Enantioselective Hydroamination of Alkenes with Sulfonamides Enabled by Proton-Coupled Electron Transfer

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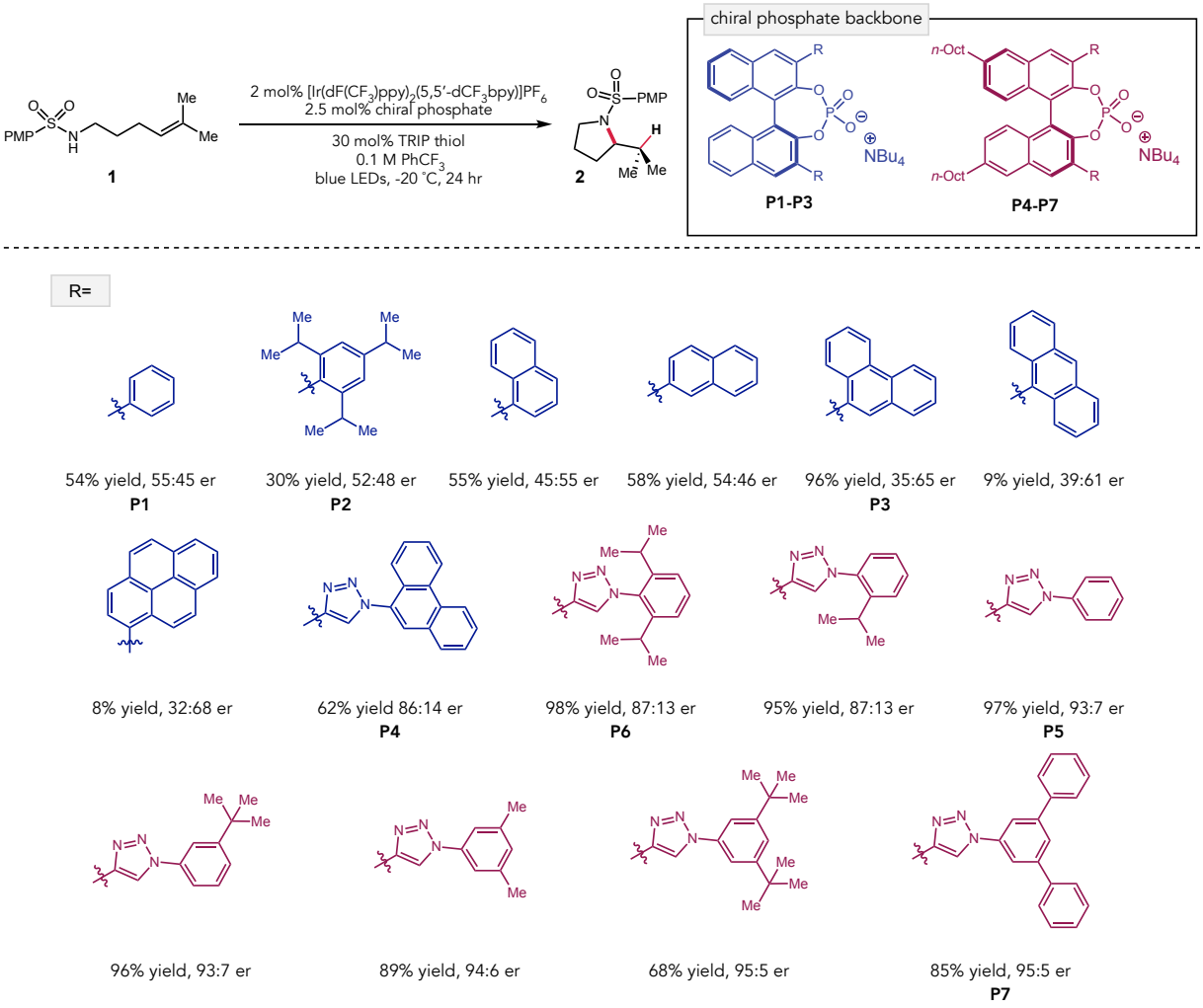
1. General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates containing indicator F-254. Visualization of the developed chromatogram was performed by irradiation with UV light and potassium permanganate stain. Normal-phase flash chromatography was performed using a Biotage Isolera One purification system equipped with a 10, 25, 50, or 100 g SNAP Ultra (HP Sphere, 25 μm silica) cartridge and an appropriate linear gradient in the mobile phase. Yields refer to purified compounds unless otherwise noted.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 500 (500, 126 and 203 MHz) instrument. The chemical shifts are calibrated by residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, hept = septet, m = multiplet, brs = broad singlet), coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift, and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Mass spectra of chiral phosphate bases and intermediates were obtained on Bruker UltraFlextreme MALDI TOF/TOF with 2,5-dihydroxybenzoic acid (DHB) matrix to assist ionization. The enantiomeric ratio (er) was determined by High-Performance Liquid Chromatography (HPLC) performed on an Agilent 1260 Infinity Series LC using commercial ChiralPak/ChiralCel columns from Daicel Chemical Industries, notably ChiralPak AD-H (5 μm particle size, 4.6 mm vs. 250 mm), ChiralCel OZ-H (5 μm particle size, 4.6 mm vs. 250 mm), and ChiralCel OD-H (5 μm particle size, 4.6 mm vs. 250 mm), ChiralCel AS-H (5 μm particle size, 4.6 mm vs. 250 mm), and ChiralCel OJ-H (5 μm particle size, 4.6 mm vs. 250 mm). Optical rotations were measured on a Jasco P-1010 polarimeter at the sodium D-line (589 nm) using a cell of 50 mm path length. The concentration values (c) are reported in g/100 mL.

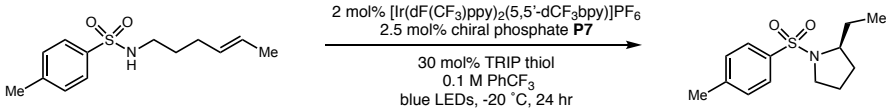
2. Optimization

Table S1: Evaluation of Chiral Phosphate Bases



Analytical reactions were run on 0.05 mmol scale. A stock solution was prepared in a 16x125mm culture tube with screw cap with substrate (0.05mmol/reaction, 1.0 equiv.) and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (0.001 mmol/reaction, 2 mol%). Phosphates (0.025 mmol/reaction, 2.5 mol%) were weighed into individual reaction vials. The vials were evacuated and refilled three times with nitrogen. Anhydrous triflourotoluene from a sure-seal bottle (0.1 M) was added to the stock solution and 0.5 mL of the stock solution was transferred to each reaction vial containing phosphate. Then 2,4,6-triisopropylbenzene thiol (0.15 mmol, 30 mol%, 35.5 mg) was added to each reaction vial. The reactions were then stirred for 24 hours under irradiation with blue LED strips at -20 ˚C. The samples were then concentrated, dissolved in 1 mL of stock solution containing trimethoxybenzene (internal standard) in $CDCl_3$ (0.05 M). Yields were determined by quantitative proton NMR integrating against internal standard. Samples were purified by preparatory TLC and enrichment was determined by HPLC on a chiral stationary phase.

Table S2: Disubstituted Olefin Optimization



Entry	Temperature	HAT catalyst	chiral phosphate	Yield (%)	e.r.
1	-20 ˚C	TRIP-thiol	P7	<5	95:5
2	0 ˚C	TRIP-thiol	P7	8	96:4
3	0 ˚C	TRIP-disulfide	P7	42	95:5
4	0 ˚C	TRIP-disulfide	P15	36	93:7
5	0 ˚C	TRIP-disulfide	P5	21	84:16

Entries 1 and 2:

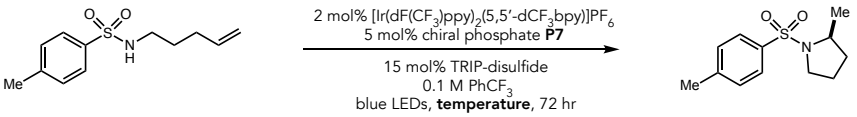
Analytical reactions were run on 0.05 mmol scale. A stock solution was prepared in a 16x125mm culture tube with screw cap with substrate (0.05mmol/reaction, 1.0 equiv.) and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)]PF_6$ (0.001 mmol/reaction, 2 mol%) and P7 (0.025 mmol/reaction). Vials were evacuated and refilled three times with nitrogen. Anhydrous, degassed triflourotoluene (0.1 M) was added to the stock solution and 0.5 mL of the stock solution was transferred to two reaction vials under inert atmosphere nitrogen. Then 2,4,6-triisopropylbenzene thiol (0.15 mmol, 30 mol%, 3.5 mg) was added to each reaction vial. The reactions were then stirred for 24 hours under irradiation with blue LED strips at the indicated temperature. The samples were then concentrated, dissolved in 1 mL of stock solution containing trimethoxybenzene (internal standard) in $CDCl_3$ (0.05 M). Yields were determined by quantitative proton NMR. Samples were purified by preparatory TLC and enrichment was determined by HPLC on a chiral stationary phase.

Entries 3 – 5:

Analytical reactions were run on 0.05 mmol scale. A stock solution was prepared in a 16x125mm culture tube with screw cap with substrate (0.05mmol/reaction, 1.0 equiv.), TRIP-disulfide (0.075 mmol/reaction, 15 mol%) and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(d(CF_3)\text{-}bpy)]PF_6$ (0.001 mmol/reaction, 2 mol%). Phosphates (0.025mmol/reaction, 2.5 mol%) were weighed into individual reaction vials. The vials were evacuated and refilled three times with nitrogen. Anhydrous, degassed triflourotoluene (0.1 M) was added to the stock solution and 0.5 mL of the stock solution was transferred to each reaction vial containing phosphate. The reactions were then stirred for 24 hours under irradiation with blue LED strips at 0 ˚C. The samples were then concentrated, dissolved in 1 mL of stock solution containing trimethoxybenzene (internal standard) in $CDCl_3$ (0.05 M). Yields were determined by quantitative proton NMR. Samples were purified by preparatory TLC and enrichment was determined by HPLC on a chiral stationary phase.

Table S3: Terminal olefins

Terminal olefins reacted efficiently under the conditions previously reported,[3] however under the conditions reported here we observed no reactivity for these substrates at 0 ˚C, and 7% yield after irradiation with blue LEDs at room temperature for 72 hours with low levels of enantioselectivity

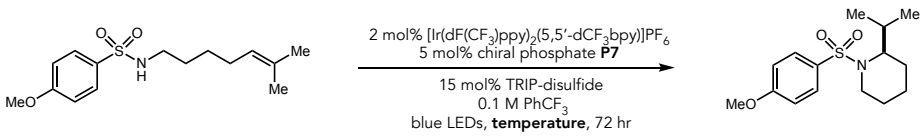


Entry	Temperature	Yield (%)	er
1	0 ˚C	<1	-
2	room temperature	7% yield	56:44

Reactions were run at 0.05 mmol scale, yield was determined by ^{1}H NMR relative to trimethoxybenzene internal standard which was added after the reaction. Enantiomeric ratio was determined by HPLC on a chiral stationary phase.

Table S4: 6-exo cyclization substrate

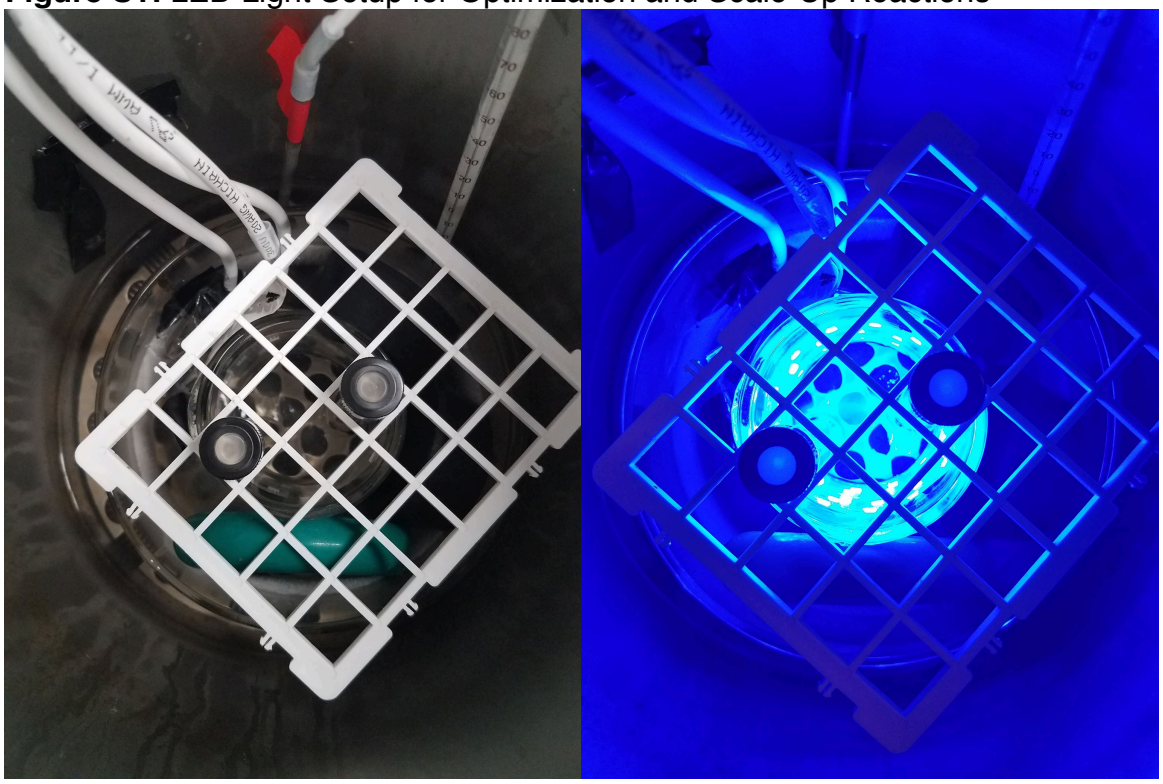
A substrate which could undergo 6-exo cyclization to furnish a chiral piperadine product provided trace reactivity at 0 ˚C, and provided the product in 10% yield after irradiation with blue LEDs at room temperature for 72 hours with low levels of enantioselectivity.



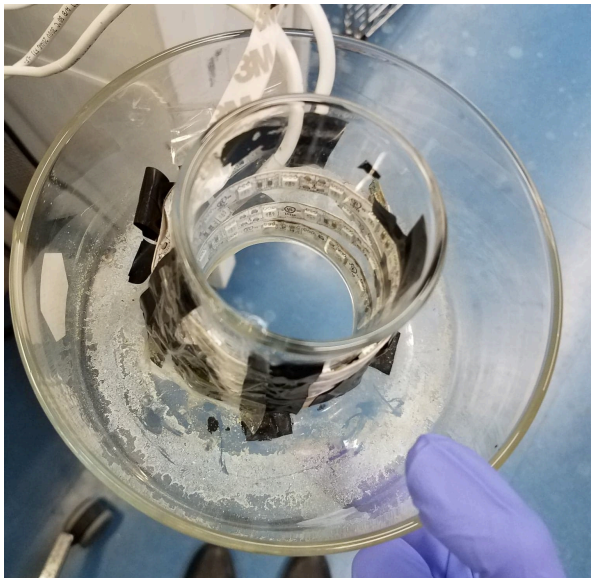
Entry	Temperature	Yield (%)	er
1	0 ˚C	<1	-
2	room temperature	10% yield	53:47

Reactions were run at 0.05 mmol scale, yield was determined by ^{1}H NMR relative to trimethoxybenzene internal standard which was added after the reaction. Enantiomeric ratio was determined by HPLC on a chiral stationary phase.

Figure S1: LED Light Setup for Optimization and Scale-Up Reactions



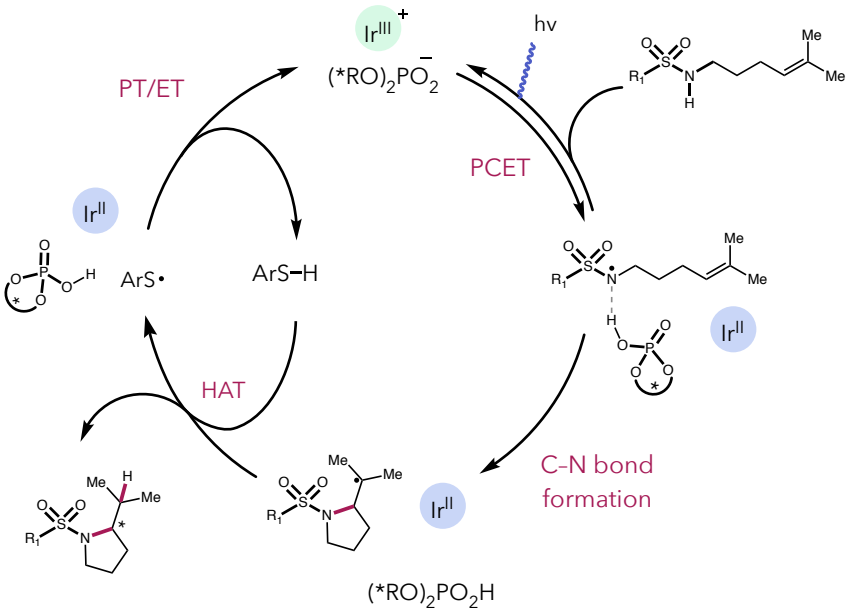
Low temperature reactions were run in a liquid submersible light set up in a cryocool for optimal temperature control. This setup was constructed from a 300 mL beaker and crystallizing dish fused together with an open bottom to allow reactions to be effectively cooled by the cryocool bath. LED strips were wrapped around the outside of the inner beaker. This allows the reactions to be submerged in the acetone bath for efficient cooling, while protecting the LED strips and associated power source from coming in contact with the solvent.



Reactions were placed in a plastic grid such that they were approximately 0.5 cm away from the light source. Up to 6 reactions could run at a time with no effect on selectivity or yield.

3. Proposed Catalytic Cycle

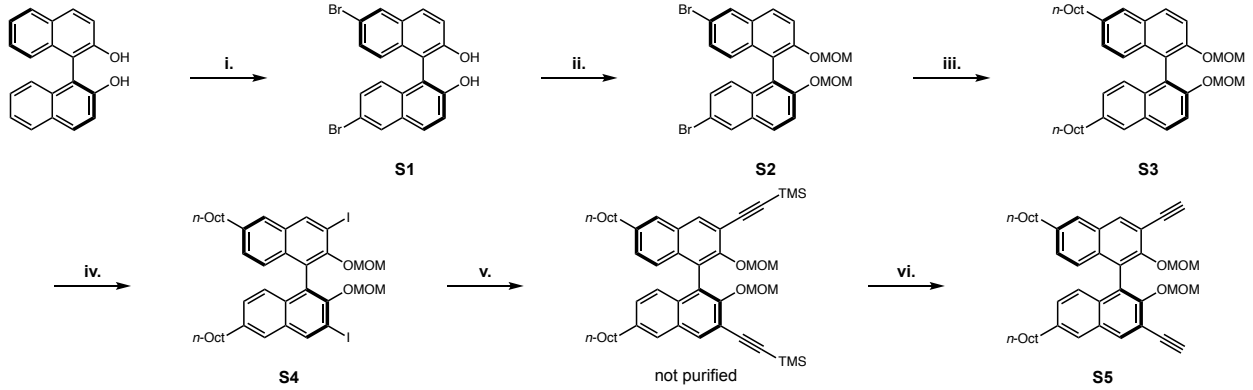
Figure S2: Proposed Catalytic Cycle



4. Synthesis of Catalysts

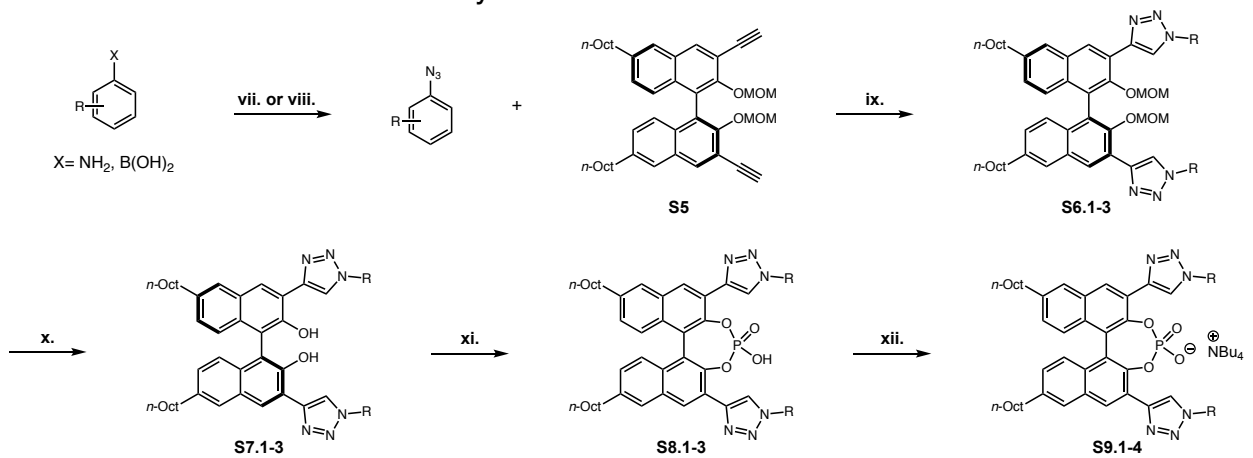
$[Ir(dF(CF_3)ppy)_2(5,5'\text{-}CF_3bpy)]PF_6$ photocatalyst.[3] TRIP-thiophenol,[4] and TRIP-disulfide[5] were synthesized according to literature precedent. 1,2,3-Triazole-containing chiral phosphate bases (**P4–P7**) were synthesized as described below.

Scheme S1: Synthesis of Alkyne Precursor



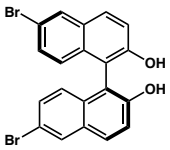
i.) Br_2 (2.7 equiv), DCM, –78 ˚C–rt **ii.)** NaH (2.3 equiv), THF, 0 ˚C, then MOM-Cl, 0 ˚C to rt **iii.)** *n-OctMgBr* (5 equiv), $Pd(dppf)Cl_2$ (4 mol%), THF, 0˚C–55˚C **iv.)** *n*-BuLi (3.5 equiv), THF, –78˚C–0˚C, then I_2 (3.7 equiv), –78 ˚C–rt **v.)** $Pd(PPh)_3Cl_2$ (5 mol%), Cu(I)Br (40 mol%), TMS-acetylene (3.1 equiv), NEt_3/Tol, 50˚C **vi.)** K_2CO_3 (10 equiv), MeOH:DCM

Scheme S2: Derivatization of Alkyne Precursor



vii.) for anilines: *t*-BuONO (3.0 equiv), $TMSN_3$ (1.12 equiv), MeCN **viii)** for boronic acids NaN_3 (3 equiv), $CuSO_4$ (30 mol%), MeOH **ix.)** CuI (1 equiv), DIPEA (2 equiv), acetonitrile, rt **x.)** conc. HCl (100 equiv), dioxane, rt **xi.)** $POCl_3$ (2 equiv), H_2O (5 mL), Pyridine, 90 ˚C–100 ˚C **xii.)** NBu_4OH, DCM/MeOH

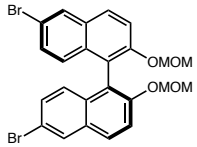
(*S*)-6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol (**S1**)



An oven-dried 2-neck, 1 L round bottom flask was charged with (*S*)-[1,1'-binaphthalene]-2,2'-diol (20.0 g, 69.9 mmol, 1.00 equiv) and dichloromethane (400 mL, 0.17 M), fitted with an addition funnel, and cooled to –78 ˚C, at which point a base bubbler was attached. The addition funnel was then charged with a solution of Br_2 (9.72 mL, 189 mmol, 2.70 equiv) in dichloromethane (100 mL), which was then added dropwise to the round bottom flask. After stirring at –78 ˚C for 2 h, the reaction was warmed to room temperature for an additional 3 h. The reaction was quenched by careful addition of a saturated solution of aqueous $Na_2S_2O_3$ at 0 ˚C while stirring vigorously until the solution was colorless. The biphasic solution was then transferred to a separatory funnel, and the organic layer was washed with brine. The aqueous layers were back-extracted 2x with dichloromethane, and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated to afford the title compound in 97% yield (30.06 g, 67.6 mmol) as a grey solid. The product was carried through to the next step without further purification. The ^{1}H NMR data for this compound matched the spectrum previously reported in the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 2.0 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H) 7.39 (d, *J* = 9.1 Hz, 2H), 7.37 (dd, *J* = 8.7, 1.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H) ppm.

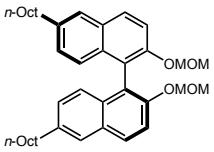
(*S*)-6,6'-dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (**S2**)



An oven-dried 500 mL round bottom flask was charged with a 60% mineral oil suspension of NaH (3.74 g, 156 mmol, 2.30 equiv), which was subsequently suspended in dry THF (100 mL, 1.5 M) under an atmophsere of nitrogen. A solution of **S1** (30.1g, 67.7 mmol, 1.00 equiv) in dry THF (100 mL, 0.7 M) was added dropwise *via* cannula to the vigorously stirring NaH suspension at 0 ºC. After stirring for 2 h at 0 ˚C, chloromethyl methyl ether (11.82 mL, 156 mmol, 2.30 equiv) was added dropwise, and the solution was allowed to warm to rt overnight. The reaction was quenched with a solution of saturated aqueous NH_4Cl, and the THF was removed carefully *in vacuo*. The remaining contents of the round bottom flask were transferred to a separatory funnel and extracted 3x with dichloromethane. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated. The crude material was purified by recrystallization from hexanes and dichloromethane to afford the title compound in 95% yield (34.2g, 64.3 mmol). The ^{1}H NMR data for this compound matched the spectrum previously reported in the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 1.8 Hz, 2H), 7.86 (d, *J* = 9.1 Hz, 2H), 7.59 (d, *J* = 9.1 Hz, 2H), 7.29 (dd, *J* = 9.0, 1.9 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 5.09 (d, *J* = 6.9 Hz, 2H), 4.98 (d, *J* = 6.9 Hz, 2H), 3.16 (s, 6H).

(*S*)-2,2'-bis(methoxymethoxy)-6,6'-dioctyl-1,1'-binaphthalene (**S3**)

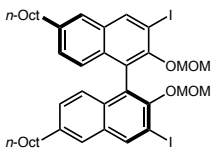


An oven-dried 1 L round-bottom flask was charged with **S2** (15.0 g, 28.2 mmol, 1 equiv) and Pd(dppf)Cl_2 · DCM (921 mg, 1.13 mmol, 4 mol%), and dry THF (400 mL) under a nitrogen atmosphere. The resulting solution was cooled to 0 °C over an ice bath. A solution of octylmagnesium bromide (2.0 M in Et_2O, 70.5 mL, 141 mmol, 5.0 equiv) was added dropwise to the vigorously stirring solution. After addition of the Grignard solution, the reaction was warmed to 55 °C and stirred overnight. The reaction was quenched by careful addition of saturated aqueous NH_4Cl solution. The excess THF was removed in vacuo and the aqueous phase was extracted 3x with EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude mixture was purified *via* silica gel column chromatography eluting with 10% EtOAc in hexanes, affording the title compound in 57% yield (9.57 g, 15.9 mmol) as an orange/yellow oil. The ^{1}H and ^{13}C NMR data for this compound matched the spectrum previously reported in the literature.[8]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.63 (s, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 1.5 Hz, 4H), 5.00 (dd, *J* = 50.9, 6.8 Hz, 4H), 3.13 (s, 6H), 2.73–2.65 (m, 4H), 1.69–1.60 (m, 4H), 1.37–1.19 (m, 20H), 0.87 (t, *J* = 6.9 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.2, 138.7, 132.6, 130.2, 128.9, 128.1, 126.3, 125.7, 121.7, 117.7, 95.6, 55.9, 36.0, 32.0, 31.4, 29.6, 29.5, 29.4, 22.8, 14.3 ppm.

(*S*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-6,6'-dioctyl-1,1'-binaphthalene (**S4**)

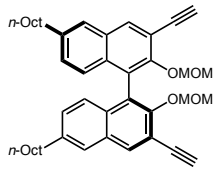


An oven-dried, 1 L round bottom flask was charged with **S3** (9.57 g, 16.0 mmol) and 320 mL (0.05 M) dry THF under a nitrogen atmosphere. The flask was cooled to –78 °C, and a solution of n-BuLi (2.5 M in hexanes, 22.4 mL, 55.9 mmol, 3.50 equiv) was added dropwise to the vigorously stirring solution. The reaction was brought to 0 ˚C for 2 h. The mixture was cooled again to –78 °C, and molecular I_2 (15.0 g, 59.1 mmol, 3.70 equiv) was added quickly in one portion. The mixture was allowed to warm to room temperature overnight, after which it was quenched by the careful addition of saturated aqueous $Na_2S_2O_3$ solution and stirring for an additional 30 min. The organic solvent was removed *in vacuo*, and the aqueous layer was extracted 3x with EtOAc. The combined organics were washed with brine, dried with Na_2SO_4, filtered, and concentrated on Celite®. The crude mixture was purified *via* silica gel column chromatography eluting with 2.5% Et_2O in hexanes, to afford the title compound in 79% yield (10.74 g, 12.6 mmol) as a yellow oil. The ^{1}H NMR data for this compound matched the spectrum previously reported in the literature.[9]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (s, 2H), 7.52 (s, 2H), 7.14 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 4.73 (dd, *J* = 58.0, 5.6 Hz, 4H), 2.77–2.66 (m, 4H), 2.59 (s, 6H), 1.66 (q, *J* = 7.4 Hz, 4H), 1.39–1.21 (m, 20H), 0.92–0.85 (m, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.5, 140.7, 139.5, 132.6, 132.4, 128.9, 126.5, 126.4, 125.1, 99.5, 92.4, 56.7, 36.0, 32.0, 31.2, 29.6, 29.5, 29.4, 22.8, 14.3 ppm.

(*S*)-3,3'-diethynyl-2,2'-bis(methoxymethoxy)-6,6'-dioctyl-1,1'-binaphthalene (**S5**)



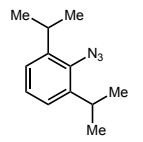
An oven-dried 100 mL round bottom flask was charged with **S4** (10.73 g, 12.6 mmol), $Pd(PPh_3)_2Cl_2$ (443 mg, 0.63 mmol, 5 mol%), and CuBr (724 mg, 5.05 mmol, 40 mol%). Toluene (32 mL, 0.5 M) was added to the flask, followed by Et_3N (32 mL, 0.5 M), and the mixture was degassed by sparging with nitrogen for 5 min. Trimethylsilylacetylene (5.50 mL, 39.4 mmol, 3.10 equiv) was added, and the reaction was stirred overnight at 50 ˚C. The resulting black suspension was filtered over Celite, and concentrated. A 9:1 mixture of MeOH/dichloromethane (160 mL) and K_2CO_3 (17.4 g, 126 mmol, 10.0 equiv) were added to the dark brown residue, which was vigorously stirred for 2 hrs. The solids were removed by filtration through Celite, and the filtrate was concentrated and partitioned between Et_2O and water. The aqueous phase was extracted 3x with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified *via* silica gel column chromatography eluting with a 9:1 mixture of hexanes/Et_2O. After column chromatography, the title compound was obtained in 62% yield (5.02 g, 7.76 mmol) as a sticky red/brown oil. The ^1H and ^{13}C NMR data for this compound matched the spectrum previously reported in the literature.**Error! Bookmark not defined.**

^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 2H), 7.60 (s, 2H), 7.23–7.11 (m, 4H), 4.98 (dd, *J* = 96.6, 6.0 Hz, 4H), 3.33 (s, 2H), 2.73 (t, *J* = 7.7 Hz, 4H), 2.55 (s, 6H), 1.68 (t, *J* = 7.5 Hz, 4H), 1.42–1.25 (m, 20H), 0.90 (m, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.4, 140.1, 134.5, 132.2, 130.2, 129.0, 126.2, 125.7, 125.6, 115.9, 98.6, 81.3, 80.6, 55.8, 35.6, 31.7, 31.0, 29.3, 29.2, 29.1, 22.5, 13.9 ppm.

Representative Azide Procedure 1:

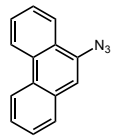
2-azido-1,3-diisopropylbenzene



An oven-dried 10 mL round bottom flask was charged with 2,6-diisopropylaniline (1.15 g, 6.48 mmol, 1.00 equiv) and MeCN (3.8 mL, 1.6 M) at 0 ˚C. Next, *tert*-butyl nitrite (2.31 mL, 19.44 mmol, 3.00 equiv) was added in one portion and the mixture was stirred for a few minutes, followed by dropwise addition of $TMSN_3$ (0.864 mL, 6.54 mmol, 1.01 equiv). The reaction mixture was stirred for 1 h at room temperature, diluted with Et_2O, and transferred to a separatory funnel. The organic layer was washed with an aqueous Na_2CO_3 solution, dried over $MgSO_4$, and filtered through a silica plug eluting with Et_2O. The filtrate was concentrated, and the resulting azide product was used without further purification.

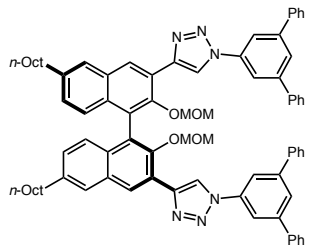
Representative Azide Procedure 2:

Phenanthren-9-azide



An oven-dried round bottom flask was charged with NaN_3 (421 mg, 6.48 mmol, 3.00 equiv), phenanthren-9-ylboronic acid (479 mg, 2.16 mmol, 1.00 equiv), and MeOH (21 mL, 0.10 M). $CuSO_4$ (103.43 mg, 0.648 mmol, 30 mol%) was added next, and the reaction mixture was allowed to stir at room temperature for 48 h. Upon consumption of the boronic acid (monitored by TLC), the reaction mixture was partitioned between a saturated aqueous solution of Na_2CO_3 and Et_2O. The organic layer was washed with saturated aqueous NH_4Cl solution, dried with Na_2SO_4, and passed through a plug of silica gel eluting with Et_2O. The filtrate was concentrated, and the resulting azide product was used without further purification. Phenanthren-9-azide and 5'-azido-1,1':3',1''-terphenyl were prepared by this procedure.

(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazole) (**S6.1**)



A 250 mL round-bottom flask was charged sequentially with **S5** (2.92 g, 4.52 mmol, 1 equiv), DIPEA (15.0 mL, 90.0 mmol, 20.0 equiv), MeCN (70 mL, 0.06 M), and 5'-azido-1,1':3',1''-terphenyl (3.65 g, 13.5 mmol, 3.00 equiv, prepared by **Representative Azide Procedure 1**). After stirring for 5 min at rt, CuI (854 mg, 4.48 mmol, 1.00 equiv) was added. The reaction mixture was stirred at room temperature overnight, after which it was diluted with ether (100 mL) and filtered through a Celite plug. The filtrate was washed with saturated aqueous NH_4Cl solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification on silica gel column chromatography using hexanes/EtOAc 80:20 afforded 3.279 g (62%, 4.48 mmol) of the title compound as a yellow oil. *Note: The reaction mixture tends to form aggregates initially, but typically transitions to a homogeneous system toward completion.* This procedure serves as a **Representative Click Procedure** in the synthesis of the other catalyst derivatives.

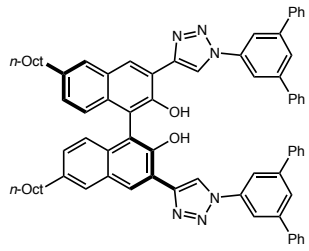
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.99 (s, 2H), 8.93 (s, 2H), 8.02 (d, *J* = 1.6 Hz, 4H), 7.87 (t, *J* = 1.6 Hz, 2H), 7.82 (s, 2H), 7.73–7.67 (m, 8H), 7.53–7.44 (m, 8H), 7.46–7.38 (m, 4H), 7.24–7.16 (m, 4H), 4.67 (d, *J* = 5.1 Hz, 2H), 4.44 (d, *J* = 5.0 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 4H), 2.72 (s, 6H), 1.71 (t, *J* = 7.5 Hz, 4H), 1.41–1.20 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): 149.3, 144.4, 143.8, 140.6, 139.9, 138.2, 132.5, 131.4, 129.3, 129.2, 129.1, 128.4, 127.5, 127.2, 126.4, 126.1, 126.0, 123.9, 121.5, 118.1, 99.1, 57.3, 36.0, 32.0, 31.3, 29.6, 29.6, 29.4, 22.8, 14.3 ppm.

HRMS: exact mass calculated for $[C_{80}H_{80}N_6O_4 + H]^+$ requires *m/z* = 1,188.624, found *m/z* = 1,188.619, difference of 4.2 ppm.

IR (neat): ν 2922, 2852, 1726, 1596, 1577, 1434, 1231, 1156, 1039, 966, 821, 756 cm^{-1}.

(*S*)-3,3'-bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (**S7.1**)



A 100 mL round bottom flask was charged with **S6.1** (2.00 g, 1.68 mmol, 1.00 equiv), dioxane (33 mL, 0.6 M), and 37% aqueous HCl 37 (5.11 mL, 168 mmol, 100 equiv), and the reaction mixture was stirred at rt overnight. The mixture was partitioned between Et_2O (100 mL) and a saturated aqueous solution of $NaHCO_3$. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification on silica gel column chromatography eluting with hexanes/EtOAc 95:5 to 80:20 afforded 1.84 g (99%, 1.67 mmol) of the title compound as a foamy beige solid. This procedure serves as a **Representative Deprotection Procedure** in the synthesis of the other catalyst derivatives.

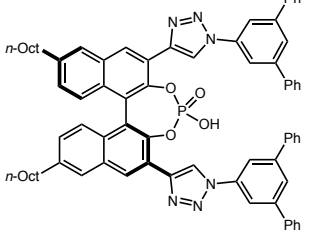
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.06 (s, 2H), 8.70 (s, 2H), 8.54 (s, 2H), 8.02 (d, *J* = 1.6 Hz, 4H), 7.91 (t, *J* = 1.6 Hz, 2H), 7.75–7.69 (m, 10H), 7.54–7.48 (m, 8H), 7.48–7.40 (m, 4H), 7.21–7.12 (m, 4H), 2.72 (t, *J* = 7.6 Hz, 4H), 1.66 (q, *J* = 7.5 Hz, 4H), 1.36–1.24 (m, 20H), 0.87 (t, *J* = 6.6 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.1, 147.2, 144.0, 139.8, 138.7, 137.9, 132.4, 129.2, 129.0, 128.5, 127.5, 126.9, 126.7, 126.7, 124.8, 119.6, 118.3, 117.3, 115.8, 36.0, 32.1, 31.4, 29.7, 29.6, 29.4, 28.4, 22.8, 14.3 ppm.

HRMS: exact mass calculated for $[C_{76}H_{72}N_6O_2 + H]^+$ requires *m/z* = 1100.572, found *m/z* = 1100.566, difference of 5.5 ppm.

IR (neat): ν 3059, 2932, 2852, 1726, 1596, 1577, 1501, 1460, 1435, 1372, 1218, 1033, 908, 798 cm^{-1}.

(4*R*,11b*S*)-2,6-bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.1**)

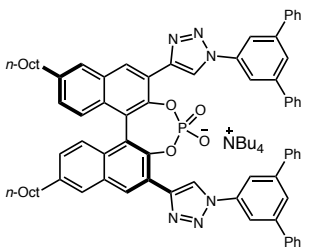


An oven-dried 50 mL round bottom flask was charged with compound **S7.1** (1.84 g, 1.67 mmol, 1.00 equiv), pyridine (33.4 mL, 0.05 M), and $POCl_3$ (311 μL, 3.34 mmol, 2.00 equiv). The mixture was stirred at 95 °C overnight. After cooling to rt, water (5 mL) was added, and the reaction mixture was stirred for an additional 4 h at 100 °C. The mixture was partitioned between DCM and aqueous HCl (3 M) in a separatory funnel, and the organic phase was then washed two more times with HCl. The organic phase was then dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by column chromatography on silica gel eluting with 10% MeOH/DCM solution. The collected fractions were then washed once more with 3 M aqueous HCl solution, dried with Na_2SO_4, filtered, and concentrated to give 1.30 g (67%, 1.12 mol) of the title compound as a foamy beige solid. This procedure serves as a **Representative Phosphoric Acid Procedure** in the synthesis of the other catalyst derivatives.

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.41 (s, 2H), 8.75 (s, 2H), 8.13 (d, *J* = 1.6 Hz, 4H), 8.03 (t, *J* = 1.7 Hz, 2H), 7.97 (s, 2H), 7.87 (d, *J* = 7.2 Hz, 8H), 7.50 (t, *J* = 7.5 Hz, 8H), 7.45–

7.39 (m, 4H), 7.21 (dd, *J* = 8.8, 1.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 4H), 1.67 (p, *J* = 7.3 Hz, 4H), 1.38–1.16 (m, 20H), 0.84 (t, *J* = 6.9 Hz, 6H) ppm.
^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 144.9 (d, *J* = 9.6 Hz), 143.3, 142.7, 139.7, 138.9, 137.8, 130.7, 130.1, 129.1, 128.4, 127.7, 127.2, 127.1, 126.0, 125.5, 123.1, 123.0, 122.5, 117.5, 35.0, 31.3, 30.6, 29.0, 28.8, 28.7, 22.1, 14.0 ppm. (Note: 28 ^{13}C peaks expected, 27 counted, likely due to overlapping peaks in the aryl region)
^{31}P NMR (203 MHz, DMSO-d$_6$): δ 3.20 ppm.
HRMS: exact mass calculated for $[C_{76}H_{71}N_6O_4P + H]^+$ requires *m/z* = 1163.535, found *m/z* 1163.530, difference of 4.3 ppm.
IR (neat): ν 3059, 2923, 2852, 1729, 1595, 1577, 1462, 1434, 1239, 1197, 1080, 1028, 910, 866, 838, 755, 733, 695 cm^{-1}.

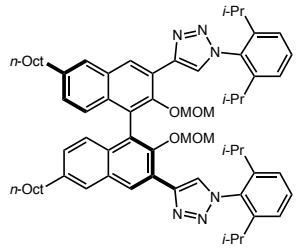
(*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.1 = P7**)



Compound **S8.1** (771 mg, 0.663 mmol, 1.00 equiv) was dissolved in a minimal amount of DCM (10 mL). To this solution, tetrabutylammonium hydroxide (650 μL, 1.0 M in MeOH, 0.98 equiv) was added, and the solution was shaken for 30 s. The reaction was then concentrated and dried overnight under high vacuum. The resulting tetrabutylammonium phosphate base was used without further purification. This procedure serves as a **Representative Deprotonation Procedure** in the synthesis of the other catalyst derivatives.

^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 9.54 (s, 2H), 8.71 (s, 2H), 8.11 (d, *J* = 1.6 Hz, 4H), 8.06 (d, *J* = 1.6 Hz, 2H), 7.95 (s, 2H), 7.89 (dt, *J* = 8.3, 1.4, 1.2 Hz, 8H), 7.52 (t, *J* = 7.6 Hz, 8H), 7.46 (tdt, *J* = 7.2, 4.7, 2.1 Hz, 4H), 7.19 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 3.15–3.07 (m, 8H), 2.74 (t, *J* = 7.7 Hz, 4H), 1.72–1.62 (m, 4H), 1.56–1.48 (m, 8H), 1.39–1.14 (m, 28H), 0.90 (t, *J* = 7.3 Hz, 12H), 0.87–0.79 (m, 6H) ppm.
^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 146.4 (d, *J* = 9.5 Hz), 143.8, 142.8, 139.0, 138.9, 138.0, 130.3, 130.2, 129.1, 128.4, 127.9, 127.2, 127.2, 127.0, 126.0, 125.5, 123.6, 123.5, 122.8, 117.6, 57.5, 35.0, 31.3, 30.6, 28.9, 28.8, 28.7, 23.0, 22.1, 19.2, 14.0, 13.5 ppm.
^{31}P NMR (203 MHz, DMSO-*d*$_6$): δ 4.86 ppm.
HRMS: exact mass calculated for $[C_{76}H_{70}N_6O_4P]^-$ requires *m/z* = 1161.5202, found *m/z* = 1161.5245, difference of 3.7 ppm.
IR (neat): ν 3052, 2958, 2926, 2854, 2872, 1596, 1577, 1499, 1474, 1435, 1286, 1264, 1232, 1098, 1041, 955, 856, 757 cm^{-1}.

(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazole) (**S6.2**)



Following the **Representative Click Procedure** as outlined for compound **S6.1**, the title compound was isolated as a yellow solid in 59% yield (506 mg, 0.48 mmol)

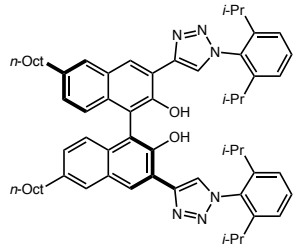
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.01 (s, 2H), 8.41 (s, 2H), 7.79 (d, *J* = 1.7 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 7.8, 2.6 Hz, 4H), 7.22–7.16 (m, 4H), 4.64 (d, *J* = 4.8 Hz, 2H), 4.40 (d, *J* = 4.7 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 4H), 2.62 (s, 6H), 2.38 (hept, *J* = 6.8 Hz, 2H), 2.32 (hept, *J* = 6.8 Hz, 2H), 1.69 (p, *J* = 7.3 Hz, 4H), 1.45–1.22 (m, 20H), 1.19 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.12 (d, *J* = 6.9 Hz, 6H), 1.10 (d, *J* = 6.9 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.0, 146.3, 146.2, 143.4, 140.4, 133.4, 132.4, 131.4, 130.9, 128.9, 128.2, 127.1, 126.4, 126.1, 125.9, 124.2, 124.0, 123.9, 98.4, 56.8, 36.0, 32.0, 31.3, 29.6, 29.5, 29.4, 28.6, 28.6, 24.5, 24.3, 24.2, 24.1, 22.8, 14.3 ppm.

HRMS: exact mass calculated for $[C_{68}H_{88}N_6O_4 + H]^+$ requires *m/z* = 1052.6867, found *m/z* = 1052.691 difference of 2.9 ppm.

IR (neat): *ν* 2961, 2925, 2854, 1474, 1461, 1385, 1332, 1228, 1205, 1160, 1049, 1058, 1037, 979, 931, 804, 759, 736, 661 cm^{-1}.

(*S*)-3,3'-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (**S7.2**)



Following the **Representative Deprotection Procedure** as outlined for compound **S7.1**, the title compound was isolated as a brown solid in 87% yield (406 mg, 0.42 mmol).

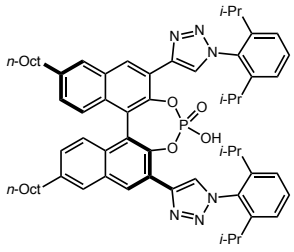
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (s, 2H), 8.40 (s, 2H), 8.21 (s, 2H), 7.68 (s, 2H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 2H), 7.33 (d, *J* = 2.2 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 3H), 2.38 (hept, *J* = 6.4 Hz, 2H), 2.33 (hept, *J* = 6.9 Hz, 2H), 1.67 (p, *J* = 7.9, 7.4 Hz, 4H), 1.43–1.22 (m, 20H), 1.22–1.15 (m, 24H), 0.87 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.4, 146.7, 146.3, 146.2, 138.4, 133.1, 132.6, 131.2, 129.1, 128.8, 126.7, 126.2, 124.9, 124.1, 124.1, 123.9, 117.1, 116.7, 36.0, 32.1, 31.4, 29.7, 29.5, 29.4, 28.6, 28.6, 24.4, 24.4, 24.2, 24.2, 22.8, 14.3 ppm.

HRMS: exact mass calculated for $[C_{64}H_{80}N_6O_2 + H]^+$ requires *m/z* = 964.634, found *m/z* = 964.635, difference of 1.0 ppm.

IR (neat): *ν* 3178, 2962, 2924, 2853, 1616, 1505, 1457, 1385, 1310, 1205, 1056, 994, 90, 803, 758, 734 cm^{-1}.

(4*R*,11b*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.2**)



Following the **Representative Phosphorylation Procedure** as outlined for compound **S8.1,** the title compound was isolated as a light green solid in 91% yield (0.395 g, 0.38 mmol).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.82 (s, 2H), 8.77 (d, *J* = 2.3 Hz, 2H), 7.98 (d, *J* = 1.7 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.42 (ddd, *J* = 7.7, 6.3, 1.4 Hz, 4H), 7.23 (dd, *J* = 8.8, 1.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 4H), 2.30 (hept, *J* = 6.8 Hz, 2H), 2.21 (hept, *J* = 6.9 Hz, 2H), 1.74–1.62 (m, 4H), 1.37–1.18 (m, 20H), 1.09 (td, *J* = 14.8, 13.9, 6.8 Hz, 24H), 0.84 (t, *J* = 6.7 Hz, 6H) ppm.

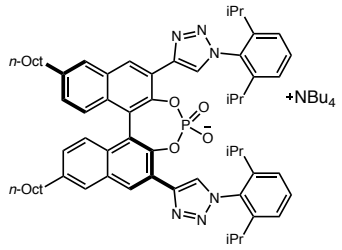
^{13}C NMR (126 MHz, DMSO-d_6): δ 145.5 (d, *J* = 10.6 Hz), 144.8, 141.9, 139.7, 132.9, 131.0, 130.7, 130.0, 128.3, 127.7, 127.5, 127.1, 126.0, 124.0, 123.0, 122.5, 35.0, 31.3, 30.6, 28.9, 28.8, 28.7, 28.1, 28.0, 24.0, 23.9, 23.8, 23.7, 22.1, 14.0 ppm. (Note: 32 ^{13}C peaks expected, only 30 observed. Possible overlapping peaks in the aryl region or unexpected increase in peak degeneracy.)

^{31}P NMR (203 MHz, DMSO-d_6): δ 3.31 ppm.

HRMS: exact mass calculated for $[C_{64}H_{79}N_6O_4P + H]^+$ requires *m/z* = 1027.597, found *m/z* = 1027.598, difference of 1.0 ppm.

IR (neat): ν 2962, 2924, 2854, 1617, 1463, 1275, 1260, 1239, 1049, 860, 802, 754 cm^{-1}.

(*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutyl ammonium salt (**S9.2 = P6**)



Following the **Representative Deprotonation Procedure** as outlined for compound **S9.1**, the title compound was isolated as a light brown solid in quantitative yield.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.91 (s, 2H), 8.74 (s, 2H), 7.94 (s, 2H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.41 (td, *J* = 8.1, 1.4 Hz, 4H), 7.18 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 3.19–3.09 (m, 8H), 2.74 (t, *J* = 7.6 Hz, 4H), 2.29 (h, *J* = 6.8 Hz, 2H), 2.19 (h, *J* = 6.7 Hz, 2H), 1.76–1.61 (m, 4H), 1.61–1.48 (m, 8H), 1.37–1.21 (m, 28H), 1.16–1.03 (m, 24H), 0.93 (t, *J* = 7.3 Hz, 12H), 0.85 (t, *J* = 6.7 Hz, 6H) ppm.

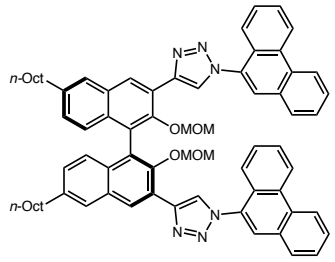
^{13}C NMR (126 MHz, DMSO-d_6): δ 146.6 (d, *J* = 9.4 Hz), 145.9, 145.9, 142.8, 139.4, 133.4, 131.4, 130.7, 130.6, 128.6, 128.3, 127.4, 127.3, 126.4, 124.4, 124.0, 123.2, 123.2, 57.9, 35.4, 31.8, 31.1, 29.3, 29.2, 29.2, 28.5, 28.5, 24.3, 24.3, 24.3, 24.2, 23.5, 22.6, 19.7, 14.4, 14.0 ppm.

^{31}P NMR (203 MHz, DMSO-d_6): δ 5.45.

HRMS: exact mass calculated for $[C_{64}H_{78}N_6O_4P]^-$ requires *m/z* = 1025.5828, found *m/z* = 1025.5786, difference of 4.1 ppm.

IR (neat): ν 2961, 2870, 2855, 1739, 1475, 1463, 1365, 1228, 1100, 1051, 956, 804, 759, 736 cm^{-1}.

(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazole) (**S6.3**)



Following the **Representative Click Procedure** as outlined for compound **S6.1**, the title compound was isolated as a yellow solid in 19% yield (57 mg, 0.05 mmol).

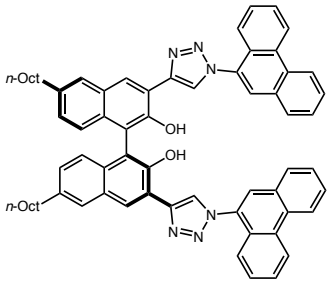
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.05 (s, 2H), 8.79 (d, *J* = 8.3 Hz, 2H), 8.77 (s, 2H), 8.75 (d, *J* = 8.4 Hz, 2H), 7.95–7.94 (m, 4H), 7.84 (s, 2H), 7.81–7.71 (m, 6H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 10.7 Hz, 2H), 7.21 (dd, *J* = 7.4, 1.2 Hz, 2H), 4.68 (d, *J* = 5.0 Hz, 2H), 4.47 (d, *J* = 5.0 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 4H), 2.70 (s, 6H), 1.73 (p, *J* = 7.4 Hz, 4H), 1.44–1.24 (m, 20H), 0.88 (t, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.4, 143.7, 140.5, 132.7, 132.5, 131.4, 131.3, 130.9, 130.5, 129.5, 129.0, 128.4, 128.4, 128.0, 127.9, 127.7, 127.6, 127.2, 126.3, 126.1, 125.8, 124.9, 124.1, 123.5, 123.2, 123.0, 98.9, 57.2, 36.0, 32.0, 31.3, 29.7, 29.6, 29.4, 22.8, 14.3 ppm.

HRMS: exact mass calculated for $[C_{72}H_{72}N_6O_4 + H]^+$ requires *m/z* = 1085.569, found *m/z* = 1085.572 difference of 3.3 ppm.

IR (neat): *ν* 2924, 2853, 1627, 1603, 1499, 1462, 1437, 1326, 1231, 1159, 1038, 978, 929, 823, 724 cm^{-1}.

(*S*)-6,6'-dioctyl-3,3'-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)-[1,1'-binaphthalene]-2,2'-diol (**S7.3**)



Following the **Representative Deprotection Procedure** as outlined for compound **S7.1,** the title compound was isolated as a beige solid in 61% yield (3.28 g, 2.76 mmol).

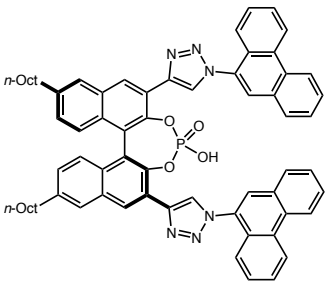
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.28 (s, 2H), 8.82 (d, *J* = 8.4 Hz, 2H), 8.78 (d, *J* = 8.3 Hz, 2H), 8.57 (s, 2H), 8.54 (s, 2H), 8.02–7.96 (m, 4H), 7.84–7.76 (m, 4H), 7.74–7.69 (m, 6H), 7.68–7.64 (m, 2H), (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 10.2 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 4H), 1.69 (p, *J* = 7.9, 7.5 Hz, 4H), 1.43–1.22 (m, 20H), 0.87 (t, *J* = 6.9 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.3, 146.5, 138.6, 132.5, 132.5, 131.3, 131.0, 130.4, 129.5, 129.2, 129.0, 128.7, 128.2, 128.1, 127.8, 127.6, 126.9, 126.6, 125.2, 124.9, 124.2, 123.3, 123.3, 123.1, 117.3, 116.1, 36.0, 32.1, 31.5, 29.7, 29.6, 29.4, 22.8, 14.3 ppm.

HRMS: exact mass calculated for $[C_{68}H_{64}N_6O_2) + H]^+$ requires *m/z* = 997.5164, found *m/z* = 997.5125, difference of 3.9 ppm.

IR (neat): *ν* 3134, 2954, 2922, 2851, 1726, 1629, 1602, 1530, 1502, 1452, 1430, 1259, 1228, 1043, 893, 748, 761cm^{-1}.

(4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.3**)



Following the **Representative Phosphorylation Procedure** as outlined for compound **S8.1**, the title compound was isolated as an orange/brown solid in 91% yield (145.7 mg, 0.14 mmol).

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.12 (s, 2H), 9.01 (d, *J* = 8.5 Hz, 2H), 8.96 (d, *J* = 8.4 Hz, 2H), 8.88 (s, 2H), 8.27 (s, 2H), 8.16 (d, *J* = 7.8 Hz, 2H), 8.01 (s, 2H), 7.82 (dt, *J* = 15.3, 7.7 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.25 (dd, *J* = 8.8, 1.4 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 4H), 1.68 (d, *J* = 50.0 Hz, 4H), 1.42–1.14 (m, 20H), 0.85 (t, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (126 MHz, DMSO-d_6): δ 145.4 (d, *J* = 9.4 Hz), 142.52, 139.56, 131.88, 130.62, 130.60, 130.18, 130.13, 130.00, 129.47, 128.69, 128.28, 128.16, 127.87, 127.50, 127.38, 127.09, 126.97, 126.06, 124.90, 123.71, 123.26, 123.16, 122.76, 122.65, 35.01, 31.32, 30.62, 28.90, 28.81, 28.72, 22.14, 14.01 ppm. (Note: 32 ^{13}C peaks expected, only 31 observed. Possible overlapping peaks in the aryl region.)

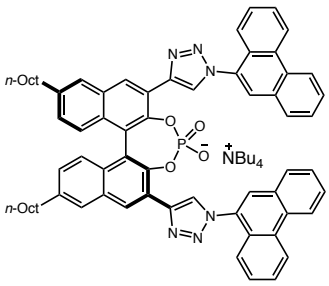
^{31}P NMR (203 MHz, DMSO-d_6): δ 8.34 ppm.

HRMS: exact mass calculated for $[C_{68}H_{63}N_6O_2P + H]^+$ requires *m/z* = 1059.472, found *m/z* = 1059.468, difference of 3.8 ppm.

IR (neat): *ν* 2952, 2921, 2852, 1719, 1500, 1462, 1452, 1230, 1085, 1039, 950, 909, 856, 759, 747 658 cm^{-1}.

(*S*)-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S10.1 = P4**)

Following the **Representative Deprotonation Procedure**, as outlined for compound **S9.1,** the title compound was isolated as a light brown solid in quantitative yield.



^{1}H NMR (500 MHz, DMSO-d_6): δ 9.21 (s, 2H), 9.02 (d, *J* = 8.5 Hz, 2H), 8.96 (d, *J* = 8.5 Hz, 2H), 8.82 (s, 2H), 8.26 (s, 2H), 8.17 (d, *J* = 7.8 Hz, 2H), 7.98 (s, 2H), 7.83 (dt, *J* = 15.0, 7.6 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 3.17–3.09 (m, 8H), 2.77 (t, *J* = 7.4 Hz, 4H), 1.75–1.60 (m, 4H), 1.61–1.47 (m, 8H), 1.38–1.19 (m, 28H), 0.92 (t, *J* = 7.3 Hz, 12H), 0.86 (t, *J* = 6.7 Hz, 6H) ppm.

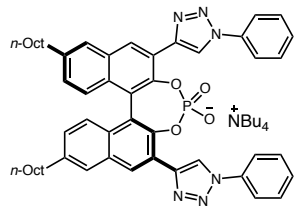
^{13}C NMR (126 MHz, DMSO-d_6): δ 146.3 (d, *J* = 9.9 Hz), 142.8, 139.1, 131.9, 130.6, 130.3, 130.1, 129.5, 128.7, 128.2, 128.0, 127.9, 127.9, 127.6, 127.1, 127.0, 126.0, 124.8, 123.7, 123.5, 123.3, 122.8, 122.7, 57.5, 35.0, 31.3, 30.6, 28.9, 28.8, 28.7, 23.1, 22.1, 19.2, 14.0, 13.5 ppm. (Note: 38 ^{13}C peaks expected, only 37 observed. Possible overlapping peaks in the aryl region.)

^{31}P NMR (203 MHz, DMSO-d_6): δ 5.21 ppm.

HRMS: exact mass calculated for $[C_{68}H_{62}N_6O_4P]^-$ requires *m/z* = 1057.4576, found *m/z* = 1057.4575, difference of 0.1 ppm.

IR (neat): ν 1958, 1955, 2853, 1463, 1453, 1287, 1237, 1098, 1041, 859, 762, 752, 726 cm^{-1}.

(*S*)-9,14-dioctyl-2,6-bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S10.3 = P5**)



Following **Representative Deprotonation Procedure** as outlined for compound **S9.1,** the title compound was isolated after deprotonation of (4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6 bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide synthesized by reported literature procedure[10] in quantitiative yield.

^{1}H NMR (500 MHz, DMSO-*d*$_6$): 9.42 (s, 2H), 8.69 (s, 2H), 7.93 (s, 2H), 7.87 (d, *J* = 8.0 Hz, 4H), 7.68 (t, *J* = 7.9 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.18 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 3.17 – 3.04 (m, 8H), 2.73 (t, *J* = 7.7 Hz, 4H), 1.70 – 1.61 (m, 4H), 1.54 (td, *J* = 7.8, 7.1, 3.9 Hz, 8H), 1.37 – 1.18 (m, 28H), 0.91 (t, *J* = 7.3 Hz, 12H), 0.88 – 0.80 (m, 6H) ppm.

^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 146.3 (d, *J* = 9.4 Hz), 143.7, 139.1, 136.7, 130.3, 130.2, 130.2, 128.9, 128.0, 127.2, 127.0, 126.0, 123.4, 123.1, 122.8, 120.2, 57.5, 35.0, 31.3, 30.6, 28.9, 28.8, 28.7, 23.1, 22.1, 19.2, 14.0, 13.5 ppm.

^{31}P NMR (203 MHz, DMSO-*d*$_6$): δ 5.39 ppm.

HRMS: exact mass calculated for $[C_{52}H_{54}N_6O_4P]^-$ requires *m/z* = 857.395, found *m/z* = 857.393, difference of 2.2 ppm.

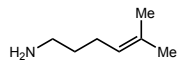
IR (neat): ν 2958, 2925, 2871, 2854, 1598, 1501, 1464, 1445, 1335, 1277, 1235, 1202, 1095, 1042, 955, 855, 825, 733 cm^{-1}.

5. Synthesis of Substrates

The following sulfonamide substrates were prepared according to Zhu et. al.[3]
4-methoxy-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
4-methyl-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
N-(5-methylhex-4-en-1-yl)benzenesulfonamide,
4-chloro-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
4-bromo-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
N-(5-methylhex-4-en-1-yl)-4- (trifluoromethyl)benzenesulfonamide,
4-cyano-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
3-methoxy-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
2-methoxy-N-(5-methylhex-4-en-1- yl)benzenesulfonamide,
N-(5-methylhex-4-en-1-yl)-2,3-dihydrobenzofuran5-sulfonamide,
N-(5-methylhex-4-en-1-yl)thiophene-2-sulfonamide,
2,4-dimethyl-N-(5-methylhex-4-en-1-yl)thiazole-5- sulfonamide,
N-(5-methylhex-4-en-1-yl)-1- phenylmethanesulfonamide

(*E*)-*N*-(hex-4-en-1-yl)-4-methylbenzenesulfonamide and (*Z*)-*N*-(hex-4-en-1-yl)-4-methylbenzenesulfonamide were prepared by methods described by Marcotullio et al.[11]

5-methylhex-4-en-1-amine (**S10**)

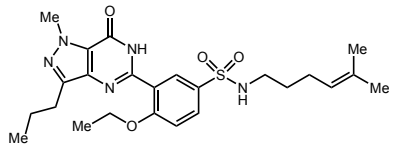


An oven-dried 1L round bottom flask was charged with Acetonitrile (6.23 ml, 119 mmol, 1.05 equiv) and THF (500 mL, 0.25 M) under N_2 atmosphere and cooled to –78 °C. A solution of *n*-BuLi (50 mL, 2.5 M in hexanes, 125 mmol, 1.1 equiv) was added dropwise stirred for 25 min. 1-bromo-3-methylbut-2-ene (13.13 mL, 114 mmol, 16.94 g, 1 equiv) was added dropwise via syringe. The mixture was allowed to warm to room temperature overnight, after which the THF was removed carefully *in vacuo*. The remaining contents of the round bottom flask were transferred to a separatory funnel and extracted 3x with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and filtered into a round bottom flask to be used directly in the following reduction step.

To the round bottom flask containing 5-methylhex-4-enenitrile in Et_2O (500 mL) at 0˚C, $LiAlH_4$ (6.5 g, 171 mmol, 1.5 equiv) was added slowly the reaction warmed to room temperature gradually overnight. The reaction was quenched following the Fieser procedure with sequential dropwise addition of water (6.5 mL), 10% sodium hydroxide (6.5 mL, aqueous), and water (20 mL).[12] When the reaction mixture turned white, magnesium sulfate was added to the flask and the mixture was filtered over a plug of Celite yielding the title compound which was concentrated and used crude in subsequent reactions.

4-ethoxy-3-(1-methyl-7-oxo-3-propyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidin-5-yl)-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (**S11**)

An oven-dried round bottom flask was charged with 4-ethoxy-3-(1-methyl-7-oxo-3-propyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidin-5-yl)benzenesulfonyl chloride (6.57g, 15.99 mmol, 1.8 equiv, prepared via literature procedure[13]) in DCM (32 mL, 0.5M) at 0 ˚C. Amine **S10** (2.00 g, 8.83 mmol, 1.00 equiv) was added followed by slow addition of triethylamine (6.7 mL, 48.0 mmol, 3.0 equiv). The reaction was allowed to stir overnight, at which point it was diluted with DCM and transferred to a separatory funnel. The organic layer was washed 2x with 0.5 M HCl and the aqueous layers were then back extracted with DCM. The combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was then purified by column chromatography on silica (5% acetone/hexanes) to afford the title product in 32% yield (1.36 g, 2.78 mmol).



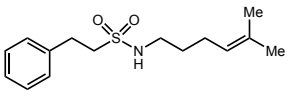
^{1}H NMR (500 MHz, $CDCl_3$): δ10.84 (s, 1H), 8.92 (d, *J* = 2.5 Hz, 1H), 7.94 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.01 (t, *J* = 7.2 Hz, 1H), 4.51 (t, *J* = 6.2 Hz, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 4.27 (s, 1H), 3.01 (q, *J* = 6.8 Hz, 2H), 2.95 – 2.89 (m, 2H), 1.99 (q, *J* = 7.3 Hz, 2H), 1.85 (h, *J* = 7.4 Hz, 2H), 1.65 (t, *J* = 7.0, 3H), 1.65 (s, 3H), 1.55 (p, *J* = 7.4 Hz, 2H), 1.55 (s, 3H), 1.02 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 153.8, 147.1, 146.7, 138.5, 133.6, 133.1, 131.3, 130.6, 124.6, 123.0, 121.3, 113.2, 66.2, 43.2, 38.4, 29.8, 27.8, 25.8, 25.2, 22.5, 17.8, 14.7, 14.2 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{24}H_{33}N_5O_4S$) from $[M+H]^+$ requires m/z 487.22533, found m/z 487.22321, difference 4.3 ppm.

IR (neat): ν 3296, 2960, 1682, 1318, 1279, 1151, 1079, 7564, 652 cm^{-1}.

N-(5-methylhex-4-en-1-yl)-2-phenylethane-1-sulfonamide (**S12**)



Adapted from a procedure from Bahrami et al.,[14] a round bottom flask was charged with a solution of 2-phenylethanethiol (3.09 g, 22.35 mmol, 1 equiv) in acetonitrile (112 mL, 0.2 M) at 0 ˚C. H_2O_2 (6.91 mL, 30 wt % in water, 67.1 mmol, 3 equiv) was added followed by the addition of $ZrCl_4$ (5.21g, 22.35 mmol, 1 equiv), added *slowly* to prevent sudden exotherm. The reaction stirred for 10 minutes at which point it was quenched carefully with water, diluted with EtOAc and washed iteratively with a saturated solution of aqueous $Na_2S_2O_3$ until the peroxide levels were undetectable by hydrogen peroxide test strips. The organic layer was dried with sodium sulfate and concentrated. The crude mixture was purified by column chromatography (5-10% EtOAc /hexanes gradient) affording the sulfonyl chloride product in 54% yield (2.54g, 12.3 mmol). The ^{1}H spectrum was consistent with reported literature.[15]

The resulting sulfonyl chloride (2.54 g. 12.3 mmol, 1 equiv) was dissolved in DCM (60 mL, 0.2 M) at 0 ˚C, followed by the addition of amine **S10** (1.38 g, 12.21 mmol, 1 equiv) and triethylamine (3.40 mL, 24.23 mmol, 2 equiv). After stirring overnight, the reaction was diluted with DCM and washed 2x with 0.5 M HCl. The aqueous layer was then back extracted with DCM, and the combined organic layers were dried with sodium

sulfate, filtered, and concentrated. The crude residue was purified by column chromatography on silica (10% EtOAc /hexanes) to afford the title product in 42% yield (1.46 g, 5.12 mmol).

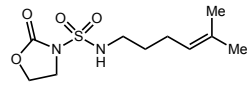
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 3H) 5.07 (dddd, *J* = 7.2, 5.8, 2.8, 1.4 Hz, 1H), 3.97 – 3.85 (m, 1H), 3.34 – 3.28 (m, 2H), 3.18 – 3.12 (m, 2H), 3.03 (q, *J* = 6.9 Hz, 2H), 2.01 (q, *J* = 7.3 Hz, 2H), 1.71 (s, 3H), 1.62 (s, 3H), 1.52 (p, *J* = 7.3 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.1, 133.1, 129.1, 128.5, 127.2, 123.0, 53.6, 43.1, 30.34, 30.2, 25.9, 25.2, 17.9 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{15}H_{23}NO_2S$) from $[M+H]^+$ requires m/z 281.14495, found m/z 281.14458, difference 0.4 ppm.

IR (neat): ν 3281, 2926, 1448, 1307, 1146, 1127, 1071, 717, 698 cm^{-1}.

N-(5-methylhex-4-en-1-yl)-2-oxooxazolidine-3-sulfonamide (**S13**)



An oven-dried round bottom flask was charged with Chlorosulfonyl isocyanate (1.918 ml, 22.08 mmol, 1 equiv) of DCM (33 mL, 0.7 M) under N_2 at , and equipped with an addition funnel. A solution of 2-chloroethanol (1.482 ml, 22.08 mmol, 1 equiv) in DCM (9.96 mL, 2.5 M) was added dropwise through an addition funnel and stirred for 30 minutes. Next, a solution of 5-methylhex-4-en-1-amine (2.5 g, 22.08 mmol, 1 equiv) and triethylamine (6.77 ml, 48.6 mmol, 2.2 equiv) in DCM (20 mL) was added dropwise and the reaction was warmed to room temperature overnight. The reaction was then diluted with DCM was washed with a solution of 2M HCl (60 mL) followed by a 0.5 M solution of HCl (60 mL). The organic layer was dried with sodium sulfate, filtered, concentrated and purified by flash chromatography providing the title compound in 26% yield (1.50 g, 5.73 mmol).

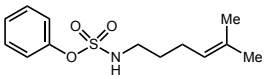
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.36 (t, *J* = 5.4 Hz, 1H), 5.07 (t, *J* = 7.2 Hz, 1H), 4.44 (dd, *J* = 8.7, 7.1 Hz, 2H), 4.06 (dd, *J* = 8.7, 7.0 Hz, 2H), 3.10 (q, *J* = 7.0 Hz, 2H), 2.06 (q, *J* = 7.2 Hz, 2H), 1.69 (s, 3H), 1.63 (p, p, *J* = 7.2 Hz, 3H), 1.61 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.7, 133.4, 122.7, 62.7, 45.3, 43.9, 29.4, 25.8, 25.1, 17.9 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{10}H_{18}N_2O_4S$) from $[M+H]^+$ requires m/z 262.09873 found m/z 262.09876, difference -0.1 ppm.

IR (neat): ν 3277, 2937, 2729, 1598, 1436, 1323, 1092, 1032, 814, 706 cm^{-1}.

phenyl (5-methylhex-4-en-1-yl)sulfamate (**S14**)



A round bottom flask was charged with **S13** (750 mg, 2.86 mmol, 1 equiv), phenol (350 mg, 3.72 mmol, 1.3 equiv), trimethylamine (1.07 mL, 7.72 mmol, 2.8 equiv), and acetonitrile (10 mL, 0.3 M), and stirred at reflux overnight. The reaction was concentrated in vacuo, diluted in DCM, and washed with aqueous solutions of 0.5 M HCl and brine. The aqueous layers were then back extracted 2x with DCM and the combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was purified by silica gel column chromatography, (7% EtOAc /hexanes) to afford the product as an clear oil in 46% yield (352mg, 1.307 mmol).

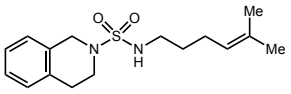
^{1}H NMR (500 MHz, $CDCl_3$): 7.43 – 7.37 (m, 2H), 7.32 – 7.27 (m, 3H), 5.07 (t, *J* = 7.2 Hz, 1H), 4.55 (s, 1H), 3.26 (q, *J* = 7.0 Hz, 2H), 2.05 (q, *J* = 7.3 Hz, 2H), 1.69 (s, 2H), 1.64 (p, *J* = 7.2 Hz, 2H), 1.60 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.3, 133.4, 130.0, 127.1, 122.8, 122.0, 44.2, 29.7, 25.9, 25.1, 17.9 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_3S$) from $[M+H]^+$ requires m/z 269.10856 found m/z 269.10853, difference 0.1 ppm.

IR (neat): ν 3308, 2928, 1741, 1588, 1488, 1430, 1360, 1195, 1170, 1150, 1074, 859, 778, 725, 690 cm^{-1}.

N-(5-methylhex-4-en-1-yl)-3,4-dihydroisoquinoline-2(1*H*)-sulfonamide (**S15**)



A round bottom flask was charged with **S13** (750 mg, 2.86 mmol, 1 equiv), 1,2,3,4-tetrahydroisoquinoline (0.464 mL, 3.72 mmol, 1.3 equiv), trimethylamine (1.07 mL, 7.72 mmol, 2.8 equiv), and acetonitrile (10 mL, 0.3 M), and stirred at reflux overnight. The reaction was concentrated in vacuo, diluted in DCM, and washed with aqueous solutions of 0.5 M HCl and brine. The aqueous layers were then back extracted 2x with DCM and the combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was purified by silica gel column chromatography, (7% EtOAc /hexanes) to afford the product as an clear oil in 83% yield (736 mg, 2.386 mmol).

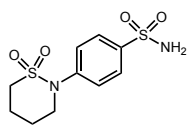
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 7.10 – 7.06 (m, 1H), 5.04 (t, *J* = 7.1 Hz, 1H), 4.42 (s, 2H), 4.17 (t, *J* = 6.2 Hz, 2H), 3.04 (q, *J* = 6.8 Hz, 2H), 2.96 (t, *J* = 5.9 Hz, 2H), 2.01 (q, *J* = 7.3 Hz, 2H), 1.67 (s, 3H), 1.58 (s, 7H), 1.58 (p, *J* = 7.4 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 133.5, 133.0, 132.4, 129.1, 126.9, 126.5, 126.5, 123.1, 47.8, 44.0, 43.4, 30.0, 29.0, 25.8, 25.3, 17.9 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{24}N_2O_2S$) from $[M+H]^+$ requires m/z 308.15585, found m/z 308.15643, difference -1.9 ppm.

