Electronic Supplementary Material (ESI) for ChemComm.

Combining cycloisomerization with trienamine catalysis: A regiochemically flexible enantio- and diastereoselective synthesis of hexahydroindoles

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Contents

1. EXPERIMENTAL

1.1 General Experimental Considerations

Nuclear Magnetic Resonance Spectroscopy: ^{1}H NMR spectra were acquired on Bruker DRX500, AVII500 (500 MHz, with cryoprobe) or AVIII400 (400 MHz) spectrometers and were referenced to residual non-deuterated solvent peaks in $CDCl_3$ (δ = 7.26) or C_6D_6 (δ = 7.16). Chemical shifts (δ_H and δ_C) are reported in parts per million (ppm) with signal splittings recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), and multiplet (m); app = apparent. Coupling constants (*J*) are measured to the nearest 0.1 Hz and are presented as observed. ^{13}C NMR spectra were obtained on Bruker AVII500 (126 MHz, with cryoprobe) or AVIII400 (101 MHz) spectrometers and were referenced to solvent peaks in $CDCl_3$ (δ = 77.16). Where diastereomeric mixtures are formed, data is given for the major diastereomer, unless specified otherwise.

Mass Spectrometry: Low-resolution mass spectra (*m/z*) were recorded on a Waters LCT Premier EX mass spectrometer, using electrospray ionization (ESI). High-resolution mass spectra (HRMS) were recorded by the Departmental Mass Spectrometry Service, University of Oxford on a Bruker MicroTOF (resolution = 5000 FWHM) using electrospray ionisation (ES^+). The parent ion $[M]^+$, $[M+H]^+$ or $[M+Na]^+$ is calculated to 4 decimal places from the molecular formula, and all values are within a tolerance of 5 ppm.

Infrared Spectroscopy: Absorption spectra were obtained in $CHCl_3$ as solvent on a Bruker Tensor 27 FT-IR spectrometer. The sample was prepared as a thin film on a diamond/ZnSe PIKE Miracle ATR module. Wavelengths of maximum absorbance (ν_{max}) are quoted in wavenubers (cm^{-1}). Only selected, characteristic IR absorption data are provided for each compound.

Specific rotations: Optical rotations were recorded on a Perkin Elmer 241 or 341 polarimeter with a path length of 1 dm (using the sodium D line, 589 nm). Specific rotations ($[\alpha]_D$) are reported in units of 10^{-1} deg cm^2 g^{-1}. Concentrations are reported in g/100 mL. Temperatures are reported in °C (typically 25 °C).

Chromatography: Flash chromatography refers to normal phase column chromatography on silica gel using a head pressure of N_2, using either Merck Geduran® Silicagel 60 (40 - 63 μm) or Macherey-Nagel Silica 60 M (40 - 63 μm). Thin-layer chromatography was performed on Merck Kieselgel 60 F_{254} plates with visualization by ultraviolet light (254 nm) and/or heating the plate after staining with vanillin or $KMnO_4$. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series running in normal phase under UV detection using a ZORBAX RX-SIL (150 mm x 4.6 mm ID) as the analytical column. Chiral analysis was carried out using DAICEL CHIRALPAK-IA, IB or IC (250 mm x 4.6 mm ID).

Materials: Unless otherwise stated, all reactions were carried out in oven-dried glassware under an atmosphere of argon, using anhydrous reaction solvents. Et_2O, CH_2Cl_2, THF and toluene were dried over activated alumina before use. All other commercially available reagents and solvents were either used as received, and/or dried and purified before use using standard procedures. Petroleum ether refers to the fraction of light petroleum ether boiling at 40-60 °C unless stated otherwise.

1.2 General Procedures

General Procedure A: *Mitsunobu Reaction*

DIAD (1.3 equiv.) was added dropwise to a stirred solution of alcohol (1.0 equiv.), triphenylphosphine (1.5 equiv.) and methyl tosylcarbamate (1.2 equiv.) in THF (3 mL / mmol of alcohol) at 0 °C. The reaction mixture was stirred at rt overnight, then it was filtered and concentrated. The residue was taken up in petroleum ether / Et_2O (1:1, 10 mL / mmol of alcohol), stirred for 5 min, then filtered and concentrated. The residue was once again taken up in petroleum ether / Et_2O (1:1, 10 mL/mmol of alcohol), stirred for 5 min, filtered, and the filtrate concentrated. Purification by flash chromatography afforded the product.

General Procedure B: *Carbamate deprotection of sulfonamide carbamates*

To a solution of the carbamate (1.0 equiv.) in MeOH (10 mL / mmol carbamate) was added K_2CO_3 (2.0 equiv.). The reaction mixture was stirred for 5 h at RT, then it was concentrated to a volume of approximately 5 mL. The mixture was then added to NH_4Cl (10 mL / mmol carbamate), and extracted with EtOAc (3 × 10 mL / mmol carbamate). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography afforded the product.

General Procedure C: *Copper(II)-catalysed enynamide formation*

According to the procedure of Hsung et al.[1] To a mixture of sulfonamide (1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (0.2 equiv.), 1,10 phenanthroline (0.4 equiv.) and K_3PO_4 (2.0 equiv.) was added a solution of bromoalkyne (1.4 equiv.) in toluene (2 mL / mmol sulfonamide). The reaction mixture was stirred at 70 °C for 15 h before being allowed to cool to RT. The reaction mixture was filtered through Celite, eluting with Et_2O, and the filtrate was concentrated. Purification by flash chromatography afforded the ynamide.

General Procedure D: *Cs_2CO_3 promoted synthesis of dichloroenamides*

According to the procedure of Anderson et al.[2] To a stirred suspension of amide (1.0 equiv.) and Cs_2CO_3 (3.0 equiv.) in DMF (0.75 mL / mmol amide), at 50 °C, was added trichloroethylene (3.0 equiv.) dropwise over ten minutes. The resulting mixture was stirred at 50 °C for 2 h. Upon cooling to rt, the mixture was partitioned between EtOAc and water, the organic layer was separated and further washed with water (x 3). The organic layer was dried (Na_2SO_4), filtered, and concentrated. Purification by flash chromatography afforded the enamide.

General Procedure E: *Synthesis of ynamides using phenyllithium*

According to the procedure of Trost et al.,[3] *and Anderson et al.*[2] To a stirred solution of 1,2-dichloroenamide (1.0 equiv.) in THF (10 mL / mmol of enamide), at –78 °C was added phenyllithium (2.0 M solution in dibutyl ether, 2.2 equiv.) dropwise over 10 minutes. The reaction mixture was stirred at –78 °C for 1 h, after which time iodomethane (1.2 equiv.) was added. The solution was allowed to warm to rt and stirred for 1 h. The reaction mixture was quenched with water and the aqueous layer extracted with Et_2O (x 2). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography afforded the product ynamide.

General Procedure F: *Palladium-catalysed cycloisomerization*

According to the procedure of Anderson et al.[4] To a solution of enynamide (1.0 equiv.) in toluene (6.5 mL / mmol of enynamide) was added *N*,*N*'-*bis*-(benzylidene)ethylenediamine (0.05 equiv.) and $Pd(OAc)_2$ (0.05 equiv.). The reaction mixture was stirred at 60 °C for 30 min, then cooled to rt and concentrated. Purification by flash chromatography afforded the product.

General Procedure G: *TBS-deprotection of silyloxy amidodienes*

To a solution of diene (1.0 equiv.) in THF (20 mL / mmol of diene) was added TBAF (1.3 equiv.). The reaction mixture was stirred at rt for 2 h, before being diluted with EtOAc, filtered through a silica plug and concentrated. Purification by flash chromatography afforded the product.

General Procedure H: *Parikh-Doering Oxidation*

Et_3N (5.0 equiv.), DMSO (7.0 equiv.) and SO_3•py (3.0 equiv.) were added to a solution of alcohol (1.0 equiv.) in DCM (6 mL / mmol of alcohol) at 0 °C. The solution was stirred at 0 °C for 2 h before being quenched with pH 7 phosphate buffer (20 mL). The mixture was extracted with EtOAc (3 x 20mL), washed with brine (2 x 20mL), dried ($MgSO_4$) and concentrated. Purification by flash chromatography afforded the product.

General Procedure I: *Dess-Martin Oxidation*

To a solution of alcohol (1.0 equiv.) in CH_2Cl_2 at 0 °C was added Dess-Martin periodinane (1.2 equiv.), and then the reaction was allowed to warm to rt and stirred for 1.5 h. After this time, $NaHCO_3$ (sat., aq.) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried (Na_2SO_4), filtered, and concentrated. Purification by flash chromatography provided the aldehyde.

General Procedure J: *Trienamine-catalysed Diels-Alder cycloaddition with nitrostyrenes and olefinic azlactones*

To a vial containing catalyst **10** (0.2 equiv.), benzoic acid (0.2 equiv.) and the respective dienophile (1.0 equiv.) was added the amidodiene (1.4 equiv.) in toluene (5 mL / mmol of amidodiene). The resulting mixture was stirred at RT for 2-5 h, then (ethoxycarbonylmethylene)triphenylphosphorane (0.15 mmol, 1.5 equiv.) was added. The reaction was then stirred overnight, then it was concentrated and the residue directly purified by flash chromatography.

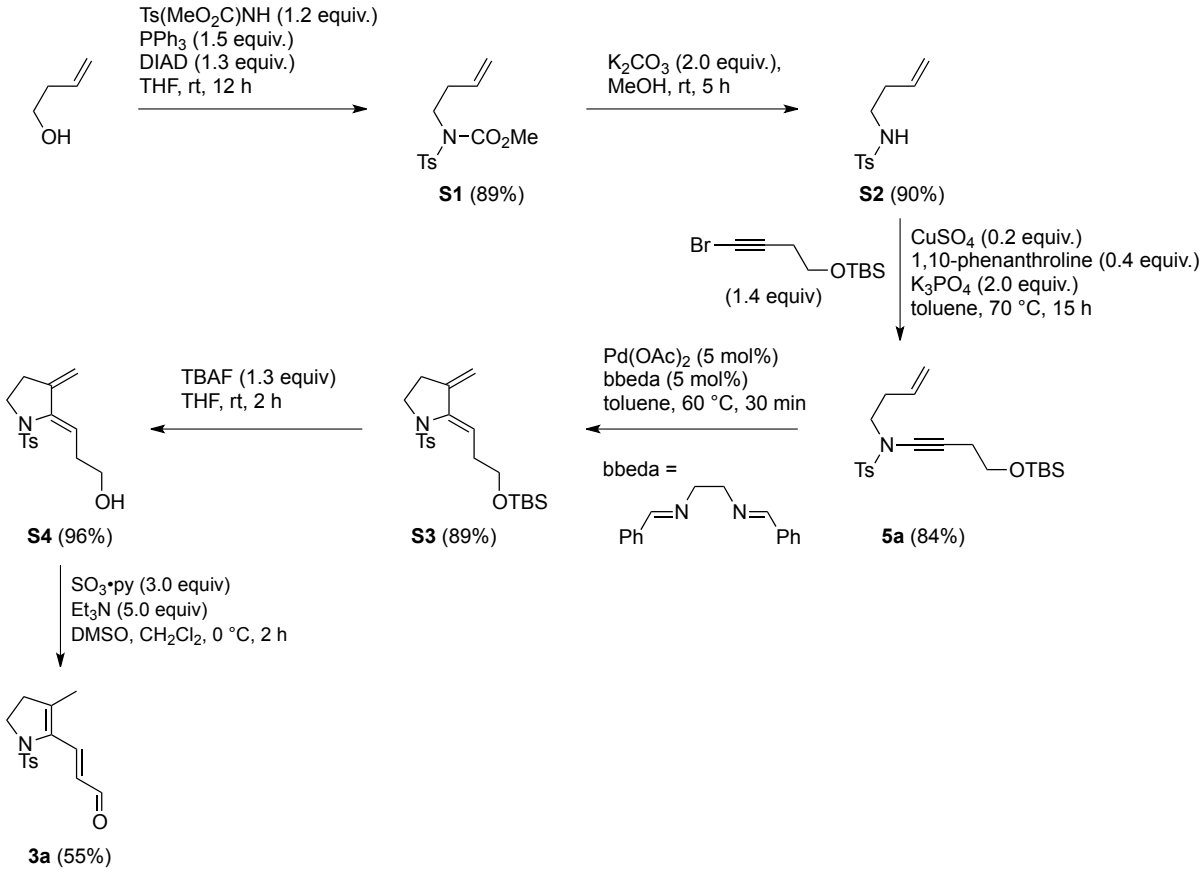
General Procedure K: *Trienamine-catalysed Diels-Alder cycloaddition with olefinic oxindoles and lactones*

To a vial containing catalyst **10** (0.2 equiv.), benzoic acid (0.2 equiv.) and the respective dienophile (1.0 equiv.) was added the amidodiene (1.5 equiv.) in toluene (5 mL / mmol of amidodiene). The resulting mixture was stirred at RT for 2-6 h before being diluted with EtOAc, filtered through a silica plug, and concentrated.

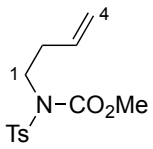
1.3 Specific experimental procedures and characterization of compounds

*1.3.1 Synthesis of dienal **3a***

Dienal **3a** was synthesized according to the following Scheme:

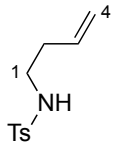


Methyl but-3-en-1-yl(tosyl)carbamate, S1



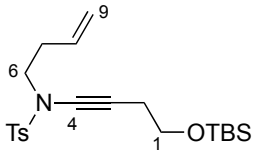
Prepared by General Procedure **A** using but-3-en-1-ol (1.20 ml, 1.00 g, 13.9 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / Et_2O (9:1)) to give **S1** as a colourless oil (3.50 g, 12.4 mmol, 89%). **IR** (thin film, ν_{max} / cm^{-1}) 2980, 1728, 1691, 1450, 1355, 1293, 1185, 767; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.82 (2H, d, *J* = 8.4 Hz, TsH), 7.29 (2H, d, *J* = 8.4 Hz, TsH), 5.77 (1H, ddt, *J* = 17.1, 10.2 and 6.9 Hz, H3), 5.12-5.05 (2H, m, H4), 4.02-3.76 (2H, m, H1), 3.67 (3H, s, CO_2Me), 2.47 (2H, dd, *J* = 14.7 and 7.3 Hz, H2), 2.41 (3H, s, $TsCH_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 152.7, 144.5, 136.5, 134.0, 129.2, 128.2, 117.5, 53.6, 46.5, 34.3, 21.5; **HRMS** (ES^+) calc. for $C_{13}H_{18}O_4NS$ $[M+H]^+$ 284.0951; found 284.0950.

***N*-(But-3-en-1-yl)-4-methylbenzenesulfonamide, S2**



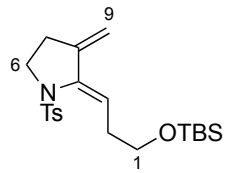
Prepared by General Procedure **B** using methyl but-3-en-1-yl(tosyl)carbamate **S1** (4.20 g, 14.8 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / Et_2O (4:1)) to give **S2** as a colourless oil (3.01 g, 13.4 mmol, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.74 (2H, d, *J* = 8.5 Hz, TsH), 7.30 (2H, d, *J* = 8.5 Hz, TsH), 5.61 (1H, ddt, *J* = 17.0, 10.5 and 7.0 Hz, H3), 5.07-4.98 (2H, m, H4), 4.63 (1H, br s, NH), 3.00 (2H, app q, *J* = 6.5 Hz, H1), 2.42 (3H, s, $TsCH_3$), 2.18 (2H, app q, *J* = 7.0 Hz, H2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.6, 137.1, 134.3, 129.9, 127.2, 118.2, 42.2, 33.7, 21.7; **HRMS** (ES^+) calc. for $C_{11}H_{16}O_2NS$ $[M+H]^+$ 226.0896; found 226.0896. Data identical to literature values.[5]

***N*-(But-3-en-1-yl)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-4-methylbenzenesulfonamide, 5a**



Prepared by General Procedure **C** using sulfonamide **S2** (1.83 g, 8.12 mmol, 1.0 equiv.) and ((4-bromobut-3-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (2.57 g, 9.75 mmol, 1.2 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **5a** as a colourless oil (2.76 g, 6.78 mmol, 84%); **IR** (thin film, ν_{max} / cm^{-1}) 2929, 2222, 1364, 1171, 1105; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, *J* = 8.0 Hz, TsH), 7.32 (2H, d, *J* = 8.0 Hz, TsH), 5.70 (1H, ddt, *J* = 17.0, 10.2 and 6.8 Hz, H8), 5.11-4.99 (2H, m, H9), 3.66 (2H, t, *J* = 7.1 Hz, H1), 3.31 (2H, t, *J* = 7.3 Hz, H6), 2.47 (2H, t, *J* = 7.1 Hz, H2), 2.43 (3H, s, $TsCH_3$), 2.35 (2H, dd, *J* = 14.8 and 6.9 Hz, H7), 0.87 (9H, s, Si*t*-Bu), 0.04 (6H, s, $SiMe_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.3, 134.6, 133.7, 129.6, 127.6, 117.4, 73.7, 67.5, 62.1, 50.7, 32.0, 25.8, 22.8, 21.5, 18.2, –5.4; **HRMS** (ES^+) calc. for $C_{21}H_{34}O_3NSSi$ $[M+H]^+$ 408.2023; found 408.2021.

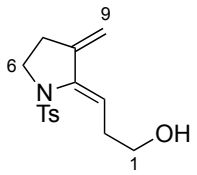
(*Z*)-2-(3-((*tert*-Butyldimethylsilyl)oxy)propylidene)-3-methylene-1-tosylpyrrolidine, S3



Prepared by General Procedure **F** using ynamide **5a** (1.02 g, 2.50 mmol). The crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **S3** as a colourless oil (0.91 g, 2.23 mmol, 89%); **IR** (thin film, ν_{max} / cm^{-1}) 2928, 2857, 1357, 1166, 1092; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.67 (2H, d, *J* = 6.5 Hz, TsH), 7.23 (2H, d, *J* = 7.8 Hz, TsH), 6.03 (1H, t, *J* = 6.7 Hz, H3), 5.22 (1H, s, H9), 4.66 (1H, s, H9), 3.76 (2H, t, *J* = 6.1 Hz, H1), 3.53 (2H, t, *J* = 6.6 Hz, H6), 2.75 (2H, app q, *J* = 6.5 Hz, H2), 2.41 (3H, s, $TsCH_3$), 1.83 (2H, t, *J* = 6.4 Hz, H7), 0.91 (9H, s, Si*t*-Bu), 0.07 (6H, s, $SiMe_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C

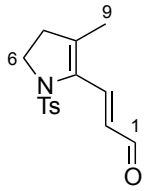
143.8, 143.1, 137.5, 135.9, 129.5, 127.7, 118.3, 103.9, 62.6, 48.5, 33.3, 29.0, 25.9, 21.6, 18.3, –5.2; **HRMS** (ES^+) calc. for $C_{21}H_{34}O_3NSSi$ $[M+H]^+$ 408.2023; found 408.2021.

(*Z*)-3-(3-Methylene-1-tosylpyrrolidin-2-ylidene)propan-1-ol, S4



Prepared by General Procedure **G** using **S3** (508 mg, 1.25 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give the title compound **S4** as a colourless oil (350 mg, 1.19 mmol, 96%); **IR** (thin film, ν_{max} / cm^{-1}) 3450, 2925, 1090, 1162, 1348, 1597; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.68 (2H, d, *J* = 8.3 Hz), 7.24 (2H, d, *J* = 8.3 Hz), 5.98 (1H, t, *J* = 7.7 Hz, H3), 5.26 (1H, t, *J* = 2.4 Hz, H9), 4.69 (1H, t, *J* = 2.2 Hz, H9), 3.85 (2H, t, *J* = 6.0 Hz, H1), 3.55 (2H, t, *J* = 7.4 Hz, H6), 2.84 (2H, app. q, *J* = 6.8 Hz, H2), 2.41 (3H, s, $TsCH_3$), 1.85-1.80 (2H, m, H7); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.1, 142.8, 138.6, 135.5, 129.6, 127.7, 118.3, 104.6, 62.3, 48.6, 32.8, 28.8, 21.6; **HRMS** (ES^+) calc. for $C_{15}H_{20}O_3NS$ $[M+H]^+$ 294.1158; found 294.1157.

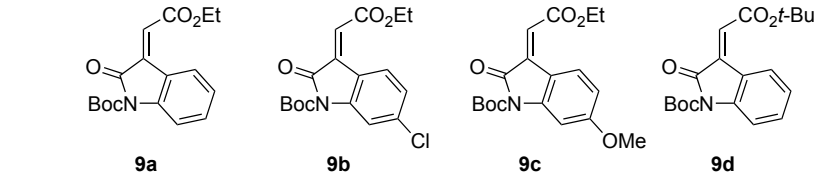
(*E*)-3-(3-Methyl-1-tosyl-4,5-dihydro-1H-pyrrol-2-yl)acrylaldehyde, 3a



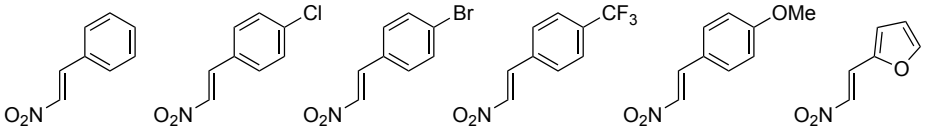
Prepared by General Procedure **H** using **S4** (199 mg, 0.68 mmol). The resulting crude material was purified by flash chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **3a** as a light yellow oil (108 mg, 0.37 mmol, 55%); **IR** (thin film, ν_{max} / cm^{-1}) 3334, 2946, 1738, 1367, 1217, 1021; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.59 (1H, d, *J* = 7.8 Hz, H1 (*this peak appears to be an unresolved ddd*)), 7.50 (2H, d, *J* = 8.0 Hz, TsH), 7.37-7.29 (3H, m, TsH and H3), 6.36 (1H, dd, *J* = 16.0 and 7.8 Hz, H2), 3.67 (2H, t, *J* = 8.3 Hz, H6), 2.35 (3H, s, $TsCH_3$), 1.96 (2H, t, *J* = 8.0 Hz, H7), 1.74 (3H, s, H9); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 193.8, 144.2, 142.0, 138.0, 133.7, 133.2, 131.7, 129.6, 127.8, 49.0, 35.3, 21.6, 14.9; **HRMS** (ES^+) calc. for $C_{15}H_{18}O_3NS$ $[M+H]^+$ 292.1002; found 292.1001.

*1.3.2 Cycloaddition reactions of dienal **3a***

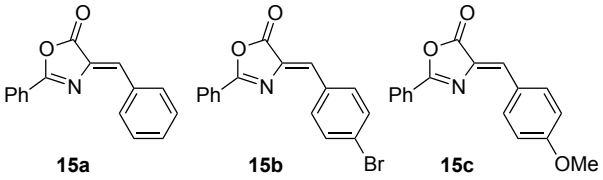
3a was reacted with the following dienophiles:



9a **9b** **9c** **9d**

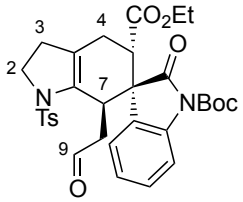


13a **13b** **13c** **13d** **13e** **13f**



15a **15b** **15c**

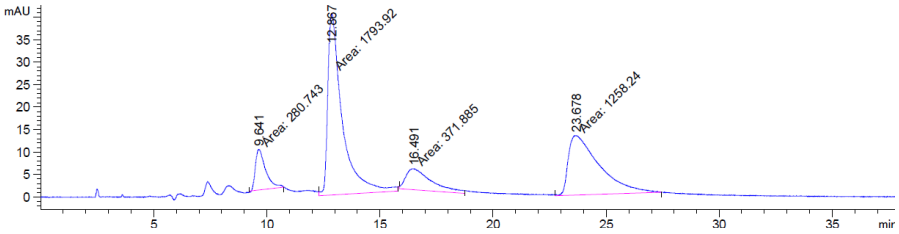
(3'*S*,5*S*,7*R*)-1'-*tert*-Butyl 5-ethyl 2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11a



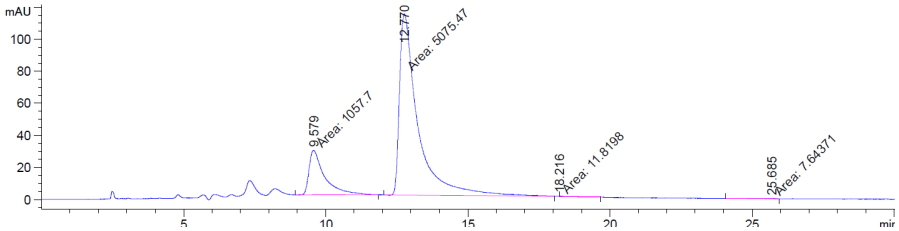
Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 *μ*L, 0.02 mmol, 0.2 equiv.), **3a** (21.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9a** (15.8 mg, 0.050 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **11a** as a yellow oil (25.5 mg, 0.042 mmol, 84%); $[\alpha]_D^{25}$ –13.7 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2925, 1716, 1598, 1348, 1210, 1369, 1346, 706; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.69 (1H, s, H9), 7.98 (1H, d, *J* = 7.8 Hz, PhH), 7.36-7.27 (3H, m, TsH and PhH), 7.03 (2H, d, *J* = 7.9 Hz, TsH), 6.76 (1H, td, *J* = 7.6 and 1.0 Hz, PhH), 6.55 (1H, d, *J* = 6.8 Hz, PhH), 4.01-3.82 (3H, m, H2 and $OC\underline{H}_2CH_3$), 3.77-3.61 (2H, m, H2 and H7), 3.32 (dd, *J* = 11.4, and 7.0 Hz, H5), 3.23 (dd, *J* = 18.9 and 9.1 Hz, H8), 3.03 (1H, dd, *J* = 19.0 and 1.4 Hz, H8), 2.71 (1H, dd, *J* = 18.5 and 6.9 Hz, H4), 2.49-2.39 (6H, m, H4, H3 and $TsCH_3$), 1.63 (9H, s, $C(CH_3)_3$), 0.99 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.2, 176.3, 171.2, 149.0, 143.6, 139.8, 135.8, 133.7, 133.6, 129.7, 128.0, 127.5, 123.7, 122.9, 120.4, 115.2, 83.9, 61.0, 49.9, 49.1, 43.3, 41.4, 36.8, 30.8, 28.0, 25.5, 21.5, 13.6; **HRMS** (ES^+) calc. for $C_{32}H_{37}O_8N_2S$ $[M+H]^+$ 609.2265; found 609.2265.

HPLC data is listed on the next page.

Chiralpak IB (15% IPA in hexane, flow rate = 1.3 mL/min, 230 nm) Minor diastereomer: $t_R$major – 9.6 min, minor – 18.2 min; Major diastereomer: $t_R$major – 12.8 min, minor – 25.7 min. (98% *ee*).

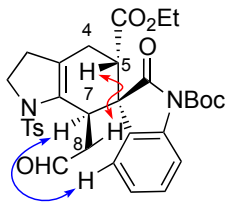


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.641	MM T	0.5163	280.74313	9.06200	7.5778
2	12.867	MM T	0.7424	1793.91882	40.27047	48.4216
3	16.491	MM T	1.3180	371.88452	4.70261	10.0379
4	23.678	MM T	1.5902	1258.24463	13.18771	33.9626

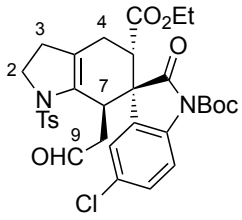


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.579	MM T	0.6346	1057.70349	27.77845	17.1911
2	12.770	MM T	0.7383	5075.47217	113.02905	82.4926
3	18.216	MM T	0.3072	11.81980	4.56006e-1	0.1921
4	25.685	MM T	0.6027	7.64371	2.11361e-1	0.1242

Proof of stereochemistry for oxindole cycloadditions: Cycloadduct **11a** was used to assign the relative stereochemistry of the cycloaddition through ^{1}H NMR nOe experiments (1D nOe / 2D NOESY). On the beta face (as depicted below), enhancements were seen between H5 and H8, indicating these groups to be on the same face. On the alpha face, enhancements between H7 and one of the aryl protons of the oxindole, indicating these groups to be on the same face.

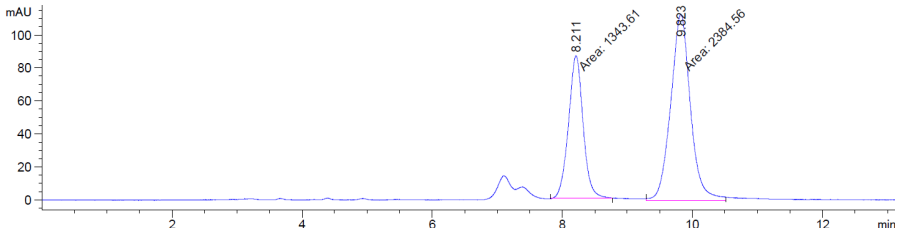


(3'*S*,5*S*,7*R*)-1'-*tert*-Butyl 5-ethyl 5'-chloro-2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11b

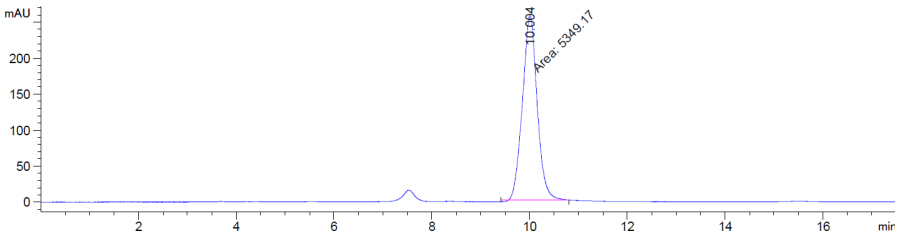


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.02 mmol, 0.2 equiv.), **3a** (21.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9b** (17.5 mg, 0.050 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **11b** as a light yellow oil (22 mg, 0.034 mmol, 68%); $[\alpha]_D^{25}$ –15.6 (*c* = 1.2, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2982, 1790, 1762, 1727, 1473, 1272, 1151, 909, 728; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 9.69 (1H, s, H9), 7.97 (1H, d, *J* = 8.7 Hz, PhH), 7.34 (2H, d, *J* = 8.2 Hz, TsH), 7.28 (1H, dd, *J* = 8.7 and 2.2, PhH), 7.09 (2H, d, *J* = 8.0 Hz, TsH), 6.44 (1H, d, *J* = 2.1 Hz, PhH), 4.01 (1H, td, *J* = 10.8 and 6.3 Hz, H2), 3.96-3.83 (2H, m, $OC\underline{H}_2CH_3$), 3.74-3.59 (2H, m, H2 and H7), 3.32 (1H, dd, *J* = 11.6 and 7.1Hz, H5), 3.21 (1H, dd, *J* =19.1and 9.0 Hz, H4), 3.08 (1H, dd, *J* = 19.1 and 1.2 Hz, H4), 2.73 (1H, dd, *J* = 18.5 and 7.0 Hz, H8), 2.54-2.44 (2H, m, H8 and H3), 2.41 (3H, s, $TsCH_3$), 2.39-2.35 (1H, m, H3), 1.63 (9H, s, $C(CH_3)_3$), 1.04 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 198.0, 175.7, 171.1, 148.9, 144.1, 138.6, 135.7, 133.4, 132.4, 130.0, 128.9, 128.1, 127.2, 123.1, 119.7, 116.4, 84.3, 61.3, 50.0, 49.1, 43.3, 41.3, 36.5, 30.6, 28.0, 25.4, 21.6, 13.7; **HRMS** (ES^+) calc. for $C_{32}H_{35}O_8N_2ClNaS$ $[M+Na]^+$ 665.1694; found 665.1686.

Chiralpak IA (20% IPA in hexane, flow rate = 1.0 mL/min, 254 nm) $t_R$major – 10.0 min, minor – 8.2 min (>99% *ee*).

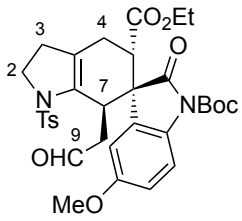


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.213	MM T	0.2660	3281.98193	205.64961	38.0026
2	9.822	MM T	0.3399	5354.21240	262.55542	61.9974



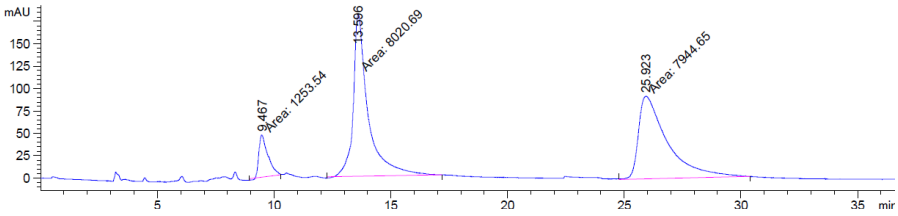
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.004	MM T	0.3477	5349.16943	256.37866	100.0000

(3'*S*,5*S*,7*R*)-1'-*tert*-Butyl 5-ethyl 5'-methoxy-2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11c

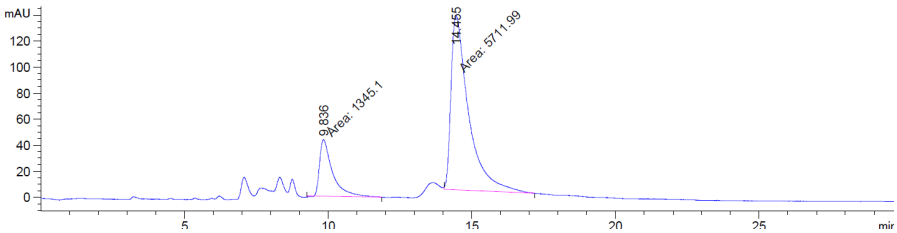


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.02 mmol, 0.2 equiv.), **3a** (21.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9c** (17.3 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **11c** as a red oil (29 mg, 0.045 mmol, 91%); $[\alpha]_D^{25}$ – 2.03 (*c* = 1.3, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2931, 1787, 1757, 1722, 1597, 1485, 1279, 1155, 771; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.63 (1H, s, H9), 7.86 (1H, d, *J* = 8.9 Hz, PhH), 7.26 (2H, d, *J* = 8.2 Hz, TsH), 6.98 (2H, d, *J* = 8.1 Hz, TsH), 6.82-6.72 (1H, m, PhH), 6.08 (1H, d, *J* = 2.6 Hz, PhH), 3.99-3.73 (3H, m, H2 and $OC\underline{H}_2CH_3$), 3.66-3.51 (2H, m, H2 and H7), 3.49 (3H, s, OCH_3), 3.28-3.13 (2H, m, H5 and H8), 2.97 (1H, d, *J* = 17.9 Hz, H8), 2.64 (1H, dd, *J* = 18.4 and 6.6 Hz, H4), 2.40-2.33 (6H, m, H4, H3 and $TsCH_3$), 1.57 (9H, s, $C(CH_3)_3$), 0.95 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 198.0, 176.2, 171.2, 155.7, 149.1, 143.6, 135.9, 133.5, 133.3, 131.7, 129.8, 127.5, 120.1, 115.9, 112.0, 110.0, 83.8, 61.1, 54.8, 50.2, 49.0, 43.4, 41.3, 36.8, 30.7, 28.0, 25.5, 21.5, 13.6; **HRMS** (ES^+) calc. for $C_{33}H_{39}O_9N_2S$ $[M+H]^+$ 639.2370; found 639.2365.

Chiralpak IB (20% IPA in hexane, flow rate = 1.3 mL/min, 230 nm) $t_R$major – 9.8 min, minor – 25.9 min and $t_R$major – 14.4 min, minor – 25.9 min (>99% *ee*).

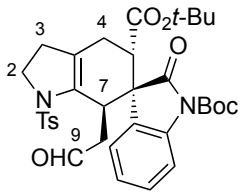


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.467	MM T	0.4832	1253.53833	47.25889	7.2800
2	13.596	MM T	0.9582	8020.68701	181.43690	46.5808
3	25.923	MM T	1.3532	7944.64795	92.29728	46.1392



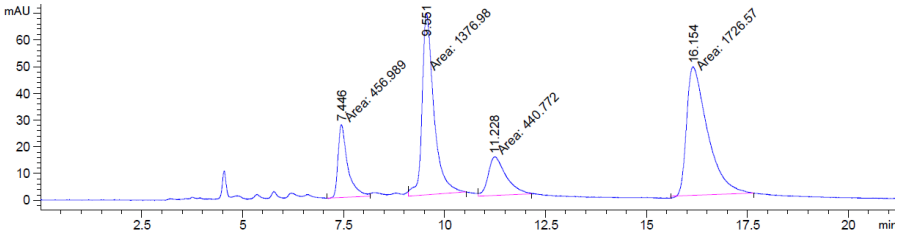
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.836	MM T	0.5172	1345.10364	43.34476	19.0603
2	14.455	MM T	0.7119	5711.99365	133.72974	80.9397

(3'*S*,5*S*,7*R*)-di-*tert*-Butyl 2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11d

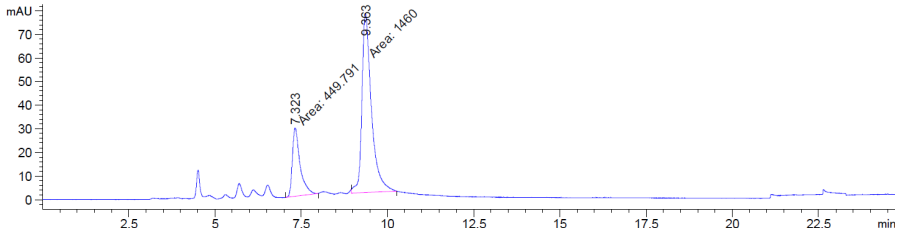


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.02 mmol, 0.2 equiv.), **3a** (21.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9d** (17.2 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **11d** as a light yellow oil (22 mg, 0.034 mmol, 69%, *dr* 3.6:1); $[\alpha]_D^{25}$ –16.9 (*c* = 1, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2926, 1791, 1760, 1722, 1604, 1479, 1348, 1152, 1090, 815; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.69 (1H, s, H9), 7.96 (1H, t, *J* = 8.4 Hz, PhH), 7.36-7.25 (3H, m, TsH and PhH), 7.02 (2H, d, *J* = 8.0 Hz, TsH), 6.77 (1H, t, *J* = 7.5 Hz, PhH), 6.56 (1H, d, *J* = 7.5 Hz, PhH), 4.00-3.87 (1H, m, H2), 3.69-3.62 (2H, m, H2 and H7), 3.27-3.19 (2H, m, H5 and H8), 2.99 (1H, d, *J* = 17.9 Hz, H8), 2.69-2.56 (1H, m, H4), 2.50-2.34 (6H, m, H4, H3 and $TsCH_3$), 1.63 (9H, s, $C(CH_3)_3$), 1.09 (9H, s, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.2, 176.0, 170.3, 149.2, 143.5, 139.6, 135.4, 133.8, 129.7, 129.7, 128.0, 127.5, 123.7, 123.0, 115.0, 83.9, 82.0, 54.5, 50.2, 49.1, 43.5, 41.6, 36.9, 30.9, 28.0, 27.3, 25.5, 21.5; **HRMS** (ES^+) calc. for $C_{34}H_{40}O_8N_2NaS$ $[M+Na]^+$ 659.2397; found 659.2391.

Chiralpak IB (20 % IPA in hexane, flow rate = 1.3 mL/min, 254 nm) Minor diastereomer: $t_R$major – 7.3 min, minor – 11.2 min; Major diastereomer: $t_R$major – 9.4 min, minor – 16.2 min (>99% *ee*).

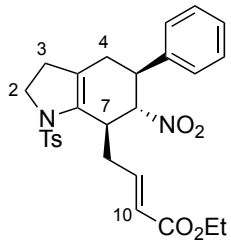


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.446	MM T	0.3082	456.98883	27.20280	11.4210
2	9.551	MM T	0.3386	1376.97815	67.77059	34.4132
3	11.228	MM T	0.4769	440.77182	14.36648	11.0157
4	16.154	MM T	0.5884	1726.56702	47.98352	43.1501



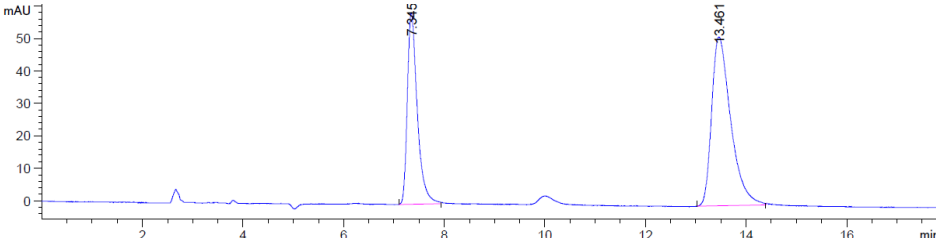
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.323	MM T	0.2619	449.79077	29.00819	23.5518
2	9.363	MM T	0.3212	1460.00476	75.75909	76.4482

(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-6-nitro-5-phenyl-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14a

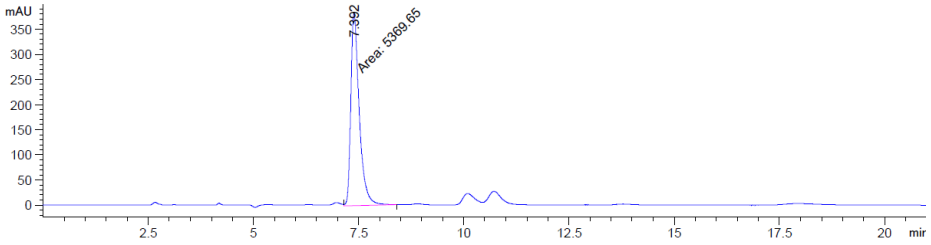


Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.020 mmol, 0.2 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and trans-β-nitrostyrene **13a** (14.9 mg, 0.10 mmol, 1.0 equiv.). Purification via column chromatography (petroleum ether / EtOAc (2:1)) to give **14a** as colourless oil (36 mg, 0.071 mmol, 71%); $[\alpha]_D^{25}$ c–127.5 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2925, 1716, 1598, 1548, 1345, 1089; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.78 (2H, d, *J* = 8.3 Hz, TsH), 7.39 (2H, d, *J* = 8.0 Hz, TsH), 7.34 - 7.25 (3H, m, PhH), 7.18 (2H, d, *J* = 6.7 Hz, PhH), 6.76 (1H, ddd, *J* = 15.5, 9.3 and 6.1 Hz, H9), 6.02 (1H, d, *J* = 15.7 Hz, H10), 4.71 (1H, dd, *J* = 11.4 and 9.4 Hz, H6), 4.21 (2H, q, *J* = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.89 (1H, ddd, *J* = 12.9, 8.3 and 1.3 Hz, H2), 3.74-3.65 (2H, m, H2 and H7), 3.39-3.36 (2H, m, H5 and H8), 2.48 (3H, s, OCH_3), 2.46-2.32 (2H, m, H8 and H4), 2.09 (1H, dd, *J* =18.3 and 5.3 Hz, H4), 1.84 (1H, dd, *J* = 15.9 and 9.5 Hz, H3), 1.68-1.57 (1H, m, H3), 1.24 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 166.3, 144.7, 142.7, 138.3, 134.5, 133.4, 131.4, 129.9, 129.1, 128.3, 127.9, 127.5, 126.0, 91.4, 60.5, 50.8, 45.3, 40.9, 31.6 (2C), 31.3, 21.8, 14.4; **HRMS** (ES^+) calc. for $C_{27}H_{31}O_6N_2S$ $[M+H]^+$ 511.1897, found 511.1898.

Chiralpak IB (20% IPA in hexane, flow rate = 1.2 mL/min, 230 nm) $t_R$major – 7.4 min, minor – 13.4 min (>99% *ee*).

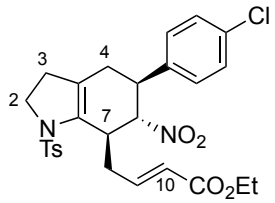


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.345	BB	0.2071	809.90680	59.02208	37.1520
2	13.461	BB	0.3969	1370.07263	52.08670	62.8480



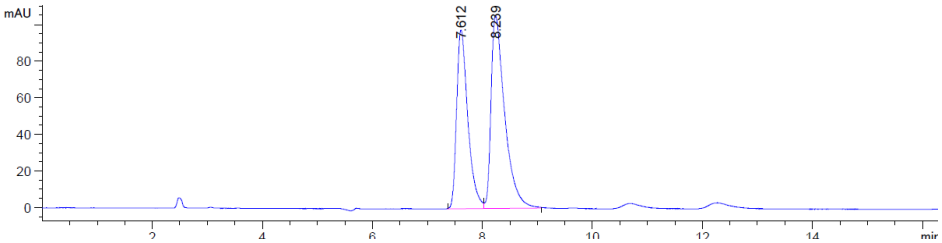
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.392	MM T	0.2344	5369.64648	381.86496	100.0000

(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-(4-chlorophenyl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14b

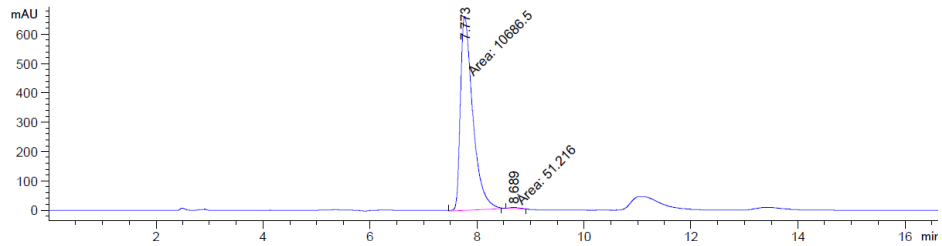


Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.020 mmol, 0.2 equiv.) and **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and (*E*)-1-chloro-4-(2-nitrovinyl)benzene **13b** (14.9 mg, 0.10 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave the cycloadduct **14b** as light yellow oil (38 mg, 0.070 mmol, 70%). Note: a small amount of the *Z*-alkene (*E*:*Z* = 20:1) was observed (*J* = 11.6 Hz), but no diastereomer from the cycloaddition could be detected. $[\alpha]_D^{25}$ –53.8 (*c* = 1.2, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2981, 1714, 1655, 1547, 1319, 1161; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, *J* = 8.3 Hz, TsH), 7.38 (2H, d, *J* = 8.0 Hz, TsH), 7.29 (2H, d, *J* = 8.5 Hz, ArH), 7.12 (2H, d, *J* = 8.5 Hz, ArH), 6.80 (1H, ddd, *J* = 15.5, 9.4 and 6.0 Hz, H9), 6.02 (1H, d, *J* = 15.6 Hz, H10), 4.65 (1H, dd, *J* = 11.5 and 9.5 Hz, H6), 4.20 (2H, q, *J* = 7.1 Hz, OCH_2CH_3), 3.95 (1H, ddd, *J* = 12.9, 8.3 and 1.3 Hz, H2), 3.76-3.63 (2H, m, H2 and H7), 3.39-3.26 (2H, m, H5 and H8), 2.48 (3H, s, $TsCH_3$), 2.44-2.26 (2H, m, H8 and H4), 2.14 (1H, dd, *J* = 18.0, 4.9 Hz, H4), 1.91 (1H, dd, *J* = 15.7, 9.1 Hz, H3), 1.68-1.64 (1H, m, H3), 1.31 (3H, t, *J* = 7.1 Hz, OCH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 166.2, 144.6, 142.4, 136.7, 134.5, 134.1, 133.3, 131.0, 129.8, 129.2, 128.8, 127.8, 126.0, 91.2, 60.5, 50.6, 44.6, 40.8, 31.4, 31.4, 31.2, 21.7, 14.2; **HRMS** (ES^+) calc. for $C_{27}H_{30}O_6N_2ClS$ $[M+H]^+$ 545.1507; found 545.1507.

Chiralpak IB (15% IPA in hexane, flow rate = 1.3 mL/min, 230 nm) $t_R$major – 7.8 min, minor – 8.7 min (>99% *ee*).

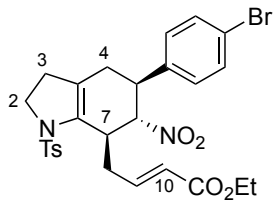


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.612	BV	0.2153	1383.88696	97.67653	43.1487
2	8.239	VB	0.2557	1823.36047	105.45750	56.8513

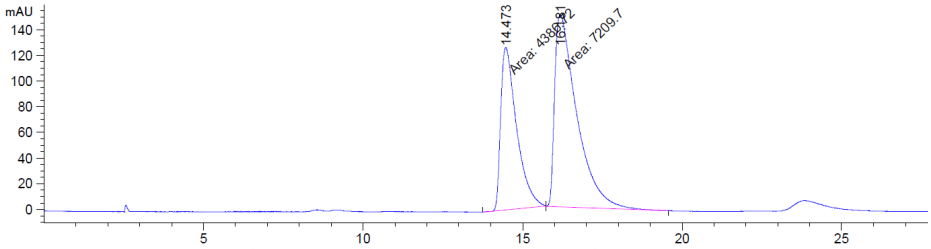


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.773	MM T	0.2694	1.06865e4	661.09607	99.5230
2	8.689	MM T	0.2175	51.21599	3.92439	0.4770

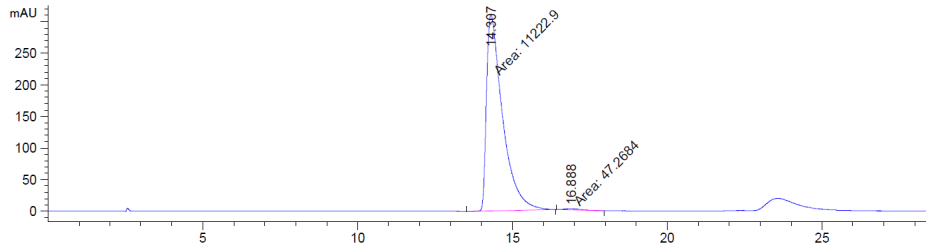
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-(4-bromophenyl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14c



Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.02 mmol, 0.2 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 eq.) and (*E*)-1-bromo-4-(2-nitrovinyl)benzene **13c** (22.6 mg, 0.10 mmol, 1.0 eq.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **14c** as a red oil (49 mg, 0.083 mmol, 83%); Note: a small amount of the *Z*-alkene (*E*:*Z* ~ 20:1) was observed (*J* = 11.6 Hz), in addition to the 13.5:1 ratio of diastereomers from the cycloaddition. $[\alpha]_D^{25}$ –56.5 (*c* = 1.5, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 1714, 1551, 1316, 1160, 982; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, *J* = 8.2 Hz, TsH), 7.43 (2H, d, *J* = 8.3 Hz, TsH), 7.38 (2H, d, *J* = 8.1 Hz, ArH), 7.06 (2H, d, *J* = 8.4 Hz, ArH), 6.80 (1H, ddd, *J* = 15.5, 9.4 and 6.0 Hz, H9), 6.02 (1H, d, *J* = 15.6 Hz, H10), 4.65 (1H, dd, *J* = 11.5 and 9.5 Hz, H6), 4.20 (2H, q, *J* = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.95 (1H, dd, *J* = 13.1 and 7.2 Hz, H2), 3.72-3.64 (2H, m, H2 and H7), 3.32 (2H, td, *J* = 11.2 and 5.3 Hz, H5 and H8), 2.47 (3H, s, $TsCH_3$), 2.45-2.26 (2H, m, H8 and H4), 2.14 (1H, dd, *J* = 18.2 and 5.1 Hz, H4), 1.90 (1H, dd, *J* = 16.0 and 9.3 Hz, H3), 1.67-1.58 (1H, m, H3), 1.31 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 166.1, 144.6, 142.3, 137.2, 134.5, 133.3, 132.1, 131.0, 129.8, 129.1, 127.7, 126.0, 122.1, 91.0, 60.4, 50.6, 44.6, 40.7, 31.4, 31.4, 31.1, 21.7, 14.2; **HRMS** (ES^+) calc. for $C_{27}H_{30}O_6N_2BrS$ $[M+H]^+$ 589.1002; found 589.0996, 591.0974. Chiralpak IB (7% IPA in hexane, flow rate = 1.3 mL/min, 230 nm) $t_R$major – 14.3 min, minor – 16.9 min (>99% *ee*).

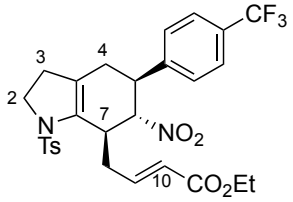


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.476	MM T	0.5752	1041.61963	30.18300	37.2898
2	16.189	MM T	0.8142	1751.69373	35.85704	62.7102

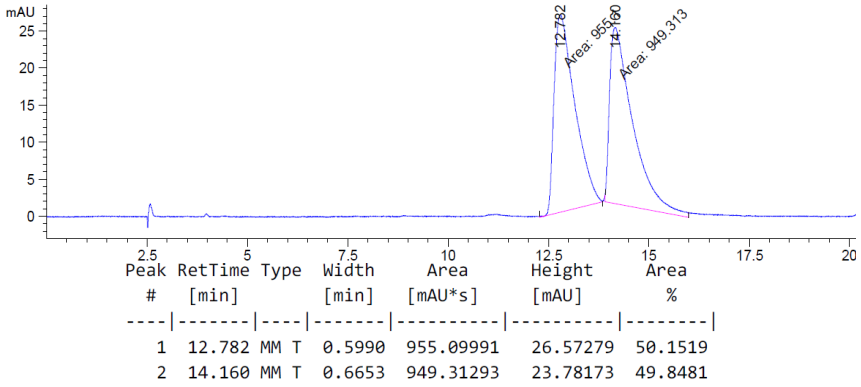


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.307	MM T	0.6915	1.12229e4	309.54282	99.5806
2	16.888	MM T	0.5025	47.26838	1.56782	0.4194

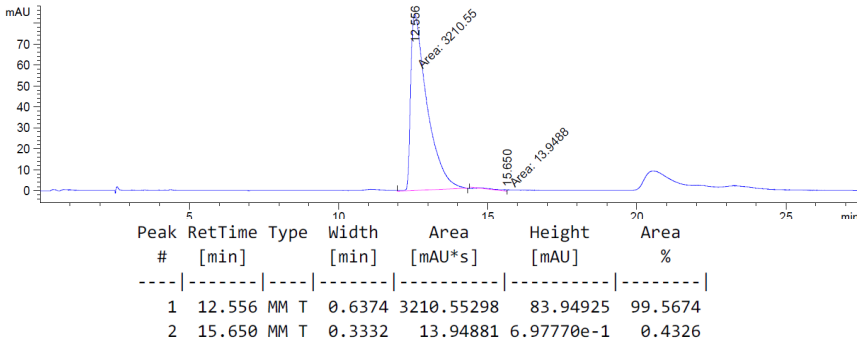
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-6-nitro-1-tosyl-5-(4-(trifluoromethyl)phenyl)-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14d



Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.02 mmol, 0.20 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and (*E*)-1-(2-nitrovinyl)-4-(trifluoromethyl)benzene **13d** (21.7 mg, 0.10 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **14d** as a colourless oil (39.5 mg, 0.068 mmol, 68%); Note: a small amount of the *Z*-alkene (*E*:*Z* ~ 20:1) was observed (J = 11.6 Hz), in addition to the 8:1 ratio of diastereomers from the cycloaddition. $[\alpha]_D^{25}$ –40.0 (c = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2926, 1716, 1551, 1651, 1348, 1324, 1160; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.77 (2H, d, J = 8.3 Hz, TsH), 7.57 (2H, d, J = 8.1 Hz, TsH), 7.32 (2H, d, J = 8.1 Hz, ArH), 7.25 (2H, d, J = 8.1 Hz, ArH), 6.81 (1H, ddd, J = 15.5, 9.4 and 6.0 Hz, H9), 6.03 (1H, d, J = 15.9 Hz, H10), 4.72 (1H, dd, J = 11.6 and 9.5 Hz, H6), 4.21 (2H, q, J = 7.1 Hz, OCH_2CH_3), 3.96 (1H, dd, J = 12.4 and 7.8 Hz, H2), 3.74-3.65 (2H, m, H2 and H7), 3.43 (1H, td, J = 11.3 and 5.4 Hz, H5), 3.37-3.30 (1H, m, H8), 2.48 (3H, s, OCH_3), 2.54-2.27 (2H, m, H8 and H4), 2.17 (1H, dd, J = 18.2 and 5.1 Hz, H4), 1.92 (1H, dd, J = 15.9 and 9.2 Hz, H3), 1.69-1.63 (1H, m, H3), 1.31 (3H, t, J = 7.1 Hz, OCH_2CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 166.1, 144.6, 142.2, 133.2, 130.8, 130.2 (q, J = 23.7 Hz), 130.0, 129.8, 127.8, 127.7, 126.1, 126.0, 126.0, 125.9, 125.9, 90.8, 60.4, 50.6, 44.9, 40.8, 31.4, 31.1, 21.7, 14.2; **HRMS** (ES^+) calc. for $C_{28}H_{30}O_6N_2F_3S$ $[M+H]^+$ 579.1771; found 579.1770. Chiralpak IA (7% IPA in hexane, flow rate = 1.3 mL/min, 254 nm) $t_R$major – 12.6 min, minor – 15.6 min (>99% *ee*).

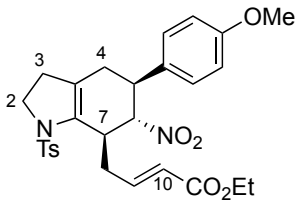


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.782	MM T	0.5990	955.09991	26.57279	50.1519
2	14.160	MM T	0.6653	949.31293	23.78173	49.8481

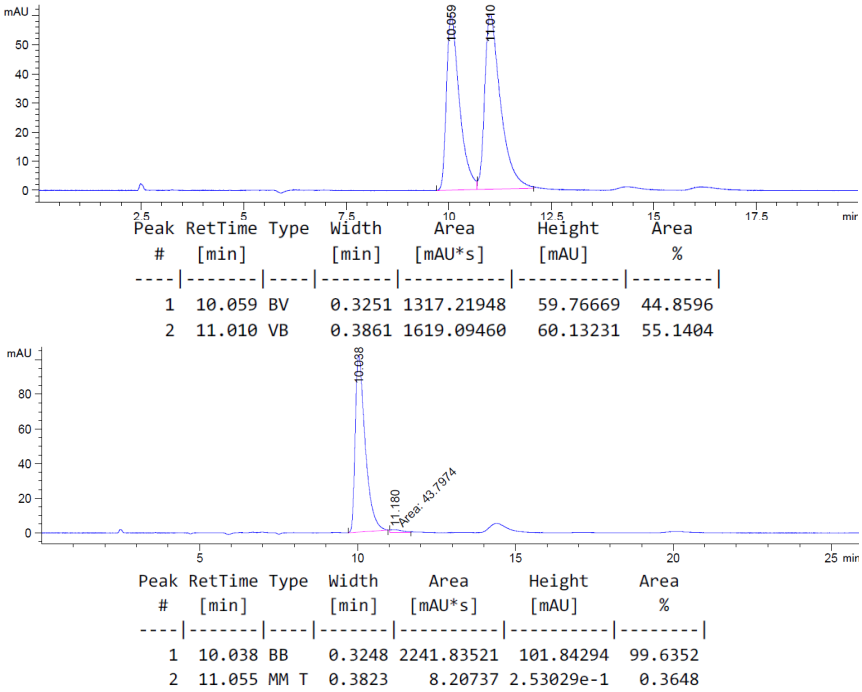


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.556	MM T	0.6374	3210.55298	83.94925	99.5674
2	15.650	MM T	0.3332	13.94881	6.97770e-1	0.4326

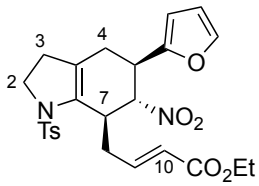
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-(4-methoxyphenyl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14e



Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.02 mmol, 0.20 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and (*E*)-1-methoxy-4-(2-nitrovinyl)benzene **13e** (17.9 mg, 0.10 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **14e** as a red oil (44 mg, 0.081 mmol, 81%); Note: a small amount of the *Z*-alkene (*E*:*Z* ~ 30:1) was observed (J = 11.6 Hz), but no diastereomer from the cycloaddition could be detected. $[\alpha]_D^{25}$ –48.1 (c = 1.2, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 1715, 1548, 1516, 1346, 1249, 1270, 1180, 1158; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.76 (2H, d, J = 8.3 Hz, TsH), 7.38 (2H, d, J = 8.0 Hz, TsH), 7.10 (2H, d, J = 8.7 Hz, ArH), 6.86 (2H, d, J = 8.8 Hz, ArH), 6.82 (1H, dd, J = 9.4 and 6.0 Hz, H9), 6.00 (1H, d, J = 15.7 Hz, H10), 4.64 (1H, dd, J = 11.4, 9.4 Hz, H6), 4.20 (2H, q, J = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.94 (1H, ddd, J = 12.9, 8.3 and 1.2 Hz, H2), 3.76 (3H, s, OCH_3), 3.73-3.64 (2H, m, H2' and H7), 3.32-3.25 (2H, m, H5 and H8), 2.47 (3H, s, $TsCH_3$), 2.43-2.29 (2H, m, H8 and H4), 2.12 (1H, dd, J = 18.3 and 5.2 Hz, H4), 1.89 (1H, dd, J = 16.0 and 9.4 Hz, H3), 1.65-1.56 (1H, m, H3'), 1.30 (3H, t, J = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 166.2, 159.2, 144.5, 142.6, 134.3, 133.2, 131.4, 130.0, 129.7, 128.4, 127.7, 125.8, 114.2, 91.6, 60.4, 55.2, 50.6, 44.4, 40.7, 31.4, 31.4, 31.1, 21.6, 14.2; **HRMS** (ES^+) calc. for $C_{28}H_{33}O_7N_2S$ $[M+H]^+$ 541.2003; found 541.1998. Chiralpak IB (15% IPA in hexane, flow rate = 1.3 mL/min,254 nm) $t_R$major – 10.0 min, minor – 11.1 min (>99% *ee*).

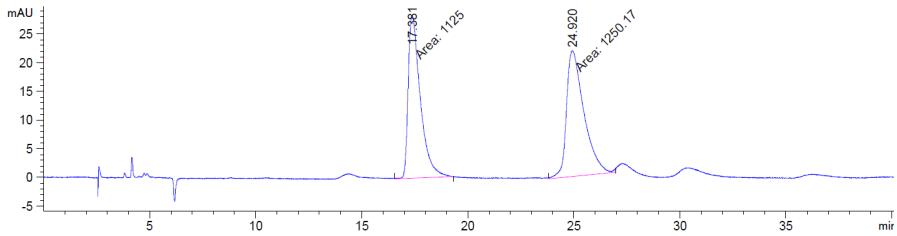


(*E*)-Ethyl 4-((5*R*,6*R*,7*R*)-5-(furan-2-yl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14f

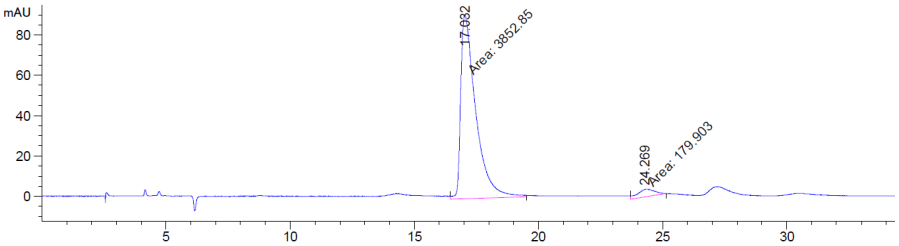


Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.02 mmol, 0.20 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and (*E*)-2-(2-nitrovinyl)furan **13f** (13.9 mg, 0.10 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave the corresponding cycloadduct **14f** as a black oil (36 mg, 0.072 mmol, 72%); Note: a small amount of the *Z*-alkene (*E*:*Z* ~ 20:1) was observed (J = 11.6 Hz), in addition to the 9:1 ratio of diastereomers from the cycloaddition. $[\alpha]_D^{25}$ –30.0 (c = 1.25, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2926, 1717, 1554, 1357, 1160, 1158, 729; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.74 (2H, d, J = 8.3 Hz, TsH), 7.39 (2H, d, J = 8.3 Hz, TsH), 7.37 (1H, dd, J = 1.8 and 0.8 Hz, FurH), 6.79 (1H, ddd, J = 15.5, 8.9 and 6.4 Hz, H9), 6.28 (1H, dd, J = 3.2 and 1.9 Hz, Fur*H*), 6.13 (1H, d, J = 3.3 Hz, FurH), 5.97 (1H, d, J = 15.6 Hz, H10), 4.69 (1H, dd, J = 10.6 and 8.8 Hz, H6), 4.19 (2H, q, J = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.92 (1H, ddd, J = 12.9, 8.5 and 1.7 Hz, H2), 3.78-3.72 (1H, m, H7), 3.68 (1H, ddd, J = 12.9, 11.8 and 9.6 Hz, H2), 3.56 (1H, td, J = 10.4 and 5.5 Hz, H5), 3.09-3.02 (1H, m, H8), 2.54-2.42 (2H, m, H8 and H4), 2.46 (3H, s, OCH_3), 2.19 (1H, dd, J = 18.1 and 5.0 Hz, H4), 1.94 (1H, dd, J = 16.0 and 9.4 Hz, H3), 1.70-1.61 (1H, m, H3), 1.29 (3H, t, J = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 166.1, 151.2, 144.5, 142.6, 142.5, 134.1, 133.2, 129.8, 129.8, 127.7, 125.8, 110.4, 107.5, 89.3, 60.4, 50.4, 39.9, 37.9, 31.5, 31.1, 27.8, 21.6, 14.2; **HRMS** (ES^+) calc. for $C_{25}H_{29}O_7N_2S$ $[M+H]^+$ 501.1690; found 501.1685.

Chiralpak IB (5% IPA in hexane, flow rate = 1.3 mL/min, 254 nm) $t_R$major – 17.0 min, minor – 24.3 min (91% *ee*).

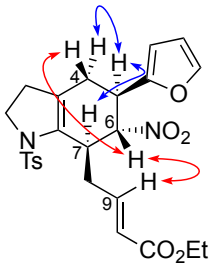


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.381	MM T	0.6612	1125.00366	28.35582	47.3652
2	24.920	MM T	1.0037	1250.16565	21.90841	52.6348

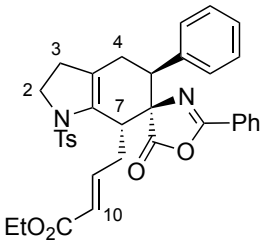


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.032	MM T	0.7041	3852.84839	91.20291	95.5390
2	24.269	MM T	0.8020	179.90282	3.73884	4.4610

Proof of stereochemistry for nitroalkene cycloadditions: Cycloadduct **14f** was used to assign the relative stereochemistry of the cycloaddition through ^{1}H NMR nOe experiments (1D nOe / 2D NOESY). On the beta face (as depicted below), enhancements were seen between H6 and H9, and H6 and one of H4, indicating these groups to be on the same face. On the alpha face, enhancements between H5 and H7, and between H5 and the second of the H4 atoms, are indicative of these groups to be on the same face.

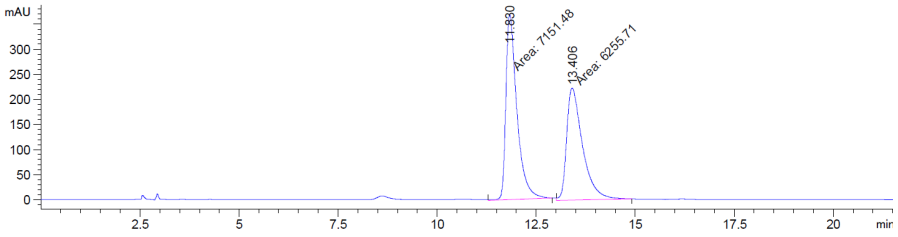


(*E*)-Ethyl 4-((4'*R*,5*S*,7*R*)-5'-oxo-2',5-diphenyl-1-tosyl-1,2,3,4,5,7-hexahydro-5'H-spiro[indole-6,4'-oxazol]-7-yl)but-2-enoate, 16a

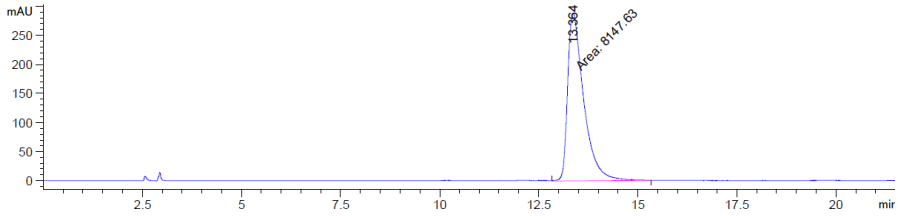


Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.02 mmol, 0.2 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and olefinic azlactone **15a** (24.9 mg, 0.1 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave the corresponding cycloadduct **16a** as a yellow oil (30.6 mg, 0.050 mmol, 50%); $[\alpha]_D^{25}$ –161.3 (*c* = 0.6, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 1810, 1712, 1652, 1552, 1347, 1159; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.96 (2H, d, *J* = 7.2 Hz, PhH), 7.83 (2H, d, *J* = 8.1 Hz, TsH), 7.62 (1H, t, *J* = 7.4 Hz, PhH), 7.52 (2H, t, *J* = 7.6 Hz, PhH), 7.33 (2H, d, *J* = 8.1 Hz, TsH), 7.23-7.12 (6H, m, H9 and PhH), 6.11 (1H, d, *J* = 15.6 Hz, H10), 4.21 (2H, q, *J* = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.80 (2H, dd, *J* = 9.8 and 6.7 Hz, H2), 3.55 (1H, br s, H7), 3.46 (1H, dd, *J* = 11.7 and 5.6 Hz, H5), 3.17-3.11 (1H, m, H8), 2.92-2.86 (1H, m, H8), 2.65 (1H, dd, *J* = 16.6 and 12.1 Hz, H4), 2.50 (3H, s, $TsCH_3$), 2.33 (1H, dd, *J* = 17.3 and 5.5 Hz, H4), 2.10-1.92 (2H, m, H3), 1.31 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 176.5, 166.5, 161.0, 145.7, 143.7, 137.5, 134.4, 133.9, 132.9, 129.5, 129.02, 128.8, 128.3, 128.1, 127.9, 127.8, 126.9, 125.8, 123.8, 75.3, 60.2, 49.8, 43.1, 42.5, 31.6, 30.8, 29.5, 21.7, 14.3; **HRMS** (ES^+) calc. for $C_{35}H_{35}O_6N_2S$ $[M+H]^+$ 611.2210; found 611.2205.

