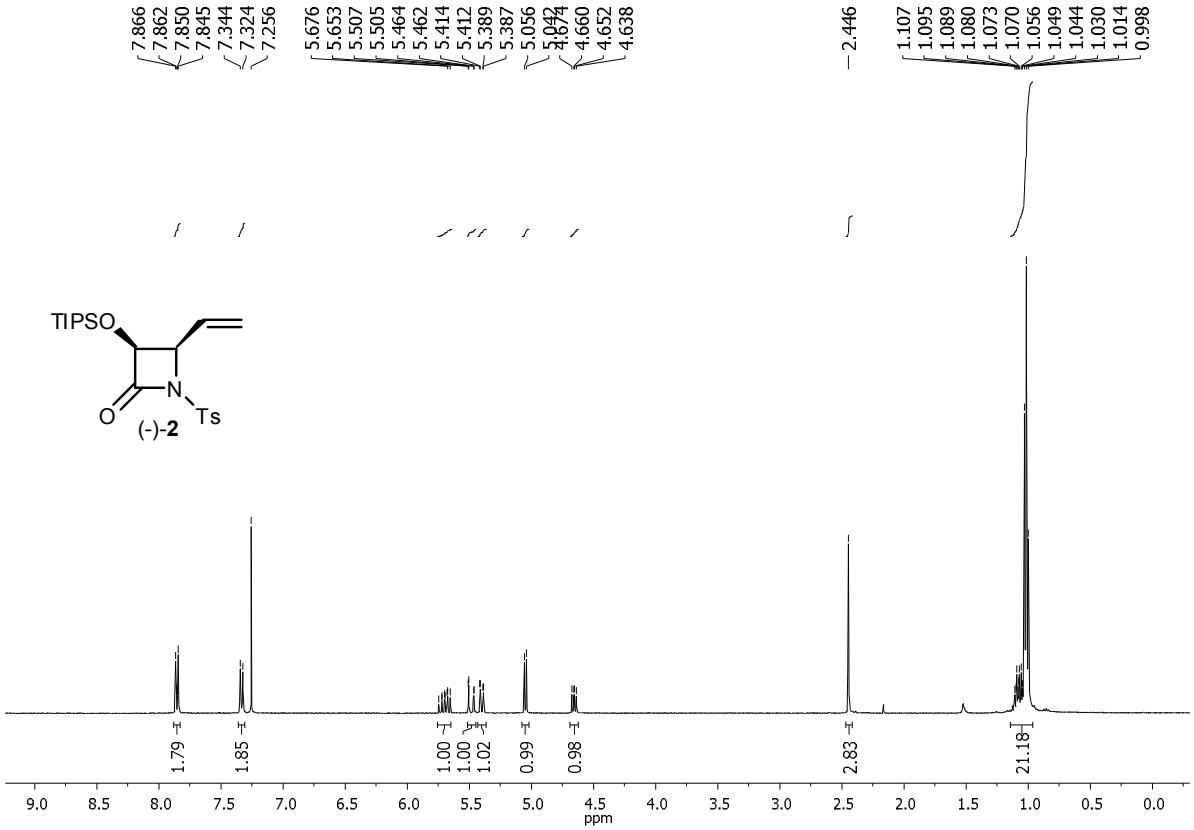
^{1}H NMR (400 MHz, $CDCl_3$)



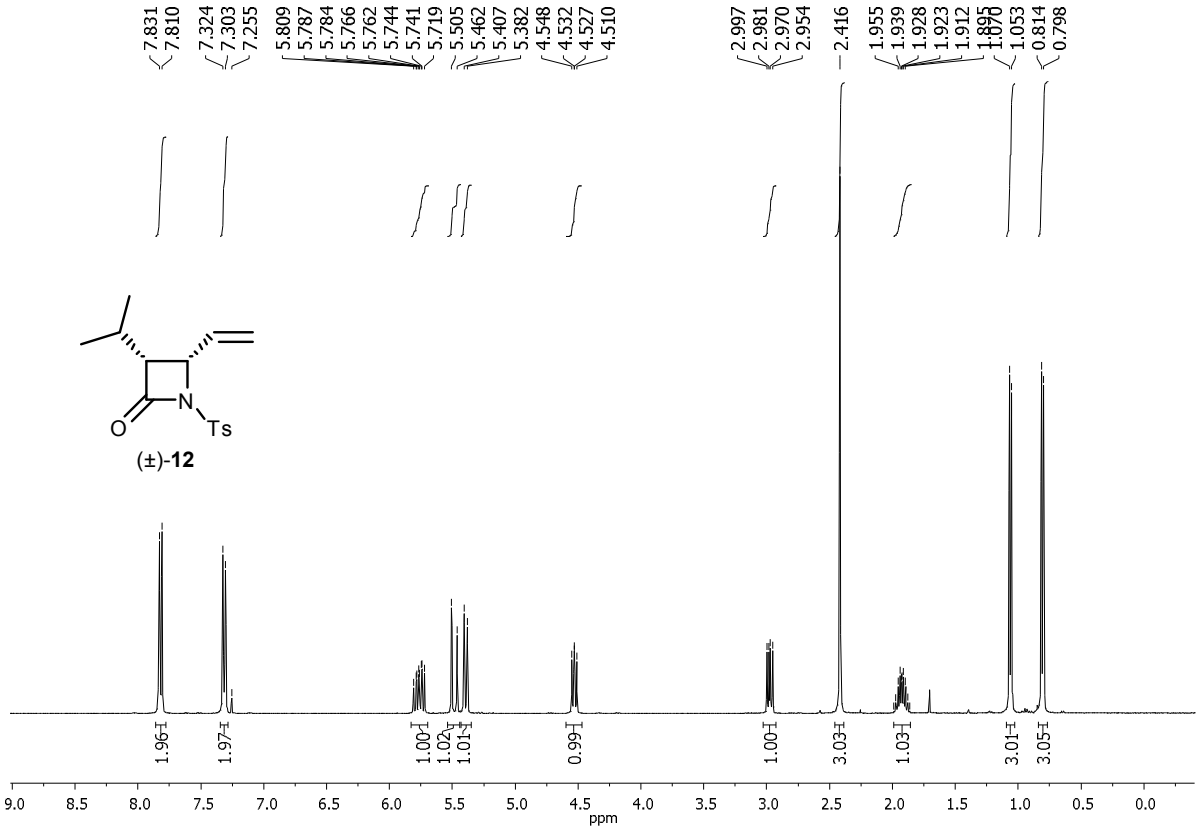
^{13}C NMR (101 MHz, $CDCl_3$)



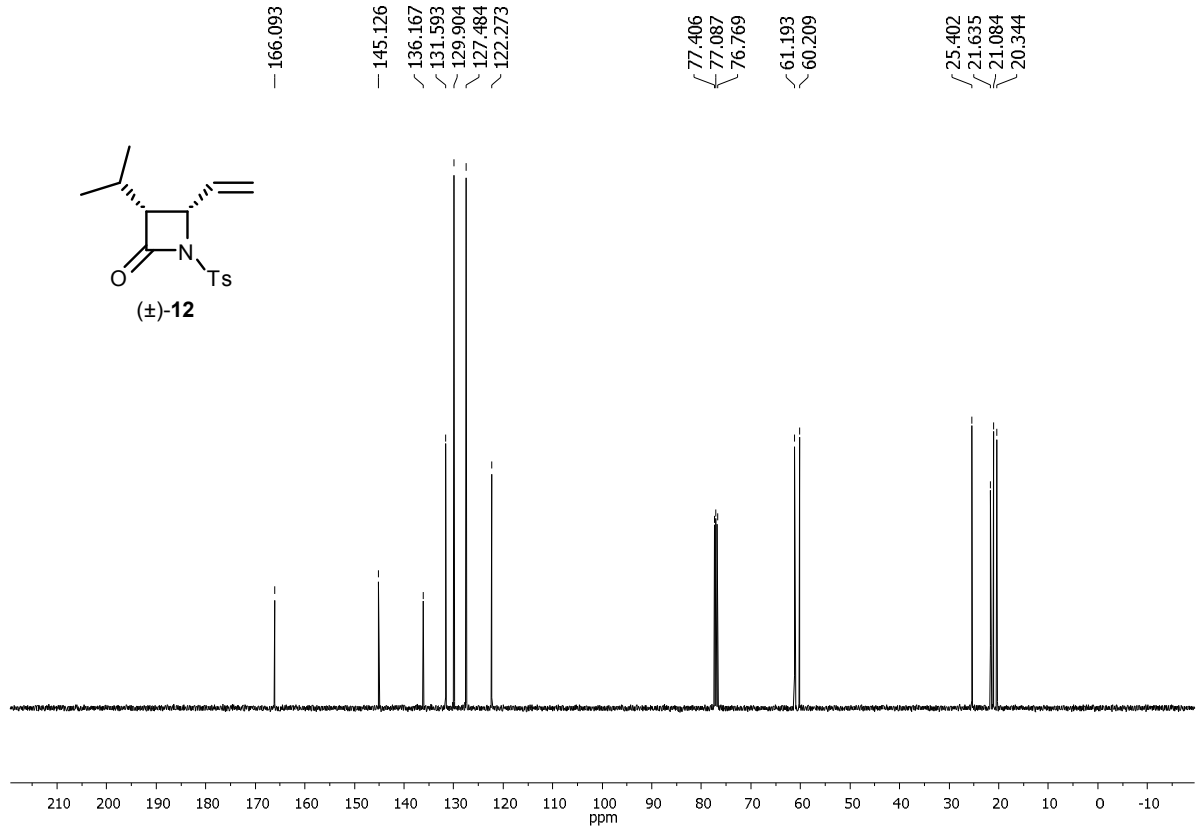
^{1}H NMR (400 MHz, $CDCl_3$)



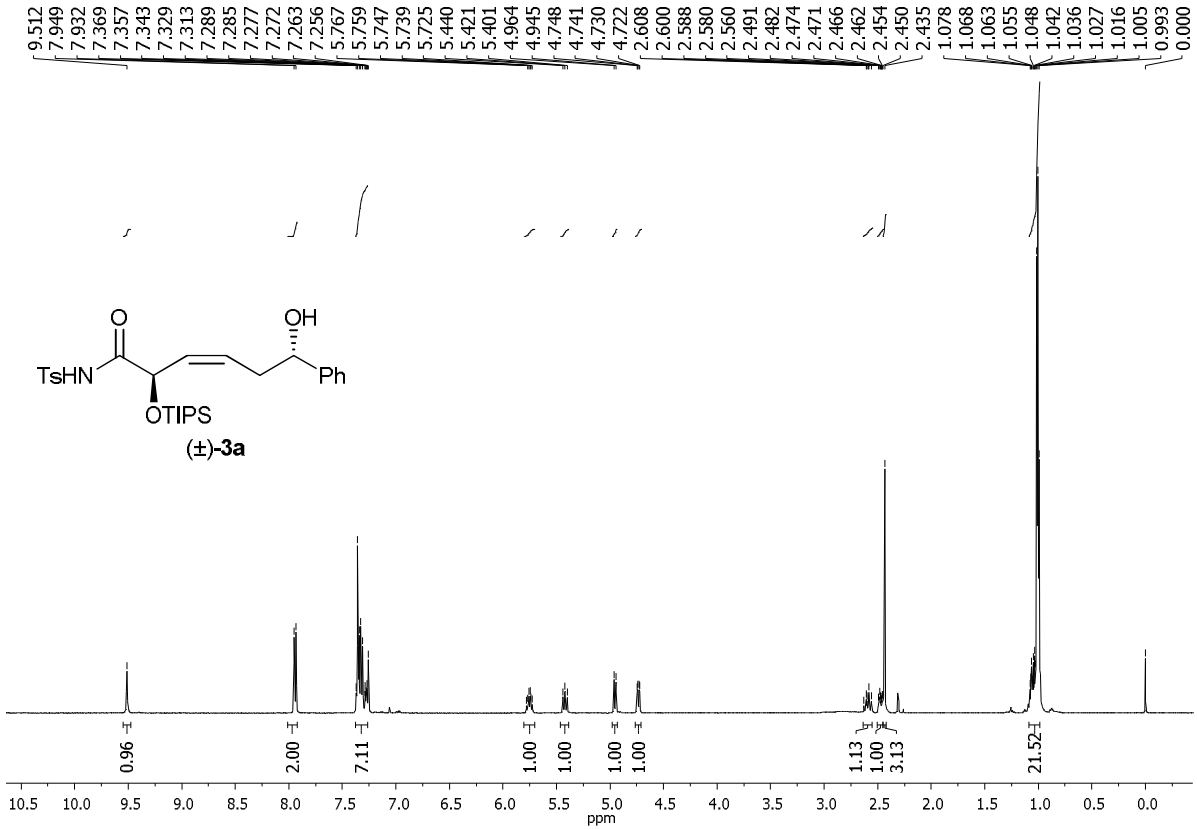
^{1}H NMR (400 MHz, $CDCl_3$)



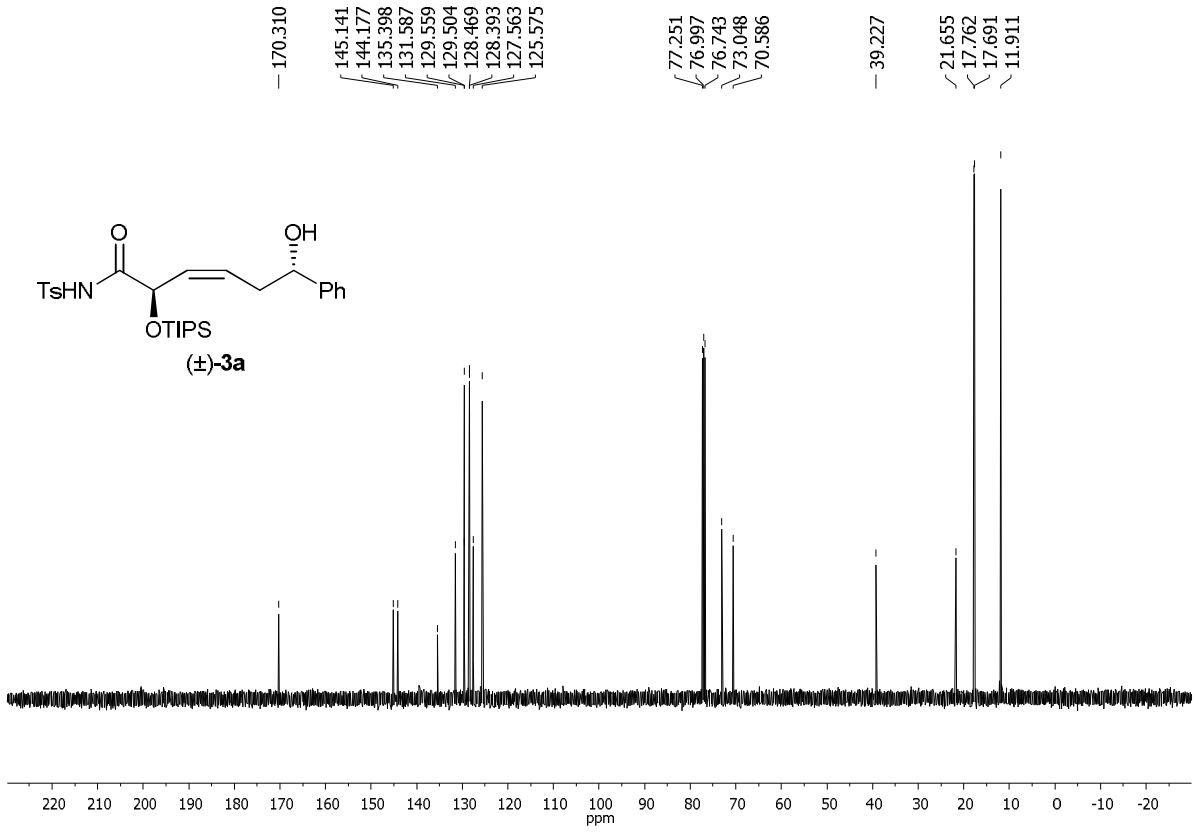
^{13}C NMR (101 MHz, $CDCl_3$)



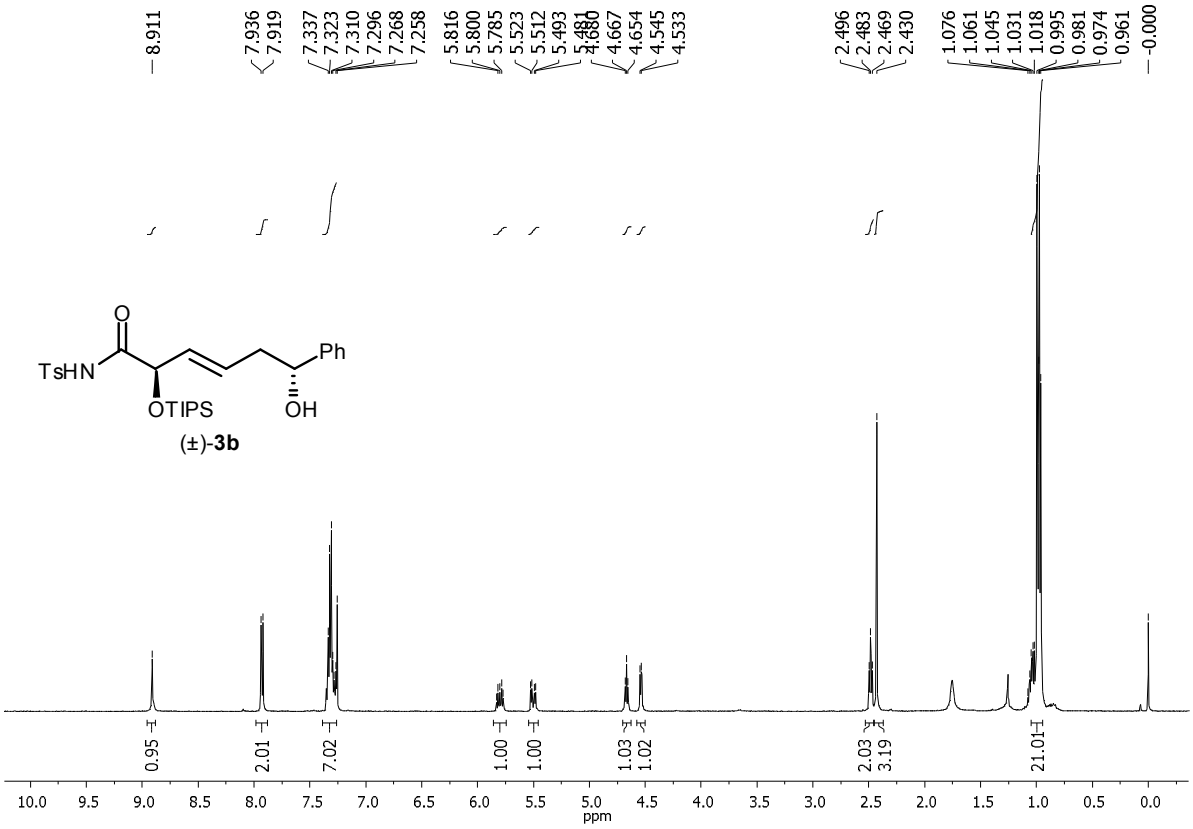
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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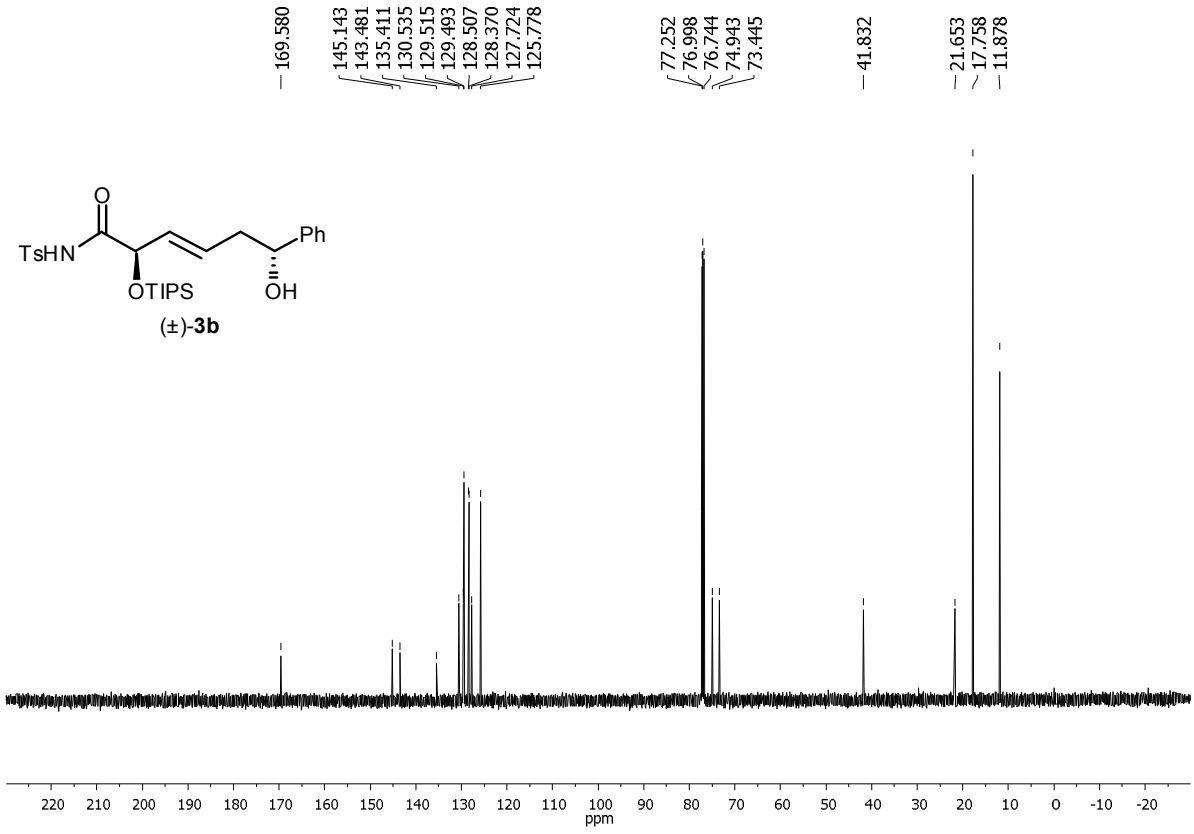

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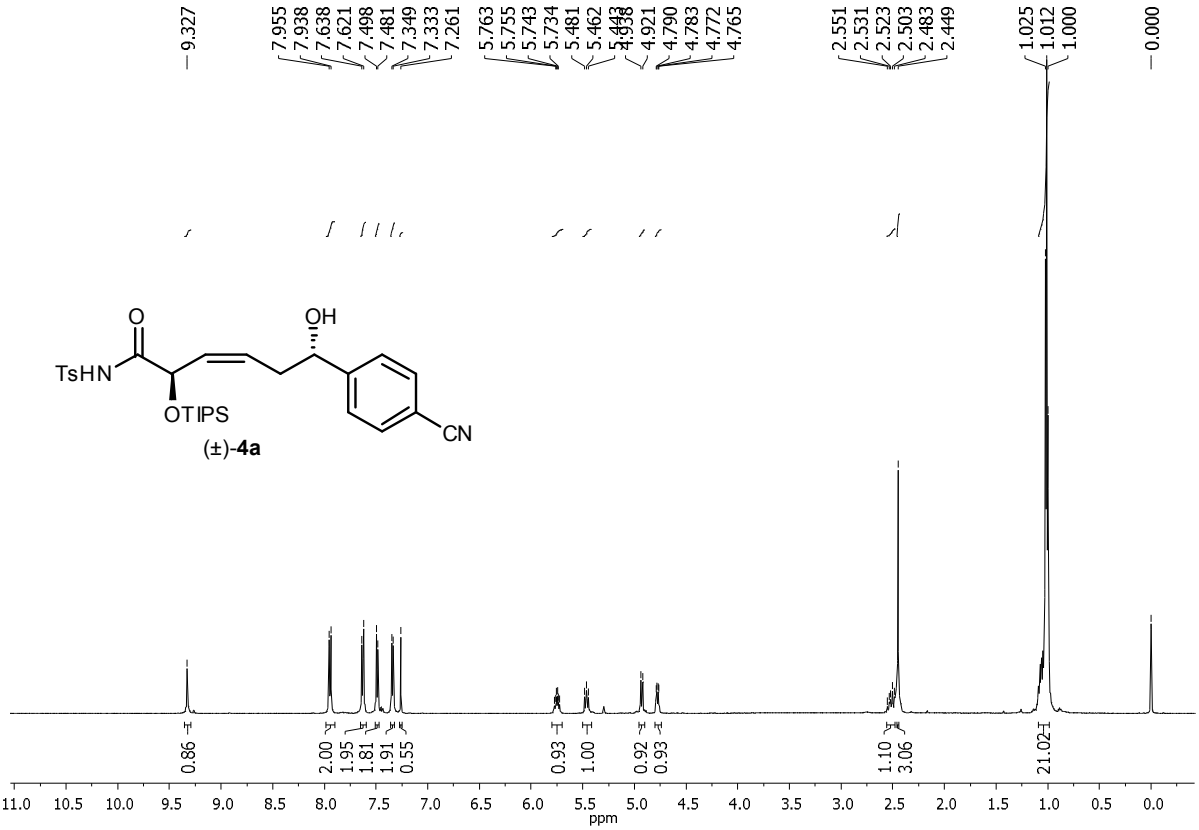