IR (neat): ν 3295, 2927, 1454,1326,1151, 1070, 1023, 955, 923, 759, 736 cm^{-1}.

4-(1,1-dioxido-1,2-thiazinan-2-yl)benzenesulfonamide (**S16**)



A round bottom flask was charged with 4-aminobenzenesulfonamide (0.850 g, 4.94 mmol, 1 equiv) in pyridine (5 ml, 1 M), and submerged in a waterbath. 4-chlorobutane-1-sulfonyl chloride (1.00 g, 5.23 mmol, 1.06 equiv) was added dropwise. The reaction was stirred for 24 h, then warmed to 40 ˚C for 5 h. The solution was poured into 200 mL of 2.5 M HCl and the resulting solid was filtered, washed with water, and transferred to a solution of sodium carbonate (0.523 g, 4.94 mmol, 1 equiv) in 16 mL H_2O and heated to 80 ˚C for 12 h. The solid initially dissolved, and then precipitated out again after several hours. This precipitate was then filtered and washed with water, yielding the title compound as a white solid in 75% yield (1.08 mg, 3.72 mmol).

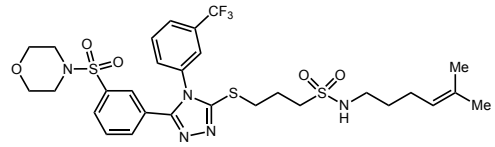
^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 7.69 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 3.67 – 3.53 (m, 2H), 3.26 – 3.20 (m, 2H), 2.11 – 1.94 (m, 2H), 1.77 – 1.64 (m, 2H) ppm.

^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 143.6, 141.7, 126.5, 126.4, 52.9, 50.1, 23.9, 23.4 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{10}H_{14}N_2O_4S_2$) from $[M+H]^+$ requires m/z 290.0395 found m/z 290.03951, difference -0.1 ppm.

IR (neat): ν 3263, 1593, 1493, 1329, 1163, 885, 720 cm^{-1}.

N-(5-methylhex-4-en-1-yl)-3-((5-(3-(morpholinosulfonyl)phenyl)-4-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-3-yl)thio)propane-1-sulfonamide (**S17)**



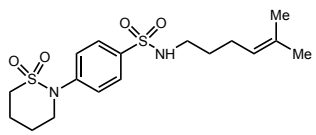
3-chloro-N-(5-methylhex-4-en-1-yl)propane-1-sulfonamide (587 mg, 2.31 mmol, 1.1 equiv) prepared by literature procedure[3] was added to a round bottom flask containing 5-(3-(morpholinosulfonyl)phenyl)-4-(3-(trifluoromethyl)phenyl)-4H-1,2,4-triazole-3-thiol (989 mg, 2.10 mmol, 1.0 equiv) and K_2CO_3 (126.13 mg, 2.10 mmol, 1.0 equiv) in DMF (10 mL, 2 M). The mixture was stirred at 100 ˚C until full consumption of the alkyl chloride starting material was observed by TLC. The reaction was then diluted with diethyl ether and washed 3x with 10% aqueous lithium chloride solution. The combined aqueous layers were back extracted 2x with diethyl ether, and the combined organic layers were dried, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (50% EtOAc /hexanes) to afford the title compound as a sticky oil in 46% yield (658, 2.10 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.79 – 7.69 (m, 3H), 7.62 (s, 1H), 7.58 – 7.53 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 5.07 (t, *J* = 7.1 Hz, 1H), 4.92 (t, *J* = 6.1 Hz, 1H), 3.67 (t, *J* = 4.7 Hz, 4H), 3.44 (t, *J* = 7.2 Hz, 2H), 3.18 (t, *J* = 7.1 Hz, 2H) 3.11 (q, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 4.2 Hz, 4H), 2.38 (p, *J* = 7.2 Hz, 2H), 2.08 – 1.93 (m, 2H), 1.67 (s, 2H), 1.67 – 1.59 (m, 2H), 1.59 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.2, 153.2, 135.9, 134.3, 132.9 (q, *J* = 33.6 Hz), 132.6, 132.5, 131.3, 131.0, 129.9, 129.1, 127.3, 127.2 (q, *J* = 3.6 Hz), 126.9, 124.4 (q, *J* = 3.7 Hz),123.1, 122.9 (q, *J* = 272.9 Hz), 65.9, 50.5, 45.8, 43.0, 30.5, 30.3, 25.7, 25.1, 24.1, 17.7 ppm.

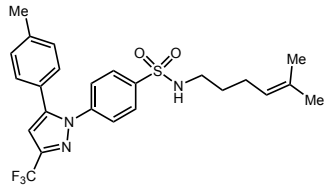
HRMS: (ESI) exact mass calculated for [M] ($C_{29}H_{36}F_3N_5O_5S$) from $[M+H]^+$ requires m/z 687.18307, found m/z 687.18254, difference 0.8 ppm.
IR (neat): ν 2922, 2860, 1668, 1454, 1333, 1170, 1095, 1070, 945, 721, 700 cm^{-1}.

4-(1,1-dioxido-1,2-thiazinan-2-yl)-*N*-(5-methylhex-4-en-1-yl)benzenesulfonamide (**S18**)



Potassium hydroxide (214 mg, 3.82 mmol) was dissolved over in DMF (7 mL) at 120 ˚C. , 4-(1,1-dioxido-1,2-thiazinan-2-yl)benzenesulfonamide (1108 mg, 3.82 mmol) was then added the solution and was allowed to stir for 30 minutes before adding a solution of adding 5-methylhex-4-en-1-yl 4-methylbenzenesulfonate (683 mg, 2.54 mmol) prepared by literature procedure[16] dropwise as a solution in DMF (7 mL). After full consumption of the starting material after 1 hour, the reaction was cooled to room temperature, diluted with diethyl ether, and washed with 3x with 10% aqueous lithium chloride solution. The combined aqueous layers were back extracted 2x with diethyl ether, and the combined organic layers were dried, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (20% EtOAc /hexanes) to afford the title compound as a pale yellow solid in 40% yield (387 mg, 1.00 mmol).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2fH), 5.02 (t, *J* = 7.2, 1H), 4.33 (t, *J* = 6.0 Hz, 1H), 3.81 (dd, *J* = 5.58, 5.54Hz, 2H), 3.23 (dd, *J* = 6.3, 5.8 Hz, 2H), 2.96 (q, *J* = 6.9 Hz, 2H), 2.36 (p, *J* = 6.1 Hz, 2H), 2.02 – 1.90 (m, 4 H), 1.67 (s, 3H), 1.56 (s, 3H), 1.52 (p, *J* = 7.4 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.4, 138.1, 133.1, 128.1, 126.7, 123.0, 53.2, 51.0, 43.2, 29.8, 25.8, 25.2, 24.6, 24.3, 17.9 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{17}H_{26}N_2O_4S_2$) from $[M+H]^+$ requires m/z 386,13340 found m/z 386.13337, difference 0.1 ppm.
IR (neat): ν 2969, 1741, 1331, 1217, 1153, 882 cm^{-1}.

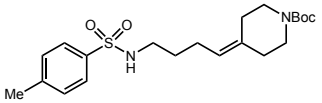
N-(5-methylhex-4-en-1-yl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (**S19**)



Following a procedure adapted from Zhu et. al.[17] 4-[5-(p-tolyl)-3-(trifluoromethyl)pyrazol-1-yl]benzenesulfonamide (2.01 g, 5.24 mmol, 1 equiv) and 5-methylhex-4-en-1-ol (658.7 mg, 5.77 mmol, 1.1 equiv) prepared by literature procedures[18] were added to a round bottom flask equipped with a reflux condenser containing $[Cp^*IrCl_2]_2$ (28.0 mg, 0.052 mmol, 0.01 equiv) and cesium carbonate (34.1 mg, 0.105 mmol, 0.02 equiv). The reaction vessel was evacuated and refilled with nitrogen 3x, followed by the addition of toluene (10 mL, 0.52 M), and the reaction was stirred at reflux for 48 hours, at which point the reaction was cooled to room temperature and concentrated. The crude residue was purified by silica gel column chromatography to afford the title compound as a white solid in 43% yield (1.08 g, 2.26 mmol)

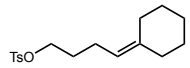
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 4.36 (t, *J* = 6.1 Hz, 1H), 2.95 (q, *J* = 6.9 Hz, 2H), 2.38 (s, 3H), 1.96 (q, *J* = 7.3 Hz, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.50 (p, *J* = 7.2 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 145.4, 144.2 (q, *J* = 38.5 Hz), 142.6, 139.9, 139.6, 133.2, 129.9, 128.8, 128.2, 125.8, 125.7, 121.1 (d, *J* = 269.2 Hz), 122.9, 106.4, 43.1, 29.7, 25.8, 25.2, 21.5, 17.9 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{26}H_{26}F_3N_3O_2S$) from $[M+H]^+$ requires m/z 477.16978, found m/z 477.16907, difference 1.5 ppm.
IR (neat): *ν* 3284, 2926, 1597, 1498, 1471, 1409, 1331m 1272, 1236, 1158, 1134, 1096, 957, 842, 759, 743 cm^{-1}.

<u>*tert*-butyl 4-(4-((4-methylphenyl)sulfonamido)butylidene)piperidine-1-carboxylate</u> (**S20**)



4-methyl-N-(pent-4-en-1-yl)benzenesulfonamide (607 mg, 2.53 mmol, 1 equiv.) and tert-butyl 4-methylenepiperidine-1-carboxylate (2 g, 10.14 mmol, 4 equiv.) were added by syringe to an oven dried three neck round bottom flask, fitted with a reflux condenser, under nitrogen atmosphere containing Grubbs II catalyst (0.065g , 0.076 mmol, 0.03 equiv.) was dissolved in DCM (10 mL, 0.25 M). The reaction was refluxed for 48 hours, at which point the remaining ruthenium byproducts were removed by stirring the product in dichloromethane with DMSO (0.27 mL, 1.5 equiv) overnight, followed by filtration through a silica plug and concentration of the crude residue. The crude mixture was purified by silica gel chromatography (15% EtOAc/hexanes) to afford the title compound as a white solid in 23% yield (240 mg, 0.857mmol).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.09 (t, *J* = 7.4 Hz, 1H), 4.52 – 4.43 (m, 1H), 3.34 (dt, *J* = 15.3, 6.1 Hz, 4H), 2.f (q, *J* = 7.2, 6.8 Hz, 2H) 2.43 (s, 3H), 2.13 – 2.06 (m, 4H), 2.00 (q, *J* = 7.4 Hz, 2H), 1.49 (p, *J* = 7.2 Hz, 2H), 1.46 (s, 9H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 155.1, 143.6, 137.0, 136.6, 130.0, 127.2, 122.4, 119.2, 79.7, 45.7, 44.7, 42.9, 36.0, 29.9, 28.6, 28.4, 24.2, 21.7 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{21}H_{32}N_2O_4S$) from $[M+H]^+$ requires m/z 408.20828, found m/z 408.20809, difference 0.5 ppm.
IR (neat): *ν* 3266, 2952, 1691, 1668, 1424, 1365, 1327, 1241, 1160, 1094, 815, 662 cm^{-1}.

4-cyclohexylidenebutyl 4-methylbenzenesulfonate (**S21**)



Lithium aluminum hydride (420 mg, 11.07 mmol, 1.05 equiv) was added to a solution of ethyl 4-cyclohexylidenebutanoate (2.07g, 10.55 mmol, 1 equiv) prepared by literature procedure[19] in a solution of diethyl ether (100 mL, 0.10 M) at 0 ˚C. The reaction was allowed to warm to room temperature over 2 hours, at which point the reaction was quenched by sequential dropwise addition of water (0.42 mL), 10% sodium hydroxide (0.42 mL, aqueous), and water (1.26 mL). When the reaction mixture turned white, magnesium sulfate was added to the flask and the mixture was filtered over a plug of silica and concentrated yielding crude 4-cyclohexylidenebutan-1-ol which was used without further purification.

4-methylbenzene-1-sulfonyl chloride (2.56 g, 13.42 mmol, 1 eq) was then added to a solution of 4-cyclohexylidenebutan-1-ol dissolved in DCM (70 mL, 0.15 M) at 0 ˚C, followed by dropwise addition of trimethylamine (5.61 mL, 40.30 mmol, 3 equiv). The reaction was allowed to stir overnight, at which point it was diluted with DCM and transferred to a separatory funnel. The organic layer was washed 2x with 0.5 M HCl and the aqueous layers were then back extracted with DCM. The combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was then purified by column chromatography on silica (5% acetone/hexanes) to afford the title product in 68% yield (2.23 g, 7.23 mmol) over two steps.

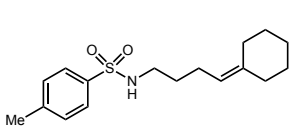
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.91 (t, *J* = 7.3 Hz, 1H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 2.11 – 1.91 (m, 6H), 1.65 (p, *J* = 6.7 Hz, 1H), 1.55 – 1.38 (m, 4H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.8, 141.5, 133.3, 129.9, 128.0, 119.0, 70.3, 37.2, 31.07, 29.3, 28.7, 27.9, 27.0, 23.0, 21.8 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{17}H_{24}O_3S$) from $[M+Na]^+$ requires m/z 308.14462, found m/z 308.14462, difference 0.03 ppm.

IR (neat): ν 2925, 2852, 1598, 1446, 1358, 1188, 1097, 921, 812, 661 cm^{-1}.

N-(4-cyclohexylidenebutyl)-4-methylbenzenesulfonamide (**S22**)

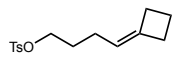


Following a procedure adapted from literature precedent,[11] potassium hydroxide (608 mg, 10.85 mmol) was dissolved over in DMF (15 mL) at 120 ˚C. 4-methylbenzenesulfonamide (1.86 mg, 10.85 mmol) was then added the solution and was allowed to stir for 30 minutes before adding 4-cyclohexylidenebutyl 4-methylbenzenesulfonate dropwise as a solution in DMF (7 mL). After full consumption of the starting material after 1 hour, the reaction was cooled to room temperature, diluted with diethyl ether, and washed with 3x with 10% aqueous lithium chloride solution. The combined aqueous layers were back extracted 2x with diethyl ether, and the combined organic layers were dried, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford the title compound as an oil in 40% yield (387 mg, 1.00 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.93 (t, *J* = 7.3 Hz, 1H), 4.44 (t, *J* = 6.2 Hz, 1H), 2.93 (q, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.02, (q, J = 8.0 Hz, 4H), 1.96 (q, *J* = 7.3 Hz, 2H), 1.52 – 1.40 (m, 8H) ppm.

^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.5, 141.2, 137.1, 129.8, 127.3, 119.7, 43.1, 37.2, 29.9, 28.8, 28.8, 27.9, 27.0, 24.3, 21.7 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{17}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 307.1606, found m/z 307.16073, difference -0.4 ppm.
IR (neat): ν 3289, 2925, 1445, 1323, 1157, 1093, 813, 662 cm^{-1}.

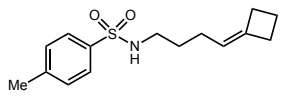
4-cyclobutylidenebutyl 4-methylbenzenesulfonate (**S23**)



Lithium aluminum hydride (179 mg, 4.72 mmol, 1.05 equiv) was added to a solution of ethyl 4-cyclohexylidenebutanoate (757 mg, 4.50 mmol, 1 equiv) prepared by literature procedure[20] in a solution of diethyl ether (45 mL, 0.10 M) at 0 ˚C. The reaction was allowed to warm to room temperature over 2 hours, at which point the reaction was quenched by sequential dropwise addition of water (0.180), 10% sodium hydroxide (0.180 mL, aqueous), and water (0.54 mL). When the reaction mixture turned white, magnesium sulfate was added to the flask and the mixture was filtered over a plug of silica and concentrated yielding crude 4-cyclohexylidenebutan-1-ol which was used without further purification.

4-methylbenzene-1-sulfonyl chloride (858 mg, 4.50 mmol, 1 eq) was then added to a solution of 4-cyclohexylidenebutan-1-ol dissolved in DCM (40 mL, 1.12 M) at 0 ˚C, followed by dropwise addition of trimethylamine (1.88 mL, 13.50 mmol, 3 equiv). The reaction was allowed to stir overnight, at which point it was diluted with DCM and transferred to a separatory funnel. The organic layer was washed 2x with 0.5 M HCl and the aqueous layers were then back extracted with DCM. The combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was then purified by column chromatography on silica (5% acetone/hexanes) to afford the title product in 76% yield (963 mg, 3.4 mmol) over two steps.
^{1}H NMR (500 MHz, $CDCl_3$): 7.79 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.90 (tm, J = 7.4, 2.4 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.63 – 2.51 (m, 4H), 2.45 (s, 3H), 1.96 – 1.84 (m, 4H), 1.66 (p, J = 6.7 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.8, 141.9, 133.4, 129.9, 128.0, 118.1, 70.2, 31.0, 29.3, 28.9, 23.8, 21.8, 17.1 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{15}H_{20}O_3S$) from $[M+Na]^+$ requires m/z 280.11332 found m/z 280.11272, difference 2.1 ppm.
IR (neat): ν 2934, 1598, 1357, 1187, 1097, 965, 919, 812, 740 cm^{-1}.

N-(4-cyclobutylidenebutyl)-4-methylbenzenesulfonamide (**S24**)



Following a procedure adapted from literature precedent,[11] potassium hydroxide (129 mg, 2.30 mmol, 1.5 equiv) was dissolved in DMF (4 mL) at 120 ˚C. 4-methylbenzenesulfonamide (393 mg, 2.30 mmol, 1.5 equiv) was then added the solution and was allowed to stir for 30 minutes before adding 4-cyclobutylidenebutyl 4-methylbenzenesulfonate **S23** dropwise as a solution in DMF (4 mL). After full consumption of the starting material after 1 hour, the reaction was cooled to room temperature, diluted with diethyl ether, and washed with 3x with 10% aqueous lithium chloride solution. The combined aqueous layers were back extracted 2x with diethyl ether, and the combined organic layers were dried, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford the title compound as an oil in 77% yield (3.29 mg, 1.18 mmol).

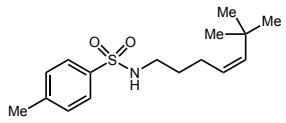
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.93 (ddq, *J* = 7.2, 4.7, 2.3 Hz, 1H), 4.38 (t, *J* = 6.3 Hz, 1H), 2.93 (q, *J* = 6.7 Hz, 2H), 2.57 (dt, *J* = 15.2, 7.9 Hz, 4H), 2.43 (s, 3H), 2.05 – 1.78 (m, 4H), 1.48 (p, *J* = 7.1 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 154.9, 143.6, 134.8, 129.8, 127.7, 64.4, 49.4, 41.0, 28.6, 27.1, 26.8, 24.6, 21.7 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{15}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 279.12930, found m/z 279.12815, difference 4.1 ppm.

IR (neat): ν 3279, 2940, 1710, 1598, 1426, 1323, 1091, 813, 662 cm^{-1}.

(*Z*)-*N*-(6,6-dimethylhept-4-en-1-yl)-4-methylbenzenesulfonamide (**S25**):



Lithium aluminum hydride (1.15 6, 30.4 mmol, 2 equiv) was added to a solution of (Z)-ethyl 6,6-dimethylhept-4-enoate (2.80 g, 15.19 mmol, 1 equiv) prepared by literature procedure[21] in a solution of diethyl ether (150 mL, 0.10 M) at 0 ˚C. The reaction was allowed to warm to room temperature over 2 hours, at which point the reaction was quenched by sequential dropwise addition of water (1.15 mL), 10% sodium hydroxide (1.15 mL, aqueous), and water (2.3 mL). When the reaction mixture turned white, magnesium sulfate was added to the flask and the mixture was filtered over a plug of silica and concentrated yielding crude 4-cyclohexylidenebutan-1-ol which was used without further purification.

Methanesulfonyl chloride (1.7 mL, 22.7 mmol, 1.5 eq) was then added to a solution of (Z)-6,6-dimethylhept-4-en-1-ol dissolved in DCM (13.5 mL, 1.12 M) at 0 ˚C, followed by dropwise addition of trimethylamine (10.6 mL, 76 mmol, 5 equiv). The reaction was allowed to stir overnight, at which point it was diluted with DCM and transferred to a separatory funnel. The organic layer was washed 2x with 0.5 M HCl and the aqueous layers were then back extracted with DCM. The combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was then purified by column chromatography on silica (5% EtOAc/hexanes) to afford the mesylate product. This intermediate was carried on without any further characterization.

Following a procedure adapted from literature precedent,[11] potassium hydroxide (1.278 g, 22.8 mmol, 1.5 equiv) was dissolved in DMF (15 mL) at 120 ˚C. 4-methylbenzenesulfonamide (3.90 g, 22.8 mmol, 1.5 equiv) was then added the solution and was allowed to stir for 30 minutes before adding (*Z*)-6,6-dimethylhept-4-en-1-yl methanesulfonate dropwise as a solution in DMF (15 mL). After full consumption of the starting material after 1 hour, the reaction was cooled to room temperature, diluted with diethyl ether, and washed with 3x with 10% aqueous lithium chloride solution. The combined aqueous layers were back extracted 2x with diethyl ether, and the combined organic layers were dried, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford the title compound as a white solid in 47% yield (2.15 g, 7.29 mmol) over 3 steps.

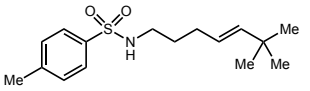
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.33 (d, *J* = 12.0 Hz, 1H), 5.04 (dt, *J* = 12.0, 7.6 Hz, 1H), 4.48 (t, *J* = 6.0 Hz, 1H), 2.98 (q, *J* = 6.8 Hz, 2H), 2.45 (s, 2H), 2.17 (qd, *J* = 7.4, 1.7 Hz, 2H), 1.54 (p, *J* = 7.3 Hz, 2H), 1.08 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 141.1, 137.0, 129.8, 127.2, 127.0, 43.1, 33.3, 31.2, 30.2, 25.5, 21.7 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 295.1606, found m/z 295.16047, difference 0.4 ppm.

IR (neat): ν 3280, 2954, 1324, 1157, 1092, 813, 662 cm^{-1}.

(*E*)-*N*-(6,6-dimethylhept-4-en-1-yl)-4-methylbenzenesulfonamide (**S26**):



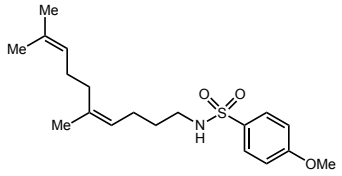
Methanesulfonyl chloride (2.38 mL, 30.0 mmol, 1.5 equiv.) was added to a solution of (E)-6,6-dimethylhept-4-en-1-ol (2.84 g, 20 mmol, 1 equiv.) prepared by literature procedure[22] dissolved in DCM (18 mL, 1.12 M) at 0 ˚C, followed by dropwise addition of trimethylamine (14 mL, 100 mmol, 5 equiv.). The reaction was allowed to stir overnight, at which point it was diluted with DCM and transferred to a separatory funnel. The organic layer was washed 2x with 0.5 M HCl and the aqueous layers were then back extracted with DCM. The combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was then purified by column chromatography on silica (5% EtOAc/hexanes) to afford the mesylate product. This intermediate was carried on without any further characterization.

Following a procedure adapted from literature precedent,[12] potassium hydroxide (1.683 g, 22.8 mmol, 1.5 equiv) was dissolved in DMF (40 mL) at 120 ˚C. 4-methylbenzenesulfonamide (5.14 g, 22.8 mmol, 1.5 equiv) was then added the solution and was allowed to stir for 30 minutes before adding (*Z*)-6,6-dimethylhept-4-en-1-yl methanesulfonate dropwise as a solution in DMF (40 mL). After full consumption of the starting material after 1 hour, the reaction was cooled to room temperature, diluted with diethyl ether, and washed with 3x with 10% aqueous lithium chloride solution. The combined aqueous layers were back extracted 2x with diethyl ether, and the combined organic layers were dried, filtered, and concentrated. The crude residue was purified by

silica gel column chromatography (20% EtOAc/hexanes) to afford the title compound as a white solid in 34% yield (2.05 g, 6.7 mmol) over 2 steps.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.39 (dt, *J* = 15.6, 1.4 Hz, 1H), 5.18 (dt, *J* = 15.6, 6.8 Hz, 1H), 4.36 (t, *J* = 6.2 Hz, 1H), 2.93 (q, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.96 (qd, *J* = 7.1, 1.4 Hz, 2H), 1.52 (p, *J* = 7.1 Hz, 2H), 0.95 (s, 9H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 143.1, 137.1, 129.8, 127.3, 123.1, 42.8, 33.0, 29.8, 29.8, 29.5, 21.7 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 295.1606, found m/z 295.16077, difference -0.6 ppm.
IR (neat): ν 3281, 2953, 1428, 1323, 1156, 1093, 972, 813 cm^{-1}.

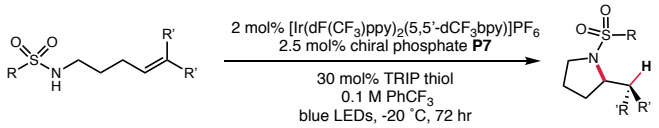
(*Z*)-*N*-(5,9-dimethyldeca-4,8-dien-1-yl)-4-methoxybenzenesulfonamide (**S27**)



A round bottom flask was charged with a solution of crude (*Z*)-5,9-dimethyldeca-4,8-dien-1-amine (7.8 g, 43 mmol, 1 equiv) prepared via literature procedure[23] at 0 ˚C in DCM (300 mL, 0.14 M), followed by sequential addition of 4-Methoxybenzenesulfonyl chloride (8.9 g, 43 mmol, 1 equiv) and triethylamine (9.8 mL, 86 mmol, 2 equiv). The solution was allowed to warm up overnight, at which point it was diluted with DCM and transferred to a separatory funnel. The organic layer was washed 2x with 0.5 M HCl and the aqueous layers were then back extracted with DCM. The combined organic layers were dried with sodium sulfate, filtered, and concentrated. The crude residue was then purified by column chromatography on silica (10-15% EtOAc/hexanes gradient) to afford the title product in 9% yield (1.5 g, 4.27 mmol) over 4 steps.
^{1}H NMR (500 MHz, $CDCl_3$): δ δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.07 (t, *J* = 6.2 Hz, 1H), 5.00 (t, *J* = 7.0 Hz, 1H), 4.31 (t, *J* = 5.9 Hz, 1H), 3.87 (s, 3H), 2.93 (q, *J* = 6.8 Hz, 2H), 2.07 – 1.87 (m, 6H), 1.67 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H), 1.48 (p, *J* = 7.2 Hz, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.96, 136.67, 131.88, 131.70, 129.36, 124.20, 123.75, 114.34, 55.74, 43.09, 32.03, 29.94, 26.61, 25.84, 25.00, 23.49, 17.79 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{19}H_{29}NO_3S$) from $[M+H]^+$ requires m/z 351.18681, found m/z 351.1952, difference -1.46 ppm.
IR (neat): ν 3278, 2942, 1596, 1498, 1441, 1257, 1094, 1025, 832, 668 cm^{-1}.

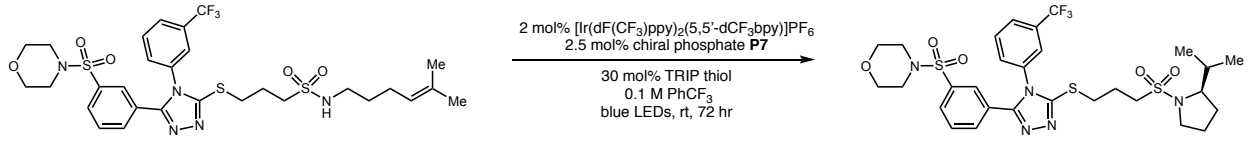
6. Synthesis of Products

Scheme S3: General Conditions for Products **2–18**, **21**,**23–25**



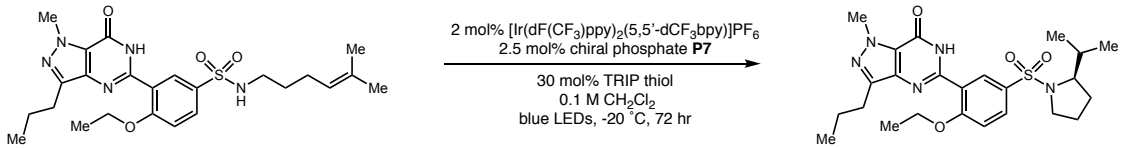
General conditions A: An oven dried 16x125mm culture tube with screw cap equipped with a teflon septum was charged with substrate (0.5 mmol, 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}CF_3bpy)]PF_6$ (0.001 mmol, 2 mol%, 1.2 mg), and chiral phosphate **P7**. The vial was evacuated and refilled three times with nitrogen, followed by the addition of degassed anhydrous trifluorotoluene (5.0 mL, 0.1 M) and 2,4,6-triisopropylbenzene thiol (0.15 mmol, 30 mol%, 35.5 mg). The vial was then sealed tightly with parafilm wrapped around the entire screwcap and stirred for 72 hours under irradiation with blue LED strips at -20 ˚C (see S5 for low temperature photoredox setup). Solvent was removed under vacuum and the crude product was purified by silica gel (25 gram) flash chromatography eluted with ethyl acetate/hexanes unless otherwise specified.

Scheme S4: Conditions for Product **19**



General conditions B: An oven dried 16x125mm culture tube with screw cap equipped with a teflon septum was charged with substrate (0.5 mmol, 1.0 equiv.), [Ir(dF-CF3-ppy)2(d(CF3)-bpy)]PF6 (0.001 mmol, 2 mol%, 1.2 mg), and chiral phosphate **P7**. The vial was evacuated and refilled three times with nitrogen, followed by the addition of degassed anhydrous trifluorotoluene (5.0 mL, 0.1 M) and 2,4,6-triisopropylbenzene thiol (0.15 mmol, 30 mol%, 35.5 mg). The vial was then sealed tightly with parafilm wrapped around the entire screwcap and stirred for 72 hours under irradiation with Kessil lamps at room temperature (see SI ## for photoredox setup). Solvent was removed under vacuum and the crude product was purified by silica gel (25 gram) flash chromatography eluted with ethylacetate/hexanes unless otherwise specified.

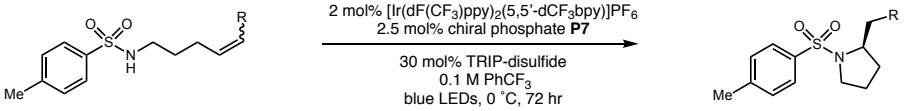
Scheme S5: Conditions for Product **22**



General conditions C: An oven dried 16x125mm culture tube with screw cap equipped with a teflon septum was charged with substrate (0.5 mmol, 1.0 equiv.), [Ir(dF-CF3-

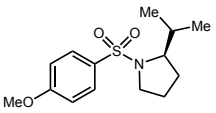
ppy)2(d(CF3)-bpy)]PF6 (0.001 mmol, 2 mol%, 1.2 mg), and chiral phosphate **P7**. The vial was evacuated and refilled three times with nitrogen, followed by the addition of degassed anhydrous dichloromethane (5.0 mL, 0.1 M) and 2,4,6-triisopropylbenzene thiol (0.15 mmol, 30 mol%, 35.5 mg). The vial was then sealed tightly with parafilm wrapped around the entire screwcap and stirred for 72 hours under irradiation with blue LED strips at -20 ˚C (see SI5 for low temperature photoredox setup). Solvent was removed under vacuum and the crude product was purified by silica gel (25 gram) flash chromatography eluted with ethyl acetate/hexanes unless otherwise specified.

Scheme S6: General Conditions for Products **26—27**



General conditions D: An oven dried 16x125mm culture tube with screw cap equipped with a teflon septum was charged with substrate (0.5 mmol, 1.0 equiv.), [Ir(dF-CF3-ppy)2(d(CF3)-bpy)]PF6 (0.001 mmol, 2 mol%, 1.2 mg), and chiral phosphate **P7**. The vial was evacuated and refilled three times with nitrogen, followed by the addition of degassed anhydrous trifluorotoluene (5.0 mL, 0.1 M) and 1,2-bis(2,4,6-triisopropylphenyl)disulfane (0.075 mmol, 15 mol%, 35.5 mg). The vial was then sealed tightly with parafilm wrapped around the entire screwcap and stirred for 72 hours under irradiation with blue LED strips at 0 ˚C (see SI S5 for low temperature photoredox setup). Solvent was removed under vacuum and the crude product was purified by silica gel (25 gram) flash chromatography eluted with ethyl acetate/hexanes unless otherwise specified.

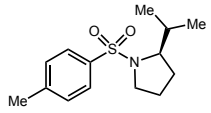
(*R*)-2-isopropyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine (**2**)



Under **General Conditions A**, the title compound was obtained as a white solid in 86% yield and 96:4 er after column chromatography (15% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$):
δ 7.77 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.56 – 3.38 (m, 1H), 3.33 – 3.25 (m, 2H), 2.20 – 2.09 (m, 1H), 1.74 – 1.55 (m, 2H), 1.52 – 1.41 (m, 1H), 1.41 – 1.28 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.9, 130.1, 129.7, 114.2, 65.7, 55.7, 49.6, 32.2, 26.3, 24.8, 20.0, 16.7 ppm.
HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 8.687min, t_r (minor) = 9.859 min.
HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12428, difference -0.2 ppm.
$[\alpha]_D^{22}$ = 88 (c = 1.00, CH_2Cl_2).

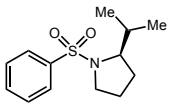
(*R*)-2-isopropyl-1-tosylpyrrolidine (**3**)



Under **General Conditions A**, the title compound was obtained as a white solid in 83% yield and 95:5 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.54 (dt, *J* = 8.1, 5.0 Hz, 1H), 3.33 (td, *J* = 6.9, 2.2 Hz, 2H), 2.45 (s, 3H), 2.19 (h , *J* = 5.9 Hz, 1H), 1.68 (dtd, *J* = 23.5, 12.2, 11.7, 6.0 Hz, 2H), 1.53 – 1.43 (m, 1H), 1.37 (dq, *J* = 12.3, 6.6, 6.1 Hz, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 1H) ppm
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 135.3, 129.7, 127.7, 65.8, 49.6, 32.2, 26.3, 24.7, 21.7, 20.0, 16.7 ppm.
HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min, 230 nm, t_r (major) = 6.546min, t_r (minor) = 5.978 min.
HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.1230, found m/z 267.12928, difference 0.1 ppm.
$[\alpha]_D^{21}$ = 82 (c = 0.99, CH_2Cl_2).

(*R*)-2-isopropyl-1-(phenylsulfonyl)pyrrolidine (**4**)

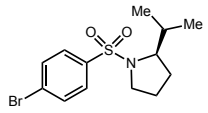


Under **General Conditions A**, the title compound was obtained as a white solid in 91% yield and 95:5 er after column chromatography (15% EtOAc/hexanes reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 – 7.79 (dt, J = 7.1, 1.2 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.49 (m, 1H), 3.54 (dt, *J* = 8.1, 5.1 Hz, 1H), 3.40 – 3.23 (m, 2H), 2.25 – 2.05 (m, 2H), 1.74 – 1.58 (m, 2H), 1.52 – 1.40 (m, 1H), 1.40 – 1.26 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H).

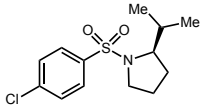
^{13}C NMR (126 MHz, $CDCl_3$): δ 138.2, 132.6, 129.1, 127.6, 77.4, 65.8, 49.6, 32.2, 26.3, 24.7, 20.0, 16.6 ppm.
HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 6.423 min, t_r (minor) = 6.818 min.
HRMS: (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 253.11365, found m/z 253.11346, difference 1.4 ppm.
$[\alpha]_D^{22}$ = 85 (c = 1.07, CH_2Cl_2).

(R)-1-((4-bromophenyl)sulfonyl)-2-isopropylpyrrolidine (**5**)



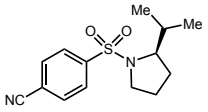
Under **General Conditions A**, the title compound was obtained as a white solid in 76% yield and 95:5 er after column chromatography (15% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 3.51 (dt, *J* = 8.1, 5.0 Hz, 1H), 3.38 – 3.18 (m, 2H), 2.17 (dp, *J* = 13.7, 6.9 Hz, 1H), 1.78 – 1.61 (m, 2H), 1.53 – 1.45 (m, 1H), 1.44 – 1.33 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 137.3, 132.4, 129.1, 127.6, 66.0, 49.6, 32.1, 26.3, 24.8, 19.9, 16.6 ppm.
HPLC: ChiralPak OD-H, 20% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 4.987 min, t_r (minor) = 5.868 min.
HRMS: (ESI) exact mass calculated for [M] ($C_{13}H_{18}BrNO_2S$) from $[M+H]^+$ requires m/z 331.02416, found m/z 331.02433, difference -0.5 ppm.
$[\alpha]_D^{21}$ = 75 (c = 1.04, CH_2Cl_2).

(R)-1-((4-chlorophenyl)sulfonyl)-2-isopropylpyrrolidine (**6**)



Under **General Conditions A**, the title compound was obtained as a white solid in 61% yield and 96:4 er after column chromatography (15% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 3.51 (dt, *J* = 8.1, 5.1 Hz, 1H), 3.36 – 3.25 (m, 2H), 2.16 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.79 – 1.61 (m, 1H), 1.54 – 1.45 (m, 1H), 1.40 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 139.1, 136.8, 129.4, 129.0, 65.9, 49.6, 32.1, 26.3, 24.8, 19.9, 16.6 ppm.
HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 5.796 min, t_r (minor) = 6.976 min.
HRMS: (ESI) exact mass calculated for [M] ($C_{13}H_{18}ClNO_2S$) from $[M+H]^+$ requires m/z 287.07468, found m/z 287.07468, difference 0.2 ppm.
$[\alpha]_D^{21}$ = 76 (c = 0.95, CH_2Cl_2).

(*R*)-4-((2-isopropylpyrrolidin-1-yl)sulfonyl)benzonitrile (**7**)



Under **General Conditions A**, the title compound was obtained as a white solid in 63% yield and 96:4 er after column chromatography (15% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 3.55 (dt, *J* = 8.1, 5.1 Hz, 1H), 3.55 (dt, m, 2H), 2.17 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.82 – 1.60 (m, 2H), 1.54 – 1.47 (m, 1H), 1.42 (dd, *J* = 12.3, 6.4 Hz, 1H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 2H) ppm.

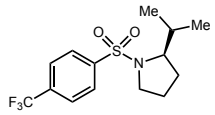
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.7, 133.0, 128.2, 117.5, 116.4, 66.2, 49.7, 32.1, 26.3, 24.8, 19.9, 16.5 ppm.

HPLC: ChiralPak OD-H, 20% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 8.653 min, t_r (minor) = 10.150 min.

HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{18}N_2O_2S$) from $[M+H]^+$ requires m/z 278.1089, found m/z 278.10873, difference 0.6 ppm.

$[\alpha]_D^{22}$ = 92 (c = 1.00, CH_2Cl_2).

(*R*)-2-isopropyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (**8**)



Under **General Conditions A**, the title compound was obtained as a white solid in 74% yield and 98:2 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 3.55 (dt, *J* = 8.1, 5.1 Hz, 1H), 3.39 – 3.28 (m, 2H), 2.28 – 2.07 (m, 1H), 1.79 – 1.64 (m, 2H), 1.54 – 1.45 (m, 1H), 1.40 (tt, *J* = 13.2, 6.9 Hz, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm.

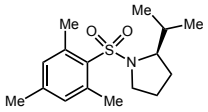
^{13}C NMR (126 MHz, $CDCl_3$): δ 141.9, 134.8 (q, J = 32.6 Hz), 128.1, 126.3 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 272.9 Hz), 66.0, 49.7, 32.1, 26.3, 24.8, 19.9, 16.5 ppm.

HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes,1 mL/min, 250 nm, t_r (major) = 5.405 min, t_r (minor) = 7.329 min.

HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{18}F_3NO_2S$) from $[M+H]^+$ requires m/z 321.10103, found m/z 321.10059, difference 1.4 ppm.

$[\alpha]_D^{21}$ = 68 (c = 0.97, CH_2Cl_2).

(R)-2-isopropyl-1-(mesitylsulfonyl)pyrrolidine (**9**)



Under **General Conditions A**, the title compound was obtained as a white solid in 91% yield and 92:8 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 2H), 3.85 (dt, *J* = 8.4, 4.6 Hz, 1H), 3.51 (dt, *J* = 10.5, 6.5 Hz, 1H), 3.03 (d, *J* = 10.4 Hz, 1H), 2.65 (s, 6H), 2.29 (s, 3H), 1.94 – 1.67 (m, 5H), 0.76 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H) ppm.

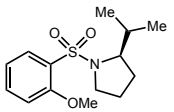
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.4, 140.2, 133.7, 132.0, 64.5, 48.8, 31.3, 26.3, 25.4, 23.04, 21.1, 19.9, 16.3 ppm.

HPLC: ChiralPak AD-H, 5% *i*-PrOH/hexanes, 0.75 mL/min, 210 nm, t_r (major) = 8.375 min, t_r (minor) = 8.914 min

HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{26}NO_2S$) from $[M+H]^+$ requires m/z 295.16060, found m/z 295.16022, difference 1.3 ppm.

$[\alpha]_D^{21}$ = 11 (c = 1.05, $CHCl_3$).

(*R*)-2-isopropyl-1-((2-methoxyphenyl)sulfonyl)pyrrolidine (**10**)



Under **General Conditions A**, the title compound was obtained as a white solid in 78% yield and 90:10 er after column chromatography (15% EtOAc/hexanes reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 3.80 (q, *J* = 6.4 Hz, 1H), 3.54 (ddd, *J* = 10.7, 7.7, 5.0 Hz, 1H), 3.27 (dt, *J* = 10.7, 7.1 Hz, 1H), 2.06 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.78 (dq, *J* = 13.1, 6.5 Hz, 1H), 1.69 (q, *J* = 6.7 Hz, 2H), 1.61 – 1.51 (m, 1H), 0.89 f(d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H) ppm.

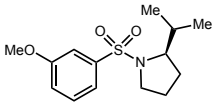
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.8, 134.2, 132.3, 127.7, 120.4, 112.1, 65.6, 55.9, 49.3, 31.8, 26.5, 25.0, 19.8, 16.6 ppm.

HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 0.75 mL/min, 230 nm, t_r (major) = 11.279 min, t_r (minor) = 11.914 min.

HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12438, difference -0.6 ppm.

$[\alpha]_D^{22}$ = 44 (c = 1.06, CH_2Cl_2).

(*R*)-2-isopropyl-1-((3-methoxyphenyl)sulfonyl)pyrrolidine (**11**)



Under **General Conditions A**, the title compound was obtained as a clear oil in 79% yield and 94:6 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ7.41 (d, *J* = 5.9 Hz, 2H), 7.34 (d, *J* = 3.0 Hz, 1H), 7.12 – 7.07 (m, 1H), 3.86 (s, 2H), 3.54 (dt, *J* = 8.1, 5.0 Hz, 1H), 3.37 – 3.26 (m, 2H), 2.23 – 2.07 (m, 1H), 1.66 (m, 2H), 1.50 (d, *J* = 7.7 Hz, 1H), 1.37 (dt, *J* = 13.4, 6.6 Hz, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H) ppm.

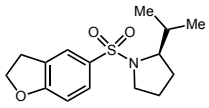
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.9, 139.3, 130.2, 119.8, 118.7, 112.6, 65.8, 55.8, 49.6, 32.2, 26.3, 24.7, 19.9, 16.6 ppm.

HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min, 210 nm, t_r (major) = 6.771 min, t_r (minor) = 7.658 min.

HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 283.12421, found m/z 283.12373, difference 1.7 ppm.

$[\alpha]_D^{22}$ = 80 (c = 1.07, CH_2Cl_2).

(*R*)-1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2-isopropylpyrrolidine (**12**)



Under **General Conditions A**, the title compound was obtained as a white solid in 92% yield and 96:4 er after column chromatography (15% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 – 7.64 (m, 1H), 7.62 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H),4.68 (t, *J* = 8.8 Hz, 2H), 3.50 (dt, *J* = 8.1, 5.0 Hz, 1H), 3.31 – 3.24 (m, 4H), 2.16 (dp, *J* = 13.7, 6.8 Hz, 1H), 1.75 – 1.59 (m, 2H), 1.54 – 1.45 (m, 1H), 1.39 (dt, *J* = 12.8, 6.4 Hz, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H) ppm.

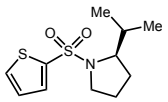
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.6, 129.9, 129.0, 124.8, 72.2, 65.5, 49.5, 32.1, 29.2, 26.2, 24.6, 19.9, 16.5 ppm.

HPLC: ChiralPak OD-H, 10% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 10.552 min, t_r (minor) = 12.204 min.

HRMS: (ESI) exact mass calculated for [M] ($C_{15}H_{21}NO_3S$) from $[M+H]^+$ requires m/z 295.12421, found m/z 295.12447, difference -0.9 ppm.

$[\alpha]_D^{21}$ = 81 (c = 1.01, CH_2Cl_2).

(*R*)-2-isopropyl-1-(thiophen-2-ylsulfonyl)pyrrolidine (**13**)



Under **General Conditions A**, the title compound was obtained as a white solid in 53% yield and 7:93 er after column chromatography (15% EtOAc/hexanes reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.12 (t, *J* = 3.8 Hz, 1H), 3.53 (dt, *J* = 8.7, 5.0 Hz, 1H), 3.37 (t, *J* = 6.6 Hz, 2H), 2.17 (dq, *J* = 13.2, 6.4 Hz, 1H), 1.80 – 1.60 (m, 2H), 1.53 – 1.45 (m, 1H), 1.45 – 1.32 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H).

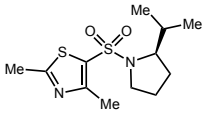
^{13}C NMR (126 MHz, $CDCl_3$): δ 132.1, 131.5, 127.4, 66.2, 49.9, 32.2, 26.3, 24.7, 19.9, 16.7 ppm.

HPLC: ChiralPak OZ-H, 20% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (minor) = 7.637 min, t_r (major = 10.096 min.

HRMS: (ESI) exact mass calculated for [M] ($C_{11}H_{17}NO_2S_2$) from $[M+H]^+$ requires m/z 259.07007, found m/z 259.06983, difference 0.9 ppm.

$[\alpha]_D^{22}$ = 77 (c = 1.00, CH_2Cl_2).

(*R*)-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)-2,4-dimethylthiazole (**14**)



Under **General Conditions A**, the title compound was obtained as a white solid in 79% yield and 97:3 er after column chromatography (25% EtOAc/hexanes) reported as an average of two trials.

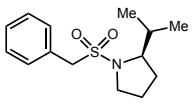
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.57 (dt, *J* = 8.0, 5.0 Hz, 1H), 3.36 (td, *J* = 6.5, 3.9 Hz, 2H), 2.69 (s, 3H), 2.67 (s, 3H), 2.18 (td, *J* = 6.9, 5.3 Hz, 1H), 1.87 – 1.68 (m, 2H), 1.68 – 1.52 (m, 2H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 156.3, 127.5, 66.1, 49.8, 32.0, 26.3, 24.9, 19.9, 19.6, 17.0, 16.5 ppm.

HPLC: ChiralPak AS-H, 15% *i*-PrOH/hexanes,1 mL/min, 250 nm, t_r (major) = 6.078 min, t_r (minor) = 6.868 min

HRMS: (ESI) exact mass calculated for [M] ($C_{12}H_{20}N_2O_2S_2$) from $[M+H]^+$ requires m/z 288.09662, found m/z 288.09632, difference 1.0 ppm.
$[\alpha]_D^{22}$ = 75 (c = 1.03, CH_2Cl_2).

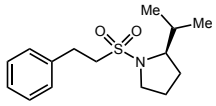
(*R*)-1-(benzylsulfonyl)-2-isopropylpyrrolidine (**15**)



Under **General Conditions A**, the title compound was obtained as a white solid in 98% yield and 91:9 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.40 (m, 2H), 7.40 – 7.33 (m, 3H), 4.22 (d, *J* = 2.6 Hz, 2H), 3.64 (dt, *J* = 7.4, 5.0 Hz, 1H), 3.37 – 3.25 (m, 1H), 3.09 (dt, *J* = 10.6, 6.6 Hz, 1H), 2.02 (dtd, *J* = 13.7, 6.9, 5.2 Hz, 1H), 1.83 – 1.60 (m, 4H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 130.9, 129.4, 128.8, 128.7, 65.6, 56.8, 49.8, 32.0, 26.2, 25.6, 19.8, 16.3 ppm.
HPLC: ChiralPak OJ-H, 20% *i*-PrOH/hexanes,1 mL/min, 210 nm, t_r (major) = 13.8988 min, t_r (minor) = 18.966 min
HRMS: (ESI) exact mass calculated for [M] ($C_{14}H_{21}NO_2S$) from $[M+H]^+$ requires m/z 267.12930, found m/z 167.12892, difference 1.4 ppm.
$[\alpha]_D^{21}$ = 33 (c = 1.03, CH_2Cl_2).

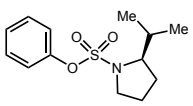
(*R*)-2-isopropyl-1-(phenethylsulfonyl)pyrrolidine (**16**)



Under **General Conditions A**, the title compound was obtained as a white solid in 98% yield and 4:96 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.20 (m, 3H), 3.80 – 3.70 (m, 1H), 3.55 (dt, *J* = 11.3, 6.3 Hz, 1H), 3.26 (dt, *J* = 11.0, 6.6 Hz, 1H), 3.21 – 3.08 (m, 4H), 2.16 – 2.05 (m, 1H), 1.93 – 1.71 (m, 4H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 138.5, 129.0, 128.6, 127.0, 65.3, 51.6, 49.4, 32.0, 29.7, 26.5, 25.7, 19.8, 16.4 ppm.
HPLC: ChiralPak AS-H, 10% *i*-PrOH/hexanes,1 mL/min, 210 nm, t_r (minor) = 16.280 min, t_r (major) = 21.111 min
HRMS: (ESI) exact mass calculated for [M] ($C_{15}H_{23}NO_2S$) from $[M+H]^+$ requires m/z 281.14495, found m/z 281.14469, difference 0.9 ppm.
IR (neat): ν 2962, 1335, 1147, 1004, 699 cm^{-1}.
$[\alpha]_D^{22}$ = 46 (c = 1.00, CH_2Cl_2).

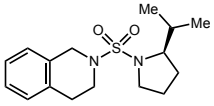
phenyl (*R*)-2-isopropylpyrrolidine-1-sulfonate (**17**)



Under **General Conditions A**, the title compound was obtained as a white solid in 87% yield and 92:8 er after column chromatography (7% EtOAc/hexanes) reported as an average of two trials.

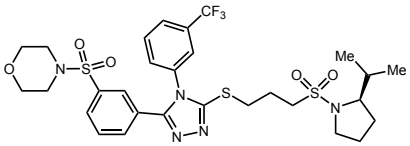
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, *J* = 7.9 Hz, 2H), 7.32 – 7.24 (m, 3H), 3.87 – 3.76 (m, 1H), 3.70 (dt, *J* = 10.6, 7.0 Hz, 1H), 3.40 (dt, *J* = 10.6, 6.6 Hz, 1H), 2.14 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.99 – 1.86 (m, 3H), 1.85 – 1.76 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 1H), 0.86 (d, *J* = 6.8 Hz, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 129.8, 126.6, 121.8, 67.2, 50.7, 31.3, 26.5, 25.1, 19.7, 16.5 ppm.
HRMS: exact mass calculated for [M] ($C_{13}H_{20}NO_3S$) from $[M+H]^+$ requires m/z 269.0856, found 269.10889 m/z, difference -1.2 ppm.
HPLC: ChiralPak OJ-H, 20% *i*-PrOH/hexanes, 1 mL/min, 210 nm, t_r (major) = 8.677 min, t_r (minor) = 13.894 min.
IR (neat): ν 2963, 1487, 1370, 1149, 1067, 1012, 847, 775, 689 cm^{-1}.
$[\alpha]_D^{21}$ = 46 (c = 1.01, $CHCl_3$).

(*R*)-2-((2-isopropylpyrrolidin-1-yl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (**18**)



Under **General Conditions A**, the title compound was obtained as a white solid in 80% yield and 94:6 er after column chromatography (7% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.16 (m, 2H), 7.16 – 7.11 (m, 1H), 7.11 – 7.06 (m, 1H), 4.44 (s, 2H), 3.81 (dt, *J* = 8.2, 5.1 Hz, 1H), 3.62 – 3.42 (m, 3H), 3.10 (dt, *J* = 10.4, 6.6 Hz, 1H), 2.94 (td, *J* = 6.1, 2.3 Hz, 2H), 2.23 – 2.07 (m, 1H), 1.94 – 1.78 (m, 3H), 1.74 (dp, *J* = 12.7, 5.9, 4.8 Hz, 1H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 133.6, 132.7, 129.1, 126.8, 126.5, 126.4, 65.8, 49.8, 47.8, 44.0, 31.5, 29.2, 26.1, 25.6, 19.9, 16.4 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{24}N_2O_2S$) from $[M+H]^+$ requires m/z 308.15585, found m/z 308.15585, difference 1.5 ppm.
HPLC: ChiralPak OJ-H, 20% *i*-PrOH/hexanes, 1 mL/min, 210 nm, t_r (major) = 17.940 min, t_r (minor) = 10.698 min.
IR (neat): ν 2961, 1328, 1148, 1073, 1023, 993, 955, 924, 759 cm^{-1}.
$[\alpha]_D^{21}$ = 20 (c = 1.01, CH_2Cl_2).

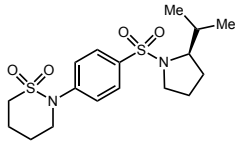
(*R*)-4-((3-(5-((3-((2-isopropylpyrrolidin-1-yl)sulfonyl)propyl)thio)-4-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-3-yl)phenyl)sulfonyl)morpholine (**19**)



Under **General Conditions B**, the title compound was obtained as a white solid in 83% yield and 13:87 er after column chromatography (5% acetone/dichloromethane) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 1.6 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 3.72 (dt, *J* = 7.2, 5.2 Hz, 1H), 3.68 (dd, *J* = 55.3, 5.0 Hz, 4H), 3.50 (ddd, *J* = 10.3, 7.1, 5.1 Hz, 1H), 3.45 (td, *J* = 6.9, 1.7 Hz, 1H), 3.23 (dt, *J* = 11.0, 6.6 Hz, 1H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.79 (dd, *J* = 6.5, 4.5 Hz, 1H), 2.41 (p, *J* = 7.1 Hz, 2H),

2.05 (pd, *J* = 6.9, 5.3 Hz, 1H), 1.94 – 1.69 (m, 4H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 153.2, 153.1, 136.1, 134.4, 133.1 (q, *J* = 33.7 Hz), 132.4, 131.3, 130.0, 129.9, 129.1, 127.4, 127.2 (q, *J* = 3.6 Hz), 127.0, 124.4 (q, *J* = 3.6 Hz), 122.9 (q, *J* = 272.9 Hz), 65.9, 65.3, 49.3, 48.1, 45.8, 31.9, 31.0, 26.3, 25.5, 23.8, 19.6, 16.3 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{29}H_{36}F_3N_5O_5S$) from $[M+H]^+$ requires m/z 687.18307, found m/z 687.18158, difference 2.2 ppm.
SFC: ChiralCel AD-H (25 x 0.46 cm), 40% IPA (DEA)/CO_2, 100 bar, 3 mL/min, 220 nm, t_r (minor) = 4.53 min, t_r (major) = 5.06 min.
IR (neat): ν 2965, 1454, 1332, 1260, 1170, 1132, 1113, 1070, 945, 722, 700 cm^{-1}.
$\mathbf{[\alpha]_D^{21}}$ = 79 (c = 1.08, CH_2Cl_2).

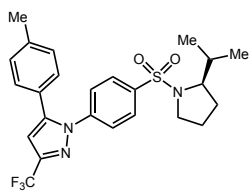
(*R*)-2-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1,2-thiazinane 1,1-dioxide (**20**)



Under **General Conditions A**, the title compound was obtained as a white solid in 88% yield and 95:5 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 3.83 – 3.79 (m, 2H), 3.52 (dt, *J* = 8.2, 5.0 Hz, 1H), 3.37 – 3.25 (m, 2H), 3.25 – 3.21 (m, 2H), 2.42 – 2.29 (m, 2H), 2.19 (dp, *J* = 13.6, 7.0 Hz, 1H), 1.94 (p, *J* = 5.9 Hz, 2H), 1.68 (dtd, *J* = 27.6, 12.4, 6.7 Hz, 2H), 1.55 – 1.47 (m, 1H), 1.42 (dq, *J* = 12.2, 6.8, 6.3 Hz, 1H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.3, 136.3, 128.6, 126.5, 65.8, 53.2, 51.0, 49.7, 32.2, 26.3, 24.8, 24.6, 24.3, 20.0, 16.6 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{17}H_{26}N_2O_4S_2$) from $[M+H]^+$ requires m/z 386.1334, found m/z 386.13287, difference 1.4 ppm.
SFC: ChiralCel AS-H (25 x 0.46 cm), 30% MeOH (DEA)/CO_2, 100 bar, 3 mL/min, 220 nm, t_r (major) = 2.55 min, t_r (minor) = 2.97 min.
IR (neat): ν 2962, 1336, 1155, 10093, 881, 737 cm^{-1}.
$\mathbf{[\alpha]_D^{21}}$ = 68 (c = 0.99, CH_2Cl_2).

(*R*)-1-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (**21**)

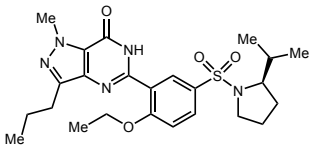
Under **General Conditions A**, the title compound was obtained as a white solid in 83% yield and 95:5 er after column chromatography (5% acetone/dichloromethane) reported as an average of two trials.



^{1}H NMR (500 MHz, $CDCl_3$): 7.83 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 3.49 (dt, *J* = 8.0, 5.1 Hz, 1H), 3.37 – 3.25 (m, 2H), 2.37 (s, 3H), 2.15 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.68 (ddq, *J* = 30.2, 12.1, 6.6 Hz, 3H), 1.52 – 1.43 (m, 1H), 1.51 – 1.44 (m, 1H), 1.38 (dq, *J* = 12.7, 6.8 Hz, 1H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H) ppm.

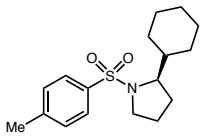
^{13}C NMR (126 MHz, $CDCl_3$): δ 145.4, 144.2 (q, *J* = 38.6 Hz) 142.5, 139.9, 137.8, 129.9, 128.9, 128.6, 125.8, 125.7, 121.2 (q, *J* = 269.1 Hz), 106.3, 66.0, 49.7, 32.1, 26.3, 24.7, 21.5, 19.9, 16.6 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{26}H_{26}F_3N_3O_2S$) from $[M+H]^+$ requires m/z 477.16978, found m/z 477.16818, difference 3.4 ppm.
HPLC: ChiralPak OZ-H, 20% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (major) = 6.815 min, t_r (minor) = 8.413 min
IR (neat): ν 2964, 1597, 1470, 2346, 1235, 1132, 1096, 975, 762 cm^{-1}.
$[\alpha]_D^{21}$ = 264 (c = 0.89, CH_2Cl_2).

(*R*)-5-(2-ethoxy-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one (**22**)



Under **General Conditions C**, the title compound was obtained as a white solid in 50% yield and 96:4 er after column chromatography (5% acetone/dichloromethane) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.84 (s, 1H), 8.91 (d, *J* = 2.4 Hz, 1H), 7.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 4.27 (s, 3H), 3.64 (dt, *J* = 7.7, 4.9 Hz, 1H), 3.35 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 3H), 2.22 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.85 (h, *J* = 7.3 Hz, 2H), 1.80 – 1.54 (m, 3H), 1.65 (t, *J* = 7.0 Hz, 3H), 1.55 – 1.41 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.0, 153.7, 147.0, 146.6, 138.4, 131.8, 131.6, 130.7, 124.5, 121.0, 112.9, 66.0, 65.9, 49.6, 38.3, 32.1, 27.8, 26.2, 24.7, 22.3, 19.8, 16.5, 14.6, 14.1 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{24}H_{33}N_5O_4S$) from $[M+H]^+$ requires m/z 487.22533, found m/z 487.2241, difference 2.5 ppm.
SFC: ChiralCel OD-H (25 x 0.46 cm), 40% MeOH (DEA)/CO_2, 100 bar, 3 mL/min, 220 nm, t_r (major) = 3.49 min, t_r (minor) = 3.90 min.
IR (neat): ν 3316, 2960, 2873, 1693, 1599, 1488, 1468, 1340, 1154, 1003, 927, 737, 653 cm^{-1}.
$[\alpha]_D^{21}$ = 179 (c = 1.07, CH_2Cl_2).

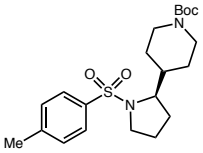
(*R*)-2-cyclohexyl-1-tosylpyrrolidine (**23**)



Under **General Conditions A**, the title compound was obtained as a white solid in 98% yield and 94:6 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ ^{1}H NMR 7.71 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.63 – 3.39 (m, 1H), 3.27 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 1.82 – 1.61 (m,

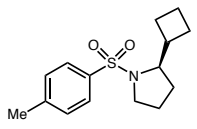
8H), 1.46 – 1.31 (m, 2H), 1.31 – 1.17 (m, 2H), 1.17 – 1.06 (m, 1H), 1.03 – 0.82 (m, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.2, 135.4, 129.7, 127.7, 65.3, 49.3, 42.4, 30.6, 27.7, 27.1, 26.8, 26.5, 26.3, 24.7, 21.7 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{17}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 307.1606, found m/z307.15999, difference 2.0 ppm.
HPLC: ChiralPak AS-H, 20% *i*-PrOH/hexanes,1 mL/min, 230 nm, t_r (major) = 10.619 min, t_r (minor) = 15.115 min
IR (neat): ν 2925, 1343, 1158, 1092, 997, 815, 665 cm^{-1}.
$[\alpha]_D^{22}$ = 110 (c = 1.01, CH_2Cl_2).

tert-butyl (*R*)-4-(1-tosylpyrrolidin-2-yl)piperidine-1-carboxylate (**24**)



Under **General Conditions A**, the title compound was obtained as a white solid in 91% yield and 90:10 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.19 (d, *J* = 12.6 Hz, 2H), 3.61 – 3.52 (m, 1H), 3.36 – 3.22 (m, 2H), 2.68 (q, *J* = 13.4 Hz, 2H), 2.45 (s, 3H), 1.99 – 1.89 (m, 1H), 1.77 – 1.61 (m, 4H), 1.48 (s, 9H), 1.43 (ddd, *J* = 17.2, 10.0, 4.4 Hz, 2H), 1.30 – 1.08 (m, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 154.8 143.4, 134.8, 129.7, 127.6, 79.4, 64.3, 49.2, 44.1, 43.8, 40.9, 29.5, 28.5, 27.0, 26.7, 24.5, 21.6 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{24}N_2O_2S$) from $[M+H\text{-}Boc]^+$ requires m/z 308.15585, found m/z 308.15573, difference 0.4 ppm.
HPLC: ChiralPak OJ-H, 20% *i*-PrOH/hexanes, 1 mL/min, 230 nm, t_r (major) = 10.738 min, t_r (minor) = 14.845 min.
IR (neat): ν 2792, 1686, 1422, 1364, 1342, 1157, 1090, 986, 817, 666 cm^{-1}.
$[\alpha]_D^{22}$ = 96 (c = 1.15, CH_2Cl_2).

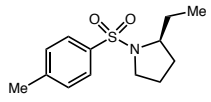
(*R*)-2-cyclobutyl-1-tosylpyrrolidine (**25**)



Under **General Conditions A**, the title compound was obtained as a white solid in 96% yield and 95:5 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.70 (td, *J* = 7.8, 2.7 Hz, 1H), 3.33 (ddd, *J* = 12.2, 7.5, 5.0 Hz, 1H), 3.23 (dt, *J* = 10.9, 7.4 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.42 (s, 3H), 2.05 – 1.97 (m, 2H), 1.91 (dtd, *J* = 9.0, 6.8, 5.9, 2.4 Hz, 1H), 1.85 – 1.64 (m, 4H), 1.54 – 1.42 (m, 2H), 1.41 – 1.32 (m, 1H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 135.5, 129.7, 127.7, 64.7, 49.1, 40.5, 28.5, 26.1, 25.0, 24.3, 21.7, 17.8 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{15}H_{22}NO_2S$) from $[M+H]^+$ requires m/z 279.1293, found m/z 279.12876, difference 2.0 ppm.

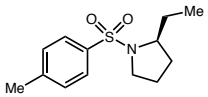
HPLC: ChiralPak AS-H, 25% *i*-PrOH/hexanes,1 mL/min, 250 nm, t_r (major) = 9.208 min, t_r (minor) = 11.650 min
IR (neat): ν 2960, 1598, 1342, 1092, 997, 816, 709 cm^{-1}.
$[\alpha]_D^{21}$ = 495 (c = 0.95, CH_2Cl_2).

(*S*)-2-ethyl-1-tosylpyrrolidine from *cis* (**26**)



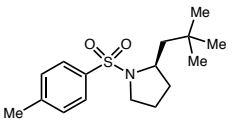
Under **General Conditions D**, the title compound was obtained as a white solid from (*Z*)-*N*-(hex-4-en-1-yl)-4-methylbenzenesulfonamide in 72% yield and 93:7 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.54 (dq, *J* = 10.4, 5.8 Hz, 1H), 3.38 (ddd, *J* = 10.5, 7.1, 5.2 Hz, 1H) , 3.19 (dt, *J* = 10.4, 7.2 Hz, 1H), 2.43 (s, 3H), 1.90 – 1.81 (m, 1H), 1.76 (dp, *J* = 12.1, 7.3 Hz, 1H), 1.57 (q, *J* = 5.8 Hz, 2H), 1.53 – 1.42 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 135.1, 129.7, 127.6, 62.0, 49.1, 30.3, 29.4, 24.3, 21.7, 10.5 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 153.11365, found m/z 253.11281, difference 3.3 ppm.
HPLC: ChiralPak AS-H, 20% IPA in Hexanes,1mL/min, 230 nm, tr (major) = 12.027 min, tr (minor) = 14.850 min
IR (neat): ν 2967, 2875, 1598, 1341, 1092, 995, 816 cm^{-1}.
$[\alpha]_D^{22}$ = 60 (c = 0.96, CH_2Cl_2).

(*S*)-2-ethyl-1-tosylpyrrolidine from *trans* (**26**)



Under **General Conditions D**, the title compound was obtained as a white solid from (*E*)-*N*-(hex-4-en-1-yl)-4-methylbenzenesulfonamide in 83% yield and 95:5 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.54 (dq, *J* = 10.4, 5.8 Hz, 1H), 3.38 (ddd, *J* = 10.5, 7.1, 5.2 Hz, 1H), 3.19 (dt, *J* = 10.4, 7.2 Hz, 1H), 2.43 (s, 3H), 1.90 – 1.81 (m, 1H), 1.76 (dp, *J* = 12.1, 7.3 Hz, 1H), 1.57 (q, *J* = 5.8 Hz, 2H), 1.53 – 1.42 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 135.1, 129.7, 127.6, 62.0, 49.1, 30.3, 29.4, 24.3, 21.7, 10.5 ppm.
HRMS: (ESI) exact mass calculated for [M] ($C_{13}H_{19}NO_2S$) from $[M+H]^+$ requires m/z 153.11365, found m/z 253.11295, difference 2.8 ppm
HPLC: ChiralPak AS-H, 20% IPA in Hexanes,1mL/min, 230 nm, tr (major) = 12.027 min, tr (minor) = 14.850 min
IR (neat): ν 2967, 2875, 1598, 1341, 1092, 995, 816 cm^{-1}.
$[\alpha]_D^{22}$ = 76 (c = 1.06, CH_2Cl_2).

(*R*)-2-neopentyl-1-tosylpyrrolidine from *cis* (**27**)



Under **General Conditions D**, the title compound was obtained from (*Z*)-*N*-(6,6-dimethylhept-4-en-1-yl)-4-methylbenzenesulfonamide (**S25**) as a white solid in 93% yield and 97:3 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.1 Hz, 2H) 7.31 (d, *J* = 8.1 Hz, 2H), 3.66 – 3.59 (m, 1H), 3.37 (dt, *J* = 11.4, 5.9 Hz, 1H), 3.13 (dt, *J* = 10.1, 7.3 Hz, 1H), 2.43 (s, 3H), 1.97 (d, *J* = 13.7 Hz, 1H), 1.78 (dq, *J* = 20.8, 7.2 Hz, 1H), 1.67 – 1.44 (m, 4H), 1.37 (dd, *J* = 13.8, 10.3 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 135.0, 129.7, 127.7, 57.9, 51.0, 48.6, 33.7, 30.5, 30.2, 24.4, 21.7 ppm.

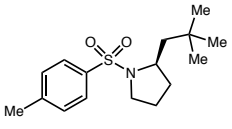
HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 295.1606, found m/z 295.1595, difference 3.7 ppm.

HPLC: ChiralPak AS-H, 20% *i*-PrOH/hexanes,1 mL/min, 230 nm, t_r (major) = 7.19 min, t_r (minor) = 10.386 min

IR (neat): ν 2953, 1343, 1158, 1092, 815, 663 cm^{-1}

$[\alpha]_D^{22}$ = 119 (c = 1.01, CH_2Cl_2).

(*R*)-2-neopentyl-1-tosylpyrrolidine from *trans* (**27**)



Under **General Conditions D**, the title compound was obtained from (*E*)-*N*-(6,6-dimethylhept-4-en-1-yl)-4-methylbenzenesulfonamide (**S26**) as a white solid in 48% yield and 96:4 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.1 Hz, 2H) 7.31 (d, *J* = 8.1 Hz, 2H), 3.66 – 3.59 (m, 1H), 3.37 (dt, *J* = 11.4, 5.9 Hz, 1H), 3.13 (dt, *J* = 10.1, 7.3 Hz, 1H), 2.43 (s, 3H), 1.97 (d, *J* = 13.7 Hz, 1H), 1.78 (dq, *J* = 20.8, 7.2 Hz, 1H), 1.67 – 1.44 (m, 4H), 1.37 (dd, *J* = 13.8, 10.3 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 135.0, 129.7, 127.7, 57.9, 51.0, 48.6, 33.7, 30.5, 30.2, 24.4, 21.7 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{16}H_{25}NO_2S$) from $[M+H]^+$ requires m/z 295.1606, found m/z 295.1601, difference 1.7 ppm.

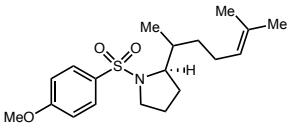
HPLC: ChiralPak AS-H, 20% *i*-PrOH/hexanes,1 mL/min, 230 nm, t_r (major) = 7.19 min, t_r (minor) = 10.386 min

IR (neat): ν 2953, 1343, 1158, 1092, 815, 663 cm^{-1}.

$[\alpha]_D^{22}$ = 107 (c = 0.97, CH_2Cl_2).

1-((4-methoxyphenyl)sulfonyl)-2-(6-methylhept-5-en-2-yl)pyrrolidine (mixture of diastereomers) (**28**)

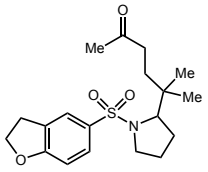
Under **General Conditions A**, the title compound was obtained from (*Z*)-*N*-(5,9-dimethyldeca-4,8-dien-1-yl)-4-methoxybenzenesulfonamide (**S27**) as a clear oil in 85% yield as a mixture of diastereomers (1.5:1 dr), inseparable by silica gel chromatography. The enantiomeric ratio for both diasteromers was determined to be 96:4 er, determined by HPLC on a chiral stationary phase.



^{1}H NMR (500 MHz, $CDCl_3$): (mixture of diastereomers) δ 7.70 (d, *J* = 8.9 Hz, 4H), 6.91 (dd, *J* = 8.8, 1.7 Hz, 4H), 5.09 – 4.98 (m, 2H), 3.80 (d, *J* = 1.3 Hz, 6H), 3.54 – 3.42 (m, 2H), 3.36 – 3.10 (m, 4H), 2.09 – 1.95 (m, 3H), 1.95 – 1.76 (m, 3H), 1.64 – 1.61 (m, 6H), 1.62 – 1.55 (m, 2H), 1.54 (s, 6H), 1.52 – 1.39 (m, 4H), 1.32 – 1.21 (m, 3.5H), 1.11 – 1.01 (m, 0.5H), 0.97 – 0.88 (m, 1.5H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): (mixture of diastereomers) δ 162.84, 131.59, 131.47, 130.22, 129.92, 129.68, 129.65, 124.88, 124.67, 114.21, 65.52, 64.43, 55.69, 49.87, 49.73, 37.21, 36.83, 34.48, 31.08, 26.97, 26.21, 26.13, 26.08, 25.87, 24.83, 24.72, 17.85, 17.84, 16.92, 13.72.
HRMS (mixture of diastereomers)**:** (ESI) exact mass calculated for [M] ($C_{19}H_{29}NO_3S$) from $[M+H]^+$ requires m/z 351.18681, found m/z 351.2065, difference 1.3 ppm.
HPLC: ChiralPak AS-H, 15% *i*-PrOH/hexanes, 1 mL/min, 250 nm, t_r (diastereomer 1, major enantiomer) = 11.740 min, t_r (diastereomer 2, major enantiomer) = 13.390 min, t_r (diastereomer 1, minor enantiomer) = 15.123 min, (diastereomer 2, minor enantiomer) = 17.830 min.
IR (neat) (mixture of diastereomers)**:** ν 2964, 1596, 1497, 1461, 1341, 1258, 1154, 1093, 1025, 834, 803 cm^{-1}.

Carboamination Procedure

(*R*)-5-(1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)pyrrolidin-2-yl)-5-methylhexan-2-one (**29**)



An oven dried 16x125mm culture tube with screw cap was charged with substrate (0.5 mmol, 1.0 equiv.), [Ir(dF-CF3-ppy)2(d(CF3)-bpy)]PF6 (0.001 mmol, 2 mol%, 1.2 mg), and chiral phosphate **P7** (0.0125 mmol, 2.5 mol%) . The vial was evacuated and refilled three times with nitrogen, followed by the addition of degassed anhydrous trifluorotoluene (5.0 mL, 0.1 M) and methyl vinyl ketone (2.0 mmol, 4 equiv., 140 mg, 167 uL). The reaction was then stirred for 72 hours under irradiation with blue LED strips at -20 ˚C (see S5 for low temperature photoredox setup). Solvent was removed under vacuum and the crude product was purified by silica gel (25 gram) flash chromatography eluted with EtOAc/hexanes to afford the title compound was obtained as a white solid in 65% yield and 95:5 er after column chromatography (10% EtOAc/hexanes) reported as an average of two trials.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.63 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.78 (dd, *J* = 8.8, 4.7 Hz, 1H), 3.54 (ddd, *J* = 11.7, 8.2, 2.8 Hz, 1H), 3.28 (t, *J* = 8.8 Hz, 2H), 3.08 (ddd, *J* = 12.7, 9.6, 6.9 Hz, 1H), 2.57 (ddd, *J* = 16.4, 11.4, 4.9 Hz, 1H), 2.39 (ddd, *J* = 16.5, 11.3, 5.1 Hz, 1H), 1.28 (s, 1H), 1.77 – 1.46 (m, 5H), 1.21 (dt, *J* = 20.0, 9.7 Hz, 1H), 0.95 (s, 3H), 0.86 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 209.7, 163.9, 131.0, 129.1, 128.4, 124.9, 109.7, 72.4, 68.0, 50.2, 38.9, 38.0, 32.9, 30.2, 29.3, 26.4, 25.2, 24.4, 23.5 ppm.

