

Stereochemical and Skeletal Diversity Arising from Amino Propargylic Alcohols

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I. Materials and Methods:

Experimental. Dry solvents were dispensed from a solvent purification system that passes solvents through packed columns (THF and CH₂Cl₂: dry neutral alumina; toluene: dry neutral alumina and Q5 reactant). Unless otherwise stated, all reagents were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Nicolet IR100 FTIR from Thermo Scientific. ¹H NMR spectra were recorded on Varian Unity/Inova I500 and I600 (500MHz and 600MHz) spectrometer. ¹H data are reported as follows: chemical shift in parts per million relative to residual protonated solvent (CHCl₃: d 7.26, C₆H₆: d 7.15, DMSO-d₆: d 2.54), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened), coupling constant (Hz), and integration. ¹³C magnetic resonance spectra were recorded on Varian Unity/Inova I500 and (126MHz) spectrometer. ¹³C chemical shifts are reported in parts per million relative to solvent (CHCl₃: d 77.0). All ¹³C spectra were determined with broadband decoupling. Microwave heating was performed using Explorer[®]-48 positions, CEM. High-resolution mass spectra were obtained through the Harvard University mass spectrometry facility. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed either on EM Science silica gel 60 (230–400 mesh) or using a CombiFlash companion system (Teledyne ISCO, Inc.) with pre-packed FLASH silica gel columns (Biotage, Inc.). Optical

rotations were obtained using digital polarimeter Autopol IV (Rudolph research Analytical) with a 1 mL cell and a 1 dm path length. SFC/MS chromatography was performed with a Berger analytic SFC (Waters ZQ Mass Spectrometer) using CO₂ and MeOH or MeOH/*i*-PrOH as the mobile phase and using a Chiralcel® OD-H column or a Chiralpak® AD-H column purchased from Chiral Technology Inc. (column length: 4.6x250mm, pore size: 5µm).

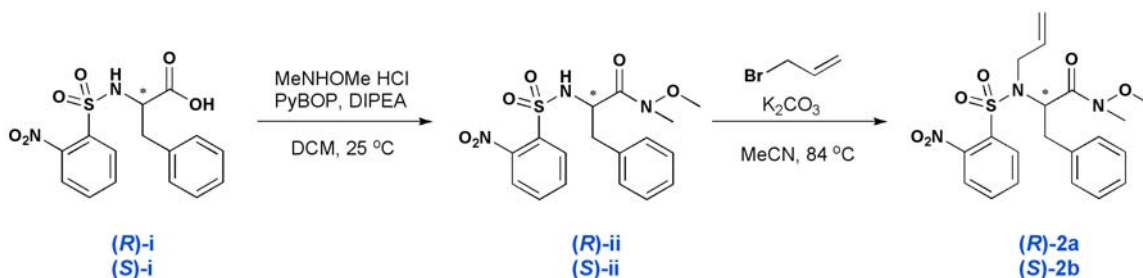
Computational. We used Pipeline Pilot (Accelrys, Inc.; San Diego, CA, USA) to generate SMILES¹ representations of all four possible stereoisomers (**a-d**) for each of the compounds studied (**1-14**). 3D models were built for each stereoisomer structure and then expanded to a set of conformers by a conformational sampling run, both performed in Molecular Operating Environment (MOE 2007.09; Chemical Computing Group; Montreal, QC, Canada) using default sampling and energy-minimization parameters and keeping only conformers with free energies within 2 kcal of the global minimum of the search. Resulting conformers were again filtered after being manually inspected for spatial defects, and unfavorable interactions.

For each compound we kept unique conformers of diastereomeric pairs (**a** and **b**) of low free energy. Because enantiomeric compounds have identical PMI ratios, we considered conformers of both **a** and **d** as “**a**”, **b** and **c** as “**b**” for PMI analysis. In order to retain the geometry of common fragments present in **1-14** throughout the 3D-models, we used the lowest energy conformer of **1** as a seed structure for new models of diastereomeric pairs of **5**, **6**, **8**, **10**, and **11**. By dialing in actual dihedral angles of **1** and performing local minimization on ring-forming atoms of the new product structures, we built 3D structures, for all **a**, that are of comparable geometry for the common molecular fragment in these compounds. We then performed an all-atom local minimization with default minimization parameters in MOE where heavy atoms were constrained to their current positions using a quadratic force constant to keep the resulting minimum close to the original coordinates. New structures of **6** and **11** were then used as seed structures for compound sets **7** and **9**, and **12**, **13**, **14**, respectively.

In our implementation of Sauer and Schwartz² PMI ratio method, we calculated ratios of the smallest and medium eigenvalues of the diagonalized mass tensor to the largest (i.e., $X = \mathbf{I}_{\text{small}}/\mathbf{I}_{\text{large}}$, $Y = \mathbf{I}_{\text{medium}}/\mathbf{I}_{\text{large}}$). The Y coordinate of these ratios was then scaled by $\sqrt{3}$ to produce an equilateral PMI space, to allow meaningful Euclidean distances between compounds to be computed in the resulting PMI space.

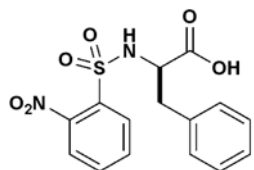
II. Experimental procedures

Scheme 1s. Synthetic route to derivatives (*R*)-**2a** and (*S*)-**2b**.^a



^a Compounds (*R*)-**i** and (*S*)-**i** were prepared from D- and L-phenylalanine respectively by the known procedure.³ Compound (*S*)-**i** is a known compound.⁴

(*R*)-2-(2-nitrophenylsulfonamido)-3-phenylpropanoic acid (*R*)-**i**



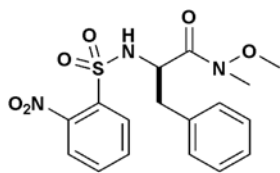
Yield 86% (white solid); IR (neat, cm^{-1}) $\nu = 3321, 3095, 3030, 1727, 1539,$
 $1355, 1168, 1103$; $[\alpha]_{\text{D}}^{20} = + 81.8 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.49 \text{ g cm}^3, \text{CHCl}_3$);

¹H NMR (500 MHz, CDCl_3) $\delta = 7.93$ (d, $J = 8.0$, 1H), 7.83 (d, $J = 8.0$, 1H),
 7.68 (t, $J = 7.5$, 1H), 7.64 (t, $J = 7.5$, 1H), $7.22 - 7.18$ (m, 3H), $7.13 - 7.11$
(m, 2H), 5.94 (d, $J = 8.5$, 1H), 4.48 (ddd, $J = 5.0, 7.5, 13.5$, 1H), 3.21 (dd, $J = 5.0, 14.0$, 1H), 3.05 (dd,
 $J = 7.5, 14.0$, 1H); ¹³C NMR (126 MHz, CDCl_3) $\delta = 175.4, 147.2, 134.4, 133.9, 133.6, 133.0,$
 $130.2, 129.2, 128.7, 127.5, 125.6, 57.4, 38.6$. HRMS (EI) calcd. for $[\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_6\text{S}]$ ($\text{M}+\text{H}$)⁺
 351.0645 , found 351.0642 .

General procedure for amidation

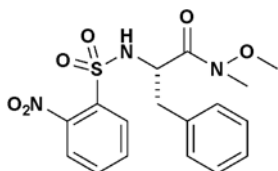
To a solution of (*R*)- or (*S*)-2-(2-nitrophenylsulfonamido)-3-phenylpropanoic acid (1 equiv.), (*R*)-**i** or (*S*)-**i** respectively, *N,N*-diisopropylethylamine (1 equiv.) in dry dichloromethane (0.2M) at 0 °C, benzotriazol-1-yloxy tripyrrolidinophosphonium hexafluorophosphate (pyBOP, 1.1 equiv.), *N,O*-dimethylhydroxylamine hydrochloride (2 equiv.) and *N,N*-diisopropylethylamine (2 equiv.) were added. The resulting solution was stirred for 30 min at 0 °C and then it was allowed to warm to room temperature and stirred under nitrogen for 4h. The mixture was diluted with dichloromethane, quenched with 3N aqueous HCl and the aqueous layer was extracted with dichloromethane. The combined organic phases were washed with saturated aqueous NaHCO_3 , brine, dried over sodium sulfate, filtered and evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography (Hex/EtOAc 1:1).

(*R*)-*N*-methoxy-*N*-methyl-2-(2-nitrophenylsulfonamido)-3-phenylpropanamide (*R*)-**ii**



Yield 83% (pale yellow solid); IR (neat, cm^{-1}) $\nu = 3300, 3095, 3028, 2939, 1662, 1541, 1441, 1412, 1385, 1349, 1168, 1079$; $[\alpha]_{\text{D}}^{20} = +12.1 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.43 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.87$ (d, $J=8.0$, 1H), 7.84 (d, $J=8.0$, 1H), 7.65 (t, $J=7.5$, 1H), 7.59 (t, $J=7.5$, 1H), $7.21 - 7.12$ (m, 5H), 6.23 (d, $J=9.0$, 1H), $4.88 - 4.83$ (m, 1H), 3.55 (s, 3H), 3.06 (dd, $J=6.0, 13.5$, 1H), 2.96 (s, 3H), 2.91 (dd, $J=7.0, 13.5$, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 170.60, 147.53, 135.66, 134.55, 133.20, 132.52, 129.98, 129.44, 128.44, 127.12, 125.47, 61.49, 55.36, 39.42, 31.99$; HRMS (EI) calcd. for $[\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_6\text{S}]$ (M+H) $^+$ 394.1067, found 394.1069.

(S)-N-methoxy-N-methyl-2-(2-nitrophenylsulfonamido)-3-phenylpropanamide (S-ii)

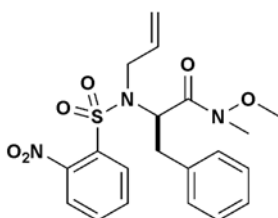


Yield 83% (pale yellow solid); IR (neat, cm^{-1}) $\nu = 3300, 3095, 3028, 2938, 1662, 1541, 1441, 1412, 1385, 1350, 1168, 1079$; $[\alpha]_{\text{D}}^{20} = -12.7 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.33 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.87$ (d, $J=8.0$, 1H), 7.83 (d, $J=8.0$, 1H), 7.65 (t, $J=7.5$, 1H), 7.59 (t, $J=7.5$, 1H), $7.19 - 7.12$ (m, 5H), 6.25 (m, 1H), $4.85 - 4.84$ (m, 1H), 3.55 (s, 3H), 3.06 (dd, $J=6.0, 13.5$, 1H), 2.96 (s, 3H), 2.90 (dd, $J=7.0, 13.5$, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 170.5, 147.4, 135.6, 134.5, 133.2, 132.5, 129.9, 129.3, 128.4, 127.0, 125.4, 61.4, 55.3, 39.3, 31.9$; HRMS (EI) calcd. for $[\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_6\text{S}]$ (M+H) $^+$ 394.1067, found 394.1064.

General procedure for N-Allylation

In a 250 mL pear flask, (*R*)- or (*S*)-*N*-methoxy-*N*-methyl-2-(2-nitrophenylsulfonamido)-3-phenylpropanamide (1 equiv.), (**R-ii**) or (**S-ii**) respectively, was dissolved in acetonitrile (0.2M) to give a pale yellow solution. Potassium carbonate (1.2 equiv.) and 3-bromoprop-1-ene (1.2 equiv.) were added and the resulting suspension was heated to 84°C and stirred under nitrogen for 3h. The solvent was evaporated under reduced pressure and the residue taken up with water and dichloromethane. The two phases were separated and the aqueous layer was extracted with dichloromethane. The combined organic phases were dried over sodium sulfate, filtered and evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography (Hex/EtOAc 3:2).

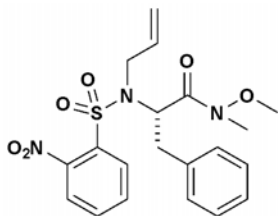
(R)-2-(N-allyl-2-nitrophenylsulfonamido)-N-methoxy-N-methyl-3-phenylpropanamide (2a)



Yield 97% (yellow oil); IR (neat, cm^{-1}) $\nu = 3088, 3028, 2940, 1665, 1544, 1440, 1372, 1165$; $[\alpha]_{\text{D}}^{20} = +50.6 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.65 \text{ g cm}^3$,

CHCl₃); SFC: Chiralcel® OD-H column; 5% MeOH, 95% sfCO₂, $t_R^{(major)} = 12$ min, area = 100% (>99% ee) (racemic compound $t_R = 12.18$ min, 13.46 min); ¹H NMR (500 MHz, CDCl₃) $\delta = 7.92$ (d, $J=8.0$, 1H), 7.68 – 7.64 (m, 1H), 7.61 – 7.57 (m, 2H), 7.27 – 7.18 (m, 5H), 5.89 – 5.81 (m, 1H), 5.30 – 5.23 (m, 2H), 5.08 (d, $J=10.0$, 1H), 4.45 (dd, $J=6.5$, 16.5, 1H), 4.30 (dd, $J=6.0$, 16.5, 1H), 3.34 (m, 4H), 3.05 – 2.93 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) $\delta = 170.0$, 148.2, 136.3, 135.3, 133.9, 133.3, 131.4, 130.9, 129.4, 128.4, 126.8, 124.0, 117.6, 61.2, 56.5, 48.2, 36.9, 31.7; HRMS (EI) calcd. for [C₂₀H₂₃N₃O₆S] (M+H)⁺ 434.1380, found 434.1388.

(S)-2-(N-allyl-2-nitrophenylsulfonamido)-N-methoxy-N-methyl-3-phenylpropanamide (2b)



Yield 98% (yellow oil); IR (neat, cm⁻¹) $\nu = 3088$, 3028, 2940, 1665, 1544, 1440, 1372, 1165, 1127, 1062; $[\alpha]_D^{20} = -47.3$ cm³ g⁻¹ dm⁻¹ (c = 0.52 g cm³, CHCl₃); SFC: Chiralcel® OD-H column; 5% MeOH, 95% sfCO₂, $t_R^{(major)} = 13.33$ min, area = 100% (>99% ee) (racemic compound $t_R = 12.18$ min, 13.46 min); ¹H NMR (500 MHz, CDCl₃) $\delta = 7.91$ (d,

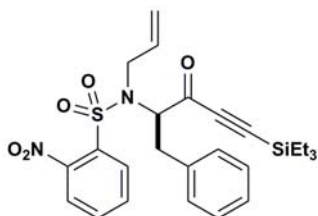
$J=8.0$, 1H), 7.65 – 7.56 (m, 3H), 7.27 – 7.18 (m, 5H), 5.83 (ddd, $J=6.0$, 11.0, 16.5, 1H), 5.29 – 5.22 (m, 2H), 5.07 (d, $J=10$, 1H), 4.43 (dd, $J=5.5$, 16.5, 1H), 4.29 (dd, $J=5.5$, 16.5, 1H), 3.40 – 3.24 (m, 4H), 3.01 – 2.93 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) $\delta = 170.0$, 148.2, 136.4, 135.3, 134.0, 133.3, 131.4, 130.9, 129.5, 128.4, 126.9, 124.0, 117.6, 61.2, 56.6, 48.2, 36.9, 31.7; HRMS (EI) calcd. for [C₂₀H₂₃N₃O₆S] (M+H)⁺ 434.1380, found 434.1386.

General procedure for the preparation of α,β -acetylenic ketones 3a-b

In a flame-dried flask, triethyl(ethynyl)silane (2.8 equiv.) was dissolved in dry THF (0.5M), the resulting colorless solution was cooled to – 78 °C and *n*-butyllithium (2.5 M in hexanes, 2.6 equiv.) was added dropwise. (NOTE: recently opened *n*-butyllithium is recommended). The reaction mixture was stirred under nitrogen for 1h, allowing the temperature to rise up to – 50 °C. Then, the reaction was cooled to – 78 °C and a solution of Weinreb amide derivative **2a** or **2b** (1 equiv.) in dry THF (0.5M) was added. The reaction mixture was stirred under nitrogen for 75 min allowing the temperature to rise up to – 45 °C. The reaction mixture was quenched with saturated aqueous NH₄Cl. The aqueous layer was extracted with diethyl ether and the combined organic phases were washed with brine, dried over sodium sulfate, filtered and evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography (Hex/EtOAc 4:1).

(R)-N-allyl-2-nitro-N-(3-oxo-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)benzenesulfonamide

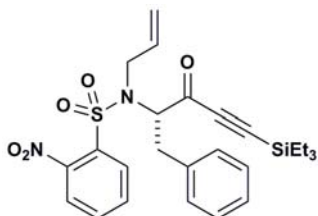
(3a)



Yield 72% (yellow oil); IR (neat, cm^{-1}) $\nu = 3089, 3029, 2957, 2913, 2876, 2147, 1681, 1545, 1371, 1167, 1008$; $[\alpha]_{\text{D}}^{20} = -47.1 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.41 \text{ g cm}^3, \text{CHCl}_3$); SFC: Chiralpak[®] AD-H (2 columns); 10% MeOH/*i*-PrOH (4:1), 95% sfCO₂, $t_{\text{R}}^{(\text{major})} = 4.32 \text{ min}$, area = 98.38 % (97% ee) (racemic compound $t_{\text{R}} = 3.81 \text{ min}, 4.31 \text{ min}$); ¹H NMR (500 MHz, CDCl₃) $\delta = 7.79 - 7.77$ (m, 1H), 7.65 – 7.62 (m, 1H), 7.57 – 7.52 (m, 2H), 7.29 – 7.24 (m, 4H), 7.23 – 7.21 (m, 1H), 5.80 (ddd, $J=6.0, 11.0, 16.5$, 1H), 5.20 (d, $J=16.5$, 1H), 5.11 (d, $J=10.0$, 1H), 5.09 – 5.07 (m, 1H), 4.10 (dd, $J=6.5, 16.5$, 1H), 3.95 (dd, $J=6.5, 16.5$, 1H), 3.60 (dd, $J=6.0, 14.5$, 1H), 3.02 (dd, $J=8.5, 14.5$, 1H), 1.00 (t, $J=8.0$, 9H), 0.67 (q, $J=8.0$, 6H); ¹³C NMR (126 MHz, CDCl₃) $\delta = 183.9, 136.3, 134.5, 133.6, 133.3, 131.5, 131.1, 129.2, 128.6, 126.9, 124.0, 118.8, 101.7, 101.7, 68.6, 49.4, 34.8, 7.2, 3.6$; HRMS (EI) calcd. for [C₂₆H₃₂N₂O₅SSi] (M+H)⁺ 513.1874, found 513.1869.

(S)-N-allyl-2-nitro-N-(3-oxo-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)benzenesulfonamide

(3b)



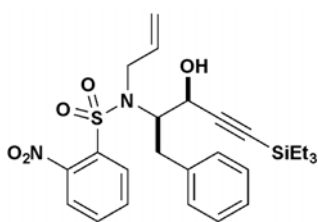
Yield 79% (yellow oil); IR (neat, cm^{-1}) $\nu = 3089, 3029, 2957, 2913, 2876, 2148, 1681, 1545, 1371, 1167, 1008$; $[\alpha]_{\text{D}}^{20} = +42.5 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.53 \text{ g cm}^3, \text{CHCl}_3$); SFC: Chiralpak[®] AD-H (2 columns); 10% MeOH/*i*-PrOH (4:1), 95% sfCO₂, $t_{\text{R}}^{(\text{major})} = 3.85 \text{ min}$, area = 98 % (96% ee) (racemic compound $t_{\text{R}} = 3.81 \text{ min}, 4.31 \text{ min}$); ¹H NMR (500 MHz, CDCl₃) $\delta = 7.79 - 7.77$ (m, 1H), 7.65 – 7.62 (m, 1H), 7.57 – 7.52 (m, 2H), 7.27 – 7.24 (m, 4H), 7.23 – 7.21 (m, 1H), 5.81 (ddd, $J=6.0, 11.0, 16.5$, 1H), 5.21 (d, $J=16.5$, 1H), 5.11 (d, $J=10.5$, 1H), 5.09 – 5.07 (m, 1H), 4.10 (dd, $J=6.5, 16.5$, 1H), 3.95 (dd, $J=6.5, 16.5$, 1H), 3.60 (dd, $J=6.0, 14.5$, 1H), 3.02 (dd, $J=8.0, 14.5$, 1H), 1.00 (t, $J=8.0$, 9H), 0.67 (q, $J=8.0$, 6H); ¹³C NMR (126 MHz, CDCl₃) $\delta = 183.9, 136.3, 134.5, 133.5, 133.3, 131.5, 131.1, 129.2, 128.5, 126.9, 124.0, 118.7, 101.7, 101.6, 68.7, 49.4, 34.8, 7.2, 3.6$; HRMS (EI) calcd. for [C₂₆H₃₂N₂O₅SSi] (M+Na)⁺ 535.1693, found 535.1696.

General procedure for diastereoselective reduction of α,β -acetylenic ketones 3a-b

In a flame-dried flask, (*R*)- or (*S*)-1-methyl-3,3-diphenylhexahydropyrrolo[1,2-*c*][1,3,2]oxazaborolidine (1.0 M in toluene, 1.1 equiv.) and borane tetrahydrofuran complex solution (1.0

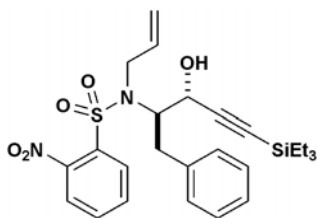
M in THF, 1.1 equiv.) were dissolved in dry THF at 0°C and the resulting colorless solution was stirred for 30 min under nitrogen. The mixture was cooled to – 78 °C and the appropriate enantiomer of the substrate (1 equiv.), dissolved in dry THF (0.1M), was slowly added by syringe pump (1.6 mL/h). The temperature was maintained between – 70 °C and – 50 °C. The reaction mixture was cautiously quenched by addition of MeOH at 0 °C. After 30 min of stirring at room temperature, the mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography (Hex/EtOAc 4:1).

***N*-allyl-*N*-((2*R*,3*S*)-3-hydroxy-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)-2-nitrobenzene sulfonamide (4a)**



Yield 80% (inseparable mixture of diastereomers, *anti/syn* = 9:91) (yellow oil); IR (neat, cm⁻¹) ν = 3523, 3087, 3028, 2955, 2912, 2875, 2169, 1544, 1372, 1350, 1163, 1005; $[\alpha]_D^{20}$ = + 3.3 cm³ g⁻¹ dm⁻¹ (c = 0.12 g cm³, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ = 7.92 (d, *J*=8, 1H), 7.65 – 7.62 (m, 1H), 7.58 – 7.53 (m, 2H), 7.21 – 7.19 (m, 4H), 7.18 – 7.16 (m, 1H), 5.95 (ddd, *J*=6.0, 11.0, 16.5, 1H), 5.32 – 5.28 (m, 2H), 5.14 (d, *J*=10.0, 1H), 4.56 (dd, *J*=7.0, 16.5, 1H), 4.46 – 4.45 (m, 1H), 4.30 – 4.25 (m, 2H), 4.27 – 4.24 (m, 1H), 3.20 (dd, *J*=8.5, 14.5, 1H), 3.12 (dd, *J*=6.5, 14.5, 1H), 2.42 (d, *J*=7.0, 1H), 1.03 (t, *J*=8.0, 9H), 0.65 (q, *J*=8.0, 6H); ¹³C NMR (126 MHz, CDCl₃) δ = 137.0, 135.8, 133.5, 133.4, 131.7, 131.6, 129.1, 128.5, 128.4, 126.8, 124.1, 117.8, 104.3, 91.3, 63.6, 63.1, 47.5, 36.0, 7.4, 4.1; HRMS (EI) calcd. for [C₂₆H₃₄N₂O₅SSi] (M+H)⁺ 515.2030, found 515.2030.

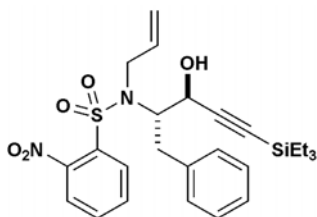
***N*-allyl-*N*-((2*R*,3*R*)-3-hydroxy-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)-2-nitrobenzene sulfonamide (4b)**



Yield 99% (inseparable mixture of diastereomers, *anti/syn* = 90:10) (yellow oil); IR (neat, cm⁻¹) ν = 3525, 3087, 3028, 2955, 2912, 2875, 2171, 1545, 1371, 1352, 1162, 1006; $[\alpha]_D^{20}$ = – 75.8 cm³ g⁻¹ dm⁻¹ (c = 0.12 g cm³, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ = 7.58 (d, *J*=8.0, 1H), 7.56 – 7.53 (m, 1H), 7.46 (d, *J*=8.0, 1H), 7.42 – 7.38 (m, 1H), 7.13 – 7.06 (m, 5H), 6.01 (ddd, *J*=6.0, 10.0, 16.5, 1H), 5.31 (d, *J*=17.5, 1H), 5.18 (d, *J*=10.0, 1H), 4.45 (m, 1H), 4.30 – 4.25 (m, 2H), 4.04 (dd, *J*=7.5, 16.5, 1H), 3.29 (dd, *J*=10.0, 15.0, 1H), 2.88 (dd, *J*=10.0, 15.0, 1H), 2.73 (br, 1H), 1.01 (t, *J*=8.0, 9H), 0.64 (q, *J*=8.0, 6H); ¹³C NMR (126 MHz, CDCl₃) δ = 147.8, 137.0, 135.7, 133.5, 133.1, 131.5, 131.0, 129.1, 128.4, 126.6, 124.0,

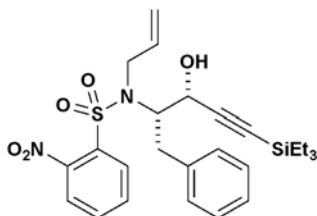
118.1, 105.3, 90.0, 65.3, 64.0, 47.7, 34.8, 7.4, 4.1; HRMS (EI) calcd. for $[C_{26}H_{34}N_2O_5SSi]$ (M+H)⁺ 515.2030, found 515.2032.

***N*-allyl-*N*-((2*S*,3*S*)-3-hydroxy-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)-2-nitrobenzene sulfonamide (4c)**



Yield 87% (inseparable mixture of diastereomers, *anti/syn* = 90:10) (yellow oil); IR (neat, cm^{-1}) ν = 3523, 3087, 3028, 2955, 2924, 2875, 2172, 1544, 1372, 1162, 1006; $[\alpha]_D^{20}$ = + 68.3 $cm^3 g^{-1} dm^{-1}$ (c = 0.36 $g cm^3$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ = 7.58 – 7.53 (m, 2H), 7.47 (d, $J=8.0$, 1H), 7.41 – 7.38 (m, 1H), 7.14 – 7.06 (m, 5H), 6.05 – 5.97 (m, 1H), 5.33 – 5.28 (m, 1H), 5.18 (d, $J=10.0$, 1H), 4.48 – 4.45 (m, 1H), 4.29 – 4.25 (m, 2H), 4.05 (dd, $J=7.5$, 16.5, 1H), 3.29 (dd, $J=5.0$, 15.0, 1H), 2.88 (dd, $J=10.0$, 15.0, 1H), 2.73 (d, $J=8.0$, 1H), 1.01 (t, $J=8.0$, 9H), 0.64 (q, $J=8.0$, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.7, 137.0, 135.7, 133.5, 133.1, 131.5, 130.9, 129.1, 128.4, 126.6, 124.0, 118.1, 105.3, 90.0, 65.3, 63.9, 47.7, 34.8, 7.4, 4.1; HRMS (EI) calcd. for $[C_{26}H_{34}N_2O_5SSi]$ (M+H)⁺ 515.2030, found 515.2031.

***N*-allyl-*N*-((2*S*,3*R*)-3-hydroxy-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)-2-nitrobenzene sulfonamide (4d)**

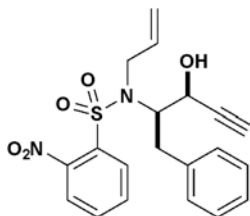


Yield 80% (inseparable mixture of diastereomers, *anti/syn* = 9:91) (yellow oil); IR (neat, cm^{-1}) ν = 3527, 2955, 2911, 2875, 2161, 1544, 1371, 1350, 1163, 1005; $[\alpha]_D^{20}$ = – 4.0 $cm^3 g^{-1} dm^{-1}$ (c = 0.65 $g cm^3$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, $J=8.0$, 1H), 7.65 – 7.62 (m, 1H), 7.57 – 7.53 (m, 2H), 7.21 – 7.19 (m, 4H), 7.18 – 7.16 (m, 1H), 5.96 (ddd, $J=6.0$, 11.0, 16.5, 1H), 5.33 – 5.27 (m, 1H), 5.15 (d, $J=10.0$, 1H), 4.57 (dd, $J=7.0$, 16.5, 1H), 4.46 – 4.44 (m, 1H), 4.30 – 4.25 (m, 3H), 3.19 (dd, $J=8.5$, 14.5, 1H), 3.12 (dd, $J=6.5$, 14.5, 1H), 2.42 (d, $J=6.5$, 1H), 1.04 (t, $J=8.0$, 9H), 0.65 (q, $J=8.0$, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 148.1, 137.3, 136.1, 133.8, 133.7, 132.0, 131.8, 129., 128.8, 127.0, 124.4, 118.1, 104.6, 91.5, 63.9, 63.3, 47.7, 36.2, 7.7, 4.4; HRMS (EI) calcd. for $[C_{26}H_{34}N_2O_5SSi]$ (M+H)⁺ 515.2030, found 515.2020.

General procedure for triethylsilyl group (TES) cleavage

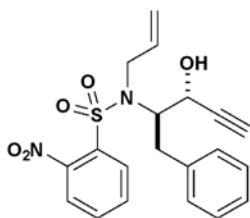
In a flask, the TES-protected propargylic alcohol was dissolved in wet THF (0.1M) and a 1:1 molar ratio tetrabutylammonium fluoride (TBAF)/acetic acid solution (1.6 equiv.) was added at 0 °C. The reaction mixture was stirred under nitrogen for 5h. The mixture was diluted with EtOAc and quenched with saturated aqueous NH₄Cl. The two phases were separated and the aqueous layer was extracted with EtOAc. The combined organic phases were washed with brine, dried over sodium sulfate, filtered and evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography (Hex/EtOAc 3:2).

***N*-allyl-*N*-((2*R*,3*S*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (1a)**



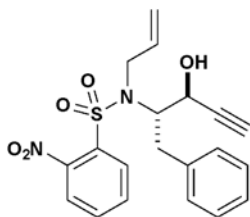
Yield 90% (pale yellow oil); IR (neat, cm⁻¹) ν = 3519, 3288, 3088, 3028, 2931, 2161, 1543, 1372, 1346, 1162, 1062; $[\alpha]_D^{20}$ = + 15.5 cm³ g⁻¹ dm⁻¹ (c = 0.52 g cm³, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ = 7.86 (d, *J*=8.0, 1H), 7.63 (t, *J*=7.5, 1H), 7.56 – 7.52 (m, 2H), 7.21 – 7.14 (m, 5H), 5.95 (ddd, *J*=6.0, 11.0, 16.5, 1H), 5.31 (d, *J*=16.5, 1H), 5.16 (d, *J*=10.0, 1H), 4.52 – 4.50 (m, 1H), 4.46 (dd, *J*=6.5, 16.5, 1H), 4.33 – 4.28 (m, 1H), 4.24 (dd, *J*=6.0, 16.5, 1H), 3.20 (dd, *J*=8.0, 14.0, 1H), 3.10 (dd, *J*=7.0, 14.0, 1H), 2.65 (d, *J*=2.5, 1H), 2.51 (d, *J*=7.0, 1H); ¹³C NMR (126 MHz, CDCl₃) δ = 147.7, 136.9, 135.7, 133.5, 133.4, 131.6, 129.1, 128.5, 128.4, 126.8, 124.1, 118.1, 81.7, 76.4, 63.4, 63.2, 47.5, 35.4; HRMS (EI) calcd. for [C₂₀H₂₀N₂O₅S] (M+H)⁺ 401.1165, found 401.1158.

***N*-allyl-*N*-((2*R*,3*R*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (1b)**



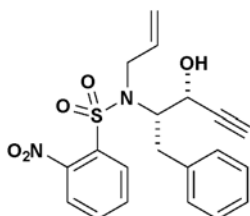
Yield 96% (white crystals). The purified compound was crystallized from CHCl₃/Hexanes. IR (neat, cm⁻¹) ν = 3523, 3289, 3088, 3028, 2930, 2118, 1543, 1372, 1347, 1162, 1063; $[\alpha]_D^{20}$ = - 51.5 cm³ g⁻¹ dm⁻¹ (c = 0.40 g cm³, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ = 7.65 (d, *J*=8.0, 1H), 7.57 (t, *J*=7.5, 1H), 7.49 – 7.42 (m, 2H), 7.17 – 7.07 (m, 5H), 6.07 – 5.98 (m, 1H), 5.33 (d, *J*=17.5, 1H), 5.20 (d, *J*=10.0, 1H), 4.45 – 4.43 (m, 1H), 4.34 – 4.27 (m, 2H), 4.08 (dd, *J*=8.0, 16.5, 1H), 3.25 (dd, *J*=7.5, 14.0, 1H), 2.90 (dd, *J*=10.0, 15.0, 1H), 2.83 (br, 1H), 2.53 (d, *J*=2.5, 1H); ¹³C NMR (126 MHz, CDCl₃) δ = 147.7, 136.8, 135.7, 133.4, 133.2, 131.5, 131.1, 129.1, 128.4, 126.7, 124.0, 118.2, 82.6, 75.3, 64.8, 63.2, 48.0, 34.9; HRMS (EI) calcd. for [C₂₀H₂₀N₂O₅S] (M+H)⁺ 401.1165, found 401.1164.

***N*-allyl-*N*-((2*S*,3*S*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (1c)**



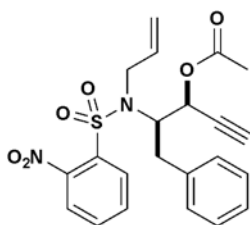
Yield 89% (white crystals). The purified compound was crystallized from $\text{CHCl}_3/\text{Hexanes}$. IR (neat, cm^{-1}) $\nu = 3523, 3289, 3089, 3028, 2930, 2118, 1543, 1372, 1347, 1162, 1063$; $[\alpha]_{\text{D}}^{20} = + 52.5 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.52 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.64$ (d, $J=8.0, 1\text{H}$), 7.56 (t, $J=7.5, 1\text{H}$), 7.48 – 7.42 (m, 2H), 7.15 – 7.08 (m, 5H), 6.06 – 5.98 (m, 1H), 5.32 (d, $J=17.5, 1\text{H}$), 5.20 (d, $J=10.0, 1\text{H}$), 4.45 – 4.43 (m, 1H), 4.33 – 4.29 (m, 2H), 4.08 (dd, $J=8.0, 16.5, 1\text{H}$), 3.26 (dd, $J=5.0, 14.0, 1\text{H}$), 2.90 (dd, $J=10.0, 15.0, 1\text{H}$), 2.90 – 2.87 (m, 1H), 2.53 (d, $J=2.5, 1\text{H}$); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 147.7, 136.8, 135.7, 133.4, 133.2, 131.5, 131.1, 129.1, 128.4, 126.7, 124.0, 118.2, 82.5, 75.3, 64.8, 63.1, 47.9, 34.9$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\text{S}] (\text{M}+\text{H})^+$ 401.1165, found 401.1160.

***N*-allyl-*N*-((2*S*,3*R*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (1d)**



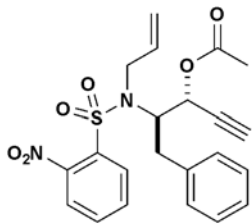
Yield 92% (pale yellow oil); IR (neat, cm^{-1}) $\nu = 3524, 3288, 3088, 3028, 2917, 2117, 1543, 1372, 1347, 1162, 1062$; $[\alpha]_{\text{D}}^{20} = - 15.2 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.47 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.87$ (d, $J=8, 1\text{H}$), 7.63 (t, $J=7.5, 1\text{H}$), 7.56 – 7.52 (m, 2H), 7.21 – 7.15 (m, 5H), 5.95 (ddd, $J=6, 11, 16.5, 1\text{H}$), 5.32 (d, $J=17, 1\text{H}$), 5.16 (d, $J=10, 1\text{H}$), 4.51 (m, 1H), 4.46 (dd, $J=6.5, 16.5, 1\text{H}$), 4.32 – 4.29 (m, 1H), 4.24 (dd, $J=7, 16.5, 1\text{H}$), 3.20 (dd, $J=8, 14, 1\text{H}$), 3.11 (dd, $J=6.5, 14, 1\text{H}$), 2.66 (d, $J=2.5, 1\text{H}$), 2.47 (br, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 147.8, 137.0, 135.7, 133.5, 133.4, 131.7, 131.6, 129.1, 128.5, 126.8, 124.1, 118.1, 81.7, 76.4, 63.4, 63.2, 47.5, 35.5$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\text{S}] (\text{M}+\text{H})^+$ 401.1165, found 401.1164.

