Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

PIFA-Mediated Ethoxyiodination of Enamides with Potassium Iodide.

R. Beltran, S. Nocquet-Thibault, F. Blanchard, R. H. Dodd* and K. Cariou*

Supplementary information contains:

1. General Remarks

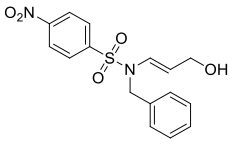
Melting points were measured in capillary tubes on a Büchi B-540 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on Bruker spectrometers: Avance 300 MHz (QNP - ^{13}C, ^{31}P, ^{19}F - probe or Dual ^{13}C probe) and Avance 500 MHz (BB0 - ATM probe or BBI - ATM probe). Carbon NMR (^{13}C) spectra were recorded at 125 or 75 MHz, using a broadband decoupled mode with the multiplicities obtained using a DEPT sequence. NMR experiments were carried out in deuterochloroform ($CDCl_3$), chemical shifts (δ) are reported in parts per million (ppm) with reference to $CDCl_3$ (^{1}H: 7.26; ^{13}C: 77.16) and deuterobenzene (C_6D_6), chemical shifts (δ) are reported in parts per million (ppm) with reference to C_6D_6 (^{1}H: 7.15; ^{13}C: 128.62). The following abbreviations are used for the proton spectra multiplicities: s: singlet, bs: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad. Coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained either with a LCT (Micromass) instrument using electrospray ionisation (ES), or from a Time of Flight analyser (ESI-MS) for the high resolution mass spectra (HRMS). Thin-layer chromatography was performed on silica gel 60 F_{254} on aluminium plates (Merck) and visualised under a UVP Mineralight UVLS-28 lamp (254 nm) and with 4-anisaldehyde and phosphomolybdic acid stains in ethanol. Flash chromatography was conducted on Merck silica gel 60 (40-63 μm) at medium pressure (300 mbar).

All reagents were obtained from commercial suppliers unless otherwise stated. Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under nitrogen.

2. Preparation and Analytical Data of Starting Enamides

Starting materials **1a-c, e, g, i-p**[1], **1d,**[2] **1f**[3] **1h,**[4] were prepared following literature procedures; starting material **1q** was prepared by reduction of **1l**, as reported for **1p**.[5]

(*E*)-*N*-benzyl-*N*-(3-hydroxyprop-1-en-1-yl)-4-nitrobenzenesulfonamide **1q**



348.37 g/mol

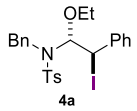
$C_{16}H_{16}N_2O_5S$

To a solution of ester **1l** (100 mg, 0.27 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) at –78 °C was added DIBAL-H (600 µL mL, 1 M in toluene, 3.19 mmol, 2.2 equiv). After 40 minutes, an additional 2.2 equiv. of DIBAL-H were added. The mixture was then allowed to slowly warm to 0 °C (over 1 h) then poured into a saturated aqueous solution of Rochelle's salt and diluted with EtOAc. After 2 h of stirring, the layers were separated and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. After purification by flash chromatography (petroleum ether/EtOAc 70:30), 86 mg (92%) of the desired alcohol **1q** were obtained as a white solid.

^{1}H NMR (500 MHz, C_6D_6): δ (ppm) = 7.46 (d, *J* = 9.0 Hz, 2H, Ar), 7.28 (d, *J* = 9.0 Hz, 2H, Ar), 7.13-7.09 (m, 2H, Ar), 7.07-7.96 (m, 3H, Ar), 6.90 (dt, *J* = 14.2, 1.5 Hz, 1H, =CHN), 4.67 (dt, *J* = 14.2, 5.9 Hz, 1H, =CH), 4.19 (s, 2H, NCH_2), 3.52 (t, 2H, *J* = 5.9 Hz, 2H).

3. Preparation and Analytical Data of Ethoxyiodination Products 4

N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide **4a**



4a

535.44 g/mol

$C_{24}H_{26}INO_3S$

To a suspension of (*E*)-*N*-benzyl-*N*-styryl-4-methylbenzenesulfonamide **1a** (50 mg, 0.138 mmol, 1 equiv) **1a** and KI (50 mg, 0.301 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (89 mg, 0.206 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with EtOAc (15 mL) and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 95:5 v:v as the mobile phase to afford 68 mg (92%) of the desired product **4a** as a yellow clear solid.

*The product was obtained as a mixture of two diastereoisomers with a ratio of 90:10 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform.*

^{1}H NMR (300 MHz, C_6D_6): δ ^{1}H NMR (300 MHz, C_6D_6) δ 7.78 (d, *J* = 7.8 Hz, 2H, **A**+ 1H, **B**), 7.63 (d, *J* = 8.0 Hz, 1H, **B**), 7.30 (d, *J* = 7.2 Hz, 2H, **A**), 7.23 (d, *J* = 7.2 Hz, 2H, **A**), 7.10 – 6.81 (m, 6H, **A** + 6H**, B**), 6.72 (d, *J* = 7.9 Hz, 2H, **A** + 2H, **B**), 6.56 (d, *J* = 8.0 Hz, 2H, **B**), 6.22 (d, *J* = 10.1 Hz, 1H, **B**), 6.02 (d, *J* = 7.2 Hz, 1H, **A**), 5.61 (d, *J* = 14.7 Hz, 1H, **B**), 5.01 (d, *J* = 7.1 Hz, 1H, **A**), 4.42 (d, *J* = 15.5 Hz, 1H, **A**+ 1H,**B**), 4.12 (d, *J* = 15.5 Hz, 1H,**A** +1H, **B**), 3.86 – 3.73 (m, 1H,**B**), 3.71 – 3.55 (m, 1H, **B**), 3.50 – 3.33 (m, 1H, **A**), 3.28 – 3.09 (m, 1H, **A**), 1.85 (s, 3H, **A**), 1.80 (s, 3H, **B**), 1.17 (t, *J* = 7.0 Hz, 3H, **B**), 0.66 (t, *J* = 6.9 Hz, 3H, **A**).

^{13}C NMR (75 MHz, C_6D_6): δ 142.9 (C), 140.9 (C), 138.3 (C), 137.3 (C), 129.3 (2*CH), 129.1

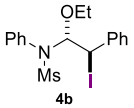
[1] S. Nocquet-Thibault, P. Retailleau, K. Cariou and R. H. Dodd, *Org. Lett.,* 2013, **15**, 1842.
[2] S. Nocquet-Thibault, A. Rayar, P. Retailleau, K. Cariou and R. H. Dodd, *Chem.–Eur. J.,* 2015, **21**, 14205.
[3] H. Lebel and O. Leogane, *Org. Lett.,* 2006, **8**, 5717.
[4] M. Nakanishi, C. Minard, P. Retailleau, K. Cariou and R. H. Dodd, *Org. Lett.* 2011, **13**, 5792.
[5] M. Barbazanges, C. Meyer, J. Cossy and P. Turner, *Chem.–Eur. J.* 2011, **17**, 4480.

(2*CH), 128.8 (2*CH), 128.2 (2*CH), 91.8 (CH), 65.8 (CH_2), 47.2 (CH_2), 33.3 (CH), 20.8 (CH_3), 13.9 (CH_3). *(Only **A**)*.

HRMS: m/z $[M+MeCN+Na]^+$ calcd 599.0835 found 599.0814; $[2M+Na]^+$ calcd 1093.1248 found 1093.1256; $[M-OEt]^+$ calcd 490.0332 found 490.0317

IR: *v*= 3063, 2976, 1598, 1495, 1454, 1339, 1155.

N-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-*N*-phenylmethanesulfonamide **4b**



4b

445.32 g/mol

$C_{17}H_{20}INO_3S$

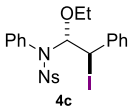
To a suspension of (*E*)-*N*-phenyl-*N*-styrylmethanesulfonamide **1b** (50 mg, 0.183 mmol, 1 equiv) and KI (73 mg, 0.439 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (118 mg, 0.274 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with EtOAc (15 mL) and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 15 g of silica gel using heptane/ethyl acetate 95:5 v:v as the mobile phase to afford 79 mg (97%) of the desired product **4b** as a yellow clear solid.
*The product was obtained as a mixture of two diastereoisomers with a ratio of 97:3 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform.*

^{1}H NMR (300 MHz, C_6D_6): δ 7.73 – 7.65 (m, 2H, **A** + 2H, **B**), 7.13 – 7.04 (m, 2H **A** + 2H, **B**), 6.98 – 6.76 (m, 6H **A** + 6H, **B**), 6.38 (d, *J* = 10.3 Hz, 1H, **B**), 6.24 (d, *J* = 10.1 Hz, 1H, **A**), 4.79 (d, *J* = 10.3 Hz, 1H, **B**), 4.61 (d, *J* = 10.1 Hz, 1H, **A**), 4.08 (dq, *J* = 9.3, 7.0 Hz, 1H, **B**), 3.93 – 3.84 (m, 1H, **B**), 3.78 (dq, *J* = 9.6, 7.0 Hz, 1H, **A**), 3.28 (dq, *J* = 9.6, 7.0 Hz, 1H, **A**), 2.62 (s, 3H, **A** + 3H, **B**), 1.21 (t, *J* = 7.0 Hz, 3H, **B**), 0.66 (t, *J* = 7.0 Hz, 3H, **A**).
^{13}C NMR (75 MHz, C_6D_6): δ 140.9 (C), 134.9 (C), 132.3 (2CH), 129.2 (CH), 129.1 (2CH), 128.4 (4CH), 127.8 (CH), 91.9 (CH), 65.9 (CH_2), 39.3 (CH_3), 34.9 (CH), 14.5 (CH_3). *(Only **A**)*

HRMS: m/z $[M-OEt]^+$ calcd 399.9863 found 399.9870.

IR: *v*= 3060, 2978, 2935, 1490, 1452, 1320, 1149, 1021 cm^{-1}.

N-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-*N*-phenyl-4-nitrobenzenesulfonamide **4c**



4c

552.38 g/mol

$C_{22}H_{22}IN_2O_5S$

To a suspension of (*E*)-*N*-phenyl-*N*-styryl-4-nitrobenzenesulfonamide **1c** (50 mg, 0.131 mmol, 1 equiv) and KI (52 mg, 0.315 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (85 mg, 0.197 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with EtOAc (15 mL) and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 95:5 v:v as the mobile phase to afford 67 mg (93%) of the desired product **4c** as a yellow solid.
The product was obtained as a single diastereoisomer. The product was unstable in deuterated chloroform.

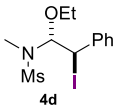
^{1}H NMR (500 MHz, C_6D_6): δ 7.60 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 6.6

Hz, 2H), 7.10 – 6.98 (m, 3H), 6.96 – 6.81 (m, 5H), 6.32 (d, *J* = 9.9 Hz, 1H), 4.52 (d, *J* = 9.9 Hz, 1H), 3.79 (dq, *J* = 14.1, 7.0 Hz, 1H), 3.29 (dq, *J* = 14.1, 7.0 Hz, 1H), 0.65 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (125 MHz, C_6D_6): δ 150.1 (C), 144.5 (C), 140.7 (C), 133.9 (C), 132.5 (2CH), 129.8 (2CH), 129.6 (CH), 129.0 (2CH), 128.4 (2CH), 128.4 (2CH), 128.0 (CH), 123.3 (2CH), 92.5 (CH), 66.4 (CH_2), 34.1 (CH), 14.4 (CH_3).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 506.9870 found 506.9872.

IR: 2922, 2850, 1525, 1490, 1452, 1348, 1166 cm^{-1}

N-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-*N*-methylmethanesulfonamide **4d**



4d

383.25 g/mol

$C_{12}H_{18}INO_3S$

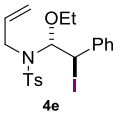
To a suspension of (*E*)-*N*-methyl-*N*-styrylmethanesulfonamide **1d** (30 mg, 0.14 mmol, 1 equiv) and KI (55 mg, 0.33 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (90 mg, 0.21 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark brown and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with EtOAc (15 mL) and washed with a solution of sodium thiosulfate until disappearance of the brown colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 15 g of silica gel using heptane/ethyl acetate 90:10 v:v as the mobile phase to afford 49 mg (75%) of the desired product **4d** as a yellow clear solid.
*The product was obtained as a mixture of two diastereoisomers with a ratio of 96:4 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform.*

^{1}H NMR (300 MHz, C_6D_6): δ 7.20 (d, *J* = 8.3 Hz, 2H, **A**), 7.00 – 6.90 (m, 3H, **A**), 5.80 (d, *J* = 9.1 Hz, 1H, **A**), 5.78 (d, *J* = 10.0 Hz, 1H, **B**), 4.90 (d, *J* = 9.1 Hz, 1H, **A**), 4.72 (d, *J* = 10.0 Hz, 1H, **B**), 3.70 – 5.53 (m, 2H, **B**), 3.47 (dq, *J* = 9.7, 7.0 Hz, 1H, **A**), 3.21 (dq, *J* = 9.7, 7.0 Hz, 1H, **A**), 2.54 (s, 3H, **A**), 2.42 (s, 3H, **A**), 1.15 (t, *J* = 7.0 Hz, 3H, **B**), 0.71 (t, *J* = 7.0 Hz, 3H, **A**).
^{13}C NMR (75 MHz, C_6D_6): δ 140.9 (C), 128.6 (2CH), 128.4 (2CH), 128.1 (CH), 89.8 (CH), 64.7 (CH_2), 39.1 (CH_3), 33.8 (CH), 26.2 (CH_3), 14.3 (CH_3). *(Only **A**)*

HRMS: m/z $[M+MeCN+Na]^+$ calcd 447.0210 found 447.0226.

IR: *v*= 3062, 3029, 2972, 2925, 2851, 1669, 1454, 1325, 1139, 1046 cm^{-1}.

N-allyl-*N*-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide **4e**



4e

585.38 g/mol

$C_{20}H_{24}INO_3S$

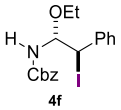
To a suspension of (*E*)-*N*-allyl-*N*-styryl-4-methylbenzenesulfonamide **1e** (50 mg, 0.160 mmol, 1 equiv) and KI (64 mg, 0.383 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (103 mg, 0.239 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 40 min, 0.2 equiv of PIFA (14 mg) in 0.2 mL of abs. EtOH was added dropwise to the reaction mixture. Ten minutes later, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 95:5 v:v as the mobile phase to afford 72 mg (92%) of the desired product **4e** as a clear yellow oil.
*The product was obtained as a mixture of two diastereoisomers with a ratio of 91:9 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform.*

^{1}H NMR (300 MHz, C_6D_6): δ 7.91 (d, *J* = 8.3 Hz, 2H, **A**), 7.83 (d, *J* = 8.2 Hz, 2H, **B**), 7.33 – 7.25 (m, 2H, **A**), 7.08 (d, *J* = 8.3 Hz, 2H, **B**), 6.99 – 6.88 (m, 3H, **A** + 3H, **B**), 6.77 (d, *J* = 8.3 Hz, 2H, **A**), 6.54 (d, *J* = 8.2 Hz, 2H, **B**), 6.15 (d, *J* = 9.8 Hz, 1H, **B**, CHNO), 5.97 (d, *J* = 7.5 Hz, 1H, **A**, CHNO), 5.78 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H, **A**, CH allyl), 5.53 – 5.29 (m, 1H, **B**, H allyl), 5.22 (d, *J* = 7.5 Hz, 1H, **A**, CHI+ 1H, **B**, CHI), 4.90 (dd, *J* = 17.2, 1.4 Hz, 1H, **A**), 4.78 (dd, *J* = 10.1, 1.4 Hz, 1H, **A** + 1H, **B**), 4.62 (dd, *J* = 10.1, 1.3 Hz, 1H, **B**), 3.88 – 3.77 (m, 1H, **A**, CH_2 Allyl + 1H, **B**, OCH_2Me), 3.75 – 3.61 (m, 1H, **A**, CH_2 allyl + 1H, **B**, OCH2Me), 3.49 (dq, *J* = 9.4, 7.0 Hz, 1H, **A**, OCH_2Me), 3.23 (dq, *J* = 9.4, 7.0 Hz, 1H, **A**, OCH_2Me), 1.87 (s, 3H, **A**), 1.78 (s, 3H, **B**), 1.19 (t, *J* = 7.0 Hz, 3H, **B**), 0.78 (t, *J* = 7.0 Hz, 3H, **A**).
^{13}C NMR (75 MHz, C_6D_6): δ 143.2 (C), 140.8 (C), 138.3 (C), 135.7 (CH), 129.3 (2CH), 129.1 (2CH), 128.5 (2CH), 128.1 (2CH), 116.8 (CH_2), 91.6 (CH), 65.7 (CH_2), 45.8 (CH_2), 33.9 (CH), 21.0 (CH_3), 14.3 (CH_3). (*Only **A***)

HRMS: m/z $[2M+Na]^+$ calcd 993.0936 found 993.1000; $[M+MeCN+Na]^+$ calcd 549.0679 found 549.0702; $[M-OEt]^+$ calcd 440.0176 found 440.0198.

IR: *v*= 3029, 2976, 2926, 1598, 1494, 1453, 1340, 1155; 1092 cm^{-1}.

benzyl ((1R, 2R*)-1-ethoxy-2-iodo-2-phenylethyl)carbamate* **4f**



4f

525.26 g/mol

$C_{18}H_{20}INO_3$

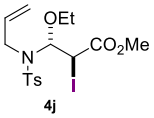
To a suspension of benzyl (*E*)-styrylcarbamate **1f** (50 mg, 0.197 mmol, 1 equiv) and KI (79 mg, 0.473 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (127 mg, 0.296 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 15 g of silica gel using heptane/ethyl acetate 95:5 v:v as the mobile phase to afford 82 mg (97%) of the desired product **4f** as a white solid.
The product was obtained as a single diastereoisomer. The product was unstable in deuterated chloroform.

^{1}H NMR (300 MHz, C_6D_6): δ 7.26 (d, *J* = 7.9 Hz, 2H), 7.19 - 7.16 (m, 2H), 7.14 – 7.02 (m, 3H), 6.99 – 6.86 (m, 3H), 5.26 (dd, *J* = 9.5, 4.9 Hz, 1H), 5.02 (s, 2H), 4.96 (d, *J* = 9.5 Hz, 1H), 4.88 (d, *J* = 4.9 Hz, 1H), 3.54 (dq, *J* = 14.2, 7.0 Hz, 1H), 3.37 (dq, *J* = 14.2, 7.0 Hz, 1H), 0.96 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 155.4 (C), 139.5 (C), 136.8 (C), 129.2 (2CH), 128.6(CH), 128.5 (2CH), 128.3 (CH), 128.2 (2CH), 128.2 (2CH), 84.6 (CH), 66.9 (CH_2), 64.3 (CH_2), 34.5 (CH), 14.8 (CH_3).

HRMS: m/z $[2M+Na]^+$ calcd 873.0868 found 873.0906; $[M+Na]^+$ calcd 448.0380 found 448.0401.

IR: *v*= 3314, 3063, 2975, 2926, 1702, 1494, 1453, 1219 cm^{-1}.

(2*S**, 3*R**)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4j**



4j

To a suspension of methyl (*E*)-3-(*N*-allyl-4-methylphenylsulfonamido)acrylate **1j** (50 mg, 0.169 mmol, 1 equiv) and KI (67 mg, 0.406 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (108 mg, 0.251 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was

467.32 g/mol
$C_{16}H_{22}INO_5S$

stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After one hour, 0.2 equiv of PIFA (14 mg) in 0.2 mL of absolute EtOH was added dropwise to the reaction mixture. Ten minutes later, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 12 g of silica gel using heptane/ethyl acetate 95:5 to 80:20, v:v as the mobile phase to afford 67 mg (85%) of the desired product **4j** as a clear oil.
The product was obtained as a single diastereoisomer. The product was unstable in deuterated chloroform.

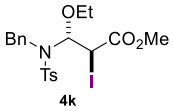
^{1}H NMR (300 MHz, C_6D_6): δ 7.86 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.08 (d, *J* = 9.7 Hz, 1H), 5.83 (ddt, *J* = 17.1, 10.1, 6.6 Hz, 1H), 4.84 (dq, *J* = 17.1, 1.4 Hz, 1H), 4.76 (dq, *J* = 10.1, 1.3 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 1H), 3.82 (dd, *J* = 6.6, 1.4 Hz, 2H), 3.72 – 3.48 (m, 2H), 3.28 (s, 3H), 1.87 (s, 3H), 0.95 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 169.8 (C), 143.3 (C), 138.2(C), 135.5 (CH), 129.3 (2*CH), 128.8 (2*CH), 117.5 (CH_2), 89.3 (CH), 65.8 (CH_2), 52.4 (CH_3), 45.8 (CH_2), 23.0 (CH), 21.2 (CH_3), 14.8 (CH_3).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 421.99 found 421.99; $[M+MeCN+Na]^+$ calcd 531.0458 found 531.0429; $[2M+Na]^+$ calcd 957.0492 found 957.0468.

IR: *v*= 2977, 2927, 1738, 1640, 1597, 1436, 1343, 1151 cm^{-1}.

methyl (2*S**, 3*R**)-3-(*N*-benzyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4k**

To a suspension of methyl (*E*)-3-(*N*-benzyl-4-methylphenylsulfonamido)acrylate **1k** (50 mg, 0.145 mmol, 1 equiv) and KI (58 mg, 0.345 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (93 mg, 0.217 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 30 min, 0.2 equiv of PIFA (13 mg) in 0.2 mL of absolute EtOH was added dropwise to the reaction mixture. Ten minutes later, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 95:5 to 90:10, v:v as the mobile phase to afford 71 mg (95%) of the desired product **4k**.
The product was obtained as a single diastereoisomer.



4k

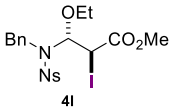
517.38 g/mol
$C_{20}H_{24}INO_5S$

^{1}H NMR (300 MHz, C_6D_6): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.11 – 6.95 (m, 3H), 6.73 (d, *J* = 8.3 Hz, 2H), 6.08 (d, *J* = 10.0 Hz, 1H), 4.38 (d, *J* = 15.3 Hz, 1H), 4.34 (d, *J* = 10 Hz, 1H), 4.30 (d, *J* = 15.3 Hz, 1H), 3.51 (q, *J* = 7 Hz, 2H), 3.20 (s, 3H), 1.87 (s, 3H), 0.83 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 169.8 (C), 143.1 (C), 138.3 (C), 136.8 (C), 129.6 (2*CH), 129.2 (2*CH), 128.6 (2*CH), 128.4 (2*CH), 128.2 (CH), 89.4 (CH), 65.9 (CH_2), 52.1 (CH_3), 47.5 (CH_2), 22.4 (CH), 20.9 (CH_3), 14.5 (CH_3).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 472.01 found 472.0074; $[M+MeCN+Na]^+$ 581.0557 found 581.0571.

IR: *v*= 3063, 3030, 2976, 2927, 1598, 1495, 1454, 1339, 1155, 1092.

methyl (2*S**, 3*R**)-3-(*N*-benzyl-4-nitrophenylsulfonamido)-3-ethoxy-2-iodopropanoate **4l**



548.35 g/mol
$C_{19}H_{21}IN_2O_5S$

To a suspension of (*E*)-*N*-benzyl-*N*-(3-hydroxyprop-1-en-1-yl)-4-nitrobenzenesulfonamide **1l** (50 mg, 0.144 mmol, 1 equiv) and KI (57 mg, 0.344 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (93 mg, 0.215 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 15 min, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 90:10 to 80:20, v:v as the mobile phase to afford 64 mg (85%) of the desired product **4l** as a white solid.
The product was obtained as a single diastereoisomer.