Chiralpak IB (7% IPA in hexane, flow rate = 1.3 mL/min, 230 nm) $t_R$major – 13.4 min, minor – 11.8 min (>99% *ee*).

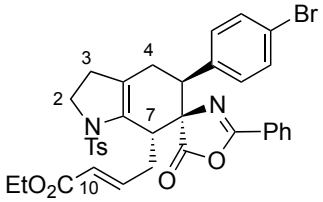


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.830	MM T	0.4122	7151.48340	369.80606	53.3406
2	13.406	MM T	0.4663	6255.71338	223.61560	46.6594



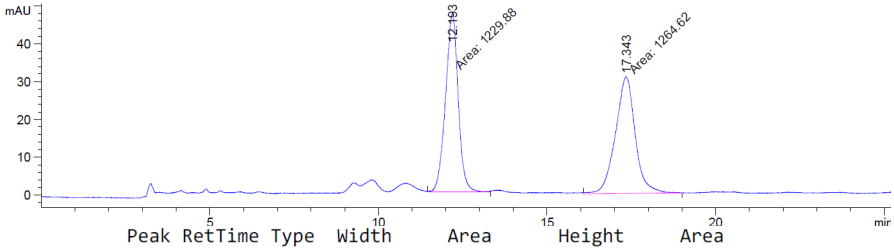
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.364	MM T	0.4702	8147.62500	288.80008	100.0000

(*E*)-Ethyl 4-((4'*R*,5*S*,7*R*)-5-(4-bromophenyl)-5'-oxo-2'-phenyl-1-tosyl-1,2,3,4,5,7-hexahydro-5'H-spiro[indole-6,4'-oxazol]-7-yl)but-2-enoate, 16b

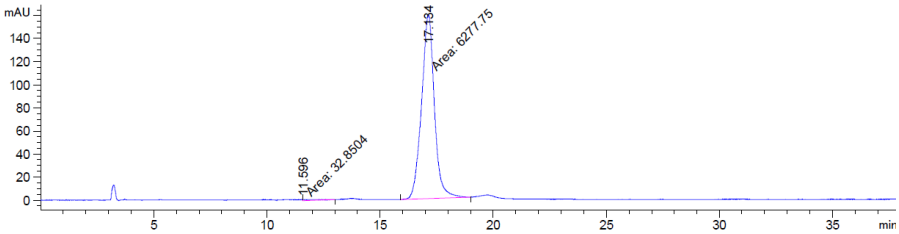


Prepared by General Procedure **J** using catalyst (*S*)-**10** (6 μL, 0.02 mmol, 0.2 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and olefinic azlactone **15b** (32.6 mg, 0.1 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave the corresponding cycloadduct **16b** as a yellow oil (27 mg, 0.039 mmol, 39%); $[\alpha]_D^{25}$ –106.2 (*c* = 1.2, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2925, 1810, 1712, 1651, 1494, 1346, 1158; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.90 (2H, d, *J* = 7.2 Hz, PhH), 7.81 (2H, d, *J* = 8.2 Hz, TsH), 7.63 (1H, t, *J* = 7.4 Hz, PhH), 7.54 (2H, t, *J* = 7.6 Hz, PhH), 7.32 (1H, d, *J* = 8.4 Hz, TsH), 7.00 (2H, d, *J* = 8.4 Hz, *p*-BrC_6H_4), 7.16 (1H, ddd, *J* = 15.5, 8.5 and 7.0 Hz, H9), 6.93 (2H, d, *J* = 8.5 Hz, *p*-BrC_6H_4), 6.10 (2H, d, *J* = 15.6 Hz, H10), 4.21 (2H, q, *J* = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.80 (2H, dd, *J* = 9.9 and 6.7 Hz, H2), 3.47 (1H, br s, H7), 3.42 (1H, dd, *J* = 11.7 and 5.6 Hz, H5), 3.09-3.02 (1H, m, H8), 2.87 (1H, ddd, *J* = 15.0, 8.5 and 4.1 Hz, H8), 2.55-2.48 (1H, m, H4), 2.43 (3H, s, TsH), 2.30 (1H, dd, *J* = 17.3 and 5.6 Hz, H4), 2.02-1.87 (2H, m, H3), 1.31 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 176.4, 166.5, 161.2, 145.5, 143.8, 136.7, 134.4, 133.9, 133.1, 131.5, 130.7, 129.6, 128.9, 128.1, 127.9, 126.5, 125.6, 124.0, 122.0, 75.1, 60.3, 49.9, 42.6, 42.5, 31.6, 30.8, 29.5, 21.8, 14.3; **HRMS** (ES^+) calc. for $C_{35}H_{33}BrN_2O_6S$ $[M]^+$ 688.1243; found 689.8211, 690.8067.

Chiralpak IA (10% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) $t_R$major – 17.13 min, minor – 11.6 min (>99% *ee*).

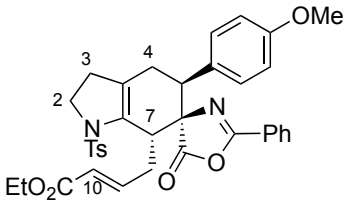


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.193	MM T	0.5279	1229.88367	47.20601	49.3037
2	17.343	MM T	0.8436	1264.62219	30.91245	50.6963



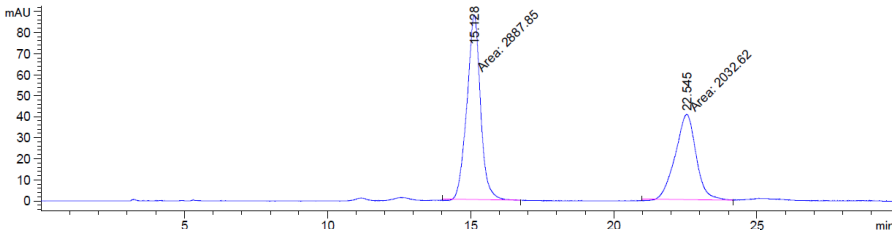
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.596	MM T	0.6851	32.85041	7.99106e-1	0.5206
2	17.134	MM T	0.6555	6277.75049	159.62878	99.4794

(*E*)-Ethyl 4-((4'*R*,5*S*,7*R*)-5-(4-methoxyphenyl)-5'-oxo-2'-phenyl-1-tosyl-1,2,3,4,5,7-hexahydro-5'H-spiro[indole-6,4'-oxazol]-7-yl)but-2-enoate, 16c

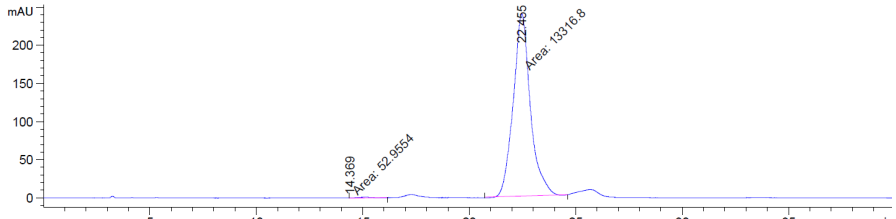


Prepared by General Procedure **J** using catalyst (*S*)-**10** (6.5 μL, 0.02 mmol, 0.2 equiv.), **3a** (40 mg, 0.14 mmol, 1.4 equiv.) and olefinic azlactone **15c** (27.9 mg, 0.1 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave the corresponding cycloadduct **16c** as a brown oil (23 mg, 0.036 mmol, 36%, *dr* 17:1); $[\alpha]_D^{25}$ –107.1 (*c* = 0.75, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 1801, 1719, 1652, 1349, 1160, 1039; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.96 (2H, d, *J* = 8.5 Hz, PhH), 7.83 (2H, d, *J* = 8.2 Hz, TsH), 7.61 (1H, t, *J* = 6.9 Hz, PhH), 7.52 (2H, t, *J* = 7.7 Hz, PhH), 7.32 (2H, d, *J* = 8.1 Hz, TsH), 7.20-7.15 (1H, m, H9), 7.04 (2H, d, *J* = 8.7 Hz, ArH), 6.66 (2H, d, *J* = 8.7 Hz, ArH), 6.10 (1H, d, *J* = 15.6 Hz, H10), 4.21 (2H, q, *J* = 7.1 Hz, $OC\underline{H}_2CH_3$), 3.79 (2H, dd, *J* = 10.0 and 6.6 Hz, H2), 3.70 (3H, s, OCH_3), 3.54 (1H, brs, H7), 3.42 (1H, dd, *J* = 11.7 and 5.6 Hz, H5), 3.16 - 3.10 (1H, m, H8), 2.91 - 2.88 (1H, m, H8), 2.60 (1H, dd, *J* = 16.7 and 12.0 Hz, H4), 2.50 (3H, s, TsH), 2.29 (1H, dd, *J* = 17.3 and 5.6 Hz, H4), 2.07 - 1.93 (2H, m, H3), 1.31 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 176.6, 166.5, 160.9, 159.0, 145.8, 143.7, 134.4, 133.8, 132.8, 130.0, 129.49, 129.4, 128.8, 128.1, 127.8, 127.0, 125.8, 123.8, 113.6, 75.5, 60.2, 55.1, 49.8, 42.4, 42.3, 31.6, 30.8, 29.7, 21.7, 14.3. **HRMS** (ES^+) calc. for $C_{36}H_{36}O_7N_2NaS$ $[M+Na]^+$ 663.2135; found 663.2133.

Chiralpak IA (10% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) $t_R$major – 22.4 min, minor – 14.4 min (>99% *ee*).

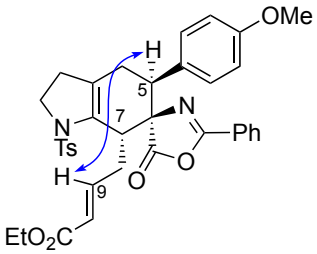


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.128	MM T	0.5489	2887.84790	87.68507	58.6906
2	22.545	MM T	1.0549	2032.61597	40.53008	41.3094



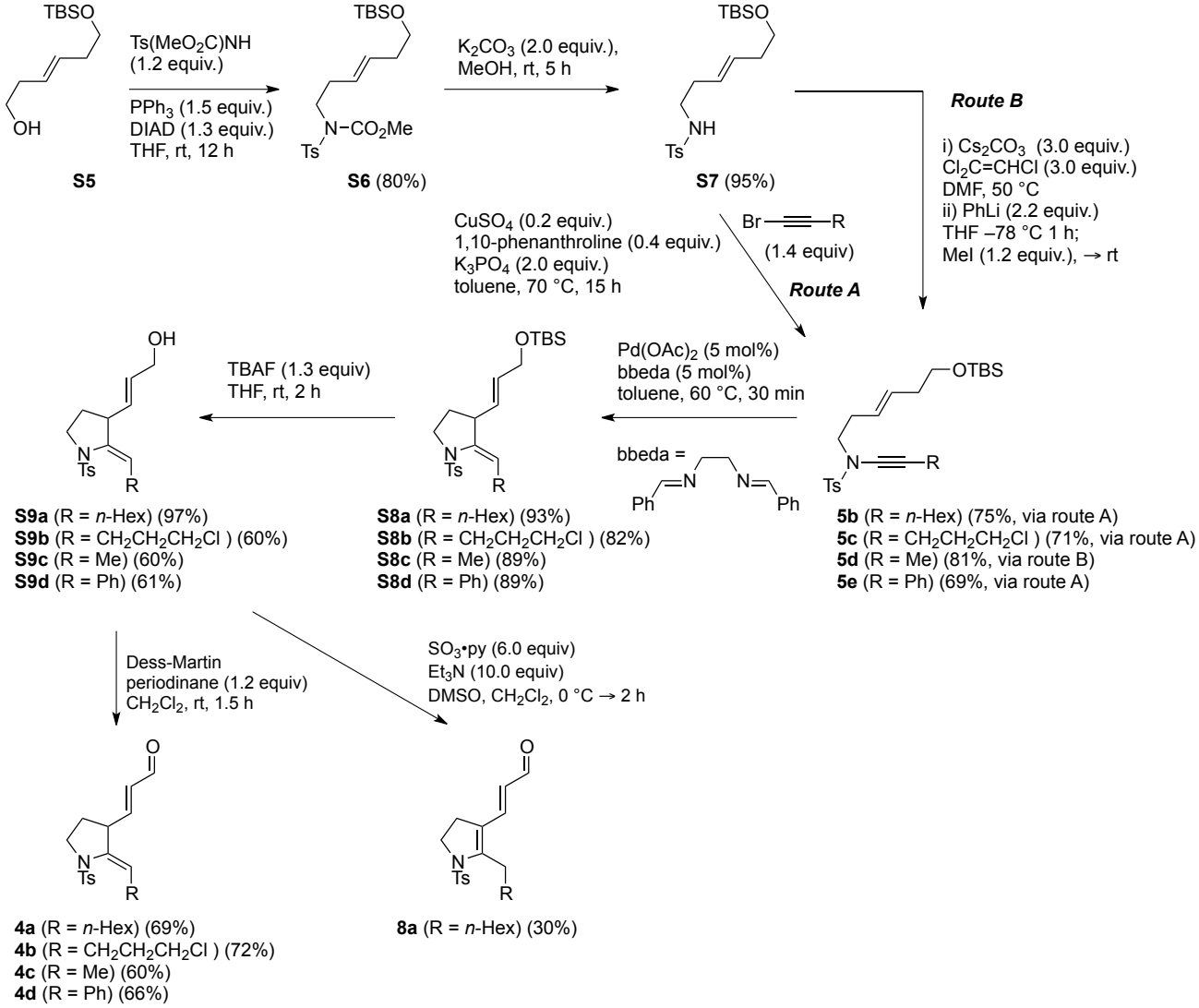
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.369	MM T	1.3973	52.95538	6.31625e-1	0.3961
2	22.455	MM T	1.1789	1.33168e4	238.57243	99.6039

Proof of stereochemistry for azlactone cycloadditions: Cycloadduct **16c** was used to assign the relative stereochemistry of the cycloaddition through ^{1}H NMR nOe experiments (1D nOe / 2D NOESY). On the alpha face (as depicted below), a strong enhancement was seen between H5 and H9, indicating these groups to be on the same face.

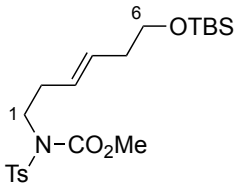


*1.3.3 Synthesis of dienals **4a-d** and **8a***

Dienals **4a-d** and **8a** were synthesized according to the following scheme:

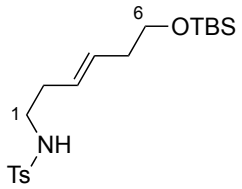


(*E*)-Methyl (6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl)(tosyl)carbamate, S6



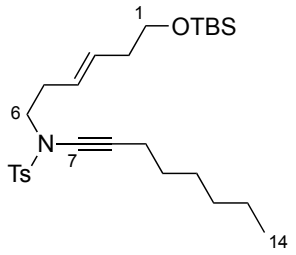
Prepared by General Procedure **A** using **S5** (1.20 g, 5.21 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / Et_2O (9:1)) to give **S6** as a colourless oil (1.85 g, 4.19 mmol, 80%); **IR** (thin film, ν_{max} / cm^{-1}) 2955, 2857, 1736, 1444, 1359, 1281, 1168, 1089, 835; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.83 (2H, d, *J* = 8.0 Hz, TsH), 7.30 (2H, d, *J* = 8.0 Hz, TsH), 5.47 (2H, m, H3 and H4), 3.86-3.82 (2H, m, H6), 3.68 (3H, s, CO_2Me), 3.60 (2H, t, *J* = 6.9 Hz, H1), 2.43 (3H, s, $TsCH_3$), 2.46-2.35 (2H, m, H5), 2.21 (2H, q, *J* = 6.6 Hz, H2), 0.89 (9H, s, $SiC(CH_3)_3$), 0.05 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 152.8, 144.5, 136.6, 130.0, 129.3, 128.3, 127.4, 63.0, 53.7, 47.0, 36.2, 33.3, 25.9, 21.6, 18.3, –5.3; **HRMS** (ES^+) calc. for $C_{21}H_{36}O_5NSSi$ $[M+H]^+$ 442.2078; found 442.2074.

(*E*)-*N*-(6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methylbenzenesulfonamide, S7



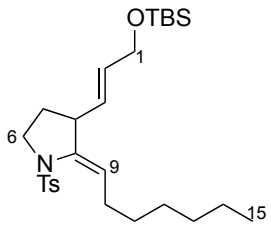
Prepared by General Procedure **B** using carbamate **S6** (1.80 g, 4.08 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / Et_2O (4:1)) to give **S7** as a colourless oil (1.49 g, 3.88 mmol, 95%); **IR** (thin film, ν_{max} / cm^{-1}) 3284, 2954, 2929, 2857, 1599, 1325, 1219, 1159, 1094, 908; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.73 (2H, d, *J* = 8.3 Hz, TsH), 7.28 (2H, t, *J* = 8.7 Hz, TsH), 5.45-5.38 (1H, m, H4), 5.29-5.22 (1H, m, H3), 4.62 (1H, br s, NH), 3.57 (2H, t, *J* = 6.7 Hz, H6), 2.96 (2H, q, *J* = 6.6 Hz, H1), 2.42 (3H, s, $TsCH_3$), 2.23-2.06 (4H, m, H2 and H5), 0.87 (9H, s, $SiC(CH_3)_3$), 0.02 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.3, 136.9, 130.7, 129.6, 127.5, 127.1, 62.8, 42.5, 36.1, 32.5, 25.9, 21.5, 18.3, –5.3; **HRMS** (ES^+) calc. for $C_{19}H_{34}O_3NSSi$ $[M+H]^+$ 384.2023; found 384.2021.

(*E*)-*N*-(6-((tert-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methyl-*N*-(oct-1-yn-1-yl)benzenesulfonamide, 5b



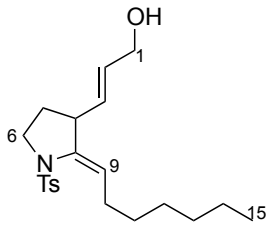
Prepared by General Procedure **C** using sulfonamide **S7** (1.50 g, 3.91 mmol, 1.0 equiv.) and 1-bromooct-1-yne (940 mg, 4.80 mmol, 1.2 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **5b** as a colourless oil (1.45 g, 2.95 mmol, 75%); **IR** (thin film, ν_{max} / cm^{-1}) 2929, 2857, 1739, 1463, 1366, 1254, 1170, 1093, 968, 836, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.73 (2H, d, *J* = 8.3 Hz, TsH), 7.28 (2H, d, *J* = 8.1 Hz, TsH), 5.51-5.37 (1H, m, H3), 5.34-5.26 (1H, m, H4), 3.54 (2H, t, *J* = 6.8 Hz, H1), 3.25-3.21 (2H, m, H6), 2.40 (3H, s, $TsCH_3$), 2.30 (2H, dt, *J* = 7.5 and 7.0 Hz, H2), 2.25 (2H, t, *J* = 7.0 Hz, H9), 2.17 (2H, dt, *J* = 6.5 and 6.5 Hz, H5), 1.46-1.39 (2H, m, H10), 1.33-1.14 (6H, m, H11-H13), 0.86-0.83 (3H, m, H14), 0.84 (9H, s, $SiC(CH_3)_3$), 0.00 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.2, 134.7, 129.9, 129.6, 127.6, 127.2, 72.9, 70.5, 63.0, 51.2, 36.3, 31.3, 31.2, 28.9, 28.5, 25.9, 22.6, 21.6, 18.5, 18.4, 14.1, –5.2; **HRMS** (ES^+) calc. for $C_{27}H_{46}O_3NSSi$ $[M+H]^+$ 492.2962; found 492.2958.

(*Z*)-3-((*E*)-3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-heptylidene-1-tosylpyrrolidine, S8a



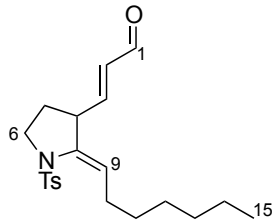
Prepared by General Procedure **F** using ynamide **5b** (1.29 g, 2.62 mmol). The crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **S8a** as a colourless oil (1.20 g, 2.44 mmol, 93%); **IR** (thin film, ν_{max} / cm^{-1}) 2955, 2928, 1355, 1253, 1164, 1091, 835; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.63 (2H, d, *J* = 8.2 Hz, TsH), 7.23 (2H, d, *J* = 8.0 Hz, TsH), 5.34 (1H, dt, *J* = 15.3 and 4.8 Hz, H2), 5.24-5.16 (1H, m, H3), 4.95-4.91 (1H, m, H9), 4.03 (2H, d, *J* = 4.1 Hz, H1), 3.55-3.47 (1H, m, H6), 3.39-3.30 (1H, m, H6), 2.44-2.19 (3H, m, H4 and H10), 2.37 (3H, s, $TsCH_3$), 1.69-1.66 (1H, m, H5), 1.37-1.14 (9H, m, H5 and H11-H14), 0.84 (9H, s, $SiC(CH_3)_3$), 0.81 (3H, t, *J* = 6.7 Hz, H15), 0.00 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.7, 139.6, 134.8, 131.8, 129.4, 129.4, 127.8, 121.5, 63.3, 49.1, 45.0, 31.7, 29.8, 29.2, 29.0, 25.9, 25.9, 22.6, 21.5, 18.4, 14.1, –5.2; **HRMS** (ES^+) calc. for $C_{27}H_{46}O_3NSSi$ $[M+H]^+$ 492.2962; found 492.2961.

(*E*)-3-((*Z*)-2-heptylidene-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9a



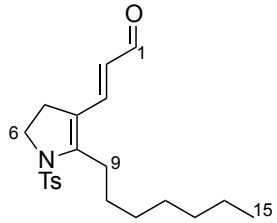
Prepared by General Procedure **G** using **S8a** (1.10 g, 2.24 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give **S9a** as a colourless oil (819 mg, 2.17 mmol, 97%); **IR** (thin film, ν_{max} / cm^{-1}) 3457, 3016, 2970, 1436, 1366, 1217, 1164, 1092, 660; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.62 (2H, d, *J* = 8.2 Hz, TsH), 7.23 (2H, d, *J* = 8.2 Hz, TsH), 5.41 (1H, dt, *J* = 15.3 and 5.6 Hz, H2), 5.17 (1H, dd, *J* = 15.4 and 8.3 Hz, H3), 4.92 (1H, ddd, *J* = 8.0, 6.3 and 1.8 Hz, H9), 3.99 (2H, br s, H1), 3.50 (1H, ddd, *J* = 11.6, 8.7 and 3.1 Hz, H6), 3.34 (1H, dt, *J* = 11.4 and 8.3 Hz, H6), 2.37 (3H, s, $TsCH_3$), 2.34-2.24 (3H, m, H10 and H4), 1.70-1.62 (1H, m, H5), 1.40-1.17 (9H, m, H5 and H11 to H14), 0.81 (3H, t, *J* = 6.7 Hz, H15); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.8, 139.3, 134.8, 131.3, 131.2, 129.4, 127.8, 121.6, 63.1, 49.1, 45.2, 31.7, 29.7, 29.1, 29.0, 29.0, 22.6, 21.5, 14.1; **HRMS** (ES^+) calc. for $C_{21}H_{32}O_3NS$ $[M+H]^+$ 378.2097; found 378.2097.

(*E*)-3-((*Z*)-2-heptylidene-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4a



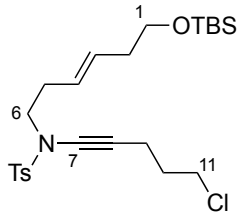
Prepared by General Procedure **I** using **S9A** (260 mg, 0.69 mmol). The resulting crude material was purified by column chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **4a** as a light yellow oil (180 mg, 0.48 mmol, 69%); **IR** (thin film, ν_{max} / cm^{-1}) 2925, 1720, 1689, 1355, 1165, 909, 815, 729, 659; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.31 (1H, d, *J* = 7.8 Hz, H1), 7.63 (2H, d, *J* = 6.8 Hz, TsH), 7.24 (2H, d, *J* = 6.8 Hz, TsH), 6.16 (1H, dd, *J* = 15.6 and 8.6 Hz, H3), 5.83 (1H, dd, *J* = 15.6 and 7.8 Hz, H2), 4.94 (1H, t, *J* = 7.1 Hz, H9), 3.65- 3.57 (1H, m, H6), 3.49-3.40 (1H, m, H6), 2.75-2.64 (1H, m, H4), 2.46-2.32 (2H, m, H10), 2.37 (3H, s, $TsCH_3$), 1.81-1.72 (1H, m, H5), 1.47-1.21 (9H, m, H5 and H11 to H14), 0.81 (3H, t, *J* = 6.2 Hz, H15); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 193.1, 155.5, 144.2, 137.5, 134.7, 133.2, 129.6, 127.8, 123.6, 49.5, 45.5, 31.6, 29.6, 29.2, 29.0, 28.6, 22.6, 21.5, 14.0; **HRMS** (ES^+) calc. for $C_{21}H_{30}O_3NS$ $[M+H]^+$ 376.1941; found 376.1940.

(*E*)-3-(2-heptyl-1-tosyl-4,5-dihydro-1H-pyrrol-3-yl)acrylaldehyde, 8a



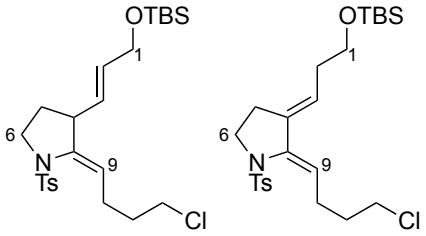
Et_3N (1.36 mL, 9.80 mmol, 10.0 equiv.), DMSO (0.97 mL, 13.7 mmol, 14.0 equiv.) and SO_3•py (935 mg, 5.88 mmol, 6.0 equiv.) were added to a solution of alcohol **S9a** (37 mg, 0.98 mmol, 1.0 equiv.) in DCM (1 mL) at 0 °C. The solution was stirred for 2 h at rt before being quenched with pH 7 phosphate buffer (20 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL), then the combined organic phases were washed with brine (2 x 20 mL), dried ($MgSO_4$) and concentrated. The resulting crude material was purified by flash chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **8a** as a light yellow oil (11.5 mg, 0.030 mmol, 30%); **IR** (thin film, ν_{max} / cm^{-1}) 2925, 2856, 1671, 1601, 1454, 1377, 1233, 1163, 1112, 1088, 813; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.46 (1H, d, *J* = 7.9 Hz, H1), 7.62 (2H, d, *J* = 8.3 Hz, TsH), 7.26 (2H, d, *J* = 8.2 Hz, TsH), 7.20 (1H, d, *J* = 6.8 Hz, H3), 5.76 (1H, dd, *J* = 15.1 and 7.9 Hz, H2), 3.86-3.74 (2H, m, H6), 2.73-2.61 (2H, m, H10), 2.42 (2H, t, *J* = 9.2 Hz, H9), 2.37 (3H, s, $TsCH_3$), 1.57 (2H, dt, *J* = 15.1 and 7.6 Hz, H5), 1.36-1.09 (8H, m, H11 to H14), 0.82 (3H, t, *J* = 6.9 Hz, H14); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 192.9, 152.0, 144.5, 135.0, 130.0, 127.1, 126.3, 119.4, 49.4, 49.4, 31.7, 29.6, 29.5, 28.9, 26.8, 26.5, 22.6, 21.6, 14.1; **HRMS** (ES^+) calc. for $C_{21}H_{29}O_3NNaS$ $[M+Na]^+$ 398.1765; found 398.1760.

(*E*)-*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-*N*-(5-chloropent-1-yn-1-yl)-4-ethylbenzene sulfonamide, 5c



Prepared by General Procedure **C** using sulfonamide **S7** (760 mg, 1.98 mmol, 1.0 equiv.) and 1-bromo-5-chloropent-1-yne (432 mg, 2.40 mmol, 1.2 equiv.). The resulting crude material was purified by column chromatography (petroleum ether / EtOAc (95:5)) to give **5c** as a colourless oil (680 mg, 1.40 mmol, 71%); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2929, 1363, 1254, 1168, 1091, 834, 813, 775; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, *J* = 8.2 Hz, TsH), 7.33 (2H, d, *J* = 8.1 Hz, TsH), 5.53-5.42 (1H, m, H3), 5.39-5.26 (1H, m, H4), 3.62-3.55 (4H, m, H1 and H6), 3.28 (2H, t, *J* = 7.4 Hz, H11), 2.46 (2H, t, *J* = 6.8 Hz, H2), 2.44 (3H, s, $TsCH_3$), 2.29 (2H, q, *J* = 7.1 Hz, H9), 2.16 (2H, q, *J* = 6.8 Hz, H5), 1.92 (2H, quint, *J* = 6.5 Hz, H10), 0.88 (9H, s, $SiC(CH_3)_3$), 0.03 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.4, 134.6, 130.0, 129.6, 127.5, 127.0, 74.0, 68.4, 62.9, 51.1, 43.5, 36.2, 31.5, 31.1, 25.9, 21.6, 18.3, 15.9, –5.3; **HRMS** (ES^+) calc. for $C_{24}H_{39}O_3NClSSi$ $[M+H]^+$ 484.2103; found 484.2102.

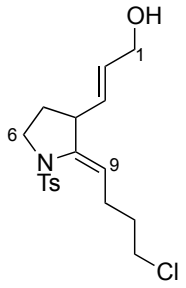
(*Z*)-3-((*E*)-3-((*tert*-Butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-(4-chlorobutylidene)-1-tosylpyrrolidine, S8b



(4:1)

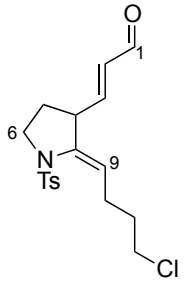
Prepared by General Procedure **F** using ynamide **5c** (604 mg, 1.25 mmol). The crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **S8b** as a colourless oil (498 mg, 1.03 mmol, 82%); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2929, 1598, 1471, 1329, 1253, 1091, 1067, 835, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.62 (2H, d, *J* = 9.0 Hz, TsH), 7.24 (2H, d, *J* = 7.4 Hz, TsH), 5.35 (1H, d, *J* = 14.2 Hz, H2), 5.18 (1H, dd, *J* = 15.3 and 8.3 Hz, H3), 4.91 (1H, t, *J* = 7.2 Hz, H9), 4.04 (2H, d, *J* = 2.1 Hz, H1), 3.77-3.68 (1H, m, H6), 3.52-3.45 (2H, m, H12), 3.36 (1H, dt, *J* = 18.5 and 7.5 Hz, H6), 2.62-2.49 (2H, m, H10), 2.38 (3H, s, $TsCH_3$), 2.25 (1H, dd, *J* = 16.9 and 8.4 Hz, H4), 1.99-1.63 (3H, m, H5 and H11), 1.67 (1H, dd, *J* = 18.4 and 9.2 Hz, H5), 0.84 (9H, s, $SiC(CH_3)_3$), 0.00 (3H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.9, 141.0, 134.6, 132.1, 129.5, 129.0, 127.8, 119.0, 76.7, 63.2, 49.1, 45.2, 44.6, 32.8, 29.1, 26.6, 25.9, 21.6, –5.2; **HRMS** (ES^+) calc. for $C_{24}H_{38}O_3NClNaSSi$ $[M+Na]^+$ 506.1922; found 506.1919.

(*E*)-3-((*Z*)-2-(4-Chlorobutylidene)-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9b



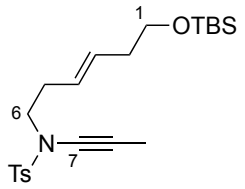
Prepared by General Procedure **G** using **S8b** (521 mg, 1.08 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give **S9b** as a colourless oil (240 mg, 0.65 mmol, 60%); **IR** (thin film, ν_{max} / cm^{-1}) 3450, 2925, 1449, 1348, 1160, 1120, 1015, 709; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.66 (2H, d, *J* = 7.8 Hz), 7.28 (2H, d, *J* = 7.8 Hz), 5.47 (1H, dt, *J* = 14.5 and 5.3 Hz, H2), 5.21 (1H, dd, *J* = 15.3 and 8.3 Hz, H3), 4.96 (1H, t, *J* = 7.2 Hz, H9), 4.03 (2H, d, *J* = 4.9 Hz, H1), 3.53 (3H, t, *J* = 6.5 Hz, H12 and H6), 3.38 (1H, dd, *J* = 18.5 and 9.4 Hz, H6), 2.54 (2H, dd, *J* = 15.1 and 7.9 Hz, H10), 2.41 (3H, s, $TsCH_3$), 2.32 (1H, q, *J* = 8.4 Hz, H4), 1.96-1.68 (3H, m, H5 and H11), 1.38-1.21 (1H, m, H5); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.0, 140.7, 134.5, 131.7, 130.5, 129.5, 127.7, 119.1, 62.8, 49.1, 45.2, 44.7, 32.6, 29.0, 26.6, 21.5; **HRMS** (ES^+) calc. for $C_{18}H_{25}O_3NClS$ $[M+H]^+$ 370.1238; found 370.1234.

(*E*)-3-((*Z*)-2-(4-chlorobutylidene)-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4b



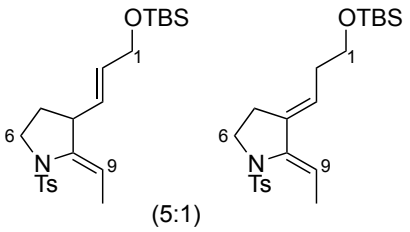
Prepared by General Procedure **I** using **S9b** (74 mg, 0.20 mmol). The resulting crude material was purified by flash chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **4b** as a light yellow oil (53 mg, 0.144 mmol, 72%); **IR** (thin film, ν_{max} / cm^{-1}) 2928, 1728, 1687, 1351, 1161, 1090, 840, 708; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.37 (1H, ddd, *J* = 7.8, 2.0 and 1.0 Hz, H1), 7.67 (2H, d, *J* = 8.1 Hz, TsH), 7.31 (2H, d, *J* = 7.4 Hz, TsH), 6.22 (1H, dd, *J* = 15.6 and 8.6 Hz, H2), 5.89 (1H, dd, *J* = 16.4 and 7.8 Hz, H3), 4.99 (1H, t, *J* = 7.2 Hz, H9), 3.67 (1H, br t, *J* = 10.1 Hz, H6), 3.57-3.46 (3H, m, H6 and 2 x H12), 2.77 (1H, app q, *J* = 8.3 Hz, H4), 2.58 (2H, app q, *J* = 7.5 Hz, H10), 2.42 (3H, s, $TsCH_3$), 1.97-1.80 (3H, m, H5 and 2 x H11), 1.54-1.43 (1H, m, H5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 193.0, 154.9, 144.4, 138.9, 134.6, 133.4, 129.7, 127.8, 121.1, 49.5, 45.6, 44.6, 32.4, 28.4, 26.9, 21.5; **HRMS** (ES^+) calc. for $C_{18}H_{23}O_3NClS$ $[M+H]^+$ 368.1081; found 368.1077.

(*E*)-*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 5d



Prepared by General Procedure **D** and **E** using sulfonamide **S7** (760 mg, 1.98 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **5d** as a colorless oil (680 mg, 1.61 mmol, 81%); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2857, 1362, 1253, 1168, 1092, 834, 812, 775; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, *J* = 8.3 Hz, TsH), 7.32 (2H, d, *J* = 8.3 Hz, TsH), 5.52-5.41 (1H, m, H3), 5.39-5.29 (1H, m, H4), 3.58 (2H, t, *J* = 6.8 Hz, H1), 3.25 (2H, t, *J* = 8 Hz, H6), 2.43 (3H, s, $TsCH_3$), 2.29 (2H, q, *J* = 7.1 Hz, H2), 2.16 (2H, q, *J* = 6.8 Hz, H3), 1.89 (3H, s, H9), 0.88 (9H, s, $SiC(CH_3)_3$), 0.03 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.2, 134.8, 129.9, 129.6, 127.5, 127.2, 71.8, 70.6, 65.7, 62.9, 51.1, 36.2, 31.1, 25.9, 21.6, 3.3, –5.3; **HRMS** (ES^+) calc. for $C_{22}H_{35}O_3NNaS$ $[M+Na]^+$ 444.1999; found 444.2000.

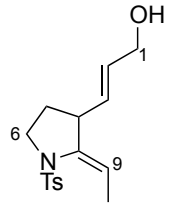
(*Z*)-3-((*E*)-3-((*tert*-Butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-ethylidene-1-tosylpyrrolidine, S8c



(5:1)

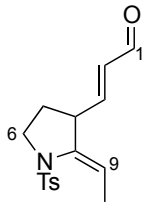
Prepared by General Procedure **F** using ynamide **5d** (600 mg, 1.42 mmol). The crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **S8c** as colourless oil (532 mg, 1.26 mmol, 89%); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2929, 1390, 1351, 1164, 1114, 1096, 1060, 954, 836, 770; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.64 (2H, d, *J* = 8.2 Hz, TsH), 7.24 (2H, d, *J* = 8.1 Hz, TsH), 5.34 (1H, dt, *J* = 15.3 and 5.0 Hz, H2), 5.19 (1H, dd, *J* = 15.3 and 8.3 Hz, H3), 5.07 (1H, qd, *J* = 7.0 and 1.9 Hz, H9), 4.03 (2H, d, *J* = 4.9 Hz, H1), 3.51 (1H, ddd, *J* = 17.1, 11.7 and 5.2 Hz, H6), 3.43-3.30 (1H, m, H6), 2.38 (3H, s, $TsCH_3$), 2.24 (1H, ddd, *J* = 10.0, 9.1 and 5.3 Hz, H4), 1.96 (3H, d, *J* = 3.9 Hz, H10), 1.86 (1H, dd, *J* = 7.1 and 2.1 Hz, H5), 1.66 (1H, ddt, *J* = 13.5, 8.7 and 4.3 Hz, H5), 0.84 (9H, s, $SiC(CH_3)_3$), -0.00 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.7, 141.0, 134.7, 131.8, 129.4, 127.8, 115.5, 76.7, 63.4, 49.1, 45.1, 29.1, 25.9, 21.5, 18.4, 15.0, –5.2; **HRMS** (ES^+) calc. for $C_{22}H_{36}O_3NSSi$ $[M+H]^+$ 422.2179; found 422.2178.

(*E*)-3-((*Z*)-2-Ethylidene-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9c



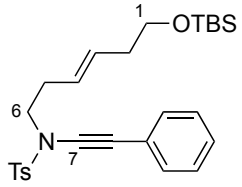
Prepared by General Procedure **G** using **S8c** (353 mg, 0.84 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give **S9c** as a colourless oil (155 mg, 0.50 mmol, 60%); **IR** (thin film, ν_{max} / cm^{-1}) 3445, 2921, 1736, 1449, 1350, 1242, 1161, 1090, 813; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.62 (2H, d, *J* = 8.0 Hz, TsH), 7.23 (2H, d, *J* = 8.0 Hz, TsH), 5.41 (1H, dt, *J* = 15.3 and 5.6 Hz, H2), 5.18 (1H, dd, *J* = 15.4 and 8.3 Hz, H3), 5.06 (1H, qd, *J* = 7.0 and 1.8 Hz, H9), 3.97 (2H, d, *J* = 5.5 Hz, H1), 3.53-3.47 (1H, m, H6), 3.37-3.30 (1H, m, H6), 2.36 (3H, s, $TsCH_3$), 2.25 (1H, q, *J* = 8.3 Hz, H4), 1.83 (3H, d, *J* = 6.1 Hz, H10), 1.69-1.62 (1H, m, H5), 1.37-1.18 (1H, m, H5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.8, 140.7, 134.6, 131.4, 130.8, 129.4, 127.7, 115.5, 62.9, 49.0, 45.1, 28.9, 21.5, 15.0; **HRMS** (ES^+) calc. for $C_{16}H_{22}O_3NS$ $[M+H]^+$ 308.1314; found 308.1313.

(*E*)-3-((*Z*)-2-Ethylidene-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4c



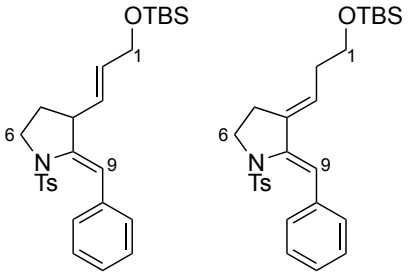
Prepared by General Procedure **I** using **S9c** (50 mg, 0.16 mmol). The resulting crude material was purified by column chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **4c** as a light yellow oil (30 mg, 0.098 mmol, 60%); **IR** (thin film, ν_{max} / cm^{-1}) 2923, 1796, 1724, 1687, 1551, 1401, 1350, 1191, 1158, 773; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.36 (1H, d, *J* = 7.8 Hz, H1), 7.69 (2H, d, *J* = 8.2 Hz, TsH), 7.30 (2H, d, *J* = 8.2 Hz, TsH), 6.23 (1H, dd, *J* = 15.6 and 8.6 Hz, H2), 5.89 (1H, dd, *J* = 15.6 and 7.8 Hz, H3), 5.18-5.10 (1H, m, H9), 3.67 (1H, ddd, *J* = 12.3, 8.5 and 4.0 Hz, H6), 3.51 (1H, dt, *J* = 11.7, 7.9 Hz, H6), 2.75 (1H, q, *J* = 8.4 Hz, H4), 2.43 (3H, s, $TsCH_3$), 1.93 (3H, d, *J* = 7.1 Hz, H10), 1.88-1.78 (1H, m, H5), 1.54-1.43 (1H, m, H5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 193.1, 155.4, 144.3, 139.0, 134.7, 133.2, 129.7, 127.8, 117.6, 49.5, 45.5, 28.5, 21.5, 15.2; **HRMS** (ES^+) calc. for $C_{16}H_{20}O_3NS$ $[M+H]^+$ 306.1158; found 306.1159.

(*E*)-*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide, 5e



Prepared by General Procedure **C** using sulfonamide **S7** (760 mg, 1.98 mmol, 1.0 equiv.) and (bromoethynyl)benzene (432 mg, 2.40 mmol, 1.2 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **5e** as a colourless oil (660 mg, 1.36 mmol, 69%); **IR** (thin film, ν_{max} / cm^{-1}) 2953, 2856, 2235, 1366, 1254, 1169, 1091, 733; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (2H, d, *J* = 8.2 Hz, TsH), 7.34-7.30 (4H, m, PhH and TsH), 7.28-7.22 (3H, m, PhH), 5.51-5.44 (1H, m, H3), 5.38-5.31 (1H, m, H4), 3.55 (2H, t, *J* = 6.8 Hz, H1), 3.38 (2H, t, *J* = 7.5 Hz, H6), 2.41 (3H, s, $TsCH_3$), 2.35 (2H, dd, *J* = 14.4 and 7.2 Hz, H2), 2.14 (2H, q, *J* = 6.8 Hz, H5), 0.84 (9H, s, $SiC(CH_3)_3$), 0.0 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.5, 134.6, 131.3, 130.2, 129.7, 128.2, 127.7, 127.6, 127.0, 122.9, 82.2, 70.9, 67.9, 51.3, 36.2, 31.3, 25.9, 21.6, 18.3, –5.3; **HRMS** (ES^+) calc. for $C_{27}H_{38}O_3NSSi$ $[M+H]^+$ 484.2336; found 484.2335.

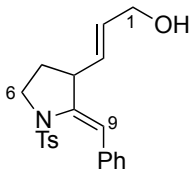
(*Z*)-2-Benzylidene-3-((*E*)-3-((tert-butyldimethylsilyl)oxy)prop-1-en-1-yl)-1-tosylpyrrolidine, S8d



(5:1)

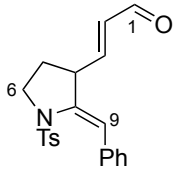
Prepared by General Procedure F using ynamide **5e** (650 mg, 1.34 mmol, 1.0 equiv.). The crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **S8d** as a yellow oil (580 mg, 1.20 mmol, 89%); **IR** (thin film, ν_{max} / cm^{-1}) 2953, 1597, 1471, 1404, 1210, 1160, 1090, 834, 814, 731; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.58 (2H, d, *J* = 8.2 Hz, TsH), 7.54 (2H, d, *J* = 7.4 Hz, PhH), 7.29-7.16 (3H, m, TsH and PhH), 7.15-7.07 (2H, m, PhH), 5.85 (1H, d, *J* = 2.1 Hz, H9), 5.44 (1H, dt, *J* = 15.3 and 4.9 Hz, H2), 5.32-5.19 (1H, m, H3), 4.06 (2H, dd, *J* = 4.9 and 1.4 Hz, H1), 3.62 (1H, ddd, *J* = 15.7, 9.4 and 5.1 Hz, H6), 3.45 (1H, ddd, *J* = 14.6, 10.4 and 7.5 Hz, H6), 2.49 (1H, q, *J* = 10.2 Hz, H4), 2.35 (3H, s, $TsCH_3$), 1.77-1.69 (1H, m, H5), 1.35 (1H, ddd, *J* = 19.5, 12.3 and 9.1 Hz, H5), 0.83 (9H, s, $SiC(CH_3)_3$), 0.00 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.9, 140.6, 136.4, 134.5, 132.6, 129.4, 129.2, 128.8, 127.9, 127.7, 126.8, 118.8, 63.4, 49.1, 46.3, 28.8, 25.9, 25.9, 21.6, –5.2; **HRMS** (ES^+) calc. for $C_{27}H_{38}O_3NSSi$ $[M+H]^+$ 484.2336; found 484.2334.

(*E*)-3-((*Z*)-2-Benzylidene-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9d



Prepared by General Procedure **G** using **S8d** (300 mg, 0.62 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give **S9d** as a yellow oil (140 mg, 0.38 mmol, 61%); **IR** (thin film, ν_{max} / cm^{-1}) 3385, 2958, 2899, 1597, 1305, 1160, 1088, 911,756; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.61 (2H, d, *J* = 8.1 Hz, TsH), 7.57 (2H, d, *J* = 7.4 Hz, PhH), 7.24 (4H, m, TsH and PhH), 7.14 (1H, t, *J* = 7.4 Hz, PhH), 5.90 (1H, d, *J* = 1.8 Hz, H9), 5.54 (1H, dt, *J* = 14.6 and 5.2 Hz, H2), 5.31 (1H, dd, *J* = 15.3 and 8.4 Hz, H3), 4.04 (2H, br s, H1), 3.75-3.62 (1H, m, H6), 3.49 (1H, dd, *J* = 19.5 and 8.4 Hz, H6), 2.56 (1H, q, *J* = 8.6 Hz, H4), 2.38 (3H, s, $TsCH_3$), 1.95 (1H, br s, OH), 1.77 (1H, dd, *J* = 18.6 and 8.6 Hz, H5), 1.46 - 1.36 (1H, m, H5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.0, 140.4, 136.2, 134.3, 132.1, 130.4, 129.4, 128.7, 127.8, 127.6, 126.7, 118.8, 62.8, 49.1, 46.1, 28.6, 21.5; **HRMS** (ES^+) calc. for $C_{21}H_{23}O_3NNaS$ $[M+Na]^+$ 392.1291; found 392.1289.

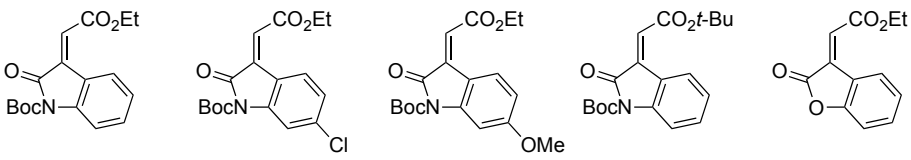
(*E*)-3-((*Z*)-2-benzylidene-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4d



Prepared by General Procedure **I** using **S9d** (70 mg, 0.19 mmol, 1.0 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether -> petroleum ether / EtOAc (1:1)) to give **4d** as a yellow oil (46 mg, 0.13 mmol, 66%); **IR** (thin film, ν_{max} / cm^{-1}) 3016, 1728, 1685, 1598, 1353, 1158, 1089, 1030, 815; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.37 (1H, d, *J* = 7.8 Hz, H1), 7.57 (2H, d, *J* = 8.3 Hz, TsH), 7.51 (2H, d, *J* = 7.3 Hz, PhH), 7.21 (4H, m, TsH and PhH), 7.12 (1H, t, *J* = 7.3 Hz, PhH), 6.31 (1H, dd, *J* = 15.6 and 8.8 Hz, H2), 5.95 (1H, dd, *J* = 15.6 and 7.8 Hz, H3), 5.84 (1H, d, *J* = 1.7 Hz, H9), 3.74 (1H, ddd, *J* = 12.2, 8.4 and 4.0 Hz, H6), 3.56 (1H, dt, *J* = 11.9 and 7.9 Hz, H6), 2.96 (1H, q, *J* = 8.6 Hz, H4), 2.35 (3H, s, $TsCH_3$), 1.89-1.81 (1H, m, H5), 1.56-1.46 (1H, m, H5); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 193.0, 155.0, 144.4, 138.4, 135.6, 134.4, 133.7, 129.6, 128.8, 127.9, 127.8, 127.3, 120.6, 49.6, 46.4, 28.3, 21.5; **HRMS** (ES^+) calc. for $C_{21}H_{22}O_3NS$ $[M+H]^+$ 368.1315; found 368.1318.

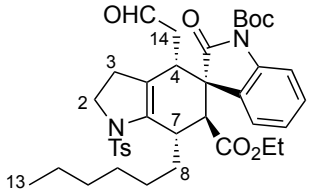
*1.3.4 Cycloaddition reactions of dienals **4a-d***

4a-d were reacted with the following dienophiles:



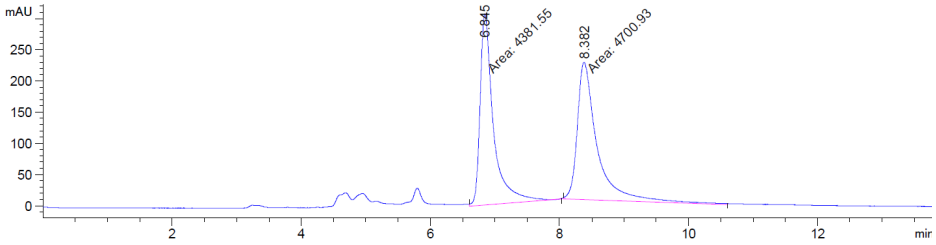
9a **9b** **9c** **9d** **17**

(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-hexyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12a

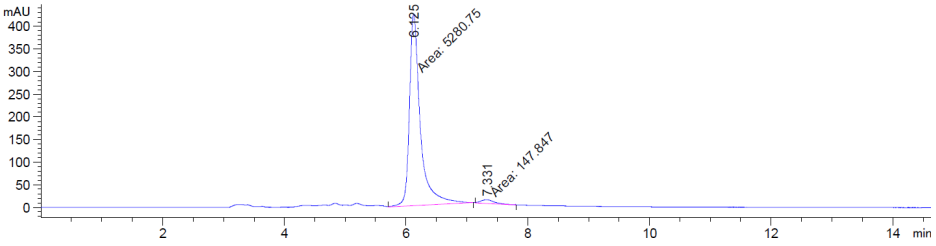


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.010 mmol, 0.2 equiv.), **4a** (28 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9a** (15.8 mg, 0.050 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12a** as a light yellow oil (27 mg, 0.039 mmol, 78%); $[\alpha]_D^{25}$ –94.3 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2128, 1750, 1730, 1605, 1464, 1353, 1304, 1253, 1162; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.67 (1H, s, H15), 7.94 (2H, d, *J* = 8.0 Hz, TsH), 7.81 (1H, d, *J* = 7.9 Hz, ArH), 7.40 (2H, d, *J* = 8.0 Hz, TsH), 7.21 (1H, td, *J* = 8.0 and 1.4 Hz, ArH), 6.63 (1H, t, *J* = 8.0 Hz, ArH), 6.55 (1H, d, *J* = 6.5 Hz, ArH),), 4.03 (1H, ddd, *J* = 11.7, 8.0 and 6.4 Hz, H2), 3.83-3.78 (3H, m, H2 and $OC\underline{H}_2CH_3$), 3.67 (1H, br s, H7), 3.33 (1H, dd, *J* = 18.6 and 8.9 Hz, H14), 3.27 (1H, d, *J* = 7.1 Hz, H6), 2.89 (1H, d, *J* = 8.6 Hz, H4), 2.51 (3H, s, $TsCH_3$), 2.28 (1H, dd, *J* = 18.7 and 3.0 Hz, H14), 2.24-2.19 (2H, m, H3), 2.00-1.93 (1H, m, H8), 1.81-1.93 (1H, m, H8), 1.60 (9H, s, $C(CH_3)_3$), 1.37-1.14 (8H, m, H9-H12), 0.89 (6H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$ and H13); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.9, 176.7, 171.0, 148.9, 144.0, 139.3, 138.8, 136.2, 130.5, 130.1, 128.4, 128.1, 123.8, 123.5, 123.3, 114.7, 84.14, 61.2, 51.6, 50.1, 47.7, 44.3, 37.4, 33.8, 33.5, 31.8, 30.3, 29.5, 27.9, 25.4, 22.7, 21.6, 14.1, 13.4; **HRMS** (ES^+) calc. for $C_{38}H_{48}O_8N_2NaS$ $[M+Na]^+$ 715.3023; found 715.3018.

Chiralpak IB (25% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) $t_R$major –6.1 min, minor – 7.3 min (94% *ee*).

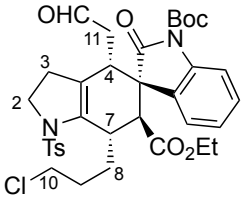


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.845	MM T	0.2385	4381.54639	306.17032	48.2418
2	8.382	MM T	0.3559	4700.92676	220.12039	51.7582



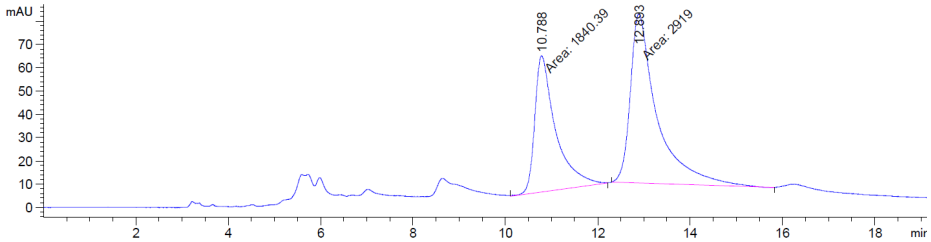
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.125	MM T	0.2072	5280.74902	424.71085	97.2765
2	7.331	MM T	0.2778	147.84732	8.86930	2.7235

(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-(3-chloropropyl)-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12b

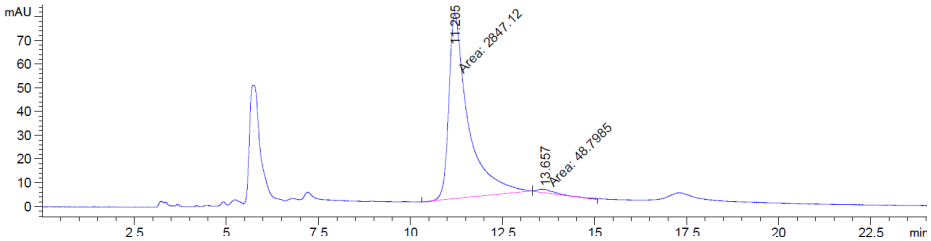


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.010 mmol, 0.2 equiv.), **4b** (27.5 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9a** (15.8 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12b** as a colourless oil (23 mg, 0.034 mmol, 67%); $[\alpha]_D^{25}$ –51.3 (*c* = 0.5, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2927, 2856, 1787, 1755, 1726, 1598, 1482, 1348, 1250; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 9.67 (1H, s, H12), 7.93 (2H, d, *J* = 8.0 Hz, TsH), 7.82 (1H, d, *J* = 8.1 Hz, ArH), 7.41 (2H, d, *J* = 8.0 Hz, TsH), 7.22 (1H, dt, *J* = 15.1 and 4.1 Hz, ArH), 6.64 (1H, t, *J* = 7.9 Hz, ArH), 6.54 (1H, d, *J* = 7.0 Hz, ArH), 4.16-4.10 (1H, m, H2), 4.05-3.99 (1H, m, H2), 3.85-3.78 (2H, m, $OC\underline{H_2}CH_3$), 3.74-3.70 (1H, m, H7), 3.62-3.53 (2H, m, H10), 3.30 (1H, dd, *J* = 18.6 and 8.7 Hz, H11), 3.23 (1H, d, *J* = 7.1 Hz, H6), 2.92 (1H , d, *J* = 6.5 Hz, H4), 2.52 (3H, s, $TsCH_3$), 2.29 (1H, dd, *J* = 18.7 and 3.1 Hz, H11), 2.23 (2H, td, *J* = 9.1 and 2.4 Hz, H3), 2.16-2.10 (1H, m, H8), 1.99-1.83 (2H, m, H9), 1.75-1.66 (1H, m, H8), 1.61 (9H, s, $C(CH_3)_3$), 0.90 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H_3}$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 198.7, 176.5, 170.9, 148.9, 144.3, 138.9, 138.6, 135.9, 130.3, 130.1, 128.6, 128.1, 124.3, 123.9, 123.2, 114.8, 84.3, 61.4, 51.6, 50.0, 47.7, 44.8, 44.2, 37.2, 33.1, 31.6, 30.3, 29.0, 28.0, 21.7, 13.4; **HRMS** (ES^+) calc. for $C_{35}H_{42}O_8N_2ClS$ $[M+H]^+$ 685.2344; found 685.2338.

Chiralpak IB (20% IPA in hexane, flow rate = 1.0 mL/min, 254 nm) $t_R$major: 11.2 min, minor: 13.6 min (97% *ee*).

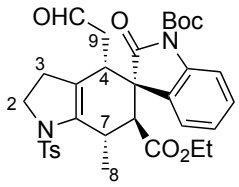


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.788	MM T	0.5753	1840.39417	58.43845	38.6687
2	12.893	MM T	0.6699	2919.00146	72.61856	61.3313



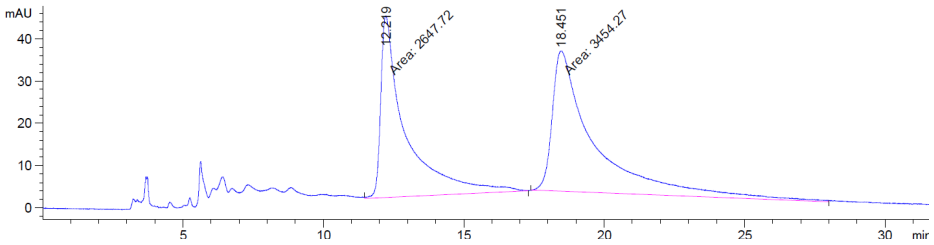
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.196	MM T	0.6682	716.36023	19.63755	98.5921
2	13.591	MM T	0.4072	10.22972	4.18751e-1	1.4079

(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-methyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12c



Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.010 mmol, 0.2 equiv.), **4c** (22.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9a** (15.8 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12c** as a light yellow oil (23 mg, 0.036 mmol, 74%); $[\alpha]_D^{25}$ –57.1 (*c* = 0.8, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2922, 2850, 1764, 1722, 1602, 1475, 1348, 1306, 1156, 986, 739; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 9.67 (1H, s, H10), 7.92 (2H, d, *J* = 8.0 Hz, TsH), 7.80 (1H, d, *J* = 8.2 Hz, ArH), 7.41 (2H, d, *J* = 8.0 Hz, TsH), 7.25-7.21 (1H, m, ArH), 6.69 (1H, t, *J* = 8.0 Hz, ArH), 6.63 (1H, d, *J* = 8.5 Hz, ArH), 4.06 (1H, ddd, *J* = 11.9, 9.1 and 4.8 Hz, H2), 3.88-3.77 (3H, m, H2 and $OC\underline{H}_2CH_3$), 3.53-3.50 (1H, m, H7), 3.32 (1H, dd, *J* = 18.6 and 8.9 Hz, H9), 3.09 (1H, d, *J* = 8.1 Hz, H6), 2.87 (1H, d, *J* = 7.0 Hz, H4), 2.51 (3H, s, $TsCH_3$), 2.31 (1H dd, *J* = 18.7 and 3.0 Hz, H9), 2.29-2.17 (2H, m, H3), 1.60 (9H, s, $C(CH_3)_3$), 1.50 (3H, d, *J* = 6.5 Hz, H8), 0.94 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 198.9, 176.6, 170.8, 148.8, 144.2, 140.4, 138.9, 136.2, 130.6, 130.1, 128.4, 128.0, 123.9, 123.1, 123.0, 114.8, 84.2, 61.2, 51.2, 51.0, 50.2, 44.1, 37.7, 30.3, 29.7, 28.0, 21.7, 21.7, 13.5; **HRMS** (ES^+) calc. for $C_{33}H_{39}O_8N_2S$ $[M+H]^+$ 623.2421; found 623.2433.

Chiralpak IB (20% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) $t_R$major: 12.2 min, minor: 18.9 min (98% *ee*).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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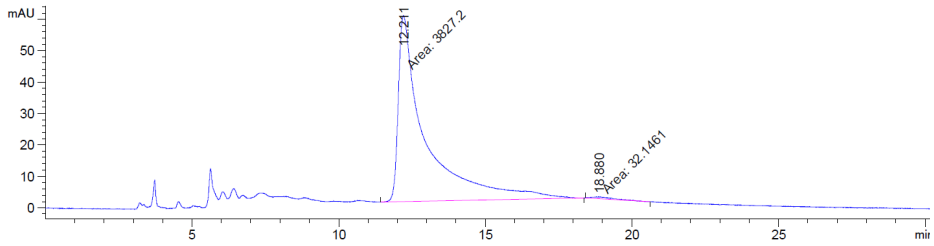
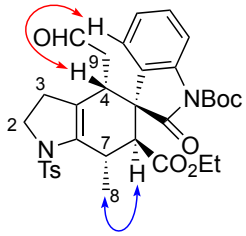
2	18.451	MM T	1.5380	3454.27222	33.21464	56.6089

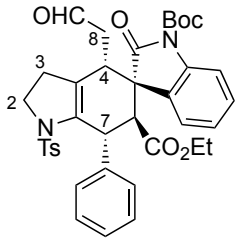


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.211	MM T	0.9924	3827.19922	59.21365	99.1671
2	18.880	MM T	0.8282	32.14612	6.46924e-1	0.8329

Proof of stereochemistry for oxindole cycloadditions: Cycloadduct **12c** was used to assign the relative stereochemistry of the cycloaddition through ^{1}H NMR nOe experiments (1D nOe / 2D NOESY). On the alpha face (as depicted below), a strong enhancement was seen between H6 and H8 (side chain methyl), indicating these groups to be on the same face; on the beta face, a strong enhancement was seen between H4 and an aryl proton.



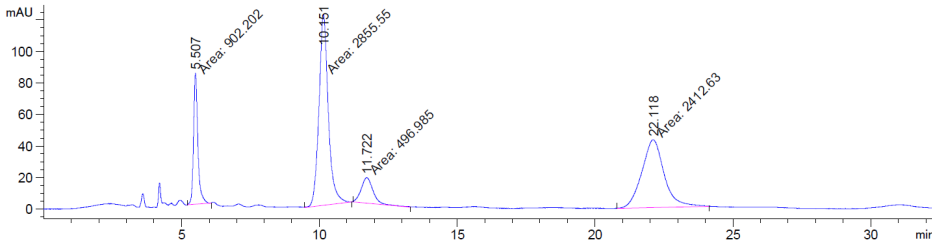
(3'*S*,4*S*,6*S*,7*R*)-1'-*tert*-Butyl 6-ethyl 2'-oxo-4-(2-oxoethyl)-7-phenyl-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12d



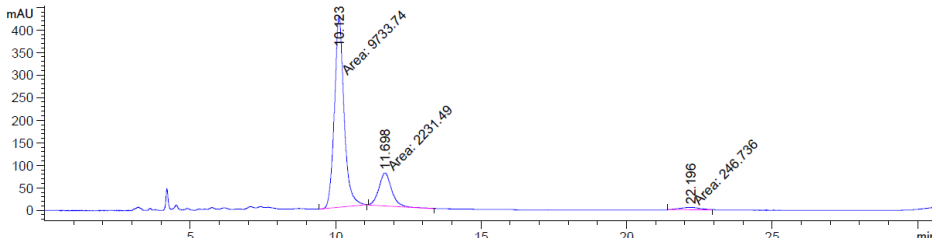
Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.01 mmol, 0.2 equiv.), **4d** (27.5 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9a** (15.8 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12d** as a yellow oil (24 mg, 0.035 mmol, 70% yield); $[\alpha]_D^{25}$ –57.4 (*c* = 1.1, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2928, 1789, 1757, 1726, 1602, 1478, 1251, 1150, 1022, 868; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.66 (1H, s, H9), 7.77 (1H, d, *J* = 8.3 Hz, ArH), 7.34-7.22 (3H, m, TsH and ArH), 7.23-6.91 (9H, m, TsH and ArH), 4.82-4.70 (1H, m, H2), 4.10-4.04 (1H, m, H2), 3.74-3.65 (2H, m, $OC\underline{H}_2CH_3$), 3.63-3.52 (2H, m, H8 and H6), 3.27 (1H, d, *J* = 8.9 Hz, H7), 3.02 (1H, dd, *J* = 11.3 and 7.9 Hz, H8), 2.56-2.40 (2H, m, H4 and H5), 2.37-2.28 (1H, m, H5), 2.32 (3H, s, $TsCH_3$), 1.52 (9H, s, $C(CH_3)_3$), 0.76 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.9, 176.0, 170.3, 148.7, 143.5, 141.5, 138.8, 138.1, 136.6, 130.1, 129.5, 128.7, 128.4, 128.3, 127.5, 126.9, 125.5, 124.6, 123.6, 114.8, 84.2, 61.1, 52.2, 51.8, 49.6, 44.3, 40.8, 37.9, 31.0, 28.0, 21.5, 13.4; **HRMS** (ES^+) calc. for $C_{38}H_{41}O_8N_2S$ $[M+H]^+$ 685.2578; found 685.2562.

HPLC data is on the next page.

Chiralpak IA (20% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) Minor diastereomer: $t_R$major – 11.7 min, minor – 5.2 min;Major diastereomer: $t_R$major – 10.1 min, minor – 22.2 min. (95% *ee*).

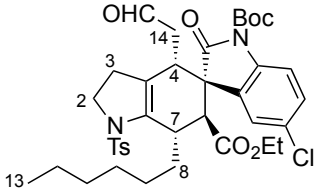


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.507	MM T	0.1813	902.20239	82.94261	13.5316
2	10.151	MM T	0.3935	2855.55420	120.93341	42.8288
3	11.722	MM T	0.5078	496.98535	16.31137	7.4540
4	22.118	MM T	0.9356	2412.63037	42.97863	36.1856



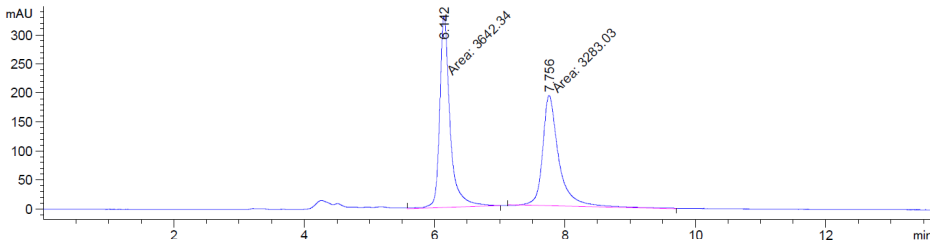
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.123	MM T	0.3829	9733.73535	423.66254	79.7066
2	11.698	MM T	0.5092	2231.48682	73.03339	18.2730
3	22.196	MM T	0.7831	246.73602	5.25150	2.0204

(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 5'-chloro-7-hexyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12e

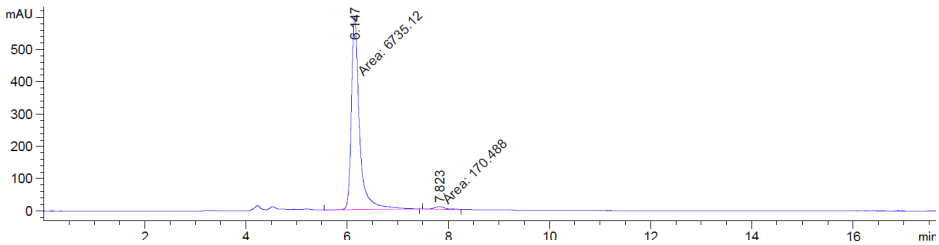


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.01 mmol, 0.2 equiv.), **4a** (28 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9b** (17.5 mg, 0.050 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12e** as a light yellow oil (27 mg, 0.037 mmol, 75%); $[\alpha]_D^{25}$ –68.2 (*c*=0.7, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2957, 2856, 1790, 1760, 1728, 1598, 1471, 1394, 1250, 1152, 1090, 1023, 815; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.66 (1H, s, H15), 7.91 (2H, d, *J* = 8.1 Hz, TsH), 7.83 (1H, d, *J* = 8.7 Hz, ArH), 7.38 (2H, d, *J* = 8.1 Hz, TsH), 7.27 (1H, dd, *J* = 8.3 and 2.6 Hz, ArH), 7.16 (1H, d, *J* = 2.2 Hz, ArH), 3.93-3.84 (3H, m, H2 and OCH_2CH_3), 3.69-3.61 (2H, m, H2 and H7), 3.25 (2H, dt, *J* = 8.8 and 7.3 Hz, H6 and H14), 2.98 (1H, d, *J* = 7.7 Hz, H4), 2.44 (3H, s, $TsCH_3$), 2.33 (1H, dd, *J* = 18.8 and 2.9 Hz, H14), 2.25-2.13 (2H, m, H3), 1.94-1.86 (1H, m, H8), 1.82-1.70 (1H, m, H8), 1.60 (9H, s, $C(CH_3)_3$), 1.36-1.23 (8H, m, H9 to H12), 0.96 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 0.89 (3H, t, *J* = 6.8 Hz, H13); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.7, 176.1, 171.0, 148.7, 144.3, 139.8, 137.5, 135.5, 132.5, 130.1, 129.7, 128.6, 127.9, 124.5, 123.5, 116.0, 84.5, 61.3, 51.8, 49.8, 47.3, 44.2, 37.1, 34.2, 32.8, 31.7, 30.5, 29.4, 28.0, 24.9, 22.6, 21.6, 14.1, 13.5; **HRMS** (ES^-) calc. for $C_{38}H_{46}O_8N_2SCl$ $[M–H]^-$ 725.2669; found 725.2682.