(3*S*,4*R*)-4-(*N*-allyl-2-nitrophenylsulfonamido)-5-phenylpent-1-yn-3-yl acetate (6a)⁵



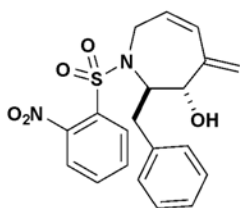
Yield 90% (white powder); IR (neat, cm^{-1}) $\nu = 3282, 3090, 3029, 2918, 2124, 1745, 1534, 1371, 1353, 1226, 1164, 1031$; $[\alpha]_{\text{D}}^{20} = + 55.4 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.50 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.84$ (d, $J=8.0, 1\text{H}$), 7.65 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 7.28 – 7.18 (m, 5H), 5.78 – 5.71 (m, 1H), 5.45 (dd, $J=2.5, 10.0, 1\text{H}$), 5.22 (d, $J=17.0, 1\text{H}$), 5.06 (dd, $J=10.0, 1\text{H}$), 4.59 (td, $J=5.0, 8.0, 1\text{H}$), 4.43 (dd, $J=5.5, 17.5, 1\text{H}$), 4.25 (dd, $J=6.5, 17.0, 1\text{H}$), 3.15 (d, $J=7.5, 2\text{H}$), 2.62 (d, $J=2.5, 1\text{H}$), 1.97 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 169.1, 147.8, 136.3, 135.0, 134.1, 133.3, 131.7, 131.5, 129.1, 128.6, 127.0, 124.1, 117.6, 78.5, 76.8, 63.8, 60.4, 47.3, 36.1, 20.7$; HRMS (EI) calcd. for $[\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_6\text{S}] (\text{M}+\text{H})^+$ 443.1271, found 443.1263.

(3*R*,4*R*)-4-(*N*-allyl-2-nitrophenylsulfonamido)-5-phenylpent-1-yn-3-yl acetate (6b)⁵



Yield 90% (white solid); IR (neat, cm^{-1}) $\nu = 3287, 3089, 3029, 2917, 2126, 1747, 1544, 1372, 1353, 1225, 1164, 1023$; $[\alpha]_{\text{D}}^{20} = +4.5 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.24 \text{ g cm}^{-3}, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.58$ (t, $J=7.5$, 1H), 7.49 (d, $J=8.0$, 1H), 7.40 – 7.34 (m, 2H), 7.30 – 7.24 (m, 5H), 5.79 (ddd, $J=6.0, 10.0, 16.5$, 1H), 5.38 (dd, $J=2.0, 7.0$, 1H), 5.29 (d, $J=17.5$, 1H), 5.15 (d, $J=10.0$, 1H), 4.72 (dd, $J=1.5, 6.5$, 1H), 4.08 – 4.06 (m, 2H), 3.29 (dd, $J=6.5, 14.0$, 1H), 3.04 (dd, $J=8.5, 14.0$, 1H), 2.43 (d, $J=2.5$, 1H), 2.09 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 169.2, 148.4, 136.8, 134.7, 133.4, 133.2, 131.3, 130.9, 129.3, 128.7, 127.0, 123.6, 118.5, 78.7, 76.1, 63.7, 62.1, 47.5, 35.5, 20.7$; HRMS (EI) calcd. for $[\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_6\text{S}]$ (M+H) $^+$ 443.1271, found 443.1267.

(2*R*,3*S*,*Z*)-2-benzyl-4-methylene-1-(2-nitrophenylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azepin-3-ol (5a)



In a 15 mL flask, **1a** (0.0947 g, 0.236 mmol) was dissolved in dry toluene (0.05M) to give a colorless solution. Hoveyda-Grubbs 2nd generation catalyst (7.41 mg, 0.012 mmol) was added and the reaction mixture was stirred at room temperature under ethylene atmosphere (balloon) for 30 min. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (Hex/EtAOc 1:1) to give **5a** in 50% yield as a pale yellow oil (0.048 mg, 0.120 mmol; *endo/exo* = 10: 1.5, inseparable on silica). Spectroscopic data for the major regioisomer: IR (neat, cm^{-1}) $\nu = 3530, 3090, 3028, 2924, 2855, 1543, 1372, 1340, 1162, 1126$; $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.81$ (d, $J=8.0$, 1H), 7.70 (t, $J=7.5$, 1H), 7.52 – 7.49 (m, 2H), 7.19 – 7.14 (m, 5H), 6.06 (d, $J=11.5$, 1H), 5.68 – 5.64 (m, 1H), 5.35 (s, 1H), 5.04 (s, 1H), 4.42 (dd, $J=6.0, 19.0$, 1H), 4.34 – 4.30 (m, 1H), 4.27 – 4.24 (m, 1H), 3.72 – 3.68 (m, 1H), 3.04 – 3.01 (m, 2H), 2.33 (d, $J=2.5$, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 145.5, 136.7, 133.3, 133.2, 131.3, 130.3, 129.6, 129.1, 128.4, 127.3, 126.8, 123.8, 118.8, 74.0, 63.1, 43.9, 37.1$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\text{S}]$ (M+Na) $^+$ 423.0985, found 423.0981.

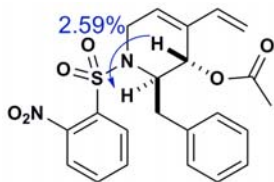
General procedure for enyne metathesis reaction of 6a-b

In a 50 mL flask, the appropriate enyne substrate **6a** or **6b** (1 equiv.) was dissolved in dry dichloromethane (0.05M) to give a colorless solution. Hoveyda-Grubbs 2nd generation catalyst (20 mol%) was added and the reaction mixture was stirred under ethylene atmosphere (balloon) at 45 °C for 7h (*syn*-diastereomer) and for 10h (*anti*-diastereomer). The solvent was removed under

reduced pressure. The residue was purified by silica gel chromatography (Hex/EtAOc 7:3). The two diastereoisomeric products **7a** and **7b** are inseparable on silica.

(2*R*,3*S*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-yl-acetate

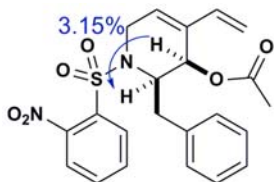
(7a)



Yield 68% (white powder); IR (neat, cm^{-1}) $\nu = 3091, 3028, 2956, 2853, 1735, 1543, 1371, 1234, 1165$; $[\alpha]_D^{20} = -22.5 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.20 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.65$ (d, $J=8.0$, 1H), 7.58 – 7.56 (m, 2H), 7.47 – 7.43 (m, 1H), 7.12 – 7.07 (m, 5H), 6.35 (dd, $J=10.5, 17.5$, 1H), 6.09 – 6.08 (m, 1H), 5.42 (s, 1H), 5.11 (m, 2H), 4.60 (dd, $J=4, 20.0$, 1H), 4.52 (td, $J=1.5, 8.0$, 1H), 4.08 (d, $J=20$, 1H), 2.81 – 2.72 (m, 2H), 1.93 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 170.9, 147.5, 136.6, 135.5, 134.3, 132.9, 131.9, 131.0, 130.7, 129.1, 128.4, 128.1, 127.0, 124.1, 113.6, 65.1, 57.7, 41.7, 35.7, 20.9$; HRMS (EI) calcd. for $[\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_6\text{S}]$ ($\text{M}+\text{Na}$) $^+$ 435.1090, found 465.1086. The relative configuration was confirmed by NOE experiment.

(2*R*,3*R*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-yl-acetate

(7b)



Yield 49% (pale yellow powder); IR (neat, cm^{-1}) $\nu = 3092, 3028, 2978, 2936, 1740, 1542, 1370, 1231, 1163$; $[\alpha]_D^{20} = -44.4 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.18 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.86$ (d, $J=8.0$, 1H), 7.58 – 7.50 (m, 3H), 7.04 – 7.06 (m, 5H), 6.20 (dd, $J=11.0, 17.5$, 1H), 6.02 – 6.01 (m, 1H), 5.76 – 5.75 (br, 1H), 5.23 (d, $J=17.5$, 1H), 5.09 (d, $J=11.5$, 1H), 4.66 (m, 1H), 4.48 – 4.44 (m, 1H), 4.06 – 4.03 (m, 1H), 2.89 (dd, $J=5.0, 14.5$, 1H), 2.73 (dd, $J=5.0, 9.5$, 1H), 1.92 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 170.1, 147.0, 137.4, 133.7, 133.3, 133.2, 132.0, 131.1, 128.9, 128.1, 128.1, 126.4, 124.6, 123.8, 115.2, 68.6, 54.7, 41.1, 32.4, 20.5$; HRMS (EI) calcd. for $[\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_6\text{S}]$ ($\text{M}+\text{Na}$) $^+$ 465.1090, found 465.1083. The relative configuration was confirmed by NOE experiment.

General procedure for the cycloisomerization reaction of enynes **1a-b**

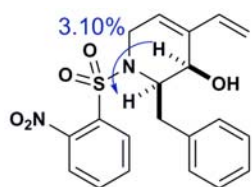
In a 10 mL microwave vial, the appropriate diastereomer **1a** or **1b** (1 equiv.) was dissolved in 1,2-dichloroethane (0.05M) to give a pale yellow solution. Indium(III) chloride (15 mol%) was added and the reaction was irradiated at 90 °C for 20 minutes. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (Hex/EtAOc 7:3).

(2*R*,3*S*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-ol (8a)



Yield 70% (colorless oil); IR (neat, cm^{-1}) $\nu = 3537, 3091, 3027, 2922, 2851, 1542, 1371, 1162, 1022$; $[\alpha]_{\text{D}}^{20} = + 53.7 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.09 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, Benzene) $\delta = 7.76$ (d, $J=8.0, 1\text{H}$), $6.98 - 6.94$ (m, 4H), $6.93 - 6.90$ (m, 1H), $6.64 - 6.61$ (m, 1H), $6.57 - 6.53$ (m, 1H), $6.47 - 6.43$ (m, 1H), 6.06 (dd, $J=11.0, 17.5, 1\text{H}$), 5.25 (d, $J=17.5, 1\text{H}$), $5.16 - 5.15$ (m, 1H), 4.92 (d, $J=12.5, 1\text{H}$), 4.31 (dd, $J=5.0, 20.0, 1\text{H}$), $4.26 - 4.24$ (m, 1H), 4.16 (d, $J=8.0, 1\text{H}$), 3.59 (d, $J=20.0, 1\text{H}$), 2.81 (dd, $J=5.5, 13.0, 1\text{H}$), 2.33 (dd, $J=10.0, 13.0, 1\text{H}$), 1.99 (br, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 147.5, 137.0, 135.8, 134.8, 133.6, 133.1, 131.9, 131.4, 129.1, 128.6, 126.8, 125.3, 124.3, 114.0, 63.4, 60.9, 41.6, 36.1$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\text{S}] (\text{M}+\text{H})^+$ 401.1165, found 401.1158. The relative configuration was determined by NOE experiment.

(2*R*,3*R*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-ol (8b)



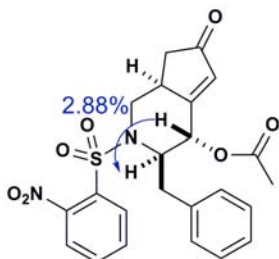
Yield 69% (white powder); IR (neat, cm^{-1}) $\nu = 3535, 3090, 3027, 2892, 1541, 1367, 1338, 1160, 1090$; $[\alpha]_{\text{D}}^{20} = - 109.0 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.11 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.67$ (dd, $J=8.0, 1\text{H}$), $7.53 - 7.52$ (m, 2H), $7.44 - 7.41$ (m, 1H), $7.06 - 7.05$ (m, 2H), $6.97 - 6.92$ (m, 3H), 6.34 (dd, $J=11.5, 17.5, 1\text{H}$), 5.89 (m, 1H), 5.50 (d, $J=18.0, 1\text{H}$), 5.20 (d, $J=12.5, 1\text{H}$), 4.81 (m, 1H), $4.40 - 4.36$ (m, 1H), 4.32 (m, 1H), $4.14 - 4.10$ (m, 1H), 3.18 (dd, $J=5.0, 14.0, 1\text{H}$), 2.61 (dd, $J=10.0, 14.0, 1\text{H}$), 2.10 (br, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 146.9, 137.9, 136.4, 134.6, 133.8, 132.9, 131.9, 130.7, 129.0, 128.0, 126.3, 124.4, 123.4, 115.8, 66.6, 59.3, 42.2, 30.8$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\text{S}] (\text{M}+\text{H})^+$ 401.1165, found 401.1172. The relative configuration was determined by NOE experiment.

General procedure for the Pauson-Khand reaction

In a flame-dried flask, the appropriate diastereomer **6a** or **6b** (1 equiv.) was dissolved in dry THF (0.05M) to give a colorless solution. Cobalt octacarbonyl (1.05 equiv) was added and the resulting orange reaction mixture was stirred for 1h under nitrogen. The solution was then cooled to 0 °C and 4-methylmorpholine 4-oxide (2 equiv) was added. The reaction was stirred for 3h at room temperature and then 2 more equiv of 4-methylmorpholine 4-oxide were added and the reaction mixture was stirred for further 3h under nitrogen. The mixture was passed through a short silica plug and eluted with EtOAc (15 mL) and DCM/EtOH 4:1 (15 mL). The filtrate was

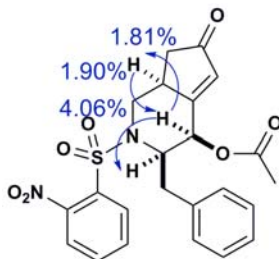
concentrated under reduced pressure and the residue purified by flash chromatography (Hex/EtOAc 1:1).

(3*R*,4*S*,7*aS*)-3-benzyl-2-(2-nitrophenylsulfonyl)-6-oxo-2,3,4,6,7,7*a*-hexahydro-1*H*-cyclopenta [c]pyridin-4-yl acetate (9a)



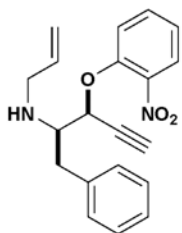
Yield 70% (white powder); IR (neat, cm^{-1}) $\nu = 3093, 3028, 2919, 2850, 1741, 1716, 1636, 1543, 1371, 1233, 1164, 1127, 1062$; $[\alpha]_{\text{D}}^{20} = -125.0 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.12 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.67$ (d, $J=8.0$, 1H), 7.63 – 7.62 (m, 2H), 7.53 – 7.49 (m, 1H), 7.20 – 7.12 (m, 5H), 6.25 (d, $J=1.5$, 1H), 5.46 (d, $J=2.0$, 1H), 4.71 (t, $J=8.0$, 1H), 4.32 (dd, $J=6.5, 13.5$, 1H), 3.50 – 3.45 (m, 1H), 3.02 – 2.97 (m, 1H), 2.82 (dd, $J=7.5, 13.5$, 1H), 2.73 (dd, $J=8.5, 13.5$, 1H), 2.65 (dd, $J=7.0, 19.0$, 1H), 2.10 (dd, $J=2.5, 19.0$, 1H), 1.96 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 206.2, 170.6, 169.9, 147.5, 135.6, 133.8, 133.3, 132.5, 132.0, 130.9, 129.0, 128.8, 127.3, 124.3, 68.2, 59.1, 47.6, 38.3, 37.2, 34.6, 20.8$; HRMS (EI) calcd. for $[\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_7\text{S}]$ (M+H) $^+$ 471.1220, found 471.1228. The relative configuration was determined by NOE experiment.

(3*R*,4*R*,7*aS*)-3-benzyl-2-(2-nitrophenylsulfonyl)-6-oxo-2,3,4,6,7,7*a*-hexahydro-1*H*-cyclopenta [c]pyridin-4-yl acetate (9b)



Yield 55% (white powder); IR (neat, cm^{-1}) $\nu = 3093, 3028, 2917, 2849, 1747, 1711, 1632, 1541, 1367, 1227, 1161, 1058$; $[\alpha]_{\text{D}}^{20} = -142.3 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.25 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.77$ (d, $J=8.0$, 1H), 7.61 – 7.56 (m, 2H), 7.51 – 7.47 (m, 1H), 6.97 – 6.93 (m, 5H), 6.19 (s, 1H), 5.85 (d, $J=6.0$, 1H), 4.74 – 4.69 (m, 1H), 4.43 (dd, $J=6.0, 13.5$, 1H), 3.27 – 3.22 (m, 1H), 3.07 (dd, $J=11.5, 14.0$, 1H), 2.90 (dd, $J=5.0, 15.0$, 1H), 2.68 – 2.58 (m, 2H), 2.21 (dd, $J=2.5, 19.0$, 1H), 2.04 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 205.0, 173.8, 169.2, 147.0, 136.3, 133.5, 133.0, 132.1, 131.1, 128.8, 128.7, 128.2, 126.6, 124.8, 72.0, 58.6, 46.5, 41.4, 38.3, 31.8, 20.4$; HRMS (EI) calcd. for $[\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_7\text{S}]$ (M+H) $^+$ 471.1220, found 471.1227. The relative configuration was determined by NOE experiment.

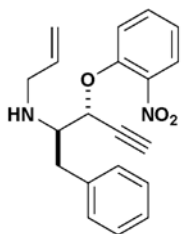
(2*R*,3*S*)-*N*-allyl-3-(2-nitrophenoxy)-1-phenylpent-4-yn-2-amine (10a)



In 10 mL-flask, **1a** (0.0083 g, 0.021 mmol) was dissolved in THF (0.207 mL, 0.1M). The resulting solution was cooled to 0 °C and TBAF (0.065 mL, 0.065

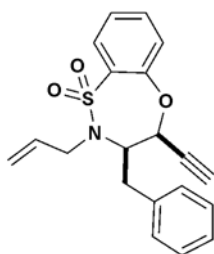
mmol) was added. The reaction mixture was stirred under nitrogen for 30 min, then it was quenched with saturated aqueous NH_4Cl , the solvent removed under reduced pressure and the residue was loaded on TLC plate. The plate was developed using Hex/EtOAc 7:3. Yield 50% (yellow oil); IR (neat, cm^{-1}) $\nu = 3287, 3062, 3027, 2923, 2858, 2116, 1605, 1524, 1484, 1349, 1277, 1248$; $[\alpha]_{\text{D}}^{20} = -4.5 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.2 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (600 Hz, CDCl_3) $\delta = 7.87$ (d, $J=7.0$, 1H), 7.51 (t, $J=7.0$, 1H), 7.32 – 7.21 (m, 6H), 7.07 (t, $J=7.0$, 1H), 5.80 (ddd, $J=5.0, 9.5, 14.0$, 1H), 5.14 (d, $J=15.0$, 1H), 5.07 (d, $J=8.5$, 1H), 4.83 (m, 1H), 3.38 – 3.36 (m, 2H), 3.36 – 3.34 (m, 1H), 3.06 (dd, $J=5.0, 12.0$, 1H), 3.00 (dd, $J=5.0, 12.0$, 1H), 2.67 (d, $J=2.5$, 1H), 1.67 (br, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 150.7, 140.2, 138.3, 137.6, 133.9, 129.4, 129.3, 128.5, 126.5, 125.7, 121.3, 116.2, 78.6, 78.0, 71.6, 61.6, 50.3, 37.2$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3\text{S}]$ (M+H) $^+$ 337.1546, found 337.1546.

(2*R*,3*R*)-*N*-allyl-3-(2-nitrophenoxy)-1-phenylpent-4-yn-2-amine (10b)



In 50 mL-flask, **1b** (0.123 g, 0.307 mmol) was dissolved in THF (6.14 mL, 0.1M) and DBU (0.139 mL, 0.921 mmol) was added. The reaction mixture was heated to 64 °C and stirred under nitrogen for 4h. Then the reaction was quenched with water, EtOAc was added and the two phases were separated. The aqueous layer was extracted with EtOAc and the combined organic phases were washed with brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (Hex/EtOAc 7:3). Yield 70% (yellow oil); IR (neat, cm^{-1}) $\nu = 3287, 3062, 3027, 2918, 2116, 1605, 1525, 1483, 1350, 1277, 1248$; $[\alpha]_{\text{D}}^{20} = +10.8 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.16 \text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 7.91$ (d, $J=8.0$, 1H), 7.53 (t, $J=7.0$, 1H), 7.30 – 7.21 (m, 6H), 7.09 (t, $J=8.0$, 1H), 5.78 (ddd, $J=5.0, 9.5, 14.0$, 1H), 5.13 (d, $J=17.0$, 1H), 5.05 (d, $J=10.0$, 1H), 4.82 (m, 1H), 3.35 – 3.34 (m, 2H), 3.32 – 3.28 (m, 1H), 3.19 (dd, $J=6.0, 14.0$, 1H), 2.89 (dd, $J=7.5, 14.0$, 1H), 2.61 (d, $J=2.0$, 1H), 1.63 (br, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) $\delta = 150.7, 140.1, 138.4, 136.7, 134.0, 129.4, 128.5, 126.4, 125.8, 121.2, 116.2, 116.1, 79.2, 70.9, 61.5, 50.4, 36.8$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3\text{S}]$ (M+H) $^+$ 337.1546, found 337.1556.

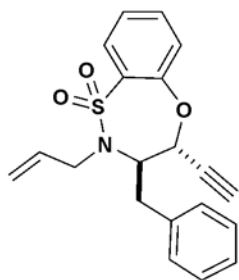
(3*R*,4*S*)-3-benzyl-4-ethynyl-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine 1,1-dioxide (11a)



In a 100 mL flame-dried flask, propargylic alcohol **1a** (0.450 g, 1.124 mmol) was dissolved in dry THF (11.24 mL). The resulting colorless solution was

cooled $-10\text{ }^{\circ}\text{C}$ and sodium hydride (0.081 g, 3.37 mmol) was added. The reaction was stirred under nitrogen for 5h, maintaining the temperature between $-10\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl at $0\text{ }^{\circ}\text{C}$. Diethyl ether and water were added and the two phases were separated. The aqueous layer was extracted with diethyl ether and the combined organic phases were dried over Na_2SO_4 , filtered and evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography (Hex/EtOAc 7:3). Yield 75% (white solid). The purified compound was crystallized from $\text{CHCl}_3/\text{Hexanes}$. IR (neat, cm^{-1}) $\nu = 3275, 3065, 3028, 2929, 2119, 1589, 1467, 1447, 1345, 1171, 1073, 1007$; $[\alpha]_{\text{D}}^{20} = -27.1\text{ cm}^3\text{ g}^{-1}\text{ dm}^{-1}$ ($c = 0.63\text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, DMSO, $T = 65\text{ }^{\circ}\text{C}$) $\delta = 7.75$ (d, $J=8.0$, 1H), 7.66 (t, $J=8.0$, 1H), 7.39 (t, $J=8.0$, 1H), 7.36 – 7.35 (m, 4H), 7.29 – 7.26 (m, 2H), 5.46 (ddd, $J=6.0, 11.0, 16.5$, 1H), 5.07 – 5.03 (m, 2H), 4.95 (d, $J=10.5$, 1H), 4.46 (br, 1H), 3.99 (dd, $J=5.0, 16.5$, 1H), 3.82 (d, $J=2.5$, 1H), 3.48 (dd, $J=5.0, 17.0$, 1H), 3.36 – 3.31 (m, 1H), 3.16 (dd, $J=6.0, 14.5$, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3 , $T = 55\text{ }^{\circ}\text{C}$) $\delta = 152.6, 136.7, 135.7, 135.5, 133.8, 129.3, 128.8, 128.7, 127.1, 125.7, 124.8, 116.9, 80.7, 77.1, 70.5, 63.2, 48.9, 35.8$; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}]$ (M+H) $^+$ 354.1158, found 354.1161.

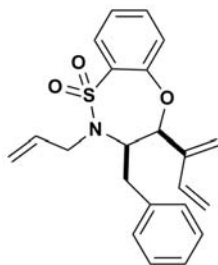
(3R,4R)-3-benzyl-4-ethynyl-2-prop-2-en-1-yl-3,4-dihydro-2H-5,1,2-benzoxathiazepine 1,1-dioxide (11b)



In a 50 mL flame-dried flask, propargylic alcohol **1b** (0.106 g, 0.264 mmol) was dissolved in dry THF (5.28 mL). The resulting colorless solution was cooled $0\text{ }^{\circ}\text{C}$ and sodium hydride (0.019 g, 0.792 mmol) was added. The reaction was stirred under nitrogen for 5h, allowing the temperature to rise to room temperature. Then, the reaction mixture was quenched with saturated aqueous NH_4Cl at $0\text{ }^{\circ}\text{C}$. Diethyl ether and water were added and the two phases were separated. The aqueous layer was extracted with diethyl ether and the combined organic phases were dried over Na_2SO_4 , filtered and evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography (Hex/EtOAc 4:1). Yield 35% (white solid); IR (neat, cm^{-1}) $\nu = 3278, 3066, 3028, 2923, 2850, 2127, 1593, 1470, 1443, 1340, 1155, 1075$; $[\alpha]_{\text{D}}^{20} = -8.8\text{ cm}^3\text{ g}^{-1}\text{ dm}^{-1}$ ($c = 0.11\text{ g cm}^3, \text{CHCl}_3$); $^1\text{H NMR}$ (500 MHz, CDCl_3 , $T = 55\text{ }^{\circ}\text{C}$) $\delta = 7.82$ (d, $J=7.5$, 1H), 7.44 (t, $J=8.0$, 1H), 7.34 – 7.32 (m, 4H), 7.28 – 7.25 (m, 1H), 7.20 (t, $J=7.5$, 1H), 7.15 (d, $J=7.5$, 1H), 5.59 (d, $J=10$, 1H), 5.02 – 4.96 (m, 1H), 4.90 (d, $J=17.0$, 1H), 4.83 (d, $J=10.0$, 1H), 3.76 (t, $J=10.0$, 1H), 3.53 (m, 2H), 3.32 – 3.27 (m, 1H), 3.17 (dd, $J=3.5, 14.0$, 1H), 2.77 (d, $J=2.0$, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3 , $T = 55\text{ }^{\circ}\text{C}$) $\delta =$

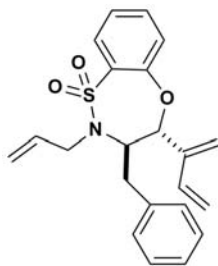
154.0, 137.7, 133.4, 132.3, 130.2, 128.4, 128.3, 126.6, 124.1, 121.9, 119.1, 79.2, 77.1, 75.7, 67.5, 55.3, 37.2; HRMS (EI) calcd. for $[C_{20}H_{19}NO_3S] (M+Na)^+$ 376.0977, found 376.0974.

(3*R*,4*S*)-3-benzyl-4-(1-methylideneprop-2-en-1-yl)-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine (12a)



In 25 mL flame-dried pear flask, **11a** (0.100 g, 0.283 mmol) was dissolved in dry benzene (5.66 mL) to give a colorless solution. Hoveyda-Grubbs 2nd generation catalyst (8.86 mg, 0.014 mmol) was added and the resulting green solution was stirred under ethylene atmosphere (balloon) for 45 min at room temperature. The reaction mixture was concentrated to about 2 mL, $Pb(OAc)_4$ (8.7 mg, 5 equiv to the amount of Grubbs catalyst) was added and the resulting mixture was stirred under nitrogen for 18h at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (Hex/EtOAc 9:1). Yield 56% (white powder); IR (neat, cm^{-1}) $\nu = 3086, 3064, 3027, 2926, 2855, 1589, 1468, 1447, 1350, 1263, 1229, 1169, 1072, 1012$; $[\alpha]_D^{20} = +91.3 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.15 \text{ g cm}^3$, $CHCl_3$); 1H NMR (500 MHz, Benzene) $\delta = 7.85$ (d, $J=8.0$, 1H), 7.47 – 7.46 (m, 2H), 7.14 – 7.10 (m, 2H), 7.03 (t, $J=7.0$, 1H), 6.85 – 6.79 (m, 2H), 6.66 (t, $J=7.0$, 1H), 6.07 (dd, $J=11.0, 18.0$, 1H), 5.74 (s, 1H), 5.22 (s, 1H), 4.99 (ddd, $J=4.0, 11.0, 17.5$, 1H), 4.80 – 4.77 (m, 2H), 4.57 (d, $J=10.0$, 1H), 4.50 (d, $J=17.0$, 1H), 4.46 (m, 1H), 4.15 – 4.10 (m, 1H), 3.87 (dd, $J=5.0, 15.0$, 1H), 3.61 – 3.57 (m, 1H), 2.89 (dd, $J=3.0, 14.0$, 1H), 2.77 (dd, $J=8.0, 15.0$, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) $\delta = 156.5, 142.5, 138.7, 136.1, 135.8, 134.2, 133.2, 130.0, 128.2, 128.0, 126.0, 124.7, 123.3, 118.7, 118.1, 114.4, 81.0, 64.5, 53.7, 32.6$; HRMS (EI) calcd. for $[C_{22}H_{23}NO_3S] (M+H)^+$ 382.1471, found 382.1475.

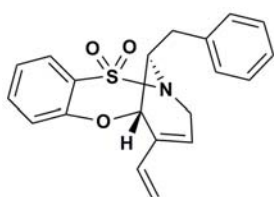
(3*R*,4*R*)-3-benzyl-4-(1-methylideneprop-2-en-1-yl)-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine (12b)



12b was obtained from **11b** (0.0115 g, 0.033 mmol) according to the procedure described for the diastereomer **12a**. 10 mol% of Hoveyda-Grubbs 2nd generation catalyst were used in this case and the reaction mixture was stirred for 6h. The residue was loaded on TLC plate. The plate was developed using Hex/EtOAc 9:1. Yield 39% (white powder); IR (neat, cm^{-1}) $\nu = 3086, 3065, 3028, 2933, 2866, 1594, 1470, 1443, 1339, 1265, 1227, 1154, 1075$; $[\alpha]_D^{20} = +23.3 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.24 \text{ g cm}^3$, $CHCl_3$); 1H NMR (500 MHz, Benzene)

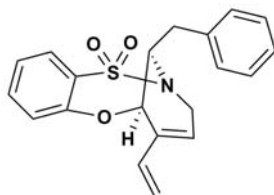
$\delta = 7.90$ (d, $J=8.0$, 1H), 7.29 – 7.28 (m, 2H), 7.09 – 7.06 (m, 2H), 7.02 – 6.89 (m, 1H), 6.79 – 6.73 (m, 2H), 6.57 (t, $J=8.0$, 1H), 6.26 (dd, $J=12.5$, 18.0, 1H), 5.76 – 5.74 (m, 1H), 5.45 (d, $J=18.0$, 1H), 5.01 (s, 1H), 4.97 – 4.95 (m, 1H), 4.95 (buried s, 1H), 4.90 – 4.87 (m, 1H), 4.58 – 4.53 (m, 2H), 3.82 (m, 1H), 3.55 – 3.45 (m, 2H), 3.43 – 3.38 (m, 1H), 2.57 (dd, $J=3.0$, 13.0, 1H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 155.04$, 143.50, 138.03, 134.75, 133.25, 132.55, 130.15, 128.35, 128.26, 126.42, 123.42, 121.58, 119.07, 119.00, 116.86, 86.74, 65.77, 55.49, 36.93; HRMS (EI) calcd. for $[\text{C}_{22}\text{H}_{23}\text{NO}_3\text{S}]$ (M+H) $^+$ 382.1471, found 382.1474.

(10R,14S)-14-benzyl-11-ethenyl-9-oxa-2-thia-1-azatricyclo[8.3.1.0^{3,8}]tetradeca-3,5,7,11-tetraene 2,2-dioxide (13a)



In 25 mL flame-dried pear flask, **11a** (0.055 g, 0.156 mmol) was dissolved dry DCM (7.78 mL) to give a colorless solution. Grubbs catalyst 1st generation (3.84 mg, 4.67 μmol) was added and the resulting pink solution was stirred under nitrogen for 2h at room temperature. The reaction mixture was concentrated to about 2 mL, $\text{Pb}(\text{OAc})_4$ (9 mg, 5 equiv to the amount of Grubbs catalyst) was added and the resulting mixture was stirred under nitrogen for 18h at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (Hex/EtOAc 1:1). The purified compound was crystallized from CHCl_3 /Hexanes. Yield 95 % (white solid); IR (neat, cm^{-1}) $\nu = 3063$, 3027, 2924, 2852, 1589, 1466, 1444, 1344, 1167, 1072; $[\alpha]_{\text{D}}^{20} = -77.7 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.09 \text{ g cm}^3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) $\delta = 7.80$ (d, $J=8.0$, 1H), 7.38 – 7.33 (m, 3H), 7.29 – 7.24 (m, 3H), 7.16 (t, $J=7.0$, 1H), 6.92 (d, $J=8.0$, 1H), 6.08 (dd, $J=11.0$, 17.5, 1H), 5.70 – 5.69 (m, 1H), 5.54 (d, $J=17.5$, 1H), 5.19 (d, $J=11.0$, 1H), 4.97 – 4.93 (m, 2H), 4.15 (dd, $J=4.0$, 21.0, 1H), 3.93 (d, $J=21.0$, 1H), 2.99 (dd, $J=7.0$, 14.0, 1H), 2.78 (dd, $J=9.5$, 14.0, 1H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 151.3$, 136.4, 134.1, 133.7, 130.2, 129.01, 128.9, 128.8, 128.2, 127.0, 125.0, 124.0, 114.6, 70.2, 58.4, 41.8, 35.8; HRMS (EI) calcd. for $[\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}]$ (M+H) $^+$ 354.1158, found 354.1162.

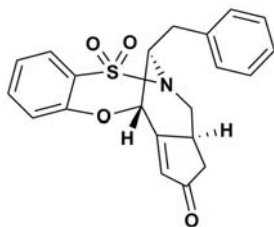
(10R,14R)-14-benzyl-11-ethenyl-9-oxa-2-thia-1-azatricyclo[8.3.1.0^{3,8}]tetradeca-3,5,7,11-tetraene 2,2-dioxide (13b)



13b was obtained from **11b** (0.0115 g, 0.033 mmol) according to the enyne metathesis procedure described for the compound **12b**. Yield 19% (white solid); IR (neat, cm^{-1}) $\nu = 3063$, 3027, 2930, 1589, 1468, 1443, 1350, 1333, 1167, 1068; $[\alpha]_{\text{D}}^{20} = +81.6 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.12 \text{ g}$

cm³, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ = 7.82 (d, *J*=8.0, 1H), 7.42 – 7.41 (m, 2H), 7.38 – 7.36 (m, 2H), 7.29 – 7.27 (m, 2H), 7.17 (t, *J*=7.5, 1H), 7.03 (d, *J*=8.0, 1H), 5.90 (dd, *J*=11.0, 17.5, 1H), 5.62 (m, 1H), 5.51 (d, *J*=17.5, 1H), 5.10 (d, *J*=11.0, 1H), 4.94 (s, 1H), 4.40 (dd, *J*=3.5, 17.0, 1H), 4.00 (d, *J*=17.0, 1H), 3.72 (dd, *J*=7.5, 11.5, 1H), 3.58 (dd, *J*=5.0, 10.0, 1H), 3.52 (dd, *J*=4.0, 11.5, 1H); ¹³C NMR (126 MHz, CDCl₃) δ = 150.7, 139.0, 135.8, 135.0, 133.4, 133.0, 129.7, 129.2, 128.7, 128.0, 126.7, 125.3, 123.9, 114.7, 68.7, 63.6, 50.0, 37.1; HRMS (EI) calcd. for [C₂₀H₁₉NO₃S] (M+H)⁺ 354.1158, found 354.1158.

Compound (14a)



14a was obtained from **11a** (0.158 g, 0.447 mmol) according to the reported general procedure for the Pauson-Khand reaction. In the work-up phase, the filtrate was washed with 5% CuSO₄ aqueous solution.

The aqueous phase was extracted with EtOAc. The combined organic layers were washed once with brine, dried over Na₂SO₄ and evaporated

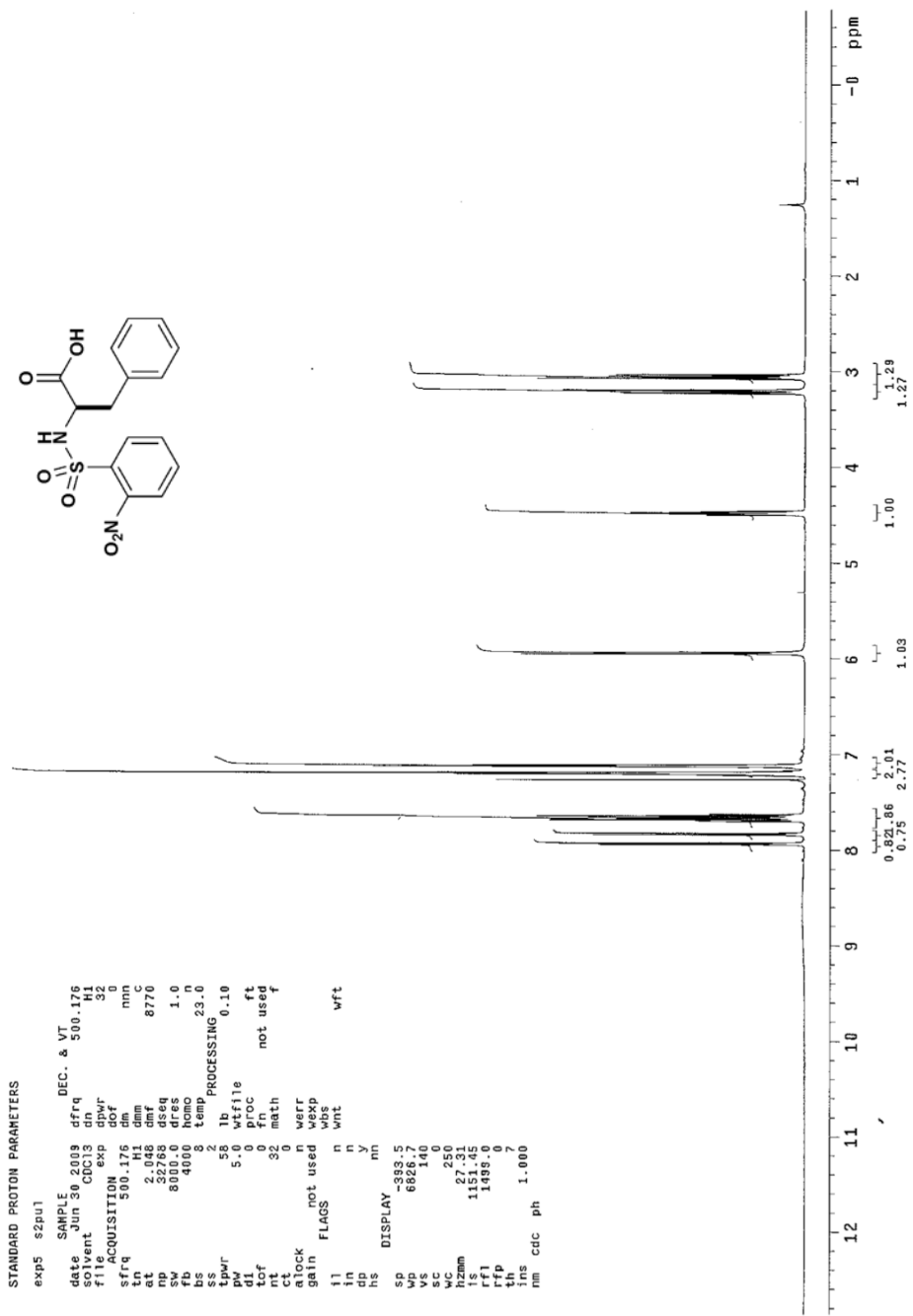
under reduced pressure. The residue was purified by silica gel chromatography (Hex/EtOAc 1:1). The purified compound was crystallized from CHCl₃/Hexanes. Yield 26% (pale yellow solid); IR (neat, cm⁻¹) ν = 3064, 3029, 2924, 2854, 1716, 1621, 1589, 1466, 1341, 1261, 1207, 1166, 1000; [α]_D²⁰ = -130.0 cm³ g⁻¹ dm⁻¹ (c = 0.04 g cm³, CHCl₃); ¹H NMR (500 MHz, Benzene) δ = 7.89 (d, *J*=8.0, 1H), 7.09 – 7.03 (m, 3H), 6.88 – 6.87 (m, 2H), 6.77 (t, *J*=8.0, 1H), 6.69 (d, *J*=8.0, 1H), 6.59 (t, *J*=8.0, 1H), 5.69 (d, *J*=2.0, 1H), 5.21 (t, *J*=8.5, 1H), 4.62 (d, *J*=2.0, 1H), 3.78 (dd, *J*=8.0, 15.0, 1H), 2.38 (dd, *J*=7.5, 14.0, 1H), 2.30 (dd, *J*=11.5, 15.0, 1H), 2.07 (dd, *J*=10.0, 15.0, 1H), 2.03 – 2.01 (m, 1H), 1.39 (dd, *J*=6.5, 18.5, 1H), 1.01 (dd, *J*=3.0, 18.5, 1H); ¹³C NMR (126 MHz, CDCl₃) δ = 205.1, 169.5, 152.5, 136.7, 135.5, 134.9, 129.2, 129.1, 128.8, 127.4, 124.9, 124.8, 73.9, 60.8, 46.5, 40.1, 35.2, 35.1; HRMS (EI) calcd. for [C₂₁H₁₉NO₄S] (M+H)⁺ 382.1107, found 382.1110.