HRMS: (ESI) exact mass calculated for [M] ($C_{19}H_{27}NO_4S$) from $[M+H]^+$ requires m/z 365.16608, found m/z 365.16579, difference 0.8 ppm.

HPLC: ChiralPak AD-H, 20% *i*-PrOH/hexanes,1 mL/min, 250 nm, t_r (minor) = 8.221 min, t_r (major) = 9.231 min

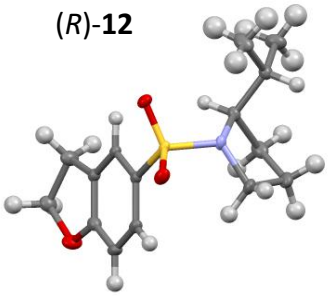
IR (neat): ν 2968, 1712, 1484, 1342, 1241, 1145, 1114, 1064, 980, 892, 696 cm^{-1}.

$[\alpha]_D^{21}$ = 496 (c = 1.05, CH_2Cl_2).

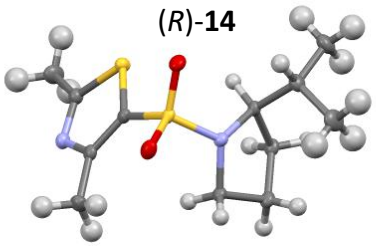
7. Determination of Absolute Configuration

The absolute configurations of products **12** and **14** were determined to be (*R*), and the rest of the products (**2-25**, **26**) were assigned by analogy.

(*R*)-**12**

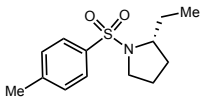


(*R*)-**14**

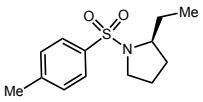


The crystal structures of **12** and **14** were obtained from a Cu X-ray source with 8.5% and 7.2% racemic twinning, respectively, consistent with the ee estimates of these products.

Further, literature reports of the optical rotation for was reported as the following: $[\alpha]_D^{23} = -81.9$ (c = 1.1 $CHCl_3$).[24] By convention the absolute configuration of **26** is assigned (*S*)-2-ethyl-1-tosylpyrrolidine, which is consistent with the facial selectivity observed for products **12** and **14**. To note, the same facial selectivity is observed for disubstituted olefins regardless of whether the alkene was cis or trans.



(*R*)-2-ethyl-1-tosylpyrrolidine
ref 23: $[\alpha]_D^{23} = -81.9$ (c = 1.1 $CHCl_3$)



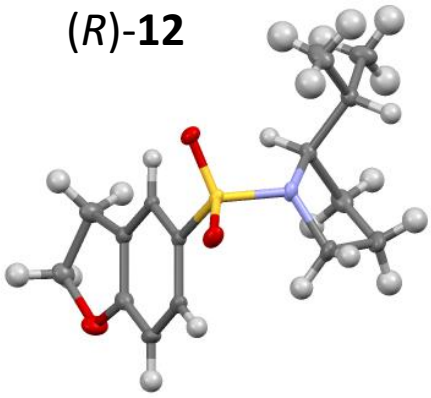
26 (from *cis* and *trans*)
(*S*)-2-ethyl-1-tosylpyrrolidine
$[\alpha]_D^{22} = 76$ (c = 1.06, CH_2Cl_2).

8. Crystallography Data

Crystal growth for products **12** and **14**

X-ray quality crystals of **12** were grown using vapor deposition method (EtOAc/pentane). To a 1 dram vial, **12** was added to a 1 dram vial and dissolved in a minimal amount of EtOAc.The opening of the vial was covered in foil and a small hole was made with a needle.the vial was then placed in a 20 mL scintillation vial and pentane was added to the outer vial. The Scintillation vial was sealed with a cap and left undisturbed for 48 hours at which point crystals formed in the inner vial, the structure of which was determined by X-ray diffraction. The same procedure was followed for compound **14**.

(*R*)-**12**



Compound **12**

Crystal data

$C_{15}H_{21}NO_3S$	D_x = 1.332 Mg m^{-3}
M_r = 295.39	Cu *K*a radiation, l = 1.54178 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 118 reflections
a = 7.5385 (3) Å	q = 6.0–39.9°
b = 11.3360 (4) Å	m = 2.02 mm^{-1}
c = 17.2319 (6) Å	*T* = 100 K
V = 1472.58 (9) Å^3	Prism
Z = 4	0.37 × 0.24 × 0.17 mm
F(000) = 632	

Data collection

Bruker Photon 100 CMOS diffractometer	2639 reflections with $I > 2\sigma(I)$
Radiation source: IμS microfocus source	$R_{int} = 0.037$
Detector resolution: 10.4167 pixels mm^{-1}	$\theta_{max} = 68.5°$, $\theta_{min} = 4.7°$
Absorption correction: multi-scan *SADABS* V2014/5 (Bruker AXS Inc.)	$h = -8 \rightarrow 9$
$T_{min} = 0.59$, $T_{max} = 0.72$	$k = -13 \rightarrow 13$
19399 measured reflections	$l = -20 \rightarrow 20$
2664 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.3211P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.10$	$\Delta\rangle_{max} = 0.14$ e Å^{-3}
2664 reflections	$\Delta\rangle_{min} = -0.26$ e Å^{-3}
184 parameters	Absolute structure: Flack x determined using 1077 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
0 restraints	Absolute structure parameter: 0.085 (16)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (PDJCBR1)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.97582 (5)	0.35248 (4)	0.29581 (2)	0.01369 (12)
O1	0.8852 (2)	0.30849 (13)	-0.04037 (8)	0.0272 (3)
O2	1.03570 (18)	0.23899 (11)	0.32243 (7)	0.0179 (3)
O3	1.07828 (18)	0.45600 (12)	0.31335 (8)	0.0205 (3)
N1	0.7796 (2)	0.37465 (13)	0.33278 (9)	0.0155 (3)
C1	0.9533 (2)	0.34349 (15)	0.19415 (10)	0.0148 (3)
C2	0.9301 (2)	0.23220 (16)	0.16042 (11)	0.0148 (4)
H2	0.92971	0.162855	0.191379	0.018*
C3	0.9077 (3)	0.22580 (17)	0.08102 (11)	0.0166 (4)
C4	0.8789 (3)	0.12253 (17)	0.02740 (11)	0.0234 (4)
H4A	0.759387	0.087928	0.034253	0.028*
H4B	0.969589	0.060548	0.035483	0.028*
C5	0.8986 (3)	0.18104 (18)	-0.05272 (11)	0.0240 (4)
H5A	1.01486	0.160852	-0.075926	0.029*
H5B	0.803668	0.153727	-0.088107	0.029*
C6	0.9070 (3)	0.32872 (17)	0.03704 (11)	0.0195 (4)
C7	0.9285 (3)	0.43948 (17)	0.06927 (12)	0.0208 (4)
H7	0.926277	0.508478	0.03799	0.025*
C8	0.9536 (3)	0.44632 (16)	0.14923 (11)	0.0187 (4)
H8	0.970891	0.520848	0.173288	0.022*
C9	0.6998 (3)	0.49352 (17)	0.31859 (12)	0.0220 (4)
H9A	0.745529	0.528409	0.26986	0.026*
H9B	0.725506	0.547915	0.362111	0.026*
C10	0.5018 (3)	0.46844 (18)	0.31266 (12)	0.0267 (4)
H10A	0.442509	0.525643	0.277863	0.032*
H10B	0.444588	0.471155	0.364331	0.032*
C11	0.4964 (3)	0.34384 (19)	0.27870 (11)	0.0249 (4)
H11A	0.521739	0.344742	0.222331	0.03*
H11B	0.379544	0.306395	0.287556	0.03*
C12	0.6430 (2)	0.27966 (17)	0.32353 (10)	0.0162 (4)
H12	0.692026	0.213862	0.291362	0.019*
C13	0.5813 (3)	0.23207 (17)	0.40256 (11)	0.0186 (4)
H13	0.517079	0.296851	0.430168	0.022*

C14	0.7352 (3)	0.1923 (2)	0.45371 (12)	0.0307 (5)
H14A	0.793449	0.123942	0.429964	0.046*
H14B	0.6902	0.170521	0.505102	0.046*
H14C	0.820857	0.256837	0.458913	0.046*
C15	0.4528 (3)	0.13030 (19)	0.39120 (13)	0.0290 (5)
H15A	0.348908	0.157843	0.362222	0.044*
H15B	0.415147	0.100307	0.441925	0.044*
H15C	0.511519	0.067091	0.362114	0.044*

Atomic displacement parameters (Å^2) for (PDJCBR1)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01118 (19)	0.0115 (2)	0.0184 (2)	0.00086 (16)	-0.00011 (15)	-0.00275 (16)
O1	0.0389 (9)	0.0254 (7)	0.0174 (7)	0.0001 (7)	-0.0026 (6)	0.0044 (6)
O2	0.0170 (6)	0.0147 (6)	0.0220 (6)	0.0031 (5)	-0.0022 (5)	-0.0001 (5)
O3	0.0163 (7)	0.0155 (6)	0.0297 (7)	-0.0014 (5)	-0.0030 (5)	-0.0044 (5)
N1	0.0133 (7)	0.0150 (7)	0.0181 (7)	0.0008 (6)	0.0021 (6)	-0.0042 (6)
C1	0.0127 (7)	0.0128 (8)	0.0189 (8)	0.0009 (7)	0.0031 (6)	0.0000 (7)
C2	0.0142 (9)	0.0114 (8)	0.0189 (8)	0.0019 (6)	0.0027 (7)	0.0007 (7)
C3	0.0153 (9)	0.0143 (9)	0.0201 (9)	0.0015 (7)	0.0021 (8)	0.0000 (7)
C4	0.0338 (11)	0.0199 (10)	0.0166 (8)	-0.0019 (8)	-0.0013 (8)	-0.0018 (8)
C5	0.0290 (11)	0.0250 (10)	0.0181 (9)	-0.0023 (8)	-0.0011 (8)	-0.0012 (8)
C6	0.0174 (9)	0.0224 (10)	0.0187 (9)	0.0016 (8)	0.0008 (7)	0.0037 (8)
C7	0.0205 (11)	0.0149 (9)	0.0270 (10)	0.0021 (8)	0.0040 (8)	0.0073 (7)
C8	0.0165 (9)	0.0121 (8)	0.0275 (9)	0.0002 (7)	0.0046 (8)	0.0007 (7)
C9	0.0200 (10)	0.0181 (9)	0.0280 (10)	0.0066 (8)	0.0051 (8)	-0.0021 (8)
C10	0.0200 (11)	0.0308 (10)	0.0293 (10)	0.0098 (9)	0.0042 (9)	0.0078 (8)
C11	0.0162 (9)	0.0373 (11)	0.0211 (9)	-0.0008 (10)	-0.0043 (7)	0.0054 (8)
C12	0.0141 (9)	0.0196 (9)	0.0150 (8)	-0.0018 (7)	0.0000 (7)	-0.0024 (7)
C13	0.0178 (9)	0.0205 (9)	0.0176 (8)	0.0004 (8)	0.0013 (7)	-0.0001 (7)
C14	0.0250 (12)	0.0464 (13)	0.0207 (10)	-0.0049 (10)	-0.0049 (9)	0.0078 (9)
C15	0.0293 (11)	0.0266 (11)	0.0312 (10)	-0.0087 (10)	-0.0053 (9)	0.0068 (9)

Geometric parameters (Å, º) for (PDJCBR1)

S1—O3	1.4371 (13)	C8—H8	0.95
S1—O2	1.4385 (13)	C9—C10	1.523 (3)
S1—N1	1.6302 (15)	C9—H9A	0.99
S1—C1	1.7630 (18)	C9—H9B	0.99
O1—C6	1.364 (2)	C10—C11	1.529 (3)
O1—C5	1.464 (2)	C10—H10A	0.99
N1—C9	1.496 (2)	C10—H10B	0.99
N1—C12	1.498 (2)	C11—C12	1.532 (3)
C1—C8	1.399 (3)	C11—H11A	0.99
C1—C2	1.400 (2)	C11—H11B	0.99
C2—C3	1.380 (3)	C12—C13	1.537 (3)
C2—H2	0.95	C12—H12	1.0
C3—C6	1.391 (3)	C13—C15	1.519 (3)
C3—C4	1.507 (3)	C13—C14	1.525 (3)
C4—C5	1.539 (3)	C13—H13	1.0
C4—H4A	0.99	C14—H14A	0.98
C4—H4B	0.99	C14—H14B	0.98
C5—H5A	0.99	C14—H14C	0.98
C5—H5B	0.99	C15—H15A	0.98
C6—C7	1.382 (3)	C15—H15B	0.98
C7—C8	1.393 (3)	C15—H15C	0.98
C7—H7	0.95		
O3—S1—O2	119.64 (8)	N1—C9—H9A	111.0
O3—S1—N1	106.24 (8)	C10—C9—H9A	111.0
O2—S1—N1	107.34 (8)	N1—C9—H9B	111.0
O3—S1—C1	107.93 (9)	C10—C9—H9B	111.0
O2—S1—C1	107.18 (8)	H9A—C9—H9B	109.0
N1—S1—C1	108.06 (8)	C9—C10—C11	102.96 (16)
C6—O1—C5	107.45 (14)	C9—C10—H10A	111.2
C9—N1—C12	110.73 (15)	C11—C10—H10A	111.2
C9—N1—S1	116.09 (12)	C9—C10—H10B	111.2
C12—N1—S1	118.11 (12)	C11—C10—H10B	111.2
C8—C1—C2	121.42 (16)	H10A—C10—H10B	109.1
C8—C1—S1	120.09 (14)	C10—C11—C12	103.09 (15)

C2—C1—S1	118.47 (13)	C10—C11—H11A	111.1
C3—C2—C1	118.30 (17)	C12—C11—H11A	111.1
C3—C2—H2	120.9	C10—C11—H11B	111.1
C1—C2—H2	120.9	C12—C11—H11B	111.1
C2—C3—C6	119.76 (18)	H11A—C11—H11B	109.1
C2—C3—C4	131.76 (17)	N1—C12—C11	102.00 (15)
C6—C3—C4	108.47 (16)	N1—C12—C13	111.47 (14)
C3—C4—C5	101.62 (15)	C11—C12—C13	113.27 (15)
C3—C4—H4A	111.4	N1—C12—H12	110.0
C5—C4—H4A	111.4	C11—C12—H12	110.0
C3—C4—H4B	111.4	C13—C12—H12	110.0
C5—C4—H4B	111.4	C15—C13—C14	109.57 (17)
H4A—C4—H4B	109.3	C15—C13—C12	110.21 (15)
O1—C5—C4	106.76 (15)	C14—C13—C12	112.67 (16)
O1—C5—H5A	110.4	C15—C13—H13	108.1
C4—C5—H5A	110.4	C14—C13—H13	108.1
O1—C5—H5B	110.4	C12—C13—H13	108.1
C4—C5—H5B	110.4	C13—C14—H14A	109.5
H5A—C5—H5B	108.6	C13—C14—H14B	109.5
O1—C6—C7	124.06 (16)	H14A—C14—H14B	109.5
O1—C6—C3	113.10 (17)	C13—C14—H14C	109.5
C7—C6—C3	122.84 (17)	H14A—C14—H14C	109.5
C6—C7—C8	117.64 (17)	H14B—C14—H14C	109.5
C6—C7—H7	121.2	C13—C15—H15A	109.5
C8—C7—H7	121.2	C13—C15—H15B	109.5
C7—C8—C1	120.04 (17)	H15A—C15—H15B	109.5
C7—C8—H8	120.0	C13—C15—H15C	109.5
C1—C8—H8	120.0	H15A—C15—H15C	109.5
N1—C9—C10	103.69 (16)	H15B—C15—H15C	109.5
O3—S1—N1—C9	45.13 (15)	C4—C3—C6—O1	-1.4 (2)
O2—S1—N1—C9	174.23 (13)	C2—C3—C6—C7	0.2 (3)
C1—S1—N1—C9	-70.48 (15)	C4—C3—C6—C7	179.36 (19)
O3—S1—N1—C12	-179.76 (13)	O1—C6—C7—C8	-178.54 (19)
O2—S1—N1—C12	-50.66 (15)	C3—C6—C7—C8	0.7 (3)
C1—S1—N1—C12	64.63 (15)	C6—C7—C8—C1	-1.1 (3)

O3—S1—C1—C8	-29.13 (17)	C2—C1—C8—C7	0.7 (3)
O2—S1—C1—C8	-159.23 (15)	S1—C1—C8—C7	-177.36 (15)
N1—S1—C1—C8	85.37 (16)	C12—N1—C9—C10	8.6 (2)
O3—S1—C1—C2	152.77 (14)	S1—N1—C9—C10	146.83 (13)
O2—S1—C1—C2	22.67 (16)	N1—C9—C10—C11	-30.97 (19)
N1—S1—C1—C2	-92.73 (15)	C9—C10—C11—C12	42.23 (19)
C8—C1—C2—C3	0.2 (3)	C9—N1—C12—C11	17.22 (18)
S1—C1—C2—C3	178.27 (14)	S1—N1—C12—C11	-120.11 (14)
C1—C2—C3—C6	-0.6 (3)	C9—N1—C12—C13	-103.95 (17)
C1—C2—C3—C4	-179.6 (2)	S1—N1—C12—C13	118.72 (15)
C2—C3—C4—C5	-170.5 (2)	C10—C11—C12—N1	-36.09 (17)
C6—C3—C4—C5	10.5 (2)	C10—C11—C12—C13	83.82 (18)
C6—O1—C5—C4	15.5 (2)	N1—C12—C13—C15	-176.06 (16)
C3—C4—C5—O1	-15.5 (2)	C11—C12—C13—C15	69.6 (2)
C5—O1—C6—C7	170.1 (2)	N1—C12—C13—C14	-53.3 (2)
C5—O1—C6—C3	-9.1 (2)	C11—C12—C13—C14	-167.68 (18)
C2—C3—C6—O1	179.49 (17)		

Hydrogen-bond geometry (Å, º) for (PDJCBR1)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O3^{i}	0.95	2.35	3.164 (2)	144
C9—H9*B*···O1^{ii}	0.99	2.48	3.370 (2)	149
C8—H8···O2^{iii}	0.95	2.47	3.354 (2)	154

Symmetry codes: (i) -*x*+2, *y*-1/2, -*z*+1/2; (ii) -*x*+3/2, -*y*+1, *z*+1/2; (iii) -*x*+2, *y*+1/2, -*z*+1/2.

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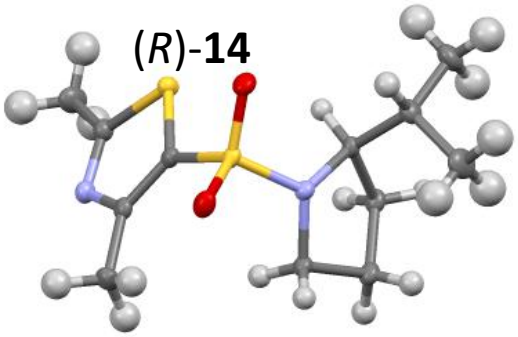


Compound **14**

Crystal data

$C_{12}H_{20}N_2O_2S_2$	D_x = 1.330 Mg m^{-3}
M_r = 288.42	Cu $K\alpha$ radiation, λ = 1.54178 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 9860 reflections
a = 7.4499 (2) Å	θ = 4.7–70.1°
b = 10.1587 (3) Å	μ = 3.33 mm^{-1}
c = 19.0266 (5) Å	T = 100 K
V = 1439.96 (7) Å^3	Prism
Z = 4	0.18 × 0.18 × 0.12 mm
F(000) = 616	

Data collection

Bruker Photon 100 CMOS diffractometer	2639 reflections with $I > 2\sigma(I)$
Radiation source: IμS microfocus source	R_{int} = 0.036
Detector resolution: 10.4167 pixels mm^{-1}	θ_{max} = 70.2°, θ_{min} = 4.7°
Absorption correction: multi-scan *SADABS* V2014/5 (Bruker AXS Inc.)	h = -8→9
T_{min} = 0.56, T_{max} = 0.69	k = -12→12
18997 measured reflections	l = -23→23
2726 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.023	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.249P]$ where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2)$ = 0.060	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.09	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
2726 reflections	$\Delta\rho_{min}$ = -0.20 e Å^{-3}
168 parameters	Absolute structure: Refined as an inversion twin.
0 restraints	Absolute structure parameter: 0.072 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (cu_PDJCBR2_0m)

	x	y	z	U_{iso}*/U_{eq}
S1	0.51416 (7)	0.67723 (5)	0.67599 (2)	0.01871 (13)
O1	0.4821 (2)	0.37292 (14)	0.67311 (8)	0.0216 (3)
N1	0.4525 (3)	0.79626 (18)	0.55974 (9)	0.0208 (4)
C1	0.4764 (4)	0.9520 (2)	0.65906 (12)	0.0308 (5)
H1A	0.374115	1.002326	0.640993	0.046*
H1B	0.588268	0.997532	0.647059	0.046*
H1C	0.466632	0.944113	0.710247	0.046*
S2	0.53200 (7)	0.41367 (5)	0.60364 (2)	0.01591 (13)
O2	0.4441 (2)	0.35803 (15)	0.54380 (8)	0.0226 (3)
N2	0.7444 (2)	0.38707 (16)	0.59466 (9)	0.0161 (4)
C2	0.4768 (3)	0.8176 (2)	0.62678 (11)	0.0204 (4)
C3	0.4653 (3)	0.6645 (2)	0.54324 (10)	0.0181 (4)
C4	0.4973 (3)	0.58475 (19)	0.59982 (10)	0.0159 (4)
C5	0.4430 (3)	0.6281 (2)	0.46740 (11)	0.0247 (5)
H5A	0.333370	0.668596	0.448947	0.037*
H5B	0.434403	0.532127	0.463104	0.037*
H5C	0.546761	0.659585	0.440567	0.037*
C6	0.8251 (3)	0.4252 (2)	0.52612 (11)	0.0184 (4)
H6A	0.780539	0.512240	0.510467	0.022*

H6B	0.798509	0.359033	0.489388	0.022*
C7	1.0250 (3)	0.4301 (2)	0.54227 (11)	0.0209 (4)
H7A	1.088170	0.491472	0.510329	0.025*
H7B	1.080121	0.341690	0.538309	0.025*
C8	1.0295 (3)	0.4798 (2)	0.61838 (11)	0.0201 (4)
H8A	1.019046	0.576908	0.619815	0.024*
H8B	1.142967	0.453719	0.641636	0.024*
C9	0.8680 (3)	0.4150 (2)	0.65477 (11)	0.0164 (4)
H9	0.810198	0.480512	0.686828	0.020*
C10	0.9071 (3)	0.2885 (2)	0.69599 (12)	0.0222 (5)
H10	0.788806	0.249305	0.709394	0.027*
C11	1.0077 (4)	0.1858 (2)	0.65343 (13)	0.0347 (6)
H11A	0.942196	0.167880	0.609811	0.052*
H11B	1.017968	0.104532	0.680877	0.052*
H11C	1.127949	0.218777	0.642155	0.052*
C12	1.0073 (4)	0.3196 (2)	0.76398 (12)	0.0317 (5)
H12A	1.122403	0.361386	0.752788	0.048*
H12B	1.028907	0.237881	0.790017	0.048*
H12C	0.935054	0.379488	0.792787	0.048*

Atomic displacement parameters (Å^2) for (cu_PDJCBR2_0m)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0233 (3)	0.0178 (2)	0.0150 (2)	0.0030 (2)	0.0010 (2)	-0.00050 (17)
O1	0.0187 (8)	0.0221 (7)	0.0240 (7)	-0.0015 (6)	0.0061 (7)	0.0040 (6)
N1	0.0217 (9)	0.0202 (8)	0.0206 (9)	0.0038 (8)	0.0006 (8)	0.0013 (7)
C1	0.0476 (15)	0.0194 (10)	0.0252 (11)	0.0071 (11)	0.0031 (12)	-0.0019 (8)
S2	0.0118 (2)	0.0158 (2)	0.0201 (2)	-0.00100 (18)	0.00128 (19)	-0.00069 (18)
O2	0.0168 (8)	0.0231 (7)	0.0277 (8)	-0.0026 (6)	-0.0029 (6)	-0.0060 (6)
N2	0.0134 (8)	0.0183 (9)	0.0165 (8)	0.0000 (7)	0.0016 (7)	0.0006 (7)
C2	0.0218 (10)	0.0188 (10)	0.0205 (9)	0.0045 (9)	0.0010 (9)	0.0011 (8)
C3	0.0138 (9)	0.0213 (10)	0.0190 (10)	0.0024 (9)	-0.0006 (8)	-0.0008 (8)
C4	0.0123 (9)	0.0196 (9)	0.0159 (8)	0.0010 (8)	0.0007 (8)	-0.0021 (7)
C5	0.0271 (12)	0.0297 (11)	0.0174 (10)	0.0017 (10)	-0.0041 (9)	-0.0004 (9)
C6	0.0159 (10)	0.0216 (10)	0.0178 (9)	0.0021 (9)	0.0031 (8)	0.0016 (8)

C7	0.0165 (10)	0.0239 (10)	0.0223 (10)	0.0014 (9)	0.0028 (9)	0.0036 (8)
C8	0.0150 (9)	0.0206 (9)	0.0247 (10)	-0.0015 (9)	0.0000 (9)	0.0011 (8)
C9	0.0155 (10)	0.0161 (10)	0.0177 (10)	0.0019 (8)	-0.0010 (8)	0.0002 (8)
C10	0.0246 (11)	0.0201 (11)	0.0218 (11)	0.0004 (9)	-0.0013 (9)	0.0044 (8)
C11	0.0493 (17)	0.0203 (10)	0.0346 (12)	0.0104 (12)	0.0009 (12)	0.0031 (9)
C12	0.0381 (14)	0.0324 (12)	0.0246 (11)	0.0049 (12)	-0.0077 (11)	0.0056 (9)

Geometric parameters (Å, º) for (cu_PDJCBR2_0m)

S1—C2	1.729 (2)	C6—H6A	0.9900
S1—C4	1.7316 (19)	C6—H6B	0.9900
O1—S2	1.4341 (15)	C7—C8	1.534 (3)
N1—C2	1.306 (3)	C7—H7A	0.9900
N1—C3	1.378 (3)	C7—H7B	0.9900
C1—C2	1.497 (3)	C8—C9	1.536 (3)
C1—H1A	0.9800	C8—H8A	0.9900
C1—H1B	0.9800	C8—H8B	0.9900
C1—H1C	0.9800	C9—C10	1.533 (3)
S2—O2	1.4300 (16)	C9—H9	1.0000
S2—N2	1.6140 (17)	C10—C11	1.519 (3)
S2—C4	1.759 (2)	C10—C12	1.527 (3)
N2—C6	1.488 (3)	C10—H10	1.0000
N2—C9	1.496 (3)	C11—H11A	0.9800
C3—C4	1.368 (3)	C11—H11B	0.9800
C3—C5	1.499 (3)	C11—H11C	0.9800
C5—H5A	0.9800	C12—H12A	0.9800
C5—H5B	0.9800	C12—H12B	0.9800
C5—H5C	0.9800	C12—H12C	0.9800
C6—C7	1.521 (3)		
C2—S1—C4	89.00 (10)	H6A—C6—H6B	109.1
C2—N1—C3	111.97 (18)	C6—C7—C8	102.88 (18)
C2—C1—H1A	109.5	C6—C7—H7A	111.2
C2—C1—H1B	109.5	C8—C7—H7A	111.2
H1A—C1—H1B	109.5	C6—C7—H7B	111.2
C2—C1—H1C	109.5	C8—C7—H7B	111.2
H1A—C1—H1C	109.5	H7A—C7—H7B	109.1

H1B—C1—H1C	109.5	C7—C8—C9	105.50 (18)
O2—S2—O1	120.06 (10)	C7—C8—H8A	110.6
O2—S2—N2	107.37 (9)	C9—C8—H8A	110.6
O1—S2—N2	107.67 (9)	C7—C8—H8B	110.6
O2—S2—C4	106.88 (10)	C9—C8—H8B	110.6
O1—S2—C4	106.57 (9)	H8A—C8—H8B	108.8
N2—S2—C4	107.77 (9)	N2—C9—C10	110.41 (17)
C6—N2—C9	111.82 (16)	N2—C9—C8	102.65 (16)
C6—N2—S2	116.47 (13)	C10—C9—C8	116.16 (18)
C9—N2—S2	119.40 (14)	N2—C9—H9	109.1
N1—C2—C1	123.48 (19)	C10—C9—H9	109.1
N1—C2—S1	114.47 (16)	C8—C9—H9	109.1
C1—C2—S1	122.04 (16)	C11—C10—C12	110.6 (2)
C4—C3—N1	114.08 (18)	C11—C10—C9	113.38 (19)
C4—C3—C5	129.07 (19)	C12—C10—C9	110.66 (18)
N1—C3—C5	116.85 (18)	C11—C10—H10	107.3
C3—C4—S1	110.47 (15)	C12—C10—H10	107.3
C3—C4—S2	130.04 (15)	C9—C10—H10	107.3
S1—C4—S2	119.40 (11)	C10—C11—H11A	109.5
C3—C5—H5A	109.5	C10—C11—H11B	109.5
C3—C5—H5B	109.5	H11A—C11—H11B	109.5
H5A—C5—H5B	109.5	C10—C11—H11C	109.5
C3—C5—H5C	109.5	H11A—C11—H11C	109.5
H5A—C5—H5C	109.5	H11B—C11—H11C	109.5
H5B—C5—H5C	109.5	C10—C12—H12A	109.5
N2—C6—C7	103.13 (16)	C10—C12—H12B	109.5
N2—C6—H6A	111.1	H12A—C12—H12B	109.5
C7—C6—H6A	111.1	C10—C12—H12C	109.5
N2—C6—H6B	111.1	H12A—C12—H12C	109.5
C7—C6—H6B	111.1	H12B—C12—H12C	109.5
O2—S2—N2—C6	50.57 (17)	O1—S2—C4—C3	-155.4 (2)
O1—S2—N2—C6	-178.86 (14)	N2—S2—C4—C3	89.2 (2)
C4—S2—N2—C6	-64.25 (16)	O2—S2—C4—S1	157.72 (12)
O2—S2—N2—C9	-170.23 (15)	O1—S2—C4—S1	28.19 (15)
O1—S2—N2—C9	-39.65 (17)	N2—S2—C4—S1	-87.14 (13)

C4—S2—N2—C9	74.96 (17)	C9—N2—C6—C7	20.3 (2)
C3—N1—C2—C1	177.9 (2)	S2—N2—C6—C7	162.49 (14)
C3—N1—C2—S1	-1.0 (3)	N2—C6—C7—C8	-34.4 (2)
C4—S1—C2—N1	0.5 (2)	C6—C7—C8—C9	37.1 (2)
C4—S1—C2—C1	-178.3 (2)	C6—N2—C9—C10	-121.95 (18)
C2—N1—C3—C4	1.0 (3)	S2—N2—C9—C10	97.10 (18)
C2—N1—C3—C5	-179.0 (2)	C6—N2—C9—C8	2.5 (2)
N1—C3—C4—S1	-0.6 (2)	S2—N2—C9—C8	-138.45 (14)
C5—C3—C4—S1	179.4 (2)	C7—C8—C9—N2	-24.4 (2)
N1—C3—C4—S2	-177.23 (17)	C7—C8—C9—C10	96.2 (2)
C5—C3—C4—S2	2.7 (4)	N2—C9—C10—C11	64.4 (2)
C2—S1—C4—C3	0.06 (17)	C8—C9—C10—C11	-52.0 (3)
C2—S1—C4—S2	177.09 (14)	N2—C9—C10—C12	-170.68 (18)
O2—S2—C4—C3	-25.9 (2)	C8—C9—C10—C12	73.0 (2)

Hydrogen-bond geometry (Å, º) for (cu_PDJCBR2_0m)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*C*···O1^{i}	0.98	2.37	3.307 (3)	161
C5—H5*B*···O2	0.98	2.34	3.104 (3)	134
C6—H6*B*···O2^{ii}	0.99	2.54	3.292 (3)	133

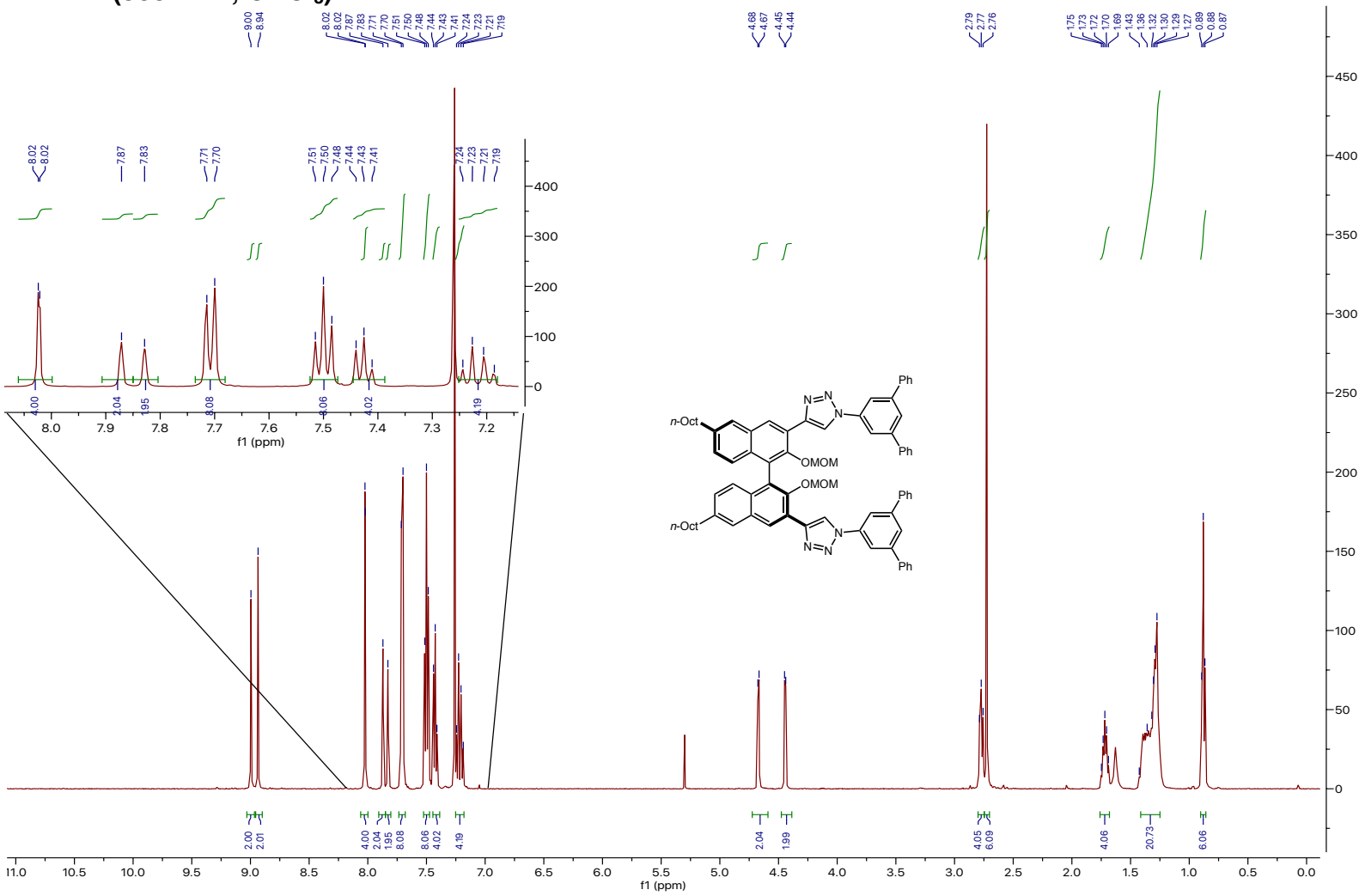
Symmetry codes: (i) -*x*+1, *y*+1/2, -*z*+3/2; (ii) *x*+1/2, -*y*+1/2, -*z*+1.

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

9. Catalyst NMR Spectra

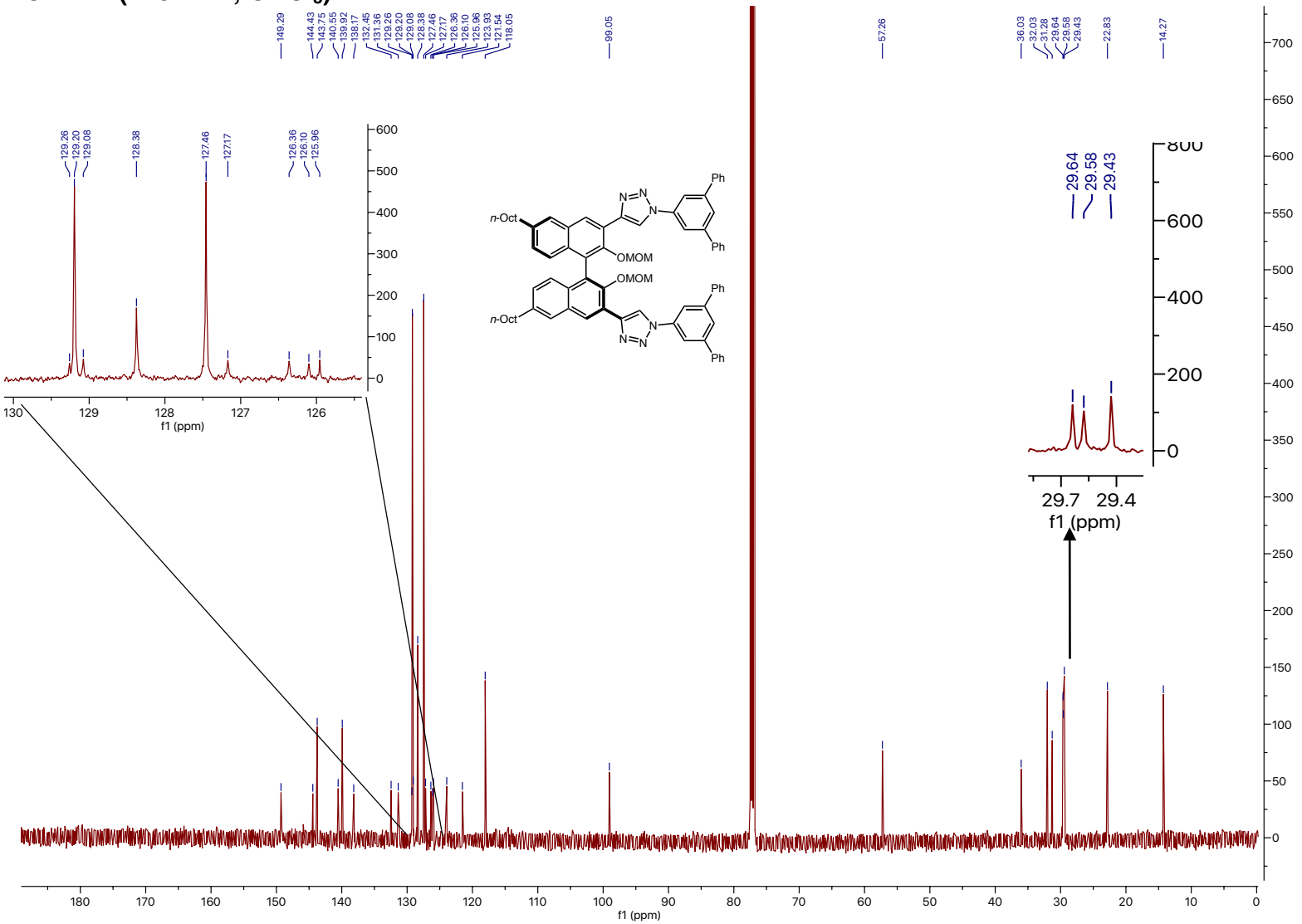
(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazole) (**S6.1**)

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



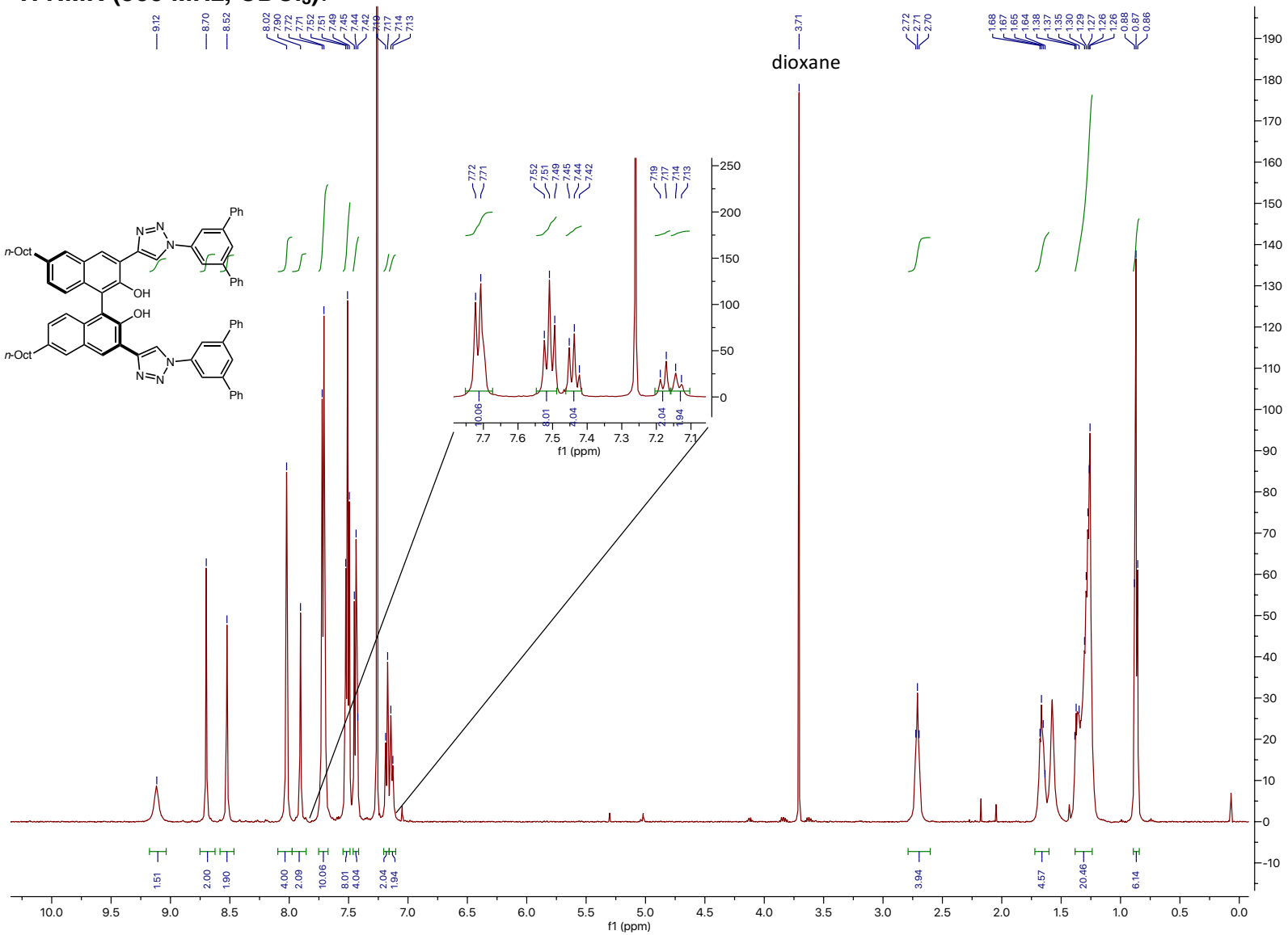
(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazole) (**S6.1**)

^{13}C NMR (126 MHz, $CDCl_3$):



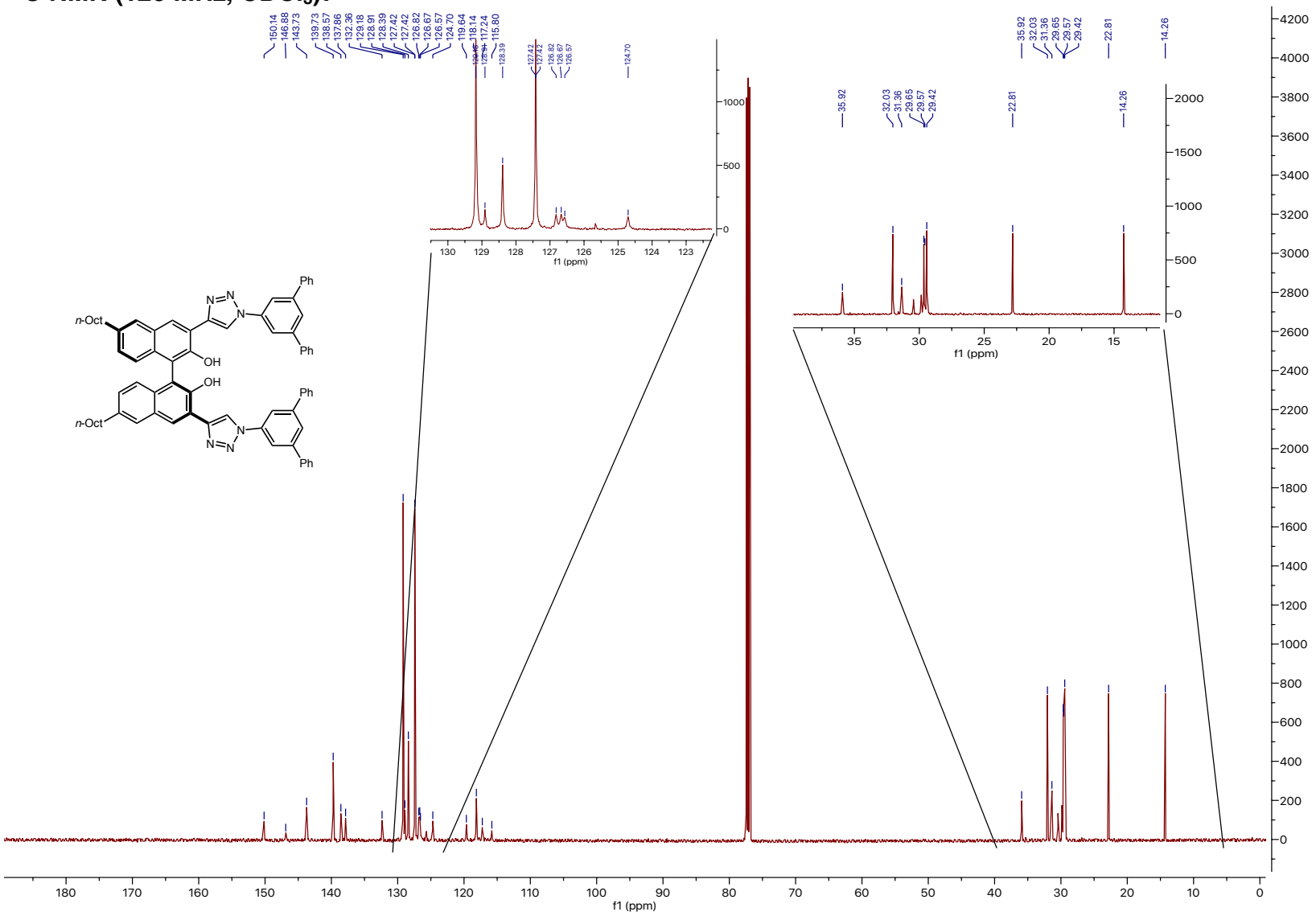
(*S*)-3,3'-bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazol-4-yl)- 6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (**S7.1**)

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



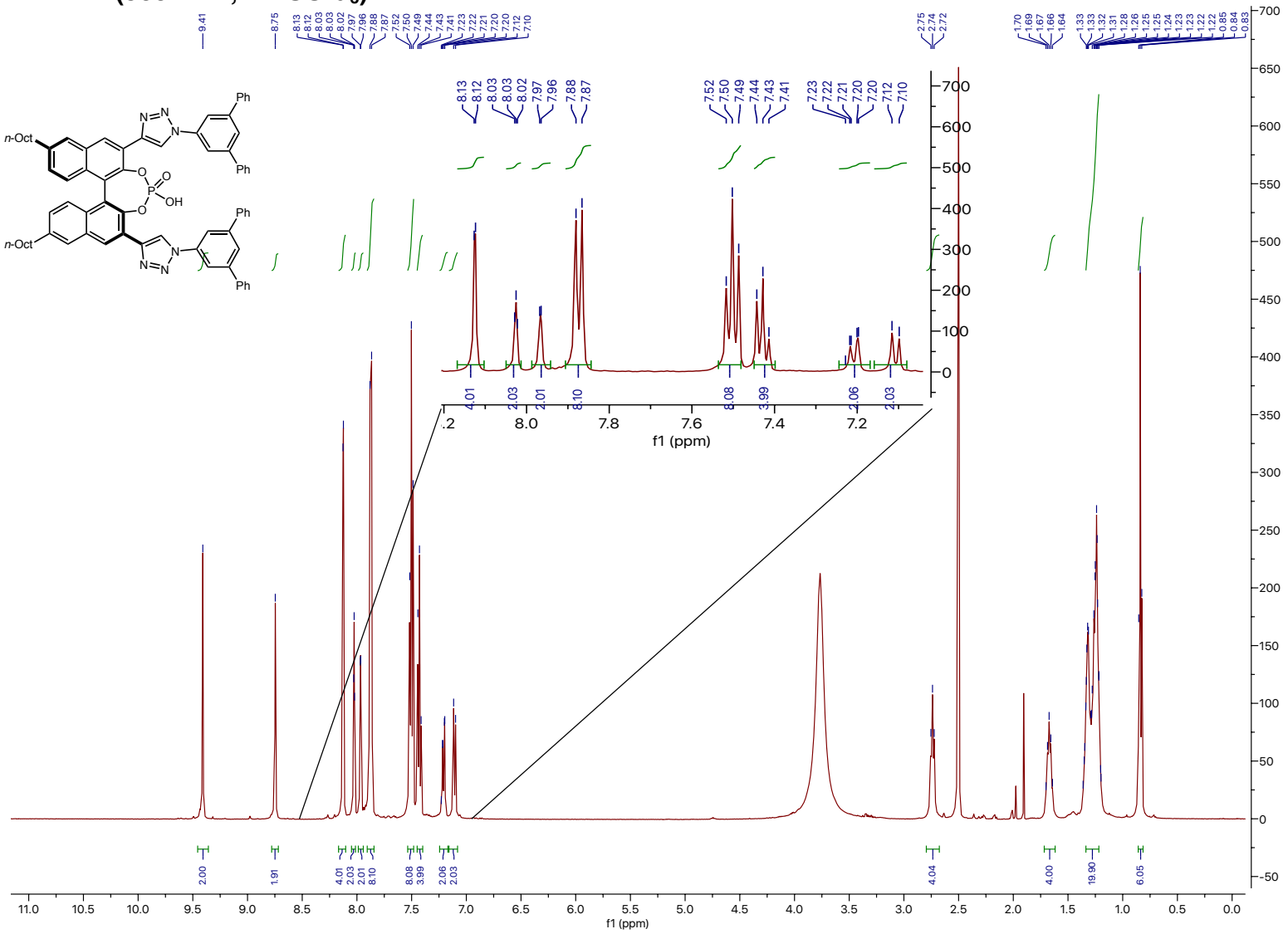
(*S*)-3,3'-bis(1-(1,1':3',1''-terphen-5'-yl)-1*H*-1,2,3-triazol-4-yl)- 6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (**S7.1**)

^{13}C NMR (126 MHz, $CDCl_3$):



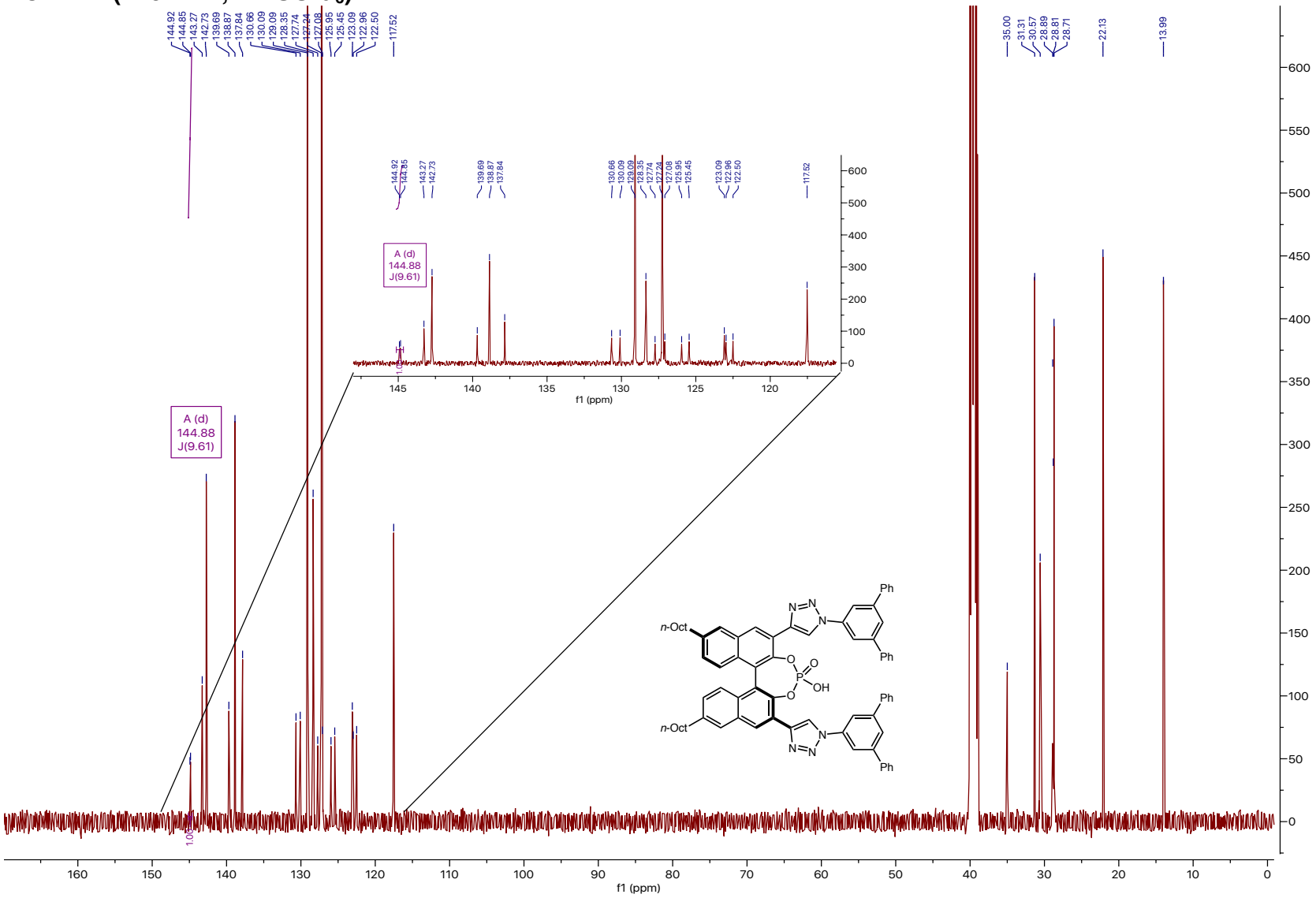
(4*R*,11b*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.1**)

^{1}H NMR (500 MHz, DMSO-d$_6$):



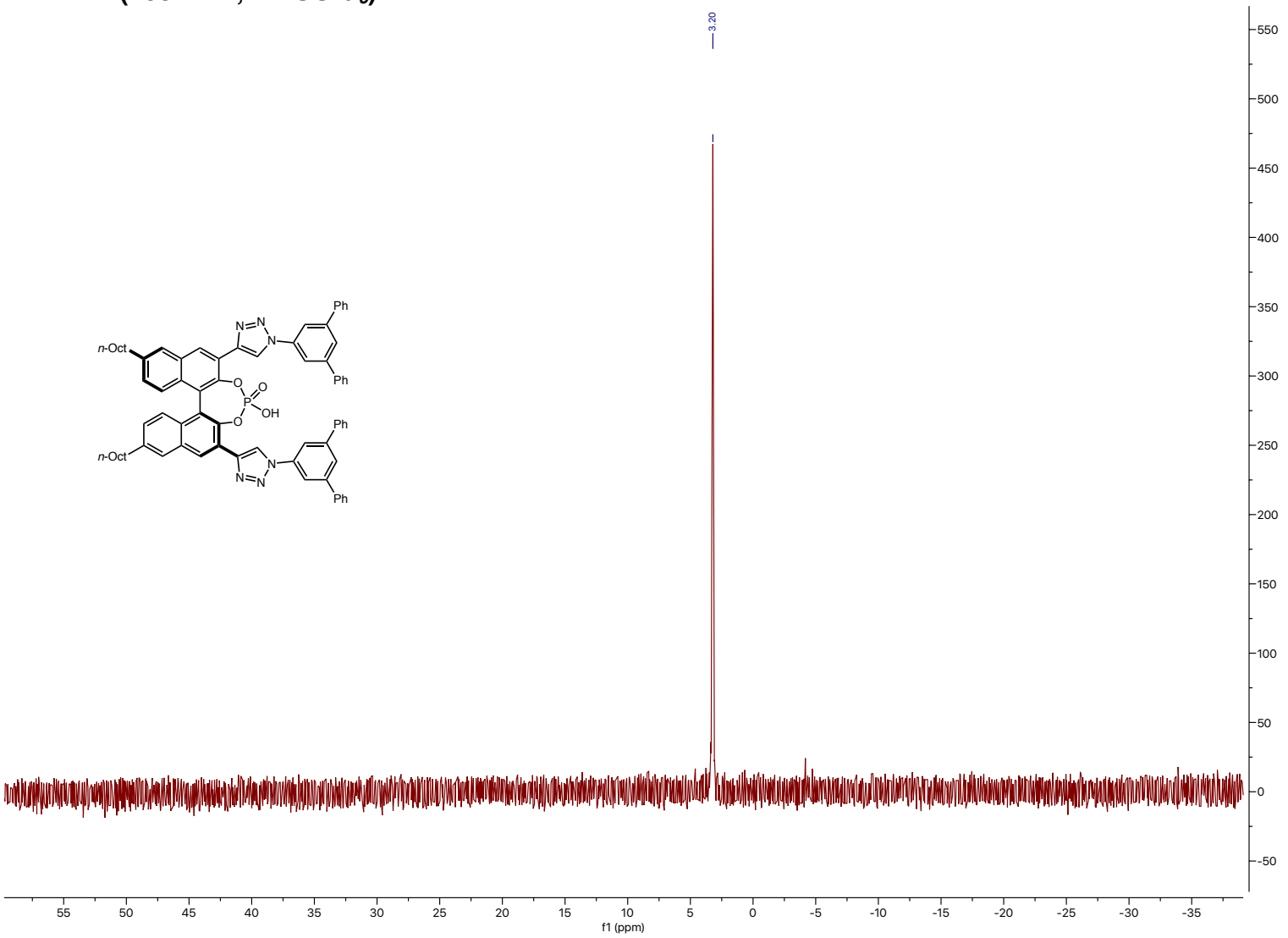
(4*R*,11b*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.1**)

^{13}C NMR (126 MHz, DMSO-d$_6$):



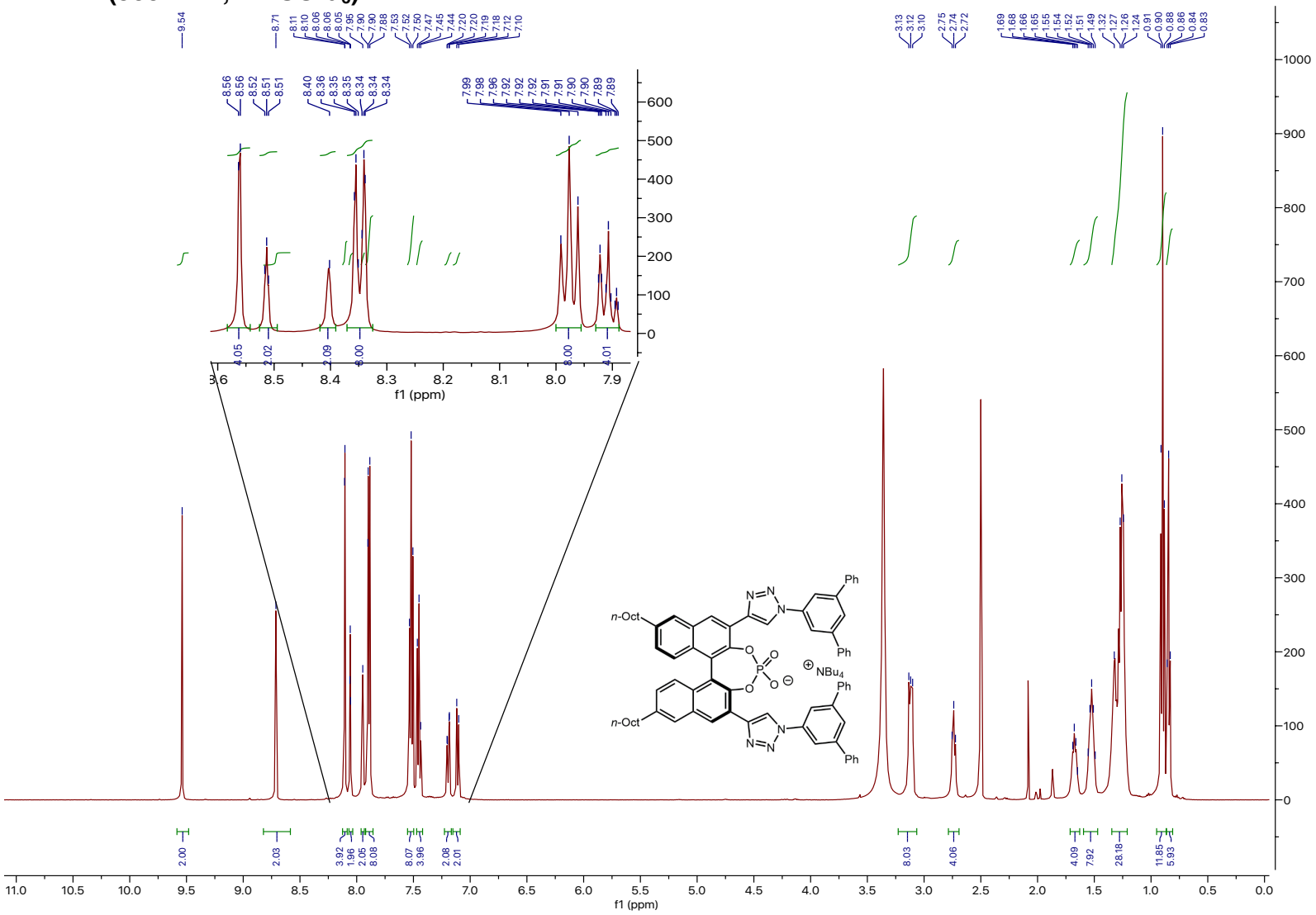
(4*R*,11b*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.1**)

^{31}P NMR (203 MHz, DMSO-d_6):



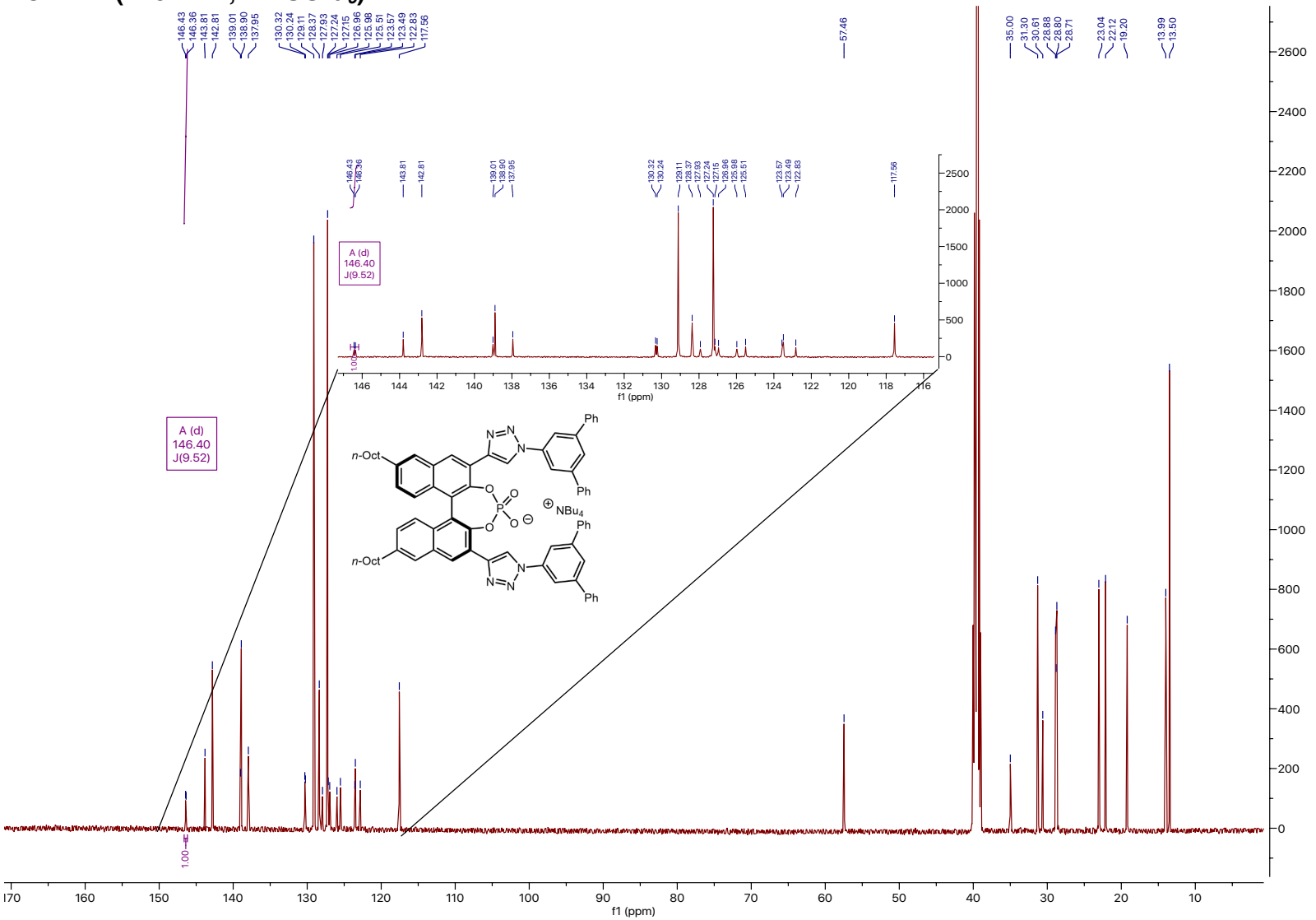
(*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.1**)

^{1}H NMR (500 MHz, DMSO-d$_6$):



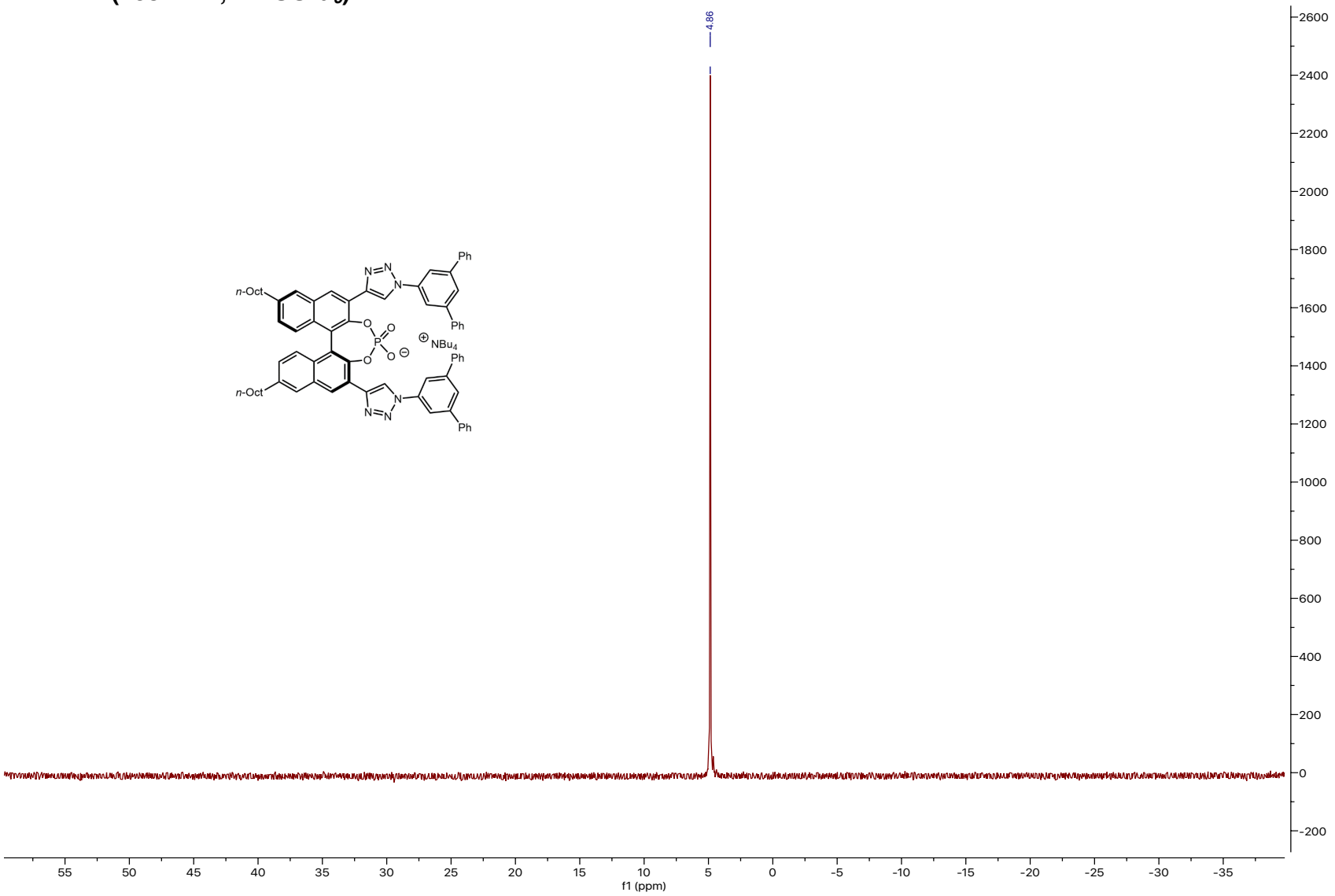
(*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.1**)

^{13}C NMR (126 MHz, DMSO-d_6):



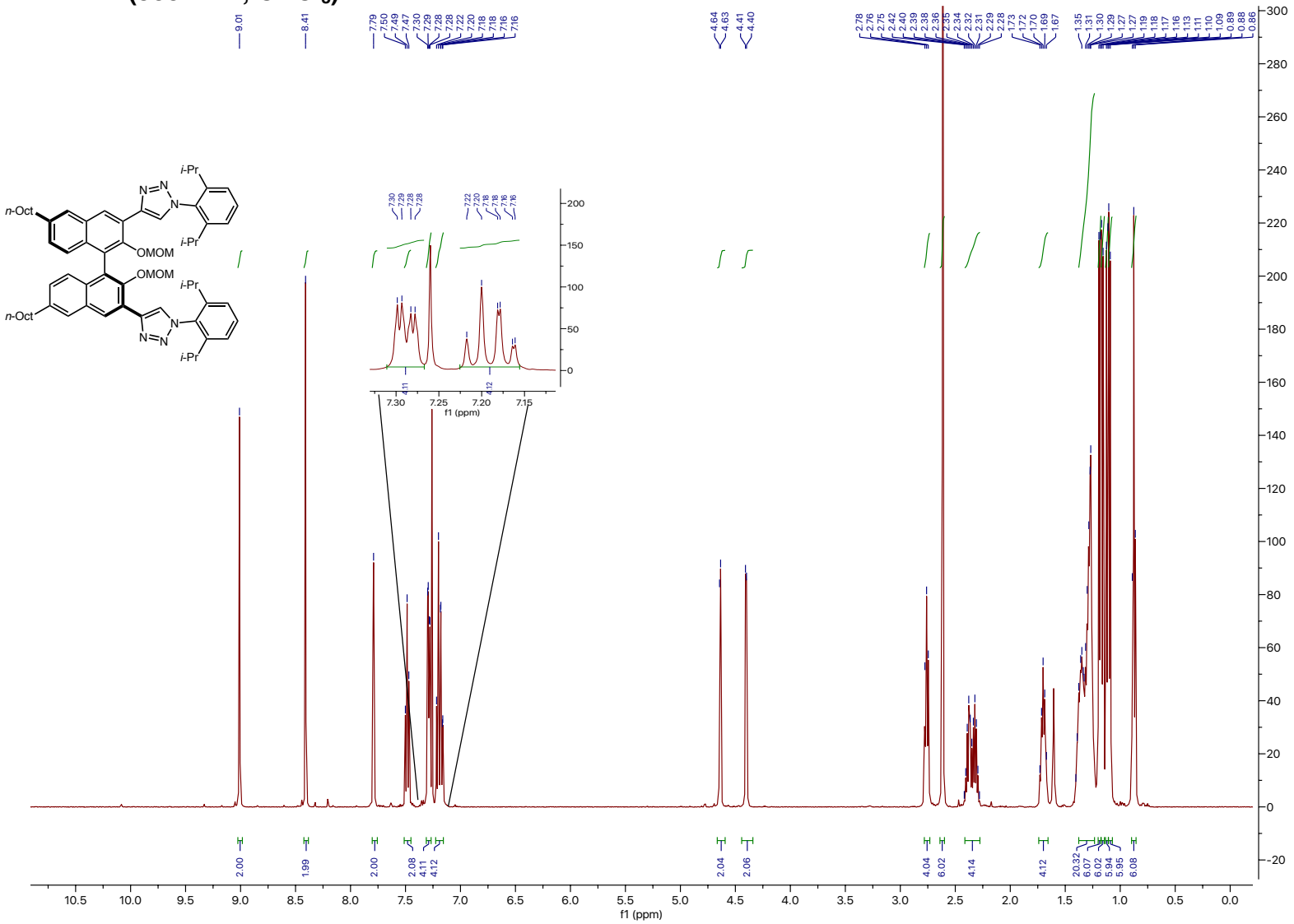
(*S*)-2,6-bis(1-([1,1':3',1''-terphenyl]-5'-yl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.1**)

^{31}P NMR (203 MHz, DMSO-d_6):



