nature portfolio

https://doi.org/10.1038/s44160-022-00107-3

Supplementary information

Combined radical and ionic approach for the enantioselective synthesis of β-functionalized amines from alcohols

In the format provided by the authors and unedited

Supplementary Information

Combined radical and ionic approach for the enantioselective synthesis of β-functionalized amines from alcohols

Kai Lang,[1] Yang Hu,[2] Wan-Chen Cindy Lee,[1] and X. Peter Zhang*,[1]

[1] Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

[2] Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

This PDF file includes:

Table of Contents

1. General Considerations

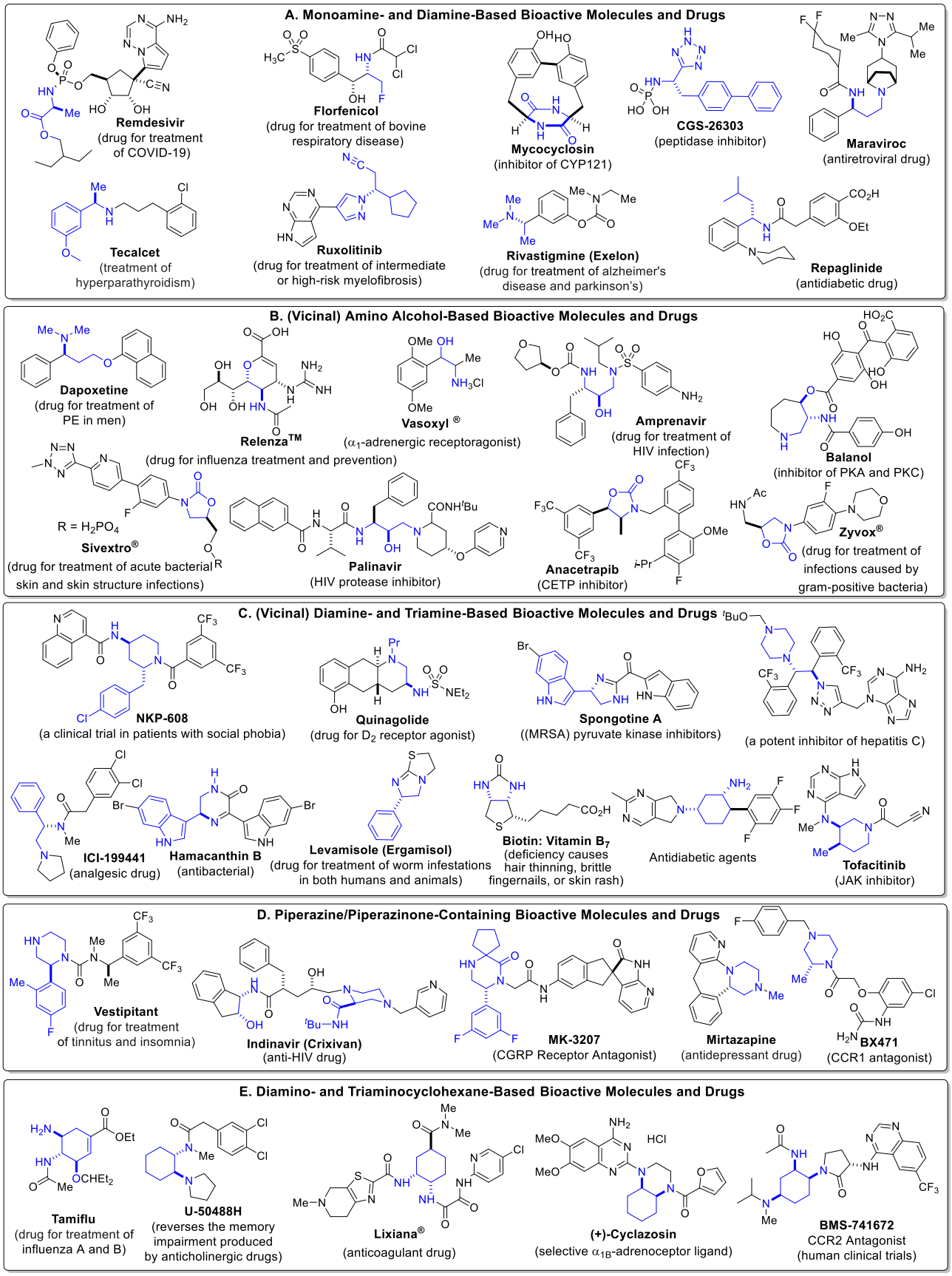
All intramolecular C–H amination reactions were performed under nitrogen in oven-dried glassware following standard Schlenk techniques. Dichloromethane was distilled under nitrogen from calcium hydride. All cross-coupling reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Tetrahydrofuran (THF) and toluene were distilled under nitrogen from sodium benzophenone ketyl. Anhydrous cobalt(II) chloride, palladium(II) acetate, and 9-dimethyl-4,5-bis(diphenylphosphino)xanthenes (Xantphos) were purchased from Strem Chemical Inc. Cesium carbonate was obtained as a gift from Chemetall Chemical Products, Inc. Thin layer chromatography was performed on SorBent Technologies TLC plates (silica gel 60 F254). Flash column chromatography was performed with SorBent Technologies silica gel (60Å, 230-400 mesh, 32-63μm). ^{1}H NMR and ^{13}C NMR were recorded on Bruker 250, Inova400, Inova500, Inova600 instruments, and referenced with respect to internal TMS standard. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OD-H, OJ-H, AS-H, AD-H, IA and IC columns. HRMS data was obtained on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electrospray ionization. Optical rotations were recorded on Rudolph Research Analytical, Autopol® IV, Automatic Polarimeter.

Notes on safety: Some azides could be explosive and should be handled carefully. When common sense is employed, the azides can be prepared, stored, and used without risk in the standard organic chemistry laboratory.[1] Face shields, leather gloves, and protective leather clothing are highly recommended. For organic azides, the "rule of six" provides us with the guidance. Six carbons (or other atoms of about the same size) per energetic functional group (azide, diazo, nitro, etc.) should provide enough dilution to render the compound relatively safe to work with given appropriate controls and safety procedures.[1]

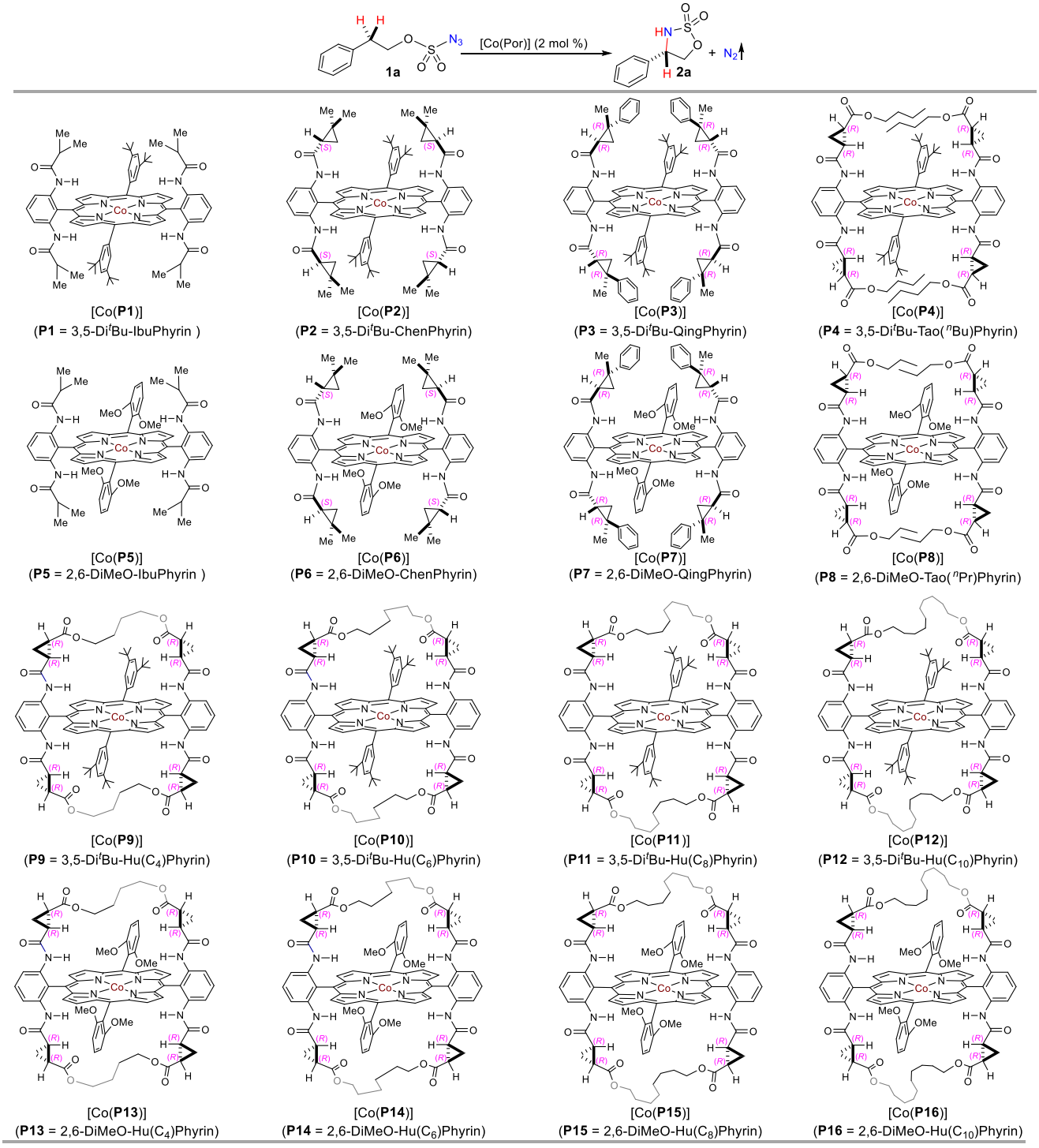
Although the C/N ratios[2] for most of the alkoxysulfonyl azides synthesized in this work are >4 ($(N_C+N_O)/N_N$ (N = number of atoms)), special attention needs to be paid when handling these type of compounds. The rotavap concentration for all azide synthesis was done at 0 ºC behind a blast shield.

1.1. Figure S1. Select Examples of Biologically Important Molecules Containing Chiral Amine Motifs.

(~40–45% of marketed drug molecules contain chiral amine as core structures)



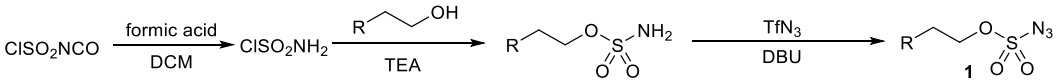
1.2. Figure S2. Catalysts Surveyed for Ligand Effect on 1,5-C(sp^3)–H Amination.



Synthesis and characterization of catalysts [Co(**P1**)], [Co(**P2**)], [Co(**P3**)], [Co(**P4**)], [Co(**P5**)], [Co(**P6**)], [Co(**P7**)], [Co(**P8**)], [Co(**P9**)], [Co(**P10**)], [Co(**P11**)], [Co(**P12**)], [Co(**P13**)], [Co(**P14**)], [Co(**P15**)] and [Co(**P16**)] can be found in our previously report and references therein.[3,4]

2. General Procedure A: Synthesis of Alkoxysulfonyl Azides

Notes on safety. Although no issues were encountered for alkoxysulfonyl azides throughout our research for this project, these azides are somewhat thermally unstable as suggested by TGA-DSC data in S19 (the onset of decomposition was approximately 134.7 ºC for the azide **1a**). Face shields, leather gloves, and protective leather clothing are highly recommended. The solvent concentration via rotavap for all azide synthesis was done at 0 ºC behind a blast shield.

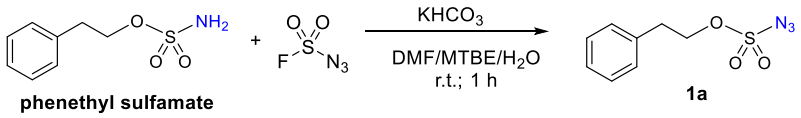


At 0 ºC, formic acid (2.0 equiv) was added dropwise to a solution of chlorosulfonyl isocyanate (2.0 equiv) in DCM (2.5 M). Then reaction mixture was slowly warmed up to rt and stirred overnight. To this freshly made sulfamoyl chloride, a solution of starting alcohol (1.0 equiv) and triethyl amine (2.2 equiv) in DCM (2.5 M) was slowly added at 0 ºC. The reaction was stirred at rt for another hour. Upon complete consumption of starting alcohol as monitored by TLC, the reaction was quenched with H_2O. The aqueous layer was then extracted with DCM (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: DCM:EtOAc 15:1) to give the desired sulfamate ester, which was used directly for next step.

Procedure for Diazo-Transfer Reactions Using TfN_3. To a solution of the above synthesized sulfamate ester (1.0 equiv) in DCM (0.25 M) was added DBU (1.5 equiv) and the reaction mixture was cooled to -78 ºC. A solution of TfN_3[5] in hexanes (0.5 M, 1.5 equiv) was then added slowly and the reaction was monitored by TLC to completion (typically 5 min). The reaction mixture was then directly loaded into the silica gel column then purified by flash column chromatography (eluent was given below). The fractions containing product were collected and concentrated at 0 ºC to afford the desired alkoxysulfonyl azides, which were stored immediately in a -20 ºC freezer. **Note:** during column purification, the first 5-7 test tubes (~ 100 mL of Hexanes/EtOAc: 40:1) before the desired azides came out were collected separately due to the presence of unreacted TfN_3; this part of solution was quenched as detailed in the following section.

Procedure for Destruction of TfN_3: Dilute the solution containing TfN_3 in a 250 mL round bottom flask with 50 mL THF assuming the full amount used still remains (1.0 equiv). A solution of triphenylphosphine (1.5 equiv, 50 mol % excess) in a 20 mL of THF is added slowly with stirring. The mixture is allowed to stand at room temperature for 24 hours or until complete consumption of the azide. The quenched mixture can then be worked up as usual or be disposed in an appropriate organic waste stream.

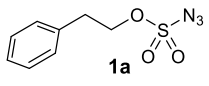
The following alternative procedure is highly recommended for the end users due to the use of much safer FSO_2N_3[6] as diazotransfer reagent.



Procedure for Diazo-Transfer Reactions Using FSO_2N_3. Taking the synthesis of **phenethyl sulfazidate** (**1a**) as an example, to a round-bottom flask was added sequentially above synthesized **phenethyl sulfamate** (1.0 mmol) and FSO_2N_3 (5 mL, 1.0 mmol, 1.0 equiv, 0.2 M in MTBE), diluted with equal volume of DMF and followed by the addition of aqueous $KHCO_3$ solution (1.3 mL, 4.0 mmol, 4.0 equiv, 3.0 M in H_2O). The reaction mixture was stirred for 1 hour at room temperature. After completion, EtOAc (40 mL) was added and the mixture was washed sequentially with brine (60 mL × 6), water (60 mL × 2) and brine (60 mL), dried over Na_2SO_4, concentrated by rotary evaporation. The residue was then loaded into the silica gel column and purified by flash column chromatography (eluent: 20:1 Hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc). The fractions containing product were collected and concentrated at 0 ºC to afford the desired alkoxysulfonyl azides **1a** as colorless oil in 90% yield (204 mg), which were stored immediately in a -20 ºC freezer.

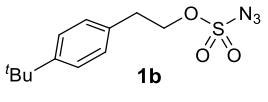
2.1. Synthesis and Characterization of Alkoxysulfonyl Azides

Phenethyl sulfazidate (1a) was synthesized following General Procedure A, from 2.4 mmol of the 2-phenyl-1-ethanol (commercially available, cas: 60-12-8) and purified by flash silica gel chromatography (eluent: 40: 1 hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc) to afford 408 mg of desired product as a colorless oil (75% yield). ^{1}H NMR (600 MHz,



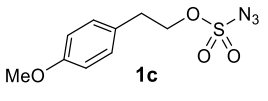
C_6D_6) δ ppm 7.07- 6.91 (m, 3H), 6.76 (d, *J* = 7.0 Hz, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.5, 129.1, 129.0, 127.5, 75.0, 35.2; IR (neat, cm^{-1}): 2143, 1403, 1183.

4-(*tert*-Butyl)phenethyl sulfazidate (1b) was synthesized following General Procedure A, from 1.0 mmol of the 2-(4-(*tert*-butyl)phenyl)ethan-1-ol (commercially available, cas: 5406-86-0) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.70 (20:1 Hexanes/EtOAc) to afford 250 mg of desired product as a colorless oil (88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.17 (dd, *J* = 8.2, 1.7 Hz, 2H), 4.54 (td, *J* = 6.9, 1.4 Hz, 2H), 3.07 (t, *J* = 6.9 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.3, 132.2, 128.6, 125.8, 77.2, 74.9, 34.5, 31.3; IR(neat, cm^{-1}): 2135, 1400, 1185.



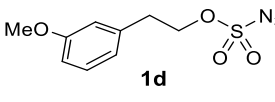
1b

4-Methoxyphenethyl sulfazidate (1c) was synthesized following General Procedure A, from 2.6 mmol of the 2-(4-methoxyphenyl)ethan-1-ol (commercially available, cas: 702-23-8) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.55 (10:1 Hexanes/EtOAc) to afford 436 mg of desired product as a colorless oil (65% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.16 (d, *J* =8.8 Hz, 2H), 6.88 (d, *J* =8.8 Hz, 2H), 4.51 (t, *J* =6.8 Hz, 2H), 3.80 (s, 3H), 3.05 (t, *J* =6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 159.0, 130.1, 127.4, 114.4, 75.2, 55.4, 34.4; IR (neat, cm^{-1}): 2133, 1402, 1183.

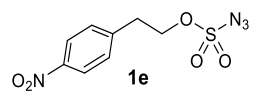


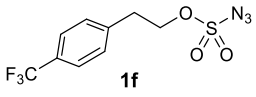
1c

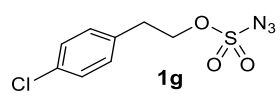
3-Methoxyphenethyl sulfazidate (1d) was synthesized following General Procedure A, from 1.1 mmol of the 2-(3-methoxyphenyl)ethan-1-ol (commercially available, cas: 5020-41-7) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.50 (20:1 Hexanes/EtOAc) to afford 231 mg of desired product as a colorless oil (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29-7.24 (m, 1H), 6.85-6.80 (m, 2H), 6.78 (d, *J* = 1.8 Hz, 1H), 4.55 (t, *J* = 6.9 Hz, 2H), 3.80 (s, 3H), 3.08 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.9, 136.9, 129.9, 121.1, 114.8, 112.6, 74.8, 55.2, 35.0; IR (neat, cm^{-1}): 2134, 1401, 1183.

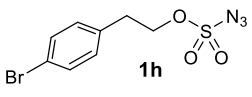


1d

4-Nitrophenethyl sulfazidate (1e) was synthesized following General Procedure A, from 1.0 mmol of  the 2-(4-nitrophenyl)ethan-1-ol (commercially available, cas: 100-27-6) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.50 (20:1 Hexanes/EtOAc) to afford 200 mg of desired product as an off-white solid (72% yield). ^{1}H NMR (500 MHz, C_6D_6) δ 7.76-7.70 (m, 2H), 6.43-6.36 (m, 2H), 3.74 (t, *J* = 6.5 Hz, 2H), 2.14 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 147.5, 143.2, 130.0, 124.2, 73.7, 35.0; IR (neat, cm^{-1}): 2147, 1519, 1403, 1346, 1183.

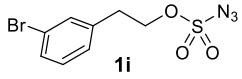
4-(Trifluoromethyl)phenethyl sulfazidate (1f) was synthesized following General Procedure A, from  1.0 mmol of the 2-(4-(trifluoromethyl)phenyl)ethan-1-ol (commercially available, cas: 2968-93-6) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.60 (20:1 Hexanes/EtOAc) to afford 250 mg of desired product as a colorless oil (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.57 (t, *J* = 6.6 Hz, 2H), 3.16 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 139.6, 129.7 (q, *J* = 32 Hz), 129.3, 125.7 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 271 Hz), 74.0, 34.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.7; IR (neat, cm^{-1}): 2135, 1401, 1185.

4-Chlorophenethyl sulfazidate (1g) was synthesized following General Procedure A, from 1.24 mmol  of the 2-(4-chlorophenyl)ethan-1-ol (commercially available, cas: 1875-88-3) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.62 (20:1 Hexanes/EtOAc) to afford 260 mg of desired product as a colorless oil (80% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.35 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 4.56 (t, *J* = 6.7 Hz, 2H), 3.11 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 133.9, 133.3, 130.3, 129.0, 74.4, 34.4; IR (neat, cm^{-1}): 2137, 1400, 1180.

4-Bromophenethyl sulfazidate (1h) was synthesized following General Procedure A, from 0.93 mmol  of the 2-(4-bromophenyl)ethan-1-ol (commercially available, cas: 4654-39-1) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc) to afford 230 mg of desired product as a colorless oil (82% yield). ^{1}H

NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.53 (t, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 134.6, 132.0, 130.7, 121.3, 74.4, 34.5; IR (neat, cm^{-1}): 2147, 1401, 1184.

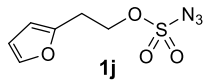
3-Bromophenethyl sulfurazidate (1i) was synthesized following General Procedure A, from 1.4 mmol



1i

3-bromobenzeneethanol (commercially available, cas: 28229-69-8) and purified by flash silica gel chromatography (eluent: 20: 1 Hexanes/EtOAc), TLC R_f = 0.40 (10:1 Hexanes/EtOAc) to afford 390 mg of desired product as a colorless oil (89% yield). ^1H NMR (600 MHz, $CDCl_3$) δ ppm 7.44-7.41 (m, 1H), 7.40 (t, *J* = 1.7 Hz, 1H), 7.24-7.20 (m, 1H), 7.20-7.16 (m, 1H), 4.54 (t, *J* = 6.8 Hz, 2H), 3.08 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 137.8, 132.1, 130.7, 130.6, 127.7, 123.0, 74.3, 34.8; IR (neat, cm^{-1}): 2144, 1405, 1186, 956, 625.

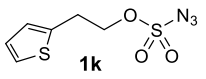
2-(Furan-2-yl)ethyl sulfazidate (1j) was synthesized following General Procedure A, from 2.2 mmol



1j

of the 2-(furan-2-yl)ethan-1-ol (commercially available, cas: 35942-95-1) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc) to afford 360 mg of desired product as a colorless oil (75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.35 (d, *J* = 1.8 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 4.57 (t, *J* = 6.6 Hz, 2H), 3.13 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.2, 142.1, 110.5, 107.6, 72.1, 27.8; IR (neat, cm^{-1}): 2133, 1401, 1185.

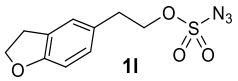
2-(Thiophen-2-yl)ethyl sulfazidate (1k) was synthesized following General Procedure A, from 2.08



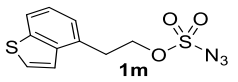
1k

mmol of the 2-(thiophen-2-yl)ethan-1-ol (commercially available, cas: 5402-55-1) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc) to afford 420 mg of desired product as a colorless oil (86% yield). ^1H NMR (250 MHz, $CDCl_3$) δ ppm 7.32-7.21 (m, 1H), 7.08-6.91 (m, 2H), 4.58 (t, *J* = 6.6 Hz, 2H), 3.36 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 137.1, 127.3, 126.6, 124.9, 74.3, 29.3; IR (neat, cm^{-1}): 2135, 1405, 1185.

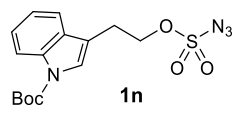
2-(2,3-Dihydrobenzofuran-5-yl)ethyl sulfurazidate (1l) was synthesized following General Procedure A, from 2.1 mmol 2-(2,3-dihydrobenzofuran-5-yl)ethan-1-ol (commercially available, cas: 87776-76-9) and purified by flash silica gel chromatography (eluent: 16: 1 Hexanes/EtOAc), TLC R_f = 0.30 (8:1 Hexanes/EtOAc) to afford 300 mg of desired product as a colorless oil (54% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.06 (s, 1H), 6.98-6.94 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 4.57 (t, *J* = 8.7 Hz, 2H), 4.50 (t, *J* = 7.0 Hz, 2H), 3.20 (t, *J* = 8.7 Hz, 2H), 3.03 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 159.6, 128.7, 127.9, 127.2, 125.7, 109.6, 75.5, 71.5, 34.7, 29.8; IR (neat, cm^{-1}): 2143, 1492, 1401, 1181, 938, 623.

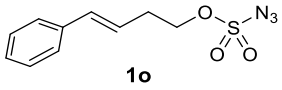


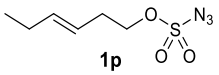
2-(Benzo[b]thiophen-4-yl)ethyl sulfurazidate (1m) was synthesized following General Procedure A, from 1.4 mmol benzo[b]thiophene-4-ethanol (commercially available, cas: 227809-74-7) and purified by flash silica gel chromatography (eluent: 20: 1 Hexanes/EtOAc), TLC R_f = 0.70 (20:1 Hexanes/EtOAc) to afford 320 mg of desired product as a colorless oil (80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.83 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 5.5 Hz, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 4.64 (t, *J* = 7.1 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 140.6, 138.8, 130.0, 127.4, 125.1, 124.6, 122.1, 121.1, 74.3, 33.4; IR (neat, cm^{-1}): 2143, 1402, 1185, 951, 760.

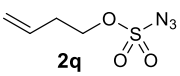


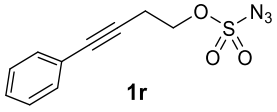
***tert*-Butyl 3-(2-((azidosulfonyl)oxy)ethyl)-1H-indole-1-carboxylate (1n)** was synthesized following General Procedure A, from 1.02 mmol of the *tert*-butyl 3-(2-hydroxyethyl)-1H-indole-1- carboxylate (commercially available, cas: 141972-32-9) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.45 (20:1 Hexanes/EtOAc) to afford 300 mg of desired product as a colorless oil (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.14 (d, *J* = 7.8 Hz, 1H), 7.38-7.31 (m, 1H), 7.29-7.25 (m, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 4.61 (t, *J* = 6.4 Hz, 2H), 3.21 (t, *J* = 6.4 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.5, 135.5, 129.7, 124.8, 124.1, 122.8, 118.5, 115.5, 114.3, 84.0, 73.5, 28.2, 24.8; IR (neat, cm^{-1}): 2135, 1675, 1405, 1180.



(*E*)-4-phenylbut-3-en-1-yl sulfazidate (1o) was synthesized following General Procedure A, from 1.69  mmol of the (*E*)-4-phenylbut-3-en-1-ol (commercially available, cas: 770-36-5) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.78 (20:1 Hexanes/EtOAc) to afford 310 mg of desired product as a colorless oil (70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.39-7.29 (m, 4H), 7.28-7.24 (m, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.19-6.09 (m, 1H), 4.47 (t, *J* = 6.6 Hz, 2H), 2.79- 2.66 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 136.7, 134.2, 128.7, 127.8, 126.3, 122.8, 74.1, 32.3; IR (neat, cm^{-1}) 2143, 1403, 1184.

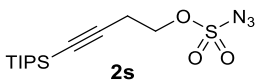
(*E*)-Hex-3-en-1-yl sulfazidate (1p) was synthesized following General Procedure A, from 2.0 mmol of  the (*E*)-hex-3-en-1-ol (commercially available, cas: 928-97-2) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.75 (20:1 Hexanes/EtOAc) to afford 340 mg of desired product as a colorless oil (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.75-5.58 (m, 1H), 5.35 (tdd, *J* = 13.7, 4.9, 3.4 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 2.49 (q, *J* = 6.8 Hz, 2H), 2.04 (p, *J* = 6.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 137.1, 121.6, 74.5, 31.8, 25.6, 13.5; IR (neat, cm^{-1}) 2137, 1401, 1185.

But-3-en-1-yl sulfazidate (2q) was synthesized following General Procedure A, from 2.0 mmol of the  but-3-en-1-ol (commercially available, cas: 627-27-0) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.75 (20:1 Hexanes/EtOAc) to afford 344 mg of desired product as a colorless oil (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.85-5.72 (m, 1H), 5.24-5.19 (m, 2H), 4.41 (t, *J* = 6.4 Hz, 2H), 2.56 (q, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 131.7, 119.3, 74.0, 33.1; IR (neat, cm^{-1}) 2135, 1404, 1185.

4-phenylbut-3-yn-1-yl sulfazidate (1r) was synthesized following General Procedure A, from 2.0  mmol of the 4-phenylbut-3-yn-1-ol (commercially available, cas: 10229-11-5) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.78 (20:1 Hexanes/EtOAc) to afford 400 mg of desired product as a colorless oil (80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.50-7.36 (m, 2H), 7.32-7.28 (m, 3H), 4.49 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 131.6, 128.4, 128.3, 122.6, 83.2, 82.8, 71.9, 20.2; IR (neat, cm^{-1}) 2180, 2117, 1410, 1194.

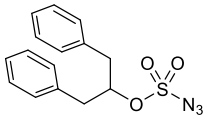
4-(Triisopropylsilyl)but-3-yn-1-yl sulfazidate (1s) was synthesized following General Procedure A,



2s

from 1.05 mmol of the 4-(triisopropylsilyl)but-3-yn-1-ol[7] and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.88 (20:1 Hexanes/EtOAc) to afford 315 mg of desired product as a colorless oil (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.41 (t, *J* = 6.9 Hz, 2H), 2.77 (t, *J* = 6.9 Hz, 2H), 1.07-0.99 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 100.8, 84.4, 72.0, 20.6, 18.5, 11.1; IR (neat, cm^{-1}) 2174, 2115, 1412, 1187.

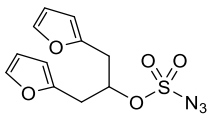
1,3-Diphenylpropan-2-yl sulfurazidate (1t) was synthesized following General Procedure A, from 2.0



1t

mmol of the 1,3-diphenyl-2-propanol (commercially available, cas: 5381-92-0) and purified by flash silica gel chromatography (eluent: 20: 1 Hexanes/EtOAc), TLC R_f = 0.60 (10:1 Hexanes/EtOAc) to afford 470 mg of desired product as a colorless oil (74% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.34 (dd, *J* = 10.4, 4.4 Hz, 4H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.1 Hz, 4H), 5.14-4.96 (m, 1H), 3.08 (dd, *J* = 14.3, 7.0 Hz, 2H), 3.04 (dd, *J* = 14.3, 5.9 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.7, 129.7, 129.0, 127.5, 89.8, 40.5; IR (neat, cm^{-1}): 2145, 1190.

1,3-Di(furan-2-yl)propan-2-yl sulfurazidate (1u) was synthesized following General Procedure A,

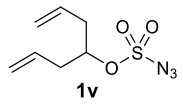


1u

from 0.9 mmol of the 1,3-di(furan-2-yl)propan-2-ol, which was prepared from 1,3-di-2-furanyl-2-propanone[8] through $NaBH_4$ reduction and purified by flash silica gel chromatography (eluent: 15: 1 Hexanes/EtOAc), TLC R_f = 0.52 (8:1 Hexanes/EtOAc) to afford 180 mg of desired product as a colorless oil (65% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.39 (d, *J* = 1.0 Hz, 2H), 6.34 (dd, *J* = 2.8, 1.8 Hz, 2H), 6.22 (d, *J* = 2.9 Hz, 2H), 5.16 (p, *J* = 6.1 Hz, 1H), 3.14 (dd, *J* = 15.5, 5.7 Hz, 2H), 3.10 (dd, *J* = 15.5, 6.5 Hz, 2H); ^{13}C NMR (150 MHz,

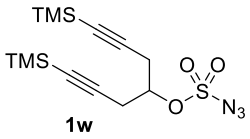
$CDCl_3$) δ ppm 149.2, 142.5, 110.8, 108.8, 84.1, 32.7; IR (neat, cm^{-1}): 2980, 2145, 1405, 1187, 903, 723, 624.

2-Allylpent-4-en-1-yl sulfurazidate (1v) was synthesized following General Procedure A, from 1.0 mmol of the 1,6-heptadien-4-ol (commercially available, cas: 2883-45-6) and purified by flash silica gel chromatography (eluent: 20: 1 Hexanes/EtOAc), TLC R_f = 0.42 (10:1 Hexanes/EtOAc) to afford 220 mg of desired product as a colorless oil (95% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.79 (ddt, *J* = 17.3, 10.5, 7.1 Hz, 2H), 5.24-5.19 (m, 4H), 4.79 (p, *J* = 6.1 Hz, 1H), 2.61-2.48 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 131.4, 120.0, 87.4, 38.2; IR (neat, cm^{-1}): 2142, 1738, 1186.



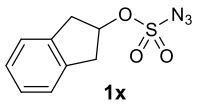
1v

1,7-Bis(trimethylsilyl)hepta-1,6-diyn-4-yl sulfurazidate (1w) was synthesized following General Procedure A, from 1.1 mmol 1,7-bis(trimethylsilyl)hepta-1,6-diyn-4-ol[9] and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.40 (40:1 Hexanes/EtOAc) to afford 300 mg of desired product as a colorless oil (79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 4.82 (p, *J* = 5.8 Hz, 1H), 2.86 (dd, *J* = 17.3, 5.9 Hz, 2H), 2.80 (dd, *J* = 17.4, 5.7 Hz, 2H), 0.17 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 99.1, 89.2, 82.6, 25.1, 0.0; IR (neat, cm^{-1}): 2960, 2182, 2144, 1410, 1191, 840.



1w

2,3-Dihydro-1H-inden-2-yl sulfazidate (1x) was synthesized following General Procedure A, from 1.0 mmol of the 2,3-dihydro-1H-inden-2-ol (commercially available, cas: 4254-29-9) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.75 (20:1 Hexanes/EtOAc) to afford 198 mg of desired product as a colorless oil (83% yield). ^{1}H NMR (600 MHz, C_6D_6) δ ppm 6.95 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.84-6.79 (m, 2H), 4.93 (dt, *J* = 9.0, 3.0 Hz, 1H), 2.81 (dd, *J* = 17.2, 2.6 Hz, 2H), 2.59 (dd, *J* = 17.2, 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 138.5, 127.5, 124.7, 88.2, 39.7; IR (neat, cm^{-1}) 2145, 1404, 1178.



1x

Cyclopent-3-en-1-yl sulfurazidate (1y) was synthesized following General Procedure A, from 2.0 mmol of 3-cyclopenten-1-ol (commercially available, cas: 14320-38-8) and purified by flash silica gel chromatography (eluent: 20: 1 Hexanes/EtOAc), TLC R_f = 0.50 (20:1 Hexanes/EtOAc) to afford 300 mg of desired product as a colorless oil (79% yield). (**Note: compound is not stable under neat condition at room temperature but it is stable at 0 ºC under neat condition.**). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.76 (d, *J* = 7.7 Hz, 2H), 5.43 (t, *J* = 6.2 Hz, 1H), 2.83 (dd, *J* = 17.6, 6.2 Hz, 2H), 2.75 (d, *J* = 18.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 127.7, 87.7, 39.9; IR (neat, cm^{-1}): 2143, 1403, 1180, 908, 743.

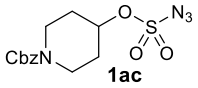
Cyclohexyl sulfazidate (1z) was synthesized following General Procedure A, from 1.52 mmol of the cyclohexanol (commercially available, cas: 108-93-0) and purified by flash silica gel chromatography (eluent: 40: 1 Hexanes/EtOAc), TLC R_f = 0.80 (20:1 Hexanes/EtOAc) to afford 260 mg of desired product as a colorless oil (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.78-4.85 (m, 1H), 2.02 (ddd, *J* = 12.9, 6.8, 3.4 Hz, 2H), 1.96-1.67 (m, 4H), 1.67-1.48 (m, 1H), 1.32-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 87.5, 31.9, 24.6, 23.2; IR (neat, cm^{-1}) 2137, 1401, 1180.

1,4-Dioxaspiro[4.5]decan-8-yl sulfazidate (1aa) was synthesized following General Procedure A, from 1.44 mmol of the 1,4-dioxaspiro[4.5]decan-8-ol (commercially available, cas: 22428-87-1) and purified by flash silica gel chromatography (eluent: 10: 1 Hexanes/EtOAc), TLC R_f = 0.30 (10:1 Hexanes/EtOAc) to afford 452 mg of desired product as a colorless oil (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.94-4.85 (m, 1H), 4.08-3.82 (m, 4H), 2.19-1.92 (m, 4H), 1.86-1.82 (m, 2H), 1.68-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 107.0, 84.8, 64.5, 64.4, 30.6, 28.8; IR (neat, cm^{-1}) 2145, 1400, 1183.

1,4-Dithiaspiro[4.5]decan-8-yl sulfurazidate (1ab) was synthesized following General Procedure A, from 1.0 mmol of the 1,4-dithiaspiro[4.5]decan-8-ol (commercially available, cas: 22428-86-0) and purified by flash silica gel chromatography (eluent: 8: 1

Hexanes/EtOAc), TLC R_f = 0.32 (4:1 Hexanes/EtOAc) to afford 230 mg of desired product as a colorless oil (77% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.01-4.78 (m, 1H), 3.37-3.27 (m, 4H), 2.33-2.22 (m, 2H), 2.15- 2.00 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 84.6, 66.5, 38.9, 38.8, 38.3, 31.2; IR (neat, cm^{-1}): 2143, 1405, 1182, 913.

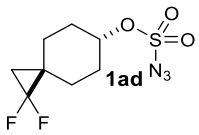
Benzyl 4-((azidosulfonyl)oxy)piperidine-1-carboxylate (1ac) was synthesized following General



1ac

Procedure A, from 1.0 mmol of the 1-(benzyloxycarbonyl)-4-piperidinol (commercially available, cas: 95798-23-5) and purified by flash silica gel chromatography (eluent: 8: 1 Hexanes/EtOAc), TLC R_f = 0.30 (4:1 Hexanes/EtOAc) to afford 306 mg of desired product as a colorless oil (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40-7.28 (m, 5H), 5.14 (s, 2H), 4.96 (tt, *J* = 7.3, 3.7 Hz, 1H), 3.74 (ddd, *J* = 13.4, 7.5, 3.9 Hz, 2H), 3.47 (ddd, *J* = 13.8, 7.5, 4.0 Hz, 2H), 2.12-1.96 (m, 2H), 1.96-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.0, 136.4, 128.5, 128.1, 127.9, 83.3, 67.4, 40.3, 30.8; IR (neat, cm^{-1}): 2105, 1684, 1402, 1185.

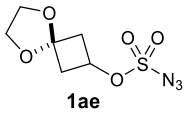
(3r,6r)-1,1-Difluorospiro[2.5]octan-6-yl sulfurazidate (1ad) was synthesized following General



1ad

Procedure A, from 2.5 mmol of 1,1-difluorospiro[2.5]octan-6-ol (synthesized through the $NaBH_4$ reduction of the corresponding ketone;[10] 1:1 mixture of diastereosomers for the resulting alcohols; once formig sulfamate esters, diastereoisomers are separatable via flash silica gel chromatography (eluent: 4: 1 Hexanes/EtOAc), less polar compound is the desired *trans* diasteromer of sulfamate ester.) and purified by flash silica gel chromatography (eluent: 20: 1 Hexanes/EtOAc), TLC R_f = 0.55 (20:1 Hexanes/EtOAc) to afford 310 mg of desired product as white solid (47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.97 (tt, *J* = 6.7, 3.5 Hz, 1H), 2.07-1.90 (m, 4H), 1.83 (dddd, *J* = 11.0, 8.7, 4.4, 2.3 Hz, 2H), 1.70-1.54 (m, 2H), 1.10 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 116.1 (t, *J* = 288.5 Hz), 85.3, 30.2, 27.2 (t, *J* = 10.0 Hz), 24.8, 22.0 (t, *J* = 10.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm -140.27; IR (neat, cm^{-1}): 2959, 2142, 1400, 1183, 904, 623.

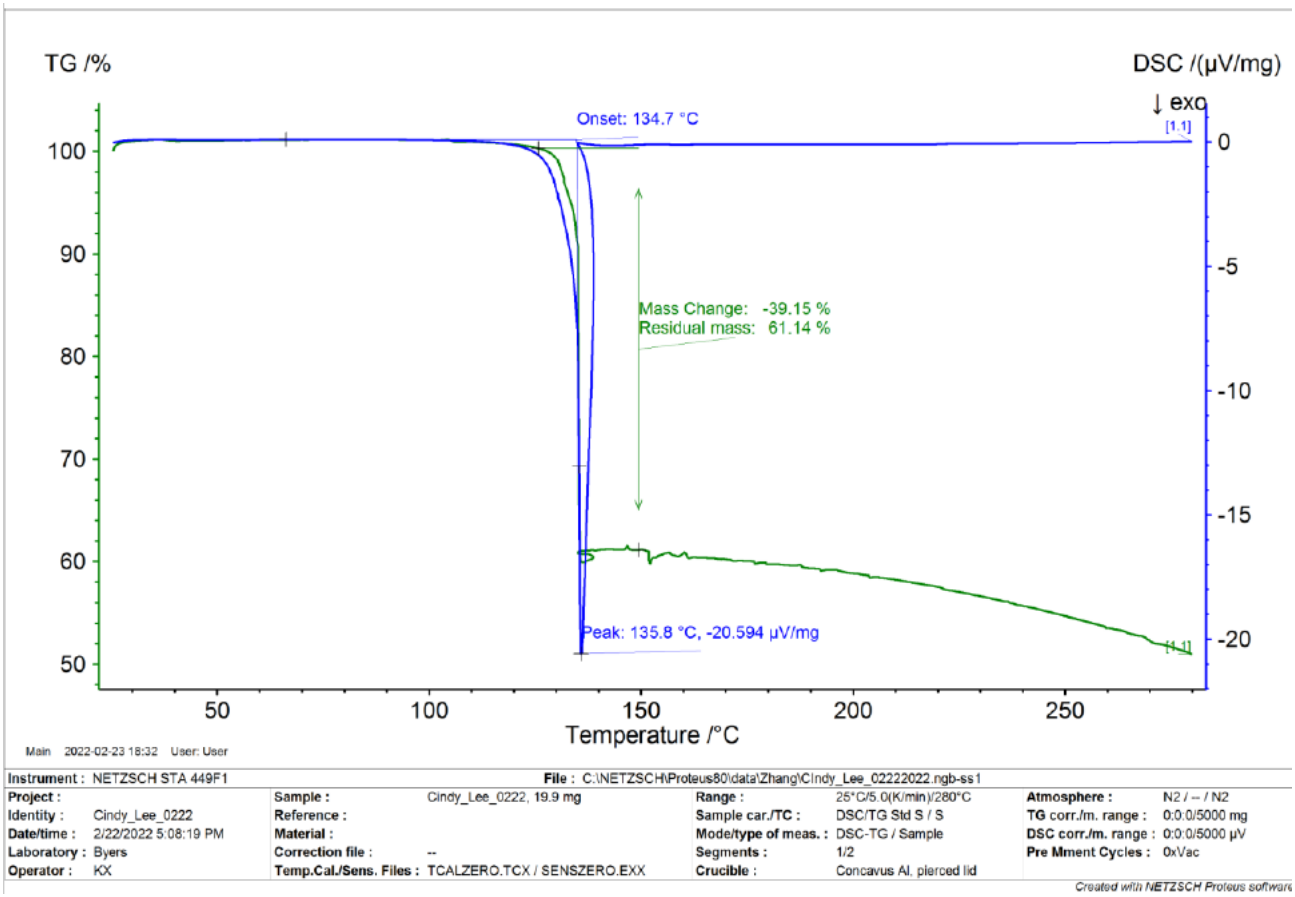
5,8-Dioxaspiro[3.4]octan-2-yl sulfurazidate (1ae) was synthesized following General Procedure A, from 2.0 mmol of the 5,8-dioxaspiro[3.4]octan-2-ol,[11] which was synthesized from 3-benzyloxycyclobutan-1-one (commercially available, cas: 30830-27-4) and purified by flash silica gel chromatography (eluent: 10: 1 Hexanes/EtOAc), TLC R_f = 0.32 (4:1 Hexanes/EtOAc) to afford 320 mg of desired product as a colorless oil (68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.02-4.96 (m, 1H), 3.91 (s, 4H), 2.87-2.72 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 103.0, 71.9, 64.8, 64.4, 44.2; IR (neat, cm^{-1}): 2143, 1405, 1185, 910.



1ae

2.2. TGA and DSC Result for **1a**

Simultaneous TGA-DSC was run on a machine of NETZSCH STA 449F1. The result was analyzed using software of Proteus Analysis. Temperature program: 25 ºC to 280 ºC at 5 ºC/min rate under N_2 in a sealed aluminum crucible. 19.9 mg of sample was used for analysis.



3. General Procedure B: Intramolecular C–H Amination

An oven-dried Schlenk tube that was previously charged with catalyst (0.002 mmol) and 4Å molecular sieves (20 mg), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum and 1.0 mL of solvent was added followed by azide (0.1 mmol). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The reaction mixture was then stirred for the desired time and temperature. Following completion of the reaction, the reaction mixture was purified via flash silica gel chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the pure compound.

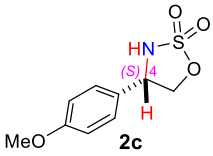
3.1. Synthesis and Characterization of Sulfamidates

(*S*)-4-Phenyl-1,2,3-oxathiazolidine 2,2-dioxide (2a) was synthesized following General Procedure B, starting from 0.2 mmol scale, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.40 (10: 1 DCM/EtOAc) to afford the desired product as white solid (98% yield). m.p. 112-114 °C. $[\alpha]^{20}_{D}$= +40.0º (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.49-7.38 (m, 5H), 5.08 (dd, *J* = 8.4, 7.0 Hz, 1H), 4.84 (dd, *J* = 8.8, 6.9 Hz, 1H), 4.78 (s, 1H), 4.45 (t, *J* = 8.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.5, 129.7, 129.6, 126.8, 75.2, 59.8. IR (neat, cm^{-1}): 1352, 1189; HRMS (ESI) *m/z* calcd for $C_8H_9NNaO_3S^+$ $[M+Na]^+$: 222.0201, obsd: 222.0195; HPLC analysis: ee = 98%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 17.33 min., Minor t = 19.59 min. 4-[*S*] absolute configuration of the product was determined by X-ray crystallography. **Reactions were successfully scaled up to 2.0 mmol** without any notable change for either enantioselectivity or yield.

(*S*)-4-(4-*tert*-Butylphenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2b) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: DCM), TLC R_f = 0.30 (DCM) to afford the desired product as white solid (98% yield). m.p. 140-142

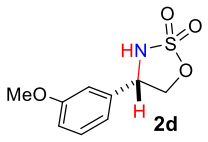
°C. $[\alpha]^{20}_D$= +115.0º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.42-7.32 (m, 2H), 7.32-7.22 (m, 2H), 5.14-4.94 (m, 1H), 4.91-4.66 (m, 2H), 4.38 (t, *J* = 8.6 Hz, 1H), 1.25 (s, 9 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 152.9, 132.1, 126.6, 126.4, 75.3, 59.5, 34.8, 31.2; IR (neat, cm^{-1}): 1345, 1155; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{17}NNaO_3S^+$ $[M+Na]^+$: 278.0827, obsd: 278.0830; HPLC analysis: ee = 97%. Chiral AD-H (10% isopropanol - 90% hexanes, 0.7 mL/min): Major t = 12.55 min., Minor t = 15.48 min.

(*S*)-4-(4-Methoxyphenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2c) was synthesized following General



Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.25 (10: 1 DCM/EtOAc) to afford the desired product as white solid (87% yield). m.p. 102-103 °C. $[\alpha]^{20}_D$= +28.0º (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.34 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.02 (dd, *J* = 15.4, 6.9 Hz, 1H), 4.78 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.74 (br. s, 1H), 4.44 (t, *J* = 8.7 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 160.7, 128.3, 127.1, 114.9, 75.4, 59.5, 55.6; IR (neat, cm^{-1}):1388, 1152; HRMS (ESI) *m*/*z* calcd for $C_9H_{11}NNaO_4S^+$ $[M+Na]^+$: 252.0306, obsd: 252.0312; HPLC analysis: ee = 95%. Chiral AD-H (10% isopropanol - 90% hexanes, 0.7 mL/min): Major t = 24.36 min., Minor t = 28.58 min. 4-[*S*] absolute configuration of the product was determined by X-ray crystallography.

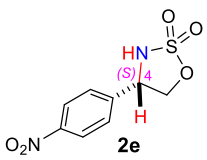
(*S*)-4-(3-Methoxyphenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2d) was synthesized following General



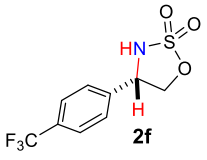
Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.28 (10: 1 DCM/EtOAc) to afford the desired product as a colorless oil (96% yield). $[\alpha]^{20}_D$= +30.0º (*c* = 1.3, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.33-7.21 (m, 1H), 6.94-6.80 (m, 3H), 5.05-4.87 (m, 1H), 4.83 (d, *J* = 6.5 Hz, 1H), 4.80-4.69 (m, 1H), 4.36 (t, *J* = 8.5 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 160.3, 136.9, 130.6, 118.7, 115.0, 112.2, 75.6, 59.5, 55.4; IR (neat, cm^{-1}): 1156; HRMS (ESI) *m*/*z* calcd for

$C_9H_{11}NNaO_4S^+$ [M+Na]$^+$: 252.0306, obsd: 252.0309; HPLC analysis: ee = 97%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 15.36 min., Minor t = 17.74 min.

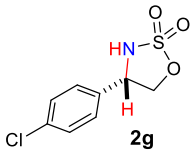
(*S*)-4-(4-Nitrophenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2e) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.20 (10: 1 DCM/EtOAc) to afford the desired product as white solid (82% yield). m.p. 130-133 °C. $[\alpha]^{20}_D$= +26.0º (*c* = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-D_6) δ ppm 8.29 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.37 (br. s, 1H), 5.48 (q, *J* = 6.7 Hz, 1H), 5.13 (dd, *J* = 8.7, 7.5 Hz, 1H), 4.48 (dd, *J* = 9.0, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, Acetone-D_6) δ ppm 148.0, 145.5, 127.9, 123.8, 74.2, 58.2; IR (neat, cm^{-1}): 1611, 1521, 1350, 1188; HRMS (ESI) *m*/*z* calcd for $C_8H_8N_2NaO_5S^+$ [M+Na]$^+$: 267.0052, obsd: 267.0054; HPLC analysis: ee = 90%, Chiral AD-H (10% isopropanol - 90% hexanes, 0.7 mL/min): Major t = 46.72 min., Minor t = 72.65 min. 4-[*S*] absolute configuration of the product was determined by X-ray crystallography.



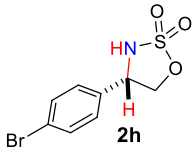
(*S*)-4-(4-Trifluoromethylphenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2f) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.35 (10: 1 DCM/EtOAc) to afford the desired product as white solid (94% yield). m.p. 74-76 °C. $[\alpha]^{20}_D$= +38.0º (*c* = 0.4, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.70 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 5.16 (dd, *J* = 14.4, 7.2 Hz, 1H), 5.04 (d, *J* = 6.7 Hz, 1H), 4.90 (dd, *J* = 8.7, 7.1 Hz, 1H), 4.41 (t, *J* = 8.3 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 139.8, 131.4 (q, *J* = 32 Hz), 127.1, 126.4 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 270 Hz), 74.5, 59.0; ^{19}F NMR(376 MHz, $CDCl_3$) δ ppm -62.9; IR(neat): 1346, 1182; HRMS (ESI) *m*/*z* calcd for $C_9H_8F_3NNaO_3S^+$ [M+Na]$^+$: 290.0075, obsd: 290.0077; HPLC analysis: ee = 94%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 9.99 min., Minor t = 15.32 min.



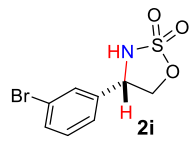
(*S*)-4-(4-Chlorophenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2g) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.35 (10: 1 DCM/EtOAc) to afford the desired product as white solid (98% yield). m.p. 130-131 °C. $[\alpha]^{20}_D$= +32.0º (*c* = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.45-7.35 (m, 4H), 5.06 (t, *J* = 7.5 Hz, 1H), 4.84 (dd, *J* = 8.8, 7.0 Hz, 1H), 4.83 (br. s, 1H). 4.40 (t, *J* = 10.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.7, 134.3, 129.8, 128.2, 74.7, 59.1; IR(neat) 1140; HRMS (ESI) *m/z* calcd for $C_8H_8ClNNaO_3S^+$ $[M+Na]^+$: 255.9811, obsd: 255.9814; HPLC analysis: ee = 95%, Chiral AD-H (5% isopropanol - 95% hexanes, 1.0 mL/min): Major t = 36.23 min., Minor t = 54.21 min.



(*S*)-4-(4-Bromophenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2h) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15:1 DCM/EtOAc), TLC R_f = 0.35 (10: 1 DCM/EtOAc) to afford the desired product as white solid (90% yield). m.p. 118-120 °C. $[\alpha]^{20}_D$= +26.0º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59-7.49 (m, 2H), 7.36-7.26 (m, 2H), 5.05-4.95 (m, 2H), 4.81 (dd, *J* = 8.8, 7.1 Hz, 1H), 4.36 (dd, *J* = 8.8, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 134.7, 132.5, 128.3, 123.6, 74.5, 58.9; IR (neat, cm^{-1}): 1178, 1055; HRMS (ESI) *m/z* calcd for $C_8H_8BrNNaO_3S^+$ $[M+Na]^+$ 299.9301, obsd: 299.9300; HPLC analysis: ee = 94%; Chiral AD-H (10% isopropanol - 90% hexanes, 0.7 mL/min): Major t = 18.93 min., Minor t = 26.81 min.

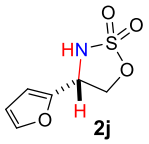


(*S*)-4-(3-Bromophenyl)-1,2,3-oxathiazolidine 2,2-dioxide (2i) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 4:1 Hexanes/Ethyl acetate), TLC R_f = 0.20 (4:1 Hexanes/EtOAc) to afford the desired product as white solid (92% yield). $[\alpha]^{20}_D$= +34.1º (*c* = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.58 (t, *J* = 1.7 Hz, 1H), 7.56-7.53 (m, 1H), 7.38-7.37 (m, 1H), 7.33-7.30 (m, 1H), 5.05 (t, *J* = 7.6 Hz, 1H), 4.85 (dd, *J* = 8.8, 7.1 Hz, 1H), 4.76 (s, 1H), 4.45-4.38 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 138.1, 132.8, 131.1, 129.9, 125.3, 123.6, 74.5, 59.0; IR (neat, cm^{-1}): 1214, 749;

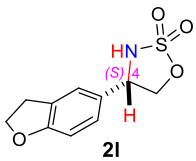


HRMS (ESI) *m/z* calcd for $C_8H_9BrNO_3S^+$ $[M+H]^+$ 277.9481, obsd: 277.9481; HPLC analysis: ee = 97%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 13.64 min., Minor t = 15.77 min.

(*S*)-4-(Furan-2-yl)-1,2,3-oxathiazolidine 2,2-dioxide (2j) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: DCM), TLC R_f = 0.27 (DCM) to afford the desired product as an oil (95% yield). $[\alpha]^{20}_D$= +9.8º (*c* = 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.48 (d, *J* = 1.0 Hz, 1H), 6.51 (d, *J* = 3.3 Hz, 1H), 6.42 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.11 (dd, *J* = 15.1, 8.1 Hz, 1H), 4.76 (dd, *J* = 8.5, 6.8 Hz, 1H), 4.73 (s, 1H), 4.66 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 146.9, 144.2, 111.2, 110.5, 73.0, 53.4; IR (neat, cm^{-1}): 1298; HRMS (ESI) *m/z* calcd for $C_6H_7NNaO_4S^+$ $[M+Na]^+$: 211.9993, obsd: 211.9994; HPLC analysis: ee = 94%. Chiral OD-H (7% isopropanol - 93% hexanes, 1.0 mL/min): Major t = 53.64 min., Minor t = 38.33 min.



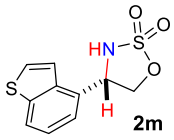
(*S*)-4-(Thiophen-2-yl)-1,2,3-oxathiazolidine 2,2-dioxide (2k) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: DCM), TLC R_f = 0.25 (DCM) to afford the desired product as white solid (98% yield). m.p. 62-64 °C. $[\alpha]^{20}_D$= +6.8º (*c* = 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (d, *J* = 5.1 Hz, 1H), 7.19-7.13 (m, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.28-5.35 (m, 1H), 4.95 (d, *J* = 6.3 Hz, 1H), 4.83 (dd, *J* = 8.6, 6.6 Hz, 1H), 4.54 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ ppm 137.4, 127.6, 127.1, 127.0, 75.3, 55,4; IR (neat, cm^{-1}): 1346, 1155; HRMS (ESI) *m/z* calcd for $C_6H_7NNaO_3S_2^+$ $[M+Na]^+$: 227.9765, obsd: 227.9769; HPLC analysis: ee = 97%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 15.02 min., Minor t = 16.21 min.



(*S*)-4-(2,3-Dihydrobenzofuran-5-yl)-1,2,3-oxathiazolidine 2,2-dioxide (2l) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 4:1 Hexanes/Ethyl acetate), to afford the desired product as white solid (67% yield) (TLC R_f = 0.25 (4:1 Hexanes/EtOAc). m.p. 131-133 °C. $[\alpha]^{20}_D$= +28.2º (*c* = 0.9,

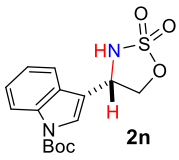
$CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ ppm 7.29 (s, 1H), 7.12 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.00 (dt, *J* = 8.7, 6.8 Hz, 1H), 4.78 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.61 (t, *J* = 8.7 Hz, 2H), 4.55 (d, *J* = 6.4 Hz, 1H), 4.44 (t, *J* = 8.8 Hz, 1H), 3.23 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 161.4, 128.8, 127.3, 127.0, 123.6, 110.0, 75.4, 71.8, 59.8, 29.6; IR (neat, cm^{-1}): 3269, 1615, 1494, 1346, 1184, 958, 789; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{12}NO_4S^+$ $[M+H]^+$: 242.0482, obsd: 242.0488; HPLC analysis: ee = 94%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 22.03 min., Minor t = 27.96 min. 4-[*S*] absolute configuration of the product was determined by X-ray crystallography.

(*S*)-4-(Benzo[b]thiophen-4-yl)-1,2,3-oxathiazolidine 2,2-dioxide (2m) was synthesized following



General Procedure B, and purified by flash silica gel chromatography (eluent: 4: 1 Hexanes/EtOAc), TLC R_f = 0.30 (3: 1 Hexanes/EtOAc) to afford the desired product as a colorless oil (97% yield). $[\alpha]^{20}_D$= +15.0º (*c* = 0.8, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ ppm 7.95 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 5.5 Hz, 1H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 5.56 (dd, *J* = 15.2, 7.2 Hz, 1H), 4.94 (dd, *J* = 8.6, 7.1 Hz, 1H), 4.79 (d, *J* = 6.6 Hz, 1H), 4.64 (t, *J* = 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CHCl_3$) δ ppm 141.4, 137.1, 129.5, 128.8, 124.6, 124.0, 122.6, 120.3, 74.1, 58.4; IR (neat, cm^{-1}): 1354, 1264, 730, 702; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{10}NO_3S_2^+$ $[M+H]^+$: 256.0097, obsd: 256.0092; HPLC analysis: ee = 81%. Chiral AS-H (20% isopropanol - 80% hexanes, 1.0 mL/min): Major t = 56.09 min., Minor t = 44.78 min.

(*S*)-*tert*-Butyl 3-(2,2-dioxido-1,2,3-oxathiazolidin-4-yl)-1H-indole-1-carboxylate (2n) was



synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.25 (10: 1 DCM/EtOAc) to afford the desired product as an off-white solid (98% yield). m.p. 134-136 °C. $[\alpha]^{20}_D$= +12.0º (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.16 (d, *J* = 8.3 Hz, 1H), 7.41-7.35 (m, 1H), 7.34-7.23 (m, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 5.40-5.23 (m, 1H), 4.85 (dd, *J* = 8.6, 6.7 Hz, 2H), 4.68 (t, *J* = 8.6 Hz, 1H), 1.68 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.1, 135.8, 127.3, 125.5, 124.6, 123.3, 118.8, 115.8, 114.2, 84.8, 73.5, 53.1, 28.1; IR (neat, cm^{-1}): 1735, 1373, 1190; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{18}N_2NaO_5S^+$ $[M+Na]^+$: 361.0834, obsd: 361.0832; HPLC analysis: ee = 89%.

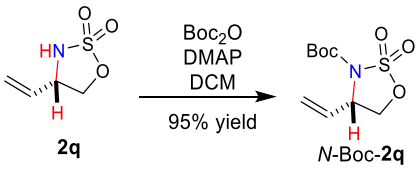
Chiral OD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 34.25 min., Minor t = 24.11 min.

(*S*,*E*)-4-Styryl-1,2,3-oxathiazolidine 2,2-dioxide (2o) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.45 (10: 1 DCM/EtOAc) to afford the desired product as white solid (89% yield). m.p. 160-162 °C. $[\alpha]^{20}_D$= +160.0º (*c* = 0.4, $CHCl_3$). ^{1}H NMR (600 MHz, Acetone-D_6) δ ppm 7.49 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 15.8 Hz, 1H), 6.81 (s, 1H), 6.36 (dd, *J* = 15.8, 7.6 Hz, 1H), 4.85-4.80 (m, 1H), 4.80-4.74 (m, 1H), 4.39 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (150 MHz, Acetone-D_6) δ ppm 136.9, 135.6, 129.6, 129.2, 127.6, 124.9, 74.9, 59.0; IR (neat, cm^{-1}): 1355, 1190; HRMS (ESI) *m*/*z* calcd for $C_{10}H_{11}NNaO_3S^+$ $[M+Na]^+$: 248.0357, obsd: 248.0361; HPLC analysis: ee = 91%. Chiral AD-H (7% isopropanol - 93% hexanes, 1.0 mL/min): Major t = 24.57 min., Minor t = 30.54 min.

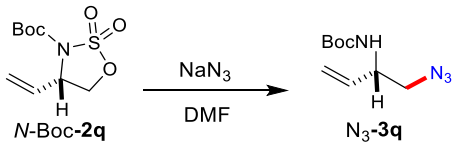
(*S*,*E*)-4-(But-1-en-1-yl)-1,2,3-oxathiazolidine 2,2-dioxide (2p) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.45 (10: 1 DCM/EtOAc) to afford the desired product as an oil (85% yield). $[\alpha]^{20}_D$= +54.0º (*c* = 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.92 (td, *J* = 15.3, 6.3 Hz, 1H), 5.39 (dd, *J* = 15.3, 7.9 Hz, 1H), 4.59 (dd, *J* = 8.3, 6.4 Hz, 1H), 4.44 (dd, *J* = 14.9, 7.9 Hz, 1H), 4.20 (t, *J* = 8.4 Hz, 1H), 2.12-2.04 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 140.7, 122.1, 74.4, 58.5, 25.2, 12.8; IR (neat, cm^{-1}):1356, 1176; HRMS (ESI) *m*/*z* calcd for $C_6H_{11}NNaO_3S^+$ $[M+Na]^+$: 200.0357, obsd: 200.0359; HPLC analysis: ee = 89%. Chiral AD-H (5 % isopropanol - 95% hexanes, 1.0 mL/min): Major t = 14.45 min., Minor t = 15.18 min.

(*S*)-4-Vinyl-1,2,3-oxathiazolidine 2,2-dioxide (2q) was synthesized following General Procedure B, starting from 0.3 mmol scale, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.45 (10: 1 DCM/EtOAc) to afford the desired product as an oil (67% yield). $[\alpha]^{20}_D$= -12.0º (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.84 (ddd, *J* = 17.3, 10.3, 7.2 Hz, 1H), 5.50-5.45 (m, 1H), 5.42 (dd, *J* = 8.6, 5.4 Hz, 1H), 4.69 (s, 1H), 4.67 (dd, *J* =8.2, 6.5

Hz, 1H), 4.55-4.47 (m, 1H), 4.27 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 131.9, 121.9, 73.9, 58.6; IR (neat, cm^{-1}): 1346, 1182; HRMS (ESI) *m/z* calcd for $C_4H_7NNaO_3S^+$ $[M+Na]^+$: 172.0044, obsd: 172.0043.



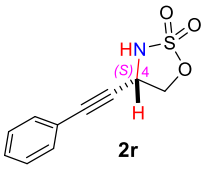
***tert*-Butyl (*S*)-4-vinyl-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide (*N*-Boc-2q)** was synthesized according to the following procedure. At 0 ºC, $(Boc)_2O$ (49 mg, 1.5 equiv) and DMAP (2 mg) were added to a solution of **2q** (30 mg, 0.15 mmol) in anhydrous DCM (2 mL). The reaction mixture was stirred for 30 min then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product *N*-Boc-**2q** as white solid (95% yield) (TLC R_f = 0.43 (8: 1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.92 (ddd, *J* = 17.0, 9.8, 7.3 Hz, 1H), 5.46 (d, *J* = 17.0 Hz, 1H), 5.41 (d, *J* = 10.3 Hz, 1H), 4.78-4.75 (m, 1H), 4.70 (dd, *J* = 8.7, 6.6 Hz, 1H), 4.30 (dd, *J* = 9.1, 2.5 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 148.4, 132.3, 120.3, 85.7, 70.1, 59.4, 28.1; IR (neat, cm^{-1}): 1710, 1334, 1210, 1201, 1148, 805; HRMS (DART) m/z calcd for $C_9H_{19}N_2O_5S^+$ $[M+NH_4]^+$: 267.1009, obsd: 267.1014.



***tert*-Butyl (*S*)-(1-azidobut-3-en-2-yl)carbamate (N$_3$-3q)** was synthesized according to the following procedure. NaN_3 (28.2 mg, 0.43 mmol) was added to a stirred solution of *N*-Boc-**2q** (0.14 mmol) in DMF (0.8 mL) at rt. After 24 h, the reaction mixture was stirred for 30 min between ether (2 mL) and 1N citric acid (5 mL). The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product N$_3$-**3q** as colorless oil (97%), TLC R_f = 0.33 (8:1 Hexanes/EtOAc). $[\alpha]^{20}_D$= -42.6º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.87-5.76 (m, 1H), 5.29 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 4.76 (br.s, 1H), 4.34 (br.s, 1H), 3.50-3.40 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 156.2, 135.5, 117.1, 80.1, 54.8, 52.4, 28.5; IR

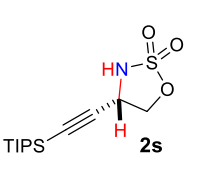
(neat, cm^{-1}): 3327, 2101, 1706, 1507, 1172; HRMS (DART) m/z calcd for $C_9H_{17}N_4O_2^+$ $[M+H]^+$: 213.1346, obsd: 213.1355; HPLC analysis: ee = 80%. Chiral IC (2% isopropanol - 98% hexanes, 1.0 mL/min): Major t = 16.04 min., Minor t = 13.20 min.

(*S*)-4-(Phenylethynyl)-1,2,3-oxathiazolidine 2,2-dioxide (2r) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: DCM), TLC R_f = 0.40 (DCM) to afford the desired product as white solid (94% yield). m.p. 65-67 °C. $[\alpha]^{20}_D$= -9.6º (*c* = 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52-7.39 (m, 2H), 7.38-7.30 (m, 3H), 4.97-4.84 (m, 1H), 4.78 (dd, *J* = 8.3, 6.5 Hz, 1H), 4.64-4.58 (m, 1H), 4.49 (t, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 131.9, 129.6, 128.5, 120.6, 88.4, 80.8, 74.2, 47.9; IR (neat, cm^{-1}): 2185, 1355, 1187; HRMS (ESI) *m/z* calcd for $C_{10}H_9NNaO_3S^+$ $[M+Na]^+$: 246.0201, obsd: 246.0203; HPLC analysis: ee = 97%. Chiral AD-H(10% isopropanol - 90% hexanes, 0.7 mL/min): Major t = 16.43 min., Minor t =18.73 min. 4-[*S*] absolute configuration of the product was determined by X-ray crystallography.



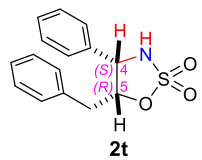
2r

(*S*)-4-((Triisopropylsilyl)ethynyl)-1,2,3-oxathiazolidine 2,2-dioxide (2s) was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: DCM), TLC R_f = 0.60 (DCM) to afford the desired product as a colorless oil (90% yield). $[\alpha]^{20}_D$= -4.0º (*c* = 2.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 4.84-4.65 (m, 2H), 4.63-4.45 (m, 1H), 4.43-4.36 (m, 1H), 1.09-1.05 (m, 21H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 98.5, 91.5, 74.5, 47.8, 18.4, 10.9; IR(neat): 2180, 1380, 1180; HRMS (ESI) *m/z* calcd for $C_{13}H_{25}NNaO_3SSi^+$ $[M+Na]^+$: 326.1222, obsd: 326.1223; HPLC analysis: ee = 93%. Chiral AD-H (5% isopropanol - 95% hexanes, 1.0 mL/min): Major t = 5.83 min., Minor t = 5.03 min.



2s

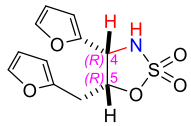
Compound 2t was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 4: 1 Hexanes/EtOAc), TLC R_f = 0.30 (3: 1 Hexanes/EtOAc) to afford product **2t** as a white solid (68% yield; 99% de). m.p. 184-186 °C. $[\alpha]^{20}_D$= +33.0º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, Acetone-D_6) δ ppm 7.59 (d, *J* = 7.3 Hz,



2t

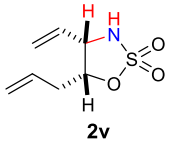
2H), 7.47 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.44-7.40 (m, 1H), 7.38 (br. s, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 5.41 (ddd, *J* = 10.5, 6.0, 3.1 Hz, 1H), 5.32 (d, *J* = 6.0 Hz, 1H), 2.67 (dd, *J* = 14.8, 3.0 Hz, 1H), 2.56 (dd, *J* = 14.8, 10.5 Hz, 1H); ^{13}C NMR (150 MHz, Acetone-D_6) δ ppm 137.6, 137.1, 130.0, 129.5, 129.4, 129.3, 128.7, 127.6, 87.8, 63.7, 37.5; IR (neat, cm^{-1}): 3236, 2161, 1737, 1181; HRMS (ESI) *m/z* calcd for $C_{15}H_{14}NO_3S^-$ [M-H]$^-$: 288.0689, obsd: 288.0689; HPLC analysis: ee = 99%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 19.26 min., Minor t = 22.69 min. 4-[*S*], 5-[*R*] absolute configuration of the product was determined by X-ray crystallography.

Compound 2u was synthesized following General Procedure B, and purified by flash silica gel chromatography (4:1 Hexanes/Ethyl acetate), TLC R_f = 0.25 (4:1 Hexanes/Ethyl acetate) to afford the desired product as white solid (92% yield; 99% de). m.p. 85-87 °C. $[\alpha]^{20}_D$= +2.7° (*c* =1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.48 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.33-7.30 (m, 1H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.43 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.28 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.08-6.05 (m, 1H), 5.30 (dt, *J* = 8.5, 5.5 Hz, 1H), 5.06 (d, *J* = 5.8 Hz, 1H), 4.86 (s, 1H), 2.99 (dd, *J* = 15.8, 8.5 Hz, 1H), 2.79 (dd, *J* = 15.8, 5.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 148.7, 147.4, 143.9, 142.2, 111.2, 111.0, 110.7, 108.0, 83.4, 57.0; IR (neat, cm^{-1}): 3285, 2980, 1347, 1185, 907, 734; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}NO_5S^+$ [M+H]$^+$: 270.0431, obsd: 270.0427; HPLC analysis: ee = 98%. Chiral AD-H (7% isopropanol - 93% hexanes, 1.0 mL/min): Major t = 27.99 min., Minor t = 32.69 min. 4-[*R*], 5-[*R*] absolute configuration of the product was determined by X-ray crystallography.



2u

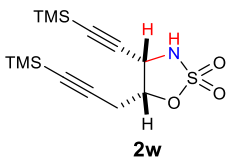
Compound 2v was synthesized following General Procedure B, and purified by flash silica gel chromatography (4:1 Hexanes/Ethyl acetate), TLC R_f = 0.25 (4:1 Hexanes/Ethyl acetate) to afford the desired product as colorless oil (84% yield; 99% de). $[\alpha]^{20}_D$= -16.0° (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.93 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.78 (ddt, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.47 (d, *J* = 9.6 Hz, 1H), 5.46-5.44 (m, 1H), 5.23 (dt, *J* = 6.2, 1.2 Hz, 1H), 5.20 (t, *J* = 1.2 Hz, 1H), 4.92 (dt, *J* = 8.6, 5.4 Hz, 1H), 4.70 (s, 1H), 4.44-4.35 (m, 1H), 2.64-



2v

2.56 (m, 1H), 2.43-2.35 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 131.2, 130.4, 121.8, 119.8, 85.6, 62.1, 34.2; IR (neat, cm^{-1}): 3261, 1738, 1348, 1186; HRMS (ESI) *m/z* calcd for $C_7H_{12}NO_3S^+$ $[M+H]^+$: 190.0532, obsd: 190.0533. Ee was determined to be 98% by derivatization into **3r** (for the detailed synthesis of **3r**, please see the section for ring opening of *N*-Boc-**2v**).

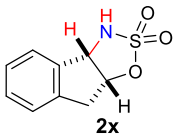
Compound 2w was synthesized following General Procedure B on 0.2 mmol scale, and purified by



2w

flash silica gel chromatography (7:1, Hexanes: Ethyl acetate), TLC R_f = 0.35 (7: 1 Hexanes: Ethyl acetate) to afford the desired product as colorless oil (84% yield; 99% de). $[\alpha]^{20}_D$= +17.1° (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 4.90-4.81 (m, 2H), 4.74 (dd, *J* = 8.8, 6.2 Hz, 1H), 2.87 (d, *J* = 5.0 Hz, 2H), 0.22 (s, 9H), 0.18 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 99.6, 96.7, 95.1, 90.1, 82.0, 51.4, 23.2, -0.1, -0.4; IR (neat, cm^{-1}): 3270, 2960, 2182, 1410, 1250, 1193, 840; HRMS (ESI) *m/z* calcd for $C_{13}H_{24}NO_3SSi_2^+$ $[M+H]^+$: 330.1010, obsd: 330.1018; HPLC analysis: ee = 98%. Chiral AD-H (4% isopropanol - 96% hexanes, 1.0 mL/min): Major t = 7.44 min., Minor t = 6.77 min.

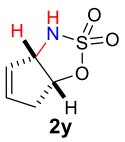
Compound 2x was synthesized following General Procedure B, and purified by flash silica gel



2x

chromatography (eluent: 15:1 DCM/EtOAc), TLC R_f = 0.45 (10: 1 DCM/EtOAc) to afford the desired product as white solid (95% yield; 99% de). m.p. 130-131 °C. $[\alpha]^{20}_D$= -129.0° (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, Acetone-D_6) δ ppm 7.42 (d, *J* = 7.2 Hz, 1H), 7.37-7.25 (m, 3H), 7.02 (s, 1H), 5.63 (td, *J* = 6.3, 1.5 Hz, 1H), 5.46 (d, *J* = 6.0 Hz, 1H), 3.49 (dd, *J* = 18.0, 6.3 Hz, 1H), 3.31 (d, *J* = 17.9 Hz, 1H); ^{13}C NMR (150 MHz, Acetone-D_6) δ ppm 140.9, 130.1, 128.4, 126.5, 126.0, 108.4, 87.1, 65.3, 38.2; IR (neat, cm^{-1}): 1155; HRMS (ESI) *m/z* calcd for $C_9H_9NNaO_3S^+$ $[M+Na]^+$: 234.0195, obsd 234.0197; HPLC analysis: ee = 98%. Chiral AD-H (7% isopropanol - 93% hexanes, 1.0 mL/min): Major t = 45.69 min., Minor t = 55.40 min.

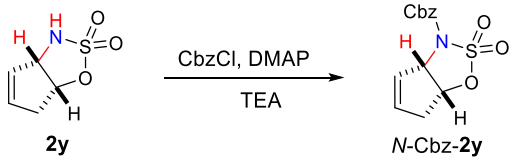
Compound 2y was synthesized following General Procedure B, and purified by flash silica gel



2y

chromatography (4:1 Hexanes/Ethyl acetate), TLC R_f = 0.35 (4:1 Hexanes/Ethyl acetate) to afford the desired product as colorless oil (93% yield; 99% de) $[\alpha]^{20}_D$= -5.2° (*c* = 1.0, $CHCl_3$);

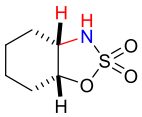
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.06-5.92 (m, 1H), 5.77-5.68 (m, 1H), 5.27 (td, *J* = 6.2, 2.5 Hz, 1H), 4.83-4.73 (m, 1H), 4.34 (s, 1H), 2.87-2.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 134.1, 128.1, 83.8, 65.6, 38.6; IR (neat, cm^{-1}): 1365, 1194, 903, 725; HRMS (ESI) *m/z* calcd for $C_5H_8NO_3S^+$ $[M+H]^+$: 162.0219, obsd: 162.0222.



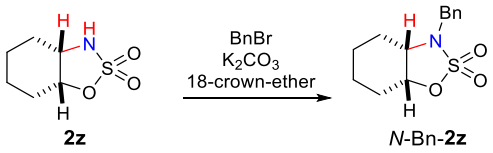
2y *N*-Cbz-**2y**

Compound *N*-Cbz-**2y** was prepared according to the following procedure. To a solution of (3a*S*,6a*R*)-3,3a,6,6a-tetrahydrocyclopenta[d][1,2,3]oxathiazole 2,2-dioxide **(2y)** (16.2 mg, 0.1 mmol, 1.0 equiv) in THF (0.4 mL); DMAP (12.0 mg, 0.1 mmol, 1.0 equiv), Et_3N (278 µL, 2.00 mmol, 20 equiv), and benzyl chloroformate (162 mg, 0.95 mmol, 9.5 equiv) were added and reaction was stirred for 2h. The solvent was then removed and the residue was purified by flash silica gel chromatography (eluent: 4:1 Hexanes/EtOAc) to afford product *N*-Cbz-**2y** as colorless oil (64%), TLC R_f = 0.30 (4:1 Hexanes/EtOAc). $[\alpha]^{20}_D$= +135.0º (*c* = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38-7.25 (m, 5H), 6.00-5.94 (m, 1H), 5.87 (dd, *J* = 5.8, 1.7 Hz, 1H), 5.31-5.23 (m, 3H), 5.11 (dd, *J* = 6.0, 1.2 Hz, 1H), 2.82-2.72 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 150.2, 134.6, 132.7, 128.9, 128.8, 128.1, 127.6, 80.6, 69.5, 66.7, 37.9; IR (neat, cm^{-1}): 1706, 1214, 748; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO_5S^+$ $[M+H]^+$: 296.0587, obsd: 296.0588; HPLC analysis: ee = 97%. Chiral ODH (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 24.00 min., Minor t = 21.99 min.

Compound 2z was synthesized following General Procedure B starting from 1.0 mmol scale, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.40 (10: 1 DCM/EtOAc) to afford the desired product as a colorless oil (79% yield; 99% de). $[\alpha]^{20}_D$= +11.0º (*c* = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.88 (q, *J* = 4.6 Hz, 1H), 4.63 (s, 1H), 3.84-3.78 (m, 1H), 2.28-2.10 (m, 1H), 2.01-1.87 (m, 2H), 1.87-1.74 (m, 1H), 1.74-1.59 (m, 2H), 1.54-1.41 (m, 1H), 1.38-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 84.0, 56.4, 27.5, 27.3, 21.4, 19.6; IR (neat, cm^{-1}): 1348, 1185; HRMS (ESI) *m/z* calcd for $C_6H_{11}NNaO_3S^+$ $[M+Na]^+$: 200.0357, obsd: 200.0353.



2z



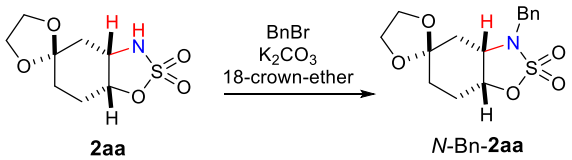
2z *N*-Bn-**2z**

Compound *N*-Bn-**2z** was prepared according to the following procedure. To a solution of **2z** (10 mg) in CH_3CN (1 mL) was added 18-crown-ether (10 mg), BnBr (20 mg) and powdered K_2CO_3 (60 mg). The reaction mixture was vigorously stirred for 1 hour prior to being filtered. The filtrate was concentrated in vacuum and the crude product was purified by flash column chromatography (4:1 Hexanes/Ethyl acetate) to afford the product *N*-Bn-**2z** (67% yield). $[\alpha]^{20}_D$= +21.0º (*c* = 0.7, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.52-7.28 (m, 5H), 4.87 (dd, *J* = 8.3, 4.1 Hz, 1H), 4.33 (d, *J* = 14.5 Hz, 1H), 4.21 (d, *J* = 14.5 Hz, 1H), 3.46-3.36 (m, 1H), 2.32-2.17 (m, 1H), 1.90-1.76 (m, 2H), 1.75-1.38 (m, 4H), 1.20-0.98 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ ppm 136.2, 128.9, 128.6, 128.4, 80.7, 58.4, 48.1, 27.8, 25.2, 21.4, 19.8; IR (neat, cm^{-1}): 1245, 1160; HRMS (ESI) *m/z* calcd for $C_{13}H_{17}NNaO_3S^+$ $[M+Na]^+$: 290.0827, obsd: 290.0830; HPLC analysis: ee = 94%. Chiral AD-H (10% isopropanol - 90% hexanes, 0.7 mL/min): Major t = 15.91 min., Minor t = 14.20 min.

N-Bn-**2z**

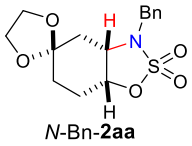
Compound 2aa was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/EtOAc), TLC R_f = 0.30 (10: 1 DCM/EtOAc) to afford the desired product as a colorless oil (89% yield; 99% de). $[\alpha]^{20}_D$= +8.7º (*c* = 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.34 (d, *J* = 10.1 Hz, 1H), 4.84-4.71 (m, 1H), 4.14-4.08 (m, 1H), 4.05-3.82 (m, 4H), 2.34-2.07 (m, 3H), 2.00-1.96 (m, 1H), 1.79-1.74 (m, 1H), 1.58-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 106.7, 82.9, 64.9, 64.5, 56.2, 33.7, 29.9, 24.6; IR (neat, cm^{-1}): 1243, 1175; HRMS (ESI) *m/z* calcd for $C_8H_{13}NNaO_5S^+$ $[M+Na]^+$: 258.0407, obsd: 258.0410.

2aa



2aa *N*-Bn-**2aa**

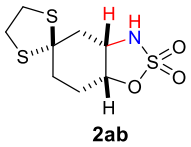
Compound *N*-Bn-**2aa** was prepared according to the following procedure. To a solution of **2aa** (10 mg)



N-Bn-**2aa**

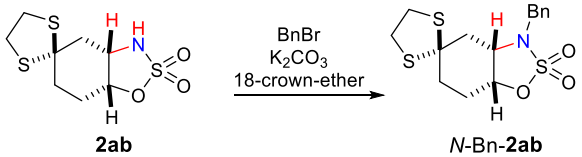
in CH_3CN (1 mL) was added 18-crown-ether (10 mg), BnBr (20 mg) and powdered K_2CO_3 (60 mg). The reaction mixture was vigorously stirred for 1 hour prior to being filtered. The filtrate was concentrated in vacuum and the crude product was purified by flash column chromatography (2:1 Hexanes/Ethyl acetate) to afford the product *N*-Bn-**2aa** as white solid (73% yield). $[\alpha]^{20}_D$= +122.0º (*c* = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39-7.32 (m, 5H), 4.88 (dd, *J* = 6.8, 3.3 Hz, 1H), 4.37, 4.11 (AB q, *J* = 14.4 Hz, each 1 H), 3.91 (dd, *J* = 9.0, 4.3 Hz, 2H), 3.85-3.67 (m, 2H), 3.57 (ddd, *J* = 10.8, 6.3, 4.2 Hz, 1H), 2.36-2.18 (m, 1H), 2.10 (dd, *J* = 13.2, 11.0 Hz, 1H), 2.02-1.73 (m, 3H), 1.67-1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 134.8, 128.8, 128.4, 128.3, 107.1, 79.1, 64.4, 58.2, 48.1, 33.8, 27.9, 24.5; IR(neat): 1176; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{19}NNaO_5S^+$ $[M+Na]^+$: 348.0876, obsd: 348.0880; HPLC analysis: ee = 95%. Chiral AD-H (20% isopropanol - 80% hexanes, 0.8 mL/min): Major t = 36.52 min., Minor t = 22.94 min.

Compound 2ab was synthesized following General Procedure B, and purified by flash silica gel



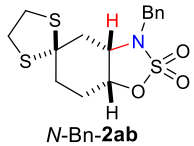
2ab

chromatography (4:1 Hexanes/Ethyl acetate), TLC R_f = 0.25 (4:1 Hexanes/Ethyl acetate) to afford product **2ab** as white solid (91% yield; 99% de). $[\alpha]^{20}_D$= +9.7º (*c* = 0.8, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.08 (d, *J* = 5.1 Hz, 1H), 4.94-4.87 (m, 1H), 3.97 (td, *J* = 10.2, 5.0 Hz, 1H), 3.51-3.18 (m, 4H), 2.50 (dd, *J* = 14.0, 9.7 Hz, 1H), 2.42-2.30 (m, 2H), 2.27-2.19 (m, 1H), 2.17-2.07 (m, 1H), 2.06-1.95 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 82.3, 64.6, 57.0, 42.5, 39.3, 38.6, 35.0, 27.3; IR (neat, cm^{-1}): 3276, 1357, 768; HRMS (ESI) *m*/*z* calcd for $C_8H_{14}NO_3S_3^+$ $[M+H]^+$: 268.0130, obsd: 268.0117.



2ab *N*-Bn-**2ab**

Compound *N*-Bn-**2ab** was prepared according to the following procedure. To a solution of **2ab** (16 mg)

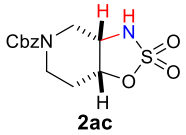


N-Bn-**2ab**

in CH_3CN (1 mL) was added 18-crown-ether (10 mg), BnBr (20 mg) and powdered K_2CO_3 (60 mg). The reaction mixture was vigorously stirred for 1 h prior to being filtered. The filtrate was concentrated in vacuum and the crude product was purified

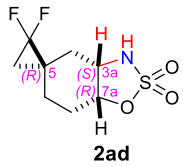
by flash column chromatography (4:1 Hexanes/Ethyl acetate) to afford the product as white solid (98% yield). m.p. 102-104 °C. $[\alpha]^{20}_{D}$= +36.0º (*c* = 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.43-7.31 (m, 5H), 4.94-4.84 (m, 1H), 4.40, 4.17 (AB q, *J* = 14.4 Hz, each 1 H), 3.56 (ddd, *J* = 10.3, 5.8, 4.2 Hz, 1H), 3.35-3.24 (m, 3H), 3.24-3.16 (m, 1H), 2.47 (dd, *J* = 13.5, 10.7 Hz, 1H), 2.38-2.27 (m, 2H), 2.20 (tt, *J* = 12.4, 6.0 Hz, 1H), 2.06-1.99 (m, 1H), 1.96 (ddt, *J* = 13.5, 4.7, 2.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 134.9, 129.0, 128.6, 128.5, 78.5, 64.6, 58.8, 48.5, 40.5, 39.4, 38.3, 35.1, 27.1; IR (neat, cm^{-1}): 1736, 1215, 772; HRMS (ESI) *m/z* calcd for $C_{15}H_{20}NO_3S_3^+$ $[M+H]^+$: 358.0600, obsd: 358.0591; HPLC analysis: ee >99%. Chiral AD-H (20% isopropanol - 80% Hexanes, 1.0 mL/min): Major t = 22.88 min., Minor t = 16.85 min.

Compound 2ac was synthesized following General Procedure B, and purified by flash silica gel chromatography (eluent: 15: 1 DCM/Ether), TLC R_f = 0.30 (10: 1 DCM/Ether) to afford the desired product as a colorless oil (83% yield; 99% de) (**note: this compound is acid-sensitive**). $[\alpha]^{20}_{D}$= -79.0º (*c* = 0.2, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ ppm 7.41-7.23 (m, 5H), 5.78-5.74 (m, 1H), 5.16-5.09 (s, 2H), 5.07-5.02 (m, 1H), 4.07-4.02 (m, 1H), 3.60-3.40 (m, 1H), 3.19-2.96 (m, 1H), 2.15-1.98 (m, 1H), 1.97-1.90 (m, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ ppm 136.6, 128.9, 128.7, 128.4, 128.0, 77.5, 68.0, 61.7, 34.7, 29.7, 26.1; IR (neat, cm^{-1}): 1738, 1365, 1228, 747; HRMS (ESI) *m/z* calcd for $C_{13}H_{16}N_2NaO_5S^+$ $[M+Na]^+$: 335.0672, obsd: 335.0677; HPLC analysis: ee = 99%. Chiral OD-H (20% isopropanol - 80% hexanes, 1.0 mL/min): Major t = 35.47 min., Minor t = 26.06 min.



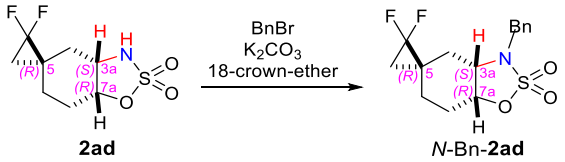
2ac

Compound 2ad was synthesized following General Procedure B with 4 mol % of [Co(**P14**)] at 40 ºC for 48 h, and purified by flash silica gel chromatography (eluent: 5:1 Hexanes/EtOAc), TLC R_f = 0.30 (3:1 Hexanes/EtOAc) to afford the desired product as a white solid (75% yield; 99% de). $[\alpha]^{20}_{D}$= -73.8º (*c* = 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.99 (t, *J* = 3.7 Hz, 1H), 4.91-4.78 (m, 1H), 3.83 (tq, *J* = 9.4, 4.4 Hz, 1H), 2.46-2.24 (m, 2H), 2.07-1.94 (m, 1H), 1.92-1.76 (m, 2H), 1.44 (ddt, *J* = 13.8, 4.9, 2.4 Hz, 1H), 1.22 (dddt, *J* = 24.7, 11.7, 7.9, 3.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 115.4 (t, *J* = 289.0 Hz), 83.5, 56.3, 30.9 (d, *J* = 5.0 Hz), 26.8,

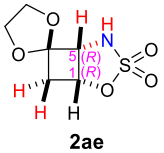


2ad

25.4 (t, *J* = 9.4 Hz), 22.6 (d, *J* = 4.7 Hz), 22.1 (t, *J* = 10.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ ppm -138.6 to -139.9 (m, 1F), -141.5 (ddt, *J* = 156.7, 11.5, 4.9 Hz, 1F); IR (neat, cm^{-1}): 3287, 2669, 1738, 1474, 1183, 818; HRMS (ESI) *m/z* calcd for $C_8H_{12}F_2NO_3S^+$ $[M+H]^+$: 240.0501, obsd: 240.0511.



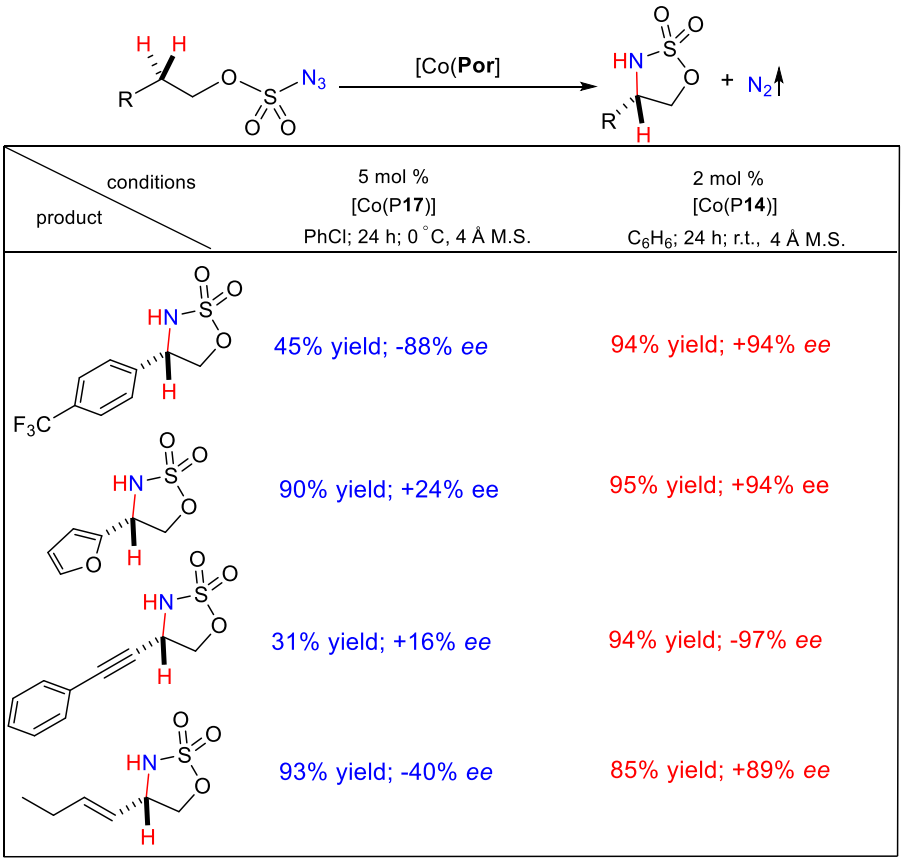
Compound *N*-Bn-**2ad** was prepared according to the following procedure. To a solution of **2ad** (10 mg) in CH_3CN (1 mL) was added 18-crown-ether (10 mg), BnBr (15 mg) and powdered K_2CO_3 (40 mg). The reaction mixture was vigorously stirred for 16 h prior to being filtered. The filtrate was concentrated in vacuum and the crude product was purified by flash column chromatography (5:1 Hexanes/Ethyl acetate) to afford the product *N*-Bn-**2ad** as white solid (79% yield). m.p. 101-103 °C. $[\alpha]^{20}_D$= +2.4° (*c* = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.43-7.21 (m, 5H), 4.95 (q, *J* = 3.6 Hz, 1H), 4.37, 4.17 (AB q, *J* = 14.3 Hz, each 1H), 3.45 (ddd, *J* = 10.5, 6.2, 4.3 Hz, 1H), 2.39-2.22 (m, 2H), 1.99 (dddd, *J* = 13.5, 10.4, 6.2, 3.2 Hz, 1H), 1.85-1.72 (m, 1H), 1.67 (dd, *J* = 13.9, 6.1 Hz, 1H), 1.45-1.34 (m, 1H), 1.19 (ddd, *J* = 12.5, 7.8, 3.7 Hz, 1H), 1.07 (ddd, *J* = 12.3, 7.8, 3.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 134.7, 129.1, 128.7, 128.6, 115.3 (t, *J* = 288.0 Hz), 79.7, 57.8, 48.5, 28.5 (d, *J* = 4.7 Hz), 26.9, 25.0 (t, *J* = 9.4 Hz), 22.8 (d, *J* = 4.9 Hz), 22.1 (t, *J* = 10.1 Hz); ^{19}F NMR (564 MHz, cdcl$_3$) δ ppm -139.0 to -139.8 (m), -141.64 (dddd, *J* = 155.7, 9.7, 6.5, 3.4 Hz); IR (neat, cm^{-1}): 2924, 1473, 1338, 1184, 829; HRMS (ESI) *m/z* calcd for $C_{15}H_{18}F_2NO_3S^+$ $[M+H]^+$: 330.0970, obsd: 330.0976; HPLC analysis: ee = 97%. Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 13.30 min., Minor t = 12.08 min. 3a-[*S*], 5-[*R*], 7a-[*R*] absolute configuration of the product was determined by X-ray crystallography.

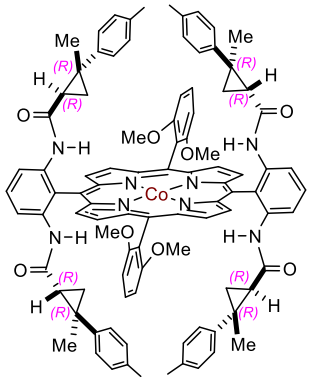


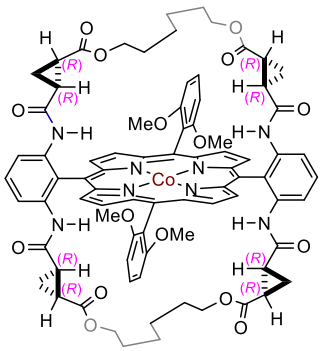
Compound 2ae was synthesized following General Procedure B, and purified by flash silica gel chromatography (2:1, Hexanes/Ethyl acetate), TLC R_f = 0.25 (1:1 Hexanes/Ethyl acetate) to afford the desired product as white solid (74% yield; 99% de). m.p. 67-69 °C. $[\alpha]^{20}_D$= -10.5° (*c* = 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.01 (br. s, 1H), 4.96 (td, *J* = 6.2, 3.1 Hz, 1H), 4.29 (d, *J* = 3.0 Hz, 1H), 4.08 (ddd, *J* = 7.8, 6.5, 5.0 Hz, 1H), 4.00 (dd, *J* = 14.0, 7.4

Hz, 1H), 3.93 (td, *J* = 7.1, 4.9 Hz, 1H), 3.88 (dd, *J* = 14.7, 7.3 Hz, 1H), 2.99 (ddd, *J* = 15.8, 6.4, 3.1 Hz, 1H), 2.93-2.77 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 103.1, 70.4, 65.7, 65.1, 64.1, 42.0; IR(neat, cm^{-1}): 3259, 1411, 1297, 926; HRMS (DART) *m/z* calcd for $C_6H_{10}NO_5S^+$ $[M+H]^+$ 208.0274, obsd: 208.0271. 1-[*R*], 5-[*R*] absolute configuration of the product was determined by X-ray crystallography. The ee was not determined due to the fact that no other catalysts showed reactivities to generate this product.

3.2. Figure S3. Ligand Effect (Open vs Bridged Catalysts) with Selected Substrates.







Note: The optimal bridged catalyst [Co(**P14**)] turned out essential for this broad C–H substrate scope. At the early stage of this study, the open catalyst [Co(**P17**)],[4] which was the derivative of [Co(**P7**)], was identified as a promising catalyst candidate. However, the amination with this catalyst only led to the effective enantiocontrol of benzylic C–H substrates. The amination of other types of C–H substrates did not provide high enough enantioselectivities. The project was opened out after we developed bridged catalysts. Please see the **Figure S3** for more details.

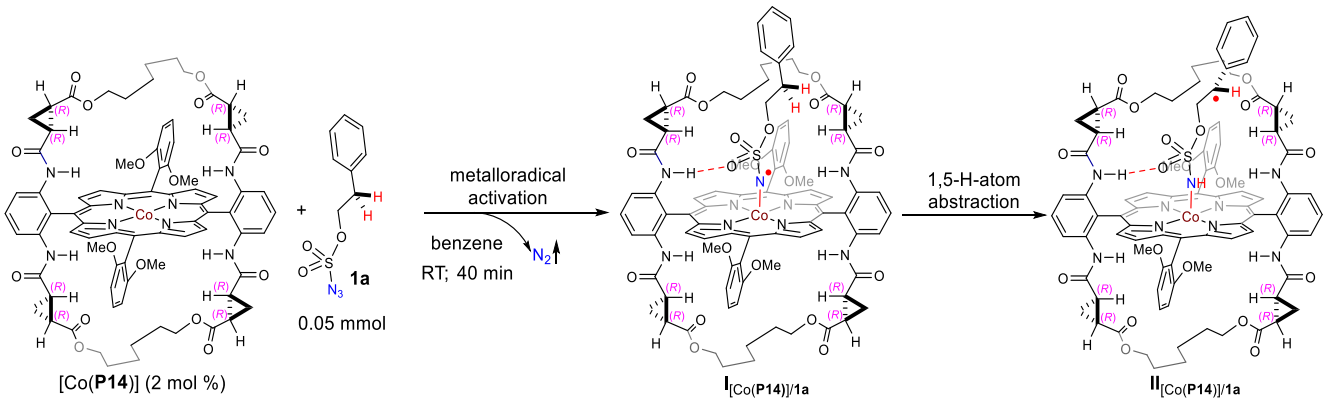
4. Mechanistic Studies on Co(II)-Catalyzed Radical 1,5-C–H Amination

4.1. EPR Studies

4.1.1. Procedure for EPR Experiment

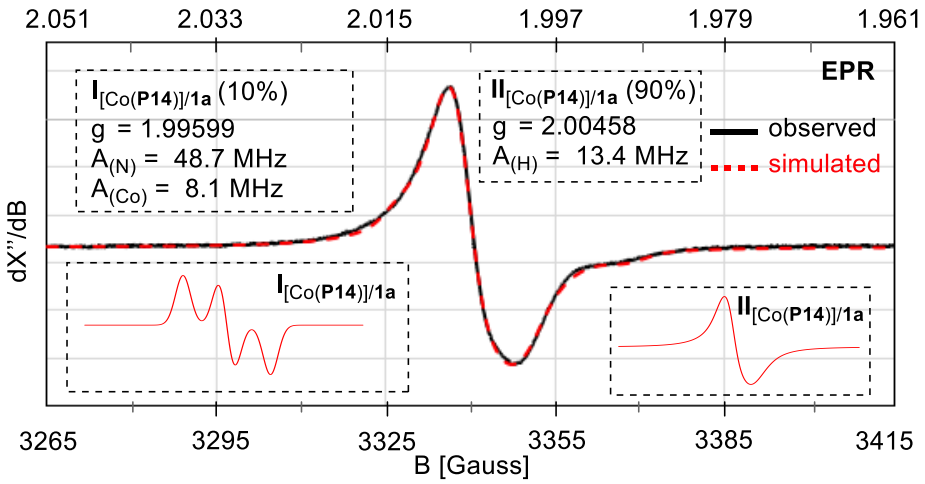
Catalyst [Co(**P14**)] (1.6 mg, 0.001 mmol) was placed into an oven-dried EPR tube. This EPR tube was then capped with a red rubber septum and was fasten with parafilm. The tube was evacuated and backfilled with nitrogen for three times. Then azide **1a** (12 mg, 0.05 mmol in 0.5 mL of anhydrous benzene) was added into this tube through a gas-tight syringe. The cap of EPR tube was further sealed with vacuum grease. The reaction mixture was shaken well at room temperature for 40 mins. Then the sample was ready for EPR experiment at room temperature.

4.1.2. Characterization of α-Co(III)-Aminyl Radical **I** and ε-Co(III)-Alkyl Radical **II** by EPR



X-band EPR spectra were recorded on a Bruker EMX-Plus spectrometer (Bruker BioSpin). Simulations of the EPR spectra were performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit in Xenon. Experimental X-band EPR isotropic spectra of α-Co(III)-Aminyl Radical $\mathbf{I}_{[Co(\mathbf{P14})]/\mathbf{1a}}$ and ε-Co(III)-alkyl radical $\mathbf{II}_{[Co(\mathbf{P14})]/\mathbf{1a}}$ in toluene were recorded at r.t. (Freq = 9.42731 GHz; mod. amp. = 1 G; microwave power = 63.25 mW) (**Figure S4**).

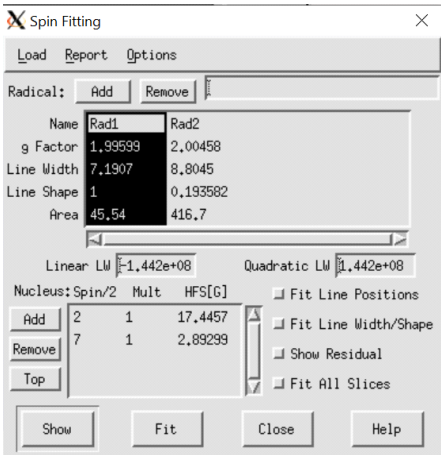
4.1.3. Figure S4. Experimental and Simulated X-Band EPR Spectra for α-Co(III)-Aminyl Radical **I**$_{[Co(\mathbf{P14})]/\mathbf{1a}}$ and ε-Co(III)-Alkyl Radical **II**$_{[Co(\mathbf{P14})]/\mathbf{1a}}$ in Benzene at RT

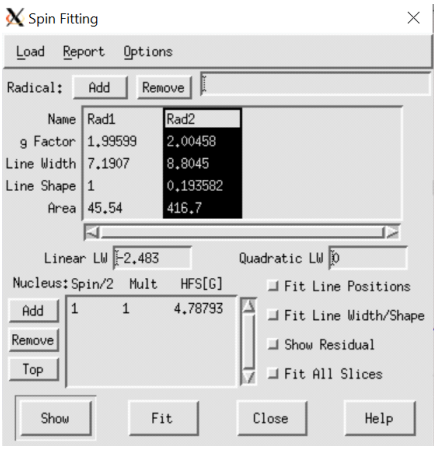


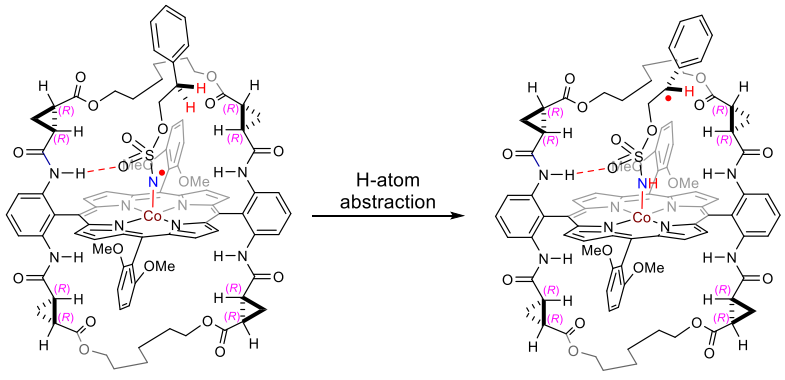
$A_{(N)}$: 17.446 x 1.99599 x 1.399611451 = 48.7 MHz

$A_{(Co)}$: 2.893 x 1.99599 x 1.399611451 = 8.1 MHz

$A_{(H)}$: 4.788 x 2.00458 x 1.399611451 = 13.4 MHz







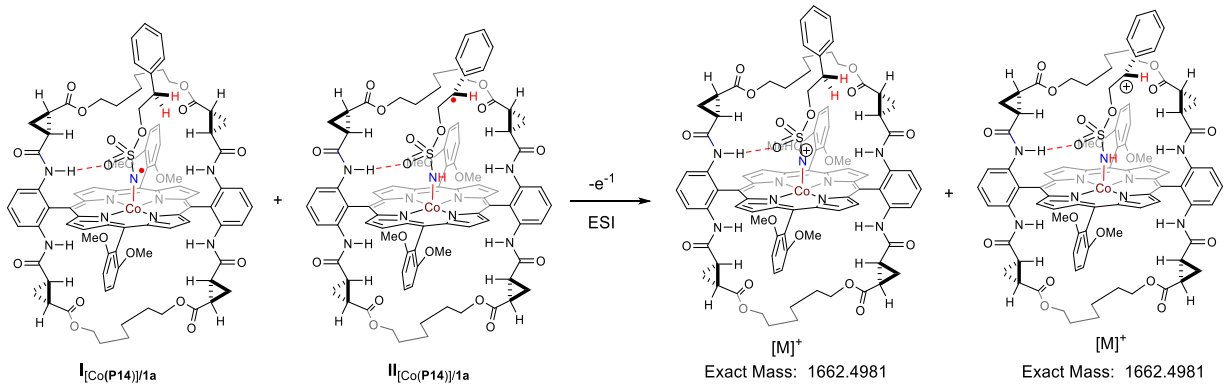
$I_{[Co(\mathbf{P14})]/\mathbf{1a}}$ (10%) $II_{[Co(\mathbf{P14})]/\mathbf{1a}}$ (90%)

From experimental: g_{iso}: 2.00522

From simulation: g_{iso}: 1.99599; 2.00458

In addition to the minor species of α-Co(III)-Aminyl Radical $\mathbf{I}_{[Co(P14)]/1a}$, the major species was proposed to be **ε-Co(III)-alkyl radical $\mathbf{II}_{[Co(P14)]/1a}$** generated through 1,5-HAA, which is consistent with our experimental observation of the high reactivity with [Co(**P14**)].

4.2. HRMS Studies

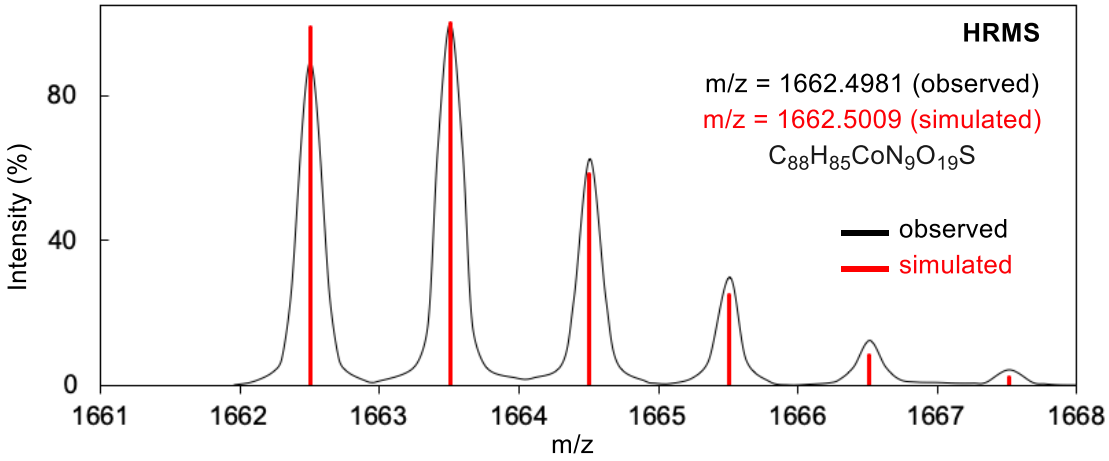


$\mathbf{I}_{[Co(P14)]/1a}$ $\mathbf{II}_{[Co(P14)]/1a}$

4.2.1. Procedure for HRMS Studies

Catalyst [Co(**P14**)] (1 mg) was dissolved into 1.0 mL of anhydrous benzene. Azide **1a** (0.1 mmol) was dissolved into 1.0 mL of anhydrous benzene. These two solutions were mixed in situ on a filter paper for direct detection of molecular ion peak by ESI-MS. The high-resolution mass spectra in the absence of any additives such as formic acids that commonly act as electron carriers for ionization allowed for the detection of the molecular ion signals corresponding to the α-Co(III)-aminyl radical $\mathbf{I}_{[Co(P14)]/1a}$ and ε-Co(III)-alkyl radical $II_{[Co(\mathbf{P14})]/\mathbf{1a}}$ ($[M]^+$ m/z = 1662.4981 (observed)), by the loss of one electron (**Figure S5**).

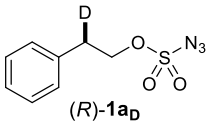
4.2.2. Figure S5. Observed and Simulated DART-MS Spectra with Isotope Distribution (Corresponding to [α-Co(III)-Aminyl Radical $\mathbf{I}_{[\mathbf{Co(P14)}]/\mathbf{1a}} - e^{-1}]^+$ and [ε-Co(III)-Alkyl Radical $\mathbf{II}_{[\mathbf{Co(P14)}]/\mathbf{1a}} - e^{-1}]^+$ ($[M]^+$ m/z = 1662.4981).



4.3. Kinetic Isotope Effect Experiment

4.3.1. Synthesis and Characterization of Optically Pure Alkoxysulfonyl Azides

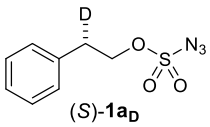
(*R*)-2-phenylethyl-2-d sulfurazidate ((*R*)-1a$_D$) was synthesized following General Procedure A, from



(*R*)-**1a$_D$**

(*R*)-2-phenylethan-2-d-1-ol (123 mg, 0.99 mmol)[12] and purified by flash silica gel chromatography (eluent: 40: 1 hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc) to afford 170 mg of desired product as a colorless oil (75% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.35 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 2H), 4.55 (d, *J* = 6.8 Hz, 2H), 3.09 (tt, *J* = 6.8, 3.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.5, 129.1, 129.0, 127.5, 75.0, 34.9 (t, *J* = 19.5 Hz); IR (neat, cm^{-1}): 2143, 1404, 1187.

(*S*)-2-phenylethyl-2-d sulfurazidate ((*S*)-1a$_D$) was synthesized following General Procedure A, from



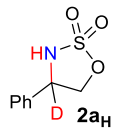
(*S*)-**1a$_D$**

(*S*)-2-phenylethan-2-d-1-ol (123 mg, 0.99 mmol)[12] and purified by flash silica gel chromatography (eluent: 40: 1 hexanes/EtOAc), TLC R_f = 0.65 (20:1 Hexanes/EtOAc) to afford 190 mg of desired product as a colorless oil (84% yield).

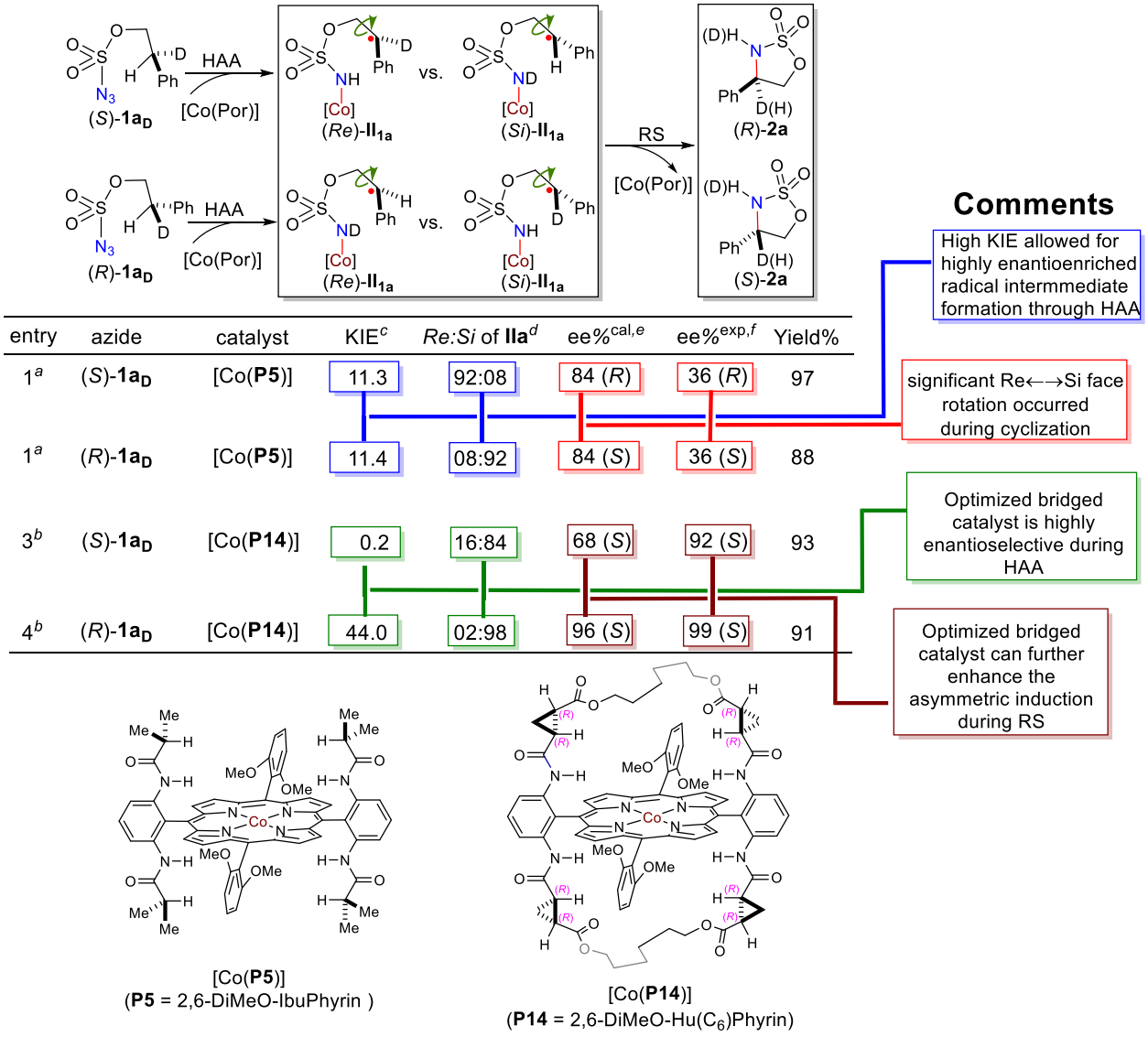
4.3.2. Procedure for KIE Studies and Characterization

An oven-dried Schlenk tube that was previously charged with catalyst [Co(**P5**)] or [Co(**P14**)] (0.002 mmol) and 4Å molecular sieves (20 mg), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum and approximately 0.5 mL of benzene was added, then azide **1a** (0.1 mmol), followed by the remaining benzene (total 1.0 mL). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The reaction mixture was then stirred for 24 hours at room temperature. After completion of the reaction, the solvent was removed and the reaction mixture was purified by flash column chromatography on silica gel (eluent: 4:1 Hexanes/EtOAc), TLC R_f = 0.35 (4:1 Hexanes/EtOAc) to afford to give the desired product **2a** as white solid. Please see **pages S330–S333** for detail on how to use integration of ^{1}H-NMR to determine KIE values. **Note:** ee values of **2a** were determined by chiral HPLC analysis, which offered no separation of (*R*)-**2a$_H$** from (*R*)-**2a$_D$** and (*S*)-**2a$_H$** from (*S*)-**2a$_D$**. Single crystal sample was obtained for the product **2a** (98% ee). [*S*] absolute configuration of the product was determined by X-ray crystallography (**pages S166–S168**). HPLC (Chiral AD-H (10% isopropanol - 90% hexanes, 1.0 mL/min) trace indicated that the retention time for *R*-enantiomer is t_{major} = 17.33 min., the *S*-enantiomer is t_{minor} = 19.59 min; see **pages S164–S165** and **pages S332–333** for the detailed spectrum and the distribution of enantiomers for the product **2a** for each reaction.

4-Phenyl-1,2,3-oxathiazolidine 2,2-dioxide-4-d (**2a$_H$**) was synthesized according to General Procedure B**,** starting with [Co(Por)] (0.002 mmol) and **1a$_D$** (0.1 mmol), and purified by flash column chromatography on silica gel (eluent: 4:1 Hexanes/EtOAc), TLC R_f = 0.35 (4:1 Hexanes/EtOAc) to afford **4-phenyl-1,2,3-oxathiazolidine 2,2-dioxide-4-*d* (2a$_H$)** together with **4-phenyl-1,2,3-oxathiazolidine 2,2-dioxide-3-*d* (2a$_D$)** as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.46-7.37 (m, 5H), 4.89 (br.s, 1H), 4.83 (d, *J* = 8.7 Hz, 1H), 4.44 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 135.4, 129.7, 129.5, 126.8, 75.1, 59.4 (t, *J* = 22.5 Hz); HRMS (DART) ($[M+H]^+$) Calcd. for $C_8H_9DNO_3S^+$ $[M+H]^+$: 201.0439, obsd: 201.0431; IR (neat, cm^{-1}): 3241, 1393, 1165, 734.



4.3.3. Table S1. Asymmetric Induction Mode Studies



entry	azide	catalyst	KIE[c]	*Re:Si* of **IIa**[d]	ee%[cal,e]	ee%[exp,f]	Yield%
1[a]	(*S*)-**1a**$_D$	[Co(**P5**)]	11.3	92:08	84 (*R*)	36 (*R*)	97
1[a]	(*R*)-**1a**$_D$	[Co(**P5**)]	11.4	08:92	84 (*S*)	36 (*S*)	88
3[b]	(*S*)-**1a**$_D$	[Co(**P14**)]	0.2	16:84	68 (*S*)	92 (*S*)	93
4[b]	(*R*)-**1a**$_D$	[Co(**P14**)]	44.0	02:98	96 (*S*)	99 (*S*)	91

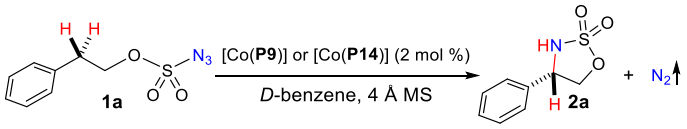
[Co(**P5**)]
(**P5** = 2,6-DiMeO-IbuPhyrin)

[Co(**P14**)]
(**P14** = 2,6-DiMeO-Hu(C_6)Phyrin)

[a] Carried out in benzene at 40 ºC for 24 h using 2 mol % [Co(Por)] on 0.10 mmol scale under N_2 in the presence of 4 Å MS; [azide **1a**$_D$] = 0.1 M; isolated yield. [b] Run at RT for 24 h. [c] Ratio of H:D determined by ^{1}H NMR spectroscopy. [d] Calculated based on the ratio of H:D. [e] ee of **2a** calculated on the basis of stereoretentive RS. [f] ee of **2a** determined by chiral HPLC analysis, which offered no separation of (*R*)-**2a**$_H$ from (*R*)-**2a**$_D$ and (*S*)-**2a**$_H$ from (*S*)-**2a**$_D$.

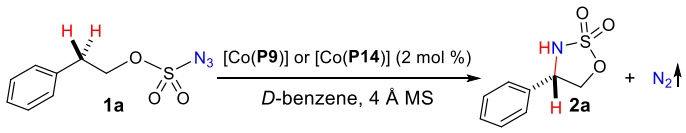
4.4 Kinetics Studies

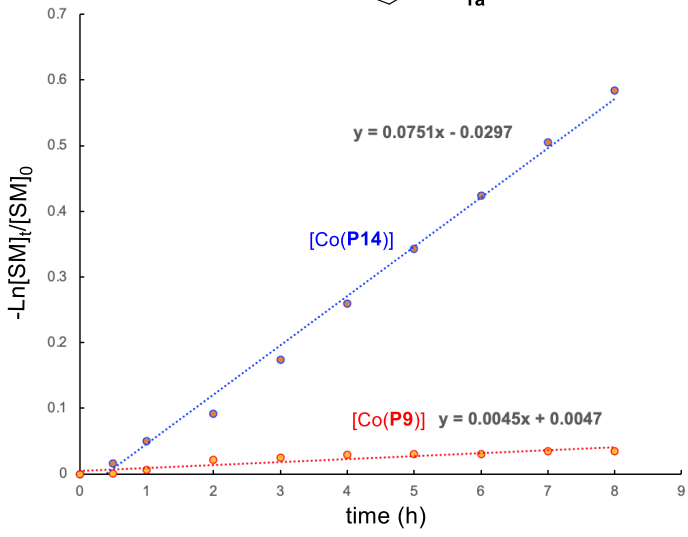
4.4.1 Procedure for Kinetics Studies



An oven-dried J-Young tube that was previously charged with catalyst [Co(**P9**)] or [Co(**P14**)] (0.001 mmol) and 4Å molecular sieves (10 mg), was evacuated and backfilled with argon gas. The Teflon screw cap was replaced with a rubber septum and azide **1a** (0.05 mmol) in 0.5 mL of degassed *D*-benzene was added via injection. The J-Young tube was then purged with argon for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The J-Young tube was then put into NMR instrument. The reaction was monitored via in-situ ^{1}H NMR (without stirring) for 8 hours. The ^{1}H NMR integration ratios between the starting materials **1a** and amination product **2a** were used to determine the yields and to calculate the ratios of $[SM]_t/[SM]_0$. The reaction rate constants (k_{obs} values) were determined through calculating the slopes of the least square lines for the plots of $-Ln([SM]_t/[SM]_0)$ vs. time.

4.4.2 Figure S6. Rate Plots of C–H Amination with [Co(**P9**)] and [Co(**P14**)]





	[Co(**P14**)]		[Co(**P9**]	
t (h)	Yield (%)	-Ln[SM]$_t$/[SM]$_0$	Yield (%)	-Ln[SM]$_t$/[SM]$_0$
0	0	0	0	0
0.5	1.54	0.0155	0.08	0.0008
1	4.88	0.0500	0.56	0.0056
2	8.75	0.0916	2.12	0.0214
3	15.95	0.1737	2.46	0.0249
4	22.85	0.2594	2.87	0.0291
5	29.02	0.3428	2.99	0.0304
6	34.55	0.4238	3.02	0.0306
7	39.68	0.5055	3.36	0.0342
8	44.22	0.5837	3.42	0.0348

[Co(**P14**)]: k_{obs} = 7.5x10^{-2}h^{-1} 7.5x10^{-2}h^{-1}/4.5x10^{-3}h^{-1} = 16.7

[Co(**P9**)]: k_{obs} = 4.5x10^{-3}h^{-1}

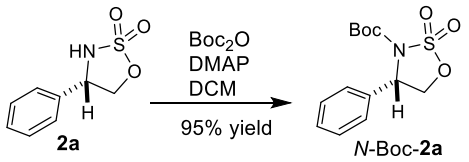
rate constant for [Co(**P14**)] is ~17 times of that for [Co(**P9**)]

According to these kinetics studies, the rate constant k_{obs} for the reaction catalyzed by [Co(**P14**)] is roughly 17 times of that for the reaction catalyzed by [Co(**P9**)].

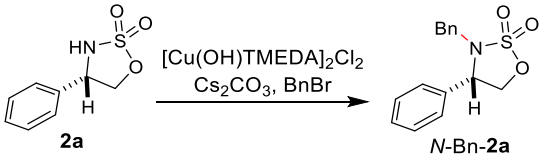
5. Synthesis of Chiral Amines

Note: for Boc-protected product, a mixture of rotamer exists for most of cases, therefore the compound peaks in ^{1}H-NMR are typically broad.

5.1. Ring-Opening by Carbon Nucleophiles

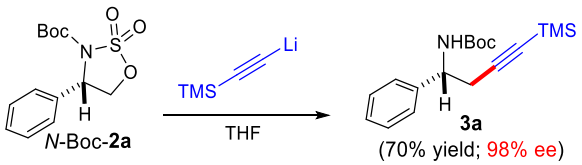


***tert*-Butyl (*S*)-4-phenyl-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide (*N*-Boc-2a)** was prepared according to the following procedure: at 0 ºC, Boc_2O (49 mg, 1.5 equiv) and DMAP (2 mg) were added to a solution of **2a** (30 mg, 0.15 mmol) in anhydrous DCM (2 mL). The reaction mixture was stirred for 30 min then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 8:1) to afford product *N*-Boc-**2a** as white solid (95% yield). m.p. 126-127 °C. $[\alpha]^{20}_D$= +29.0º (*c* = 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.46-7.35 (m, 5H), 5.28 (dd, *J* = 6.7, 4.2 Hz, 1H), 4.87 (dd, *J* = 9.3, 6.7 Hz, 1H), 4.41 (dd, *J* = 9.3, 4.2 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 148.4, 137.1, 129.4, 129.3, 126.3, 85.7, 71.9, 60.9, 28.0; IR (neat, cm^{-1}): 1684; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{17}NNaO_5S^+$ $[M+Na]^+$: 322.0725, obsd: 322.0726.



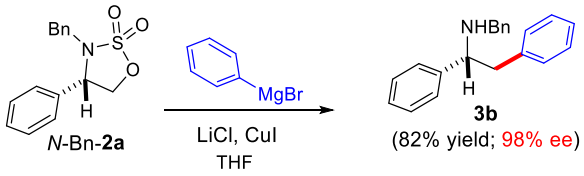
(*S*)-3-Benzyl-4-phenyl-1,2,3-oxathiazolidine 2,2-dioxide (*N*-Bn-2a) was prepared according to the following procedure: in a flame-dried flask, sulfamidate **2a** (0.45 mmol), $[Cu(OH)TMEDA]_2Cl_2$ (5 mol %) (10.5 mg, 0.02 mmol) and Cs_2CO_3 (294 mg, 0.9 mmol) were charged, and the flask was evacuated and back-filled with argon three times. The solids were dissolved in anhydrous CH_3CN (7 mL) at room temperature. To this suspension, benzyl bromide (160 µL, 1.36 mmol) was added slowly via syringe, and stirred for 6 h at room temperature. Then, the reaction mixture was filtered through a

celite pad, solids were washed with EtOAc (2 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product *N*-Bn-**2a** as colorless oil (80% yield), TLC R_f = 0.33 (8:1 Hexanes/EtOAc). **Known compound.**[13] $[\alpha]^{20}_D$= -92.0º (*c* = 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.41-7.37 (m, 3H), 7.36-7.32 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.17 (m, 2H), 4.68 (dd, *J* = 8.6, 7.0 Hz, 1H), 4.61-4.56 (m, 1H), 4.36 (t, *J* = 8.5 Hz, 1H), 4.28, 4.09 (AB q, *J* = 14.6 Hz, each 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 134.8, 133.8, 129.7, 129.4, 128.6, 128.4, 127.9, 72.7, 63.2, 49.4; IR (neat, cm^{-1}): 1456, 1342, 1182, 756, 696; HRMS (DART) *m/z* calcd for $C_{15}H_{16}NO_3S^+$ $[M+H]^+$: 290.0845, obsd: 290.0842.

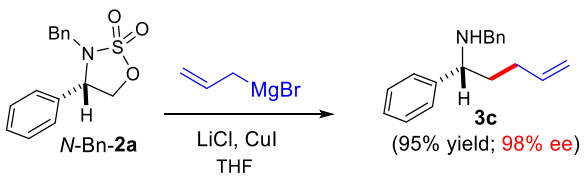


***tert*-Butyl (*R*)-(1-phenyl-4-(trimethylsilyl)but-3-yn-1-yl)carbamate (3a)** was prepared according to the following procedure: an oven-dried Schlenk tube was evacuated and backfilled with nitrogen gas. Under positive pressure of nitrogen, the Teflon screw cap was replaced with a rubber septum and the solution of ethynyltrimethylsilane (0.16 mmol) in THF (2 mL) was added. Then the reaction solution was cooled to -78 ºC, followed by the addition of *n*-BuLi (64 µL, 0.16 mmol, 2.5 M in hexanes). The reaction was stirred for 15 min, taken out of the ice-bath for 10 min, and then cooled back to -78 ºC. *N*-Boc-**2a** (0.1 mmol) in THF (2 mL) was added to this solution. The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The reaction mixture was stirred for 30 mins before being allowed to warm to 0 ºC over 1 h. The reaction was quenched by the addition of 1N citric acid (5 mL). Then the reaction mixture was stirred for 30 min. The aqueous layer was extracted with DCM (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 10:1 Hexanes/EtOAc) to afford product **3a** as colorless oil (70% yield), TLC R_f = 0.43 (8:1 Hexanes/EtOAc). $[\alpha]^{20}_D$= +21.2º (*c* = 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.39-7.25 (m, 5H), 5.14 (s, 1H), 4.85 (s, 1H), 2.79-2.52 (m, 2H), 1.43 (s, 9H), 0.12 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 156.2, 141.4, 128.5, 127.6, 126.5, 102.7, 88.3, 79.8, 53.0, 28.5, 28.2, 0.1; IR (neat, cm^{-1}): 2176, 1702, 1494, 841; HRMS (DART)

m/*z* calcd for $C_{18}H_{28}NO_2Si^+$ $[M+H]^+$: 318.1884, obsd: 318.1884; HPLC analysis: ee = 98%. Chiral IC (5% isopropanol - 95% hexanes, 1.0 mL/min): Major t = 4.78 min., Minor t = 5.08 min.

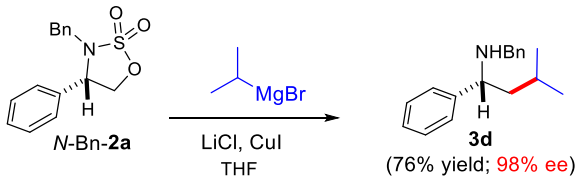


(*R*)-*N*-Benzyl-1,2-diphenylethan-1-amine (**3b**) was prepared according to the following procedure: an oven-dried Schlenk tube that was charged with CuI (1.3 mg, 0.007 mmol) and *N*-Bn-**2a** (20 mg, 0.07 mmol) was evacuated and backfilled with nitrogen three times. Under positive pressure of nitrogen, the Teflon screw cap was replaced with a rubber septum. LiCl (0.15 mg, 0.0035 mmol in stock solution of THF) and anhydrous THF (1.0 mL) were added and the reaciton mixture was cooled down to 0 ºC. To this solution, 2.5 M solution of PhMgBr in THF (86 µL, 0.17 mmol) was added slowly via syringe, and then stirred for 6 h at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (5 mL) and 1N citric acid (5 mL). Then the reaction mixture was stirred for 30 mins and tuned to pH value to 13.0 with 1 M of NaOH solution. The aqueous layer was extracted with DCM (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 4:1) to afford product **3b** as yellow oil (82% yield) (TLC R_f = 0.30 (Hexanes/EtOAc 4: 1). $[\alpha]^{20}_D$ = +20.4º (*c* = 0.5, $CHCl_3$); for HCl salt of **3b**: ^{1}H NMR (500 MHz, CD_3OD) δ ppm 7.48-7.39 (m, 8H), 7.39-7.34 (m, 2H), 7.18-7.12 (m, 3H), 6.99 (dd, *J* = 7.5, 1.9 Hz, 2H), 4.51 (dd, *J* = 11.3, 4.3 Hz, 1H), 4.17, 3.94 (AB q, *J* = 13.1 Hz, each 1H), 3.57 (dd, *J* = 13.1, 4.3 Hz, 1H), 3.24 (dd, *J* = 13.1, 11.3 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ ppm 135.1, 133.7, 130.9, 129.6, 129.5, 129.4, 129.1, 129.0, 128.9, 128.3, 128.1, 126.7; 64.2, 49.5, 39.1; IR (neat, cm^{-1}): 2920, 1494, 1453, 698; HRMS (DART) *m*/*z* calcd for $C_{21}H_{22}N^+$ $[M+H]^+$: 288.1747, obsd: 288.1751; HPLC analysis: ee = 98%. Chiral OJH (6% isopropanol - 94% hexanes, 0.8 mL/min): Major t = 14.34 min., Minor t = 19.84 min.



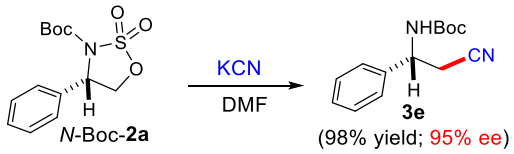
(*R*)-*N*-Benzyl-1-phenylpent-4-en-1-amine (**3c**) was prepared according to the following procedure:

an oven-dried Schlenk tube that was charged with CuI (1.3 mg, 0.007 mmol) and *N*-Bn-**2a** (20 mg, 0.07 mmol) was evacuated and backfilled with nitrogen three times. Under positive pressure of nitrogen, the Teflon screw cap was replaced with a rubber septum. LiCl (0.15 mg, 0.0035 mmol in stock solution of THF) and anhydrous THF (1.0 mL) was added and the reaciton mixture was cooled down to 0 ºC. To this solution, 1M solution of allylMgBr in THF (172 µL, 0.17 mmol) was added slowly via syringe, and then stirred for 6 h at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (5 mL) and 1N citric acid (5 mL). Then the reaction mixture was stirred for 30 mins and tuned to pH value to 13.0 with 1 M of NaOH solution. The aqueous layer was extracted with DCM (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 4:1) to afford product **3c** as yellow oil (95% yield) (TLC R_f = 0.30 (Hexanes/EtOAc 4: 1). $[\alpha]^{20}_D$ = +24.6º (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38-7.20 (m, 10H), 5.76 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 4.99-4.89 (m, 2H), 3.66-3.61 (m, 2H), 3.53 (d, *J* = 13.2 Hz, 1H), 1.99 (ddd, *J* = 23.5, 14.7, 7.9 Hz, 2H), 1.88-1.65 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 144.13, 140.8, 138.5, 128.6, 128.5, 128.3, 127.5, 127.2, 127.0, 114.8, 62.2, 51.7, 37.5, 30.7; IR (neat, cm^{-1}): 1265, 904, 724; HRMS (DART) *m/z* calcd for $C_{18}H_{22}N^+$ $[M+H]^+$: 252.1746, obsd: 252.1746; HPLC analysis: ee = 98%. Chiral IA (3% isopropanol - 97% hexanes, 0.5 mL/min): Major t = 9.44 min., Minor t = 10.80 min.

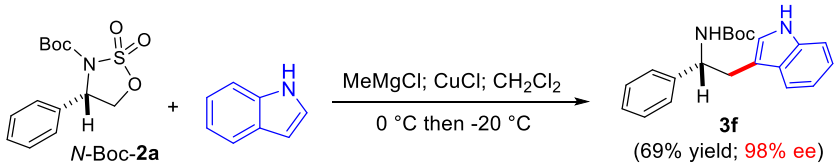


(*R*)-*N*-Benzyl-3-methyl-1-phenylbutan-1-amine (3d) was prepared according to the following procedure: an oven-dried Schlenk tube that was charged with CuI (2.9 mg, 0.015 mmol) and *N*-Bn-**2a** (44 mg, 0.15 mmol) was evacuated and backfilled with nitrogen three times. Under positive pressure of nitrogen, the Teflon screw cap was replaced with a rubber septum. LiCl (0.15 mg, 0.0035 mmol in stock solution of THF) and anhydrous THF (1.5 mL) were added and the reaciton mixture was cooled down to 0 ºC. To this solution, 1M solution of iPrMgBr in THF (382 µL, 0.38 mmol) was added slowly via syringe, and then reaction mixtures were stirred for 6 h at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (5 mL) and 1N citric acid (5 mL). Then the reaction mixture

was stirred for 30 min and tuned to pH value to 13.0 with 1 M of NaOH solution. The aqueous layer was extracted with DCM (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 4:1 Hexanes/EtOAc) to afford product **3d** as yellow oil (76% yield), TLC R_f = 0.30 (4:1 Hexanes/EtOAc). $[\alpha]^{20}_D$ = +18.9º (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.40-7.17 (m, 5H), 3.75-3.63 (m, 1H), 3.63, 3.51 (AB q, *J* = 13.1 Hz, each 1H), 1.61-1.55 (m, 2H), 1.55-1.44 (m, 2H), 0.88 (d, *J* = 6.0 Hz, 3H), 0.82 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 144.8, 140.9, 128.5, 128.4, 128.3, 127.4, 127.0, 126.9, 60.6, 51.7, 47.9, 25.1, 22.9, 22.8; IR (neat, cm^{-1}): 2953, 1493, 1452, 1126; HRMS (DART) *m*/*z* calcd for $C_{18}H_{24}N^+$ $[M+H]^+$: 254.1903, obsd: 254.1910; HPLC analysis: ee = 98%. Chiral OJH (1% isopropanol - 99% hexanes, 1.1 mL/min): Major t = 17.79 min., Minor t = 10.39 min.

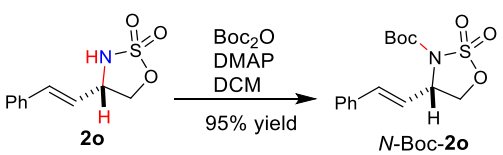


(*S*)-*tert*-Butyl (2-cyano-1-phenylethyl)carbamate (3e) was prepared according to the following procedure: KCN (10.4 mg, 0.16 mmol) was added to a stirred solution of *N*-Boc-**2a** (0.10 mmol) in DMF (0.8 mL) at rt. After 4 h, the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and a H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product **3e** as white solid (98% yield), TLC R_f = 0.43 (4:1 Hexanes/EtOAc). **Known compound.**[14] m.p.110-112 °C. $[\alpha]^{20}_D$= +34.0º (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53-7.31 (m, 5H), 5.23-4.98 (m, 2H), 3.09-2.98 (m, 1H), 2.97-2.83 (m, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 154.8, 138.4, 129.2, 128.7, 126.2, 116.9, 80.6, 51.2, 28.2, 25.2; IR (neat, cm^{-1}): 1684; HPLC analysis: ee = 95%. Chiral AD-H (10% isopropanol - 90% hexanes, 0.8 mL/min): Major t = 14.26 min., Minor t =17.60 min.



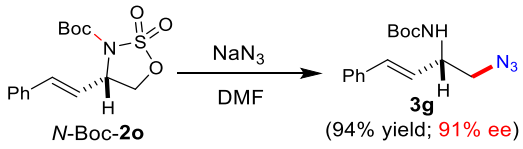
***tert*-Butyl (*R*)-(2-(1H-indol-3-yl)-1-phenylethyl)carbamate (3f)** was prepared according to the following procedure: an oven-dried Schlenk tube that was previously charged with mixture of indole (16 mg, 0.13 mmol) and CuCl (11 mg, 0.11 mmol) in CH_2Cl_2 (0.3 mL) was cooled down to 0 ºC. Then MeMgCl (3.0 M in THF, 36 µL, 0.11 mmol) was added over 10 min at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 h and cooled to -20 ºC. A solution of *N*-Boc-**2a** (25 mg, 0.08 mmol) in CH_2Cl_2 (0.2 mL) was added into the reaction mixture over 30 min at -20 ºC. The reaction mixture was then stirred at -20 ºC for 18 h, quenched with 10% aqueous citric acid (1.0 mL) at 0 ºC, filtered, extracted with CH_2Cl_2 (10.0 mL x 2), washed with saturated brine (20.0 mL x 2), dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash silica gel chromatography (eluent: 4:1 Hexanes/EtOAc) to afford product **3f** as light pink solid (69% yield), TLC R_f = 0.20 (4:1 Hexanes/EtOAc). $[\alpha]^{20}_D$= +5.8º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.93 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.23-7.19 (m, 2H), 7.16 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.69 (s, 1H), 4.99 (s, 1H), 4.90 (s, 1H), 3.15 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 155.4, 143.0, 136.2, 128.5, 127.9, 127.2, 126.5, 122.9, 122.1, 119.6, 119.0, 111.7, 111.2, 79.6, 55.0, 33.1, 28.5; IR (neat, cm^{-1}): 1733, 1264, 732, 703; HRMS (DART) *m*/*z* calcd for $C_{21}H_{25}N_2O_2^+$ $[M+H]^+$: 337.1911, obsd: 337.1899; HPLC analysis: ee = 98%. Chiral ADH (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 25.10 min., Minor t = 17.41 min.

5.2. Ring-Opening by Nitrogen Nucleophiles



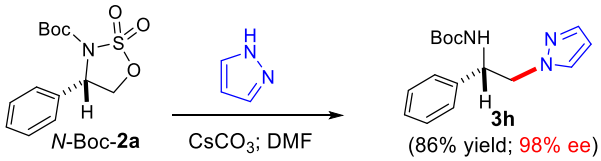
***tert*-Butyl (*S*,*E*)-4-styryl-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide dioxide (*N*-Boc-2o)** was prepared according to the following procedure: at 0 ºC, Boc_2O (32 mg, 1.5 equiv) and DMAP (2 mg) were added to a solution of **2o** (22 mg, 0.15 mmol) in anhydrous DCM (2 mL). The reaction mixture

was stirred for 30 mins and then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: 4:1 Hexanes/EtOAc) to afford product *N*-Boc-**2o** as white solid (95% yield), TLC R_f = 0.33 (4:1 Hexanes/EtOAc). m.p. 141-143 °C. $[\alpha]^{20}_D$= +12.0º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.43-7.39 (m, 2H), 7.38-7.32 (m, 2H), 7.32-7.28 (m, 1H), 6.73 (d, *J* = 15.7 Hz, 1H), 6.24 (dd, *J* = 15.7, 8.1 Hz, 1H), 4.99-4.88 (m, 1H), 4.77 (dd, *J* = 9.2, 6.3 Hz, 1H), 4.38 (dd, *J* = 9.3, 3.5 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 148.4, 135.8, 135.2, 128.9, 128.8, 127.0, 122.8, 85.7, 70.4, 59.6, 28.1; IR (neat, cm^{-1}): 1714, 1369, 1244, 752; HRMS (DART) *m/z* calcd for $C_{15}H_{23}N_2O_5S^+$ $[M+NH_4]^+$ 343.1322, obsd: 343.1311.

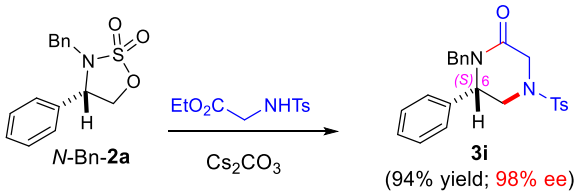


N-Boc-**2o**

***tert*-Butyl (*S*,*E*)-(1-azido-4-phenylbut-3-en-2-yl)carbamate (3g)** was synthesized according to the following procedure: NaN_3 (15.6 mg, 0.24 mmol) was added to a stirred solution of *N*-Boc-**2o** (0.08 mmol) in DMF (0.8 mL) at r.t. After 24 h, the reaction mixture was stirred for 30 min between ether (2 mL) and 1N citric acid (5 mL). The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 10:1 Hexanes/EtOAc) to afford product **3g** as white solid (94% yield), TLC R_f = 0.43 (8:1 Hexanes/EtOAc). m.p. 80-82 °C. $[\alpha]^{20}_D$= +13.8º (*c* = 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.37 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28-7.23 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.2 Hz, 1H), 4.83 (br.s, 1H), 4.50 (br.s, 1H), 3.63-3.44 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 156.1, 136.3, 132.5, 128.8, 128.2, 126.7, 126.6, 80.2, 55.2, 52.4, 28.5; IR (neat, cm^{-1}): 2103, 1707, 1496, 1169, 769; HRMS (DART) m/z calcd for $C_{15}H_{21}N_4O_2^+$ $[M+H]^+$: 289.1659, obsd: 289.1659; HPLC analysis: ee = 91%. Chiral ADH (5% isopropanol - 95% hexanes, 1.0 mL/min): Major t = 12.65 min., Minor t = 14.99 min.

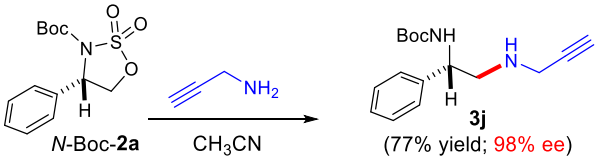


***tert*-Butyl (*S*)-(1-phenyl-2-(1H-pyrazol-1-yl)ethyl)carbamate (3h)** was prepared according to the following procedure. Cesium carbonate (65 mg, 0.2 mmol) was added to a stirred solution of *N*-Boc-**2a** (0.1 mmol) and pyrazole (13.6 mg, 0.2 mmol) in DMF (0.5 mL) at rt. After 24 h, the reaction was quenched by addition of 1N citric acid (5 mL) and the mixture was stirred for 30 min. The aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 2:1) to afford product **3h** as white solid (86% yield) (TLC R_f = 0.40 (Hexanes/EtOAc 2: 1). m.p.146-148 °C. $[\alpha]^{20}_D$= +53.4° (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.53-7.55 (m, 1H), 7.30-7.21 (m, 3H), 7.06 (d, *J* = 6.9 Hz, 2H), 6.99 (s, 1H), 6.13 (s, 1H), 6.02 (br.s, 1H), 5.07 (br.s, 1H), 4.58-4.49 (m, 1H), 4.39-4.29 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 156.3, 140.1, 139.6, 130.6, 128.7, 127.8, 126.3, 105.6, 79.8, 57.0, 55.5, 28.5; IR (neat, cm^{-1}): 3367, 1686, 1525, 1250, 1169; HRMS (DART) *m*/*z* calcd for $C_{16}H_{22}N_3O_2^+$ $[M+H]^+$: 288.1707, obsd: 288.1696; HPLC analysis: ee = 98%. Chiral IC (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 11.84 min., Minor t = 17.37 min.



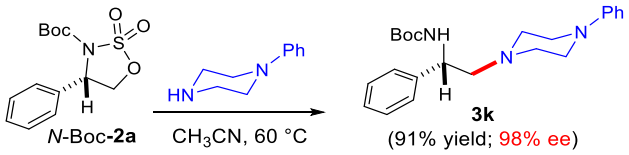
(*S*)-1-Benzyl-6-phenyl-4-tosylpiperazin-2-one (3i) was prepared according to the following procedure: Ethyl 2-(4-methylphenylsulfonamido)acetate (17 mg, 0.07 mmol, commercially available, cas: 5465-67-8) and Cs_2CO_3 (23 mg, 0.07 mmol) were added to a stirred solution of *N*-Bn-**2a** (20 mg, 0.07 mmol) in DMF (0.4 mL) at room temperature. After 16 h, the reaction was quenched by addition of 1N citric acid (5 mL) and the mixture was stirred for 6 h. After tuning the pH to 12 by adding NaOH (1M), the aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was dissolved into toluene (1 mL) and the reaction mixture was heated to 120 ºC for overnight to induce the lactamization. Then the solvent was removed and the residue was

purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 4:1) to afford product **3i** as yellow solid (94% yield) (TLC R_f = 0.35 (Hexanes/EtOAc 4: 1). m.p. 130-132 °C. $[\alpha]^{20}_D$= -45.0º (*c* = 1.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.55 (d, *J* = 8.2 Hz, 2H), 7.43-7.36 (m, 3H), 7.33-7.24 (m, 5H), 7.17 (dd, *J* = 2.9, 6.5 Hz, 2H), 7.09-7.04 (m, 2H), 5.48, 3.41 (AB q, *J* = 14.7 Hz, 1H), 4.44 (t, *J* = 4.4 Hz, 1H), 4.00 (d, *J* = 16.4 Hz, 1H), 3.80 (d, *J* = 16.4 Hz, 1H), 3.38 (dd, *J* = 5.3, 12.3 Hz, 1H), 3.27 (dd, *J* = 4.4, 12.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 165.1, 144.7, 137.4, 136.2, 132.4, 130.3, 129.4, 129.1, 129.1, 128.8, 128.2, 128.1, 127.6, 59.1, 50.4, 49.5, 47.4, 21.9; IR (neat, cm^{-1}): 2921, 1656, 1166, 1264; HRMS (DART) *m/z* calcd for $C_{24}H_{25}N_2O_3S^+$ $[M+H]^+$: 421.1580, obsd: 421.1588; HPLC analysis: ee = 98%. Chiral ADH (30% isopropanol - 70% hexanes, 1.0 mL/min): Major t = 14.27 min., Minor t = 19.36 min. 6-[*S*] absolute configuration of the product was determined by X-ray crystallography.

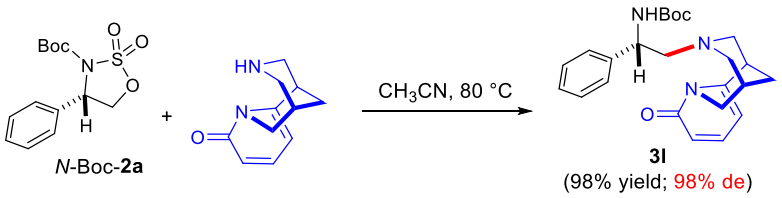


N-Boc-**2a**

***tert*-Butyl (*S*)-(1-phenyl-2-(prop-2-yn-1-ylamino)ethyl)carbamate (3j)** was prepared according to the following procedure: propargylamine (24 mg, 0.44 mmol) was added to a stirred solution of *N*-Boc-**2a** (0.15 mmol) in CH_3CN (1.0 mL) at 40 ºC. After 24 h, the reaction was quenched by addition of 1N citric acid (5 mL) and the mixture was stirred for 8 h. After tuning the pH to 12 by adding NaOH (1M), the aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 2:1 Hexanes/EtOAc) to afford product **3j** as yellow solid (77% yield), TLC R_f = 0.40 (1:1 Hexanes/EtOAc). m.p.146-148 °C. $[\alpha]^{20}_D$= +22.6º (*c* = 1.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.46-7.14 (m, 5H), 5.45 (s, 1H), 4.80 (s, 1H), 3.38 (qd, *J* = 17.1, 2.3 Hz, 2H), 3.04 (br. s, 1H), 2.95 (dd, *J* = 11.9, 4.9 Hz, 1H), 2.19 (t, *J* = 2.3 Hz, 1H), 1.42 (s, 9H), 1.19 (br. s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 155.6, 141.2, 128.8, 127.4, 126.3, 81.9, 79.6, 71.7, 54.0, 53.7, 38.2, 28.5; IR (neat, cm^{-1}): 3303, 1703, 1493, 1264, 701; HRMS (DART) *m/z* calcd for $C_{16}H_{23}N_2O_2^+$ $[M+H]^+$: 275.1754, obsd: 275.1763; HPLC analysis: ee = 98%. Chiral ADH (5% isopropanol - 95% hexanes, 1.0 mL/min): Major t = 18.18 min., Minor t = 24.04 min.



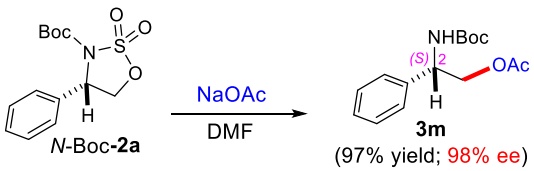
***tert*-Butyl (*S*)-(1-phenyl-2-(4-phenylpiperazin-1-yl)ethyl)carbamate (3k)** was prepared according to the following procedure. 1-Phenylpiperazine (49 mg, 0.3 mmol) was added to a stirred solution of *N*-Boc-**2a** (0.1 mmol) in CH_3CN (1.0 mL) at 60 ºC. After 24 h, the reaction was quenched by addition of 1 N citric acid (5 mL) and the mixture was stirred for 8 h. After tuning the pH to 12 by adding NaOH (1 M), the aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 3:1 Hexanes/EtOAc) to afford product **3k** as white solid (91% yield), TLC R_f = 0.40 (2:1 Hexanes/EtOAc). m.p.77-79 °C. $[\alpha]^{20}_D$= +11.5º (*c* = 2.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.38-7.29 (m, 4H), 7.28-7.22 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.89-6.80 (m, 1H), 5.48 (br.s, 1H), 4.71 (br.s, 1H), 3.28-3.10 (m, 4H), 2.81-2.66 (m, 2H), 2.64-2.47 (m, 4H), 1.40 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 155.9, 151.4, 129.2, 128.6, 127.3, 126.3, 119.9, 116.2, 79.6, 64.0, 53.2, 49.3, 28.5; IR (neat, cm^{-1}): 3263, 1685, 1215, 773; HRMS (DART) *m*/*z* calcd for $C_{23}H_{32}N_3O_2^+$ $[M+H]^+$: 382.2489, obsd: 382.2500; HPLC analysis: ee = 98%. Chiral IB (2.5% isopropanol - 97.5% hexanes, 1.0 mL/min): Major t = 16.52 min., Minor t = 14.10 min.



***tert*-Butyl((*S*)-2-((1*R*,5*S*)-8-oxo-1,5,6,8-tetrahydro-2H-1,5-methanopyrido[1,2-a][1,5]diazocin-3 (4H)-yl)-1-phenylethyl)carbamate (3l)** was prepared according to the following procedure: an oven-dried Schlenk tube that was previously charged with Cytisine (25 mg, 0.13 mmol) and *N*-Boc-**2a** (0.067 mmol) was evacuated and backfilled with nitrogen. The Teflon screw cap was replaced with a rubber septum and 1.0 ml of CH_3CN was added. The Schlenk tube was then purged with nitrogen for 2 min and the rubber septum was replaced with a Teflon screw cap. The reaction mixture was stirred at 80 ºC

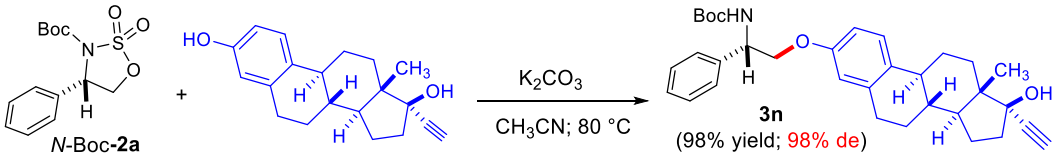
for 24 h. Then the reaction was quenched by addition of 1 N citric acid (5 mL) and the mixture was stirred for 30 mins. After tuning the pH to 12 by adding NaOH (1 M), the aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: EtOAc only) to afford product **3l** as off white oil (98% yield) (TLC R_f = 0.30 (EtOAc only). $[\alpha]^{20}_D$= -86.0º (*c* = 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.29-7.24 (m, 3H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.45 (t, *J* = 13.8 Hz, 1H), 5.94 (t, *J* = 10.6 Hz, 1H), 4.89 (br. s, 1H), 4.47 (br. s, 1H), 4.02 (d, *J* = 15.3 Hz, 1H), 3.82 (dd, *J* = 15.3, 6.5 Hz, 1H), 2.95-2.93 (m, 2H), 2.67 (d, *J* = 10.9 Hz, 1H), 2.51-2.32 (m, 5H), 1.87 (d, *J* = 12.8 Hz, 1H), 1.75 (d, *J* = 12.8 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 163.6, 155.4, 151.0, 141.7, 138.8, 128.6, 127.2, 126.0, 117.0, 104.6, 79.3, 62.9, 61.1, 59.9, 52.4, 50.0, 35.5, 28.4, 28.2, 25.9; IR (neat, cm^{-1}): 1699, 1648, 1546, 1363, 1165, 734; HRMS (DART) *m/z* calcd for $C_{24}H_{32}N_3O_3^+$ $[M+H]^+$: 410.2438, obsd: 410.2440; ^{1}H NMR (600 MHz, C_6D_6) analysis: de = 98%.

5.3. Ring-Opening by Oxygen, Fluorine, Phosphine and Sulfur Nucleophiles



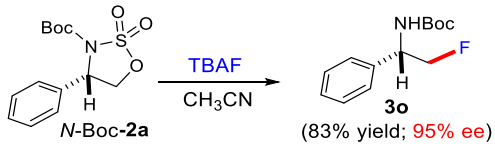
(*S*)-*tert*-Butyl (2-acetyloxy-1-phenylethyl)carbamate (3m) was prepared according to the following procedure: NaOAc (14.7 mg, 0.16 mmol) was added to a stirred solution of *N*-Boc-**2a** (0.10 mmol) in DMF (0.8 mL) at rt. After 4 h, the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 8:1) to afford product **3m** as white solid (97% yield) (TLC R_f = 0.30 (Hexanes/EtOAc 4: 1). **Known compound.**[15] m.p. 114-116 °C. $[\alpha]^{20}_D$= +30.0º (*c* = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.32 (m, 2H), 7.32-7.27 (m, 3H), 5.10 (br. s, 1H), 4.98 (br. s, 1H), 4.37-4.23 (m, 2H), 2.04 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 171.1, 155.3, 139.0, 128.8, 128.0, 126.7, 80.0, 66.8, 53.9, 28.5, 21.0; IR (neat, cm^{-1}): 1715, 1684;

HPLC analysis: ee = 98%. Chiral AD-H (7% isopropanol - 93% hexanes, 1.0 mL/min): Major t = 14.93 min., Minor t =12.57 min. 2-[*S*] absolute configuration of the product was determined by X-ray crystallography.

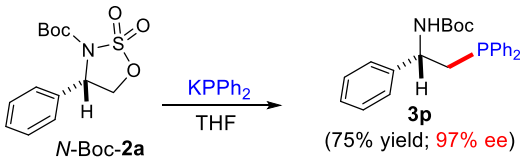


***tert*-Butyl((*S*)-2-(((8*R*,9*S*,13*S*,14*S*,17*R*)-17-ethynyl-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-1-phenylethyl)carbamate (3n)** was prepared according to the following procedure: 17α-Ethynylestradiol (89 mg, 0.3 mmol) and K_2CO_3 (17 mg, 0.1 mmol) were added to a stirred solution of *N*-Boc-**2a** (0.1 mmol) in CH_3CN (1.0 mL) at 80 ºC. After 24 h, the reaction was quenched by addition of 1 N citric acid (5 mL) and the mixture was stirred for 30 min. After tuning the pH to 12 by adding NaOH (1 M), the aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 3:1) to afford product **3n** as colorless oil (98% yield) (TLC R_f = 0.30 (Hexanes/EtOAc 2:1). $[\alpha]^{20}_D$= +5.0º (*c* = 2.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.41-7.31 (m, 4H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.60 (d, *J* = 2.5 Hz, 1H), 5.34 (br.s, 1H), 5.04 (br.s, 1H), 4.18 (br.s, 1H), 4.11 (br.s, 1H), 2.91-2.73 (m, 2H), 2.59 (s, 1H), 2.38-2.29 (m, 2H), 2.26-2.16 (m, 1H), 2.06-2.01 (m, 1H), 2.01-1.96 (m, 1H), 1.95-1.83 (m, 2H), 1.82-1.74 (m, 1H), 1.75-1.65 (m, 2H), 1.63 (br. s, 1H), 1.55-1.28 (m, 12H), 0.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 156.4, 155.5, 140.1, 138.2, 133.3, 128.6, 127.7, 126.9, 126.5, 114.8, 112.3, 87.7, 80.0, 79.9, 74.2, 70.7, 54.0, 49.6, 47.3, 44.6, 43.7, 39.5, 39.1, 32.9, 29.9, 28.5, 27.3, 26.5, 22.9, 12.8; IR (neat, cm^{-1}): 3399, 2159, 1696, 1496, 1165, 734; HRMS (DART) *m*/*z* calcd for $C_{33}H_{42}NO_4^+$ $[M+H]^+$: 516.3108, obsd 516.3082; HPLC analysis: de = 98%. Chiral ADH (10% isopropanol - 90% hexanes, 1.0 mL/min): Major t = 51.22 min., Minor t = 33.10 min. (Note the chiral center formed via amination was remote to the chiral centers in 17α-ethynylestradiol moiety and the ring-opening products from (±)-*N*-Boc-**2a** and (+)-*N*-Boc-**2a** are idential in ^{1}H NMR. The HPLC was the next option for de determination, since two diastereomers generatated behave more like enantiomers due to the remoteness between nitrogen-centered chriality and the enantiopure chiral

centers in 17α-ethynylestradiol moiety. Using 210 nm in the HPLC, the two diastereomers generated from (±)-*N*-Boc-**2a** were integrated to be 50% and 50% on HPLC; the similar concentration of **3n** generated from (+)-*N*-Boc-**2a** was determined to be 98% de).