References

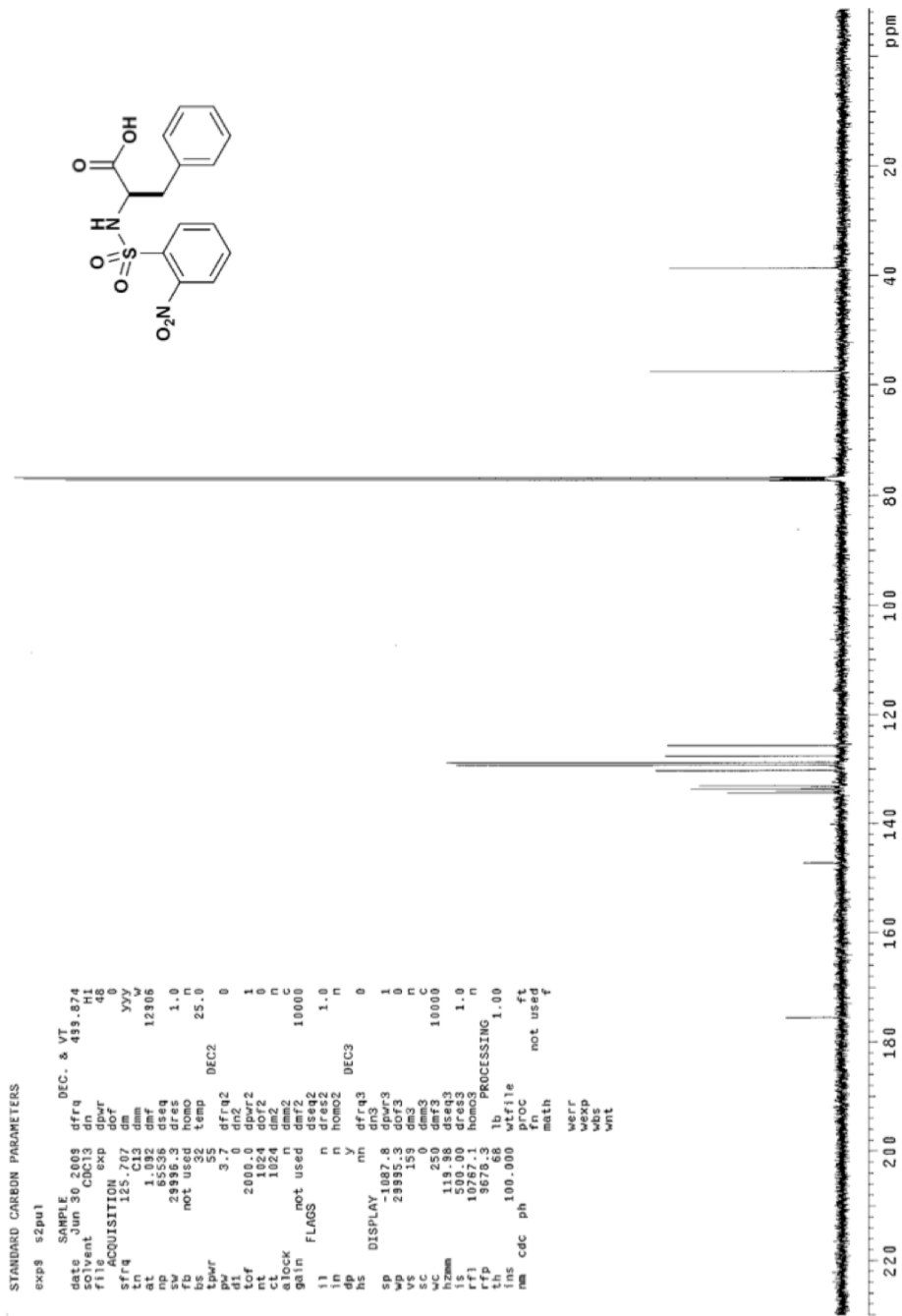
- (1) Weininger, D. A. *J. Chem. Inf. Comput. Sci.* **1988**, *28*, 31-36.
- (2) Sauer, W. H.; Schwarz, M. K. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 987-1003.
- (3) Fukuyama, T.; Jow, C-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36*, 6373-6374.
- (4) Miller, S. C.; Scanlan, T. S. *J. Am. Chem. Soc.* **1998**, *120*, 2690-2691.
- (5) For the acetylation of the amino propargylic alcohols **1a** and **1b** see: Hofle, G.; Steglich, W.; Vorbruggen, H. *Angew. Chemie* **1978**, *90*, 602-615; *Angew. Chemie Int. Ed.* **1978**, *17*, 569-583;

III. ¹H and ¹³C NMR spectra

Spectral data for (R)-2-(2-nitrophenylsulfonamido)-3-phenylpropanoic acid (R)-i

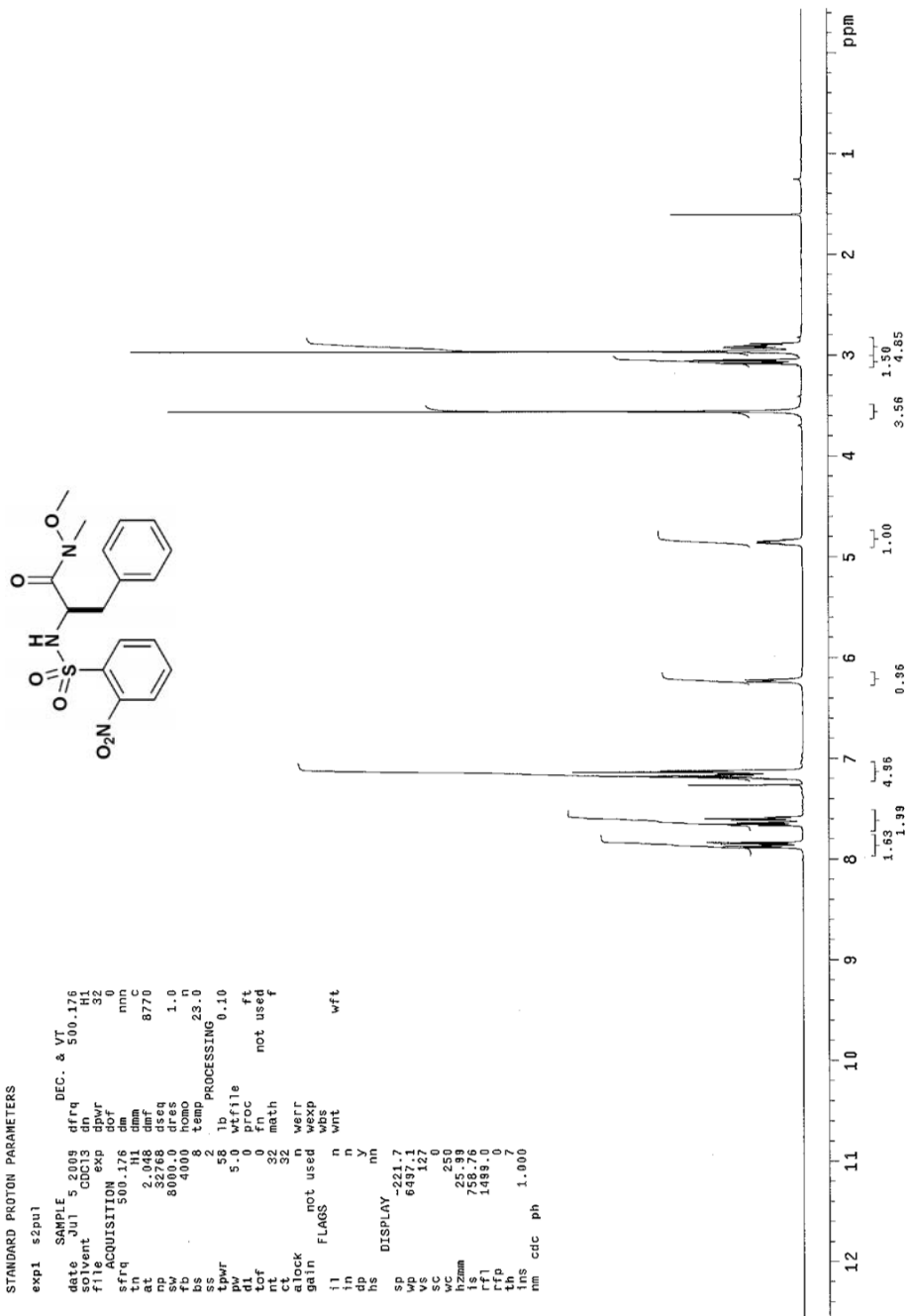


¹H NMR (500 MHz, CDCl₃) of compound (R)-i

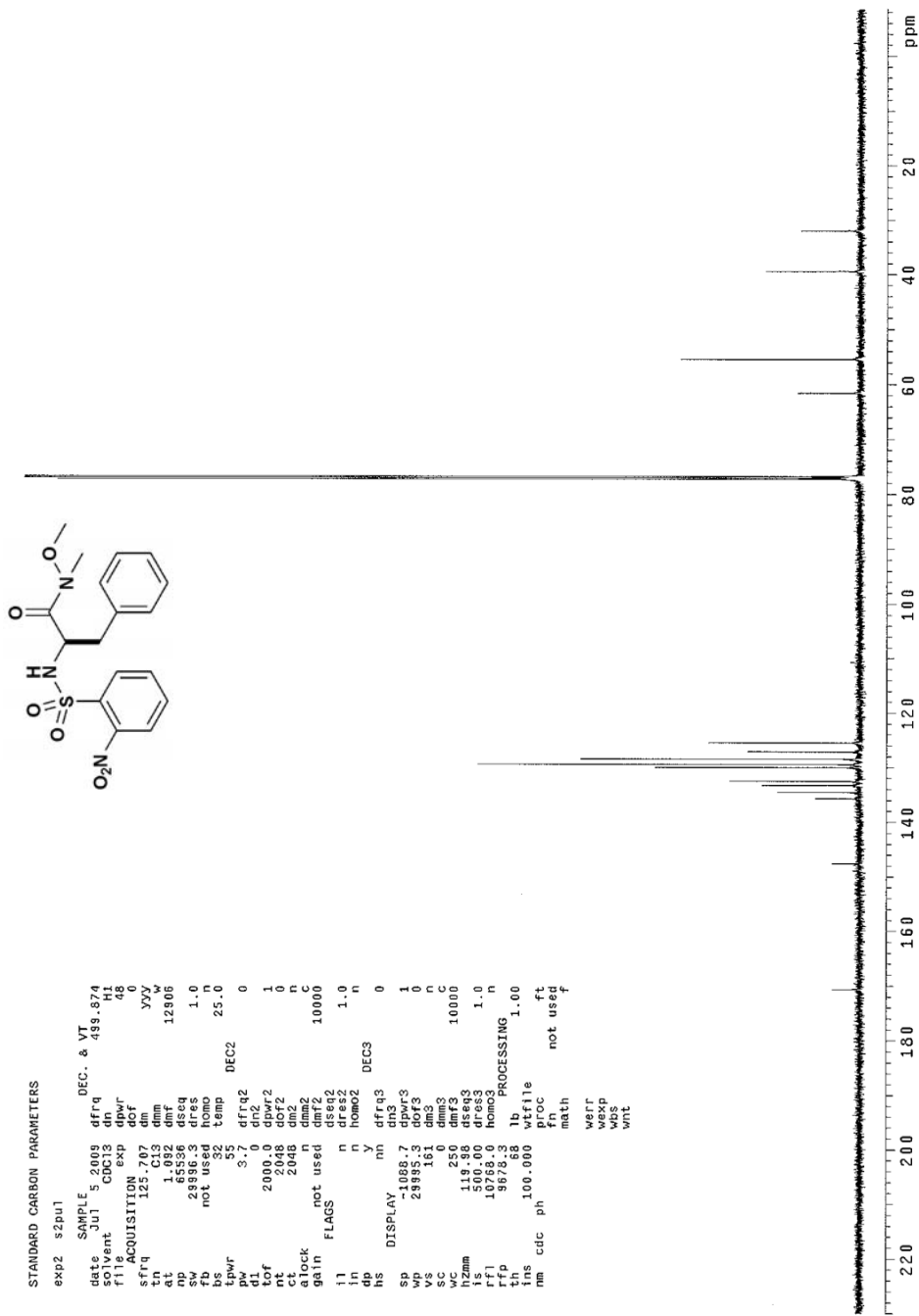


^{13}C NMR (500 MHz, CDCl_3) of compound (R)-i

Spectral data for (*R*)-*N*-methoxy-*N*-methyl-2-(2-nitrophenylsulfonamido)-3-phenylpropanamide (*R*)-ii

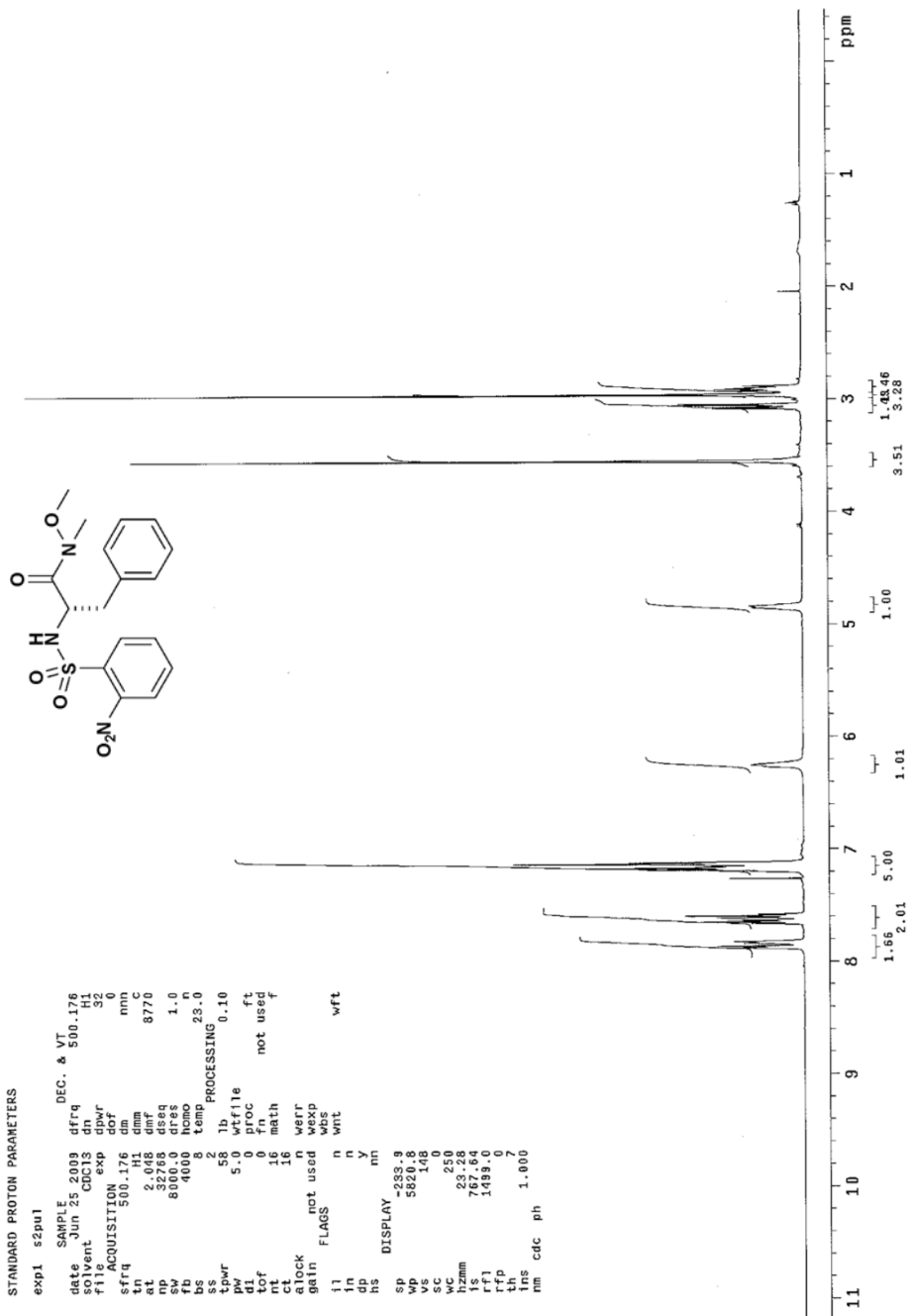


¹H NMR (500 MHz, CDCl₃) of compound (*R*)-ii

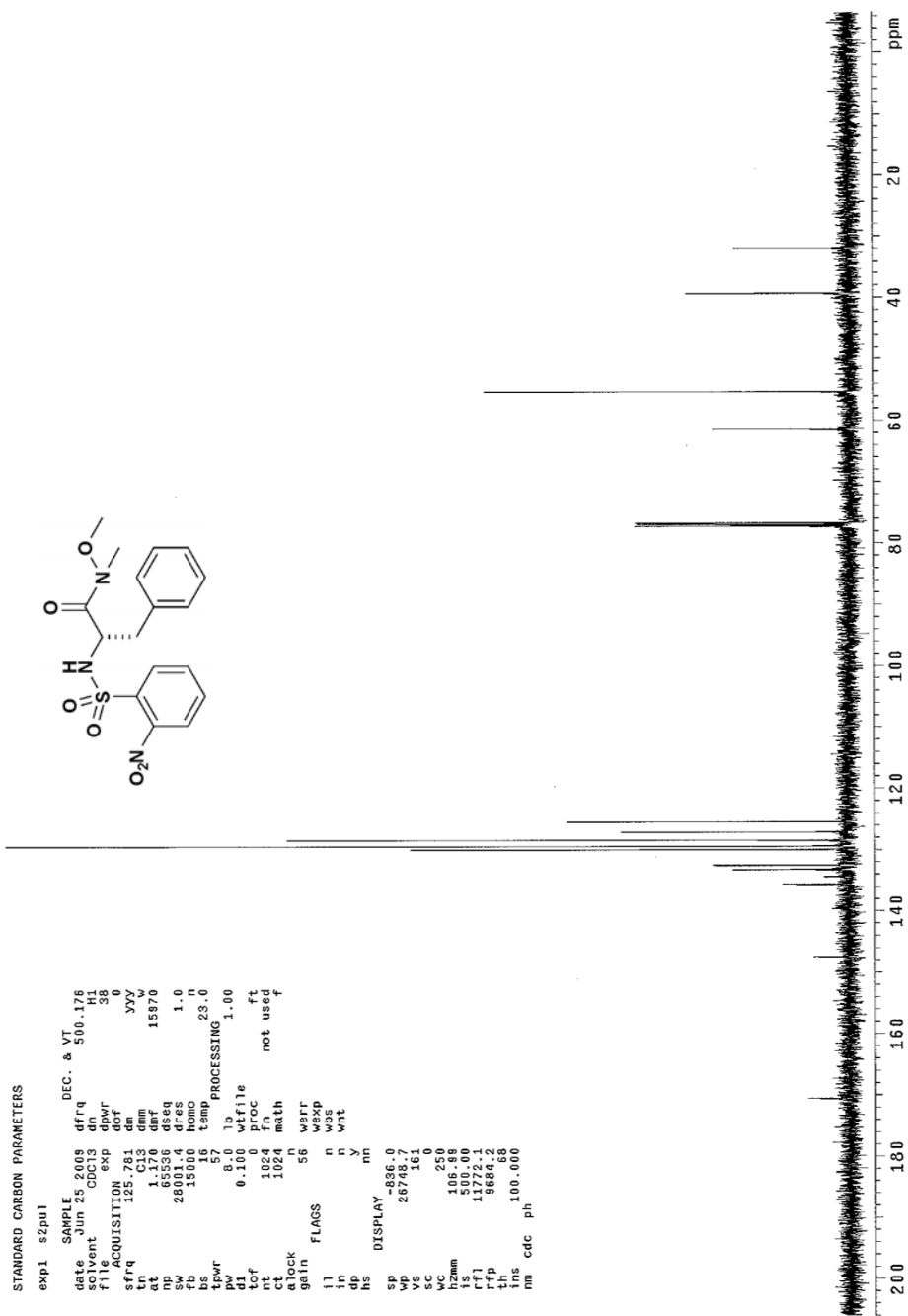


¹³C NMR (126 MHz, CDCl₃) of compound (R)-ii

Spectral data for *S*-*N*-methoxy-*N*-methyl-2-(2-nitrophenylsulfonamido)-3-phenylpropanamide (*S*)-ii

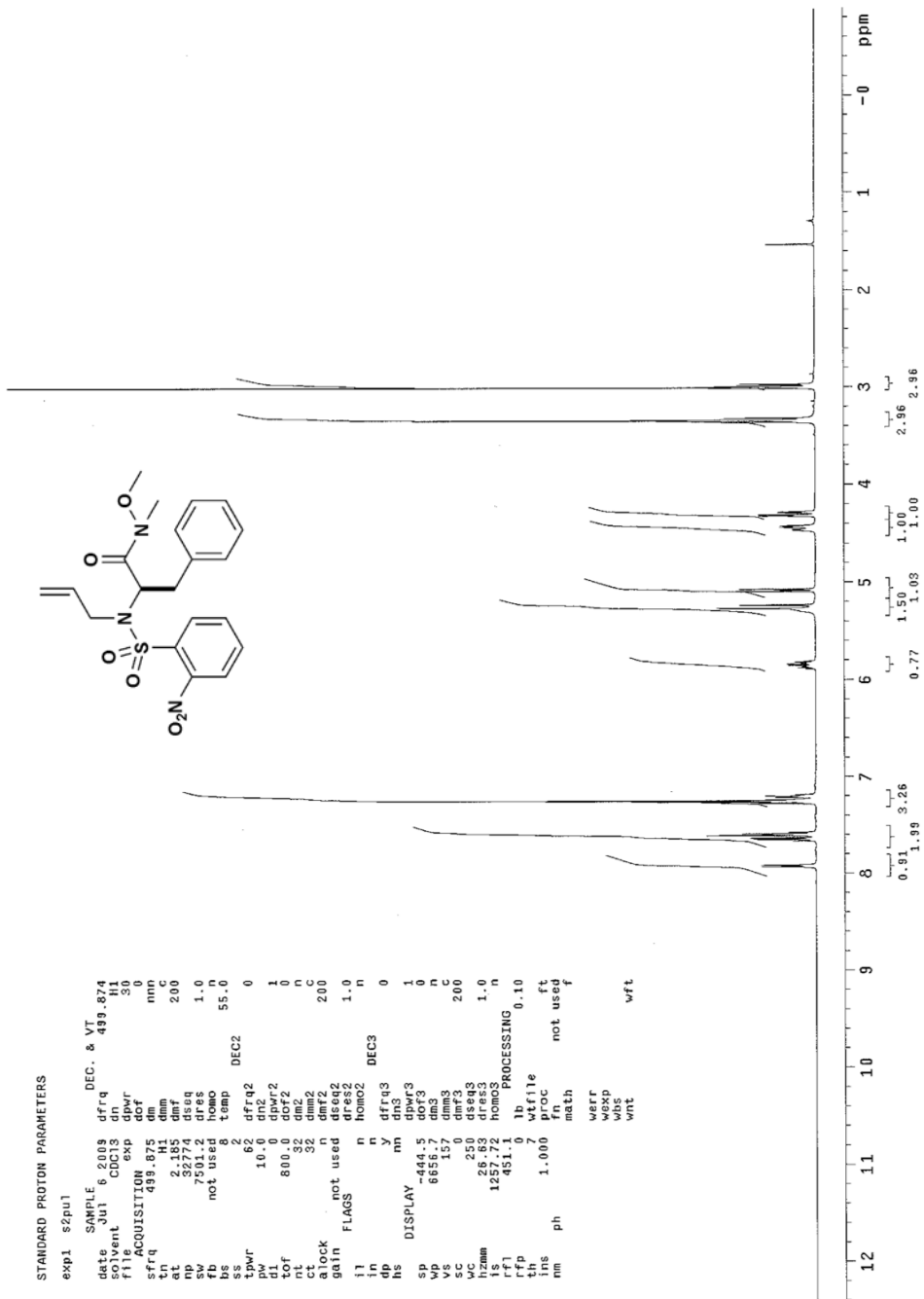


¹H NMR (500 MHz, CDCl₃) of compound (*S*)-ii



^{13}C NMR (126 MHz, CDCl_3) of compound (S)-ii

Spectral data for (*R*)-2-(*N*-allyl-2-nitrophenylsulfonamido)-*N*-methoxy-*N*-methyl-3-phenylpropanamide (**2a**)

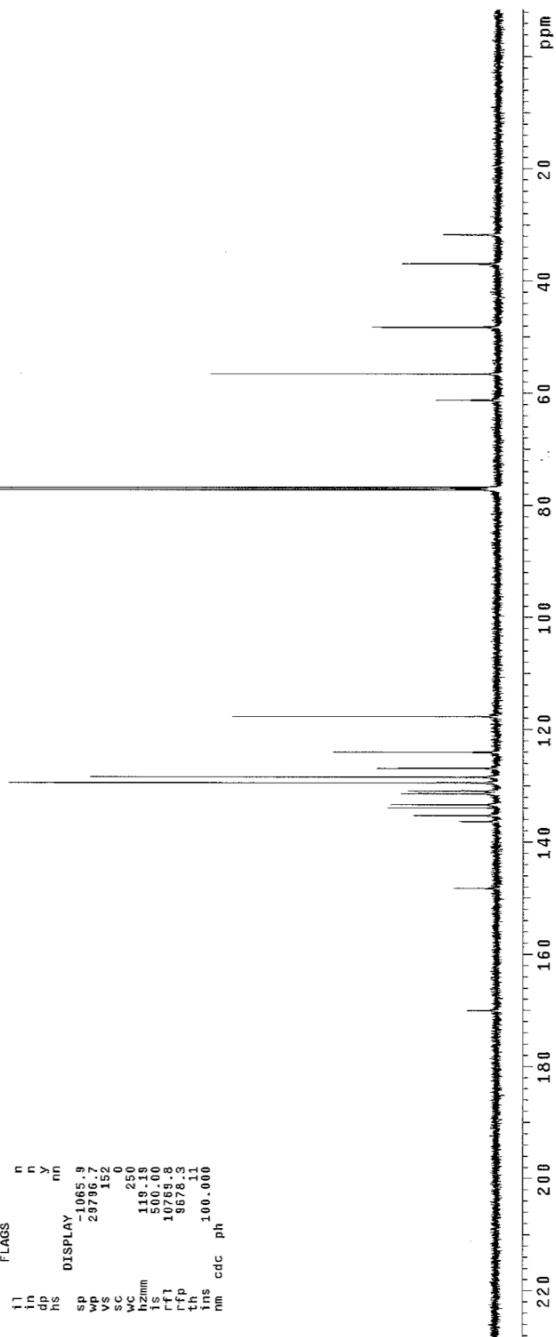
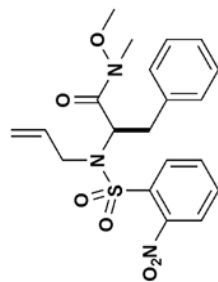


¹H NMR (500 MHz, CDCl₃) of compound **2a**

STANDARD CARBON PARAMETERS

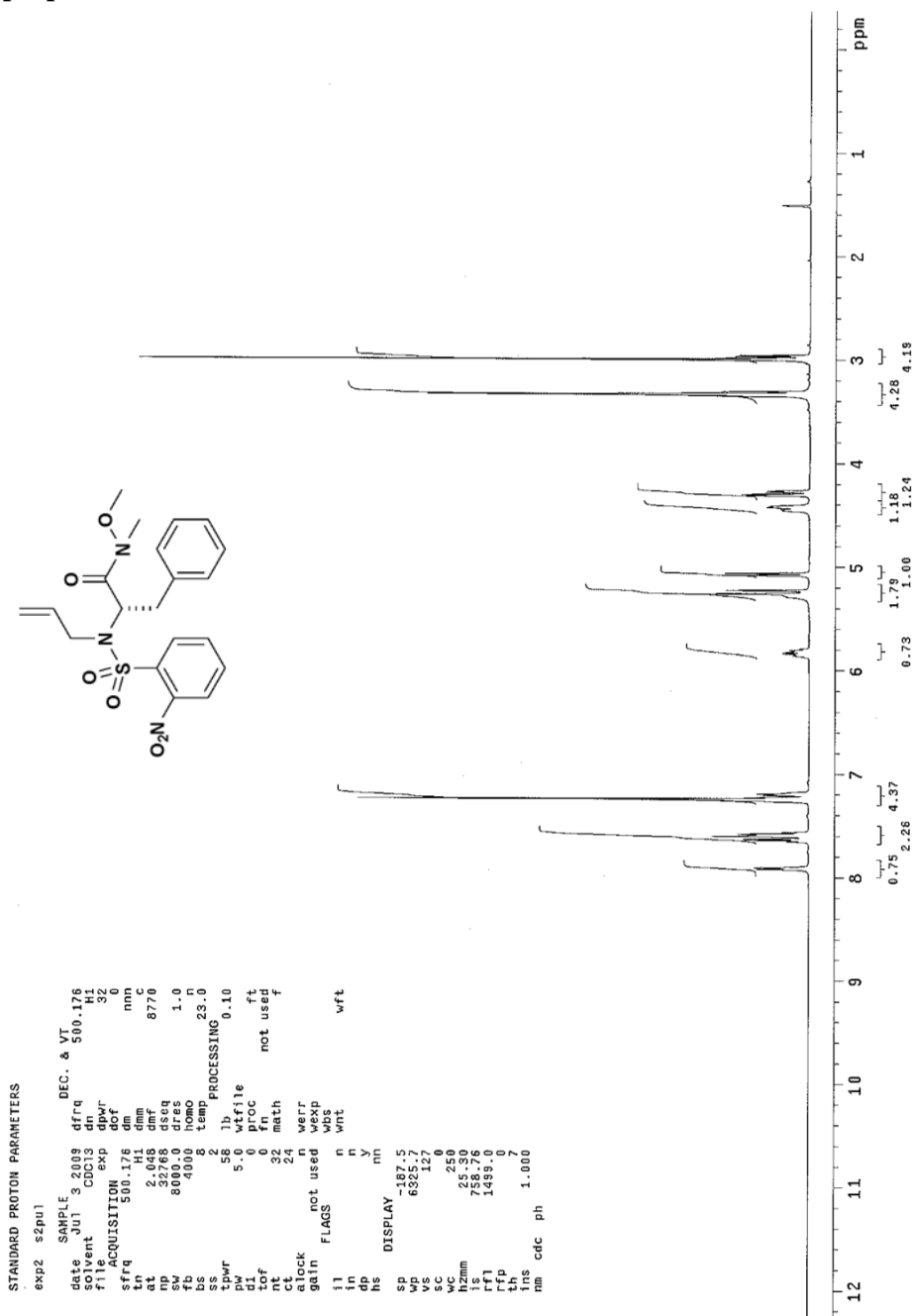
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et 1.082 temp 25.0
np 65596 th PROCESSING 1.00
% 299862
tb not used wtf file
bs not used proc ft
tpwr 55 fn not used f
pw 3.7 math
t 2000.0 werr
tof 2048 wexp
ct 1600 wbs
dlock not used n
gain not used n
flags n
11 n
in n
dp y
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sp DISPLAY -1065.9
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nm cdc ph
  
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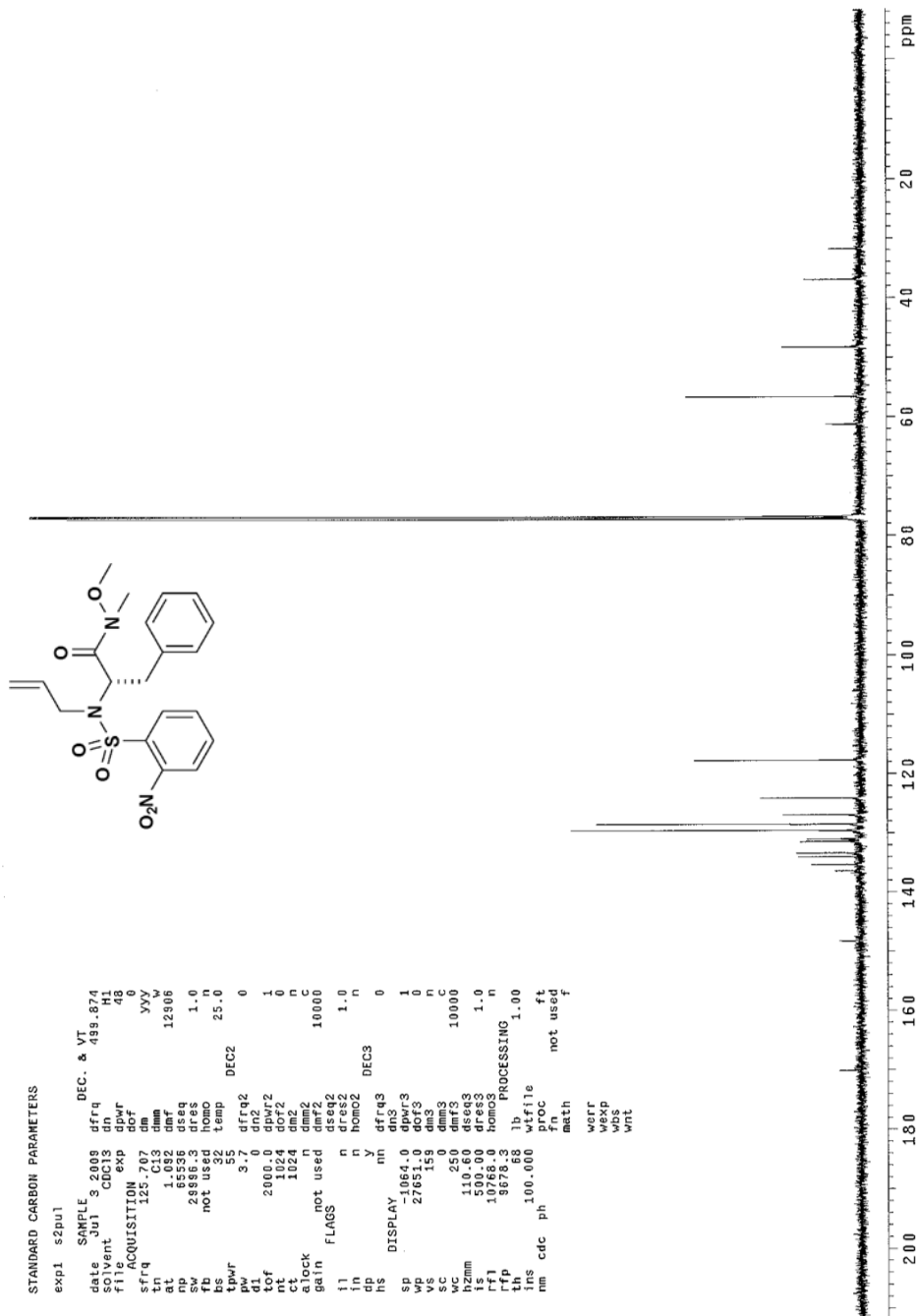