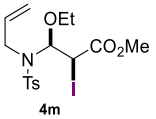
^{1}H NMR (300 MHz, C_6D_6): δ 7.53 (d, *J* = 9.1 Hz, 2H), 7.41 (d, *J* = 9.1 Hz, 2H), 7.13 – 7.08 (m, 2H), 6.94 – 6.84 (m, 3H), 5.57 (d, *J* = 9.4 Hz, 1H), 4.20 (d, *J* = 15.5 Hz, 1H), 4.07 (d, *J* = 15.5 Hz, 1H), 3.88 – 3.77 (m, 1H), 3.67 (ddd, *J* = 12.4, 8.9, 3.7 Hz, 1H), 3.50 (ddd, *J* = 11.8, 7.0, 3.7 Hz, 2H), 3.35 (dq, *J* = 9.4, 7.0 Hz, 1H), 1.96 (dd, *J* = 8.9, 4.4 Hz, 1H), 0.76 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 149.7 (C), 145.7 (C), 135.7 (C), 129.6 (2*CH), 129.3 (2*CH), 128.3 (2*CH), 127.9 (CH), 123.2 (2*CH), 90.6, 66.2 (CH_2), 65.2 (CH_2), 47.6 (CH_2), 36.7 (CH_3), 14.4 (CH_3).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 502.9768 found 502.9770.

IR: *v*= 3473, 3117,2920, 2850, 1607, 1527, 1349, 1332, 1310, 1159, 1022.

Mp: 124 –126 °C

methyl (2*S**, 3*S**)-3-(*N*-allyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4m**



467.32 g/mol
$C_{16}H_{22}INO_5S$

To a suspension of methyl (*Z*)-3-(*N*-allyl-4-methylphenylsulfonamido)acrylate **1m** (15 mg, 0.052 mmol, 1 equiv) and KI (21 mg, 0.124 mmol, 2.4 equiv) in 0.5 mL of EtOH was added dropwise a solution of PIFA (34 mg, 0.077 mmol, 1.5 equiv) in 0.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with 7 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 5 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 10 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 2.5 g of silica gel using heptane/ethyl acetate 95:5 to 80:20, v:v as the mobile phase to afford 19 mg (79%) of the desired product **4m** as a yellow clear oil.
*The product was obtained as a mixture of two diastereoisomers with a ratio of 25:75 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform.*

^{1}H NMR (300 MHz, C_6D_6): δ 7.84 (d, *J* = 8.3 Hz, 2H, **A**), 7.77 (d, *J* = 8.3 Hz, 2H, **B**), 6.74 (d, *J* = 8.3 Hz, 2H, **A**), 6.69 (d, *J* = 8.3 Hz, 2H, **B**), 6.05 (d, *J* = 9.7 Hz, 1H, **A**, CHNO), 5.90 (d, *J* = 9.9 Hz, 1H, **B**), 5.81 (ddt, *J* = 17.1, 10.1, 6.6 Hz, 1H, **A**), 5.51 (ddt, *J* = 17.2, 10.2, 6.5 Hz, 1H, **B**), 4.89 – 4.67 (m, 5H, 2H CH_2 allyl **A** + 2H CH_2 allyl **B** + 1H CHI **B**), 4.63 (d, *J* = 9.7 Hz, 1H, **A**, CHI), 3.89 (ddt, *J* = 16.8, 6.5, 1.5 Hz, 1H, **B**), 3.81 (dd, *J* = 6.6, 1.3 Hz, 2H, **A**), 3.71 (ddt, *J* = 16.8, 6.5, 1.5 Hz, 1H, **B**), 3.58 (dq, *J* = 9.4, 7.0 Hz, 1H, **B**), 3.72 – 3.48 (m, 2H, OCH_2 **A**), 3.42 (dq, *J* = 9.4, 7.0 Hz, 1H, **B**), 3.27 (s, 3H, **A**), 3.18 (s, 3H, **B**), 1.86 (s, 3H, **A**), 1.82 (s, 3H, **B**), 1.02 (t, *J* = 7.0 Hz, 3H, **B**), 0.93 (t, *J* = 7.0 Hz, 3H, **A**).

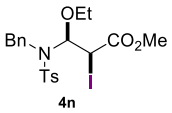
^{13}C NMR (75 MHz, C_6D_6): δ 169.2 (C), 143.2 (C, **A**), 143.1 (C, **B**), 138.4 (C, **B**), 138.1 (C, **A**), 135.4 (CH, **A**), 135.1 (CH, **B**), 129.2 (2*CH, **A**), 129.1 (2*CH, **B**), 128.7 (2*CH, **A**), 128.4 (2*CH, **B**), 117.7 (CH_2, **B**), 117.4 (CH_2, **A**), 89.2 (CH, **A**), 88.3 (CH, **B**), 65.7 (CH_2, **A**), 65.3 (CH_2, **B**), 52.2 (CH_3, **A+B**), 45.7 (CH_2, **A+B**), 22.9 (CH, **A**), 22.6 (CH, **B**), 20.9 (CH_3, **A**), 20.9 (CH_3, **B**), 14.6 (CH_3, **A**), 14.3 (CH_3, **B**).

HRMS: m/z $[2M+Na]^+$ calcd 957,0418 found 957,0468; $[M+MeCN+Na]^+$ calcd 531,0421 found 531,0429; $[M-OEt]^+$ calcd 421.9917 found 421.9917.

IR: *v*= 2977, 2927, 1738, 1640, 1597, 1436, 1343, 1151 cm^{-1}.

(2*S**, 3*S**)-methyl 3-(*N*-benzyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4n**

To a suspension of methyl (*Z*)-3-(*N*-benzyl-4-methylphenylsulfonamido)acrylate **1n** (50 mg, 0.145 mmol, 1 equiv) and KI (58 mg, 0.345 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (93 mg, 0.217 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 95:5 to 90:10, v:v as the mobile phase to afford 74 mg (98%) of the desired product **4n** as a white powder.



4n

517.38 g/mol

$C_{20}H_{24}INO_5S$

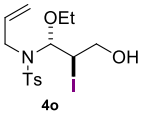
*The product was obtained as a mixture of two diastereoisomers with a ratio of 25:75 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform.*

^{1}H NMR (500 MHz, C_6D_6): δ 7.76 (d, *J* = 8.3 Hz, 2H, **A**), 7.70 (d, *J* = 8.3 Hz, 2H, **B**), 7.31 (d, *J* = 7.7 Hz, 2H, **A**), 7.06 – 6.98 (m, 3H, **A**), 6.96 – 6.88 (m, 5H, **B**), 6.73 (d, *J* = 8.3 Hz, 2H, **A**), 6.67 (d, *J* = 8.3 Hz, 2H, **B**), 6.06 (d, *J* = 9.6 Hz, 1H, **A**), 6.02 (d, *J* = 9.8 Hz, 1H, **B**), 4.52 (d, *J* = 9.8 Hz, 1H, **B**), 4.47 (d, *J* = 15.6 Hz, 1H, **B**), 4.38 (d, *J* = 15.4 Hz, 1H, **A**), 4.37 (d, *J* = 9.6 Hz, 1H, **A** CHI), 4.30 (d, *J* = 15.4 Hz, 1H, **A**), 4.23 (d, *J* = 15.6 Hz, 1H, **B**), 3.64 (dq, *J* = 14.1, 7.0 Hz, 1H, **B**), 3.55 – 3.41 (m, 3H, 1H**B**2 H**A**, OCH_2Me), 3.21 (s, 3H, **A**), 3.15 (s, 3H, **B**), 1.87 (s, 3H, **A**), 1.84 (s, 3H, **B**), 1.03 (t, *J* = 7.0 Hz, 3H, **B**), 0.84 (t, *J* = 7.0 Hz, 3H, **A**).

^{13}C NMR (126 MHz, C_6D_6): δ 169.8 (C, **A**), 169.2 (C, **B**), 143.1 (C, **A**), 142.9 (C, **B**), 138.5 (C, **B**), 138.3 (C, **A**), 137.2 (C, **B**), 136.8 (C, **B**), 129.6 (2*CH, **A**), 129.2 (2*CH, **A**), 129.1 (2*CH, **B**), 129.0 (2*CH, **B**), 128.6 (2*CH, **A**), 128.4 (2*CH, **A**), 128.4 (2*CH, **B**), 128.3 (2*CH, **B**), 128.2 (CH, **A**), 127.9 (CH, **B**), 89.4 (CH, **A**), 88.3 (CH, **B**), 65.9 (CH_2, **A**), 65.6 (CH_2, **B**), 52.1 (CH_3, **A**), 52.0 (CH_3, **B**), 47.7 (CH_2, **A**), 46.9 (CH_2,**B**), 22.8 (CH, **B**), 22.4 (CH, **A**), 20.9 (CH_3, **A**), 20.9 (CH_3, **B**), 14.5 (CH_3, **A**), 14.3 (CH_3, **B**).

N-allyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-methylbenzenesulfonamide **4o**

To a suspension of (*E*)-*N*-allyl-*N*-(3-hydroxyprop-1-en-1-yl)-4-methylbenzenesulfonamide **1o** (50 mg, 0.187 mmol, 1 equiv) and KI (75 mg, 0.449 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (121 mg, 0.281 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 15 min, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on



4o

439.31 g/mol

$C_{15}H_{22}INO_4S$

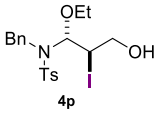
10 g of silica gel using heptane/ethyl acetate 90:10 to 70:30, v:v as the mobile phase to afford 80 mg (98%) of the desired product **4o** as a white powder.
The product was obtained as a single diastereoisomer.

^{1}H NMR (300 MHz, C_6D_6): δ 7.87 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 5.80 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.64 (d, *J* = 9.1 Hz, 1H), 4.88 (dq, *J* = 17.2, 1.4 Hz, 1H), 4.77 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.10 (ddd, *J* = 9.3, 5.6, 4.1 Hz, 1H), 3.90 – 3.72 (m, 3H), 3.72 – 3.64 (m, 1H), 3.63 – 3.52 (m, 1H), 3.40 (dq, *J* = 9.5, 7.0 Hz, 1H), 2.37 (s, 1H), 1.85 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 143.2 (C), 137.9 (C), 135.7 (CH), 129.1 (2*CH), 128.8 (2*CH), 116.9 (CH_2), 89.9 (CH), 66.6 (CH_2), 64.9 (CH_2), 45.3 (CH_2), 37.1 (CH), 20.9 (CH_3), 14.6 (CH_3).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 393.9968 found 393.9902; $[M+MeCN+Na]^+$ calcd 503.0458 found 503.0476; $[2M+Na]^+$ calcd 901.0492 found 901.0542.

IR: v= 3521, 2975, 2925, 1598, 1336, 1159.

N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-methylbenzenesulfonamide **4p**



4p

489.05 g/mol
$C_{19}H_{24}INO_4S$

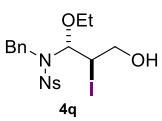
To a suspension of (*E*)-*N*-benzyl-*N*-(3-hydroxyprop-1-en-1-yl)-4-methylbenzenesulfonamide **1p** (50 mg, 0.158 mmol, 1 equiv) and KI (63 mg, 0.378 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (102 mg, 0.236 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 10 min, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 90:10 to 80:20, v:v as the mobile phase to afford 64 mg (85%) of the desired product **4p** as a clear oil.
The product was obtained as a single diastereoisomer.

^{1}H NMR (300 MHz, C_6D_6): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.27 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.08 – 6.91 (m, 3H), 6.71 (d, *J* = 8.3 Hz, 2H), 5.71 (d, *J* = 9.1 Hz, 1H), 4.38 (d, *J* = 15.8 Hz, 1H), 4.28 (d, *J* = 15.8 Hz, 1H), 3.94 (ddd, *J* = 9.1, 5.5, 3.9 Hz, 1H), 3.73 (ddd, *J* = 13.0, 9.1, 4.1 Hz, 1H), 3.63 – 3.48 (m, 2H), 3.37 (dq, *J* = 9.5, 7.0 Hz, 1H), 2.25 (dd, *J* = 9.1, 4.1 Hz, 1H), 1.85 (s, 3H), 0.76 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 143.1 (C), 138.1 (C), 137.0 (C), 129.4 (2*CH), 129.1 (2*CH), 128.7 (2*CH), 128.3 (2*CH), 127.6 (CH), 90.6 (CH), 66.6 (CH_2), 65.1 (CH_2), 47.1 (CH_2), 36.9 (CH), 20.9 (CH_3), 14.4 (CH_3).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 444.0125 found 444.0092; $[M+Na]^+$ calcd 512.0363 found 512.0367.

IR: *v*= 3526, 2975, 2928, 1735, 1598, 1495, 1455, 1336, 1159, 1093, 1059, 1025.

N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-nitrobenzenesulfonamide **4q**



4q

To a suspension of (*E*)-*N*-benzyl-*N*-(3-hydroxyprop-1-en-1-yl)-4-nitrobenzenesulfonamide **1q** (50 mg, 0.144 mmol, 1 equiv) and KI (57 mg, 0.344 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (93 mg, 0.215 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot.

520.34 g/mol
$C_{18}H_{21}IN_2O_6S$

After 15 min, the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 90:10 to 80:20, v:v as the mobile phase to afford 64 mg (85%) of the desired product **4q** as a white solid.
The product was obtained as a single diastereoisomer.

^{1}H NMR (300 MHz, C_6D_6): δ 7.53 (d, *J* = 9.1 Hz, 2H), 7.41 (d, *J* = 9.1 Hz, 2H), 7.13 – 7.08 (m, 2H), 6.94 – 6.84 (m, 3H), 5.57 (d, *J* = 9.4 Hz, 1H), 4.20 (d, *J* = 15.5 Hz, 1H), 4.07 (d, *J* = 15.5 Hz, 1H), 3.88 – 3.77 (m, 1H), 3.67 (ddd, *J* = 12.4, 8.9, 3.7 Hz, 1H), 3.50 (ddd, *J* = 11.8, 7.0, 3.7 Hz, 2H), 3.35 (dq, *J* = 9.4, 7.0 Hz, 1H), 1.96 (dd, *J* = 8.9, 4.4 Hz, 1H), 0.76 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, C_6D_6): δ 149.7 (C), 145.7 (C), 135.7 (C), 129.6 (2*CH), 129.3 (2*CH), 128.3 (2*CH), 127.9 (CH), 123.2 (2*CH), 90.6, 66.2 (CH_2), 65.2 (CH_2), 47.6 (CH_2), 36.7 (CH_3), 14.4 (CH_3).

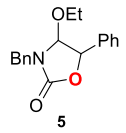
HRMS: m/z $[M\text{-}OEt]^+$ calcd 474.9819 found 474.9814.

IR: *v*= 3473, 3117,2920, 2850, 1607, 1527, 1349, 1332, 1310, 1159, 1022.

Mp: 120 –122 °C

4. Preparation and Analytical Data of Products 5-8

3-benzyl-4-ethoxy-5-phenyloxazolidin-2-one **5**



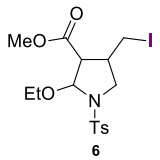
5

297.35 g/mol
$C_{18}H_{19}NO_3$

To a suspension of (*E*)-*tert*-butyl benzyl(styryl)carbamate **1f** (50 mg, 0.16 mmol, 1 equiv) and KI (64 mg, 0.39 mmol, 2.4 equiv) in 1.5 mL of EtOH was added dropwise a solution of PIFA (104 mg, 0.224 mmol, 1.5 equiv) in 1.5 mL of EtOH. Following the addition, the mixture became dark red and homogeneous. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR analysis of an aliquot. After 20 min, 15 mg of PIFA (0.2 equiv) were added and after 5 min the reaction mixture was diluted with 15 mL of EtOAc and washed with a solution of sodium thiosulfate until disappearance of the red colour, then with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure (without heating, although even using a cold bath, the crude residue rapidly turns black). The crude residue was purified using flash column chromatography on 10 g of silica gel using heptane/ethyl acetate 90:10 to 80:20, v:v as the mobile phase to afford 15 mg (31%) of the desired product **5** as yellow oil.
*The product was obtained as a mixture of two diastereoisomers with a ratio of 4:1 (**A**:**B**) according to the crude NMR. The product was unstable and decomposed rapidly.*

^{1}H NMR (300 MHz, C_6D_6): δ ^{1}H NMR (300 MHz, C_6D_6) δ 7.10– 6.87 (m, 10H, **A** + **B**), 4.97 (d, *J* = 1.7 Hz, 1H, **A**), 4.92 (d, *J* = 14.9 Hz, 1H, **B**), 4.70 (d, *J* = 15.1 Hz, 1H, **A**), 4.67 (d, *J* = 5.3 Hz, 1H, **B**), 4.42 (d, *J* = 1.7 Hz, 1H, **A**), 4.18 (d, *J* = 5.3 Hz, 1H, **B**), 4.02 (d, *J* = 15.1 Hz, 1H, **A**), 3.95 (d, *J* = 14.9 Hz, 1H, **B**), 2.95 (dq, *J* = 9.1, 7.0 Hz, 1H, **A**), 2.89 (dq, *J* = 9.1, 7.0 Hz, 1H, **A**), 2.54 (dq, *J* = 9.1, 7.1 Hz, 1H, **B**), 2.29 (dq, *J* = 9.1, 7.1 Hz, 1H, **B**), 0.85 (t, *J* = 7.0 Hz, 3H, **A**), 0.47 (t, *J* = 7.1 Hz, 3H, **B**).
^{13}C NMR (75 MHz, C_6D_6): δ 138.0 (C), 136.5 (C), 138.3 (C), 128.9 (2CH), 128.8 (2CH), 128.7 (2CH), 127.7 (CH), 127.6 (CH), 125.3 (2CH), 91.5 (CH), 80.3 (CH), 61.4 (CH_2), 45.6 (CH_2), 15.1 (CH_3). *(Only **A**)*.

methyl 2-ethoxy-4-(iodomethyl)-1-tosylpyrrolidine-3-carboxylate **6**



6

467.32 g/mol

$C_{16}H_{22}INO_5S$

To a 10 mL oven-dried flask containing a magnetic stirring bar was added methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4j** (50 mg, 0.107 mmol, 1equiv) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol, 10 mol%) under argon. After the addition of 2.7 mL of dry THF, the reaction mixture was degassed through two freeze-pump-thaw cycles, and then stirred at room temperature during 3 h at which time all starting material was consumed according to TLC analysis. The black reaction mixture was filtered on a pad of silica gel using EtOAc, washed with 1M HCl solution and brine. The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on 20 g of silica gel using heptane/ethyl acetate 90:10 to 80:20, v:v as the mobile phase to afford 41 mg of **6** (81%).

*The product was obtained as a mixture of two diastereoisomers with a ratio of 2:1 (**A**:**B**) according to the crude NMR. The product was unstable in deuterated chloroform; during the acquisition of the ^{13}C spectrum in $CDCl_3$, **7** began forming. The peaks for **6A** and **6B** were differentiated using the ^{13}C spectrum of **7**.*

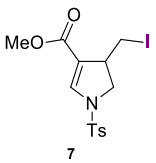
^{1}H NMR (300 MHz, C_6D_6): δ 7.77 (d, *J* = 8.2 Hz, 4H, 2H**A** + 2H**B**), 6.77 (d, *J* = 8.0 Hz, 2H, **B**), 6.76 (d, *J* = 8.0 Hz, 2H, **A**), 5.82 (d, *J* = 2.3 Hz, 1H, **A**, C**H**NO), 5.51 (s, 1H, **B**, C**H**NO), 3.98-3.85 (m, 2H, 1H**A** OC**H**$_2$Me + 1H**B** OC**H**$_2$Me), 3.65 (d, *J* = 11.3, 7.4 Hz, 1H**A**, NC**H**$_2$CH), 3.65-3.43 (m, 4H, 1H**A** OC**H**$_2$Me + 1H**B** OC**H**$_2$Me, 1H**B** NC**H**$_2$CH, 1H**B**), 3.27-3.10 (m, 1H, **B**), 3.08 (dd, *J* = 11.3, 7.3 Hz, 1H, **A**, NC**H**$_2$CH),3.01 (s, 3H, **A**), 2.96 (s, 3H, **B**), 2.85 (m, 2H, **B**)2.84 (dd, *J* = 9.9, 6.2 Hz, 1H, **A**, C**H**$_2$I), 2.76 (dd, *J* = 6.2, 2.3 Hz, 1H, **A**, C**H**CO$_2$Me), 2.61 (m, 1H, **B**, C**H**CH$_2$I), 2.58 (dd, *J* = 9.9, 8.2 Hz, 1H, **A**, C**H**$_2$I), 2.31-2.19 (m, 1H, **A**, C**H**CH$_2$I), 1.86 (s, 3H, **B**), 1.82 (s, 3H, **A**), 1.07 (t, J = 7.0 Hz, 3H, **B**), 1.05 (t, *J* = 7.0 Hz, 3H, **A**).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8 (C=O, **A**), 168.6 (C=O, **B**), 143.2 (C, **A**), 143.0 (C, **B**), 135.1 (C, **A**), 129.0 (2CH, **A**), 128.9 (2CH, **B**), 127.0 (2CH, **B**), 126.9 (2CH, **A**), 92.2 (CH, **A**), 91.3 (CH, **B**), 63.7 (CH_2, **B**), 63.6 (CH_2, **A**), 56.7 (CH, **A**), 53.8 (CH, **B**), 52.6 (CH_2, **A**), 51.9 (CH, **A**), 51.4 (CH, **B**), 50.9 (CH_2, **B**), 42.9 (CH, **A**), 41.8 (CH, B), 43.5 (CH, **A**), 21.0 (CH_3, **A**), 17.8 (CH_3, **B**), 14.4 (CH_3, **B**), 14.3 (CH_3, **B**), 6.0 (CH_2, **A**), 0.0 (CH_2, **B**).

HRMS: m/z $[M\text{-}OEt]^+$ calcd 421,9917 found 421,9926; $[M+MeCN+Na]^+$ calcd 531.0421 found 531.0425.

IR: *v*= 2975, 2889, 1733, 1597, 1434, 1345, 1165 cm^{-1}.

methyl 4-(iodomethyl)-1-tosyl-4,5-dihydro-1H-pyrrole-3-carboxylate **7**



7

421.25 g/mol

$C_{14}H_{16}INO_4S$

Over prolonged time in chloroform ($CDCl_3$) methyl 2-ethoxy-4-(iodomethyl)-1-tosylpyrrolidine-3-carboxylate **6** transformed into methyl 4-(iodomethyl)-1-tosyl-4,5-dihydro-1H-pyrrole-3-carboxylate **7**.