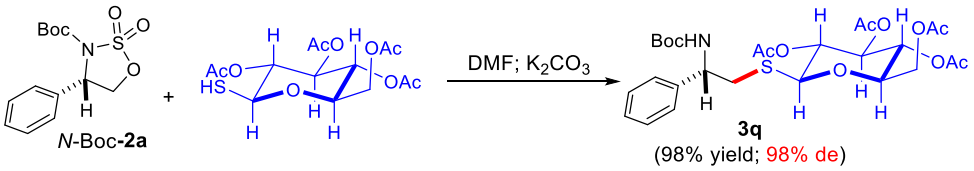


(*S*)-*tert*-Butyl (2-fluoro-1-phenylethyl)carbamate (3o) was prepared according to the following procedure: TBAF (41.7 mg, 0.16 mmol) was dissolved in anhydrous CH_3CN (0.8 mL). *N*-Boc-**2a** (0.1 mmol) was added and the mixture was stirred for 30 mins at rt. Then the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 8:1) to afford product **3o** as white solid (83% yield) (TLC R_f = 0.50 (Hexanes/EtOAc 4: 1). **Known compound.**[16] m.p.81-82 °C. $[\alpha]^{20}_D$= +33.0° (*c* = 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48-7.25 (m, 5H), 5.19 (s, 1H), 5.08-4.81 (m, 1H), 4.61 (ddd, *J* = 15.6, 13.7, 4.1 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.2, 138.3, 128.7, 127.9, 126.8, 85.1 (d, *J* =175 Hz), 80.0, 54.5(br), 28.3; ^{19}F NMR(376 MHz, $CDCl_3$) δ ppm -227.0; IR (neat, cm^{-1}): 1684, 1523, 1456, 1173; HPLC analysis: ee = 95%. Chiral AD-H (5% isopropanol - 95% hexanes, 0.7 mL/min): Major t = 13.48 min., Minor t =14.68 min.



***tert*-Butyl (*S*)-(2-(diphenylphosphanyl)-1-phenylethyl)carbamate (3p)** was prepared according to the following procedure: $KPPh_2$ (0.32 mL, 0.16 mmol, 0.5 M in THF) was diluted in anhydrous THF (0.8 mL). *N*-Boc-**2a** (0.1 mmol) was added and the mixture was stirred for 30 mins at rt. Then the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution

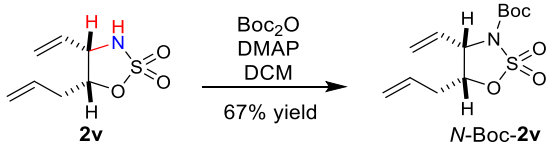
(1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 8:1) to afford product **3p** as white solid (75% yield) (TLC R_f = 0.33 (Hexanes/EtOAc 4: 1). **Known compound.**[17] $[\alpha]^{20}_D$= +5.9° (*c* = 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.10-7.41 (m, 15H), 5.07-4.90 (m, 1H), 4.80-4.60 (m, 1H), 2.60-2.40 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 154.8, 143.2, 137.9 (d, *J* = 13.0 Hz), 132.9 (d, *J* = 20.0 Hz), 132.8 (d, *J* =19.0 Hz), 128.7 (d, *J* = 7.0 Hz), 128.6, 128.5 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 2.0 Hz), 127.3, 126.1 (d, *J* = 1.0 Hz), 79.4, 52.9, 37.3 (d, *J* = 16.0 Hz), 28.3; ^{31}P NMR (100 MHz, $CDCl_3$) δ ppm -23.3; IR (neat, cm^{-1}): 1684, 1500, 1365, 1172; HPLC analysis: ee = 97%. Chiral OD-H (5% isopropanol - 95% hexanes, 0.8 mL/min): Major t = 9.58 min., Minor t =12.67 min.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((*S*)-2-((tert-butoxycarbonyl)amino)-2-phenylethyl)thio) tetrahydro-2H-pyran-3,4,5-triyl triacetate (3q) was prepared according to the following procedure: an oven-dried Schlenk tube that was previously charged with 1-thio-*β*-D-glucose tetraacetate (25 mg, 0.13 mmol), K_2CO_3 (10 mg, 0.73 mmol) and *N*-Boc-**2a** (0.067 mmol) was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum and 0.5 ml of DMF was added. The Schlenk tube was then purged with nitrogen for 2 min and the rubber septum was replaced with a Teflon screw cap. The reaction mixture was stirred for 24 h. Then the reaction was quenched by addition of 1 N citric acid (5 mL) and the mixture was stirred for 30 min. After tuning the pH to 12 by adding NaOH (1 M), the aqueous layer was then extracted with DCM (5 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: EtOAc only) to afford product **3q** as off-white solid (98% yield), TLC R_f = 0.30 (2:1 Hexanes/EtOAc). $[\alpha]^{20}_D$= -11.1° (*c* = 2.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.39-7.31 (m, 2H), 7.27 (dd, *J* = 7.7, 5.4 Hz, 3H), 5.60 (br. s, 1H), 5.17 (t, *J* = 9.3 Hz, 1H), 5.11 (t, *J* = 9.7 Hz, 1H), 4.99 (t, *J* = 9.6 Hz, 1H), 4.88 (br. s, 1H), 4.39 (d, *J* = 9.9 Hz, 1H), 4.30 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.22 (dd, *J* = 12.4, 2.1

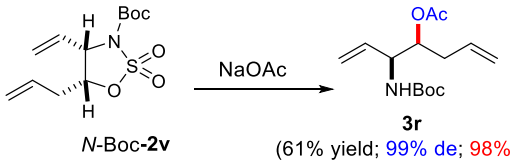
Hz, 1H), 3.68 (ddd, *J* = 9.9, 4.2, 2.3 Hz, 1H), 3.20-3.10 (m, 1H), 2.98 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.11 (s, 3H), 2.03 (s, 6H), 1.99 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 170.6, 170.1, 169.3, 155.1, 140.9, 128.6, 127.6, 126.3, 83.3, 79.7, 75.9, 73.6, 69.8, 67.9, 61.8, 54.1, 36.7, 28.3, 20.7, 20.6, 20.5; IR (neat, cm^{-1}): 1754, 1214, 745; HRMS (DART) *m*/*z* calcd for $C_{27}H_{38}NO_{11}S^+$ $[M+H]^+$: 584.2160, obsd: 584.2164; **Note:** the chiral center formed via amination was remote to the chiral centers in 1-thio-*β*-D-glucose tetraacetate moiety and the ring-opening products from (±)-*N*-Boc-**2a** and (+)-*N*-Boc-**2a** were identical in ^{1}H NMR and ^{13}C NMR. The HPLC results with all representative columns (more than 20) for the ring-opening products from (±)-*N*-Boc-**2a** and (+)-*N*-Boc-**2a** were identical as a single peak. This is due to the strong interaction between the HPLC stationary phase and sugar moiety. Based on our observation that no racemization was observed during ring-opening processes for all the other reactions, we propose the de is >98%.

5.4. Ring-Opening of α,β-Disubstituted Sulfamidates



2v *N*-Boc-**2v**

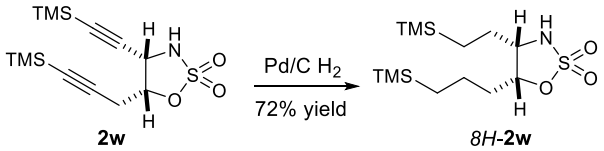
tert*-Butyl (4*S*,5*R*)-5-allyl-4-vinyl-1,2,3-oxathiazolidine-3-carboxylate 2,2-dioxide (N*-Boc-**2v)** was synthesized according to the following procedure: at 0 ºC, Boc_2O (69 mg, 1.5 equiv) and DMAP (2 mg) were added to a solution of **2v** (40 mg, 0.21 mmol) in anhydrous DCM (3 mL). The reaction mixture was stirred for 30 min then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) TLC R_f = 0.22 (8: 1 Hexanes/Ethyl acetate) to afford product *N*-Boc-**2v** as colorless oil (67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.88 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.77-5.67 (m, 1H), 5.50 (d, *J* = 10.7 Hz, 1H), 5.46 (s, 1H), 5.26-5.23 (m, 1H), 5.23-5.20 (m, 1H), 4.95-4.89 (m, 1H), 4.70-4.64 (m, 1H), 2.58 (ddd, *J* = 14.6, 7.9, 6.5 Hz, 1H), 2.39 (dt, *J* = 14.7, 6.7 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 148.3, 130.1, 129.0, 122.2, 120.3, 85.6, 81.7, 63.1, 33.5, 28.1; IR (neat, cm^{-1}): 1729, 1369, 1318, 1191,1151; HRMS (DART) *m*/*z* calcd for $C_{12}H_{23}N_2O_5S^+$ $[M+NH_4]^+$ 307.1322, obsd 307.1325.



N-Boc-**2v** **3r** (61% yield; 99% de; 98% ee)

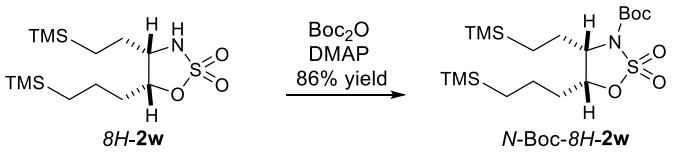
(3*S*,4*S*)-3-((*tert*-Butoxycarbonyl)amino)hepta-1,6-dien-4-yl acetate (3r) was prepared according to the following procedure: NaOAc (17.3 mg, 0.21 mmol) was added to a stirred solution of *N*-Boc-**2v** (0.13 mmol) in DMF (0.8 mL) at rt. After 24 h, the reaction was quenched by addition of 1N citric acid (5 mL) and the mixture was stirred for 30 min. The aqueous layer was then extracted with DCM (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 10:1) to afford product **3r** as colorless oil (61% yield; 99% de) (TLC R_f = 0.40 (Hexanes/EtOAc 8:1). $[\alpha]^{20}_D$= -50.0º (*c* = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 5.75 (tt, *J* = 10.8, 5.9 Hz, 2H), 5.24-5.19 (m, 1H), 5.18-5.08 (m, 3H), 5.03 (br. s, 1H), 4.75 (d, *J* = 8.0 Hz, 1H), 4.37 (br. s, 1H), 2.42-2.31 (m, 2H), 2.03 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 170.4, 155.6, 135.9, 133.0, 118.7, 116.2, 79.8, 74.2, 54.7, 36.1, 28.5, 21.0; IR (neat, cm^{-1}): 1708, 1498, 1368, 1216, 759; HRMS (DART) *m*/*z* calcd for $C_{14}H_{24}NO_4^+$ $[M+H]^+$: 270.1700, obsd: 270.1699; HPLC analysis: ee = 98%. Chiral IC (3% isopropanol - 97% hexanes, 1.0 mL/min): Major t = 11.75 min., Minor t = 9.05 min.

5.5. Synthesis of β-Azido-α-Amine Derivatives

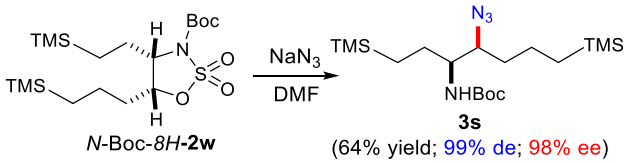


2w *8H*-**2w**

To a round bottom flask, Pd/C (7.0 mg, 10 wt. %) was added, followed by the addition of the amination product **2w** (35 mg, 0.1 mmol) in EtOAc (0.1 mL), and pentane (0.4 mL).The reaction flask was sealed with septum. By connecting to a hydrogen balloon and an oil bubbler through two needles, the hydrogen gas was bubbled through the reaction solution for 30 mins. Then reaction was stirred overnight in hydrogen atmosphere. After removing the Pd/C through filtration with a plug of celite, the reaciton mixture was concentrated to afford hydrogenated product *8H*-**2w** as white solid (72% yield), which was used directly for next step.



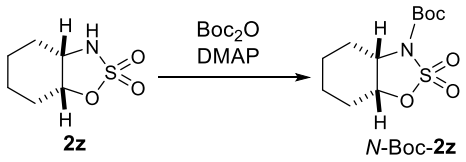
The above hydrogenated product *8H*-**2w** (26 mg, 0.079 mmol) was dissolved in 0.2 mL DCM and the reaction solution was cooled to 0 ºC. Boc_2O (0.12 mmol) and DMAP (1 mg) were added. The reaction mixture was stirred for 1 h and then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: 20:1 Hexanes/EtOAc) to afford Boc-protected product *N*-Boc-*8H*-**2w** as white solid (86% yield; 99% de), TLC R_f = 0.35 (20:1 Hexanes/EtOAc). $[\alpha]^{20}_D$= -1.3º (*c* = 1.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.87 (dt, *J* = 9.3, 4.5 Hz, 1H), 4.23 (dd, *J* = 10.7, 5.4 Hz, 1H), 1.95-1.85 (m, 1H), 1.84-1.73 (m, 1H), 1.71-1.61 (m, 2H), 1.55 (s, 9H), 1.46-1.35 (m, 2H), 0.64-0.48 (m, 4H), 0.01 (s, 9H), -0.00 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 149.2, 85.2, 83.8, 62.9, 32.5, 28.1, 23.2, 20.4, 16.6, 11.9, -1.6, -1.8; IR (neat, cm^{-1}): 1214, 749, 730; HRMS (DART) *m*/*z* calcd for $C_{18}H_{43}N_2O_5SSi_2^+$ $[M+NH_4]^+$ 455.2426, obsd 455.2418.



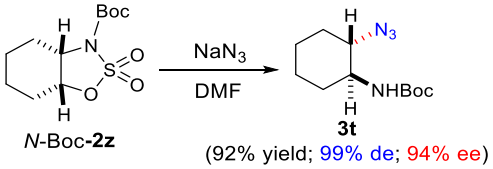
***tert*-Butyl ((3*S*,4*S*)-4-azido-1,7-bis(trimethylsilyl)heptan-3-yl)carbamate (3s)** was prepared according to the following procedure: NaN_3 (12.9 mg, 0.19 mmol) was added to a stirred solution of Boc-protected product *N*-Boc-*8H*-**2w** (0.07 mmol) in DMF (0.4 mL) at rt. After 24 h, the reaction mixture was stirred for 30 min between ether (2 mL) and 1N citric acid (2 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 20:1 Hexanes/EtOAc) to afford product **3s** as colorless oil (64% yield; 99% de), TLC R_f = 0.53 (20: 1 Hexanes/EtOAc). $[\alpha]^{20}_D$ = -12.5º (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.47 (d, *J* = 9.8 Hz, 1H), 3.61-3.56 (m, 1H), 3.56-3.50 (m, 1H), 1.68-1.52 (m, 3H), 1.52-1.45 (m, 3H), 1.44 (s, 9H), 0.61-0.44 (m, 4H), -0.00 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 160.0, 79.4, 65.3, 55.9, 35.8, 28.5, 28.0, 20.9, 16.7, 13.1, -1.54, -1.67; IR (neat, cm^{-1}): 2952, 2098, 1703, 1499, 1247, 1167, 831, 754; HRMS (DART) *m*/*z* calcd for

$C_{18}H_{41}N_4O_2Si_2^+$ $[M+H]^+$: 401.2763, obsd 401.2760; this product is not UV active, ee was determined to be >98% based on the ^1H NMR analysis of racemic and enantioenriched samples by adding chiral lanthanide shift reagent Eu(hfc)$_3$ (2.0 equiv) in $CDCl_3$ (see the spectrum section for detail).

5.6. Ring-Opening of Fused-Bicyclic Sulfamidates

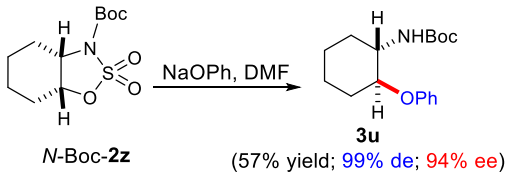


***tert*-Butyl (3a*S*,7a*R*)-hexahydro-3H-benzo[d][1,2,3]oxathiazole-3-carboxylate 2,2-dioxide (*N*-Boc-2z)** was prepared according to the following procedure: at 0 ºC, Boc_2O (130 mg, 1.5 equiv) and DMAP (2 mg) were added to a solution of **2z** (80 mg, 0.45 mmol) in anhydrous DCM (4 mL). The reaction mixture was stirred for 30 mins and then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 8:1) to afford product *N*-Boc-**2z** as white solid (90% yield). m.p. 131-132 °C. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 4.95 (dd, *J* = 6.6, 3.4 Hz, 1H), 4.14 (ddd, *J* = 10.6, 6.0, 4.3 Hz, 1H), 2.30 (ddd, *J* = 8.1, 4.7, 2.4 Hz, 2H), 1.86-1.58 (m, 5H), 1.53 (s, 9H) 1.22 (ddd, *J* = 12.9, 8.4, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 148.4, 85.0, 79.1, 57.5, 27.9, 27.2, 27.0, 21.8, 18.9; IR (neat, cm^{-1}): 1686; HRMS (DART) *m*/*z* calcd for $C_{11}H_{19}NNaO_5S^+$ $[M+Na]^+$: 300.0876, obsd: 300.0880.



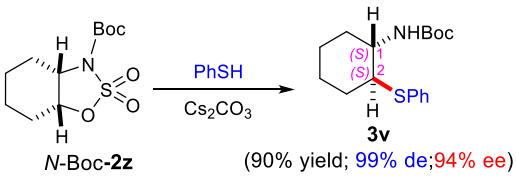
***tert*-Butyl ((1*S*,2*S*)-2-azidocyclohexyl)carbamate (3t)** was prepared according to the following procedure: NaN_3 (10.2 mg, 0.16 mmol) was added to a stirred solution of *N*-Boc-**2z** (0.10 mmol) in DMF (0.8 mL) at r.t. After 24 h, the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified

by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product **3t** as white solid (92% yield; 99% de), TLC R_f = 0.33 (4:1 Hexanes/EtOAc). **Known compound.**[18] m.p. 58-60 °C. $[\alpha]^{20}_D$= -2.0º (*c* = 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.61-4.35 (m, 1H), 3.40 (d, *J* = 9.4 Hz, 1H), 3.15-3.05 (m, 1H), 2.12-1.97 (m, 2H), 1.82-1.62 (m, 2H), 1.45 (m, 9H), 1.41-1.11 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.3, 79.6, 64.3, 53.9, 32.2, 30.6, 28.3, 24.3, 24.0. IR (neat, cm^{-1}): 3359, 2954, 2107, 1684, 1166; HPLC analysis: ee = 94%. Chiral AD-H (3% isopropanol - 97% hexanes, 0.8 mL/min): Major t = 15.87 min., Minor t = 12.77 min.



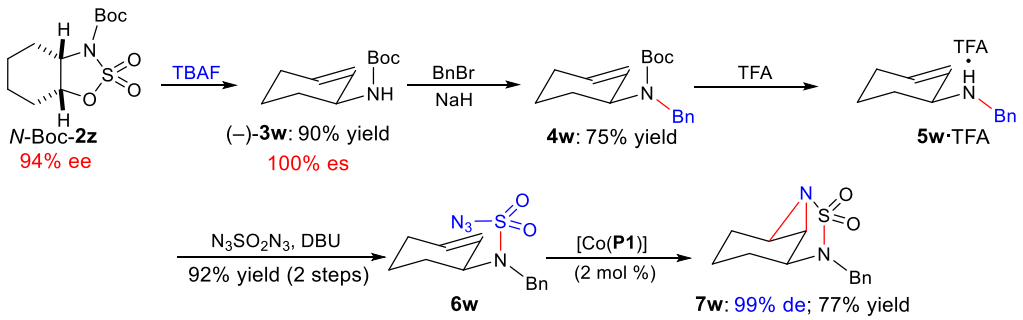
N-Boc-**2z** **3u** (57% yield; 99% de; 94% ee)

***tert*-Butyl ((1*S*,2*S*)-2-phenoxycyclohexyl)carbamate (3u)** was prepared according to the following procedure: NaOPh (18.5 mg, 0.16 mmol) was added to a stirred solution of *N*-Boc-**2z** (0.1 mmol) in DMF (0.8 mL) at r.t. After 4 h, the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product **3u** as white solid (57% yield; 99% de), TLC R_f = 0.23 (4:1 Hexanes/EtOAc). **Known compound.[19]** m.p. 107-108 °C. $[\alpha]^{20}_D$= +9.0º (*c* = 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30-7.25 (m, 2H), 6.96-6.91 (m, 3H), 4.66-4.37 (m, 1H), 4.03 (td, *J* = 9.09, 3.90 Hz, 1H), 3.84-3.56 (m, 1H), 2.13-2.03 (m, 2H), 1.84-1.73 (m, 1H), 1.67-1.60 (m, 1H), 1.52-1.22 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.1, 155.6, 129.4, 120.8, 116.1, 77.2, 53.2, 36.8, 30.9, 29.8, 28.3, 23.7, 23.2; IR (neat, cm^{-1}): 1698, 1492, 1242, 1170; HPLC analysis: ee = 94%. Chiral AS-H (3% isopropanol - 97% hexanes, 0.8 ml/min); Major t = 12.29 min., Minor t = 15.83 min.



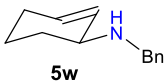
***tert*-Butyl ((1*S*,2*S*)-2-(phenylthio)cyclohexyl)carbamate (3v)** was prepared according to the following procedure: powdered Cs_2CO_3 (87.7 mg, 0.27 mmol) was added to a stirred solution of *N*-Boc-**2z** (0.1 mmol) and PhSH (29.7 mg, 0.27 mmol) in DMF (0.8 mL) at r.t. After 4 h, the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product **3v** as white solid (90% yield; 99% de), TLC R_f = 0.33 (4:1 Hexanes/EtOAc). m.p. 102-104 °C. $[\alpha]^{20}_D$= +38.0° (*c* = 0.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.45 (d, *J* = 7.1 Hz, 2H), 7.33-7.23 (m, 3H), 4.67 (s, 1H), 3.39 (d, *J* = 5.5 Hz, 1H), 2.87 (td, *J* = 10.6, 3.5 Hz, 1H), 2.19 (d, *J* = 10.8 Hz, 1H), 2.06 (dd, *J* = 9.9, 4.0 Hz, 1H), 1.68 (dd, *J* = 23.7, 10.0 Hz, 2H), 1.45 (s, 9H), 1.43-1.38 (m, 1H), 1.36-1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.3, 133.8, 133.2, 128.8, 127.3, 79.2, 53.5, 52.2, 33.7, 33.0, 28.4, 25.6, 24.4; IR (neat, cm^{-1}): 3346, 2932, 1698, 1532; HRMS (DART) *m*/*z* calcd for $C_{17}H_{26}NO_2S^+$ $[M+H]^+$: 308.1679, obsd: 308.1678; HPLC analysis: ee = 94%. Chiral AD-H (2% isopropanol - 98% hexanes, 1.0 mL/min); Major t = 26.31 min., Minor t = 21.07 min. 1-[*S*], 2-[*S*] absolute configuration of the product was determined by X-ray crystallography.

5.7. Synthesis of 1,2,3-Trifunctionalized Cyclohexane Derivatives via Ring-Opening of Cyclohexane-Fused Sulfamidates



***tert*-Butyl (*S*)-cyclohex-2-en-1-ylcarbamate (3w)** was prepared according to the following procedure: TBAF (41.7 mg, 0.16 mmol) was dissolved in anhydrous CH_3CN (0.8 mL). *N*-Boc-**2z** (0.1 mmol) was added and the mixture was stirred for 30 min at rt. Then the solvent was removed and the resulting residue was stirred overnight between ether (2 mL) and H_2SO_4 solution (1 mL, 2M). A solution of NaOH (4 mL, 1M) was added to tune pH to 10 and the resulting solution was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layers were combined, dried, and concentrated. The residue was purified by flash silica gel chromatography (eluent: 8:1 Hexanes/EtOAc) to afford product **3w** as white solid (90% yield), TLC R_f = 0.43 (4:1 Hexanes/EtOAc). **Known compound.**[20] m.p. 40-42 °C. $[\alpha]^{20}_D$= -89.0º (*c* = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.80 (dtd, *J* = 9.5, 3.6, 1.9 Hz, 1H), 5.60 (ddd, *J* = 9.9, 5.2, 2.3 Hz, 1H), 4.51 (br. s, 1H), 4.14 (br. s, 1H), 2.02-1.94 (m, 2H), 1.92-1.83 (m, 1H), 1.68-1.58 (m, 2H), 1.56-1.49 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 155.4, 130.5, 128.3, 79.3, 45.9, 30.0, 28.6, 25.0, 19.8; IR (neat, cm^{-1}): 1702, 1500, 1170; HPLC analysis: ee = 94%. Chiral IC (2% isopropanol - 98% hexanes, 1.0 mL/min): Major t = 11.39 min., Minor t = 10.52 min. **Note:** a scale-up process provided 80.0 mg of product for the following further transformation.

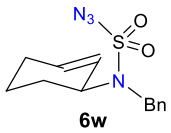
(*S*)-*N*-Benzylcyclohex-2-en-1-amine (5w) was synthesized according to the following procedure: in a flame-dried Schlenk tube, the above synthesized ***tert*-butyl (*S*)-cyclohex-2-en-1-ylcarbamate (3w)** (80.0 mg, 0.41 mmol), NaH (23.0 mg, 0.60 mmol) were charged. The tube was evacuated and back-filled with argon three times. The solids were dissolved in anhydrous THF (4 mL) at 0 ºC. To this suspension, benzyl bromide (50 µL, 0.45 mmol) was added slowly via syringe. The tube was sealed and stirred for 16 h at room temperature. Then the solvent was removed. The residue was purified by flash silica gel chromatography (eluent: 20:1 Hexanes/EtOAc) to afford product 84.0 mg of **4w** as colorless oil (71% yield), TLC R_f = 0.63 (10:1 Hexanes/EtOAc), which was used directly for next step. The above synthesized **4w** (80.0 mg. 0.28 mmol) was dissolved in DCM (1 mL). Then trifluoroacetic acid (214 µL, 2,78 mmol) was added. The reaction mixture was stirred at room temperature for 16 hours. Then the solvent was removed and **5w·TFA** salt was used for next step (full conversion). For **5w** free base: ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.38-7.29 (m, 4H), 7.26-7.20



5w

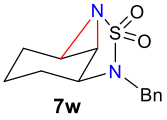
(m, 1H), 5.77 (dtd, *J* = 10.2, 3.3, 1.5 Hz, 1H), 5.73 (dd, *J* = 10.2, 2.2 Hz, 1H), 3.86, 3.82 (AB q, *J* = 13.0 Hz, each 1H), 3.21 (ddt, *J* = 7.2, 4.9, 2.5 Hz, 1H), 2.05-1.92 (m, 2H), 1.89 (dddd, *J* = 12.9, 7.8, 5.1, 2.5 Hz, 1H), 1.74 (ddtd, *J* = 12.3, 7.1, 5.1, 2.4 Hz, 1H), 1.56 (dddt, *J* = 12.8, 10.3, 4.6, 2.5 Hz, 1H), 1.49 (dddd, *J* = 13.1, 10.4, 7.3, 2.5 Hz, 1H), 1.34 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 140.9, 130.1, 129.1, 128.5, 128.3, 127.0, 52.5, 51.1, 29.6, 25.5, 20.4; IR (neat, cm^{-1}): 3023, 2927, 1738, 1452, 1216, 697; HRMS (DART) *m*/*z* calcd for $C_{13}H_{18}N^+$ $[M+H]^+$: 188.1434, obsd: 188.1444.

(*S*)-(((Azidosulfonyl)(cyclohex-2-en-1-yl)amino)methyl)benzene (6w) was synthesized according to the following procedure: **sulphuryl diazide** ($N_3SO_2N_3$) was prepared according to the following procedure: sulfuryl chloride (9.72 mL, 120 mmol) was added dropwise for 1 hour to a solution of sodium azide (29.25 g, 450 mmol) and pyridine (19.44 mL, 250 mmol) in acetonitrile (600 mL) at 0 ºC. Then the reaction mixture was stirred for one hour at room temperature followed by the addition of 100 mL DCM. The mixture was poured into ice-cold water and extracted with DCM (3 x 100 mL). The combined organic layer was washed sequentially with hydrochloric acid (1 mol/L in H_2O), water, potassium hydroxide (1 mol/L in H_2O), hydrochloric acid (1 mol/L in H_2O), and water. After drying (Na_2SO_4), the sulphuryl azide solution was used directly for the further reaction. This solution (0.3 M in DCM) can be stored in the refrigerator at -20 ºC for at least two years without significant decomposition. A mixture of above synthesized **5w·TFA** (**(*S*)-*N*-benzylcyclohex-2-en-1-amine TFA salt)** (0.27 mmol) and DBU (230.0 mg, 0.86 mmol) in DCM (0.5 mL) was added dropwise via pipette to a solution of $N_3SO_2N_3$ in DCM (0.3 M) (1.8 mL, 0.54 mmol) at 0 ºC. After the reaction was completed based on TLC (~ 1 hour), the majority of the solvent was removed under reduced pressure at room temperature. The residue was purified by flash silica gel chromatography (eluent: 20:1 Hexanes/EtOAc) to afford 74.0 mg of product **6w** as colorless oil (92% yield, TLC R_f = 0.65 (10:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.39-7.32 (m, 4H), 7.31-7.26 (m, 1H), 6.01-5.93 (m, 1H), 5.61 (dt, *J* = 10.2, 2.0 Hz, 1H), 4.62 (ddd, *J* = 8.6, 5.5, 2.9 Hz, 1H), 4.52, 4.34 (AB q, *J* = 16.3 Hz, each 1H), 2.02-1.92 (m, 3H), 1.81-1.71 (m, 1H), 1.64-1.48 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 137.3, 133.7, 128.7, 127.8, 127.6, 126.1, 58.0, 49.2, 28.3, 24.4, 21.6; IR (neat, cm^{-1}): 2936, 2119, 1378, 1168, 729.



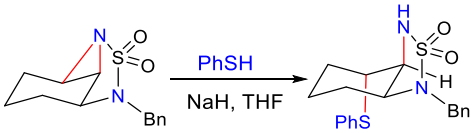
6w

(2a1*R*,2b*R*,5a*S*)-1-benzylhexahydro-1H-2-thia-1,2a-diazacyclopropa[cd]indene 2,2-dioxide (7w)



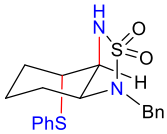
7w

was synthesized according to the following procedure: an oven-dried Schlenk tube that was previously charged with catalyst [Co(**P1**)] (11.8 mg, 0.0095 mmol) and 4Å molecular sieves (50 mg), was evacuated and backfilled with nitrogen gas. The Teflon screw cap was replaced with a rubber septum and 2.5 mL of benzene was added followed by azide (70 mg, 0.24 mmol). The Schlenk tube was then purged with nitrogen for 2 minutes and the rubber septum was replaced with a Teflon screw cap. The reaction mixture was then stirred for 8 hours at 80 ºC. The residue was purified by flash silica gel chromatography (eluent: 5:1 Hexanes/EtOAc) to afford 49.2 mg of **7w** as white solid (77% yield; 99% de), TLC R_f = 0.53 (3:1 Hexanes/EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.40-7.29 (m, 5H), 4.41, 3.87 (AB q, *J* = 15.2 Hz, each 1H), 3.85-3.83 (m, 1H), 3.47 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.89 (ddd, *J* = 6.5, 5.2, 1.6 Hz, 1H), 2.61-2.52 (m, 1H), 2.11-2.02 (m, 1H), 1.67-1.58 (m, 2H), 1.58-1.50 (m, 1H), 1.24 (dt, *J* = 5.6, 1.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.0, 128.9, 128.7, 128.3, 51.2, 47.6, 42.9, 42.6, 22.1, 17.6, 14.0; IR (neat, cm^{-1}): 2925, 1741, 1306, 1157. HRMS (DART) *m*/*z* calcd for $C_{13}H_{17}N_2O_2S^+$ $[M+H]^+$: 265.1005, obsd: 265.1007.



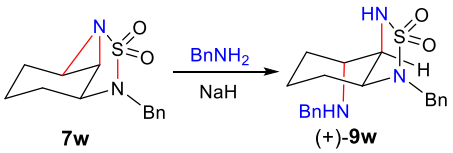
7w **(+)-8w**

Compound 8w was prepared according to the following procedure: at 0 ºC, to a solution of PhSH (9.4 mg, 0.085 mmol) in THF (0.5 mL) was added NaH (3.3 mg, 0.085 mmol). After stirring for 0.5 h at the same tempareture, a solution of **7w** (15 mg, 0.056 mmol) in THF (0.5 mL) was added dropwise. The reaction mixture was strirred at 0 ºC for 1 hour, quenched by 1 M HCl solution (1 mL). The organic phase was extracted by DCM (15.0 mL) with three times, the combined organic layers were dired over ($NaSO_4$), filtered, concentrated. The residue was purified by flash silica gel chromatography (eluent: 7:1 Hexanes/EtOAc) to afford 18 mg of ring-opening product **8w** as white solid (80% yield; 99% de), TLC R_f = 0.50 (5:1 Hexanes/EtOAc). $[\alpha]^{20}_D$ = +48.0º (*c* = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.47 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 5H), 7.31-7.27 (m, 1H), 5.13 (s, 1H), 4.46, 3.91 (AB q, *J* = 15.4 Hz, each 1H),



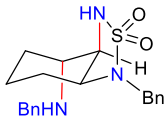
8w

3.78 (q, *J* = 3.9 Hz, 1H), 3.38 (td, *J* = 11.3, 10.7, 3.8 Hz, 1H), 3.27 (ddd, *J* = 9.7, 4.8, 1.3 Hz, 1H), 2.10-1.95 (m, 1H), 1.92-1.81 (m, 1H), 1.47-1.36 (m, 1H), 1.36-1.21 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 136.0, 134.9, 130.9, 129.4, 128.8, 128.7, 128.6, 128.0, 59.7, 57.1, 49.8, 48.8, 31.0, 26.3, 19.9; **the 5-membered ring structure was assigned unambiguously with H-H COSY, see spectrum section for details**; IR (neat cm^{-1}): 3462, 3015, 2969, 2944, 1738, 1365, 1228, 1216; HRMS (DART) *m*/*z* calcd for $C_{19}H_{23}N_2O_2S_2^+$ $[M+H]^+$: 375.1196, obsd: 375.1194; HPLC analysis: ee = 93%. Chiral IA (30% isopropanol - 70% hexanes, 1.0 mL/min); Major t = 12.41 min., Minor t = 8.76 min.

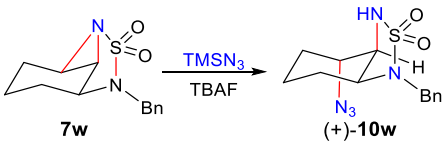


7w (+)-**9w**

Compound 9w was prepared according to the following procedure: to a solution of **7w** (15 mg, 0.056 mmol) in THF (1 mL) and $BnNH_2$(12 mg, 0.11 mmol) was added triethyl amine (11 mg, 0.11 mmol). The reaction mixture was strirred under reflux for 16 h. Then the solvent was removed and the residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 1:1 with triethyl amine-neutralized silica gel) to afford 15 mg of ring opening product **3y** as colorless oil (71% yield; 99% de) (TLC R_f = 0.10 (EtOAc only)). $[\alpha]^{20}_D$ = +104.0 (*c* = 0.8, $CHCl_3$); for HCl salt of **9w**: ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 10.15 (s, 1H), 8.88 (s, 1H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 3H), 7.27-7.21 (m, 5H), 4.43 (dt, *J* = 13.7, 4.3 Hz, 1H), 4.38, 3.87 (AB q, *J* = 16.1 Hz, each 1H), 4.05 (ddd, *J* = 29.2, 9.3, 3.9 Hz, 2H), 3.89 (s, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 1.96-1.89 (m, 1H), 1.79-1.64 (m, 2H), 1.49 (ddd, *J* = 15.8, 10.7, 3.9 Hz, 1H), 1.33 (dt, *J* = 13.8, 3.8 Hz, 1H), 0.95-0.82 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 136.1, 130.3, 129.8, 129.7, 129.3, 128.6, 128.3, 127.9, 62.2, 56.1, 55.0, 48.6, 47.9, 25.6, 25.3, 17.9; **the 5-membered ring structure was assigned unambiguously with H-H COSY, see spectrum section for details**; IR (neat, cm^{-1}): 3267, 2935, 1454, 1154, 697; HRMS (DART) *m*/*z* calcd for $C_{20}H_{26}N_3O_2S^+$ $[M+H]^+$: 372.1740, obsd: 372.1748; HPLC analysis: ee = 94%. Chiral IA (20% isopropanol - 80% hexanes, 1.2 mL/min); Major t = 13.26 min., Minor t = 11.42 min.

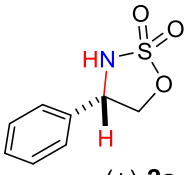


(+)-**9w**



Compound 10w was prepared according to the following procedure: to a solution of **7w** (15 mg, 0.056 mmol) and $TMSN_3$(7.2 mg, 0.062 mmol) in THF (1 mL) was added tetrabutylammonium fluoride (18 µL, 1 M solution in THF, 0.062 mmol). The reaction mixture was strirred at room tempareture for 1 h. The solvent was removed and the residue was purified by flash silica gel chromatography (eluent: Hexanes/EtOAc 4:1) to afford 17 mg of ring-opening product **10w** as colorless oil (97% yield; 99% de) (TLC R_f = 0.25 (Hexanes/EtOAc 3:1)). $[\alpha]^{20}_D$ = +110.6 (*c* = 0.8, $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.44-7.28 (m, 5H), 4.82 (s, 1H), 4.46, 3.95 (AB q, *J* = 15.6 Hz, each 1H), 3.93-3.90 (m, 1H), 3.78 (t, *J* = 4.1 Hz, 1H), 3.28 (dd, *J* = 9.1, 4.9 Hz, 1H), 2.05-1.97 (m, 1H), 1.89 (dd, *J* = 15.6, 3.7 Hz, 1H), 1.53-1.37 (m, 2H), 1.36-1.23 (m, 2H); **the 5-membered ring structure was assigned unambiguously with H-H COSY, see spectrum section for details**; ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 135.8, 128.8, 128.5, 128.1, 61.2, 60.3, 58.2, 48.4, 28.4, 26.0, 18.1; IR (neat cm^{-1}): 3252, 2928, 2100, 1738, 1365, 1160; HRMS (DART) *m/z* calcd for $C_{13}H_{18}N_5O_2S^+$ $[M+H]^+$: 308.1176, obsd: 308.1180; HPLC analysis: ee = 94%. Chiral IC (30% isopropanol - 70% hexanes, 1.0 mL/min); Major t = 20.36 min., Minor t = 17.09 min.

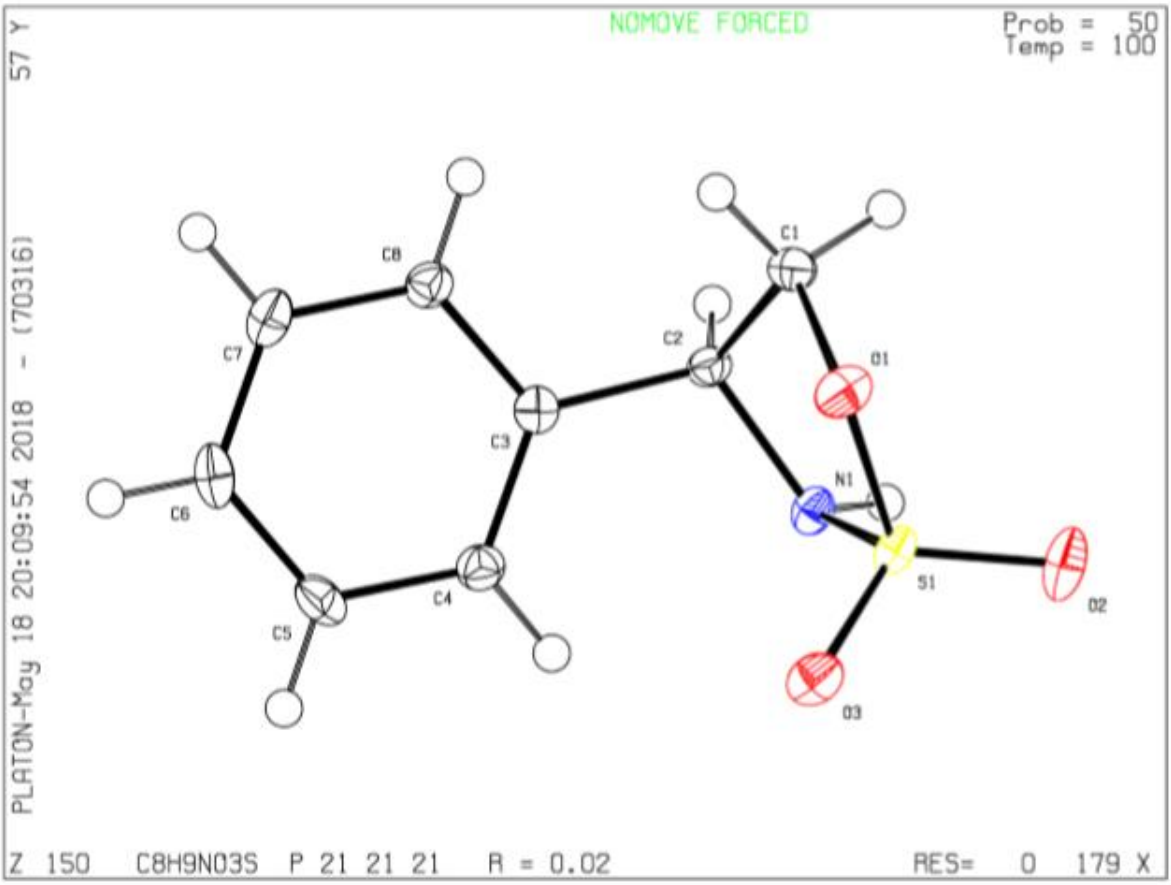
6. X-ray Crystallography

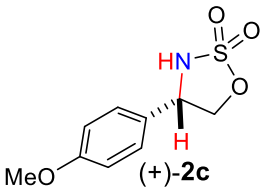


(+)-**2a**

Table 1. Crystal data and structure refinement for **2a**. (CCDC 2097084)

Identification code	C8H9NO3S	
Empirical formula	C8 H9 N O3 S	
Formula weight	199.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 4.7540(2) Å	α= 90°.
	b = 11.9215(4) Å	β= 90°.
	c = 15.2976(5) Å	γ = 90°.
Volume	866.99(5) $Å^3$	
Z	4	
Density (calculated)	1.526 Mg/m^3	
Absorption coefficient	3.128 mm^{-1}	
F(000)	416	
Crystal size	0.460 x 0.240 x 0.130 mm^3	
Theta range for data collection	4.702 to 70.187°.	
Index ranges	-5<=h<=5, -14<=k<=14, -18<=l<=18	
Reflections collected	12526	
Independent reflections	1637 [R(int) = 0.0295]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5852	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1637 / 1 / 121	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0615	
R indices (all data)	R1 = 0.0229, wR2 = 0.0616	
Absolute structure parameter	-0.001(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.230 and -0.272 e.$Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 100
57 Y
PLATON-May 18 20:09:54 2018 - (70316)
C8
C1
C7
C2
O1
C3
N1
C6
S1
O2
C4
C5
O3
Z 150 C8H9N03S P 21 21 21 R = 0.02
RES= 0 179 X

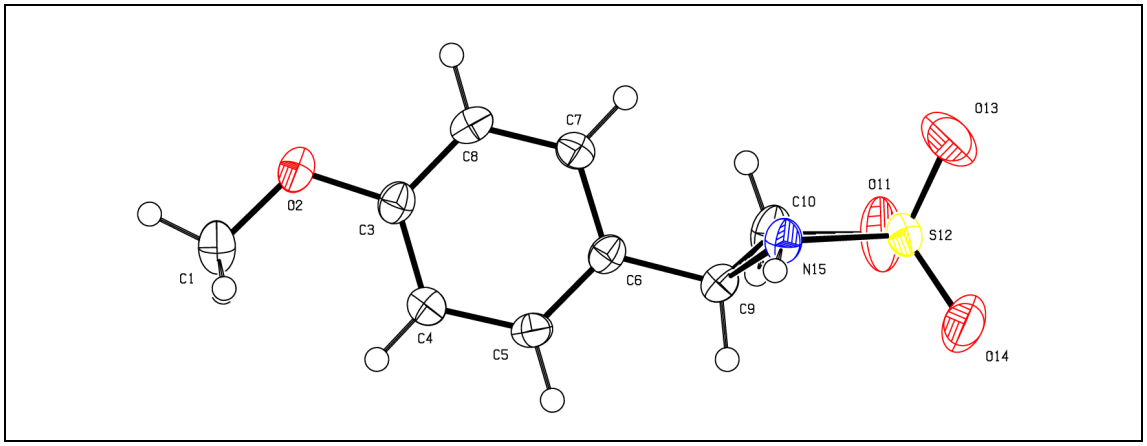


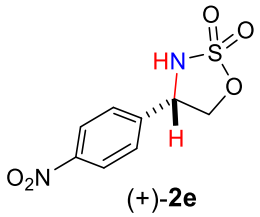
(+)-**2c**

Table 2. Crystal data and structure refinement for **2c.** (CCDC 2097091)

Identification code	**2c**
Empirical formula	$C_9H_{11}NO_4S$
Formula weight	229.25
Temperature/K	228.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.32350(9)
b/Å	8.25340(10)
c/Å	22.6205(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	993.88(2)
Z	4
ρ_{calc}g/cm^3	1.532
μ/mm^{-1}	2.888
F(000)	480.0
Crystal size/mm^3	0.4 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.816 to 141.884

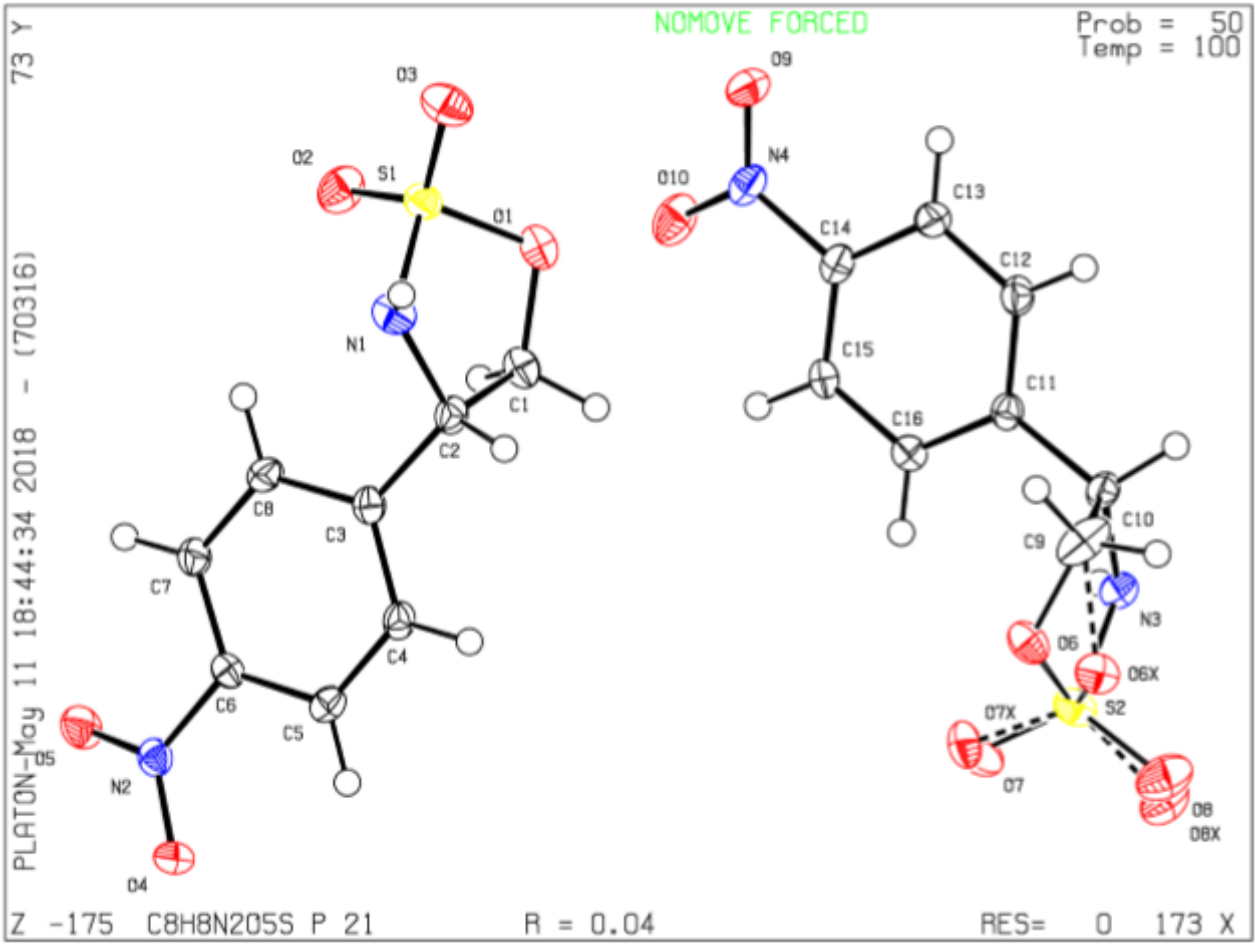
Index ranges	$-5 \leq h \leq 6$, $-9 \leq k \leq 10$, $-27 \leq l \leq 27$
Reflections collected	12145
Independent reflections	1817 [R_{int} = 0.0408, R_{sigma} = 0.0244]
Data/restraints/parameters	1817/0/141
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, wR_2 = 0.0811
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0816
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.27
Flack parameter	0.043(12)

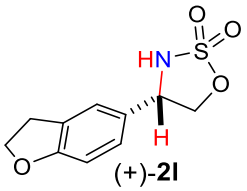

C1
O2
C3
C4
C5
C6
C7
C8
C9
C10
N15
O11
S12
O13
O14



(+)-**2e**

Table 3. Crystal data and structure refinement for **2e**. (CCDC 2097083)		
Identification code	C8H8N2O5S	
Empirical formula	C8 H8 N2 O5 S	
Formula weight	244.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.1996(2) Å	α= 90°.
	b = 9.8838(3) Å	β= 98.7700(10)°.
	c = 13.6772(5) Å	γ = 90°.
Volume	961.88(5) $Å^3$	
Z	4	
Density (calculated)	1.686 Mg/m^3	
Absorption coefficient	3.144 mm^{-1}	
F(000)	504	
Crystal size	0.320 x 0.240 x 0.200 mm^3	
Theta range for data collection	3.269 to 68.271°.	
Index ranges	-8<=h<=8, -11<=k<=11, -16<=l<=16	
Reflections collected	11893	
Independent reflections	3496 [R(int) = 0.0232]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.5919	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3496 / 10 / 323	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0916	
R indices (all data)	R1 = 0.0352, wR2 = 0.0917	
Absolute structure parameter	0.002(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.771 and -0.363 $e.Å^{-3}$	

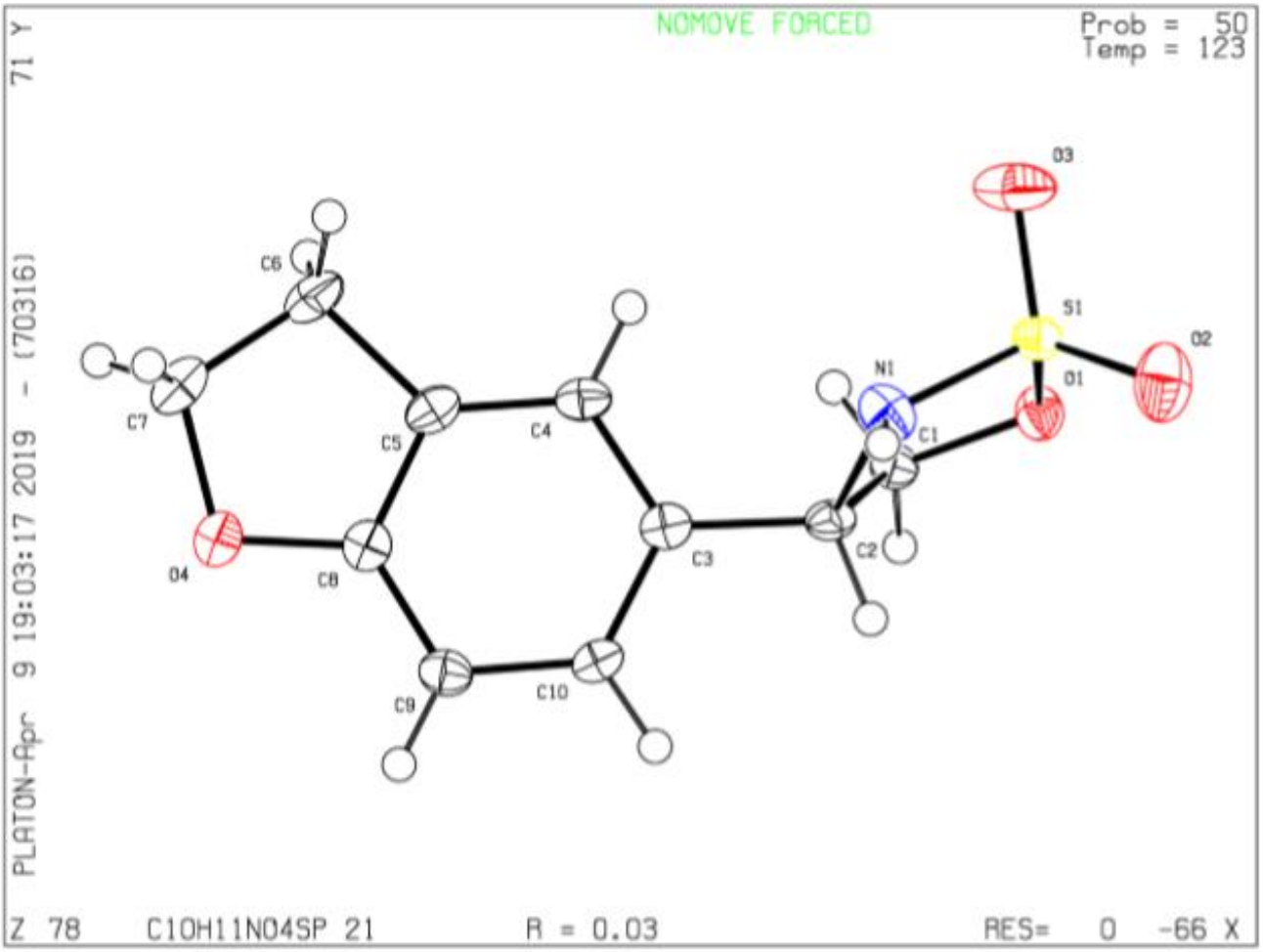

NOMOVE FORCED
Prob = 50
Temp = 100
PLATON-May 11 18:44:34 2018 - (70316)
73 Y
O3
O2
S1
O1
N1
C1
C2
C8
C3
C7
C4
C6
C5
O5
N2
O4
O9
N4
O10
C13
C14
C12
C15
C11
C16
C10
C9
N3
O6
O6X
O7X
S2
O7
O8
O8X
Z -175 C8H8N2O5S P 21
R = 0.04
RES= 0 173 X

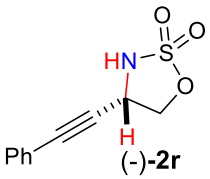


(+)-**2l**

Table 4. Crystal data and structure refinement for **2l**. (CCDC 2097080)

Identification code	C10H11NO4S	
Empirical formula	C10 H11 N O4 S	
Formula weight	241.26	
Temperature	123(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.6416(7) Å	α= 90°.
	b = 6.1950(5) Å	β= 91.217(5)°.
	c = 10.8388(9) Å	γ = 90°.
Volume	512.99(8) $Å^3$	
Z	2	
Density (calculated)	1.562 Mg/m^3	
Absorption coefficient	2.832 mm^{-1}	
F(000)	252	
Crystal size	0.380 x 0.260 x 0.060 mm^3	
Theta range for data collection	4.079 to 66.411°.	
Index ranges	-8<=h<=8, -7<=k<=7, -12<=l<=12	
Reflections collected	5469	
Independent reflections	1777 [R(int) = 0.0503]	
Completeness to theta = 66.411°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5799	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1777 / 2 / 149	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0323, wR2 = 0.0840	
R indices (all data)	R1 = 0.0328, wR2 = 0.0845	
Absolute structure parameter	-0.007(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.301 and -0.198 e.$Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 123
71 Y
PLATON-Apr 9 19:03:17 2019 - (70316)
O3
S1
O2
O1
N1
C1
C2
C3
C4
C5
C6
C7
O4
C8
C9
C10
Z 78 C10H11NO4SP 21 R = 0.03 RES= 0 -66 X

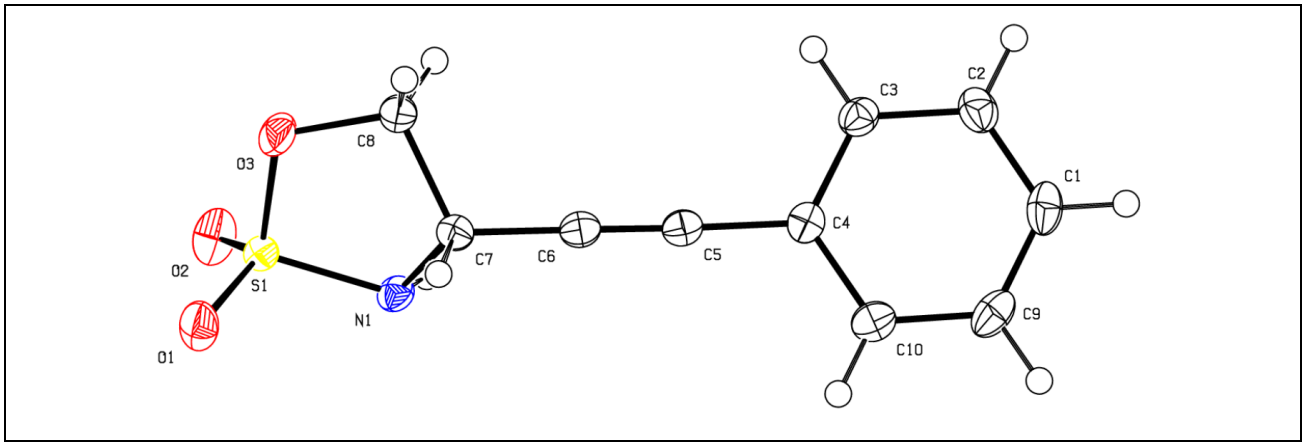


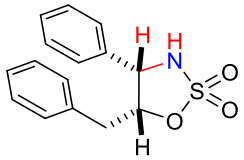
(-)-**2r**

Table 5. Crystal data and structure refinement for **2r.** (CCDC 2097090)

Identification code	**2r**
Empirical formula	$C_{10}H_9NO_3S$
Formula weight	223.24
Temperature/K	105.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.4916(3)
b/Å	7.9553(5)
c/Å	23.5357(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1028.21(10)
Z	4
ρ_{calc}g/cm^3	1.442
μ/mm^{-1}	2.708
F(000)	464.0
Crystal size/mm^3	0.21 × 0.15 × 0.03
Radiation	CuKα (λ = 1.54178)

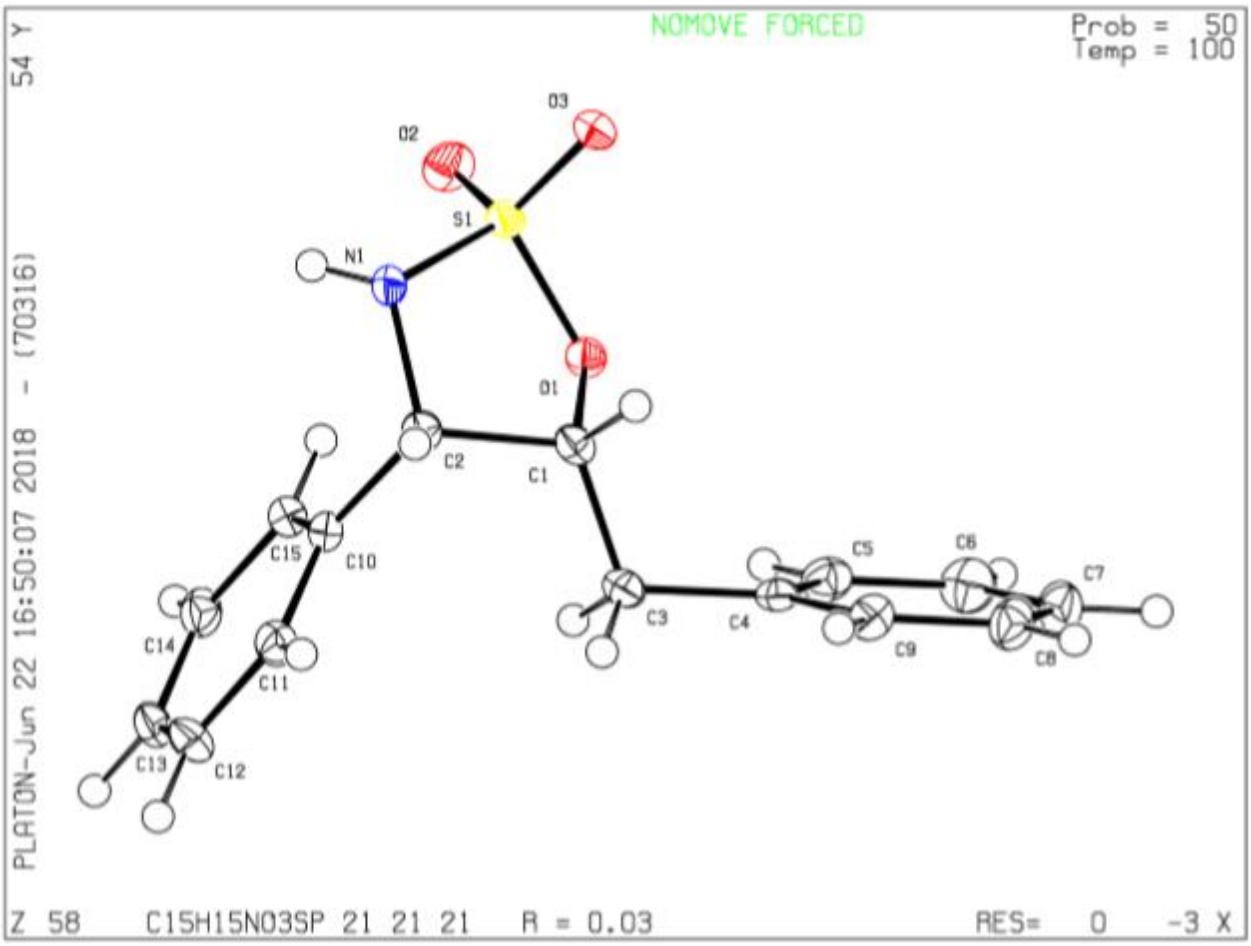
2Θ range for data collection/°	7.512 to 138.292
Index ranges	$-6 \leq h \leq 6$, $-9 \leq k \leq 9$, $-28 \leq l \leq 28$
Reflections collected	12863
Independent reflections	1879 [R_{int} = 0.0378, R_{sigma} = 0.0238]
Data/restraints/parameters	1879/0/140
Goodness-of-fit on F^2	1.134
Final R indexes [I>=2σ (I)]	R_1 = 0.0287, wR_2 = 0.0724
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0726
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.26
Flack parameter	0.032(5)

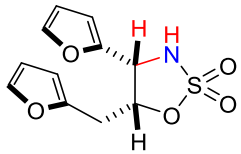

C3
C2
C8
O3
C1
C4
O2
S1
C7
C6
C5
N1
C9
O1
C10



(+)-**2t**

Table 6. Crystal data and structure refinement for **2t.** (CCDC 2097081)		
Identification code	**2t**	
Empirical formula	C15 H15 N O3 S	
Formula weight	289.34	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.1826(3) Å	α= 90°.
	b = 8.8713(4) Å	β= 90°.
	c = 24.9596(12) Å	γ = 90°.
Volume	1368.98(11) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	2.166 mm^{-1}	
F(000)	608	
Crystal size	0.480 x 0.140 x 0.080 mm^3	
Theta range for data collection	3.541 to 66.600°.	
Index ranges	-7<=h<=7, -8<=k<=10, -29<=l<=29	
Reflections collected	9270	
Independent reflections	2400 [R(int) = 0.0343]	
Completeness to theta = 66.600°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5951	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2400 / 1 / 185	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0711	
R indices (all data)	R1 = 0.0272, wR2 = 0.0714	
Absolute structure parameter	0.040(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.316 and -0.307 $e.Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 100
54 Y
PLATON-Jun 22 16:50:07 2018 - (70316)
O3
O2
S1
N1
O1
C2
C1
C15
C10
C5
C6
C7
C3
C4
C14
C11
C9
C8
C13
C12
Z 58 C15H15NO3SP 21 21 21 R = 0.03
RES= 0 -3 X



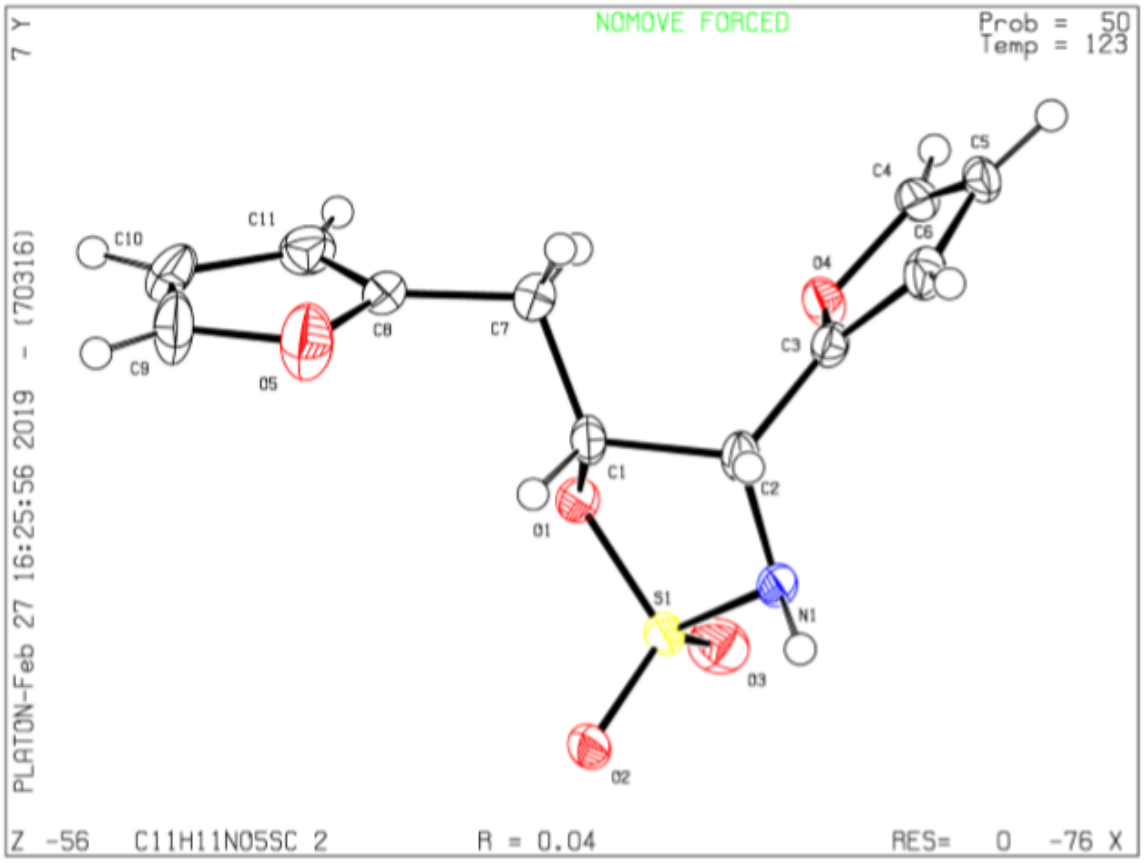
(+)-**2u**

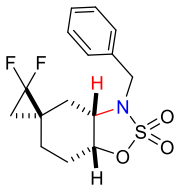
Table 7. Crystal data and structure refinement for **2u.** (CCDC 2097089)

Identification code	**2u**	
Empirical formula	C11 H11 N O5 S	
Formula weight	269.27	
Temperature	123(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 17.9291(12) Å	α= 90°.
	b = 5.4403(4) Å	β= 124.469(3)°.
	c = 14.8271(9) Å	γ = 90°.
Volume	1192.32(14) $Å^3$	
Z	4	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	2.569 mm^{-1}	
F(000)	560	
Crystal size	0.480 x 0.120 x 0.100 mm^3	
Theta range for data collection	3.616 to 66.693°.	
Index ranges	-21<=h<=17, -6<=k<=6, -17<=l<=17	
Reflections collected	4718	
Independent reflections	2078 [R(int) = 0.0276]	
Completeness to theta = 66.693°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5510	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2078 / 2 / 166	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.1042	
R indices (all data)	R1 = 0.0380, wR2 = 0.1046	
Absolute structure parameter	-0.010(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.304 and -0.246 $e.Å^{-3}$	

PLATON version of 18/02/2019; check.def file version of 18/02/2019

Datablock C11H11NO5S - ellipsoid plot

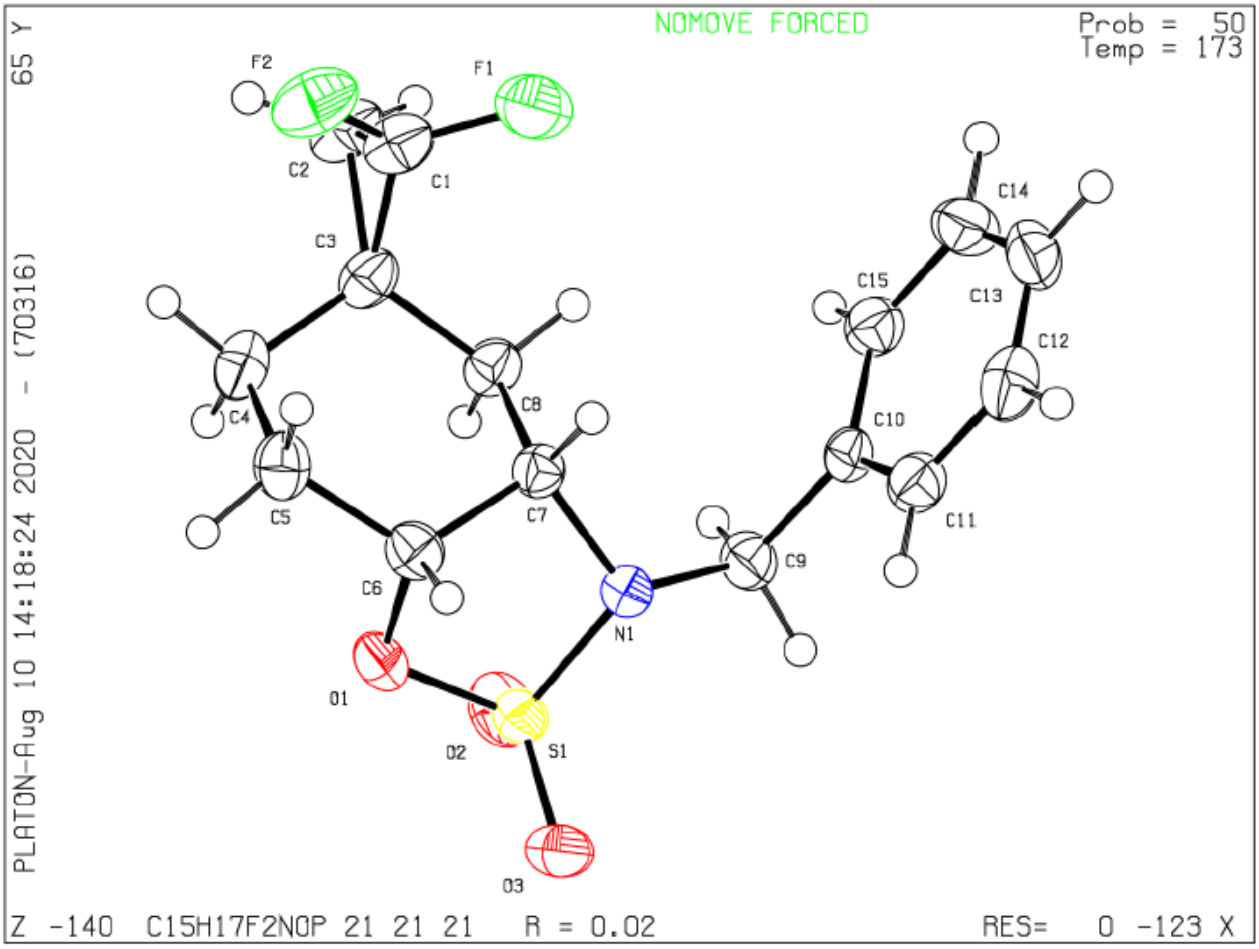


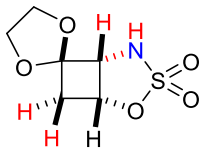


(+)-*N*-Bn-**2ad**

Table 8. Crystal data and structure refinement for *N*-Bn-**2ad**. (CCDC 2097088)

Identification code	C15H17F2NO3S	
Empirical formula	C15 H17 F2 N O3 S	
Formula weight	329.35	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.0047(7) Å	α= 90°.
	b = 10.8944(7) Å	β= 90°.
	c = 13.8830(9) Å	γ = 90°.
Volume	1513.18(17) $Å^3$	
Z	4	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	2.223 mm^{-1}	
F(000)	688	
Crystal size	0.420 x 0.220 x 0.120 mm^3	
Theta range for data collection	5.161 to 66.631°.	
Index ranges	-11<=h<=11, -12<=k<=12, -16<=l<=16	
Reflections collected	28574	
Independent reflections	2622 [R(int) = 0.0253]	
Completeness to theta = 66.631°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6183	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2622 / 0 / 200	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0683	
R indices (all data)	R1 = 0.0230, wR2 = 0.0686	
Absolute structure parameter	0.019(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.161 and -0.210 e.$Å^{-3}$	

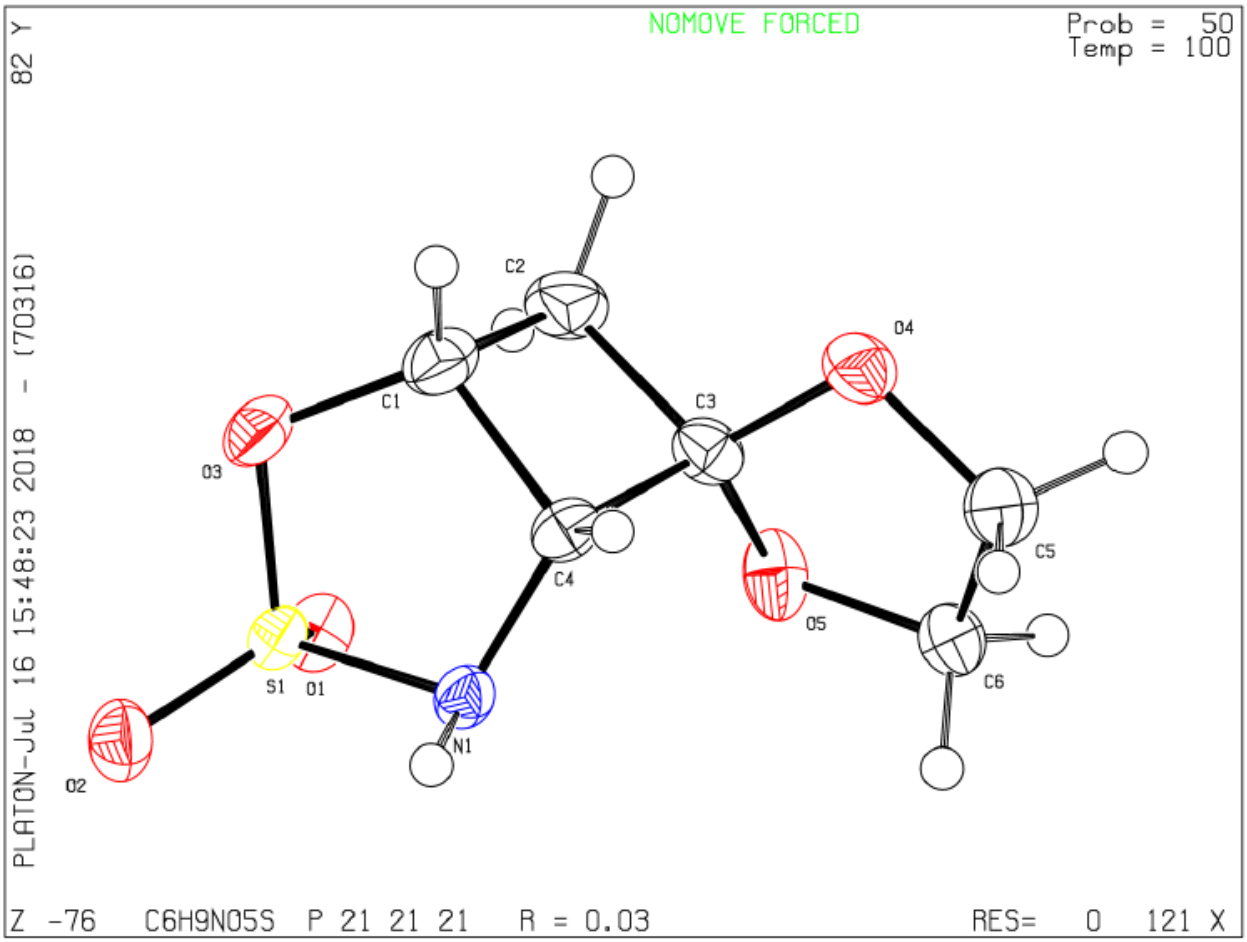

NOMOVE FORCED
Prob = 50
Temp = 173
65 Y
PLATON-Aug 10 14:18:24 2020 - (70316)
F2
F1
C2
C1
C3
C14
C15
C13
C12
C4
C8
C10
C5
C7
C11
C9
C6
N1
O1
O2
S1
O3
Z -140 C15H17F2NOP 21 21 21 R = 0.02
RES= 0 -123 X

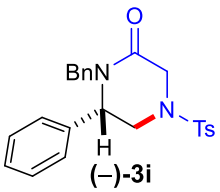


(–)-2ae

Table 9. Crystal data and structure refinement for **2ae.** (CCDC 2097082)

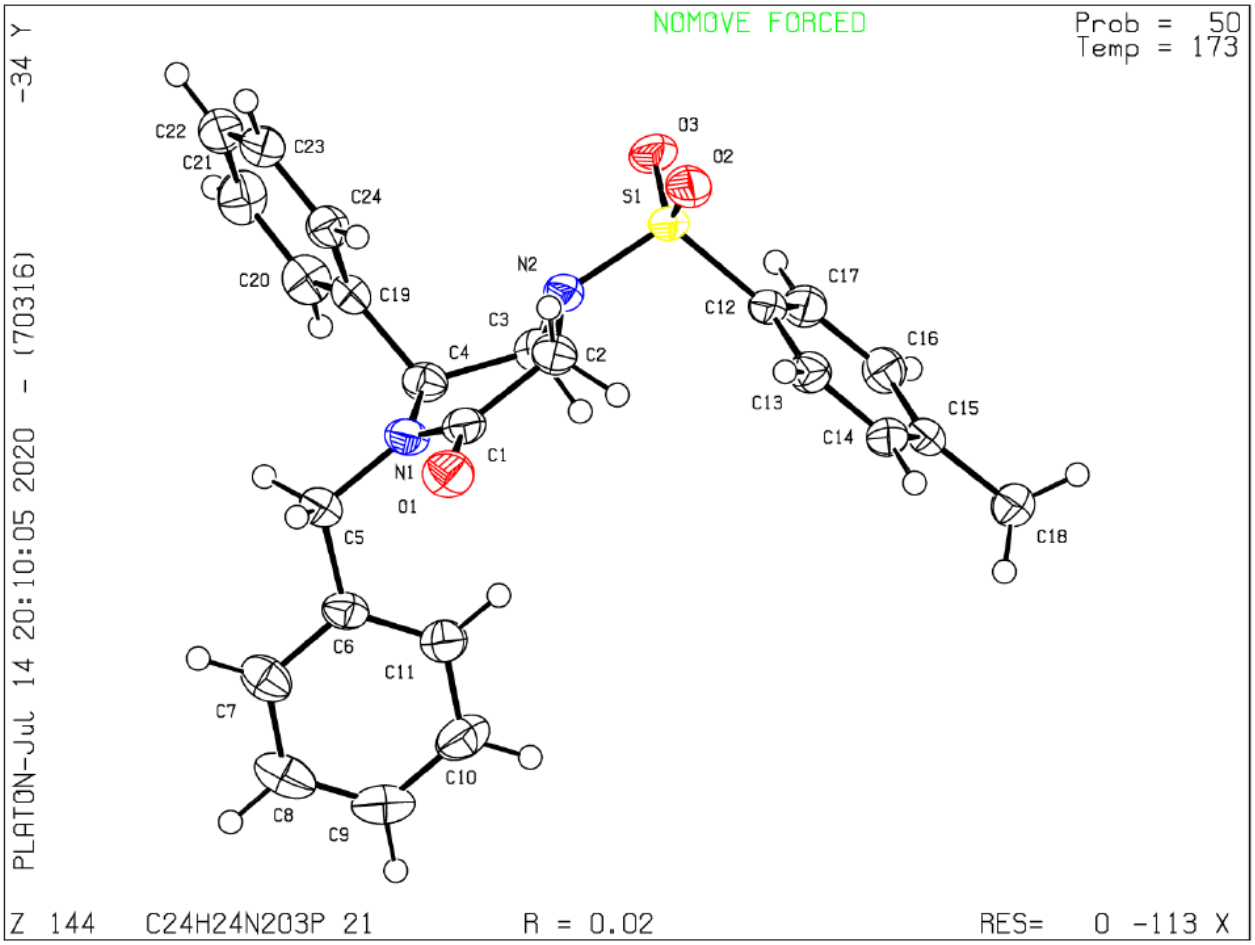
Identification code	**2ae**	
Empirical formula	C6 H9 N O5 S	
Formula weight	207.20	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.2382(3) Å	α= 90°.
	b = 10.1883(6) Å	β= 90°.
	c = 15.0152(9) Å	γ = 90°.
Volume	801.34(8) $Å^3$	
Z	4	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	3.598 mm^{-1}	
F(000)	432	
Crystal size	0.380 x 0.100 x 0.080 mm^3	
Theta range for data collection	5.246 to 66.836°.	
Index ranges	-6<=h<=6, -12<=k<=11, -17<=l<=17	
Reflections collected	8547	
Independent reflections	1418 [R(int) = 0.0653]	
Completeness to theta = 66.836°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5720	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1418 / 1 / 121	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0830	
R indices (all data)	R1 = 0.0318, wR2 = 0.0833	
Absolute structure parameter	0.005(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.455 and -0.300 $e.Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 100
82 Y
PLATON-Jul 16 15:48:23 2018 - (70316)
C1
C2
C3
C4
C5
C6
O1
O2
O3
O4
O5
S1
N1
Z -76 C6H9NO5S P 21 21 21 R = 0.03
RES= 0 121 X



(–)-3i

Table 10. Crystal data and structure refinement for **3i.** (CCDC 2097087)		
Identification code	C24H24N2O3S	
Empirical formula	C24 H24 N2 O3 S	
Formula weight	420.51	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.0355(12) Å	α= 90°.
	b = 10.0246(14) Å	β= 97.020(4)°.
	c = 11.7191(16) Å	γ = 90°.
Volume	1053.5(2) $Å^3$	
Z	2	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	1.595 mm^{-1}	
F(000)	444	
Crystal size	0.380 x 0.240 x 0.150 mm^3	
Theta range for data collection	4.931 to 66.661°.	
Index ranges	-10<=h<=10, -11<=k<=11, -13<=l<=13	
Reflections collected	18180	
Independent reflections	3597 [R(int) = 0.0230]	
Completeness to theta = 66.661°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6187	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3597 / 1 / 273	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0653	
R indices (all data)	R1 = 0.0228, wR2 = 0.0654	
Absolute structure parameter	-0.004(4)	
Extinction coefficient	0.010(3)	
Largest diff. peak and hole	0.145 and -0.163 e.$Å^{-3}$	


NOMOVE FORCED
Prob = 50
Temp = 173
-34 Y
PLATON-Jul 14 20:10:05 2020 - (70316)
O3
O2
S1
N2
C22
C23
C21
C24
C20
C19
C3
C4
C2
C17
C12
C16
C13
C15
C14
N1
C1
O1
C5
C18
C6
C11
C7
C10
C8
C9
Z 144 C24H24N2O3P 21
R = 0.02
RES= 0 -113 X

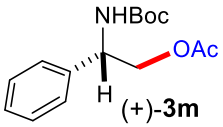
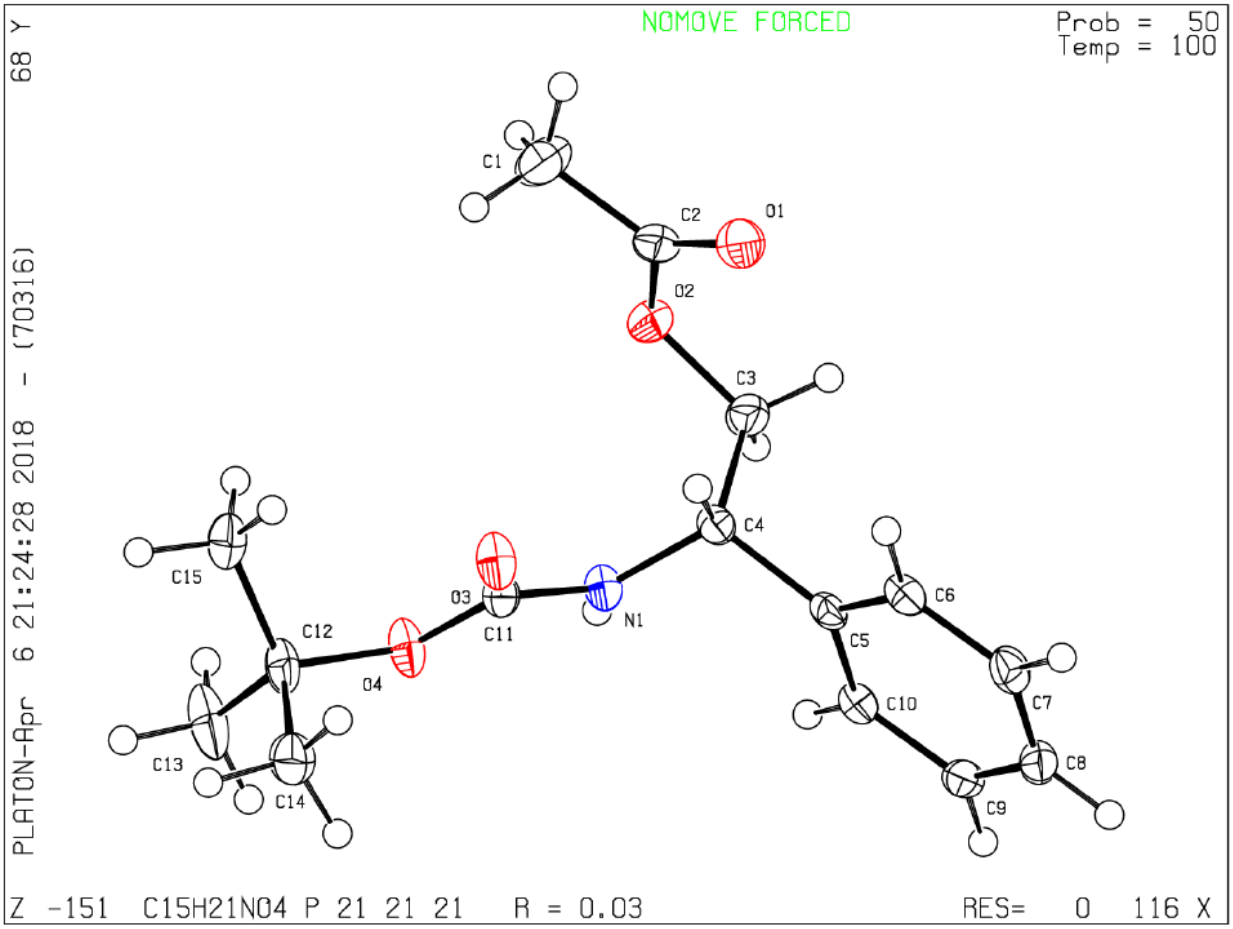
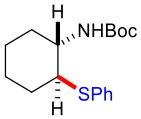


Table 11. Crystal data and structure refinement for **3m**. (CCDC 2097085)		
Identification code	**3m**	
Empirical formula	C15 H21 N O4	
Formula weight	279.33	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.2404(2) Å	α= 90°.
	b = 10.6394(4) Å	β= 90°.
	c = 27.3903(10) Å	γ = 90°.
Volume	1527.14(10) $Å^3$	
Z	4	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	0.721 mm^{-1}	
F(000)	600	
Crystal size	0.480 x 0.090 x 0.080 mm^3	
Theta range for data collection	3.227 to 66.566°.	
Index ranges	-6<=h<=6, -12<=k<=12, -24<=l<=32	
Reflections collected	11554	
Independent reflections	2682 [R(int) = 0.0316]	
Completeness to theta = 66.566°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6603	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2682 / 1 / 188	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0721	
R indices (all data)	R1 = 0.0296, wR2 = 0.0726	
Absolute structure parameter	0.06(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.182 and -0.199 $e.Å^{-3}$	

Datablock C15H21NO4 - ellipsoid plot





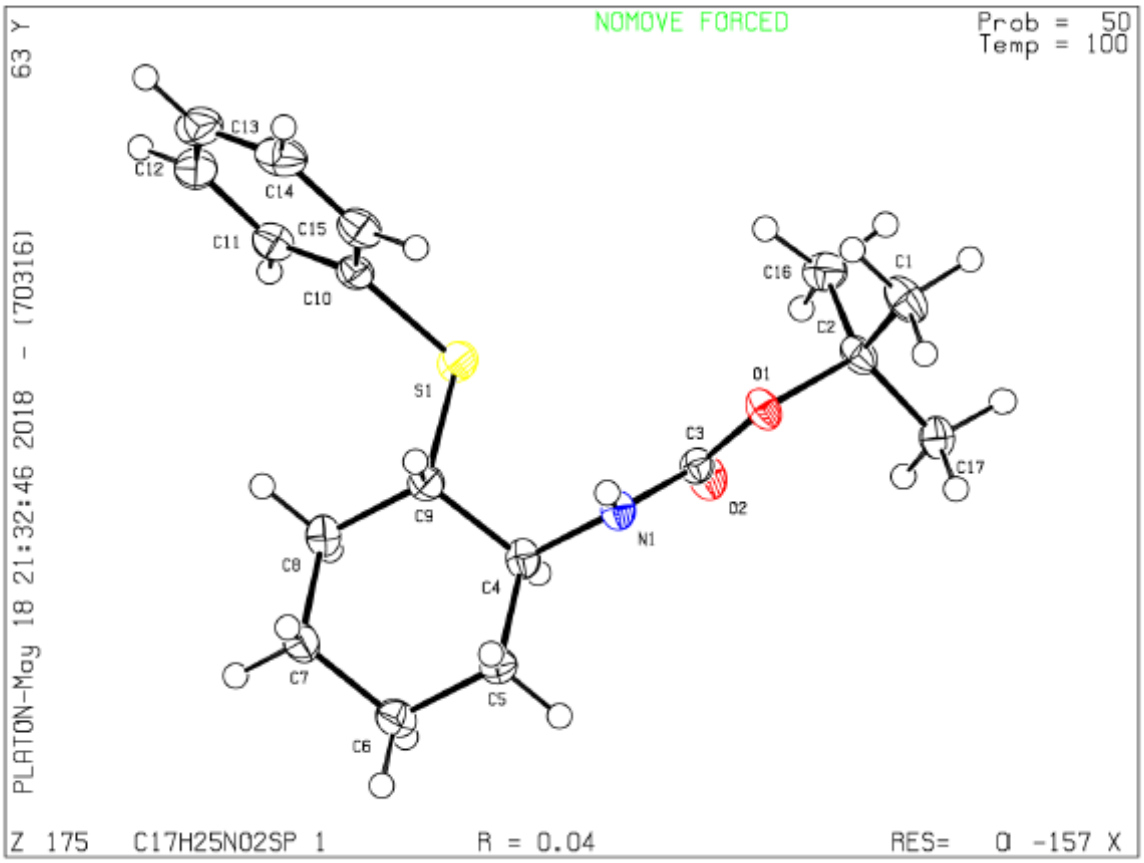
(+)-**3v**

Table 12. Crystal data and structure refinement for **3v**. (CCDC 2097086)

Identification code	**3v**	
Empirical formula	C17 H25 N O2 S	
Formula weight	307.44	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 5.1618(4) Å	α= 112.852(4)°.
	b = 8.6542(7) Å	β= 96.462(4)°.
	c = 10.5664(8) Å	γ = 99.605(4)°.
Volume	420.62(6) $Å^3$	
Z	1	
Density (calculated)	1.214 Mg/m^3	
Absorption coefficient	1.735 mm^{-1}	
F(000)	166	
Crystal size	0.550 x 0.340 x 0.220 mm^3	
Theta range for data collection	5.657 to 69.773°.	
Index ranges	-6<=h<=6, -10<=k<=10, -12<=l<=12	
Reflections collected	6021	
Independent reflections	2898 [R(int) = 0.0304]	
Completeness to theta = 67.679°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6045	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2898 / 4 / 196	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1111	
R indices (all data)	R1 = 0.0416, wR2 = 0.1115	
Absolute structure parameter	-0.03(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.314 and -0.222 $e.Å^{-3}$	

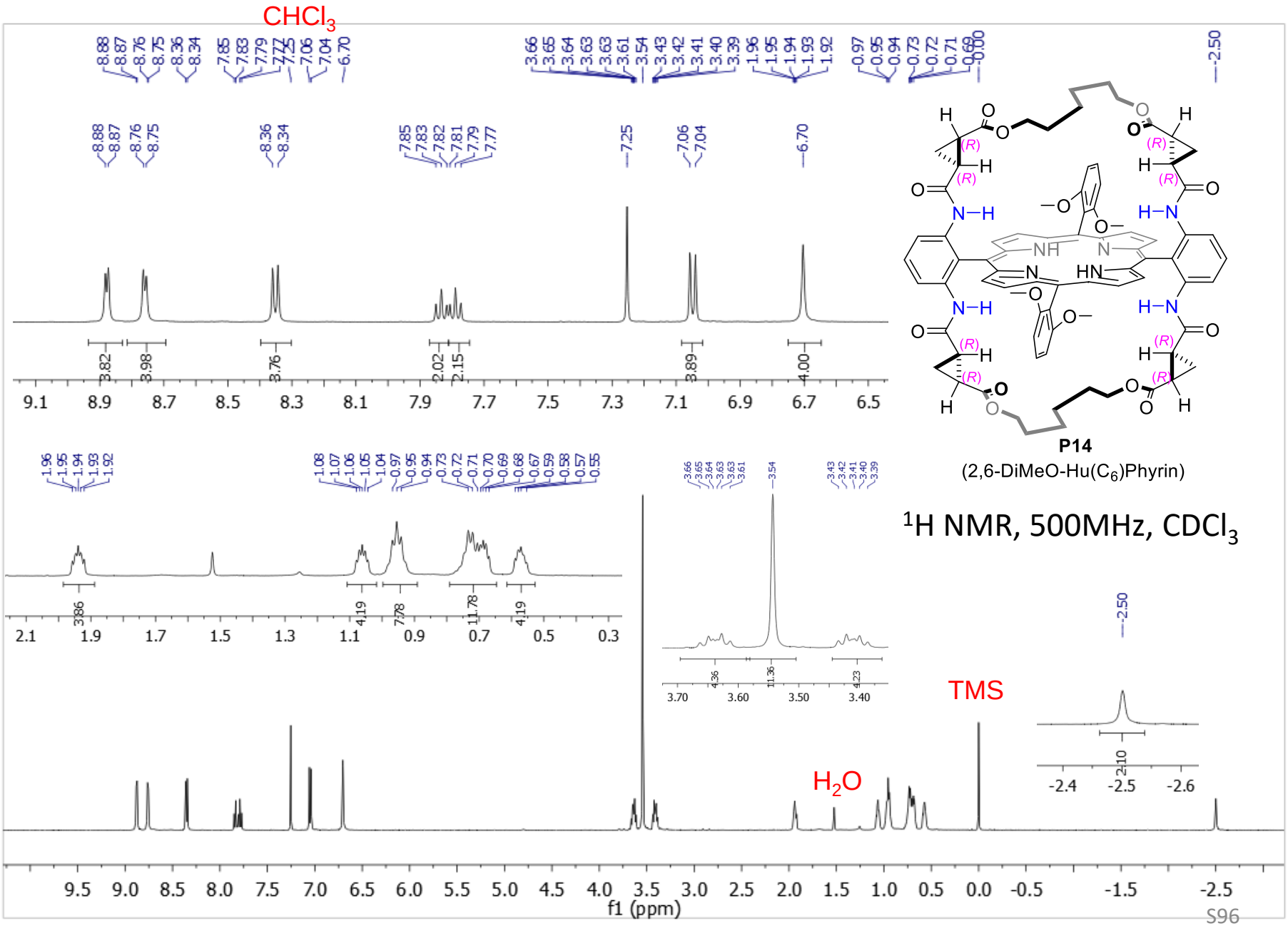
PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock: C17H25NO2S - ellipsoid plot



7. References

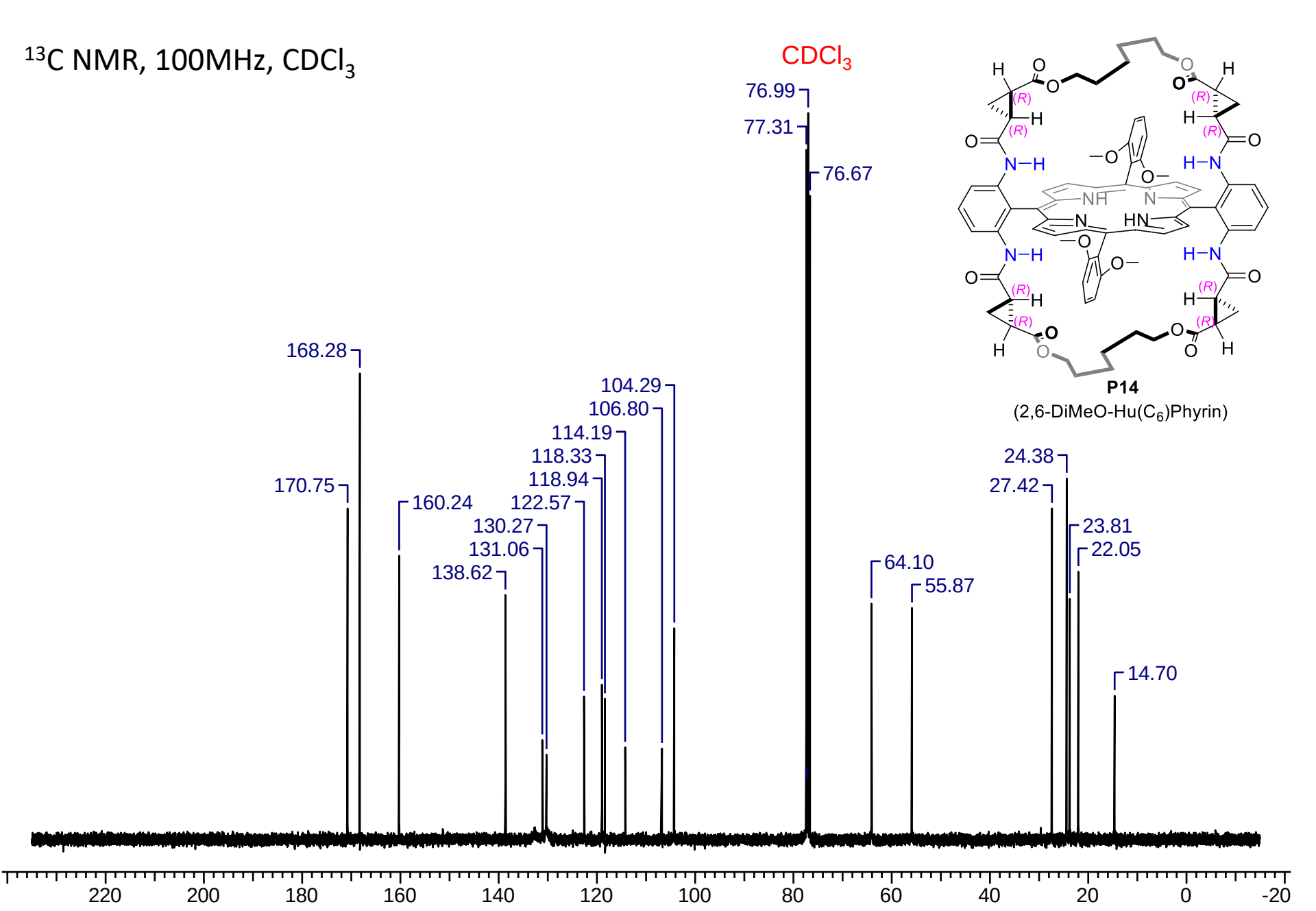
1. H. C. Kolb, M. G. Finn, K. B. Sharpless, Click chemistry: diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.* **40**, 2004–2021 (2001).
2. S. Bräse, C. Gil, K. Knepper, V. Zimmermann, Organic azides: an exploding diversity of a unique class of compounds. *Angew. Chem. Int. Ed.* **44**, 5188–5240 (2005).
3. K. Lang, S. Torker, L. Wojtas, X. P. Zhang, Asymmetric induction and enantiodivergence in catalytic radical C–H amination via enantiodifferentiative H-atom abstraction and stereoretentive radical substitution. *J. Am. Chem. Soc*. **141**, 12388–12396 (2019).
4. Y. Hu, K. Lang, C. Li, J. B. Gill, I. Kim, H. Lu, K. B. Fields, M. Marshall, Q. Cheng, X. Cui, L. Wojtas, X. P. Zhang, Enantioselective radical construction of 5-membered cyclic sulfonamides by metalloradical C–H amination. *J. Am. Chem. Soc*. **141**, 18160−18169 (2019).
5. Cavender, C. J. & Shiner, V. J. Trifluoromethanesulfonyl azide. Its reaction with alkyl amines to form alkyl azides. *J. Org. Chem*. **37**, 3567-3569 (1972).
6. Meng, G.; Guo, T.; Ma, T.; Zhang, J.; Shen, Y.; Sharpless, K. B.; Dong, J. Modular click chemistry libraries for functional screens using a diazotizing reagent. *Nature* **574**, 86-89 (2019).
7. M. W. Giese, W. H. Moser, Stereoselective synthesis of the rocaglamide skeleton via a silyl vinylketene formation/[4 + 1] annulation sequence. *Org. Lett.* **10**, 4215−4218 (2008).
8. A. J. Wommack, J. S. Kingsbury, Synthesis of acyclic ketones by catalytic, bidirectional homologation of formaldehyde with nonstabilized diazoalkanes. application of a chiral diazomethyl(pyrrolidine) in total syntheses of erythroxylon alkaloids. *J. Org. Chem.* **78**, 10573−10587 (2013).
9. E. Hartmann, M. Oestreich, Two-directional desymmetrization by double 1,4-addition of silicon and boron nucleophiles. *Org. Lett.* **14**, 2406−2409 (2012).
10. R. M. Bychek, V. V. Levterov, I. V. Sadkova, A. A. Tolmachev, P. K. Mykhailiuk, Synthesis of functionalized difluorocyclopropanes: unique building blocks for drug discovery. *Chem. Eur. J.* **24**, 12291−12297 (2018).
11. Z. Wan, M. L. Vazquez, X. Li, Benzamides of pyrazolyl-amino-pyrimidinyl derivatives, and compositions and methods thereof. WO2020119819A1, 2020.
12. M. N. Alberti, G. Vassilikogiannakis, M. Orfanopoulos, Stereochemistry of the singlet oxygenation of simple alkenes: a stereospecific transformation. *Org. Lett.* **10**, 3997−4000 (2008).
13. Y.-Q. Wang, C.-B. Yu, D.-W. Wang, X.-B. Wang, Y.-G. Zhou, Enantioselective synthesis of cyclic sulfamidates via Pd-catalyzed hydrogenation. *Org. Lett.* **10**, 2071−2074 (2008).
14. T. Kaseda, T. Kikuchi, C. Kibayashi, Enantioselective total synthesis of (+)-(*S*)-dihydroperiphylline. *Tetrahedron Lett.* **30**, 4539–4542 (1989).
15. M. Duan, W. M. Kazmierski, M. Tallant, J. H. Jun, M. Edelstein, R. Ferris, D. Todd, P. Wheelan, Z. Xiong, Discovery of a novel series of cyclic urea as potent CCR5 antagonists. *Bioorganic Med. Chem. Lett.* **21**, 6381−6385 (2011).
16. S. Mizuta, N. Shibata, Y. Goto, T. Furukawa, S. Nakamura, T. Toru, Cinchona alkaloid-catalyzed enantioselective monofluoromethylation reaction based on fluorobis(phenylsulfonyl)methane chemistry combined with a Mannich-type reaction. *J. Am. Chem. Soc*. **129**, 6394−6395 (2007).
17. H. Xiao, Z. Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang, G. Zhao, Asymmetric [3+2] cycloadditions of allenoates and dual activated olefins catalyzed by simple bifunctional *N*-acyl aminophosphines. *Angew. Chem. Int. Ed.* **49**, 4467−4470 (2010).
18. N. Pendem, C. Douat, P. Claudon, M. Laguerre, S. Castano, B. Desbat, D. Cavagnat, E. Ennifar, B. Kauffmann, G. Guichard, Helix-forming propensity of aliphatic urea oligomers incorporating noncanonical residue substitution patterns. *J. Am. Chem. Soc.* **135**, 4884–4892 (2013).
19. X.-L. Hou, R.-H. Fan, L.-X. Dai, Tributylphosphine: a remarkable promoting reagent for the ring-opening reaction of aziridines. *J. Org. Chem.* **67**, 5295−5300 (2002).
20. P. O'Brien, C. M. Rosser, D. Caine, On the α-lithiation-rearrangement of *N*-toluensulfonyl aziridines: mechanistic and synthetic aspects. *Tetrahedron* **59**, 9779–9791 (2003).



P14
(2,6-DiMeO-Hu(C_6)Phyrin)

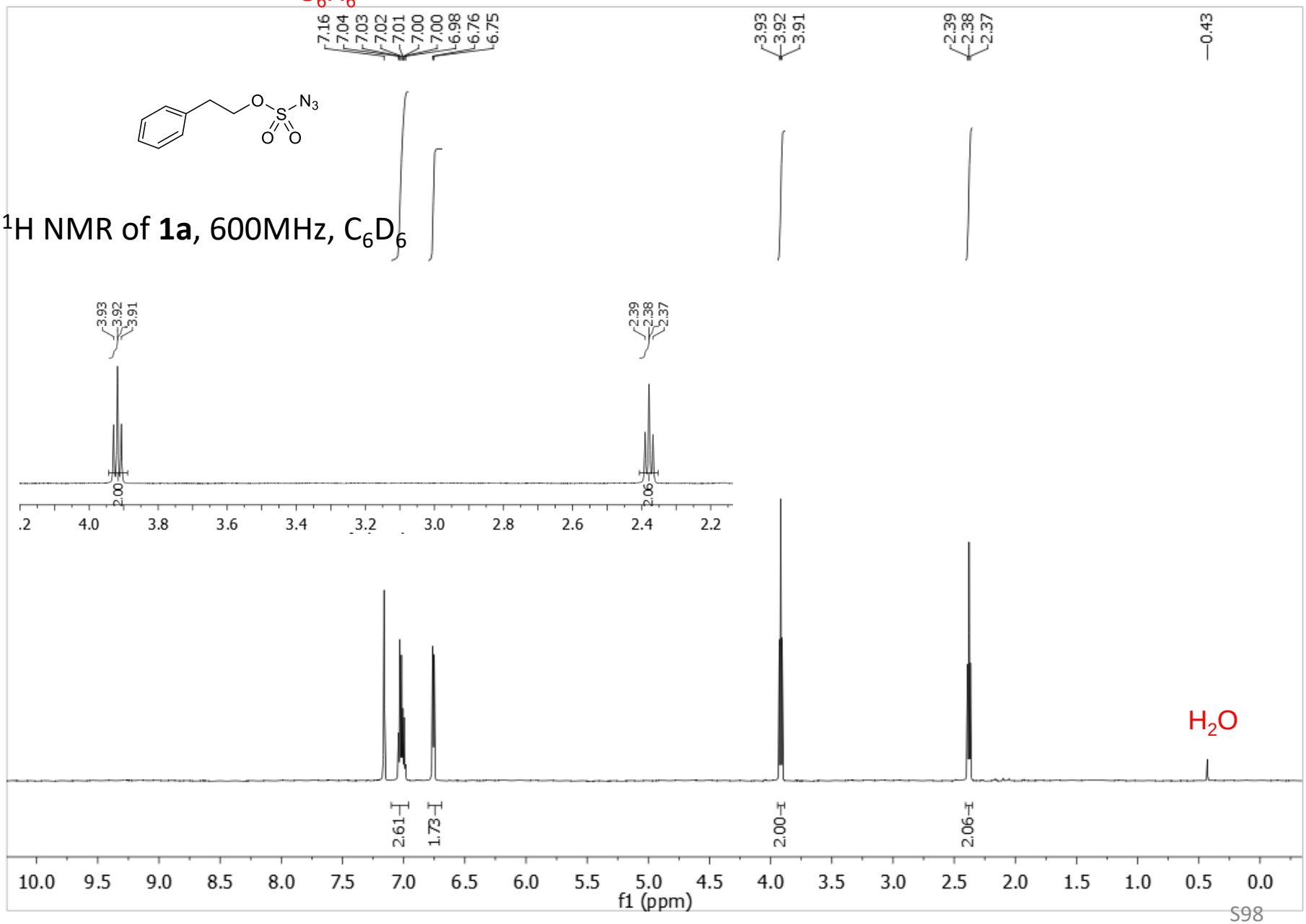
^{1}H NMR, 500MHz, $CDCl_3$

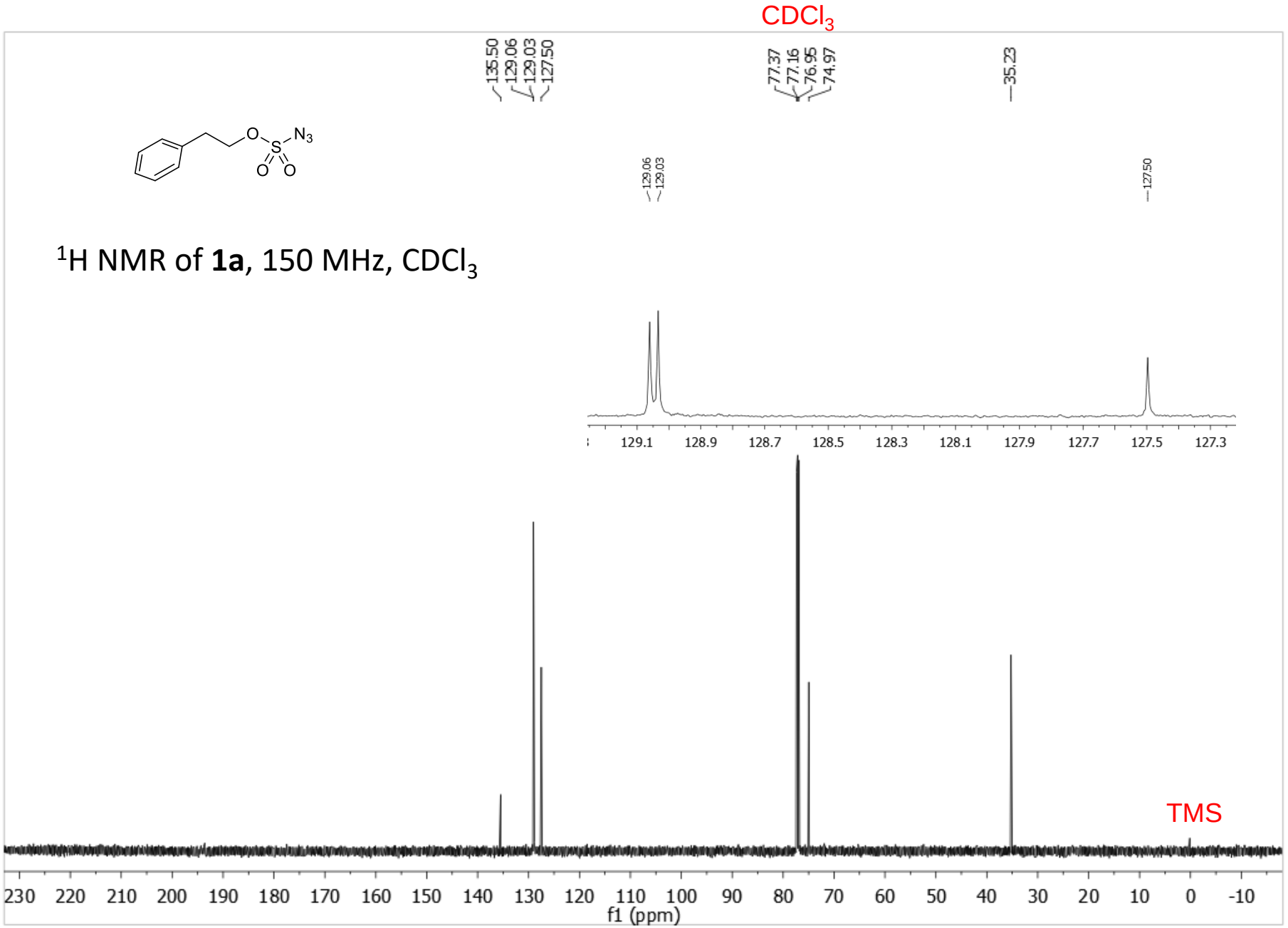
^{13}C NMR, 100MHz, $CDCl_3$

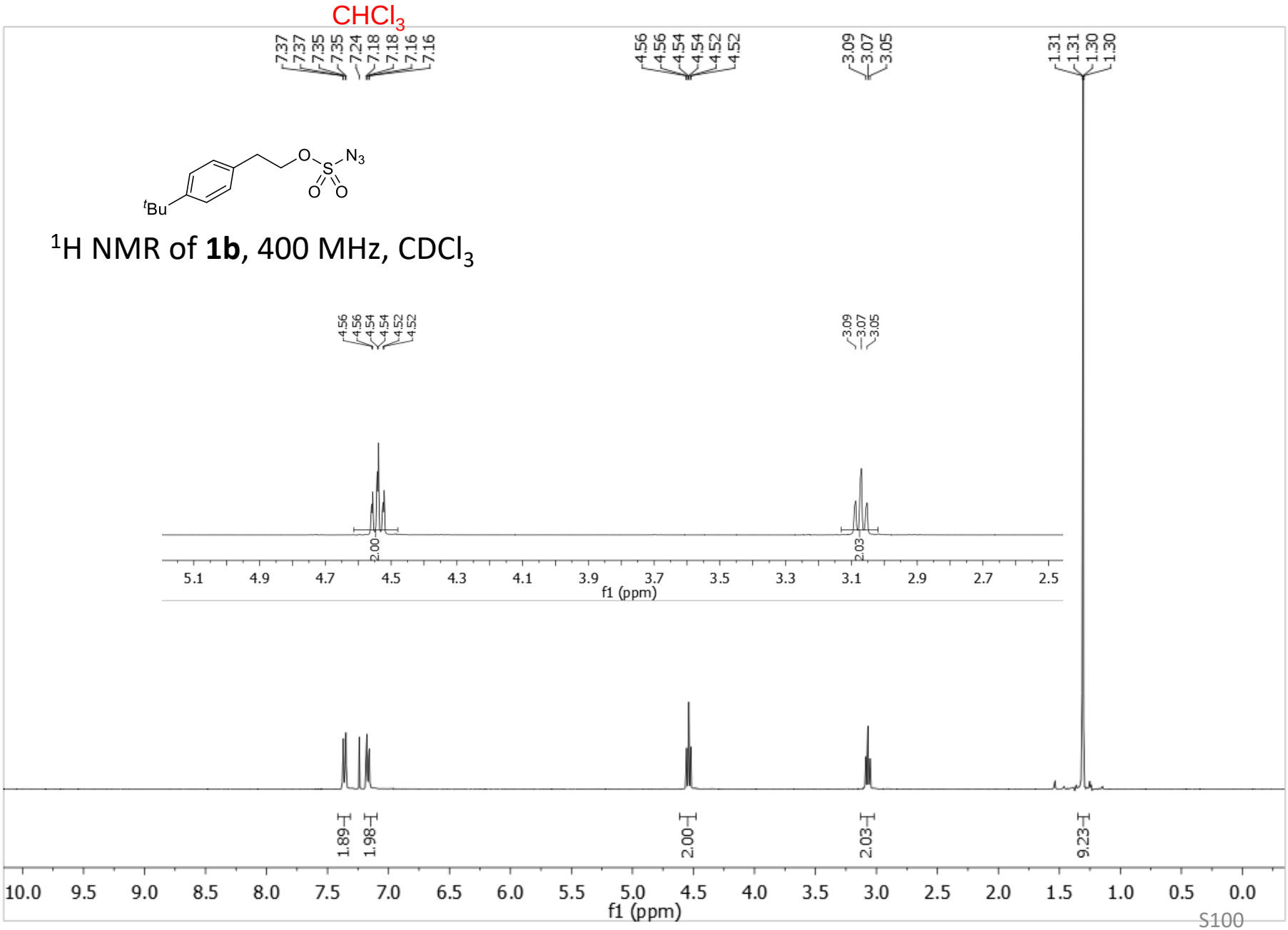


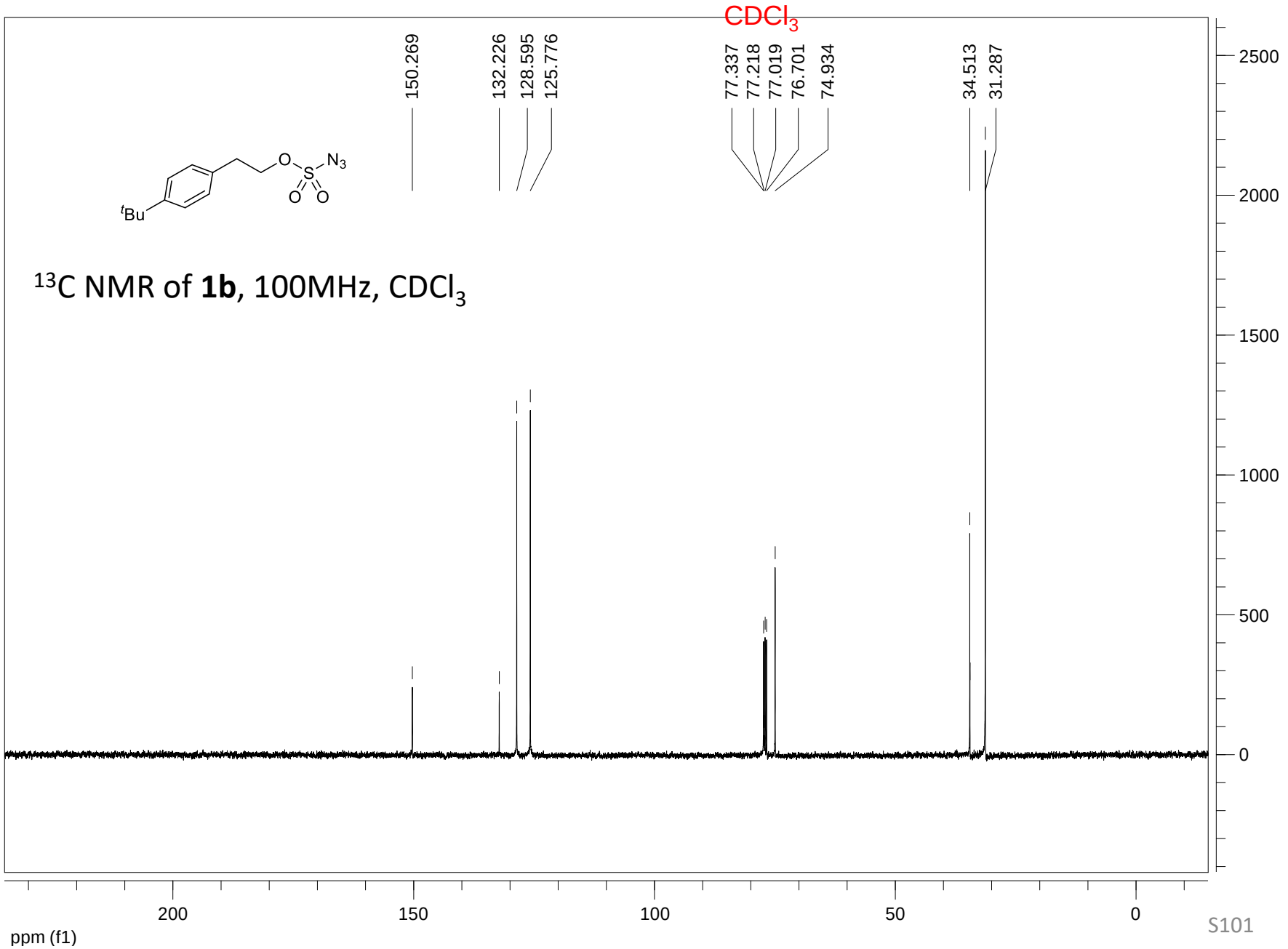
P14

(2,6-DiMeO-Hu(C_6)Phyrin)

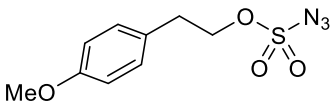

C6H6
7.16
7.04
7.03
7.02
7.01
7.00
7.00
6.98
6.76
6.75
3.93
3.92
3.91
2.39
2.38
2.37
0.43
O
S
N3
O
O
1H NMR of 1a, 600MHz, C6D6
2.00
2.06
2.61
1.73
2.00
2.06
H2O
f1 (ppm)


CDCl3
135.50
129.06
129.03
127.50
77.37
77.16
76.95
74.97
35.23
129.06
129.03
127.50
O
S
N3
O
O
1H NMR of 1a, 150 MHz, CDCl3
129.1
128.9
128.7
128.5
128.3
128.1
127.9
127.7
127.5
127.3
TMS
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

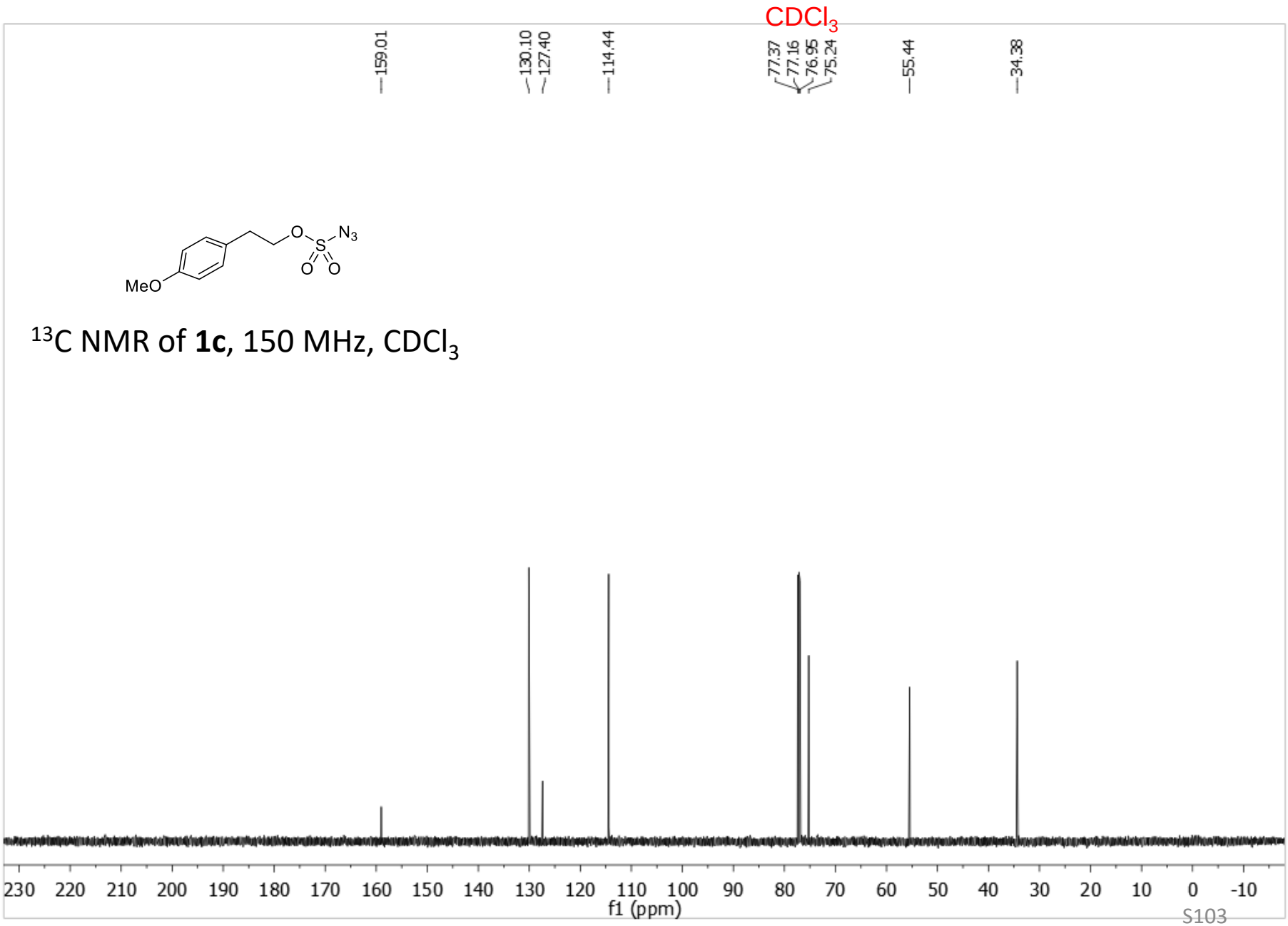

CHCl3
7.37
7.37
7.35
7.35
7.24
7.18
7.18
7.16
7.16
4.56
4.56
4.54
4.54
4.52
4.52
3.09
3.07
3.05
1.31
1.31
1.30
1.30
O
S
N3
O
O
tBu
1H NMR of 1b, 400 MHz, CDCl3
2.00
2.03
f1 (ppm)
1.89
1.98
2.00
2.03
9.23
f1 (ppm)


CDCl3
150.269
132.226
128.595
125.776
77.337
77.218
77.019
76.701
74.934
34.513
31.287
O
S
N3
O
O
tBu
13C NMR of 1b, 100MHz, CDCl3
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (f1)

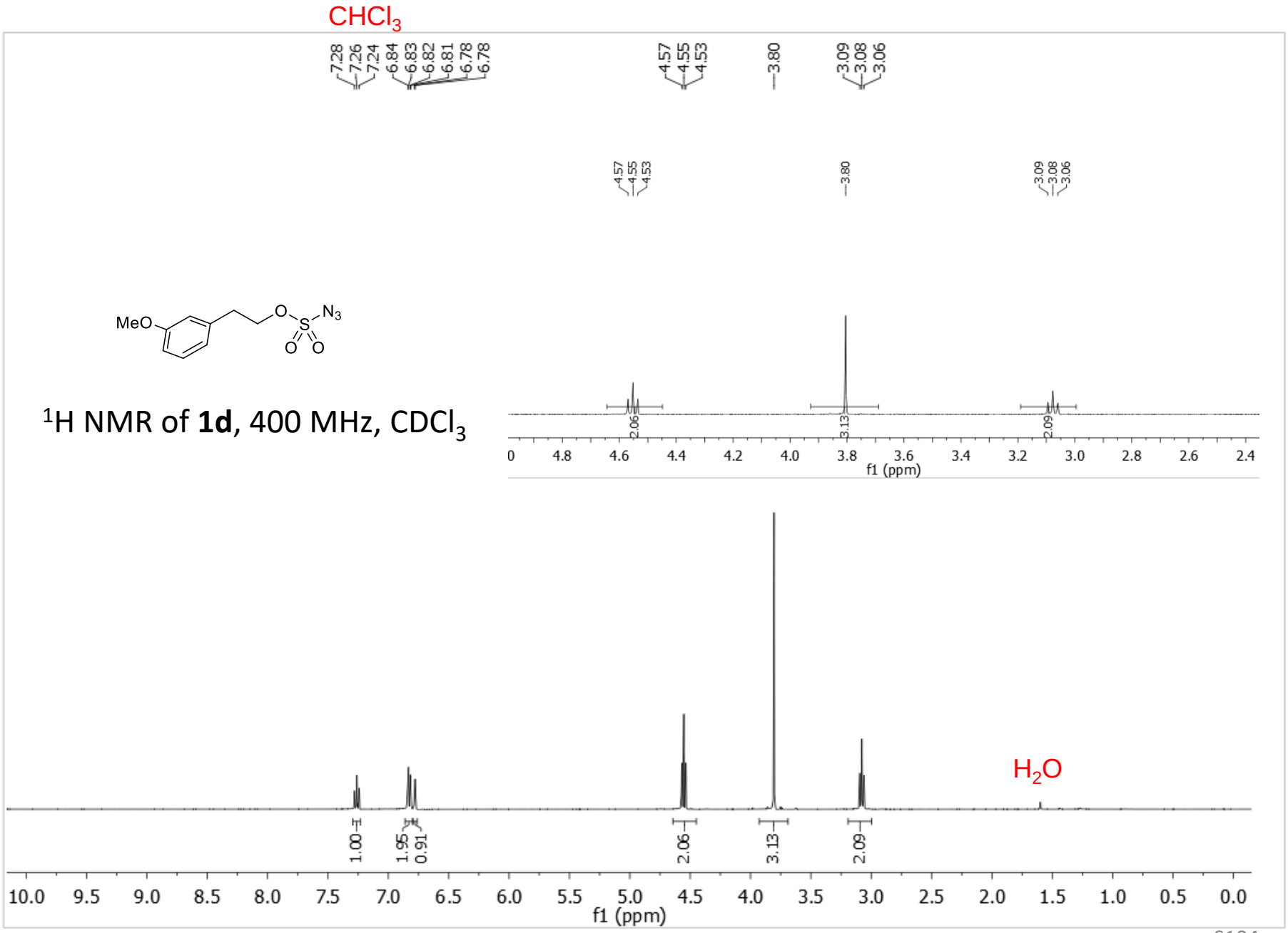
$CHCl_3$

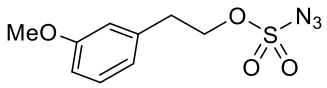


^{1}H NMR of **1c**, 250 MHz, $CDCl_3$

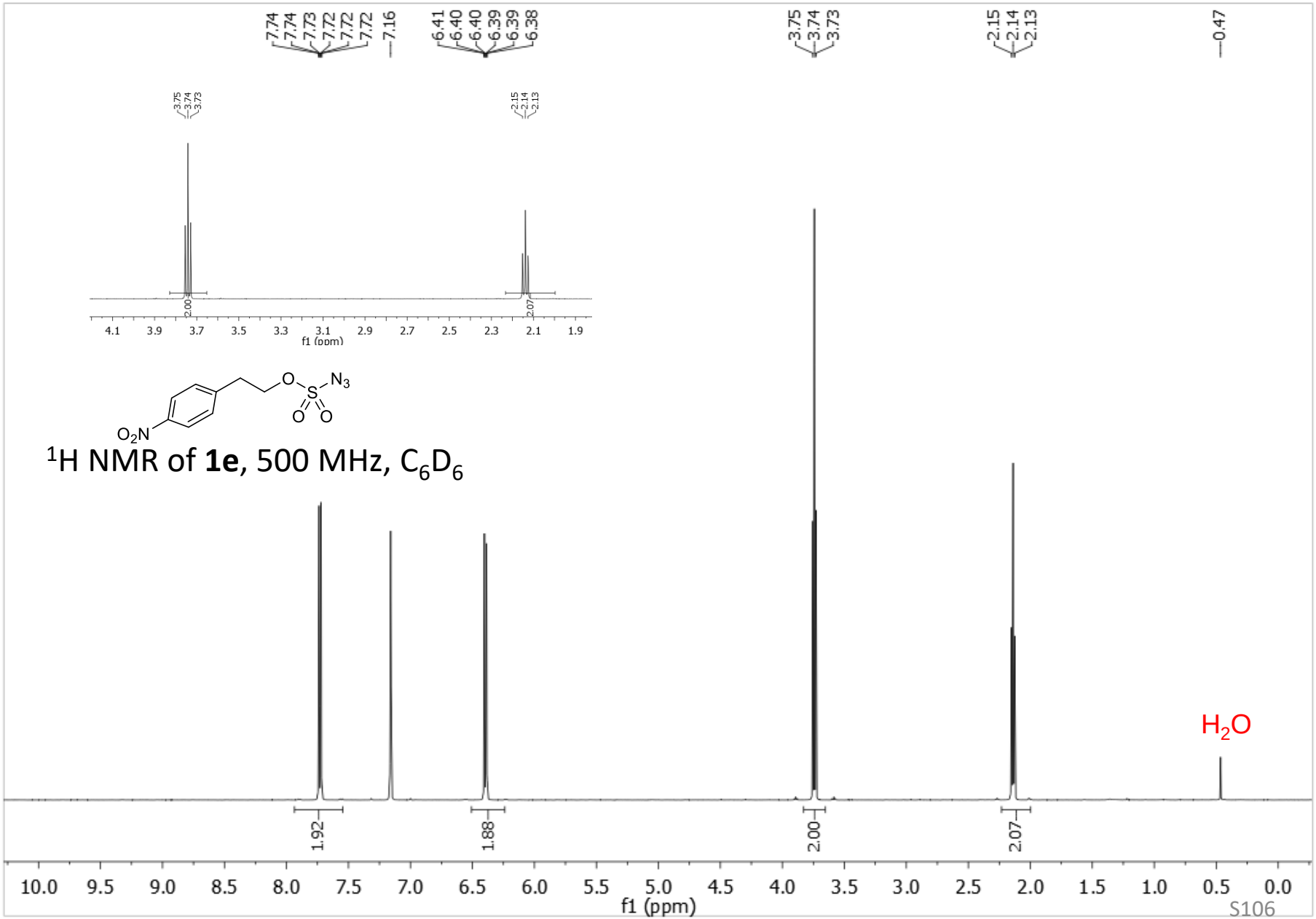


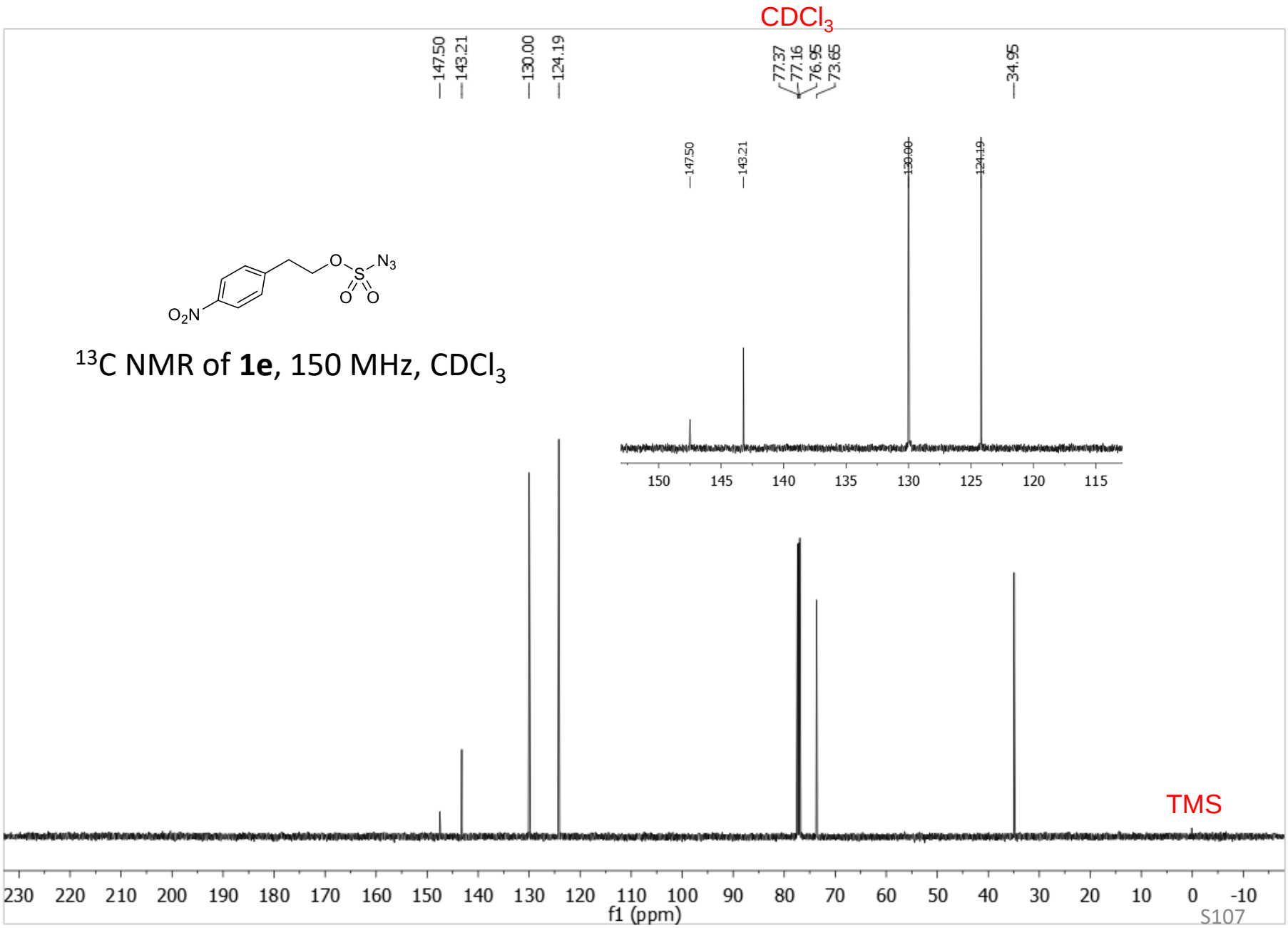
^{13}C NMR of **1c**, 150 MHz, $CDCl_3$


CHCl3
7.28
7.26
7.24
6.84
6.83
6.82
6.81
6.78
6.78
4.57
4.55
4.53
3.80
3.09
3.08
3.06
MeO
O
S
N3
O
O
1H NMR of 1d, 400 MHz, CDCl3
2.06
3.13
2.09
f1 (ppm)
H2O
1.00
1.95
0.91
2.06
3.13
2.09
f1 (ppm)

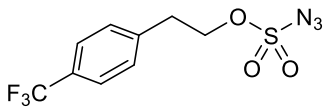


^{13}C NMR of **1d**, 100 MHz, $CDCl_3$

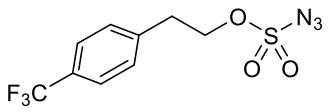

C6H6
7.74
7.74
7.73
7.72
7.72
7.72
7.16
6.41
6.40
6.40
6.39
6.39
6.38
3.75
3.74
3.73
2.15
2.14
2.13
0.47
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
f1 (ppm)
O2N
O
S
O
O
N3
1H NMR of 1e, 500 MHz, C6D6
H2O
1.92
1.88
2.00
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CDCl3
147.50
143.21
130.00
124.19
77.37
77.16
76.95
73.65
34.95
O2N
O
S
N3
O
O
13C NMR of 1e, 150 MHz, CDCl3
150
145
140
135
130
125
120
115
TMS
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

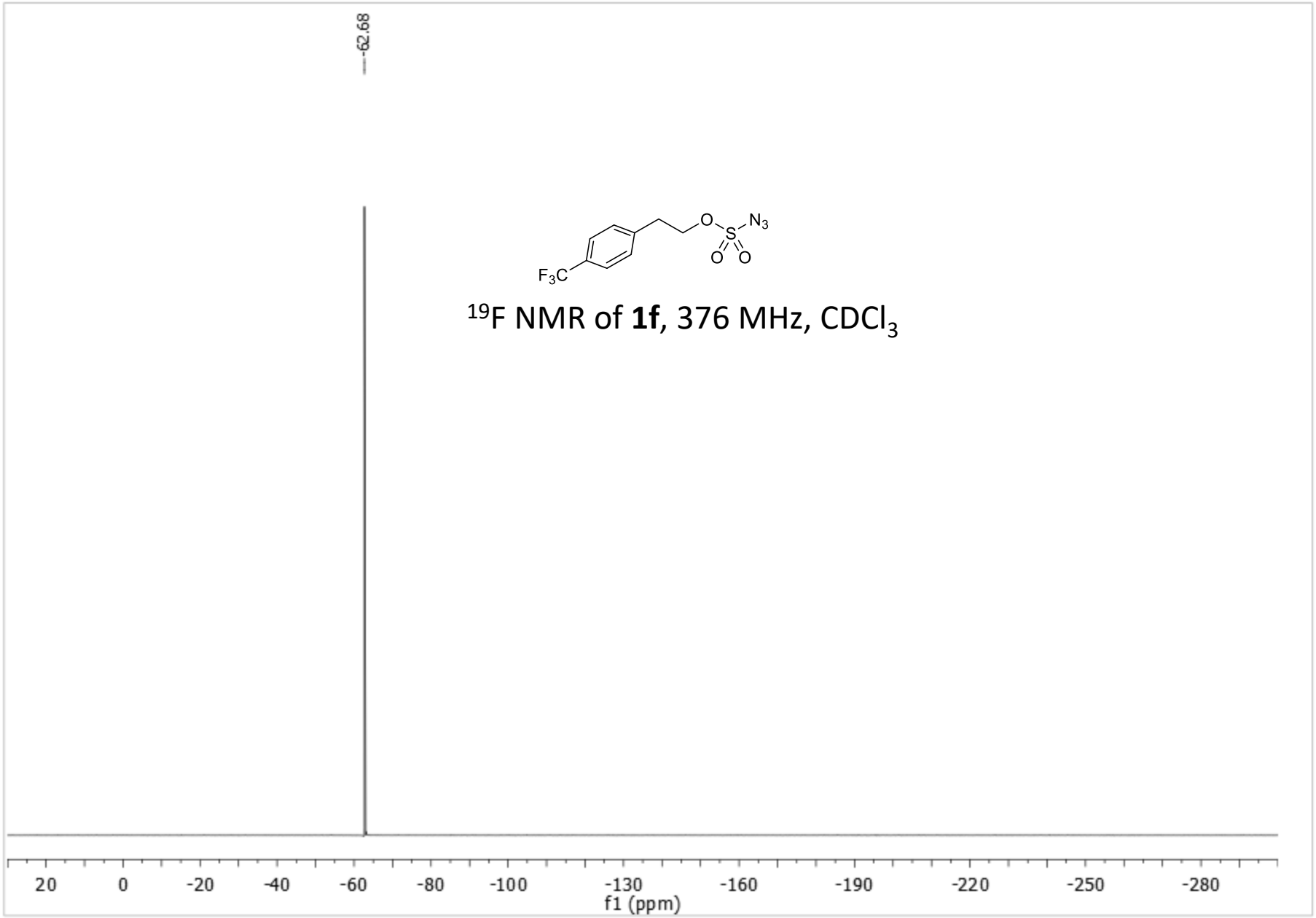
$CHCl_3$



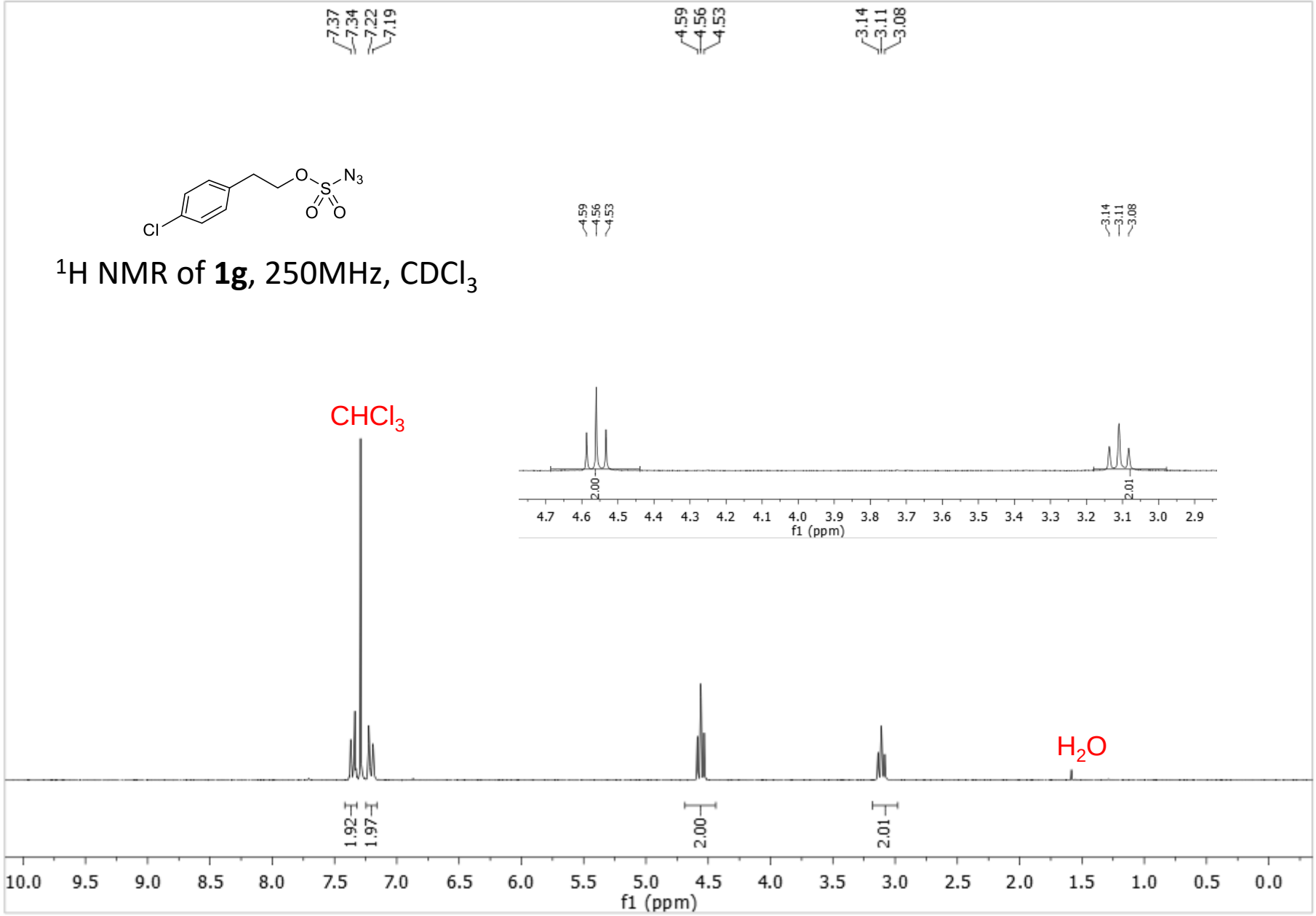
^{1}H NMR of **1f**, 400 MHz, $CDCl_3$



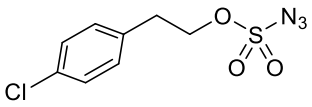
^{13}C NMR of **1f**, 100 MHz, $CDCl_3$



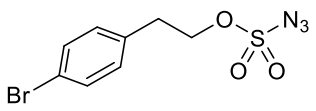
^{19}F NMR of **1f**, 376 MHz, $CDCl_3$



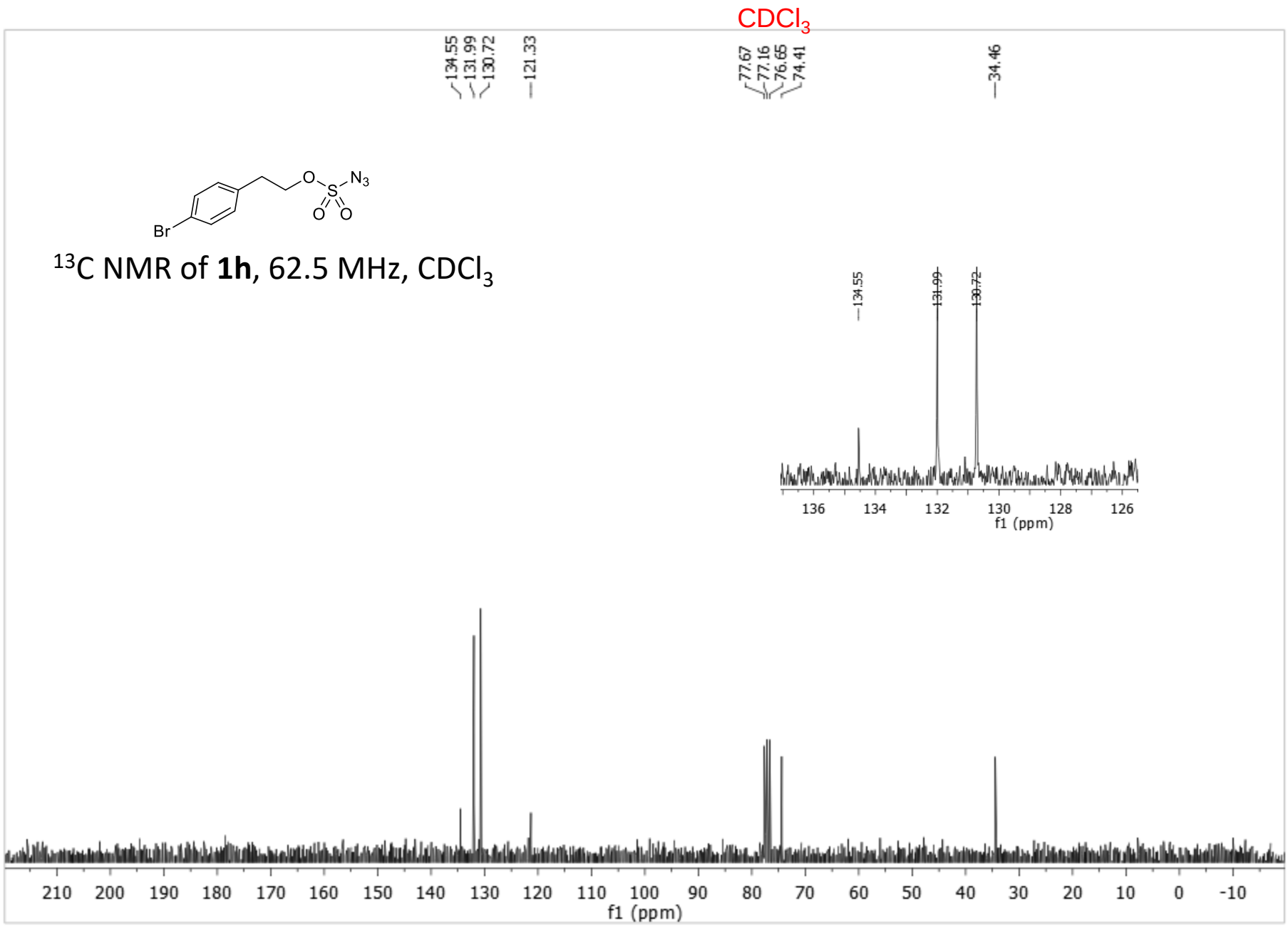
^{1}H NMR of **1g**, 250MHz, $CDCl_3$

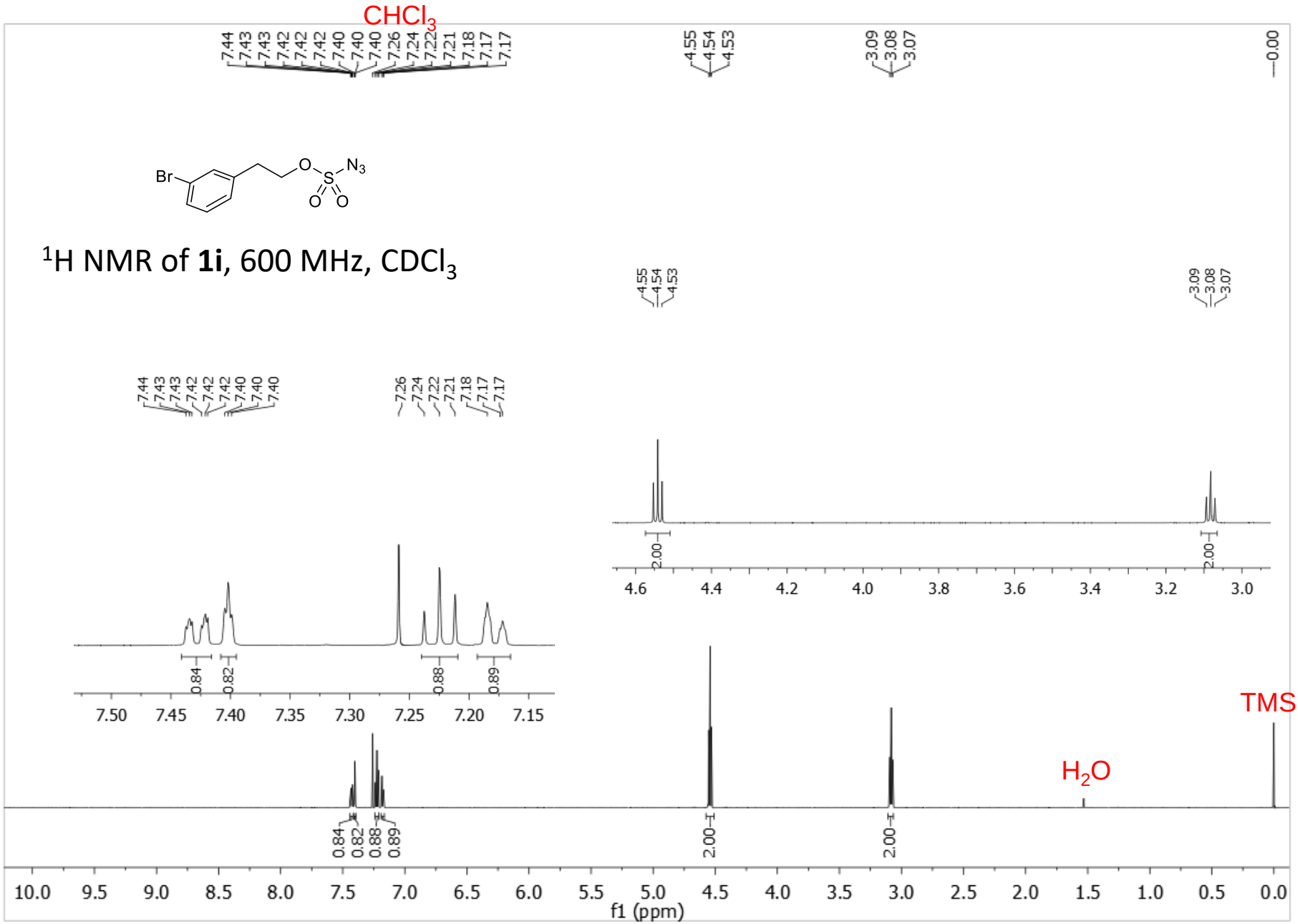


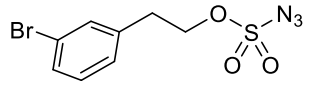
^{13}C NMR of **1g**, 62.5 MHz, $CDCl_3$



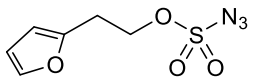
^{1}H NMR of **1h**, 400 MHz, $CDCl_3$


CDCl3
134.55
131.99
130.72
121.33
77.67
77.16
76.65
74.41
34.46
O
S
N3
O
O
Br
13C NMR of 1h, 62.5 MHz, CDCl3
134.55
131.99
130.72
136
134
132
130
128
126
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

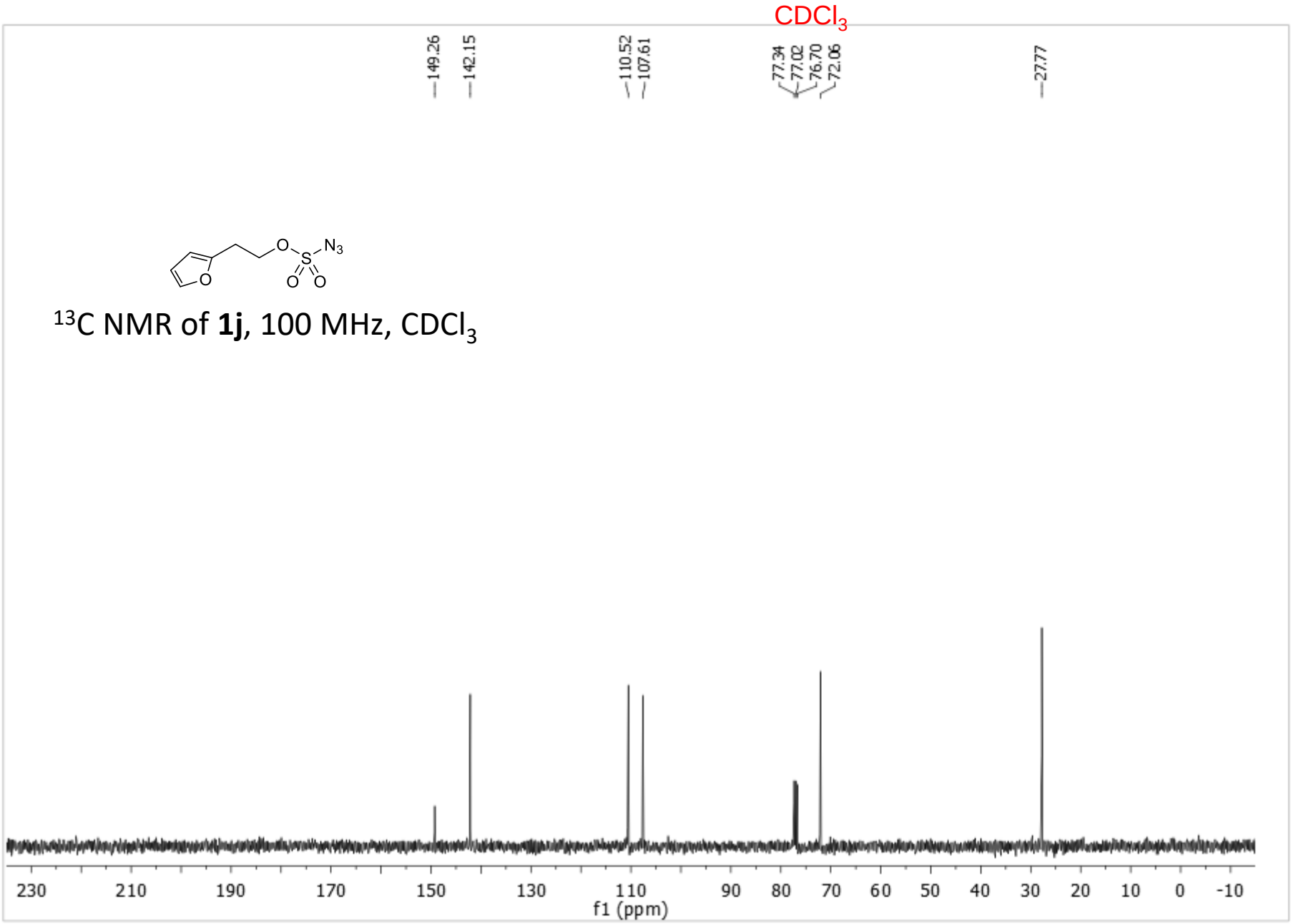

CHCl3
7.44 7.43 7.43 7.42 7.42 7.42 7.40 7.40 7.40 7.26 7.24 7.22 7.21 7.18 7.17 7.17
4.55 4.54 4.53
3.09 3.08 3.07
0.00
Br
O
S
N3
O
O
1H NMR of 1i, 600 MHz, CDCl3
0.84 0.82 0.88 0.89
2.00
2.00
H2O
TMS
f1 (ppm)