¹³C NMR (126 MHz, CDCl₃) of compound 2a

Spectral data for (*S*)-2-(*N*-allyl-2-nitrophenylsulfonamido)-*N*-methoxy-*N*-methyl-3-phenylpropanamide (**2b**)

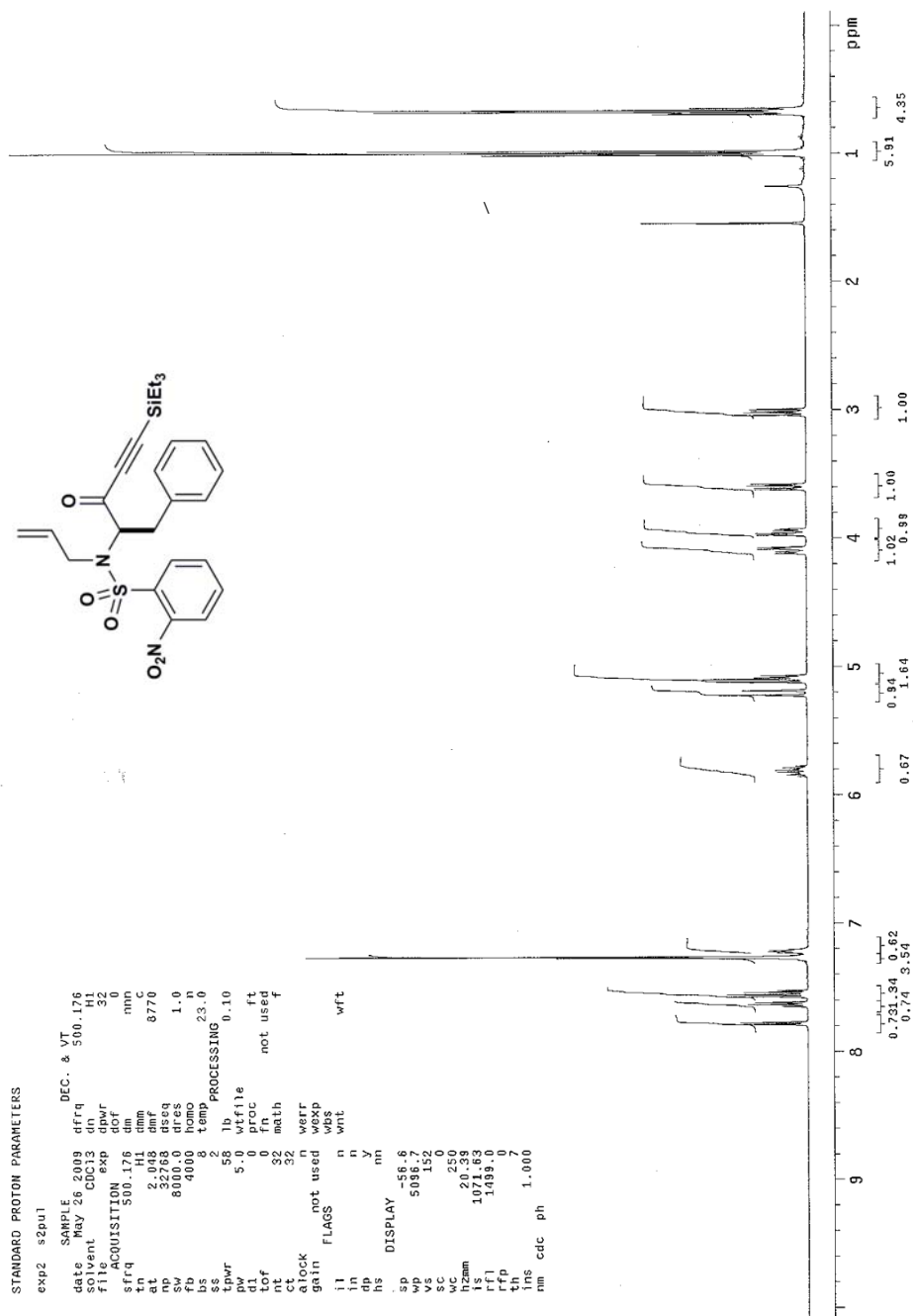


¹H NMR (500 MHz, CDCl₃) of compound **2b**

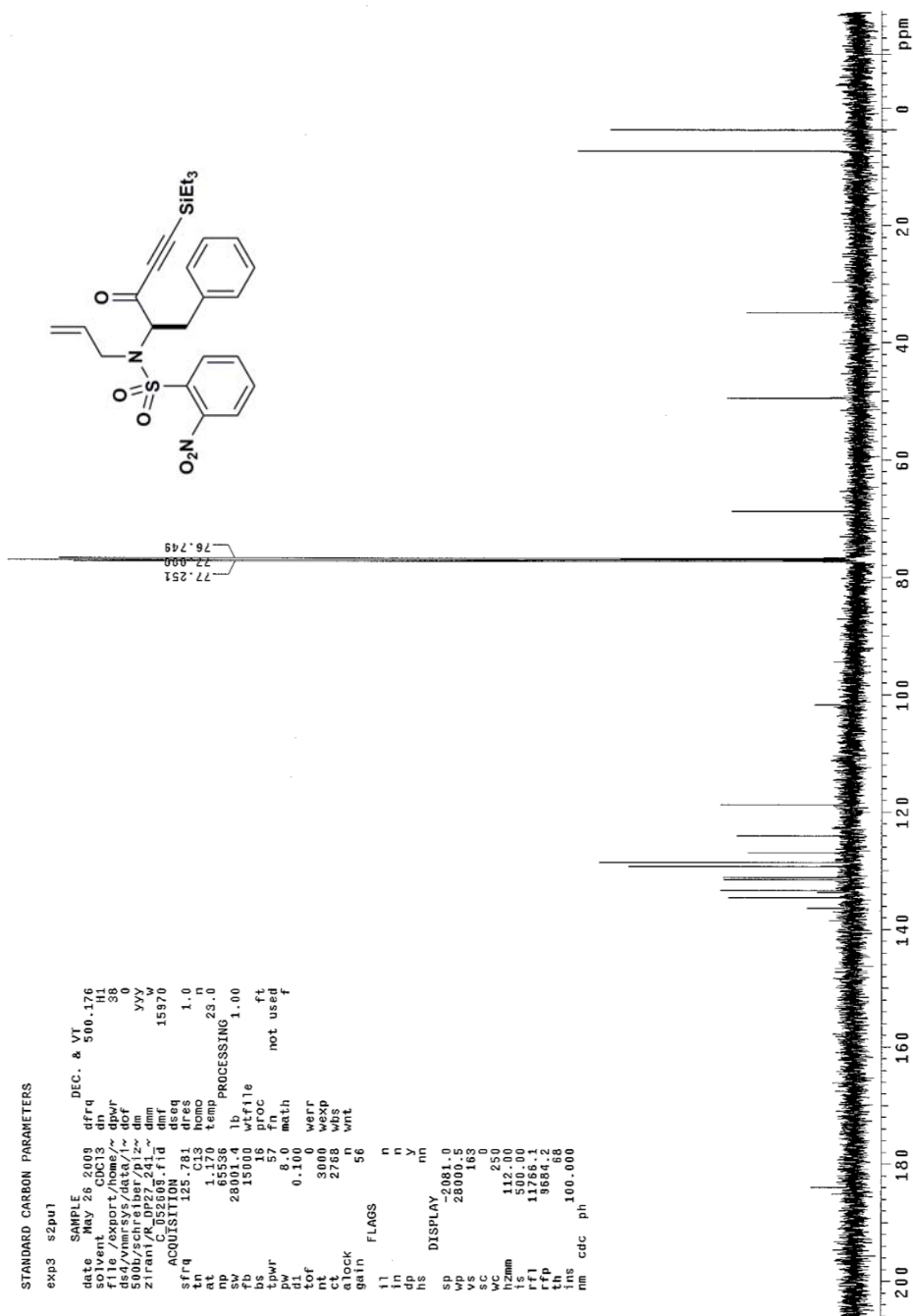


^{13}C NMR (126 MHz, CDCl_3) of compound **2b**

Spectral data for (*R*)-*N*-allyl-2-nitro-*N*-(3-oxo-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)benzenesulfonamide (**3a**)

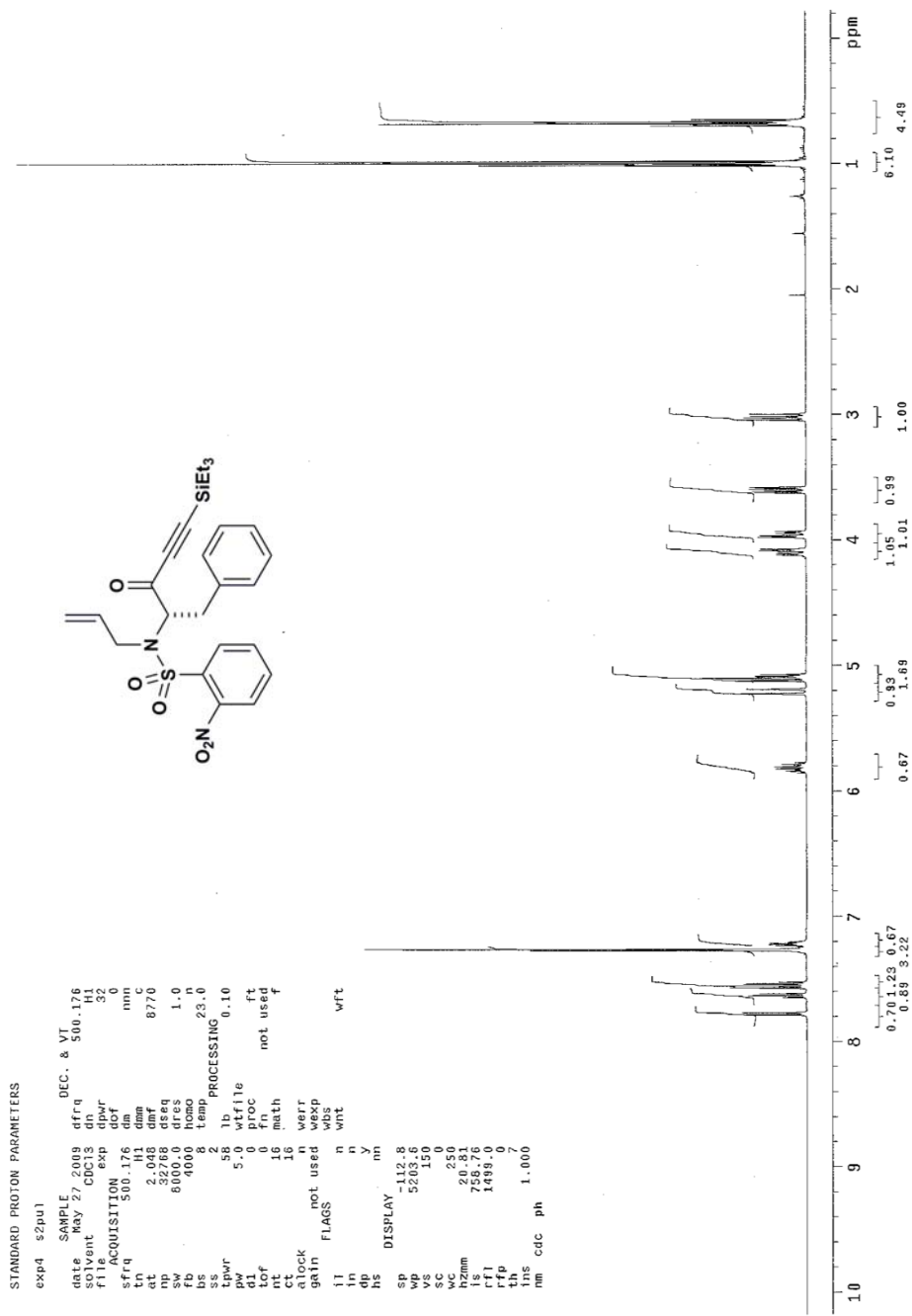


¹H NMR (500 MHz, CDCl₃) of compound **3a**

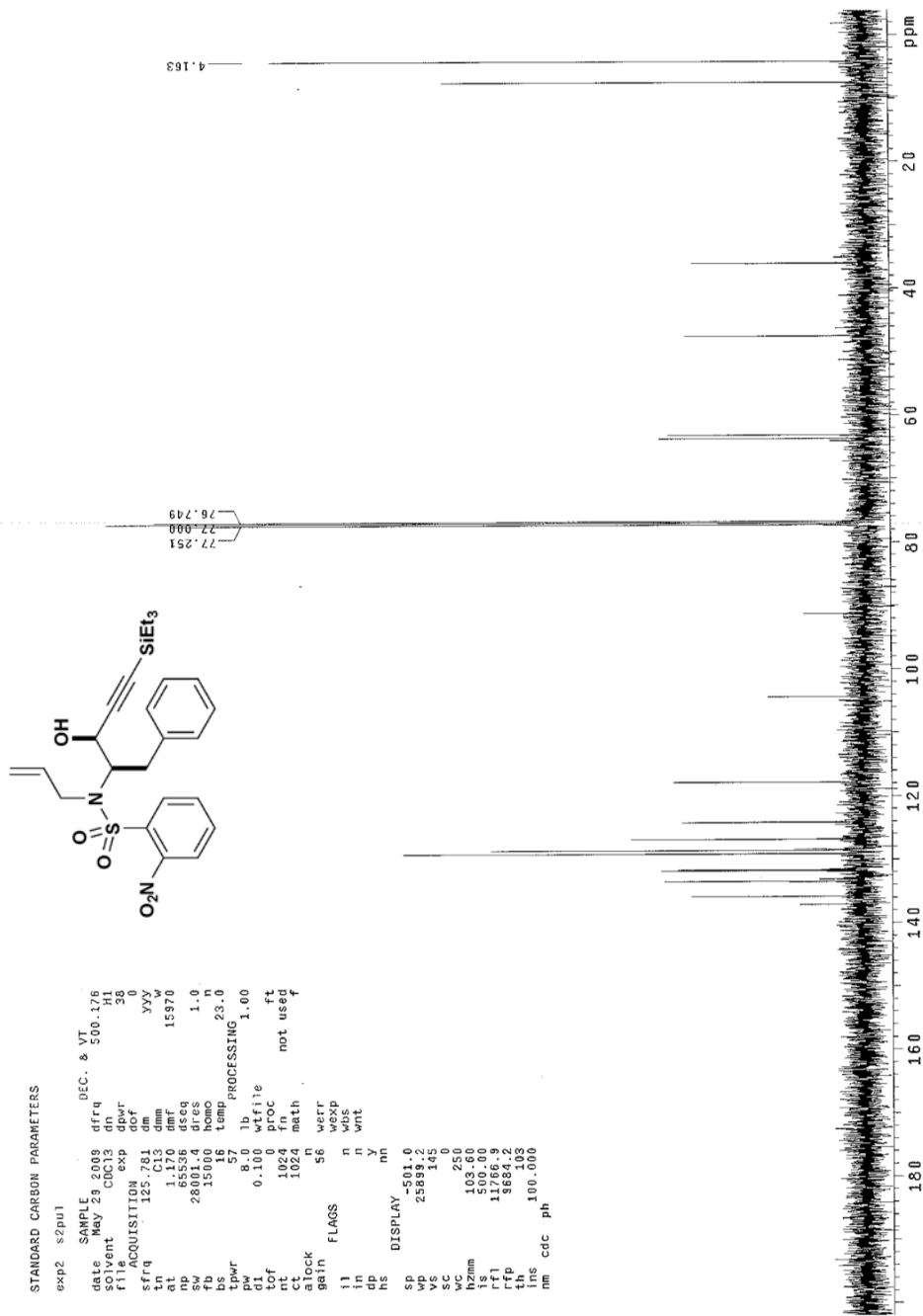


^{13}C NMR (126 MHz, CDCl_3) of compound **3a**

Spectral data for (*S*)-*N*-allyl-2-nitro-*N*-(3-oxo-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)benzenesulfonamide (**3b**)

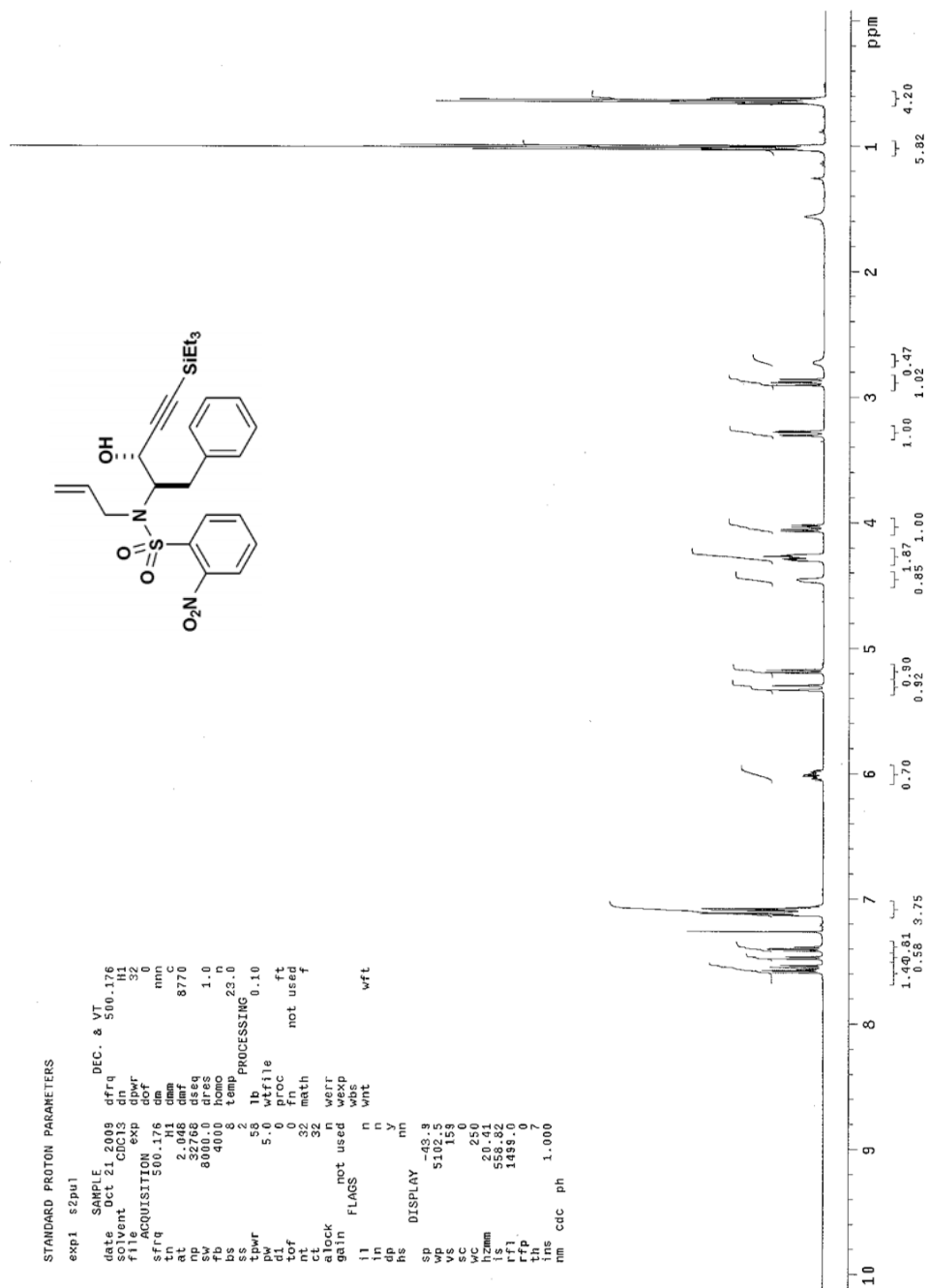


¹H NMR (500 MHz, CDCl₃) of compound **3b**

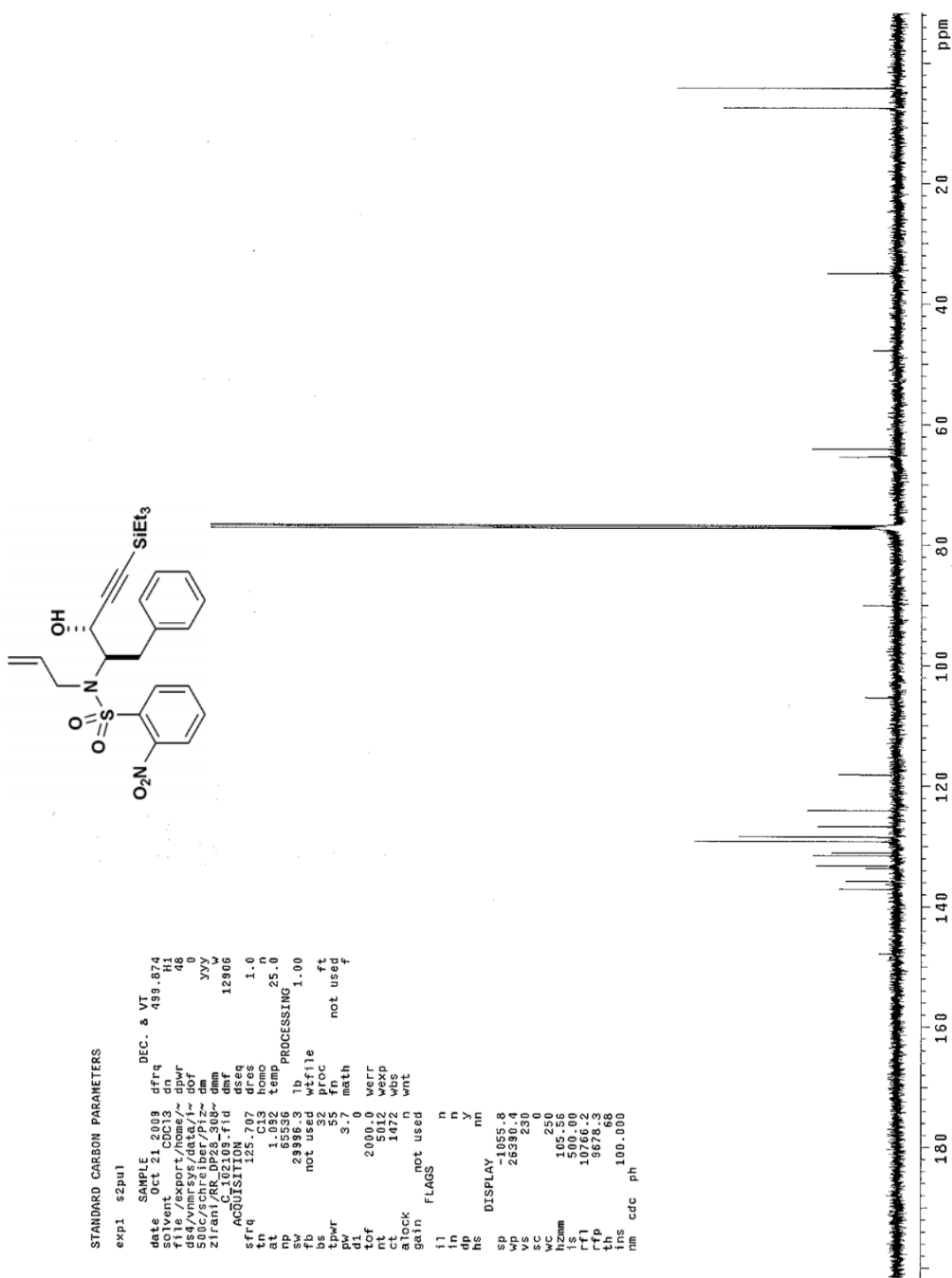


^{13}C NMR (126 MHz, CDCl_3) of compound **4a**

Spectral data for *N*-allyl-*N*-((2*R*,3*R*)-3-hydroxy-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)-2-nitrobenzene sulfonamide (**4b**)



¹H NMR (500 MHz, CDCl₃) of compound **4b**

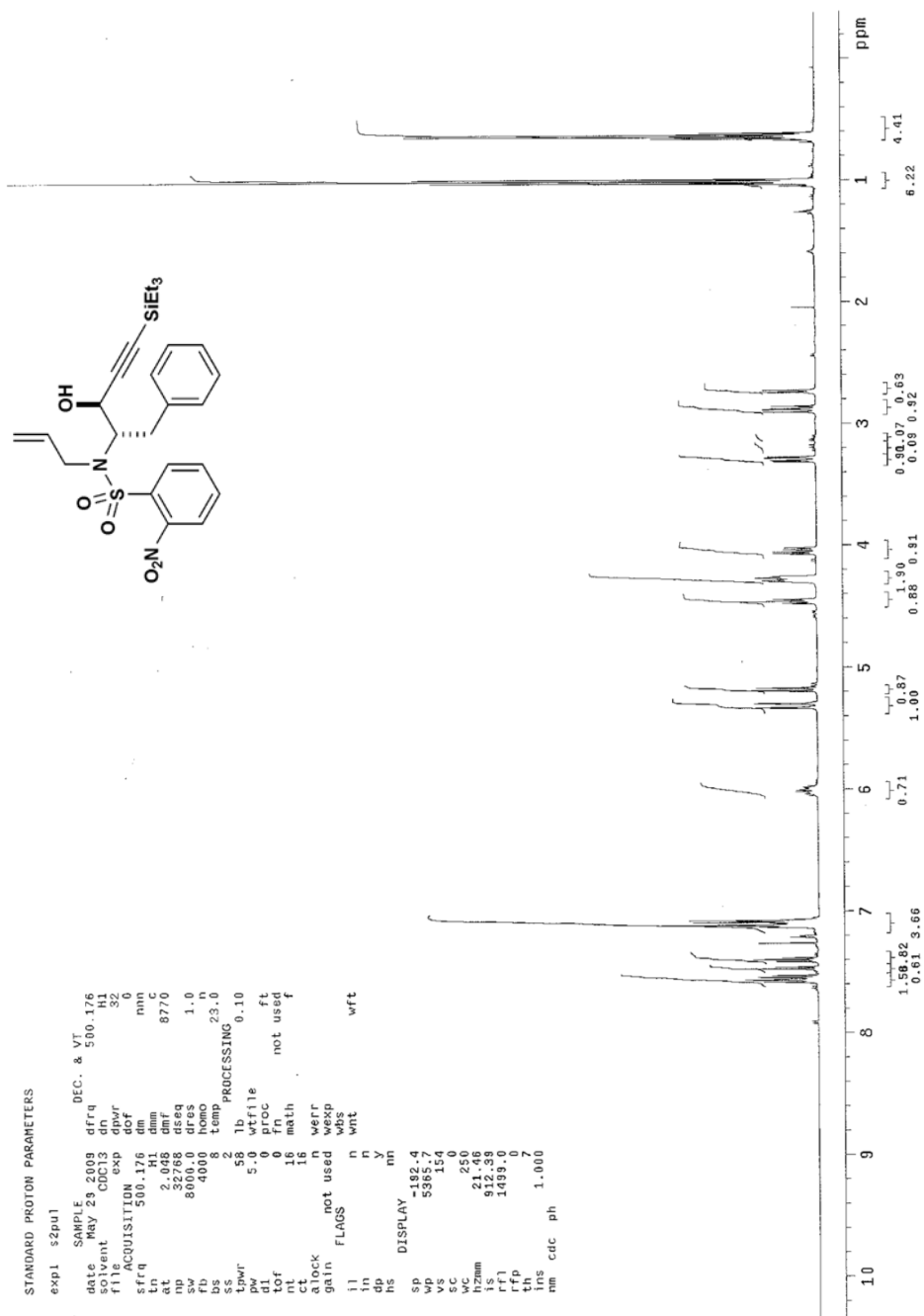


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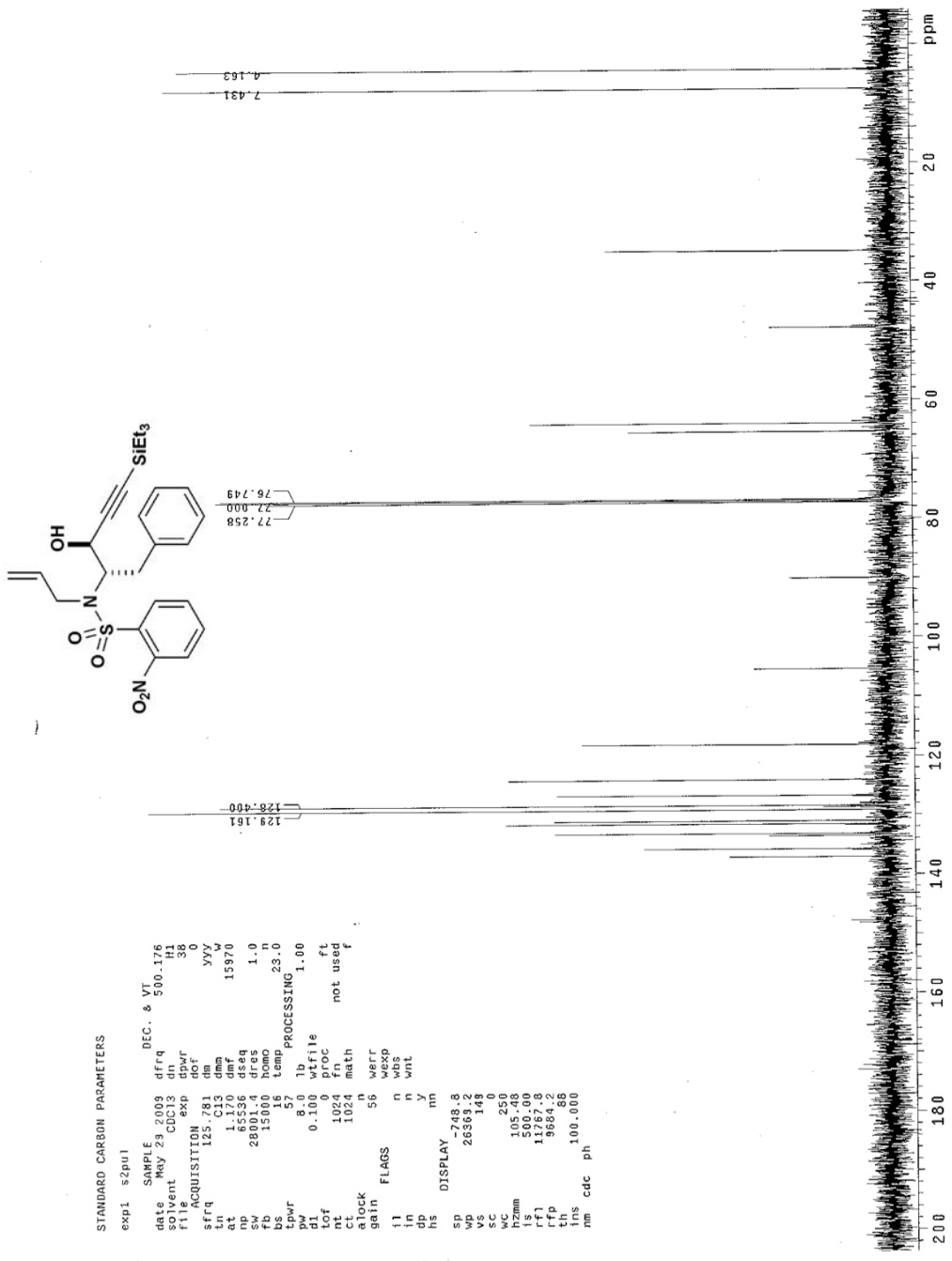
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Zifam/CR DP5/302~ dmf 12966
C_102109-fid dmf 12966
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tpwr 55 proc ft
pw 3.7 math not used f
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tof 5012 wbp
ct 1472 wbs
gain not used wnt
il FLAG n
in n
dp y
hs nn
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wp 26390.4
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SC 0
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tpp 9877.68
lms 100.000
nm cdc ph
  
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¹³C NMR (126 MHz, CDCl₃) of compound **4b**

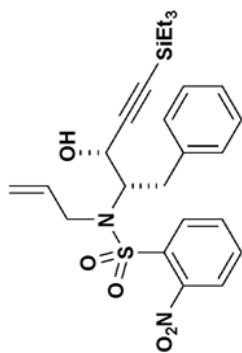
Spectral data for *N*-allyl-*N*-((2*S*,3*S*)-3-hydroxy-1-phenyl-5-(triethylsilyl)pent-4-yn-2-yl)-2-nitrobenzene sulfonamide (**4c**)



¹H NMR (500 MHz, CDCl₃) of compound **4c**



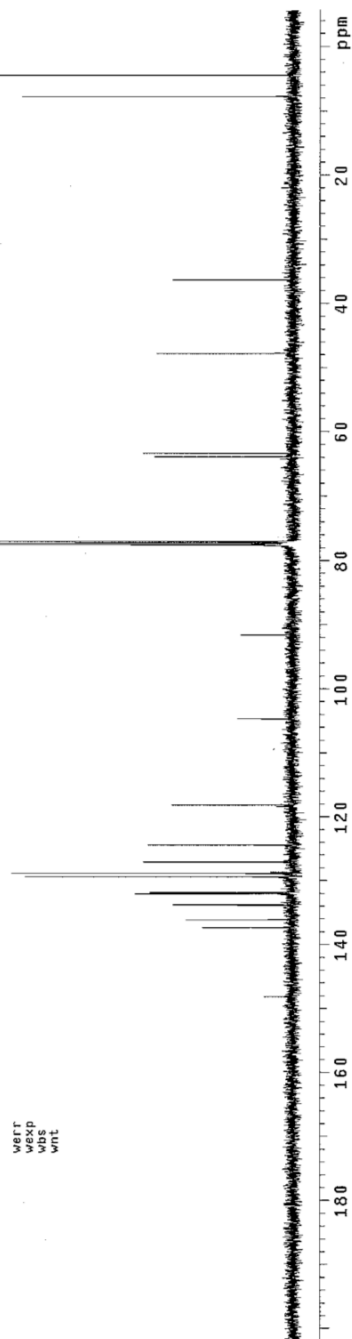
¹³C NMR (126 MHz, CDCl₃) of compound **4c**



STANDARD CARBON PARAMETERS

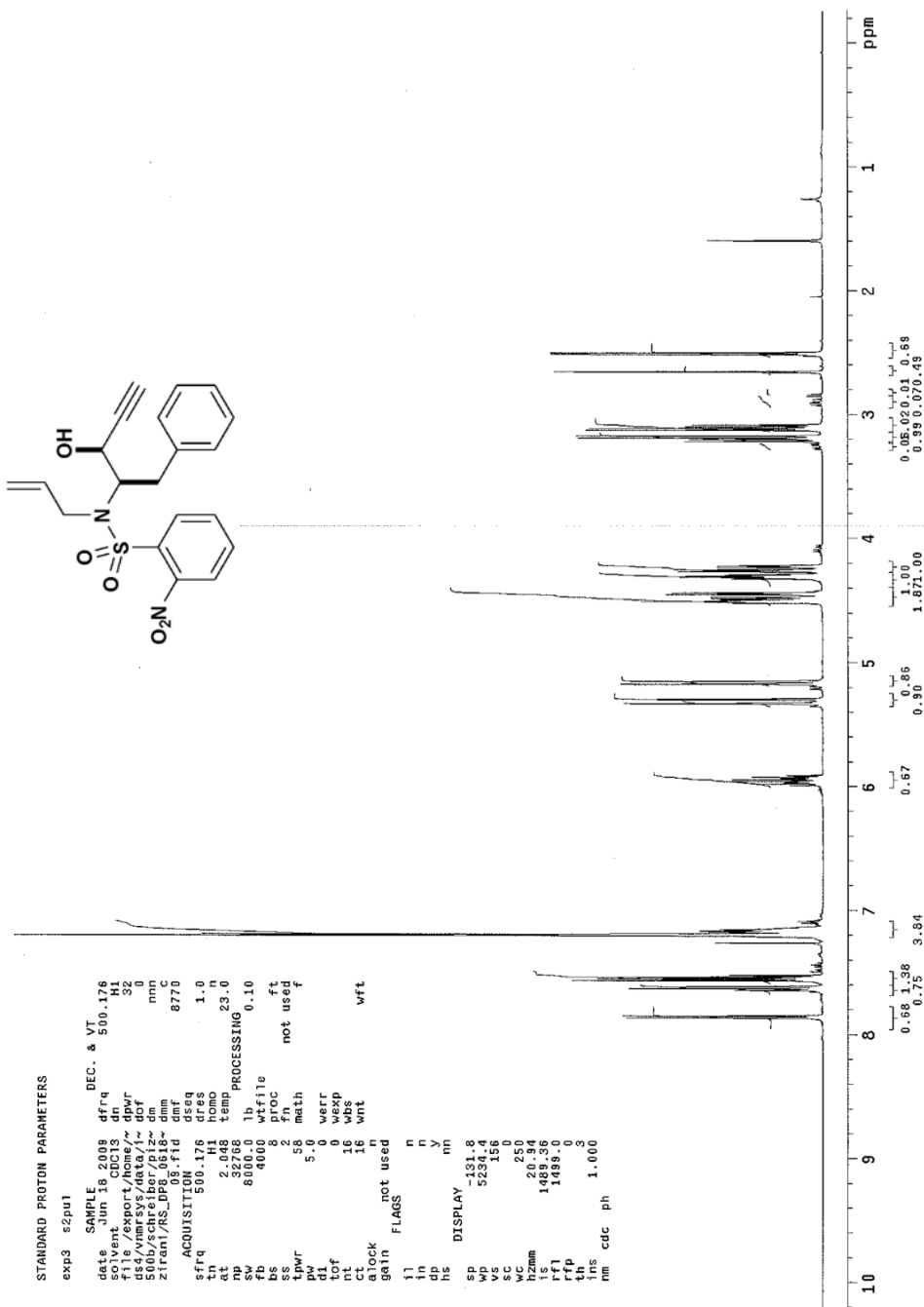
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at 1.092 dmf 12000
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fb not used homo 1.0
bs S2 temp 25.0 DEC2
tpwr 55
pw 4.2 dfrq2 0
tof 2000.0 dpr2 1
nt 2048 dof2 0
ct 0 dm2 n
atock not used dm2 10000
gain FLAGS dseq2 1.0
il n homo2 n
in y dfrq3 0
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wp 26095.7 dof3 0
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wc 250 dm3 10000
h2mm 104.38 dseq3 1.0
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rfp 1055.0 homo PROCESSING n
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proc not used
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wsp
wnt
  