Chiralpak IB (20% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) $t_R$major – 6.1 min, minor – 7.8 min (95% *ee*).

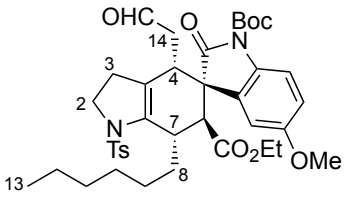


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.142	MM T	0.3091	3642.33618	329.55859	52.5941
2	7.756	MM T	0.2879	3283.02783	190.04253	47.4059



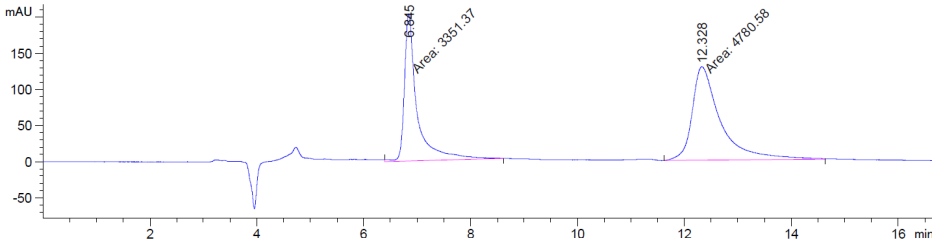
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.147	MM T	0.3285	6735.12305	597.91882	97.5312
2	7.823	MM T	0.3229	170.48836	8.79898	2.4688

(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-hexyl-5'-methoxy-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12f

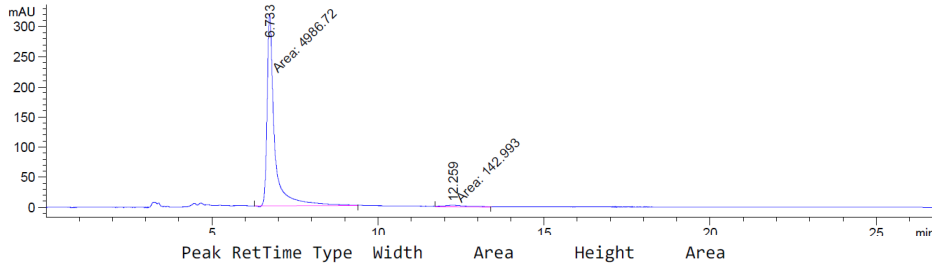


Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.01 mmol, 0.2 equiv.), **4a** (28 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9b** (17.3 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12f** as a red oil (24 mg, 0.033 mmol, 67%); $[\alpha]_D^{25}$ –64.6 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2928, 2856, 1787, 1754, 1724, 1598, 1486, 1471, 1249, 1152, 814; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.67 (1H, s, H15), 7.89 (2H, d, *J* = 8.2 Hz, TsH), 7.77 (1H, d, *J* = 8.9 Hz, ArH), 7.36 (2H, d, *J* = 8.1 Hz, TsH), 6.89 (1H, d, *J* = 2.6 Hz, ArH), 6.81 (1H, dd, *J* = 8.9 and 2.6 Hz, ArH), 3.96 (1H, ddd, *J* = 11.7, 9.0 and 2.9 Hz, H2), 3.91-3.83 (2H, m, H14), 3.80 (3H, s, OCH_3), 3.70 (1H, br s, H2), 3.54 (1H, app q, *J* = 10.7 Hz, H7), 3.30 (1H, dd, *J* = 18.6 and 8.8 Hz, H14), 3.22 (1H, d, *J* = 8.1 Hz, H6), 3.01 (1H, d, *J* = 7.6 Hz, H4), 2.45 (3H, s, $TsCH_3$), 2.40-2.30 (1H, m, H3), 2.32 (1H, dd, *J* = 18.6 and 3.0 Hz, H14), 2.15-2.09 (1H, m, H3), 1.81-1.76 (2H, m, H8), 1.60 (9H, s, $C(CH_3)_3$), 1.33-1.24 (8H, m, H9 to H12), 0.95 (3H, t, *J* = 7.1 Hz, H15), 0.88 (3H, t, *J* = 6.8 Hz, H13); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.9, 176.7, 171.1, 156.8, 149.0, 144.0, 139.4, 136.1, 132.1, 131.8, 129.9, 127.8, 125.8, 115.5, 113.3, 110.1, 83.8, 61.1, 56.0, 51.8, 49.9, 47.1, 44.3, 37.4, 34.2, 32.1, 31.7, 30.8, 29.5, 28.0, 24.6, 22.6, 21.6, 14.1, 13.5; **HRMS** (ES^+) calc. for $C_{39}H_{50}O_9N_2NaS$ $[M+H]^+$ 745.3129; found 745.3130.

Chiralpak IB (20% IPA in hexane, flow rate = 1.0 mL/min, 210 nm) $t_R$major – 6.7 min, minor – 12.2 min (94% *ee*).

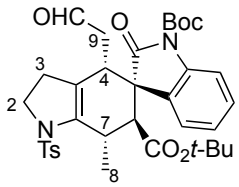


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.842	MM T	0.2959	1090.36829	61.40505	45.1111
2	12.330	MM T	0.5636	1326.70276	39.23417	54.8889



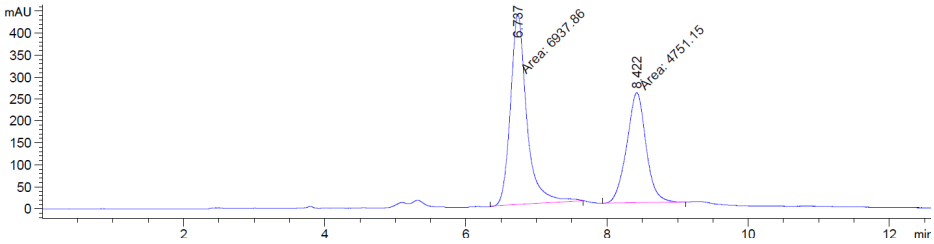
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.733	MM T	0.2609	4986.72119	318.54617	97.2125
2	12.259	MM T	0.9144	142.99287	2.60638	2.7875

(3'*S*,4*S*,6*S*,7*S*)-di-*tert*-Butyl 7-methyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12g

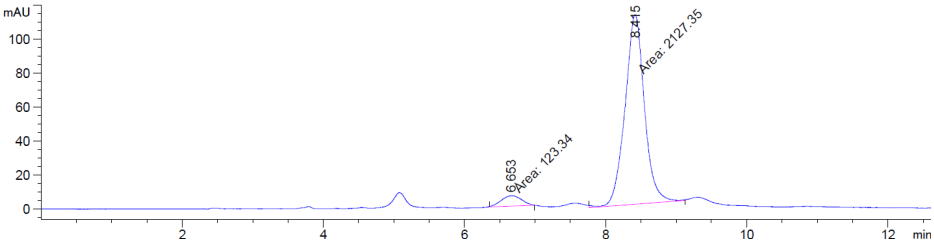


Prepared by General Procedure k using catalysts catalyst (*S*)-**10** (3 μL, 0.010 mmol, 0.2 equiv.), **4c** (22.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic oxindole **9d** (17.2 mg, 0.050 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12g** as a light yellow oil (25 mg, 0.038 mmol, 76%); $[\alpha]_D^{25}$ –98.0 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2923, 1790, 1759, 1723, 1394, 1296, 1152; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.67 (1H, s, H10), 7.94 (2H, d, *J* = 8.0 Hz, TsH), 7.82 (1H, d, *J* = 7.9 Hz, ArH), 7.40 (2H, d, *J* = 8.0 Hz, TsH), 7.21 (1H, td, *J* = 8.2 and 1.3 Hz, ArH), 6.63 (1H, td, *J* = 7.6 and 0.9 Hz, ArH), 6.48 (1H , dd, *J* = 7.6 and 0.8 Hz, ArH), 4.03 (1H, dt, *J* = 11.7 and 7.3 Hz, H2), 3.89-3.79 (1H, m, H2), 3.63-3.55 (1H, m, H7), 3.34 (1H, dd, *J* = 18.6 and 9.0 Hz, H9), 3.00 (1H, d, *J* = 7.6 Hz, H6), 2.83 (1H, dd, *J* = 8.7 and 1.8 Hz, H4), 2.51 (3H, s, $TsCH_3$), 2.28 (1H, dd, *J* = 18.7 and 2.9 Hz, H9), 2.24-2.18 (2H, m, H3), 1.59 (9H, s, $C(CH_3)_3$), 1.46 (3H, d, *J* = 6.6 Hz, H8), 1.06 (9H, s, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 199.0, 176.5, 169.5, 148.9, 144.1, 140.7, 138.9, 136.2, 130.8, 130.1, 128.3, 128.1, 123.8, 123.1, 122.3, 114.7, 84.1, 81.9, 51.5, 51.3, 50.1, 44.2, 37.9, 30.2, 29.1, 28.0, 27.2, 21.9, 21.7; **HRMS** (ES^+) calc. for $C_{35}H_{42}O_8N_2NaS$ $[M+Na]^+$ 673.2559; found 673.2553.

Chiralpak IA (15% IPA in hexane, flow rate = 1.3 mL/min, 254 nm) $t_R$major: 8.4 min, minor: 6.6 min (89% *ee*).

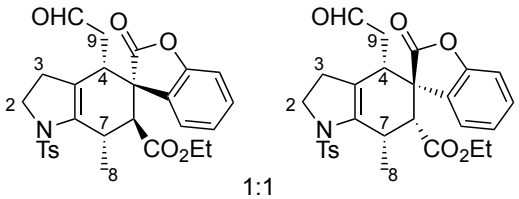


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.737	MM T	0.2672	6937.85889	432.72406	59.3537
2	8.422	MM T	0.3163	4751.14746	250.37030	40.6463



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.653	MM T	0.3350	123.33982	6.13571	5.4801
2	8.415	MM T	0.3179	2127.34912	111.53680	94.5199

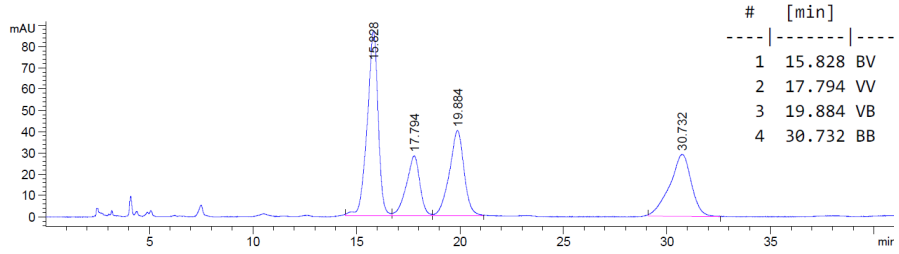
(3*S*,4'*S*,6'*S*,7'*S*)- and (3*R*,4'*S*,6'*R*,7'*S*)-Ethyl 7'-methyl-2-oxo-4'-(2-oxoethyl)-1'-tosyl-1',2',3',4',6',7'-hexahydro-2H-spiro[benzofuran-3,5'-indole]-6'-carboxylate, 18a and 18b



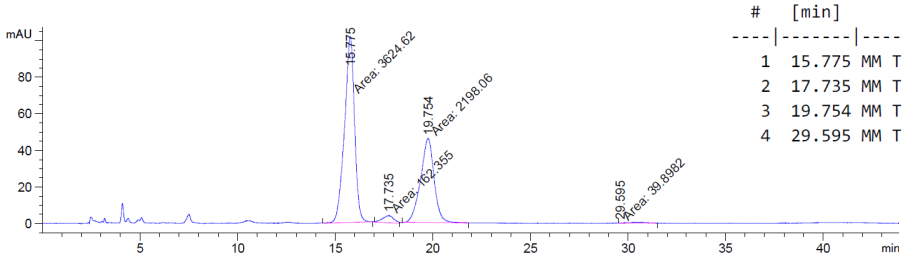
1:1

Prepared by General Procedure **K** using catalyst (*S*)-**10** (3.2 μL, 0.010 mmol, 0.2 equiv.), **4c** (22.8 mg, 0.075 mmol, 1.5 equiv.) and olefinic lactone **17** (10.9 mg, 0.05 mmol, 1.0 equiv.). Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadducts **18a** and **18b** (dr: 1:1) as a colourless oil (20 mg, 0.038 mmol, 77% yield); $[\alpha]_D^{25}$ –6.02 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2924, 1796, 1723, 1461, 1348, 1161; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.71 (1H, s, H10), 9.42 (1H, s, H10), 7.91 (2H, d, *J* = 8.2 Hz, TsH), 7.70 (1H, d, *J* = 8.2 Hz, TsH), 7.42-7.34 (5H, m, TsH and ArH), 7.27-7.18 (4H, m, TsH and ArH), 7.13-7.06 (2H, m, ArH), 6.75 (1H, t, *J* = 7.9 Hz, ArH), 6.66 (1H, d, *J* = 7.6 Hz, ArH), 4.16-4.06 (4H, m, $OC\underline{H}_2CH_3$), 3.97-3.90 (4H, m, H2), 3.82-3.73 (2H, m, H7), 3.49-3.35 (3H, m, H9 and H4), 3.11-2.95 (3H, m, H4 and H6), 2.51 (3H, s), 2.50 (3H, s), 2.42 (2H, dd, *J* = 18.8 and 3.5 Hz, H9), 2.35-2.20 (2H, m, H3), 1.96-1.72 (2H, m, H3), 1.50 (3H, d, *J* = 6.5 Hz, H8), 1.33 (3H, d, *J* = 7.1 Hz, H8), 1.27-1.21 (3H, m, $OCH_2C\underline{H}_3$), 1.01 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 198.8, 198.3, 179.2, 177.6, 170.5, 170.4, 154.4, 152.7, 144.5, 144.3, 140.6, 140.5, 136.3, 134.2, 130.1, 130.1, 129.8, 129.7, 129.2, 128.0, 127.2, 126.1, 125.8, 124.6, 124.0, 123.8, 123.6, 123.2, 111.2, 110.8, 61.6, 60.4, 52.9, 51.4, 51.0, 50.3, 50.2, 50.2, 44.2, 43.5, 38.1, 37.2, 30.7, 30.5, 30.4, 29.9, 21.7, 21.3, 14.6, 14.2, 14.0, 13.6; **HRMS** (ES^+) calc. for $C_{28}H_{29}O_7NNaS$ $[M+Na]^+$ 546.1562; found 546.1562.

Chiralpak IA (10% IPA in hexane, flow rate = 1.3 mL/min, 230 nm) $t_R$major: 15.8 min, minor: 17.7 min, and $t_R$major: 19.7 min, minor: 29.6 min (93% *ee* & 89% *ee*).



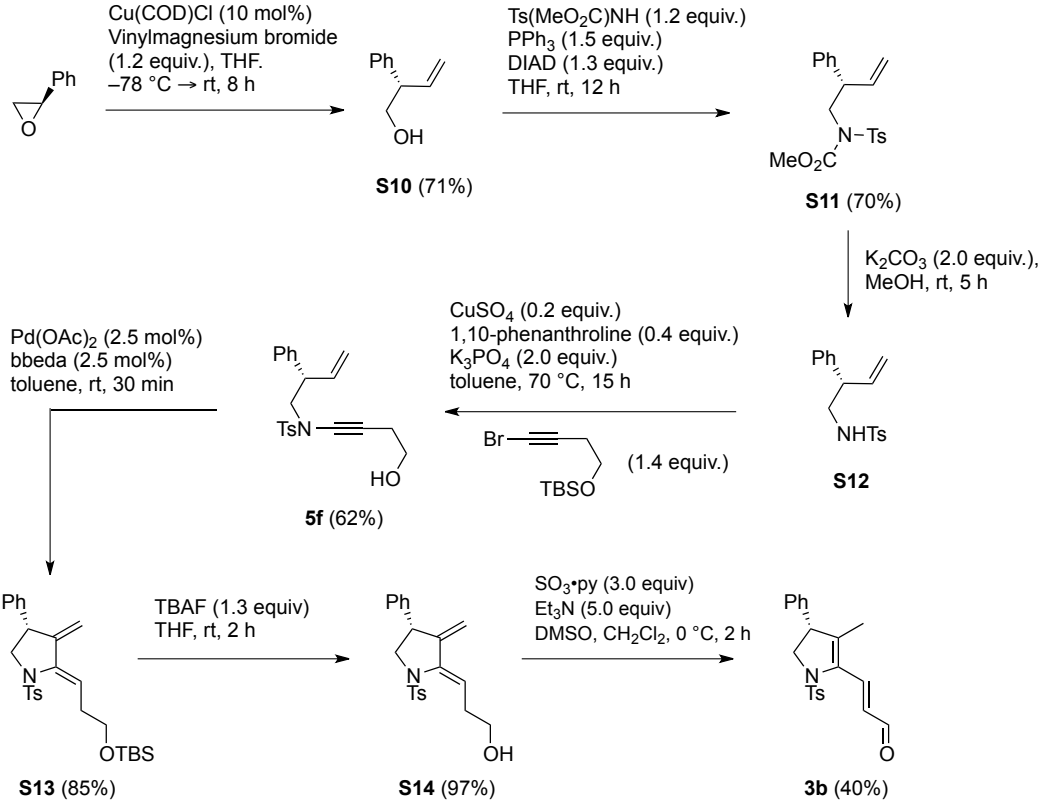
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.828	BV	0.5392	3180.07544	86.84036	37.3797
2	17.794	VV	0.6418	1265.46460	28.18340	14.8747
3	19.884	VB	0.7132	1961.32581	39.92118	23.0541
4	30.732	BB	0.8838	2100.62769	29.11183	24.6915



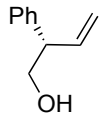
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.775	MM T	0.8497	3624.62402	101.65768	60.1603
2	17.735	MM T	0.6837	162.35490	3.95761	2.6947
3	19.754	MM T	0.7984	2198.06470	45.88548	36.4828
4	29.595	MM T	1.6314	39.89817	2.88817e-1	0.6622

*1.3.5 Synthesis of dienals **3b** and **4e***

3b was synthesized according to the following scheme:

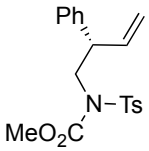


(*S*)-2-phenylbut-3-en-1-ol, S10



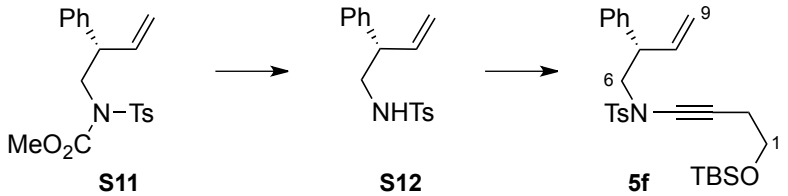
S10 was prepared according to the procedure of Tan *et al.*[6] To a solution of (*R*)-phenyloxirane (1.00 g, 8.32 mmol, 1.0 equiv.) and Cu(COD)Cl (172 mg, 0.83 mmol, 0.1 equiv.) in THF (12 mL) at –78 °C was added vinylmagnesium bromide (10.0 mL, 10.0 mmol, 1.0 M solution in THF,). The reaction was allowed to warm to rt over 8 h, then it was quenched by the addition of NH_4Cl (30 mL, sat., aq.) and extracted with EtOAc (3 x 40 mL). The combined organics were dried ($MgSO_4$), and concentrated. The crude residue was purified by flash chromatography (petroleum ether / EtOAc (90:10)) to afford **S10** as a colourless oil (870 mg, 5.87 mmol, 71%); $[\alpha]_D^{25}$ +67.3 (*c* = 1.0, $CHCl_3$); ***lit*:** +67.5 (*c* = 0.545, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3448, 3028, 1493, 1452, 1055, 1026, 992, 916, 756; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.25 (2H, t, *J* = 7.3 Hz, PhH), 7.18-7.14 (3H, m, PhH), 5.99-5.85 (1H, m, H3), 5.16-5.04 (2H, m, H4), 3.72 (2H, d, *J* = 7.1 Hz H1), 3.43 (1H, app q, *J* = 7.3 Hz, H2), 1.64 (1H, br s, OH); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 140.8, 138.3, 128.8, 128.0, 127.0, 117.1, 66.1, 52.6. Data identical to literature values.[6]

(*S*)-methyl (2-phenylbut-3-en-1-yl)(tosyl)carbamate, S11



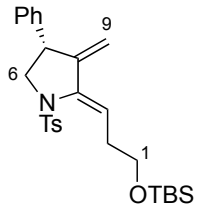
Prepared by General Procedure **A** using alcohol **S10** (1.00 g, 6.75 mmol, 1.0 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether / Et_2O (9:1)) to give **S11** as a colourless oil (1.70 g, 4.73 mmol, 70%); $[\alpha]_D^{25}$ +9.56 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2957, 2923, 1728, 1597, 1551, 1350, 1290, 1163, 1088, 764; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.63 (2H, d, *J* = 8.4 Hz, TsH), 7.26 (3H, t, *J* = 6.2 Hz, TsH and PhH), 7.21-7.17 (4H, m, PhH), 6.00 (1H, ddd, *J* = 16.9, 10.4 and 8.6 Hz, H3), 5.12-5.01 (2H, m, H4), 4.06 (2H, dd, *J* = 14.6 and 7.8 Hz, H1), 3.77 (1H, d, *J* = 8.4 Hz, H2), 3.52 (3H, s, $CO_2C\underline{H}_3$), 2.34 (3H, s, $TsCH_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 153.1, 144.7, 140.9, 138.1, 136.7, 129.4, 128.8, 128.6, 128.2, 127.1, 117.5, 53.7, 51.8, 50.4, 21.8; **HRMS** (ES^+) calc. for $C_{19}H_{21}NNaO_4S$ $[M+Na]^+$ 382.1080; found 382.1079.

(*S*)-4-methyl-*N*-(2-phenylbut-3-en-1-yl)benzenesulfonamide, S12, and (*S*)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-4-methyl-*N*-(2-phenylbut-3-en-1-yl)benzenesulfonamide, 5f



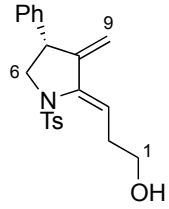
S12 was prepared by General Procedure **B** using (*S*)-methyl (2-phenylbut-3-en-1-yl)(tosyl)carbamate, **S11** (1.12 g, 3.12 mmol); the sulfonamide was obtained in quantitative yield. **S12** (750 mg, 2.49 mmol, 1.0 equiv.) was then converted to **5f** using General Procedure **C** and ((4-bromobut-3-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (979 mg, 3.74 mmol, 1.5 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (90:10)) to give **5f** as a colourless oil (740 mg, 1.53 mmol, 62%); **IR** (thin film, ν_{max}/ cm^{-1}); $[\alpha]_D^{25}$ +5.94 (*c* = 0.9, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2955, 2855, 1677, 1471, 1364, 1254, 1169, 1106, 1058, 916, 835; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.60 (2H, d, *J* = 8.2 Hz, TsH), 7.26-7.15 (5H, m, TsH and PhH), 7.12 (2H, d, *J* = 7.0 Hz, PhH), 5.92 (1H, ddd, *J* = 17.5, 10.4 and 7.5 Hz, H8), 5.06 (2H, dd, *J* = 13.7 and 8.2 Hz, H9), 3.69 (1H, app q, *J* = 7.6 Hz, H7), 3.61-3.53 (3H, m, H1 and H6), 3.40 (1H, dd, *J* = 12.5 and 7.2 Hz, H6), 2.41 (2H, t, *J* = 7.2 Hz, H2), 2.36 (3H, s, $TsCH_3$), 0.83 (10H, s, $SiC(CH_3)_3$), 0.00 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.4, 140.4, 137.8, 134.7, 129.7, 128.7, 128.2, 127.8, 127.1, 117.2, 74.0, 68.0, 62.3, 55.5, 48.1, 26.0, 23.1, 21.7, 18.4, –5.1; **HRMS** (ES^+) calc. for $C_{27}H_{37}O_3NNaSSi$ $[M+Na]^+$ 506.2155; found 506.2149.

(*R*,*Z*)-2-(3-((*tert*-butyldimethylsilyl)oxy)propylidene)-3-methylene-4-phenyl-1-tosylpyrrolidine, S13



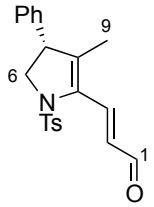
Prepared by General Procedure **F** using ynamide **5f** (300 mg, 0.62 mmol, 1.0 equiv.). The crude material was purified by flash chromatography (petroleum ether / EtOAc (90:10)) to give **S13** as a colourless oil (256 mg, 0.53 mmol, 85%); $[\alpha]_D^{25}$ +102.9 (*c* = 0.8, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2955, 1471, 1358, 1254, 1165, 1090, 834; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.75 (2H, d, *J* = 8.3 Hz, TsH), 7.31 (2H, d, *J* = 8.1 Hz, TsH), 7.28-7.17 (3H, m, PhH), 6.90 (2H, d, *J* = 6.4 Hz, PhH), 6.13-6.05 (1H, m, H3), 5.34 (1H, d, *J* = 3.2 Hz, H9), 4.35 (1H, d, *J* = 2.7 Hz, H9), 4.14-3.99 (1H, m, H7), 3.81 (2H, td, *J* = 6.0 and 2.0 Hz, H1), 3.26 (1H, dd, *J* = 12.8 and 10.9 Hz, H6), 2.93-2.73 (3H, m, H6 and H2), 2.47 (3H, s, $TsCH_3$), 0.93 (9H, s, $SiC(CH_3)_3$), 0.10 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 148.3, 144.2, 140.6, 138.1, 136.0, 129.8, 128.7, 128.5, 128.0, 127.7, 127.2, 118.6, 106.0, 62.7, 56.9, 47.2, 33.5, 26.1, 21.8, –5.0; **HRMS** (ES^+) calc. for $C_{27}H_{37}O_3NNaSSi$ $[M+Na]^+$ 506.2155; found 506.2150.

(*R*,*Z*)-3-(3-methylene-4-phenyl-1-tosylpyrrolidin-2-ylidene)propan-1-ol, S14



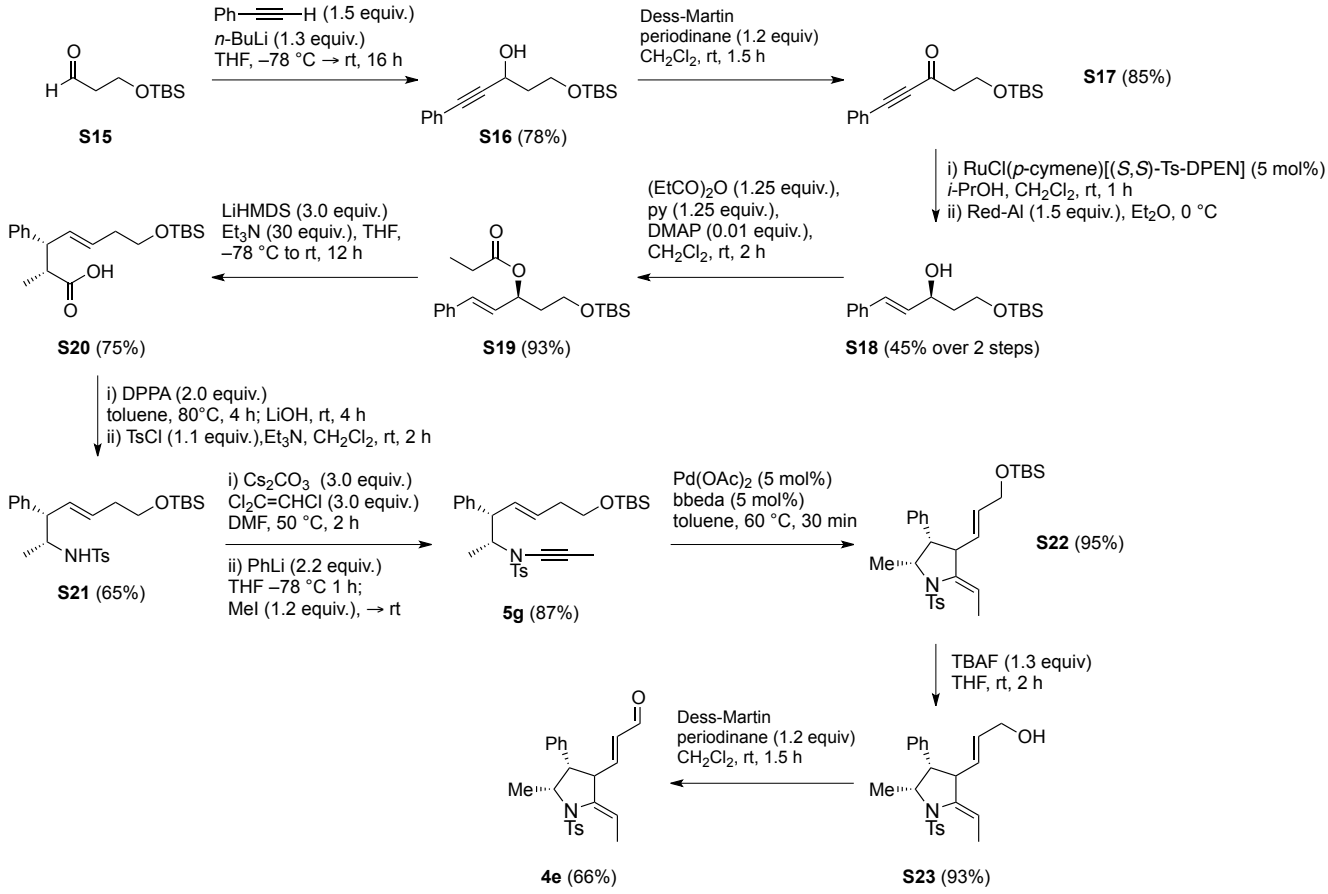
Prepared by General Procedure **G** using **S13** (240 mg, 0.496 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give **S14** as a colourless oil (178 mg, 0.482 mmol, 97%); $[\alpha]_D^{25}$ +164.1 (*c* = 0.7, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3410, 2950, 1598, 1351, 1254, 1163, 1067, 1090, 814, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.77 (2H, d, *J* = 8.2 Hz, TsH), 7.31 (2H, d, *J* = 8.2 Hz, TsH), 7.23-7.21 (3H, m, PhH), 6.90 (2H, d, *J* = 6.6 Hz, PhH), 6.04 (1H, t, *J* = 7.7 Hz, H3), 5.38 (1H, d, *J* = 2.7 Hz, H9), 4.38 (1H, d, *J* = 2.5 Hz, H9), 4.09 (1H, dd, *J* = 12.9 and 8.5 Hz, H7), 3.96-3.90 (1H, m, H1), 3.88-3.82 (1H, m, H1), 3.29 (1H, dd, *J* = 12.7 and 11.0 Hz, H6), 3.09-3.00 (1H, m, H2), 2.90-2.84 (1H, m, H6), 2.80-2.71 (1H, m, H2), 2.47 (3H, s, $TsCH_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 148.06, 144.47, 140.36, 139.13, 135.72, 129.89, 129.70, 128.86, 128.76, 128.48, 128.35, 128.03, 127.69, 127.45, 127.32,118.34, 106.66, 62.51, 57.01, 47.07, 33.08, 21.82, 21.75; **HRMS** (ES^+) calc. for $C_{21}H_{23}O_3NNaS$ $[M+Na]^+$ 392.1290; found 392.1288.

(*R*,*E*)-3-(3-methyl-4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)acrylaldehyde, 3b

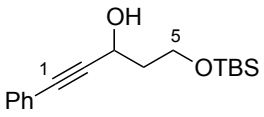


Prepared by General Procedure **H** using **S14** (36 mg, 0.97 mmol). The resulting crude material was purified by flash chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **3b** as a light yellow oil (14.2 mg, 0.39 mmol, 40%); $\mathbf{R_f}$ 0.18 (petroleum ether /EtOAc (2:1)); $\mathbf{[\alpha]_D^{25}}$ +32.6 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2962, 2923, 1682, 1598, 1350, 1132, 1089, 1029, 732; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.74 (1H, d, *J* = 7.8 Hz, H1), 7.58 (2H, d, *J* = 8.3 Hz, TsH), 7.51 (1H, d, *J* = 16.1 Hz, H3), 7.32 (2H, d, *J* = 8.0 Hz, PhH), 7.21-7.12 (3H, m, PhH), 6.65 (2H, d, *J* = 8.1Hz, PhH), 6.42 (1H, dd, *J* = 16.1 and 7.8 Hz, H2), 4.46-3.95 (1H, m, H7), 3.68-3.40 (1H, m, H6), 2.49 (3H, s, $TsCH_3$), 1.58 (3H, s, H9); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 194.0, 144.5, 143.1, 140.7, 135.7, 134.3, 132.8, 132.7, 130.0, 129.0, 128.3, 127.8, 127.5, 56.8, 52.7, 21.8, 14.0; **HRMS** (ES^+) calc. for $C_{21}H_{21}O_3NNaS$ $[M+Na]^+$ 390.1134; found 390.1135.

4e was synthesized according to the following scheme:

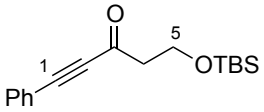


5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-1-yn-3-ol, S16



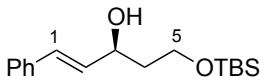
To a solution of phenylacetylene (2.46 mL 22.5 mmol, 1.5 equiv.) in THF (150 mL) at –78 °C was added *n*-BuLi (2.4 M in hexanes, 8.1 mL, 19.5 mmol, 1.3 equiv.). The reaction mixture was stirred for 15 min. A solution of aldehyde **S15**[7] (2.80 g, 15.0 mmol, 1.0 equiv.) in THF (21 mL) and added by cannula. The reaction was allowed to warm to rt, and was stirred for 16 h. The reaction was queched via addition of NH_4Cl (50 mL, sat., aq.), and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and concentrated. Purification by flash chromatography (petroleum ether / EtOAc (9:1)) gave alcohol **S16** as a yellow oil (3.39 g, 11.7 mmol, 78%); **IR** (thin film, ν_{max} / cm^{-1}) 3398, 2954, 2857, 1490, 1254, 1082, 833, 776; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.45-7.41 (2H, m, PhH), 7.32-7.29 (3H, m, PhH), 4.85 (1H, dd, *J* = 10.1 and 5.6 Hz, H3), 4.12 (1H, ddd, *J* = 10.3, 8.0 and 3.8 Hz, H5), 3.89 (1H, ddd, *J* = 10.2, 6.0 and 4.3 Hz, H5), 3.58 (1H, d, *J* = 5.4 Hz, OH), 2.14-2.06 (1H, m, H4), 1.97 (1H, dtd, *J* = 14.2, 6.2 and 3.8 Hz, H4), 0.92 (9H, s, $SiC(CH_3)_3$), 0.11 (3H, s, $Si(CH_3)_2$), 0.10 (3H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 131.6, 131.6, 128.1, 122.8, 89.6, 84.7, 61.9, 61.0, 38.8, 25.7, 18.1, –5.6; **HRMS** (ES^+) calc. for $C_{17}H_{26}O_2NaSi$ $[M+Na]^+$ 313.1605; found 313.1598.

5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-1-yn-3-one, S17



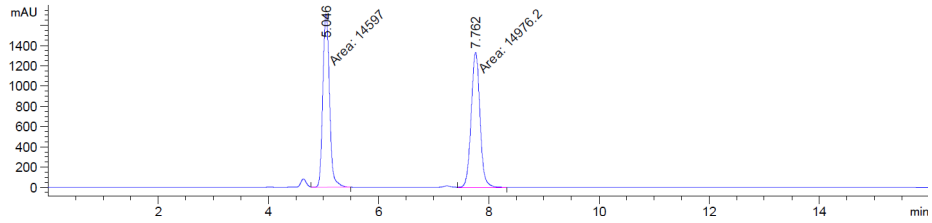
Prepared by General Procedure **I** using **S16** (870 mg, 3.00 mmol, 1.0 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether → petroleum ether / EtOAc (9:1)) to give **S17** as a yellow oil (734 mg, 2.54 mmol, 85%); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2857, 2200, 1668, 1490, 1280, 1089, 1032, 926, 833; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.58-7.56 (2H, m, PhH), 7.48-7.43 (1H, m, PhH), 7.40-7.36 (2H, m, PhH), 4.05 (2H, t, *J* = 6.2 Hz, H5), 2.87 (2H, t, *J* = 6.2 Hz, H4), 0.88 (9H, s, $SiC(CH_3)_3$), 0.07 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 186.3, 133.0, 130.7, 128.6, 120.0, 90.9, 87.9, 58.5, 48.5, 25.8, 18.2, –5.4; **HRMS** (ES^+) calc. for $C_{17}H_{25}O_2Si$ $[M+H]^+$ 289.1629, found 289.1621.

(*S*,*E*)-5-((*tert*-butyldimethylsilyl)oxy)-1-phenylpent-1-en-3-ol, S18

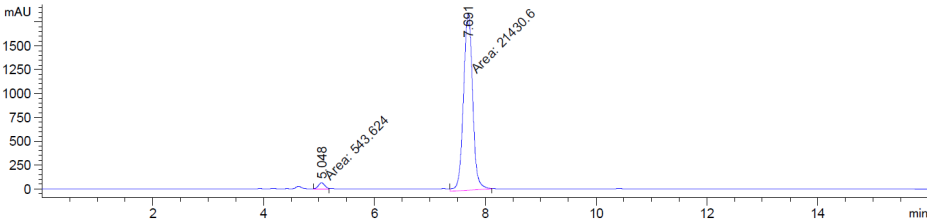


To a solution of **S17** (576 mg, 2.00 mmol, 1.0 equiv.) in *i*-PrOH (20 mL) under Ar at rt was added dropwise a solution of RuCl(*p*-cymene)[(*S*,*S*)-Ts-DPEN] (63.6 mg, 0.10 mmol, 0.05 equiv.) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1 h, and then concentrated. Purification by flash chromatography (petroleum ether / EtOAc (9:1)) gave (*S*)-propargyl alcohol **S16** (452 mg, 1.56 mmol, 78%); $[\alpha]_D^{25}$ –22.2 (c = 0.9, $CHCl_3$); other data for this compound were identical to **S16** above.

Chiralpak IB (15% IPA in hexane, flow rate = 1.0 mL/min, 230 nm) $t_R$major – 7.7 min, minor – 5.0 min.



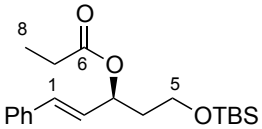
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.046	MM T	0.1960	1.45970e4	1714.13611	49.3589
2	7.762	MM T	0.1869	1.49762e4	1335.23193	50.6411



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.048	MM T	0.1372	543.62360	66.04488	2.4739
2	7.691	MM T	0.2534	2.14306e4	1855.92432	97.5261

To a solution of (*S*)-**S16** (840 mg, 2.90 mmol, 1.0 equiv.) in Et_2O at 0 °C was added Red Al (65% wt solution in toluene, 1.3 mL, 4.35 mmol, 1.5 equiv.) dropwise, and the reaction was stirred for 2 h at rt. The reaction was quenched by addition of 1N HCl, and extracted with Et_2O. The combined organic phases were washed with $NaHCO_3$ (sat., aq.), dried ($MgSO_4$) and concentrated. The crude residue was purified by flash chromatography (petroleum ether / EtOAc (9:1)) to give **S18** as a light yellow oil (490 mg, 1.68 mmol, 58%); $[\alpha]_D^{25}$ –1.83 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3417, 2953, 2929, 1494, 1292, 1093, 965, 834 and 775; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.30-7.27 (2H, m, PhH), 7.23-7.18 (2H, m, PhH), 7.16-7.11 (1H, m, PhH), 6.54 (1H, dd, *J* = 15.9 and 3.4 Hz, H2), 6.14 (1H, d, *J* = 15.9 Hz, H1), 4.45 (1H, br s, H3), 3.83 (1H, td, *J* = 10.1 and 5.1 Hz, H5), 3.79-3.72 (1H, m, H5), 3.45 (1H, br s, OH), 1.78-1.71 (2H, m, H2), 0.82 (9H, m, $SiC(CH_3)_3$), 0.00 (3H, s, $Si(CH_3)_2$), –0.01 (3H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 137.0, 132.1, 129.5, 128.5, 127.4, 126.4, 72.3, 62.0, 38.6, 25.9, 18.2, –5.5; **HRMS** (ES^+) calc. for $C_{17}H_{28}O_2NaSi$ $[M+Na]^+$ 315.1761, found 315.1749.

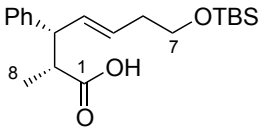
(*S*,*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-1-en-3-yl propionate, S19



Pyridine (49 mg, 0.625 mmol, 1.25 equiv.), propanoic anhydride (81mg, 0.625 mmol, 1.25 equiv.) and DMAP (0.6 mg, 0.005 mmol, 0.01 equiv.) were added to a solution of **S18** (145 mg, 0.50 mmol, 1.0 equiv.) in Et_2O (20 mL) at rt. The reaction mixture was stirred for 2 h, then it was diluted with toluene (10 mL) and concentrated. Purification by flash chromatography (petroleum ether / EtOAc (19:1)) gave **S19** as a colourless oil (160 mg, 0.46 mmol, 93%); $[\alpha]_D^{25}$ –1.2 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2859,

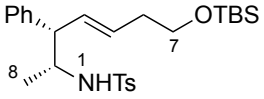
1737, 1604, 1471, 1254, 1180, 1095, 963, 834; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.33 (2H, d, *J* = 7.1 Hz, PhH), 7.26 (2H, t, *J* = 7.4 Hz, PhH), 7.20 (1H, m, PhH), 6.57 (1H, d, *J* = 15.9 Hz, H1), 6.11 (1H, dd, *J* = 15.9 and 7.3 Hz, H2), 5.53 (1H, dd, *J* = 13.6 and 6.8 Hz, H3), 3.65 (2H, t, *J* = 6.1 Hz, H5), 2.30 (2H, q, *J* = 7.6 Hz, H7), 1.98-1.71 (2H, m, H4), 1.11 (3H, t, *J* = 7.6 Hz, H8), 0.85 (9H, s, $SiC(CH_3)_3$), 0.00 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 173.6, 136.4, 132.4, 128.6, 127.9, 127.7, 126.6, 71.7, 59.1, 37.6, 27.9, 25.9, 18.3, 9.2, –5.4; **HRMS** (ES^+) calc. for $C_{20}H_{33}O_3Si$ $[M+H]^+$ 349.2193; found 349.2190.

(2*R*,3*R*,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-3-phenylhept-4-enoic acid, S20



A solution of **S19** (576 mg, 1.65 mmol, 1.0 equiv.) in toluene (16 mL) was added dropwise to a solution of LiHMDS (4.9 mL, 4.96 mmol, 3.0 equiv.) and Et_3N (6.9 mL, 4.96 mmol, 30 equiv.) in toluene (16 mL) at –78 °C. The reaction was stirred for 1 h at –78 °C, then it was allowed to warm to rt and stirred for 12 h. 1N NaOH was added to the reaction mixure, which was stirred for a further 1h and then extracted with ether. The aqueous layer was neutralized with 1N citric acid, then extracted with ether and concentrated to give acid **S20** as a colourless oil (430 mg, 1.23 mmol, 75%); $[\alpha]_D^{25}$ +30.8 (*c* = 1.4, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 1820, 1713, 1462, 1288, 1150, 1092, 834, 755; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 10.69 (1H, s, CO_2H), 7.26-7.20 (2H, m, PhH), 7.16 (3H, d, *J* = 7.3 Hz, PhH), 5.59-5.48 (2H, m, H4 and H5), 3.59 (2H, t, *J* = 6.6 Hz, H7), 3.44 (1H, t, *J* = 8.7 Hz, H3), 2.79-2.70 (1H, m, H2), 2.20 (2H, q, *J* = 6.2 Hz, H6), 1.19 (3H, d, *J* = 6.9 Hz, H8), 0.86 (9H, s, $SiC(CH_3)_3$), 0.01 (6H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 181.4, 142.5, 131.8, 129.5, 128.4, 127.6, 126.4, 62.8, 52.1, 45.0, 36.1, 25.9, 18.3, 15.5, -5.4; **HRMS** (ES^+) calc. for $C_{20}H_{33}O_3Si$ $[M+H]^+$ 349.2199; found 349.2194.

***N*-((2*R*,3S,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-3-phenylhept-4-en-2-yl)-4-methylbenzenesulfonamide, S21**

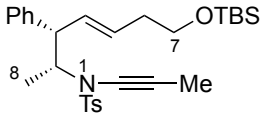


To a solution of carboxylic acid **S20** (170 mg, 0.48 mmol, 1.0 equiv.) in toluene (5 mL) were added Et_3N (0.25 mL, 1.79 mmol, 3.0 equiv.) and diphenylphosphoryl azide (DPPA) (0.25 mL, 1.16 mmol, 2.0 equiv.). The mixture was stirred at rt for 30 min, then stirred at 80 °C for 4 h. The reaction mixture was concentrated and re-dissolved in THF (5 mL). 4N LiOH (2.8 mL) was added, and the mixture was stirred for 4 h at rt, then it was diluted with water and extracted with EtOAc. The organic layer was dried (Na_2SO_4) and concentrated to give the crude amine as an oil, which was used without further purification.

To a stirred solution of the crude amine (assumed 0.48 mmol, 1.0 equiv.) and TsCl (91 mg, 0.48 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was added Et_3N (0.75 mL, 5.36 mmol) dropwise. The mixture was stirred for 2 h, then it was concentrated and purified by flash chromatography (petroleum ether / EtOAc (9:1)) to give **S21** (150 mg, 0.317 mmol, 65%) as a colorless oil; $[\alpha]_D^{25}$ +13.0 (*c* = 0.8, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3280, 2954, 2928, 1599, 1304, 1253, 1158, 1093, 835; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.68 (2H, d, *J* = 8.2 Hz, TsH),

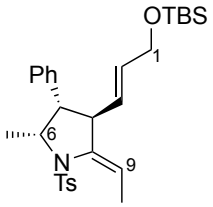
7.32-7.28 (3H, m, 2 x TsH and PhH), 7.23 (2H, d, *J* = 7.9 Hz, PhH), 7.05 (2H, d, *J* = 6.4 Hz, PhH), 5.67 (1H, dd, *J* = 15.2 and 9.4 Hz, H4), 5.55-5.46 (1H, m, H5), 4.42 (1H, d, *J* = 7.8 Hz, NHTs), 3.65 (2H, t, *J* = 6.5 Hz, H7), 3.58 (1H, dt, *J* = 13.2 and 6.6 Hz, H2), 3.22 (1H, dd, *J* = 9.3 and 6.3 Hz, H3), 2.47 (3H, s, $TsCH_3$), 2.26 (2H, q, *J* = 6.5 Hz, H6), 1.11 (3H, d, *J* = 6.6 Hz, H8), 0.91 (9H, s, $SiC(CH_3)_3$), 0.07 (3H, s, $Si(CH_3)_2$), 0.07 (3H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_H 143.1, 140.6, 137.8, 131.6, 129.6, 129.2, 128.6, 127.8, 127.1, 126.8, 62.6, 54.4, 53.5, 36.3, 25.9, 21.5, 18.6, 18.3, –5.3; **HRMS** (ES^+) calc. for $C_{26}H_{39}O_3NNaSSi$ $[M+Na]^+$ 496.2317; found 496.2308.

_N_-((2_R_,3_S_,_E_)-7-((_tert_-Butyldimethylsilyl)oxy)-3-phenylhept-4-en-2-yl)-4-methyl-_N_-(prop-1-yn-1-yl)benzenesulfonamide, 5g



Prepared by General Procedures **D** and **E** using sulfonamide **S21** (230 mg, 0.49 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (95:5)) to give **5g** as a colourless oil (217 mg, 0.42 mmol, 87%); $[\alpha]_D^{25}$ +28.3 (*c* = 0.7, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2955, 2855, 1714, 1551, 1479, 1349, 1162, 1089, 815, 756; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.31 (2H, d, *J* = 8.2 Hz, TsH), 7.22-7.17 (5H, m, TsH and PhH), 7.11 (2H, d, *J* = 8.1 Hz, PhH), 5.63 (1H, dd, *J* = 15.2 and 9.1 Hz, H4), 5.55-5.48 (1H, m, H5), 4.31 (1H, dq, *J* = 10.4 and 6.5 Hz, H2), 3.59 (2H, t, *J* = 6.7 Hz, H7), 3.38 (1H, t, *J* = 9.7 Hz, H3), 2.38 (3H, s, Me), 2.21 (2H, q, *J* = 6.6 Hz, H6), 1.93 (3H, s, $TsCH_3$), 1.22 (3H, d, *J* = 6.5 Hz, H8), 0.86 (9H, s, $SiC(CH_3)_3$), 0.00 (3H, s, $Si(CH_3)_2$), 0.00 (3H, s, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.6, 142.0, 135.6, 131.6, 129.9, 129.2, 128.4, 127.8, 127.4, 126.4, 68.8, 68.2, 62.7, 59.2, 54.3, 36.2, 25.8, 21.5, 18.3, 17.6, 3.5, –5.4; **HRMS** (ES^+) calc. for $C_{29}H_{41}O_3NNaSSi$ $[M+Na]^+$ 534.2474; found 534.2464.

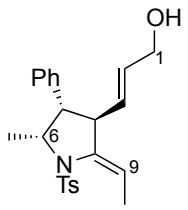
(3_R_,4_S_,5_R_,_Z_)-3-((_E_)-3-((_tert_-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-ethylidene-5-methyl-4-phenyl-1-tosylpyrrolidine, S22



Prepared by General Procedure **F** using ynamide **5g** (100 mg, 0.195 mmol). The crude material was purified by column chromatography (petroleum ether / EtOAc (95:5)) to give **S22** as colorless oil (95 mg, 0.185 mmol, 95%); $[\alpha]_D^{25}$ +68.2 (*c* = 0.7, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2954, 2856, 1471, 1354, 1353, 1197, 1072, 835, 776; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.81 (2H, d, *J* = 8.3 Hz, TsH), 7.35 (2H, d, *J* = 8.0 Hz, TsH), 7.24-7.20 (2H, m, PhH), 7.16 (1H, t, *J* = 6.7 Hz, PhH), 6.94 (2H, d, *J* = 7.3 Hz, PhH), 5.49 (1H, dt, *J* = 15.1 and 5.3 Hz, H2), 5.39 (1H, qd, *J* = 7.1 and 1.6 Hz, H9), 4.98 (1H, dd, *J* = 15.1 and 8.8 Hz, H3), 4.28 (1H, d, *J* = 6.8 Hz, H6), 3.99 (2H, dd, *J* = 5.2 and 1.5 Hz, H1), 3.53 (1H, t, *J* = 10.0 Hz, H4), 2.44 (3H, s, $TsCH_3$), 2.31 (1H, dt, *J* = 13.1 and 9.8 Hz, H5), 1.98 (3H, dd, *J* = 7.2 and 1.9 Hz, H10), 0.86 (3H, d, *J* = 6.8 Hz, H11), 0.84 (9H, s, $SiC(CH_3)_3$) –0.02 (3H, s, $Si(CH_3)_2$), –0.04 (3H, s, $Si(CH_3)_2$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 143.9, 138.5,

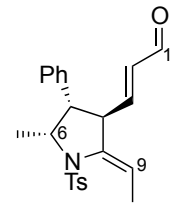
137.1, 136.4, 131.7, 130.6, 129.6, 128.4, 128.2, 127.8, 126.8, 118.4, 63.4, 61.9, 50.6, 48.3, 25.9, 21.6, 18.3, 15.9, 15.9, –5.2; **HRMS** (ES^+) calc. for $C_{29}H_{41}O_3NNaSSi$ $[M+Na]^+$ 534.2474; found 534.2468.

(*E*)-3-((3*R*,4*S*,5*R*,*Z*)-2-ethylidene-5-methyl-4-phenyl-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S23



Prepared by General Procedure **G** using **S22** (80 mg, 0.156 mmol). The resulting crude material was purified by flash chromatography (petroleum ether / EtOAc (1:1)) to give **S23** as a colourless oil (58 mg, 0.146 mmol, 93%); $[\alpha]_D^{25}$ +145.7 (*c* = 0.7, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3378, 3028, 2919, 1677, 1452, 1304, 1164, 1053, 977, 814; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.82 (2H, d, *J* = 8.3 Hz, TsH), 7.36 (2H, d, *J* = 8.0 Hz, TsH), 7.27-7.21 (2H, m, PhH), 7.18 (1H, t, *J* = 6.2 Hz, PhH), 6.97 (2H, d, *J* = 7.3 Hz, PhH), 5.59 (1H, dt, *J* = 11.3 and 5.5 Hz, H2), 5.46-5.35 (1H, m, H9), 5.01 (1H, dd, *J* = 14.6 and 9.3 Hz, H3), 4.31 (1H, quint, *J* = 6.9 Hz, H6), 3.97 (2H, d, *J* = 4.5 Hz, H1), 3.55 (1H, t, *J* = 9.6 Hz, H4), 2.48-2.42 (1H, m, H5), 2.45 (3H, s, $TsCH_3$), 1.97 (3H, dd, *J* = 7.1 and 1.8 Hz, H10), 0.85 (3H, d, *J* = 6.8 Hz, H11); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 144.1, 138.4, 137.0, 136.4, 132.4, 131.0, 129.6, 128.5, 128.2, 127.9, 126.9, 118.8, 63.2, 62.0, 50.7, 48.2, 21.6, 15.9, 15.8; **HRMS** (ES^+) calc. for $C_{23}H_{27}O_3NNaS$ $[M+Na]^+$ 420.1609; found 420.1599.

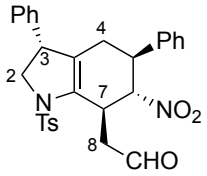
(*E*)-3-((3*R*,4*S*,5*R*,*Z*)-2-ethylidene-5-methyl-4-phenyl-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4e



Prepared by General Procedure **I** using **S23** (46 mg, 0.115 mmol, 1.0 equiv.). The resulting crude material was purified by flash chromatography (petroleum ether → petroleum ether / EtOAc (1:1)) to give **4e** as a light yellow oil (30 mg, 0.076 mmol, 66%); $[\alpha]_D^{25}$ +136.8 (*c* = 0.7, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 3030, 2919, 1686, 1632, 1453, 1165, 1053, 978, 815; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.22 (1H, d, *J* = 7.7 Hz, H1), 7.76 (2H, d, *J* = 8.3 Hz, TsH), 7.30 (2H, d, *J* = 8.0 Hz, TsH), 7.22-7.12 (3H, m, PhH), 6.92 (2H, d, *J* = 8.5 Hz, PhH), 6.01 (1H, dd, *J* = 15.5 and 8.5 Hz, H3), 5.86 (1H, dd, *J* = 15.8 and 7.7 Hz, H2), 5.36 (1H, qd, *J* = 7.0 and 1.4 Hz, H9), 4.33 (1H, qt, *J* = 6.8 Hz, H6), 3.75 (1H, t, *J* = 9.5 Hz, H4), 2.63 (1H, dd, *J* = 10.6 and 7.1 Hz, H5), 2.38 (3H, s, $TsCH_3$), 1.92 (3H, dd, *J* = 7.1 and 1.8 Hz, H10), 0.82 (3H, d, *J* = 6.8 Hz, H11); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 193.1, 156.4, 144.5, 136.6, 136.1, 135.9, 132.7, 129.8, 128.7, 127.9, 127.9, 127.4, 121.1, 62.2, 50.9, 48.7, 21.6, 16.0, 15.9; **HRMS** (ES^+) calc. for $C_{23}H_{25}O_3NNaS$ $[M+Na]^+$ 418.1452; found 418.1436.

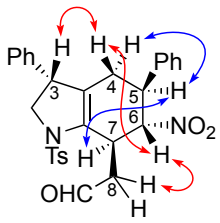
*1.3.6 Double stereodifferentiating cycloaddition reactions of dienals **3b** and **4e***

2-((3*R*,5*S*,6*S*,7*R*)-6-nitro-3,5-diphenyl-1-tosyl-2,3,4,5,6,7-hexahydro-1*H*-indol-7-yl)acetaldehyde, 19a

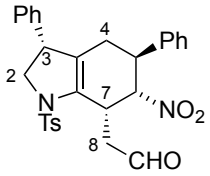


Prepared by General Procedure **J** using catalyst (*S*)-**10** (1.9 μL, 0.006 mmol, 0.2 equiv.), **3b** (11 mg, 0.030 mmol, 1.0 equiv.) and trans-β-nitrostyrene **13a** (13.4 mg, 0.09 mmol, 3.0 equiv.) under Ar. Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **19a** as a colourless oil (9.0 mg, 0.017 mmol, 58%, 8:1 dr); $[\alpha]_D^{25}$ +9.35 (*c* = 0.6, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2926, 1716, 1651, 1553, 1348, 1324, 1160; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 9.77 (1H, s), 7.66 (2H, d, *J* = 8.3 Hz, TsH), 7.34 (2H, d, *J* = 8.0 Hz, TsH), 7.30-7.23 (3H, m, PhH), 7.18 (2H, d, *J* = 7.0 Hz, PhH), 7.07 (1H, t, *J* = 7.4 Hz, PhH), 6.96 (2H, t, *J* = 6.8 Hz, PhH), 6.24 (2H, d, *J* = 7.1 Hz, PhH), 5.14 (1H, dd, *J* = 10.2 and 7.3 Hz, H6), 4.23 (1H, dd, *J* = 12.3 and 11.7 Hz, H2), 3.98 (1H, br s, H7), 3.78 (1H, br d, *J* = 10.4 Hz, H3), 3.51 (1H, dd, *J* = 12.4 and 4.8 Hz, H2), 3.45 (1H, td, *J* = 9.9 and 5.1 Hz, H5), 3.35 (1H, dd, *J* = 19.4 and 6.1 Hz, H8), 3.04 (1H, dd, *J* = 19.4 and 2.9 Hz, H8), 2.53 (3H, s, $TsCH_3$), 2.42 (1H, dddd, *J* = 17.9, 9.6, 3.0 and 1.8 Hz, H4), 2.04 (1H, dd, *J* = 17.9 and 4.9 Hz, H4); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 199.8, 144.7, 140.9, 138.6, 134.8, 132.1, 130.3, 129.1, 128.7, 128.6, 128.2, 127.7, 127.5, 127.1, 126.8, 92.5, 57.4, 48.9, 44.6, 43.6, 36.4, 28.9, 21.8; **HRMS** (ES^+) calc. for $C_{29}H_{28}O_5N_2NaS$ $[M+Na]^+$ 539.1611; found 539.1610.

Assignment of stereochemistry: The stereochemistry of cycloadduct **19a** was assigned by ^{1}H NMR nOe experiments (2D NOESY). On the alpha face (as depicted below), enhancements were seen between H7 and H5, and between H5 and H4α, indicating these protons to be on the same face. On the beta face, enhancements was seen between H3 and H4β, between H4β and H6, and between H6 and H8 (sidechain), indicating these protons to be on the opposite face. This analysis is consistent with a top face attack of nitrostyrene, with the nitro group oriented *exo* and the phenyl ring oriented *endo*. This is consistent with the acyclic trienamine catalysis reported by Chen.[8] As such, the facial and diastereoselectivity of the reaction is under catalyst stereocontrol.

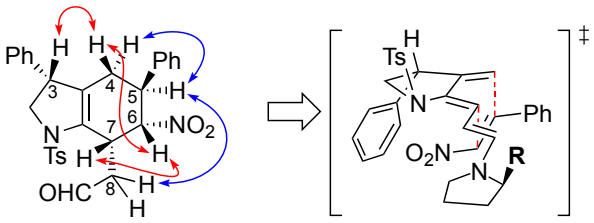


2-((3*R*,5*R*,6*R*,7*S*)-6-nitro-3,5-diphenyl-1-tosyl-2,3,4,5,6,7-hexahydro-1*H*-indol-7-yl)acetaldehyde, 19b

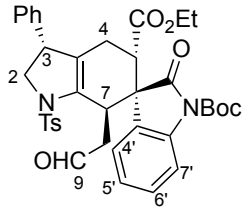


Prepared by General Procedure **J** using catalyst (***R***)-**10** (i.e. ***ent*-10**) (1.9 μL, 0.006 mmol, 0.2 equiv.), **3b** (11 mg, 0.030 mmol, 1.0 equiv.) and trans-β-nitrostyrene **13a** (13.4 mg, 0.09 mmol, 3.0 equiv.) under Ar. Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **19b** as a colourless oil (8.2 mg, 0.016 mmol, 53%, 20:1 dr); $[\alpha]_D^{25}$ –46.0 (*c* = 0.5, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2961, 2923, 1723, 1598, 1379, 1100, 1088, 728; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 9.77 (1H, s, H9), 7.76 (2H, d, *J* = 8.3 Hz, TsH), 7.44 (2H, d, *J* = 8.0 Hz, TsH), 7.32 (2H, t, *J* = 7.4 Hz, PhH), 7.28-7.25 (3H, m), 7.22 (1H, d, *J* = 7.2 Hz, PhH), 7.12 (2H, d, *J* = 7.0 Hz, PhH), 7.07 (2H, d, *J* = 7.0 Hz, PhH), 5.19 (1H, dd, *J* = 10.8 and 5.4 Hz, H6), 4.47-4.42 (1H, m, H7), 4.12 (1H, dd, *J* = 12.0 and 9.7 Hz, H2), 3.83 (1H, dd, *J* = 12.0 and 7.7 Hz, H2), 3.54 (1H, br t, *J* = 8.5 Hz, H3), 3.37 (1H, td, *J* = 9.7 and 6.5 Hz, H5), 3.27 (1H, dd, *J* = 18.5 and 2.2 Hz, H8), 3.09 (1H, dd, *J* = 18.3 and 8.3 Hz, H8), 2.53 (3H, s, $TsCH_3$), 2.15 (1H, dd, *J* = 18.2 and 6.5 Hz, H4), 2.00 (1H, ddt, *J* = 18.3, 9.4 and 1.8 Hz, H4); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 198.1, 144.8, 140.8, 139.2, 135.3, 133.9, 130.3, 129.3, 129.1, 128.0, 127.9, 127.8, 127.6, 127.4, 127.1, 89.0, 58.6, 49.0, 43.4, 39.9, 32.2, 29.8, 21.9; **HRMS** (ES^+) calc. for $C_{29}H_{28}O_5N_2NaS$ $[M+Na]^+$ 539.1611; found 539.1610.

Assignment of stereochemistry: The stereochemistry of cycloadduct **19b** was assigned through ^{1}H NMR nOe experiments (2D NOESY). On the alpha face (as depicted below), enhancements were seen between H5 and H4α, and between H5 and H8 (sidechain), indicating these protons to be on the same face. On the beta face, enhancements was seen between H3 and H4β, between H4β and H6, and between H6 and H7, indicating these protons to be on the opposite face. This analysis is consistent with a bottom face attack of nitrostyrene, with the nitro group oriented *endo* and the phenyl ring oriented *exo*. This *reverses* the diastereoselectivity of trienamine catalysis observed by Chen,[8] and likely arises from an avoidance of steric interactions between the C3-phenyl group, and the phenyl ring of nitrostyrene, in the Diels-Alder transition state. As such, the facial selectivity of the reaction is under catalyst stereocontrol, but the diastereoselectivity is under substrate control.

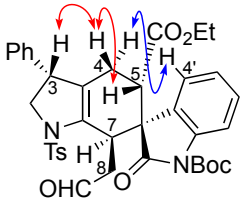


(3*R*,3'*S*,5*S*,7*R*)-1'-*tert*-butyl 5-ethyl 2'-oxo-7-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11e

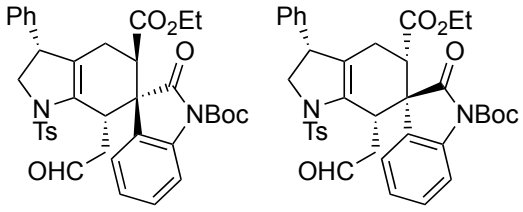


Prepared by General Procedure **K** using catalyst (*S*)-**10** (1.9 μL, 0.011 mmol, 0.2 equiv.), **3b** (11 mg, 0.030 mmol, 1.0 equiv.) and olefinic oxindole **9a** (28 mg, 0.090 mmol, 3.0 equiv.) under Ar. Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave **11e** as a colourless oil (13 mg, 0.019 mmol, 63%, 7:1 dr); $[\alpha]_D^{25}$ –67.8 (*c* = 0.8, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2930, 1787, 1756, 1722, 1597, 1484, 1278, 1155, 771; **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 9.74 (1H, s, H9), 8.02 (1H, d, *J* = 8.1 Hz, oxindole H7'), 7.37 (1H, t, *J* = 8.8 Hz, oxindole H6'), 7.33 (2H, d, *J* = 8.3 Hz, TsH), 7.20 (1H, t, *J* = 7.9 Hz, PhH), 7.15-7.11 (4H, m, TsH and PhH), 6.81 (1H, t, *J* = 7.1 Hz, oxindole H5'), 6.58 (1H, d, *J* = 6.9 Hz, oxindole H4'), 6.51 (2H, d, *J* = 8.3 Hz, PhH), 4.36 (1H, t, *J* = 11.6 Hz, H2), 3.89-3.81 (3H, m, OCH_2CH_3, H3 and H7), 3.77 (1H, dq, *J* = 10.9 and 7.1 Hz, OCH_2CH_3), 3.58 (1H, dd, *J* = 11.9 and 6.3 Hz, H2), 3.35-3.27 (2H, m, H5 and H8), 3.15 (1H, d, *J* = 17.8 Hz, H8), 2.52 (3H, $TsCH_3$), 2.58-2.48 (1H, m, H4), 2.03 (1H, dd, *J* = 18.4 and 11.8 Hz, H4), 1.65 (9H, s, $C(CH_3)_3$), 0.95 (3H, t, *J* = 7.1 Hz, OCH_2CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 198.1, 176.5, 171.3, 149.2, 144.1, 141.0, 140.0, 136.2, 133.1, 130.8, 130.2, 128.8, 128.4, 128.4, 127.6, 127.3, 123.6, 123.4, 122.5, 115.5, 84.2, 61.3, 56.8, 50.1, 49.9, 43.8, 41.3, 37.5, 28.2, 24.5, 21.8, 13.7; **HRMS** (ES^+) calc. for $C_{38}H_{40}O_8N_2NaS$ $[M+Na]^+$ 707.2397; found 707.2391.