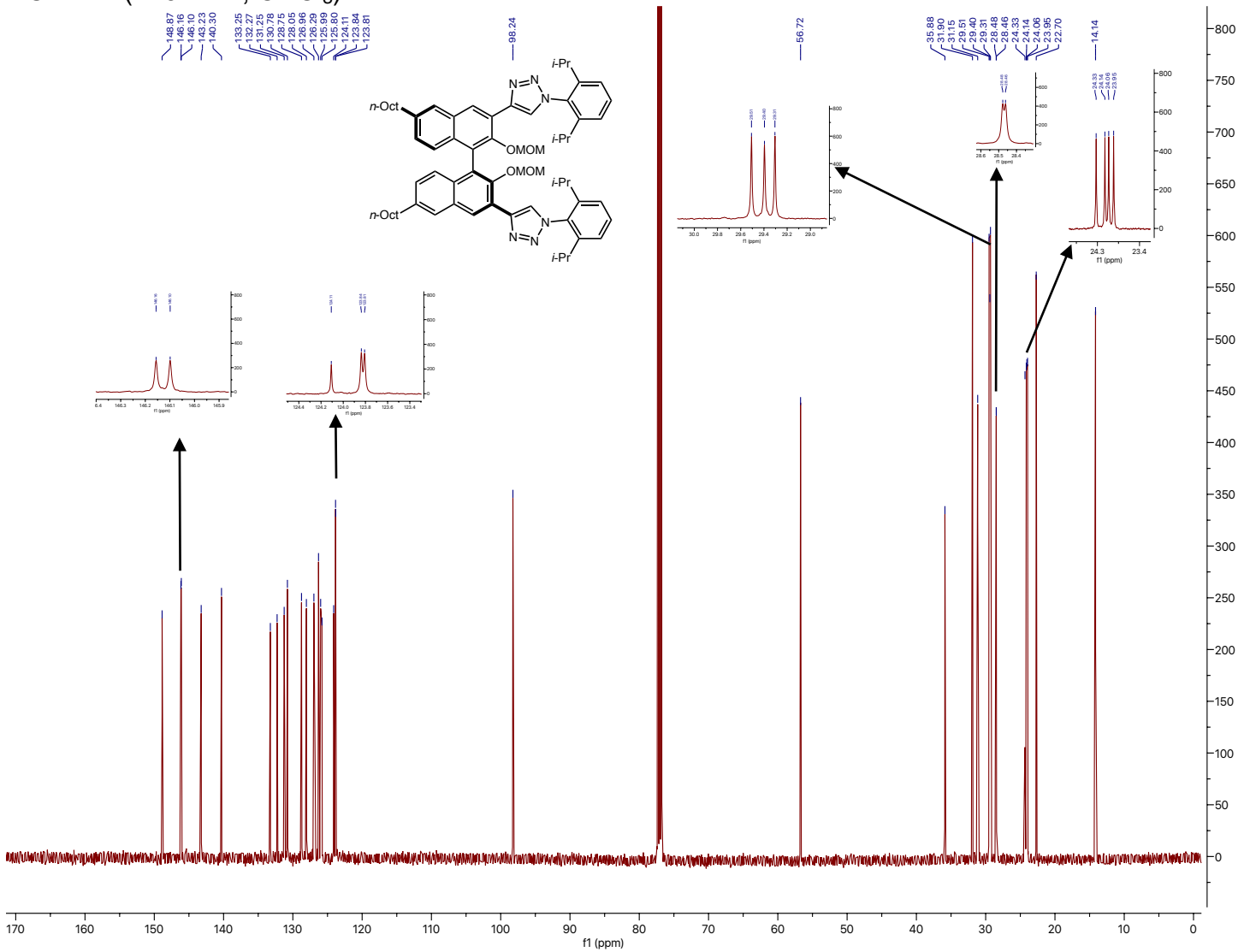
(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazole) (**S6.2**)

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



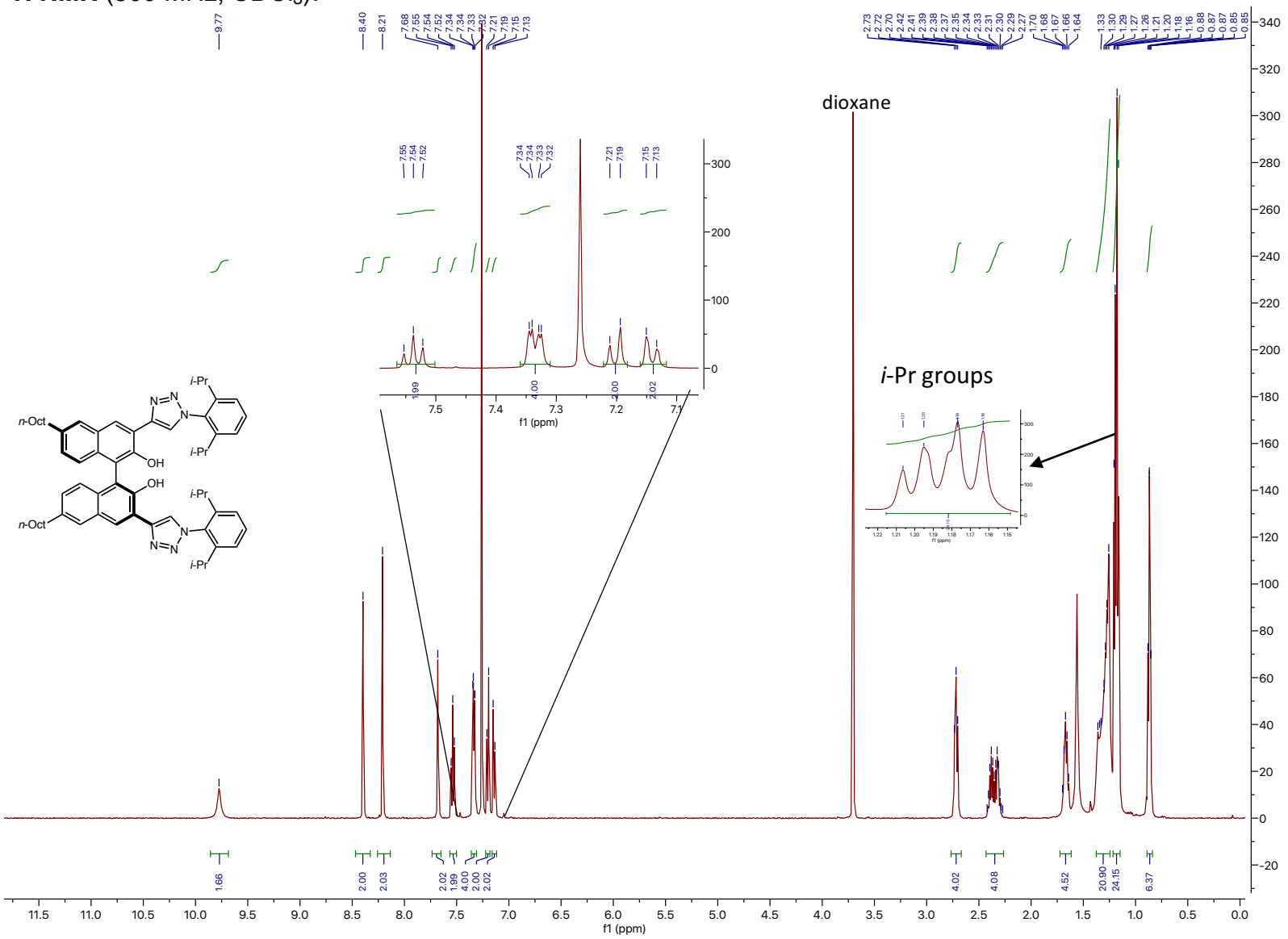
(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazole) (**S6.2**)

^{13}C NMR (126 MHz, $CDCl_3$):



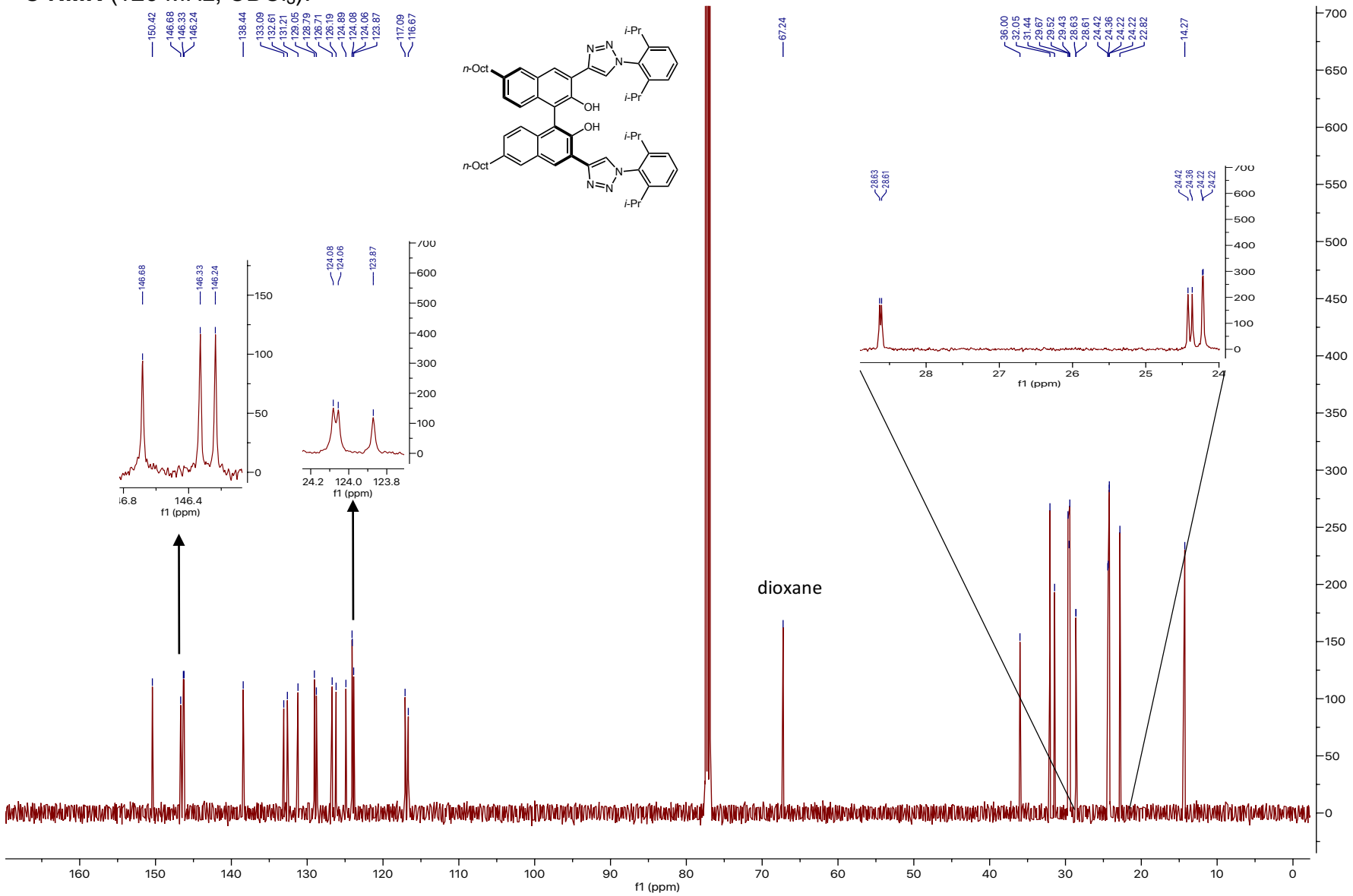
(*S*)-3,3'-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)- 6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (**S7.2**)

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



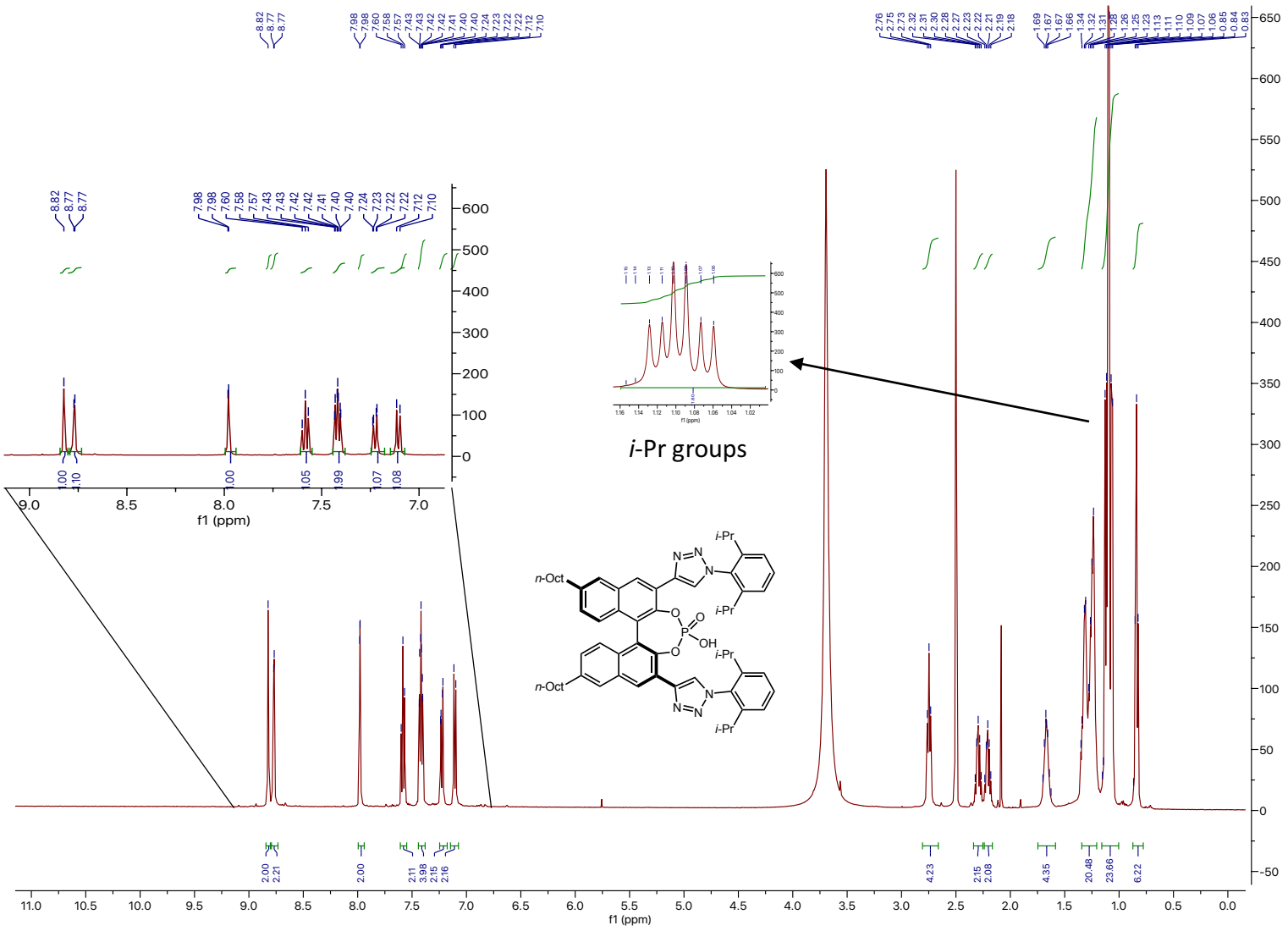
(*S*)-3,3'-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)- 6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (**S7.2**)

^{13}C NMR (126 MHz, $CDCl_3$):



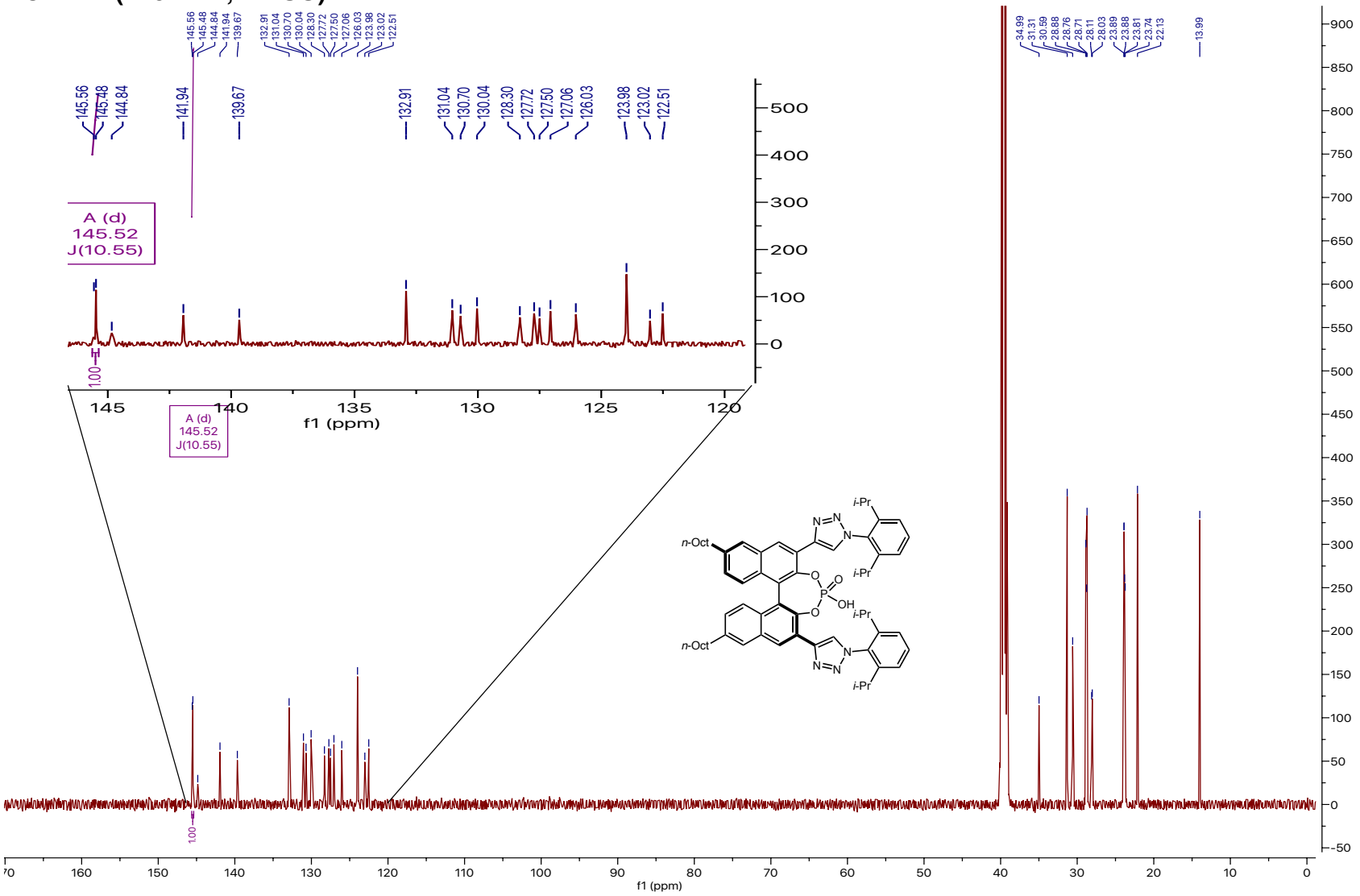
(4*R*,11b*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.2**)

^{1}H NMR (500 MHz, DMSO):



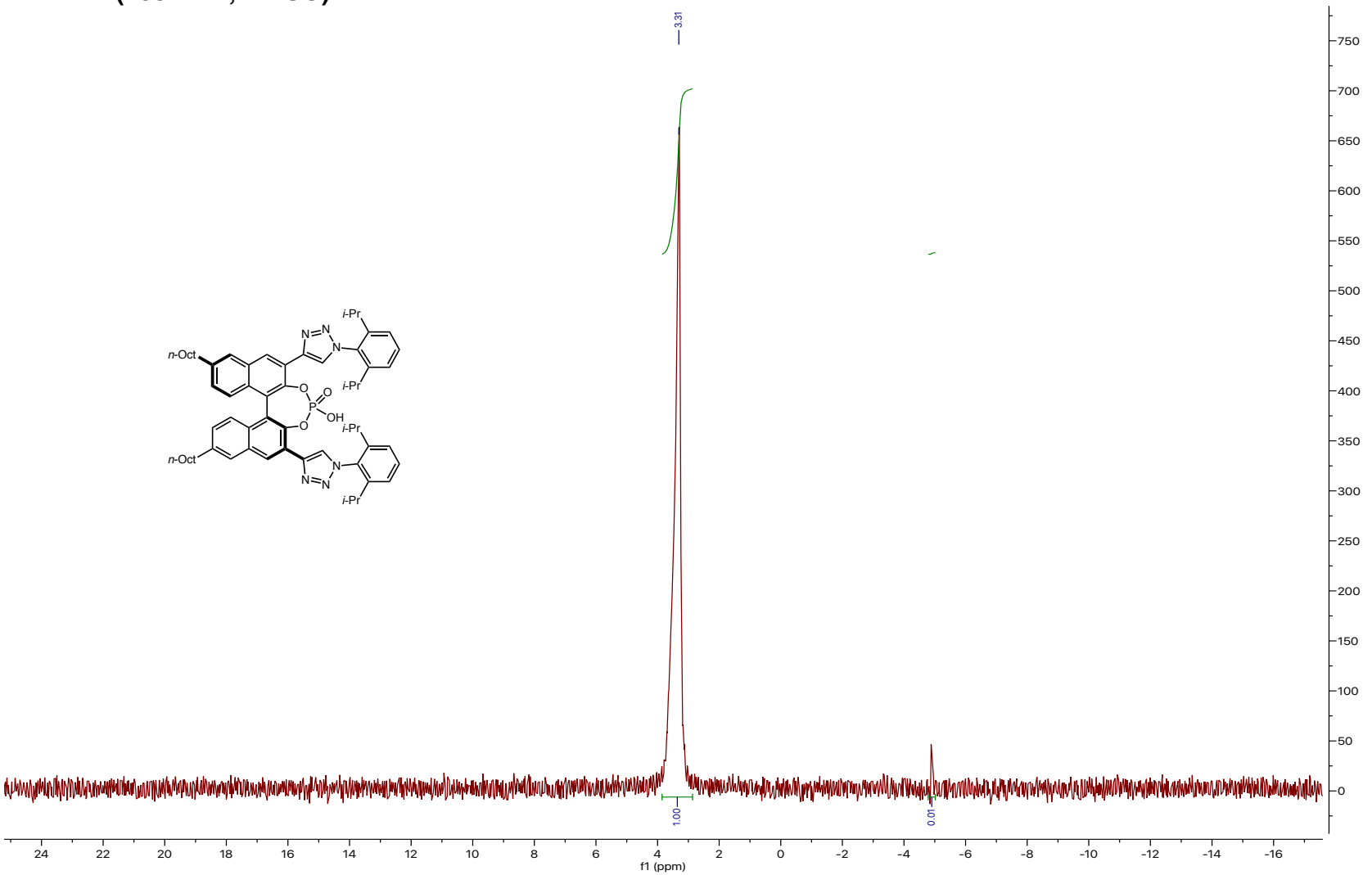
(4*R*,11b*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.2**)

^{13}C NMR (126 MHz, DMSO):



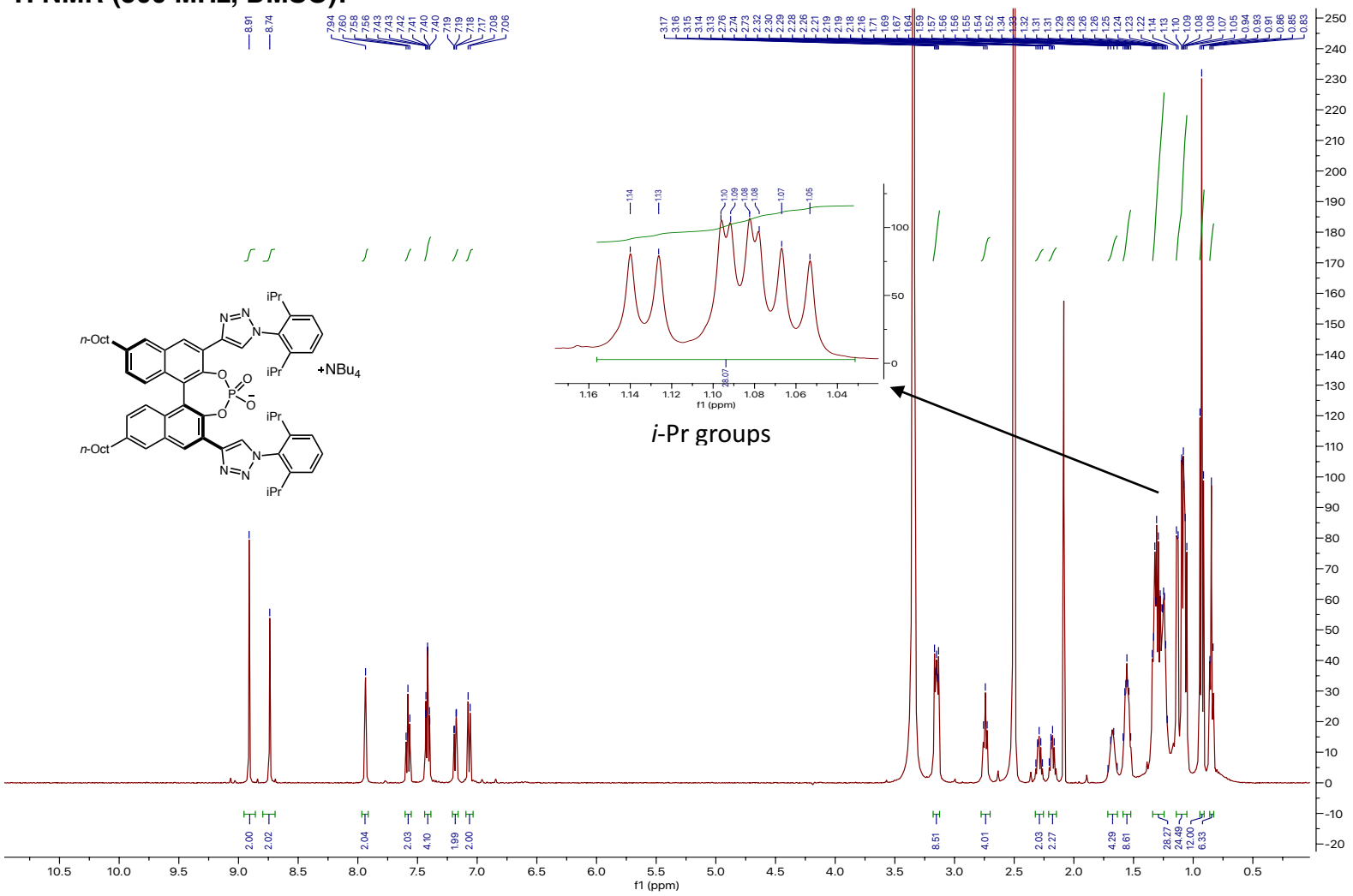
(4*R*,11b*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.2**)

^{31}P NMR (203 MHz, DMSO):



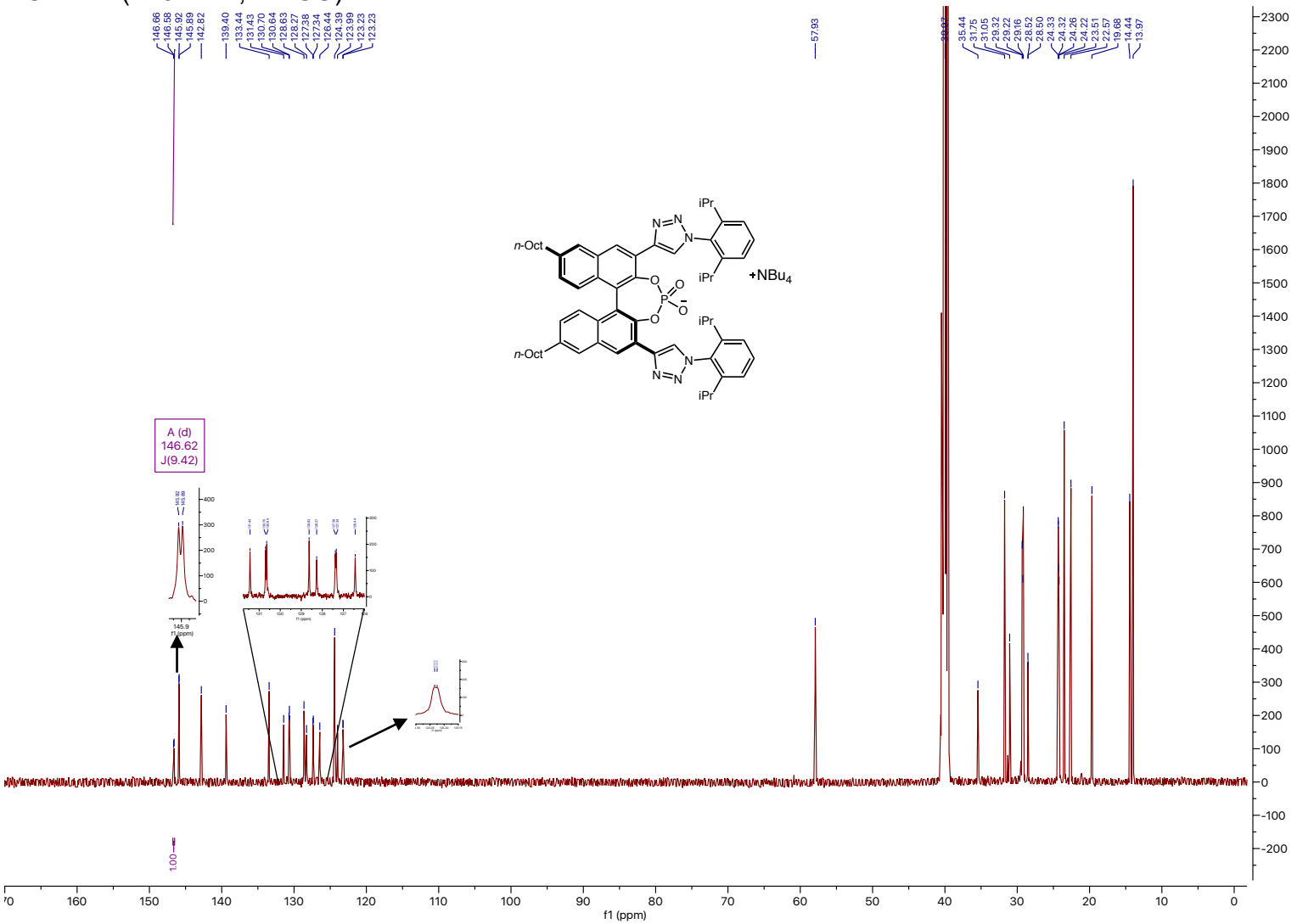
(*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutyl ammonium salt (**S9.2**)

^{1}H NMR (500 MHz, DMSO):



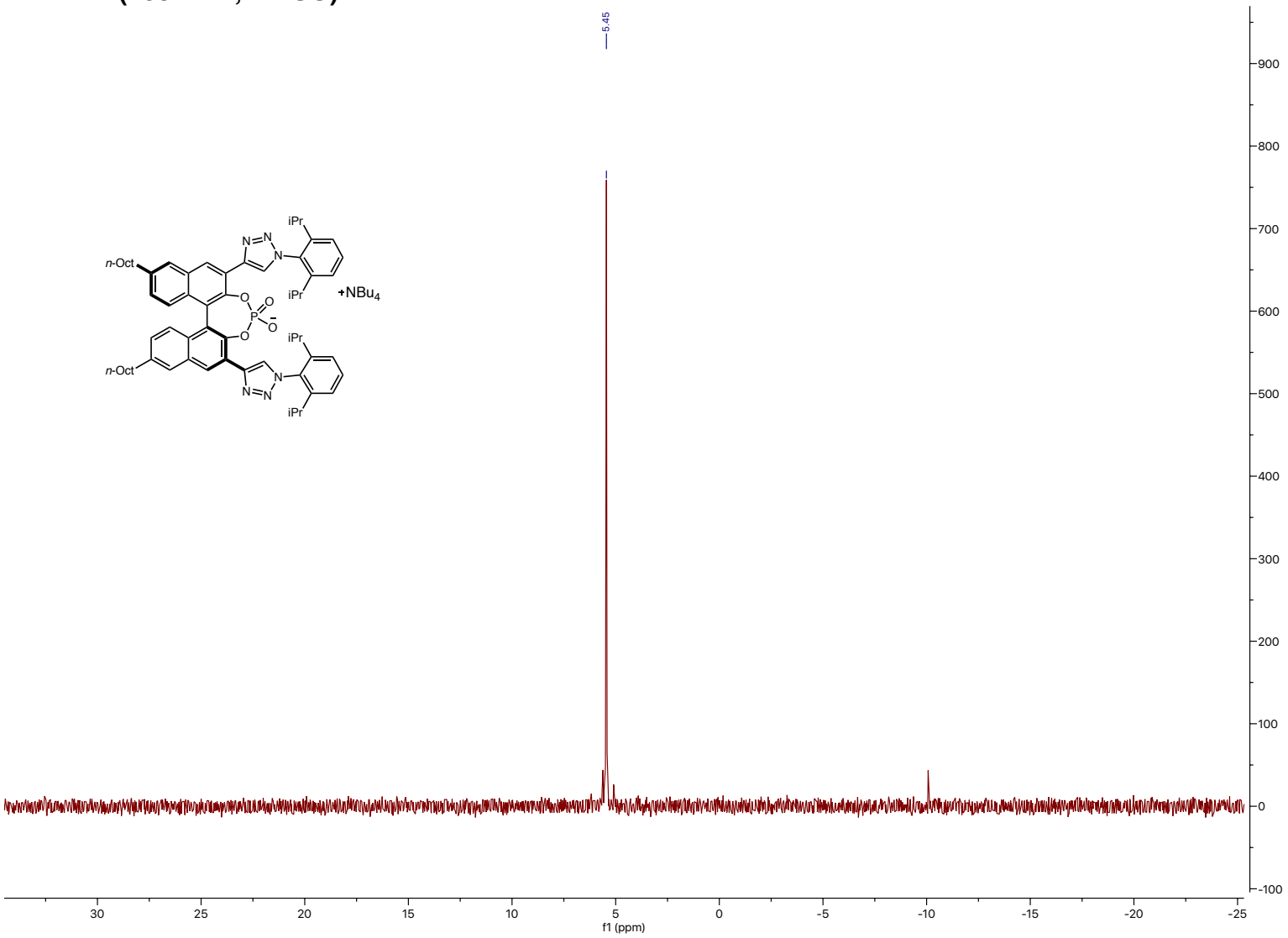
(*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutyl ammonium salt (**S9.2**)

^{13}C NMR (126 MHz, DMSO):



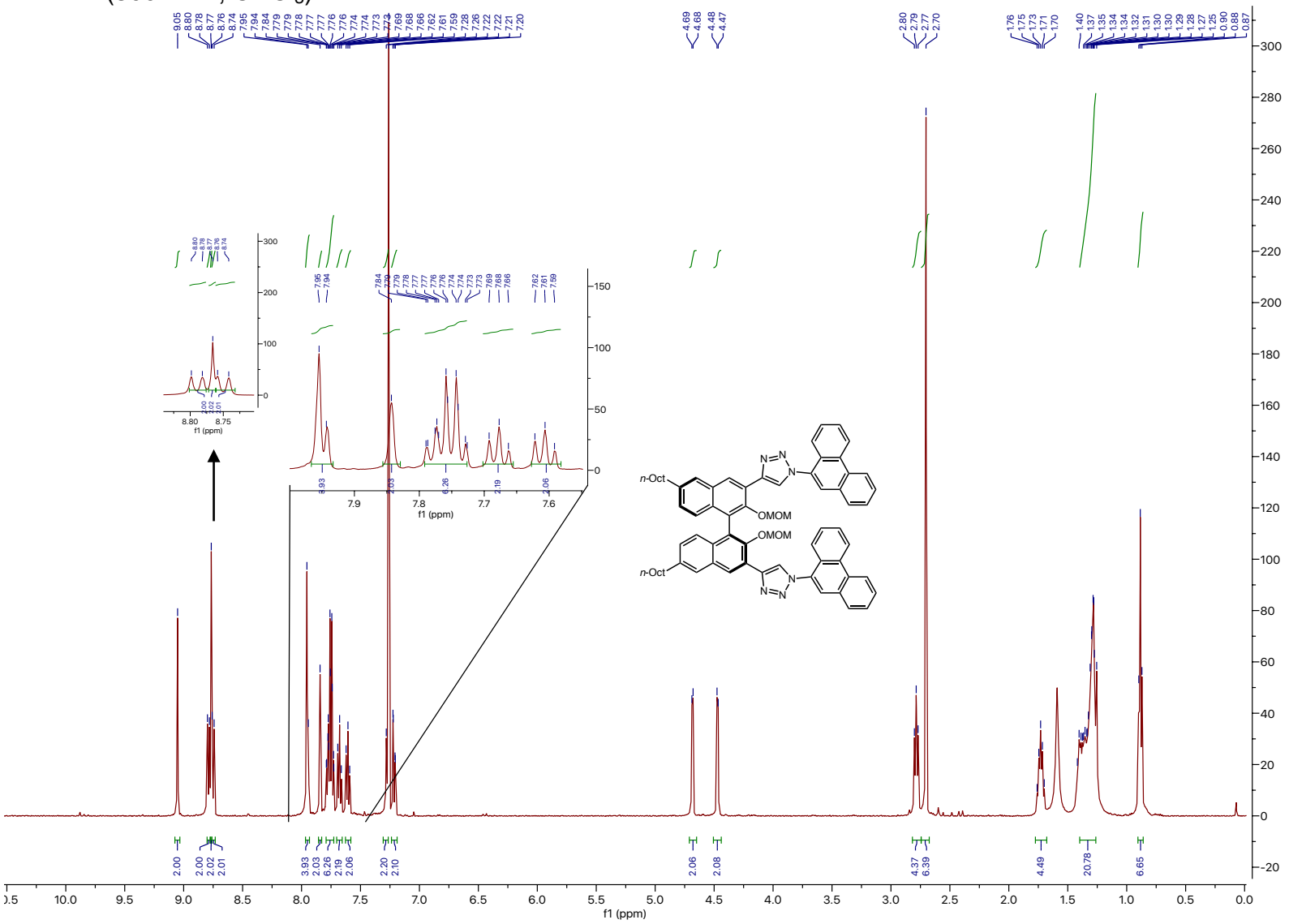
(*S*)-2,6-bis(1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutyl ammonium salt (**S9.2**)

^{31}P NMR (203 MHz, DMSO):



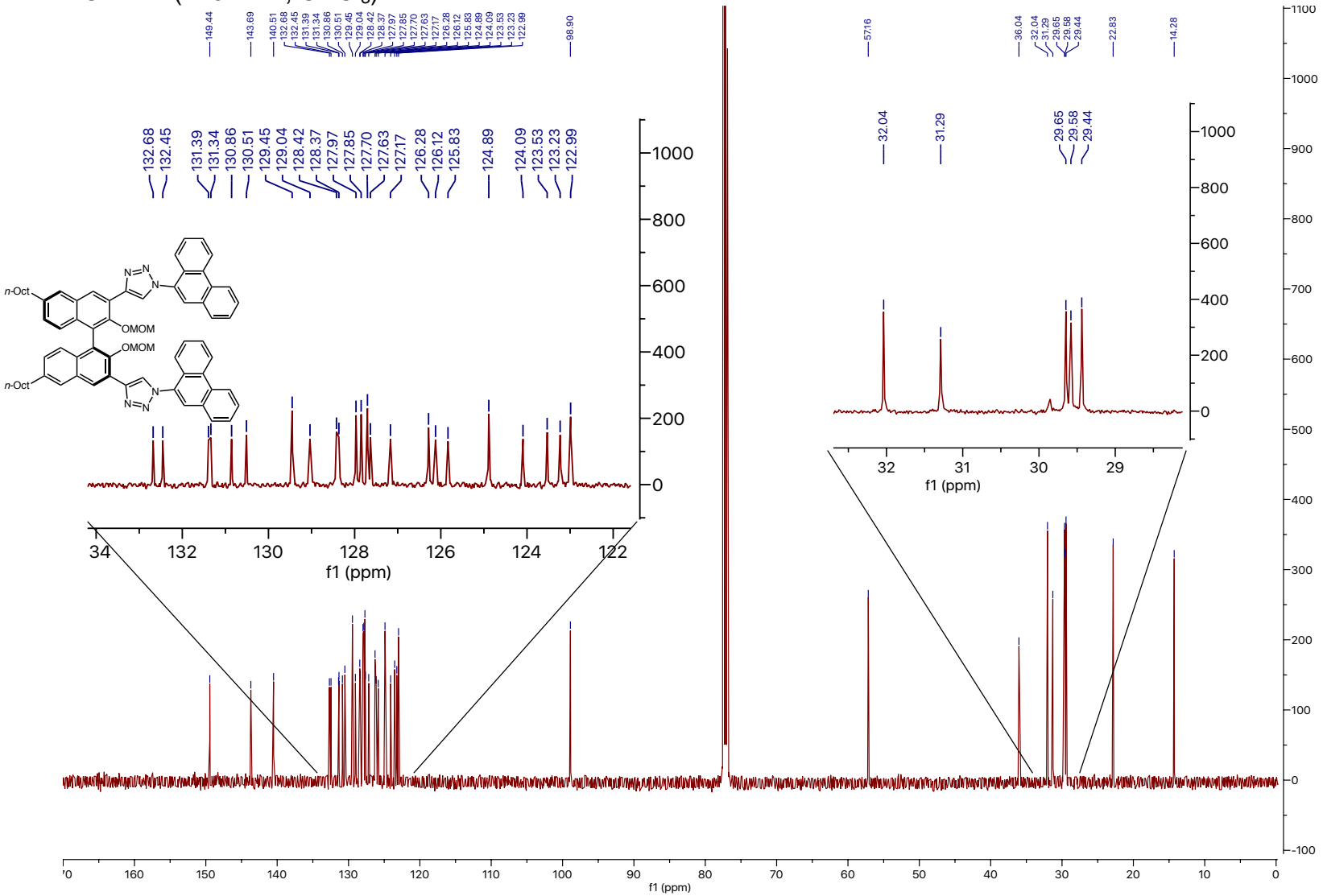
(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol (**S6.3**)

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



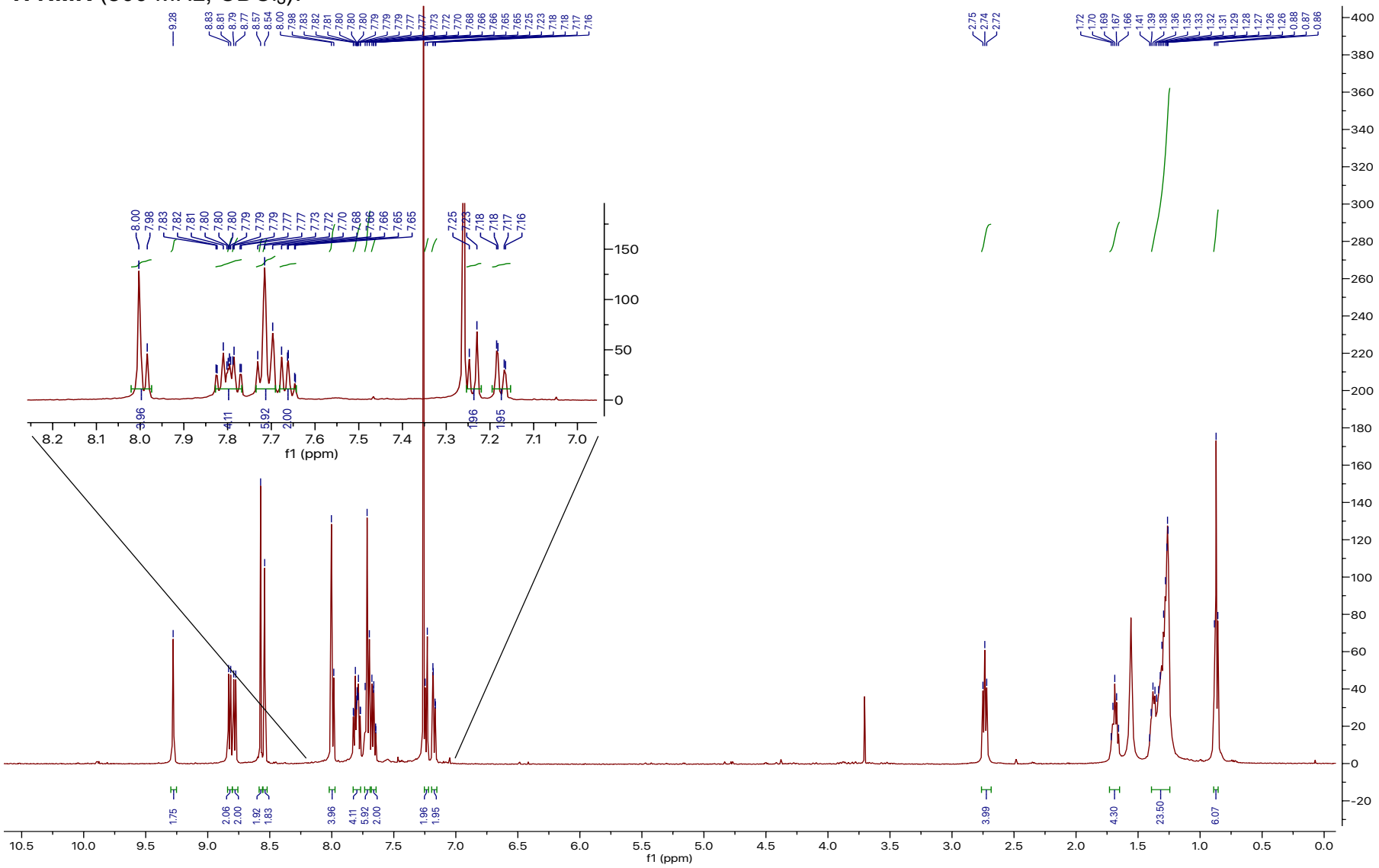
(*S*)-4,4'-(2,2'-bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol (**S6.3**)

^{13}C NMR (126 MHz, $CDCl_3$):



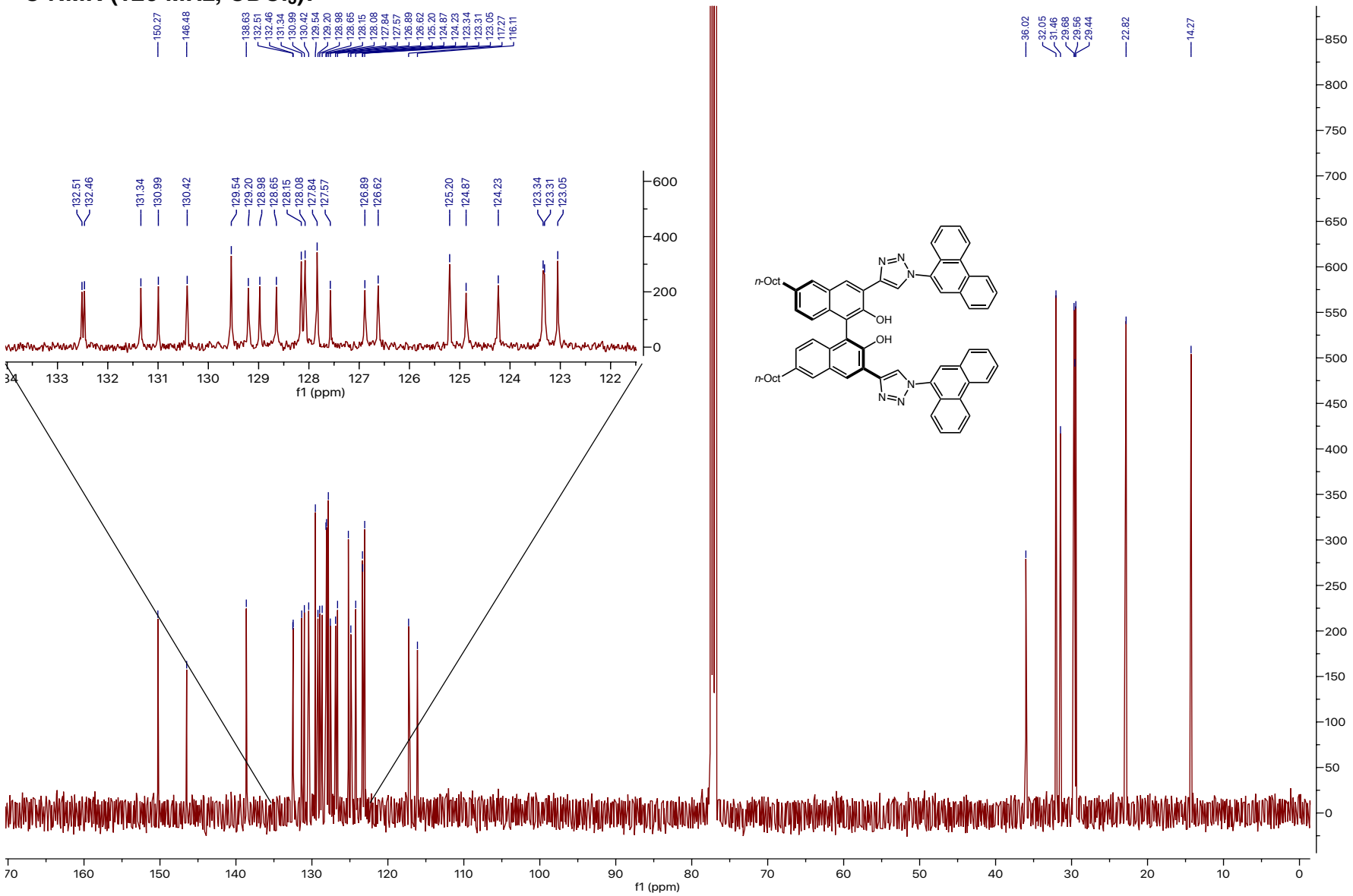
(*S*)-6,6'-dioctyl-3,3'-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)-[1,1'-binaphthalene]-2,2'-diol (**S7.3**)

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



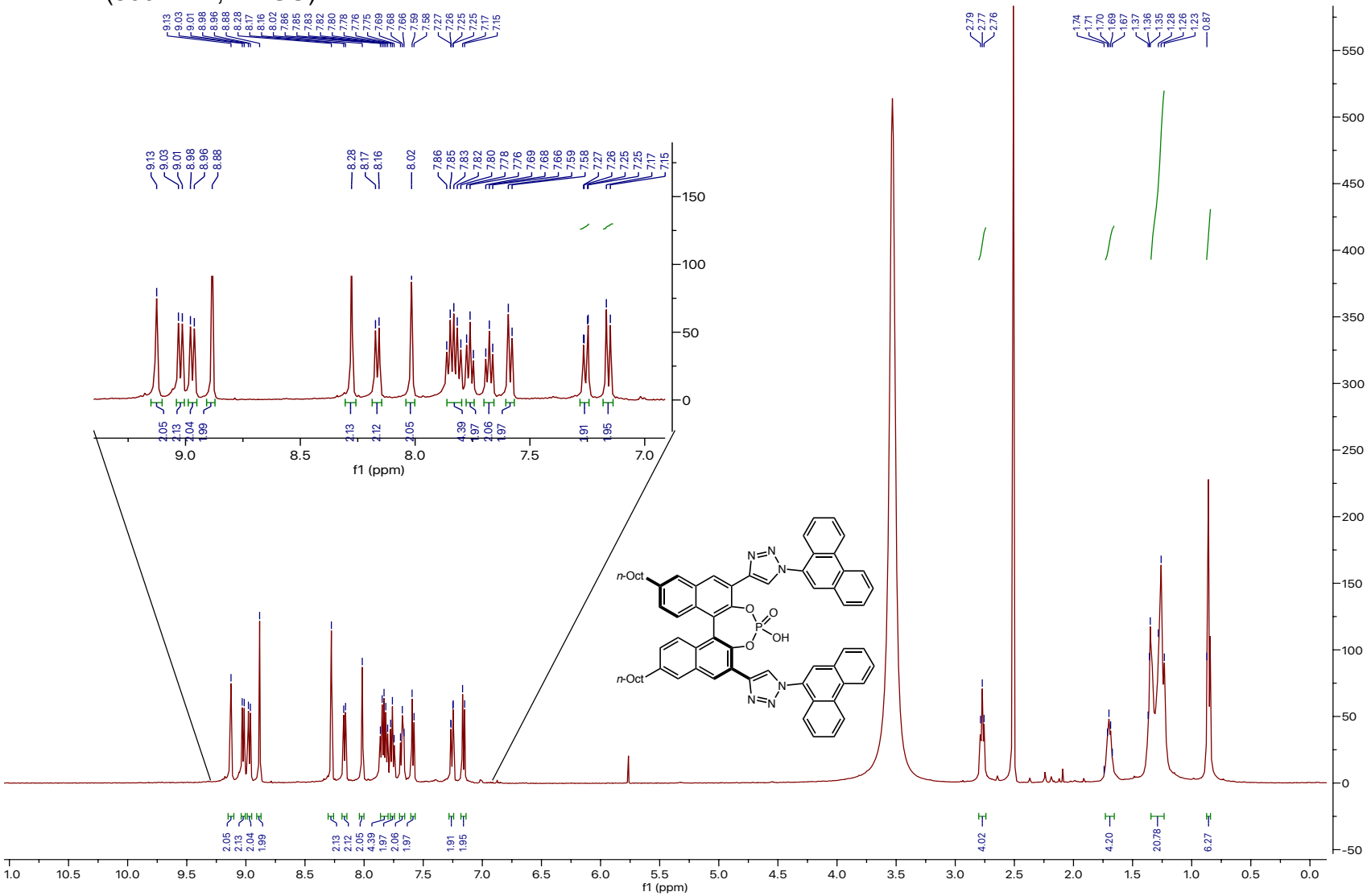
(*S*)-6,6'-dioctyl-3,3'-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)-[1,1'-binaphthalene]-2,2'-diol (**S7.3**)

^{13}C NMR (126 MHz, $CDCl_3$):



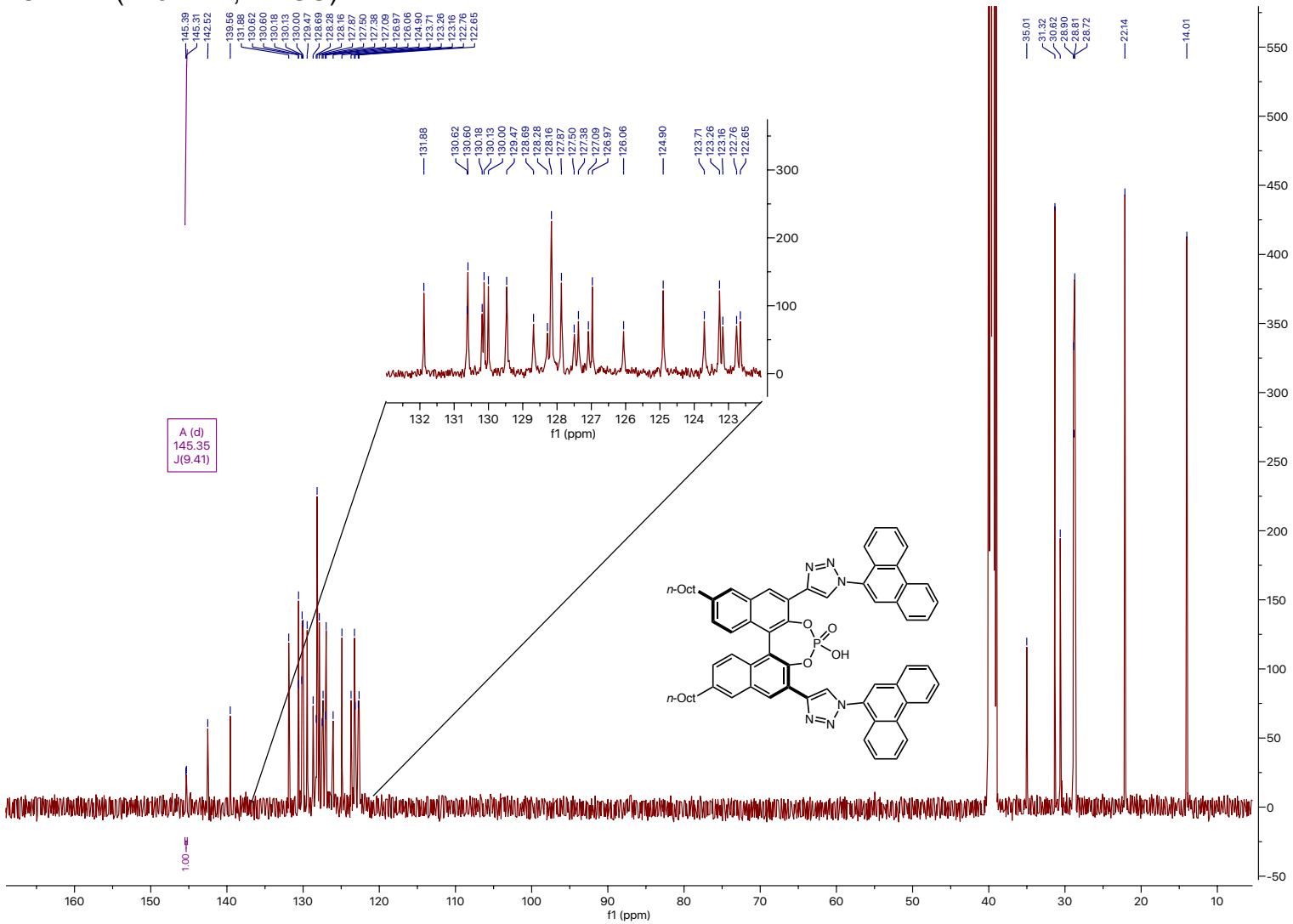
(4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.3**)

^{1}H NMR (500 MHz, DMSO):



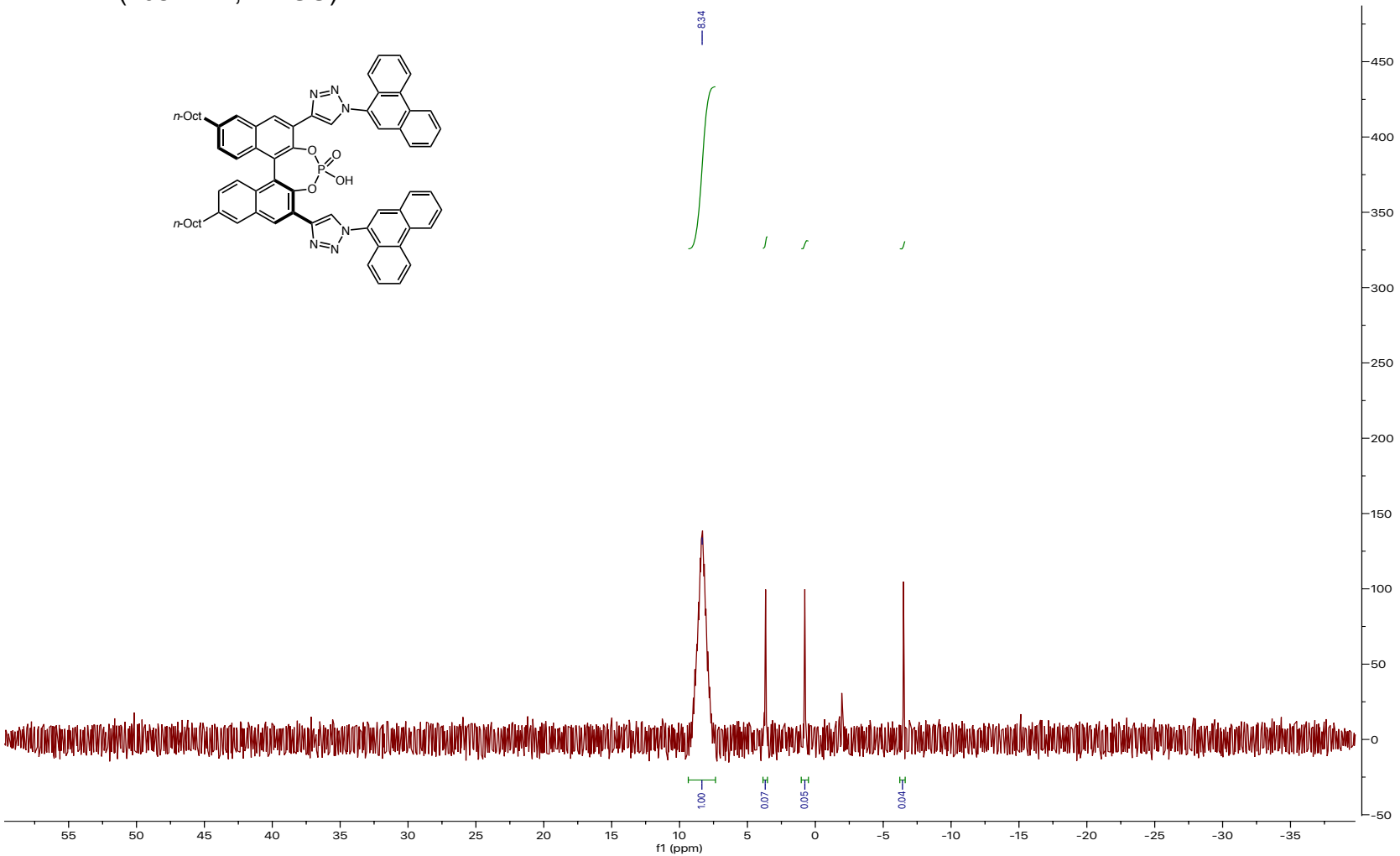
(4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.3**)

^{13}C NMR (126 MHz, DMSO):



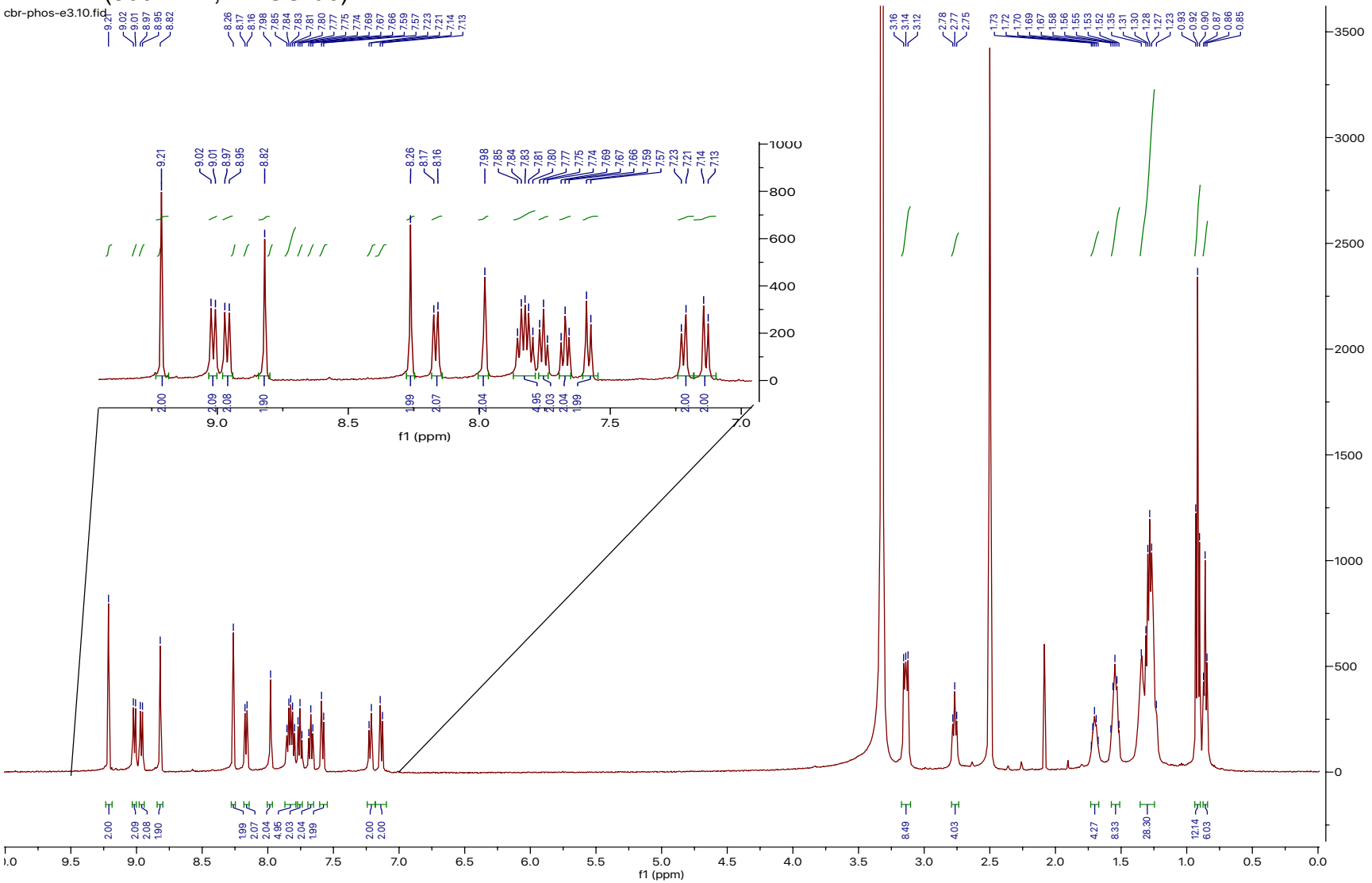
(4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (**S8.3**)

^{31}P NMR (203 MHz, DMSO):



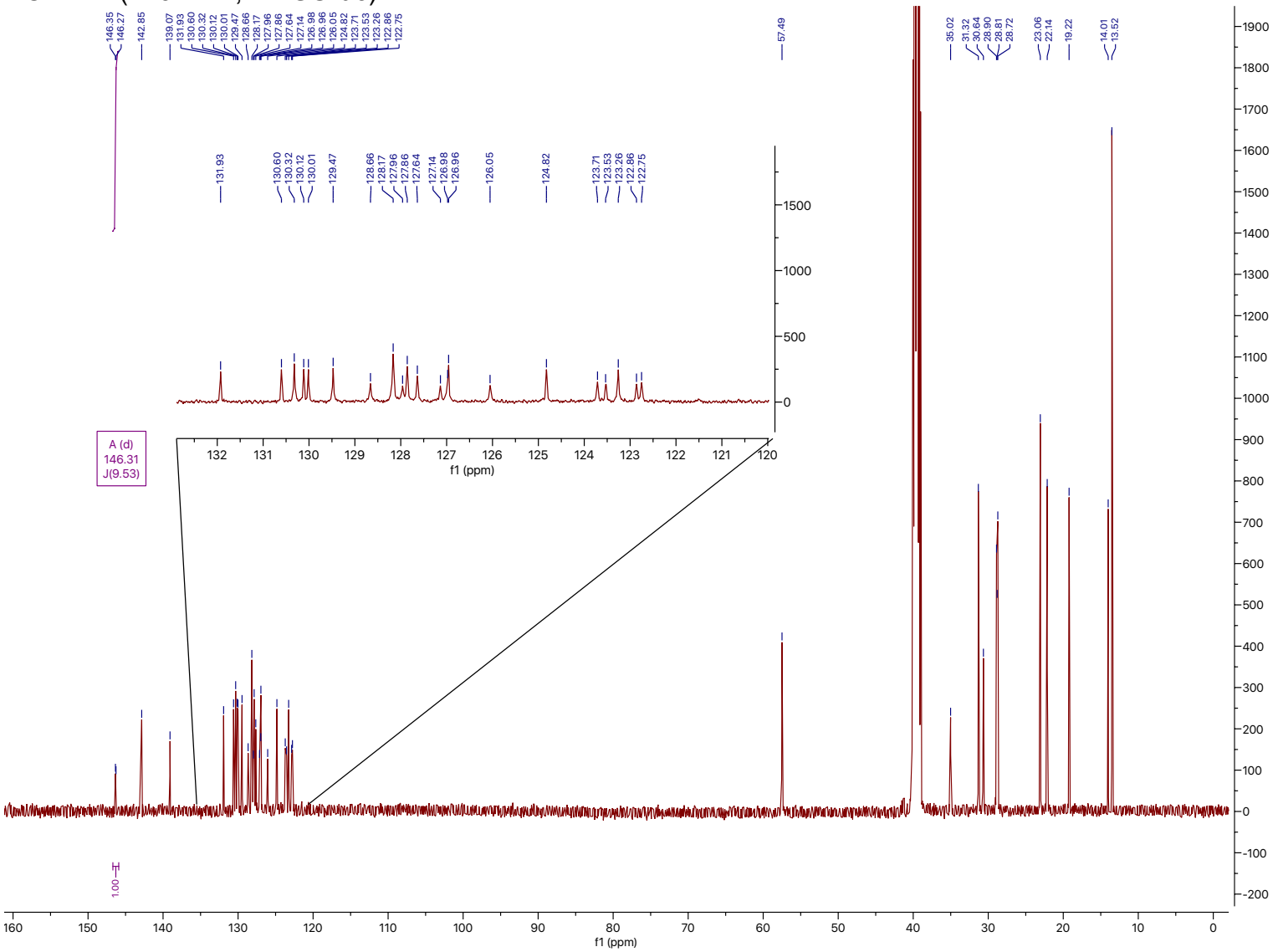
(*S*)-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.3**)

^{1}H NMR (500 MHz, DMSO-d6):



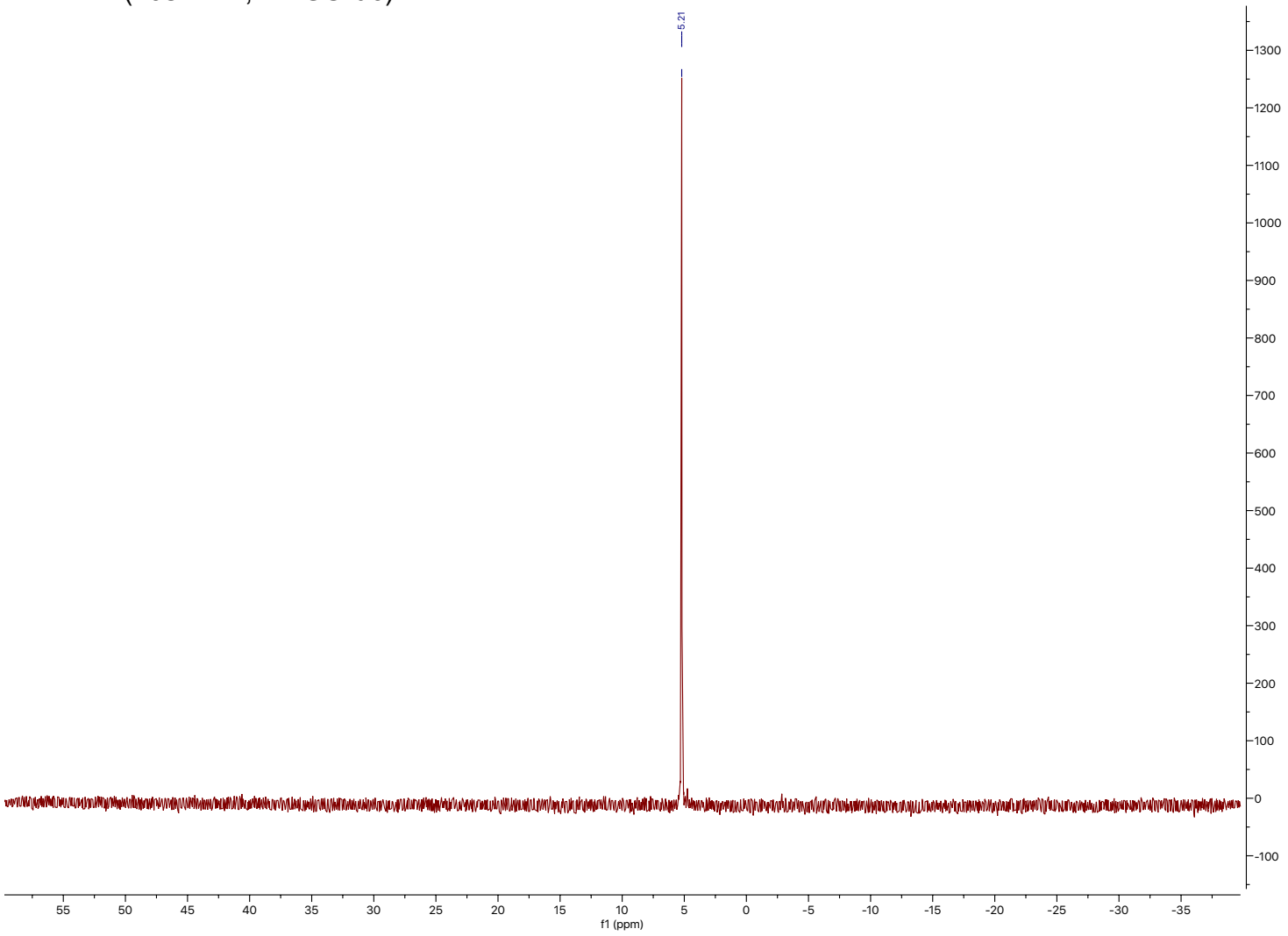
(*S*)-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.3**)

^{13}C NMR (126 MHz, DMSO-d6):



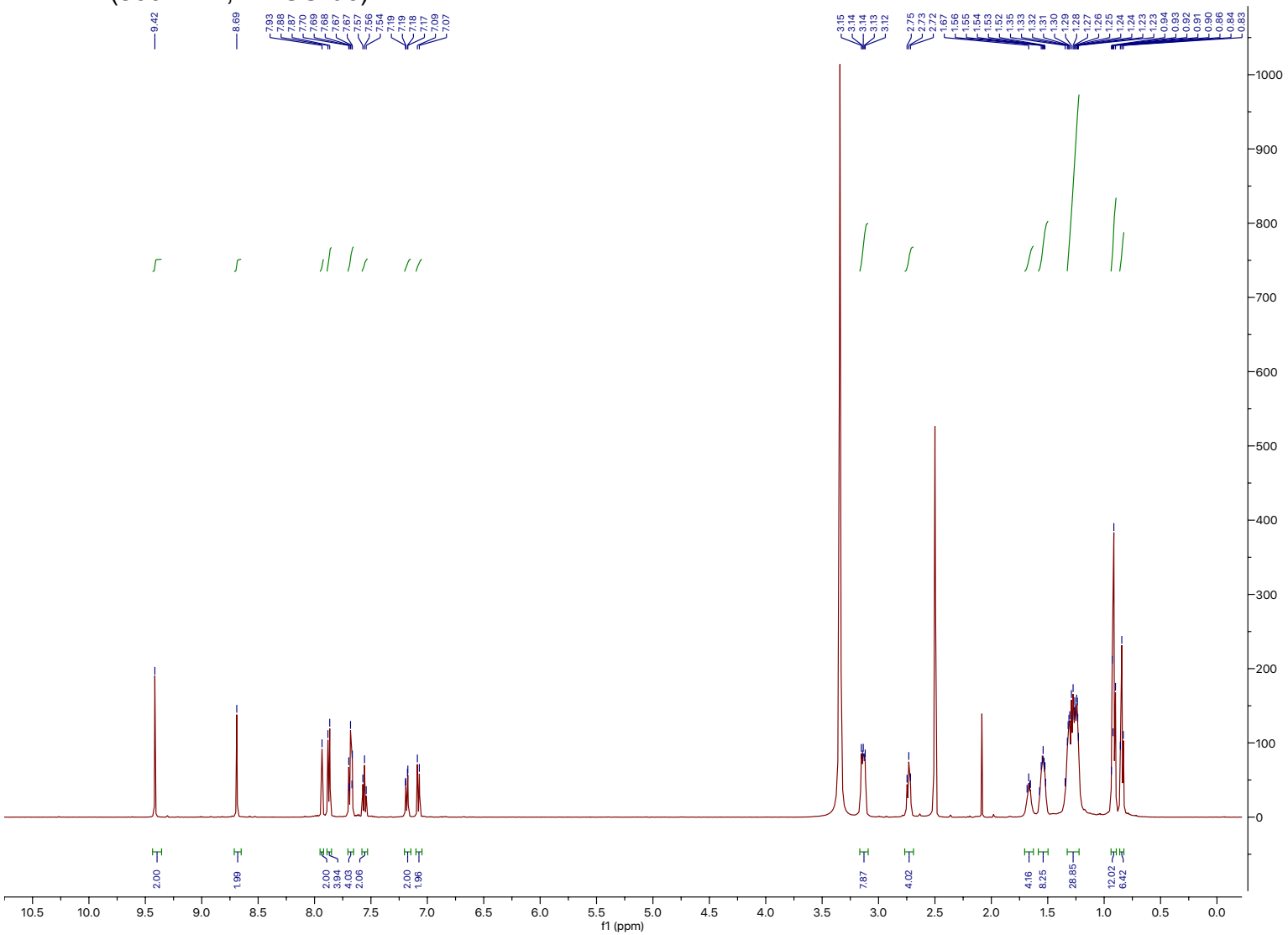
(*S*)-9,14-dioctyl-2,6-bis(1-(phenanthren-9-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.3**)