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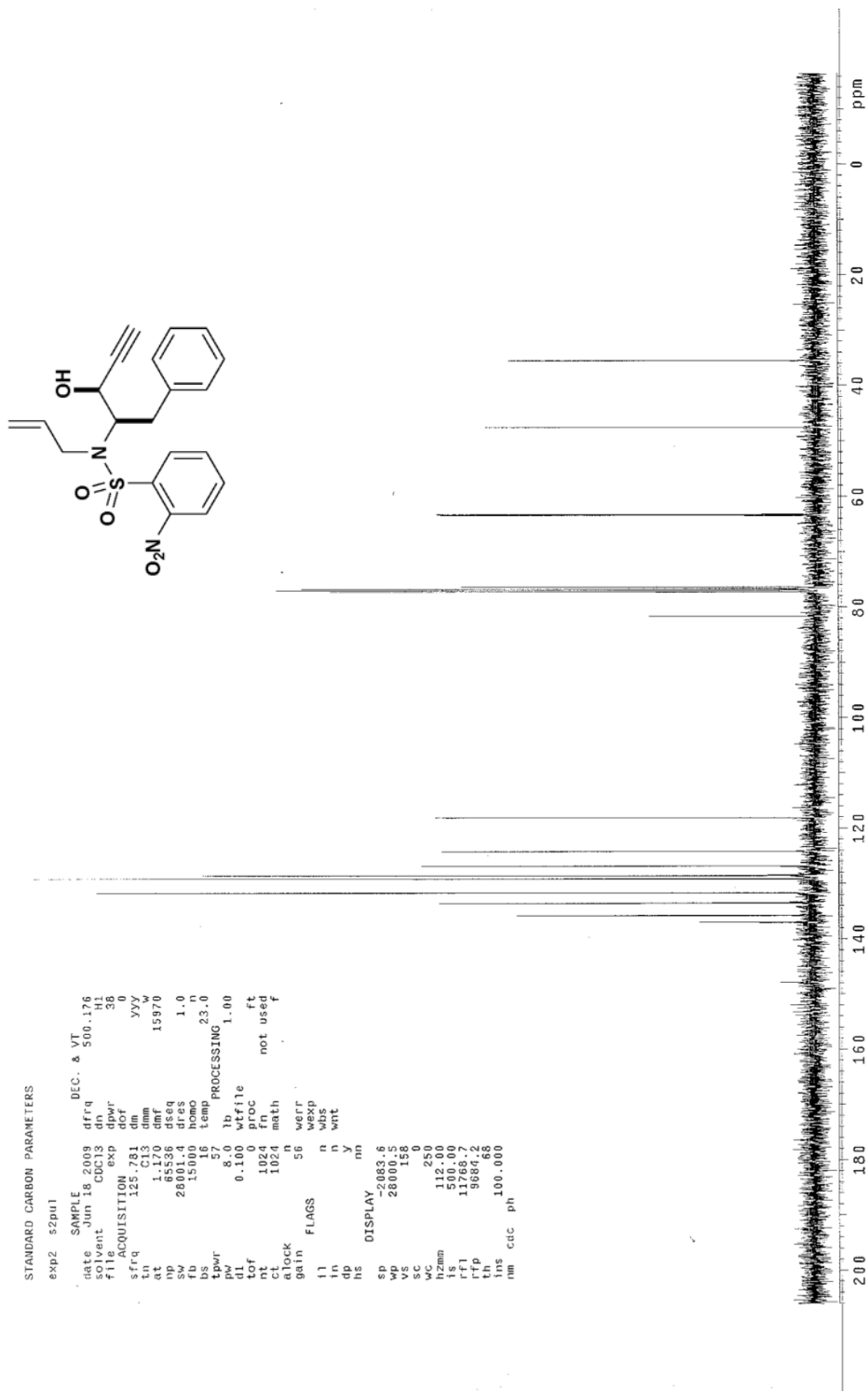


¹³C NMR (126 MHz, CDCl₃) of compound **4d**

Spectral data for *N*-allyl-*N*-((2*R*,3*S*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (**1a**)

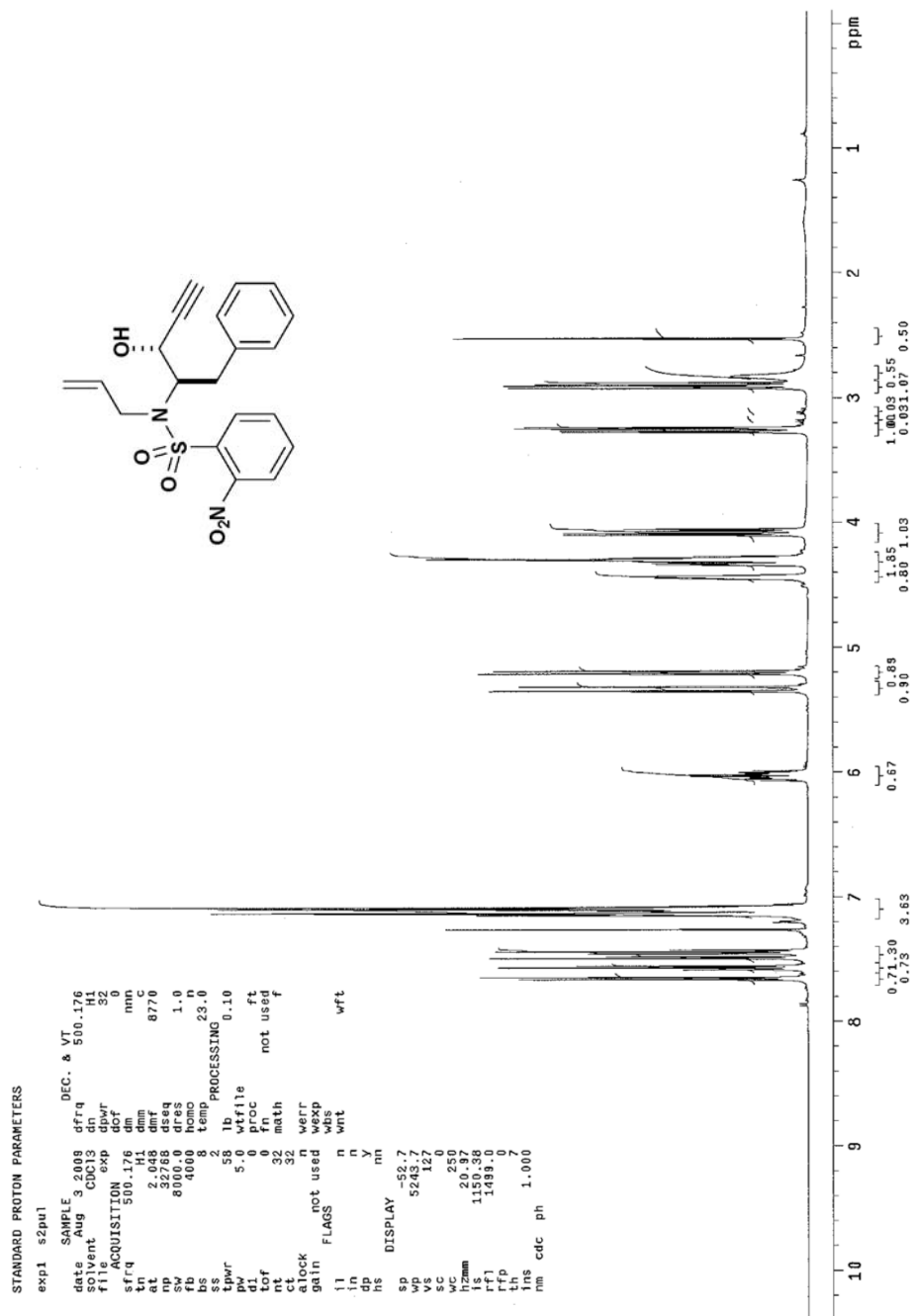


¹H NMR (500 MHz, CDCl₃) of compound **1a**

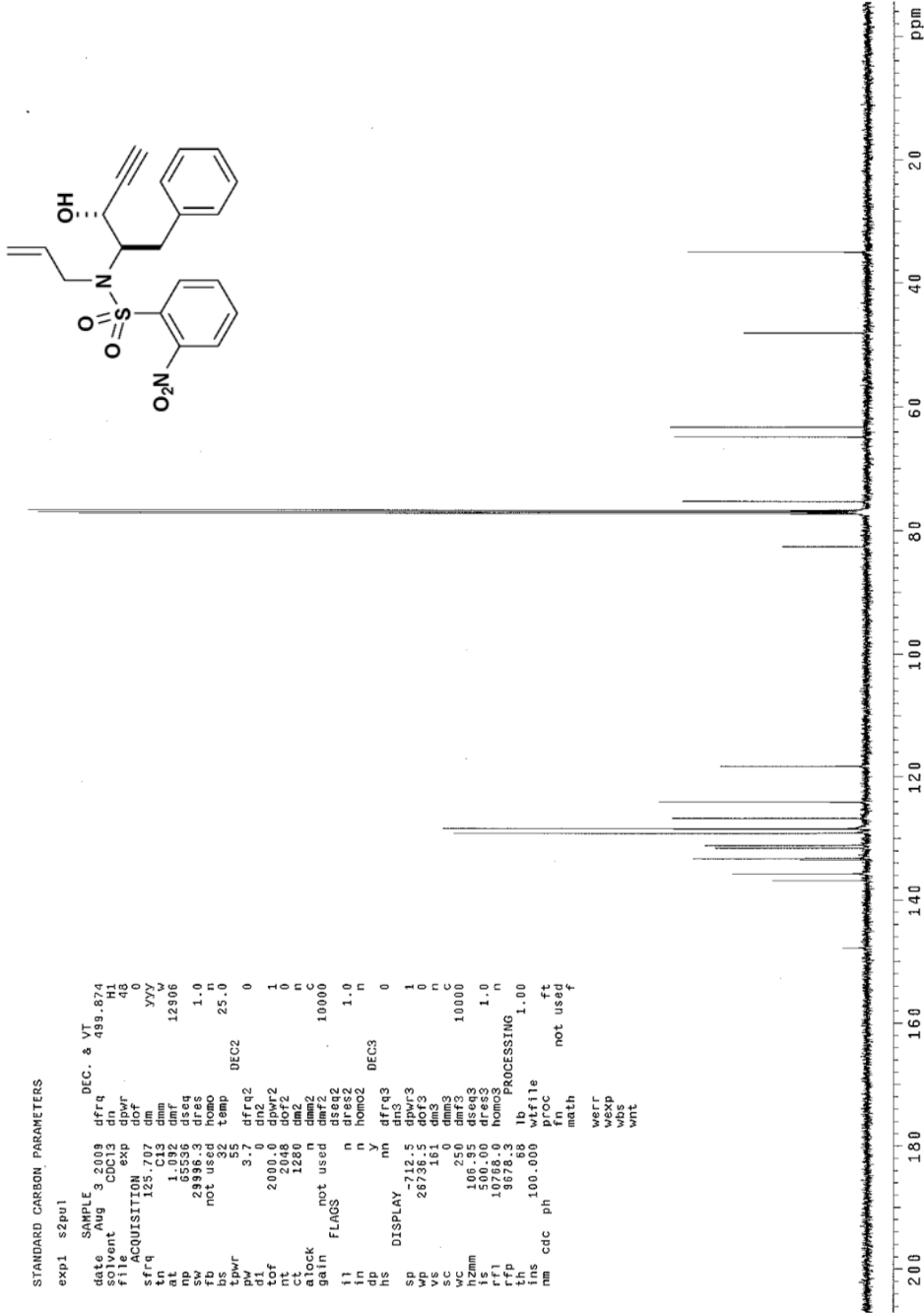


^{13}C NMR (126 MHz, CDCl_3) of compound **1a**

Sectral data for *N*-allyl-*N*-((2*R*,3*R*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (**1b**)

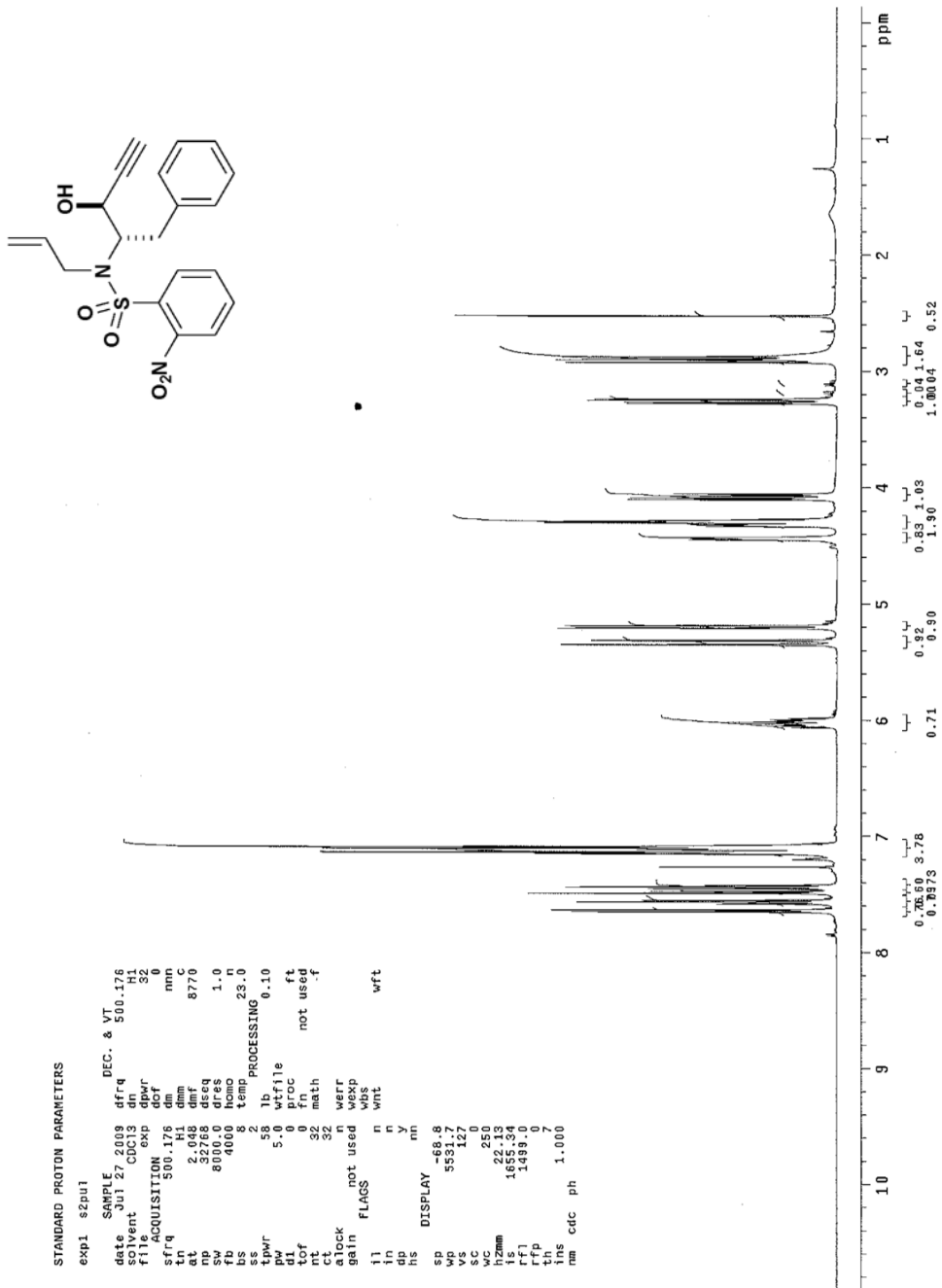


¹H NMR (500 MHz, CDCl₃) of compound **1b**

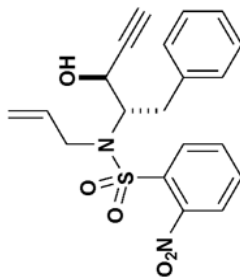


^{13}C NMR (126 MHz, CDCl_3) of compound **1b**

Spectral data for *N*-allyl-*N*-((2*S*,3*S*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (**1c**)



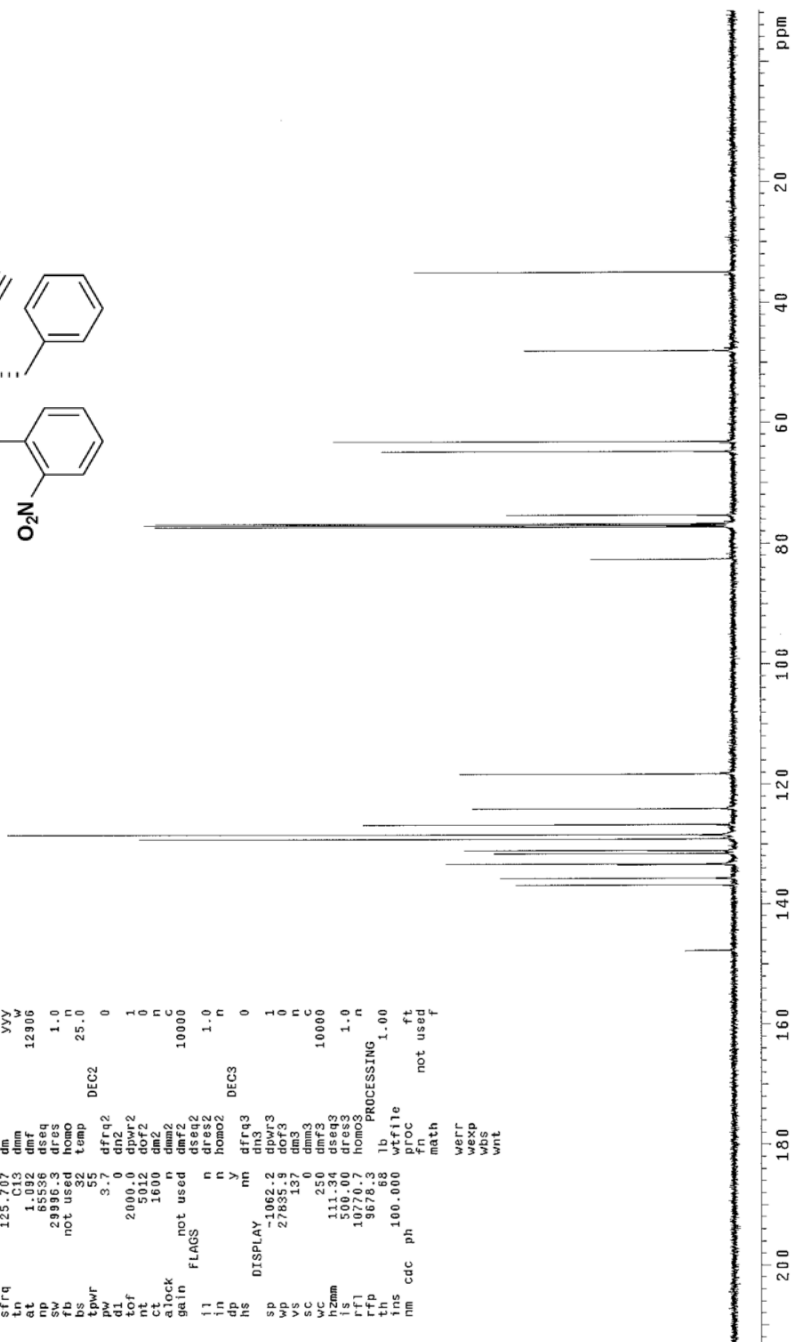
¹H NMR (500 MHz, CDCl₃) of compound **1c**



STANDARD CARBON PARAMETERS

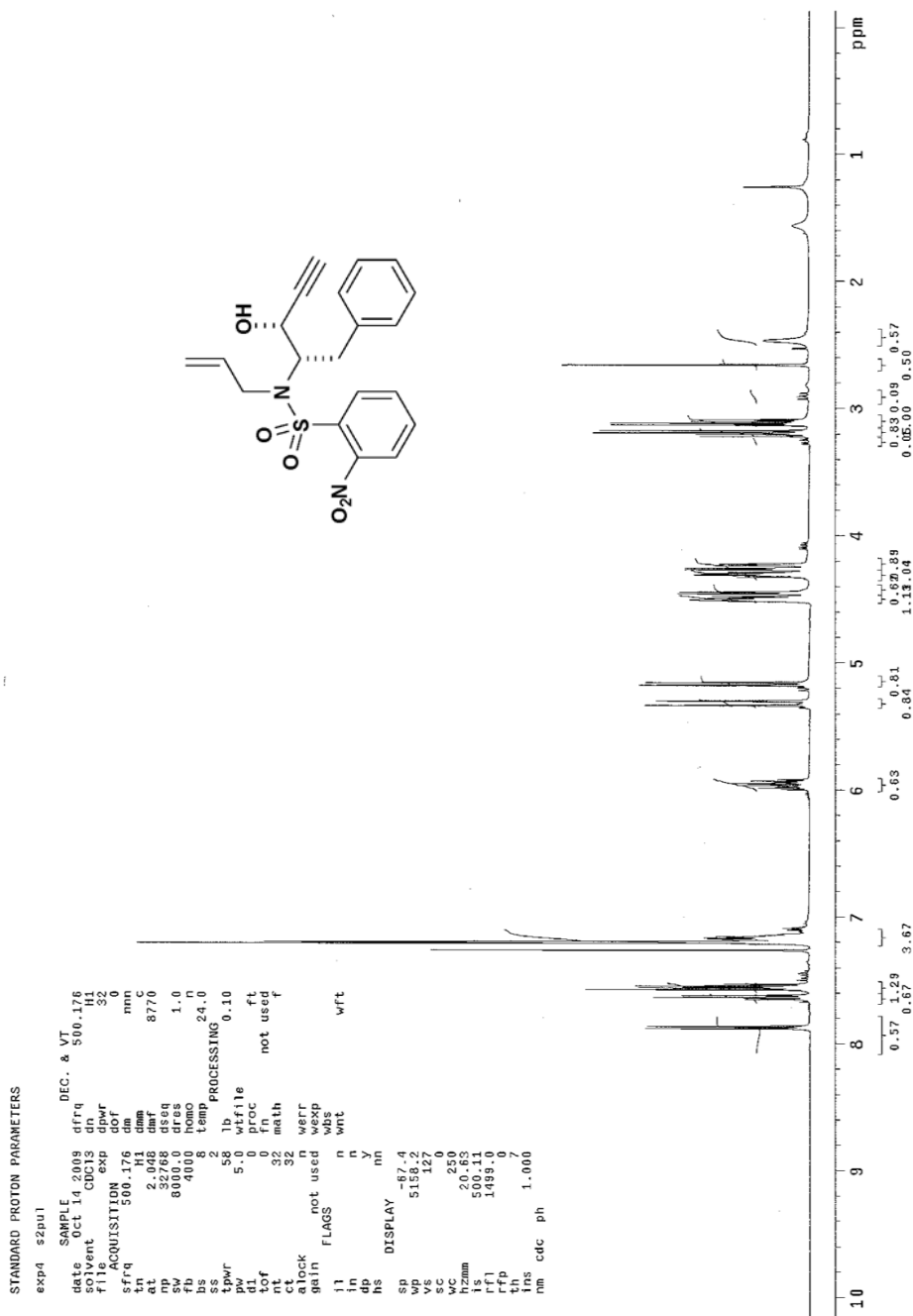
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tpwr 55
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ln n homo2 1.0
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rf2 107.07 homo3 1.0
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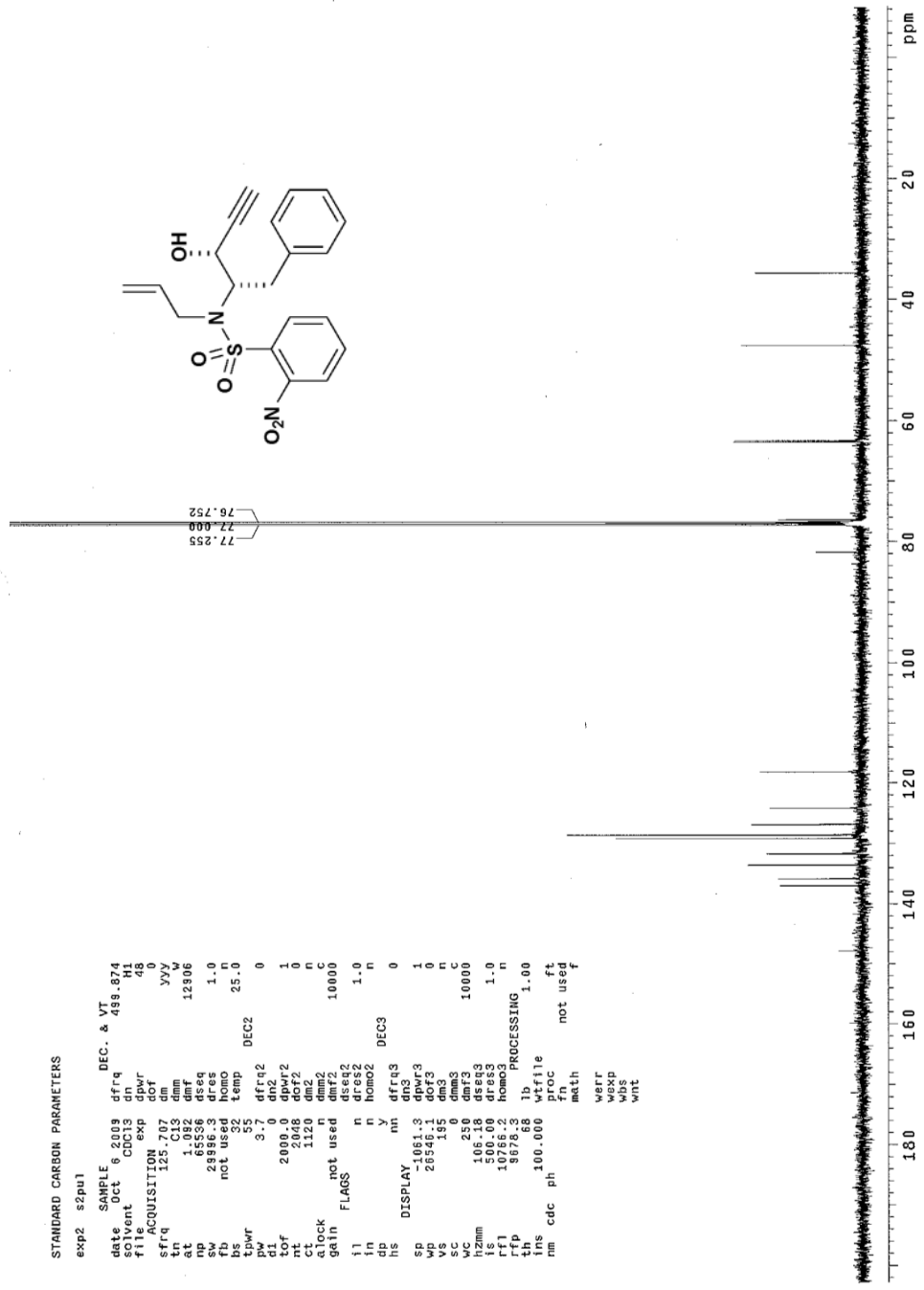


^{13}C NMR (126 MHz, CDCl_3) of compound 1c

Spectral data for *N*-allyl-*N*-((2*S*,3*R*)-3-hydroxy-1-phenylpent-4-yn-2-yl)-2-nitrobenzenesulfonamide (**1d**)



¹H NMR (500 MHz, CDCl₃) of compound **1d**



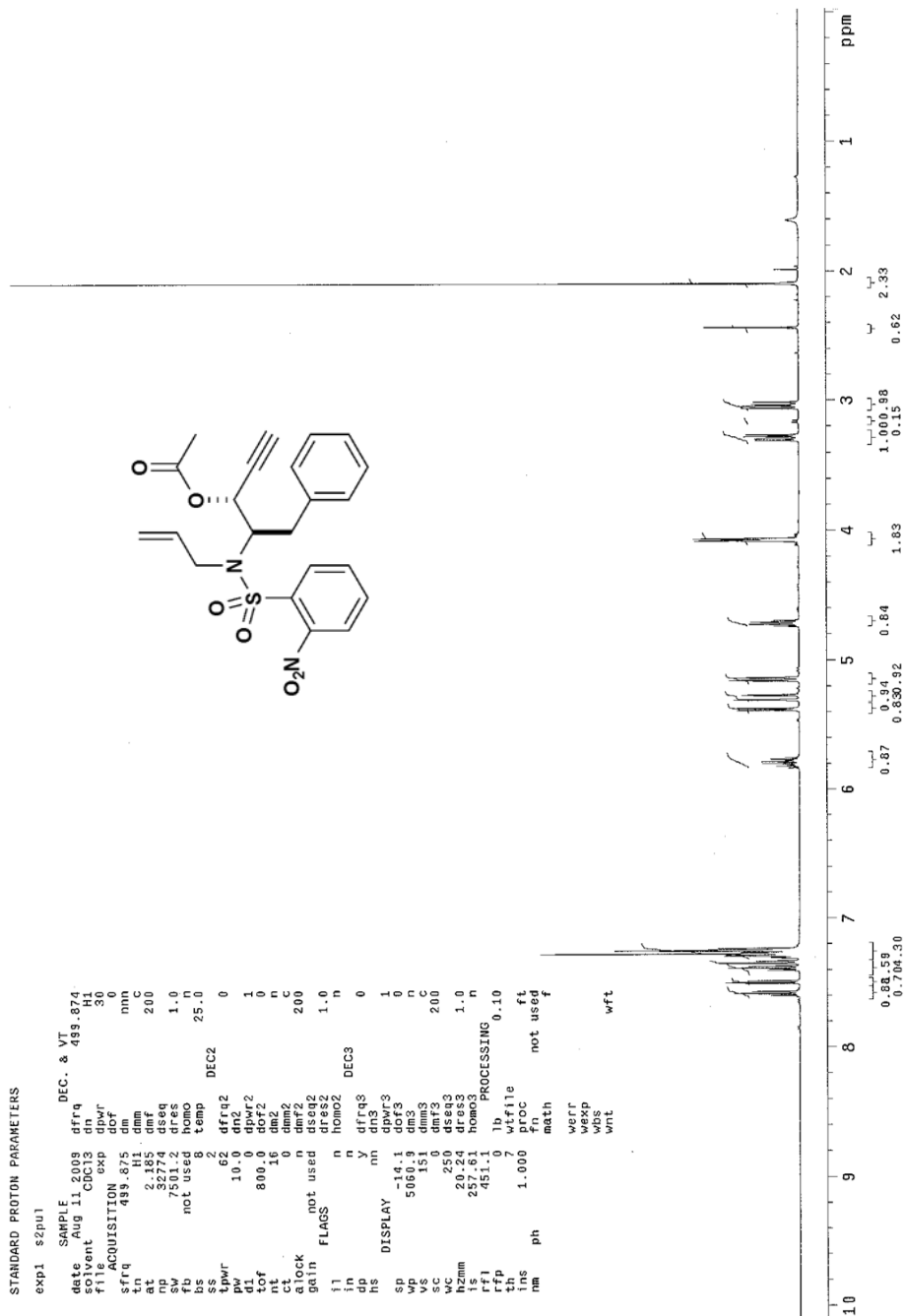
STANDARD CARBON PARAMETERS

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 sw 28986.3 dres 1.0
 fb not used homo n
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 d2 0 dn2 0
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 gain not used dmf2 10000
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 l n homo2 1.0
 dp n y
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 vs 26566.1 dfr3 0
 vs 195 dm3 n
 sc 0 dnm3 C
 wc 1050 dmf3 10000
 is 500.00 dres3 1.0
 rfl 10766.2 homo3 n
 rfp 9676.3 1b PROCESSING n
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 ms 100.000 proc ft
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 math
 werr
 wexp
 wbs
 wnt

¹³C NMR (126 MHz, CDCl₃) of compound 1d

Spectral data for (3*R*,4*R*)-4-(*N*-allyl-2-nitrophenylsulfonamido)-5-phenylpent-1-yn-3-yl acetate (**6b**)

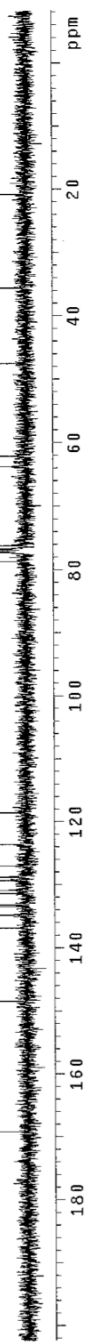
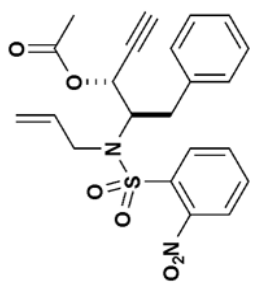


¹H NMR (500 MHz, CDCl₃) of compound **6b**

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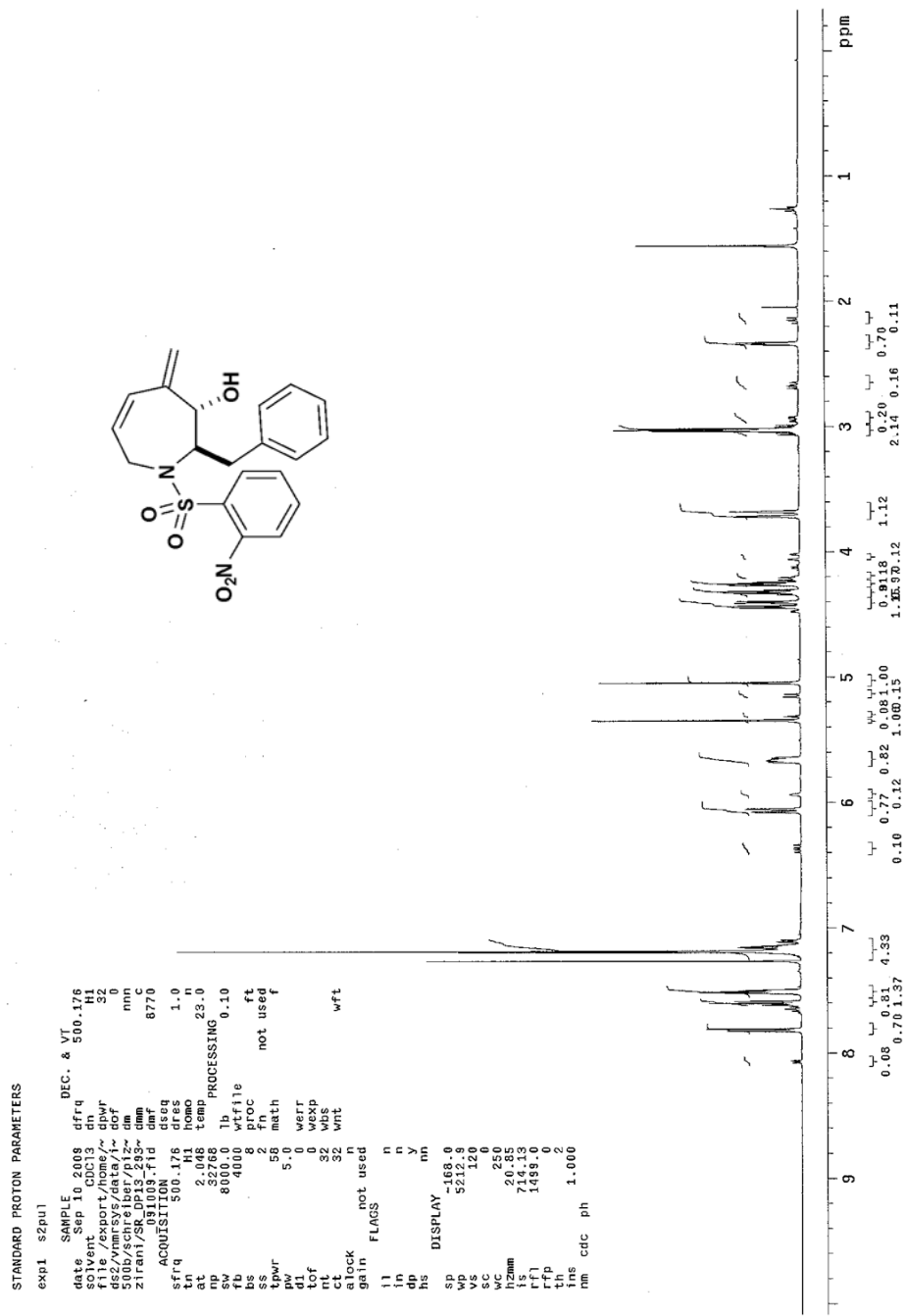
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solvent Aug 11 2009 dfrq H1
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sw 28936.3 dres 1.0
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rfi 10758.3 homo3 n
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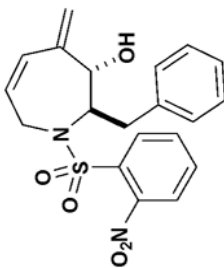


¹³C NMR (126 MHz, CDCl₃) of compound **6b**

Spectral data for (2*R*,3*S*,*Z*)-2-benzyl-4-methylene-1-(2-nitrophenylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azepin-3-ol (**5a**)