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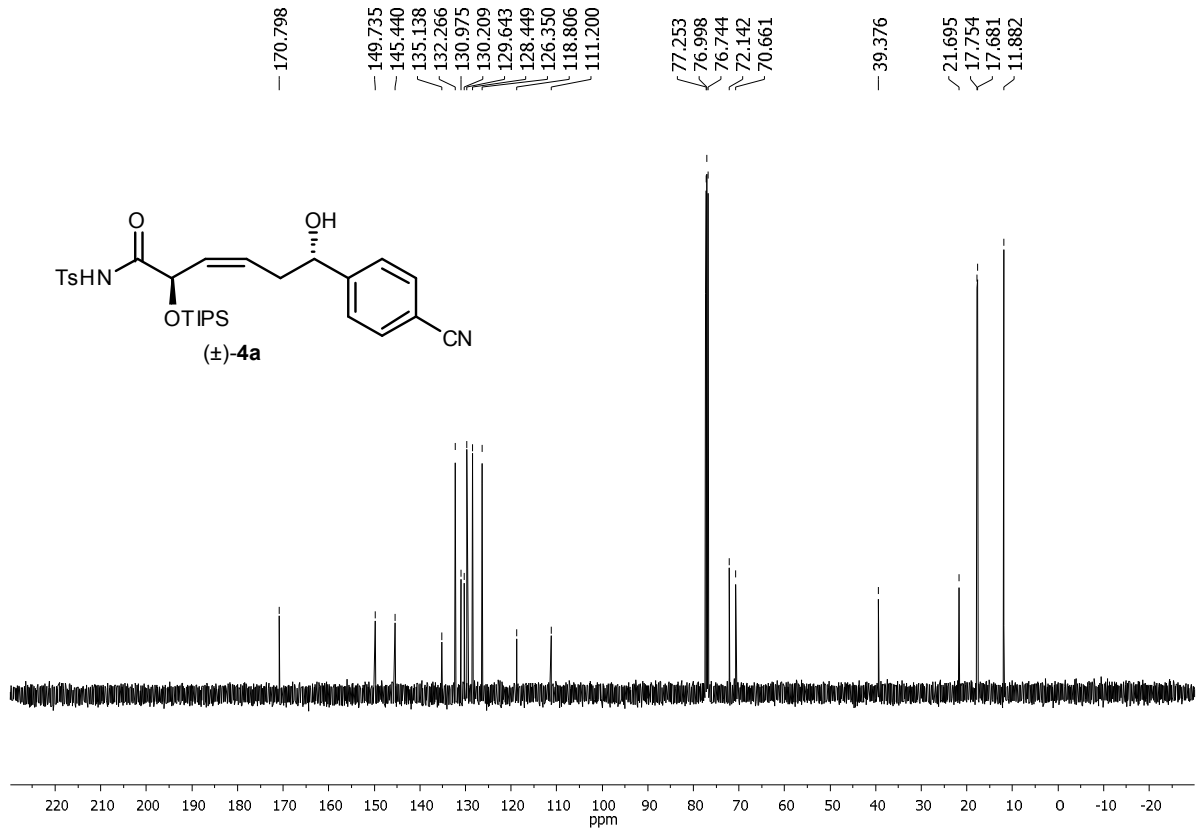

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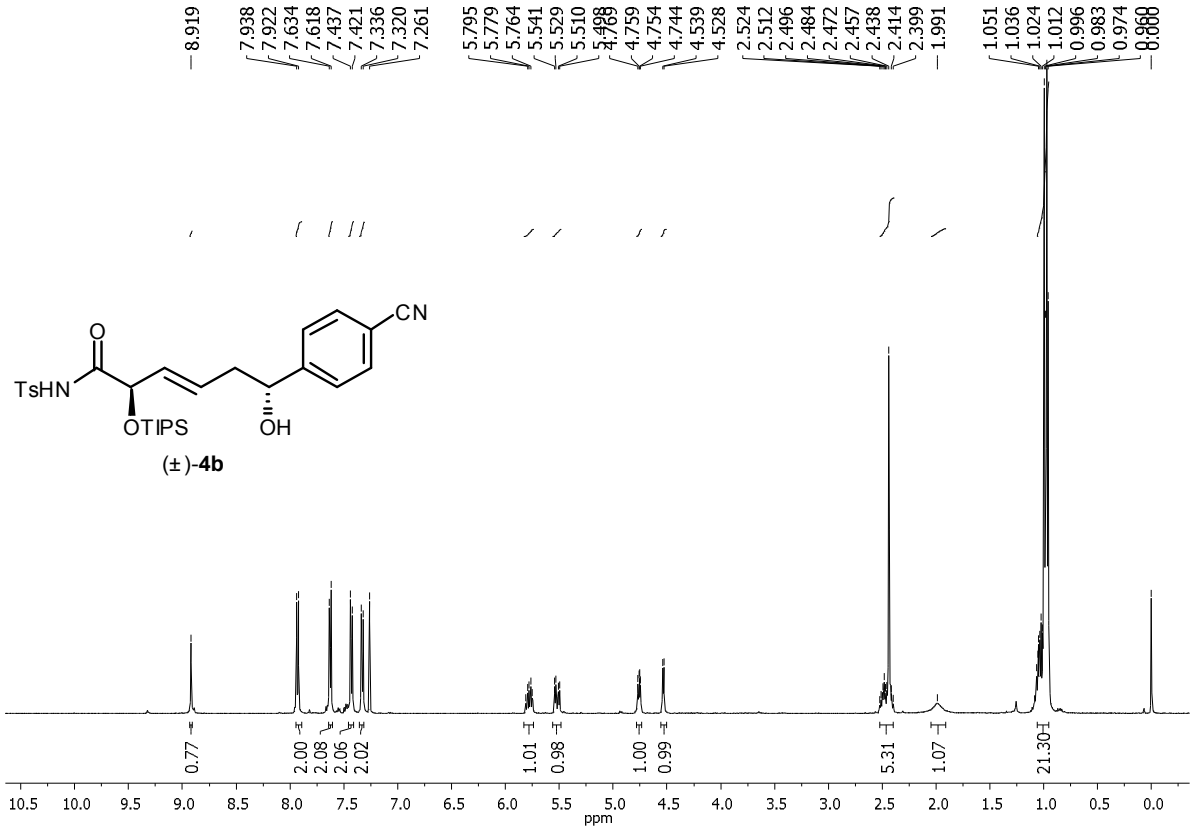

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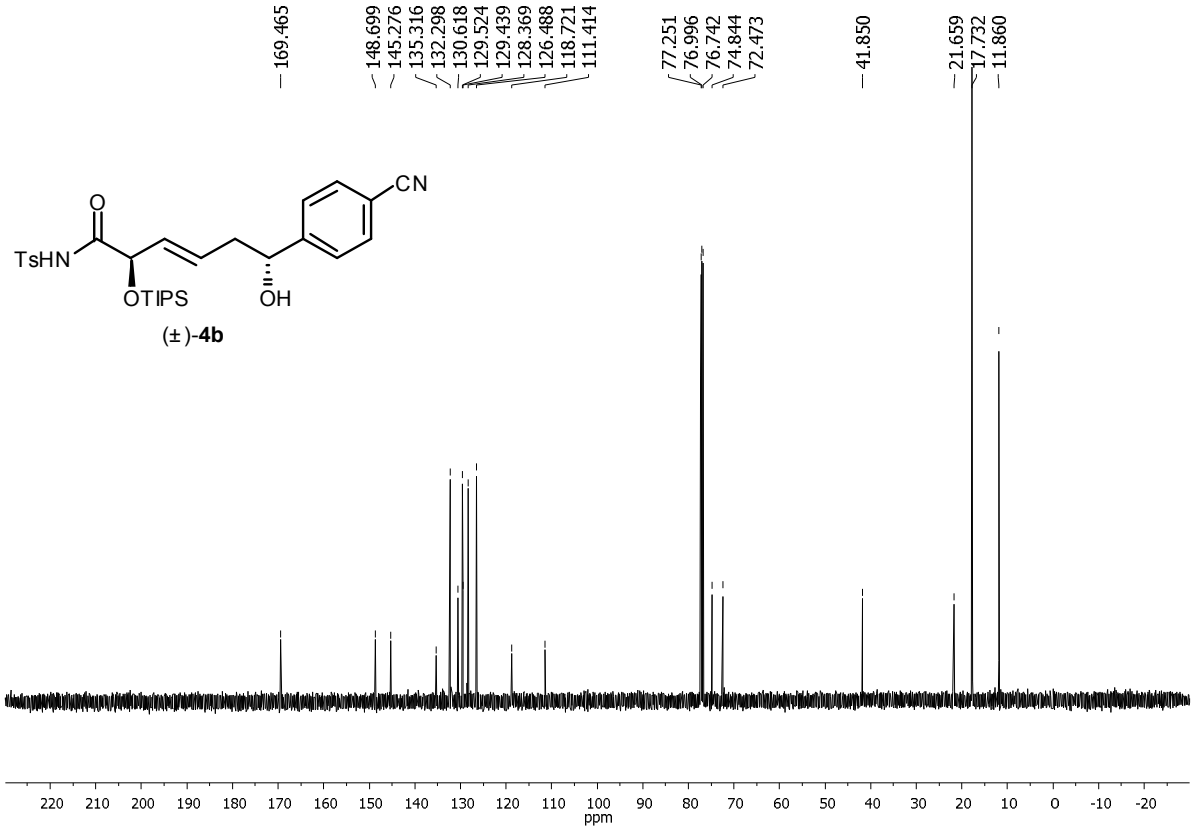

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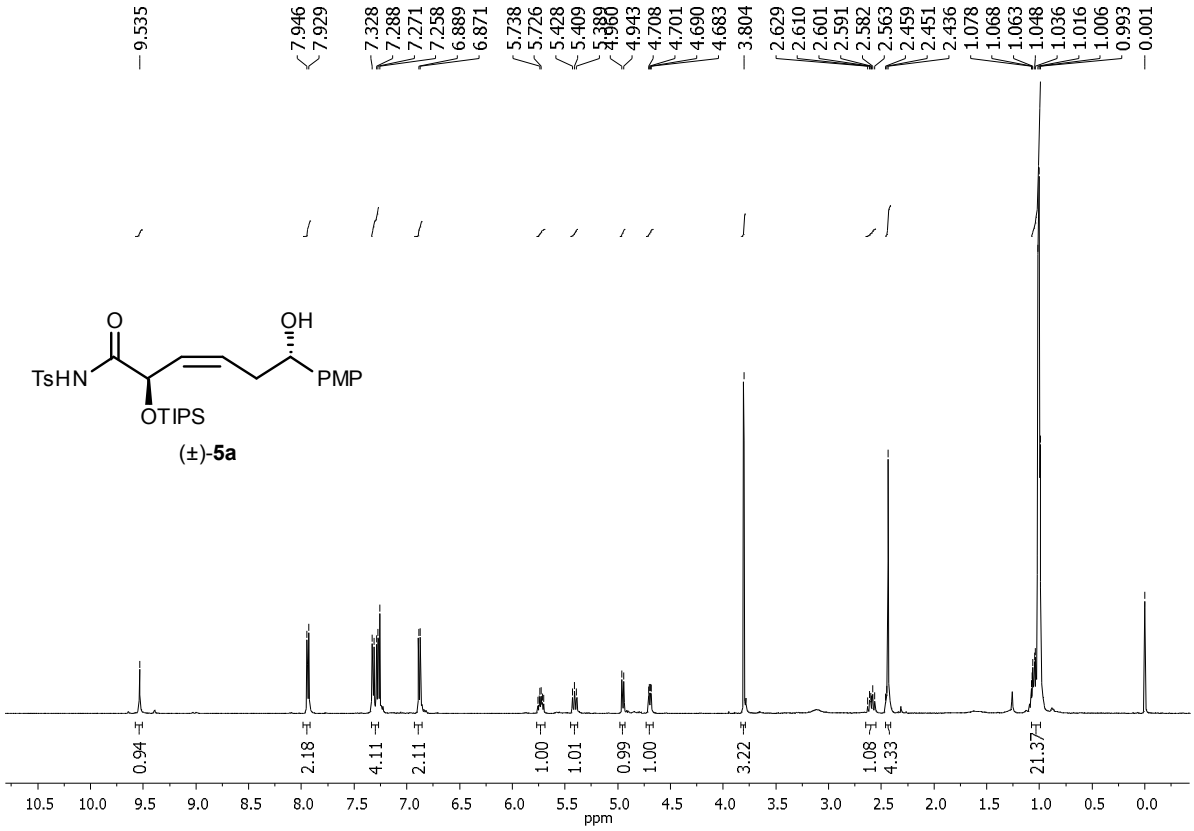

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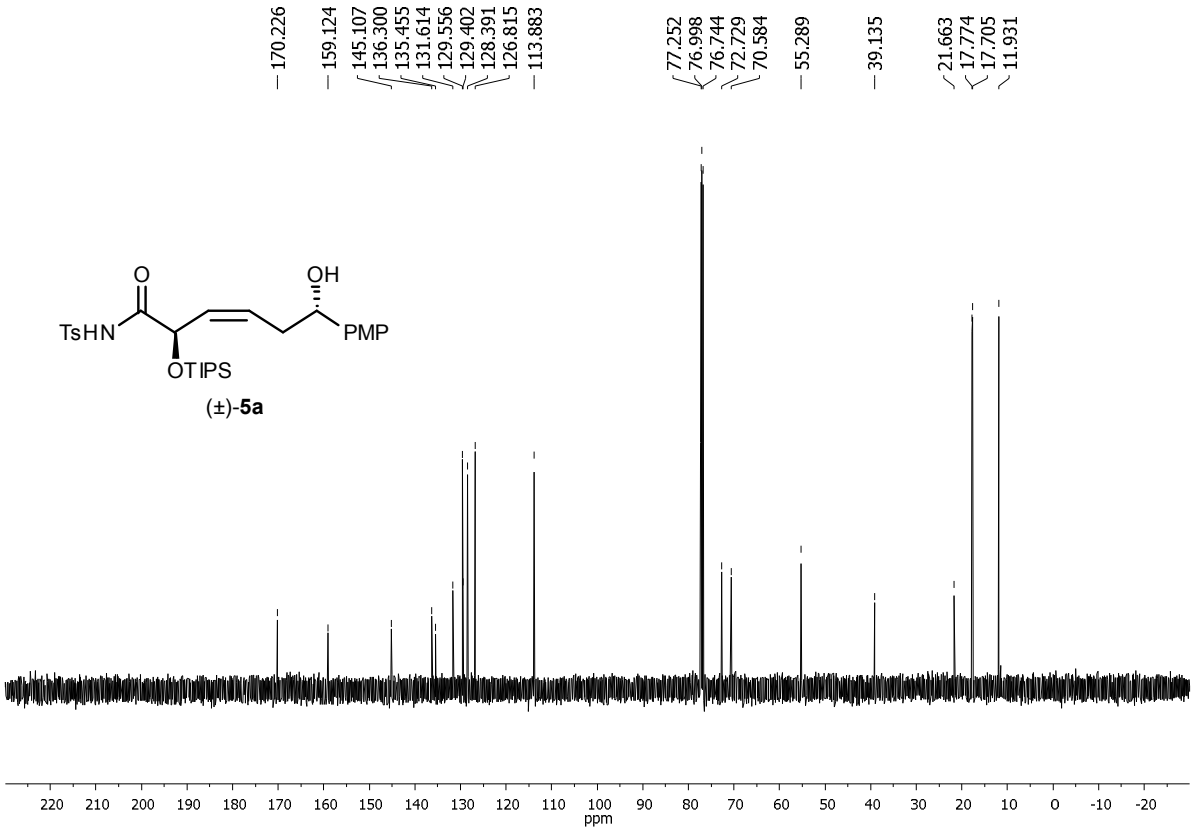

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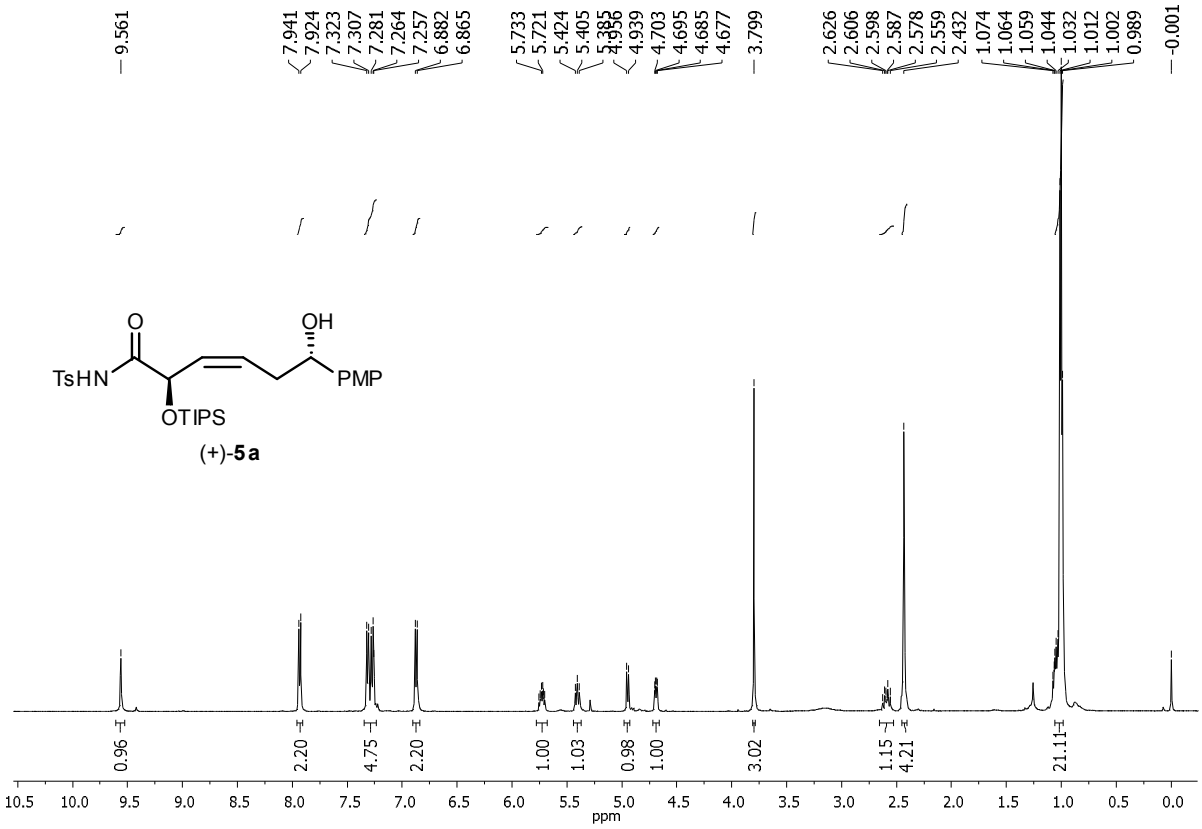

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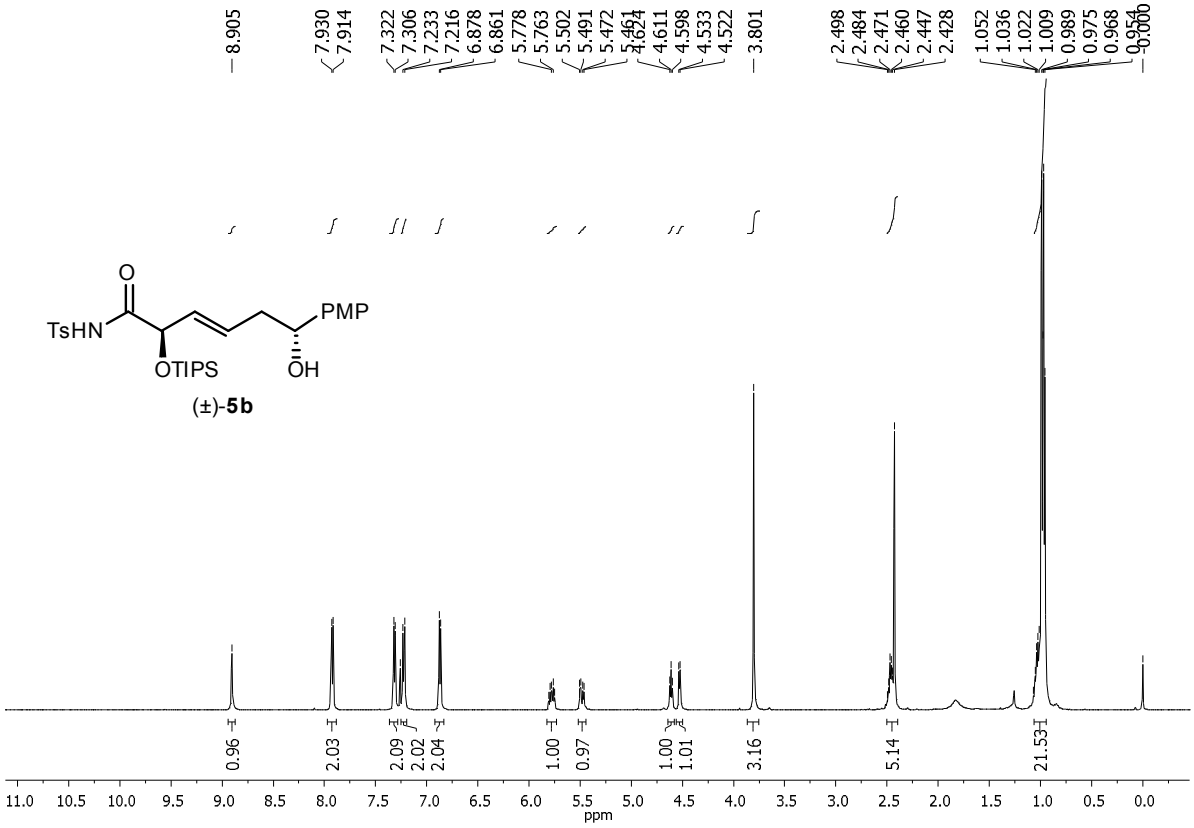

