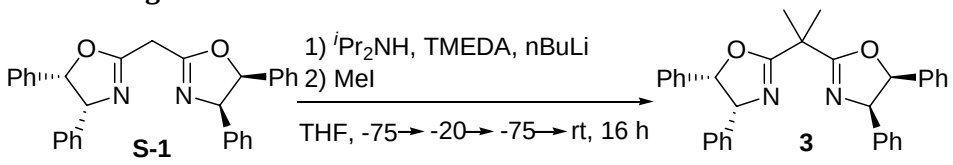
SUPPORTING INFORMATION

General Information:

All reactions were performed under an Ar atmosphere with stirring. The (*R*,*R*)-Ph-box ligand **(2)** and the 2,2'-methylenebis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline **(S-1)** were purchased from Aldrich. All other reagents were purchased from Aldrich or Acros. The MnO_2 used is <5 micron, 85%, from Aldrich. Solvents were purified using a solvent filtration system purchased from Contour Glass Co (Irvine, California). ^{1}H NMR spectra were recorded at 400 or 500 MHz using Varian instruments. ^{13}C NMR data were recorded at 75.5 MHz. Coupling constants (*J*) are in hertz. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad singlet, and dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets. IR spectra were taken neat using a Nicolet-Impact 420 FTIR. Wave numbers in cm^{-1} are reported for characteristic peaks. High resolution mass spectra were obtained at SUNY, Buffalo's mass spec. facility on a ThermoFinnigan MAT XL spectrometer. Optical rotations were obtained using a JASCO P-2000 Polarimeter fitted with a micro cell with a 1 dm path length. Enantiomeric excess was determined by high-performance liquid chromatography (HPLC) using, Chiralpak AD-RH or Regis (*S*,*S*) Whelk-O 1 chiral analytical column (UV detection at 254 nm). Melting points were obtained on an electrothermal melting point apparatus and are reported uncorrected.

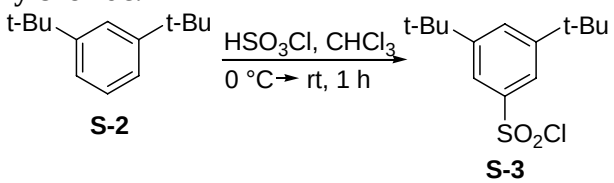
Synthesis of Ligand:



2,2-Bis{2-[4(R),5(S)-diphenyl-1,3-oxazolinyl]}propane (3)[1]

Alkylation of **S-1** was conducted following a procedure used by Denmark for similar substrates.[2] 2,2'-Methylenebis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] (**S-1**) (1.00 g, 2.18 mmol) was dissolved in dry THF (67 mL) under an argon atmosphere. To this solution, diisopropylamine (0.31 mL, 0.22 g, 2.19 mmol) and *N*,*N*,*N*,*N*-tetramethylethylenediamine (0.66 mL, 0.51 g, 4.40 mmol) were added via syringe. The solution was then cooled to -70 °C in a 2-propanol/dry ice bath. Once cooled, n-butyl lithium (2.73 mL, 4.40 mmol, 1.6 M solution in hexanes), was added dropwise. After the addition the reaction mixture was warmed to -20 °C and allowed to stir for 30 min. The mixture was then cooled to -70 °C and iodomethane (0.28 mL, 0.64 g, 4.49 mmol) was added via syringe. The cold bath was removed and the reaction was allowed to proceed for an additional 16 h at rt. The reaction mixture was quenched with sat. NH_4Cl (aq.) (75 mL) and then diluted with water (50 mL). The mixture was extracted with Et_2O (3 x 100 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Flash chromatography of the resulting crude solid on SiO_2 (50% v/v EtOAc in hexanes) afforded the (4*R*,5*S*)-di-Ph-box ligand **3** (1.04 g, 2.14 mmol) in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 10H), 6.96 (s, 10H), 5.97 (d, 10.0 Hz, 2H), 5.59 (d, 10.4 Hz, 2H), 1.92 (s, 6H) ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.4, 137.5, 136.2, 127.9, 127.6, 127.4 (2 signals overlapped), 126.9, 126.6, 86.3, 73.8, 39.6, 24.8; IR (neat): 3029, 2924, 1656, 1496, 1454, 1143, 1114, 975, 697 cm^{-1}; HRMS (ESI) calcd for $[M+H]^+$ $C_{33}H_{31}O_2N_2$ 487.2380, found 487.2374.

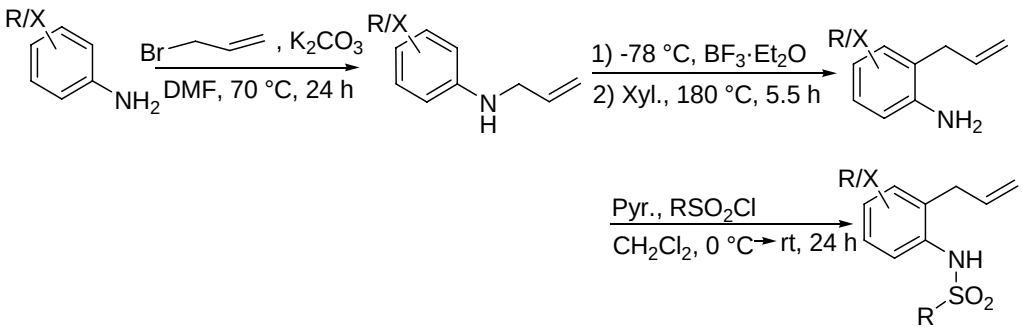
Synthesis of arylsulfonylchoride:



3,5-Di-*tert*-butylbenzenesulfonyl chloride (**S-3**)[3]

The known sulfonyl chloride **S-3** was synthesized as reported by Huntress.[3]
3,5-Di-*tert*-butylbenzene (0.58 mL, 0.50 g, 2.6 mmol) was dissolved in $CHCl_3$ (2.5 mL) at 0 °C with stirring. To the solution chlorosulfonic acid (2.45 mL, 4.29 g, 36.8 mmol) was added cautiously, dropwise, and the solution was allowed to stir for 30 min. The reaction was warmed to rt and allowed to stir for an additional 30 min. The mixture was then poured over crushed ice and the organic layer separated. The aqueous layer was then extracted with $CHCl_3$ (2 x 10 mL), and the organics were pooled. The combined organics were washed with cold water (25 mL), dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. Flash chromatography of the resulting crude solid on SiO_2 (0-20% v/v CH_2Cl_2 in hexanes gradient) afforded 3,5-di-*tert*-butylbenzenesulfonyl chloride (**S-3**) in 53% yield (unoptimized). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 2H), 7.78 (s, 1H), 1.38 (s, 18H).

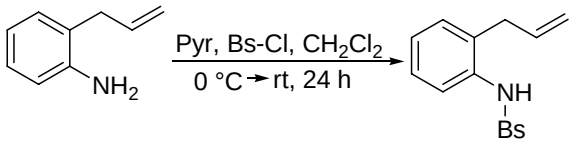
Synthesis of 2-allylaniline substrates:



R/X
H, **1a**
p-Me, **1b**
p-CN, **1c**
p-F, **1d**
P-Cl, **1e**
p-OMe, **1f**
m-OMe, **1g**
o-OMe, **1h**

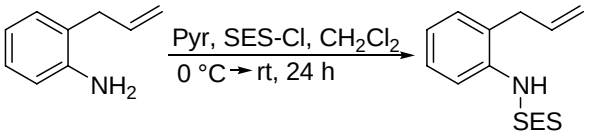
Substrates **1a-h**[4-6] were synthesized analogous to the procedure previously described by Muniz.[7] In this procedure the desired aniline is first alkylated via the S_N2 reaction of the aniline and allyl bromide. The N-allylaniline is then converted to the o-allylaniline via a 3,3'-sigmatropic rearrangement, facilitated by $BF_3{\cdot}Et_2O$, in a sealed vessel at 180°C. Lastly, the o-allylaniline was sulfonylated by treatment with the desired sulfonyl chloride under basic conditions. *N*-(2-Allyl-phenyl)-4-methyl-benzenesulfonamide (**1a**)[5] was obtained from tosylation of 2-allylaniline.[8] *N*-(2-Allyl-4-methyl-phenyl)-4-methyl-benzenesulfonamide (**1b**)[6] was obtained from tosylation of 4-methyl-2-allylaniline. *N*-(2-Allyl-4-cyano-phenyl)-4-methyl-benzenesulfonamide (**1c**)[4] was obtained from tosylation of 4-cyano-2-allylaniline.[7] *N*-(2-Allyl-4-fluoro-phenyl)-4-methyl-benzenesulfonamide (**1d**)[6] was obtained from tosylation of 4-fluoro-2-allylaniline. *N*-(2-Allyl-4-chloro-phenyl)-4-methyl-benzenesulfonamide (**1e**)[6] was obtained by tosylation of 2-allyl-4-chloro-phenylamine.[7] *N*-(2-Allyl-4-methoxy-phenyl)-4-methyl-benzenesulfonamide (**1f**)[6] was obtained from tosylation of 4-methoxy-2-allylaniline. *N*-(2-Allyl-5-methoxy-phenyl)-4-methyl-benzenesulfonamide (**1g**)[4] was obtained from tosylation of 5-methoxy-2-allylaniline.[9] *N*-(2-Allyl-phenyl)-4-nitro-benzenesulfonamide[10] (**1j**) was synthesized as previously reported from the sulfonylation of 2-allylaniline.[6] *N*-(2-Allyl-phenyl)-methyl-sulfonamide (**1k**)[5] was synthesized as previously reported from the sulfonylation of 2-allylaniline.[6]

***N*-(2-Allyl-6-methoxy-phenyl)-4-methyl-benzenesulfonamide** (**1h**)
The sulfonamide **1h** (0.3200 g, 1.01 mmol) was obtained in 76% yield from tosylation of 6-methoxy-2-allylaniline[11] (0.2179 g, 1.34 mmol). mp = 117-119 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 2H), 7.18-7.11 (m, 3H), 6.89 (d, J = 8.0 Hz, 1H), 6.48 (d, J = 8.5 Hz, 1H), 6.20 (s, 1H), 5.98-5.93 (m, 1H), 5.14-5.07 (m, 2H), 3.74 (d, J = 6.5 Hz, 2H), 3.15 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 154.2, 143.1, 140.9, 136.9, 136.7, 128.7, 128.1, 127.5, 122.8, 122.3, 116.1, 108.1, 54.7, 35.8, 21.4; IR (neat): 3274, 3076, 2973, 1640, 1590, 1473, 1333, 1272, 1162, 1080, 911 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{17}H_{20}O_3NS$ 318.1158, found 318.1152.



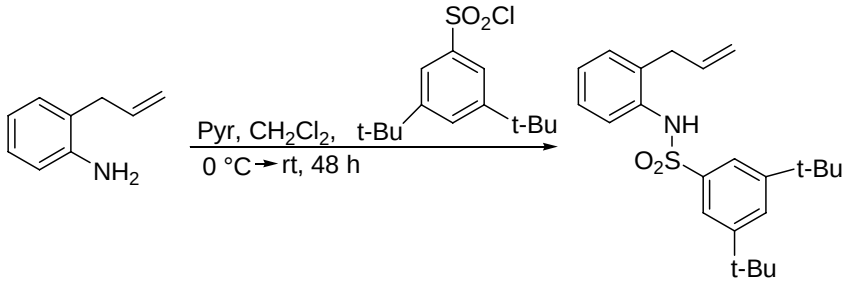
***N*-(2-allylphenyl)benzene sulfonamide (1i)**

The procedure for the synthesis of substrate **1i** was the same as stated above except that the solution was treated with benzenesulfonyl chloride. Sulfonamide **1i** (1.40 g, 5.00 mmol) was obtained from sulfonylation of 2-allylaniline[8] (1.00 g, 7.50 mmol) as a light brown solid in 66% yield (unoptimized). mp = 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 2H), 7.57-7.54 (m, 1H), 7.46-7.41 (m, 3H), 7.24-7.20 (m, 1H), 7.15-7.11 (m, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.53 (bs, 1H), 5.81-5.73 (m, 1H), 5.11 (dd, J = 1.2, 10.0 Hz, 1H), 4.94 (dd, J = 1.6, 17.2 Hz, 1H), 2.98 (d, J = 6.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.7, 135.6, 134.8, 132.9, 132.2, 130.5, 129.0, 127.7, 127.0, 126.5, 124.7, 117.1, 36.1; IR (neat): 3281, 3067, 2913, 1637, 1583, 1491, 1447, 1393, 1330, 1162, 1091, 918 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{15}H_{16}O_2NS$ 274.0896, found 274.0899.



***N*-(2-allylphenyl)-2-(trimethylsilyl)ethane sulfonamide (1l)**

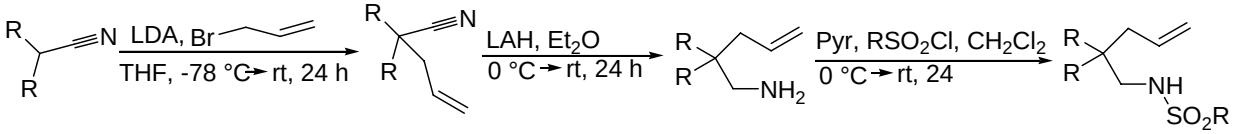
The procedure for the synthesis of substrate **1l** was the same as stated above except that the solution was treated with 2-(trimethylsilyl)ethanesulfonyl chloride. Sulfonamide **1l** (0.30 g, 1.00 mmol) was obtained from sulfonylation of 2-allylaniline[8] (0.25 g, 1.90 mmol) as a dark red oil in 55% yield (unoptimized). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.6 Hz, 1H), 7.26-7.20 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H), 6.28 (bs, 1H), 6.01-5.91 (m, 1H), 5.19 (dd, J = 1.6, 10.0 Hz, 1H), 5.09 (dd, J = 1.6, 17.2 Hz, 1H), 3.44 (d, J = 5.6 Hz, 2H), 3.07-3.03 (m, 2H), 1.07-1.03 (m, 2H), 0.01 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.6, 135.4, 130.8, 127.8, 125.6, 123.5, 122.0, 117.1, 48.7, 36.3, 10.4, -2.1; IR (neat): 3279, 3077, 2954, 1638, 1585, 1494, 1407, 1330, 1252, 1148, 918, 860, 840, 754, 698 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{23}O_2NSSiNa$ 320.1111, found 320.1115.



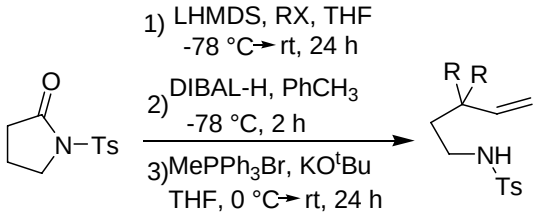
***N*-(2-allylphenyl)-3,5-di-*tert*-butylbenzenesulfonamide (1m)**

The procedure for the synthesis of substrate **1m** was the same as stated above except that the solution was treated with 3,5-di-*tert*-butylbenzenesulfonyl chloride[3] and the reaction time was prolonged to 48 h. Sulfonamide **1m** (0.36 g, 0.93 mmol) was obtained from sulfonylation of 2-allylaniline[8] (0.14 g, 1.04 mmol) as a pale brown solid in 90% yield. mp = 132 – 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.44 (s, 1H), 7.27-7.24 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.41 (bs, 1H), 5.67-5.63 (m, 1H), 5.07 (dd, J = 1.6, 10.0 Hz, 1H), 4.88 (dd, J = 1.2, 17.2 Hz, 1H), 2.74 (d, J = 6.0 Hz, 2H), 1.23 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.1, 138.5, 135.5, 135.2, 132.5, 130.3, 127.8, 126.8, 126.6, 125.7, 121.1, 117.0, 35.9, 35.1, 31.1; IR (neat): 3266, 3076, 2958, 1596, 1483, 1333, 1166 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{23}H_{32}O_2NS$ 386.2148, found 386.2141.

Synthesis of 4-pentenylsulfonamide substrates:



Substrates **7a-d, 11**[12-15] were synthesized according to the procedures previously reported by Bender and Tamaru.[12-15] *N*-(2, 2-Dimethyl-pent-4-enyl)-4-methyl-benzenesulfonamide (**7a**)[12] was obtained from sulfonylation of 2,2-dimethyl-pent-4-enylamine[13] with tosyl chloride. *N*-(2, 2-Dimethyl-pent-4-enyl)-methyl-sulfonamide (**7b**)[16] was obtained from sulfonylation of 2,2-dimethyl-pent-4-enylamine[13] with methane sulfonyl chloride. *N*-(2, 2-Dimethyl-pent-4-enyl)-4-nitro-benzenesulfonamide (**7c**)[17] was obtained from sulfonylation of 2,2-dimethyl-pent-4-enylamine[13] with 4-nitro-benzenesulfonyl chloride. *N*-(2, 2-Diphenyl-pent-4-enyl)-4-methyl-benzenesulfonamide (**7d**)[14] was obtained from sulfonylation of 2,2-diphenyl-pent-4-enylamine[13] with tosyl chloride. *N*-(2,2,4-trimethyl-pent-4-enyl)- 4-Methyl-benzenesulfonamide (**11**)[15] was obtained from sulfonylation of 2,2,4-trimethyl-pent-4-enylamine with tosyl chloride. *N*-(5-allyl-2,2-di-tert-butyl-[1,3,2]dioxasilinan-5-ylmethyl)-4-methyl-benzenesulfonamide (**7g**)[4] was synthesized by the procedure previously reported by Fuller.[4] *N*-(Pent-4-enyl)-4-methyl-benzenesulfonamide (**7e**)[5] was synthesized by the replacement of the alcohol on pent-4-en-1-ol by the sulfonamide via the Mitsonobu reaction as previously reported.[5] *N*-(2-allylbenzyl)-4-methylbenzenesulfonamide (**13**)[5] was obtained from the Stille coupling of *N*-(2-bromobenzyl)-4-methylbenzenesulfonamide with allyltributyltin as previously reported.[5]



R
Me
Allyl

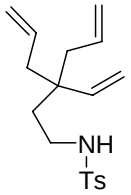
***N*-(3,3-dimethylpent-4-enyl)-4-methylbenzenesulfonamide** (**9**) was synthesized according to the procedure previously reported by Haque.[18,19]

1,1,1,3,3,3-Hexamethyldisilizane (1.86 mL, 1.41 g, 8.80 mmol) was dissolved in dry THF (20 mL) and cooled to -78 °C under an Argon atmosphere. To this solution n-Butyl lithium (3.5 mL, 2.5 M solution in hexanes), was added dropwise and the solution was allowed to stir for 20 minutes. A solution of 1-tosylpyrrolidin-2-one[18] (1.00 g, 4.20 mmol) in dry THF (20 mL) was added dropwise and the solution was allowed to stir for an additional 20 min. Next, iodomethane (0.55 mL, 1.25 g, 8.80 mmol) was added dropwise to the reaction and the resulting mixture was then left to stir and come to rt over 24 h. The reaction was quenched with 40 mL of water and extracted with 4 x 30 mL of EtOAc. The combined organics were washed with brine (2 x 60 mL), dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The resulting crude solid (0.998 g) was used without further purification.

The crude 3,3-dimethyl-1-tosylpyrrolidin-2-one (0.998 g, 3.70 mmol) was dissolved in dry toluene (37 mL) and cooled to -78 °C under an Argon atmosphere. To this mixture DIBAL-H (6.87 mL, 1.2 M solution in toluene, 8.20 mmol), was added dropwise with stirring and the reaction was allowed to continue for 2 h. The reaction was quenched with 60 mL of sat. sodium potassium tartrate (aq.) and then left to stir at rt for 24 h. The organic layer was separated and the aqueous layer was then extracted with EtOAc (3 x 30 mL). The combined organics were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. The resulting crude material (1.01 g) was used without further purification.

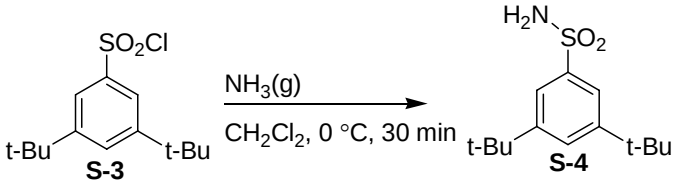
A solution of $MePPh_3Br$ (3.30 g, 9.20 mmol) in dry THF (10 mL) was prepared and cooled to 0 °C under an Argon atmosphere. To this solution KO^tBu (1.05 g, 9.20 mmol) was added in two portions and the mixture was allowed to stir for 10 min. The crude 3,3-dimethyl-1-tosylpyrrolidin-2-ol (1.01 g, 3.70 mmol) dissolved in dry THF (20 mL), was added dropwise and the resulting mixture was then left to stir and come to rt over 24 h. The reaction was quenched with 35 mL of water and the organic layer was

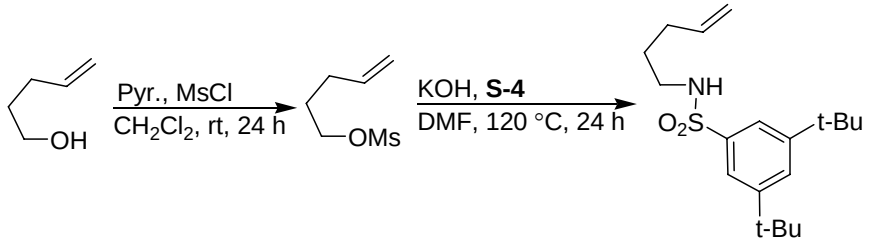
separated. The aqueous layer was then extracted with EtOAc (3 x 30 mL) and the combined organics were dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. Flash chromatography of the resulting crude oil on SiO_2 (0-30% v/v EtOAc in hexanes gradient) afforded the known sulfonamide (0.75 g, 2.80 mmol) (**9**)[19] in 67% yield over 3 steps (unoptimized). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.68 (dd, J = 10.8, 17.2 Hz, 1H), 4.93 (d, J = 11.2 Hz, 1H), 4.87 (d, J = 18.4 Hz, 1H), 4.25 (bs, 1H), 2.94-2.87 (m, 2H), 2.43 (s, 3H), 1.47 (apparent t, J = 8.0 Hz, 2H), 0.94 (s, 6H).



***N*-(3-allyl-3-vinylhex-5-enyl)-4-methylbenzenesulfonamide** (**15**)

The sulfonamide **15** was prepared the same as above except allyl bromide was used in place of methyl iodide for the alkylation. The desired sulfonamide **15** was obtained in 51% yield over 3 steps. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.67-5.58 (m, 3H), 5.10-4.86 (m, 6H), 4.32 (t, J = 6.0 Hz, 1H), 2.93-2.89 (m, 2H), 2,43 (s, 3H), 2.02 (d, J = 7.5 Hz, 4H), 1.47 (dd, J = 8.0, 9.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.3, 143.4, 136.9, 133.7, 129.7, 127.1, 117.9, 113.8, 41.3, 40.7, 38.9, 36.5, 21.5; IR (neat): 3282, 3076, 2977, 2923, 1639, 1599, 1418, 1327, 1160, 1095, 999, 915, 815 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{18}H_{26}O_2NS$ 320.1679, found 320.1680.





3,5-Di-*tert*-butyl-*N*-(pent-4-enyl)benzenesulfonamide (**7f**) was synthesized analogous to the protocol developed by Marcotullio.[20]

Sulfonamide **S-4** was synthesized following the analogous procedure described by Flemer.[21]

To an oven dried flask with a stir bar, under argon, was added 3,5-di-*tert*-butylbenzenesulfonyl chloride (**S-3**) (0.8 g, 2.76 mmol) and methylene chloride (15 mL) and the flask was placed in a 0 °C ice bath. Gaseous ammonia was introduced through a needle inlet such that it bubbled through the reaction mixture at a steady flow. With a steady flow of ammonia the reaction mixture was allowed to stir at 0 °C, under argon for 30 minutes. After the time had elapsed the reaction mixture was diluted with brine and extracted with methylene chloride (3 x 15 mL). The organic extracts were combined, dried over Na_2SO_4, filtered, and the solvent removed *in vacuo* providing the crude sulfonamide **S-4** ~0.8 g, which was used without further purification. mp = 145 – 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 1.6 Hz, 2H), 7.63 (t, J = 1.6 Hz, 1H), 4.88 (bs, 2H), 1.35 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.3, 141.3, 127.1, 120.5, 35.2, 31.3; IR (neat): 3342, 3260, 2960, 1599, 1551, 1475, 1336, 1311, 1248, 1169, 904, 734 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{23}O_2NSNa$ 292.1342 found 292.1341.

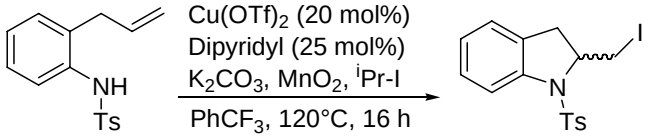
To a stirred solution of pent-4-en-1-ol (0.6 mL 0.5 g, 5.81 mmol) and MsCl (0.54 mL, 0.799 g, 6.98 mmol) in CH_2Cl_2 (30 mL), at 0 °C, Et_3N (2.45 mL, 1.779 g, 17.57 mmol) was added dropwise. After 1 h

the reaction mixture was diluted with H_2O (40 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with H_2O (2 × 50 mL), brine (2 × 50 mL), dried over Na_2SO_4, filtered, and the solvent removed *in vacuo* providing the crude mesylate, 0.96 g, which was used in the next step without further purification.

Potassium carbonate (0.77 g, 5.57 mmol) was dissolved in DMF (9 mL) at 120 °C and 3,5-di-*tert*-butylbenzenesulfonamide **S-4** (0.75 g, 2.78 mmol) was added to the resulting solution. After 30 min a solution of the mesylate (0.304 g, 1.85 mmol) in DMF (1 mL) was added. After 1 h the reaction mixture was cooled, diluted with H_2O (10 mL) and extracted with Et_2O (4 × 5 mL). The combined organic layers were washed with H_2O (3 × 5 mL), brine (3 × 5 mL), dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo.* The crude residue was further purified via flash chromatography on SiO_2 (0-40% Et_2O in hexanes eluent) providing pure 3,5-di-*tert*-butyl-*N*-(pent-4-enyl)benzenesulfonamide **(7f)**, (0.46 g, 1.36 mmol) in 70% yield over two steps as a viscous clear oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 2.0 Hz, 2H), 7.62 (t, J = 2.0 Hz, 1H), 5.73-5.63 (m, 1H), 4.97-4.92 (m, 2H), 4.40 (t, J = 6.0 Hz, 1H), 2.99 (q, J = 6.8 Hz, 2H), 2.04 (qd, J = 1.2, 7.2 Hz, 2H), 1.60-1.52 (m, 2H), 1.35 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.1, 139.2, 137.2, 126.7, 121.1, 115.5, 42.6, 35.1, 31.2, 30.6, 28.6; IR (neat): 3279, 3020, 2964, 1600, 1439, 1328, 1311, 1248, 1163, 883, 703 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{19}H_{31}O_2NSNa$ 360.1968, found 360.1970.

Catalytic Methods for Aniline Substrates:

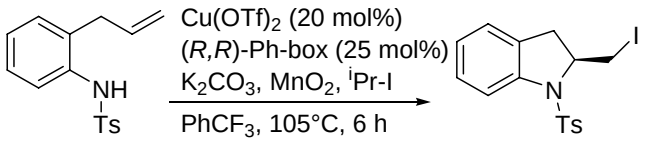
Representative procedure for the catalytic racemic aminohalogenation of alkenes:



(±)-2-(Iodomethyl)-1-tosylindoline (4a)

Copper (II) triflate (13.0 mg, 0.036 mmol) was added to an oven dried pressure tube (10 mL) equipped with a stir bar, in a glovebox. Upon removal from the glove box the pressure tube was flushed with argon any time it was opened. To the tube, dipyridyl (7.10 mg, 0.045 mmol) was added and the mixture was dissolved in $PhCF_3$ (1.80 mL), the tube was then sealed and heated to 60 °C for 2 h in an oil bath with stirring. Upon cooling to rt, the following reagents were then added sequentially: sulfonamide (**1a**) (51.2 mg, 0.178 mmol), MnO_2 (46.9 mg, 0.539 mmol), K_2CO_3 (24.9 mg, 0.180 mmol), ^{i}Pr-I (0.108 mL, 183.6 mg, 1.08 mmol) and ~36 mg of flame activated 4Å molecular sieves. The tube was then flushed with argon, sealed, and sonicated to ensure that all reagents were in solution. The mixture was stirred at 120 °C (oil bath) for 16 h. The room temperature reaction mixture was then filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient) afforded **4a** in good yield. Further purification using HPLC 10% EtOAc in hexanes, isocratic, was used prior to chiral HPLC analysis.

Representative procedure for the catalytic enantioselective aminohalogenation of aniline derived alkenes:

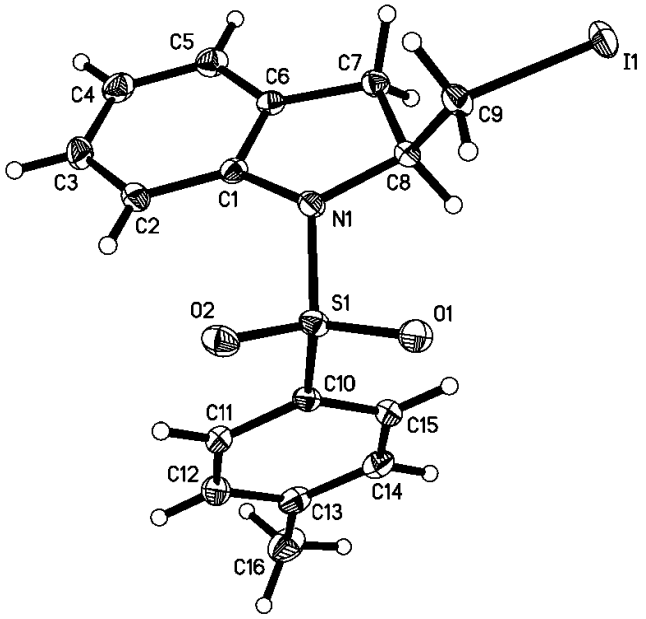


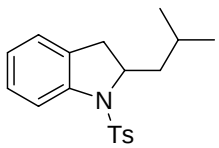
(*S*)-2-(Iodomethyl)-1-tosylindoline (**4a**)

Copper (II) triflate (12.5 mg, 0.035 mmol) was added to an oven dried pressure tube (10 mL) equipped with a stir bar, in a glovebox. Upon removal from the glove box the pressure tube was flushed with argon any time it was opened. To the tube, (*R,R*)-Ph-box (**2**) (14.5 mg, 0.045 mmol) in $PhCF_3$ (0.54 mL, 0.08 M) was added and the mixture was dissolved in additional $PhCF_3$ (1.21 mL). The tube was sealed and the mixture was stirred at 60 °C (oil bath) for 2 h. Upon cooling to rt, the following reagents were added

sequentially: N-(2-allylphenyl)-4-methyl-benzenesulfonamide[5] (**1a**) (50.7 mg, 0.176 mmol), MnO_2 (47.7 mg, 0.549 mmol), K_2CO_3 (24.5 mg, 0.177 mmol), ^{i}Pr-I (0.104 mL, 177.5 mg, 1.04 mmol) and ~36 mg of flame activated 4Å molecular sieves. The tube was then flushed with argon, sealed, and the mixture was sonicated to ensure that all reagents were in solution. The reaction mixture was then stirred at 105 °C (oil bath) for 6 h. Upon cooling to rt, the mixture was filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent was removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient) afforded indoline **4a** (62.7 mg, 0.152 mmol) as opaque crystals in 86% yield. Further purification by HPLC 10% EtOAc in hexanes, isocratic, was used prior to chiral HPLC analysis. mp = 123-125 °C; $[\alpha]_D^{24}$ = 49.2 ° (c = 0.5, $CHCl_3$), ee = 89%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 14.92 min, t(minor) = 18.83 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.25-7.18 (m, 3H), 7.06-7.03 (m,2H), 4.37-4.35 (m, 1H), 3.67 (dd, J = 3.6, 9.6 Hz, 1H), 3.27 (apparent t, J = 10.0 Hz, 1H), 2.95-2.84 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.2, 141.2, 134.5, 130.4, 129.7, 128.0, 127.0, 125.2, 124.9, 116.8, 62.5, 34.8, 21.5, 11.4; IR (neat): 3032, 2916, 1597, 1479, 1355, 1167, 1013, 961, 757, 666 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{16}H_{16}O_2NIS$ 412.9941, found 412.9939.

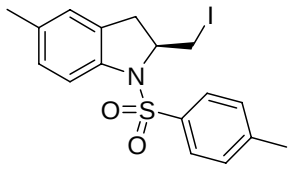
Assignment of Absolute Stereochemistry of Indoline Products:
The crystal structure of indoline **4a** (CCDC 858586) showing the S stereochemistry was obtained by William W. Brennessel at the University of Rochester. The absolute configuration of all other indoline products was assigned by analogy to this structure.





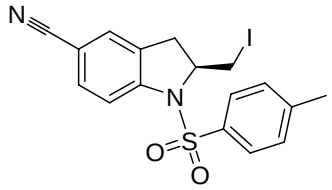
2-Isobutyl-1-tosylindoline (**6**)
In a duplicate run, Indoline **6** (4.2 mg, 0.013 mmol) was obtained as a clear oil in 7% yield, as a minor product, from the corresponding sulfonamide **1a**[5] (51.9 mg, 0.181 mmol): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.23-7.19 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 5.2 Hz, 1H), 4.30-4.25 (m, 1H), 2.67 (dd, J = 9.6, 16.4 Hz, 1H), 2.40 (dd, J = 1.6, 15.6 Hz, 1H), 2.35 (s, 3H), 1.89-1.83 (m, 1H), 1.76-1.69 (m, 1H), 1.39-1.32 (m, 1H), 0.98 (dd, J = 6.4, 20.8 Hz, 6H); ^{13}C NMR

(75.5 MHz, $CDCl_3$): δ 143.6, 141.3, 135.4, 132.9, 129.4, 127.6, 127.0, 125.1, 124.9, 118.5, 61.2, 45.7, 34.5, 24.4, 22.8, 22.4, 21.5; IR (neat): 3031, 2955, 1677, 1592, 1479, 1456, 1353, 1167, 1091, 758 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{19}H_{23}O_2NSNa$ 352.1342, found 352.1343.



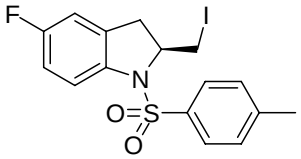
(*S*)-2-(Iodomethyl)-5-methyl-1-tosylindoline (**4b**)

Indoline **4b** (62.9 mg, 0.147 mmol) was obtained as a white solid in an 85% yield from the corresponding sulfonamide[6] **1b** (52.2 mg, 0.173 mmol): mp = 74-75°C; $[\alpha]_D^{24}$ = 65.8 ° (c = 0.5, $CHCl_3$), ee = 90%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 12.96 min, t(minor) = 16.02 min]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.86 (s, 1H), 4.34-4.31 (m,1H), 3.65 (dd, J = 4.0, 10.0 Hz, 1H), 3.25 (apparent t, J = 10.0 Hz, 1H), 2.90-2.78 (m, 2H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.1, 138.8, 134.7, 134.5, 130.5, 129.7, 128.6, 127.1, 125.8, 116.7, 62.7, 34.7, 21.5, 21.0, 11.4; IR (neat): 3029, 2919, 1597, 1486, 1354, 1166, 1090, 1024, 963, 814, 754, 666, 608 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{17}H_{19}O_2NIS$ 428.0176, found 428.0189.



(*S*)-2-(Iodomethyl)-1-tosylindoline-5-carbonitrile (**4c**)

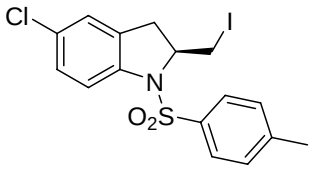
Indoline **4c** (63.7 mg, 0.145 mmol) was obtained as white crystals in 85% yield from *N*-(2-Allyl-4-cyano-phenyl)-4-methyl-benzenesulfonamide (**1c**)[4](53.4 mg, 0.171 mmol). mp = 151-153°C; $[\alpha]_D^{24}$ = 107.1 ° (c = 0.5, $CHCl_3$), ee = 84%, determined by HPLC analysis [Chiralpak AD-RH, 4% IPA/hexane, 1 mL/min, λ = 254 nm, t(minor) = 26.83 min, t(major) = 35.90 min]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 4.41-4.37 (m, 1H), 3.67 (dd, J = 3.2, 10.0 Hz, 1H), 3.34 (apparent t, J = 10.0 Hz, 1H), 3.06 (dd, J = 9.6, 12.8 Hz, 1H),2.91 (dd, J = 3.2 Hz, 12.0 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 145.3, 145.1, 134.3, 132.9, 131.2, 130.1, 128.9, 126.9, 118.7, 116.2, 107.8, 62.5, 34.7, 21.6, 11.0; IR (neat): 3022, 2923, 2226, 1607, 1482, 1359, 1167, 1090, 963, 814, 752, 666 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{17}H_{15}O_2NIS$ 437.9893, found 437.9887.



(*S*)-5-Fluoro-2-(iodomethyl)-1-tosylindoline (**4d**)

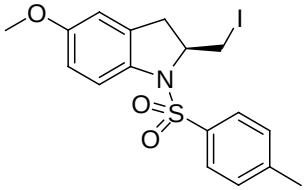
Indoline **4d** (64.3 mg, 0.149 mmol) was obtained as a white solid in an 80% yield from the corresponding sulfonamide[6] **1d** (57.6 mg, 0.189 mmol). mp = 118-120°C; $[\alpha]_D^{24}$ = 43.9° (c = 0.5, $CHCl_3$), ee = 89%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 14.21 min, t(minor) = 16.80 min]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 8.8 Hz, 1H), 6.77(d, J = 8.0 Hz, 1H), 4.38-4.32 (m, 1H), 3.63 (dd, J = 3.2, 10.0 Hz, 1H), 3.26 (t, J = 10.0 Hz, 1H), 2.86-2.80 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.4 (d, J = 243.1 Hz), 144.4, 137.2, 134.1, 132.7 (d, J = 9.2 Hz), 129.8, 127.1, 118.1 (d,

J = 8.1 Hz), 114.7 (d, J = 23 Hz), 112.3 (d, J = 24 Hz), 62.9, 34.8, 21.5, 10.9; IR (neat): 3031, 2921, 1598, 1481, 1356, 1166, 1090, 934, 814, 755, 667 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{16}H_{15}O_2NISF$ 430.9847, found 430.9837.



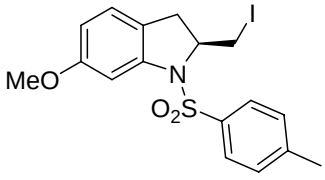
(*S*)-5-Chloro-2-(iodomethyl)-1-tosylindoline (**4e**)

Indoline **4e** (59.9 mg, 0.134 mmol) was obtained as a white solid in 83% yield from *N*-(2-Allyl-4-chloro-phenyl)-4-methyl-benzenesulfonamide (**1e**)[6] (57.4 mg, 0.178 mmol). mp = 108-110°C; $[\alpha]_D^{24}$ = 52.9° (c = 0.5, $CHCl_3$), ee =87%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 12.63 min, t(minor) = 14.73 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 3H), 7.23-7.18 (m, 3H), 7.04 (s, 1H), 4.37-4.31 (m, 1H), 3.64 (dd, J = 3.6, 10.0 Hz, 1H), 3.28 (apparent t, J = 9.6 Hz, 1H), 2.95-2.80 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.5, 139.9, 134.1, 132.3, 130.1, 129.9, 128.1, 127.0, 125.4, 117.7, 62.7, 34.7, 21.5, 11.0; IR (neat): 3029, 2924, 1598, 1473, 1357, 1167, 1023, 814, 666 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{15}O_2NClINaS$ 469.9449, found 469.9429.



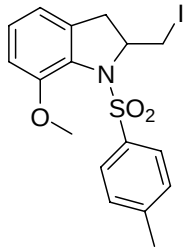
(*S*)-2-(Iodomethyl)-5-methoxy-1-tosylindoline (**4f**)

Indoline **4f** (55.9 mg, 0.126 mmol) was obtained as a white solid in a 72% yield from the corresponding sulfonamide[6] **1f** (55.7 mg, 0.175 mmol). mp = 137-139°C; $[\alpha]_D^{24}$ = 91.6 ° (c = 0.5, $CHCl_3$), ee = 87%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 22.87 min, t(minor) = 28.69 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.76 (dd, J = 2.4, 8.8 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 4.33-4.31 (m, 1H), 3.76 (s, 3H), 3.62 (dd, J = 4.0, 10.0 Hz, 1H), 3.23 (apparent t, J = 9.6 Hz, 1H), 2.81-2.77 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 157.6, 144.1, 134.5, 134.2, 132.4, 129.7, 127.1, 118.2, 113.2, 110.9, 62.9, 55.6, 34.9, 21.5, 11.1; IR (neat): 3027, 2955, 1598, 1487, 1353, 1263, 1165, 1090, 1032, 813, 751, 667 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{17}H_{19}O_3NIS$ 444.0125, found 444.0124.



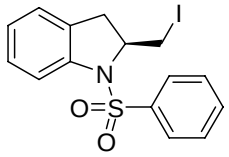
(*S*)-2-(Iodomethyl)-6-methoxy-1-tosylindoline (**4g**)

Indoline **4g** (47.9 mg, 0.108 mmol) was obtained as a clear oil in a 71% yield from the corresponding sulfonamide[4] **1g** (48.5 mg, 0.153 mmol). $[\alpha]_D^{24}$ = 80.3 ° (c = 0.64, $CHCl_3$), ee = 88%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 14.01 min, t(minor) = 18.02 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.58 (dd, J = 2.4, 8.4 Hz, 1H), 4.38-4.30 (m, 1H), 3.82 (s, 3H), 3.64 (dd, J = 3.2, 10.0 Hz, 1H), 3.26 (apparent t, J = 10.0 Hz, 1H), 2.90-2.73 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.9, 144.3, 142.4, 134.6, 129.8, 127.1, 125.5, 122.1, 111.1, 102.7, 63.4, 55.7, 34.1, 21.6, 11.4; IR (neat): 3050, 2922, 1615, 1497, 1354, 1285, 1165, 1111, 1032, 812 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{17}H_{18}O_3NISNa$ 465.9944, found 465.9955.



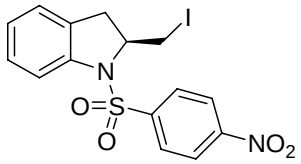
2-(Iodomethyl)-7-methoxy-1-tosylindoline (**4h**)

Indoline **4h** (55.8 mg, 0.126 mmol) was obtained as opaque crystals in 80% yield from the corresponding sulfonamide **1h** (49.9 mg, 0.157 mmol). mp = 123-124°C; $[\alpha]_D^{24}$ = -4.7° (c = 0.67, $CHCl_3$), ee = 15%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 30.64 min, t(minor) = 36.97 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 6.4 Hz, 2H), 7.22 (d, J = 6.0 Hz, 2H), 7.08 (t, J = 6.4 Hz, 1H), 6.81 (d, J = 6.4 Hz, 1H), 6.72 (d, J = 6.0 Hz, 1H), 4.80-4.76 (m,1H), 3.78 (s, 3H), 3.45 (dd, J = 3.6, 8.0 Hz, 1H), 3.11 (apparent t, J = 8.0 Hz, 1H), 2.73-2.71 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 151.9, 143.7, 136.2, 135.8, 129.9, 129.3, 127.44, 127.42, 117.6, 112.3, 64.3, 56.0, 34.6, 21.6, 9.6; IR (neat): 3027, 2925, 1595, 1488, 1333, 1277, 1158, 1088, 935, 813, 762, 675 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{17}H_{19}O_3NIS$ 444.0125, found 444.0122.



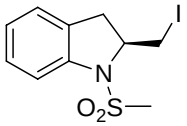
(*S*)-2-(Iodomethyl)-1-(phenylsulfonyl)indoline (**4i**)

Indoline **4i** (53.2 mg, 0.133 mmol) was obtained as a white solid in a 77% yield from N-(2-allylphenyl)benzene sulfonamide (**1i**) (47.2 mg, 0.173 mmol). mp = 82-84°C; $[\alpha]_D^{24}$ = 37.5° (c = 0.5, $CHCl_3$), ee = 88%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 12.61 min, t(minor) = 14.74 min]; mp = 82-84°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.65 (m, 3H), 7.56-7.52 (m, 1H), 7.42-7.39 (m, 2H), 7.26-7.21 (m, 1H), 7.10-7.05 (m, 2H), 4.40-4.34 (m, 1H), 3.66 (dd, J = 3.2, 10.0 Hz, 1H), 3.26 (apparent t, J = 10.0 Hz, 1H), 2.92-2.82 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.0, 137.4, 133.3, 130.4, 129.1, 128.1, 127.0, 125.3, 125.0, 116.8, 62.6, 34.8, 11.2; IR (neat): 3067, 2921, 1596, 1479, 1357, 1169, 1091, 1016, 962, 756, 718, 688 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{15}H_{14}O_2NIS$ 398.9784, found 398.9781.



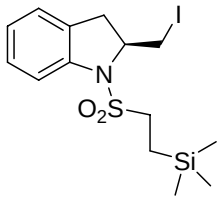
(*S*)-2-(Iodomethyl)-1-((4-nitrophenyl)sulfonyl)indoline (**4j**)

Indoline **4j** (57.2 mg, 0.129 mmol) was obtained as pale yellow crystals in 72% yield from the corresponding sulfonamide[10] **1j** (57.0 mg, 0.179 mmol). For this reaction the (4*R*,5*S*)-di-Ph-box ligand was used and the catalyst/ligand loadings were doubled to 40 and 50 mol%, respectively. mp = 135-136°C; $[\alpha]_D^{24}$ = 87.8 ° (c = 0.5, $CHCl_3$), ee = 80%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 22.24 min, t(minor) = 25.38 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 9.6 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.27 (m, 1H), 7.10 (m, 2H), 4.41-4.35 (m,1H), 3.65 (dd, J = 3.6, 10.0 Hz, 1H), 3.29 (apparent t, J = 10.0 Hz, 1H), 3.00-2.85 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 150.5, 143.0, 140.1, 130.3, 128.4, 128.2, 125.7, 124.4, 116.6, 62.9, 34.8, 10.5; IR (neat): 3104, 2921, 1605, 1530, 1479, 1349, 1171, 1010, 855, 757, 620 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{15}H_{13}O_4N_2IS$ 443.9635, found 443.9641.



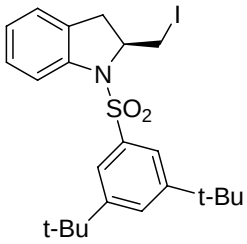
(*S*)-2-(Iodomethyl)-1-(methylsulfonyl)indoline (**4k**)

Indoline **4k** (54.6 mg, 0.162 mmol) was obtained as white crystals in 85% yield from *N*-(2-Allyl-phenyl)-methyl-sulfonamide (**1k**)[5] (38.0 mg, 0.180 mmol). For this reaction the (4*R*,5*S*)-di-Ph-box ligand (**3**) was used. mp = 163-165°C; $[\alpha]_D^{24}$ =-44.1° (c = 0.5, $CHCl_3$), ee = 81%, determined by HPLC analysis [Chiralpak AD-RH, 2% water/MeOH, 1 mL/min, λ = 254 nm, t(major) = 3.56 min, t(minor) = 5.12 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 1H), 7.25-7.21 (m, 2H), 7.09 (t, J = 7.2 Hz, 2H), 4.43-4.46 (m, 1H), 3.63 (dd, J = 3.2, 9.6 Hz, 1H), 3.48 (dd, J = 10.0, 12.0 Hz, 1H), 3.31 (apparent t, J = 9.6 Hz, 1H), 3.05 (dd, J = 4.0, 16.8 Hz, 1H), 2.86 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.1, 129.5, 128.3, 125.5, 124.7, 115.1, 62.6, 36.3, 35.5, 11.6; IR (neat): 3009, 2924, 1479, 1344, 1157, 1018, 972, 770, 752 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{10}H_{12}O_2NIS$ 336.9628, found 336.9628.



(*S*)-2-(Iodomethyl)-1-((2-(trimethylsilyl)ethyl)sulfonyl)indoline (**4l**)

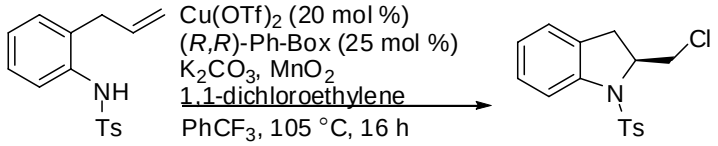
Indoline **4l** (62.3 mg, 0.147 mmol) was obtained as a white solid in an 85% yield from *N*-(2-allylphenyl)-2-(trimethylsilyl)ethane sulfonamide (**1l**) (51.5 mg, 0.173 mmol). For this reaction the (4*R*,5*S*)-di-Ph-box ligand (**3**) was used. mp = 94-95°C; $[\alpha]_D^{24}$ = -32.2° (c = 0.5, $CHCl_3$), ee = 82%, determined by HPLC analysis [Chiralpak AD-RH, 4% water/MeOH, 0.5 mL/min, λ = 254 nm, t(major) = 5.97 min, t(minor) = 7.07 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.6 Hz, 1H), 7.22-7.18 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 4.56-4.52 (m, 1H), 3.61 (dd, J = 3.2, 10 Hz, 1H), 3.46 (dd, J = 9.6, 16.8 Hz, 1H), 3.28 (apparent t, J = 9.6 Hz, 1H), 3.07 (dd, J = 3.2, 16.4 Hz, 1H), 3.00-2.94 (m, 2H), 1.09-1.02 (m, 2H), -0.03 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.3, 129.1, 128.2, 125.5, 124.1, 114.4, 62.9, 46.8, 35.2, 11.8, 9.9, -2.1; IR (neat): 3010, 2950, 1603, 1479, 1348, 1252, 1149, 1105, 1023, 966, 841, 754 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{14}H_{22}O_2NINaSSi$ 446.0077, found 446.0078.



(*S*)-2-(Iodomethyl)-1-(3,5-ditertbutylbenzene sulfonyl)indoline (**4m**)

Indoline **4m** (64.2 mg, 0.126 mmol) was obtained as an orange solid in 90% yield from *N*-(2-allylphenyl)-3,5-di-*tert*-butylbenzenesulfonamide (**1m**) (53.8 mg, 0.140 mmol). mp = 126-127°C; $[\alpha]_D^{24}$ = 17.3° (c = 0.83, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J= 8.0 Hz, 1H), 7.54 (s, 1H), 7.42 (s, 2H), 7.26-7.22 (m, 1H), 7.07-7.03 (m, 2H), 4.32-4.25 (m, 1H), 3.62 (dd, J= 3.2, 9.6 Hz, 1H), 3.25 (t, J= 9.6 Hz, 1H), 2.81-2.67 (m, 2H), 1.20 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.1, 141.6, 136.4, 130.9, 127.9, 127.1, 125.1, 125.0, 121.1, 117.6, 62.7, 35.1, 34.7, 31.1, 11.1; IR (neat): 3031, 2961, 1598, 1478, 1360, 1248, 1170, 1012, 757 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{23}H_{31}O_2NIS$ 512.1115, found 512.1112.