^{31}P NMR (203 MHz, DMSO-d6):



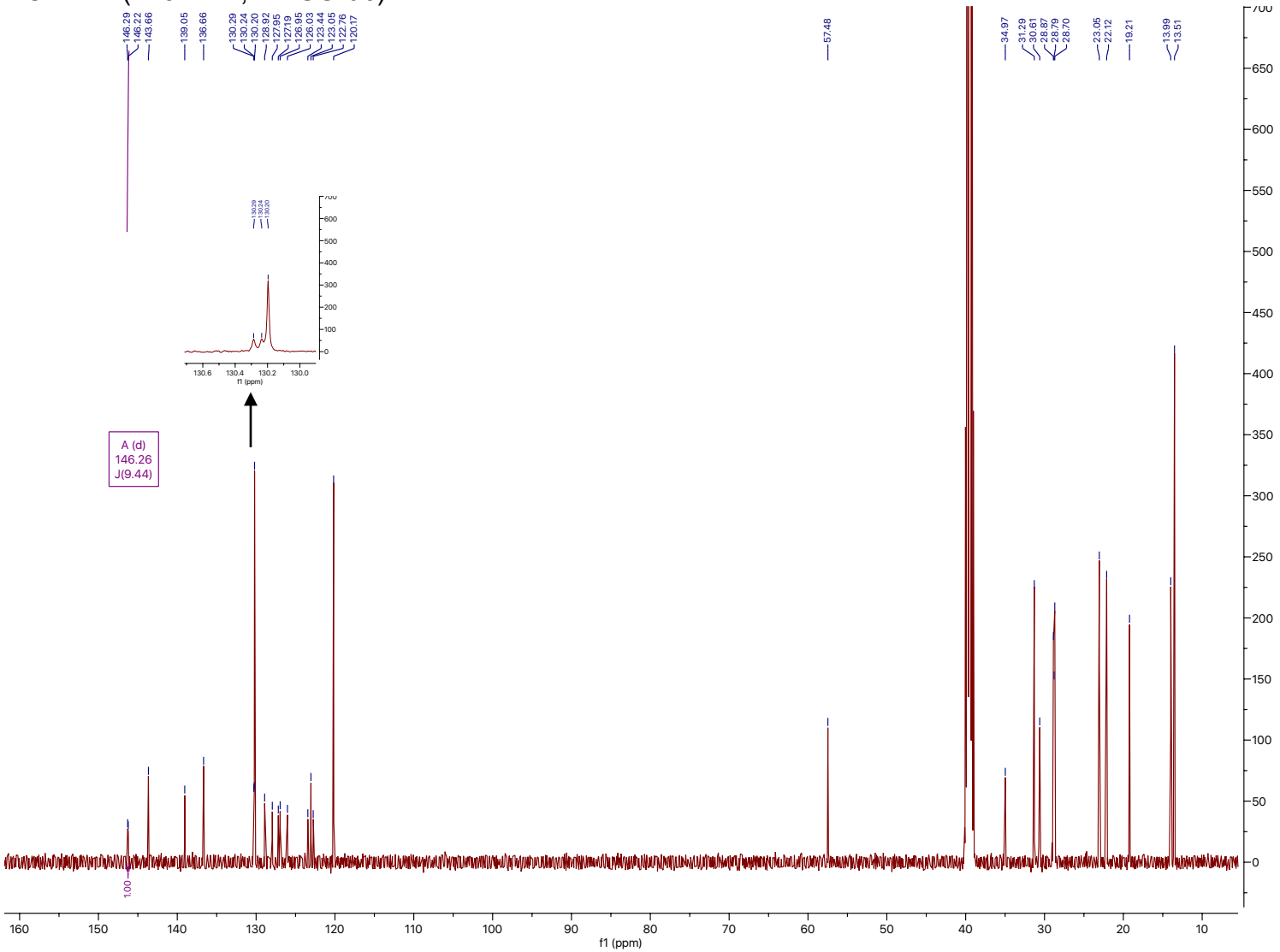
(*S*)-9,14-dioctyl-2,6-bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.4**)

^{1}H NMR (500 MHz, DMSO-d6):



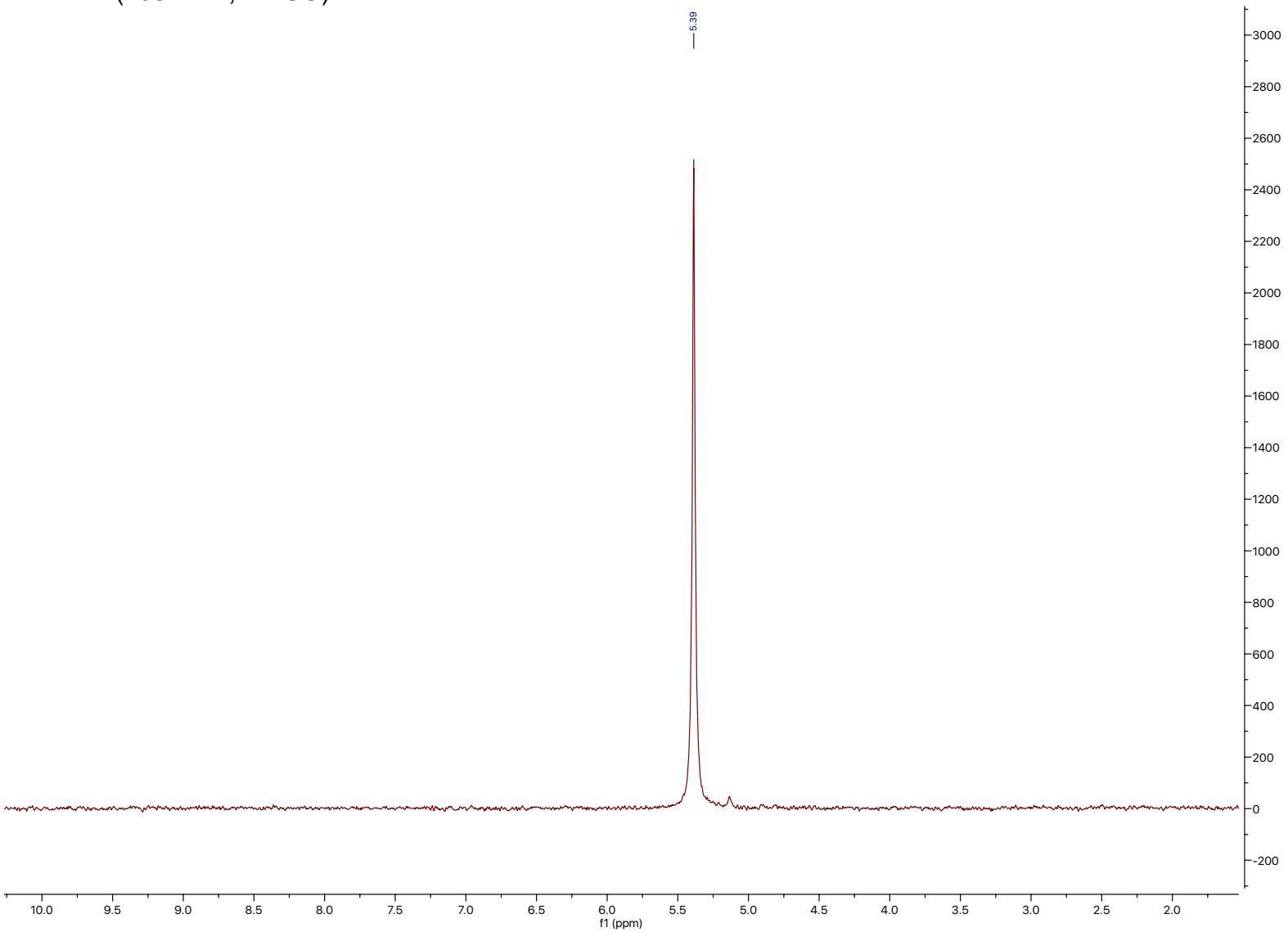
(*S*)-9,14-dioctyl-2,6-bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.4**)

^{13}C NMR (126 MHz, DMSO-d6):



(*S*)-9,14-dioctyl-2,6-bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-olate 4-oxide tetrabutylammonium salt (**S9.4**)

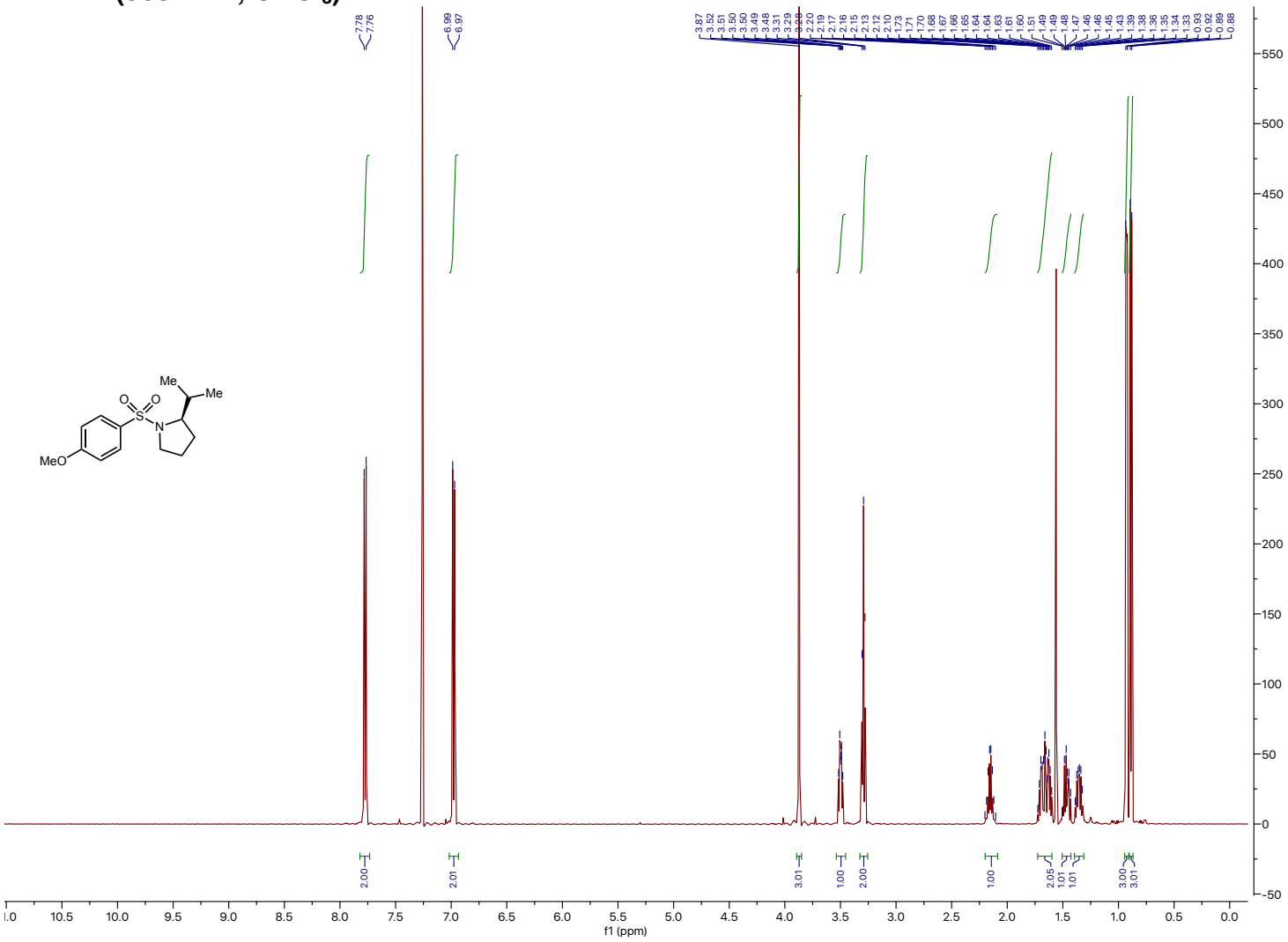
^{31}P NMR (203 MHz, DMSO):



10. Product NMR Spectra

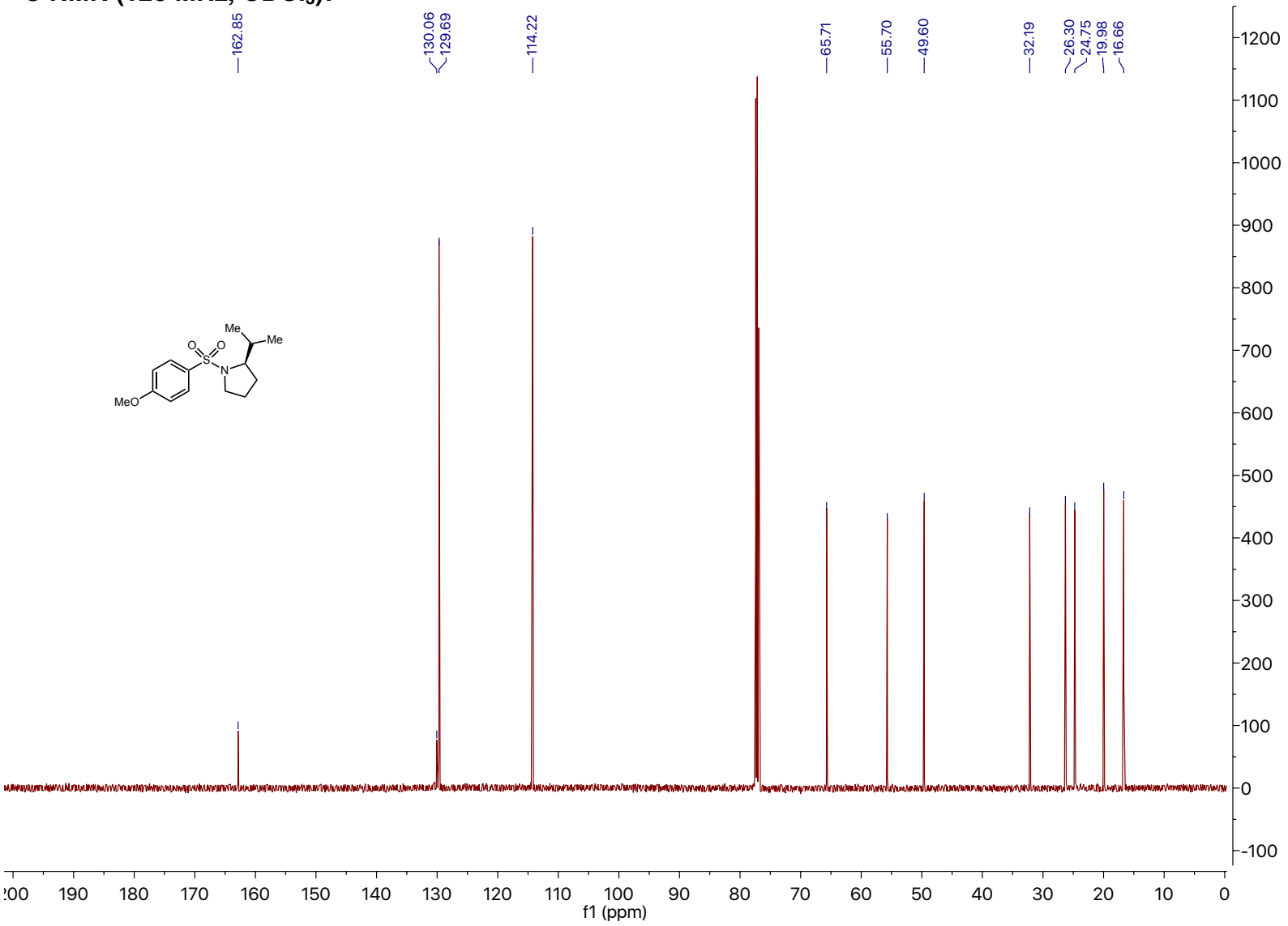
(*R*)-2-isopropyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine (**2**)

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



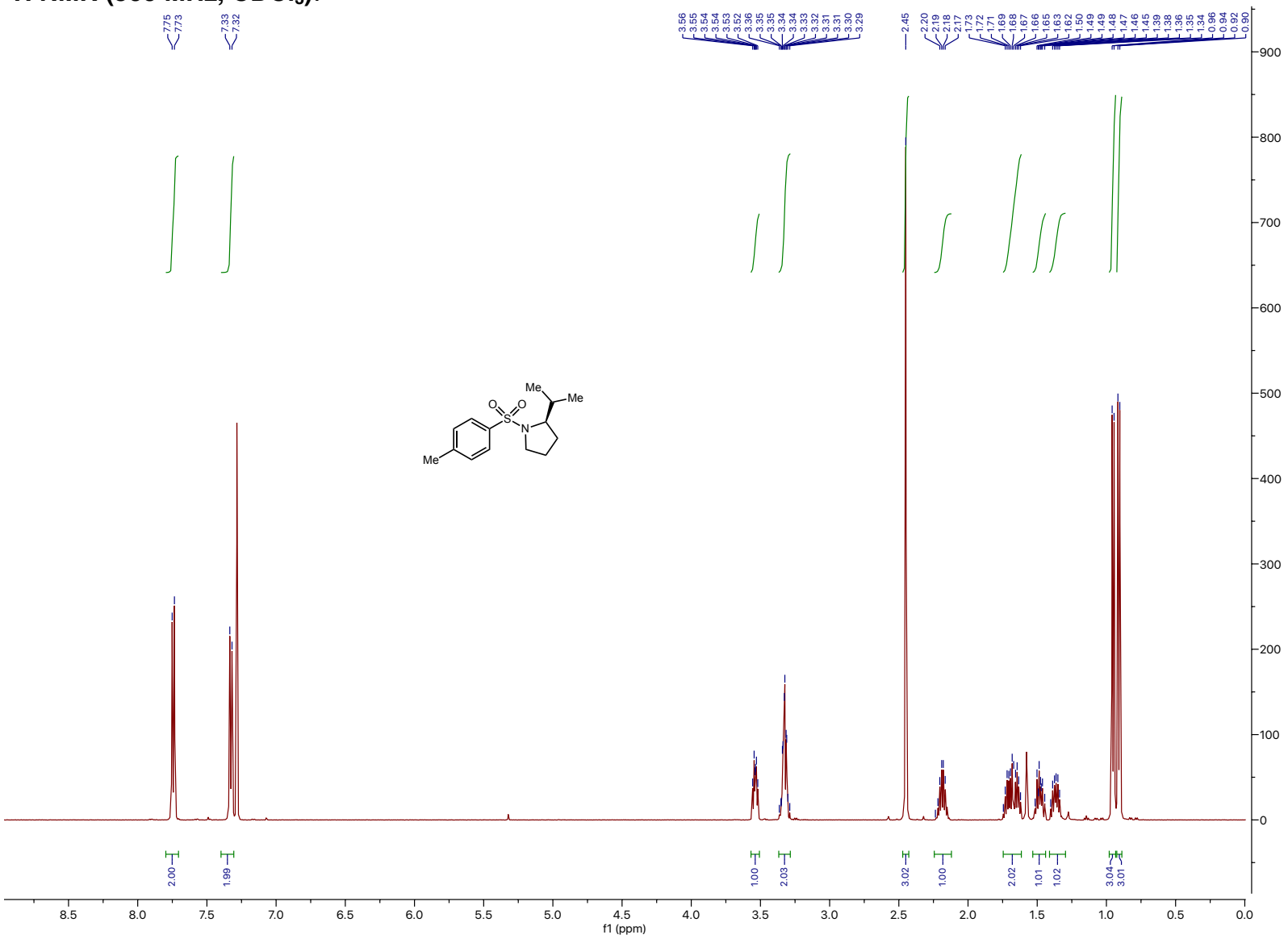
(*R*)-2-isopropyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine (**2**)

^{13}C NMR (126 MHz, $CDCl_3$):



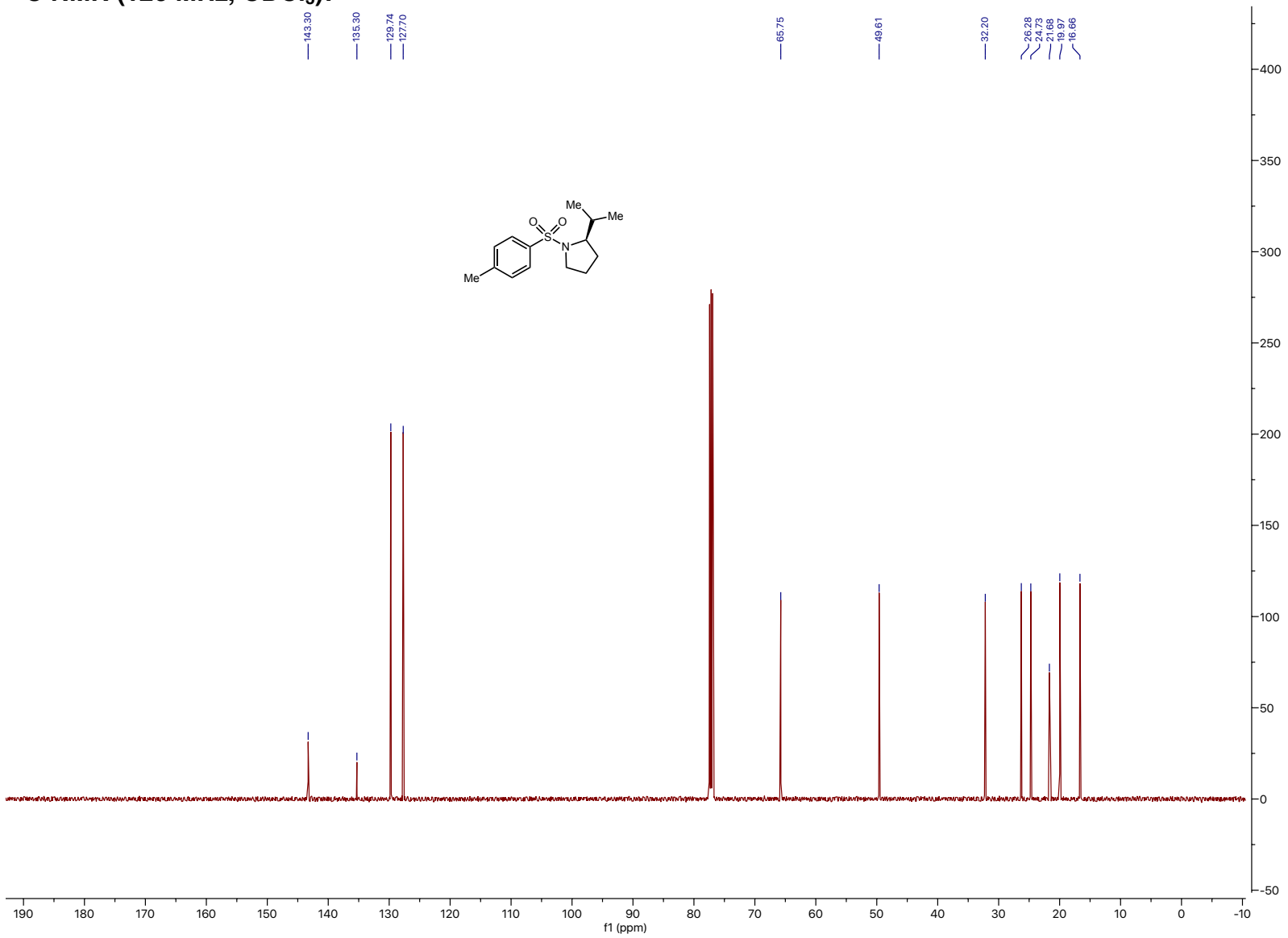
(R)-2-isopropyl-1-tosylpyrrolidine (**3**)

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



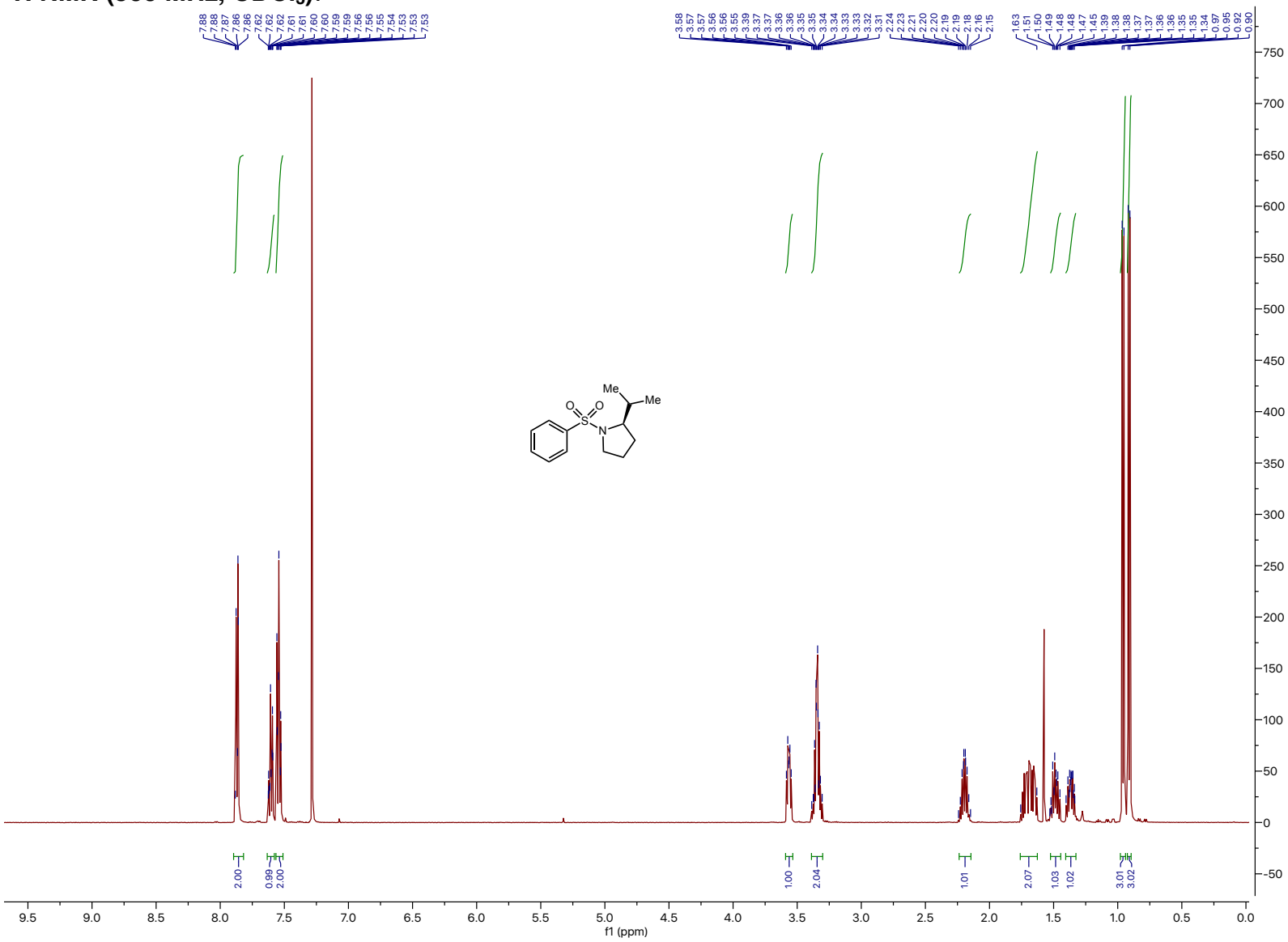
(R)-2-isopropyl-1-tosylpyrrolidine (**3**)

^{13}C NMR (126 MHz, $CDCl_3$):



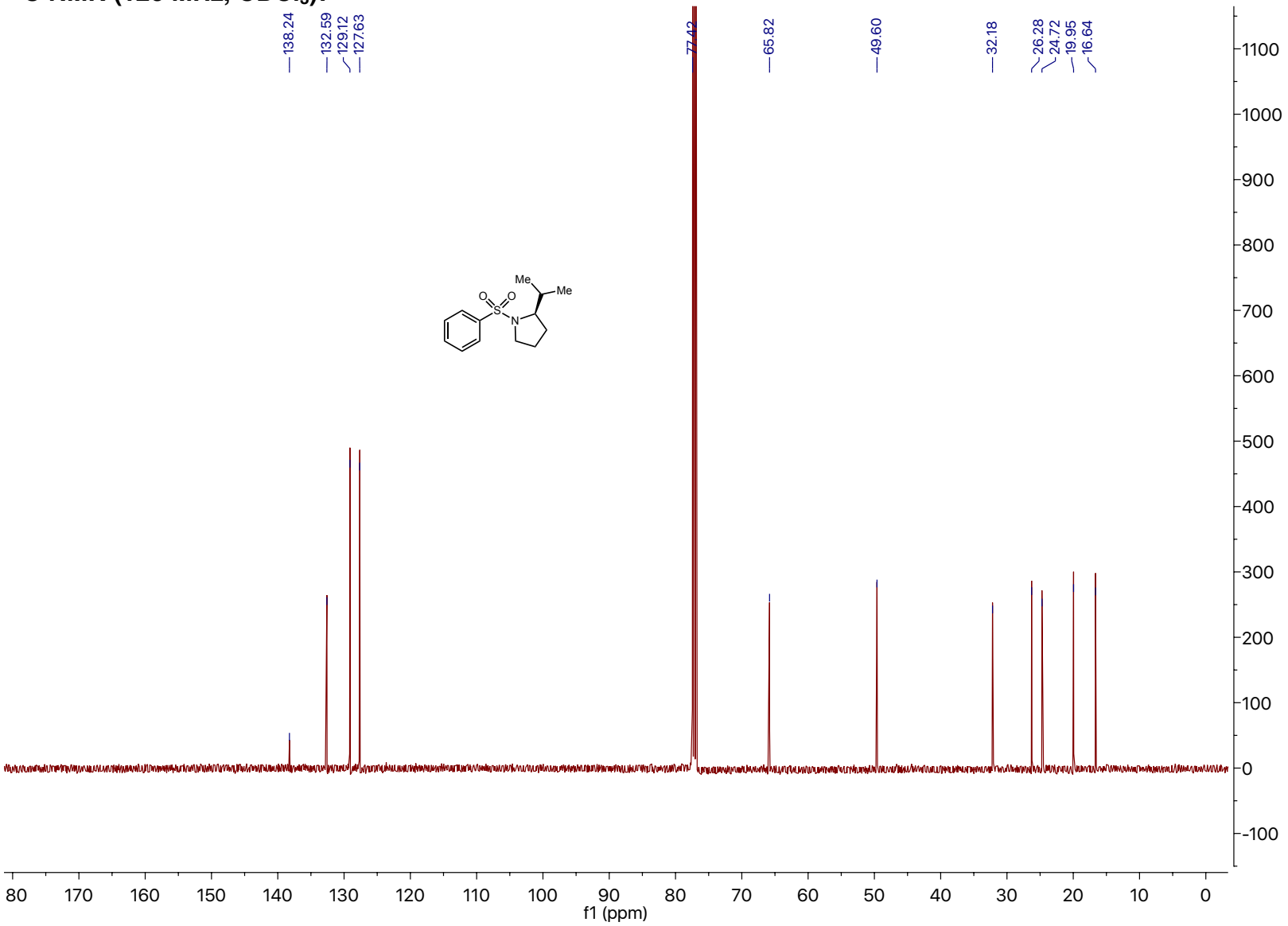
(*R*)-2-isopropyl-1-(phenylsulfonyl)pyrrolidine (**4**)

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



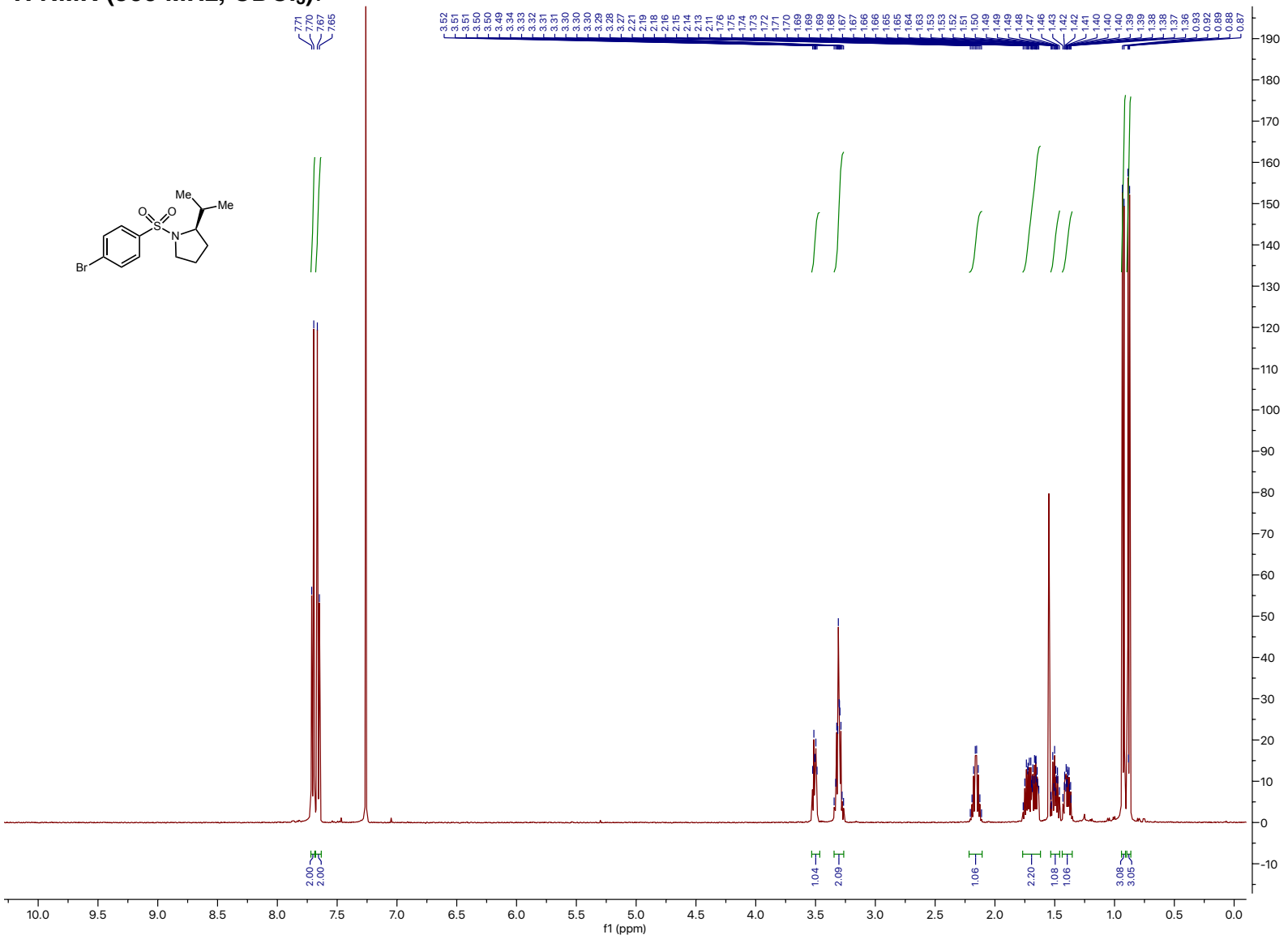
(*R*)-2-isopropyl-1-(phenylsulfonyl)pyrrolidine (**4**)

^{13}C NMR (126 MHz, $CDCl_3$):



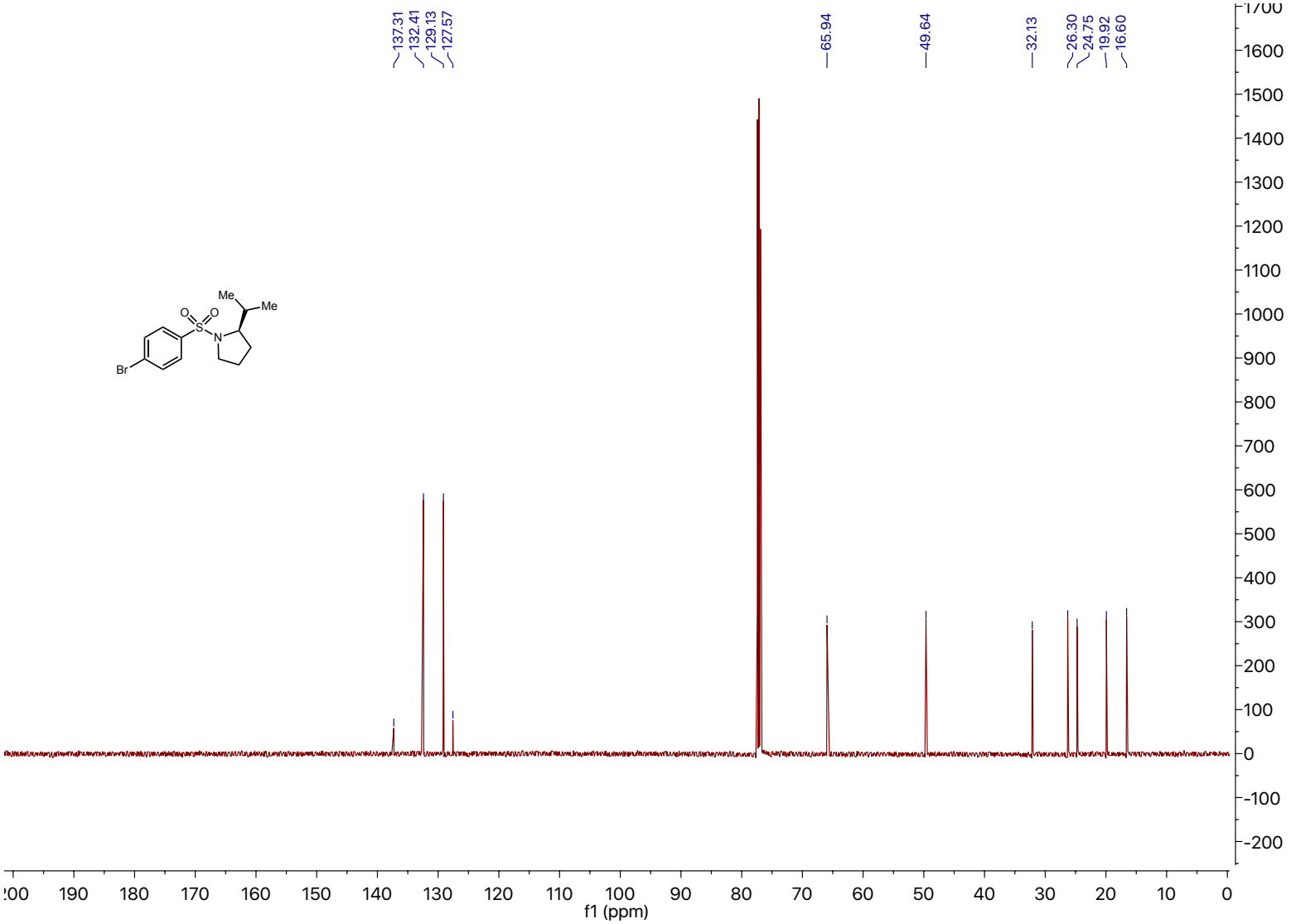
(R)-1-((4-bromophenyl)sulfonyl)-2-isopropylpyrrolidine (**5**)

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



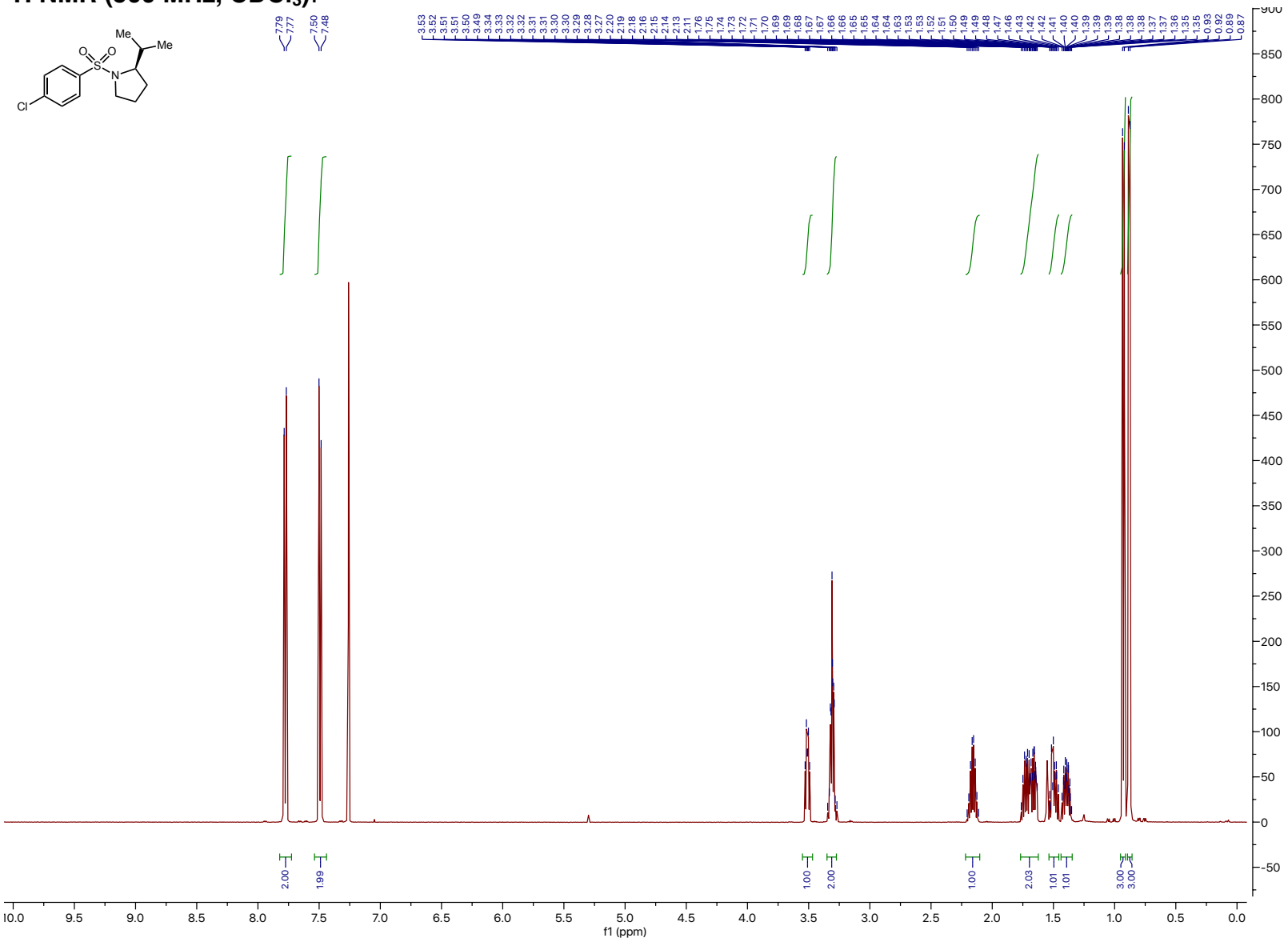
(R)-1-((4-bromophenyl)sulfonyl)-2-isopropylpyrrolidine (**5**)

^{13}C NMR (126 MHz, $CDCl_3$):



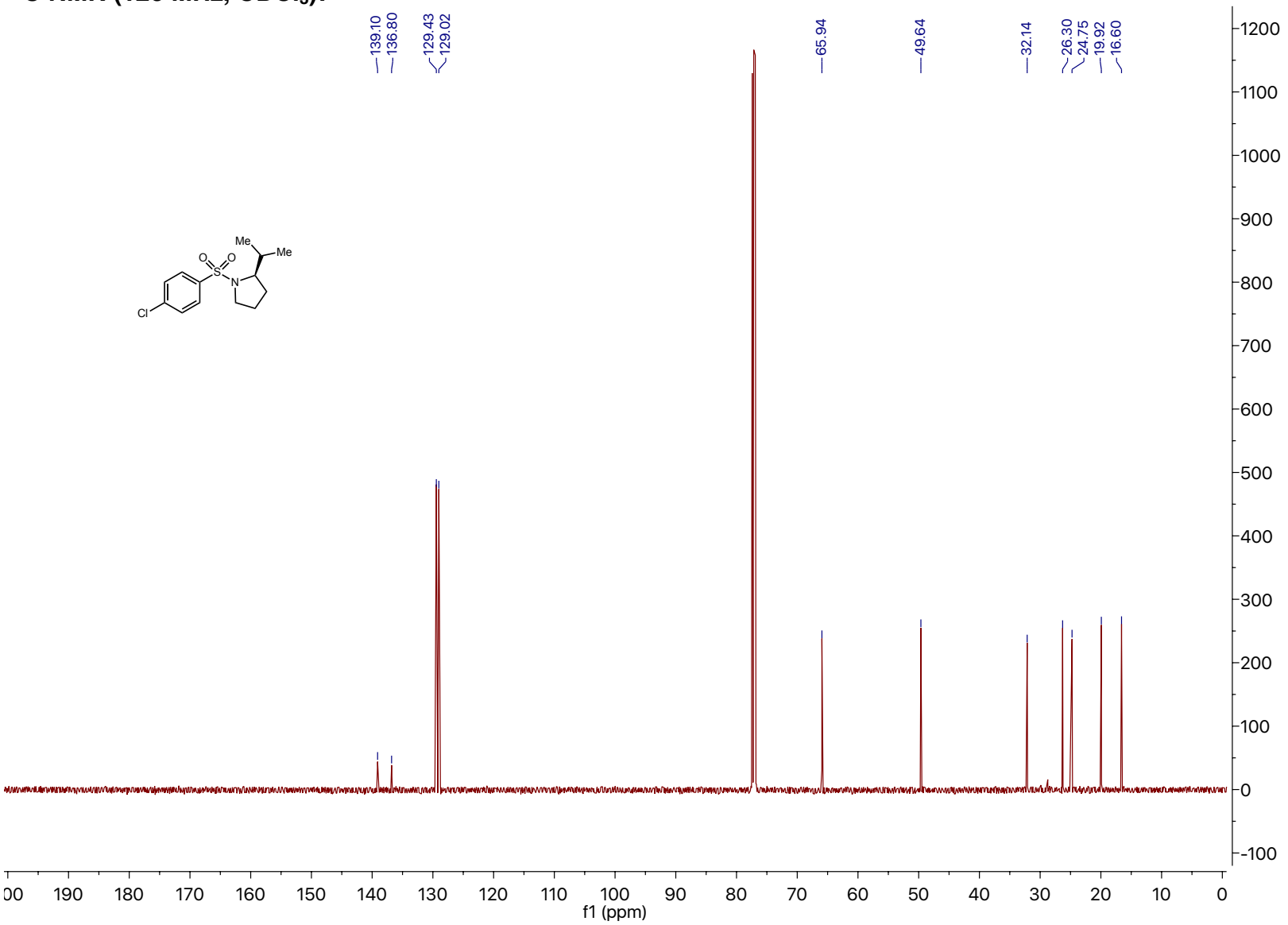
(R)-1-((4-chlorophenyl)sulfonyl)-2-isopropylpyrrolidine (**6**)

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



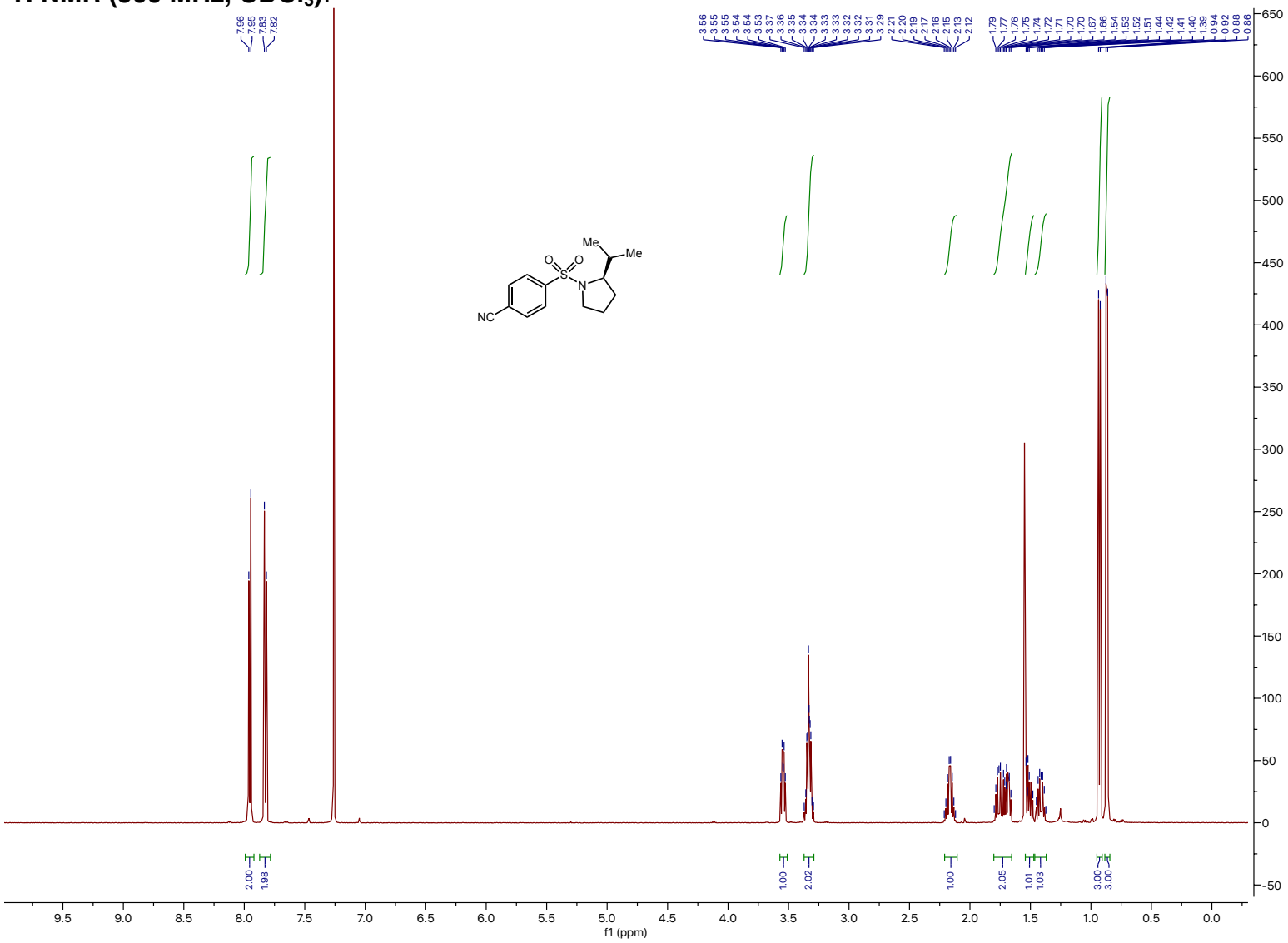
(R)-1-((4-chlorophenyl)sulfonyl)-2-isopropylpyrrolidine (**6**)

^{13}C NMR (126 MHz, $CDCl_3$):



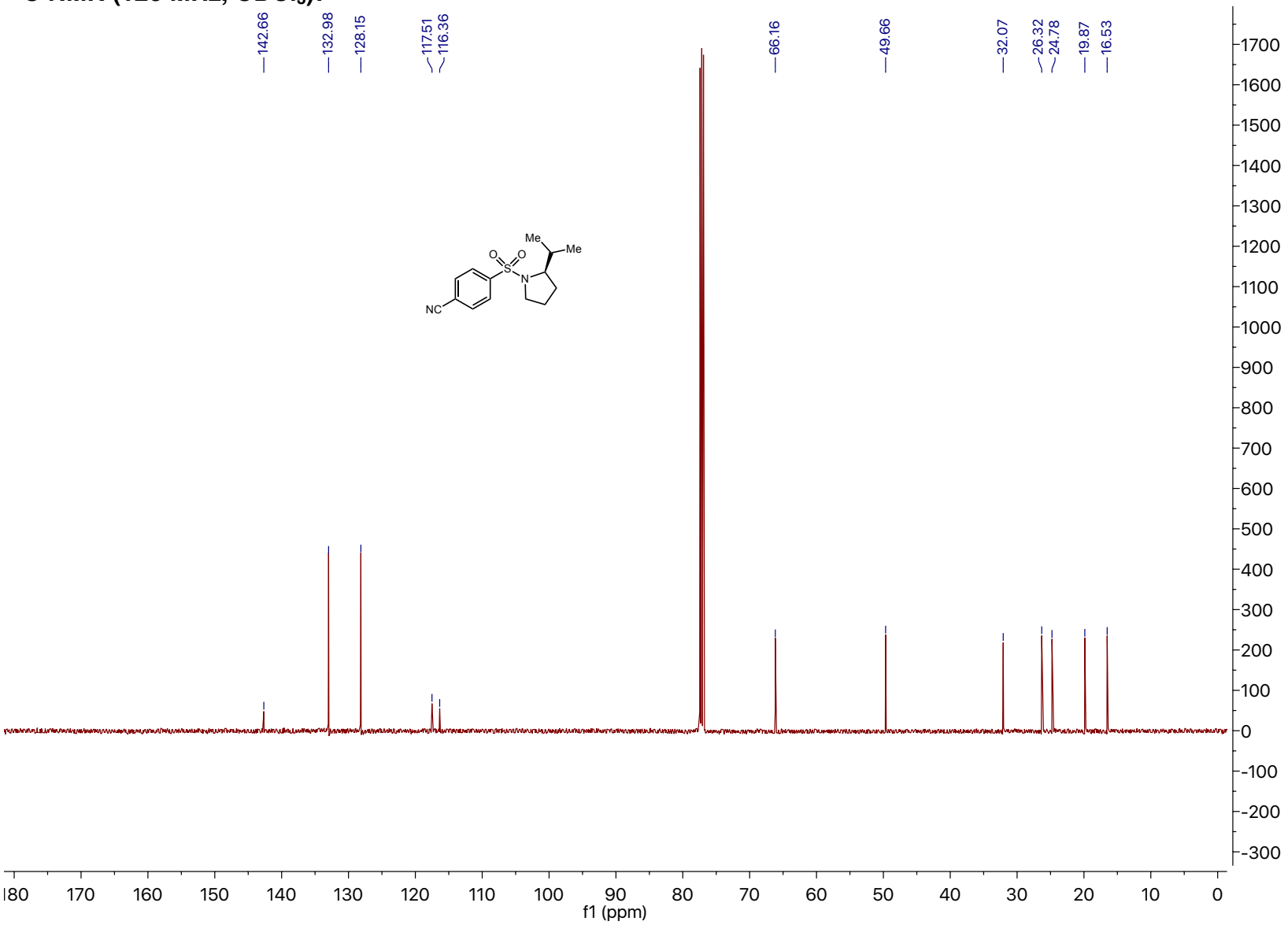
(*R*)-4-((2-isopropylpyrrolidin-1-yl)sulfonyl)benzonitrile (**7**)

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



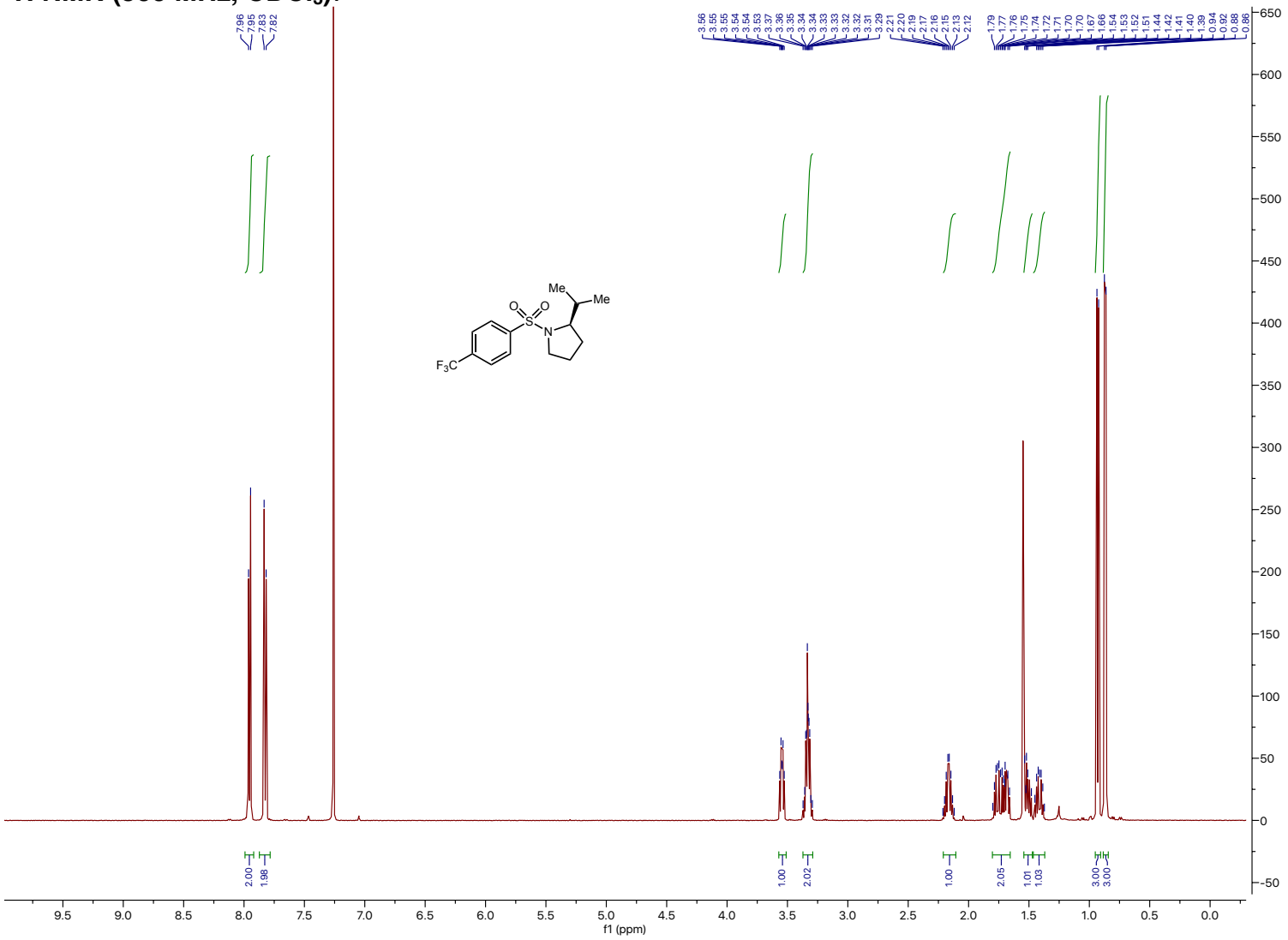
(*R*)-4-((2-isopropylpyrrolidin-1-yl)sulfonyl)benzonitrile (**7**)

^{13}C NMR (126 MHz, $CDCl_3$):



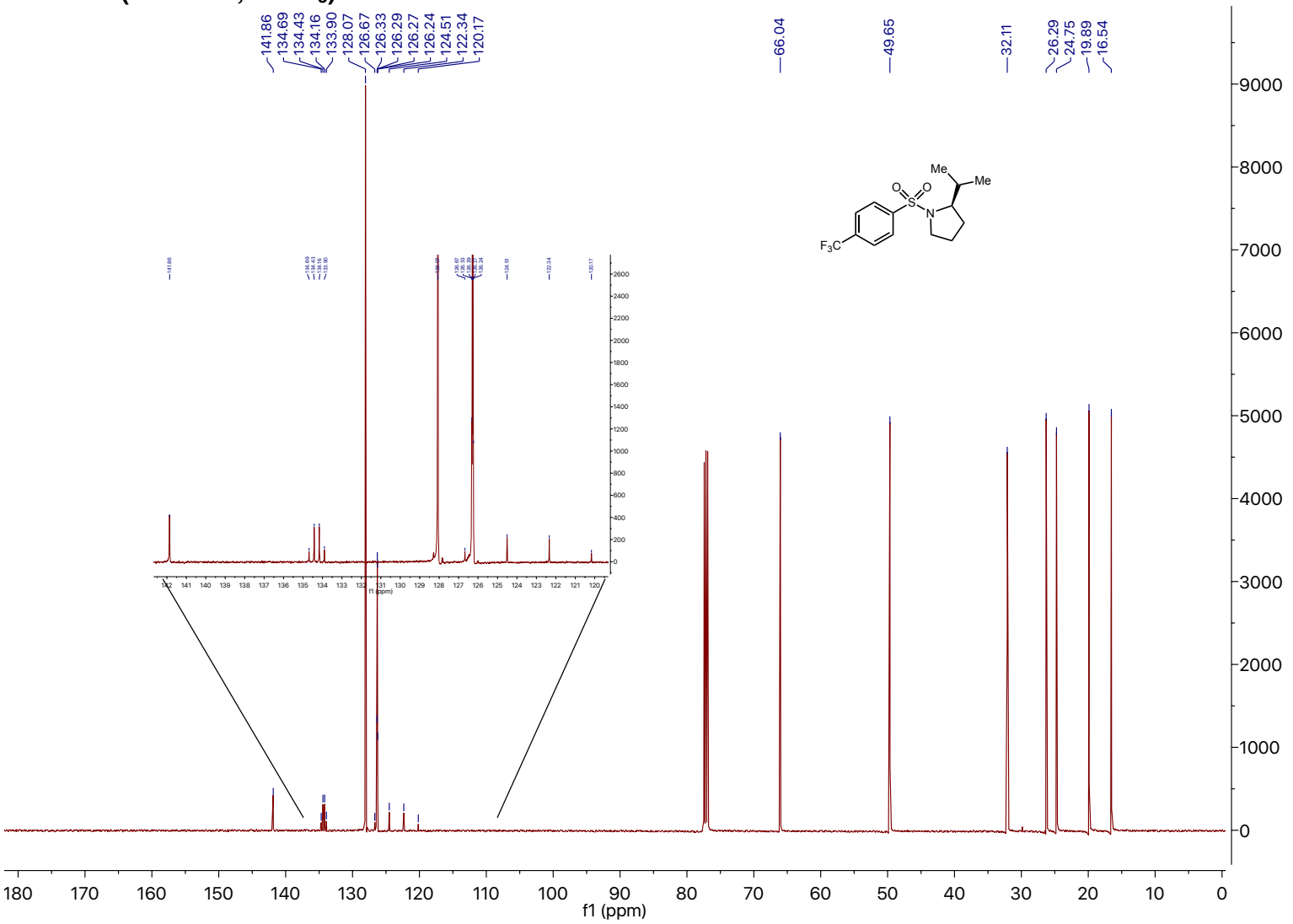
(*R*)-2-isopropyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (**8**)

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



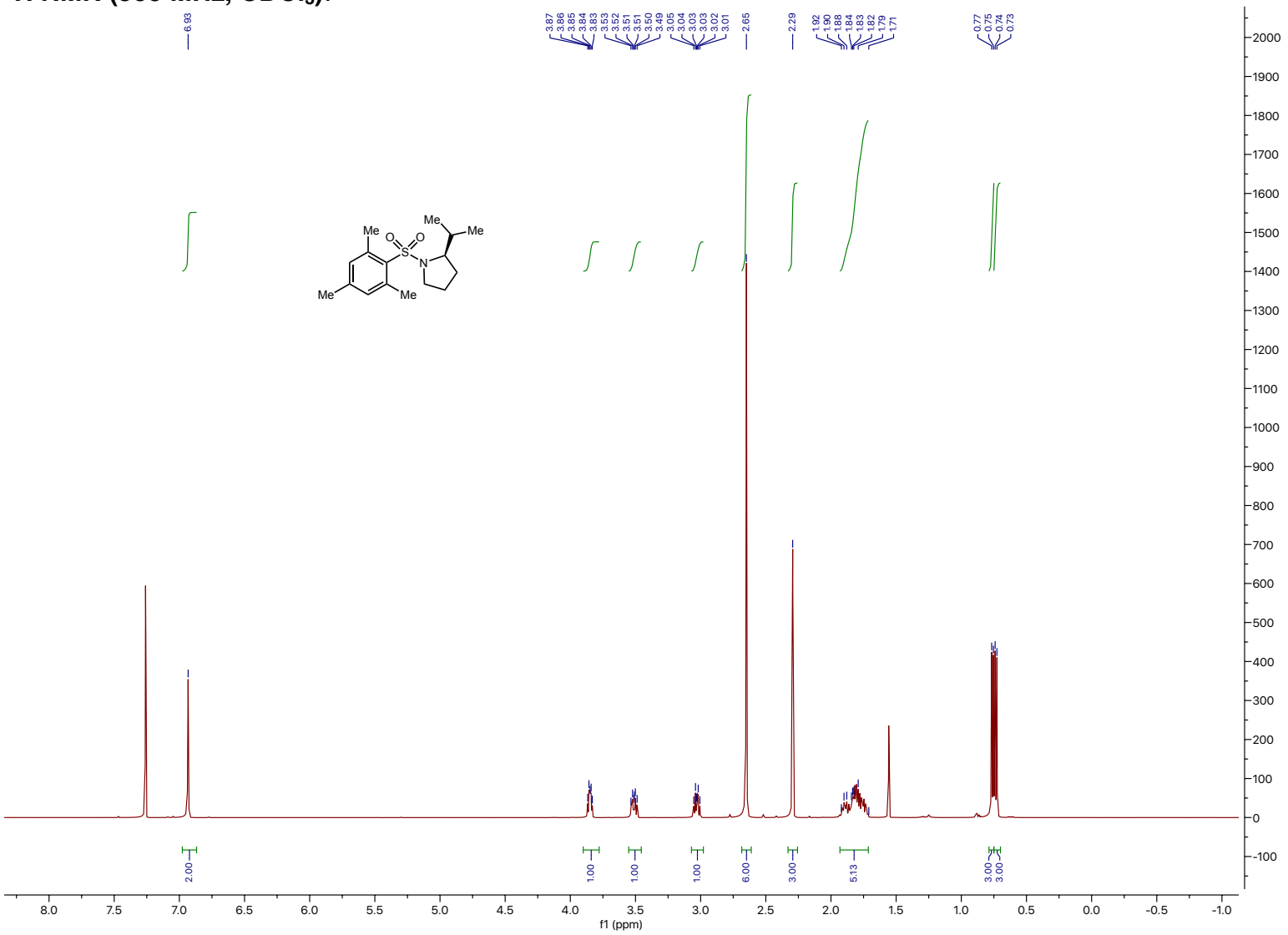
(*R*)-2-isopropyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (**8**)

^{13}C NMR (126 MHz, $CDCl_3$):



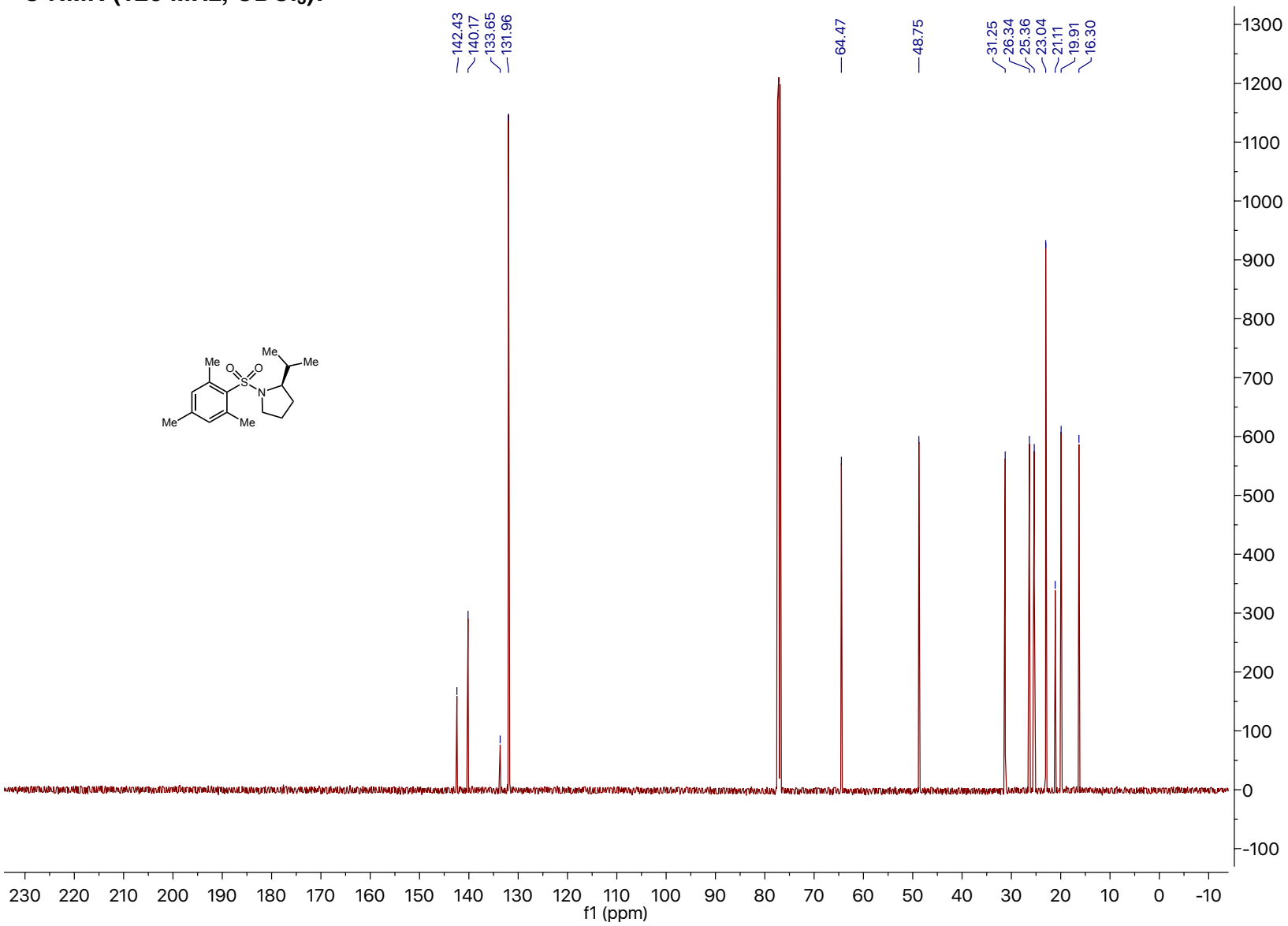
(R)-2-isopropyl-1-(mesitylsulfonyl)pyrrolidine (**9**)

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



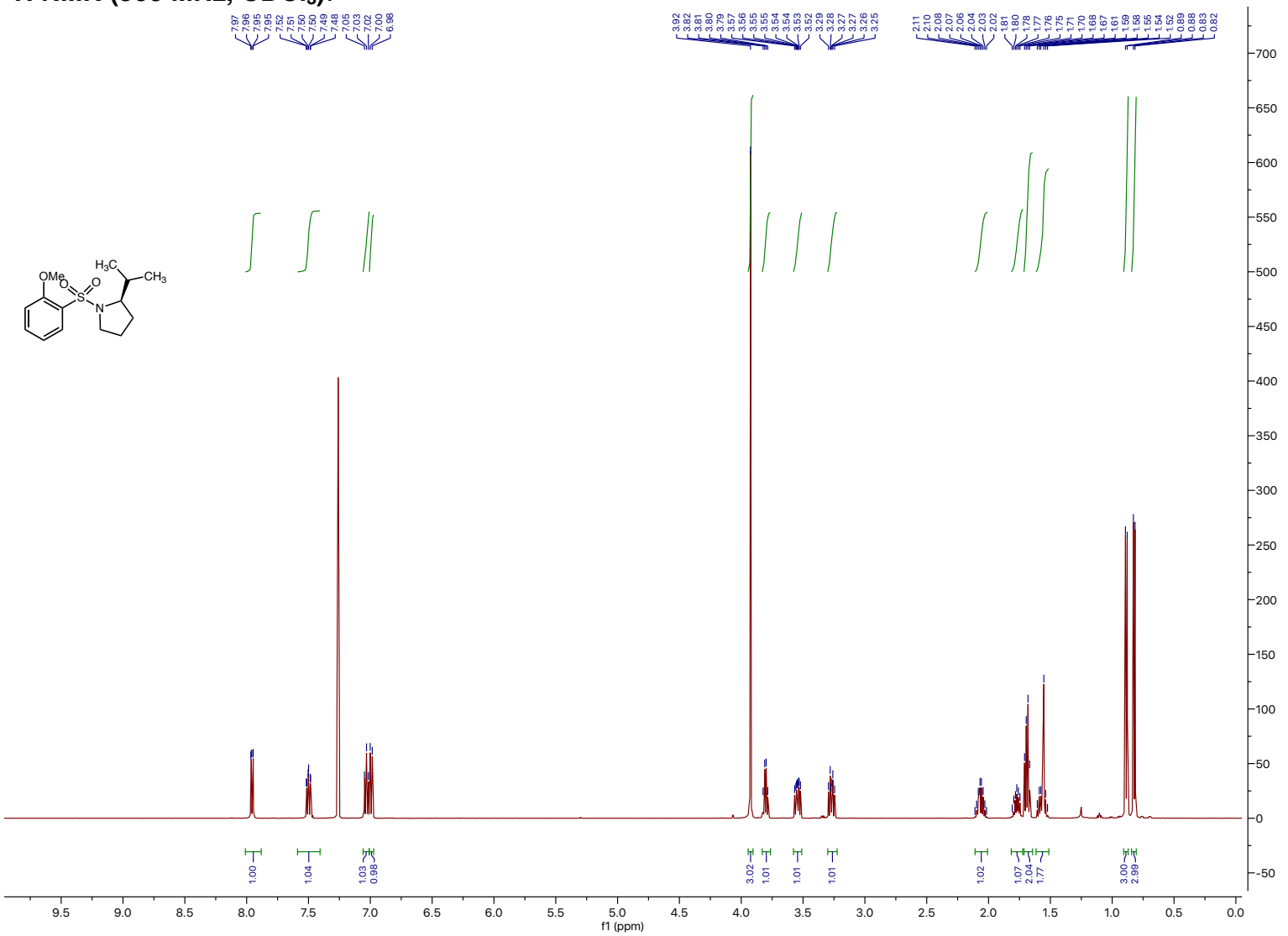
(R)-2-isopropyl-1-(mesitylsulfonyl)pyrrolidine (**9**)