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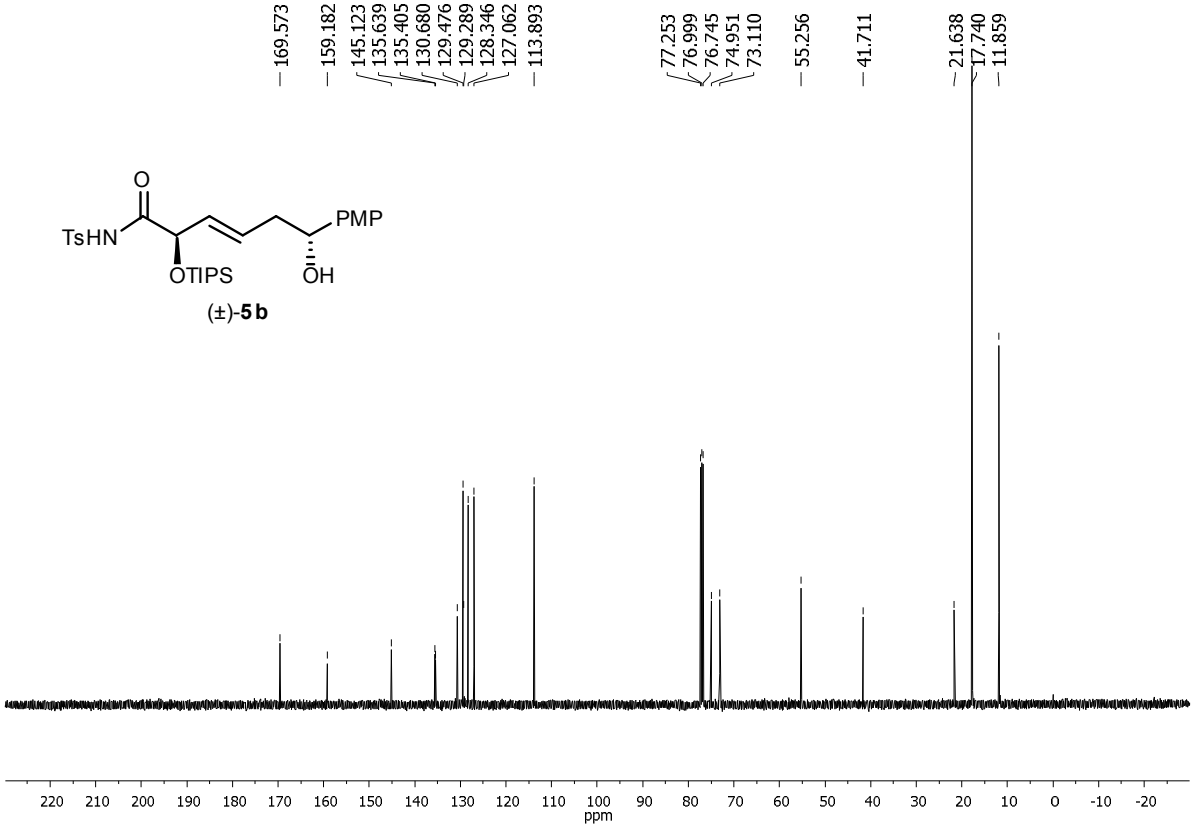

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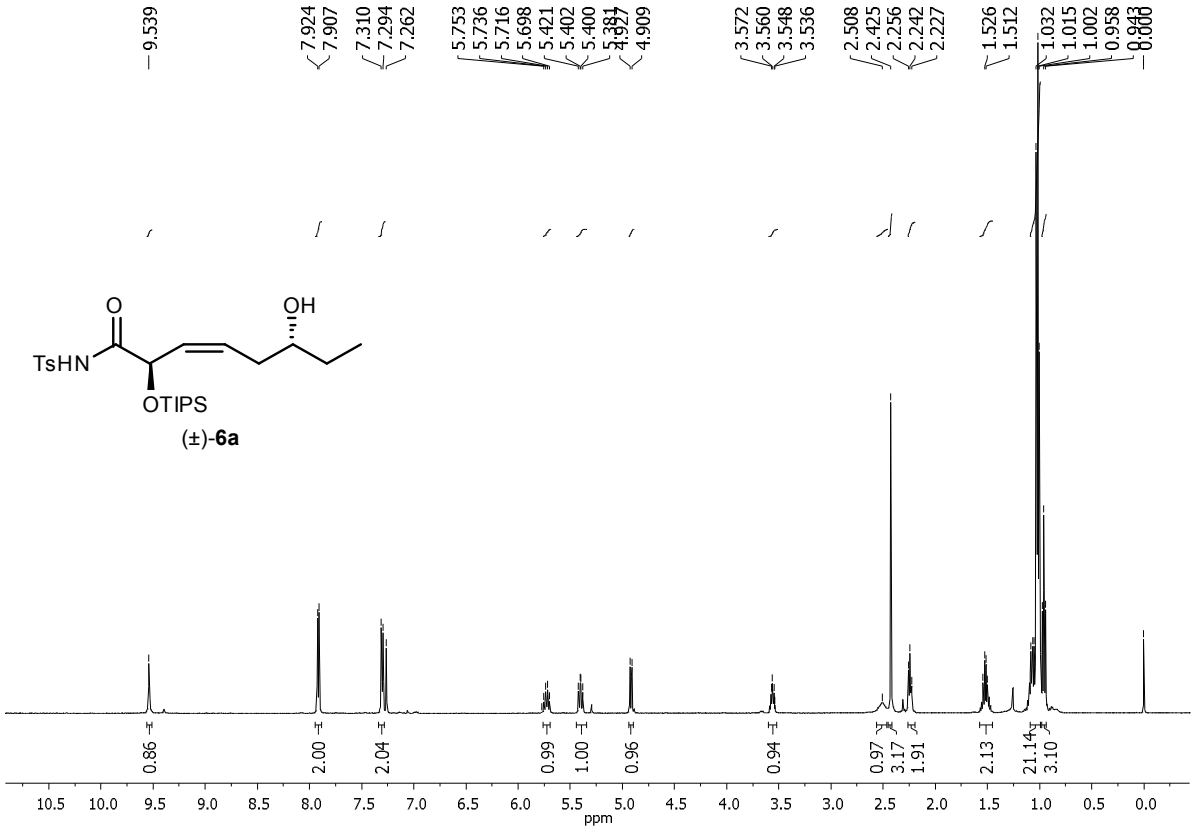

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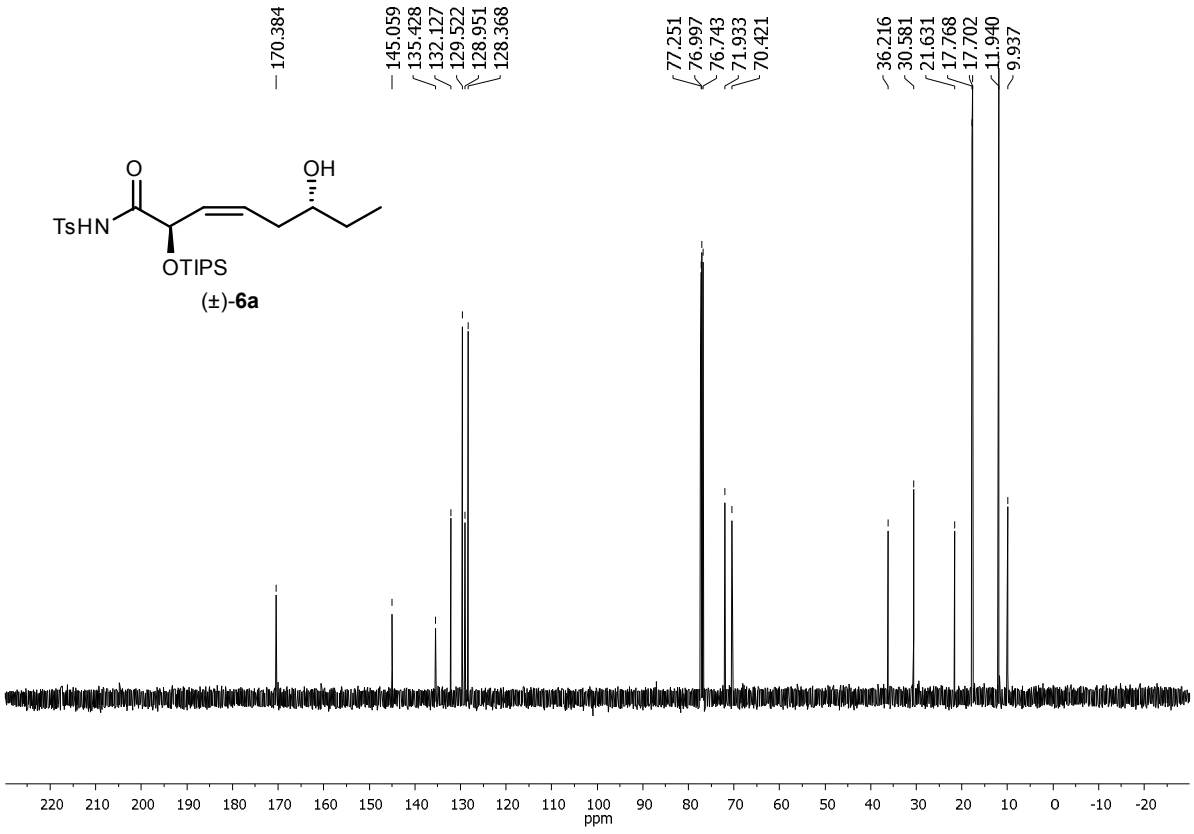

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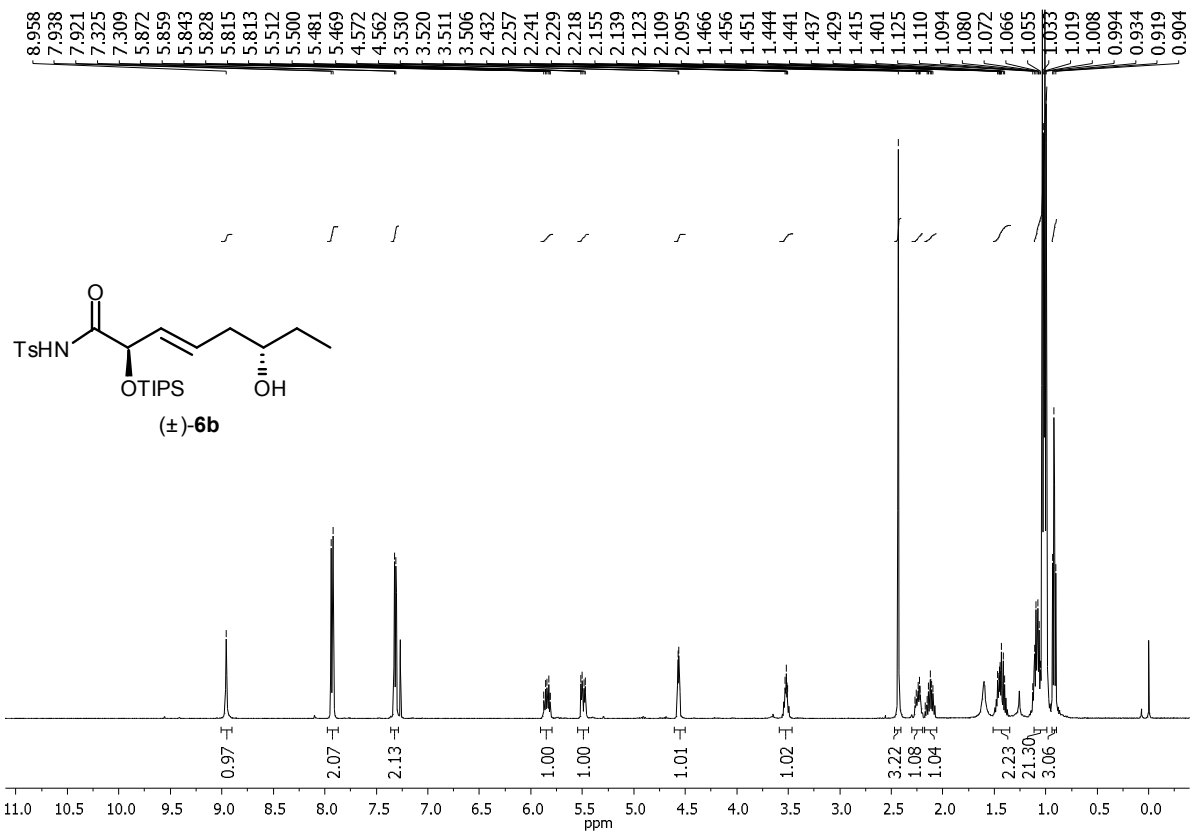

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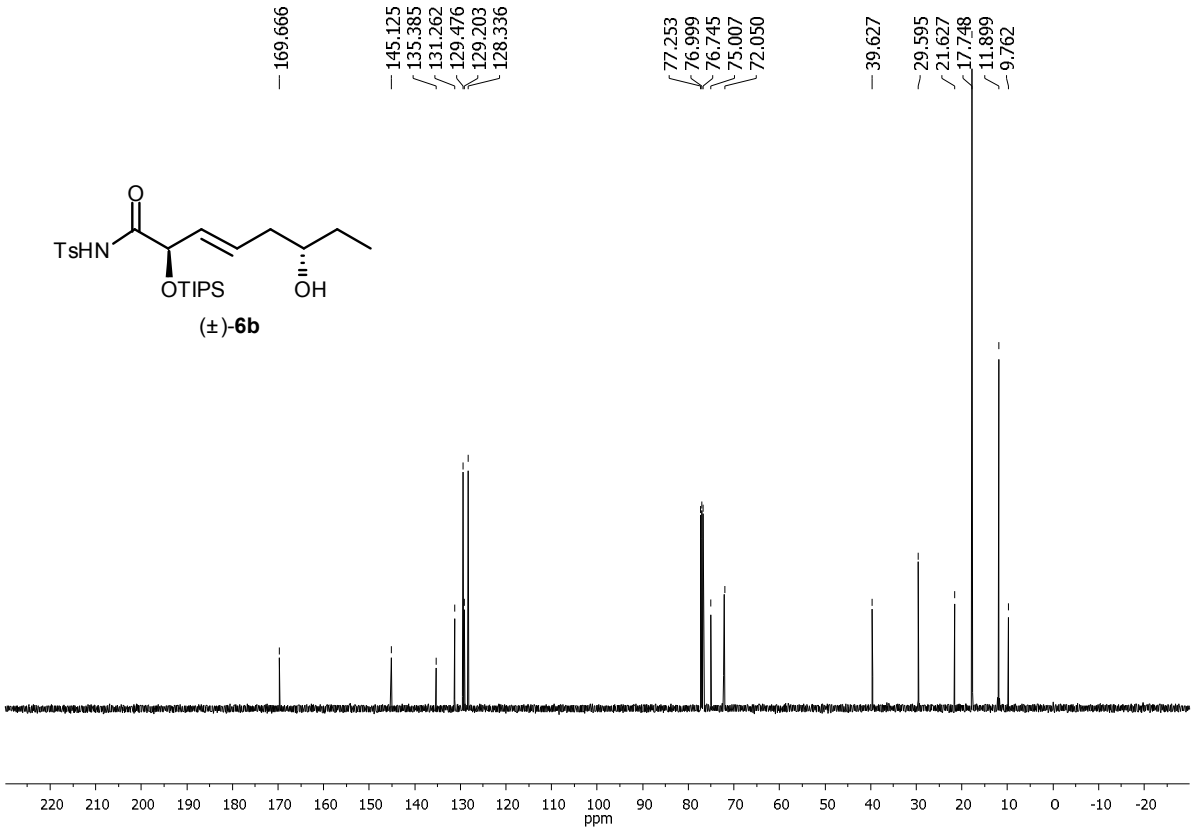

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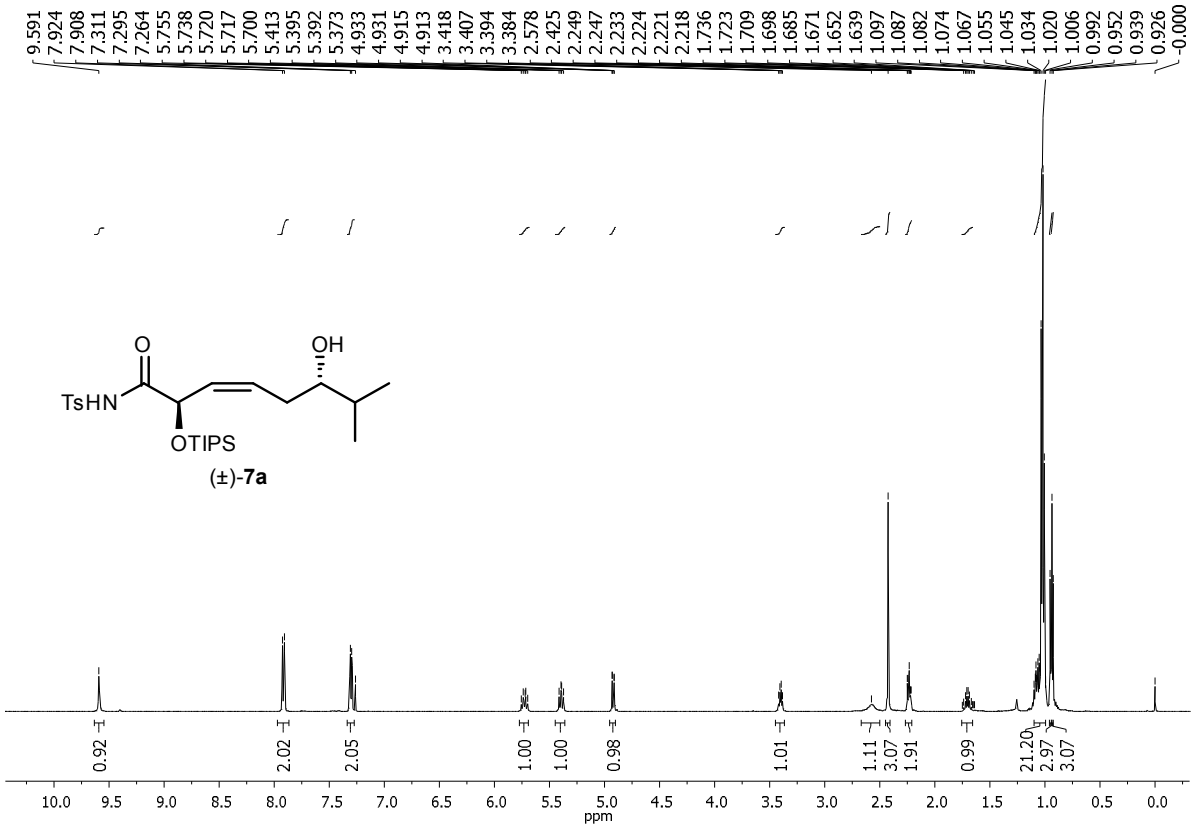

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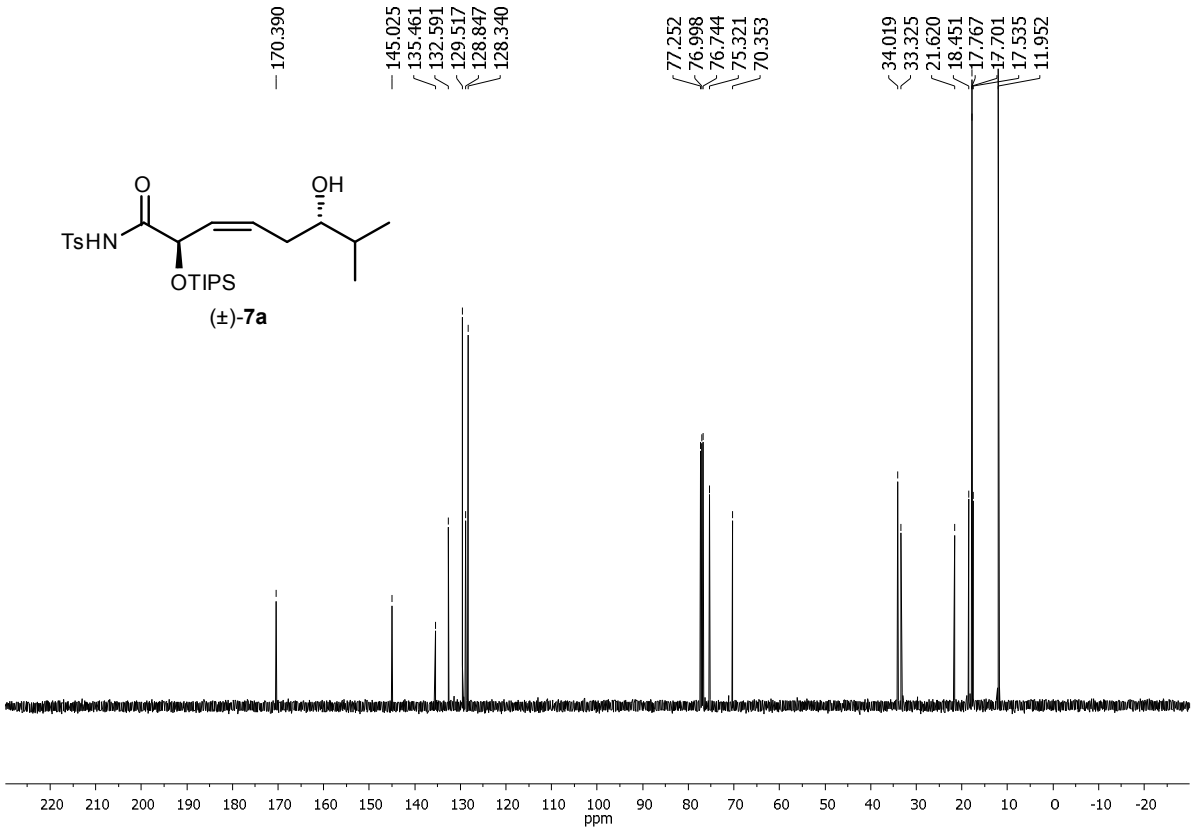

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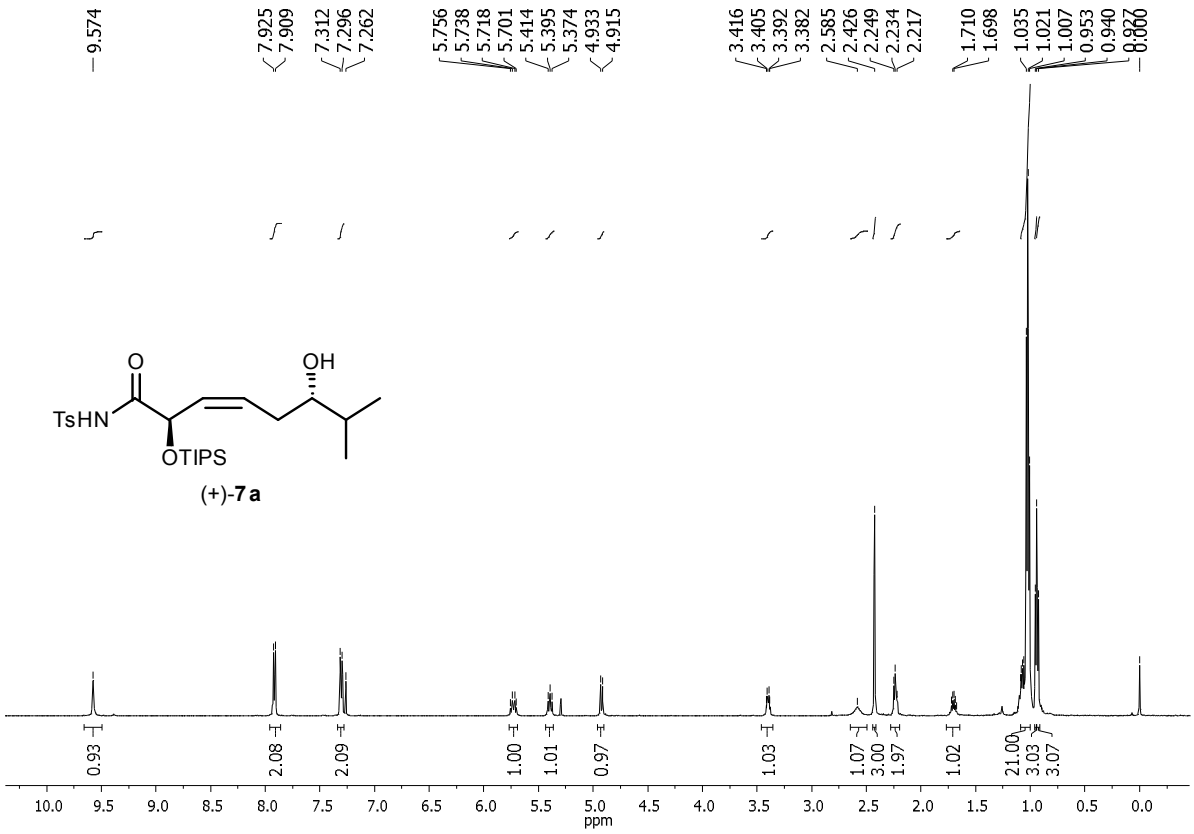