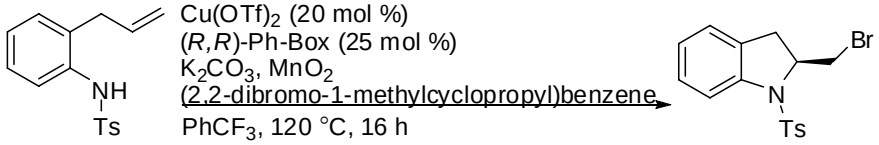
Procedure for the catalytic enantioselective aminochlorination of N-(2-allylphenyl)-4-methyl-benzenesulfonamide:



(*S*)-2-(chloromethyl)-1-tosylindoline (**4n**)

Copper (II) triflate (12.6 mg, 0.035 mmol) was added to an oven-dried pressure tube (10 mL) equipped with a stir bar, in a glovebox. Upon removal from the glovebox the pressure tube was flushed with argon any time it was opened. To the tube, (*R,R*)-Ph-box (**2**) (14.5 mg, 0.043 mmol) in $PhCF_3$ (0.54 mL, 0.08 M) was added and the mixture was dissolved in additional $PhCF_3$ (1.20 mL), the tube was then sealed and heated to 60 °C for 2 h in an oil bath with stirring. The following reagents were then added sequentially: N-(2-allylphenyl)-4-methyl-benzenesulfonamide[5] (51.8 mg, 0.180 mmol), MnO_2 (45.5 mg, 0.523 mmol), K_2CO_3 (24.8 mg, 0.179 mmol), 1,1-dichloroethylene (0.125 mL, 152.3 mg, 1.57 mmol) and ~35 mg of flame activated 4Å molecular sieves. The tube was then flushed with argon, sealed, and sonicated to ensure that all reagents were in solution. The mixture was stirred at 105 °C (oil bath) for 16 h. Upon cooling to rt and the mixture was filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent was removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient) afforded indoline **4n** (37.7 mg, 0.117 mmol) as a white solid in 65% yield. Further purification by HPLC 10% EtOAc in hexanes, isocratic, was used prior to chiral HPLC analysis. mp = 140-141°C; $[\alpha]_D^{24}$ = 93.7° (c = 0.63, $CHCl_3$), ee = 93%, determined by HPLC analysis [Regis (*S,S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 12.35 min, t(minor) = 15.58 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J= 8.4 Hz, 1H), 7.56 (d, J= 8.4 Hz, 2H), 7.25-7.17 (m, 3H), 7.08-7.02 (m, 2H), 4.44-4.37 (m, 1H), 3.93 (dd, J= 3.6, 10.8 Hz, 1H), 3.55 (dd, J= 9.6, 10.4 Hz, 1H), 2.96-2.85 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.3, 141.1, 134.5, 130.7, 129.7, 127.9, 127.1, 125.3, 124.9, 116.9, 62.3, 46.9, 32.2, 21.6; IR (neat): 3031, 2923, 1598, 1480, 1355, 1168, 1092, 1035, 755 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{16}O_2NClSNa$ 344.0482, found 344.0485.

Procedure for the catalytic enantioselective aminobromination of N-(2-allylphenyl)-4-methyl-benzenesulfonamide:

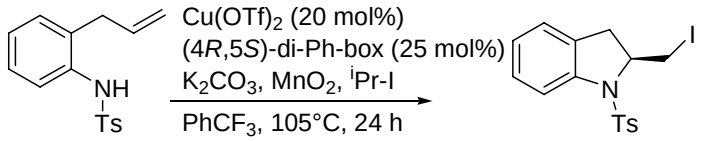


(*S*)-2-(bromomethyl)-1-tosylindoline (**4o**)

Copper (II) triflate (13.7 mg, 0.038 mmol) was added to an oven dried pressure tube (10 mL) equipped with a stir bar, in a glovebox. Upon removal from the glovebox the pressure tube was flushed with argon any time it was opened. To the tube, (*R,R*)-Ph-box (**2**) (15.8 mg, 0.047 mmol) in $PhCF_3$ (0.59 mL, 0.08 M) was added and the mixture was dissolved in additional $PhCF_3$ (1.30 mL), the tube was then sealed and heated to 60 °C for 2 h in an oil bath with stirring. The following reagents were then added sequentially: N-(2-allylphenyl)-4-methyl-benzenesulfonamide[5] (55.3 mg, 0.192 mmol), MnO_2 (49.7 mg, 0.572 mmol), K_2CO_3 (26.1 mg, 0.189 mmol), (2,2-dibromo-1-methylcyclopropyl)benzene (0.185 mL, 329.5 mg, 1.14 mmol) and ~38 mg of flame activated 4Å molecular sieves. Once all reagents were added the tube was flushed with argon, sealed, and sonicated to ensure that all reagents were in solution, and placed in a 120 °C oil bath for 16 h. The tube was then allowed to come to rt and the mixture was filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent was removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient) afforded indoline **4o** (40.2 mg, 0.110 mmol) as a white solid in 57% yield. Further purification by HPLC 10% EtOAc in hexanes, isocratic, was used prior to chiral HPLC analysis:

mp = 98-99°C; $[\alpha]_D^{24}$ = 27.9° (c = 0.79, $CHCl_3$), ee = 87%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 13.25 min, t(minor) = 16.43 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J= 8.4 Hz, 1H), 7.57 (d, J= 8.4 Hz, 2H), 7.25-7.18 (m, 3H), 7.08-7.02 (m, 2H), 4.45-4.41 (m, 1H), 3.82 (dd, J= 3.6, 10.0 Hz, 1H), 3.41 (t, J= 10.4 Hz, 1H), 2.94-2.90 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.3, 141.1, 134.5, 130.6, 129.8, 127.9, 127.1, 125.3, 124.9, 116.9, 62.2, 35.9, 33.2, 21.6; IR (neat): 3031, 2923, 1598, 1479, 1355, 1168, 1092, 1026, 758 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{16}O_2NBrSNa$ 387.9977, found 387.9986.

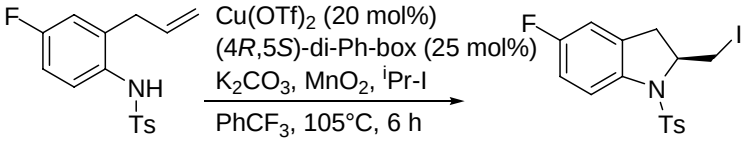
Procedure for the catalytic enantioselective aminohalogenation on a 0.5 g scale:



(*S*)-2-(Iodomethyl)-1-tosylindoline (**4a**)

Copper (II) triflate (125.2 mg, 0.346 mmol) was added to an oven dried pressure tube (60 mL) equipped with a stir bar, in a glovebox. Upon removal from the glovebox the pressure tube was flushed with argon any time it was opened. To the tube, (4*R*,5*S*)-di-Ph-box ligand (**3**) (211.4 mg, 0.434 mmol) was added and the mixture was dissolved in $PhCF_3$ (17.0 mL), the tube was then sealed and heated to 60 °C for 2 h in an oil bath with stirring. The following reagents were then added sequentially: *N*-(2-allylphenyl)-4-methyl-benzenesulfonamide[5] (504.6 mg, 1.756 mmol), MnO_2 (611.3 mg, 7.031 mmol), K_2CO_3 (242.8 mg, 1.757 mmol), ^{i}Pr-I (2.11 mL, 3.59 g, 21.1 mmol) and ~340 mg of flame activated 4Å molecular sieves. Once all reagents were added the tube was flushed with argon, sealed, and sonicated to ensure that all reagents were in solution. The reaction was then stirred at 105 °C (oil bath) for 24 h. The tube was then allowed to come to rt and the mixture was filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent was removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient) afforded the corresponding indoline **4a** (537.0 mg, 1.30 mmol) in 74% yield and 88% ee. Further purification by HPLC 10% EtOAc in hexanes, isocratic, was used prior to chiral HPLC analysis. The ee was further enriched to >98% via recrystalization from CH_2Cl_2/hexanes.

Procedure for the catalytic enantioselective aminohalogenation of 1d on a 0.25 g scale:

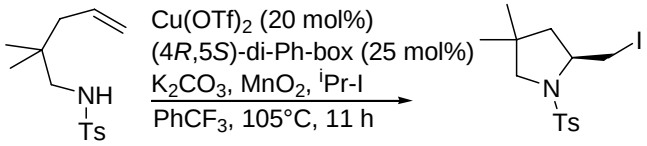


(*S*)-5-Fluoro-2-(iodomethyl)-1-tosylindoline (**4d**)

Copper (II) triflate (59.7 mg, 0.165 mmol) was added to an oven dried pressure tube (40 mL) equipped with a stir bar, in a glovebox. Upon removal from the glovebox the pressure tube was flushed with argon any time it was opened. To the tube, (4*R*,5*S*)-di -Ph-box ligand (**3**) (100.7 mg, 0.207 mmol) was added and the mixture was dissolved in $PhCF_3$ (8.2 mL), the tube was then sealed and heated to 60 °C for 2 h in an oil bath with stirring. The following reagents were then added sequentially: *N*-(2-Allyl-4-fluoro-phenyl)-4-methyl-benzenesulfonamide (**1d**)[6] (252.5 mg, 0.827 mmol), MnO_2 (216.3 mg, 2.488 mmol), K_2CO_3 (114.3 mg, 0.827 mmol), ^{i}Pr-I (0.75 mL, 1.28 g, 7.50 mmol) and ~164 mg of flame activated 4Å molecular sieves. Once all reagents were added the tube was flushed with argon, sealed, and sonicated to ensure that all reagents were in solution. The reaction was then stirred at 105 °C (oil bath) for 6 h. The tube was then allowed to come to rt and the mixture was filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent was removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient)

afforded the corresponding indoline **4d** (267.0 mg, 0.619 mmol) in 75% yield and 92% ee. Further purification by HPLC 10% EtOAc in hexanes, isocratic, was used prior to chiral HPLC analysis.

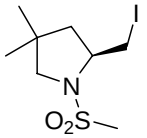
Catalytic Methods for 4-Pentenyl Sulfonamide Substrates:



(*S*)-2-(Iodomethyl)-4,4-dimethyl-1-tosylpyrrolidine (**8a**) (Representative procedure)

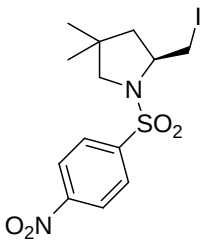
Copper (II) triflate (13.9 mg, 0.039 mmol) was added to an oven dried pressure tube (10 mL) equipped with a stir bar, in a glovebox. Upon removal from the glovebox the pressure tube was flushed with argon any time it was opened. To the tube, (4*R*,5*S*)-di-Ph-box ligand (**3**) (21.0 mg, 0.043 mmol) was added and the mixture was dissolved in $PhCF_3$ (1.73 mL), the tube was then sealed and heated to 60 °C for 2 h in an oil bath with stirring. The following reagents were then added sequentially: *N*-(2, 2-dimethyl-pent-4-enyl)-4-methyl-benzenesulfonamide (**7a**)[12](51.5 mg, 0.193 mmol), MnO_2 (45.1 mg, 0.518 mmol), K_2CO_3 (23.9 mg, 0.173 mmol), ^{i}Pr-I (0.103 mL, 175.1 mg, 1.03 mmol) and ~35 mg of flame activated 4Å molecular sieves. Once all reagents were added the tube was flushed with argon, sealed, and sonicated to ensure that all reagents were in solution. The reaction was then stirred at 105 °C (oil bath) for 11 h. The tube was then allowed to come to rt and the mixture was filtered through a pad of Celite with EtOAc. The filtrate was collected and the solvent was removed *in vacou* to yield the crude product as a solid. Flash chromatography of the resulting crude material on SiO_2 (0-20% v/v EtOAc in hexanes gradient) afforded the corresponding pyrrolidine **8a** in 81% yield. Further purification using HPLC (10% EtOAc in hexanes, isocratic) was performed prior to chiral HPLC analysis.

Pyrrolidine **8a** (61.3 mg, 0.156 mmol) was obtained as an oil in 81% yield from *N*-(2, 2-dimethyl-pent-4-enyl)-4-methyl-benzenesulfonamide (**7a**)[12](51.5 mg, 0.193 mmol): mp = 65-67 °C; $[\alpha]_D^{24}$ = -110.0 ° (c = 0.5, $CHCl_3$), ee = 88%, determined by HPLC analysis [Chiralpak AD-RH, 4% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 7.34 min, t(minor) = 8.61 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.77 (dd, J = 2.8, 9.2 Hz, 1H), 3.74-3.65 (m, 1H), 3.37 (apparent t, J = 8.8 Hz, 1H), 3.21 (apparent t, J = 8.8 Hz, 2H), 2.44 (s, 3H), 1.92 (dd, J = 7.6, 12.8 Hz, 1H), 1.60 (dd, J = 8.4, 12.8 Hz, 1H), 1.05 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.7, 134.9, 129.7, 127.5, 62.0, 60.1, 47.8, 37.5, 26.0, 25.8, 21.5, 13.2; IR (neat): 3029, 2958, 1598, 1465, 1347, 1157, 1092, 816, 662 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{14}H_{21}O_2NIS$ 394.0332, found 394.0336.



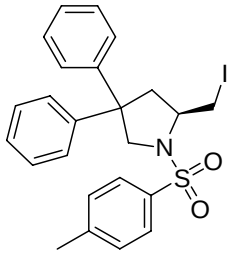
(*S*)-2-(Iodomethyl)-4,4-dimethyl-1-(methylsulfonyl)pyrrolidine (**8b**)

Pyrrolidine **8b** (49.8 mg, 0.157 mmol) was obtained as a white solid in a 78% yield from the corresponding sulfonamide[16] **7b** (38.5 mg, 0.201 mmol): mp = 79-80°C; $[\alpha]_D^{24}$ = -16.7° (c = 0.5, $CHCl_3$), ee = 43%, determined by HPLC analysis [Chiralpak AD-RH, 2% water/MeOH, 1 mL/min, λ = 254 nm, t(minor) = 3.57 min, t(major) = 4.09 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88-3.82 (m, 1H), 3.55-3.47 (m, 2H), 3.24 (ABq, J_{AB} = 10.0 Hz, Δν = 60.4 Hz, 2H), 2.95 (s, 3H), 2.04-1.98 (m, 1H), 1.70-1.64 (m, 1H), 1.14 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 61.4, 59.4, 47.3, 39.4, 38.0, 26.5, 25.7, 13.7; IR (neat): 2958, 1466, 1331, 1148, 1050, 963 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_8H_{16}O_2NISNa$ 339.9839, found 339.9847.



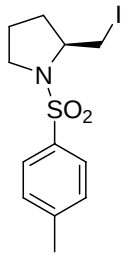
(*S*)-2-(Iodomethyl)-4,4-dimethyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine (**8c**)

Pyrrolidine **8c** (61.7 mg, 0.146 mmol) was obtained as pale yellow crystals in a 80% yield from *N*-(2, 2-dimethyl-pent-4-enyl)-4-nitro-benzenesulfonamide (**7c**)[17](54.4 mg, 0.182 mmol), the reaction time was increased to 24 h for this reaction: mp = 93-95°C; $[\alpha]_D^{24}$ = -51.1° (c = 1.00, $CHCl_3$), ee = 60%, determined by HPLC analysis [Chiralpak AD-RH, 2% IPA/Hex , 1 mL/min, λ = 254 nm, t(major) = 15.27 min, t(minor) = 20.06 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 12.8 Hz, 2H), 8.05 (d, J = 12.0 Hz, 2H), 3.81-3.75 (m, 1H), 3.65 (dd, J = 2.8, 10.0 Hz, 1H), 3.44 (dd, J = 8.0 Hz, 9.6 Hz, 1H), 3.28-3.20 (m, 2H), 1.95 (dd, J = 7.2, 12.8 Hz, 1H), 1.65 (dd, J = 8.4, 12.8 Hz, 1H), 1.08 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 150.1, 144.3, 128.5, 124.4, 61.9, 60.2, 47.4, 37.9, 26.0, 25.6, 12.7; IR (neat): 3104, 2960, 2875, 1605, 1530, 1349, 1161, 1091, 856, 743, 615 cm^{-1}; HRMS (ESI) calcd for $[M-I]^+$ $C_{13}H_{17}O_4N_2S$ 297.0900, found 297.1000.



(*S*)-2-(Iodomethyl)-4,4-diphenyl-1-tosylpyrrolidine (**8d**)

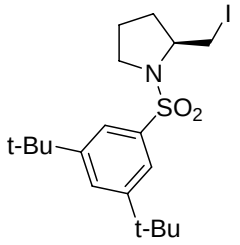
Pyrrolidine **8d** (75.9 mg, 0.147 mmol) was obtained as white crystals in 85% yield from *N*-(2, 2-diphenyl-pent-4-enyl)-4-methyl-benzenesulfonamide (**7d**)[14](67.6 mg, 0.173 mmol): mp = 78-80°C; $[\alpha]_D^{24}$ = 6.7° (c = 0.5, $CHCl_3$), ee = 93%, determined by HPLC analysis [Chiralpak AD-RH, 2% IPA/hexane, 0.5 mL/min, λ = 254 nm, t(minor) = 29.47 min, t(major) = 31.39 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 2H), 7.30-7.07 (m, 12H), 4.43 (d, J = 10.0 Hz, 1H), 3.88-3.84 (m, 1H), 3.75 (d, J = 10.0 Hz, 1H), 3.67 (dd, J = 3.0, 9.5 Hz, 1H), 2.85-2.78 (m, 2H), 2.66 (dd, J = 5.0, 13.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.6, 144.4, 143.6, 134.0, 129.8, 128.7, 128.6, 127.4, 126.8, 126.6, 126.5, 126.3, 60.4, 59.2, 52.2, 43.8, 21.5, 11.3; IR (neat): 3026, 2962, 1598, 1495, 1448, 1344, 1262, 1162, 1091, 1029, 813, 753, 701, 665 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{24}H_{25}O_2NIS$ 518.0645, found 518.0658.



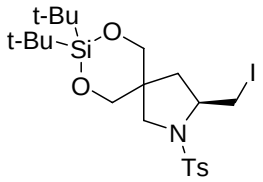
(*S*)-2-(Iodomethyl)-1-tosylpyrrolidine (**8e**)

Pyrrolidine **8e** (49.7 mg, 0.136 mmol) was obtained as a white solid in a 77% yield from *N*-(pent-4-enyl)-4-methyl-benzenesulfonamide (**7e**)[5](42.3 mg, 0.177 mmol): mp = 89-91°C; $[\alpha]_D^{24}$ = -103.2° (c = 0.5, $CHCl_3$), ee = 73%, determined by HPLC analysis [Chiralpak AD-RH, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 10.85 min, t(minor) = 12.73 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.77-3.72 (m, 1H), 3.62 (dd, J = 2.8, 9.6 Hz, 1H), 3.51-3.47 (m, 1H), 3.25-

3.16 (m, 2H), 2.44 (s, 3H), 1.91-1.80 (m, 3H), 1.56-1.50 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.8, 134.2, 129.8, 127.5, 60.7, 50.1, 32.0, 23.8, 21.6, 11.5; IR (neat): 3027, 2971, 1597, 1448, 1346, 1159, 1092, 986, 816, 665 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{12}H_{16}O_2NIS$ 364.9941, found 364.9952.

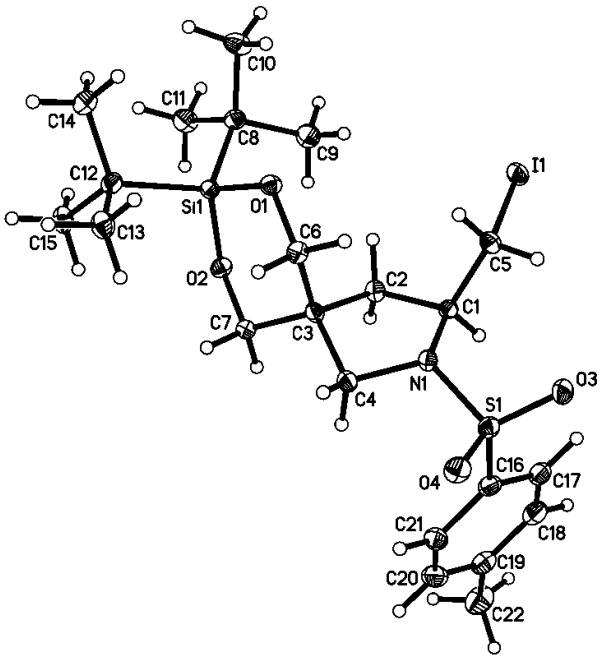


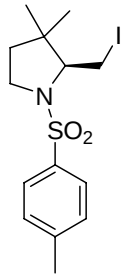
(*S*)-1-((3,5-Di-*tert*-butylphenyl)sulfonyl)-2-(iodomethyl)pyrrolidine (**8f**)
Pyrrolidine **8f** (58.3 mg, 0.126 mmol) was obtained as white crystals in 85% yield from the corresponding sulfonamide **7f**(50.0 mg, 0.148 mmol): mp = 94-95°C; $[\alpha]_D^{24}$ = -63.8° (c = 1.00, $CHCl_3$), ee = 82%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1.0 mL/min, λ = 254 nm, t(major) = 9.30 min, t(minor) = 10.59 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 3H), 3.78-3.71 (m, 1H), 3.61 (dd, J = 2.8, 9.6 Hz, 1H), 3.49-3.44 (m, 1H), 3.27-3.17 (m, 2H), 1.89-1.81 (m, 3H), 1.55-1.50 (m, 1H), 1.36 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.3, 136.7, 126.9, 121.6, 60.7, 50.0, 35.1, 32.1, 31.3, 39.9, 23.9, 11.7; IR (neat): 3067, 2963, 1599, 1476, 1348, 1248, 1164, 1114, 1024, 985, 789 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{19}H_{30}O_2NISNa$ 486.0934, found 486.0935.



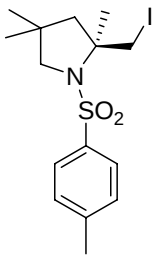
(*S*)-8,8-Di-*tert*-butyl-3-(iodomethyl)-2-tosyl-7,9-dioxa-2-aza-8-silaspiro[4.5]decane (**8g**)
Pyrrolidine **8g** (35.0 mg, 0.062 mmol) was obtained as white crystals in 78% yield from the corresponding sulfonamide **7g**[4] (34.9 mg, 0.079 mmol): mp = 123-125°C; $[\alpha]_D^{24}$ = -25.6° (c = 0.23, $CHCl_3$), ee = 92%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 4% IPA/hexane, 1.0 mL/min, λ = 254 nm, t(major) = 15.77 min, t(minor) = 18.98 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 3.94 (ABq, J_{AB} = 10.8, Δν = 42.3 Hz, 2H), 3.73-3.38 (m, 2H), 3.33 (ABq, J_{AB} = 11.6, Δν = 165.4 Hz, 2H), 3.40-3.33 (m, 2H), 2.46 (s, 3H), 1.96 (dd, J = 7.6, 14 Hz, 1H), 1.53 (dd, J = 7.6, 14 Hz, 1H), 1.02 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.1, 134.1, 129.9, 127.5, 71.6, 69.7, 59.1, 56.1, 45.3, 39.9, 29.7, 28.0, 27.5, 22.6, 21.6, 21.2, 12.9; IR (neat): 3010, 2928, 1599, 1471, 1348, 1160, 1064, 909, 824, 764 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{22}H_{37}O_4NISSi$ 566.1252, found 566.1267.

Assignment of Absolute Stereochemistry of Pyrrolidine Products:
The crystal structure of pyrrolidine **8g** (CCDC 858585) showing the S stereochemistry was obtained by William W. Brennessel at the University of Rochester. The absolute configuration of all other pyrrolidine products was assigned by analogy to this structure.



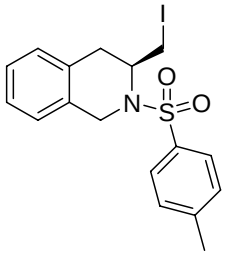


(*S*)-2-(Iodomethyl)-3,3-dimethyl-1-tosylpyrrolidine (**10**)
Pyrrolidine **10** (52.5 mg, 0.134 mmol) was obtained as a white solid in a 78% yield from *N*-(3,3-dimethylpent-4-enyl)-4-methylbenzenesulfonamide **(9)**[19](45.8 mg, 0.171 mmol): mp = 61-63°C; $[\alpha]_D^{24}$ = -67.1° (c = 0.5, $CHCl_3$), ee = 82%, determined by HPLC analysis [Chiralpak AD-RH, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 9.21 min, t(minor) = 10.69 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.51-3.33 (m, 4H), 3.13-3.08 (m, 1H), 2.44 (s, 3H), 2.03-1.98 (m, 1H), 1.35-1.31 (m, 1H), 1.16 (s, 3H), 0.52 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.7, 134.1, 129.6, 127.6, 67.7, 46.3, 42.1, 37.6, 28.5, 22.8, 21.6, 7.8; IR (neat): 3031, 2962, 1598, 1466, 1345, 1163, 1094, 1050, 816, 665 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{14}H_{20}O_2NIS$ 393.0254, found 393.0244.



(*S*)-2-(Iodomethyl)-2,4,4-trimethyl-1-tosylpyrrolidine (**12**)

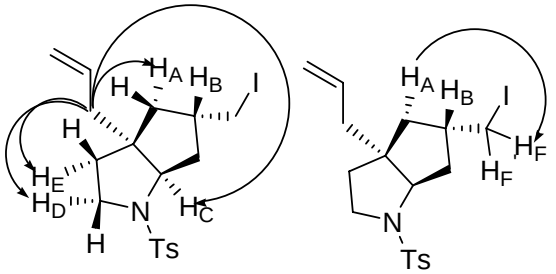
Pyrrolidine **12** (52.1 mg, 0.128 mmol) was obtained as a yellow oil in a 74% yield from *N*-(2,2,4-trimethyl-pent-4-enyl)- 4-methyl-benzenesulfonamide (**11**)[15](48.8 mg, 0.173 mmol):$[\alpha]_D^{24}$ = 7.2° (c = 0.67, $CHCl_3$), ee = 16%, determined by HPLC analysis [Chiralpak AD-RH, 2% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 7.56 min, t(minor) = 8.98 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.74 (ABq, J_{AB} = 10.0 Hz, Δν = 72.3 Hz, 2H), 3.17 (ABq, J_{AB} = 9.2 Hz, Δν = 39.1 Hz, 2H), 2.43 (s, 3H), 1.90 (ABq, J_{AB} = 12.8 Hz, Δν = 186.6 Hz, 2H), 1.71 (s, 3H), 1.08 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.1, 137.7, 129.5, 127.4, 67.3, 62.1, 55.3, 36.1, 27.4, 27.1, 25.9, 21.5, 19.8; IR (neat): 3027, 2957, 1598, 1448, 1338, 1212, 1155, 1092, 1044, 970, 815, 713, 659 cm^{-1}; HRMS (EI) calcd for $[M]^+$ $C_{15}H_{22}O_2NIS$ 407.0410, found 407.0403.



(*S*)-3-(Iodomethyl)-2-tosyl-1,2,3,4-tetrahydroisoquinoline (**14**)

Tetrahydroisoquinoline **14** (54.6 mg, 0.128 mmol) was obtained as a yellow oil in a 73% yield from *N*-(2-allylbenzyl)-4-methylbenzenesulfonamide (**13**)[5](52.8 mg, 0.175 mmol). The (*R,R*)-Ph-box ligand (**2**) was used for this reaction:$[\alpha]_D^{24}$ = 29.2° (c = 0.37, $CHCl_3$), ee = 27%, determined by HPLC analysis [Regis (*S,S*) Whelk-O 1, 4% IPA/hexane, 1 mL/min, λ = 254 nm, t(major) = 28.09 min, t(minor) = 34.05 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 2H), 7.27-7.25 (m, 2H), 7.18-7.16 (m, 2H), 7.10-7.05 (m, 2H), 4.39 (ABq, J_{AB} = 15.6 Hz, Δν = 21.3 Hz, 2H), 4.34-4.31 (m, 1H), 3.28 (dd, J = 3.6, 6.0 Hz, 1H), 3.08 (dd, J = 3.2, 16.0 Hz, 1H), 2.96 (apparent t, J = 10.4 Hz, 1H), 2.82 (dd, J = 5.2, 12.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.7, 135.8, 131.9, 131.8, 129.8, 129.1, 127.5, 127.3, 126.8, 126.1, 53.8, 44.5, 31.9, 21.5, 7.4; IR (neat): 3027, 2922, 1598, 1495, 1456, 1335, 1161, 1091, 1038, 907, 814, 745, 664 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{17}H_{19}O_2NIS$ 428.0176, found 428.0169. The absolute stereochemistry of **14** was assigned by analogy to **8e**.

Assignment of Relative Stereochemistry of Pyrrolidine Product 16:

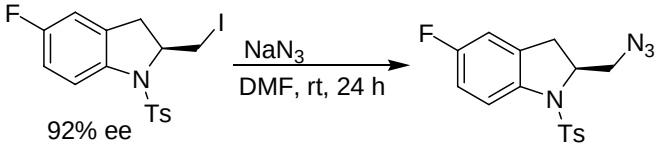


(3a*R*,5*S*,6a*R*)-3a-allyl-5-(iodomethyl)-1-tosyloctahydrocyclopenta[b]pyrrole (**16**)

Pyrrolidine **16** (52.6 mg, 0.118 mol) was obtained as a clear oil in a 70% yield from the corresponding sulfonamide **15** (53.9 mg, 0.169 mmol). The stereochemistry of H_C was assigned by analogy to crystal structure **8g**. An nOe experiment showing a strong signal between the allyl methylene protons and H_C was used to assign the stereochemistry of the quaternary carbon center, this experiment also showed a strong signal between the allyl methylene protons and H_A. The stereochemistry of the last chiral center was assigned based on an nOe experiment showing a strong signal between H_A and H_F :$[\alpha]_D^{24}$ = -25.5° (c = 0.5, $CHCl_3$), ee = 91%, determined by HPLC analysis [Chiralpak AD-RH, 2% water/MeOH, 1 mL/min, λ = 254 nm, t(major) = 4.70 min, t(minor) = 6.75 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 10.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.43-5.36 (m, 1H), 4.90 (d, J = 12.0 Hz, 1H), 4.82 (d, J = 18.8 Hz, 1H) 3.49-3.41 (m, 2H), 3.43-3.23 (m, 1H), 3.16-3.12 (m, 1H), 2.99-2.92 (m, 1H), 2.45 (s, 3H), 2.39-2.32 (m, 2H), 1.86 (dd, J = 3.2, 7.6 Hz, 2H), 1.74-1.62 (m, 3H), 1.47-1.43 (m, 1H), 1.18 (dd, J = 11.2, 12.8 Hz,

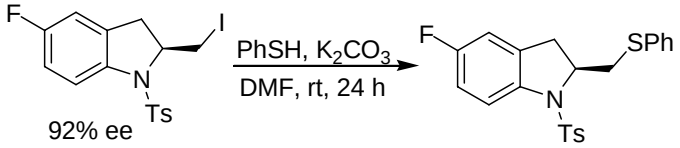
1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 143.6, 133.8, 133.2, 129.6, 127.9, 118.4, 69.3, 54.2, 48.9, 45.0, 43.8, 41.2, 40.1, 36.0, 21.5, 11.1; IR (neat): 3070, 2948, 1639, 1598, 1451, 1344, 1162, 1093, 919, 816, 657 cm^{-1}; HRMS (ESI) calcd for $[M+1]^+$ $C_{18}H_{25}O_2NIS$ 446.0645, found 446.0638.

Substitution and Cross-Coupling Reactions:



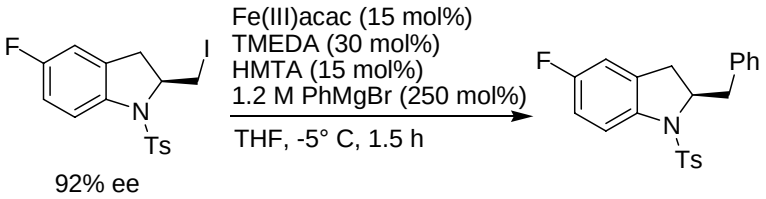
(*S*)-2-(Azidomethyl)-5-fluoro-1-tosylindoline (**17**)

To an oven dried flask with a stir bar, under argon, was added (*S*)-5-fluoro-2-(iodomethyl)-1-tosylindoline (**4d**) (44.8 mg, 0.104 mmol, 92% ee), sodium azide (20.5 mg, 0.315 mmol) and 1.05 mL of DMF. The flask was then allowed to stir under an inert atmosphere at room temperature for 24 h. The reaction mixture was then filtered through a pad of Celite with ethyl acetate. The filtrate was collected and the solvent removed *in vacuo* providing 79.1 mg of crude material. The crude product was further purified via flash chromatography on SiO_2 (0-30% EtOAc in hexanes eluent) providing pure alkyl azide **17** (35.3 mg, 0.102 mmol) as white crystals in 98% yield: mp = 98-99 °C; $[\alpha]_D^{24}$ = 144.2° (c = 0.85, $CHCl_3$), ee = 92%, determined by HPLC analysis [Regis (*S*,*S*) Whelk-O 1, 2% IPA/hexane, 1.0 mL/min, λ = 254 nm, t(major) = 20.71 min, t(minor) = 24.96 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 4.8, 8.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.95 (td, J = 2.4, 8.8 Hz, 1H), 6.76 (dd, J = 2.8, 8.0 Hz, 1H), 4.39-4.29 (m, 1H), 3.60-3.50 (m, 2H), 2.80-2.65 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.6 (d, J = 244.2 Hz), 144.4, 137.3, 134.2, 133.5 (d, J = 8.1 Hz), 129.8, 127.1, 118.5 (d, J = 8.1 Hz), 114.6 (d, J = 24.2 Hz), 112.3 (d, J = 24.2 Hz), 61.5, 55.2, 32.1, 21.6; IR (neat): 3030, 2924, 1599, 1482, 1356, 1166, 1091, 893, 815 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{16}H_{15}O_2N_4FSNa$ 369.0792, found 369.0799.



(*S*)-5-Fluoro-2-(phenylthiomethyl)-1-tosylindoline (**18**)

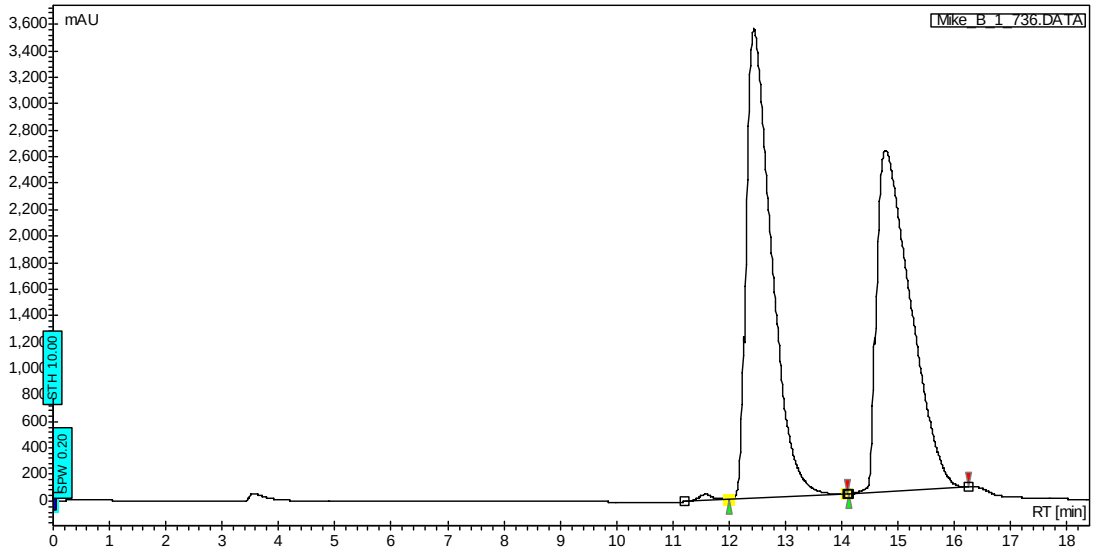
To an oven dried flask with a stir bar, under argon, was added (*S*)-5-fluoro-2-(iodomethyl)-1-tosylindoline (**4d**) (44.1 mg, 0.102 mmol, 92% ee), thiophenol (31 μL, 33.4 mg, 0.303 mmol), K_2CO_3 (14.5 mg, 0.105 mmol) and 1.00 mL of DMF. The flask was then allowed to stir under an inert atmosphere at room temperature for 24 h. The reaction mixture was then filtered through a pad of Celite with ethyl acetate, the filtrate was collected and the solvent removed *in vacuo* providing 146.4 mg of crude material. The crude product was further purified via flash chromatography on SiO_2 (0-30% EtOAc in hexanes eluent). Indoline **18** (41.3 mg, 0.100 mmol) was obtained as a clear oil in 98% yield:$[\alpha]_D^{24}$ = -15.5° (c = 0.57, $CHCl_3$), ee = 92%, determined by HPLC analysis [Chiralpak AD-RH, 2% IPA/hexane, 1.0 mL/min, λ = 254 nm, t(major) = 21.11 min, t(minor) = 14.21 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, J = 4.8, 8.4 Hz, 1H), 7.44 (d, J = 7.6 Hz, 2H), 7.39-7.34 (m, 4H), 7.27-7.23 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.91 (td, J = 2.4, 9.2 Hz, 1H), 6.74 (dd, J = 2.8, 8.0 Hz, 1H), 4.30-4.22 (m, 1H), 3.67 (dd, J = 3.6, 13.6 Hz, 1H), 2.92-2.73 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.4 (d, J = 243.2 Hz), 144.1, 137.2 (d, J = 2.3 Hz), 134.7, 134.2, 133.3 (d, J = 9.2 Hz), 129.6, 129.1 (d, J = 2.3 Hz), 126.9, 126.3, 118.2 (d, J = 8.1 Hz), 114.5 (d, J = 24.2 Hz), 112.4 (d, J = 24.2 Hz), 61.2, 38.5, 33.2, 21.5; IR (neat): 3058, 2923, 1599, 1482, 1356, 1166, 1090, 1026, 935, 814 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{22}H_{20}O_2NFS_2Na$ 436.0812, found 436.0812.



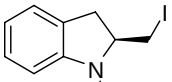
(*R*)-2-Benzyl-5-fluoro-1-tosylindoline (**19**) was prepared by a procedure analogous to that developed by Cahiez.[22]

To an oven dried flask with a stir bar, under argon, was added $Fe(acac)_3$ (5.8 mg, 0.016 mmol), HMTA (2.6 mg, 0.019 mmol), TMEDA (5 μL, 3.9 mg, 0.033 mmol,), (*S*)-5-fluoro-2-(iodomethyl)-1-tosylindoline (**4d**) (48.6 mg, 0.113 mmol, 92% ee) and 0.145 mL of THF. The reaction was then stirred and cooled to -5 °C over the course of a few minutes. Once the mixture had cooled, 1.2M phenyl magnesium bromide (0.203 mL, 0.276 mmol) was added dropwise over an hour. Once the addition was complete the reaction was allowed to stir for an additional 30 minutes before being quenched with aqueous HCl 1M (1.0 mL). The mixture was then extracted with Et_2O (3 x 1.5 mL), the organics were combined and the solvent removed *in vacuo* providing 77.6 mg of crude material. The crude product was further purified via flash chromatography on SiO_2 (0-20% EtOAc in hexanes eluent) to provide indoline **20** (34.4 mg, 0.090 mmol) as white crystals in 80% yield: mp = 99-100°C; $[\alpha]_D^{24}$ = 39.1° (c = 0.78, $CHCl_3$), ee = 90%, determined by HPLC analysis [Chiralpak AD-RH, 8% IPA/hexane, 1.0 mL/min, λ = 254 nm, t(major) = 10.91 min, t(minor) = 6.12 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, J = 4.8, 9.2 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.32-7.21 (m, 5H), 7.16 (d, J = 8.0 Hz, 2H), 6.91 (td, J = 2.0, 8.4 Hz, 1H), 6.69 (dd, J = 1.6, 7.6 Hz, 1H), 4.49-4.43 (m, 1H), 3.30 (dd, J = 4.4, 13.6 Hz, 1H), 2.79 (dd, J = 10.0, 13.2 Hz, 1H), 2.53 (d, J = 6.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.3 (d, J = 243.2 Hz), 143.9, 137.4, 137.3, 136.9, 134.9, 134.1 (d, J = 9.2 Hz), 129.6, 128.5, 126.9, 126.7, 118.6 (d, J = 8.1 Hz), 114.3 (d, J = 23.1 Hz), 112.4 (d, J = 24.2 Hz), 63.9, 42.4, 32.8, 21.5; IR (neat): 3029, 2922, 1599, 1481, 1354, 1165, 1090, 1031, 814 cm^{-1}; HRMS (ESI) calcd for $[M+Na]^+$ $C_{22}H_{20}O_2NFSNa$ 404.1091, found 404.1095.

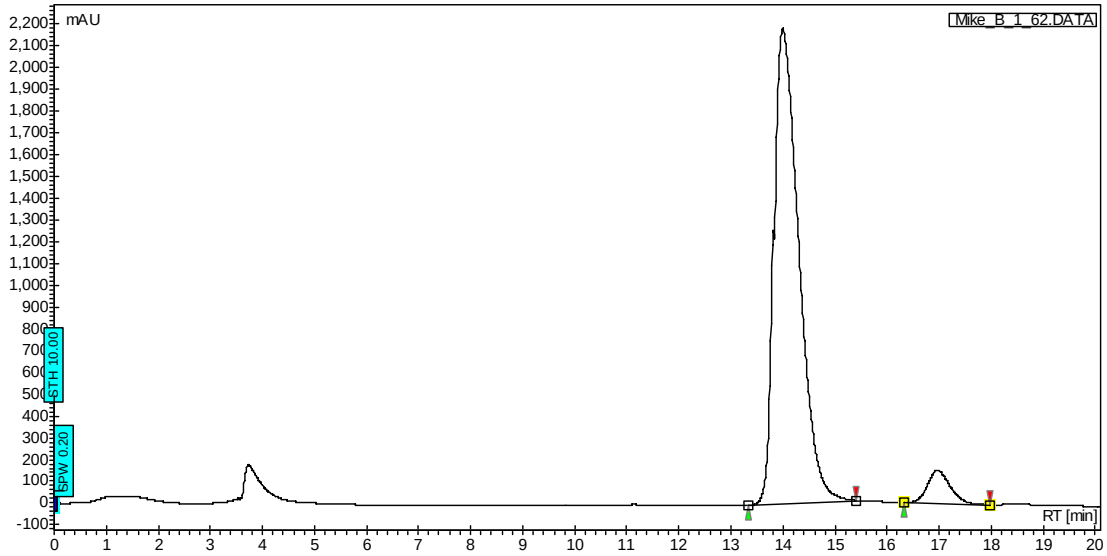
Chiral HPLC Traces:



Time (min)	Area (%)
12.44	50.403
14.78	49.597

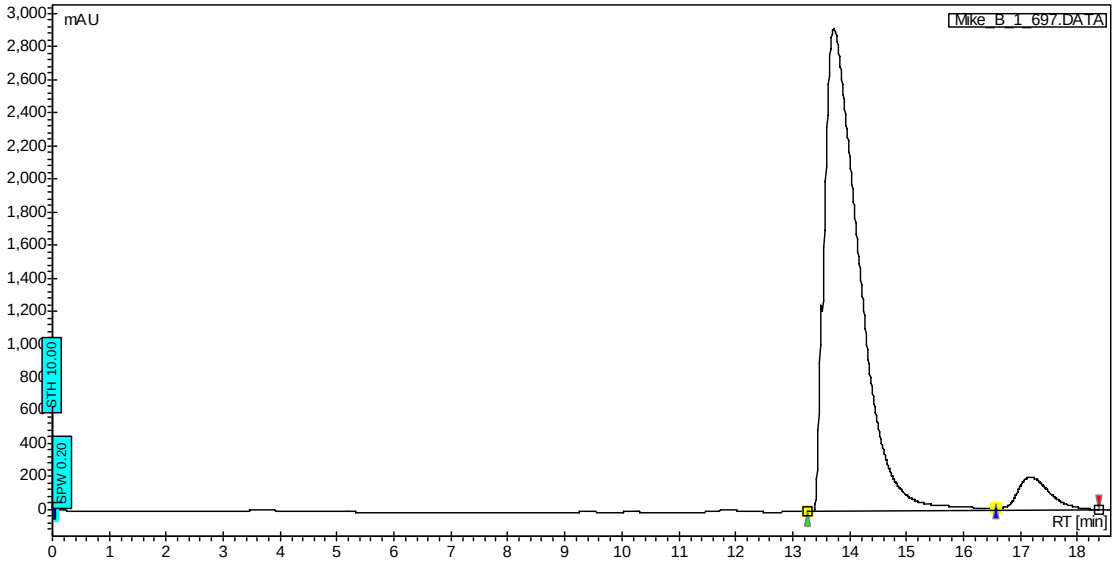


4a



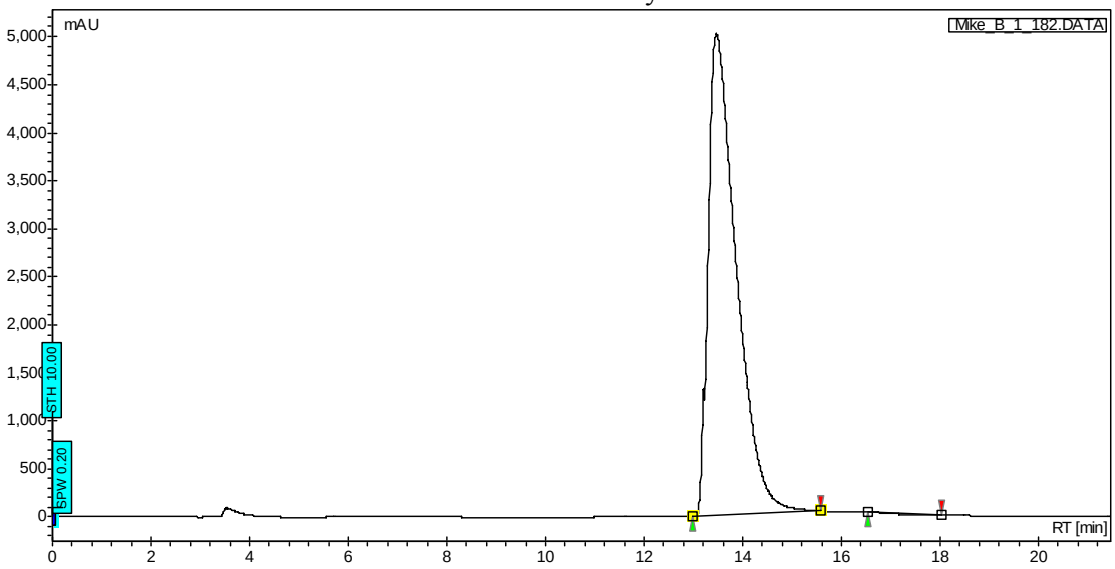
Time (min)	Area (%)
13.99	94.037
16.97	5.963

0.5 g scale:

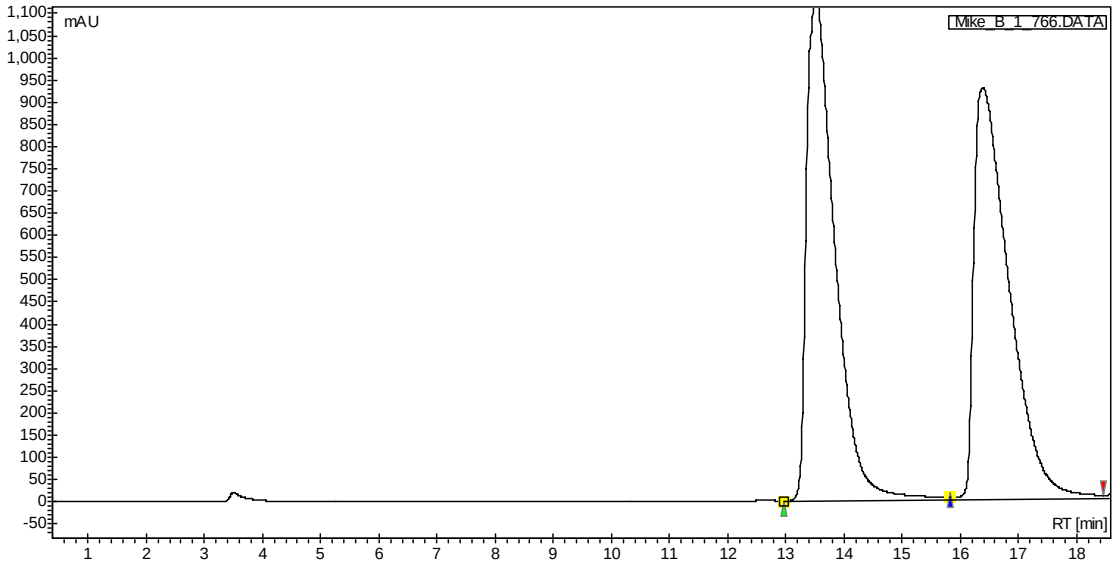


Time (min)	Area (%)
13.73	93.931
17.18	6.069

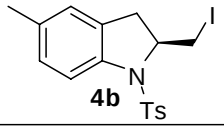
After 1 recrystalization:



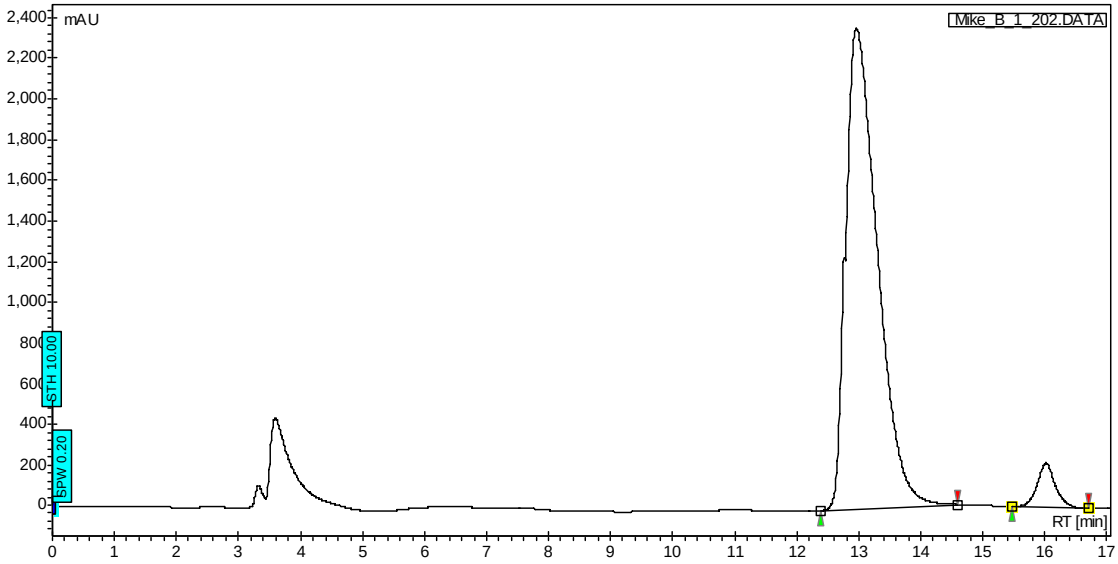
Time (min)	Area (%)
13.47	99.824
17.27	0.176



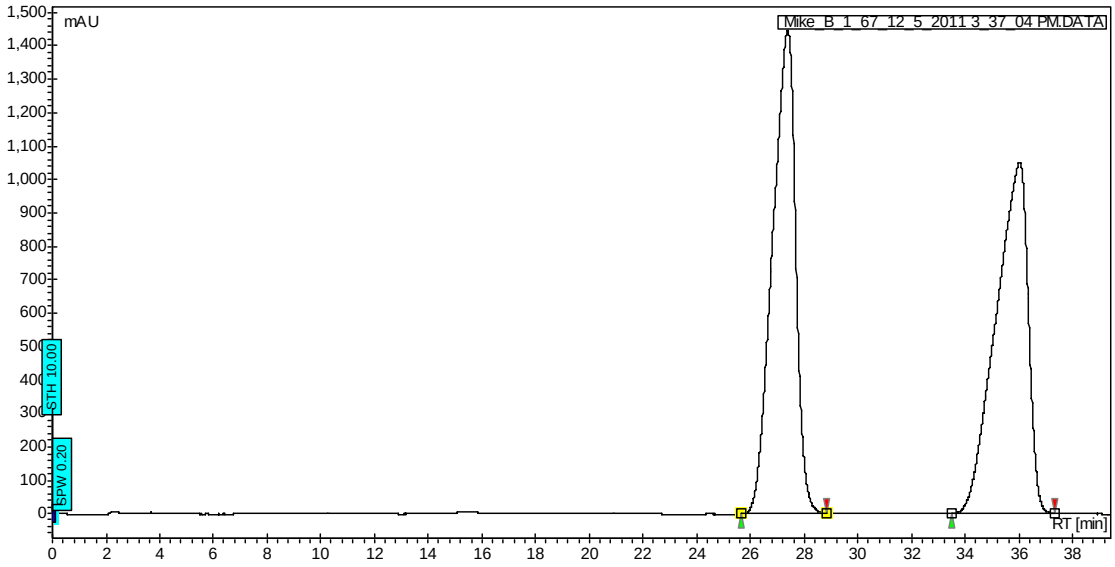
Time (min)	Area (%)
13.5	49.526
16.39	50.474