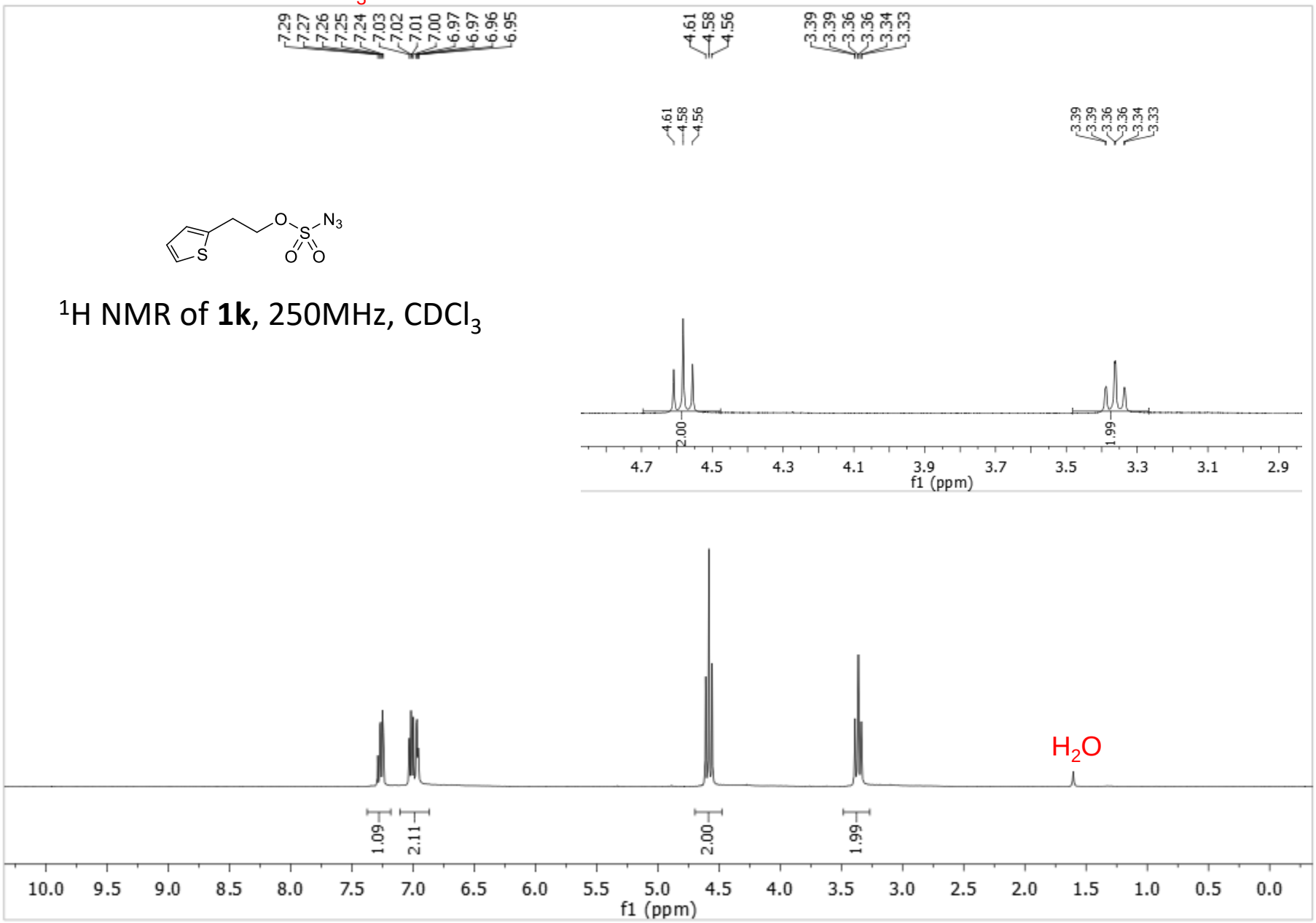
^{13}C NMR of **1i**, 150 MHz, $CDCl_3$

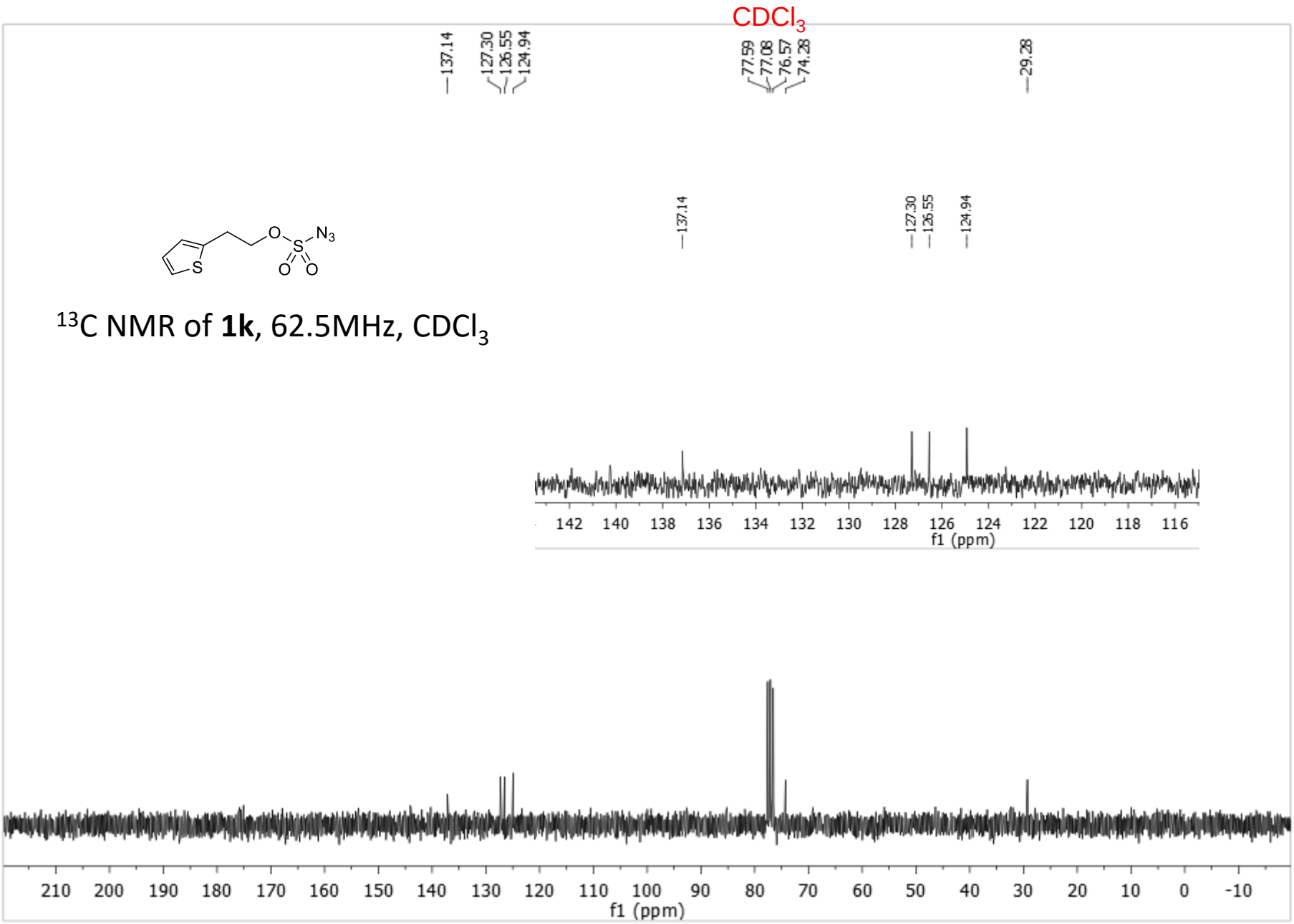


^{1}H NMR of **1j**, 400 MHz, $CDCl_3$

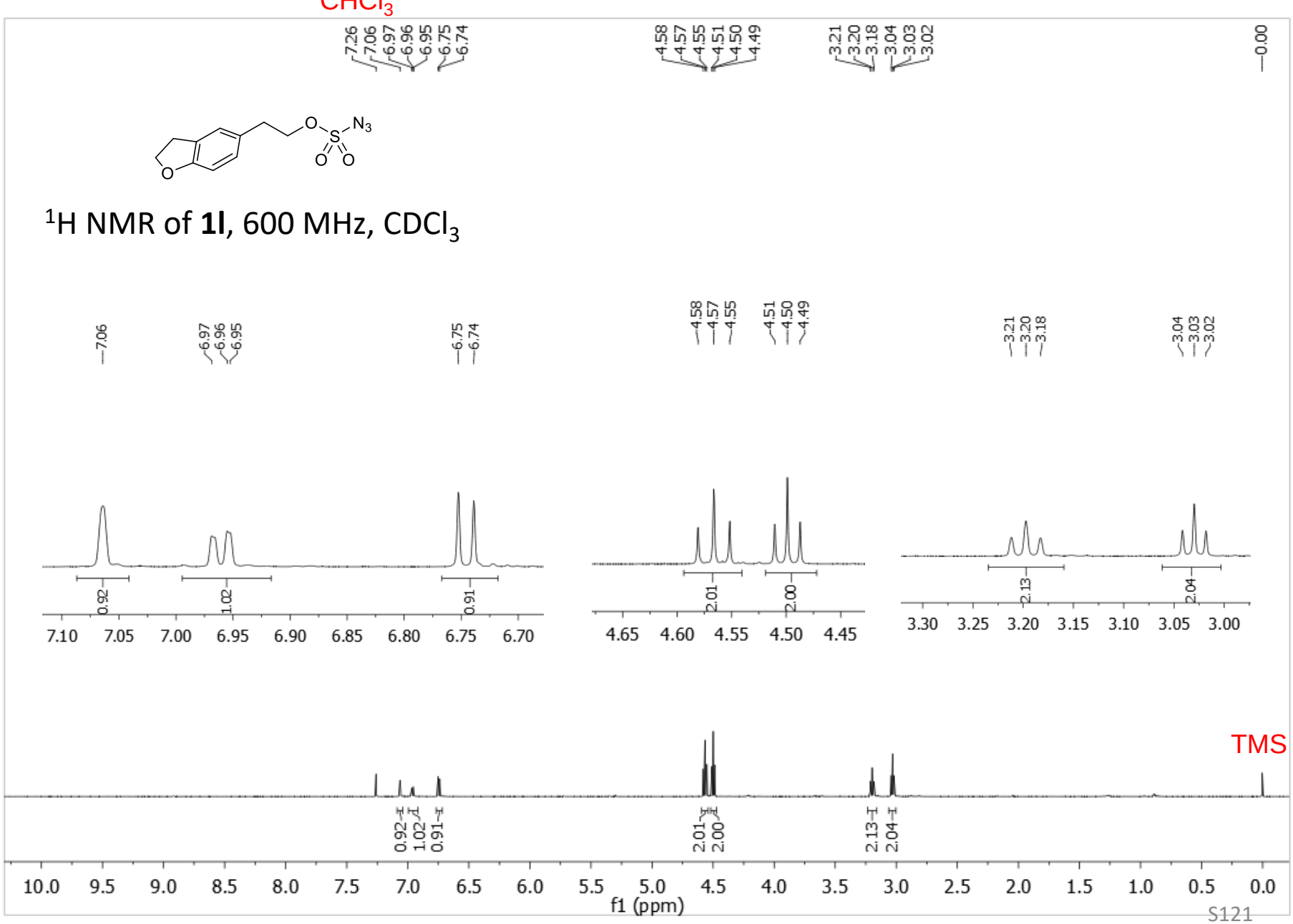


^{13}C NMR of **1j**, 100 MHz, $CDCl_3$

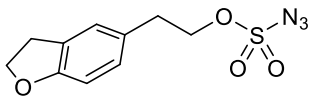

CHCl3
7.29
7.27
7.26
7.25
7.24
7.03
7.02
7.01
7.00
6.97
6.97
6.96
6.95
4.61
4.58
4.56
3.39
3.39
3.36
3.36
3.34
3.33
O
S
N3
O
O
S
1H NMR of 1k, 250MHz, CDCl3
2.00
1.99
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
f1 (ppm)
H2O
1.09
2.11
2.00
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



^{13}C NMR of **1k**, 62.5MHz, $CDCl_3$

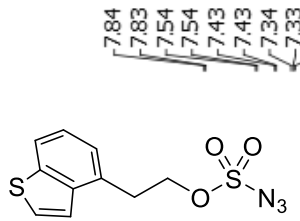

CHCl3
7.26
7.06
6.97
6.96
6.95
6.75
6.74
4.58
4.57
4.55
4.51
4.50
4.49
3.21
3.20
3.18
3.04
3.03
3.02
0.00
O
O
S
N3
O
O
1H NMR of 1l, 600 MHz, CDCl3
0.92
1.02
0.91
2.01
2.00
2.13
2.04
TMS
f1 (ppm)

$CDCl_3$

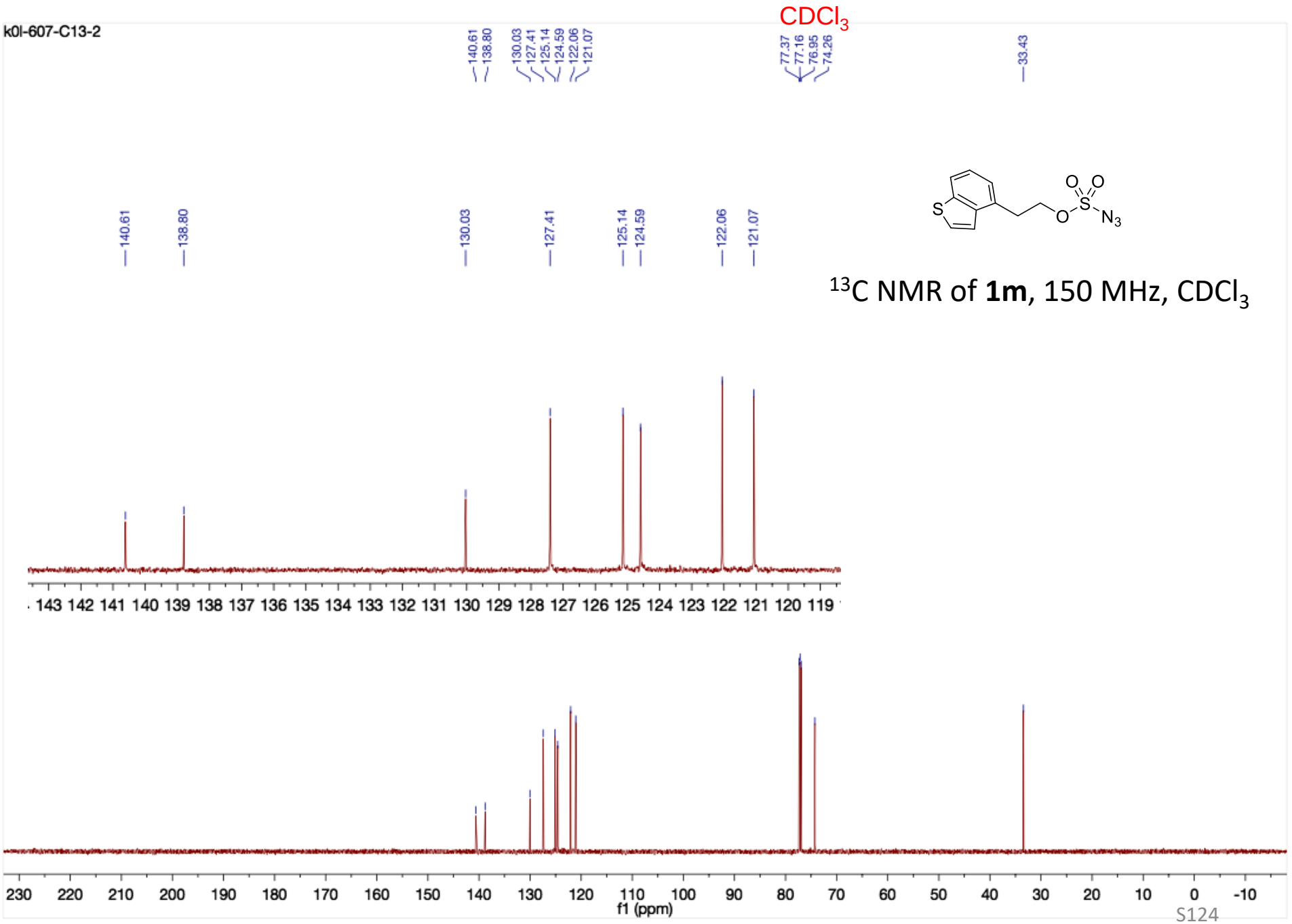


^{13}C NMR of **1l**, 150 MHz, $CDCl_3$

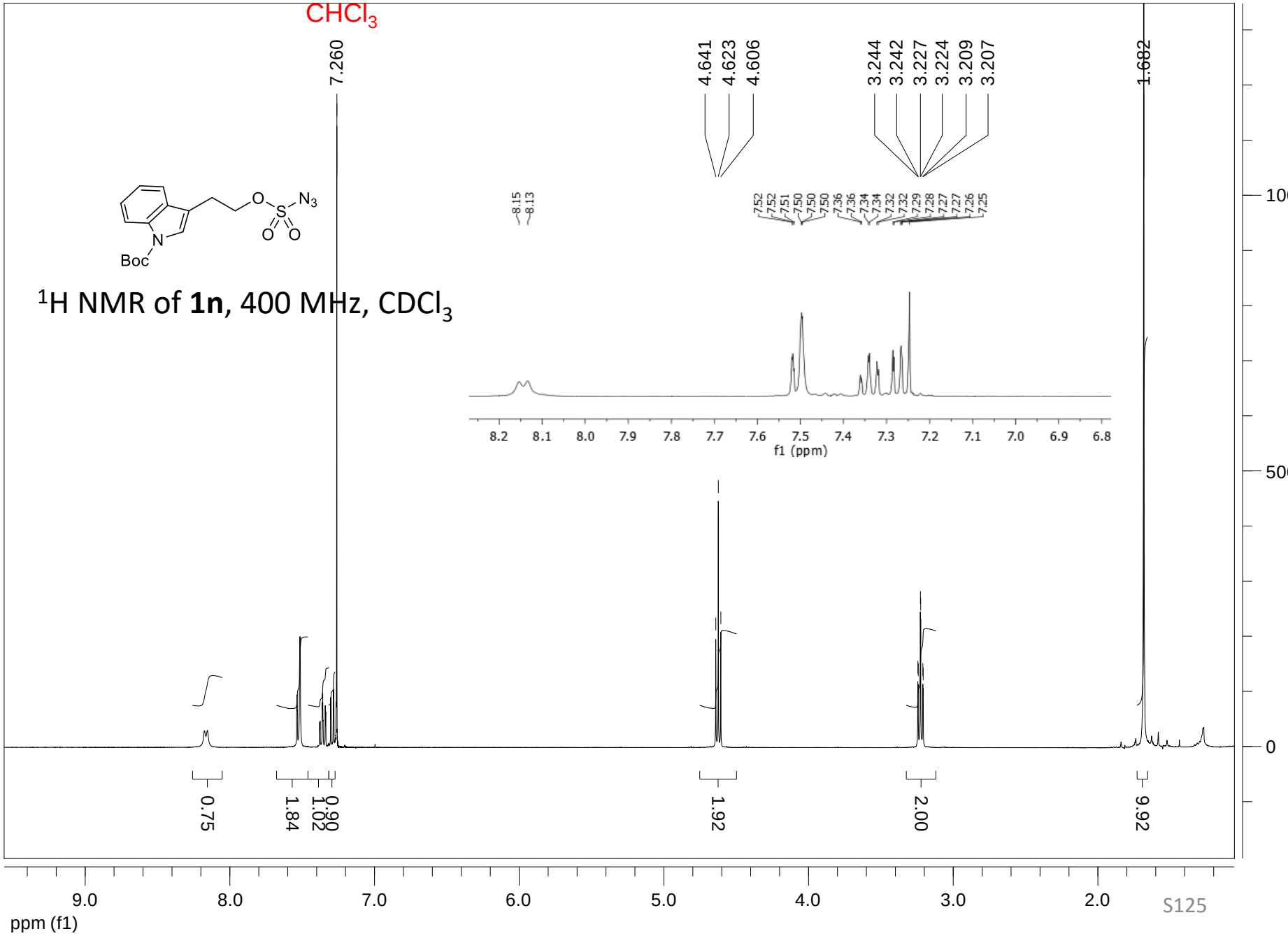
$CHCl_3$

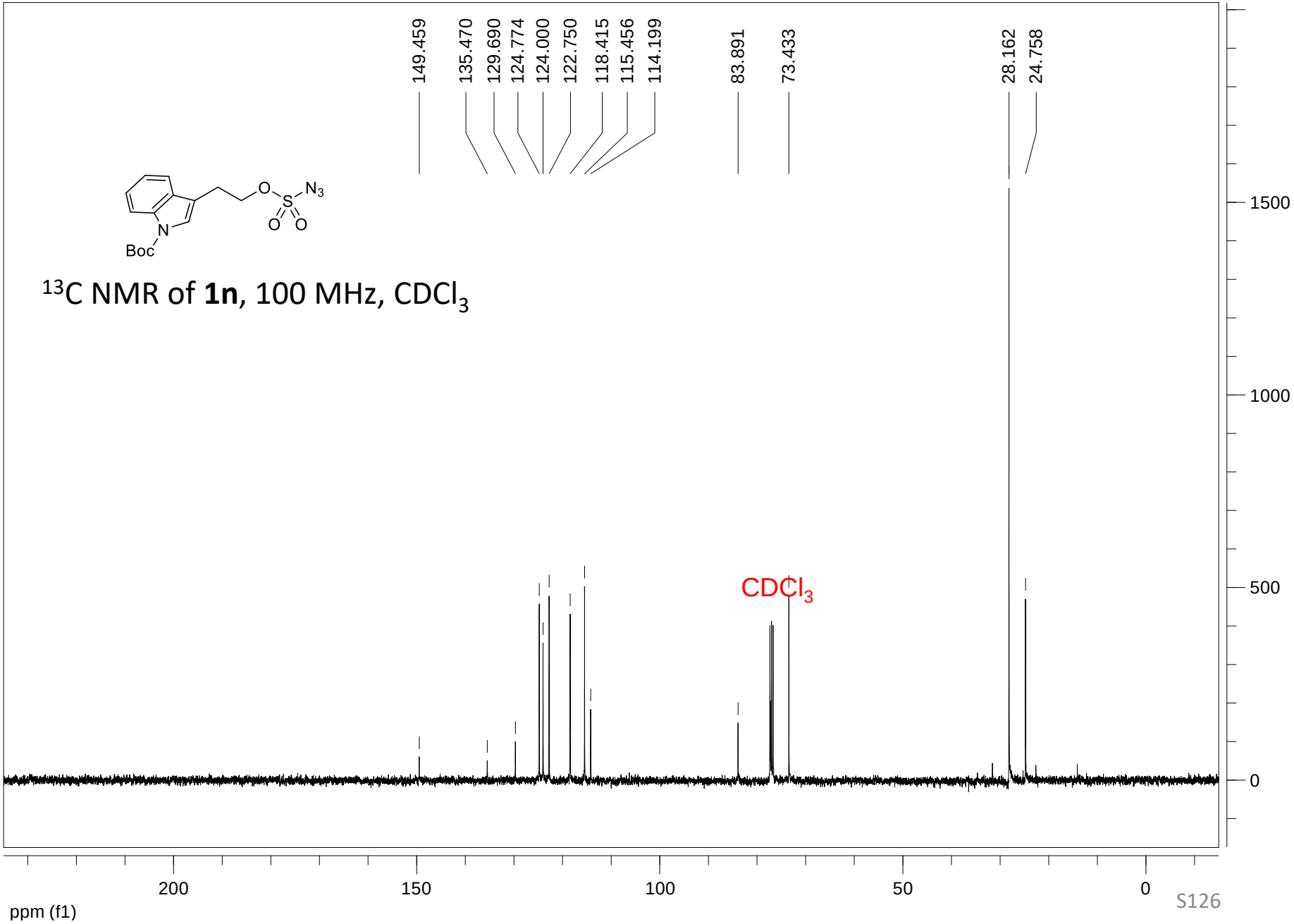


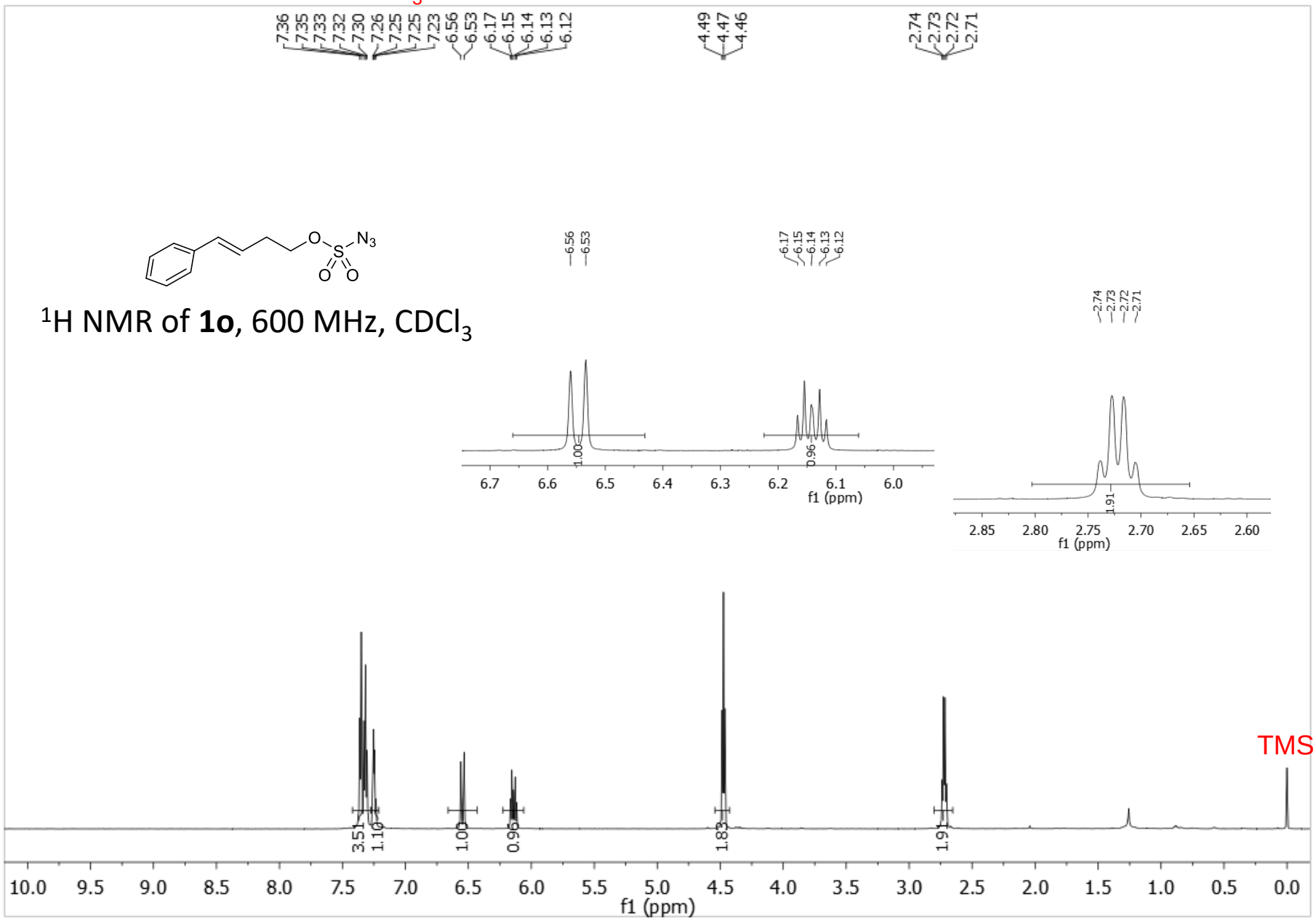
^{1}H NMR of **1m**, 600 MHz, $CDCl_3$

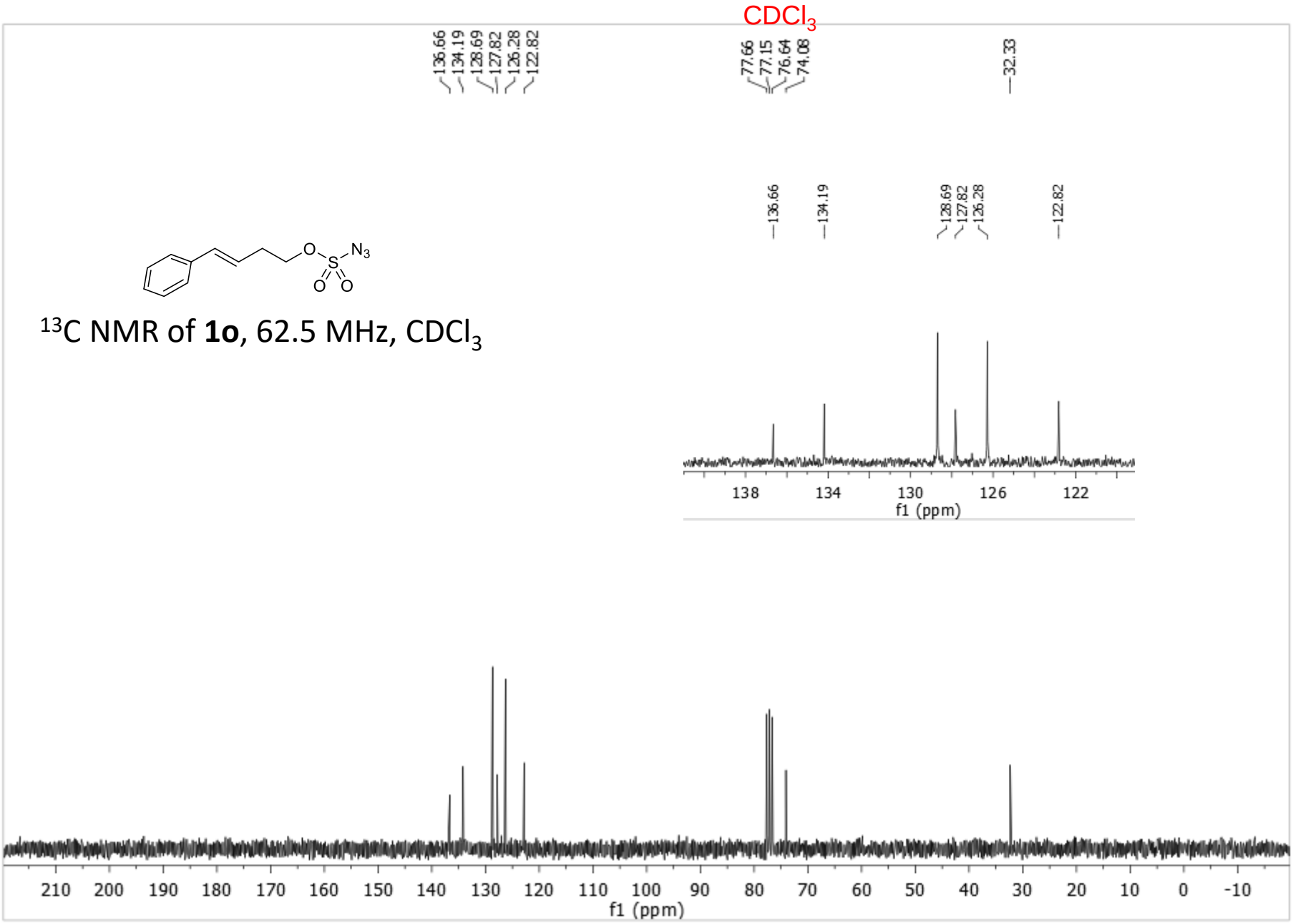


^{13}C NMR of **1m**, 150 MHz, $CDCl_3$

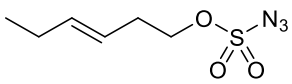

CHCl3
7.260
4.641
4.623
4.606
3.244
3.242
3.227
3.224
3.209
3.207
1.682
8.15
8.13
7.52
7.52
7.51
7.50
7.50
7.50
7.36
7.36
7.34
7.34
7.32
7.32
7.29
7.28
7.27
7.27
7.26
7.25
O
S
N3
O
O
N
Boc
1H NMR of 1n, 400 MHz, CDCl3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
0.75
1.84
1.02
0.90
1.92
2.00
9.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)


149.459
135.470
129.690
124.774
124.000
122.750
118.415
115.456
114.199
83.891
73.433
28.162
24.758
O
S
N3
O
O
N
Boc
13C NMR of 1n, 100 MHz, CDCl3
CDCl3
1500
1000
500
0
200
150
100
50
0
ppm (f1)

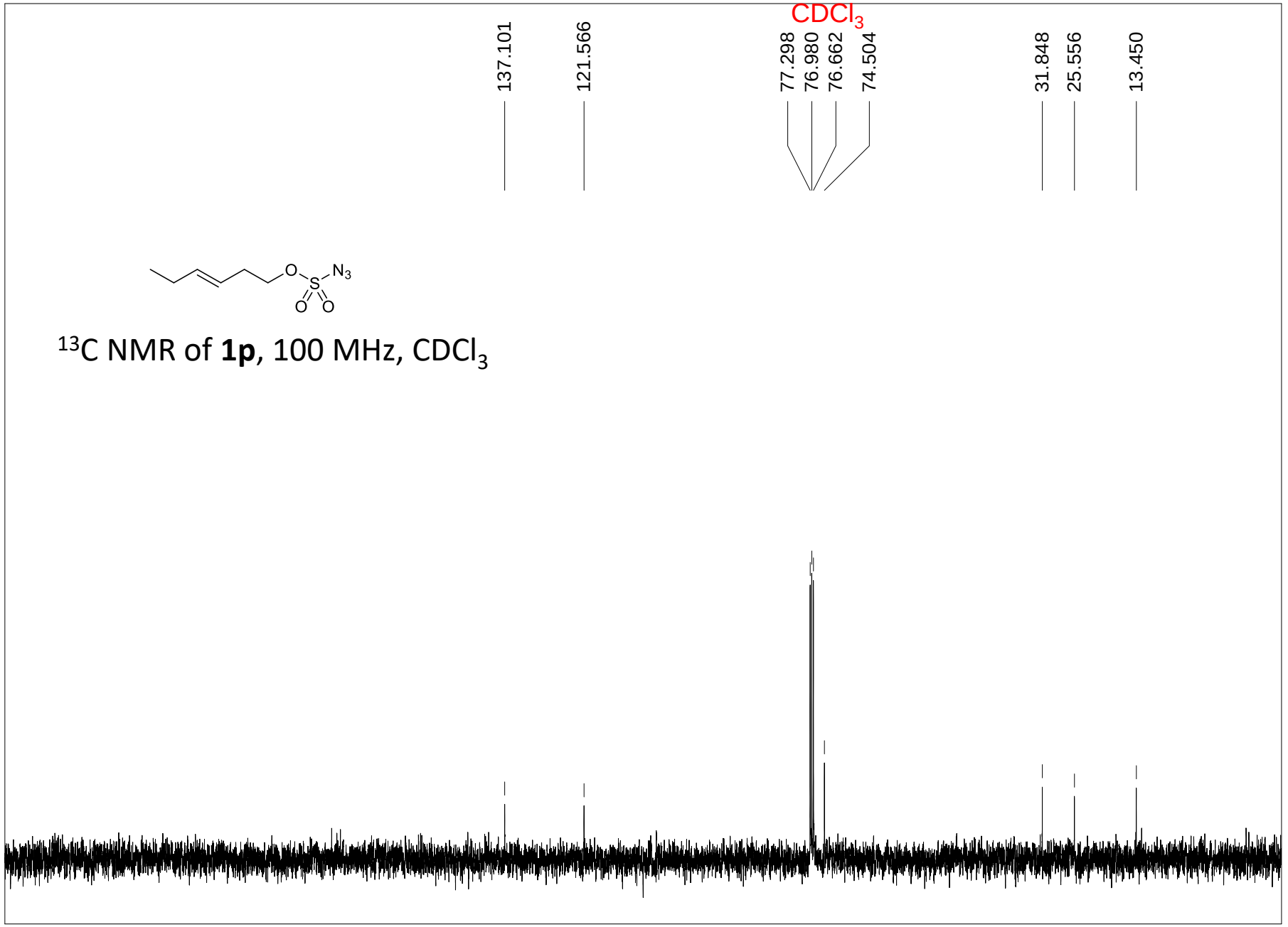

CHCl3
7.36
7.35
7.33
7.32
7.30
7.26
7.25
7.25
7.23
6.56
6.53
6.17
6.15
6.14
6.13
6.12
4.49
4.47
4.46
2.74
2.73
2.72
2.71
O
S
N3
O
O
1H NMR of 1o, 600 MHz, CDCl3
6.56
6.53
6.17
6.15
6.14
6.13
6.12
1.00
0.96
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)
2.74
2.73
2.72
2.71
1.91
2.85
2.80
2.75
2.70
2.65
2.60
f1 (ppm)
3.51
1.10
1.00
0.96
1.83
1.91
TMS
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



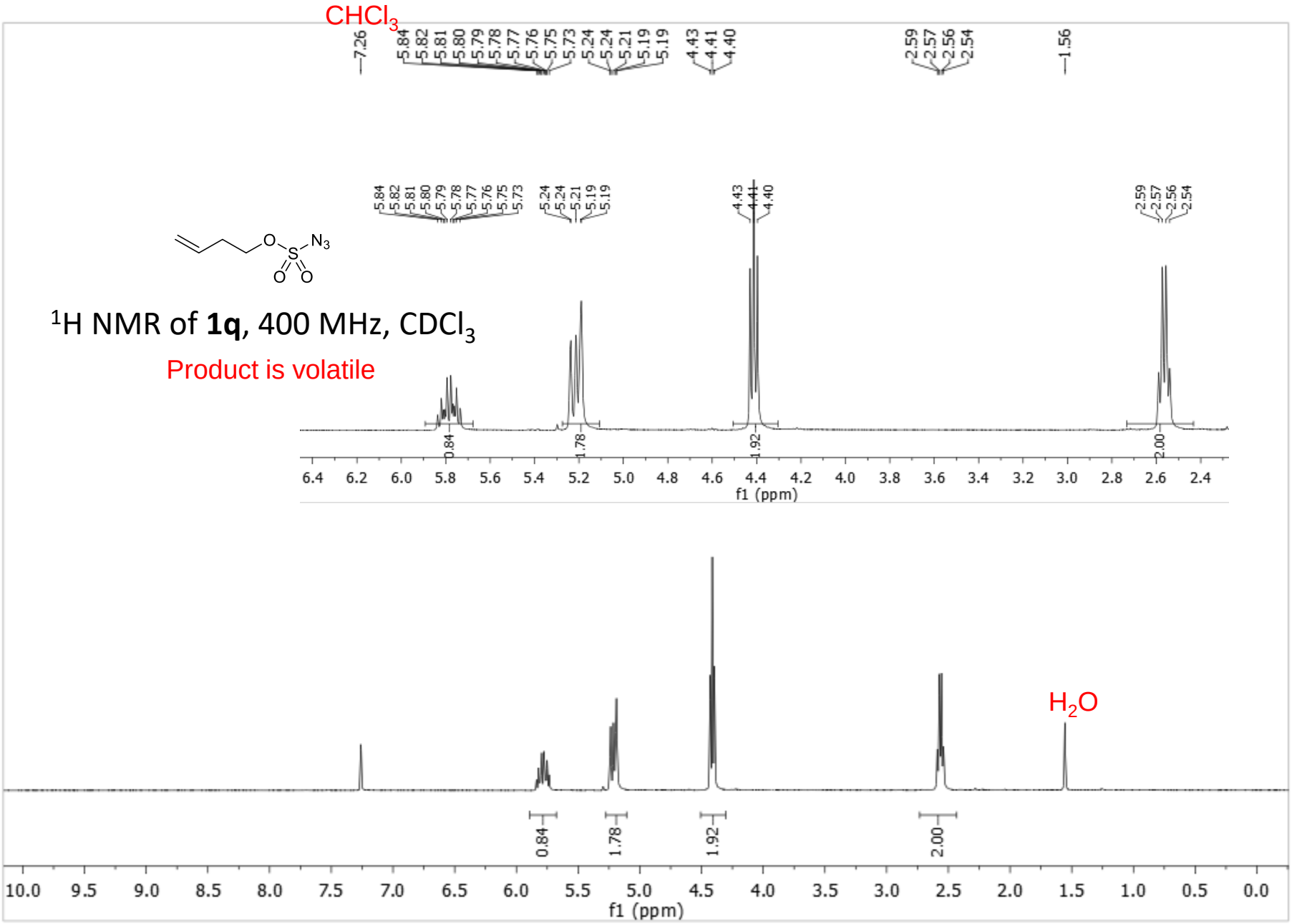
^{13}C NMR of **1o**, 62.5 MHz, $CDCl_3$

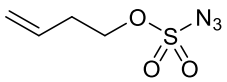


^{1}H NMR of **1p**, 400 MHz, $CDCl_3$

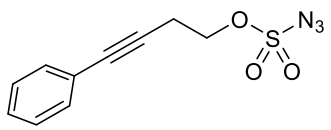


^{13}C NMR of **1p**, 100 MHz, $CDCl_3$

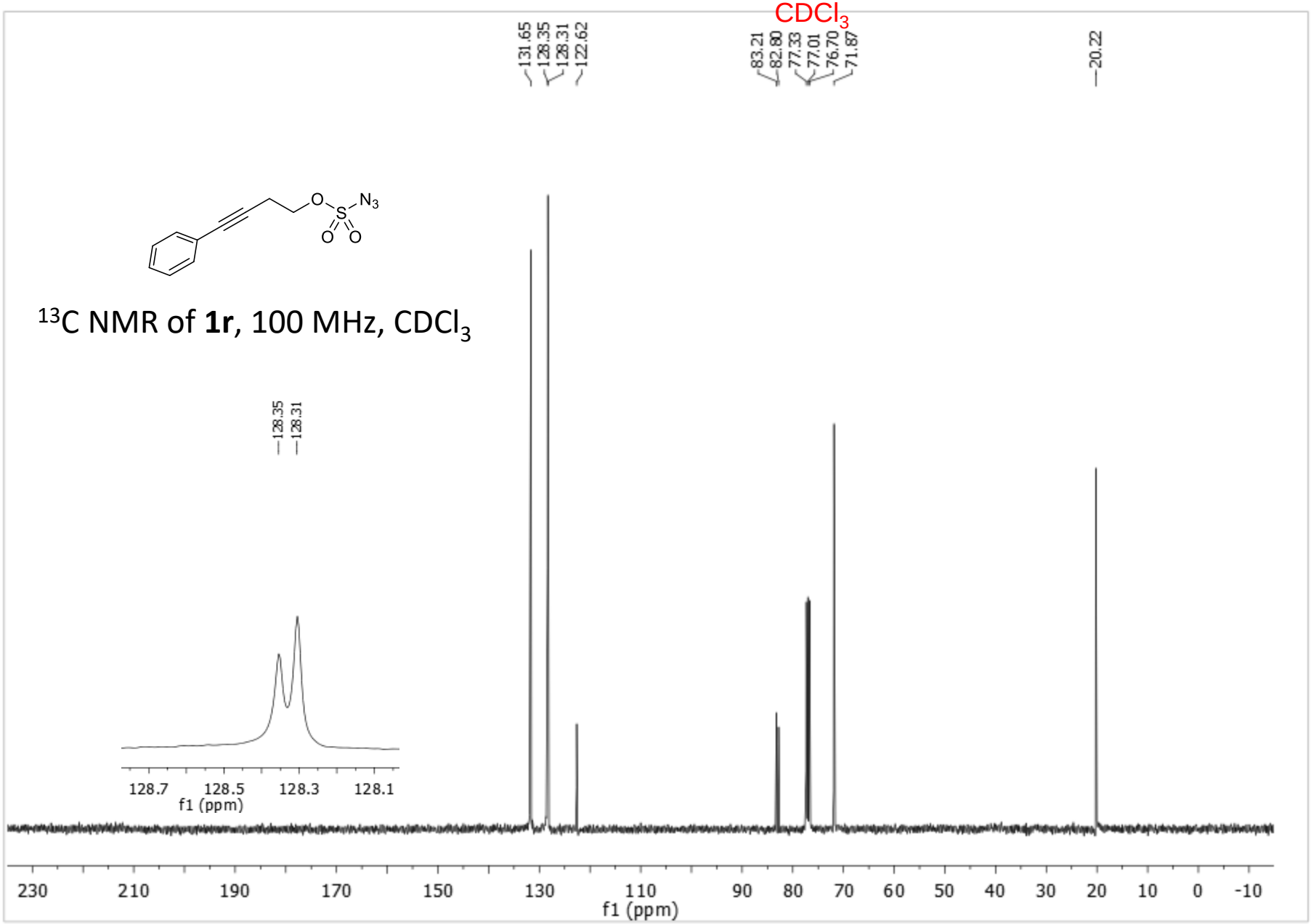

CHCl3
7.26
5.84
5.82
5.81
5.80
5.79
5.78
5.77
5.76
5.75
5.73
5.24
5.24
5.21
5.19
5.19
4.43
4.41
4.40
2.59
2.57
2.56
2.54
1.56
O
S
N3
O
O
1H NMR of 1q, 400 MHz, CDCl3
Product is volatile
0.84
1.78
1.92
2.00
f1 (ppm)
H2O



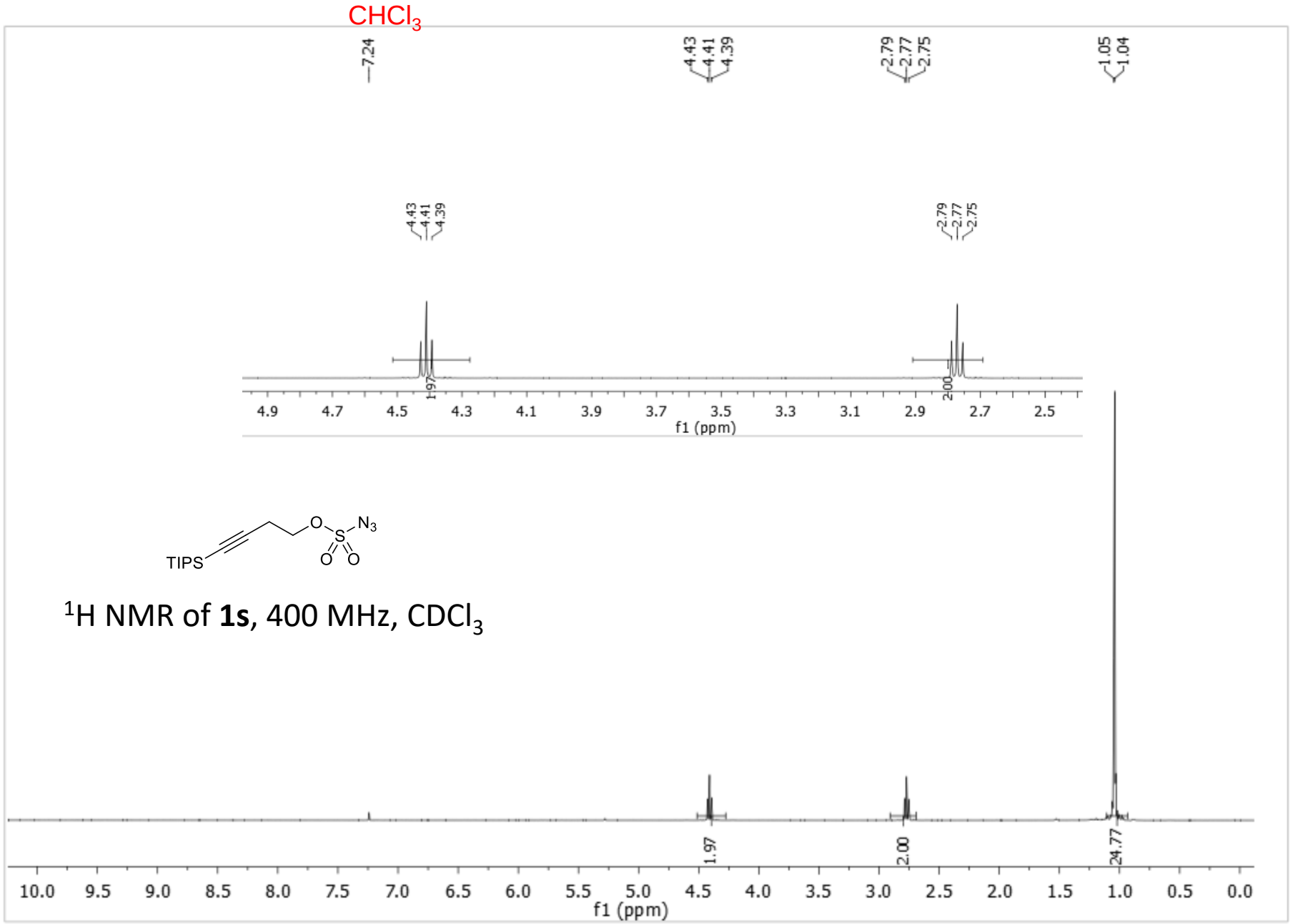
^{13}C NMR of **1q**, 100 MHz, $CDCl_3$



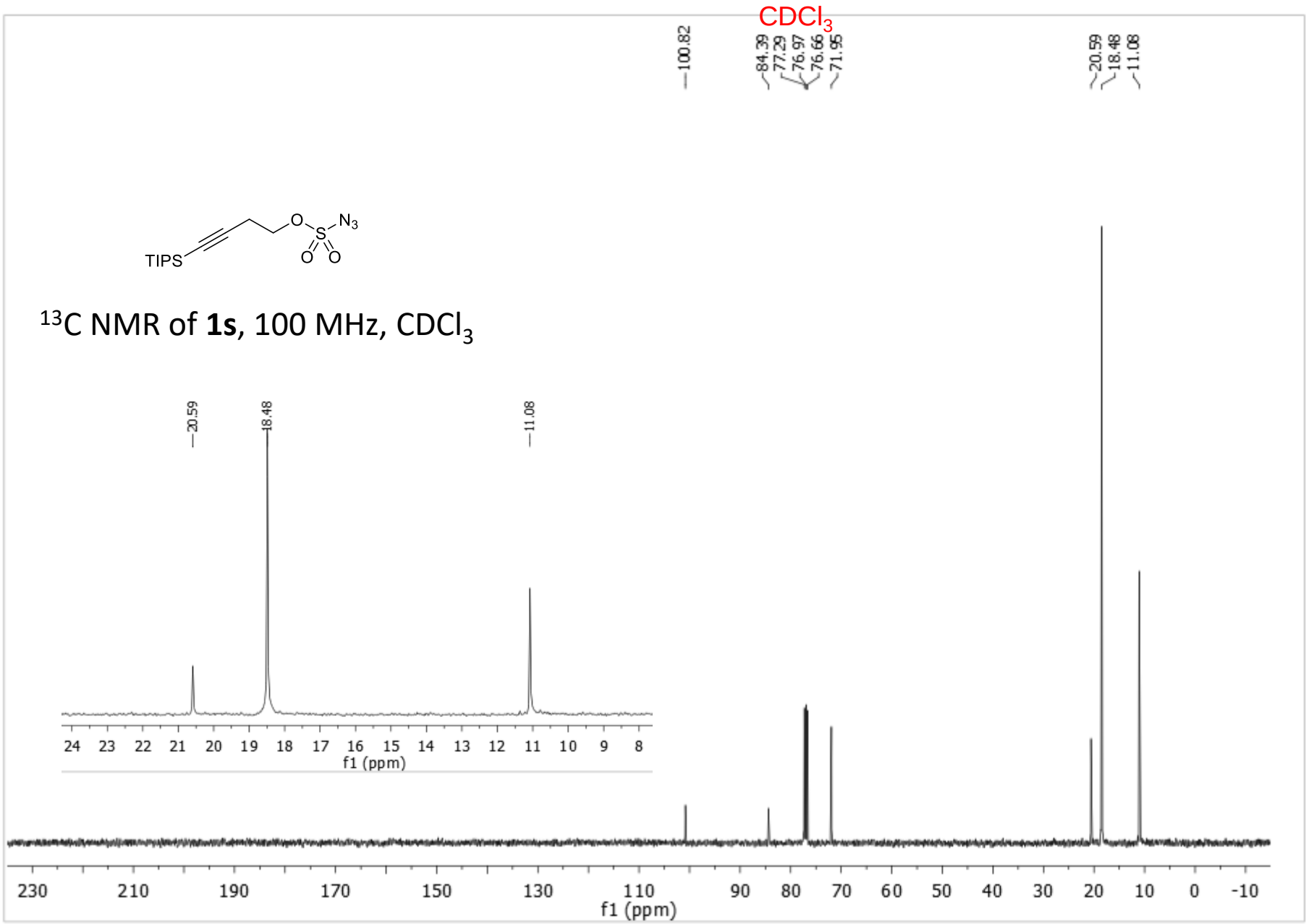
^{1}H NMR of **1r**, 400 MHz, $CDCl_3$

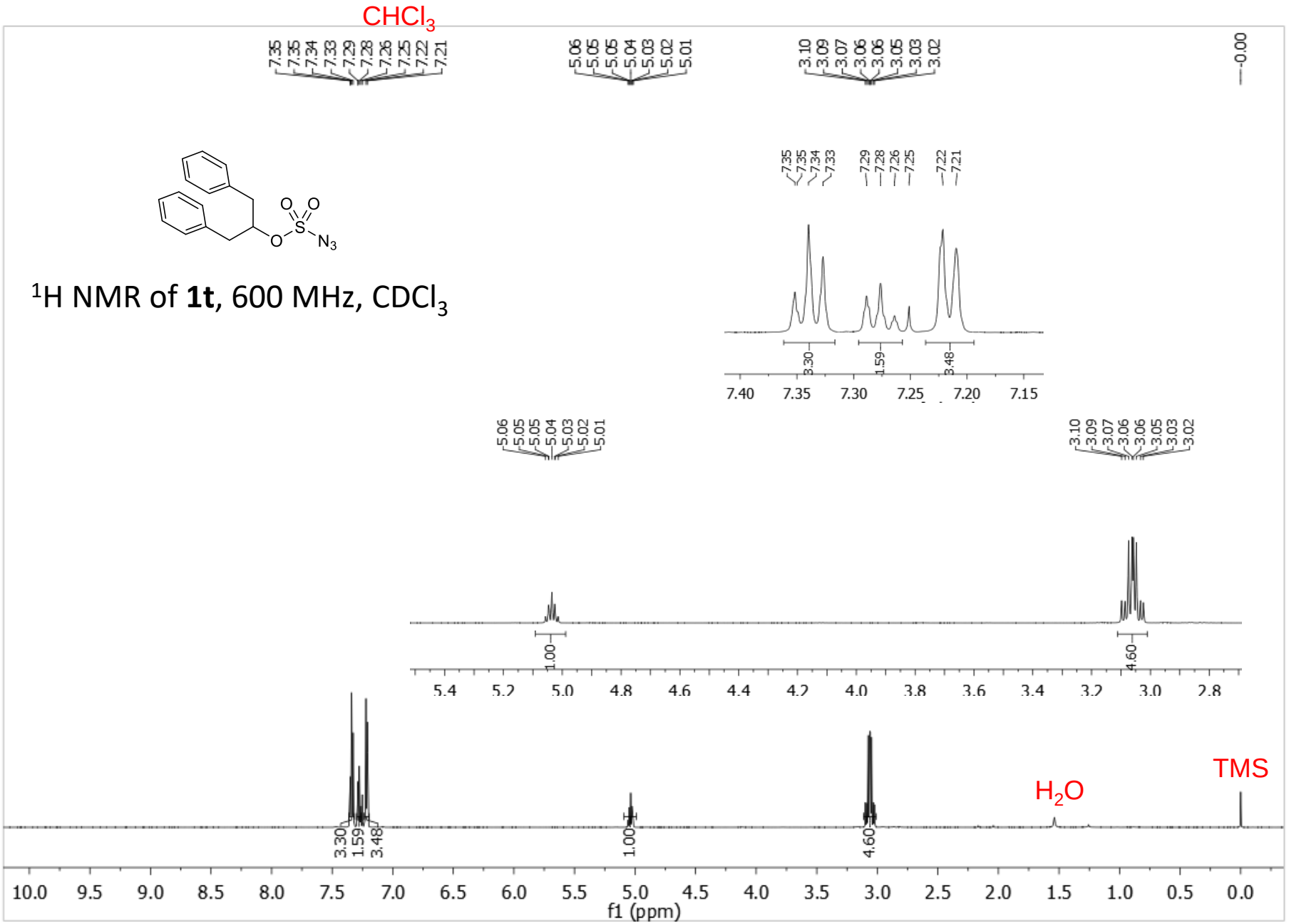


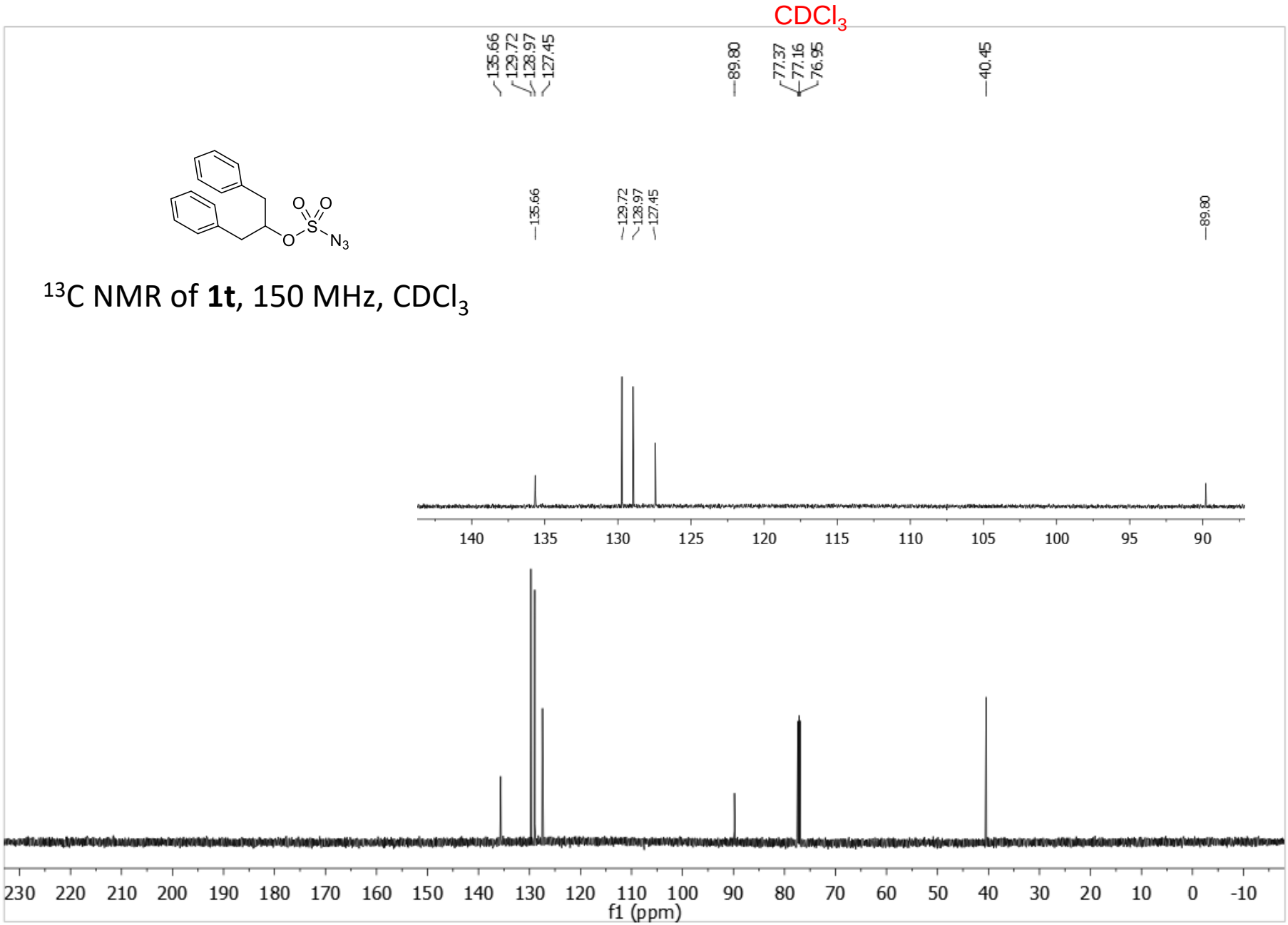
^{13}C NMR of **1r**, 100 MHz, $CDCl_3$



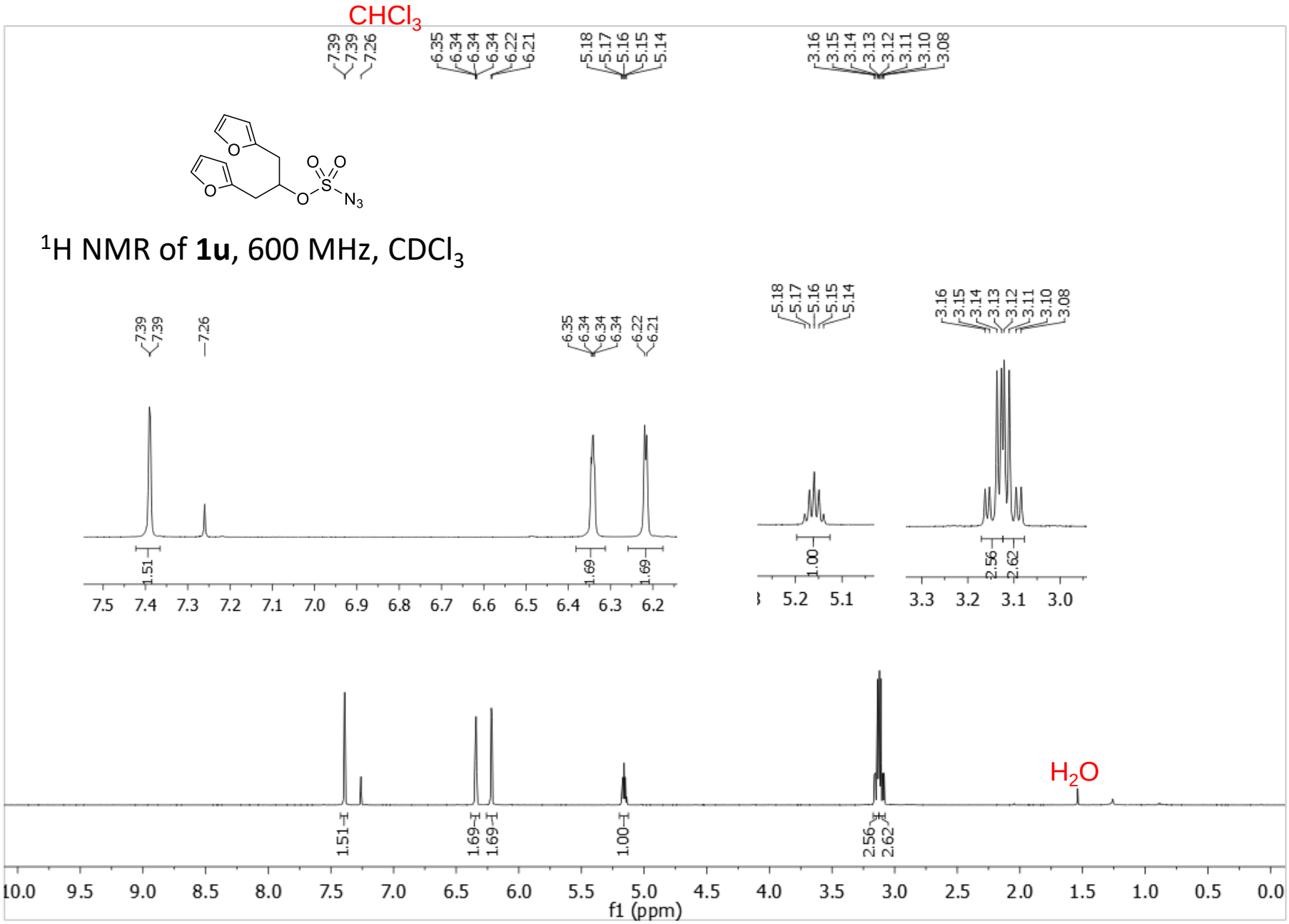
^{1}H NMR of **1s**, 400 MHz, $CDCl_3$

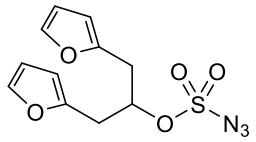

CDCl3
100.82
84.39
77.29
76.97
76.66
71.95
20.59
18.48
11.08
TIPS
O
S
N3
O
O
13C NMR of 1s, 100 MHz, CDCl3
f1 (ppm)
f1 (ppm)


CHCl3
7.35
7.35
7.34
7.33
7.29
7.28
7.26
7.25
7.22
7.21
5.06
5.05
5.05
5.04
5.03
5.02
5.01
3.10
3.09
3.07
3.06
3.06
3.05
3.03
3.02
0.00
O
O
S
O
N3
1H NMR of 1t, 600 MHz, CDCl3
3.30
1.59
3.48
7.40
7.35
7.30
7.25
7.20
7.15
1.00
4.60
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
H2O
TMS
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

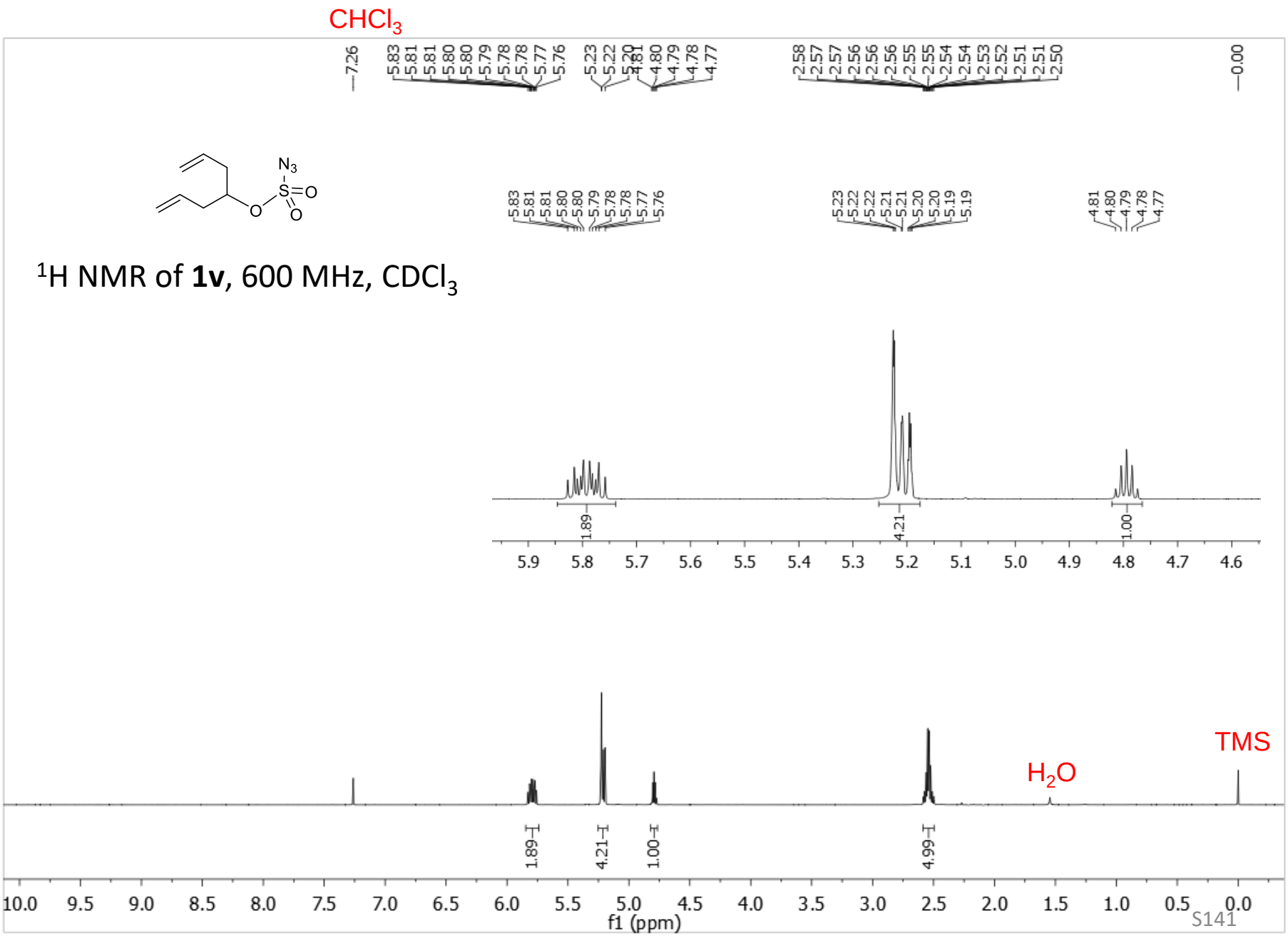


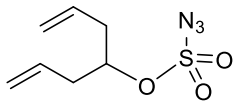
^{13}C NMR of **1t**, 150 MHz, $CDCl_3$


CHCl3
7.39
7.39
7.26
6.35
6.34
6.34
6.34
6.22
6.21
5.18
5.17
5.16
5.15
5.14
3.16
3.15
3.14
3.13
3.12
3.11
3.10
3.08
O
O
O
S
O
N3
1H NMR of 1u, 600 MHz, CDCl3
1.51
1.69
1.69
1.00
2.56
2.62
H2O
f1 (ppm)

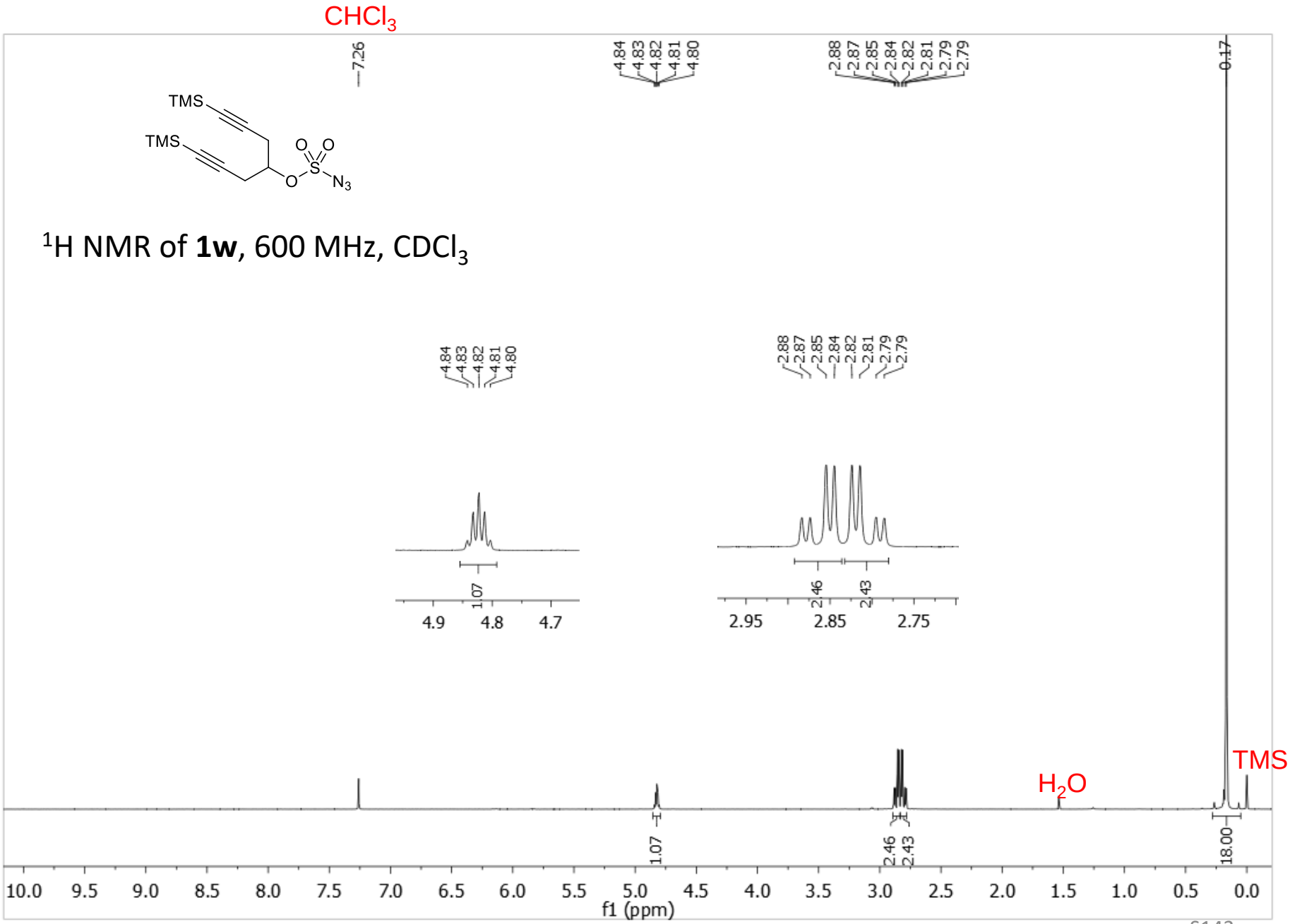


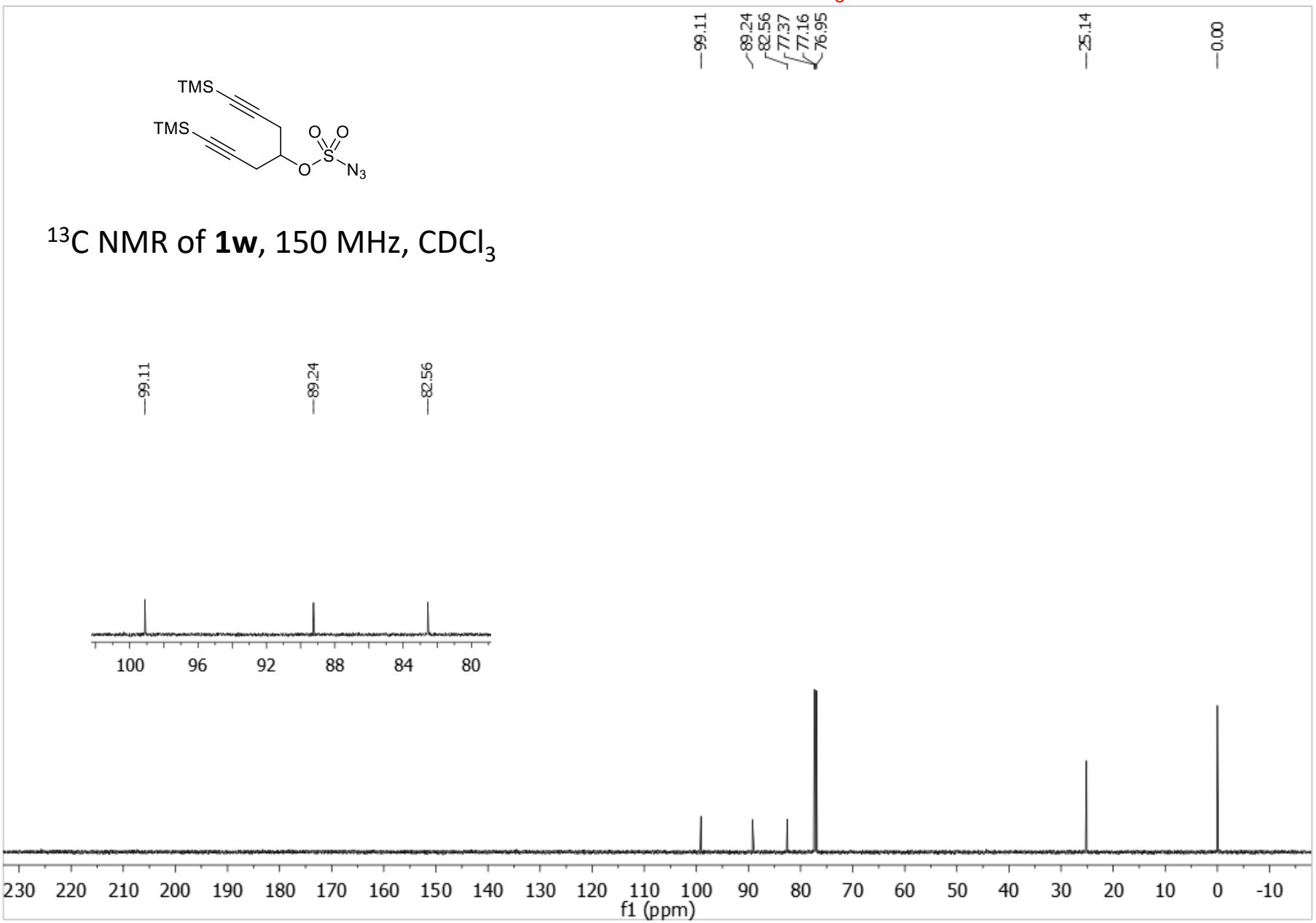
^{13}C NMR of **1u**, 150 MHz, $CDCl_3$


CHCl3
7.26
5.83 5.81 5.81 5.80 5.80 5.79 5.78 5.78 5.77 5.76
5.23 5.22 5.20 4.81 4.80 4.79 4.78 4.77
2.58 2.57 2.57 2.56 2.56 2.56 2.55 2.55 2.54 2.54 2.53 2.52 2.51 2.51 2.50
0.00
N3
S
O
O
O
1H NMR of 1v, 600 MHz, CDCl3
1.89
4.21
1.00
4.99
TMS
H2O
f1 (ppm)

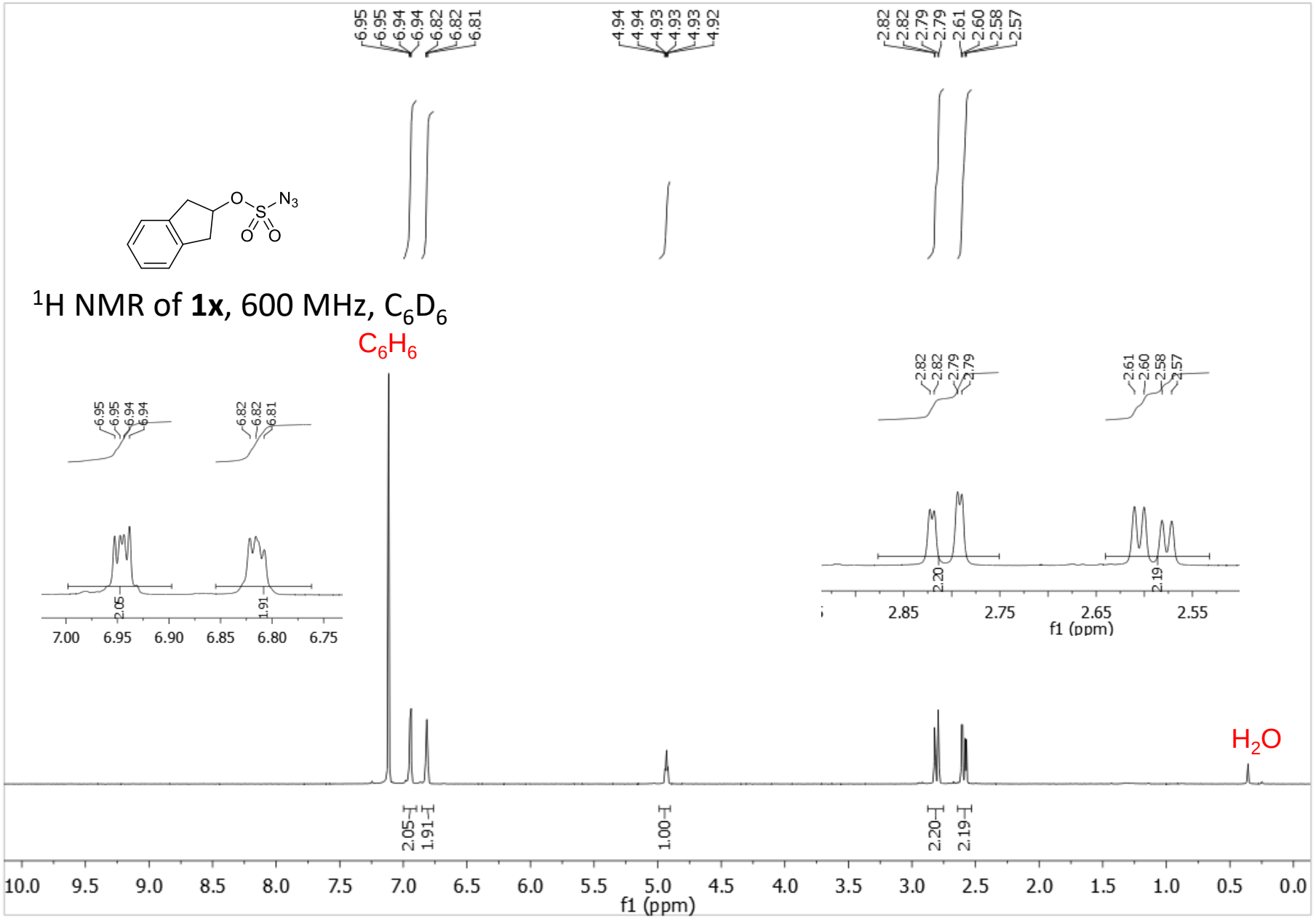


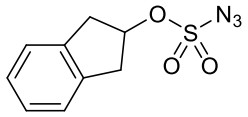
^{13}C NMR of **1v**, 150 MHz, $CDCl_3$


CHCl3
7.26
4.84
4.83
4.82
4.81
4.80
2.88
2.87
2.85
2.84
2.82
2.81
2.79
2.79
0.17
TMS
TMS
O
O
S
O
N3
1H NMR of 1w, 600 MHz, CDCl3
1.07
2.46
2.43
4.9
4.8
4.7
2.95
2.85
2.75
H2O
TMS
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

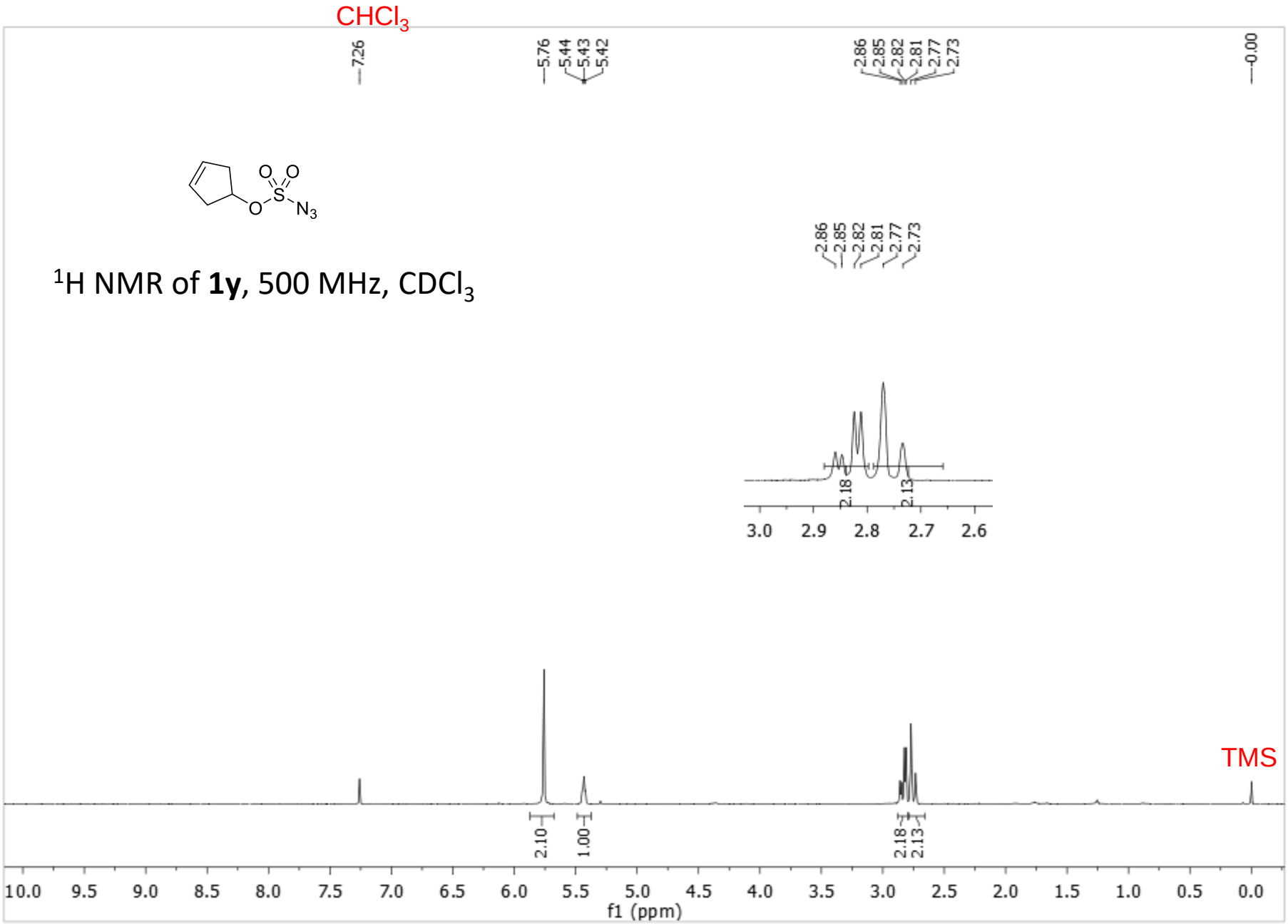


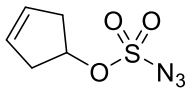
^{13}C NMR of **1w**, 150 MHz, $CDCl_3$


6.95
6.95
6.94
6.94
6.82
6.82
6.81
4.94
4.94
4.93
4.93
4.93
4.92
2.82
2.82
2.79
2.79
2.61
2.60
2.58
2.57
O
S
N3
O
O
1H NMR of 1x, 600 MHz, C6D6
C6H6
2.05
1.91
2.20
2.19
7.00
6.95
6.90
6.85
6.80
6.75
2.85
2.75
2.65
2.55
f1 (ppm)
1.00
H2O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

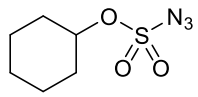


^{13}C NMR of **1x**, 100 MHz, $CDCl_3$

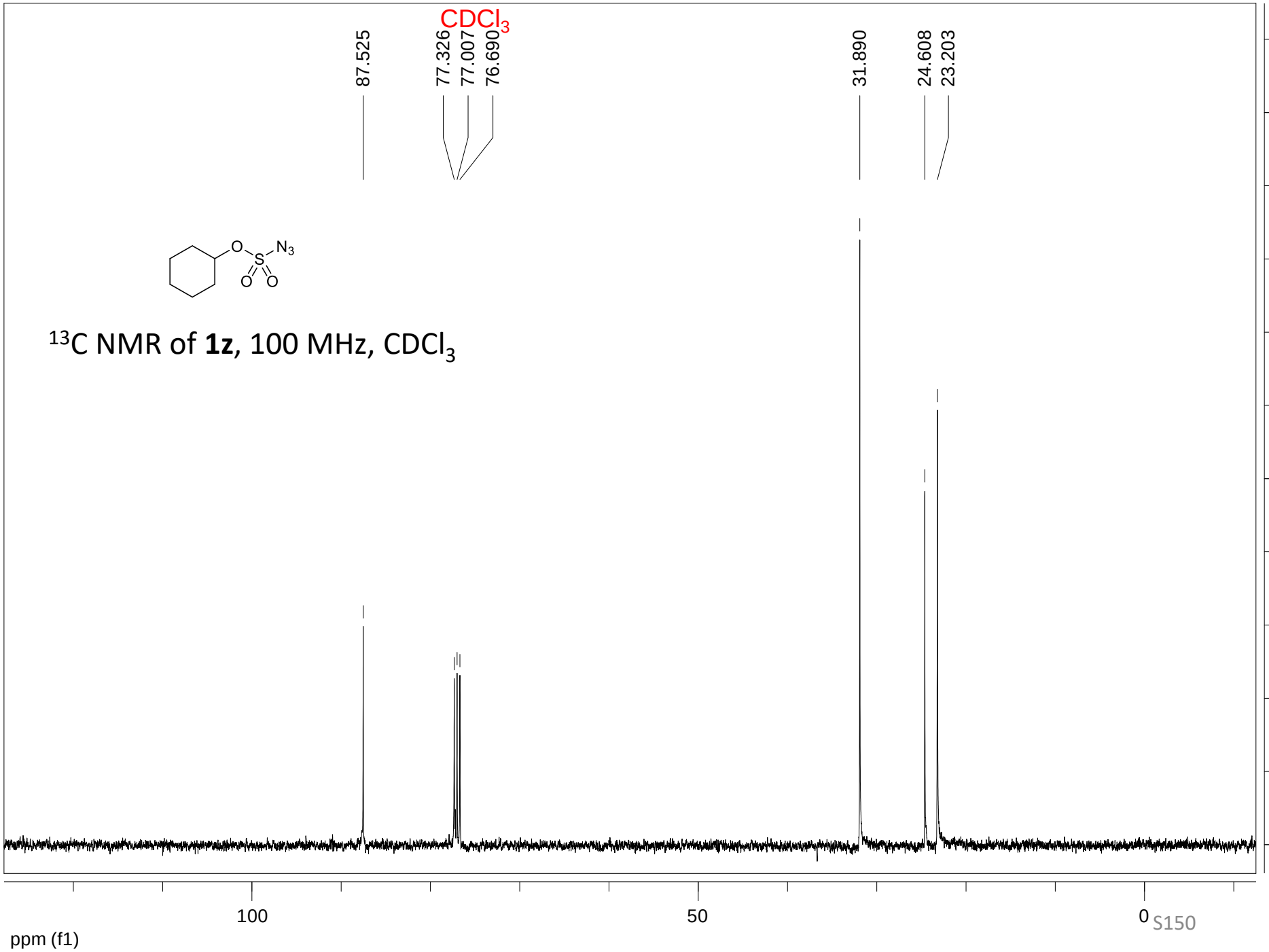

CHCl3
7.26
5.76
5.44
5.43
5.42
2.86
2.85
2.82
2.81
2.77
2.73
0.00
O
O
S
O
N3
1H NMR of 1y, 500 MHz, CDCl3
2.18
2.13
3.0
2.9
2.8
2.7
2.6
TMS
2.10
1.00
2.18
2.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



^{13}C NMR of **1y**, 125 MHz, $CDCl_3$

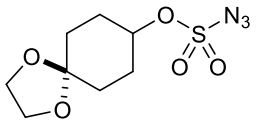


^{1}H NMR of **1z**, 400 MHz, $CDCl_3$

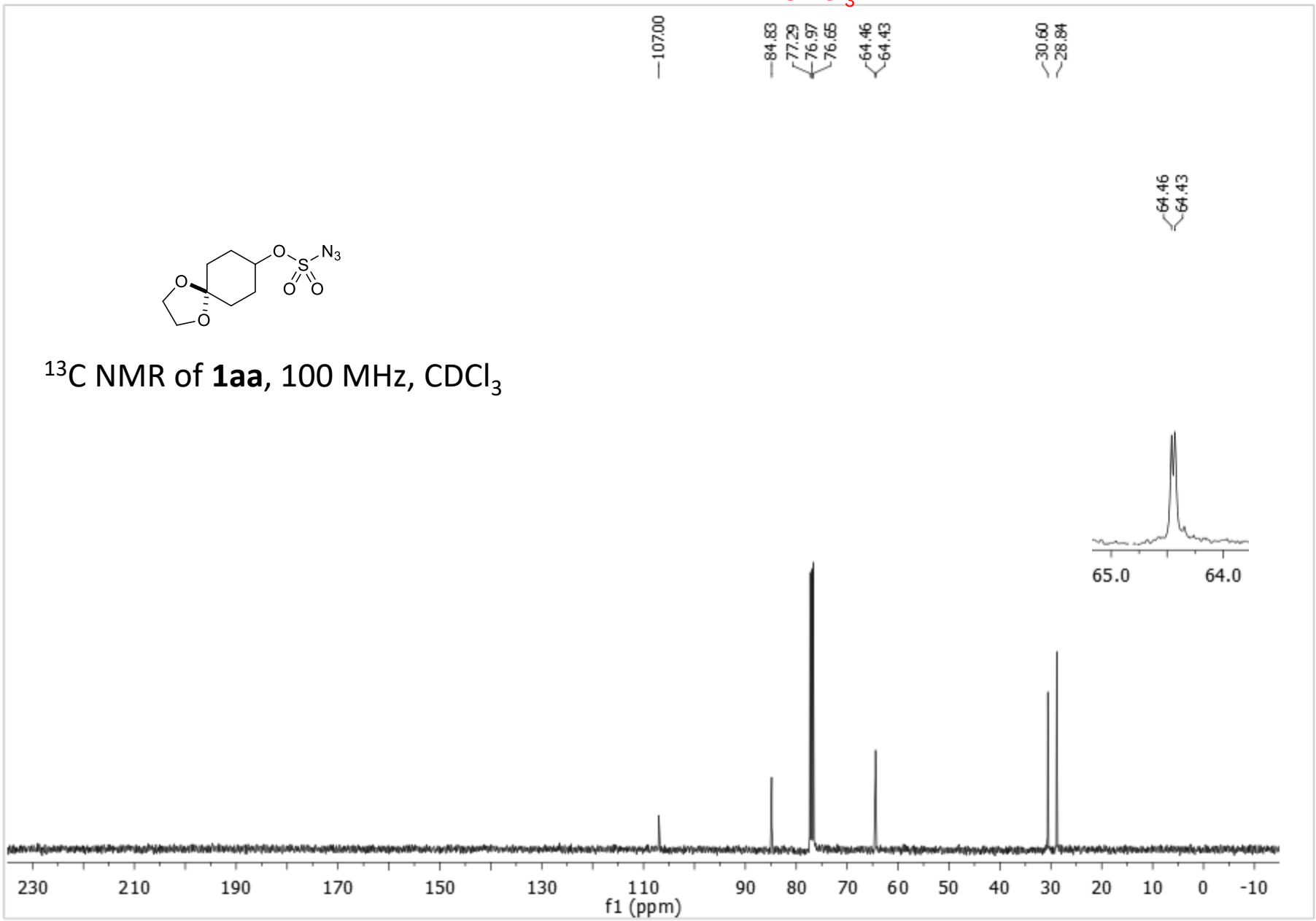


^{13}C NMR of **1z**, 100 MHz, $CDCl_3$

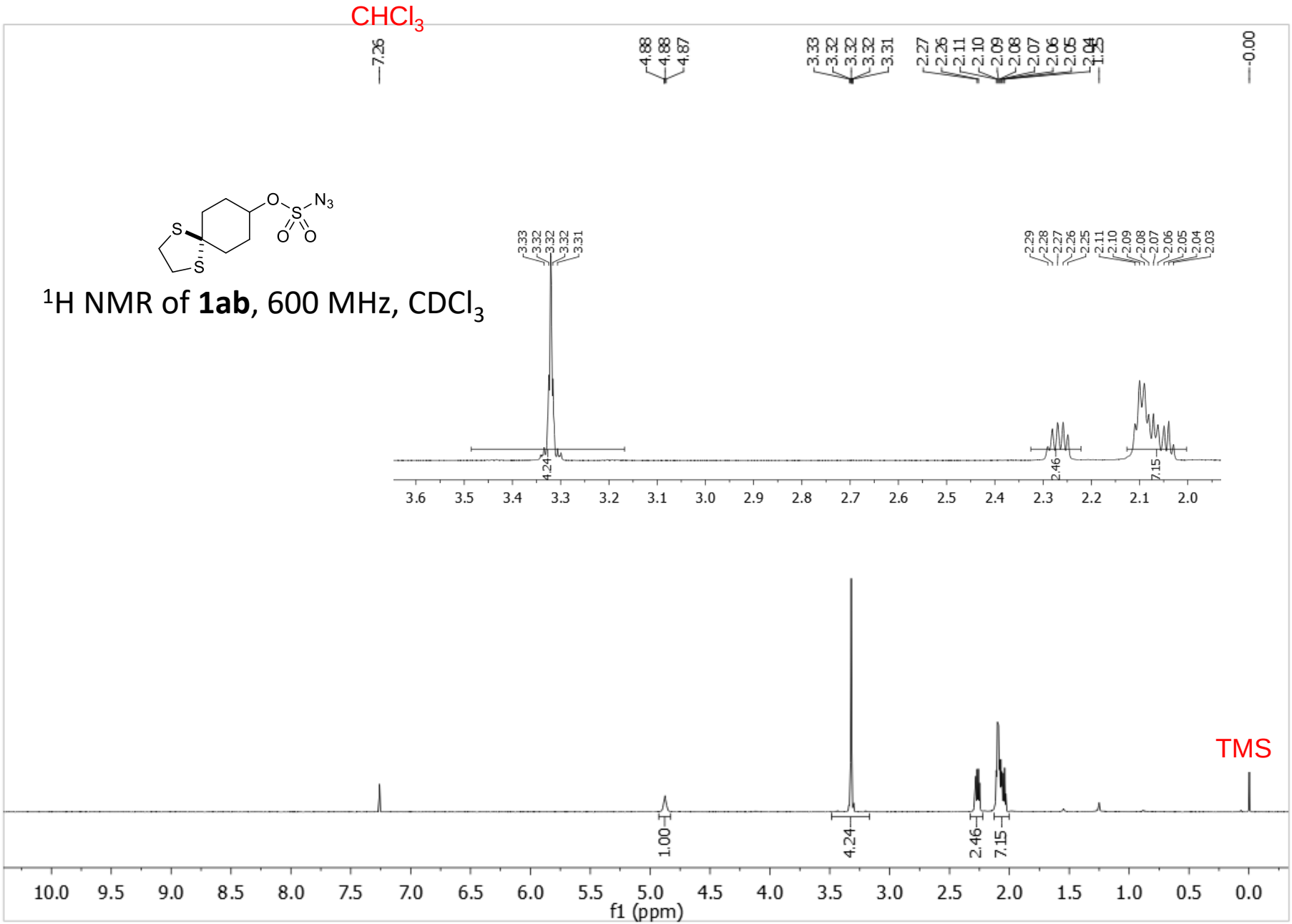
$CHCl_3$

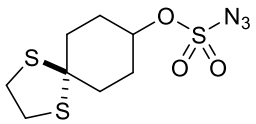


^{1}H NMR of **1aa**, 400 MHz, $CDCl_3$



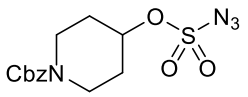
^{13}C NMR of **1aa**, 100 MHz, $CDCl_3$


CHCl3
7.26
4.88
4.88
4.87
3.33
3.32
3.32
3.32
3.31
2.27
2.26
2.11
2.10
2.09
2.08
2.07
2.06
2.05
2.04
1.25
0.00
O
S
N3
O
O
S
S
1H NMR of 1ab, 600 MHz, CDCl3
4.24
2.46
7.15
TMS
1.00
4.24
2.46
7.15
f1 (ppm)

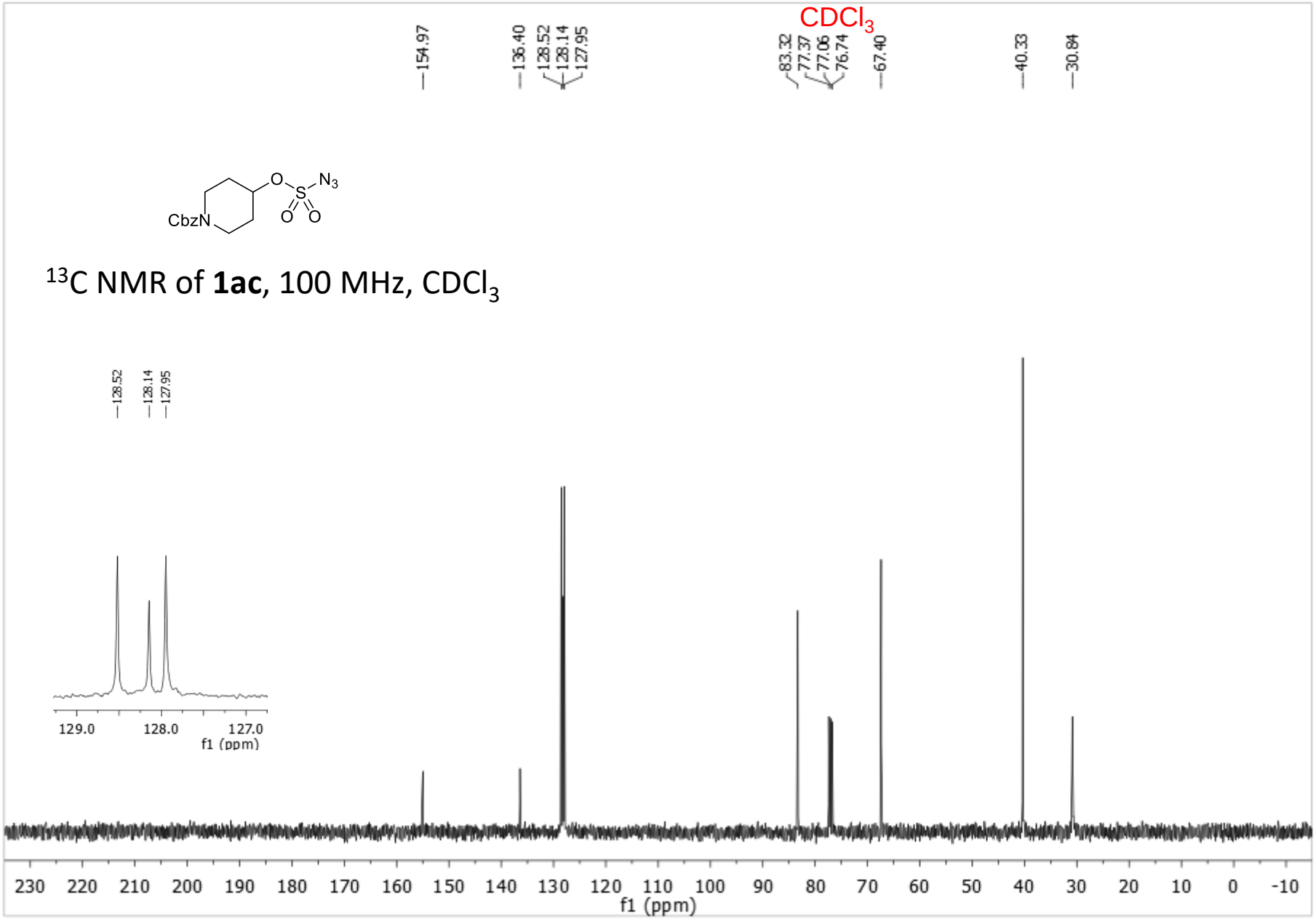


^{13}C NMR of **1ab**, 150 MHz, $CDCl_3$

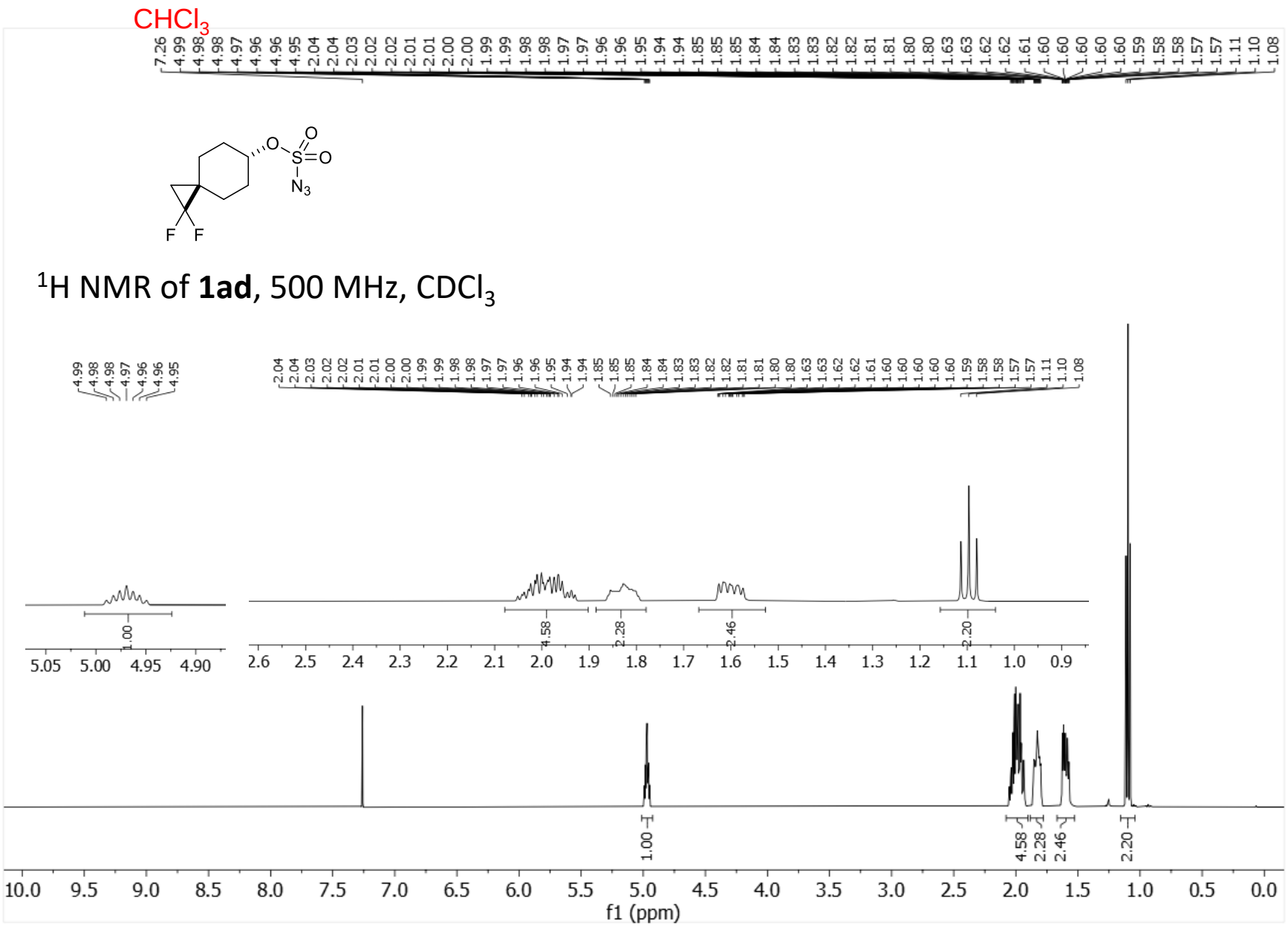
$CHCl_3$

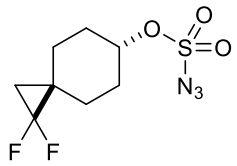


^{1}H NMR of **1ac**, 400 MHz, $CDCl_3$

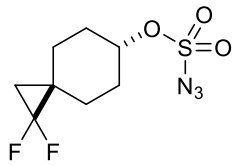


^{13}C NMR of **1ac**, 100 MHz, $CDCl_3$

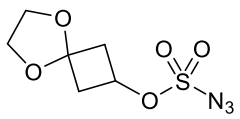

CHCl3
7.26
4.99 4.98 4.98 4.97 4.96 4.96 4.95 2.04 2.04 2.03 2.02 2.02 2.01 2.01 2.00 2.00 1.99 1.99 1.98 1.98 1.97 1.97 1.96 1.96 1.95 1.94 1.94 1.85 1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.82 1.81 1.81 1.80 1.80 1.63 1.63 1.62 1.62 1.61 1.60 1.60 1.60 1.60 1.59 1.58 1.58 1.57 1.57 1.11 1.10 1.08
O
O
S
O
N3
F F
1H NMR of 1ad, 500 MHz, CDCl3
1.00
4.58
2.28
2.46
2.20
5.05 5.00 4.95 4.90
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



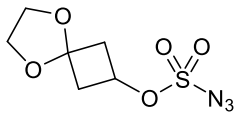
^{13}C NMR of **1ad**, 125 MHz, $CDCl_3$



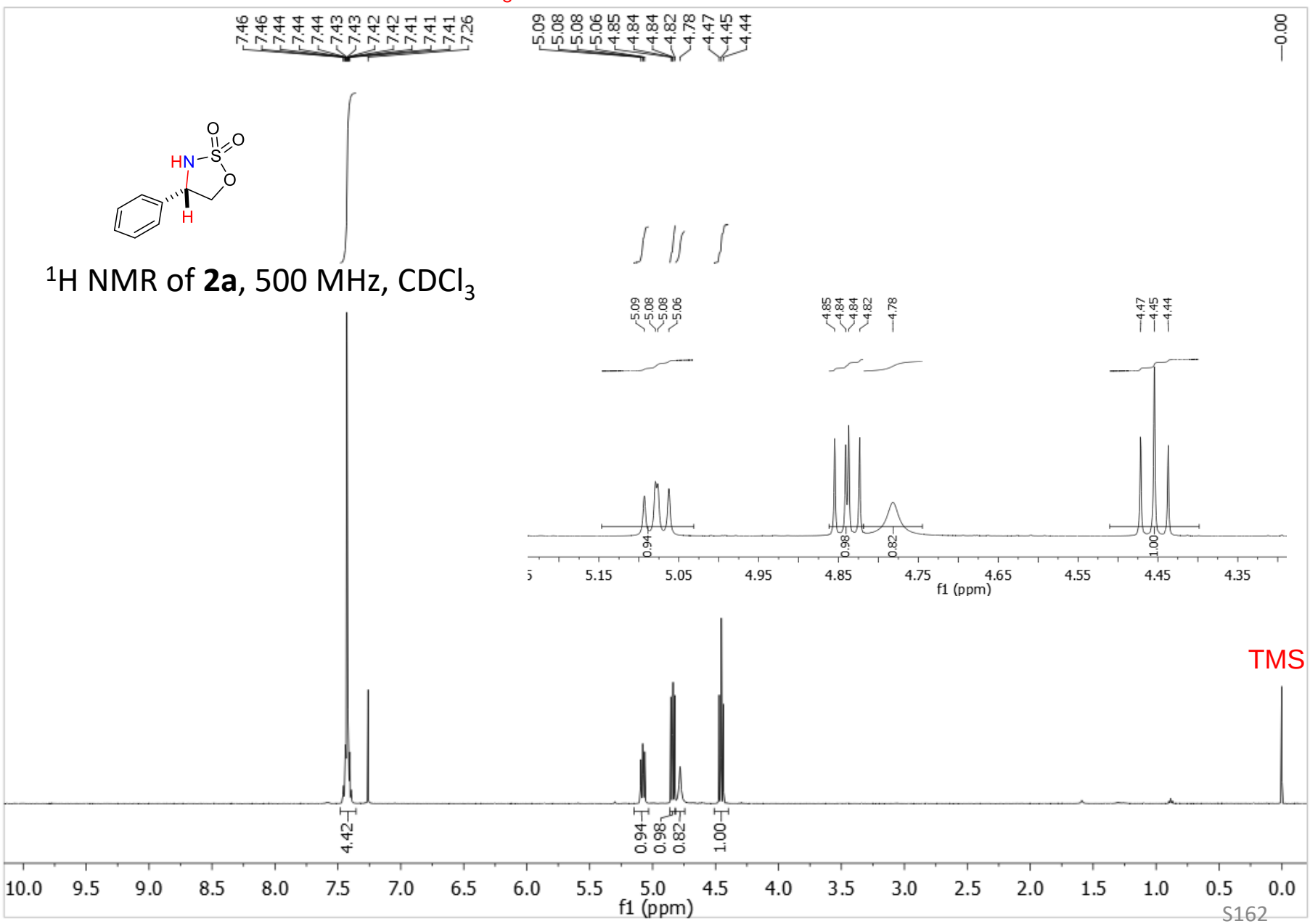
^{19}F NMR of **1ad**, 470 MHz, $CDCl_3$

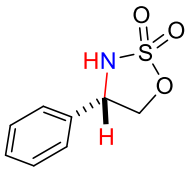


^{1}H NMR of **1ae**, 600 MHz, $CDCl_3$



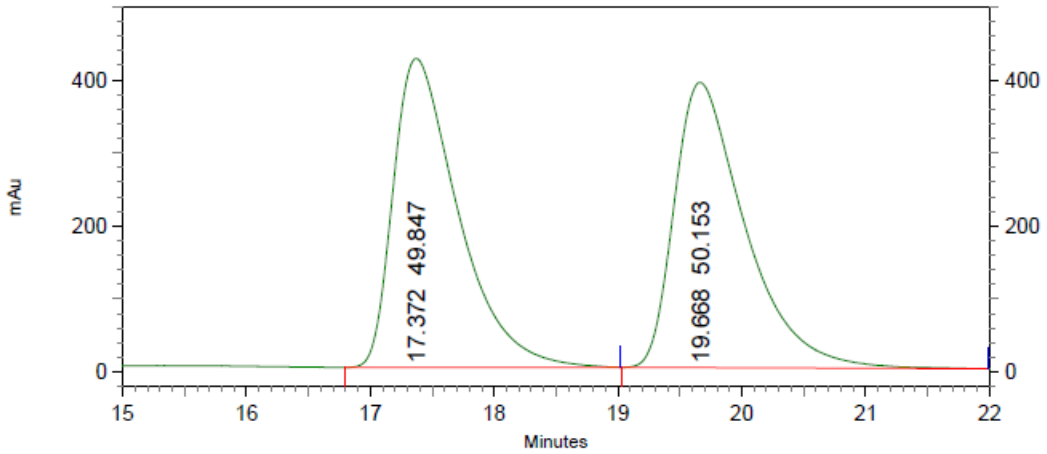
^{13}C NMR of **1ae**, 150 MHz, $CDCl_3$

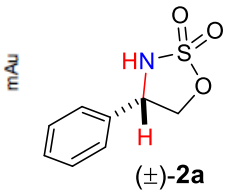

CHCl3
7.46 7.46 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.26
5.09 5.08 5.08 5.06 4.85 4.84 4.84 4.82 4.78 4.47 4.45 4.44
0.00
HN
S
O
O
O
H
1H NMR of 2a, 500 MHz, CDCl3
5.09 5.08 5.08 5.06
4.85 4.84 4.84 4.82
4.78
4.47 4.45 4.44
0.94 0.98 0.82 1.00
5.15 5.05 4.95 4.85 4.75 4.65 4.55 4.45 4.35
f1 (ppm)
TMS
4.42
0.94 0.98 0.82 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



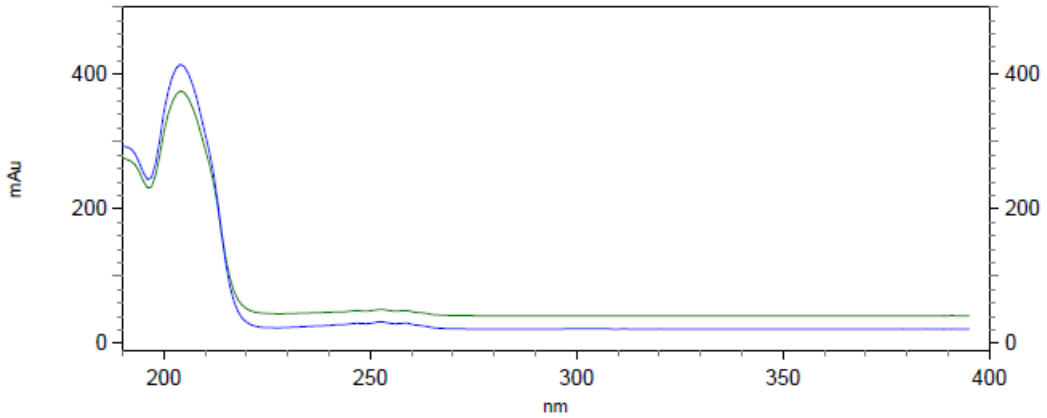
^{13}C NMR of **2a**, 150 MHz, $CDCl_3$

C:\EZStart\Projects\Default\Data\K0L-350-ADH-10%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





(±)-**2a**

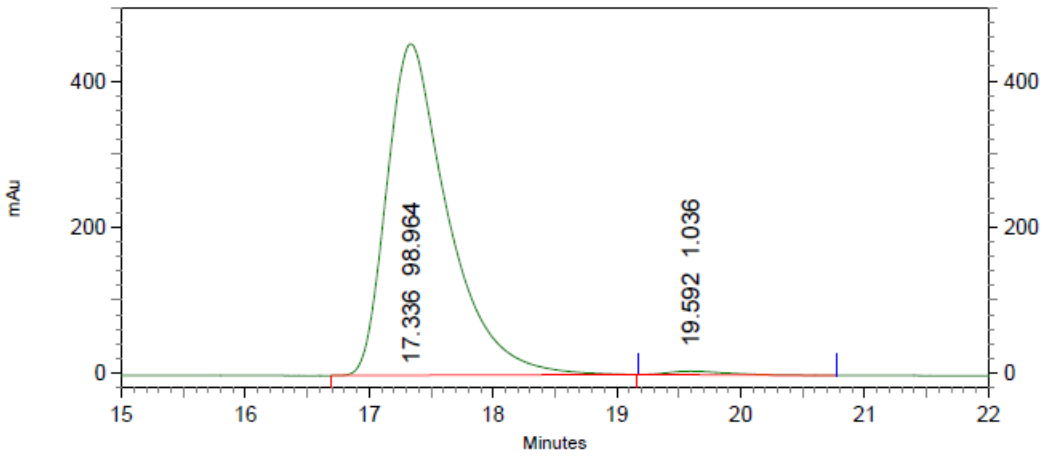


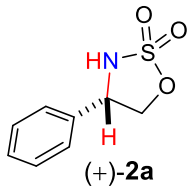
5: 208 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	17.372	49.847
2	19.668	50.153

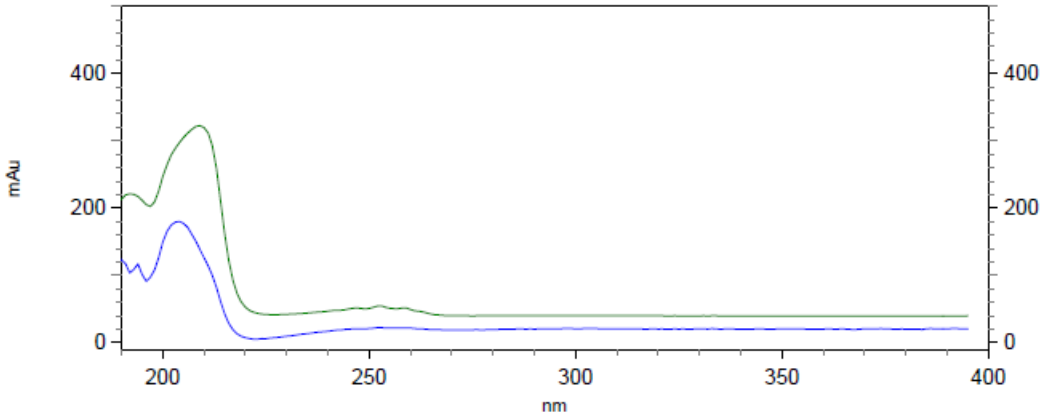
Totals	
	100.000

C:\EZStart\Projects\Default\Data\K0L-349ADH-10%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





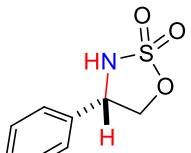
(+)-**2a**



5: 221 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	17.336	98.964
2	19.592	1.036

Totals	
	100.000



(+)-**2a**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C8H9NO3S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C8H9NO3S

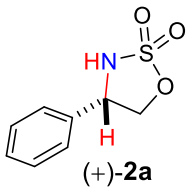
```
Bond precision:  C-C = 0.0030 A          Wavelength=1.54178

Cell:            a=4.7540(2)      b=11.9215(4)      c=15.2976(5)
                 alpha=90         beta=90           gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	866.99(5)	866.99(5)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C8 H9 N O3 S	C8 H9 N O3 S
Sum formula	C8 H9 N O3 S	C8 H9 N O3 S
Mr	199.22	199.22
Dx,g cm-3	1.526	1.526
Z	4	4
Mu (mm-1)	3.128	3.128
F000	416.0	416.0
F000'	418.58	
h,k,lmax	5,14,18	5,14,18
Nref	1660[1002]	1637
Tmin,Tmax	0.467,0.666	0.585,0.753
Tmin'	0.206	

```
Correction method= # Reported T Limits: Tmin=0.585 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.63/0.99      Theta(max)= 70.187

R(reflections)= 0.0228( 1625)     wR2(reflections)= 0.0616( 1637)

S = 1.094                 Npar= 121
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

```
Alert level G
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          2 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O1             109.9 Degree
PLAT791_ALERT_4_G Model has Chirality at C2          (Chiral SPGR)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          8 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```



(+)-**2a**

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

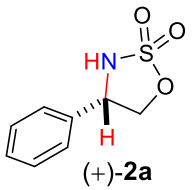
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

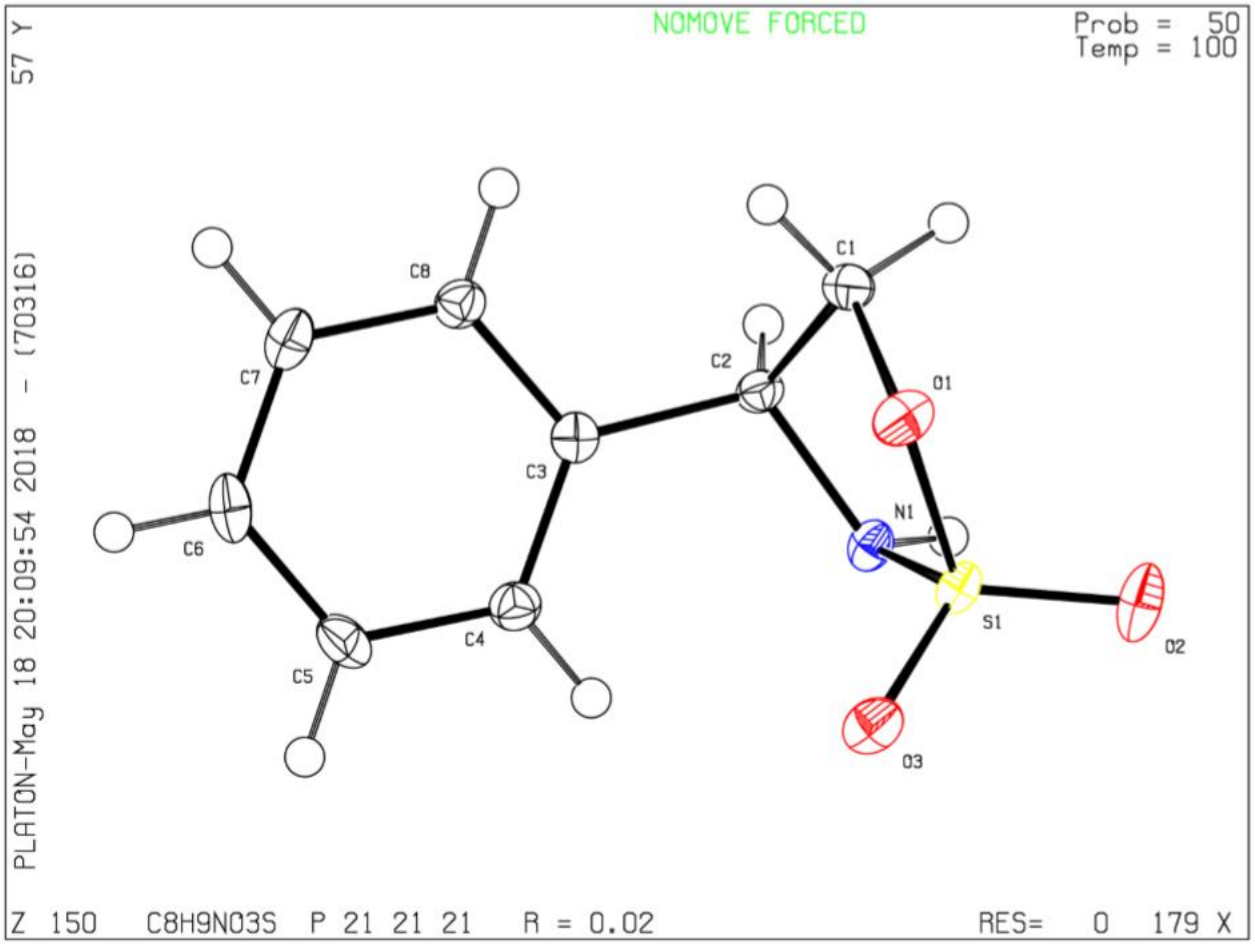
Publication of your CIF in other journals

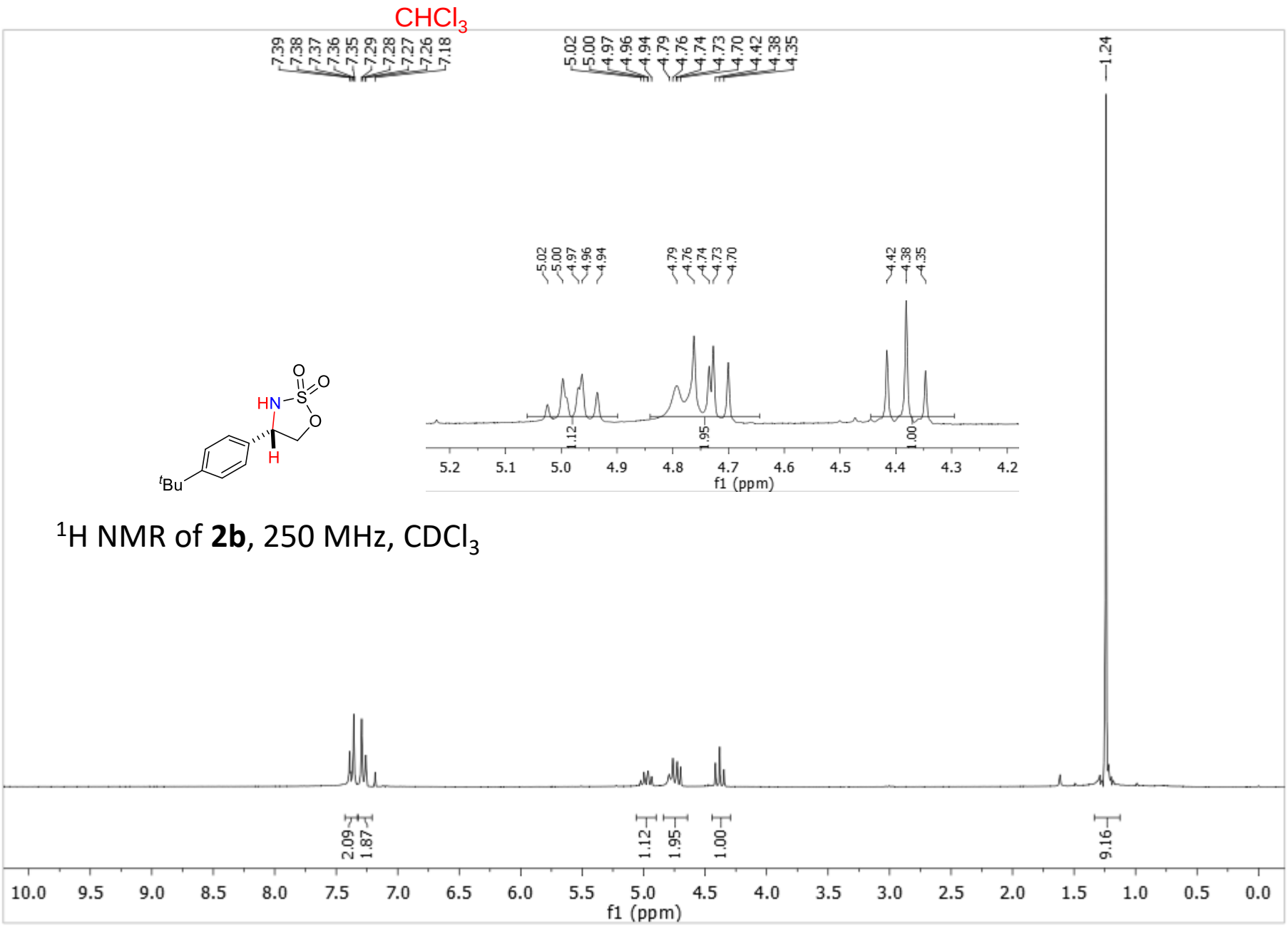
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.



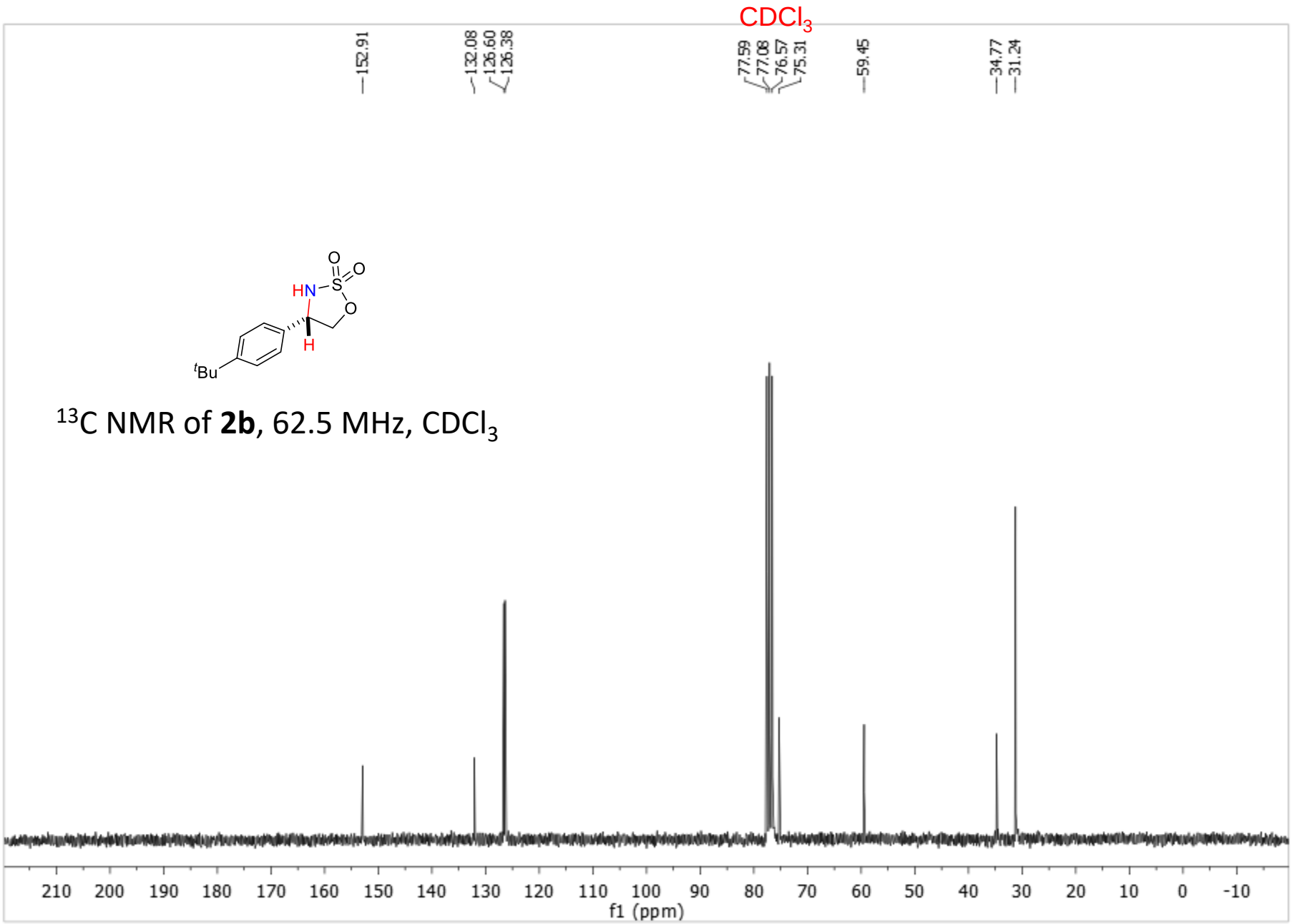
(+)-**2a**

Datablock C8H9NO3S - ellipsoid plot

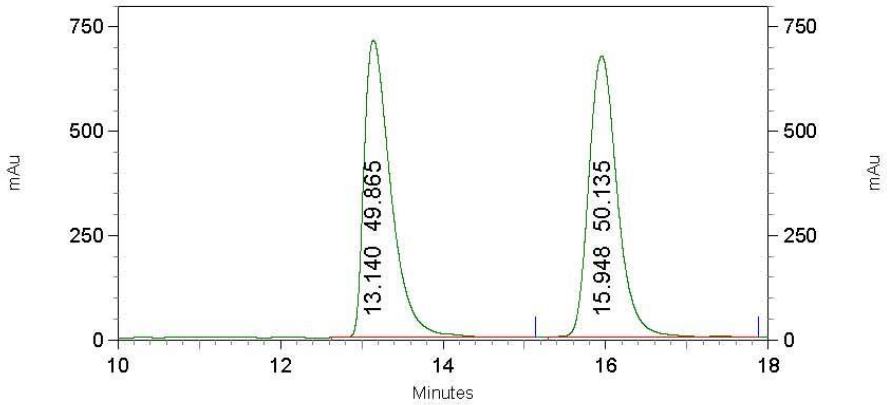


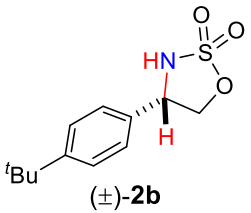


^{1}H NMR of **2b**, 250 MHz, $CDCl_3$

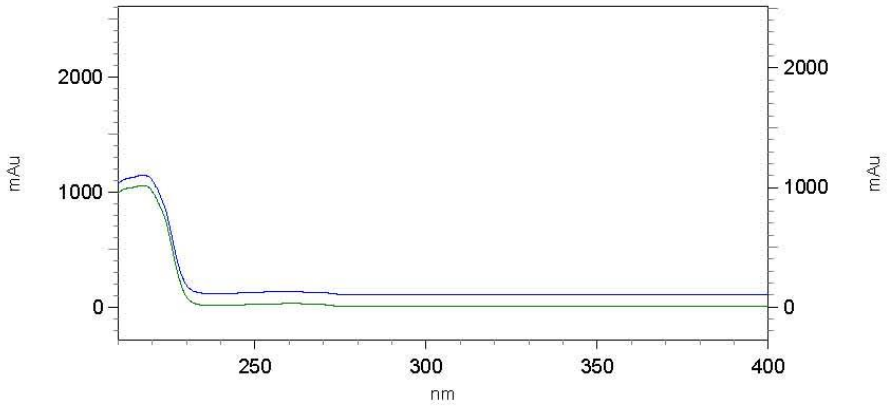


^{13}C NMR of **2b**, 62.5 MHz, $CDCl_3$



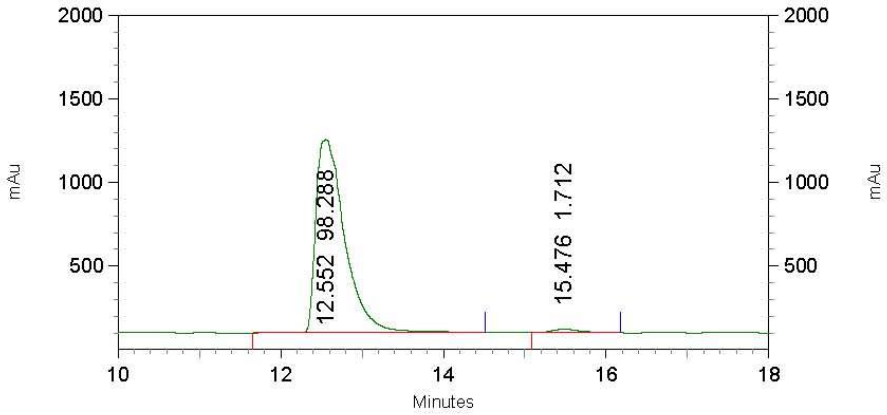


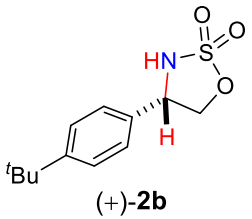
(±)-**2b**



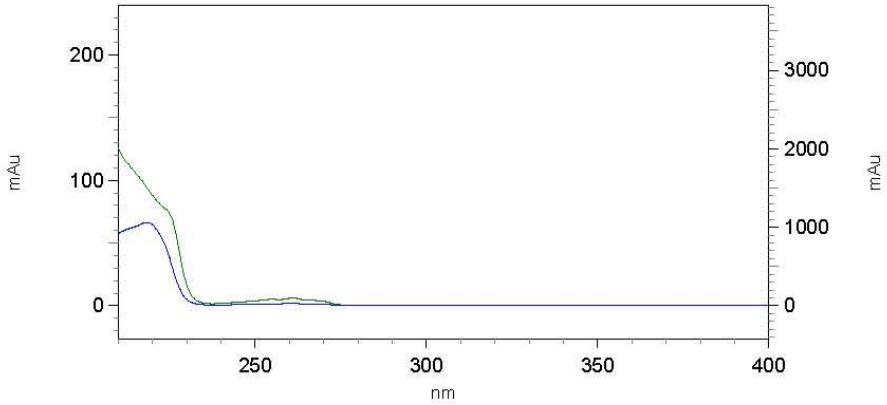
7: 224 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		13.140	49.865
2		15.948	50.135
Totals			100.000





(+)-**2b**

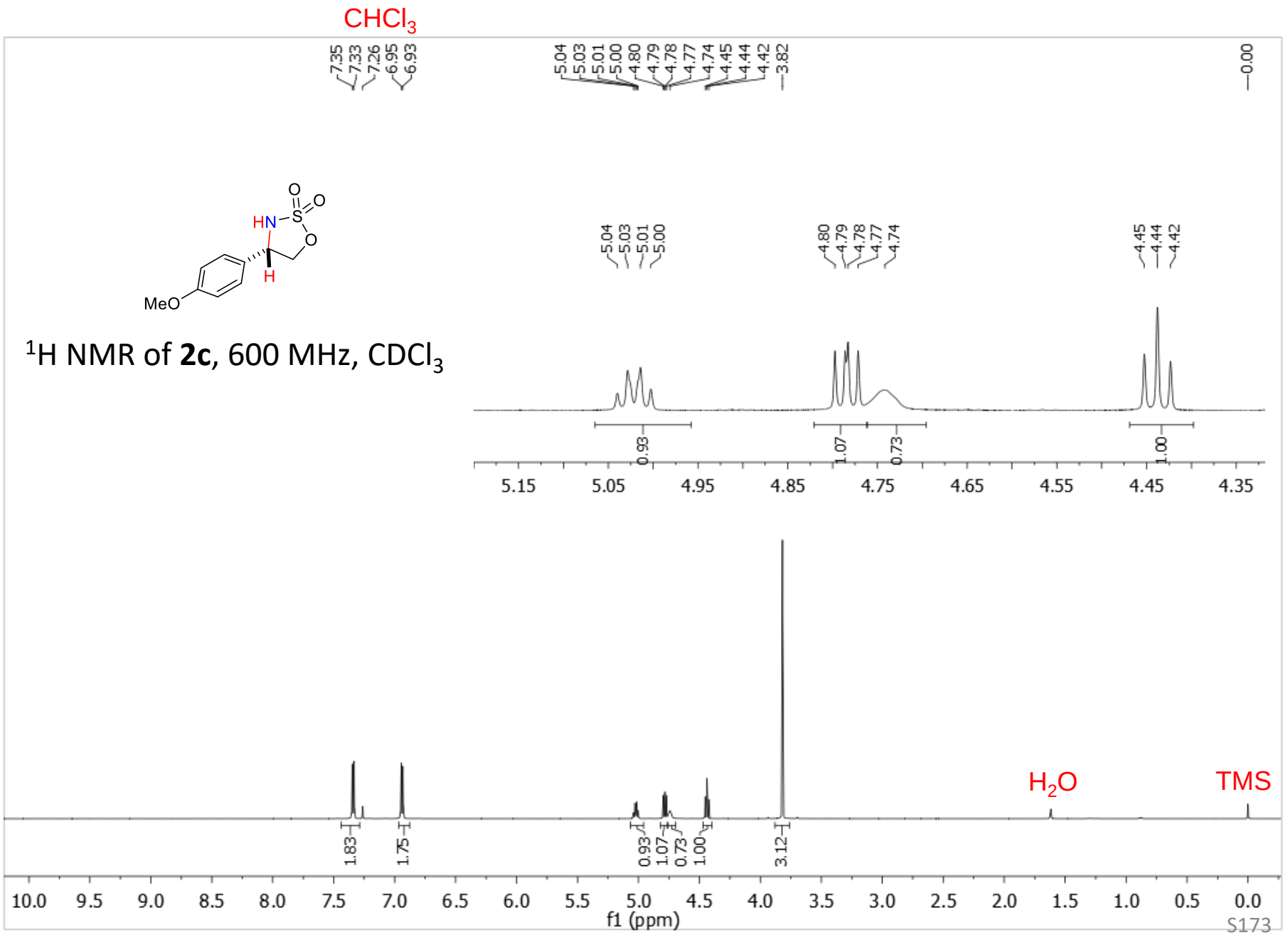


9: 207 nm, 4 nm

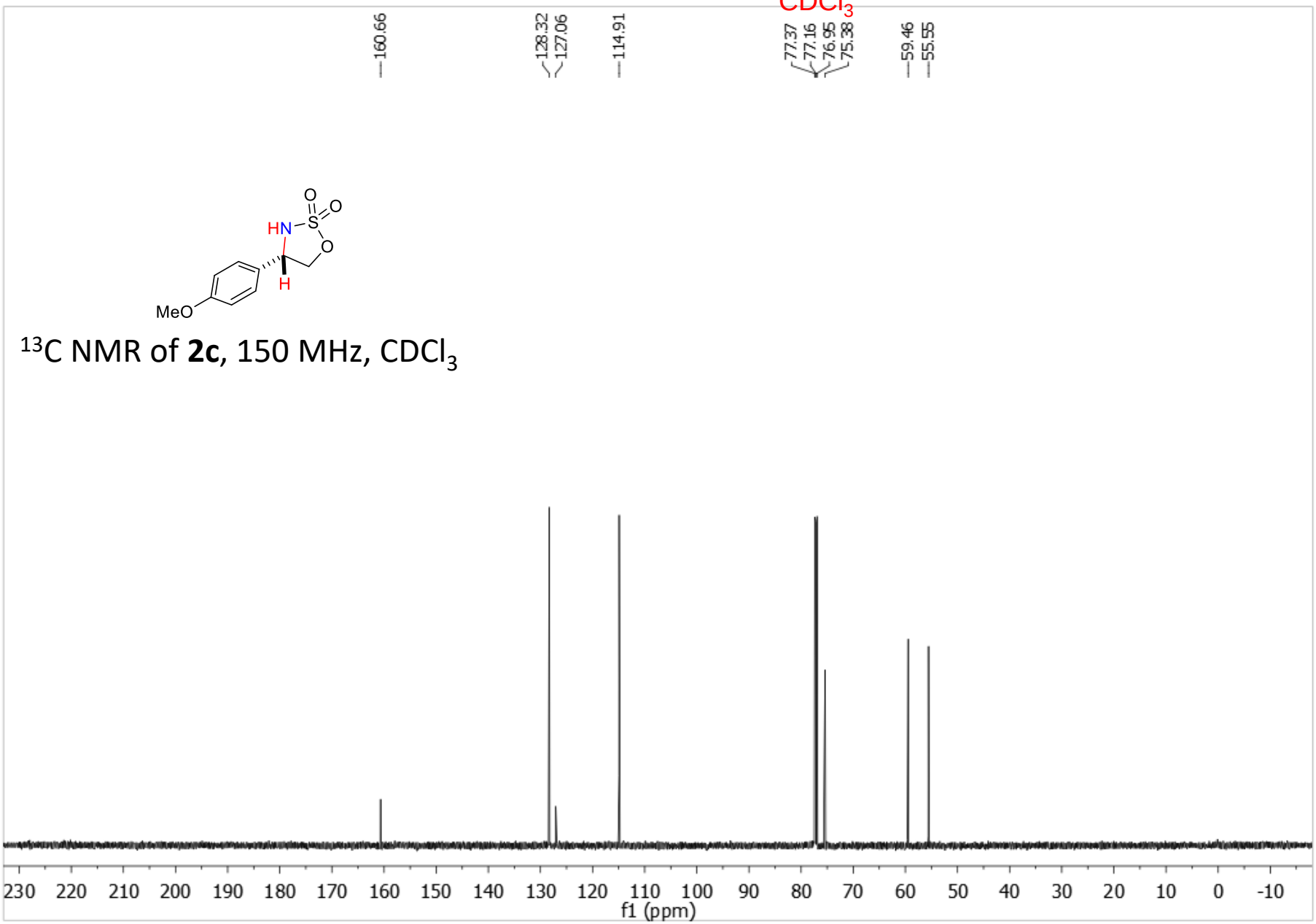
Results

Name	Retention Time	Area Percent	Pk #
	12.552	98.288	1
	15.476	1.712	2

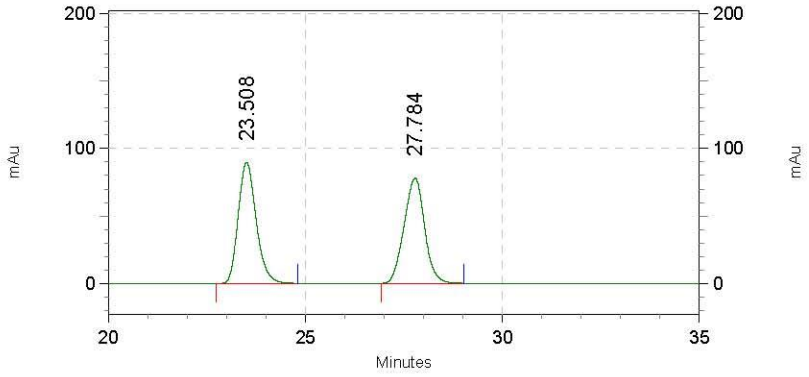
Totals		100.000	

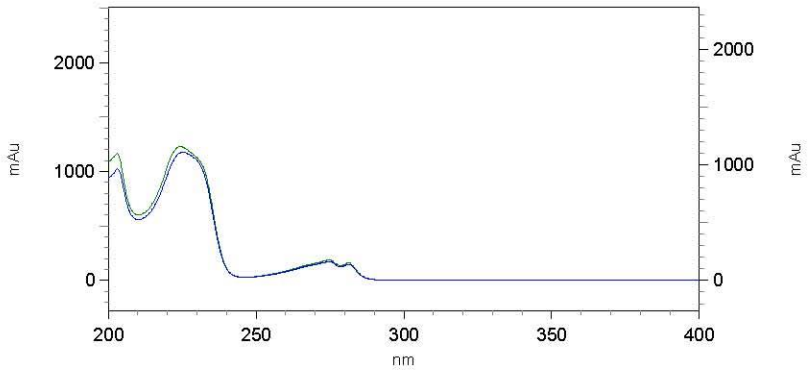


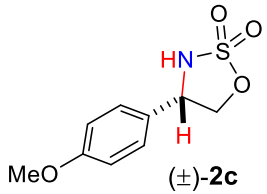
^{1}H NMR of **2c**, 600 MHz, $CDCl_3$



^{13}C NMR of **2c**, 150 MHz, $CDCl_3$



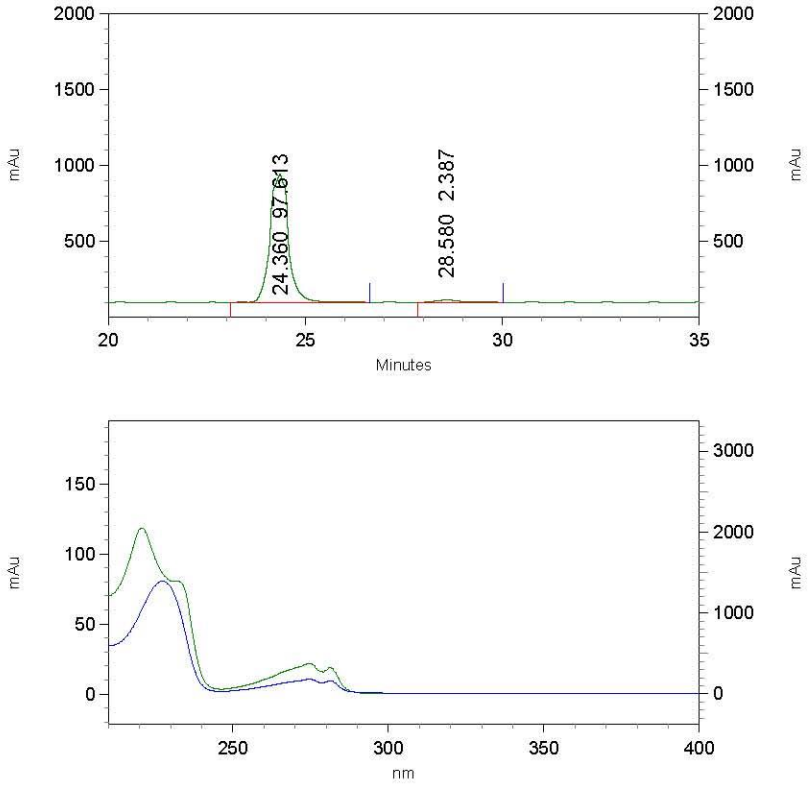


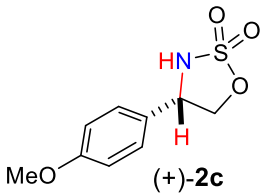


(±)-**2c**

10: 274 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		23.508	50.126
2		27.784	49.874
Totals			100.000

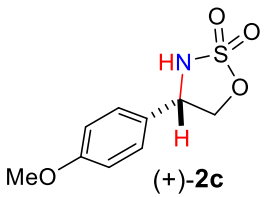




(+)-**2c**

8: 204 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	24.360	97.613	1
	28.580	2.387	2
Totals		100.000	



(+)-**2c**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) yh_iv_56

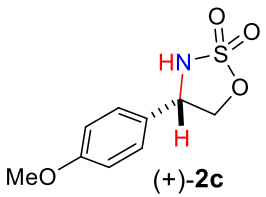
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yh_iv_56

```
Bond precision:  C-C = 0.0040 A          Wavelength=1.54178

Cell:            a=5.32350(9)      b=8.2534(1)      c=22.6205(3)
                 alpha=90          beta=90          gamma=90
Temperature:     228 K

                 Calculated                Reported
Volume           993.88(2)                 993.88(2)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C9 H11 N O4 S             C9 H11 N O4 S
Sum formula      C9 H11 N O4 S             C9 H11 N O4 S
Mr               229.25                    229.25
Dx,g cm-3        1.532                     1.532
Z                4                         4
Mu (mm-1)        2.888                     2.888
F000             480.0                     480.0
F000'            482.84
h,k,lmax         6,10,27                   6,10,27
Nref             1912[ 1152]               1817
Tmin,Tmax        0.525,0.561               0.621,1.000
Tmin'            0.300

Correction method= # Reported T Limits: Tmin=0.621 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.58/0.95      Theta(max)= 70.942

R(reflections)= 0.0322( 1772)     wR2(reflections)= 0.0816( 1817)

S = 1.076                 Npar= 141
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(+)-**2c**

Alert level C

```
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.966 Why?
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        O11 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        S12 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         37 Report
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level G

```
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.043 Note
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O11           112.5 Degree
PLAT791_ALERT_4_G Model has Chirality at C9          (Chiral SPGR)        S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        14 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         7 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  5 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  2 ALERT type 3 Indicator that the structure quality may be low
  3 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

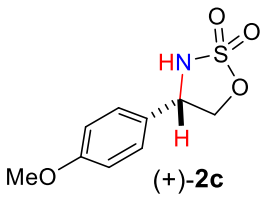
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

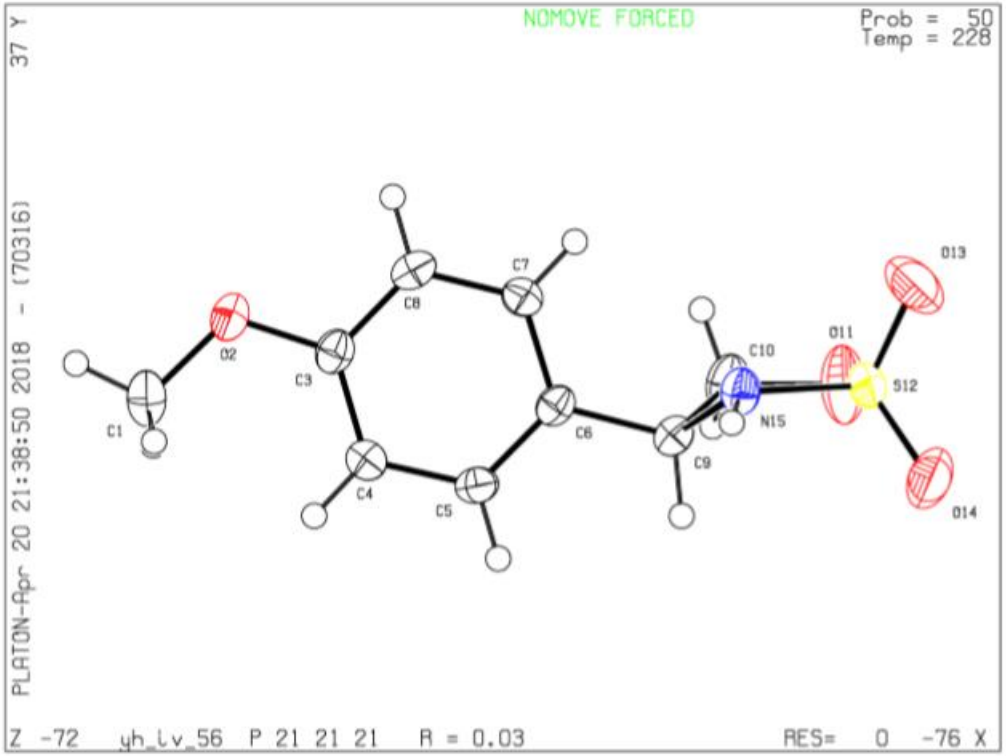
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

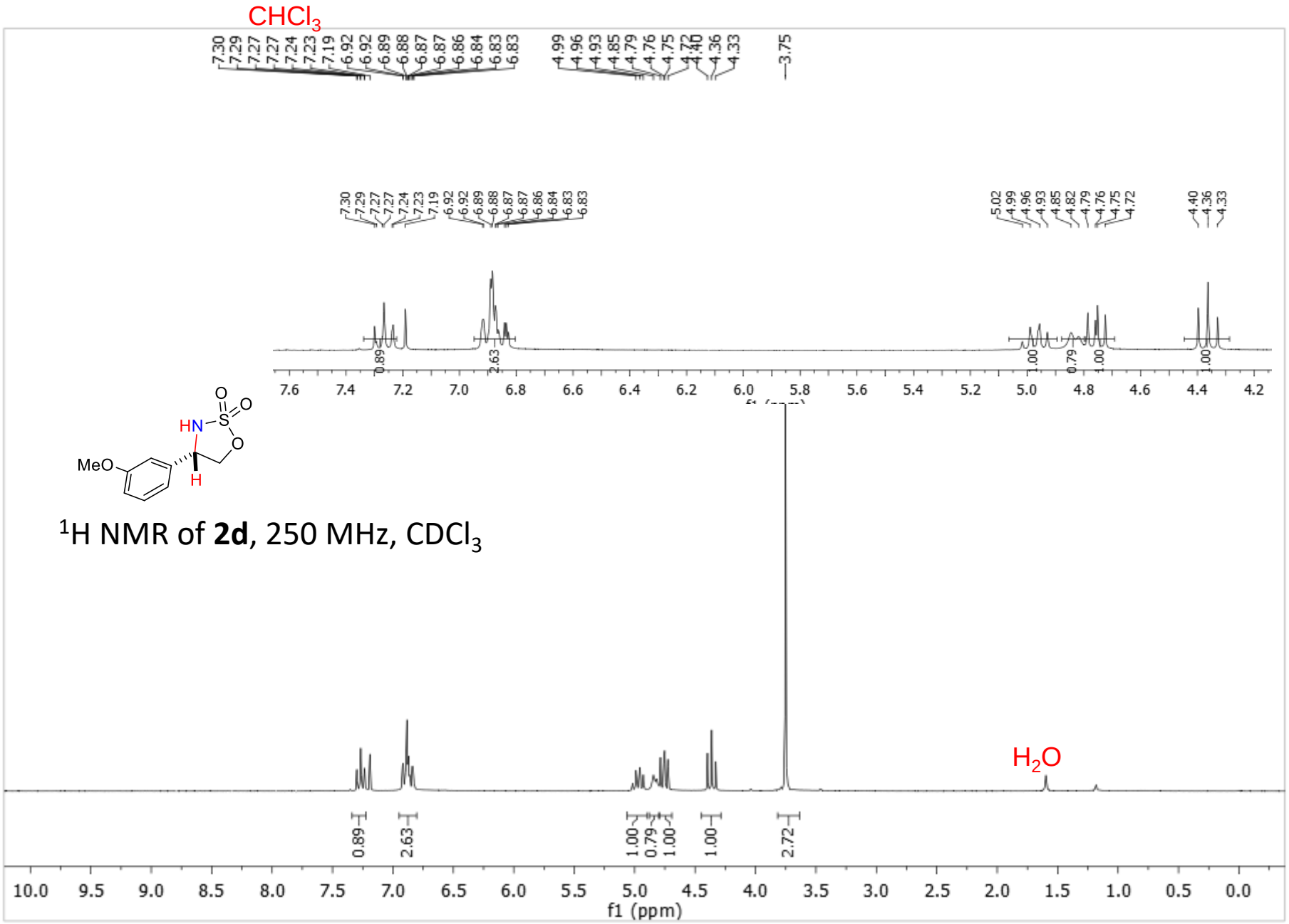


(+)-**2c**

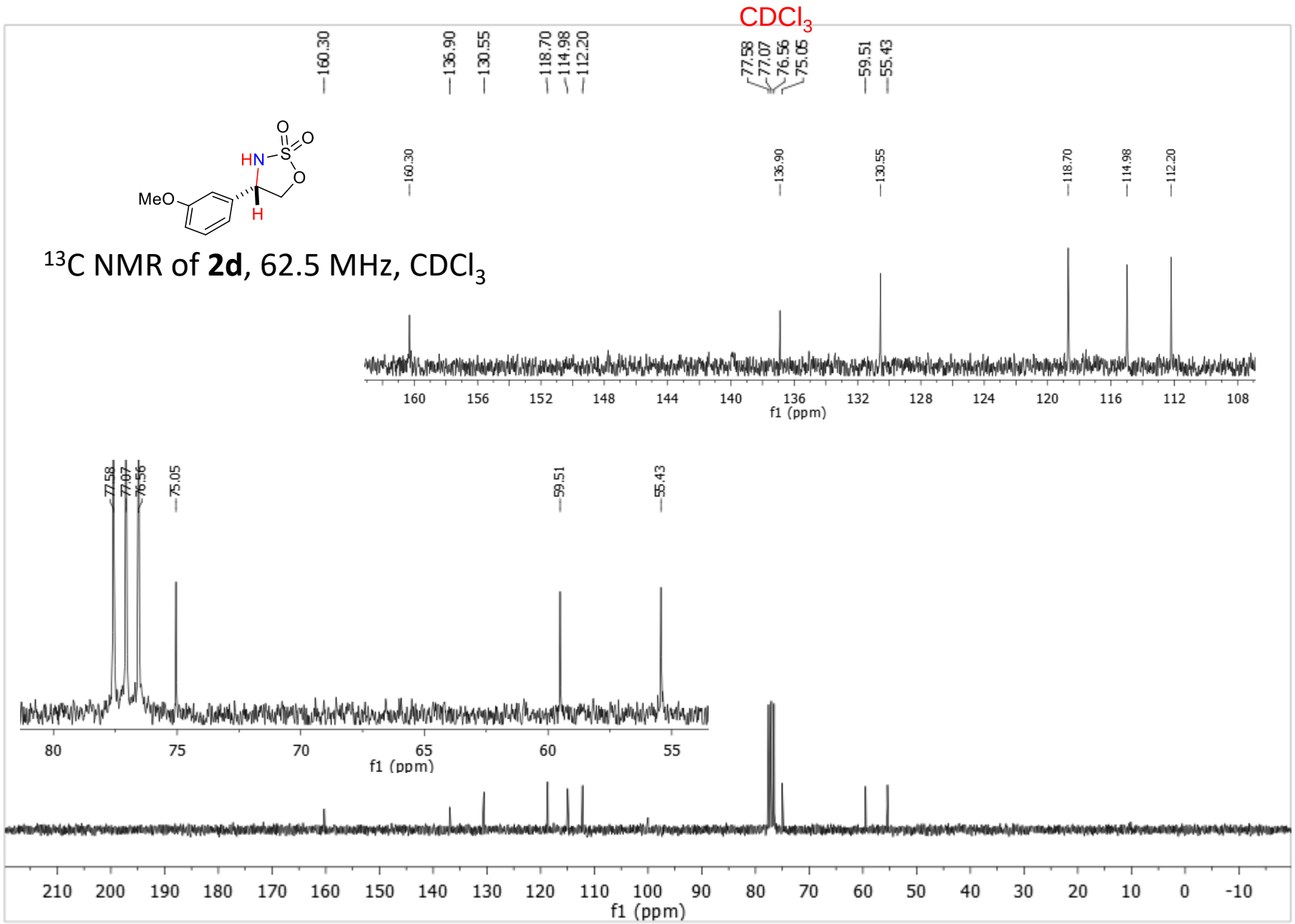
PLATON version of 30/01/2018; check.def file version of 30/01/2018