Alternatively: to a solution of **6** (76 mg, 0.16 mmol, 1 equiv) in 2.0 mL of CH_2Cl_2 at room temperature was added boron trifluoride diethyl etherate (25 µL, 0.2 mmol, 1.2 equiv). After 1 h, the reaction mixture was quenched with 10 mL of a saturated solution of $NaHCO_3$. The aqueous layer was extracted with 20 mL of CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography on 25 g of silica gel using heptane/ethyl acetate 95:5 v:v as the mobile phase to afford 57 mg (84%) of the desired product **7** as a white powder.

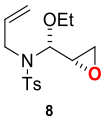
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 1.2 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 3.79- – 3.70 (m, 1H), 3.72 (s, 3H), 3.53 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.44- – 3.34 (m, 1H), 3.36 (dd, *J* = 8.9, 2.5 Hz, 1H) , 3.07 (dd, *J* = 10.2, 8.9 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.3 (C=O), 145.0 (C), 142.1 (CH), 133.1 (C), 130.2 (2CH), 127.6 (2CH), 115.4 (C), 54.8 (CH_2), 51.5 (CH_3), 43.5 (CH), 21.6 (CH_3), 10.4 (CH_2).

HRMS: m/z $[M+H]^+$ calcd 421.9918 found 421.9904; $[M+H]^+$ calcd 463.0183 found 463.0173.

IR: *v*= 3104, 3046, 2953, 2926, 1684, 1610, 1432, 1362, 1243, 1159, 1125 cm^{-1}.

N-allyl-*N*-((*R**)-ethoxy((*S**)-oxiran-2-yl)methyl)-4-methylbenzenesulfonamide **8**



8

371.40 g/mol

$C_{15}H_{21}NO_4S$

A solution of *N*-allyl-*N*-(1-ethoxy-3-hydroxy-2-iodopropyl)-4-methylbenzenesulfonamide **4o** (50 mg, 0.114 mmol, 1 equiv) and sodium hydroxide (5.0 mg, 0.125 mmol, 1.1 equiv) in a mixture of 2.5 mL of MTBE and 0.5 mL of THF was stirred at room temperature. The reaction mixture was monitored by TLC during 24 h until full conversion at which time the mixture was quenched with distilled water. The organic layer was separated, washed with a saturated solution of NaCl, dried with $MgSO_4$ and concentrated to afford the epoxide **8** (36 mg, quantitative yield) as a colourless oil.
The product was obtained as a single diastereoisomer. Analytical data are consistent with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.81 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.22 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.1 Hz, 1H), 4.81(d, *J* = 5.1 Hz, 1H), 3.94-3.90 (m, 2H), 3.46-3.29 (m, 2H), 3.07 (ddd, *J* = 5.1, 4.1, 2.7Hz, 1H), 2.70-2.62 (m, 2H), 2.43 (s, 3H), 1.11 (t, *J* = 6.9 Hz, 3H).

5. X-Ray Data

Single crystals formed from slow evaporation using MTBE for **4l** and **4q**. X-ray diffraction data were obtained on a Rigaku XtaLabPro diffractometer equipped with a microfocus source (MicroMax003_Mo) and multilayer confocal mirrors (Mo Kα radiation, λ = 0.71073 Å). Data were indexed, integrated and scaled using CrysalisPro.[6] They were also corrected for polarisation, Lorentz and absorption effects (CrysalisPro). For each compound, the structure (Figure) was solved with the ShelXT[7] structure solution program using Direct Methods and refined with the ShelXL[8] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms have been added geometrically and treated as riding on their parent atoms.

methyl (2*S**, 3*R**)-3-(*N*-benzyl-4-nitrophenylsulfonamido)-3-ethoxy-2-iodopropanoate **4l**

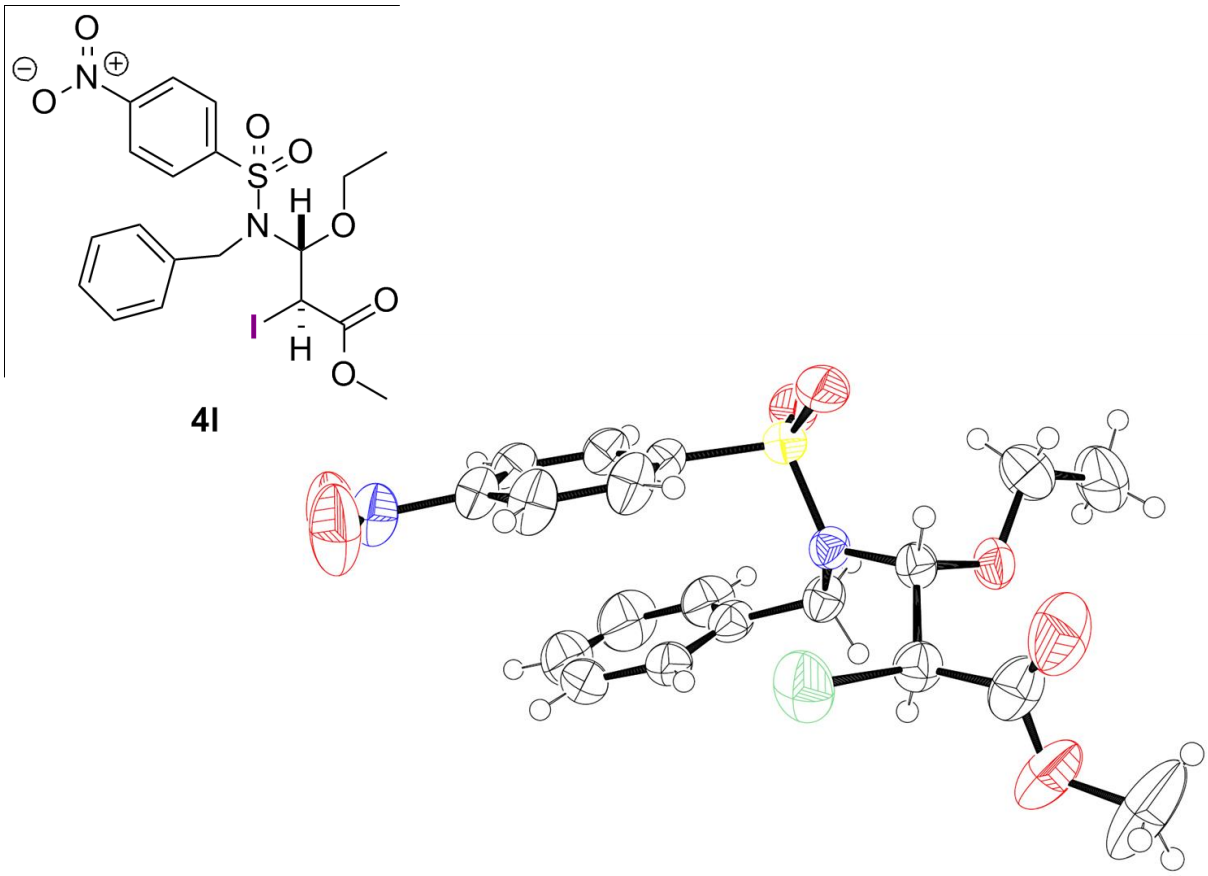
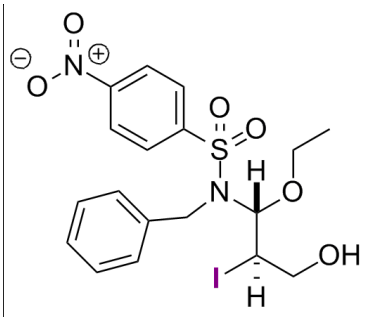


Figure 1: ORTEP-3 plot of 4l. Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius.

Crystal Data for **4l** (*M* =548.34 g/mol): monoclinic, space group I2/a (no. 15), *a* = 14.1684(3) Å, *b* = 6.6657(2) Å, *c* = 47.1845(14) Å, *β* = 91.503(2)°, *V* = 4454.7(2) Å^3, *Z* = 8, *T* = 292.87(11) K, μ(MoKα) = 1.573 mm^{-1}, *Dcalc* = 1.635 g/cm^3, 18178 reflections measured (7.486° ≤ 2Θ ≤ 59.368°), 5599 unique (R_{int} = 0.0323, R_{sigma} = 0.0326) which were used in all calculations. The final R_1 was 0.0377 (I > 2σ(I)) and wR_2 was 0.1027 (all data).

[6] Rigaku Oxford Diffraction, CrysAlisPro Software system, version 38.41o, Rigaku Corporation, Oxford, UK. (2015).
[7] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. Found. Adv.* 2015 **71,** 3.
[8] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71,** 3.

N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-nitrobenzenesulfonamide **4q**



4q

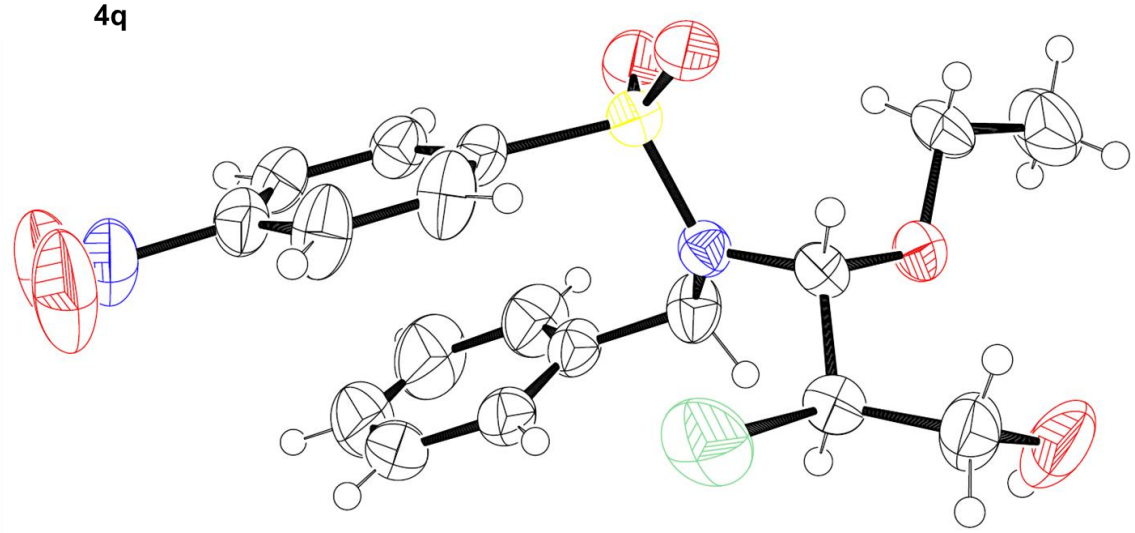


Figure 2: ORTEP-3 plot of 4q. Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius.

Crystal Data for **4q** (*M* =520.33 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 6.7507(4) Å, *b* = 14.1829(7) Å, *c* = 43.847(3) Å, *V* = 4198.1(4) Å^3, *Z* = 8, *T* = 292.8(2) K, μ(MoKα) = 1.661 mm^{-1}, *Dcalc* = 1.647 g/cm^3, 19785 reflections measured (6.748° ≤ 2Θ ≤ 59.436°), 5384 unique (R_{int} = 0.0375, R_{sigma} = 0.0440) which were used in all calculations. The final R_1 was 0.0597 (I > 2σ(I)) and wR_2 was 0.1827 (all data).

Molecular graphics were computed with Ortep 3[9] CCDC 1488802 - 1488803 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

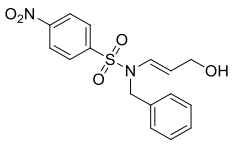
Table 1 Crystal data and structure refinement parameters

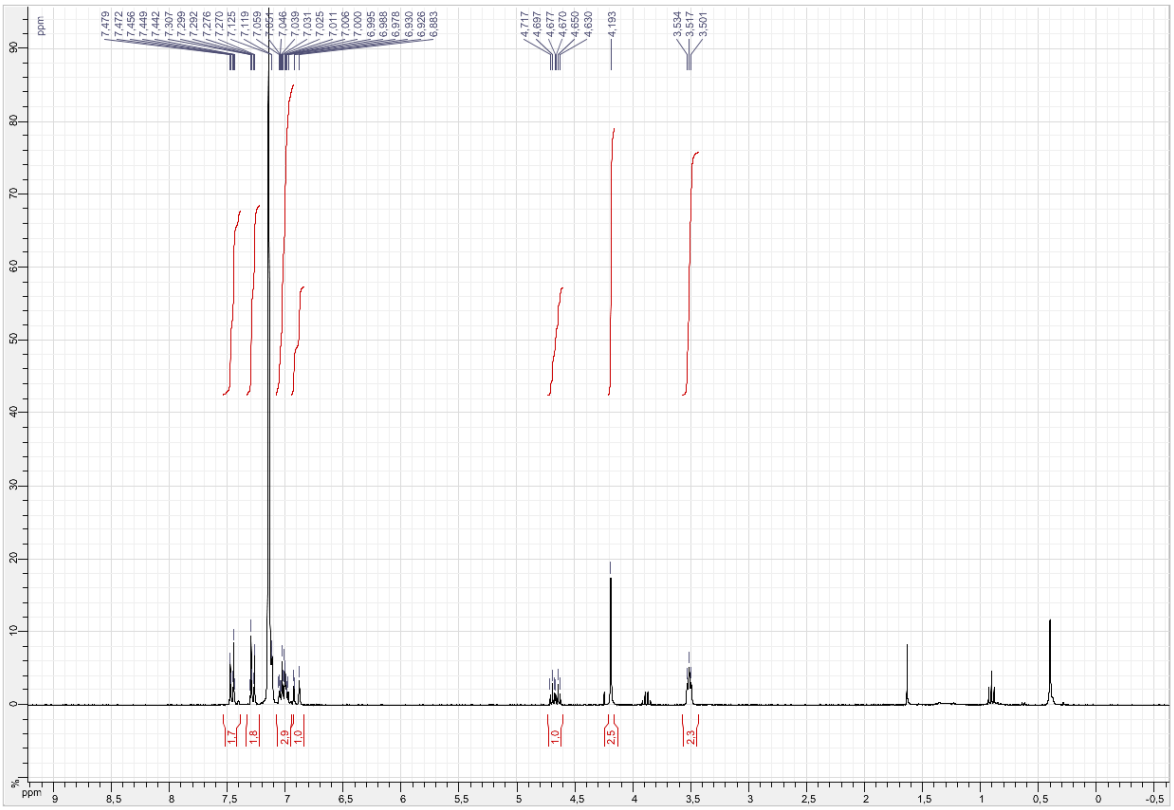
Product number	**4l**	**4q**
CCDC number	1488802	1488803
Empirical formula	$C_{19}H_{21}IN_2O_7S$	$C_{18}H_{21}IN_2O_6S$
Formula weight	548.34	520.33
Temperature/K	292.87(11)	292.8(2)
Crystal system	monoclinic	orthorhombic
Space group	I2/a	Pbca
a/Å	14.1684(3)	6.7507(4)
b/Å	6.6657(2)	14.1829(7)
c/Å	47.1845(14)	43.847(3)
α/°	90	90
β/°	91.503(2)	90
γ/°	90	90
Volume/Å^3	4454.7(2)	4198.1(4)
Z	8	8
ρ_{calc}g/cm^3	1.635	1.647
μ/mm^{-1}	1.573	1.661
F(000)	2192.0	2080.0
Crystal size/mm^3	0.1 × 0.1 × 0.04	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection/°	7.486 to 59.368	6.748 to 59.436
Index ranges	-14 ≤ h ≤ 19, -8 ≤ k ≤ 9, -65 ≤ l ≤ 52	-9 ≤ h ≤ 8, -19 ≤ k ≤ 14, -42 ≤ l ≤ 58
Reflections collected	18178	19785
Independent reflections	5599 [R_{int} = 0.0323, R_{sigma} = 0.0326]	5384 [R_{int} = 0.0375, R_{sigma} = 0.0440]
Data/restraints/parameters	5599/0/273	5384/0/275
Goodness-of-fit on F^2	1.061	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0945	R_1 = 0.0597, wR_2 = 0.1650
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.1027	R_1 = 0.1043, wR_2 = 0.1827
Largest diff. peak/hole / e Å^{-3}	0.52/-0.94	0.73/-1.06

[9] Farrugia, L. J. *WinGX* and *ORTEP for Windows* : an update. *J. Appl. Crystallogr.* 2012, **45,** 849.

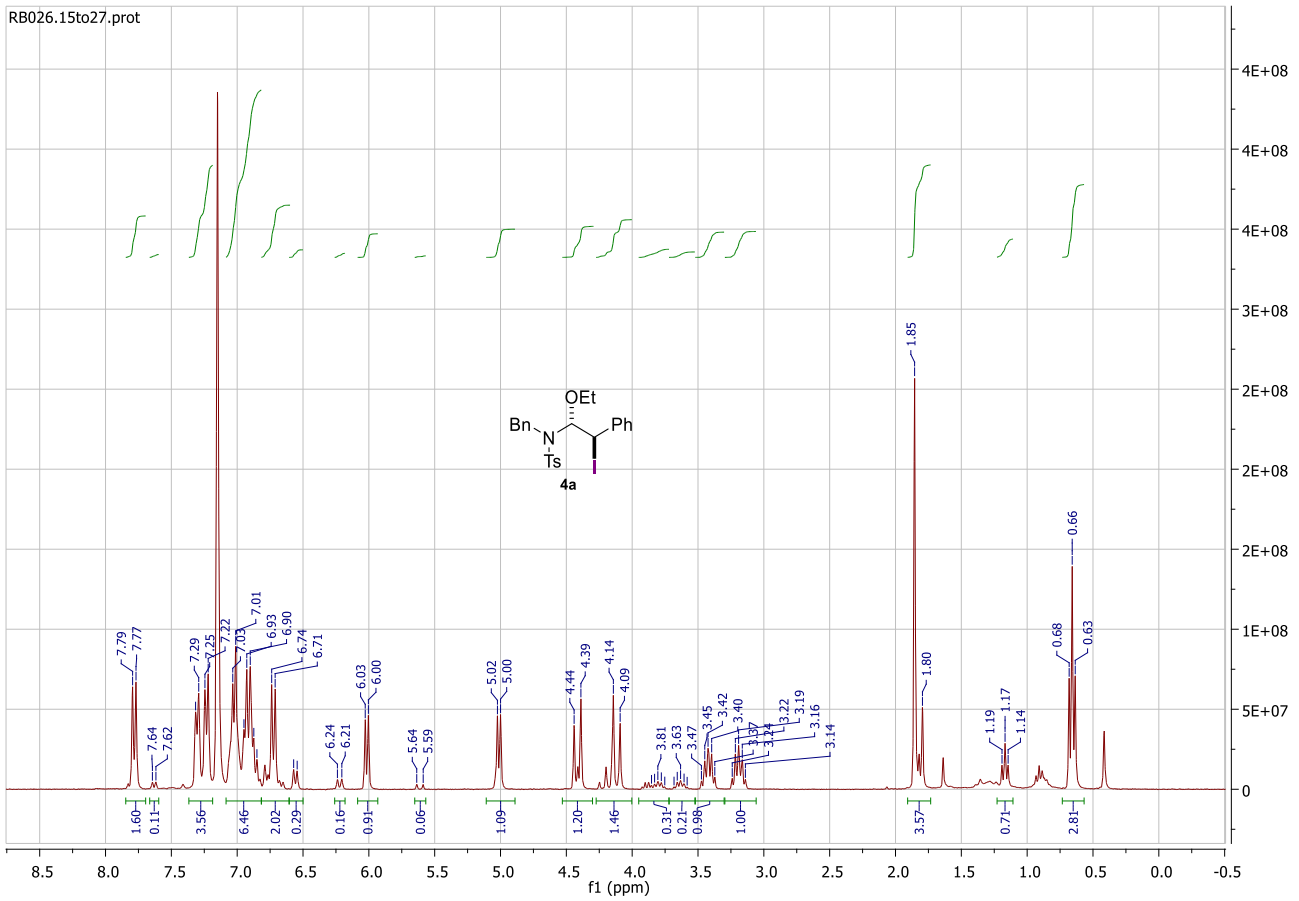
6. NMR Spectra

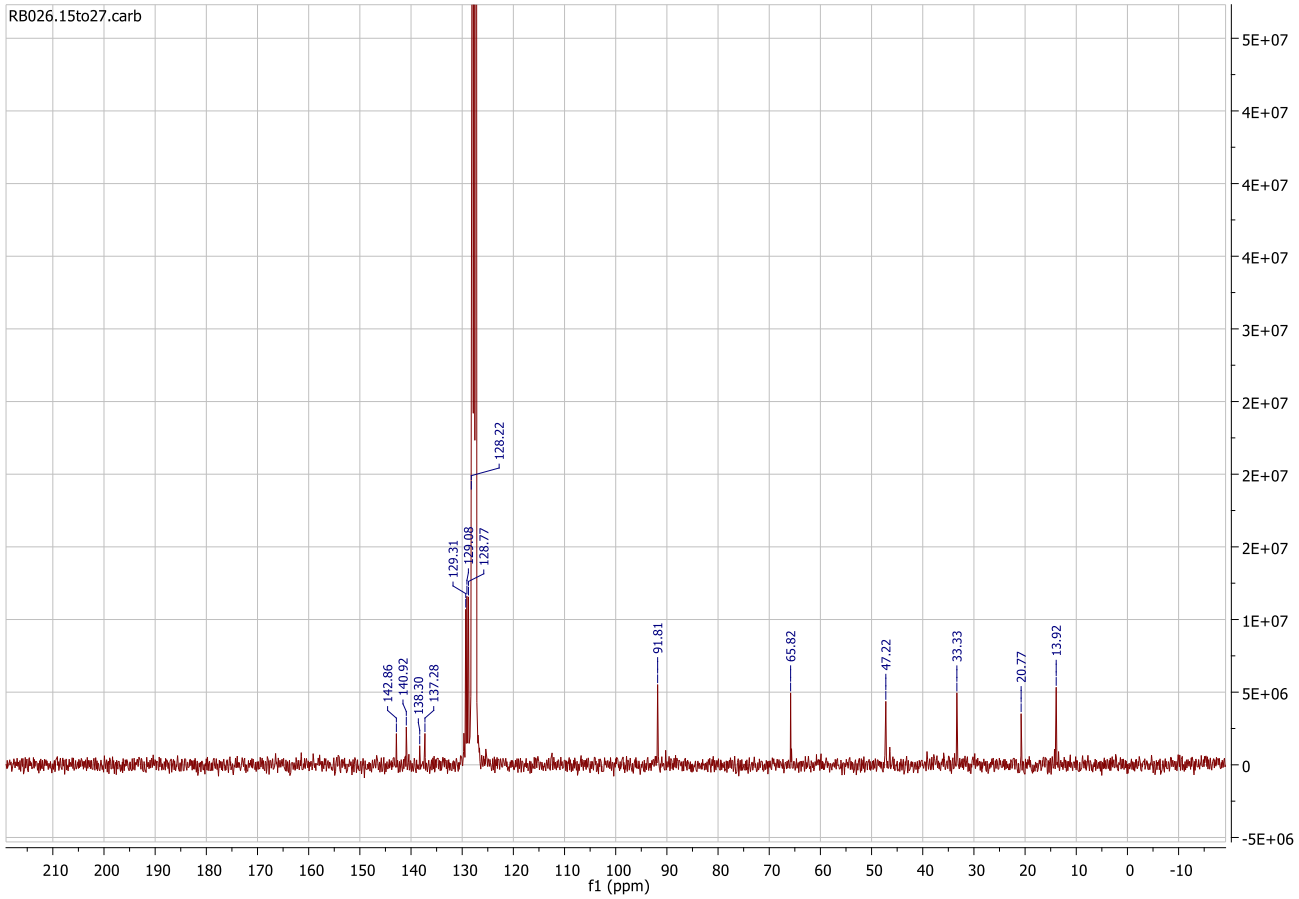
E)-*N*-benzyl-*N*-(3-hydroxyprop-1-en-1-yl)-4-nitrobenzenesulfonamide **1q**