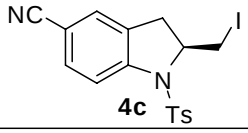
4b



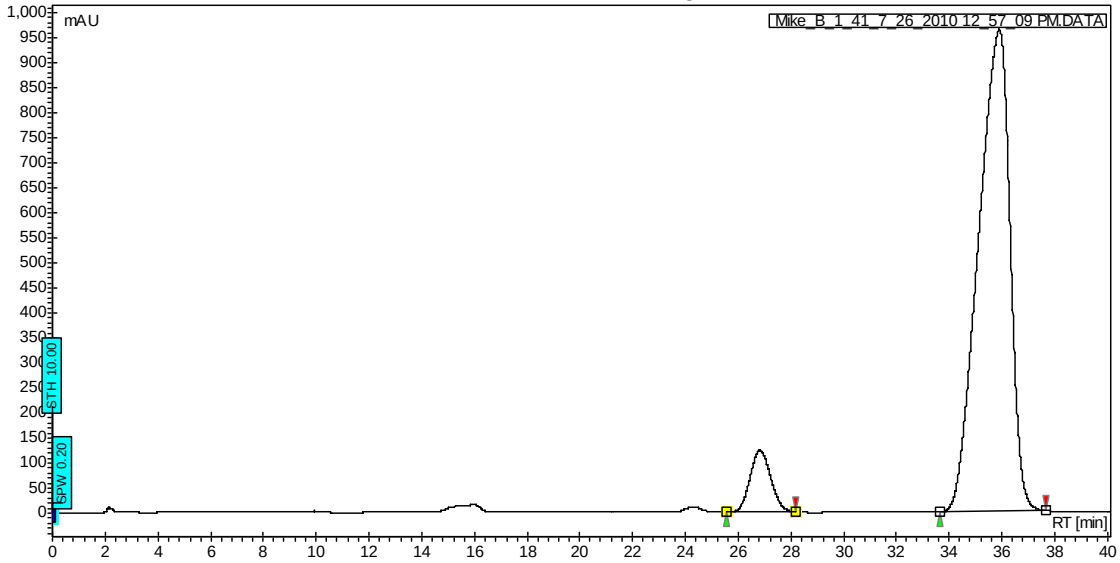
Time (min)	Area (%)
12.96	94.916
16.02	5.084



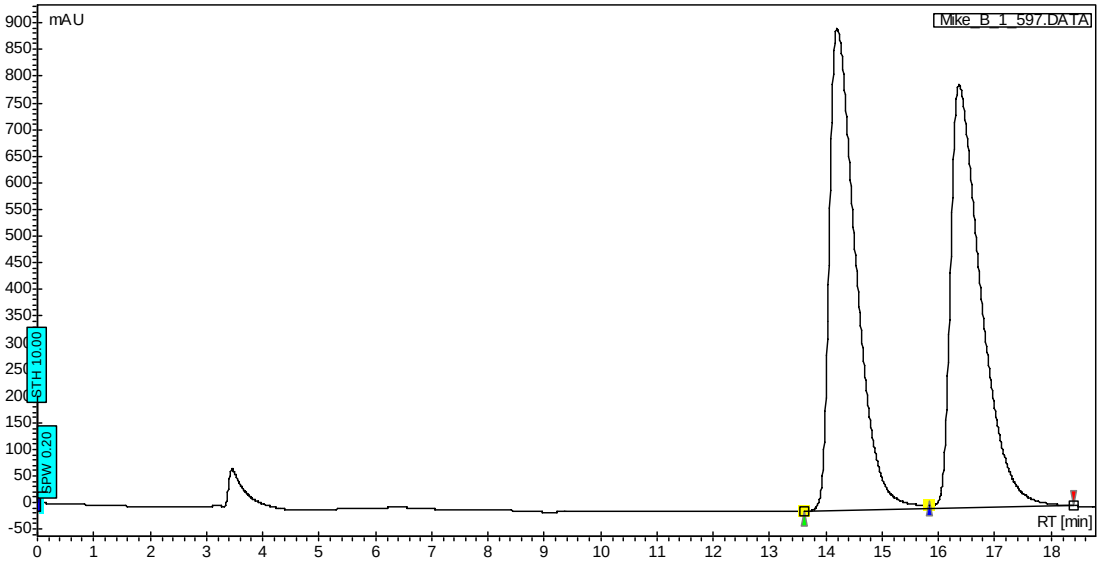
Time (min)	Area (%)
27.38	49.770
36.02	50.23



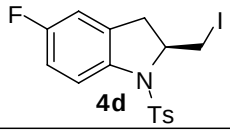
4c



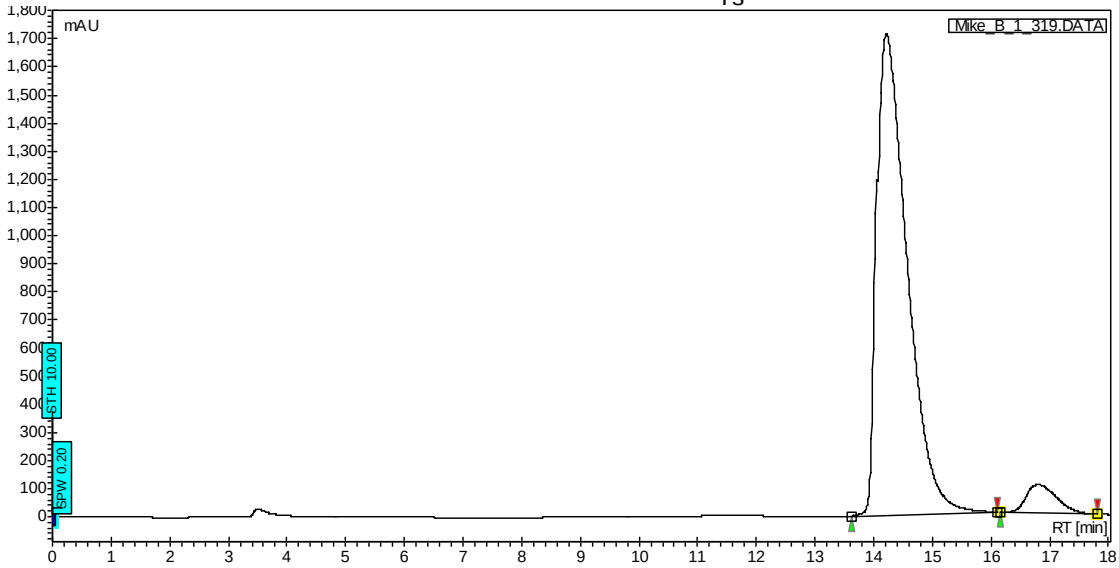
Time (min)	Area (%)
26.83	7.815
35.9	92.185



Time (min)	Area (%)
14.2	49.938
16.37	50.062

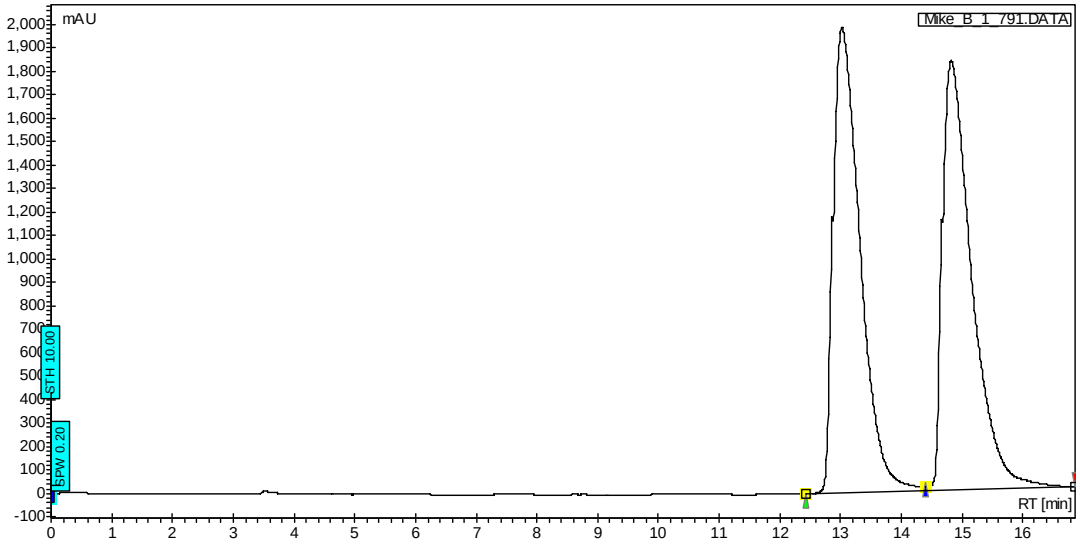


4d

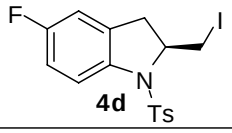


Time (min)	Area (%)
14.21	94.45
16.8	5.55

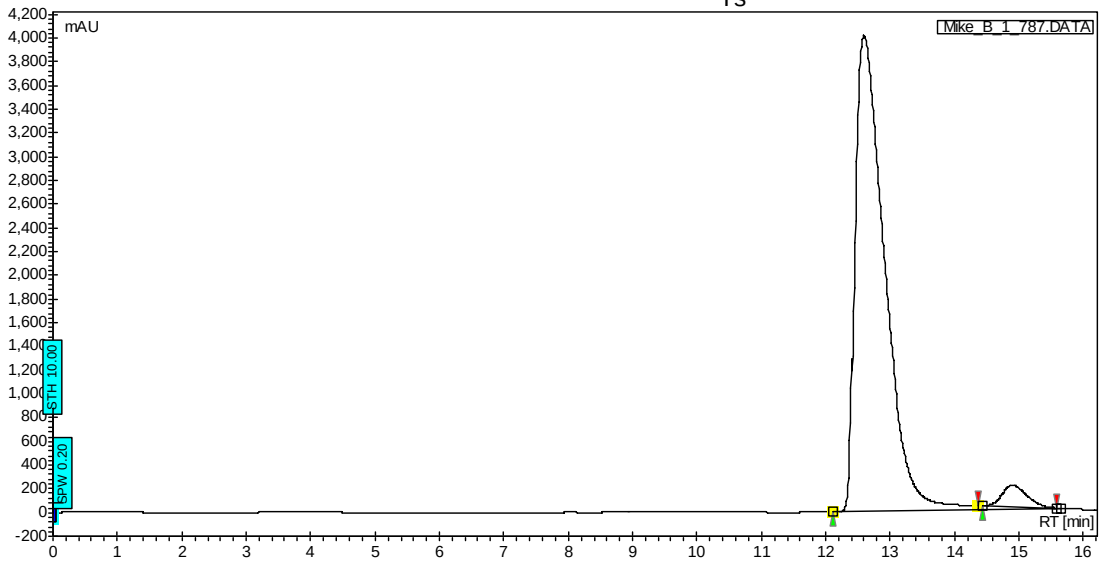
0.25 g scale with the (4*R*,5*S*)-di-Ph-box ligand:



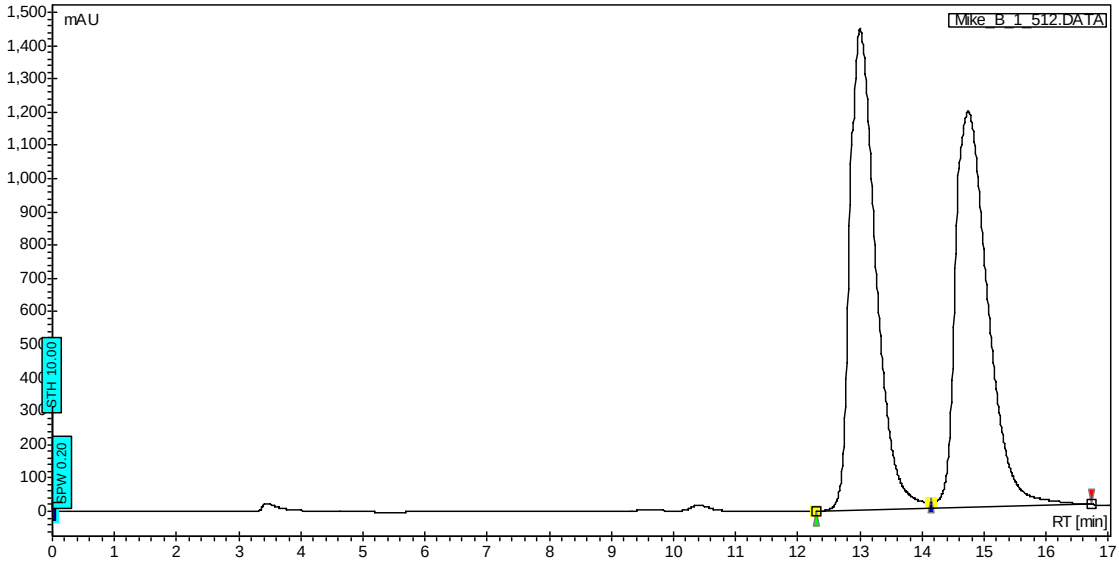
Time (min)	Area (%)
13.02	49.965
14.82	50.035



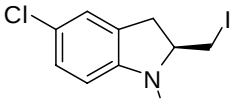
4d



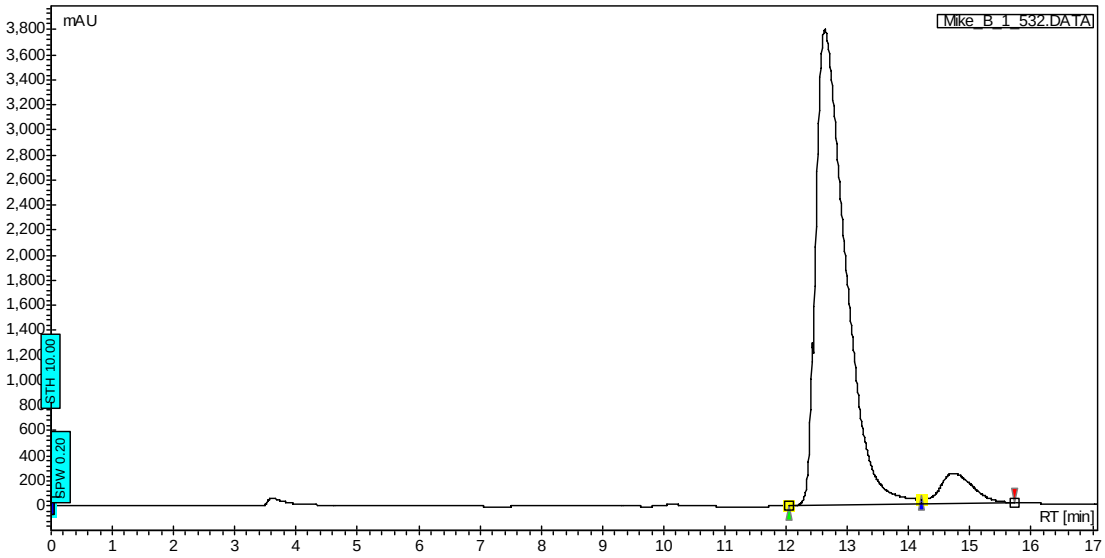
Time (min)	Area (%)
12.59	96.297
14.9	3.703



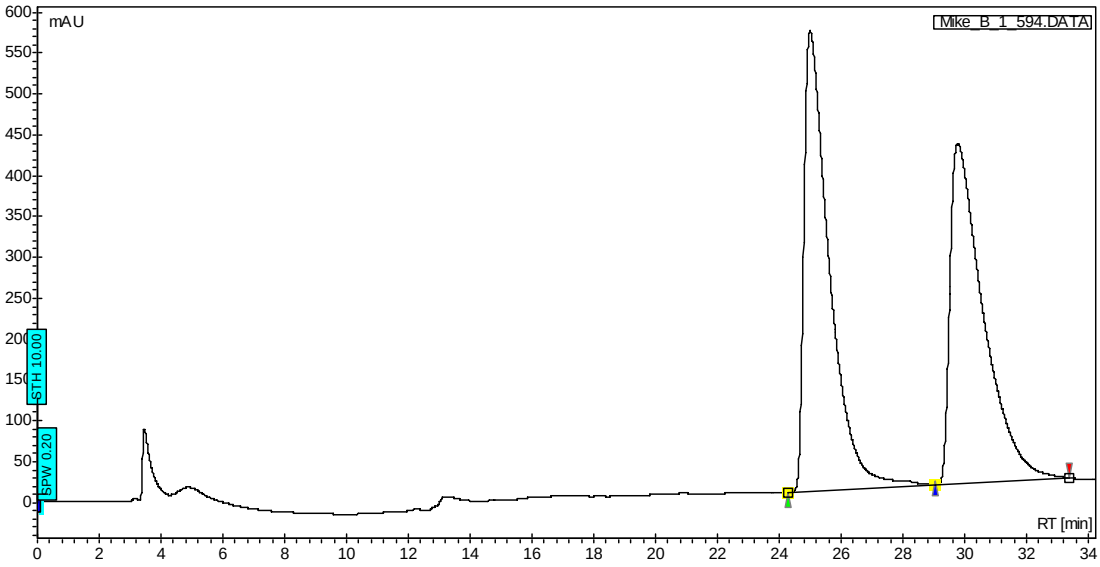
Time (min)	Area (%)
13.01	49.315
14.75	50.685



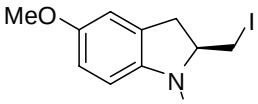
4e



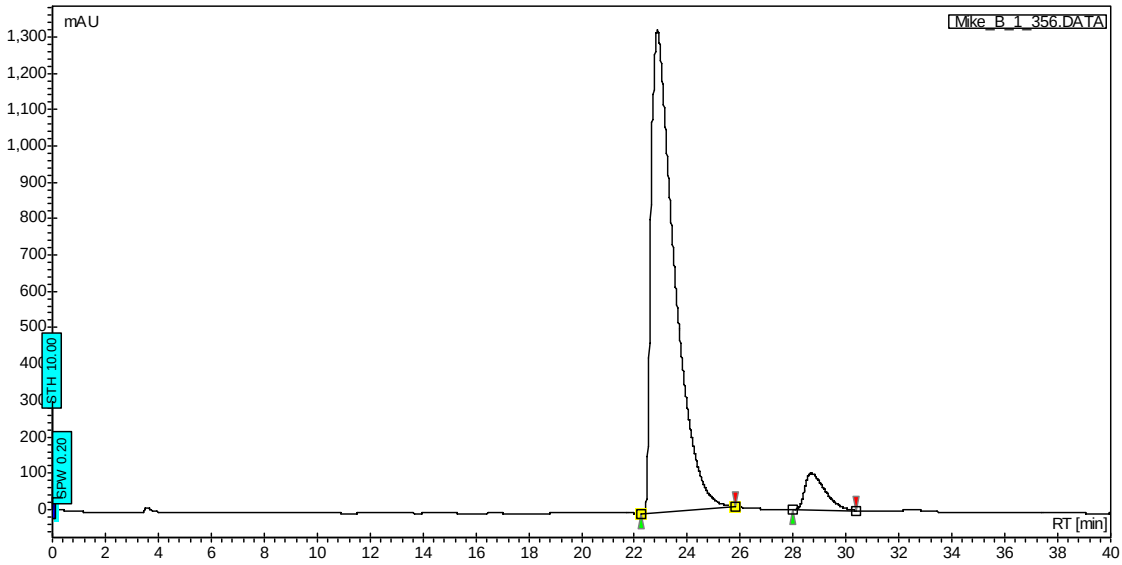
Time (min)	Area (%)
12.63	93.368
14.73	6.632



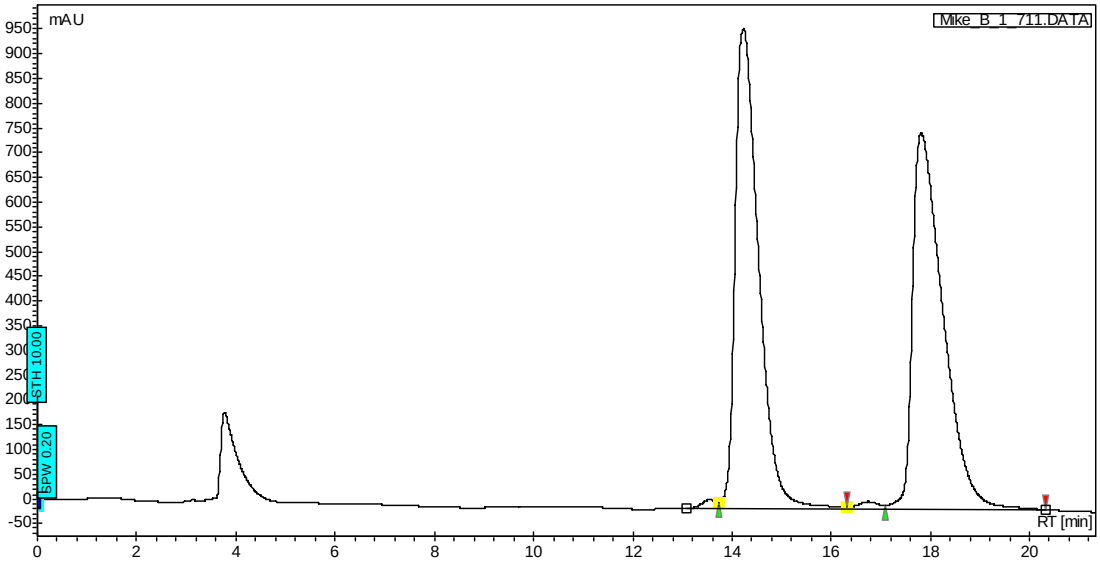
Time (min)	Area (%)
25.01	50.898
29.79	49.102



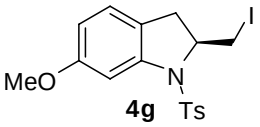
4f



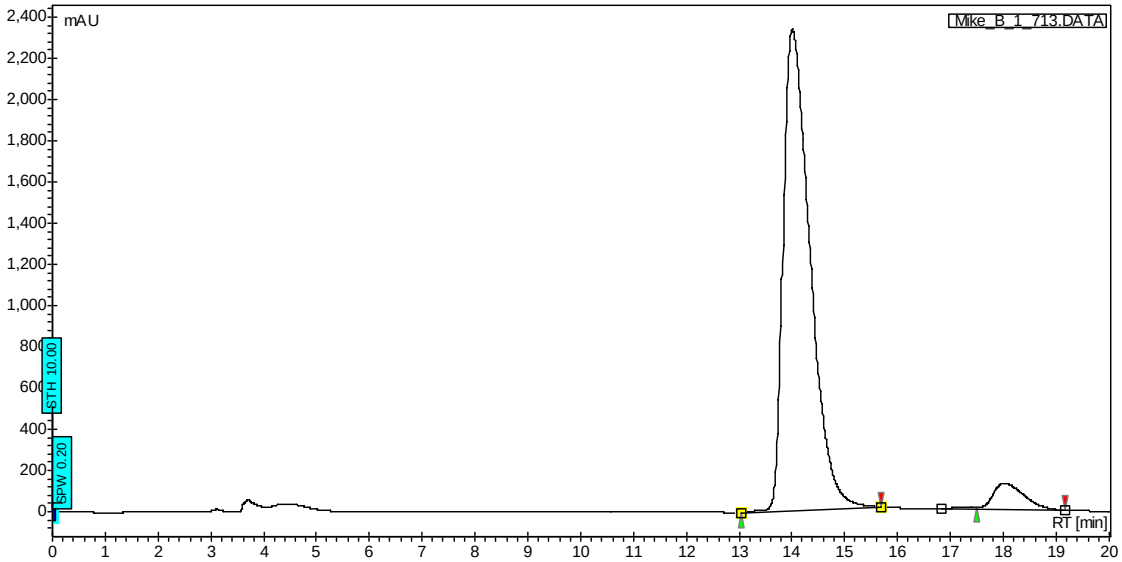
Time (min)	Area (%)
22.87	93.715
28.69	6.285



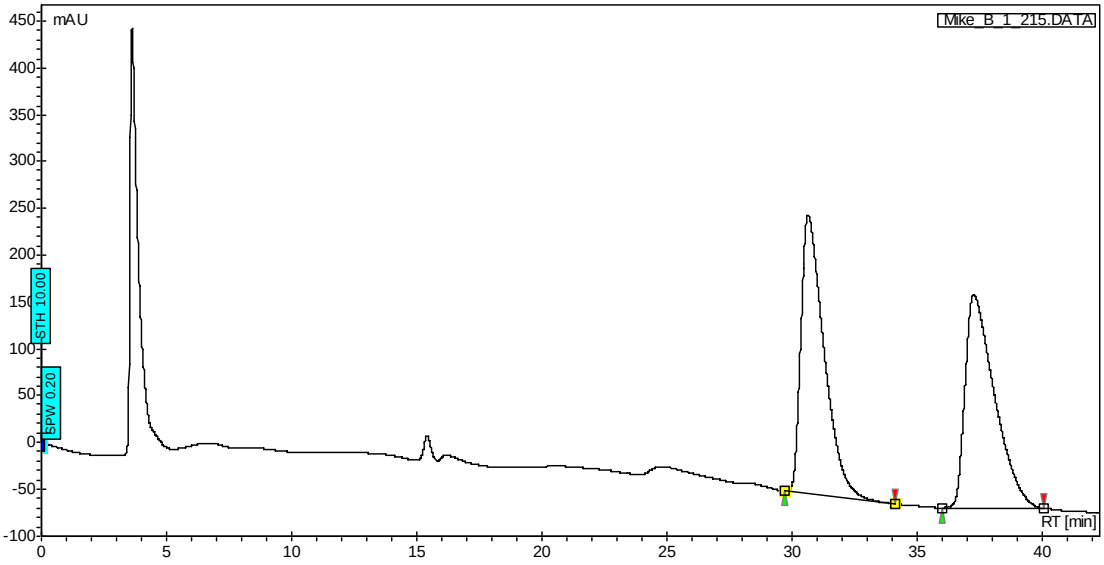
Time (min)	Area (%)
14.23	49.587
17.81	50.413



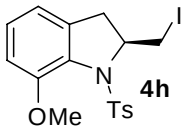
4g



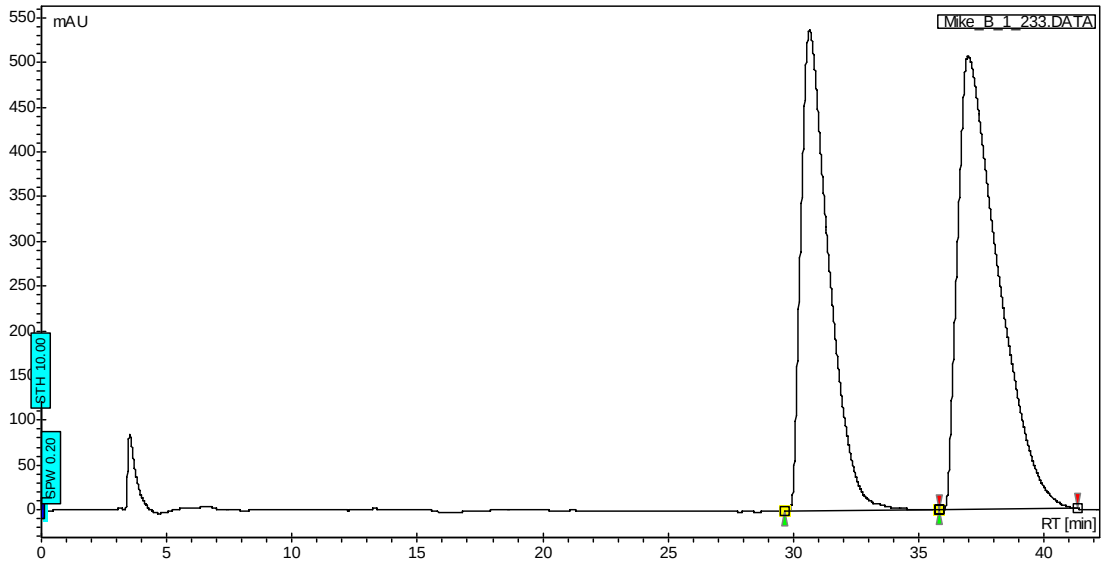
Time (min)	Area (%)
14.01	93.969
18.02	6.031



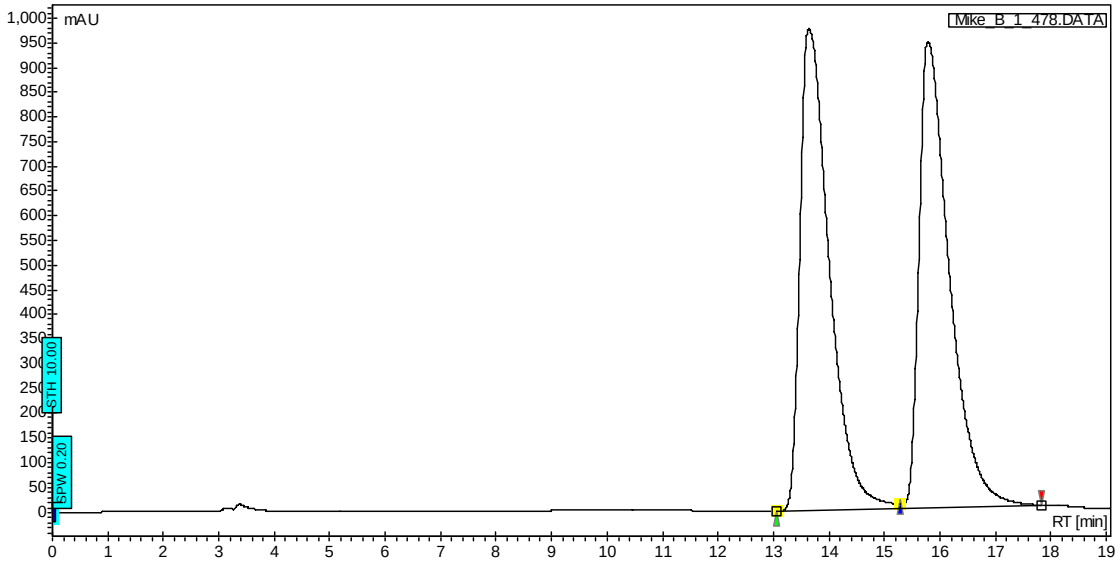
Time (min)	Area (%)
30.63	50.698
37.25	49.302



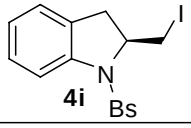
4h



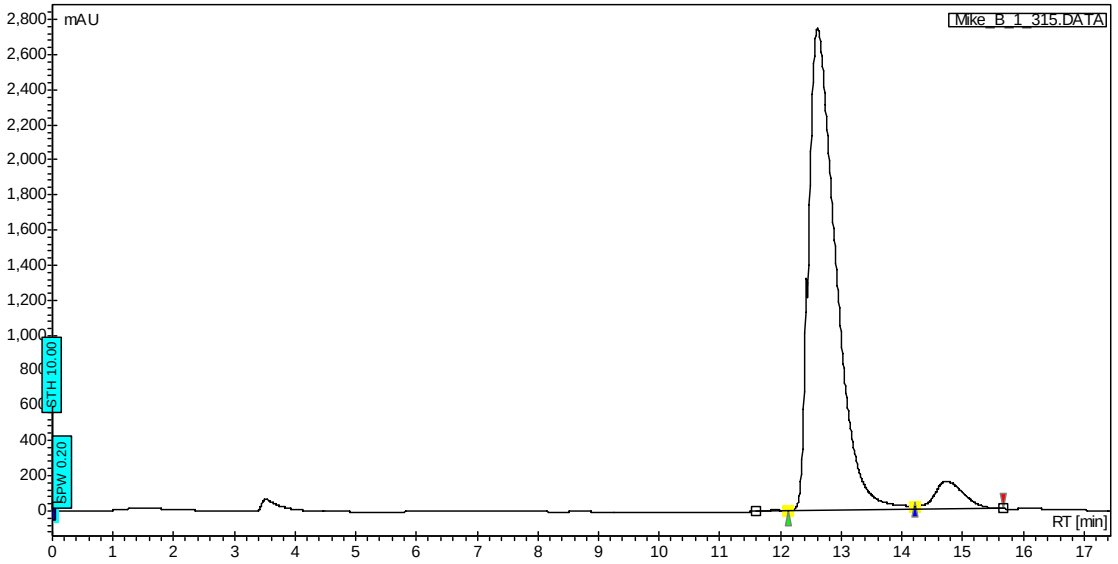
Time (min)	Area (%)
30.64	42.414
36.97	57.586



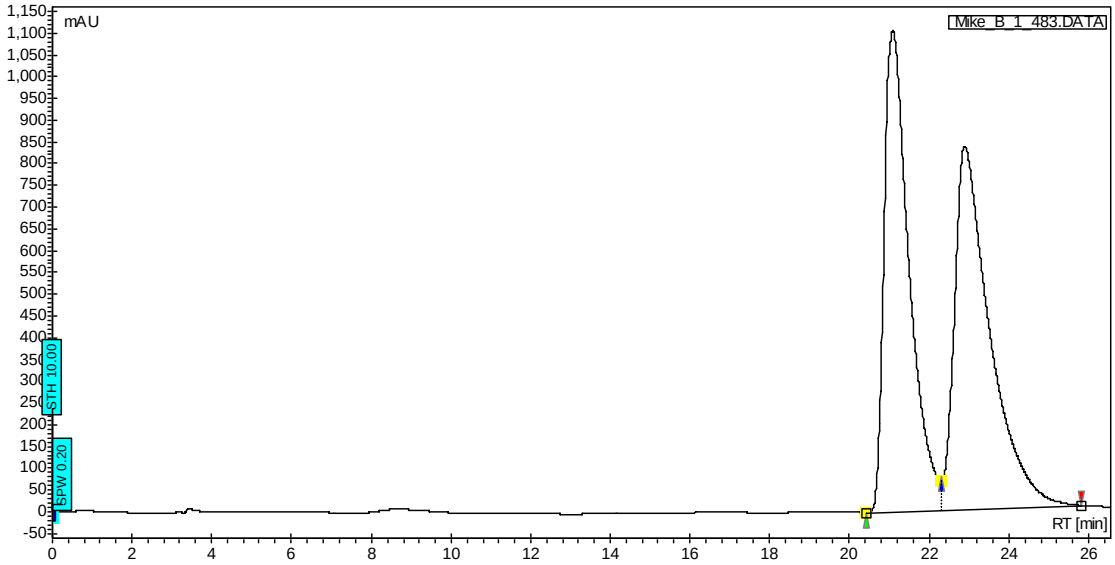
Time (min)	Area (%)
13.65	49.656
15.79	50.344



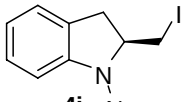
4i



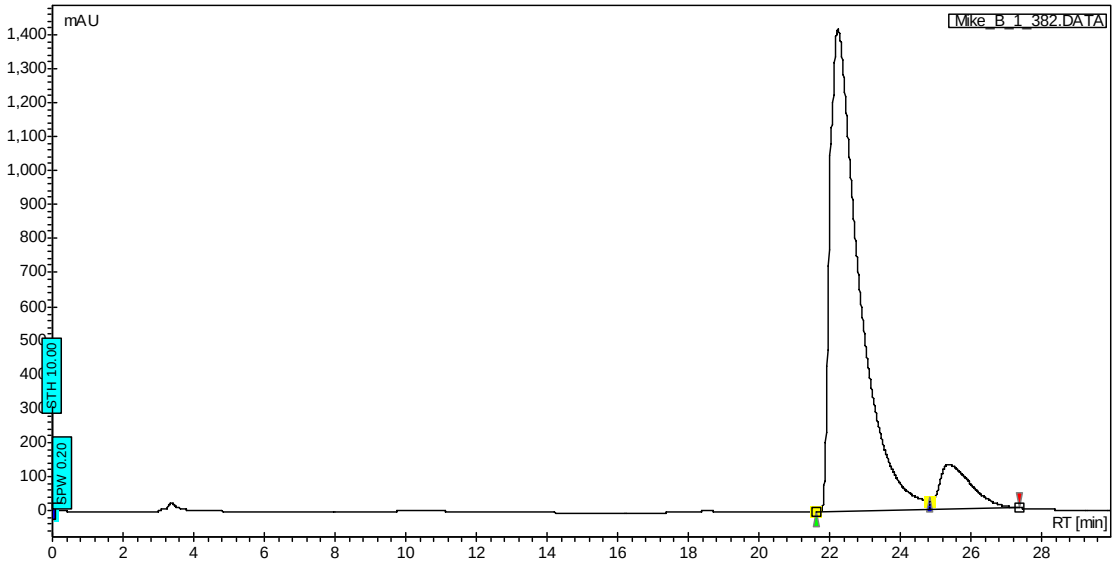
Time (min)	Area (%)
12.61	93.947
14.74	6.053



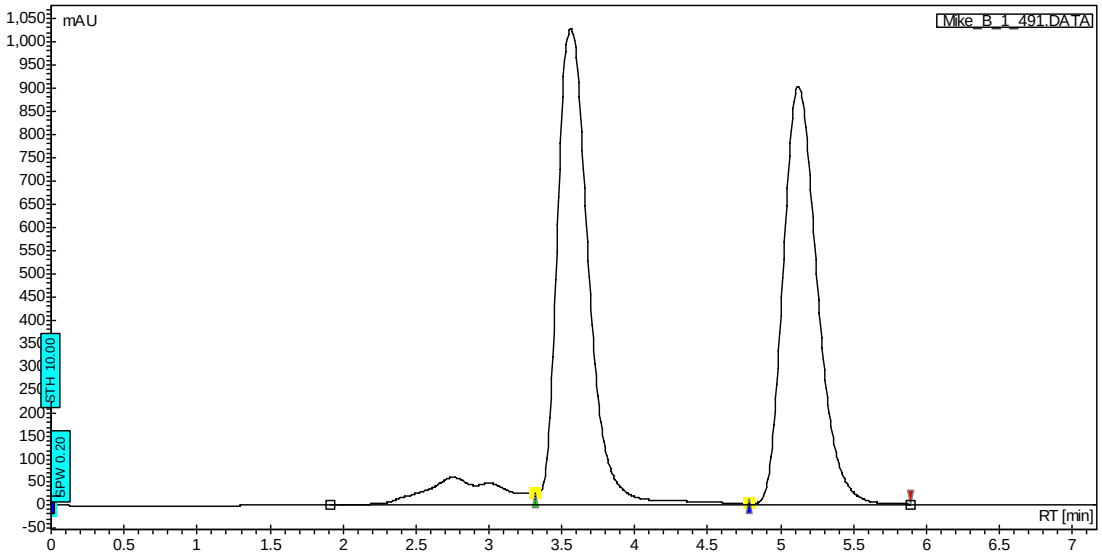
Time (min)	Area (%)
21.09	48.43
22.89	51.57



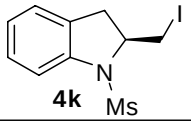
4j



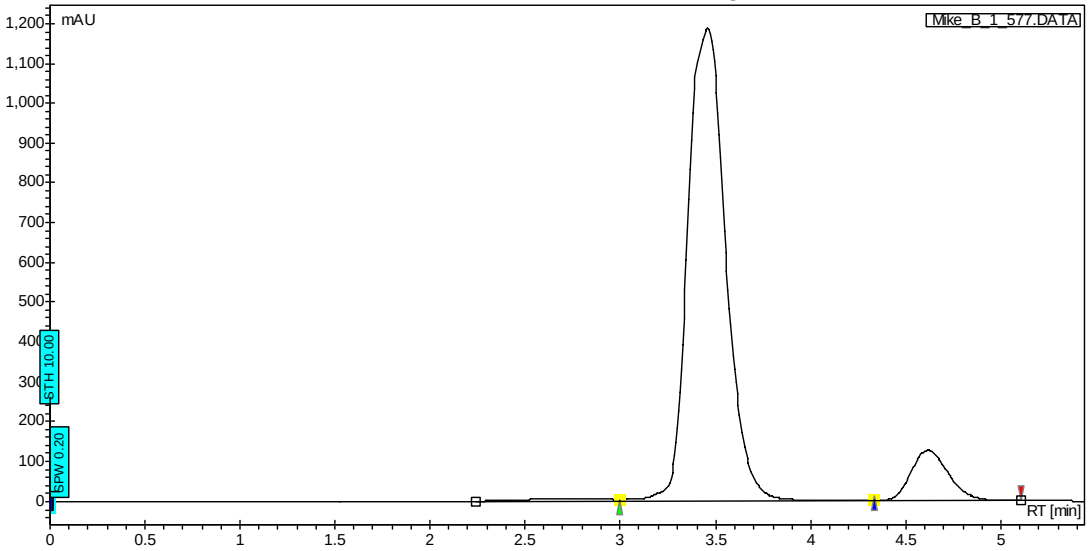
Time (min)	Area (%)
22.24	90.705
25.38	9.295



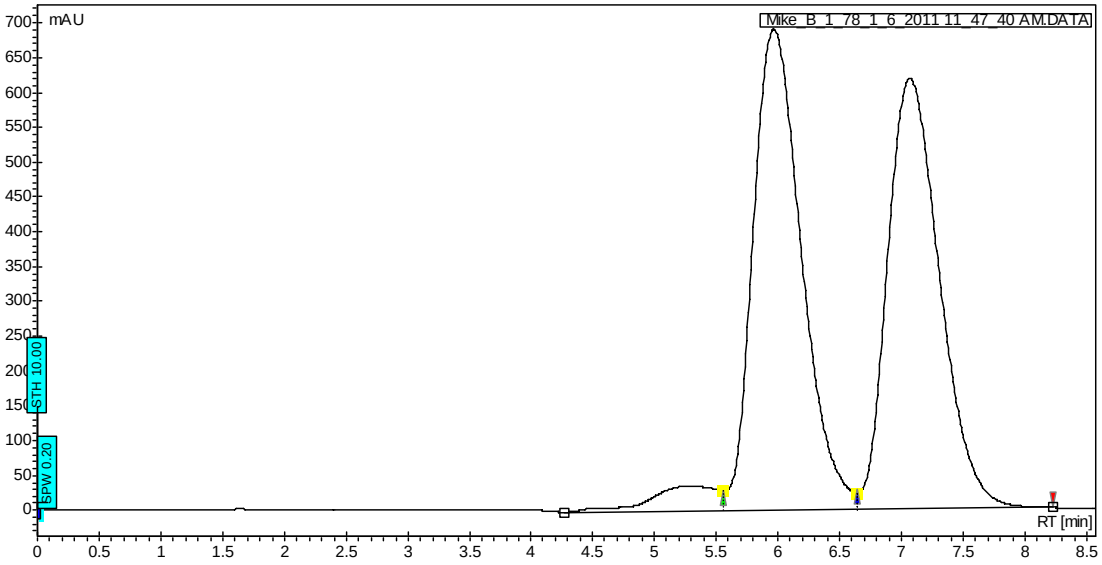
Time (min)	Area (%)
3.56	50.796
5.12	49.204



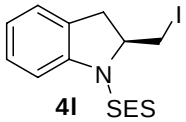
4k



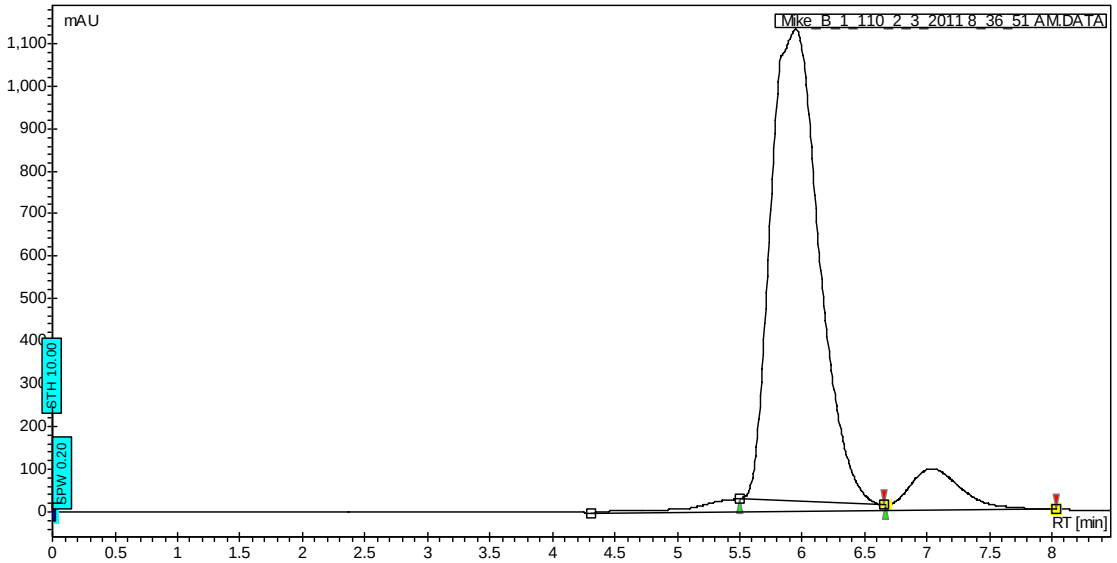
Time (min)	Area (%)
3.46	90.35
4.62	9.65



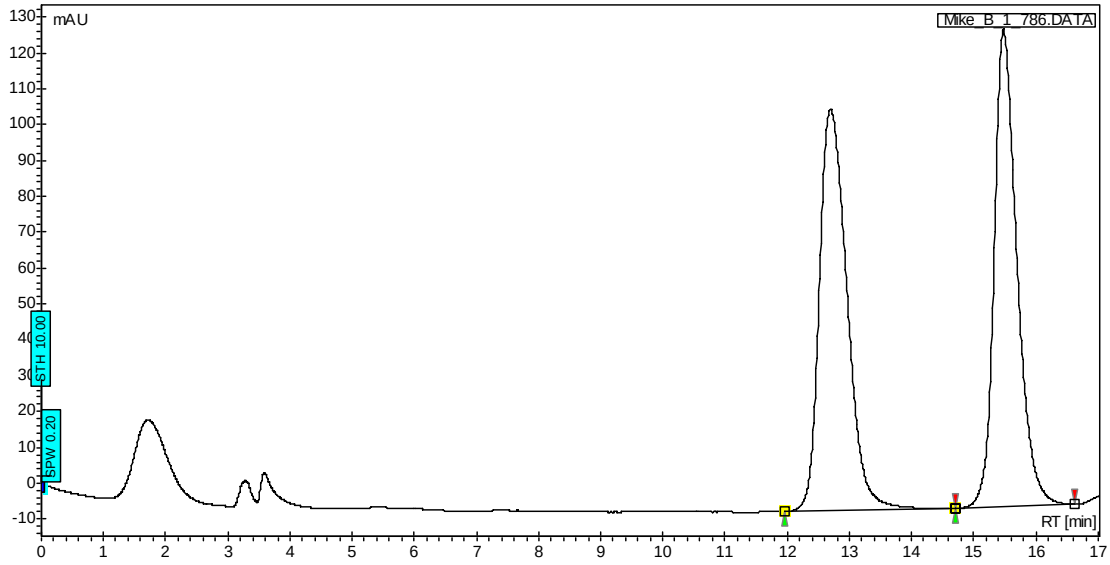
Time (min)	Area (%)
5.97	50.965
7.07	49.035



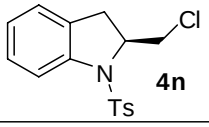
4l



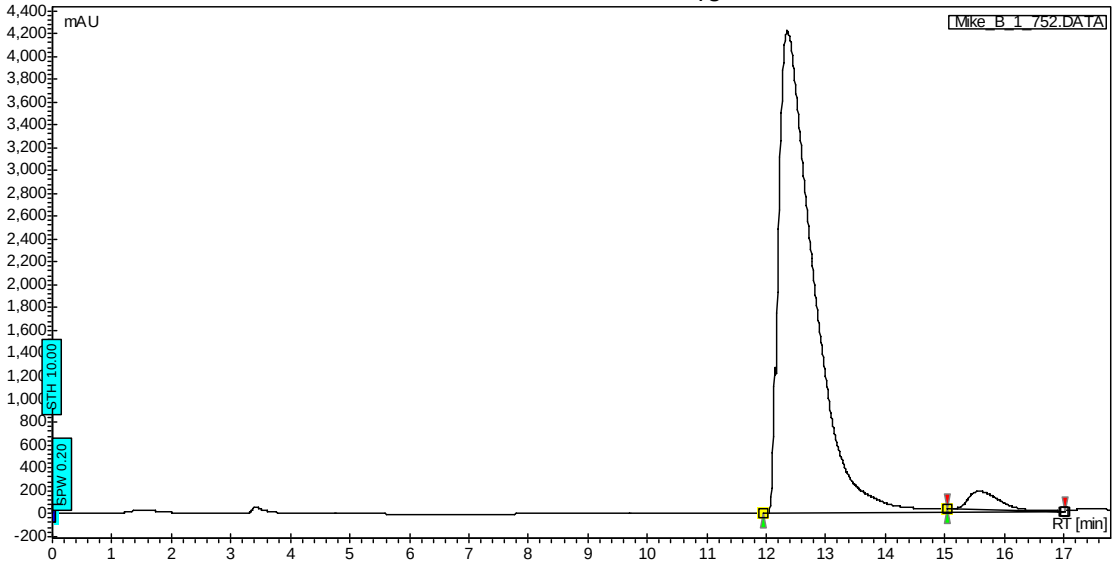
Time (min)	Area (%)
5.95	91.146
7.03	8.854



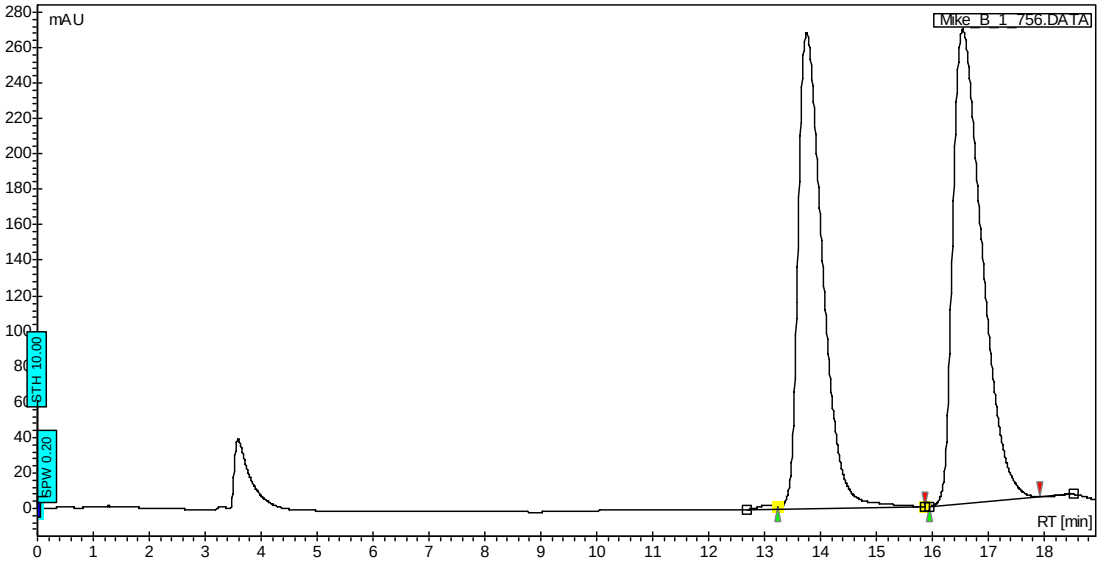
Time (min)	Area (%)
12.69	50.584
15.48	49.416