Datablock yh_lv_56 - ellipsoid plot

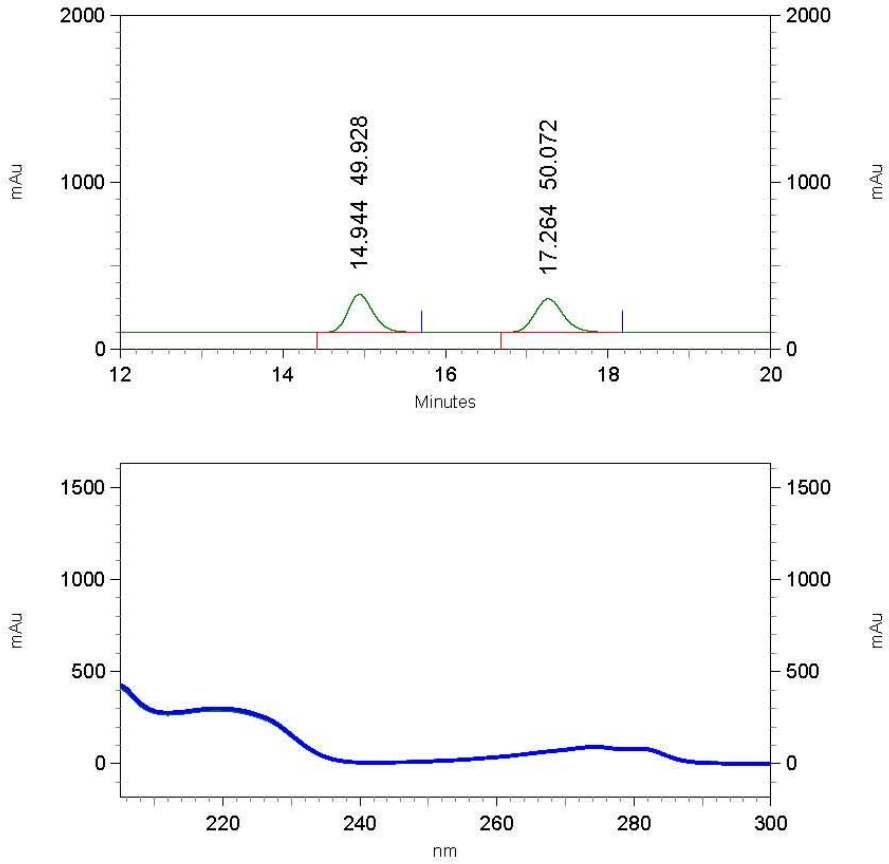


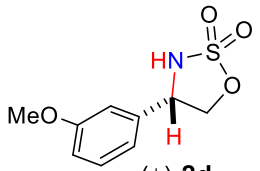


^{1}H NMR of **2d**, 250 MHz, $CDCl_3$



^{13}C NMR of **2d**, 62.5 MHz, $CDCl_3$

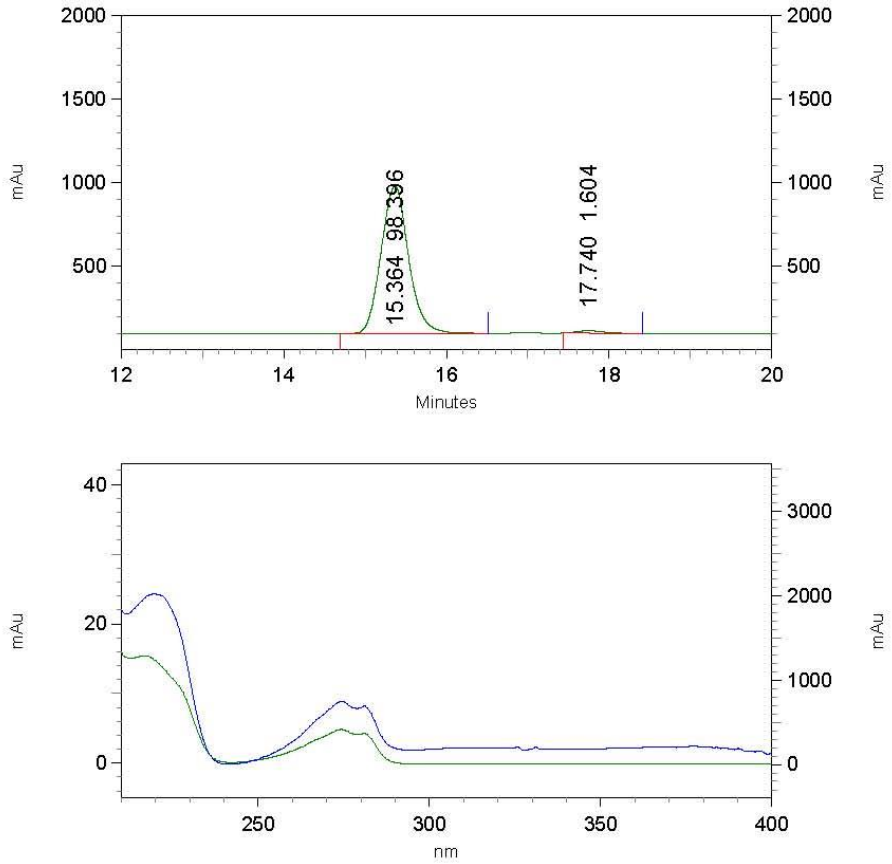


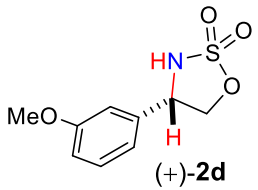


(±)-**2d**

18: 232 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		14.944	49.928
2		17.264	50.072
Totals			100.000



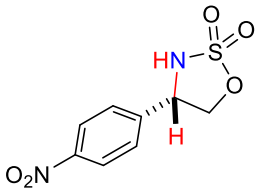


(+)-**2d**

1: 232 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	15.364	98.396	1
	17.740	1.604	2

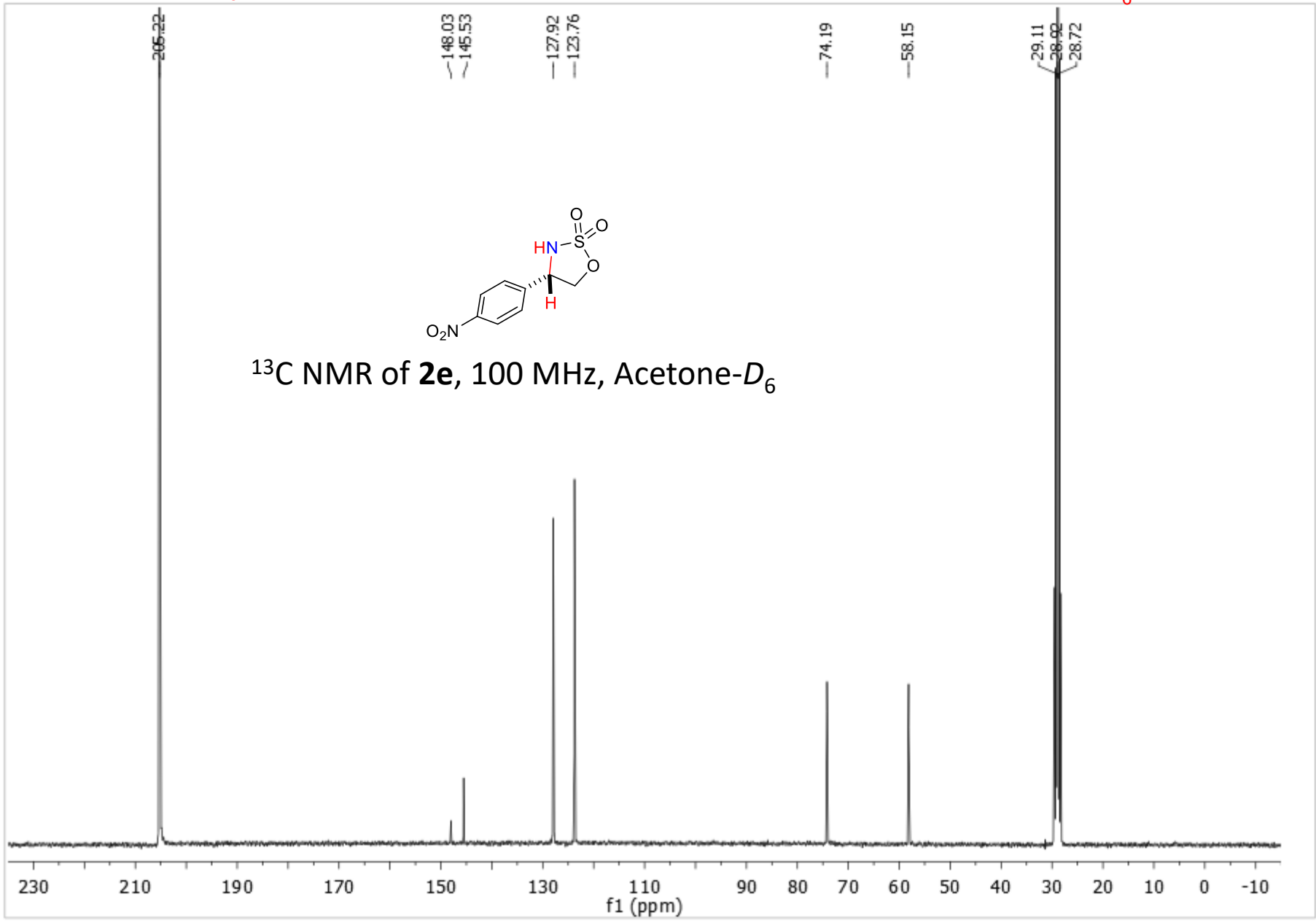
Totals		100.000	



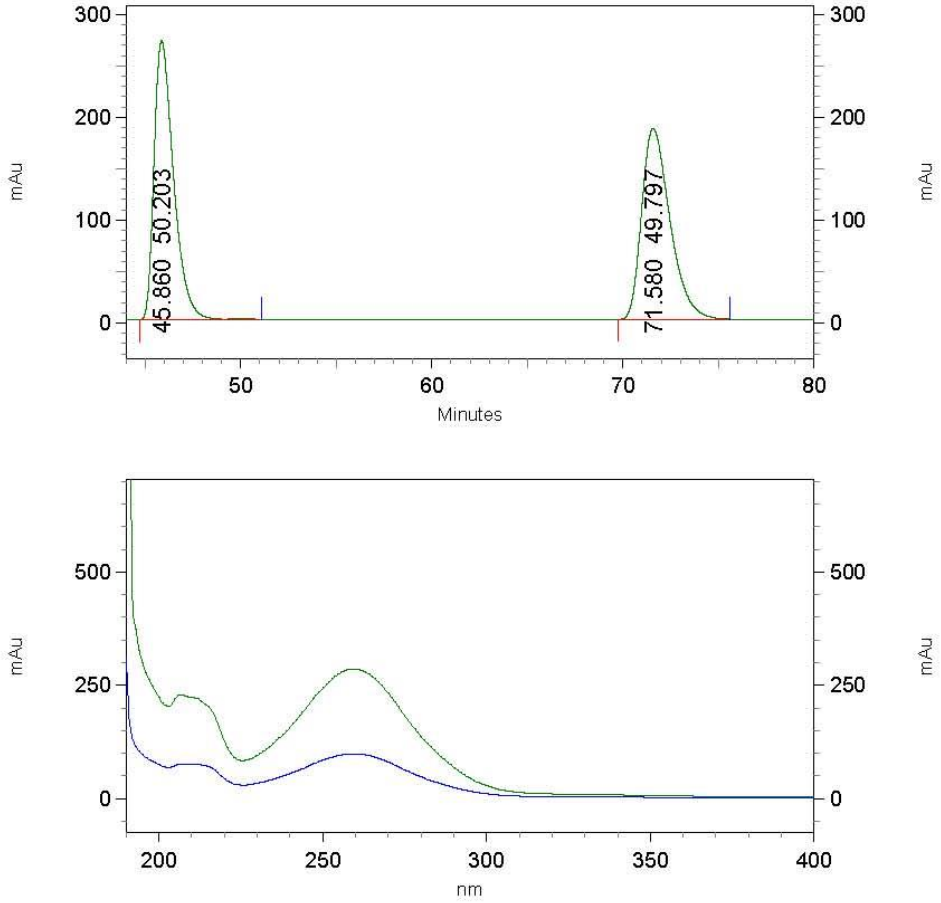
^{1}H NMR of **2e**, 400 MHz, Acetone-D_6

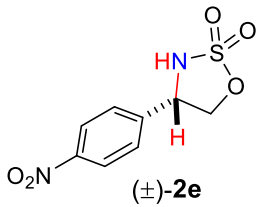
Acetone-D_6

Acetone-D_6



^{13}C NMR of **2e**, 100 MHz, Acetone-D_6





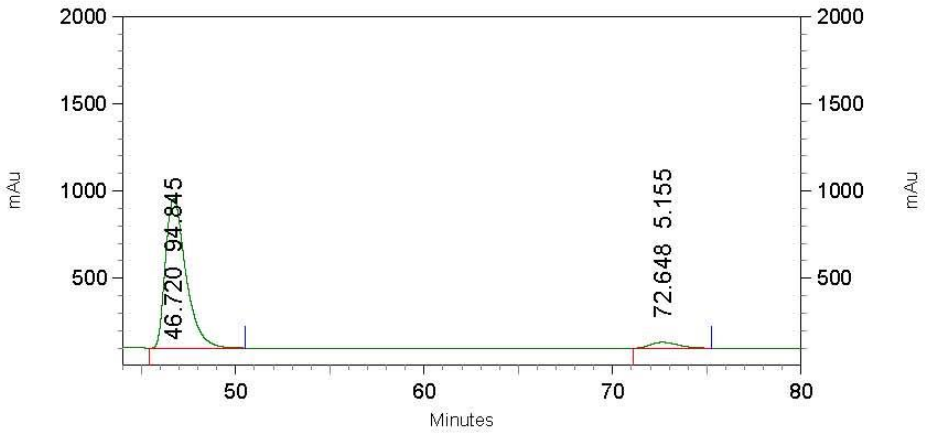
(±)-**2e**

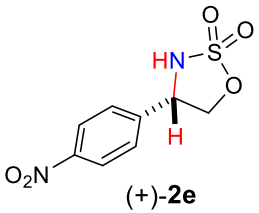
8: 264 nm, 4 nm

Results

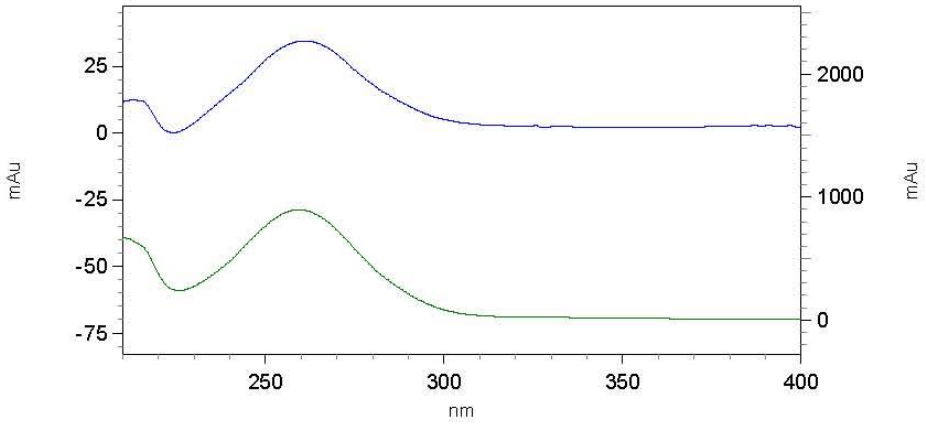
Name	Retention Time	Area Percent	Pk #
	45.860	50.203	1
	71.580	49.797	2

Totals		100.000	





(+)-**2e**

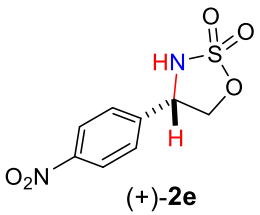


4: 264 nm, 4 nm

Results

Name	Retention Time	Area Percent	Pk #
	46.720	94.845	1
	72.648	5.155	2

Totals		100.000	



(+)-**2e**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C8H8N2O5S

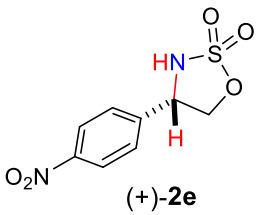
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C8H8N2O5S

```
Bond precision:  C-C = 0.0048 A          Wavelength=1.54178

Cell:            a=7.1996(2)     b=9.8838(3)         c=13.6772(5)
                 alpha=90        beta=98.770(1)      gamma=90
Temperature:     100 K

                Calculated                Reported
Volume          961.88(5)                 961.88(5)
Space group     P 21                      P 21
Hall group      P 2yb                     P 2yb
Moiety formula  C8 H8 N2 O5 S             C8 H8 N2 O5 S
Sum formula     C8 H8 N2 O5 S             C8 H8 N2 O5 S
Mr              244.22                    244.22
Dx,g cm-3       1.686                     1.686
Z               4                         4
Mu (mm-1)       3.144                     3.144
F000            504.0                     504.0
F000'           507.07
h,k,lmax        8,11,16                   8,11,16
Nref            3521[ 1871]               3496
Tmin,Tmax       0.465,0.533               0.592,0.753
Tmin'           0.318

Correction method= # Reported T Limits: Tmin=0.592 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.87/0.99      Theta(max)= 68.271

R(reflections)= 0.0351( 3485)     wR2(reflections)= 0.0917( 3496)

S = 1.055                 Npar= 323
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(+)-**2e**

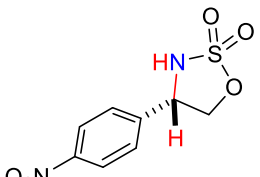
Alert level C

```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........        5.78 Note
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....        2.12 Report
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.00481 Ang.
PLAT430_ALERT_2_C Short Inter D...A Contact  O5       ..O6X              2.90 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          4 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         12 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          4 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for   O6       --C9        .        10.0 s.u.
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )         19% Note
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O6              111.1 Degree
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O6X             107.8 Degree
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O1              106.3 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact  O8       ..C9               3.01 Ang.
PLAT791_ALERT_4_G Model has Chirality at C2          (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C10         (Chiral SPGR)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         10 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          2 Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities .......     Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          5 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 16 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  9 ALERT type 2 Indicator that the structure model may be wrong or deficient
  6 ALERT type 3 Indicator that the structure quality may be low
  5 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```



(+)-**2e**

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

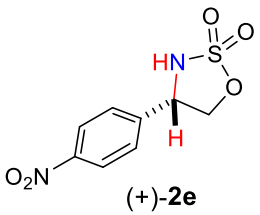
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

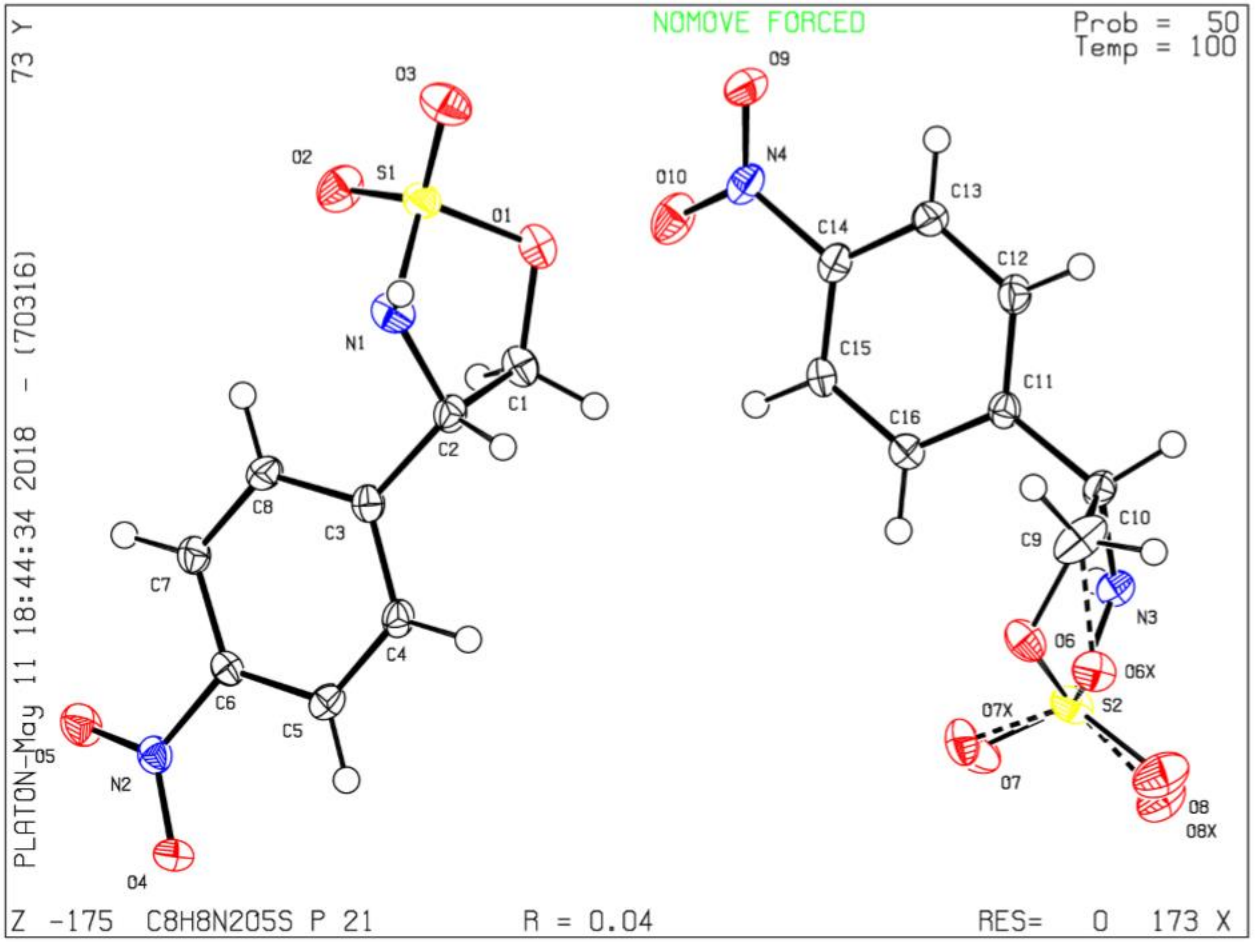
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

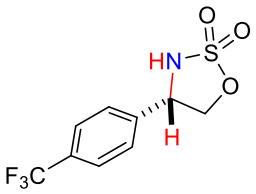
PLATON version of 23/04/2018; check.def file version of 23/04/2018



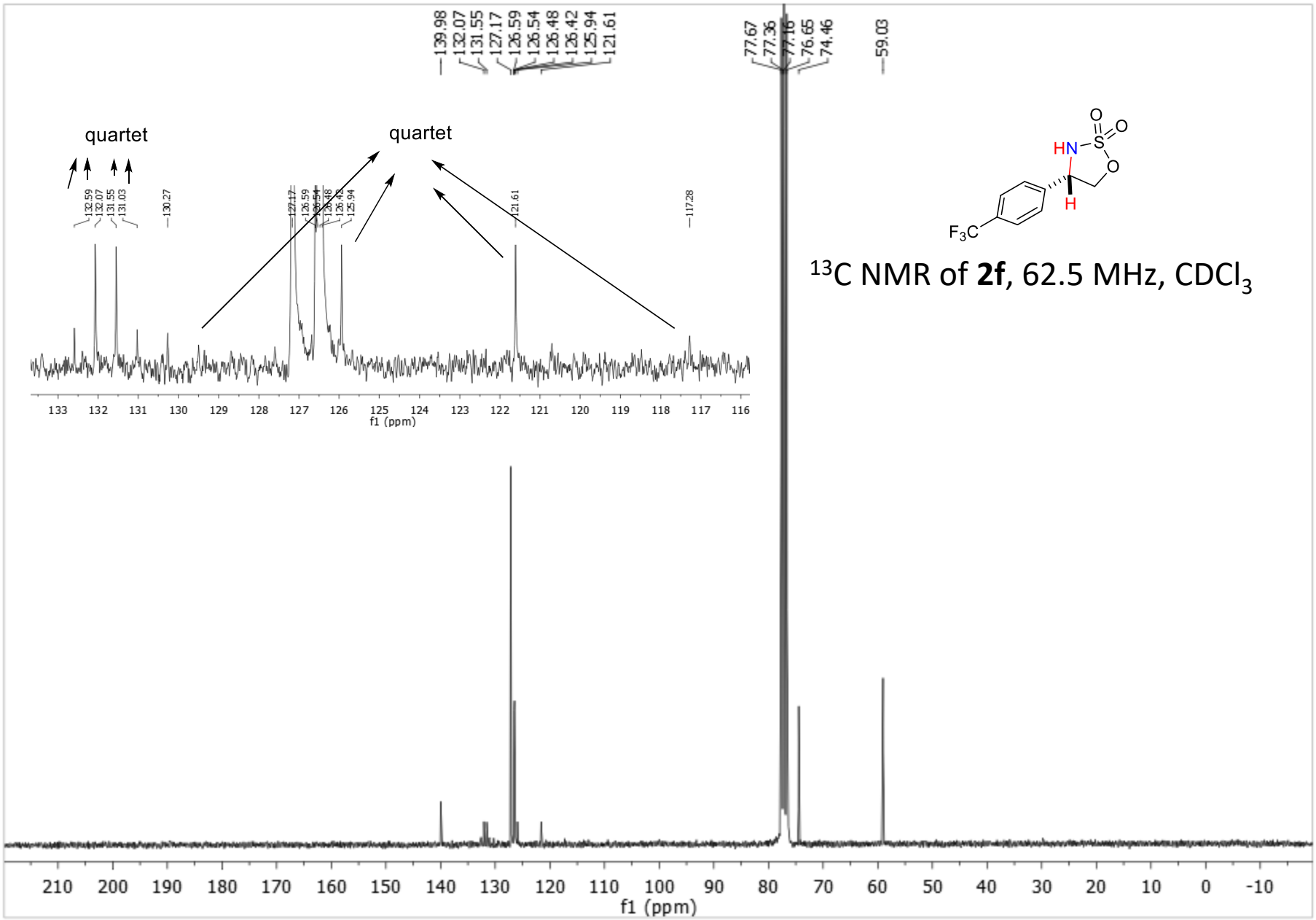
(+)-**2e**

Datablock C8H8N2O5S - ellipsoid plot

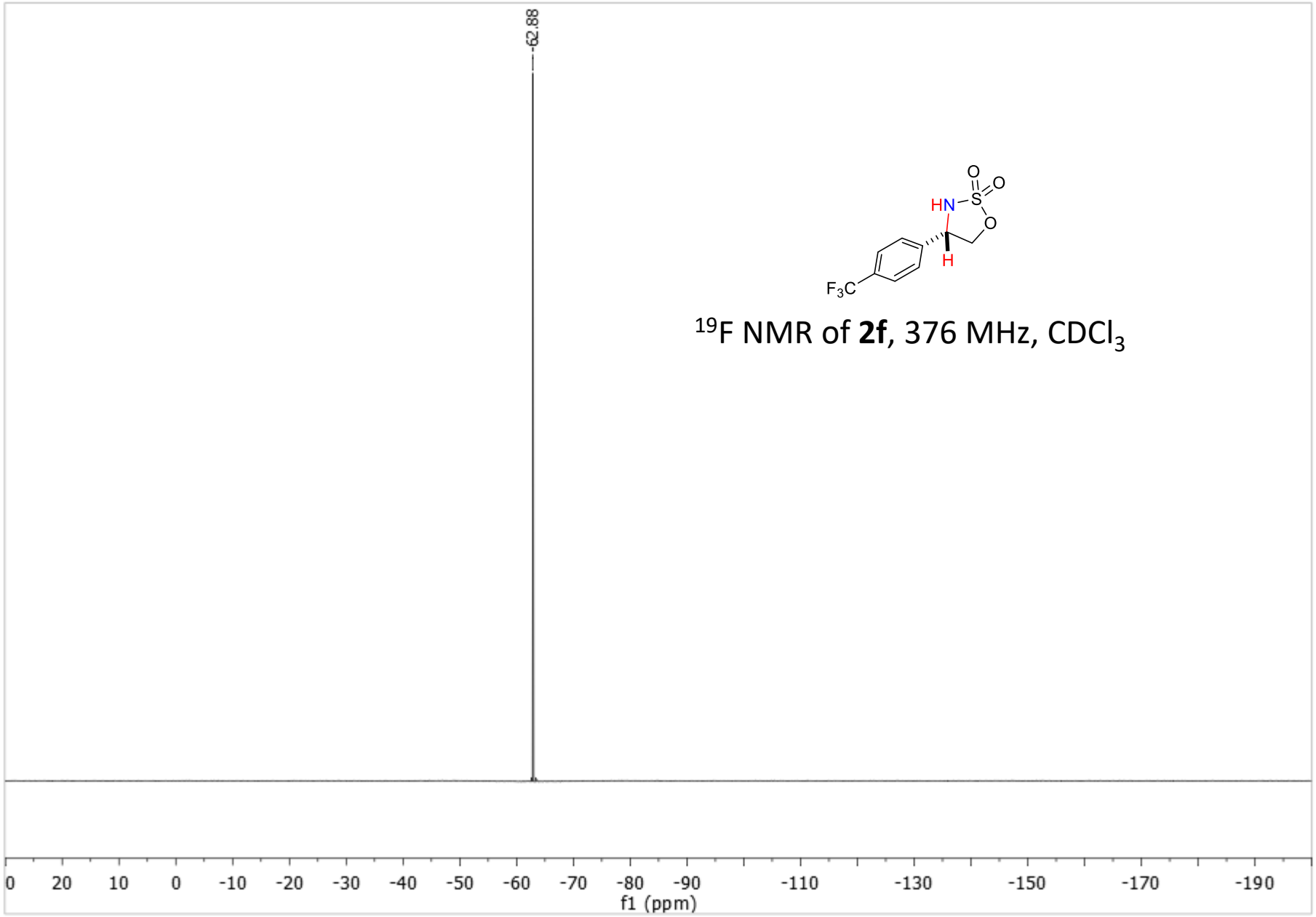




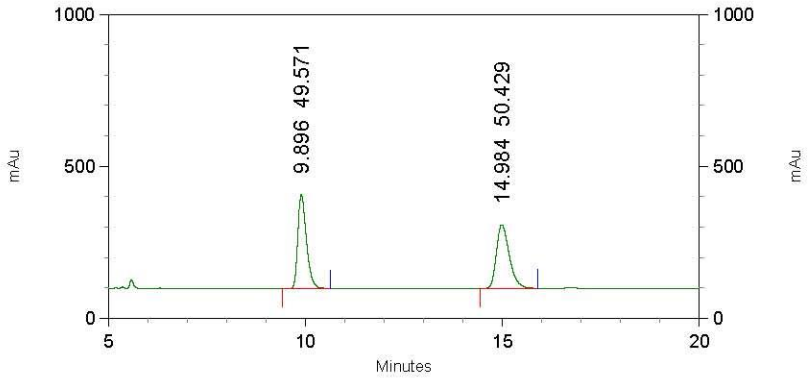
^{1}H NMR of **2f**, 250 MHz, $CDCl_3$

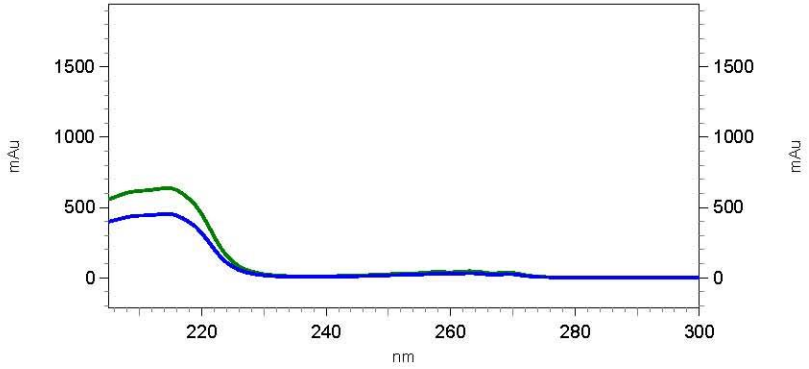


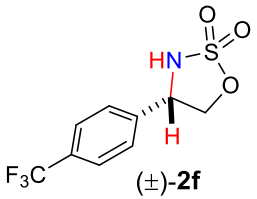
^{13}C NMR of **2f**, 62.5 MHz, $CDCl_3$



^{19}F NMR of **2f**, 376 MHz, $CDCl_3$





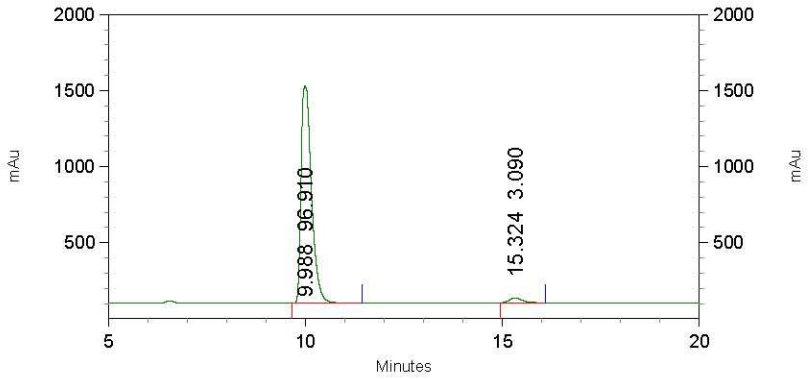


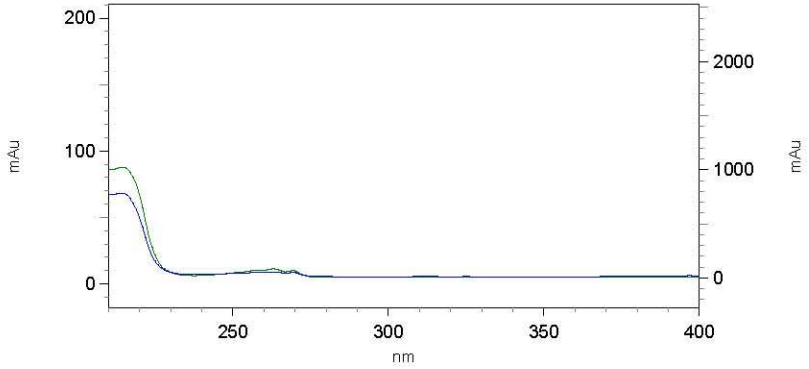
(±)-**2f**

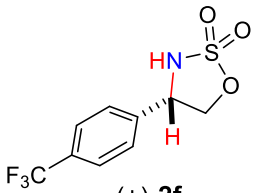
18: 222 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		9.896	49.571
2		14.984	50.429

Totals			100.000





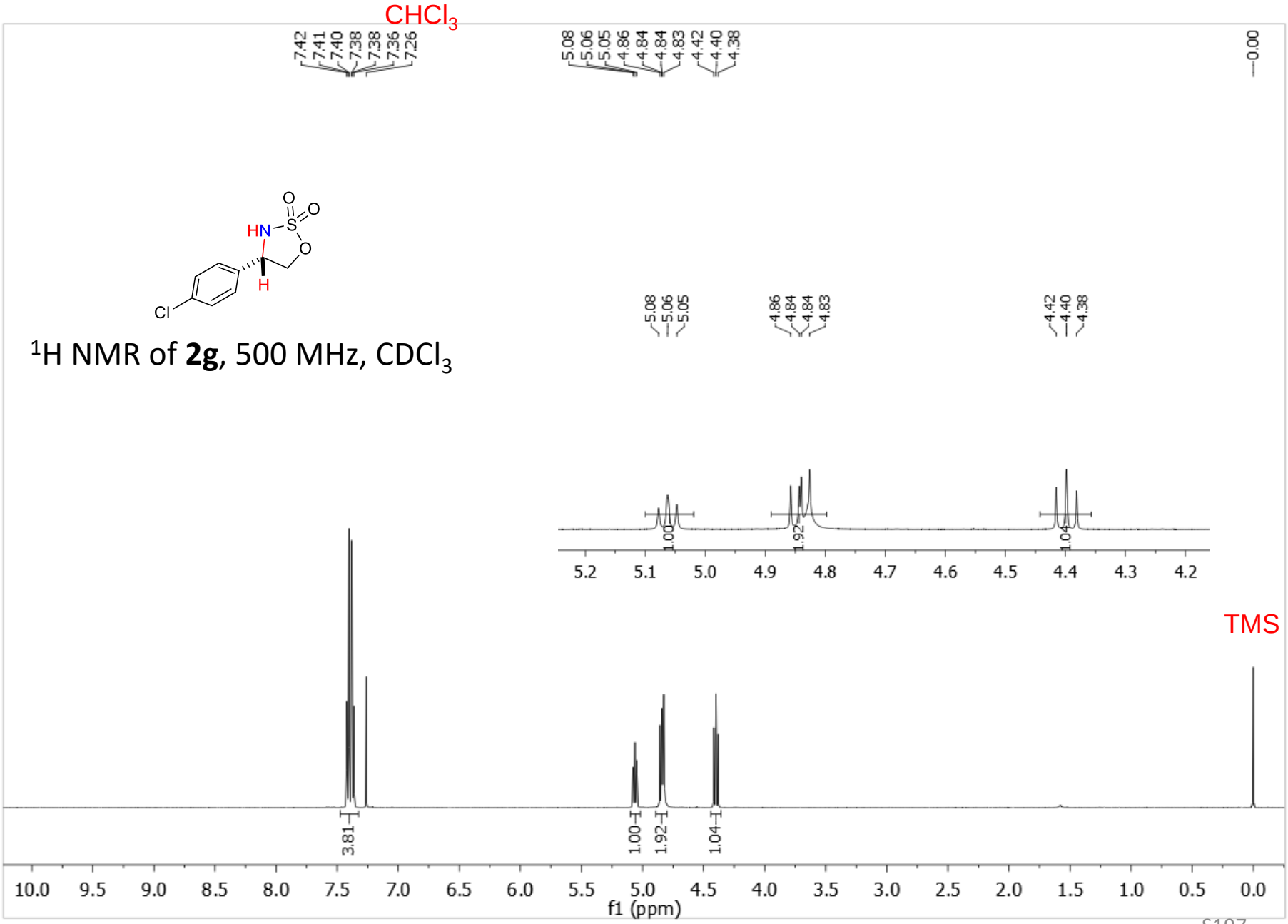


(+)-**2f**

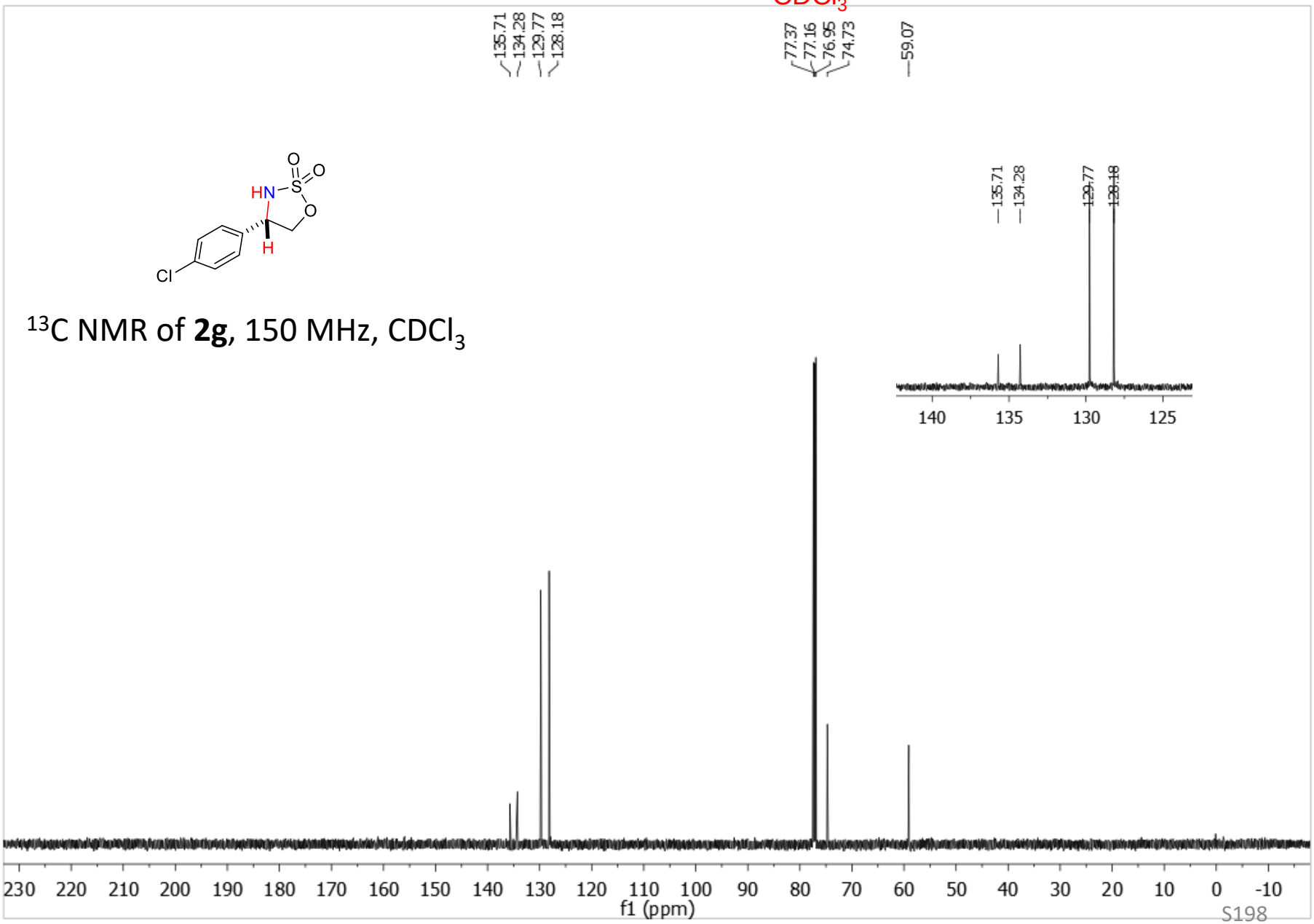
9: 204 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	9.988	96.910	1
	15.324	3.090	2

Totals			
		100.000	

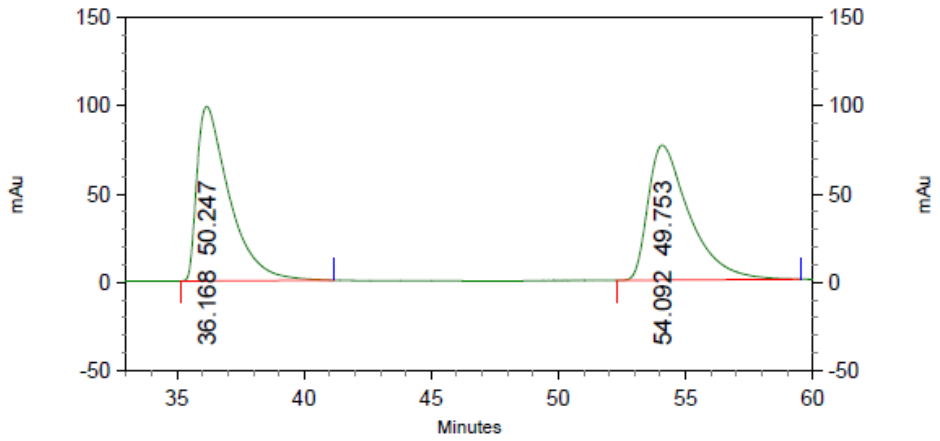


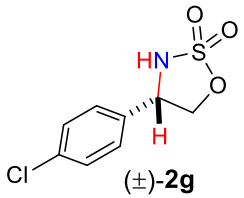
^{1}H NMR of **2g**, 500 MHz, $CDCl_3$



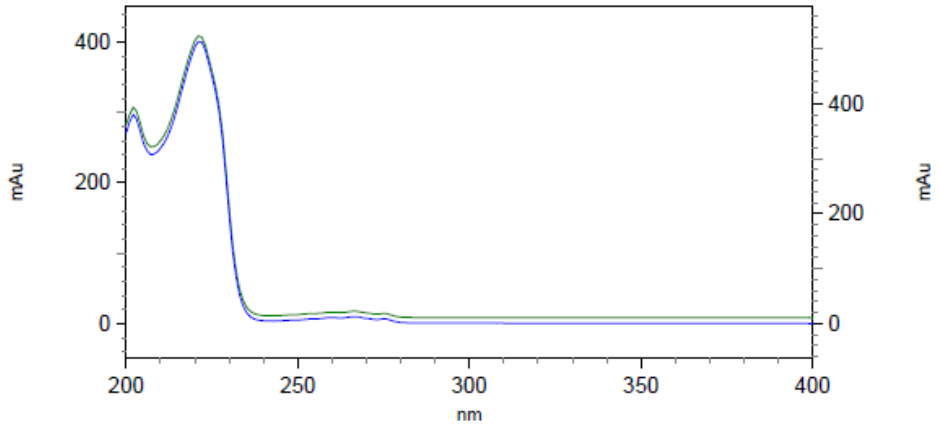
^{13}C NMR of **2g**, 150 MHz, $CDCl_3$

K0L-389-ADH-5%1.0
C:\EZStart\Projects\Default\Method\lk-5%1.0.met
C:\EZStart\Projects\Default\Data\K0L-389-ADH-5%1.0





(±)-**2g**

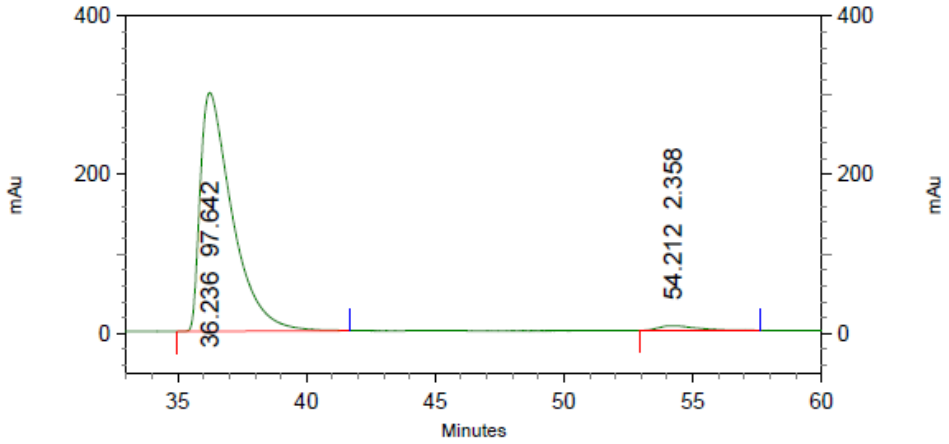


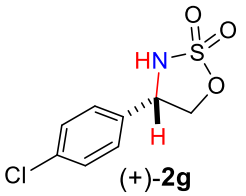
1: 232 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	36.168	50.247	1
	54.092	49.753	2

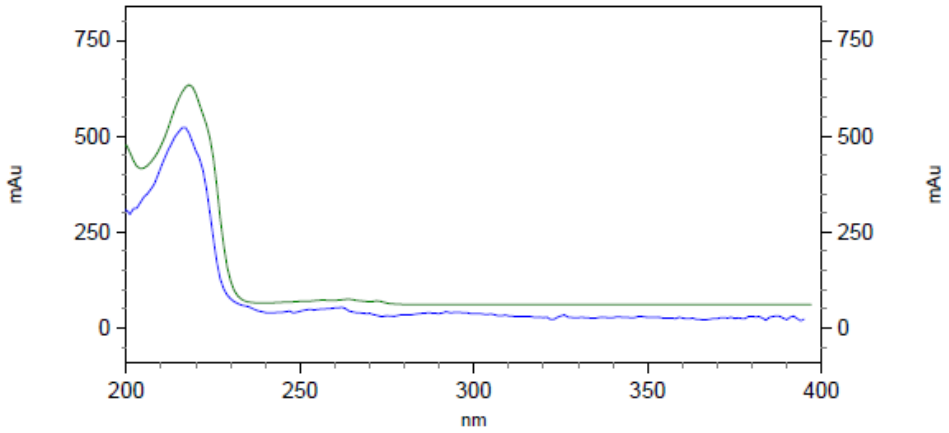
Totals	
	100.000

K0L-388-ADH-5%1.0
C:\EZStart\Projects\Default\Method\lk-5%1.0.met
C:\EZStart\Projects\Default\Data\K0L-388-ADH-5%1.0





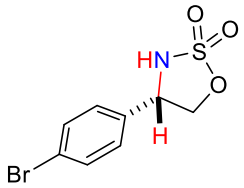
(+)-**2g**



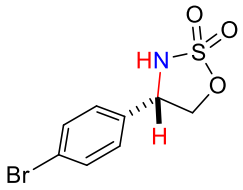
1: 232 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	36.236	97.642	1
	54.212	2.358	2

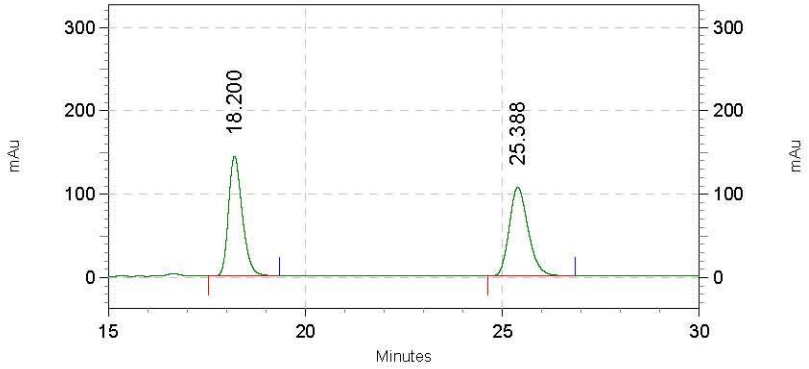
Totals	
	100.000

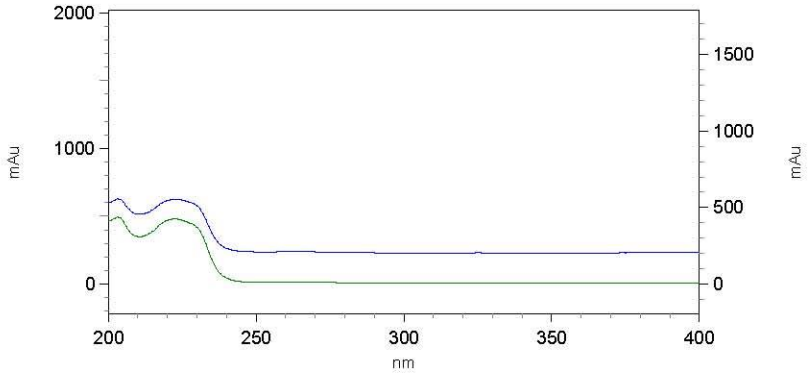


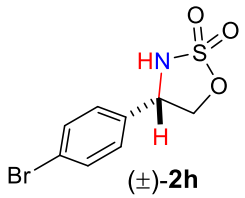
^{1}H NMR of **2h**, 400 MHz, $CDCl_3$



^{13}C NMR of **2h**, 100 MHz, $CDCl_3$



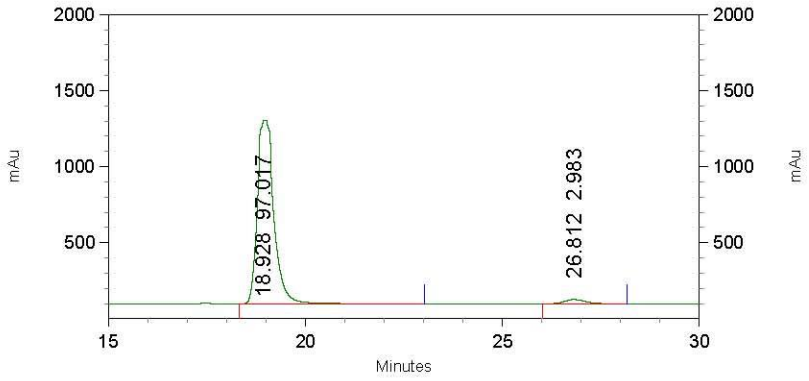


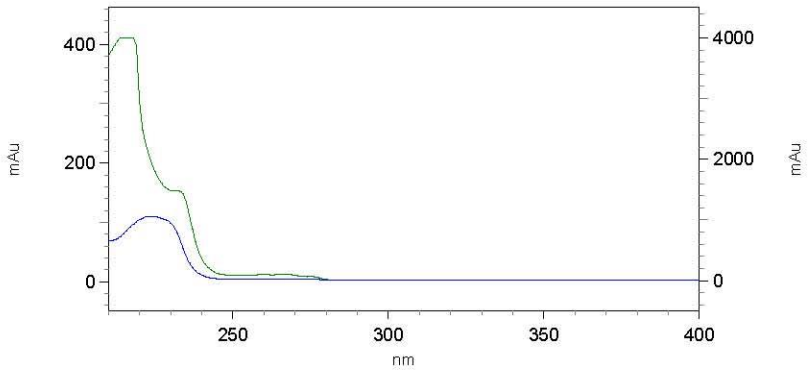


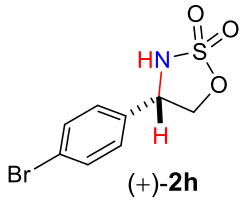
(±)-**2h**

9: 233 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		18.200	49.588
2		25.388	50.412
Totals			100.000







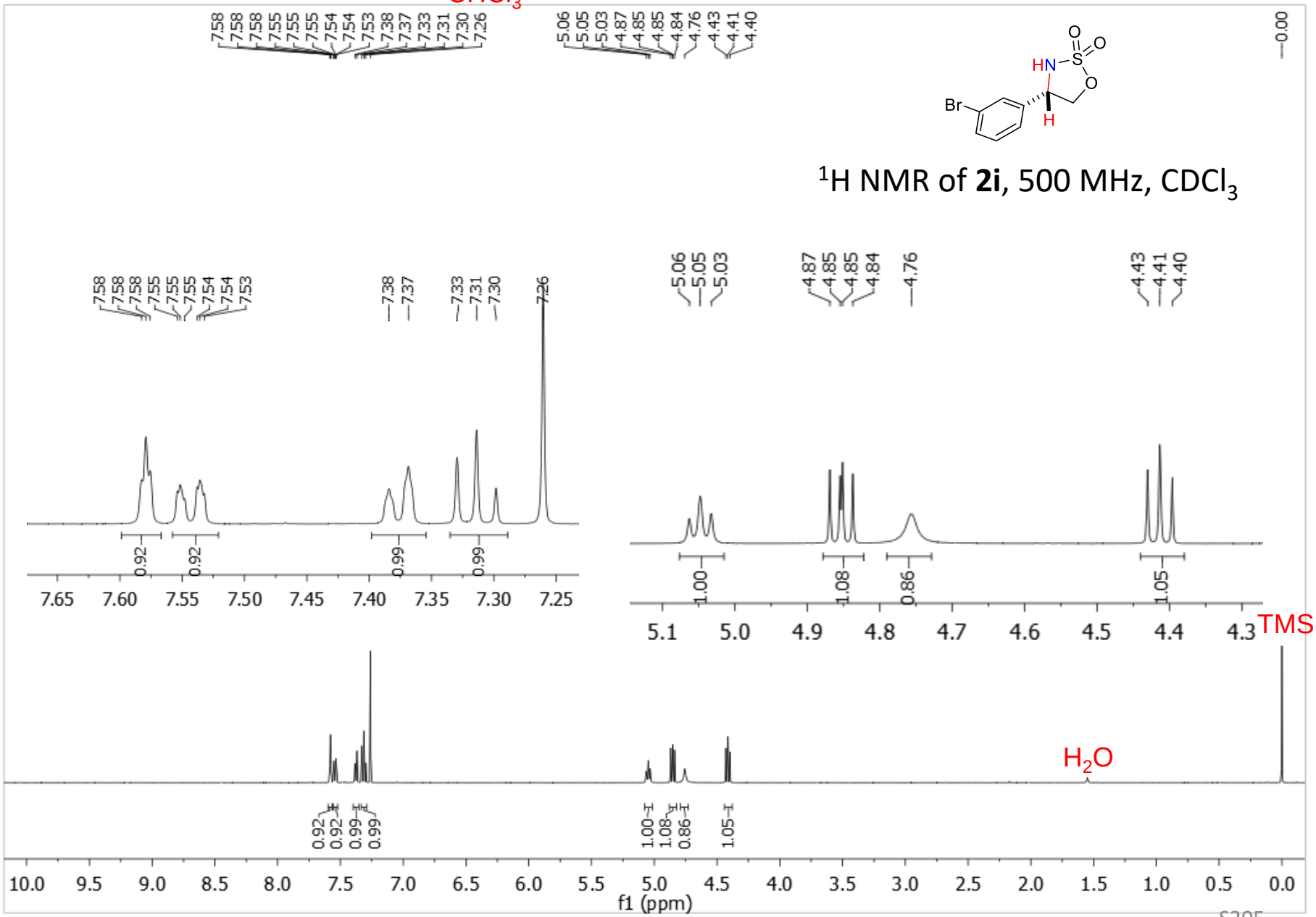
(+)-**2h**

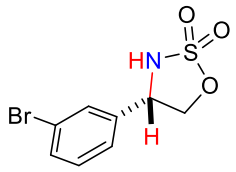
7: 217 nm, 4 nm

Results

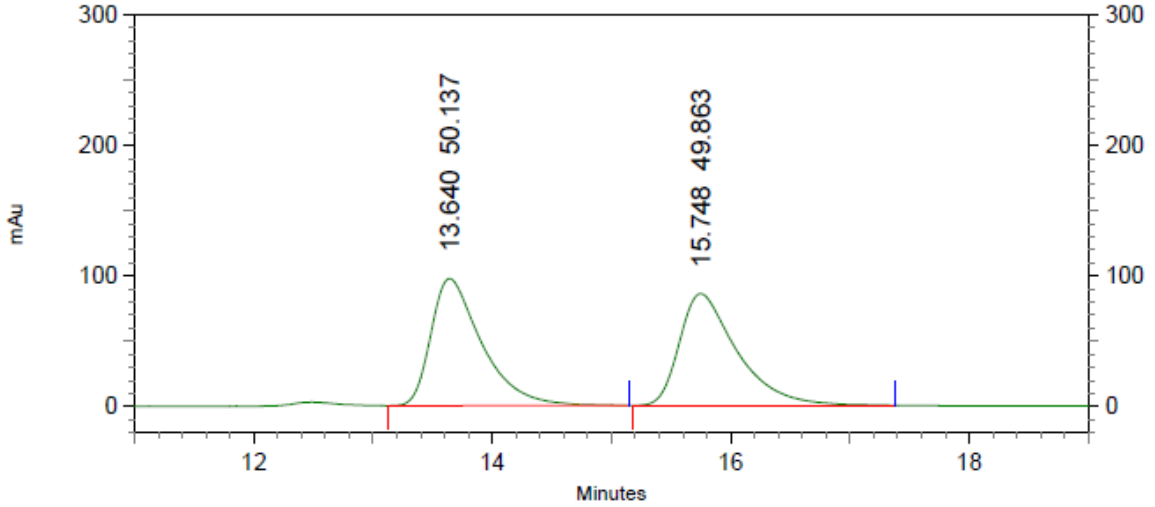
Name	Retention Time	Area Percent	Pk #
	18.928	97.017	1
	26.812	2.983	2

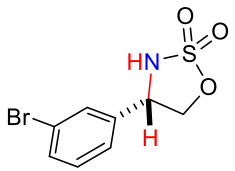
Totals			
		100.000	


CHCl3
7.58 7.58 7.58 7.55 7.55 7.55 7.54 7.54 7.53 7.38 7.37 7.33 7.31 7.30 7.26
5.06 5.05 5.03 4.87 4.85 4.85 4.84 4.76 4.43 4.41 4.40
0.00
HN
S
O
O
O
Br
H
1H NMR of 2i, 500 MHz, CDCl3
0.92 0.92 0.99 0.99
1.00 1.08 0.86 1.05
TMS
H2O
f1 (ppm)

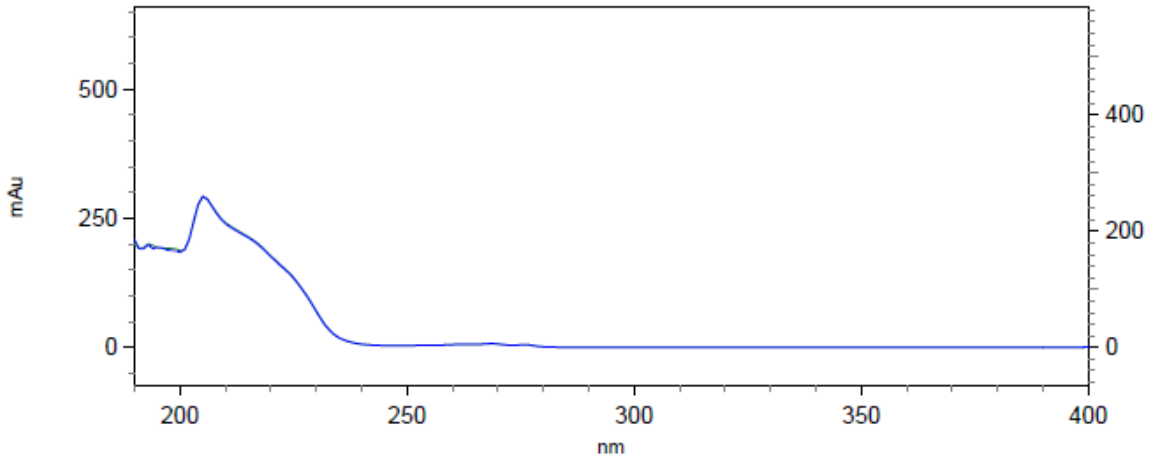


^{13}C NMR of **2i**, 150 MHz, $CDCl_3$





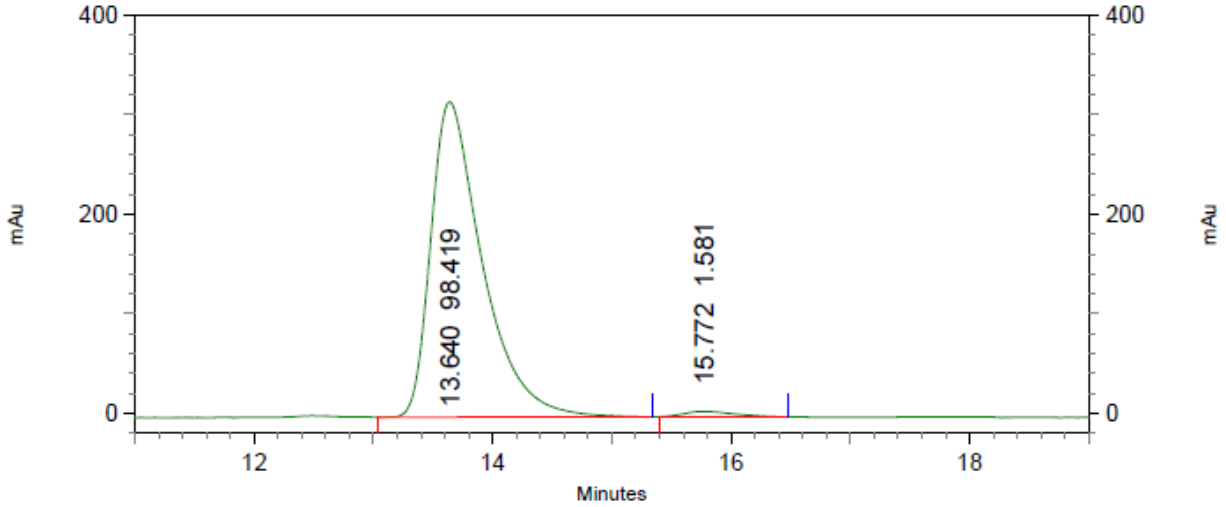
(±)-**2i**

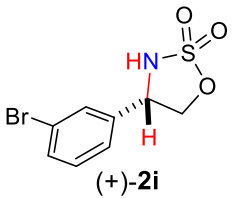


4: 228 nm, 4
nm Results

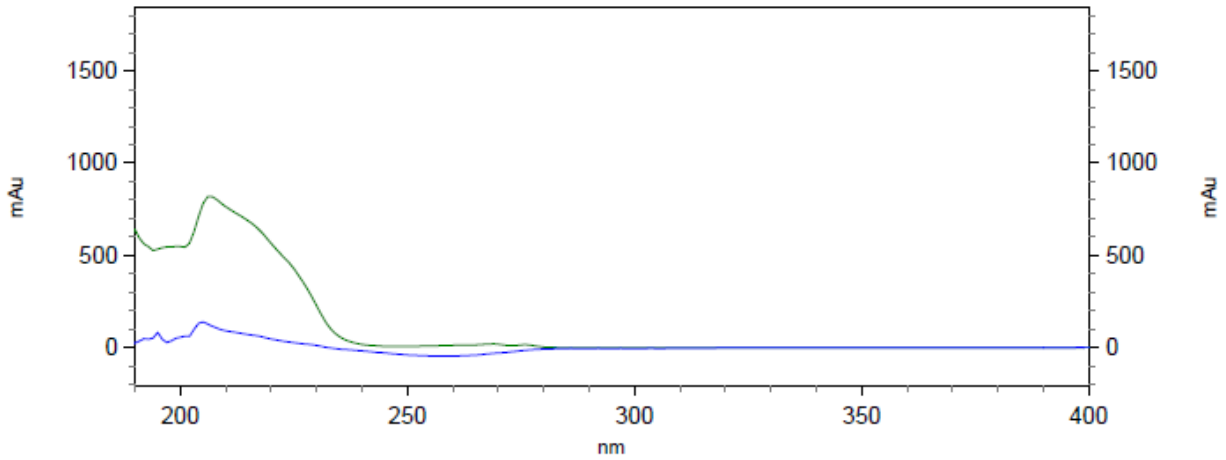
Pk #	Retention Time	Area Percent
1	13.640	50.137
2	15.748	49.863

Totals	
	100.000





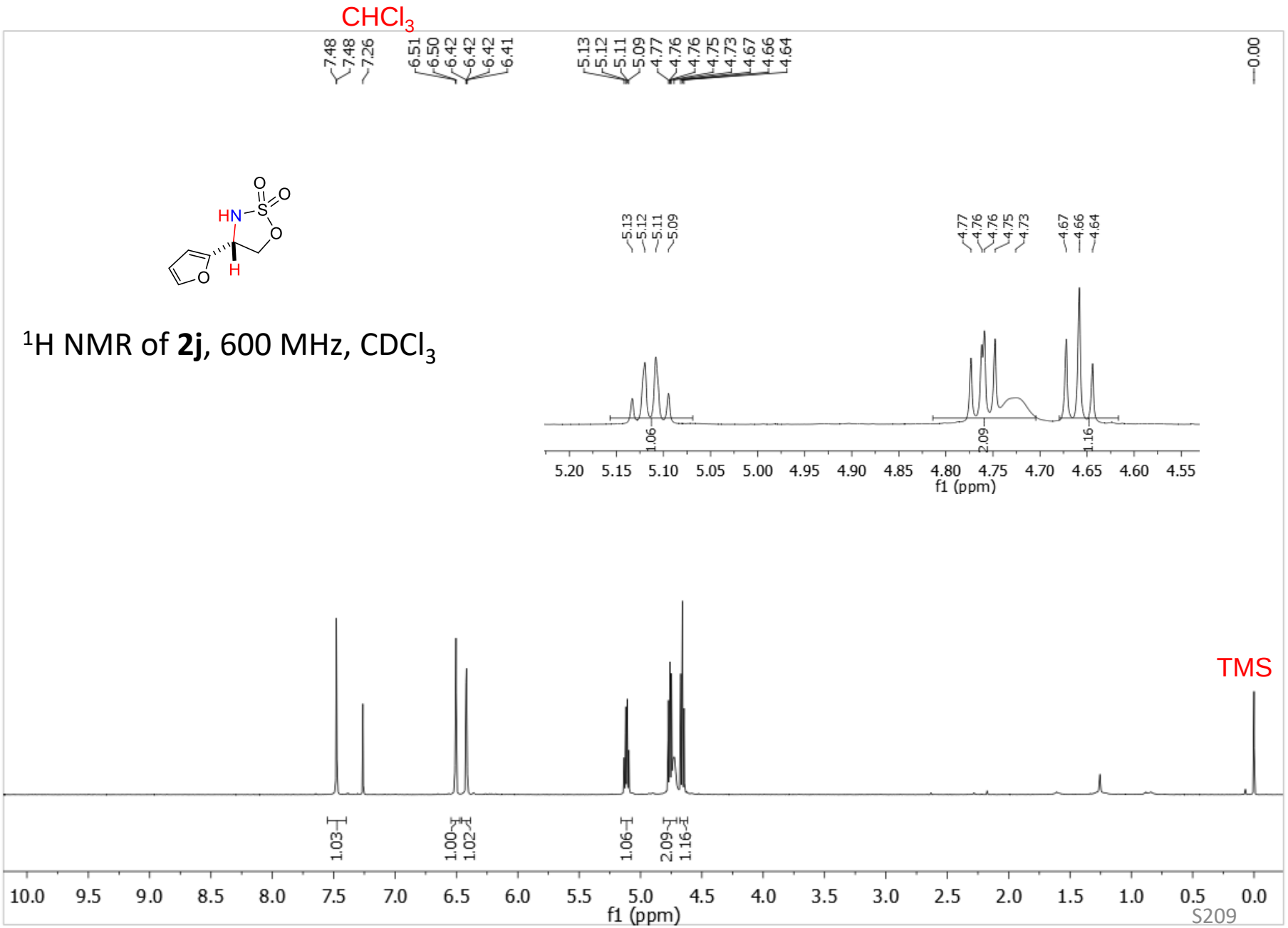
(+)-**2i**



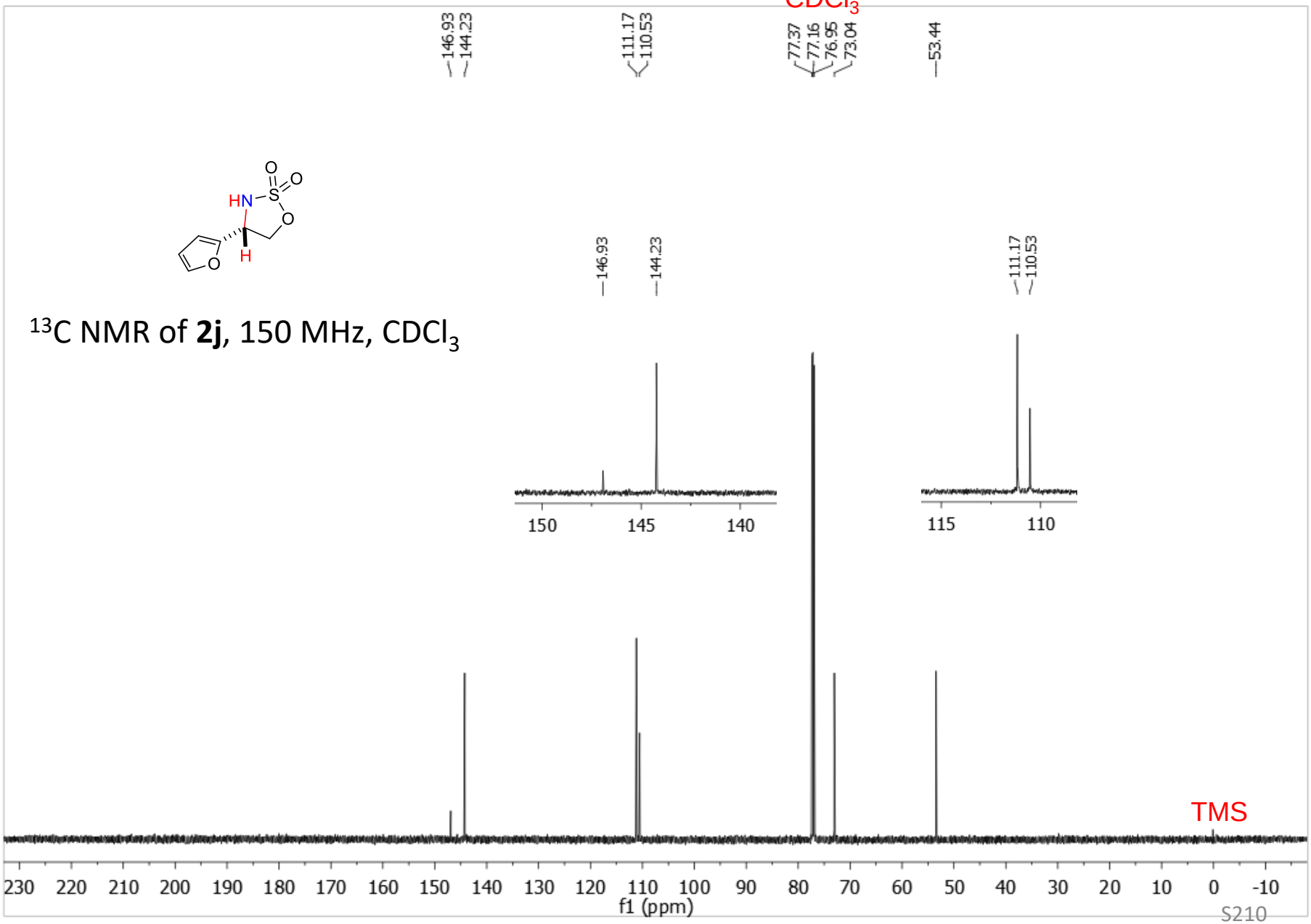
4: 228 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	13.640	98.419
2	15.772	1.581

Totals	
	100.000

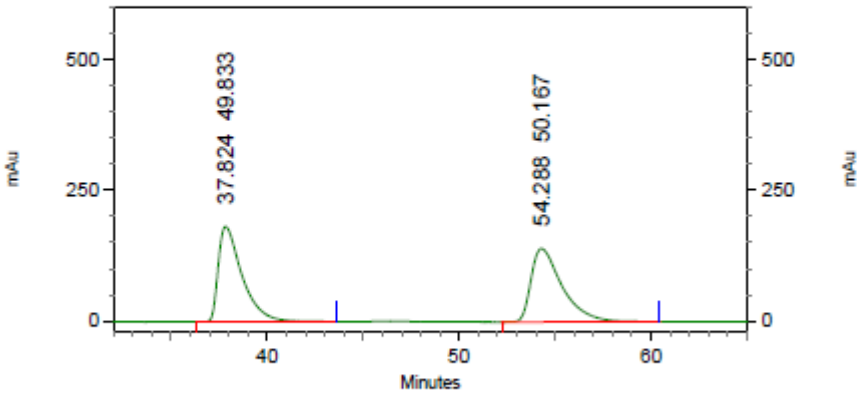


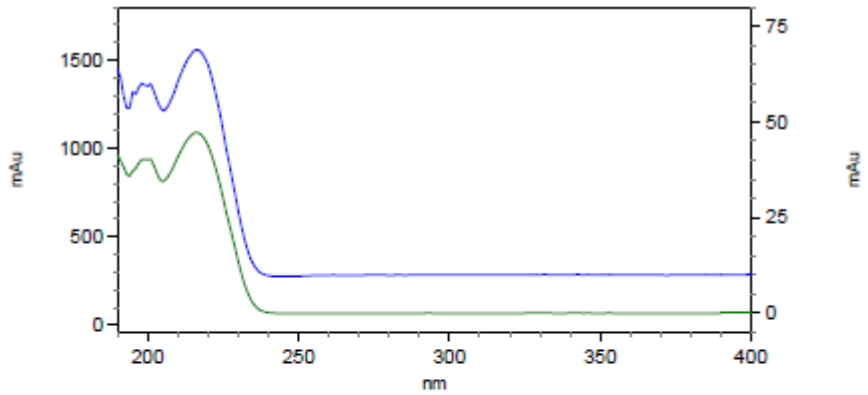
^{1}H NMR of **2j**, 600 MHz, $CDCl_3$

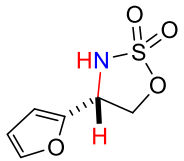


^{13}C NMR of **2j**, 150 MHz, $CDCl_3$

K0L-358ODH-10%
C:\EZStart\Projects\Default\Method\lk7%1.0.met
C:\EZStart\Projects\Default\Data\K0L-358ODH-10%





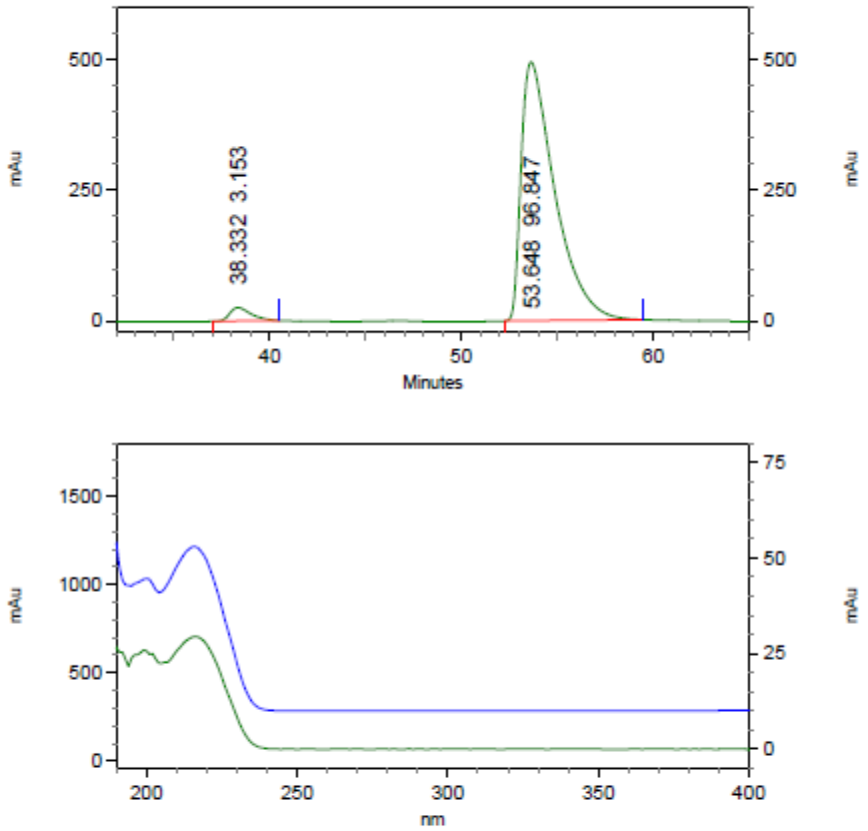


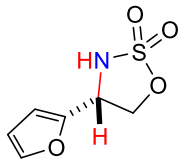
(±)-**2j**

4: 221 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	37.824	49.833	1
	54.288	50.167	2
Totals		100.000	

K0L-357-ODH-10%-1
C:\EZStart\Projects\Default\Method\1k7%1.0.met
C:\EZStart\Projects\Default\Data\K0L-357-ODH-10%-1

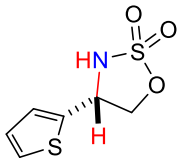




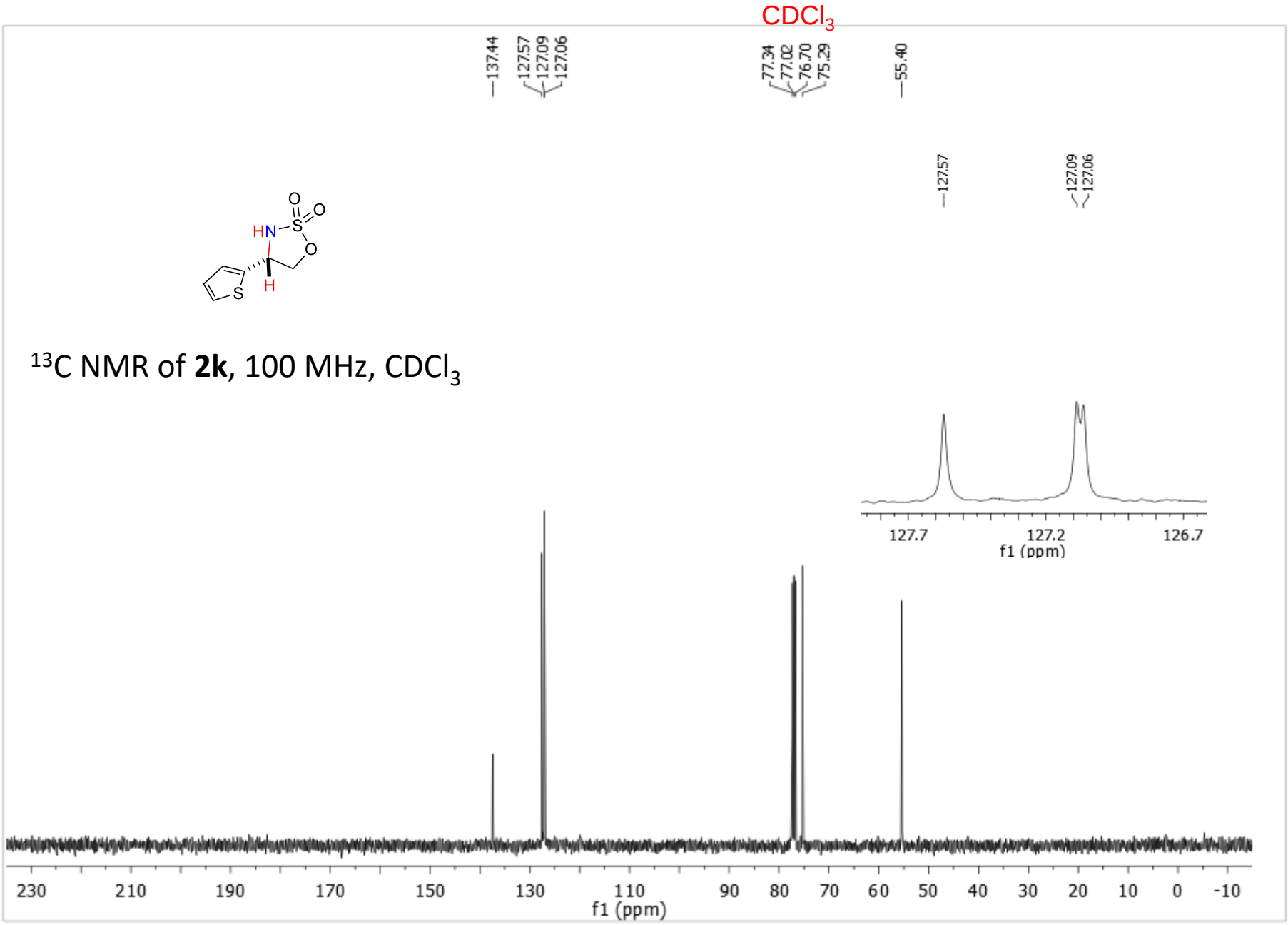
(+)-**2j**

4: 224 nm, 4 nm
Results

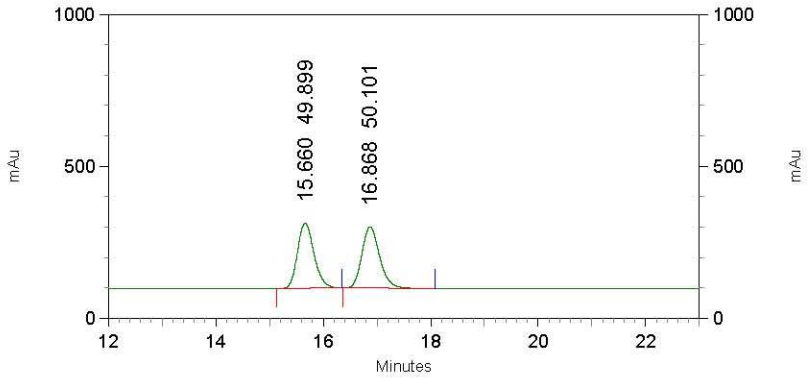
Name	Retention Time	Area Percent	Pk #
	38.332	3.153	1
	53.648	96.847	2
Totals		100.000	

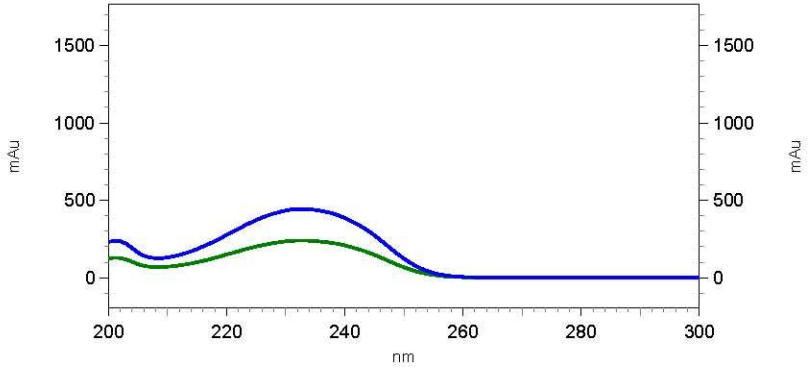


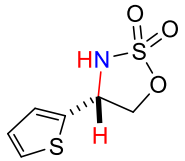
^{1}H NMR of **2k**, 400 MHz, $CDCl_3$



^{13}C NMR of **2k**, 100 MHz, $CDCl_3$



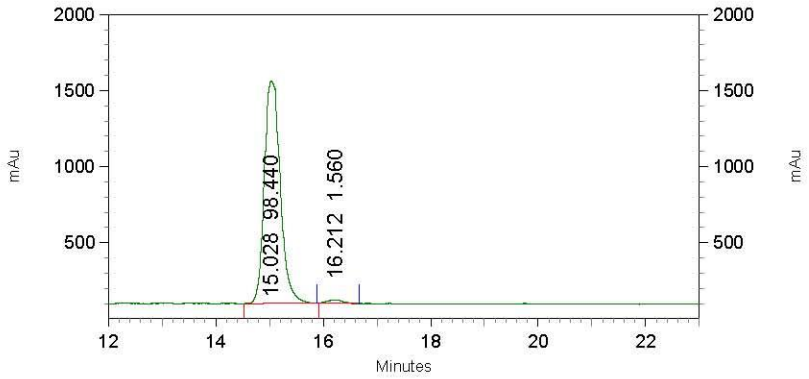


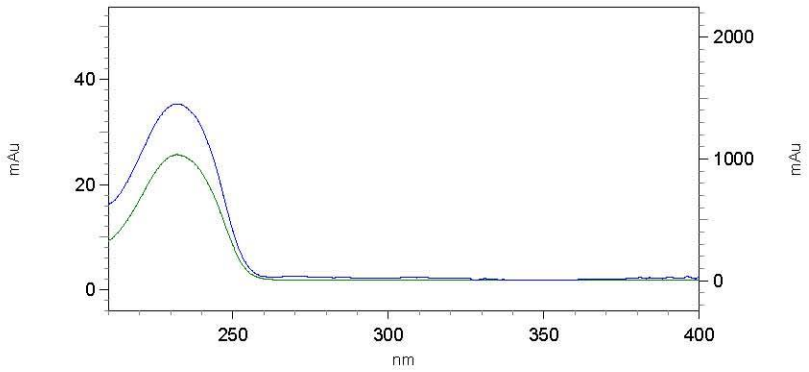


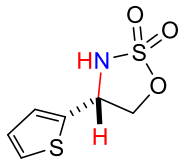
(±)-**2k**

19: 239 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		15.660	49.899
2		16.868	50.101
Totals			100.000





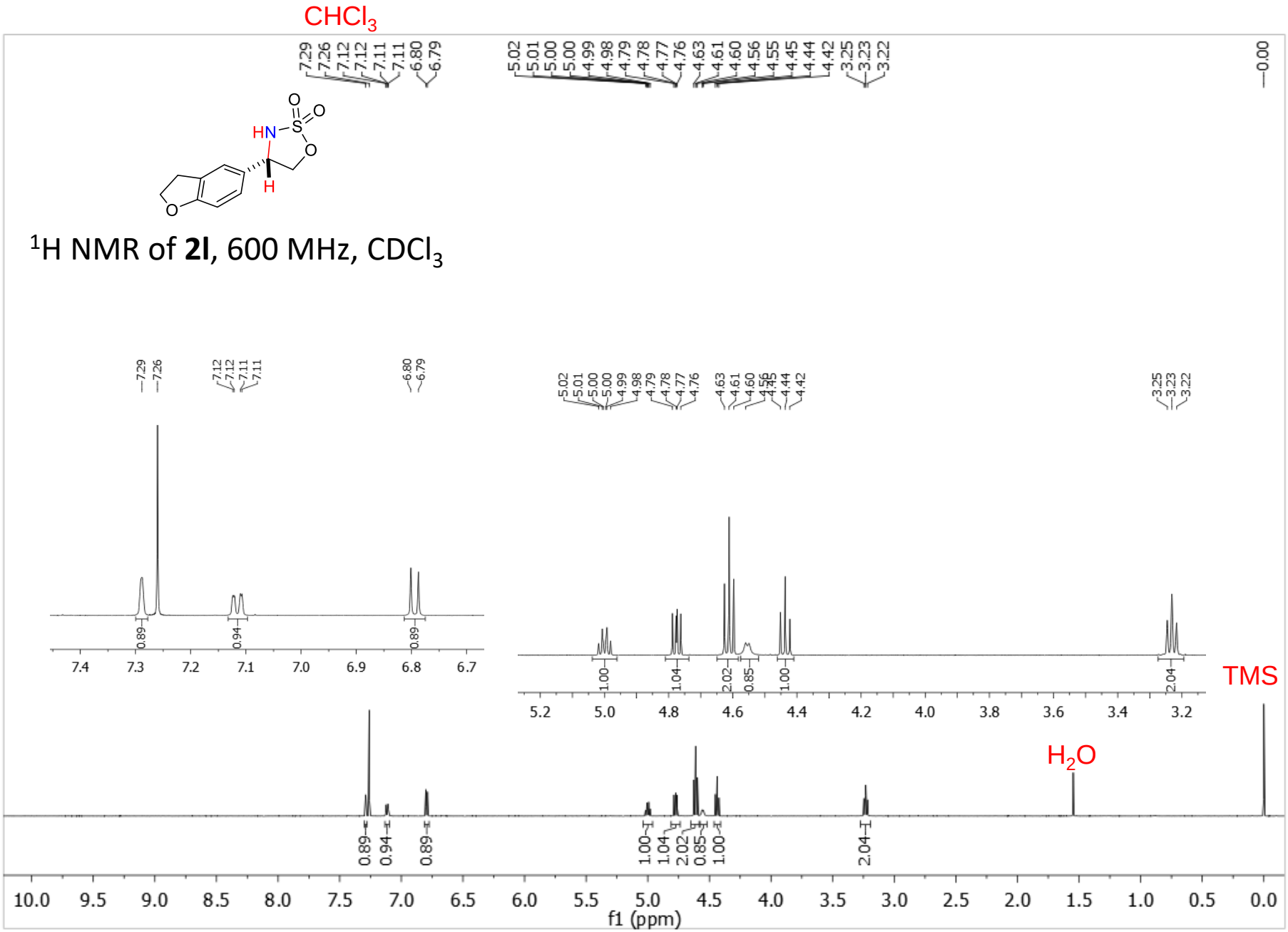


(+)-**2k**

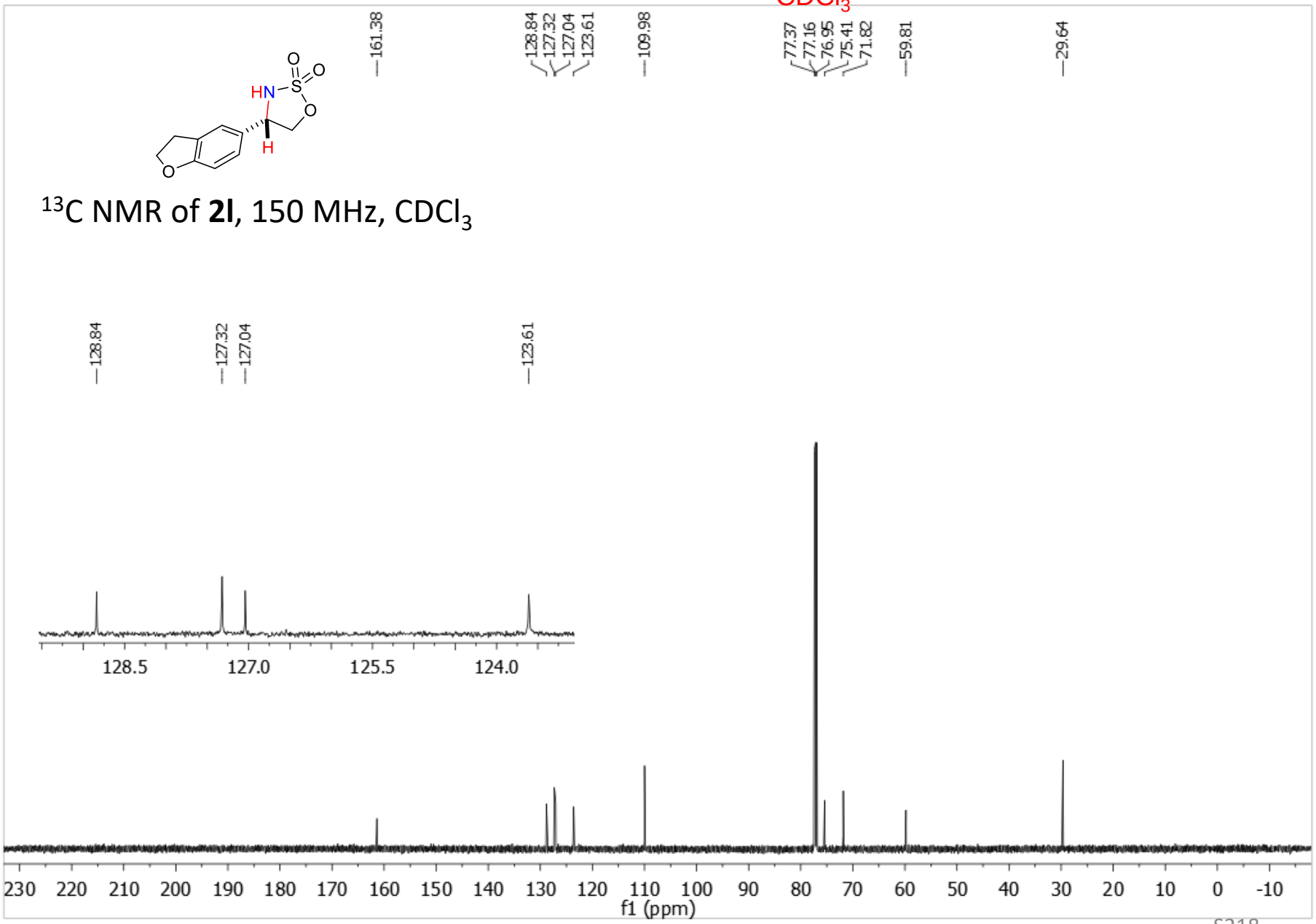
8: 193 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	15.028	98.440	1
	16.212	1.560	2

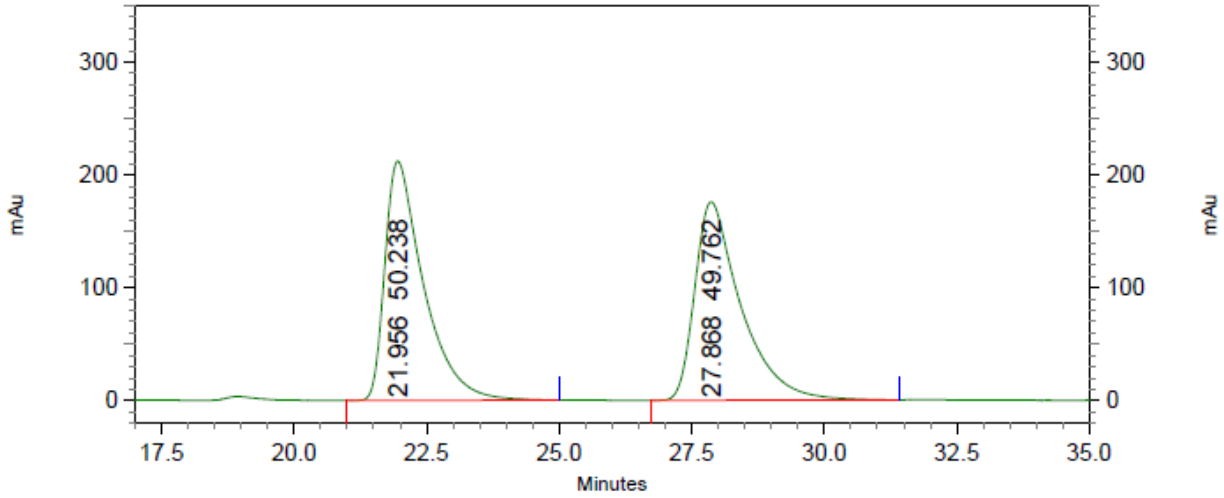
Totals		100.000	

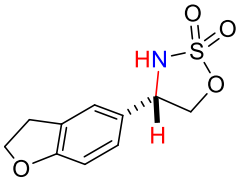


^{1}H NMR of **2l**, 600 MHz, $CDCl_3$

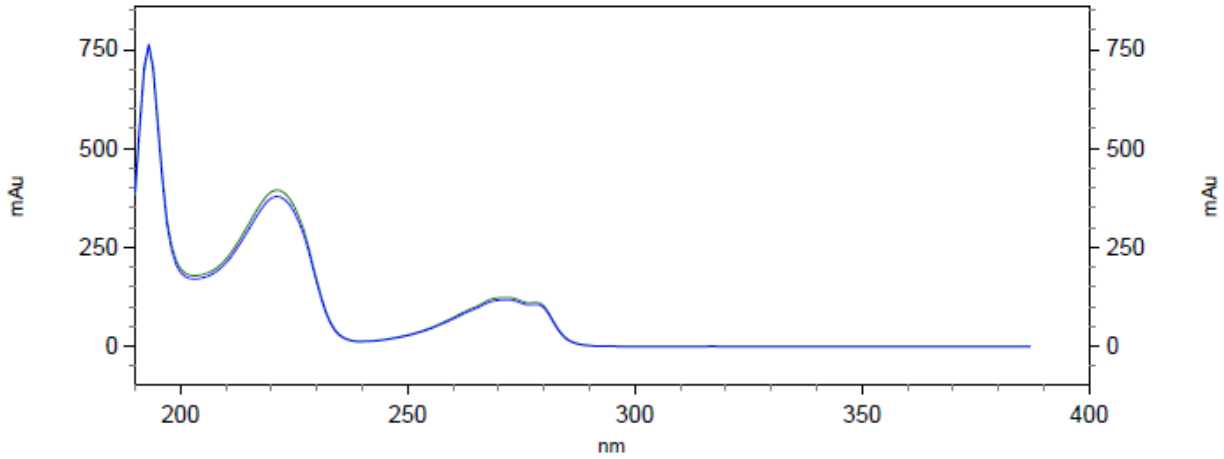


^{13}C NMR of **2l**, 150 MHz, $CDCl_3$





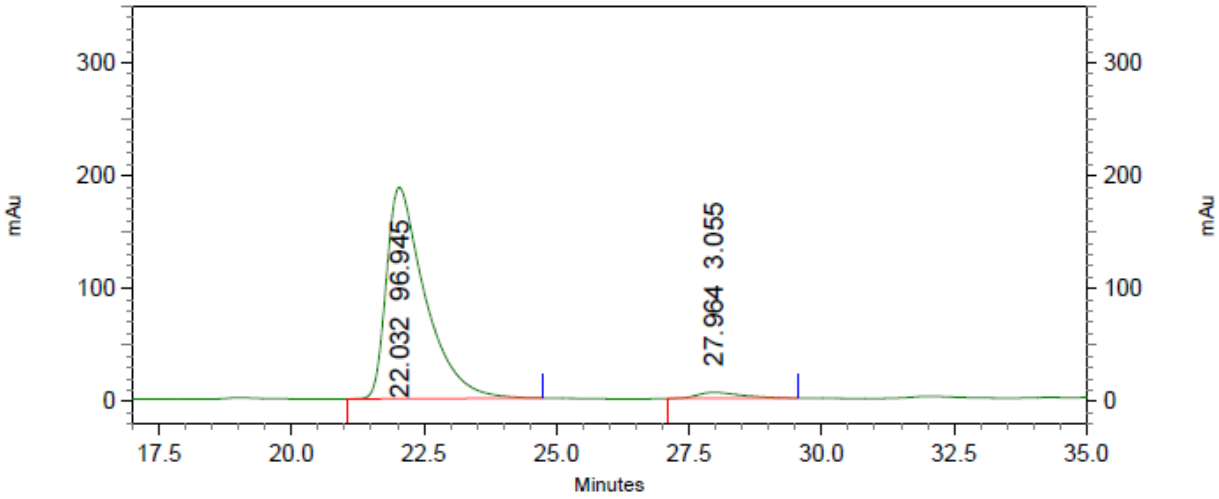
(±)-**2l**

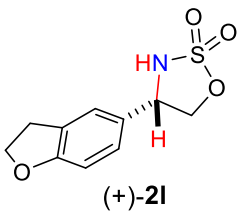


4: 237 nm, 4
nm Results

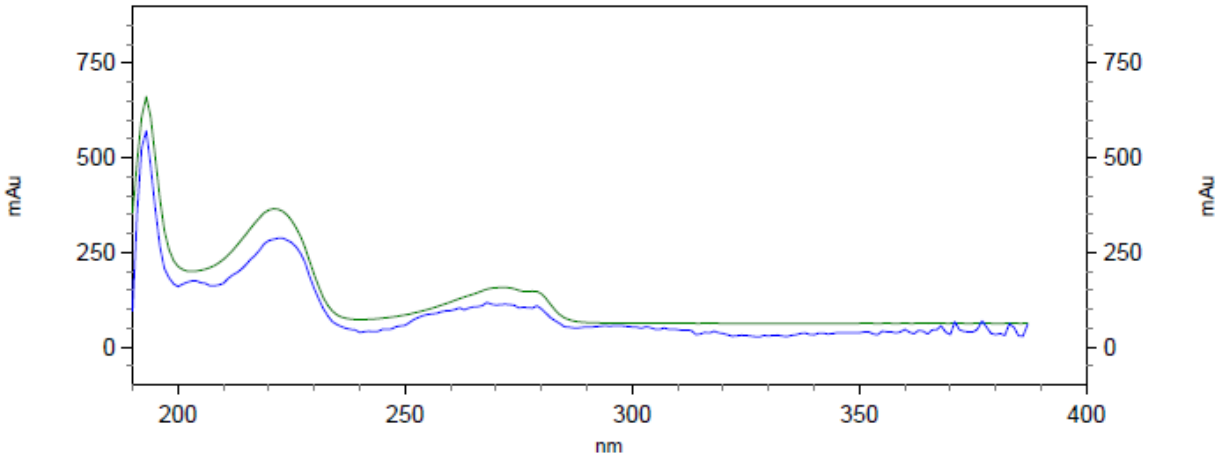
Pk #	Retention Time	Area Percent
1	21.956	50.238
2	27.868	49.762

Totals	
	100.000





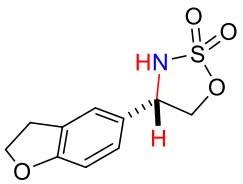
(+)-**2l**



4: 237 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	22.032	96.945
2	27.964	3.055

Totals	
	100.000



(+)-**2l**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C10H11NO4S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C10H11NO4S

Bond precision: C-C = 0.0044 A Wavelength=1.54178

Cell: a=7.6416(7) b=6.1950(5) c=10.8388(9)
alpha=90 beta=91.217(5) gamma=90
Temperature: 123 K

	Calculated	Reported
Volume	512.99(8)	512.99(8)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C10 H11 N O4 S	C10 H11 N O4 S
Sum formula	C10 H11 N O4 S	C10 H11 N O4 S
Mr	241.26	241.26
Dx,g cm-3	1.562	1.562
Z	2	2
Mu (mm-1)	2.832	2.832
F000	252.0	252.0
F000'	253.46	
h,k,lmax	9,7,12	8,7,12
Nref	1807[995]	1777
Tmin,Tmax	0.434,0.844	0.580,0.753
Tmin'	0.325	

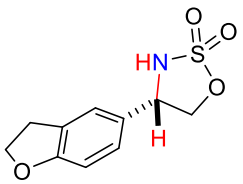
Correction method= # Reported T Limits: Tmin=0.580 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.79/0.98 Theta(max)= 66.411

R(reflections)= 0.0323(1740) wR2(reflections)= 0.0845(1777)

S = 1.036 Npar= 149

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(+)-**2l**

Alert level C

```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.64 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0044 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.594         2 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         2 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         1 Report
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O1            109.8 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O4            106.7 Degree
PLAT791_ALERT_4_G Model has Chirality at C2          (Chiral SPGR)         S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         2 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        94% Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         7 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  9 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  5 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
  2 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

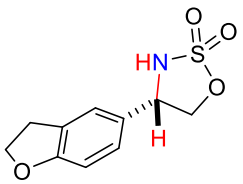
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

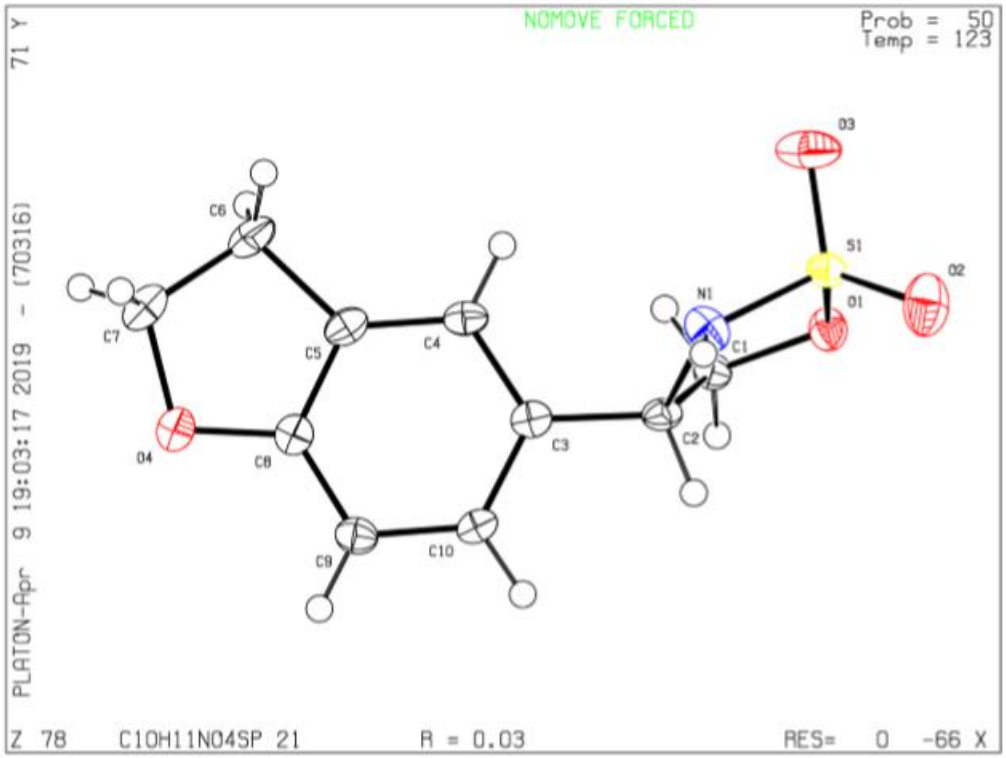
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

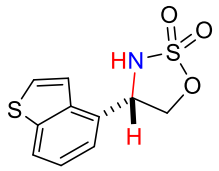


(+)-**2l**

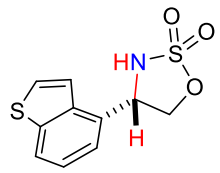
PLATON version of 17/03/2019; check.def file version of 04/03/2019

Datablock C10H11NO4S - ellipsoid plot

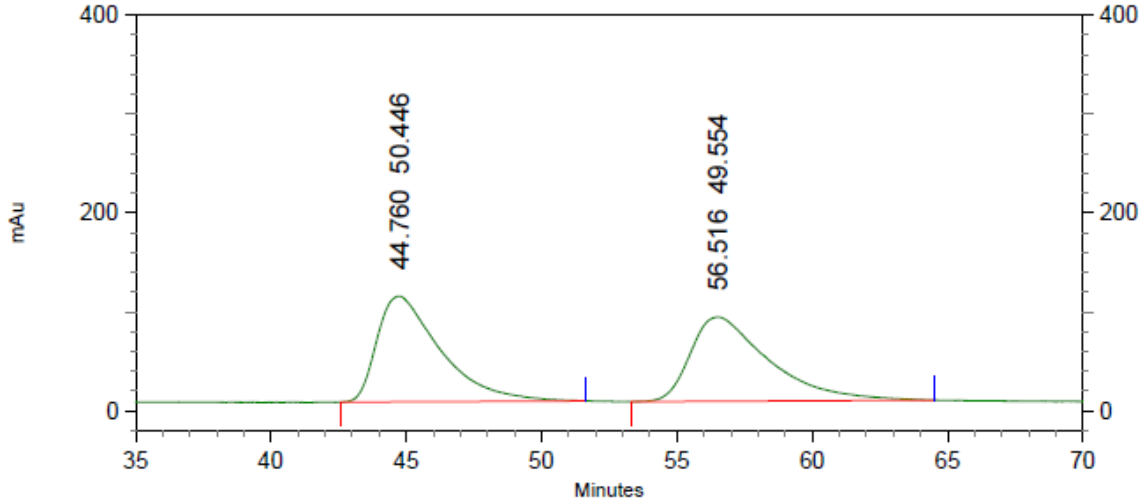


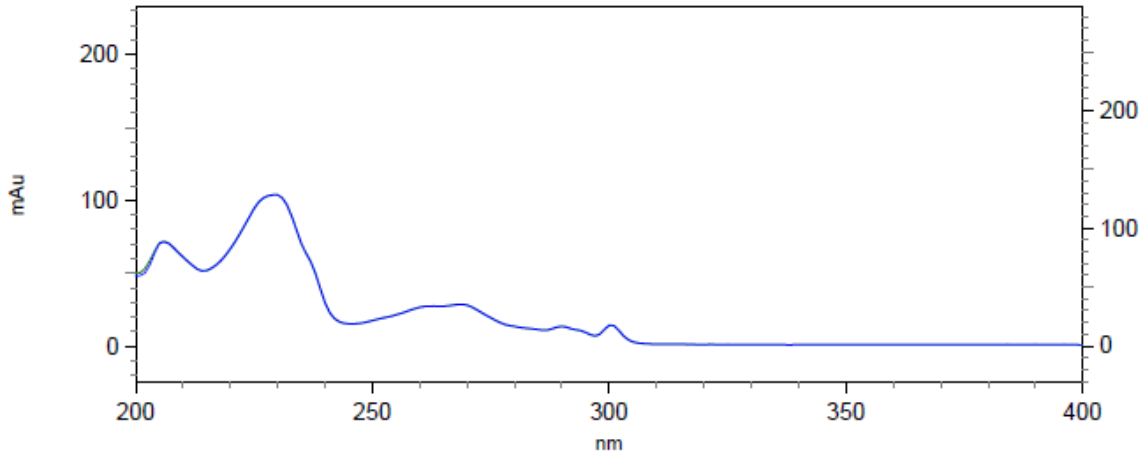


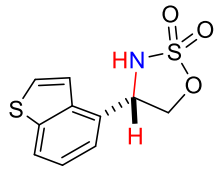
^{1}H NMR of **2m**, 600 MHz, $CDCl_3$



^{13}C NMR of **2m**, 150 MHz, $CDCl_3$





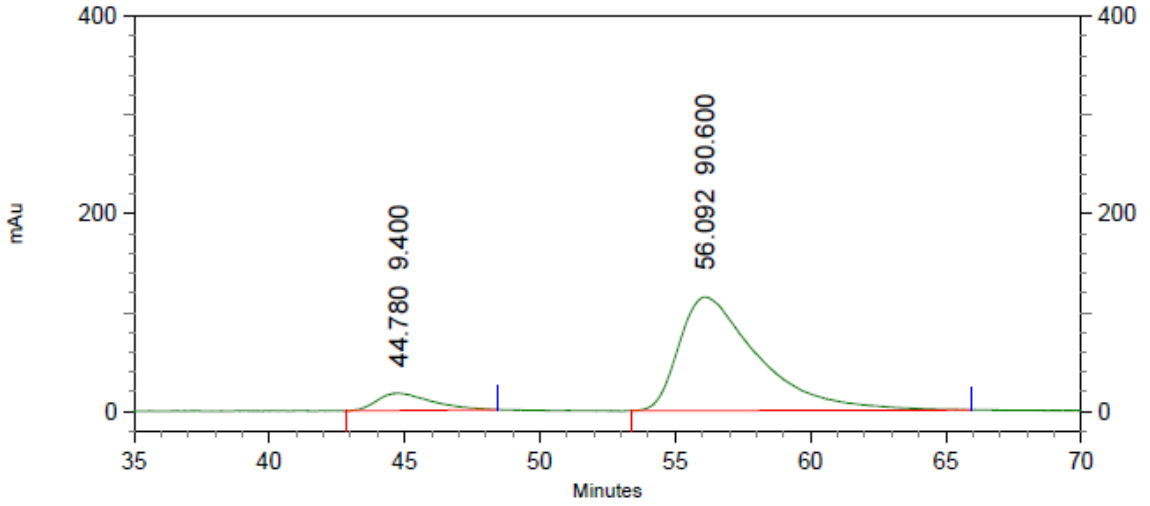


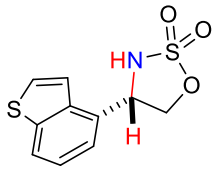
(±)-**2m**

4: 245 nm, 4
nm Results

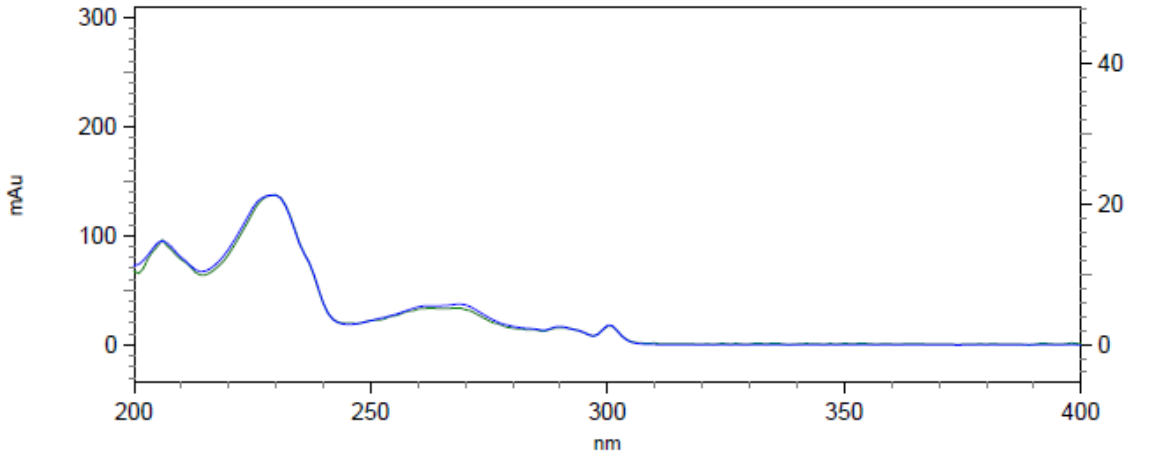
Pk #	Retention Time	Area Percent
1	44.760	50.446
2	56.516	49.554

Totals	
	100.000





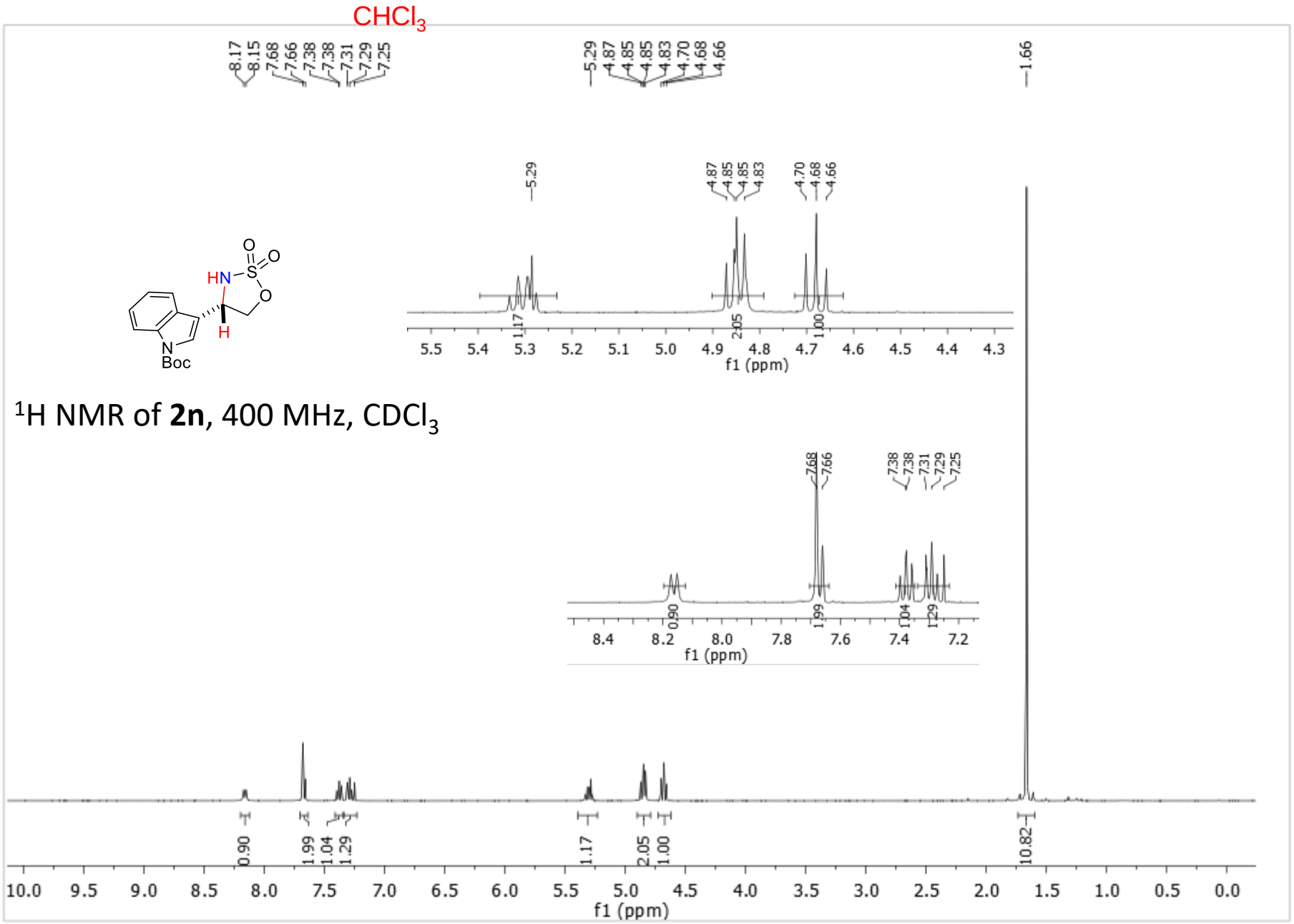
(+)-**2m**



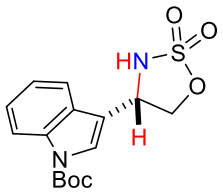
4: 245 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	44.780	9.400
2	56.092	90.600

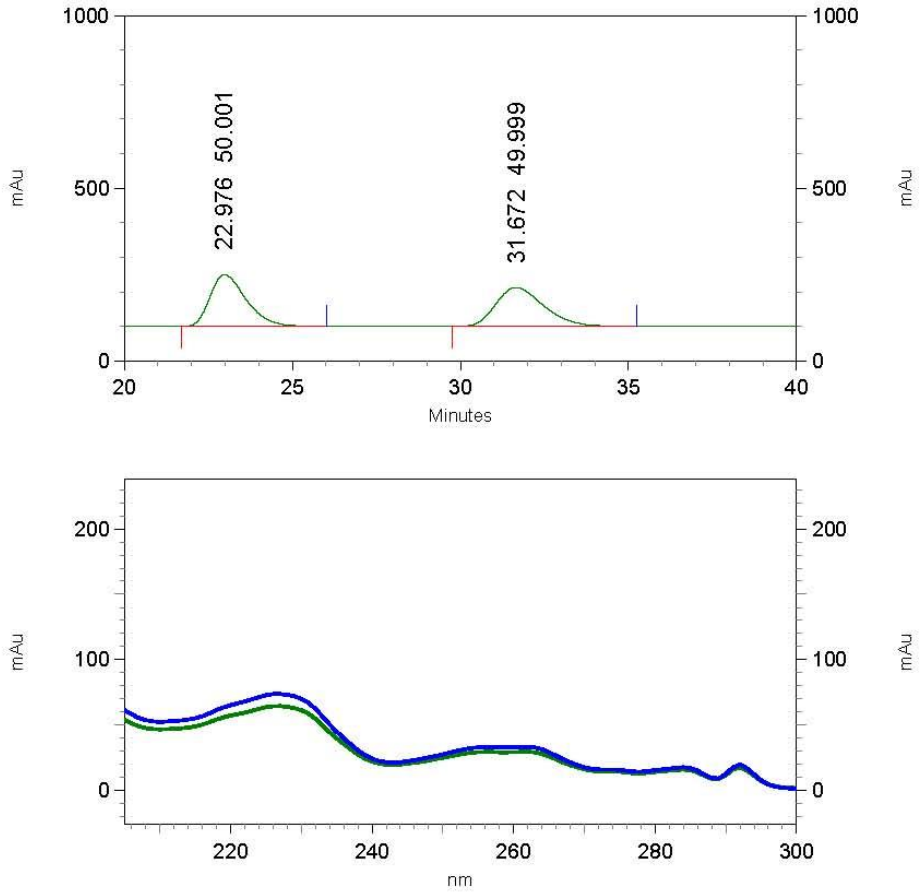
Totals	
	100.000

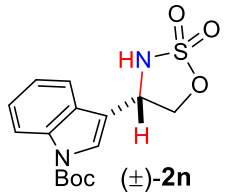


^{1}H NMR of **2n**, 400 MHz, $CDCl_3$



^{13}C NMR of **2n**, 100 MHz, $CDCl_3$

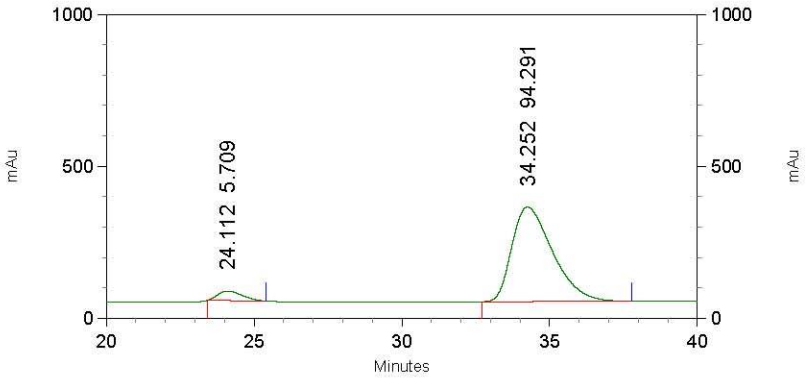


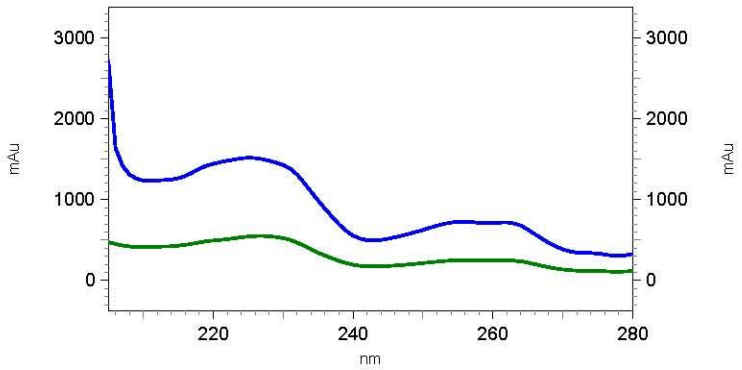


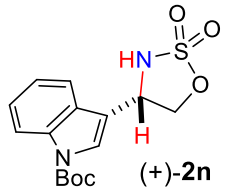
(±)-**2n**

15: 224 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		22.976	50.001
2		31.672	49.999
Totals			100.000





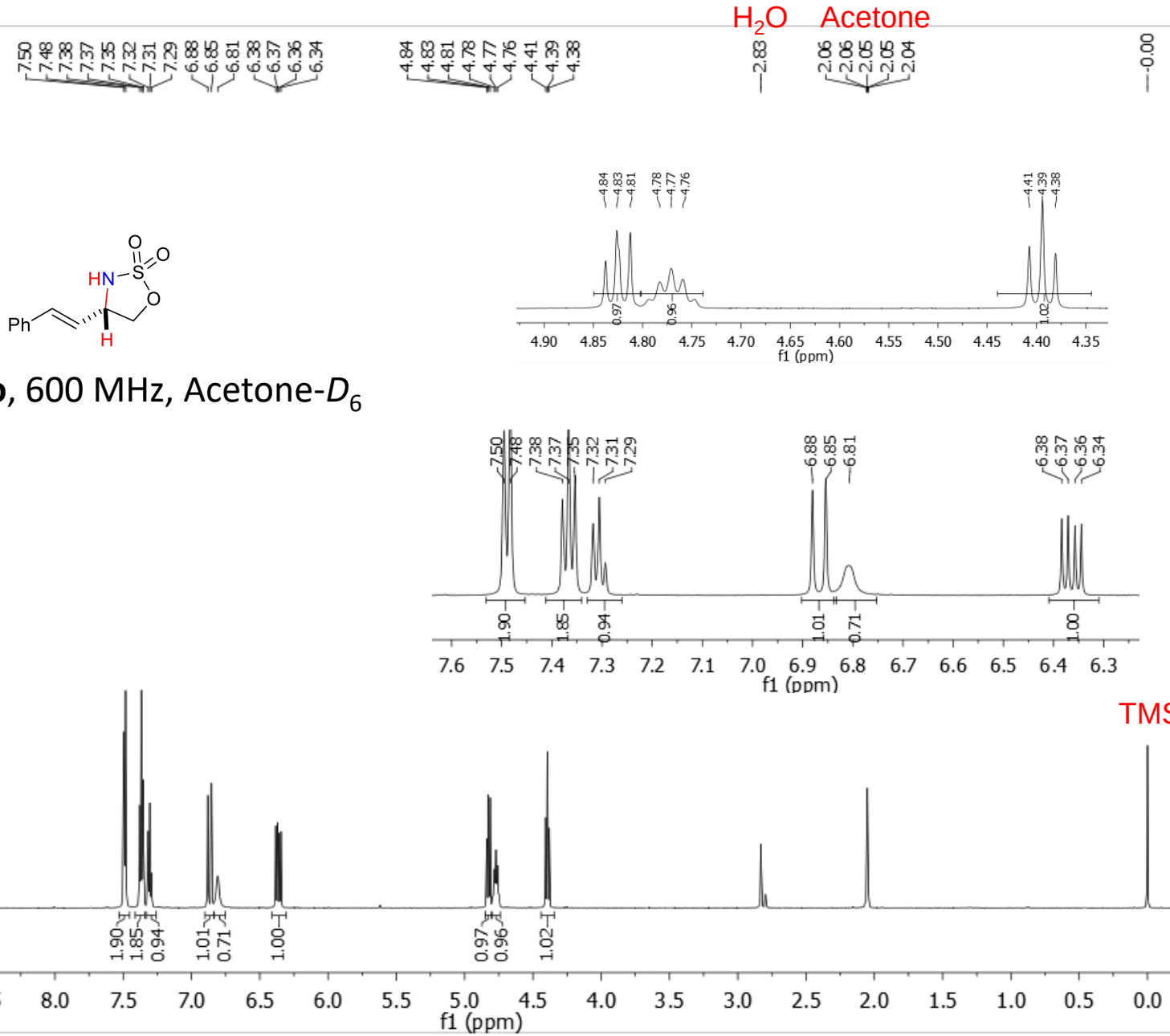


(+)-**2n**

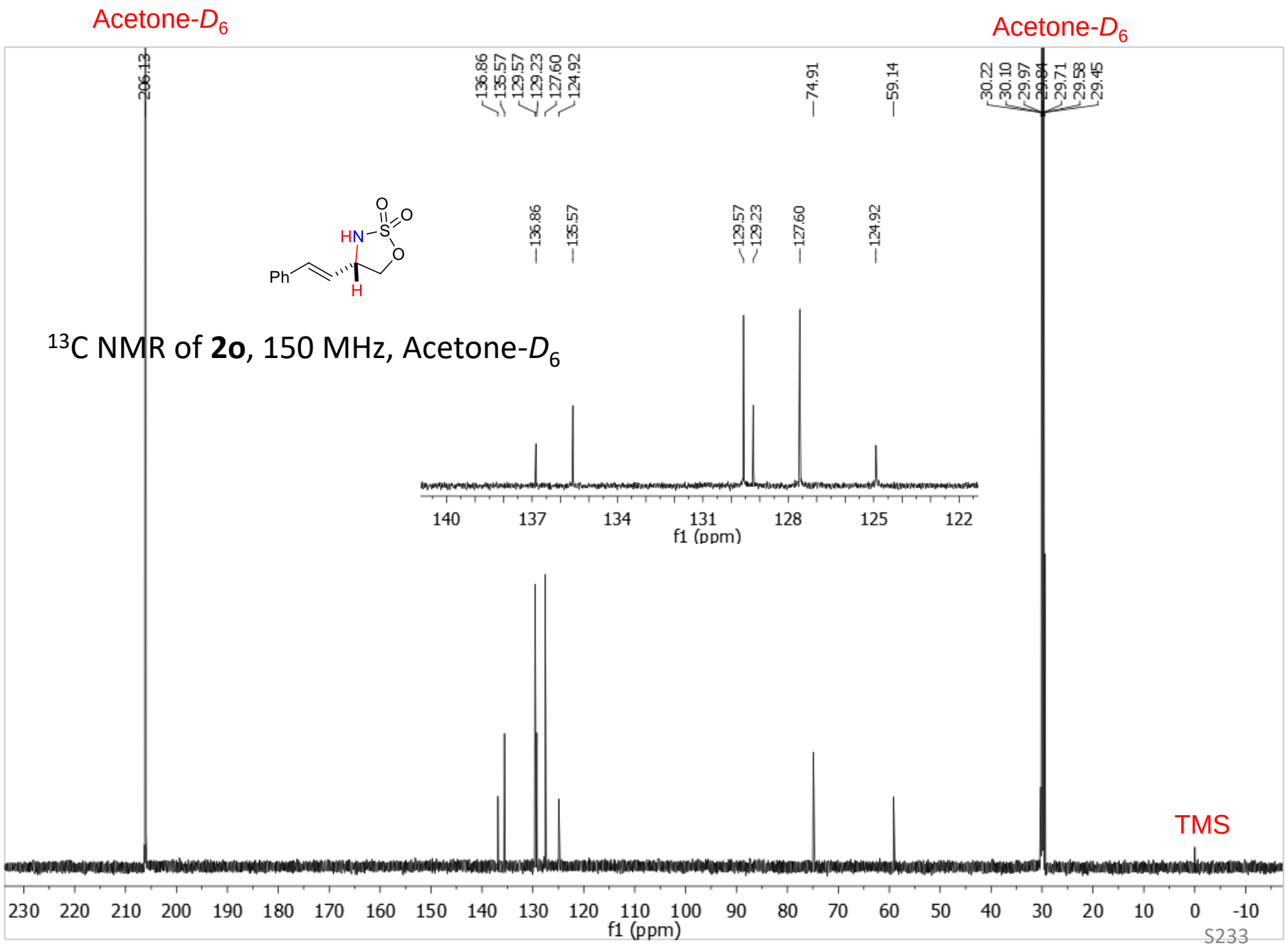
9: 277 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		24.112	5.709
2		34.252	94.291

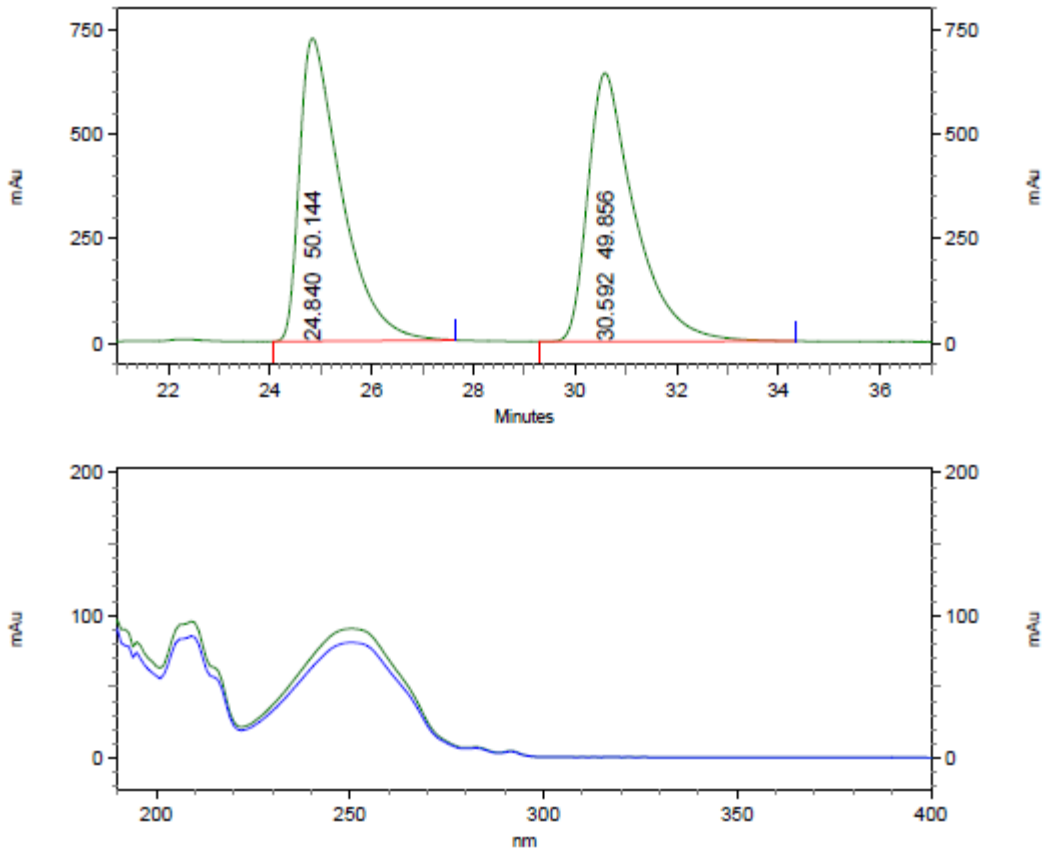
Totals			100.000

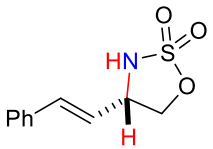


^{1}H NMR of **2o**, 600 MHz, Acetone-D_6


Acetone-D_6
Acetone-D_6
206.13
136.86
135.57
129.57
129.23
127.60
124.92
74.91
59.14
30.22
30.10
29.97
29.84
29.71
29.58
29.45
HN
S
O
O
O
Ph
H
^{13}C NMR of **2o**, 150 MHz, Acetone-D_6
140
137
134
131
128
125
122
f1 (ppm)
TMS
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

C:\EZStart\Projects\Default\Data\K0L-365-ADH-7%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





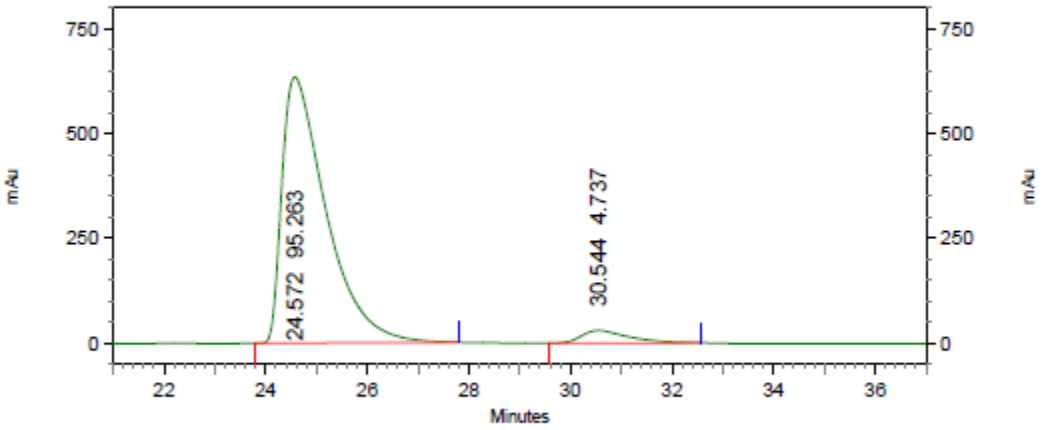
(±)-**2o**

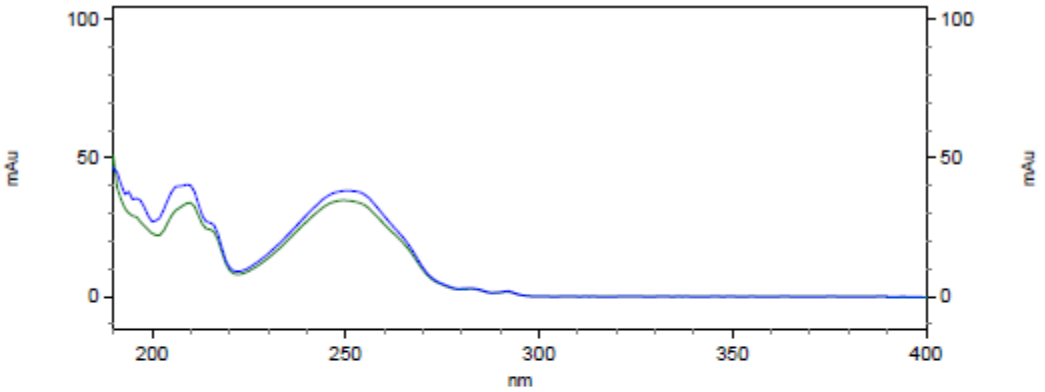
4: 250 nm, 4
nm Results

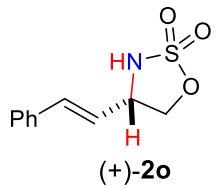
Pk #	Retention Time	Area Percent
1	24.840	50.144
2	30.592	49.856

Totals	
	100.000

C:\EZStart\Projects\Default\Data\K0L-364-ADH-7%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





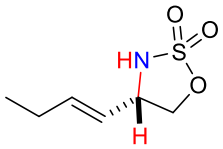


(+)-**2o**

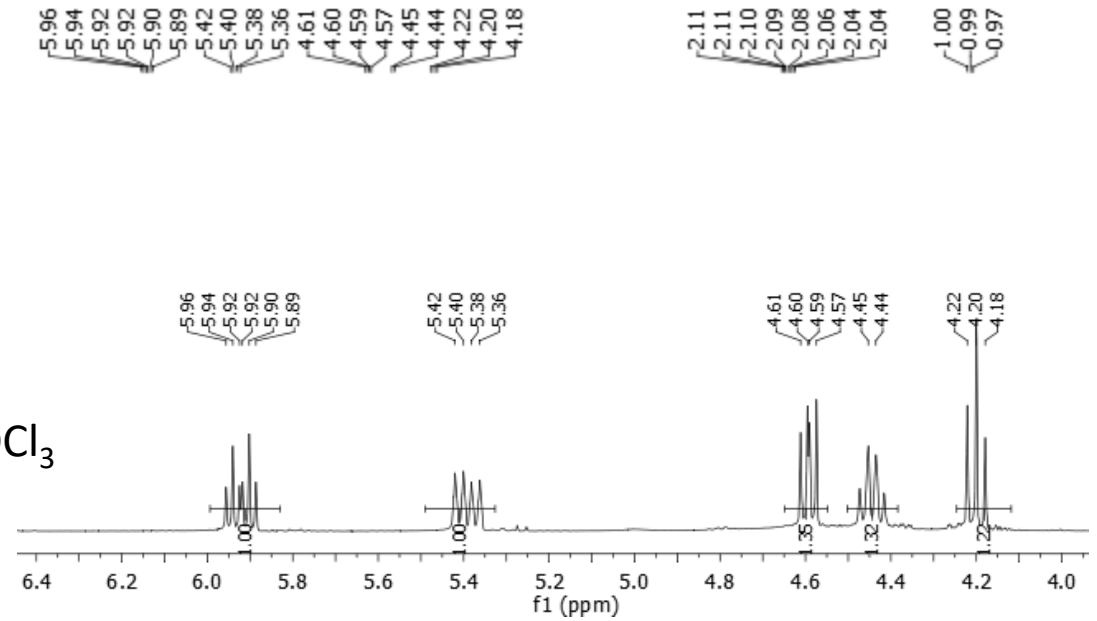
4: 250 nm, 4
nm Results

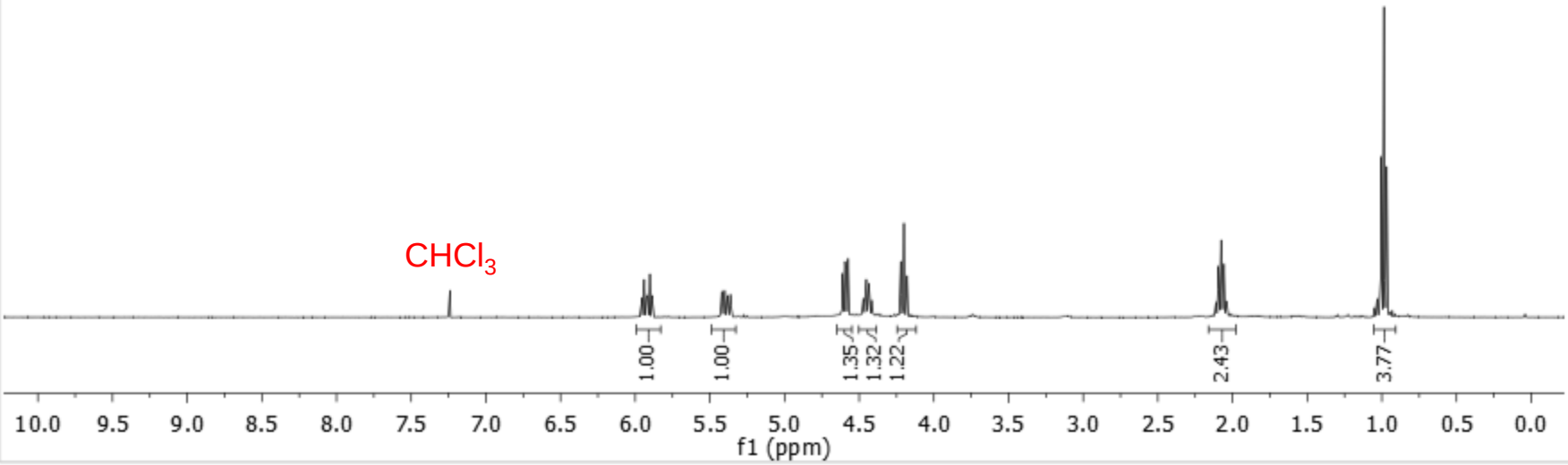
Pk #	Retention Time	Area Percent
1	24.572	95.263
2	30.544	4.737

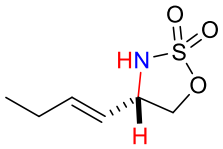
Totals	
	100.000



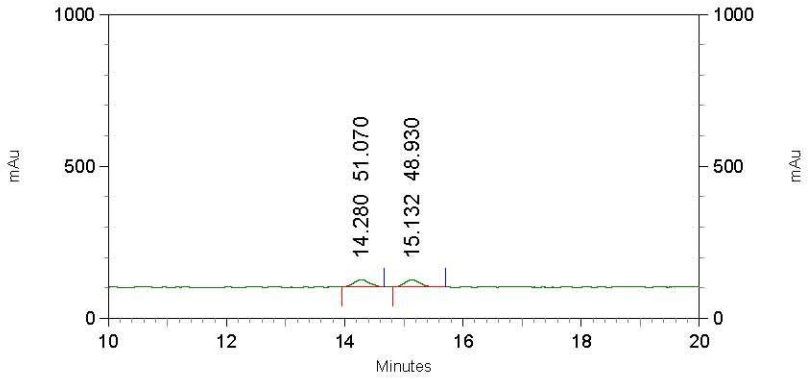
^{1}H NMR of **2p**, 400 MHz, $CDCl_3$

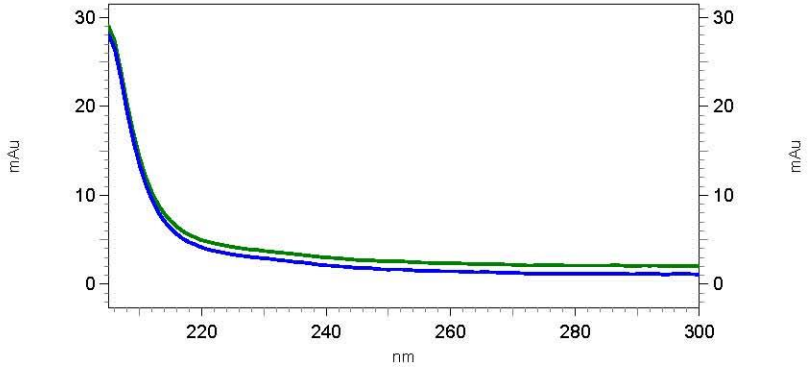


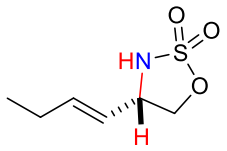




^{13}C NMR of **2p**, 100 MHz, $CDCl_3$





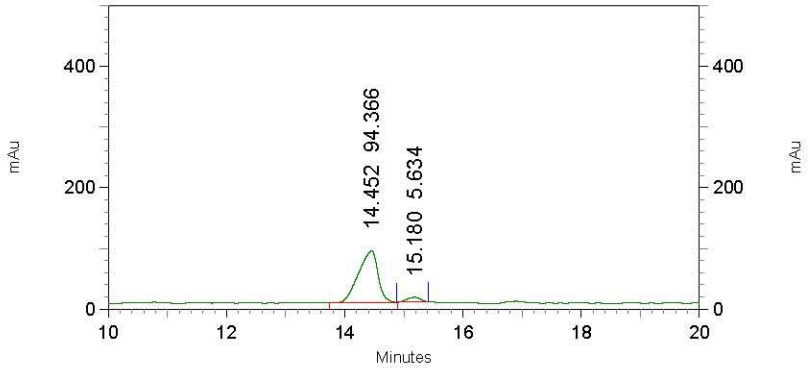


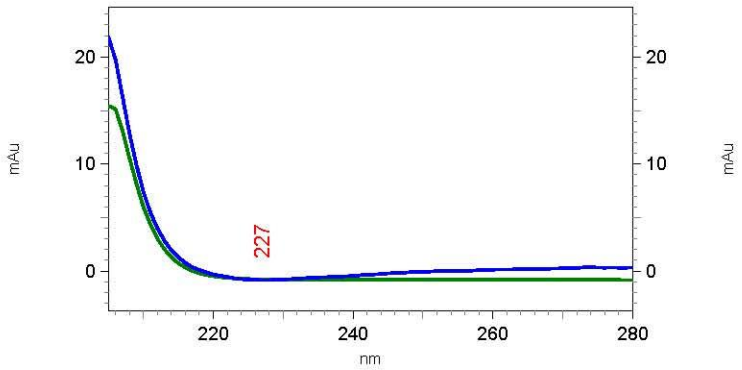
(±)-**2p**

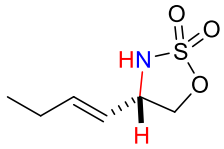
20: 205 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		14.280	51.070
2		15.132	48.930

Totals			100.000





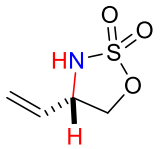


(+)-**2p**

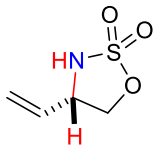
6: 205 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		14.452	94.366
2		15.180	5.634

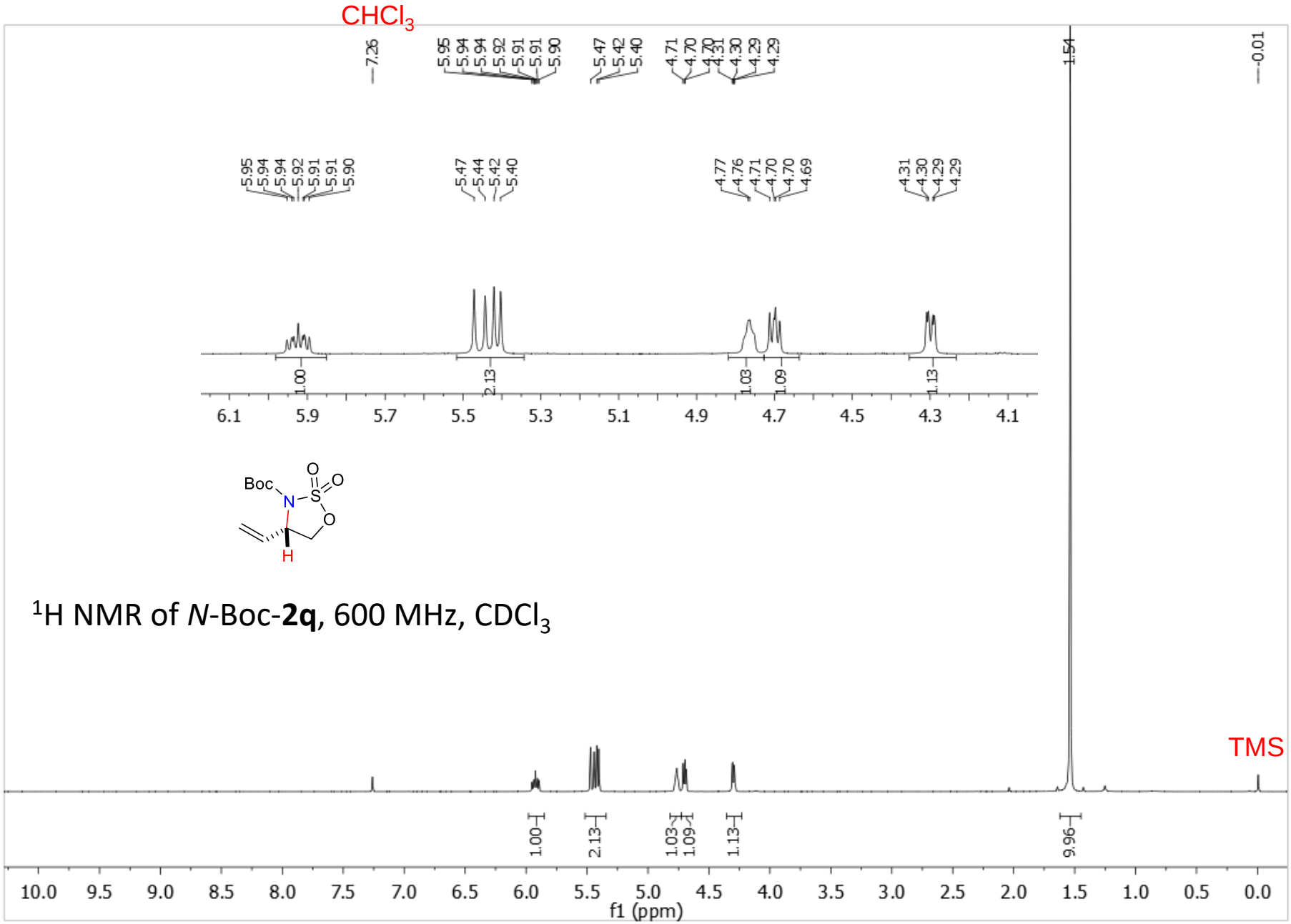
Totals			100.000



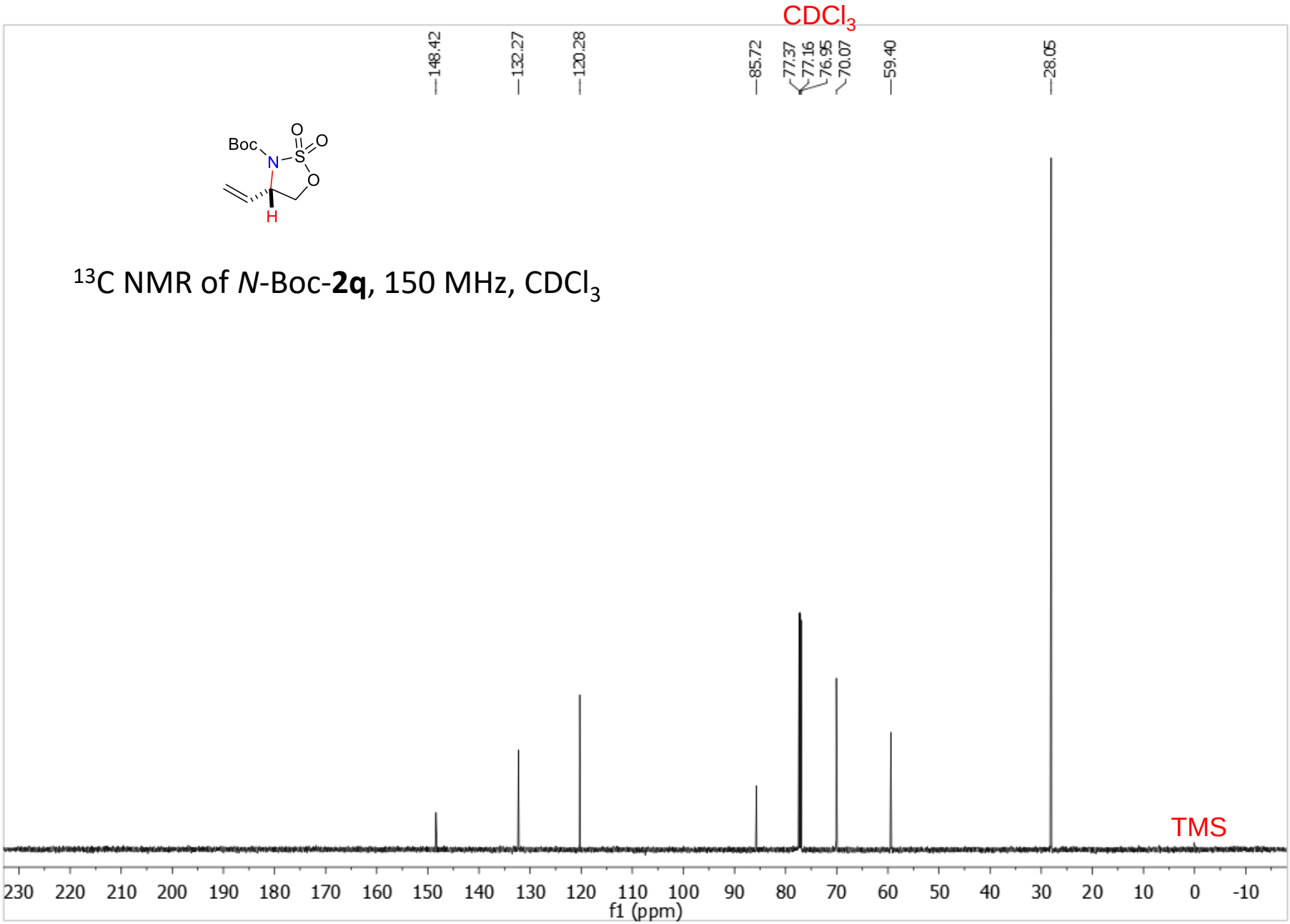
^{1}H NMR of **2q**, 500 MHz, $CDCl_3$



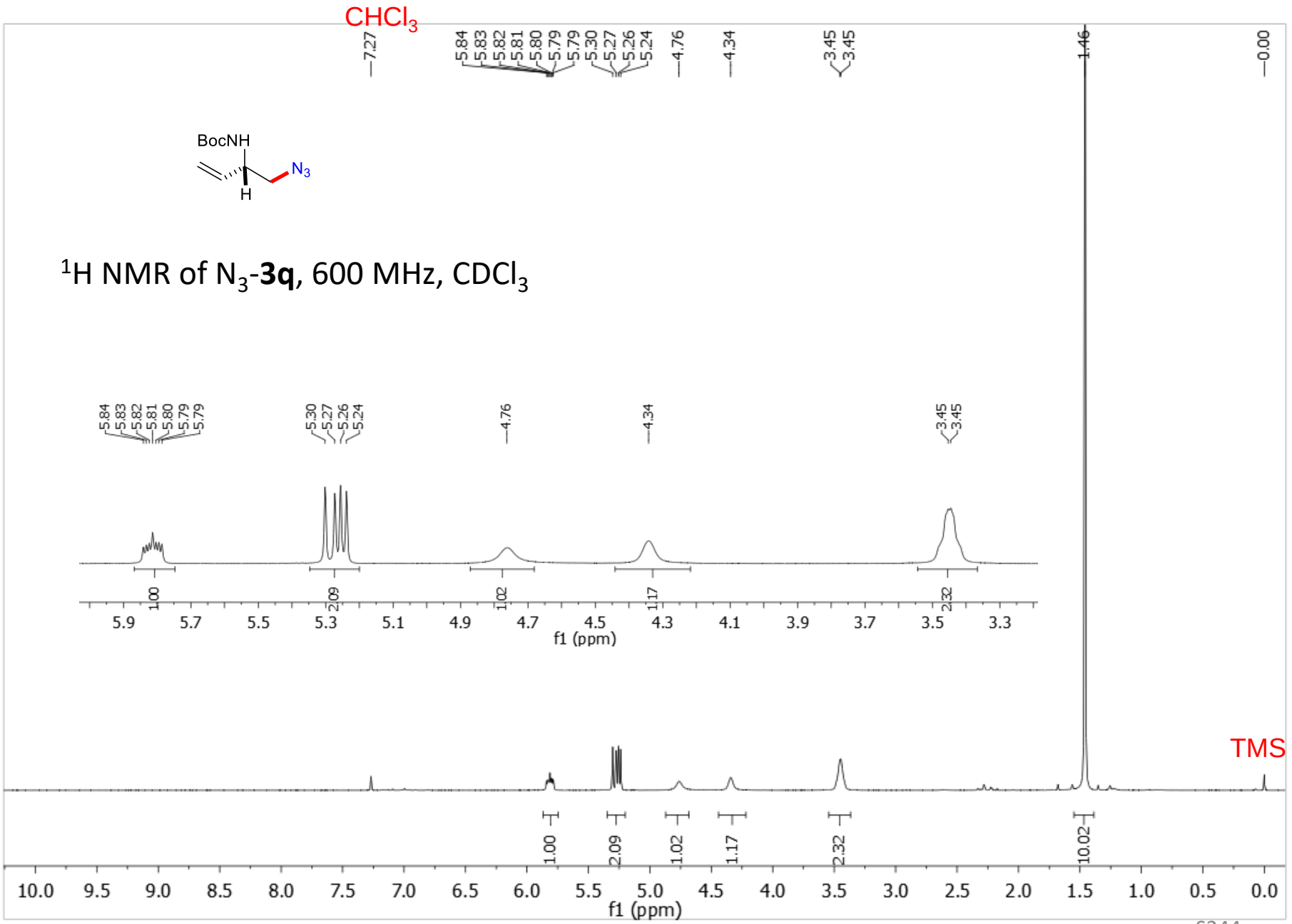
^{13}C NMR of **2q**, 150 MHz, $CDCl_3$

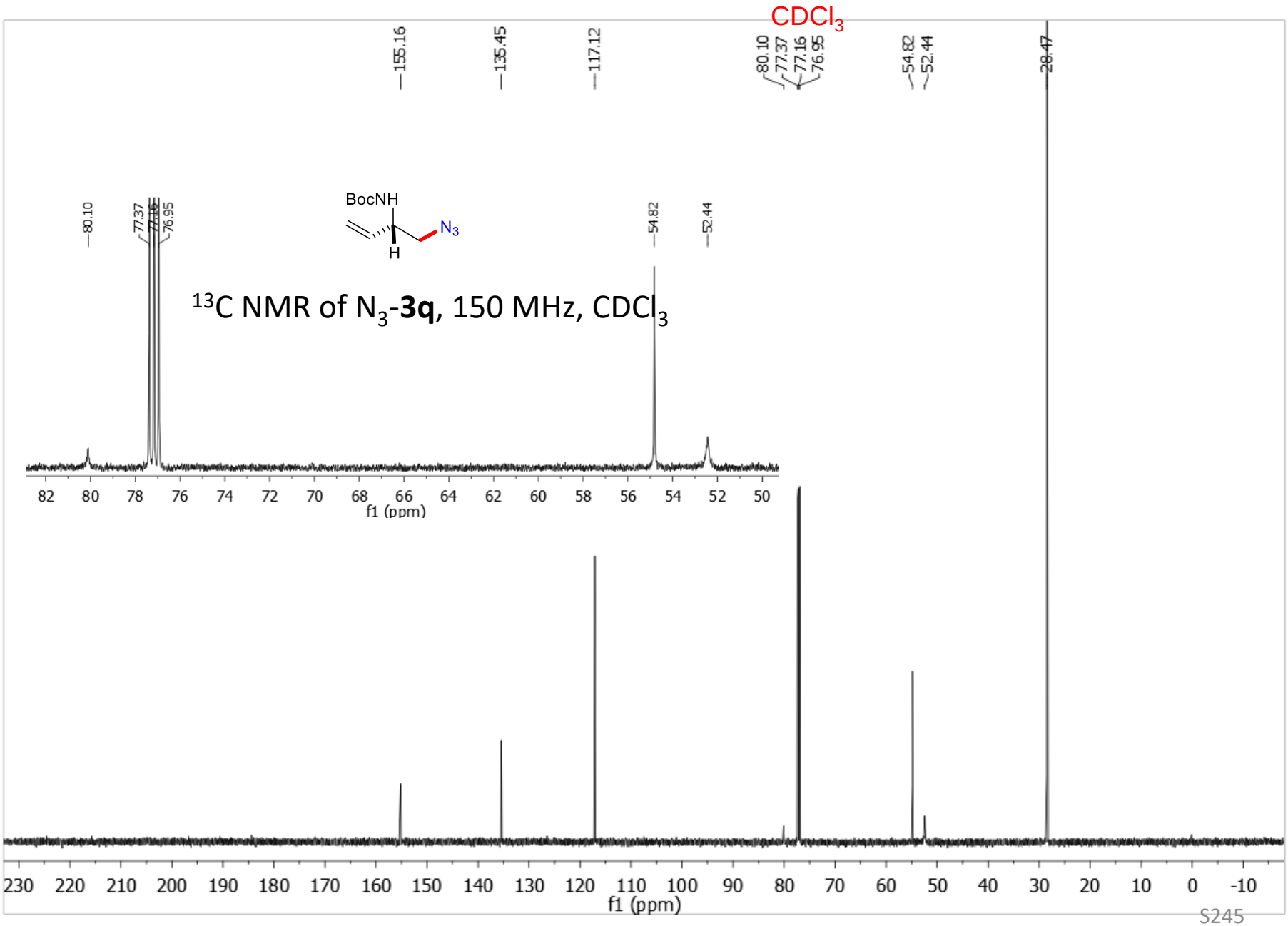


^{1}H NMR of *N*-Boc-**2q**, 600 MHz, $CDCl_3$

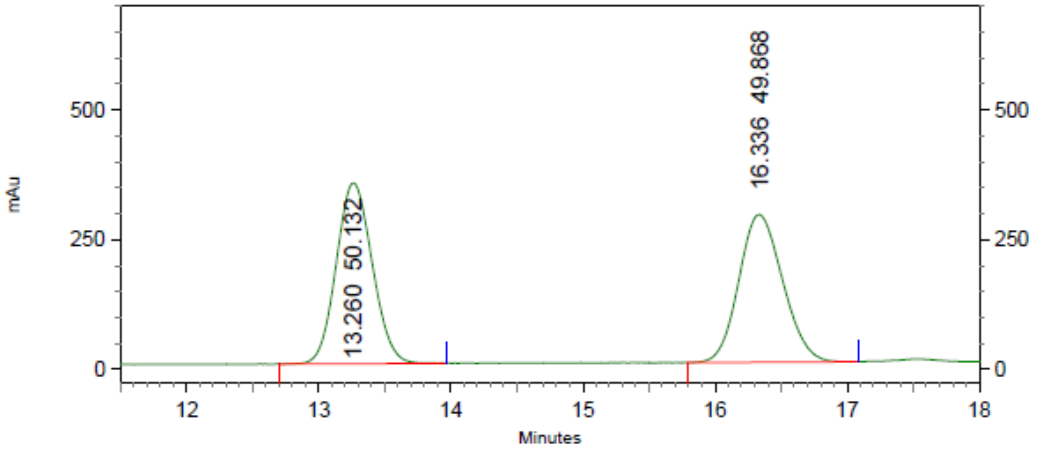


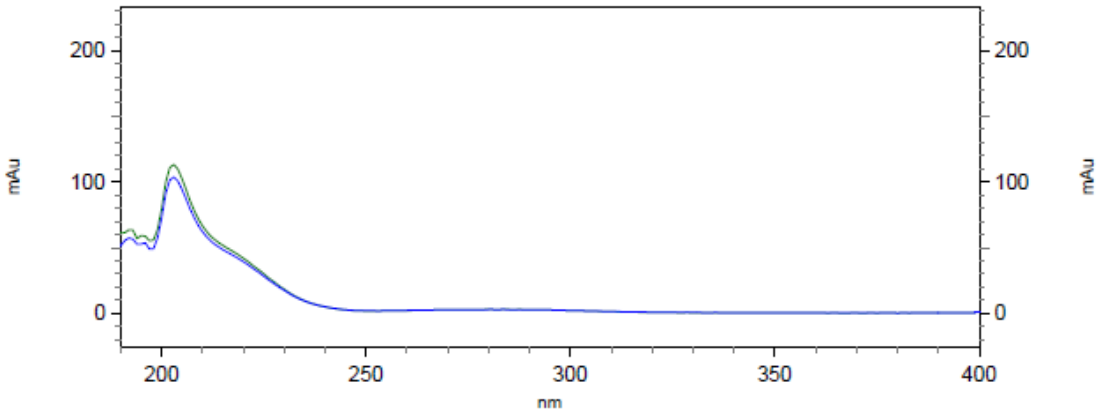
^{13}C NMR of *N*-Boc-**2q**, 150 MHz, $CDCl_3$

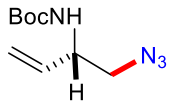

CHCl3
7.27
5.84
5.83
5.82
5.81
5.80
5.79
5.79
5.30
5.27
5.26
5.24
4.76
4.34
3.45
3.45
1.46
0.00
BocNH
N3
H
1H NMR of N3-3q, 600 MHz, CDCl3
1.00
2.09
1.02
1.17
2.32
10.02
f1 (ppm)
TMS


CDCl3
155.16
135.45
117.12
80.10
77.37
77.16
76.95
54.82
52.44
28.47
BocNH
N3
H
13C NMR of N3-3q, 150 MHz, CDCl3
f1 (ppm)
f1 (ppm)

C:\EZStart\Projects\Default\Data\K0L-401-IC-2-1mL-3
C:\Documents and Settings\zhang\Desktop\DSW\04042018.met





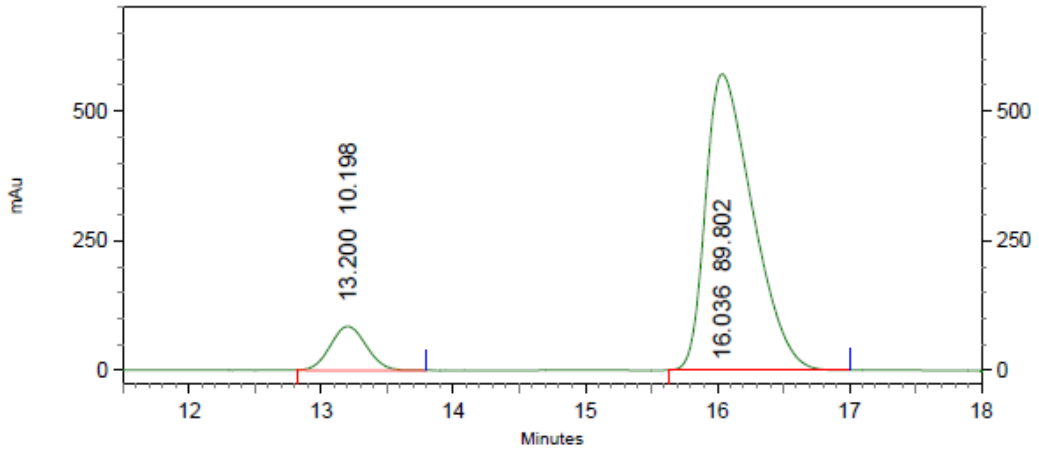


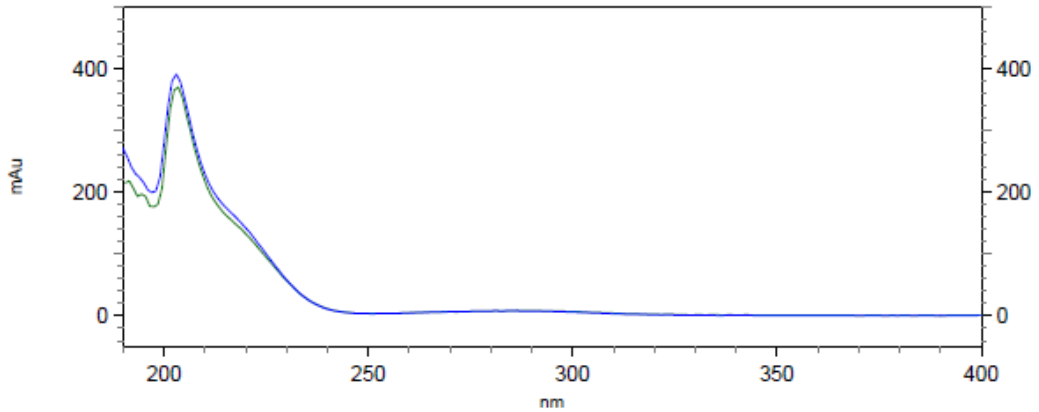
(±)-N_3-**3q**

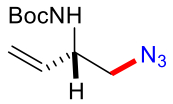
4: 221 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	13.260	50.132
2	16.336	49.868
Totals		100.000

C:\EZStart\Projects\Default\Data\K0L-400-IC-2%-1mL
C:\Documents and Settings\zhang\Desktop\DSW\04042018.met



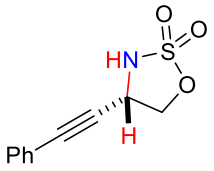




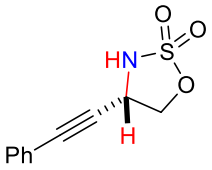
(-)-N_3-**3q**

4: 221 nm, 4
nm Results

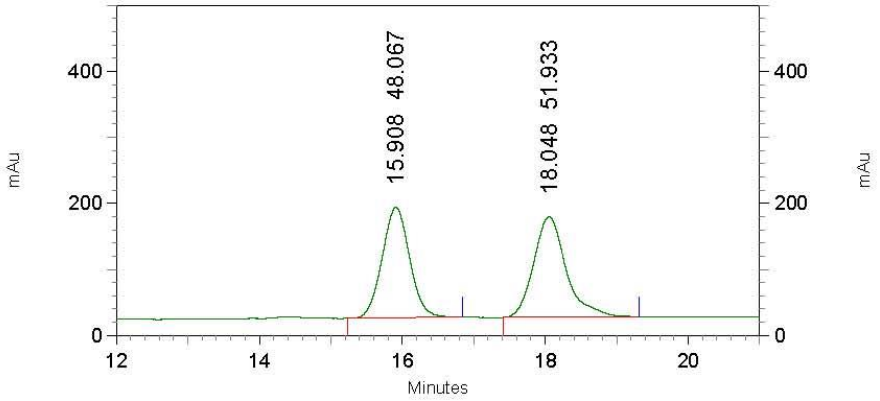
Pk #	Retention Time	Area Percent
1	13.200	10.198
2	16.036	89.802
Totals		100.000

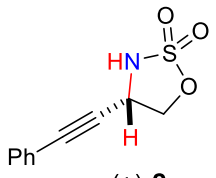


^{1}H NMR of **2r**, 400 MHz, $CDCl_3$

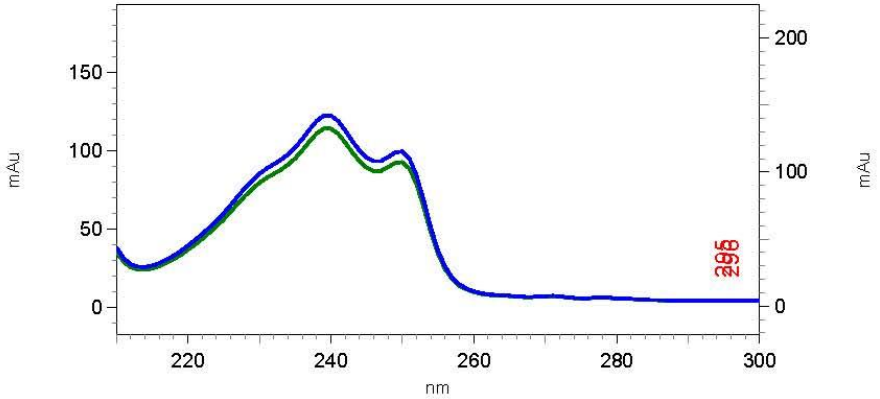


^{13}C NMR of **2r**, 100 MHz, $CDCl_3$



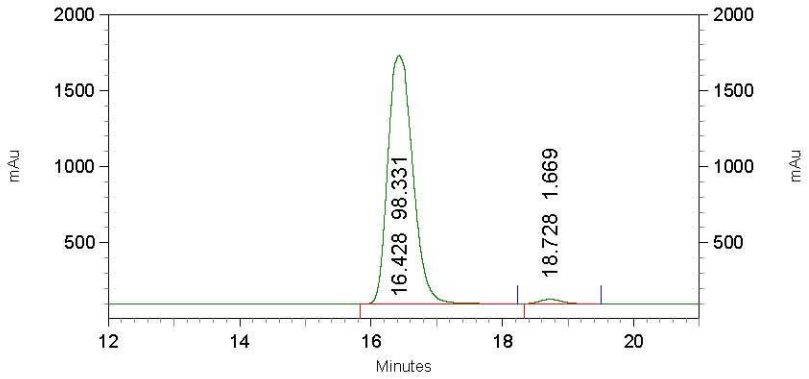


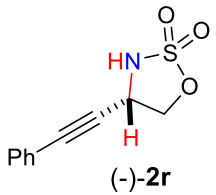
(±)-**2r**



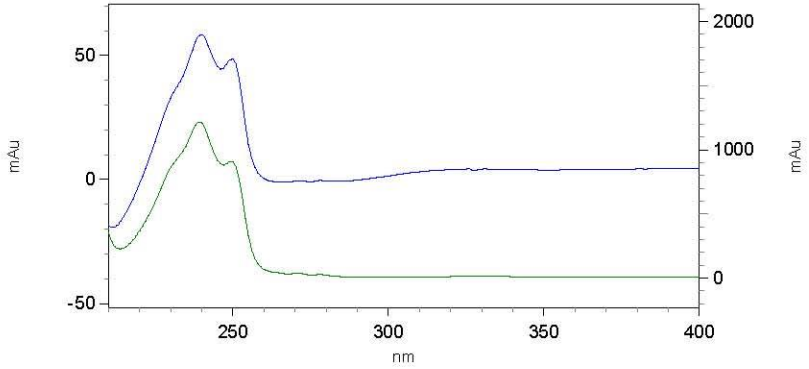
8: 257 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		15.908	48.067
2		18.048	51.933
Totals			100.000





(-)-**2r**

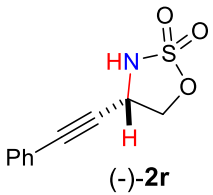


1: 239 nm, 4 nm

Results

Name	Retention Time	Area Percent	Pk #
	16.428	98.331	1
	18.728	1.669	2

Totals		100.000	



(-)-**2r**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) yh_ix_91

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: yh_ix_91