Assignment of stereochemistry: The stereochemistry of cycloadduct **11e** was assigned through ^{1}H NMR nOe experiments (2D NOESY). Several key protons are overlapping, but assignment can be made on the following basis: On the alpha face (as depicted below), a key enhancement was seen between oxindole H4' and H4α, indicating these protons to be on the same face. H4α did not show enhancements to any aliphatic protons aside from H4β. On the beta face, enhancements was seen between H4β and the overlapped H3/H7 peak (this must be an enhancement with H3 based on other compounds), and between H4β and H5, indicating these protons all to be on the opposite face. This analysis is consistent with a top face attack of the oxindole, with the oxindole carbonyl oriented *endo* and the ester group oriented *exo*. These observations are consistent with the model proposed by Jørgensen and Chen for acyclic trienamine reactions with oxindole alkene dienophiles.[8]



(3*R*,3'*R*,5*R*,7*S*)-1'-*tert*-butyl 5-ethyl 2'-oxo-7-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11f

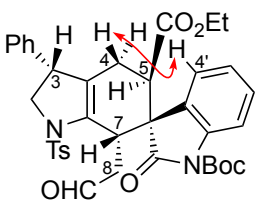


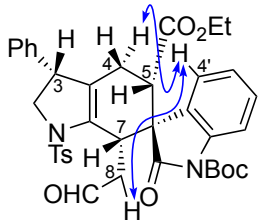
11f 1:1 *dr*

Prepared by General Procedure **K** using catalyst (*R*)-**10** (i.e. ***ent*-10**) (1.9 μL, 0.011 mmol, 0.2 equiv.), **3b** (11 mg, 0.030 mmol, 1.0 equiv.) and olefinic oxindole **9a** (28 mg, 0.090 mmol, 3.0 equiv.) under Ar. Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadducts **11f** as a light yellow oil (11 mg, 0.016 mmol, 53%, 1:1 dr); $[\alpha]_D^{25}$ –6.2 (*c* = 1.0, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2985, 2929, 1792, 1759, 1723, 1479, 1395, 1350, 1164, 1108, 775; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 9.74 (1H, s, H9A), 9.38 (1H, s, H9B), 7.98 (1H, d, *J* = 8.1 Hz, PhH), 7.93 (1H, d, *J* = 7.9 Hz, PhH), 7.84 (2H, d, *J* = 8.3 Hz, TsH), 7.44 (2H, d, *J* = 8.0 Hz, TsH), 7.41-7.29 (10H, m, TsH and PhH), 7.19 (2H, d, *J* = 6.9 Hz, PhH), 7.10 (2H, d, *J* = 7.1 Hz, PhH), 7.05 (3H, d, *J* = 8.0 Hz, PhH), 6.89 (1H, d, *J* = 7.5 Hz, PhH), 6.76 (1H, t, *J* = 7.6 Hz, oxindole H4'B), 6.63 (1H, d, *J* = 7.6 Hz, oxindole H4'A), 4.28 (1H, dd, *J* = 13.4 and 8.3 Hz, H2), 4.04-3.91 (3H, m, H2), 3.87-3.72 (6H, m, OCH_2CH_3 and H3), 3.38-3.24 (1H, m, H7 and H8A), 3.25-3.12 (3H, m, H5, H7, and H8A), 2.76 (1H, dt, *J* = 17.7 and 2.3 Hz, H8B), 2.53 (3H, s, $TsCH_3$), 2.53-2.50 (1H, m, H8B), 2.50-2.46 (1H, m, H4A/B), 2.42 (3H, s), 2.45-2.37 (1H, m, H4), 2.35-2.20 (2H, m, H4A and H4B), 2.19-2.11 (1H, m, H4A/B), 1.67 (9H, s, $C(CH_3)_3$), 1.65 (9H, s, $C(CH_3)_3$), 0.96-0.90 (6H, m, OCH_2CH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 199.2, 198.1, 177.3, 176.3, 171.3, 170.2, 149.2, 149.1, 145.0, 143.9, 141.9, 141.0, 139.9, 139.2, 137.3, 136.9, 133.5, 133.2, 132.1, 130.6, 130.1, 130.0, 129.7, 129.4, 129.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.4, 126.1, 124.6, 124.2, 123.9, 123.6, 123.0, 115.7, 115.34, 84.7, 84.3, 61.5, 61.2, 58.6, 57.7, 52.8, 50.7, 50.0, 48.5, 46.5, 43.9, 41.9, 41.5, 41.0, 37.0, 28.3, 28.2, 26.0, 23.9, 23.7, 21.9, 21.8, 13.7, 13.6; **HRMS** (ES^+) calc. for $C_{38}H_{40}O_8N_2NaS$ $[M+Na]^+$ 707.2397; found 707.2391.

Assignment of stereochemistry: The two diastereomers produced in this reaction are different to those prepared in the matched reaction (to give **11e**) assigned above. This supports an opposite (catalyst controlled) facial selectivity, and a 1:1 mixture of *endo* and *exo* adducts, which would be consistent with a steric effect imposed by the C3-phenyl affecting the mismatched catalyst-imposed diastereoselectivity. Additional evidence for the stereochemistry of these diastereomers is as follows: For isomer **11fA**, an enhancement was seen between the oxindole H4' and H4(β), but no enhancement was seen from oxindole H4' to H8. For isomer **11fB**, enhancements were seen between oxindole H4'B and H4(α), as well as between oxindole H4'B and H8, implying these protons to be on the same face.

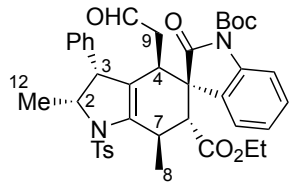
11f_A





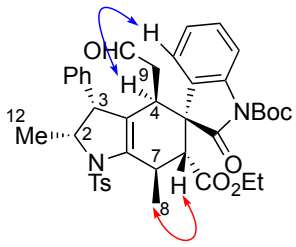
11f_B

(2*R*,3*R*,3'*R*,4*R*,6*R*,7*R*)-1'-*tert*-Butyl 6-ethyl 2,7-dimethyl-2'-oxo-4-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12h

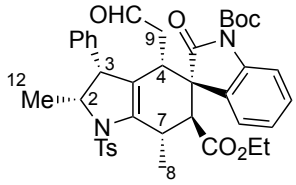


Prepared by General Procedure **K** using catalyst (*R*)-**10** (i.e. ***ent*-12a**) (3.56 μL, 0.011 mmol, 0.2 equiv.), **4e** (21 mg, 0.055 mmol, 1.0 equiv.) and olefinic oxindole **9a** (52 mg, 0.165 mmol, 3.0 equiv.) under Ar. Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12h** as a colourless oil (24 mg, 0.033 mmol, 60% yield, 20:1 dr); $[\alpha]_D^{25}$ –10.38 (*c* = 1.1, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}) 2980, 2931, 1789, 1758, 1726, 1291, 1252, 1150; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.50 (s, 1H, H10), 7.85-7.81 (3H, m, TsH and PhH), 7.38-7.26 (5H, m, TsH and PhH), 7.11-7.04 (2H, m, PhH), 6.95 (2H, t, *J* = 7.6 Hz, PhH), 6.58 (2H, d, *J* = 7.2 Hz, PhH), 4.54 (1H, dq, *J* = 13.9 and 6.9 Hz, H2), 3.91-3.80 (4H, m, $OC\underline{H_2}CH_3$, H7 and H3), 3.22 (1H, d, *J* = 7.3 Hz, H6), 3.20 (1H, dd, *J* = 16.6 and 7.4 Hz, H9), 2.78 (1H, dd, *J* = 7.3 and 4.9 Hz, H4), 2.47 (3H, s, $TsCH_3$), 2.38 (1H, ddd, *J* = 17.5, 4.8 and 1.5 Hz, H9), 1.59 (9H, s, *t*-Bu), 1.51 (1H, d, *J* = 6.5 Hz, H8), 1.09 (1H, d, *J* = 6.9 Hz, H12), 0.91 (1H, t, *J* = 7.1 Hz, $OCH_2C\underline{H_3}$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 199.4, 176.6, 171.0, 149.1, 143.7, 142.9, 139.5, 139.3, 135.1, 130.4, 130.0, 129.7, 129.0, 128.3, 127.4, 127.0, 124.6, 123.6, 122.3, 115.1, 84.4, 64.7, 61.4, 52.8, 52.0, 51.3, 44.9, 36.3, 30.5, 28.2, 23.7, 21.7, 17.2, 13.6; **HRMS** (ES^+) calc. for $C_{40}H_{44}O_8N_2NaS$ $[M+Na]^+$ 735.2716; found 735.2711.

Assignment of stereochemistry: The stereochemistry of cycloadduct **12h** was assigned through ^{1}H NMR nOe experiments (1D nOe / 2D NOESY). On the beta face (as depicted below), an enhancement was seen between H6 and H8 (side chain methyl), indicating these groups to be on the same face; on the alpha face, an enhancement was seen between H4 and oxindole H4', indicating this arene to positioned on the top face of the molecule and oriented into / over the indoline ring system.

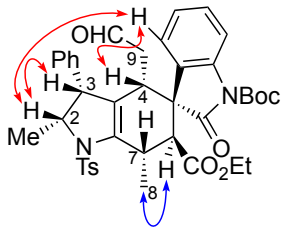


(2*R*,3*R*,3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 2,7-dimethyl-2'-oxo-4-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12i



Prepared by General Procedure **K** using catalyst (*S*)-**10** (1.6 μL, 0.005 mmol, 0.2 equiv.), **4e** (10 mg, 0.025 mmol, 1.0 equiv.) and olefinic oxindole **9a** (23.7 mg, 0.075 mmol, 3.0 equiv.) under Ar. Purification via flash chromatography (petroleum ether / EtOAc (2:1)) gave cycloadduct **12i** as a colourless oil (8 mg, 0.011 mmol, 45% yield, 7:1 dr); $[\alpha]_D^{25}$ –117.6 (*c* = 0.6, $CHCl_3$); **IR** (thin film, ν_{max} / cm^{-1}); 2980, 2931, 1789, 1758, 1726, 1291, 1252, 1150; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 9.12 (1H, s, H10), 7.98 (2H, d, *J* = 8.0 Hz, TsH), 7.78 (1H, d, *J* = 7.9 Hz, PhH), 7.42 (2H, d, *J* = 8.0 Hz, TsH), 7.27-7.22 (5H, m, PhH), 7.20-7.14 (1H, m, PhH), 7.03 (2H, dd, *J* = 7.6 and 1.7 Hz, PhH), 6.41 (1H, td, *J* = 7.6 and 0.9 Hz, PhH), 6.31 (1H, d, *J* = 7.6 Hz, PhH), 4.39-4.33 (1H, m, H2), 3.98-3.93 (1H, m, H7), 3.86-3.78 (2H, m, $OC\underline{H}_2CH_3$), 3.48 (1H, dd, *J* = 9.5 and 2.3 Hz, H3), 3.26 (1H, d, *J* = 6.0 Hz, H6), 3.00 - 2.91 (2H, m, H9 and H4), 2.53 (3H, s, $TsCH_3$), 1.67-1.60 (4H, m, H9 and H12), 1.56 (9H, s), 1.27 (3H, d, *J* = 6.6 Hz, H8), 0.86 (3H, t, *J* = 7.1 Hz, $OCH_2C\underline{H}_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C 198.2, 176.6, 171.0, 148.9, 144.3, 143.7, 139.1, 137.8, 135.3, 130.7, 130.1, 129.5, 128.6, 128.5, 128.2, 127.8, 123.5, 122.9, 121.9, 114.7, 84.1, 62.4, 61.2, 55.5, 52.0, 51.2, 44.0, 37.5, 29.1, 27.9, 24.2, 21.7, 18.3, 13.3; **HRMS** (ES^+) calc. for $C_{40}H_{44}O_8N_2NaS$ $[M+Na]^+$ 735.2710; found 735.2709.

Assignment of stereochemistry: The stereochemistry of cycloadduct **12i** was assigned through ^{1}H NMR nOe experiments (1D nOe / 2D NOESY). On the alpha face (as depicted below), a strong enhancement was seen between H6 and H8 (side chain methyl), indicating these groups to be on the same face; on the beta face, a strong enhancement was seen between H4 and oxindole H4', and also between H2 and H3, and H2 and oxindole H4', indicating this arene to positioned on the top face of the molecule and oriented into / over the indoline ring system.



*Notably, the minor diastereomers produced in the above two reactions were also different – the matched and mismatched cycloadditions thus giving two different sets of diastereoisomers, each corresponding to endo and exo isomers from the opposite sense of facial selectivity – i.e. the facial selectivity of cycloaddition in each case is very high, as observed for the equivalent oxindole cycloadditions with **3b**.*

2. REFERENCES

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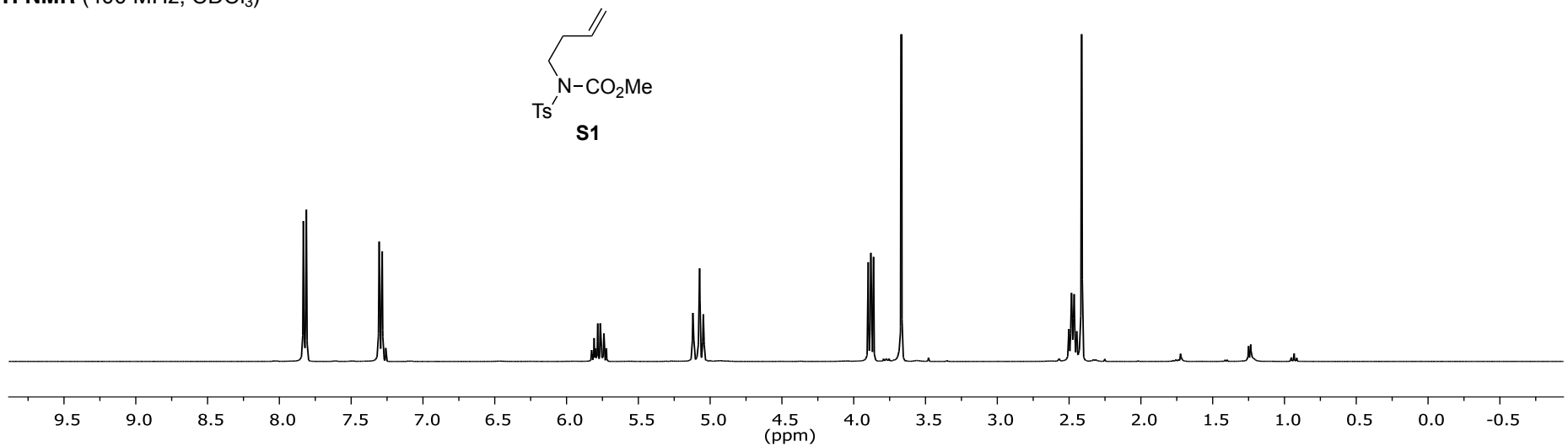
3.NMR SPECTRA

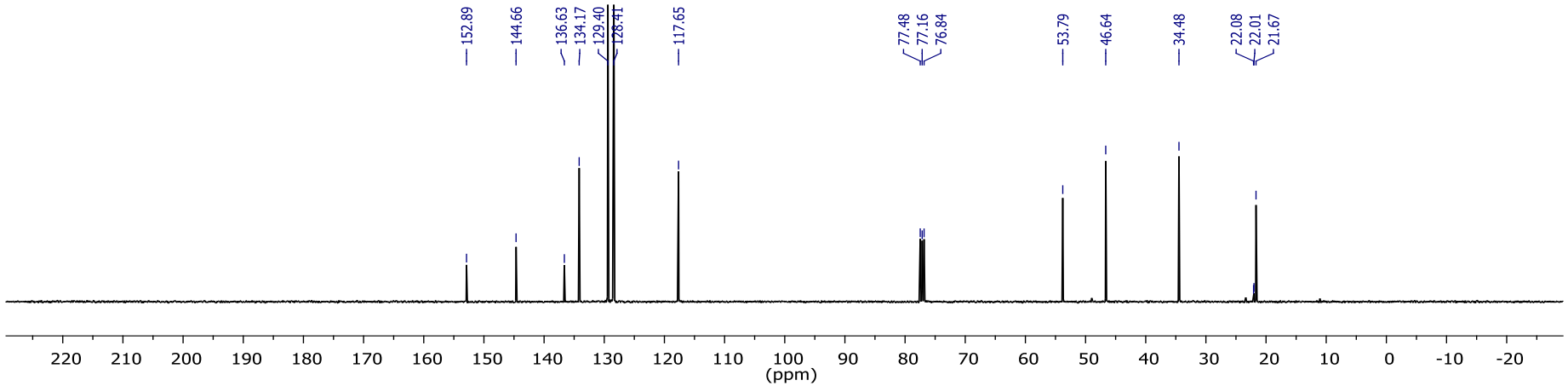
*3.1 Intermediates in the synthesis of dienal **3a***

Methyl but-3-en-1-yl(tosyl)carbamate, S1

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

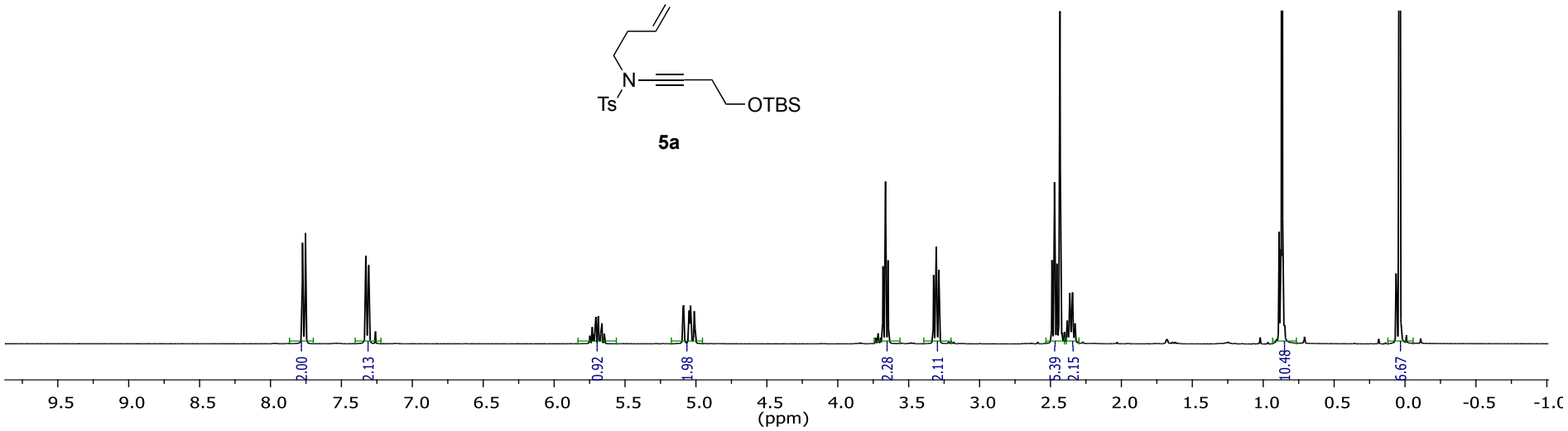


^{13}C NMR (101 MHz, $CDCl_3$)

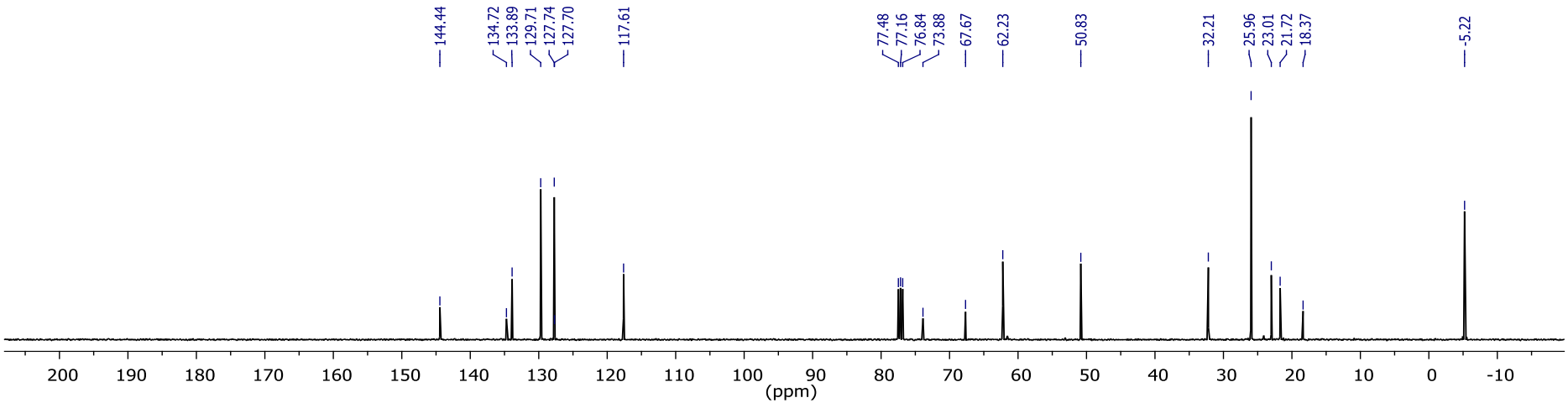


***N*-(But-3-en-1-yl)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-4-methylbenzenesulfonamide, 5a**

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

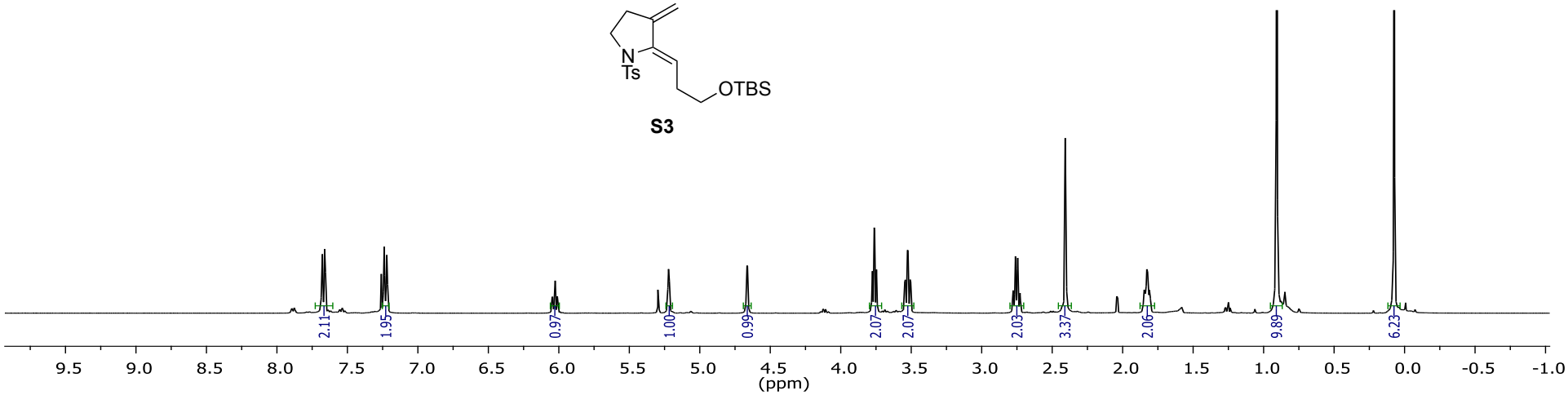


^{13}C NMR (101 MHz, $CDCl_3$)

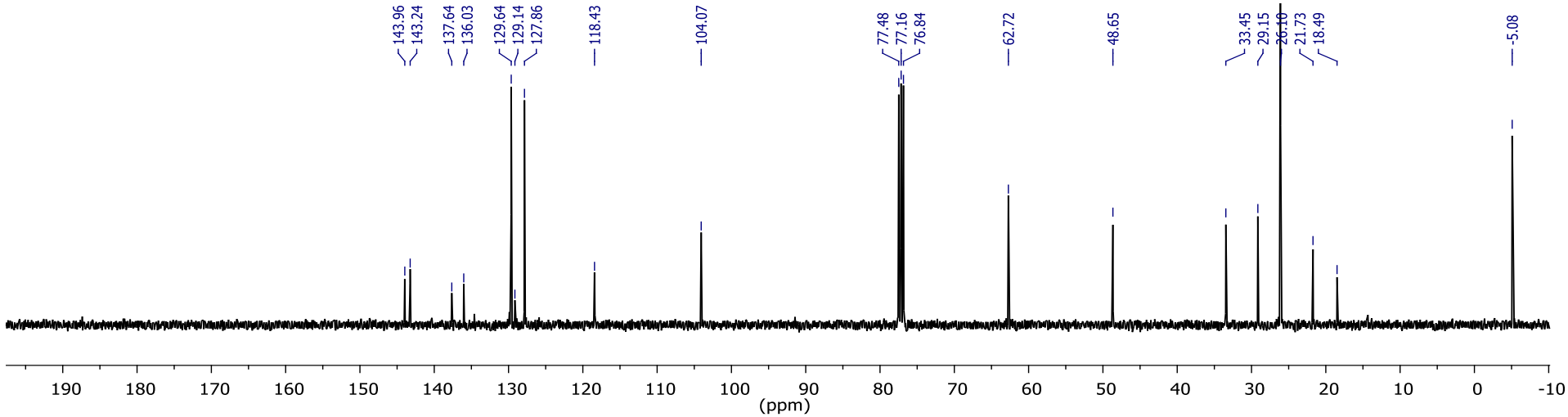


(*Z*)-2-(3-((*tert*-Butyldimethylsilyl)oxy)propylidene)-3-methylene-1-tosylpyrrolidine, S3

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

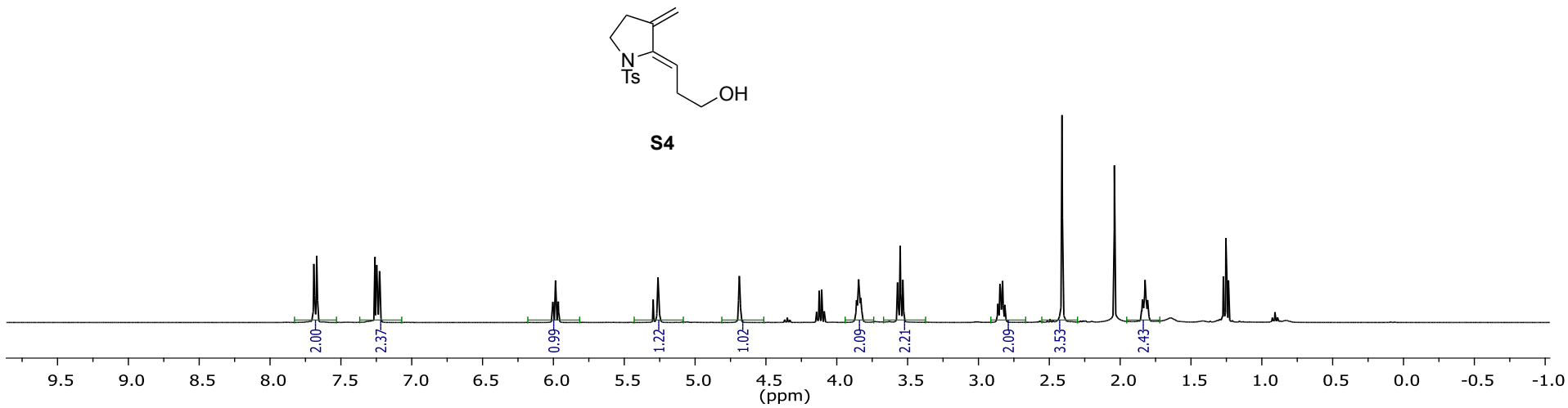


^{13}C NMR (101 MHz, $CDCl_3$)

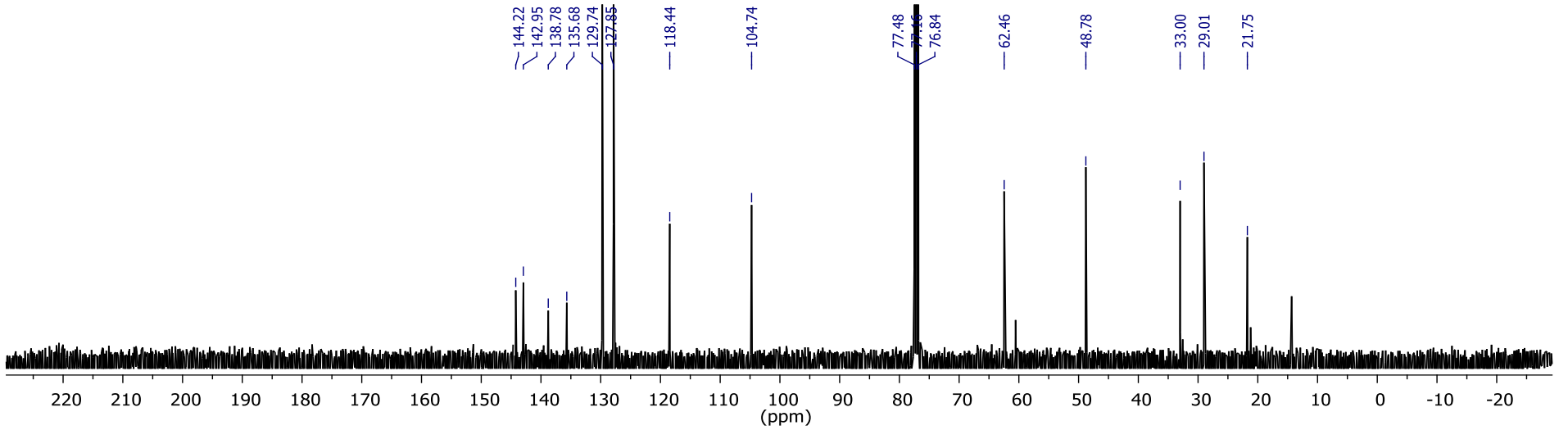


(*Z*)-3-(3-Methylene-1-tosylpyrrolidin-2-ylidene)propan-1-ol, S4

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



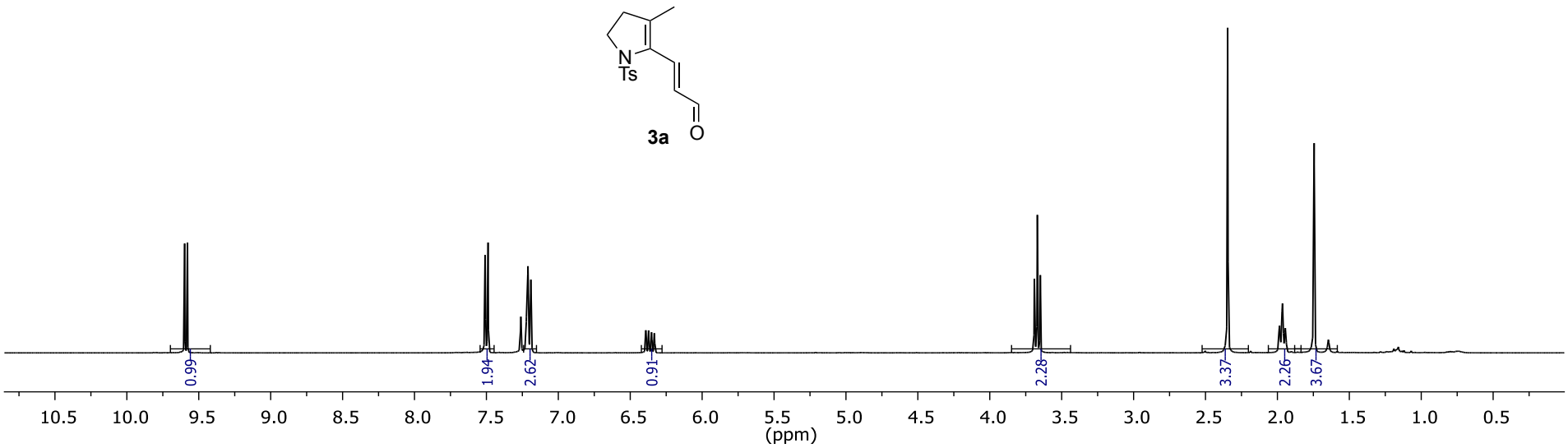
^{13}C NMR (101 MHz, $CDCl_3$)



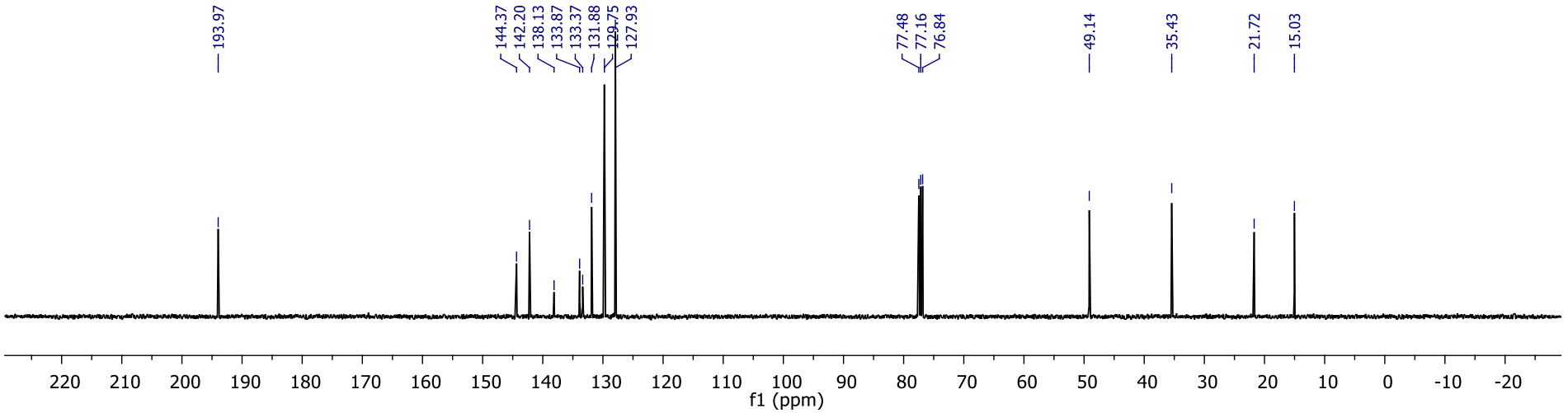
Note: EtOAc contamination.

(*E*)-3-(3-Methyl-1-tosyl-4,5-dihydro-1H-pyrrol-2-yl)acrylaldehyde, 3a

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



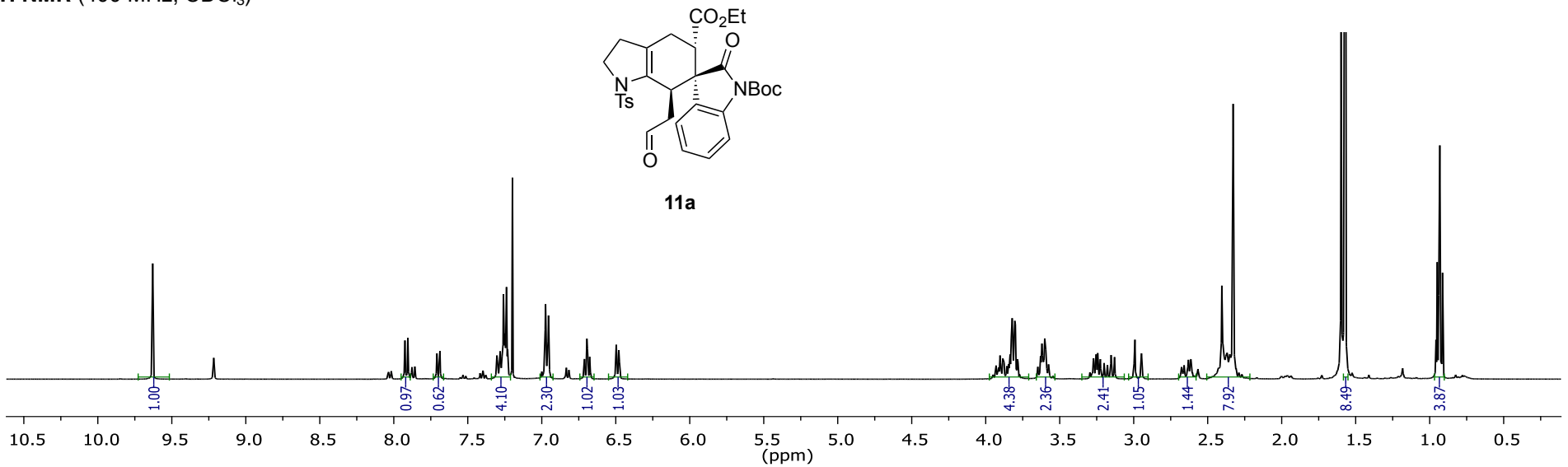
^{13}C NMR (101 MHz, $CDCl_3$)



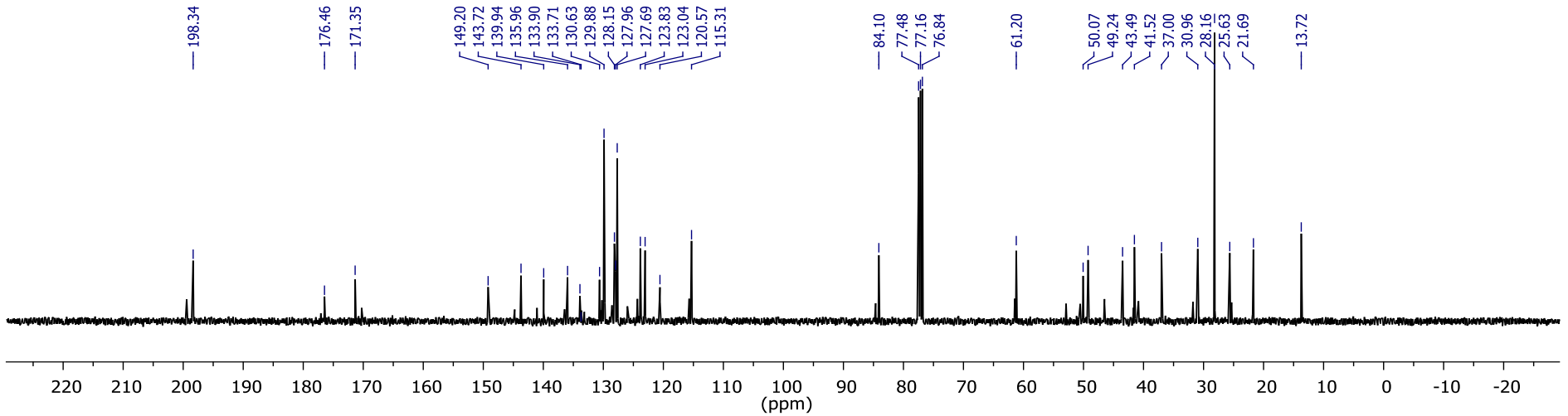
*3.2 Cycloaddition products of dienal **3a***

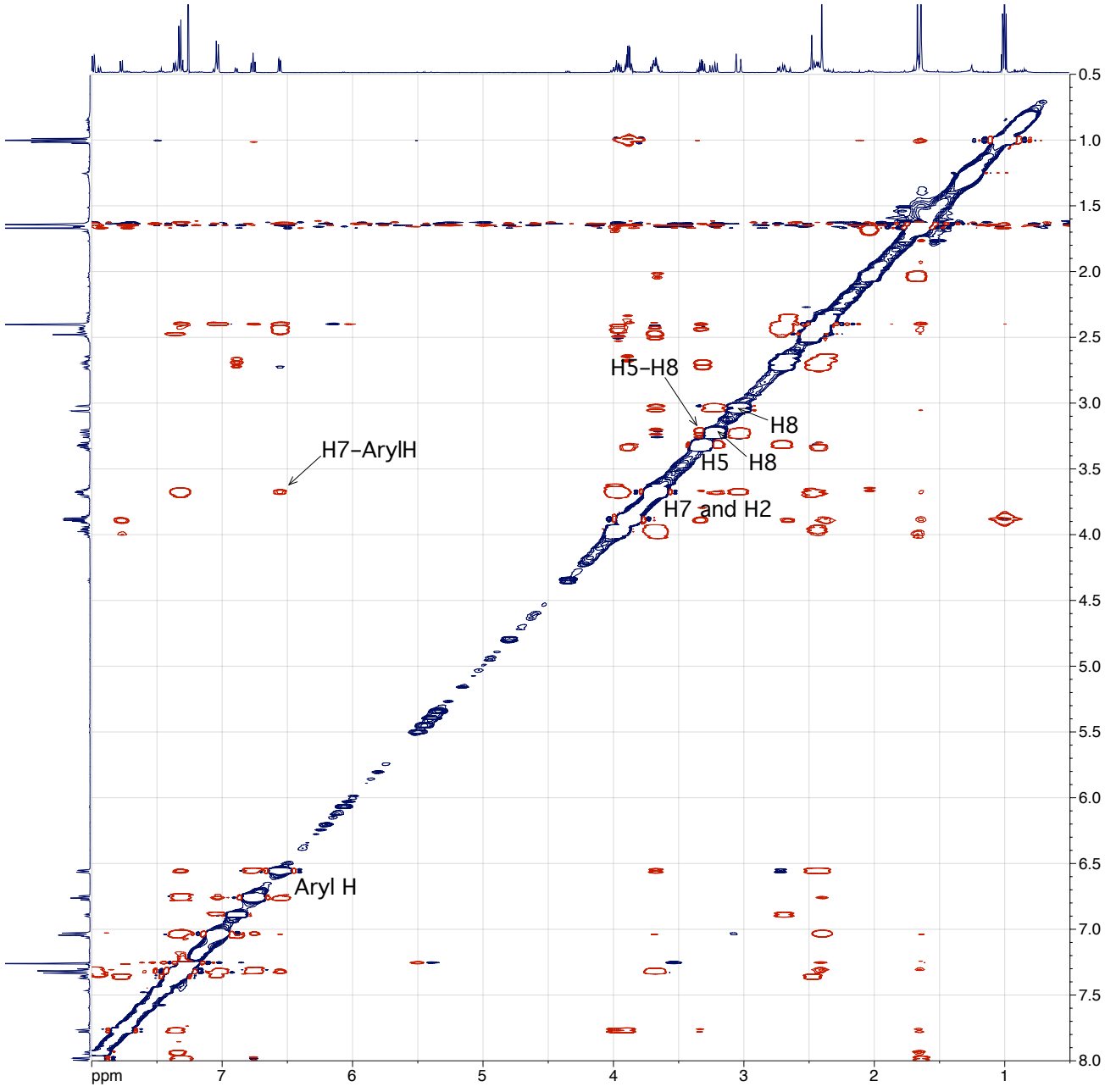
(3'*S*,5*S*,7*R*)-1'-*tert*-Butyl 5-ethyl 2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11a

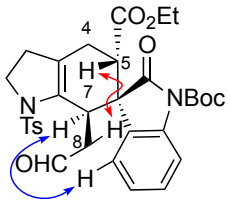
^{1}H NMR (400 MHz, $CDCl_3$)



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

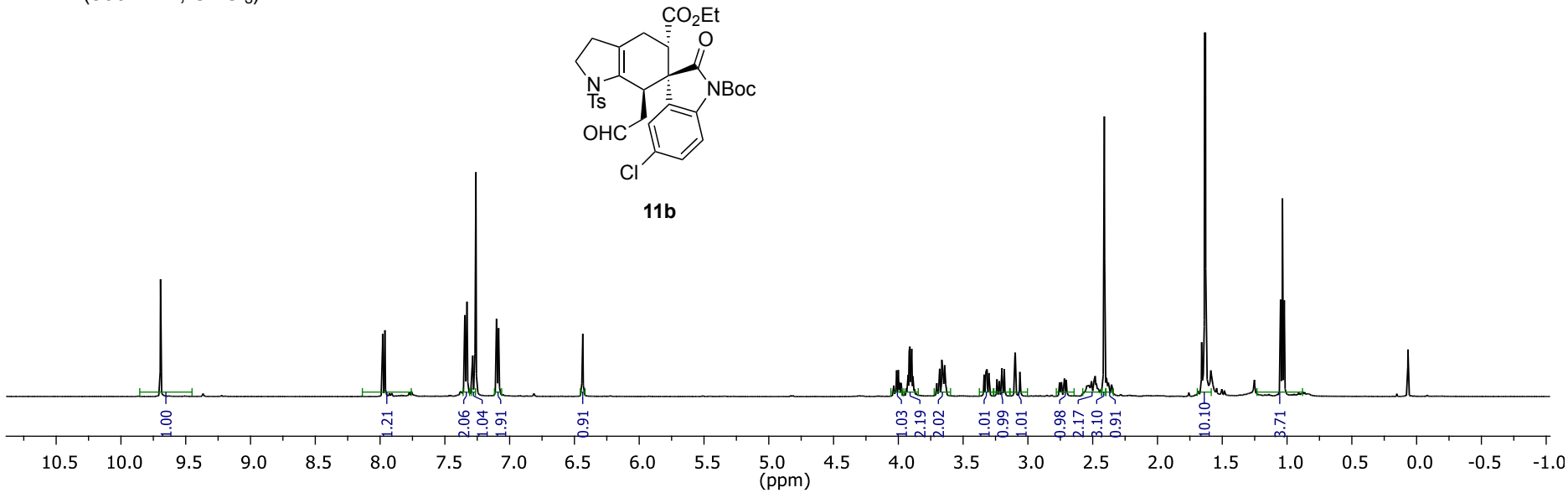



H5–H8
H8
H5
H8
H7–ArylH
H7 and H2
Aryl H
ppm
7
6
5
4
3
2
1
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

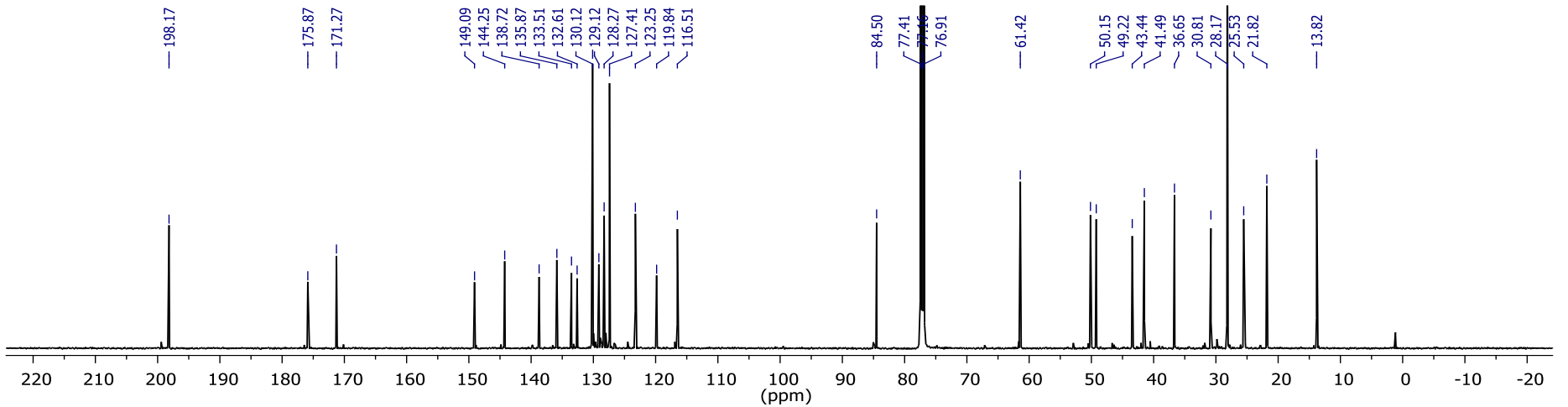

CO2Et
4
O
H
5
7
N
NBoc
Ts
H
8
H
OHC
H

(3'*S*,5*S*,7*R*)-1'-*tert*-Butyl 5-ethyl 5'-chloro-2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11b

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

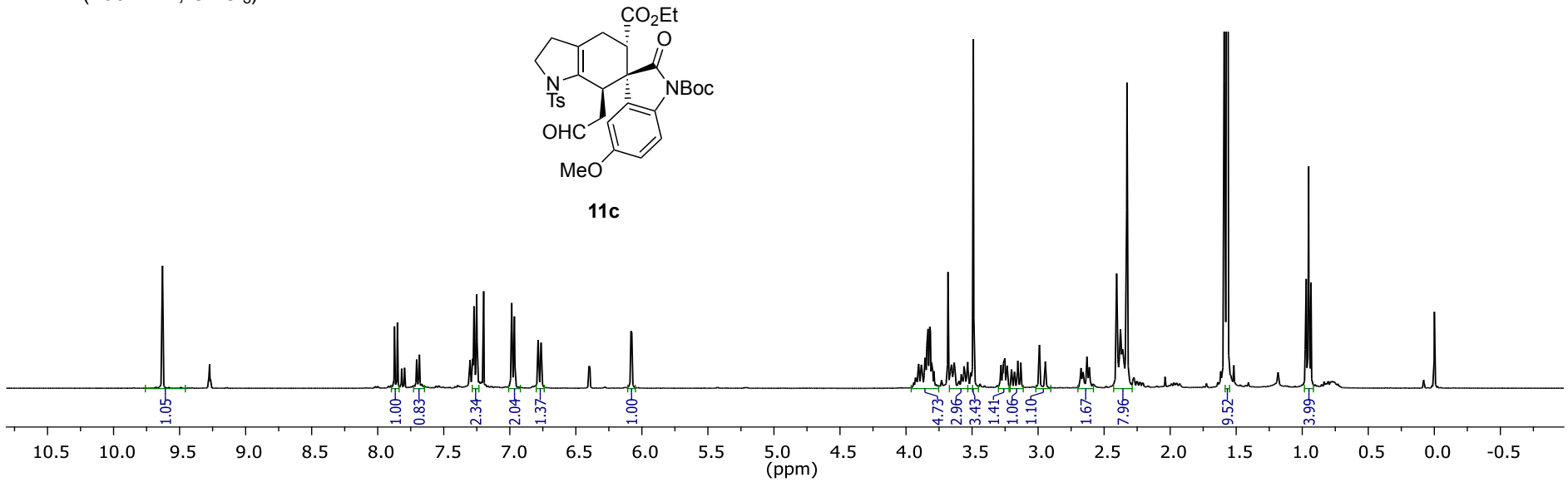


^{13}C NMR (125 MHz, $CDCl_3$)

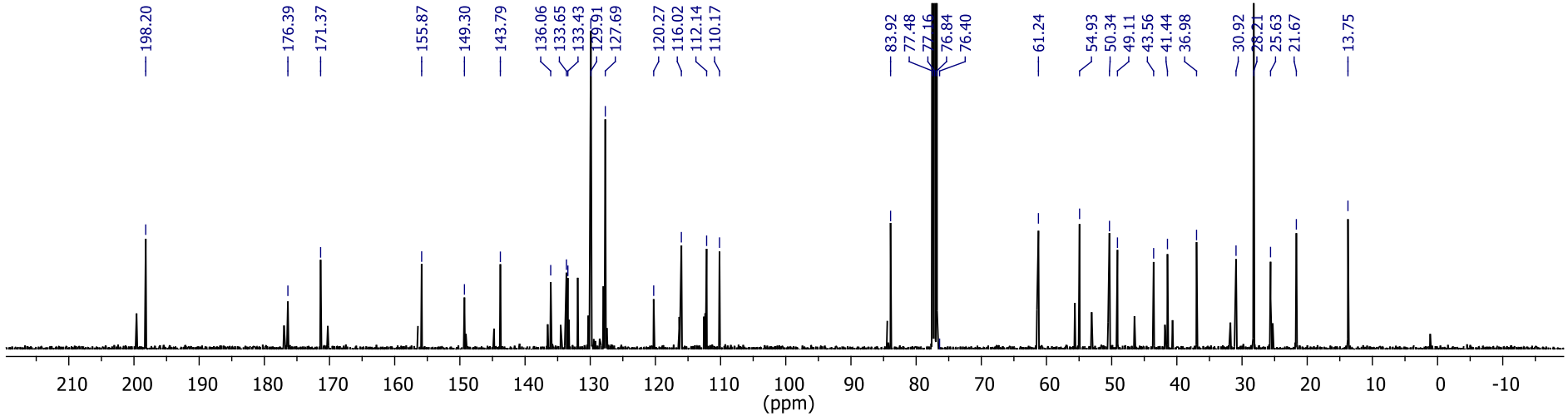


(3'*S*,5*S*,7*R*)-1'-*tert*-Butyl 5-ethyl 5'-methoxy-2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11c

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

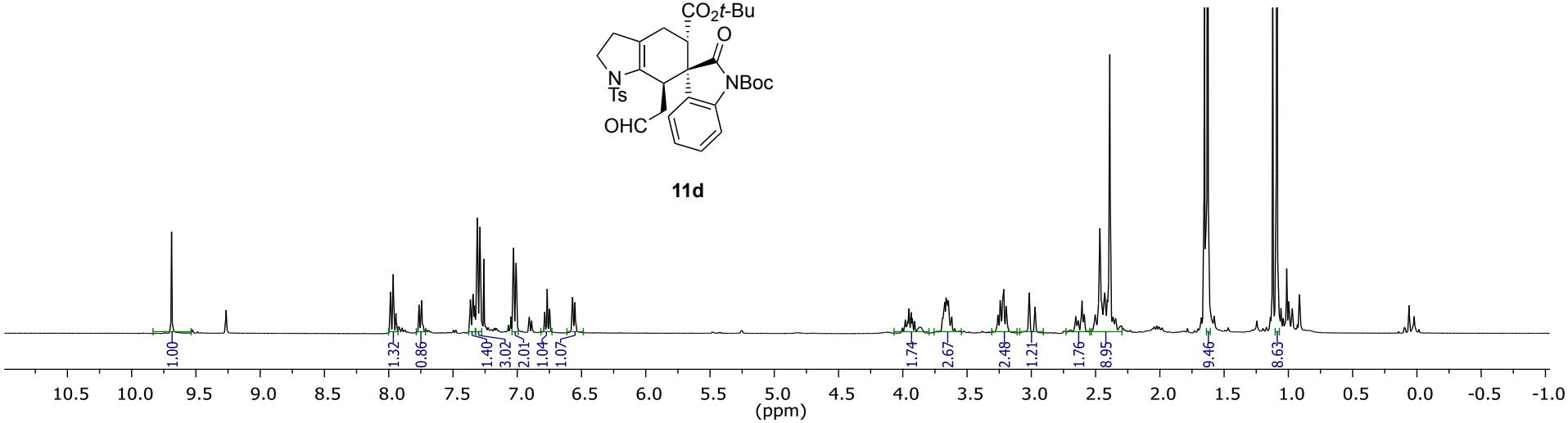


^{13}C NMR (101 MHz, $CDCl_3$)

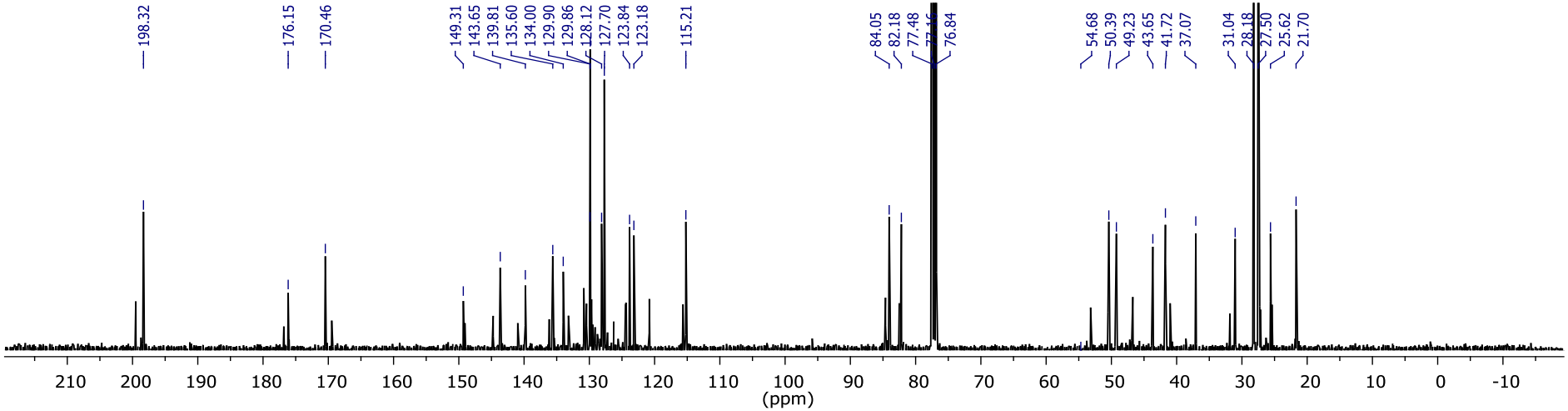


(3'*S*,5*S*,7*R*)-di-*tert*-Butyl 2'-oxo-7-(2-oxoethyl)-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11d

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

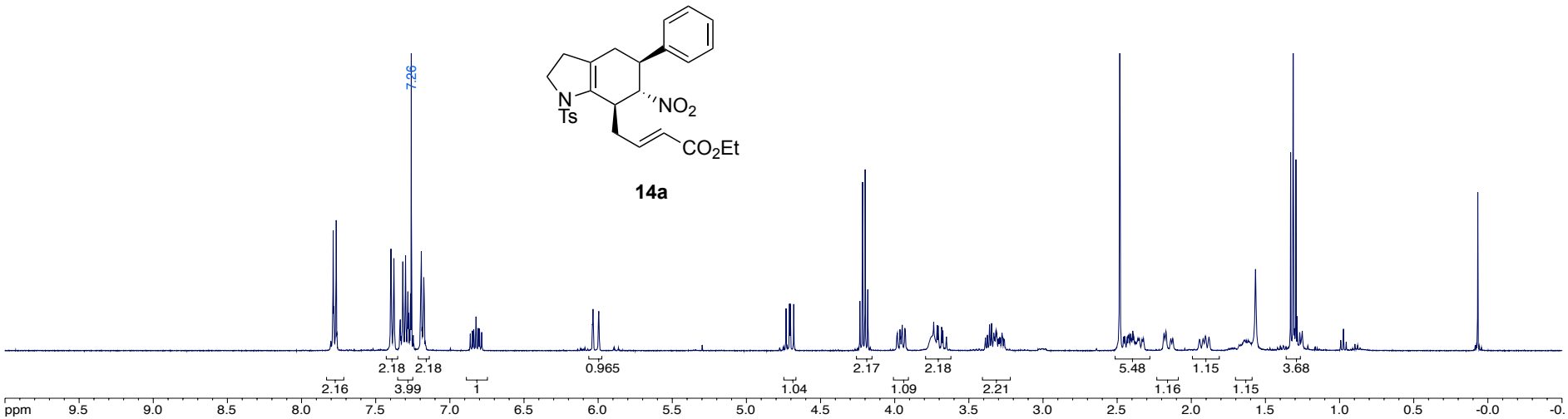


^{13}C NMR (101 MHz, $CDCl_3$)

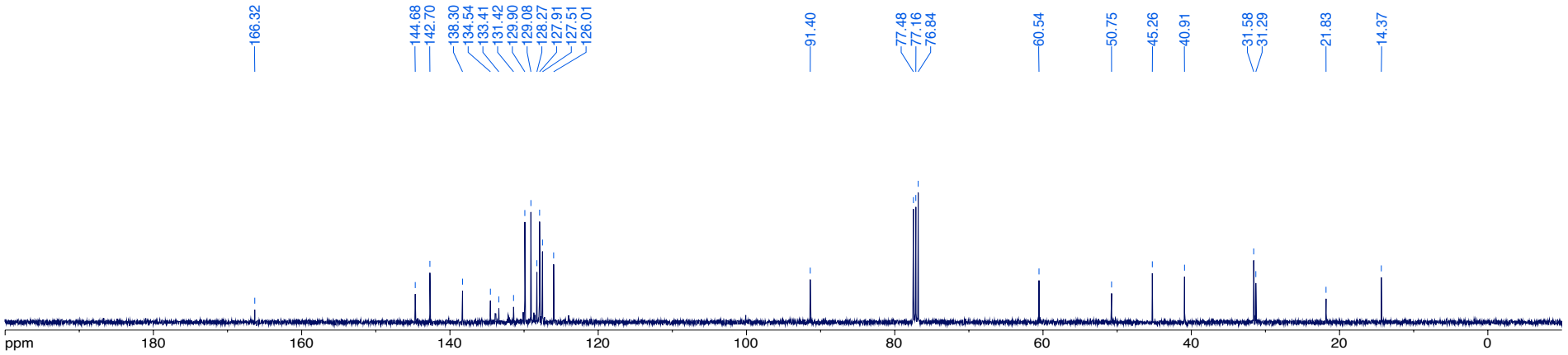


(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-phenyl-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14a

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



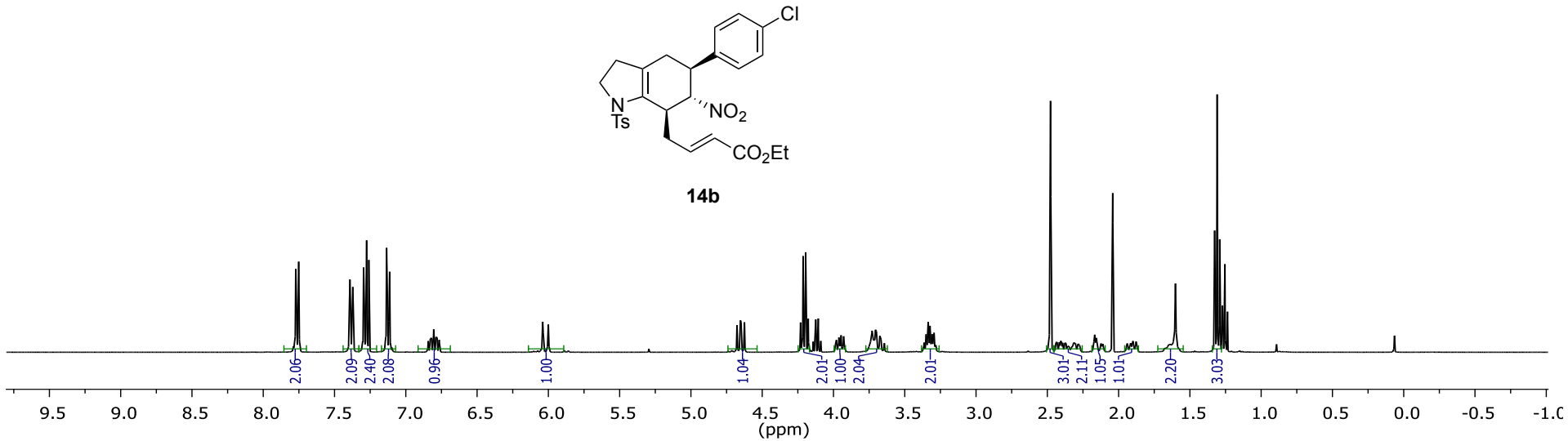
^{13}C NMR (101 MHz, $CDCl_3$)



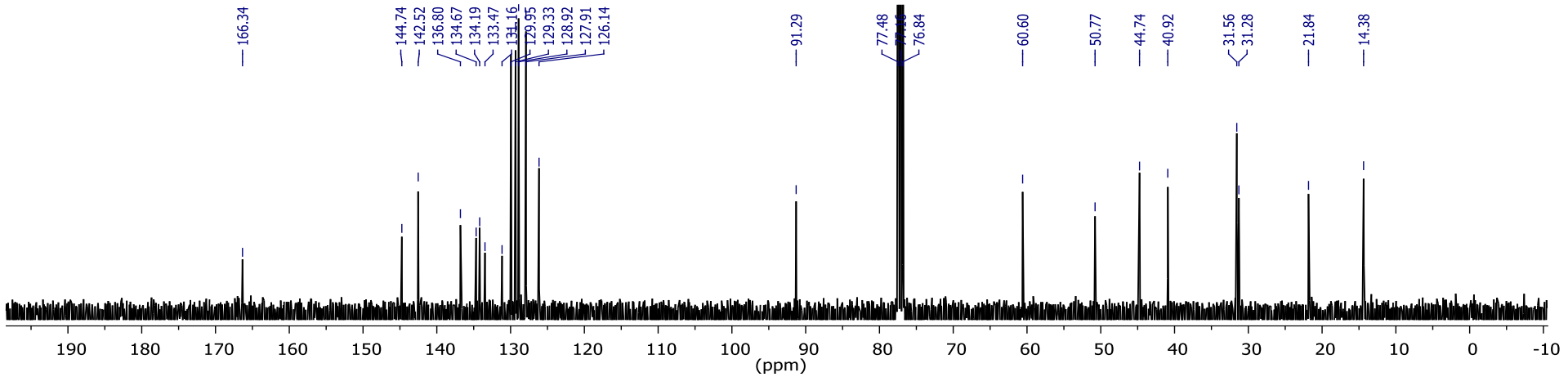
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-(4-chlorophenyl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14b

Note: a small amount of the Z-alkene (E:Z = 20:1) is observed (J = 11.6 Hz), but no diastereomer from the cycloaddition could be detected.

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



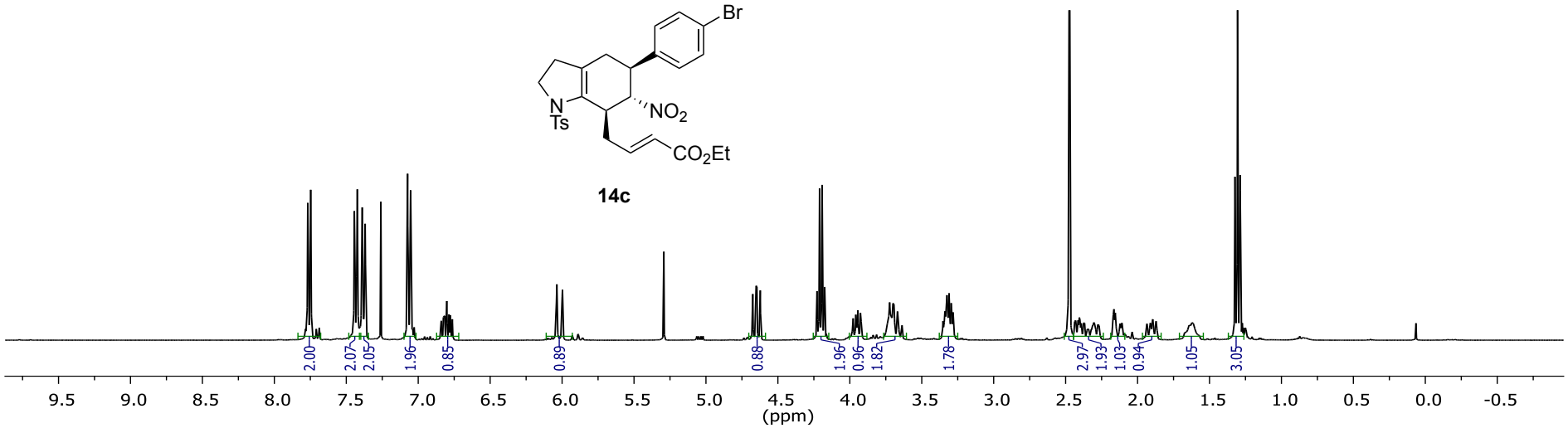
^{13}C NMR (101 MHz, $CDCl_3$)



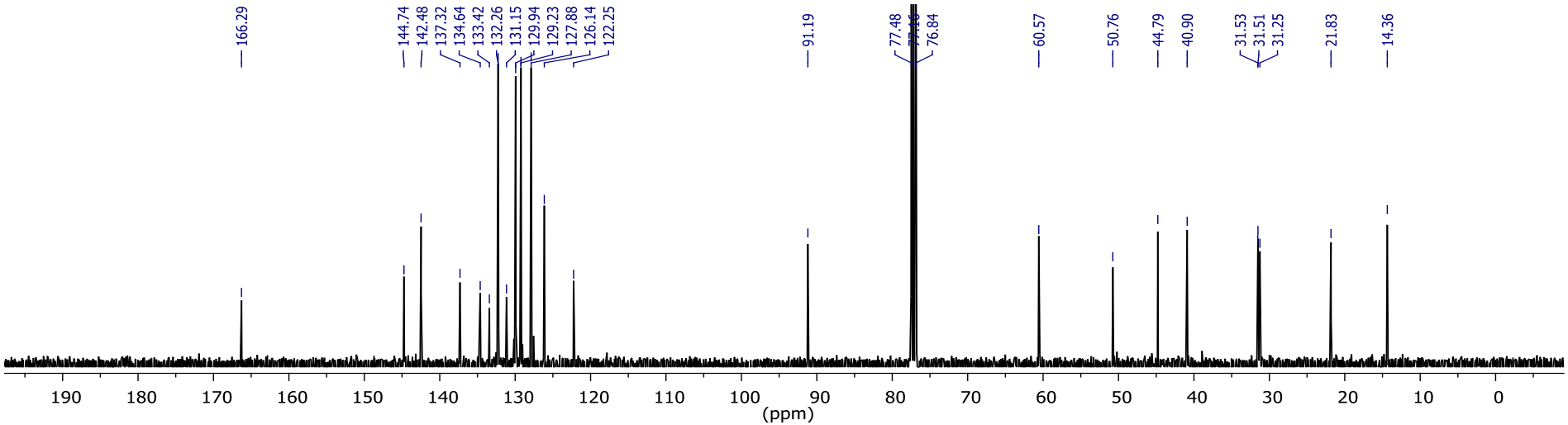
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-(4-bromophenyl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14c

Note: a small amount of the Z-alkene (E:Z ~ 20:1) is observed (J = 11.6 Hz), in addition to the 13.5:1 ratio of diastereomers from the cycloaddition.

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



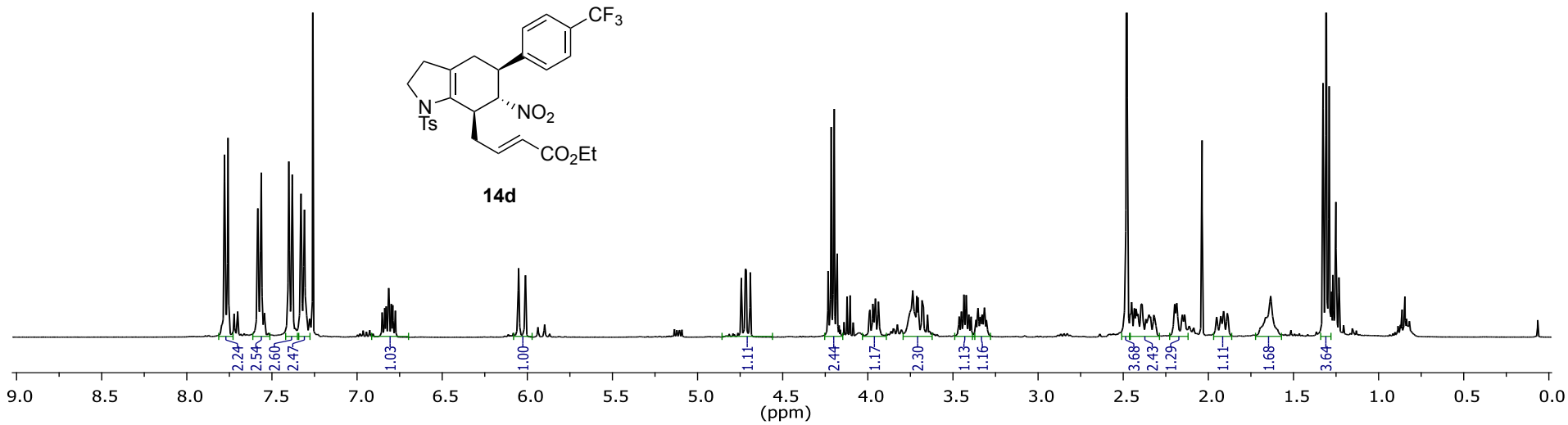
^{13}C NMR (101 MHz, $CDCl_3$)



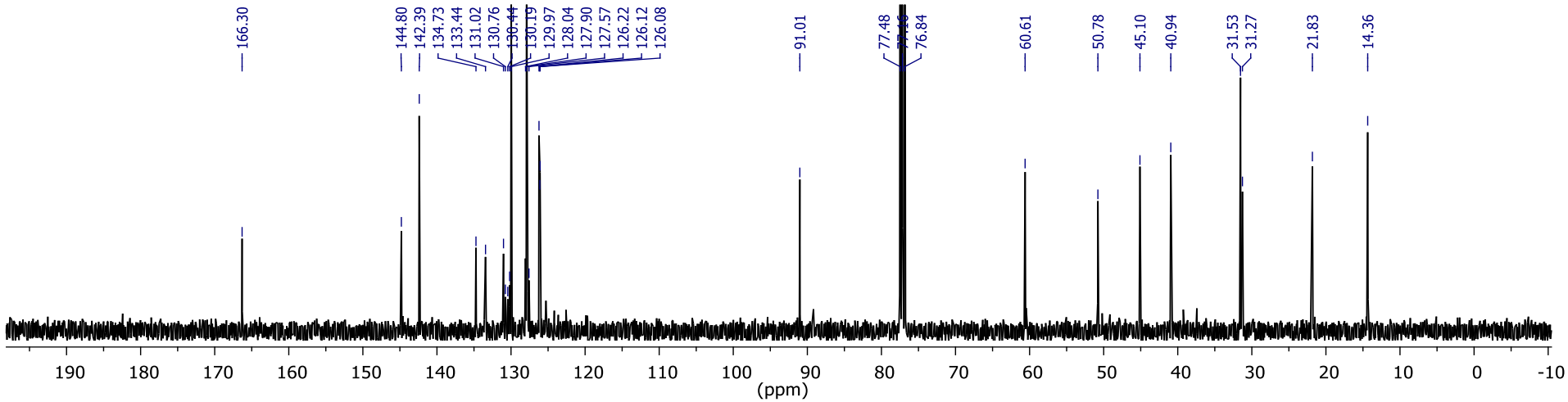
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-6-nitro-1-tosyl-5-(4-(trifluoromethyl)phenyl)-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14d

Note: a small amount of the Z-alkene (E:Z ~ 20:1) is observed (J = 11.6 Hz), in addition to the 8:1 ratio of diastereomers from the cycloaddition.