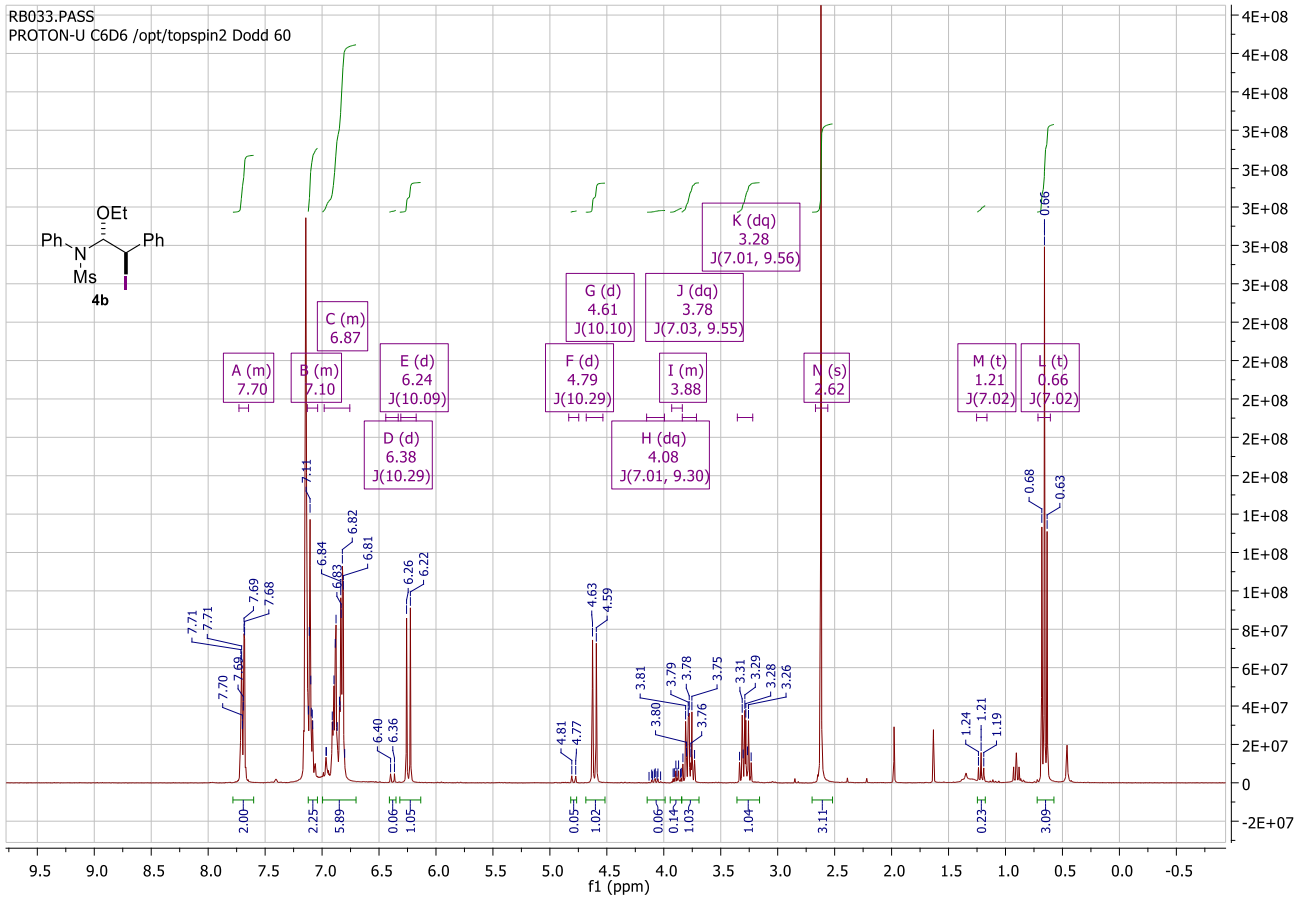


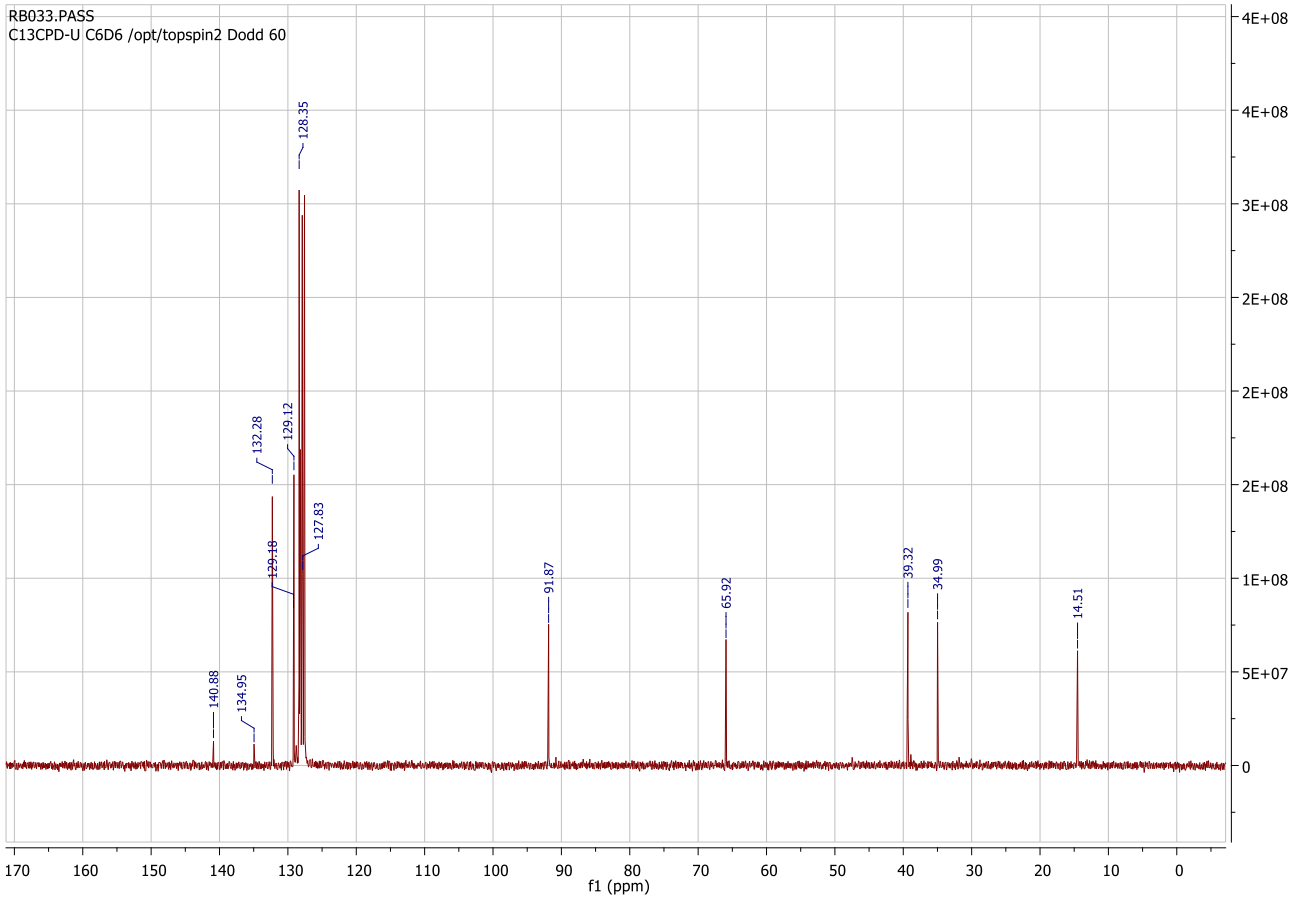
N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide **4a**



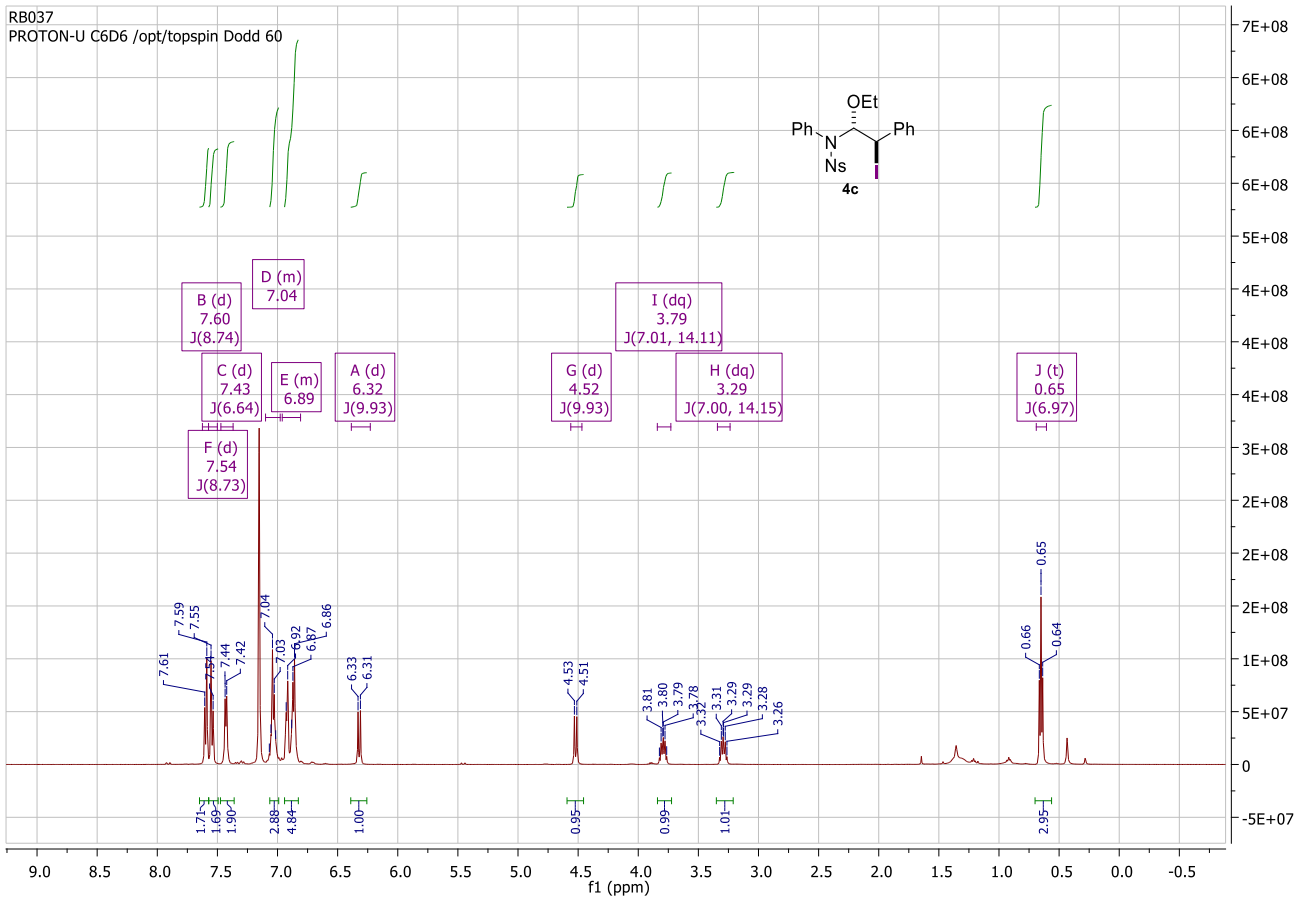


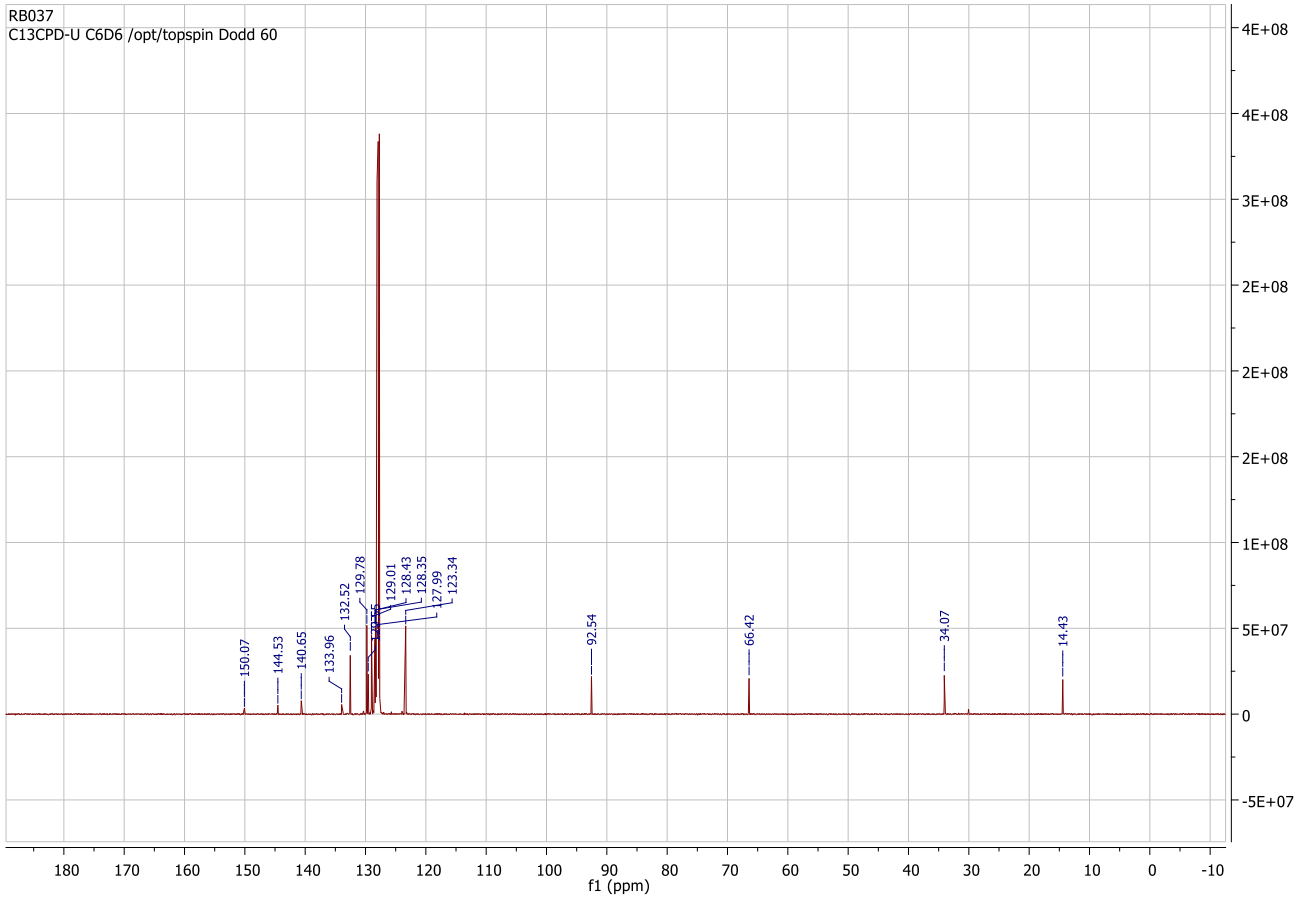
N-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-*N*-phenylmethanesulfonamide **4b**



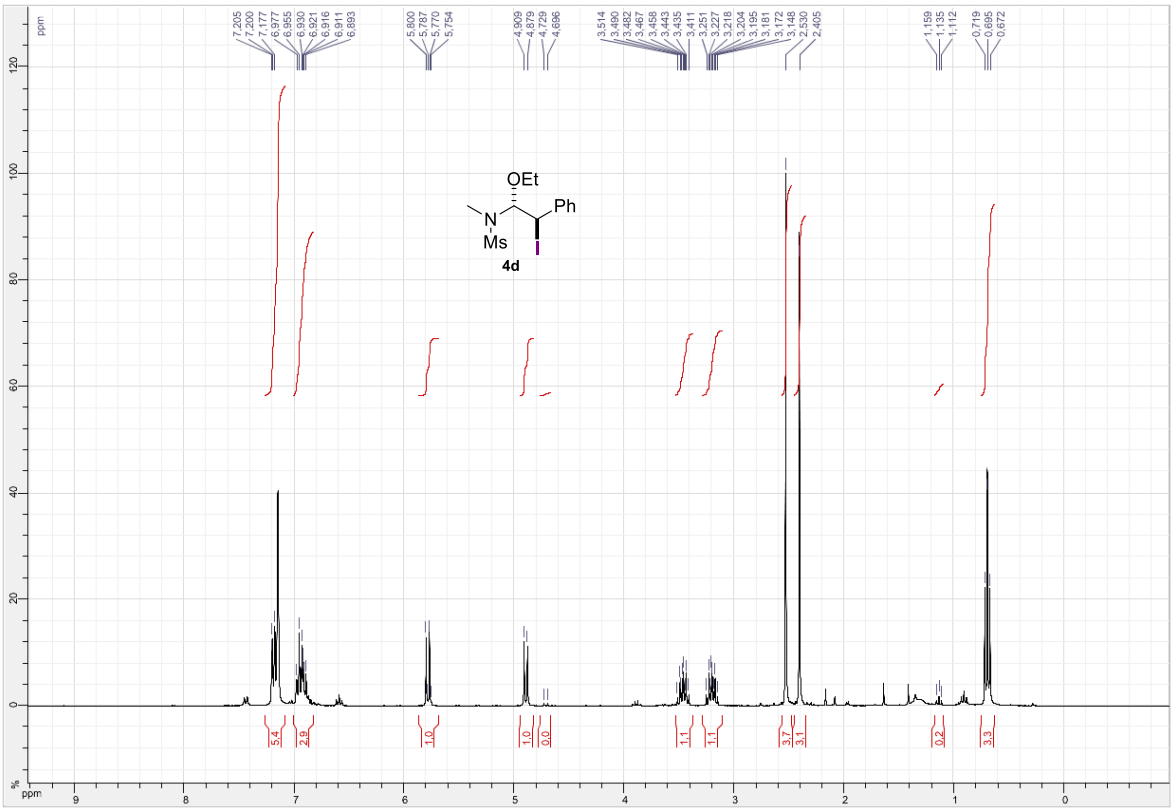


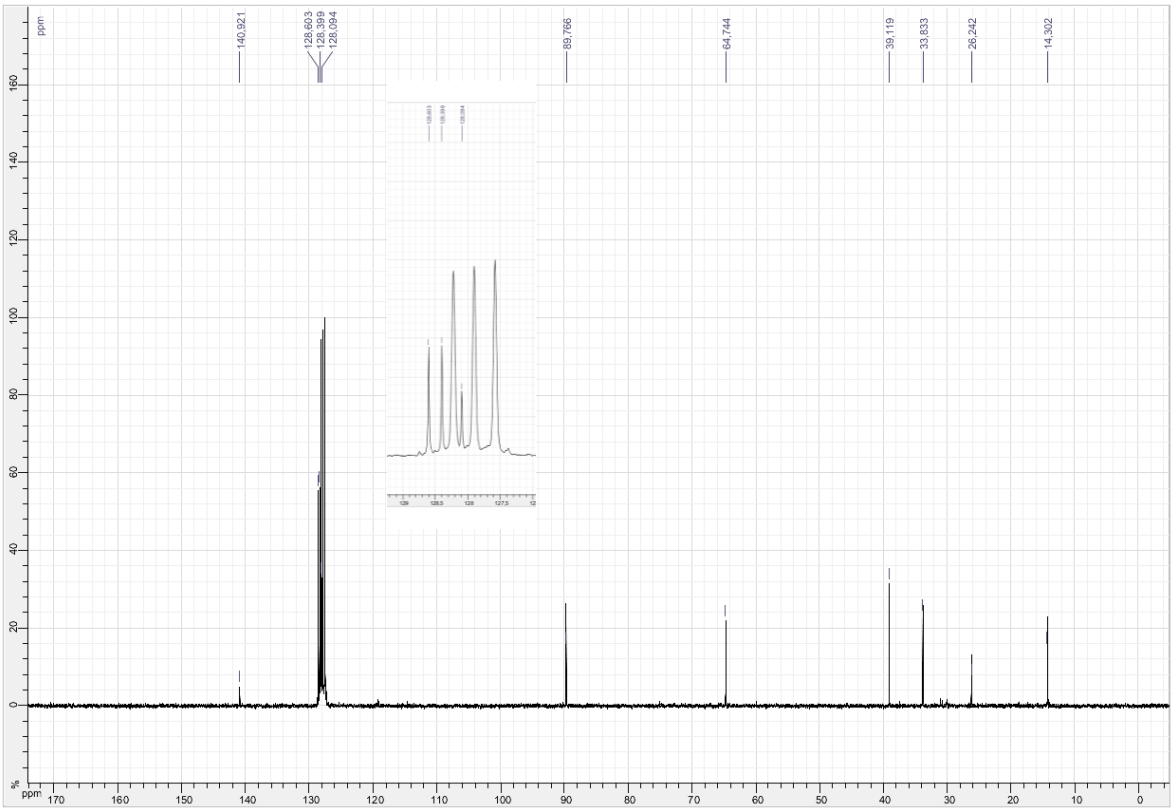
N-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-*N*-phenyl-4-nitrobenzenesulfonamide **4c**