```
Bond precision:  C-C = 0.0032 A          Wavelength=1.54178

Cell:            a=5.4916(3)     b=7.9553(5)     c=23.5357(13)
                 alpha=90        beta=90         gamma=90
Temperature:     105 K

                 Calculated                Reported
Volume           1028.21(10)               1028.21(10)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C10 H9 N O3 S             C10 H9 N O3 S
Sum formula      C10 H9 N O3 S             C10 H9 N O3 S
Mr               223.24                    223.24
Dx,g cm-3        1.442                     1.442
Z                4                         4
Mu (mm-1)        2.708                     2.708
F000             464.0                     464.0
F000'            466.72
h,k,lmax         6,9,28                    6,9,28
Nref             1925[ 1159]               1879
Tmin,Tmax        0.645,0.922               0.589,1.000
Tmin'            0.539

Correction method= # Reported T Limits: Tmin=0.589 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.62/0.98      Theta(max)= 69.146

R(reflections)= 0.0287( 1857)     wR2(reflections)= 0.0726( 1879)

S = 1.134                 Npar= 140
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

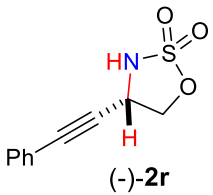
Alert level C

```
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level G

```
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.032 Note
PLAT371_ALERT_2_G Long   C(sp2)-C(sp1) Bond  C6       - C7       .       1.44 Ang.
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O11           111.9 Degree
PLAT791_ALERT_4_G Model has Chirality at C9          (Chiral SPGR)          S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          2 Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities .......     Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```



(-)-**2r**

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

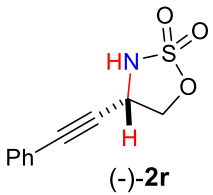
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

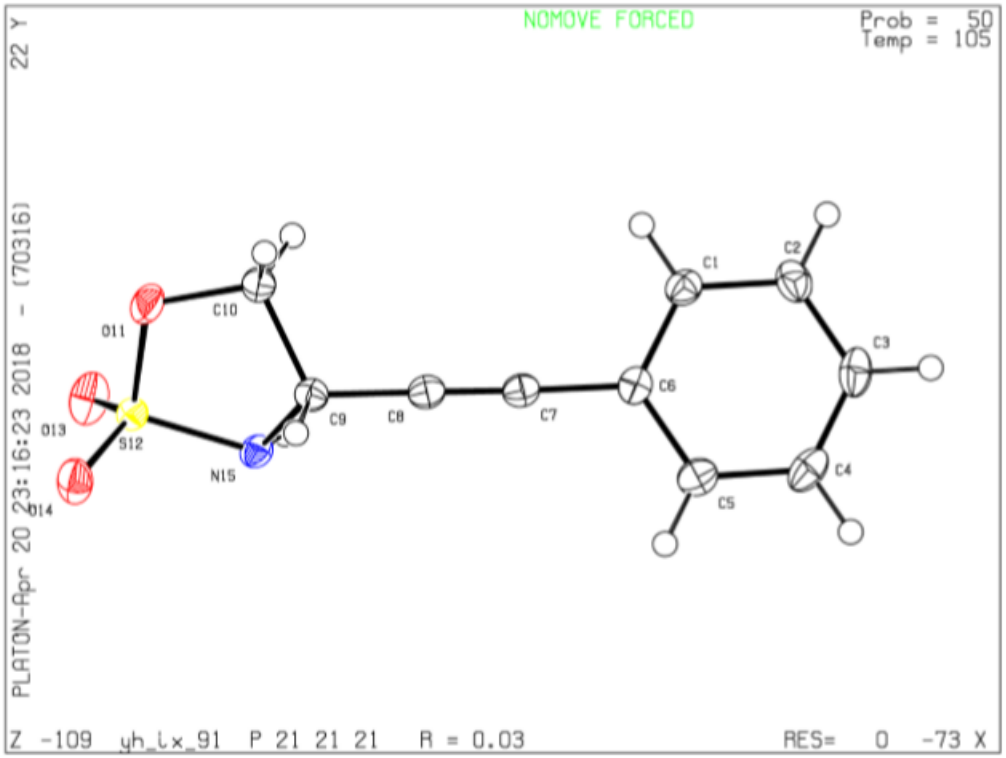
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 30/01/2018; check.def file version of 30/01/2018

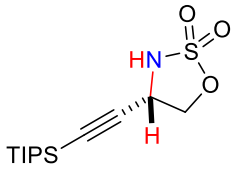


(-)-**2r**

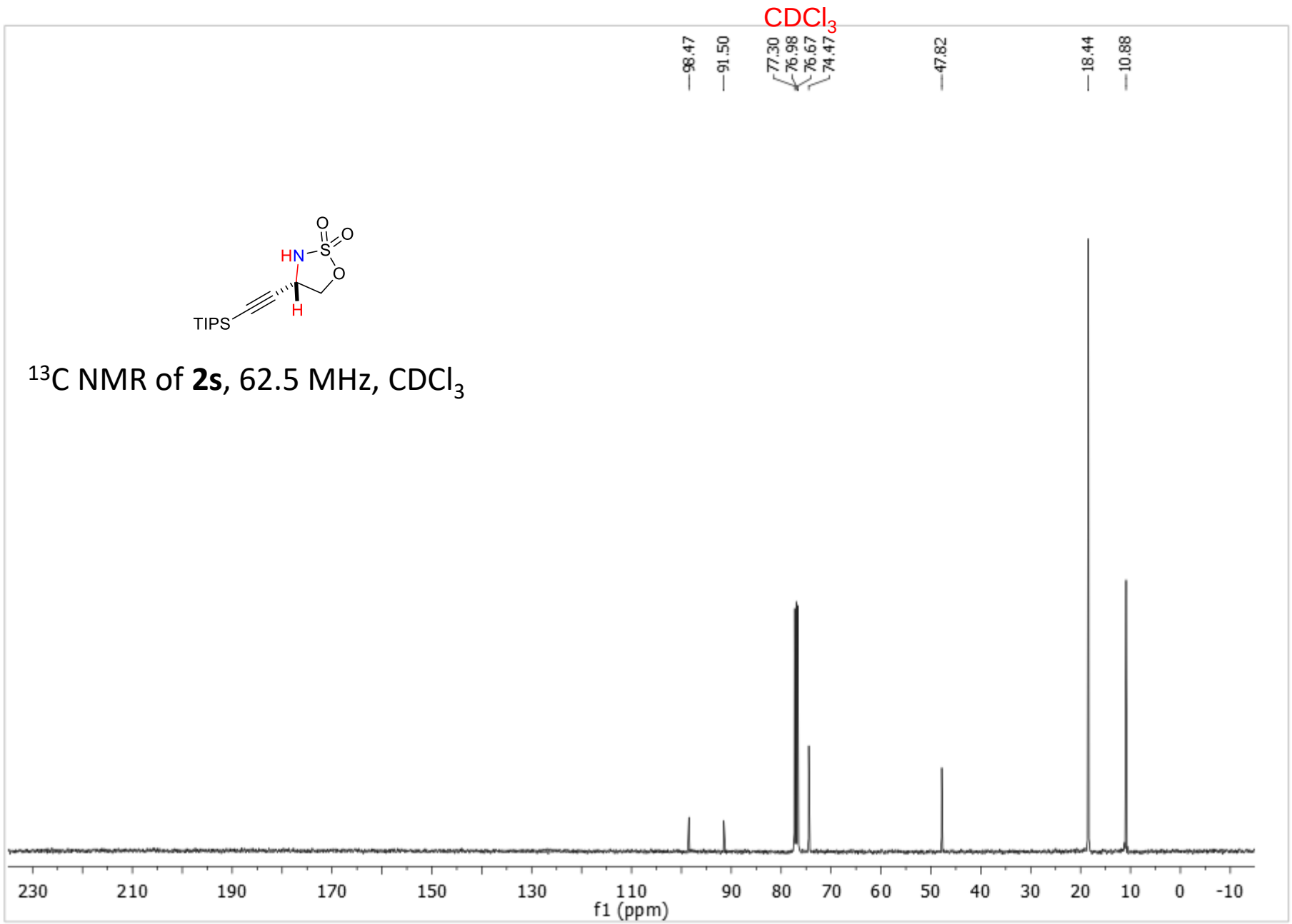
Datablock yh_ix_91 - ellipsoid plot



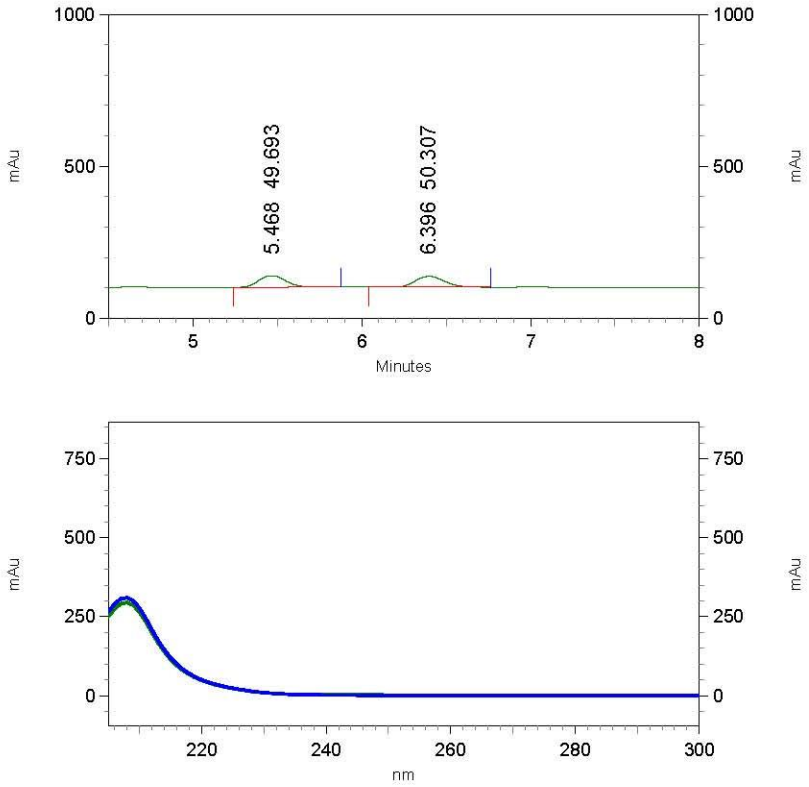
$CHCl_3$

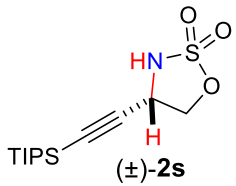


^{1}H NMR of **2s**, 250 MHz, $CDCl_3$



^{13}C NMR of **2s**, 62.5 MHz, $CDCl_3$



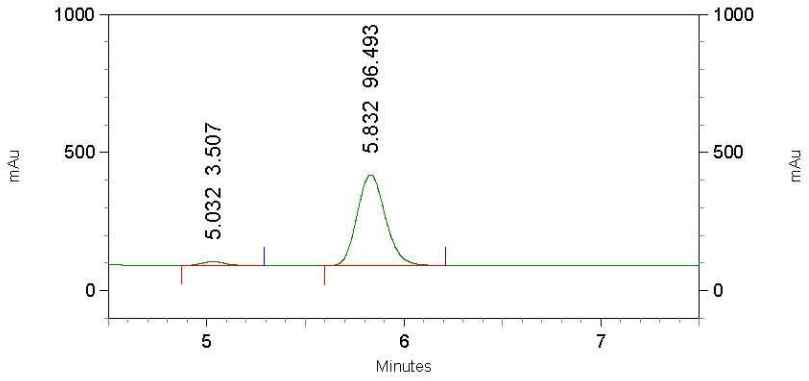


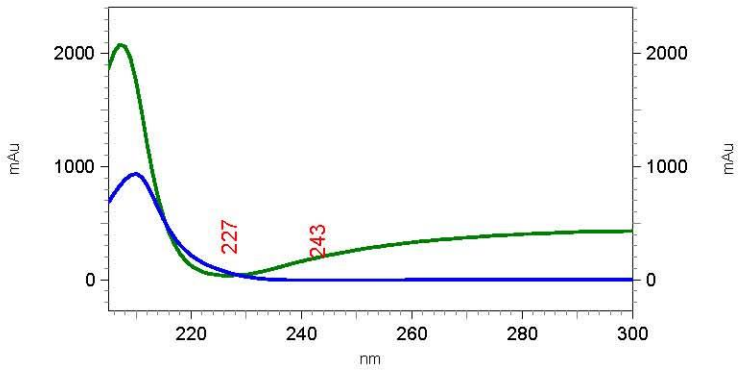
(±)-**2s**

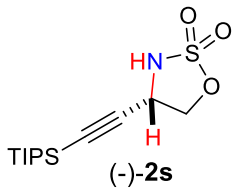
18: 222 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		5.468	49.693
2		6.396	50.307

Totals			100.000





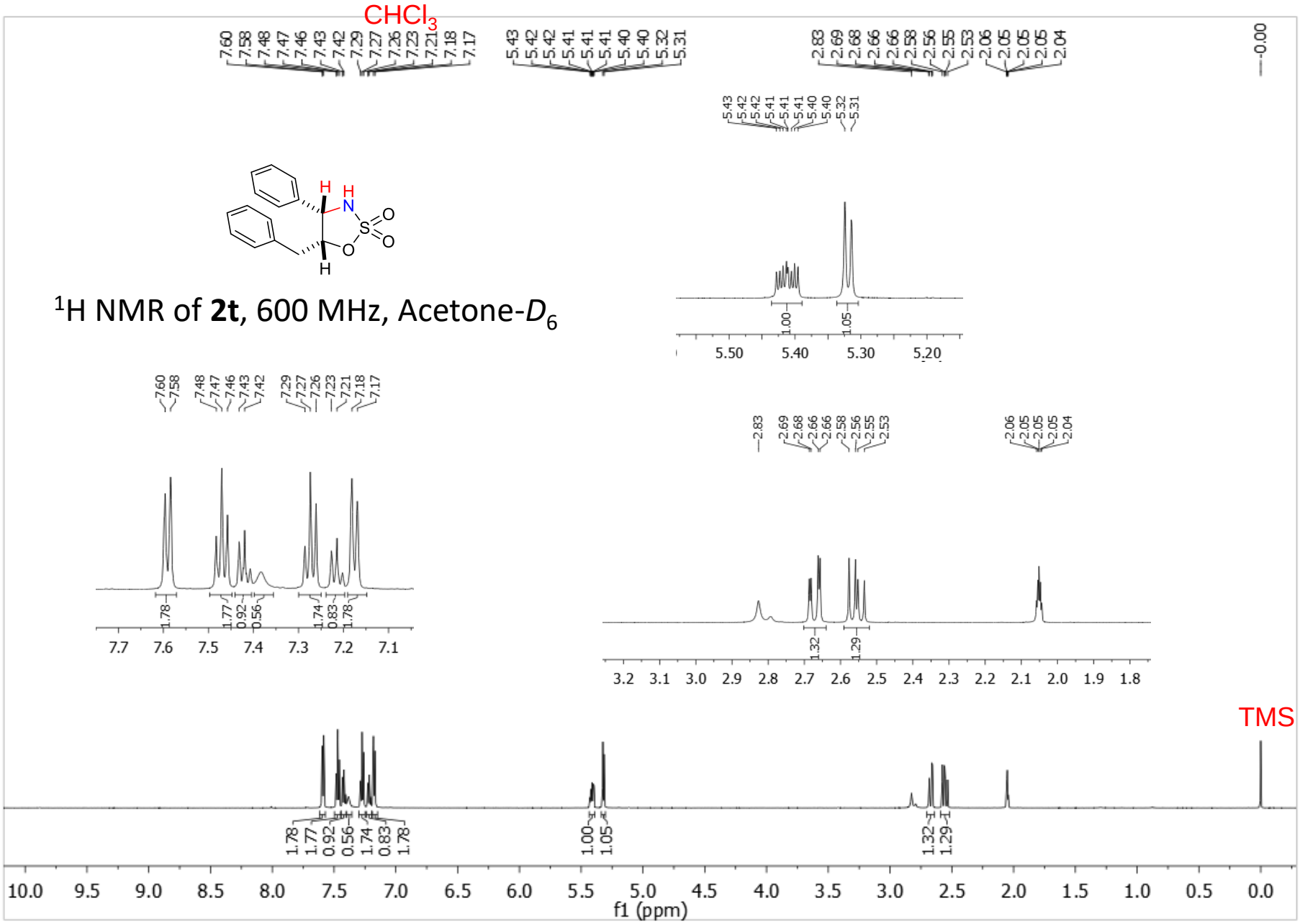


(-)-**2s**

17: 214 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		5.032	3.507
2		5.832	96.493

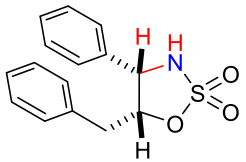
Totals			100.000



^{1}H NMR of **2t**, 600 MHz, Acetone-D_6

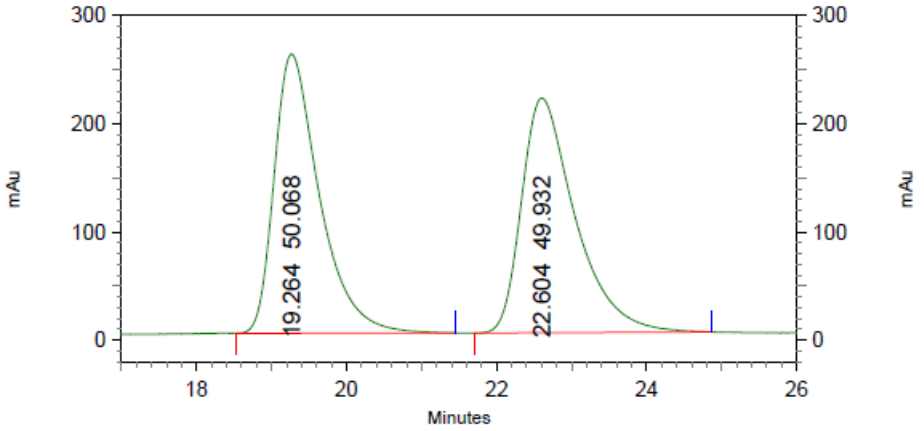
Acetone-D_6

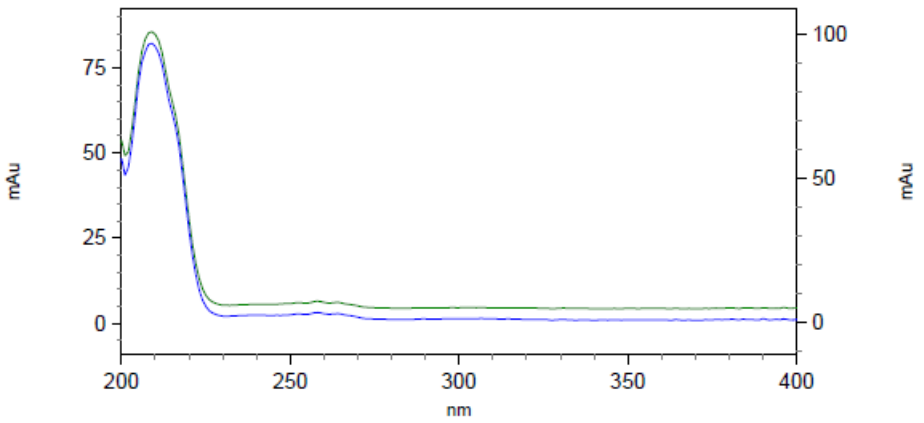
Acetone-D_6

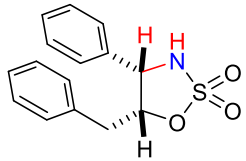


^{13}C NMR of **2t**, 150 MHz, Acetone-D_6

K0L-454-ADH-10%-1.0
C:\EZStart\Projects\Default\Method\lk-5%1.0.met
C:\EZStart\Projects\Default\Data\K0L-454-ADH-10%-1.0







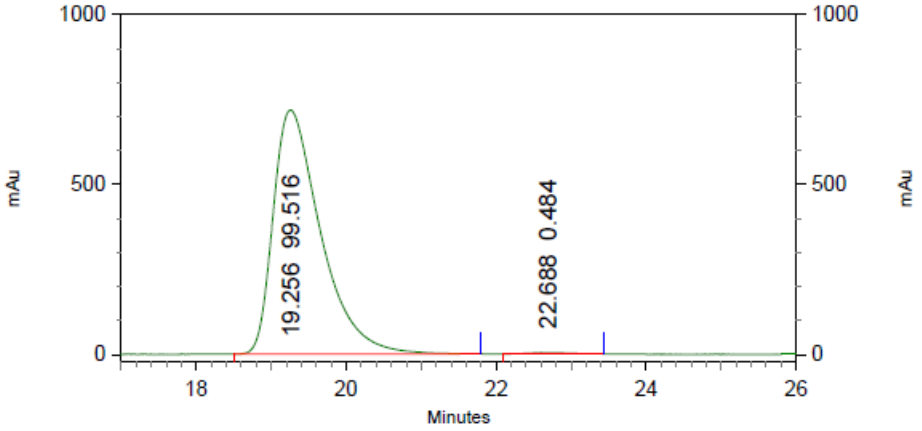
(±)-**2t**

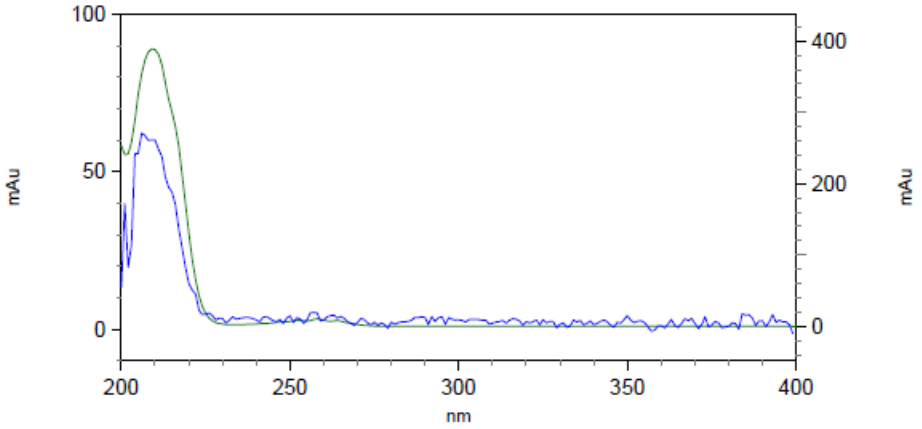
1: 212 nm, 4 nm
Results

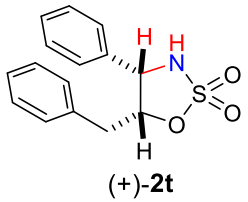
Name	Retention Time	Area Percent	Pk #
	19.264	50.068	1
	22.604	49.932	2

Totals	
	100.000

K0L-453-ADH-10%-1.0
C:\EZStart\Projects\Default\Method\lk-5%1.0.met
C:\EZStart\Projects\Default\Data\K0L-453-ADH-10%-1.0





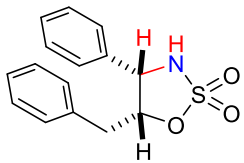


(+)-**2t**

1: 212 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	19.256	99.516	1
	22.688	0.484	2

Totals	
	100.000



(+)-**2t**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C15H15NO3S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C15H15NO3S

Bond precision: C-C = 0.0037 A Wavelength=1.54178

Cell: a=6.1826(3) b=8.8713(4) c=24.9596(12)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1368.98(11)	1368.98(11)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C15 H15 N O3 S	C15 H15 N O3 S
Sum formula	C15 H15 N O3 S	C15 H15 N O3 S
Mr	289.34	289.34
Dx,g cm-3	1.404	1.404
Z	4	4
Mu (mm-1)	2.166	2.166
F000	608.0	608.0
F000'	611.06	
h,k,lmax	7,10,29	7,10,29
Nref	2426[1442]	2400
Tmin,Tmax	0.730,0.841	0.595,0.753
Tmin'	0.337	

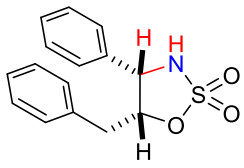
Correction method= # Reported T Limits: Tmin=0.595 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.66/0.99 Theta(max)= 66.600

R(reflections)= 0.0267(2353) wR2(reflections)= 0.0714(2400)

S = 1.086 Npar= 185

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(+)-**2t**

Alert level C

```
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         2 Note
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.040 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O1             106.6 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact  O2       ..C1              3.01 Ang.
PLAT791_ALERT_4_G Model has Chirality at C1          (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C2          (Chiral SPGR)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         1 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still       95% Note
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities .......     Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         6 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 11 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  2 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

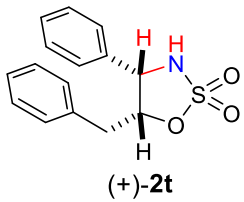
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

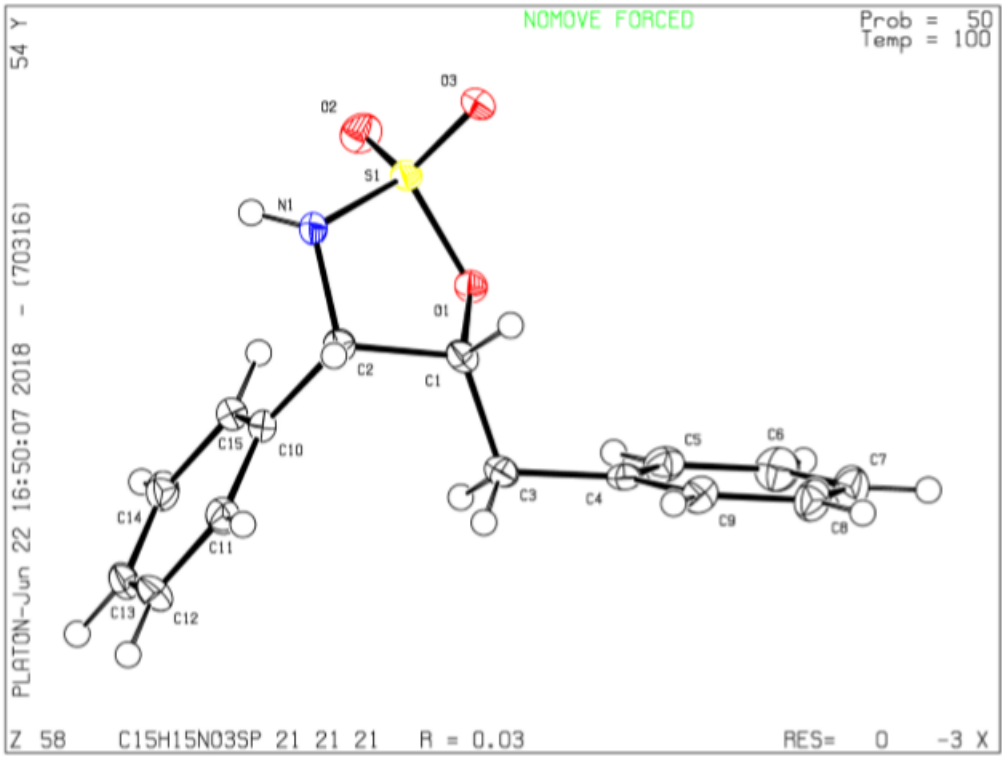
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

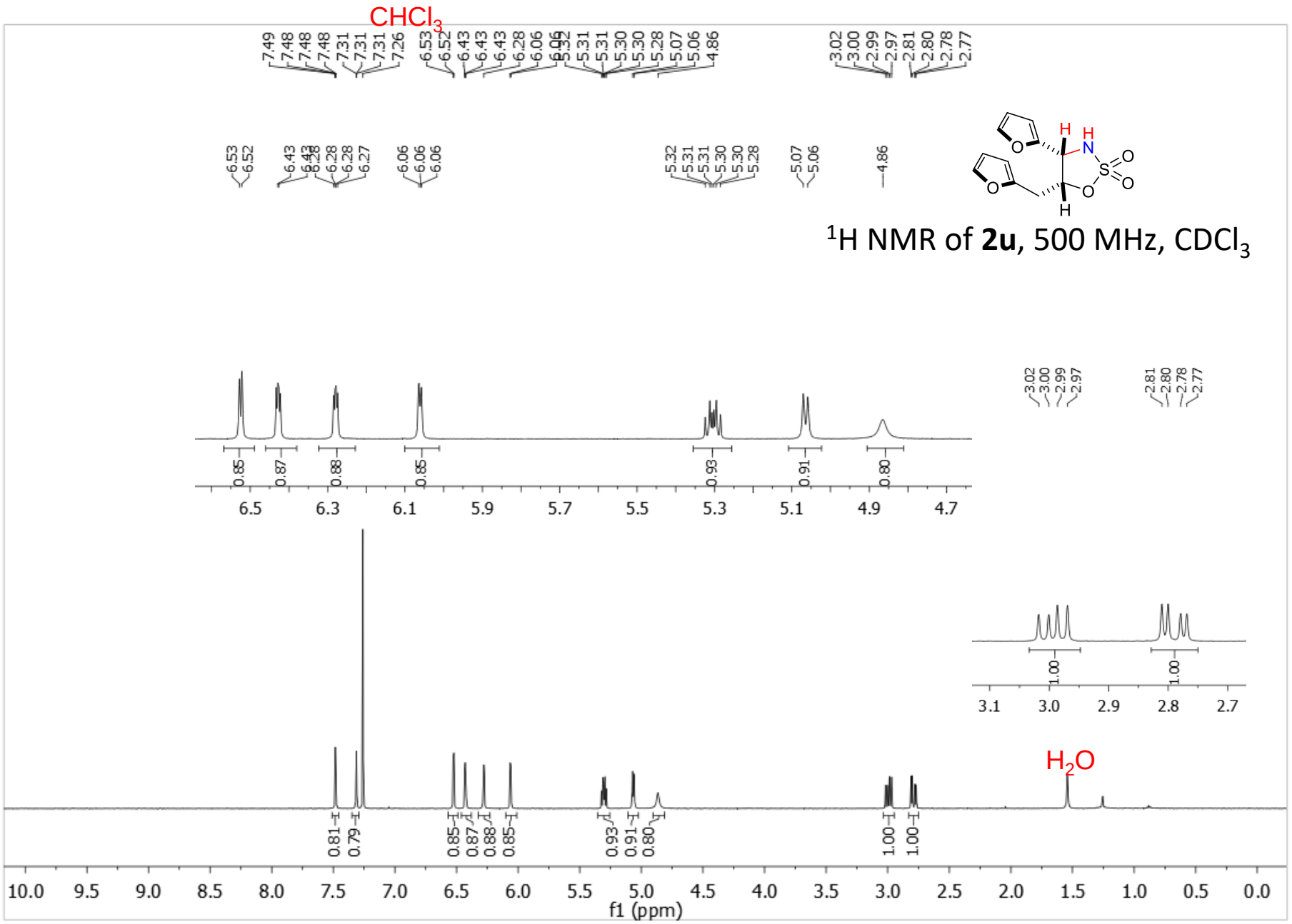


(+)-**2t**

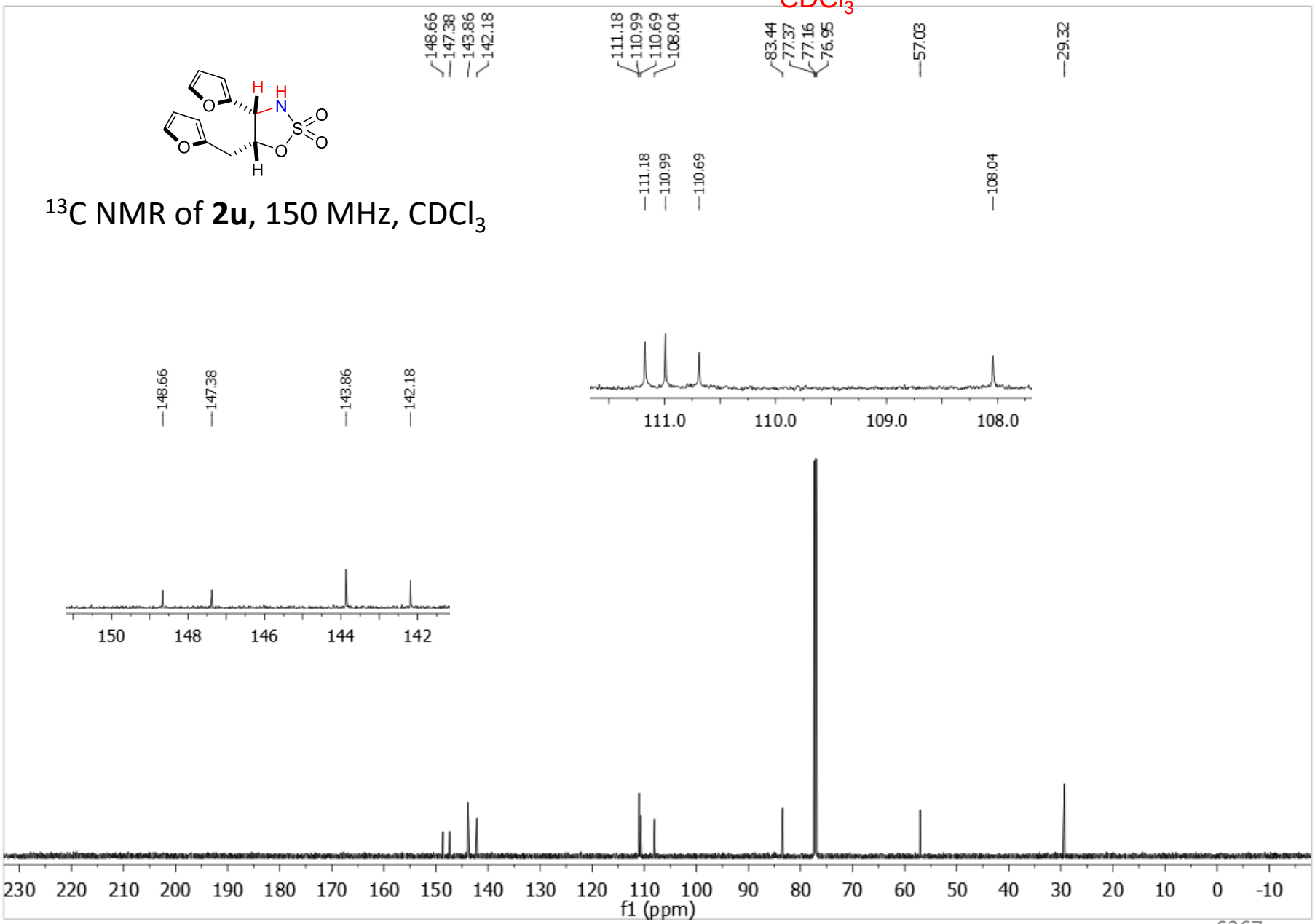
PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock C15H15NO3S - ellipsoid plot

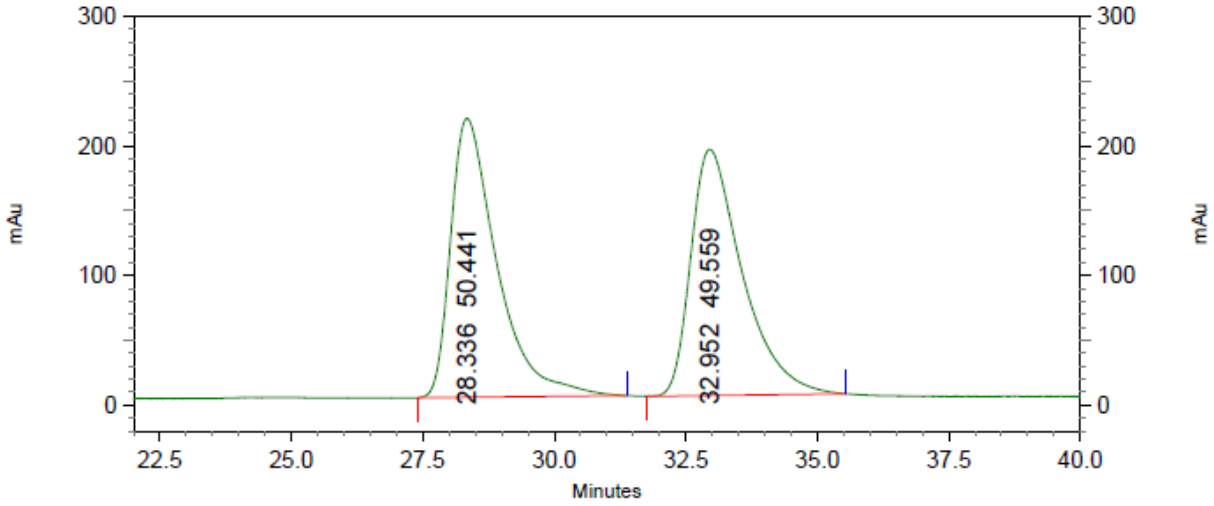


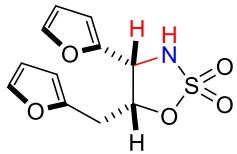


^{1}H NMR of **2u**, 500 MHz, $CDCl_3$

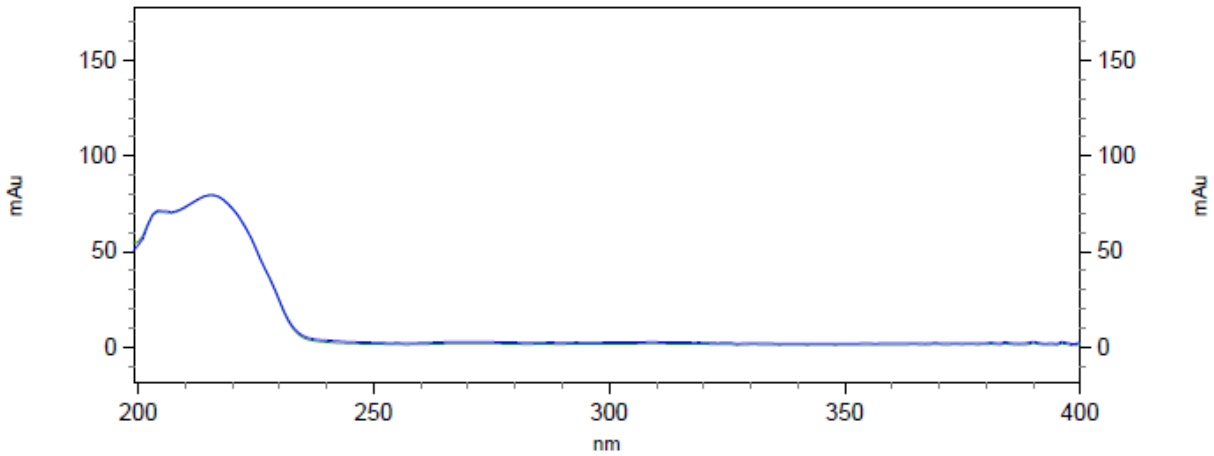


^{13}C NMR of **2u**, 150 MHz, $CDCl_3$





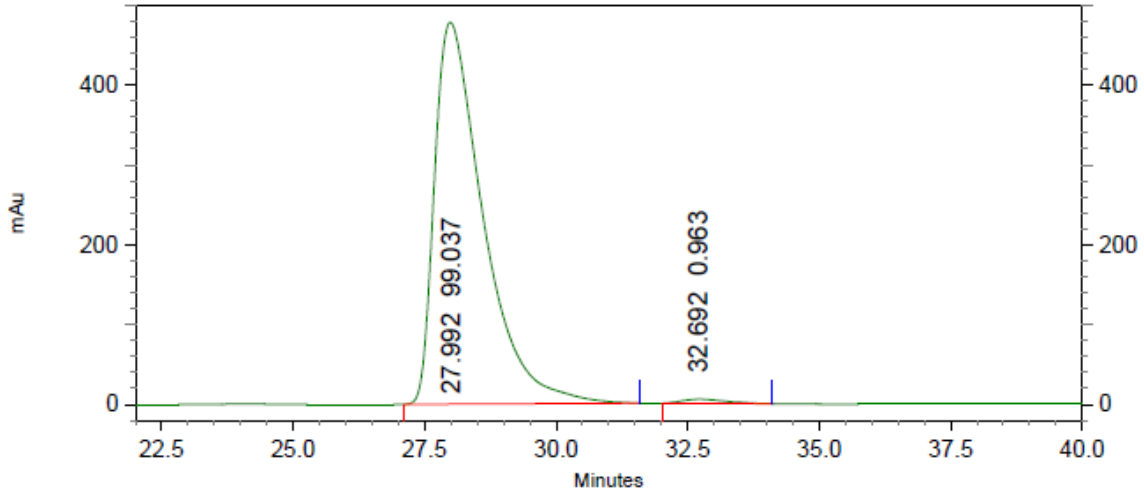
(±)-**2u**

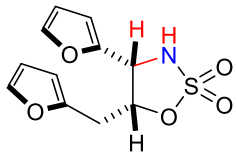


3: 222 nm, 4
nm Results

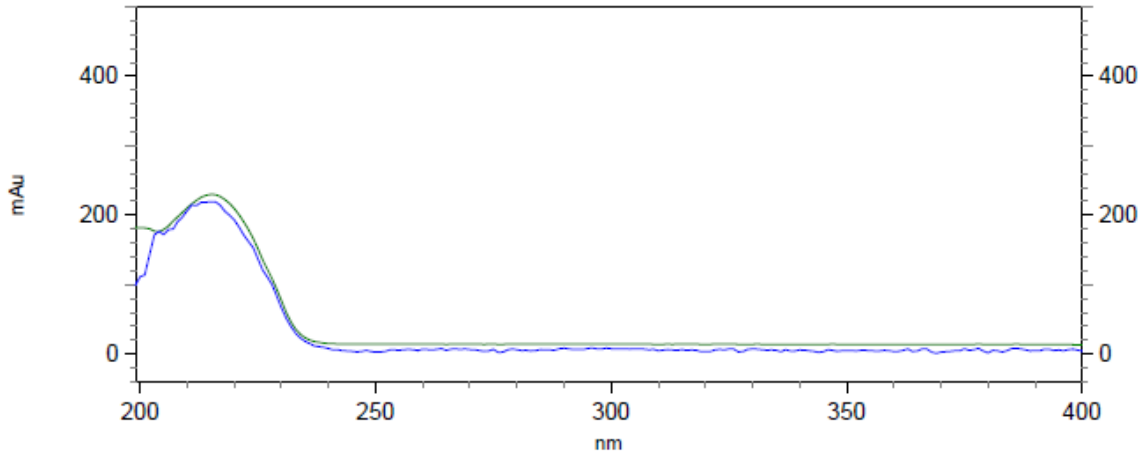
Pk #	Retention Time	Area Percent
1	28.336	50.441
2	32.952	49.559

Totals	
	100.000



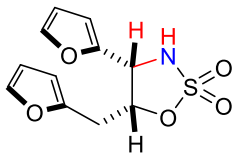


(+)-**2u**



3: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	27.992	99.037
2	32.692	0.963
Totals		100.000



(+)-**2u**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C11H11NO5S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C11H11NO5S

Bond precision: C-C = 0.0061 A Wavelength=1.54178

Cell: a=17.9291(12) b=5.4403(4) c=14.8271(9)
alpha=90 beta=124.469(3) gamma=90
Temperature: 123 K

	Calculated	Reported
Volume	1192.32(15)	1192.32(14)
Space group	C 2	C 2
Hall group	C 2y	C 2y
Moiety formula	C11 H11 N O5 S	C11 H11 N O5 S
Sum formula	C11 H11 N O5 S	C11 H11 N O5 S
Mr	269.27	269.27
Dx,g cm-3	1.500	1.500
Z	4	4
Mu (mm-1)	2.569	2.569
F000	560.0	560.0
F000'	563.18	
h,k,lmax	21,6,17	21,6,17
Nref	2117[1181]	2078
Tmin,Tmax	0.725,0.773	0.551,0.753
Tmin'	0.278	

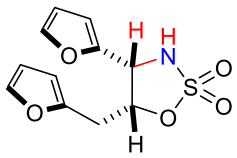
Correction method= # Reported T Limits: Tmin=0.551 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.76/0.98 Theta(max)= 66.693

R(reflections)= 0.0377(2048) wR2(reflections)= 0.1046(2078)

S = 1.105 Npar= 166

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(+)-**2u**

Alert level C

```
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       7.11 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0061 Ang.
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         2 Note
PLAT128_ALERT_4_G Alternate Setting for Input Space Group  C2             I2 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         1 Report
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O1            109.0 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O4            106.1 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O5            106.3 Degree
PLAT791_ALERT_4_G Model has Chirality at C1          (Chiral SPGR)       R Verify
PLAT791_ALERT_4_G Model has Chirality at C2          (Chiral SPGR)       R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         2 Note
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  9 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  3 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

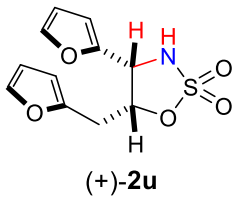
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

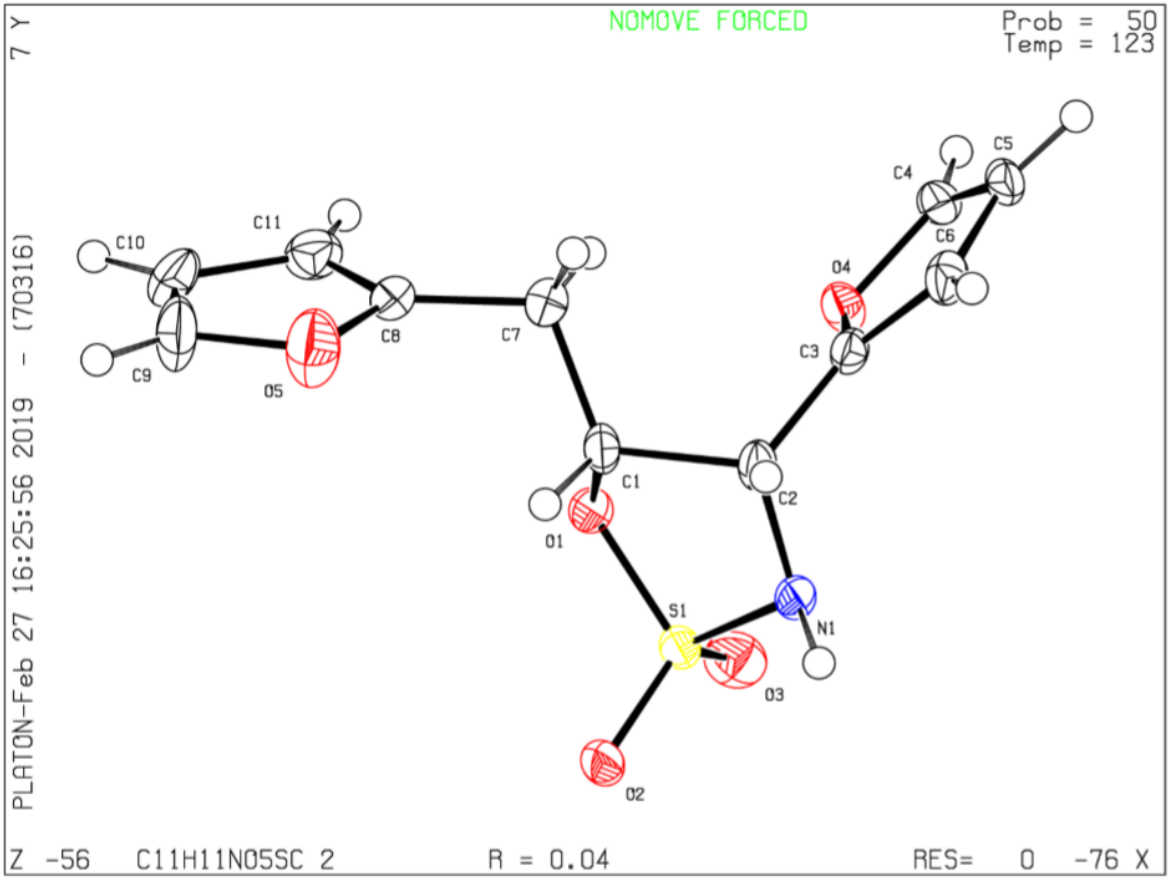
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

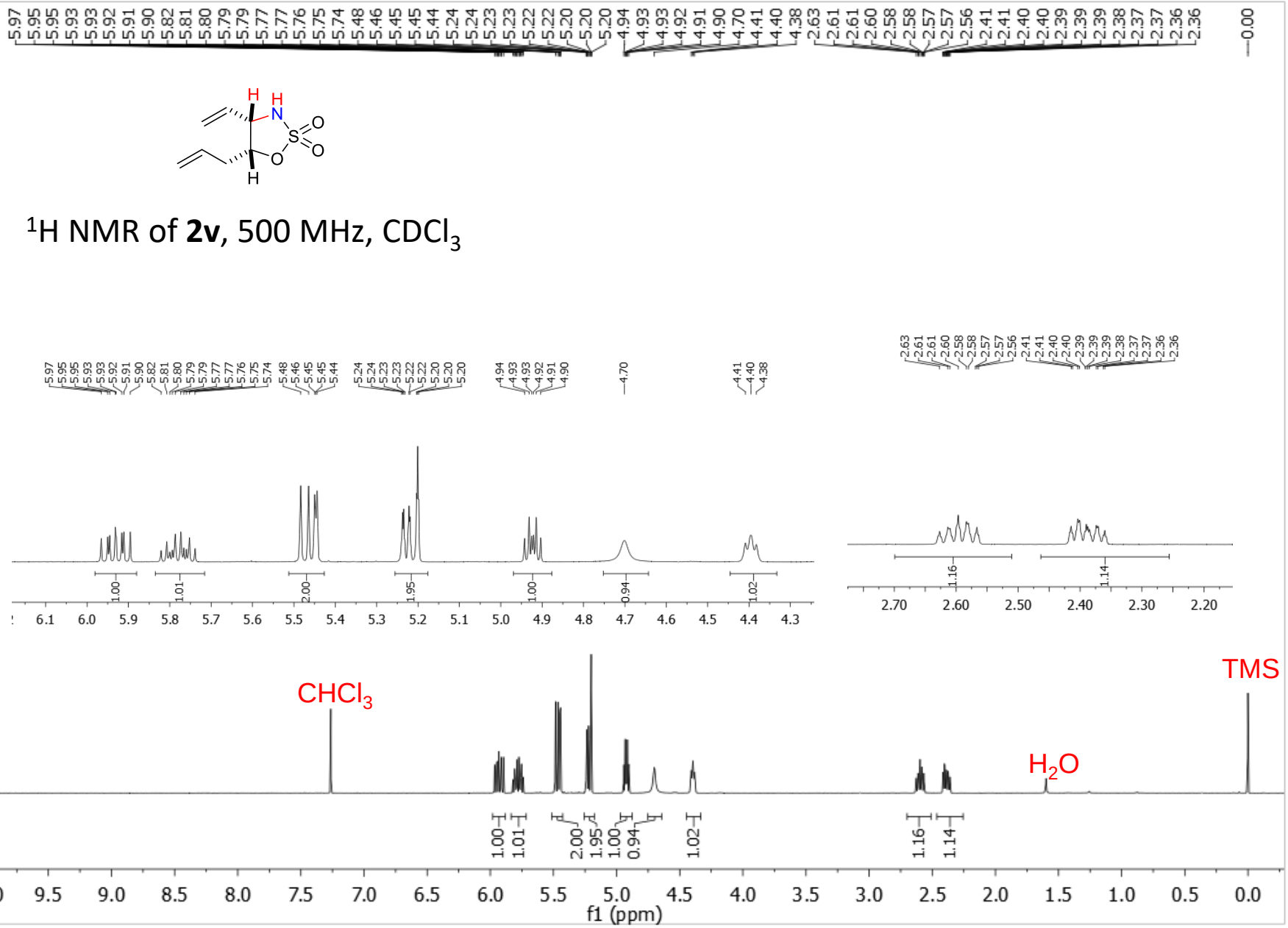


(+)-**2u**

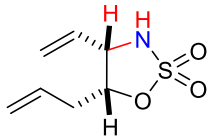
PLATON version of 18/02/2019; check.def file version of 18/02/2019

Datablock C11H11NO5S - ellipsoid plot

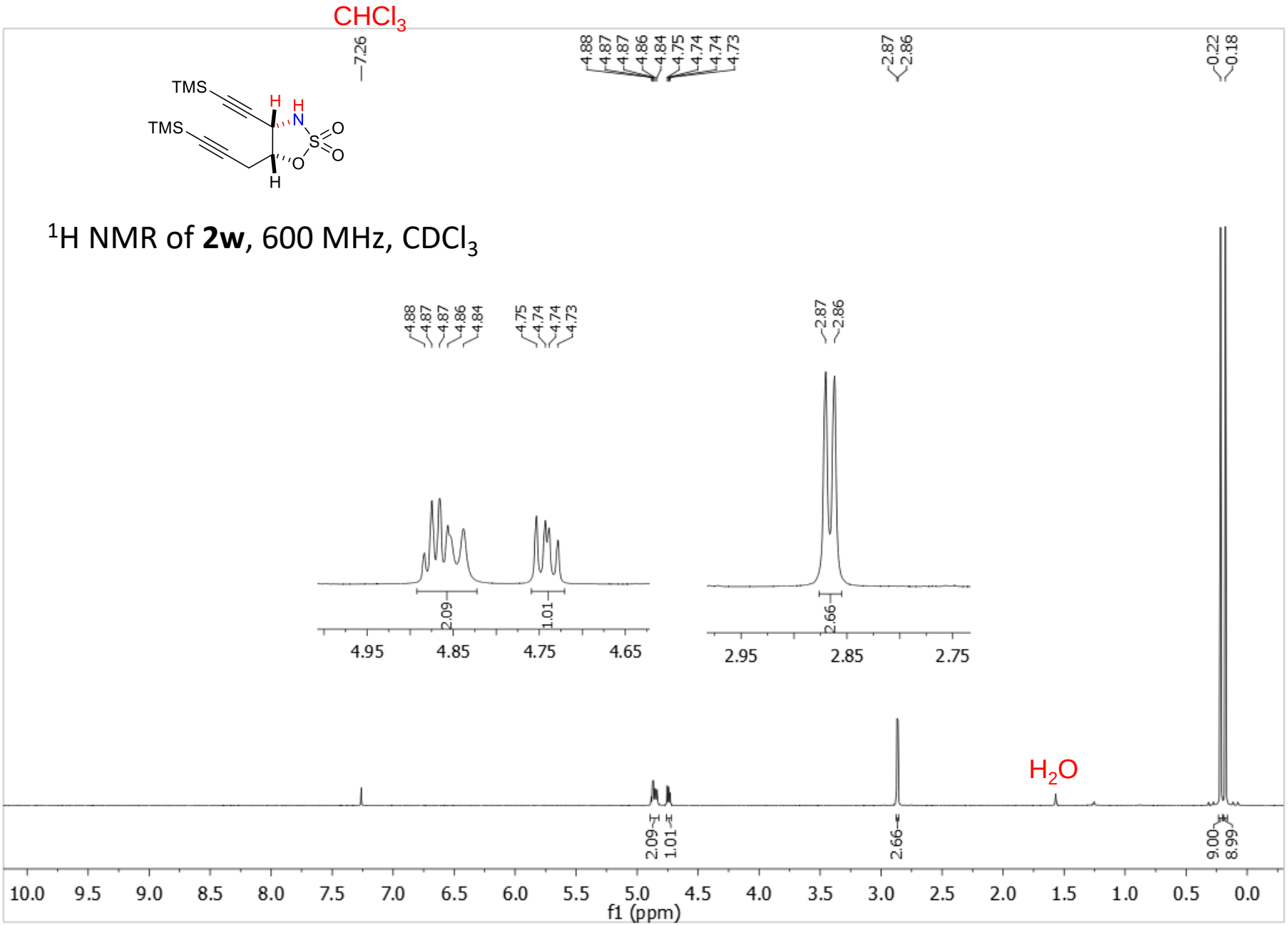


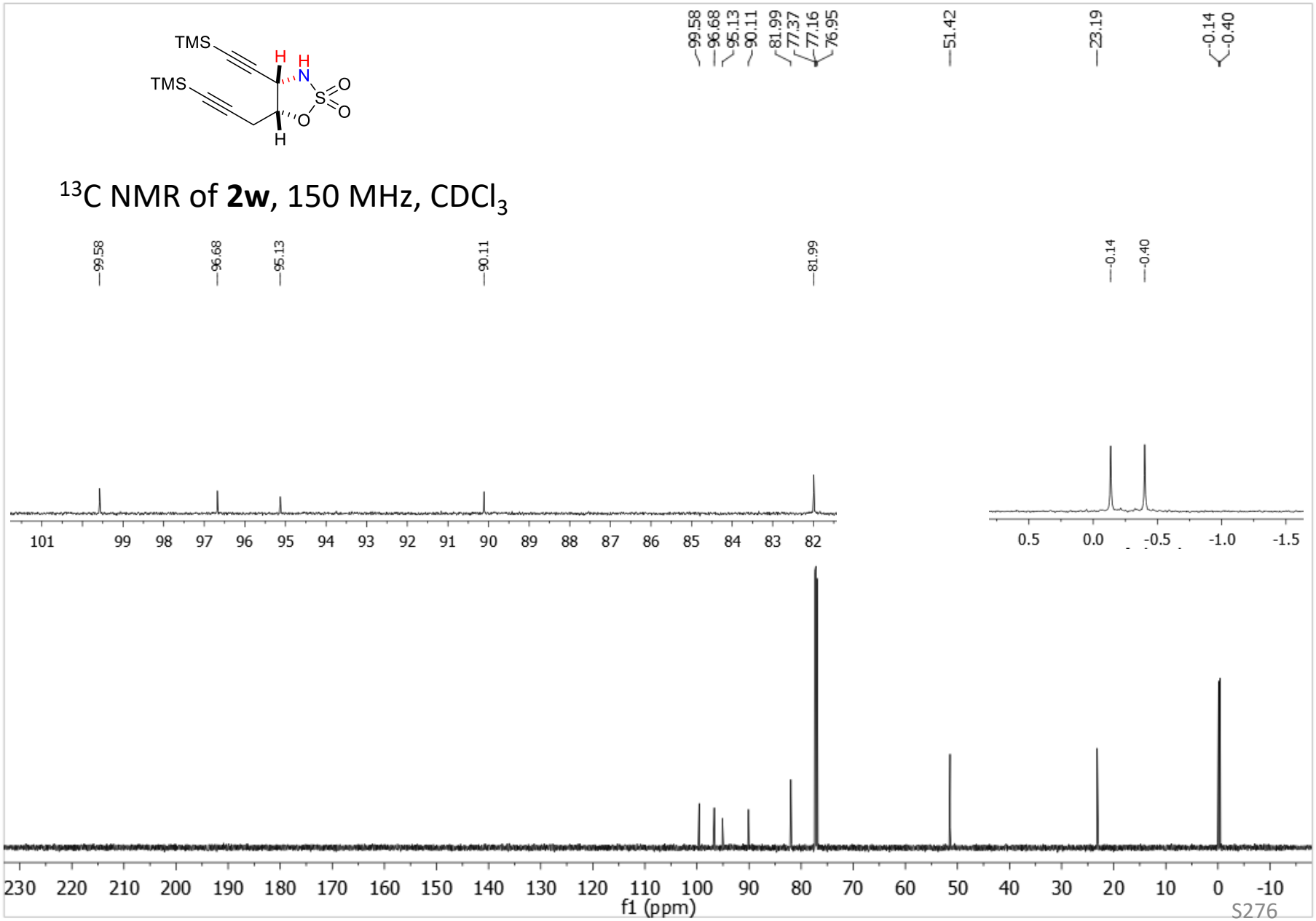


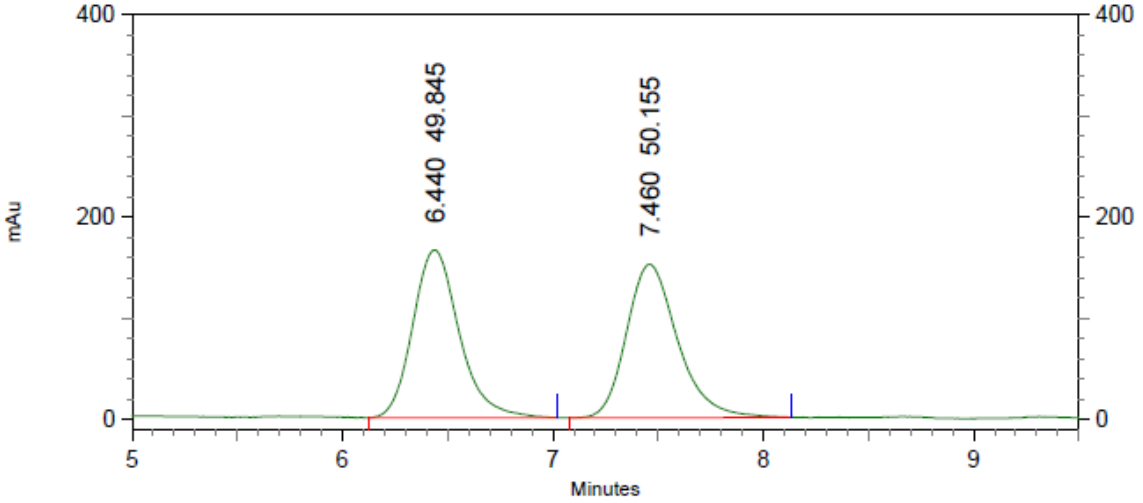
^{1}H NMR of **2v**, 500 MHz, $CDCl_3$

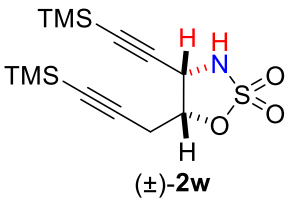


^{13}C NMR of **2v**, 150 MHz, $CDCl_3$

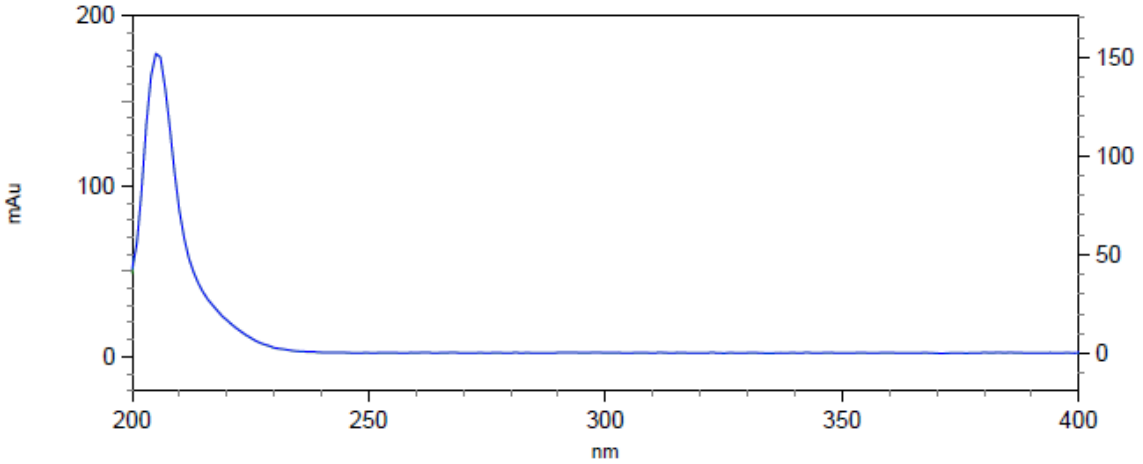

CHCl3
TMS
TMS
H
H
N
S
O
O
O
H
7.26
4.88
4.87
4.87
4.86
4.84
4.75
4.74
4.74
4.73
2.87
2.86
0.22
0.18
1H NMR of 2w, 600 MHz, CDCl3
2.09
1.01
2.66
4.95
4.85
4.75
4.65
2.95
2.85
2.75
H2O
9.00
8.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CDCl3
TMS
TMS
H
H
N
S
O
O
O
H
99.58
96.68
95.13
90.11
81.99
77.37
77.16
76.95
51.42
23.19
-0.14
-0.40
13C NMR of 2w, 150 MHz, CDCl3
f1 (ppm)





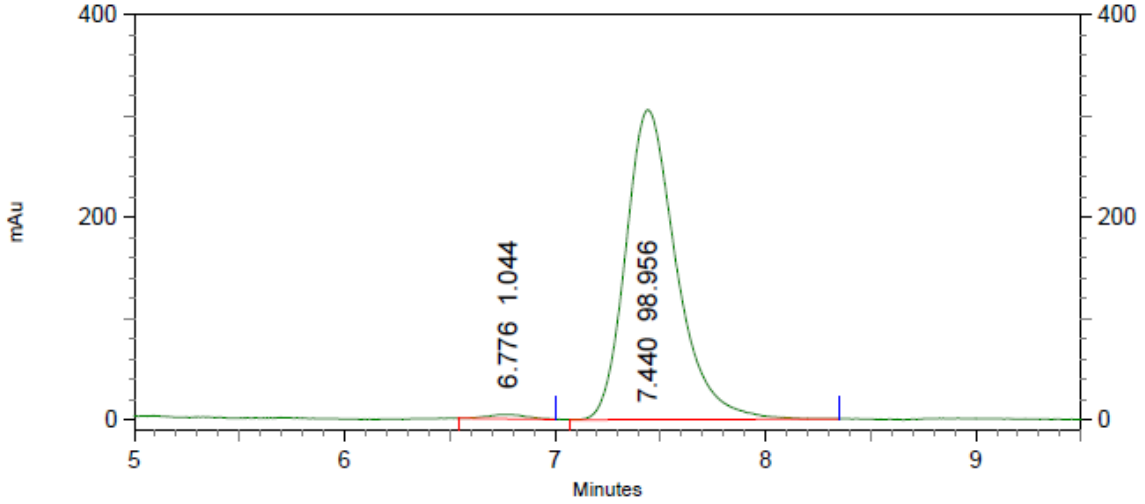
(±)-**2w**

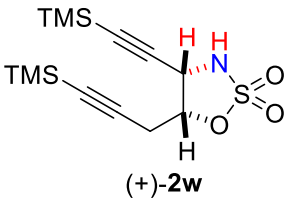


3: 210 nm, 4
nm Results

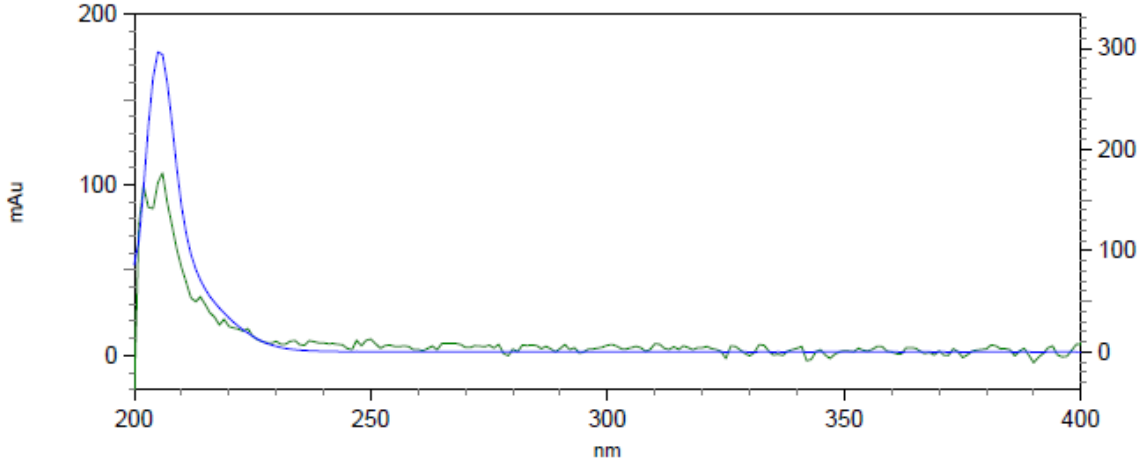
Pk #	Retention Time	Area Percent
1	6.440	49.845
2	7.460	50.155

Totals	
	100.000





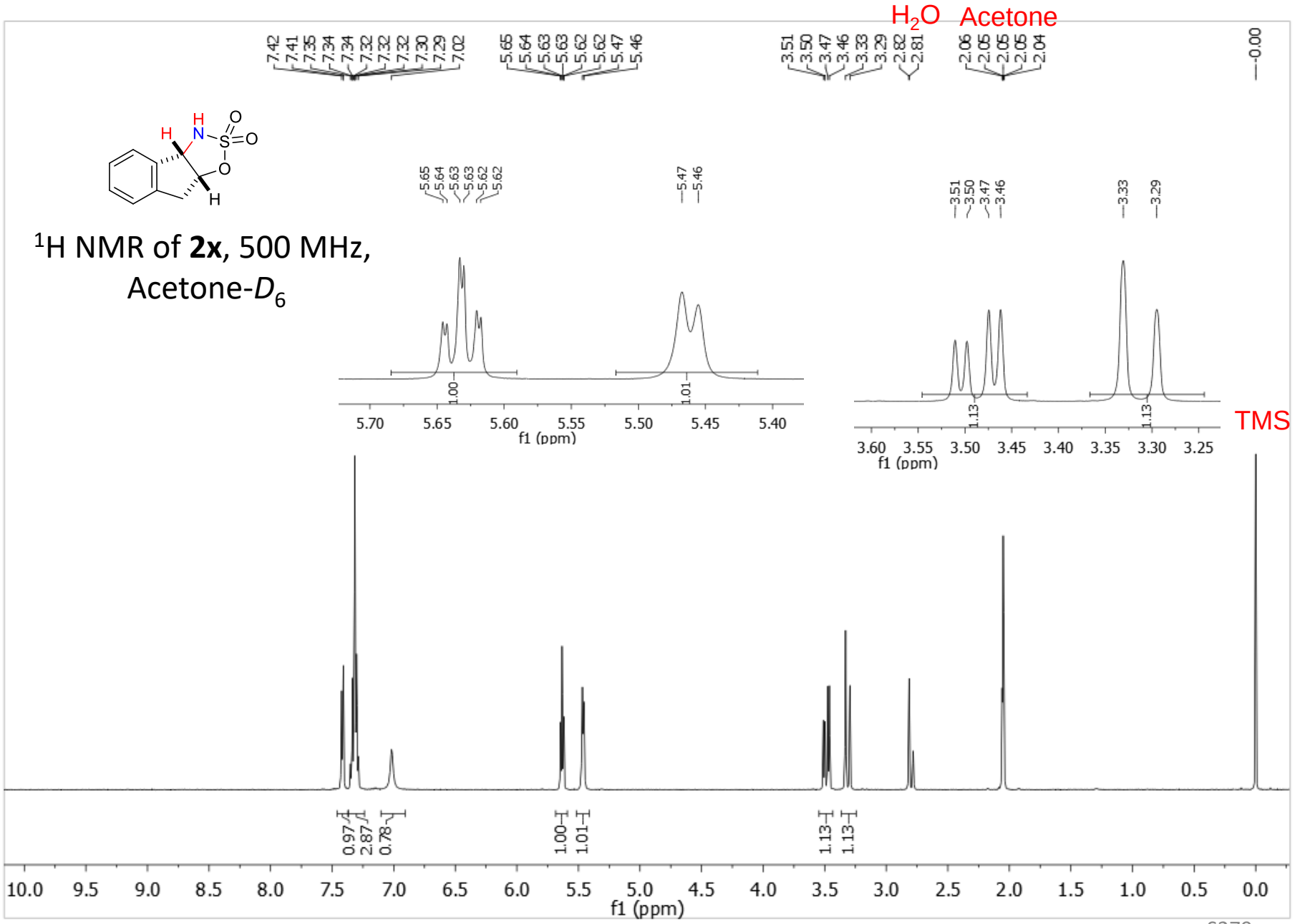
(+)-**2w**

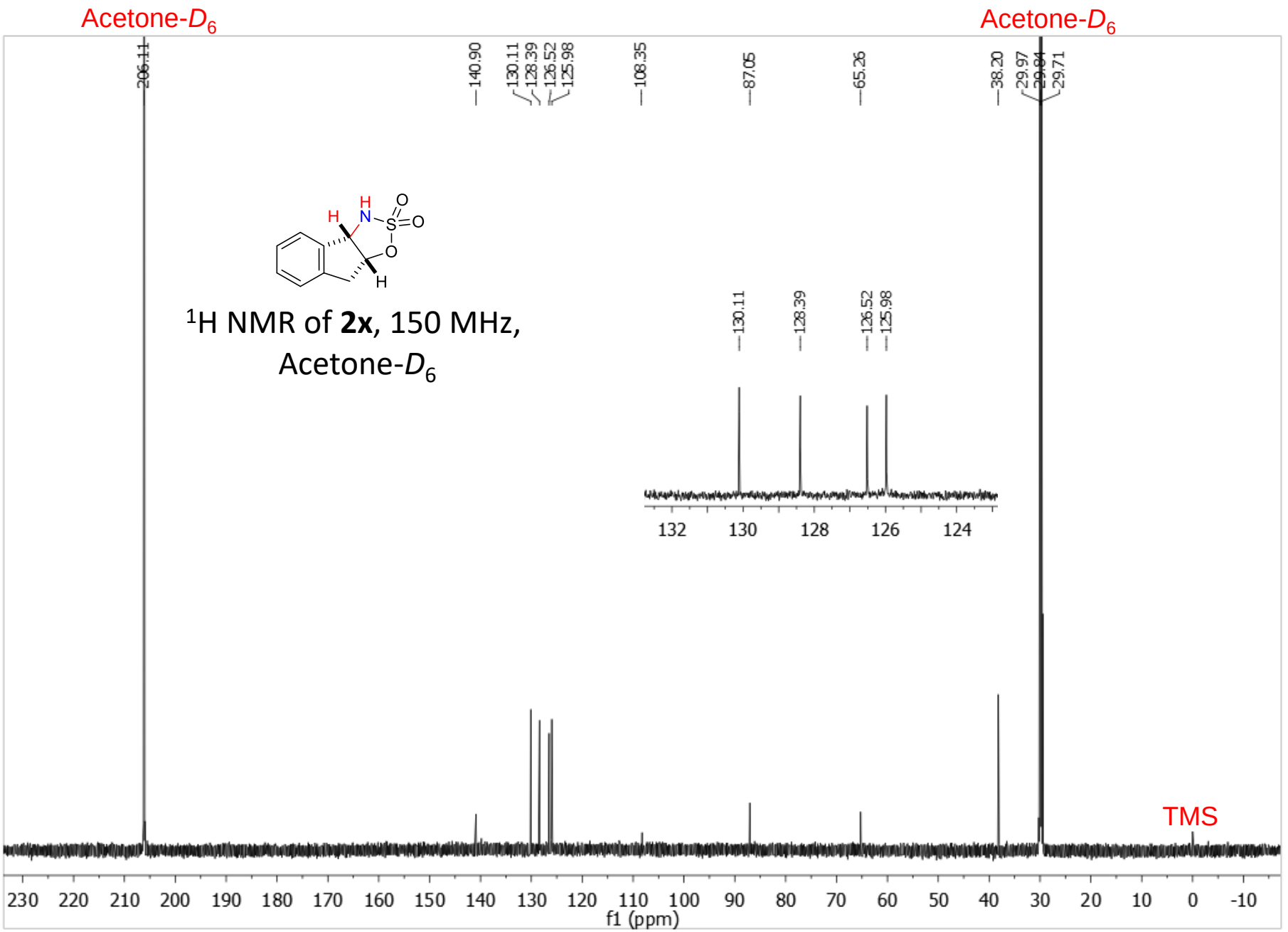


3: 210 nm, 4
nm Results

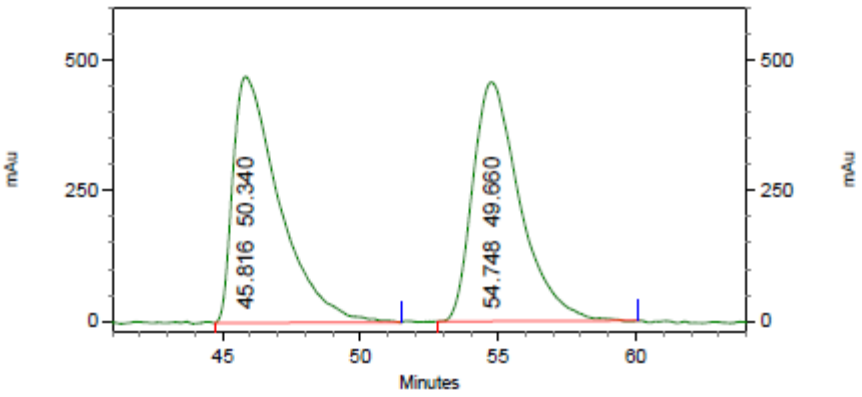
Pk #	Retention Time	Area Percent
1	6.776	1.044
2	7.440	98.956

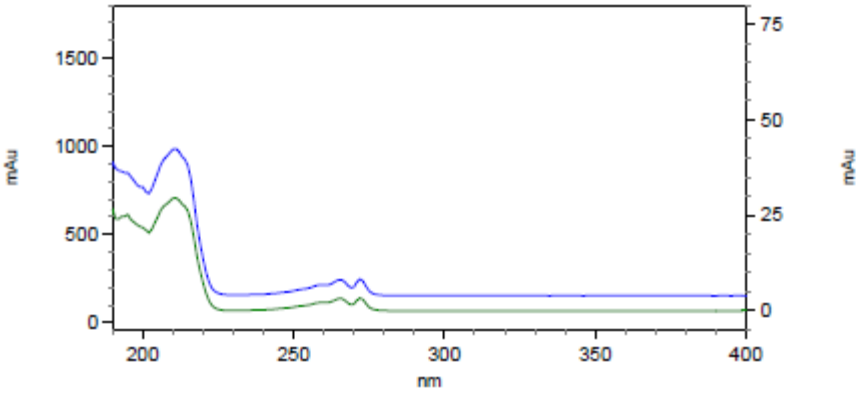
Totals	
	100.000

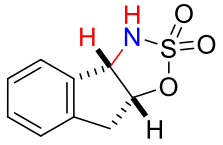

H2O
Acetone
TMS
1H NMR of 2x, 500 MHz,
Acetone-D6
f1 (ppm)


Acetone-D_6
Acetone-D_6
206.11
140.90
130.11
128.39
126.52
125.98
108.35
87.05
65.26
38.20
29.97
29.84
29.71
TMS
^{1}H NMR of **2x**, 150 MHz,
Acetone-D_6
130.11
128.39
126.52
125.98
132
130
128
126
124
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

K0L-361-ODH-10%
C:\EZStart\Projects\Default\Method\lk7%1.0.met
C:\EZStart\Projects\Default\Data\K0L-361-ODH-10%





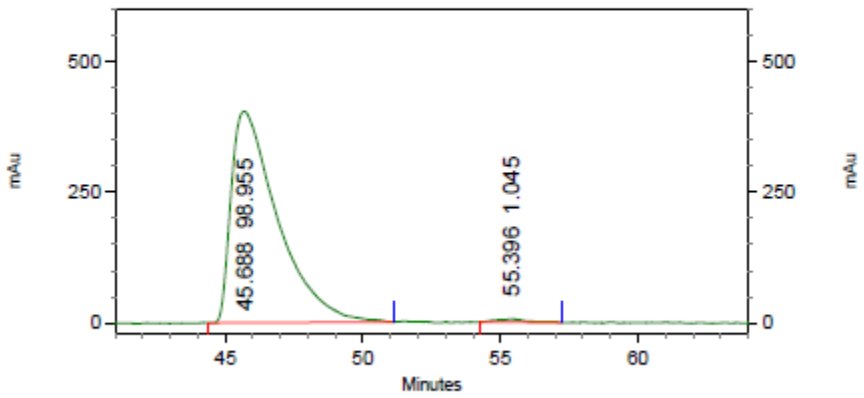


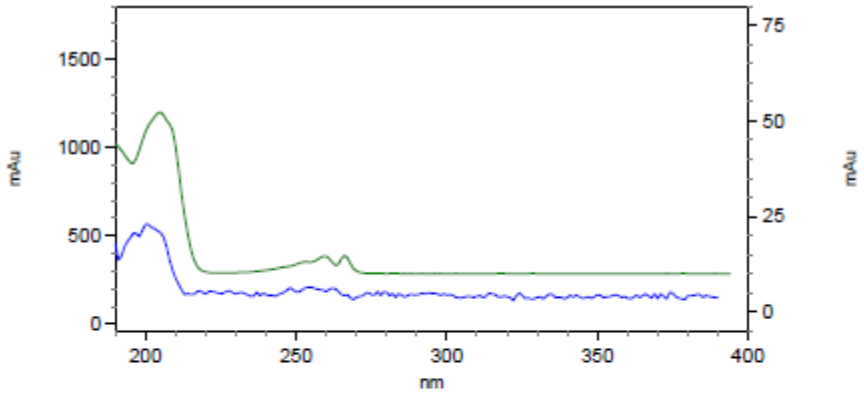
(±)-**2x**

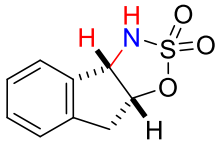
4: 208 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	45.816	50.340	1
	54.748	49.660	2
Totals		100.000	

K0L-360-ODH-10%
C:\EZStart\Projects\Default\Method\1k7%1.0.met
C:\EZStart\Projects\Default\Data\K0L-360-ODH-10%



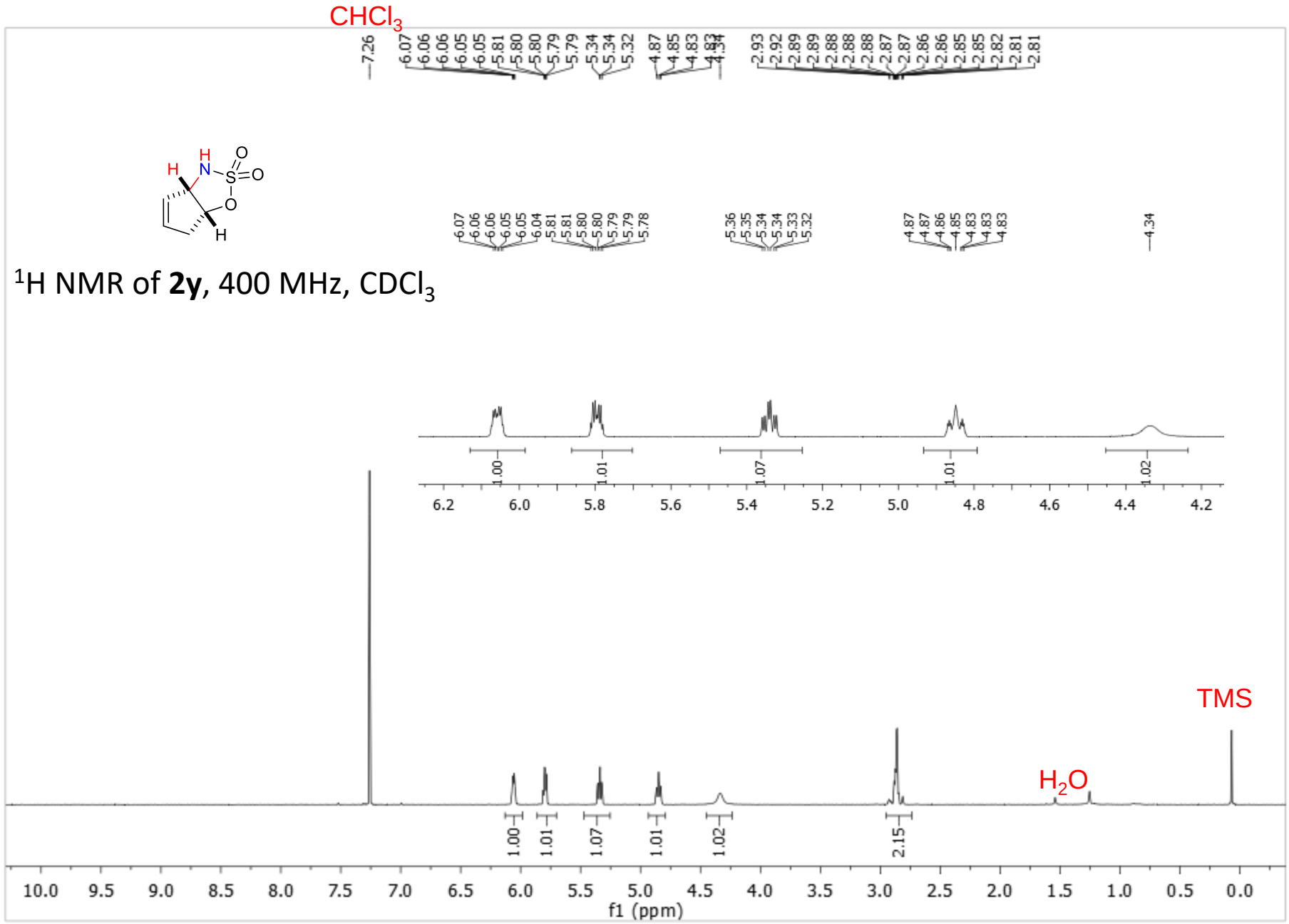




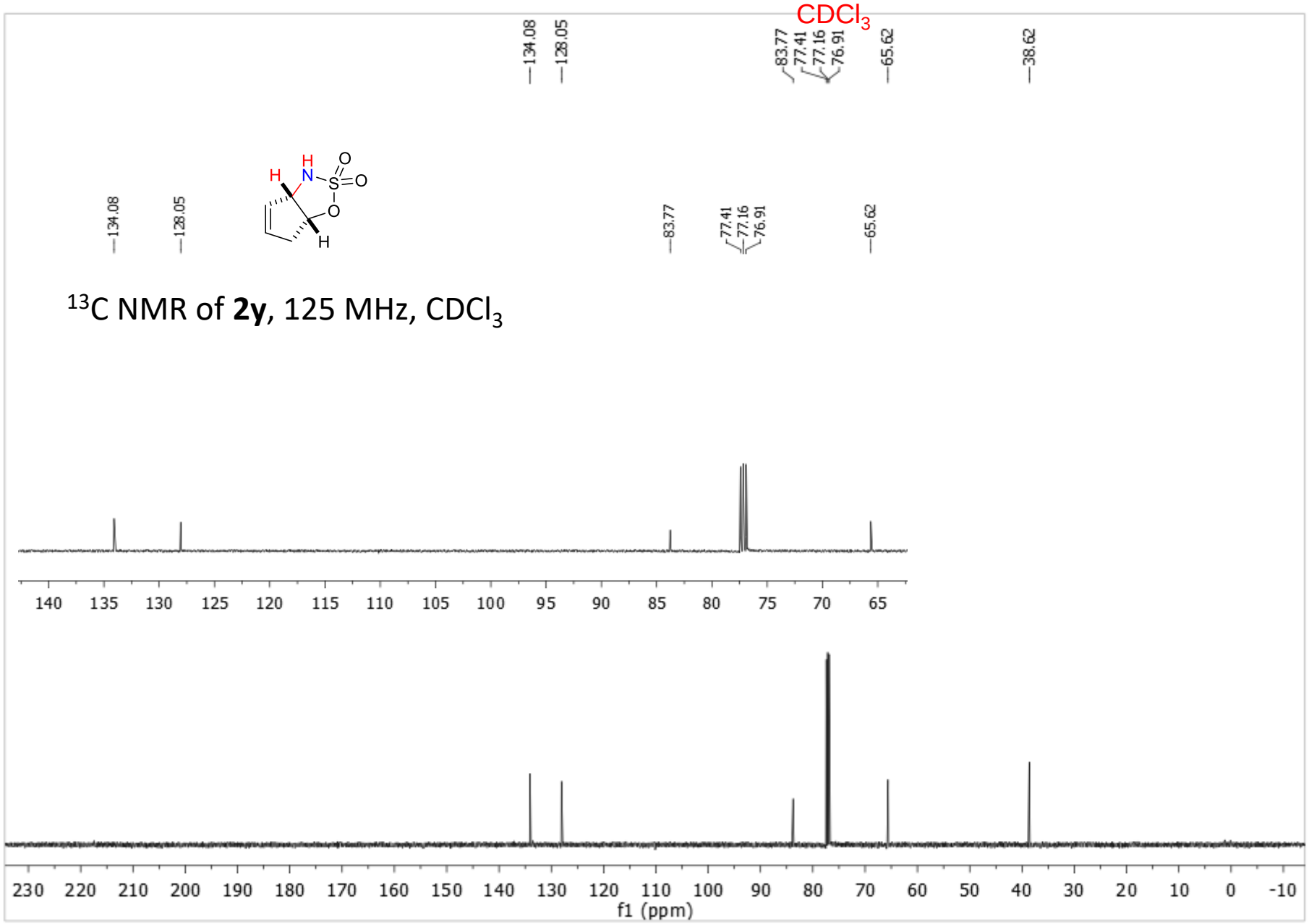
(-)-**2x**

4: 208 nm, 4 nm
Results

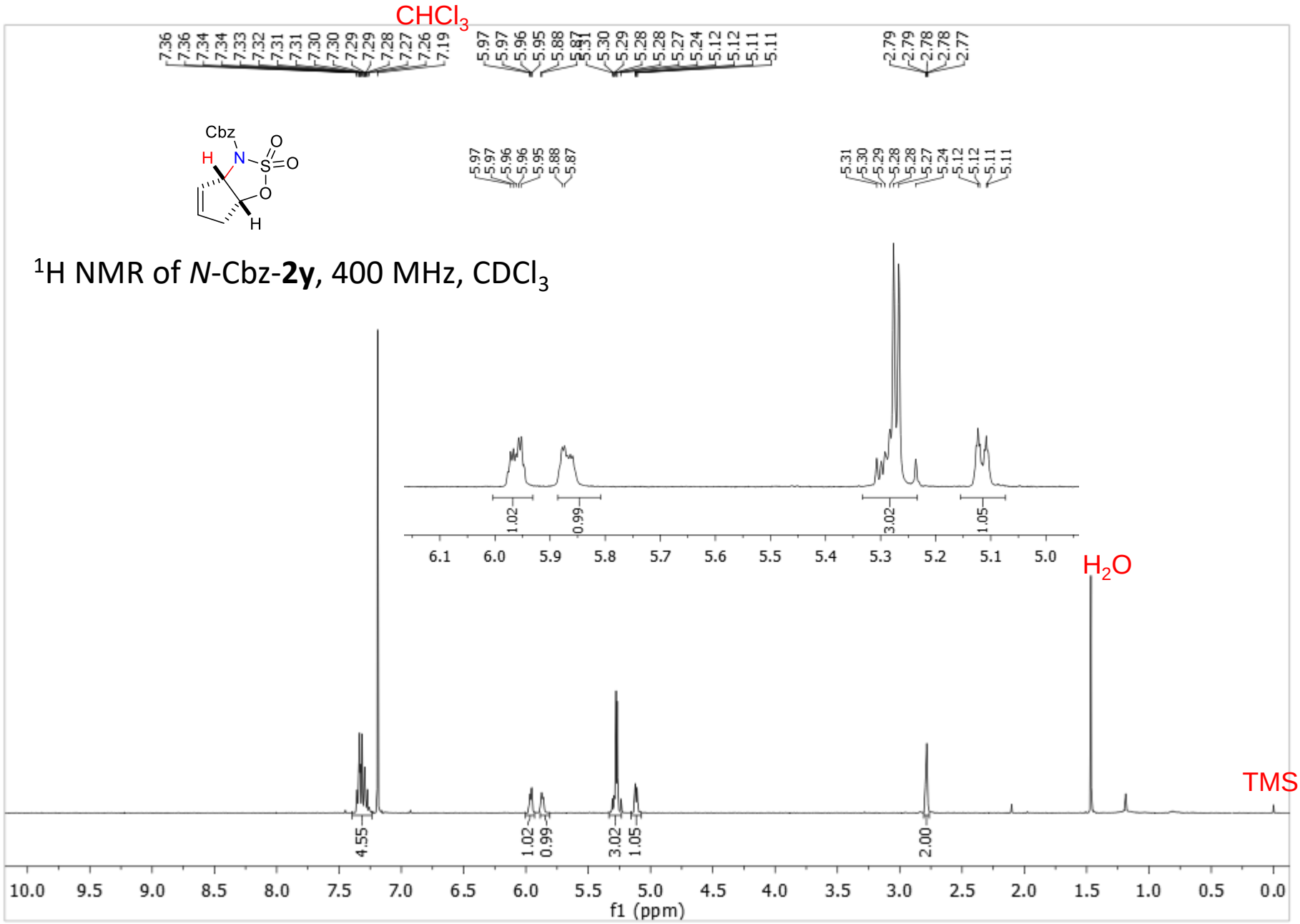
Name	Retention Time	Area Percent	Pk #
	45.688	98.955	1
	55.396	1.045	2
Totals		100.000	

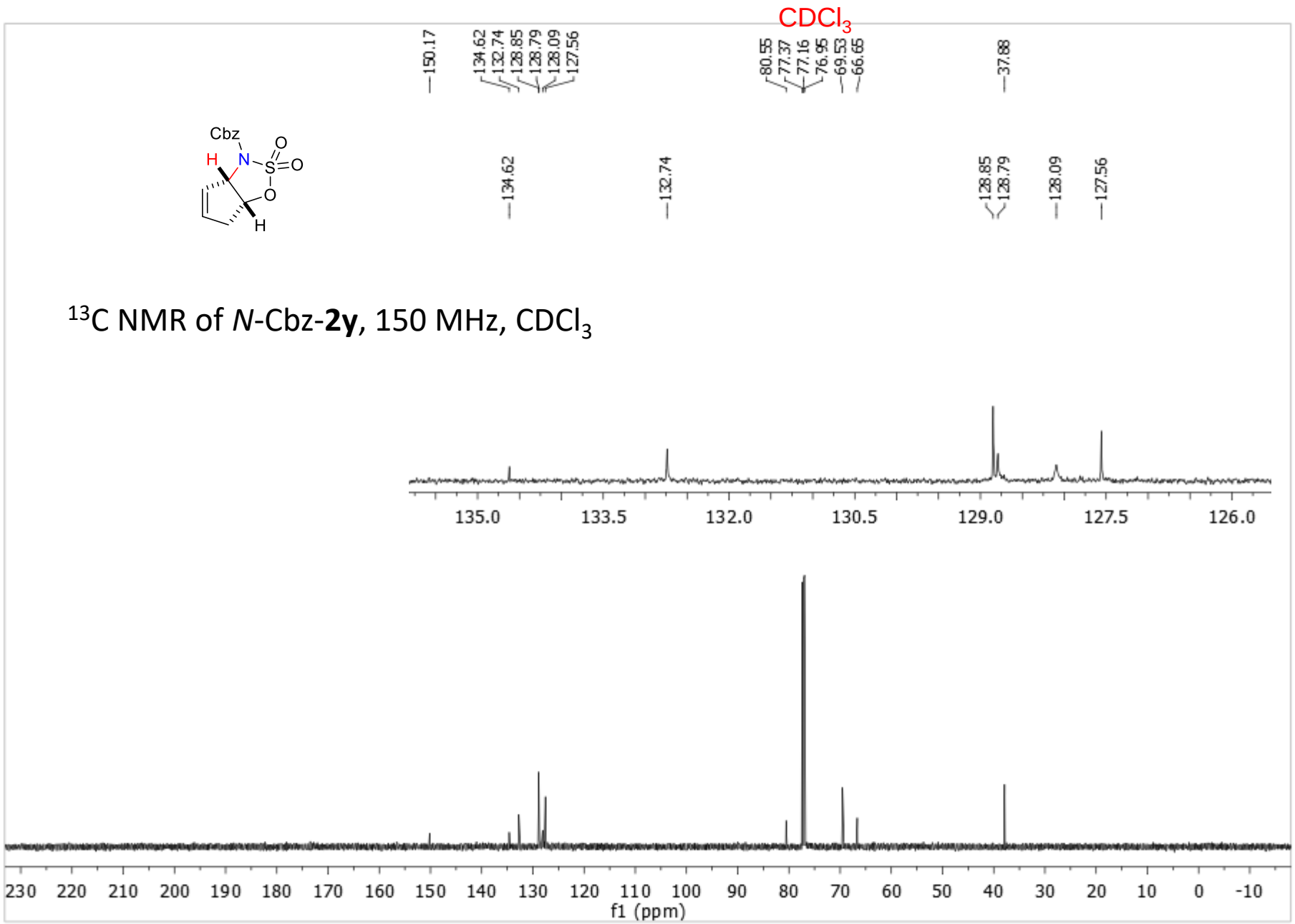


^{1}H NMR of **2y**, 400 MHz, $CDCl_3$

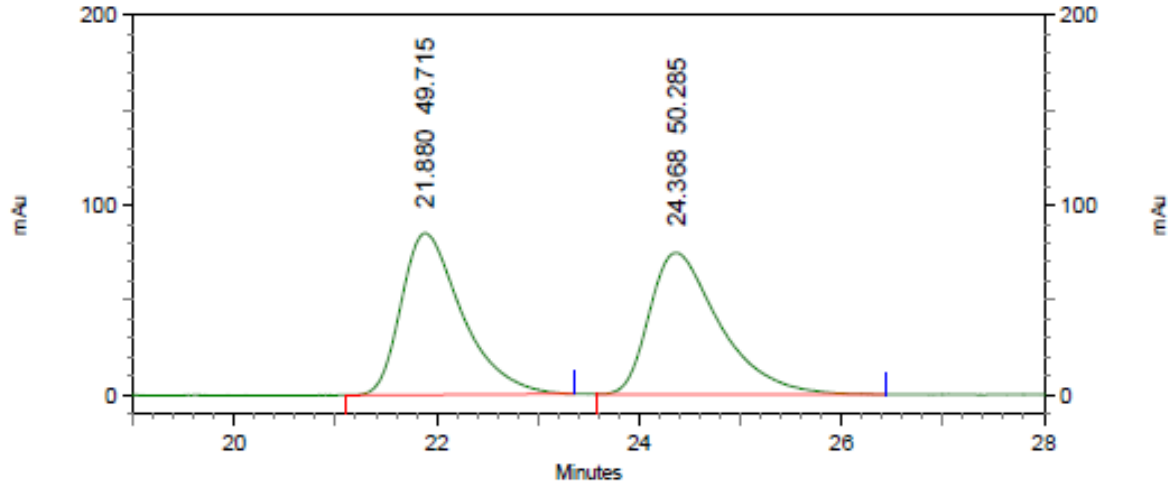


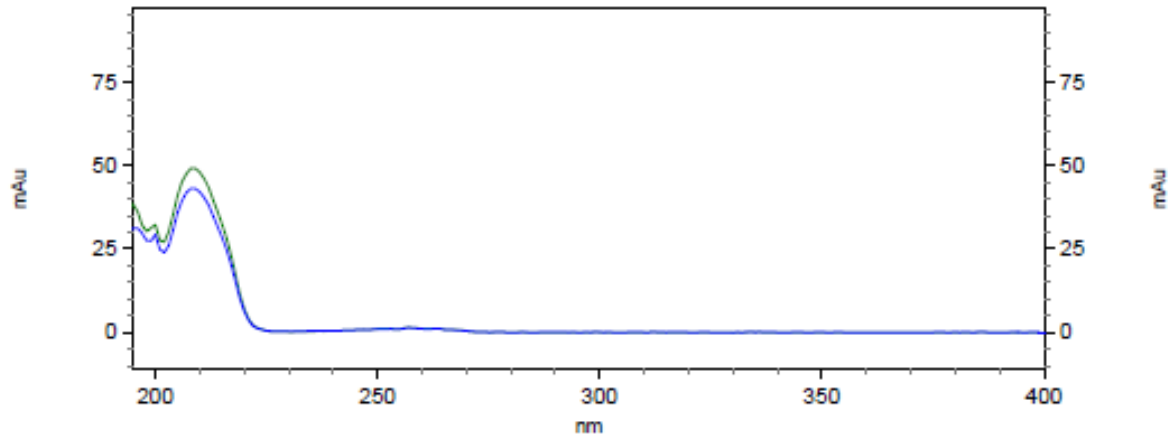
^{13}C NMR of **2y**, 125 MHz, $CDCl_3$

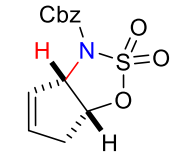

CHCl3
Cbz
H
N
S
O
O
O
H
1H NMR of N-Cbz-2y, 400 MHz, CDCl3
H2O
TMS
4.55
1.02
0.99
3.02
1.05
2.00
f1 (ppm)



^{13}C NMR of *N*-Cbz-**2y**, 150 MHz, $CDCl_3$





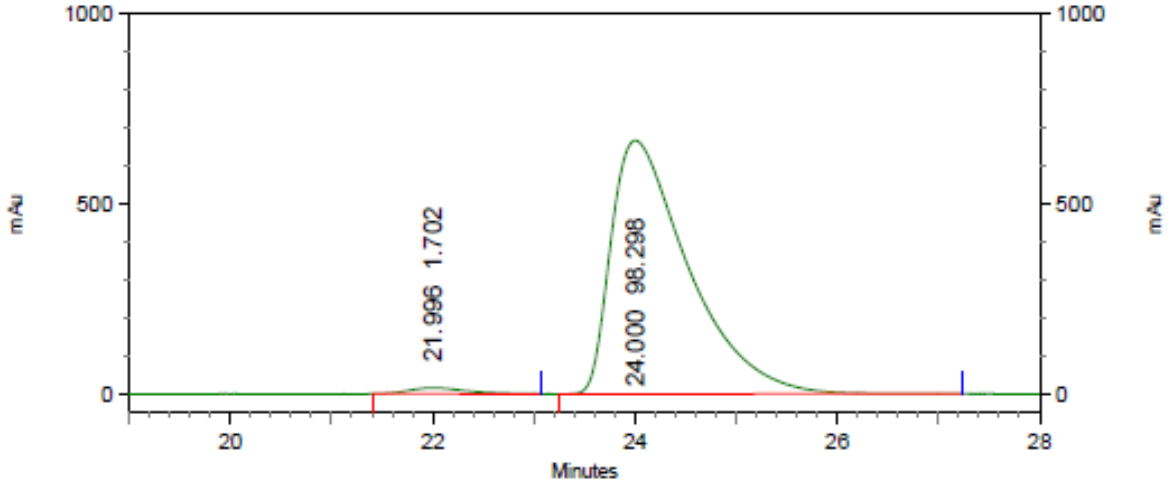


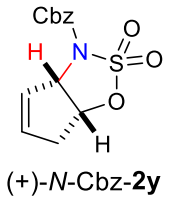
(±)-*N*-Cbz-**2y**

4: 212 nm, 4
nm Results

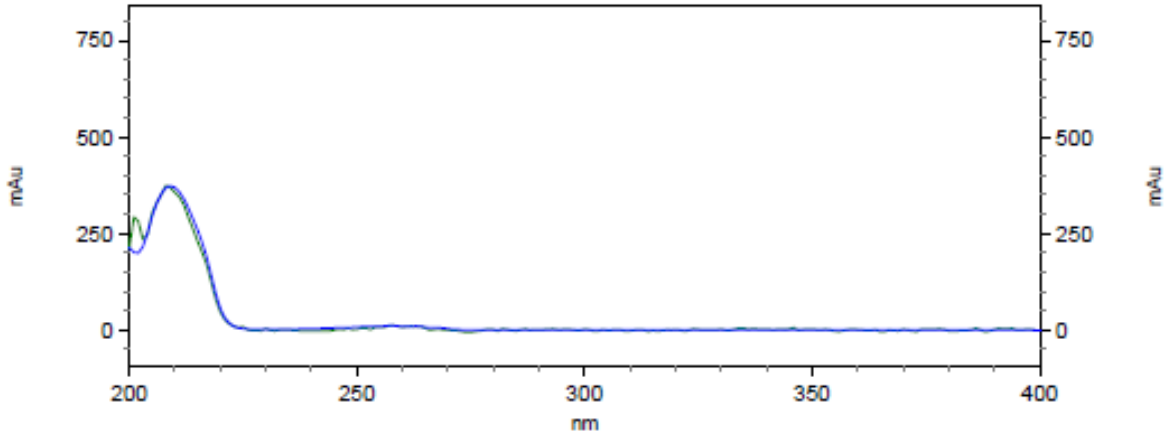
Pk #	Retention Time	Area Percent
1	21.880	49.715
2	24.368	50.285

Totals	
	100.000





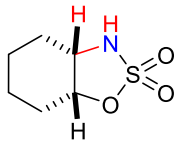
(+)-*N*-Cbz-**2y**



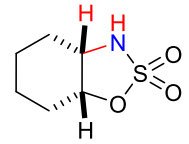
4: 212 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	21.996	1.702
2	24.000	98.298
Totals		100.000

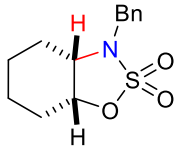
$CHCl_3$



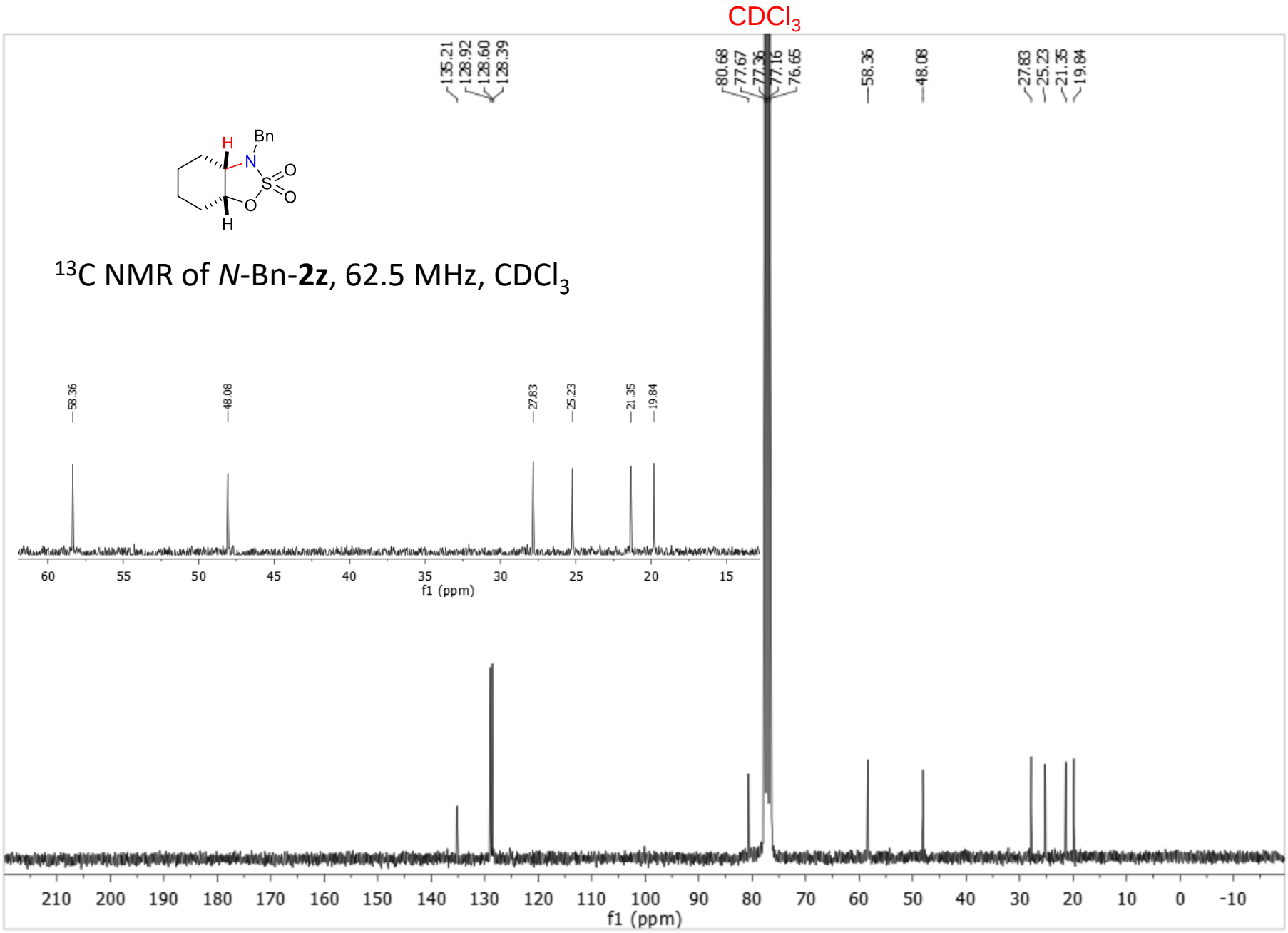
^{1}H NMR of **2z**, 400 MHz, $CDCl_3$

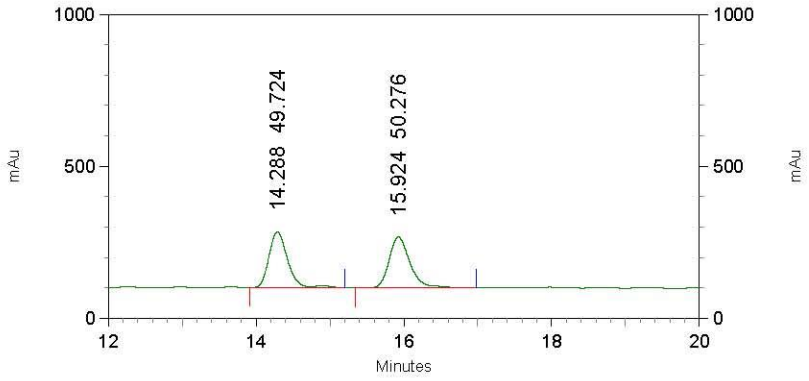


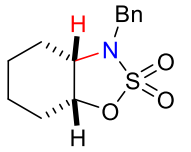
^{13}C NMR of **2z**, 100 MHz, $CDCl_3$



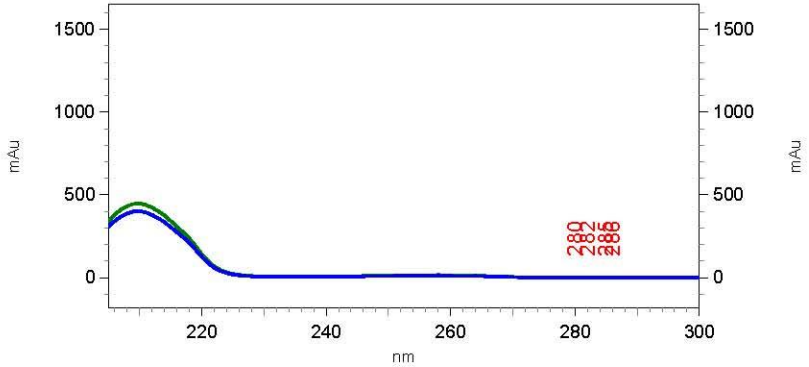
^{1}H NMR of *N*-Bn-**2z**, 250 MHz, $CDCl_3$


CDCl3
135.21
128.92
128.60
128.39
80.68
77.67
77.36
77.16
76.65
58.36
48.08
27.83
25.23
21.35
19.84
H
Bn
N
S
O
O
O
H
13C NMR of N-Bn-2z, 62.5 MHz, CDCl3
f1 (ppm)
f1 (ppm)





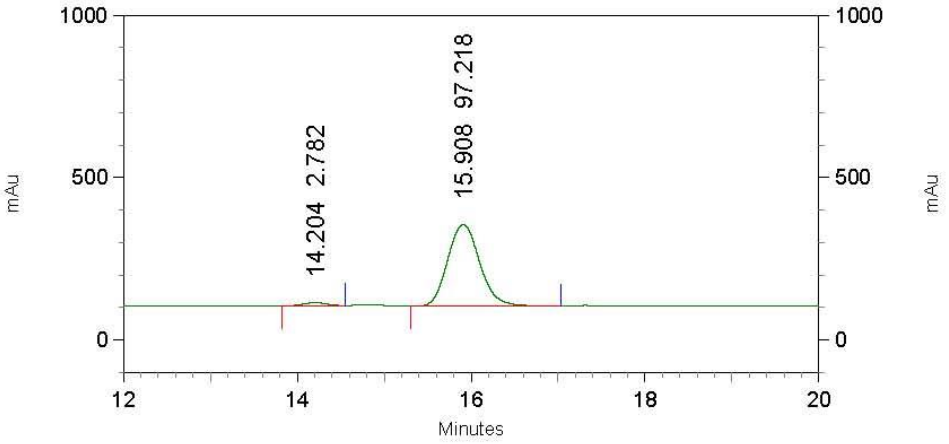
(±)-*N*-Bn-**2z**

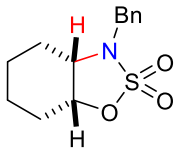


18: 219 nm, 4 nm
Results

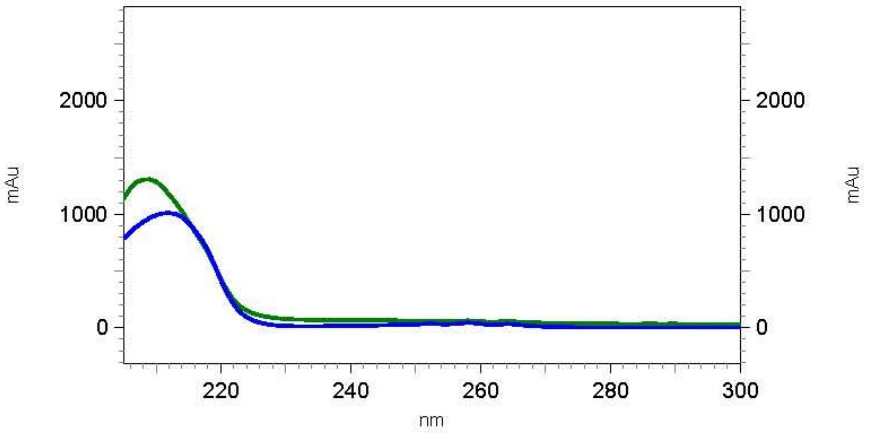
Pk #	Name	Retention Time	Area Percent
1		14.288	49.724
2		15.924	50.276

Totals			100.000





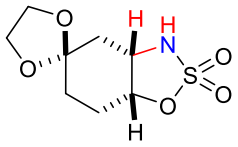
(+)-*N*-Bn-**2z**



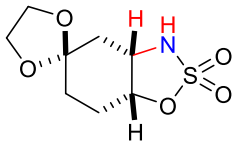
17: 221 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		14.204	2.782
2		15.908	97.218
Totals			100.000

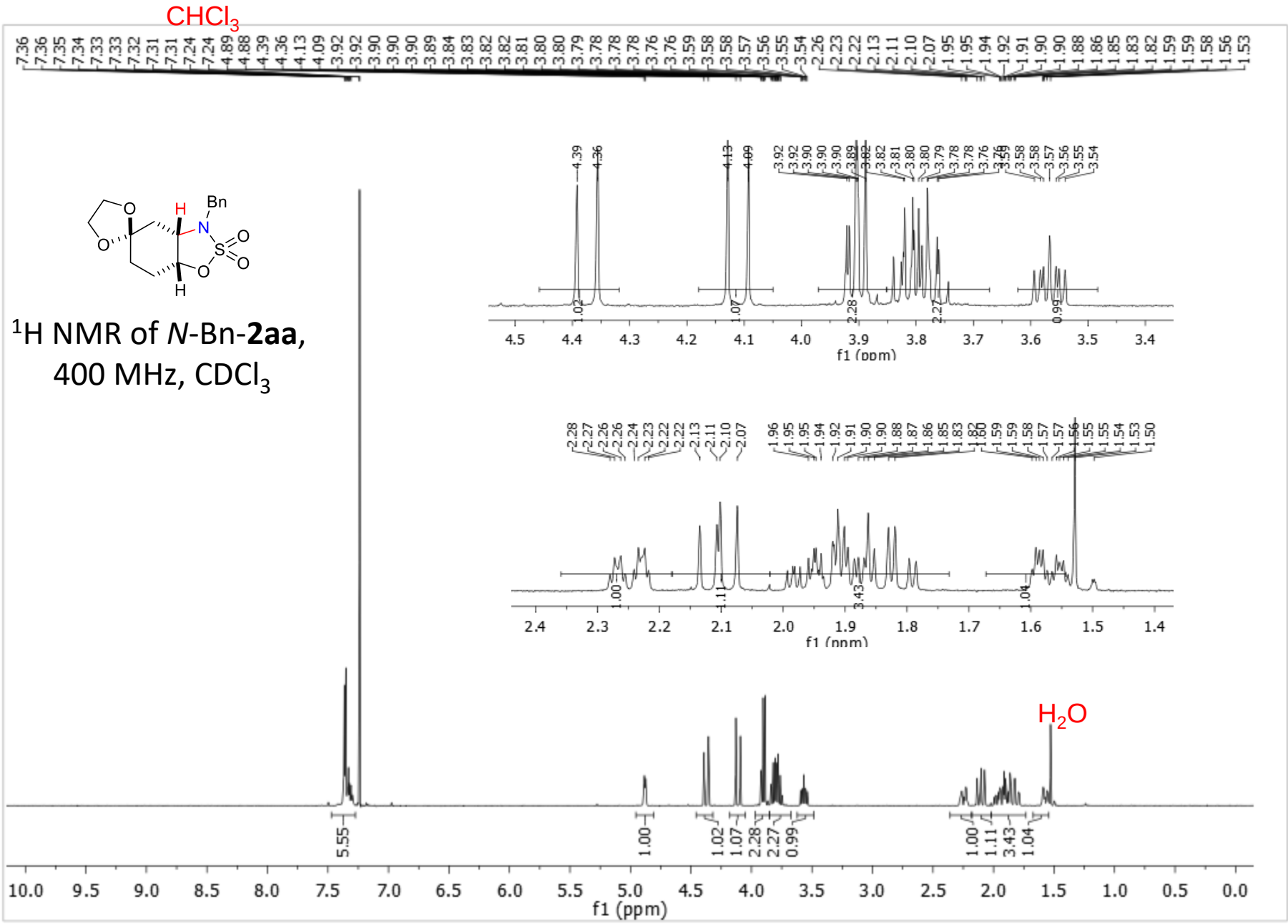
$CHCl_3$



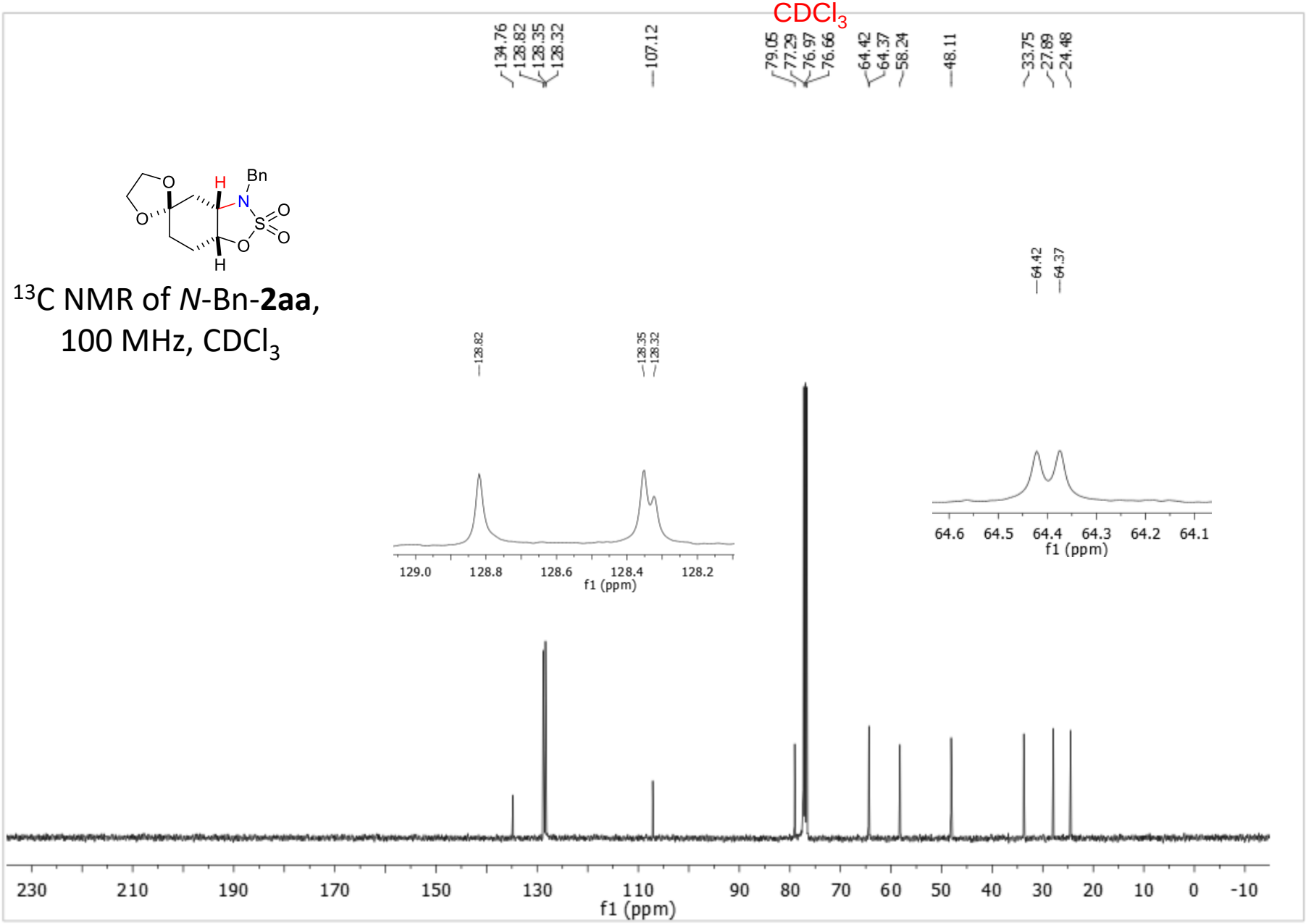
^{1}H NMR of **2aa**, 400 MHz, $CDCl_3$



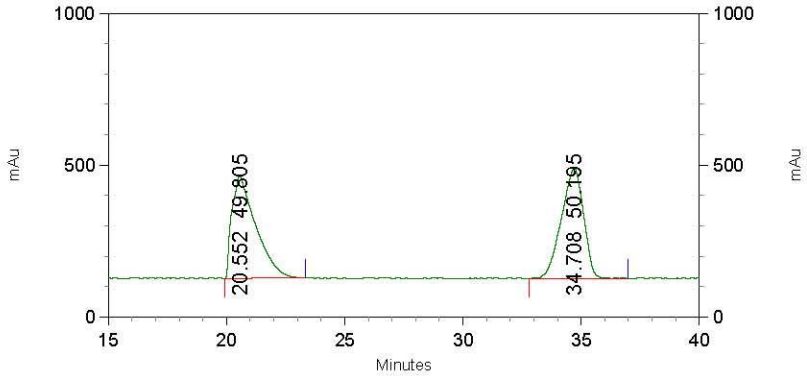
^{13}C NMR of **2aa**, 100 MHz, $CDCl_3$

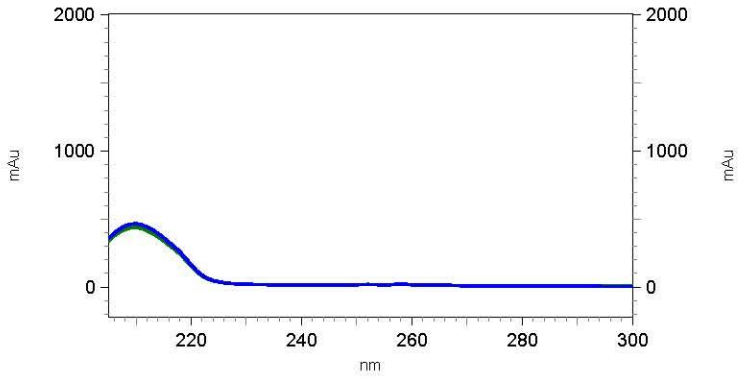


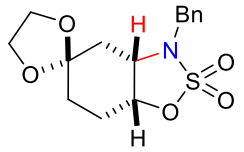
^{1}H NMR of *N*-Bn-**2aa**,
400 MHz, $CDCl_3$



^{13}C NMR of *N*-Bn-**2aa**, 100 MHz, $CDCl_3$



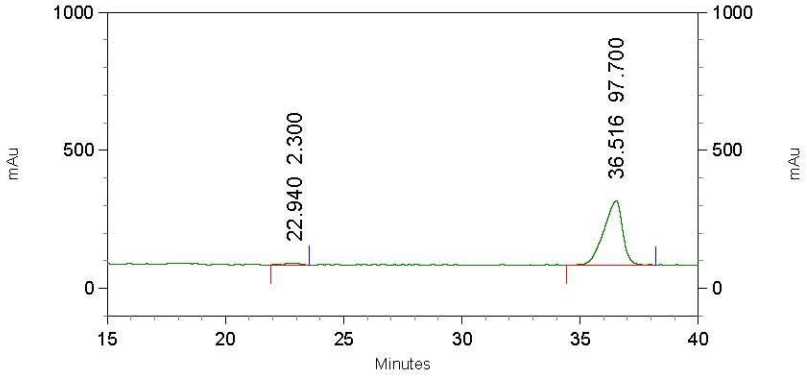


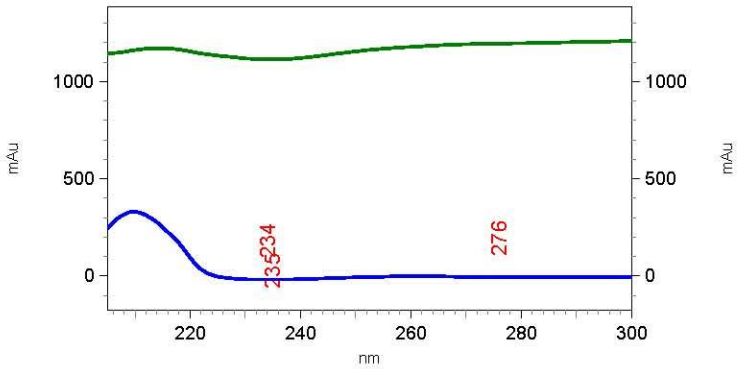


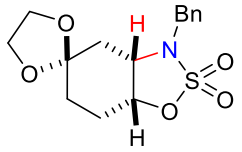
(±)-*N*-Bn-**2aa**

17: 214 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		20.552	49.805
2		34.708	50.195
Totals			100.000



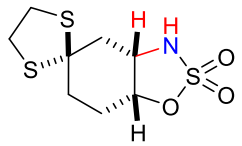




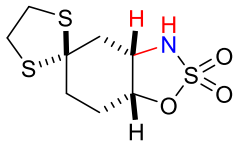
(+)-*N*-Bn-**2aa**

19: 214 nm, 4 nm
Results

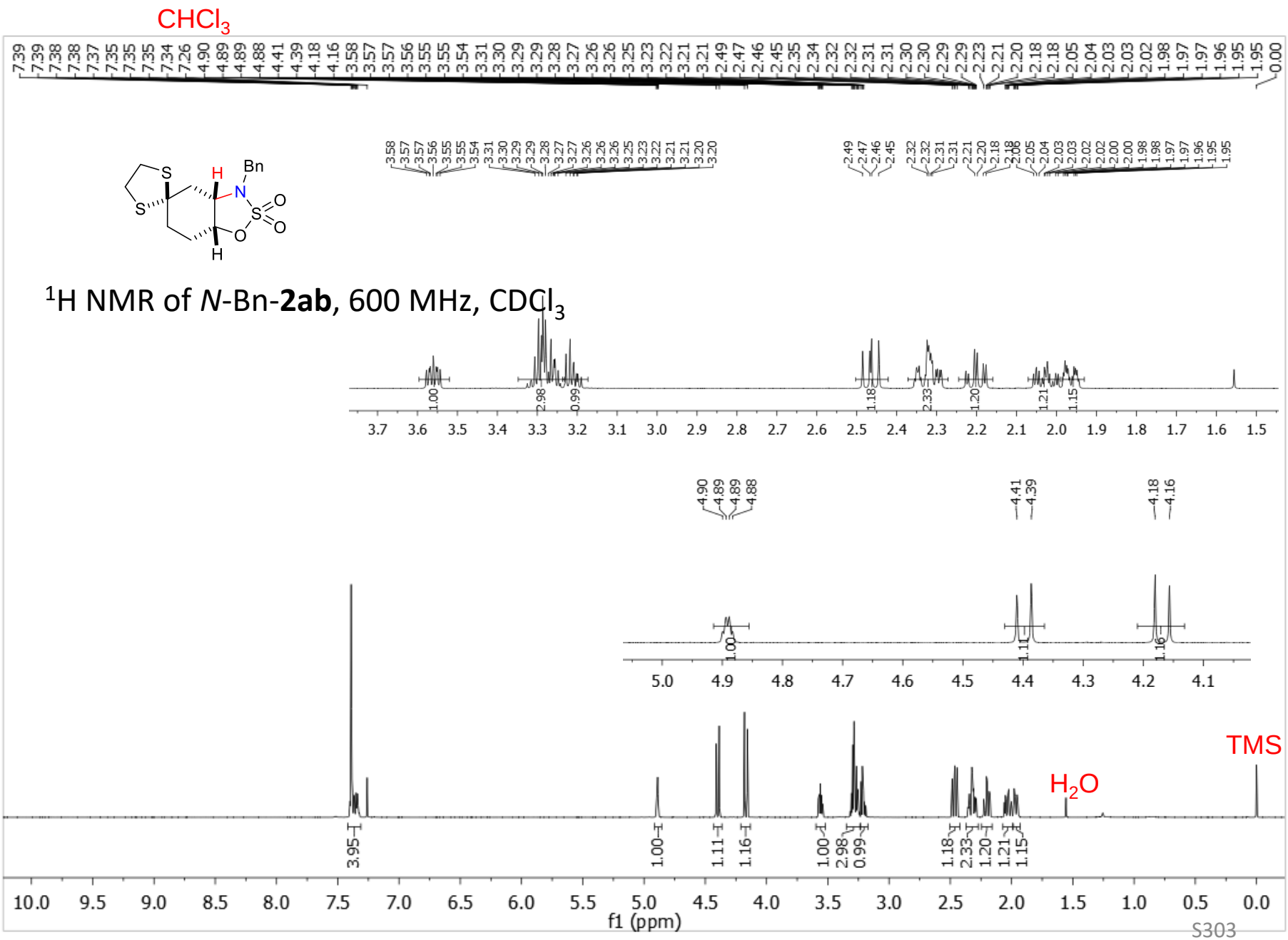
Pk #	Name	Retention Time	Area Percent
1		22.940	2.300
2		36.516	97.700
Totals			100.000

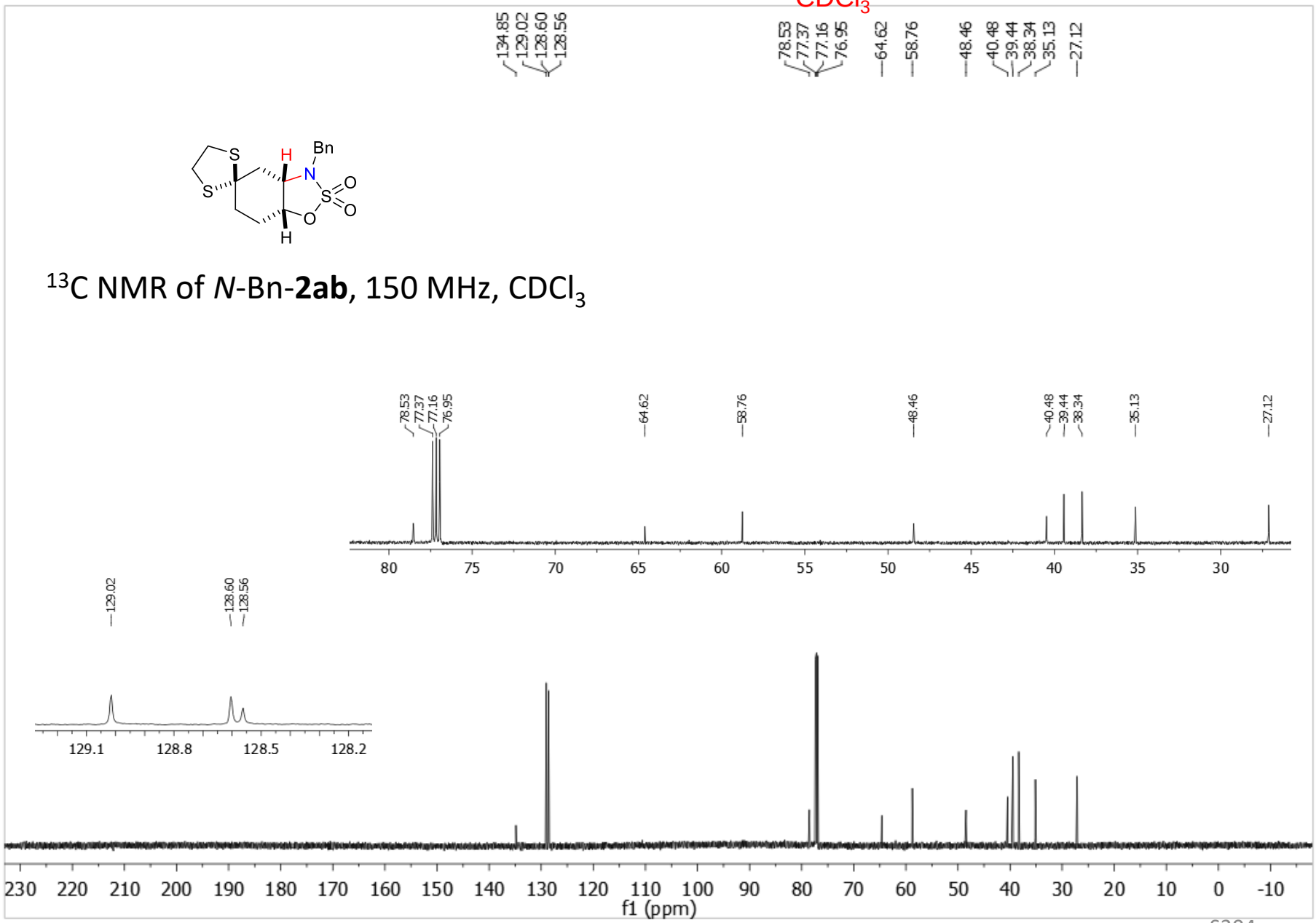


^{1}H NMR of **2ab**, 600 MHz, $CDCl_3$



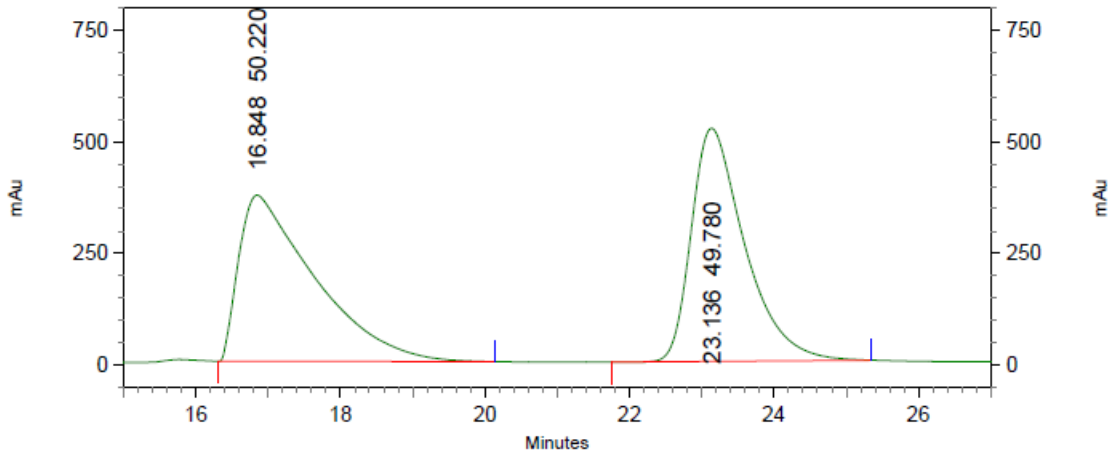
^{13}C NMR of **2ab**, 150 MHz, $CDCl_3$

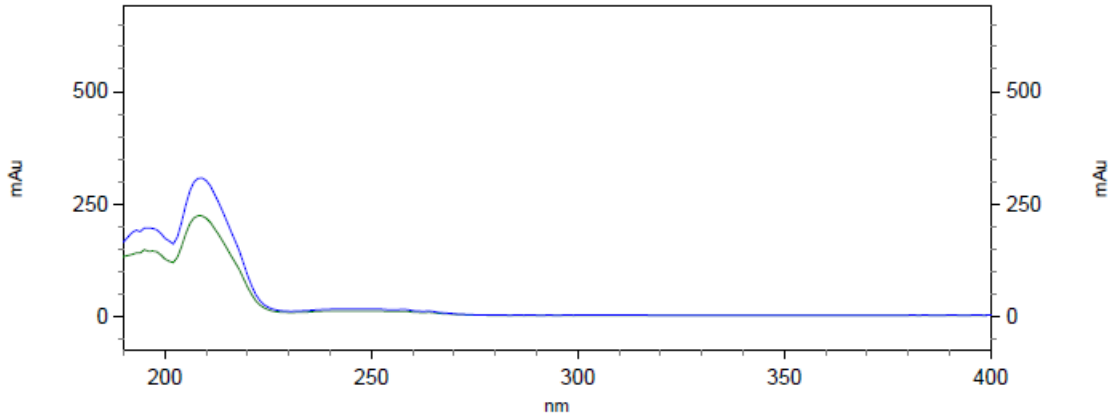

CHCl3
S
H
Bn
N
S
O
O
O
H
1H NMR of N-Bn-2ab, 600 MHz, CDCl3
TMS
H2O
f1 (ppm)

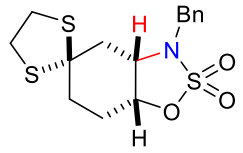


^{13}C NMR of *N*-Bn-**2ab**, 150 MHz, $CDCl_3$

C:\EZStart\Projects\Default\Data\K0L-459-ADH-20%1.0
C:\Documents and Settings\zhang\Desktop\DSW\06052018.met





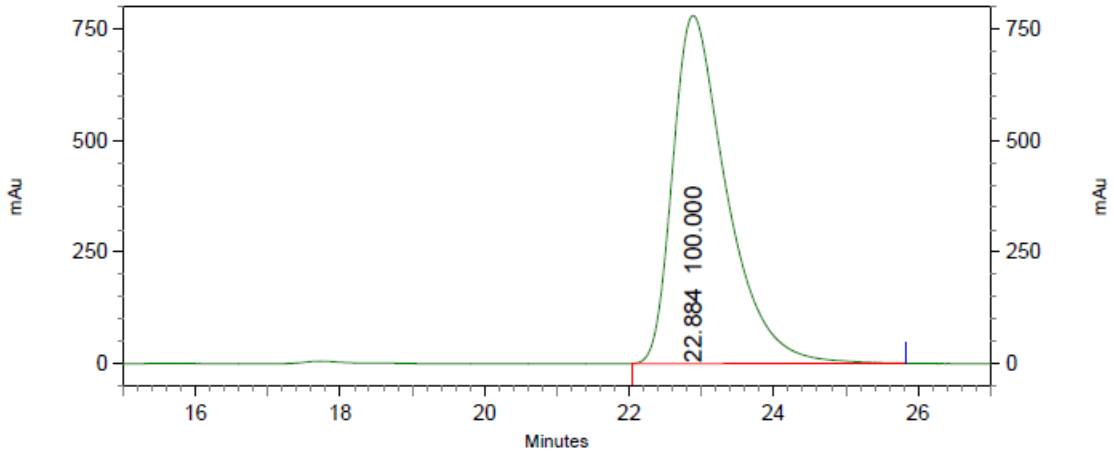


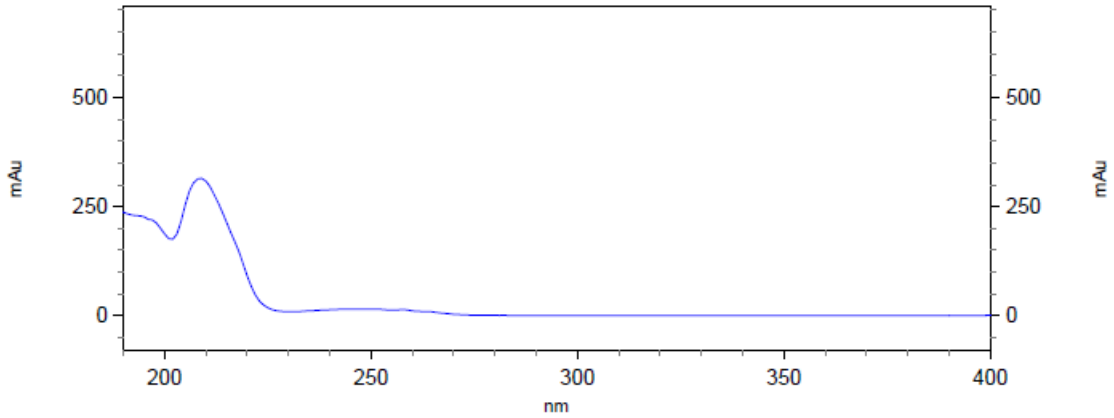
(±)-*N*-Bn-**2ab**

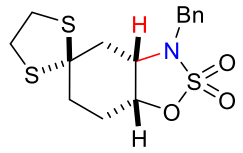
4: 215 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	16.848	50.220
2	23.136	49.780
Totals		100.000

C:\EZStart\Projects\Default\Data\K0L-458-ADH-20%1.0
C:\Documents and Settings\zhang\Desktop\DSW\06052018.met





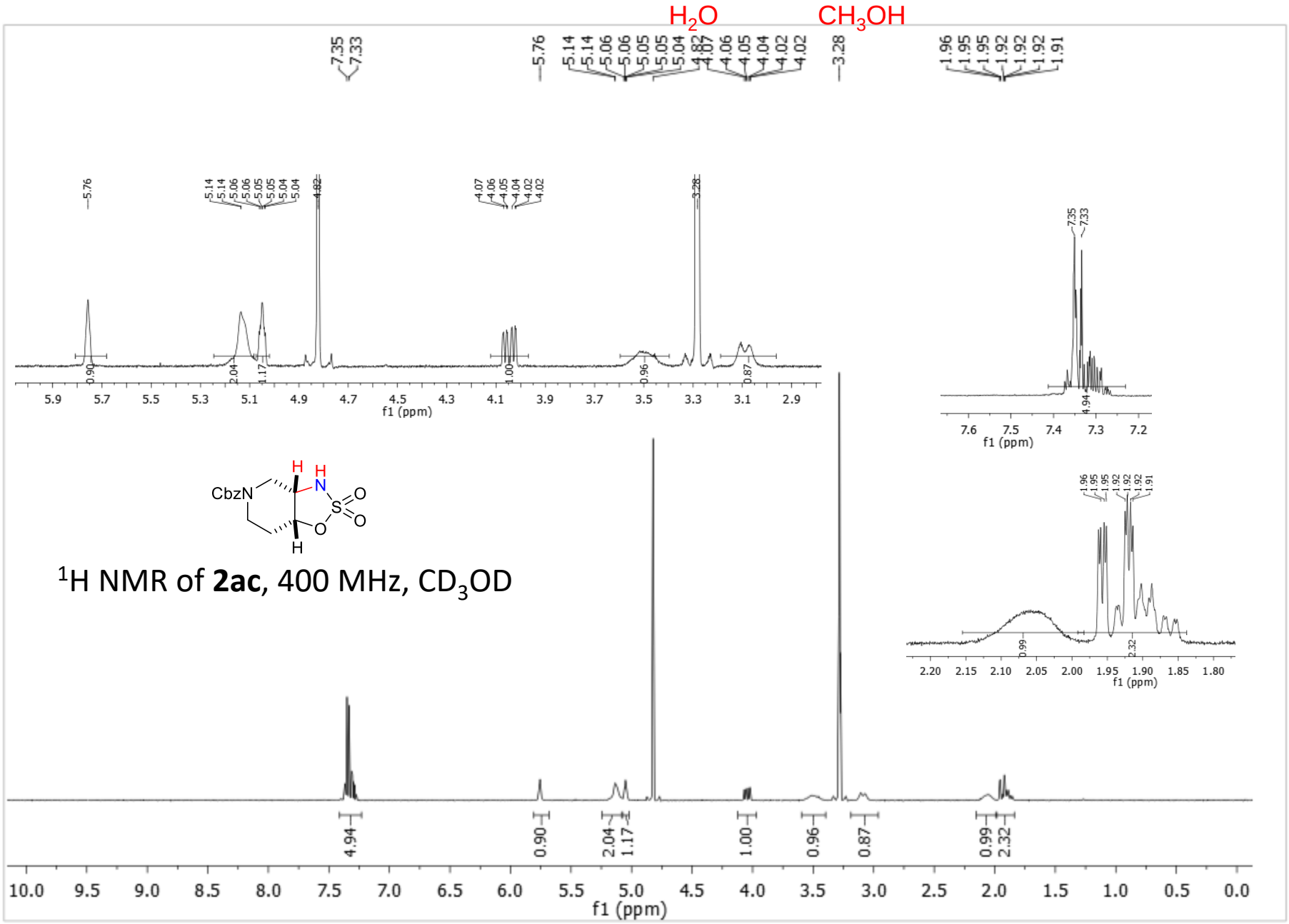


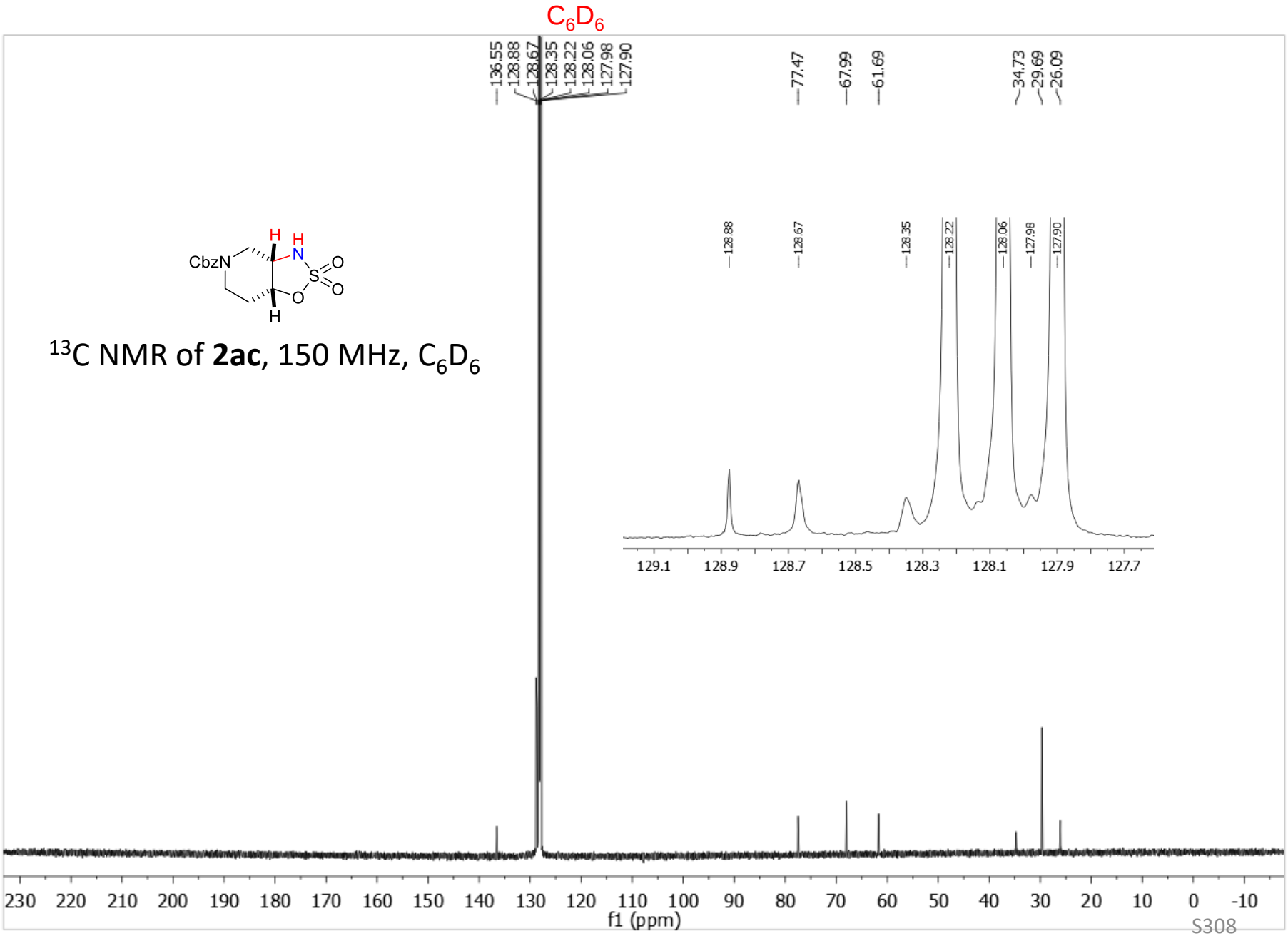
(+)-*N*-Bn-**2ab**

4: 213 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	22.884	100.000

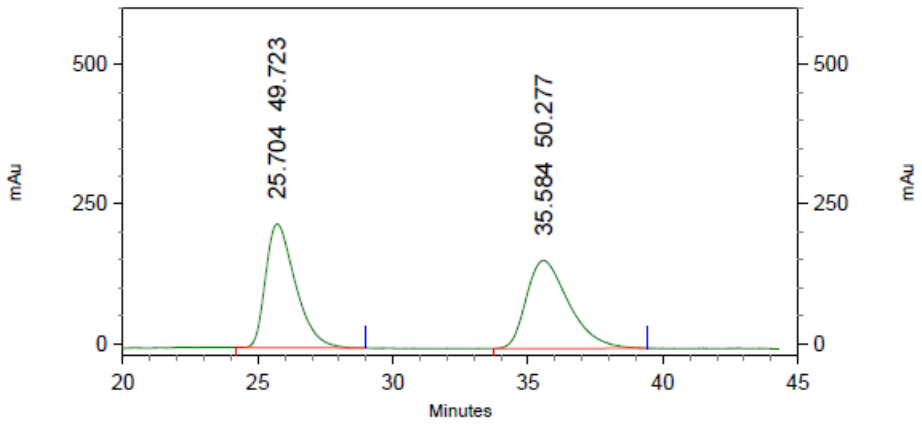
Totals	
	100.000

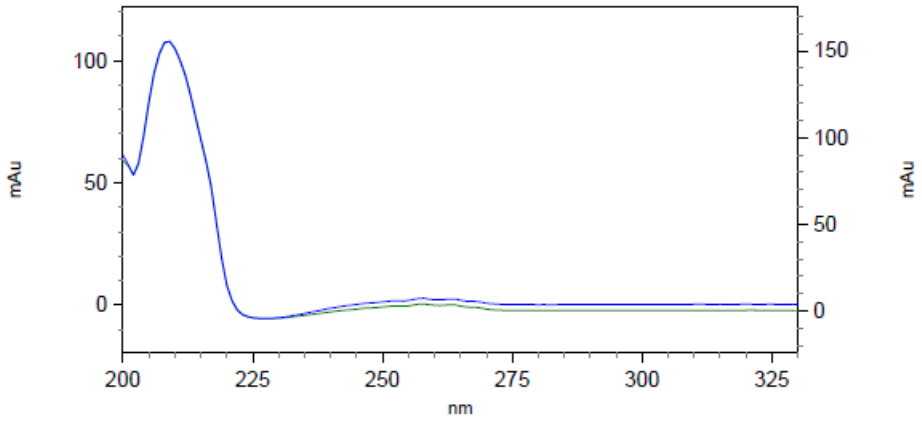

H2O
CH3OH
CbzN
H
N
S
O
O
O
H
1H NMR of 2ac, 400 MHz, CD3OD
f1 (ppm)

