Supporting Information for

Synthesis of 3-Borylated Cyclobutanols from Epihalohydrins or Epoxy Alcohol Derivatives

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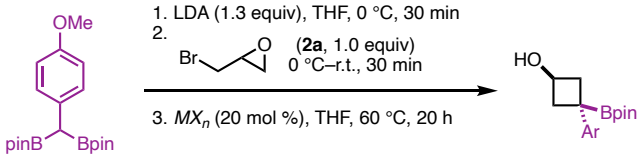
A. General Information

Unless otherwise noted, all reactions were set up on the benchtop and run under an atmosphere of Ar or N_2 using flame-dried glassware and anhydrous solvents. DCM, Et_2O, MeCN, PhMe, and THF were purchased as HPLC-grade (inhibitor-free) from Caledon or Sigma–Aldrich, and were dried using a PureSolv MD 5 solvent purification system and used without further manipulation. 1,4-Dioxane was purchased as anhydrous from Sigma–Aldrich in a Sure/Seal bottle and was degassed by sonicating under vacuum for 15 min prior to use. Zn(II) and Li(I) salts were purchased as anhydrous-grade and were stored and weighed in a glovebox, with the exception of $Zn(CN)_2$, in which case it was stored under normal atmosphere and weighed on the benchtop. CuCl was purchased from Sigma–Alrich and was measured out open to air, so a small amount of $CuCl_2$ was assumed to be present. All other commercial reagents were used as received.

Compounds were purified by flash column chromatography using SiliCycle SilicaFlash P60 silica gel. The 8- and 16-mL threaded culture tubes used for reactions were purchased from Fisher (catalogue nos. 14-957-76A and 14-959-35A) and were sealed using a size 19 rubber septum and electrical tape. 1,1-Diborylalkanes are typically stable to atmospheric conditions however they were stored under Ar at –20 °C as a precaution. ^{1}H and ^{13}C NMR spectra were recorded on Varian MercuryPlus 400 MHz, Agilent DD2 500 MHz, or Bruker AvanceIII 400 MHz spectrometers. NMR yields were measured via integration relative to a 1,3,5-trimethoxybenzene internal standard. Diastereomeric ratios were determined by ^{1}H NMR, although when the product contained a fluorine nucleus ^{19}F{H} NMR was used. TLC samples were run on EMD Millipore TLC Silica gel 60 F254 plates and were visualized by UV or by staining with standard KMnO4, phosphomolybdic acid (PMA), p-anisaldehyde, or vanillin stains. IR spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond/ZnSe ATR accessory as solids or thin films. Melting points were obtained on a Fisher-Johns Melting Point Apparatus. High-resolution mass spectra (HRMS) were recorded on a JEOL AccuTOF JMST1000LV mass spectrometer equipped with a Direct Analysis in Real Time (DART) ion source. Chiral HPLC analysis was performed on a Shimadzu 20A series system using a Daicel Chiralpak column (IA or IG).

B. Additional Optimization

Table S1. *Reaction optimization for 1b.*



1a (1.2 equiv)

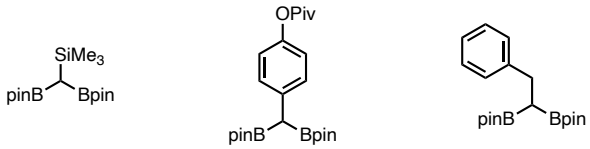
3a Ar = *p*-anisyl

Entry	MX_n	Solvent	Ligand	% **3a**	d.r.
1	–	THF	–	58	6:1
2	CuCl	THF	–	75	2:1
3	$ZnCl_2$	THF	–	67	4:1
4	$ZnCl_2$	THF	bpy	60	5:1
5	$ZnCl_2$	THF	TMEDA	78	5:1
6	$Zn(OTf)_2$	THF	–	77	4:1
7	$Zn(CN)_2$	THF	–	96	6:1
8	$Zn(CN)_2$	Toluene	–	< 1	–
9	$Zn(CN)_2$	Toluene /HMPA[b]	–	55	4:1
10[c]	$Zn(CN)_2$	THF	–	0	–

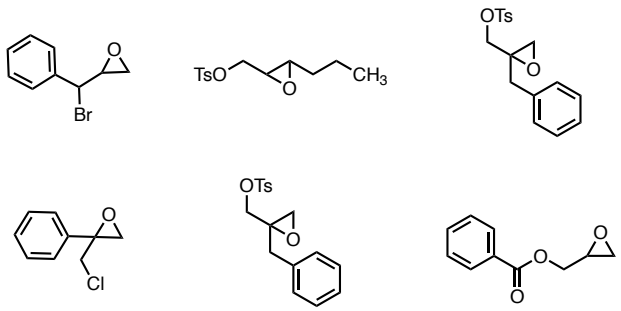
[a]Reactions were performed using 1.0 equiv of epibromohydrin, 1.2 equiv of lithiated diborylalkane, and 20 mol % of MX_n; lithiated diborylalkane was generated via deprotonation using 1.3 equiv (with respect to epibromohydrin) of LDA (generated *in situ* via the addition of *n*BuLi to diisopropylamine in THF at 0 °C). Yields and diastereomeric ratios determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]Toluene/HMPA ratio of 15/1 (v/v); HMPA (0.10 mL) was added to the reaction 10 minutes after adding the metal. [c]Reaction performed without the addition of LDA (step 1 omitted).

Table S2. *Unsuccessful substrates.*

unsuccessful 1,1-diborylalkanes (< 20% yield)

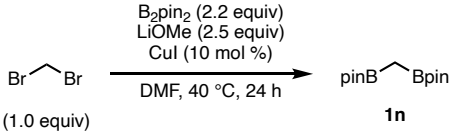


unsuccessful electrophiles (< 20% yield)



C. Synthesis of Starting Materials

Synthesis of 1,1-diborylalkanes



bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (1n): This procedure was adapted from Xiao, Fu and coworkers.[1] To a flame dried 250 mL round bottom flask equipped with a stir bar was added B_2pin_2 (11.2 g, 44.0 mmol, 2.20 equiv), CuI (0.38 g, 2.0 mmol, 10 mol %), and LiOMe (1.90 g, 50 mmol, 2.5 equiv). The flask was sealed with a size 24 septum and backfilled with nitrogen (x3). Anhydrous DMF (60 mL) was added, and the mixture was left to stir for 15 min (the solution rapidly becomes a dark blue/black upon addition of DMF). The solution was placed in an ice bath and CH_2Br_2 (1.40 mL, 20.0 mmol, 1.00 equiv) was added portion wise (3 portions) over a period of approximately 15 minutes. Once addition was complete, the ice bath was removed and the solution was heated to 40 °C for 24 h. The reaction mixture was diluted with EtOAc, filtered through a silica gel plug, and concentrated under reduced pressure. The crude solution (crude material + DMF) left after concentration was then transferred to a 250 mL separation flask, diluted with hexanes (ca. 150 mL), and rinsed with water (5x). The organic fractions were dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography (gradient of 5–10% EtOAc in hexanes) affording the desired product as a white solid (3.75 g, 14.0 mmol, 70%). The spectral data are consistent with literature precedence.[1]

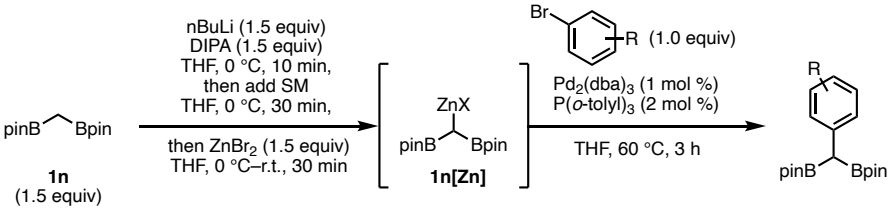
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.23 (s, 24H), 0.35 (s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.2, 24.9 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.5 ppm.

R_f: 0.3 (10% EtOAc in hexanes, stains dark blue with vanillin).

General Procedure A: Synthesis of 1-aryl-1,1-bis[(pinacolato)boryl]methane

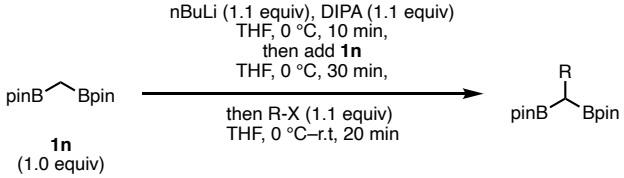


This procedure was adapted from Cho and coworkers.[2] A 16-mL threaded culture tube equipped with a stir bar and a size 19 septum was flame dried under vacuum and cooled under an atmosphere of N_2. The septum was secured with electrical tape, and anhydrous THF (2.2 mL) was added followed by DIPA (0.63 mL, 4.5 mmol, 1.5 equiv). The solution was cooled to 0 °C and nBuLi (1.74 mL of a 2.58 M solution in hexanes, 4.50 mmol, 1.50 equiv) was added dropwise. The solution was stirred for 10 min at 0 °C, after which bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**1n**, 1.2 g, 4.5 mmol, 1.5 equiv) was added as a solution in THF (2.0

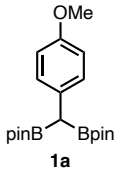
mL). A white precipitate rapidly formed, and the mixture was left to stir for 30 min at 0 °C. During this period, a separate flame dried 16-mL threaded culture tube equipped with a stir bar and size 19 septum was put under an atmosphere of N_2 and transported into a glovebox where $ZnBr_2$ (1.0 g, 4.5 mmol, 1.5 equiv) was added. After addition of the $ZnBr_2$, the tube was capped, sealed with electrical tape, removed from the glovebox and put in an ice bath. After the 30-minute stir period was complete, the lithiated **1** was transferred via syringe to the tube containing the $ZnBr_2$, and additional anhydrous THF (1.0 mL) was used as rinse. After the addition was complete, the mixture was removed from the ice bath and left to warm to r.t. over a period of 30 min, after which time the mixture became homogenous yielding **1n[Zn]** (used directly in the next step).

To a separate flame dried 16-mL threaded culture tube equipped with a stir bar and size 19 septum was added $Pd_2(dba)_3$ (28 mg, 0.030 mmol, 1.0 mol %) and P(*o*-tolyl)$_3$ (18 mg, 0.060 mmol, 2.0 mol %). The tube was sealed with the septum and electrical tape, evacuated and backfilled with N_2 (x3), and to it was added anhydrous THF (2.0 mL) with stirring. After 5 min, the aryl bromide (3.0 mmol, 1.0 equiv) was added. The mixture was stirred at r.t. for an additional 10 min, after which **1n[Zn]** was carefully added. When addition was complete, the tube was placed in a pre-heated 60 °C oil bath and stirred for 3 h. The reaction was then filtered over celite, concentrated under reduced pressure, and purified by flash column chromatography yielding the desired product.

General Procedure B: Synthesis of 1-alkyl-1,1-bis[(pinacolato)boryl]methane



This procedure was adapted from Morken and coworkers.[3] An 8-mL threaded culture tube equipped with a stir bar and size 19 septum was flame dried under vacuum and cooled under an atmosphere of N_2. The septum was secured with electrical tape and anhydrous THF (2.0 mL) was added followed by DIPA (0.15 mL, 1.1 mmol, 1.1 equiv). The solution was cooled to 0 °C and nBuLi (0.42 mL of a 2.60 M solution in hexanes, 1.1 mmol, 1.1 equiv) was added dropwise. The solution was stirred at 0 °C for 10 min, after which bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**1n**, 0.27 g, 1.0 mmol, 1.0 equiv) was added as a solution in THF (2.0 mL). A white precipitate rapidly formed, and the mixture was left to stir for 30 min at 0 °C. Alkyl halide (1.1 mmol, 1.1 equiv) was added at 0 °C (reaction became homogenous upon addition), and the mixture was removed from the ice bath. The reaction was left to warm to r.t. over a period of 20 mins and then filtered over celite, concentrated under reduced pressure, and purified by flash column chromatography yielding the desired product.



1a

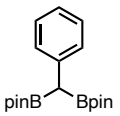
2,2'-((4-methoxyphenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1a): Prepared using 4-bromoanisole (0.38 mL, 3.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–10% EtOAc in hexanes) to afford the desired product as a white solid (0.84 g, 2.2 mmol, 75%). The spectral data are consistent with literature precedence.[2]

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.19–7.16 (m, 2H), 6.79–6.75 (m, 2H), 3.76 (s, 3H), 2.23 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ 156.6, 131.4, 129.9, 113.5, 83.3, 55.2, 24.7, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.8 ppm.

R_f: 0.2 (10% EtOAc in hexanes, stains blue/black with vanillin).



1b

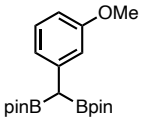
2,2'-(phenylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1b): Prepared using bromobenzene (0.11 mL, 1.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–5% EtOAc in hexanes) to afford the desired product as a white solid (0.20 g, 0.57 mmol, 57%). The spectral data are consistent with literature precedence.[2]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.28–7.24 (m, 2H, overlapping with $CHCl_3$), 7.21 (t, J = 7.5 Hz, 2H), 7.07 (t, J = 7.2 Hz, 1H), 2.30 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 139.5, 129.2, 127.9, 124.2, 83.4, 24.7, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.9 ppm.

R_f: 0.2 (10% EtOAc in hexanes, stains blue/black with vanillin).



1c

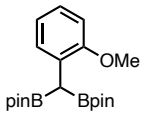
2,2'-((3-methoxyphenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1c): Prepared using 3-bromoanisole (0.25 mL, 2.0 mmol, 1.0 equiv) General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–15% EtOAc in hexanes) to afford the desired product as a white solid (0.49 g, 1.31 mmol, 66%). The spectral data are consistent with literature precedence.[4]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.88–6.83 (m, 2H), 6.66–6.61 (m, 1H), 3.78 (s, 3H), 2.28 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.4, 141.2, 128.8, 122.0, 115.1, 110.0, 83.5, 55.2, 24.9, 24.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.8 ppm.

R_f: 0.2 (10% EtOAc in hexanes, stains blue/black with vanillin).



1d

2,2'-((2-methoxyphenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1d): Prepared using 2-bromoanisole (0.12 mL, 1.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (4:26:70 EtOAc:toluene:hexanes) to afford the desired product as a white solid (0.11 g, 0.30 mmol, 30%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.41 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.08 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 6.85 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.76 (s, 3H), 2.47 (s, 1H), 1.24 (s, 12H), 1.23 (s, 12H) ppm.

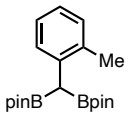
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 157.2, 130.2, 128.9, 125.6, 120.5, 110.0, 83.2, 55.4, 25.0, 24.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.3 ppm

HRMS (DART): calc'd for $C_{12}H_{33}B_2N_6O_4Si$ $[M+H]^+$: 375.2513; found 375.2512.

IR (neat): 2979, 2930, 1738, 1599, 1493, 1466, 1440, 1373, 1356, 1316, 1292, 1137, 968, 854 cm^{-1}.

R_f: 0.4 (10% EtOAc in toluene, stains blue/black with vanillin).



1e

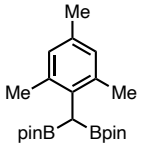
2,2'-(*o*-tolylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1e): Prepared using 2-bromotoluene (0.12 mL, 1.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 3–5% EtOAc in hexanes) to afford the desired product as a white solid (0.11 g, 0.32 mmol, 32%). The spectral data are consistent with literature precedence.[2]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.44 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.12–7.06 (m, 2H), 7.02–6.97 (m, 1H), 2.39 (s, 1H), 2.24 (s, 3H), 1.23 (s, 12H), 1.22 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 138.3, 135.9, 129.8, 129.3, 125.8, 124.5, 83.5, 24.9, 24.8, 20.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.0 ppm.

R_f: 0.2 (10% EtOAc in hexanes, stains blue/black with vanillin).



1f

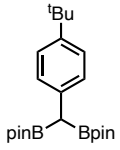
2,2'-(mesitylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1f): Prepared using 2-bromomesitylene (0.24 mL, 1.6 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–10% EtOAc in hexanes) to afford the desired product as a white solid (0.48 g, 1.2 mmol, 79%). The spectral data are consistent with literature precedence.[5]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.78 (s, 2H), 2.37 (s, 1H), 2.26 (s, 6H), 2.21 (s, 3H), 1.22 (s, 12H), 1.20 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 136.2, 134.3, 133.2, 128.9, 83.2, 25.0, 24.8, 21.7, 21.0 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.0 ppm.

R_f: 0.3 (10% EtOAc in hexanes).



1g

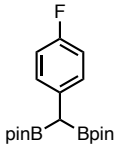
2,2'-((4-(*tert*-butyl)phenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1g): Prepared using 1-bromo-4-tert-butylbenzene (0.27 mL, 1.6 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–10% EtOAc in hexanes) to afford the desired product as a white solid (0.39 g, 0.97 mmol, 62%). The spectral data are consistent with literature precedence.[6]

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.23–7.20 (m, 2H), 7.19–7.16 (m, 2H), 2.28 (s, 1H), 1.28 (s, 9H), 1.23 (s, 12H), 1.22 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 146.7, 136.2, 128.9, 125.0, 83.4, 34.3, 31.6, 24.8, 24.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

R_f: 0.2 (5% EtOAc in hexanes, stains yellow with $KMnO_4$).



1h

2,2'-((4-fluorophenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1h): Prepared using 1-bromo-4-fluorobenzene (0.18 mL, 1.6 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 1–5% EtOAc in toluene) to afford the desired product as a white solid (0.41 g, 1.1 mmol, 71%). The spectral data are consistent with literature precedence.[2]

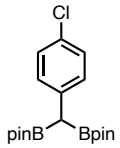
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.23–7.17 (m, 2H), 6.92–6.86 (m, 2H), 2.26 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.6 (d, J = 241.0 Hz), 135.1 (d, J = 3.1 Hz), 130.4 (d, J = 7.6 Hz), 114.8 (d, J = 20.9 Hz), 83.6, 24.8, 24.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ -120.4 ppm.

R_f: 0.5 (10% EtOAc in toluene, stains blue/black with vanillin)



1i

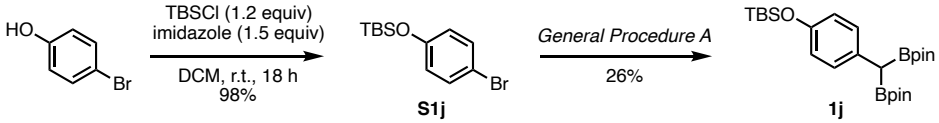
2,2'-((4-chlorophenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1i): Prepared using 1-bromo-4-chlorobenzene (0.38 g, 2.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 1–5% EtOAc in toluene) to afford the desired product as a white solid (0.28 g, 0.73 mmol, 36%). The spectral data are consistent with literature precedence.[2]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.21–7.14 (m, 4H), 2.26 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 138.3, 130.6, 130.0, 128.1, 83.7, 24.8, 24.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.8 ppm.

R_f: 0.49 (15% EtOAc in hexanes, stains blue with vanillin)



(4-bromophenoxy)(*tert*-butyl)dimethylsilane (S1j): To a flame dried round bottom flask equipped with a stir bar was added 3-bromophenol (2.1 g, 12 mmol, 1.0 equiv), *tert*-butyldimethylsilyl chloride (TBSCl, 2.2 g, 14 mmol, 1.2 equiv), and imidazole (1.2 g, 18 mmol, 1.5 equiv). The flask was sealed with a size 24 septum and then evacuated and backfilled with nitrogen (x3). DCM (25 mL) was then added and the reaction was left to stir for 18 h at 23 °C. The reaction mixture was then concentrated under reduced pressure and purified by flash column chromatography (0–5% EtOAc in hexanes) to afford the desired product as a colorless oil (3.4 g, 12 mmol, 98% yield). The spectral data are consistent with literature precedence.[7]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.34–7.29 (m, 2H), 6.74–6.69 (m, 2H), 0.97 (s, 9H), 0.18 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 155.0, 132.4, 122.1, 113.8, 25.8, 18.3, -4.3 ppm.
R_f: 0.7 (5% EtOAc in hexanes)

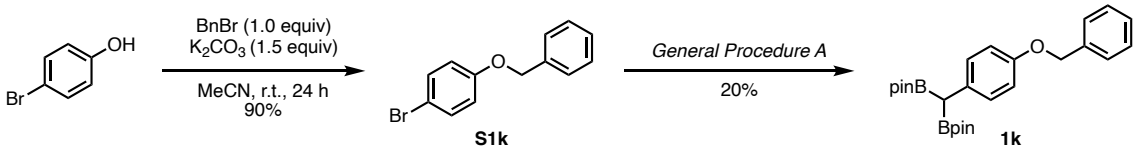
(4-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenoxy)(*tert*-butyl)dimethylsilane (1j): Prepared using **S1j** (0.57 g, 2.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–10% EtOAc in hexanes) to afford the desired product as a white solid (0.25 g, 0.52 mmol, 26%). The spectral data are consistent with literature precedence.[2]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.13–7.08 (m, 2H), 6.71–6.67 (m, 2H), 2.22 (s, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 0.96 (s, 9H), 0.17 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 152.6, 132.0, 130.0, 119.7, 83.4, 25.9, 24.8, 24.7, 18.3, -4.3 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.6 ppm.