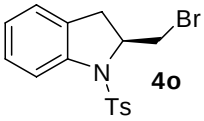
4n



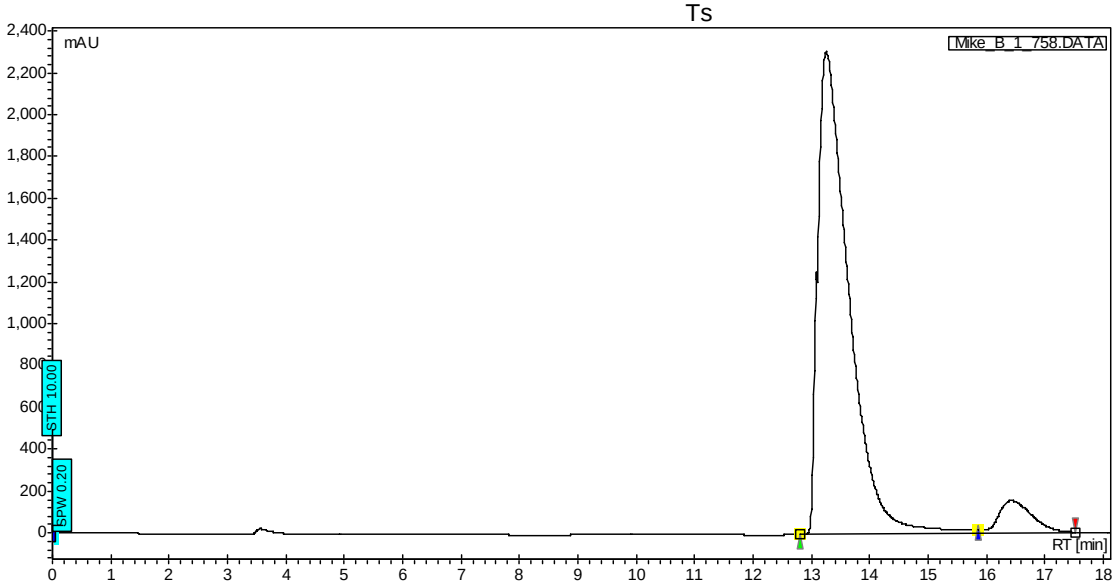
Time (min)	Area (%)
12.35	96.792
15.58	3.208



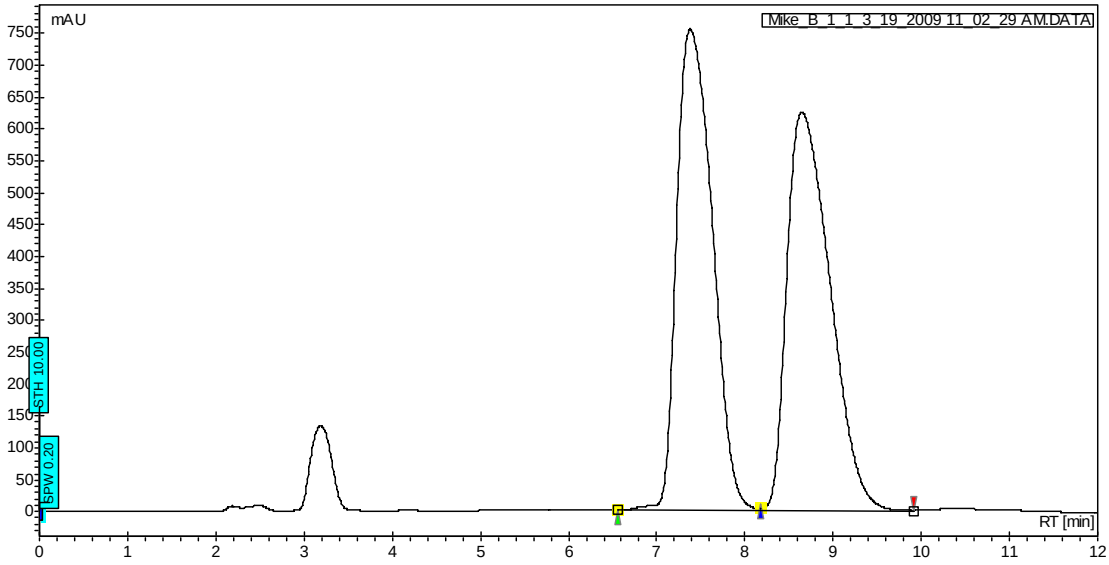
Time (min)	Area (%)
13.76	45.531
16.55	54.469



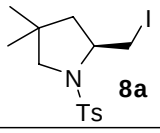
4o



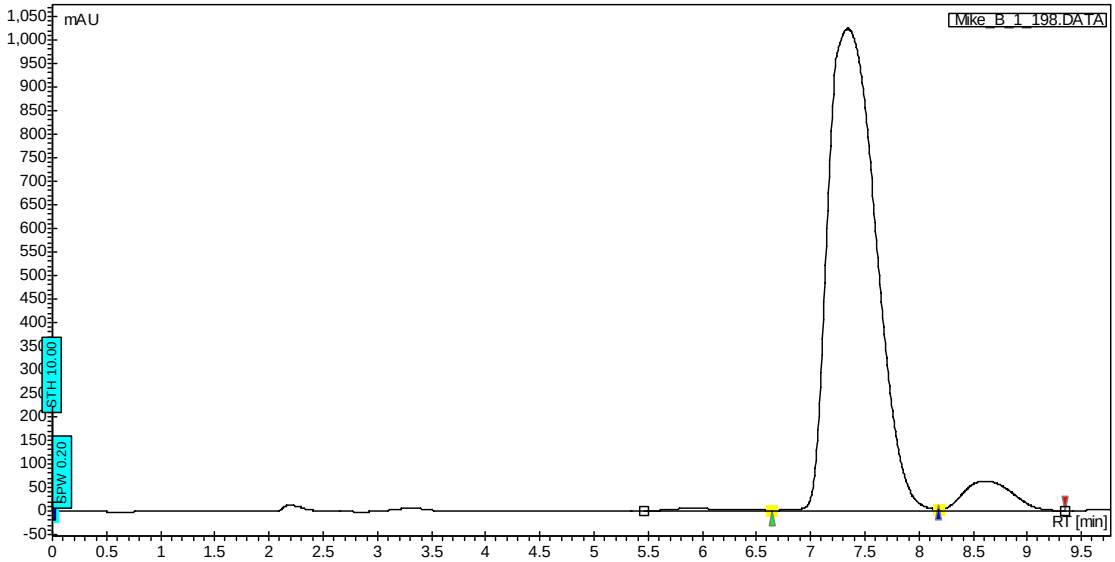
Time (min)	Area (%)
13.25	93.345
16.43	6.655



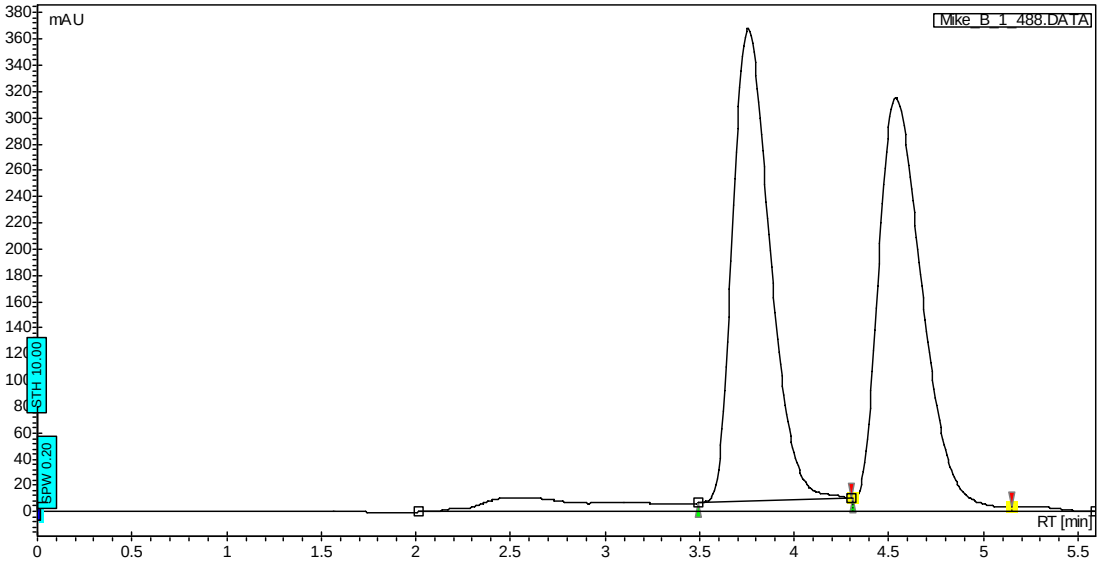
Time (min)	Area (%)
7.38	50.015
8.65	49.985



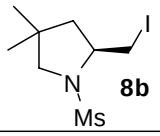
8a



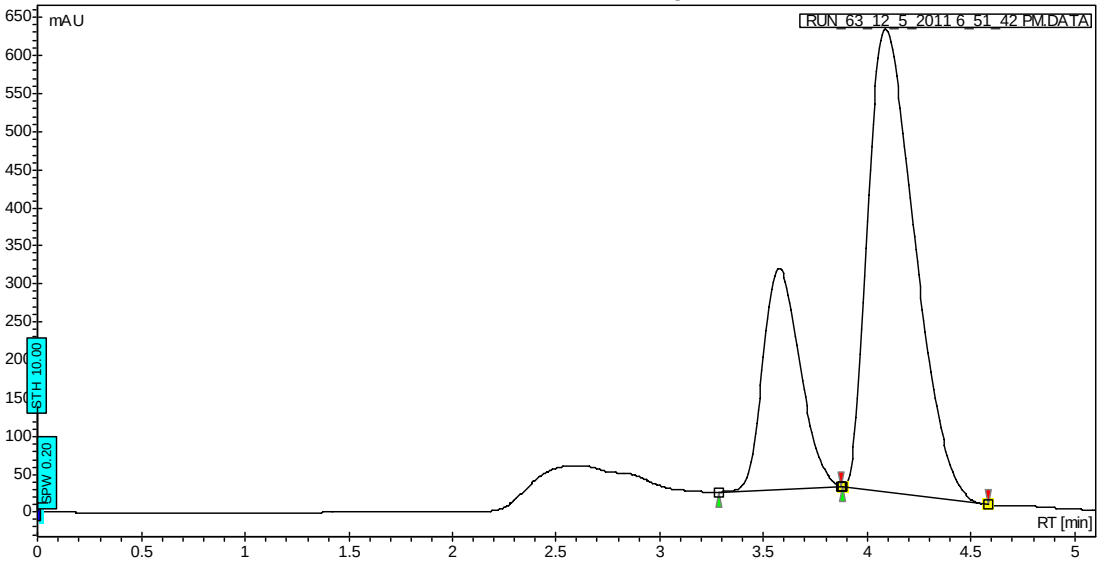
Time (min)	Area (%)
7.34	94.099
8.61	5.901



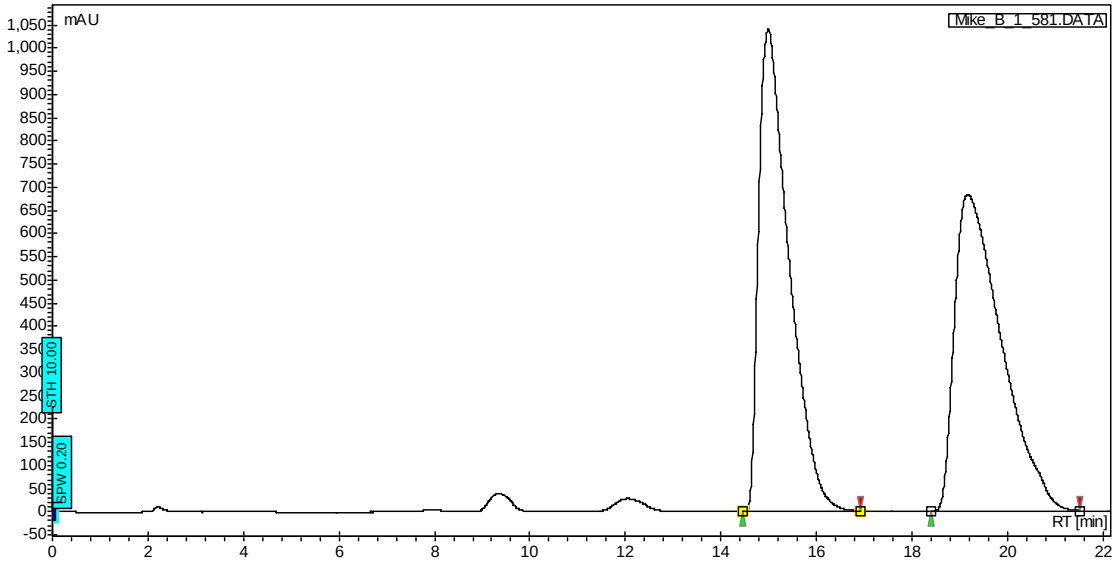
Time (min)	Area (%)
3.76	49.108
4.54	50.892



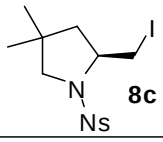
8b



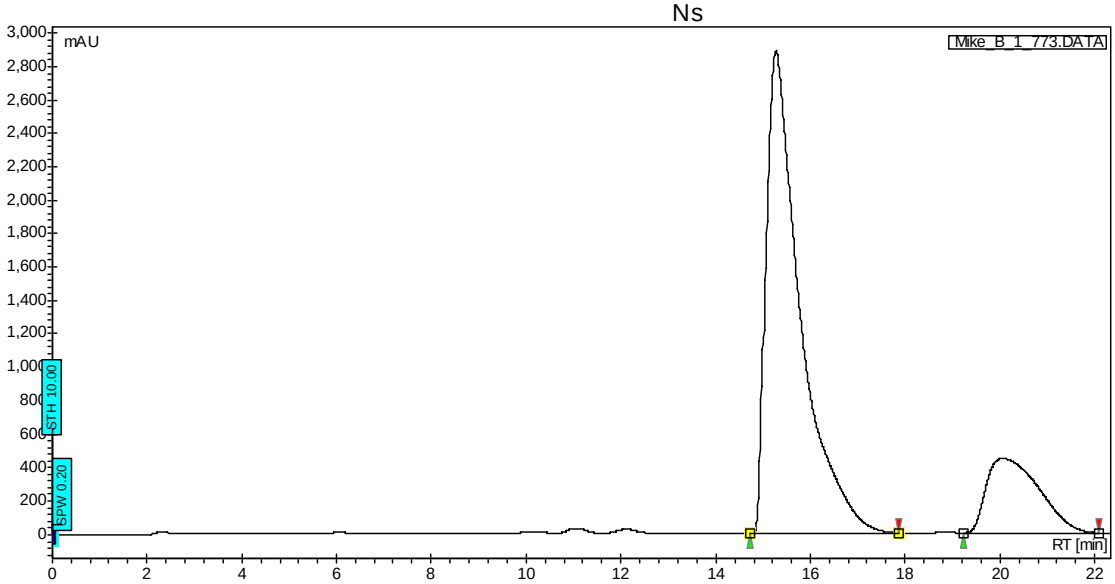
Time (min)	Area (%)
3.57	27.234
4.09	72.766



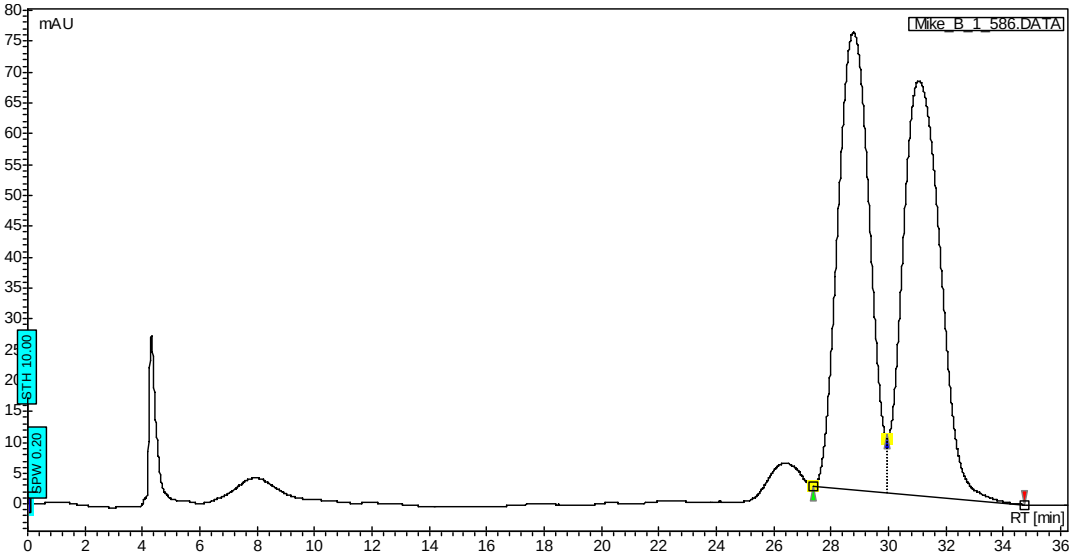
Time (min)	Area (%)
14.99	49.699
19.17	50.301



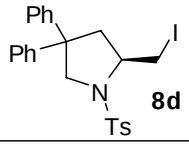
8c



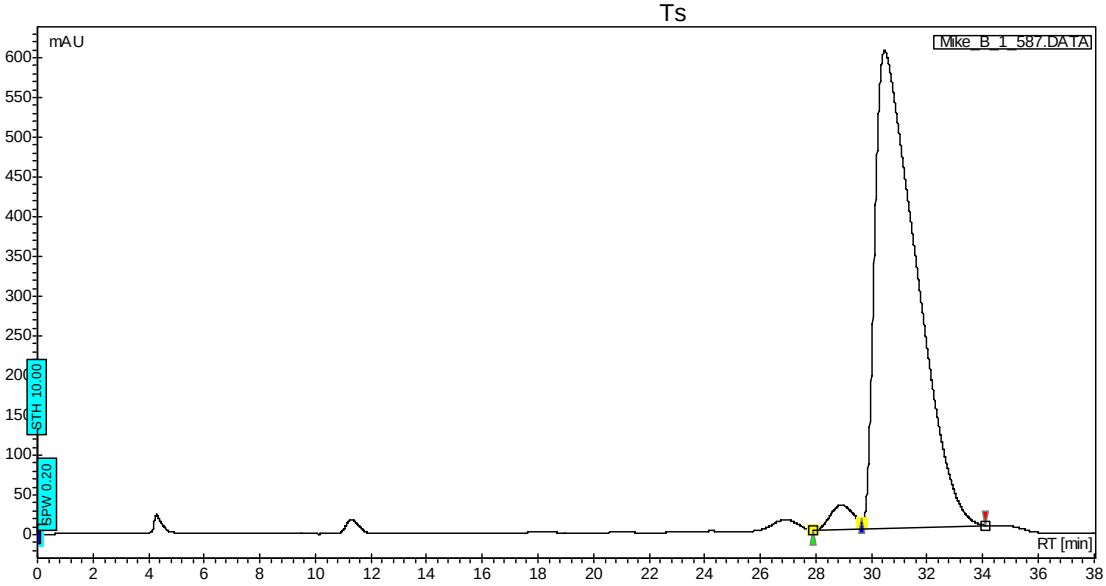
Time (min)	Area (%)
15.27	80.678
20.06	19.322



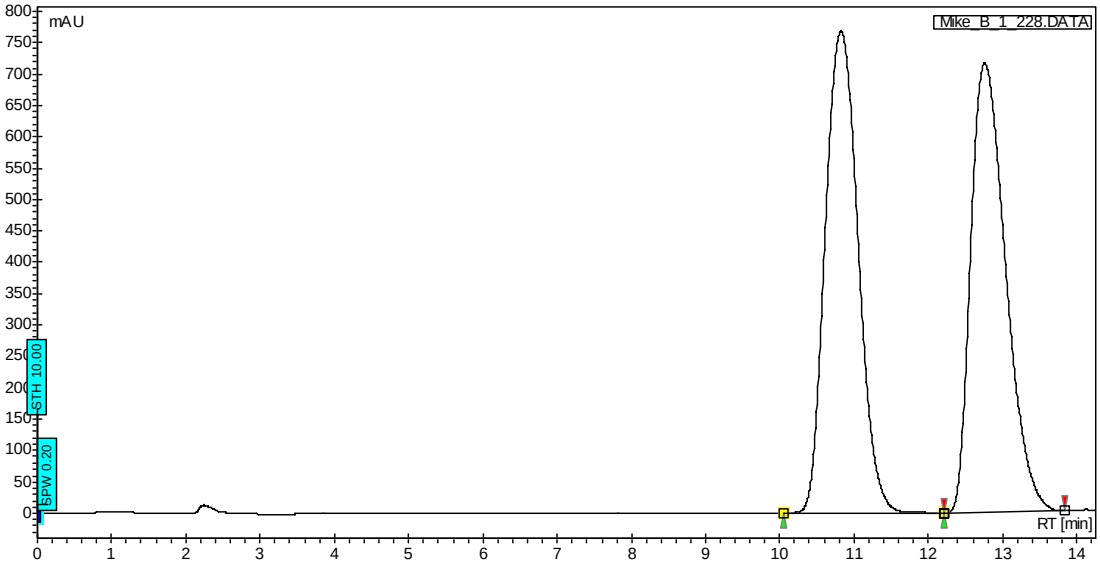
Time (min)	Area (%)
28.79	48.24
31.07	51.76



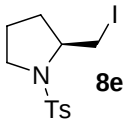
8d



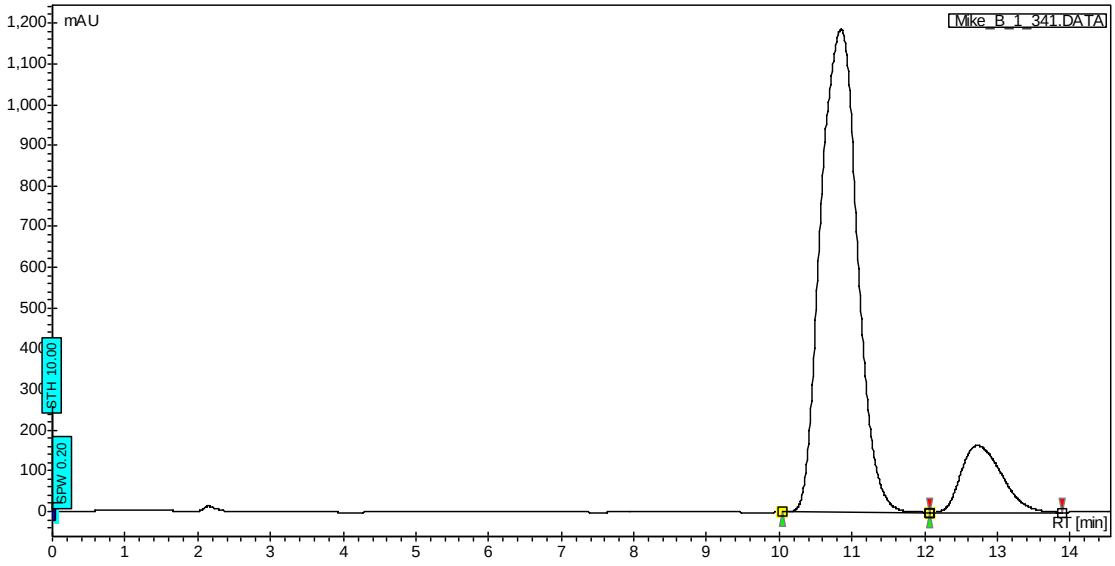
Time (min)	Area (%)
28.93	2.777
30.47	97.223



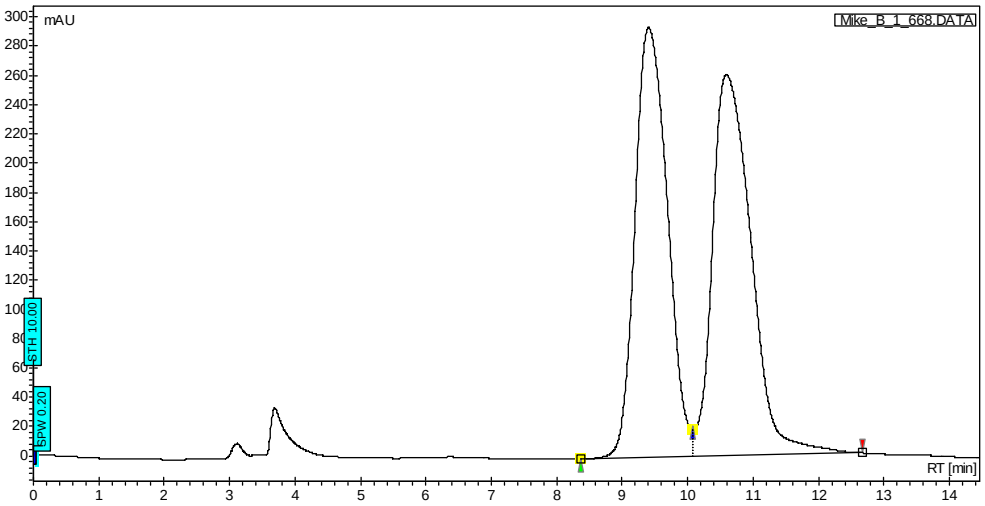
Time (min)	Area (%)
10.83	50.157
12.76	49.843



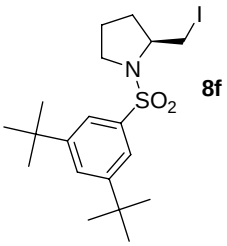
8e



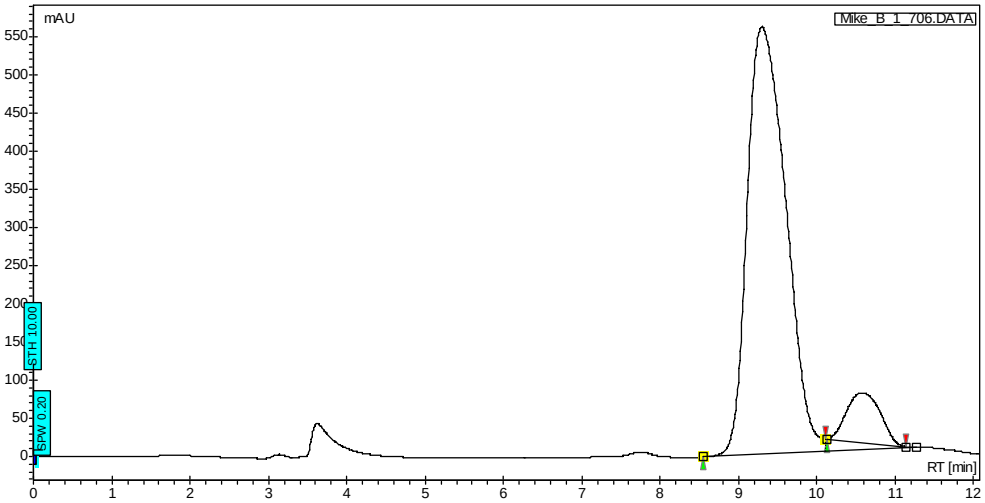
Time (min)	Area (%)
10.85	86.645
12.73	13.355



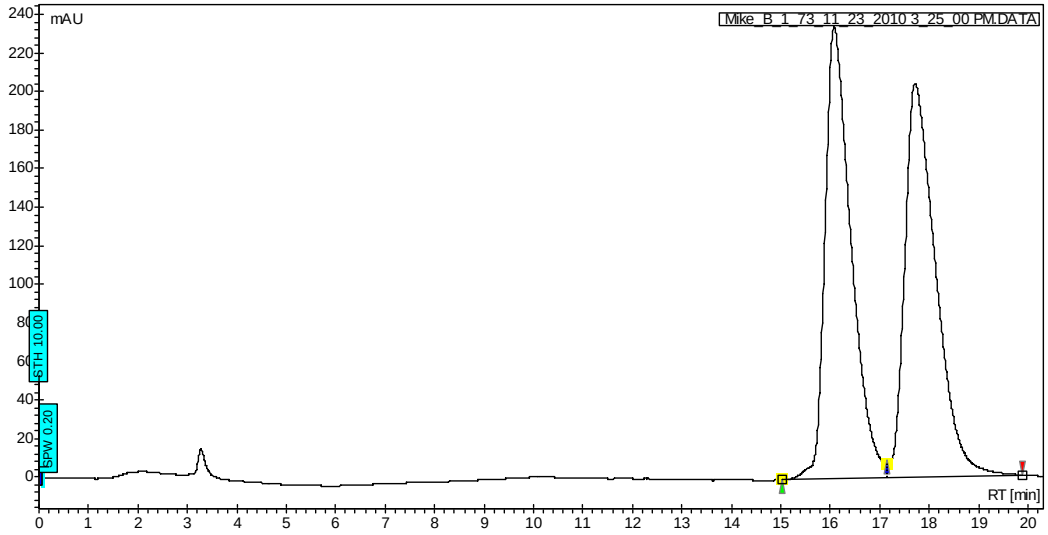
Time (min)	Area (%)
9.4	48.655
10.59	51.345



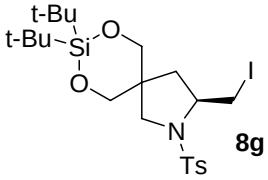
8f



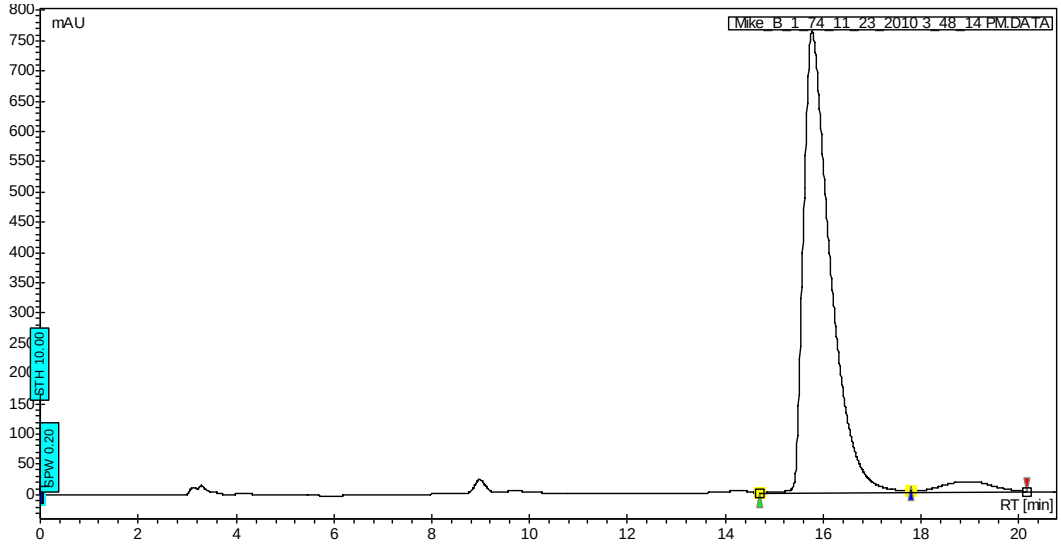
Time (min)	Area (%)
9.3	90.72
10.59	9.28



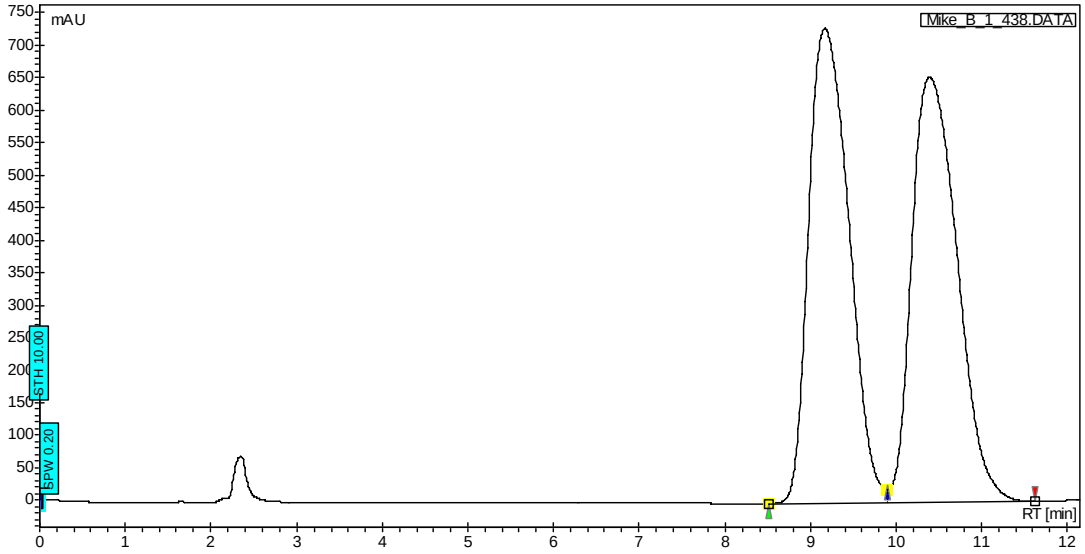
Time (min)	Area (%)
16.07	49.236
17.71	50.764



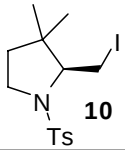
8g



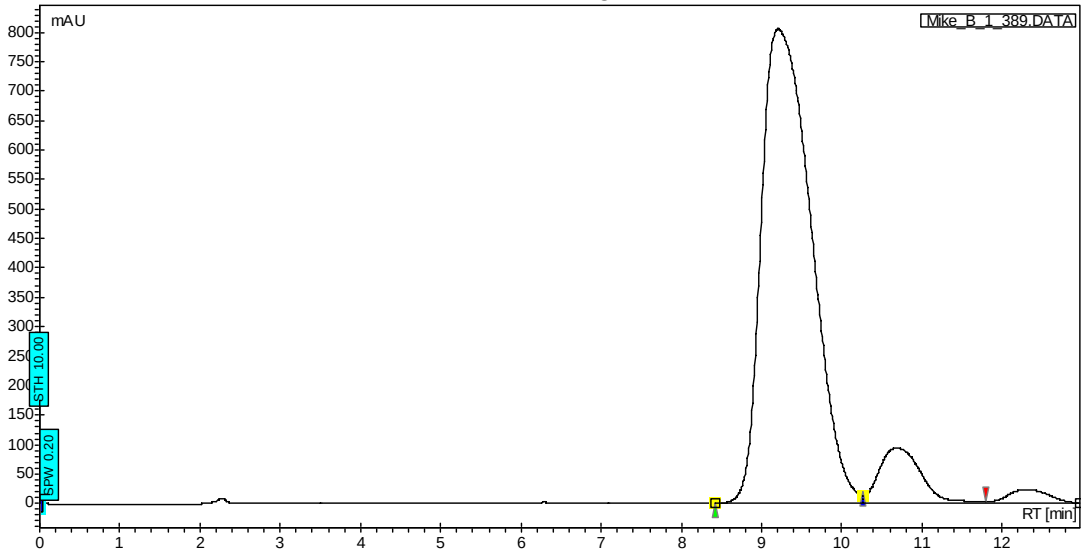
Time (min)	Area (%)
15.77	95.943
18.98	4.057



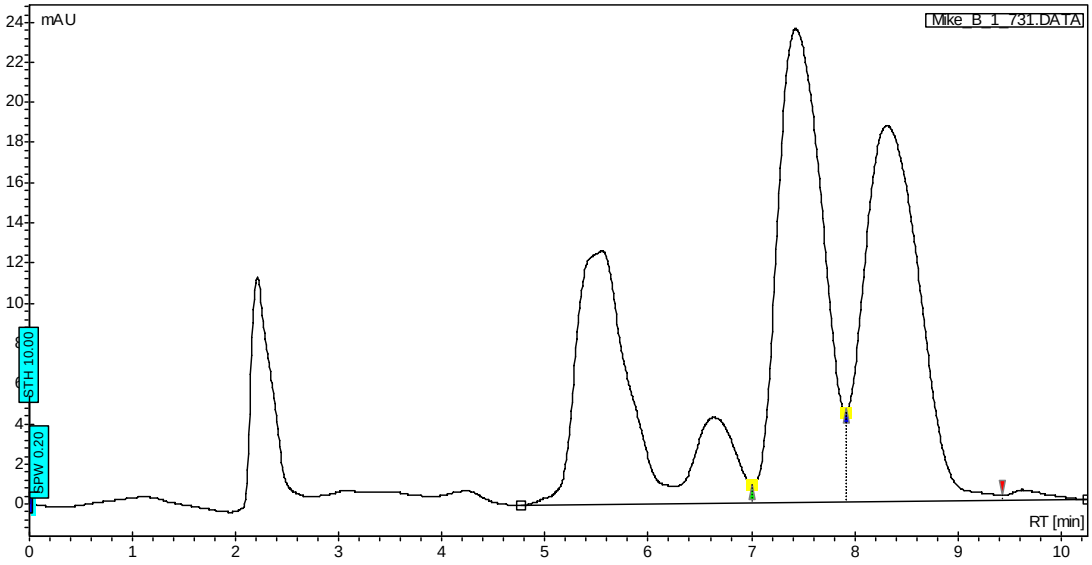
Time (min)	Area (%)
9.17	49.685
10.39	50.315



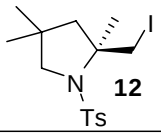
10



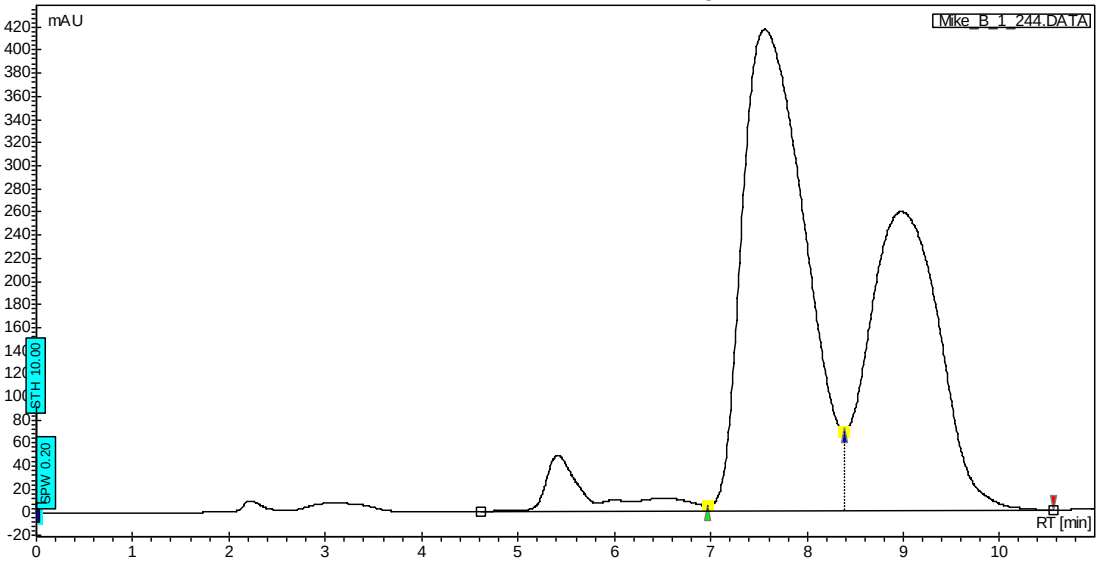
Time (min)	Area (%)
9.21	91.09
10.69	8.91



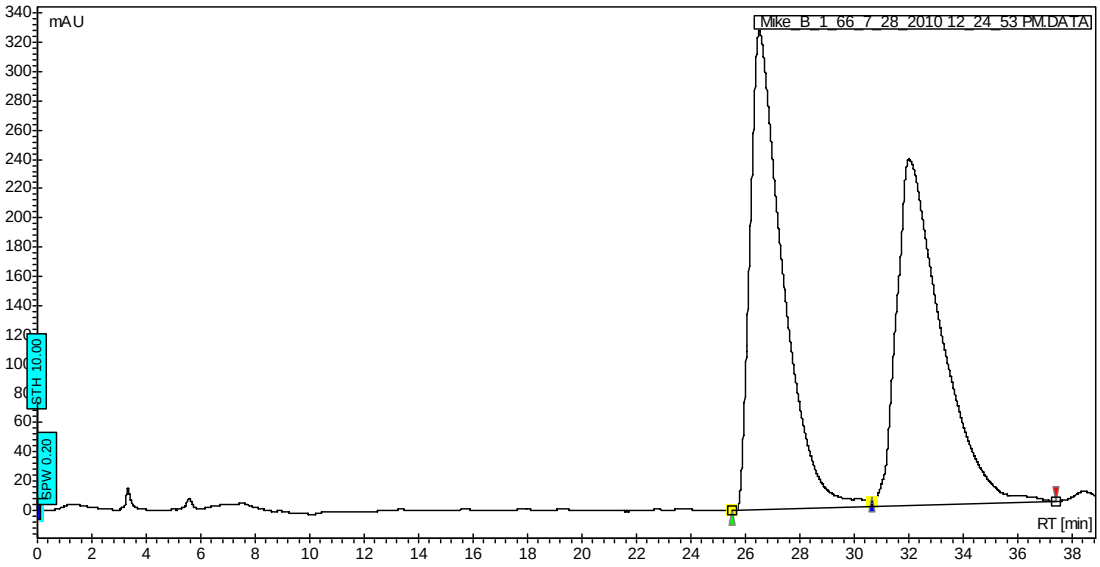
Time (min)	Area (%)
7.43	50.383
8.31	49.617



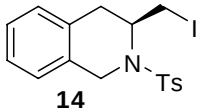
12



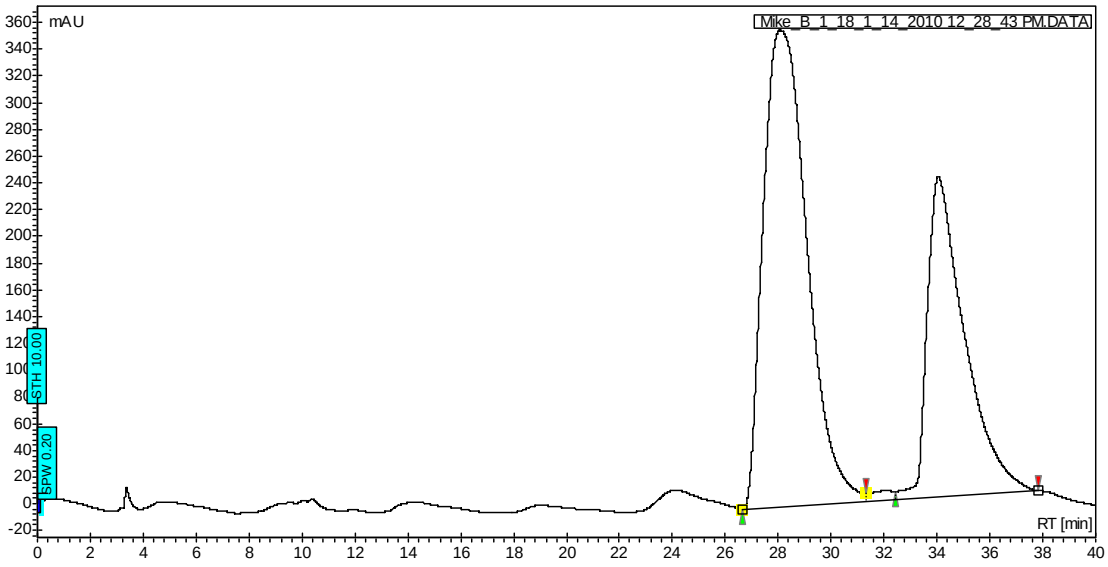
Time (min)	Area (%)
7.56	58.445
8.98	41.555



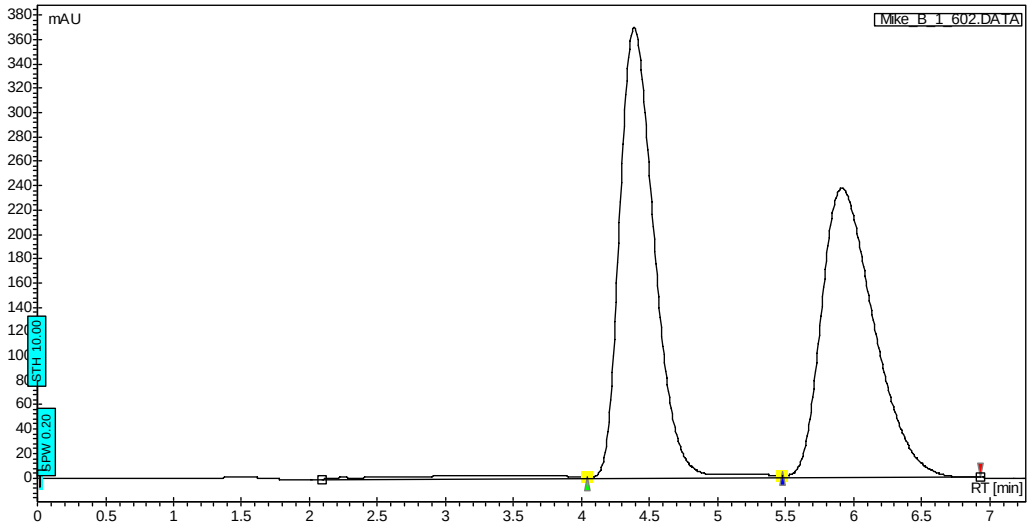
Time (min)	Area (%)
26.52	50.187
32.02	49.813



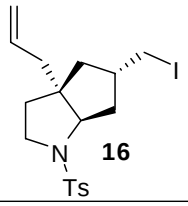
14



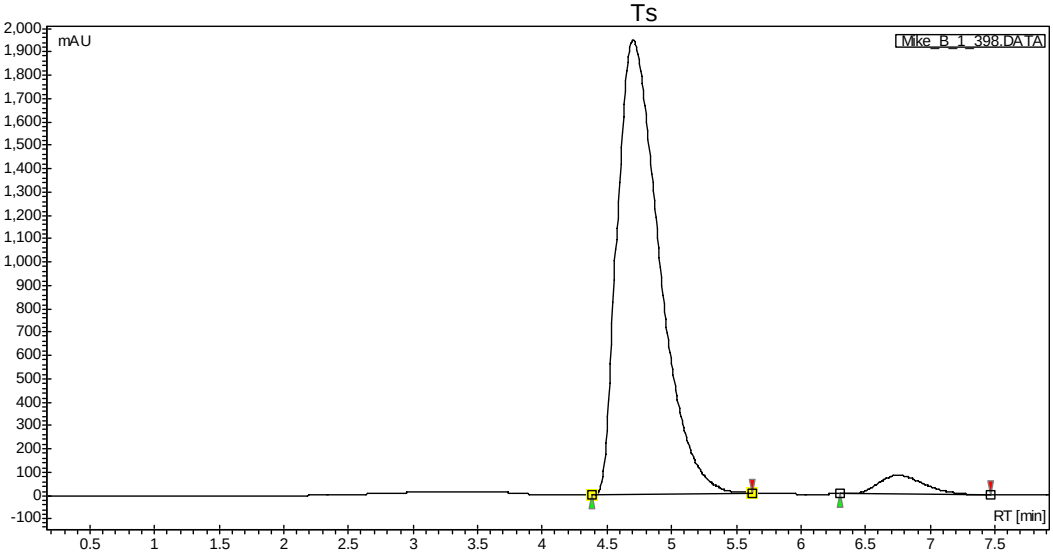
Time (min)	Area (%)
28.09	63.492
34.05	36.508



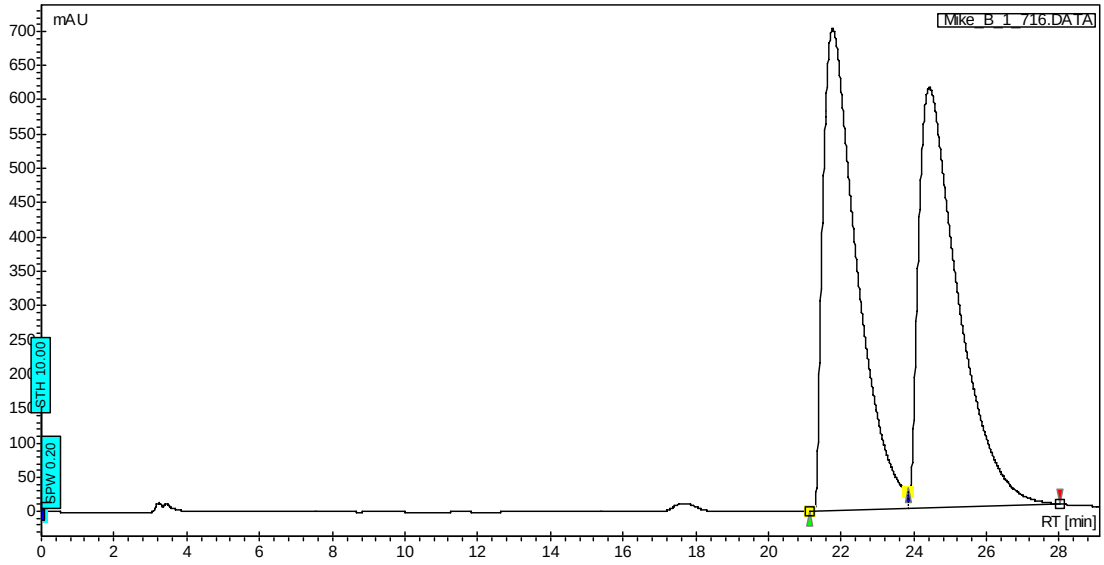
Time (min)	Area (%)
4.39	50.724
5.91	49.276