¹H NMR (500 MHz, CDCl₃) of compound **5a**

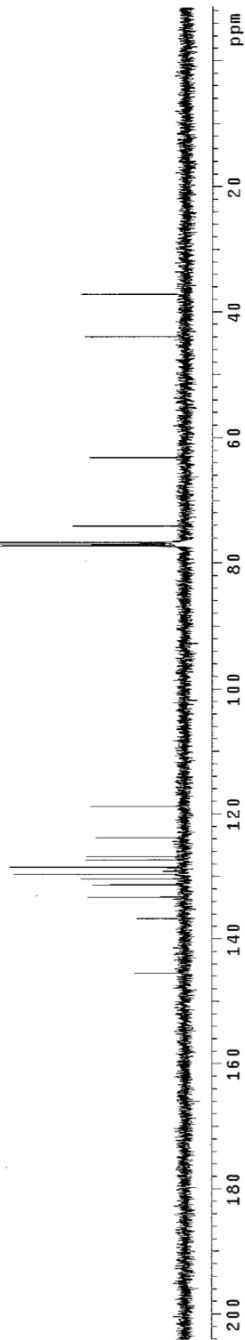


STANDARD CARBON PARAMETERS

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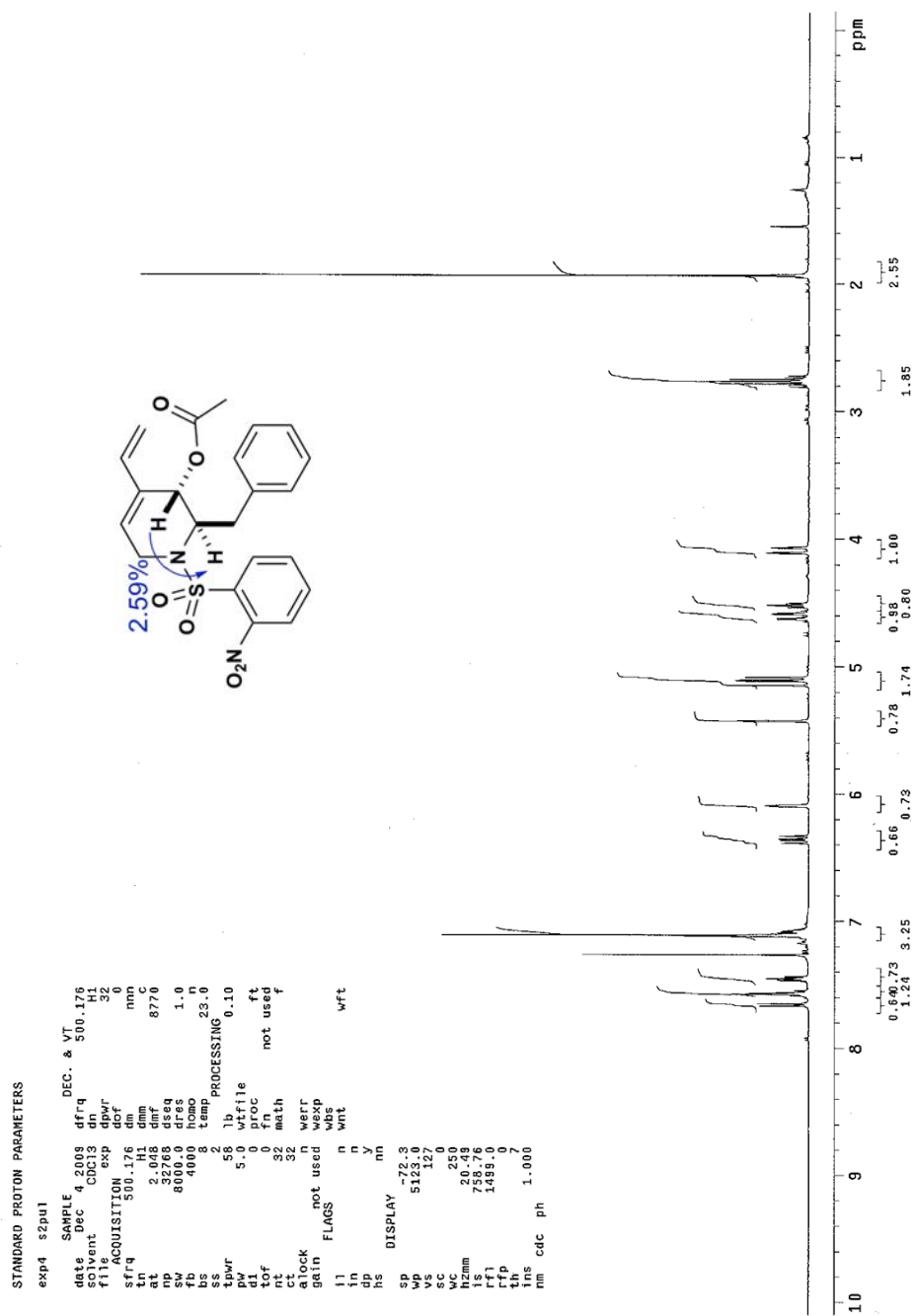
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acq CEC13 exp 49
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sp 2885.28 dseq
ps 1.00 pas
fb not used homo 1.0
bs 32 temp 25.0
tpwr 55
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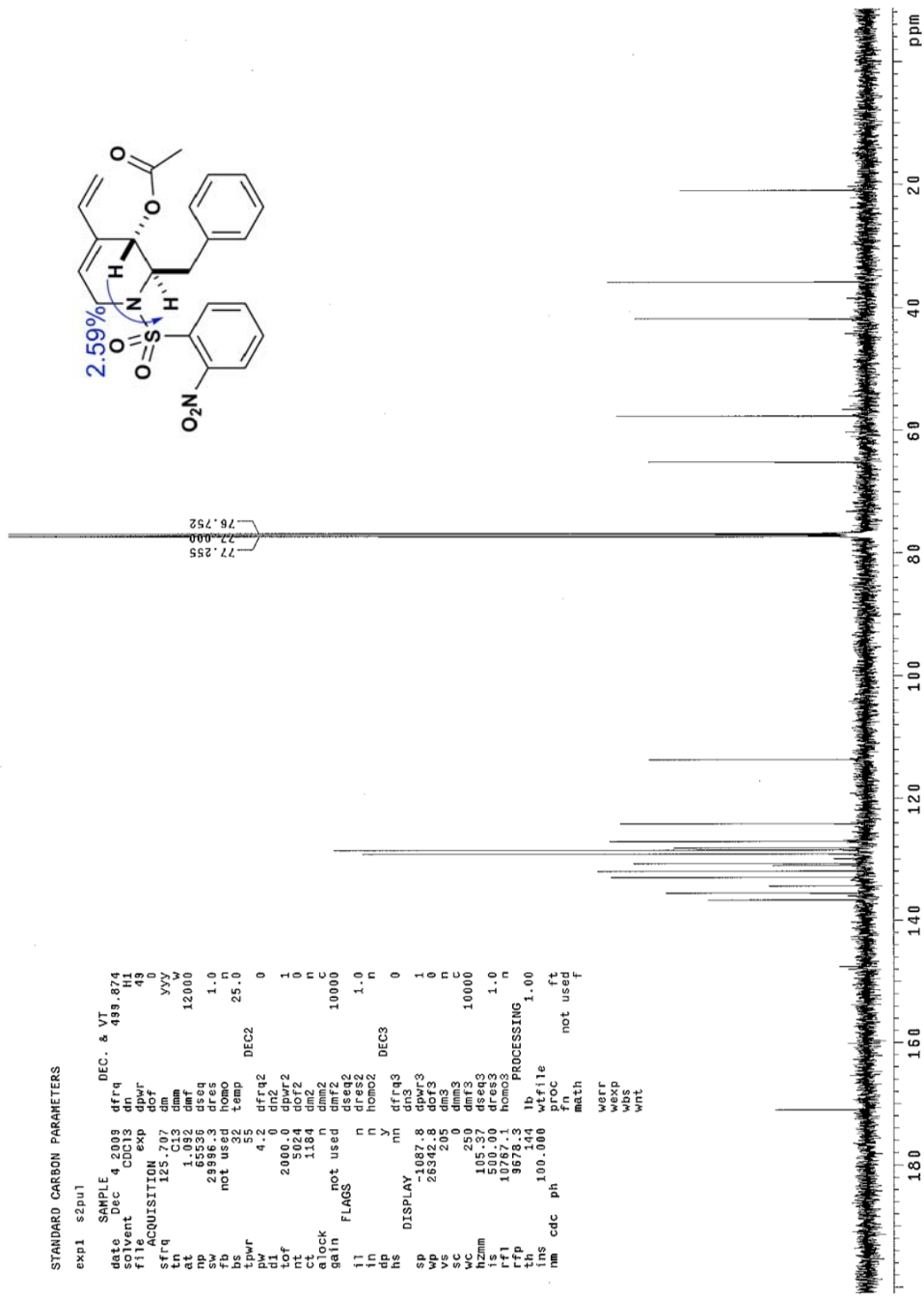


¹³C NMR (126 MHz, CDCl₃) of compound **5a**

Spectral data for (2*R*,3*S*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-yl-acetate (**7a**)

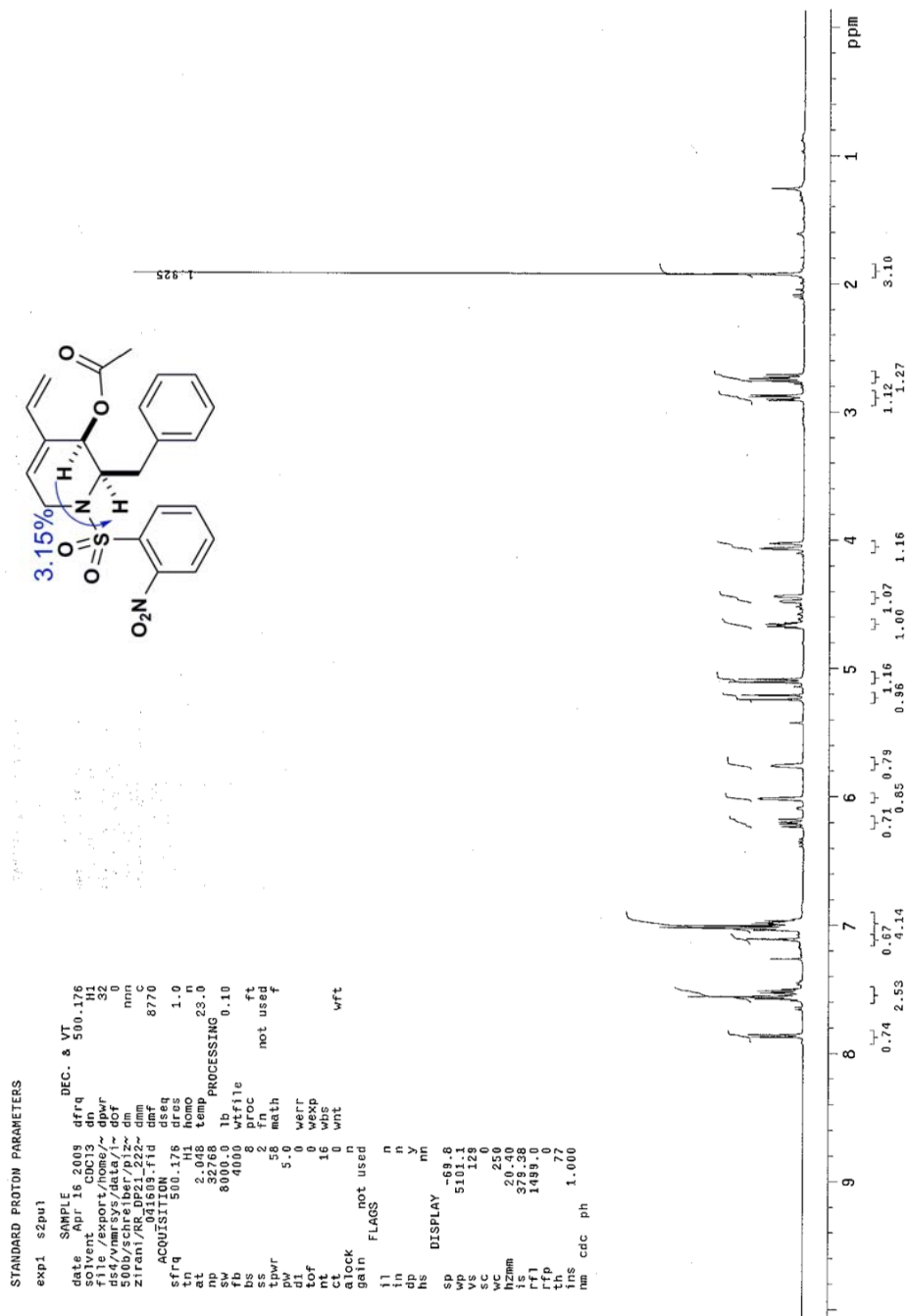


¹H NMR (500 MHz, CDCl₃) of compound **7a**



^{13}C NMR (126 MHz, CDCl_3) of compound **7a**

Spectral data for (2*R*,3*R*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-yl-acetate (**7b**)

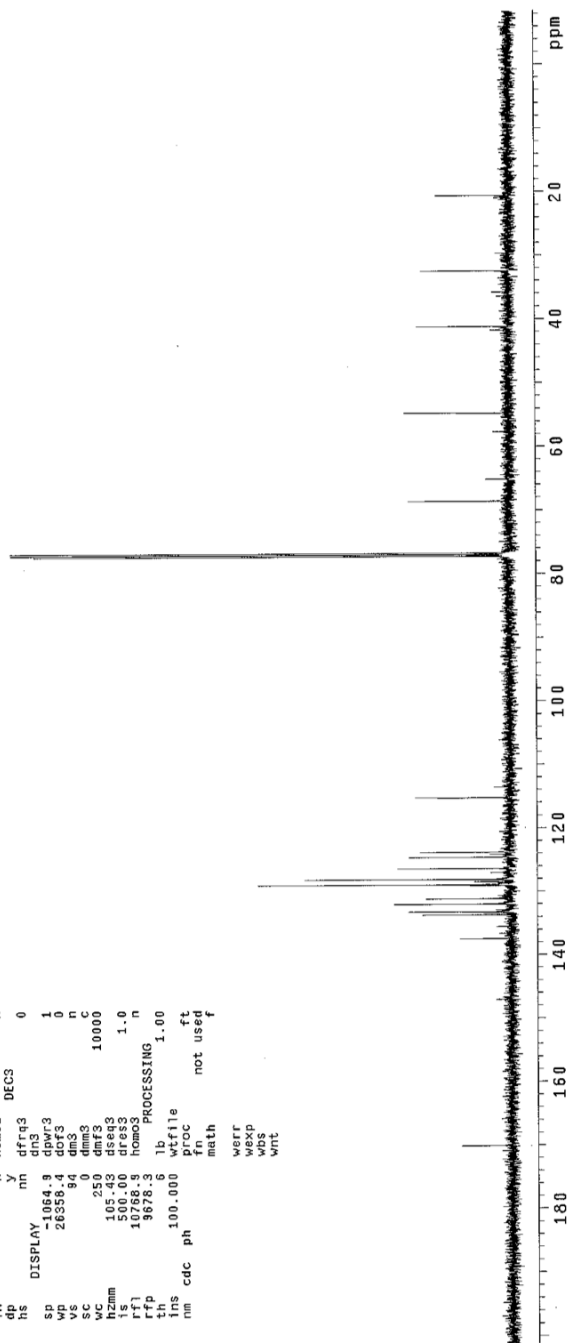
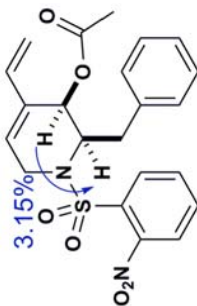


¹H NMR (500 MHz, CDCl₃) of compound **7b**

STANDARD CARBON PARAMETERS

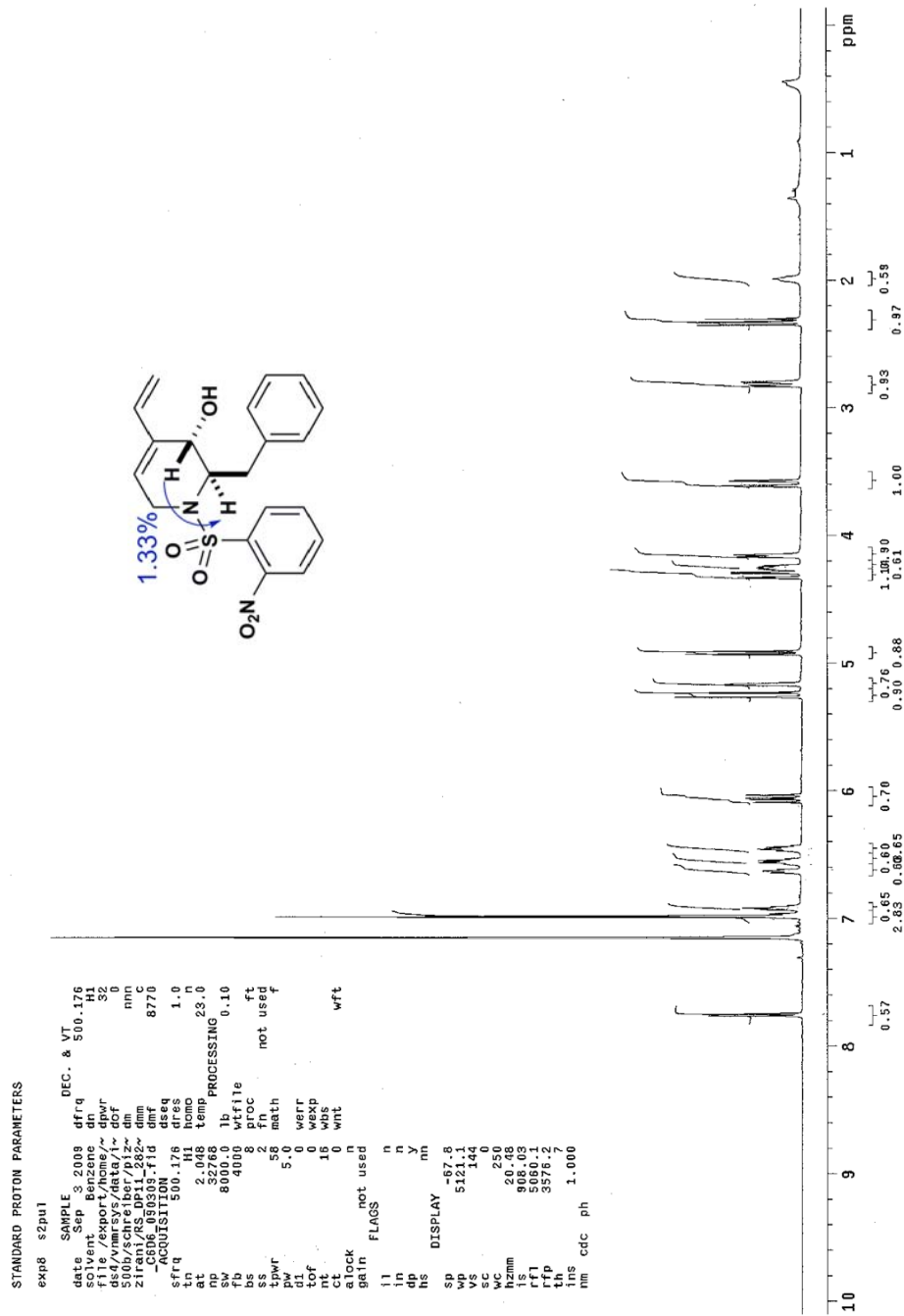
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fb not used homo 29996.3 dres 1.0
bs not used temp 32 temp 25.0
tpwr 4.2 dfrq2 0
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atlock 84 dn3 0
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^{13}C NMR (126 MHz, CDCl_3) of compound **7b**

Spectral data for (2*R*,3*S*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-ol (**8a**)



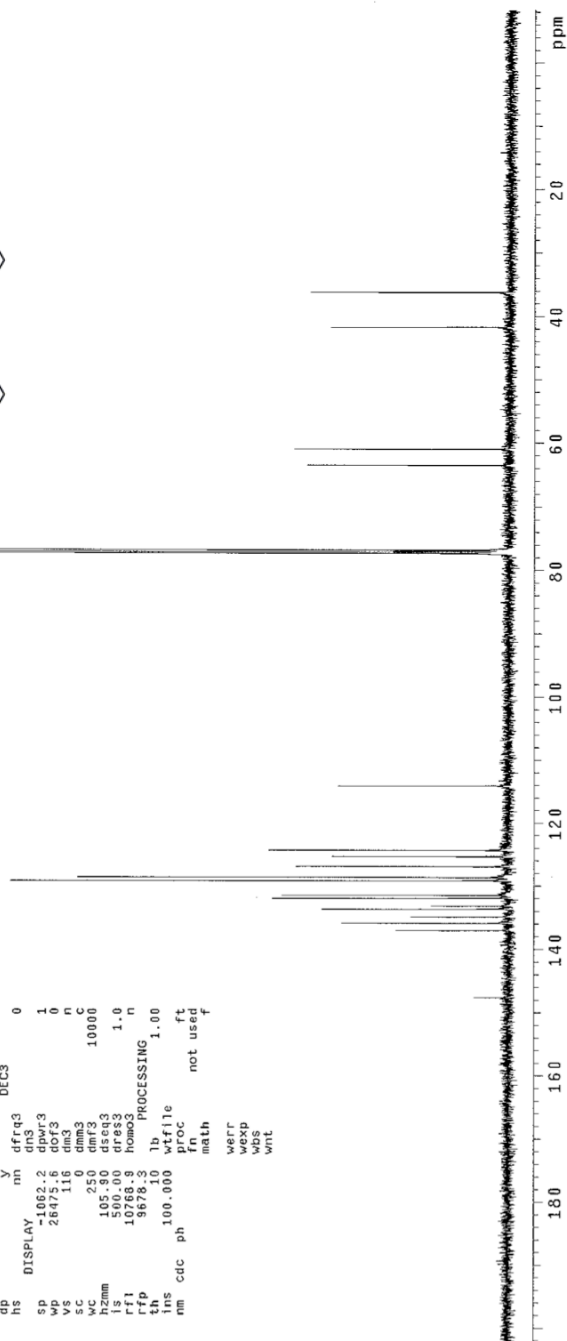
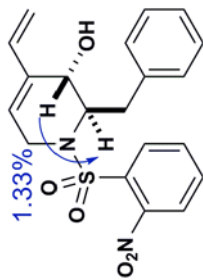
¹H NMR (500 MHz, Benzene) of compound **8a**

STANDARD CARBON PARAMETERS

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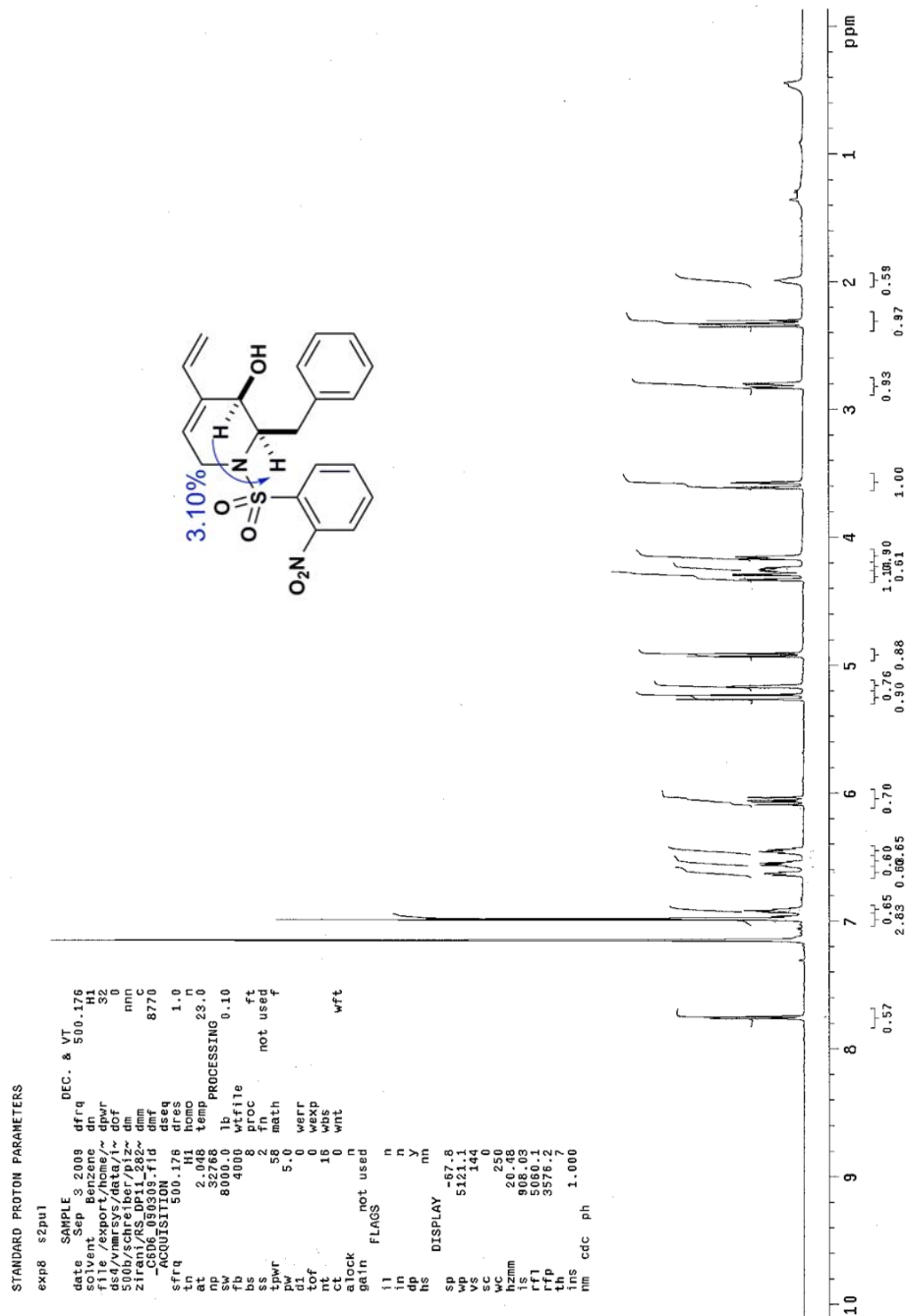
exp1 s2pu1
SAMPLE 1 2009 dfrc DEC. & VT
date Sep dnc 499.874
solvent CDC13 dn 48
fl ACQUISITION exp dpwr 48
at C13 dnm 123.707
tn C13 dnm 123.707
at 1.032 dmf 12306
pw 29886.3 dseq 1.0
fb not used homo 1.0
bs 32 temp 25.0
tpwr 55 dfrc2 DEC2
dl 3.0 dr2 0
tcf 2000.0 dpwr2 1
nt 2048 dcf2 0
clock 0 dm2 n
gain not used dmf2 10000
FLAGS n dseq2
f1 n dres2 1.0
f2 n homo2 n
f3 n homo3 DEC3
f4 n homo4 n
f5 n homo5 n
f6 n homo6 n
f7 n homo7 n
f8 n homo8 n
f9 n homo9 n
f10 n homo10 n
f11 n homo11 n
f12 n homo12 n
f13 n homo13 n
f14 n homo14 n
f15 n homo15 n
f16 n homo16 n
f17 n homo17 n
f18 n homo18 n
f19 n homo19 n
f20 n homo20 n
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f24 n homo24 n
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f26 n homo26 n
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f38 n homo38 n
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f73 n homo73 n
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f88 n homo88 n
f89 n homo89 n
f90 n homo90 n
f91 n homo91 n
f92 n homo92 n
f93 n homo93 n
f94 n homo94 n
f95 n homo95 n
f96 n homo96 n
f97 n homo97 n
f98 n homo98 n
f99 n homo99 n
f100 n homo100 n

```



¹³C NMR (126 MHz, CDCl₃) of compound **8a**

Spectral data for (2*R*,3*R*)-2-benzyl-1-(2-nitrophenylsulfonyl)-4-vinyl-1,2,3,6-tetrahydropyridin-3-ol (**8b**)



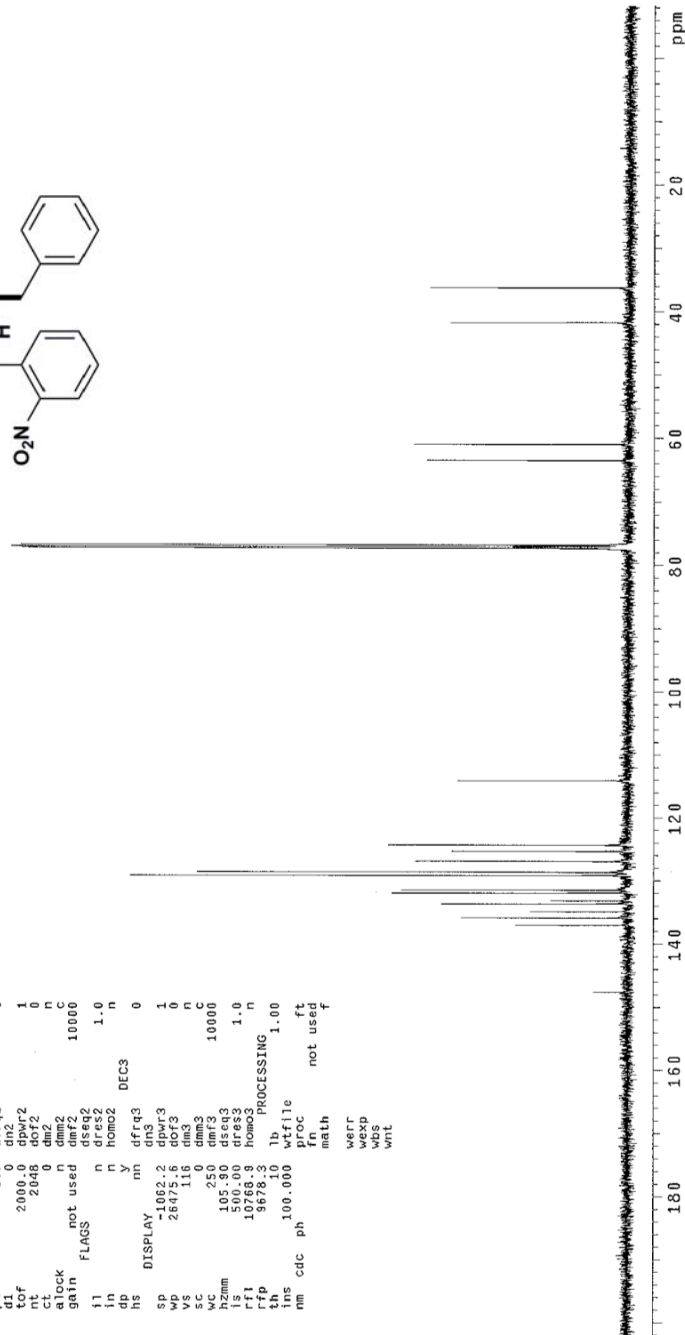
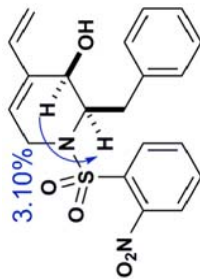
¹H NMR (500 MHz, Benzene) of compound **8b**

STANDARD CARBON PARAMETERS

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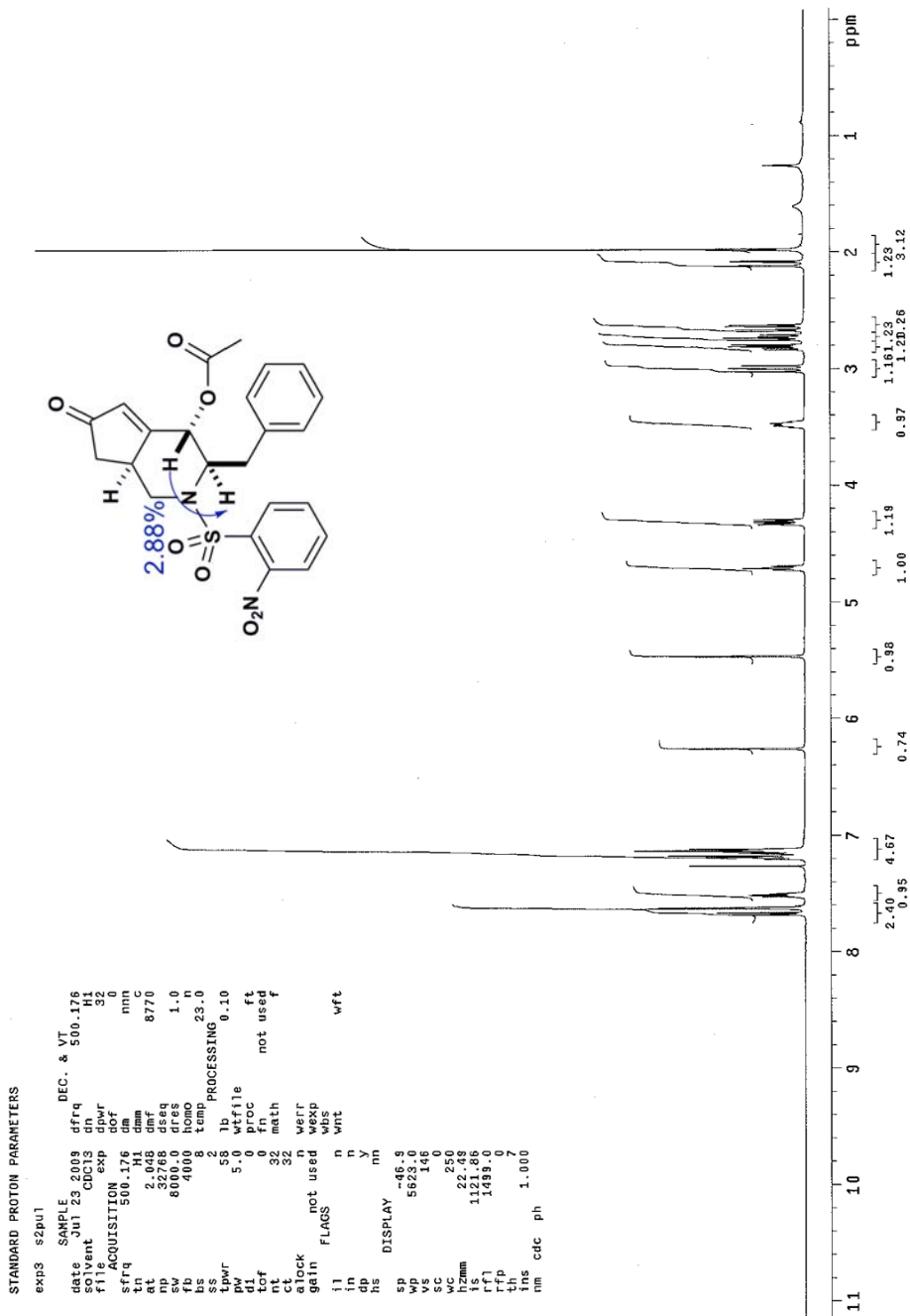
exp1 s2pu1
SAMPLE
date Sep 1 2008 DEC. & VT
solvent CDCl3 d1 499.874
file ACQUISITION exp d1vr 48
f1 125.767 dm vvy
at 1.042 dmf 12908
np 65536 dseq
sw 29386.3 dres 1.0
lg not used homo n
lp 35 temp 25.0
pwr 3.7 dfrq2 0
dl 0 dnt 0
df 2000.0 dprf2 1
nt 2048 dnt2 0
ct 0 dnt3 0
alock n dnm2 C
gain not used dnt2 10000
flags dseq dres2
l1 n homo2 1.0
in n y
dp n DEC3
hs DISPLAY nm dfrq3 0
sp -1062.2 dprf3 1
wp 28475.6 ddf3 0
vs 116 dms3 n
sc 0 dms3 C
hzmm 250 dms3 10000
ls 105.30 dseq3
l1 500.00 dres3 1.0
rf1 10769.3 homo3 n
tpp 3676.10 lb PROCESSING n
ins 100.000 wtfile 1.00
nm cdc ph proc ft
math not used f
weff
wexp
wbs
wnt

```



^{13}C NMR (126 MHz, CDCl_3) of compound **8b**

Spectral data for (3*R*,4*S*,7*aS*)-3-benzyl-2-(2-nitrophenylsulfonyl)-6-oxo-2,3,4,6,7,7*a*-hexahydro-1*H*-cyclopenta [c]pyridin-4-yl acetate (**9a**)



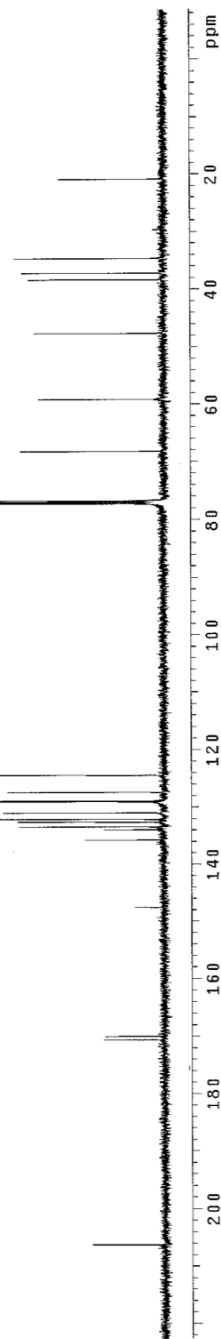
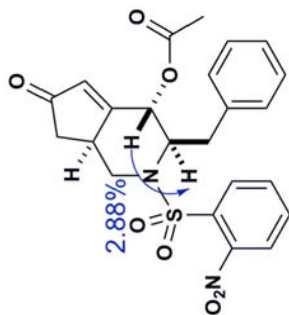
¹H NMR (500 MHz, CDCl₃) of compound **9a**