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



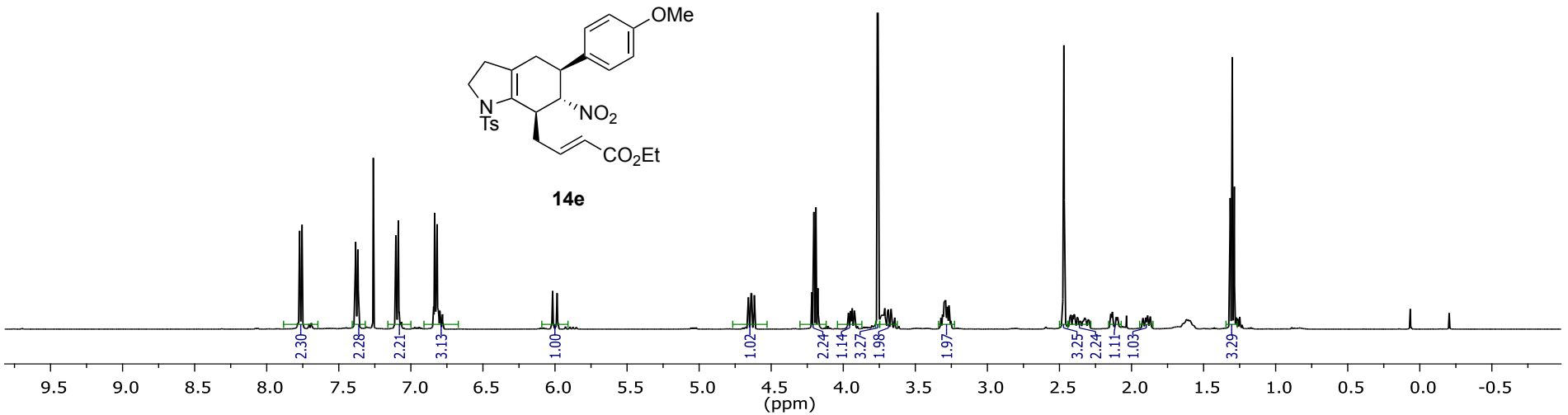
^{13}C NMR (101 MHz, $CDCl_3$)



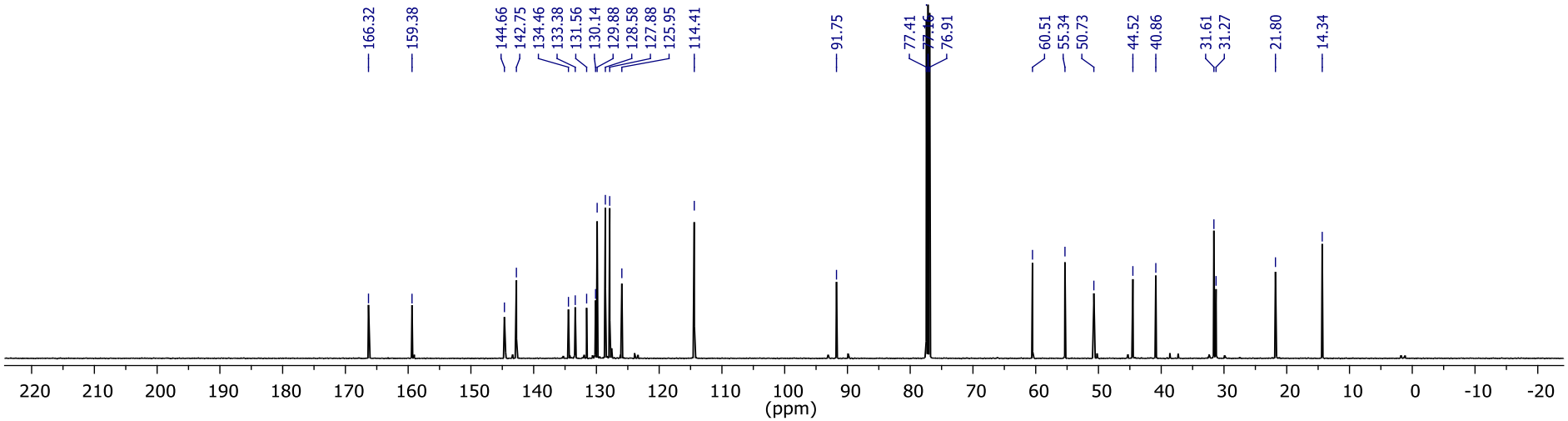
(*E*)-Ethyl 4-((5*S*,6*S*,7*R*)-5-(4-methoxyphenyl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14e

Note: a small amount of the Z-alkene (E:Z ~ 30:1) is observed (J = 11.6 Hz), but no diastereomer from the cycloaddition could be detected.

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



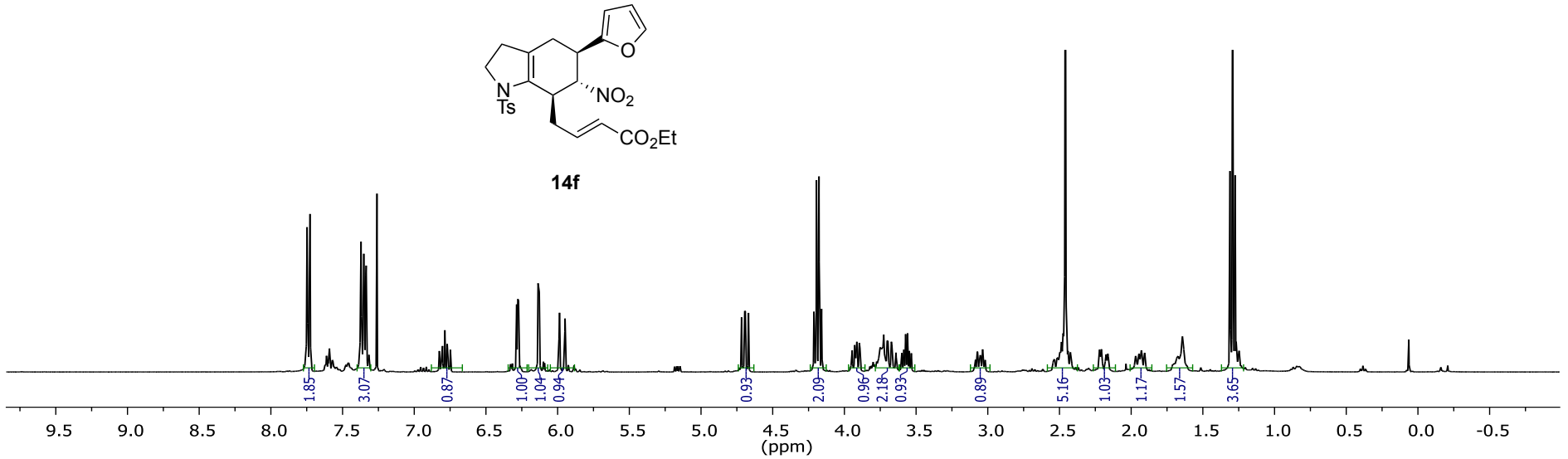
^{13}C NMR (101 MHz, $CDCl_3$)



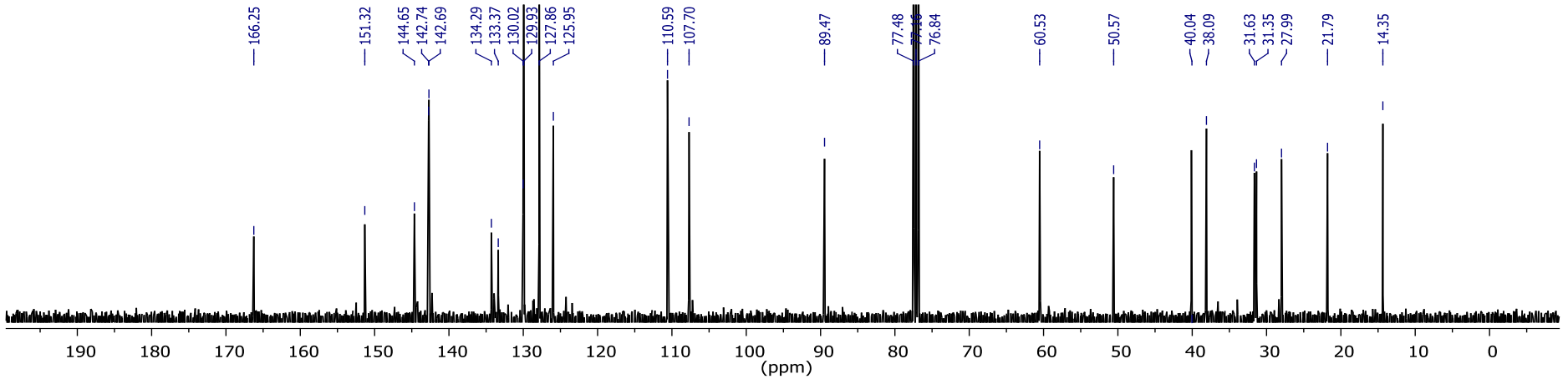
(*E*)-Ethyl 4-((5*R*,6*R*,7*R*)-5-(furan-2-yl)-6-nitro-1-tosyl-2,3,4,5,6,7-hexahydro-1H-indol-7-yl)but-2-enoate, 14f

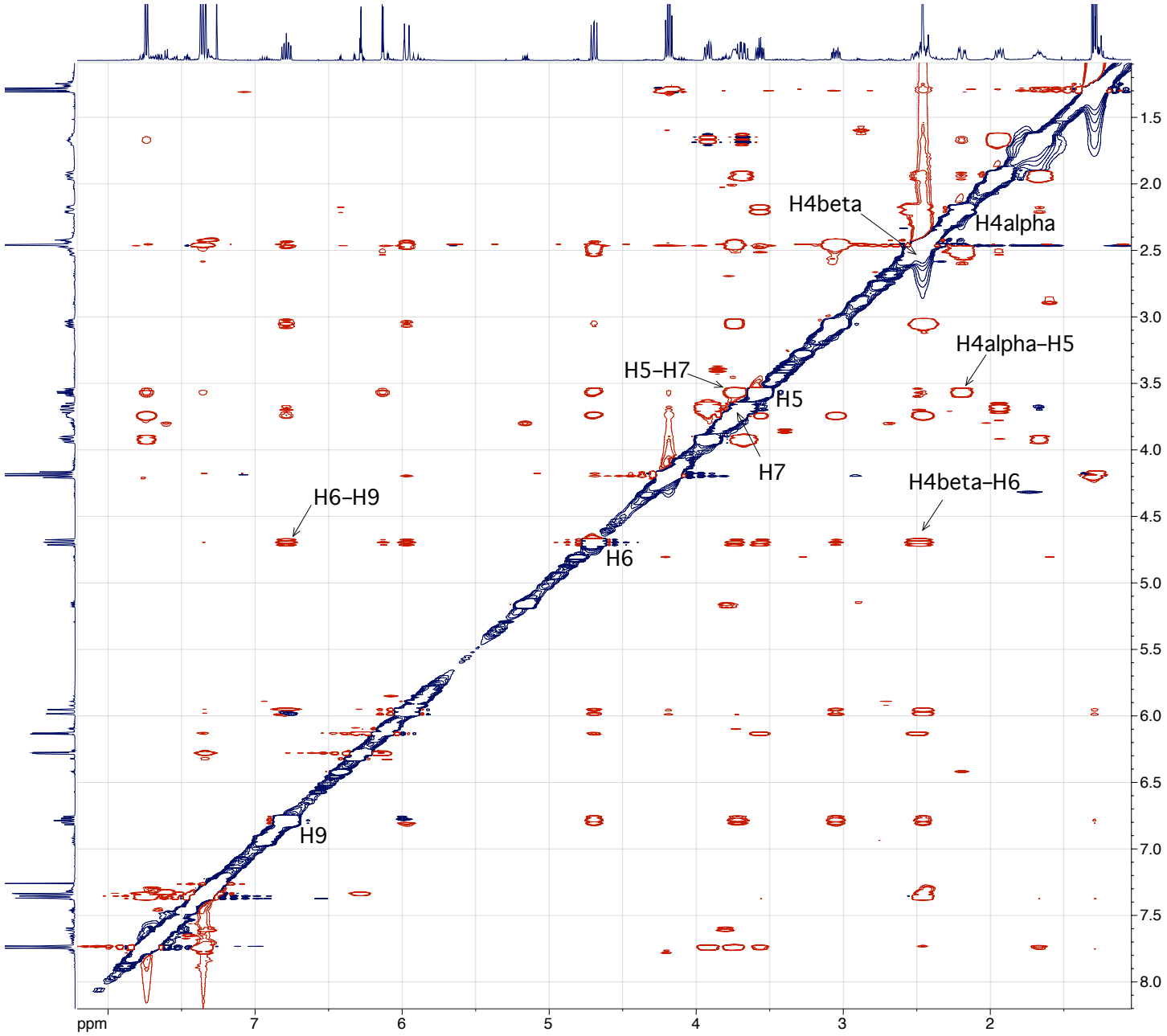
Note: a small amount of the Z-alkene (E:Z ~ 20:1) is observed (J = 11.6 Hz), in addition to the 9:1 ratio of diastereomers from the cycloaddition.

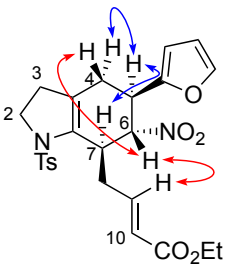
^{1}H NMR (400 MHz, $CDCl_3$)



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

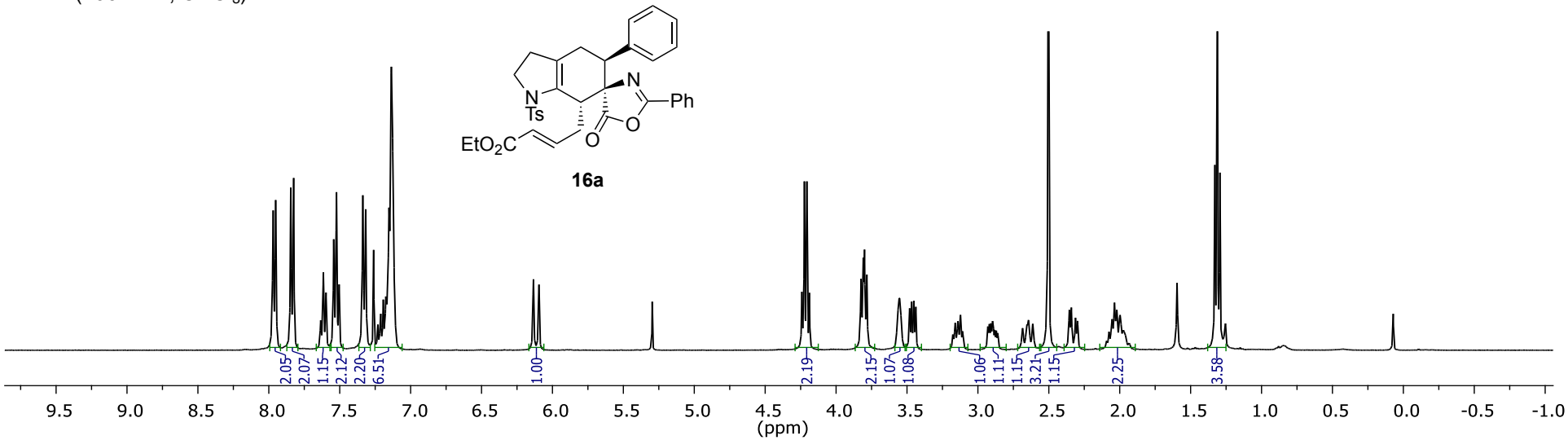



H4beta
H4alpha
H4alpha–H5
H5–H7
H5
H7
H6–H9
H6
H4beta–H6
H9
ppm
7
6
5
4
3
2
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

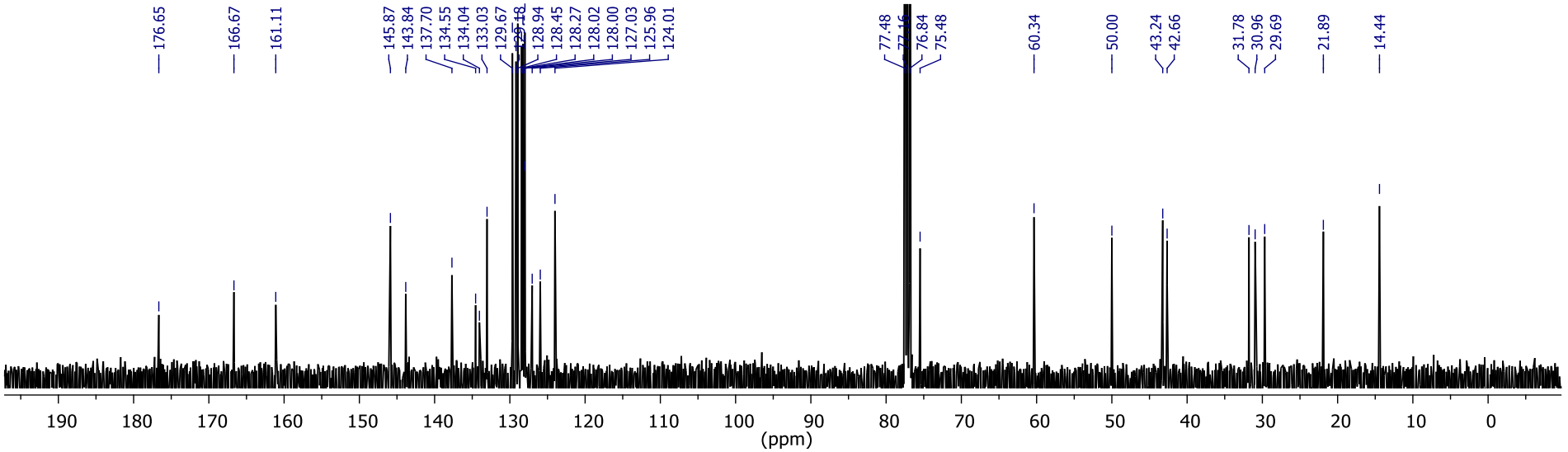

H
H
H
3
4
O
2
H
6
NO2
N
Ts
7
H
H
10
CO2Et

(*E*)-Ethyl 4-((4'*R*,5*S*,7*R*)-5'-oxo-2',5-diphenyl-1-tosyl-1,2,3,4,5,7-hexahydro-5'H-spiro[indole-6,4'-oxazol]-7-yl)but-2-enoate, 16a

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

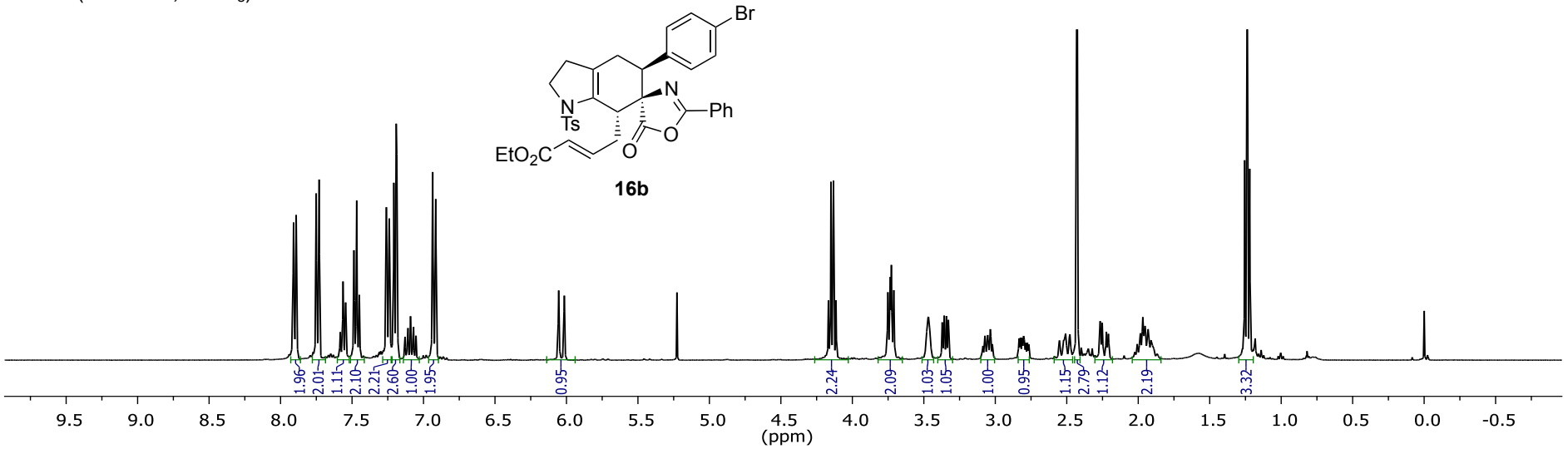


^{13}C NMR (101 MHz, $CDCl_3$)

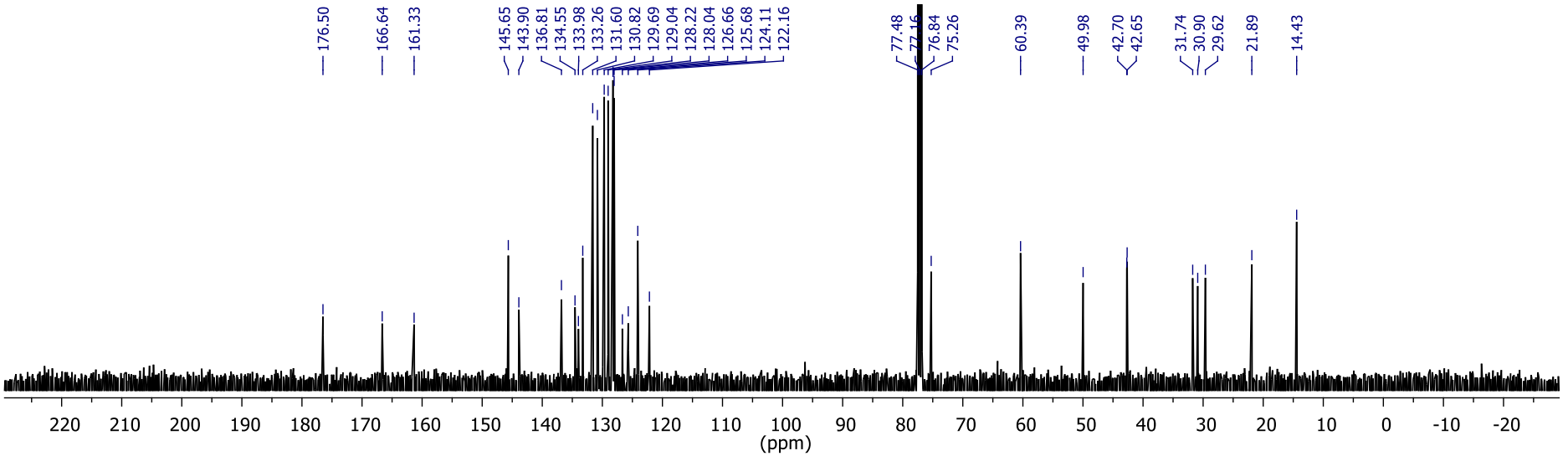


(*E*)-Ethyl 4-((4'*R*,5*S*,7*R*)-5-(4-bromophenyl)-5'-oxo-2'-phenyl-1-tosyl-1,2,3,4,5,7-hexahydro-5'H-spiro[indole-6,4'-oxazol]-7-yl)but-2-enoate, 16b

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

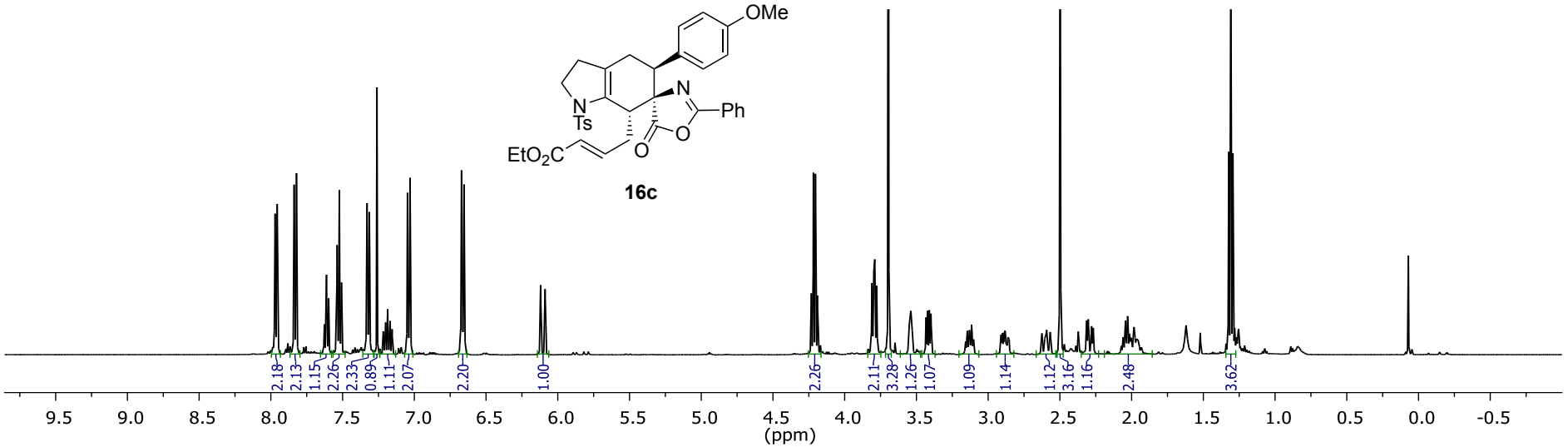


^{13}C NMR (101 MHz, $CDCl_3$)

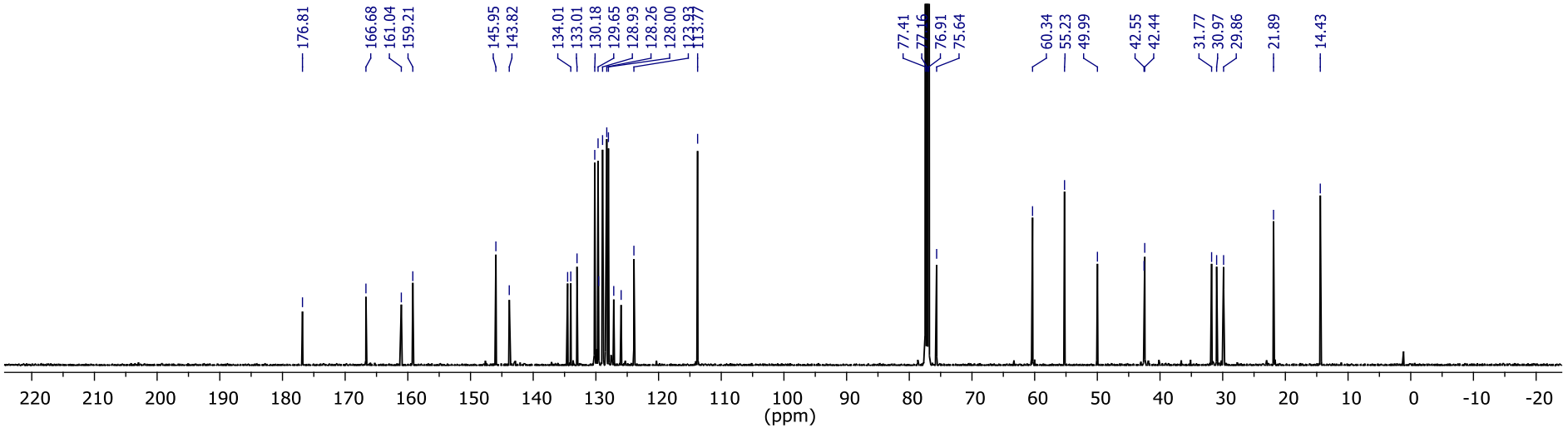


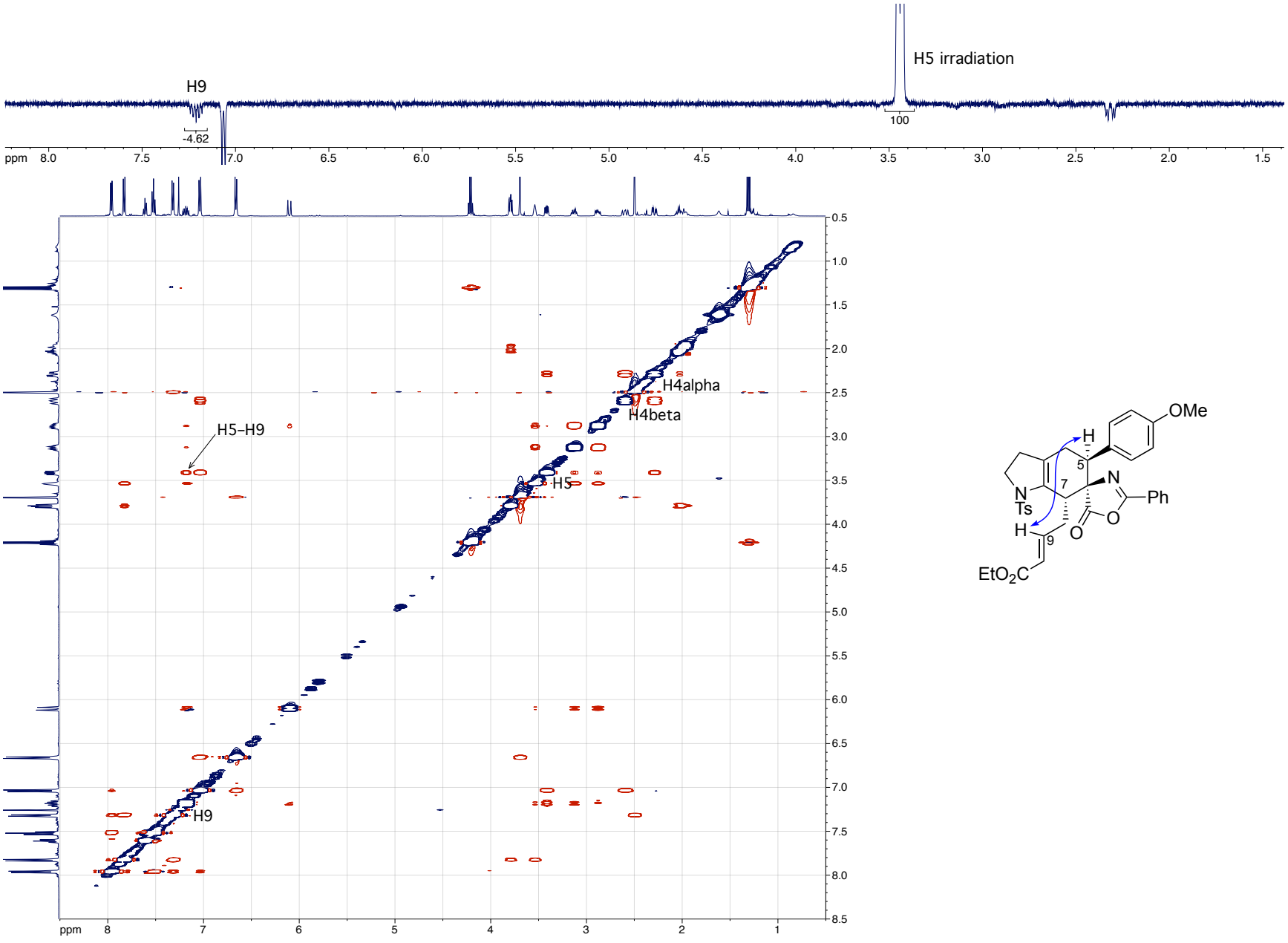
(*E*)-Ethyl 4-((4'*R*,5*S*,7*R*)-5-(4-methoxyphenyl)-5'-oxo-2'-phenyl-1-tosyl-1,2,3,4,5,7-hexahydro-5'H-spiro[indole-6,4'-oxazol]-7-yl)but-2-enoate, 16c

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



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

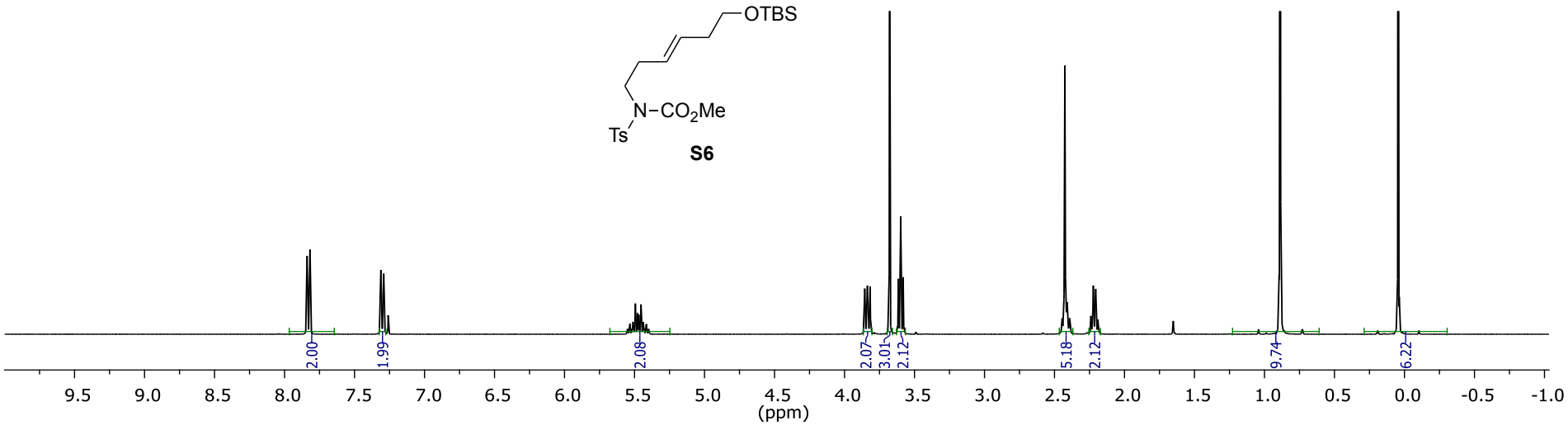



H5 irradiation
H9
-4.62
100
ppm 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
H4alpha
H4beta
H5–H9
H5
H9
ppm 8 7 6 5 4 3 2 1
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
OMe
H
5
7
N
Ts
N
Ph
O
H
O
9
EtO2C

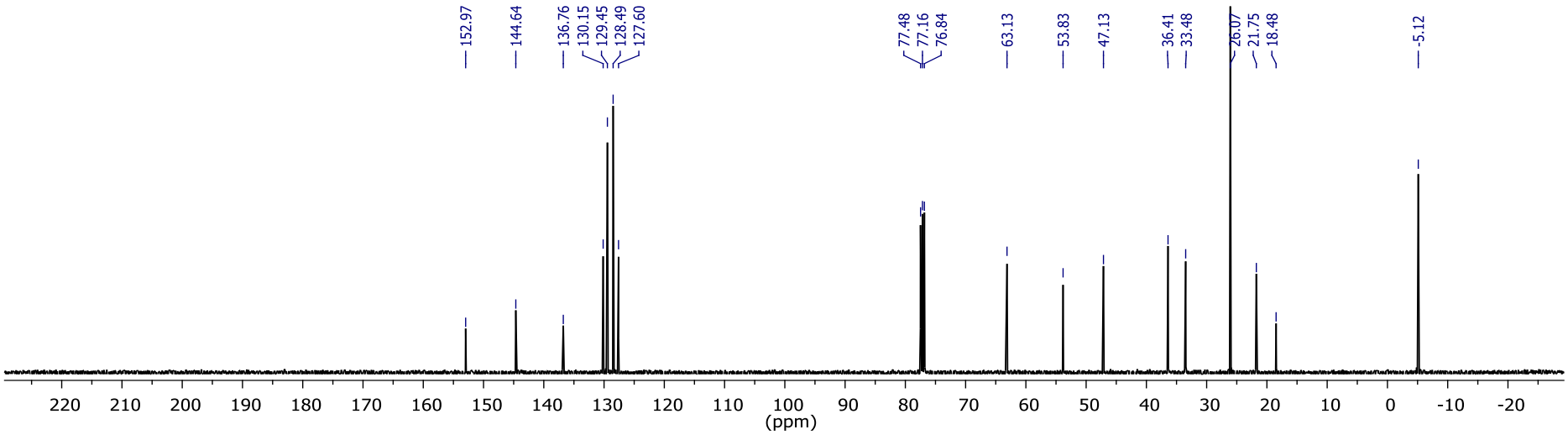
*3.3 Intermediates in the synthesis of dienals **4a**-**d** and 8**a***

(*E*)-Methyl (6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl)(tosyl)carbamate, S6

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

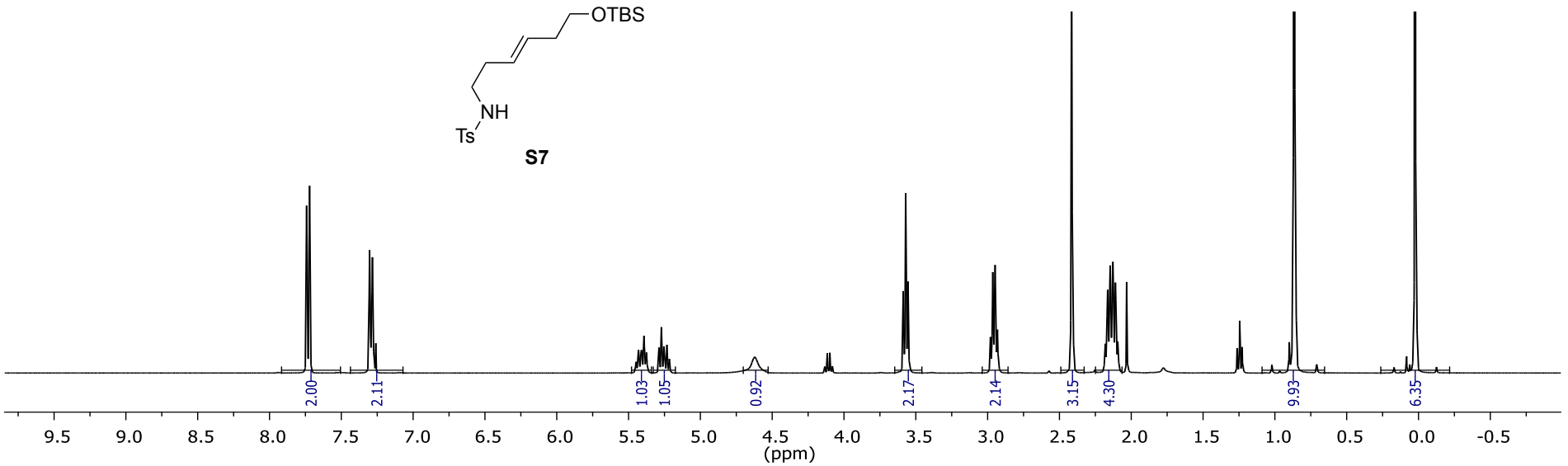


^{13}C NMR (101 MHz, $CDCl_3$)

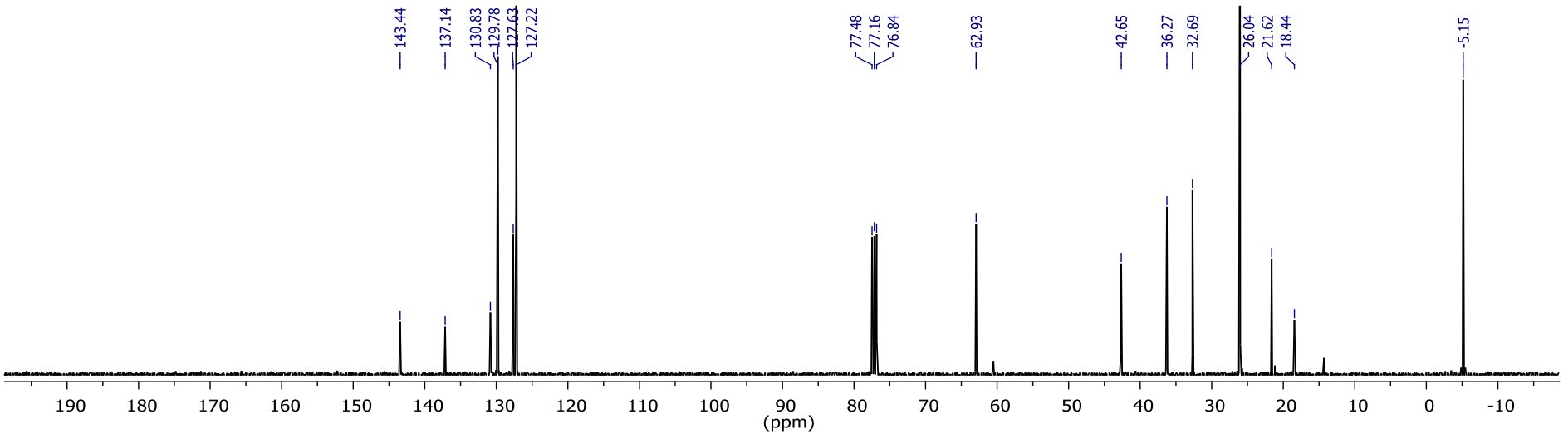


(*E*)-*N*-(6-((tert-butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methylbenzenesulfonamide, S7

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

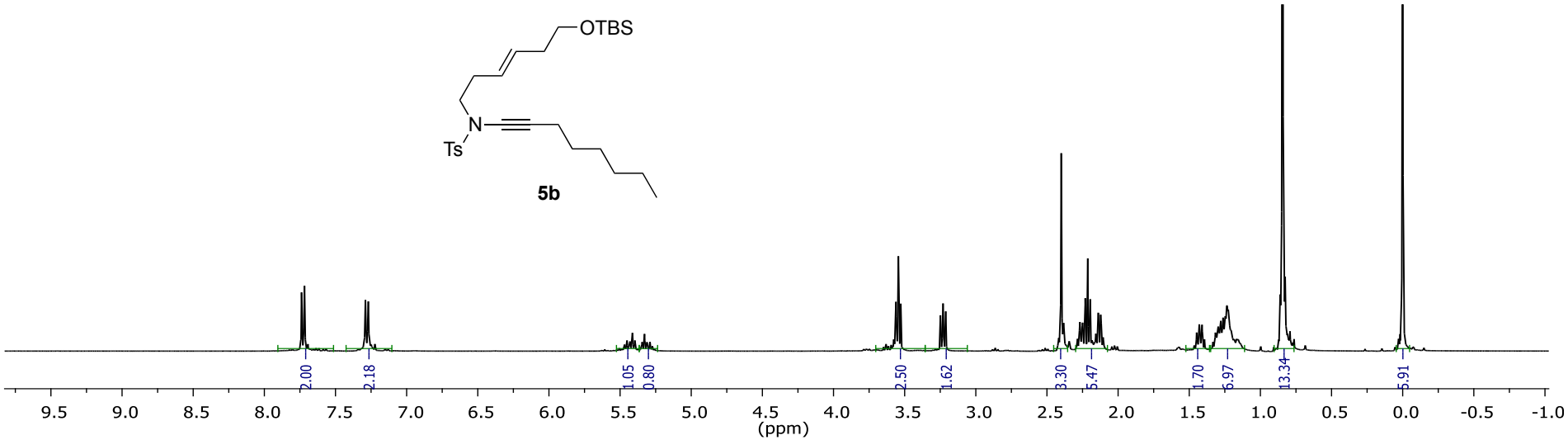


^{13}C NMR (101 MHz, $CDCl_3$)

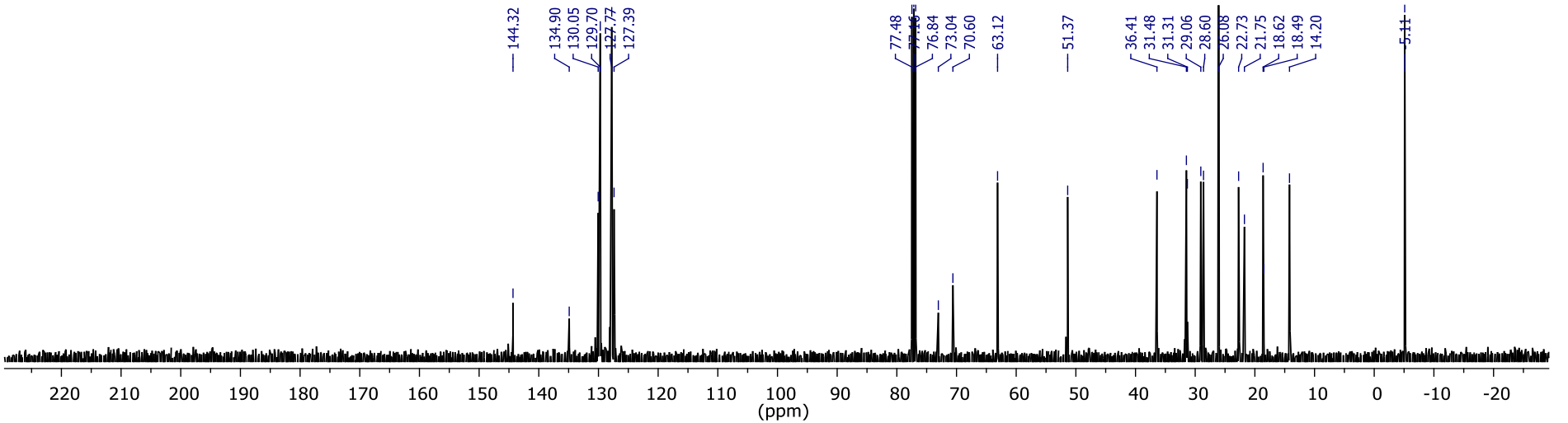


(*E*)-*N*-(6-((tert-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methyl-*N*-(oct-1-yn-1-yl)benzenesulfonamide, 5b

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

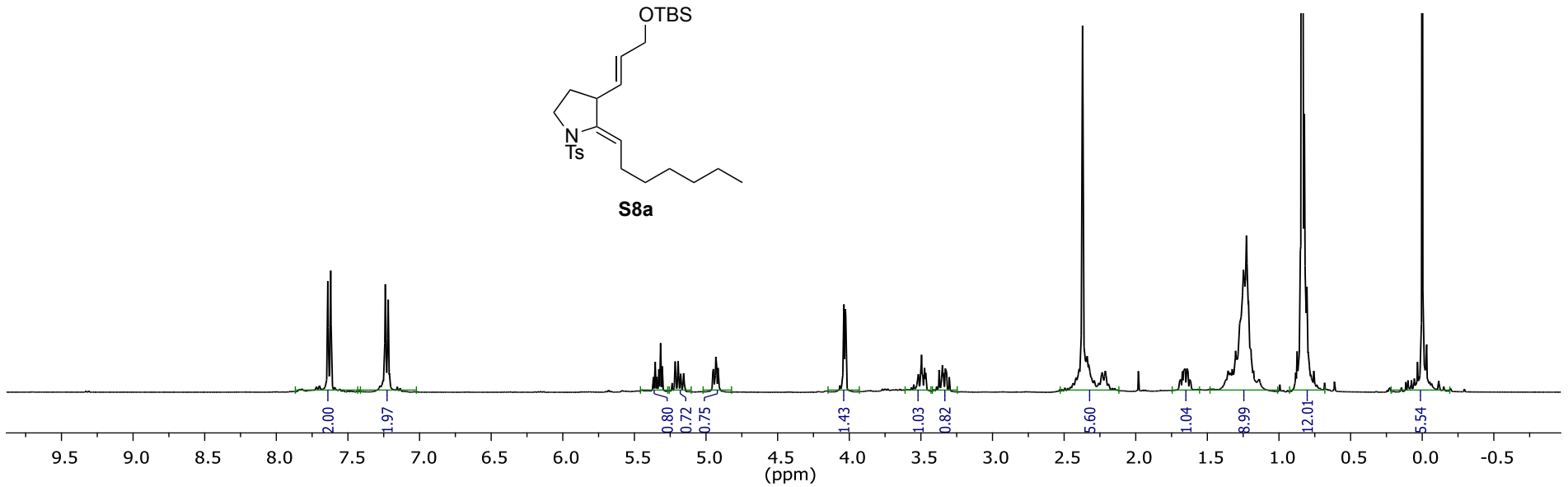


^{13}C NMR (101 MHz, $CDCl_3$)

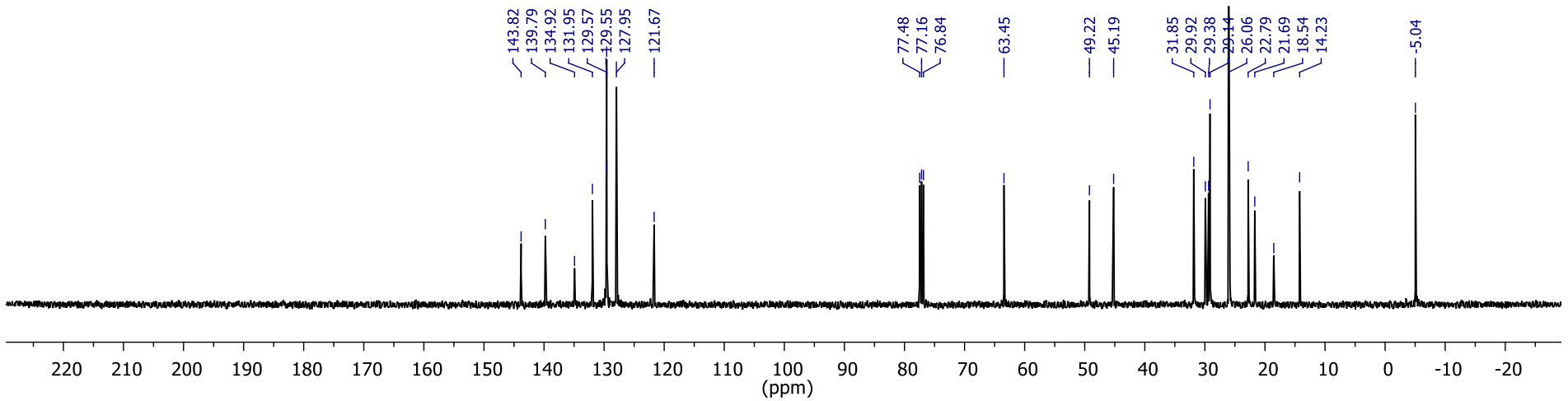


(*Z*)-3-((*E*)-3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-heptylidene-1-tosylpyrrolidine, S8a

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

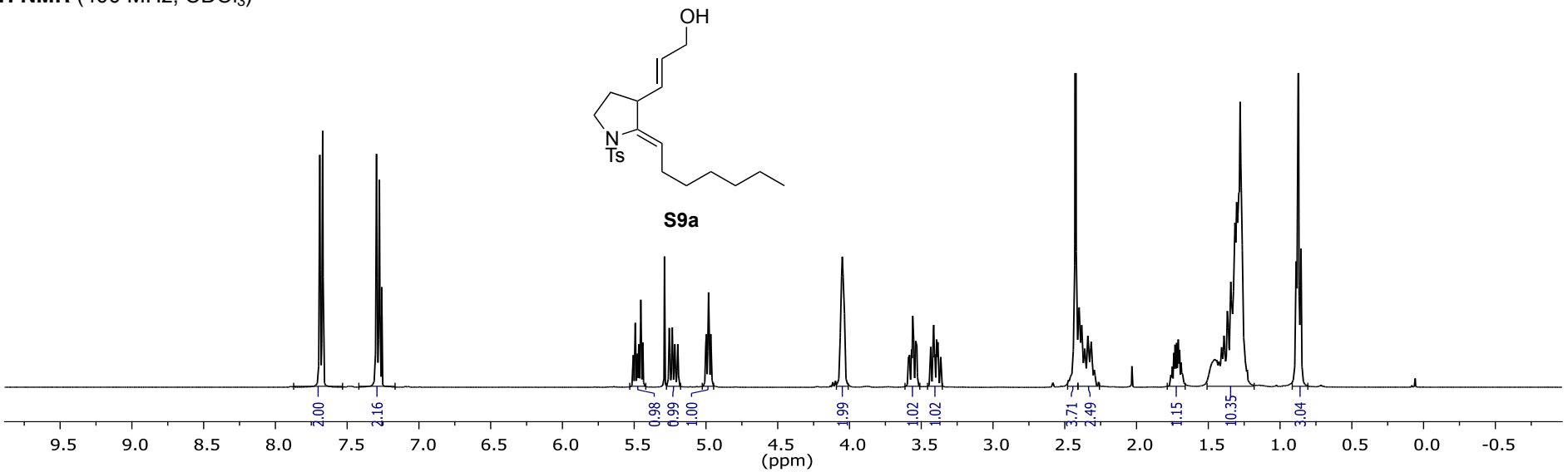


^{13}C NMR (101 MHz, $CDCl_3$)

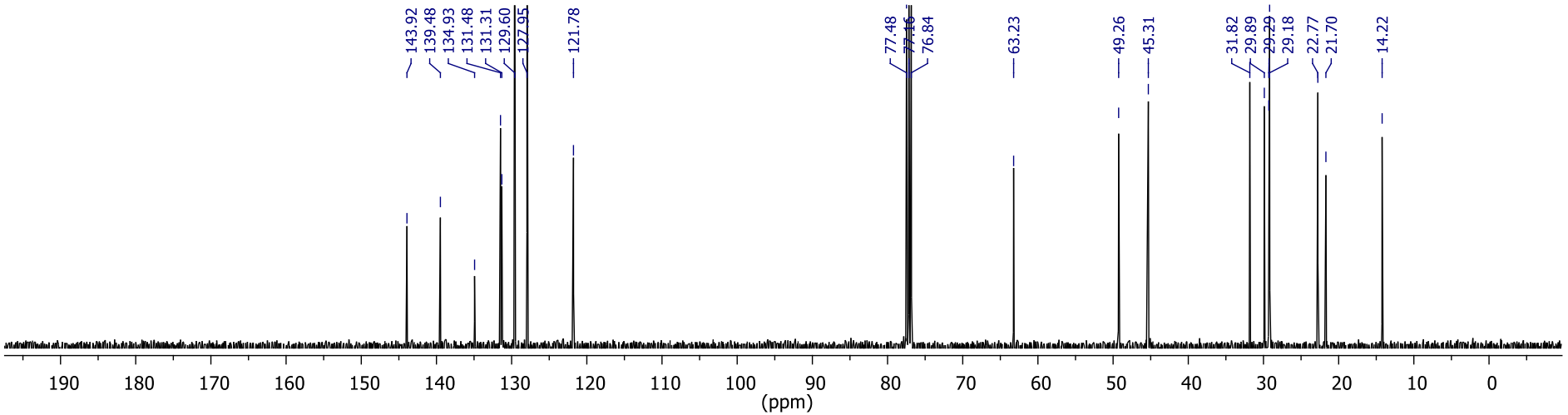


(*E*)-3-((*Z*)-2-heptylidene-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9a

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

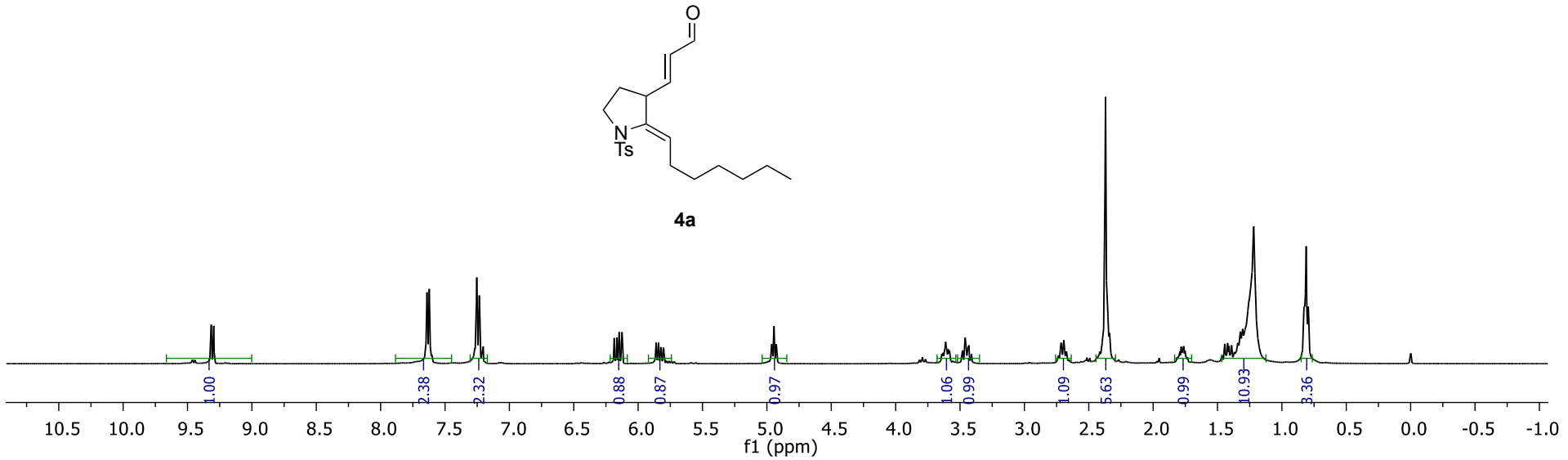


^{13}C NMR (101 MHz, $CDCl_3$)

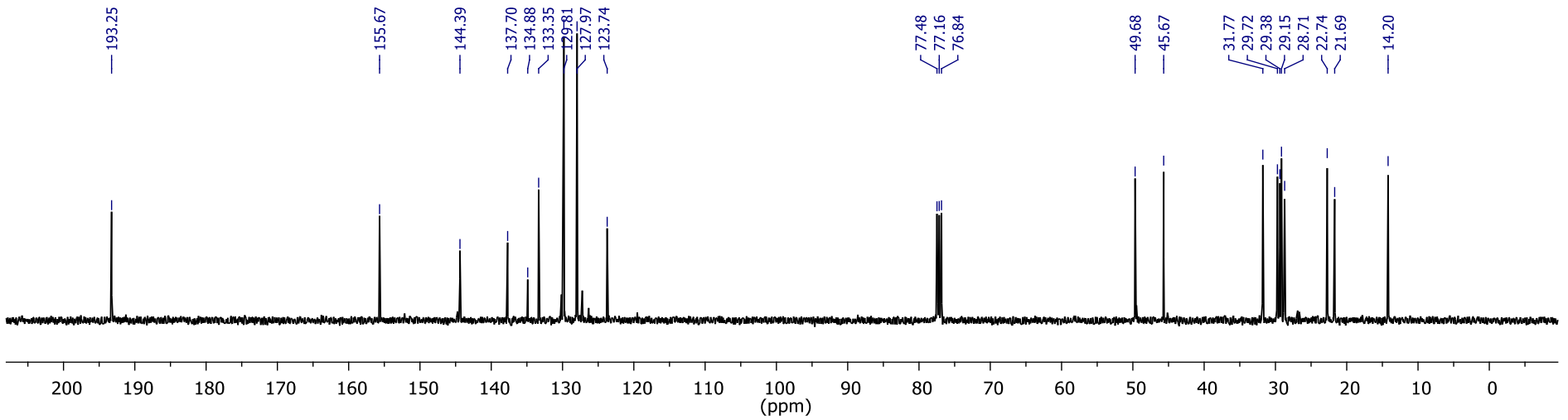


(*E*)-3-((*Z*)-2-heptylidene-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4a

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

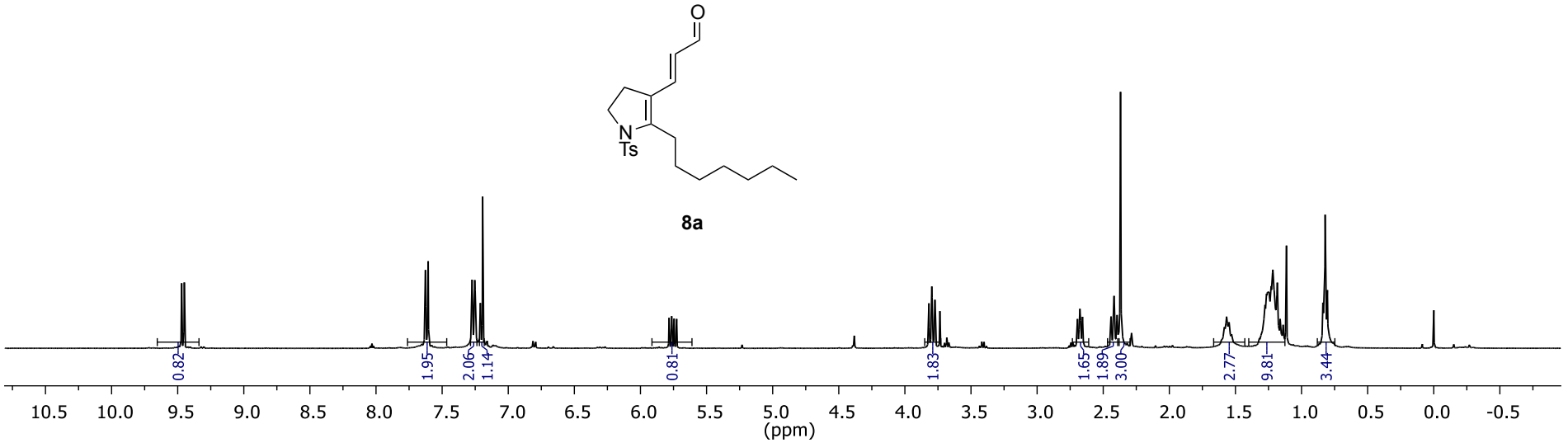


^{13}C NMR (101 MHz, $CDCl_3$)

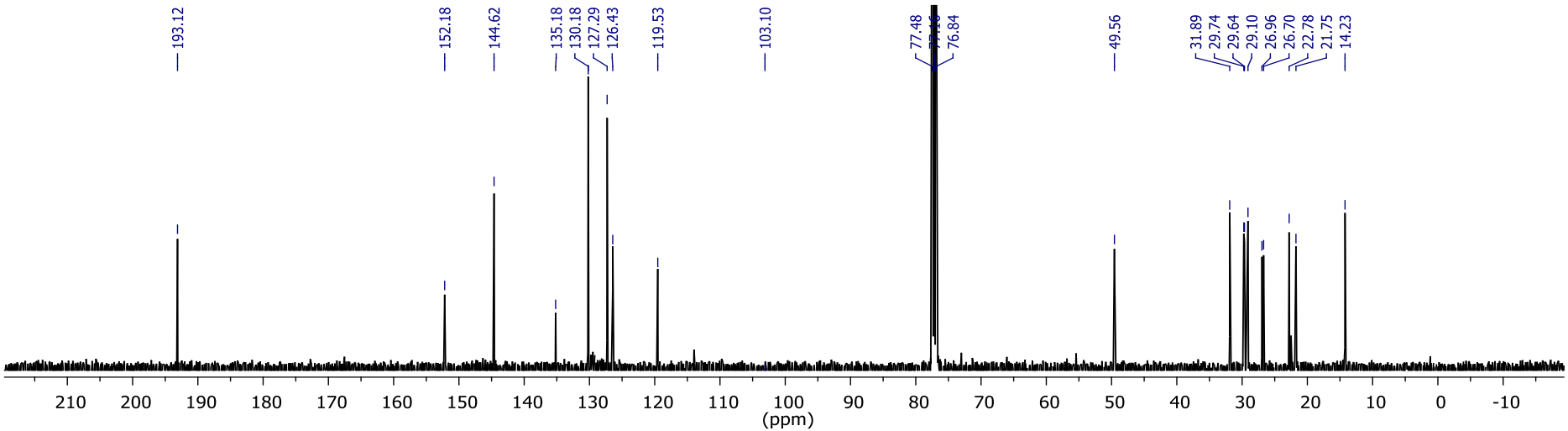


(*E*)-3-(2-heptyl-1-tosyl-4,5-dihydro-1H-pyrrol-3-yl)acrylaldehyde, 8a

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

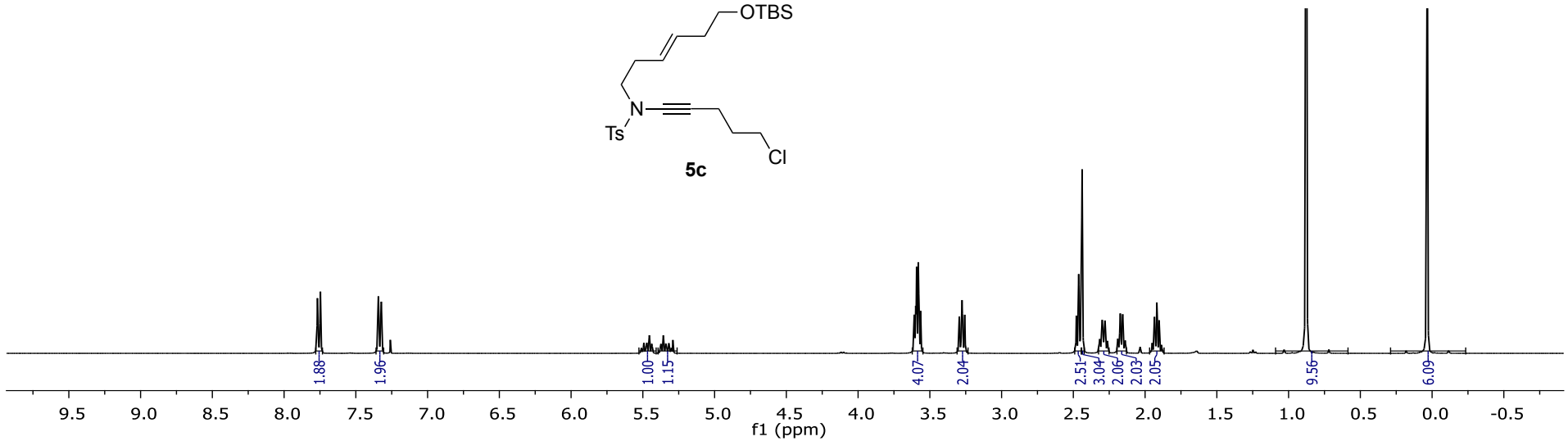


^{13}C NMR (101 MHz, $CDCl_3$)

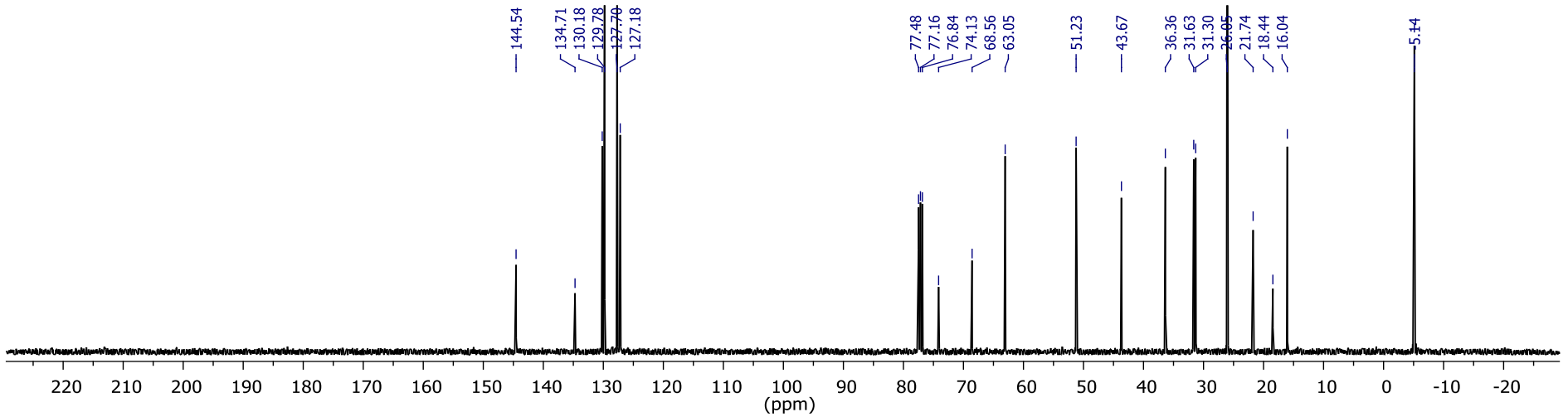


(*E*)-*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-*N*-(5-chloropent-1-yn-1-yl)-4-ethylbenzenesulfonamide, 5c