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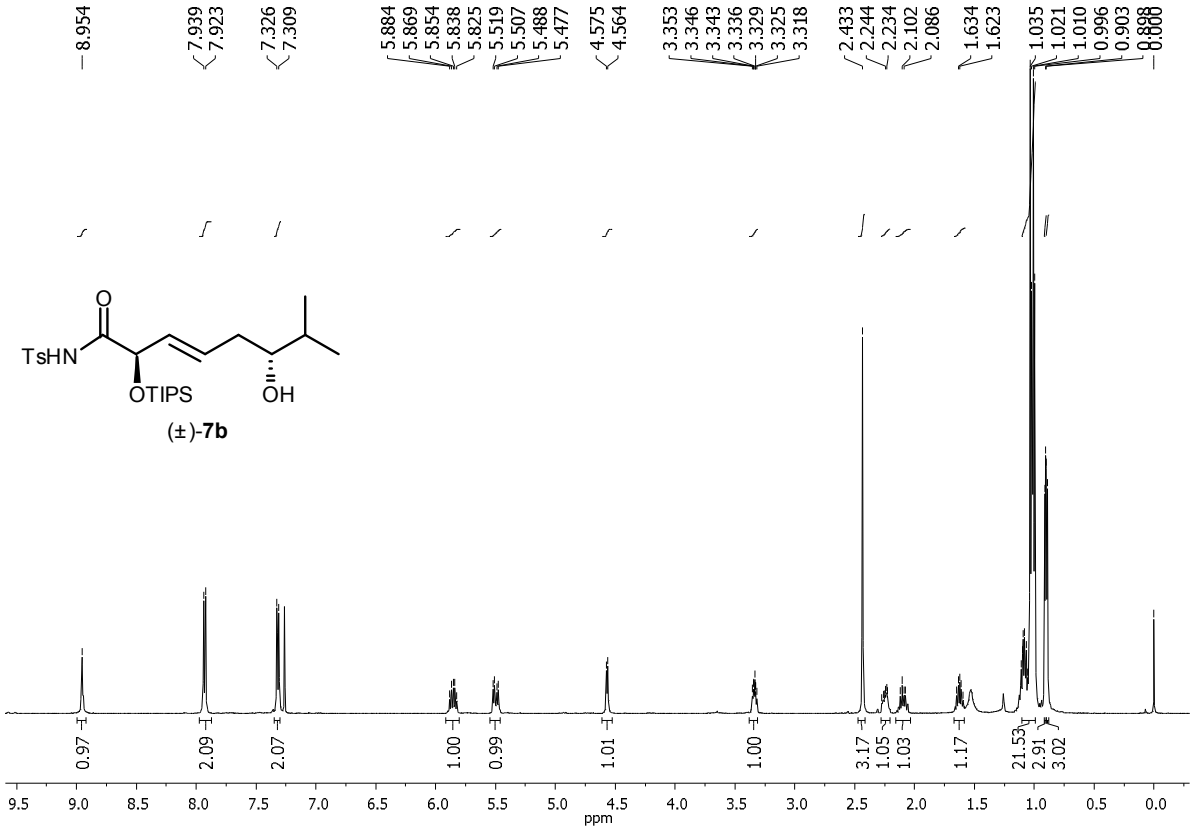

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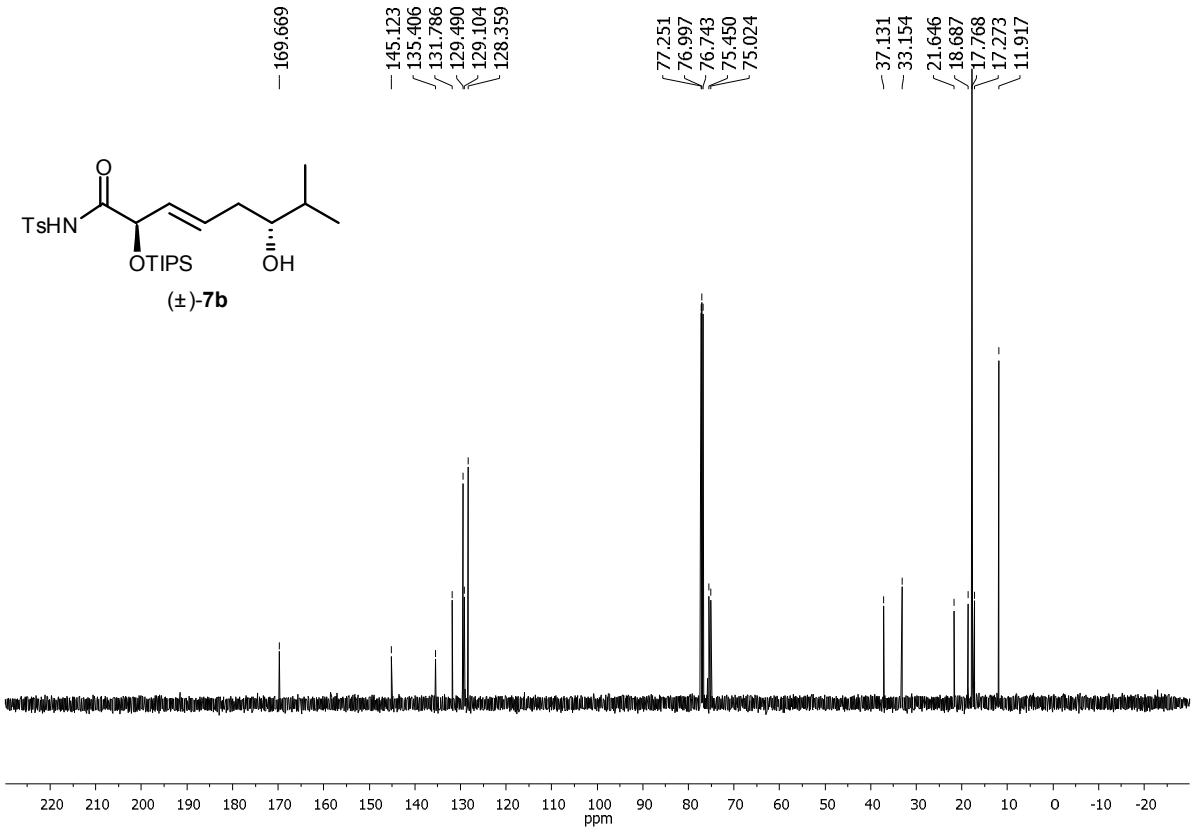

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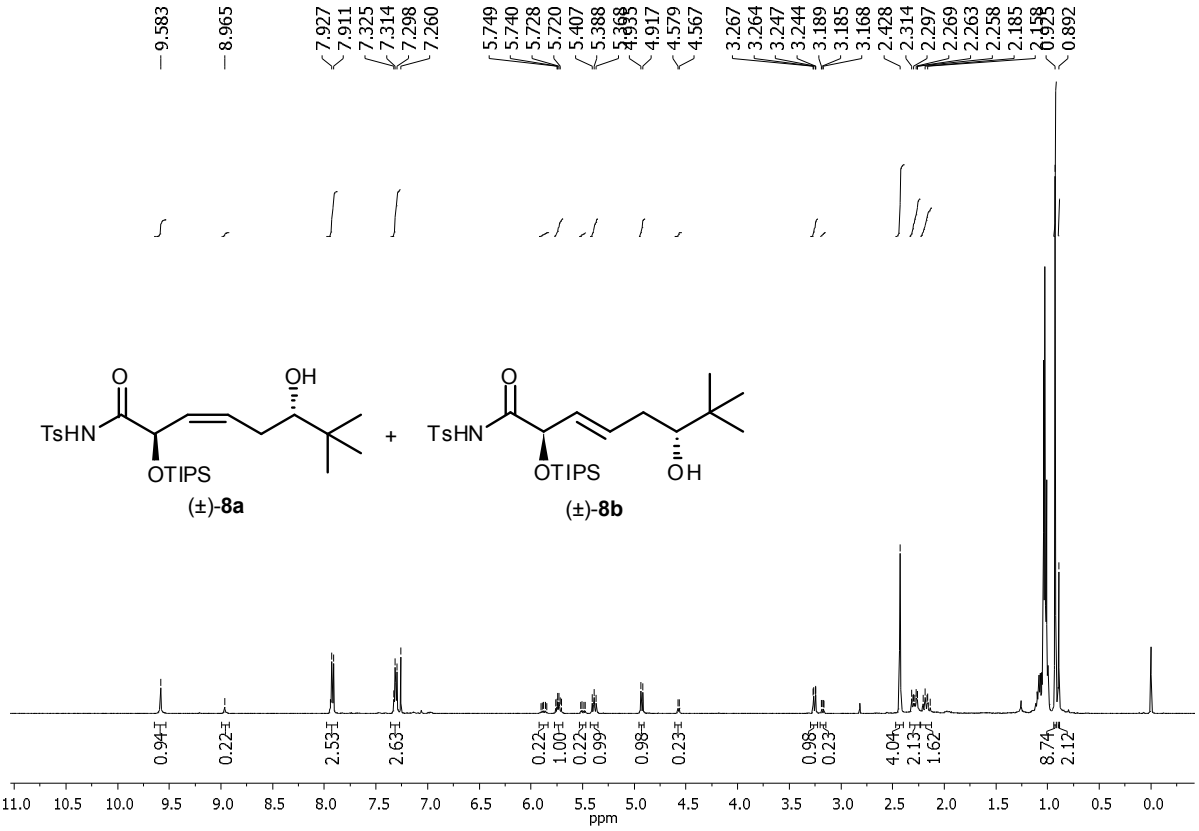

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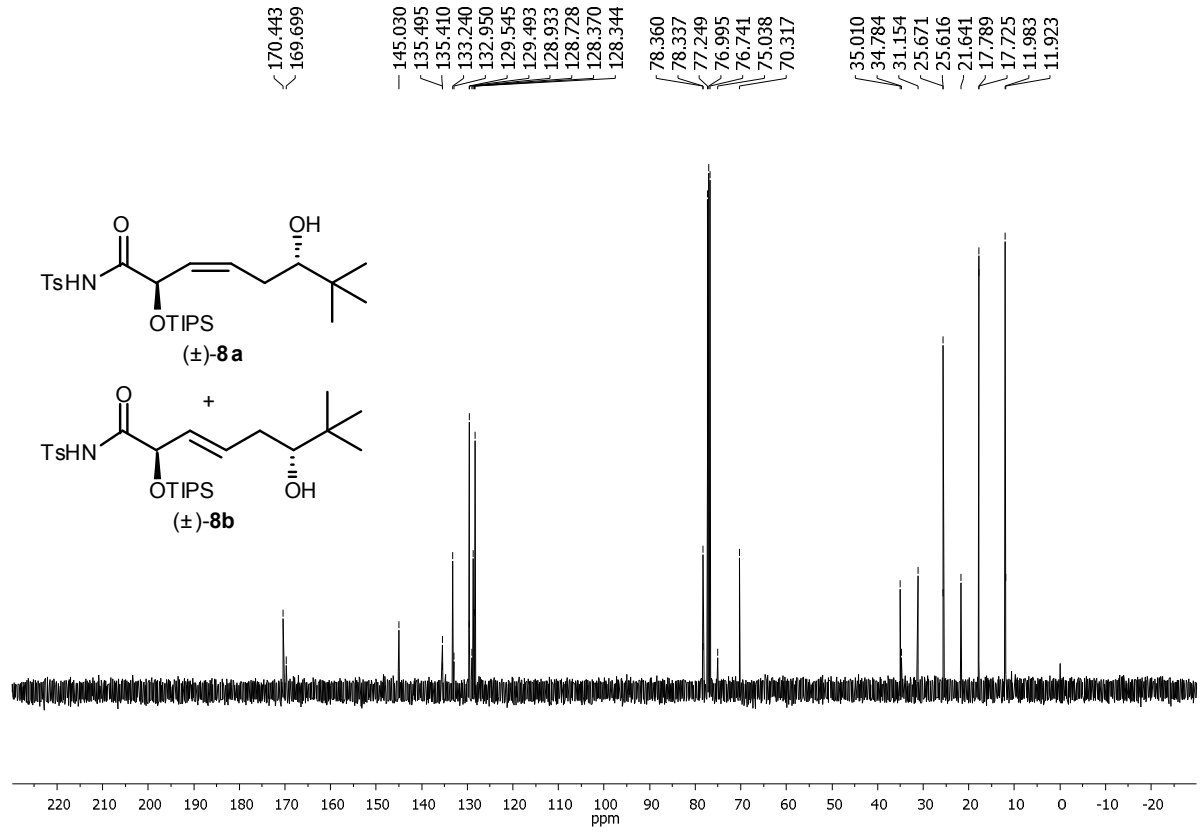

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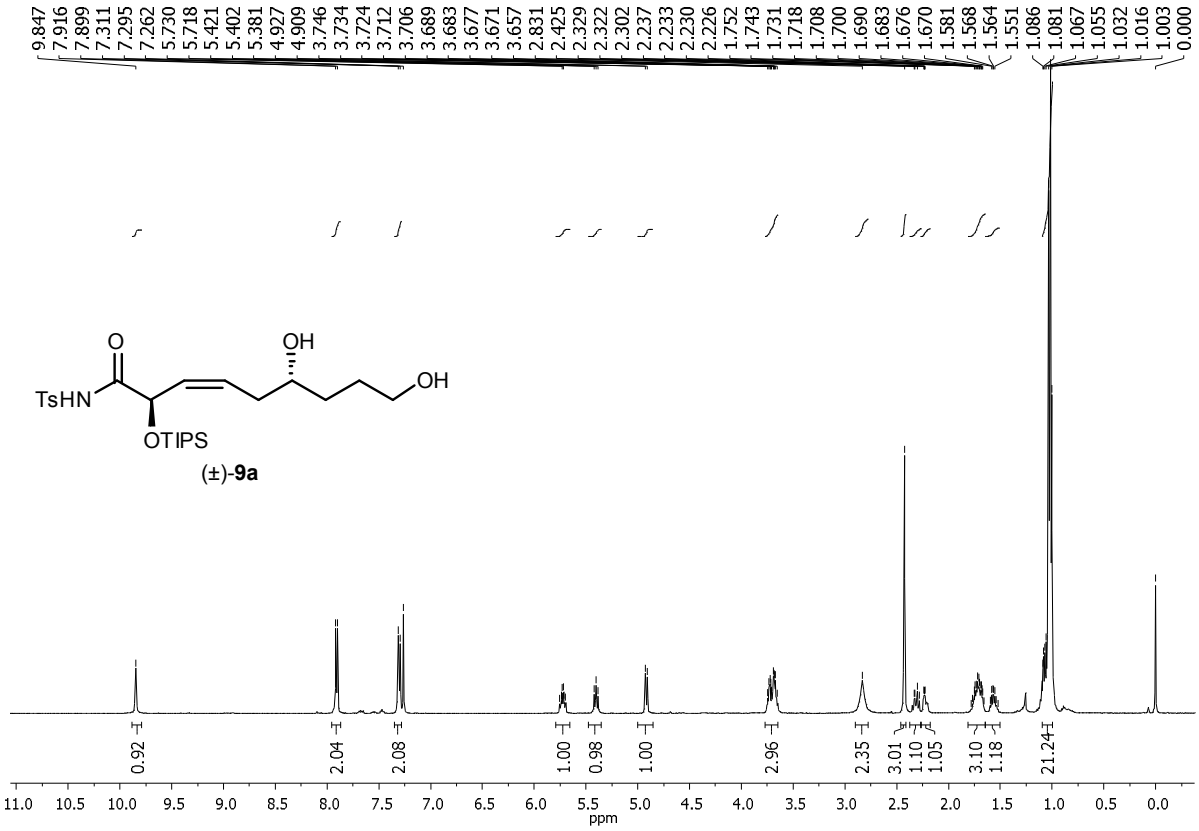

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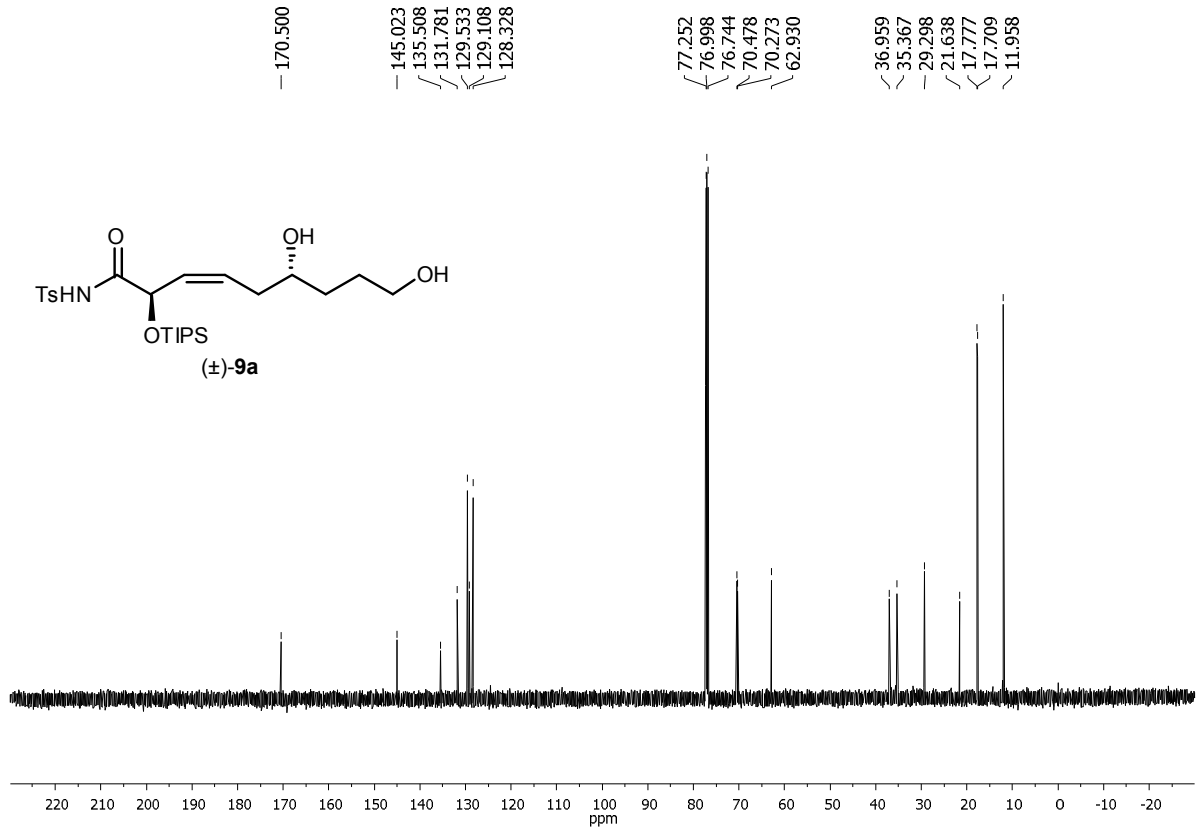

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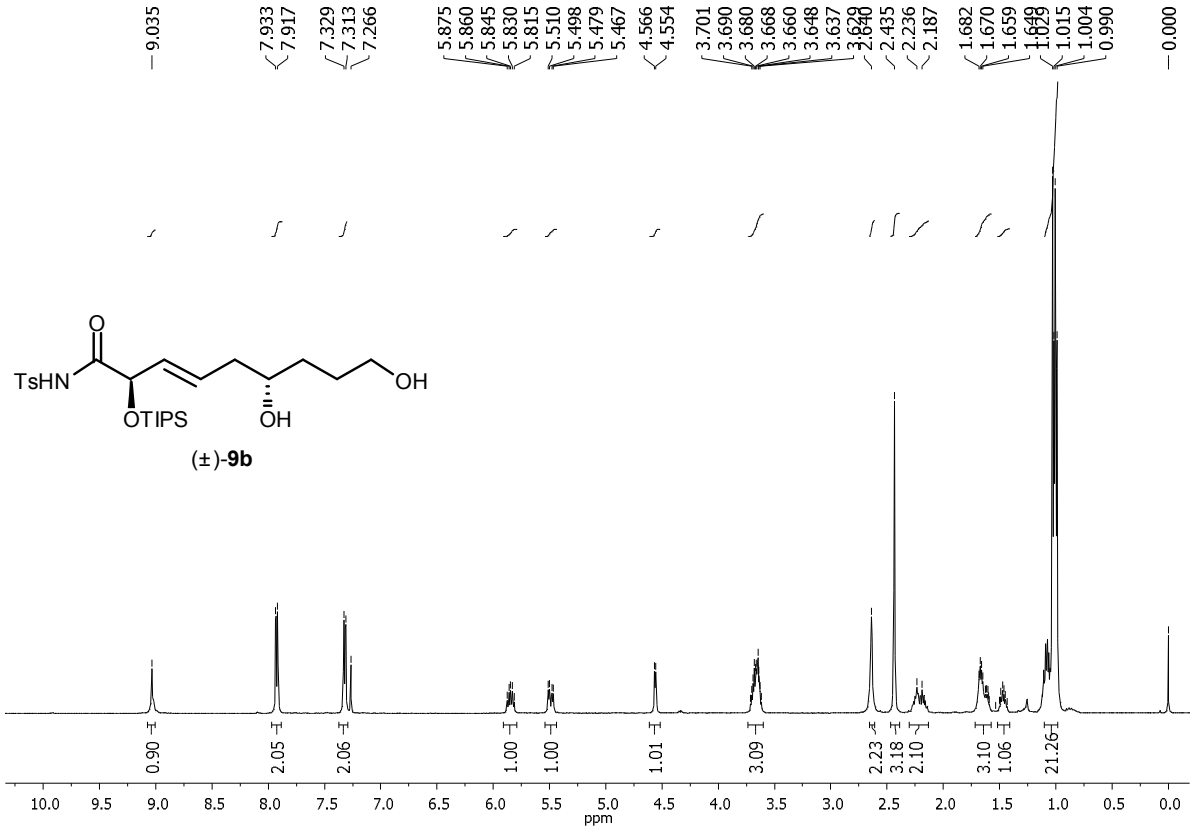

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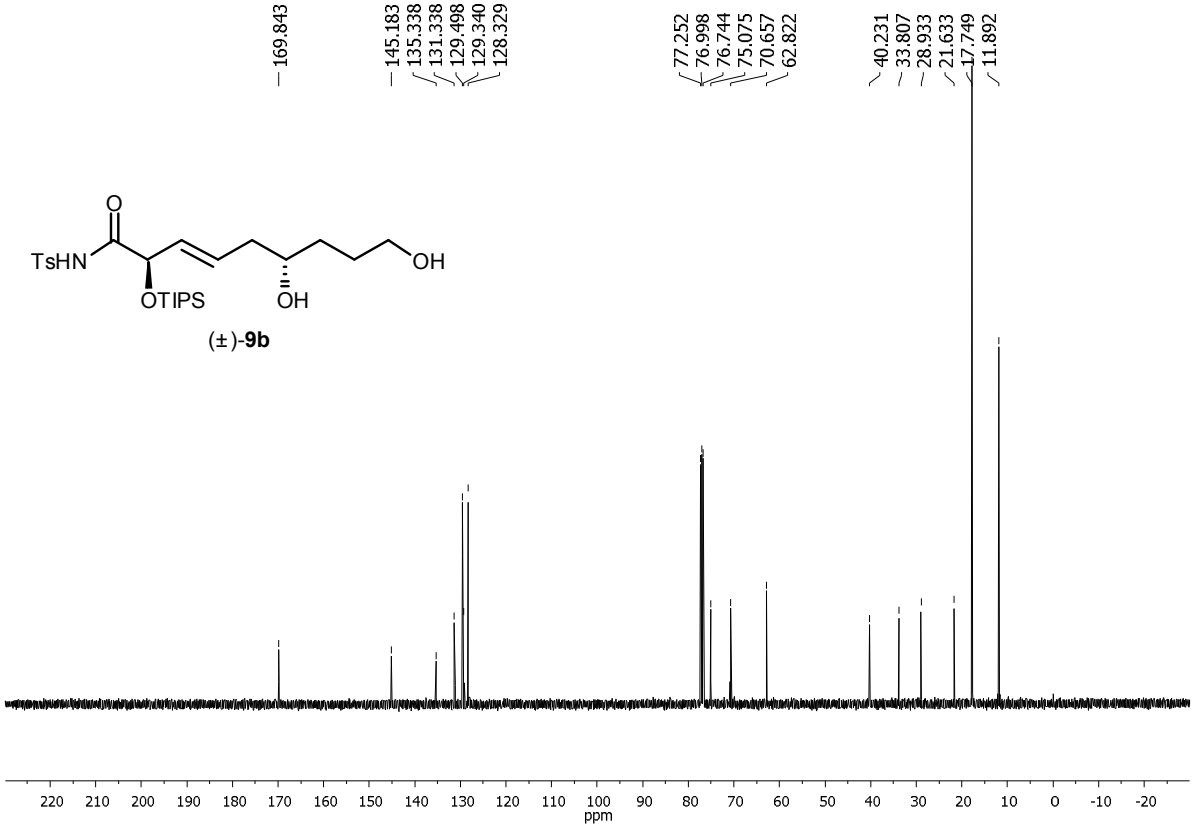