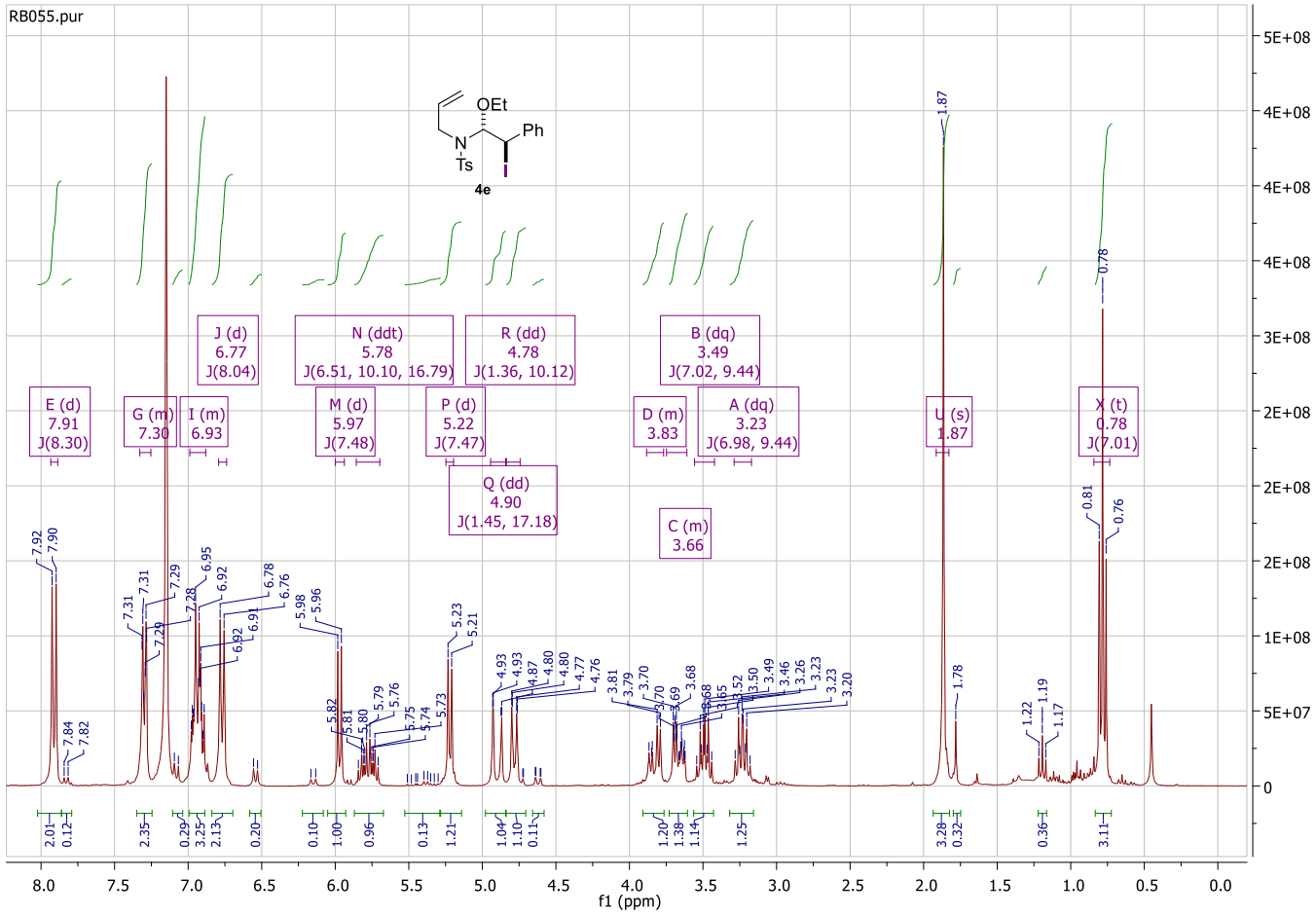


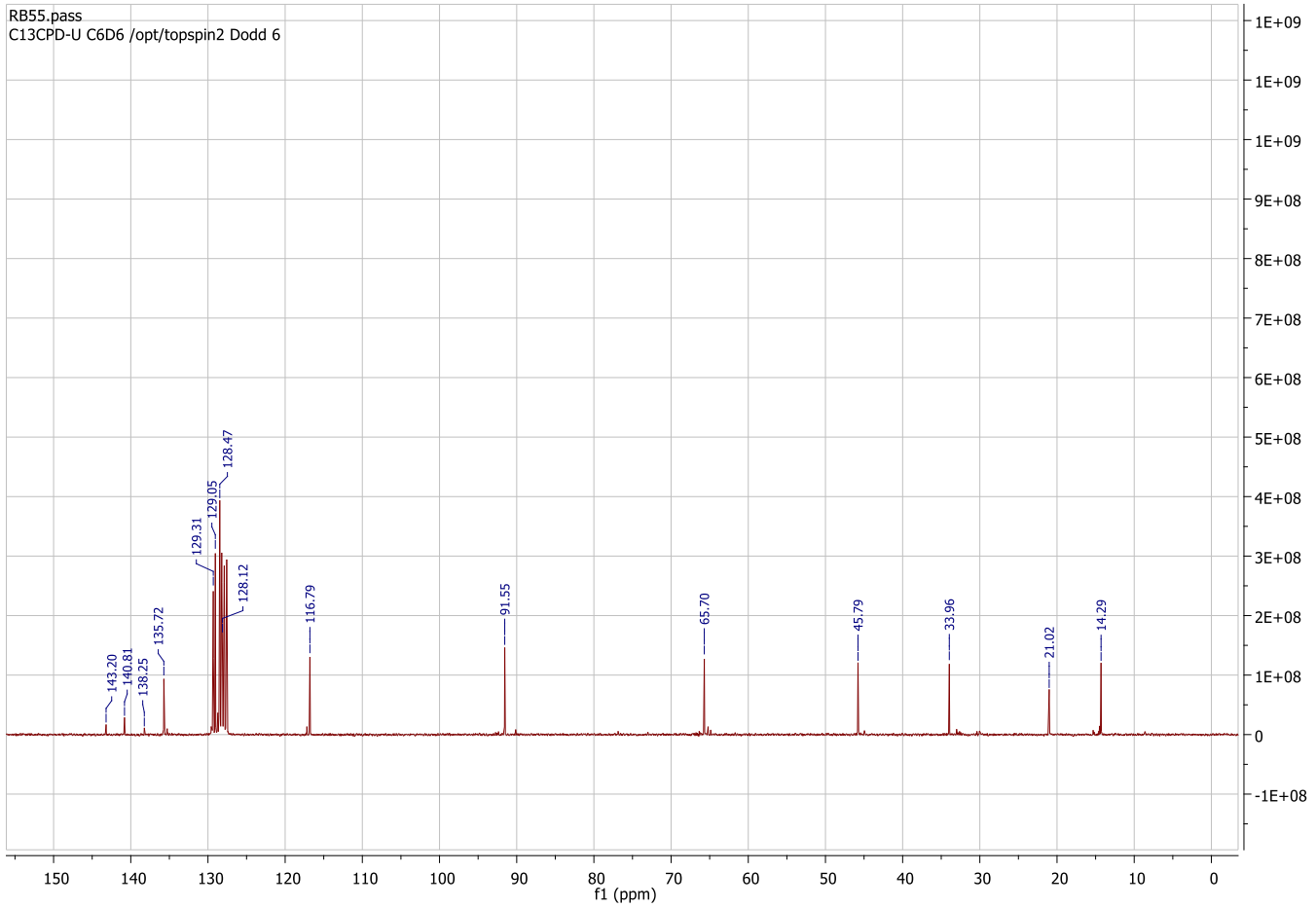
N-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-*N*-methylmethanesulfonamide **4d**



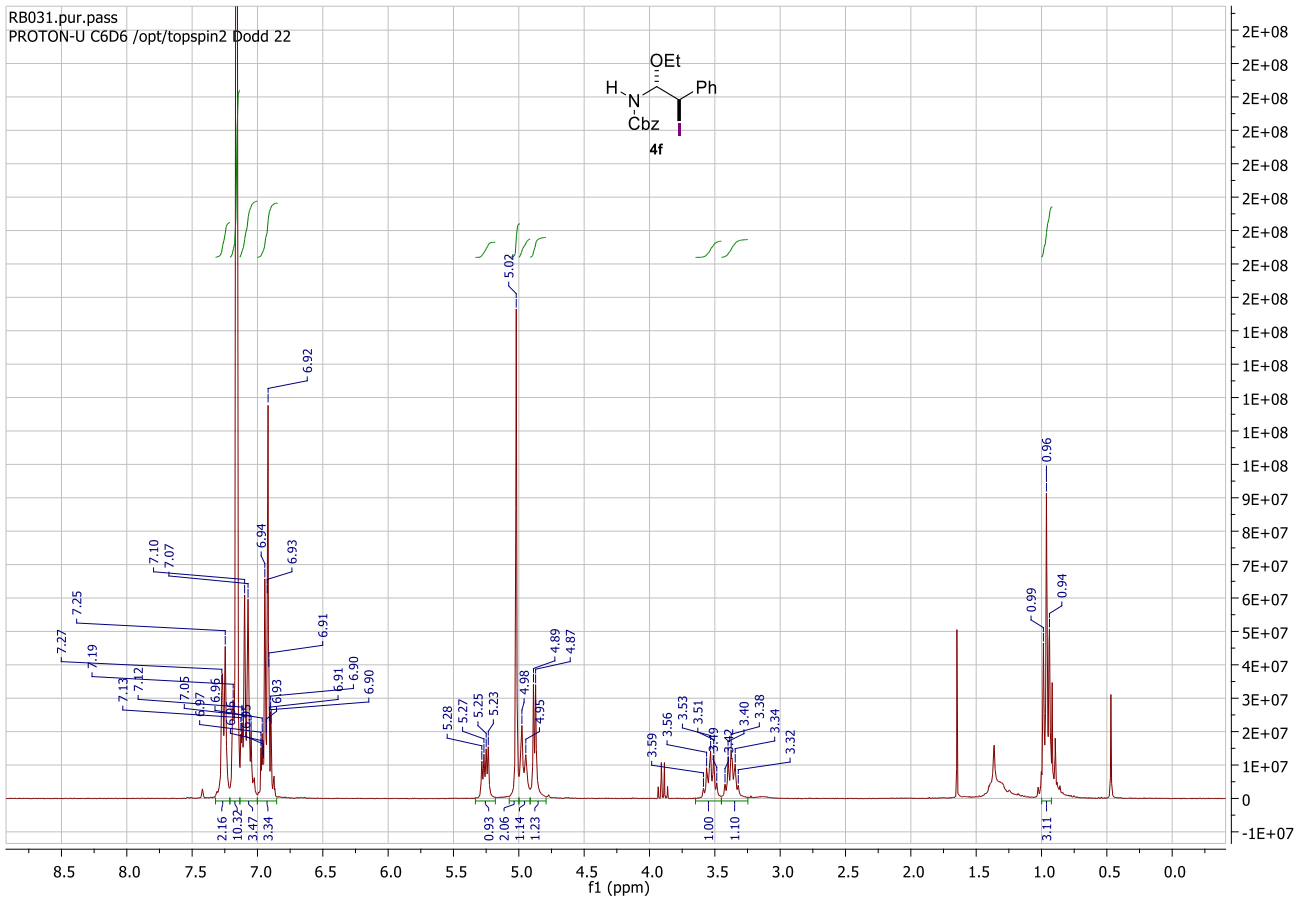


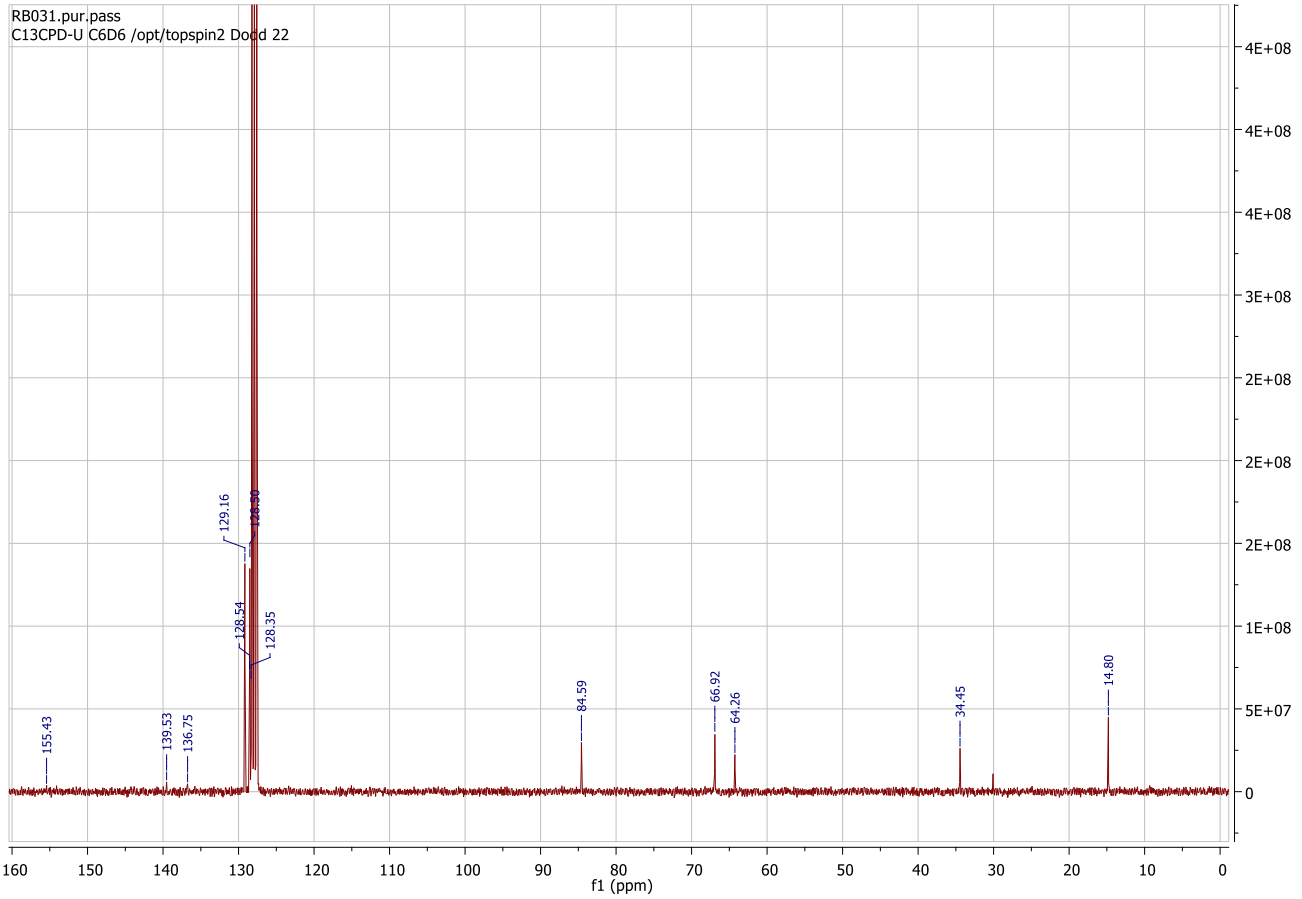
N-allyl-*N*-((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide **4e**



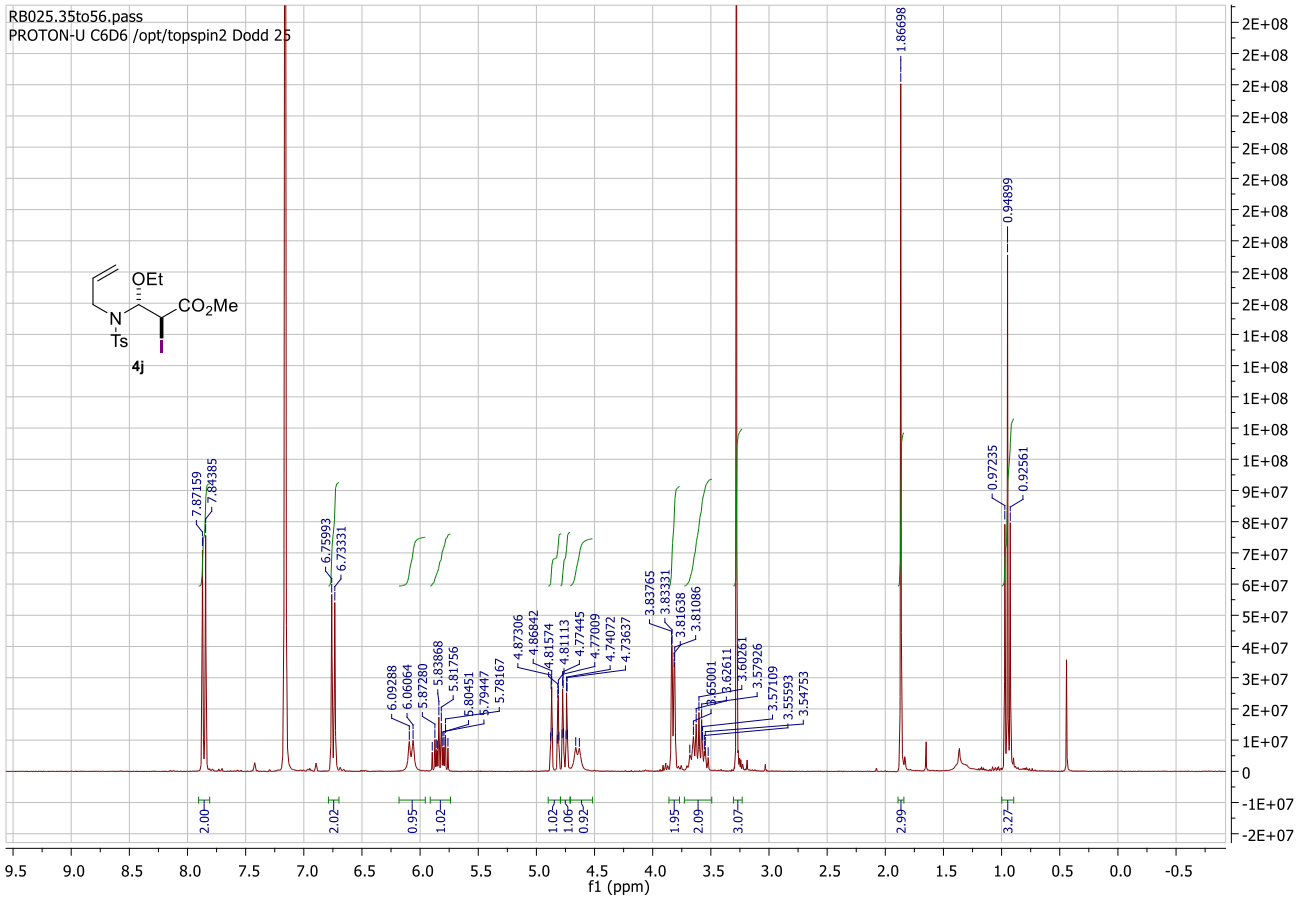


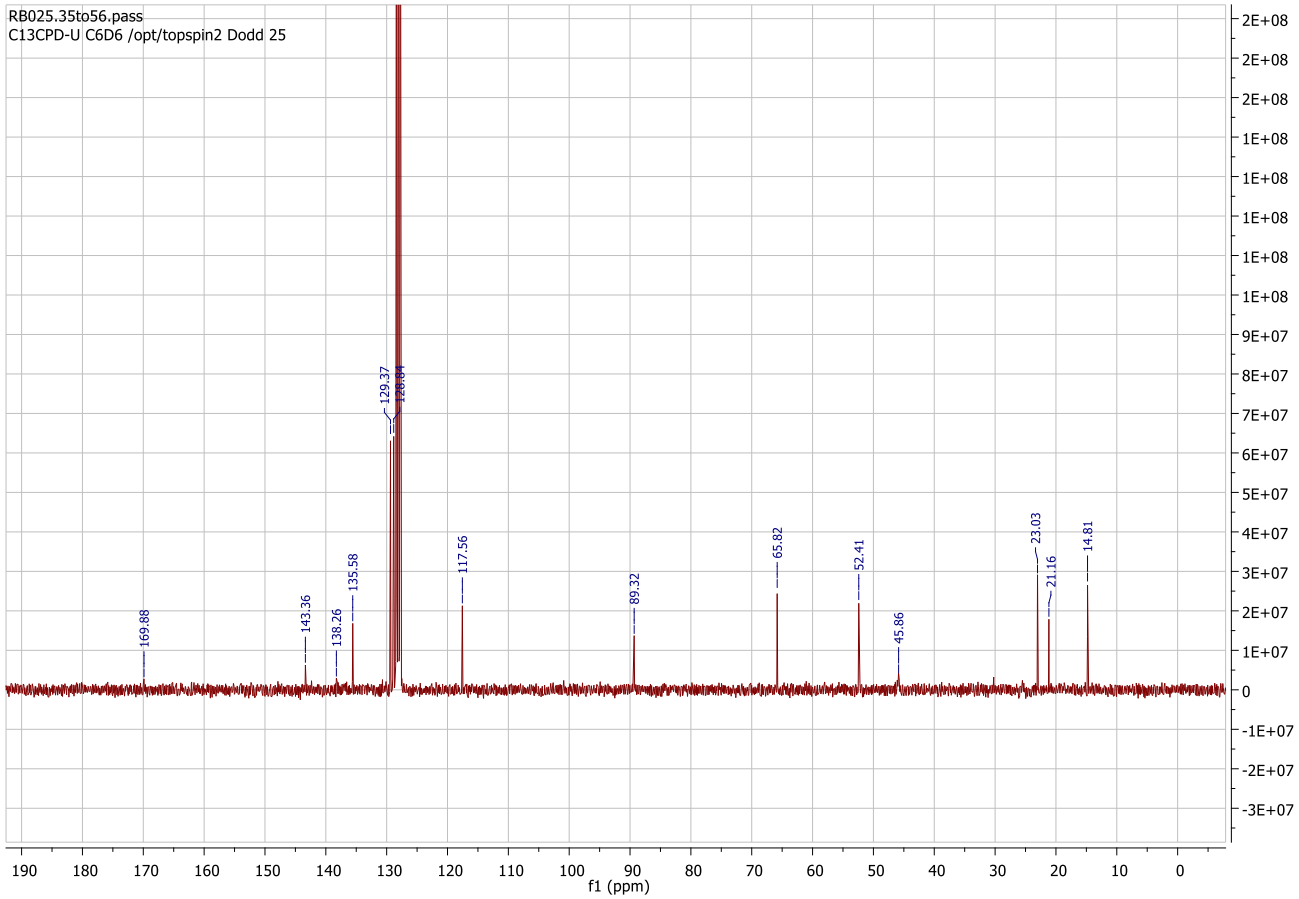
benzyl ((1*R**, 2*R**)-1-ethoxy-2-iodo-2-phenylethyl)carbamate **4f**