R_f: 0.5 (60% toluene, 30% hexanes, 10% EtOAc)



1-(benzyloxy)-4-bromobenzene (S1k): To a flame dried round bottom flask equipped with a stir bar was added K_2CO_3 (4.1 g, 30 mmol, 1.5 equiv) and 4-bromophenol (3.5 g, 20 mmol, 1.0 equiv). The flask was sealed with a size 24 septum and then evacuated and backfilled with nitrogen (x3). Acetonitrile (50 mL) was added, followed by benzyl bromide (2.4 mL, 20 mmol, 1.0 equiv). The reaction was stirred for 24 h and then filtered over celite, concentrated under reduced pressure and purified by flash column chromatography (gradient of 0–5% EtOAc in hexanes) to afford the desired product as a white solid (4.8 g, 18 mmol, 90%). The spectral data are consistent with literature precedence.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.44–7.30 (m, 7H), 6.88–6.83 (m, 2H), 5.04 (s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 158.0, 136.7, 132.4, 128.8, 128.3, 127.6, 116.9, 113.3, 70.4 ppm.

R_f: 0.6 (10% EtOAc in hexanes).

2,2'-((4-(benzyloxy)phenyl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1k): Prepared using **S1k** (0.41 g, 1.6 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–10% EtOAc in hexanes) to afford the desired product as a white solid (0.14 g, 0.31 mmol, 20%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.44–7.41 (m, 2H), 7.39–7.35 (m, 2H), 7.33–7.29 (m, 1H), 7.20–7.16 (m, 2H), 6.87–6.83 (m, 2H), 5.01 (s, 2H), 2.24 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H) ppm.

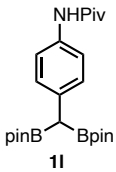
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 156.1, 137.7, 131.8, 130.1, 128.6, 127.9, 127.7, 114.6, 83.5, 70.1, 24.8, 24.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

HRMS (DART): calc'd for $C_{26}H_{40}B_2NO_5$ $[M+NH_4]^+$: 468.3087; found 468.3096.

IR (neat): 2982, 2935, 1693, 1604, 1579, 1515, 1469, 1380, 1362, 1326, 1308, 1273, 1244, 1223, 1145, 1031 cm^{-1}.

R_f: 0.2 (10% EtOAc in hexanes, stains blue/black with vanillin)



1l

***N*-(4-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)pivalamide (1l):** Prepared using *N*-(4-bromophenyl)pivalamide (0.51 g, 2.0 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–

25% EtOAc in hexanes) to afford the desired product as an off-white solid (0.30 g, 0.68 mmol, 34%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.38–7.33 (m, 2H), 7.23–7.19 (m, 2H), 2.25 (s, 1H), 1.29 (s, 9H), 1.22 (s, 12H), 1.20 (s, 12H) ppm.

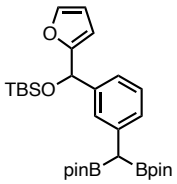
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 176.2, 135.6, 134.5, 129.5, 119.9, 83.4, 39.5, 27.7, 24.7, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.5 ppm.

HRMS (DART): calc'd for $C_{24}H_{40}B_2NO_5$ $[M+H]^+$: 444.3087; found 444.3095.

IR (neat): 3350, 2983, 2939, 2874, 1672, 1604, 1520, 1484, 1473, 1321, 1303, 1270, 1140, 970, 854 cm^{-1}.

R_f: 0.35 (30% EtOAc in hexanes, $KMnO_4$)



1m

((3-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)(furan-2-yl)methoxy)(*tert*-butyl)dimethylsilane (1m): Prepared using ((3-bromophenyl)(furan-2-yl)methoxy)(tert-butyl)dimethylsilane (0.71 g, 1.9 mmol, 1.0 equiv) following General Procedure A. The crude material was purified by flash column chromatography (gradient of 0–5% EtOAc in hexanes) to afford the desired product as an colourless oil (0.80 g, 1.44 mmol, 72%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.32–7.28 (m, 2H), 7.19–7.15 (m, 2H), 7.14–7.09 (m, 1H), 6.24 (dd, J = 3.2, 1.8 Hz, 1H), 6.04 (dt, J = 3.2, 0.9 Hz, 1H), 5.74 (s, 1H), 2.29 (s, 1H), 1.21 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 0.91 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm.

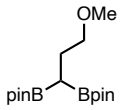
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 157.7, 141.8, 141.4, 139.4, 128.4, 127.9, 127.8, 122.5, 110.1, 106.9, 83.4, 71.0, 26.1, 24.8, 24.7(2), 24.7(1), 18.6, -4.7, -4.9 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.0 ppm.

HRMS (ESI+): calc'd for $C_{30}H_{47}B_2O_6Si$ $[M+H]^+$: 554.3357; found 554.3354.

IR (neat): 2983, 2936, 2863, 1672, 1604, 1517, 1477, 1325, 1263, 1140, 1068, 850, 782 cm^{-1}.

R_f: 0.13 (3% EtOAc in hexanes, stains blue with vanillin)



1o

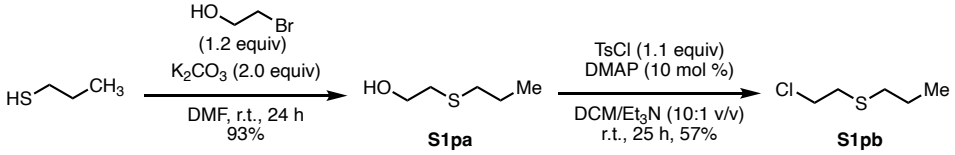
2,2'-(3-methoxypropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1o): Prepared using 2-bromoethyl methyl ether (0.12 mL, 1.3 mmol, 1.1 equiv) and **1n** (0.31 g, 1.2 mmol, 1.0 equiv) following General Procedure B to afford a colorless oil (0.34 g, 1.0 mmol, 89%). The crude material was sufficiently pure to be used without further purification. The spectral data are consistent with literature precedence.[9]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.33 (t, *J* = 6.6 Hz, 2H), 3.29 (s, 3H), 1.81 (dt, *J* = 7.8, 6.6 Hz, 2H), 1.22 (s, 12H), 1.22 (s, 12H), 0.72 (t, *J* = 7.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.0, 74.6, 58.4, 25.6, 24.8, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.7 ppm.

R_f: 0.2 (10% EtOAc in hexanes, stains blue/black with vanillin).



2-(propylthio)ethan-1-ol (S1pa): To a flame dried round bottom flask equipped with a stir bar was added K_2CO_3 (5.5 g, 40 mmol, 2.0 equiv). The flask was sealed with a size 24 septum and then evacuated and backfilled with nitrogen (x3). DMF (80 mL) was added, followed by 2-bromoethanol (1.7 mL, 24 mmol, 1.2 equiv) and 1-propanethiol (1.8 mL, 20 mmol, 1.0 equiv). The reaction was left to stir for 24 h at 23 °C then diluted with EtOAc, filtered, and concentrated under reduced pressure. The crude residue was then diluted with EtOAc, washed with brine (x5), dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the desired product as a light yellow oil (2.2 g, 19 mmol, 93%). The crude product was sufficiently pure to be used directly in the next step. The spectral data are consistent with literature precedence.[10]

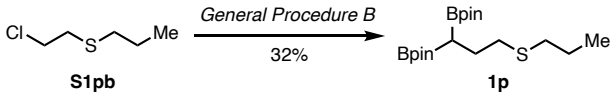
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.71 (t, *J* = 6.0 Hz, 2H), 2.75–2.69 (m, 2H), 2.53–2.47 (m, 2H), 2.20 (s, 1H), 1.61 (sextet, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 60.3, 35.4, 33.8, 23.2, 13.6 ppm.

R_f: 0.3 (30% EtOAc in hexanes, stains yellow with $KMnO_4$).

(2-chloroethyl)(propyl)sulfane (S1pb): To a flame dried round bottom flask equipped with a stir bar was added DMAP (61 mg, 0.50 mmol, 0.10 equiv). The flask was sealed with a size 24

septum and then evacuated and backfilled with nitrogen (x3). A solution of 2-(propylthio)ethan-1-ol (0.60 g, 5.0 mmol, 1.0 equiv) in DCM (10 mL) was then added, followed by Et_3N (2 mL). A solution of TsCl (1.1 g, 5.5 mmol, 1.1 equiv) in DCM (10 mL) was added, and the reaction was stirred for 25 h at 23 °C. The reaction mixture was then filtered over a silica gel plug and concentrated under reduced pressure to afford the desired product as a yellow oil (0.40 g, 2.8 mmol, 57%). The crude product was sufficiently pure to be used directly in the next step.



S1pb **1p**

2,2'-(3-(propylthio)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1p): Prepared using **S1pb** (0.10 g, 0.74 mmol, 1.1 equiv) and **1n** (0.18 g, 0.67 mmol, 1.0 equiv) following General Procedure B. The crude material was purified by flash column chromatography (gradient of 0–15% EtOAc in hexanes) to afford the desired product as a light yellow oil (80 mg, 0.22 mmol, 32%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.49–2.41 (m, 4H), 1.79 (app q, J = 7.7 Hz, 2H), 1.56 (app sext, J = 7.4 Hz, 2H), 1.20–1.19 (m, 24H), 0.94 (t, J = 7.3 Hz, 3H), 0.80–0.75 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.2, 34.2, 33.9, 26.3, 25.0, 24.7, 23.1, 13.7 ppm.

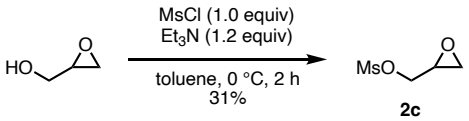
^{11}B NMR (128 MHz, $CDCl_3$, 298K): δ 33.8 ppm.

HRMS (DART): calc'd for $C_{18}H_{37}B_2O_4S$ $[M+H]^+$: 371.2593; found 371.2594

IR (neat): 2983, 2934, 2870, 1474, 1374, 1318, 1275, 1218, 1143, 1115, 973, 856 cm^{-1}.

R_f: 0.4 (10% EtOAc in hexanes, yellow in $KMnO_4$).

Synthesis of epihalohydrin/epoxy alcohol derivatives



2c

oxiran-2-ylmethyl methanesulfonate (2c): This procedure was adapted from Tietze and coworkers.[11] To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 24 septum was added toluene (20 mL) followed by glycidol (0.67 mL, 10 mmol, 1.0 equiv) and triethylamine (1.7 mL, 12 mmol, 1.2 equiv). The solution was cooled to 0 °C, and methanesulfonyl chloride (0.77 mL, 10 mmol, 1.0. equiv) was then added over a period of 10 min. The mixture was stirred at 0 °C for 2 h and then filtered over celite and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (50% EtOAc in hexanes) to afford the desired product as a colourless oil (0.48 g, 3.1 mmol, 31%).

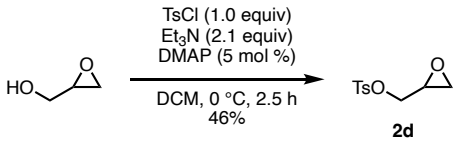
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.53 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.11 (dd, *J* = 12.0, 6.4 Hz, 1H), 3.30 (ddt, *J* = 6.7, 4.1, 2.7 Hz, 1H), 3.09 (s, 3H), 2.91 (dd, *J* = 4.7, 4.1 Hz, 1H), 2.72 (dd, *J* = 4.7, 2.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 70.1, 49.2, 44.8, 38.0 ppm.

HRMS (DART): calc'd for $C_4H_9O_4S$ $[M+H]^+$: 153.0216; found 153.0215.

IR (neat): 3026, 2945, 2860, 1737, 1460, 1424, 1349, 1339, 1261, 1175, 980, 955, 920, 838, 824 cm^{-1}.

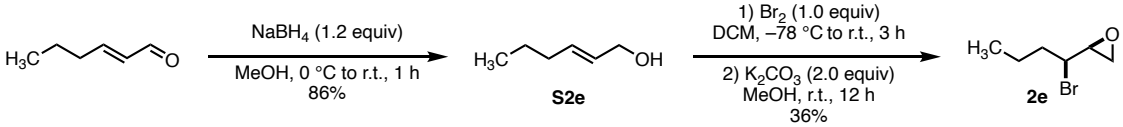
R_f: 0.3 (50% EtOAc in hexanes)



oxiran-2-ylmethyl 4-methylbenzenesulfonate (2d): This procedure was adapted from Gaich and coworkers.[12] To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 24 septum were added glycidol (0.70 mL, 11 mmol, 1.1 equiv), DMAP (61 mg, 0.50 mmol, 5.0 mol %), and triethylamine (2.9 mL, 21 mmol, 2.1 equiv). DCM (10 mL) was added, and the solution was cooled to 0 °C. Once cooled, 4-toluenesulfonyl chloride (1.9 g, 10 mmol, 1.0 equiv) in DCM (10 mL) was added over a period of approx. 5 min. The mixture was stirred for 2.5 h and then quenched with sat. aq. $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with DCM (x3). The organic fractions were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 20–40% EtOAc in hexanes) to afford the desired product as a colourless oil (1.0 g, 4.6 mmol, 46%). The spectral data are consistent with literature precedence.[13]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.84–7.77 (m, 2H), 7.38–7.33 (m, 2H), 4.25 (dd, *J* = 11.4, 3.5 Hz, 1H), 3.96 (dd, *J* = 11.5, 6.1 Hz, 1H), 3.19 (dddd, *J* = 6.0, 4.1, 3.5, 2.6 Hz, 1H), 2.81 (dd, *J* = 4.8, 4.0 Hz, 1H), 2.59 (dd, *J* = 4.8, 2.5 Hz, 1H), 2.45 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 145.3, 132.9, 130.1, 128.1, 70.5, 49.0, 44.8, 21.8 ppm.



(*E*)-hex-2-en-1-ol (S2e): To a round bottom flask equipped with a stir bar was added *trans-2*-hexenal (1.2 mL, 10 mmol, 1.0 equiv) followed by MeOH (20 mL). The solution was cooled to 0 °C and $NaBH_4$ (0.45 g, 12 mmol, 1.2 equiv) was added portion wise over a period of 10 minutes. Once the addition of $NaBH_4$ was complete, the flask was removed from the ice bath, allowed to warm to room temperature, and stirred for an additional 1 h. The reaction was quenched upon the

addition of 5 mL of acetone and concentrated under reduced pressure. NH_4Cl was added and the crude residue was extracted with Et_2O (x3). The organic fractions were combined, washed with brine (x1), dried over $MgSO_4$, and concentrated under reduced pressure to afford the desired product as a colorless oil (0.86 g, 0.86 mmol, 86%). The product was sufficiently pure to be used in the next step without further purification. The spectral data are consistent with literature precedence.[14]

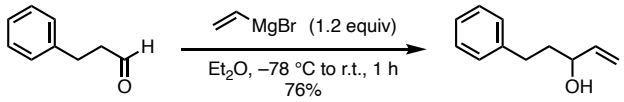
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.74–5.59 (m, 2H), 4.11–4.06 (m, 2H), 2.06–1.99 (m, 2H), 1.46–1.35 (m, 3H, overlapping with OH proton), 0.90 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 133.5, 129.2, 64.0, 34.4, 22.4, 13.8 ppm.

2-(1-bromobutyl)oxirane (2e): To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 24 septum was added (*E*)-hex-2-en-1-ol (**S2e**, 0.86 g, 0.86 mmol, 1.0 equiv) followed by DCM (20 mL). The solution was cooled to –78 ºC and Br_2 (0.44 mL, 8.6 mmol, 1.0 equiv) was added dropwise over a period of 10 minutes. The mixture was left to stir at –78 ºC for 1 h, and then warmed to r.t. and stirred for an additional 2 h. The reaction was then quenched with $Na_2S_2O_3$ (aq, 10% w/w) and $NaHCO_3$ (sat. aq) and extracted with DCM (x3). The organic fractions were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was then redissolved in MeOH (20 mL) and to it was added K_2CO_3 (2.4 g, 17 mmol, 2.0 equiv). The reaction was stirred at r.t. for 12 h, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 5–10% EtOAc in hexanes) to afford the desired product as a colorless oil (0.56 g, 3.1 mmol, 36%). The spectral data are consistent with literature precedence.[15]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.72–3.65 (m, 1H), 3.21 (ddd, *J* = 7.6, 3.9, 2.5 Hz, 1H), 2.97 (dd, *J* = 4.8, 3.9 Hz, 1H), 2.74 (dd, *J* = 4.8, 2.5 Hz, 1H), 1.90–1.83 (m, 2H), 1.67–1.55 (m, 1H), 1.52–1.38 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 55.8, 55.8, 49.0, 37.1, 20.8, 13.6 ppm.



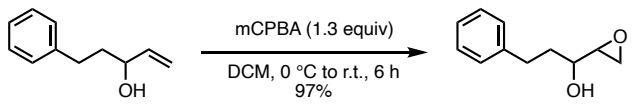
S2fa

5-phenylpent-1-en-3-ol (S2fa): To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 24 septum was added vinylmagnesium bromide (12 mL of a 1.0 M solution in THF, 12 mmol, 1.2 equiv). The flask was cooled to –78 °C and to it was added hydrocinnamaldehyde (1.3 mL, 10 mmol, 1.0 equiv) as a solution in Et_2O (24 mL). The reaction was stirred at –78 °C for 1 h, after which it was warmed to room temperature and NH_4Cl (sat. aq.) was added. The mixture was stirred for 15 min and then HCl (1.0 M aq.) was added. The layers were separated and the aqueous layer was extracted with Et_2O (x3), washed with brine (x1), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc in hexanes) to afford the desired product as a colorless oil (1.2 g, 7.6 mmol, 76%). The spectral data are consistent with literature precedence.[16]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32–7.26 (m, 2H), 7.23–7.16 (m, 3H), 5.91 (ddd, *J* = 17.3, 10.4, 6.1 Hz, 1H), 5.25 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.14 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.17–4.11 (m, 1H), 2.81–2.64 (m, 2H), 1.91–1.82 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 142.0, 141.2, 128.6, 128.6, 126.0, 115.1, 72.6, 38.7, 31.8 ppm.

R_f: 0.3 (20% EtOAc in hexanes, $KMnO_4$).



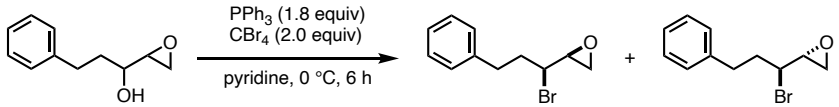
S2fa **S2fb**

1-(oxiran-2-yl)-3-phenylpropan-1-ol (S2fb): To a round bottom flask equipped with a stir bar and size 24 septum was added **S2fa** (0.49 g, 3.0 mmol, 1.0 equiv) and CH_2Cl_2 (20 mL). The flask was cooled to 0 °C and mCPBA (0.96 g, 3.9 mmol, 1.3 equiv) was added in 3 portions. The reaction was stirred for 6 h and was allowed to warm to room temperature as the ice bath melted (approx. 1 h), after which $NaHCO_3$ (sat. aq.) was added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (x3). The organic fractions were combined, washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc in hexanes) to afford the desired product as a colorless oil (0.52 g, 2.9 mmol, 97%) as an inseparable mixture of diastereomers (1.6:1 major/minor)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32–7.27 (m, 5.1H), 7.24–7.17 (m, 7.8 H), 3.87 (dt, *J* = 8.5, 3.6 Hz, 1H), 3.48 (dt, *J* = 9.0, 4.9 Hz, 1H), 3.03–2.98 (m, 2.5H), 2.92–2.69 (m, 10.3H), 2.00–1.78 (m, 6.3H) ppm.

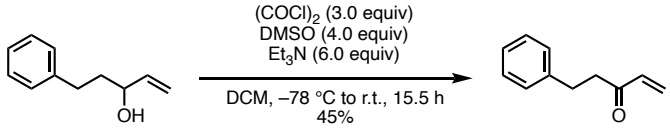
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 141.7, 141.5, 128.5, 128.5, 128.4, 128.4, 126.0, 126.0, 70.7, 67.7, 55.3, 54.4, 45.1, 43.4, 36.0, 35.0, 31.6, 31.5 ppm.

R_f: 0.14 (20% EtOAc in hexanes, stains black with vanillin)



S2fb **2f** **2g**

Syn-2-(1-bromo-3-phenylpropyl)oxirane (**2f**) and *anti*-2-(1-bromo-3-phenylpropyl)oxirane (**2g**): prepared following the same procedure used for **2h** and **2h-anti**. The spectral data were consistent with **2h** and **2h-anti**.