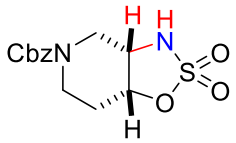


^{13}C NMR of **2ac**, 150 MHz, C_6D_6

K0L-374-ODH-20%
C:\EZStart\Projects\Default\Method\LK-2%1mL60MIN.met
C:\EZStart\Projects\Default\Data\K0L-374-ODH-20%







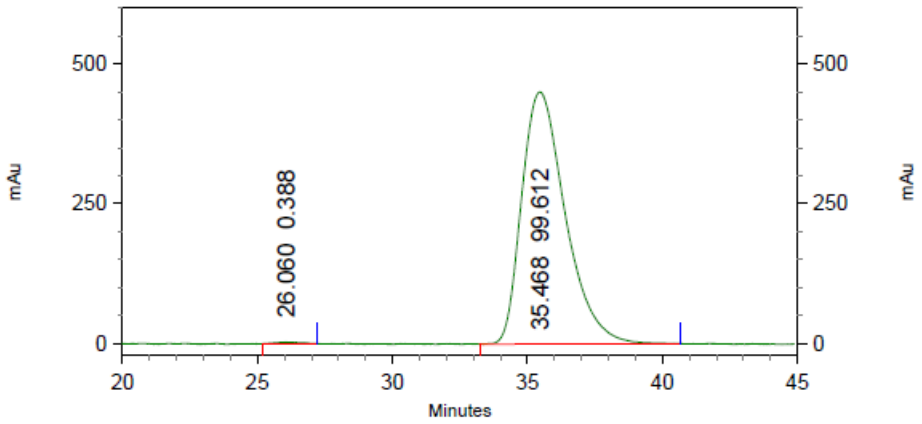
(±)-**2ac**

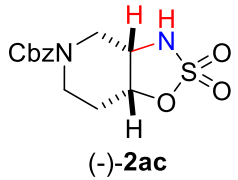
3: 207 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	25.704	49.723	1
	35.584	50.277	2

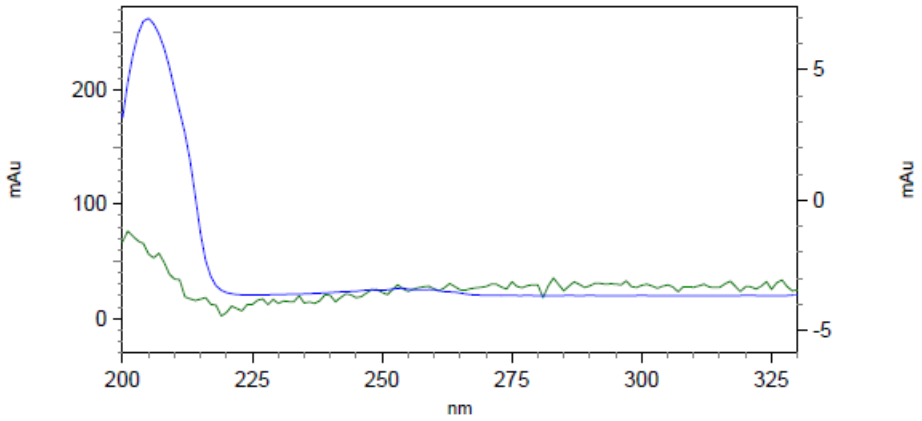
Totals	
	100.000

K0L-373-ODH-20%
C:\EZStart\Projects\Default\Method\LK-2%1mL60MIN.met
C:\EZStart\Projects\Default\Data\K0L-373-ODH-20%





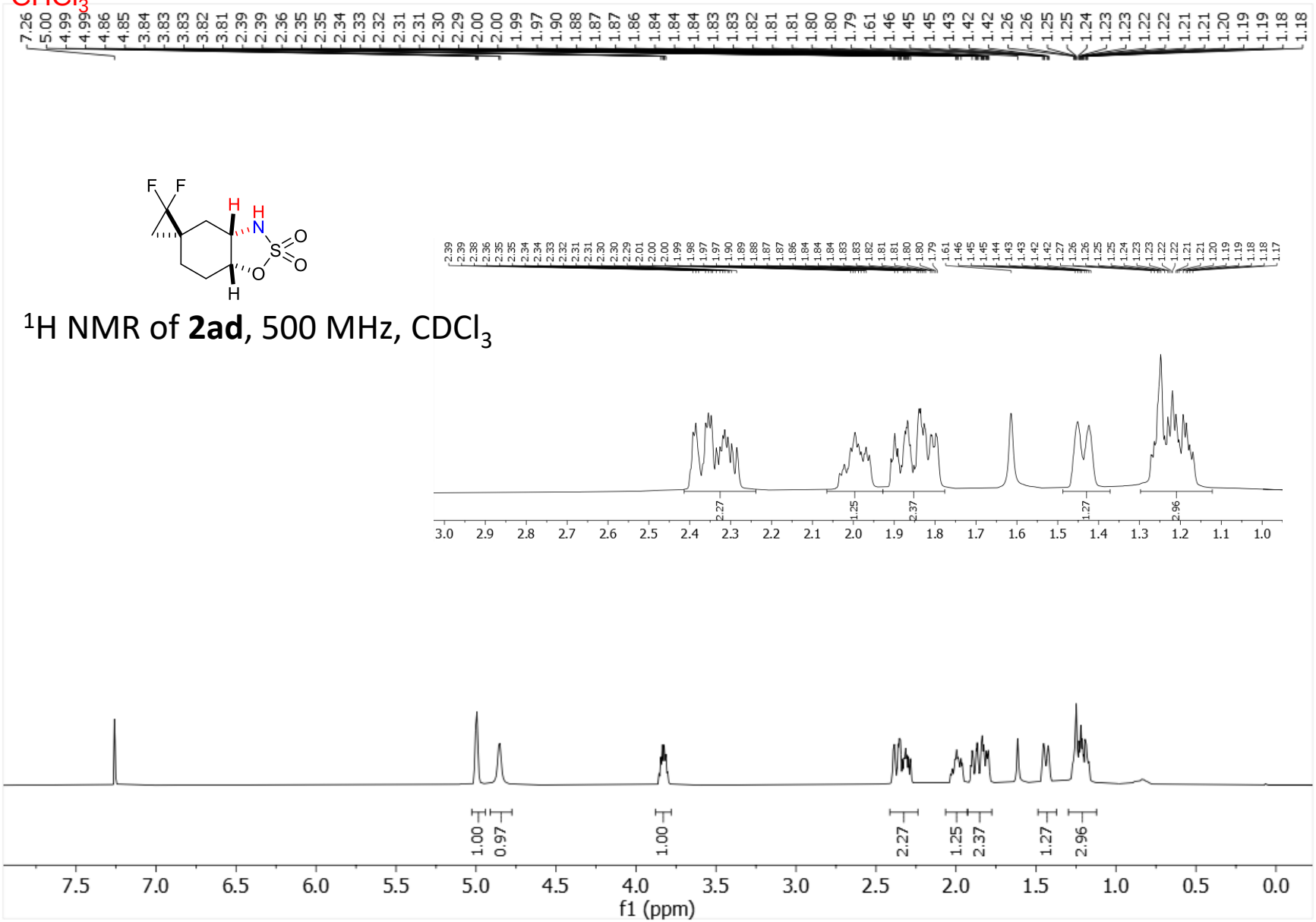
(-)-**2ac**



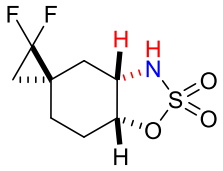
3: 207 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	26.060	0.388	1
	35.468	99.612	2

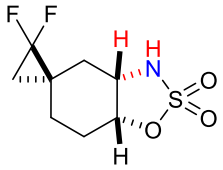
Totals	
	100.000



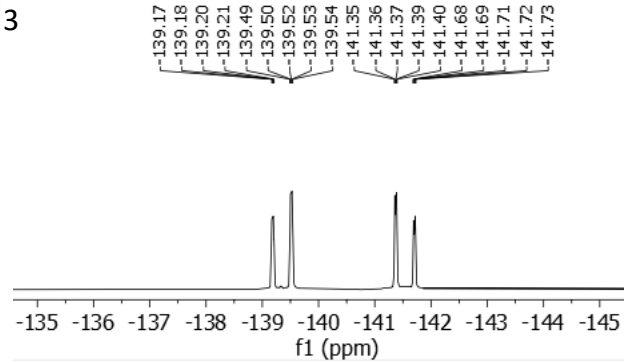
^{1}H NMR of **2ad**, 500 MHz, $CDCl_3$

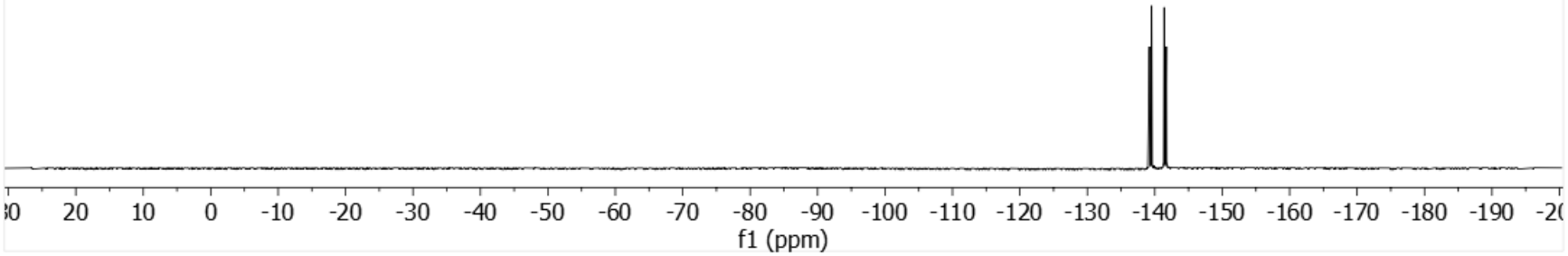


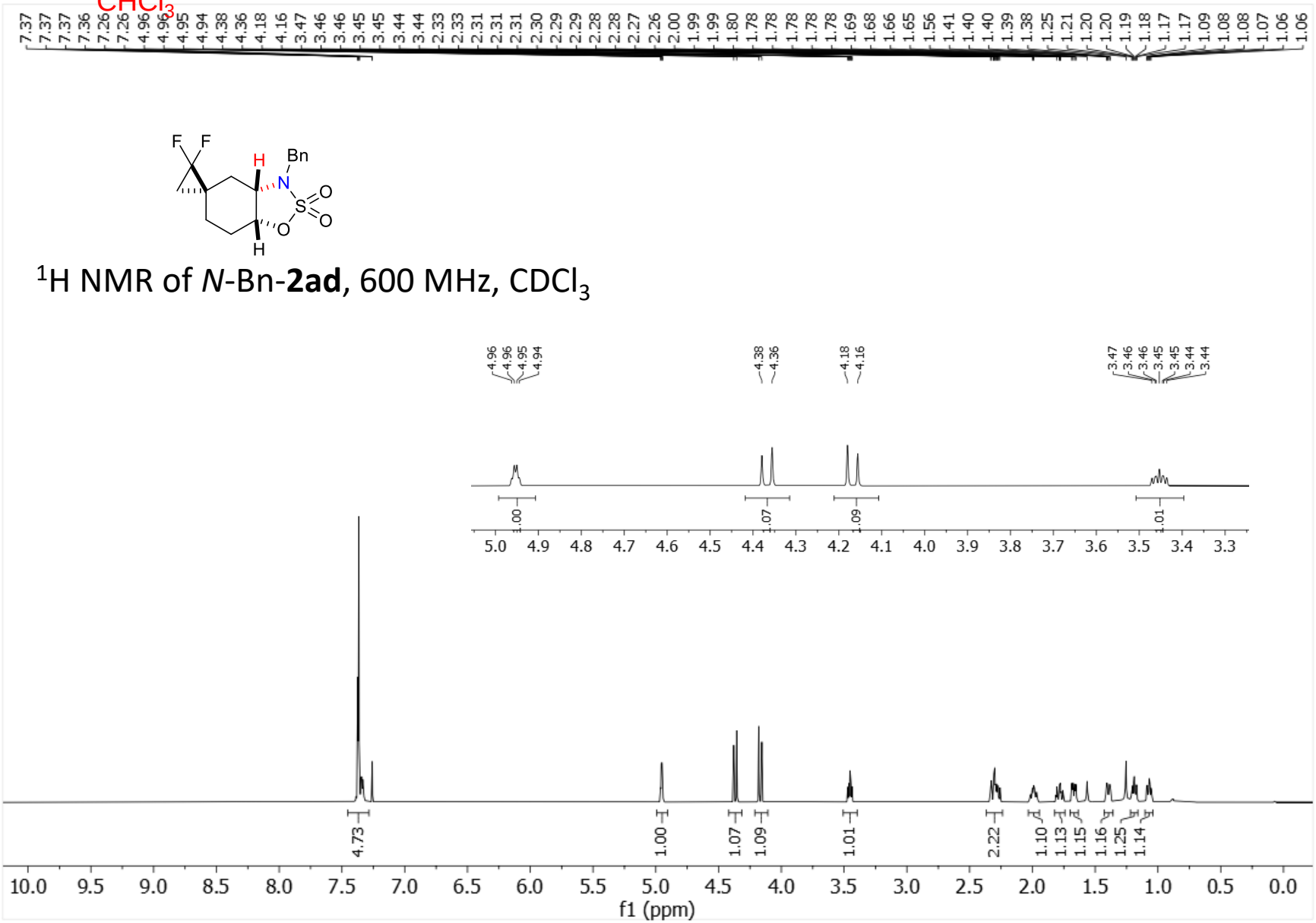
^{13}C NMR of **2ad**, 125 MHz, $CDCl_3$

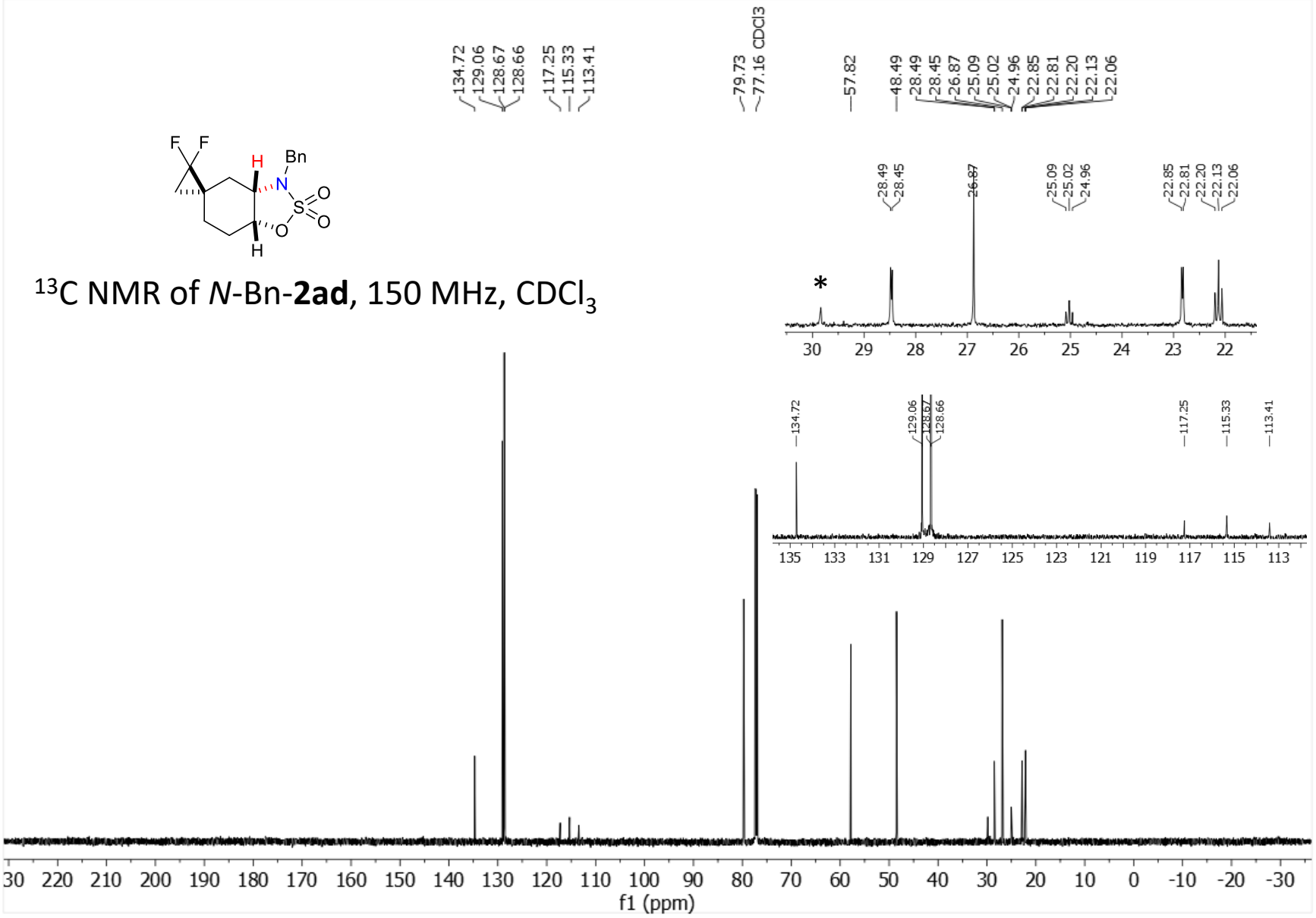


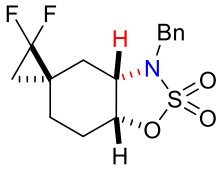
^{19}F NMR of **2ad**, 470 MHz, $CDCl_3$



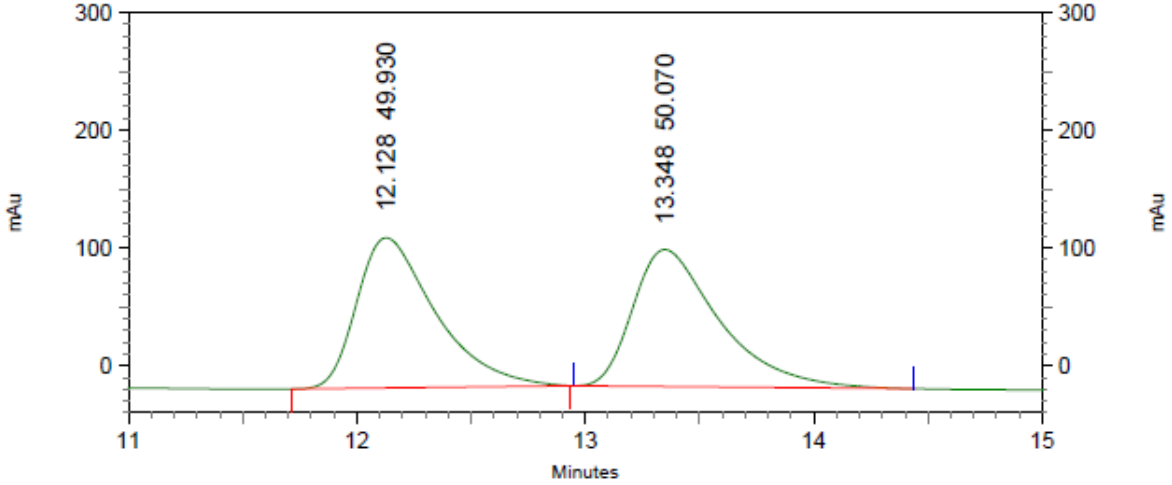


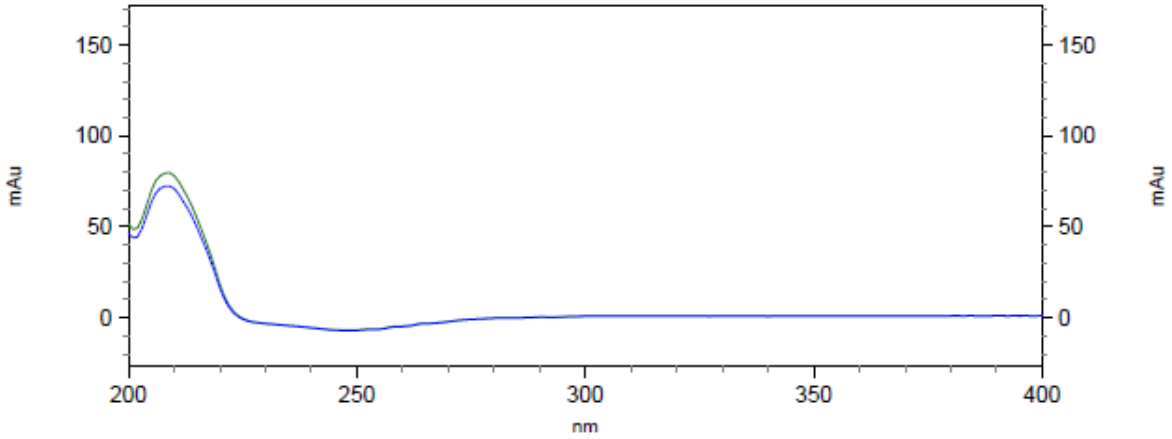

CHCl3
F
F
H
Bn
N
S
O
O
O
H
1H NMR of N-Bn-2ad, 600 MHz, CDCl3
f1 (ppm)

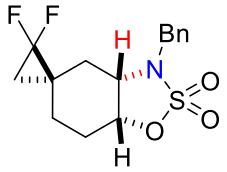

F
F
H
Bn
N
S
O
O
O
H
^{13}C NMR of *N*-Bn-**2ad**, 150 MHz, $CDCl_3$
134.72
129.06
128.67
128.66
117.25
115.33
113.41
79.73
77.16 CDCl3
57.82
48.49
28.49
28.45
26.87
25.09
25.02
24.96
22.85
22.81
22.20
22.13
22.06
*
f1 (ppm)



^{19}F NMR of *N*-Bn-**2ad**, 564 MHz, $CDCl_3$



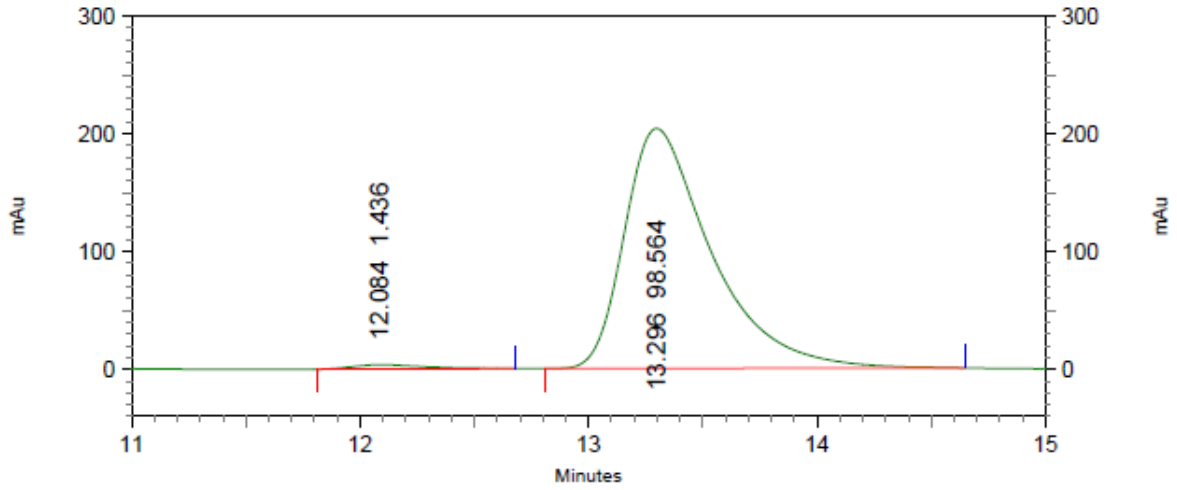


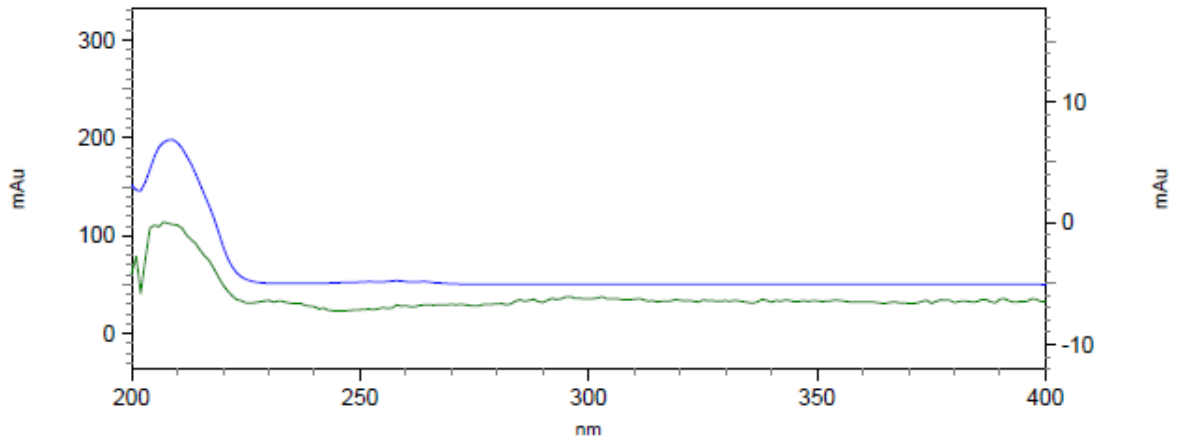


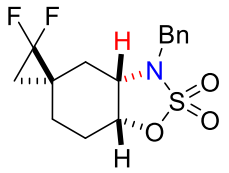
(±)-*N*-Bn-**2ad**

4: 215 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.128	49.930
2	13.348	50.070







(+)-*N*-Bn-**2ad**

4: 215 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.084	1.436
2	13.296	98.564

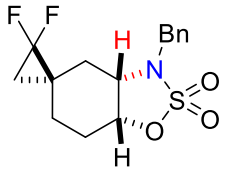
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C15H17F2NO3S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C15H17F2NO3S



(+)-*N*-Bn-**2ad**

Bond precision: C-C = 0.0029 A Wavelength=1.54178

Cell: a=10.0047(7) b=10.8944(7) c=13.8830(9)
alpha=90 beta=90 gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	1513.18(17)	1513.18(17)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C15 H17 F2 N O3 S	C15 H17 F2 N O3 S
Sum formula	C15 H17 F2 N O3 S	C15 H17 F2 N O3 S
Mr	329.36	329.35
Dx,g cm-3	1.446	1.446
Z	4	4
Mu (mm-1)	2.223	2.223
F000	688.0	688.0
F000'	691.64	
h,k,lmax	11,12,16	11,12,16
Nref	2668[1544]	2622
Tmin,Tmax	0.584,0.766	0.618,0.753
Tmin'	0.374	

Correction method= # Reported T Limits: Tmin=0.618 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.70/0.98 Theta(max)= 66.631

R(reflections)= 0.0228(2592) wR2(reflections)= 0.0686(2622)

S = 1.038 Npar= 200

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

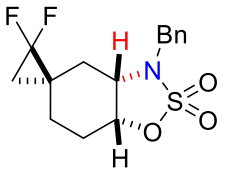
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.595	23 Report
PLAT913_ALERT_3_C	Missing # of Very Strong Reflections in FCF	9 Note

Alert level G

PLAT791_ALERT_4_G	Model has Chirality at C3 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C6 (Sohnke SpGr)	R Verify
PLAT791_ALERT_4_G	Model has Chirality at C7 (Sohnke SpGr)	S Verify
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	97% Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	2 Note
PLAT965_ALERT_2_G	The SHELXL WEIGHT Optimisation has not Converged	Please Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	6 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check



(+)-*N*-Bn-**2ad**

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

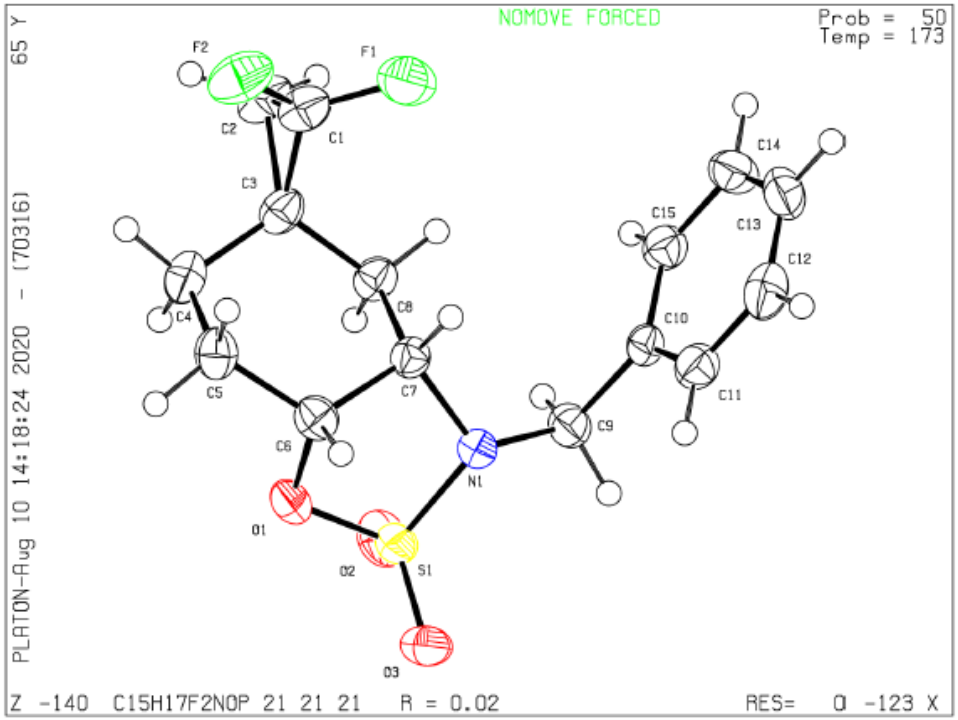
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

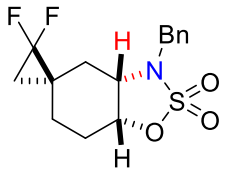
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

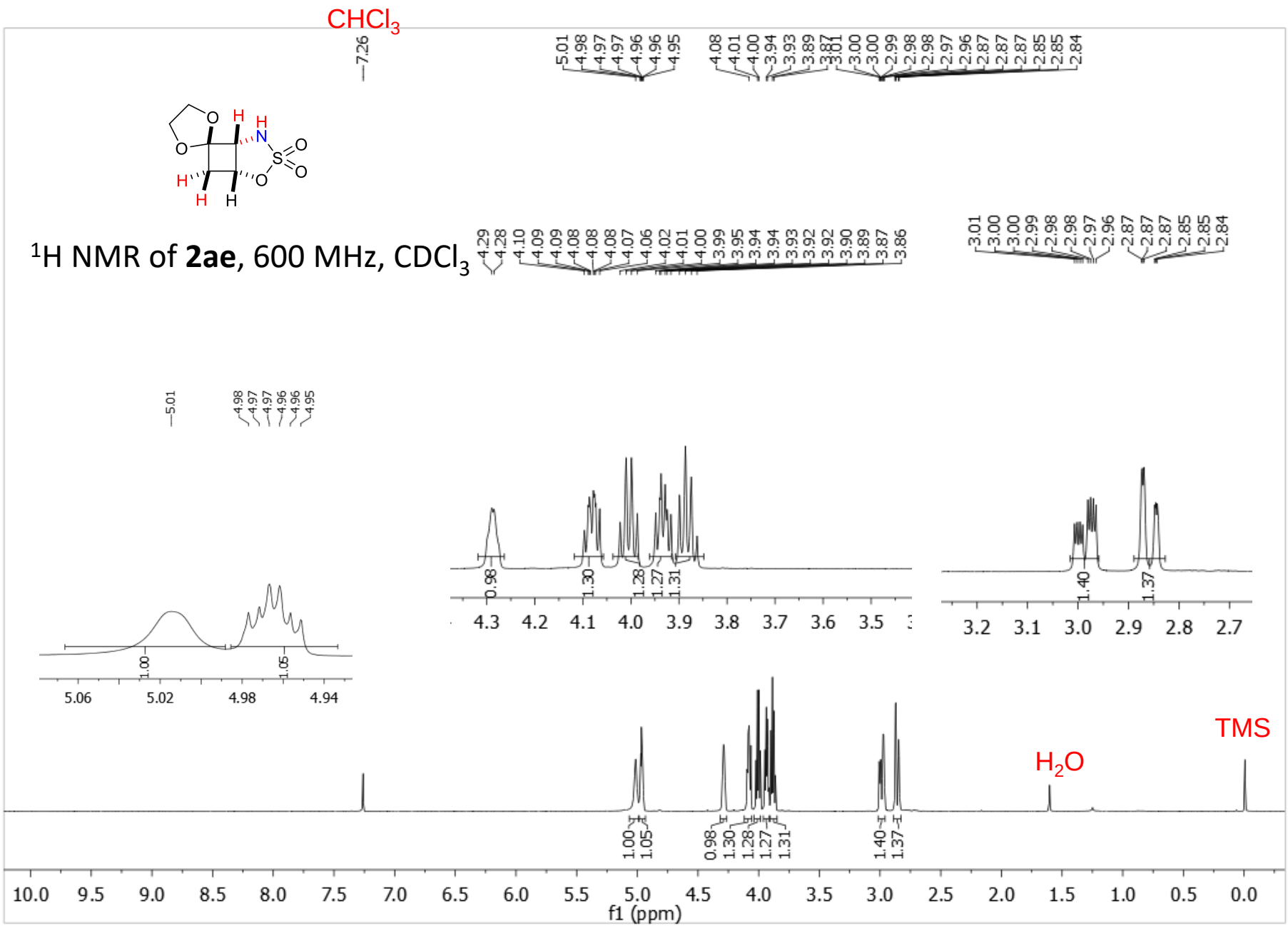
PLATON version of 16/07/2020; check.def file version of 12/07/2020

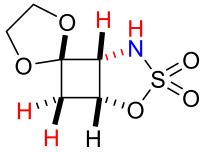
Datablock: C15H17F2NO3S - ellipsoid plot



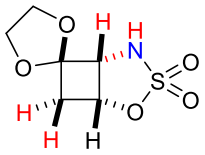


(+)-*N*-Bn-**2ad**


CHCl3
7.26
5.01 4.98 4.97 4.97 4.96 4.96 4.95
4.08 4.01 4.00 3.94 3.93 3.89 3.87 3.01 3.00 3.00 2.99 2.98 2.98 2.97 2.96 2.87 2.87 2.87 2.85 2.85 2.84
O
H
H
N
O
O
S
O
O
H
O
H
H
1H NMR of 2ae, 600 MHz, CDCl3
4.29 4.28 4.10 4.09 4.09 4.08 4.08 4.08 4.07 4.06 4.02 4.01 4.00 3.99 3.95 3.94 3.94 3.93 3.92 3.92 3.90 3.89 3.87 3.86
3.01 3.00 3.00 2.99 2.98 2.98 2.97 2.96 2.87 2.87 2.87 2.85 2.85 2.84
5.01
4.98 4.97 4.97 4.96 4.96 4.95
1.00
1.05
5.06 5.02 4.98 4.94
0.98
1.30
1.28
1.27
1.31
4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5
1.40
1.37
3.2 3.1 3.0 2.9 2.8 2.7
TMS
H2O
1.00 1.05 0.98 1.30 1.28 1.27 1.31 1.40 1.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



^{13}C NMR of **2ae**, 150 MHz, $CDCl_3$



(–)-**2ae**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C6H9NO5S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

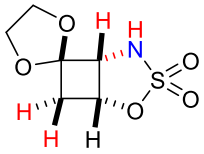
Datablock: C6H9NO5S

```
Bond precision:  C-C = 0.0042 A          Wavelength=1.54178

Cell:            a=5.2382(3)     b=10.1883(6)     c=15.0152(9)
                 alpha=90        beta=90          gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	801.34(8)	801.34(8)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C6 H9 N O5 S	C6 H9 N O5 S
Sum formula	C6 H9 N O5 S	C6 H9 N O5 S
Mr	207.20	207.20
Dx,g cm-3	1.717	1.717
Z	4	4
Mu (mm-1)	3.598	3.598
F000	432.0	432.0
F000'	434.83	
h,k,lmax	6,12,17	6,12,17
Nref	1425[862]	1418
Tmin,Tmax	0.682,0.750	0.572,0.753
Tmin'	0.243	

```
Correction method= # Reported T Limits: Tmin=0.572 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.65/1.00      Theta(max)= 66.836

R(reflections)= 0.0315( 1398)     wR2(reflections)= 0.0833( 1418)

S = 1.085                  Npar= 121
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(–)-2ae

Alert level C

PLAT089 ALERT 3 C	Poor Data / Parameter Ratio (Zmax < 18)	7.09 Note
PLAT340 ALERT 3 C	Low Bond Precision on C-C Bonds	0.0042 Ang.
PLAT420 ALERT 2 C	D-H Without Acceptor N1 --H1N	Please Check
PLAT480 ALERT 4 C	Long H...A H-Bond Reported H1N ..O5	2.62 Ang.
PLAT480 ALERT 4 C	Long H...A H-Bond Reported H1N ..N1	2.64 Ang.
PLAT911 ALERT 3 C	Missing FCF Refl Between Thmin & STh/L= 0.596	4 Report

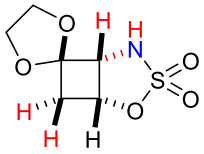
Alert level G

PLAT002 ALERT 2 G	Number of Distance or Angle Restraints on AtSite	2 Note
PLAT172 ALERT 4 G	The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT395 ALERT 2 G	Deviating X-O-Y Angle From 120 for O3	109.2 Degree
PLAT398 ALERT 2 G	Deviating C-O-C Angle From 120 for O4	106.1 Degree
PLAT398 ALERT 2 G	Deviating C-O-C Angle From 120 for O5	106.3 Degree
PLAT791 ALERT 4 G	Model has Chirality at C1 (Chiral SPGR)	R Verify
PLAT791 ALERT 4 G	Model has Chirality at C4 (Chiral SPGR)	R Verify
PLAT860 ALERT 3 G	Number of Least-Squares Restraints	1 Note
PLAT909 ALERT 3 G	Percentage of I>2sig(I) Data at Theta(Max) Still	98% Note
PLAT978 ALERT 2 G	Number C-C Bonds with Positive Residual Density.	3 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.



(–)-**2ae**

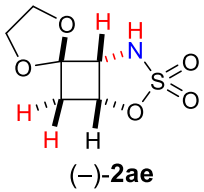
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

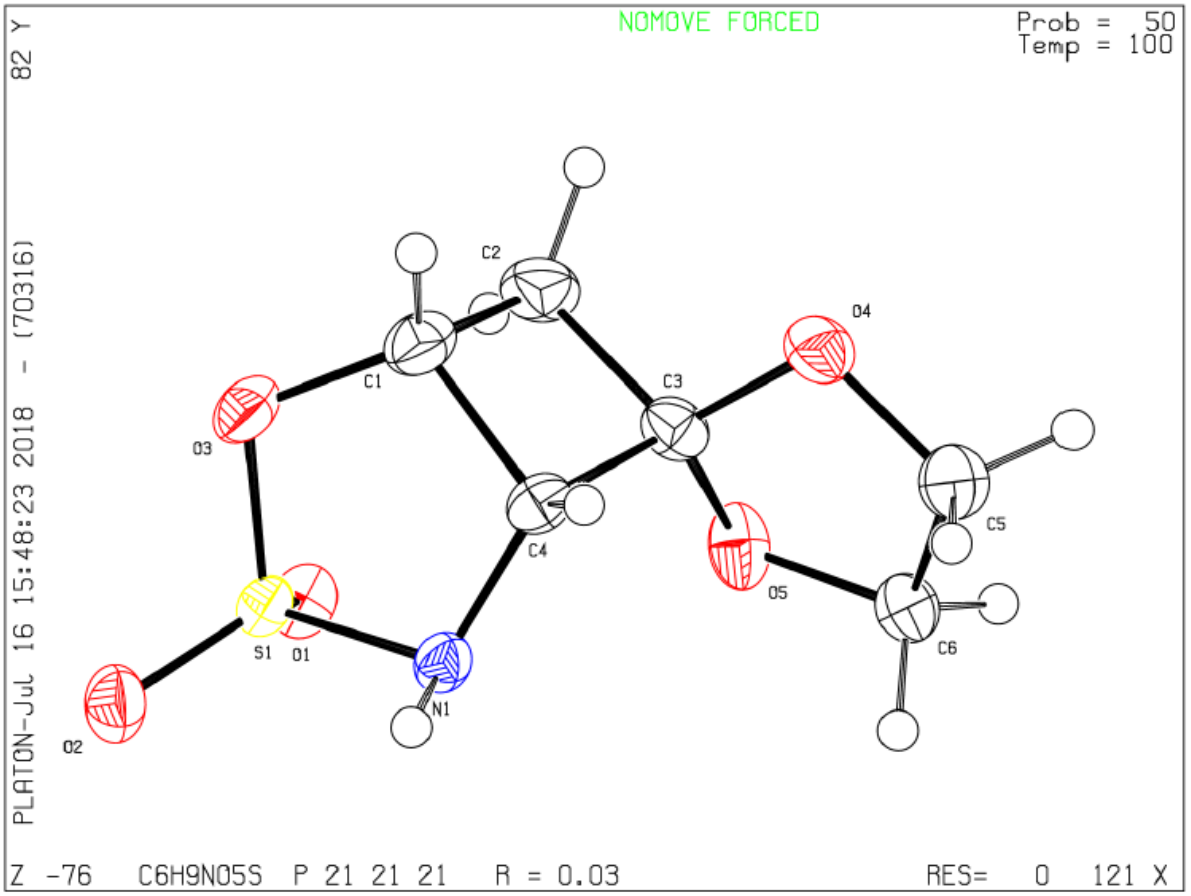
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

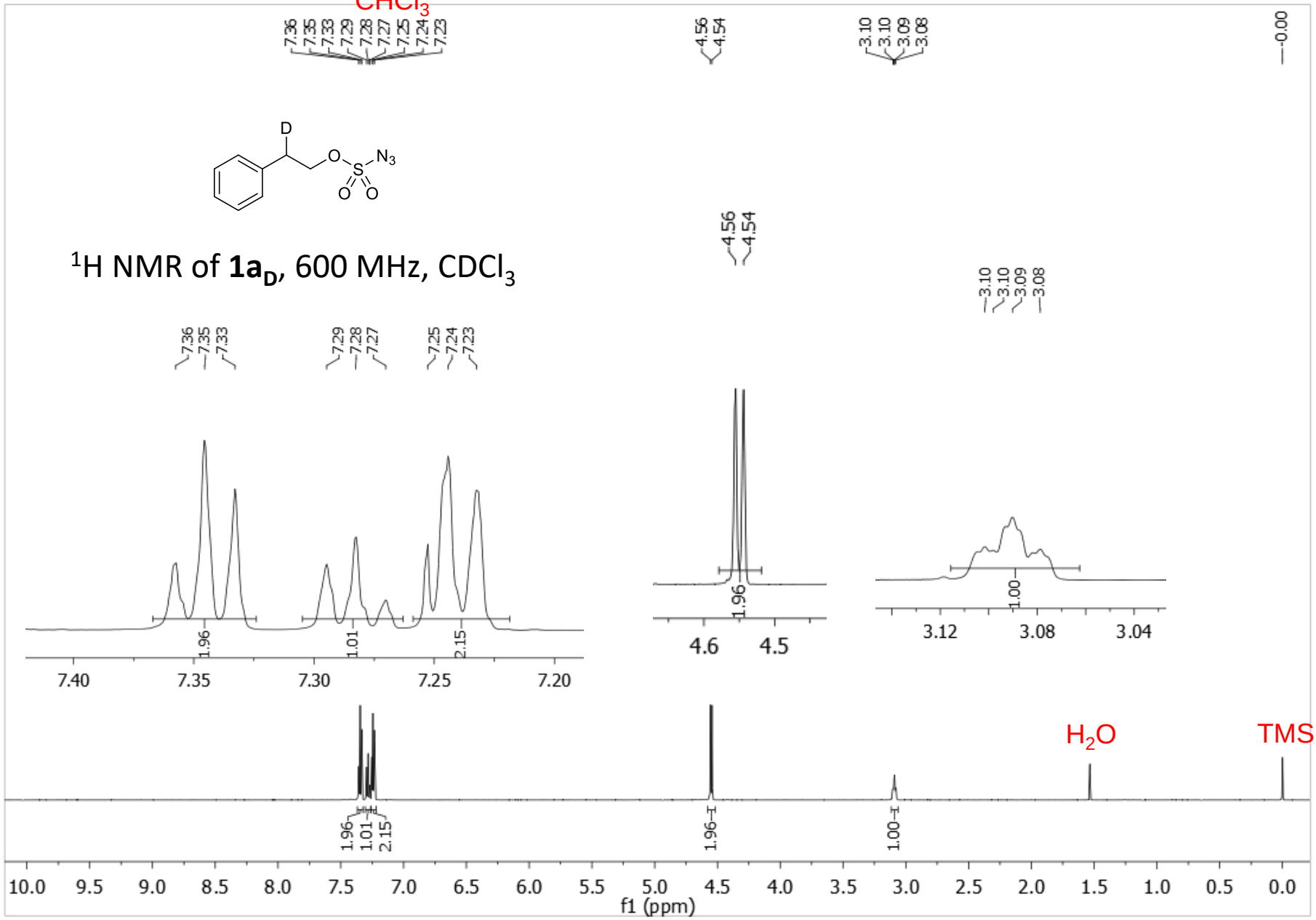
PLATON version of 23/04/2018; check.def file version of 23/04/2018

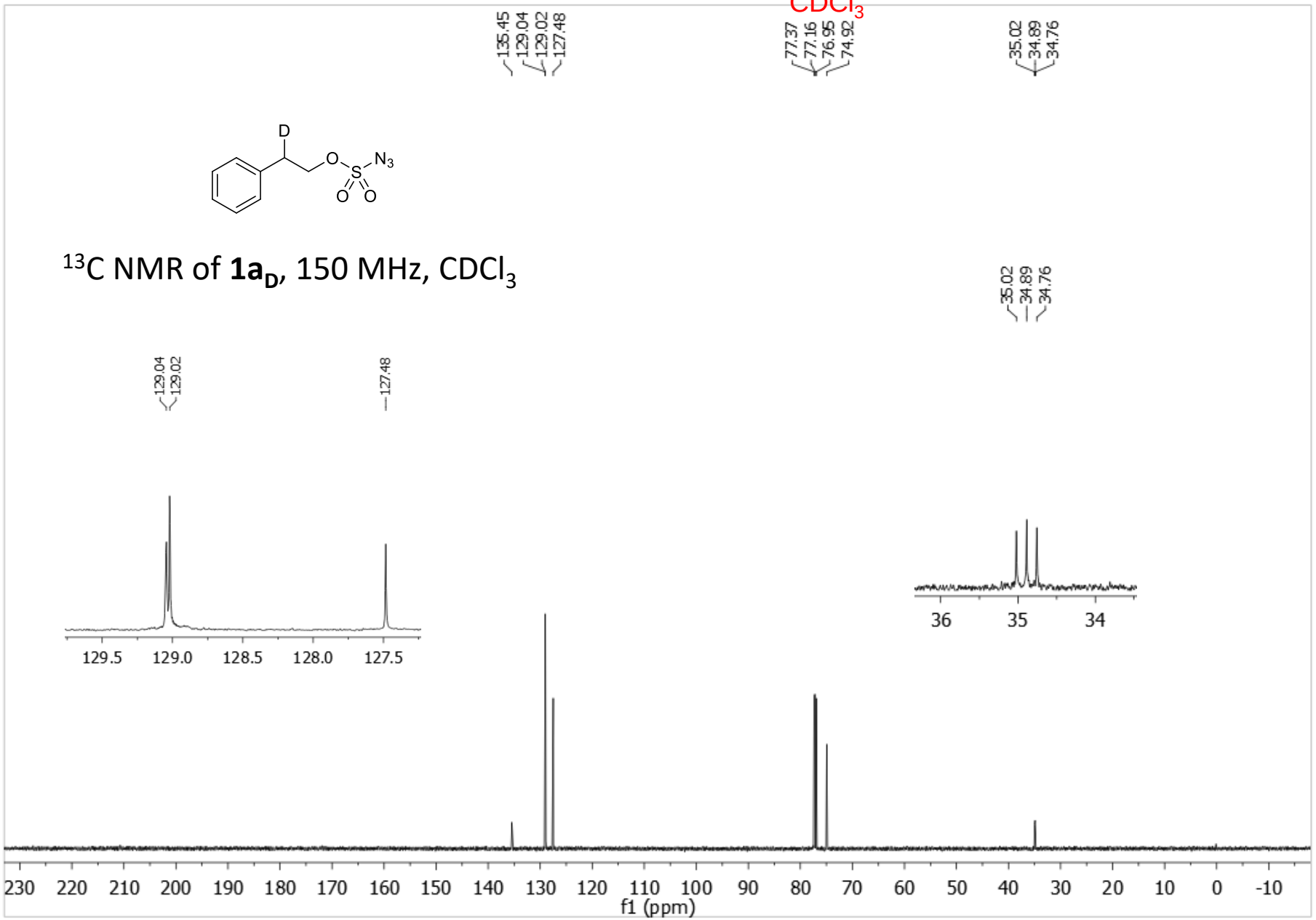


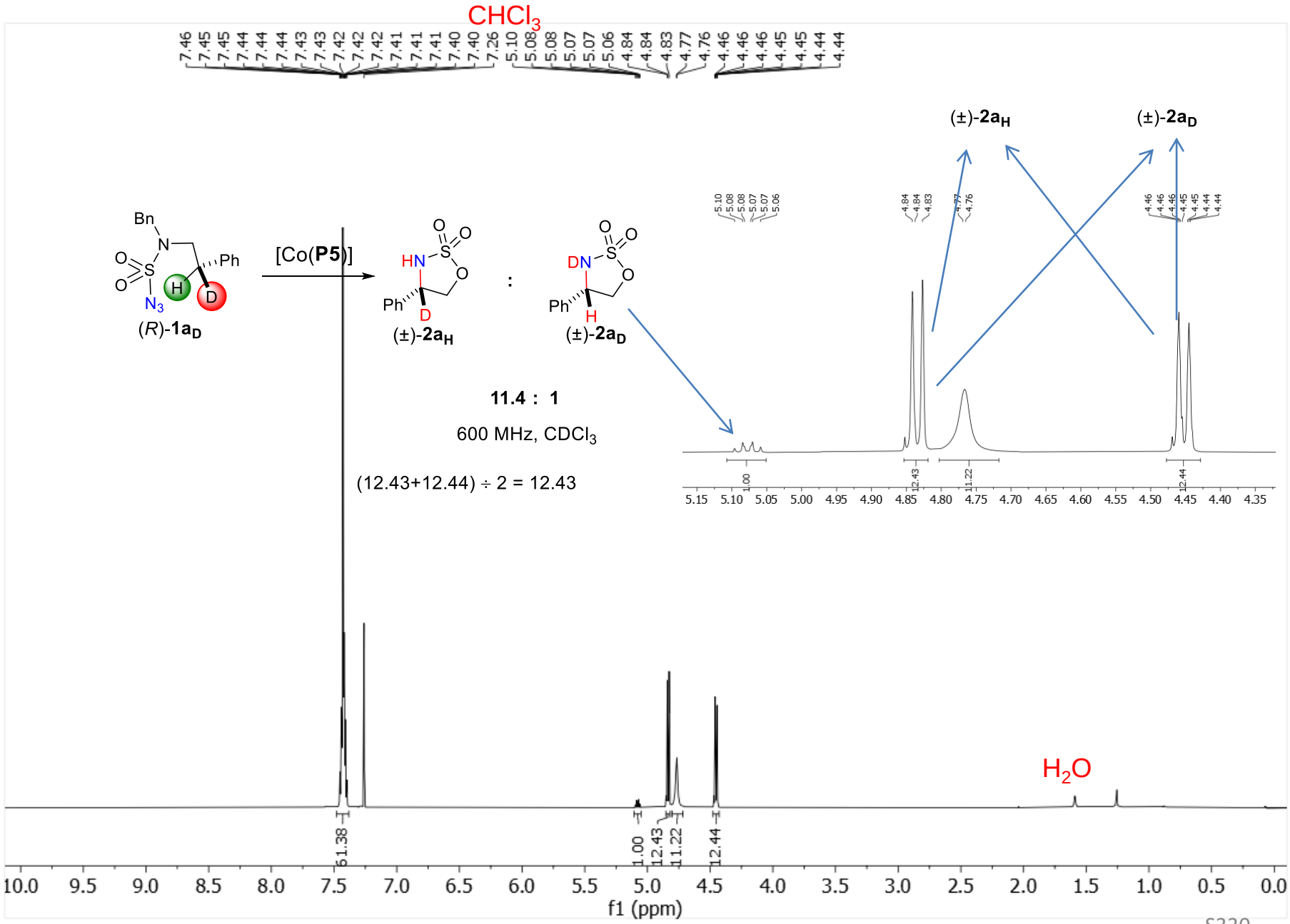
(–)-**2ae**

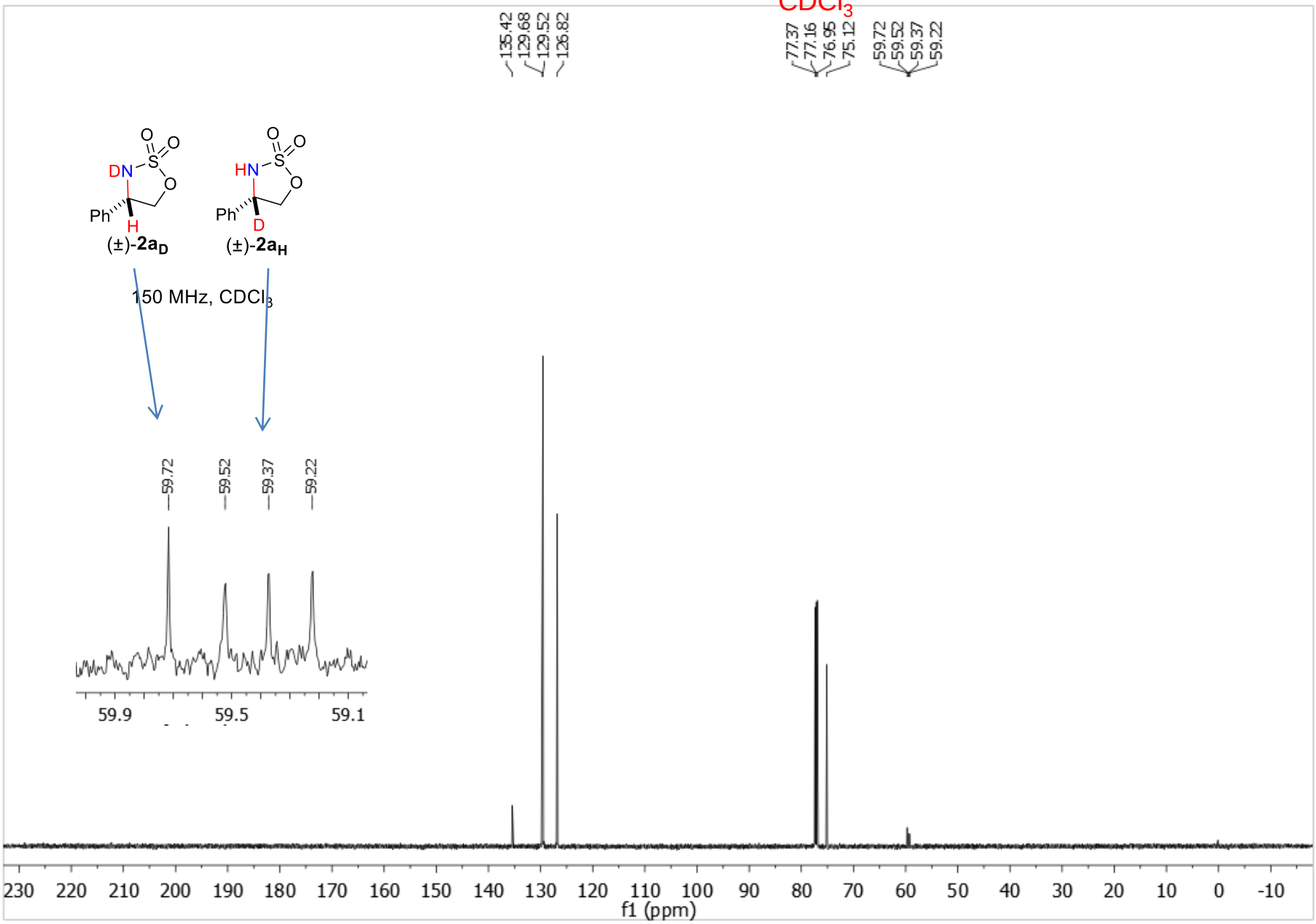
Datablock C6H9NO5S - ellipsoid plot

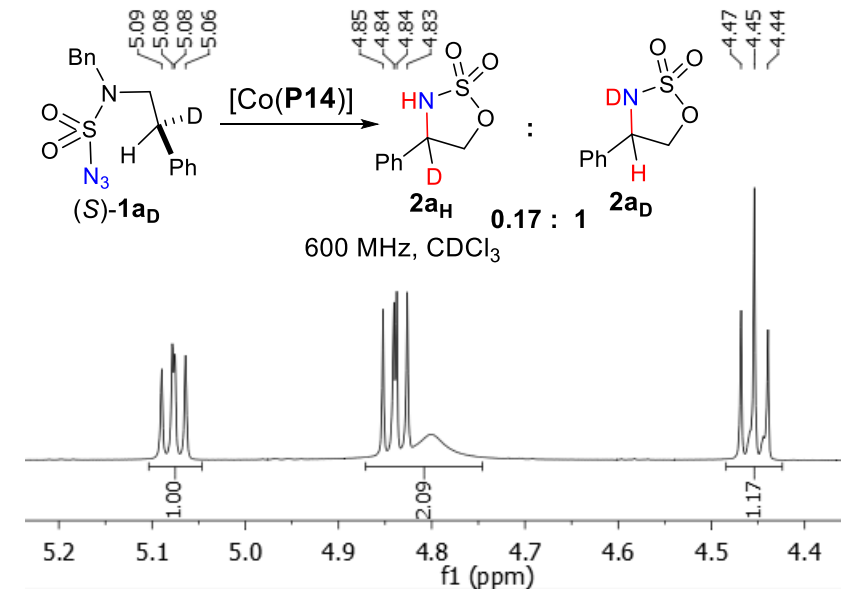


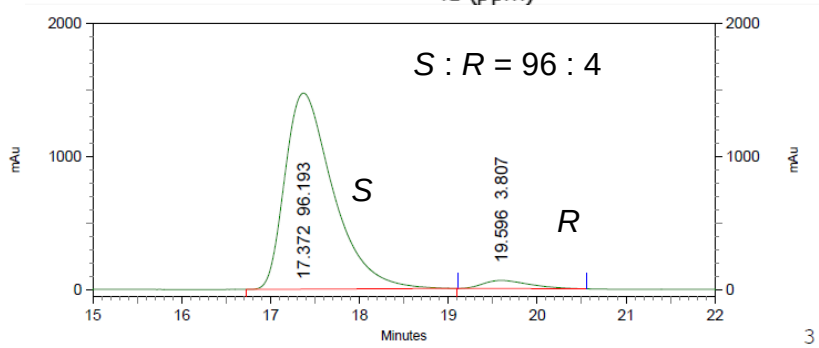

CHCl3
7.36
7.35
7.33
7.29
7.28
7.27
7.25
7.24
7.23
4.56
4.54
3.10
3.10
3.09
3.08
0.00
D
O
S
N3
O
O
1H NMR of 1aD, 600 MHz, CDCl3
1.96
1.01
2.15
1.96
1.00
4.6
4.5
3.12
3.08
3.04
7.40
7.35
7.30
7.25
7.20
H2O
TMS
1.96
1.01
2.15
1.96
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

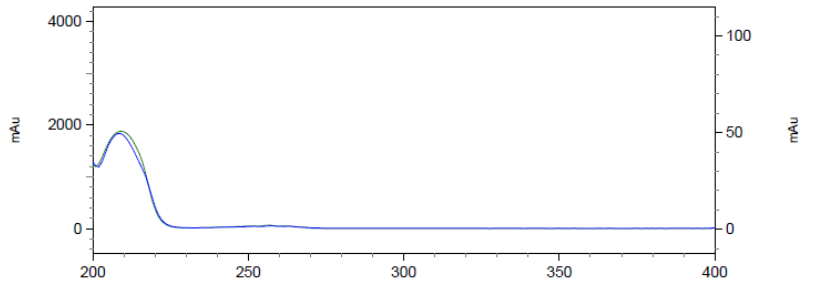

CDCl3
135.45
129.04
129.02
127.48
77.37
77.16
76.95
74.92
35.02
34.89
34.76
D
O
S
N3
O
O
13C NMR of 1aD, 150 MHz, CDCl3
129.5
129.0
128.5
128.0
127.5
36
35
34
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

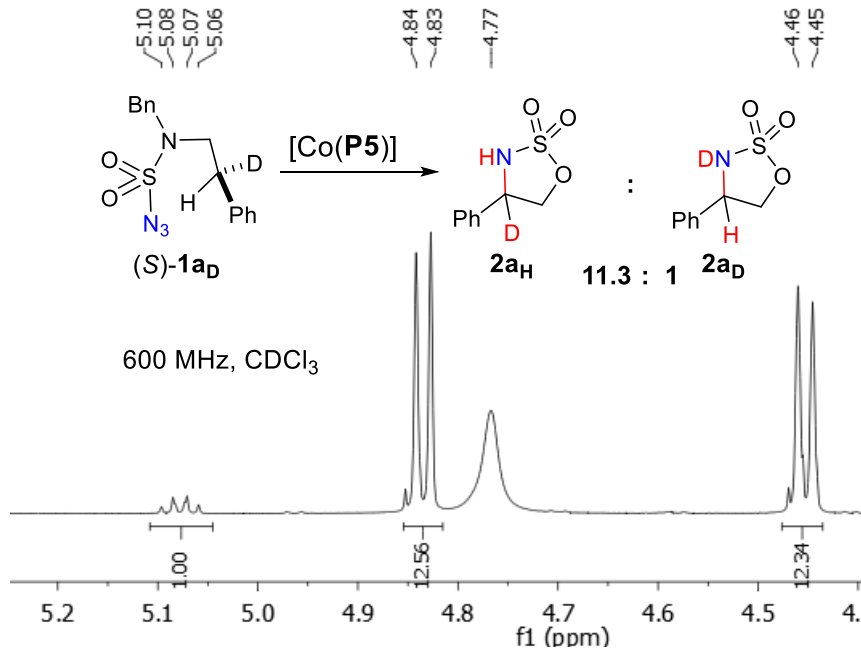

CHCl3
7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.26
5.10 5.08 5.08 5.07 5.07 5.06 4.84 4.84 4.83 4.77 4.76 4.46 4.46 4.46 4.45 4.45 4.44 4.44
Bn
N
Ph
O
S
O
H
D
N3
(R)-1aD
[Co(P5)]
HN
Ph
D
(±)-2aH
:
DN
Ph
H
(±)-2aD
11.4 : 1
600 MHz, CDCl3
(12.43+12.44) ÷ 2 = 12.43
(±)-2aH
(±)-2aD
5.10 5.08 5.08 5.07 5.07 5.06
4.84 4.84 4.83 4.77 4.76
4.46 4.46 4.46 4.45 4.45 4.44 4.44
1.00 12.43 11.22 12.44
5.15 5.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35
H2O
6.38 1.00 12.43 11.22 12.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

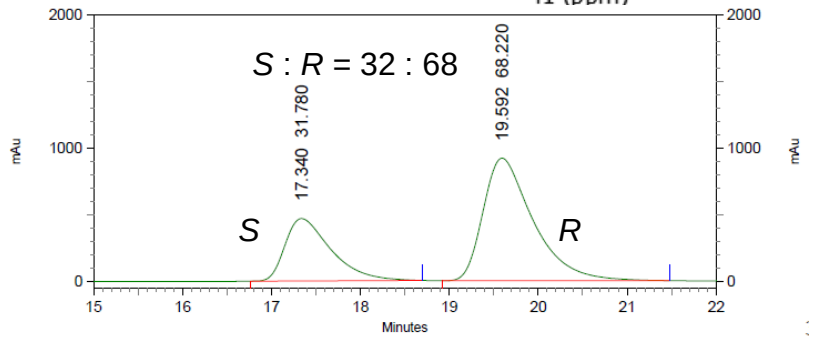

CDCl3
135.42
129.68
129.52
126.82
77.37
77.16
76.95
75.12
59.72
59.52
59.37
59.22
(±)-2aD
(±)-2aH
150 MHz, CDCl3
59.9
59.5
59.1
f1 (ppm)

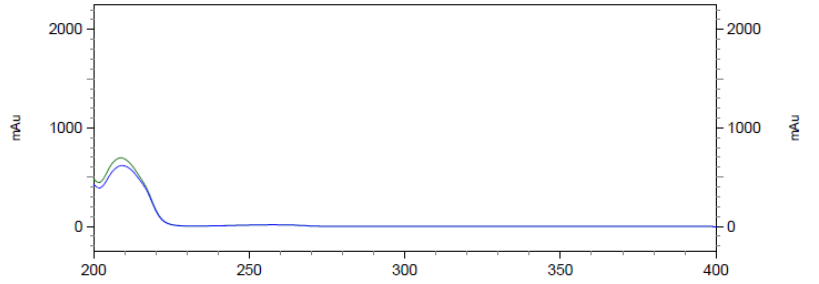

[Co(P14)]
(S)-1a_D
2a_H
2a_D
0.17 : 1
600 MHz, CDCl3
f1 (ppm)

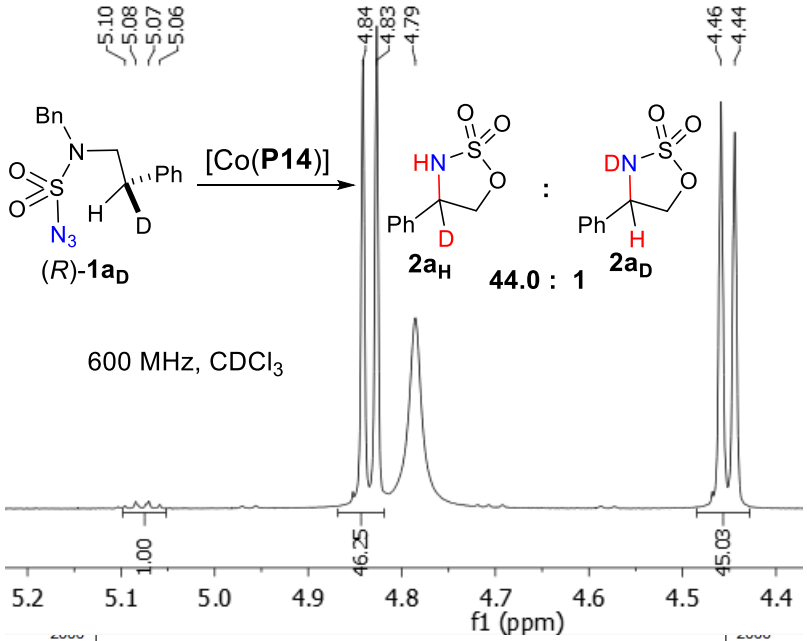

S : R = 96 : 4
17.372 96.193
19.596 3.807
S
R
Minutes
mAu

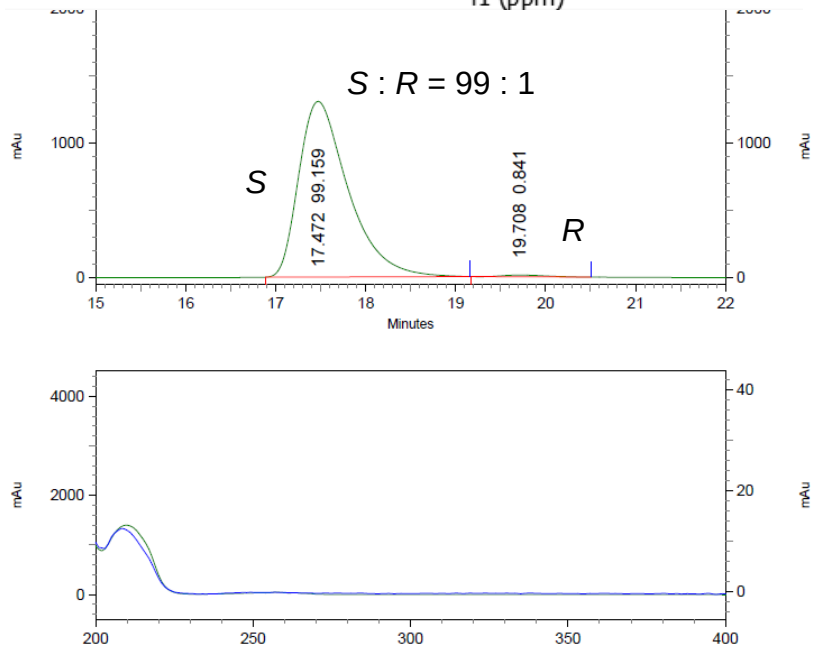

mAu


[Co(P5)]
(S)-1a_D
2a_H
2a_D
11.3 : 1
600 MHz, CDCl3
f1 (ppm)

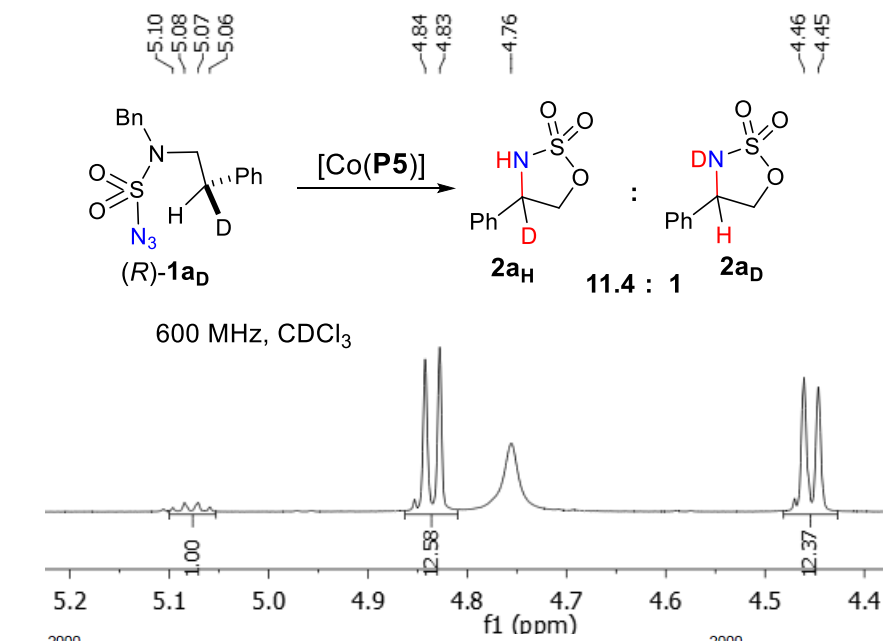

S : R = 32 : 68
17.340 31.780
19.592 68.220
S
R
Minutes
mAu

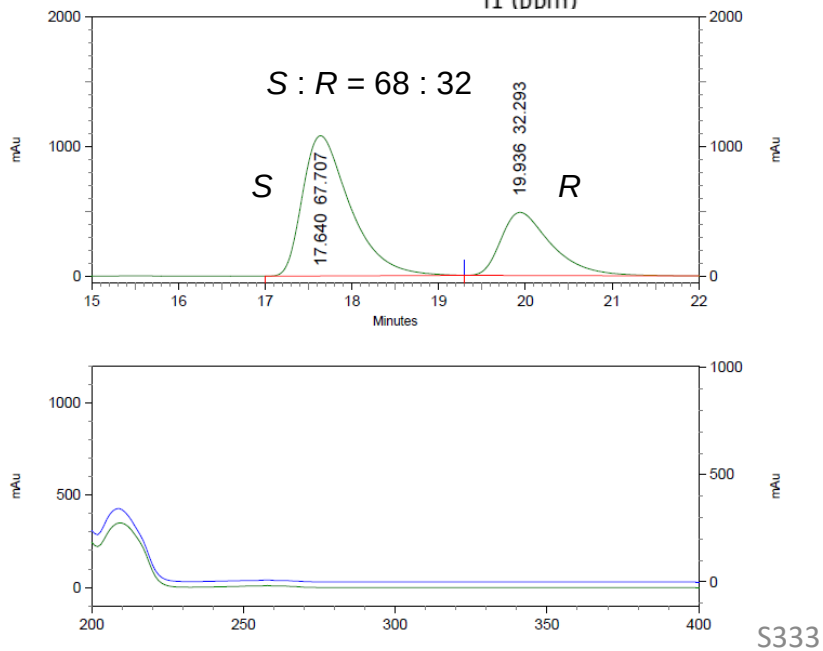

mAu


5.10
5.08
5.07
5.06
4.84
4.83
4.79
4.46
4.44
Bn
N
S
O
O
N3
Ph
H
D
[Co(P14)]
HN
DN
Ph
D
H
2aH
44.0 : 1
2aD
(R)-1aD
600 MHz, CDCl3
1.00
46.25
45.03
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
f1 (ppm)

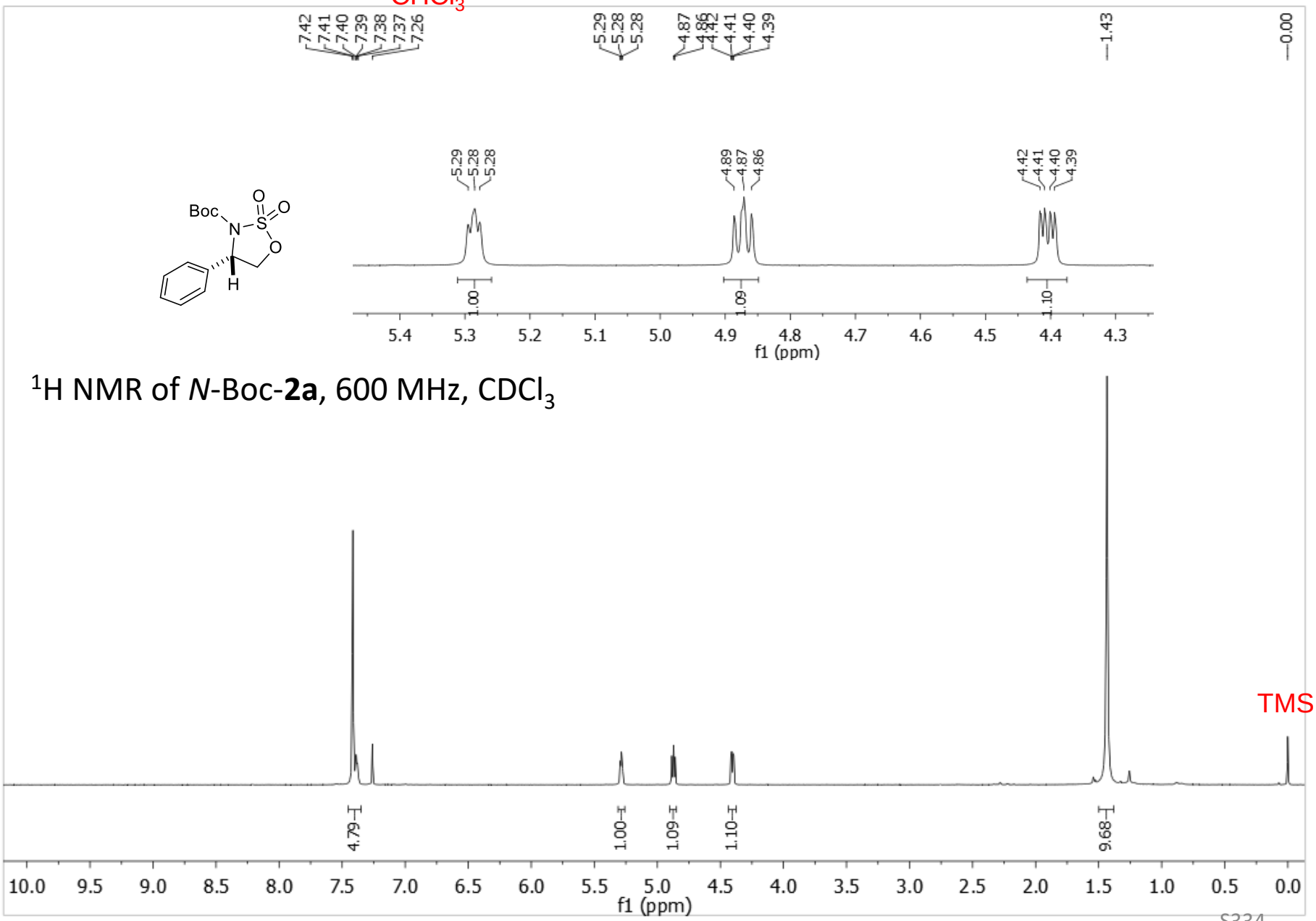

S : R = 99 : 1
S
R
17.472 99.159
19.708 0.841
mAu
Minutes
15
16
17
18
19
20
21
22

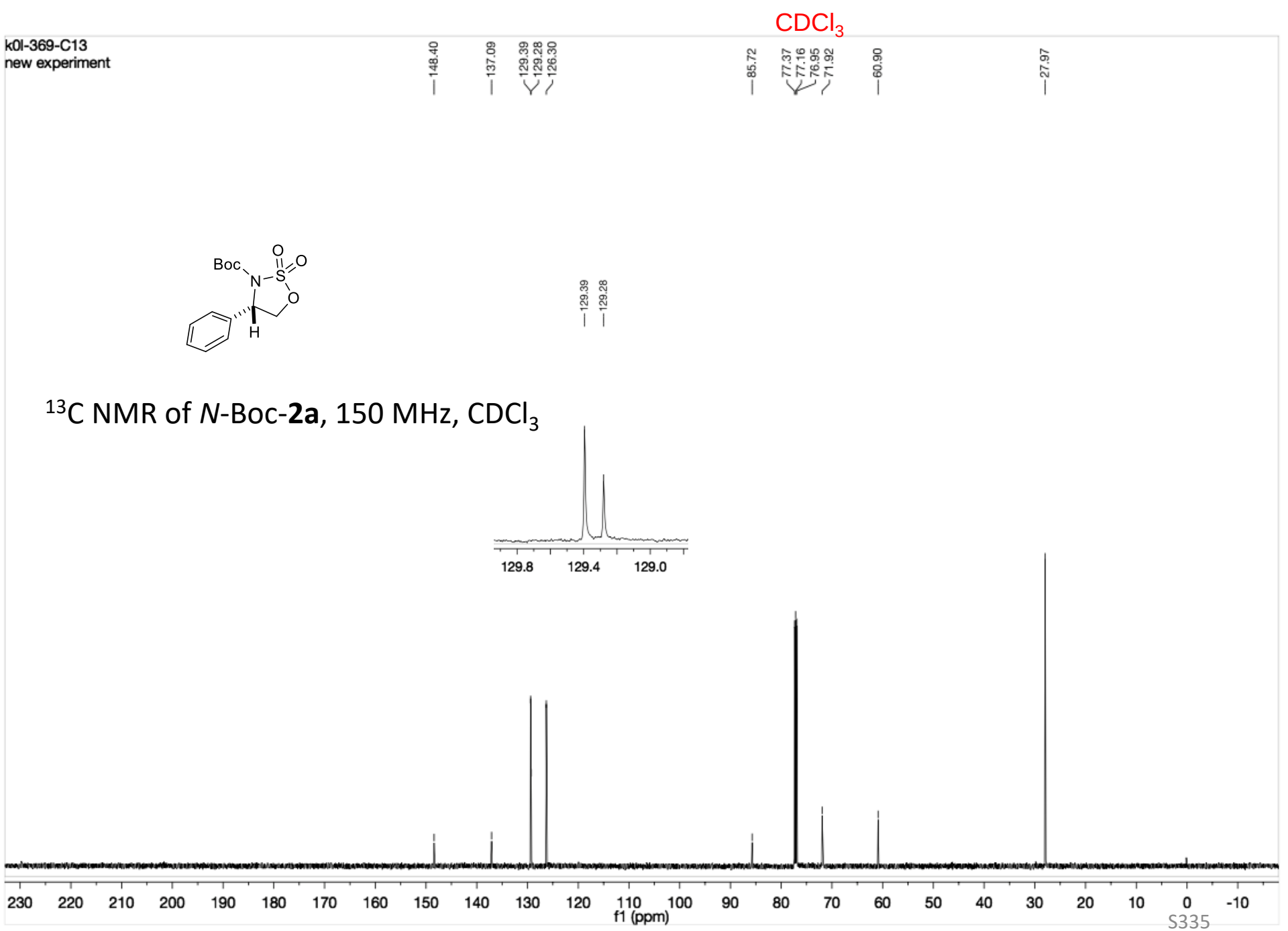
4000
2000
0
40
20
200
250
300
350
400


5.10
5.08
5.07
5.06
4.84
4.83
4.76
4.46
4.45
Bn
N
S
O
O
N3
Ph
H
D
[Co(P5)]
HN
DN
Ph
D
H
2aH
11.4 : 1
2aD
(R)-1aD
600 MHz, CDCl3
1.00
12.58
12.37
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
f1 (ppm)

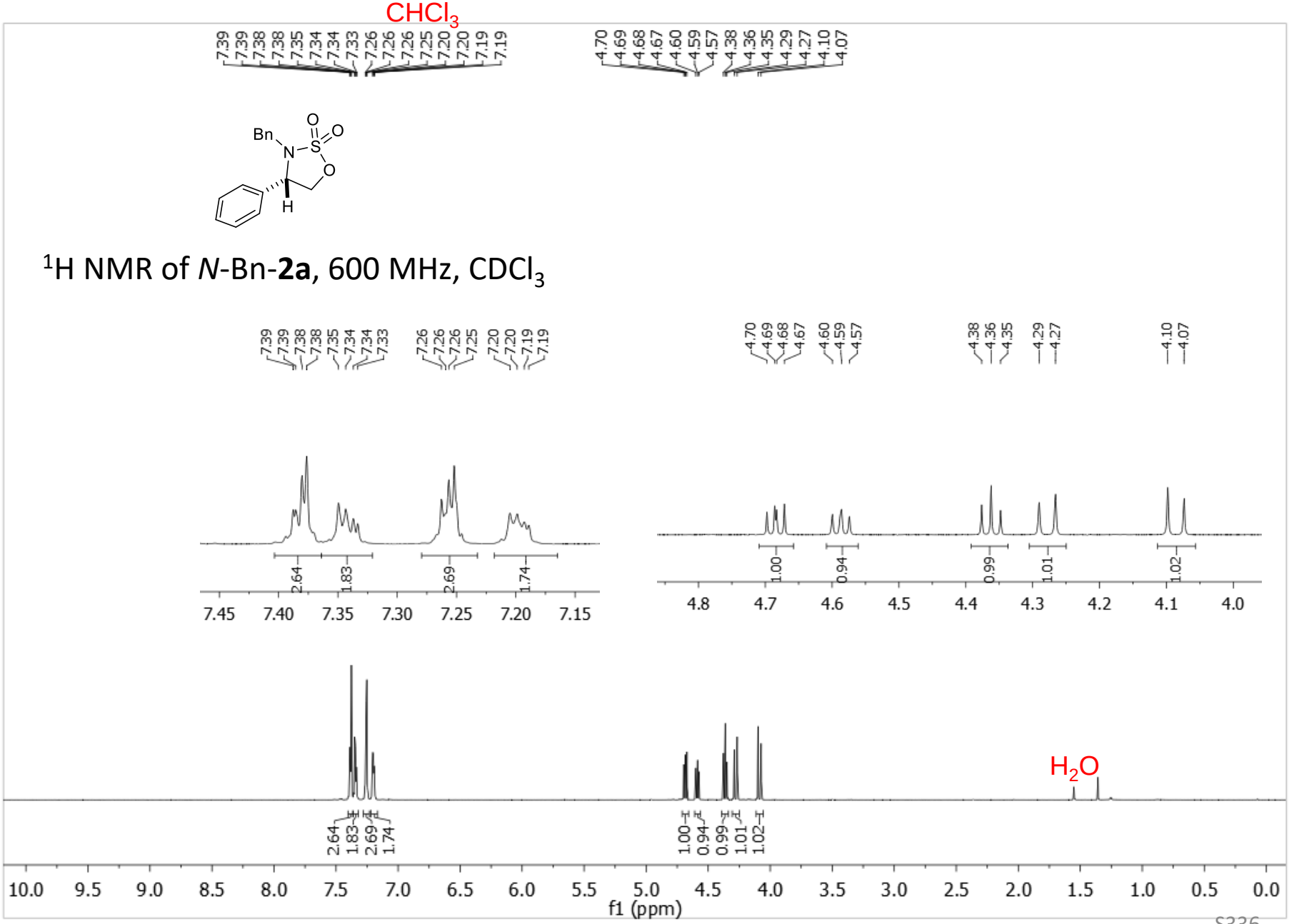

S : R = 68 : 32
S
R
17.640 67.707
19.936 32.293
mAu
Minutes
15
16
17
18
19
20
21
22

1000
500
0
200
250
300
350
400

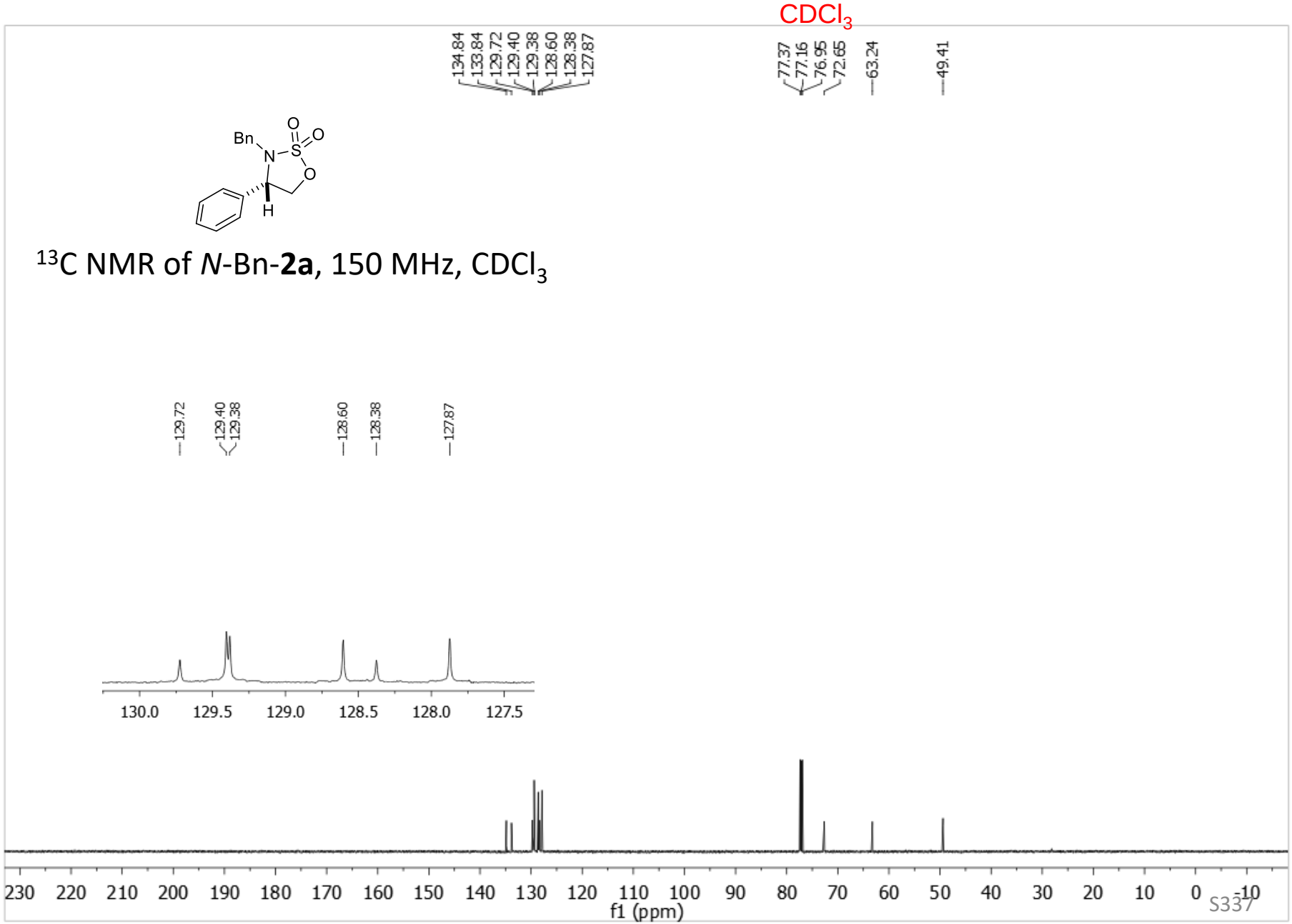

CHCl3
7.42
7.41
7.40
7.39
7.38
7.37
7.26
5.29
5.28
5.28
4.87
4.86
4.42
4.41
4.40
4.39
1.43
0.00
Boc
N
S
O
O
O
H
5.29
5.28
5.28
4.89
4.87
4.86
4.42
4.41
4.40
4.39
1.00
1.09
1.10
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
f1 (ppm)
1H NMR of N-Boc-2a, 600 MHz, CDCl3
TMS
4.79
1.00
1.09
1.10
9.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



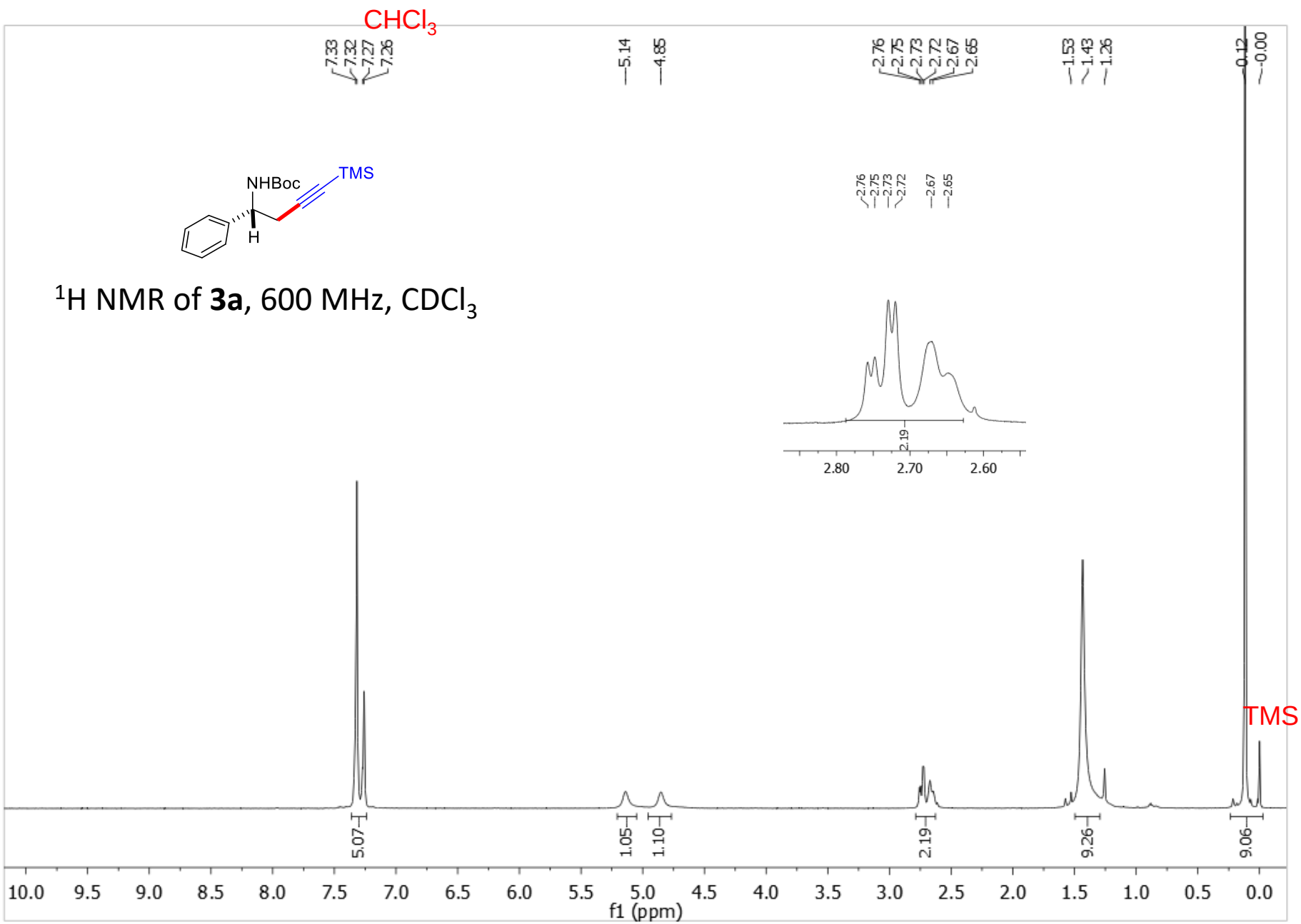
^{13}C NMR of *N*-Boc-**2a**, 150 MHz, $CDCl_3$



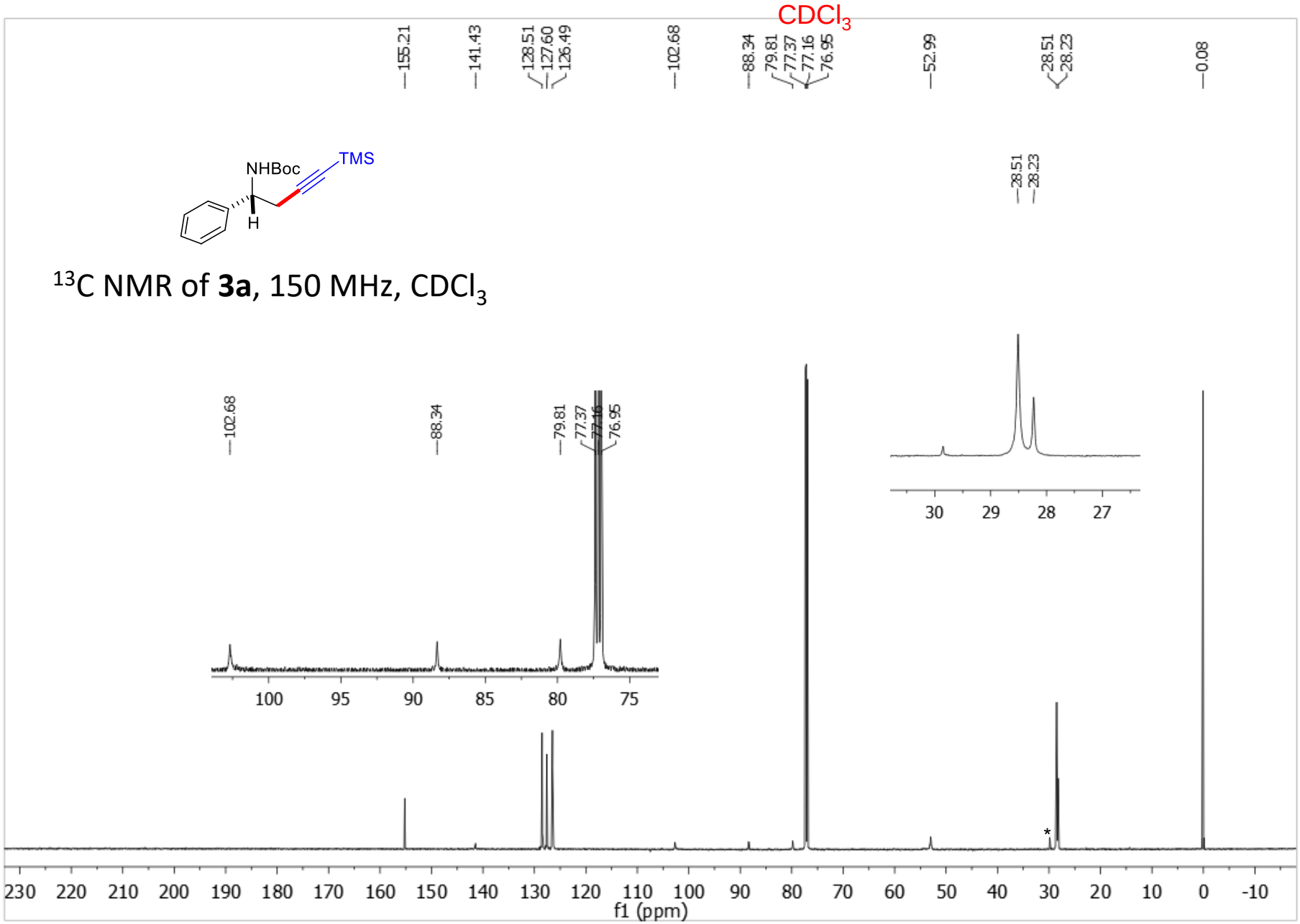
^{1}H NMR of *N*-Bn-**2a**, 600 MHz, $CDCl_3$



^{13}C NMR of *N*-Bn-**2a**, 150 MHz, $CDCl_3$

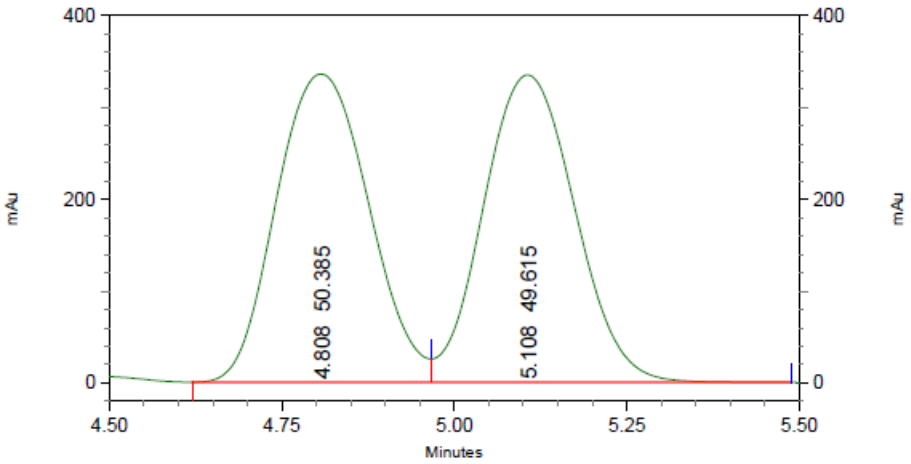


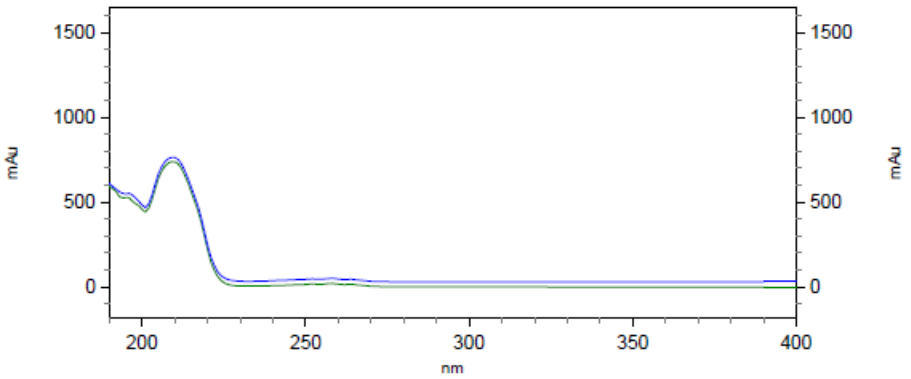
^{1}H NMR of **3a**, 600 MHz, $CDCl_3$

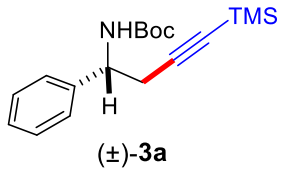


^{13}C NMR of **3a**, 150 MHz, $CDCl_3$

K0L-397-IC-1.5%-1mL-4
C:\EZStart\Projects\Default\Data\K0L-397-IC-5%-1mL-4
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met







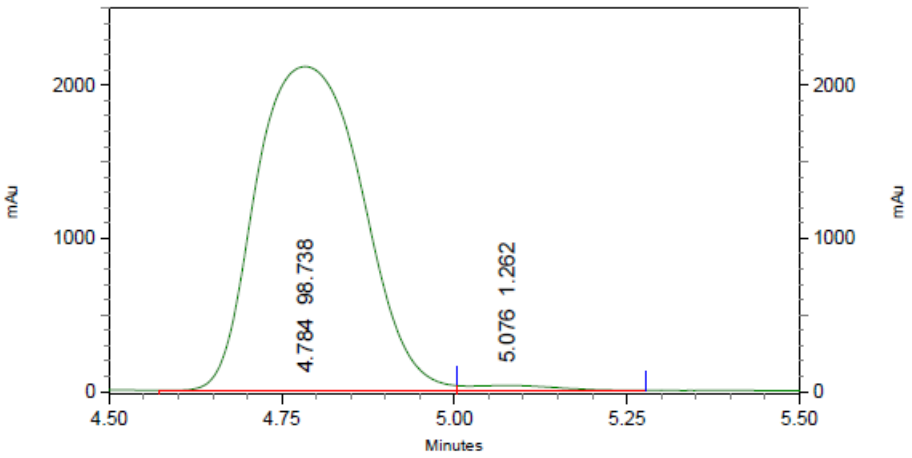
(±)-**3a**

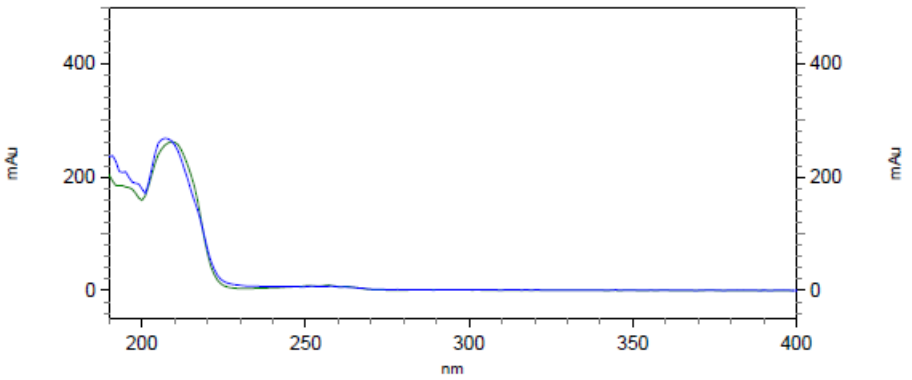
2: 215 nm, 4
nm Results

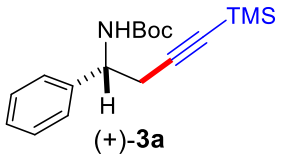
Pk #	Retention Time	Area Percent
1	4.808	50.385
2	5.108	49.615

Totals		100.000

K0L-396-IC-5%-1mL-4
C:\EZStart\Projects\Default\Data\K0L-396-IC-5%-1mL-4
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met



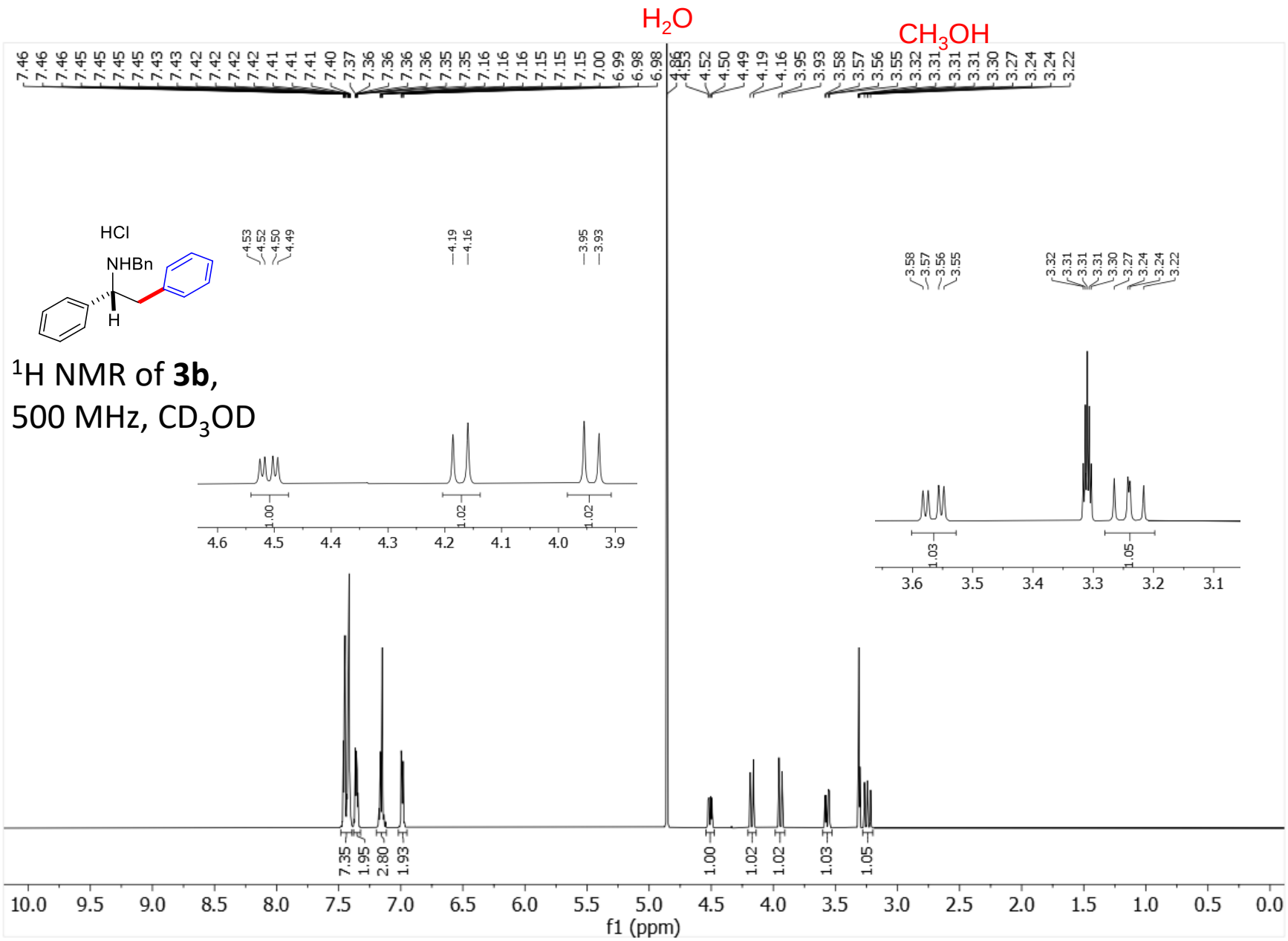


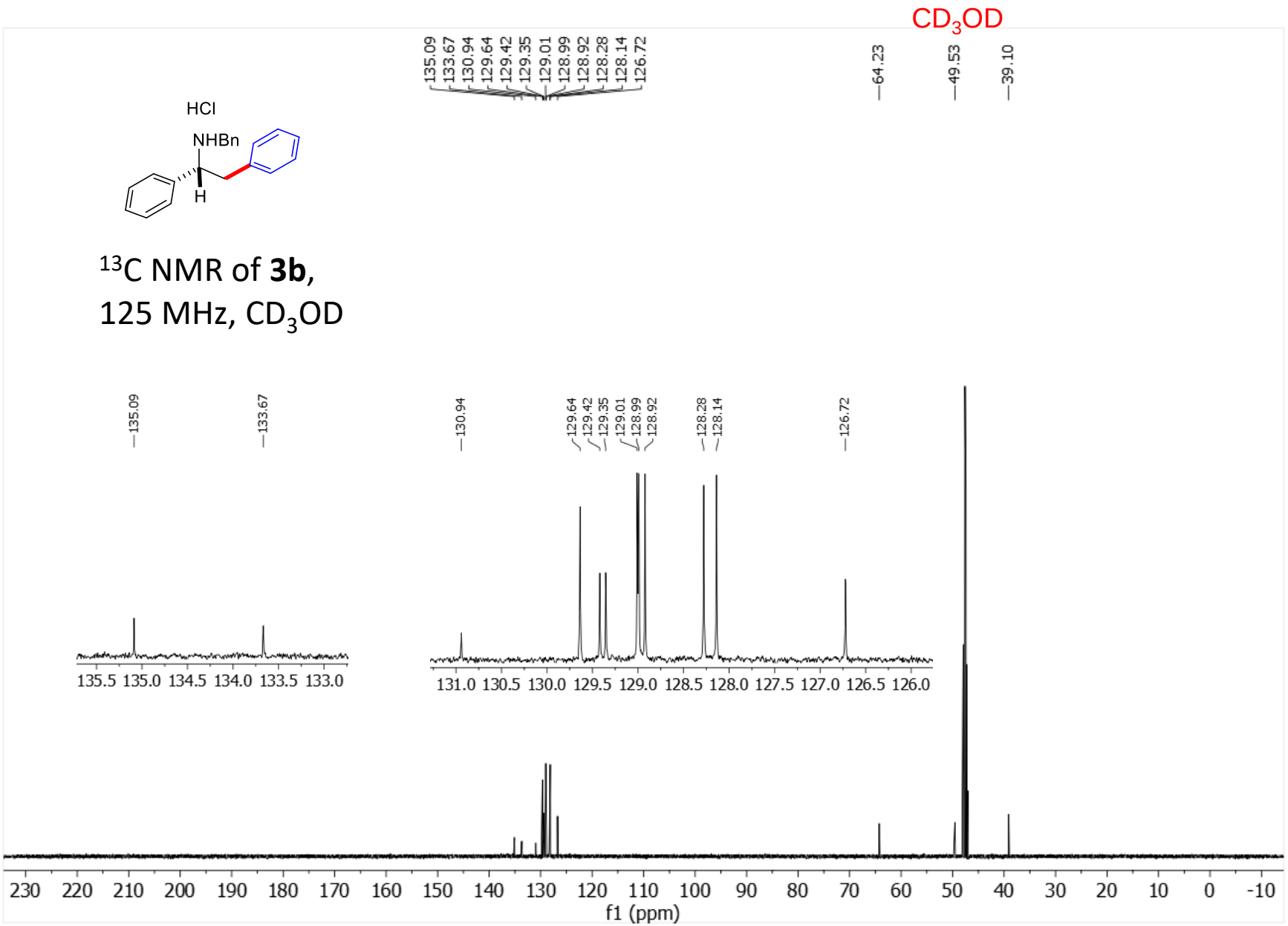


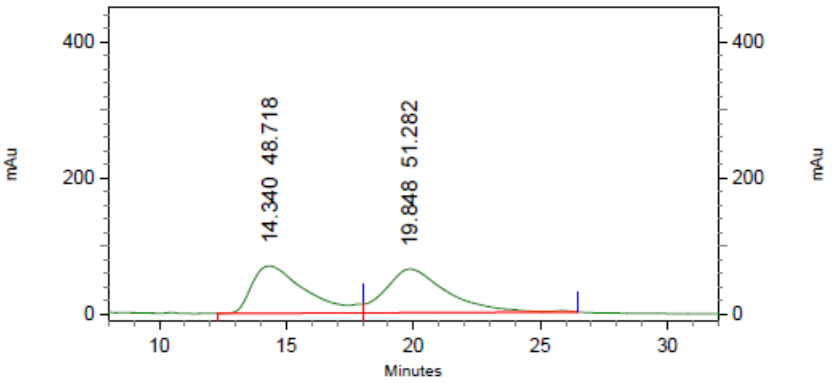
(+)-**3a**

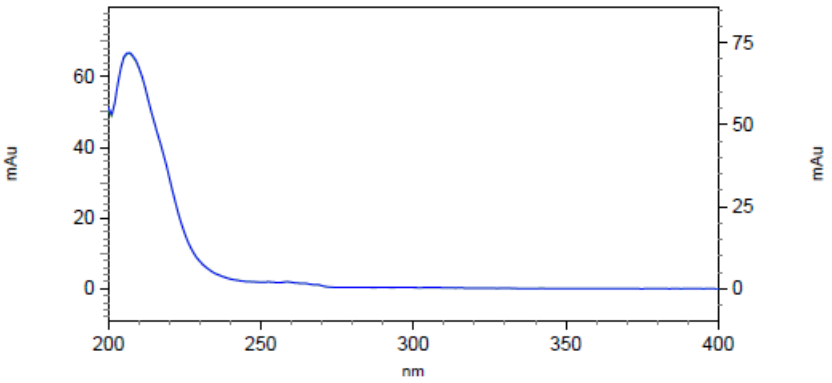
2: 220 nm, 4
nm Results

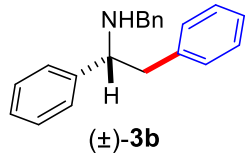
Pk #	Retention Time	Area Percent
1	4.784	98.738
2	5.076	1.262
Totals		100.000


H2O
CH3OH
HCl
NHBn
H
1H NMR of 3b,
500 MHz, CD3OD
f1 (ppm)


CD3OD
135.09
133.67
130.94
129.64
129.42
129.35
129.01
128.99
128.92
128.28
128.14
126.72
64.23
49.53
39.10
HCl
NHBn
H
13C NMR of 3b,
125 MHz, CD3OD
135.5 135.0 134.5 134.0 133.5 133.0
131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



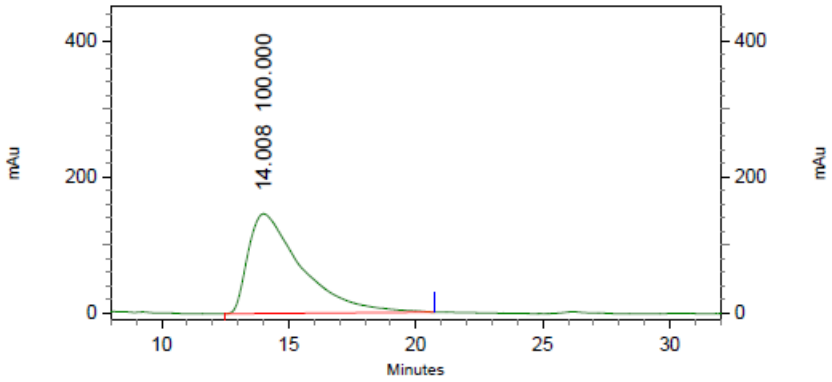


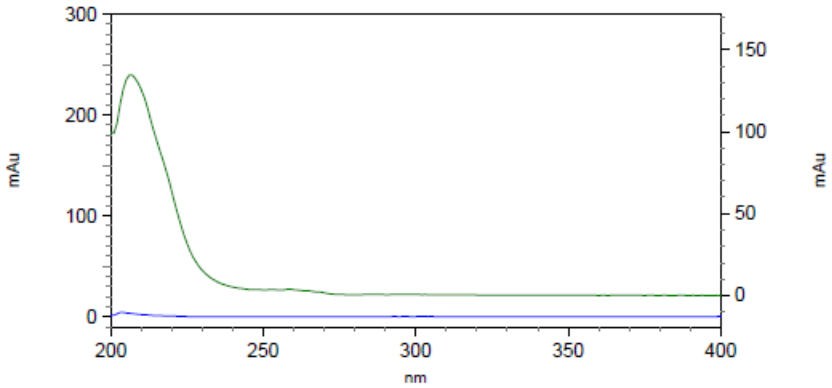


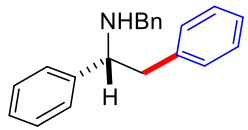
(±)-**3b**

1: 207 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	14.340	48.718	1
	19.848	51.282	2
Totals		100.000	





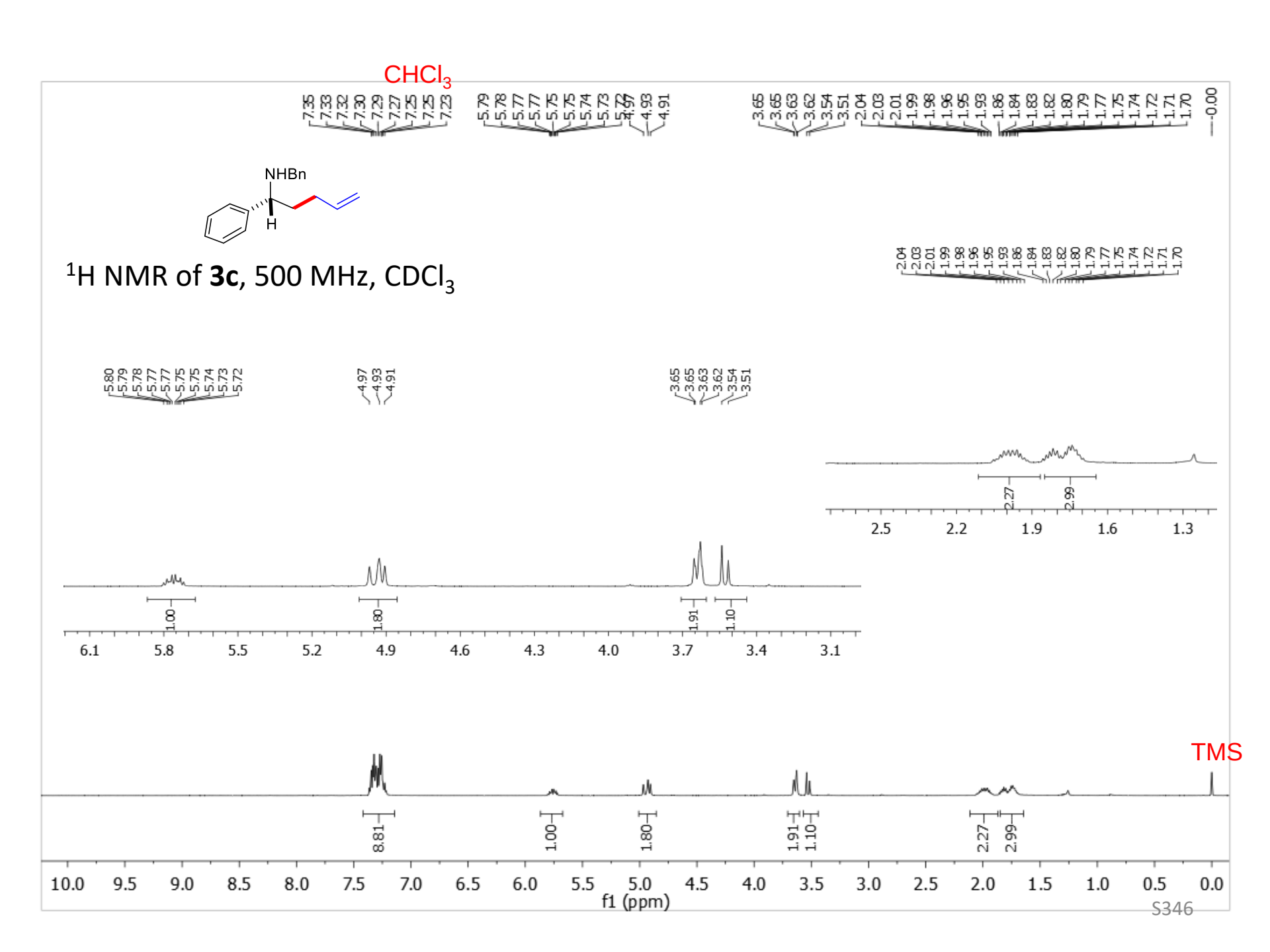


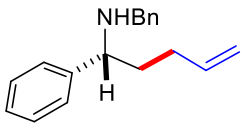
(+)-**3b**

1: 207 nm, 4 nm
Results

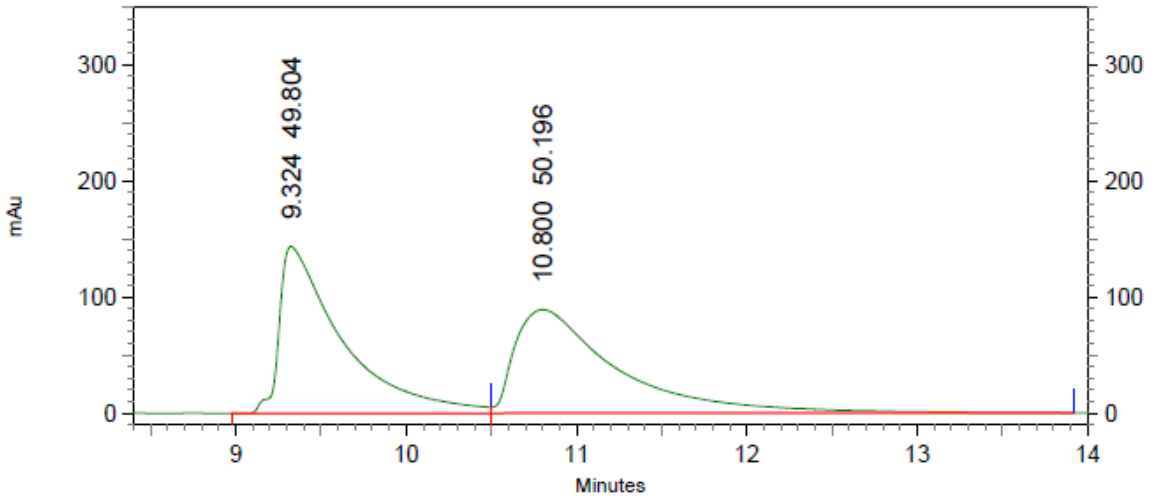
Name	Retention Time	Area Percent	Pk #
	14.008	100.000	1

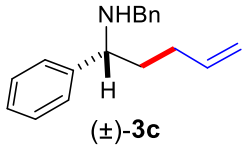
Totals		
	100.000	


CHCl3
NHBn
H
1H NMR of 3c, 500 MHz, CDCl3
TMS
f1 (ppm)

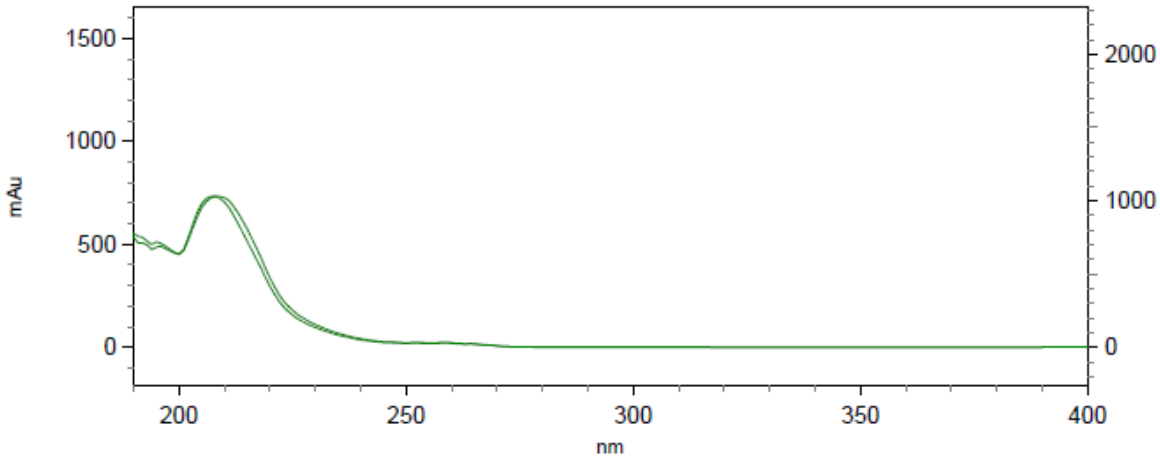


^{13}C NMR of **3c**, 150 MHz, $CDCl_3$





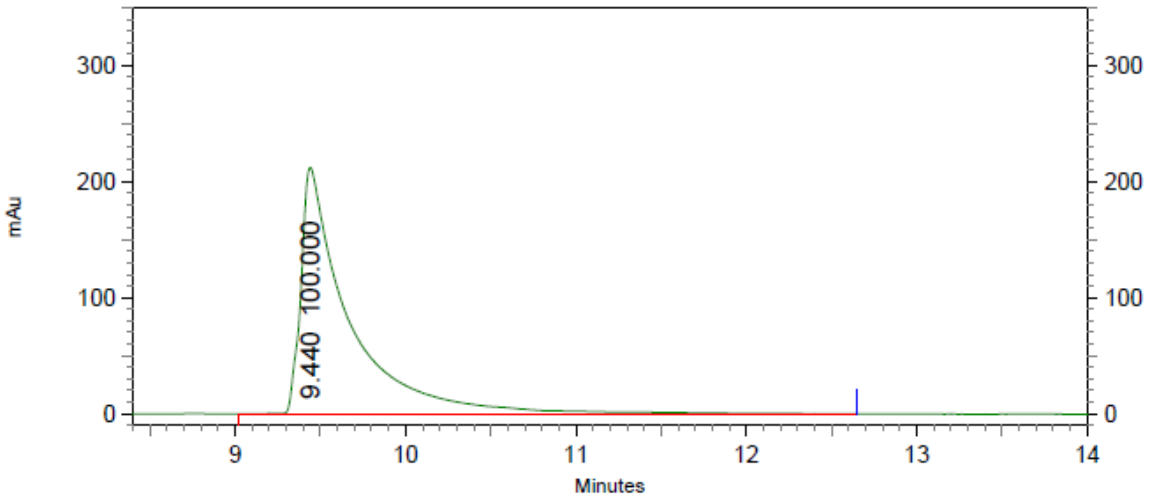
(±)-**3c**

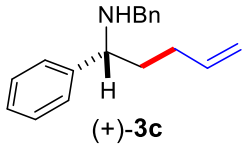


4: 224 nm, 4
nm Results

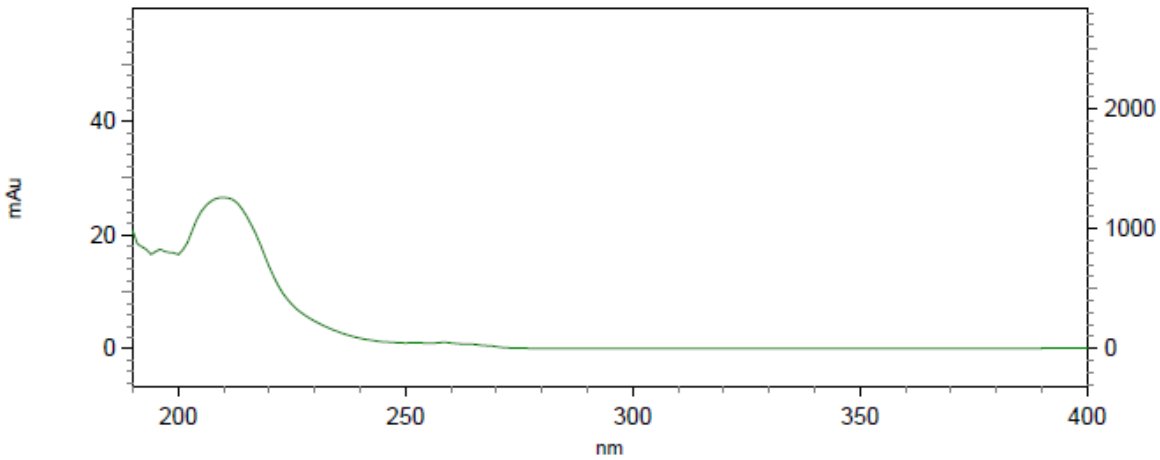
Pk #	Retention Time	Area Percent
1	9.324	49.804
2	10.800	50.196

Totals	
	100.000





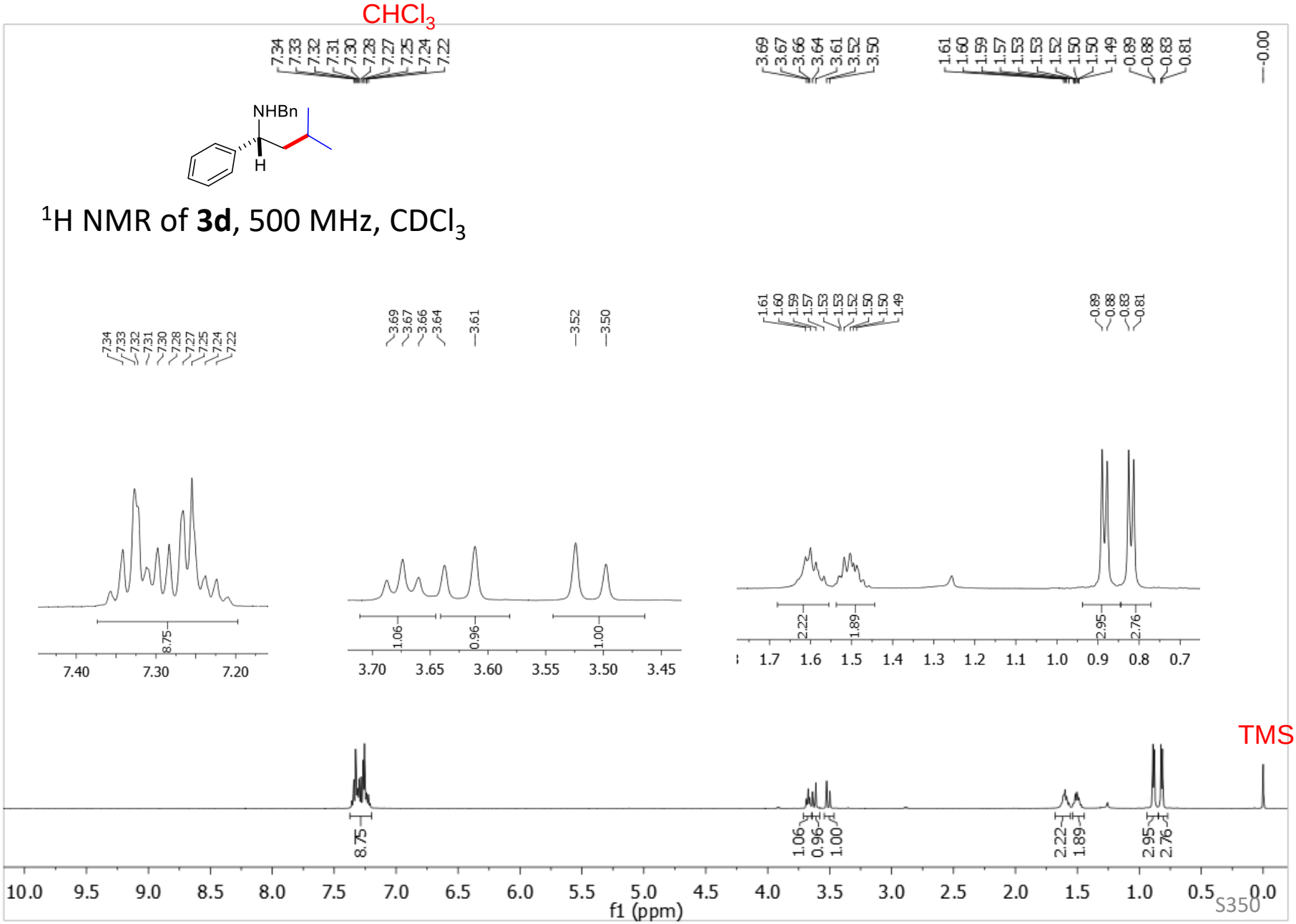
(+)-**3c**



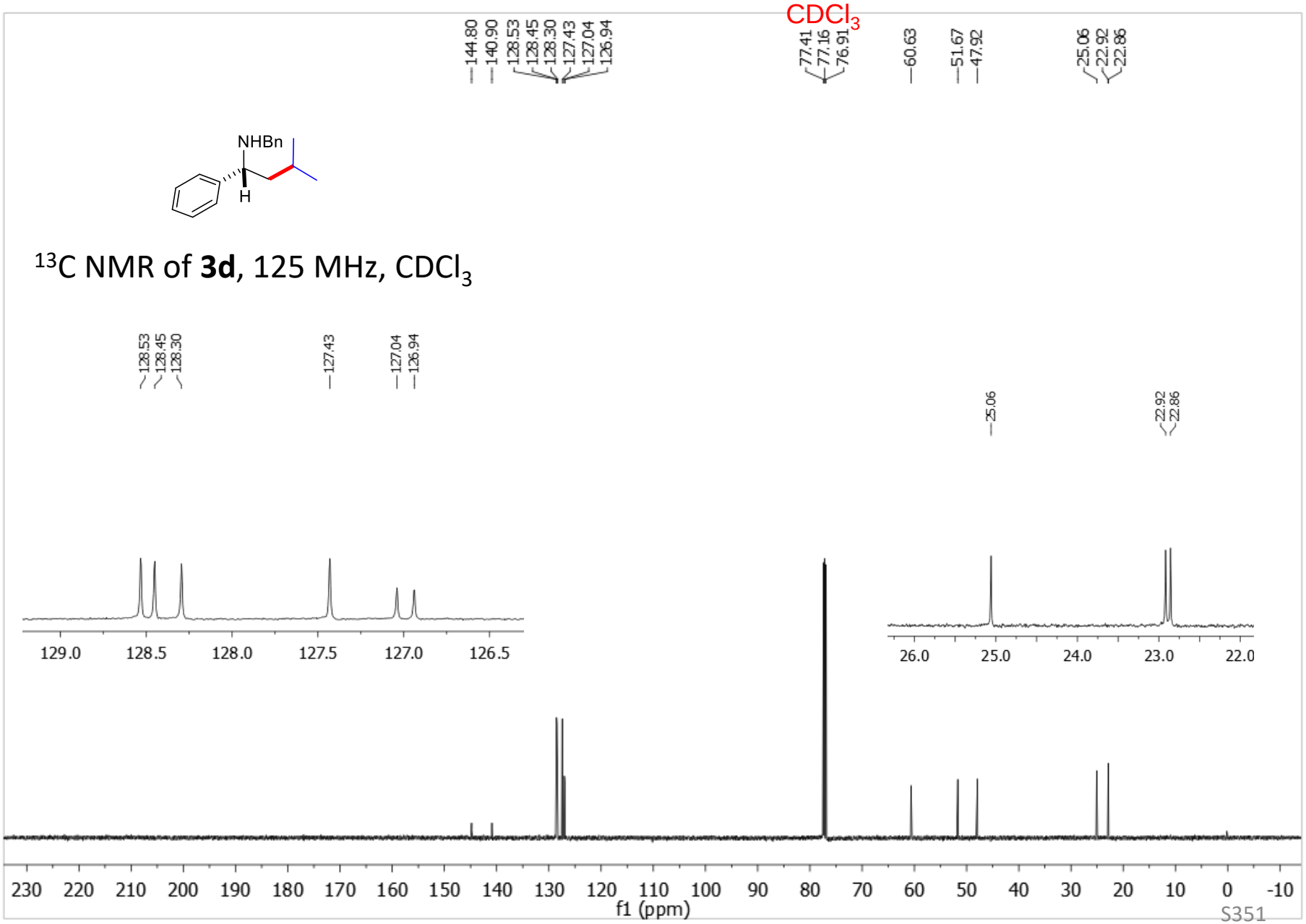
4: 224 nm, 4
nm Results

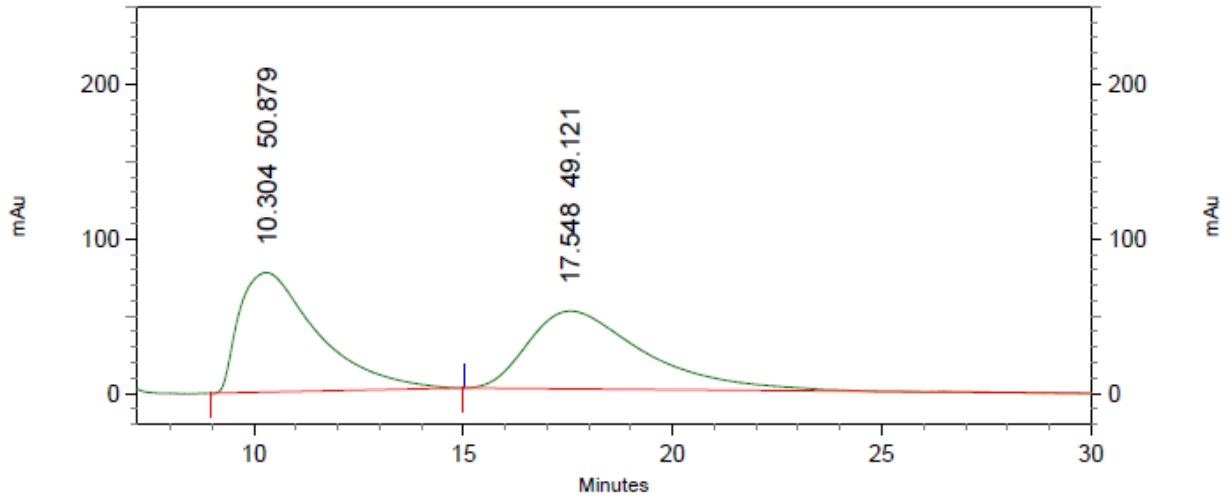
Pk #	Retention Time	Area Percent
1	9.440	100.000

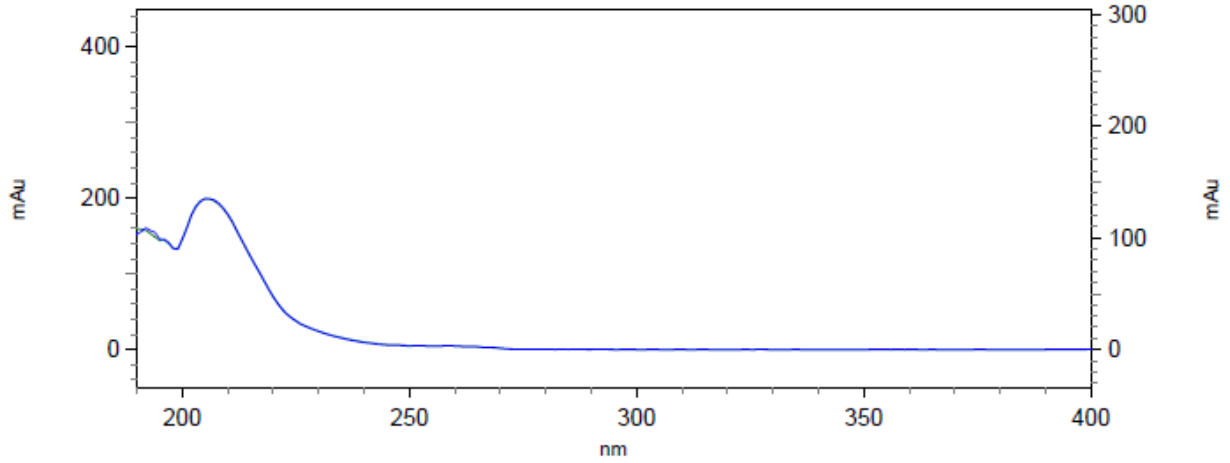
Totals	
	100.000

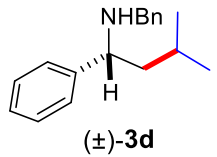


^{1}H NMR of **3d**, 500 MHz, $CDCl_3$


144.80
140.90
128.53
128.45
128.30
127.43
127.04
126.94
CDCl3
77.41
77.16
76.91
60.63
51.67
47.92
25.06
22.92
22.86
NHBn
H
13C NMR of 3d, 125 MHz, CDCl3
128.53
128.45
128.30
127.43
127.04
126.94
25.06
22.92
22.86
129.0
128.5
128.0
127.5
127.0
126.5
26.0
25.0
24.0
23.0
22.0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



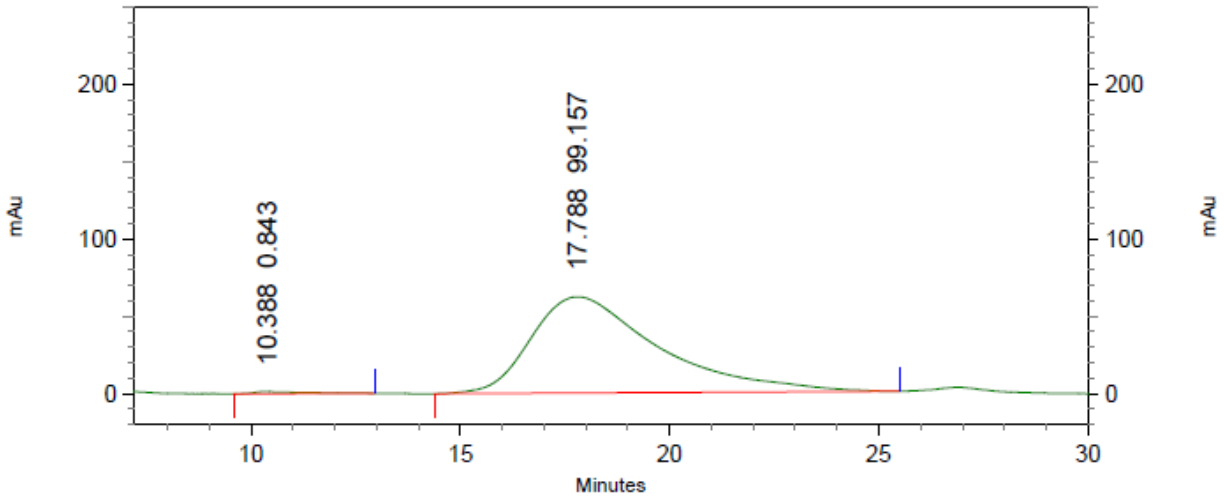


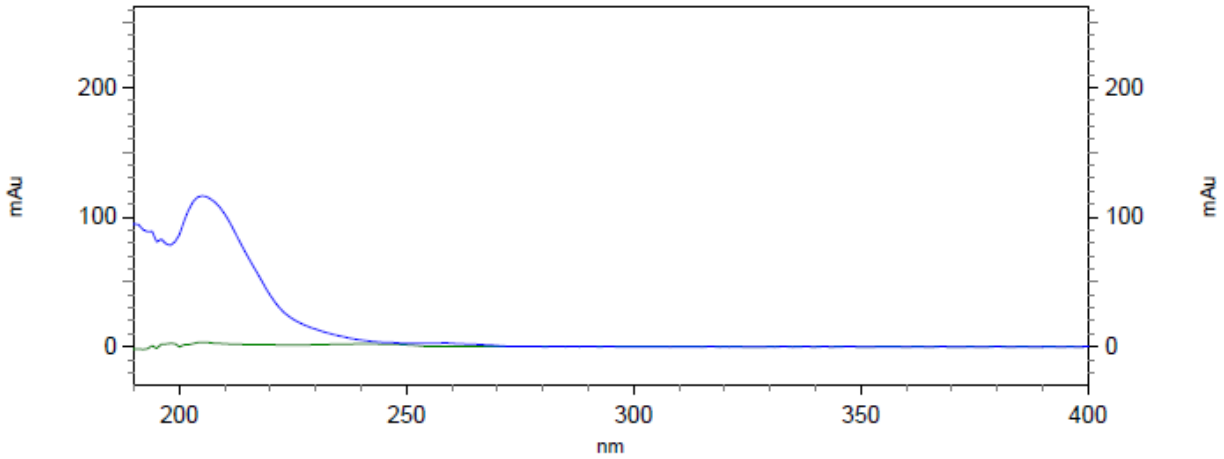


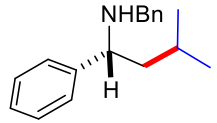
(±)-**3d**

4: 212 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	10.304	50.879
2	17.548	49.121
Totals		100.000





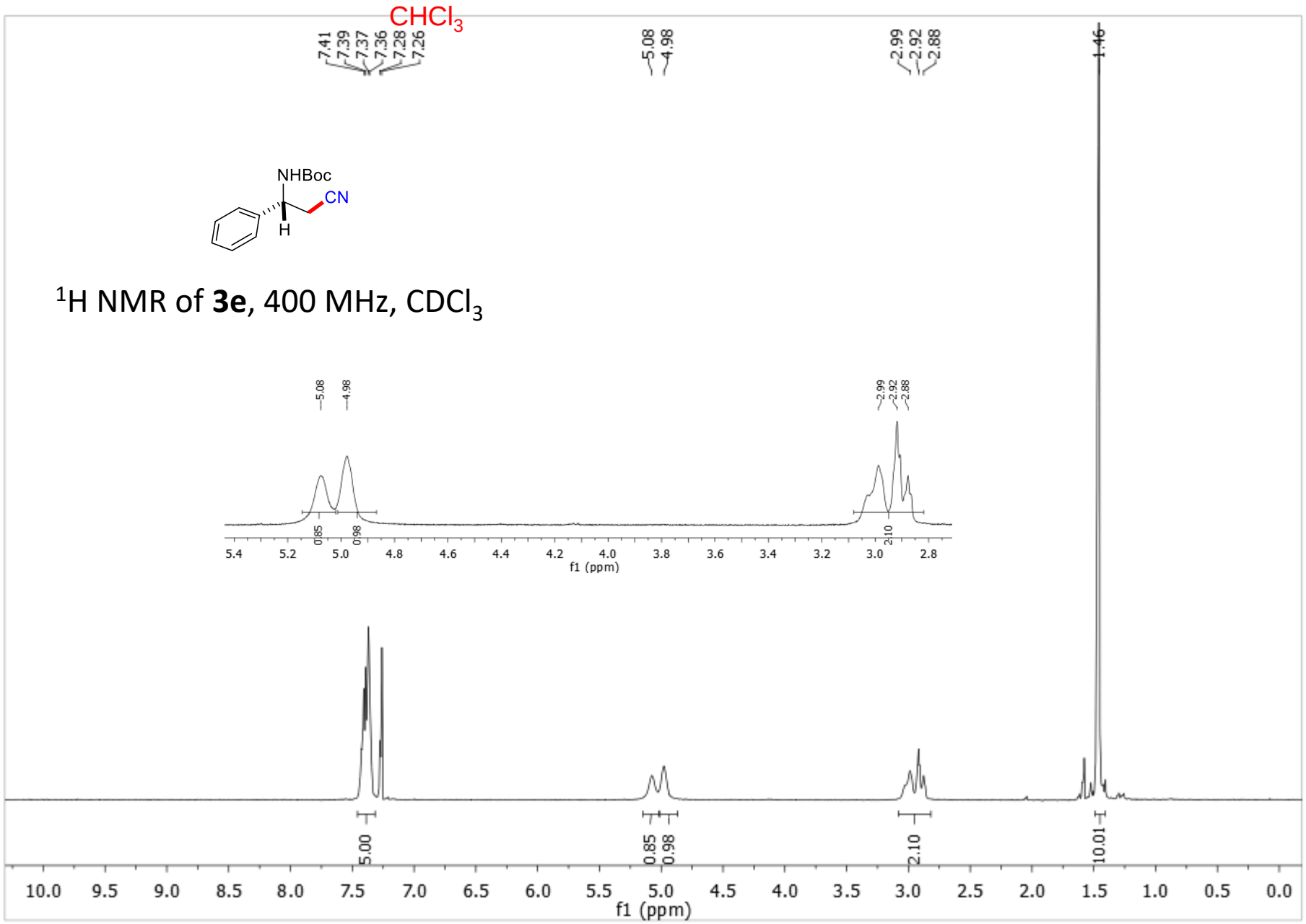


(+)-**3d**

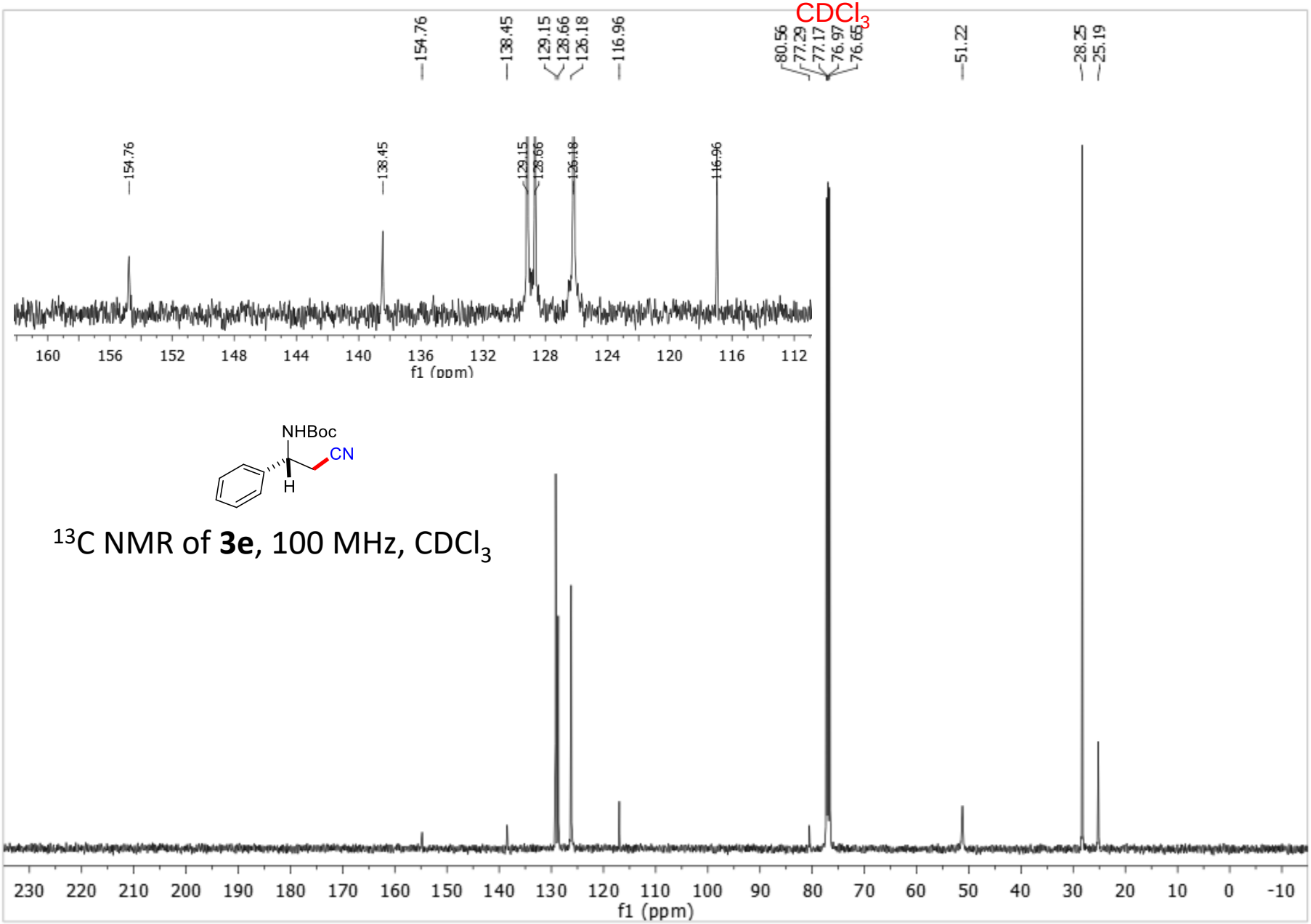
4: 212 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	10.388	0.843
2	17.788	99.157

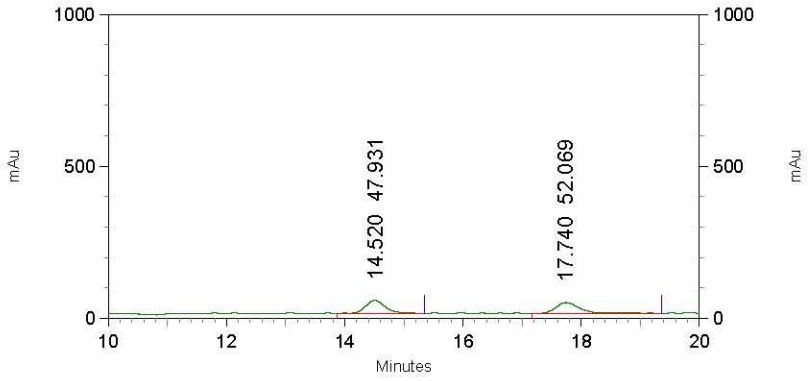
Totals	
	100.000

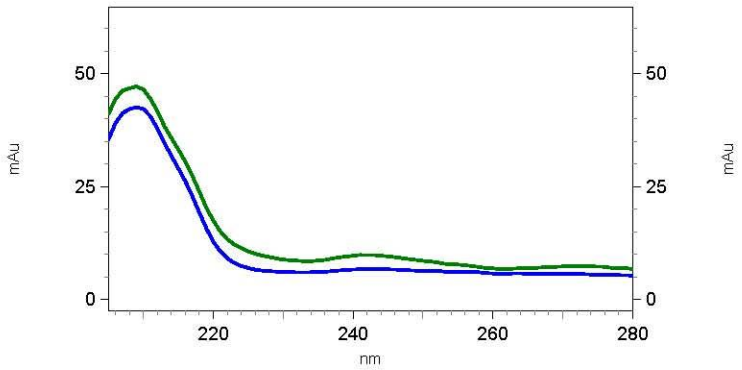


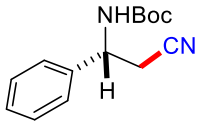
^{1}H NMR of **3e**, 400 MHz, $CDCl_3$



^{13}C NMR of **3e**, 100 MHz, $CDCl_3$





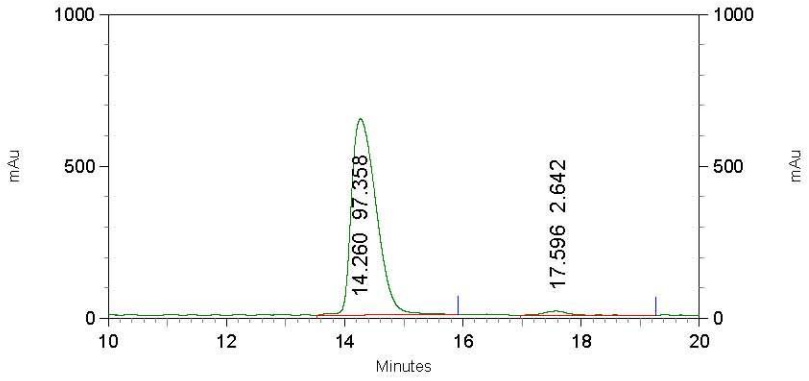


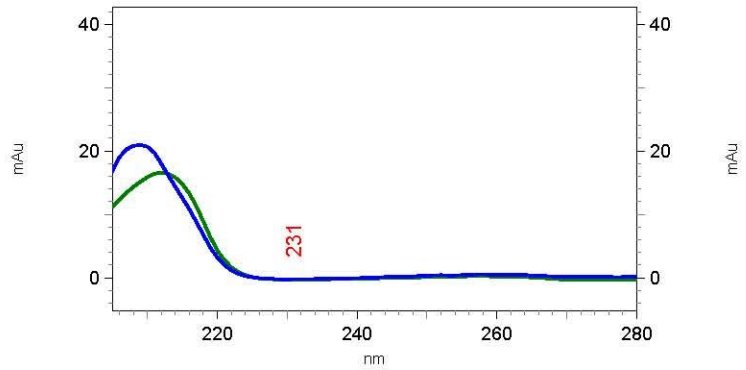
(±)-**3e**

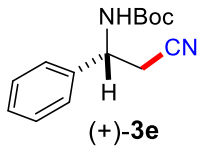
4: 202 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		14.520	47.931
2		17.740	52.069