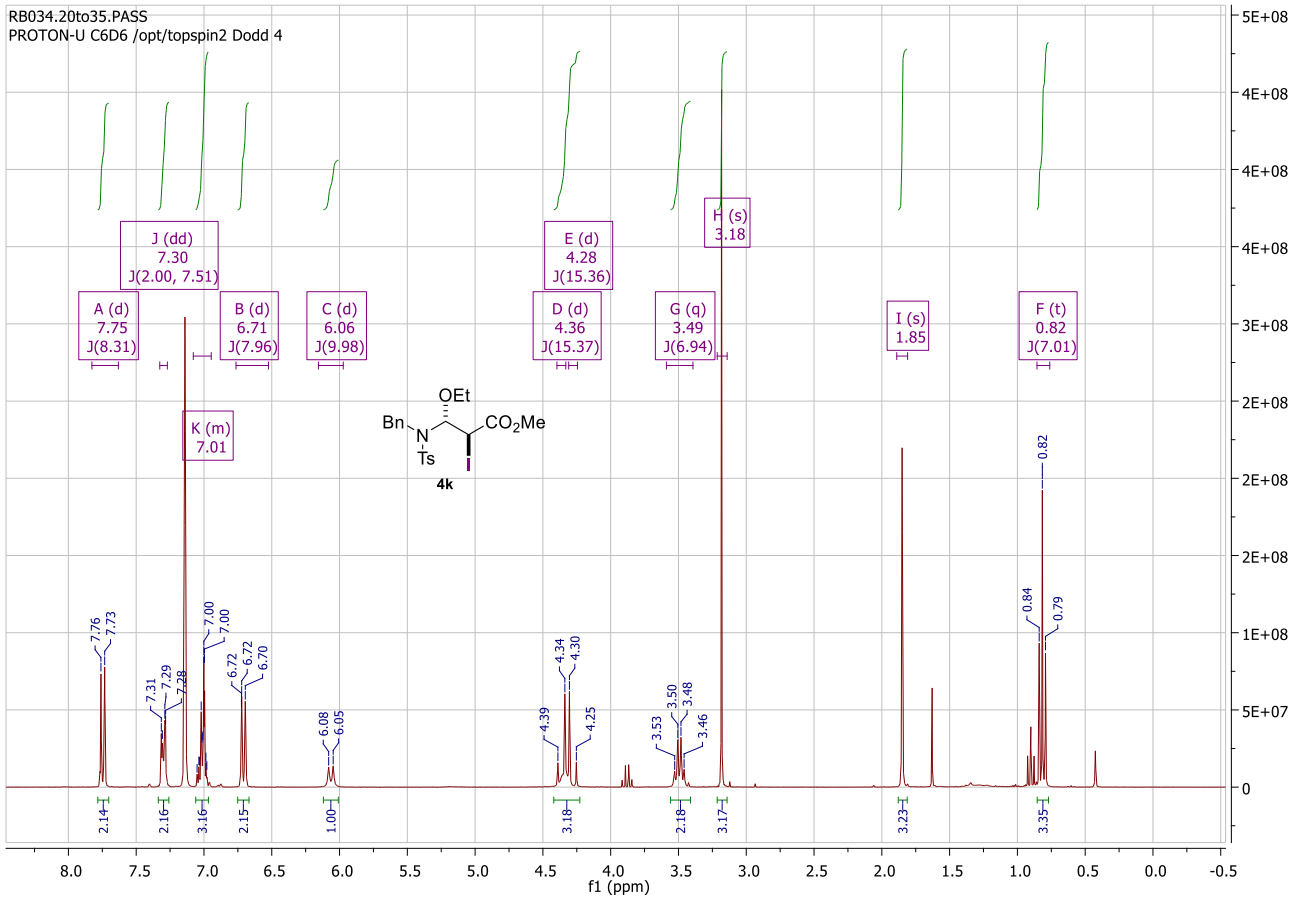


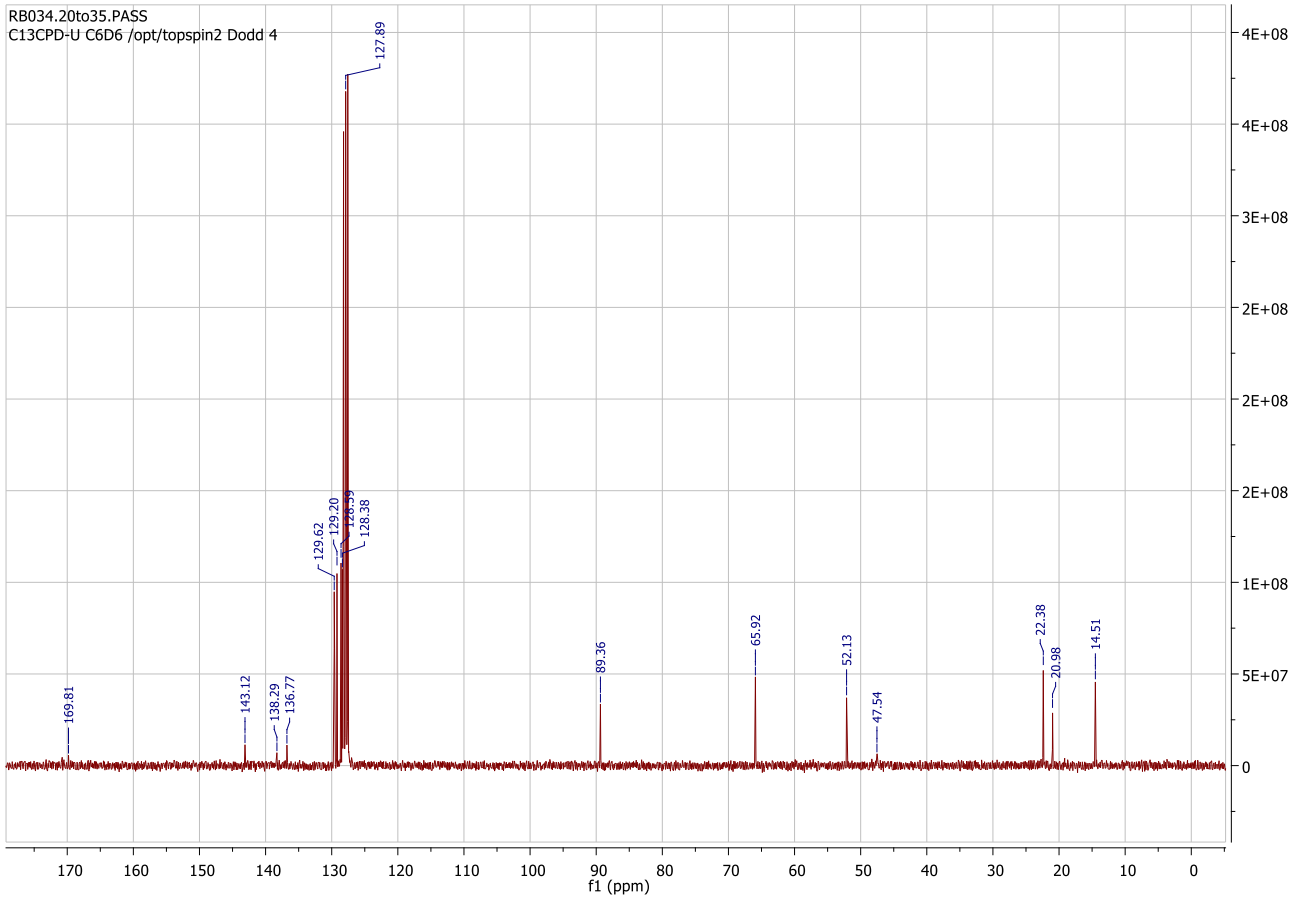
(2*S**, 3*R**)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4j**



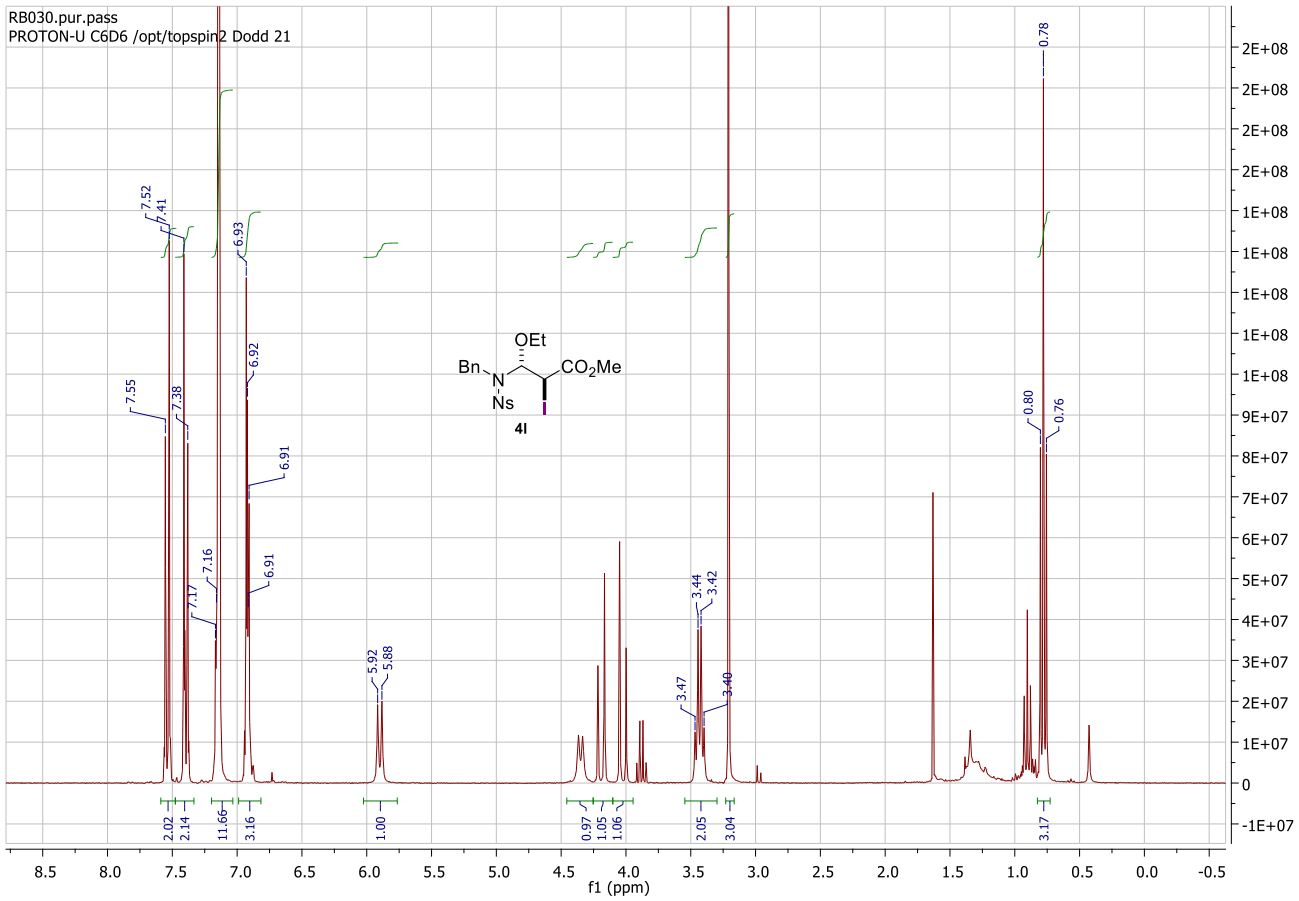


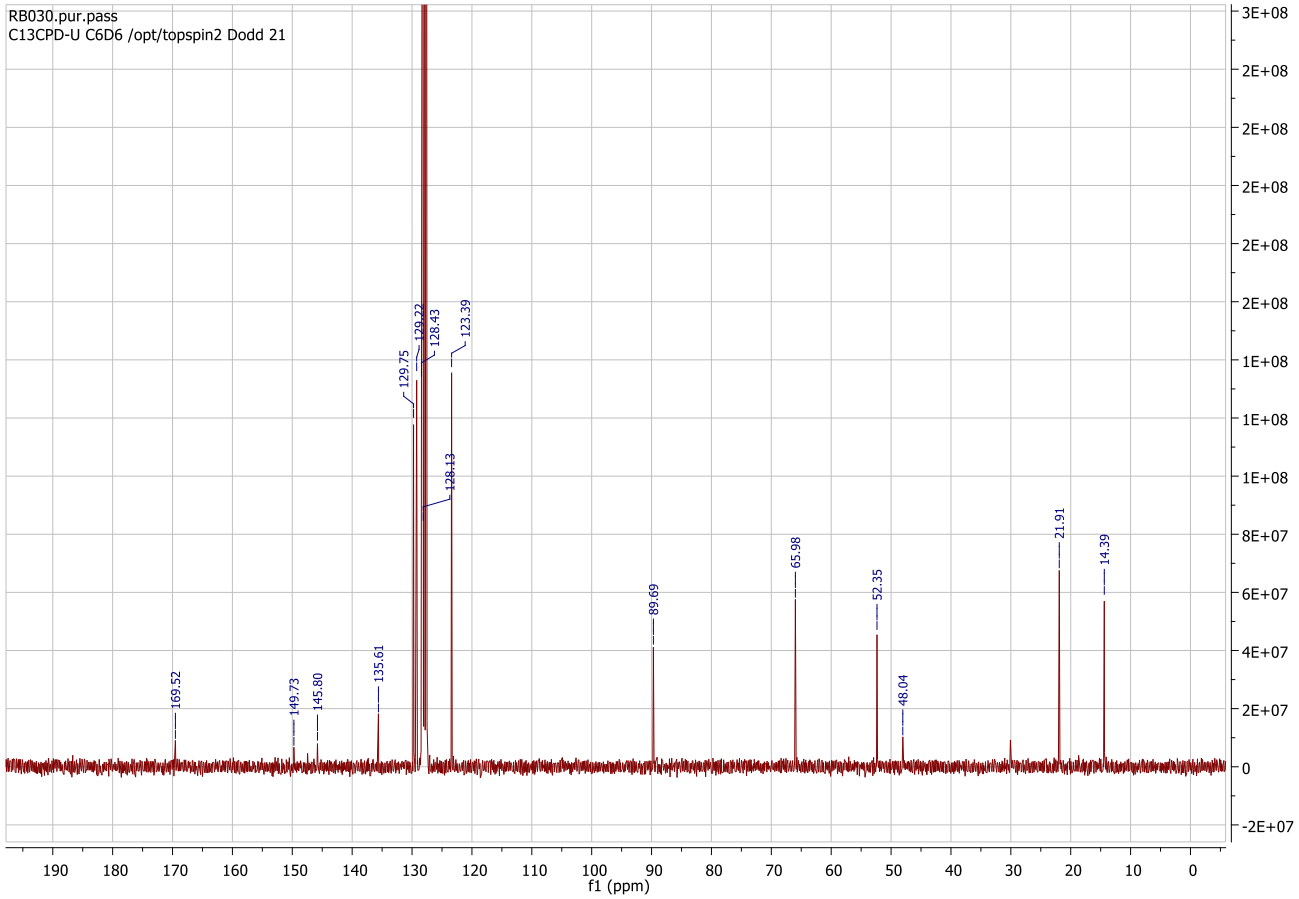
methyl (2*S**, 3*R**)-3-(*N*-benzyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4k**



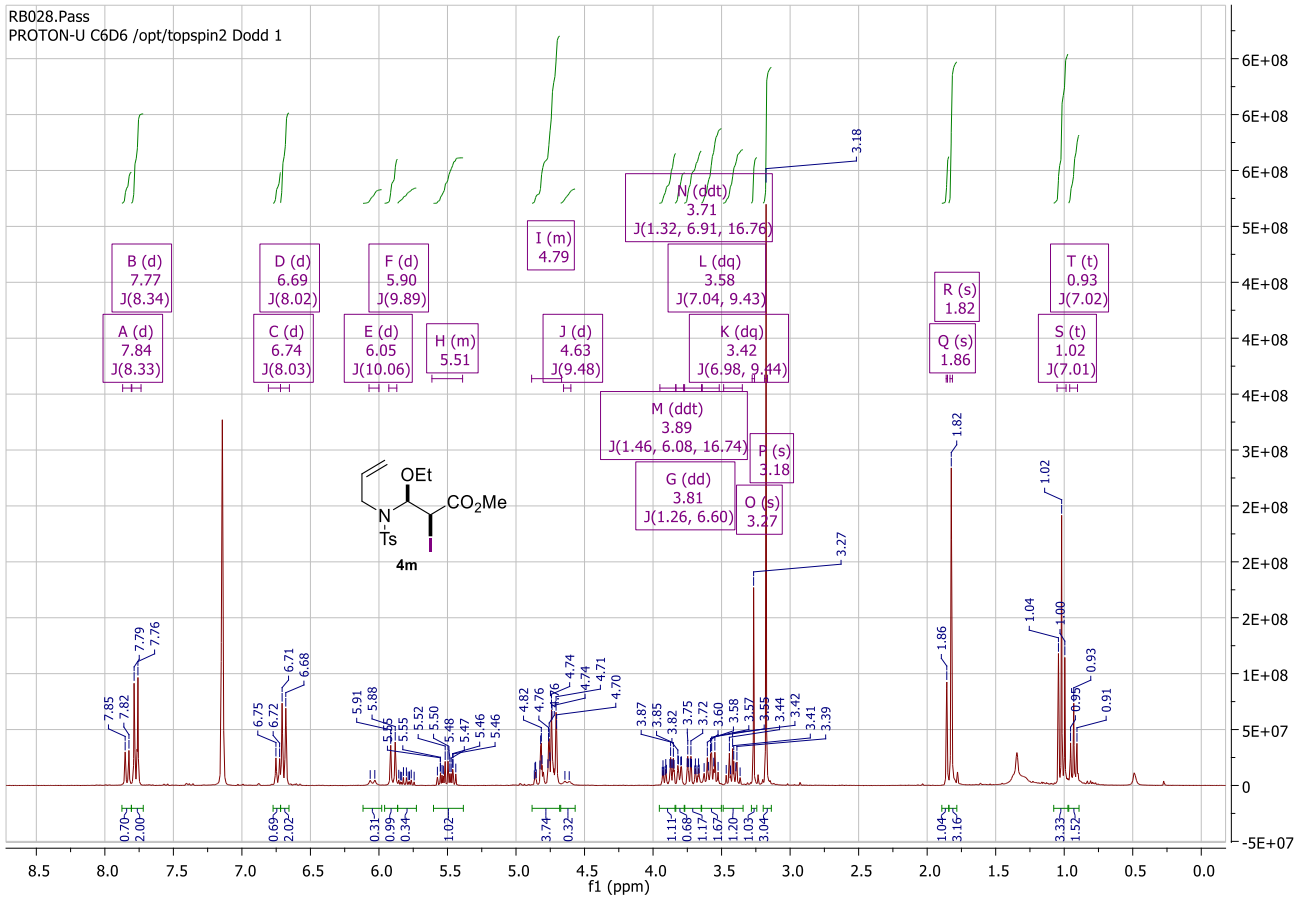


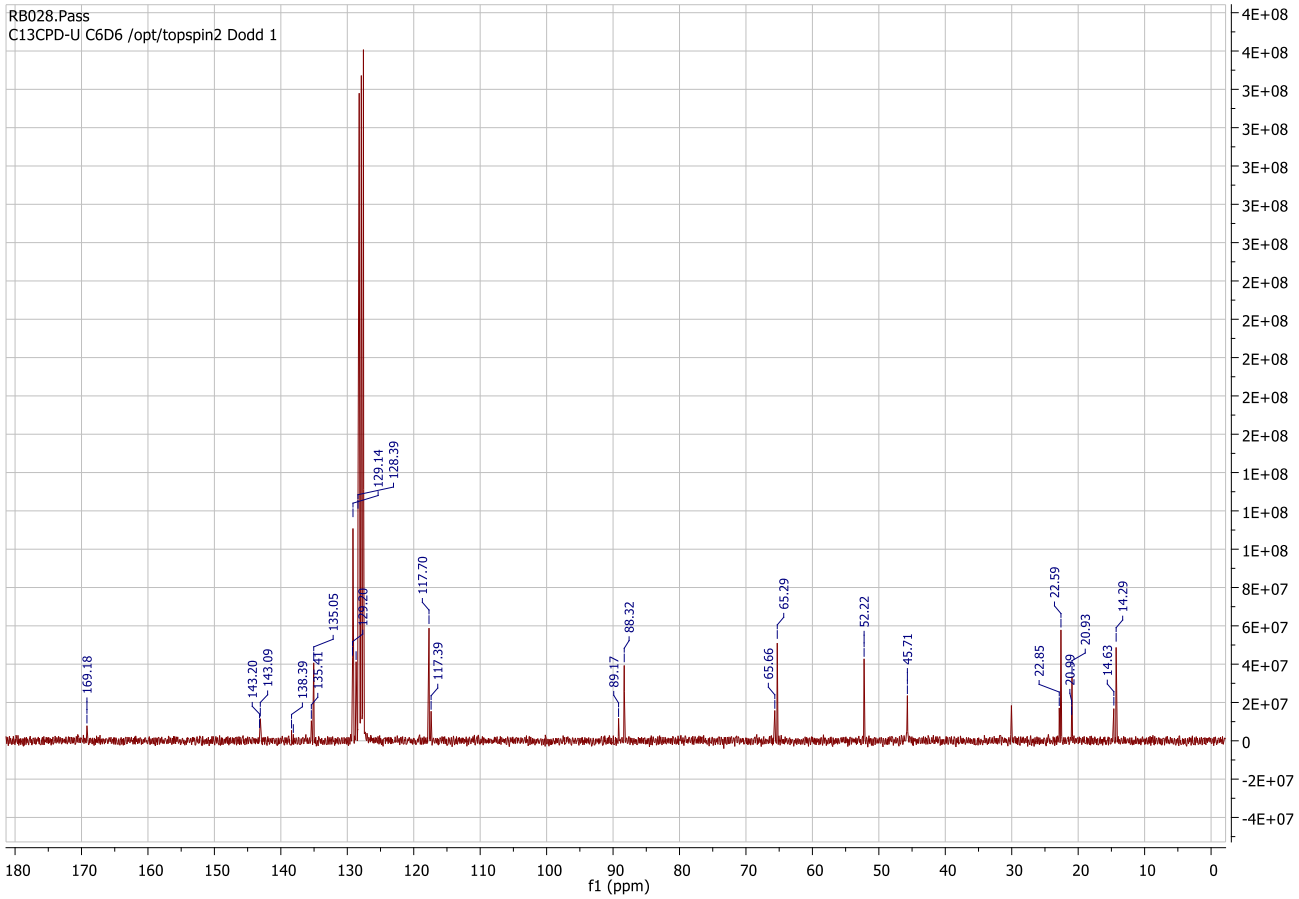
methyl (2*S**, 3*R**)-3-(*N*-benzyl-4-nitrophenylsulfonamido)-3-ethoxy-2-iodopropanoate **4l**