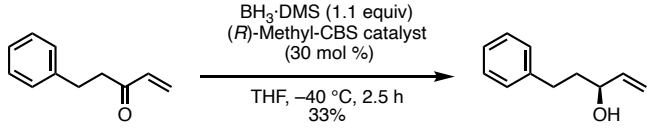
S2fa **S2ha**

5-phenylpent-1-en-3-one (S2ha): To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 24 septum was added oxalyl chloride (2.6 mL, 30 mmol, 3.0 equiv) and CH_2Cl_2 (50 mL). The solution was cooled to –78 °C and DMSO (2.9 mL, 40 mmol, 4.0 equiv) was added and stirred for 15 min. 5-phenylpent-1-en-3-ol (**S2fa**, 1.6 g, 10 mmol, 1.0 equiv) in CH_2Cl_2 (24 mL) was added dropwise and stirred for an additional 30 min, after which Et_3N was added, stirred for 30 min, warmed to room temperature, and stirred for 15.5 h. The reaction was quenched with HCl (1M aq.) and extracted with CH_2Cl_2 (x3). The organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–10% EtOAc in hexanes) to afford the desired product as a light-yellow oil (0.72 g, 4.5 mmol, 45%). The spectral data are consistent with literature precedence.[17]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32–7.25 (m, 2H), 7.24–7.17 (m, 3H), 6.36 (dd, *J* = 17.7, 10.5 Hz, 1H), 6.21 (dd, *J* = 17.8, 1.2 Hz, 1H), 5.83 (dd, *J* = 10.5, 1.2 Hz, 1H), 2.99–2.89 (m, 4H) ppm.

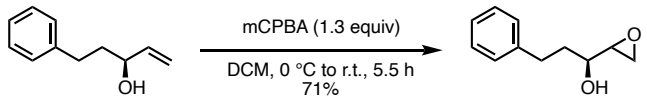
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 190.9, 141.2, 136.7, 128.7, 128.5, 128.4, 126.3, 41.4, 30.0 ppm.

R_f: 0.6 (20% EtOAc in hexanes, $KMnO_4$).



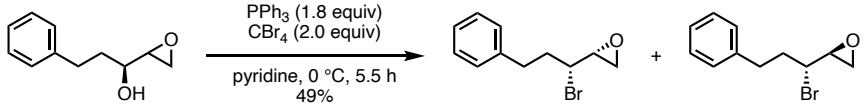
S2ha **S2hb**

(*S*)-5-phenylpent-1-en-3-ol (S2hb): To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 19 septum was added **S2ha** (0.48 g, 3.0 mmol, 1.0 equiv). The flask was cooled to –40 °C and (*R*)-Me-CBS catalyst (0.90 mL of a 1.0 M solution in toluene, 0.90 mmol, 0.30 equiv) was added. $BH_3{\cdot}SMe_3$ (1.7 mL of a 2.0 M solution in THF, 3.3 mmol, 1.1 equiv) was added dropwise and the reaction was stirred at -40 °C for 2.5 h. MeOH (0.10 M in Et_2O) was added at –40 °C and the mixture was warmed to room temperature. $NaHCO_3$ (sat. aq.) was added, the layers were separated, and the aqueous layer was extracted with Et_2O (x3). The organic fractions were combined, washed with brine (x1), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–25% EtOAc in hexanes) to afford the desired product as a colorless oil (0.16 g, 1.0 mmol, 33%). The spectral data were consistent with **S2fa**.



S2hb **S2hc**

(1*S*)-1-(oxiran-2-yl)-3-phenylpropan-1-ol (S2hc): Following the procedure outlined for **S2fb**, **S2hc** was prepared using **S2hb** (0.16 g, 1.0 mmol, 1.0 equiv) and mCPBA (0.32 g, 1.3 mmol, 1.3 equiv) to afford the desired product as a colorless oil (0.13 g, 71%) containing an inseparable mixture of diastereomers. The spectral data were consistent with **S2fb**.



S2hc **2h** **2h-anti**

(*R*)-2-((*R*)-1-bromo-3-phenylpropyl)oxirane (2h) and (*S*)-2-((*R*)-1-bromo-3-phenylpropyl)oxirane (2h-anti): To a flame dried round bottom flask under an atmosphere of N_2 equipped with a stir bar and size 19 septum was added **S2hc** (0.13 g 0.70 mmol, 1.0 equiv) and CBr_4 (0.47 g, 1.4 mmol, 2.0 equiv) in pyridine (10 mL). The mixture was cooled to 0 °C and PPh_3 (0.32 g, 1.2 mmol, 1.8 equiv) in pyridine (10 mL) was added dropwise over 1 h. The reaction was stirred at 0 °C for an additional 5.5 h, after which HCl (1.0 M aq.) was added and the mixture was extracted with EtOAc (x3). The organic fractions were combined, washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc in hexanes) to afford the desired products as colorless oils (**2h-anti**: 35 mg, 21% and **2h**: 47 mg, 28%; 58.9% ee).

2h:

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.32–7.28 (m, 2H), 7.23–7.18 (m, 3H), 3.68–3.63 (m, 1H), 3.24 (ddd, *J* = 7.4, 3.9, 2.5 Hz, 1H), 2.96–2.90 (m, 2H), 2.77 (dt, *J* = 13.8, 7.9 Hz, 1H), 2.69 (dd, *J* = 4.8, 2.48 Hz, 1H), 2.24–2.13 (m, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 140.3, 128.8, 128.6, 126.5, 55.7, 55.0, 48.7, 36.3, 33.4 ppm.

R_f: 0.7 (30% EtOAc in hexanes, $KMnO_4$).

HRMS (DART): calc'd for $C_{11}H_{17}NOBr$ $[M+NH_4]^+$: 258.0488; found 258.0482.

IR (neat): 3068, 3035, 3002, 2926, 2861, 1609, 1501, 1461, 1413, 1257, 1214, 931, 866, 811, 753, 699 cm^{-1}.

HPLC: Daicel Chiralpak column IA, hexane/IPA: 99.7:0.3, flow rate = 1.5 mL/min, wavelength: 188 nm, t_R = 10.0 min (minor), t_R = 11.0 min (major).

2h-anti:

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.22–7.18 (m, 2H), 7.14–7.09 (m, 3H), 3.33 (ddd, *J* = 9.3, 8.4, 4.3 Hz, 1H), 3.10 (ddd, *J* = 8.5, 3.9, 2.5 Hz, 1H), 2.85 (ddd, *J* = 13.5, 9.2, 5.2, 1H), 2.81 (dd, *J* = 4.8, 3.9 Hz, 1H), 2.69 (ddd, *J* = 13.9, 9.1, 7.1 Hz, 1H), 2.52 (dd, *J* = 4.8, 2.5 Hz, 1H), 2.28 (dddd, *J* = 14.5, 9.1, 7.1, 4.3 Hz, 1H), 2.12 (dtd, *J* = 14.4, 9.2, 5.2 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 140.5, 128.7, 128.7, 126.4, 55.3, 54.2, 48.3, 38.2, 33.4 ppm.

R_f: 0.8 (30% EtOAc in hexanes, $KMnO_4$).

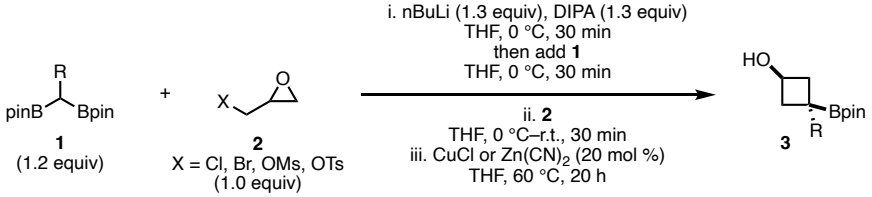
HRMS (DART): calc'd for $C_{11}H_{17}NOBr$ $[M+NH_4]^+$: 258.0488; found 258.0489.

IR (neat): 3064, 3031, 3002, 2926, 2868, 1794, 1765, 1602, 1497, 1457, 1221, 1196, 866, 753, 702, 633 cm^{-1}.

HPLC: Daicel Chiralpak column IG, hexane/IPA: 99:1, flow rate = 1.0 mL/min, wavelength: 190 nm, t_R = 7.6 min (minor), t_R = 8.0 min (major).

D. Synthesis of Borylated Cyclobutanols

General Procedure C: Synthesis of borylated cyclobutanols from epihalohydrins

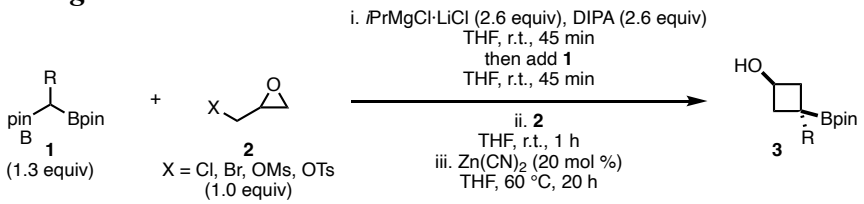


To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) were added THF (0.25 mL) and diisopropylamine (37 μL, 0.26 mmol, 1.3 equiv). The mixture was cooled to 0 °C and freshly titrated nBuLi (0.10 mL of a 2.6 M solution in hexanes, 0.26 mmol, 1.3 equiv) was added dropwise. The solution was stirred at 0 °C for 30 min. 1,1-Diborylalkane (**1**, 0.24 mmol, 1.2 equiv) was measured out into a 1-dram vial, which was sealed with a size 19 septum and electrical tape, evacuated and backfilled with N_2 (x3). THF (0.40 mL) was then added to the vial to dissolve the **1**. The solution was then added to the nBuLi/DIPA mixture (0.20 mL of THF used as rinse) and the reaction mixture was stirred at 0 °C for 30 min. Epihalohydrin or epoxy alcohol derivative (**2**, 0.20 mmol, 1.0 equiv) was added as a solution in THF (0.30 mL + 0.20 mL rinse). The reaction mixture was next removed from the ice bath and stirred for 30 min as the reaction vessel warmed to room temp. During this time, a separate 8-mL culture tube equipped with a stir bar was flame dried under vacuum and to it was added CuCl (4.0 mg, 0.040 mmol, 20 mol %) or $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 20 mol %). The tube was sealed with a size 19 septum and electrical tape, and evacuated/backfilled with N_2 (x3). Once the 30 min stir period was complete, the reaction mixture was transferred to the culture tube containing CuCl (or $Zn(CN)_2$), using THF (0.50 mL) as a rinse. The top of the septum was sealed with electrical tape (to prevent evaporation of solvent) and the mixture was stirred at 60 °C for 20 h. Once complete, the mixture was cooled to

room temp and quenched with sat. aq. NH_4Cl (stirred for ca. 30 min) and diluted with EtOAc. The organic and aqueous layers were separated, and the aqueous layer was extracted with EtOAc (x3). The organic fractions were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford the desired cyclobutanol.

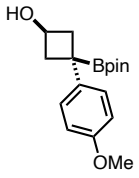
Note: As a precaution, all quenches involving NH_4Cl and $Zn(CN)_2$ were done a well ventilated fumehood with a stir period of no less than 10 min. Alternatively, sat. aq. $NaHCO_3$ can be used as a quench, though it was found that NH_4Cl was more efficient at hydrolyzing the pinB–OR bond that forms after boryl migration, which facilitated spectral analysis/d.r. calculations on crude materials. However, typically hydrolysis of this bond occurs on silica, so purification via column chromatography using silica gel renders both $NaHCO_3$ and NH_4Cl workup procedures equally efficient.

General Procedure D: Synthesis of borylated cyclobutanols from epihalohydrins using iPrMgCl·LiCl



To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) were added THF (0.13 mL) and diisopropylamine (37 μL, 0.26 mmol, 1.3 equiv). Freshly titrated *i*PrMgCl·LiCl (0.29 mL of a 0.90 M solution in THF, 0.26 mmol, 1.3 equiv) was added dropwise. The solution was stirred at r.t. for 45 min. 1,1-Diborylalkane (**1**, 0.13 mmol, 1.3 equiv) was measured out into a 1-dram vial, which was sealed with a size 19 septum and electrical tape, evacuated and backfilled with N_2 (x3). THF (0.30 mL) was then added to the vial to dissolve the **1**. The solution was then added to the *i*PrMgCl·LiCl/DIPA mixture (0.20 mL of THF used as rinse) and the reaction mixture was stirred at r.t. for 45 min. Epihalohydrin or epoxy alcohol derivative (**2**, 0.10 mmol, 1.0 equiv) was added as a solution in THF (0.20 mL + 0.20 mL rinse) and stirred for 1 h. During this time, a separate 8-mL culture tube equipped with a stir bar was flame dried under vacuum and to it was added $Zn(CN)_2$ (2.4 mg, 0.020 mmol, 20 mol %). The tube was sealed with a size 19 septum and electrical tape, and evacuated/backfilled with N_2 (x3). Once the 1 h stir period was complete, the reaction mixture was transferred to the culture tube containing $Zn(CN)_2$ using THF (0.50 mL) as a rinse. The top of the septum was sealed with electrical tape (to prevent evaporation of solvent) and the mixture was stirred at 60 °C for 20 h. Once complete, the mixture was cooled to room temp and quenched with sat. aq. NH_4Cl (stirred for ca. 30 min) and diluted with EtOAc. The organic and aqueous layers were separated, and the aqueous layer was extracted with EtOAc (x3). The organic fractions were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford the desired cyclobutanol.

Note: As a precaution, all quenches involving NH_4Cl and $Zn(CN)_2$ were done a well ventilated fumehood with a stir period of no less than 10 min.



3a

3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3a): Prepared using **1a** (90 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 0–30% EtOAc in hexanes) to afford the desired product as a white solid (44 mg, 72%, 6:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.11–7.06 (m, 2H), 6.85–6.81 (m, 2H), 4.31 (tt, J = 6.8, 4.5 Hz, 1H), 3.78 (s, 3H), 2.65–2.58 (m, 2H), 2.46–2.39 (m, 2H), 1.19 (s, 12H) ppm.

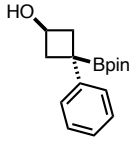
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 157.1, 138.9, 127.2, 113.7, 83.9, 66.3, 55.3, 41.8, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.7 ppm.

HRMS (DART): calc'd for $C_{17}H_{26}BO_4$ $[M+H]^+$: 305.1919; found 305.1926.

IR (neat): 3384, 2982, 2939, 2839, 1611, 1511, 1497, 1437, 1351, 1316, 1244, 1170, 1148, 1113 cm^{-1}.

R_f: 0.3 (30% EtOAc in hexanes, stains blue/black with vanillin).



3b

Major Diastereomer: 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3b): Prepared using **1b** (83 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 0–30% EtOAc in hexanes) to afford the desired product as a white solid (47 mg, 85%, 5:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.31–7.27 (m, 2H), 7.18–7.09 (m, 3H), 4.35–4.28 (m, 1H), 2.71–2.64 (m, 2H), 2.50–2.44 (m, 2H), 1.20 (s, 12H) ppm.

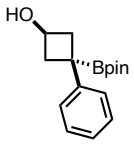
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 147.1, 128.2, 126.3, 124.9, 84.0, 66.5, 41.8, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.6 ppm.

HRMS (DART): calc'd for $C_{16}H_{27}BNO_3$ $[M+NH_4]^+$: 292.2079; found 292.2084.

IR (neat): 3280, 2982, 2928, 2864, 1604, 1497, 1440, 1355, 1323, 1241, 1148, 1123 cm^{-1}.

R_f: 0.28 (30% EtOAc in hexanes, stains blue/black with vanillin).



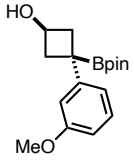
3b-*minor*

Minor Diastereomer (3b-*minor*):
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.29–7.23 (m, 3H), 7.14–7.08 (m, 2H), 4.31 (p, *J* = 7.6 Hz, 1H), 3.01–2.94 (m, 2H), 2.15–2.07 (m, 2H), 1.17 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 148.0, 128.1, 125.7, 124.8, 83.7, 64.1, 43.3, 24.4 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.8 ppm.

R_f: 0.30 (30% EtOAc in hexanes, stains blue/black with vanillin).



3c

3-(3-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3c):
Prepared using **1c** (90 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 0–40% EtOAc in hexanes) to afford the desired product as a white solid (56 mg, 91%, 4:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.21–7.16 (m, 1H), 6.78–6.74 (m, 1H), 6.72–6.70 (m, 1H), 6.69–6.63 (m, 1H), 4.31 (tt, *J* = 7.0, 4.4 Hz, 1H), 3.79 (s, 3H), 2.68–2.61 (m, 2H), 2.47–2.41 (m, 2H), 1.20 (s, 12H) ppm.

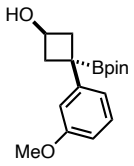
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.6, 148.8, 129.1, 118.9, 112.3, 110.1, 84.0, 66.3, 55.2, 41.7, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.2 ppm.

HRMS (DART): calc'd for $C_{17}H_{26}BO_4$ $[M+H]^+$: 305.1919; found 305.1928.

IR (neat): 3327, 2976, 2938, 1592, 1490, 1460, 1372, 1351, 1314, 1269, 1239, 1213, 1162, 1139, 1114, 854 cm^{-1}.

R_f: 0.28 (30% EtOAc in hexanes, stains blue/black with vanillin).



3c-*minor*

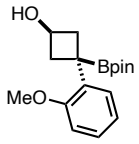
Minor Diastereomer (3c-*minor*):
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.20–7.15 (m, 1H), 6.72–6.64 (m, 3H), 4.28 (tt, *J* = 8.3, 6.9 Hz, 1H), 3.79 (s, 3H), 2.98–2.92 (m, 2H), 2.14–2.07 (m, 2H), 1.18 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.6, 149.8, 129.2, 118.4, 111.8, 110.3, 83.8, 64.1, 55.3, 43.4, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.5 ppm.

IR (neat): 3370, 2978, 2946, 2864, 1600, 1493, 1465, 1358, 1319, 1273, 1141, 1113, 1038 cm^{-1}.

R_f: 0.33 (30% EtOAc in hexanes, stains blue/black with vanillin).



3d

3-(2-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3d):
Prepared using **1d** (90 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in toluene) to afford the desired product as a white solid (38 mg, 63%, 5:1 d.r.).
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.20–7.13 (m, 2H), 6.93 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.27 (tt, *J* = 7.1, 4.1 Hz, 1H), 3.76 (s, 3H), 2.62–2.54 (m, 2H), 2.41–2.34 (m, 2H), 1.24 (s, 12H) ppm.

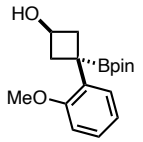
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 157.0, 135.6, 126.5, 125.3, 120.5, 109.8, 83.8, 66.5, 55.0, 40.2, 24.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.0 ppm.

HRMS (DART): calc'd for $C_{17}H_{26}BO_4$ $[M+H]^+$: 305.1919; found 305.1927

IR (neat): 3316, 2985, 2943, 1778, 1738, 1604, 1440, 1365, 1316, 1244, 1152, 1113, 1031, 984, 853.

R_f: 0.42 (40% EtOAc in toluene, stains blue/black with vanillin).



3d-*minor*

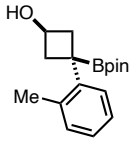
Minor Diastereomer (3d-*minor*):

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.16–7.10 (m, 2H), 6.93 (m, 1H), 6.80–6.76 (m, 1H), 4.50–4.41 (m, 1H), 3.76 (s, 3H), 2.89–2.82 (m, 2H), 2.04–1.97 (m, 2H), 1.20 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 156.9, 136.6, 126.3, 125.9, 120.7, 109.7, 83.3, 64.1, 55.0, 41.9, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.0 ppm.

R_f: 0.42 (40% EtOAc in toluene, stains blue/black with vanillin).



3e

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*o*-tolyl)cyclobutan-1-ol (3e):
Prepared using **1e** (86 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 5–15% EtOAc in toluene) to afford the desired product as a white solid (39 mg, 68%, 5:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.19–7.12 (m, 1H), 7.12–7.03 (m, 3H), 4.26 (tt, J = 6.9, 2.4 Hz, 1H), 2.72–2.65 (m, 2H), 2.53–2.47 (m, 2H), 2.17 (s, 3H), 1.25 (s, 12H) ppm.

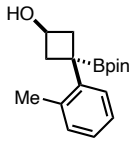
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 145.5, 135.6, 130.5, 125.7, 125.6, 125.3, 84.2, 66.3, 41.3, 24.6, 20.3 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.1 ppm.

HRMS (DART): calc'd for $C_{17}H_{26}BO_3$ $[M+H]^+$: 289.1970; found 289.1978.

IR (neat): 3405, 2985, 2935, 1447, 1355, 1316, 1234, 1158, 1120 cm^{-1}.

R_f: 0.32 (20% EtOAc in toluene, stains blue/black with vanillin).



3e-*minor*

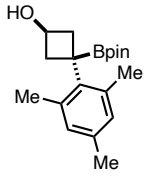
Minor Diastereomer (3e-*minor*):

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.19–7.12 (m, 1H), 7.12–7.03 (m, 3H), 4.38 (tt, *J* = 8.3, 6.9 Hz, 1H), 3.04–2.98 (m, 2H), 2.20 (s, 3H), 2.14–2.08 (m, 2H), 1.19 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 146.2, 135.4, 130.3, 126.2, 125.9, 125.2, 83.7, 63.7, 43.3, 24.6, 20.4 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.1 ppm.

R_f: 0.34 (20% EtOAc in toluene, stains blue/black with vanillin).



3f

3-mesityl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3f): Prepared using **1f** (93 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a white solid (46 mg, 73%, 4:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.76 (s, 2H), 4.20–4.15 (m, 1H), 2.73–2.65 (m, 2H), 2.61–2.55 (m, 2H), 2.24 (s, 3H), 2.15 (s, 6H), 1.27 (s, 12H) ppm.