STANDARD CARBON PARAMETERS

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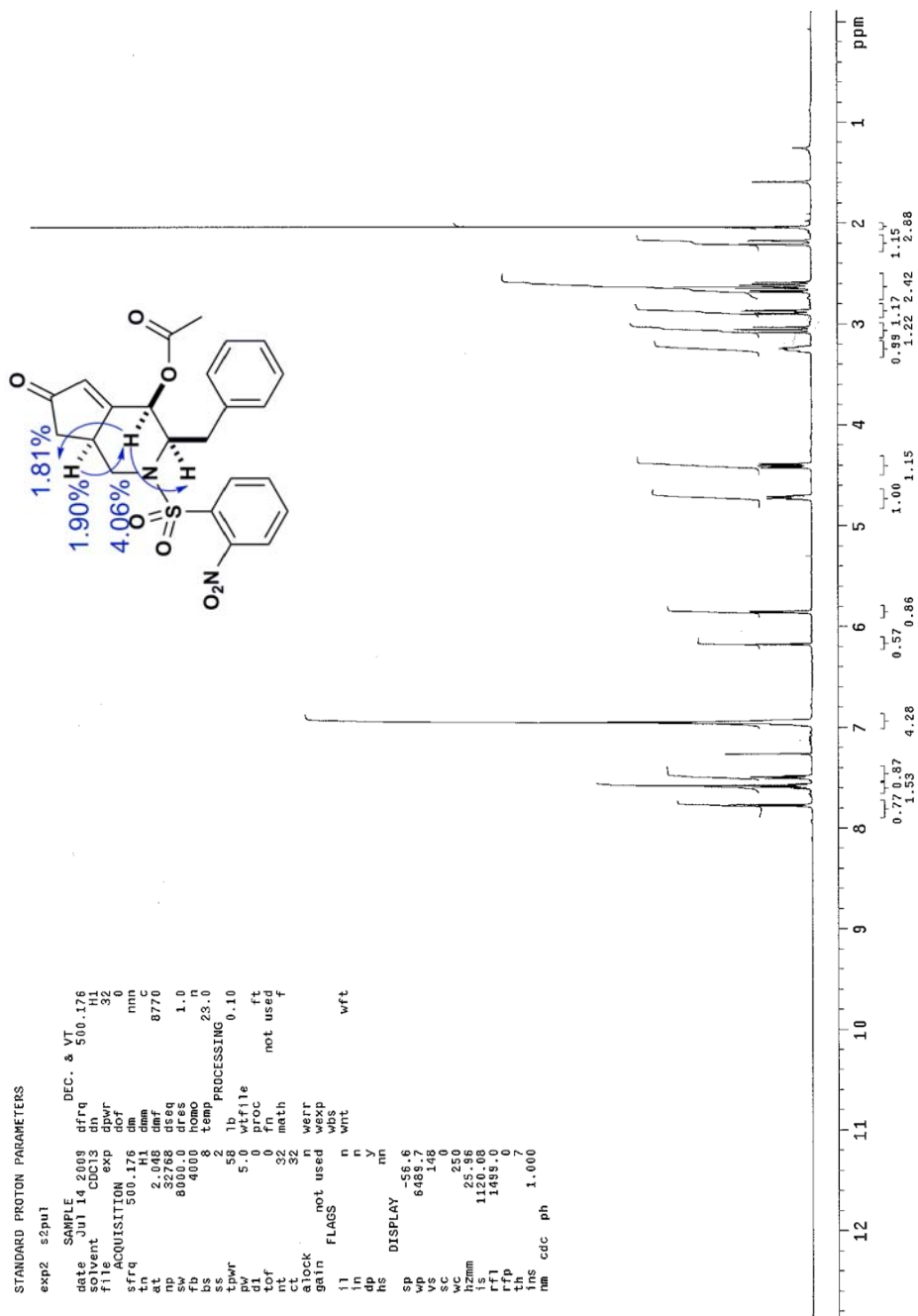
exp1 s2put
SAMPLE
date Jul 23 2009 DEC. & VT
file CDC13 d1 493.874
solvent exp H1
file dpwr 48
ACQUISITION exp dof 0
sfreq 125.713 dmh yy
in 123.713 dmh 12905
at 1.082 dmf
np 65536 ds0q 1.0
sw 29996.3 dres
bs not us32 temp 25.0
tpwr 55 DEC2
pw 3.7 dfrq2 0
td 0 dmwr2 1
nt 2000.0 dofr2 0
ct 2048 dof2 0
atlock n dnm2
gain not used ds02 10000
FLAGS n homo2 1.0
il n y dfrq3 0
dp n y dfrq3 0
hs DISPLAY dm3
SP -1088.7 dpvr3 1
wp 29080.8 dofs 0
vs 143 dm3 C
vc 250 dmf3 10000
hzmm 116.32 dseq3
ls 500.00 dres3 1.0
rf1 18978.0 homo3
rfp 3678.3 lb PROCESSING n
ins 100.000 wf1file 1.00
nm cdc ph proc not used
math
werr
wexp
wof
wnt

```

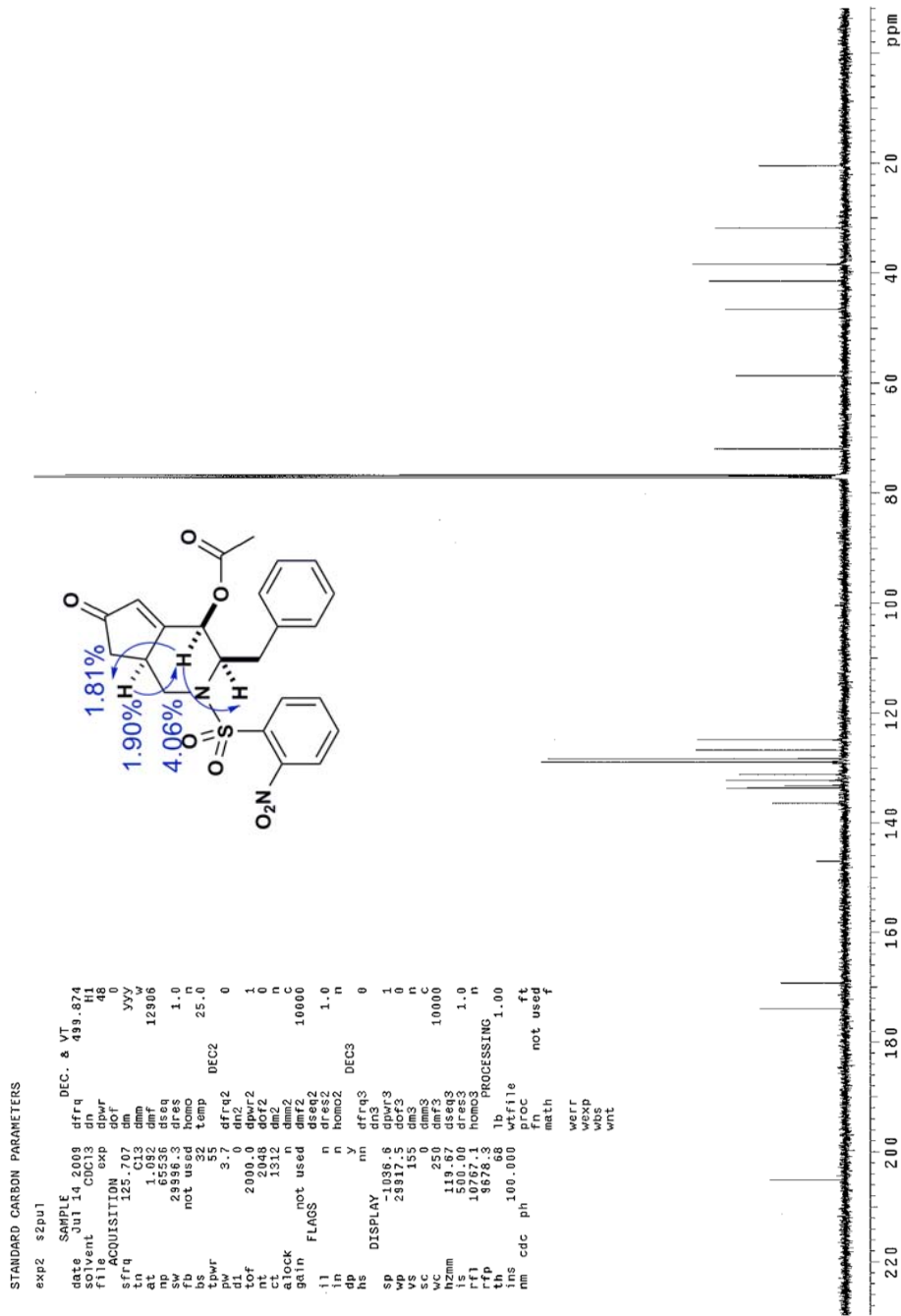


^{13}C NMR (126 MHz, CDCl_3) of compound **9a**

Spectral data for (3*R*,4*R*,7*aS*)-3-benzyl-2-(2-nitrophenylsulfonyl)-6-oxo-2,3,4,6,7,7*a*-hexahydro-1*H*-cyclopenta [c]pyridin-4-yl acetate (**9b**)

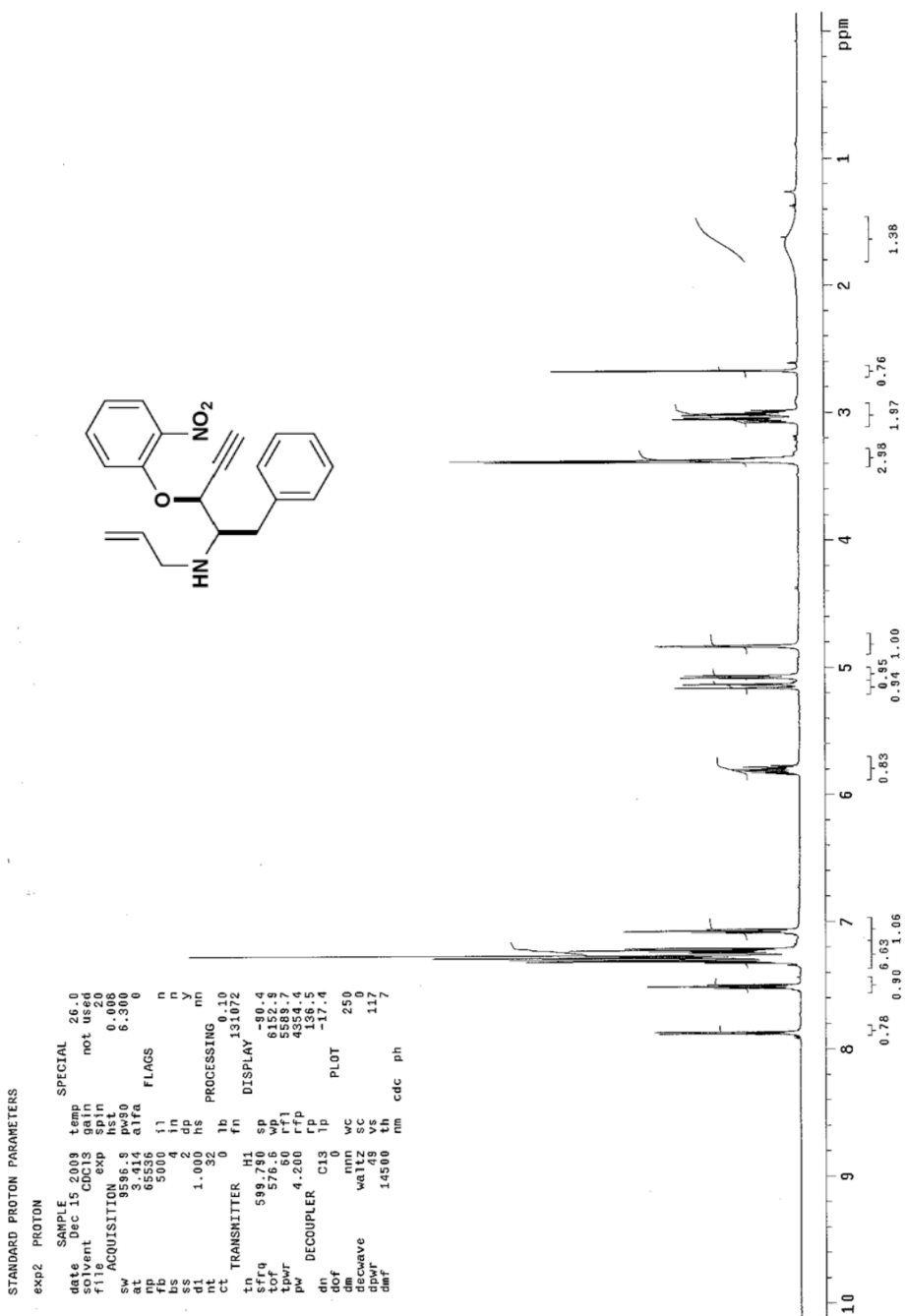


¹H NMR (500 MHz, CDCl₃) of compound **9b**



^{13}C NMR (126 MHz, CDCl_3) of compound **9b**

Spectral data for (2*R*,3*S*)-*N*-allyl-3-(2-nitrophenoxy)-1-phenylpent-4-yn-2-amine (10a)



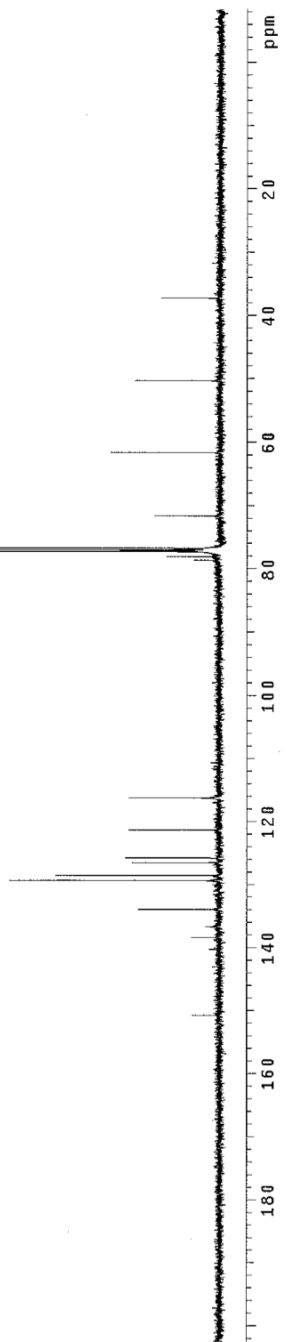
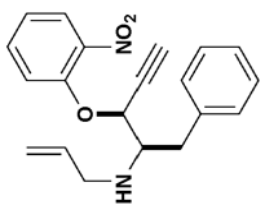
¹H NMR (600 MHz, CDCl₃) of compound 10a

STANDARD CARBON PARAMETERS

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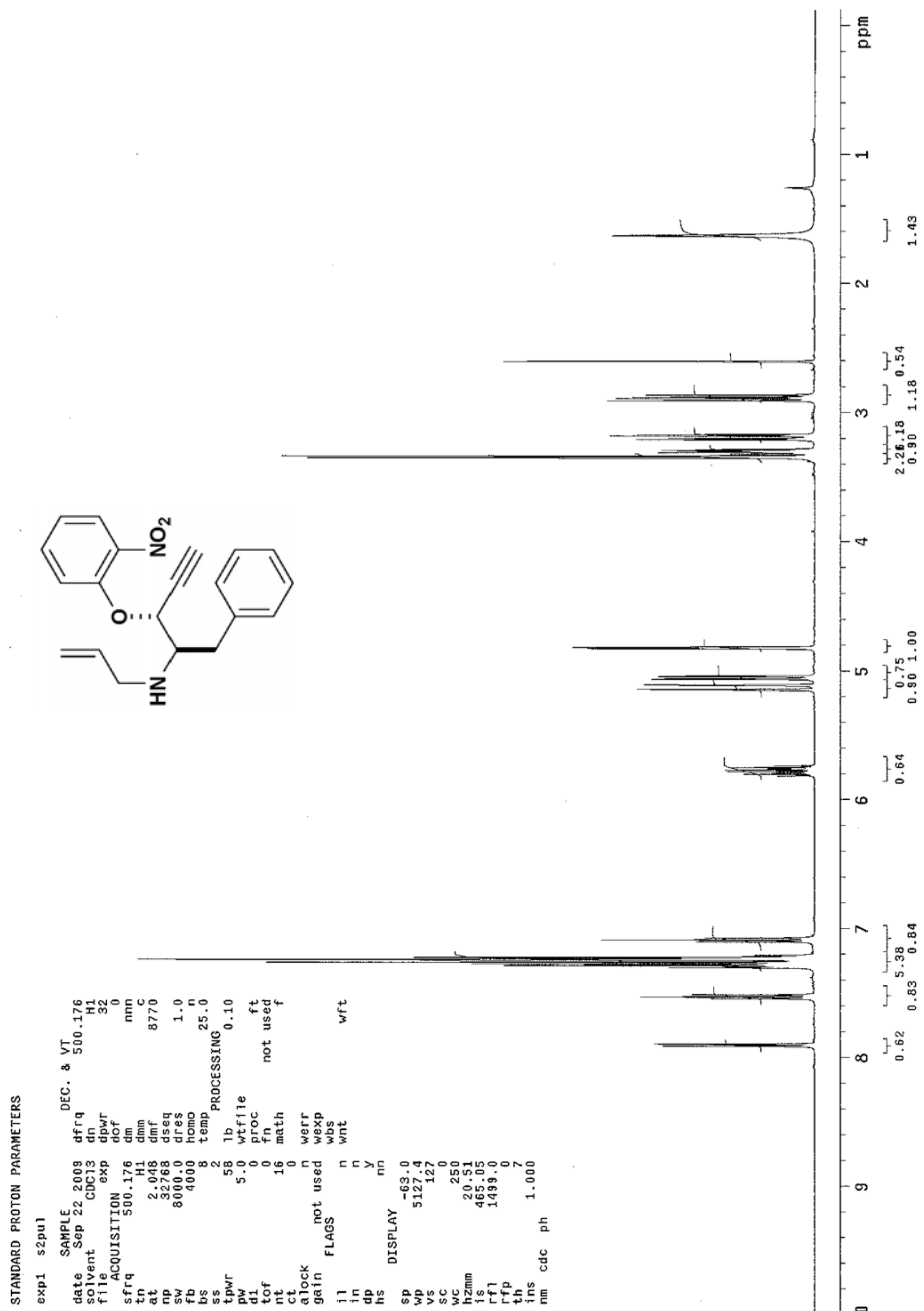
exp2 szpu1
SAMPLE DEC. & VT
date Dec 15 2009 dfrq 499.874
time 12.50.00 dm3 49
file 12.50.00 dpmr 49
ACQUISITION exp 0
sfrq 125.707 dm yxy
at 1.082 dmp 12000
np 55336 dseq
sw 23896.3 dres 1.0
fb not used homo
ts 55 temp 25.0
tavr 4.2 dfrq2 0
d1 2000.0 dn2 1
tof 1580.0 dpmr2 1
ct 5824 dm2 n
atlock not used dmm2 C
gain 10000 dmf2
ll in homo2 1.0
in in homo2 1.0
dp y dfrq3 0
hs DISPLAY dn3 0
sp 1059.4 dof3 1
wp 26510.4 dof3 0
vs 177 dm3 n
sc 0 dmm3 C
sz 0 dm3 10000
h2mm 105.04 dres
is 500.00 dres 1.0
rf1 10766.2 homo3 n
rfp 9676.3 lb PROCESSING
ins 100.000 wf1file ft
nm cdc ph proc fn not used f
math werr
wexp wbs
wnt

```



¹³C NMR (126 MHz, CDCl₃) of compound 10a

Spectral data for (2*R*,3*R*)-*N*-allyl-3-(2-nitrophenoxy)-1-phenylpent-4-yn-2-amine (10b)



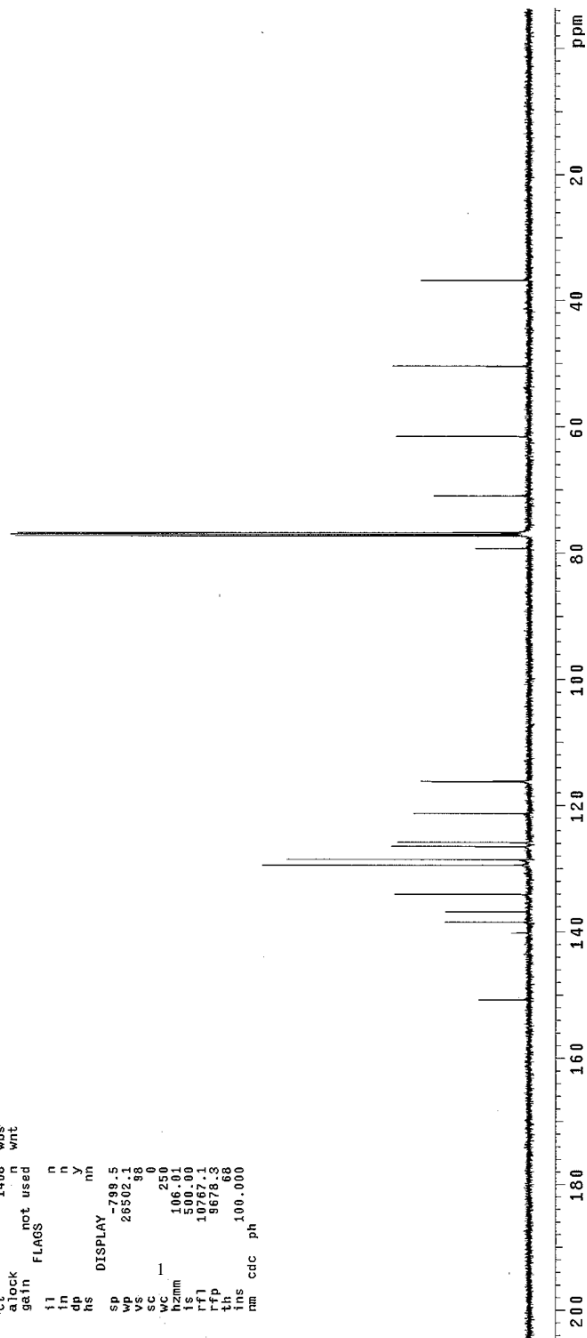
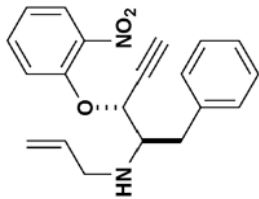
¹H NMR (500 MHz, CDCl₃) of compound 10b

STANDARD CARBON PARAMETERS

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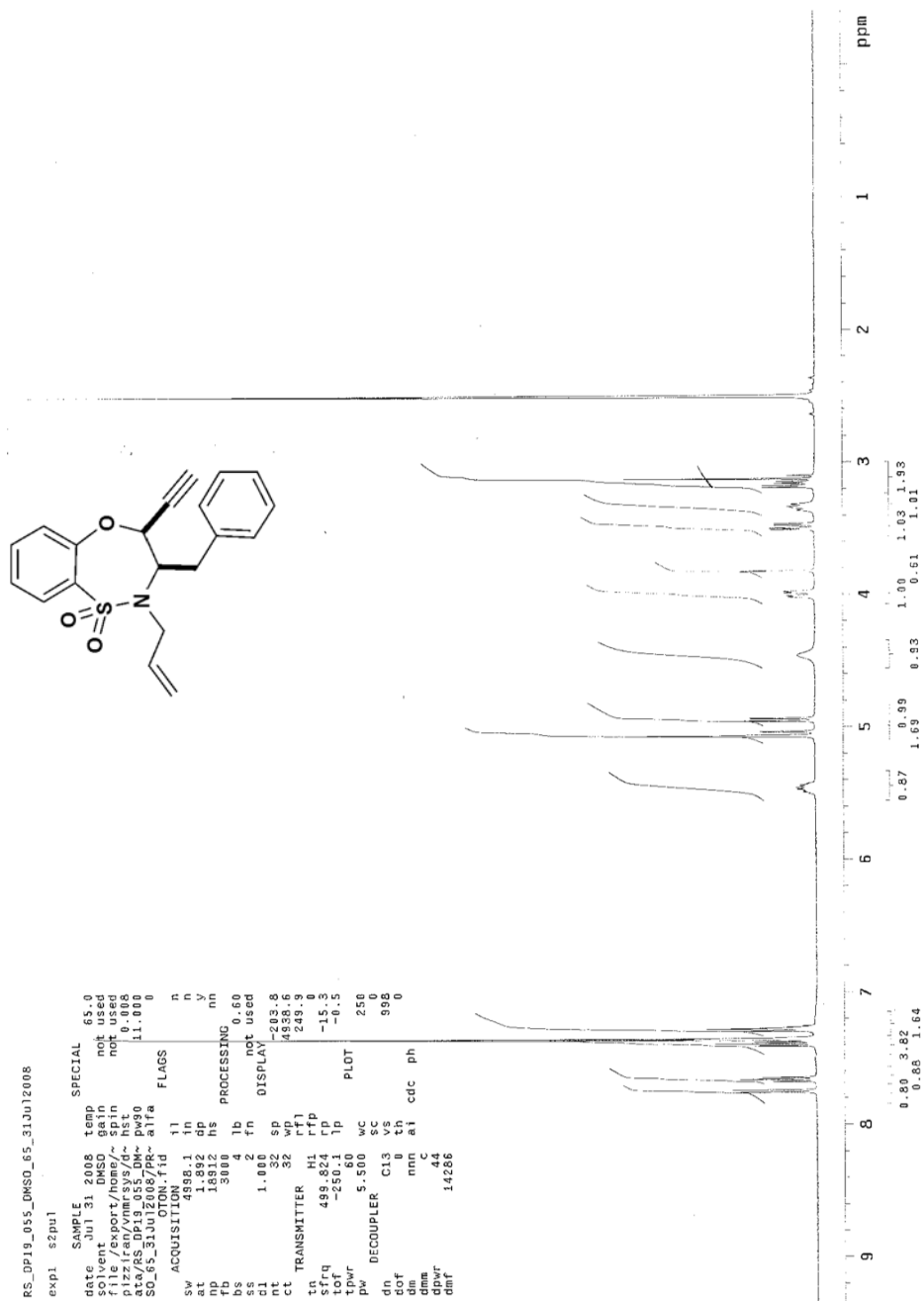
exp8 s2pu1
SAMPLE
date Sep 22 2009 DEC. & VT
dfrq 489.874
dpc 48
file /export/home/~dpcw/
ds4/vnmrSYS/data/1~ dof 0
500c/schreiber/plz~ dm VVY
zitrarr/NO2_108_11~ dmp 12906
C082208.fid dseq
ACQUISITION
sfrq 125.707 dres 1.0 n
tn 1 C13 homo
np 65536 temp 25.0 n
sw 29996.3 lb PROCESSING 1.00
fb not used wtfile
ts 52 proc not used ft
dpc 3.7 math
d1 0
tof 2000.0 werr
ct 2008 wexp
atock 1408 wnt
gain not used
flags n
in n
dp y
hs nh
SP DISPLAY 788.5
wp 26502.1
vs 98
sc 0
vc 250
wmm 106.30
fs 500.00
rf1 10767.1
rfp 9678.3
h1 0
ins 100.000
nm cdc ph

```

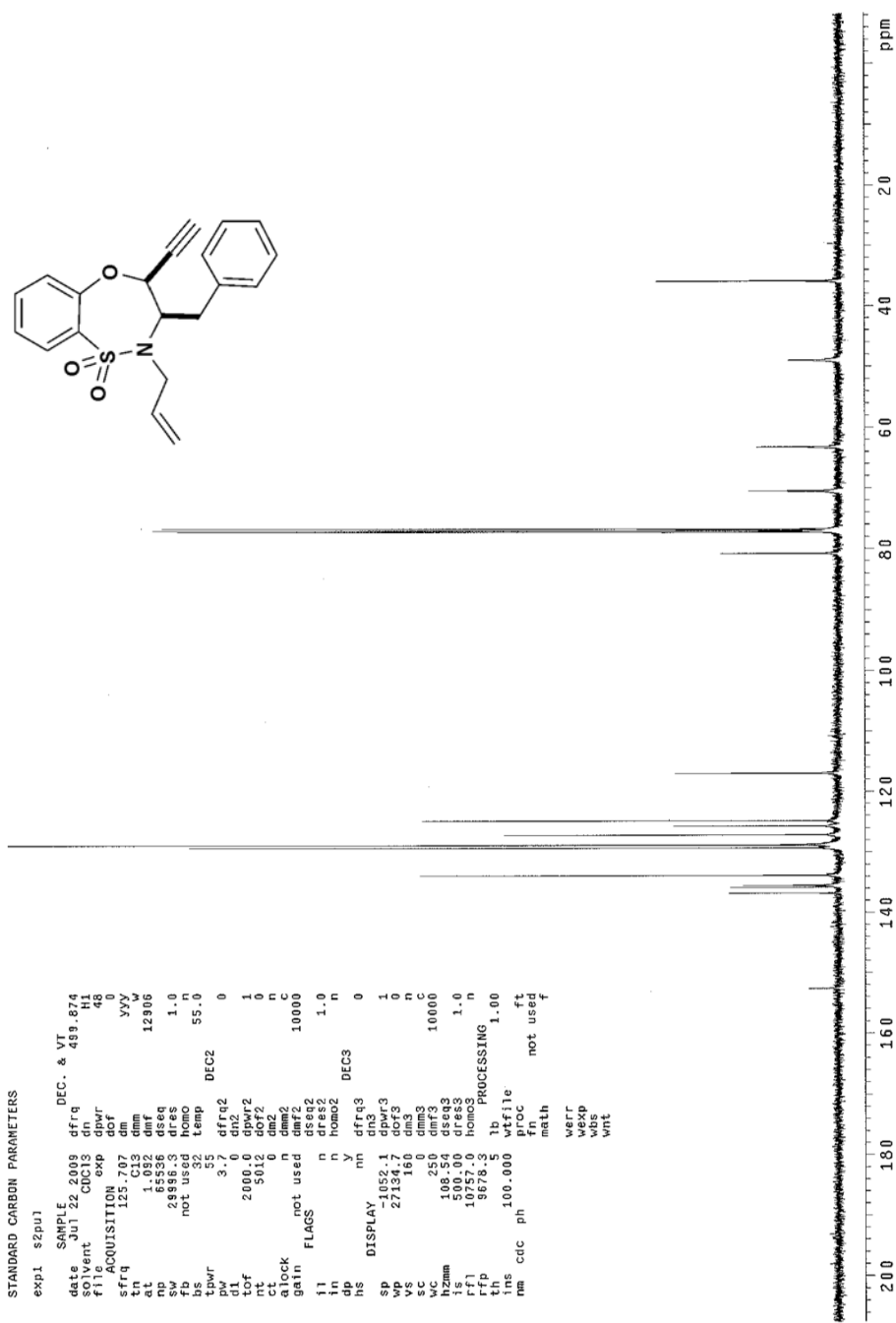


¹³C NMR (126 MHz, CDCl₃) of compound 10b

Spectral data for (3*R*,4*S*)-3-benzyl-4-ethynyl-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine 1,1-dioxide (11a)

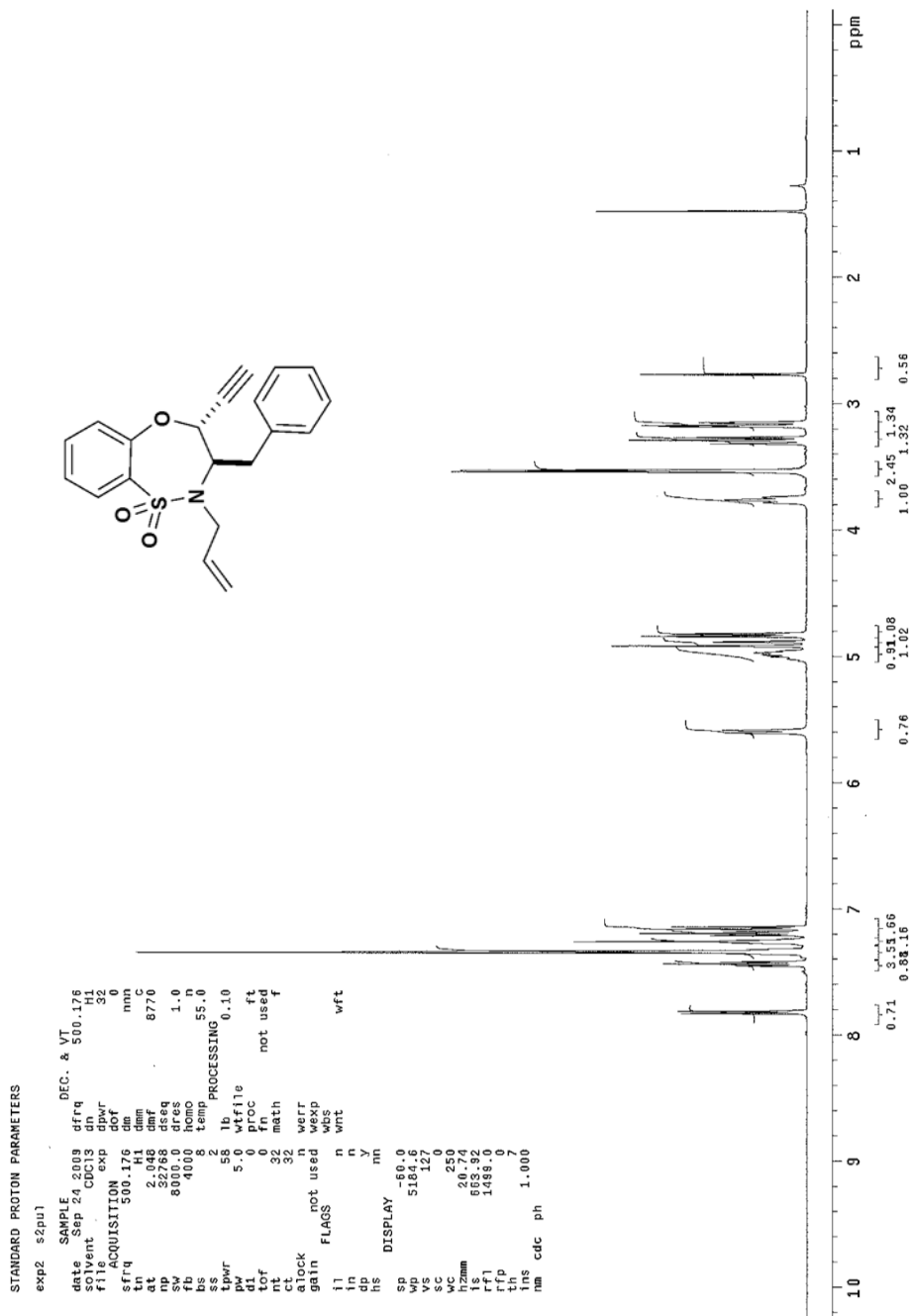
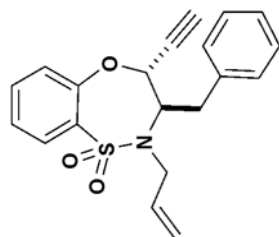


¹H NMR (500 MHz, DMSO, T = 65 °C) of compound 11a



^{13}C NMR (126 MHz, CDCl_3 , $T = 55\text{ }^\circ\text{C}$) of compound **11a**

Spectral data for (3*R*,4*R*)-3-benzyl-4-ethynyl-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine 1,1-dioxide (**11b**)

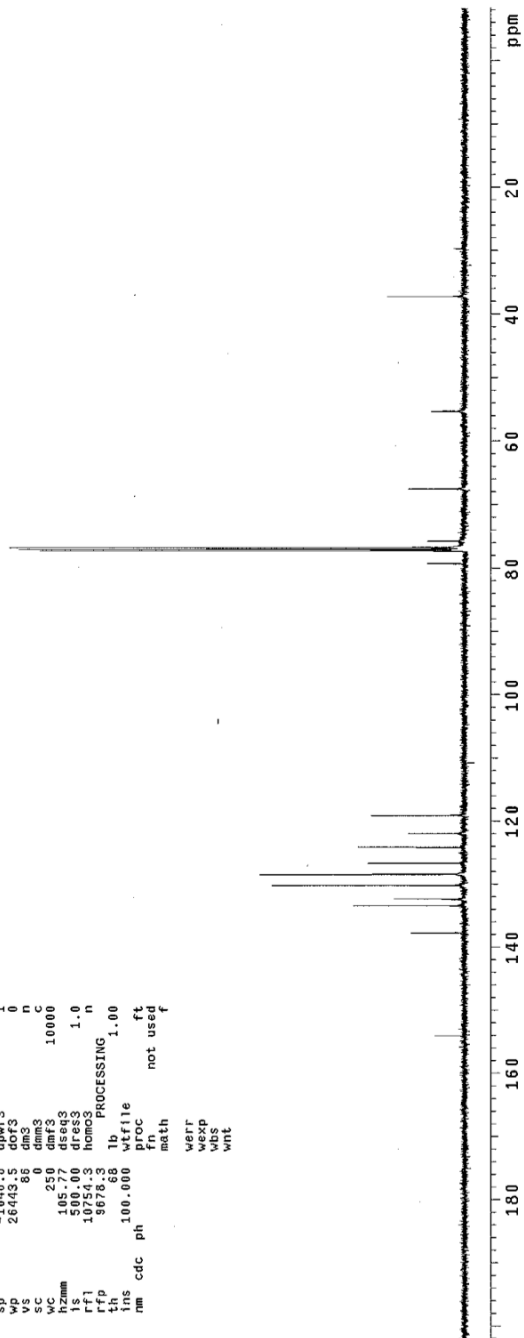
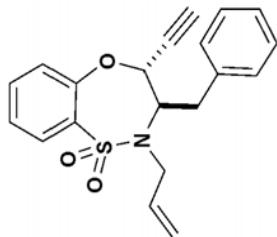


^1H NMR (500 MHz, CDCl_3 , $T = 55\text{ }^\circ\text{C}$) of compound **11b**

STANDARD CARBON PARAMETERS

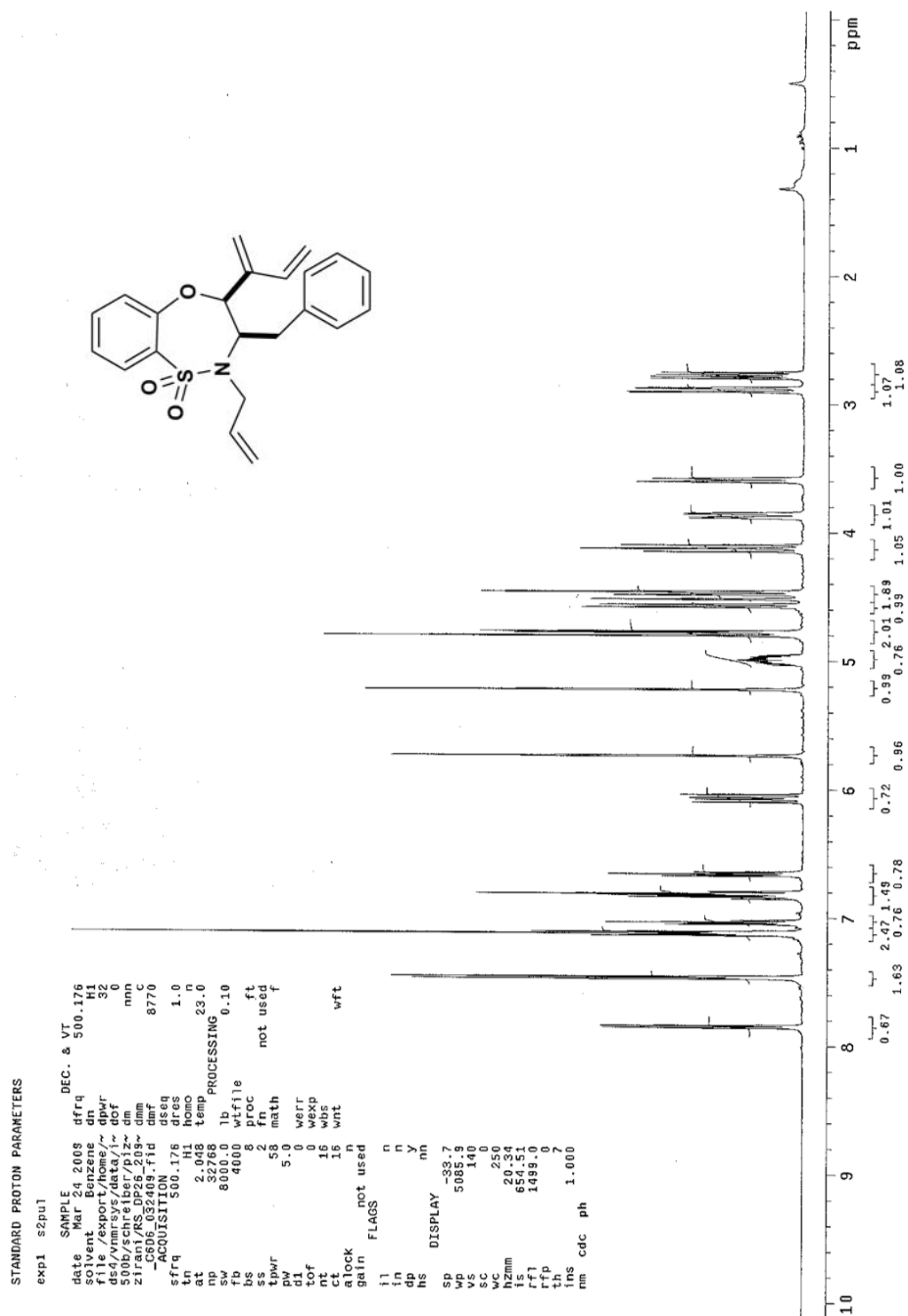
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exp1 s2pu1
date 22.2008 dfrq DEC. & VT
solvent Sep CDCl3 dn H1
f1 ACQUISITION 2-sp dnr 40
sfrq 125.707 dm YYY
tn 1.0 C13 dnm 12806
at 55.56 dfrq
sv 29996.3 dres 1.0
fb not used homo n
bs 32 temp 55.0
pwr 3.7 dfrq2 DEC2
d1 3.7 dn2
tof 2000.0 dpwr2 1
rt 5012 dor2 0
st 211n dnm C
stoc not used dm2 10000
gain
flags n n
l1 n homo2 DEC3 1.0
l2 Y
l3 mn dfrq3 0
hs
sp DISPLAY dn3 0
vs 1846.5 dpwr3 1
vs 26443.5 dnr3 0
vs 86 dms n
sc 0 dnm3 C
wc 105250 dmF3 10000
ls 500.00 dres3
rfi 10754.3 homo3 1.0
rff 9678.3
tr 68
trc 100.000 proc ft
mm cdc ph fn not used
math werr
wexp wbs
wnt
  