^{13}C NMR (126 MHz, $CDCl_3$):



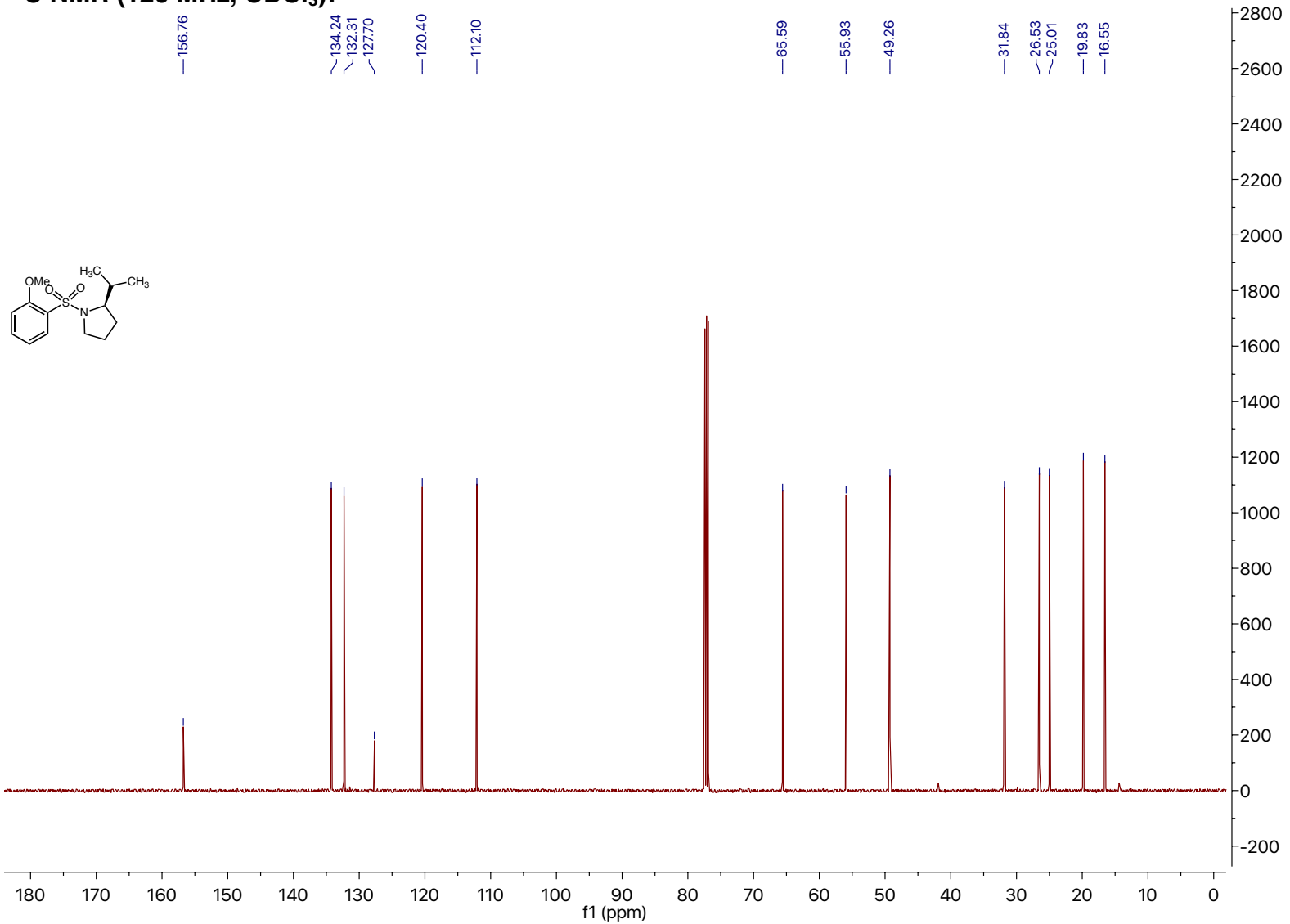
(*R*)-2-isopropyl-1-((2-methoxyphenyl)sulfonyl)pyrrolidine (**10**)

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



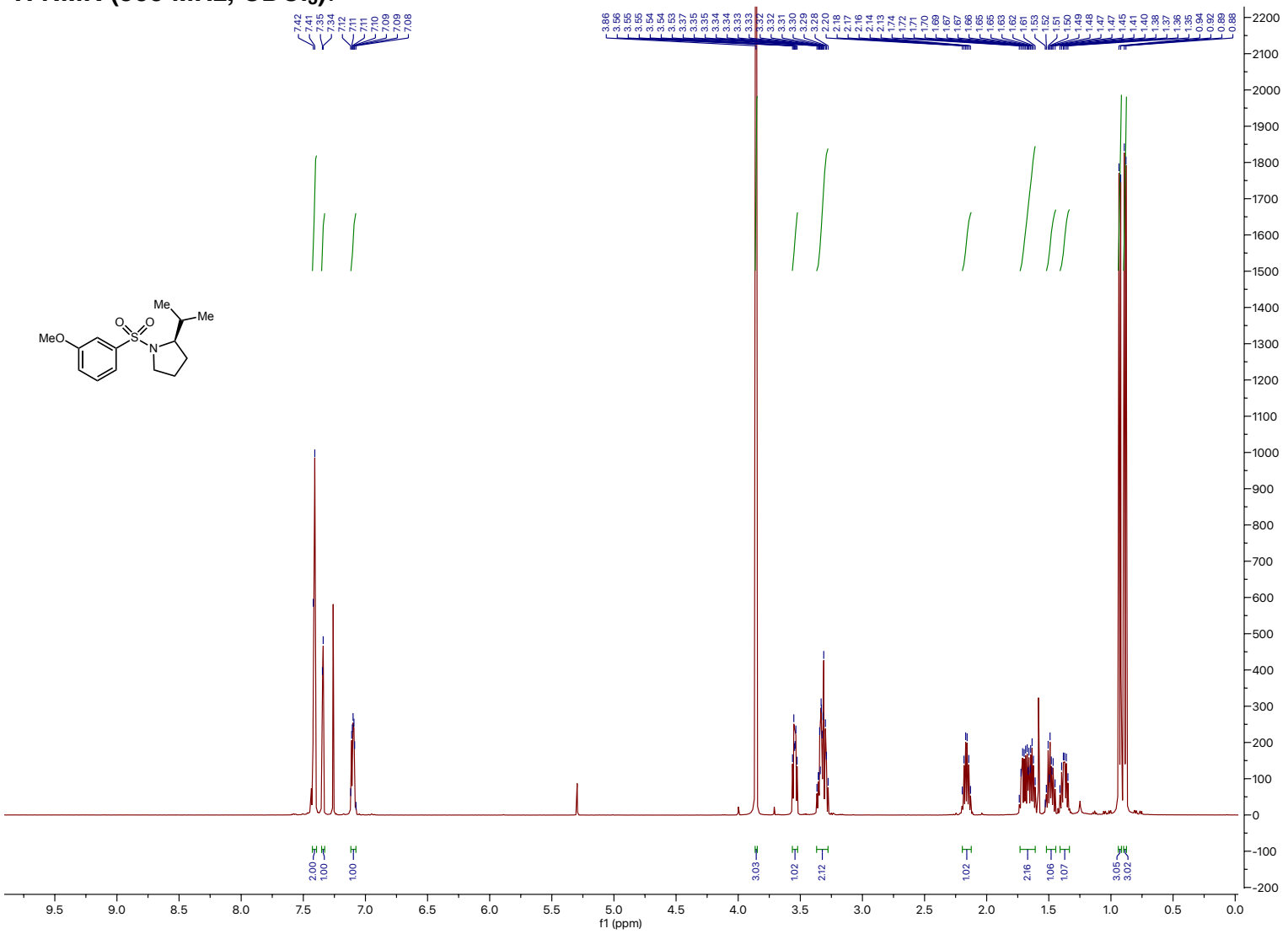
(*R*)-2-isopropyl-1-((2-methoxyphenyl)sulfonyl)pyrrolidine (**10**)

^{13}C NMR (126 MHz, $CDCl_3$):



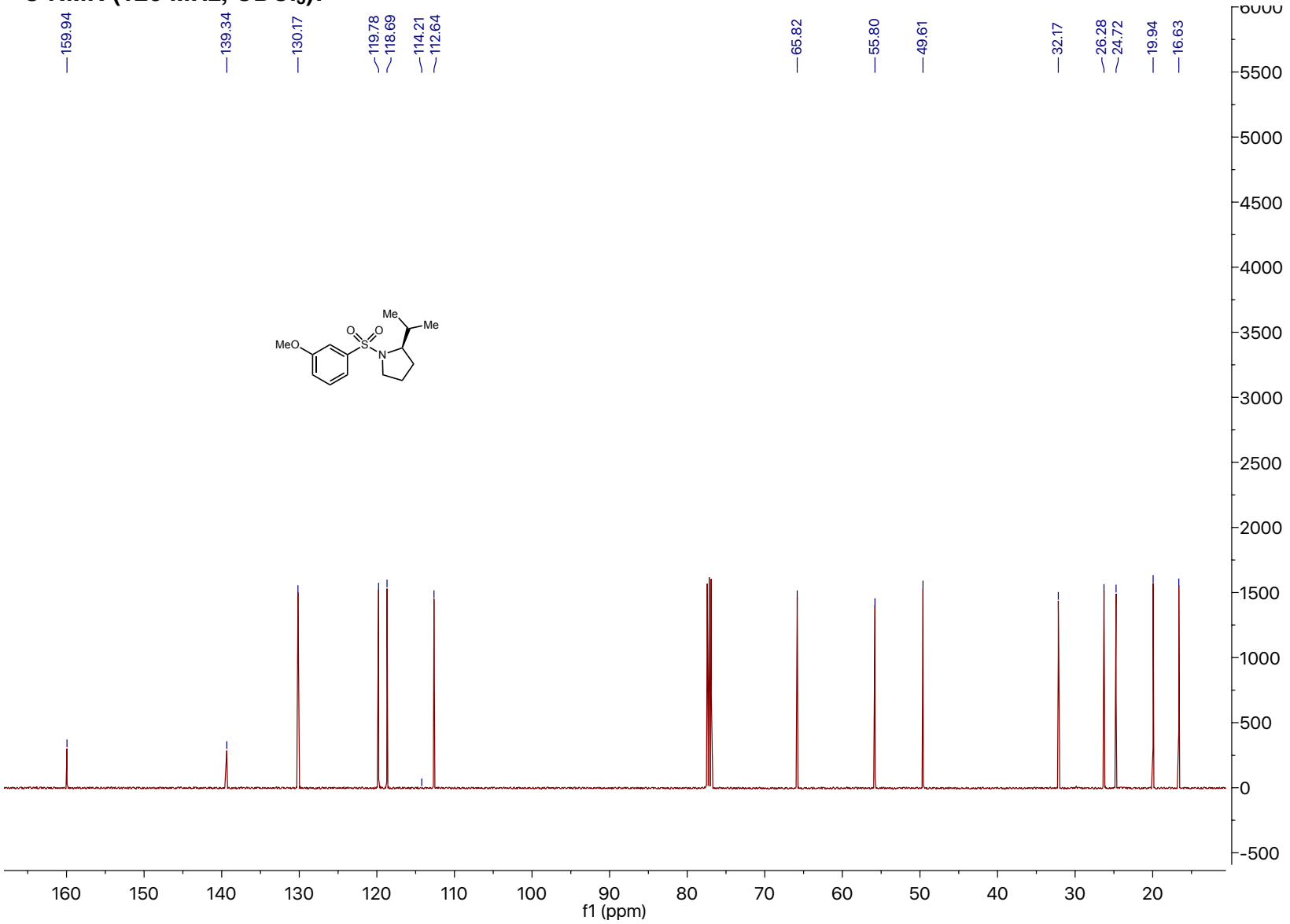
(*R*)-2-isopropyl-1-((3-methoxyphenyl)sulfonyl)pyrrolidine (**11**)

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



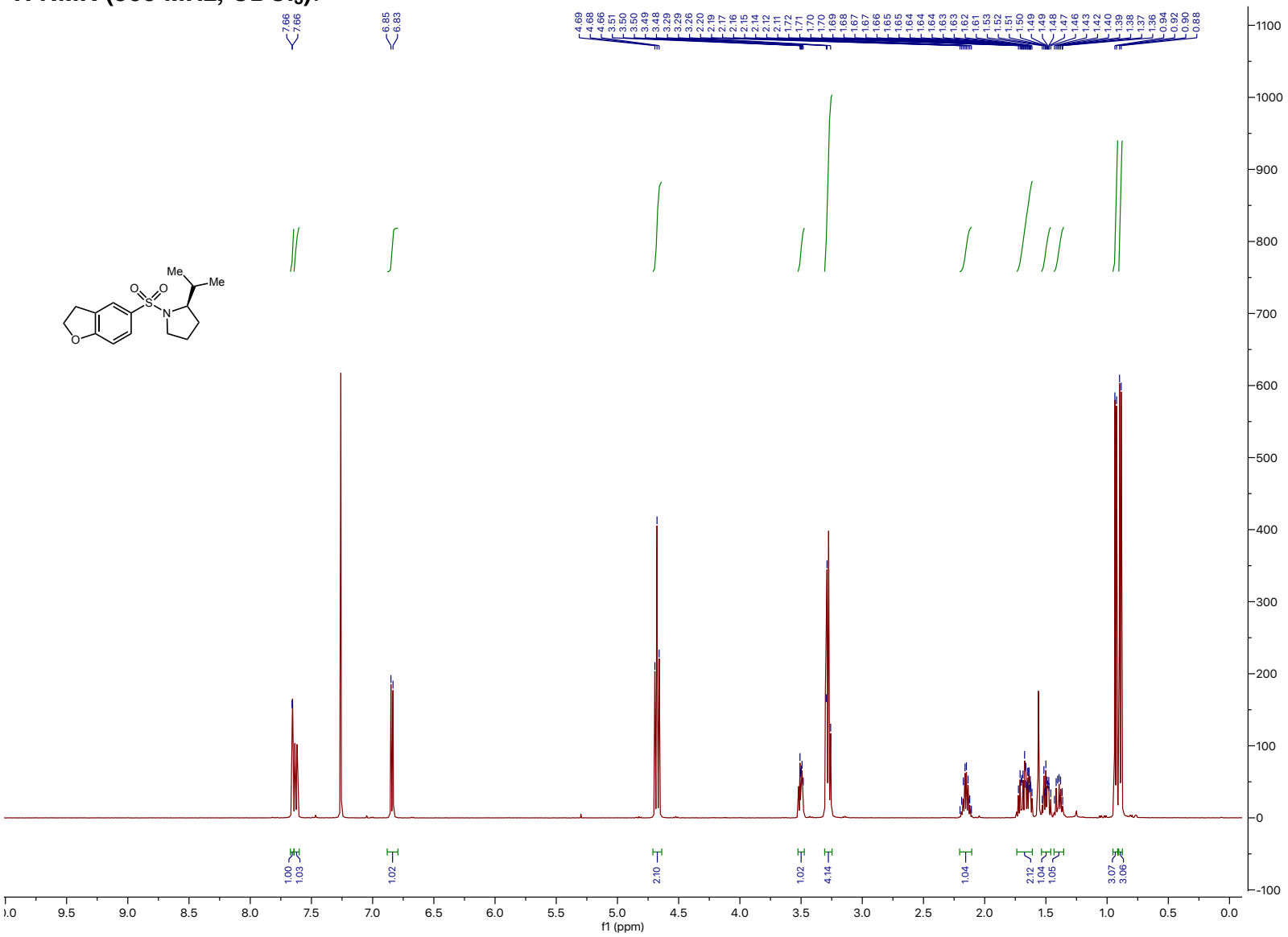
(*R*)-2-isopropyl-1-((3-methoxyphenyl)sulfonyl)pyrrolidine (**11**)

^{13}C NMR (126 MHz, $CDCl_3$):



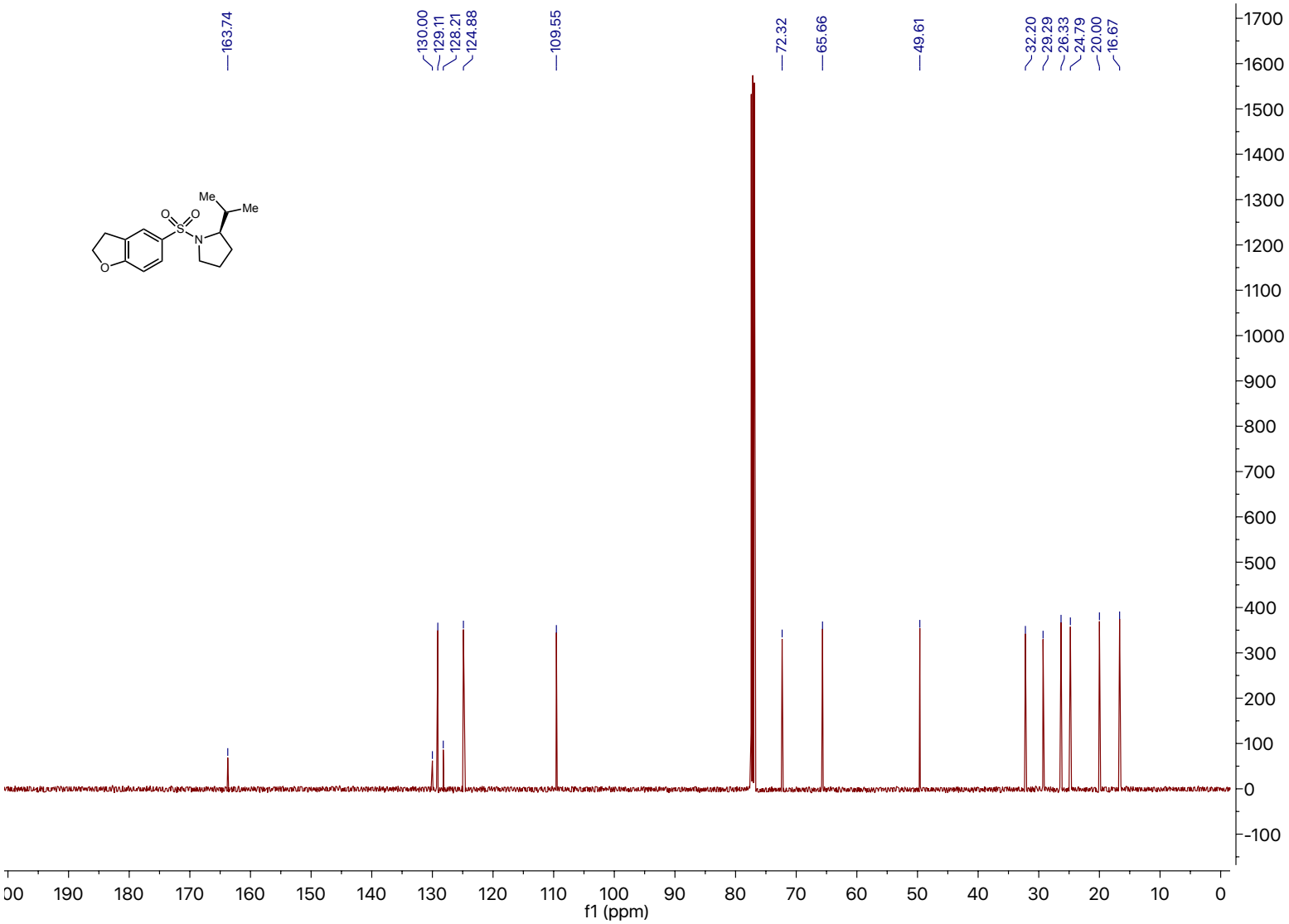
(*R*)-1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2-isopropylpyrrolidine (**12**)

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



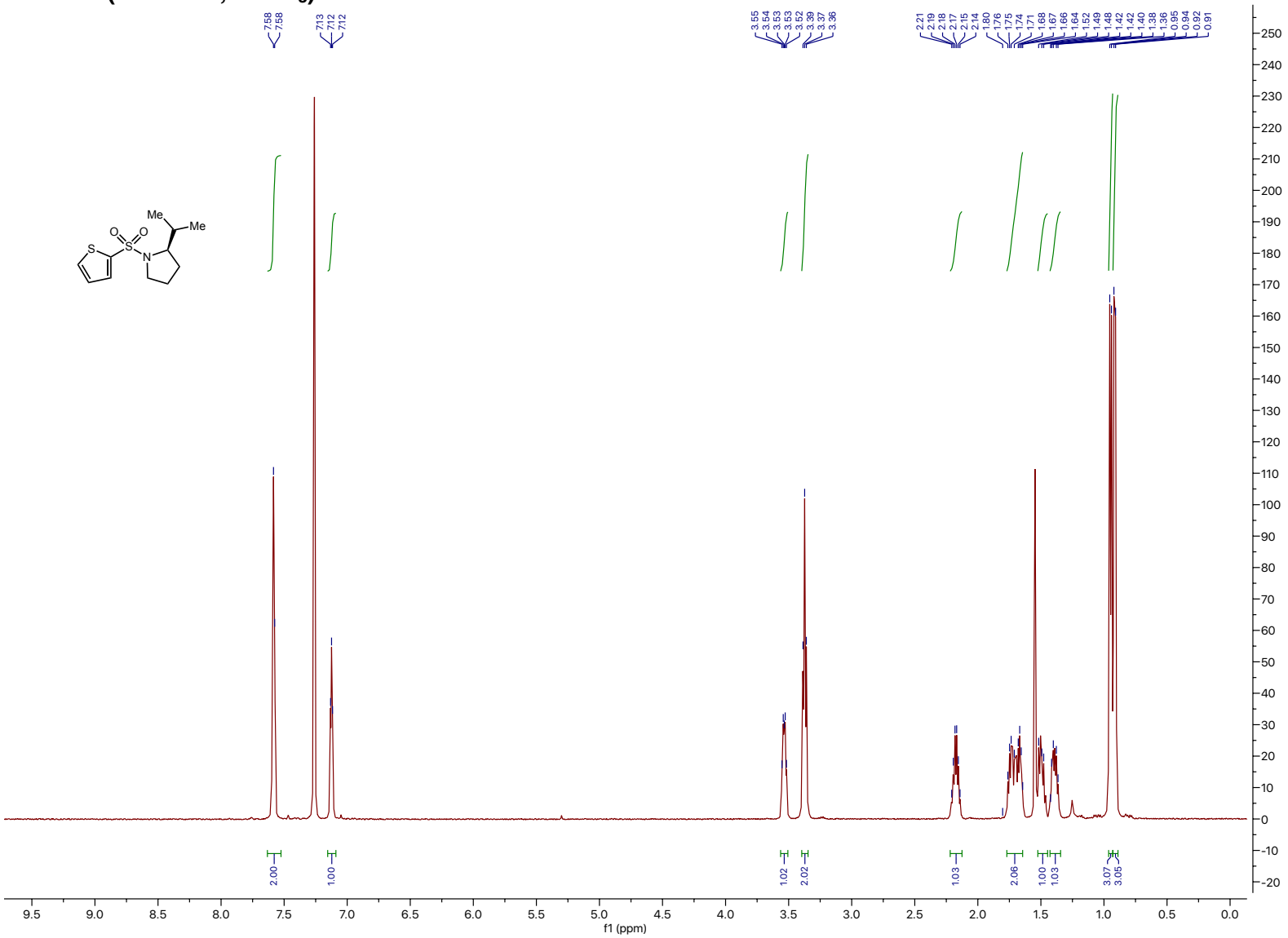
(*R*)-1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2-isopropylpyrrolidine (**12**)

^{13}C NMR (126 MHz, $CDCl_3$):



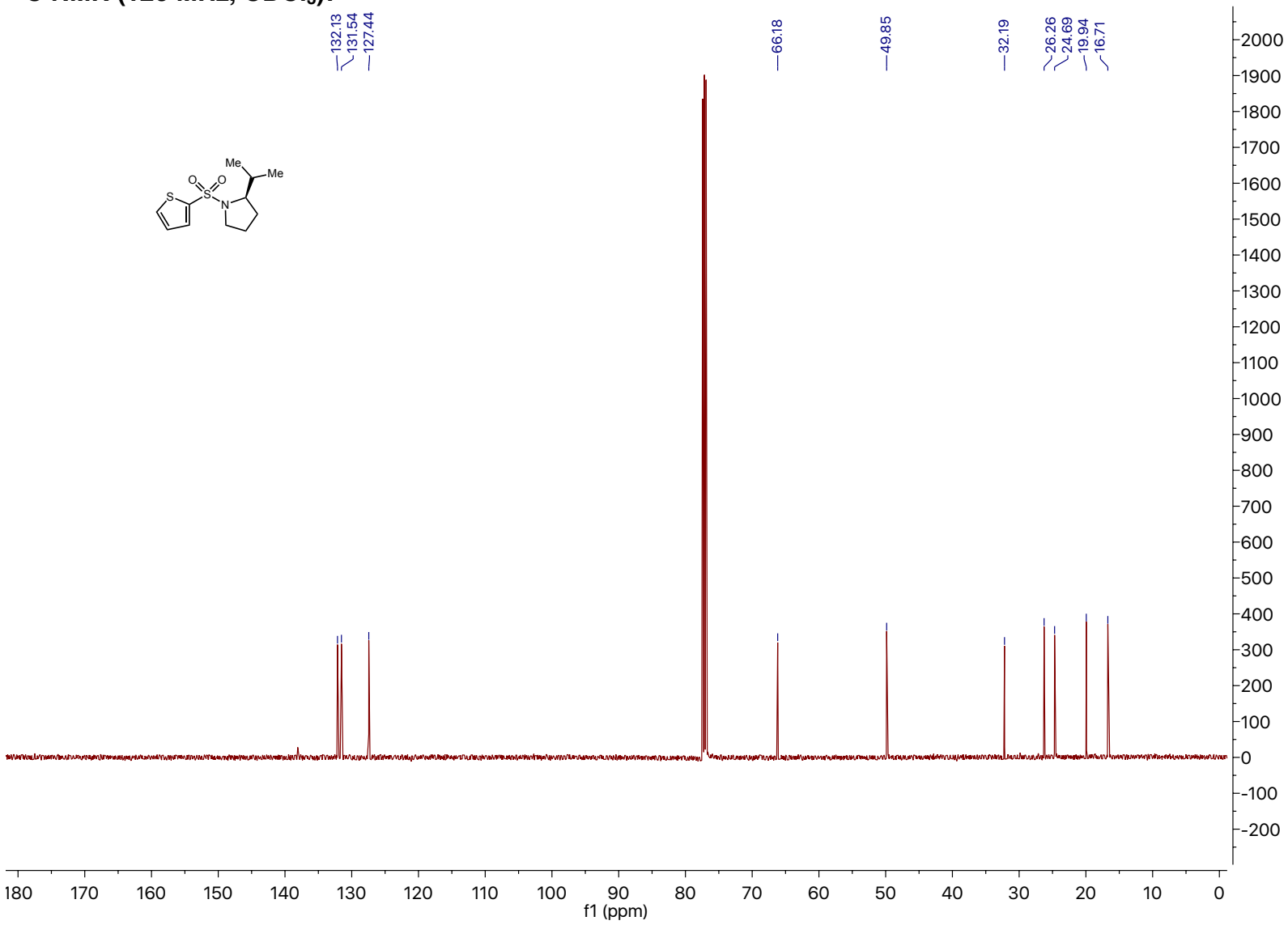
(*R*)-2-isopropyl-1-(thiophen-2-ylsulfonyl)pyrrolidine (**13**)

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



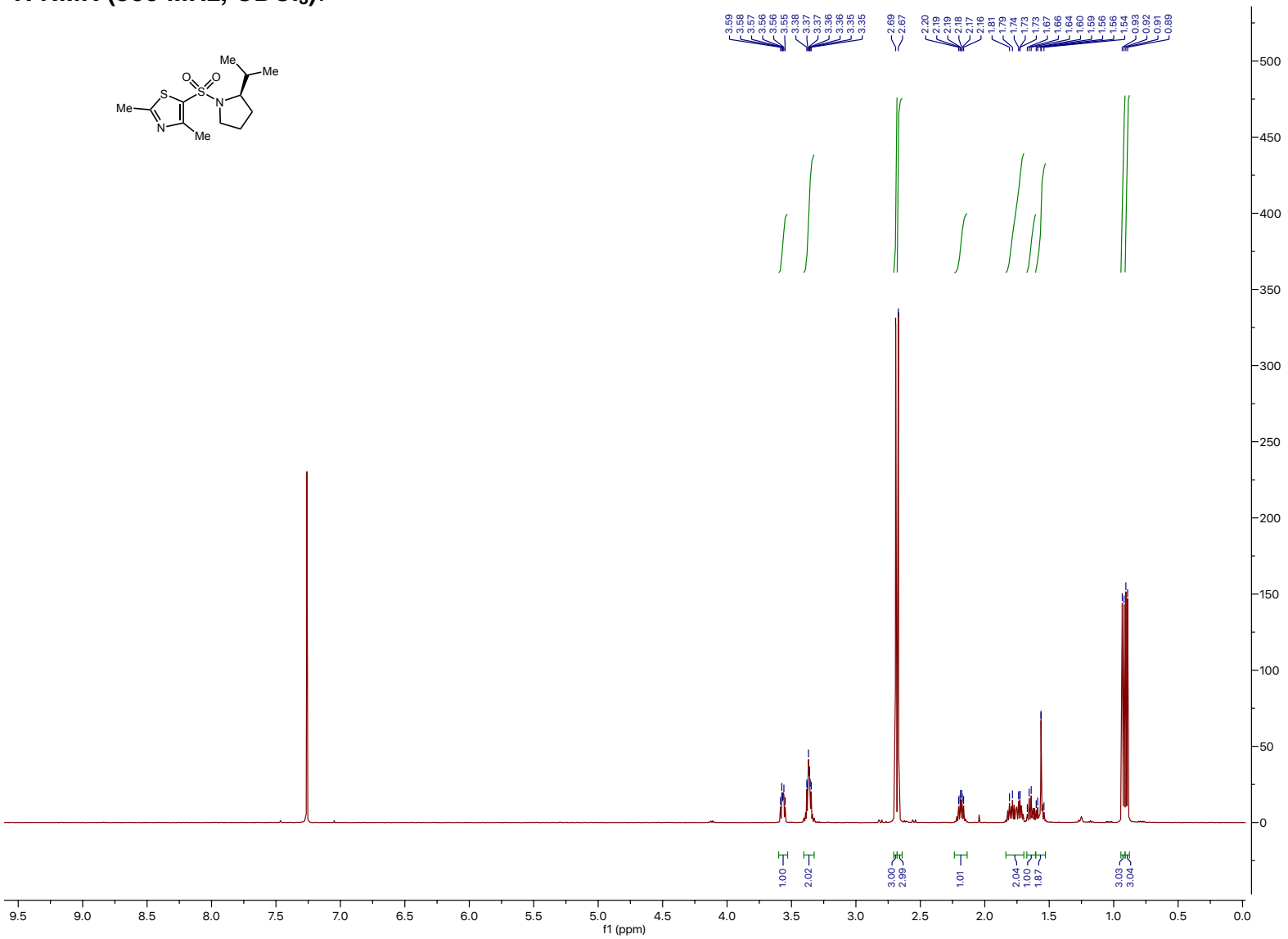
(*R*)-2-isopropyl-1-(thiophen-2-ylsulfonyl)pyrrolidine (**13**)

^{13}C NMR (126 MHz, $CDCl_3$):



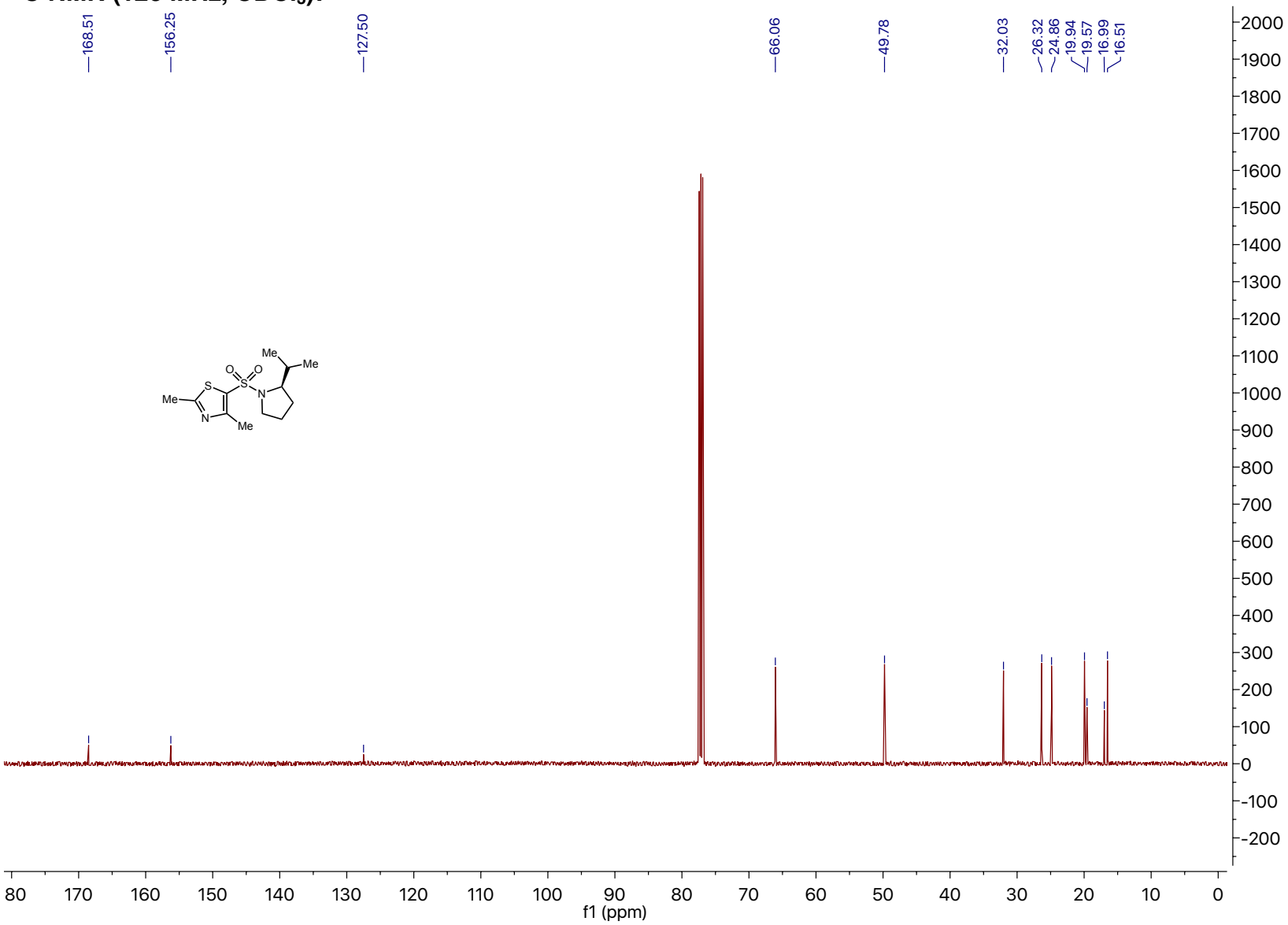
(*R*)-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)-2,4-dimethylthiazole (**14**)

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



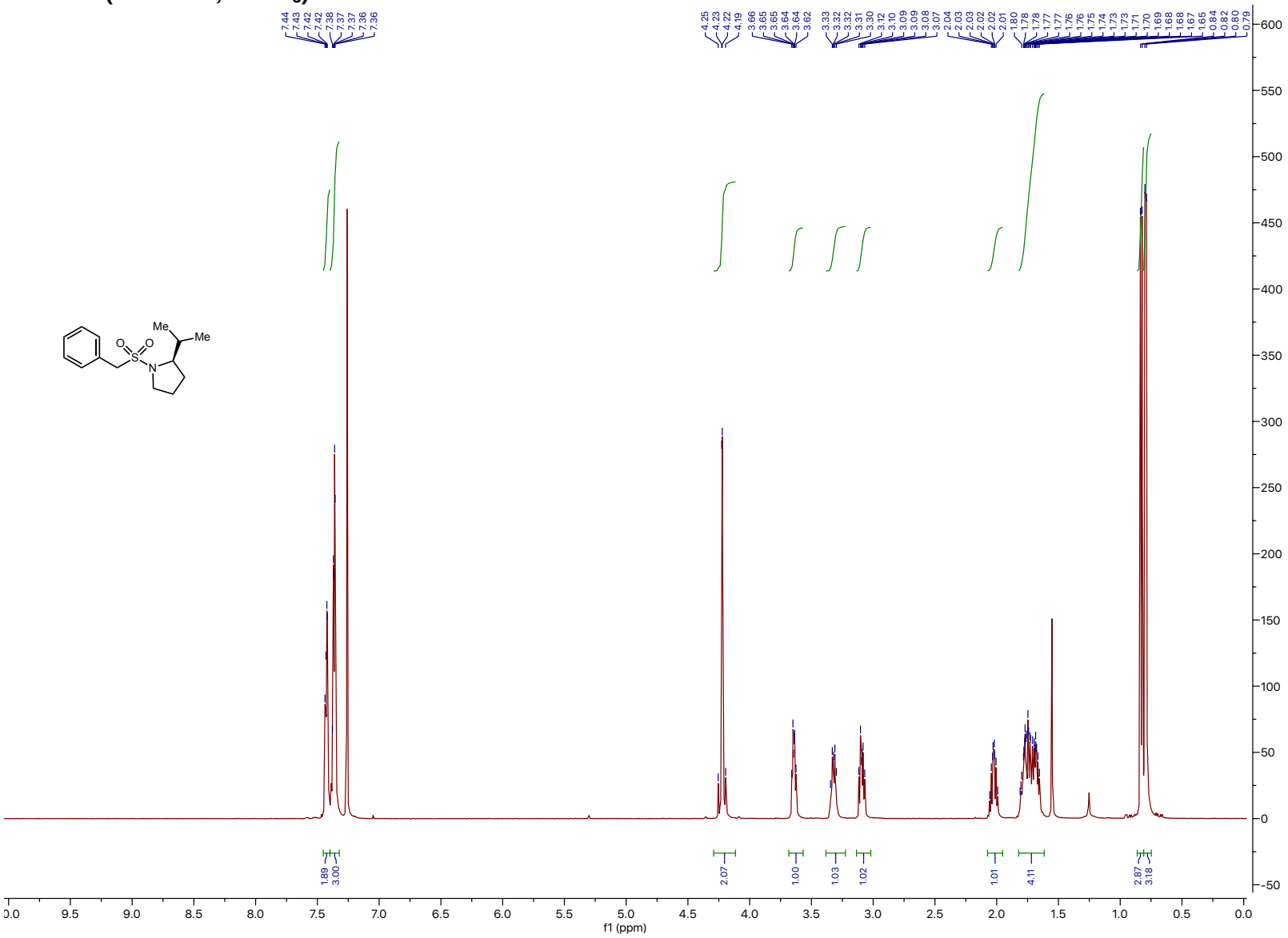
(*R*)-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)-2,4-dimethylthiazole (**14**)

^{13}C NMR (126 MHz, $CDCl_3$):



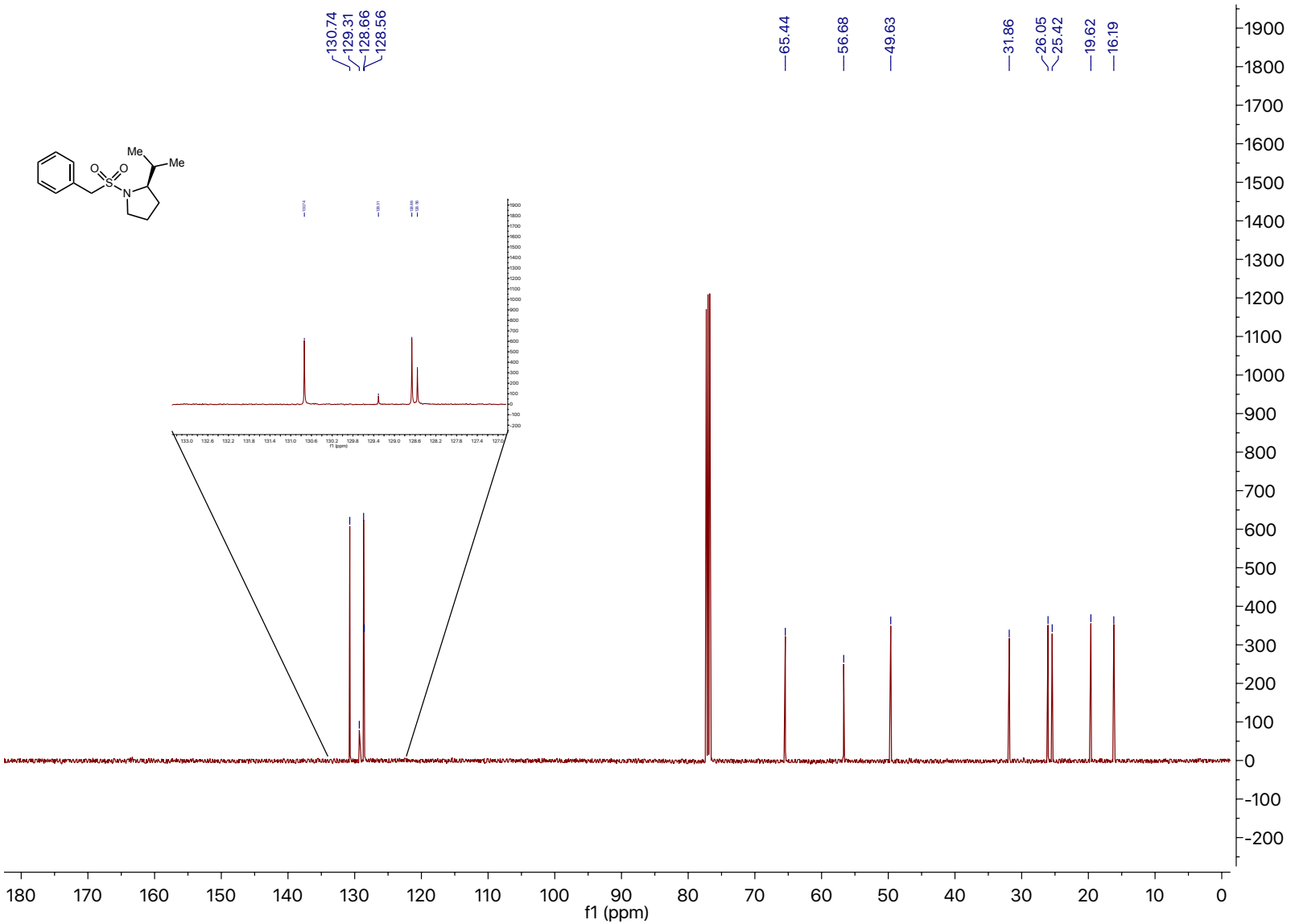
(*R*)-1-(benzylsulfonyl)-2-isopropylpyrrolidine (**15**)

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



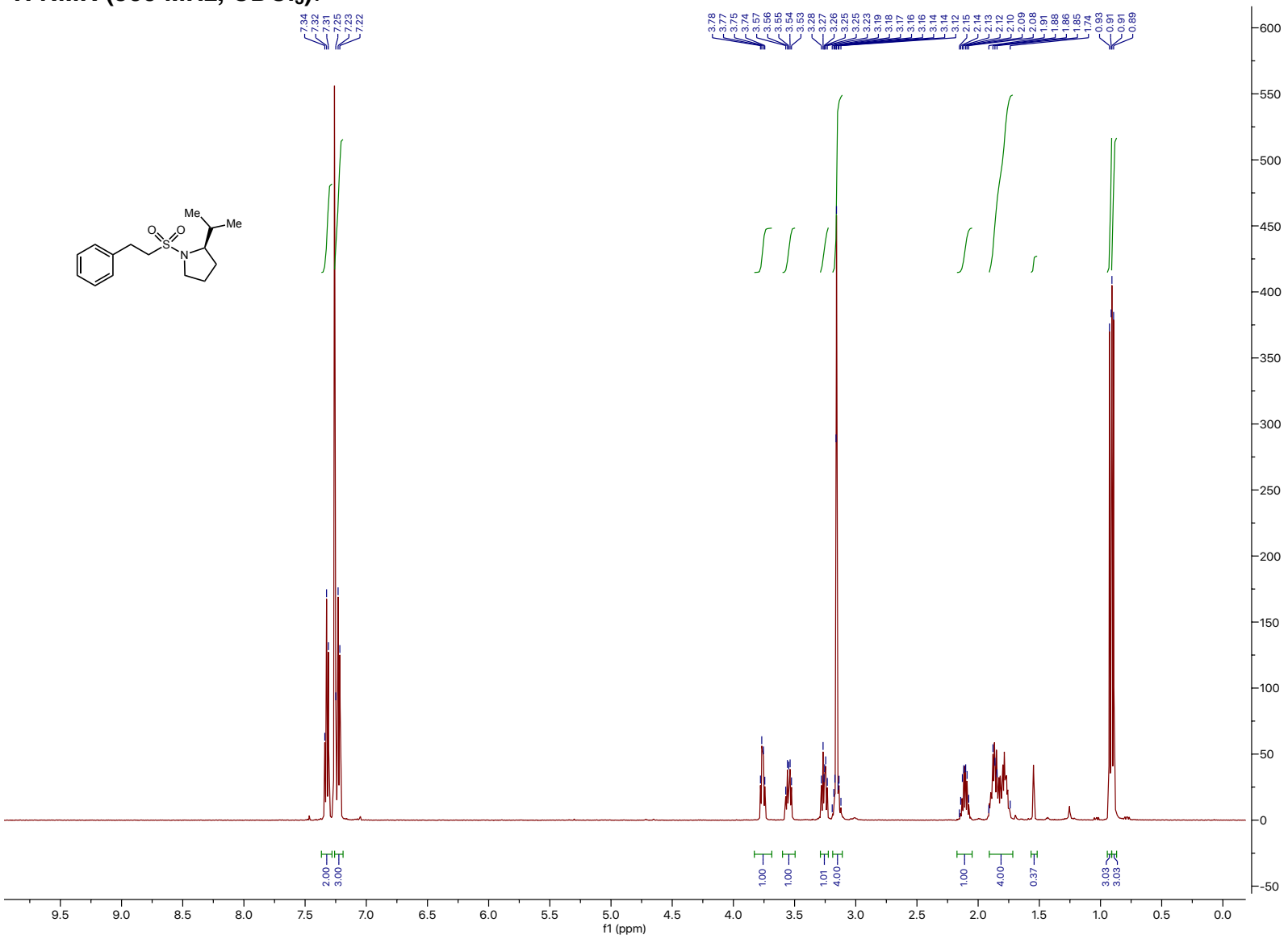
(*R*)-1-(benzylsulfonyl)-2-isopropylpyrrolidine (**15**)

^{13}C NMR (126 MHz, $CDCl_3$):



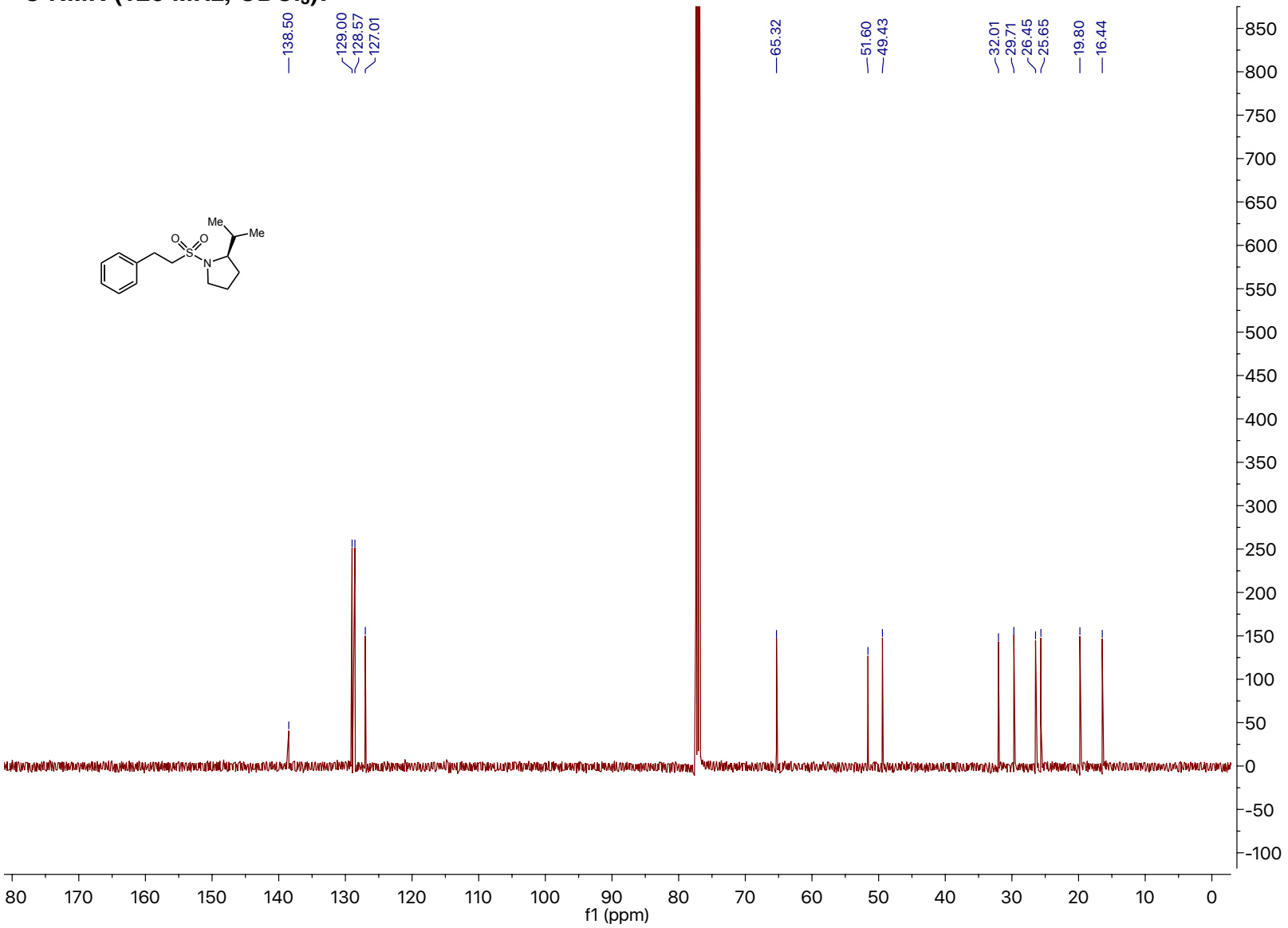
(*R*)-2-isopropyl-1-(phenethylsulfonyl)pyrrolidine (**16**)

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



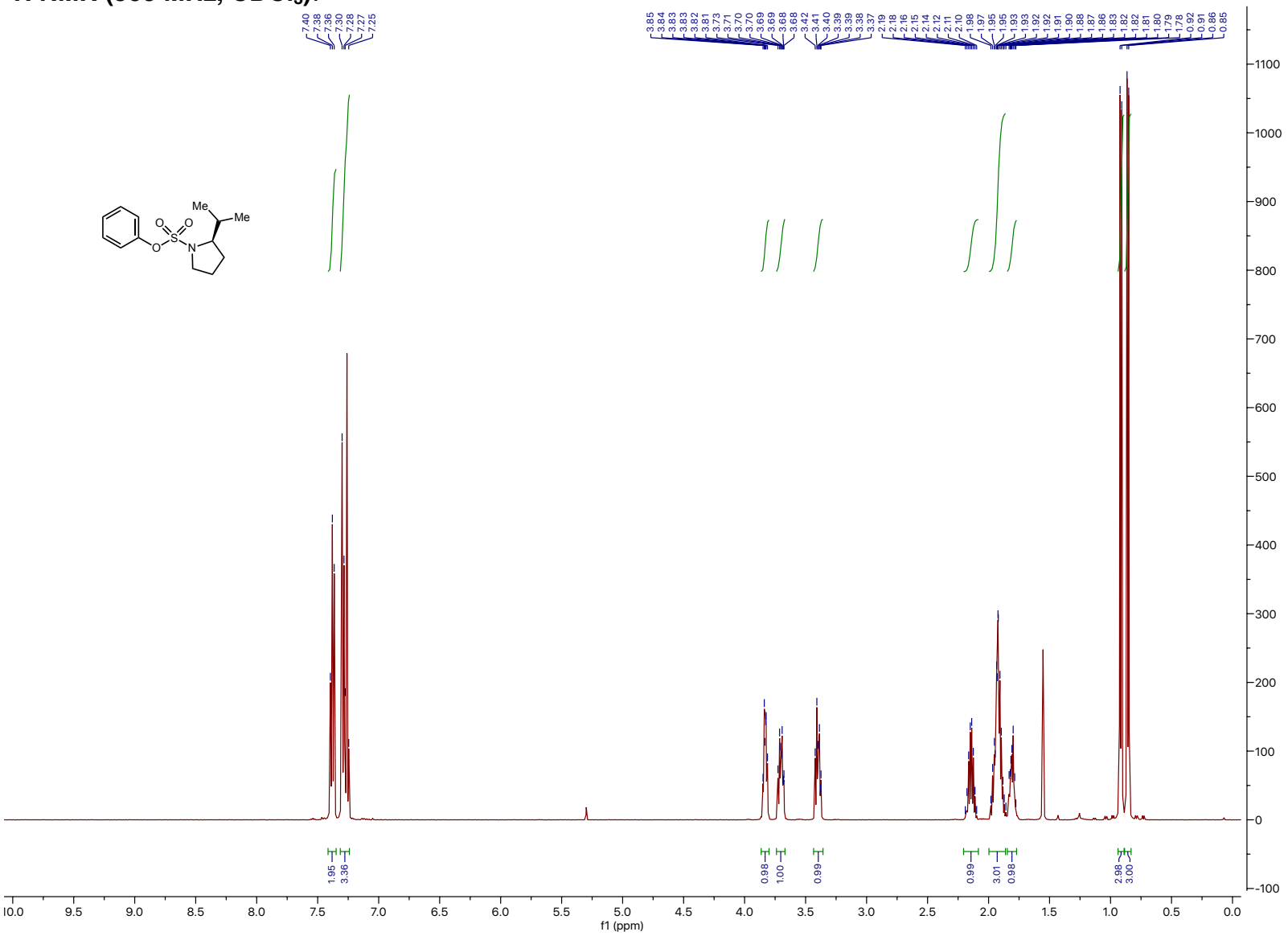
(*R*)-2-isopropyl-1-(phenethylsulfonyl)pyrrolidine (**16**)

^{13}C NMR (126 MHz, $CDCl_3$):



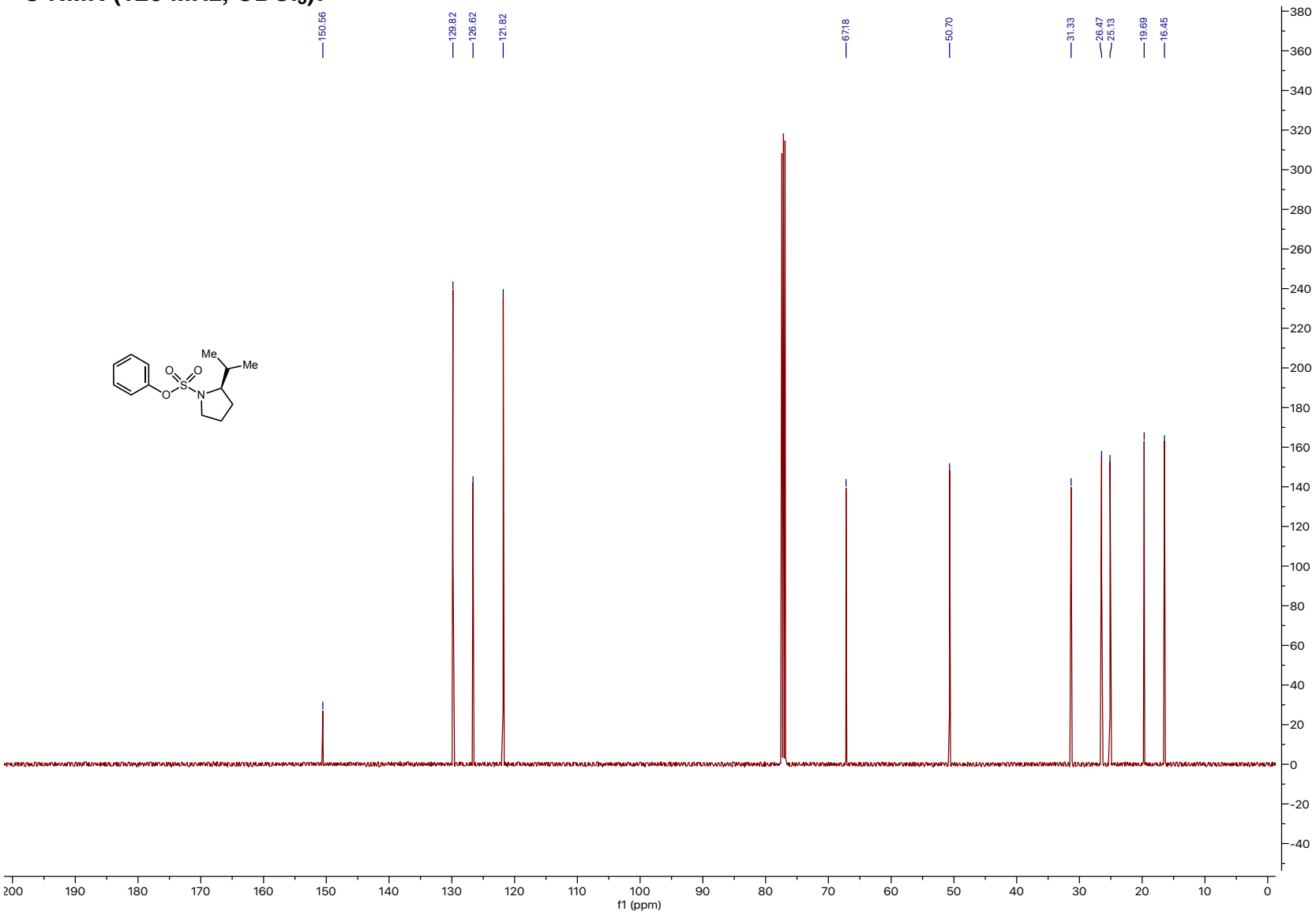
phenyl (*R*)-2-isopropylpyrrolidine-1-sulfonate (**17**)

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



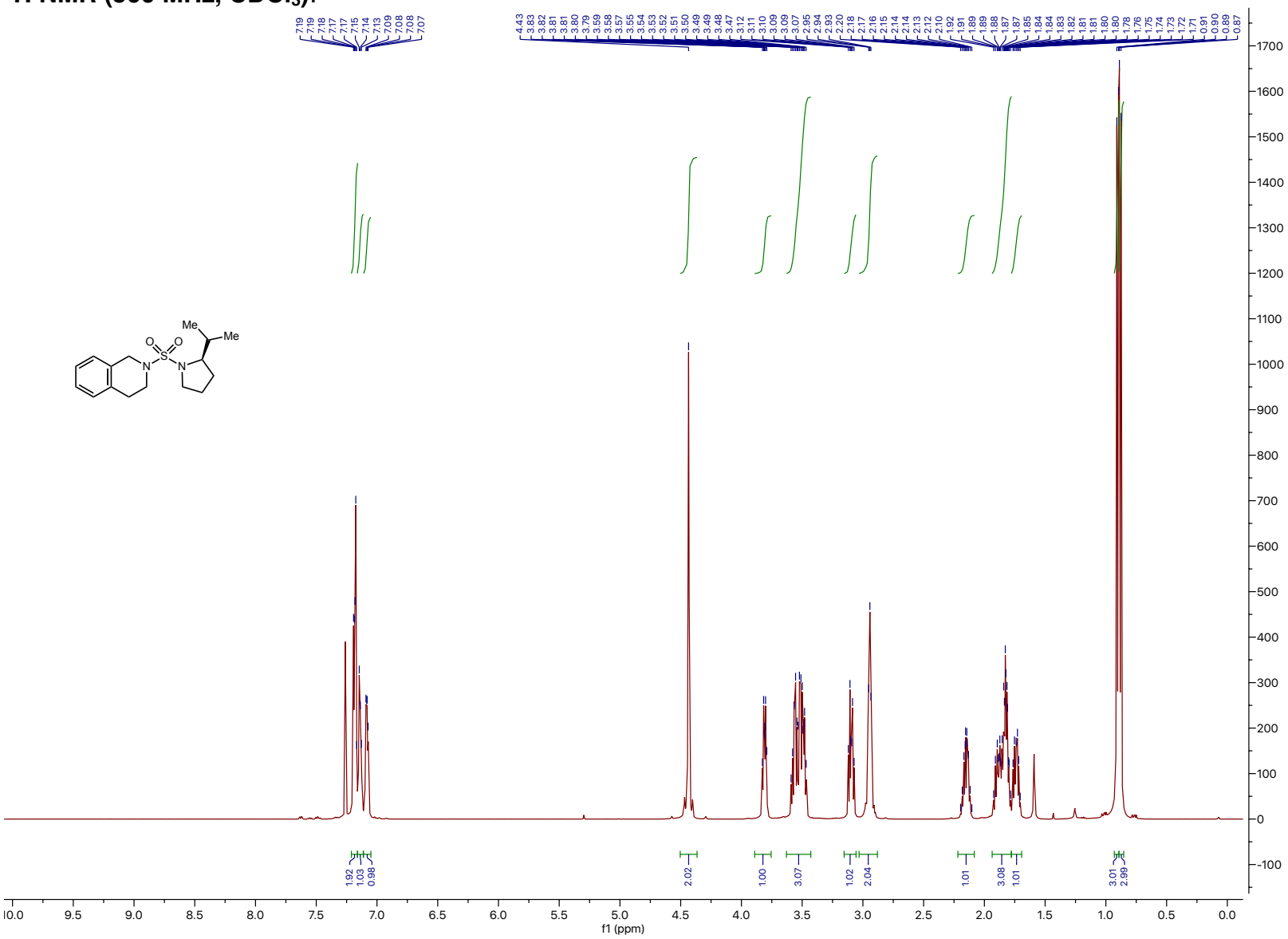
phenyl (*R*)-2-isopropylpyrrolidine-1-sulfonate (**17**)

^{13}C NMR (126 MHz, $CDCl_3$):



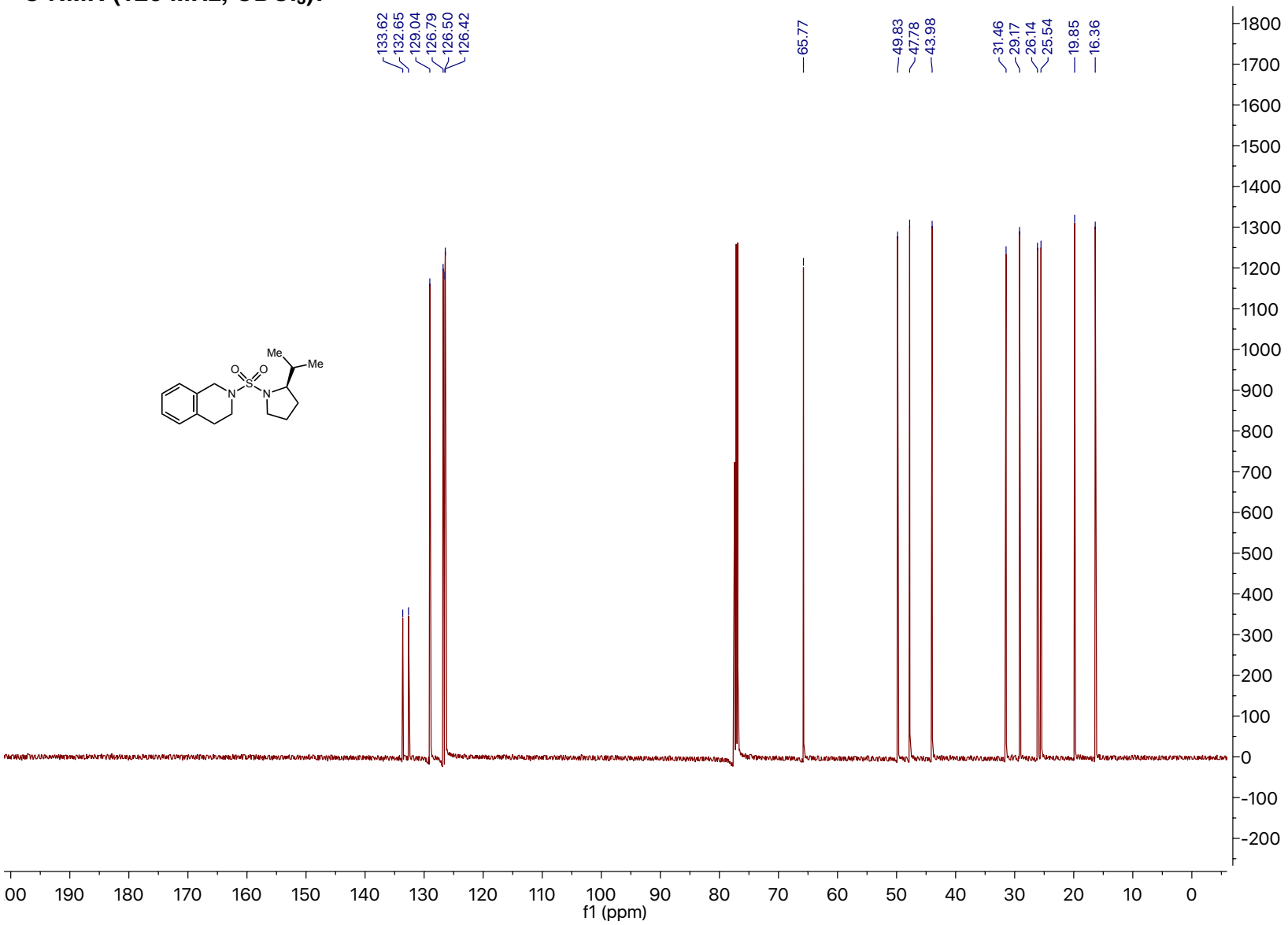
(*R*)-2-((2-isopropylpyrrolidin-1-yl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (**18**)

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



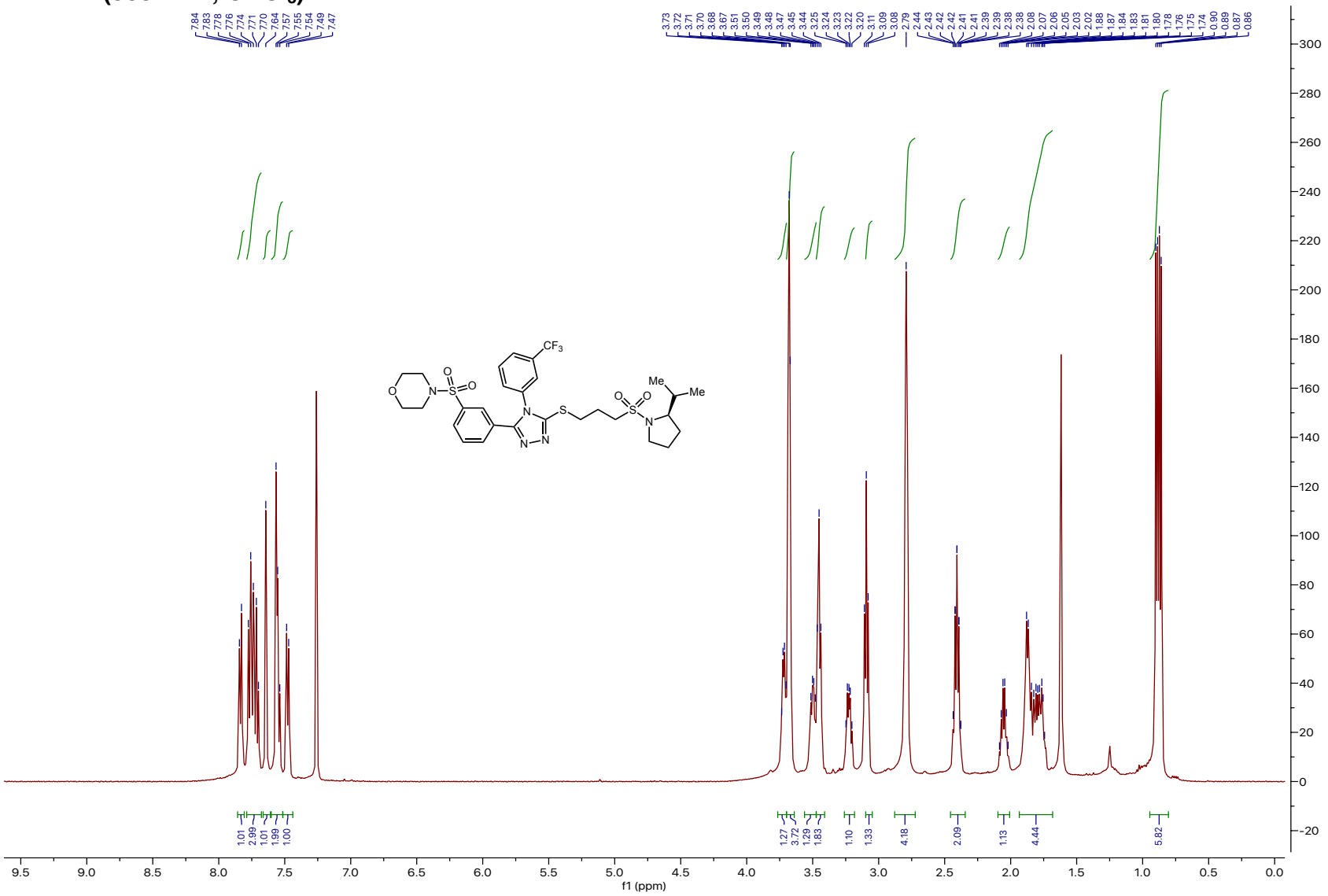
(*R*)-2-((2-isopropylpyrrolidin-1-yl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (**18**)

^{13}C NMR (126 MHz, $CDCl_3$):



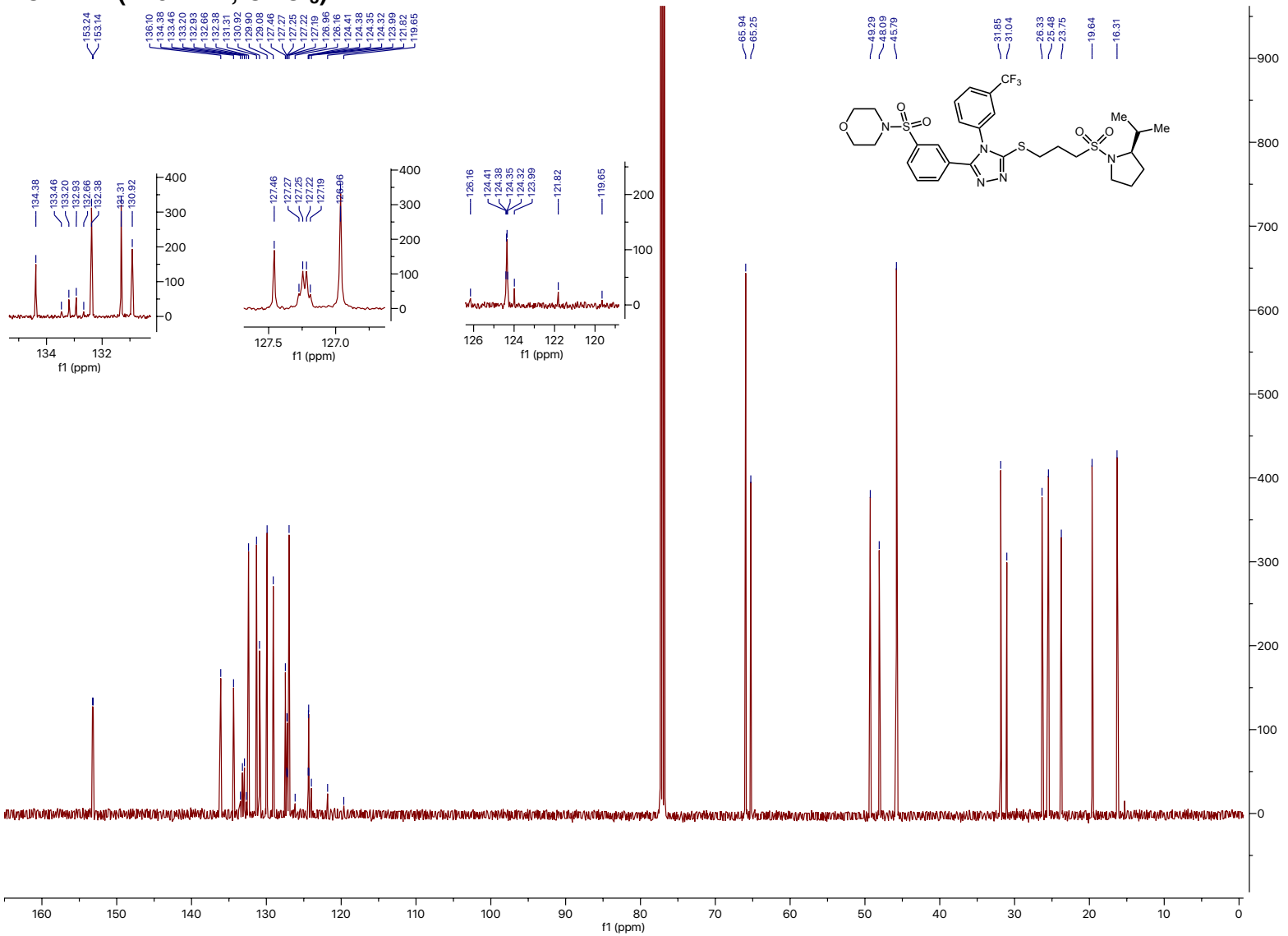
(*R*)-4-((3-(5-((3-((2-isopropylpyrrolidin-1-yl)sulfonyl)propyl)thio)-4-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-3-yl)phenyl)sulfonyl)morpholine (**19**)