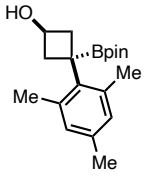
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 143.0, 135.5, 134.0, 129.6, 84.3, 66.7, 43.6, 24.6, 21.6, 20.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.7 ppm.

HRMS (DART): calc'd for $C_{19}H_{30}BO_3$ $[M+H]^+$: 317.2283; found 317.2288.

IR (neat): 3249, 2985, 2939, 1736, 1458, 1355, 1305, 1145, 1109, 860 cm^{-1}.

R_f: 0.4 (30% EtOAc in hexanes, stains blue/black with vanillin).



3f-*minor*

Minor Diastereomer (3f-*minor*):

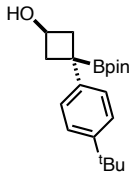
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.74 (s, 2H), 4.23 (tt, *J* = 8.6, 6.9 Hz, 1H), 3.11–3.04 (m, 2H), 2.22 (s, 3H), 2.19 (s, 6H), 2.15–2.07 (m, 2H), 1.19 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 142.9, 135.8, 133.9, 129.8, 83.6, 63.8, 45.6, 24.6, 21.9, 20.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.3 ppm.

IR (neat): 3267, 2975, 2932, 2864, 1732, 1469, 1344, 1316, 1145, 1097 cm^{-1}.

R_f: 0.3 (30% EtOAc in hexanes, stains blue/black with vanillin).



3g

3-(4-(*tert*-butyl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3g): Prepared using **1g** (96 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a white solid (60 mg, 91%, 5.5:1 d.r).

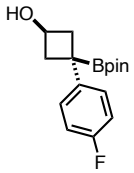
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.30–7.26 (m, 2H), 7.10–7.06 (m, 2H), 4.32 (tt, *J* = 6.8, 4.4 Hz, 1H), 2.70–2.62 (m, 2H), 2.47–2.40 (m, 2H), 1.31 (s, 9H), 1.21 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 147.4, 143.7, 125.9, 125.1, 83.9, 66.5, 41.8, 34.4, 31.6, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.7 ppm.

HRMS (DART): calc'd for $C_{20}H_{32}BO_3$ $[M+H]^+$: 331.2439; found 331.2441.

IR (neat): 3263, 2971, 2932, 2879, 1739, 1508, 1355, 1312, 1145, 1123 cm^{-1}.
R_f: 0.30 (30% EtOAc in hexanes, stains blue/black with vanillin).



3h

3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3h): Prepared using **1h** (87 mg, 0.24 mmol, 1.2 equiv) and epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv) following General Procedure C using $Zn(CN)_2$ (trial 1, 4.7 mg, 0.040 mmol, 0.20 equiv) and $ZnCl_2$ (trial 2, 5.5 mg, 0.040 mmol, 0.20 equiv). In both cases, the crude material was purified by flash column chromatography (gradient of 0–30% EtOAc in hexanes) to afford the desired product as a white solid. Trial 1: 26 mg, 44%, 5:1 d.r. Trial 2: 54 mg, 92%, 5:1 d.r. When epichlorohydrin (16 μL, 0.20 mmol, 1.0 equiv) was used in place of epibromohydrin: 51 mg, 87%, 5:1 d.r. When **2c** (30 mg, 0.20 mmol, 1.0 equiv), LiBr (17 mg, 0.20 mmol, 1.0 equiv) was used in place of epibromohydrin: 29 mg, 50%, 3:1 d.r. When **2d** (46 mg, 0.20 mmol, 1.0 equiv) was used in place of epibromohydrin: 32 mg, 55%, 7:1 d.r.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.12–7.08 (m, 2H), 6.99–6.93 (m, 2H), 4.30 (tt, *J* = 6.8, 4.3 Hz, 1H), 2.64–2.58 (m, 2H), 2.48–2.42 (m, 2H), 1.19 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 160.7 (d, *J* = 242.6 Hz), 142.7 (d, *J* = 3.0 Hz), 127.6 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 21.2 Hz), 84.1, 66.3, 41.9, 24.6 ppm.

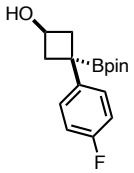
^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.2 ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -119.2 ppm

HRMS (DART): calc'd for $C_{16}H_{23}BO_3F$ $[M+H]^+$: 293.1719; found 293.1729.

IR (neat): 3405, 2982, 2939, 2864, 1604, 1511, 1444, 1358, 1323, 1227, 1145, 1120 cm^{-1}.

R_f: 0.26 (30% EtOAc in hexanes, stains blue/black with vanillin).



3h-*minor*

Minor Diastereomer (**3h-*minor*,** isolated as a 1.0:1.1 **3h**/**3h-*minor*** mixture):
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.07–7.02 (m, 2H), 6.96–6.91 (m, 2H), 4.33–4.26 (m, 1H), 2.98–2.92 (m, 2H), 2.10–2.03 (m, 2H), 1.17 (s, 12H) ppm.

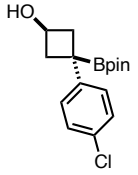
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 160.7 (d, *J* = 242.4 Hz), 143.8 (d, *J* = 3.1 Hz), 127.2 (d, *J* = 7.8 Hz), 115.0 (d, *J* = 21.1 Hz), 83.9, 63.9, 43.4, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.5 ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K): δ -119.1 ppm.

IR (neat): 3252, 2982, 2935, 2871, 1604, 1508, 1444, 1358, 1319, 1219, 1148, 1105 cm^{-1}.

R_f: 0.28 (30% EtOAc in hexanes, stains blue/black with vanillin).



3i

3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3i): Prepared using **1i** (45 mg, 0.12 mmol, 1.2 equiv) and epibromohydrin (8.6 μL, 0.10 mmol, 1.0 equiv) following General Procedure C using $Zn(CN)_2$ (2.3 mg, 0.020 mmol, 0.20 equiv). The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a white solid (28 mg, 92%, 2:1 d.r).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.26–7.22 (m, 2H), 7.10–7.06 (m, 2H), 4.33–4.26 (m, 1H), 2.65–2.58 (m, 2H), 2.52–2.43 (m, 3H), 1.20 (s, 12H) ppm.

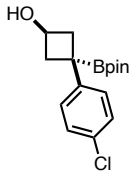
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 145.6, 130.5, 128.2, 127.6, 84.0, 66.2, 41.7, 24.5 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

HRMS (DART): calc'd for $C_{16}H_{23}BO_3Cl$ $[M+H]^+$: 309.1423; found 309.1426.

IR (neat): 3280, 2979, 2932, 2863, 1495, 1354, 1325, 1245, 1144, 1122, 1017, 963, 865, 832 cm^{-1}.

R_f: 0.31 (40% EtOAc in hexanes, stains blue/black with vanillin).



3i-*minor*

Minor Diastereomer (3i-*minor*)

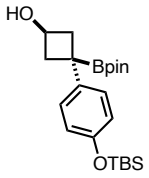
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.24–7.19 (m, 2H), 7.05–7.00 (m, 2H), 4.36–4.26 (m, 1H), 2.99–2.91 (m, 2H), 2.11–2.03 (m, 2H), 1.64 (d, J = 6.5 Hz, 1H, O–H), 1.17 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 146.8, 130.6, 128.4, 127.3, 84.0, 63.9, 43.3, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.8 ppm.

IR (neat): 3262, 2979, 2936, 2860, 1491, 1466, 1354, 1318, 1238, 1147, 1108, 1017, 984, 970, 850, 832 cm^{-1}.

R_f: 0.39 (40% EtOAc in hexanes, stains blue/black with vanillin).



3j

3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3j): Prepared using **1j** (0.11 g, 0.24 mmol, 1.2 equiv), epibromohydrin (17 µL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a colorless residue that solidifies on standing (60 mg, 74%, 6:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.03–6.99 (m, 2H), 6.77–6.72 (m, 2H), 4.31 (tt, *J* = 6.7, 4.5 Hz, 1H), 2.64–2.57 (m, 2H), 2.44–2.38 (m, 2H), 1.18 (s, 12H), 0.97 (s, 9H), 0.18 (s, 6H) ppm.

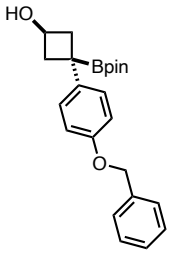
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 152.9, 139.4, 127.1, 119.7, 83.8, 66.3, 41.7, 25.8, 24.6, 18.3, -4.3 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

HRMS (DART): calc'd for $C_{22}H_{36}BO_4Si$ $[M-H]^-$: 403.2470; found 403.2478.

IR (neat): 3341, 2985, 2964, 2939, 2864, 1604, 1511, 1469, 1372, 1333, 1173, 1148, 915, 851 cm^{-1}.

R_f: 0.31 (30% EtOAc in hexanes, stains blue/green with vanillin)



3k

3-(4-(benzyloxy)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3k): Prepared using **1k** (0.11 g, 0.24 mmol, 1.2 equiv), epibromohydrin (17 µL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The

crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a white solid (39 mg, 51%, 4.2:1 d.r).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.46–7.41 (m, 2H), 7.40–7.36 (m, 2H), 7.34–7.30 (m, 1H), 7.11–7.07 (m, 2H), 6.93–6.89 (m, 2H), 5.03 (s, 2H), 4.31 (tt, *J* = 6.7, 4.4 Hz, 1H), 2.65–2.59 (m, 2H), 2.46–2.41 (m, 2H), 1.20 (s, 12H) ppm.

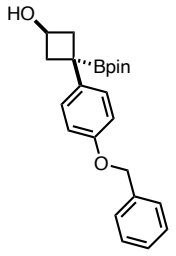
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 156.4, 139.3, 137.4, 128.7, 128.0, 127.7, 127.3, 114.6, 83.9, 70.2, 66.3, 41.8, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.5 ppm.

HRMS (DART): calc'd for $C_{23}H_{33}BNO_4$ $[M+NH_4]^+$: 398.2497; found 398.2497.

IR (neat): 3391, 2989, 2935, 2871, 1742, 1679, 1607, 1508, 1440, 1365, 1326, 1216, 1145, 1016 cm^{-1}.

R_f: 0.2 (30% EtOAc in hexanes, stains blue/black with vanillin)



3k-*minor*

Minor Diastereomer (3k-*minor*):

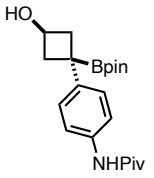
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.45–7.41 (m, 2H), 7.40–7.35 (m, 2H), 7.34–7.29 (m, 1H), 7.05–7.00 (m, 2H), 6.91–6.87 (m, 2H), 5.03 (s, 2H), 4.28 (tt, *J* = 8.3, 6.8 Hz, 1H), 2.94 (ddt, *J* = 10.6, 6.8, 2.3 Hz, 2H), 2.06 (td, *J* = 8.3, 2.8 Hz, 2H), 1.17 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 156.4, 140.4, 137.5, 128.7, 128.0, 127.7, 126.8, 114.7, 83.8, 70.2, 64.1, 43.5, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.4 ppm.

IR (neat): 3235, 2978, 2932, 2857, 1739, 1607, 1515, 1454, 1355, 1316, 1241, 1145, 1105, 1027 cm^{-1}.

R_f: 0.2 (30% EtOAc in hexanes, stains blue/black with vanillin)



3l

3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3l): Prepared using **1l** (58 mg, 0.12 mmol, 1.2 equiv), epibromohydrin (8.6 μL, 0.10 mmol, 1.0 equiv), and $Zn(CN)_2$ (2.3 mg, 0.020 mmol, 0.20 equiv) following General Procedure D. The crude material was purified by flash column chromatography (gradient of 10–35% EtOAc in hexanes) to afford the desired product as a white solid (35 mg, 94%, 2:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.46–7.41 (m, 2H), 7.14–7.09 (m, 2H), 4.34–4.25 (m, 1H), 2.67–2.58 (m, 2H), 2.48–2.41 (m, 2H), 1.30 (s, 9H), 1.19 (s, 12H) ppm.

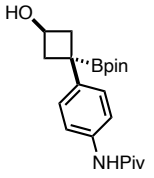
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 176.6, 143.1, 135.0, 126.8, 120.0, 84.0, 66.4, 41.8, 39.7, 27.8, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.1 ppm.

HRMS (DART): calc'd for $C_{21}H_{33}BNO_4$ $[M+H]^+$: 374.2497; found 374.2501.

IR (neat): 3309, 2976, 2936, 2878, 1640, 1604, 1538, 1524, 1361, 1325, 1234, 1151, 1129, 1122, 1021 cm^{-1}.

R_f: 0.31 (40% EtOAc in hexanes, stains blue/green with vanillin)



3l-*minor*

Minor Diastereomer (3l-*minor*):

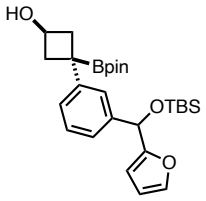
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.44–7.39 (m, 2H), 7.08–7.03 (m, 2H), 4.29 (m, 1H), 2.95 (ddt, J = 10.6, 6.8, 2.3 Hz, 2H), 2.10–2.03 (m, 2H), 1.62 (d, J = 7.0 Hz, 1H, O–H), 1.30 (s, 9H), 1.16 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 176.6, 144.2, 135.1, 126.3, 120.1, 83.8, 64.1, 43.4, 39.7, 27.8, 24.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.3 ppm.

IR (neat): 3309, 2972, 2928, 2871, 1647, 1600, 1535, 1520, 1404, 1354, 1325, 1241, 1147, 1097, 840 cm^{-1}.

R_f: 0.39 (40% EtOAc in hexanes, stains blue/black with vanillin)



3m

3-(3-(((*tert*-butyldimethylsilyl)oxy)(furan-2-yl)methyl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3m): Prepared using **1m** (0.13 g, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a light yellow oil (66 mg, 68%, 8:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.27–7.24 (m, 1H), 7.23–7.20 (m, 1H), 7.18–7.14 (m, 1H), 7.09–7.06 (m, 1H), 6.25 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.01 (dt, *J* = 3.2, 0.8 Hz, 1H), 5.75 (s, 1H), 4.35–4.25 (m, 1H), 2.70–2.61 (m, 2H), 2.54–2.41 (m, 3H), 1.17 (s, 12H), 0.91 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm.

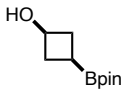
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 157.4, 146.9, 142.0, 141.8, 127.9, 125.2, 124.7, 123.1, 110.1, 106.9, 83.9, 70.9, 66.5, 41.8, 41.7, 26.0, 24.6, -4.8, -4.9 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.3 ppm.

HRMS (DART): calc'd for $C_{27}H_{45}BNO_5Si$ $[M+NH_4]^+$: 502.3155; found 502.3160.

IR (neat): 3410, 2979, 2957, 2936, 2860, 1603, 1470, 1350, 1310, 1256, 1144, 1122, 1075, 1013, 912, 861, 843, 782, 742 cm^{-1}.

R_f: 0.26 (30% EtOAc in hexanes, stains blue/black with vanillin)



3n

***syn*-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3n):** Prepared using **1n** (0.26 g, 0.97 mmol, 1.2 equiv), epibromohydrin (69 μL, 0.80 mmol, 1.0 equiv), and CuCl (16 mg, 0.16 mmol, 0.20 equiv) following General Prodedure C. The crude material was purified (gradient of 0–40% EtOAc in hexanes) to afford the desired product as a white solid. (0.12 g, 0.58 mmol, 72%)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.25 (p, *J* = 7.4 Hz, 1H), 2.44–2.35 (m, 2H), 1.91–1.81 (m, 2H), 1.33–1.24 (m, 1H), 1.25–1.23 (m, 13H) ppm.

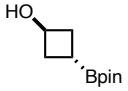
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.4, 67.4, 35.8, 24.9 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

HRMS (DART)**:** calc'd for $C_{10}H_{20}BO_3$ $[M+H]^+$: 199.1500; found 199.1502.

IR (neat): 3487, 2985, 2939, 2864, 1465, 1376, 1340, 1241, 1223, 1148, 1109 cm^{-1}.

R_f: 0.3 (40% EtOAc in hexanes, stains blue/black with vanillin).



3n-*minor*

Minor diastereomer (3n-*minor*):
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.38–4.29 (m, 1H), 2.35–2.28 (m, 2H), 2.10–2.01 (m, 2H), 1.61–1.52 (m, 1H), 1.25 (s, 12H) ppm.

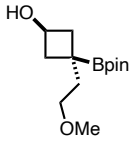
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.3, 67.2 35.3, 24.9 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.4 ppm.

HRMS (DART): calc'd for $C_{10}H_{20}BO_3$ $[M+H]^+$: 199.1500; found 199.1500.

IR (neat): 3270, 3195, 2978, 2939, 1743, 1469, 1376, 1319, 1219, 1145, 1105 cm^{-1}.

R_f: 0.3 (40% EtOAc in hexanes, stains blue/black with vanillin).



3o

3-(2-methoxyethyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3o):
Prepared using **1o** (78 mg, 0.24 mmol, 1.2 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and CuCl (20 mg, 0.20 mmol, 1.0 equiv) General Procedure C. The crude material was purified by flash column chromatography (gradient of 20–40% EtOAc in hexanes) to afford the desired product as a light yellow oil (16 mg, 30%, 2:1 d.r.).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.35 (tt, J = 7.1, 4.9 Hz, 1H), 3.32 (t, J = 6.6 Hz, 2H), 3.28 (s, 3H), 2.19–2.14 (m, 2H), 2.05–2.00 (m, 2H), 1.84–1.81 (m, 2H), 1.25 (s, 12H) ppm.

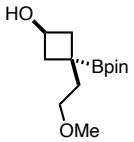
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.6, 70.9, 66.5, 58.7, 40.1, 37.9, 24.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.1 ppm.

HRMS (DART): calc'd for $C_{13}H_{26}BO_4$ $[M+H]^+$: 257.1919; found 257.1921.

IR (neat): 3402, 2978, 2928, 2868, 1743, 1462, 1380, 1312, 1212, 1148, 1116, 952, 860 cm^{-1}.

R_f: 0.2 (30% EtOAc in hexanes, stains blue/black with vanillin)



3o-*minor*

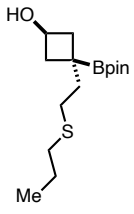
Minor Diastereomer (3o-*minor*):

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.18 (tt, *J* = 8.1, 7.1 Hz, 1H), 3.30 (t, *J* = 6.6 Hz, 2H), 3.27 (s, 3H), 2.56–2.51 (m, 2H), 1.84–1.79 (m, 2H), 1.63–1.58 (m, 2H), 1.23 (s, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 83.3, 70.5, 64.0, 58.6, 42.5, 40.5, 24.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.1 ppm.

R_f: 0.1 (30% EtOAc in hexanes, stains blue/black with vanillin)



3p

3-(2-(propylthio)ethyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3p): Prepared using **1p** (81 mg, 0.22 mmol, 1.1 equiv), epibromohydrin (17 μL, 0.20 mmol, 1.0 equiv), and CuCl (20 mg, 0.20 mmol, 1.0 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–30% EtOAc in hexanes) to afford the desired product as a faint yellow oil (28 mg, 47%, 1.4:1 d.r).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.34 (tt, *J* = 7.1, 4.7 Hz, 1H), 2.56–2.35 (m, 4H), 2.18–2.11 (m, 2H), 2.06–2.00 (m, 2H), 1.84–1.78 (m, 2H), 1.63–1.57 (m, 2H), 1.26 (s, 12H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. Note that this product coeluted with approx. 20% of the minor diastereomer (5.0:1.0 ratio), resulting in slightly higher than expected integrations at 1.80, 1.60 and 0.98 ppm. HSQC experiments were performed to confirm the assigned integration.

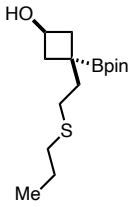
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 83.8, 66.5, 40.2, 38.7, 34.1, 29.4, 24.8, 23.0, 13.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.0 ppm.

HRMS (DART): calc'd for $C_{15}H_{29}BO_3S$ $[M+H]^+$: 301.2003; found 301.2011.

IR (neat): 3373, 2964, 2925, 2864, 1736, 1458, 1422, 1383, 1312, 1237, 1219, 1141, 1113 cm^{-1}.

R_f: 0.3 (30% EtOAc in hexanes, stains blue/black with vanillin).



3p-*minor*

Minor Diastereomer (3p-*minor*):

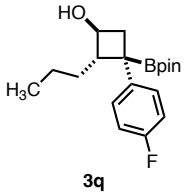
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.26–4.17 (m, 1H), 2.57–2.33 (m, 6H), 1.85–1.77 (m, 2H), 1.65–1.55 (m, 4H), 1.24 (s, 12H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. Note that this product coeluted with approx. 39% of the major diastereomer (1.0:2.6 **3p**/**3p-*minor*),** resulting in slightly higher than expected integrations at 2.57–2.33, 1.85–1.77, 1.65–1.55 and 0.98 ppm. HSQC experiments were performed to confirm the assigned integration.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 83.5, 63.8, 42.5, 41.0, 34.1, 29.0, 24.8, 23.0, 13.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.0 ppm.

IR (neat): 3366, 2971, 2928, 2864, 1746, 1465, 1383, 1312, 1141 cm^{-1}.

R_f: 0.4 (30% EtOAc in hexanes, stains blue/black with vanillin).