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

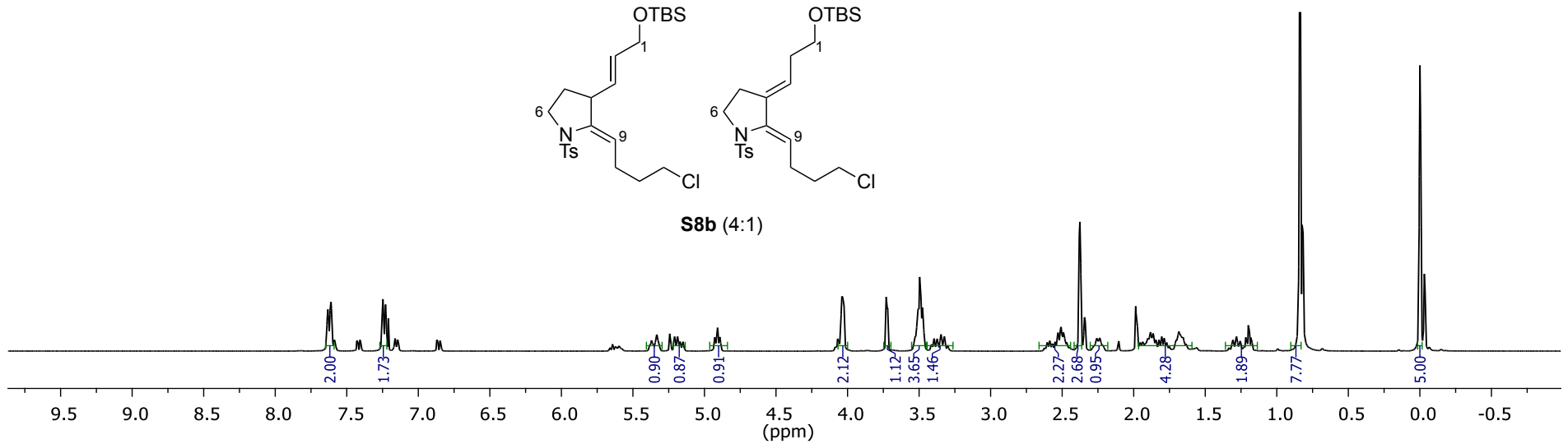


^{13}C NMR (101 MHz, $CDCl_3$)

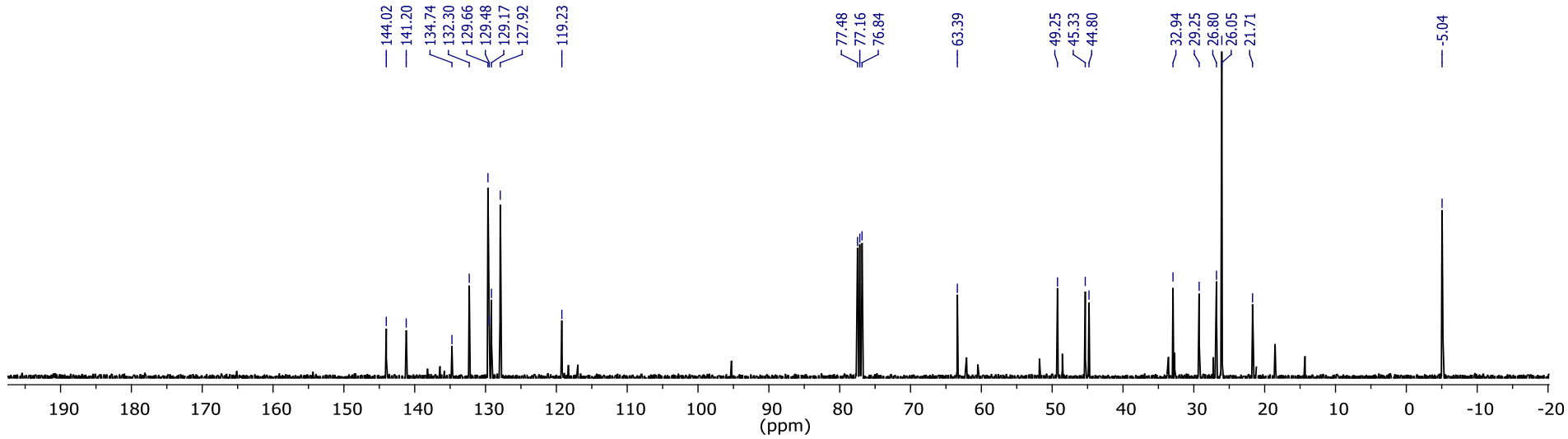


(*Z*)-3-((*E*)-3-((*tert*-Butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-(4-chlorobutylidene)-1-tosylpyrrolidine, S8b

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

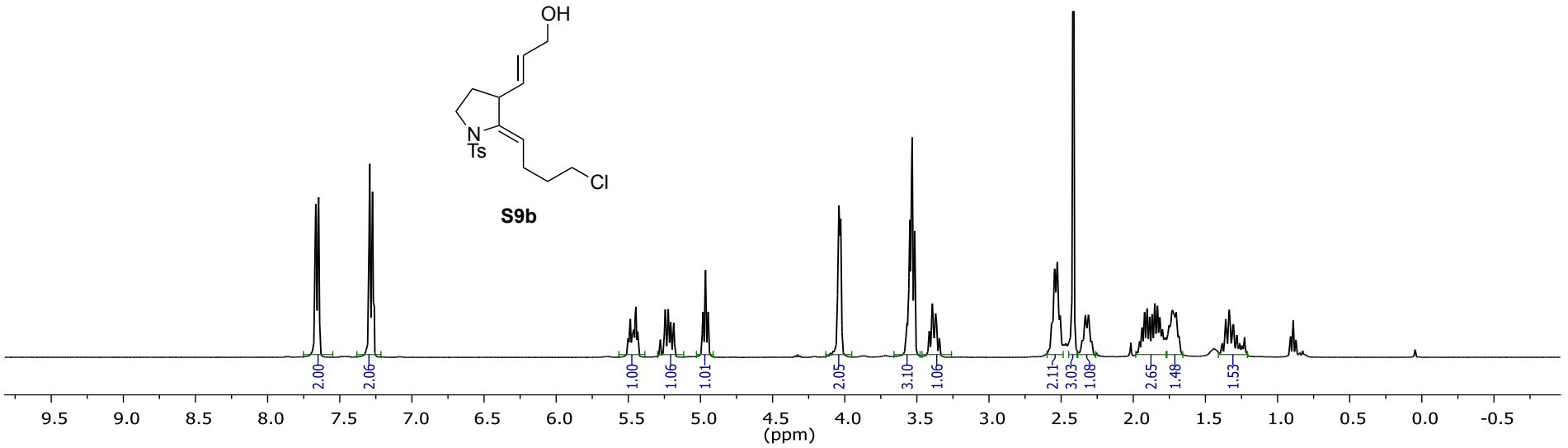


^{13}C NMR (101 MHz, $CDCl_3$)

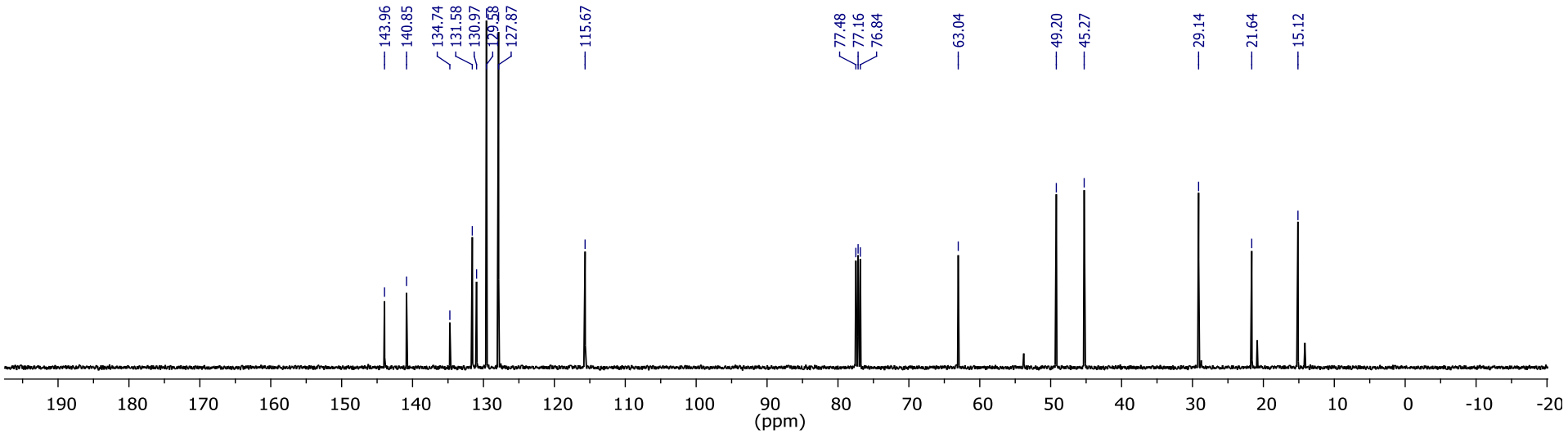


(*E*)-3-((*Z*)-2-(4-Chlorobutylidene)-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9b

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

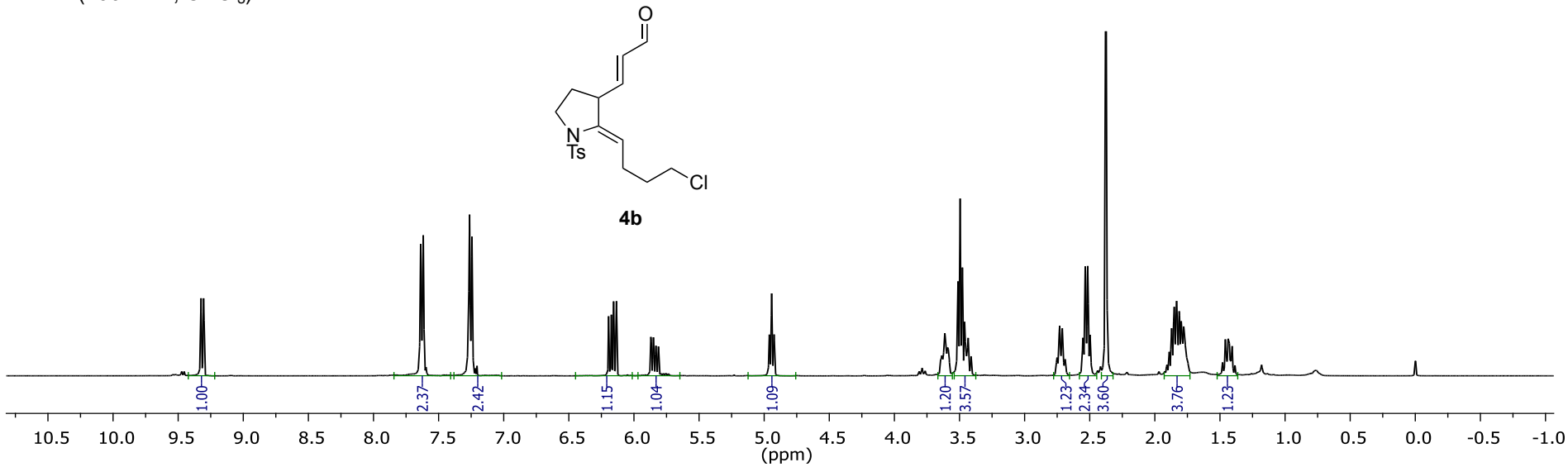


^{13}C NMR (101 MHz, $CDCl_3$)

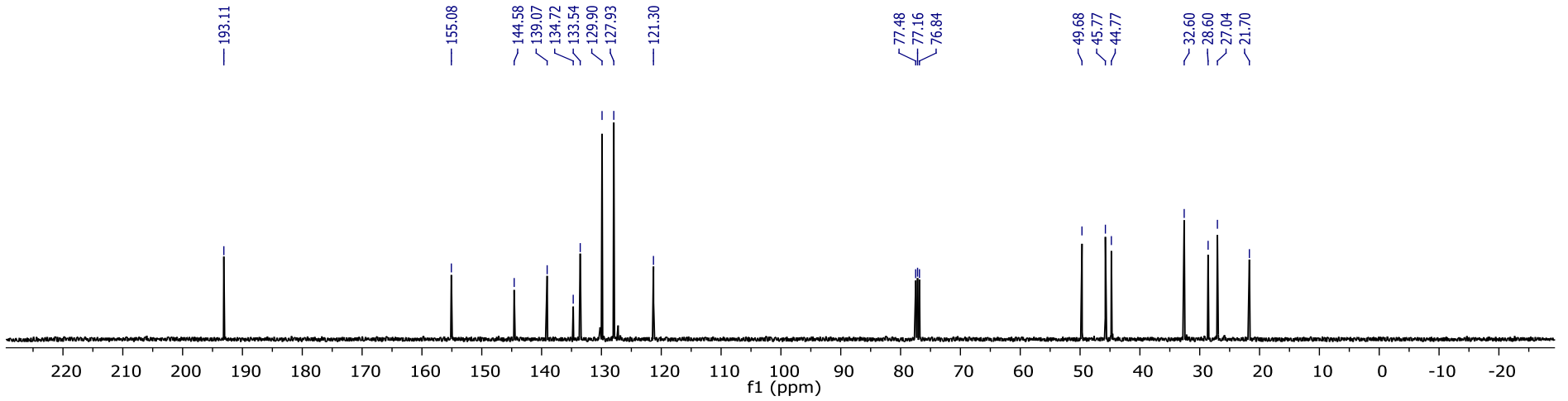


(*E*)-3-((*Z*)-2-(4-chlorobutylidene)-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4b

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

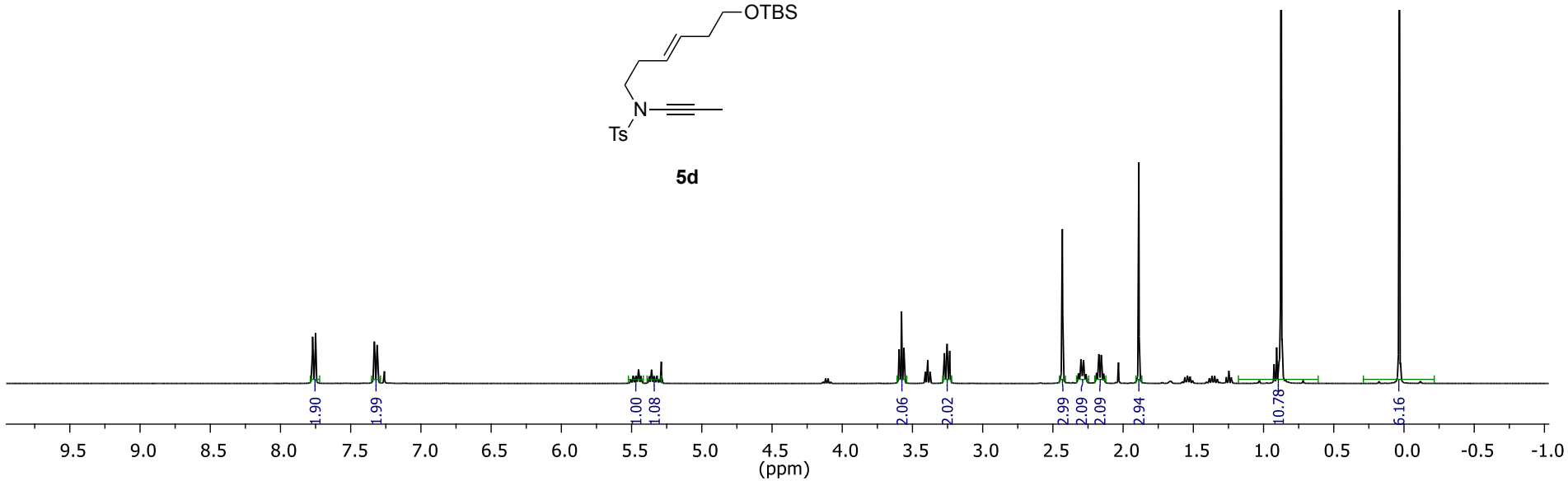


^{13}C NMR (101 MHz, $CDCl_3$)

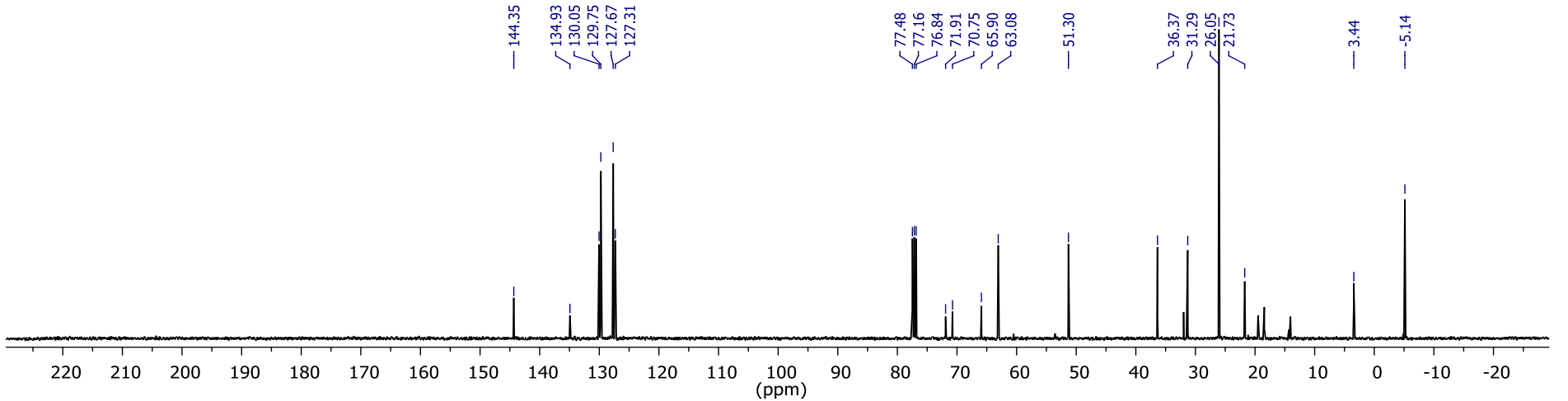


(*E*)-*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 5d

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

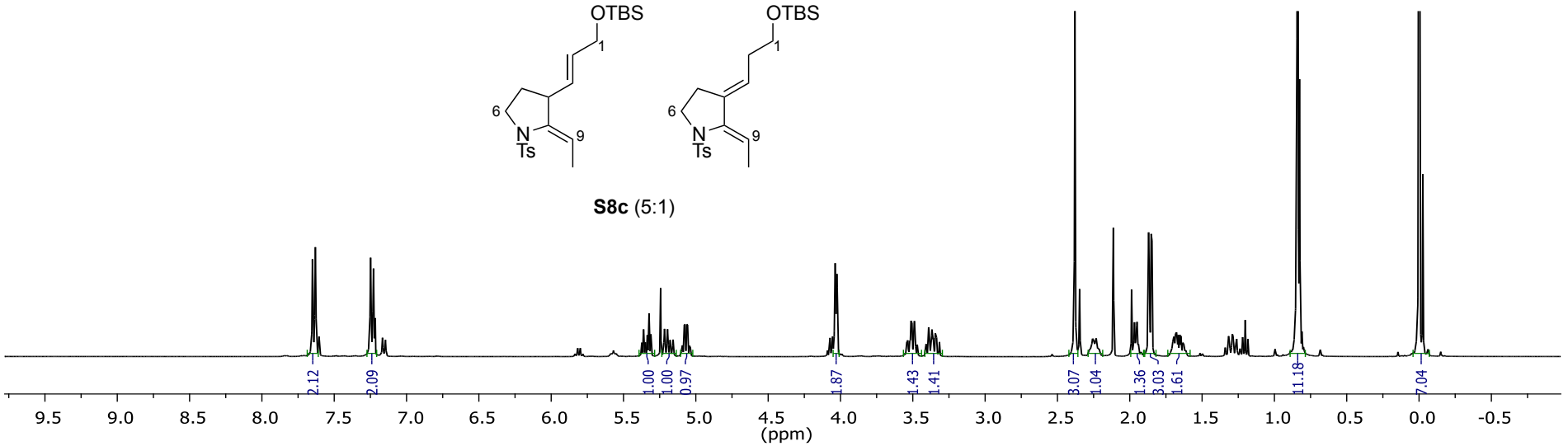


^{13}CNMR (101 MHz, $CDCl_3$)

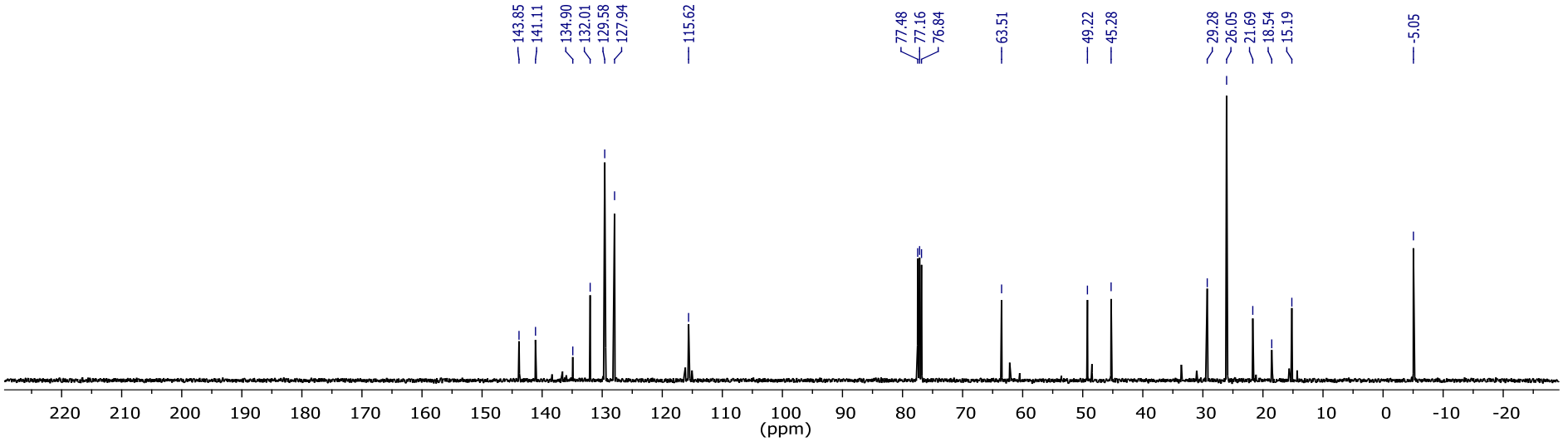


(*Z*)-3-((*E*)-3-((*tert*-Butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-ethylidene-1-tosylpyrrolidine, S8c

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

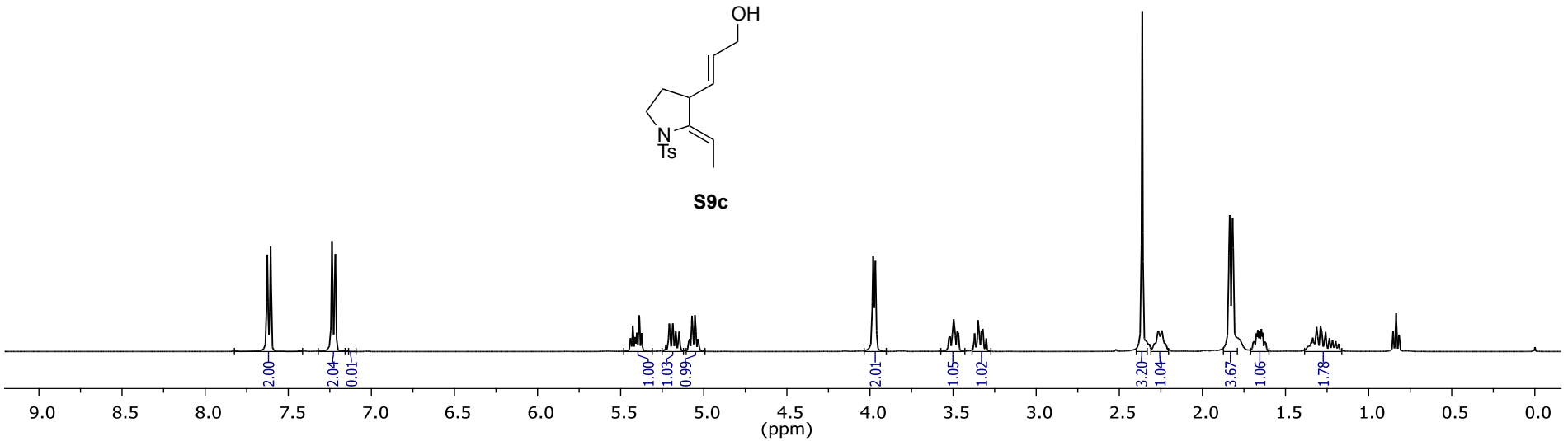


^{13}C NMR (101 MHz, $CDCl_3$)



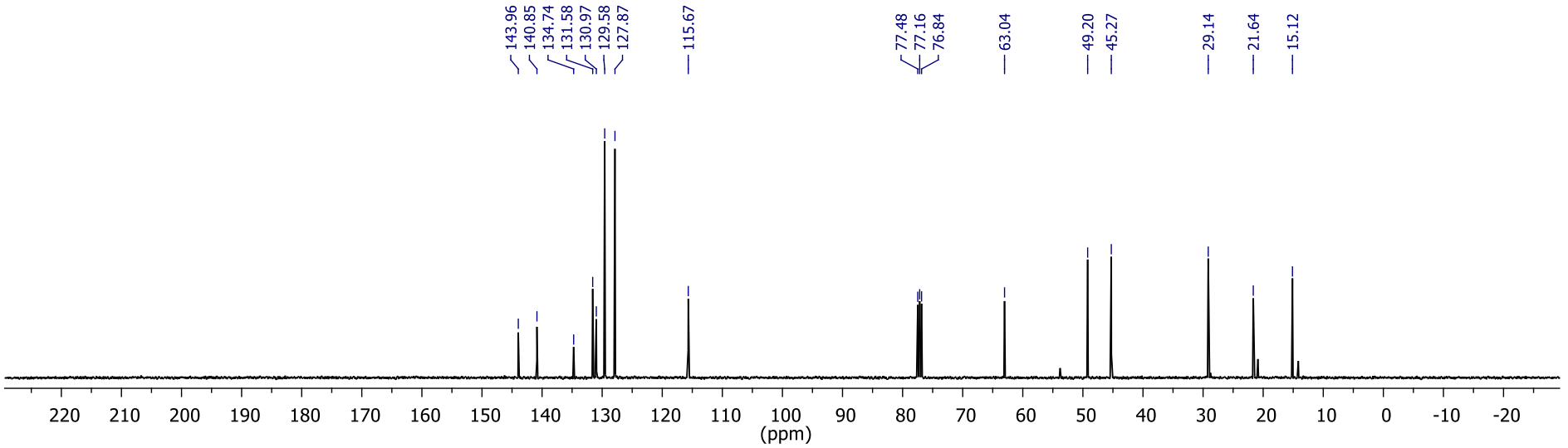
(*E*)-3-((*Z*)-2-Ethylidene-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9c

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



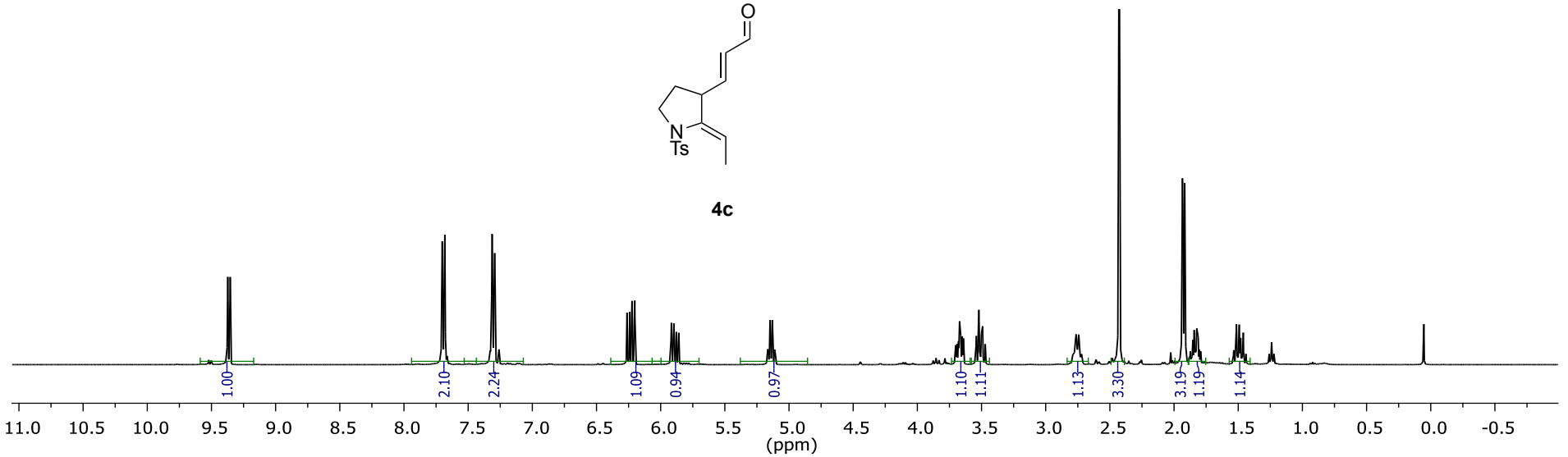
S9c

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

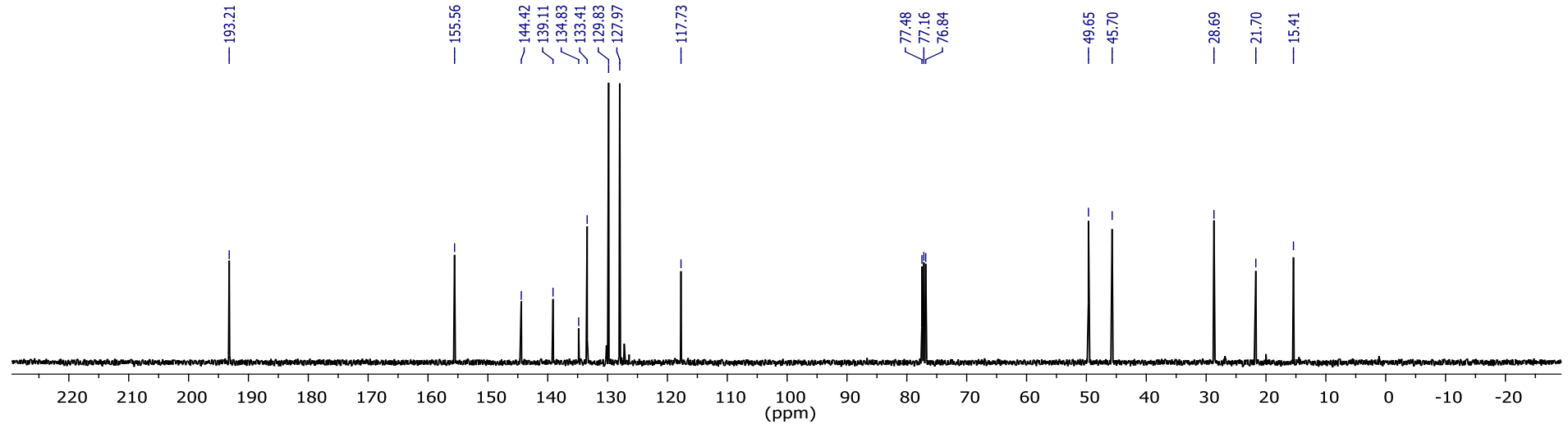


(*E*)-3-((*Z*)-2-Ethylidene-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4c

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

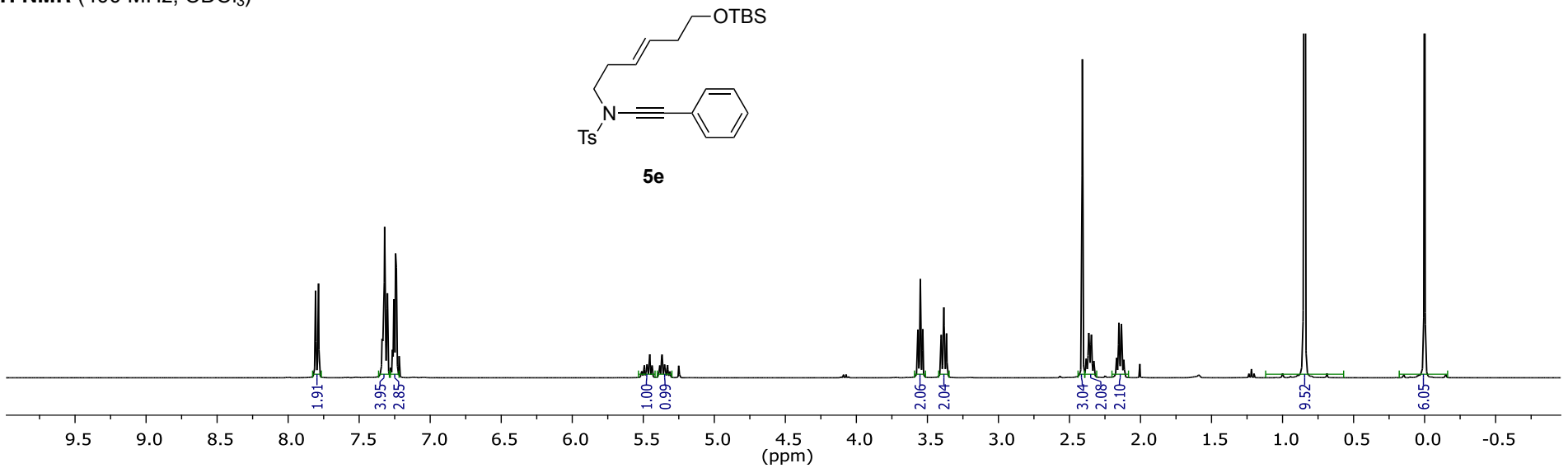


^{13}C NMR (101 MHz, $CDCl_3$)

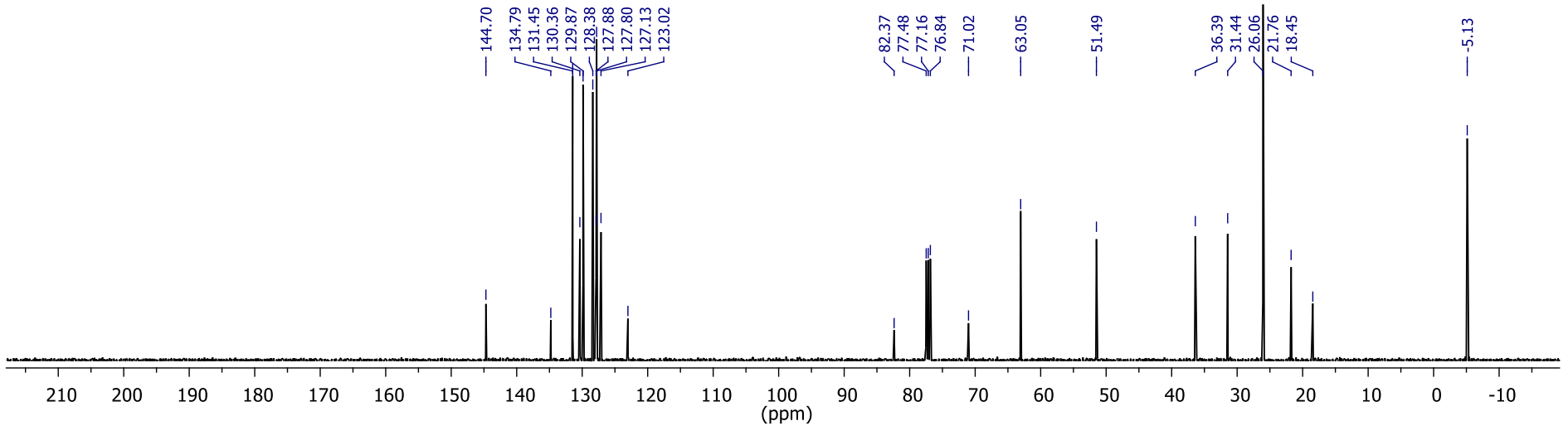


(*E*)-*N*-(6-((*tert*-Butyldimethylsilyl)oxy)hex-3-en-1-yl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide, 5e

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

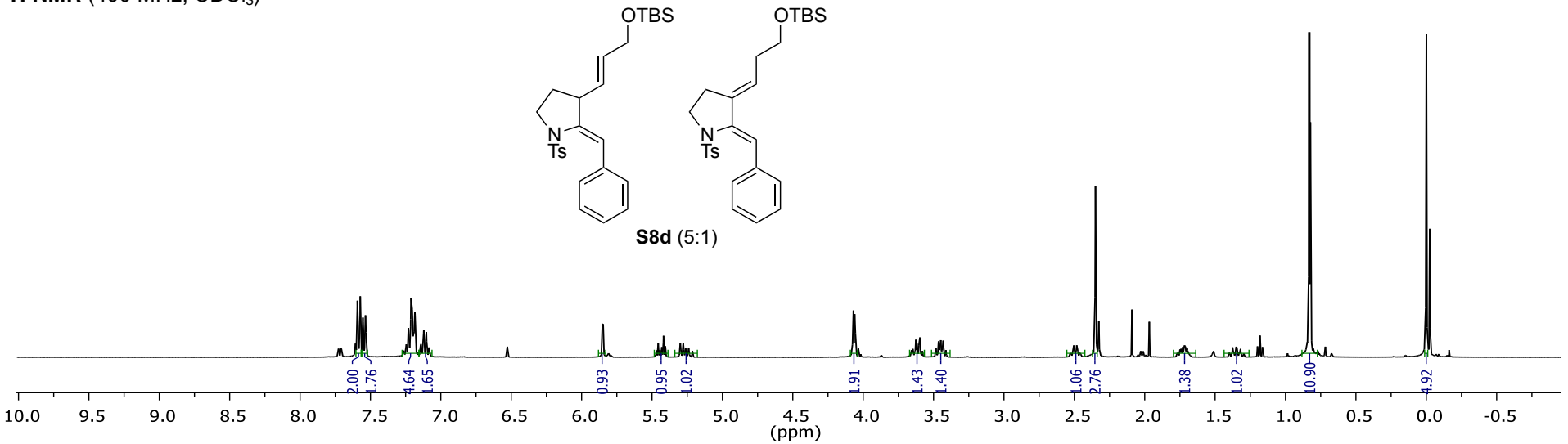


^{13}C NMR (101 MHz, $CDCl_3$)



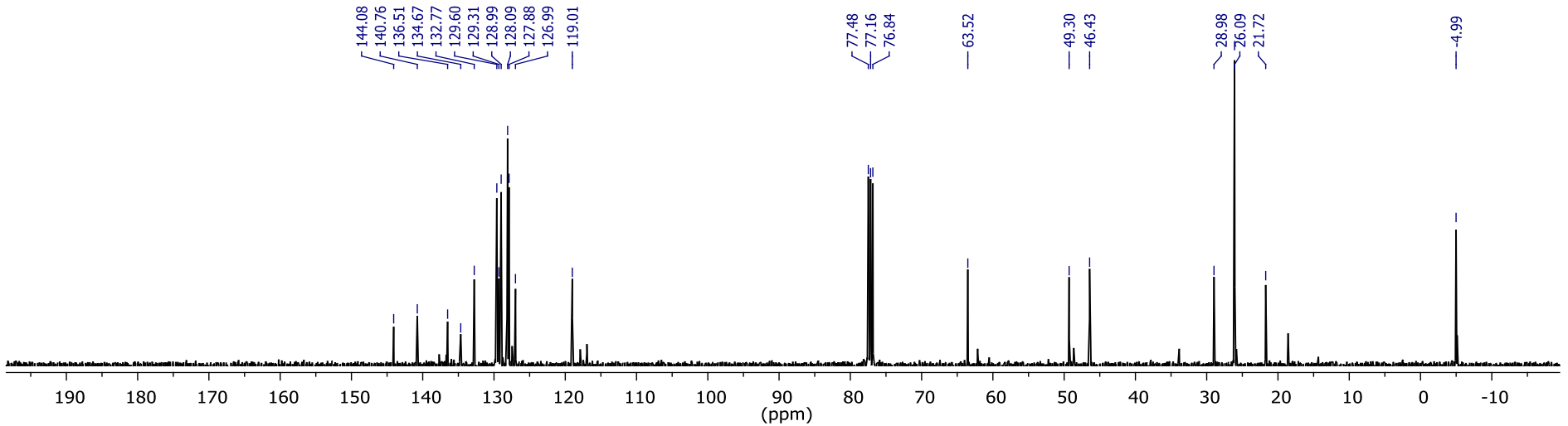
(*Z*)-2-Benzylidene-3-((*E*)-3-((tert-butyldimethylsilyl)oxy)prop-1-en-1-yl)-1-tosylpyrrolidine, S8d

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



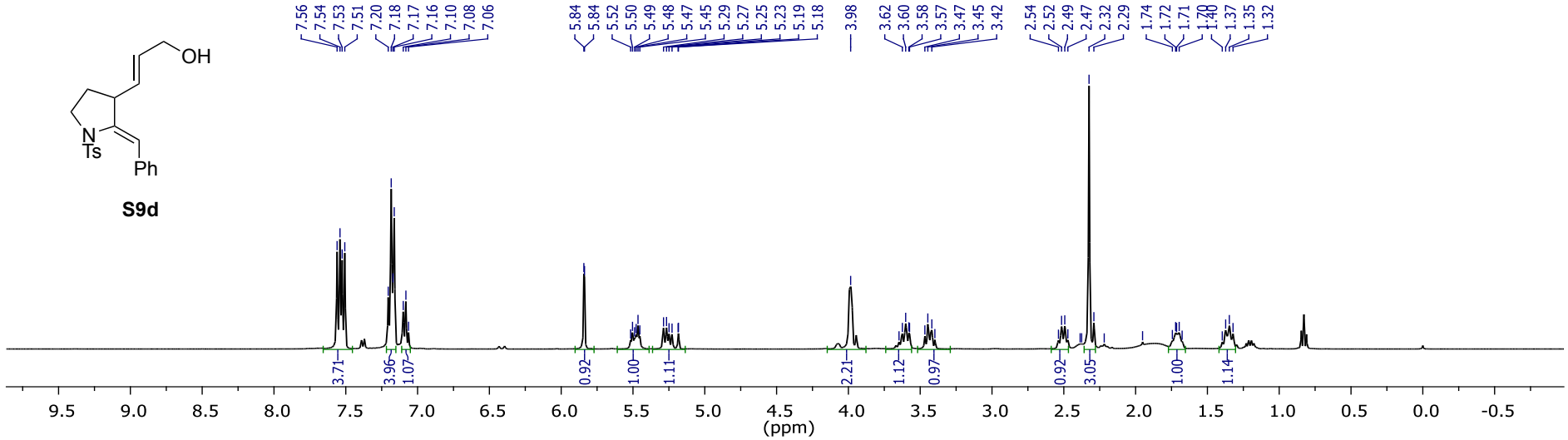
S8d (5:1)

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

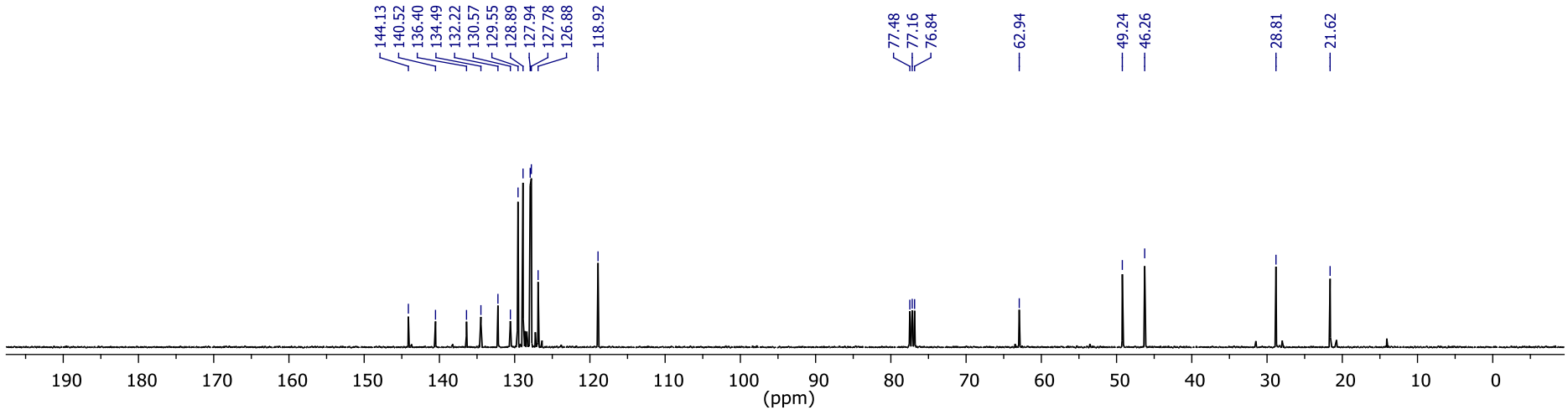


(*E*)-3-((*Z*)-2-Benzylidene-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S9d

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

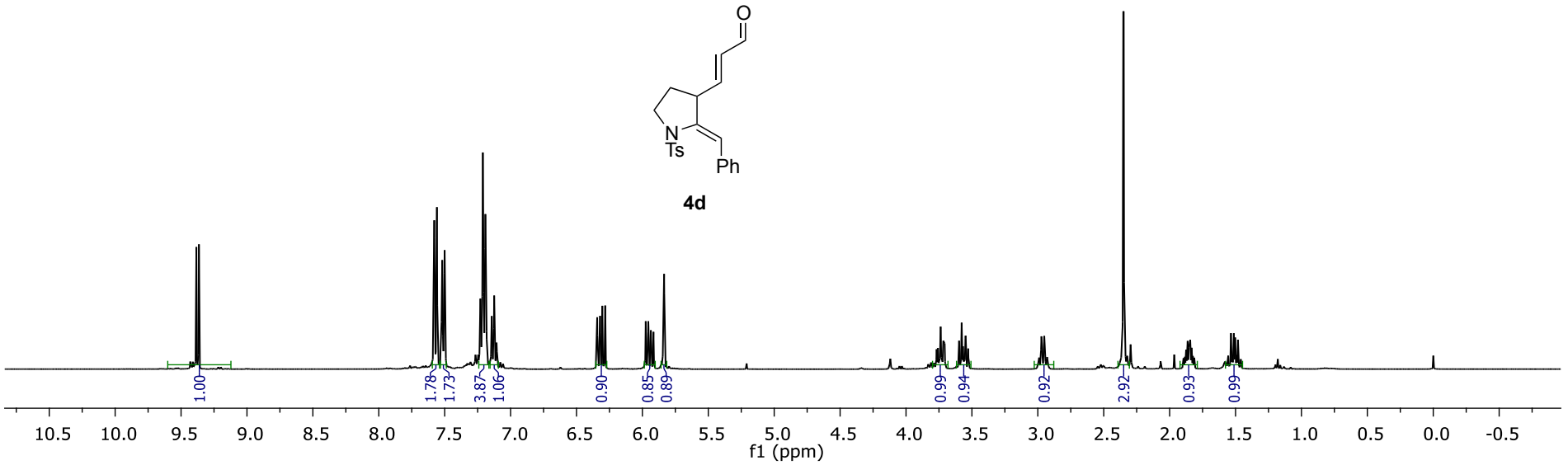


^{13}C NMR (101 MHz, $CDCl_3$)

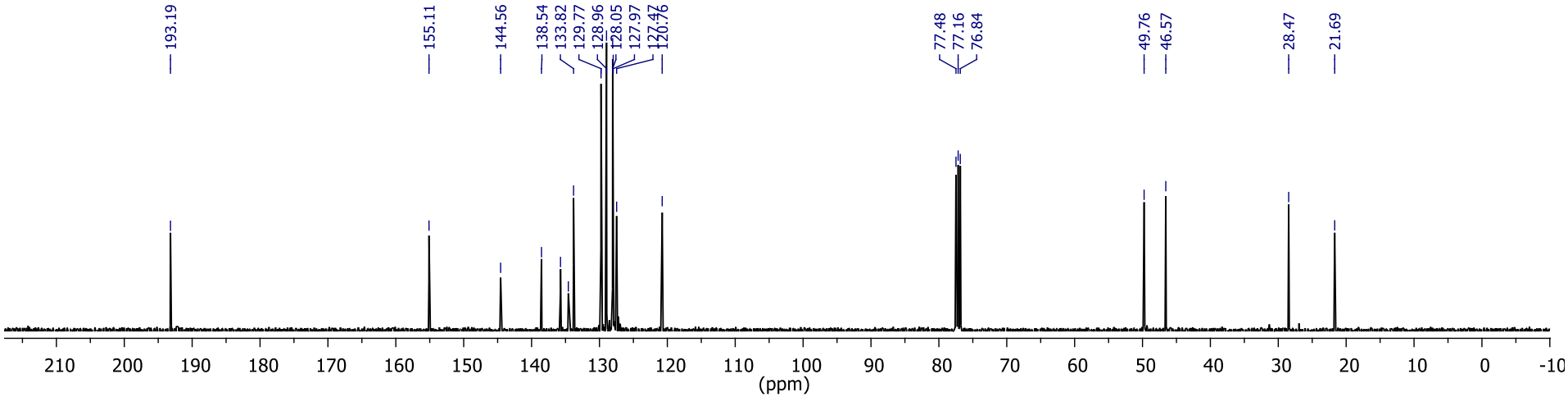


(*E*)-3-((*Z*)-2-benzylidene-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4d

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



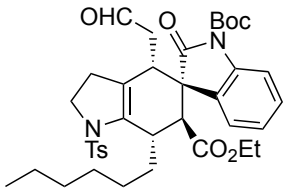
^{13}C NMR (101 MHz, $CDCl_3$)



*1.3.4 Cycloaddition reactions of dienals **4a-d***

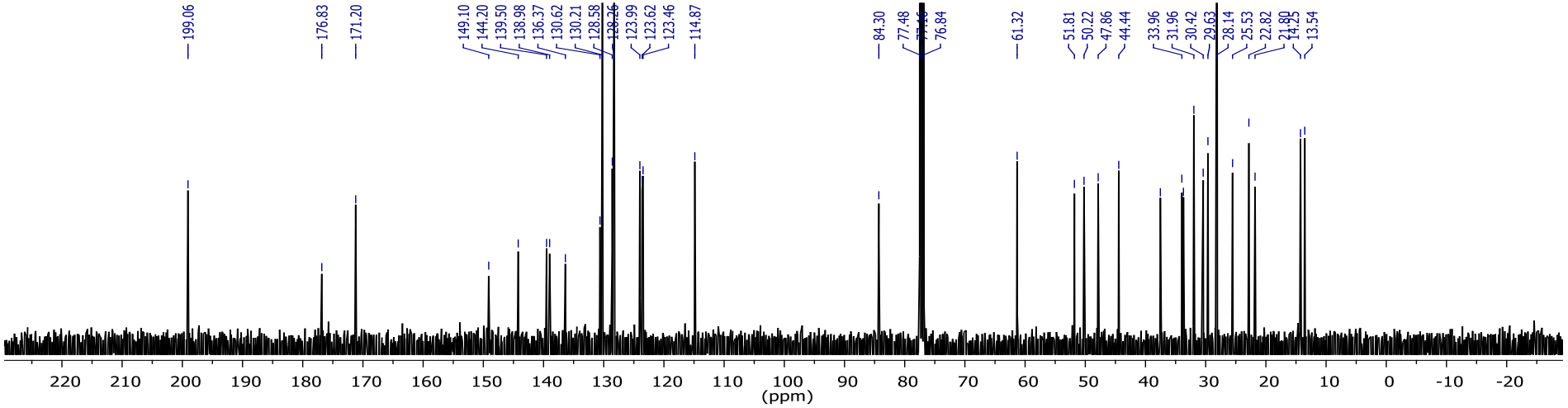
(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-hexyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12a

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



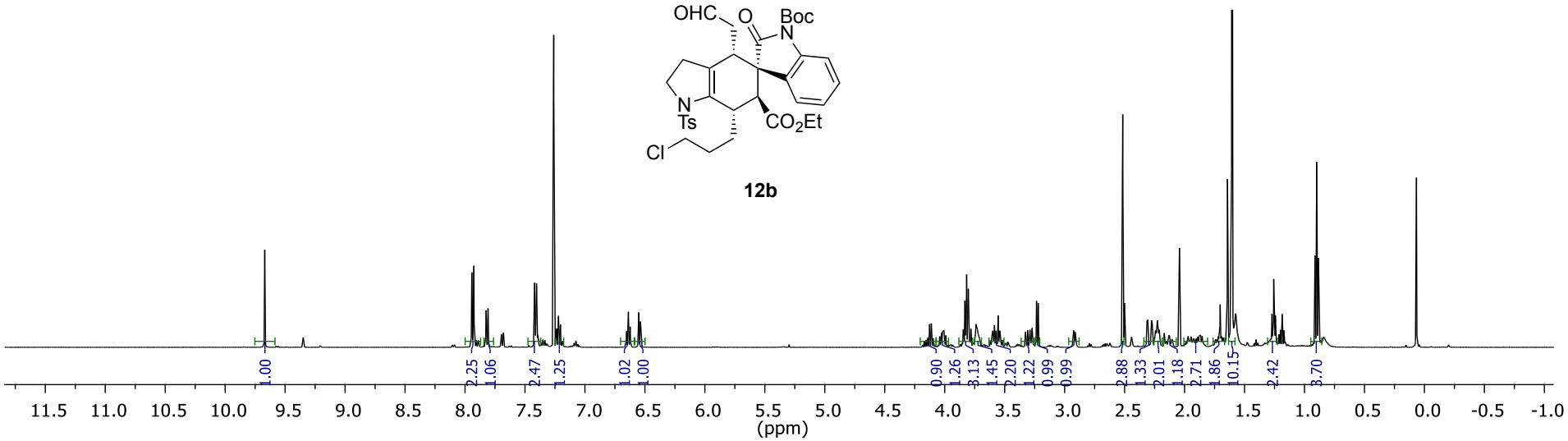
12a

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

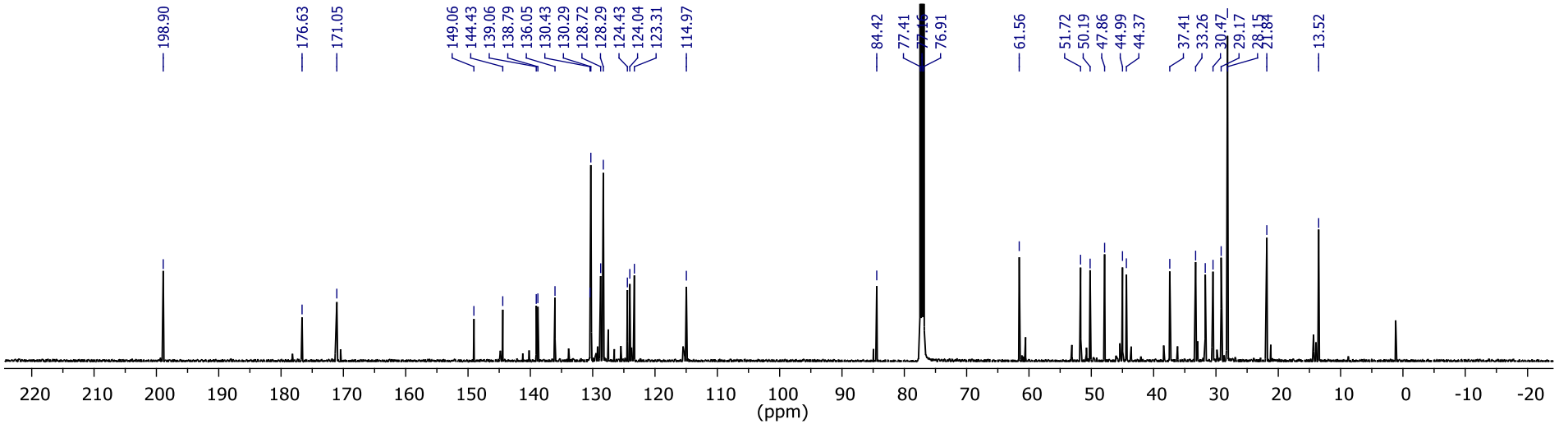


(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-(3-chloropropyl)-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12b

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

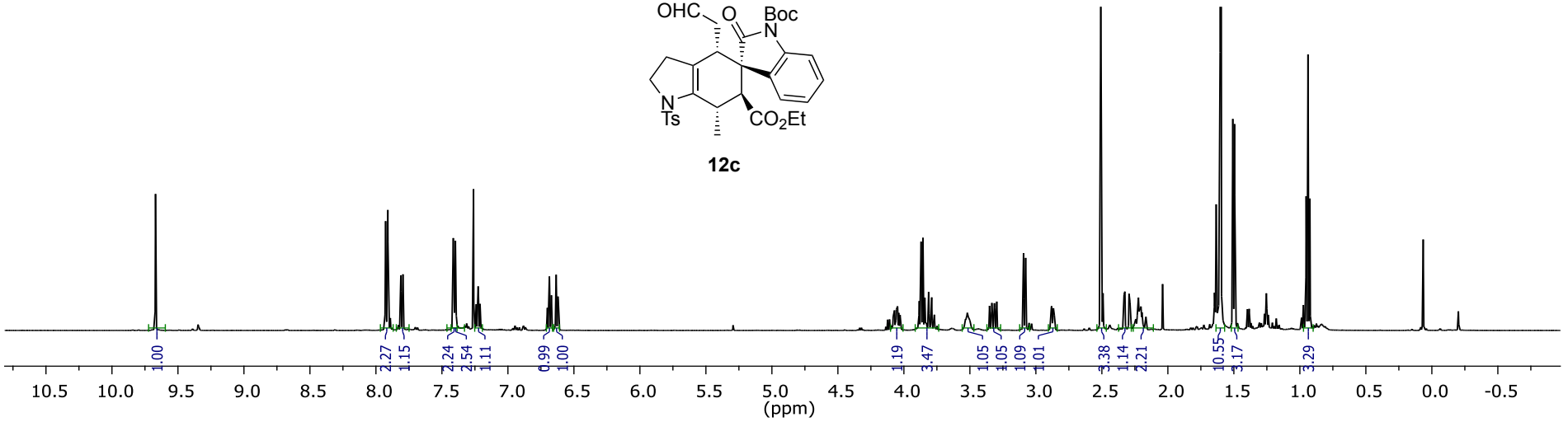


^{13}C NMR (125 MHz, $CDCl_3$)

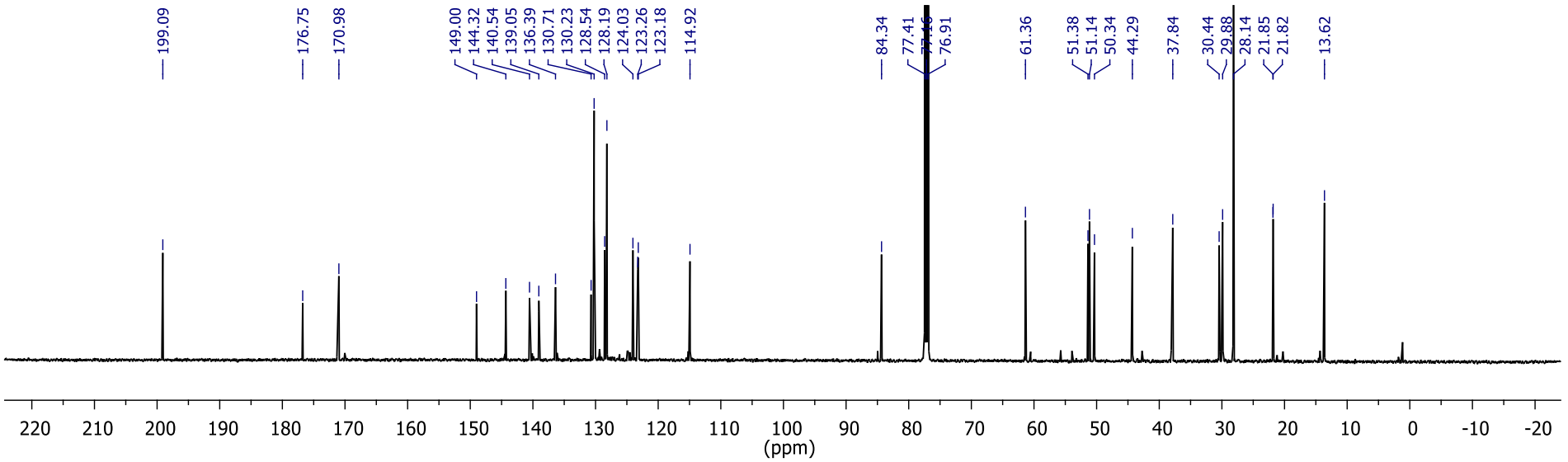


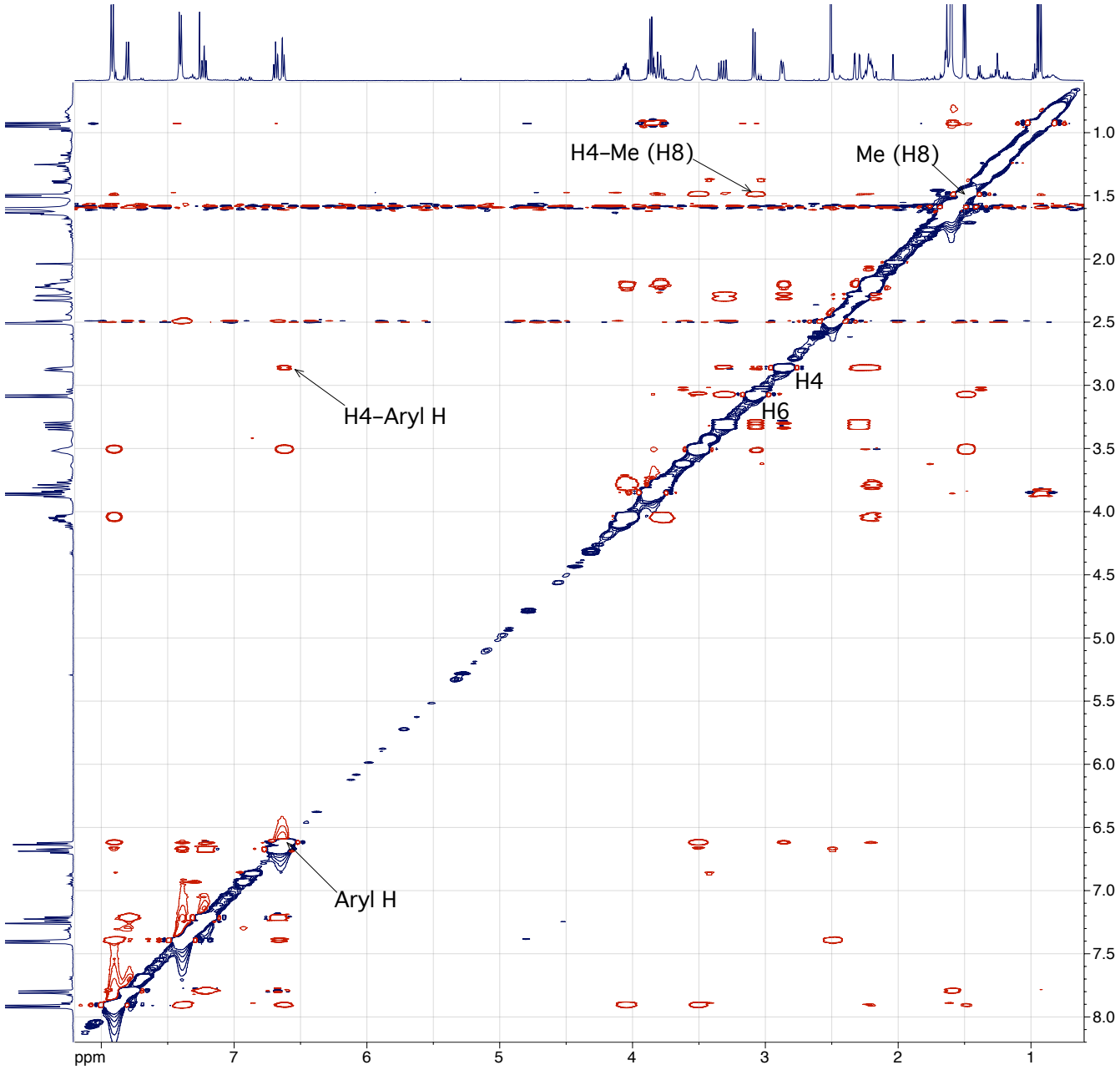
(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-methyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12c

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



^{13}C NMR (125 MHz, $CDCl_3$)




H4–Me (H8)
Me (H8)
H4–Aryl H
H4
H6
Aryl H
ppm
7
6
5
4
3
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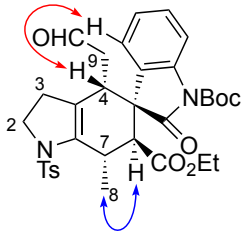
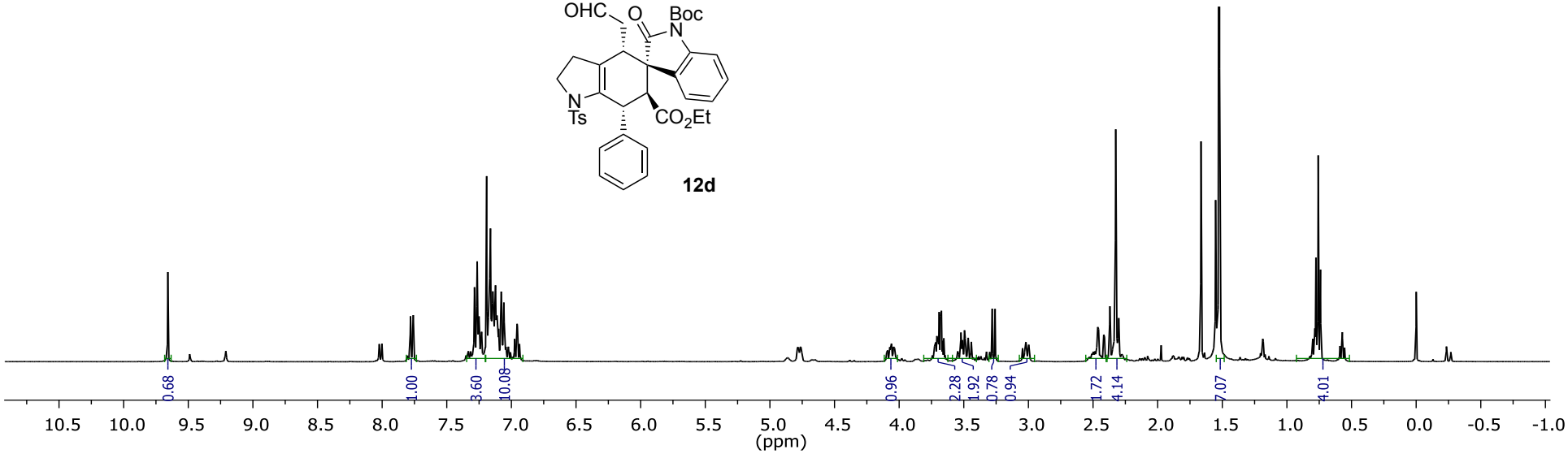
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

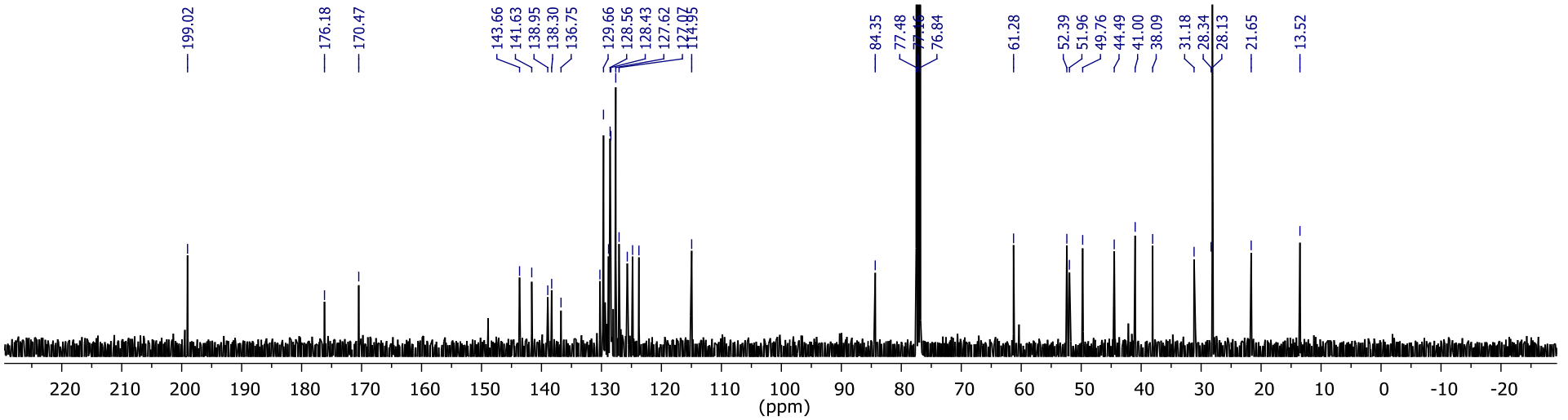

OHC
H
H
9
3
4
2
N
Ts
7
8
H
NBoc
O
CO2Et

(3'*S*,4*S*,6*S*,7*R*)-1'-*tert*-Butyl 6-ethyl 2'-oxo-4-(2-oxoethyl)-7-phenyl-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12d