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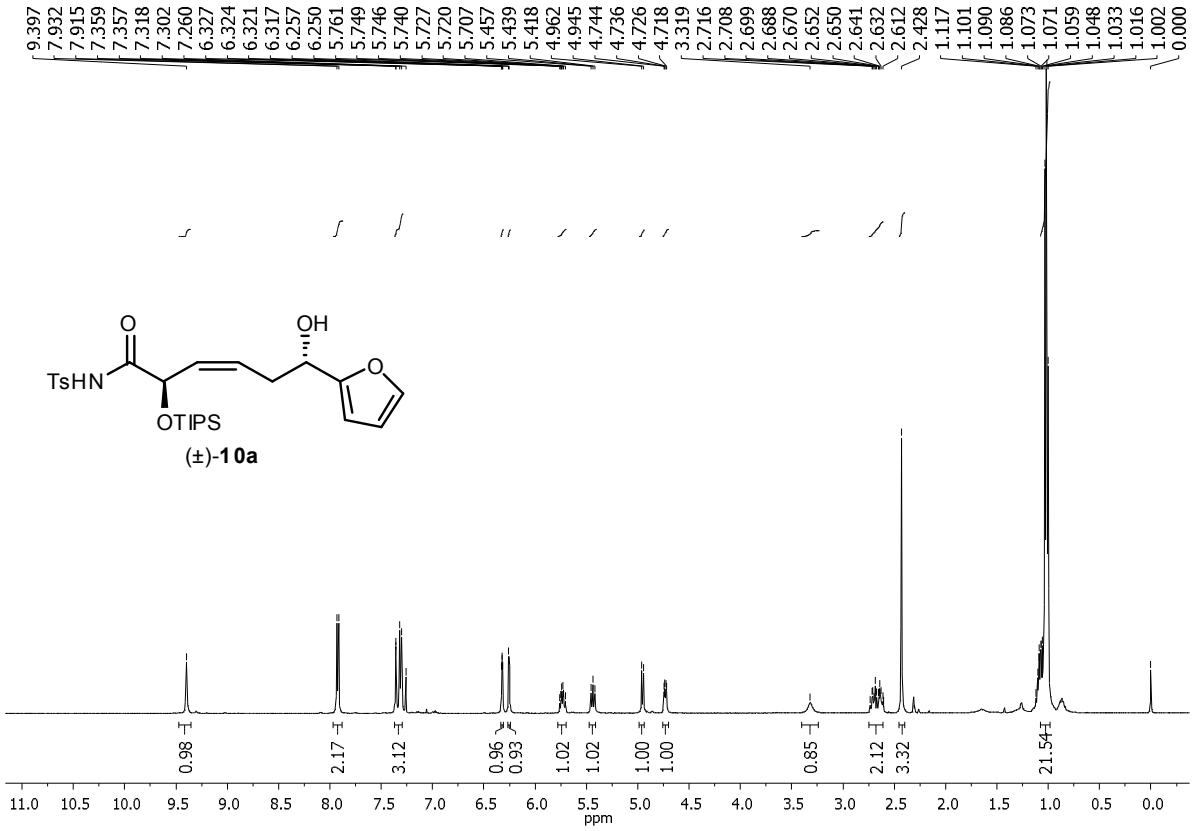

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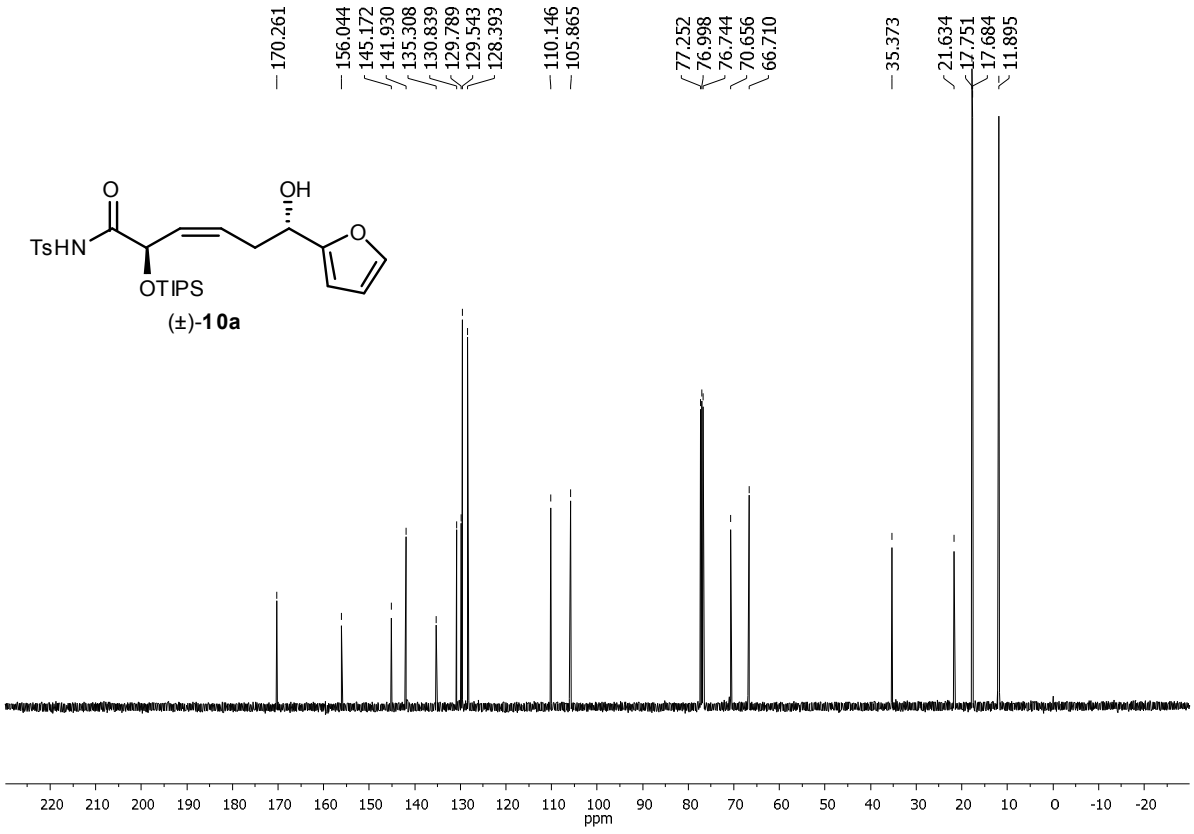

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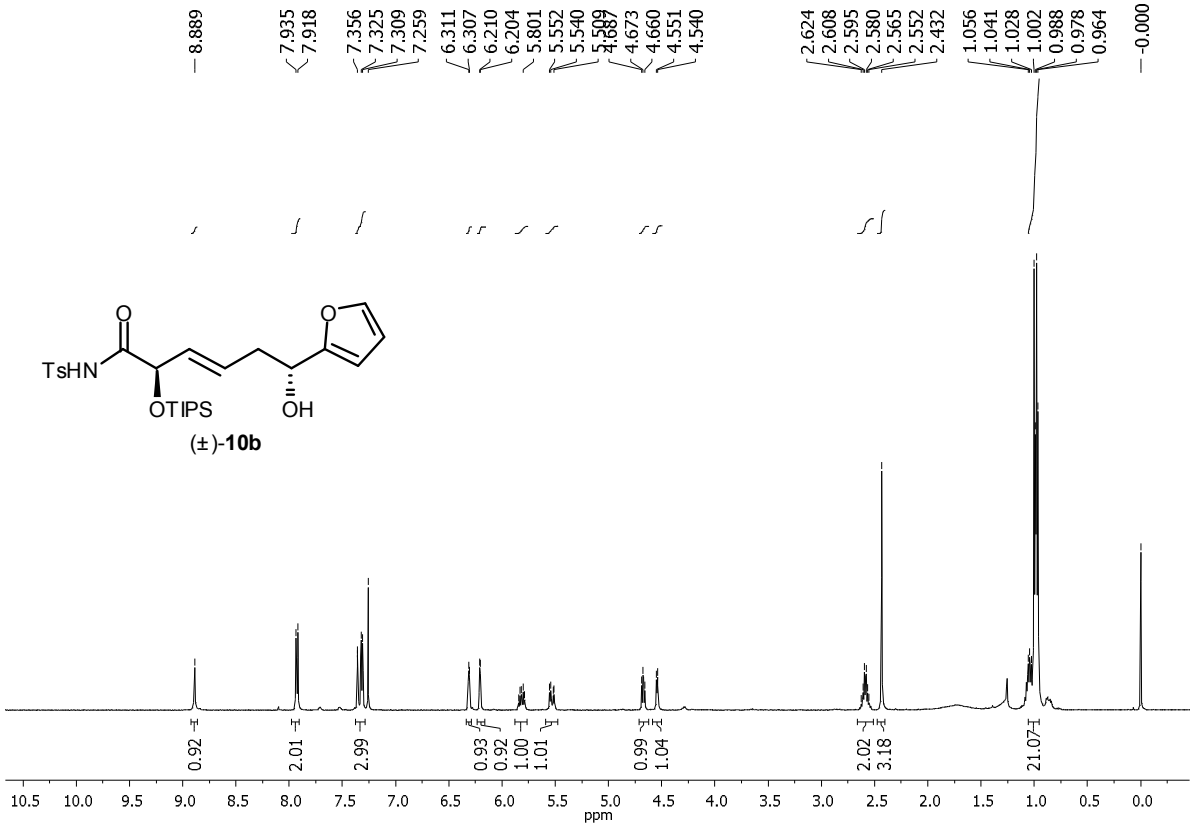
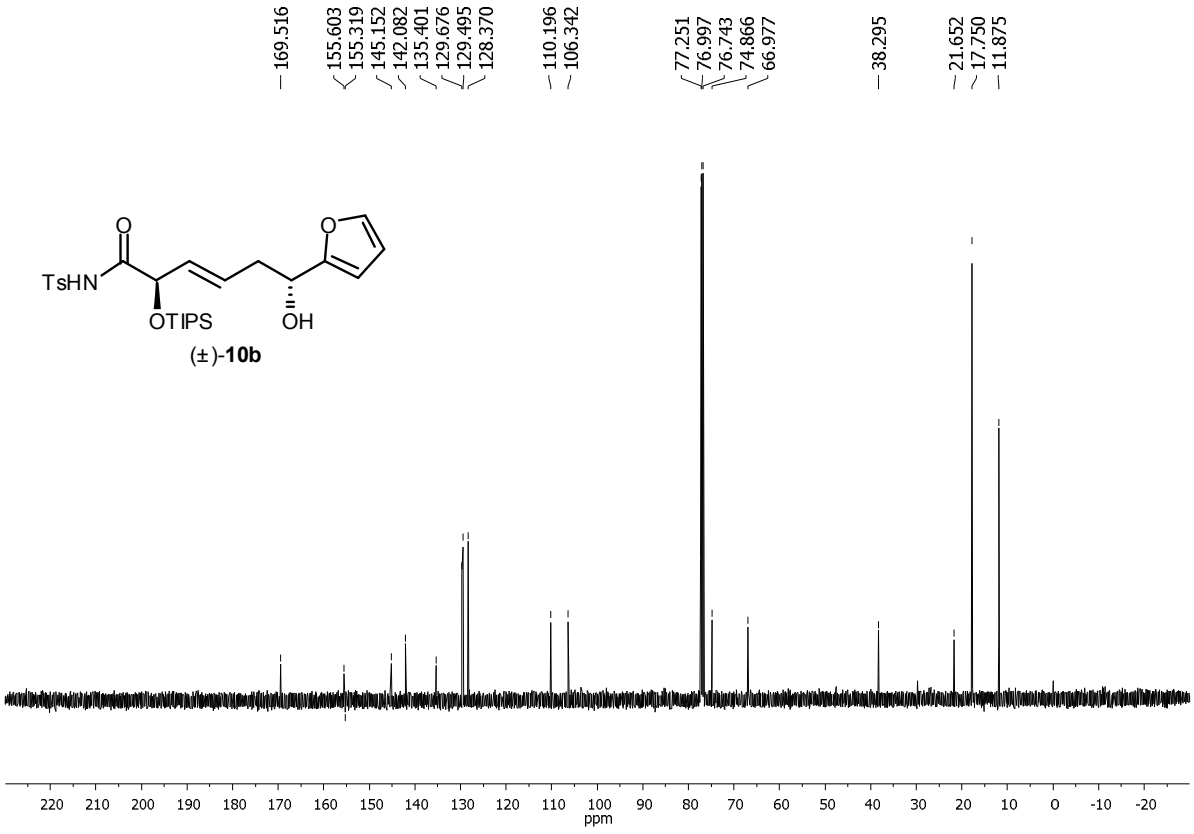
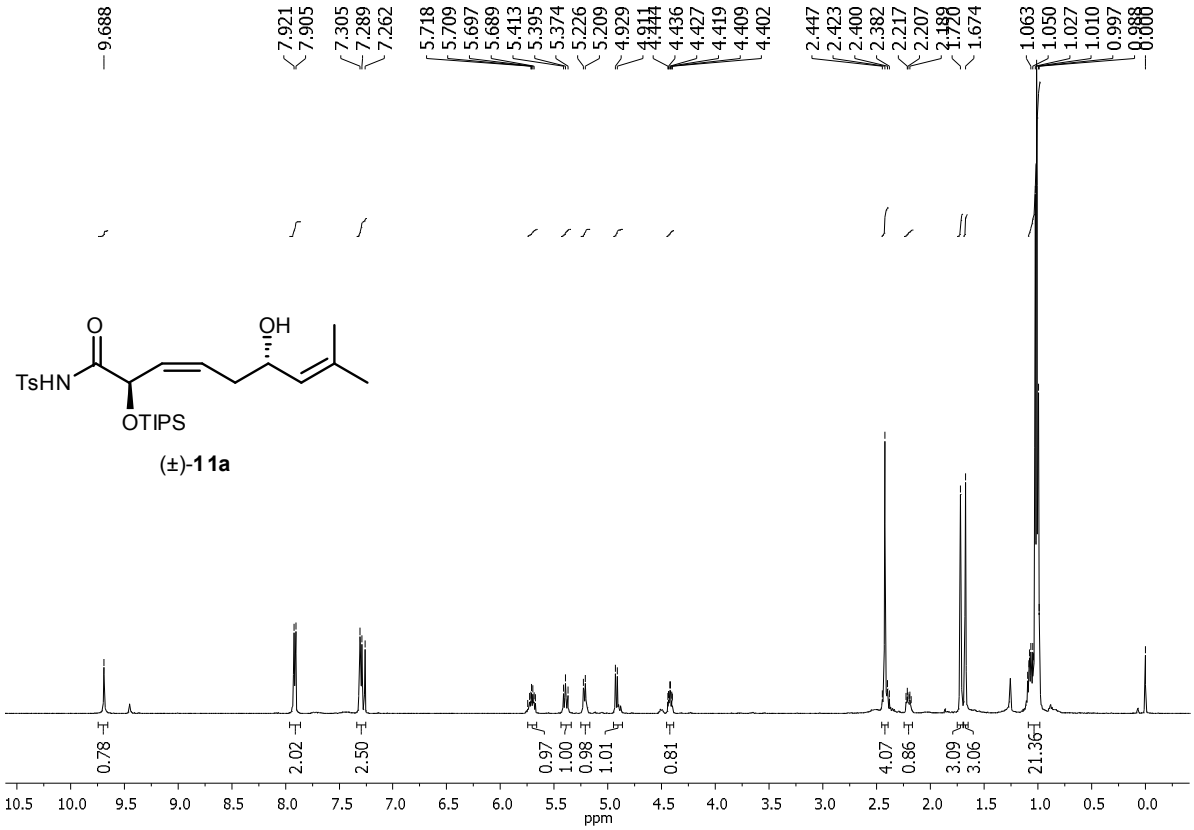


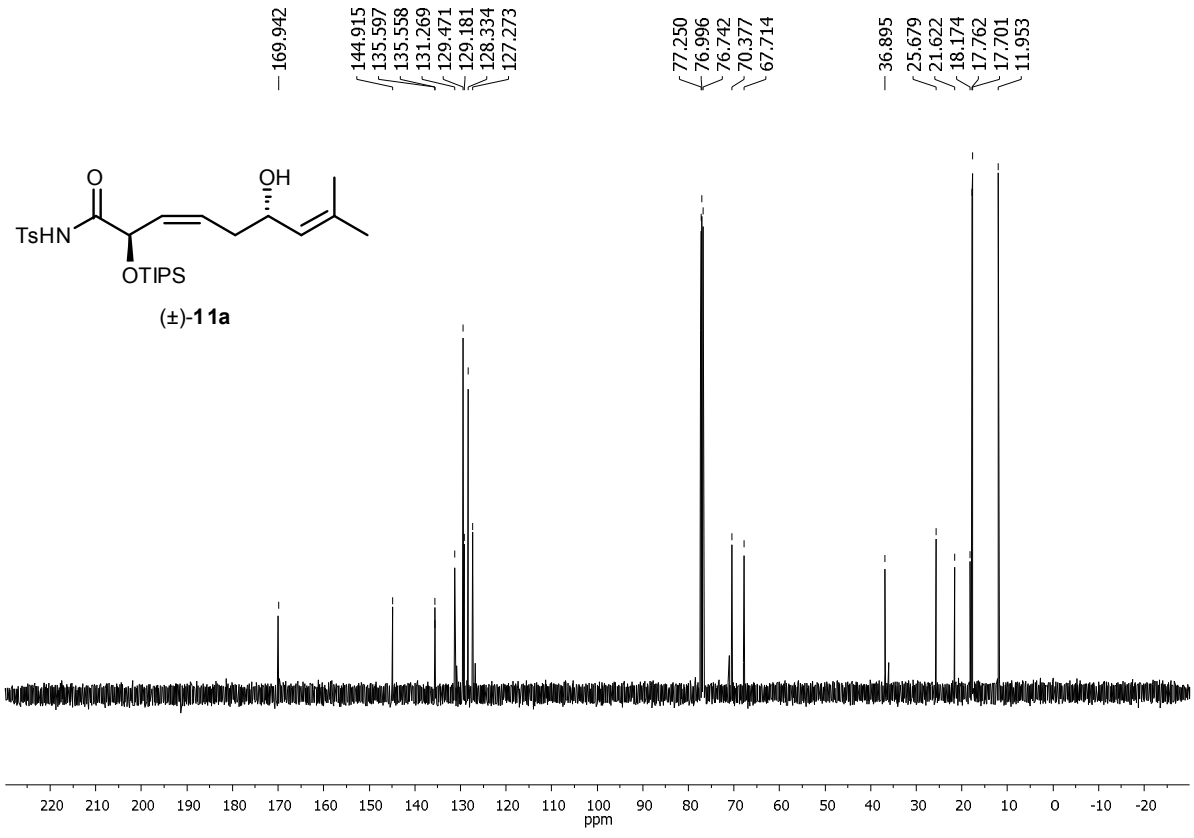
^{13}C NMR (126 MHz, $CDCl_3$)



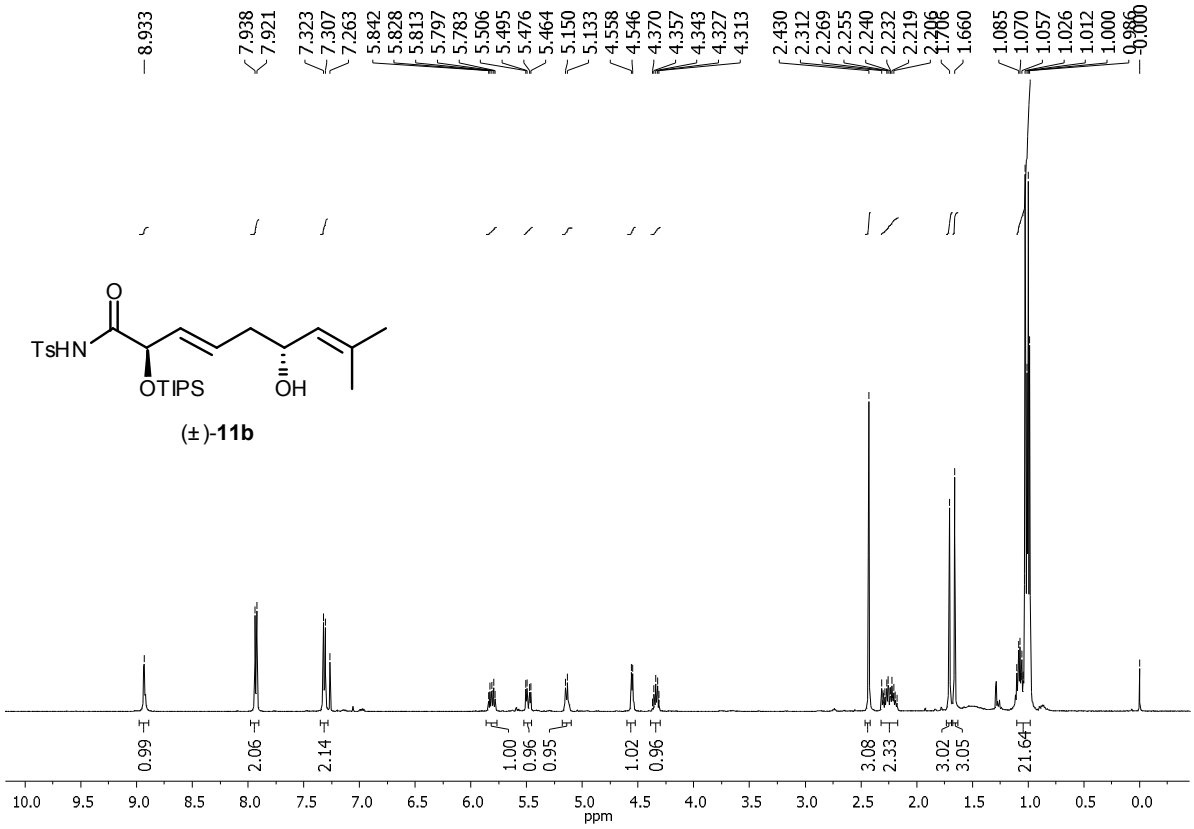
^{1}H NMR (500 MHz, $CDCl_3$)