3q

3-(4-fluorophenyl)-2-propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3q): Prepared using **1h** (87 mg, 0.24 mmol, 1.2 equiv), **2e** (36 mg, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 10–20% EtOAc in hexanes) to afford the desired product as a light yellow residue (17 mg, 25%)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.16–7.11 (m, 2H), 7.00–6.94 (m, 2H), 4.00–3.96 (m, 1H), 2.82 (ddd, *J* = 12.1, 7.0, 0.9 Hz, 1H), 2.51–2.45 (m, 1H), 2.19 (ddd, *J* = 12.1, 6.2, 1.5 Hz, 1H), 1.33–1.15 (m, 15H), 1.13–1.05 (m, 1H), 0.81 (t, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 161.0 (d, *J* = 243.2 Hz), 137.4 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 7.7 Hz), 114.8 (d, *J* = 20.9 Hz), 83.9, 71.3, 52.2, 36.3, 32.5, 24.7, 24.7, 20.4, 14.4 ppm.

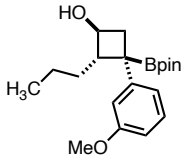
^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.3 ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 298 K): δ -118.8 ppm.

HRMS (DART): calc'd for $C_{19}H_{32}BNO_3F$ $[M+NH_4]^+$: 352.2454; found 352.2465.

IR (neat): 3396, 2963, 2931, 2877, 1602, 1509, 1463, 1445, 1374, 1357, 1318, 1307, 1278, 1232, 1147, 1101, 1019 cm^{-1}.

R_f: 0.3 (30% EtOAc in hexanes, stains blue/black with vanillin).



3r

3-(3-methoxyphenyl)-2-propyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3r): Prepared using **1c** (90 mg, 0.24 mmol, 1.2 equiv), **2e** (36 mg, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 25–30% EtOAc in hexanes) to afford the desired product as a light yellow oil (29 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.19 (t, *J* = 7.9 Hz, 1H), 6.79–6.75 (m, 2H), 6.72–6.68 (m, 1H), 4.03–3.98 (m, 1H), 3.79 (s, 3H), 2.86 (dd, *J* = 12.1, 7.0 Hz, 1H), 2.50 (dt, *J* = 10.8, 5.8 Hz, 1H), 2.15 (ddd, *J* = 12.1, 6.2, 1.4), 1.24 (s, 6H), 1.23 (s, 6H), 1.23–1.10 (m, 4H), 0.81 (t, *J* = 7.3 Hz, 3H) ppm.

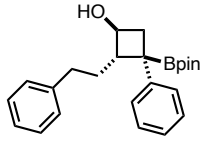
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 159.4, 143.5, 128.8, 120.9, 114.3, 110.5, 83.8, 71.3, 55.2, 52.4, 36.1, 32.4, 24.7, 20.4, 14.4 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.3 ppm.

HRMS (DART): calc'd for $C_{20}H_{35}BNO_4$ $[M+NH_4]^+$: 364.2654; found 364.2661.

IR (neat): 3427, 2960, 2932, 2875, 1604, 1590, 1486, 1437, 1376, 1358, 1319, 1287, 1266, 1230, 1145 cm^{-1}.

R_f: 0.38 (30% EtOAc in hexanes, stains blue/black with vanillin).



3s

2-phenethyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3s): Prepared using **1b** (0.11 g, 0.33 mmol, 1.2 equiv), **2f** (66 mg, 0.27 mmol, 1.0 equiv), and $Zn(CN)_2$ (6.4 mg, 0.055 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 0–35% EtOAc in hexanes) to afford the desired product as a colorless oil (43 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32–7.05 (m, 10H), 4.05 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H), 2.91 (dd, *J* = 12.1, 7.1 Hz, 1H), 2.68–2.51 (m, 3H), 2.20 (ddd, *J* = 12.1, 6.6, 1.2 Hz, 1H), 1.50 (ddt, *J* = 13.7, 9.9, 6.0 Hz, 1H), 1.26 (s, 6H), 1.25–1.14 (m, 7H) ppm.

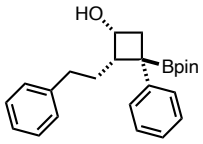
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 142.7, 141.4, 128.5, 128.3, 128.3, 128.1, 125.8, 125.4, 83.8, 71.2, 52.2, 36.0, 33.6, 32.2, 24.7, 24.7 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm

HRMS (DART): calc'd for $C_{24}H_{35}BNO_3$ $[M+NH_4]^+$: 396.2705; found 396.2700

IR (neat): 3372, 3031, 2977, 2937, 2865, 1606, 1501, 1453, 1377, 1359, 1308, 1272, 1218, 1149, 1112, 1014, 858, 746, 706 cm^{-1}.

R_f: 0.3 (30% EtOAc in hexanes, stains blue/black with vanillin)



3t

2-phenethyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3t): Prepared using **1b** (83 mg, 0.24 mmol, 1.2 equiv), **2g** (48 mg, 0.20 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.7 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 0–30% EtOAc in hexanes) to afford the desired product as a colorless oil (34 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.29–7.23 (m, 2H), 7.21–7.15 (m, 2H), 7.15–7.07 (m, 4H), 7.03–6.98 (m, 2H), 4.49–4.40 (m, 1H), 3.00 (ddt, *J* = 10.4, 7.4, 4.0 Hz, 1H), 2.74 (ddd, *J* = 10.3, 7.0, 3.5 Hz, 1H), 2.71–2.63 (m, 1H), 2.48–2.39 (m, 2H), 1.59–1.49 (m, 1H), 1.46–1.37 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H) ppm.

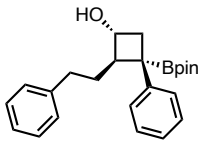
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 143.3, 141.8, 128.5, 128.3, 128.1, 127.8, 125.6, 125.2, 83.8, 65.5, 48.9, 37.6, 35.4, 27.1, 24.6, 24.5 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.1 ppm.

HRMS (DART): calc'd for $C_{24}H_{35}BNO_3$ $[M+NH_4]^+$: 396.2705; found 396.2708.

IR (neat): 3472, 3035, 2981, 2933, 2868, 1606, 1501, 1457, 1374, 1348, 1316, 1283, 1158, 1221, 1145, 1094, 1062, 1036, 1004, 971, 855, 757, 699, 677 cm^{-1}.

R_f: 0.5 (30% EtOAc in hexanes, stains blue/black with vanillin)

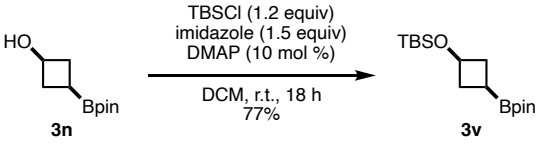


3u

(1*R*,2*R*,3*R*)-2-phenethyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3u): Prepared using **1b** (80 mg, 0.23 mmol, 1.2 equiv), **2h** (47 mg, 0.19 mmol, 1.0 equiv), and $Zn(CN)_2$ (4.6 mg, 0.040 mmol, 0.20 equiv) following General Procedure C. The crude material was purified by flash column chromatography (gradient of 0–35% EtOAc in hexanes) to afford the desired product as a colorless oil (34 mg, 45%, 58.6% ee, >98% es). The spectral data is identical to that of **3s**.

HPLC: Daicel Chiralpak column IA, hexane/IPA: 99.4:0.6, flow rate = 1.0 mL/min, wavelength: 190 nm, t_R = 38.0 min (minor), t_R = 41.7 min (major).

E. Derivatization Studies



3n 3v

***tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)silane (3v)**: To a flame dried round bottom flask equipped with a stir bar were added *tert*-butyldimethylsilyl chloride (TBSCl, 18 mg, 0.12 mmol, 1.2 equiv), imidazole (10 mg, 0.15 mmol, 1.5 equiv) and DMAP (1.2 mg, 0.010 mmol, 0.10 equiv). The flask was sealed with a size 24 septum and then evacuated and backfilled with nitrogen (x3). 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (**3n**, 20 mg, 0.10 mmol, 1.0 equiv) was added as a solution in DCM (1.5 mL) and the reaction was left to stir for 18 h at 23 °C, after which point it was diluted with EtOAc, filtered over a silica gel plug and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–30% EtOAc in hexanes) to afford the desired product as a light yellow oil (24 mg, 0.077 mmol, 77%)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.21 (tt, J = 8.4, 6.8 Hz, 1H), 2.30–2.20 (m, 2H), 1.96–1.86 (m, 2H), 1.23 (s, 12H), 1.20–1.14 (m, 1H), 0.87 (s, 9H), 0.03 (s, 6H) ppm.

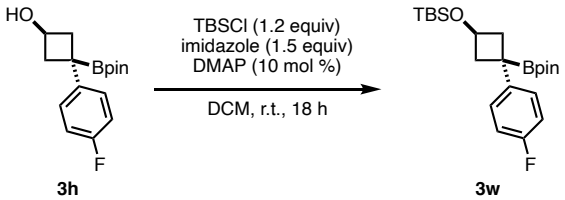
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 83.2, 67.2, 36.0, 26.1, 24.9, 18.3, -4.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.3 ppm.

HRMS (DART): calc'd for $C_{16}H_{34}BO_3Si$ $[M+H]^+$: 313.2365; found 313.2374.

IR (neat): 2964, 2939, 2893, 2857, 1736, 1462, 1426, 1383, 1323, 1244, 1173, 1145, 1120, 1066, 988 cm^{-1}.

R_f: 0.8 (30% EtOAc in hexanes, stains blue/black in vanillin/yellow in $KMnO_4$).



3h **3w**

***tert*-butyl(3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)dimethylsilane (3w)**: To a flame dried round bottom flask equipped with a stir bar was added *tert*-butyldimethylsilyl chloride (TBSCl, 65 mg, 0.43 mmol, 1.2 equiv), imidazole (37 mg, 0.54 mmol, 1.5 equiv) and DMAP (4.4 mg, 0.040 mmol, 0.10 equiv). The flask was sealed with a size 24 septum and backfilled with nitrogen (x3) and DCM (2.0 mL) was added. 3-(4-Fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (**3h**, 0.11 g, 0.36 mmol, 1.0 equiv) was added as a solution in DCM (2.0 mL) and the reaction was stirred for 18 h at 23 °C, at which point it was diluted with EtOAc, filtered over a silica gel plug and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–20% EtOAc in hexanes) to afford the desired product as a white solid (80 mg, 0.20 mmol, 54%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.22–7.15 (m, 2H), 7.00–6.93 (m, 2H), 4.25 (app p, J = 6.7 Hz, 1H), 2.60–2.53 (m, 2H), 2.50–2.42 (m, 2H), 1.16 (s, 12H), 0.88 (s, 9H), 0.02 (s, 6H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 160.7 (d, J = 242.5 Hz), 142.1 (d, J = 3.0 Hz), 128.0 (d, J = 7.7 Hz), 115.0 (d, J = 21.2 Hz), 83.7, 65.8, 42.2, 26.0, 24.6, 18.3, -4.6 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 32.8 ppm.

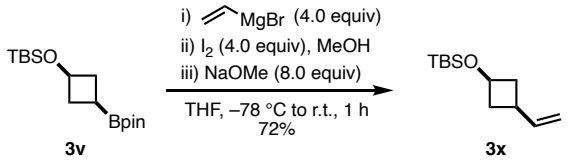
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -119.3 ppm.

HRMS (ESI+): calc'd for $C_{22}H_{36}BFO_3SiNa$ $[M+Na]^+$: 428.2439; found 428.2438.

IR (neat): 2973, 2934, 2899, 2860, 1605, 1509, 1474, 1467, 1396, 1374, 1357, 1318, 1250, 1239, 1222, 1143, 1115, 1083, 1030, 1012, 838, 774 cm^{-1}.

R_f: 0.6 (10% EtOAc in hexanes, stains blue/black in vanillin).

Bpin derivatizations



***tert*-butyldimethyl(3-vinylcyclobutoxy)silane (3x)**: This procedure was adapted from Aggarwal and coworkers.[18] To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) was added *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)silane (**3v**, 94 mg, 0.30 mmol, 1.0 equiv) as a solution in THF (1.5 mL). Vinyl magnesium bromide (2.8 mL of a 0.42 M solution in THF, 1.2 mmol, 4.0 equiv) was then added dropwise at room temperature. The mixture was stirred at this temperature for 30 min, and then it was cooled to –78 °C. A solution of iodine (0.30 g, 1.2 mmol, 4.0 equiv) in MeOH (4.0 mL) was added dropwise over a period of 10 min. The reaction was stirred for an additional 30 min and then NaOMe (0.45 mL of a 30% w/w solution in MeOH, 2.4 mmol, 8.0 equiv) was added. The reaction was warmed to room temperature and stirred for 1 h, diluted with pentane, 10% aq. $Na_2S_2O_3$, and water. The aqueous phase was separated, extracted with pentane (x3) and the combined organic layers were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (pentane) to afford the desired product as a light yellow oil (46 mg, 0.22 mmol, 72%).

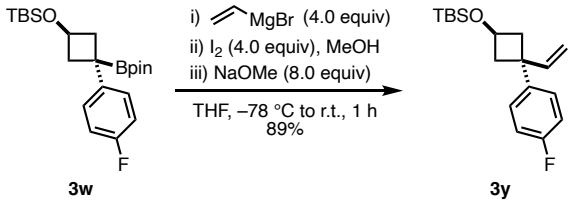
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.86 (ddd, J = 17.0, 10.2, 6.8 Hz, 1H), 4.95 (ddd, J = 17.1, 1.9, 1.3 Hz, 1H), 4.90 (ddd, J = 10.2, 1.8, 1.1 Hz, 1H), 4.11 (tt, J = 8.2, 6.6 Hz, 1H), 2.44–2.37 (m, 2H), 2.35–2.26 (m, 1H), 1.81–1.73 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 142.5, 112.9, 64.0, 40.1, 29.3, 26.0, 18.2, -4.6 ppm.

HRMS (DART): calc'd for $C_{12}H_{25}OSi$ $[M+H]^+$: 213.1669; found 213.1676.

IR (neat): 2960, 2932, 2896, 2857, 1739, 1640, 1476, 1369, 1259, 1234, 1173, 1123 cm^{-1}.

R_f: 0.4 (hexanes, stains yellow in $KMnO_4$).



***tert*-butyl(3-(4-fluorophenyl)-3-vinylcyclobutoxy)dimethylsilane (3y)**: This procedure was adapted from Aggarwal and coworkers.[18] To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) was added *tert*-butyl(3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)dimethylsilane (**3w**, 80 mg, 0.20 mmol, 1.0 equiv) as a solution in THF (2.0 mL). Vinyl magnesium bromide (1.8 mL of a 0.42 M solution in THF, 0.78 mmol, 4.0 equiv) was then added dropwise at room temperature. The mixture was stirred at this temperature for 30 min, at

which point it was cooled to –78 °C. A solution of iodine (0.20 g, 0.78 mmol, 4.0 equiv) in MeOH (3.0 mL) was added dropwise over a period of 10 min. The reaction was stirred for an additional 30 min followed by the addition of NaOMe (0.29 mL of a 30% w/w solution in MeOH, 1.6 mmol, 8.0 equiv). The reaction was warmed to room temperature and stirred for 1 h, diluted with pentane, washed with 10% aq. $Na_2S_2O_3$ and water. The aqueous phase was separated and extracted with pentane (x3) and the combined organic layers were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 0–5% EtOAc in hexanes) to afford the desired product as a colorless oil (53 mg, 0.17 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32–7.25 (m, 2H), 7.08–7.02 (m, 2H), 6.08 (dd, *J* = 17.1, 10.3 Hz, 1H), 4.93 (dd, *J* = 10.3, 1.2 Hz, 1H), 4.68 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.16 (app p, *J* = 7.5 Hz, 1H), 2.86–2.78 (m, 2H), 2.39–2.32 (m, 2H), 0.92 (s, 9H), 0.06 (s, 6H) ppm.

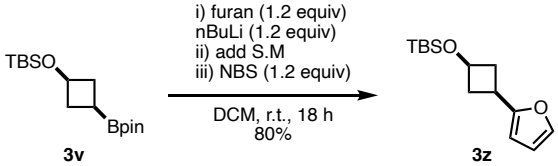
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 161.3 (d, *J* = 244.4 Hz), 147.7, 141.3 (d, *J* = 3.2 Hz), 128.9 (d, *J* = 7.8 Hz), 115.1 (d, *J* = 21.2 Hz), 111.6, 63.1, 45.0, 41.7, 26.0, 18.2, -4.6 ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -117.6 ppm.

HRMS (DART): calc'd for $C_{18}H_{28}OFSi$ $[M+H]^+$: 307.1888; found 307.1898.

IR (neat): 3083, 2955, 2934, 2899, 2863, 1744, 1637, 1609, 1513, 1477, 1466, 1364, 1254, 1236, 1161, 1119, 1108, 1044, 944, 920, 873, 838, 781 cm^{-1}.

R_f: 0.7 (5% EtOAc in hexanes, stains blue/black with vanillin).



***tert*-butyl(3-(furan-2-yl)cyclobutoxy)dimethylsilane (3z)**: This procedure was adapted from Harvey, Leonori, Aggarwal and coworkers.[19] To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) was added furan (15 μL, 0.21 mmol, 1.2 equiv) and THF (0.60 mL). The solution was cooled to –78 °C and nBuLi (87 μL of a 2.36 M solution in hexanes, 0.21 mmol, 1.2 equiv) was added to it. The reaction mixture was warmed to room temperature and stirred for 1 h. The solution was again cooled to –78 °C, and *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)silane (**3v**, 53 mg, 0.17 mmol, 1.0 equiv) was added as a solution in THF (0.9 mL). The reaction mixture was stirred at –78 °C for 1 h followed by the addition of NBS (37 mg, 0.21 mmol, 1.2 equiv) in THF (1.0 mL). The reaction was stirred for 1.5 h and quenched upon the addition of 10% aq. $Na_2S_2O_3$ at –78 °C. The mixture was left to warm to room temperature and diluted with EtOAc. The phases were separated and the aqueous layer was extracted with EtOAc (x3). The combined organic layers were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash

column chromatography (gradient of 5–10% toluene in hexanes) to afford the desired product as a light yellow oil (35 mg, 0.14 mmol, 80%).

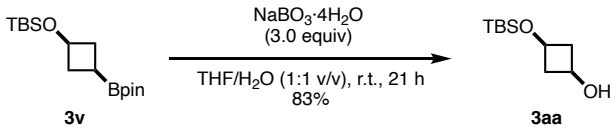
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.30 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.28 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.00 (dd, *J* = 3.1, 1.9 Hz, 1H), 4.19 (tt, *J* = 8.1, 6.7 Hz, 1H), 2.89 (tt, *J* = 10.3, 7.4 Hz, 1H), 2.63–2.54 (m, 2H), 2.19–2.09 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 158.3, 141.1, 110.3, 104.1, 63.6, 40.2, 26.0, 24.2, 18.2, -4.6 ppm.

HRMS (DART): calc'd for $C_{14}H_{25}O_2Si$ $[M+H]^+$: 253.1618; found 253.1634.

IR (neat): 2957, 2932, 2896, 2864, 1739, 1604, 1511, 1472, 1376, 1255, 1241, 1194, 1123 cm^{-1}.

R_f: 0.3 (10% toluene in hexanes, stains blue/black in vanillin).



3-((*tert*-butyldimethylsilyl)oxy)cyclobutan-1-ol (3aa): To a 8-mL culture tube with a stir bar was added *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)silane (**3v**, 94 mg, 0.30 mmol, 1.0 equiv) in THF (1.0 mL). Water (1.0 mL) was added followed by sodium perborate tetrahydrate (0.14 g, 0.90 mmol, 3.0 equiv). The tube was capped with a lid and the reaction was stirred for 21 h at 23 °C. The reaction was diluted with EtOAc and the phases were separated. The aqueous layer was extracted with EtOAc (x3) and the combined organic layers were washed with brine (x1), dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 20–25% EtOAc) to afford the desired product as a light yellow oil (50 mg, 0.25 mmol, 83%).

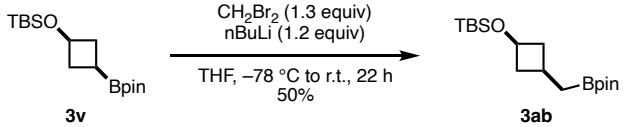
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.87–3.78 (m, 2H), 2.75–2.66 (m, 2H), 1.94–1.84 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 59.6, 58.9, 44.8, 26.0, 18.2, -4.7 ppm.

HRMS (DART): calc'd for $C_{10}H_{23}O_2Si$ $[M+H]^+$: 203.1462; found 203.1475.

IR (neat): 3320, 2960, 2935, 2900, 2854, 1465, 1365, 1259, 1241, 1166, 1056, 881, 838, 774 cm^{-1}.

R_f: 0.6 (40% EtOAc in hexanes, stains blue/black with vanillin).