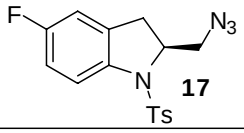
16



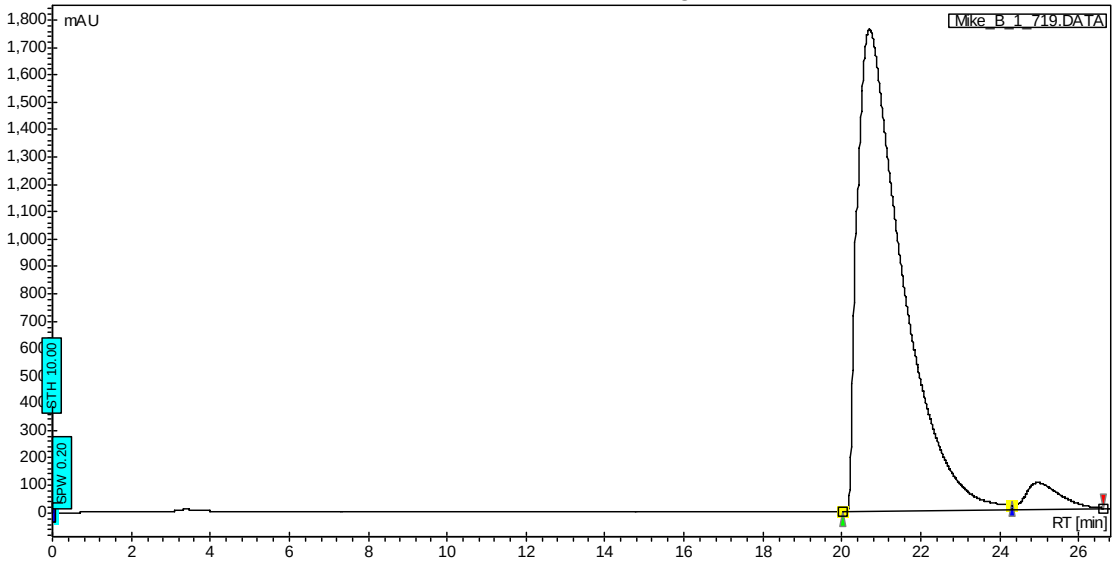
Time (min)	Area (%)
4.7	95.56
6.75	4.44



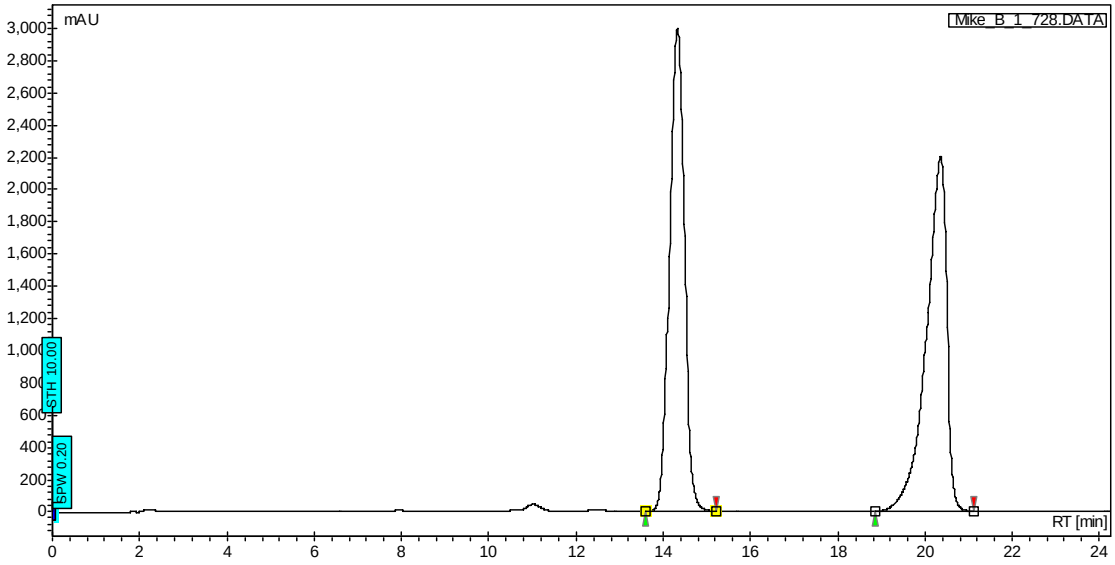
Time (min)	Area (%)
21.86	49.384
24.42	50.616



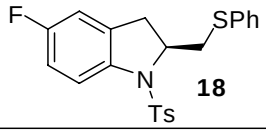
17



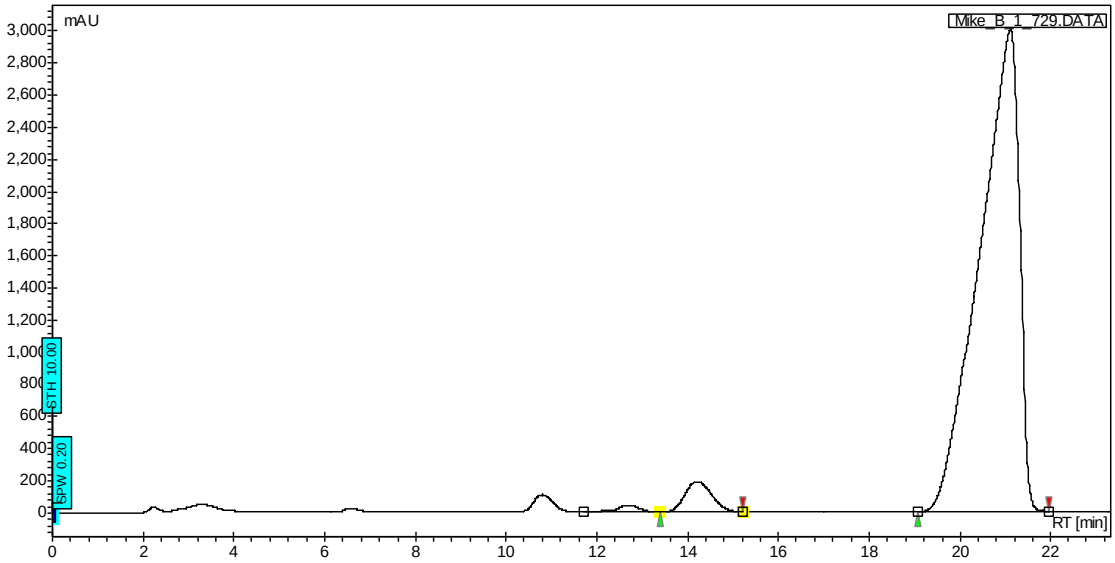
Time (min)	Area (%)
20.71	95.956
24.96	4.044



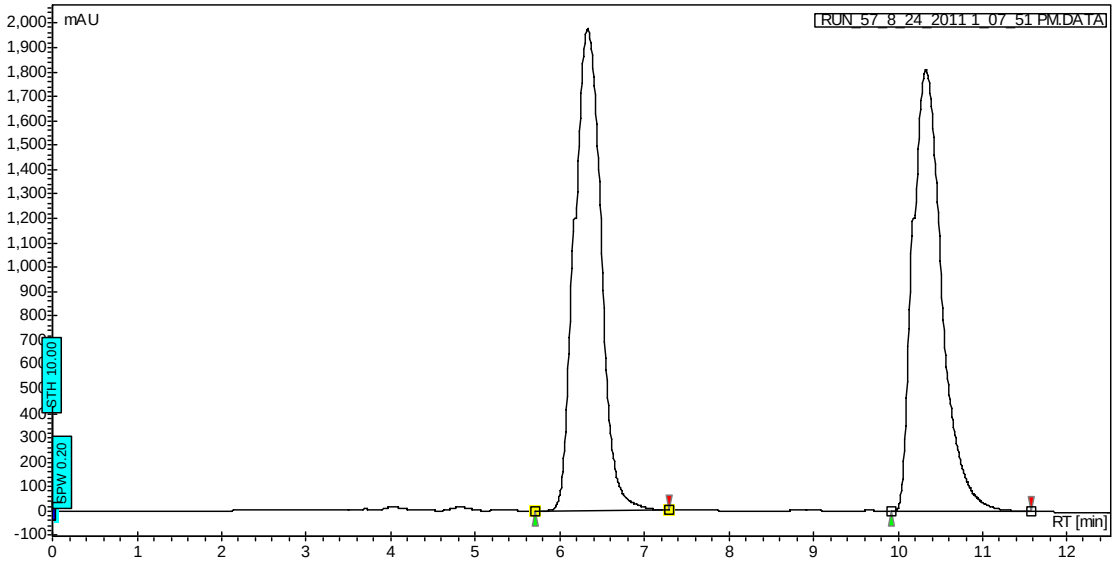
Time (min)	Area (%)
14.32	49.822
20.35	50.178



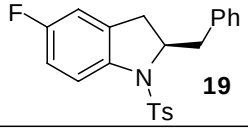
18



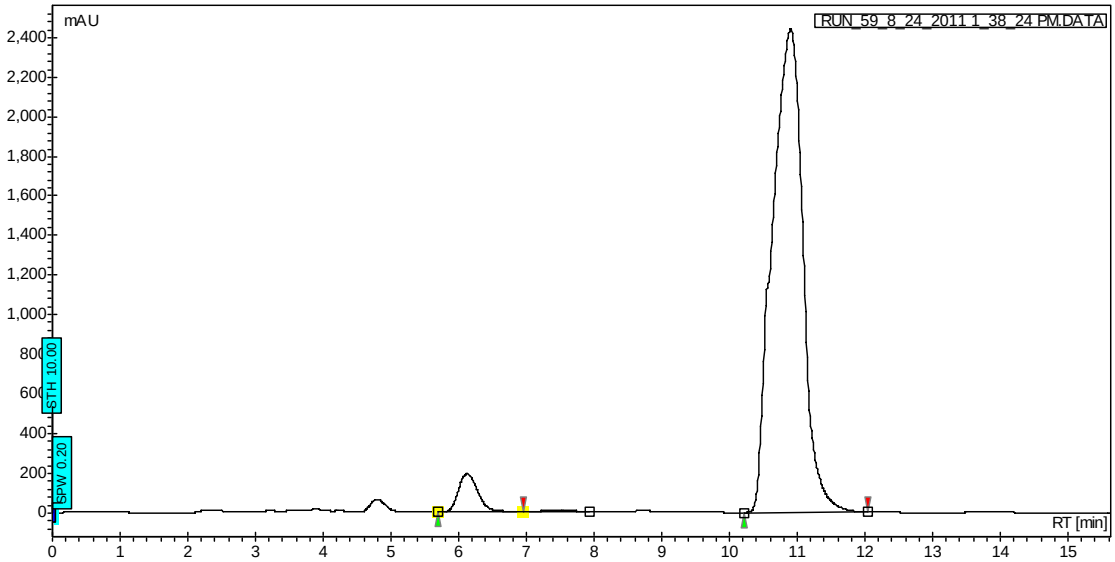
Time (min)	Area (%)
14.21	4.087
21.11	95.913



Time (min)	Area (%)
6.33	50.062
10.33	49.938



19

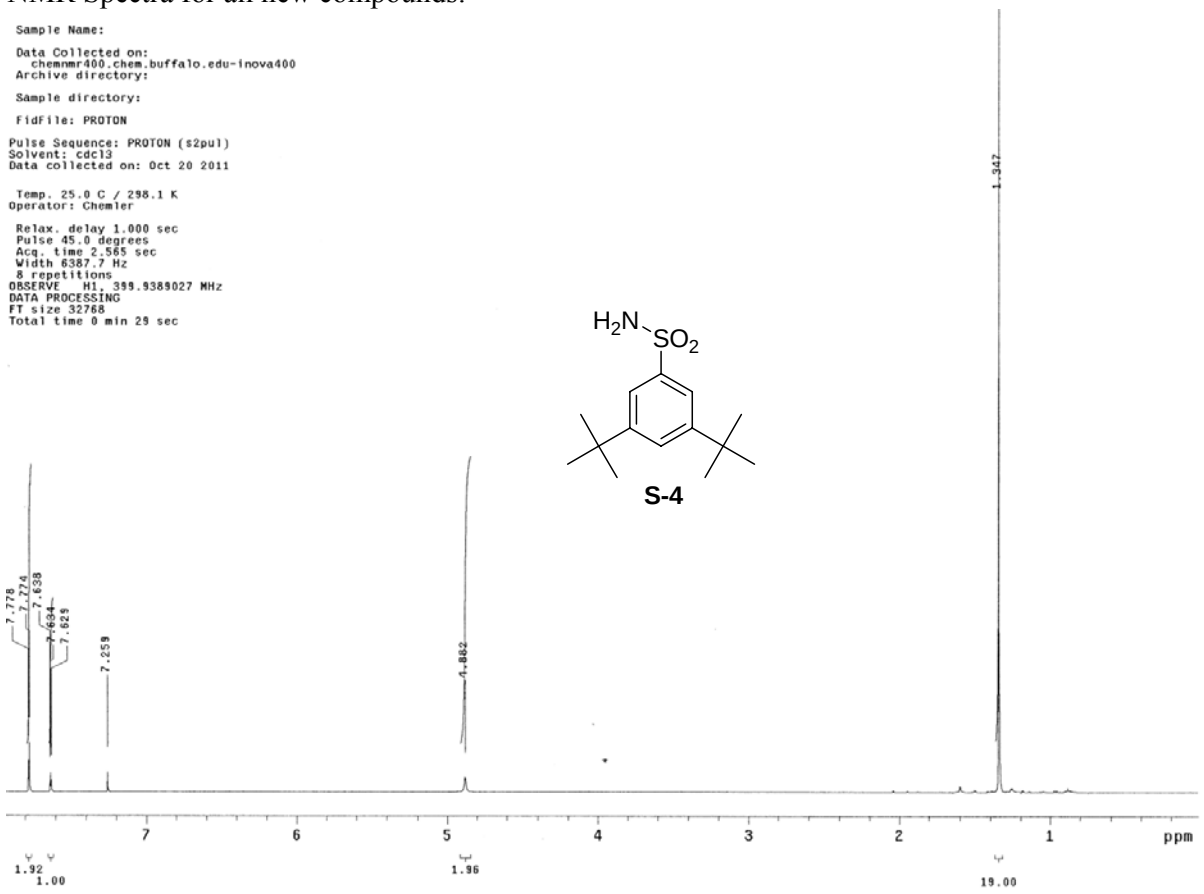


Time (min)	Area (%)
6.12	4.841
10.91	95.159

References:

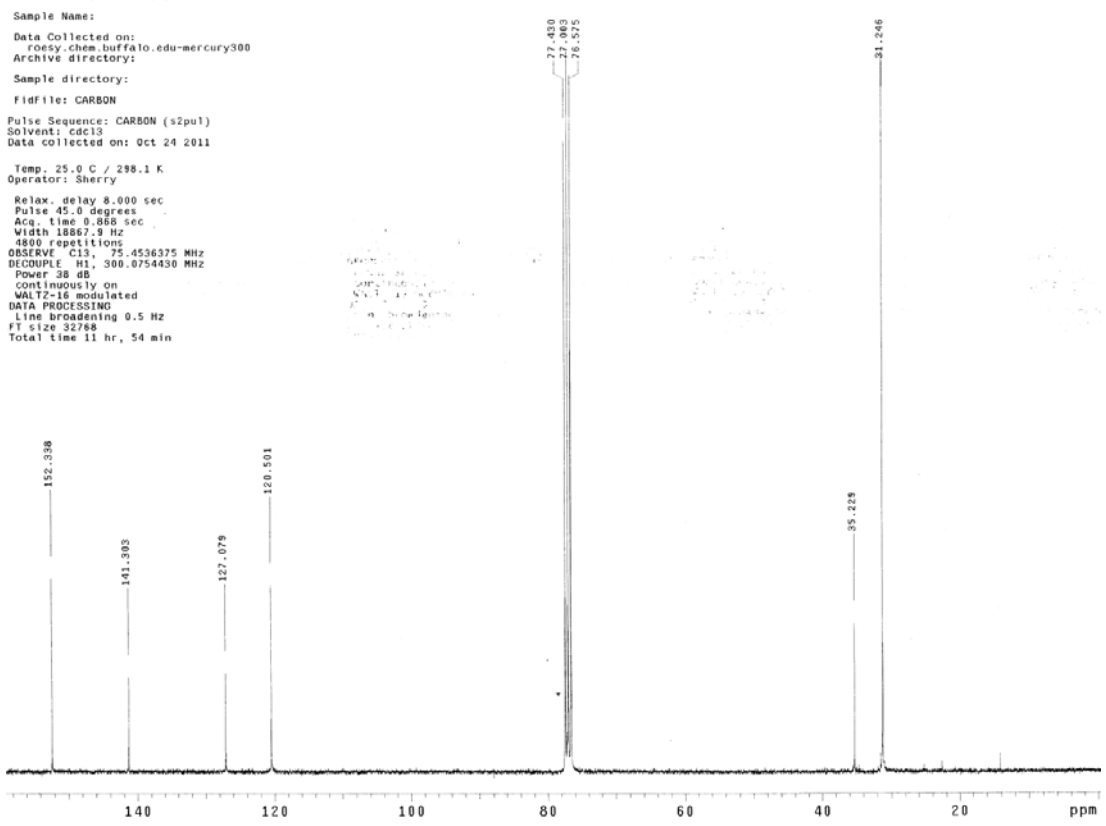
(1) Masamune, S.; Lowenthal, R. *Patent # US19910789748 19911108* **1994**.
(2) Denmark, S. E., Stiff, C. *J. Org. Chem.* **2000**, *65*, 5875-5878.
(3) Huntress, E. H.; Carten, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 511-514.
(4) Fuller, P. H.; Kim, J.-W.; Chemler, S. R. *J. Am. Chem. Soc.* **2008**, *130*, 17638-17639.
(5) Hegedus, L. S. M. J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444-2451.
(6) Yin, Y.; Z., G. *J. Fluor. Chem.* **2007**, *128*, 40-45.
(7) Muniz, K.; Hovelmann, C. H.; Streuff, J. *J. Am. Chem. Soc.* **2008**, *130*, 763-773.
(8) Bennasar, M. L. R., T.; Monerris, M.; Garcia-Diaz, D. J. *J. Org. Chem.* **2006**, *71*, 7028-7034.
(9) Lira, R.; Wolfe, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 13906-13907.
(10) Sherman, E. S.; Chemler, S. R.; Tan, T. B.; Gerlits, O. *Org. Lett.* **2004**, *6*, 1573-1575.
(11) El Ali, B.; Okuro, K.; Vasapollo, G.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 4264-4270.
(12) Michael, F. E. C., B. M. *J. Am. Chem. Soc.* **2006**, *128*, 4246-4247.
(13) Bender, C. F. W., R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070-1071.
(14) Zhang, J. Y.; C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798-1799.
(15) Tamaru, Y. H., M.; Higashimura, H.; Yoshida, Z.-I. *J. Am. Chem. Soc.* **1988**, *110*, 3994-4002.
(16) de Haro, T.; Nevado, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 906-910.
(17) Sherman, E. S.; Fuller, P. H.; Kasi, D.; Chemler, S. R. *J. Org. Chem.* **2007**, *72*, 3896-3905.
(18) Miao, L.; Haque, I.; Manzoni, M. R.; Tham, W. S.; Chemler, S. R. *Org. Lett.* **2011**, *12*, 4739-4741.
(19) Haque, I. Master's dissertation, University at Buffalo, 2009.
(20) Marcotullio, M. C.; Campagna, V.; Sternativo, S.; Costantino, F.; Curini, M. *Synthesis* **2006**, 2760-2766.
(21) Flemer, S.; Madalengoitia, J. S. *Synthesis* **2007**, 1848-1860.
(22) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 4364-4366.

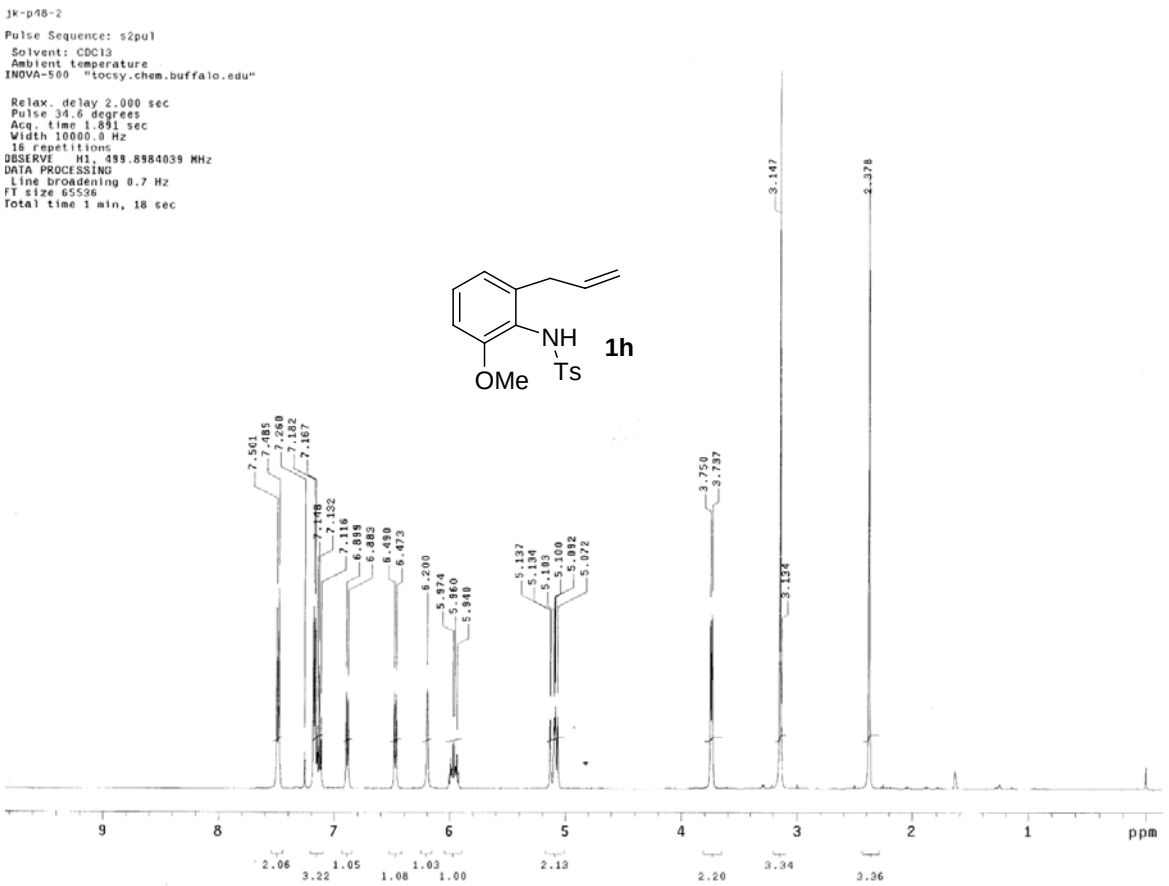
NMR Spectra for all new compounds:

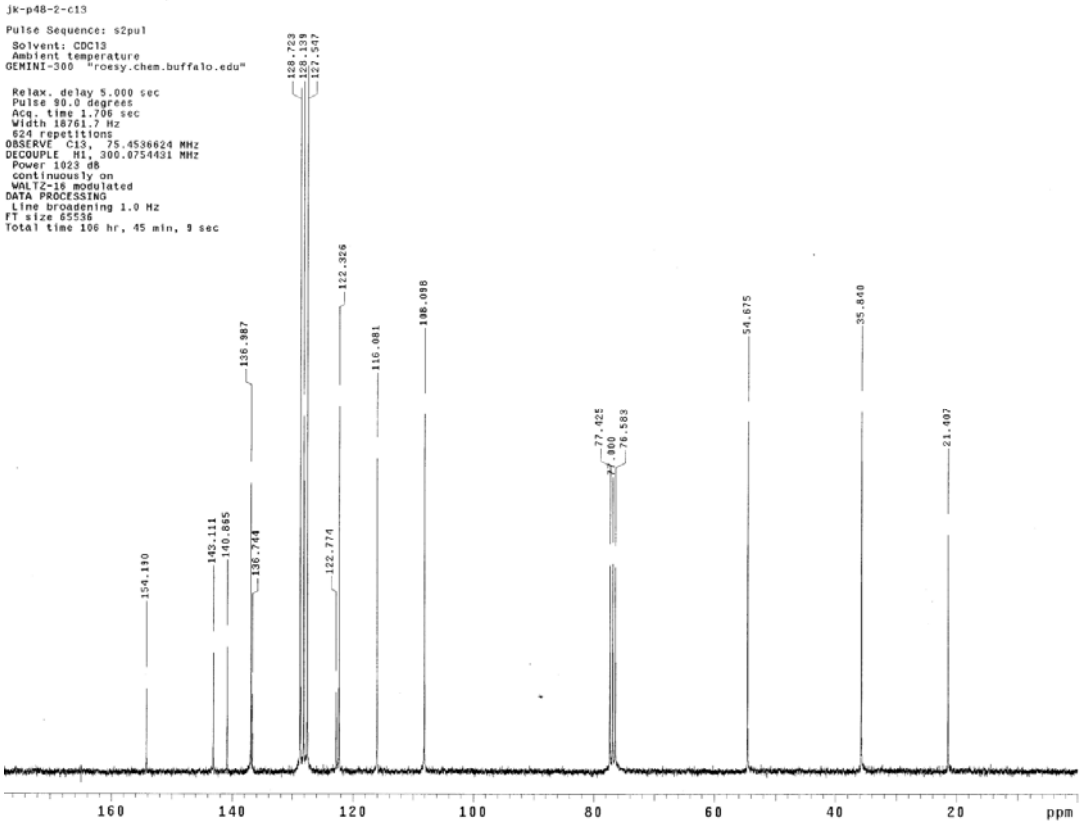


H_2N SO_2

S-4




jk-p48-2
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 499.8984039 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
NH
Ts
OMe
1h
7.561
7.485
7.260
7.182
7.167
7.148
7.132
7.116
6.899
6.883
6.490
6.473
6.200
5.974
5.860
5.940
5.137
5.134
5.103
5.100
5.092
5.072
3.750
3.737
3.147
3.134
2.378
9
8
7
6
5
4
3
2
1
ppm
2.06
3.22
1.05
1.08
1.03
1.00
2.13
2.20
3.34
3.36


jk-p48-2-c13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
624 repetitions
OBSERVE C13, 75.4536624 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 106 hr, 45 min, 9 sec
154.130
143.111
140.865
136.744
136.387
128.723
128.139
127.547
122.774
122.326
116.081
108.098
77.425
77.000
76.583
54.675
35.840
21.407
160
140
120
100
80
60
40
20
ppm

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

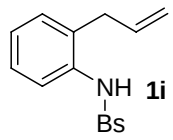
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 17 2010

Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4810.0 Hz
8 repetitions
OBSERVE H1, 300.0238602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 24 sec



1i

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

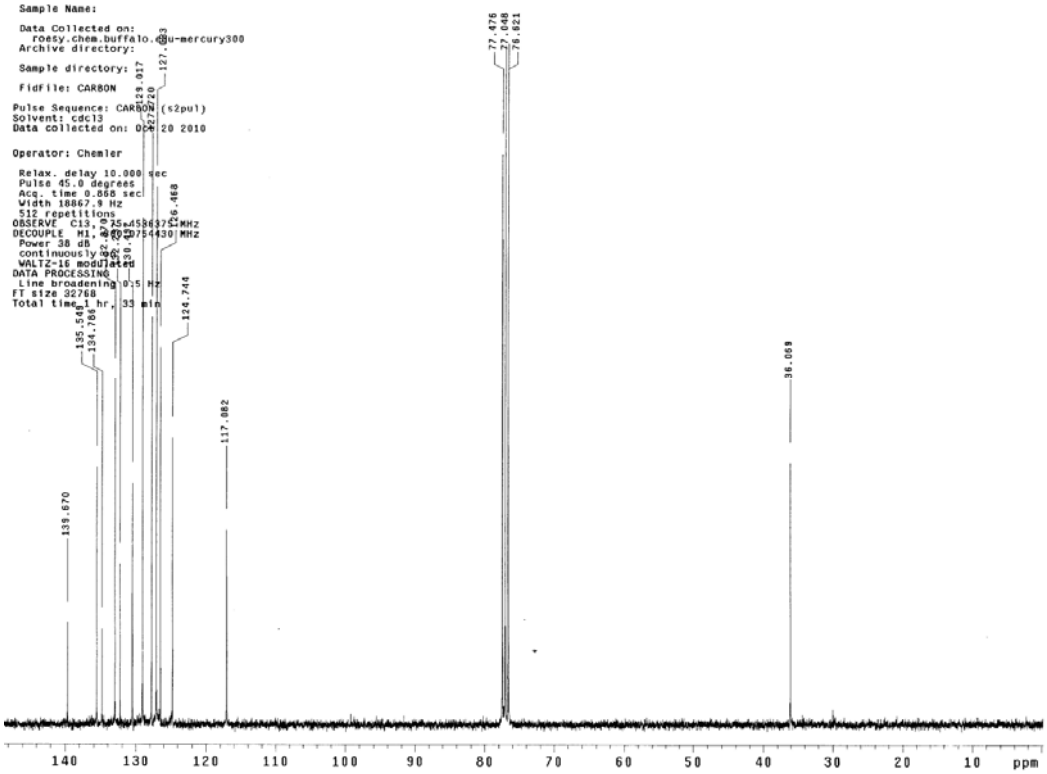
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 20 2010

Operator: Chemler

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
512 repetitions
OBSERVE C13, 75.4586375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 33 min



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

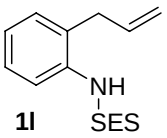
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 29 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



1l

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

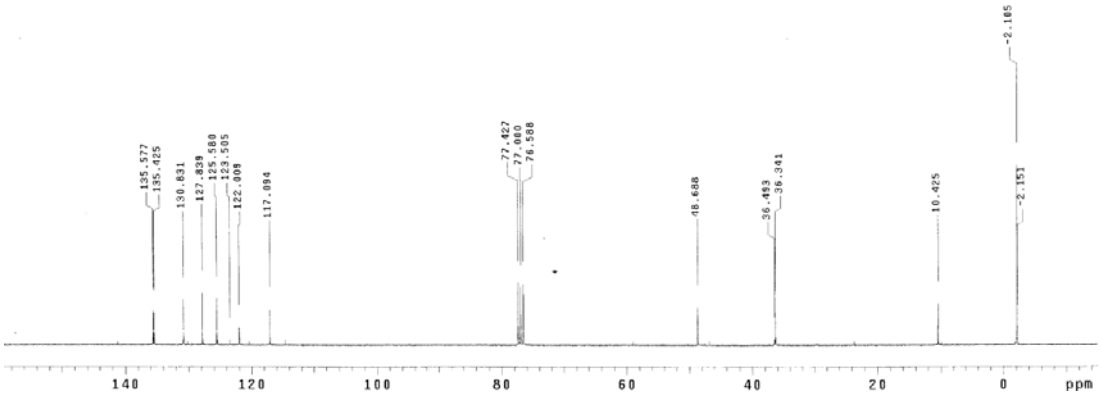
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 3 2011

Temp. 22.0 C / 295.1 K
Operator: Sherry

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1088 repetitions
OBSERVE C13, 75.4536412 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 2 hr, 41 min



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

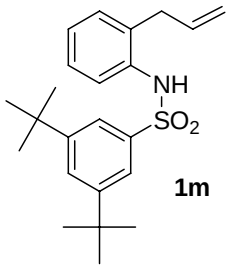
Sample directory:

FidFile: MTB-1-67

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 26 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389071 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



1m

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

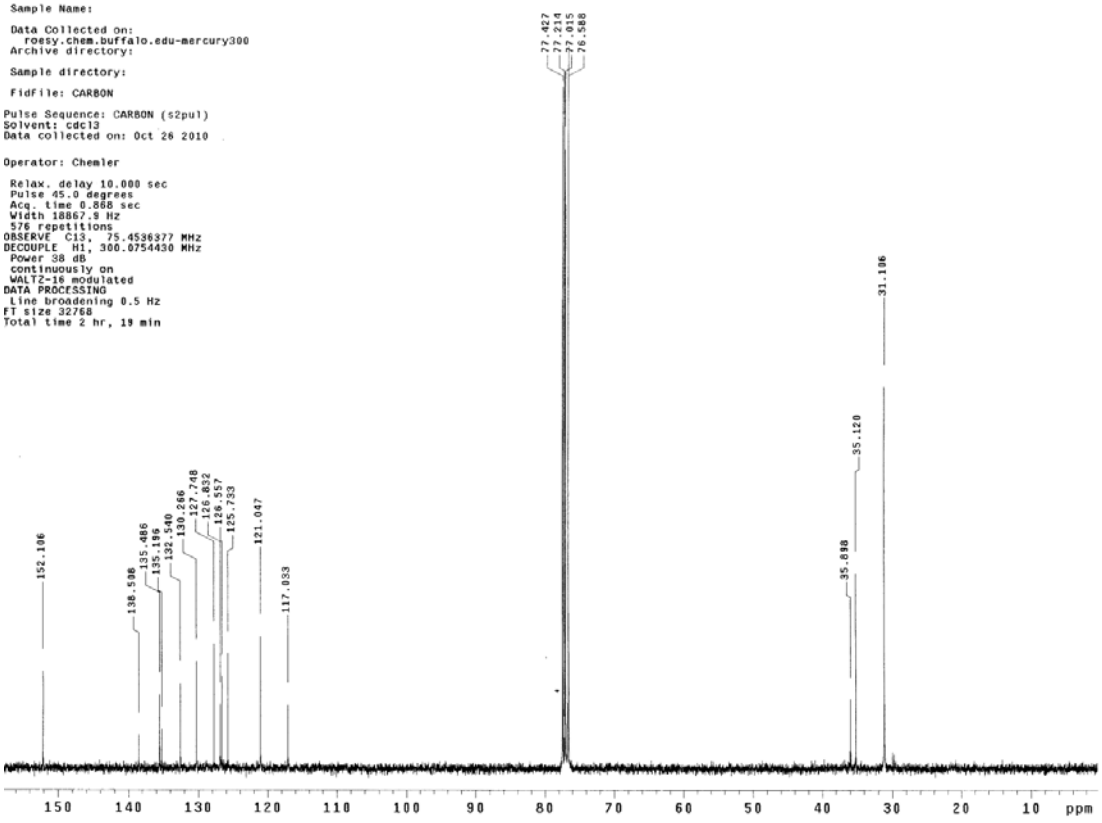
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 26 2010

Operator: Chemler

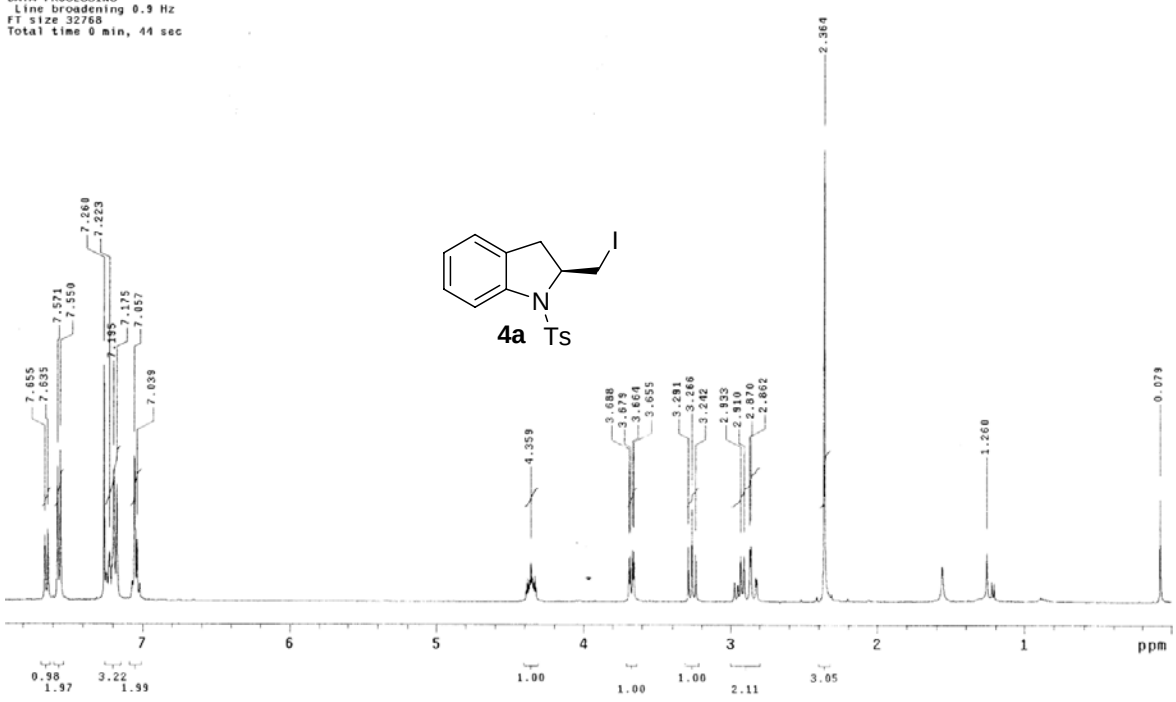
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
576 repetitions
OBSERVE C13, 75.4536377 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 2 hr, 19 min



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

Relax. delay 1.000 sec
Pulse 47.9 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389106 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 32768
Total time 0 min, 44 sec

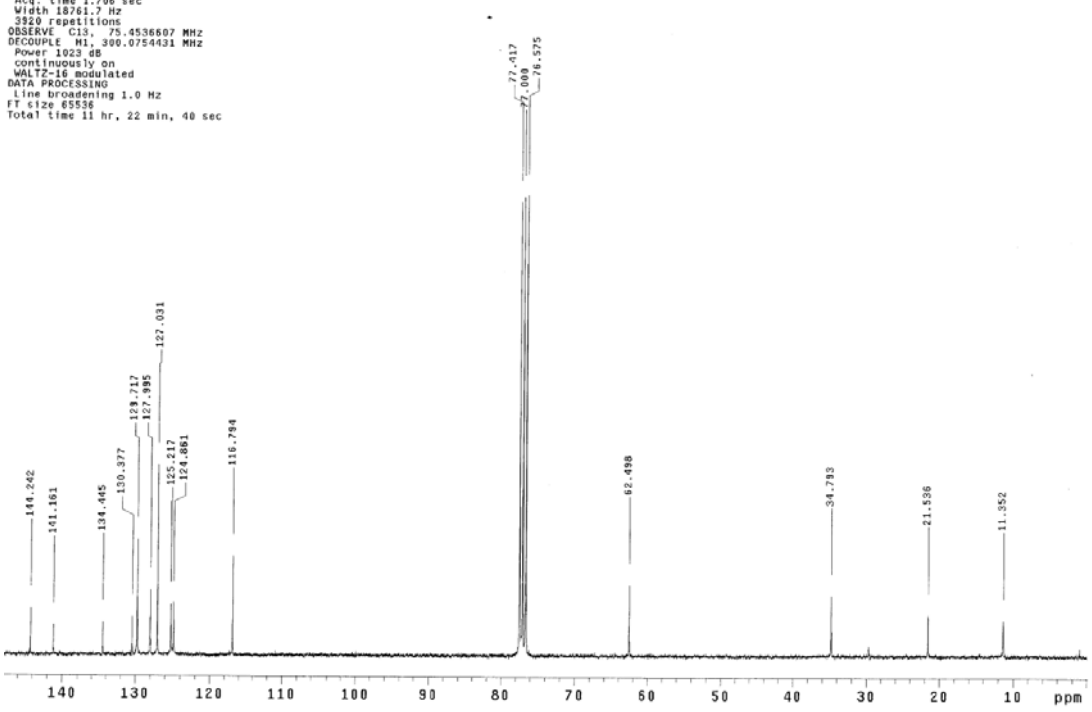


4a

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

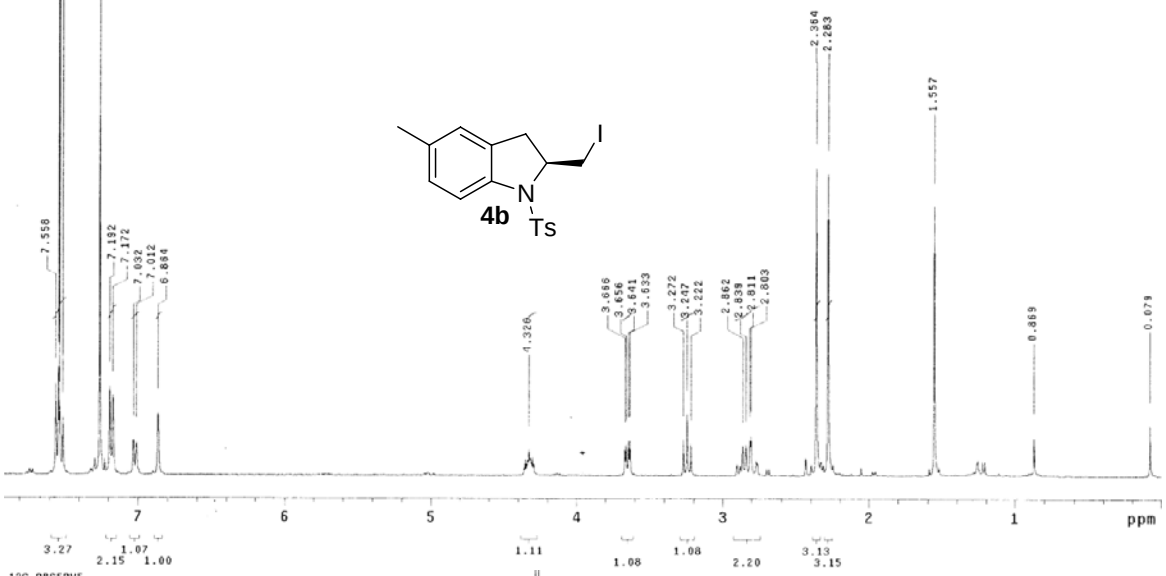
Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
3920 repetitions
OBSERVE C13, 75.4536607 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

Relax. delay 1.000 sec
Pulse 47.9 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389095 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 32768
Total time 0 min, 44 sec

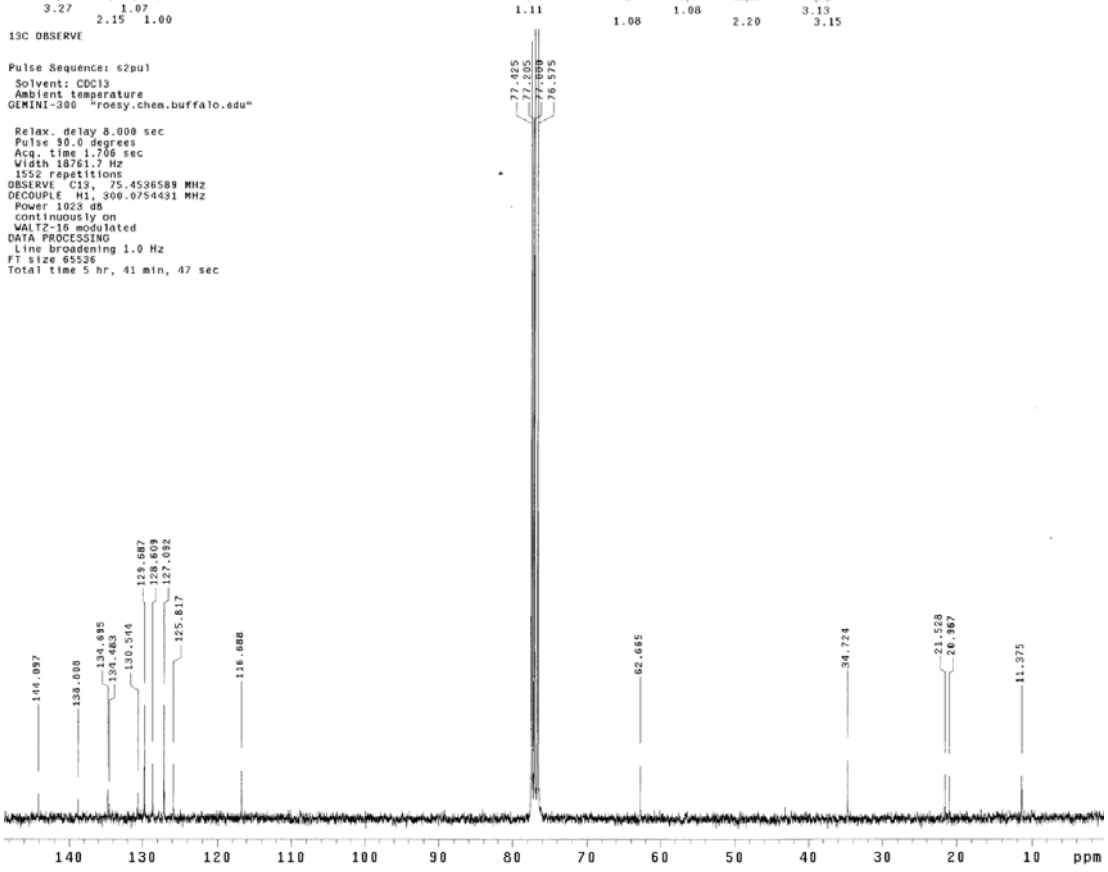


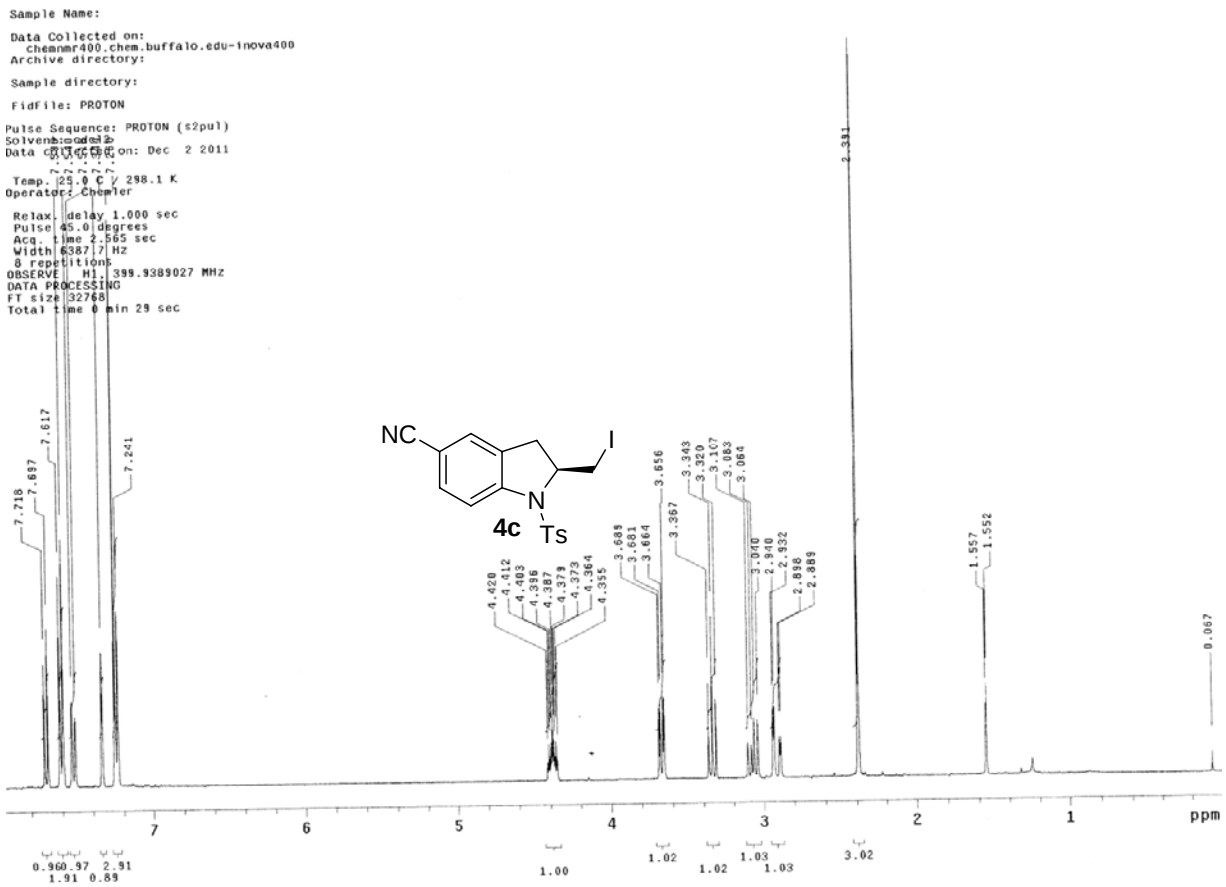
4b

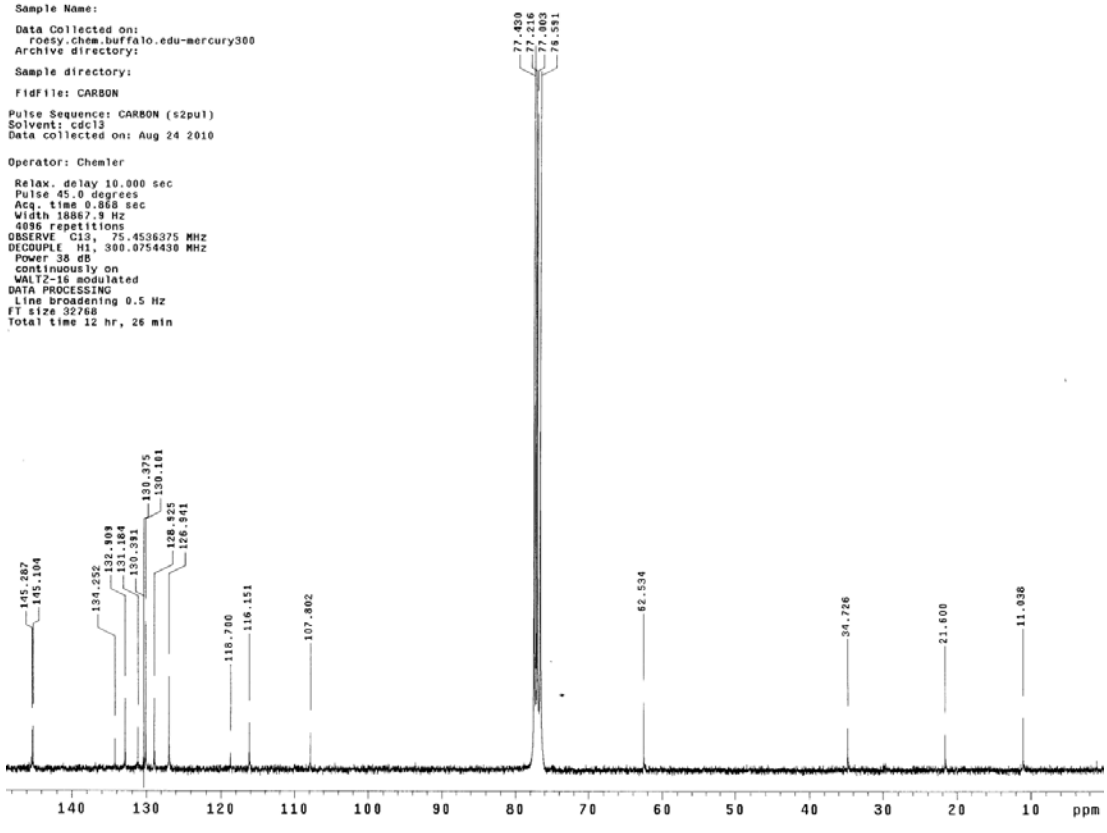
13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
1552 repetitions
OBSERVE C13, 75.4536588 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 41 min, 47 sec




Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 2 2011
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
NC
I
N
Ts
4c
7.718
7.697
7.617
7.241
4.420
4.412
4.403
4.398
4.387
4.379
4.373
4.364
4.355
3.688
3.681
3.664
3.656
3.367
3.343
3.320
3.167
3.083
3.064
3.040
2.940
2.932
2.838
2.689
2.331
1.557
1.552
0.067
ppm
0.96 0.97 2.91
1.91 0.89
1.00
1.02
1.02
1.03
1.03
3.02


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 24 2010
Operator: Chemler
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4096 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min
77.490
77.216
77.003
76.591
145.287
145.104
134.252
132.909
131.184
130.391
130.375
130.161
128.825
126.941
118.700
116.151
107.802
62.534
34.726
21.600
11.038
ppm