Totals			100.000





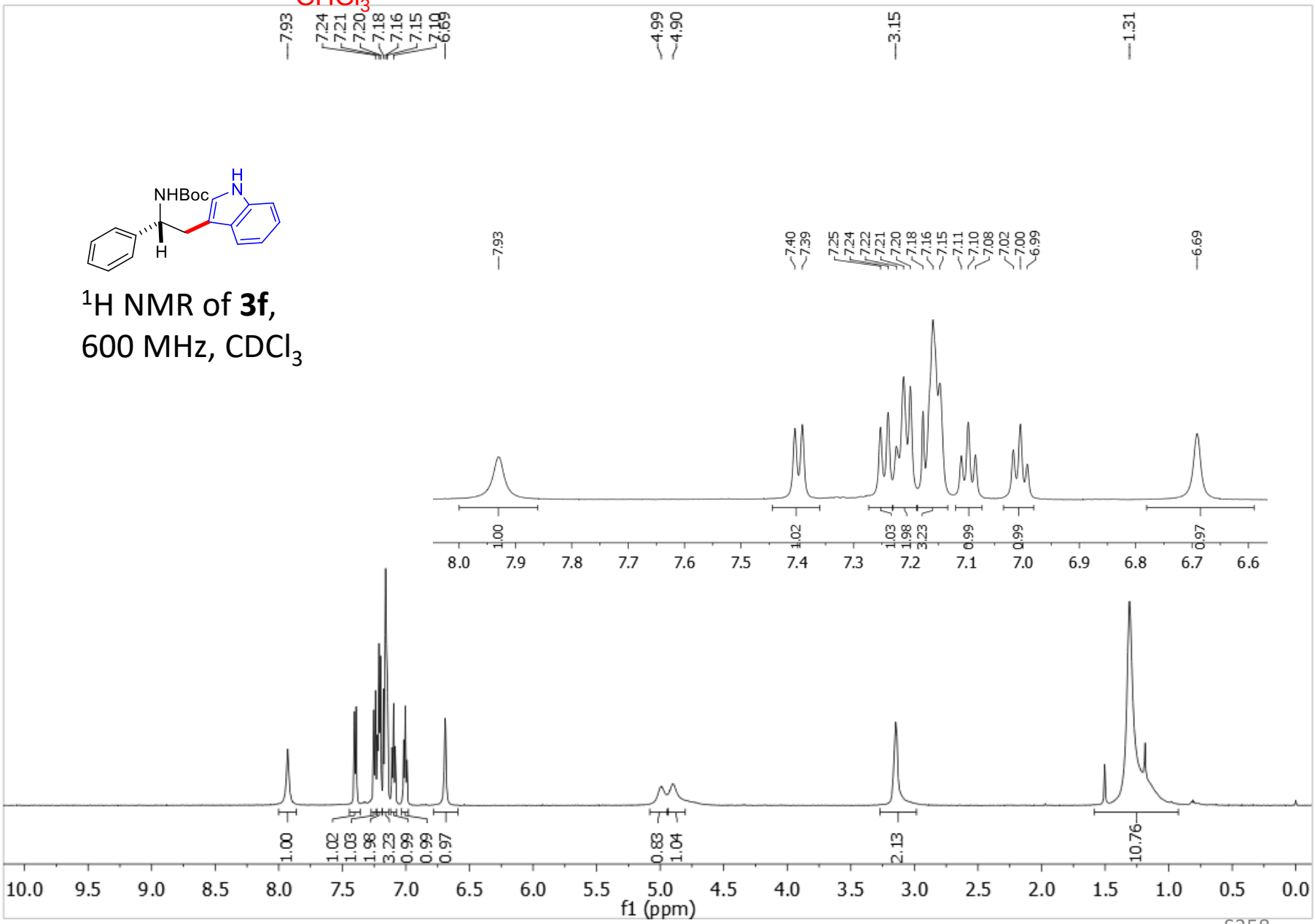


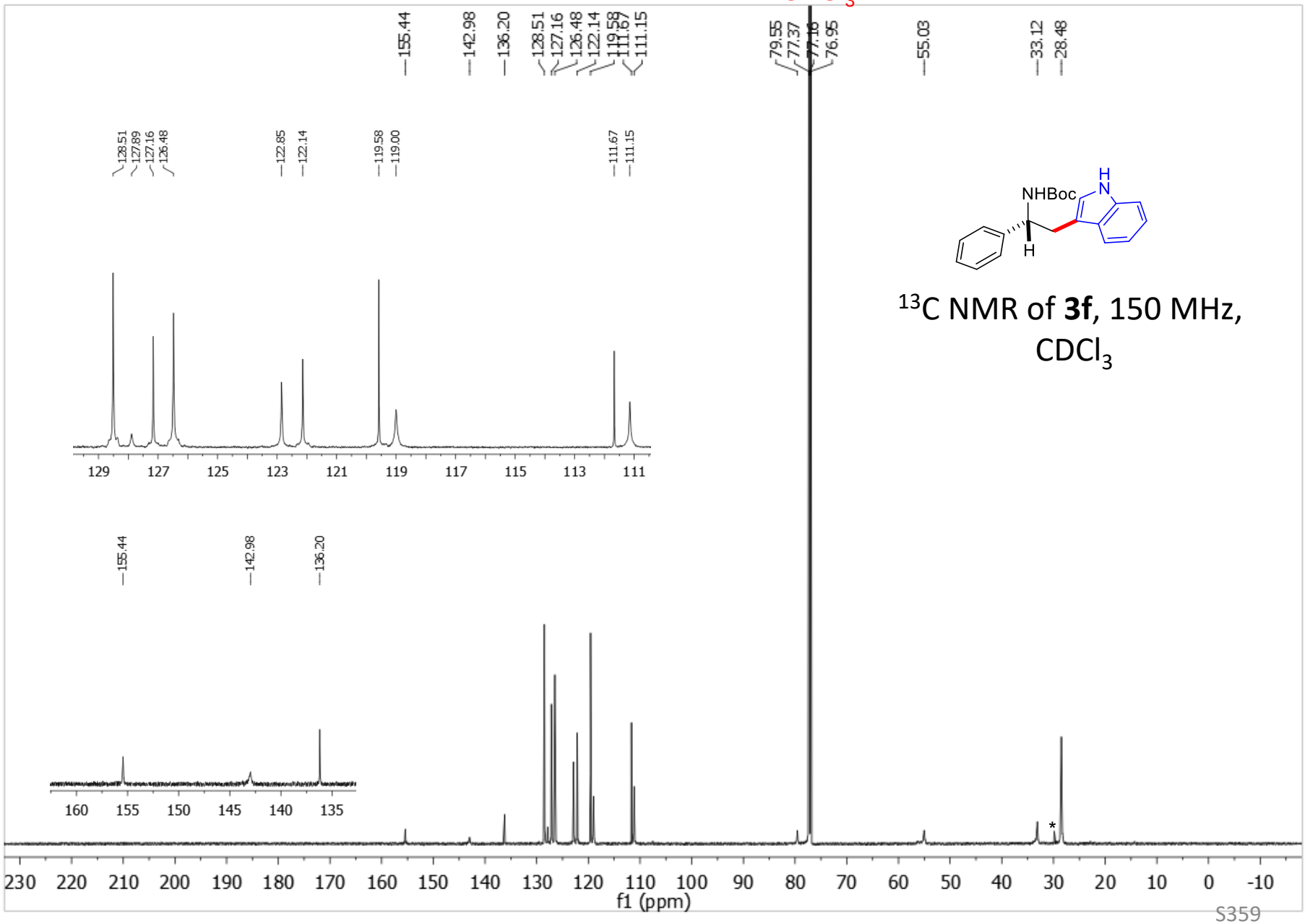
(+)-**3e**

4: 202 nm, 4 nm
Results

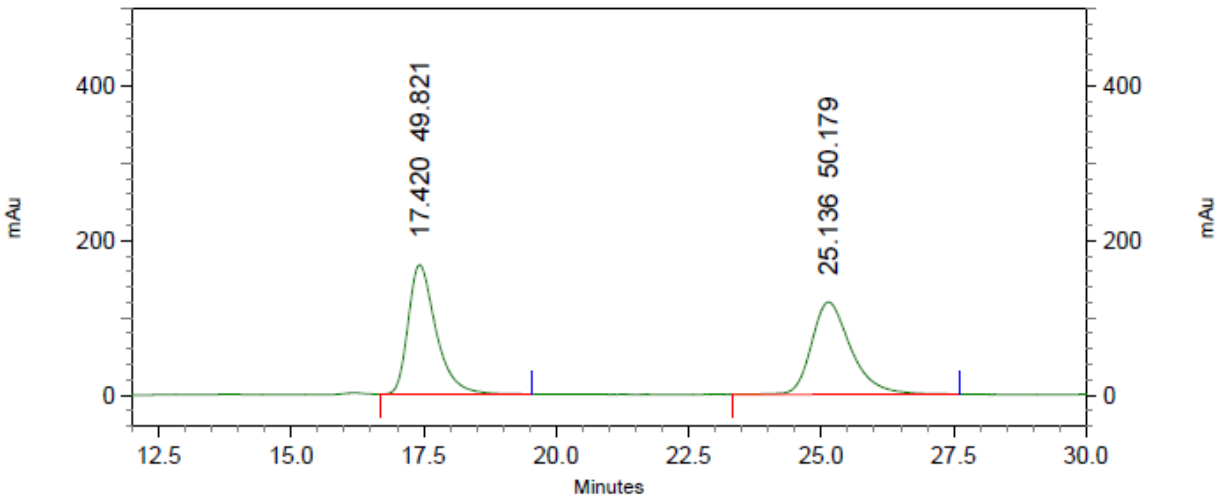
Pk #	Name	Retention Time	Area Percent
1		14.260	97.358
2		17.596	2.642

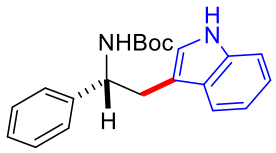
Totals			100.000


CHCl3
NHBoc
H
N
H
1H NMR of 3f,
600 MHz, CDCl3
f1 (ppm)

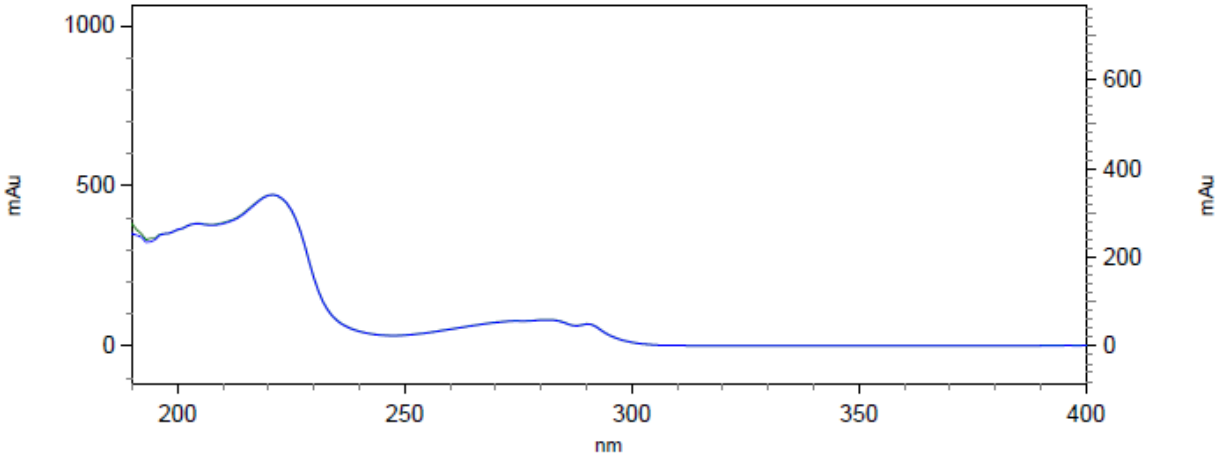


^{13}C NMR of **3f**, 150 MHz, $CDCl_3$





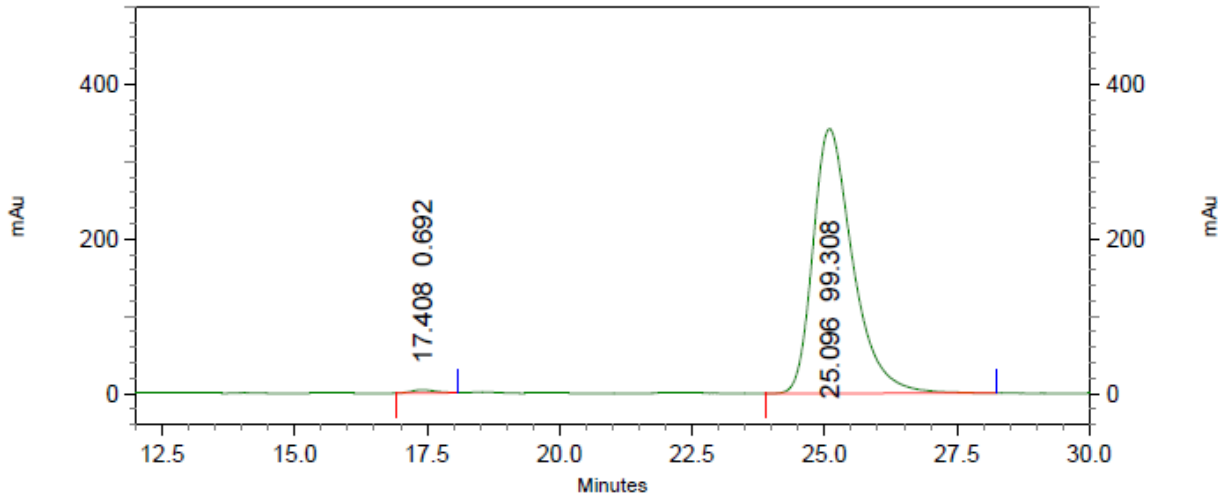
(±)-3f

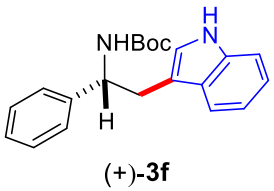


4: 235 nm, 4
nm Results

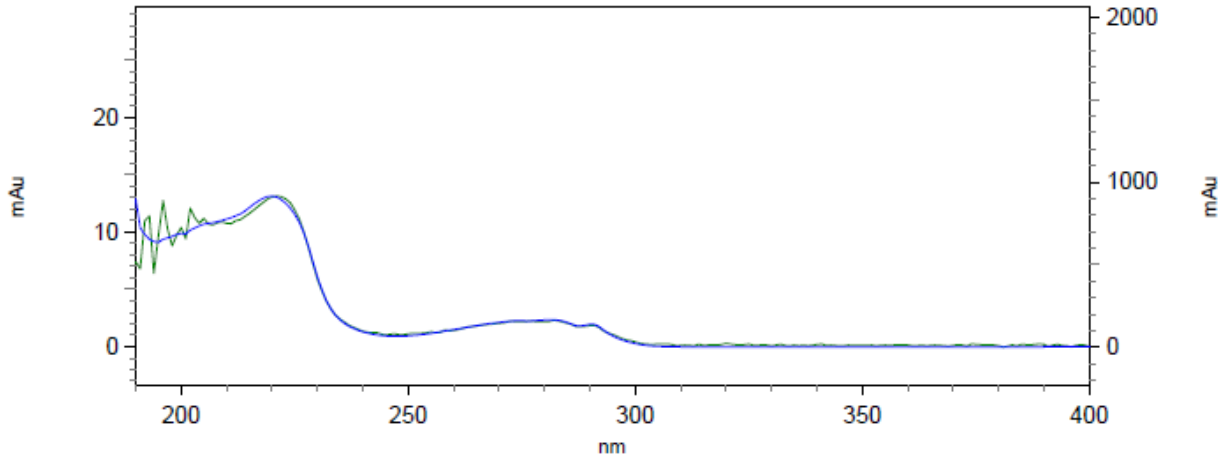
Pk #	Retention Time	Area Percent
1	17.420	49.821
2	25.136	50.179

Totals	
	100.000





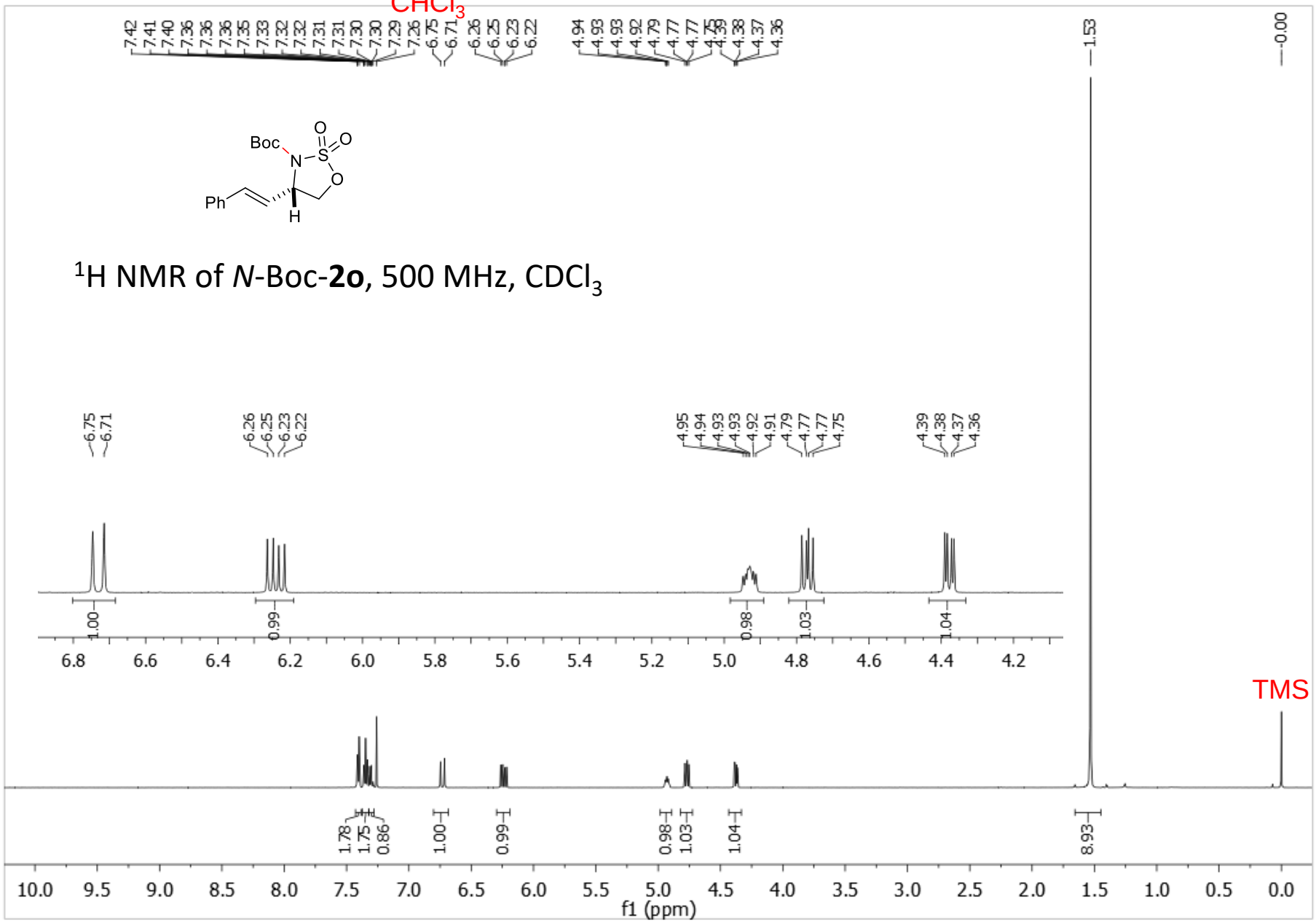
(+)-**3f**

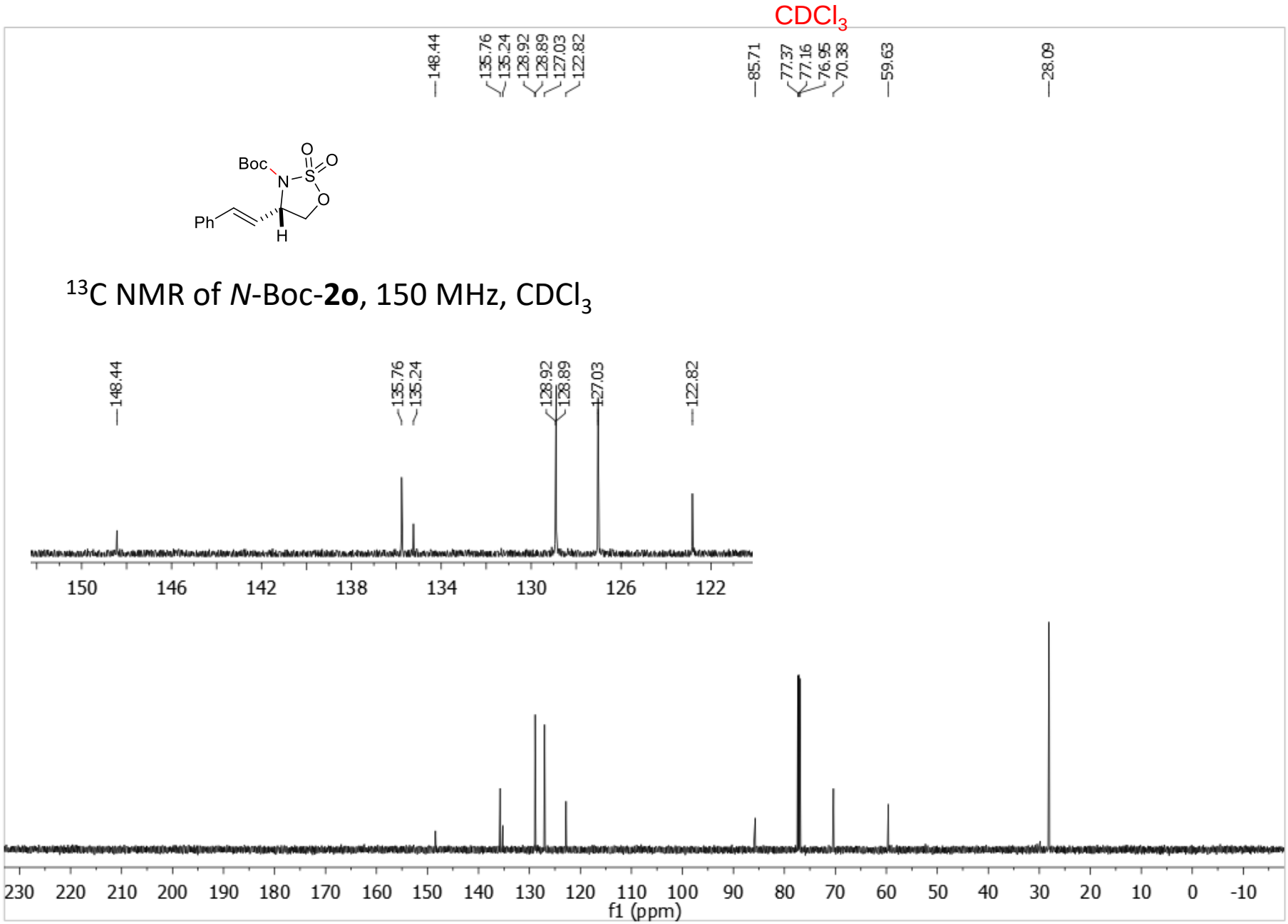


4: 235 nm, 4
nm Results

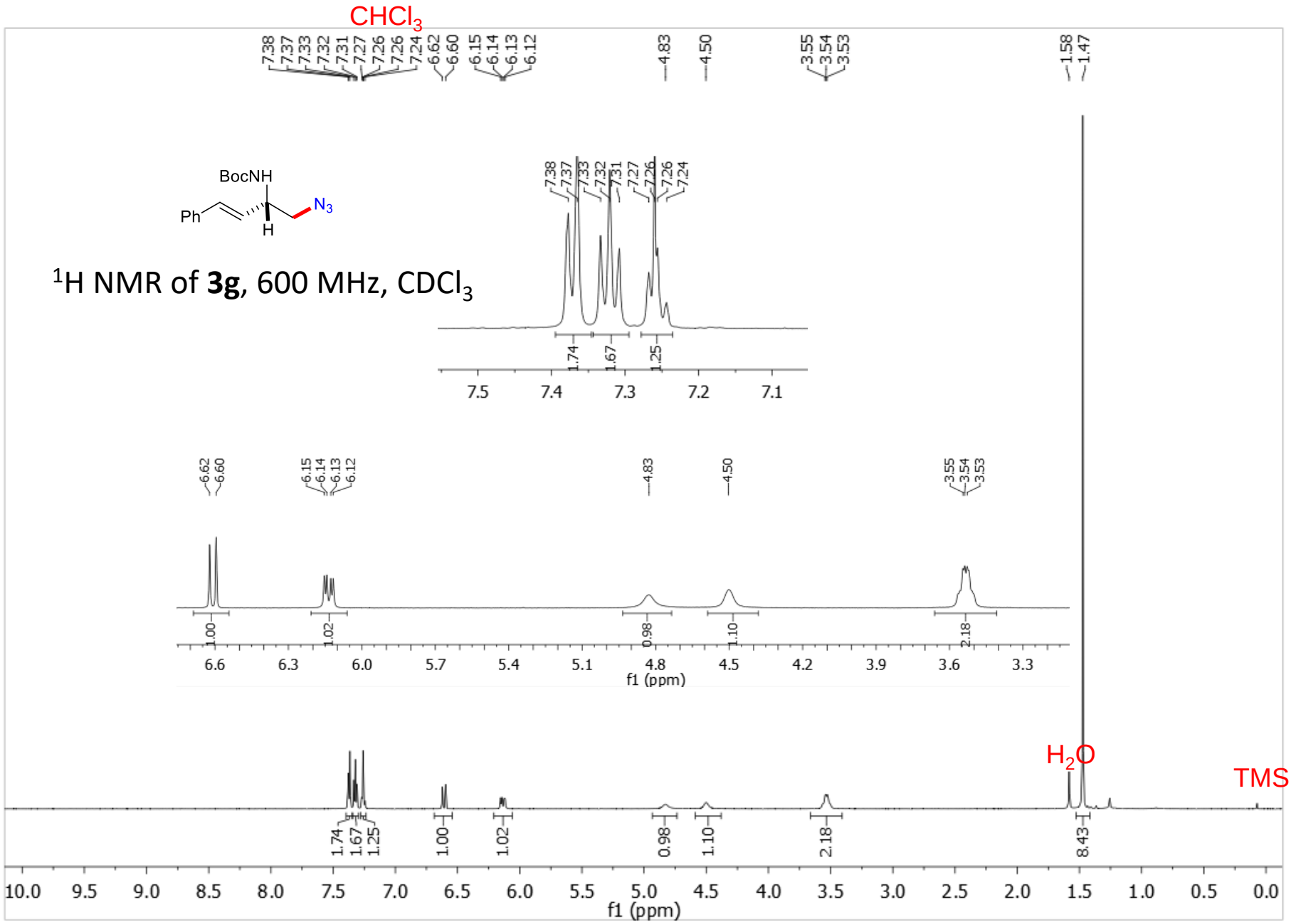
Pk #	Retention Time	Area Percent
1	17.408	0.692
2	25.096	99.308

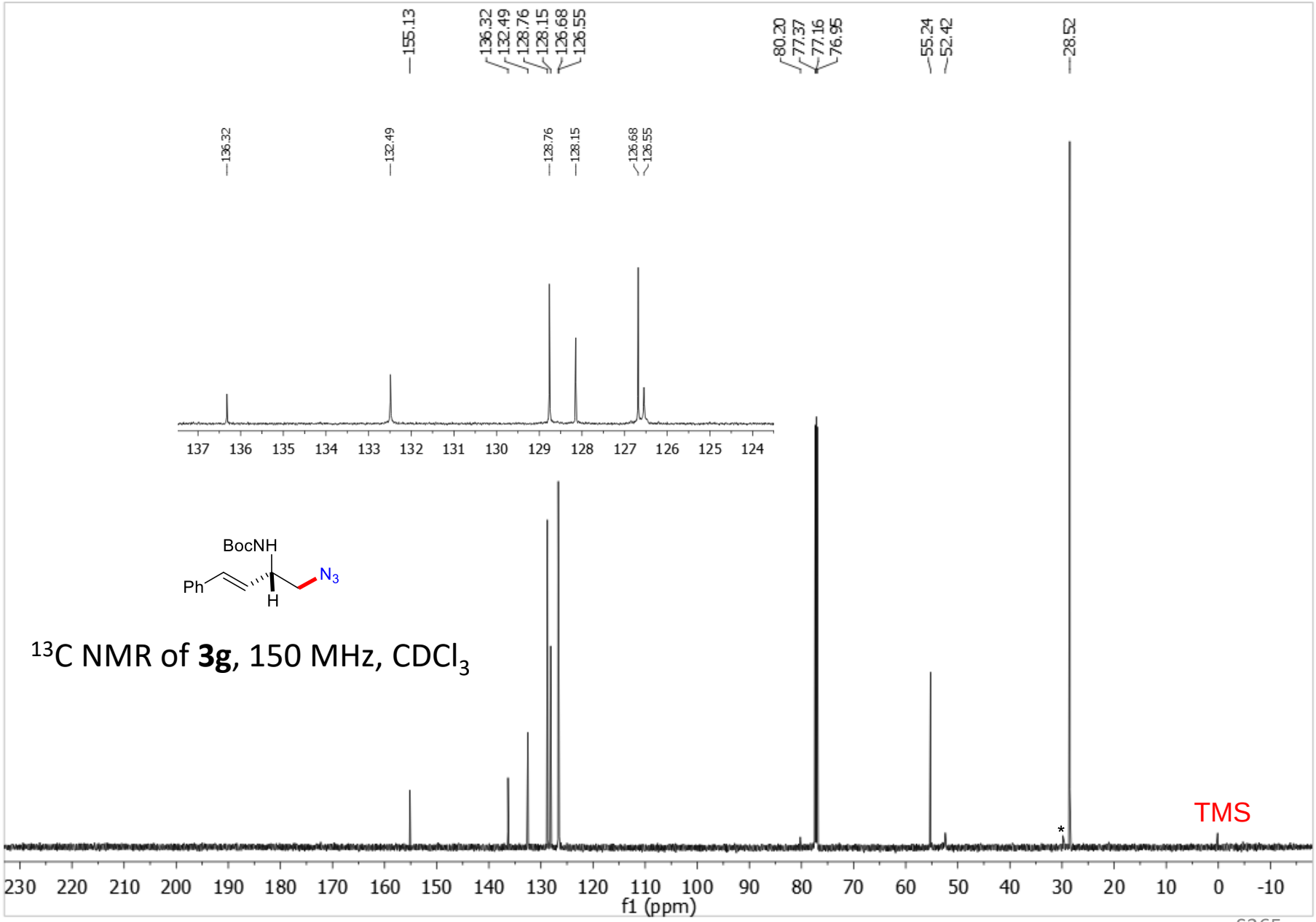
Totals	
	100.000


CHCl3
Boc
N
S
O
O
O
Ph
H
1H NMR of N-Boc-2o, 500 MHz, CDCl3
TMS
f1 (ppm)



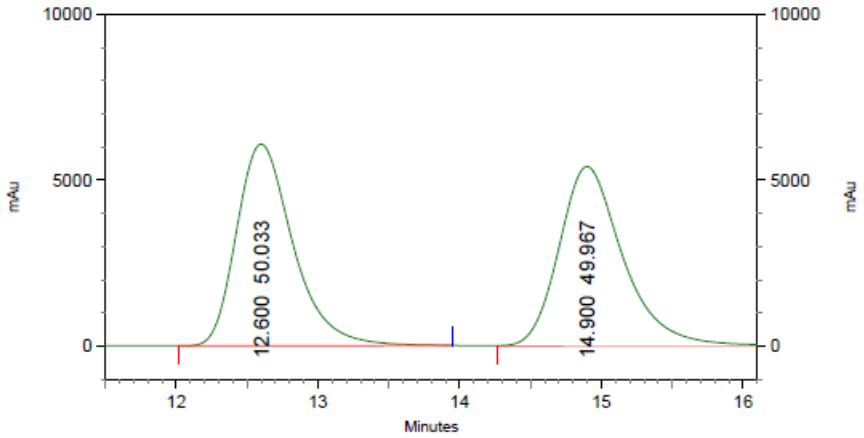
^{13}C NMR of *N*-Boc-**2o**, 150 MHz, $CDCl_3$

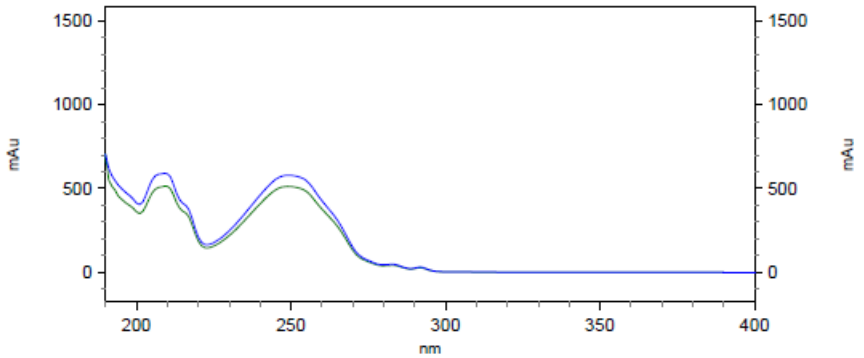

CHCl3
BocNH
Ph
N3
H
1H NMR of 3g, 600 MHz, CDCl3
H2O
TMS
f1 (ppm)

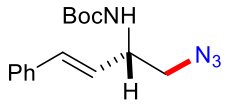


^{13}C NMR of **3g**, 150 MHz, $CDCl_3$

K0L-426-ADH-5%-1.0-2
C:\EZStart\Projects\Default\Data\K0L-426-ADH-5%-1.0-2
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met







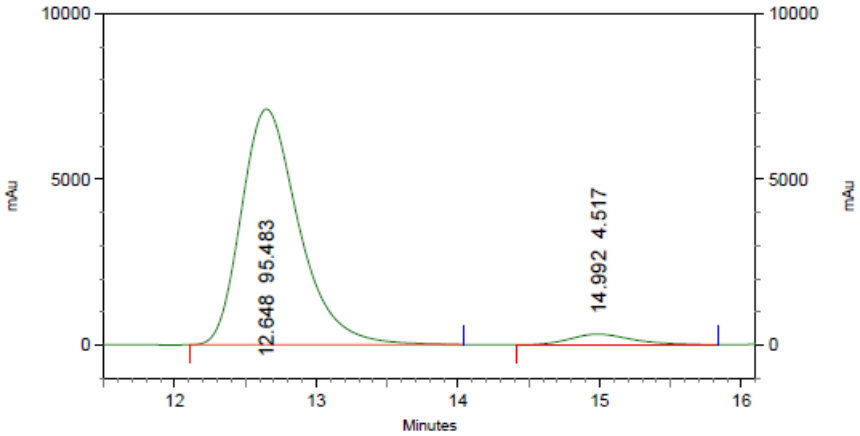
(±)-**3g**

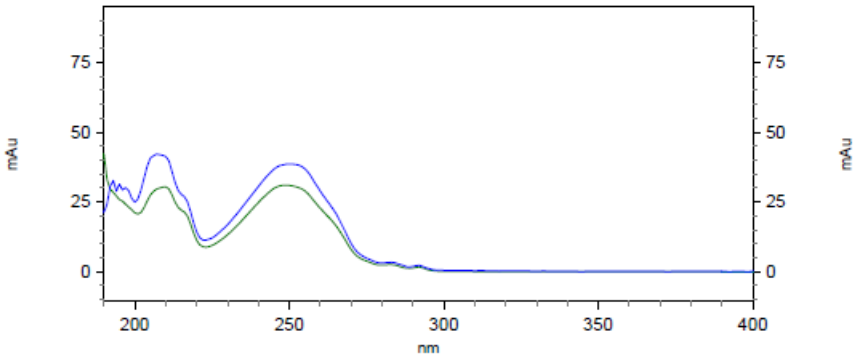
1: 261 nm, 4
nm Results

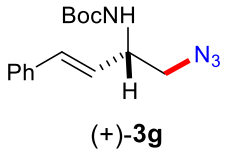
Pk #	Retention Time	Area Percent
1	12.600	50.033
2	14.900	49.967

Totals	
	100.000

K0L-416-ADH-5%-1.0
C:\EZStart\Projects\Default\Data\K0L-416-ADH-5%-1.0
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met





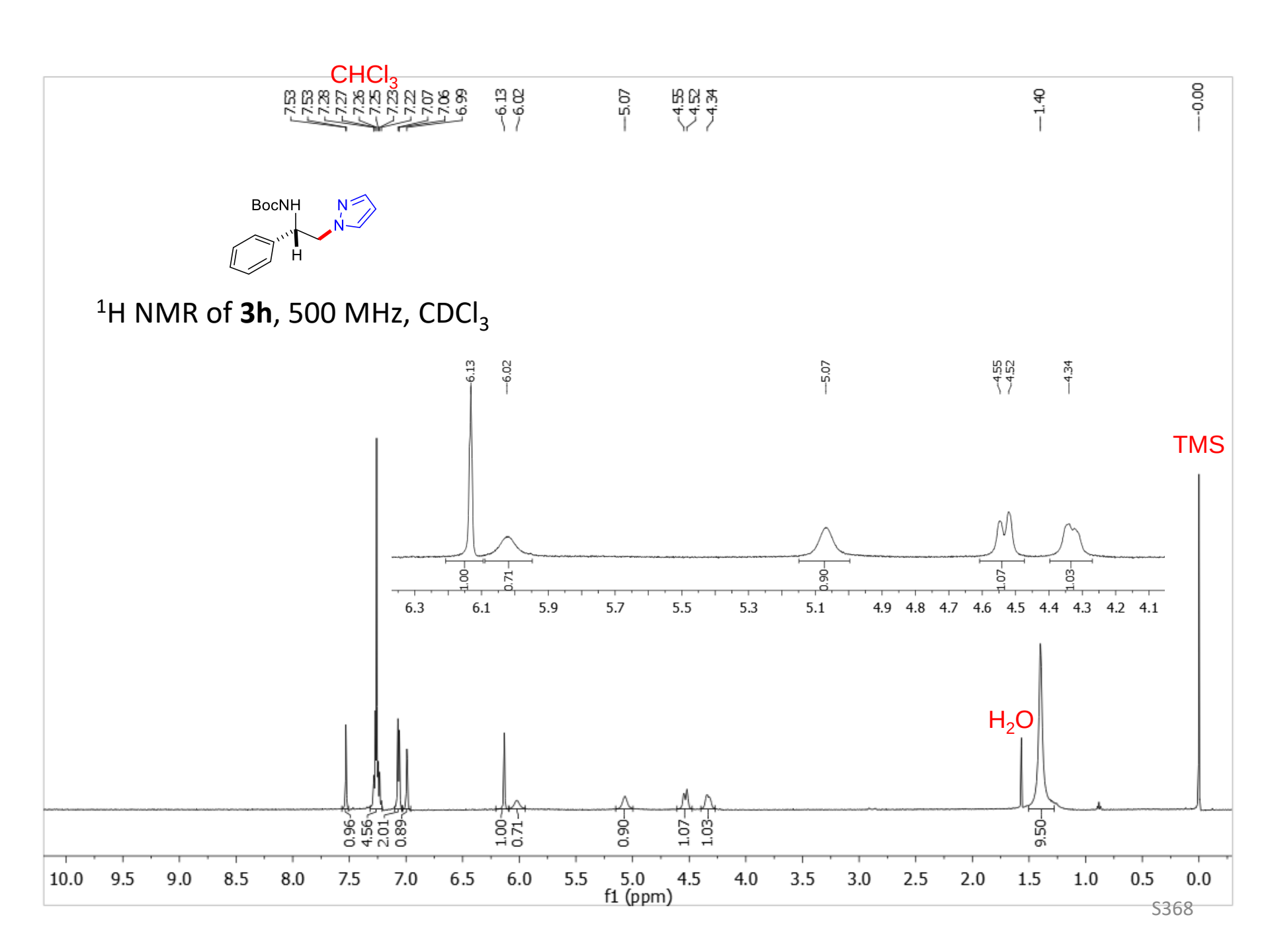


(+)-**3g**

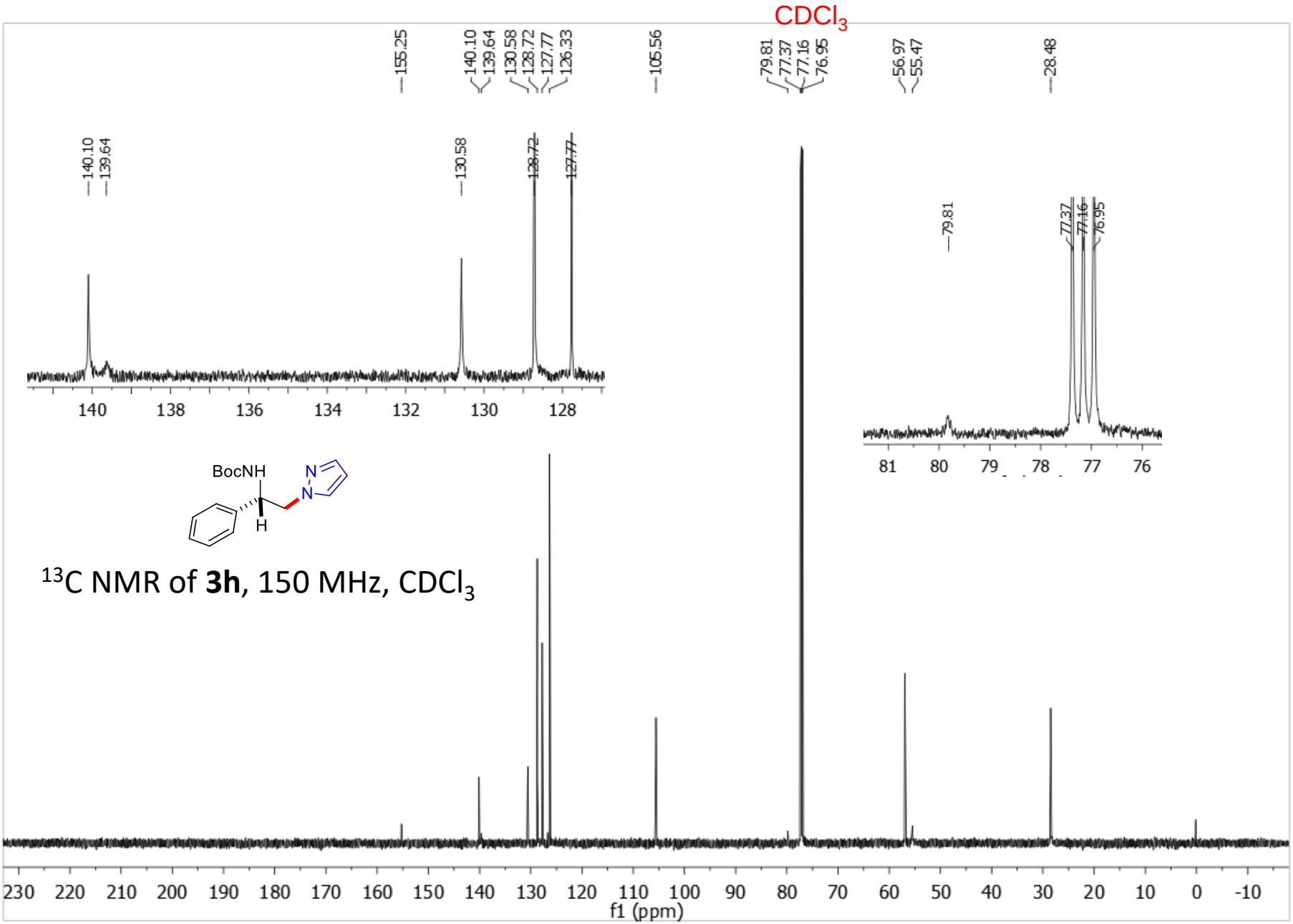
1: 261 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.648	95.483
2	14.992	4.517

Totals	
	100.000

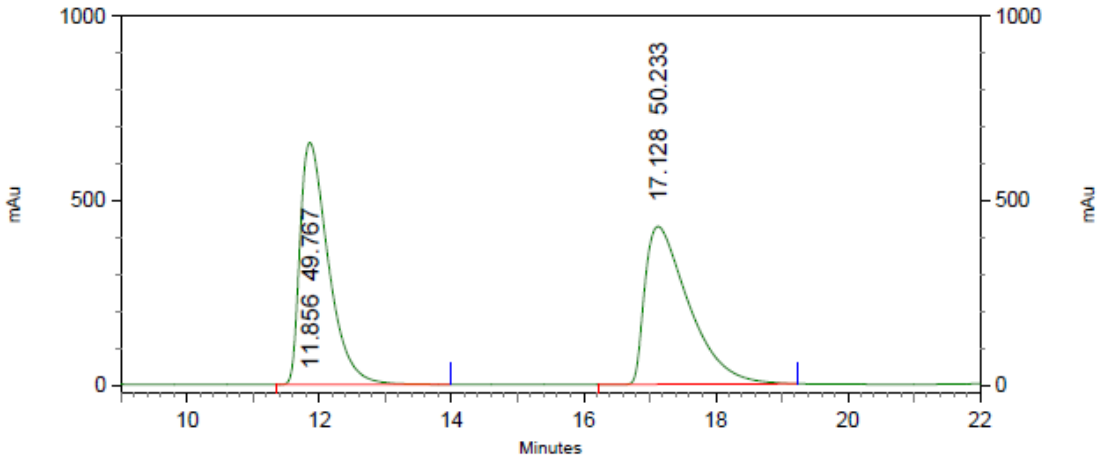


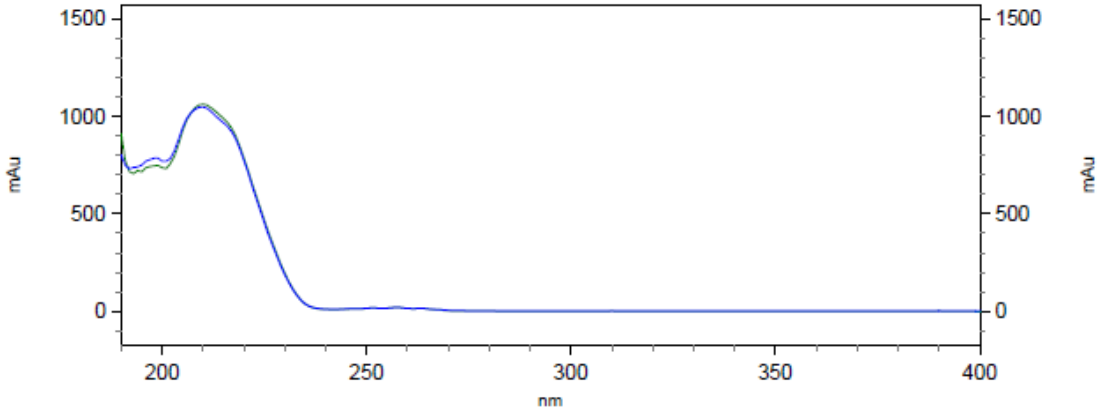
^{1}H NMR of **3h**, 500 MHz, $CDCl_3$

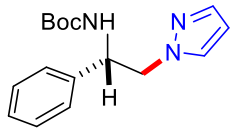


^{13}C NMR of **3h**, 150 MHz, $CDCl_3$

C:\EZStart\Projects\Default\Data\K0L-407-IC-10-1mL
C:\Documents and Settings\zhang\Desktop\DSW\04042018.met





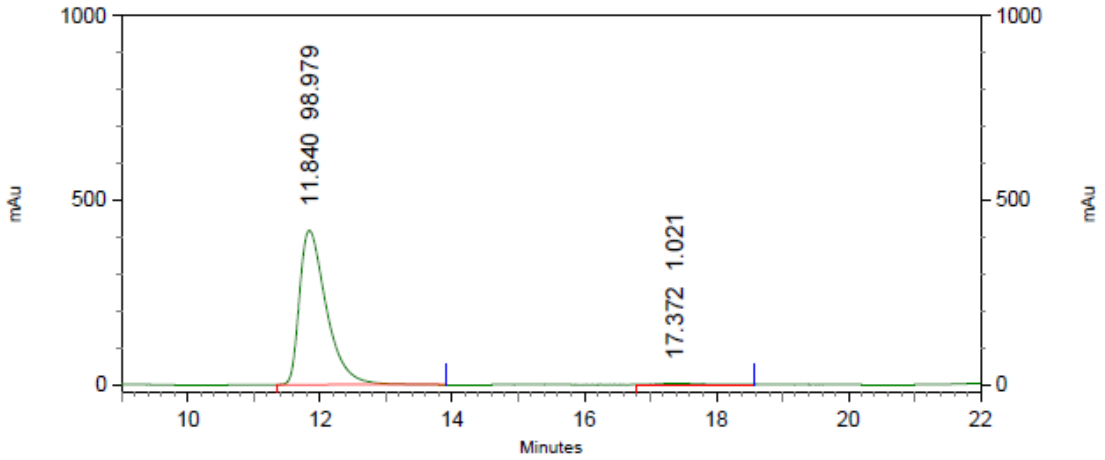


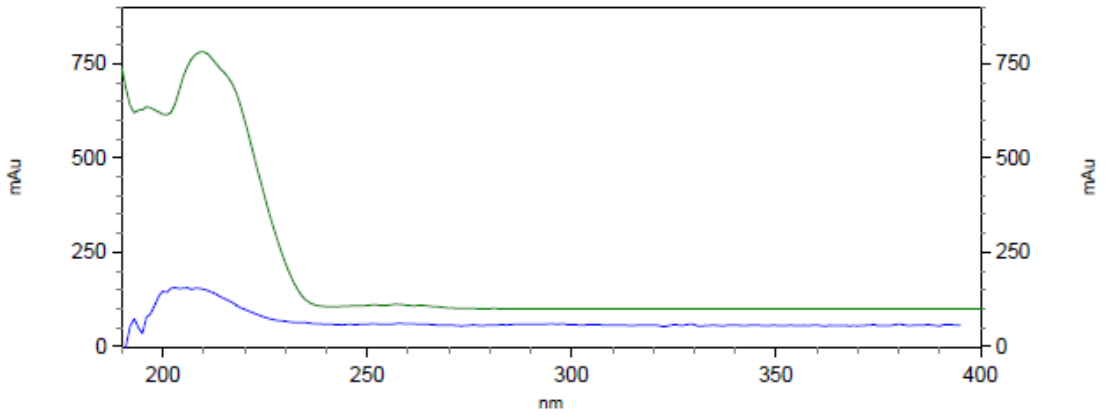
(±)-**3h**

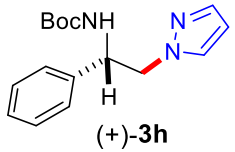
4: 222 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	11.856	49.767
2	17.128	50.233
Totals		100.000

C:\EZStart\Projects\Default\Data\K0L-406-IC-10%-1mL
C:\Documents and Settings\zhang\Desktop\DSW\04042018.met



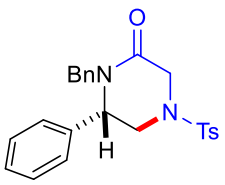




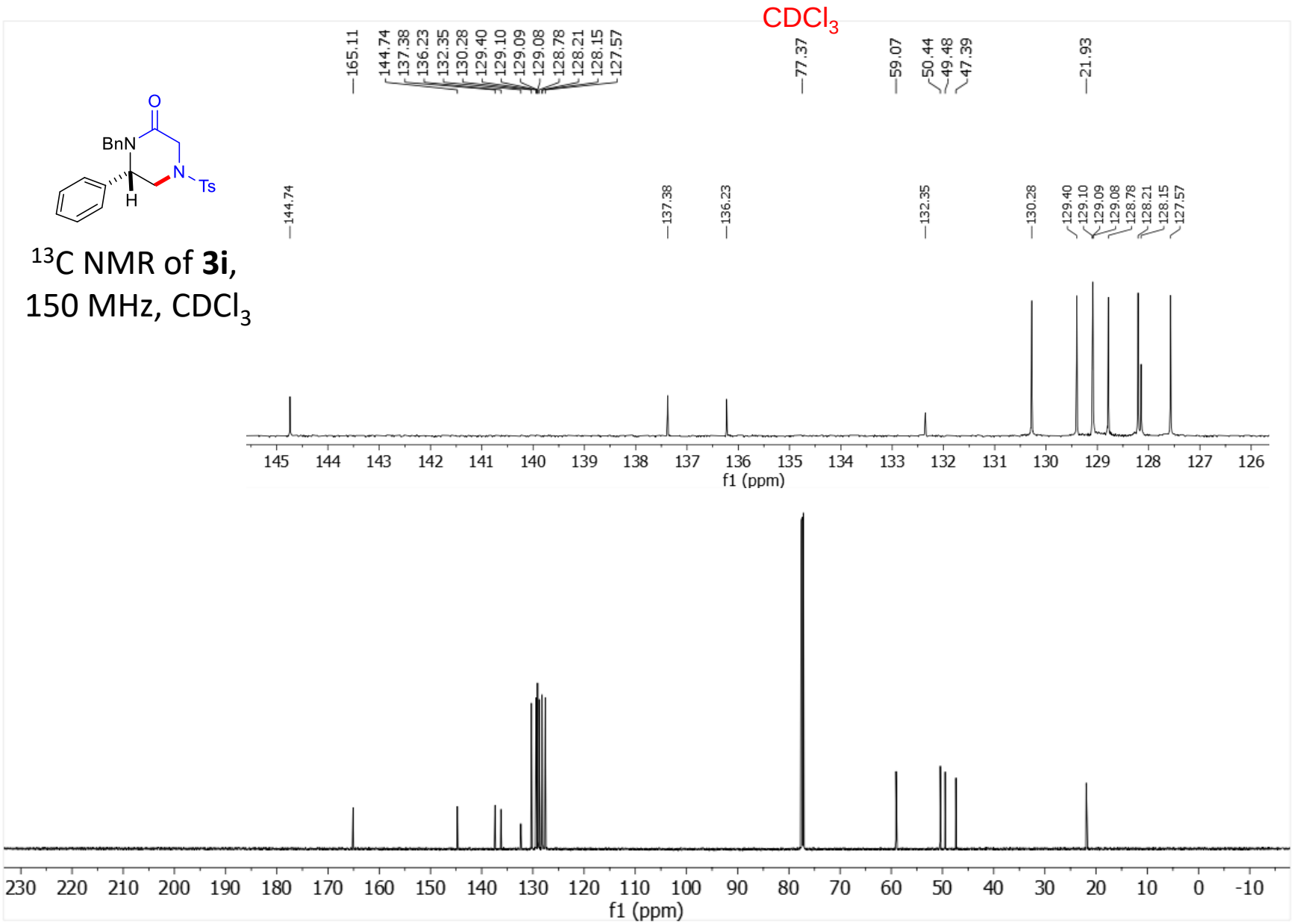
(+)-**3h**

4: 222 nm, 4
nm Results

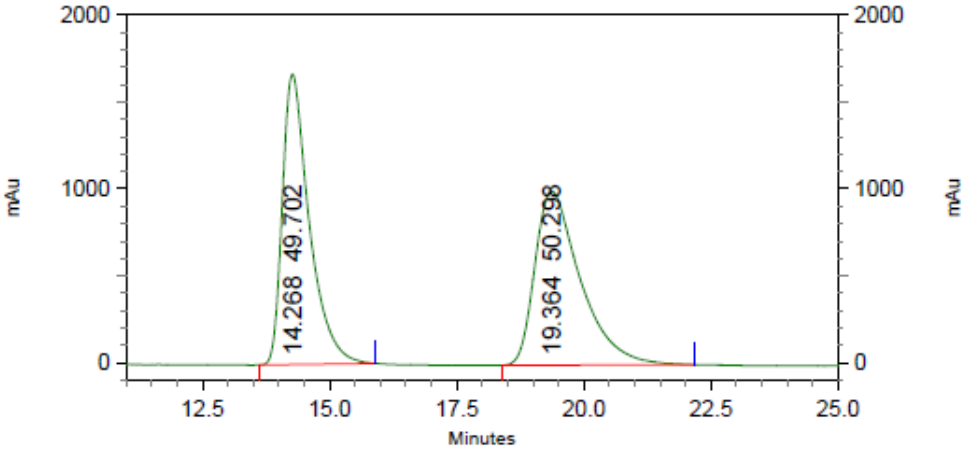
Pk #	Retention Time	Area Percent
1	11.840	98.979
2	17.372	1.021
Totals		100.000

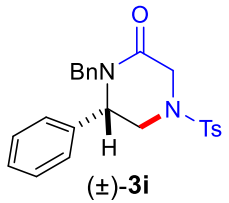


^{1}H NMR of **3i**,
600 MHz, $CDCl_3$

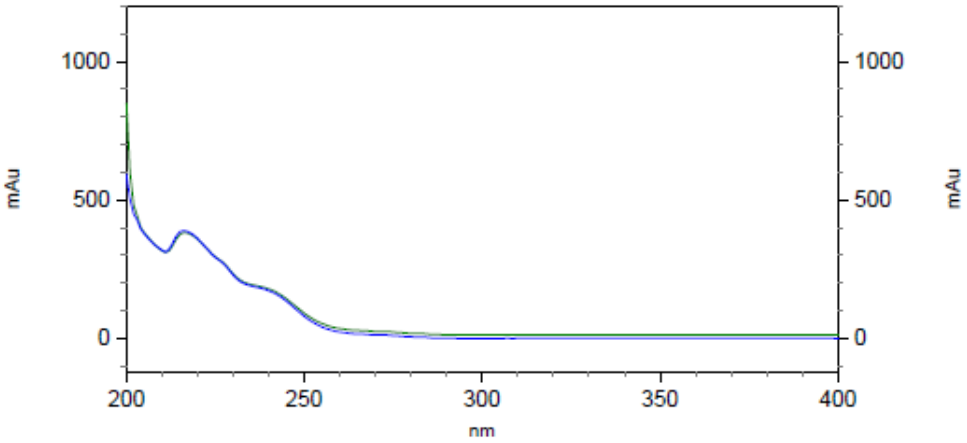


^{13}C NMR of **3i**, 150 MHz, $CDCl_3$





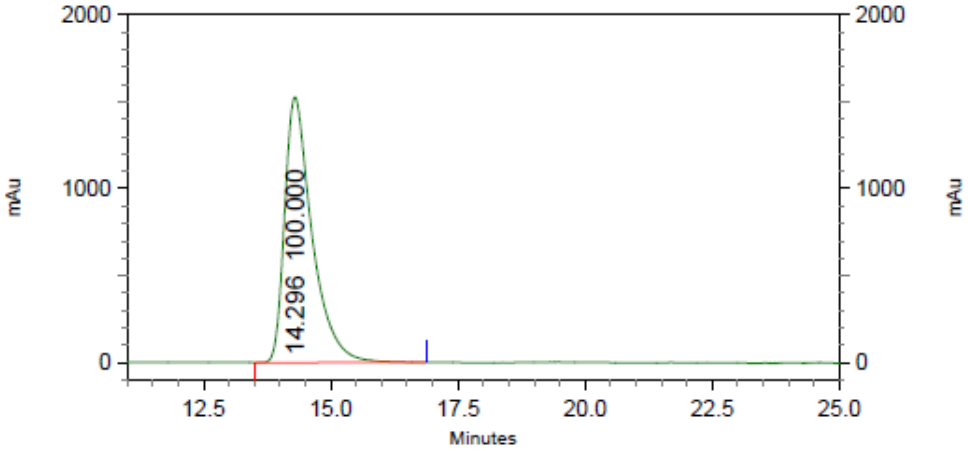
(±)-**3i**

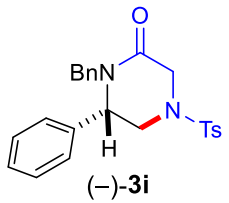


5: 205 nm, 4 nm
Results

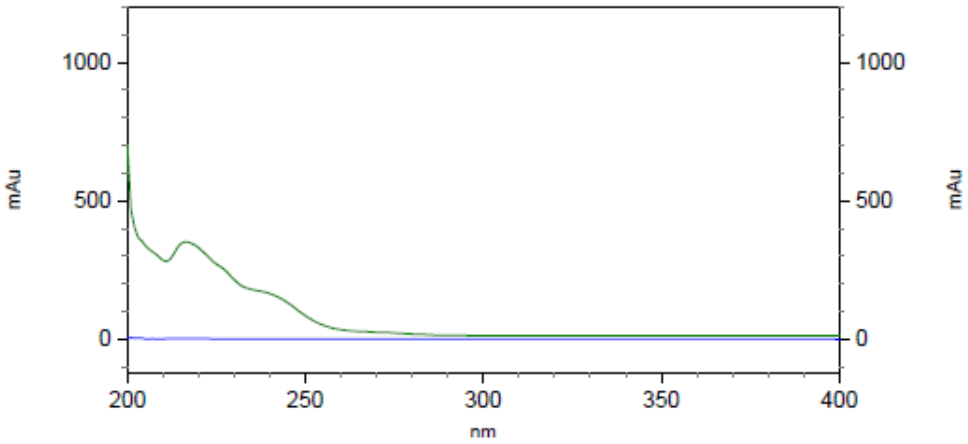
Name	Retention Time	Area Percent	Pk #
	14.268	49.702	1
	19.364	50.298	2

Totals		
	100.000	





(−)-**3i**



5: 205 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	14.296	100.000	1

Totals		
	100.000	

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C24H24N2O3S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C24H24N2O3S

Bond precision: C-C = 0.0030 A Wavelength=1.54178

Cell: a=9.0355(12) b=10.0246(14) c=11.7191(16)
alpha=90 beta=97.020(4) gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	1053.5(2)	1053.5(2)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C24 H24 N2 O3 S	C24 H24 N2 O3 S
Sum formula	C24 H24 N2 O3 S	C24 H24 N2 O3 S
Mr	420.51	420.51
Dx,g cm-3	1.326	1.326
Z	2	2
Mu (mm-1)	1.595	1.595
F000	444.0	444.0
F000'	445.89	
h,k,lmax	10,11,13	10,11,13
Nref	3724[1978]	3597
Tmin,Tmax	0.663,0.787	0.619,0.753
Tmin'	0.519	

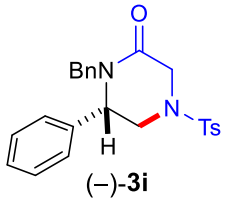
Correction method= # Reported T Limits: Tmin=0.619 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.82/0.97 Theta(max)= 66.661

R(reflections)= 0.0228(3583) wR2(reflections)= 0.0654(3597)

S = 1.067 Npar= 273

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(−)-3i

Alert level C

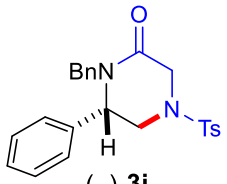
PLAT029_ALERT_3_C	_diffrn_measured_fraction_theta_full value Low .	0.975 Why?
PLAT089_ALERT_3_C	Poor Data / Parameter Ratio (Zmax < 18)	7.07 Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.596	48 Report
PLAT913_ALERT_3_C	Missing # of Very Strong Reflections in FCF	12 Note

Alert level G

PLAT791_ALERT_4_G	Model has Chirality at C4 (Sohnke SpGr)	S Verify
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	99% Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	1 Note
PLAT965_ALERT_2_G	The SHELXL WEIGHT Optimisation has not Converged	Please Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	8 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check



(−)-**3i**

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

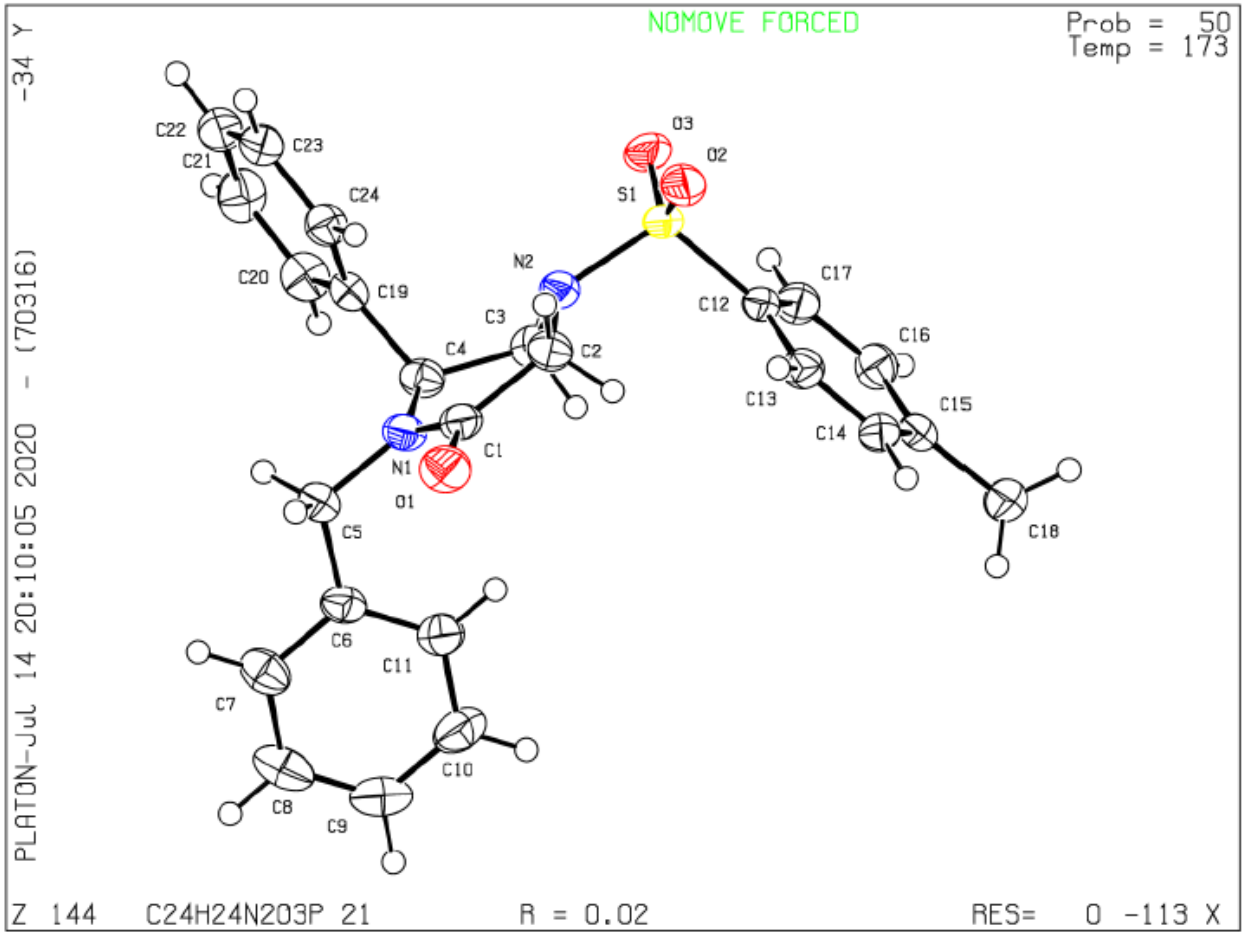
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

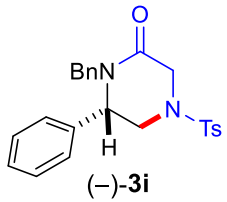
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

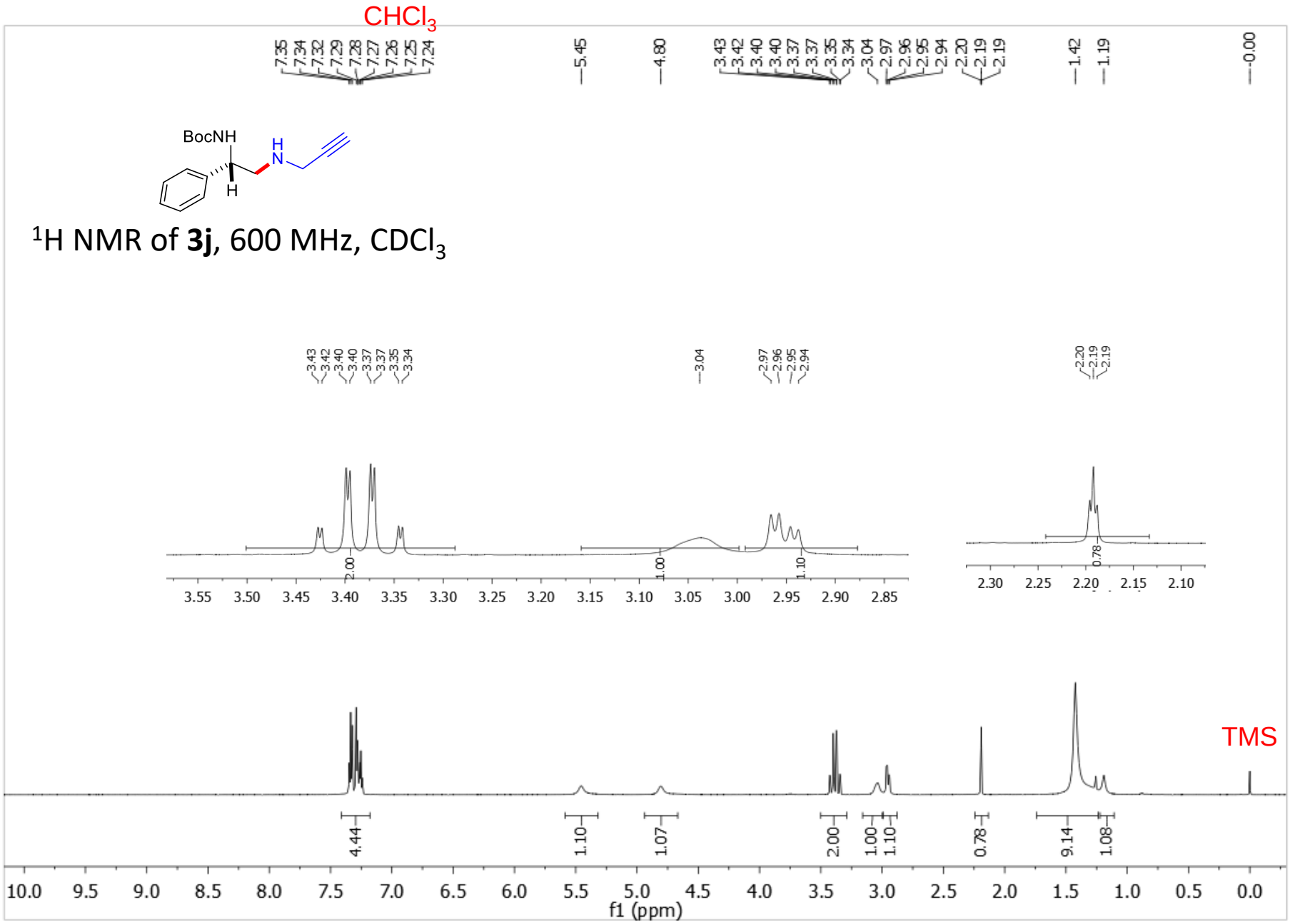
PLATON version of 08/07/2020; check.def file version of 17/06/2020

Datablock: C24H24N2O3S - ellipsoid plot

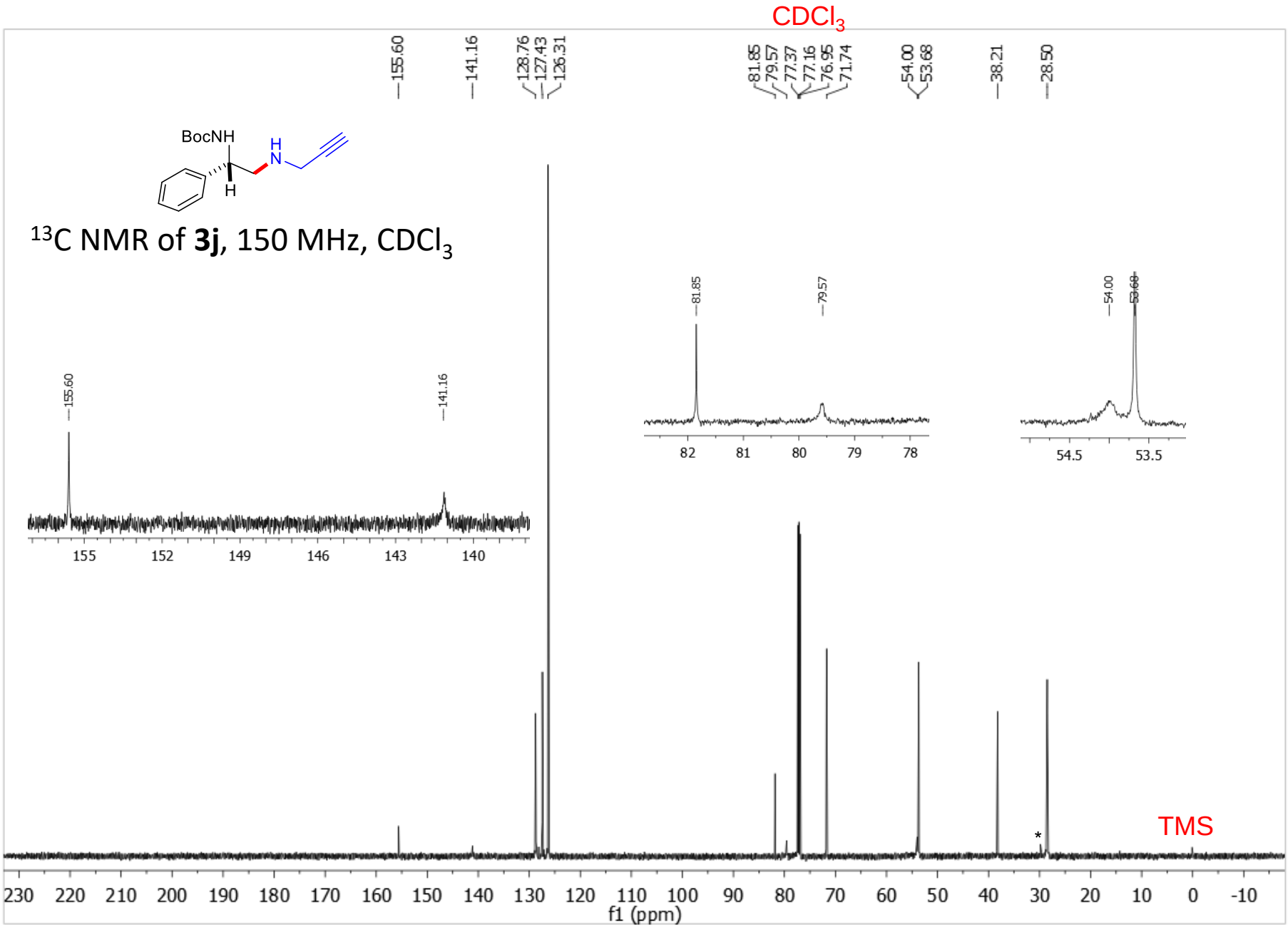




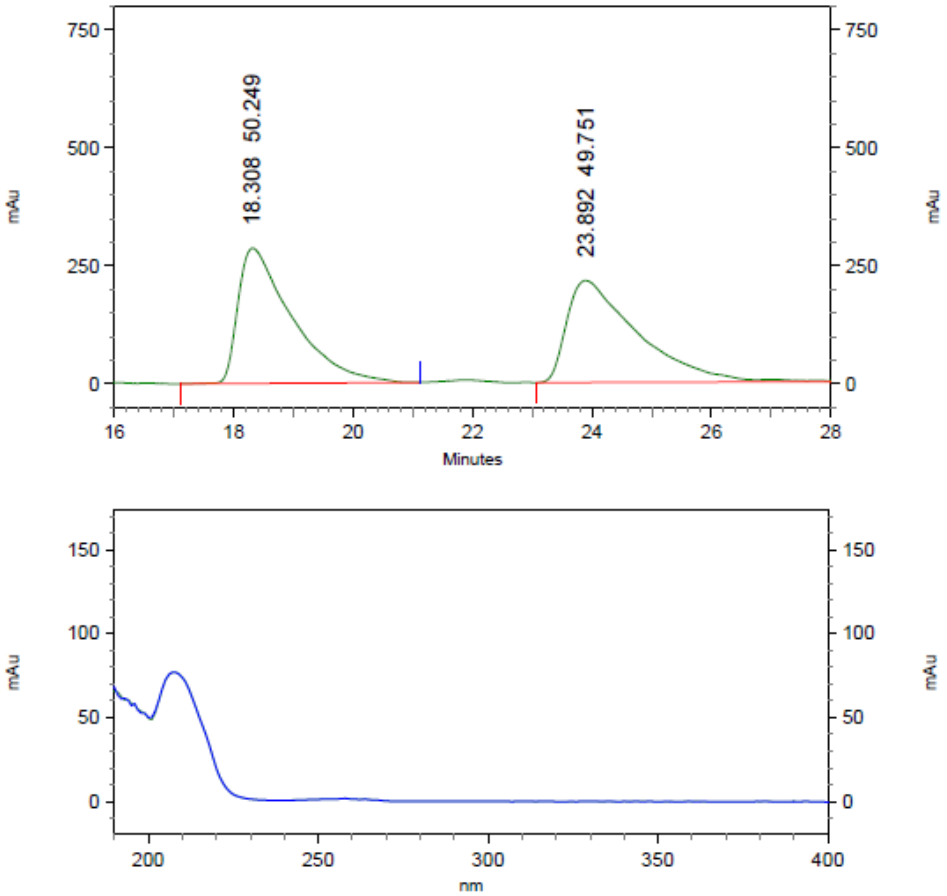
(–)-**3i**

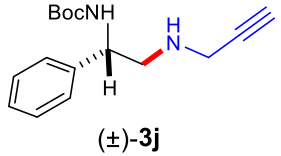


^{1}H NMR of **3j**, 600 MHz, $CDCl_3$


CDCl3
155.60
141.16
128.76
127.43
126.31
81.85
79.57
77.37
77.16
76.95
71.74
54.00
53.68
38.21
28.50
BocNH
H
N
H
13C NMR of 3j, 150 MHz, CDCl3
155.60
141.16
81.85
79.57
54.00
53.68
TMS
*
f1 (ppm)

K0L-420-ADH-5%1.0-2
C:\EZStart\Projects\Default\Data\K0L-420-ADH-5%1.0-2
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met





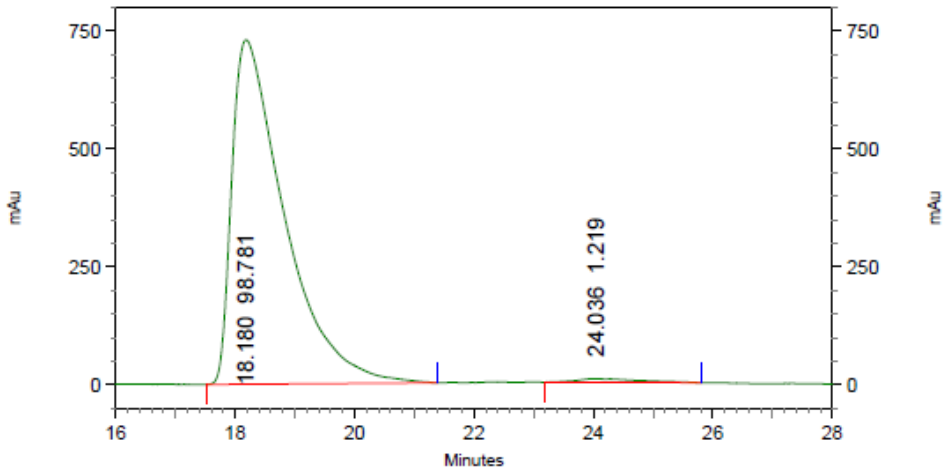
(±)-3j

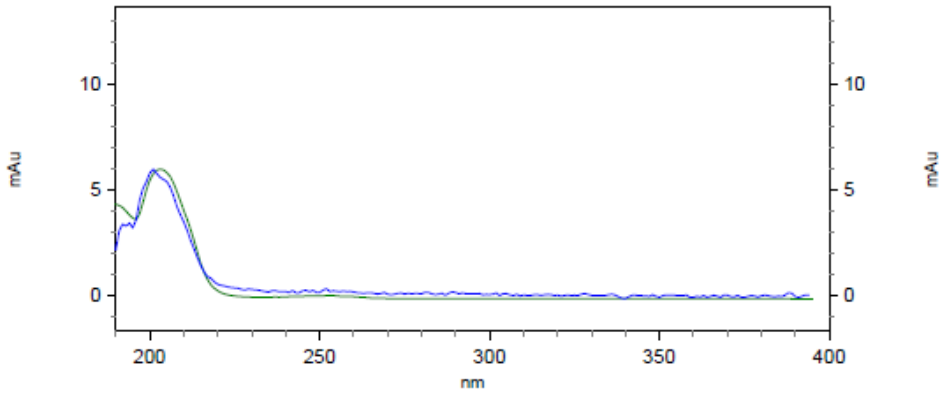
3: 210 nm, 4
nm Results

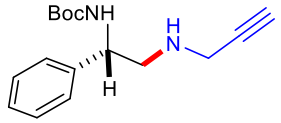
Pk #	Retention Time	Area Percent
1	18.308	50.249
2	23.892	49.751

Totals	
	100.000

K0L-427-ADH-5%1.0
C:\EZStart\Projects\Default\Data\K0L-427-ADH-5%1.0
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met





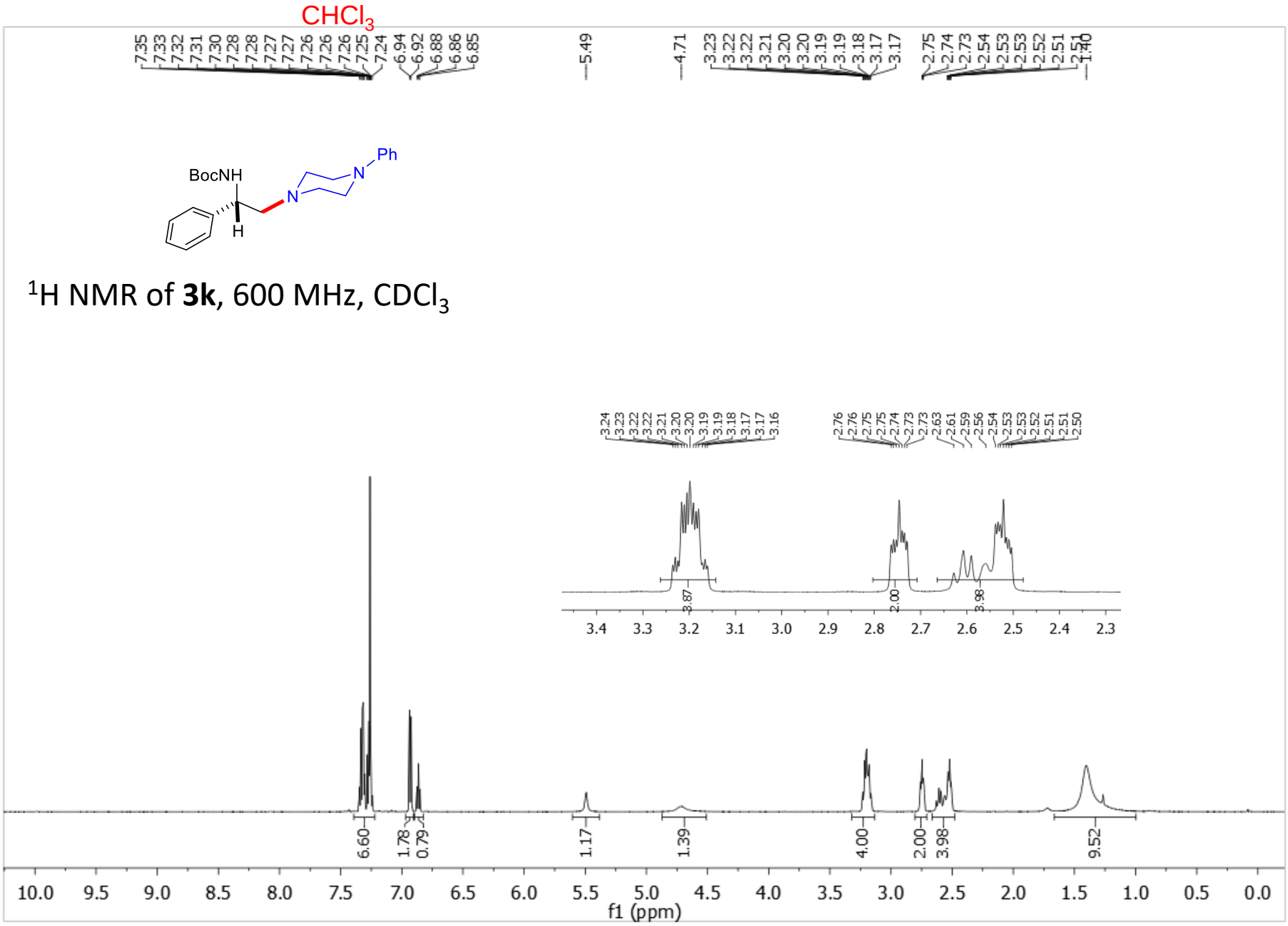


(+)-**3j**

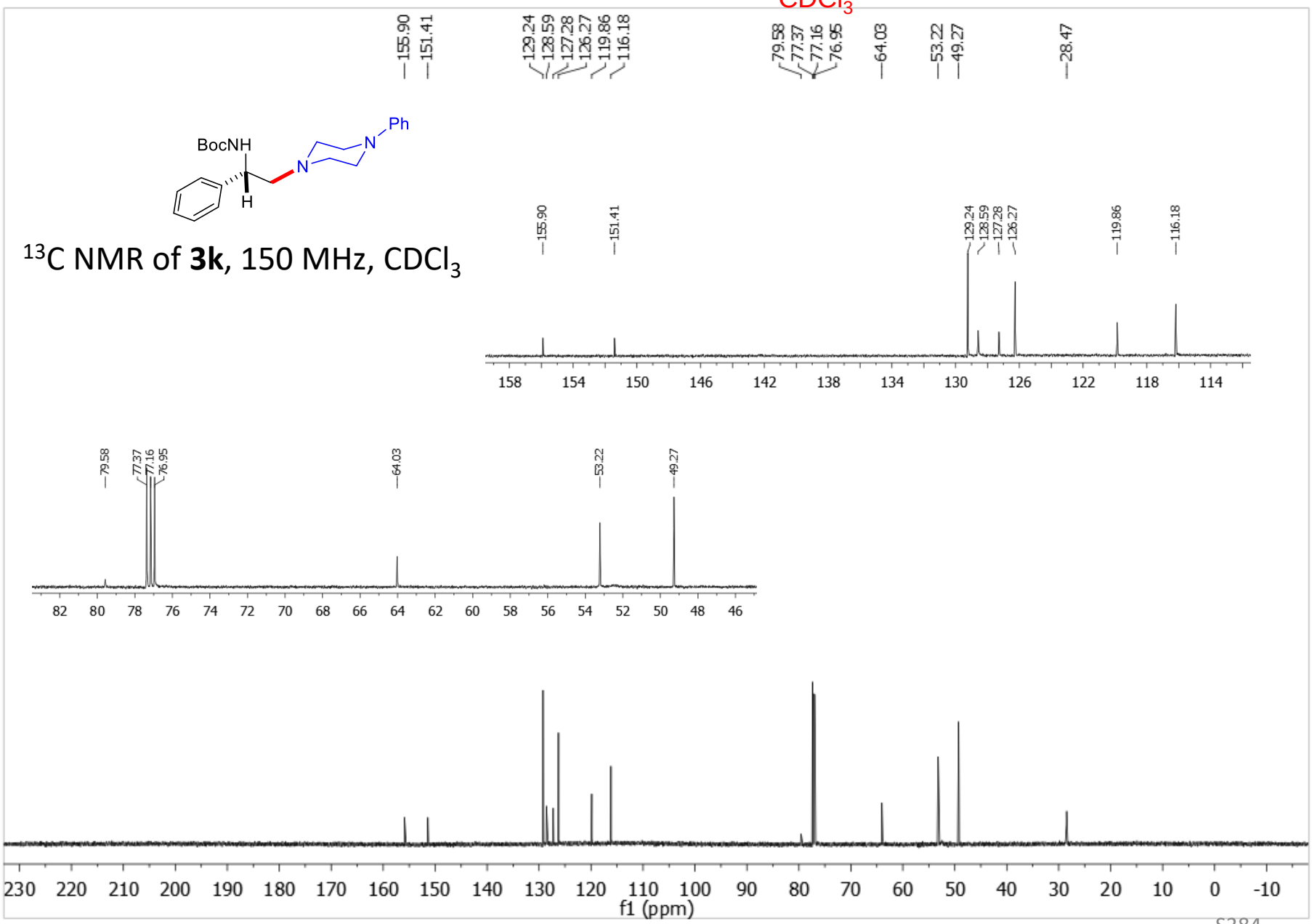
3: 210 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	18.180	98.781
2	24.036	1.219

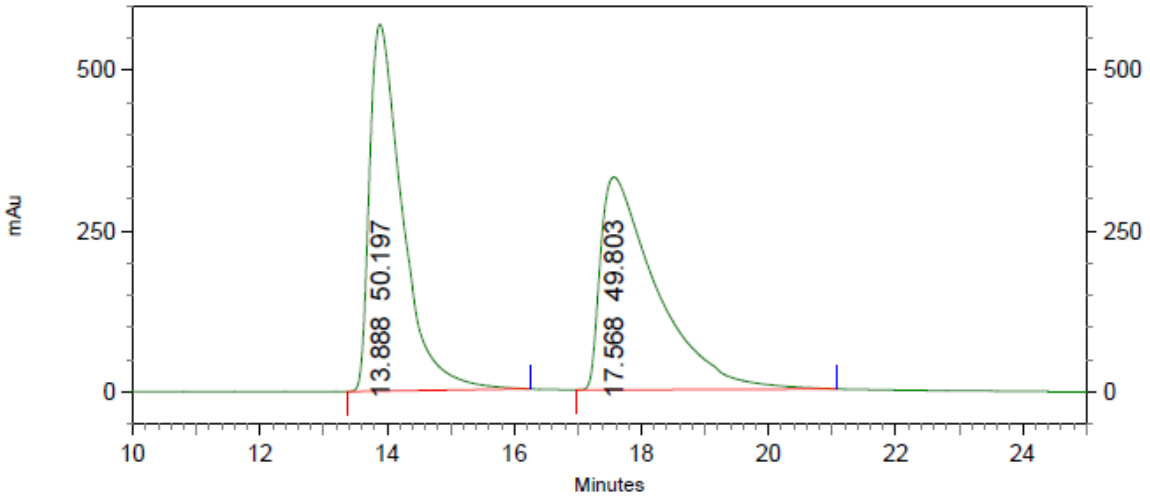
Totals	
	100.000

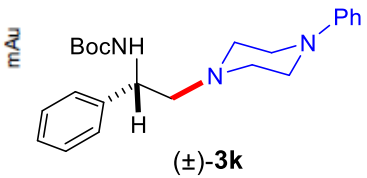


^{1}H NMR of **3k**, 600 MHz, $CDCl_3$

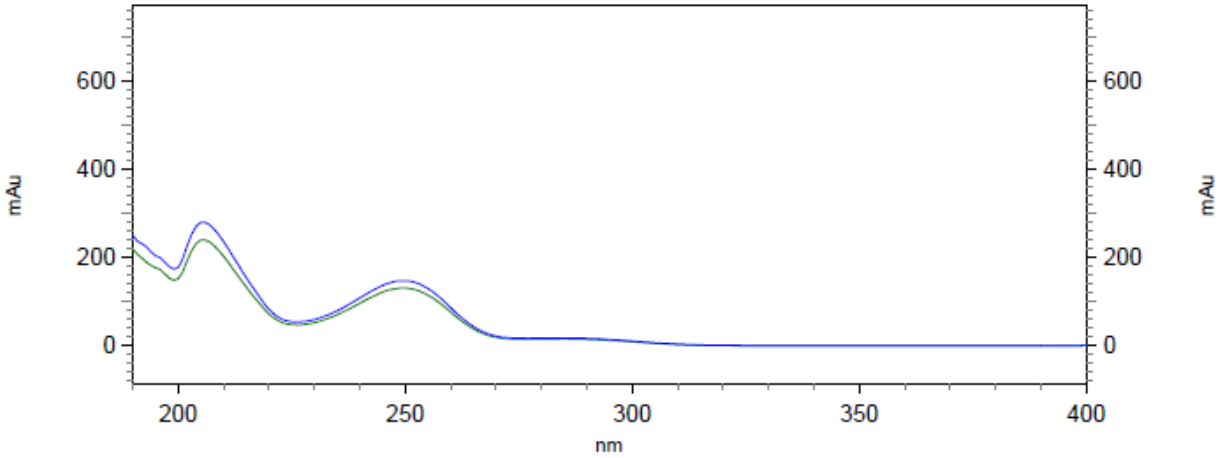

CDCl3
155.90
151.41
129.24
128.59
127.28
126.27
119.86
116.18
79.58
77.37
77.16
76.95
64.03
53.22
49.27
28.47
BocNH
N
N
Ph
H
13C NMR of 3k, 150 MHz, CDCl3
f1 (ppm)

C:\EZStart\Projects\Default\Data\K0L-445-IB-2.5%1.0
C:\Documents and Settings\zhang\Desktop\DSW\04042018.met





(±)-**3k**

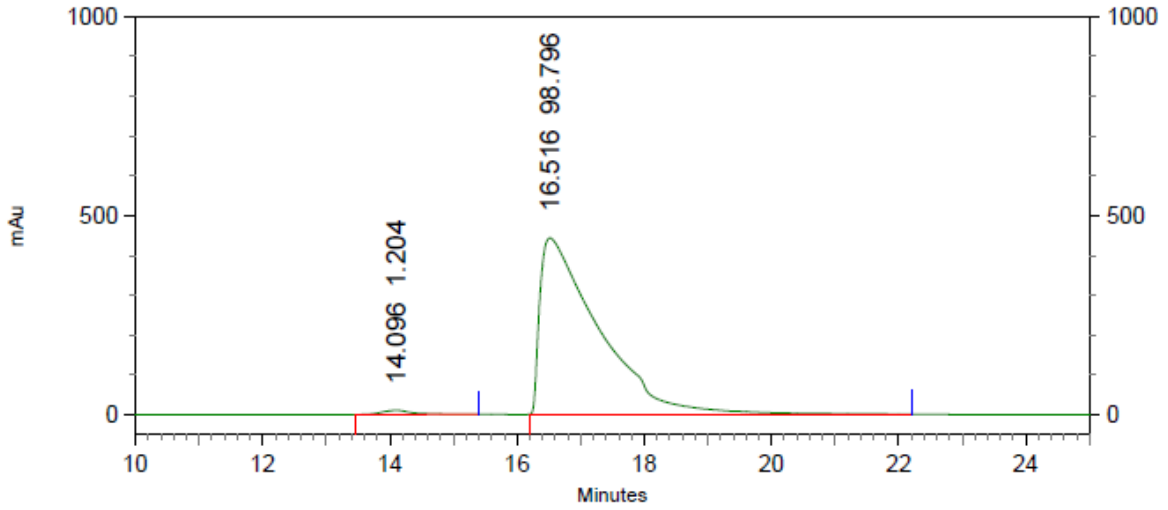


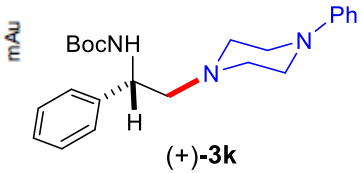
4: 240 nm, 4
nm Results

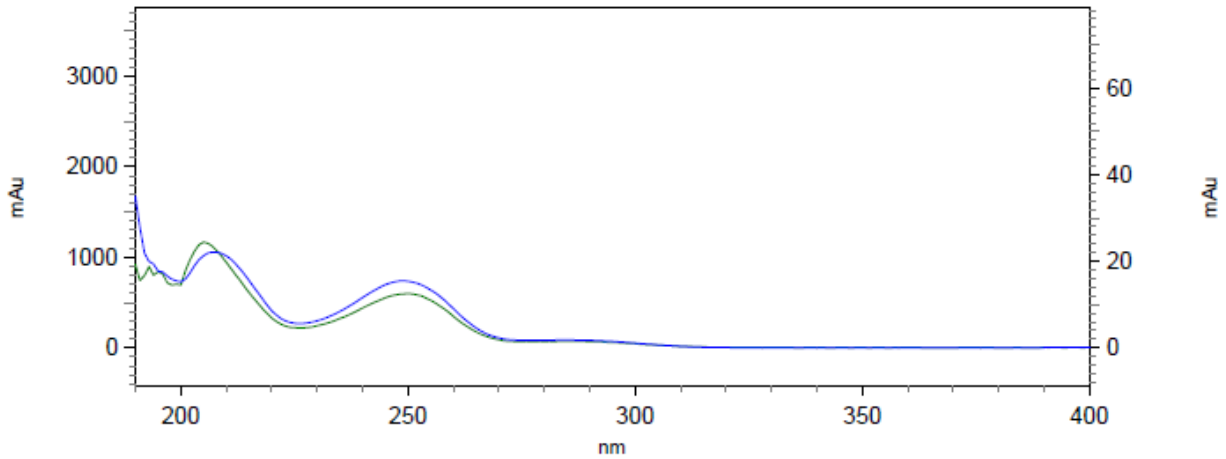
Pk #	Retention Time	Area Percent
1	13.888	50.197
2	17.568	49.803

Totals	
	100.000

C:\EZStart\Projects\Default\Data\K0L-444-IB-2.5%1.0-1
C:\Documents and Settings\zhang\Desktop\DSW\04042018.met



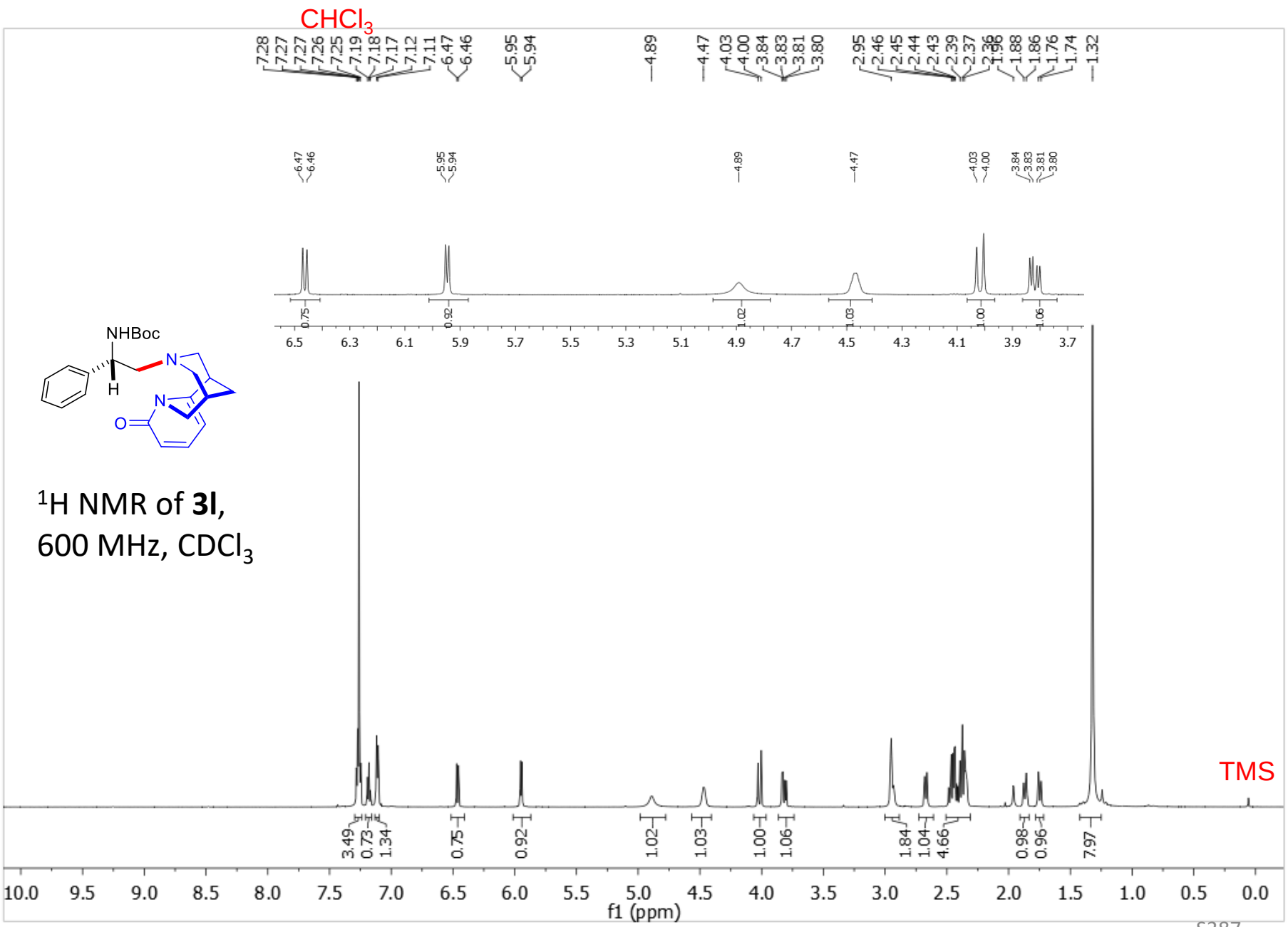




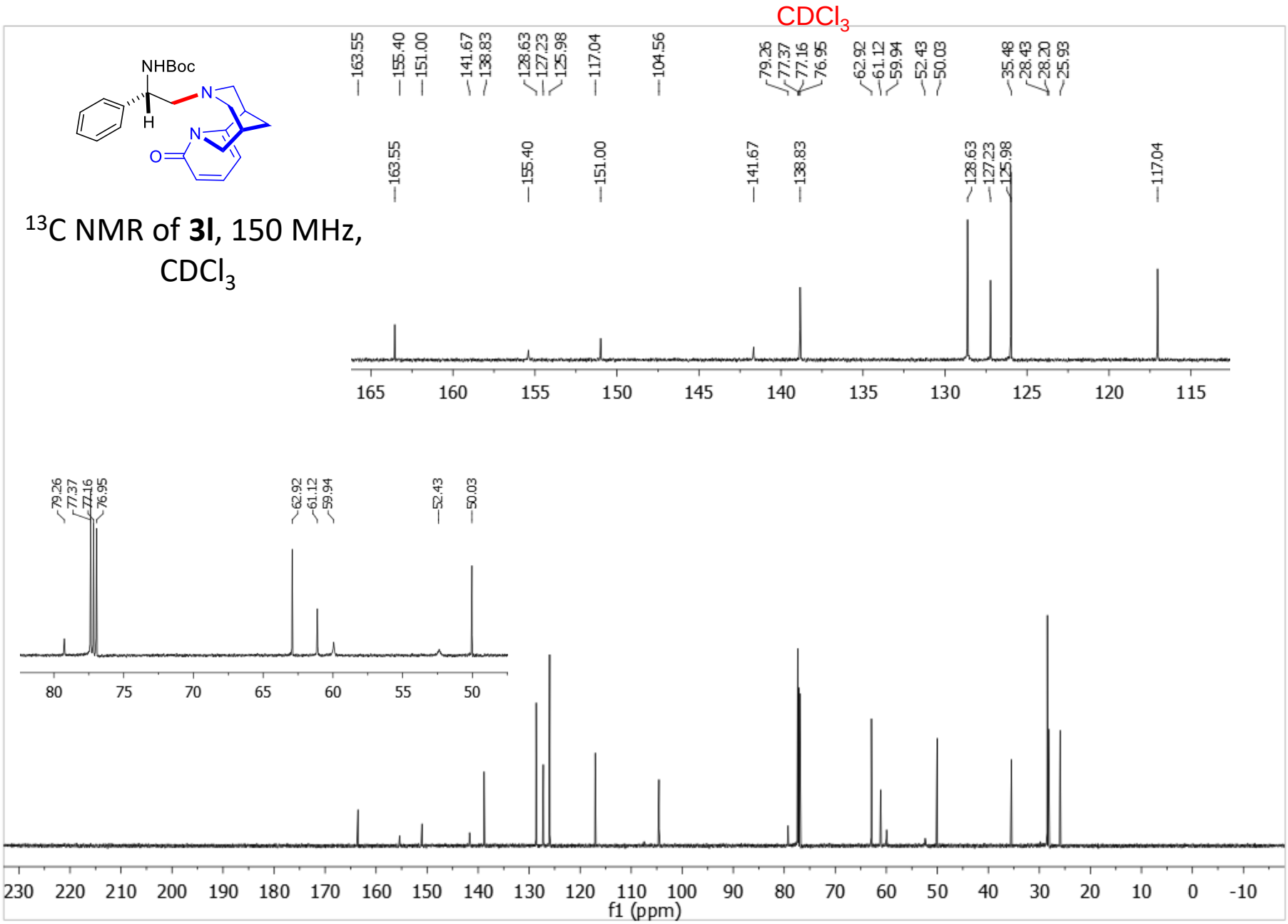
4: 240 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	14.096	1.204
2	16.516	98.796

Totals	
	100.000

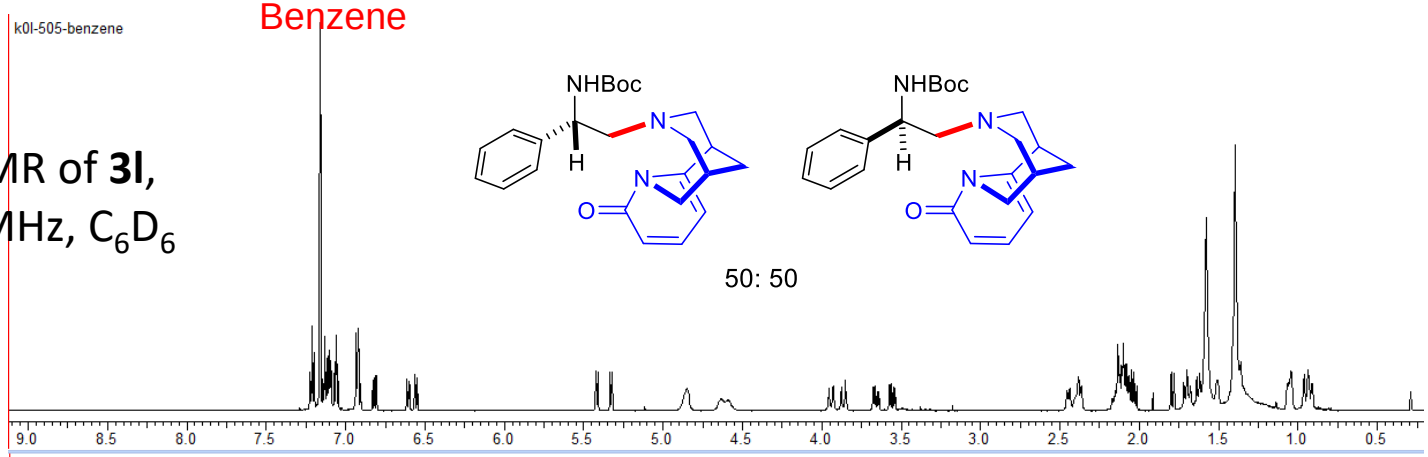


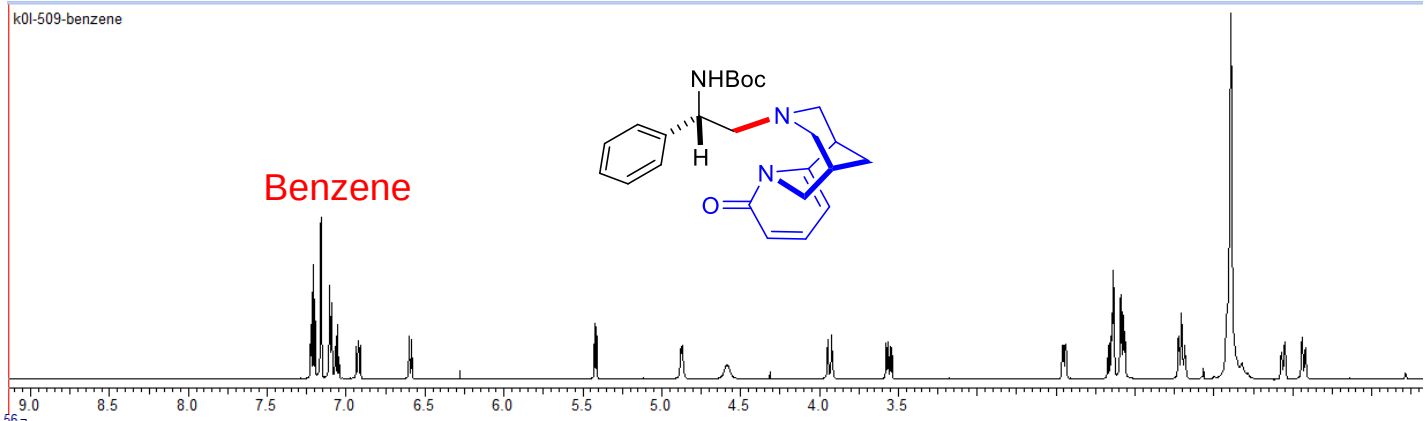
^{1}H NMR of **3l**,
600 MHz, $CDCl_3$

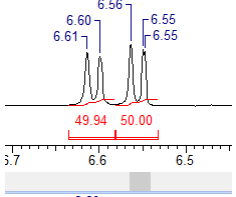


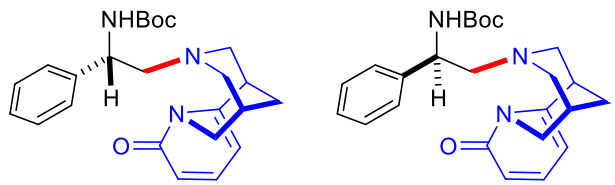
^{13}C NMR of **3l**, 150 MHz, $CDCl_3$

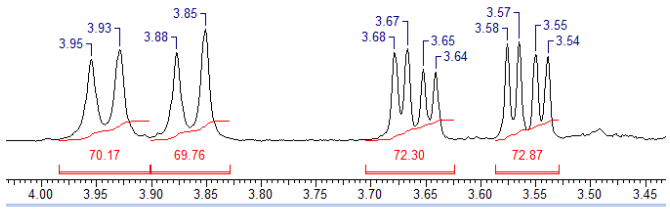
^{1}H NMR of **3l**,
600 MHz, C_6D_6

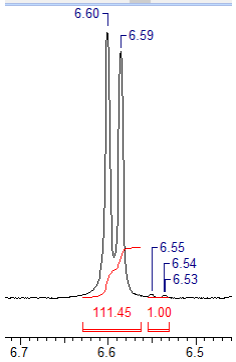


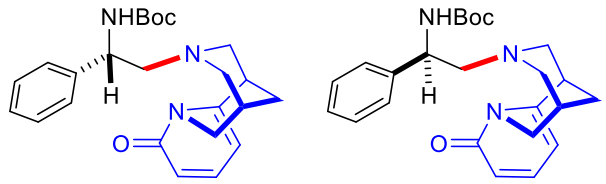


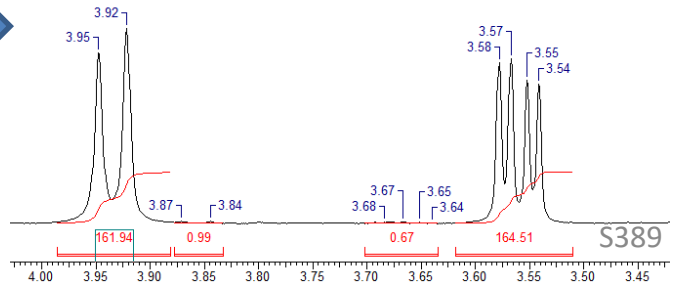


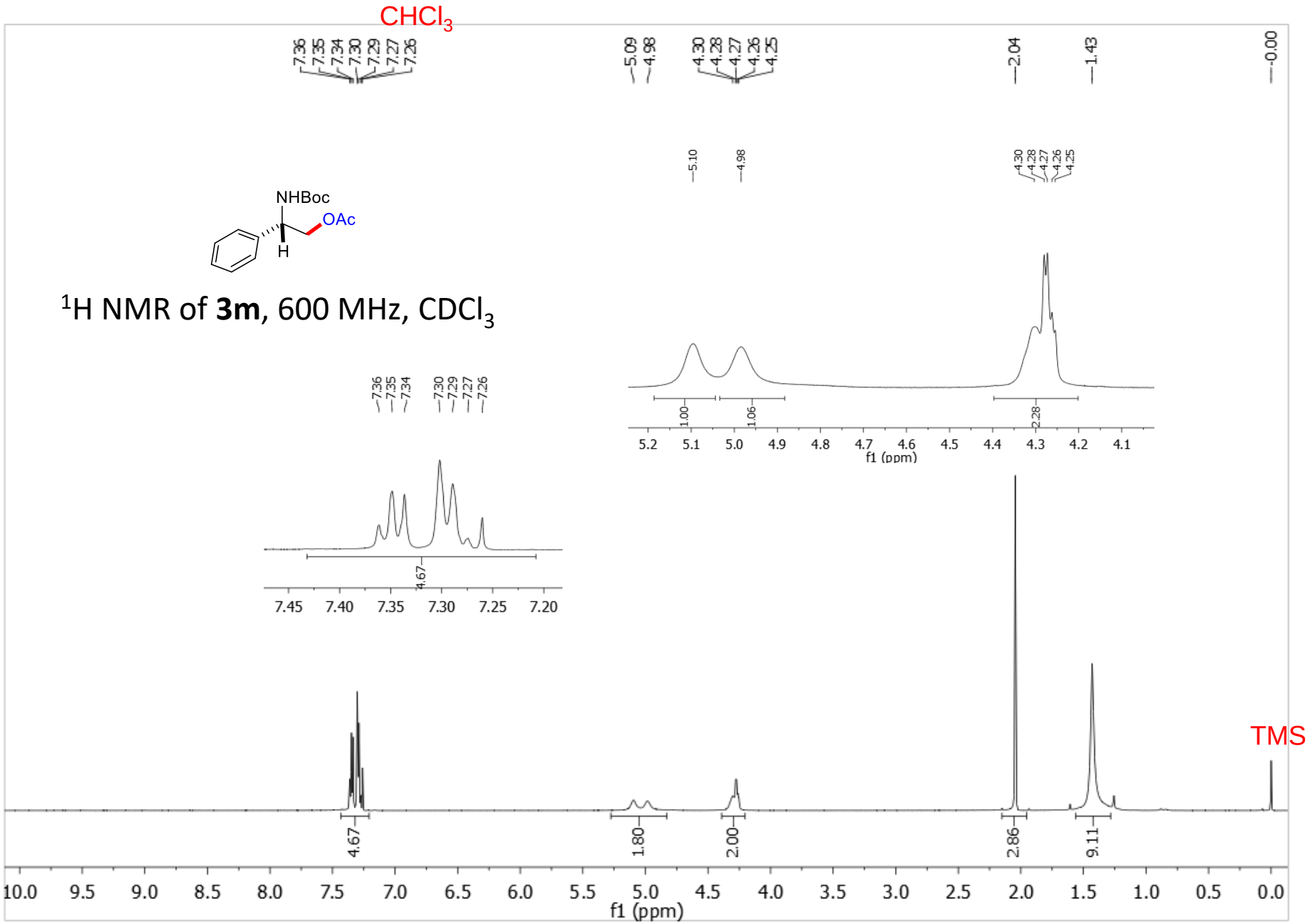


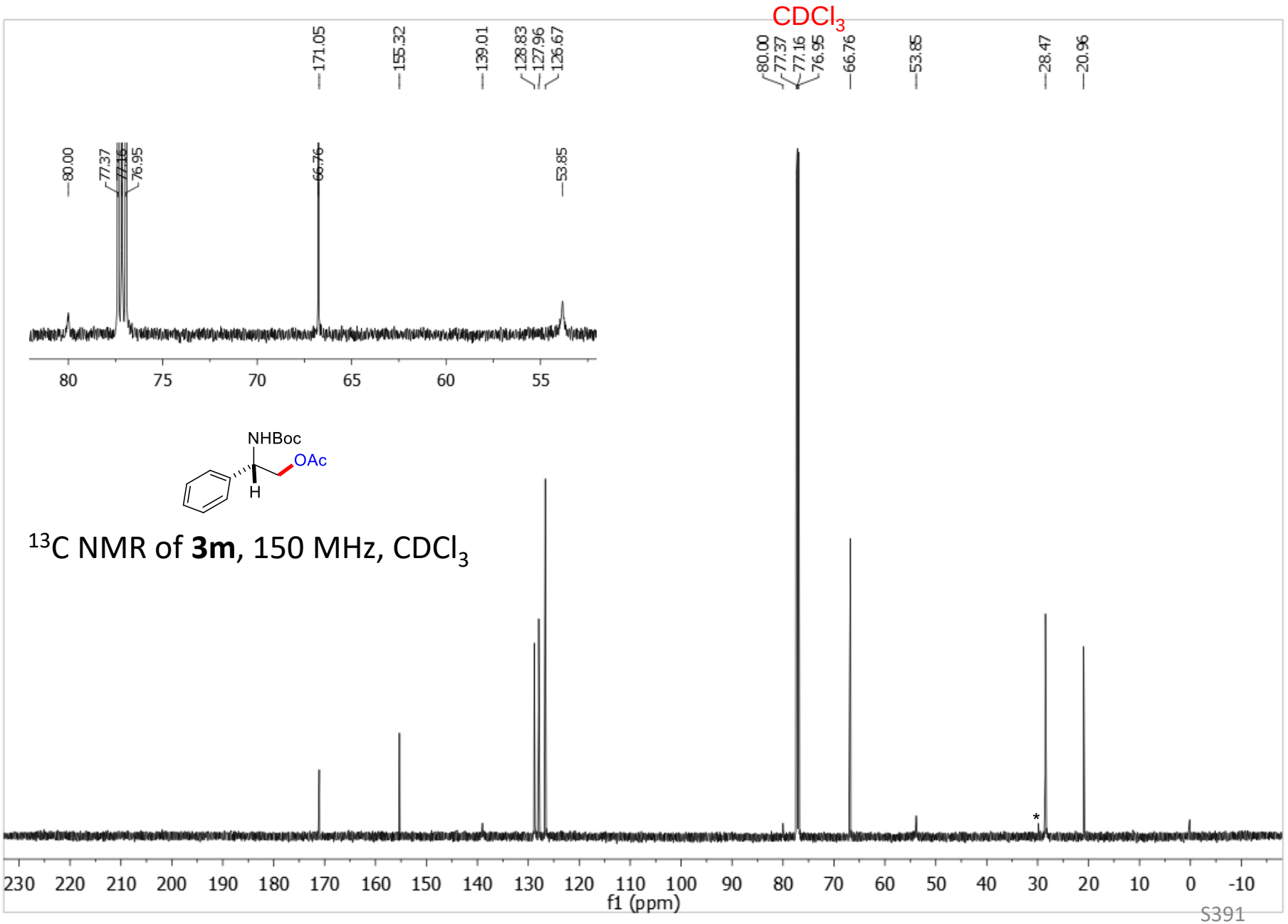






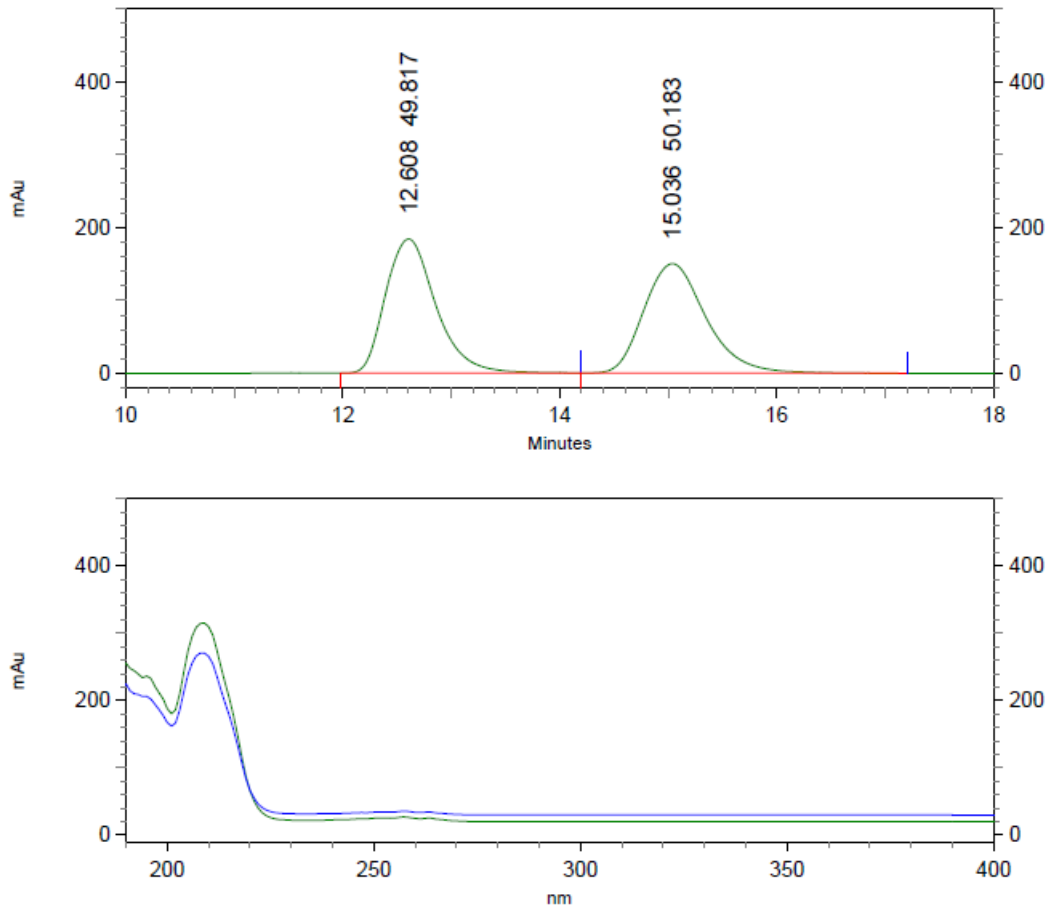


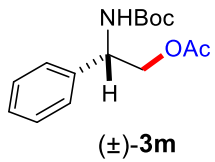

CHCl3
7.36
7.35
7.34
7.30
7.29
7.27
7.26
5.09
4.98
4.30
4.28
4.27
4.26
4.25
2.04
1.43
0.00
NHBoc
OAc
H
1H NMR of 3m, 600 MHz, CDCl3
5.10
4.98
4.30
4.28
4.27
4.26
4.25
1.00
1.06
2.28
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
f1 (ppm)
7.36
7.35
7.34
7.30
7.29
7.27
7.26
4.67
7.45
7.40
7.35
7.30
7.25
7.20
TMS
4.67
1.80
2.00
2.86
9.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



^{13}C NMR of **3m**, 150 MHz, $CDCl_3$

C:\EZStart\Projects\Default\Data\K0L-378-ADH-7%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





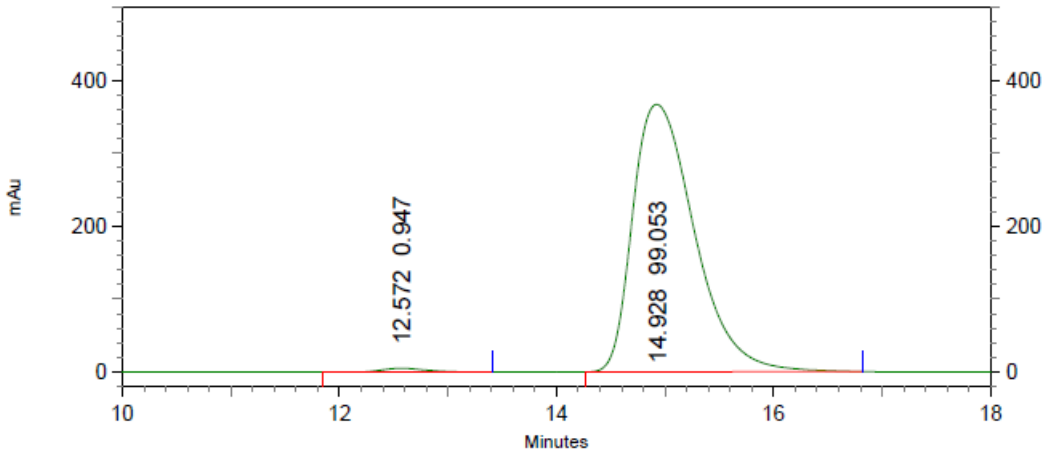
(±)-**3m**

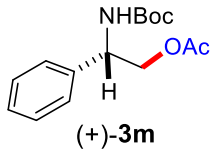
5: 213 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.608	49.817
2	15.036	50.183

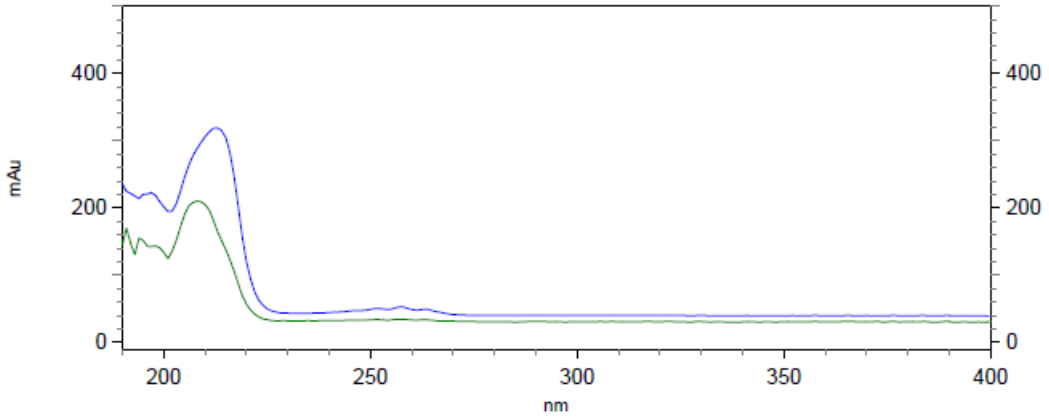
Totals	
	100.000

C:\EZStart\Projects\Default\Data\K0L-377-ADH-7%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





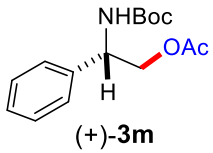
(+)-3m



5: 216 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.572	0.947
2	14.928	99.053

Totals	
	100.000



(+)-**3m**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C15H21NO4

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: C15H21NO4

```
Bond precision:  C-C = 0.0024 A          Wavelength=1.54178

Cell:            a=5.2404(2)     b=10.6394(4)     c=27.3903(10)
                 alpha=90        beta=90          gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	1527.14(10)	1527.14(10)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C15 H21 N O4	C15 H21 N O4
Sum formula	C15 H21 N O4	C15 H21 N O4
Mr	279.33	279.33
Dx,g cm-3	1.215	1.215
Z	4	4
Mu (mm-1)	0.721	0.721
F000	600.0	600.0
F000'	601.92	
h,k,lmax	6,12,32	6,12,32
Nref	2700[1611]	2682
Tmin,Tmax	0.925,0.944	0.660,0.753
Tmin'	0.707	

```
Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.66/0.99      Theta(max)= 66.566

R(reflections)= 0.0289( 2622)     wR2(reflections)= 0.0726( 2682)

S = 1.051                  Npar= 188
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

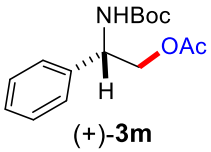
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.595	4 Report

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2 Note
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT791_ALERT_4_G	Model has Chirality at C4 (Chiral SPGR)	S Verify
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	1 Note
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still	96% Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	1 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	2 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check



(+)-**3m**

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

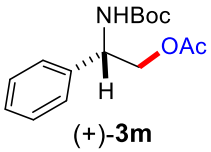
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

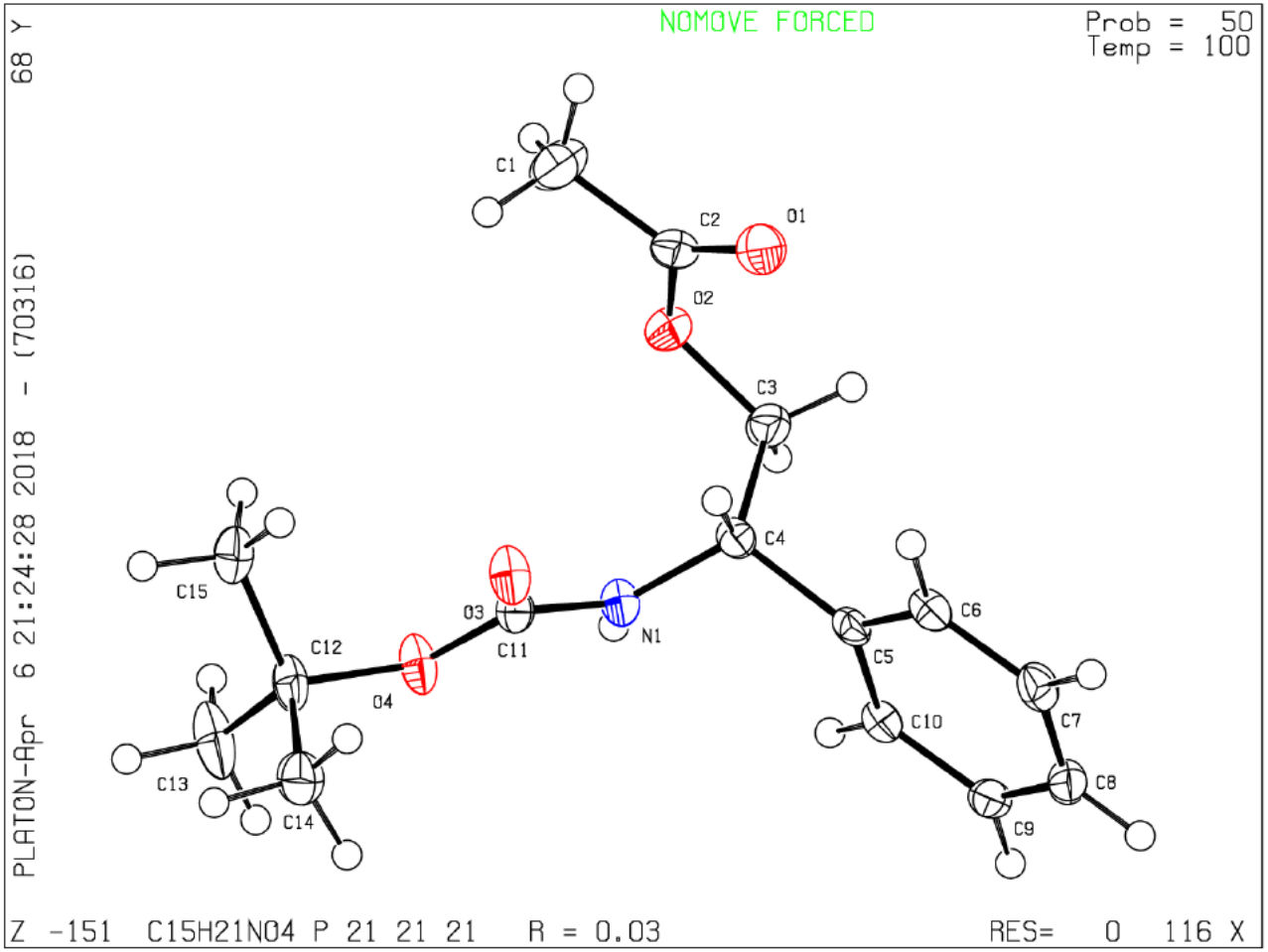
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

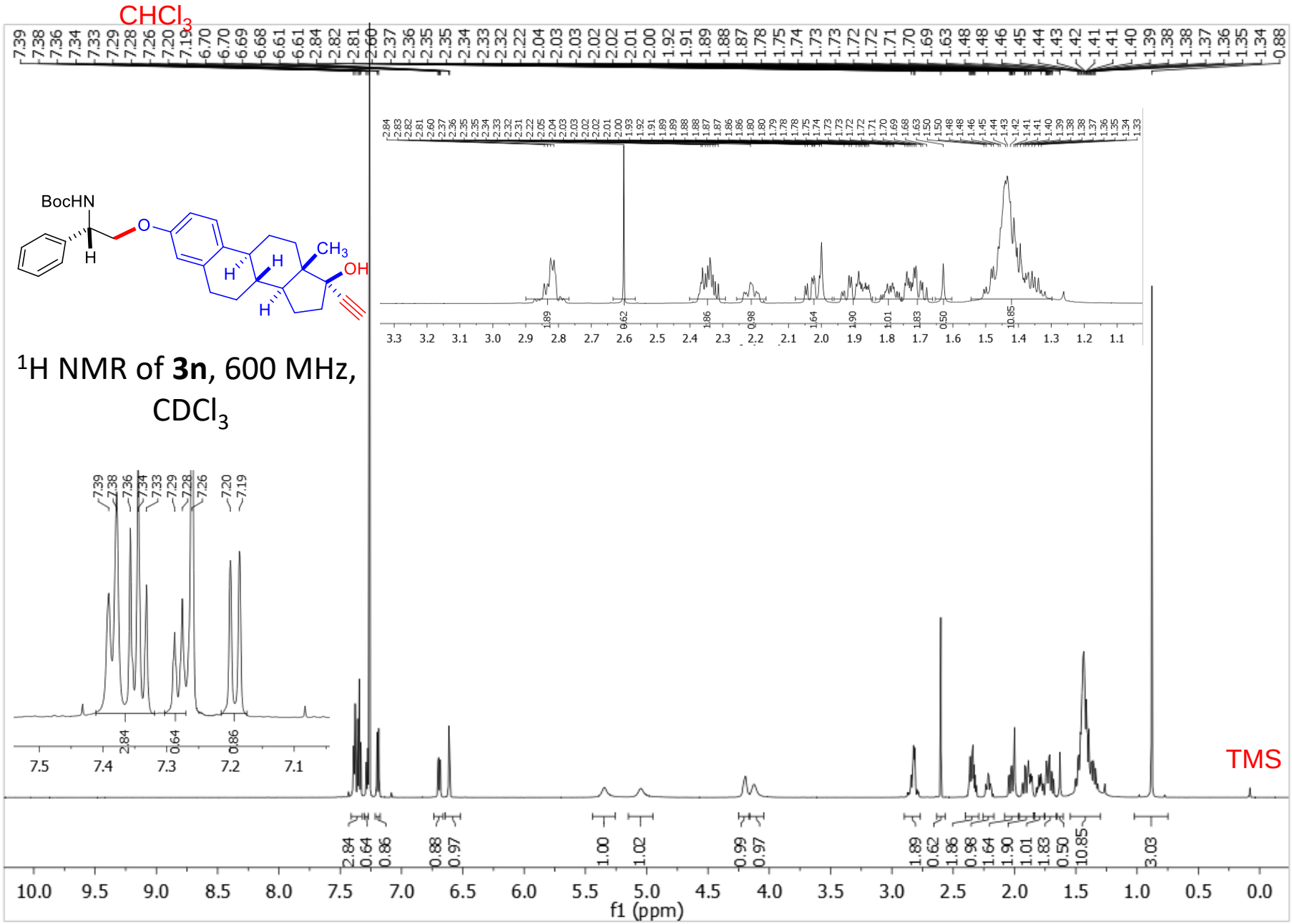
PLATON version of 30/01/2018; check.def file version of 30/01/2018

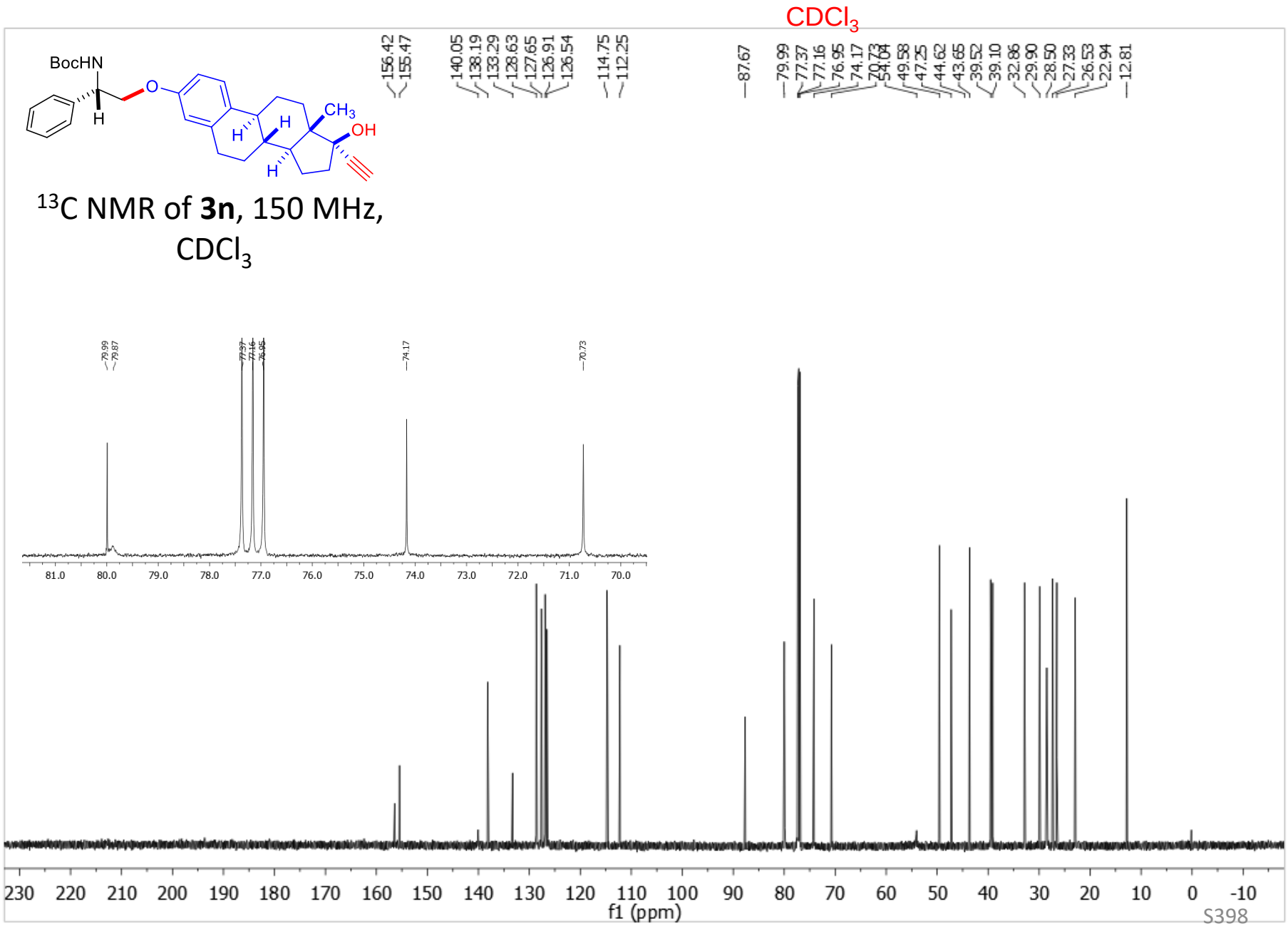


(+)-**3m**

Datablock C15H21NO4 - ellipsoid plot

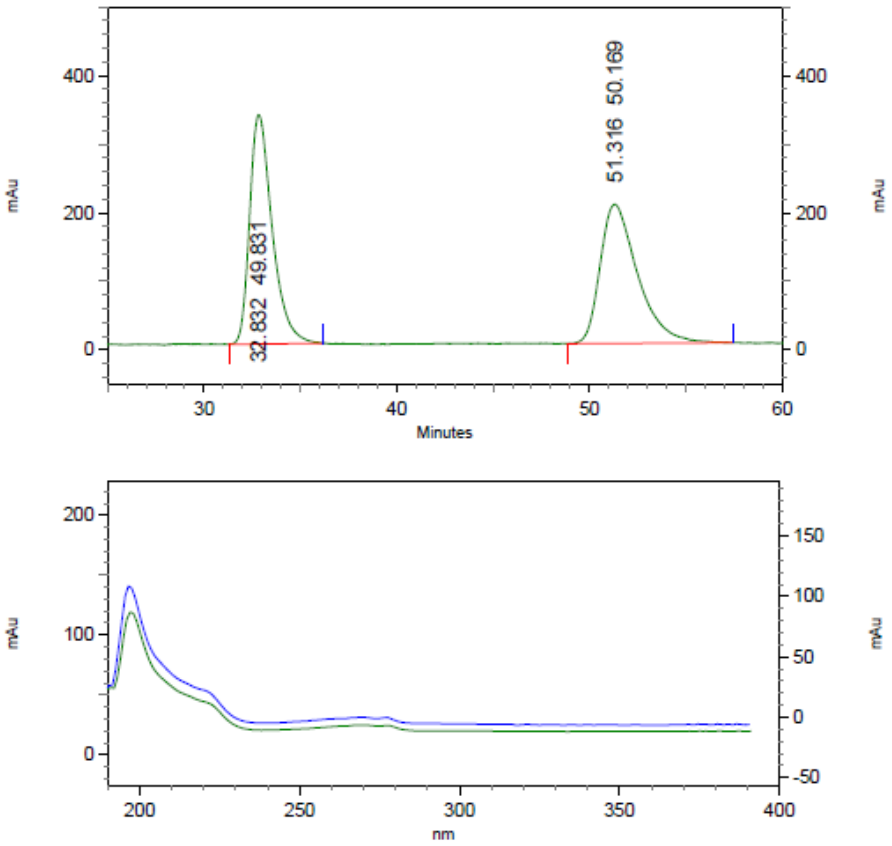


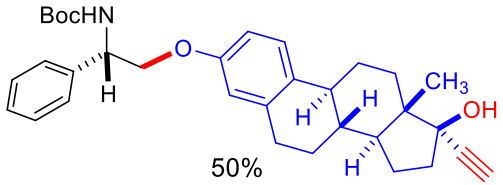

CHCl3
BocHN
O
H
H
H
CH3
OH
1H NMR of 3n, 600 MHz, CDCl3
TMS
f1 (ppm)



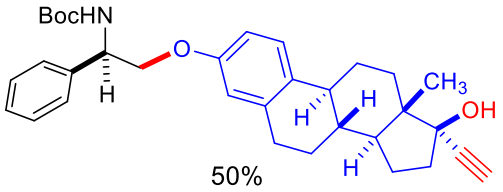
^{13}C NMR of **3n**, 150 MHz, $CDCl_3$

K0L-478-ADH-10%1.0
C:\EZStart\Projects\Default\Data\K0L-478-ADH-10%1.0
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met





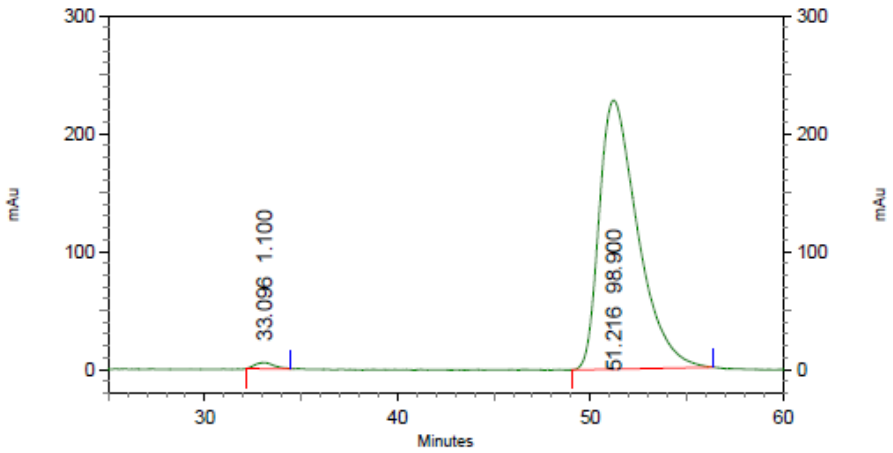
3n (from (±)-*N*-Boc-**2a**)

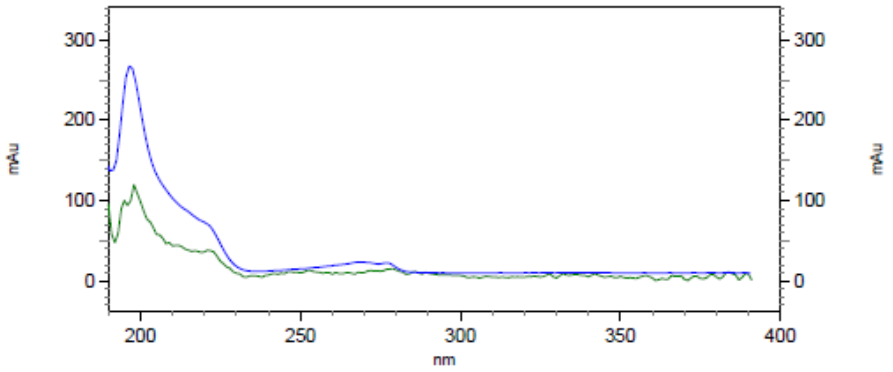


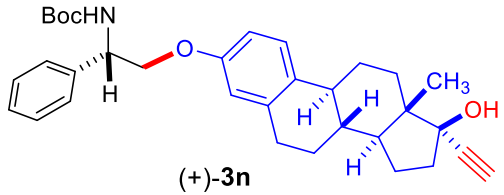
2: 210 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	32.832	49.831
2	51.316	50.169
Totals		100.000

K0L-477-ADH-10%1.0
C:\EZStart\Projects\Default\Data\K0L-477-ADH-10%1.0
C:\EZStart\Projects\Default\Method\SMG-OJ-H-20%1ml-report.met



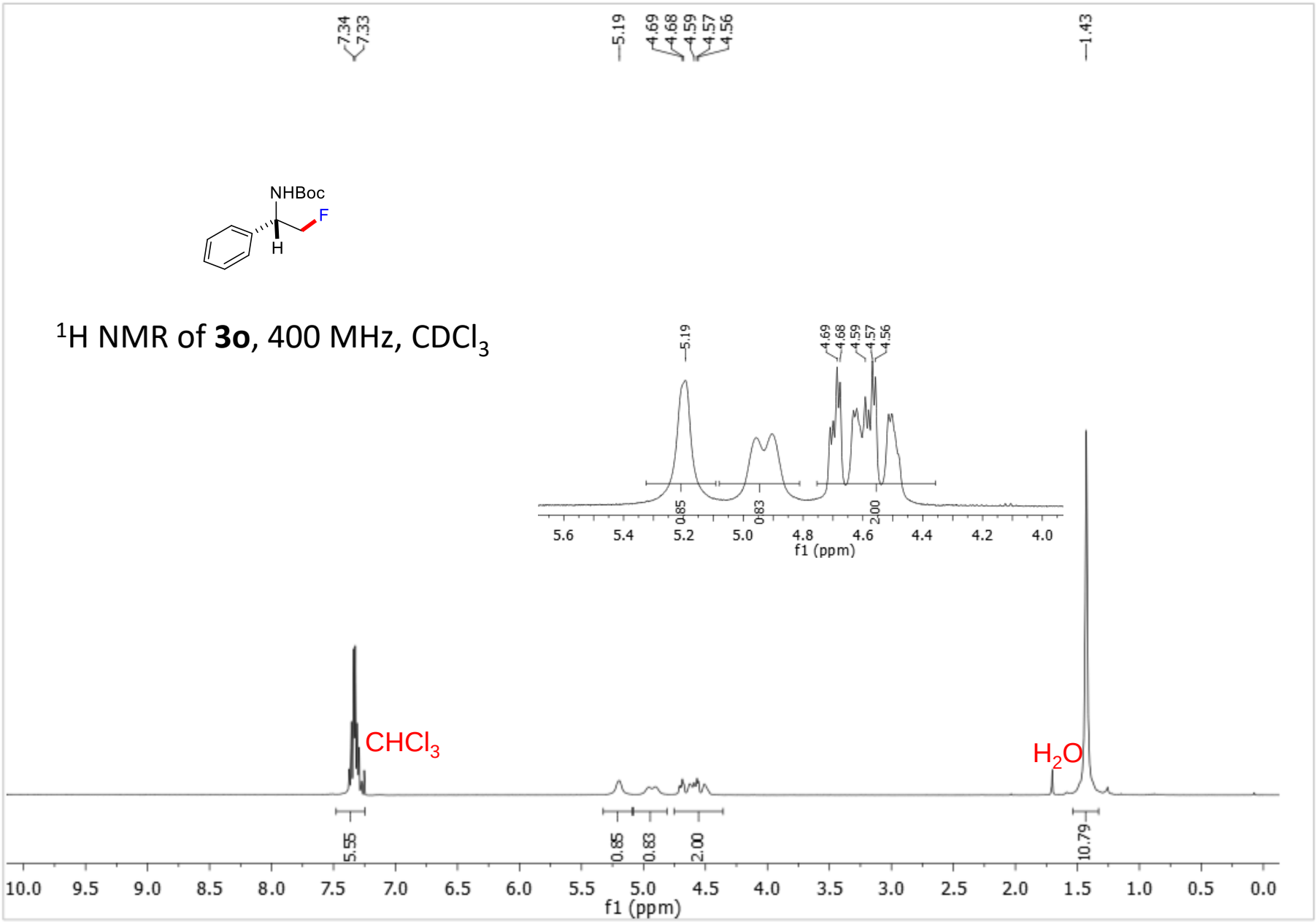


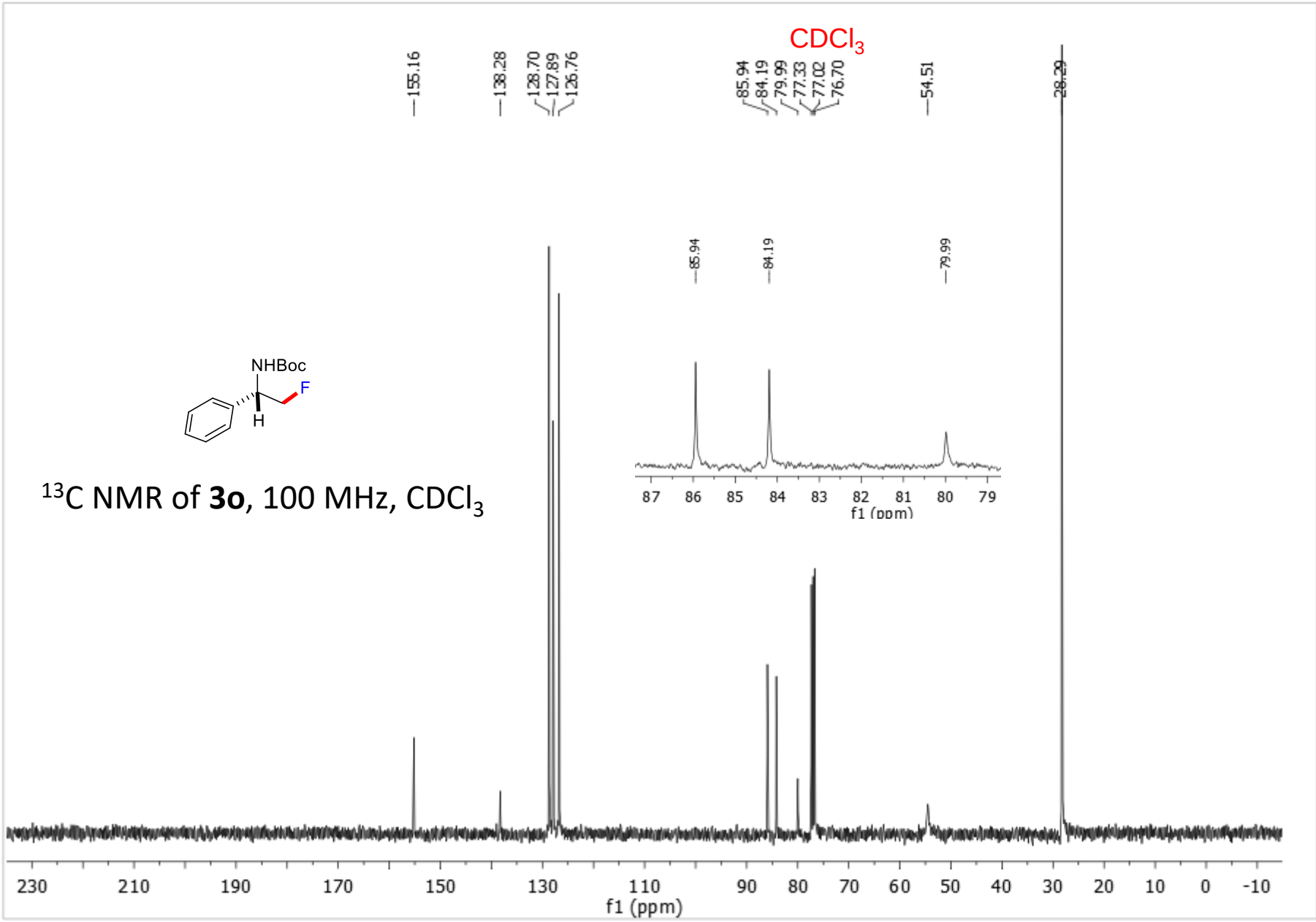


(+)-**3n**

2: 210 nm, 4
nm Results

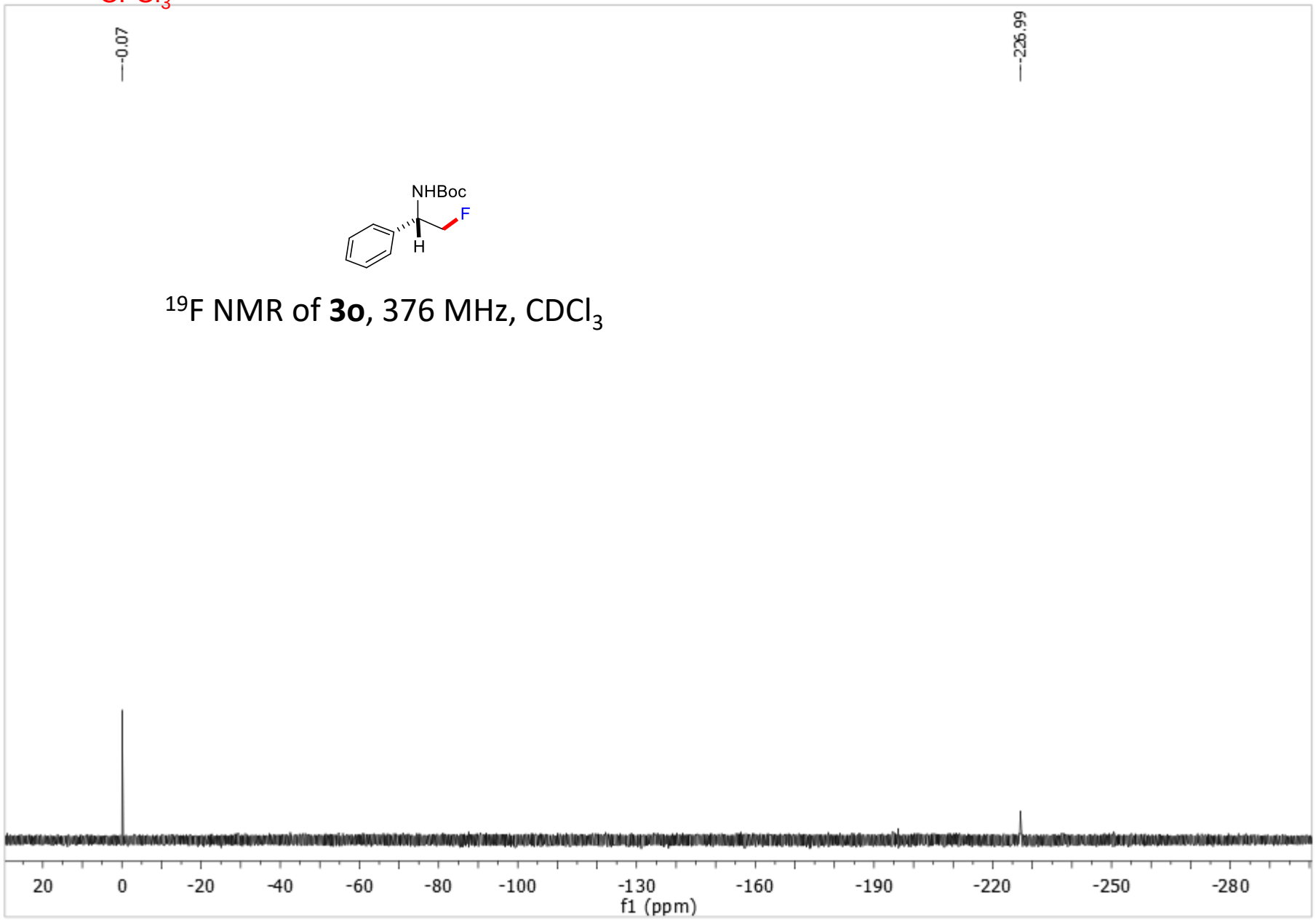
Pk #	Retention Time	Area Percent
1	33.096	1.100
2	51.216	98.900
Totals		100.000


7.34
7.33
5.19
4.69
4.68
4.59
4.57
4.56
1.43
NHBoc
F
H
^{1}H NMR of **3o**, 400 MHz, $CDCl_3$
CHCl3
H2O
5.55
0.85
0.83
2.00
10.79
f1 (ppm)

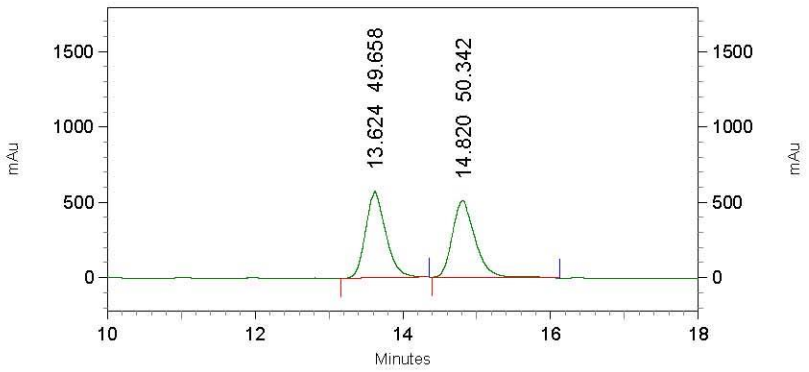


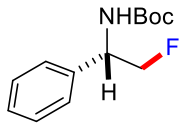
^{13}C NMR of **3o**, 100 MHz, $CDCl_3$

$CFCl_3$

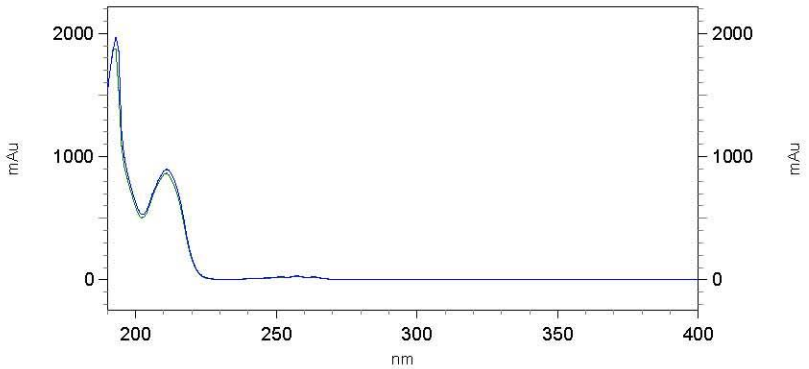


^{19}F NMR of **3o**, 376 MHz, $CDCl_3$



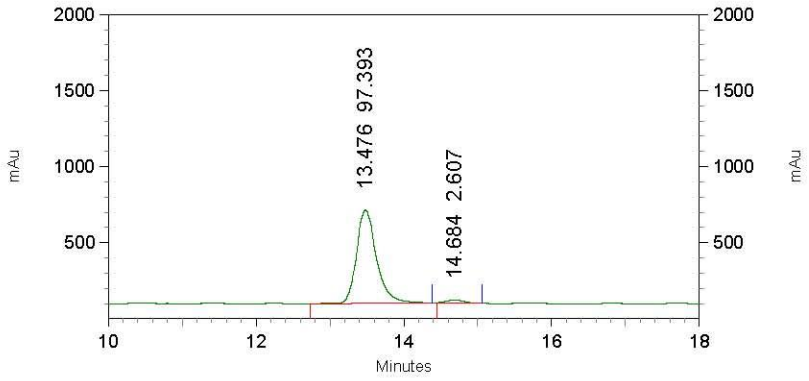


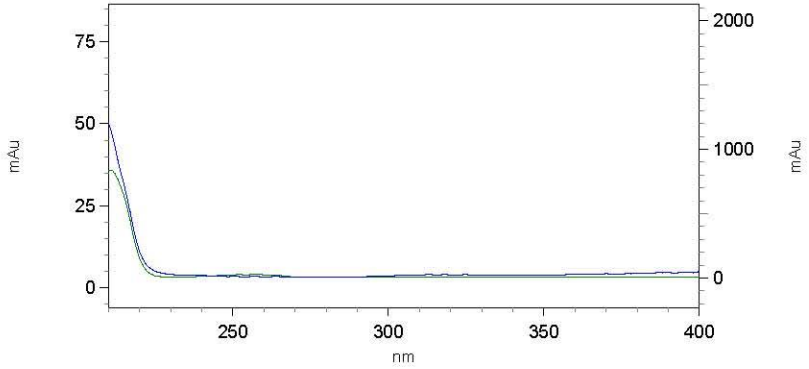
(±)-**3o**

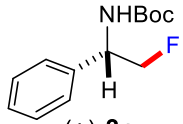


7: 196 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		13.624	49.658
2		14.820	50.342
Totals			100.000