***tert*-butyldimethyl(3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutoxy)silane (3ab)**: This procedure was adapted from Kazmaier and coworkers.[20] To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) were added *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)silane (**3v**, 80 mg, 0.26 mmol, 1.0 equiv), dibromomethane (22 μL, 0.32 mmol, 1.3 equiv), and THF (1.6 mL). The solution was cooled to –78 °C and nBuLi (0.13 mL of a 2.36 M solution in hexanes, 0.31 mmol, 1.2 equiv) was added dropwise. The reaction mixture was brought to room temperature and stirred for 22 h, at which point sat. aq. NH_4Cl was added followed by Et_2O. The phases were separated, the aqueous layer was extracted with Et_2O (x3), and the combined organic layers were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified using flash column chromatography (gradient of 0–5% EtOAc in hexanes) to afford the desired product as a light yellow oil (41 mg, 0.13 mmol, 50%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 4.00 (tt, J = 8.1, 6.7 Hz, 1H), 2.40 (dddd, J = 9.8, 6.9, 5.6, 2.9 Hz, 2H), 1.85–1.75 (m, 1H), 1.57–1.48 (m, 2H), 1.22 (s, 12H), 0.95–0.92 (m, 2H), 0.87 (s, 9H), 0.02 (s, 6H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 83.0, 64.0, 42.4, 26.1, 24.9, 22.2, 18.2, -4.6 ppm.

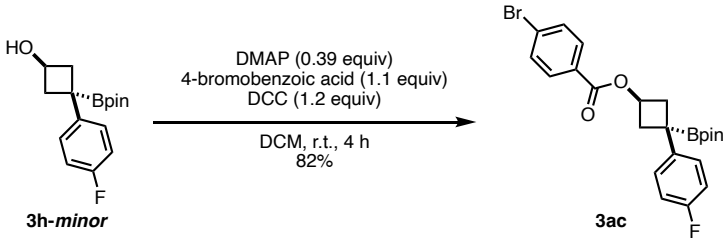
^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

HRMS (DART): calc'd for $C_{17}H_{36}BO_3Si$ $[M+H]^+$: 327.2521; found 327.2524.

IR (neat): 2960, 2935, 2861, 1750, 1469, 1365, 1319, 1259, 1237, 1166, 1148, 1066 cm^{-1}.

R_f: 0.6 (10% EtOAc in hexanes, stains blue/black in vanillin).

OH derivatizations



Syn*-3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutyl 4-bromobenzoate (3ac)**: To a flame dried 8-mL culture tube with a stir bar were added DMAP (1.0 mg, 0.0082 mmol, 0.39 equiv) and 4-bromobenzoic acid (4.7 mg, 0.023 mmol, 1.1 equiv). The tube was capped with a size 19 septum, sealed with electrical tape and then evacuated and backfilled with N_2 (x3). *Syn*-3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (**3h-*minor, 6.2 mg, 0.021 mmol, 1.0 equiv) was added as a solution in DCM (0.5 mL), followed by DCC (5.0 mg, 0.025 mmol, 1.2 equiv) in DCM (0.5 mL). The reaction was stirred for 4 h at room temperature and quenched with sat. aq. $NaHCO_3$. The phases were separated, the aqueous layer was extracted with EtOAc (x3) and the combined organic layers

were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (toluene) to afford the desired product as a white solid (8.3 mg, 0.017 mmol, 82%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.87–7.84 (m, 2H), 7.57–7.53 (m, 2H), 7.09–7.04 (m, 2H), 6.99–6.94 (m, 2H), 5.28 (tt, *J* = 8.2, 7.1 Hz, 1H), 3.14–3.08 (m, 2H), 2.42–2.36 (m, 2H), 1.20 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 165.3, 160.8 (d, *J* = 242.9 Hz), 143.5 (d, *J* = 3.0 Hz), 131.8, 131.2, 129.3, 128.2, 127.1 (d, *J* = 7.8 Hz), 115.1 (d, *J* = 21.2 Hz), 84.1, 66.3, 40.0, 24.6 ppm.

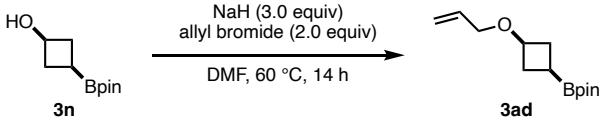
^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.4 ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -118.7 ppm.

HRMS (DART): calc'd for $C_{23}H_{29}BNO_4FBr$ $[M+NH_4]^+$: 492.1352; found 492.1364.

IR (neat): 2978, 2932, 2861, 1714, 1597, 1515, 1355, 1323, 1280, 1237, 1109, 1013 cm^{-1}.

R_f: 0.3 (10% EtOAc in hexanes, stains purple/pink with vanillin).



2-(3-(allyloxy)cyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ad):

Safety note: NaH/DMF reaction mixtures can suffer from thermal decomposition and therefore pose an explosion hazard.[21] Ensuring that the proper temperature is maintained throughout the course of this reaction is extremely important and in all cases an ice and/or dry ice/acetone bath should be prepared in case of rapid decomposition. The use of a blast shield is recommended, as is doing the reaction on small scale.

To a flame dried 8-mL culture tube with a stir bar was added NaH (12 mg of a 60% dispersion on mineral oil, 0.30 mmol, 3.0 equiv). The tube was capped with a size 19 septum, sealed with electrical tape and then evacuated and backfilled with N_2 (x3). 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (**3n**, 20 mg, 0.10 mmol, 1.0 equiv) in DMF (1.0 mL) was added and the reaction mixture was stirred for 10 min at 0 °C, warmed to room temperature, and stirred for an additional 30 min, at which point all bubbling had stopped. Allyl bromide (17 μL, 0.20 mmol, 2.0 equiv) was added, and the reaction was warmed to 60 °C and stirred for 14 h. The reaction mixture was diluted with EtOAc, washed with brine (x5), and the combined aqueous layers were back-extracted with EtOAc (x3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (15% Et_2O in pentane) to afford the desired product as a colorless oil (23 mg, 0.095 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.90 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.28–5.21 (m, 1H), 5.16–5.11 (m, 1H), 3.99 (tt, *J* = 8.3, 6.8 Hz, 1H), 3.87 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.33–2.23 (m, 2H), 1.98–1.88 (m, 2H), 1.32–1.25 (m, 1H), 1.23 (s, 12H) ppm.

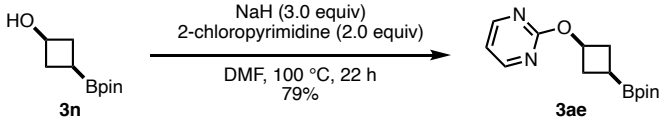
^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 135.2, 116.9, 83.3, 72.6, 68.9, 32.5, 24.9 ppm.

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 33.2 ppm.

HRMS (DART): calc'd for $C_{13}H_{24}BO_3$ $[M+H]^+$: 239.1813; found 239.1820.

IR (neat): 2978, 2939, 2864, 1739, 1465, 1422, 1387, 1323, 1241, 1148, 1120 cm^{-1}.

R_f: 0.6 (40% Et_2O in pentanes, stains blue/black in vanillin).



2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutoxy)pyrimidine (3ae):

<u>Safety note: NaH/DMF reaction mixtures can suffer from thermal decomposition and therefore pose an explosion hazard.[22] Ensuring that the proper temperature is maintained throughout the course of this reaction is extremely important and in all cases an ice and/or dry ice/acetone bath should be prepared in case of rapid decomposition. The use of a blast shield is recommended, as is doing the reaction on small scale.</u>

To a flame dried 8-mL culture tube with a stir bar was added NaH (12 mg of a 60% dispersion on mineral oil, 0.30 mmol, 3.0 equiv). The tube was capped with a size 19 septum, sealed with electrical tape and then evacuated and backfilled with N_2 (x3). 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (**3n**, 20 mg, 0.10 mmol, 1.0 equiv) in DMF (0.75 mL) was added and the reaction mixture was stirred for 10 min at 0 °C, warmed to room temperature, and stirred for an additional 20 min, at which point all bubbling had stopped. 2-chloropyrimidine (23 mg, 0.20 mmol, 2.0 equiv) was added as a solution in DMF (0.50 mL) and the reaction was stirred for 22 h at 100 °C. The reaction mixture was diluted with EtOAc, filtered over a silica gel plug, and concentrated under reduced pressure. The crude residue was them redissolved in EtOAc and washed with brine (x5). The aqueous layers were back-extracted with EtOAc (x3), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 20–40% EtOAc in hexanes) to afford the desired product as a faint light yellow (22 mg, 0.079 mmol, 79%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.48 (d, *J* = 4.8 Hz, 2H), 6.89 (t, *J* = 4.8 Hz, 1H), 5.27 (pd, *J* = 7.2, 1.3 Hz, 1H), 2.51 (dddd, *J* = 9.9, 7.0, 4.2, 2.6 Hz, 2H), 2.40 (dddd, *J* = 11.7, 9.9, 7.3, 2.6 Hz, 2H), 1.80 (m, 1H), 1.28 (s, 12H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 164.6, 159.4, 114.9, 83.4, 71.4, 31.8, 24.9 ppm.

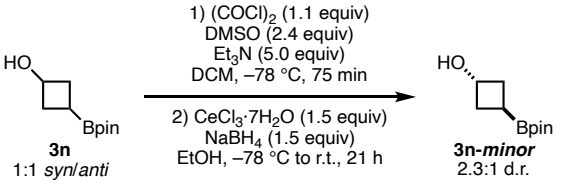
^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 34.3 ppm.

HRMS (DART): calc'd for $C_{14}H_{22}BN_2O_3$ $[M+H]^+$: 277.1718; found 277.1720.

IR (neat): 2982, 2939, 2868, 1739, 1583, 1565, 1429, 1380, 1319, 1219, 1145 cm^{-1}.

R_f: 0.3 (30% EtOAc in hexanes, stains blue with vanillin).

Oxidation/Reduction sequence to access the minor diastereomer

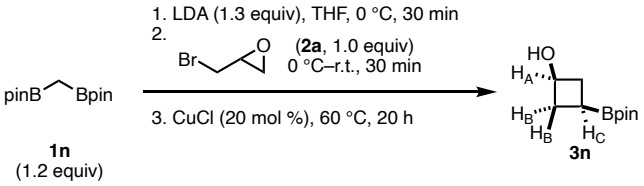


3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (3n-*minor*): To a flame dried 8-mL culture tube under an atmosphere of N_2 equipped with a stir bar and size 19 septum (sealed with electrical tape) were added oxalyl chloride (25 μL, 0.30 mmol, 1.1 equiv) and DCM (0.60 mL). The solution was cooled to –78 °C and DMSO (47 μL, 0.66 mmol, 2.4 equiv) was added. The reaction was stirred for 10 min followed by the addition of a 1:1 mixture of syn/anti diastereomers of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutan-1-ol (**3n + 3n-*minor***, 54 mg, 0.27 mmol, 1.0 equiv) as a solution in DCM (1.0 mL). The reaction was stirred for 15 min, after which Et_3N (0.19 mL, 1.4 mmol, 5.0 equiv) was added. The reaction mixture was stirred for an additional 75 min, after which 10% aq. $Na_2S_2O_3$ was added. The phases were separated, the aqueous layer was extracted with DCM (x3) and the combined organic layers were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. During solvent removal, another 8-mL culture tube with a stir bar was flame dried under reduced pressure and then backfilled with N_2 (x3). $CeCl_3 \cdot 7H_2O$ (0.15 g, 0.41 mmol, 1.5 equiv) was added and the tube capped with a size 19 septum, sealed with electrical tape, and backfilled with N_2 (x3). When the solvent was removed from the crude residue, it was added to the tube containing $CeCl_3 \cdot 7H_2O$ as a solution in EtOH (2.0 mL) and the mixture was cooled to –78 °C. $NaBH_4$ (16 mg, 0.41 mmol, 1.5 equiv) was added dropwise as a solution in EtOH (2.0 mL) and the reaction mixture was allowed to warm to room temperature and stirred for 21 h. The reaction mixture was diluted with EtOAc and sat. aq. NH_4Cl was added. The phases were separated, the aqueous layer was extracted with EtOAc (x3), and the combined organic layers were washed with brine (x1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (gradient of 20–30% EtOAc in hexanes) to afford the desired product as a white solid (**3n-*minor***, 15 mg, 0.074 mmol, 27%, 2.3:1 d.r.). Spectral data is consistent with **3n-*minor***.

F. Determination of Stereochemistry:

1D and 2D NMR experiments were performed to determine the relative stereochemistry of the products. The results of these experiments are detailed below and are consistent with a *syn* relationship between the alcohol and the boronic ester. This was found to be the case for both substituted and unsubstituted 1,1-diborylalkanes, as well as for when 1-substituted epibromohydrins are used, and therefore the results of these experiments were generalized for the remainder of the substrates.

Major diastereomer isolated after treating 1n to standard reaction conditions:



The COSY spectrum of **3n** is shown below (Figure S1).

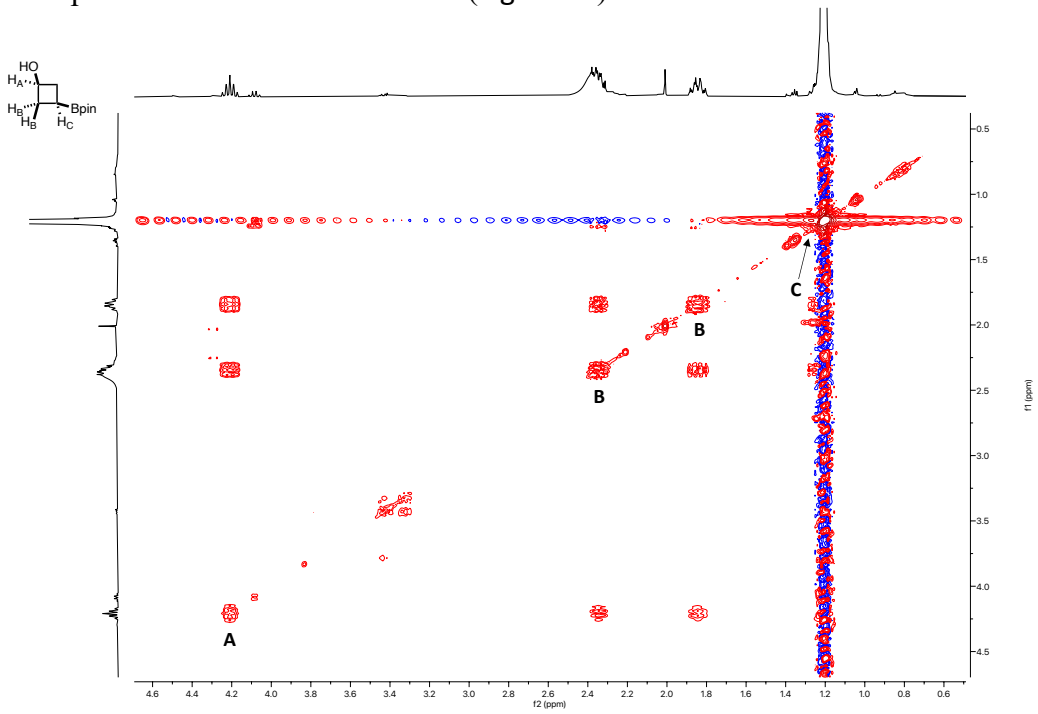


*Figure S1 - COSY spectrum of **3n***

Importantly, for the COSY spectrum there is no ^4J coupling between the two methine protons H_A/H_C. With that in mind, the 2D NOESY for **3n** was obtained (Figure S2). The nOe signal of interest is shown in the circle. This correlation is the nOe signal between H_A and H_C. Since this correlation is not observed in the COSY spectrum, we propose that this is a through space correlation of the two methine protons across the cyclobutane ring, and it strongly suggests that the major diastereomer has a syn relationship between the OH and the boronic ester.

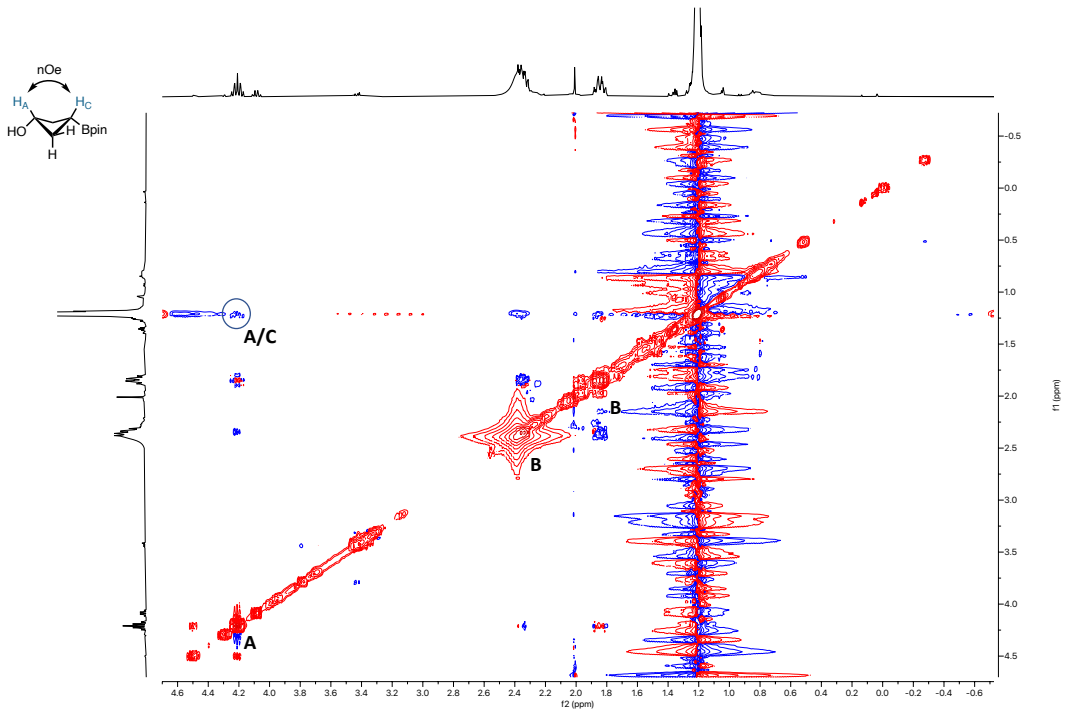


*Figure S2 – 2D NOESY spectrum of **3n***

To ensure that this analysis was correct, a sample containing a mixture of diastereomers (~1.5:1 *syn*:*anti*) was tested. The COSY spectrum (Figure S3) shows that, for both diastereomers, there is no ^{4}J coupling between the H_A and H_C protons. When the 2D NOESY spectrum was obtained (Figure S4), it became clear that only the major diastereomer had a H_A/H_C through space interaction (circled). This provided further evidence that the major product was the syn diastereomer.