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



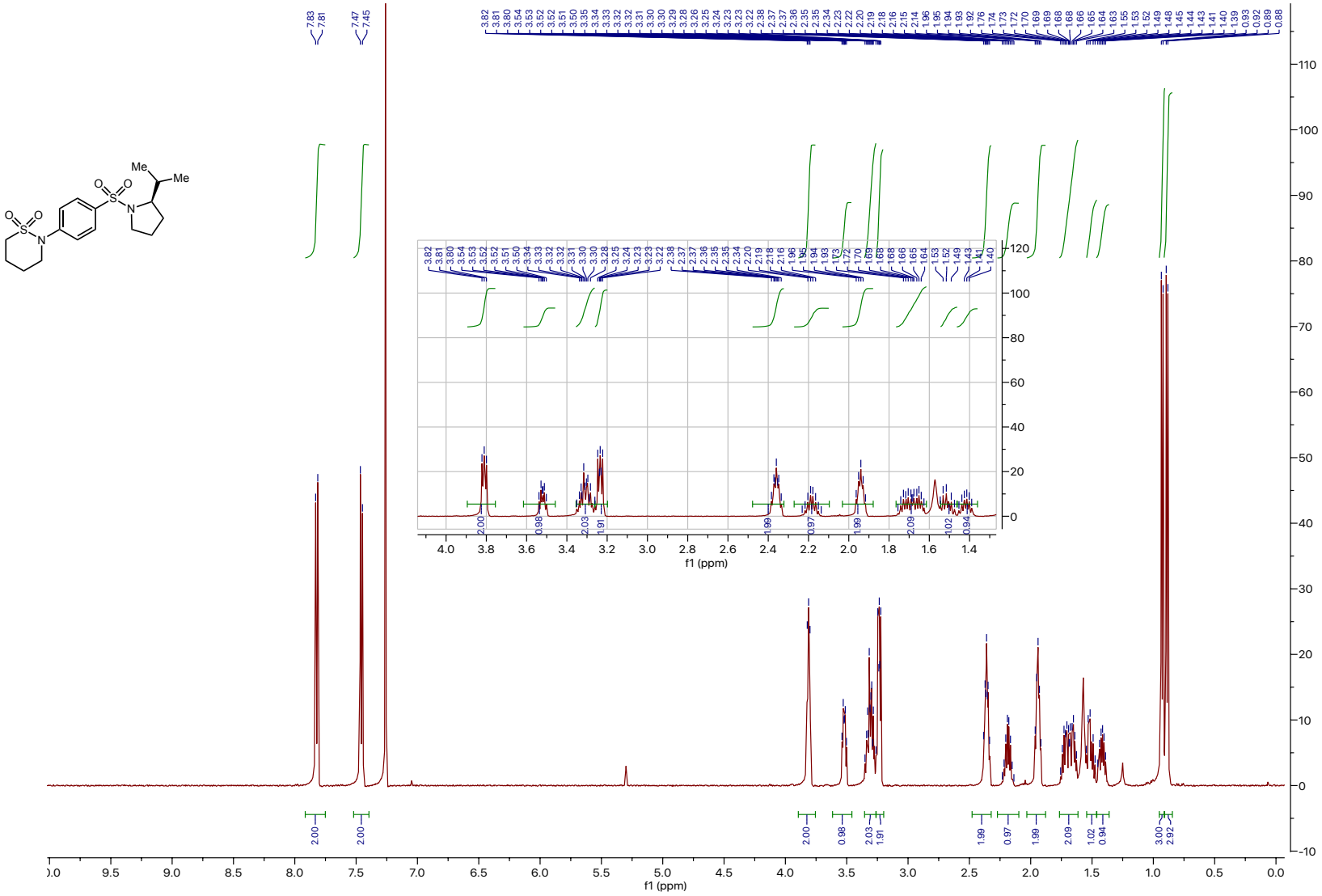
(*R*)-4-((3-(5-((3-((2-isopropylpyrrolidin-1-yl)sulfonyl)propyl)thio)-4-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-3-yl)phenyl)sulfonyl)morpholine (**19**)

^{13}C NMR (126 MHz, $CDCl_3$):



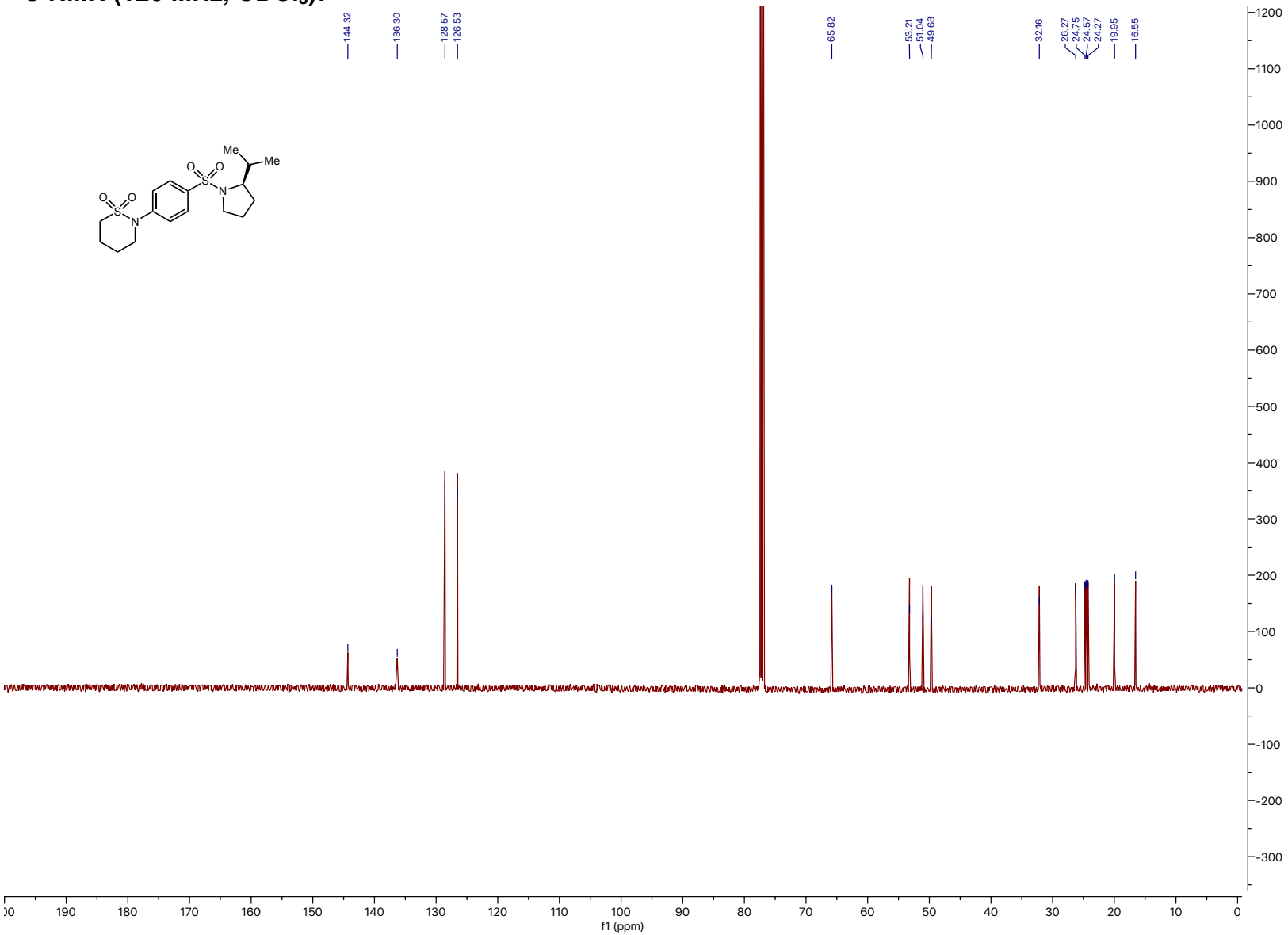
(*R*)-2-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1,2-thiazinane 1,1-dioxide (**20**)

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



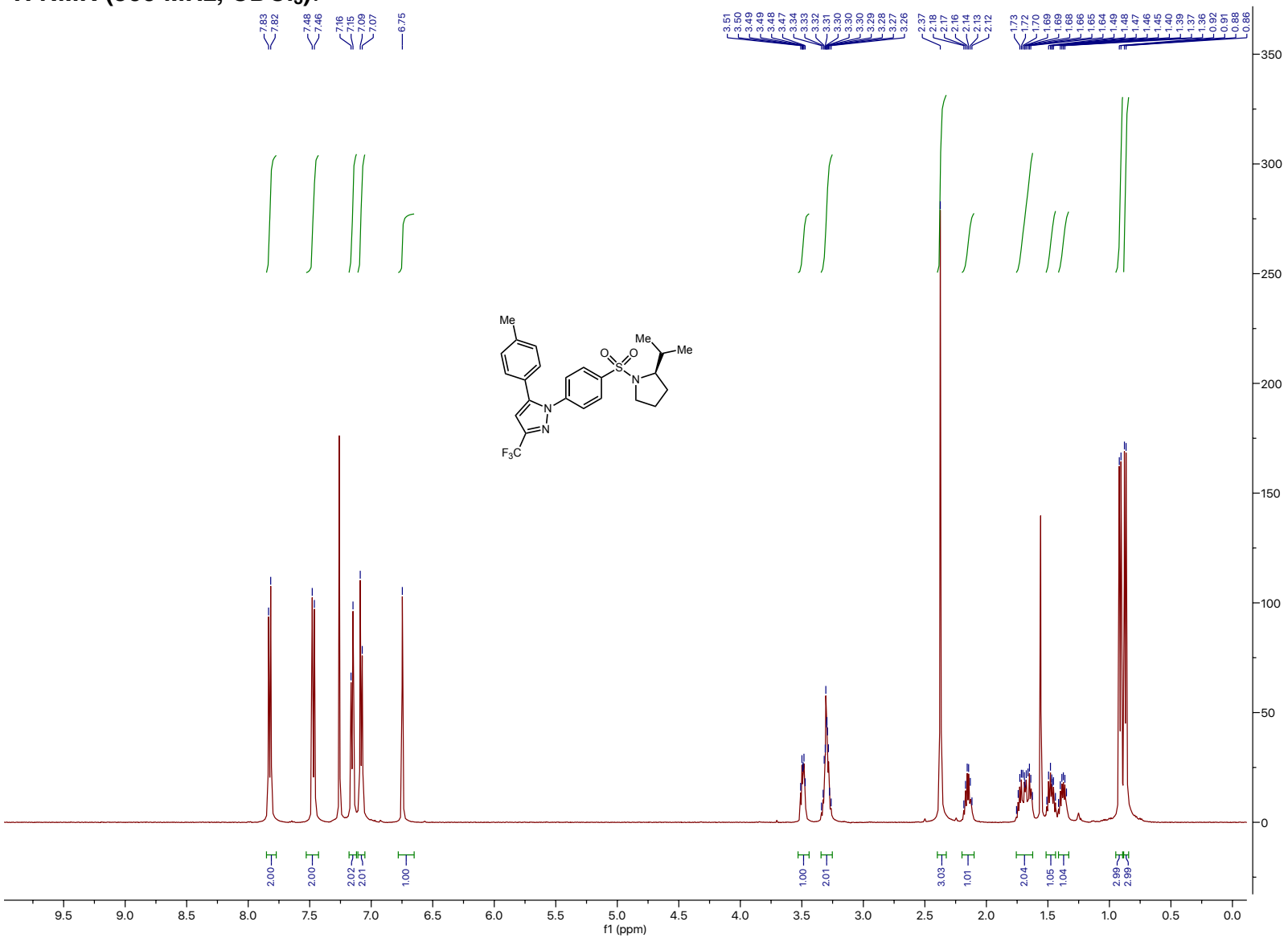
(*R*)-2-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1,2-thiazinane 1,1-dioxide (**20**)

^{13}C NMR (126 MHz, $CDCl_3$):



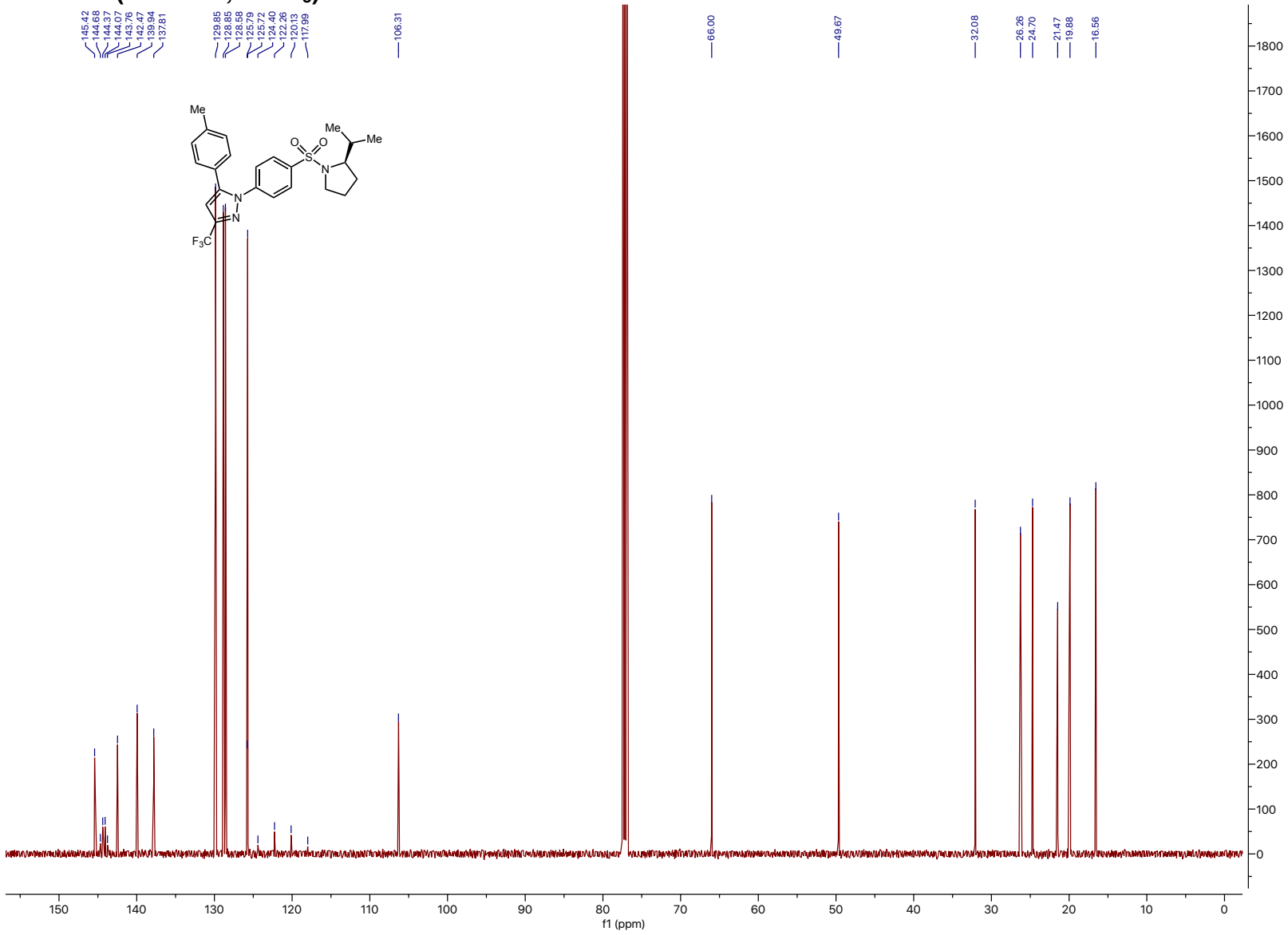
(*R*)-1-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (**21**)

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



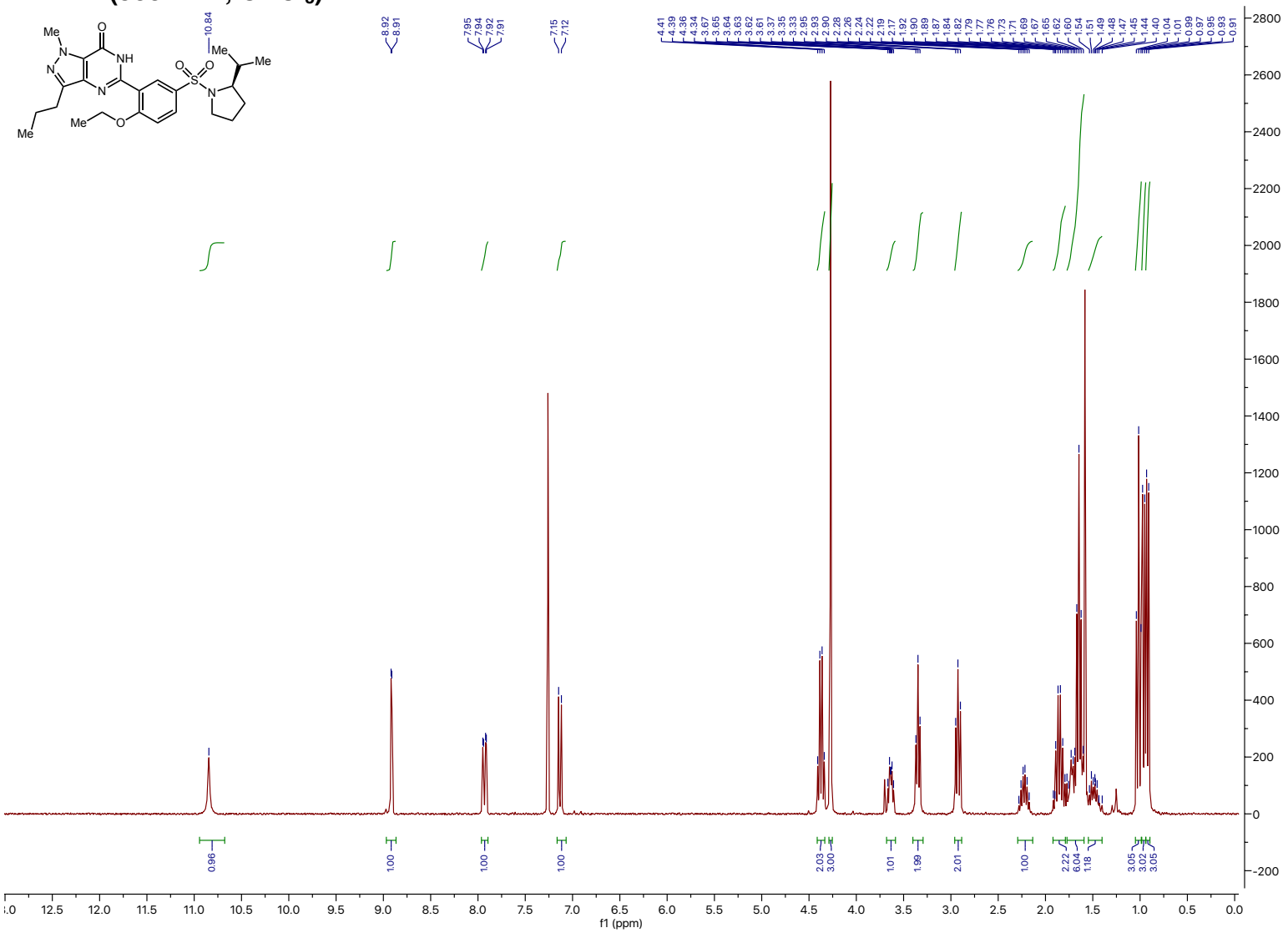
(*R*)-1-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (**21**)

^{13}C NMR (126 MHz, $CDCl_3$):



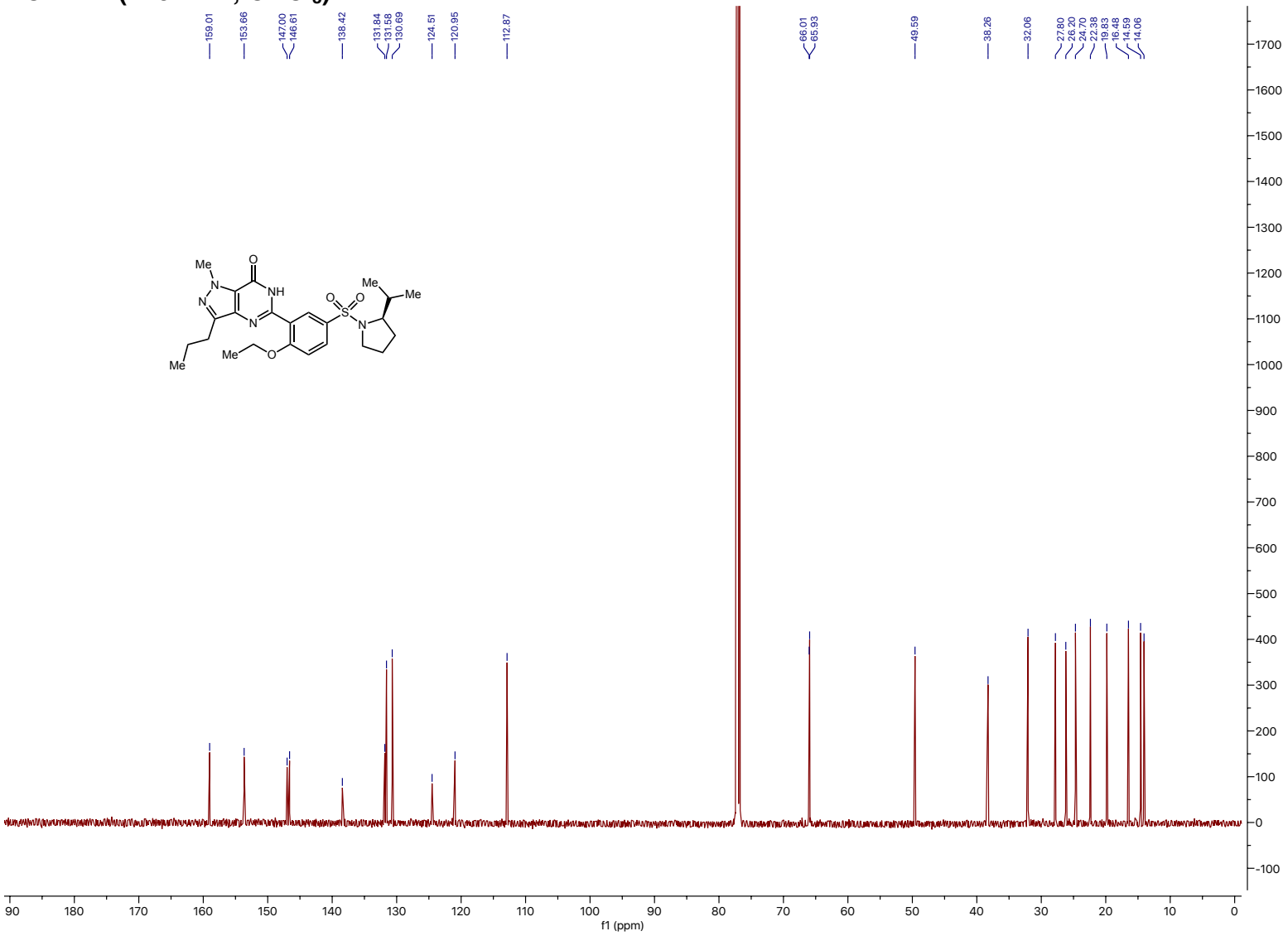
(*R*)-5-(2-ethoxy-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one (**22**)

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



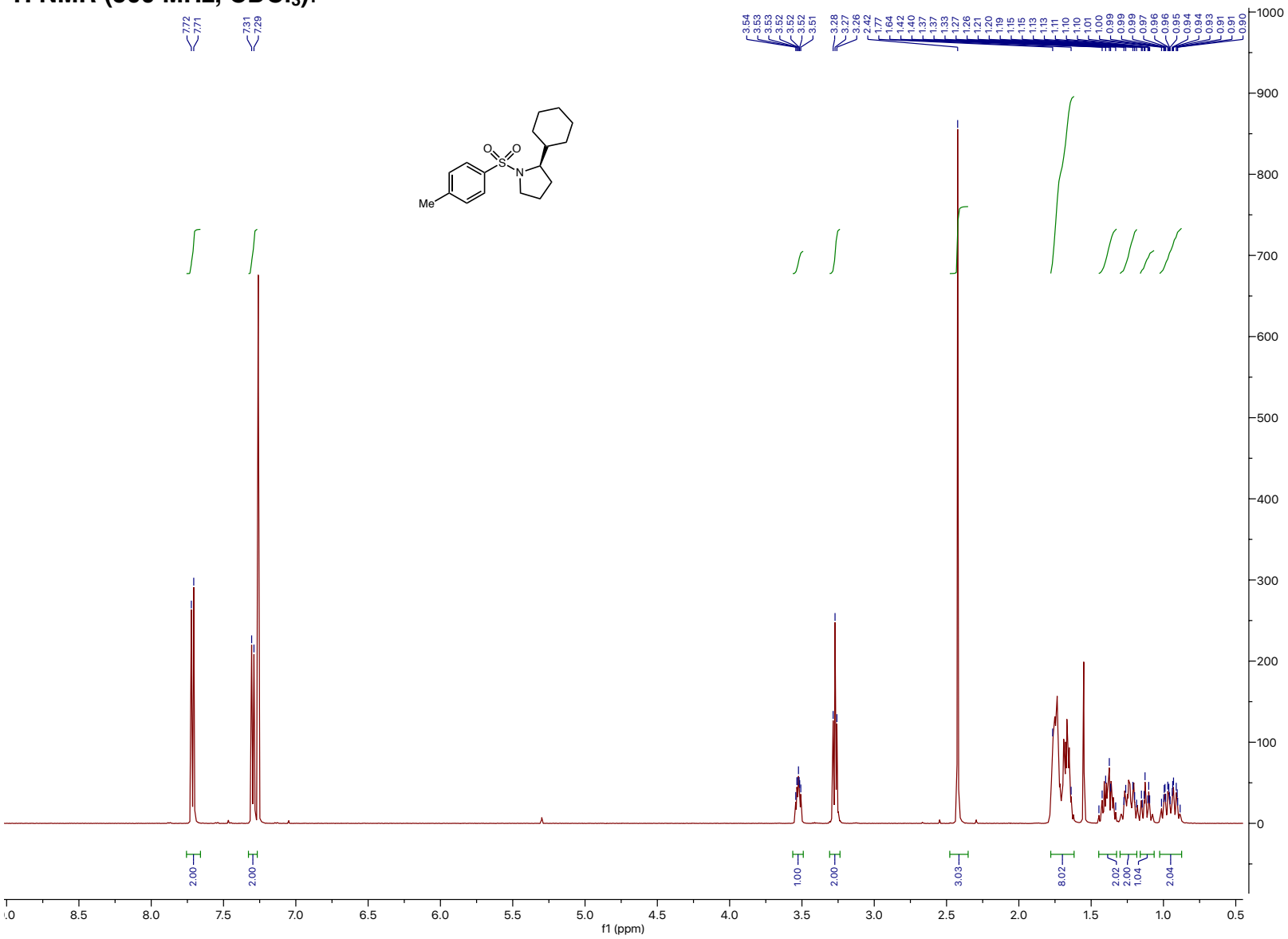
(*R*)-5-(2-ethoxy-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one (**22**)

^{13}C NMR (126 MHz, $CDCl_3$):



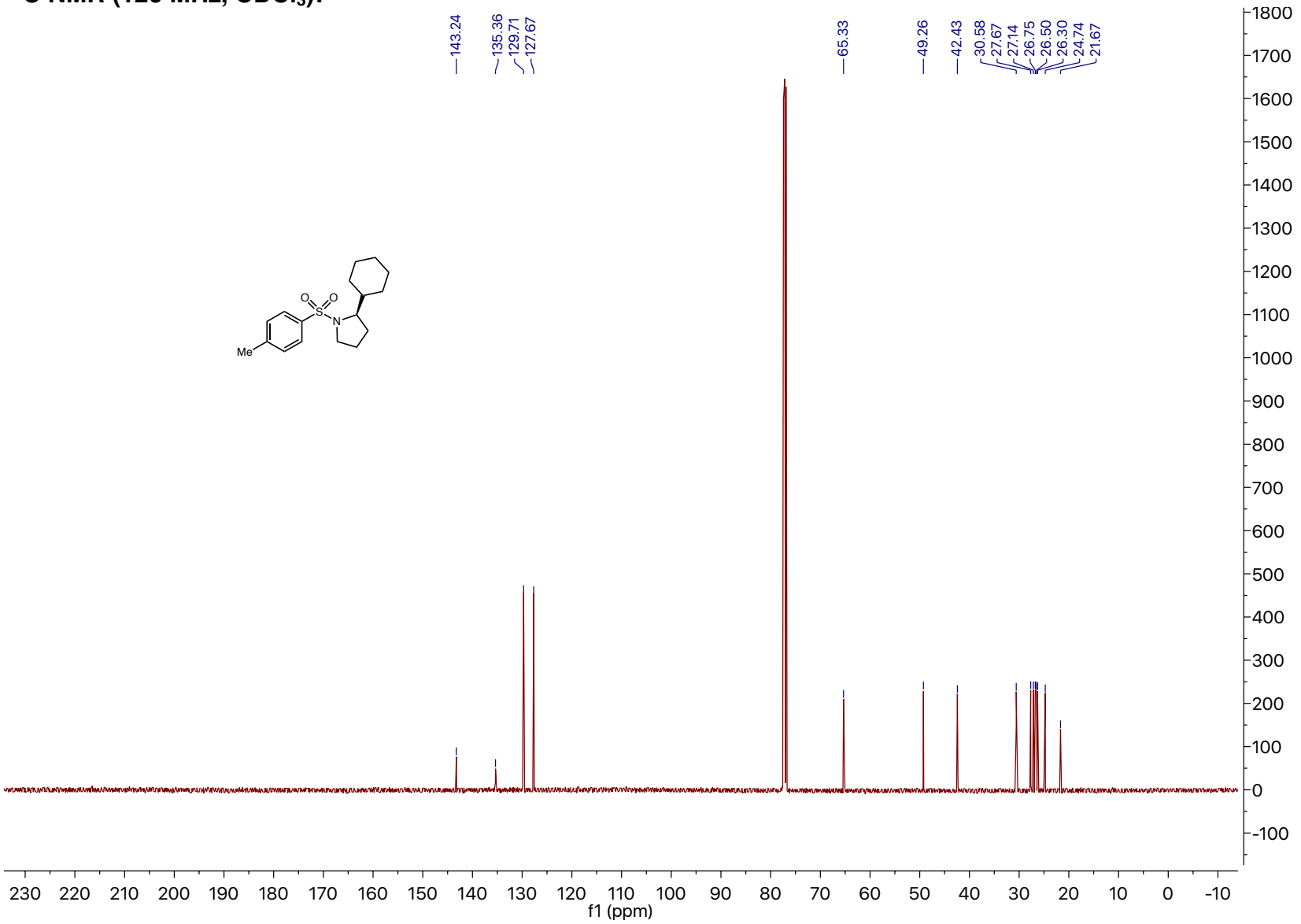
(*R*)-2-cyclohexyl-1-tosylpyrrolidine (**23**)

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



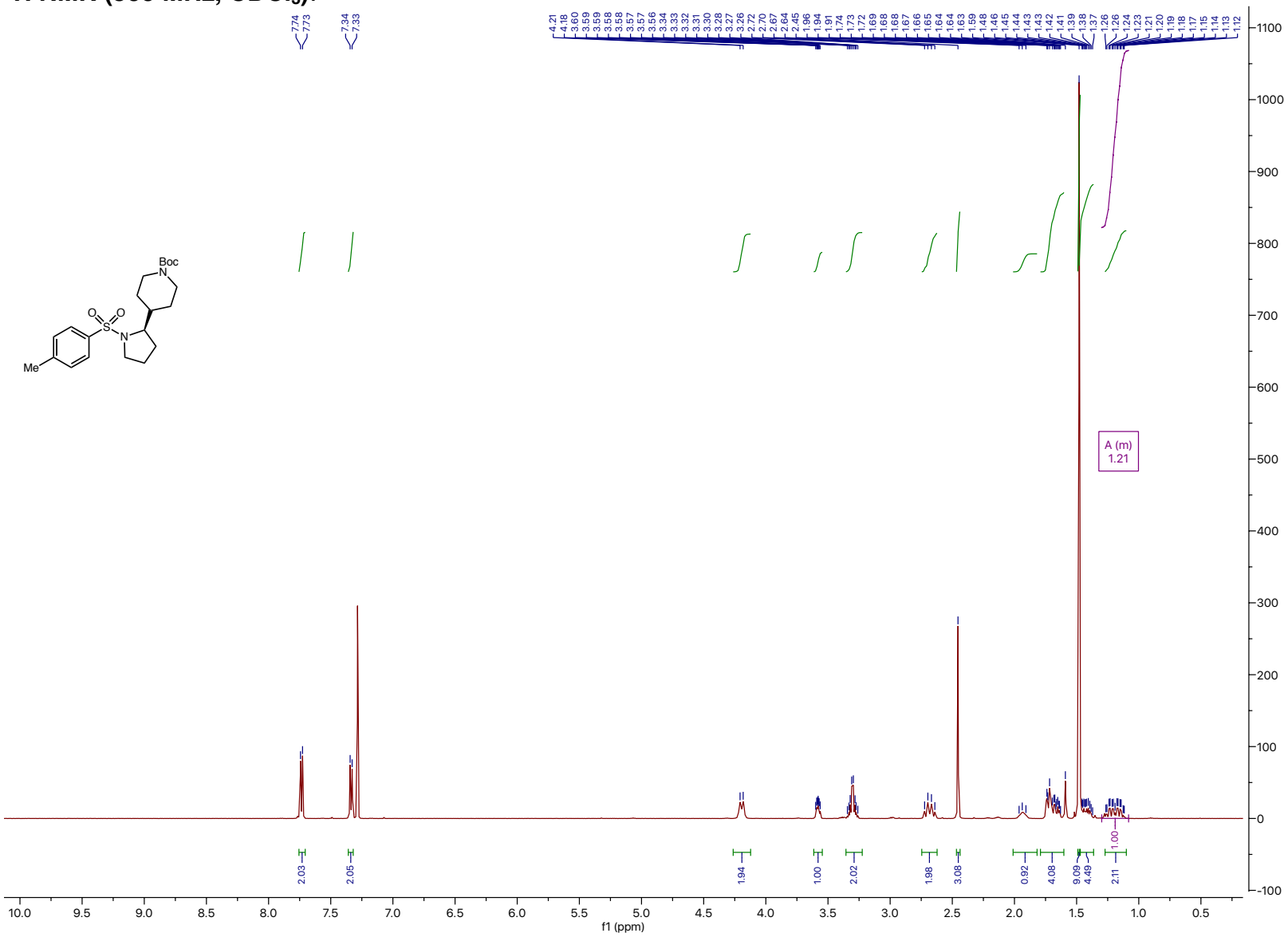
(*R*)-2-cyclohexyl-1-tosylpyrrolidine (**23**)

^{13}C NMR (126 MHz, $CDCl_3$):



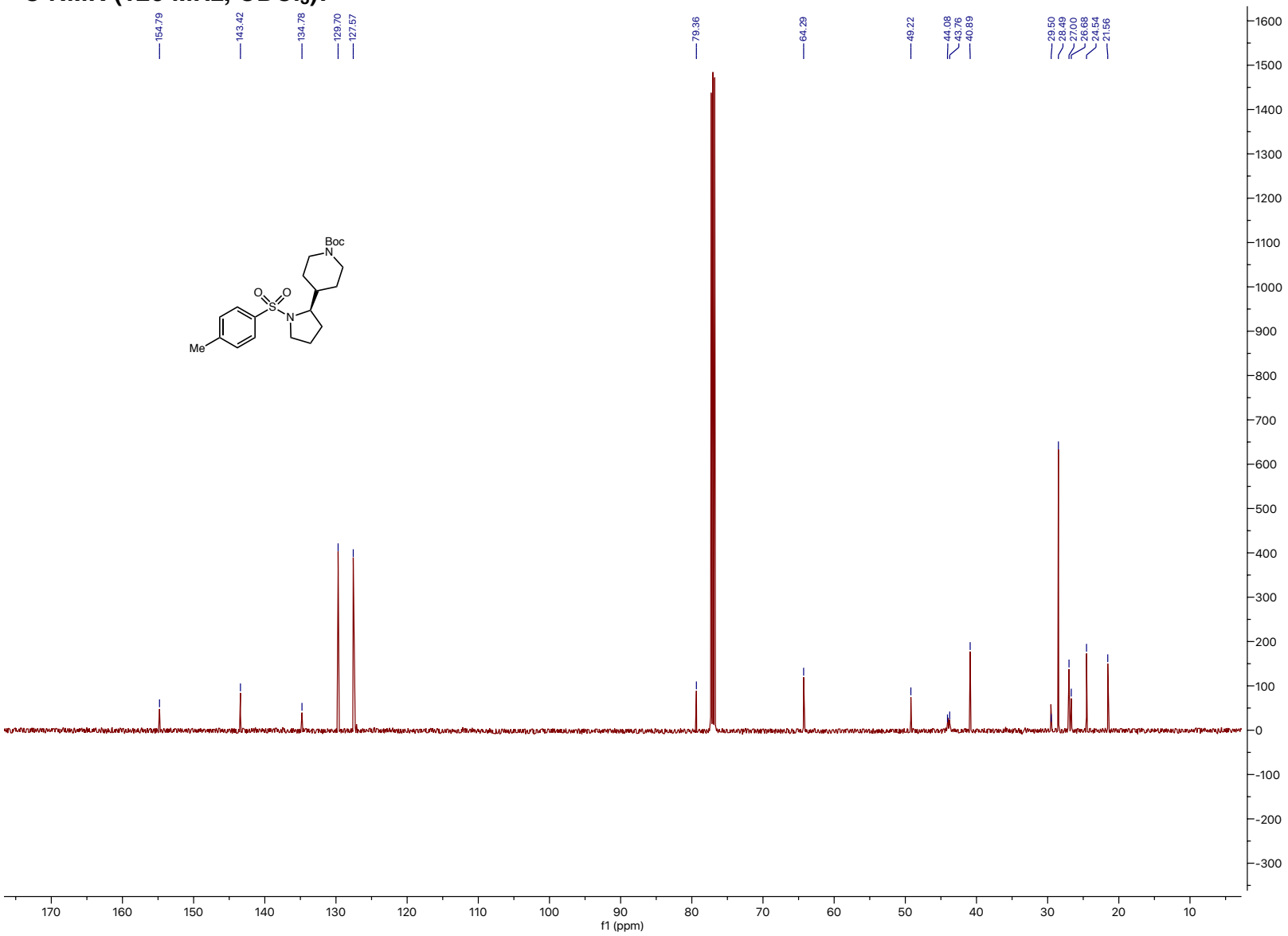
tert-butyl (*R*)-4-(1-tosylpyrrolidin-2-yl)piperidine-1-carboxylate (**24**)

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



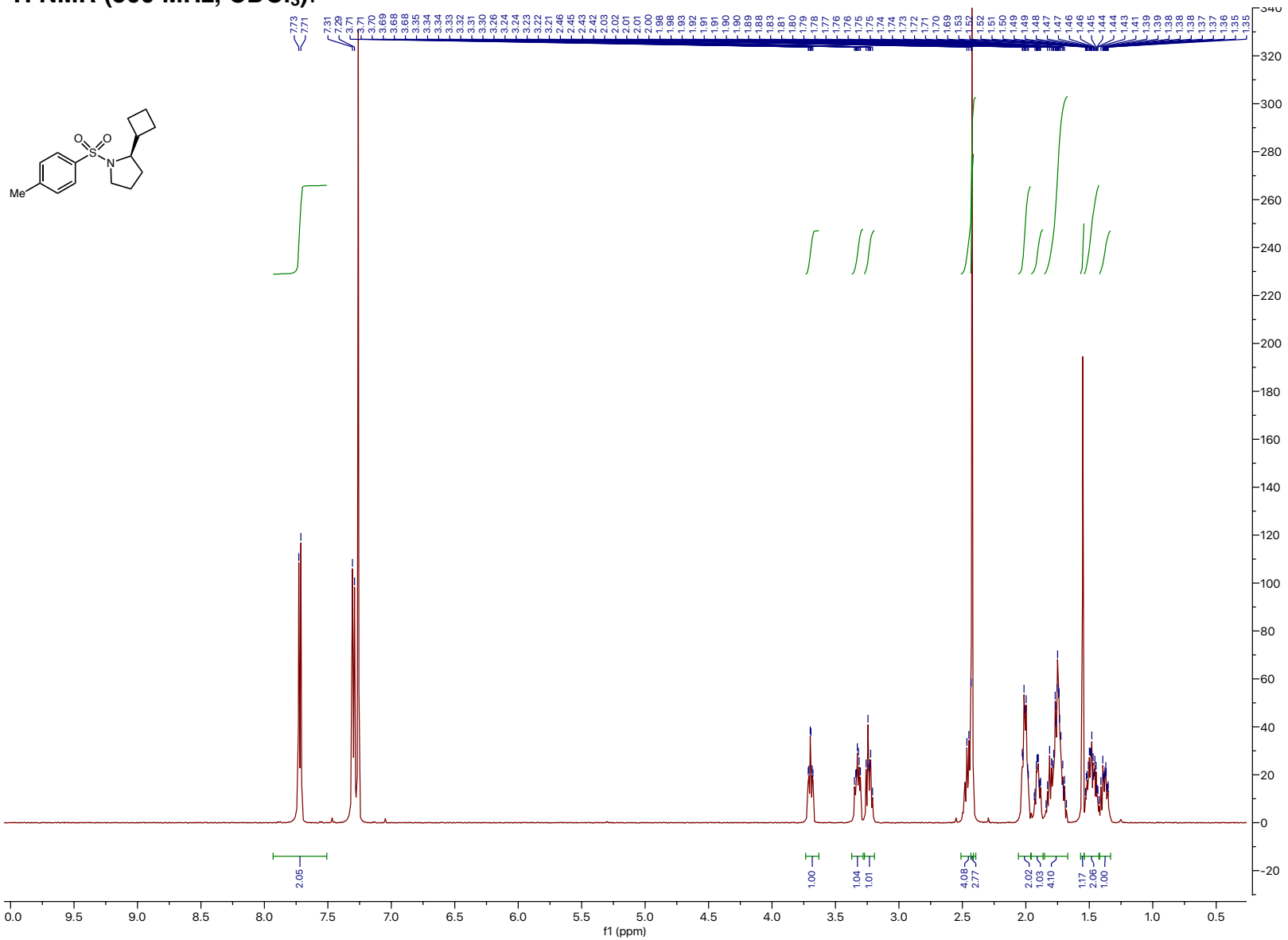
tert-butyl (*R*)-4-(1-tosylpyrrolidin-2-yl)piperidine-1-carboxylate (**24**)

^{13}C NMR (126 MHz, $CDCl_3$):



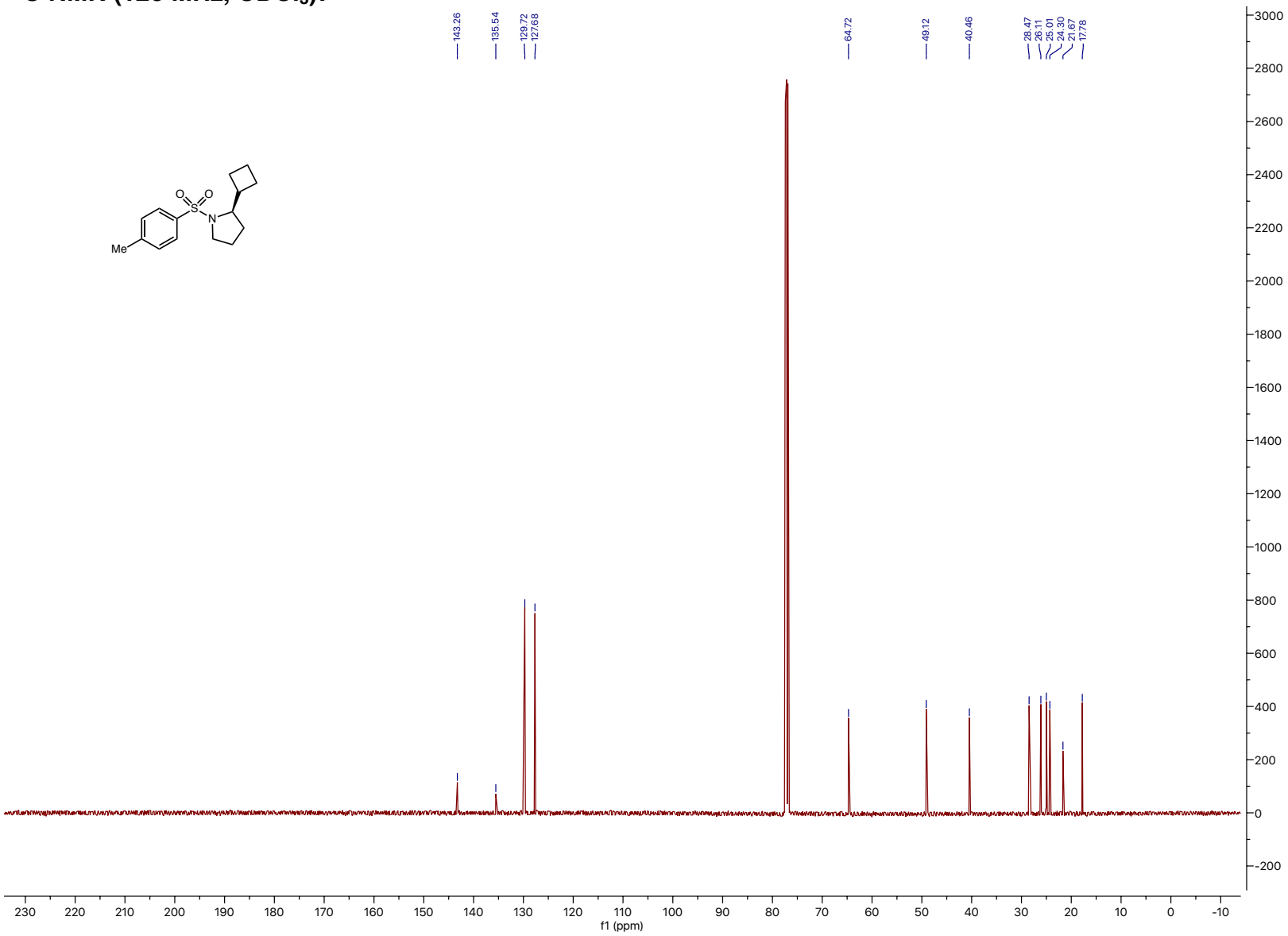
(R)-2-cyclobutyl-1-tosylpyrrolidine (**25**)

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



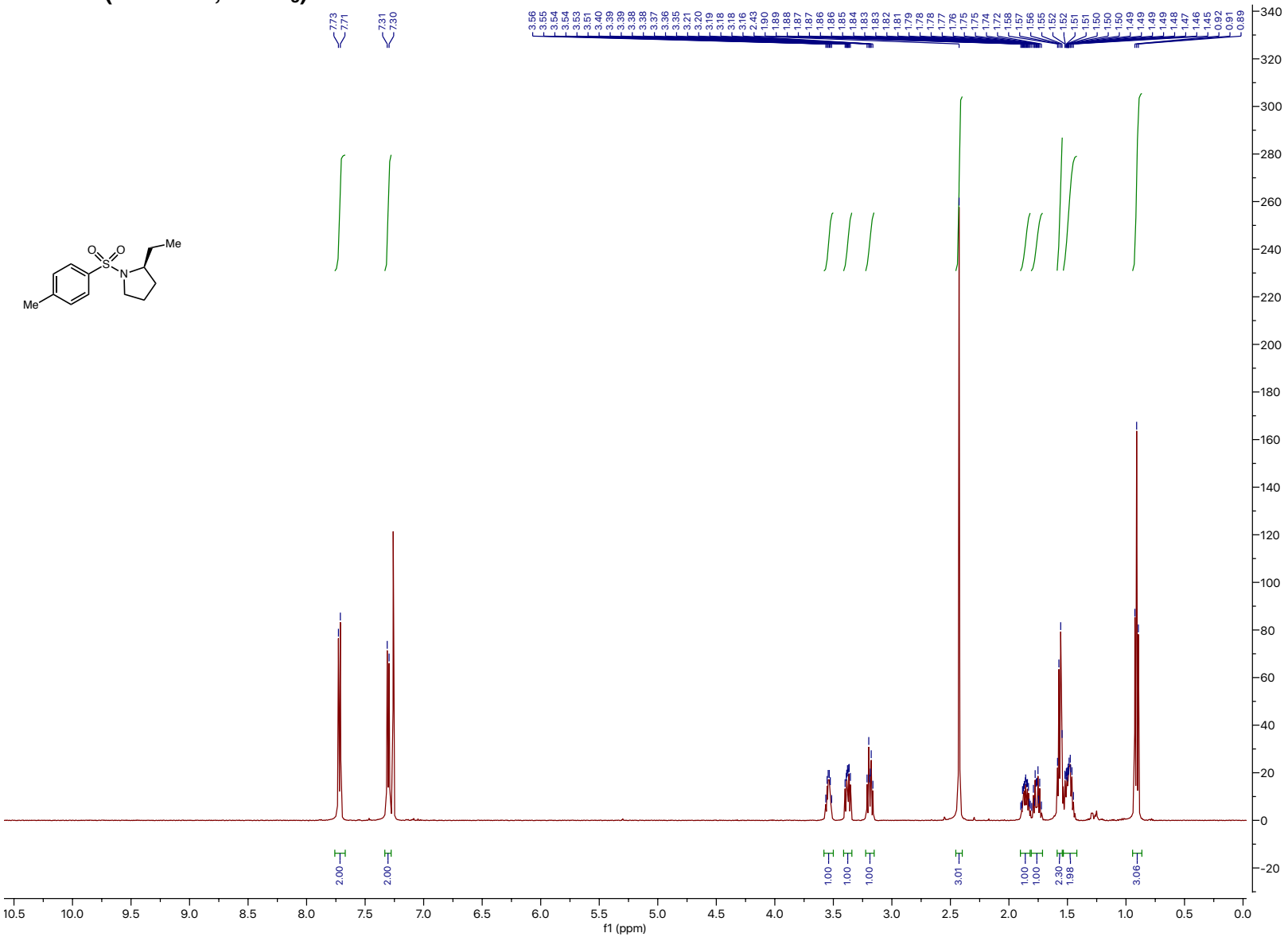
(R)-2-cyclobutyl-1-tosylpyrrolidine (**25**)

^{13}C NMR (126 MHz, $CDCl_3$):



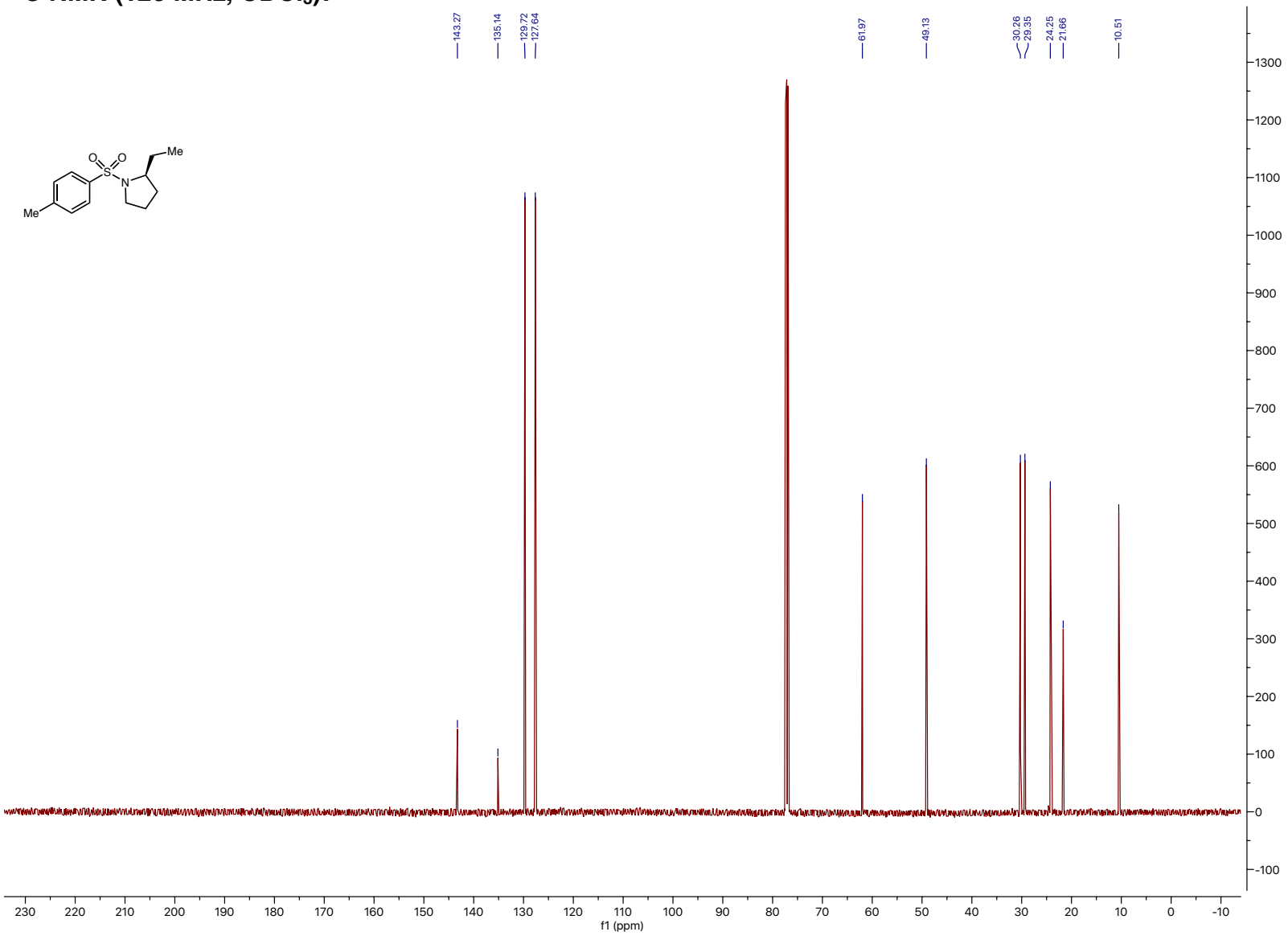
(*S*)-2-ethyl-1-tosylpyrrolidine from *cis* (**26**)

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



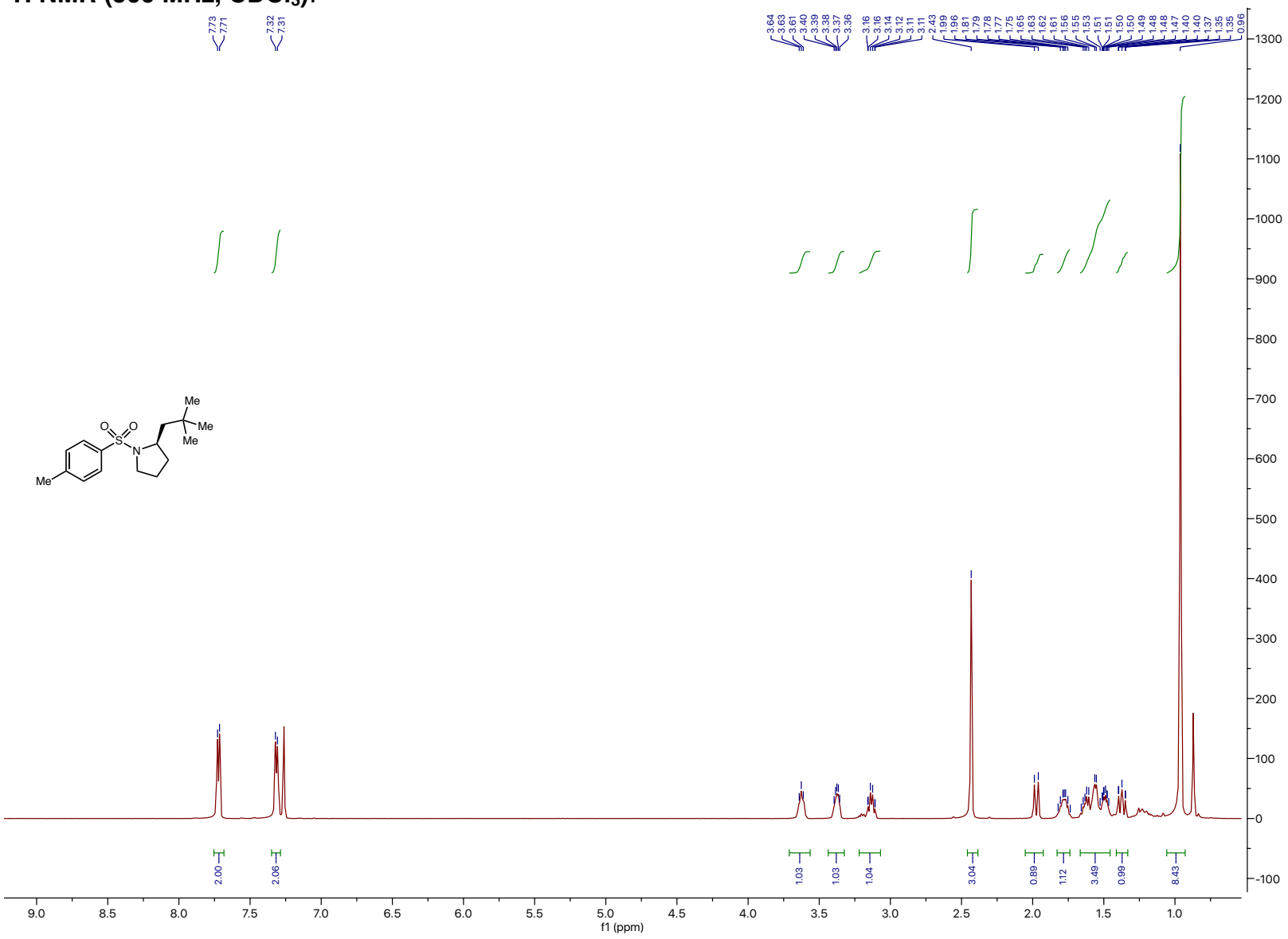
(*S*)-2-ethyl-1-tosylpyrrolidine from *cis* (**26**)

^{13}C NMR (126 MHz, $CDCl_3$):



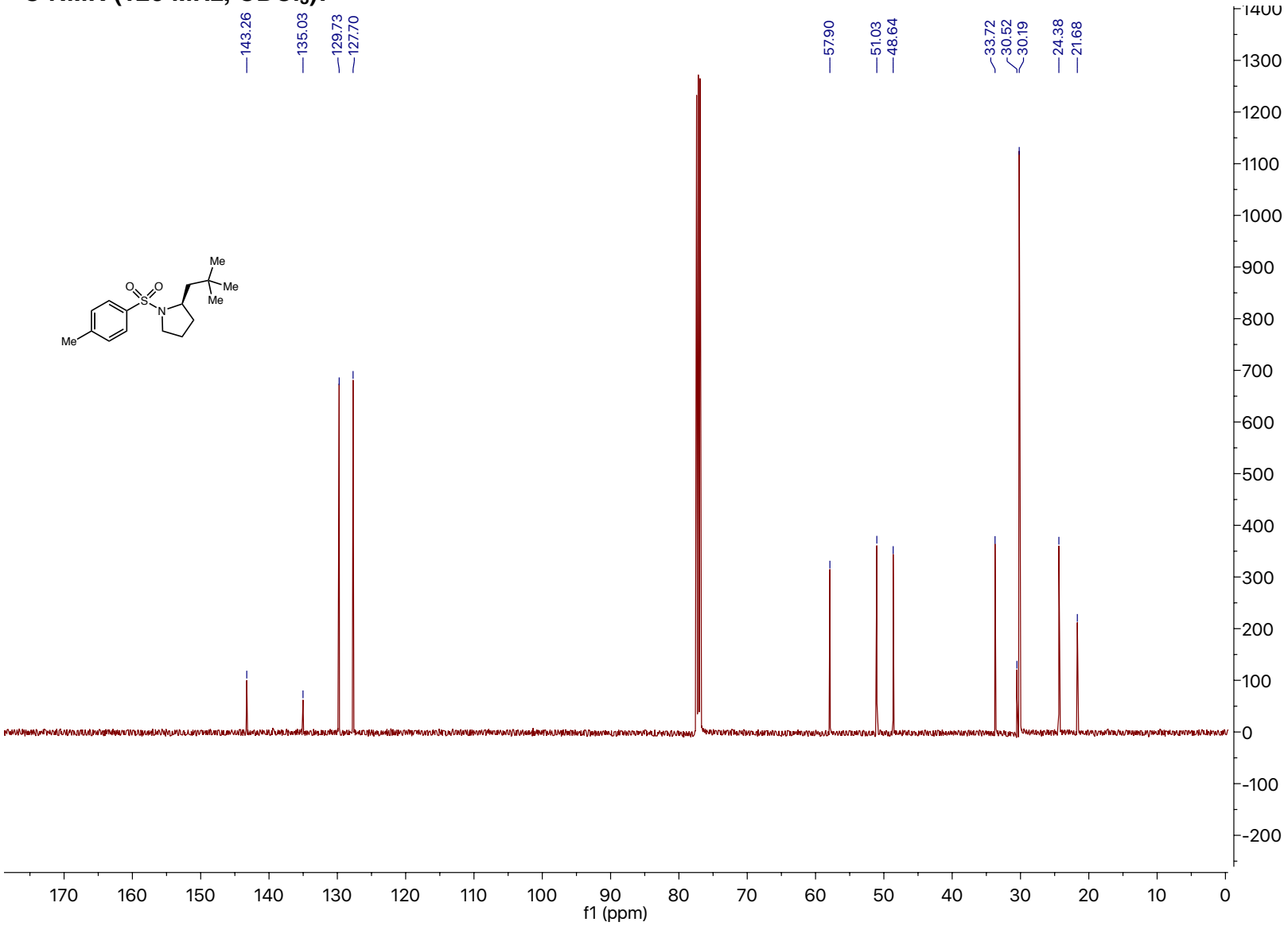
(*R*)-2-neopentyl-1-tosylpyrrolidine from *cis* (**27**)

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



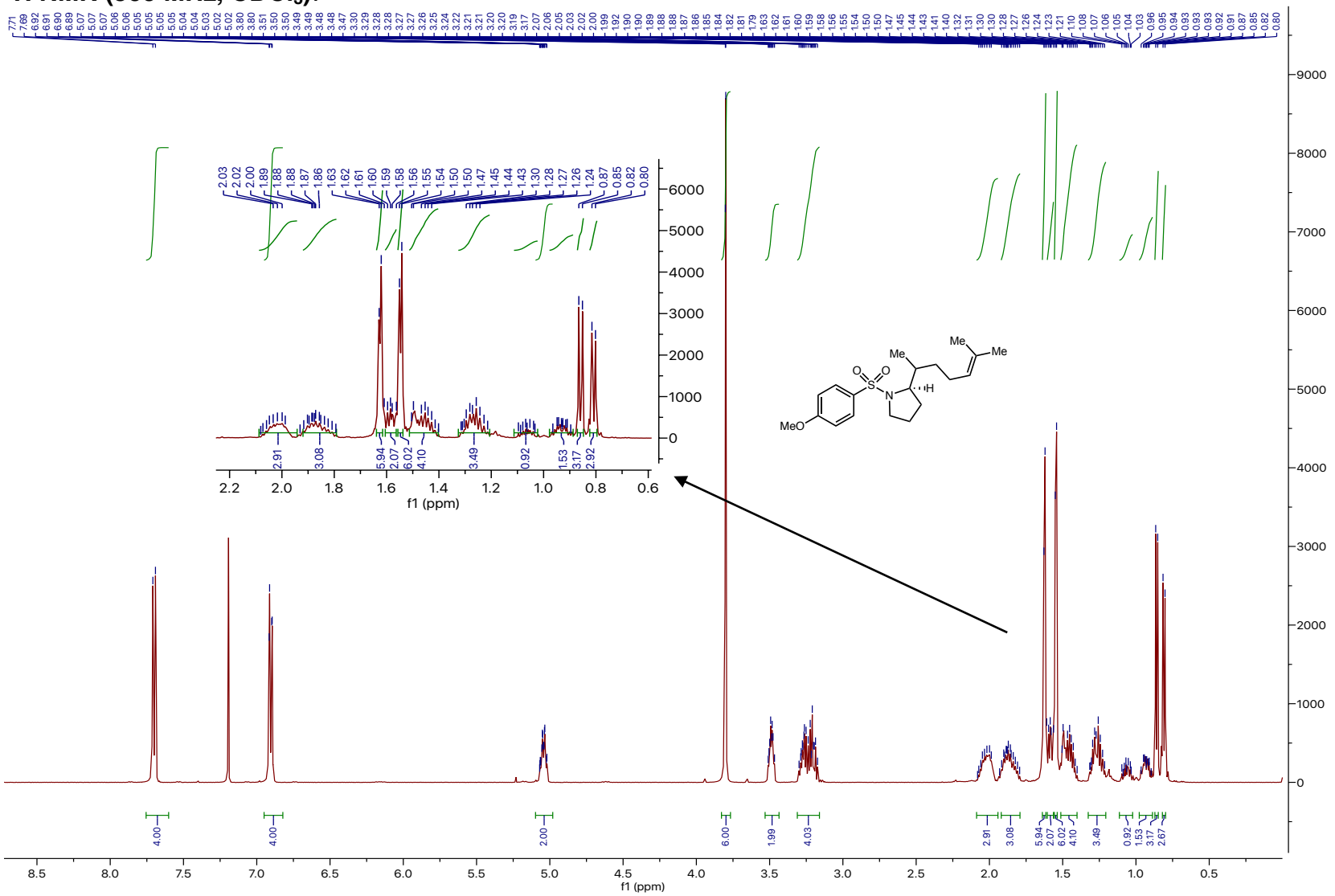
(*R*)-2-neopentyl-1-tosylpyrrolidine from *cis* (**27**)

^{13}C NMR (126 MHz, $CDCl_3$):



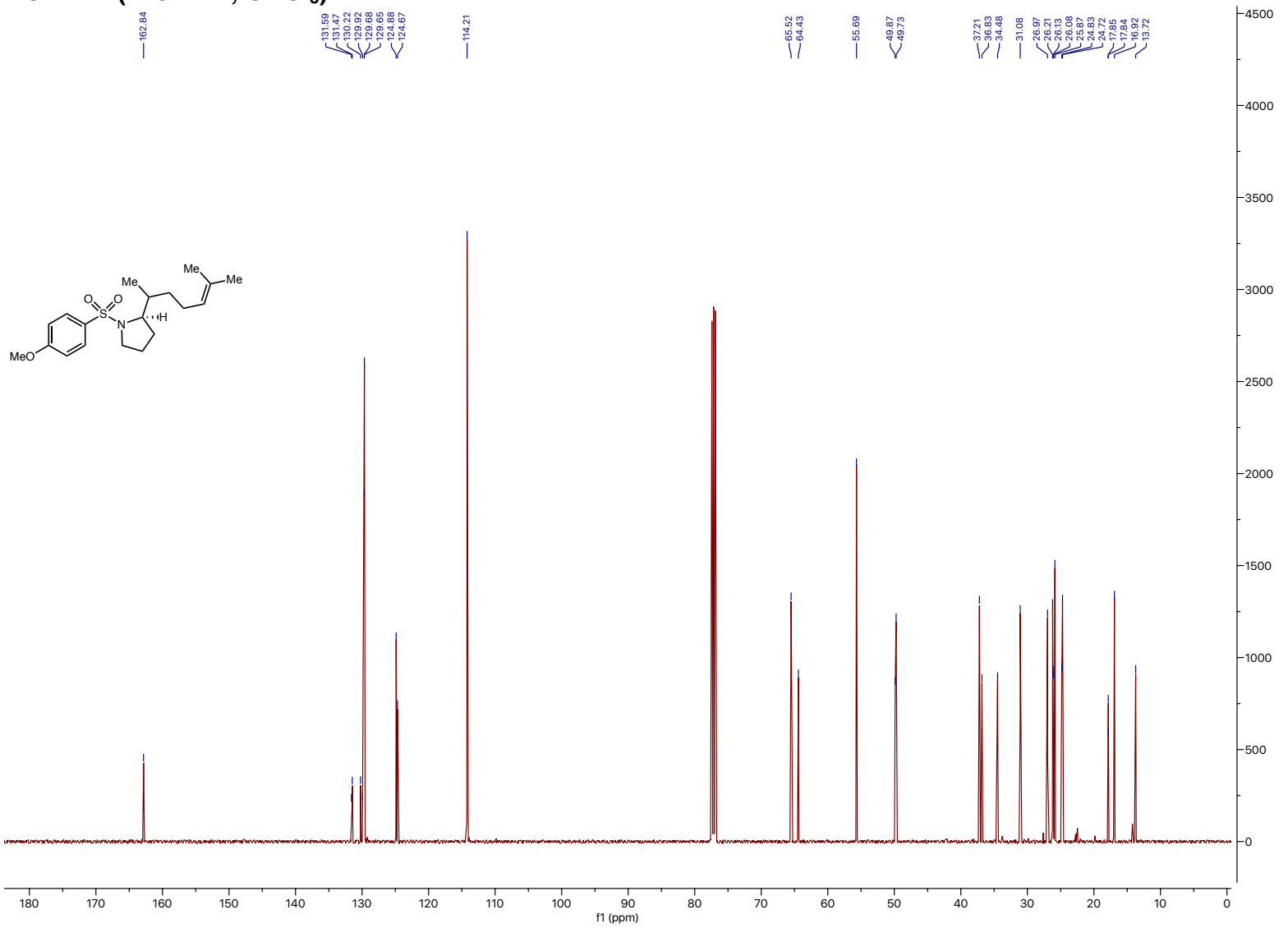
1-((4-methoxyphenyl)sulfonyl)-2-(6-methylhept-5-en-2-yl)pyrrolidine (**28**) (mixture of diastereomers)

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



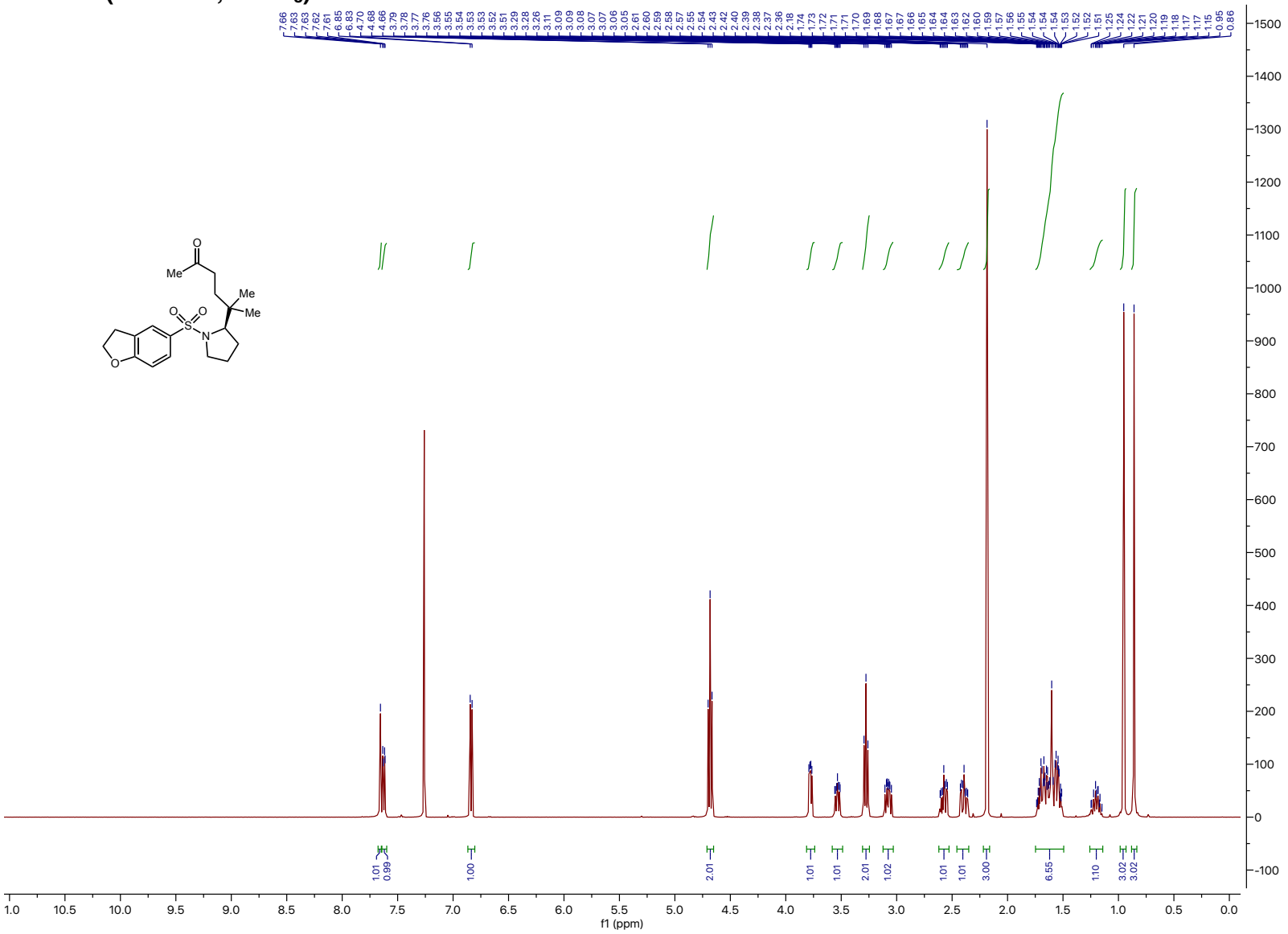
1-((4-methoxyphenyl)sulfonyl)-2-(6-methylhept-5-en-2-yl)pyrrolidine (**28**) (mixture of diastereomers)

^{13}C NMR (126 MHz, $CDCl_3$):



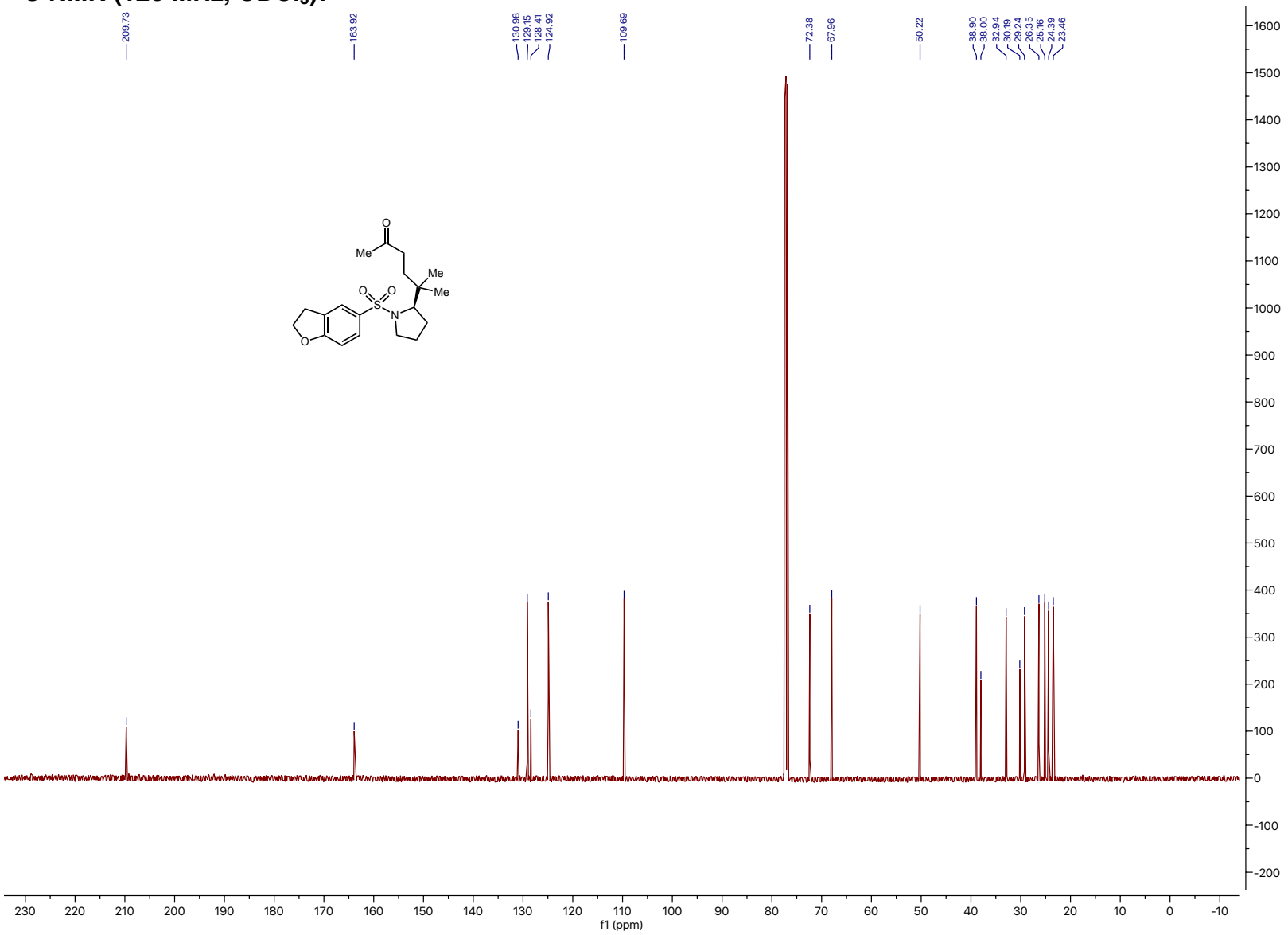
(*R*)-5-(1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)pyrrolidin-2-yl)-5-methylhexan-2-one (**29**)