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

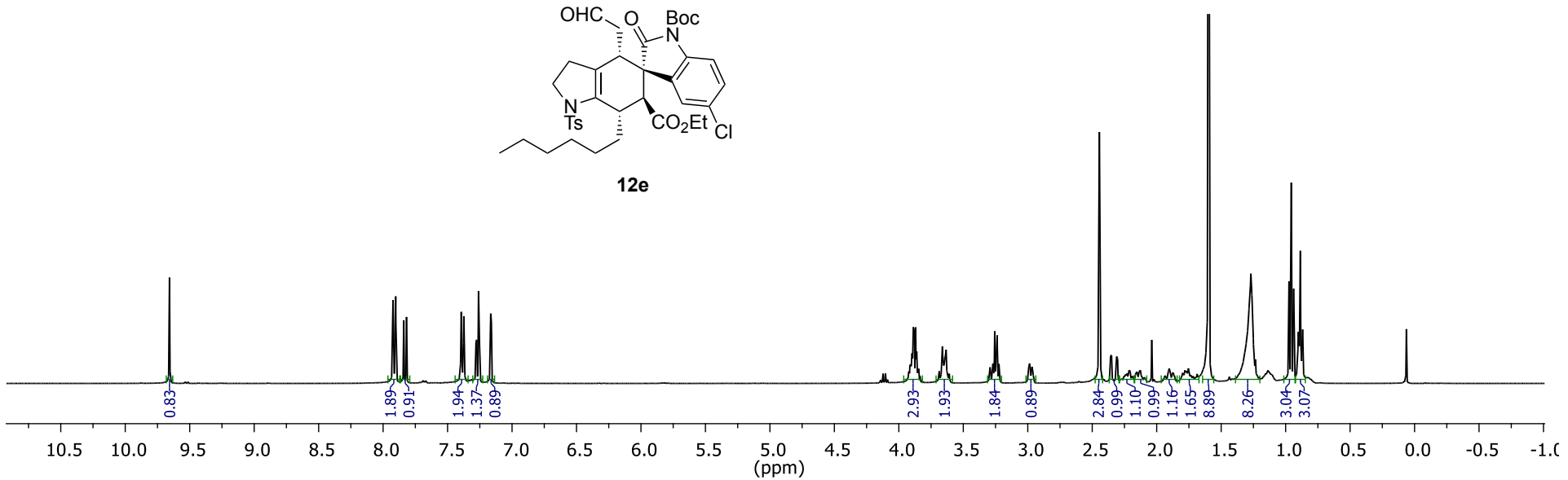


^{13}C NMR (101 MHz, $CDCl_3$)

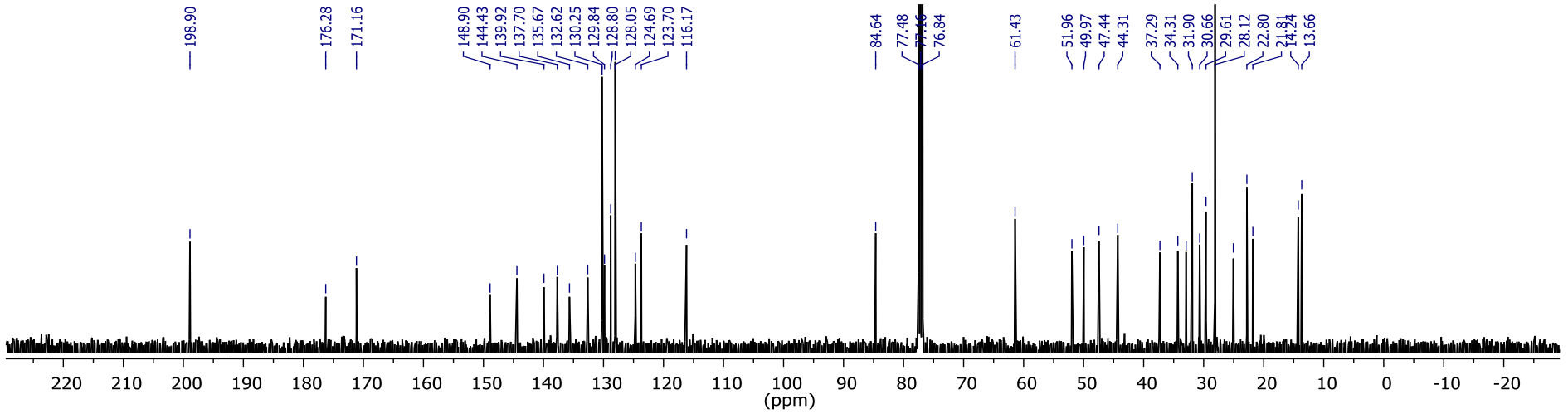


(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 5'-chloro-7-hexyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12e

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

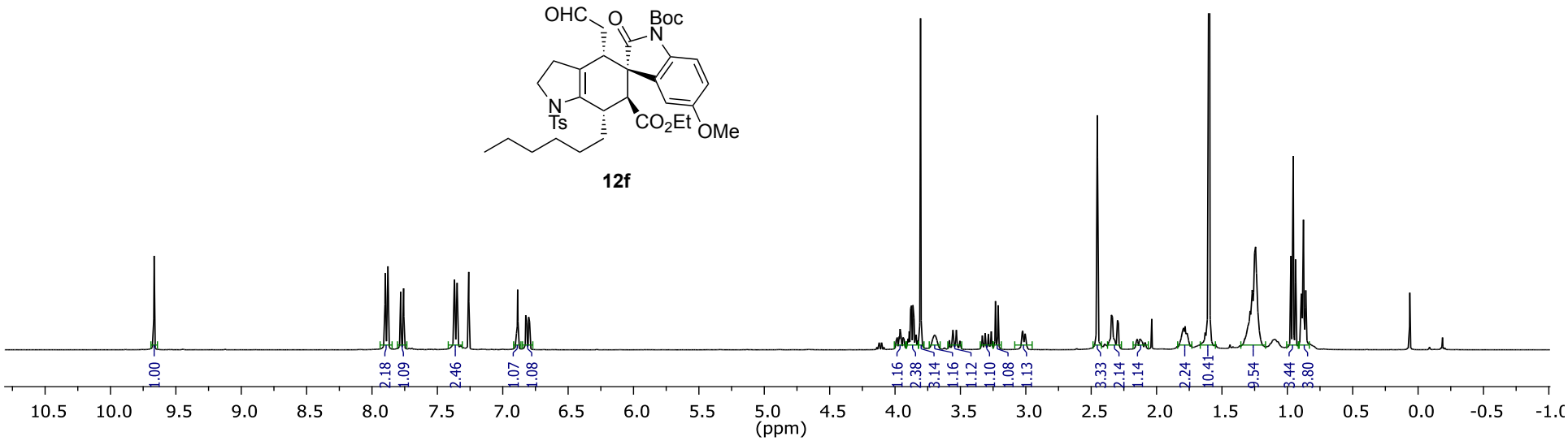


^{13}C NMR (101 MHz, $CDCl_3$)

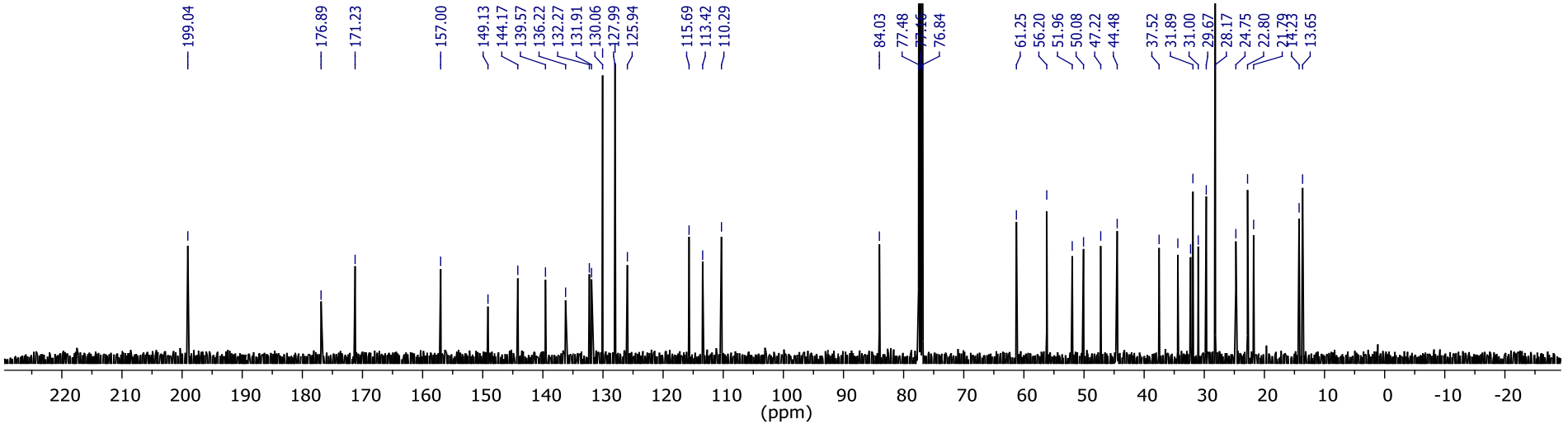


(3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 7-hexyl-5'-methoxy-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12f

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

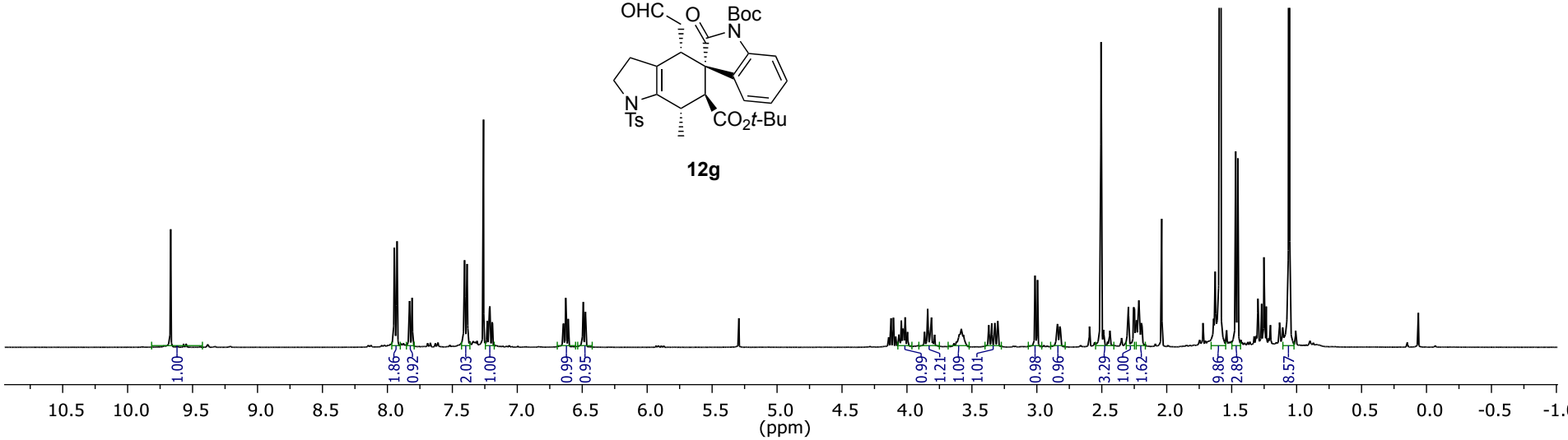


^{13}C NMR (101 MHz, $CDCl_3$)

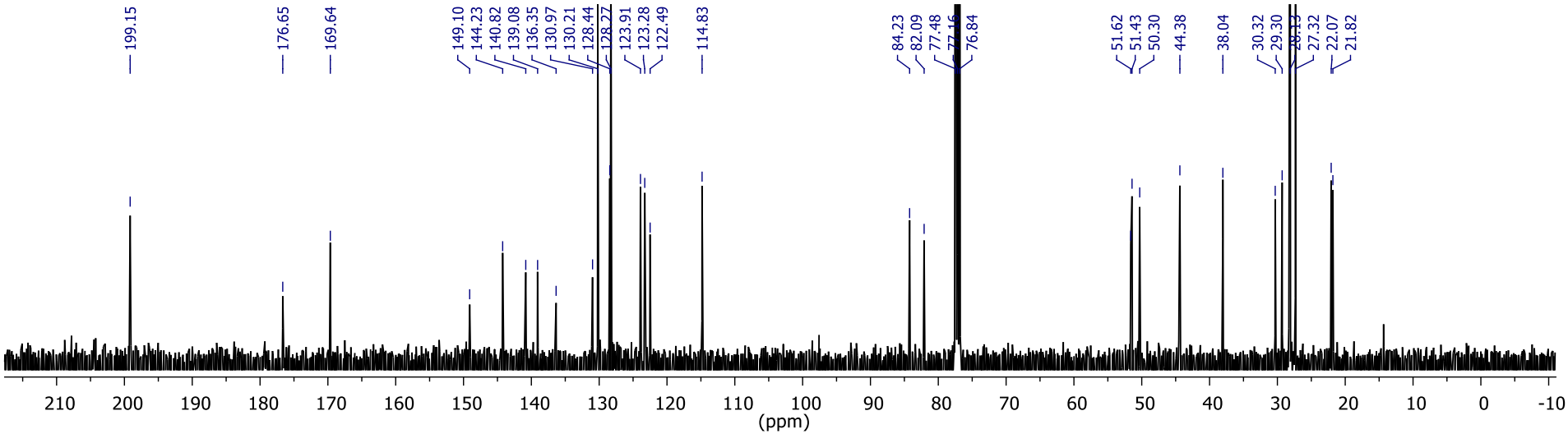


(3'*S*,4*S*,6*S*,7*S*)-di-*tert*-Butyl 7-methyl-2'-oxo-4-(2-oxoethyl)-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12g

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

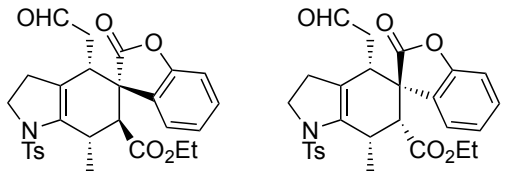


^{13}C NMR (101 MHz, $CDCl_3$)

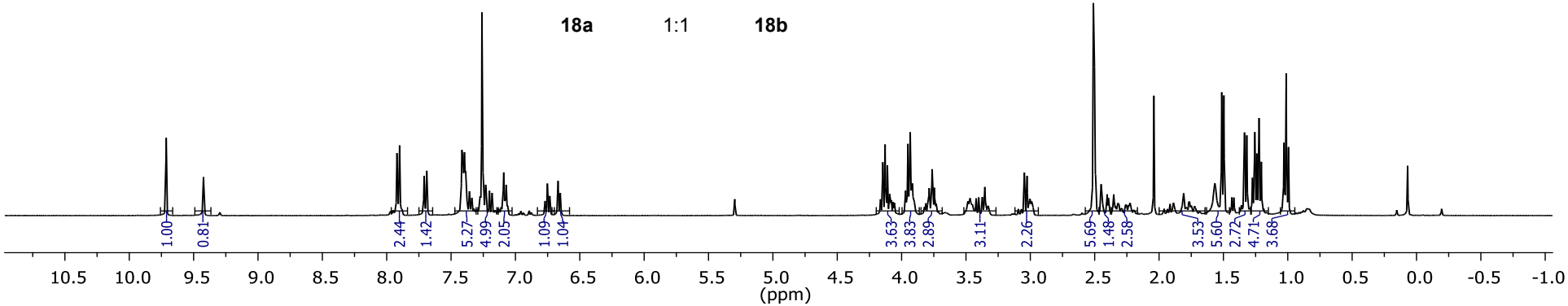


(3*S*,4'*S*,6'*S*,7'*S*)- and (3*R*,4'*S*,6'*R*,7'*S*)-Ethyl 7'-methyl-2-oxo-4'-(2-oxoethyl)-1'-tosyl-1',2',3',4',6',7'-hexahydro-2H-spiro[benzofuran-3,5'-indole]-6'-carboxylate, 18a and 18b

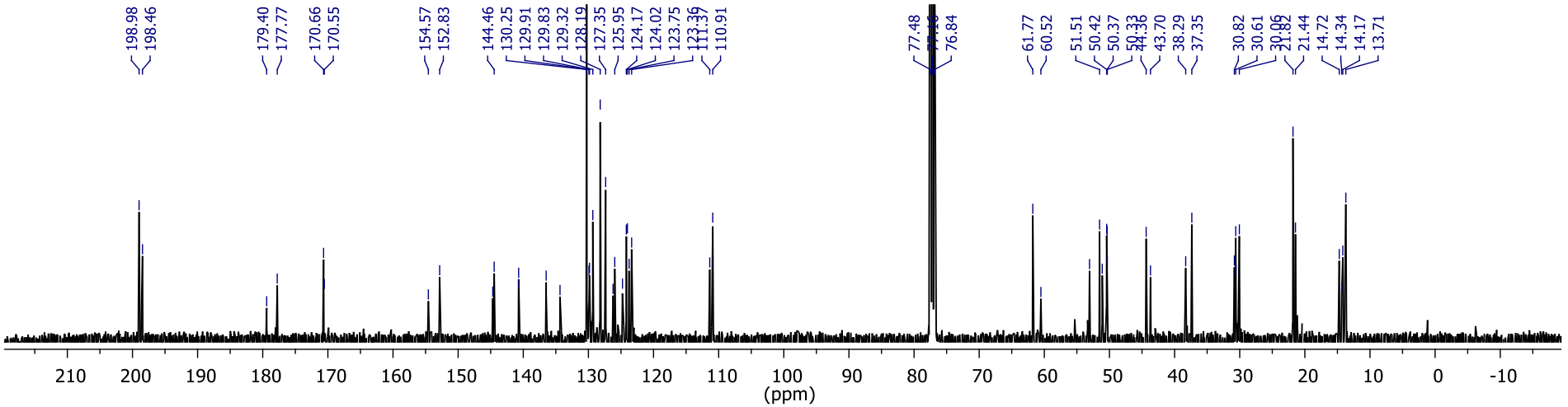
^{1}H NMR (400 MHz, $CDCl_3$)



18a 1:1 **18b**



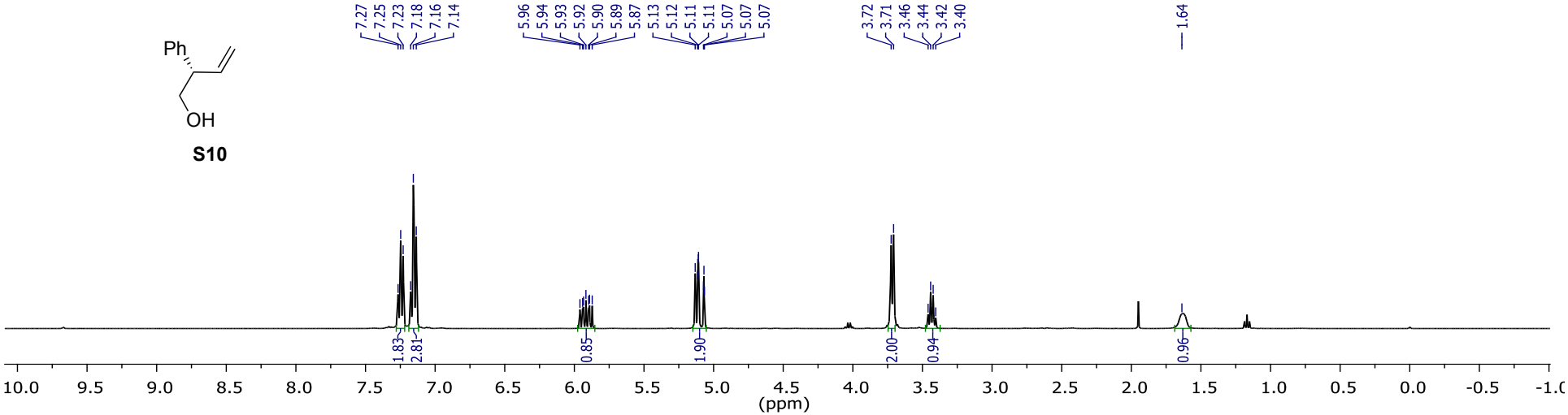
^{13}C NMR (101 MHz, $CDCl_3$)



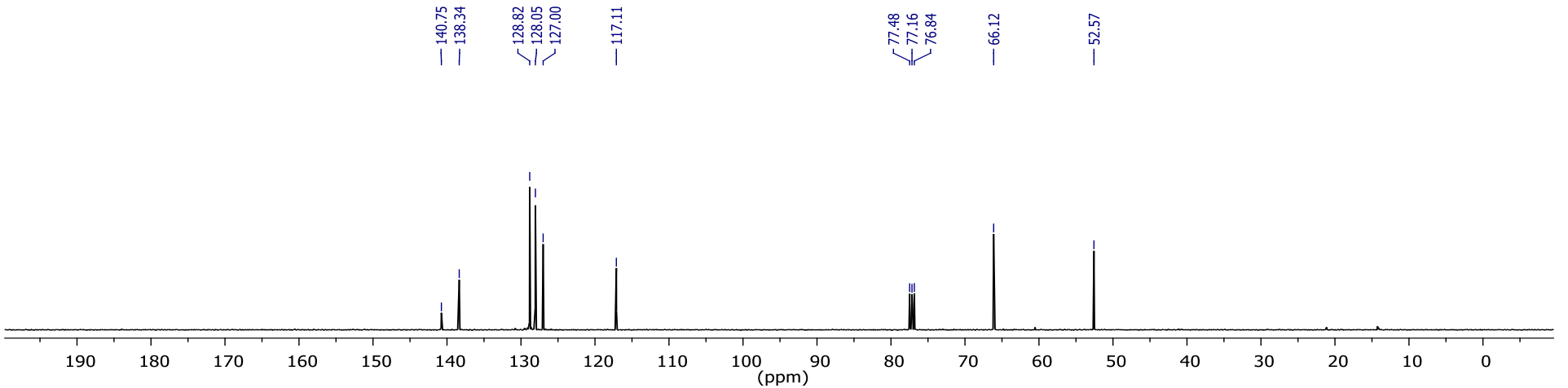
*3.5 Synthesis of dienals **3b** and **4e***

(*S*)-2-phenylbut-3-en-1-ol, S10

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

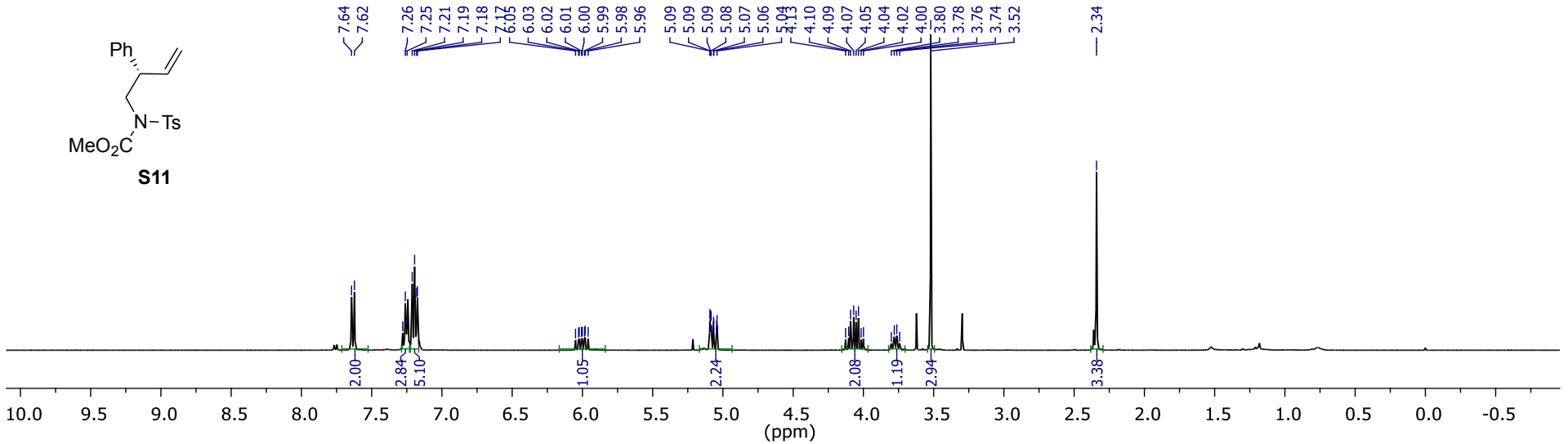


^{13}C NMR (101 MHz, $CDCl_3$)

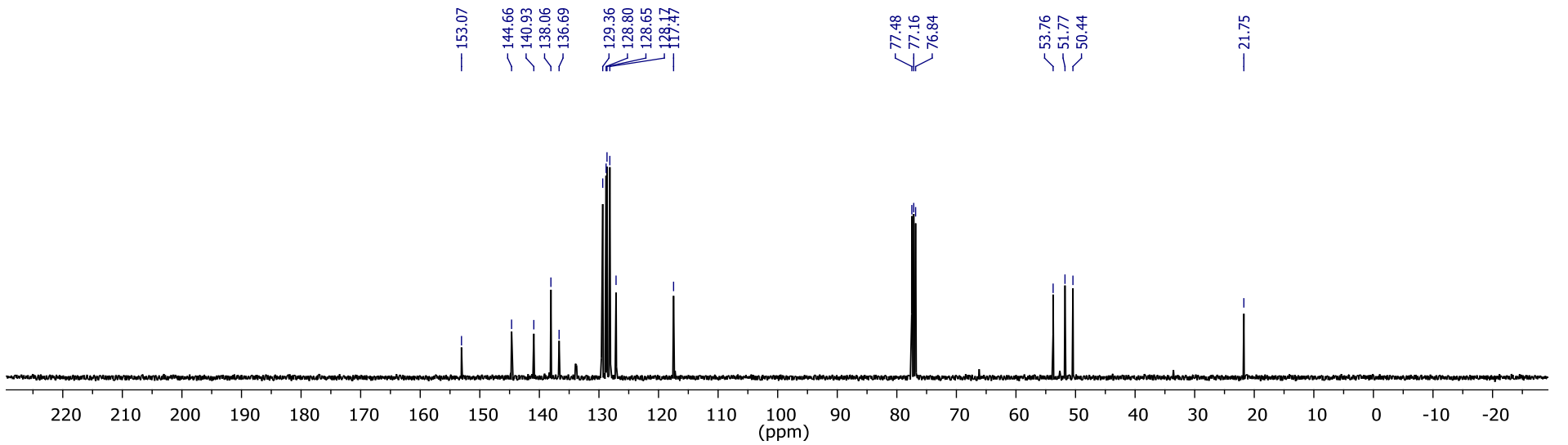


(*S*)-methyl (2-phenylbut-3-en-1-yl)(tosyl)carbamate, S11

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

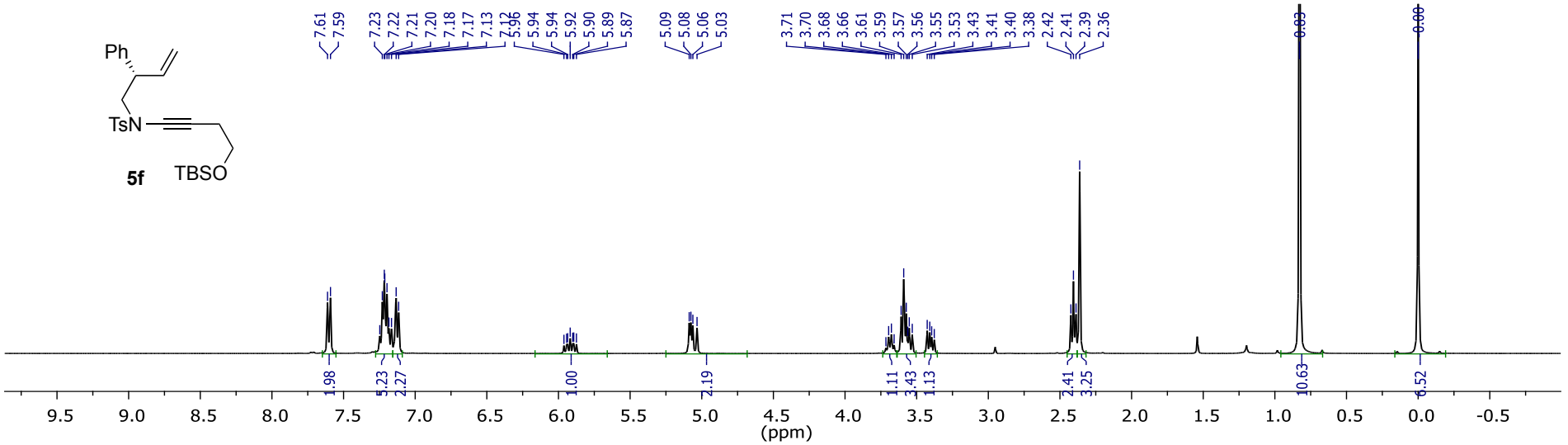


^{13}C NMR (101 MHz, $CDCl_3$)

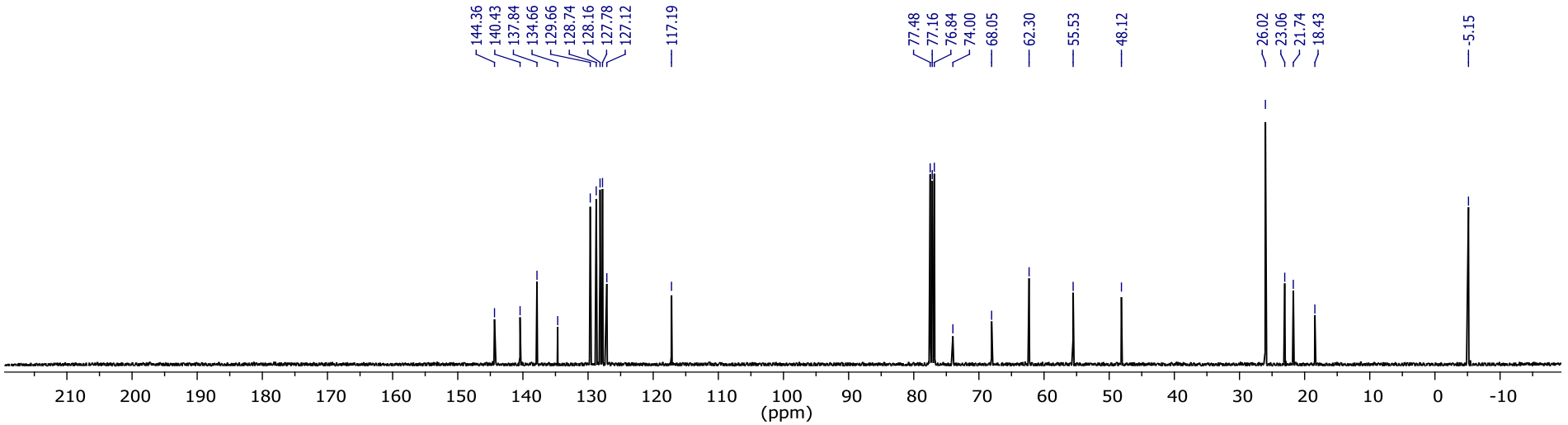


(*S*)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-4-methyl-*N*-(2-phenylbut-3-en-1-yl)benzenesulfonamide, 5f

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

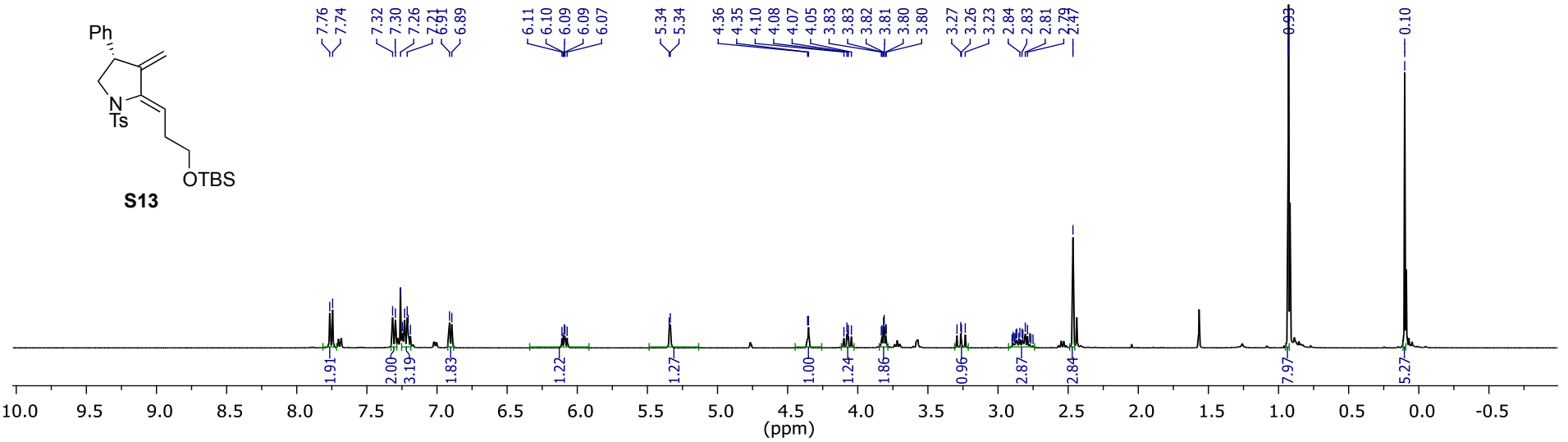


^{13}C NMR (101 MHz, $CDCl_3$)

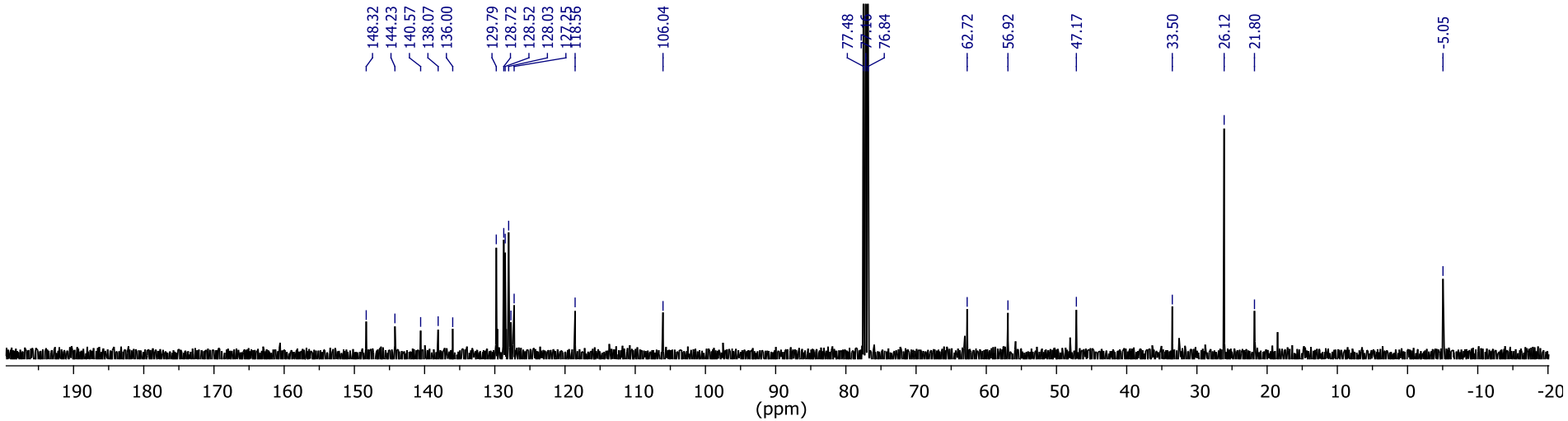


(*R*,*Z*)-2-(3-((*tert*-butyldimethylsilyl)oxy)propylidene)-3-methylene-4-phenyl-1-tosylpyrrolidine, S13

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

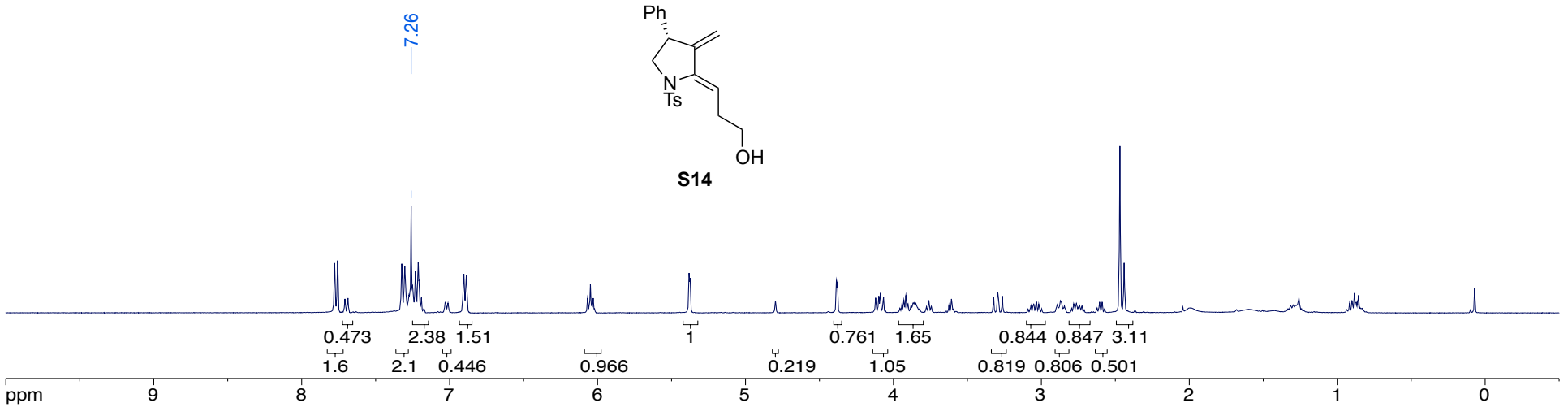


^{13}C NMR (101 MHz, $CDCl_3$)

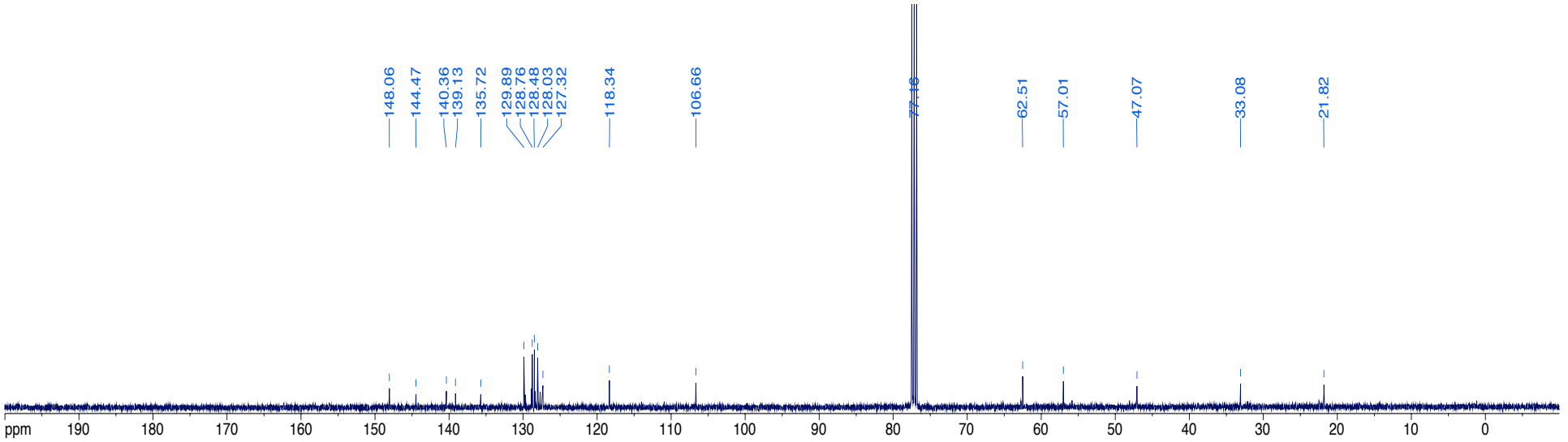


(*R*,*Z*)-3-(3-methylene-4-phenyl-1-tosylpyrrolidin-2-ylidene)propan-1-ol, S14

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

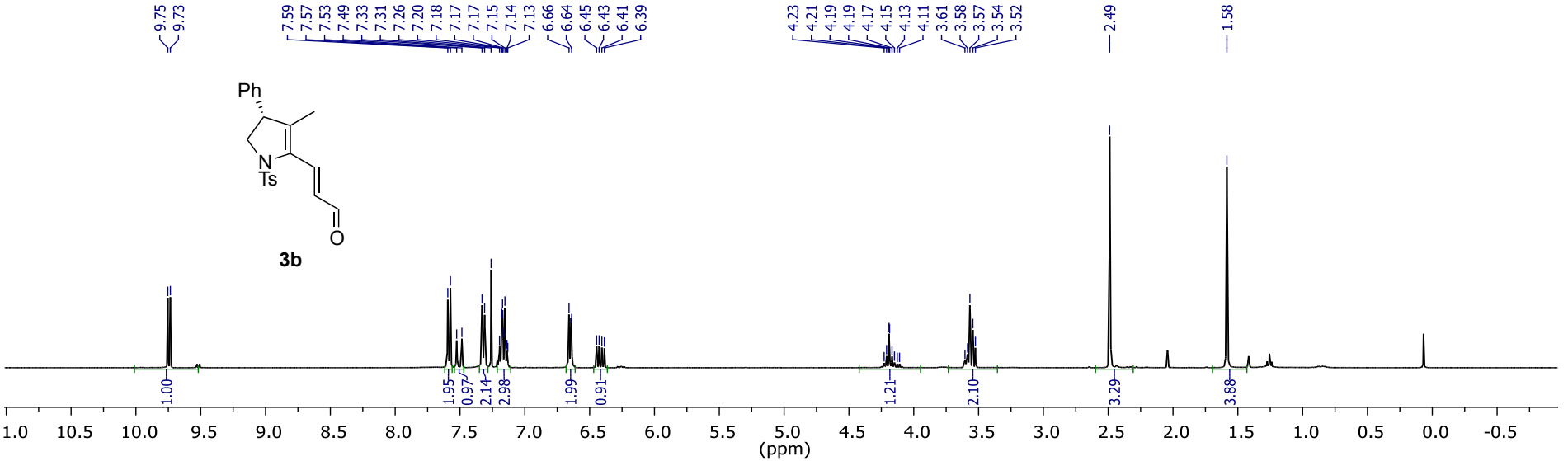


^{13}C NMR (101 MHz, $CDCl_3$)

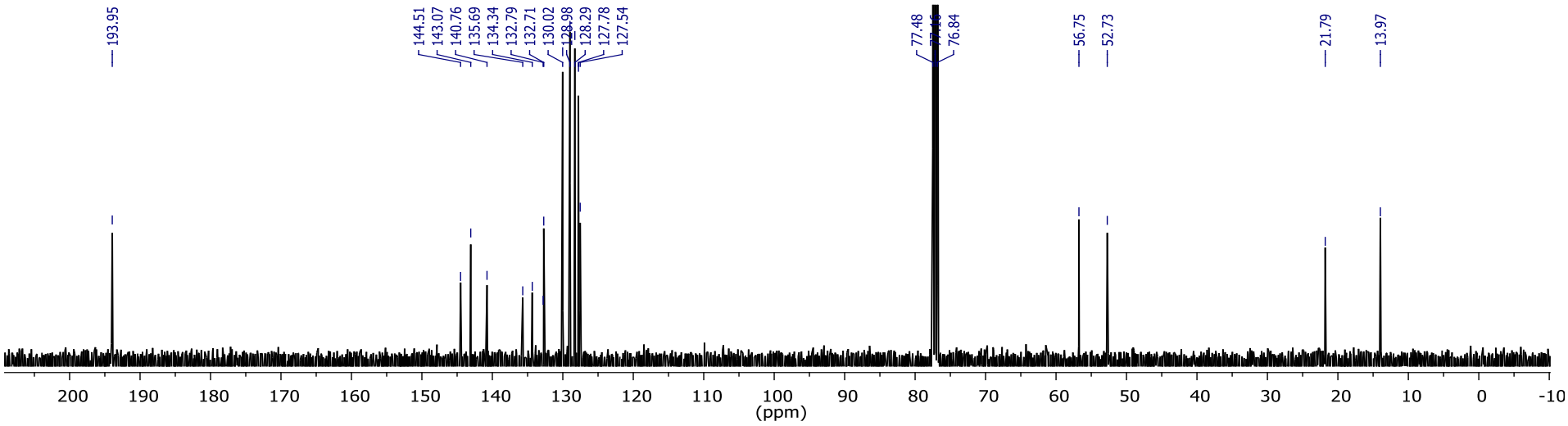


(*R*,*E*)-3-(3-methyl-4-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrrol-2-yl)acrylaldehyde, 3b

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

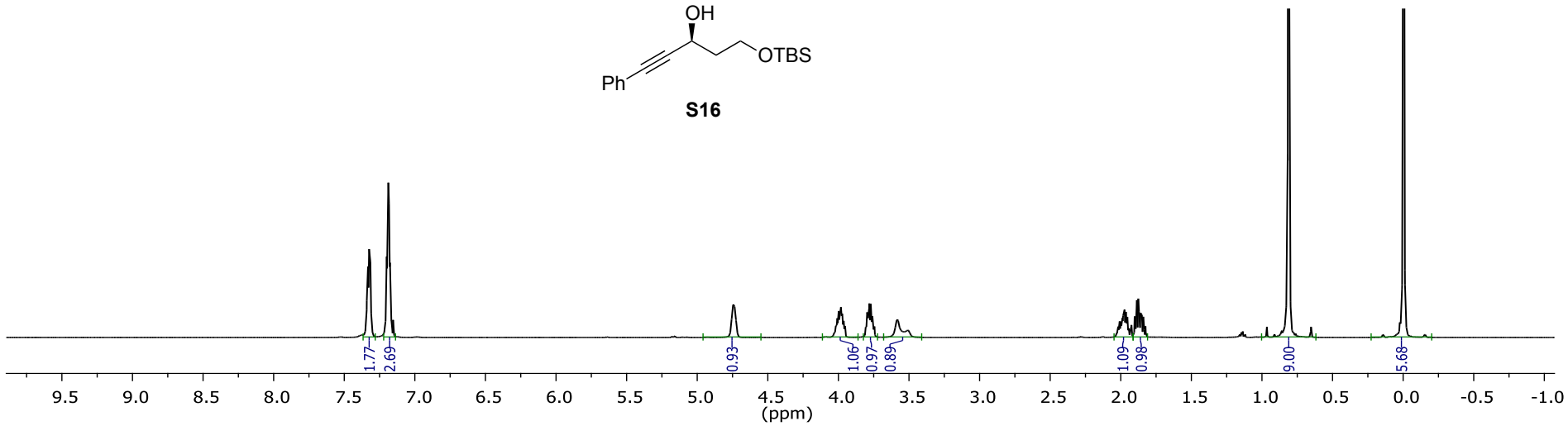


^{13}C NMR (101 MHz, $CDCl_3$)

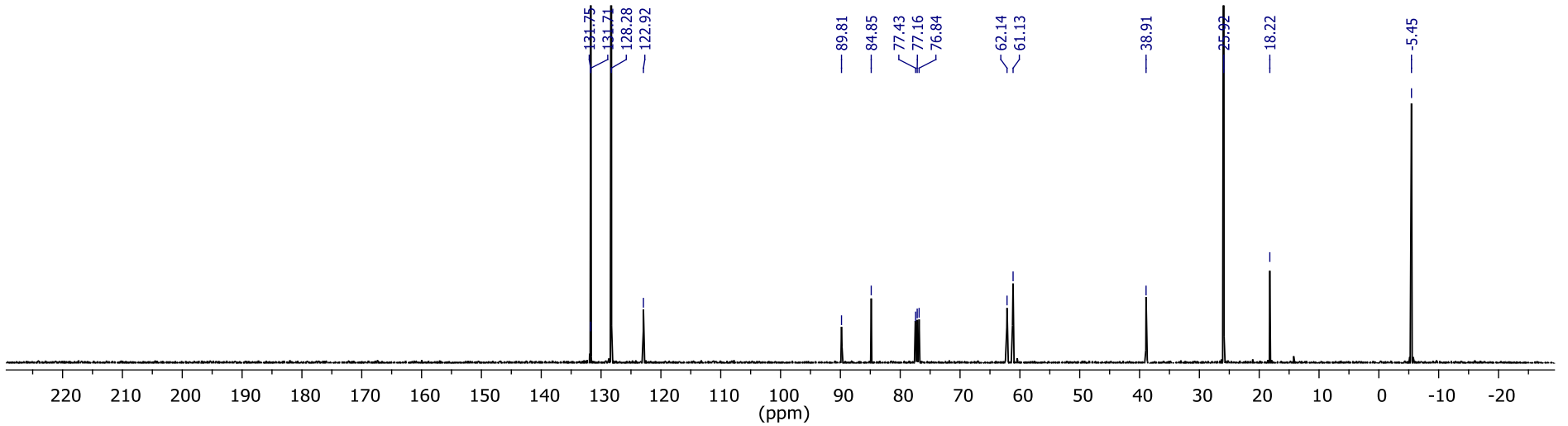


5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-1-yn-3-ol, S16

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

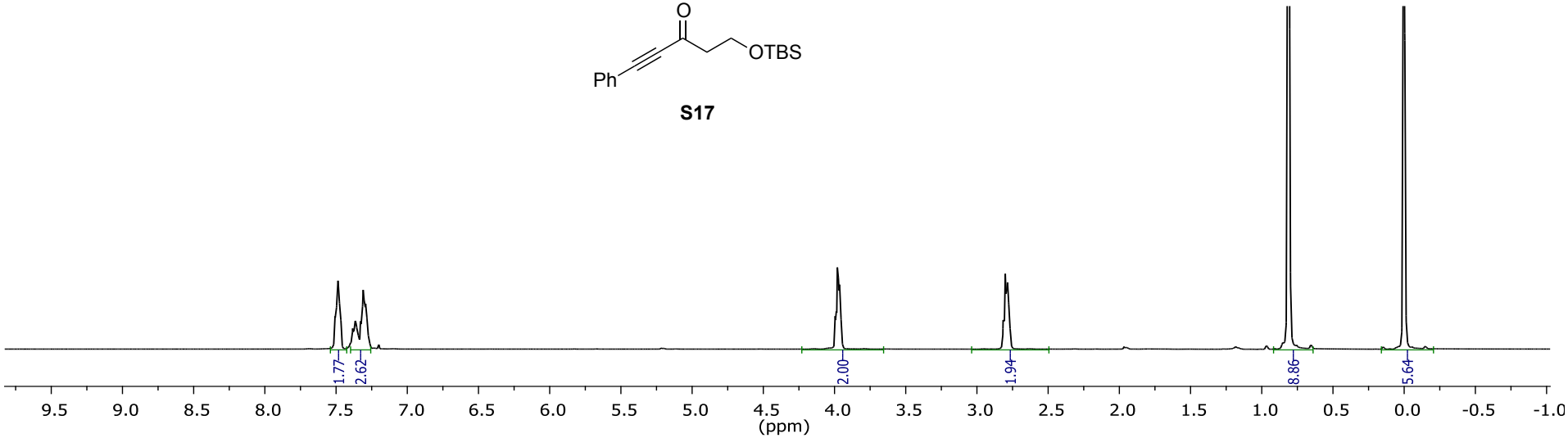


^{13}C NMR (101 MHz, $CDCl_3$)



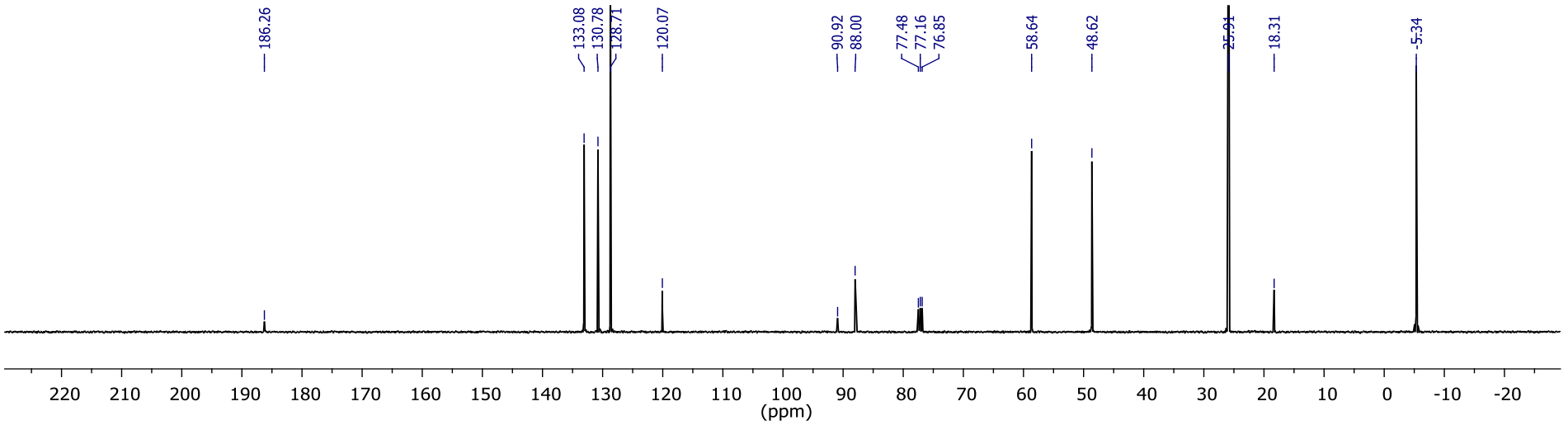
5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-1-yn-3-one, S17

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



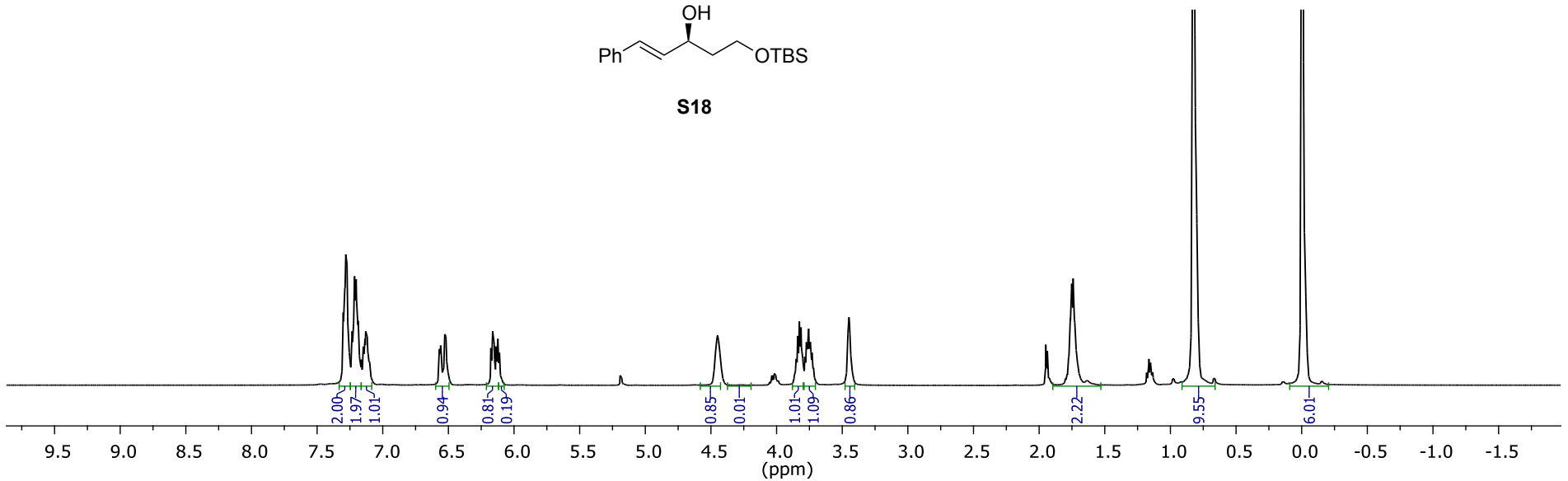
S17

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

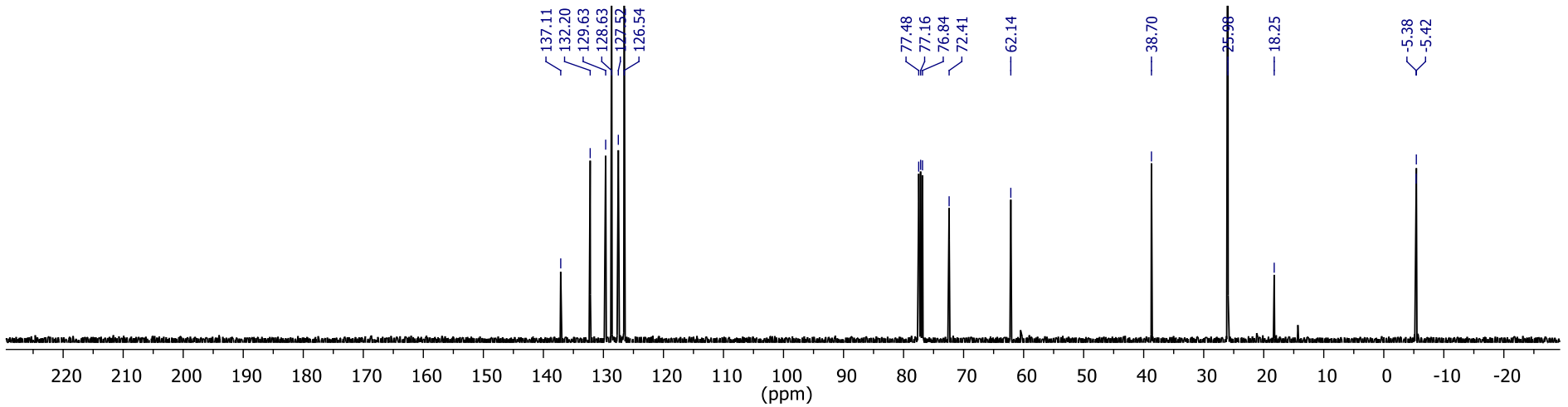


(*S*,*E*)-5-((*tert*-butyldimethylsilyl)oxy)-1-phenylpent-1-en-3-ol, S18

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

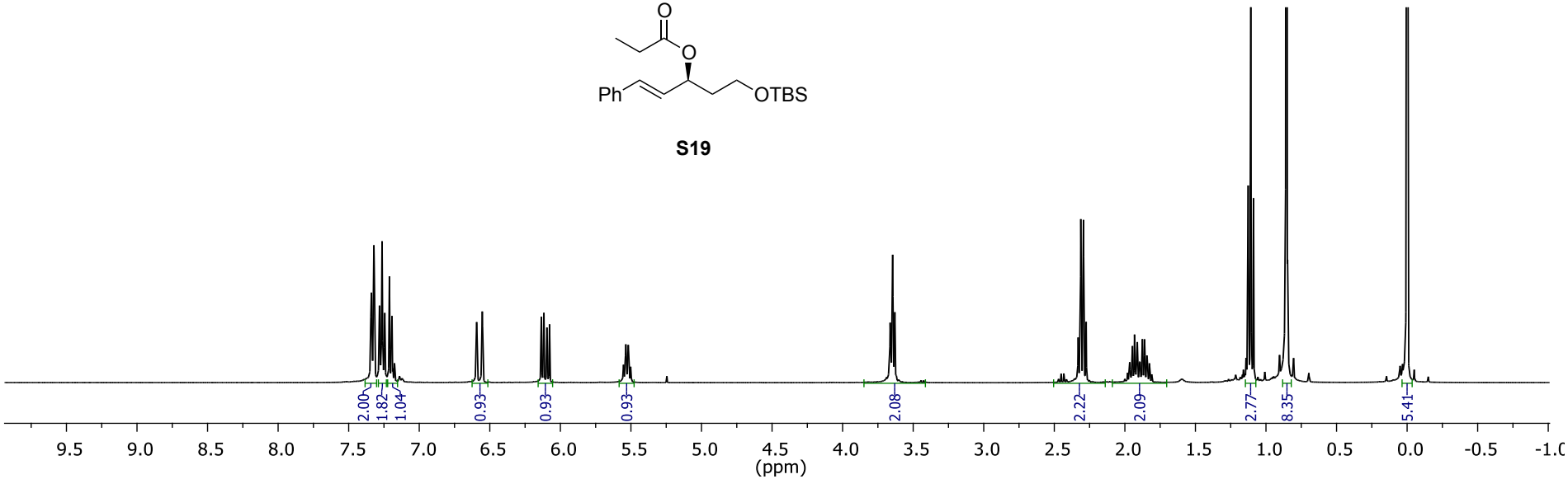


^{13}C NMR (101 MHz, $CDCl_3$)



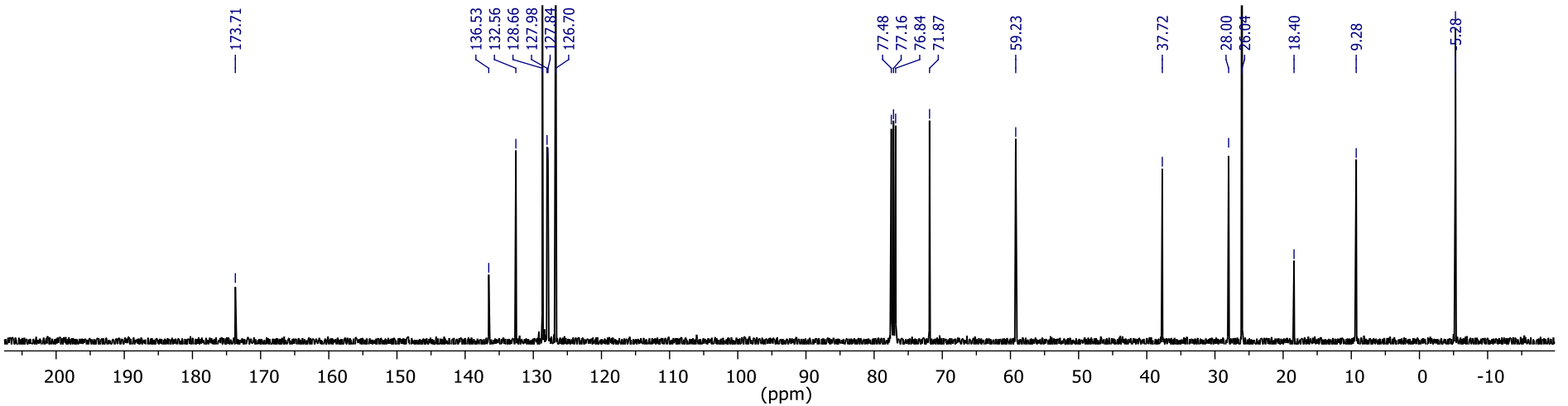
(*S*,*E*)-5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-1-en-3-yl propionate, S19

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



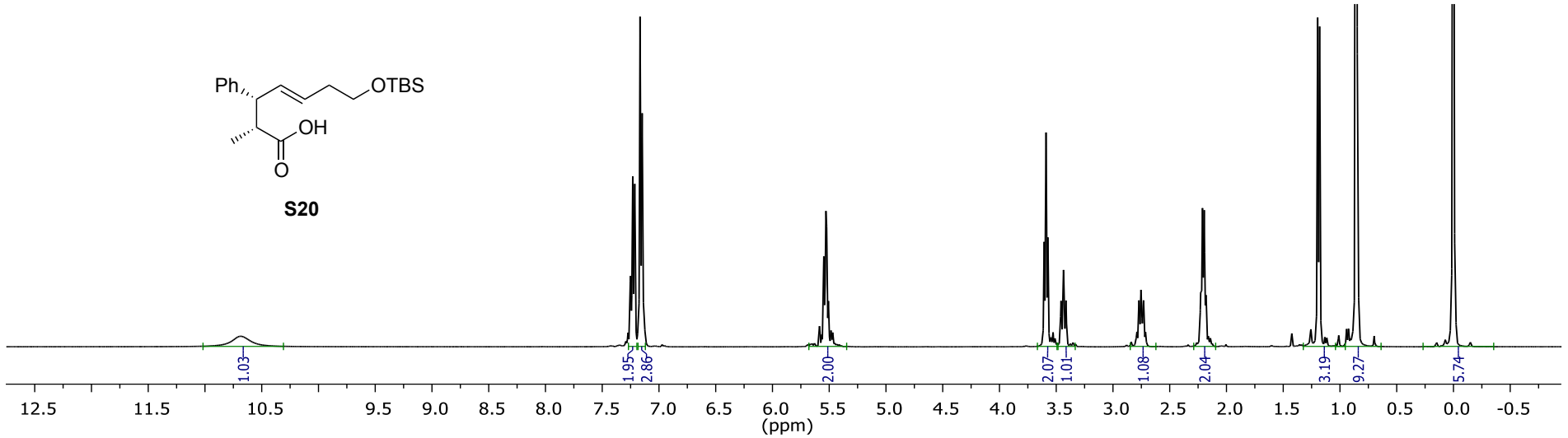
S19

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

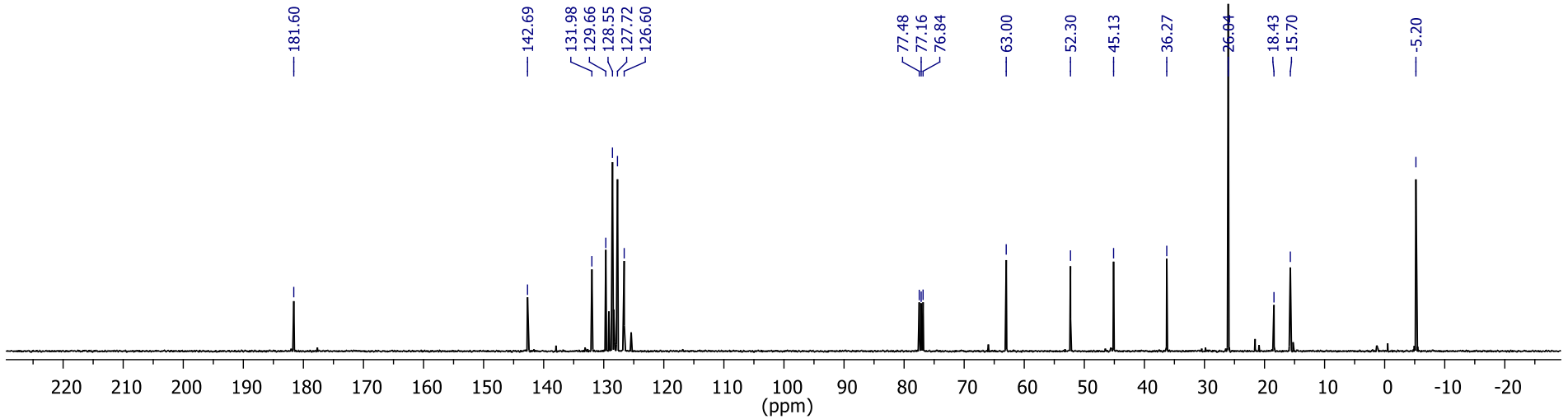


(2*R*,3*R*,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-3-phenylhept-4-enoic acid, S20

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

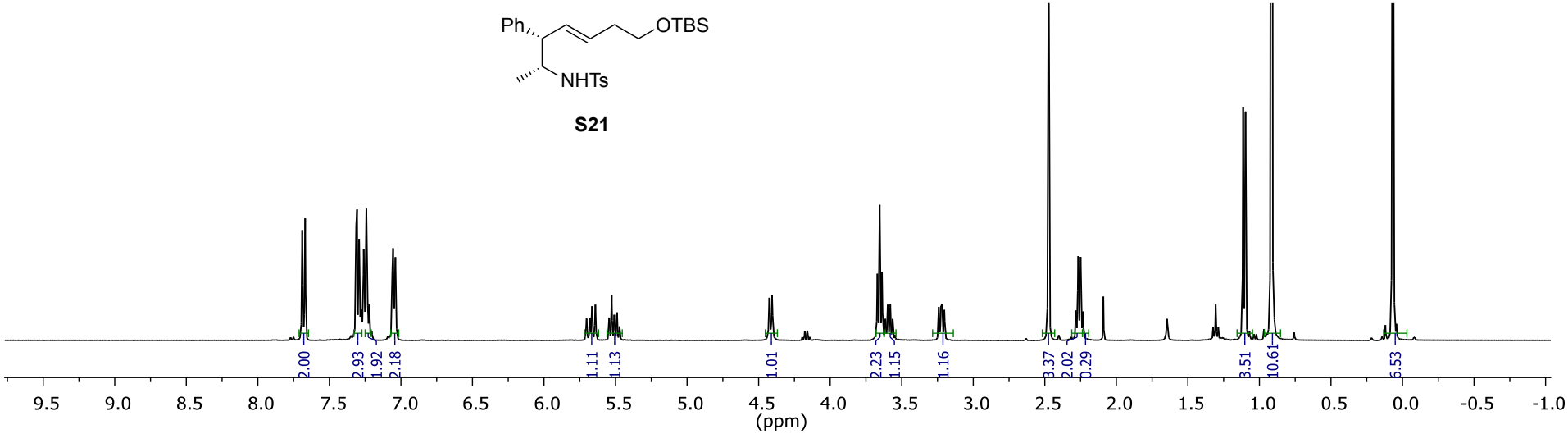


^{13}C NMR (101 MHz, $CDCl_3$)