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

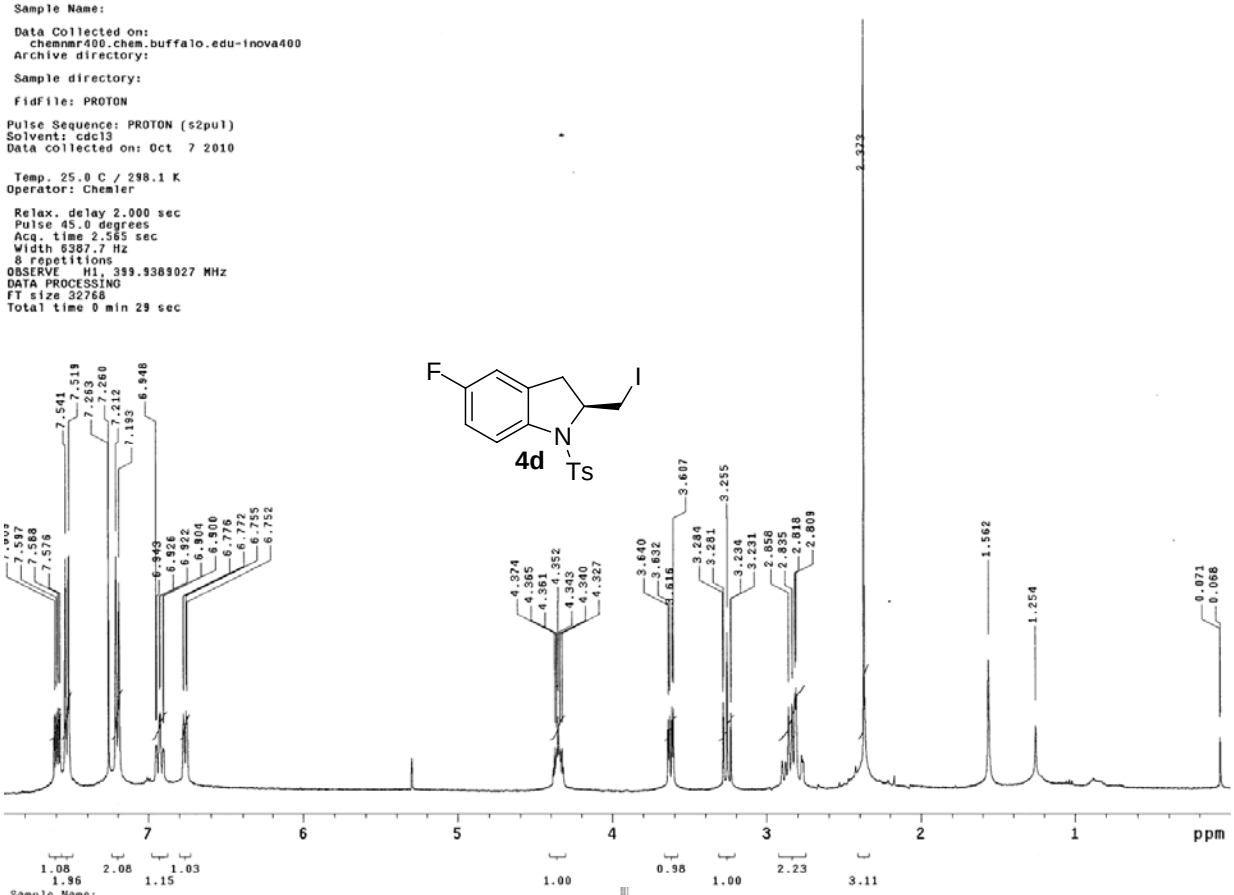
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 7 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



1.08 2.08 1.03
1.96 1.15 1.00 0.98 1.00 2.23 3.11

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

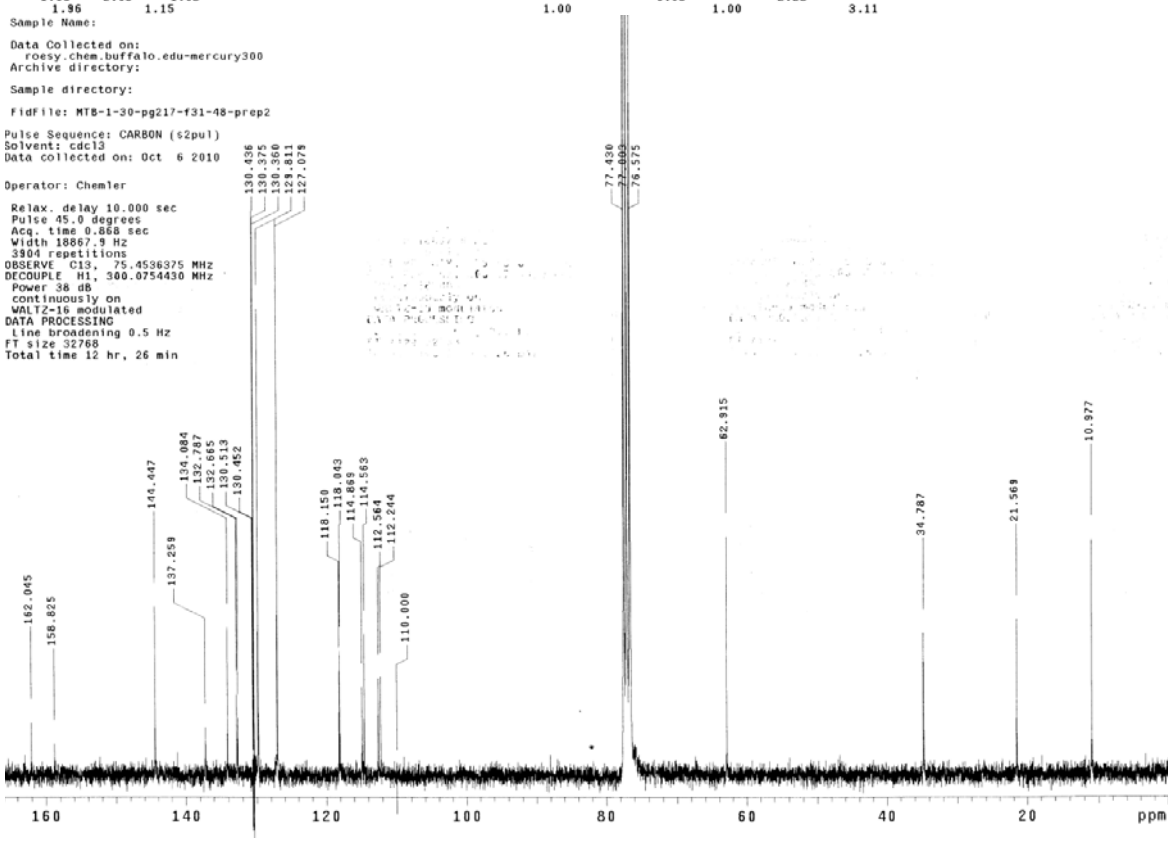
Sample directory:

FidFile: MTB-1-30-pg217-f31-48-prep2

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 6 2010

Operator: Chemler

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3304 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

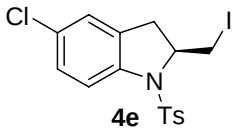
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 19 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 399.9389021 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec



4e

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

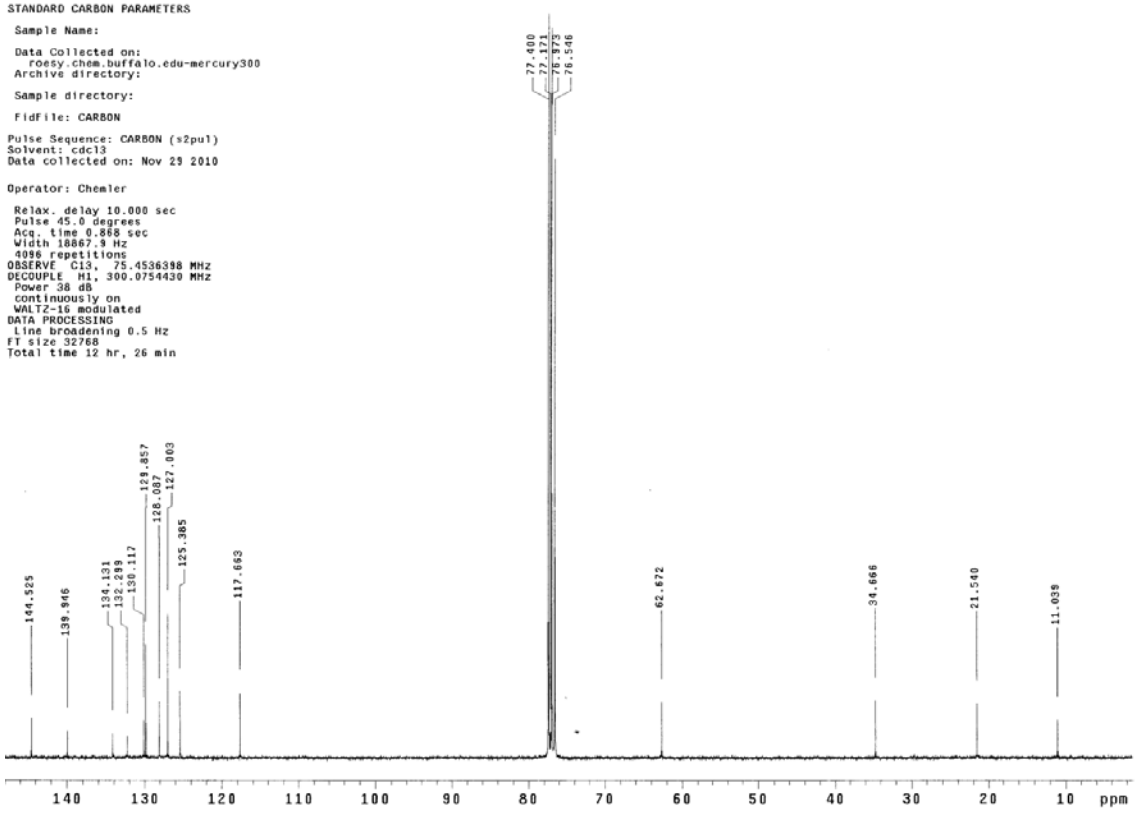
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov 29 2010

Operator: Chemler

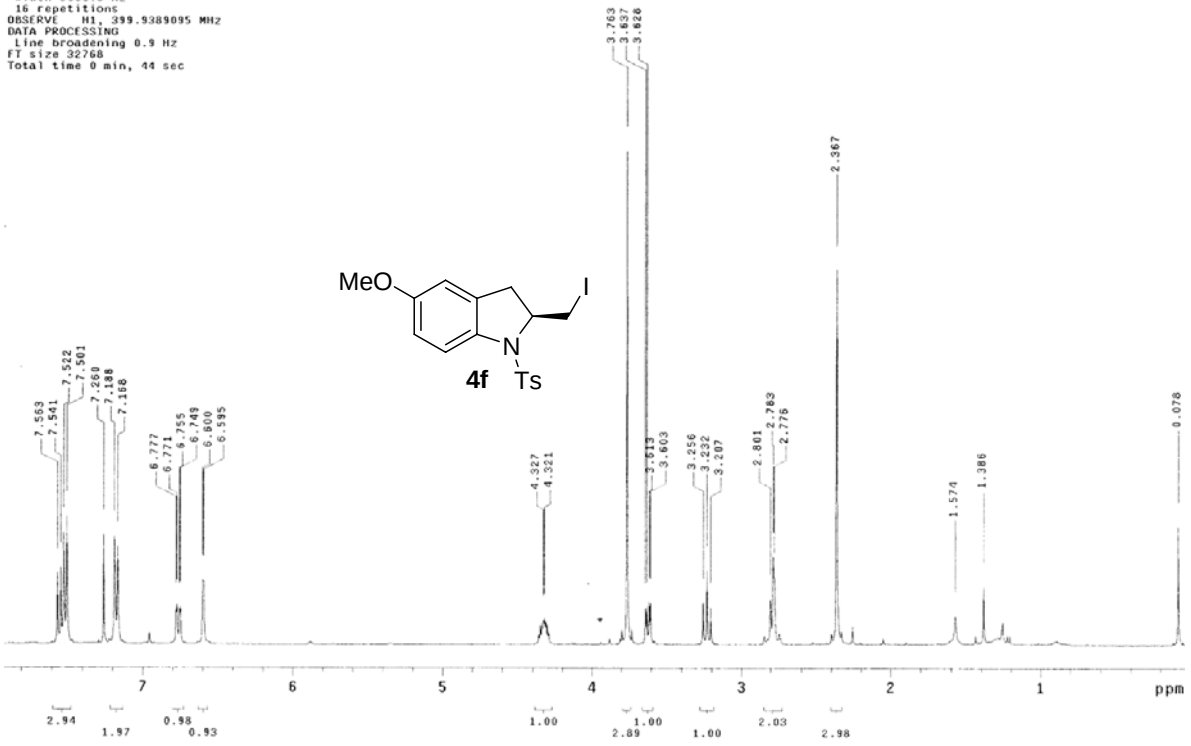
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4096 repetitions
OBSERVE C13, 75.4536398 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

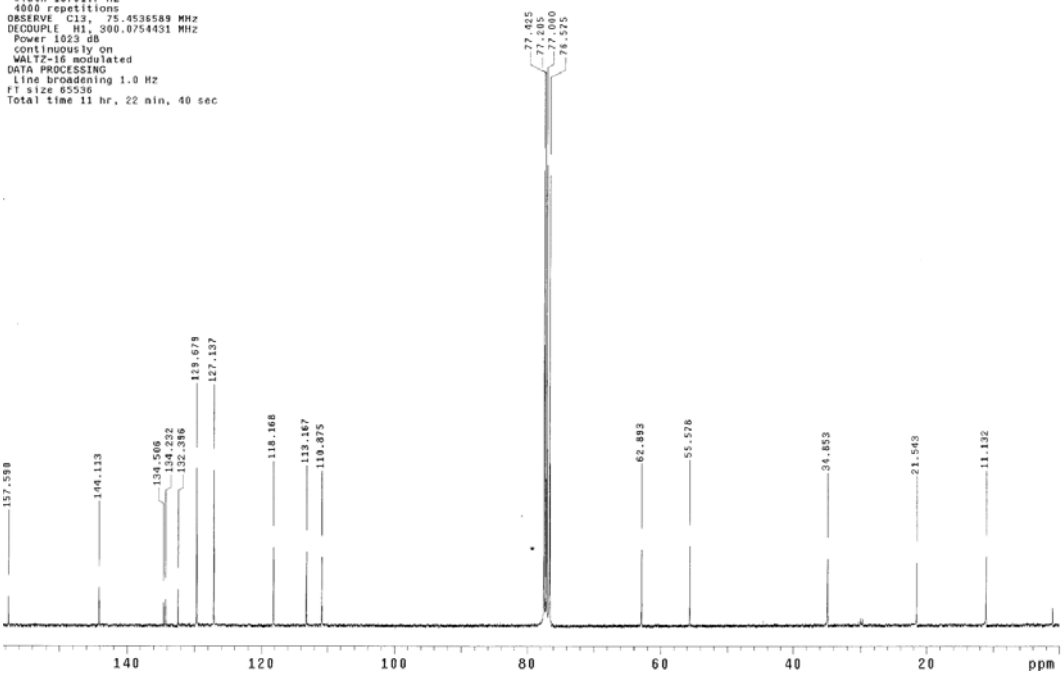
Relax. delay 1.000 sec
Pulse 47.9 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389095 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 32768
Total time 0 min, 44 sec

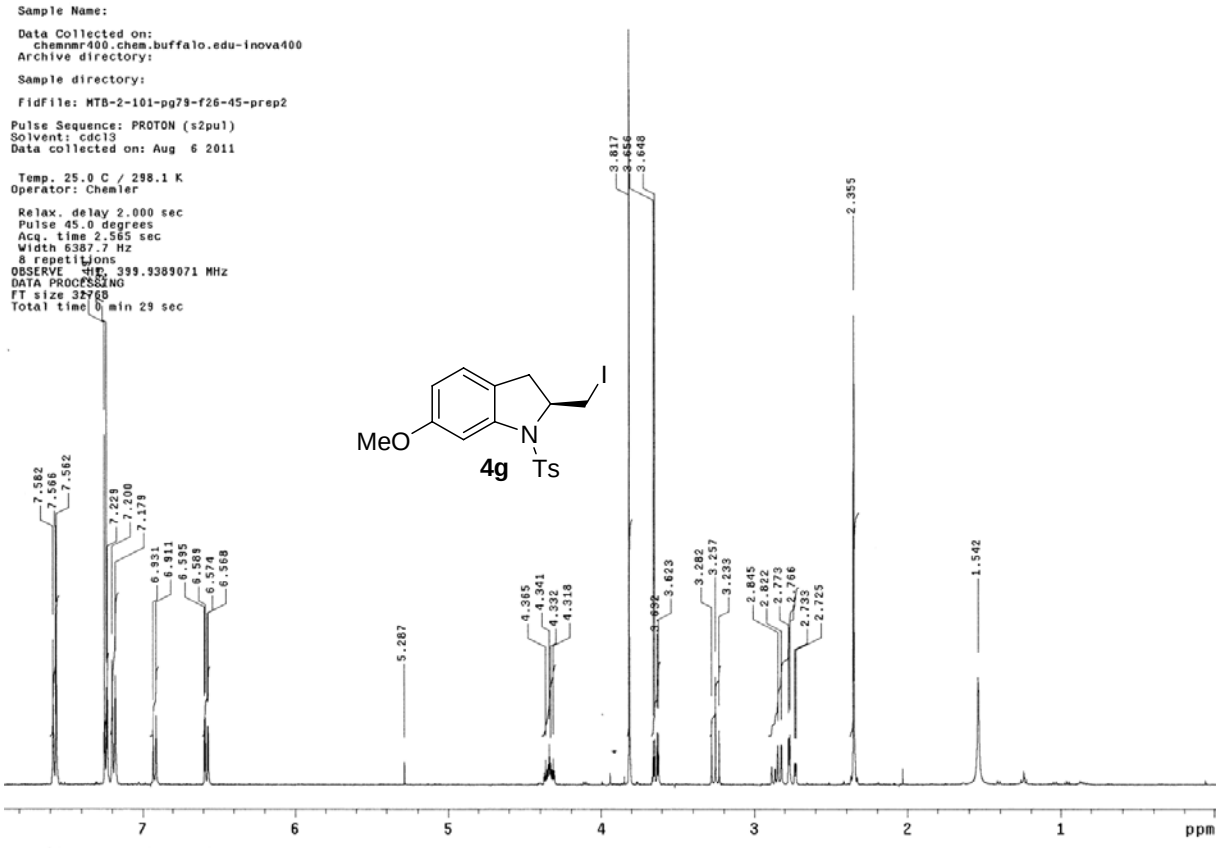


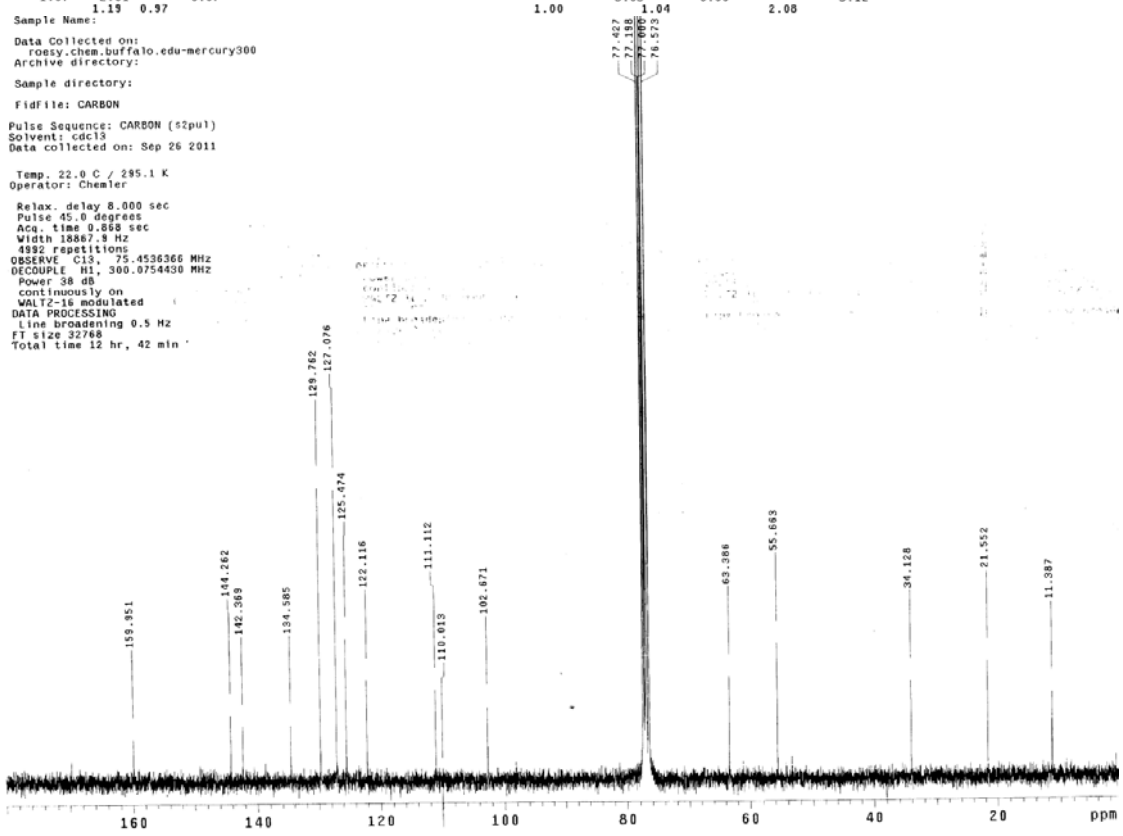
13C OBSERVE

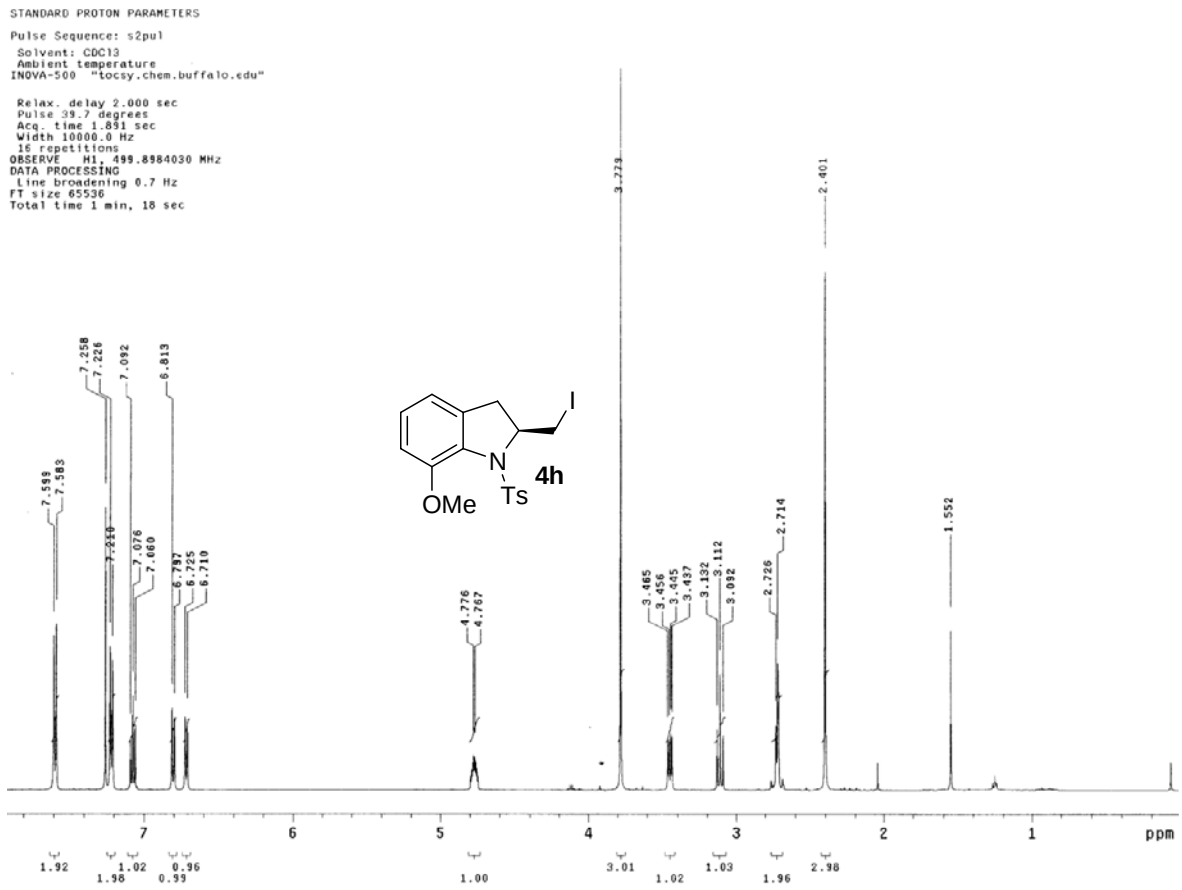
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

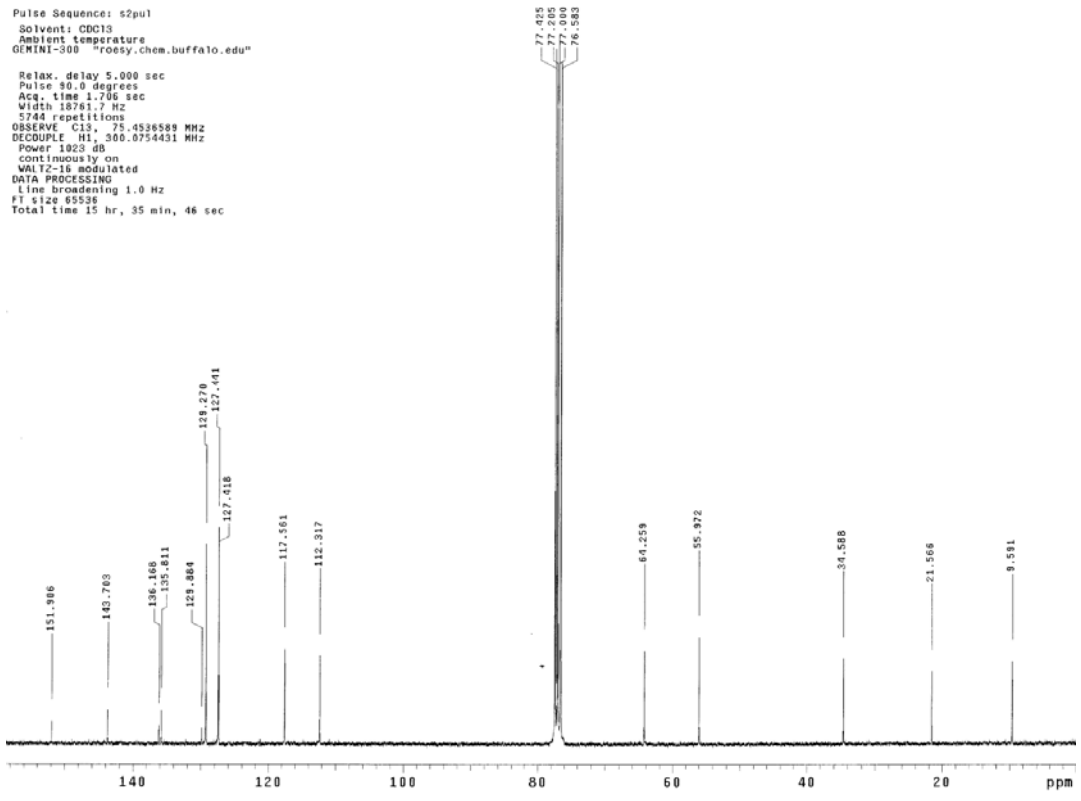
Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
4000 repetitions
OBSERVE C13, 75.4536589 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec




Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: MTB-2-101-pg79-f26-45-prep2
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 6 2011
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389071 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
MeO
N
Ts
I
4g
7.582
7.566
7.562
7.229
7.200
7.179
6.931
6.911
6.595
6.589
6.574
6.568
5.287
4.365
4.341
4.332
4.318
3.817
3.656
3.648
3.623
3.282
3.257
3.233
2.845
2.832
2.773
2.766
2.733
2.725
2.355
1.542
ppm
1.97
2.01
1.19
0.97
0.97
1.00
3.03
1.04
0.99
2.08
3.12


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 26 2011
Temp. 22.0 C / 295.1 K
Operator: Chemler
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4992 repetitions
OBSERVE C13, 75.4536366 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 42 min
77.422
77.188
77.000
76.573
159.951
144.262
142.369
134.585
129.762
127.076
125.474
122.116
111.112
110.013
102.671
63.386
55.683
34.128
21.552
11.387
ppm


STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 2.000 sec
Pulse 39.7 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 499.8984030 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
I
N
Ts
OMe
4h
7.599
7.583
7.258
7.226
7.092
7.076
7.060
6.813
6.787
6.725
6.710
4.776
4.767
3.473
3.465
3.456
3.445
3.437
3.132
3.112
3.092
2.726
2.714
2.401
1.552
ppm
1.92
1.02
1.98
0.96
0.99
1.00
3.01
1.02
1.03
1.96
2.98


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
5744 repetitions
OBSERVE C13, 75.4536589 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 15 hr, 35 min, 46 sec
77.425
77.205
77.000
76.583
151.986
143.703
136.168
135.811
129.884
129.270
127.441
127.418
117.561
112.317
64.259
55.972
34.588
21.566
9.591
ppm

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

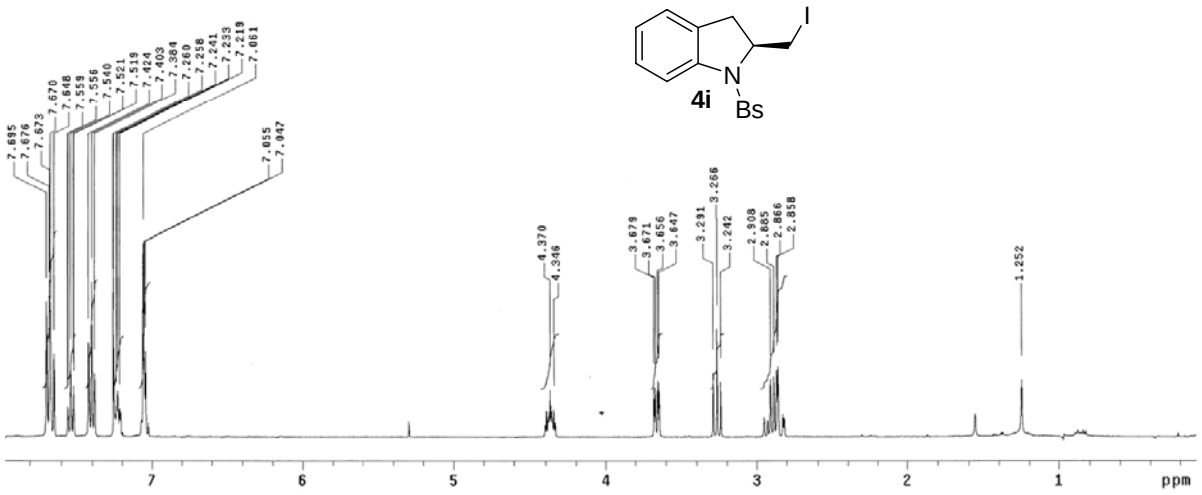
Sample directory:

FidFile: MTB-1-32

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 2 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



2.90 2.00 1.96
1.00 0.97
1.00
1.02
1.01
2.08

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

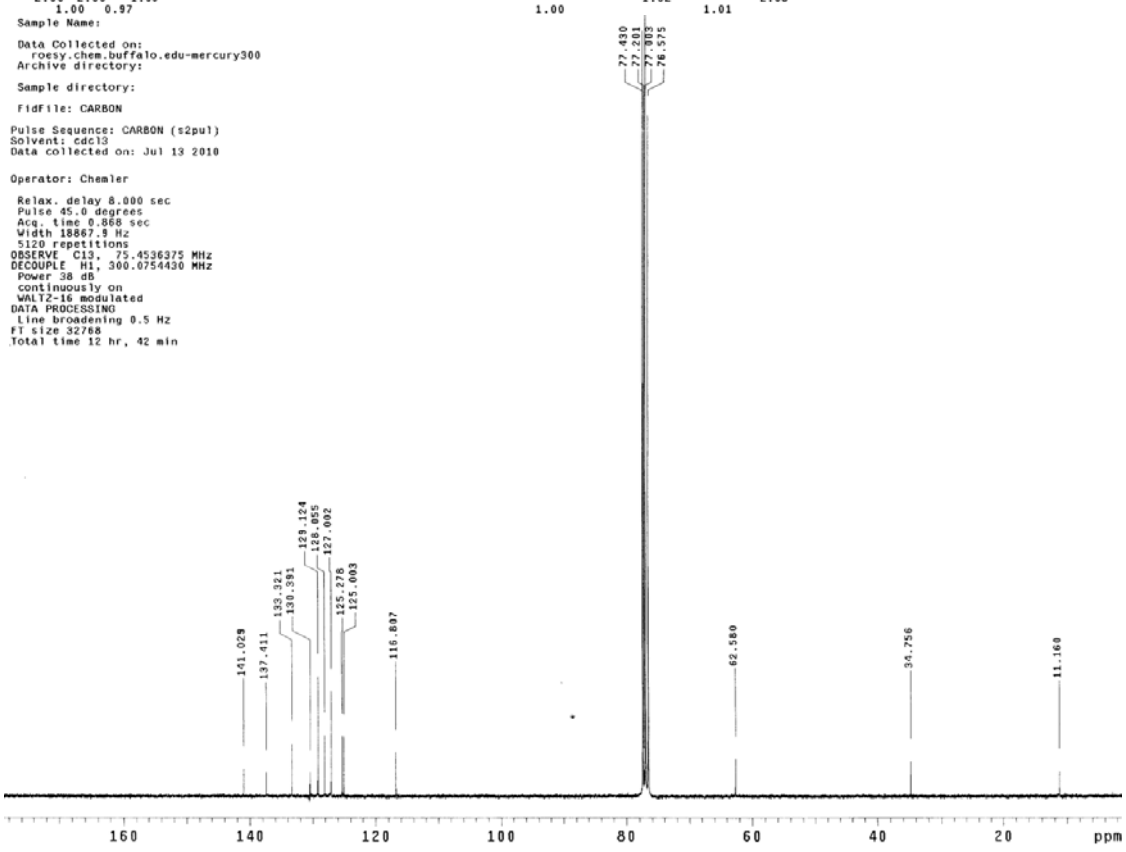
Sample directory:

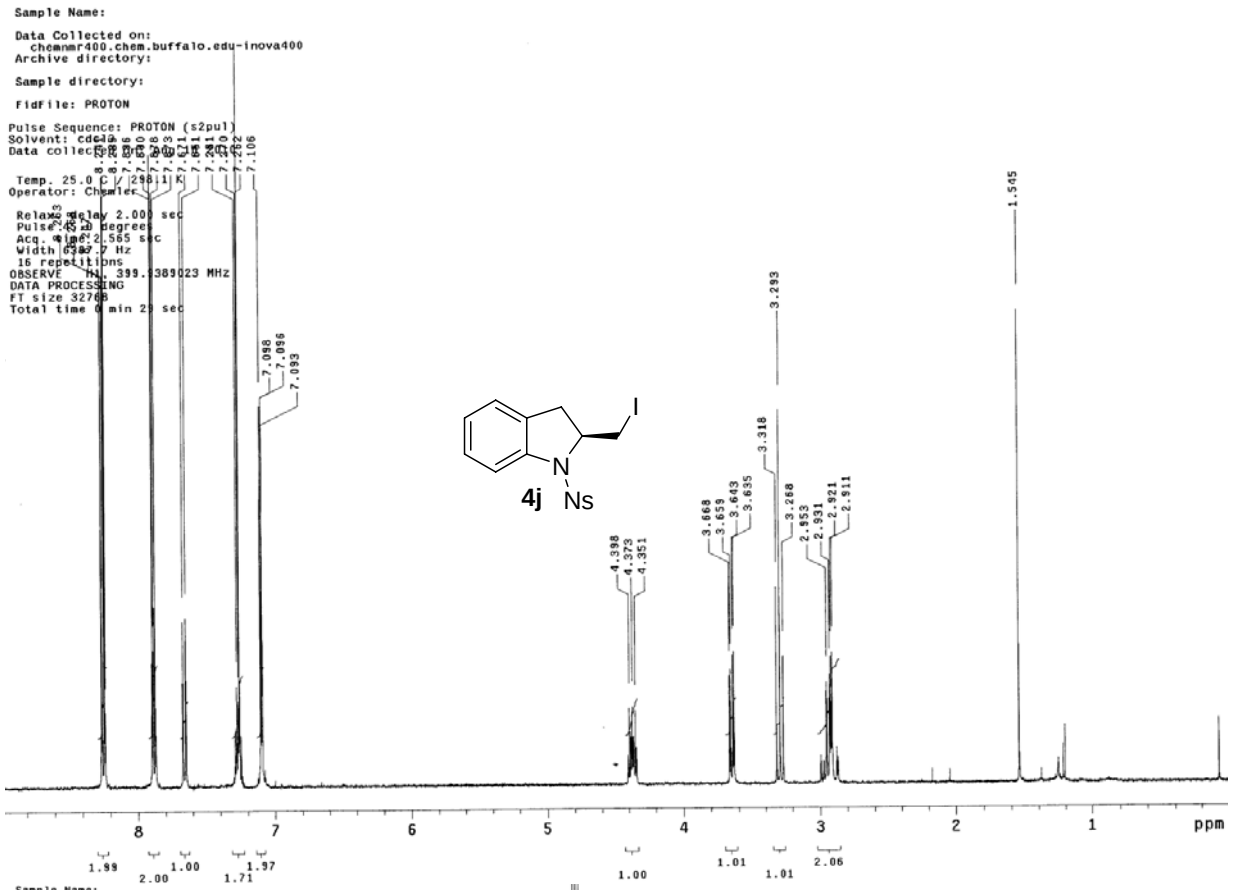
FidFile: CARBON

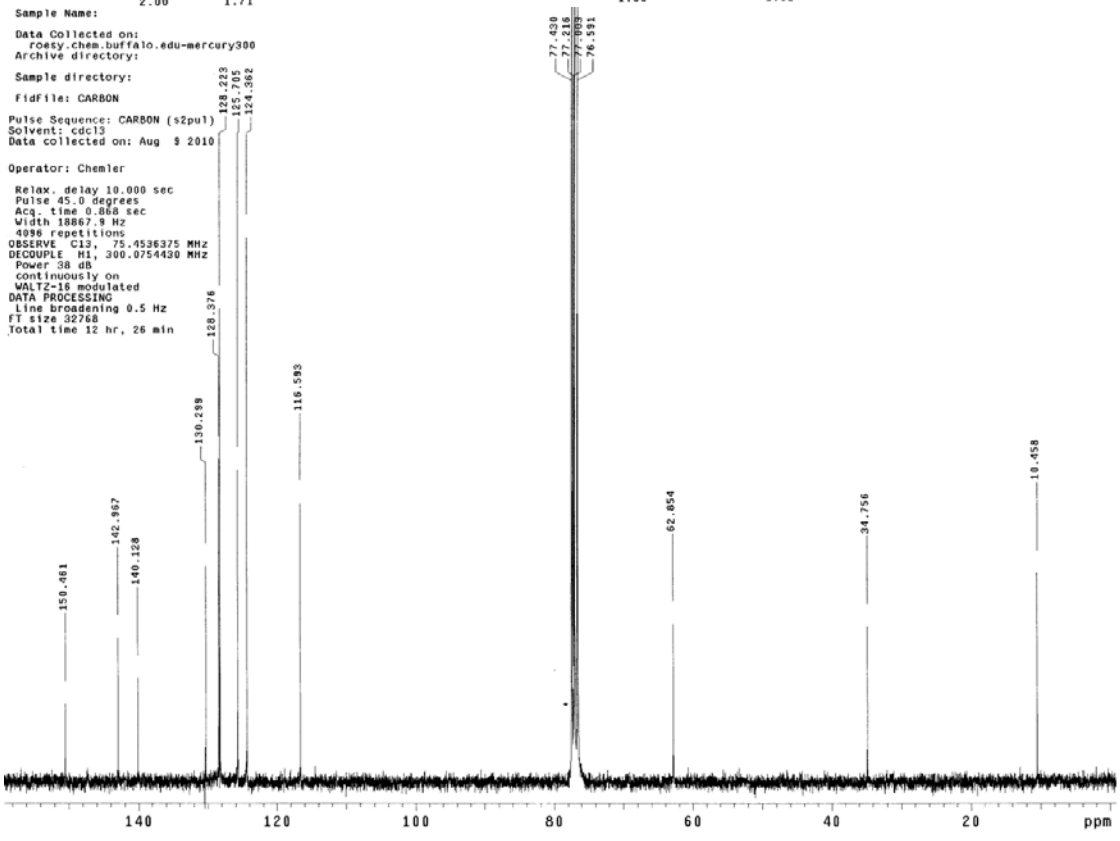
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 13 2010

Operator: Chemler

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
5120 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 42 min




Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
16 repetitions
DATA PROCESSING
FT size 32768
7.106
7.098
7.096
7.093
3.293
3.318
3.668
3.659
3.643
3.635
3.268
2.953
2.931
2.921
2.911
4.398
4.373
4.351
1.545
4j
Ns
ppm


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 9 2010
Operator: Chemler
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4096 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min
77.430
77.216
77.003
76.591
128.223
125.705
124.362
128.376
130.299
116.593
150.461
142.967
140.128
62.854
34.756
18.458
ppm

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

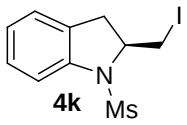
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 15 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9388929 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 37 sec



4k

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

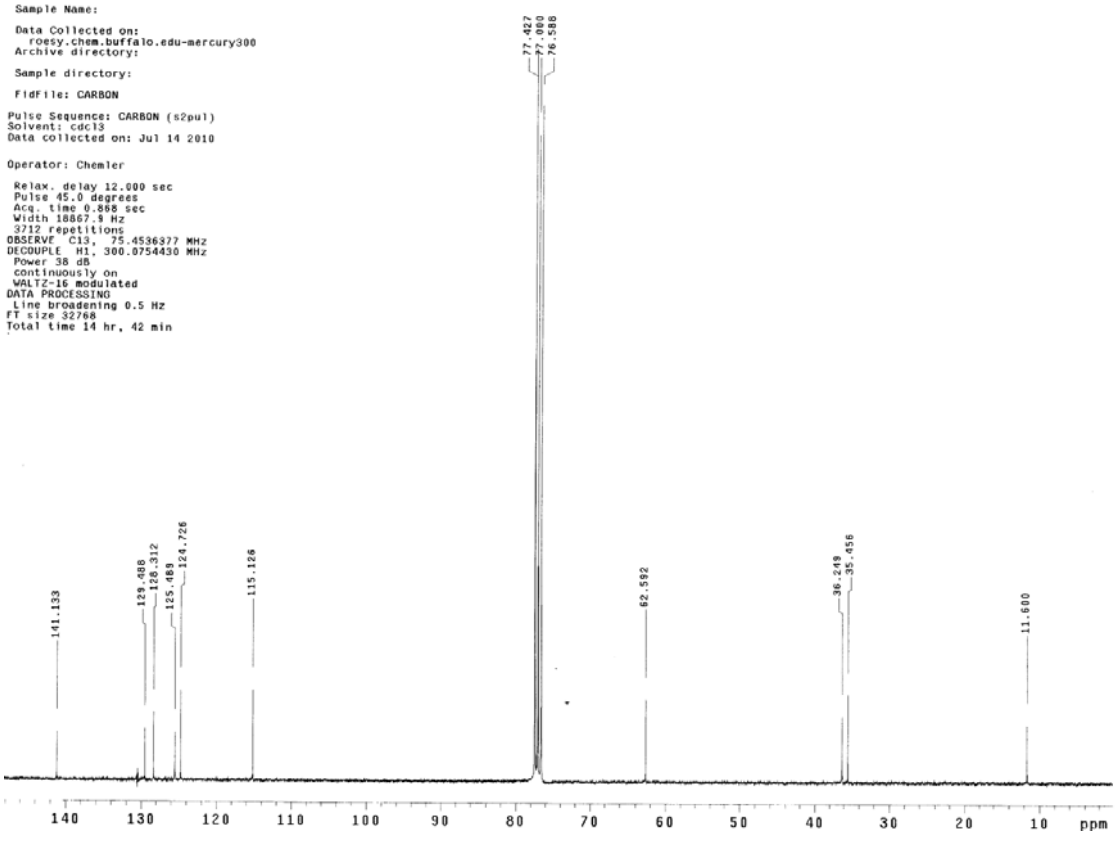
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 14 2010

Operator: Chemler

Relax. delay 12.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3712 repetitions
OBSERVE C13, 75.4536377 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 14 hr, 42 min



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

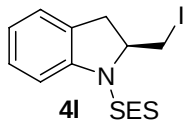
Sample directory:

FidFile: MTB-1-66-pg255-f15-36-prep1

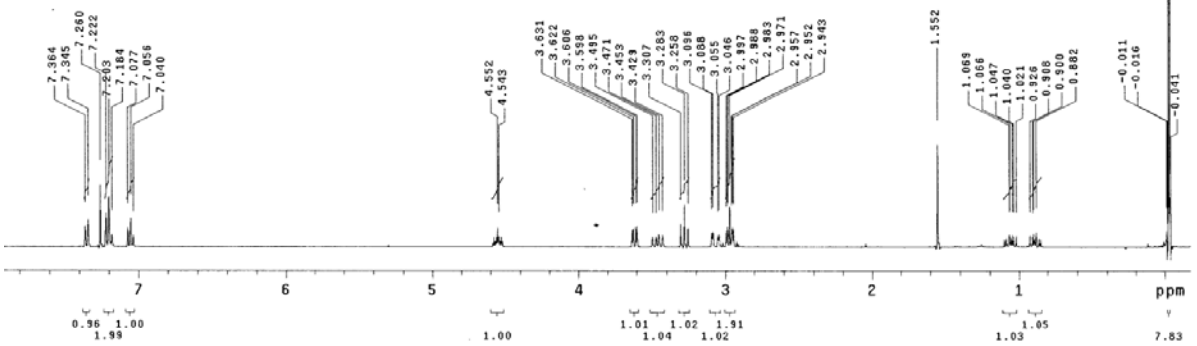
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 22 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



4l



Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

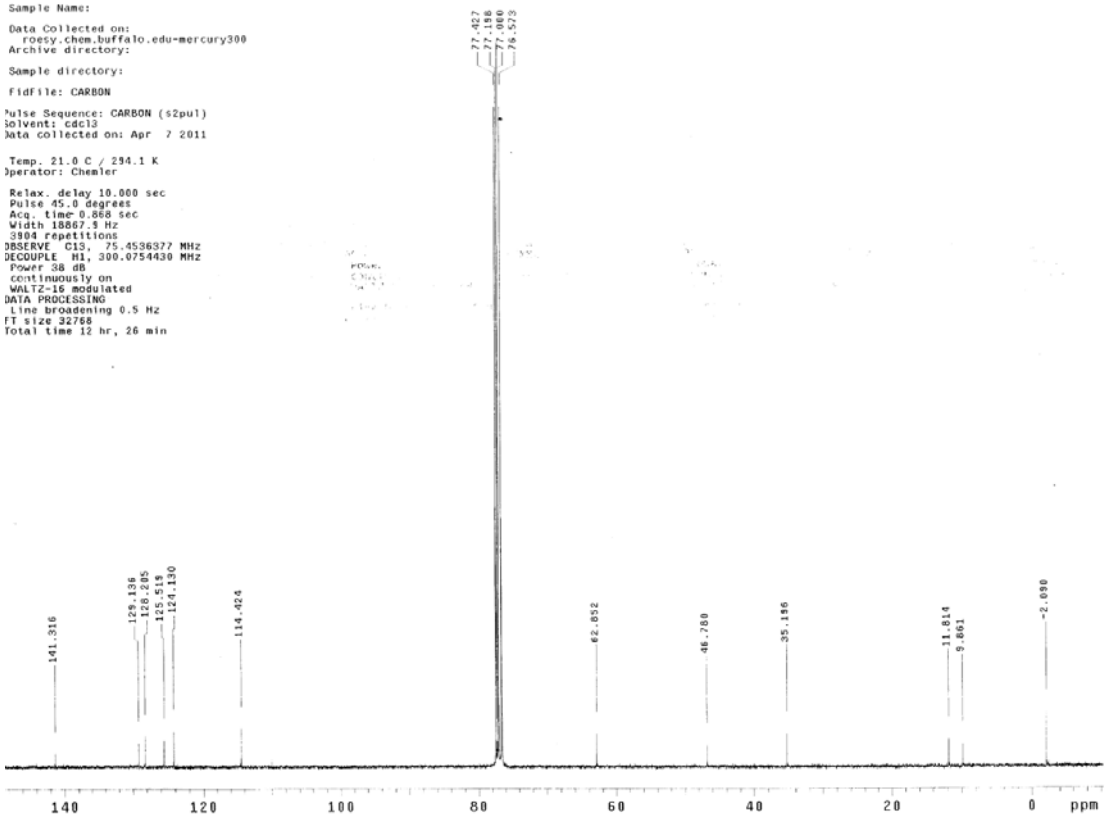
Sample directory:

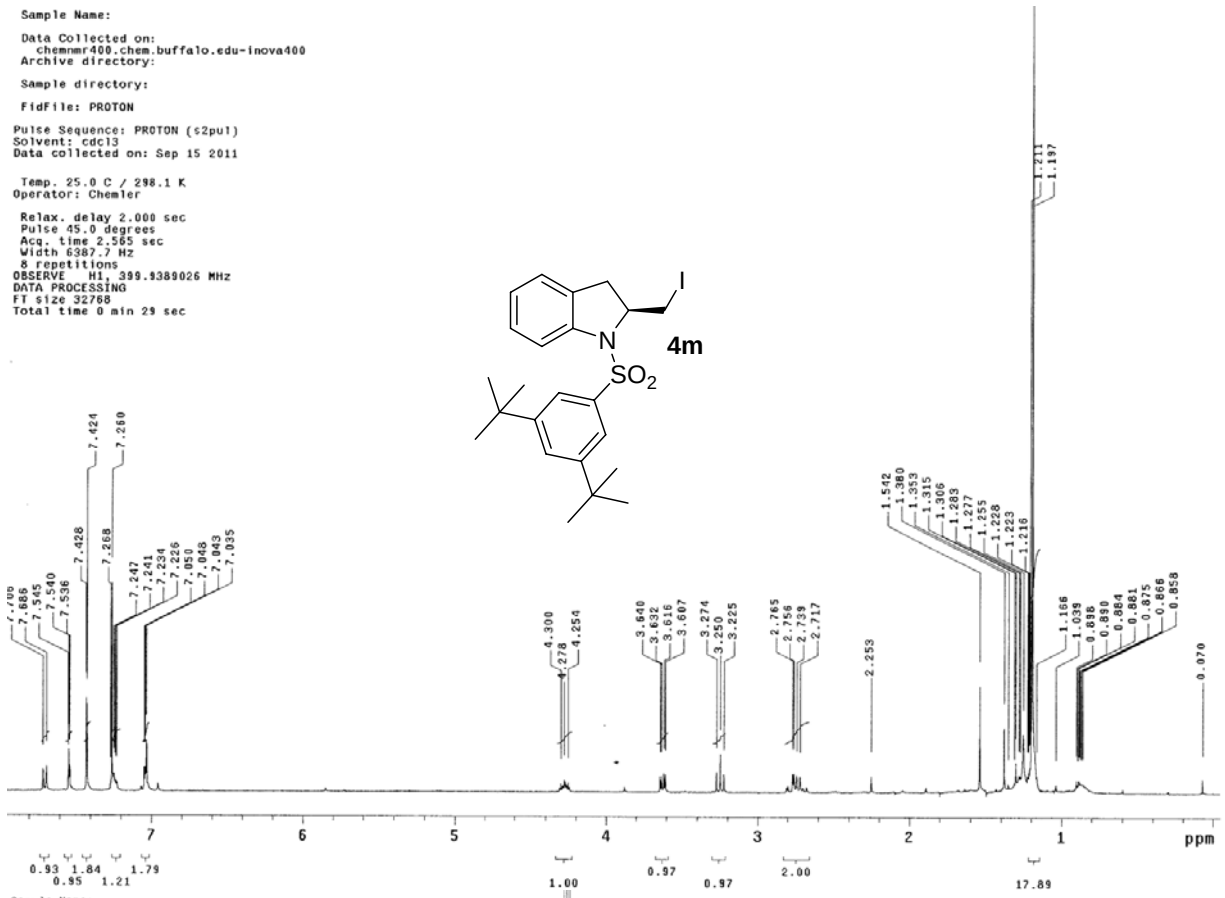
FidFile: CARBON

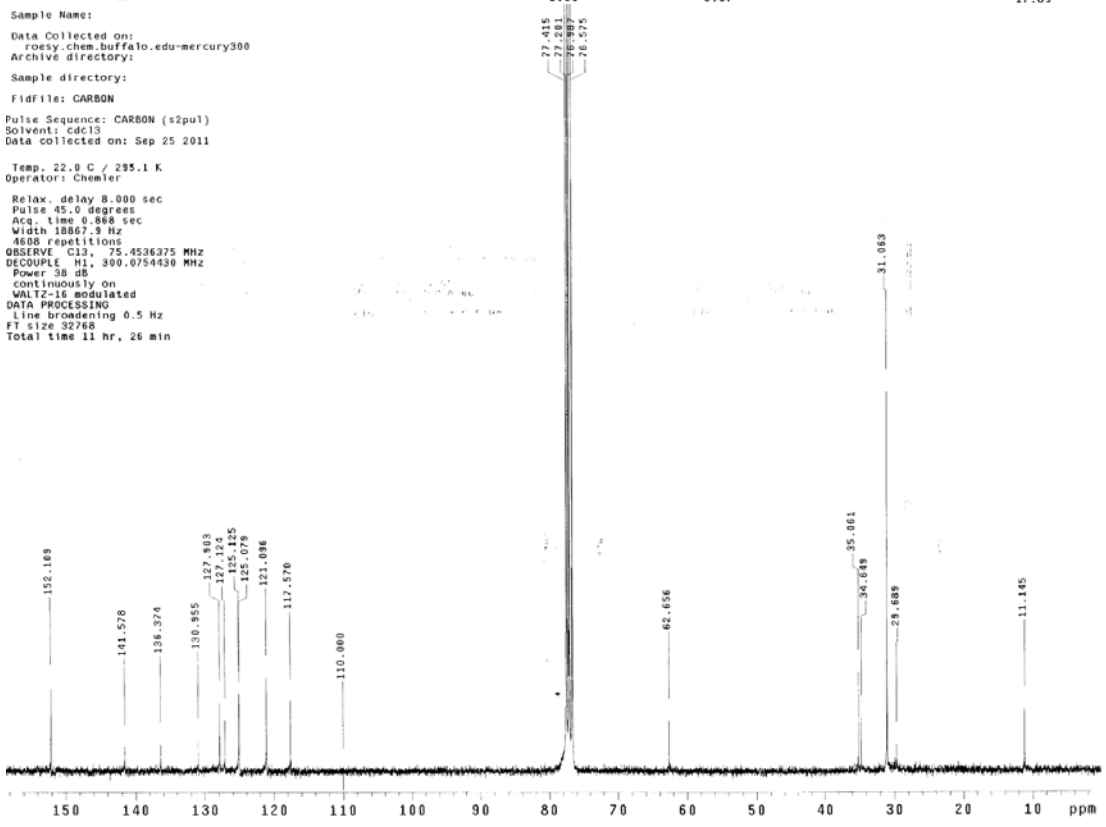
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 7 2011