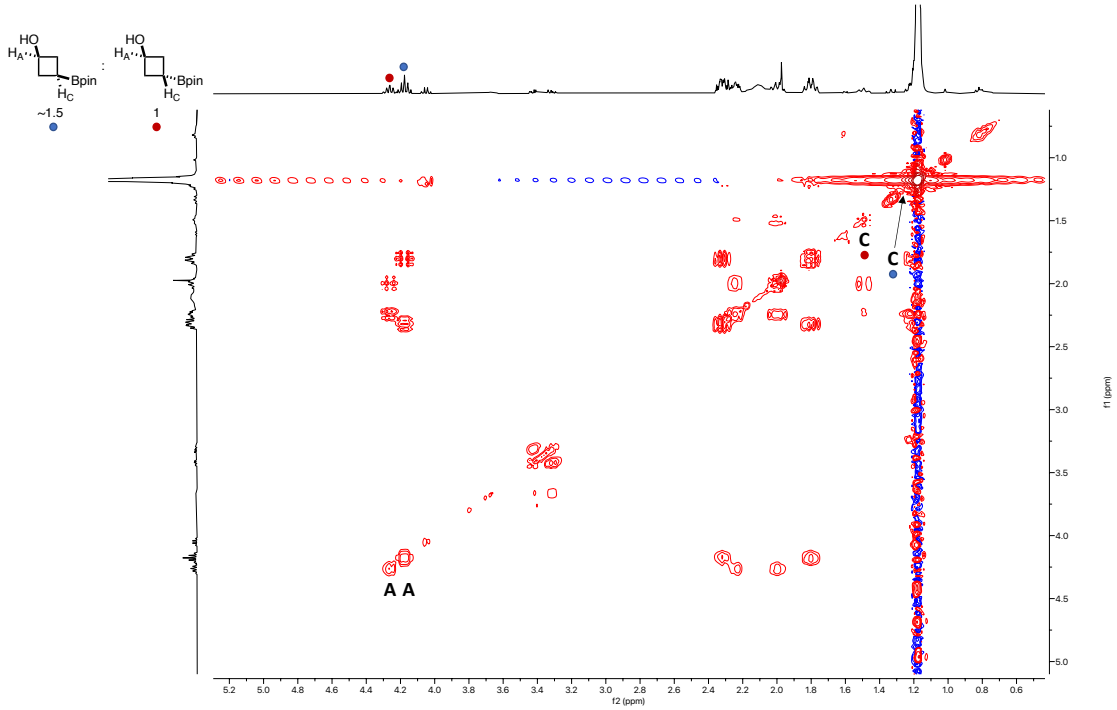


*Figure S3 – COSY spectrum of a mixture of diastereomers of **3n***

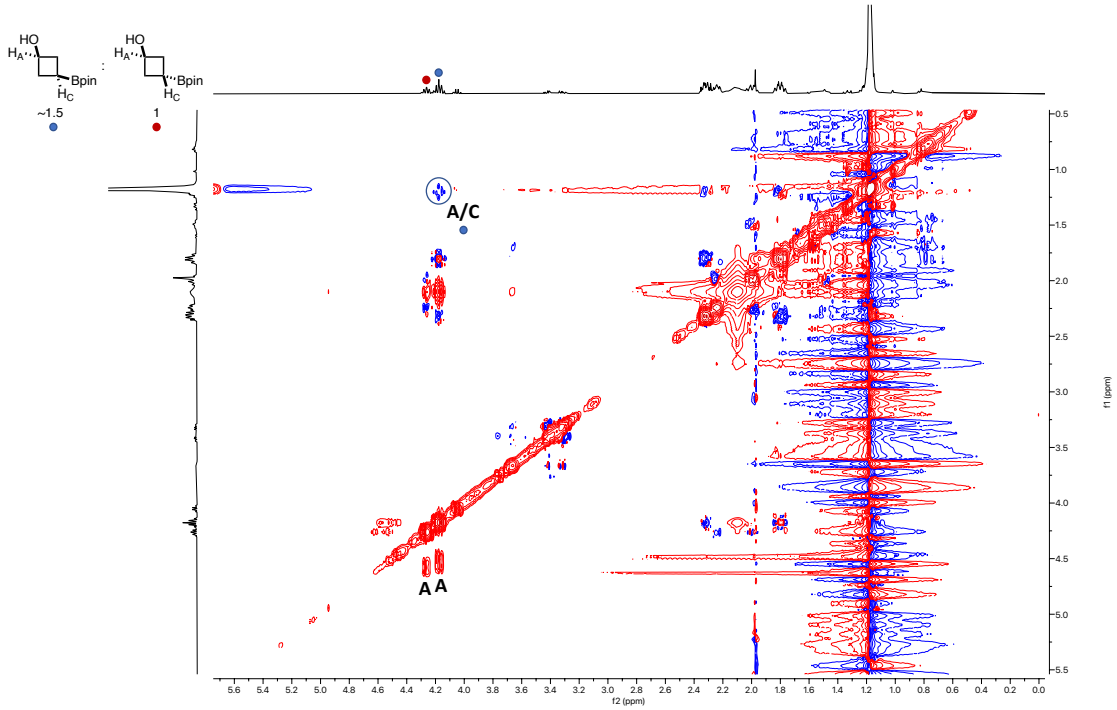
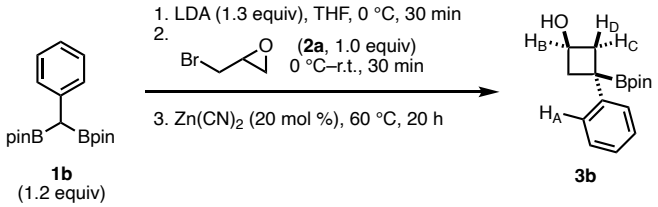


*Figure S4 - 2D NOESY spectrum of a mixture of diastereomer of **3n**. Circled cross-peak shows NOE correlation between H_A/H_C on the syn diastereomer. Blue dot represents the major product; red dot represents minor product. A cross-peak between H_A/H_C protons of the minor diastereomer at (4.26, 1.50) ppm is not observed.*

Major diastereomer isolated after treating 1b to standard reaction conditions:



1b
(1.2 equiv)

3b

3b was useful for determining the relative stereochemistry of the products because the ortho protons of the phenyl ring can act as nOe handles. The COSY spectrum of **3b** is included below (Figure S5 and Figure S6).

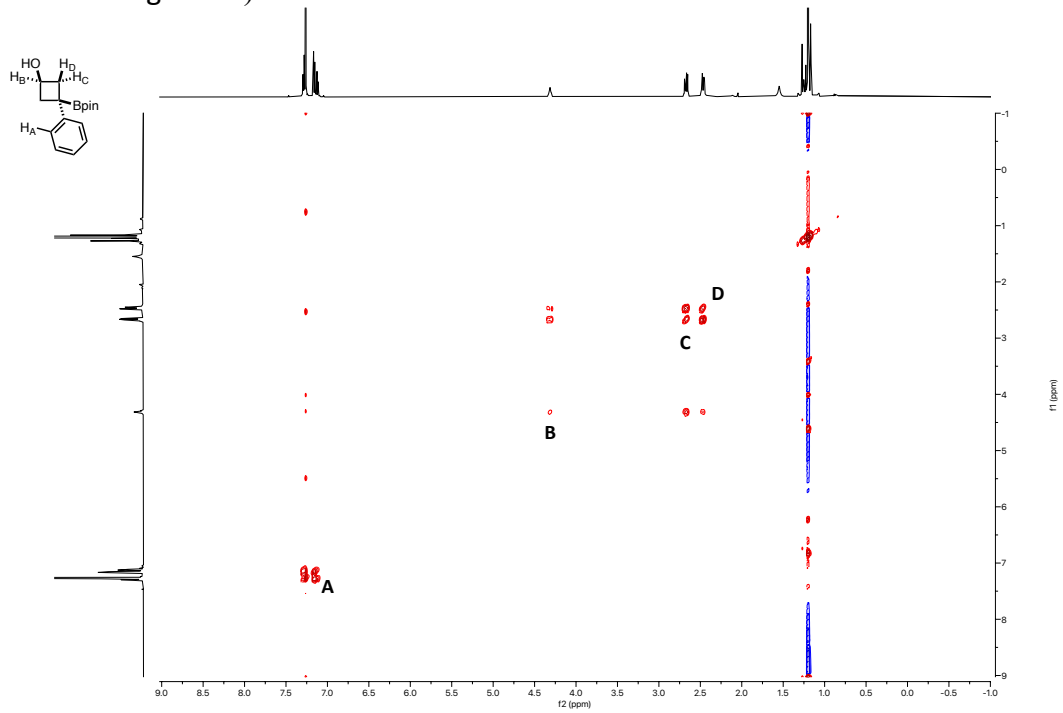


*Figure S5 - COSY spectrum of **3b***

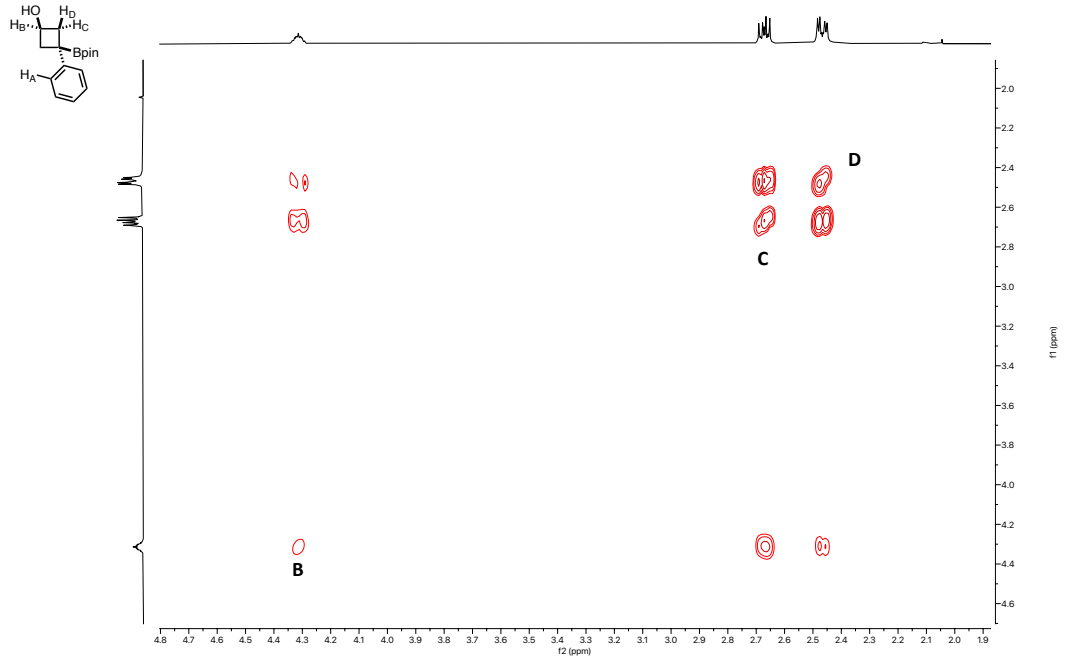


*Figure S6 - Expanded COSY spectrum of **3b***

Below is the corresponding 2D NOESY spectrum (Figure S7). The nOe correlations of interest are circled. There is a correlation through space between H_B and one of the diastereotopic methylene protons on the cyclobutane ring (H_C), and importantly, the same methylene proton (H_C) has an nOe correlation with the ortho proton on the arene ring (H_A). This suggests that the H_B, H_C, and H_A are on the same side of the ring, suggesting a syn relationship between the alcohol OH and the boronic ester.

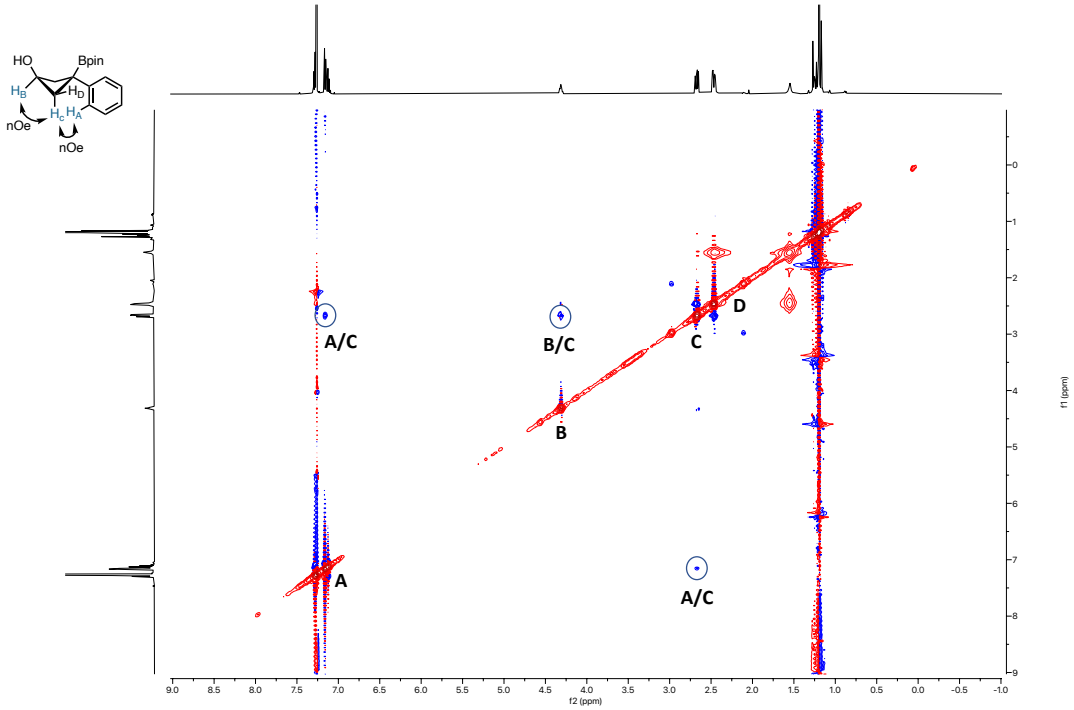


*Figure S7 - 2D NOESY spectrum of **3b***

Minor diastereomer isolated after treating 1b to standard reaction conditions:

To confirm this conclusion, 1D NOESY experiments were performed on the minor diastereomer that was isolated from the reaction. The ^{1}H spectrum of the minor diastereomer is shown below (Figure S8), along with the associated 1D nOe difference spectra after selectively irradiating the methine proton (H_C, Figure S9) and the Bpin methyl protons (H_F) (Figure S10).

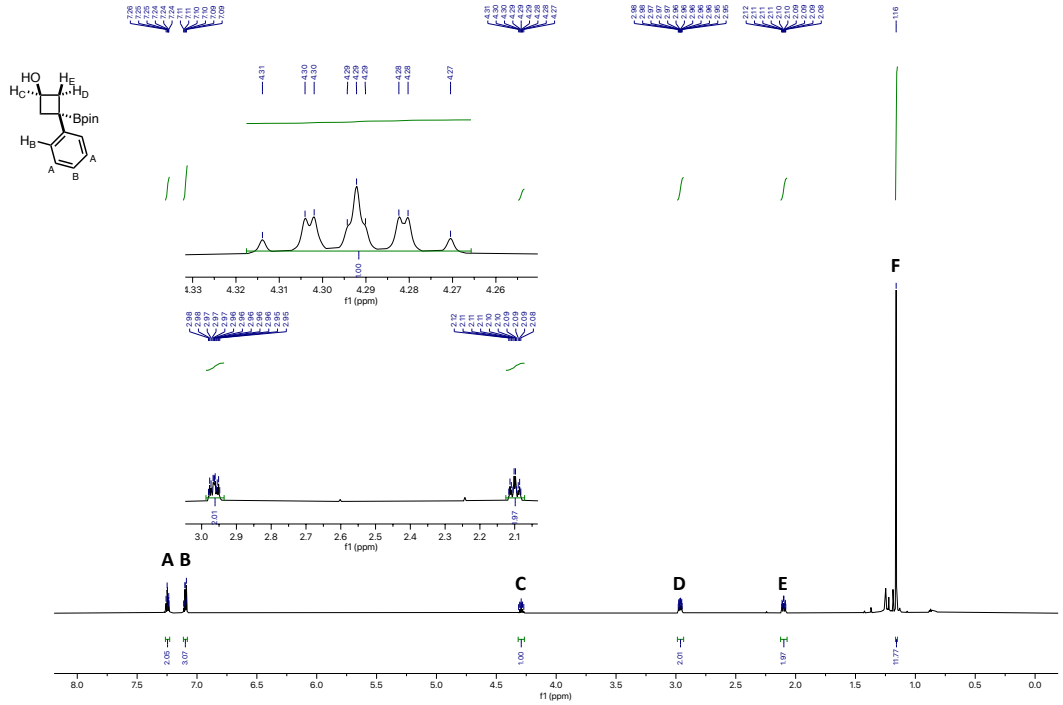


*Figure S8 - 1H NMR spectrum of **3b-minor***

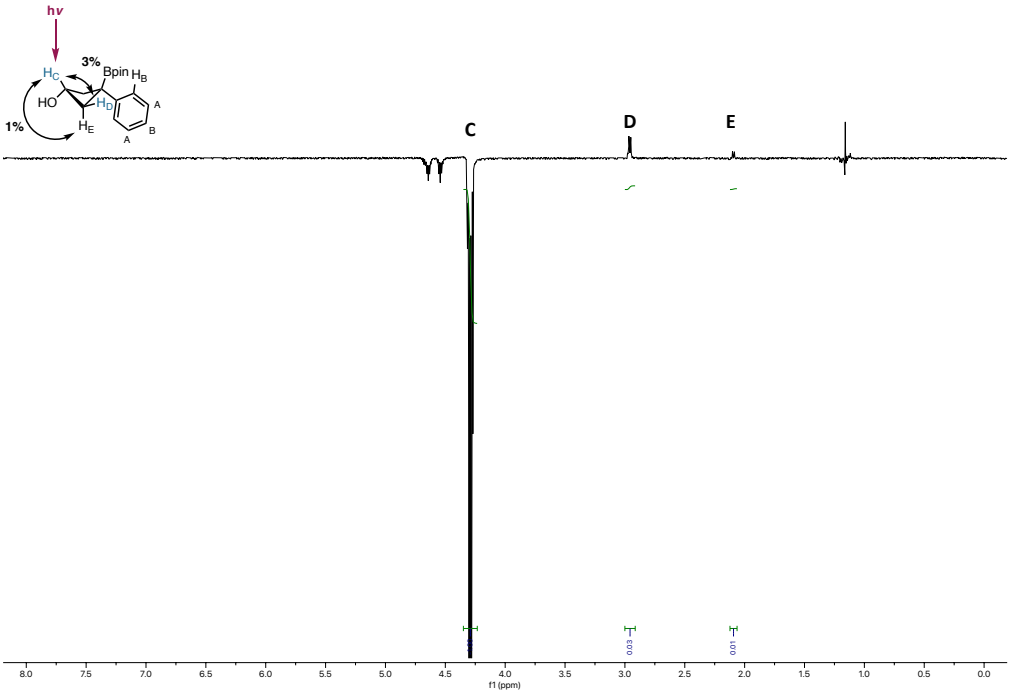


*Figure S9 - 1D NOESY spectrum of **3b-minor**. Selective irradiation of H_C*

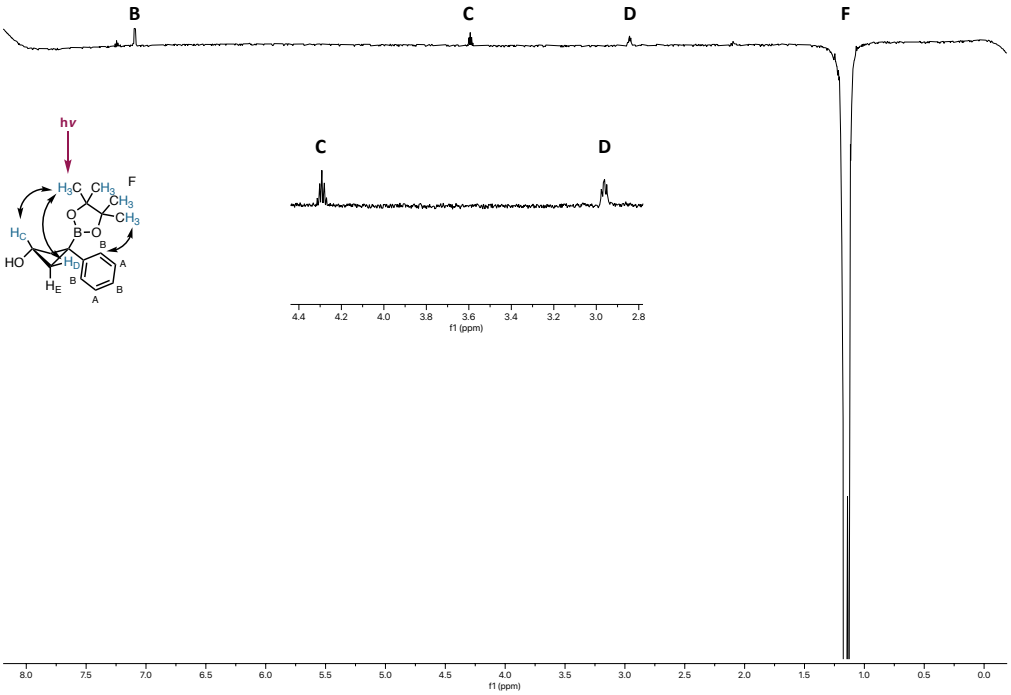
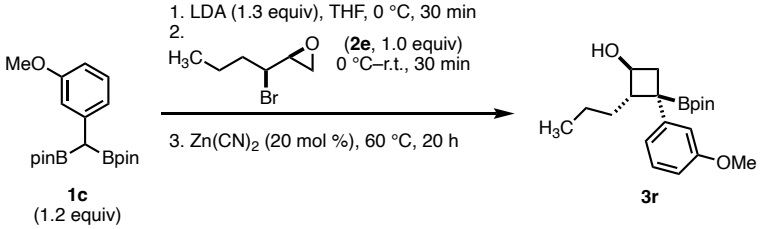


*Figure S10- 1D NOESY spectrum of **3b-minor**. Selective irradiation of H_F*

Upon irradiating H_C (4.29 ppm, Figure S9), nOe's are observed for both of the methylene protons on the cyclobutane ring, however the nOe of the signal at 2.96 ppm (H_D) is stronger than the nOe for the signal at 2.10 ppm (H_E). This suggests that H_C and H_D are on the same side of the ring. When the protons on the methyl groups of the Bpin ester (H_F, Figure S10) are irradiated, significant nOe's are observed for both H_C and H_D. This

suggests that the boronic ester, H_C and H_D are on the same face of the cyclobutane ring. Overall, these experiments support that the minor diastereomer has an *anti* relationship with respect to the OH and Bpin, which is consistent with our earlier findings that the major product has a *syn* relationship between these groups.

Product isolated after treating 1c and 2e to standard reaction conditions:



Finally, we needed to determine the stereochemistry of **3r** that is obtained from using **1c** and **2e**. To do so, both 1D and 2D NOESY experiments were performed. The ^{1}H (Figure S11) and COSY (Figure S12) spectra are shown below.