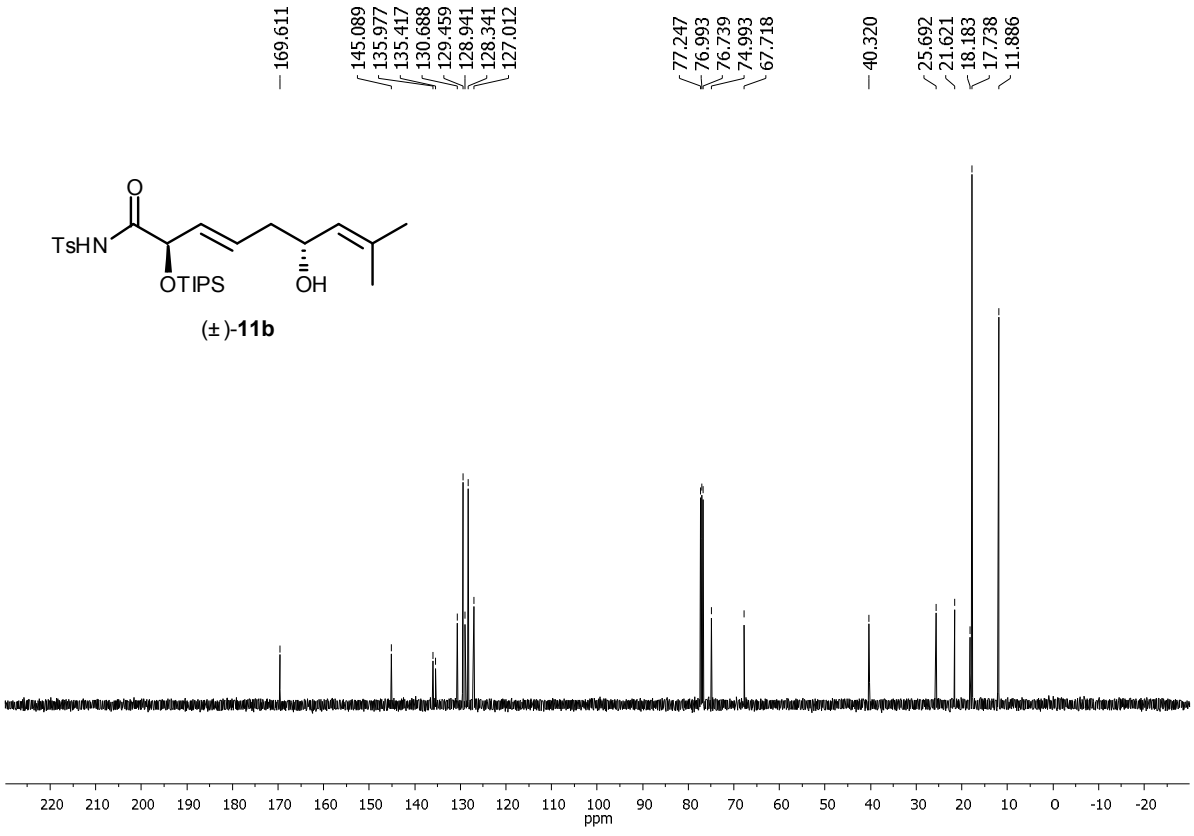
^{13}C NMR (126 MHz, $CDCl_3$)



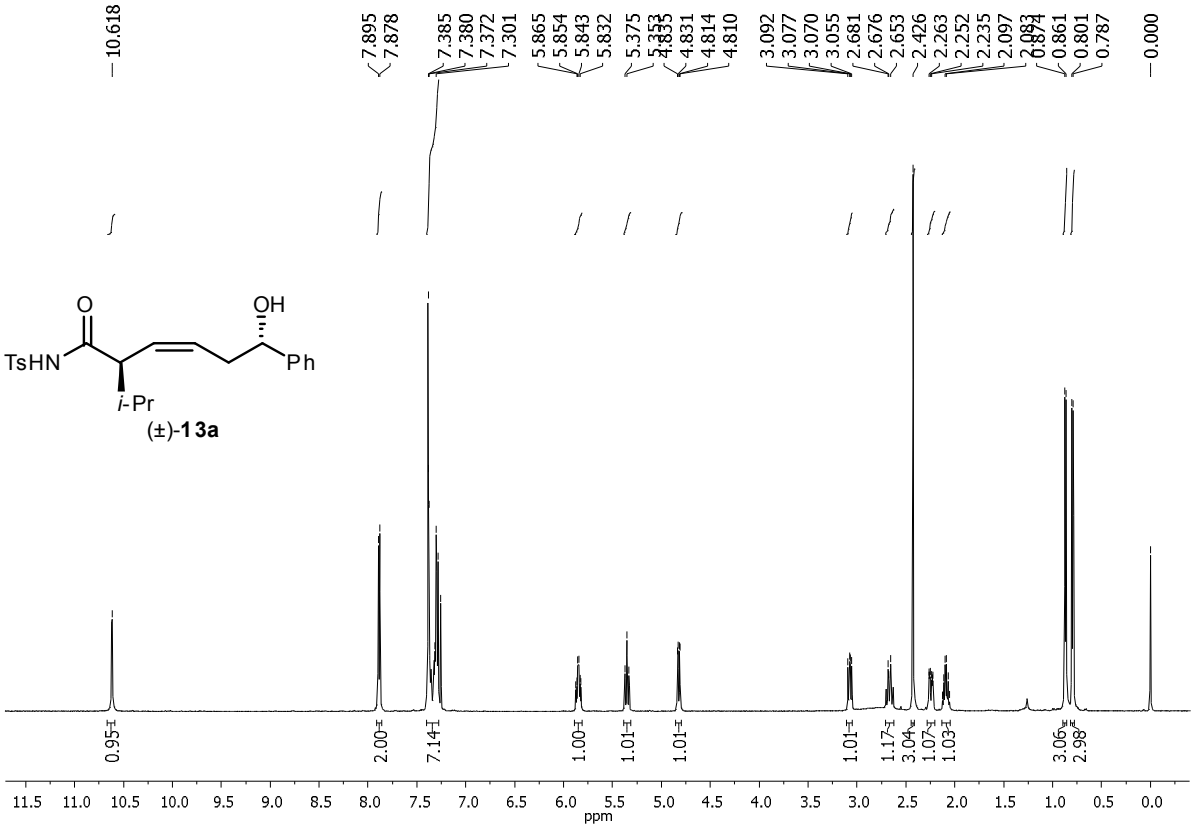
^{1}H NMR (500 MHz, $CDCl_3$)



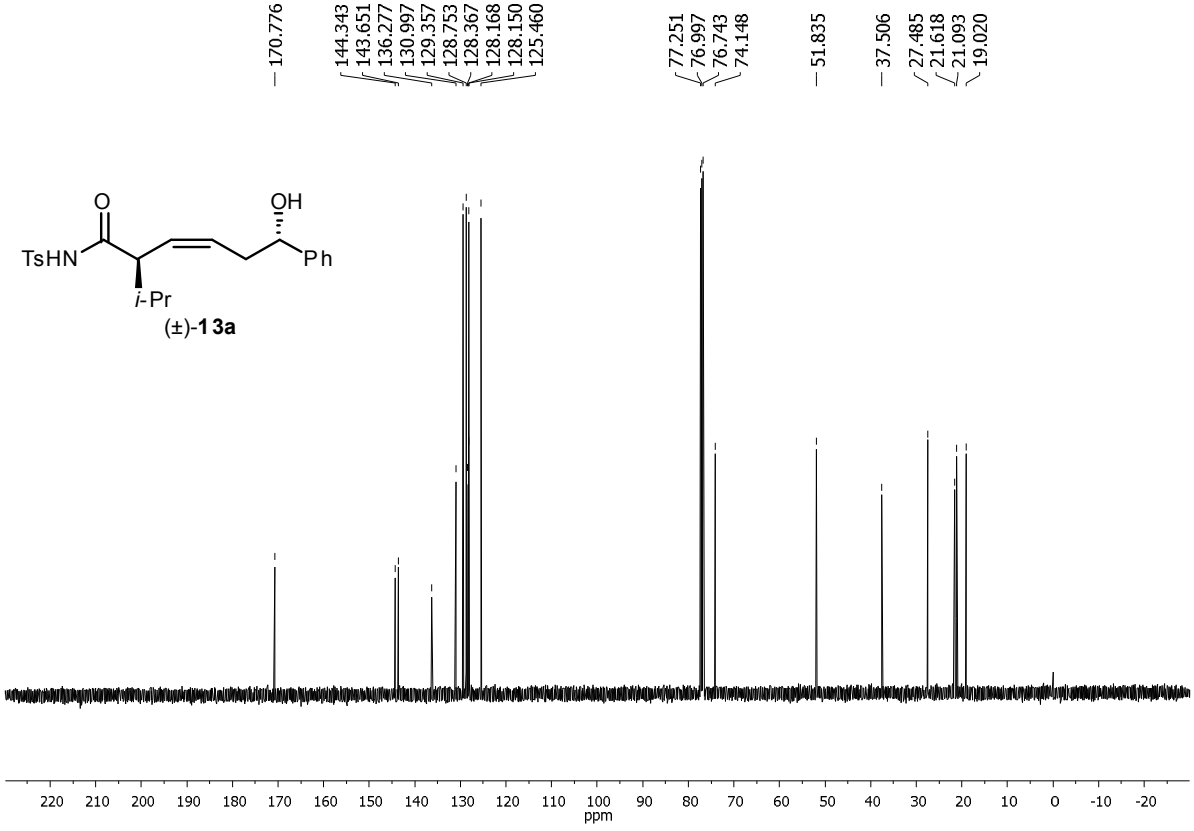
^{13}C NMR (126 MHz, $CDCl_3$)



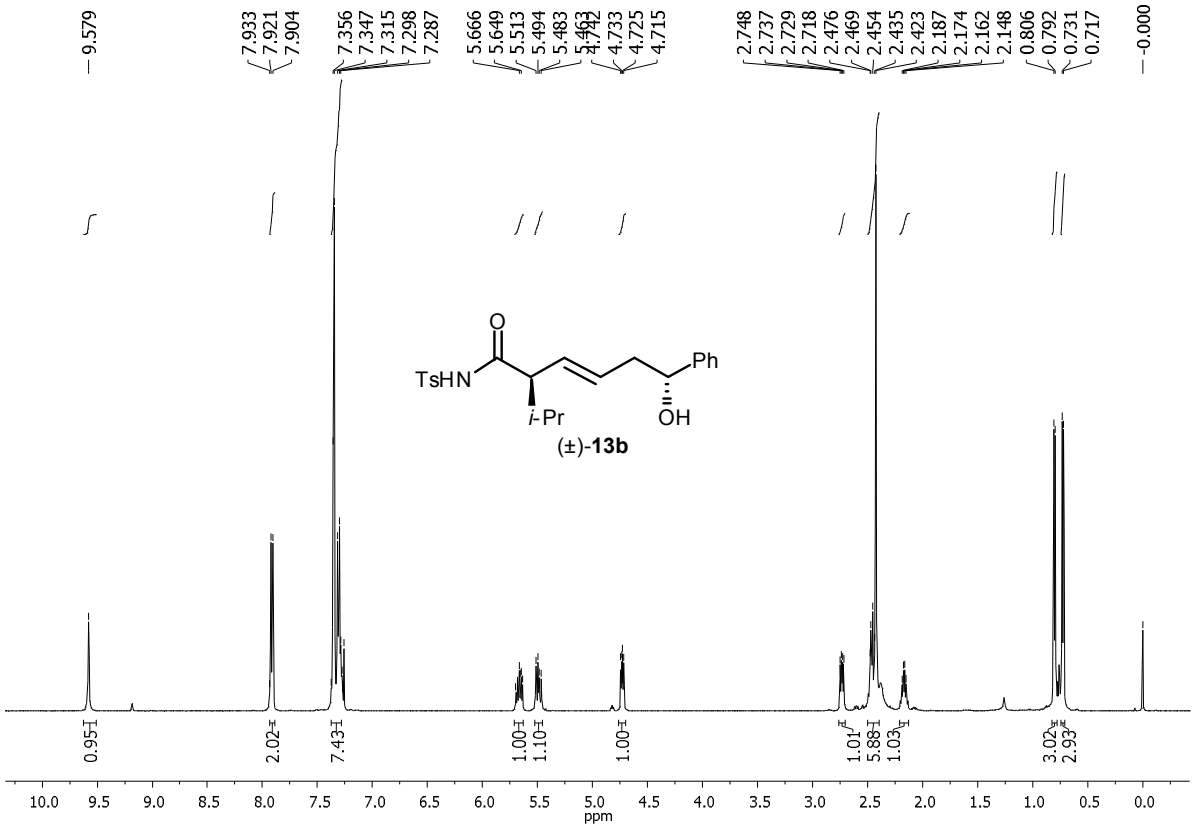
^{1}H NMR (500 MHz, $CDCl_3$)



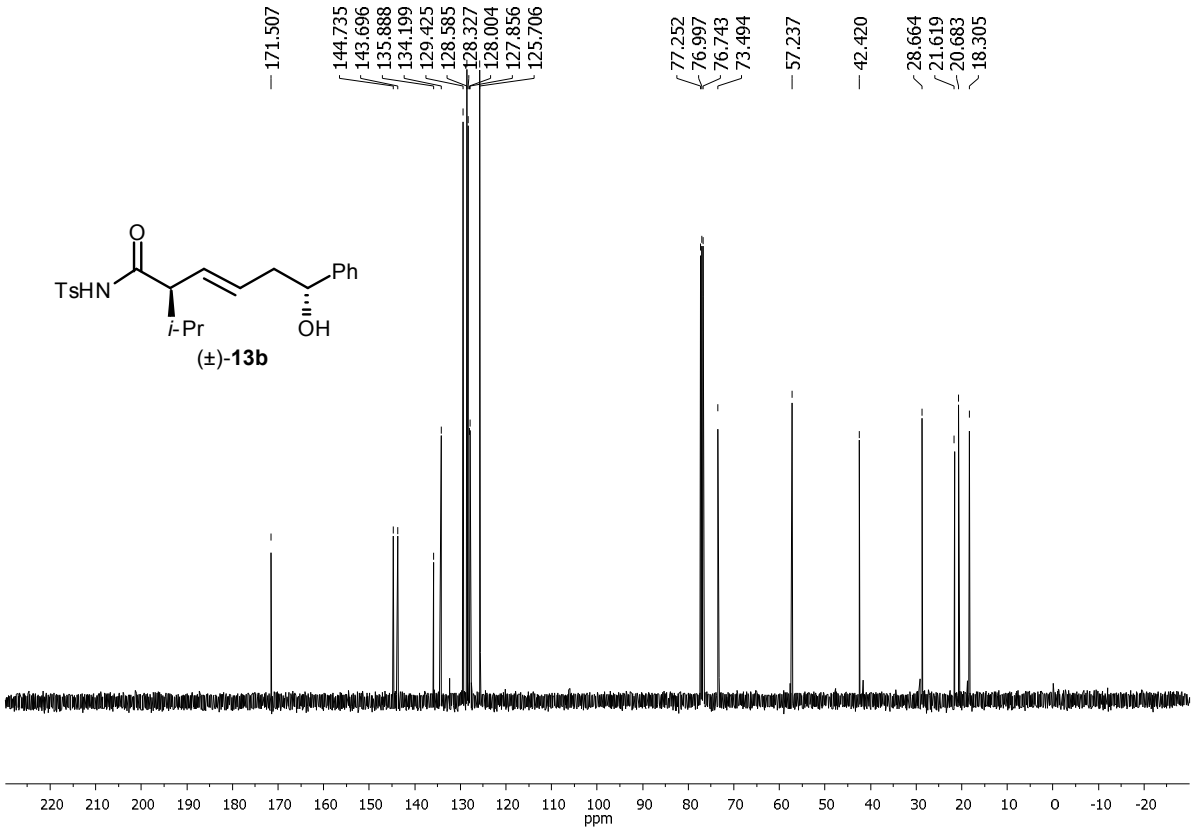
^{13}C NMR (126 MHz, $CDCl_3$)



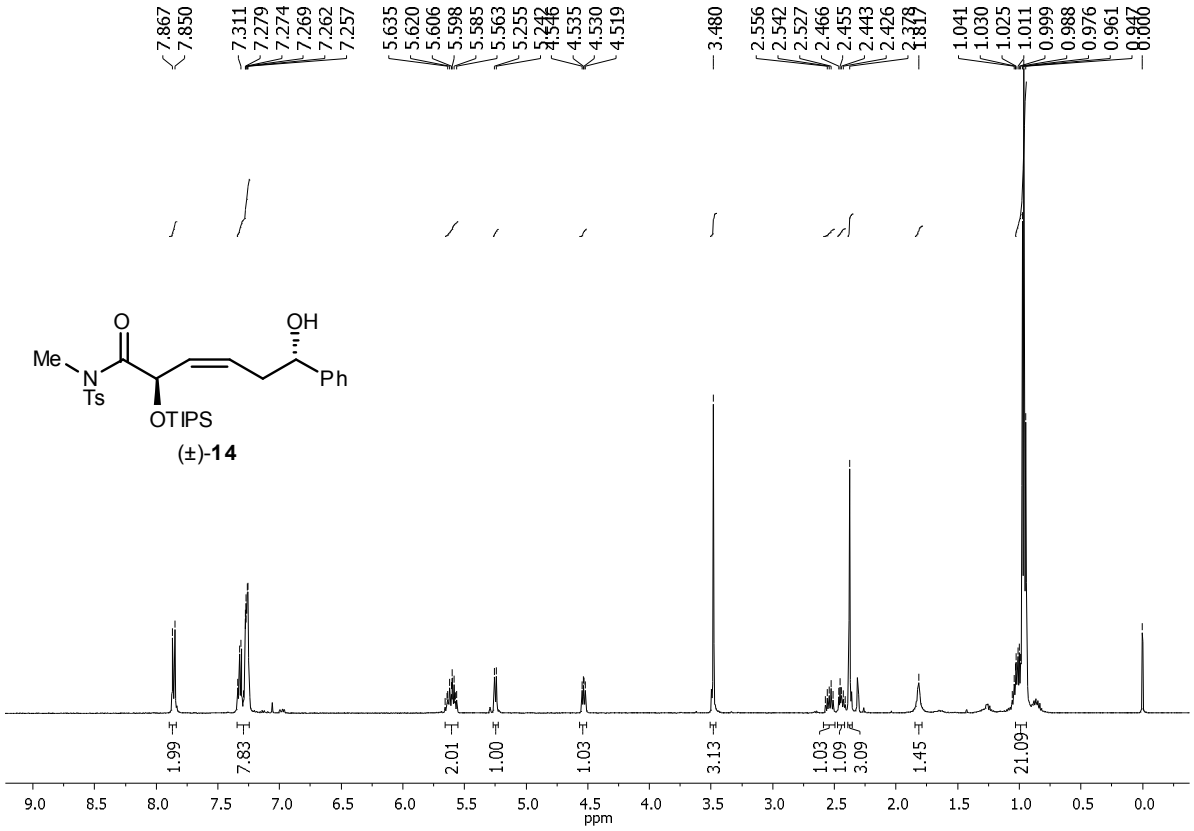
^{1}H NMR (500 MHz, $CDCl_3$)



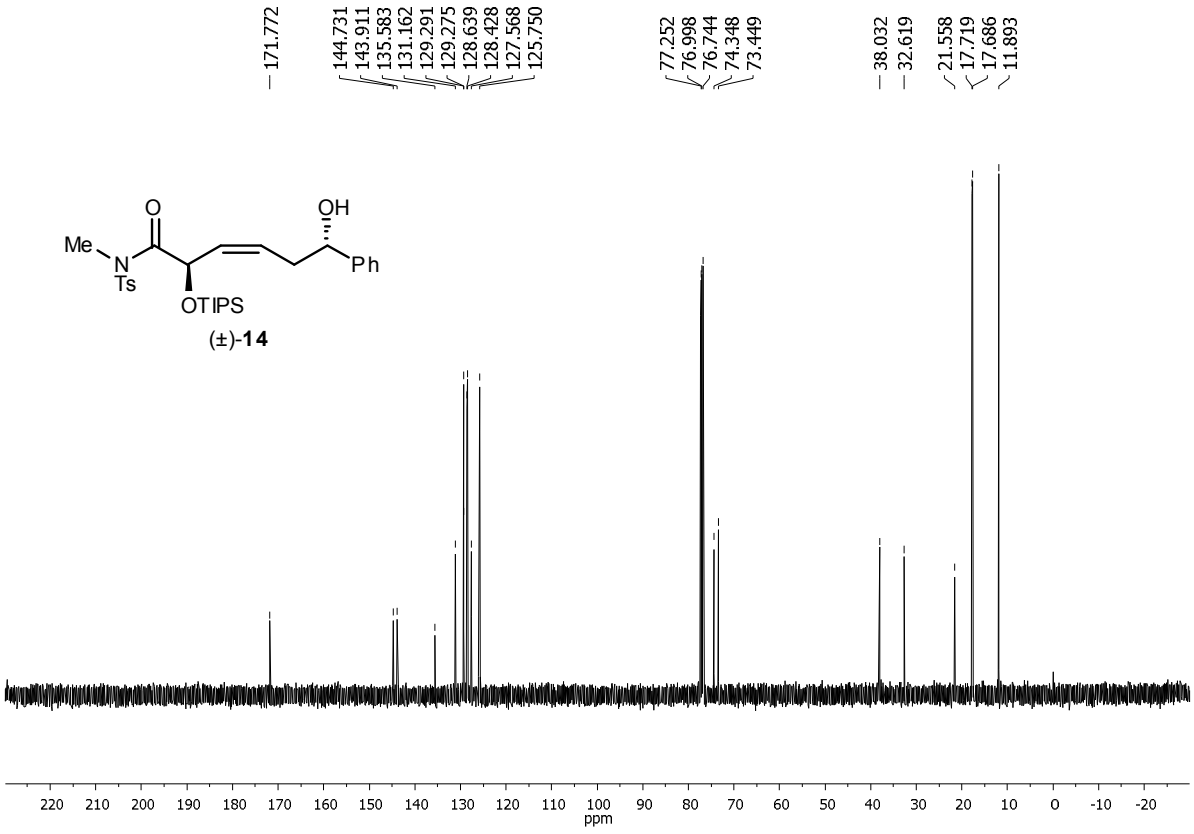
^{13}C NMR (126 MHz, $CDCl_3$)



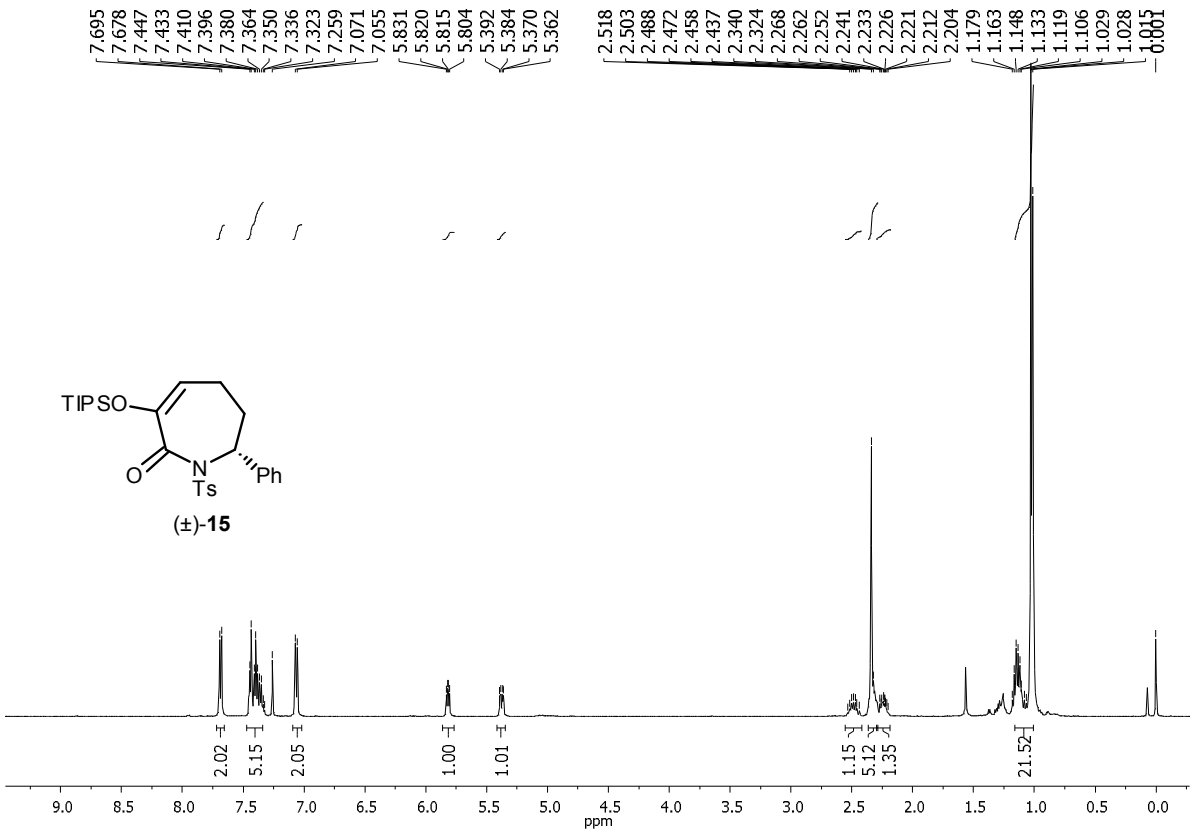
^{1}H NMR (500 MHz, $CDCl_3$)