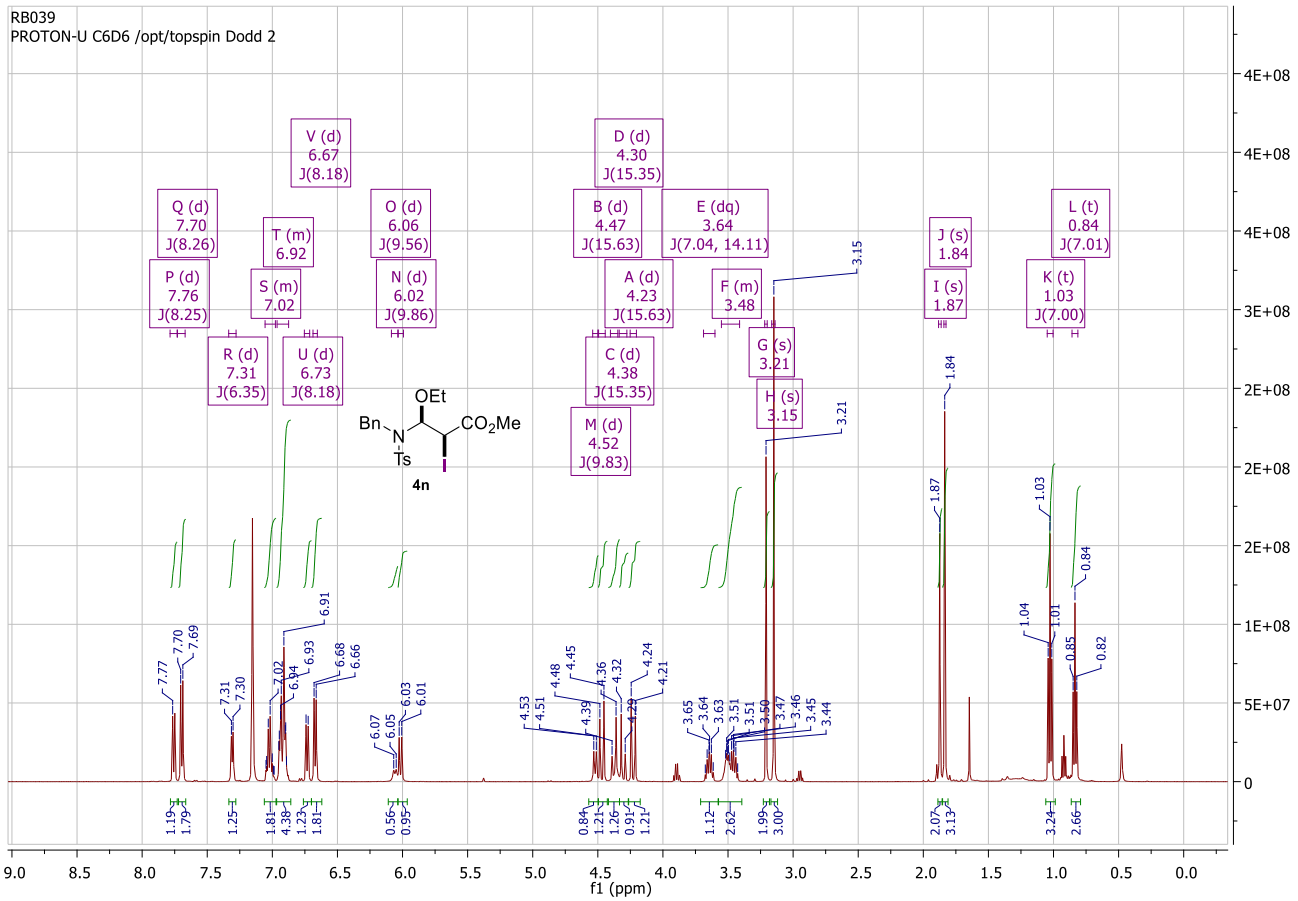


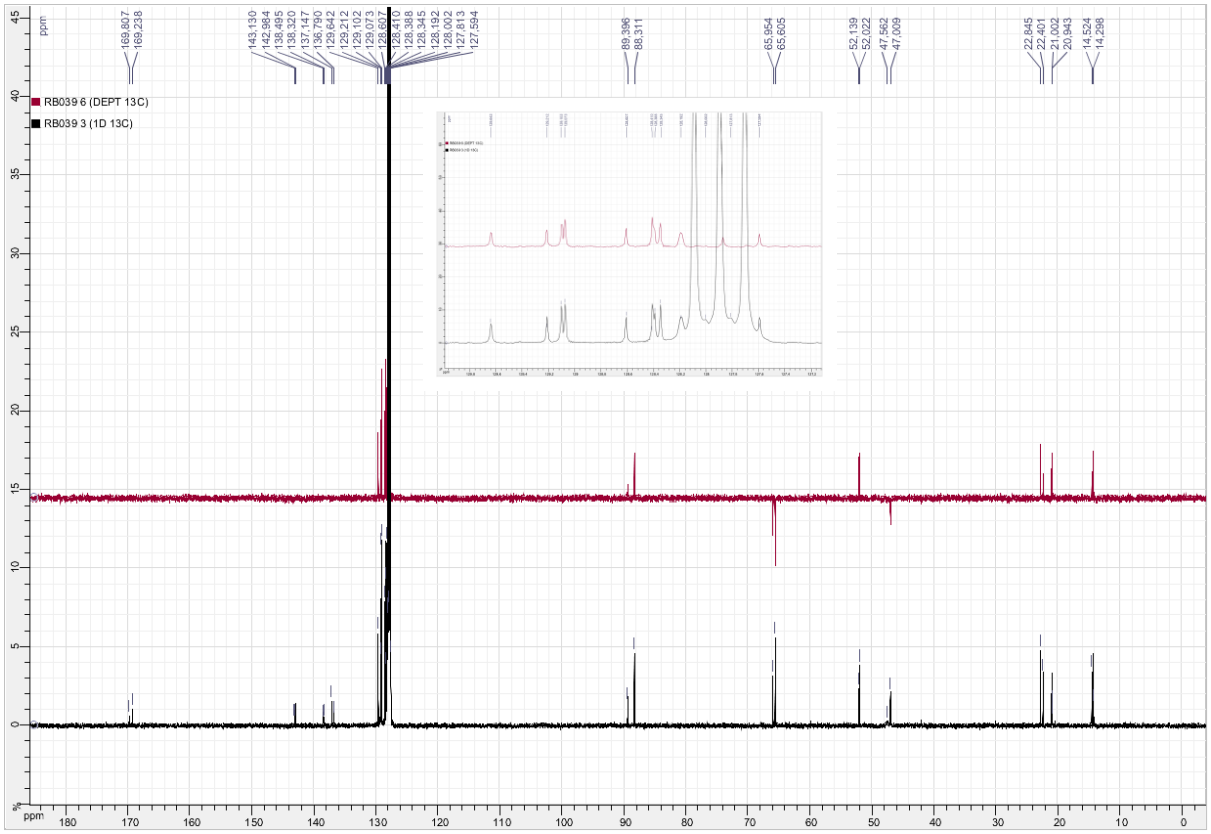
methyl (2*S**, 3*S**)-3-(*N*-allyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4m**



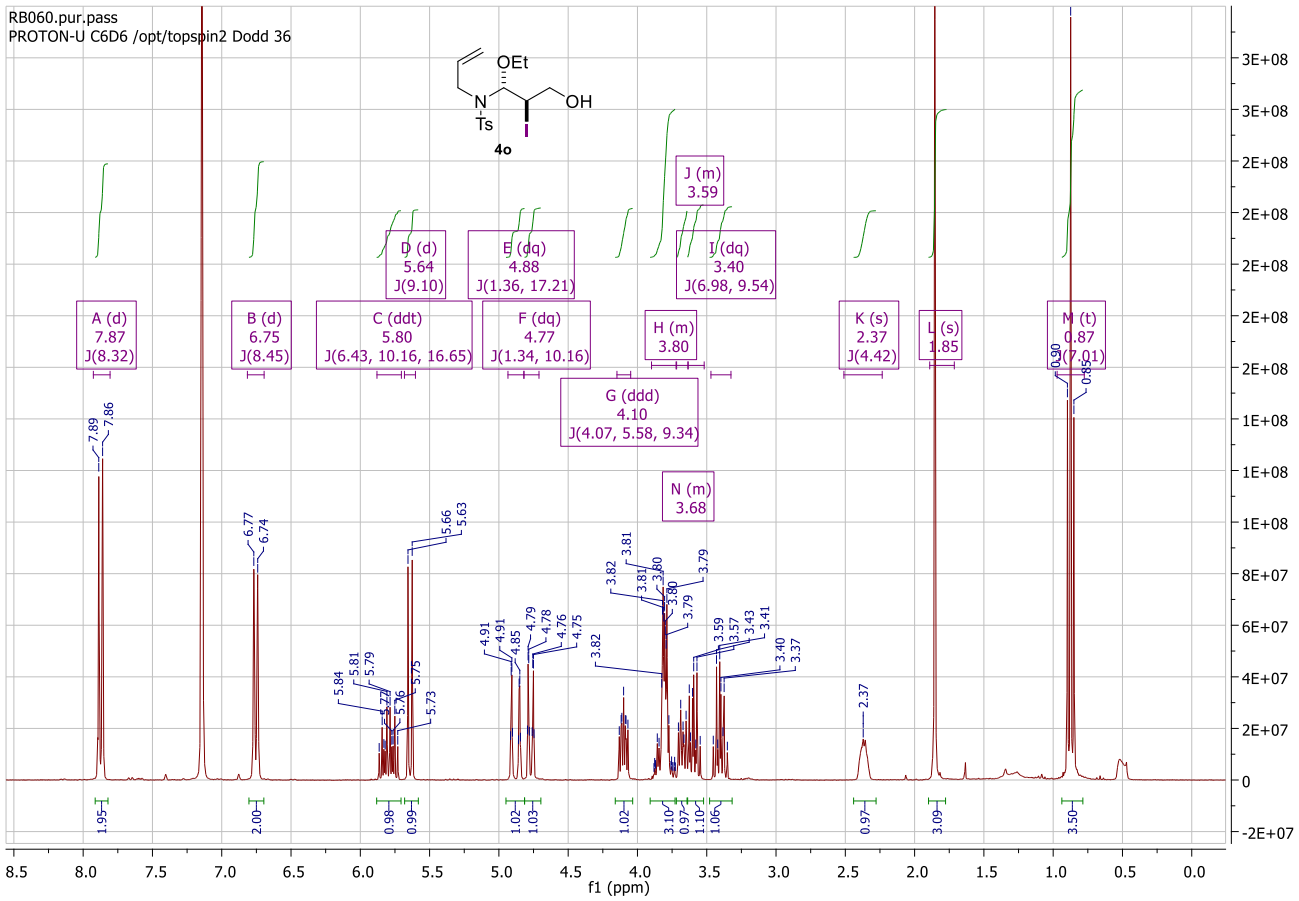


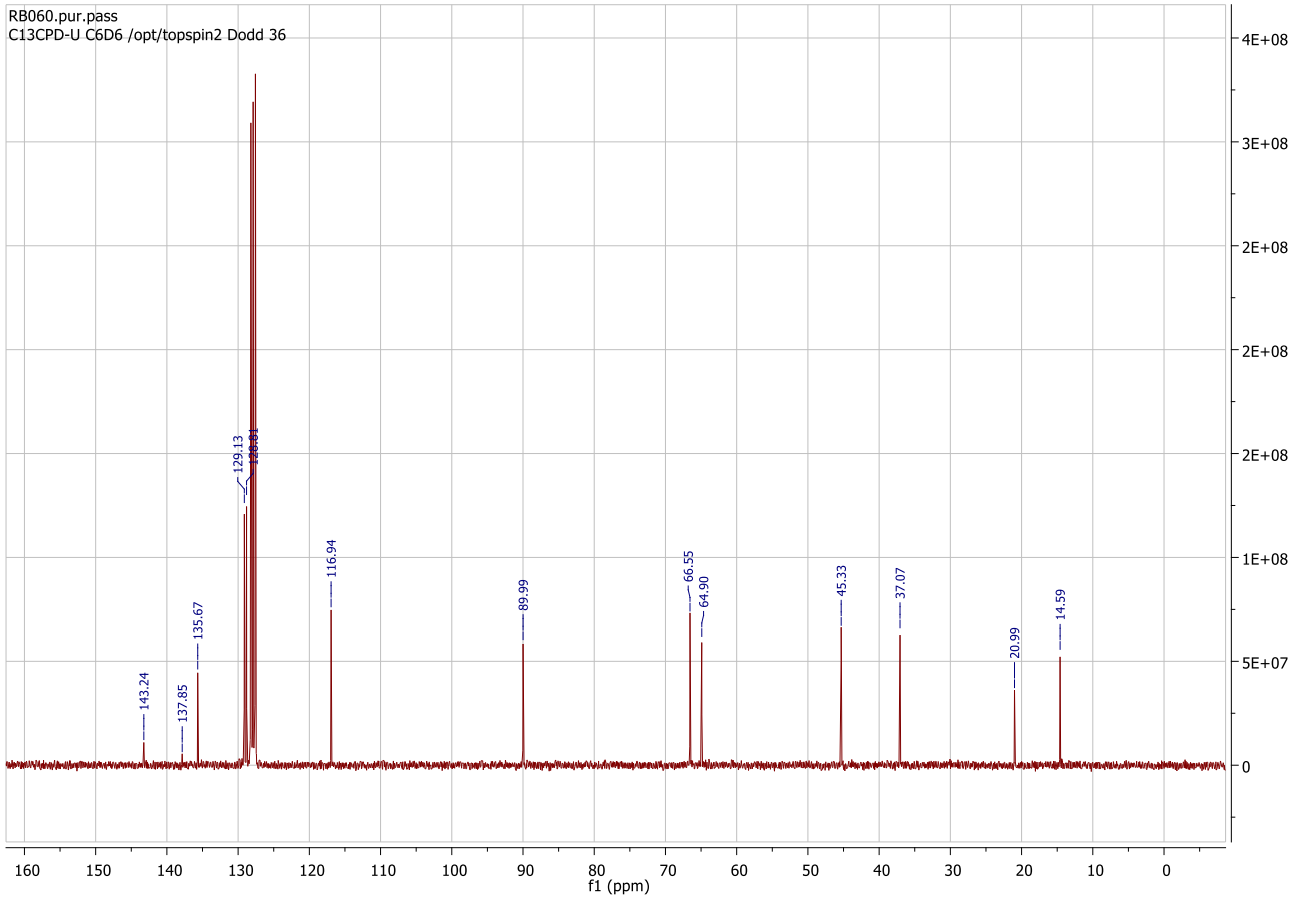
(2*S**, 3*S**)-methyl 3-(*N*-benzyl-4-methylphenylsulfonamido)-3-ethoxy-2-iodopropanoate **4n**



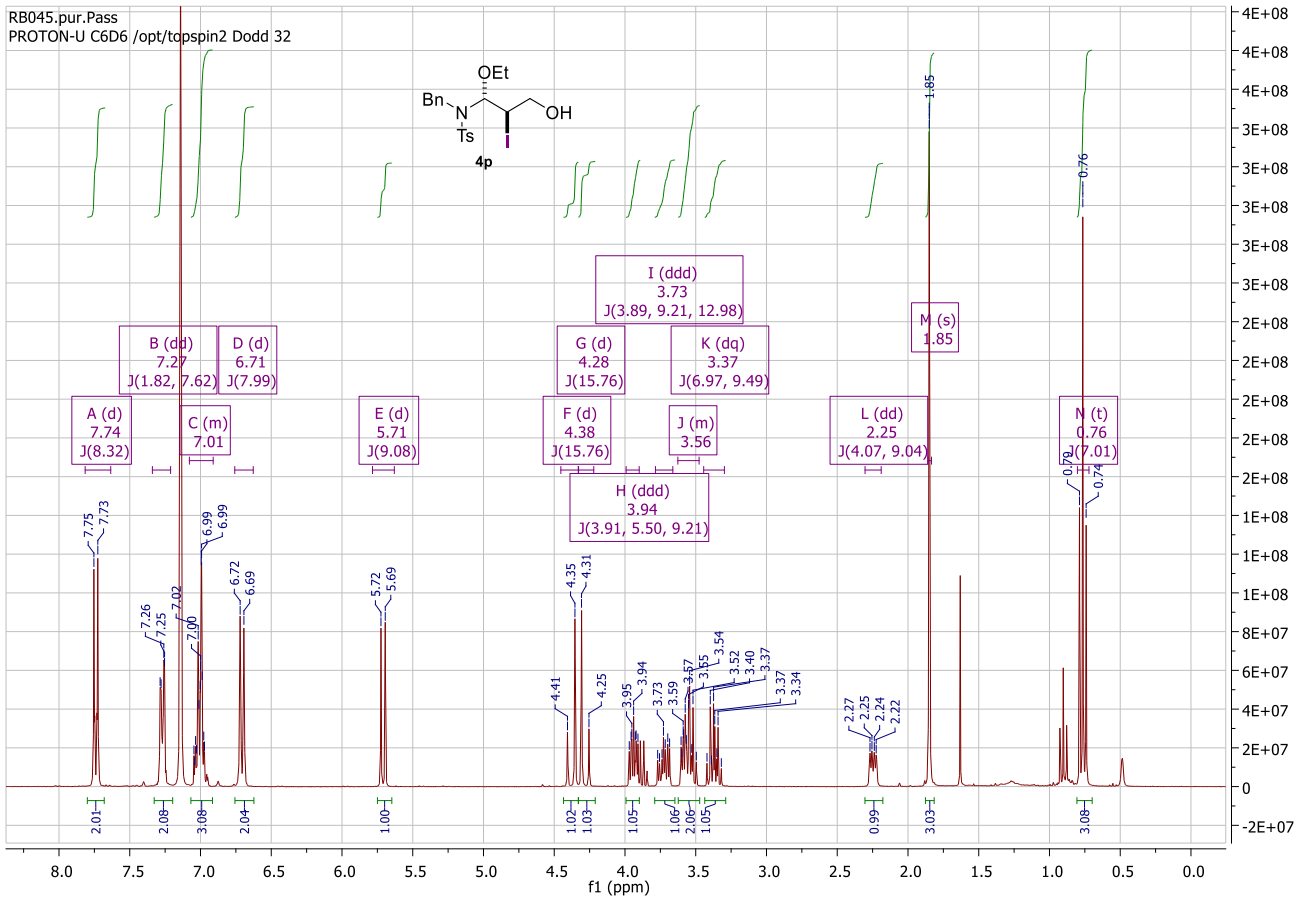


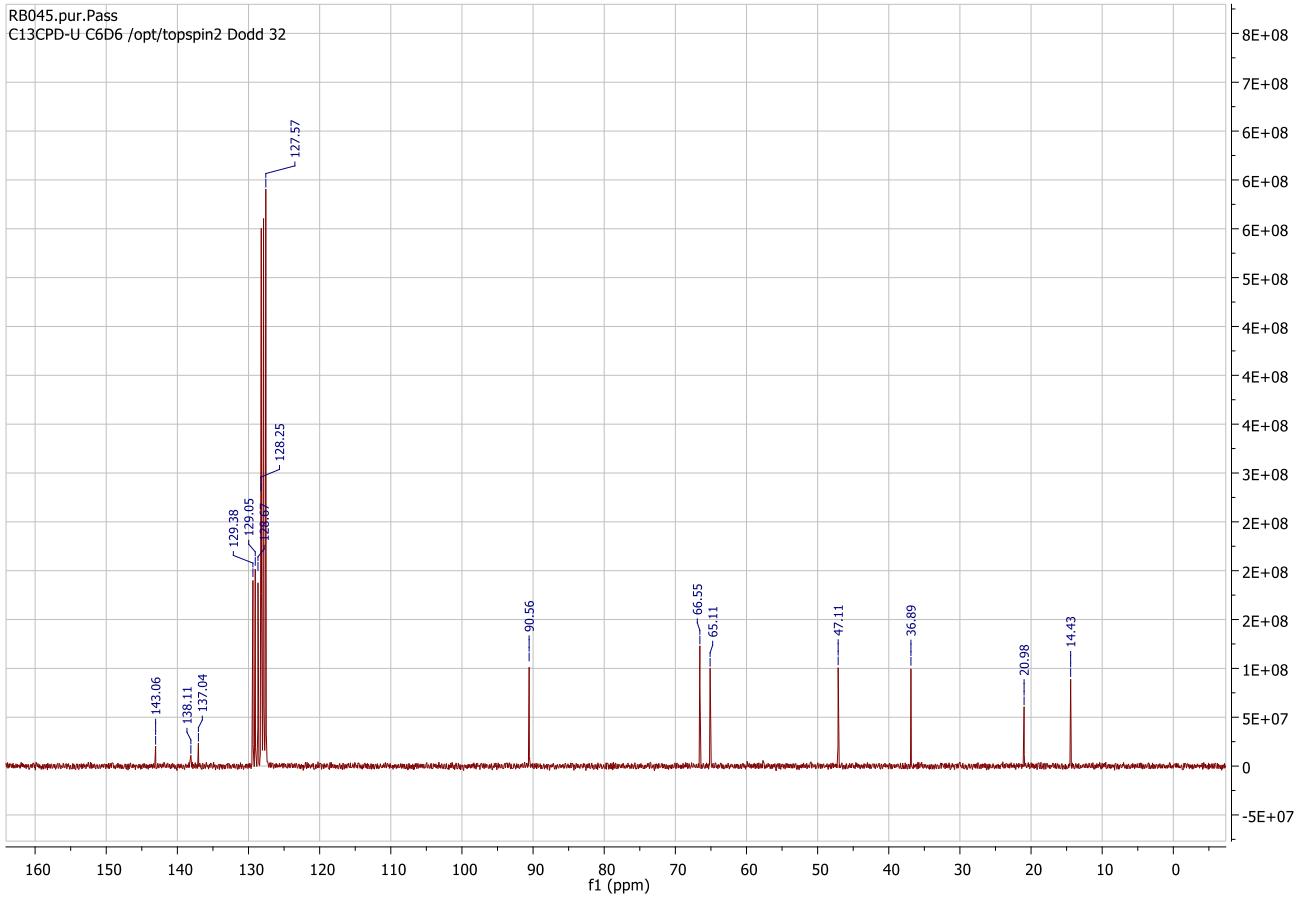
N-allyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-methylbenzenesulfonamide **4o**