```



¹³C NMR (126 MHz, CDCl₃, T = 55 °C) of compound **11b**

Spectral data for (3*R*,4*S*)-3-benzyl-4-(1-methyleneprop-2-en-1-yl)-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine (12a)

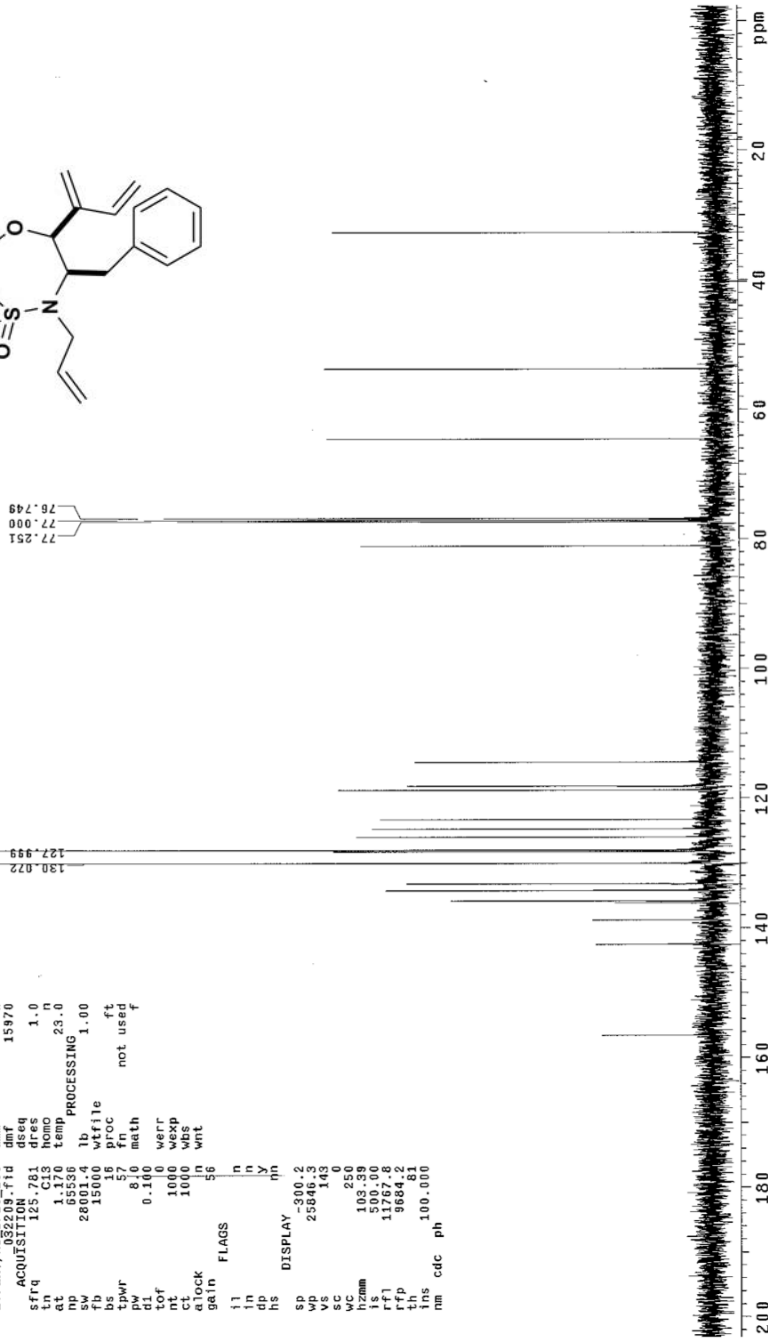
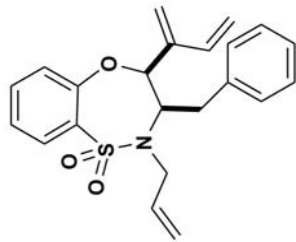


¹H NMR (500 MHz, Benzene) of compound 12a

STANDARD CARBON PARAMETERS

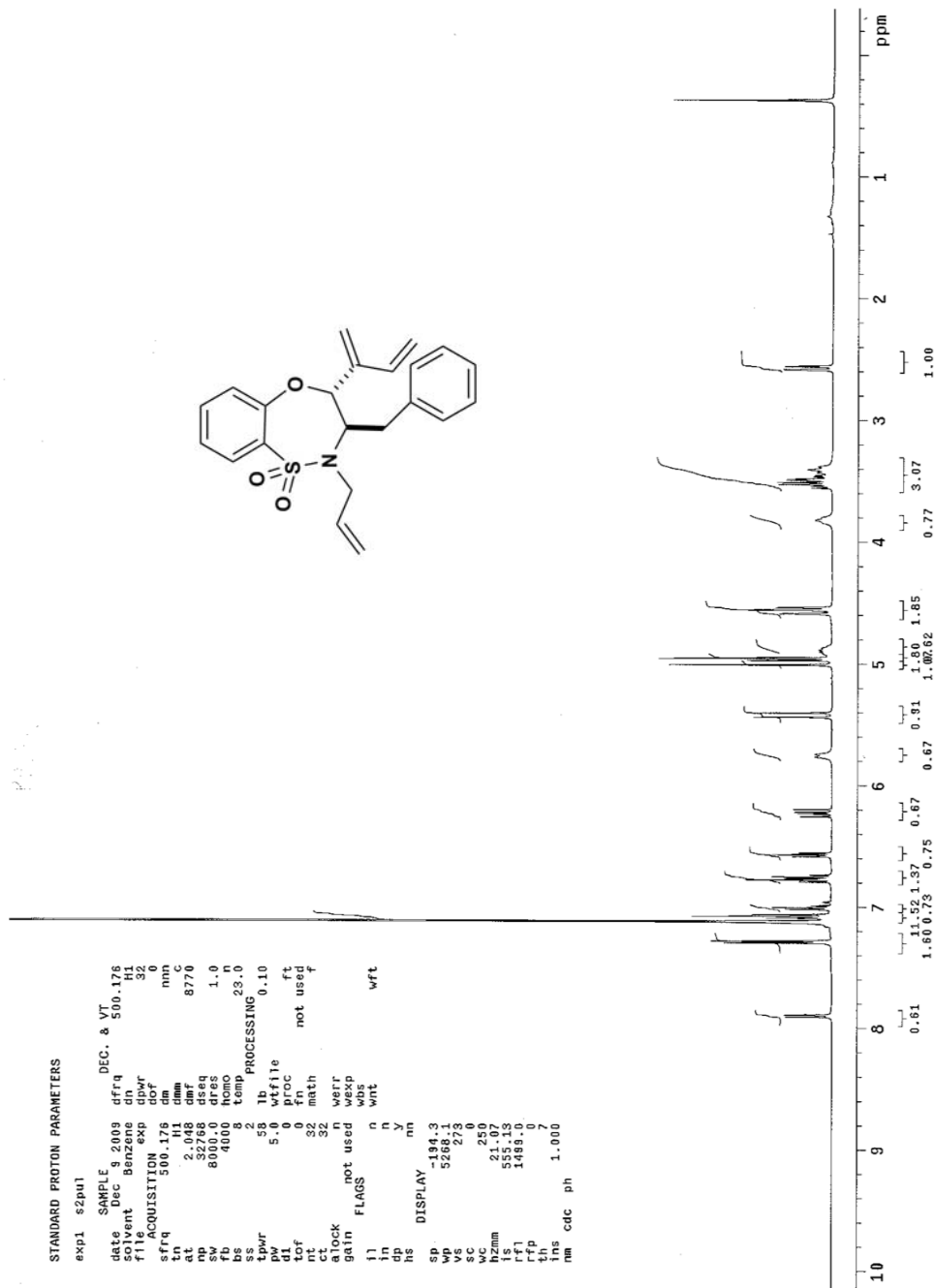
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exp4 s2pu1
SAMPLE
date Mar 22 2009 dfrq DEC. & VT
solvent CDC13 dn 500.175
file /export/home/~ dpwr 38
dsc/vmrxy/data/~ dor 0
ziran/rs dp26 208- dim 15670
032209 fid dmf
ACQUISITION
sfrq 125.251 dseq 1.0
at 1.170 pres 23.0
np 65536 lb 1.00
sw 28001.4 lb 1.00
bs 15008 wpc file
ps 57 pcc not used
tpwr 8.10 math
di 0.100 wscr
nt 1000 wexp
ct 1000 wbs
gain 56 wnt
FLAGS
f1 in
f2 in
f3 in
f4 in
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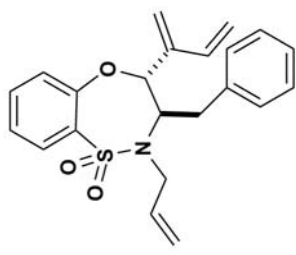


¹³C NMR (126 MHz, CDCl₃) of compound 12a

Spectral data for (3*R*,4*R*)-3-benzyl-4-(1-methylideneprop-2-en-1-yl)-2-prop-2-en-1-yl-3,4-dihydro-2*H*-5,1,2-benzoxathiazepine (**12b**)



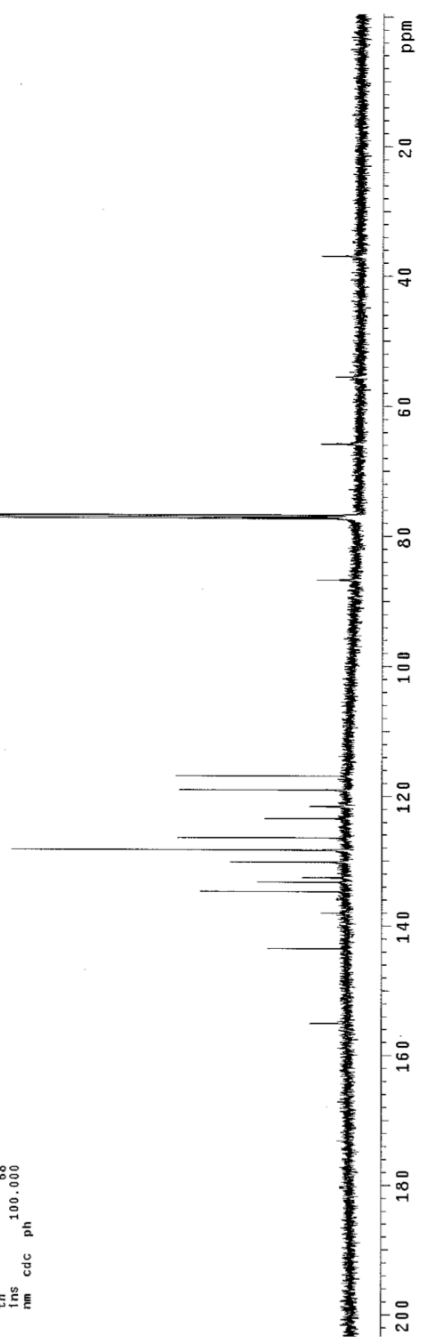
¹H NMR (500 MHz, Benzene) of compound **12b**



STANDARD CARBON PARAMETERS

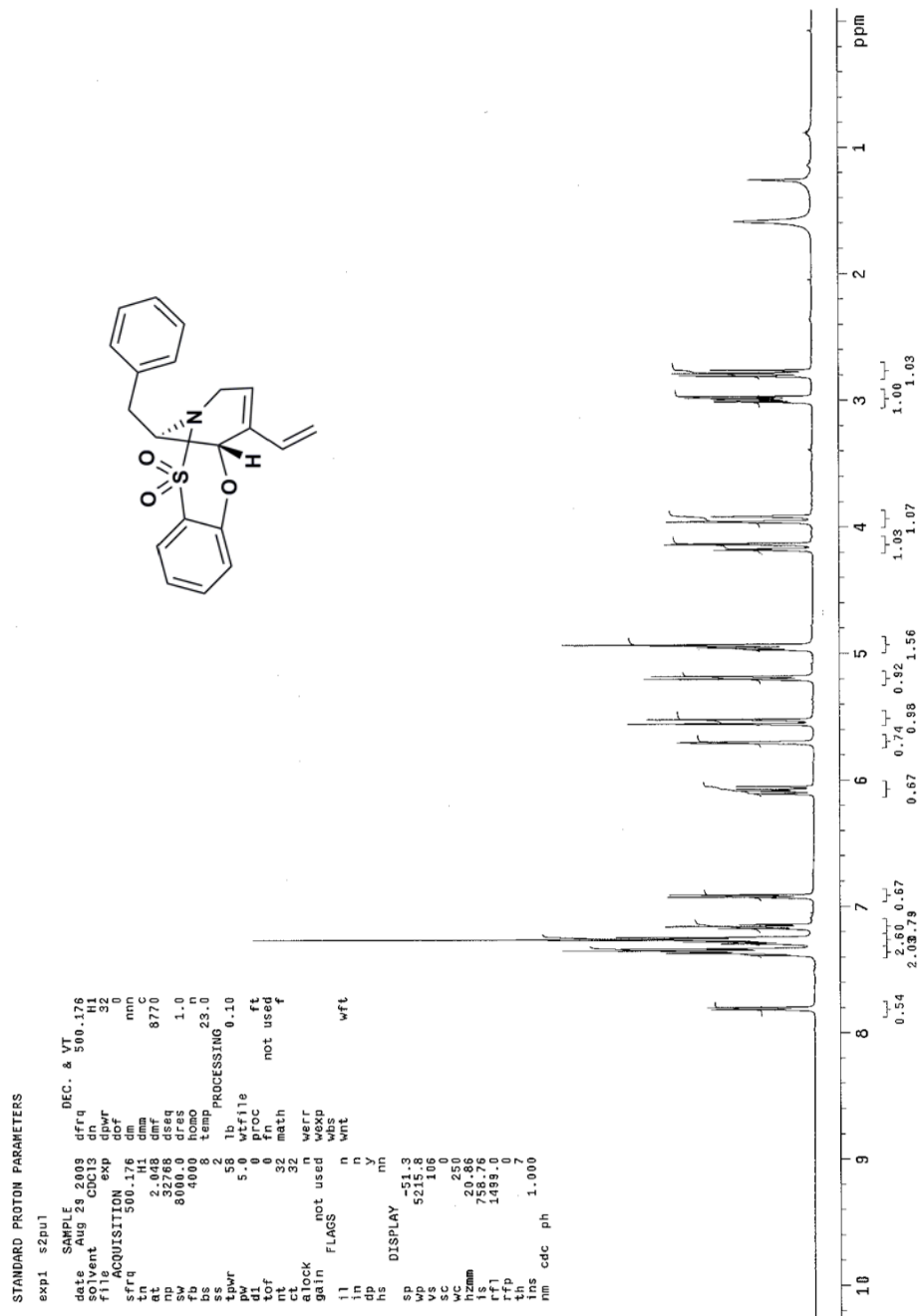
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date Dec 2009 dfrq DEC. & VT 500.176
solvent CDCl3 dm dec 38
fl ACQUISITION exp dcf 0
sfrq 125.781 dm xvy 15970
tn 1.013 dnm
np 65596 dresq
sw 28001.4 dres 1.0
fb 15000 homo
ts 57 temp PROCESSING 23.0
pw 8.70 lb wtfile 1.00
d1 0.100 wfile ft
tcf 100000 proc
ct 28304 fn not used
atlock math
gain 56 werr
il n wexp
in n
dp y wht
hs DISPLAY mn
SP -65.8
WP 25697.8
VS 188
SC 0
WC 250
IS 500.00
rfl 11766.1
rfp 9684.2
rfs 100.00
nm cdc ph
  
```



¹³C NMR (126 MHz, CDCl₃) of compound **12b**

Spectral data for (10*R*,14*S*)-14-benzyl-11-ethenyl-9-oxa-2-thia-1-azatricyclo[8.3.1.0^{3,8}]tetradeca-3,5,7,11-tetraene 2,2-dioxide (13a)



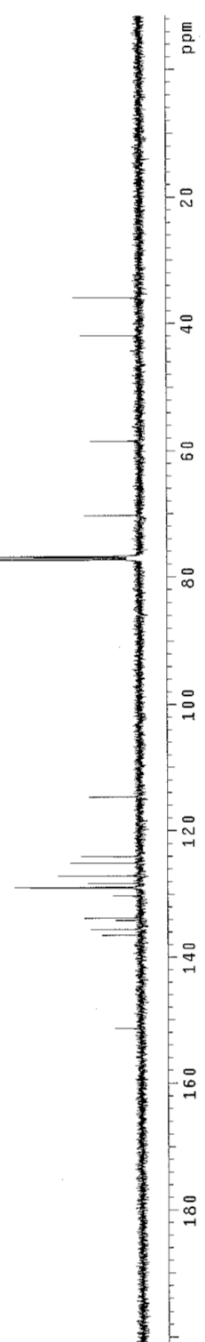
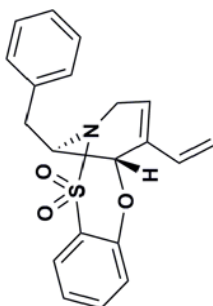
¹H NMR (500 MHz, CDCl₃) of compound **13a**

STANDARD CARBON PARAMETERS

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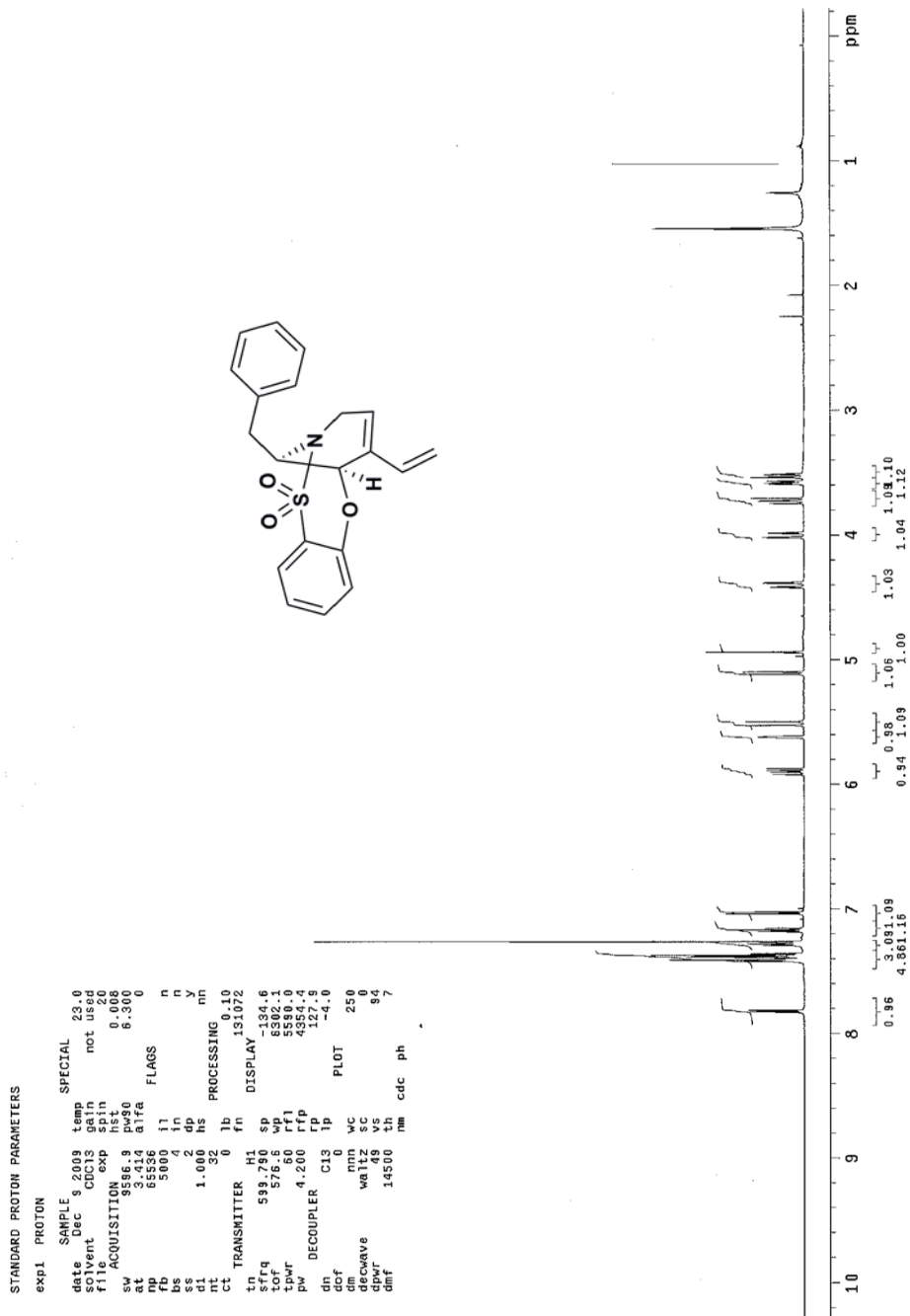
exp2 s2pu1
SAMPLE DEC. & VT
date Aug 28 2008 dfrq 439.874
solvent CDCl3 dn H1
file exp 48
ACQUISITION exp dpr 0
sfrq 125.707 dpr 0
trq 125.707 dm 399
at 1.082 dmf 12306
np 65836 dseq 1.0
sw 29996.3 dres 1.0
bs not used temp 25.0
tpwr 55 DEC2
pw 3.7 dfrq2 0
td 2000.0 dnr2 1
ct 2648 doff2 0
nl 0 dm2 n
gain not used dm2 10000
alock
il not used dres2 1.0
in n homo2 n
hs y dfrq3 0
DISPLAY dn3 0
SP -1086.9 dpwr3 1
WP 26426.1 doff3 0
VS 165 dm3 n
WC 250 dm3 10000
hzmm 185.70 dseq3 1.0
is 500.00 dres3 1.0
rf 18678.3 homo3
rfp 3878.5 lb PROCESSING n
tpr 100.000 wfile 1.00
nm cdc ph proc not used
math
werr
wexp
wps
wnt

```



¹³C NMR (126 MHz, CDCl₃) of compound 13a

Spectral data for (10*R*,14*R*)-14-benzyl-11-ethenyl-9-oxa-2-thia-1-azatricyclo[8.3.1.0^{3,8}]tetradeca-3,5,7,11-tetraene 2,2-dioxide (13b)



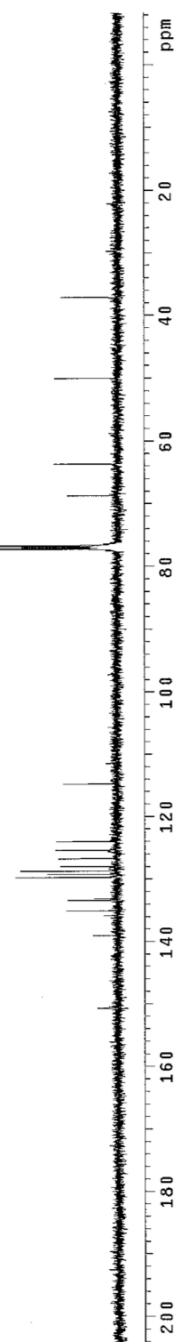
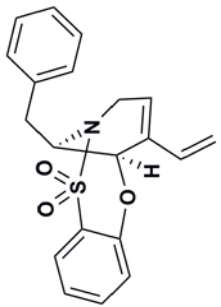
¹H NMR (600 MHz, CDCl₃) of compound **13b**

STANDARD CARBON PARAMETERS

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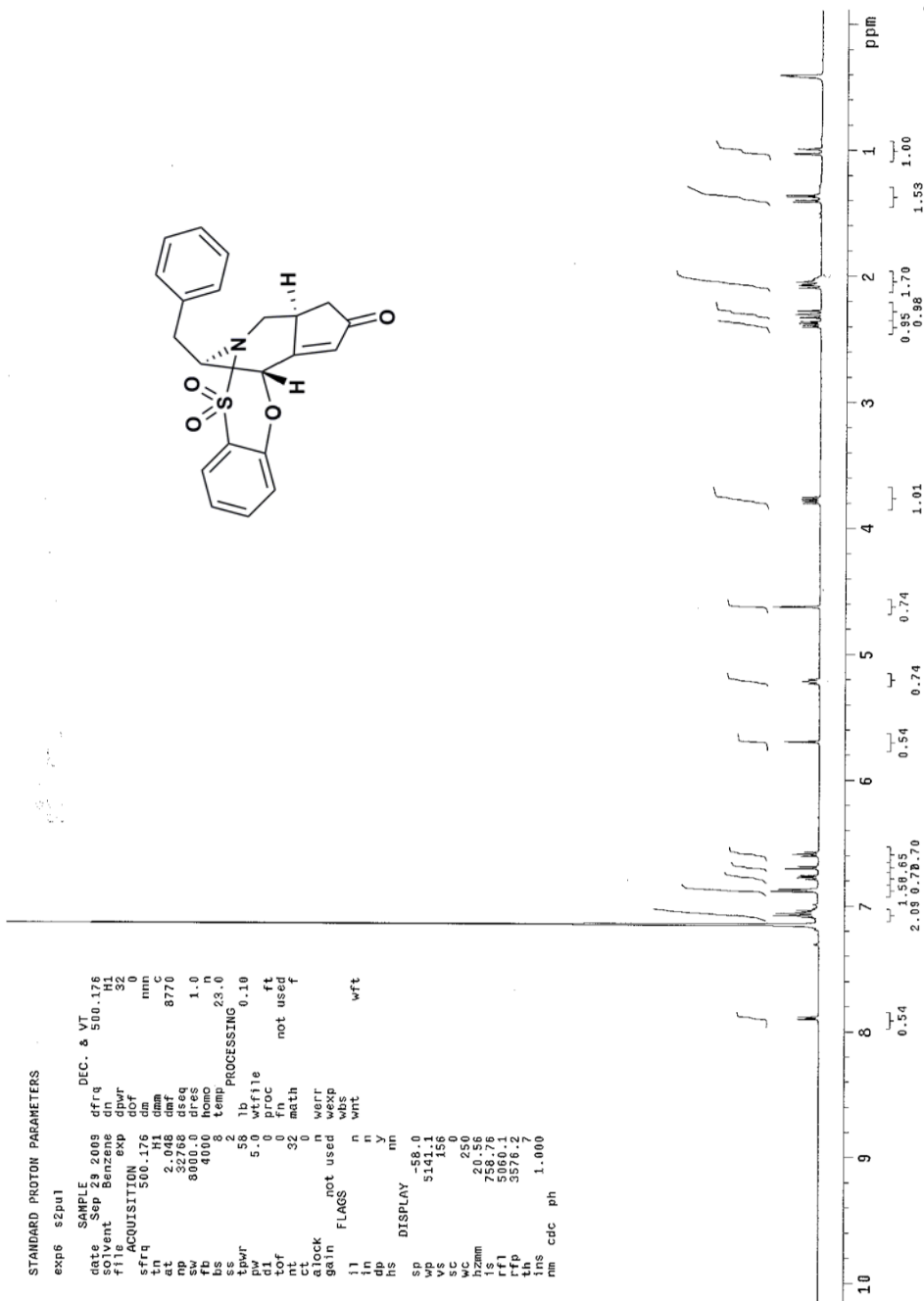
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date SAMPLE 2009 DEC. & WT
dec 9 CDC13 489.874
solvent CDC13 dn H1
file CDC13 exp 49
ACQUISITION exp dof 0
frq 125.707 dm yy
at 1.082 dmf 12000
np 65536 dseq 1.0
sw 29336.3 dres 1.0
to 0.000 dtemp 25.0
bs not used tump DEC2
tpwr 55
pv 4.2 dfrq2 0
dl 0 dn2 0
df 2000.0 dfr 1
nt 10000 dof2 0
ct 5728 dm2 n
alock n dm2 10000 C
gain not used dfr2
flags n dres2 1.0
ll n homo2 n
in n homo2 DEC3
dp n y dfrq3 0
hs DISPLAY nm dfr3 0
sp -1058.5 dpwr3 1
wp 26731.9 dofs 0
ve 230 dms n
vc 0 dms 10000
wc 250 dms3
hzmm 106.83 dseq3
is 500.00 dres3 1.0
rfi 10766.2 homo3
rfp 3676.1 lb PROCESSING n
tfr 11 lb 1.00
ins 100.000 wfile
nm cdc ph proc ft
in math not used
werr
wexp
wps
wnt

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¹³C NMR (126 MHz, CDCl₃) of compound 13b

Spectral data for compound (14a)



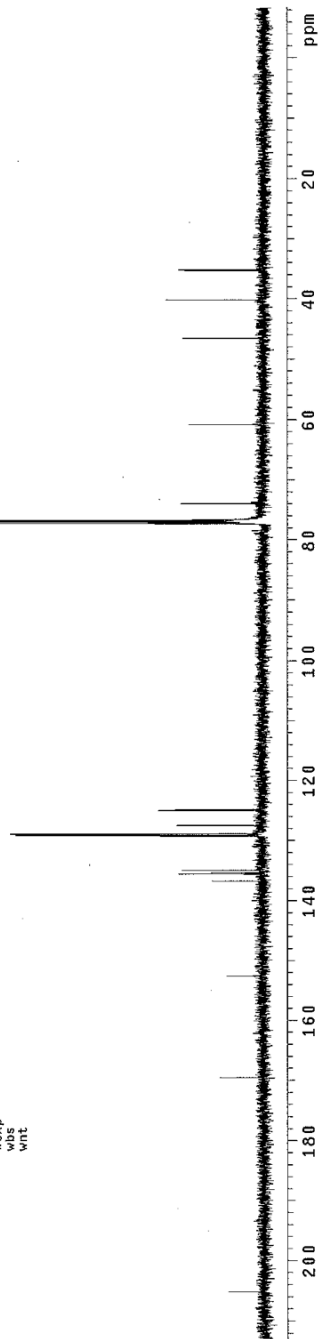
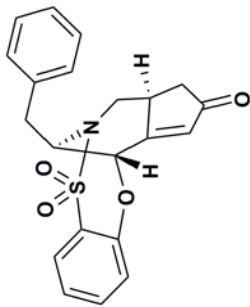
¹H NMR (500 MHz, Benzene) of compound 14a

STANDARD CARBON PARAMETERS

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SAMPLE DEC. & VT
date Oct 5 2009 dfrq 489.874
solvent CDCl3 dnu H1
f1 ACQ dnr 0
ACQUISITION EXP dof 0
sfrq 125.787 dm vvy W
t1 1 C13 dnm 12906
rt 65536 dfrq
sw 29986.9 dres 1.0
fb not used homo n
bs S2 temp DEC2 25.0
lpwr S7 dfrq2 0
d1 0 dnt 0
tof 2000.0 dper2 1
nt 10000 dcz 0
c S10 n
alock c
gain not used
flags dseq2 10000
l1 n dse2 1.0
l2 n homo2 1.0
dp Y homo3 0
hs n dfrq3 0
SP DISPLAY 1081.8 dnu3 1
VS 27891.8 dper3 0
VS 288 dnc3 0
SC 0 dnm3 C
WC 11.250 dmF3 10000
Hzmm 500.130 dres3 1.0
rf1 10766.2 homo3 n
rfp 8878.3 PROCESSING
th 100.000 1.00
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nm cdc ph
proc not used
fn math
werr wexp
wbs wnt

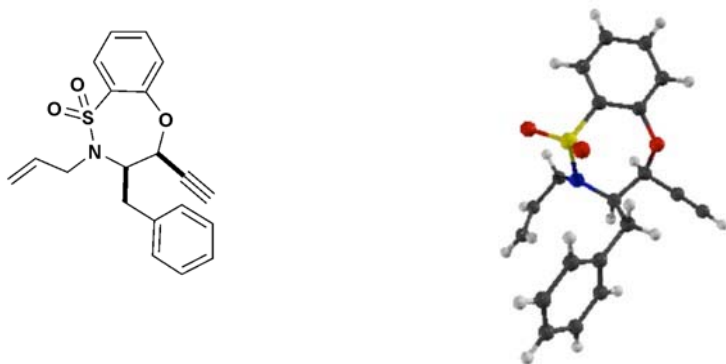
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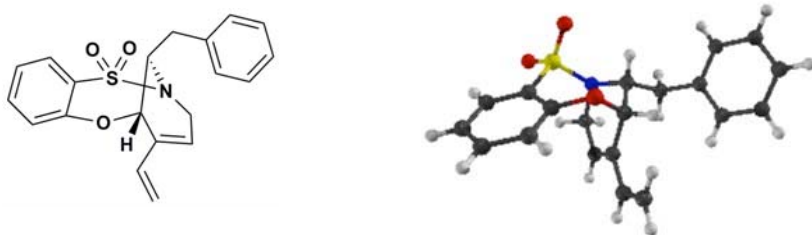
¹³C NMR (126 MHz, CDCl₃) of compound 14a

IV. X-Ray structures for compounds 11a, 13a and 14a

X-Ray structure of compound 11a (CCDC 768364)



X-Ray structure of compound 13a (CCDC 768365)



X-Ray structure of compound 14a (CCDC 768366)