Temp. 21.0 C / 294.1 K
Operator: Chemler

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3904 repetitions
OBSERVE C13, 75.4536377 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min




Sample Name:
Data Collected on:
chemmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 15 2011
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389026 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
4m
ppm
0.93 1.84 1.79
0.95 1.21
1.00
0.97
0.97
2.00
17.89


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 25 2011
Temp. 22.0 C / 295.1 K
Operator: Chemler
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4608 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 26 min
ppm

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

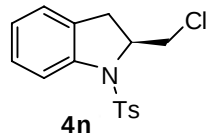
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 2 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



4n

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

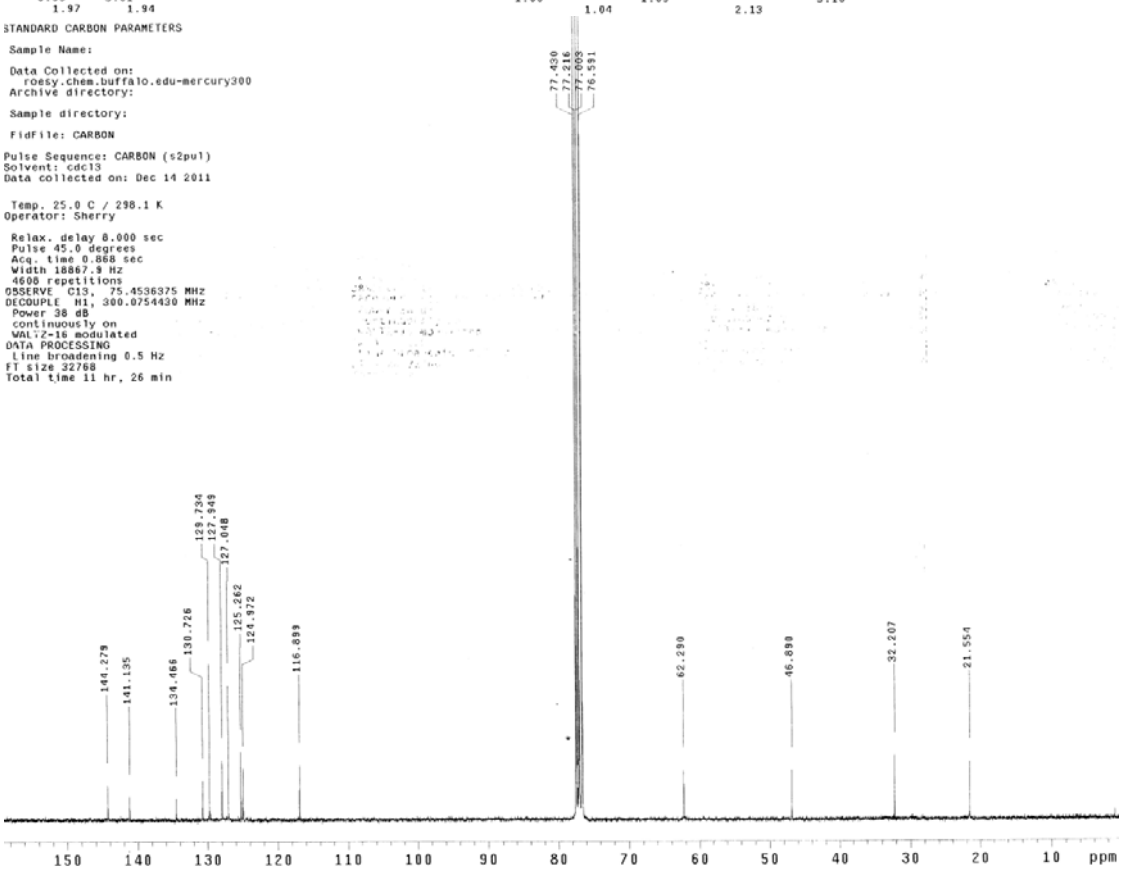
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 14 2011

Temp. 25.0 C / 298.1 K
Operator: Sherry

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4608 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 26 min



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

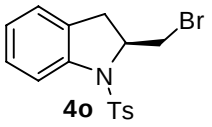
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 16 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389015 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



4o

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

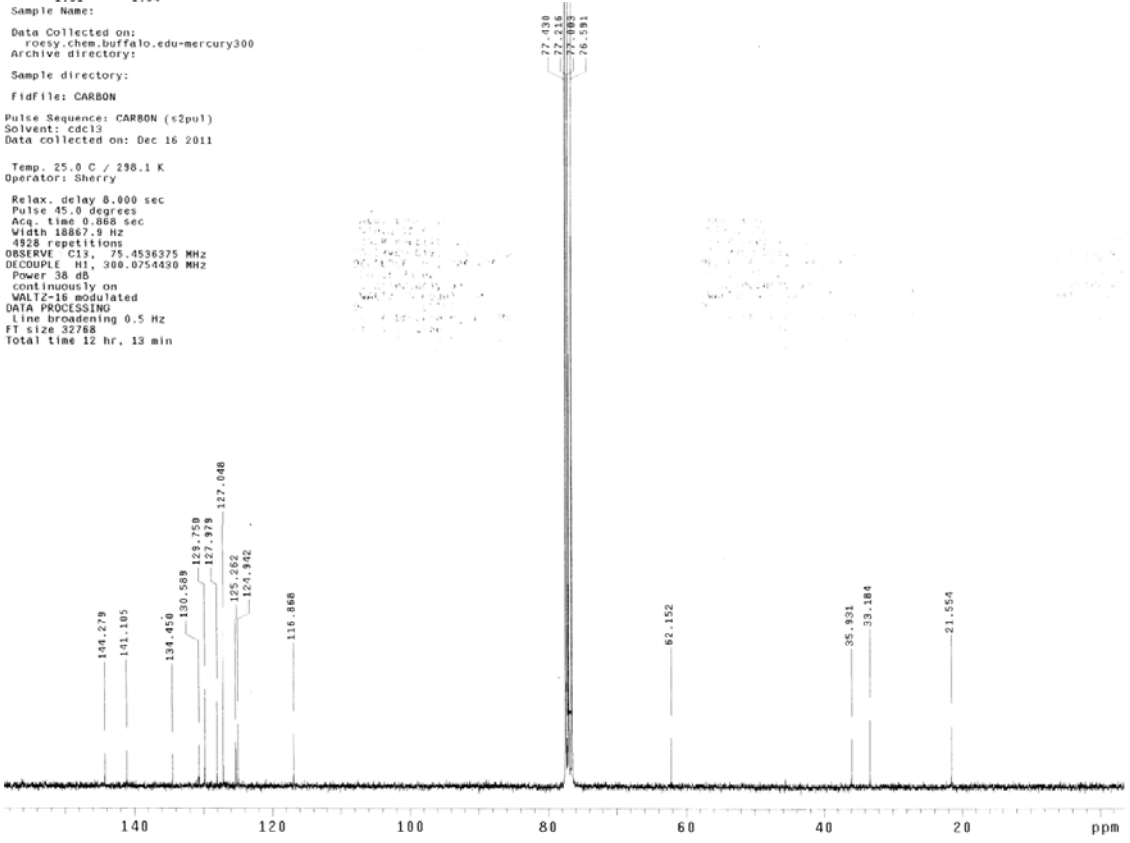
Sample directory:

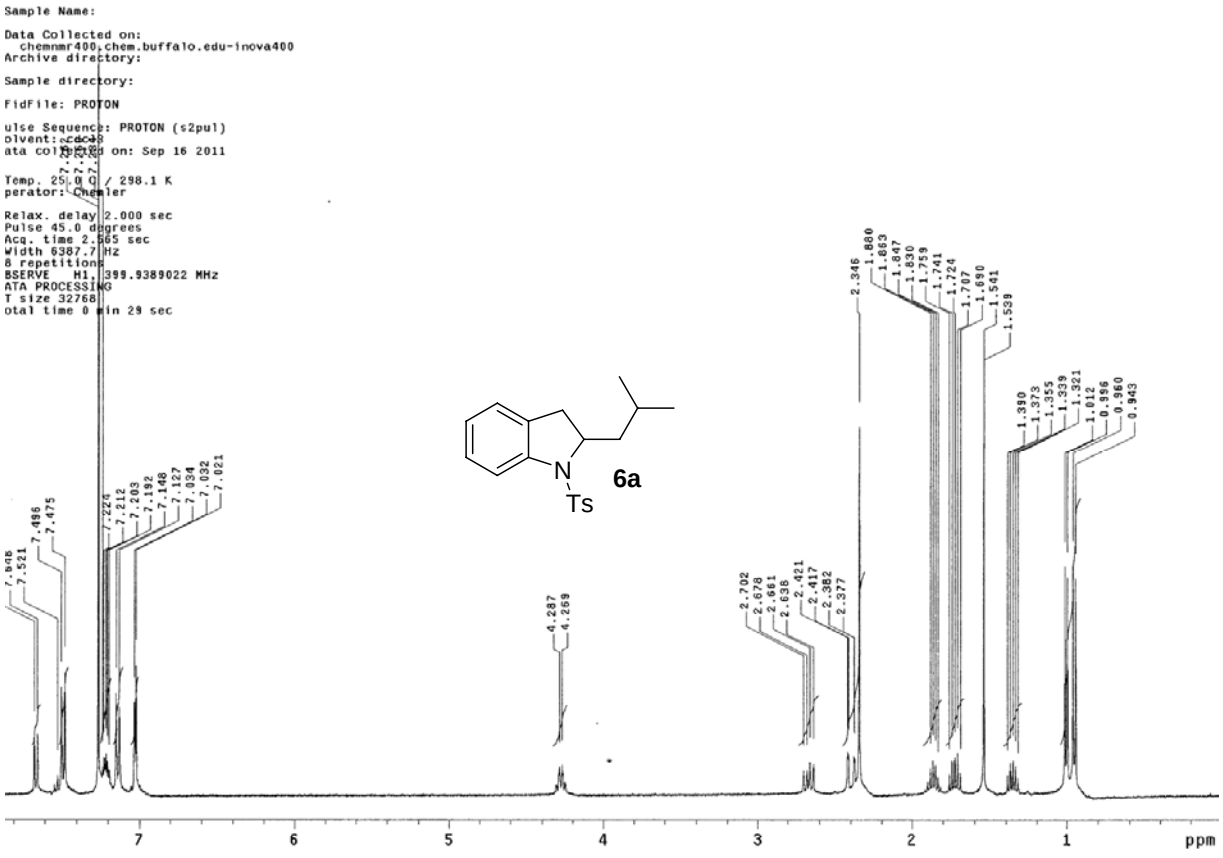
FidFile: CARBON

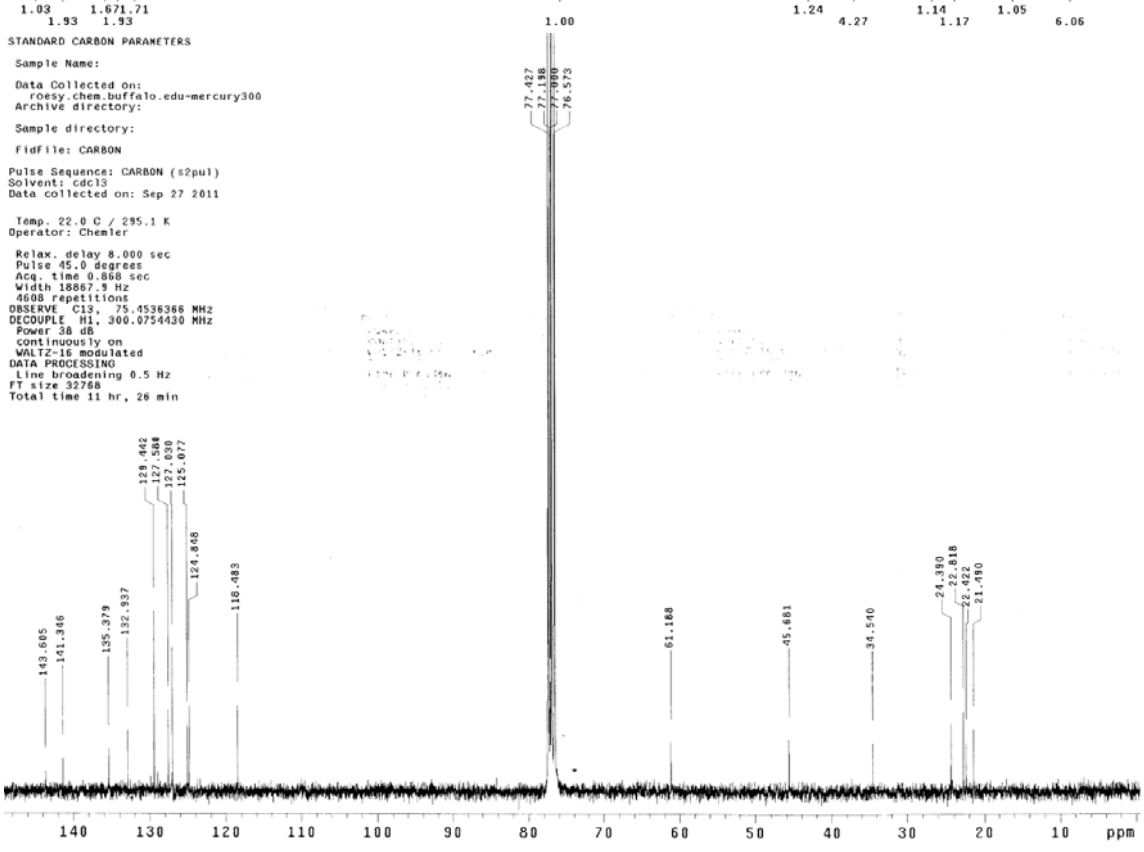
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 16 2011

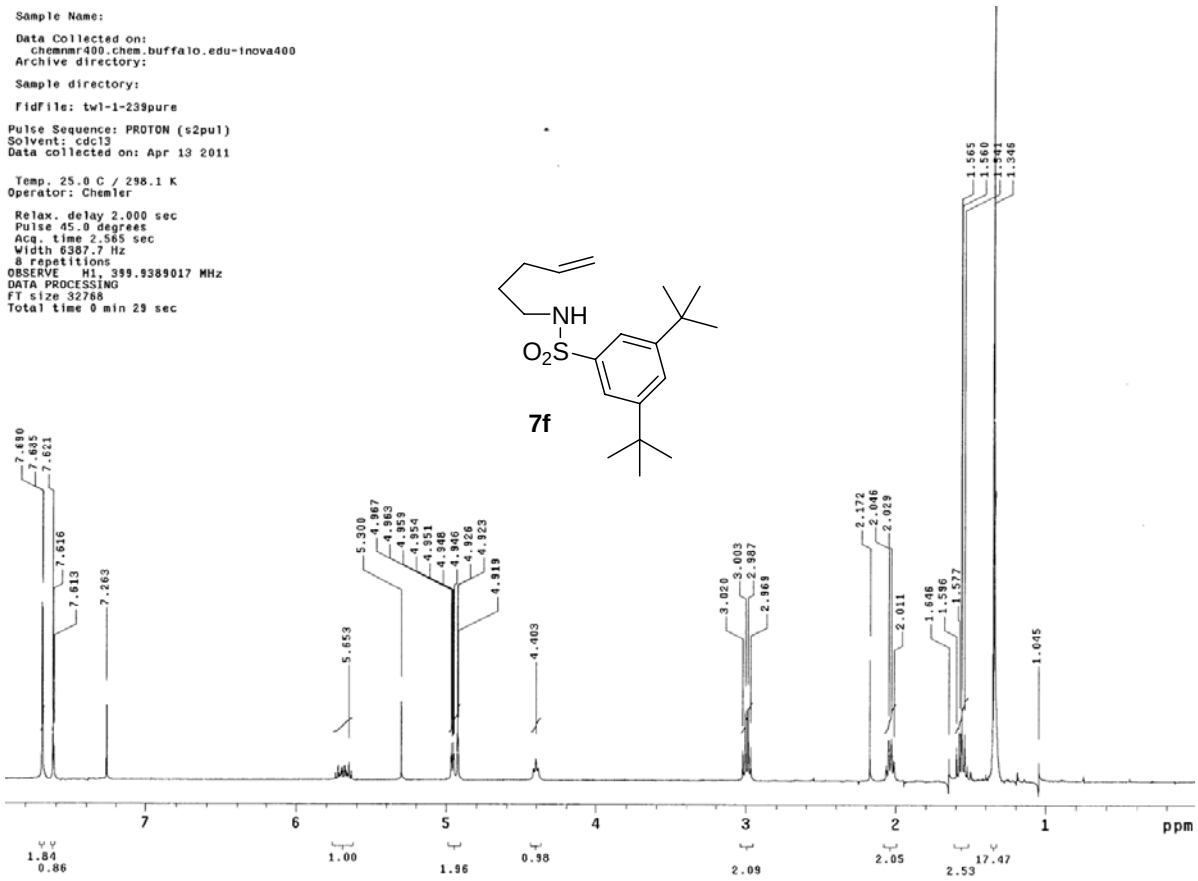
Temp. 25.0 C / 298.1 K
Operator: Sherry

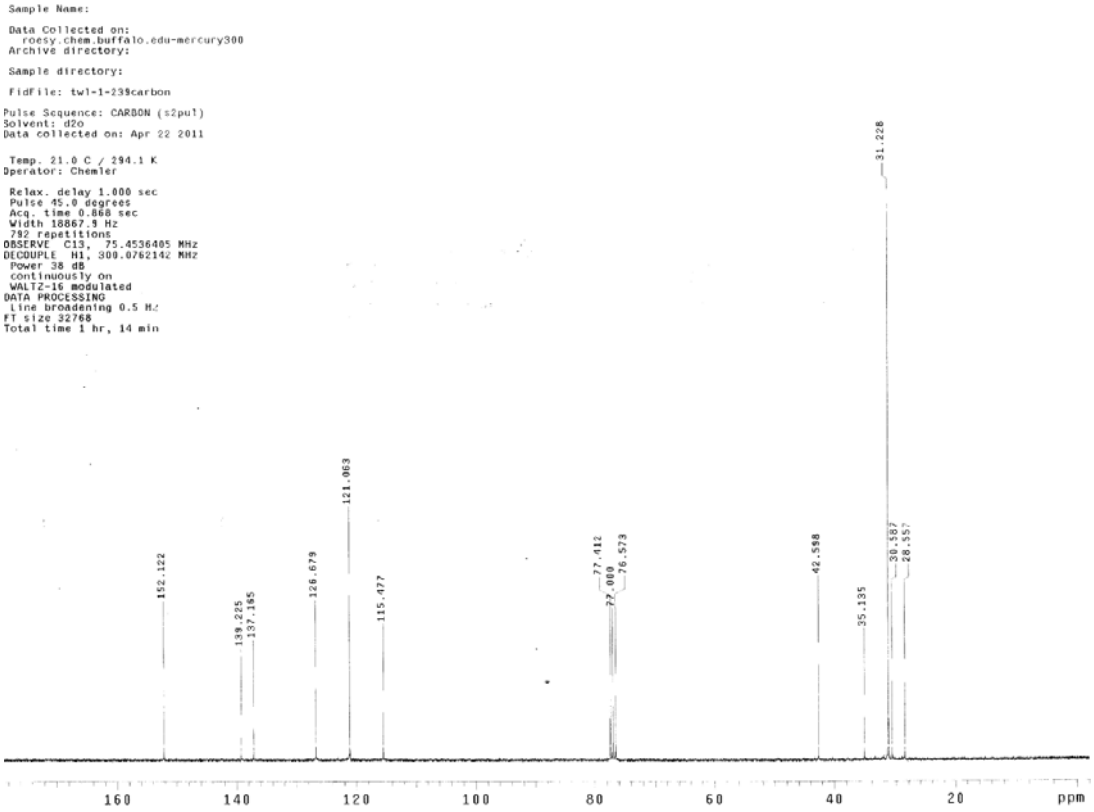
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4928 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 13 min




Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
ulse Sequence: PROTON (s2pul)
olvent: cdcl3
ata collected on: Sep 16 2011
Temp. 25.0 C / 298.1 K
perator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
BSERVE H1, 399.9389022 MHz
ATA PROCESSING
T size 32768
otal time 0 min 29 sec
6a
Ts
ppm
1.03
1.93
1.671.71
1.93
1.24
4.27
1.14
1.17
1.05
6.06


STANDARD CARBON PARAMETERS
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 27 2011
Temp. 22.0 C / 295.1 K
Operator: Chemler
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.5 Hz
4608 repetitions
OBSERVE C13, 75.4536366 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 26 min
1.00
ppm

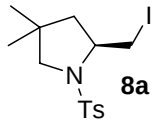

Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: twl-1-239pure
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 13 2011
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389017 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
NH
O2S
7f
7.690
7.645
7.621
7.616
7.613
7.263
5.300
4.967
4.963
4.959
4.954
4.951
4.948
4.946
4.926
4.923
4.919
5.653
4.403
3.020
3.003
2.987
2.968
2.172
2.046
2.029
2.011
1.646
1.596
1.577
1.565
1.560
1.541
1.346
1.045
7
6
5
4
3
2
1
ppm
1.84
0.86
1.00
1.96
0.98
2.09
2.05
2.53
17.47


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: twl-1-239carbon
Pulse Sequence: CARBON (s2pul)
Solvent: d2o
Data collected on: Apr 22 2011
Temp. 21.0 C / 294.1 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
782 repetitions
OBSERVE C13, 75.4536405 MHz
DECOUPLE H1, 309.0762142 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 14 min
31.228
152.122
139.225
137.165
126.679
121.063
115.477
77.412
77.089
76.573
42.598
35.135
30.587
28.357
160
140
120
100
80
60
40
20
ppm

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

Relax. delay 1.000 sec
Pulse 47.9 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389099 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 32768
Total time 0 min, 44 sec

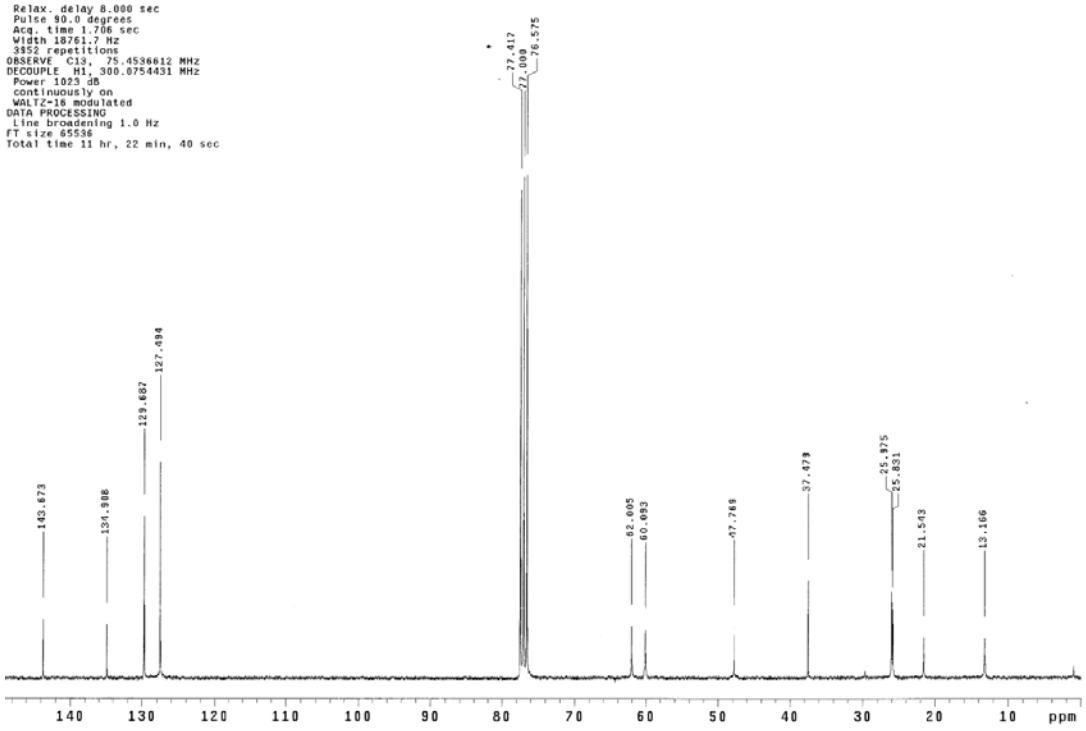


8a

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

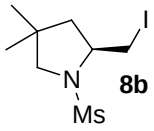
Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
3952 repetitions
OBSERVE C13, 75.4536612 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

Relax. delay 1.000 sec
Pulse 52.3 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389029 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min, 44 sec



8b

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

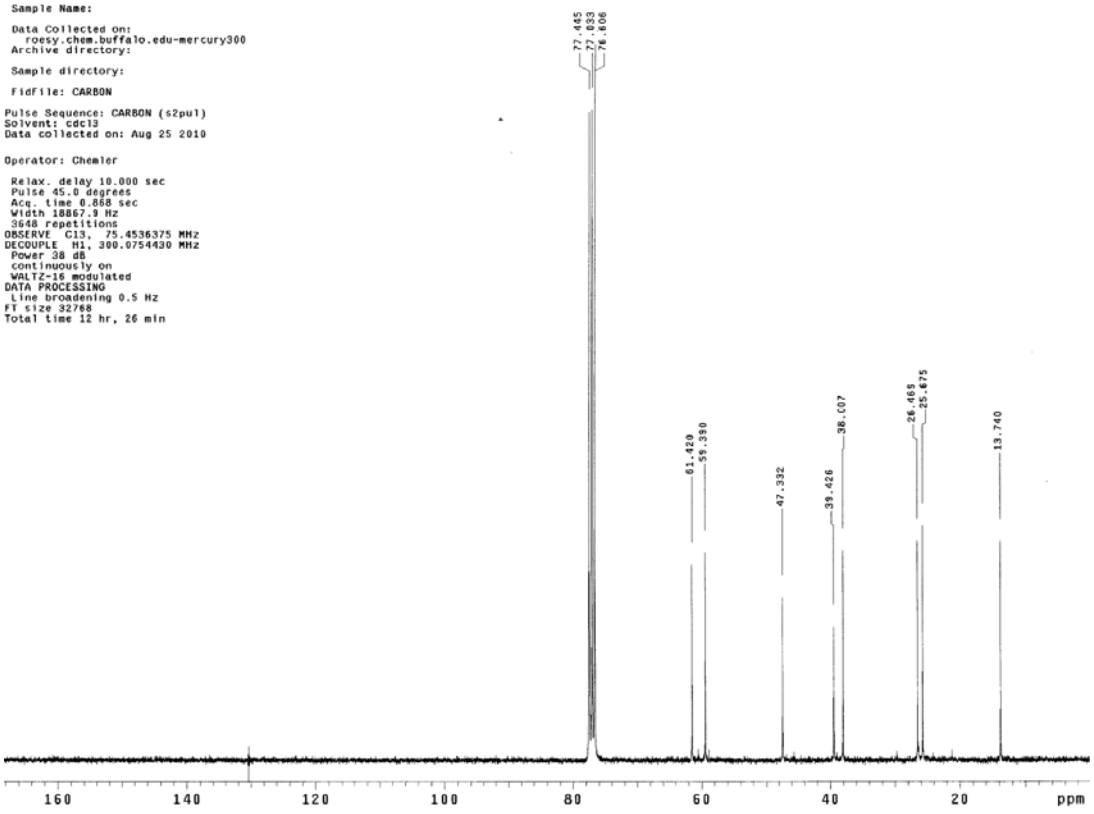
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 25 2010

Operator: Chemler

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3648 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

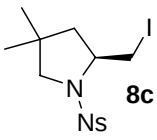
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 13 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389035 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



8c

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

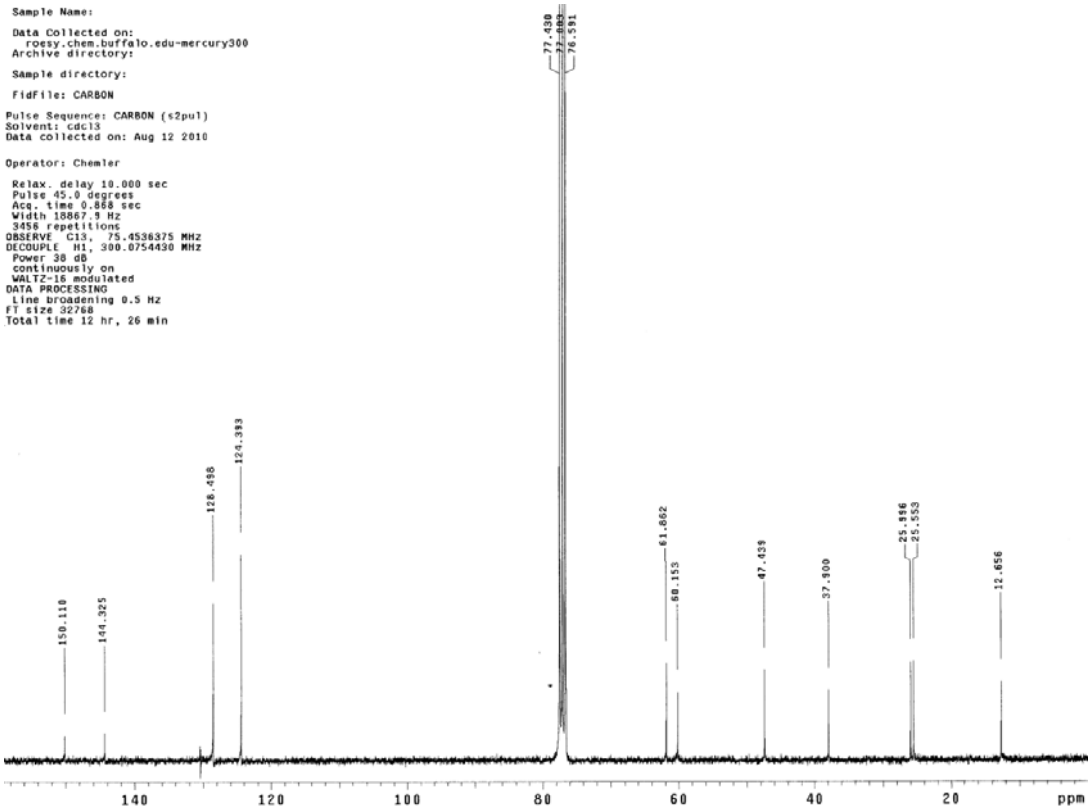
Sample directory:

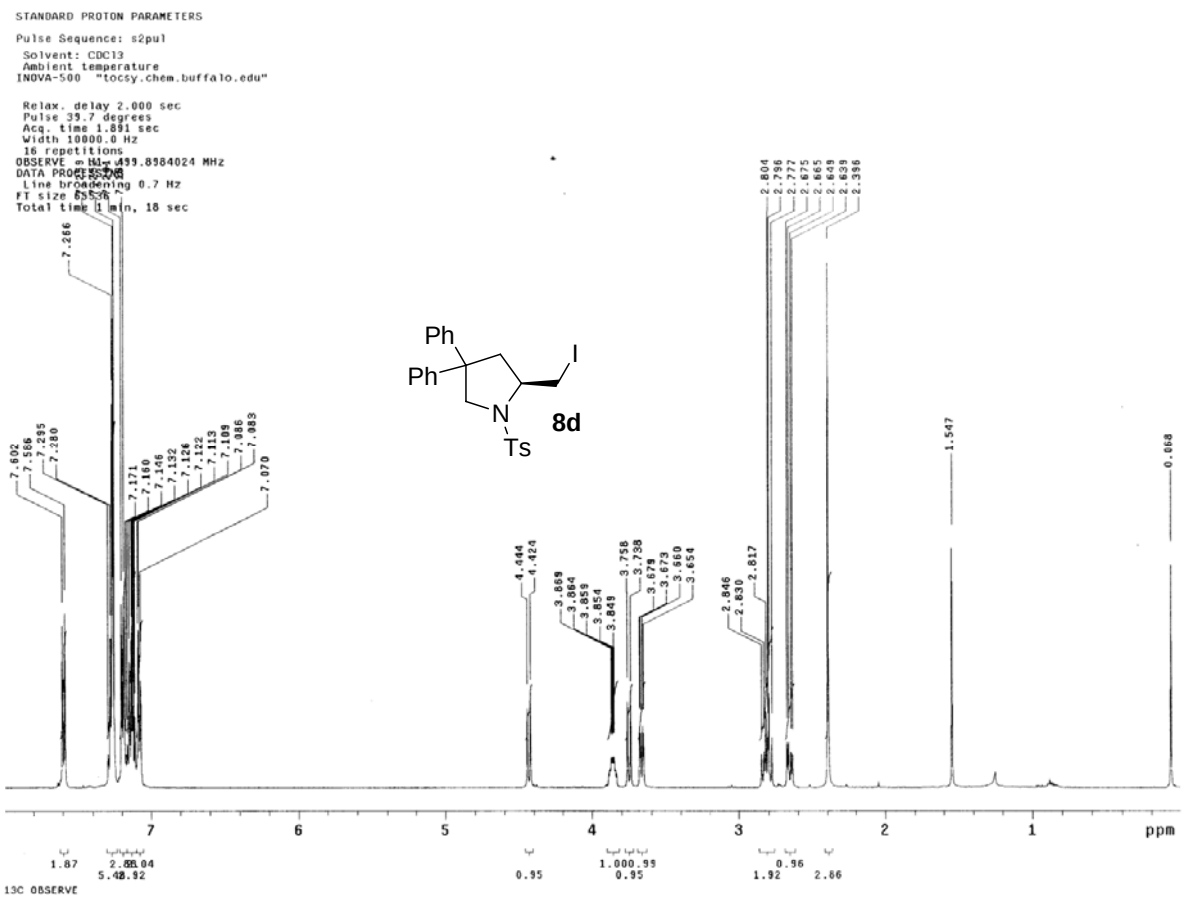
FidFile: CARBON

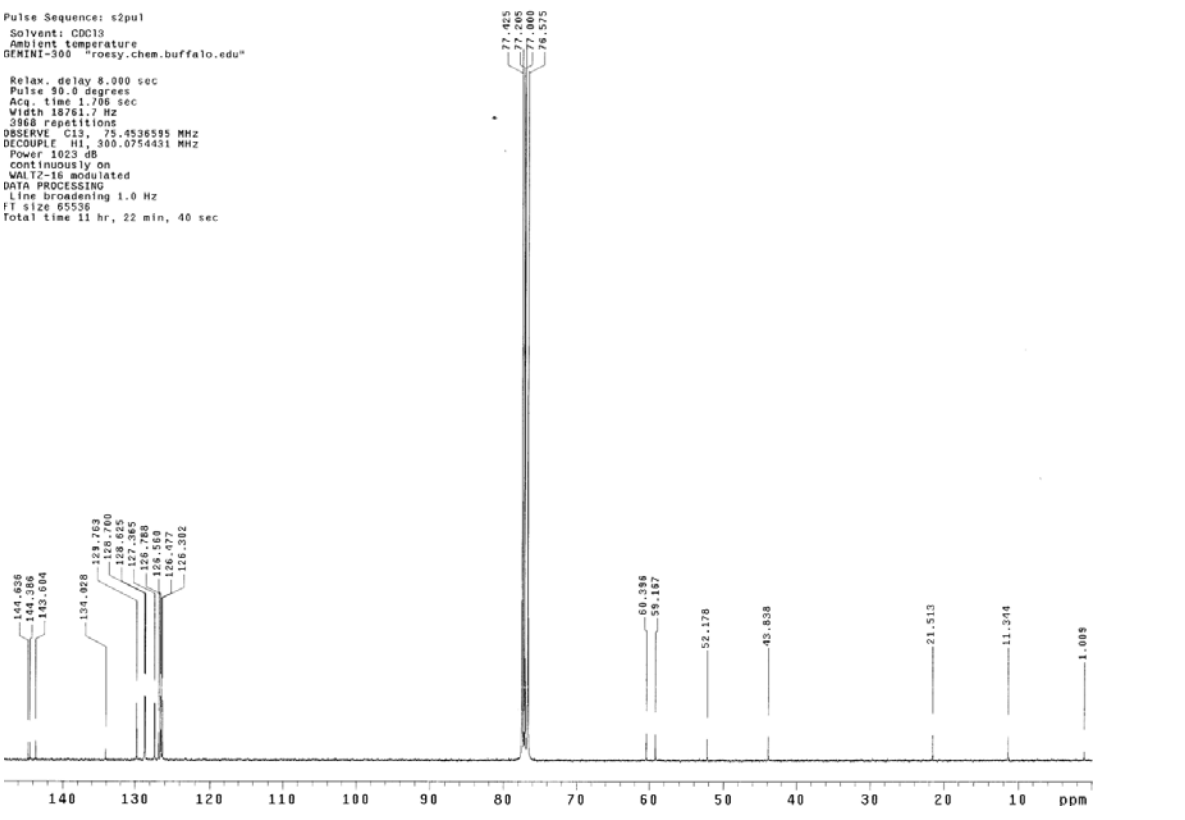
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 12 2010

Operator: Chemler

Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3456 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min




STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "tocsy.chem.buffalo.edu"
Relax. delay 2.000 sec
Pulse 39.7 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
16 repetitions
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec
Ph
Ph
I
N
Ts
8d
ppm


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
3868 repetitions
OBSERVE C13, 75.4536595 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec
ppm

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

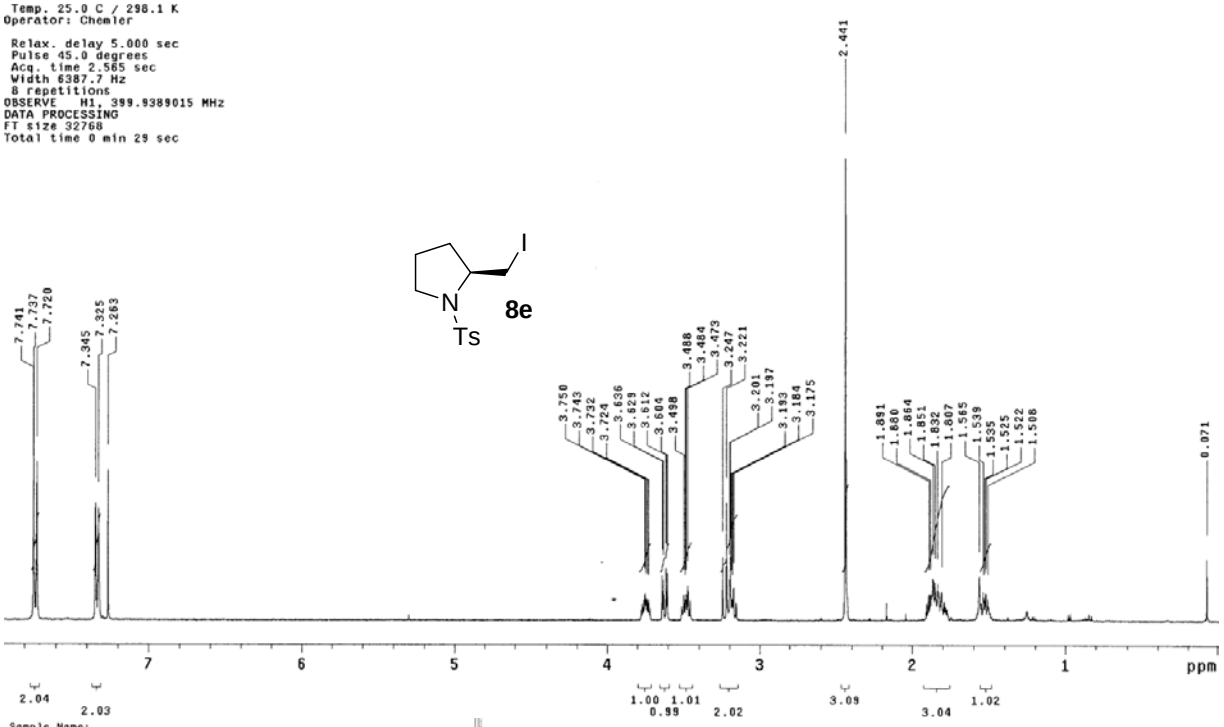
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 5 2010

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389015 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

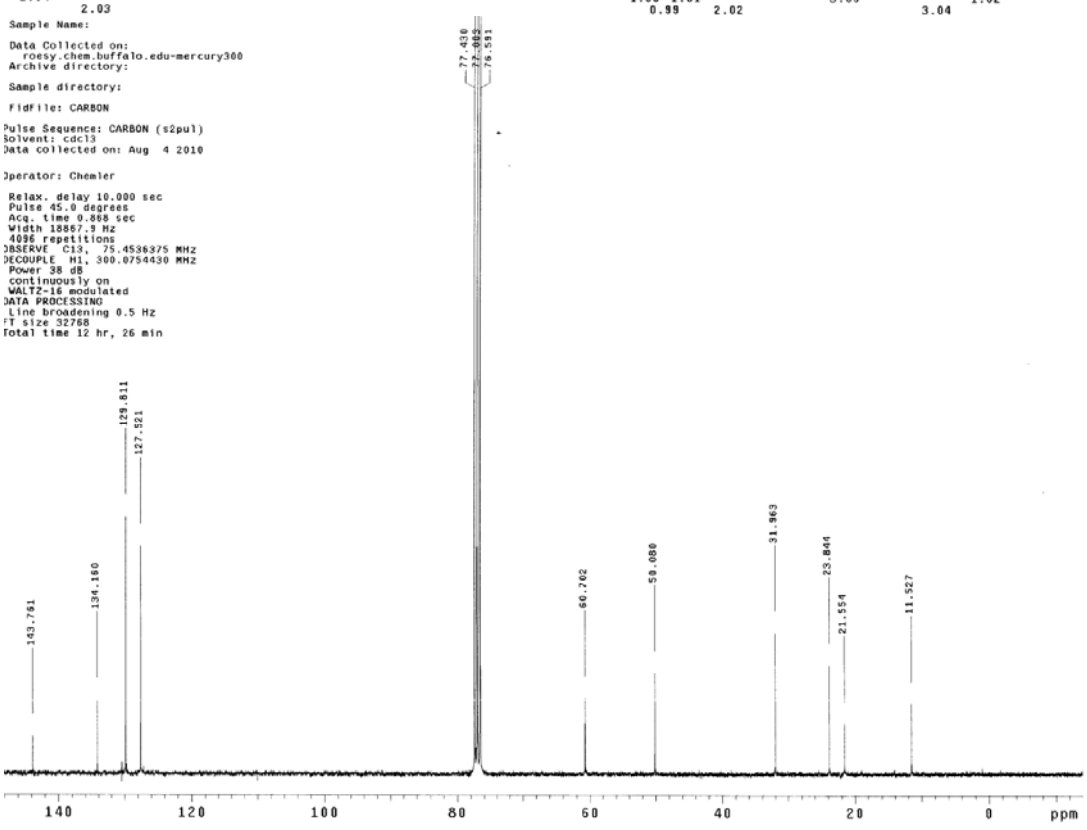
Sample directory:

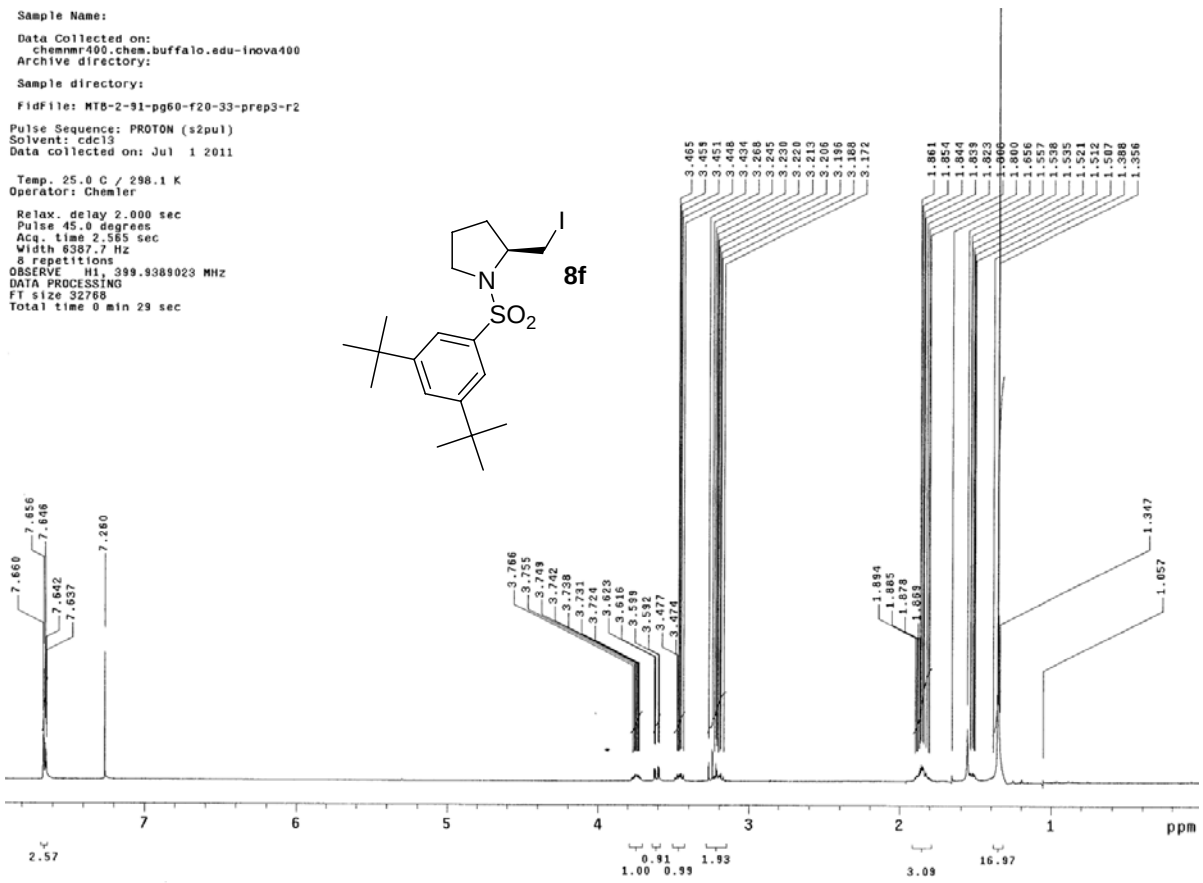
FidFile: CARBON

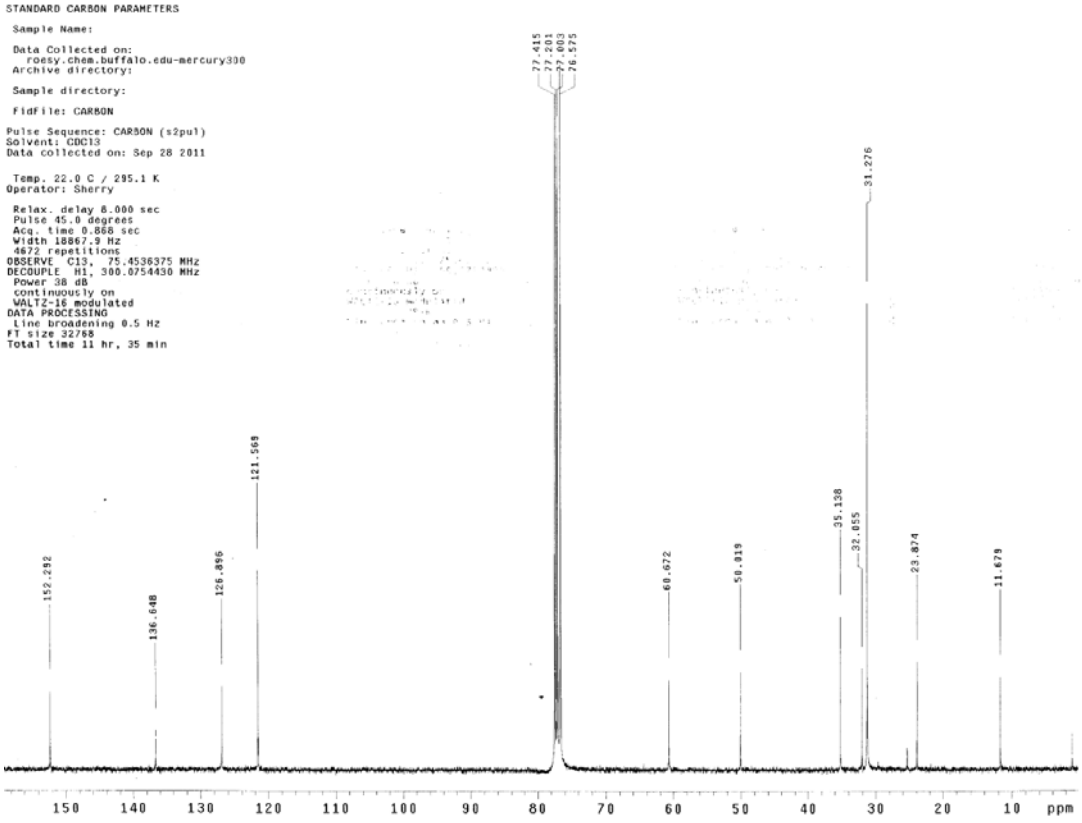
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 4 2010