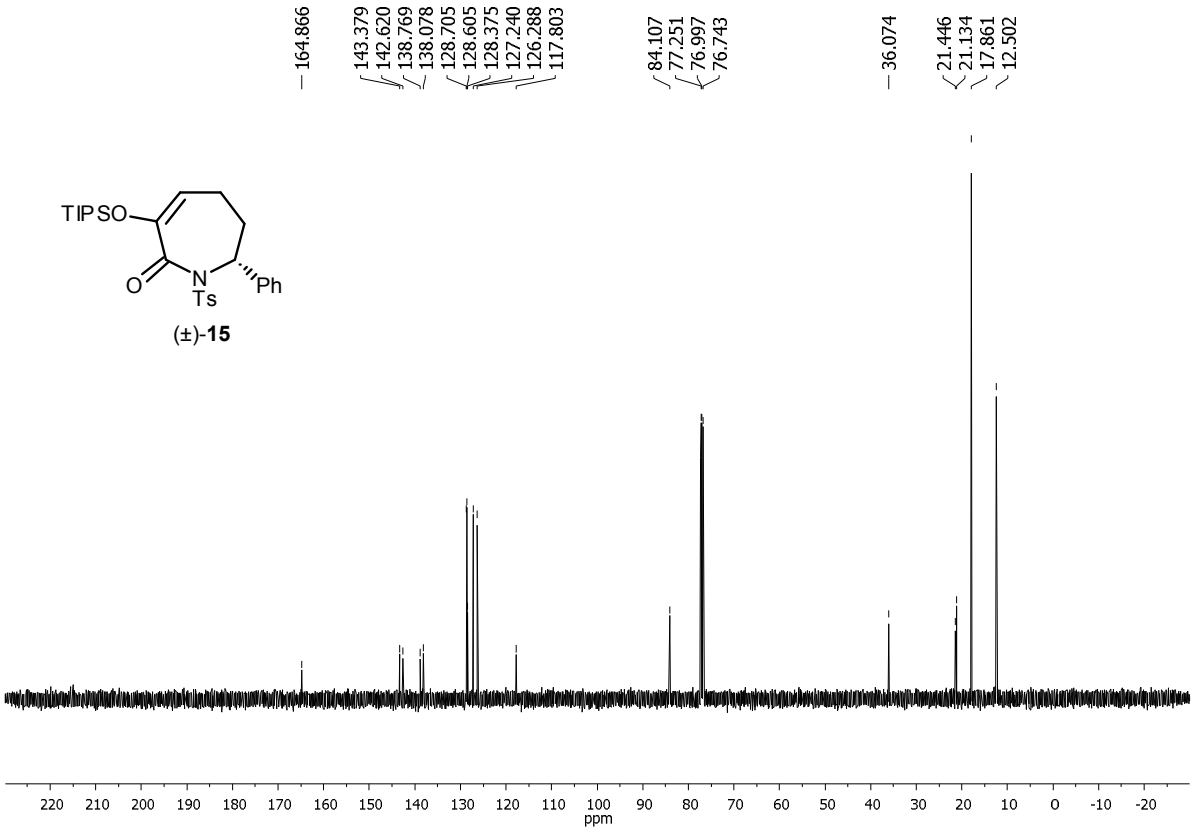
^{13}C NMR (126 MHz, $CDCl_3$)



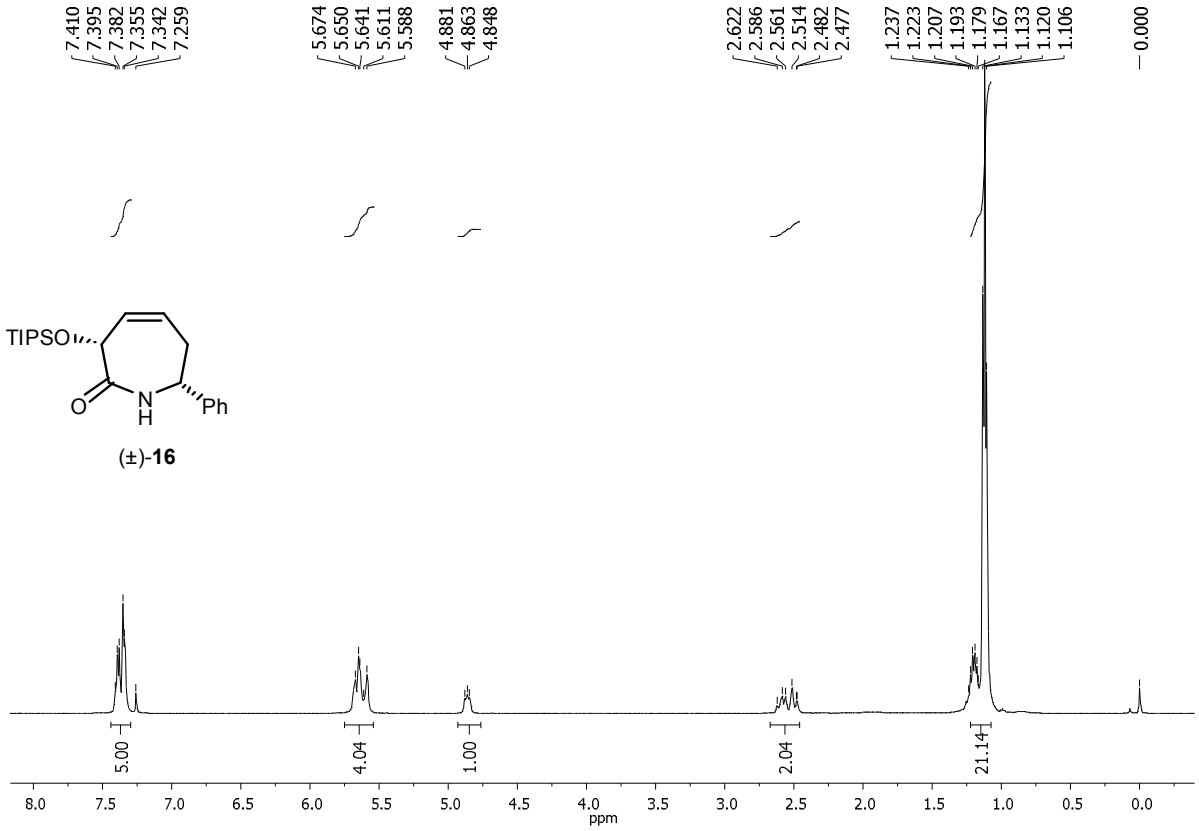
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

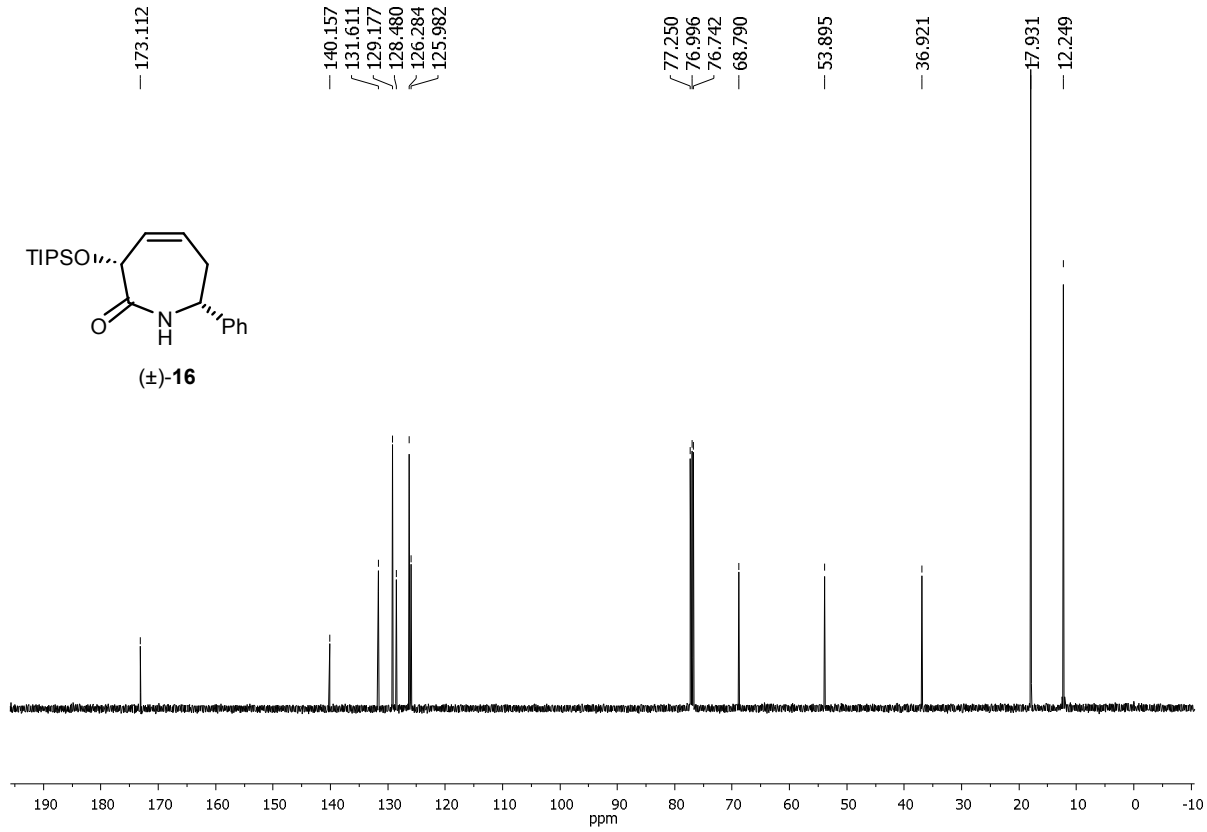


^{1}H NMR (500 MHz, $CDCl_3$)



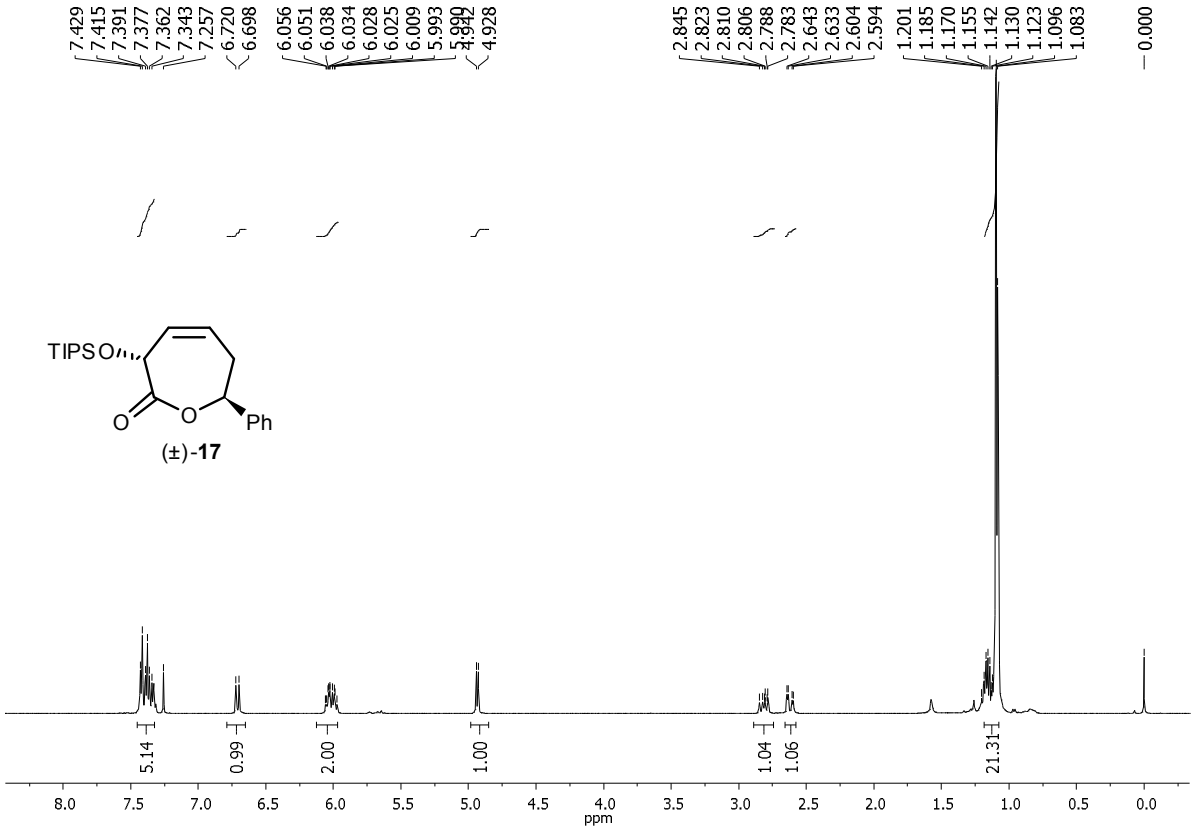
(±)-**16**

^{13}C NMR (126 MHz, $CDCl_3$)

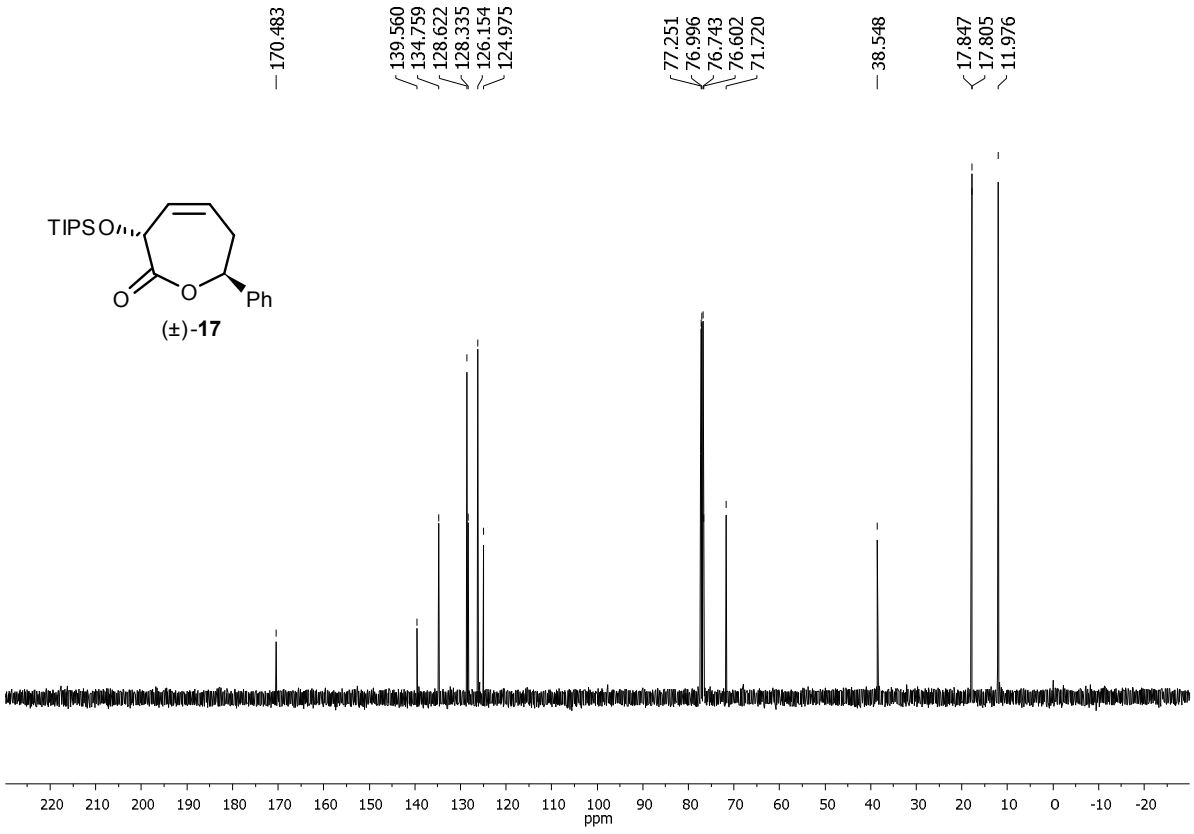


(±)-**16**

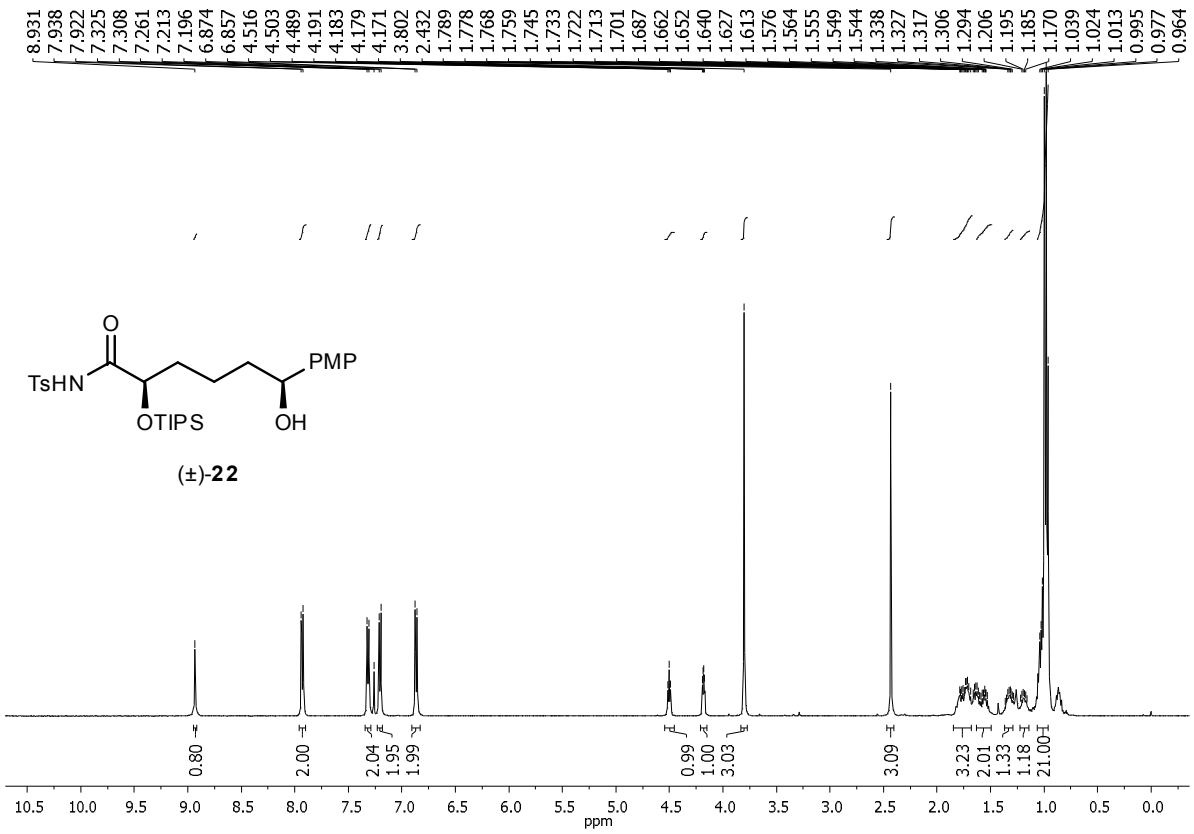
^{1}H NMR (500 MHz, $CDCl_3$)



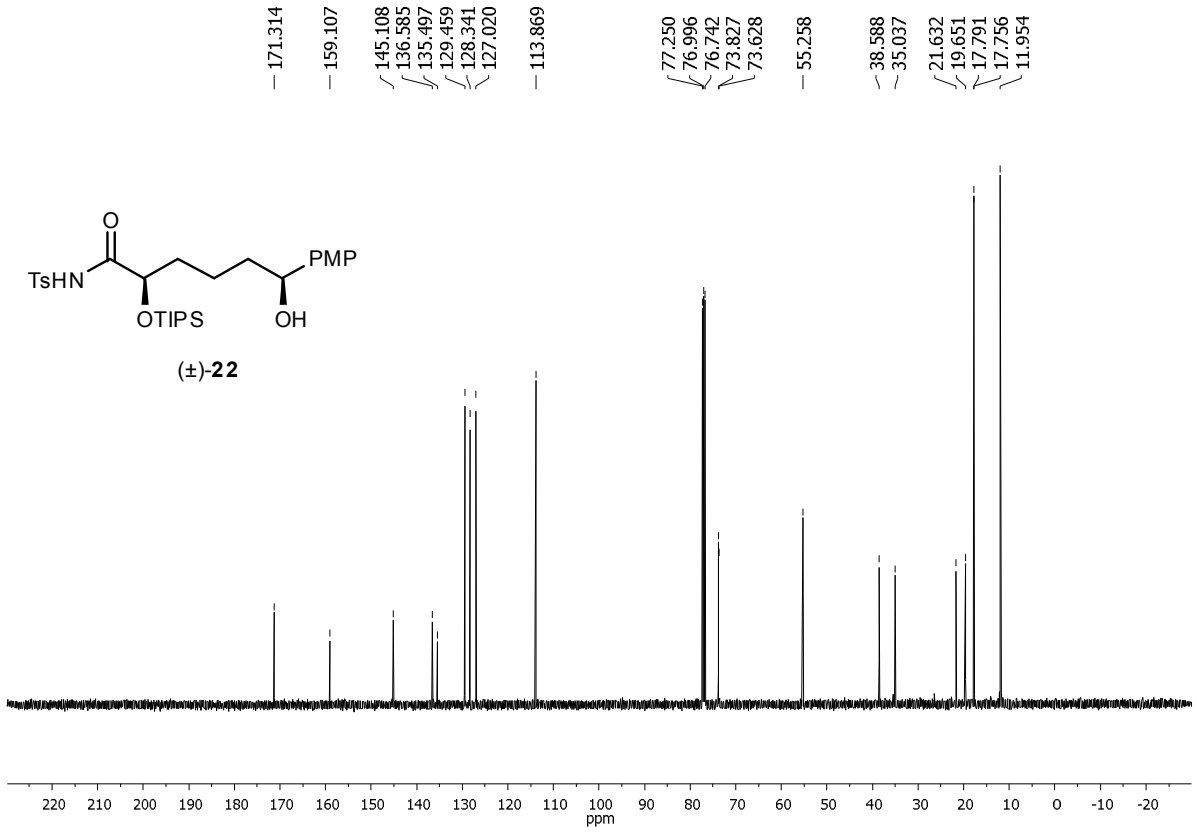
^{13}C NMR (126 MHz, $CDCl_3$)



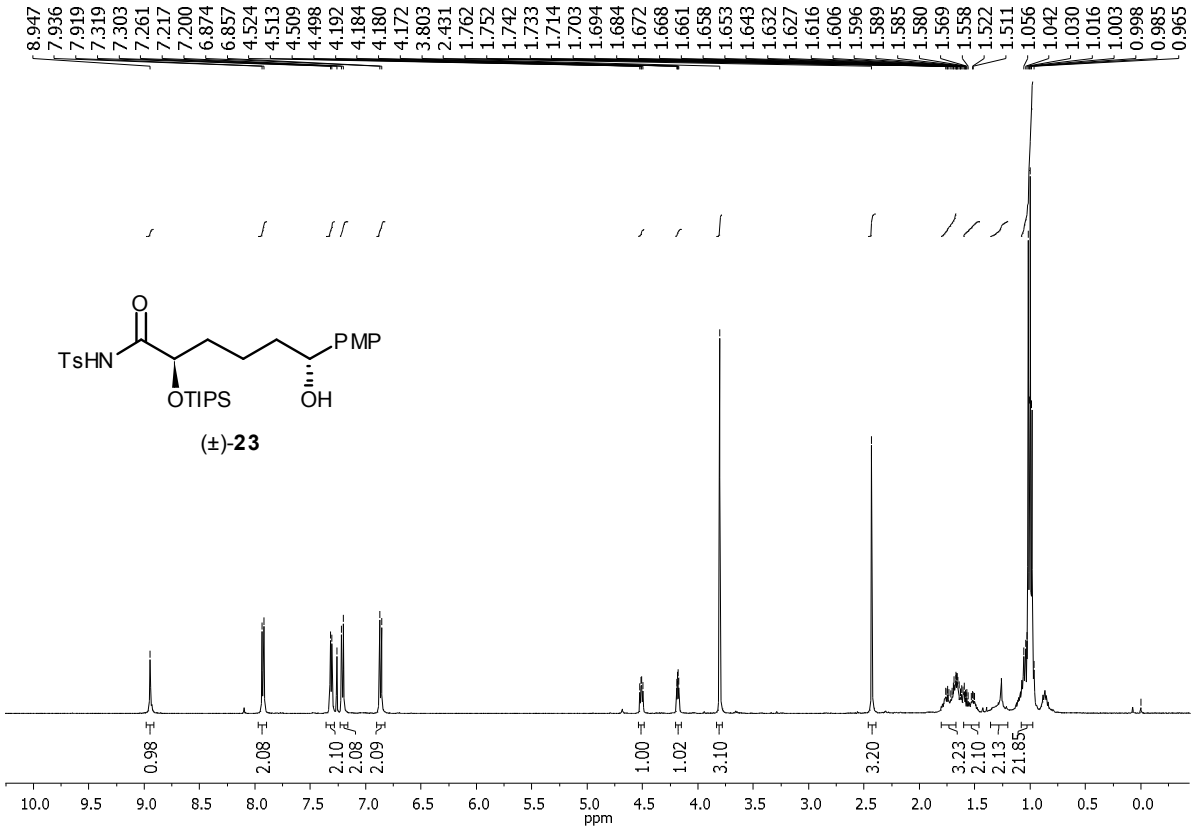
^{1}H NMR (500 MHz, $CDCl_3$)