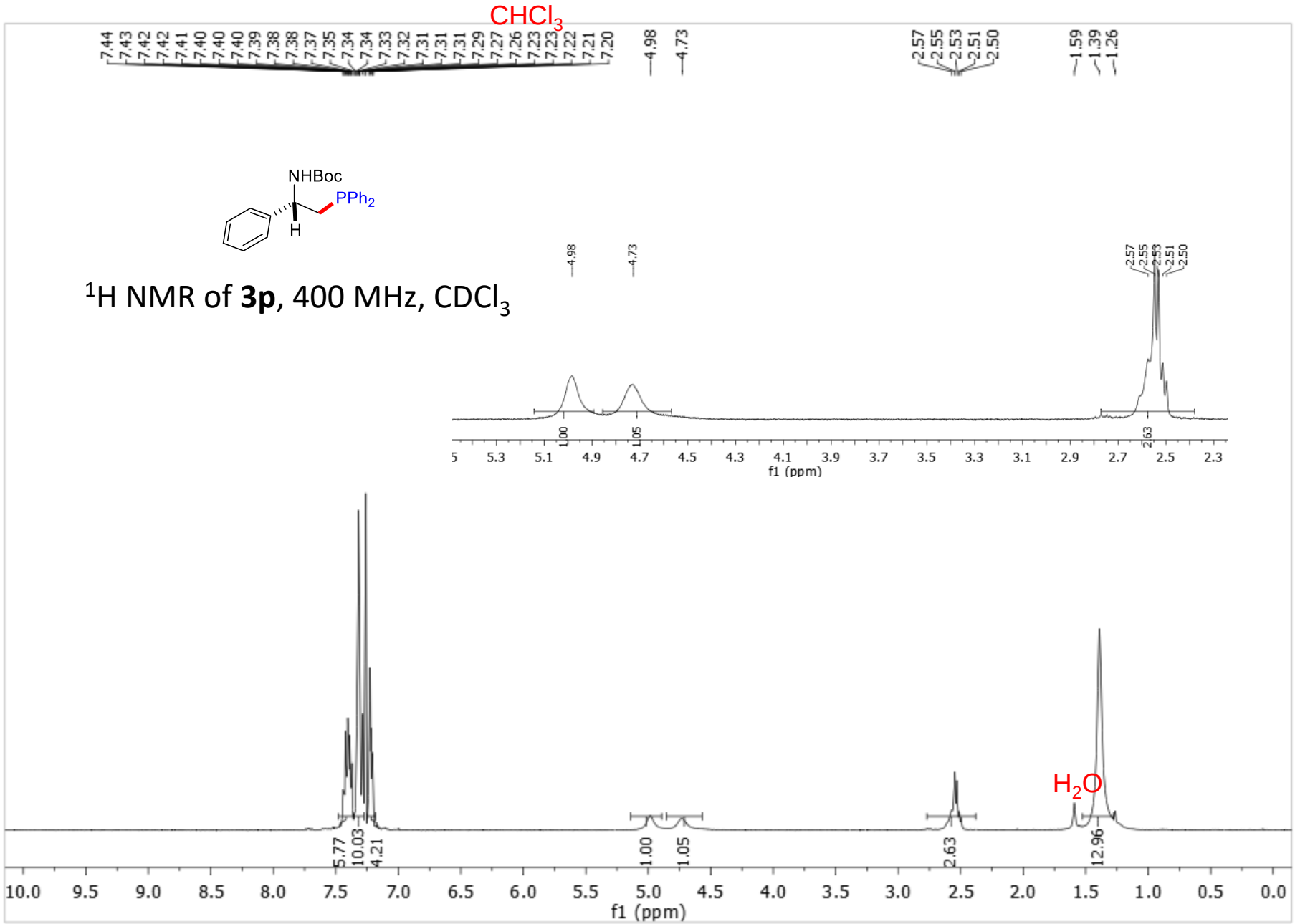


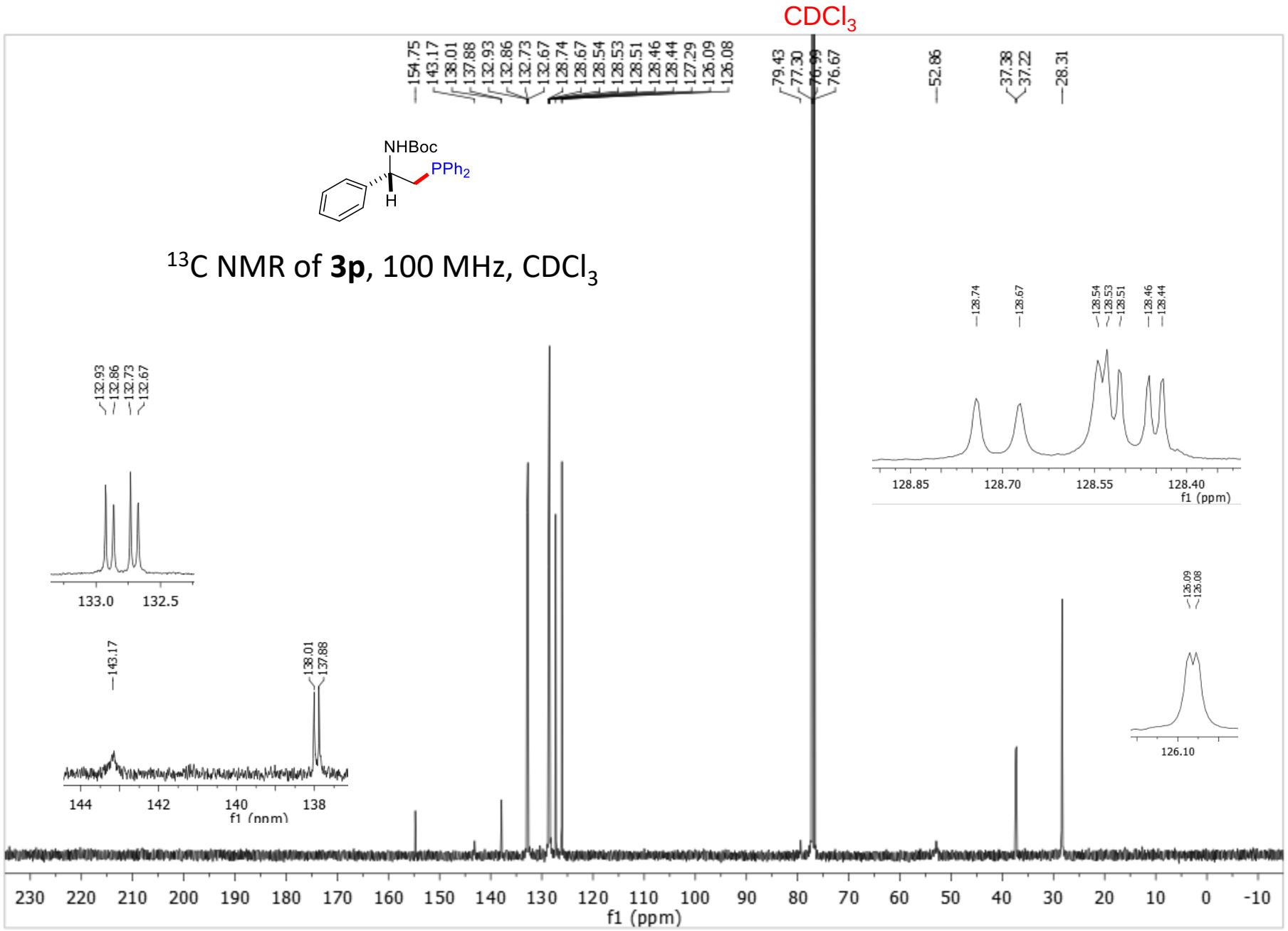
(+)-**3o**

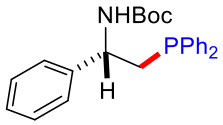
8: 195 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	13.476	97.393	1
	14.684	2.607	2

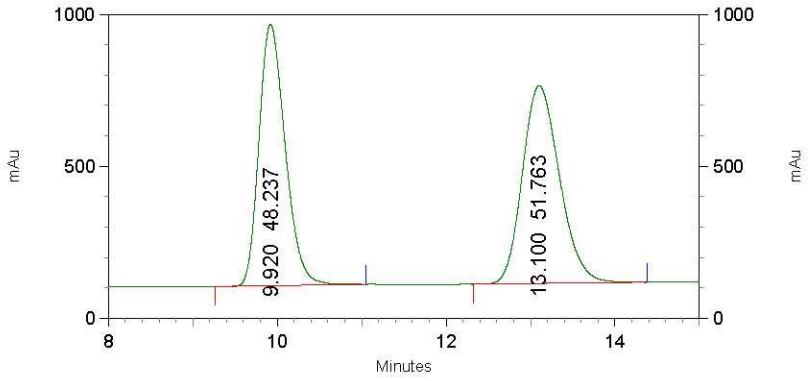
Totals		100.000	

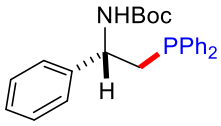

CHCl3
NHBoc
PPh2
H
1H NMR of 3p, 400 MHz, CDCl3
H2O
f1 (ppm)


CDCl3
154.75
143.17
138.01
137.88
132.93
132.86
132.73
132.67
128.74
128.67
128.54
128.53
128.51
128.46
128.44
127.29
126.09
126.08
79.43
77.30
76.99
76.67
52.86
37.38
37.22
28.31
NHBoc
PPh2
H
13C NMR of 3p, 100 MHz, CDCl3
f1 (ppm)

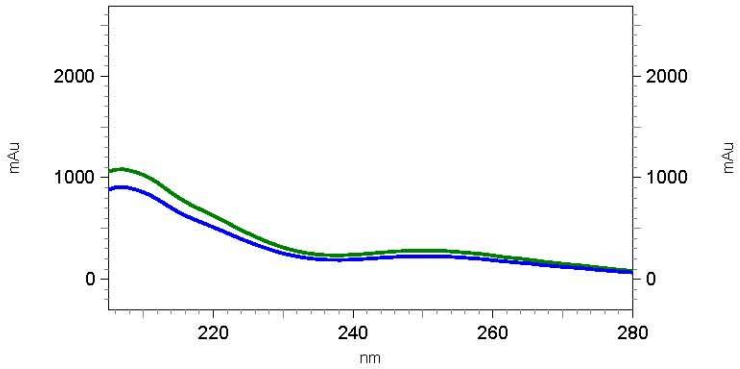


^{31}P NMR of **3p**, 100 MHz, $CDCl_3$





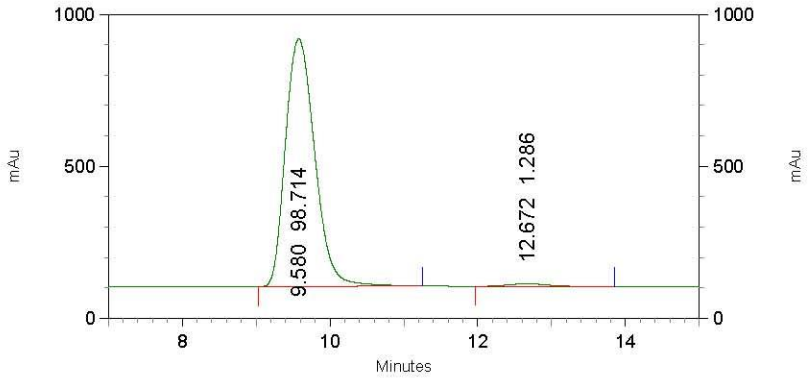
(±)-**3p**

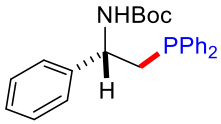


16: 215 nm, 4 nm
Results

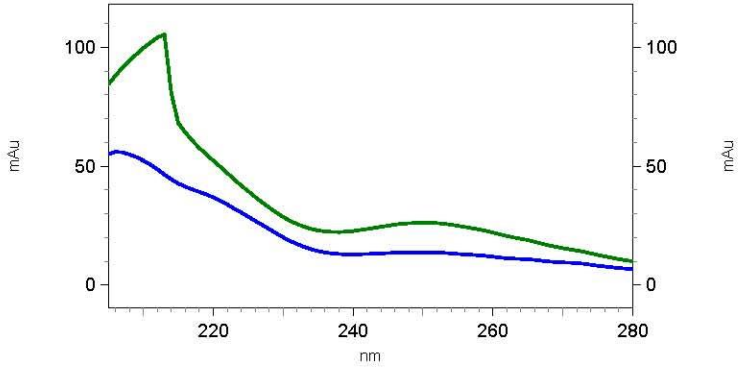
Pk #	Name	Retention Time	Area Percent
1		9.920	48.237
2		13.100	51.763

Totals			100.000





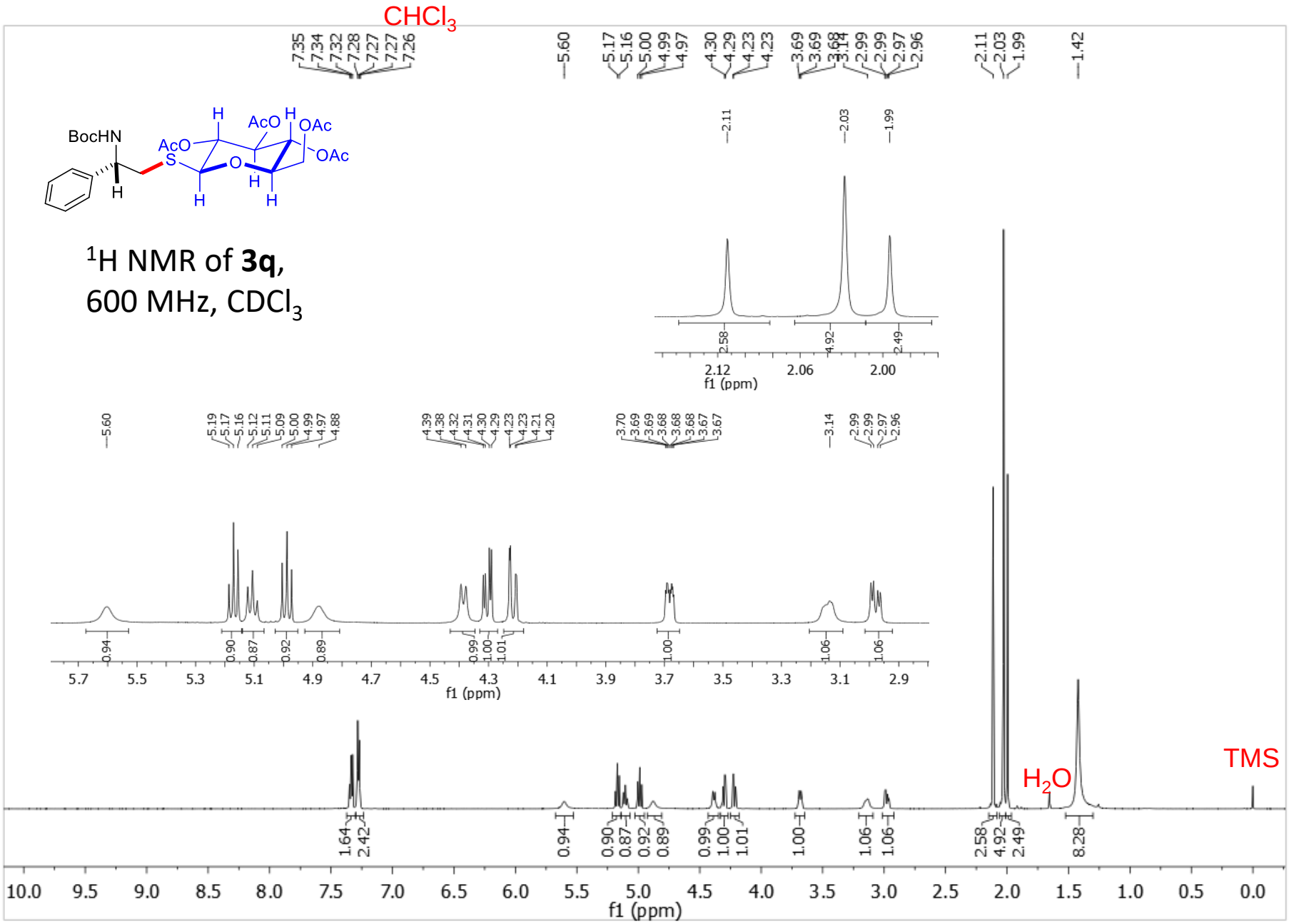
(+)-**3p**



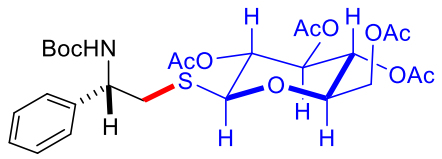
3: 256 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		9.580	98.714
2		12.672	1.286

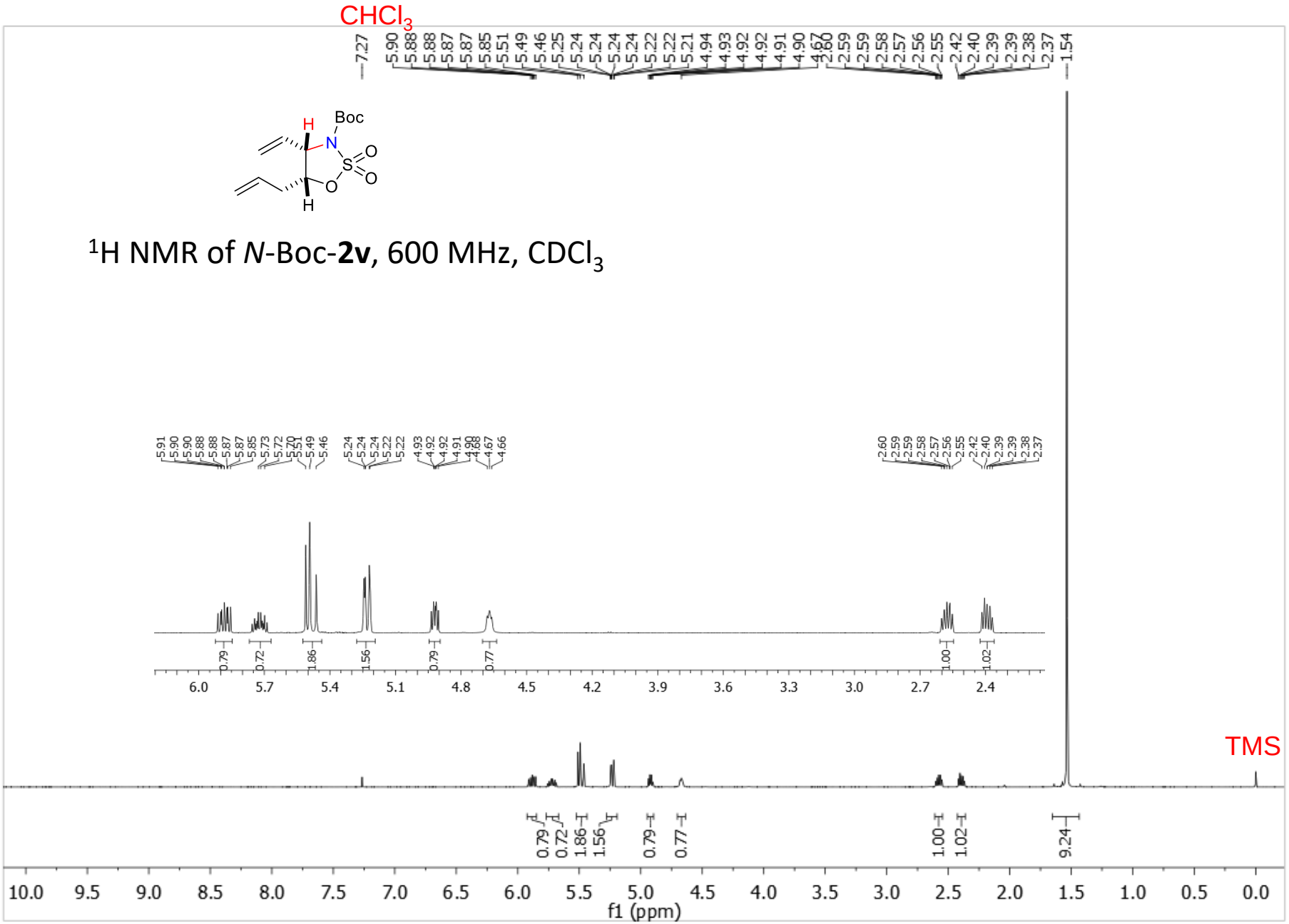
Totals			100.000

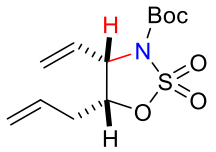

CHCl3
BocHN
AcO
AcO
OAc
OAc
H
H
H
H
H
S
O
1H NMR of 3q,
600 MHz, CDCl3
f1 (ppm)
H2O
TMS

k0l-527-2-C13

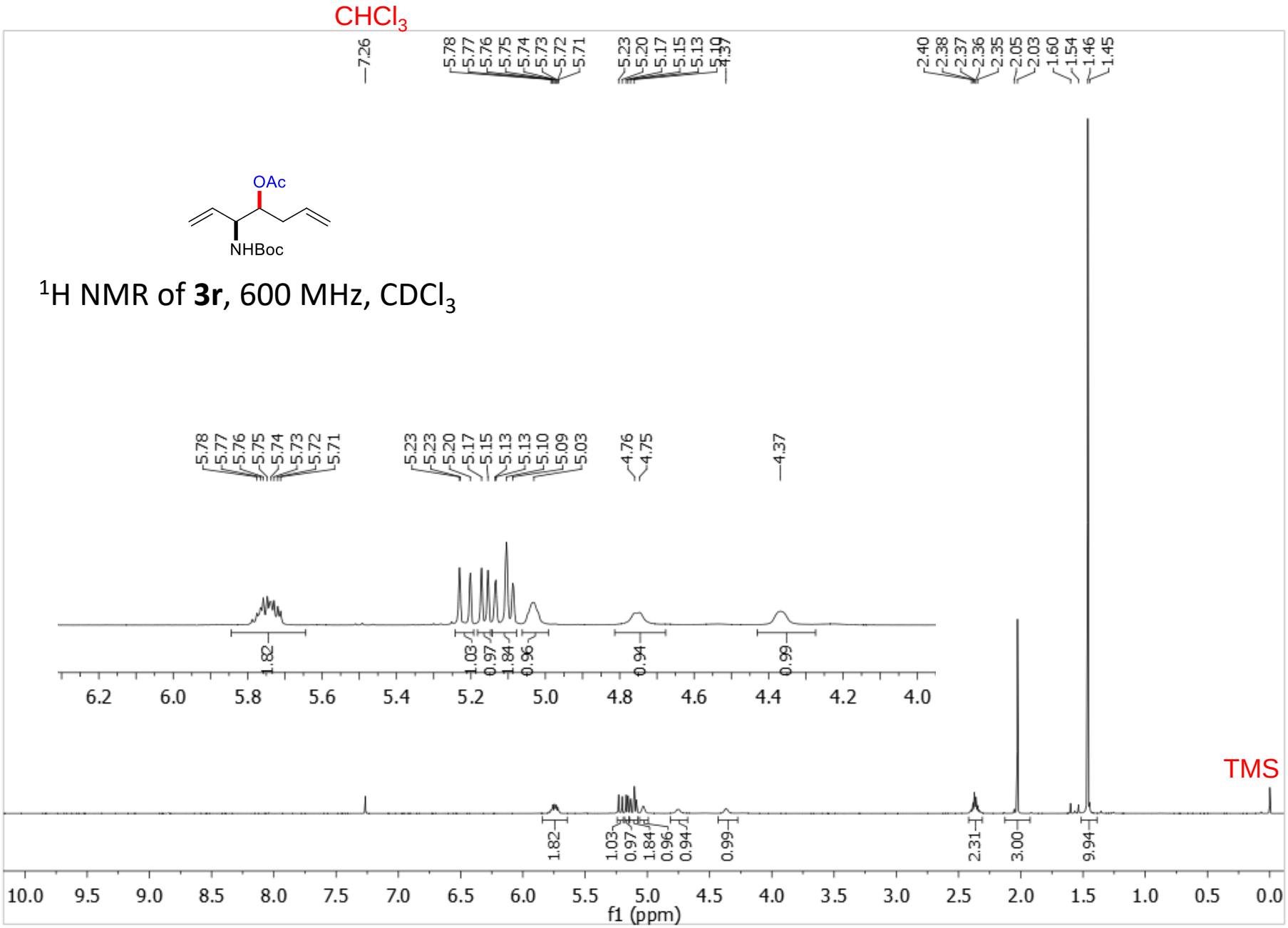


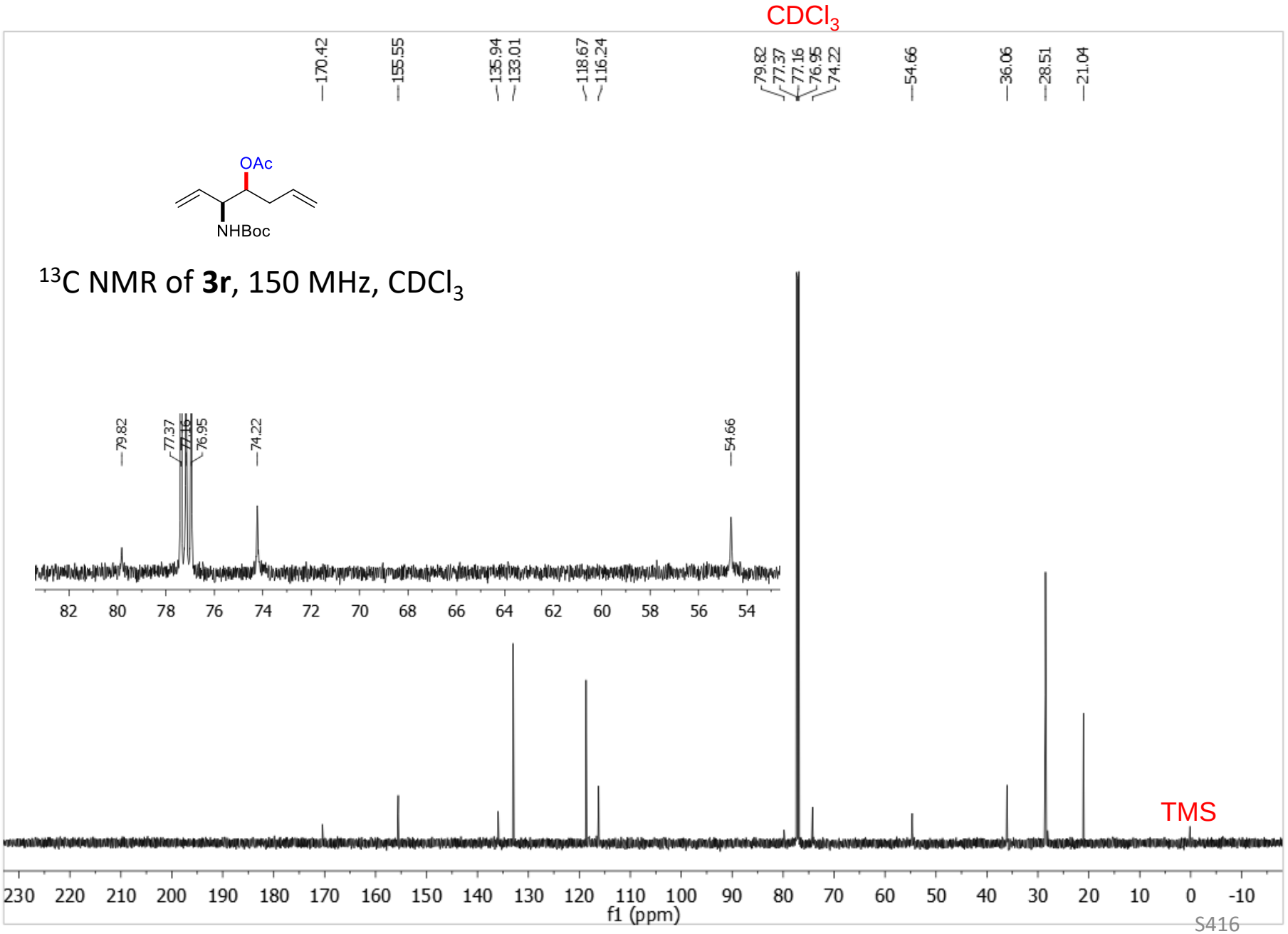
^{13}C NMR of **3q**, 150 MHz, $CDCl_3$

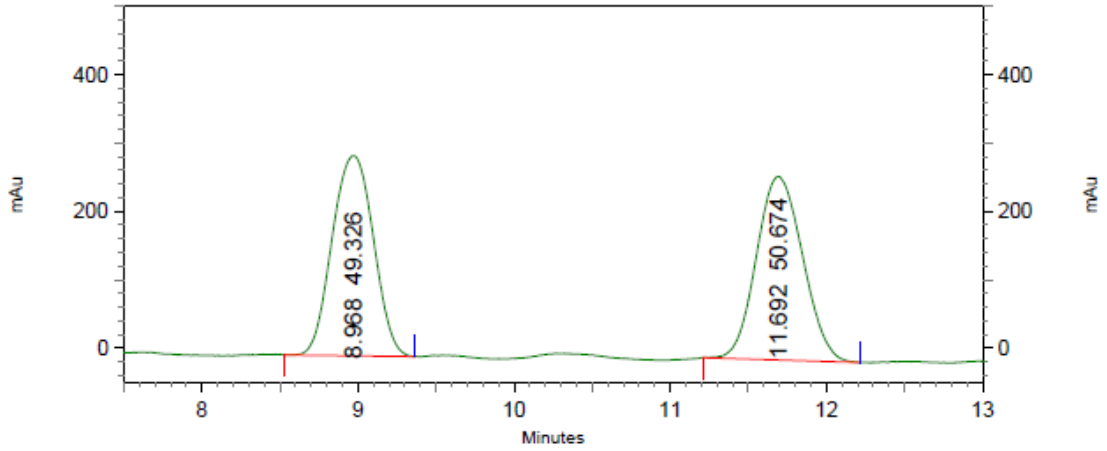

CHCl3
Boc
H
N
S
O
O
O
H
1H NMR of N-Boc-2v, 600 MHz, CDCl3
TMS
f1 (ppm)

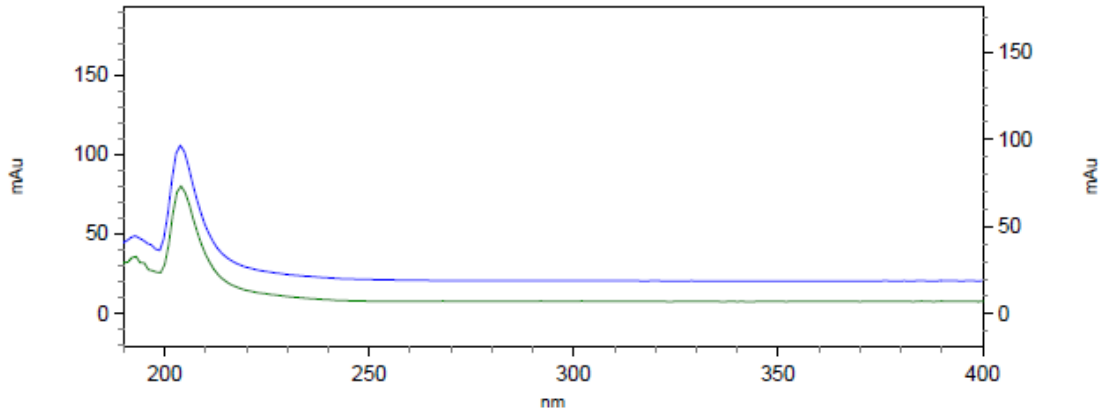


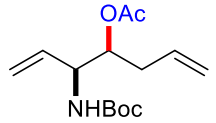
^{13}C NMR of *N*-Boc-**2v**, 150 MHz, $CDCl_3$


CHCl3
OAc
NHBoc
1H NMR of 3r, 600 MHz, CDCl3
TMS
f1 (ppm)


CDCl3
170.42
155.55
135.94
133.01
118.67
116.24
79.82
77.37
77.16
76.95
74.22
54.66
36.06
28.51
21.04
OAc
NHBoc
13C NMR of 3r, 150 MHz, CDCl3
TMS
f1 (ppm)





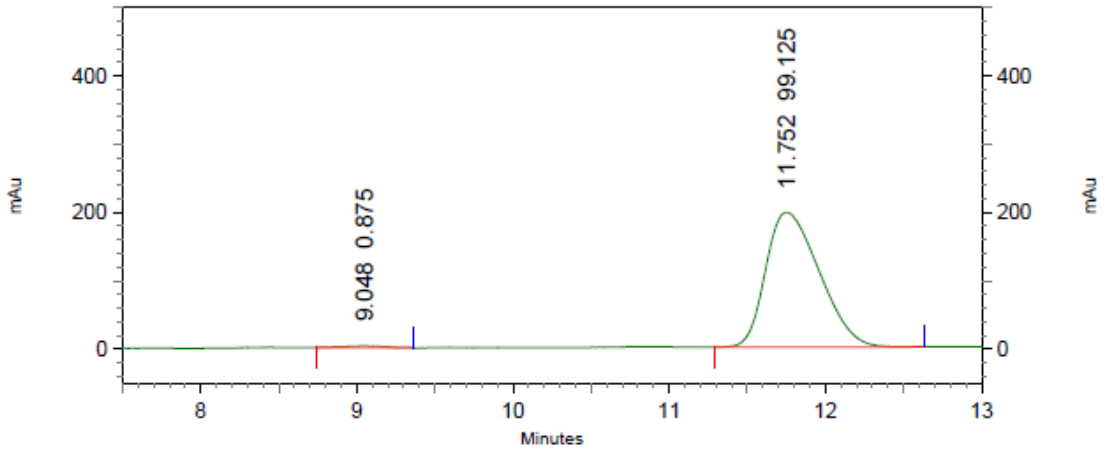


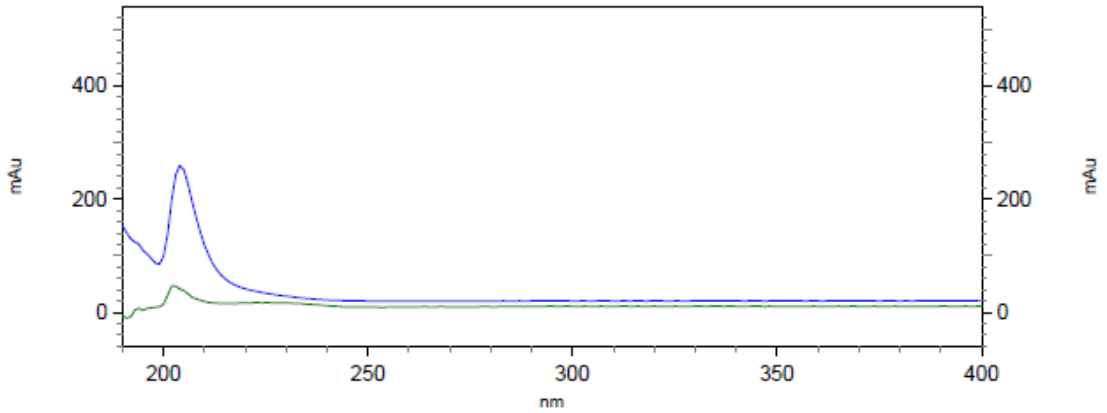
(±)-**3r**

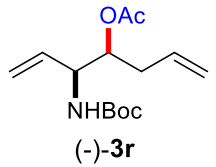
4: 206 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	8.968	49.326
2	11.692	50.674

Totals		100.000



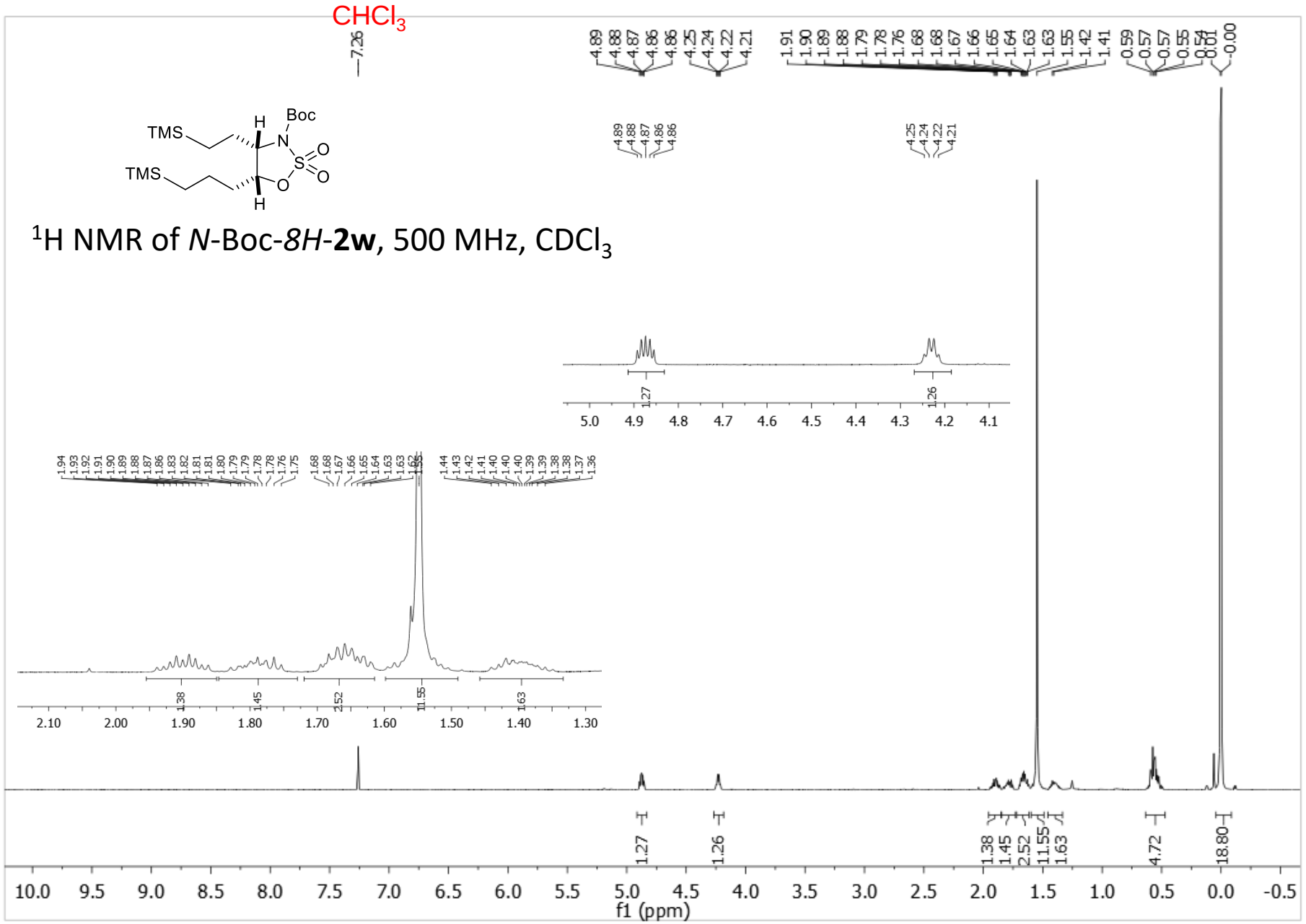


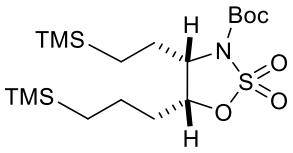


(-)-**3r**

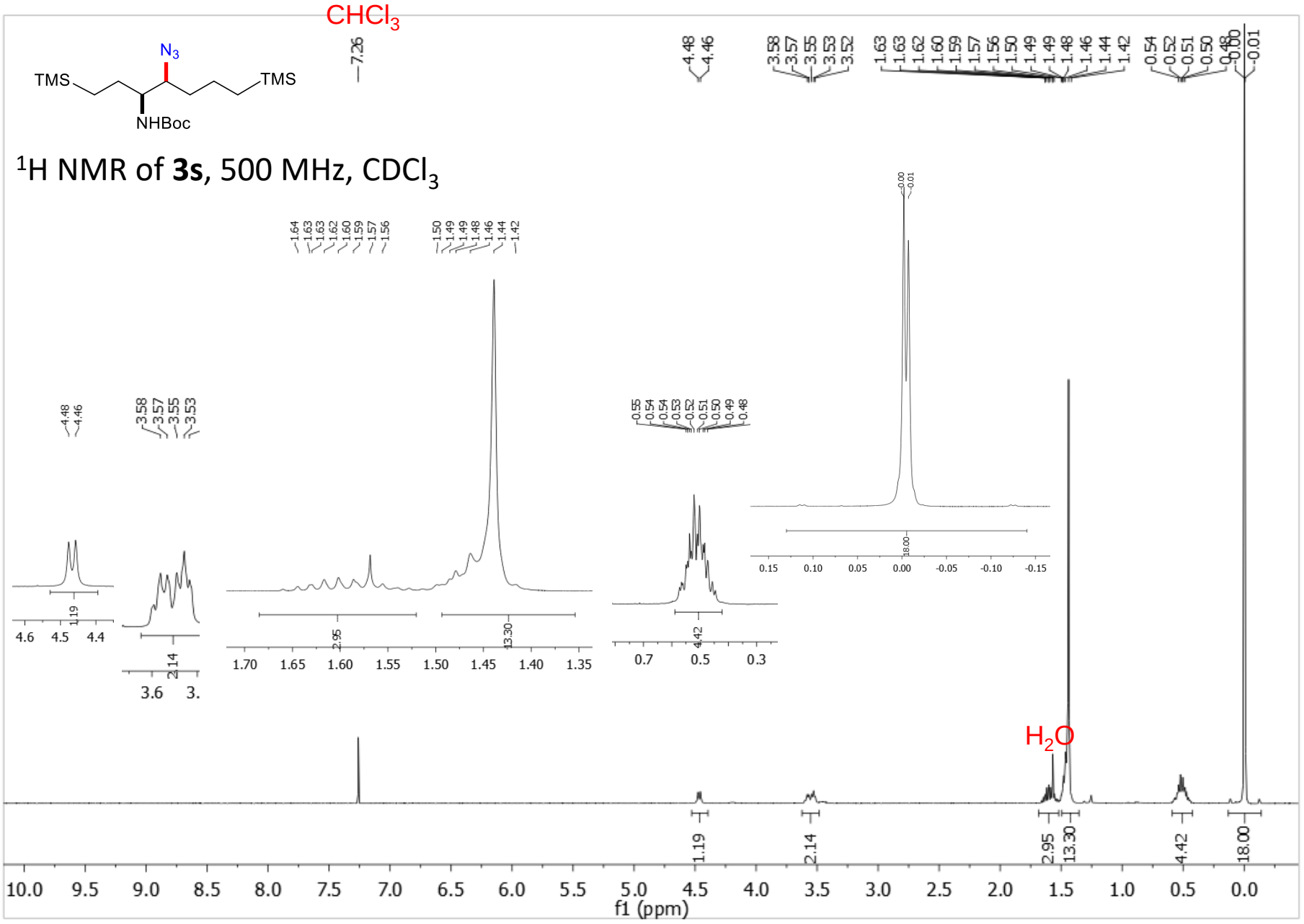
4: 206 nm, 4
nm Results

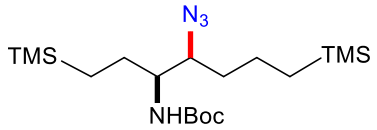
Pk #	Retention Time	Area Percent
1	9.048	0.875
2	11.752	99.125
Totals		100.000


CHCl3
TMS
TMS
H
Boc
N
S
O
O
O
H
1H NMR of N-Boc-8H-2w, 500 MHz, CDCl3
f1 (ppm)



^{13}C NMR of *N*-Boc-*8H*-**2w**, 150 MHz, $CDCl_3$

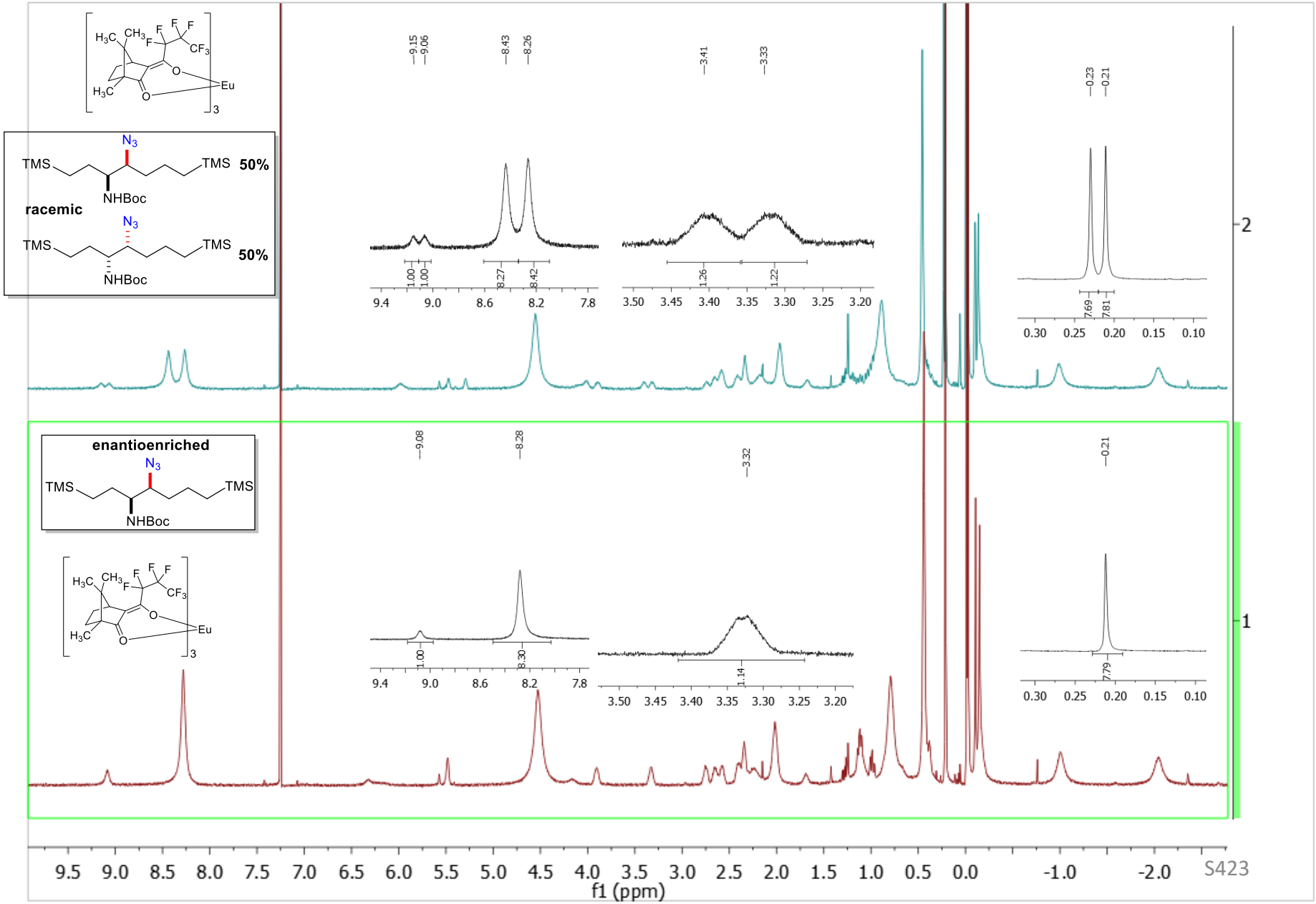

CHCl3
N3
TMS
TMS
NHBoc
1H NMR of 3s, 500 MHz, CDCl3
H2O
f1 (ppm)

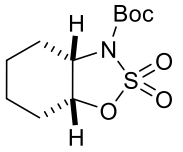


$CDCl_3$

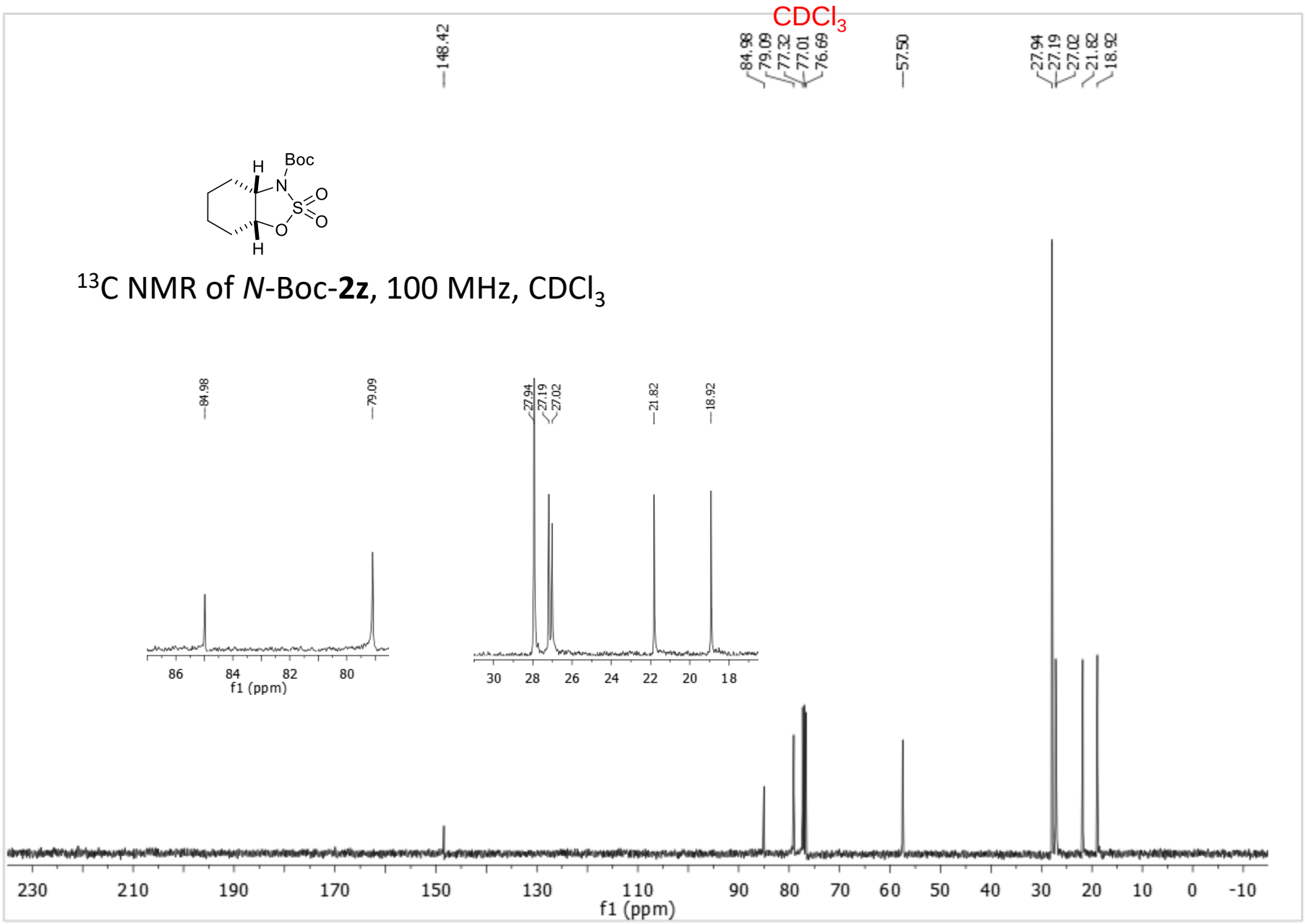
^{13}C NMR of **3s**, 150 MHz, $CDCl_3$

$CHCl_3$ ^{1}H NMR of **3s with Eu(hfc)$_3$**, 600 MHz, $CDCl_3$

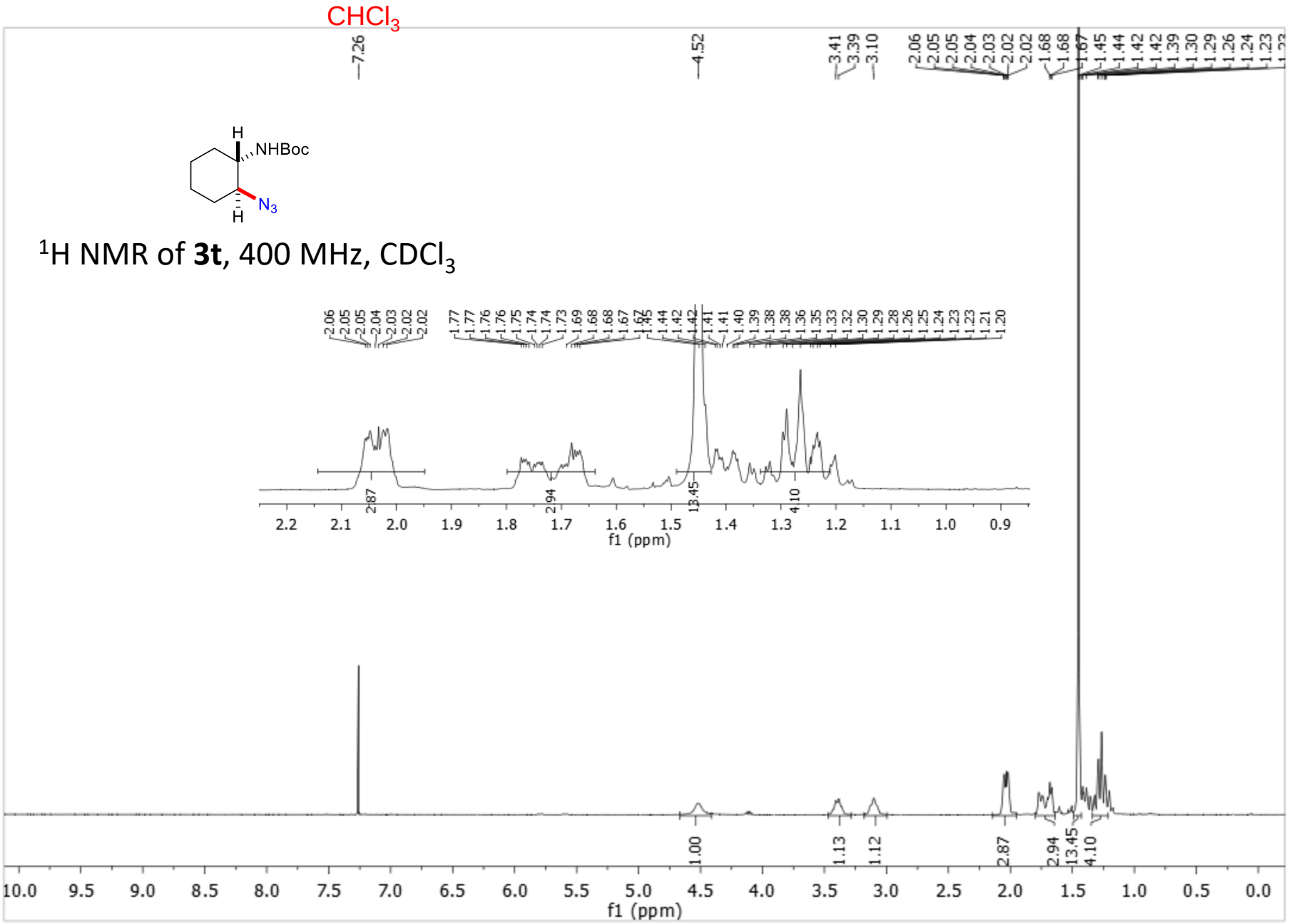


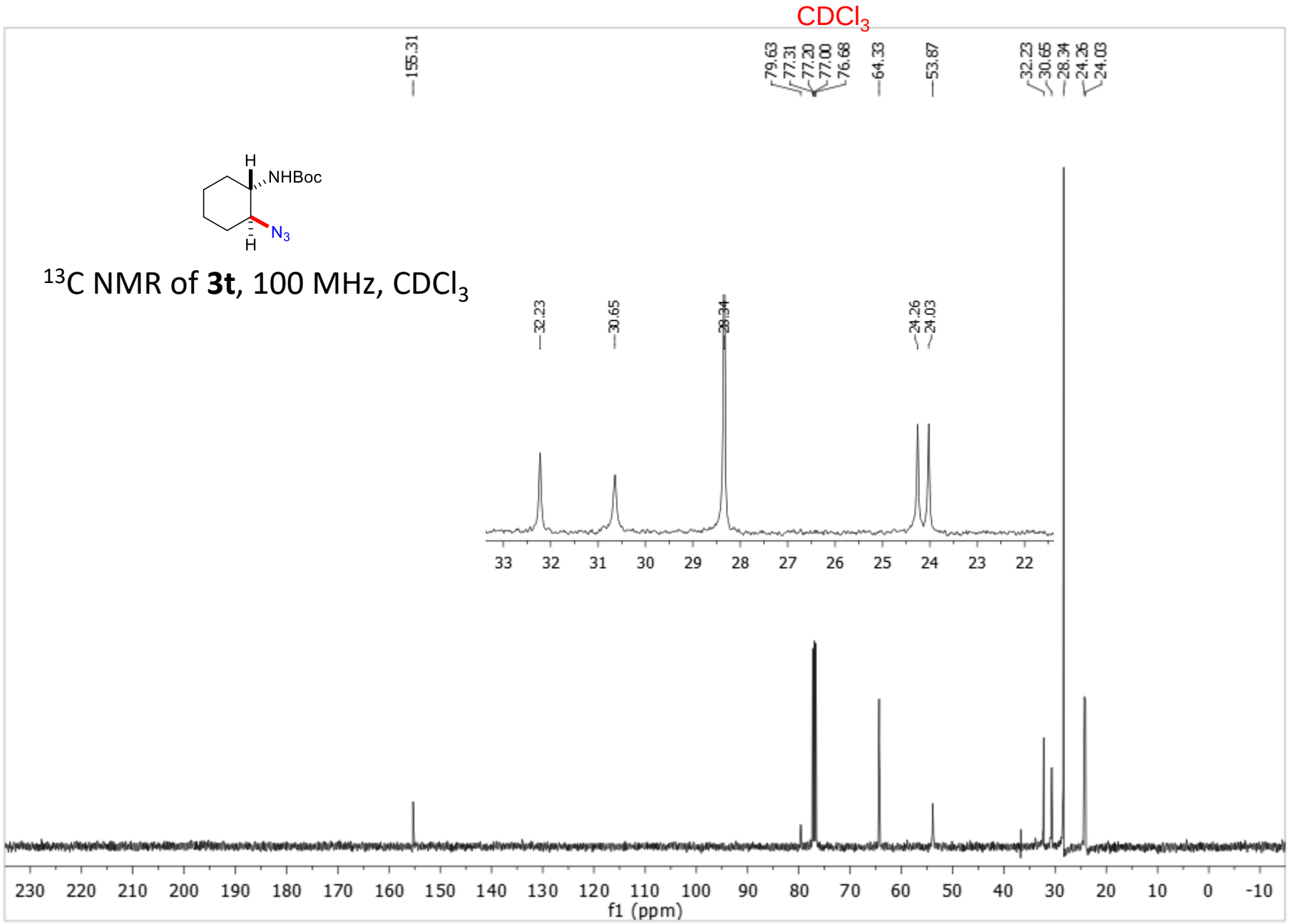


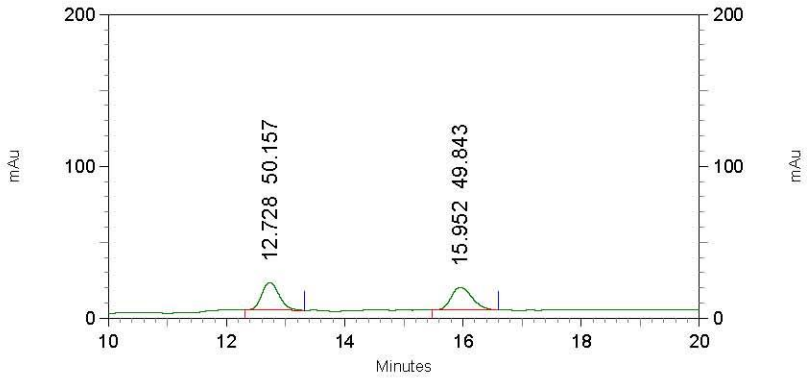
^{1}H NMR of *N*-Boc-**2z**, 400 MHz, $CDCl_3$

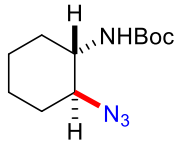


^{13}C NMR of *N*-Boc-**2z**, 100 MHz, $CDCl_3$

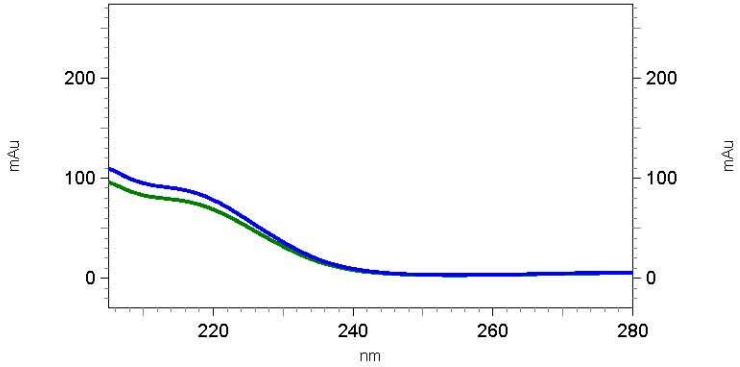

CHCl3
H
NHBoc
N3
H
1H NMR of 3t, 400 MHz, CDCl3
f1 (ppm)


CDCl3
155.31
79.63
77.31
77.20
77.00
76.68
64.33
53.87
32.23
30.65
28.34
24.26
24.03
H
NHBoc
N3
H
13C NMR of 3t, 100 MHz, CDCl3
f1 (ppm)





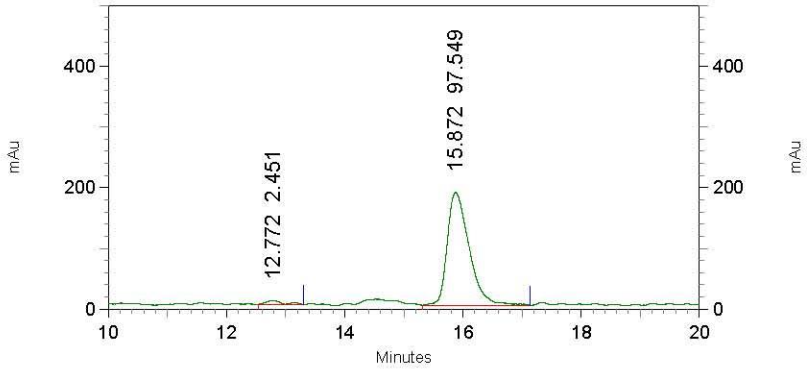
(±)-**3t**

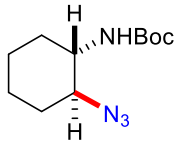


19: 235 nm, 4 nm
Results

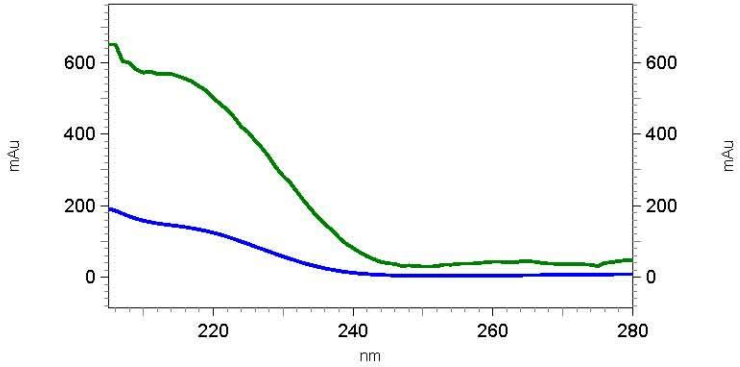
Pk #	Name	Retention Time	Area Percent
1		12.728	50.157
2		15.952	49.843

Totals			100.000





(-)-**3t**



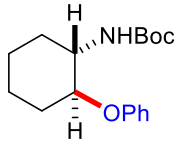
1: 197 nm, 4 nm

Results

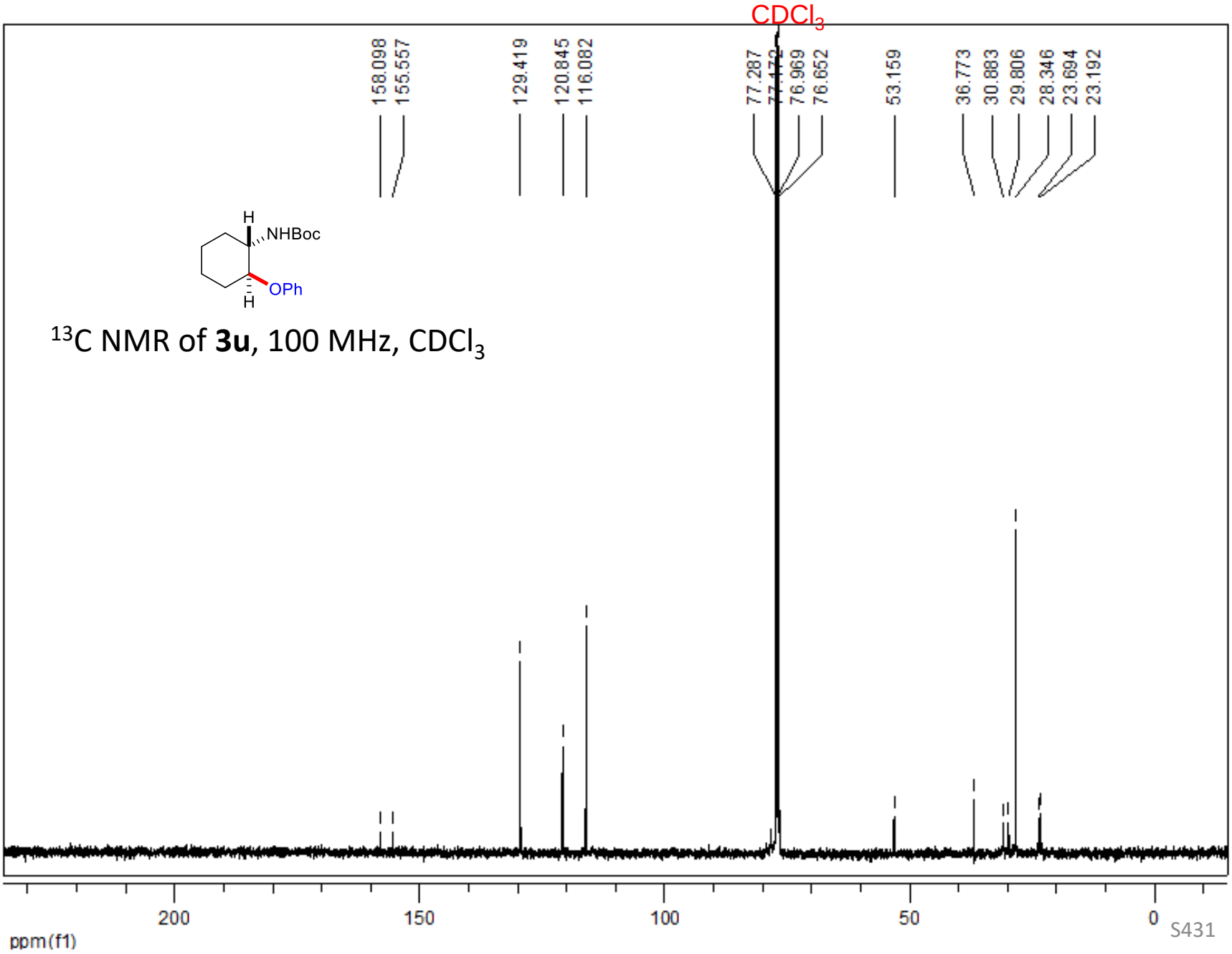
Pk #	Name	Retention Time	Area Percent
1		12.772	2.451
2		15.872	97.549

Totals			100.000

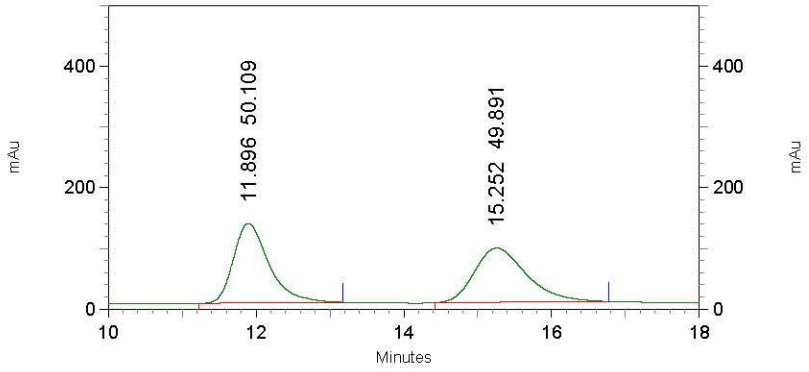
$CHCl_3$

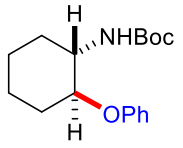


^{1}H NMR of **3u**,
400 MHz, $CDCl_3$

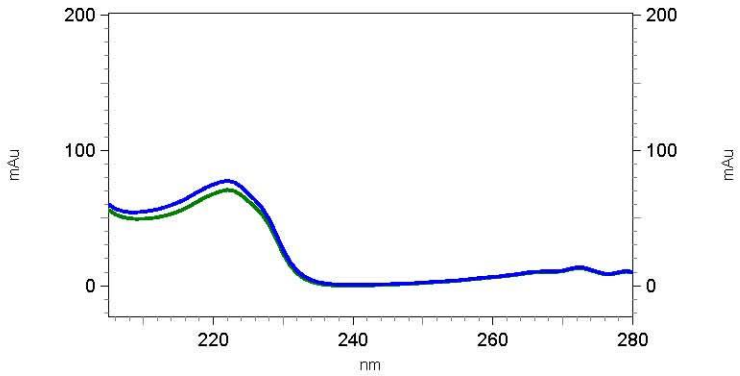


^{13}C NMR of **3u**, 100 MHz, $CDCl_3$





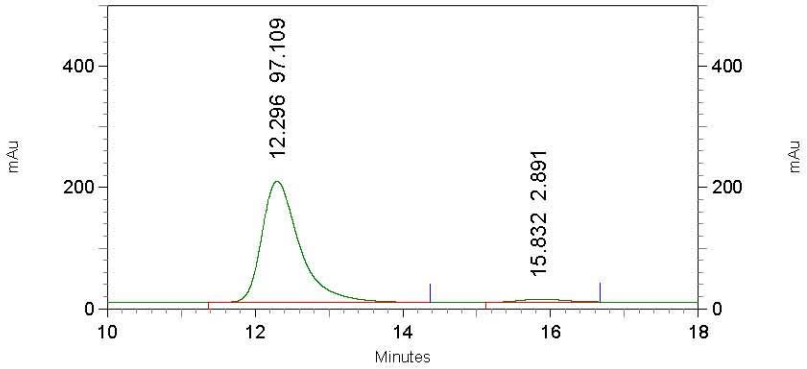
(±)-**3u**

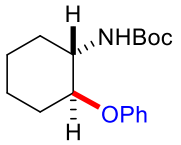


19: 230 nm, 4 nm
Results

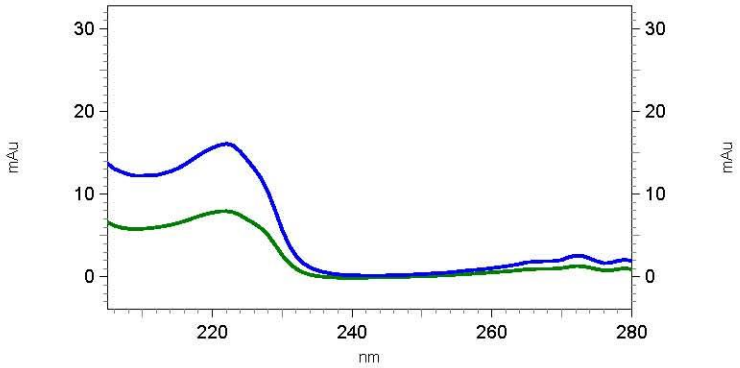
Pk #	Name	Retention Time	Area Percent
1		11.896	50.109
2		15.252	49.891

Totals			100.000



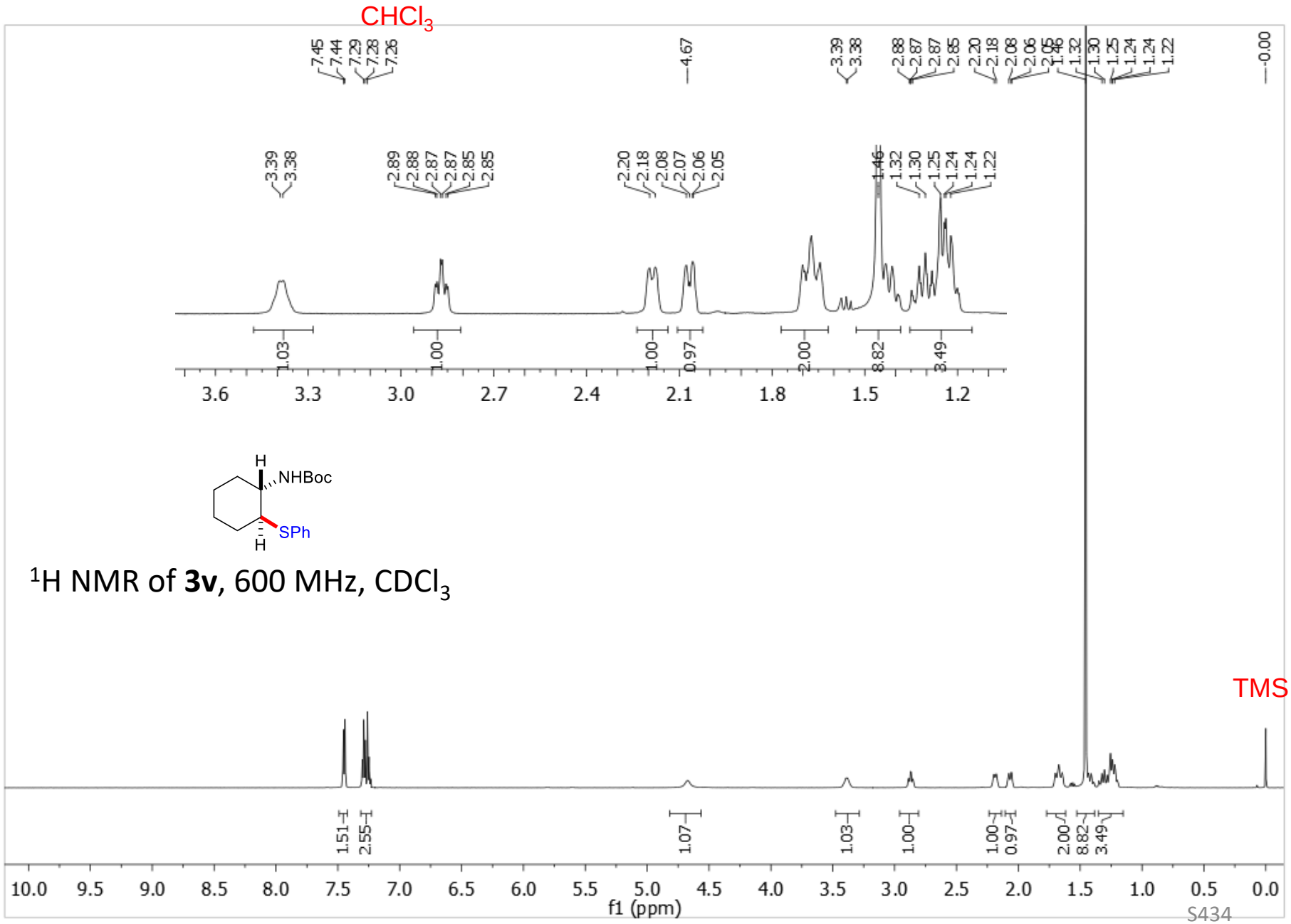


(+)-**3u**

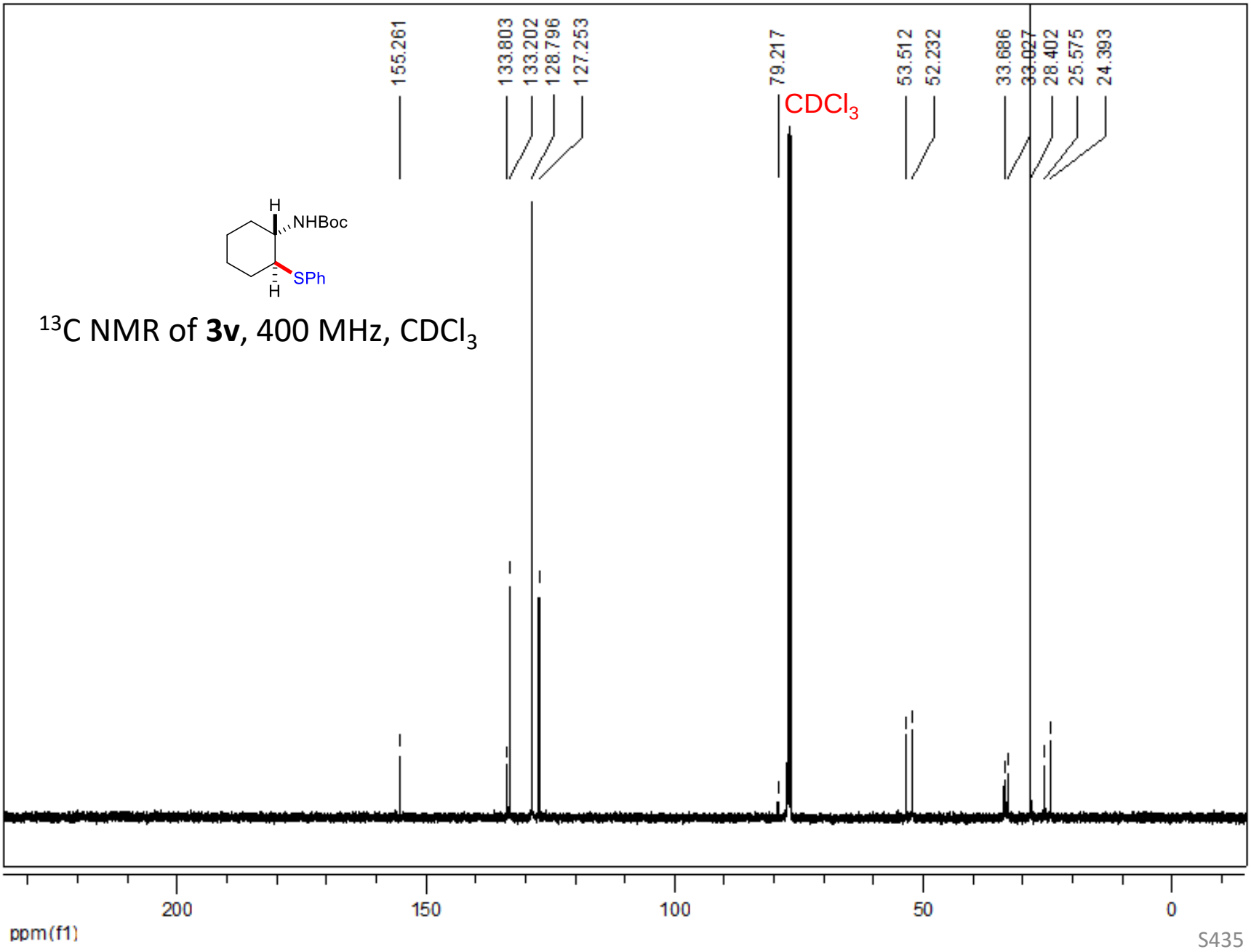


19: 230 nm, 4 nm
Results

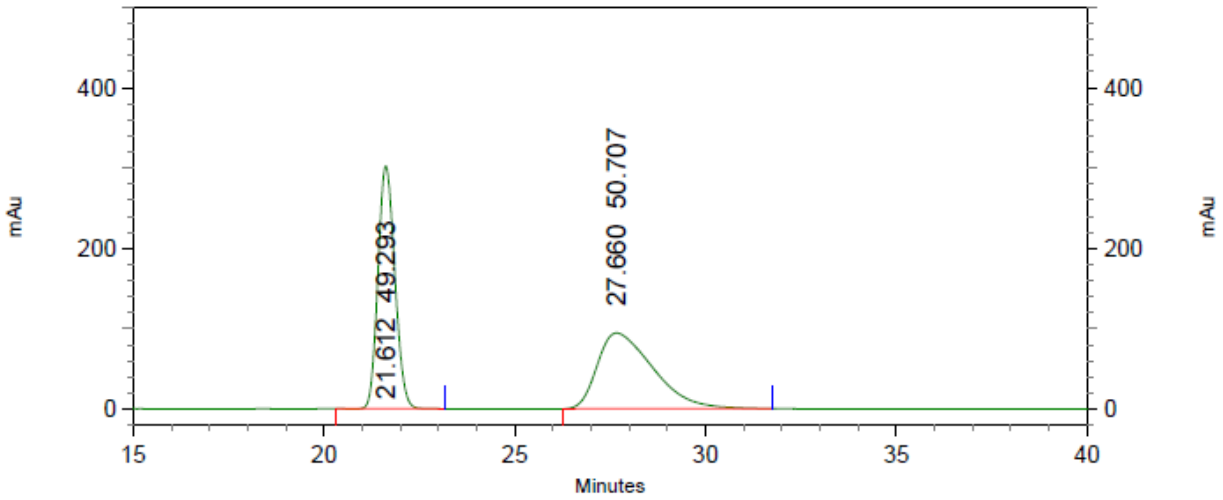
Pk #	Name	Retention Time	Area Percent
1		12.296	97.109
2		15.832	2.891
Totals			100.000

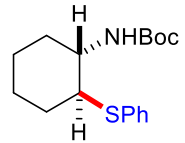


^{1}H NMR of **3v**, 600 MHz, $CDCl_3$

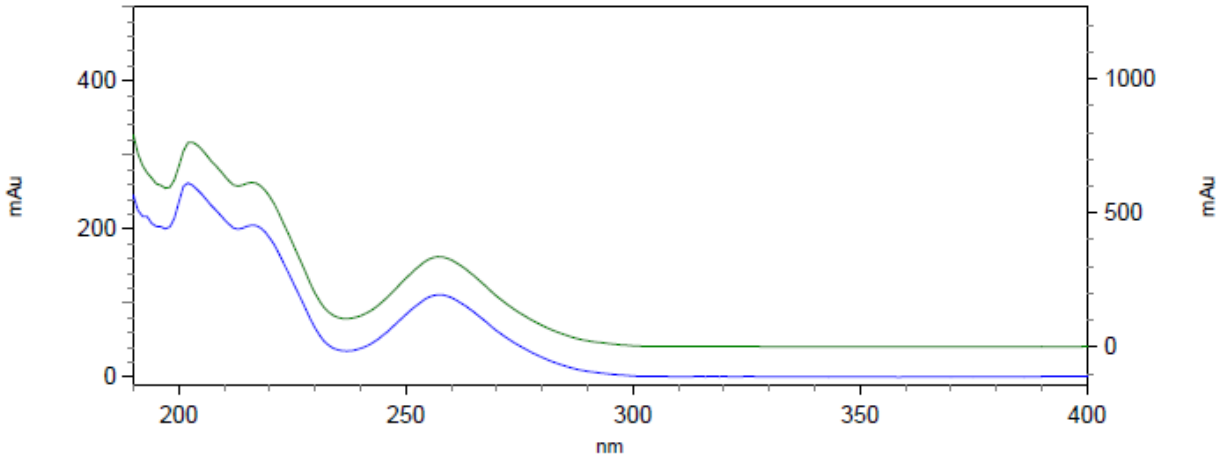

155.261
133.803
133.202
128.796
127.253
79.217
CDCl3
53.512
52.232
33.686
33.027
28.402
25.575
24.393
H
NHBoc
SPh
H
13C NMR of 3v, 400 MHz, CDCl3
200
150
100
50
0
ppm (f1)

C:\EZStart\Projects\Default\Data\K0L-384-ADH-2%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





(±)-**3v**

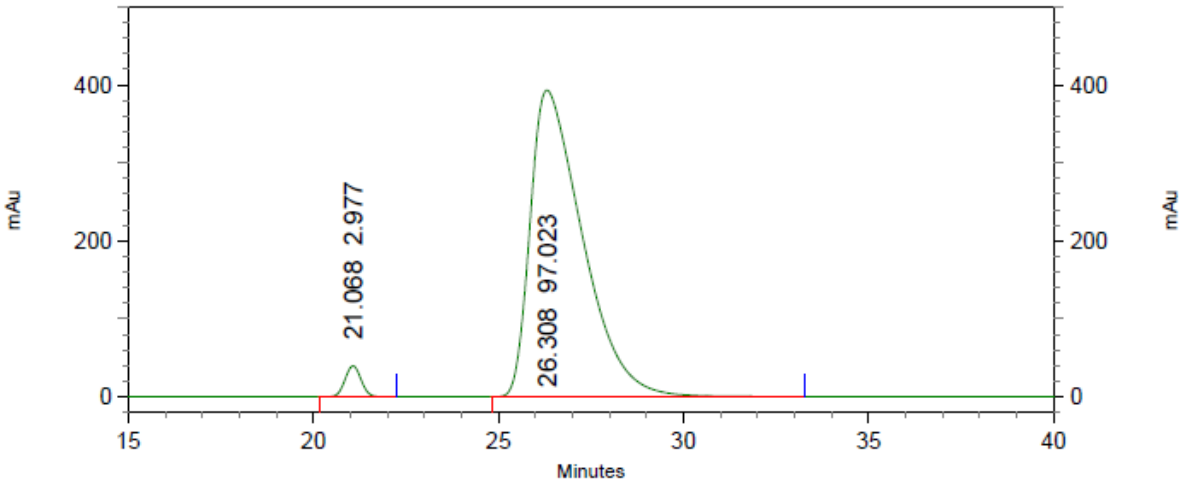


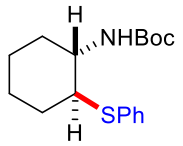
5: 221 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	21.612	49.293
2	27.660	50.707

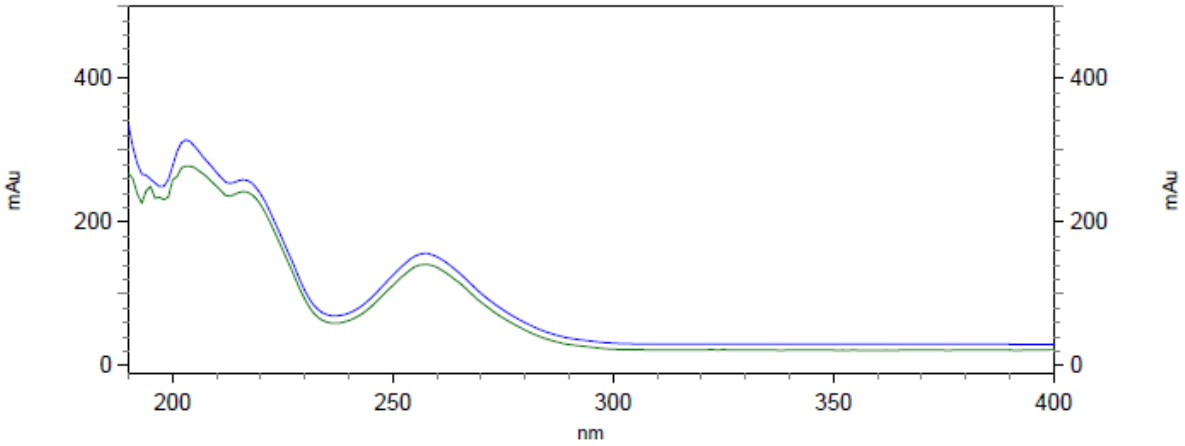
Totals	
	100.000

C:\EZStart\Projects\Default\Data\K0L-383-ADH-2%
C:\Documents and Settings\zhang\Desktop\DSW\0210.met





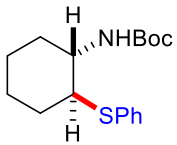
(+)-**3v**



5: 221 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	21.068	2.977
2	26.308	97.023

Totals	
	100.000



(+)-**3v**

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C17H25NO2S

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

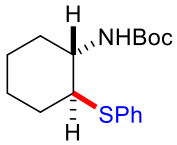
Datablock: C17H25NO2S

```
Bond precision:  C-C = 0.0053 A          Wavelength=1.54178

Cell:          a=5.1618(4)        b=8.6542(7)      c=10.5664(8)
               alpha=112.852(4)   beta=96.462(4)   gamma=99.605(4)
Temperature:   100 K
```

	Calculated	Reported
Volume	420.62(6)	420.62(6)
Space group	P 1	P 1
Hall group	P 1	P 1
Moiety formula	C17 H25 N O2 S	C17 H25 N O2 S
Sum formula	C17 H25 N O2 S	C17 H25 N O2 S
Mr	307.44	307.44
Dx,g cm-3	1.214	1.214
Z	1	1
Mu (mm-1)	1.735	1.735
F000	166.0	166.0
F000'	166.75	
h,k,lmax	6,10,12	6,10,12
Nref	3166[1583]	2898
Tmin,Tmax	0.517,0.683	0.604,0.753
Tmin'	0.367	

```
Correction method= # Reported T Limits: Tmin=0.604 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.83/0.92      Theta(max)= 69.773

R(reflections)= 0.0412( 2863)     wR2(reflections)= 0.1115( 2898)

S = 1.068                  Npar= 196
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.



(+)-**3v**

Alert level C

PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.00527 Ang.
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	20 Report
PLAT915_ALERT_3_C	No Flack x Check Done: Low Friedel Pair Coverage	85 %

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2 Note
PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)	0.004 Degree
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT791_ALERT_4_G	Model has Chirality at C4 (Chiral SPGR)	S Verify
PLAT791_ALERT_4_G	Model has Chirality at C9 (Chiral SPGR)	S Verify
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	4 Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	1 Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	12 Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	1 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	5 Info

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 10 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  2 ALERT type 2 Indicator that the structure model may be wrong or deficient
  6 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

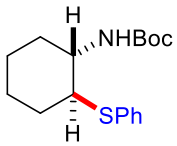
It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

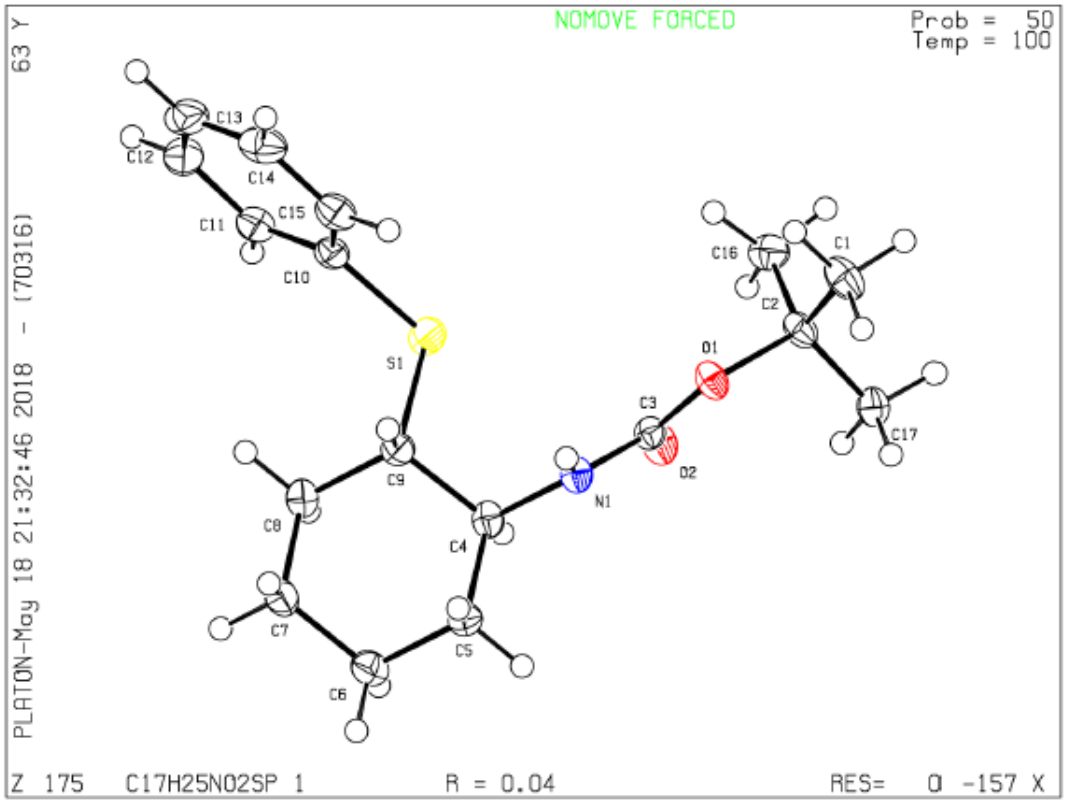
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

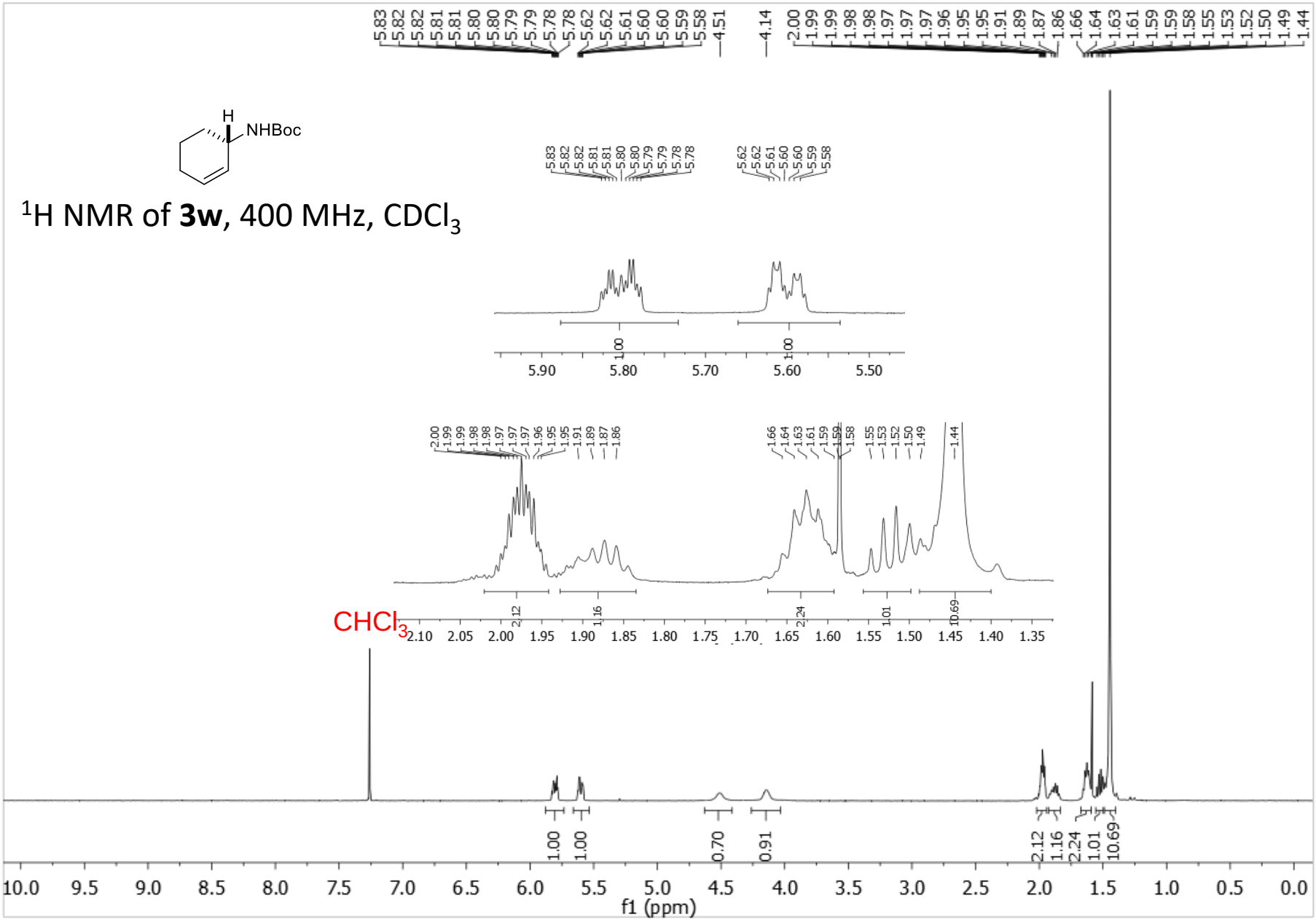


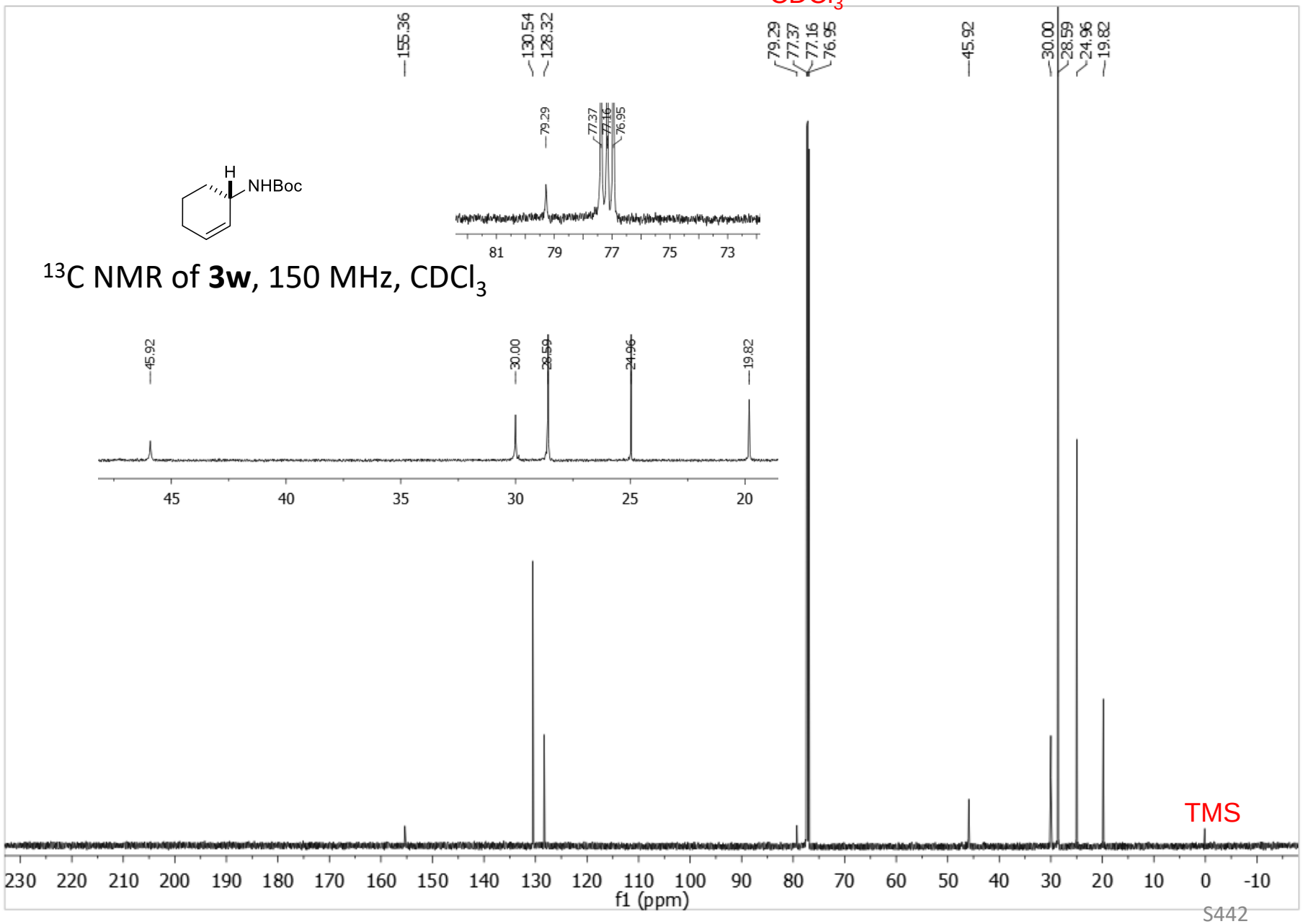
(+)-**3v**

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock: C17H25NO2S - ellipsoid plot

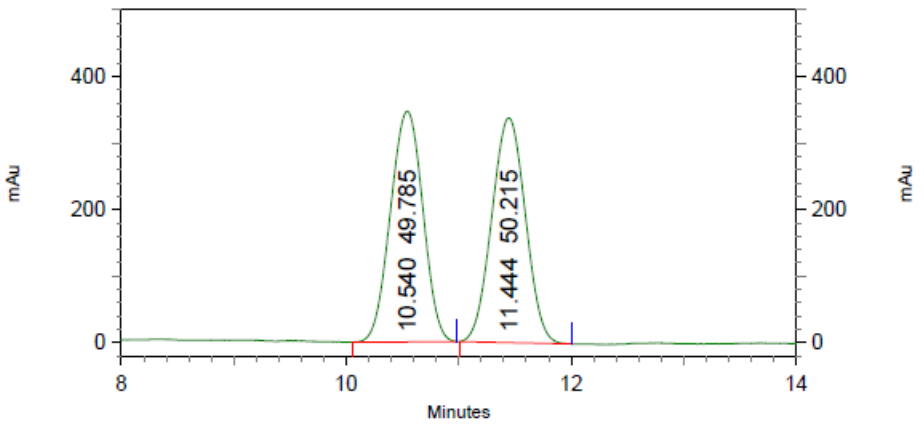


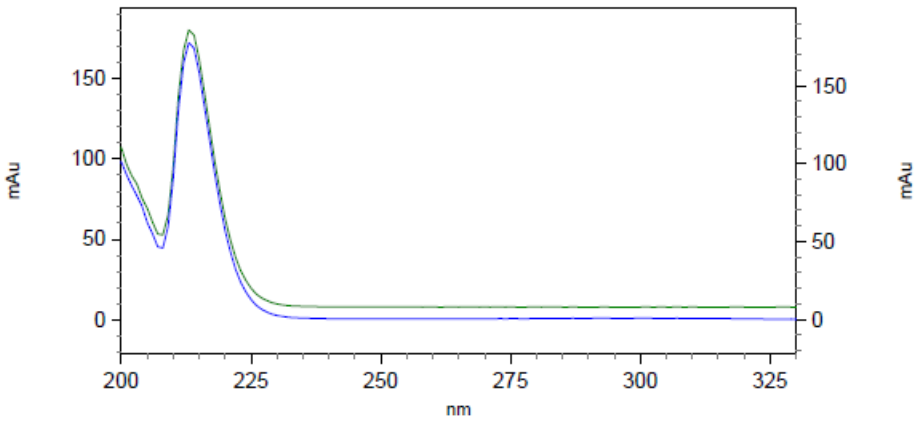

H
NHBoc
1H NMR of 3w, 400 MHz, CDCl3
CHCl3
f1 (ppm)

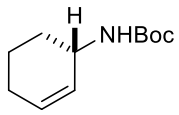


^{13}C NMR of **3w**, 150 MHz, $CDCl_3$

K0L-386-IC-2%-4
C:\EZStart\Projects\Default\Method\LK-2%1mL60MIN.met
C:\EZStart\Projects\Default\Data\K0L-386-IC-2%-4







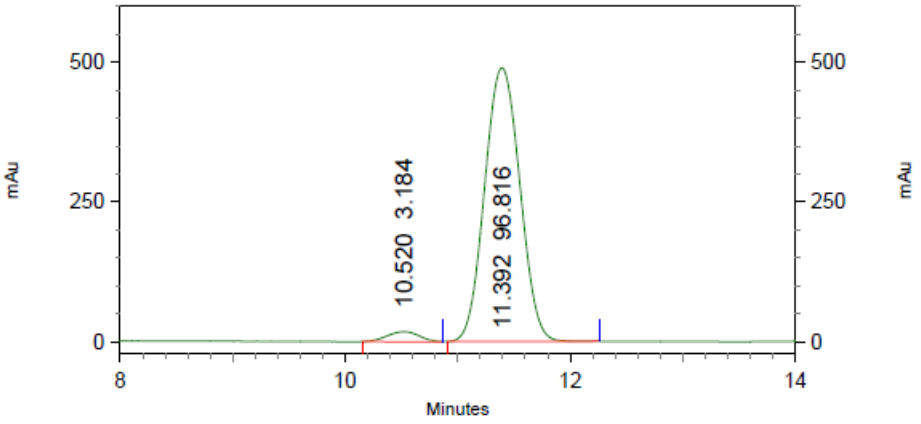
(±)-**3w**

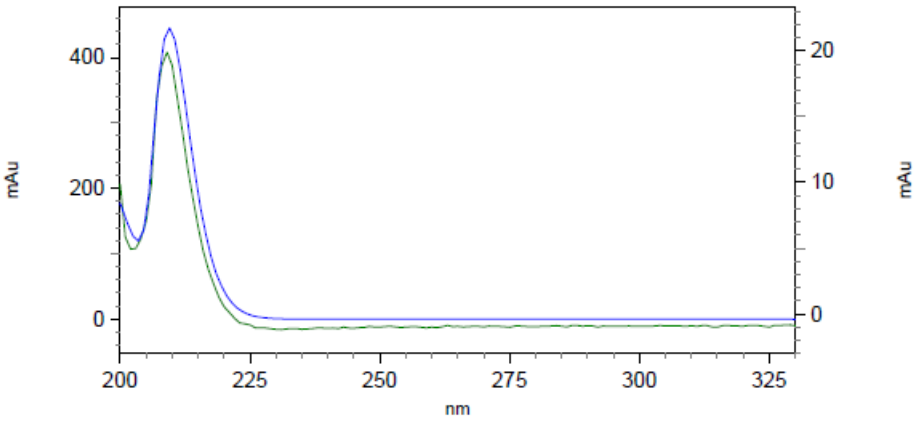
3: 207 nm, 4 nm
Results

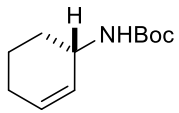
Name	Retention Time	Area Percent	Pk #
	10.540	49.785	1
	11.444	50.215	2

Totals	
	100.000

K0L-385-IC-2%-4
C:\EZStart\Projects\Default\Method\LK-2%1mL60MIN.met
C:\EZStart\Projects\Default\Data\K0L-385-IC-2%-4





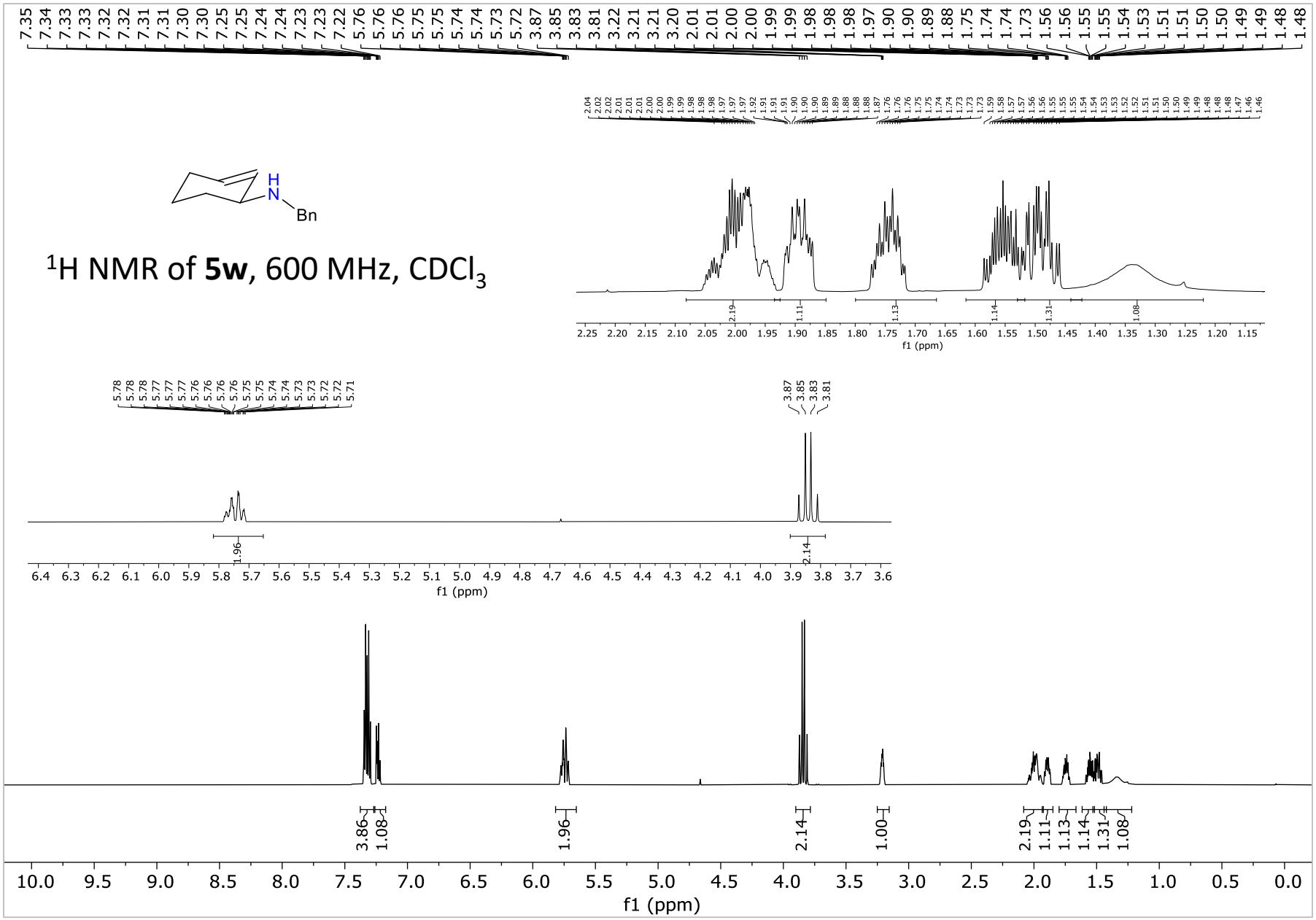


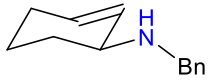
(-)-**3w**

3: 207 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	10.520	3.184	1
	11.392	96.816	2

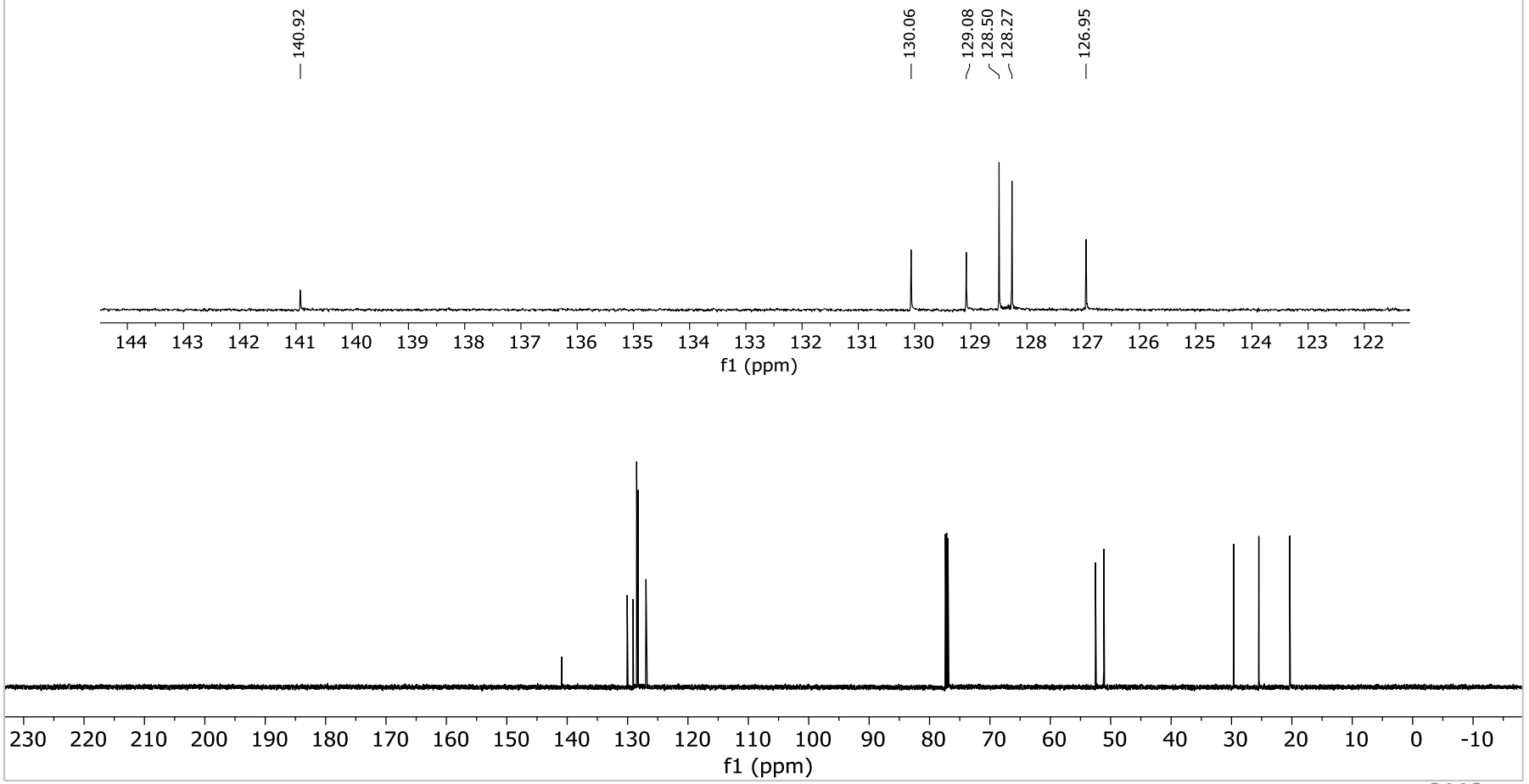
Totals	
	100.000

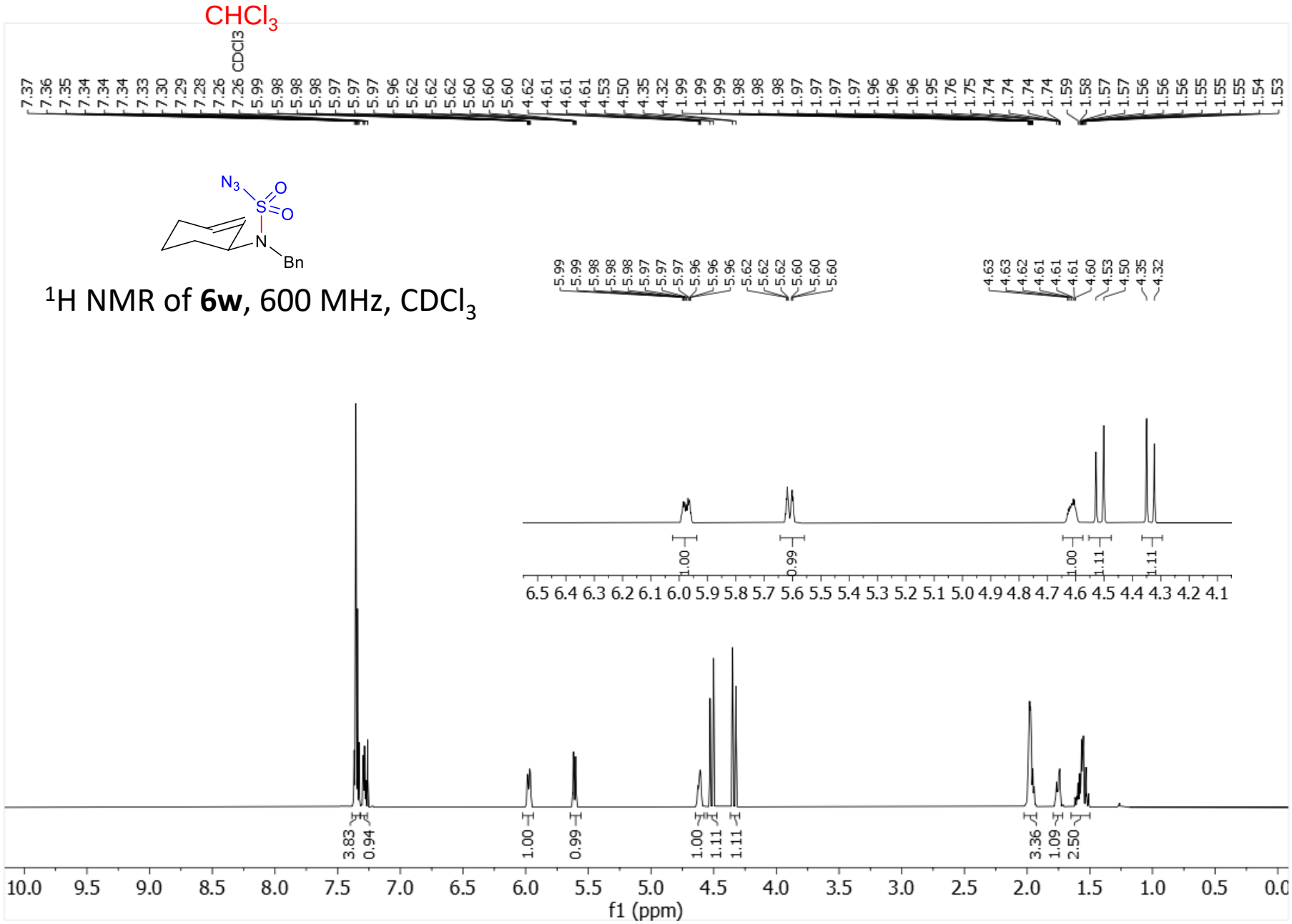

CHCl3
7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.76 7.76 7.76 7.75 7.75 7.74 7.74 7.73 7.72 3.87 3.85 3.83 3.81 3.22 3.21 3.21 3.20 2.01 2.01 2.00 2.00 1.99 1.99 1.98 1.98 1.98 1.97 1.90 1.90 1.89 1.88 1.75 1.74 1.74 1.73 1.56 1.56 1.55 1.55 1.54 1.53 1.51 1.51 1.50 1.50 1.49 1.49 1.48 1.48
H
N
Bn
1H NMR of 5w, 600 MHz, CDCl3
2.19 1.11 1.13 1.14 1.31 1.08
f1 (ppm)
1.96 2.14
f1 (ppm)
3.86 1.08 1.96 2.14 1.00 2.19 1.11 1.13 1.14 1.31 1.08
f1 (ppm)

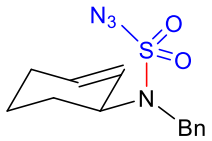


140.92
130.06
129.08
128.50
128.27
126.95
77.37
77.16 CDCl3
76.95
52.53
51.14
29.63
25.47
20.35

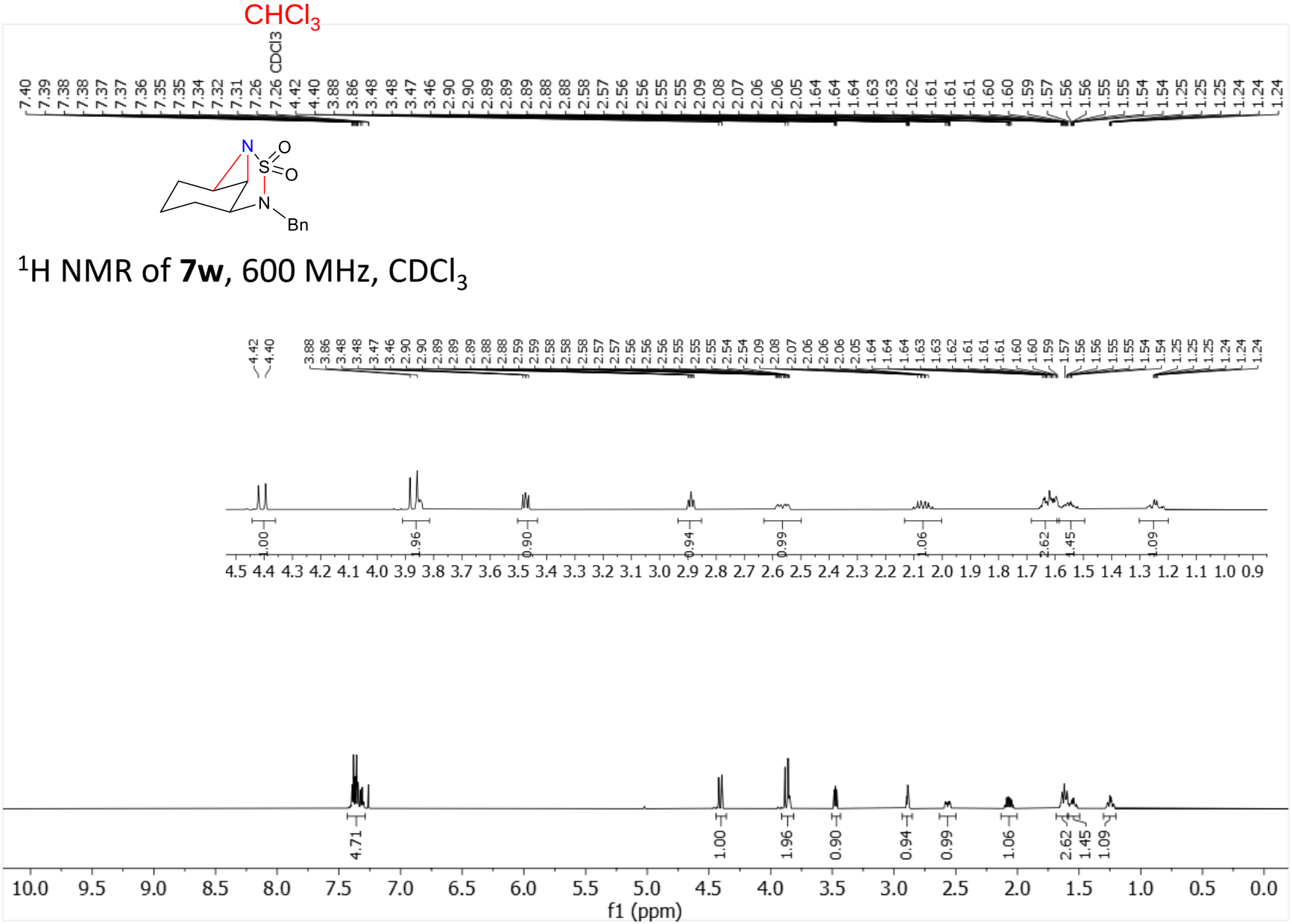
^{13}C NMR of **5w**, 150 MHz, $CDCl_3$



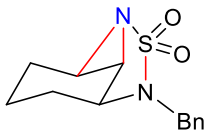

CHCl3
CDCl3
N3
O
S
O
N
Bn
1H NMR of 6w, 600 MHz, CDCl3
f1 (ppm)



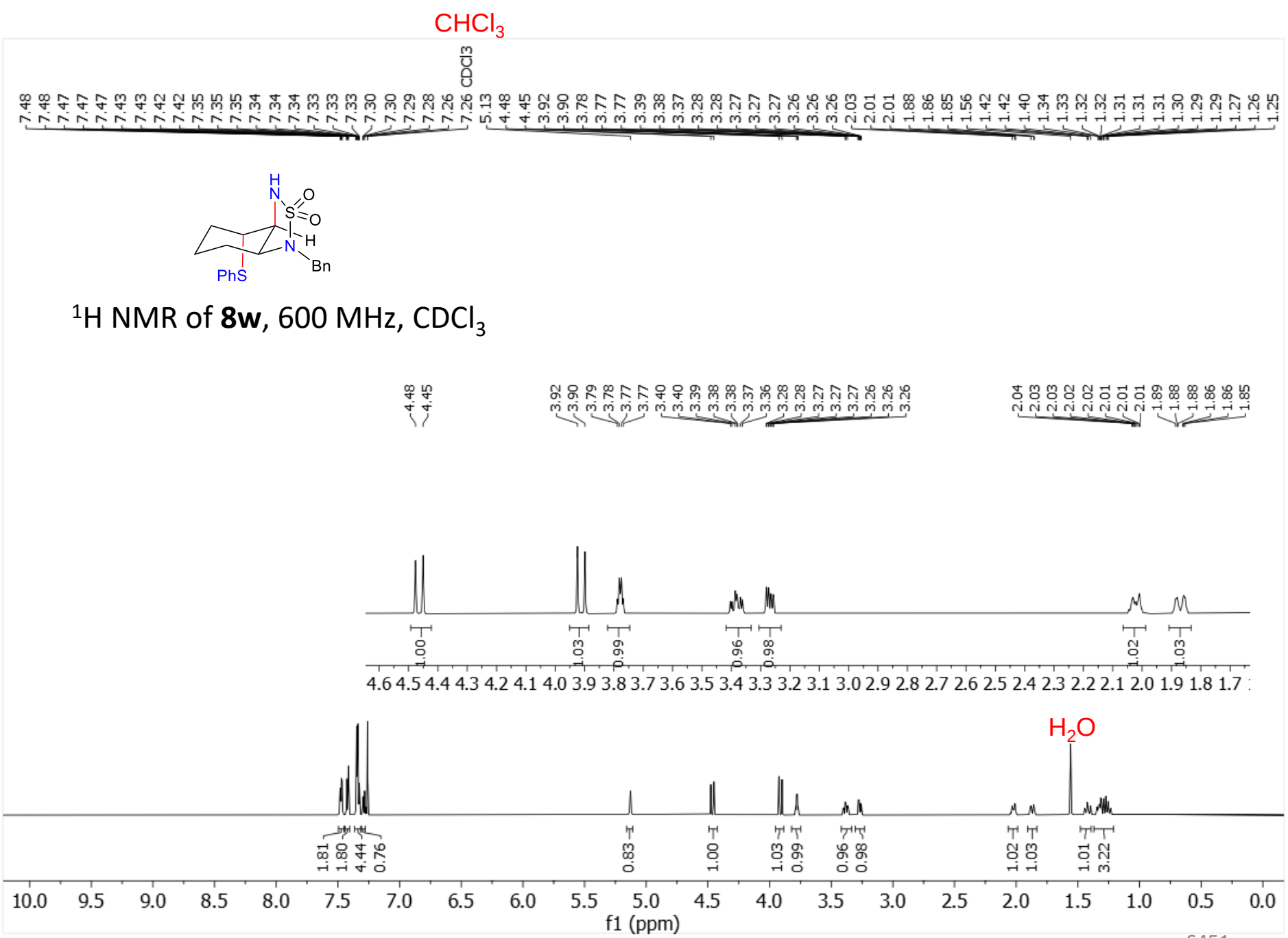
^{13}C NMR of **6w**, 150 MHz, $CDCl_3$



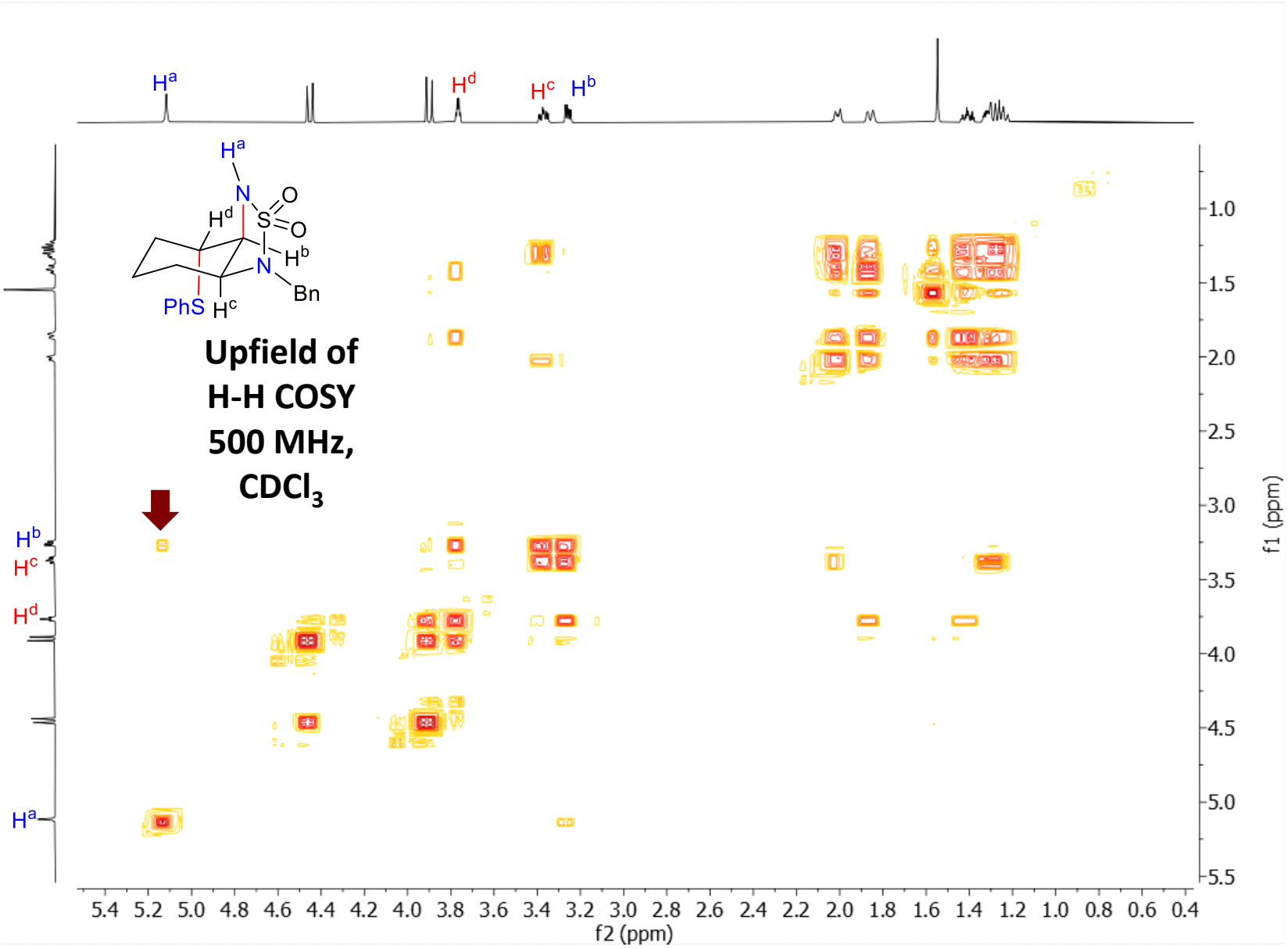
^{1}H NMR of **7w**, 600 MHz, $CDCl_3$

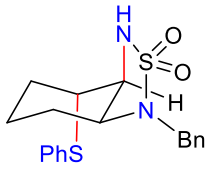


^{13}C NMR of **7w**, 150 MHz, $CDCl_3$

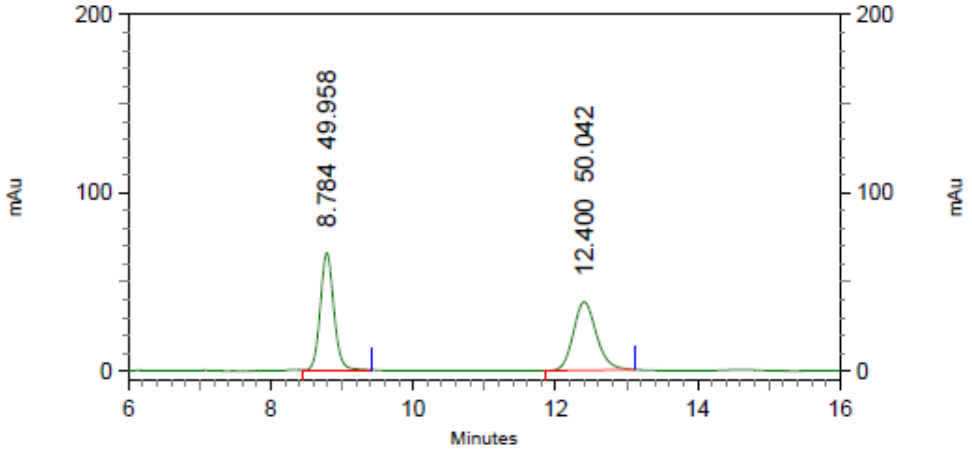


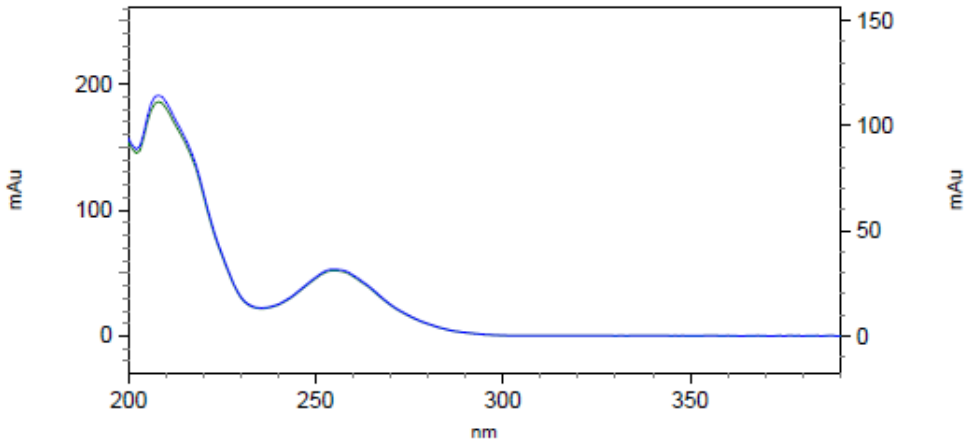
^{1}H NMR of **8w**, 600 MHz, $CDCl_3$

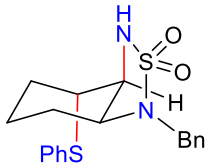

Ha
Hd
Hc
Hb
Ha
N
O
S
O
Hd
Hb
N
Bn
PhS
Hc
Upfield of
H-H COSY
500 MHz,
CDCl3
Hb
Hc
Hd
Ha
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)



^{13}C NMR of **8w**, 125 MHz, $CDCl_3$



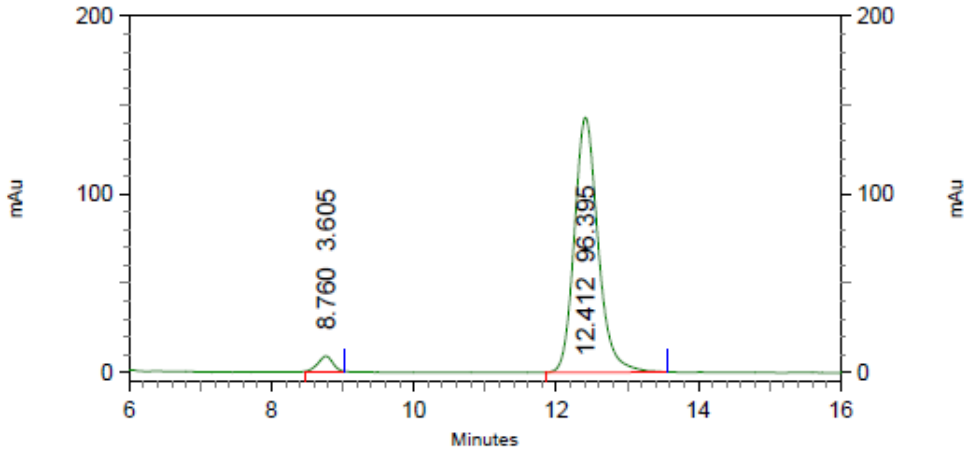


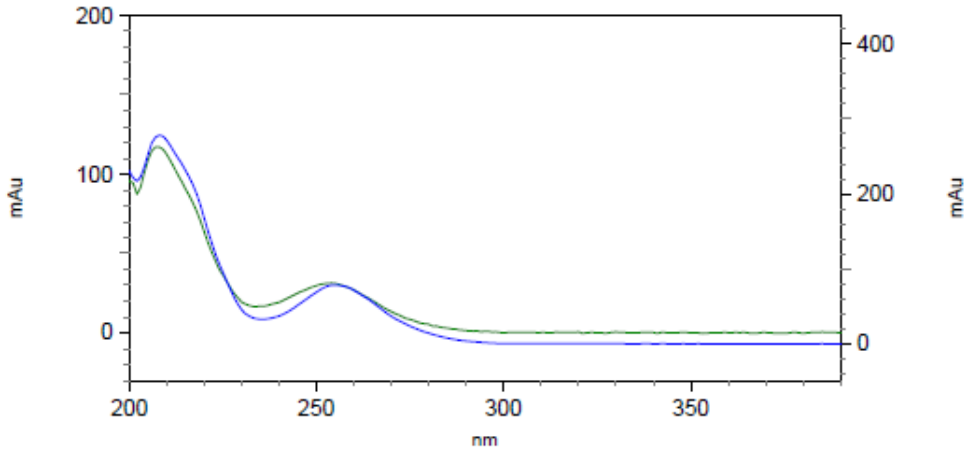


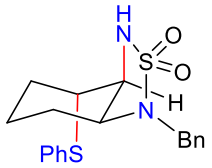
(±)-**8w**

5: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	8.784	49.958	1
	12.400	50.042	2



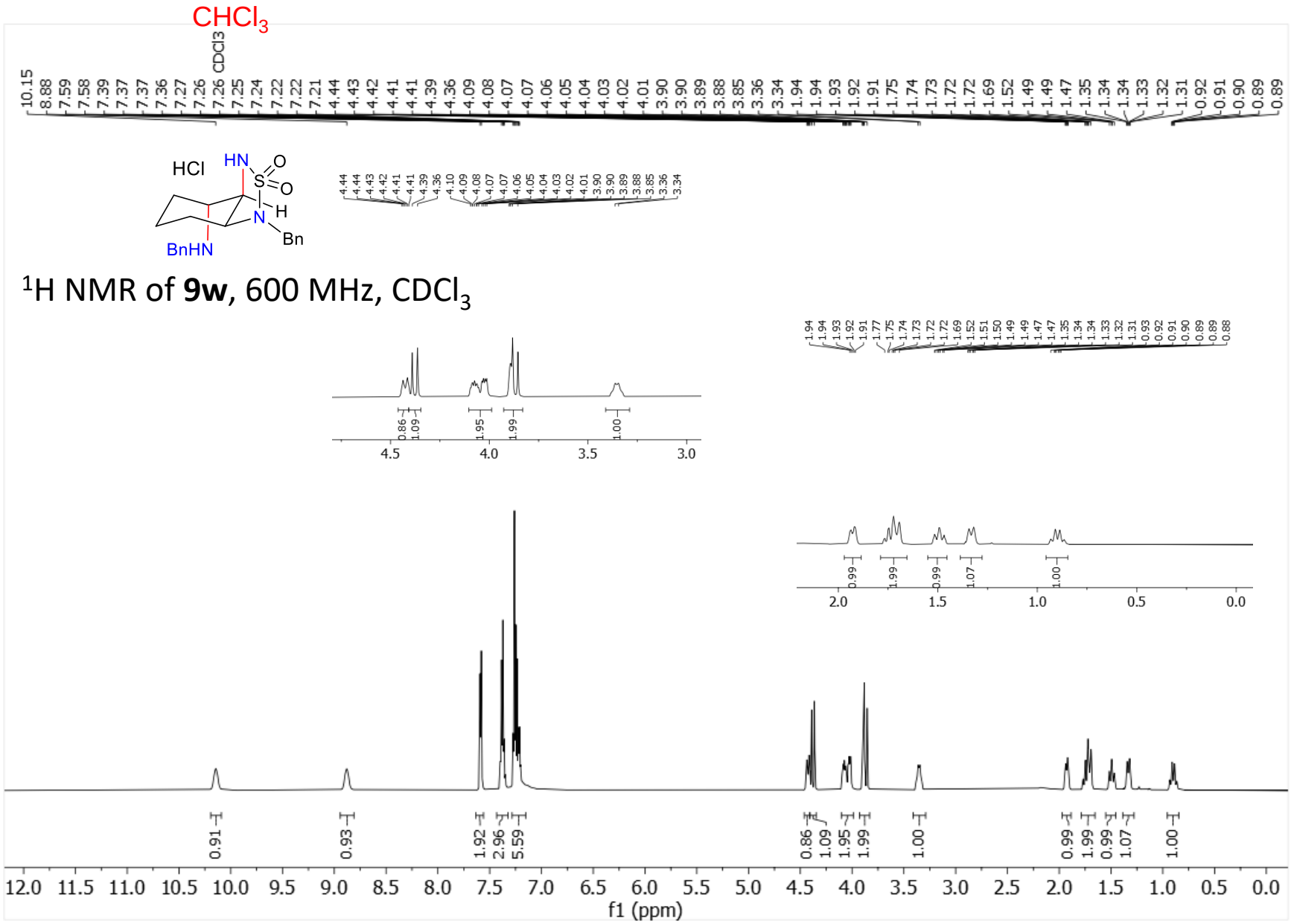




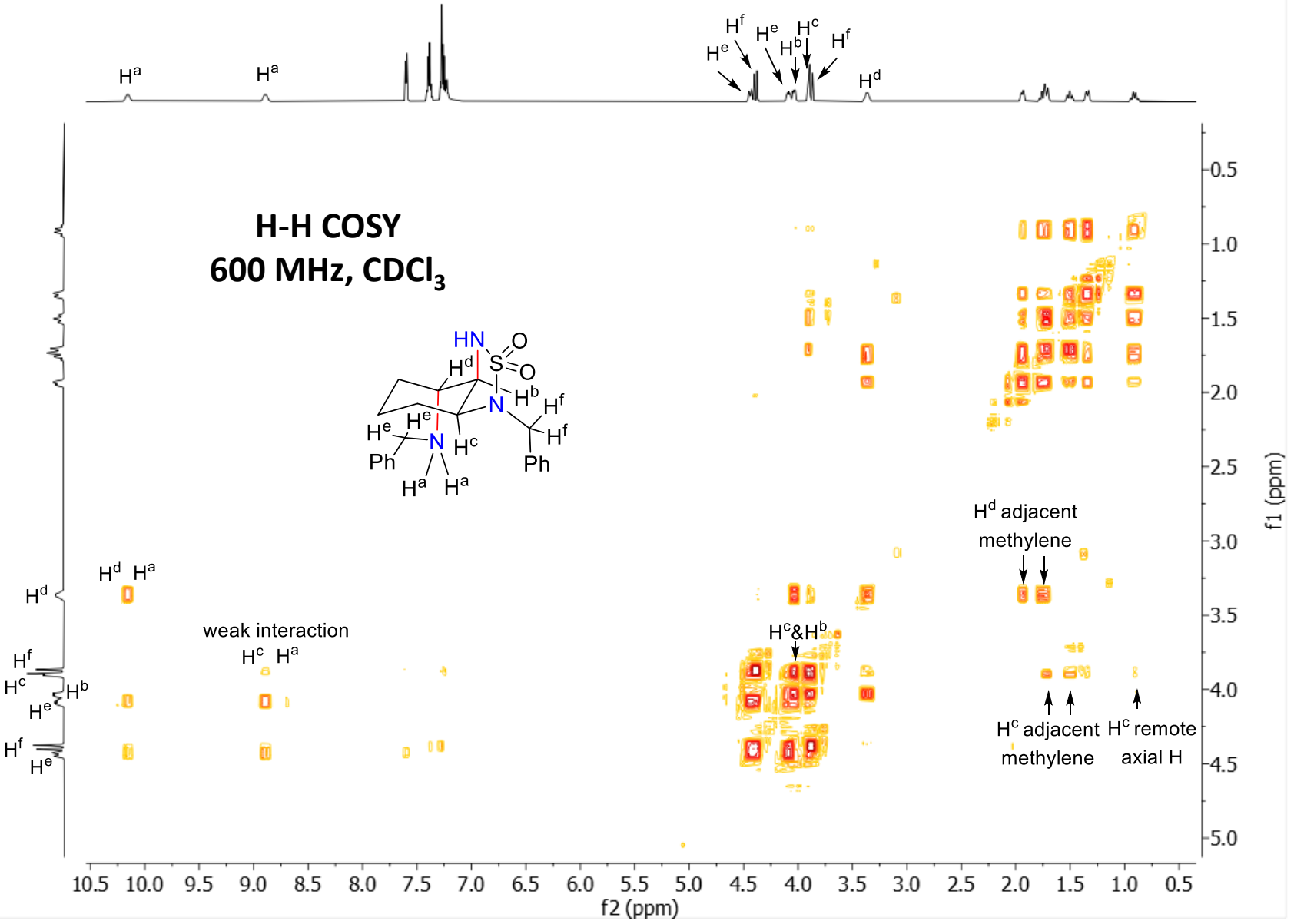
(+)-**8w**

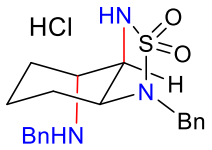
5: 225 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	8.760	3.605	1
	12.412	96.395	2

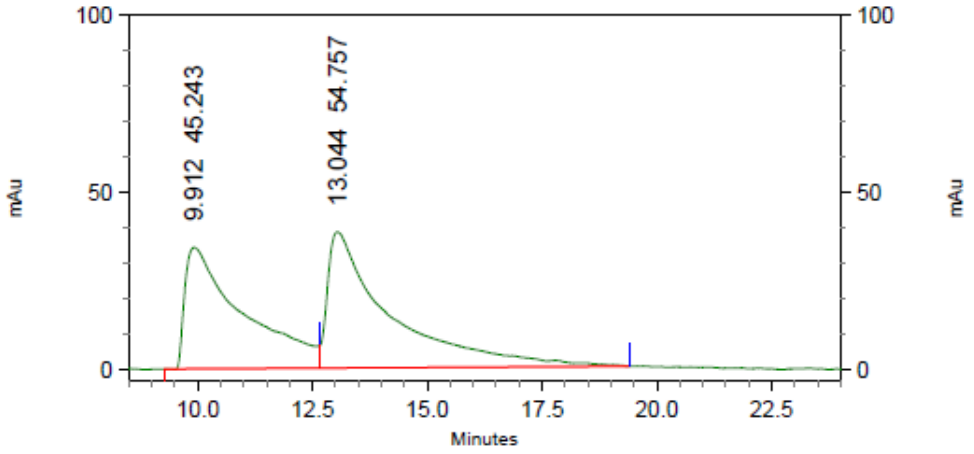


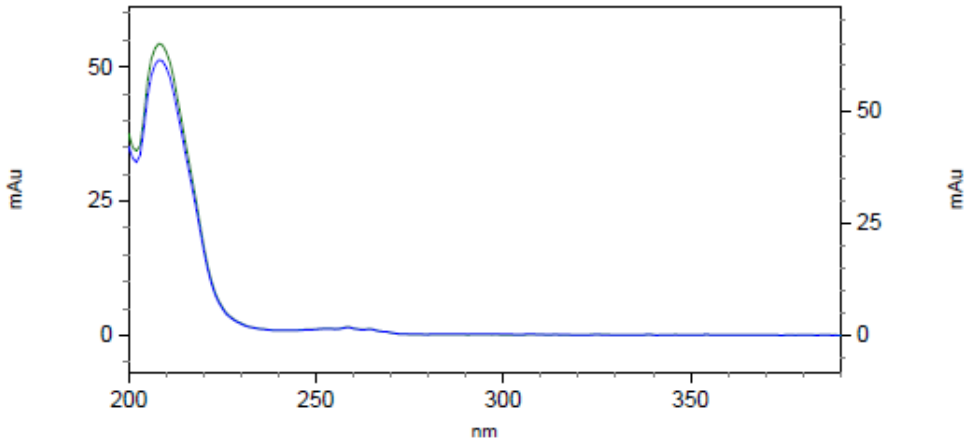
^{1}H NMR of **9w**, 600 MHz, $CDCl_3$

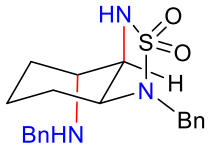

H-H COSY
600 MHz, CDCl3
Ha
Hb
Hc
Hd
He
Hf
HN
O
S
N
Ph
weak interaction
Hc Ha
Hd Ha
Hc&Hb
Hd adjacent methylene
Hc adjacent methylene
Hc remote axial H
f2 (ppm)
f1 (ppm)



^{13}C NMR of **9w**,
150 MHz, $CDCl_3$



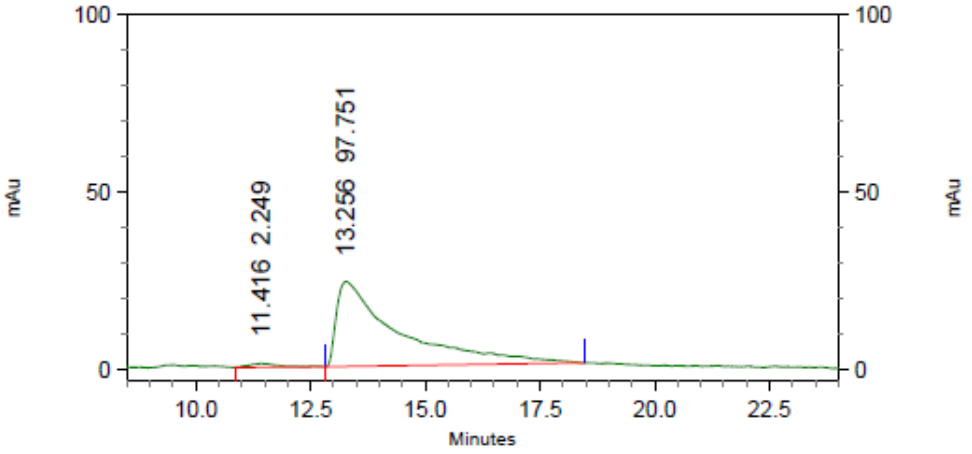


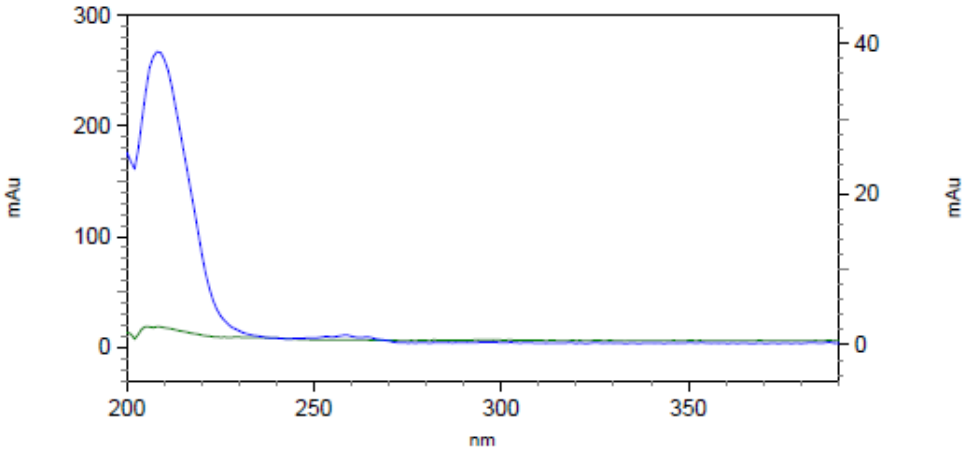


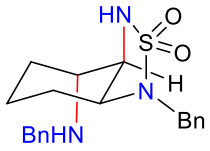
(±)-**9w**

5: 206 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	9.912	45.243	1
	13.044	54.757	2



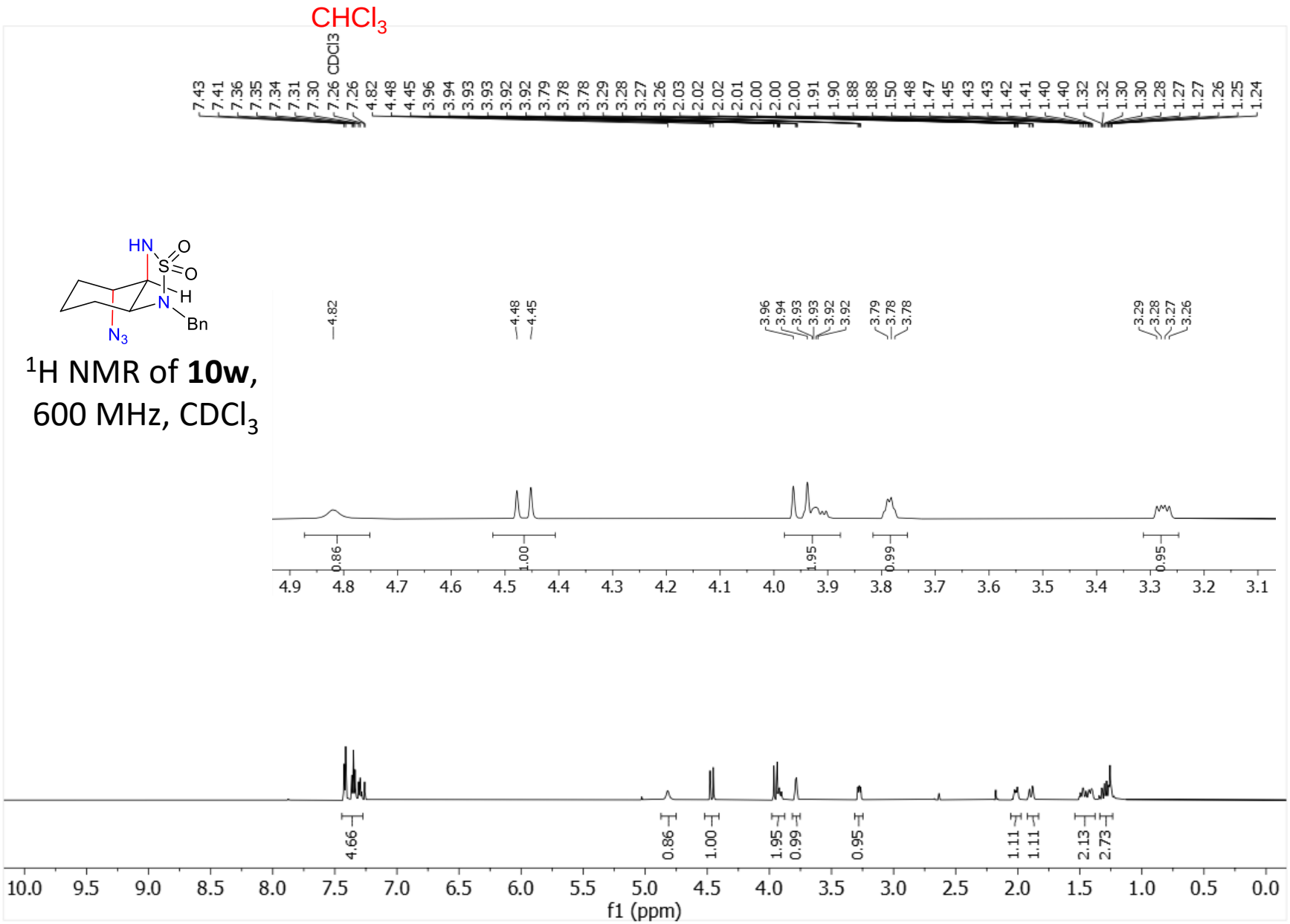




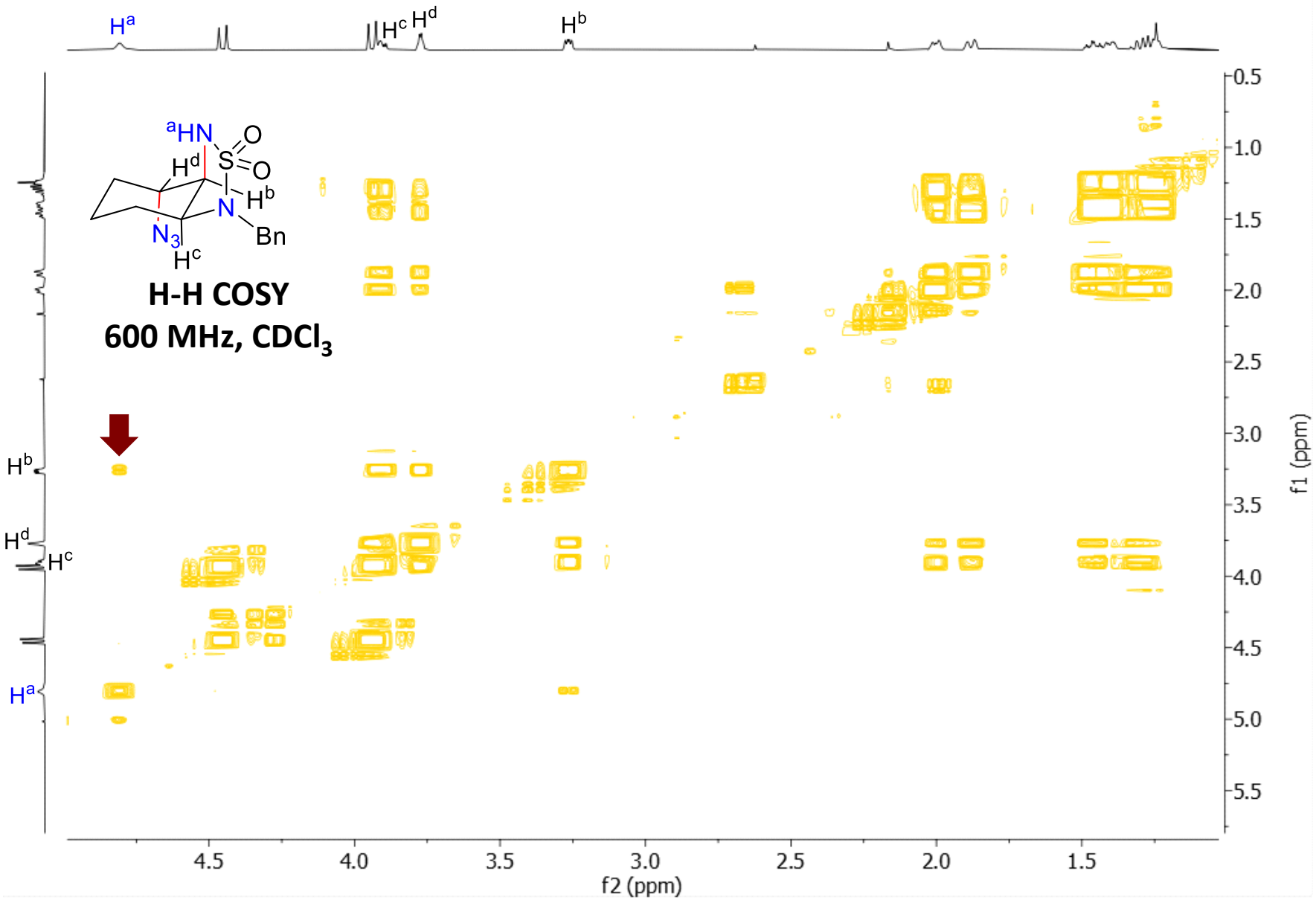
(+)-**9w**

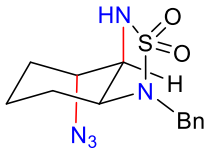
5: 206 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	11.416	2.249	1
	13.256	97.751	2

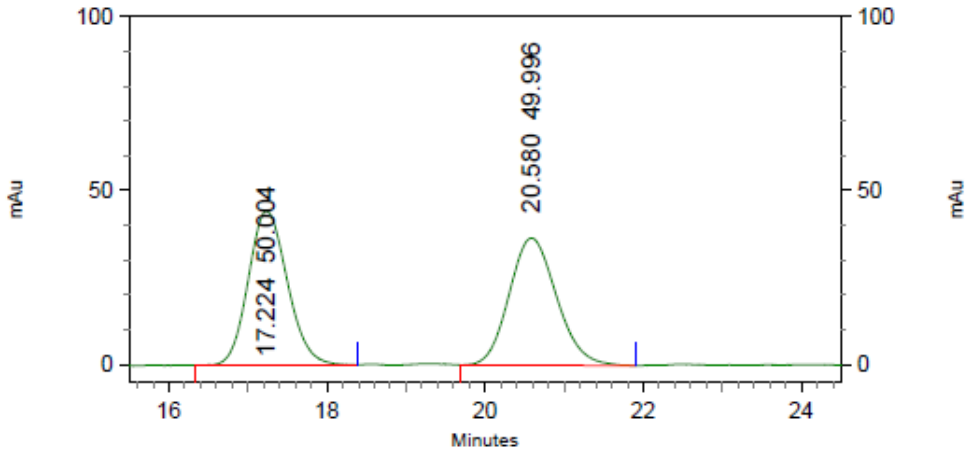


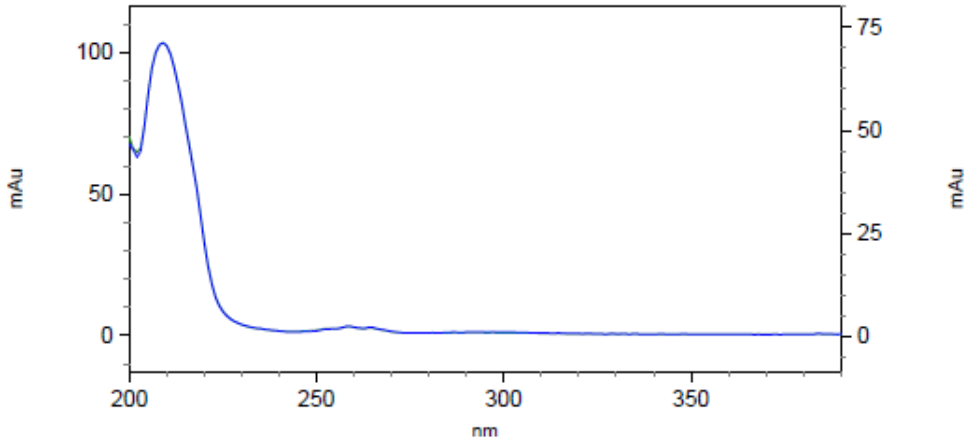
^{1}H NMR of **10w**, 600 MHz, $CDCl_3$

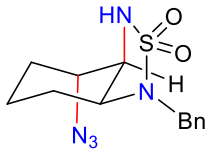

H^a
H^c H^d
H^b
aHN
O
S
O
H^d
H^b
N
N3
Bn
H^c
H-H COSY
600 MHz, CDCl3
H^b
H^d
H^c
H^a
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)



^{13}C NMR of **10w**,
150 MHz, $CDCl_3$



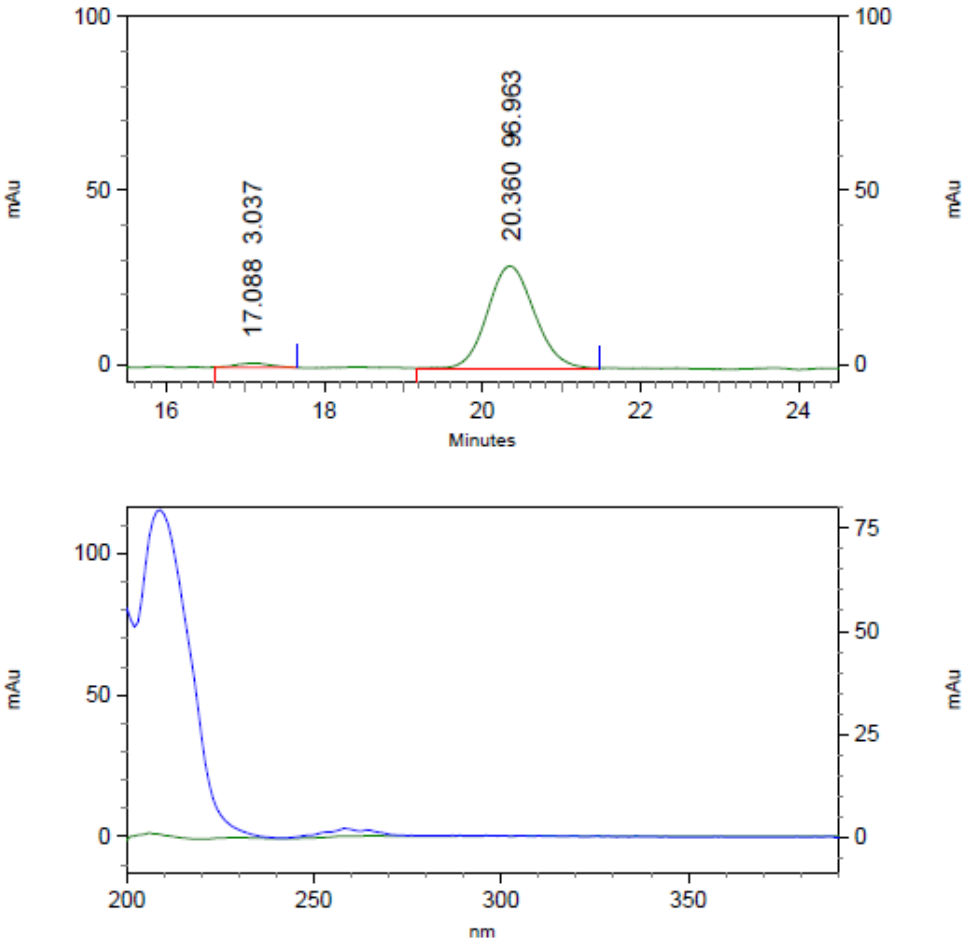


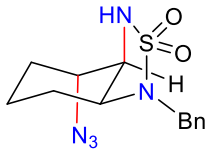


(±)-**10w**

5: 206 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	17.224	50.004	1
	20.580	49.996	2





(+)-**10w**

5: 206 nm, 4 nm
Results

Name	Retention Time	Area Percent	Pk #
	17.088	3.037	1
	20.360	96.963	2