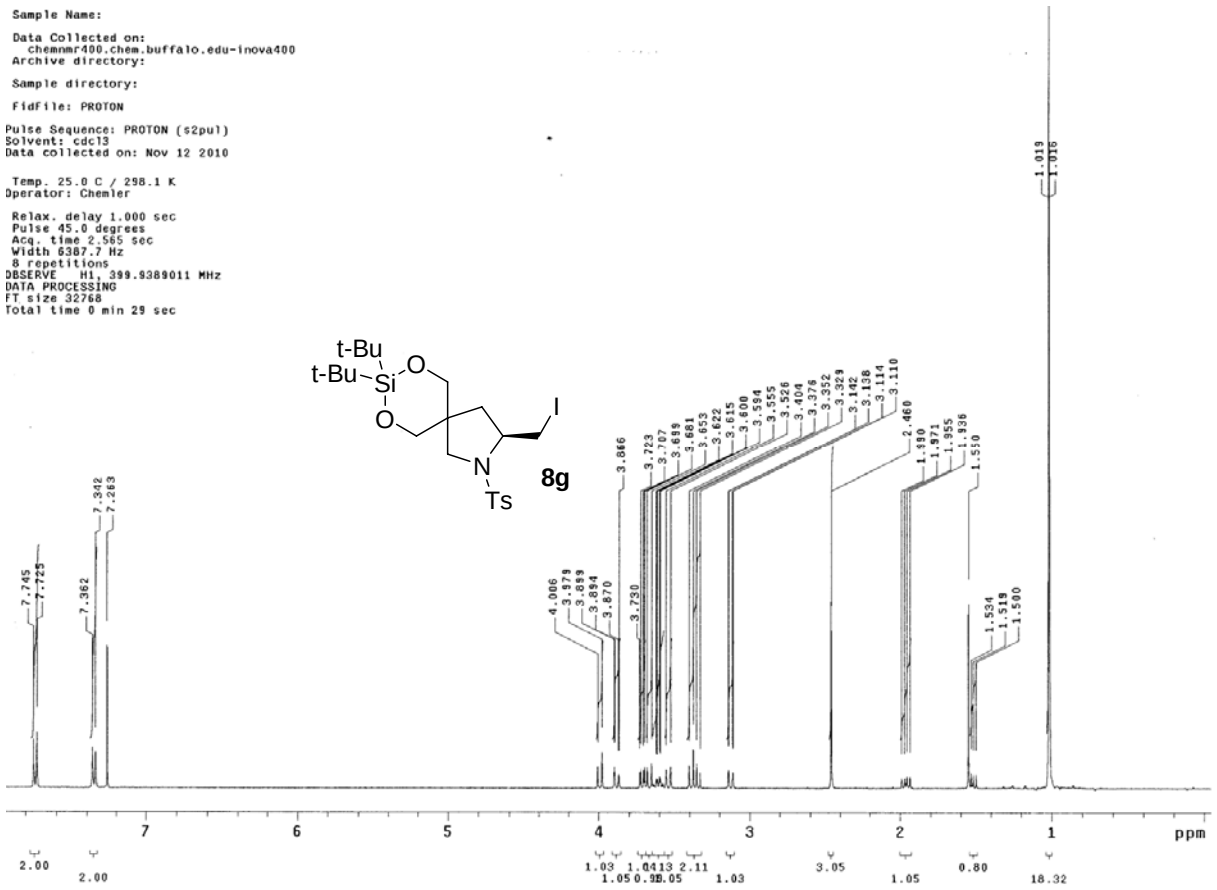
Operator: Chemler

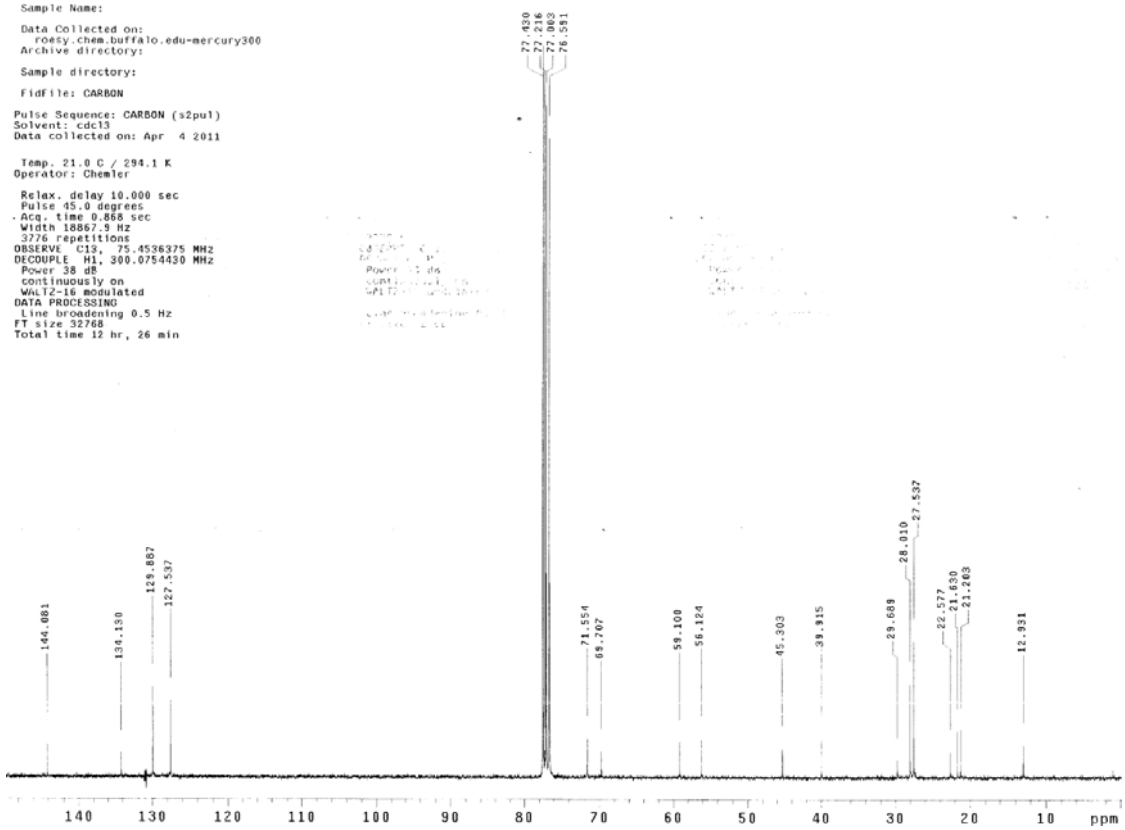
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4096 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min




Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: MTB-2-91-pg60-f20-33-prep3-r2
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 1 2011
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389023 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
8f
7.660
7.656
7.646
7.642
7.637
7.260
3.766
3.755
3.749
3.742
3.738
3.731
3.724
3.623
3.616
3.599
3.592
3.477
3.474
3.465
3.459
3.451
3.448
3.434
3.268
3.245
3.230
3.220
3.213
3.206
3.196
3.188
3.172
1.894
1.885
1.878
1.869
1.861
1.854
1.844
1.839
1.823
1.800
1.656
1.557
1.538
1.535
1.521
1.512
1.507
1.388
1.356
1.347
1.057
ppm
2.57
1.00
0.99
0.91
1.93
3.09
16.97


STANDARD CARBON PARAMETERS
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Sep 28 2011
Temp. 22.0 C / 295.1 K
Operator: Sherry
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4672 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 35 min
77.415
77.201
77.003
76.575
152.282
136.648
126.896
121.569
60.672
50.819
35.138
32.655
31.276
23.874
11.679
ppm

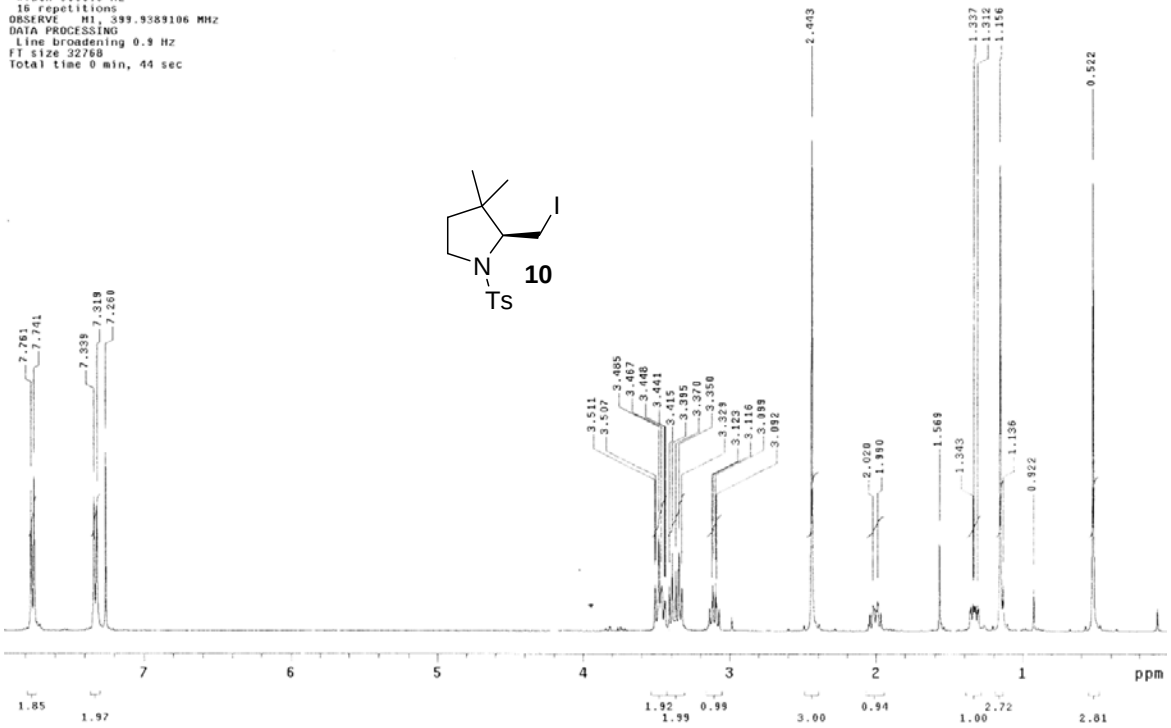

Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 12 2010
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389011 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
t-Bu
t-Bu
Si
O
O
O
I
N
Ts
8g
7.745
7.725
7.362
7.342
7.283
4.006
3.979
3.859
3.854
3.670
3.730
3.866
3.723
3.707
3.699
3.681
3.653
3.622
3.615
3.600
3.584
3.555
3.526
3.404
3.378
3.332
3.329
3.142
3.118
3.114
3.110
2.460
1.990
1.971
1.955
1.936
1.510
1.534
1.519
1.500
1.019
1.016
7
6
5
4
3
2
1
ppm
2.00
2.00
1.03
1.04
13
2.11
1.05
0.93
0.05
1.03
3.05
1.05
0.80
18.32


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 4 2011
Temp. 21.0 C / 294.1 K
Operator: Chemler
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3776 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min
77.430
77.216
77.003
76.591
144.081
134.130
129.887
127.537
71.554
69.707
59.100
56.124
45.303
39.915
29.689
28.010
27.537
22.577
21.630
21.263
12.931
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"

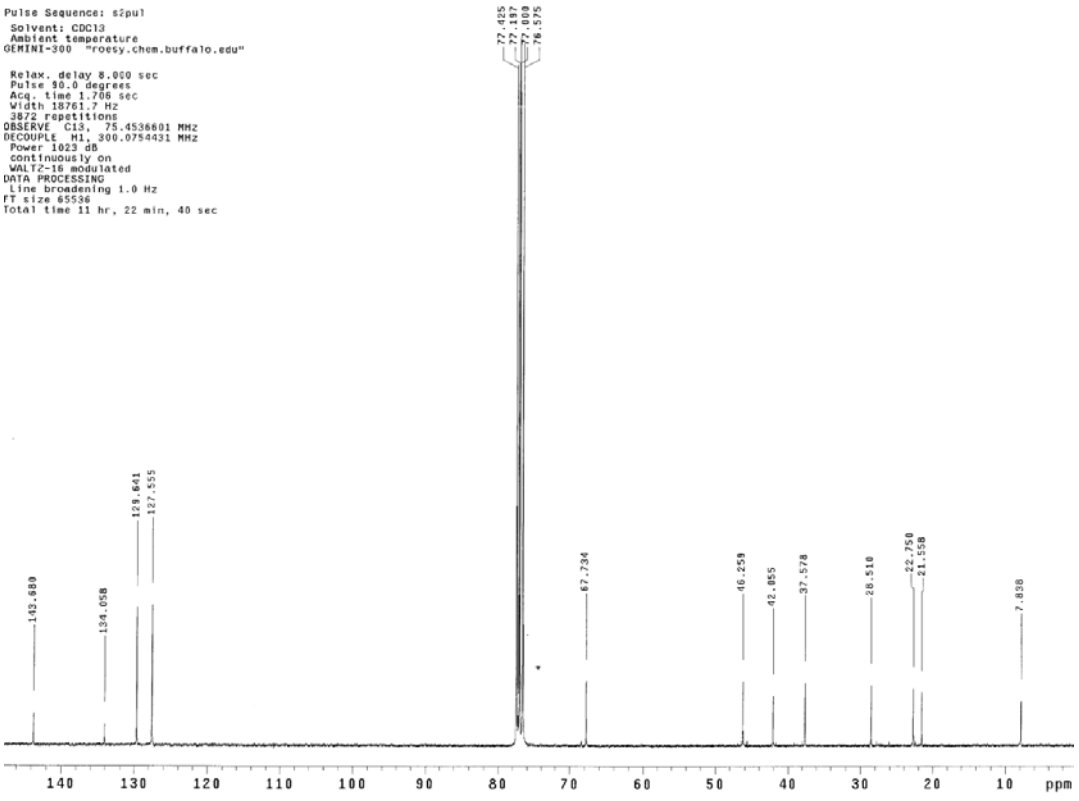
Relax. delay 1.000 sec
Pulse 47.9 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389106 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 32768
Total time 0 min, 44 sec



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

Relax. delay 8.000 sec
Pulse 30.0 degrees
Acq. time 1.708 sec
Width 18761.7 Hz
3872 repetitions
OBSERVE C13, 75.4536601 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec



Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

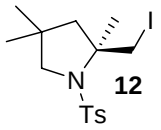
Sample directory:

FidFile: MTB-1-26

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 2 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec

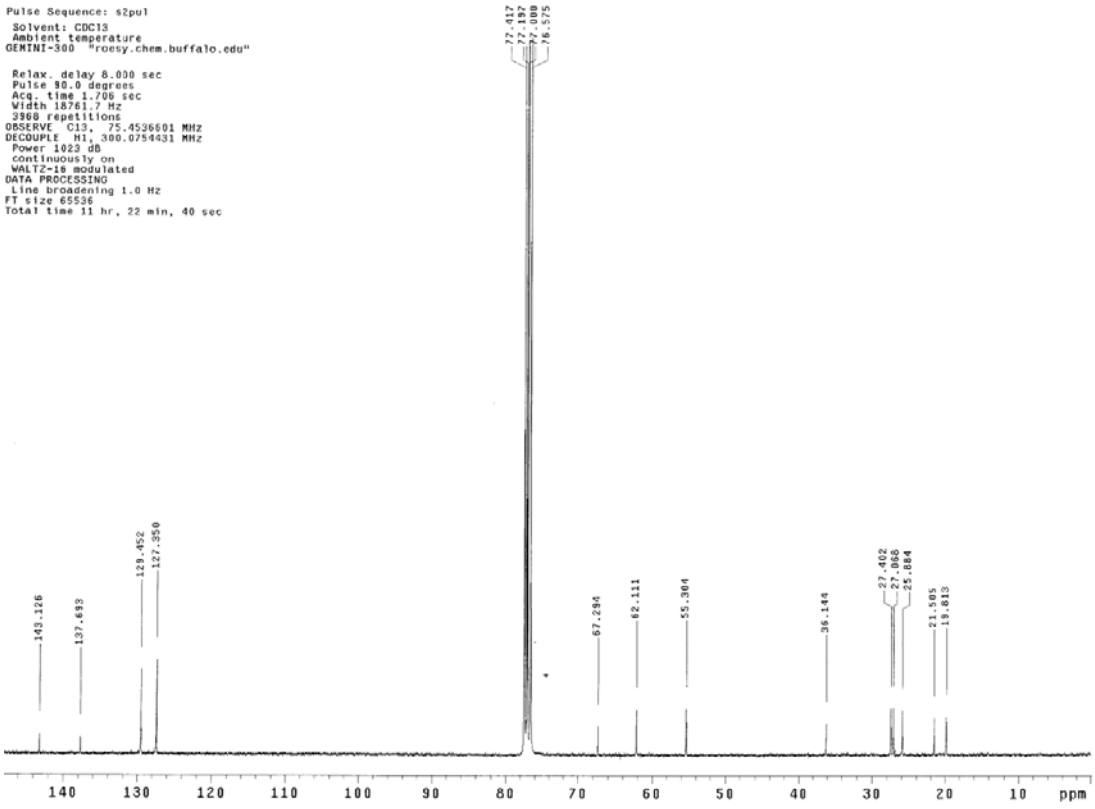


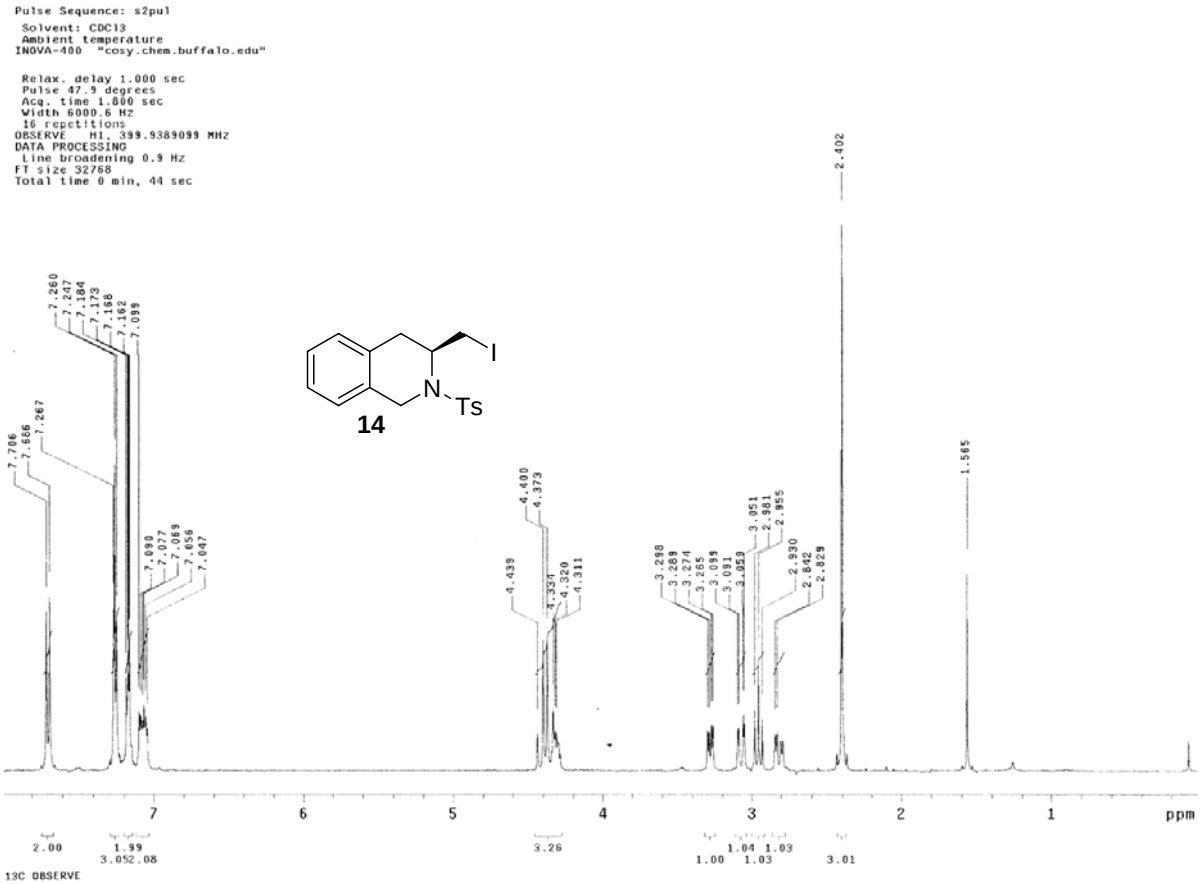
12

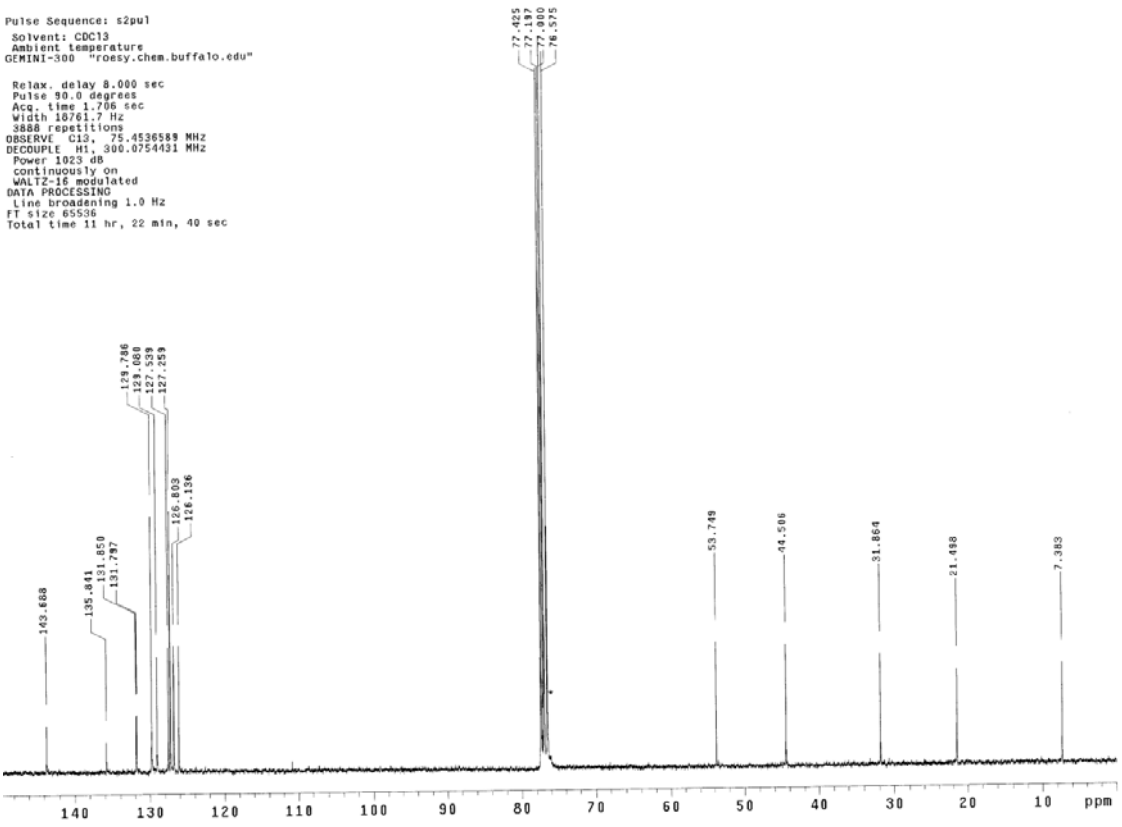
13C OBSERVE

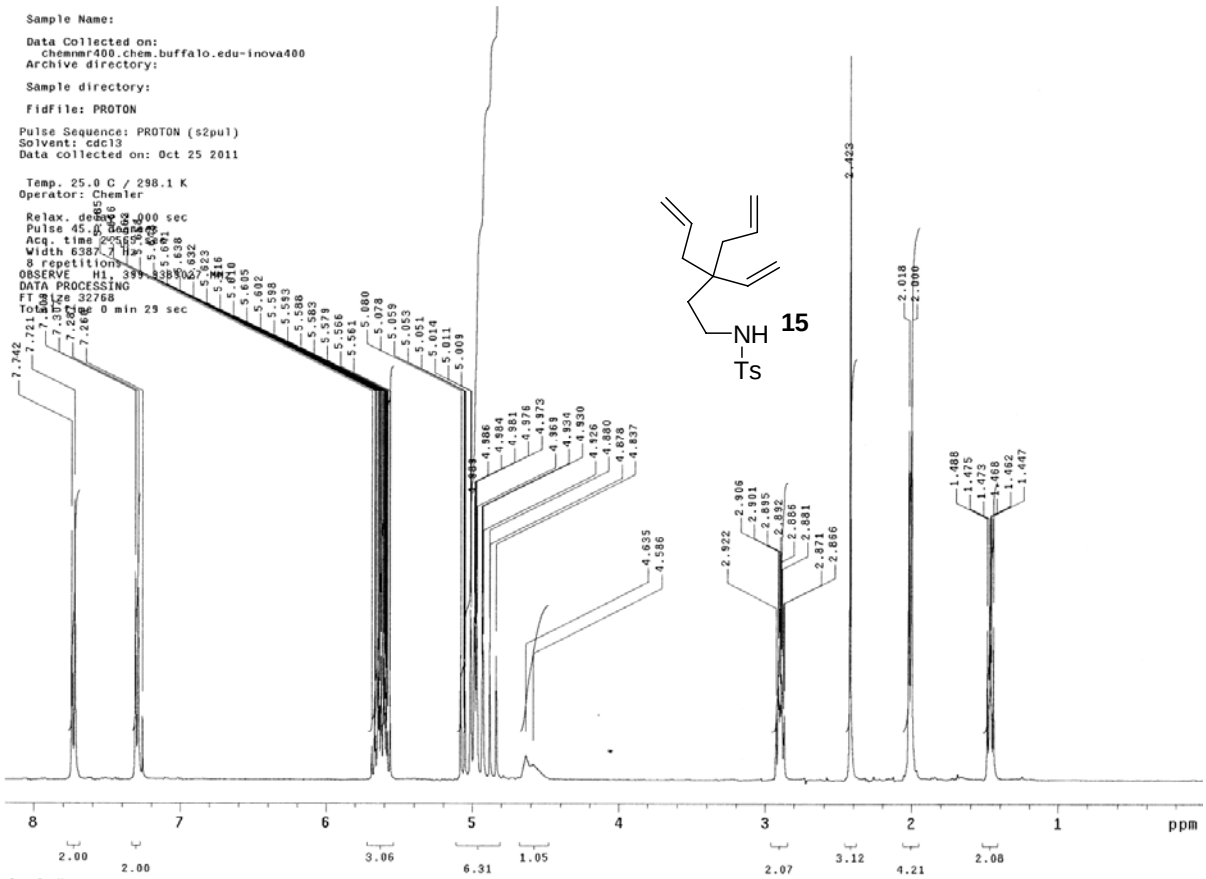
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

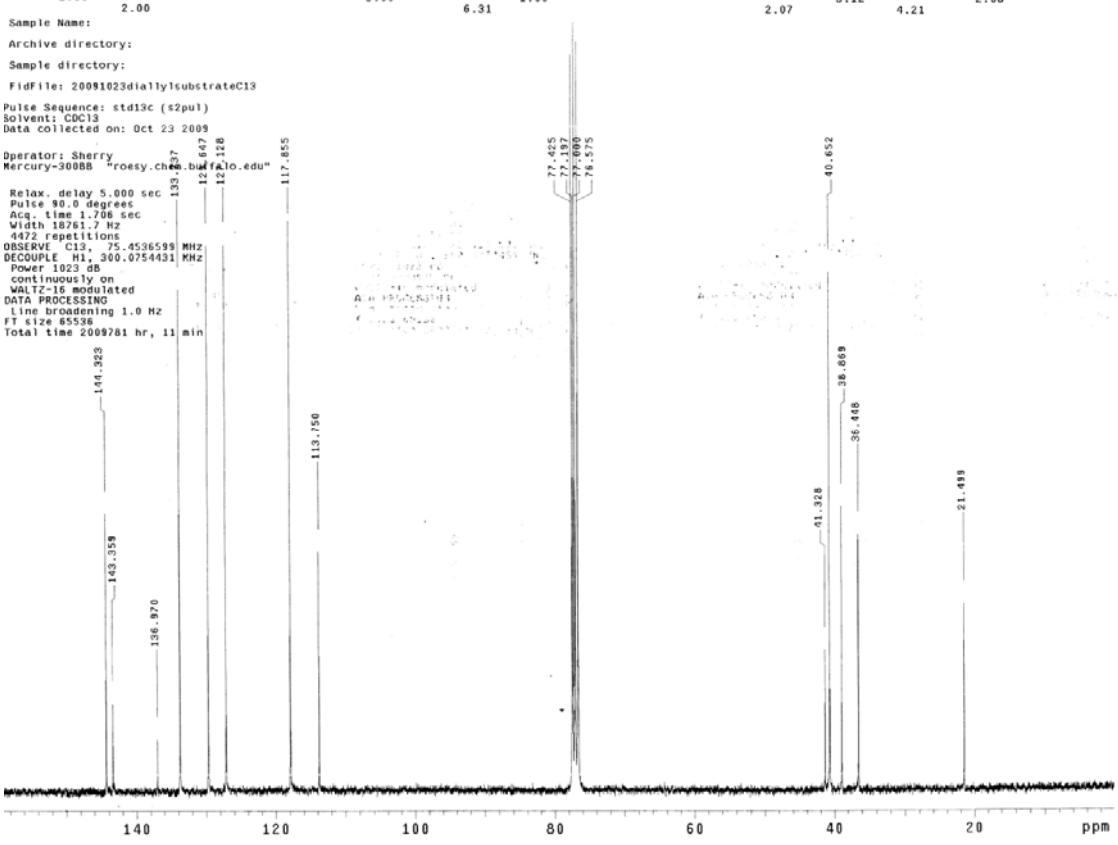
Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
3968 repetitions
OBSERVE C13, 75.4536601 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec

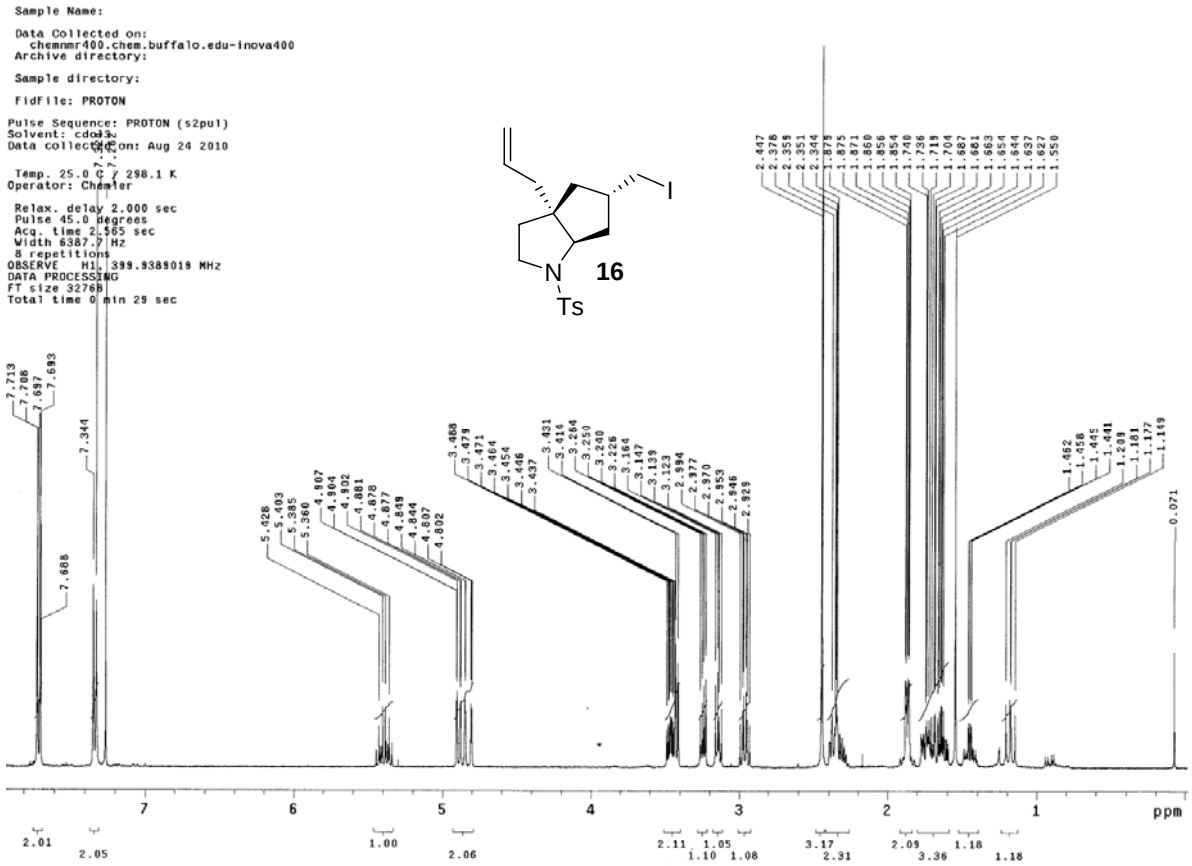


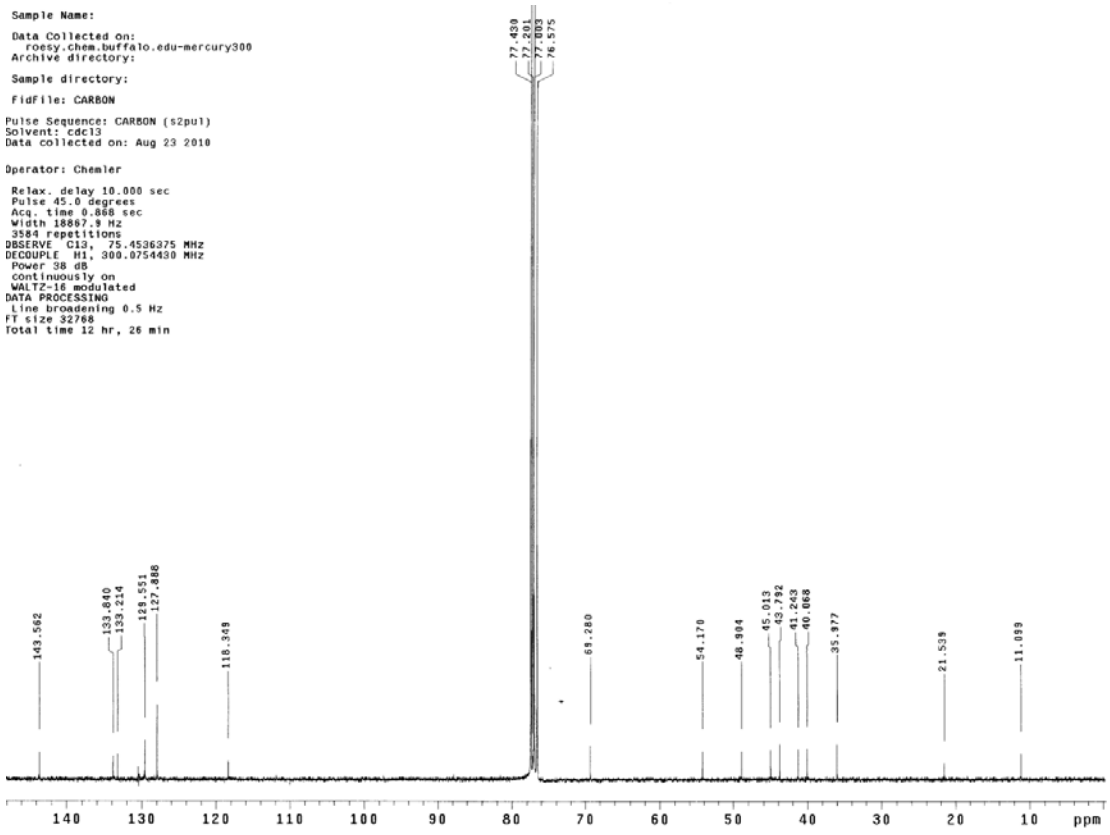

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"
Relax. delay 1.000 sec
Pulse 47.9 degrees
Acq. time 1.800 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.9389099 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 32768
Total time 0 min, 44 sec
I
N
Ts
14
2.402
1.565
ppm
2.00
1.99
3.052.08
3.26
1.00
1.04
1.03
1.03
3.01

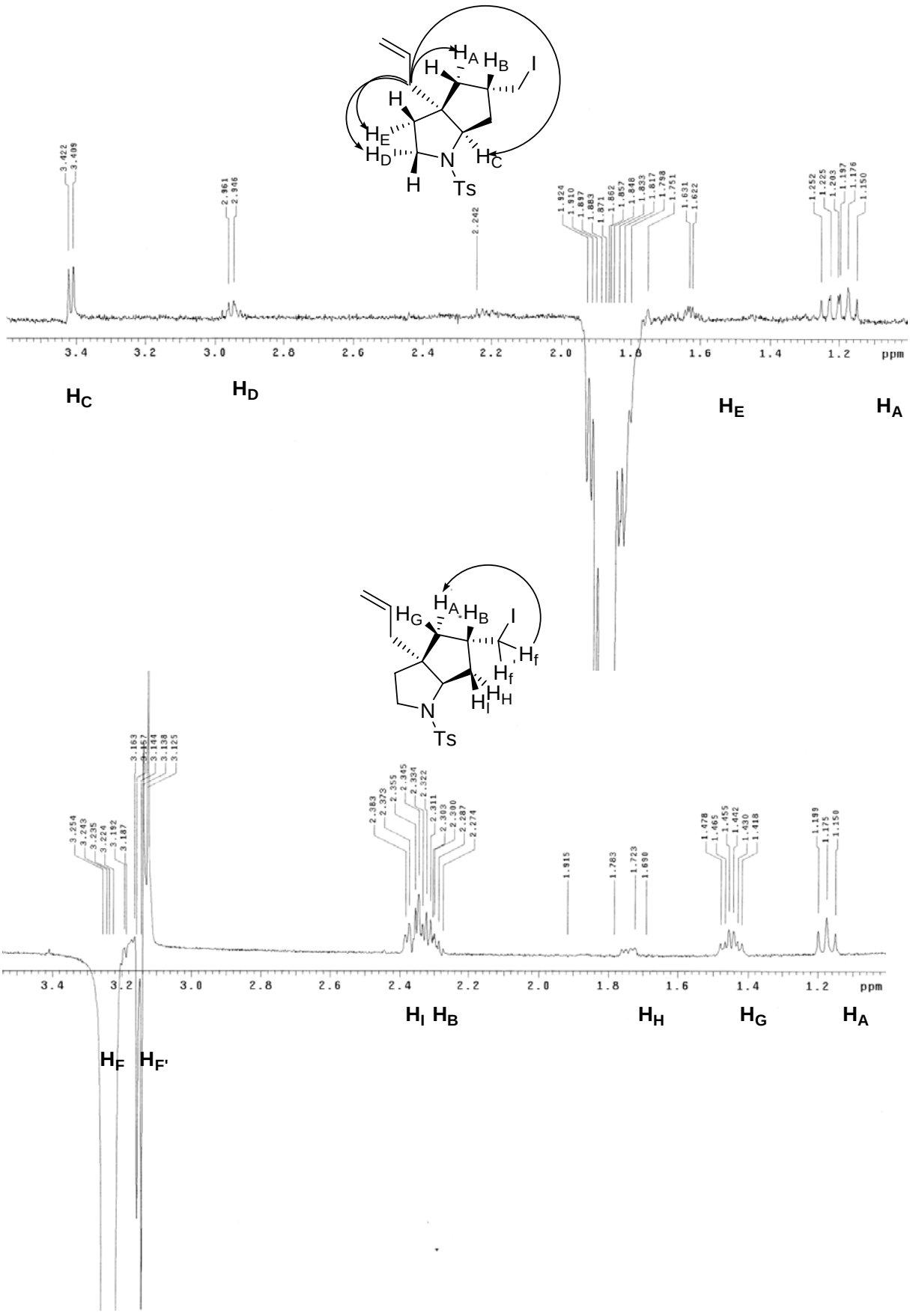

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"
Relax. delay 8.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
3888 repetitions
OBSERVE C13, 75.4536589 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 22 min, 40 sec
143.688
135.841
131.850
131.797
129.786
129.668
128.358
127.259
126.803
126.136
77.425
77.100
76.775
76.575
53.749
44.596
31.864
21.498
7.383
ppm


Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 25 2011
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.055556 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.8381027 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
NH
Ts
15
ppm


Sample Name:
Archive directory:
Sample directory:
FidFile: 20091023diallylsubstrateC13
Pulse Sequence: std13c (s2pul)
Solvent: CDCl3
Data collected on: Oct 23 2009
Operator: Sherry
Mercury-300BB "roesy.chem.buffalo.edu"
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
4472 repetitions
OBSERVE C13, 75.4536599 MHz
DECOUPLE H1, 300.0754431 MHz
Power 1023 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2009781 hr, 11 min
ppm


Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 24 2010
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389019 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
16
Ts
ppm


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 23 2010
Operator: Chemler
Relax. delay 10.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3584 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 26 min
ppm


H
H_A H_B
I
H
H_E
H_D
N
H_C
H
Ts
3.422
3.409
2.961
2.946
2.242
1.924
1.910
1.897
1.883
1.871
1.862
1.857
1.848
1.833
1.817
1.798
1.751
1.631
1.622
1.252
1.225
1.203
1.197
1.176
1.150
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm
H_C
H_D
H_E
H_A
H_G
H_A H_B
I
H_f
H_f
H_H
H_I
N
Ts
3.254
3.243
3.235
3.224
3.192
3.187
3.163
3.147
3.144
3.138
3.125
2.383
2.373
2.355
2.345
2.334
2.322
2.311
2.303
2.300
2.287
2.274
1.915
1.783
1.723
1.690
1.478
1.465
1.455
1.442
1.430
1.418
1.199
1.175
1.150
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm
H_I H_B
H_H
H_G
H_A
H_F
H_F'

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

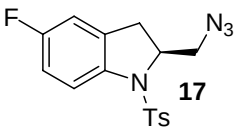
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 5 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389019 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



17

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

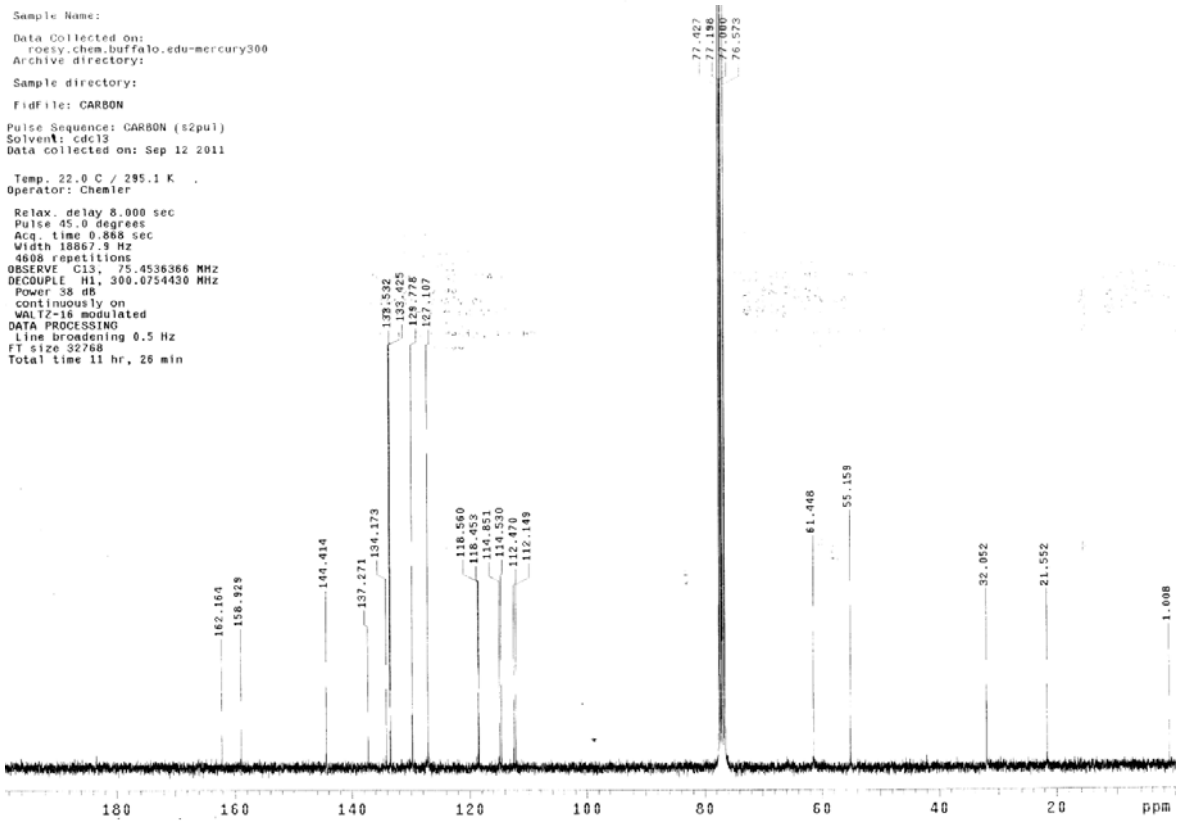
Sample directory:

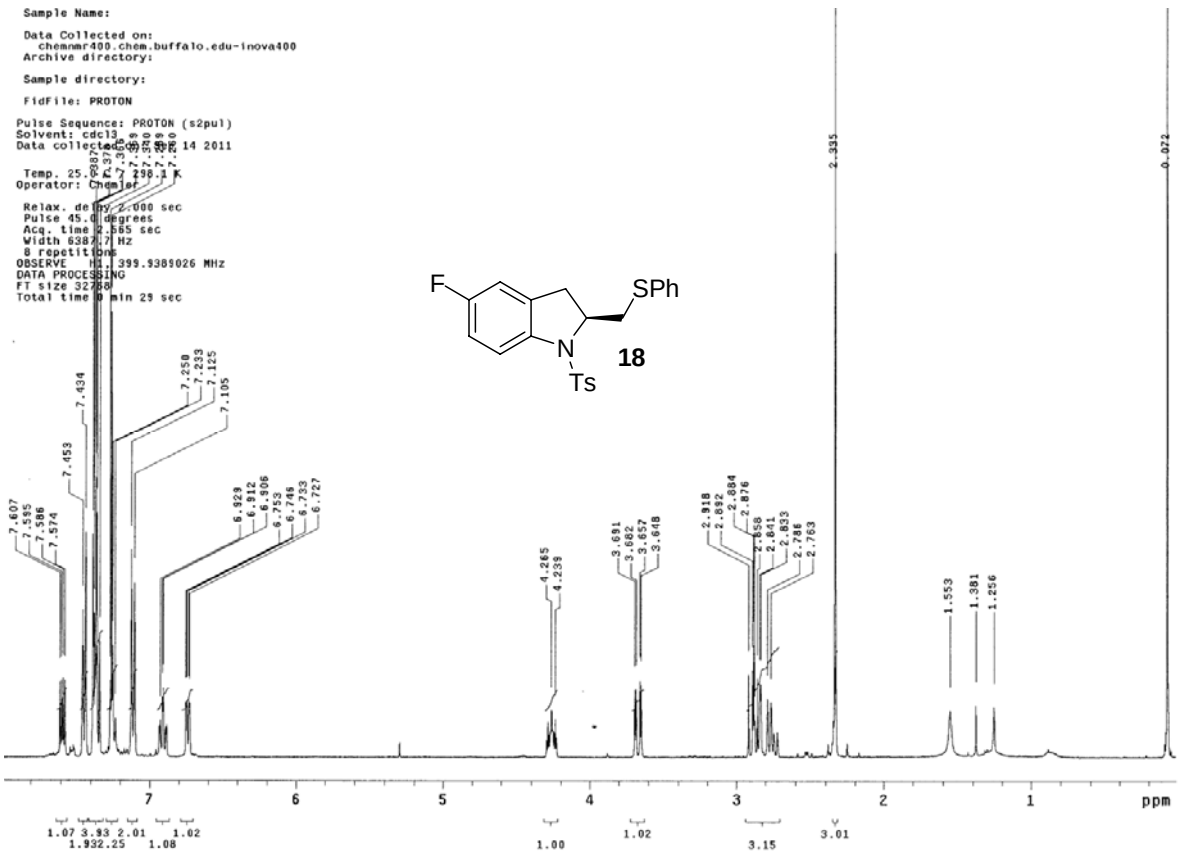
FidFile: CARBON

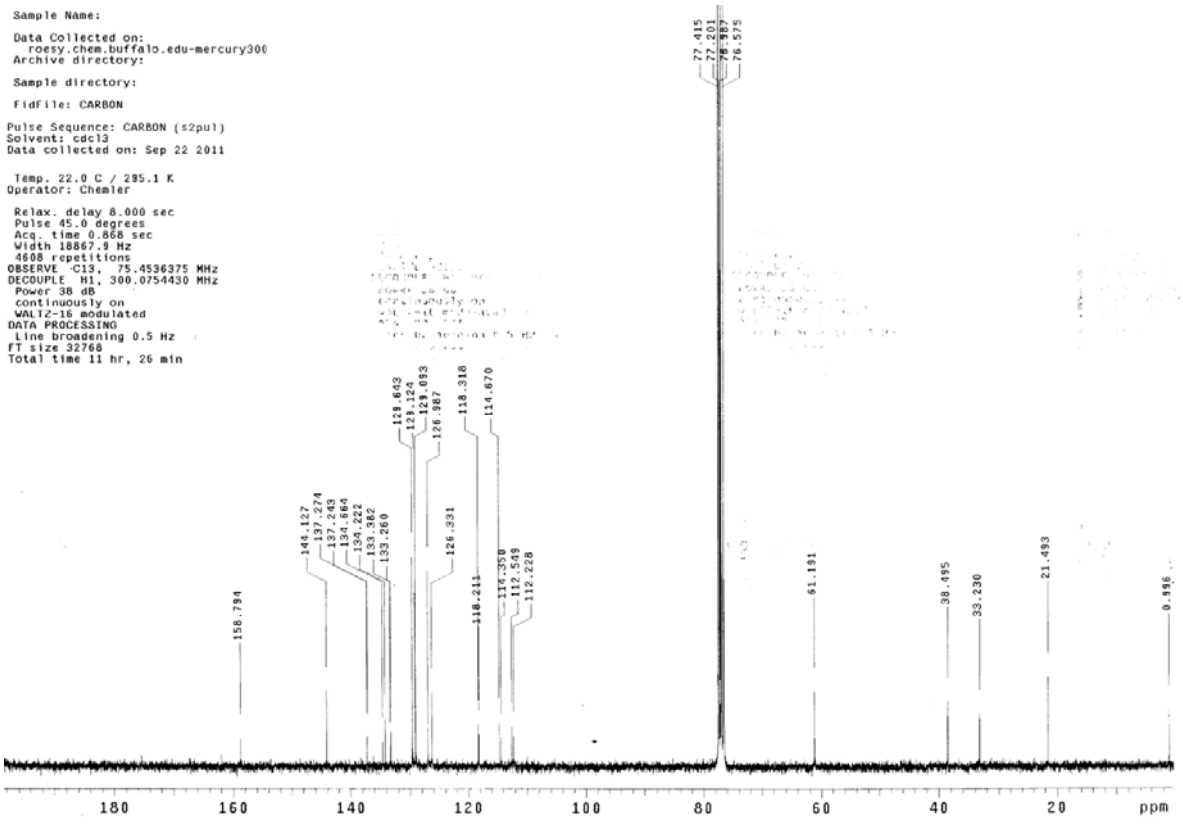
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 12 2011

Temp. 22.0 C / 295.1 K
Operator: Chemler

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4608 repetitions
OBSERVE C13, 75.4536366 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 28 min




Sample Name:
Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
DATA PROCESSING
FT size 32768
F
SPh
N
Ts
18
ppm


Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 22 2011
Temp. 22.0 C / 295.1 K
Operator: Chemler
Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4608 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 26 min
ppm

Sample Name:

Data Collected on:
chemnmr400.chem.buffalo.edu-inova400
Archive directory:

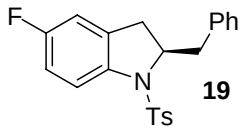
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 18 2011

Temp. 25.0 C / 298.1 K
Operator: Chemler

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6387.7 Hz
8 repetitions
OBSERVE H1, 399.9389026 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec



19

STANDARD CARBON PARAMETERS

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 6 2011

Temp. 26.3 C / 299.4 K
Operator: Chemler

Relax. delay 8.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4928 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 12 hr, 42 min