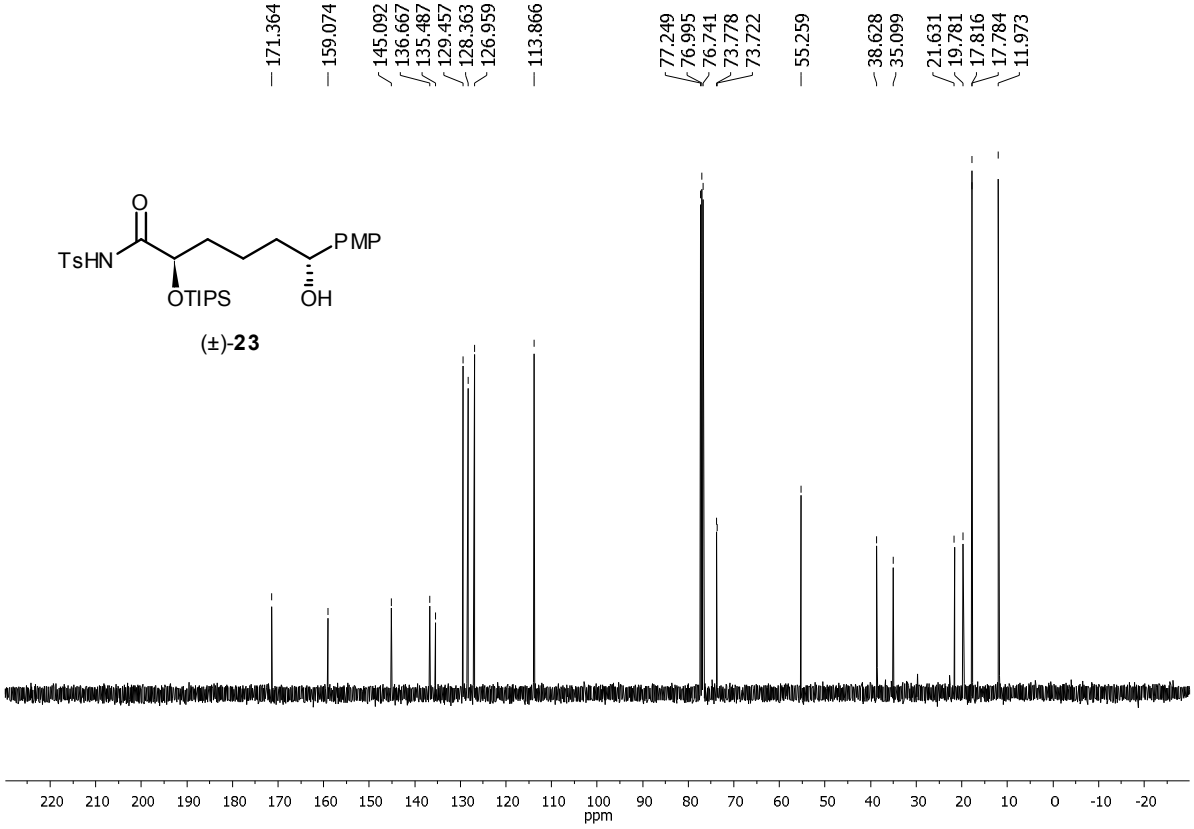
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

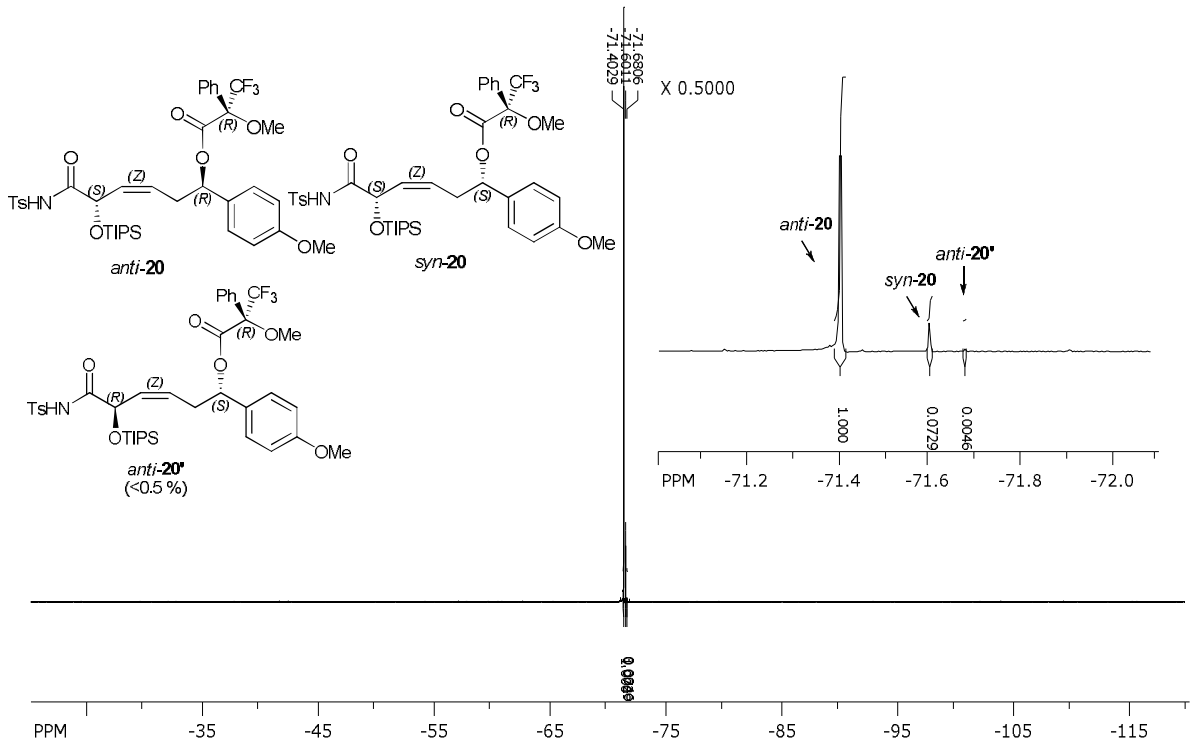


^{13}C NMR (126 MHz, $CDCl_3$)

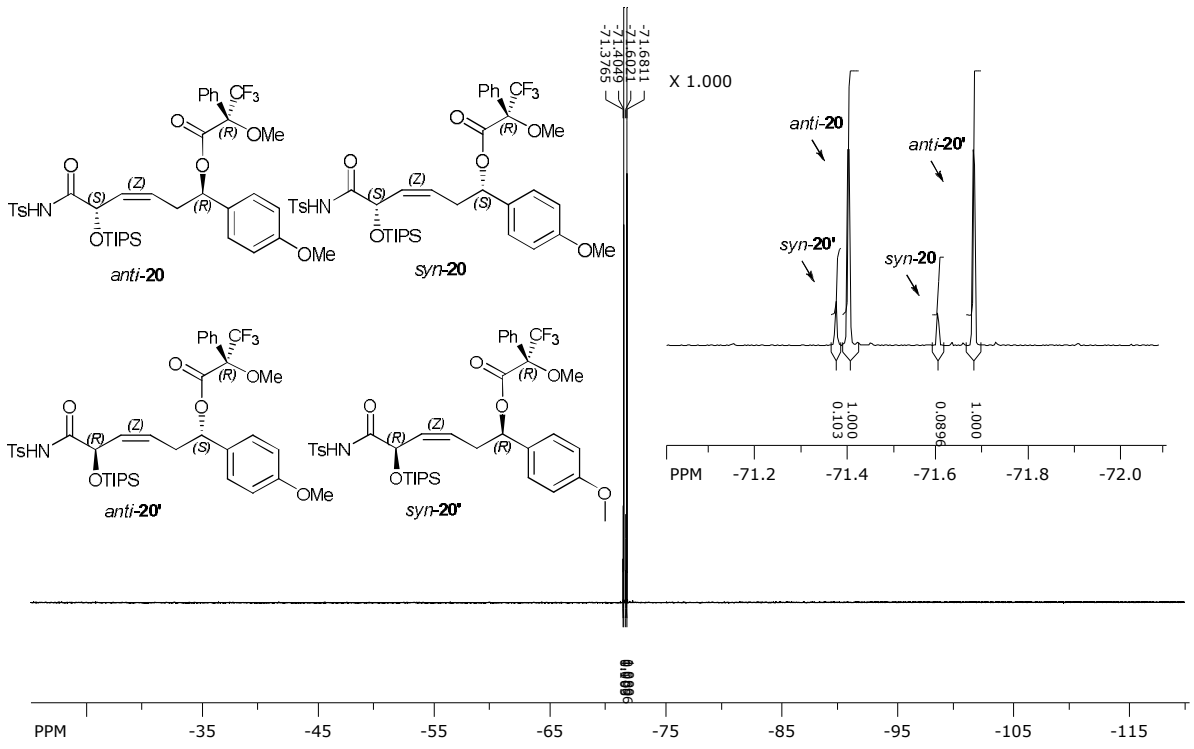


4. ^{19}F NMR spectra of Mosher's esters 20, 21, 20/20' and 21/21'.

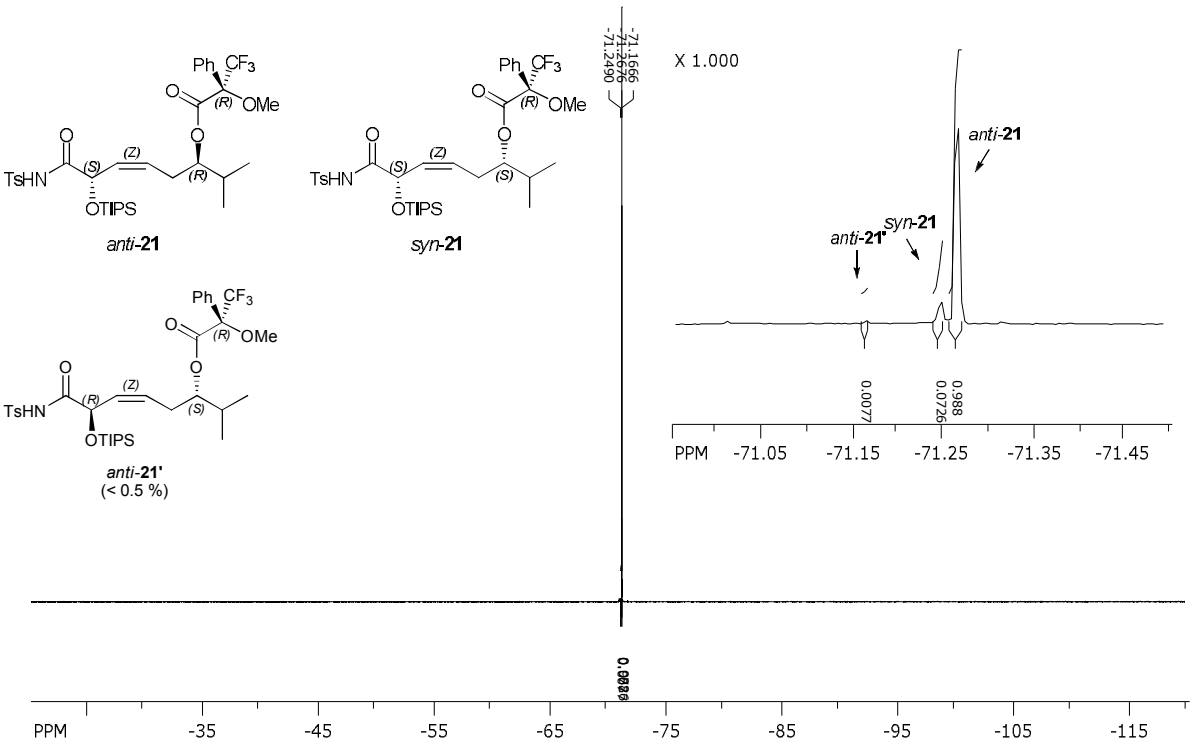
^{19}F NMR (376 MHz, $CDCl_3$)



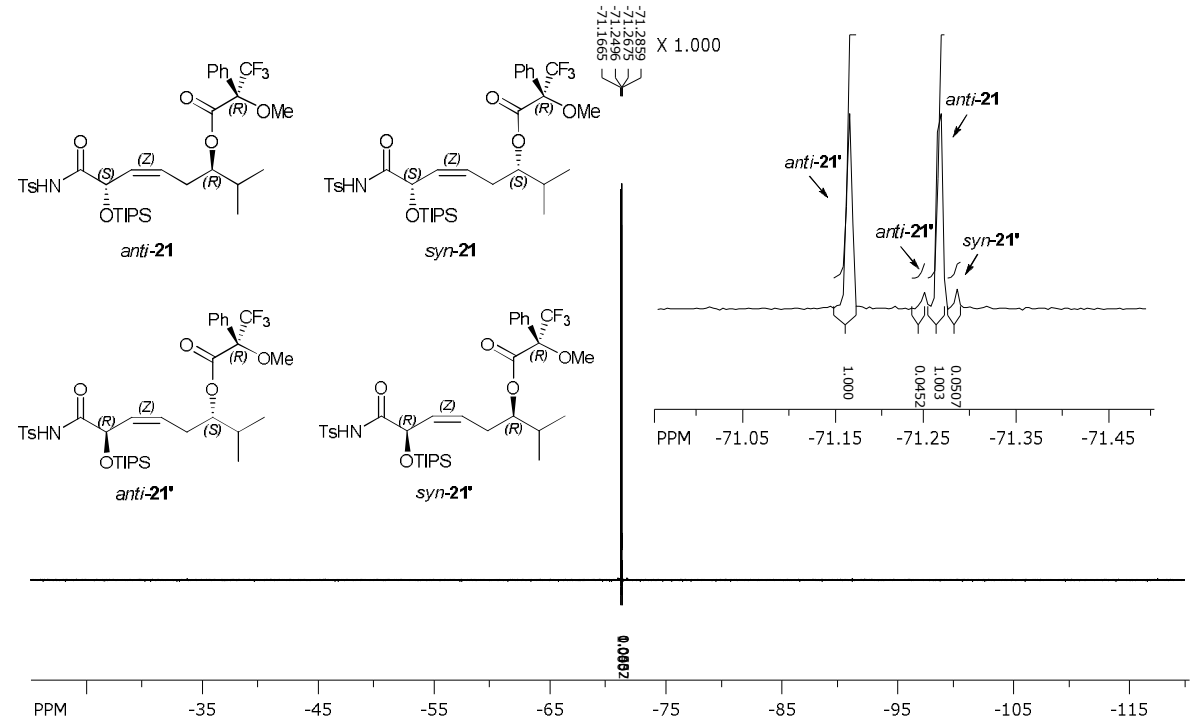
^{19}F NMR (376 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

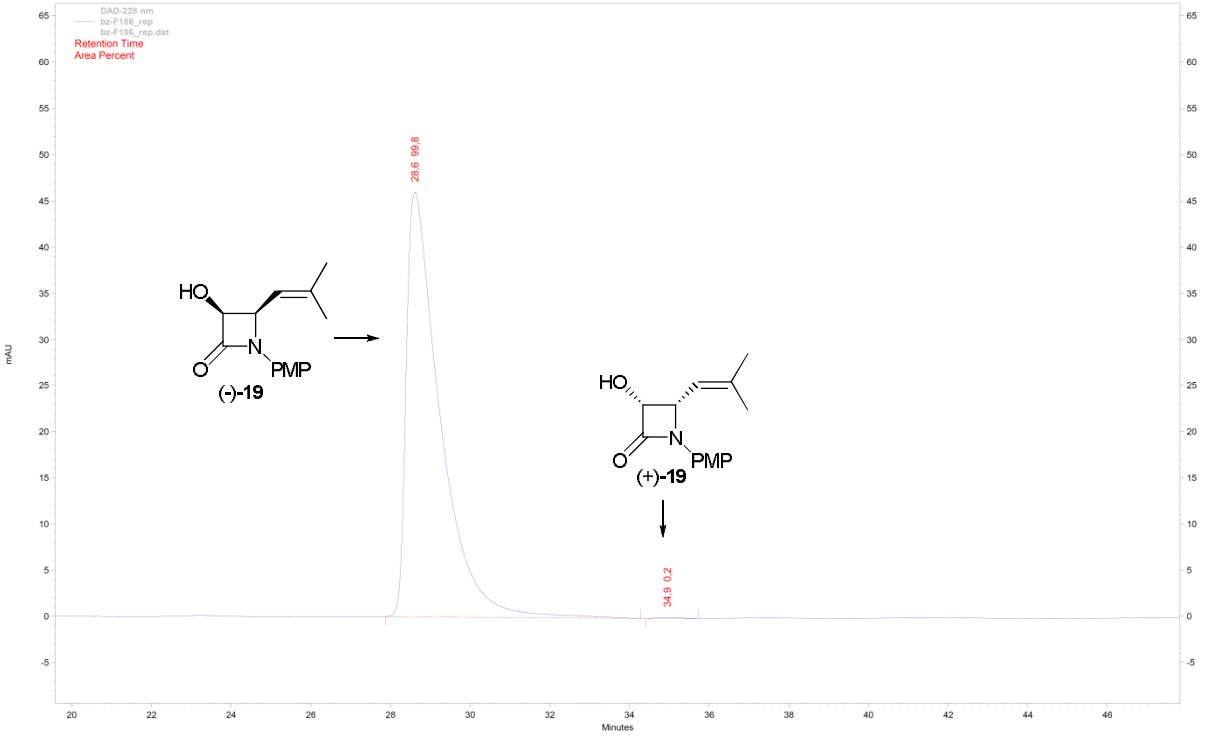


^{19}F NMR (376 MHz, $CDCl_3$)

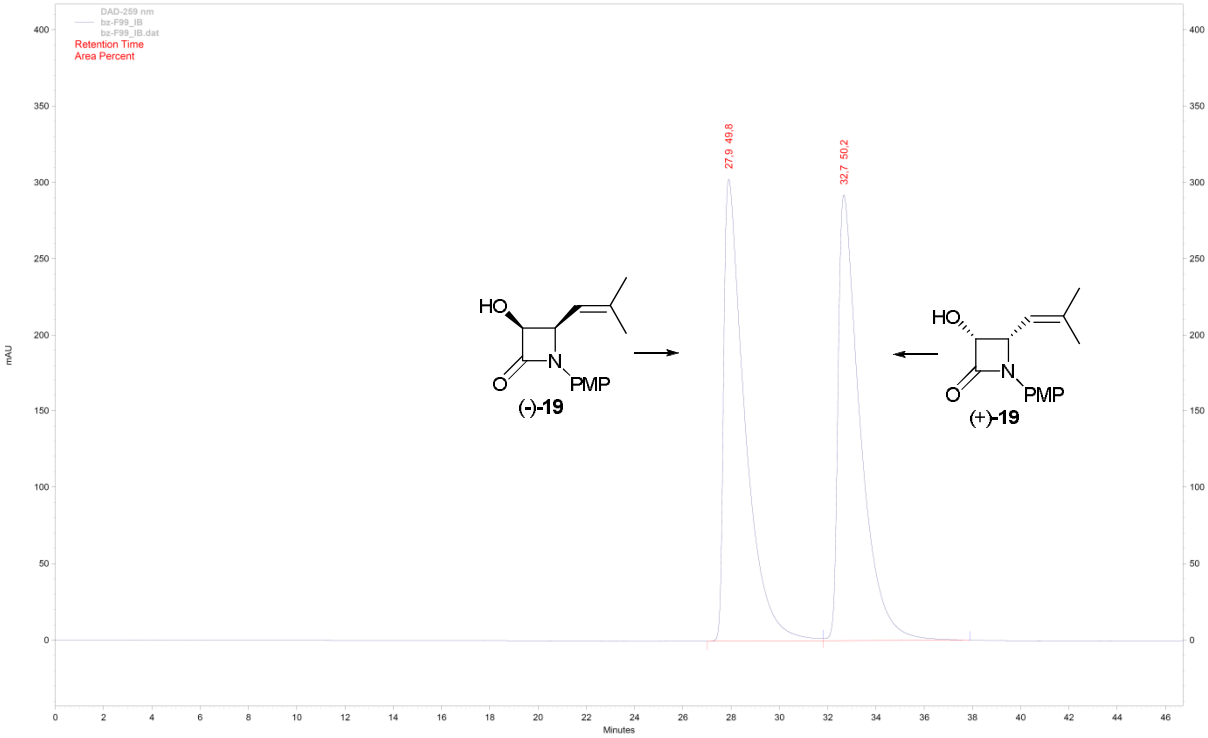


5. HPLC chromatograms of (-)-19 and (±)-19.

HPLC (Daicel Chiralpak IB column), hexane/i-PrOH = 97:3, flow rate 1.0 mL/min, λ = 212 nm): tR(-)-**19** = 28.6 min, tR (+)-**19**= 34.9 min,

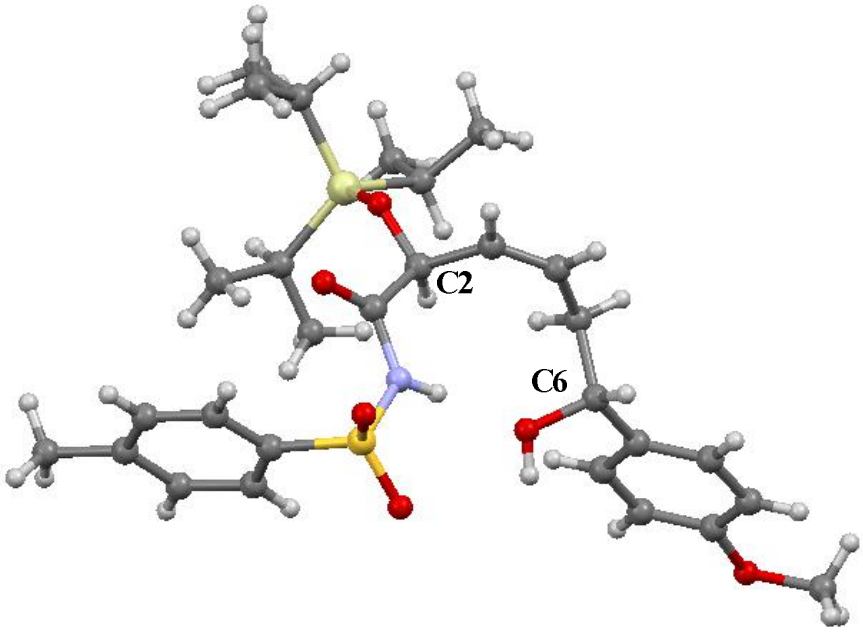


(-)-19



(±)-19

6. X-ray structure of (±)-5a.



7. References.

1. **(**a) L. Kuznetsova, I. M. Ungureanu, A. Pepe, I. Zanardi, X. Wu and I. Ojima, *J. Fluorine Chem.*, 2004 , **125**, 487; (b) I. Ojima, S. Lin, T. Inoue, M. L. Miller, C. P. Borella, X. Geng and J. J. Walsh, *J. Am. Chem. Soc.*, 2000, **122**, 5343.
2. D. C. Ha, D. J. Hart and T. K. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 4819.
3. K. Kojima, M. Kimura, S. Ueda and Y. Tamaru, *Tetrahedron*, 2006, **62**, 7512.