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



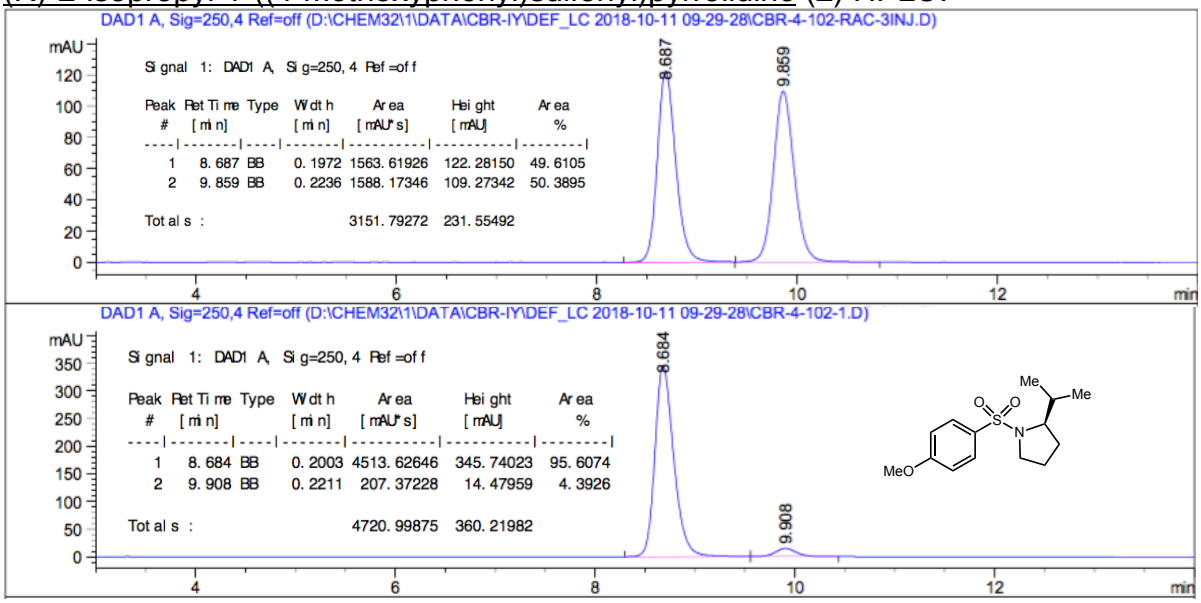
(*R*)-5-(1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)pyrrolidin-2-yl)-5-methylhexan-2-one (**29**)

^{13}C NMR (126 MHz, $CDCl_3$):

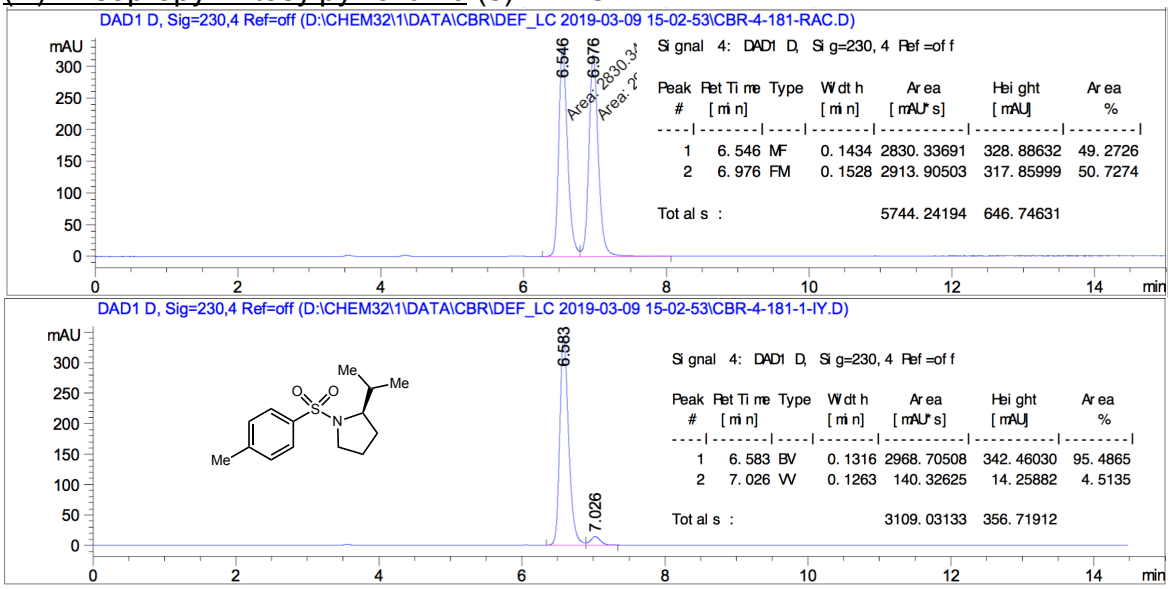


11. Product HPLC/SFC Traces

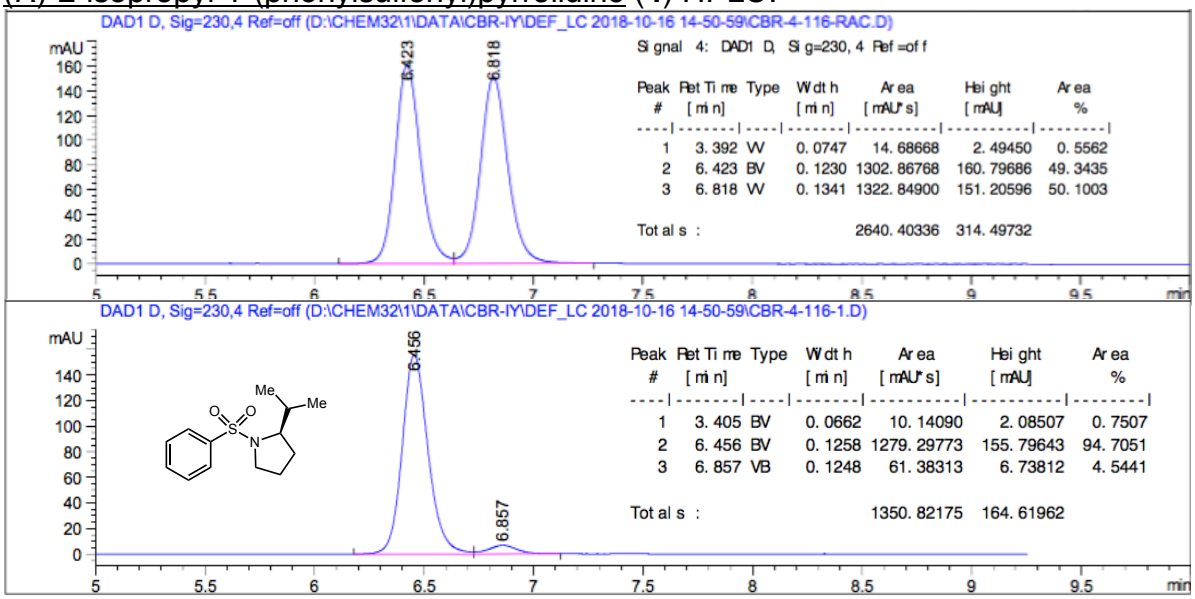
(*R*)-2-isopropyl-1-((4-methoxyphenyl)sulfonyl)pyrrolidine (**2**) HPLC:



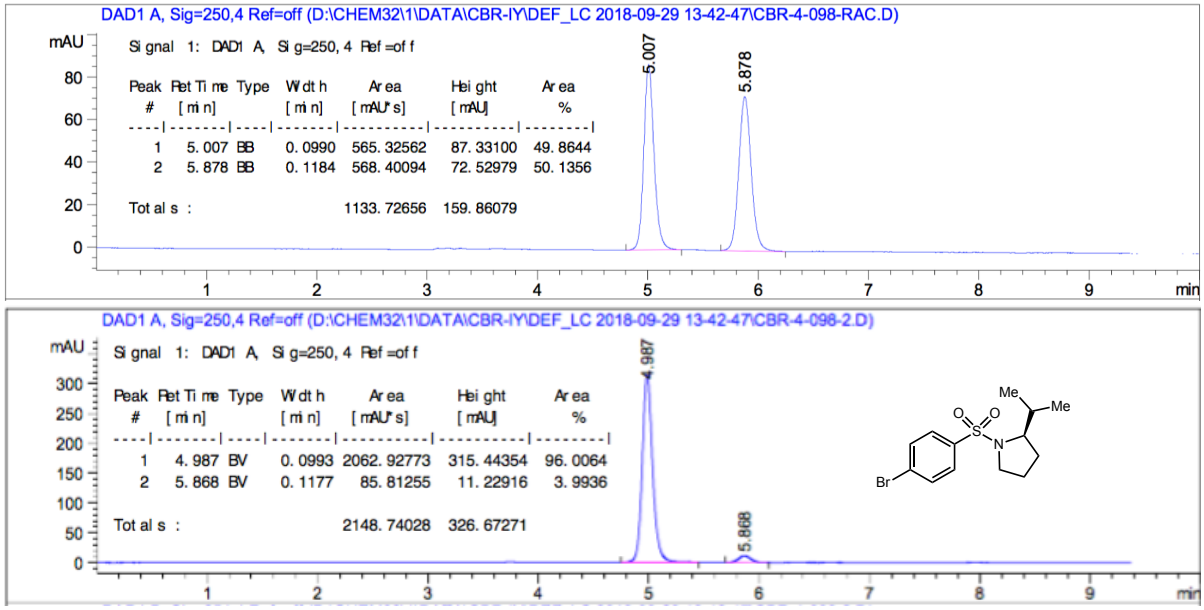
(*R*)-2-isopropyl-1-tosylpyrrolidine (**3**) HPLC:



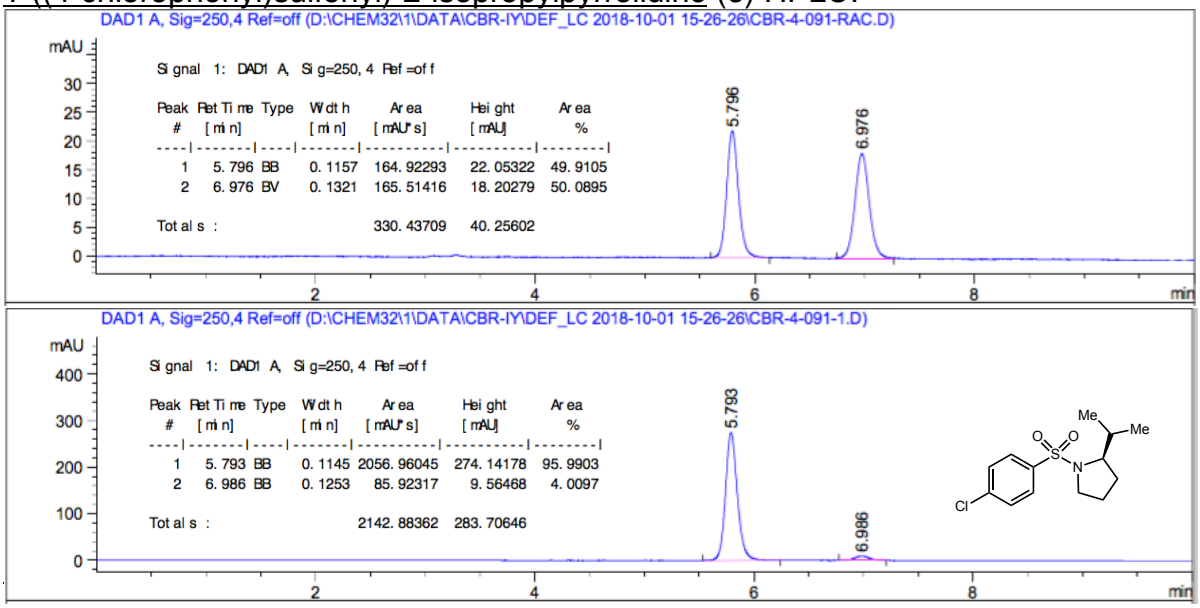
(*R*)-2-isopropyl-1-(phenylsulfonyl)pyrrolidine (**4**) HPLC:



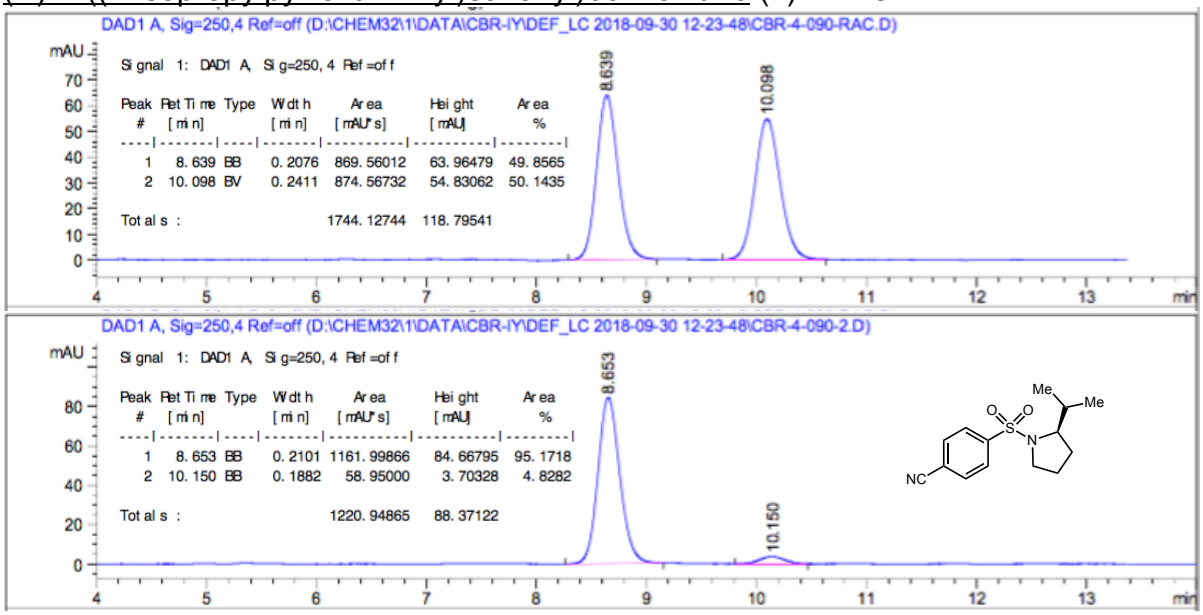
(*R*)-1-((4-bromophenyl)sulfonyl)-2-isopropylpyrrolidine (**5**) HPLC:



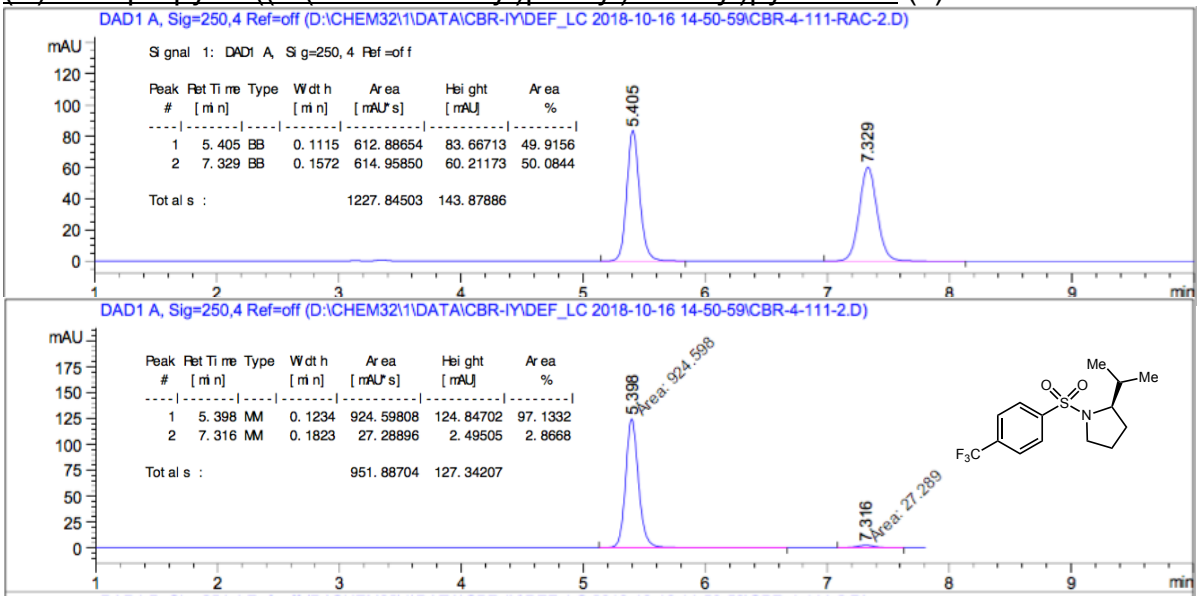
1-((4-chlorophenyl)sulfonyl)-2-isopropylpyrrolidine (**6**) HPLC:



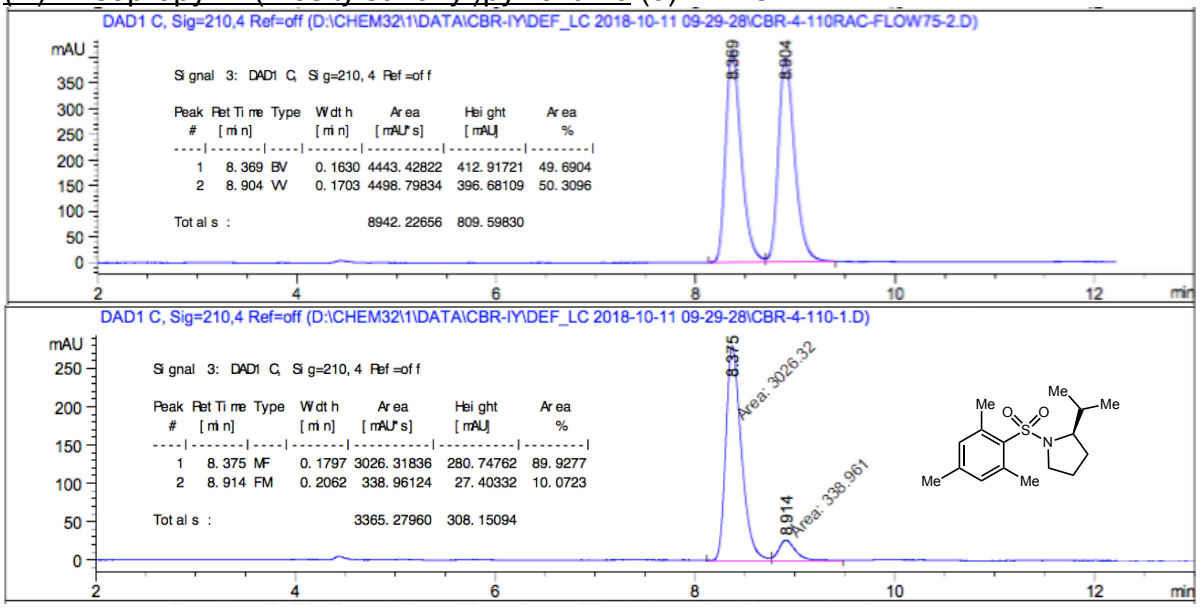
(*R*)-4-((2-isopropylpyrrolidin-1-yl)sulfonyl)benzonitrile (**7**) HPLC:



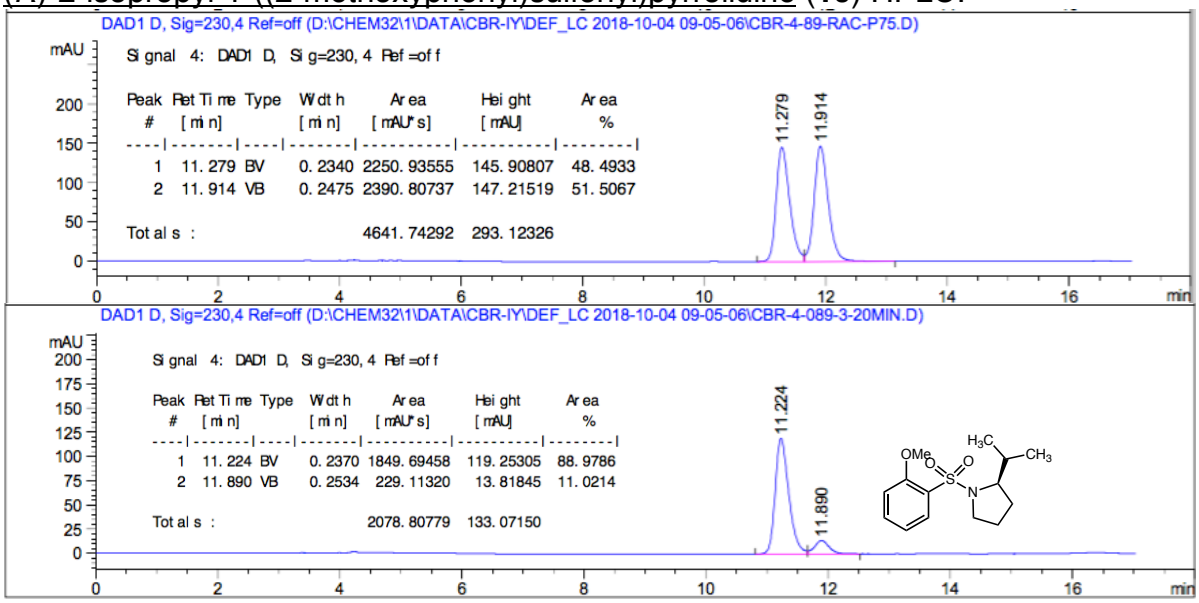
(*R*)-2-isopropyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (**8**) HPLC:



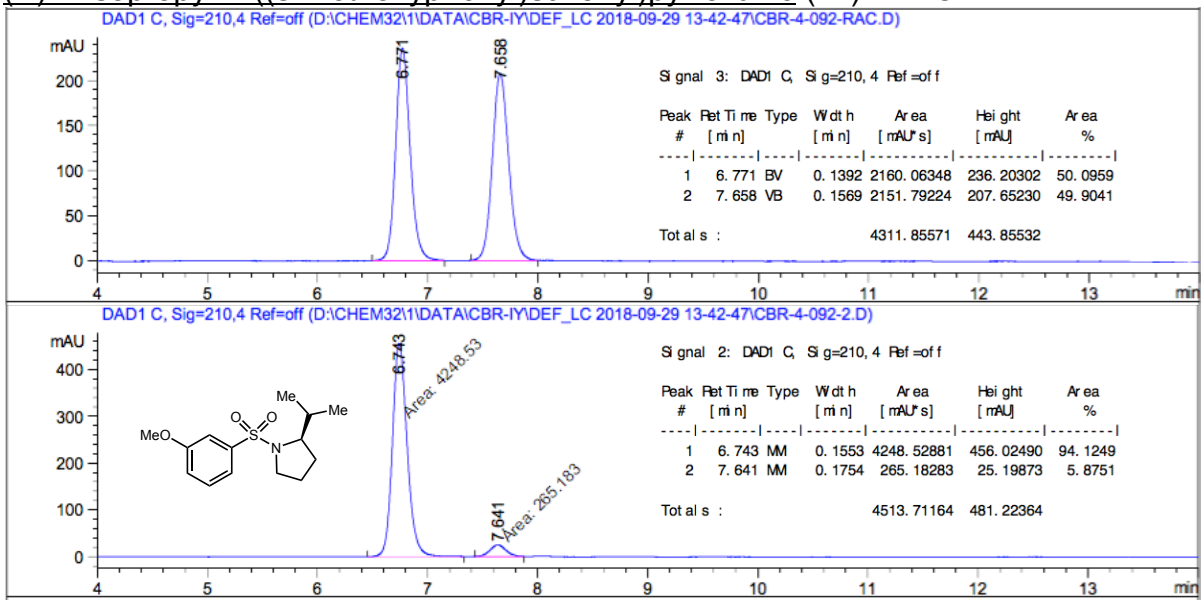
(*R*)-2-isopropyl-1-(mesitylsulfonyl)pyrrolidine (**9**) HPLC:



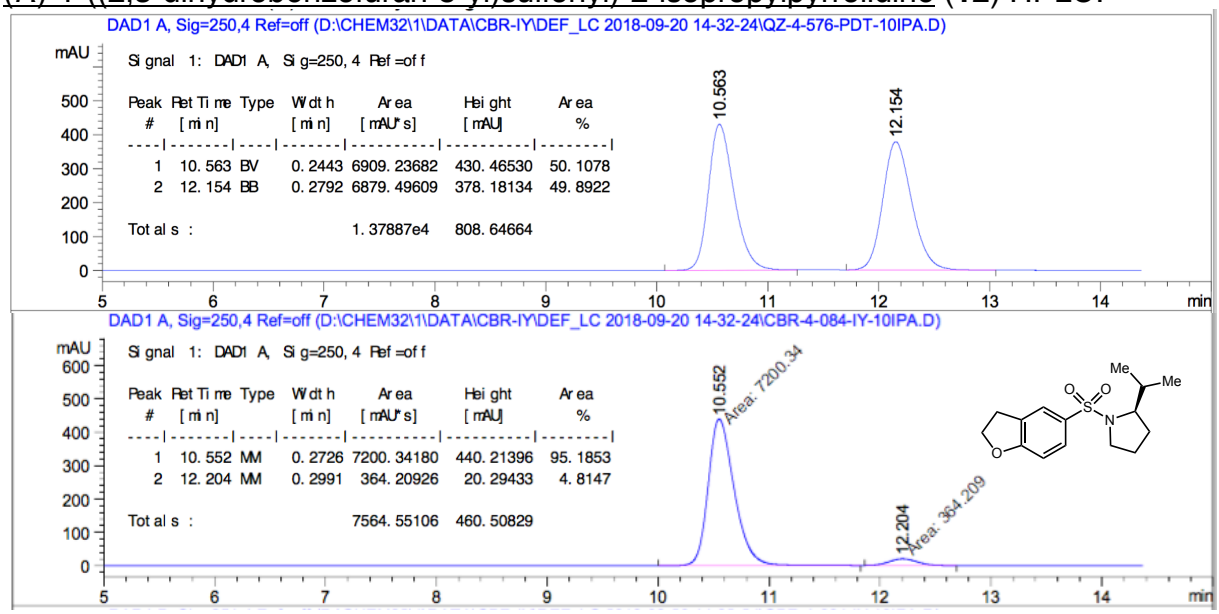
(*R*)-2-isopropyl-1-((2-methoxyphenyl)sulfonyl)pyrrolidine (**10**) HPLC:



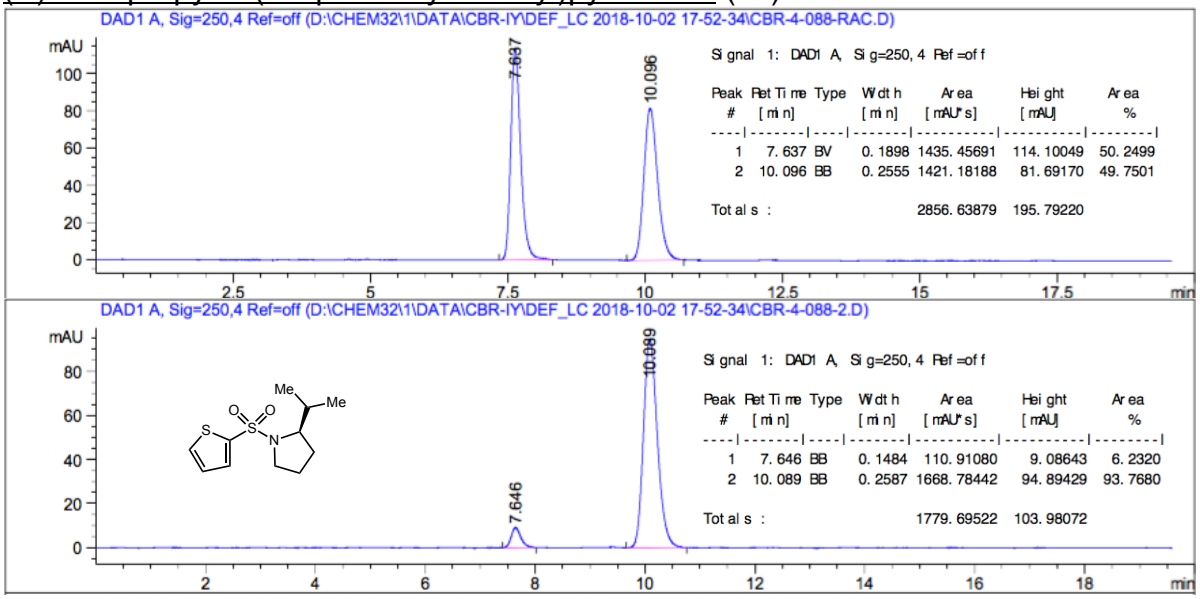
(*R*)-2-isopropyl-1-((3-methoxyphenyl)sulfonyl)pyrrolidine (**11**) HPLC:



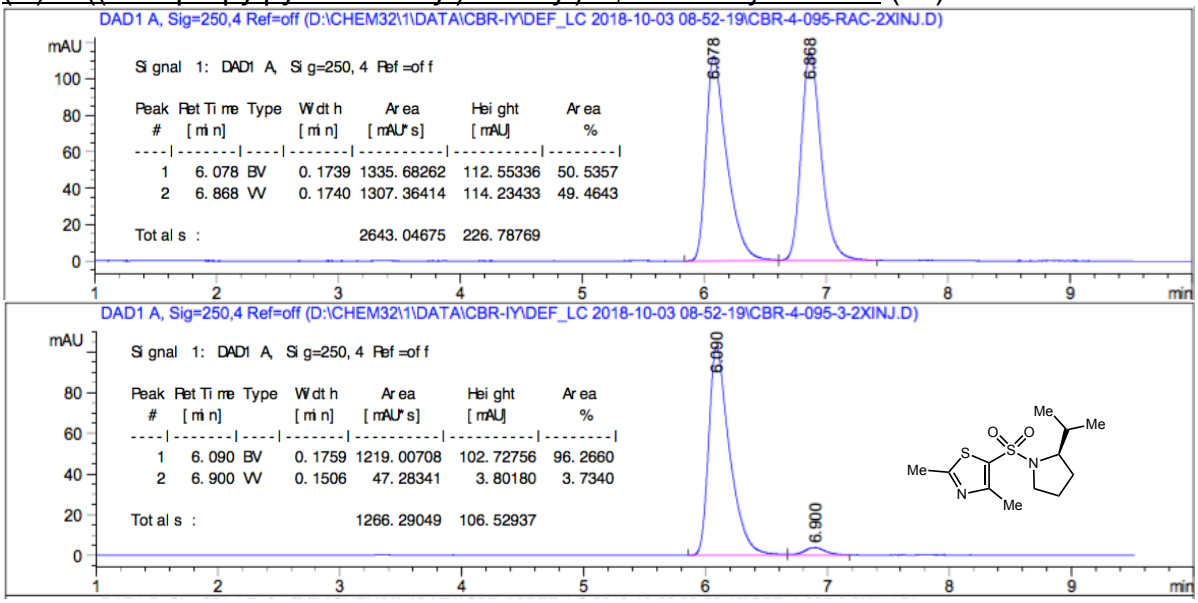
(*R*)-1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2-isopropylpyrrolidine (**12**) HPLC:



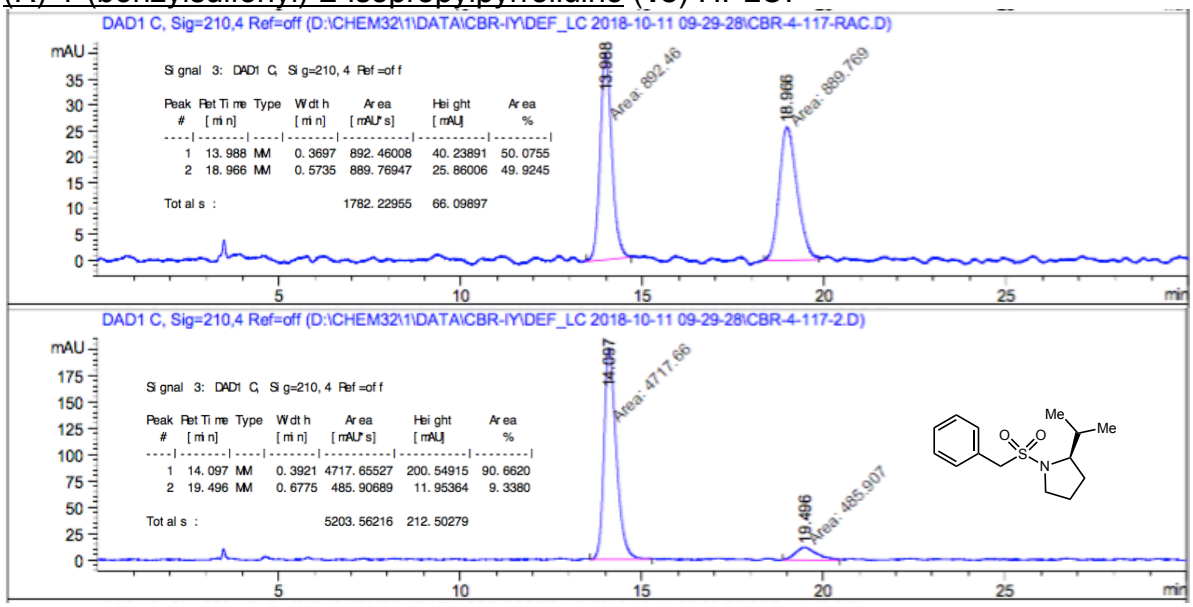
(*R*)-2-isopropyl-1-(thiophen-2-ylsulfonyl)pyrrolidine (**13**) HPLC:



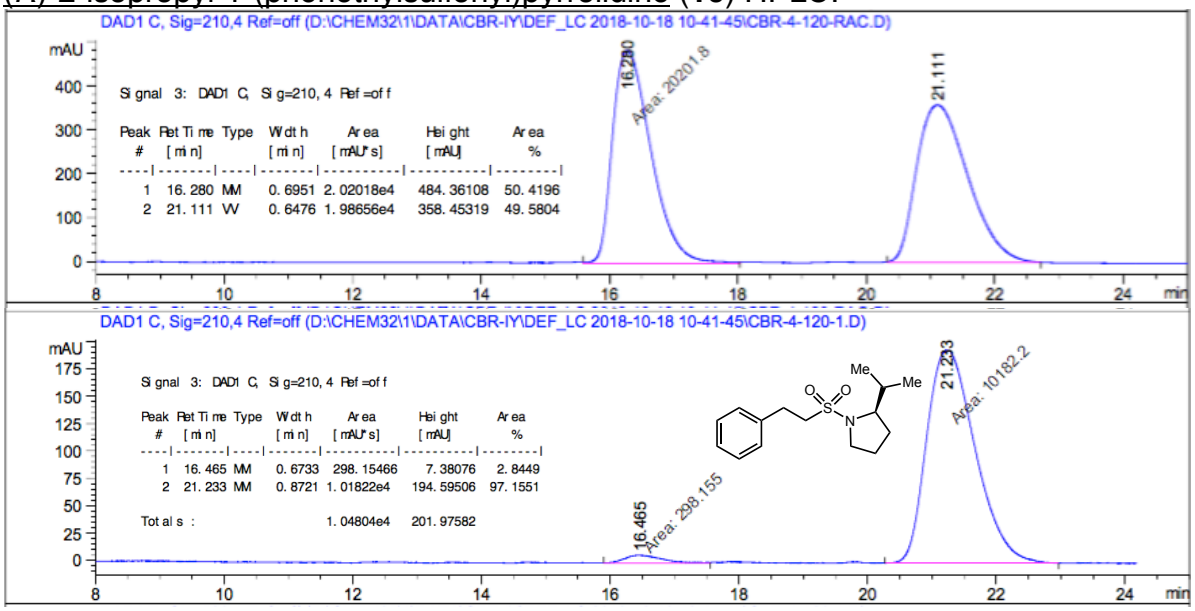
(*R*)-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)-2,4-dimethylthiazole (**14**) HPLC:



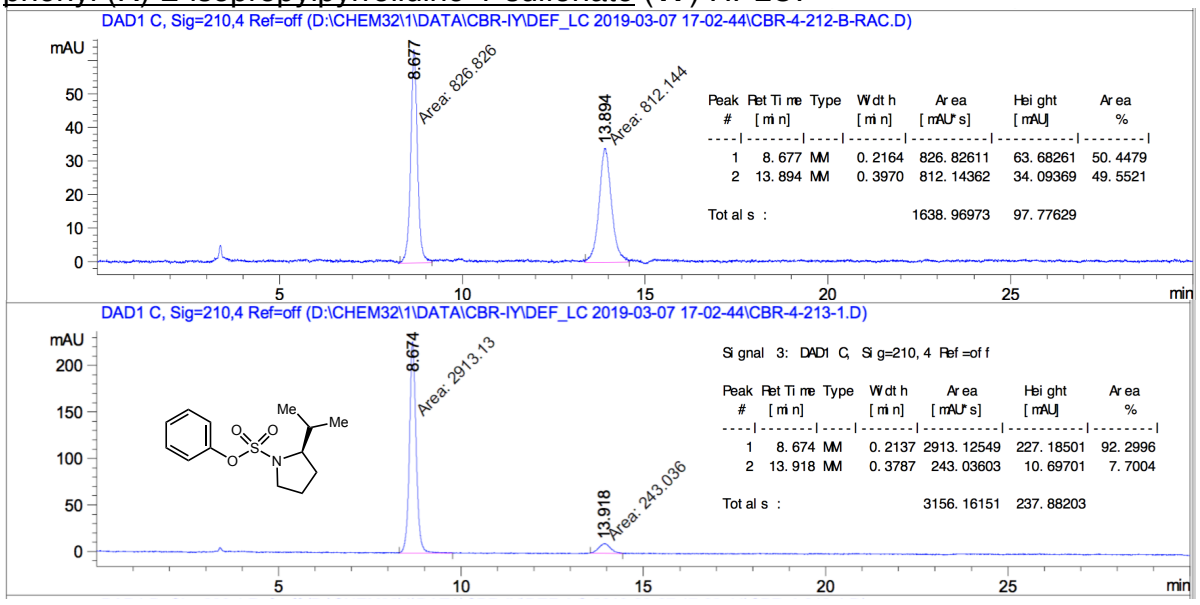
(*R*)-1-(benzylsulfonyl)-2-isopropylpyrrolidine (**15**) HPLC:



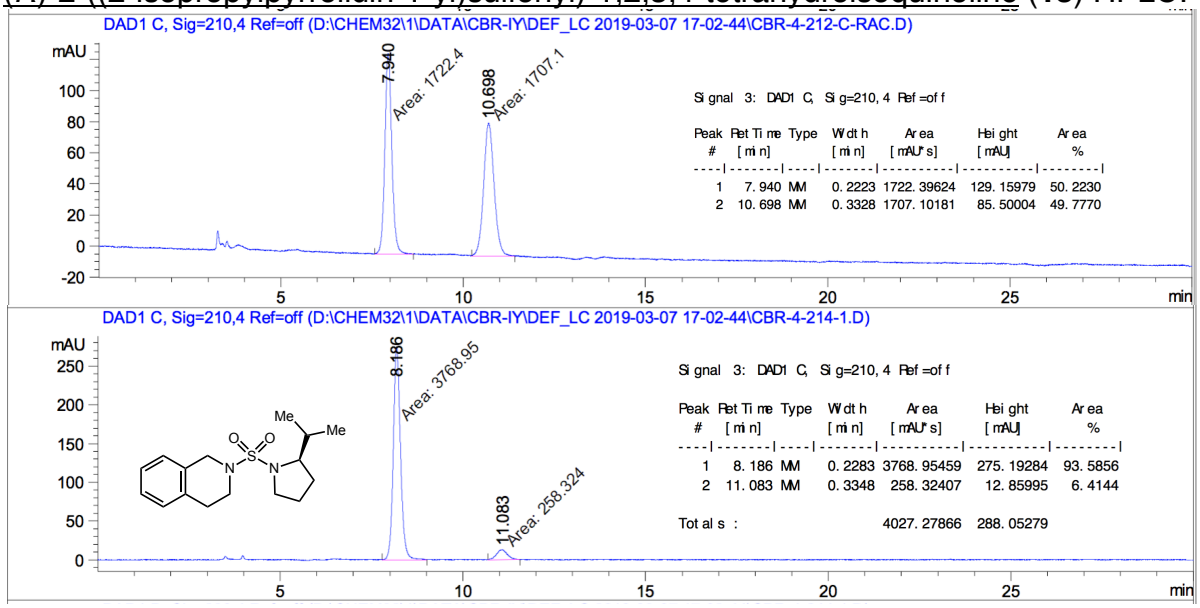
(*R*)-2-isopropyl-1-(phenethylsulfonyl)pyrrolidine (**16**) HPLC:



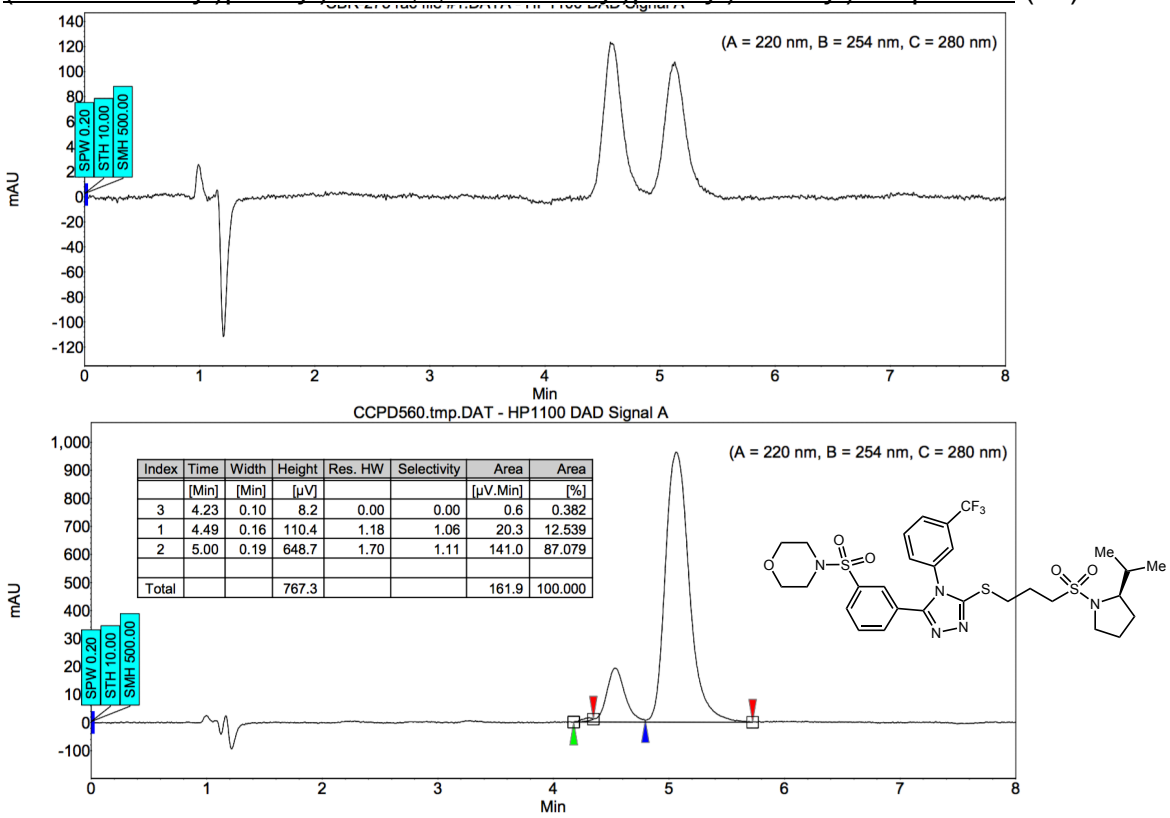
phenyl (*R*)-2-isopropylpyrrolidine-1-sulfonate (**17**) HPLC:



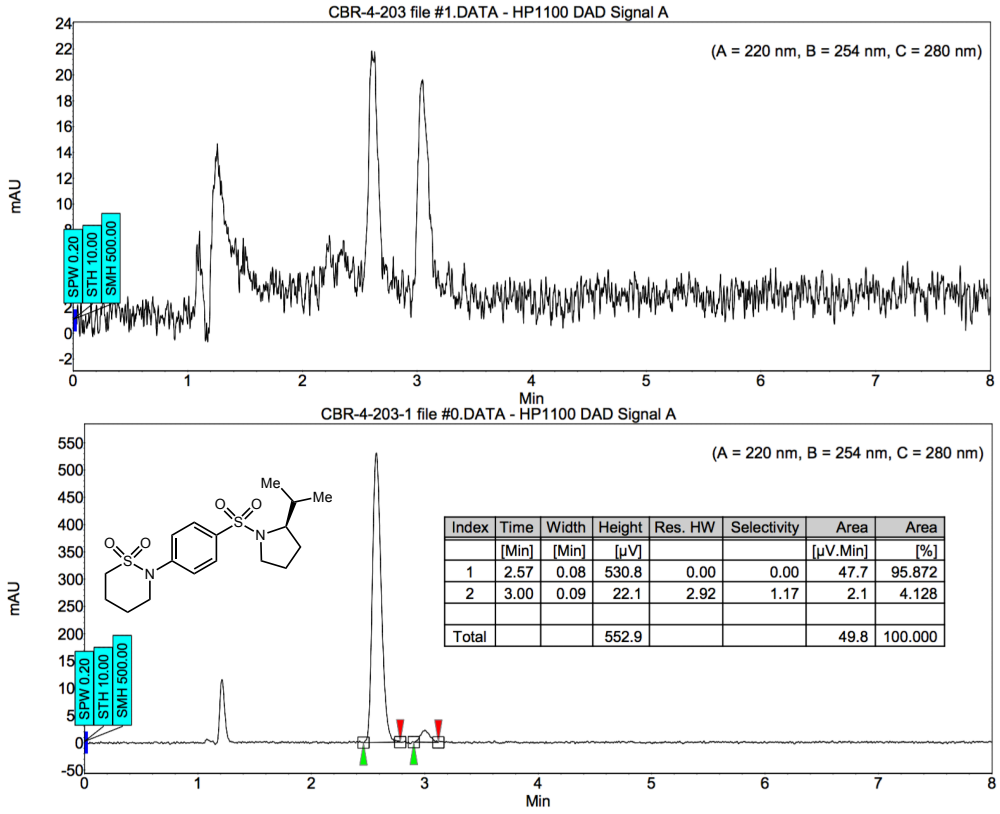
(*R*)-2-((2-isopropylpyrrolidin-1-yl)sulfonyl)-1,2,3,4-tetrahydroisoquinoline (**18**) HPLC:



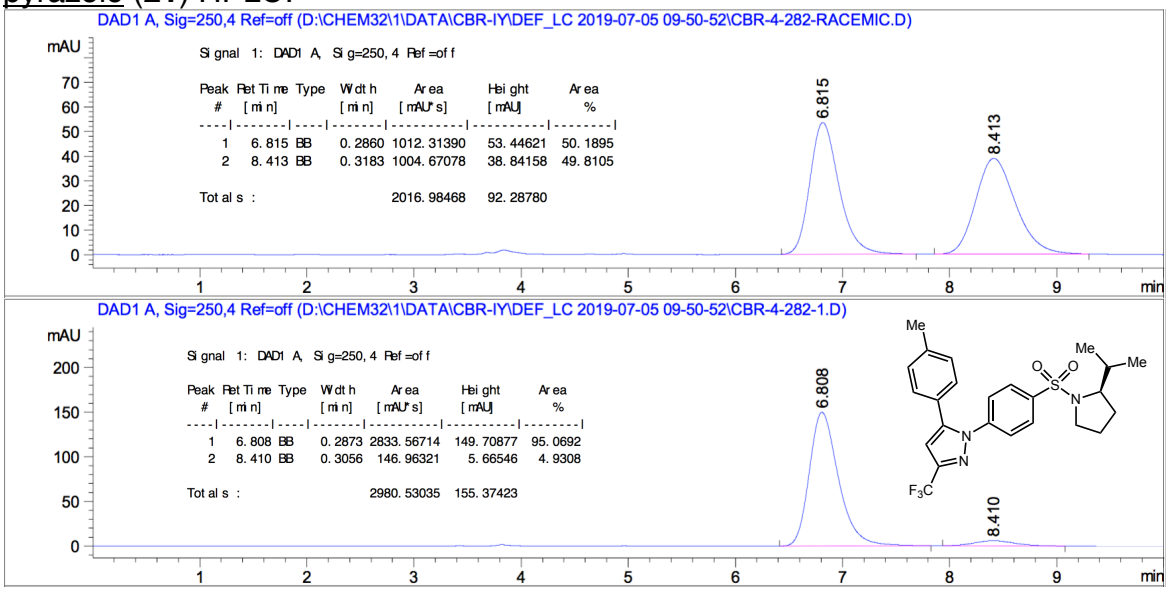
(*R*)-4-((3-(5-((3-((2-isopropylpyrrolidin-1-yl)sulfonyl)propyl)thio)-4-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-3-yl)phenyl)sulfonyl)morpholine (**19**) SFC:



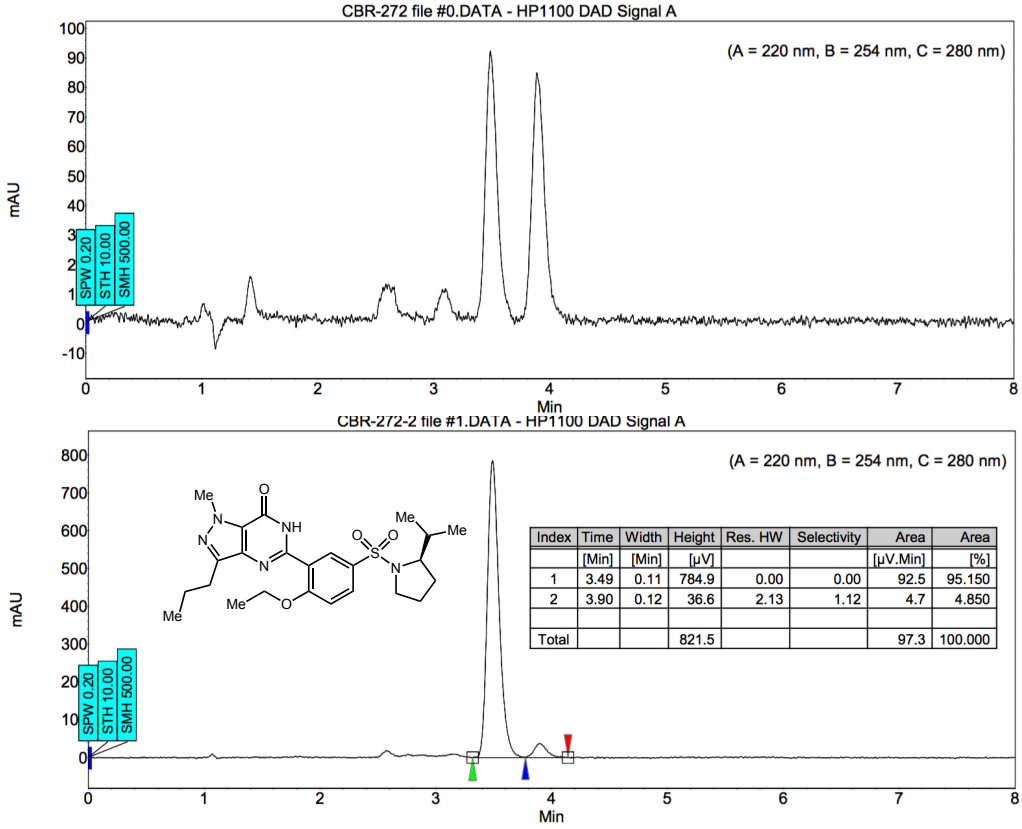
(*R*)-2-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1,2-thiazinane 1,1-dioxide (**20**) SFC:



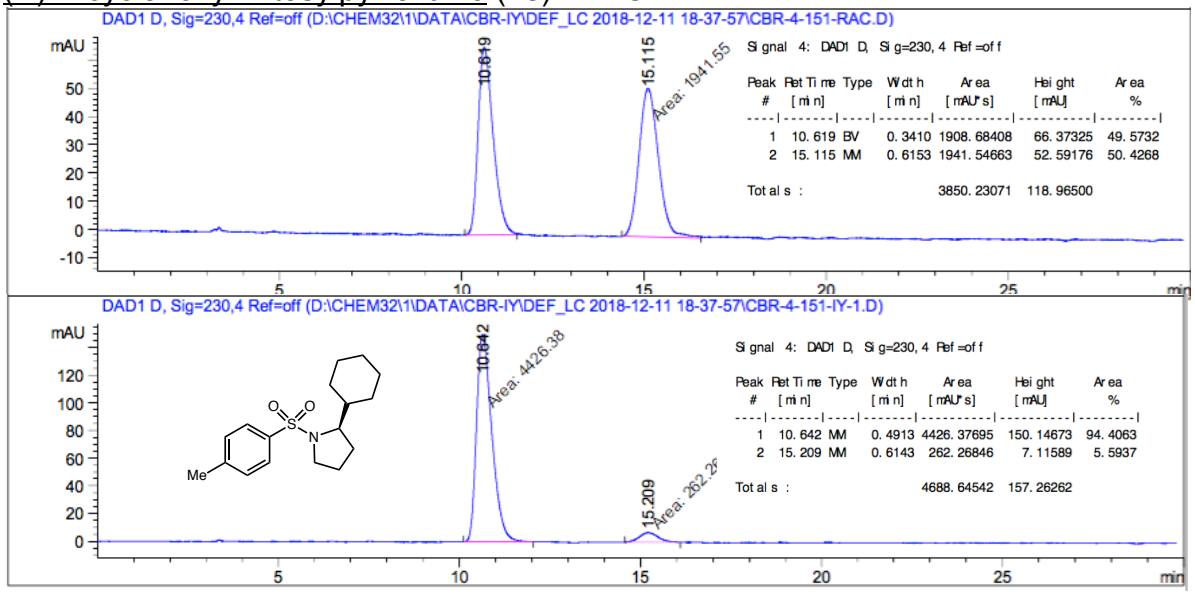
(*R*)-1-(4-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (**21**) HPLC:



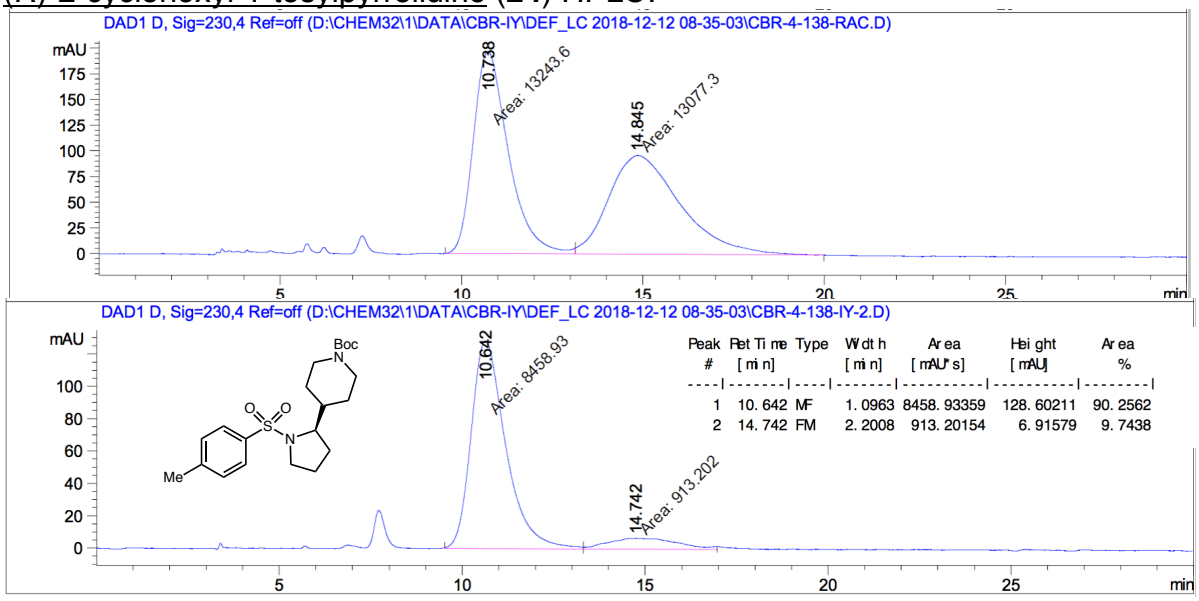
(*R*)-5-(2-ethoxy-5-((2-isopropylpyrrolidin-1-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one (**22**) SFC:



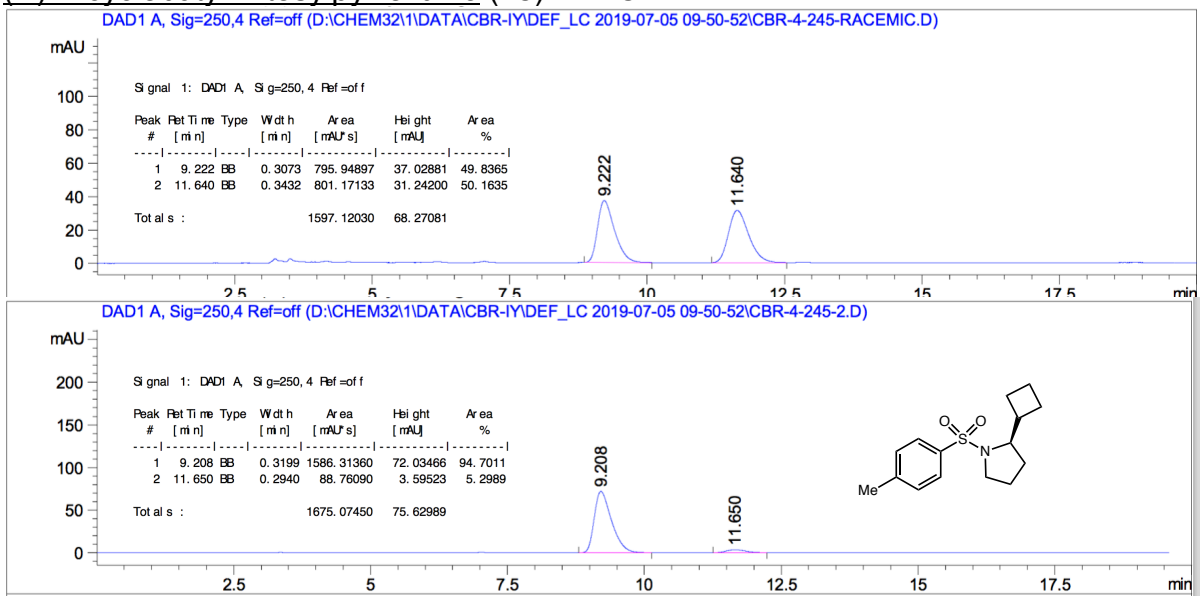
(*R*)-2-cyclohexyl-1-tosylpyrrolidine (**23**) HPLC:



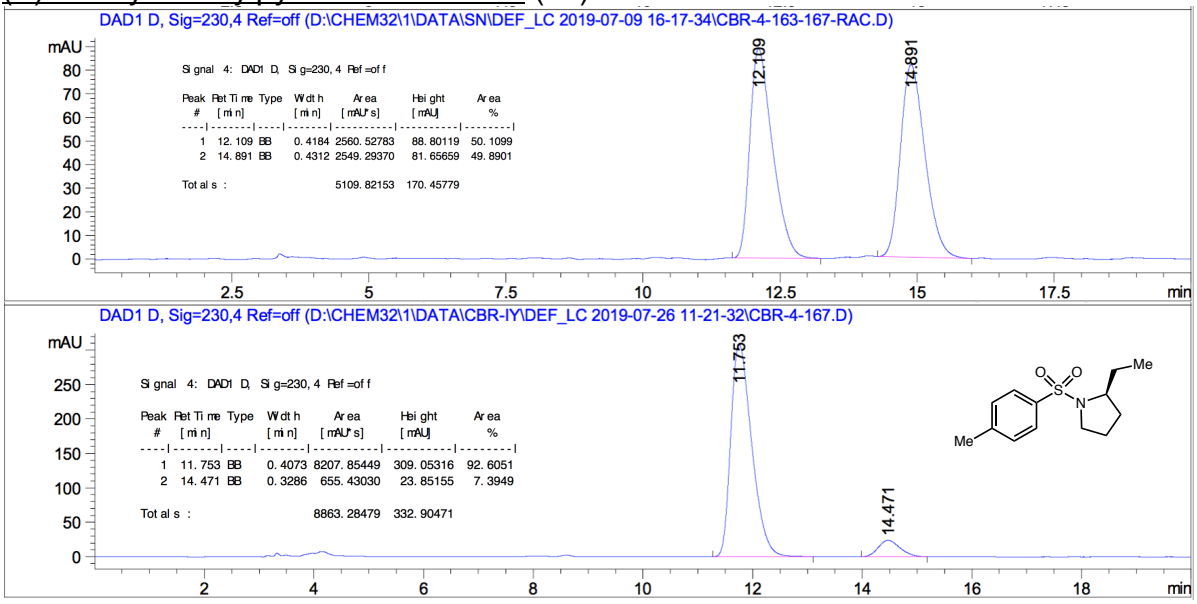
(*R*)-2-cyclohexyl-1-tosylpyrrolidine (**24**) HPLC:



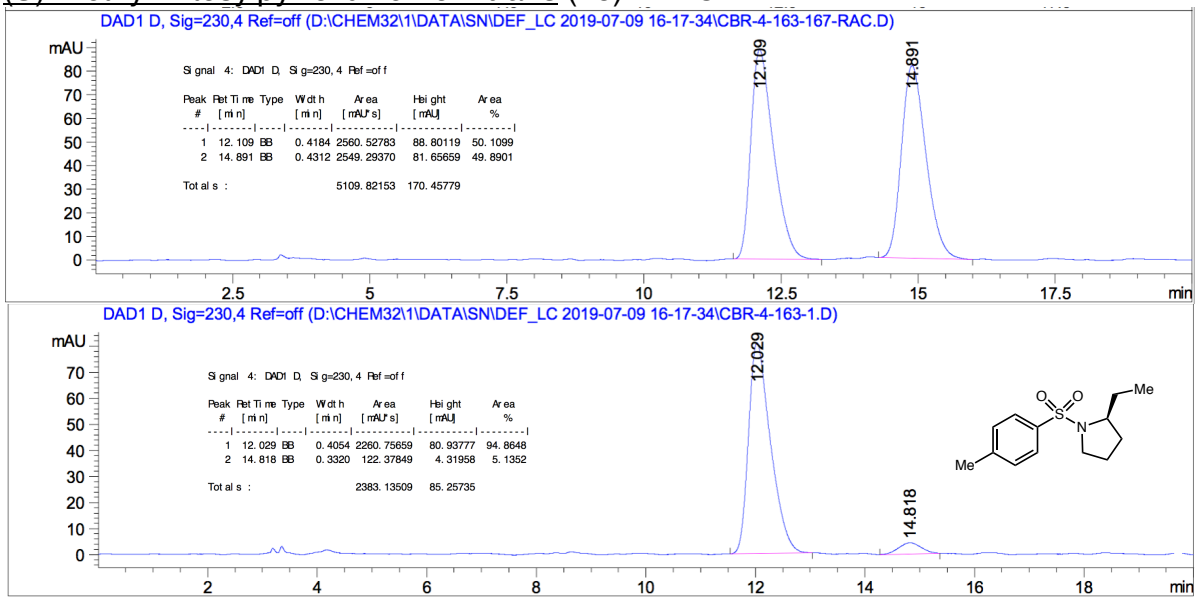
(*R*)-2-cyclobutyl-1-tosylpyrrolidine (**25**) HPLC:



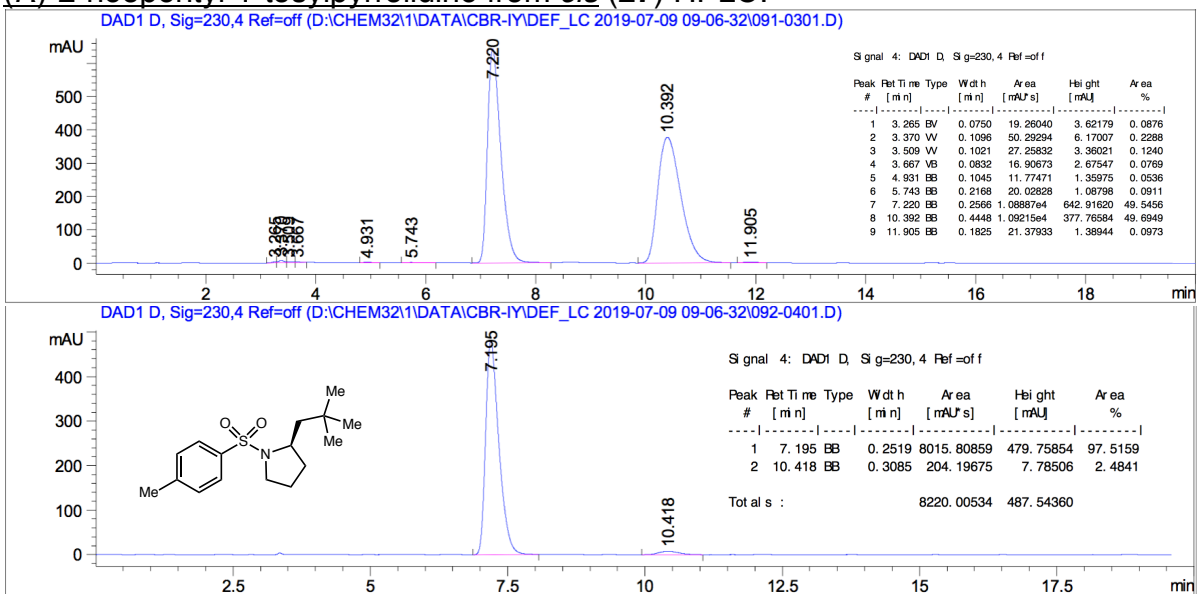
(*S*)-2-ethyl-1-tosylpyrrolidine from *cis* (**26**) HPLC:



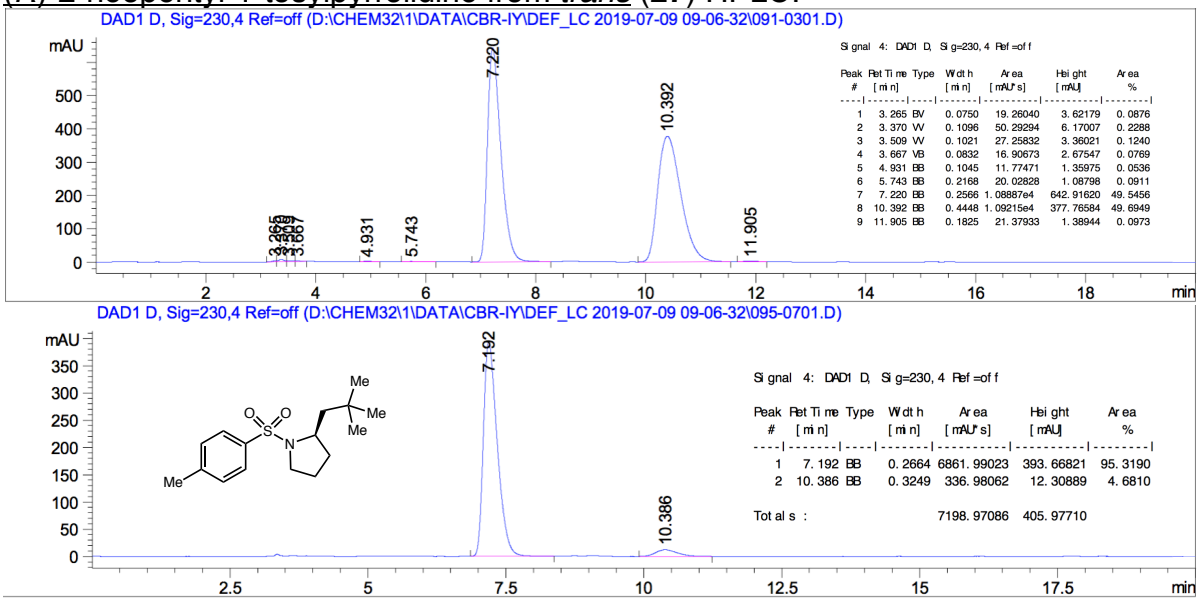
(*S*)-2-ethyl-1-tosylpyrrolidine from *trans* (**26**) HPLC:



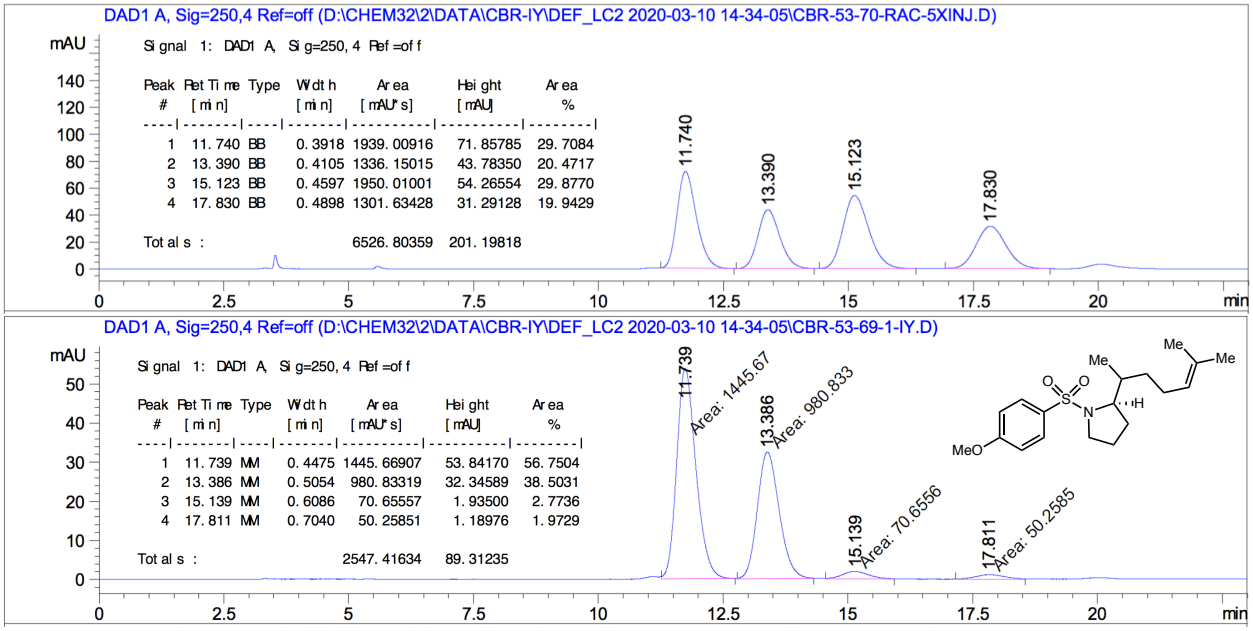
(*R*)-2-neopentyl-1-tosylpyrrolidine from *cis* (**27**) HPLC:



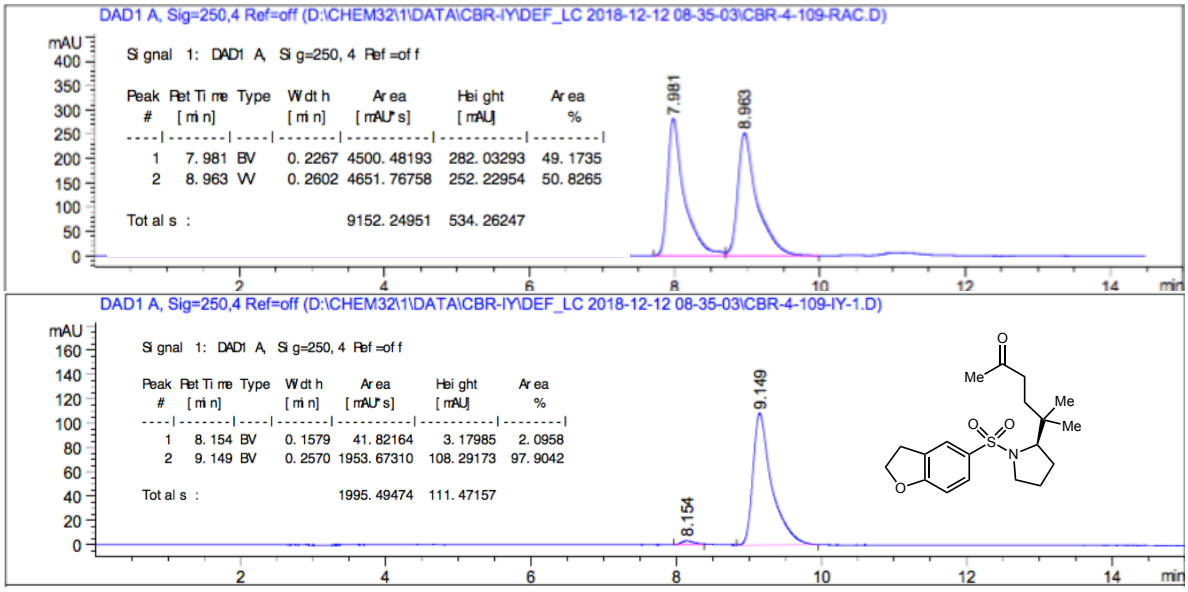
(*R*)-2-neopentyl-1-tosylpyrrolidine from *trans* (**27**) HPLC:



1-((4-methoxyphenyl)sulfonyl)-2-(6-methylhept-5-en-2-yl)pyrrolidine (mixture of diastereomers) (**28**)
HPLC:



(*R*)-5-(1-((2,3-dihydrobenzofuran-5-yl)sulfonyl)pyrrolidin-2-yl)-5-methylhexan-2-one (**29**)
HPLC:



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