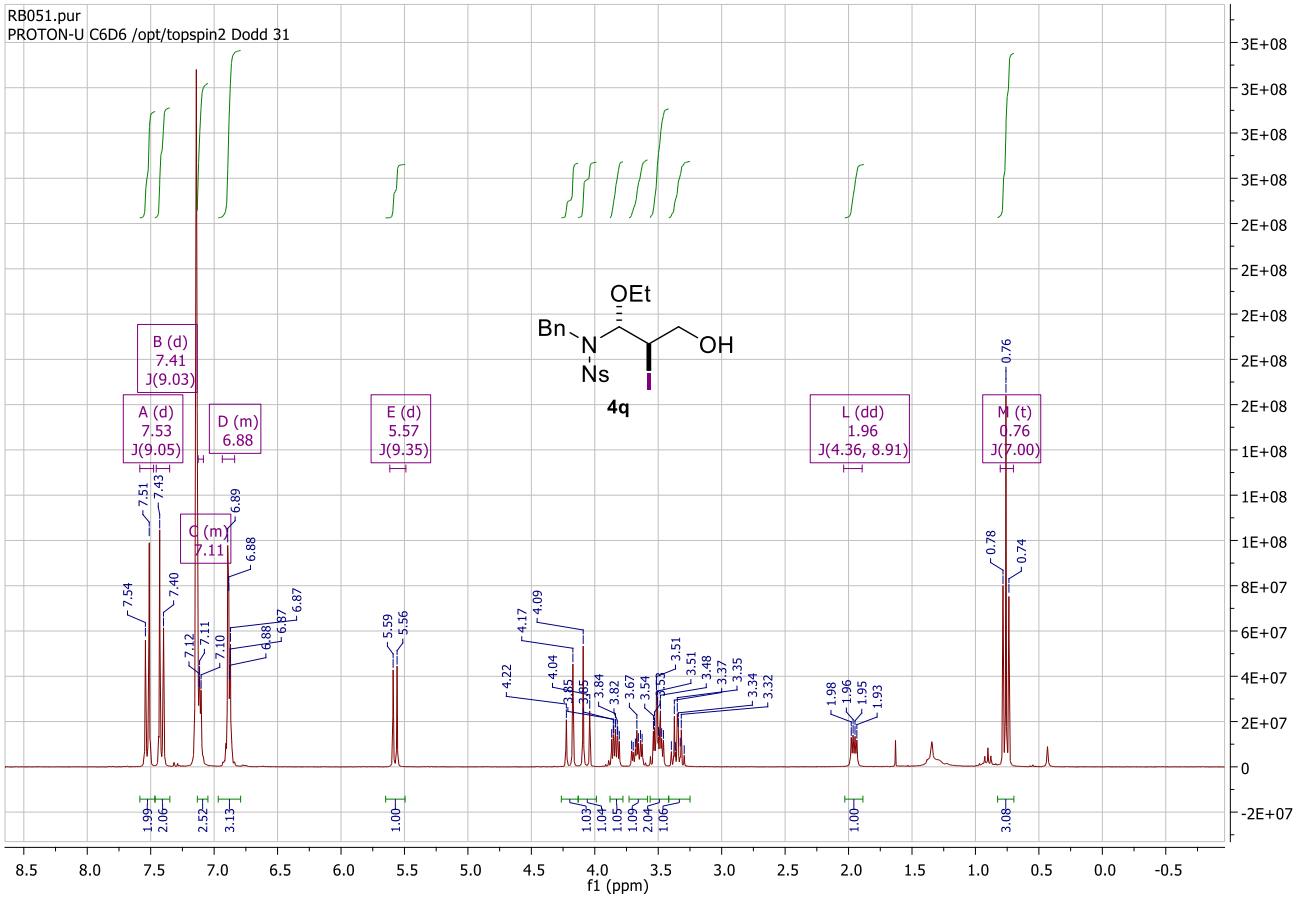


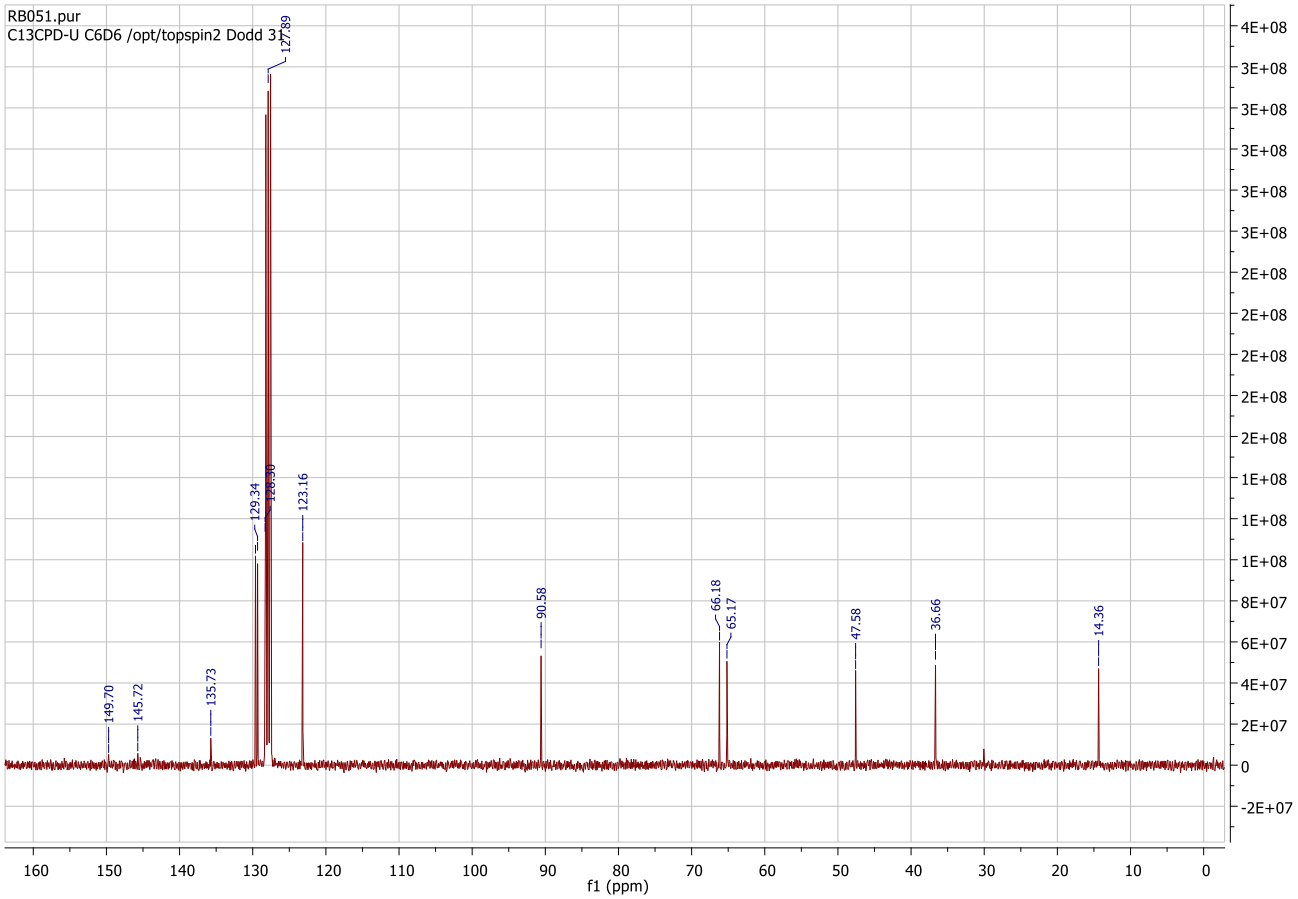
N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-methylbenzenesulfonamide **4p**



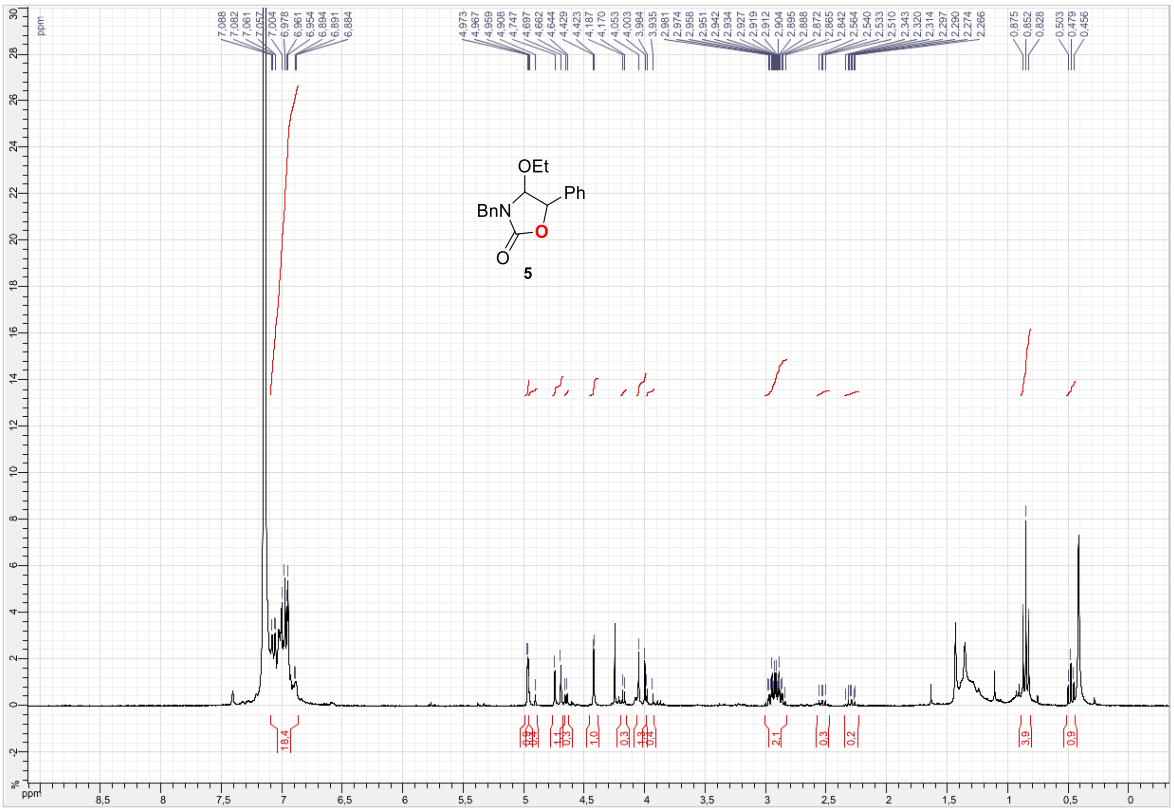


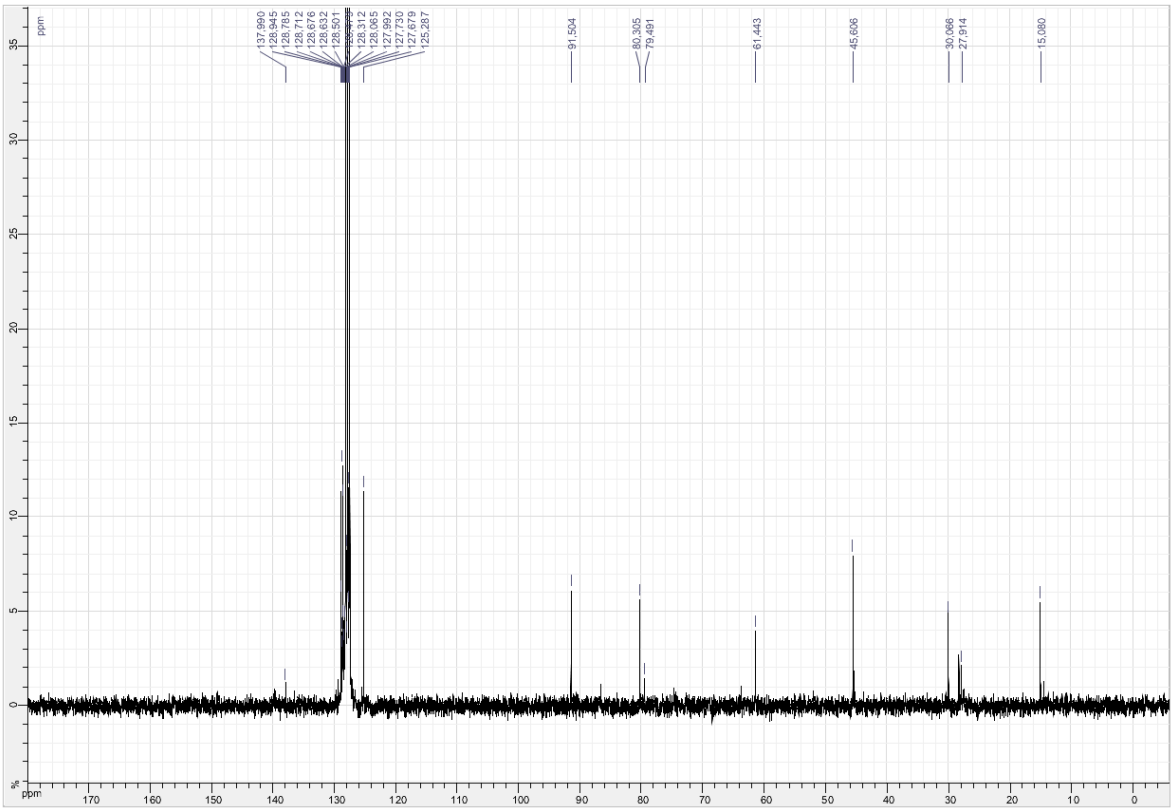
N-benzyl-*N*-((1*R**, 2*R**)-1-ethoxy-3-hydroxy-2-iodopropyl)-4-nitrobenzenesulfonamide **4q**



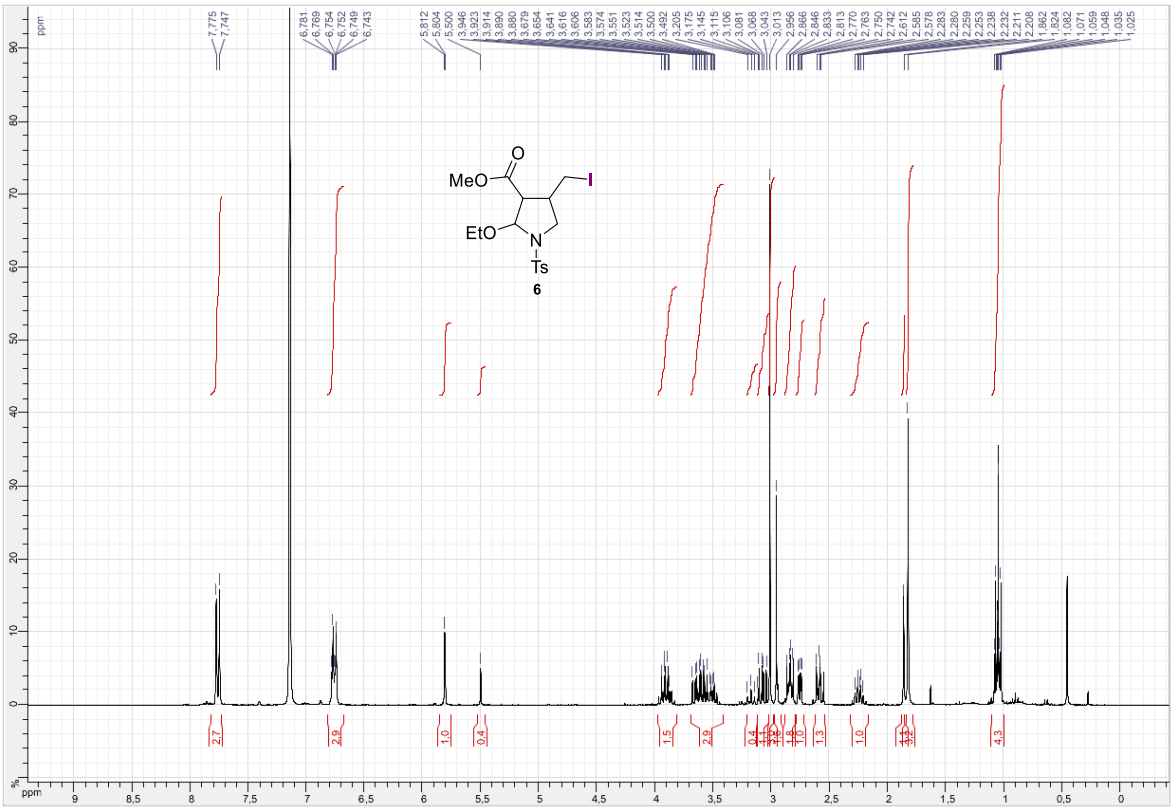


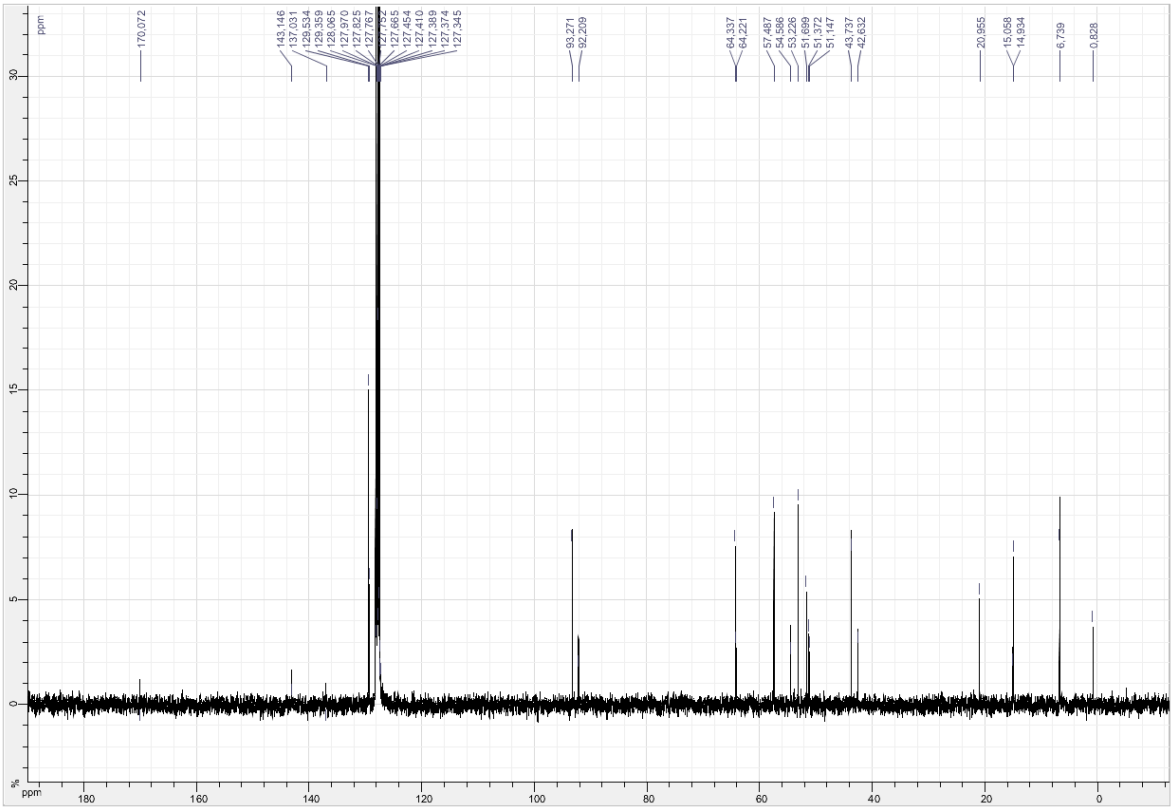
3-benzyl-4-ethoxy-5-phenyloxazolidin-2-one **5**



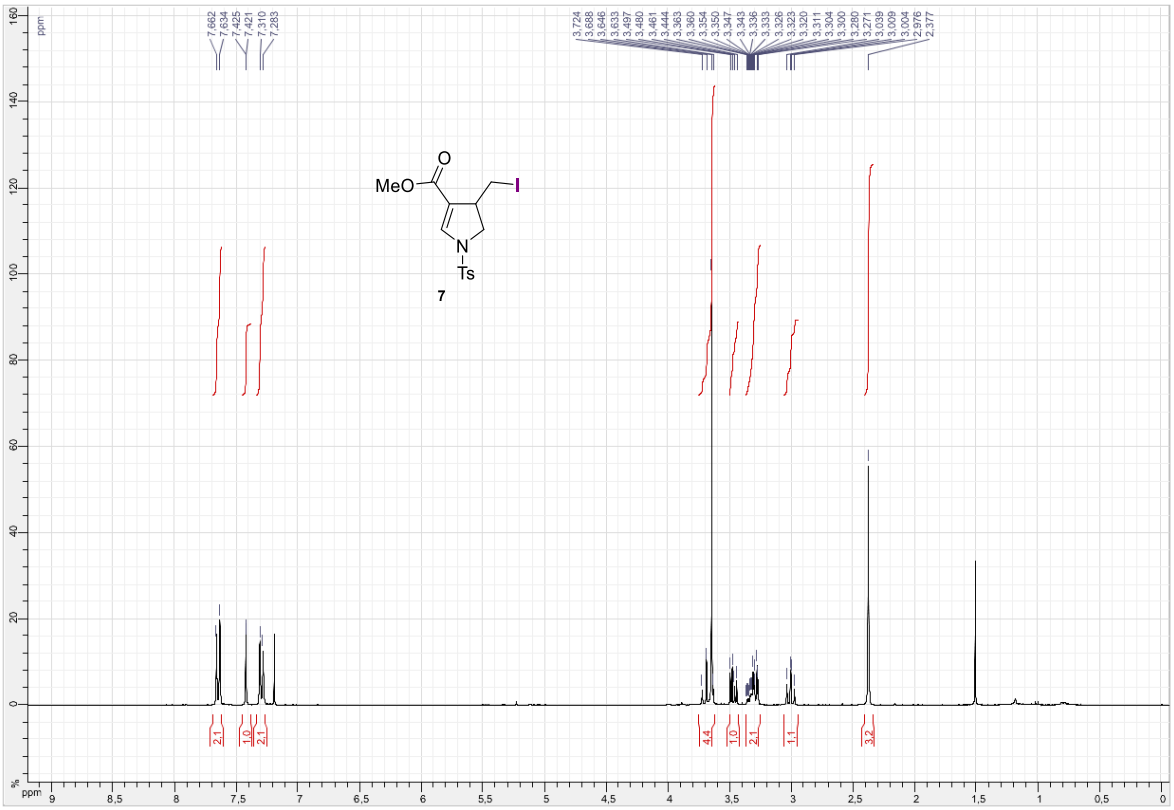


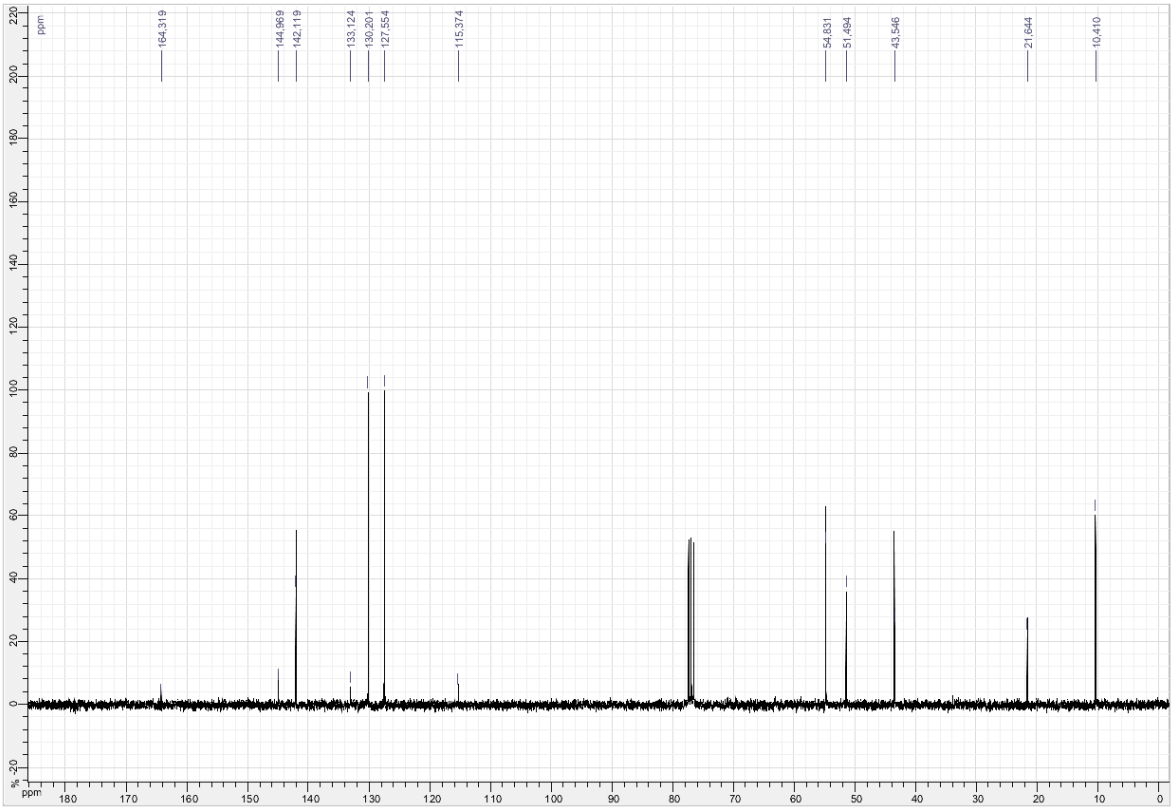
methyl 2-ethoxy-4-(iodomethyl)-1-tosylpyrrolidine-3-carboxylate **6**





methyl 4-(iodomethyl)-1-tosyl-4,5-dihydro-1H-pyrrole-3-carboxylate **7**





N-allyl-*N*-((*R**)-ethoxy((*S**)-oxiran-2-yl)methyl)-4-methylbenzenesulfonamide **8**