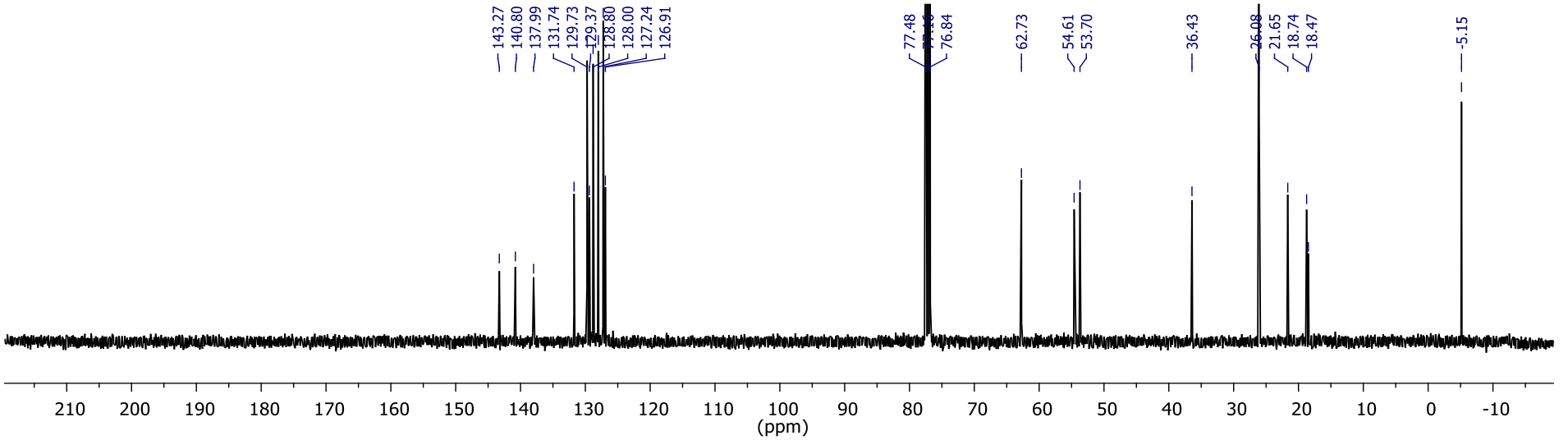
***N*-((2*R*,3S,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-3-phenylhept-4-en-2-yl)-4-methylbenzenesulfonamide, S21**

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



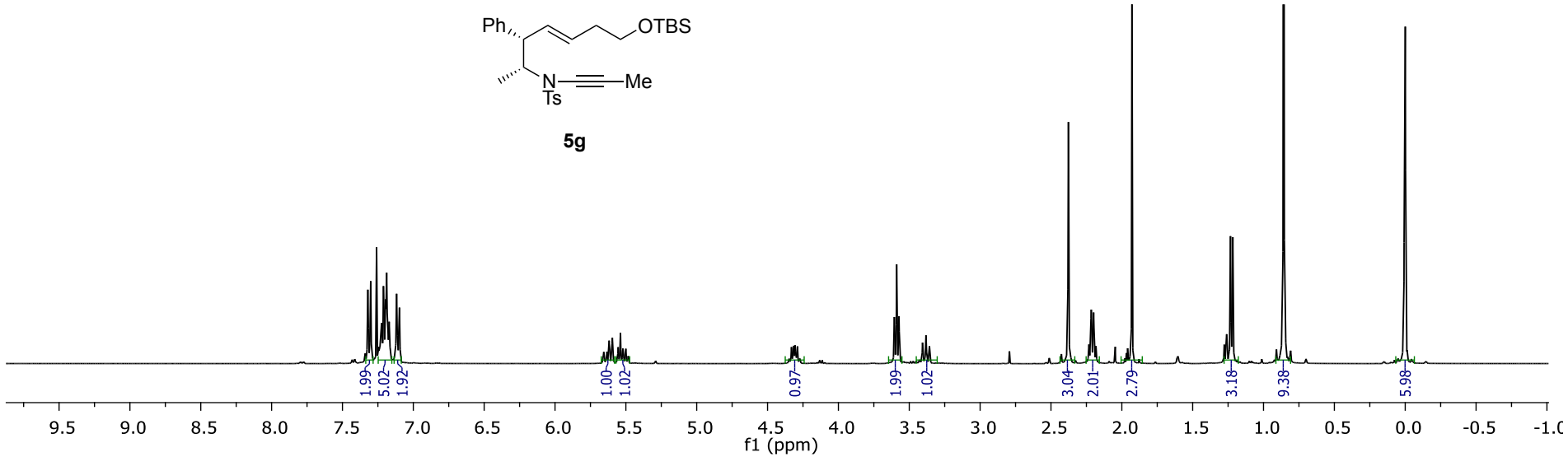
S21

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

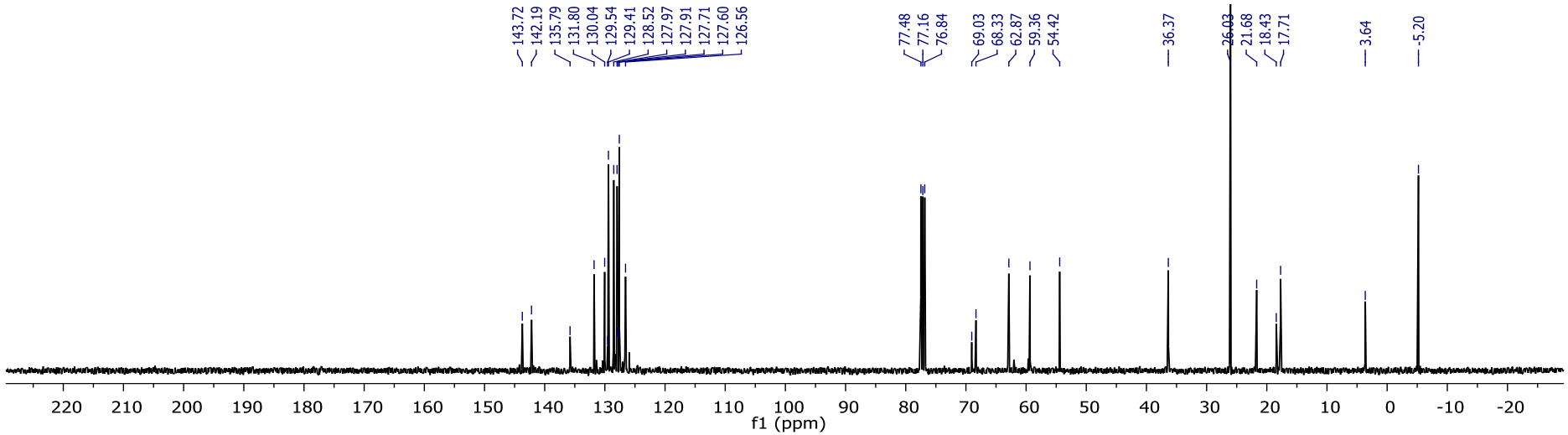


***N*-((2*R*,3*S*,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-3-phenylhept-4-en-2-yl)-4-methyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, 5g**

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

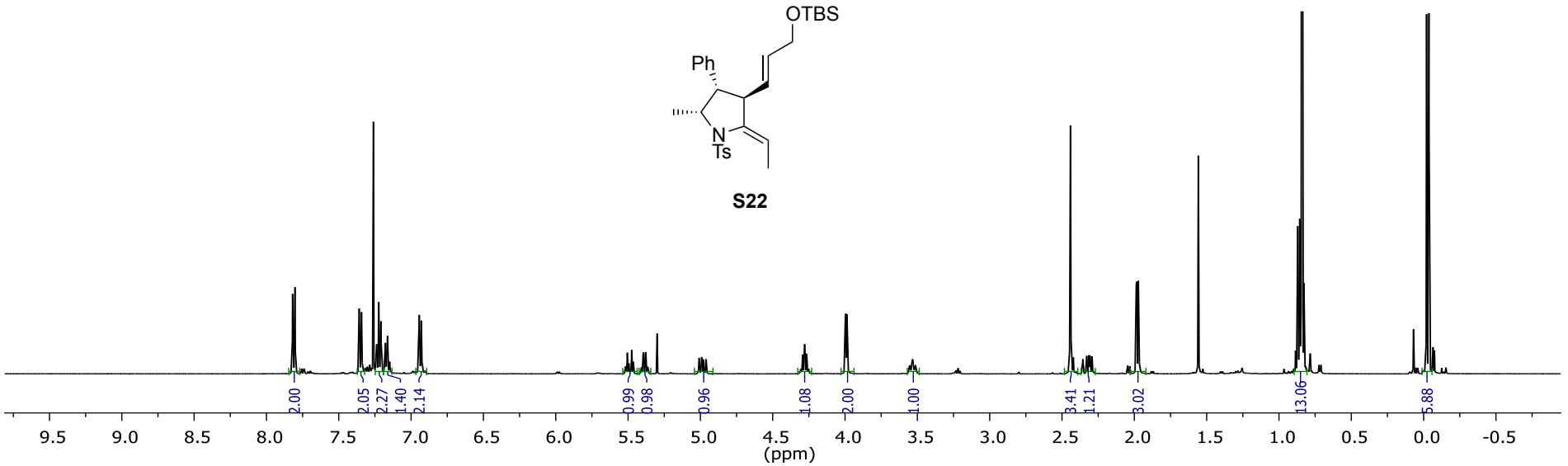


^{13}C NMR (101 MHz, $CDCl_3$)

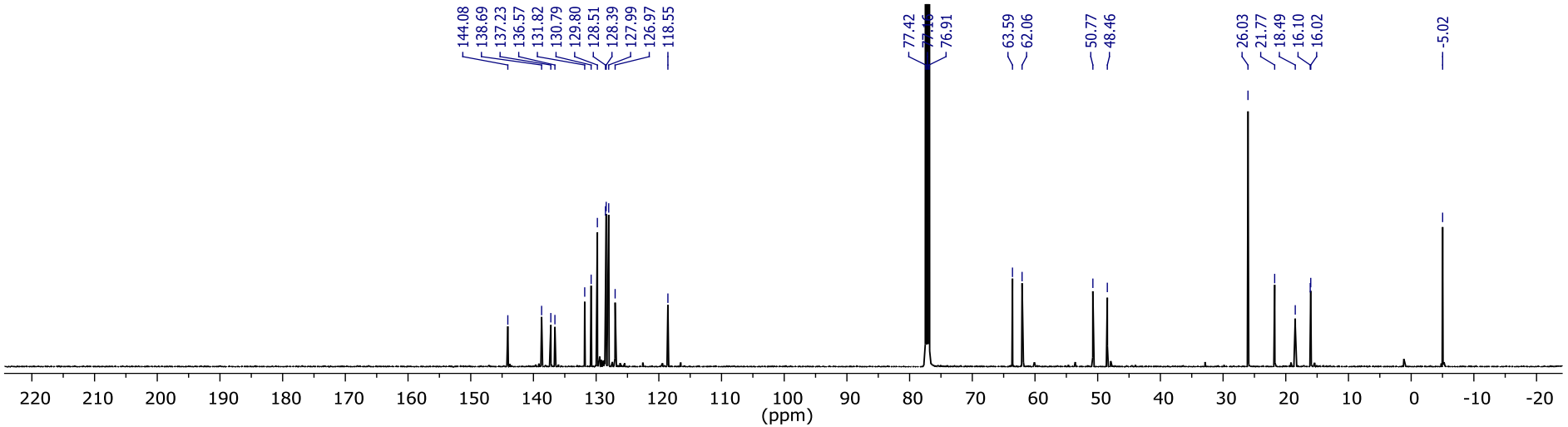


(3*R*,4*S*,5*R*,*Z*)-3-((*E*)-3-((*tert*-butyldimethylsilyl)oxy)prop-1-en-1-yl)-2-ethylidene-5-methyl-4-phenyl-1-tosylpyrrolidine, S22

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

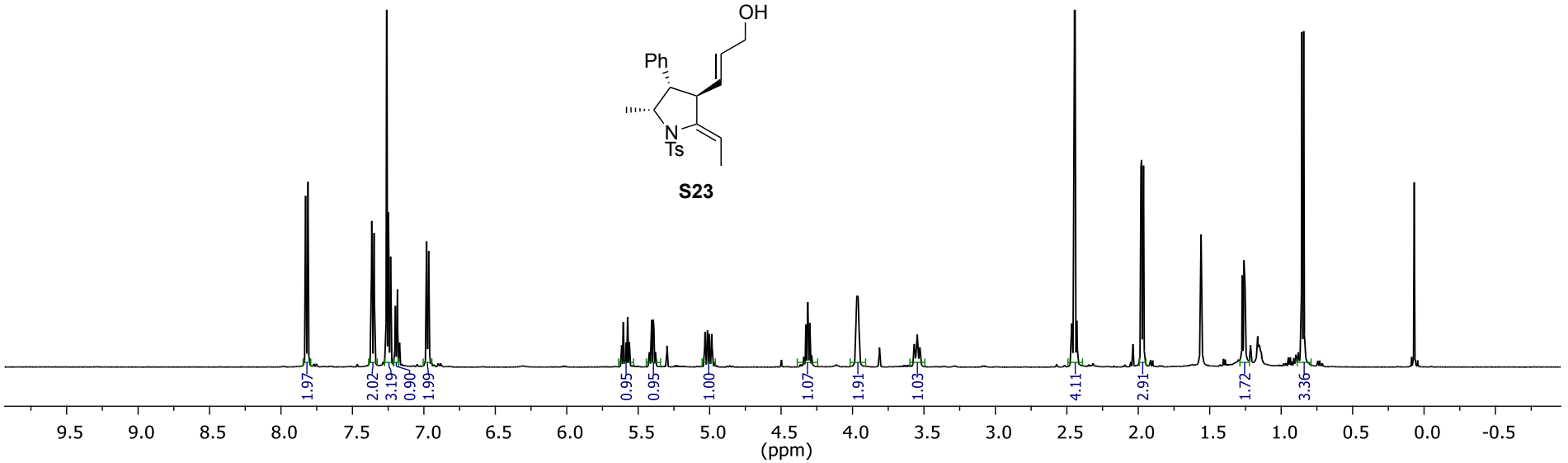


^{13}C NMR (125 MHz, $CDCl_3$)

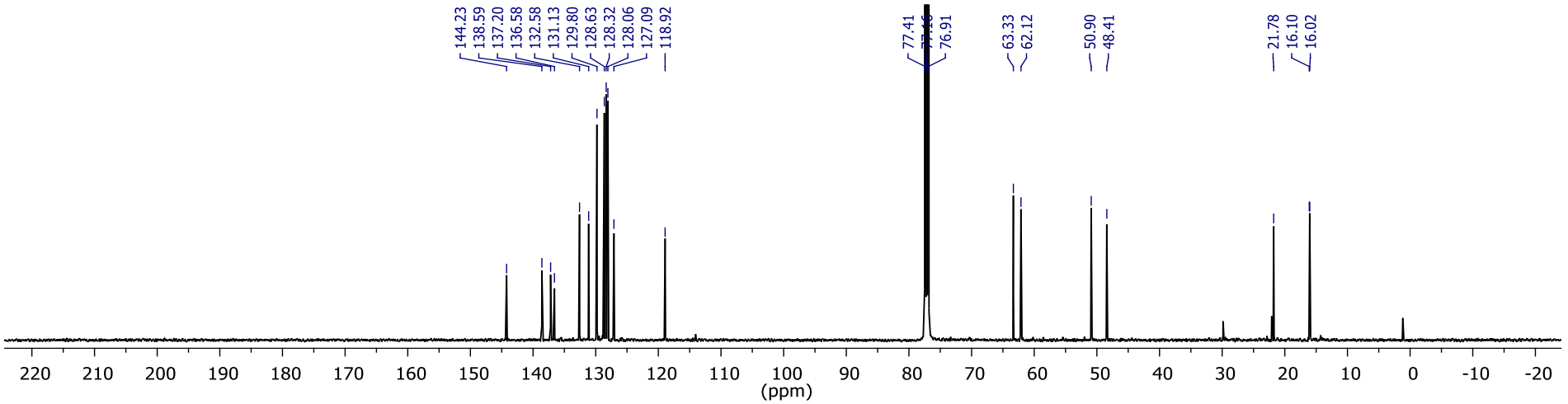


(*E*)-3-((4*S*,5*R*,*Z*)-2-ethylidene-5-methyl-4-phenyl-1-tosylpyrrolidin-3-yl)prop-2-en-1-ol, S23

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

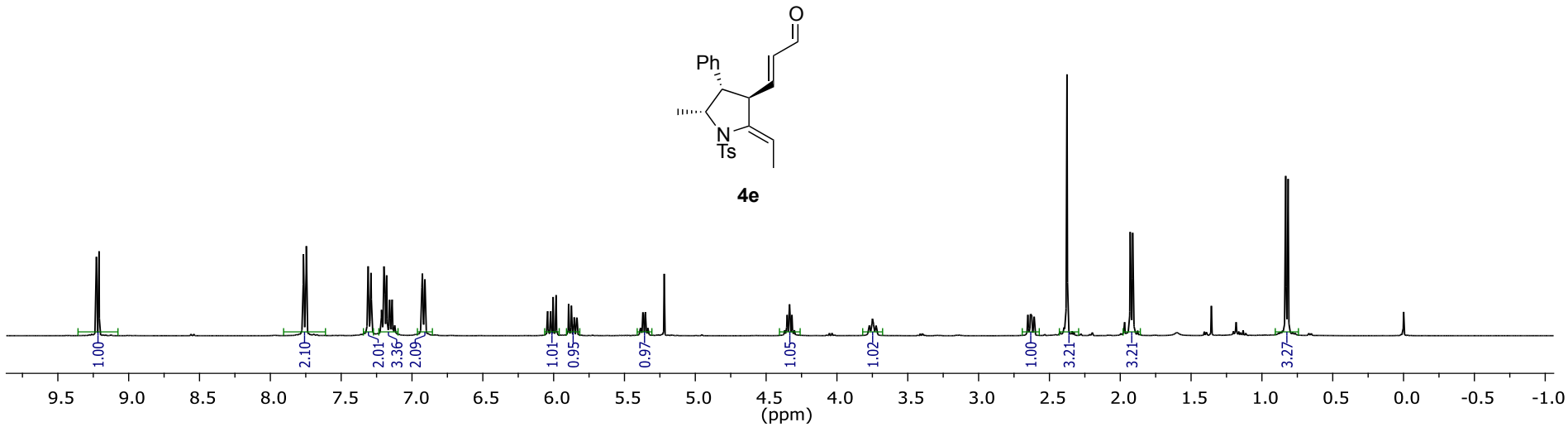


^{13}C NMR (125 MHz, $CDCl_3$)

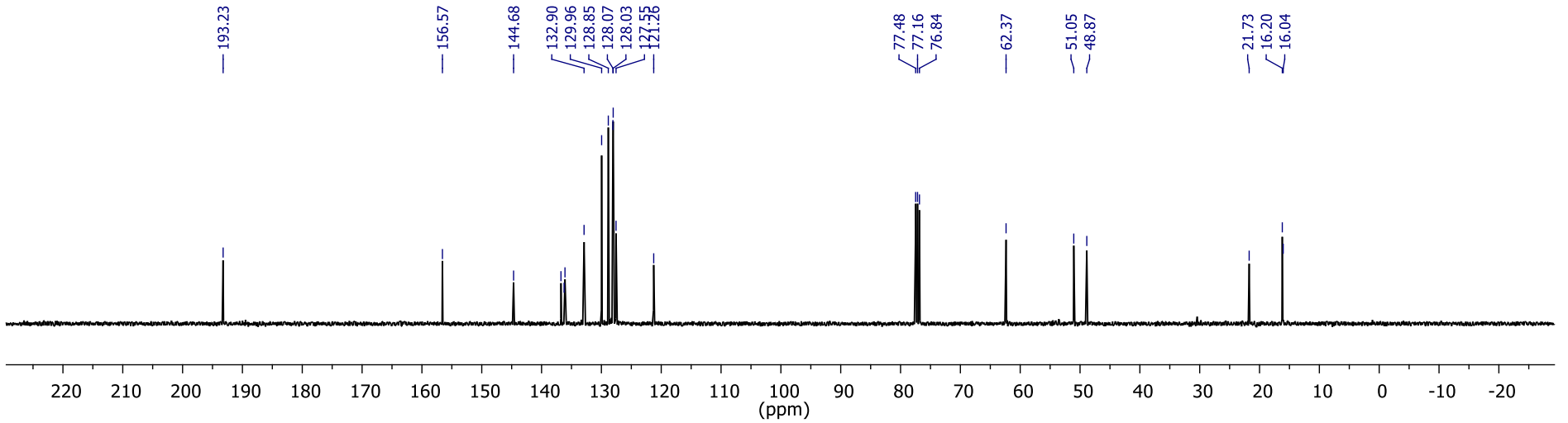


(*E*)-3-((4*S*,5*R*,*Z*)-2-ethylidene-5-methyl-4-phenyl-1-tosylpyrrolidin-3-yl)acrylaldehyde, 4e

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



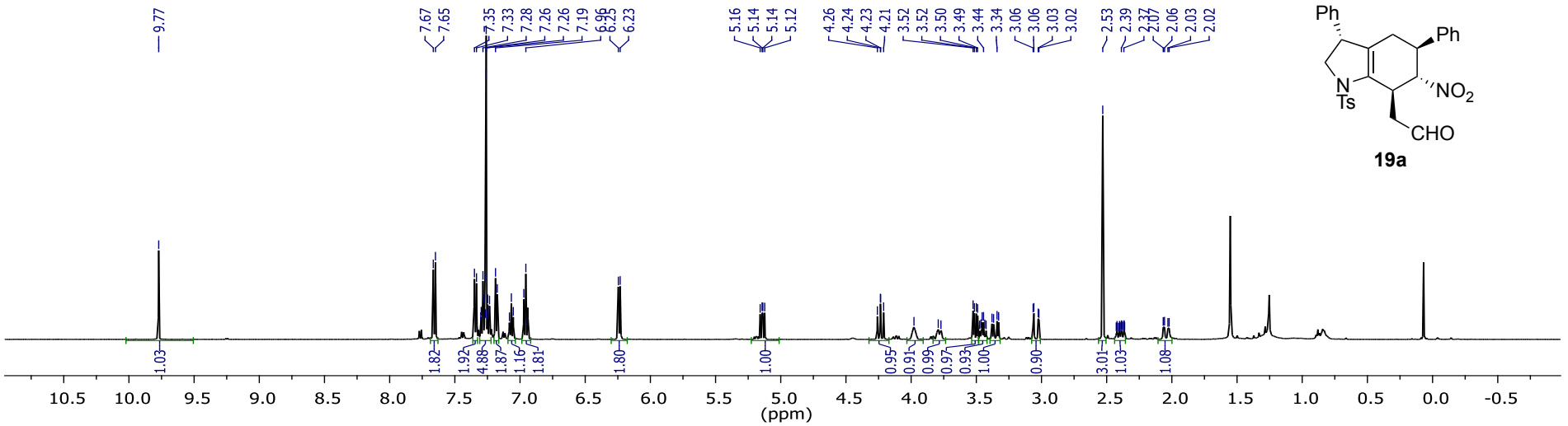
^{13}C NMR (101 MHz, $CDCl_3$)



*3.6 Double stereodifferentiating cycloaddition reactions of dienals **3b** and **4e***

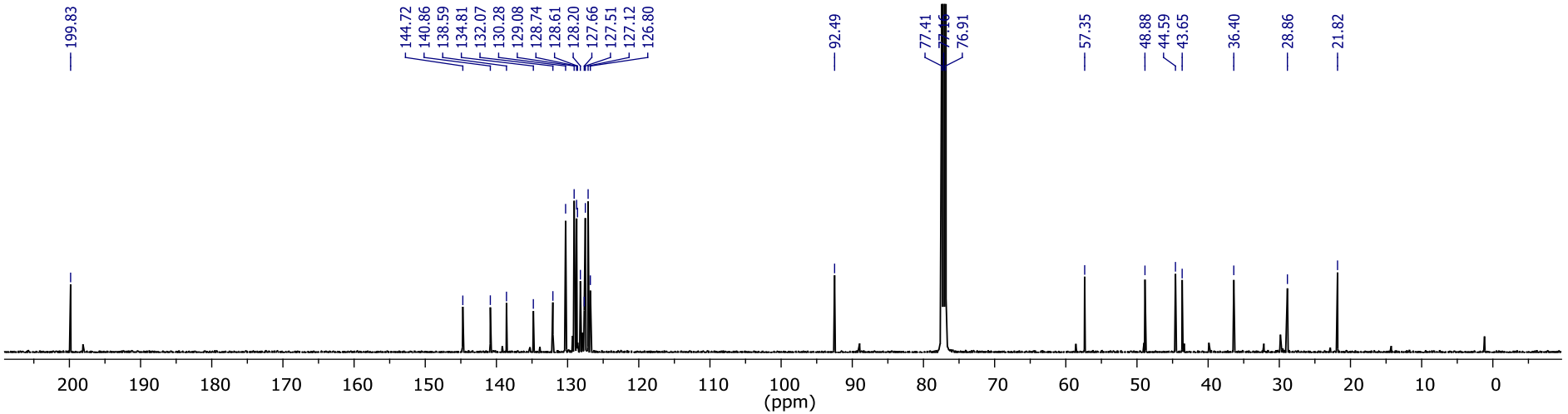
2-((3*R*,5*S*,6*S*,7*R*)-6-nitro-3,5-diphenyl-1-tosyl-2,3,4,5,6,7-hexahydro-1*H*-indol-7-yl)acetaldehyde, 19a

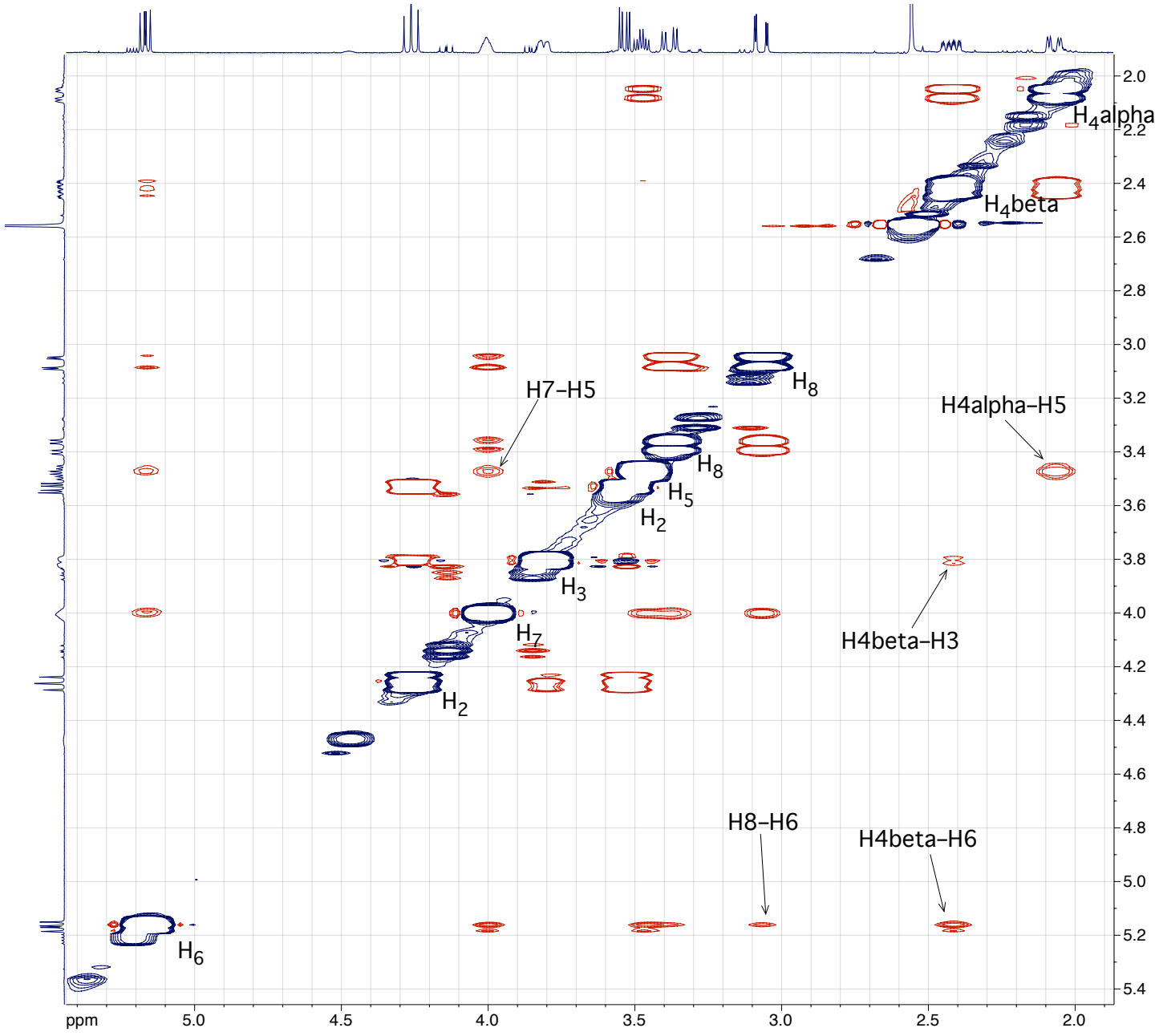
^{1}H NMR (500 MHz, $CDCl_3$)

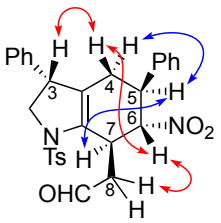


19a

^{13}C NMR (125 MHz, $CDCl_3$)

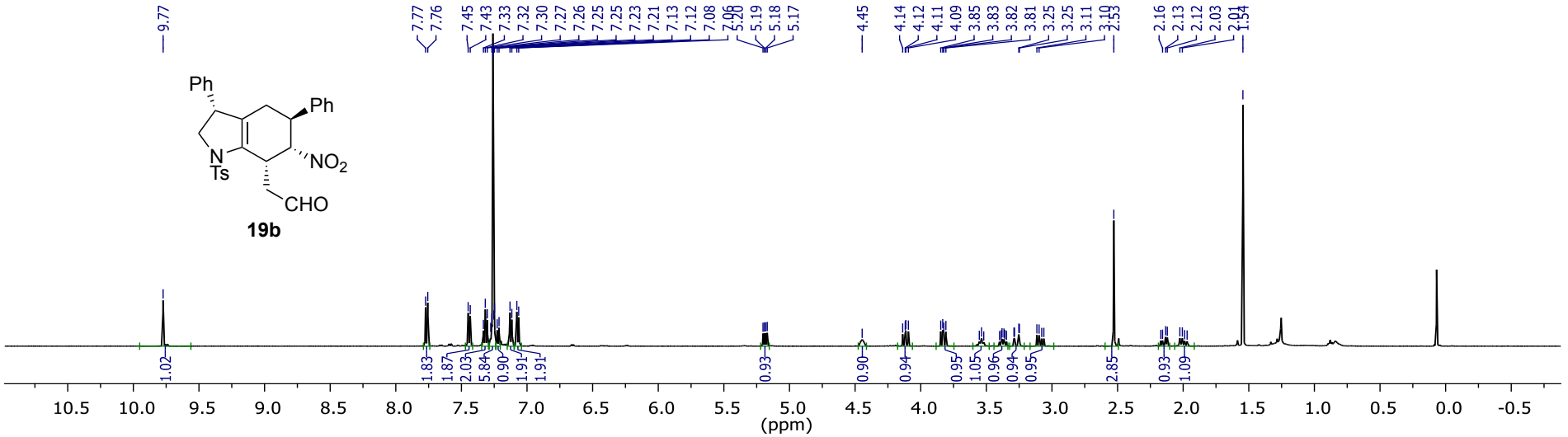



H4alpha
H4beta
H7–H5
H8
H4alpha–H5
H8
H5
H2
H3
H7
H2
H4beta–H3
H8–H6
H4beta–H6
H6
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4

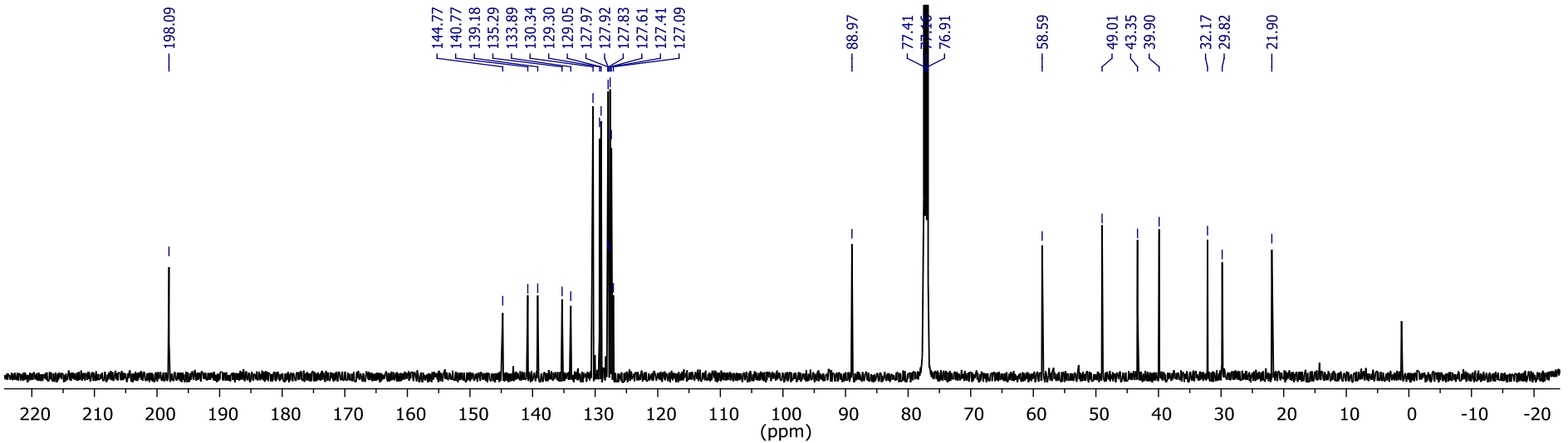

Ph
H
H
H
Ph
3
4
5
H
6
NO2
7
N
Ts
H
H
OHC
8
H
H

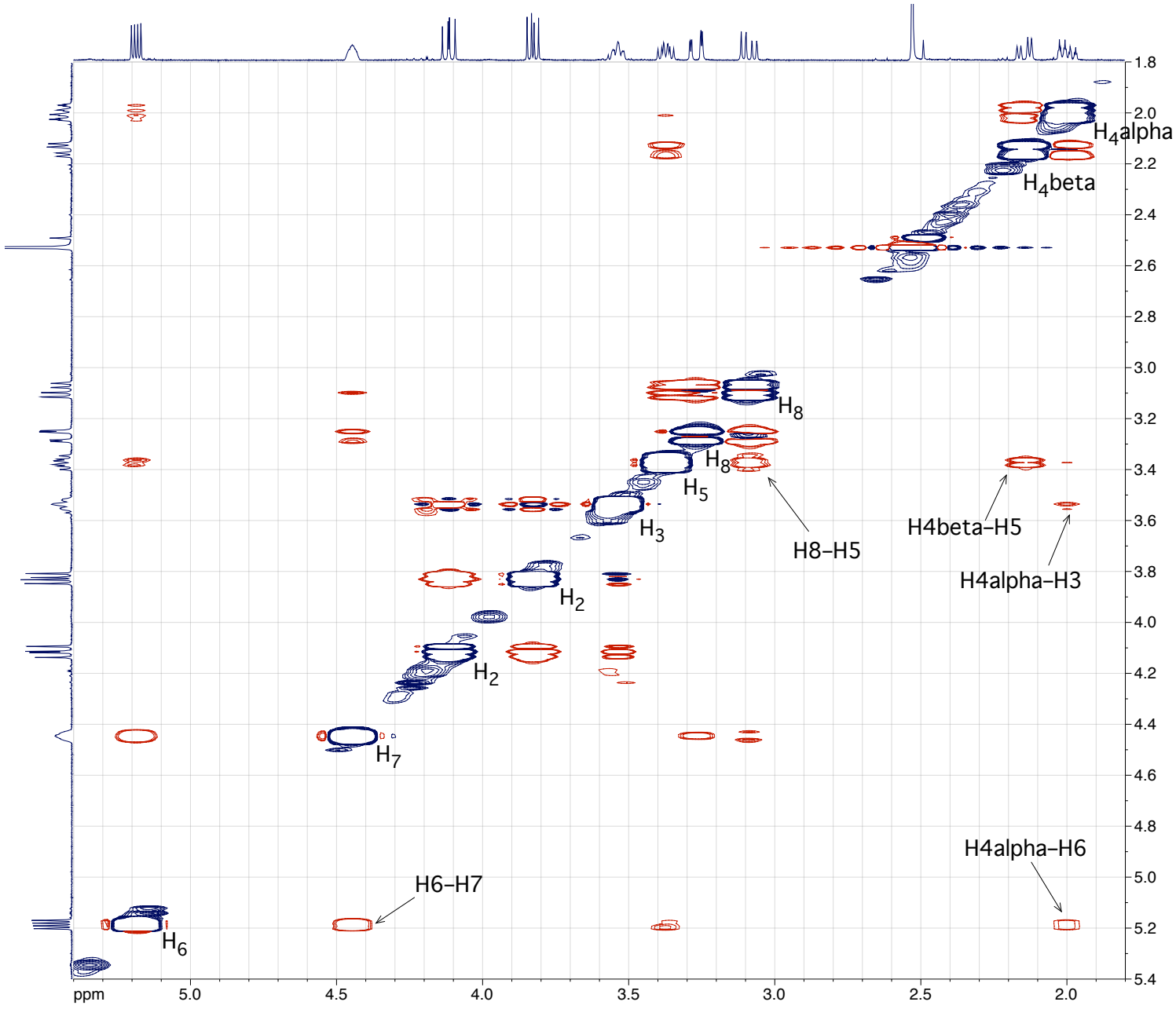
2-((3*R*,5*R*,6*R*,7*S*)-6-nitro-3,5-diphenyl-1-tosyl-2,3,4,5,6,7-hexahydro-1*H*-indol-7-yl)acetaldehyde, 19b

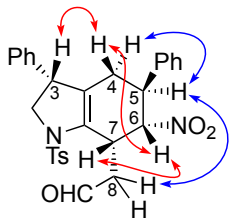
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

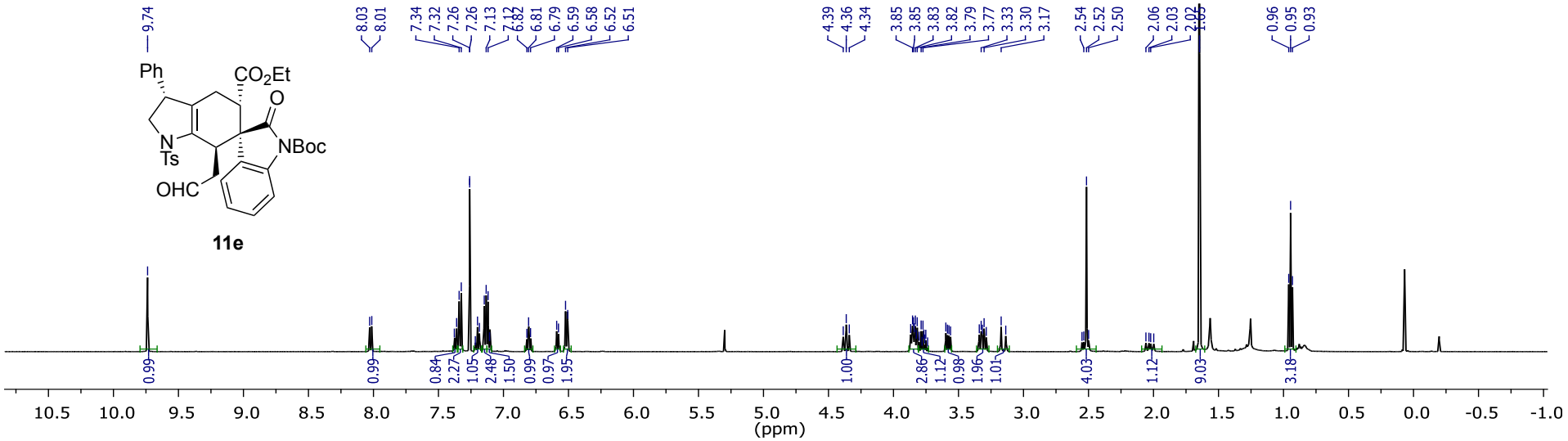



H4alpha
H4beta
H8
H8
H5
H3
H8–H5
H4beta–H5
H4alpha–H3
H2
H2
H7
H6–H7
H6
H4alpha–H6
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4

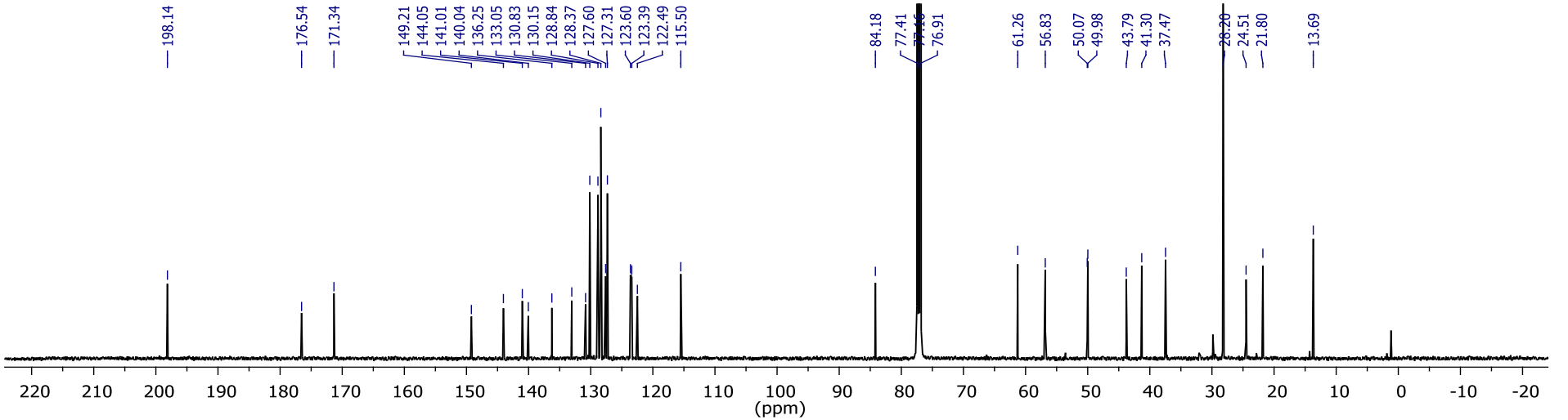

Ph
H
H
H
Ph
3
4
5
H
6
NO2
N
7
Ts
H
H
OHC
8
H
H

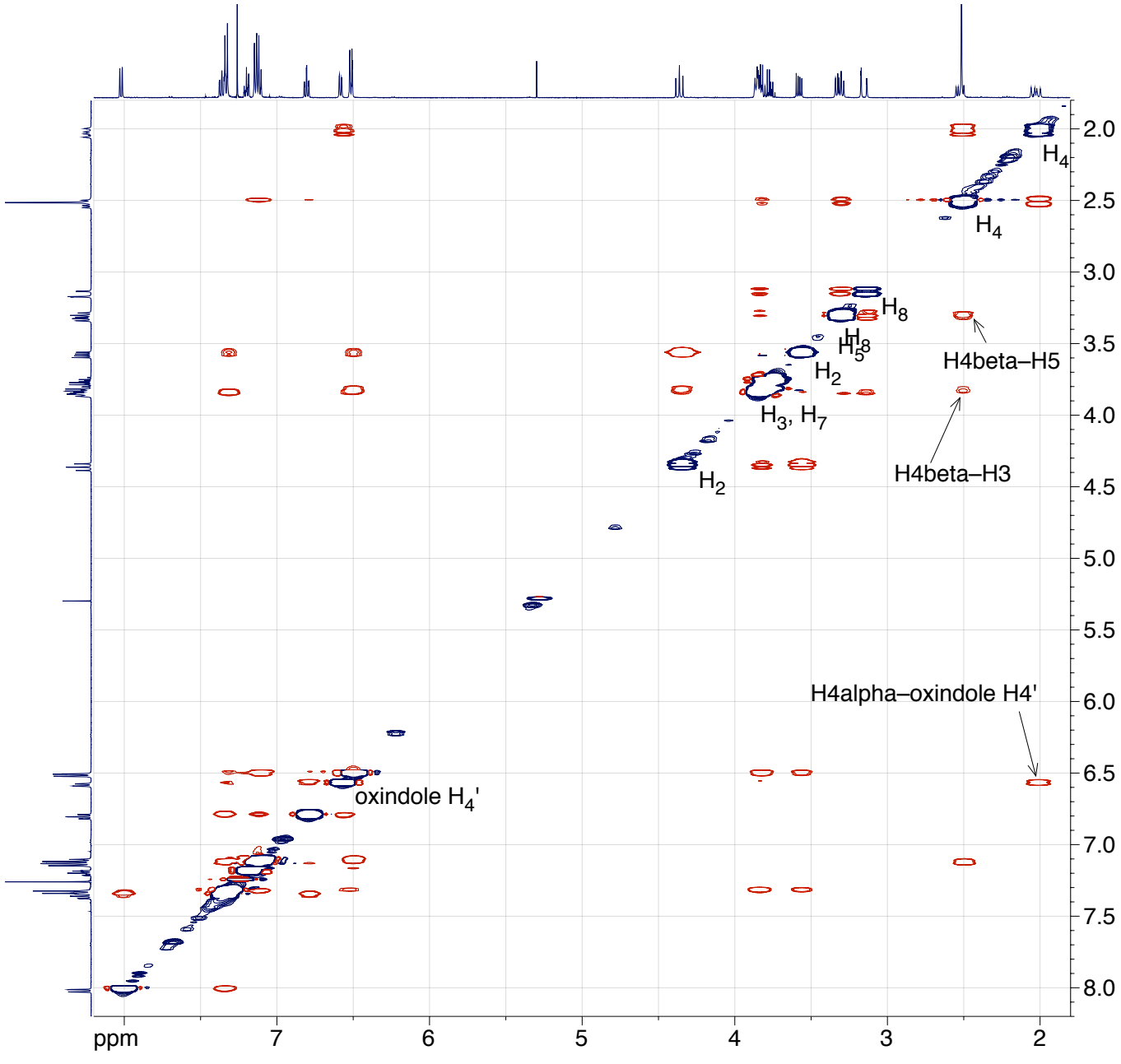
(3*R*,3'*S*,5*S*,7*R*)-1'-*tert*-butyl 5-ethyl 2'-oxo-7-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11e

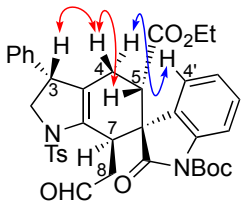
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

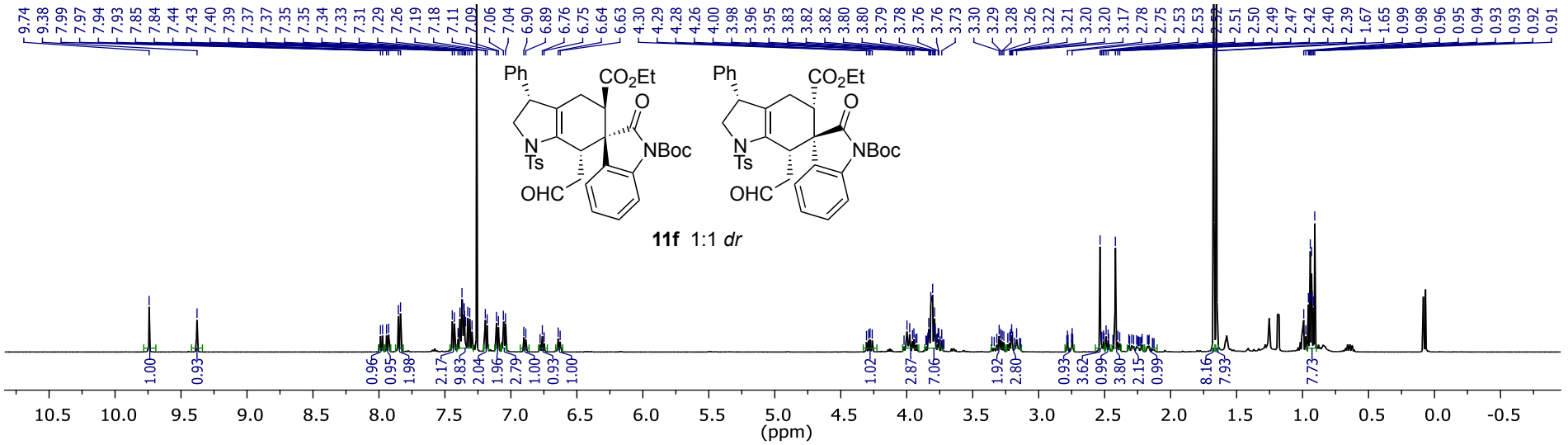



H4
H4
H8
H8
H5
H2
H3, H7
H2
H4beta–H5
H4beta–H3
H4alpha–oxindole H4'
oxindole H4'
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm
7
6
5
4
3
2

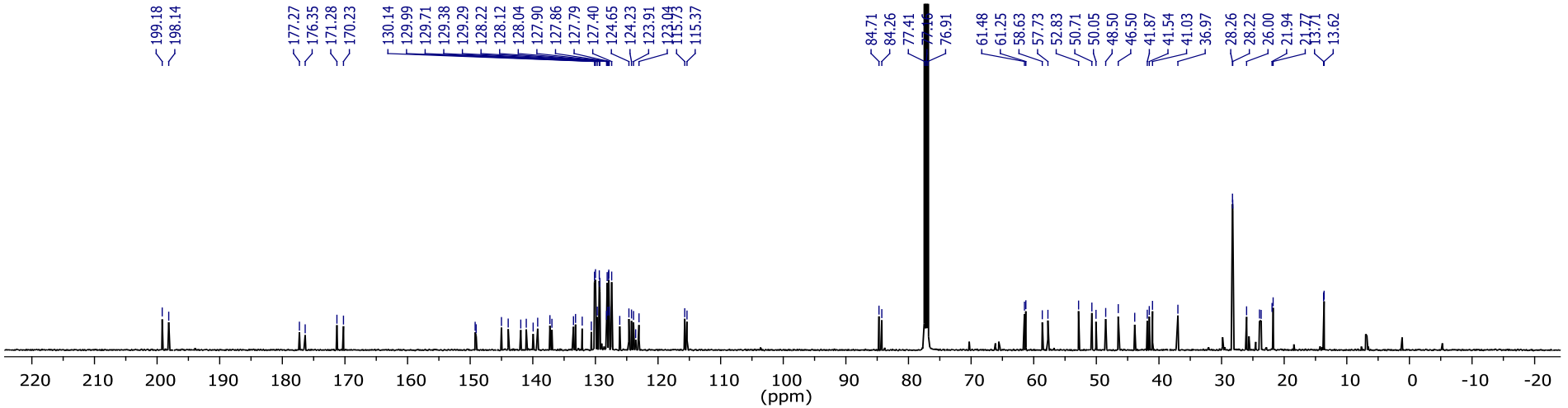

Ph
H
H
H
CO2Et
H
4
4'
5
3
H
7
N
Ts
H
8
NBoc
OHC
O

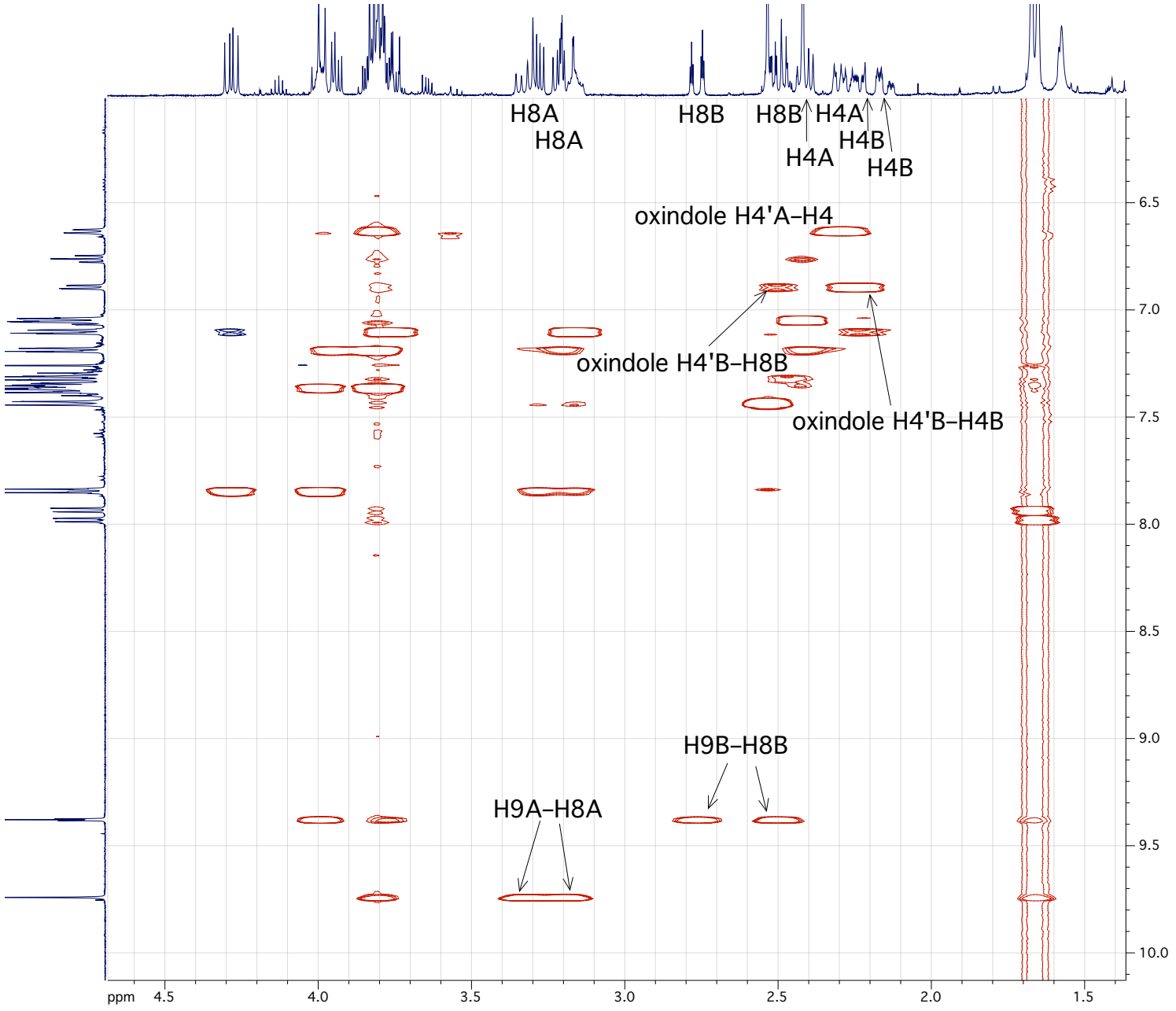
(3*R*,3'*R*,5*R*,7*S*)-1'-*tert*-butyl 5-ethyl 2'-oxo-7-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,5,7-hexahydrospiro[indole-6,3'-indoline]-1',5-dicarboxylate, 11f

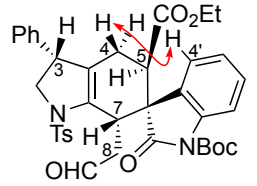
^{1}H NMR (500 MHz, $CDCl_3$)



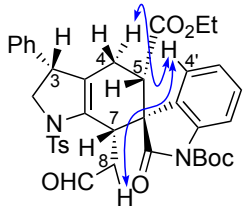
^{13}C NMR (125 MHz, $CDCl_3$)




H8A
H8A
H8B
H8B
H4A
H4A
H4B
H4B
oxindole H4'A–H4
oxindole H4'B–H8B
oxindole H4'B–H4B
H9B–H8B
H9A–H8A
ppm
4.5
4.0
3.5
3.0
2.5
2.0
1.5
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0


Ph
H
H
H
CO2Et
H
4'
4
5
3
H
N
7
Ts
H
8
NBoc
OHC
O

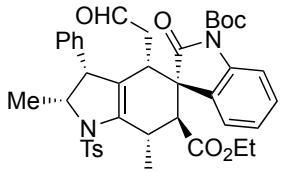
11f_A


Ph
H
H
H
CO2Et
H
4'
4
5
3
H
N
7
Ts
H
8
NBoc
OHC
O
H

11f_B

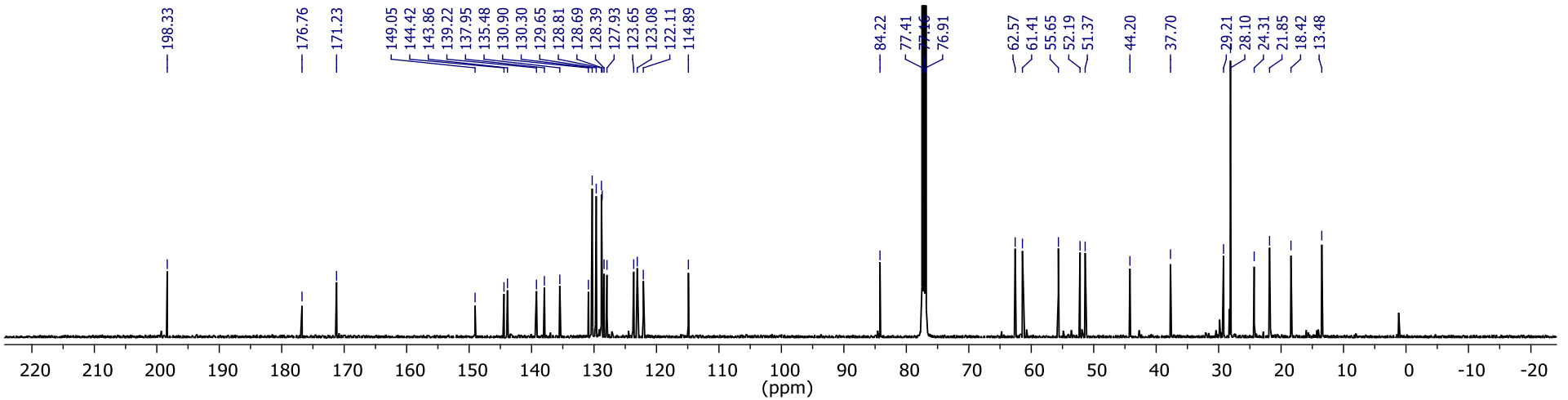
(2*R*,3*R*,3'*S*,4*S*,6*S*,7*S*)-1'-*tert*-Butyl 6-ethyl 2,7-dimethyl-2'-oxo-4-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12h

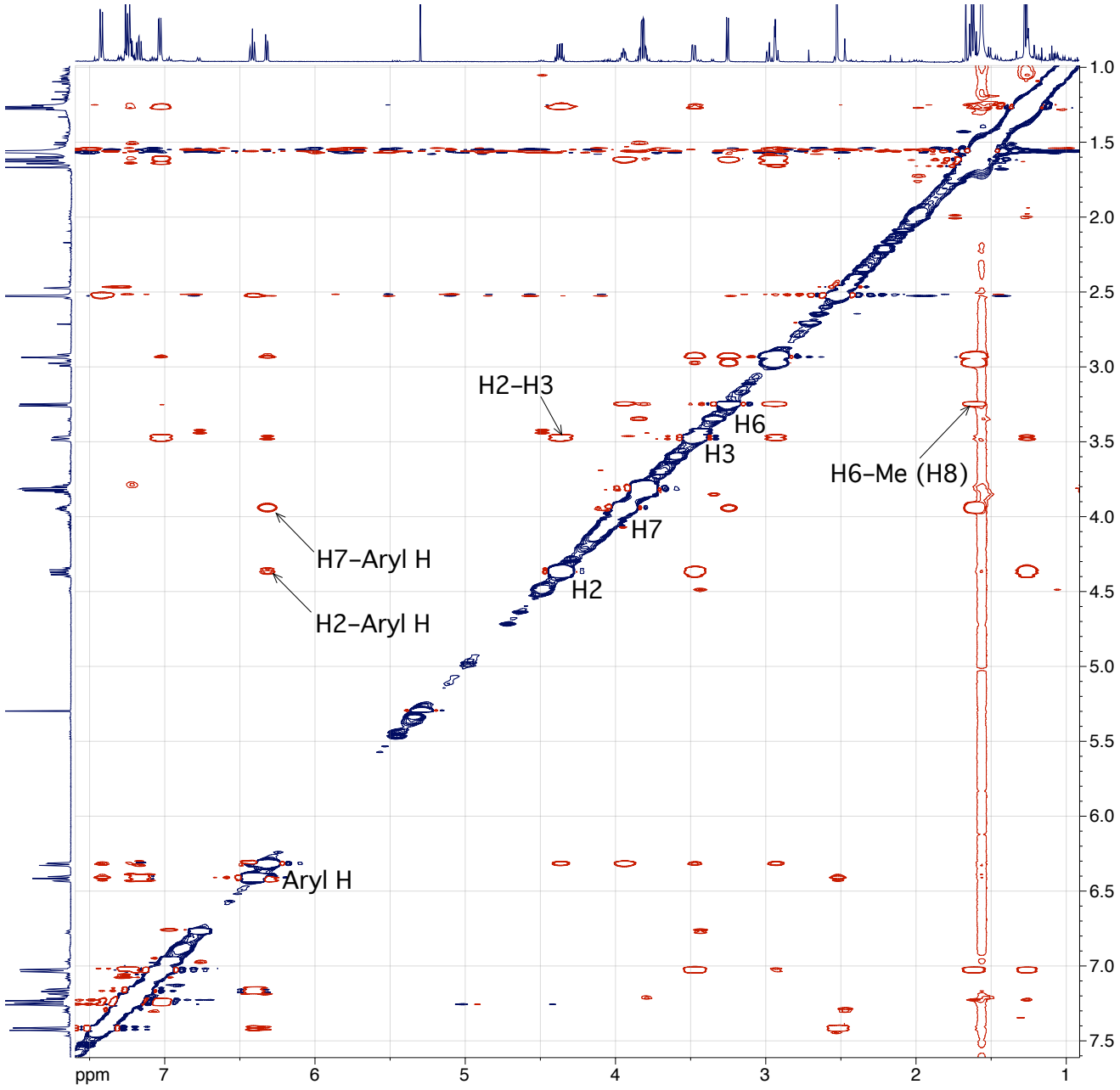
^{1}H NMR (500 MHz, $CDCl_3$)

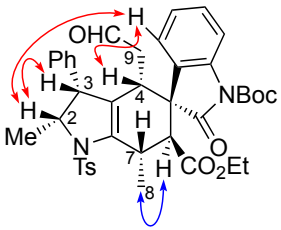


12h

^{13}C NMR (125 MHz, $CDCl_3$)

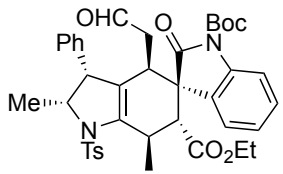



H2–H3
H6
H3
H6–Me (H8)
H7
H7–Aryl H
H2
H2–Aryl H
Aryl H
ppm
7
6
5
4
3
2
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5


H
OHC
Ph
H
H
3
H
9
4
NBoc
H
2
Me
N
Ts
H
7
H
CO2Et
O
8

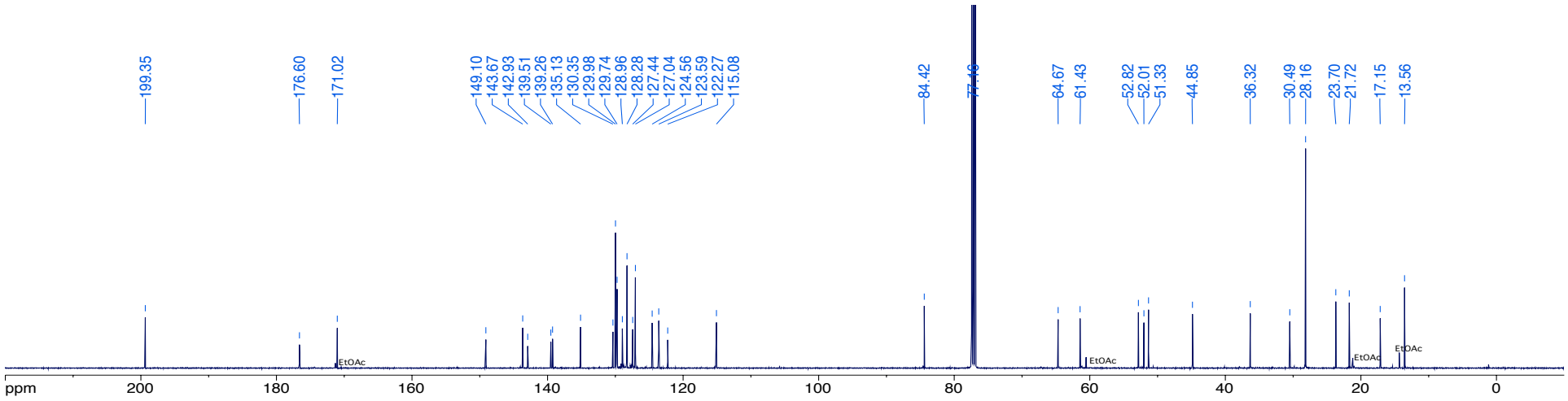
(2*R*,3*R*,3'*R*,4*R*,6*R*,7*R*)-1'-*tert*-Butyl 6-ethyl 2,7-dimethyl-2'-oxo-4-(2-oxoethyl)-3-phenyl-1-tosyl-1,2,3,4,6,7-hexahydrospiro[indole-5,3'-indoline]-1',6-dicarboxylate, 12i

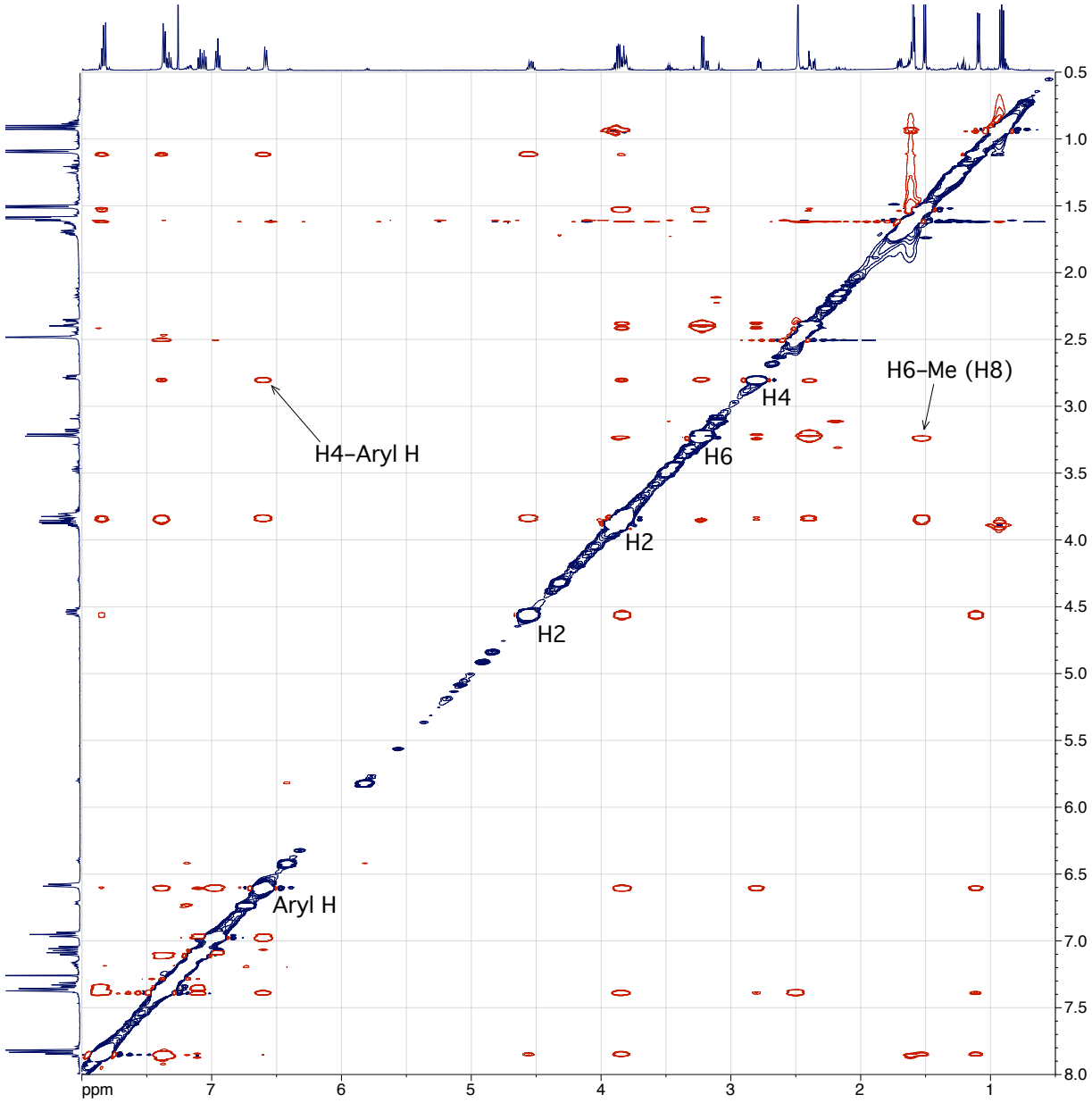
^{1}H NMR (500 MHz, $CDCl_3$)

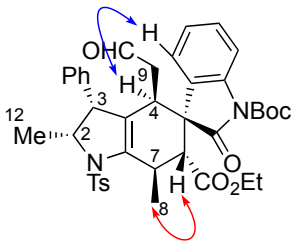


12i

^{13}C NMR (125 MHz, $CDCl_3$)




H4–Aryl H
H6–Me (H8)
H4
H6
H2
H2
Aryl H
ppm
7
6
5
4
3
2
1
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0


H
OHC
Ph
H
9
3
4
NBoc
12
Me
2
N
Ts
7
O
H
CO2Et
8