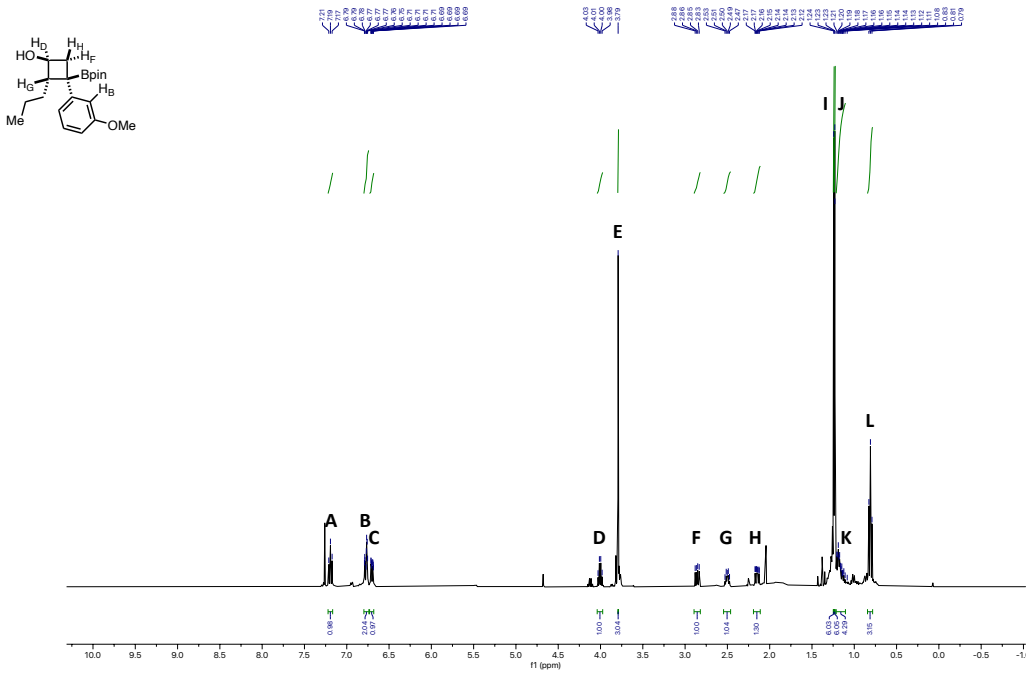


*Figure S11 - 1H NMR spectrum of **3r***

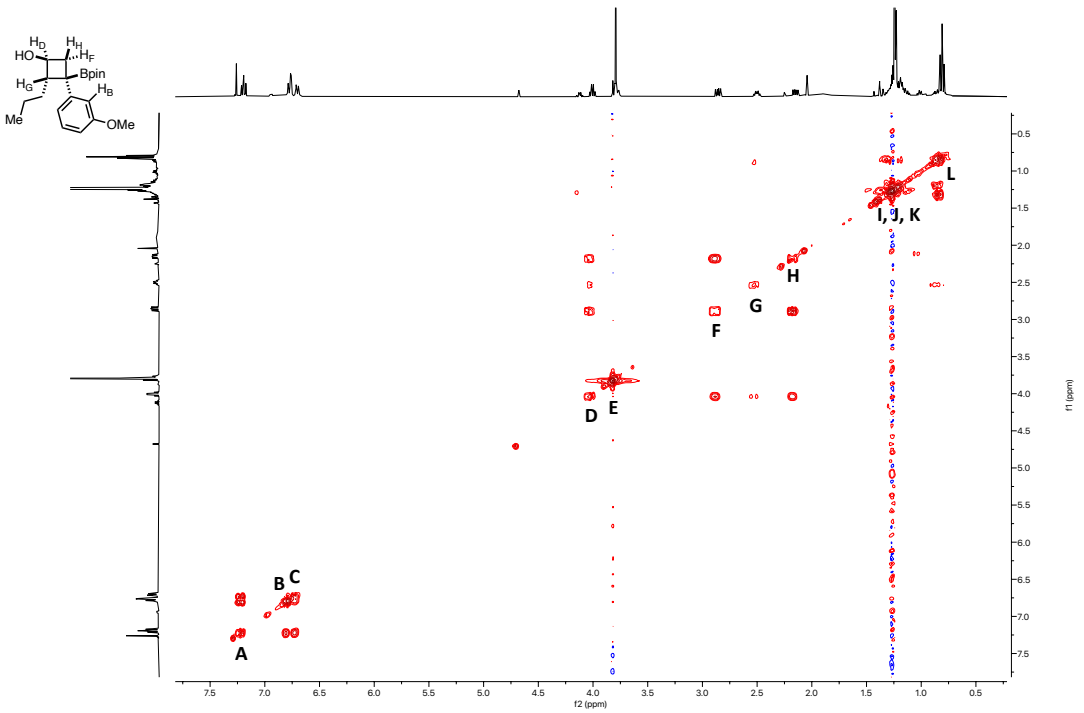


*Figure S12 - COSY spectrum of **3r***

Importantly, the COSY spectrum shows that there are no ^4J couplings between the methine proton H_G and the other two diastereotopic methylene protons (H_H and H_F) on the cyclobutane ring. With that information, the 2D NOESY spectrum was obtained. The nOe correlations of interest are circled (Figure S13).

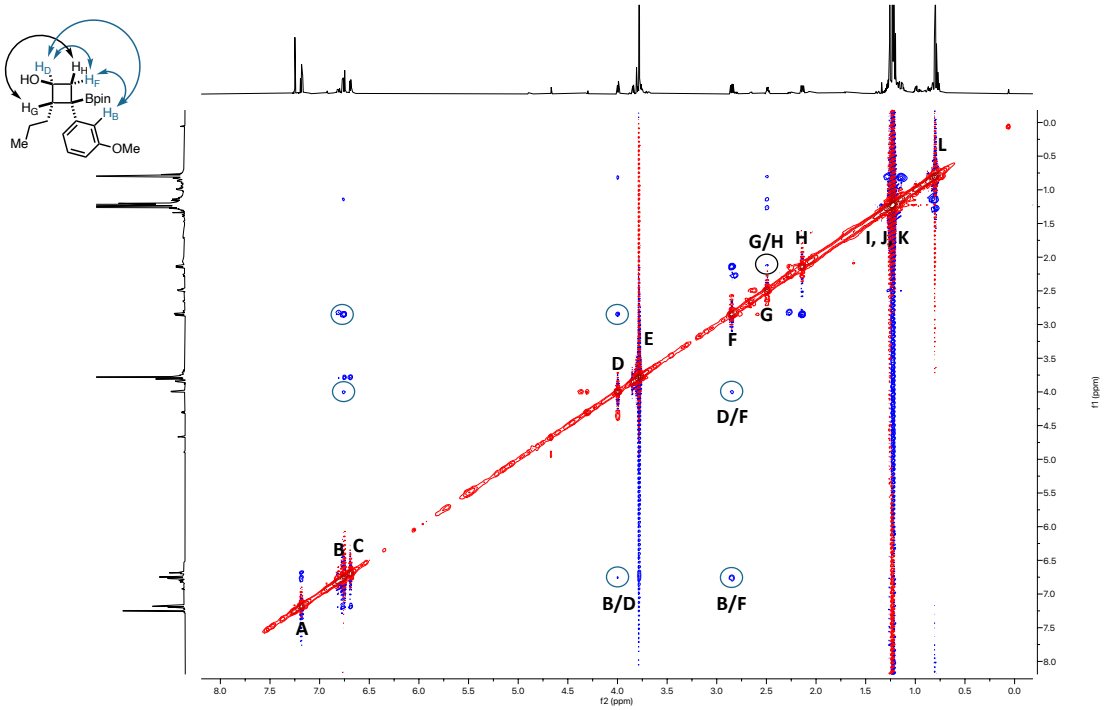


*Figure S13 - 2D NOESY spectrum of **3r***

The 2D NOESY spectrum shows nOe correlations between the ortho protons on the arene and (i) the methine proton H_D, and (ii) one of the two diastereotopic methylene protons (H_F) on the cyclobutane ring. This suggests that these three protons are on the same side of the ring and therefore establishes an *anti* relationship between the arene and the alcohol (and by extension, a *syn* relationship between the OH and the Bpin). H_D also has an nOe with H_F. Along with that, there is an nOe correlation between H_G the other diastereotopic methylene proton on the cyclobutane ring (H_H). This suggests that these two protons are on the same side of the cyclobutane ring (black circle).

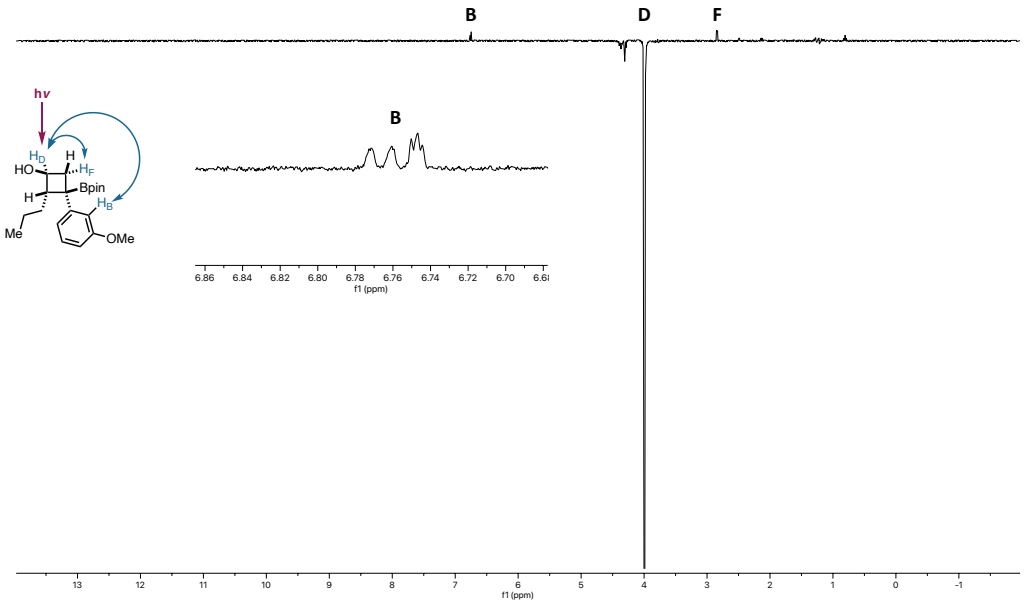


*Figure S14 - 1D NOESY spectrum of **3r**. Selective irradiation of H_D*

To verify these results, 1D NOESY difference spectra were obtained. Upon irradiating H_D (Figure S14), nOe's were observed for H_B and H_F. Along with that, H_G was selectively irradiated (Figure S15), an nOe was observed for the signal corresponding to the other methylene proton on the cyclobutane ring (H_H), confirming the *syn* relationship between these protons.

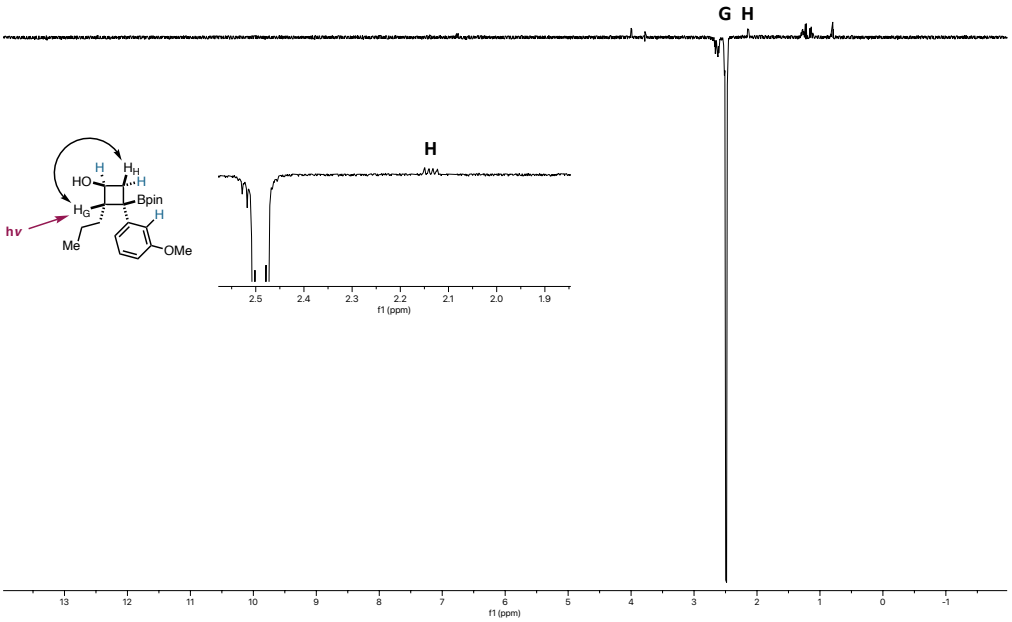
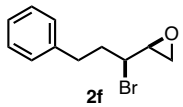


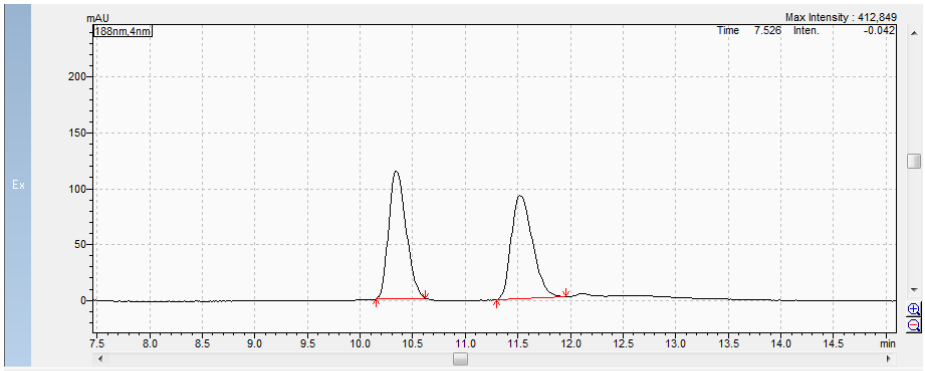
*Figure S15 - 1D NOESY spectrum of **3r**. Selective irradiation of H_G*

G. Measurement of Enantiospecificity

Racemic Traces



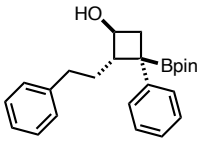
2f



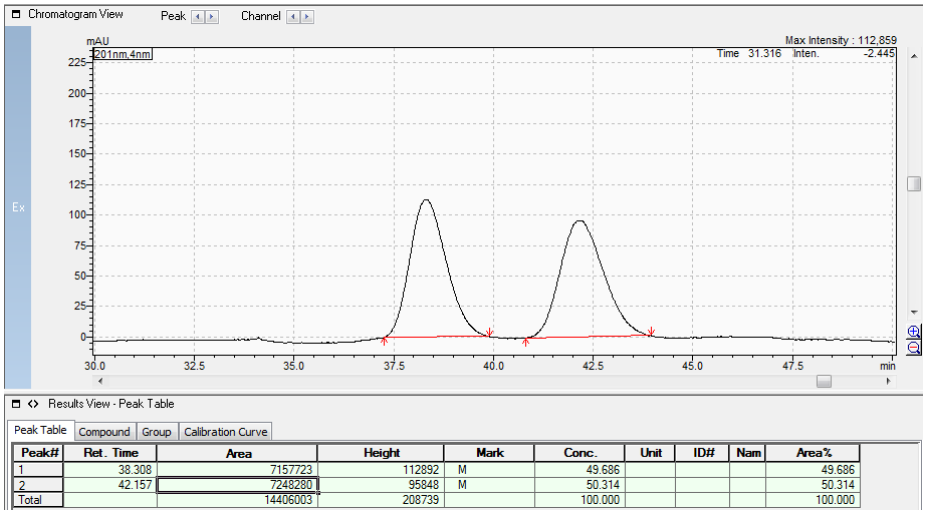
Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Nam	Area%
1	10.343	1322698	114630	M	50.318				50.318
2	11.522	1305984	92322	M	49.682				49.682
Total		2628682	206952		100.000				100.000



3s



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Nam	Area%
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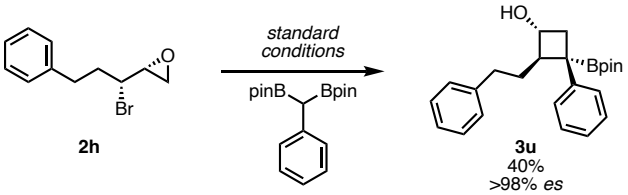
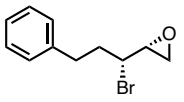
2	42.157	7248280	95848	M	50.314				50.314
Total		14406003	208739		100.000				100.000

Enantioenriched Traces

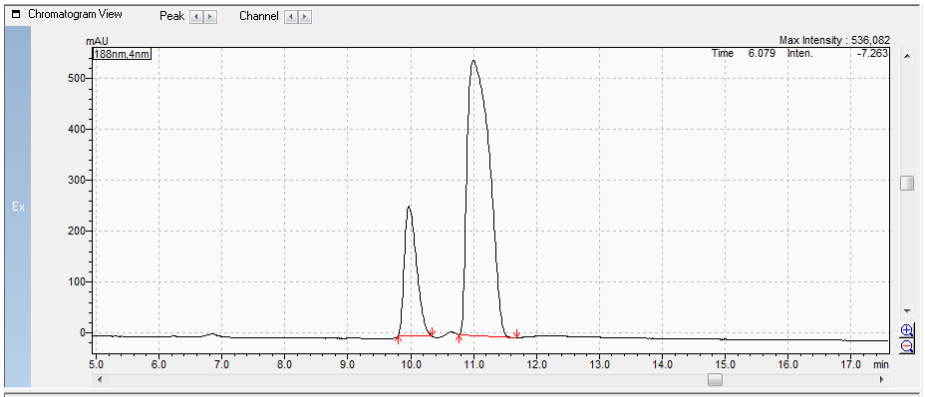


2h

3u
40%
>98% *es*



2h



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Nam	Area%
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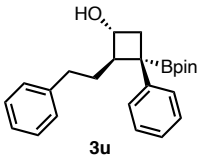
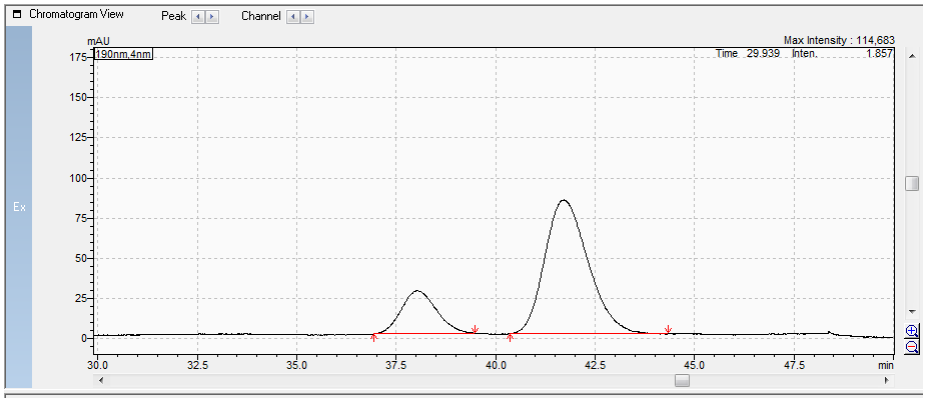
2	11.001	13166238	540478	M	79.456				79.456
Total		16570466	796077		100.000				100.000



3u
40%
>98% *es*



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Nam	Area%
1	38.027	1650745	26854	M	20.683				20.683
2	41.717	6330350	83607	M	79.317				79.317
Total		7981095	110461		100.000				100.000

H. Mechanistic Proposal

Proposed mechanism with aryl substituted 1,1-diborylalkanes

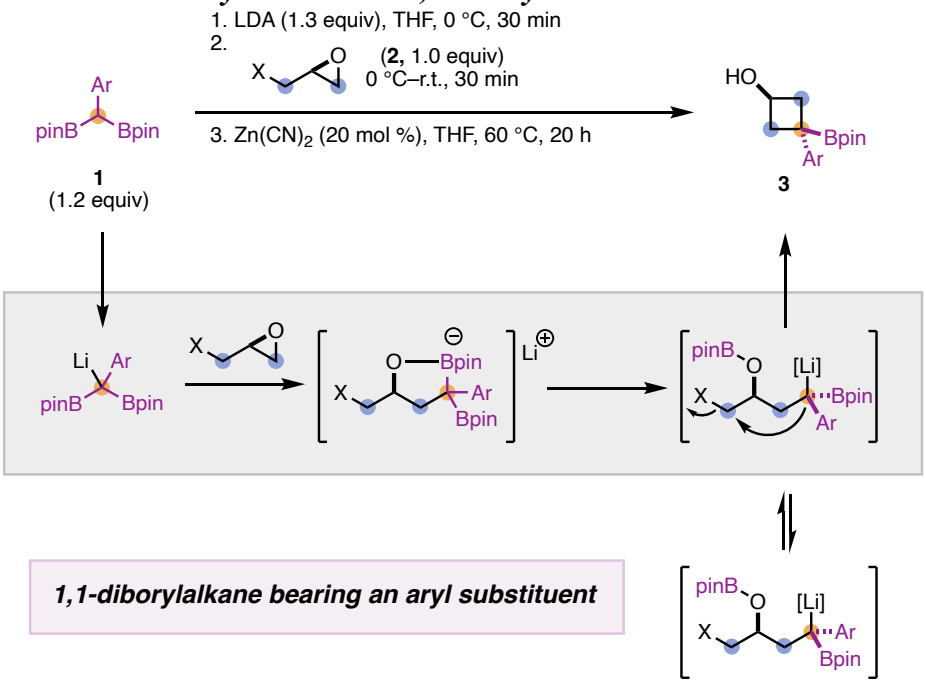


Figure S16 – Proposed mechanism with aryl substituted 1,1-diborylalkanes

Proposed mechanism with alkyl substituted 1,1-diborylalkanes

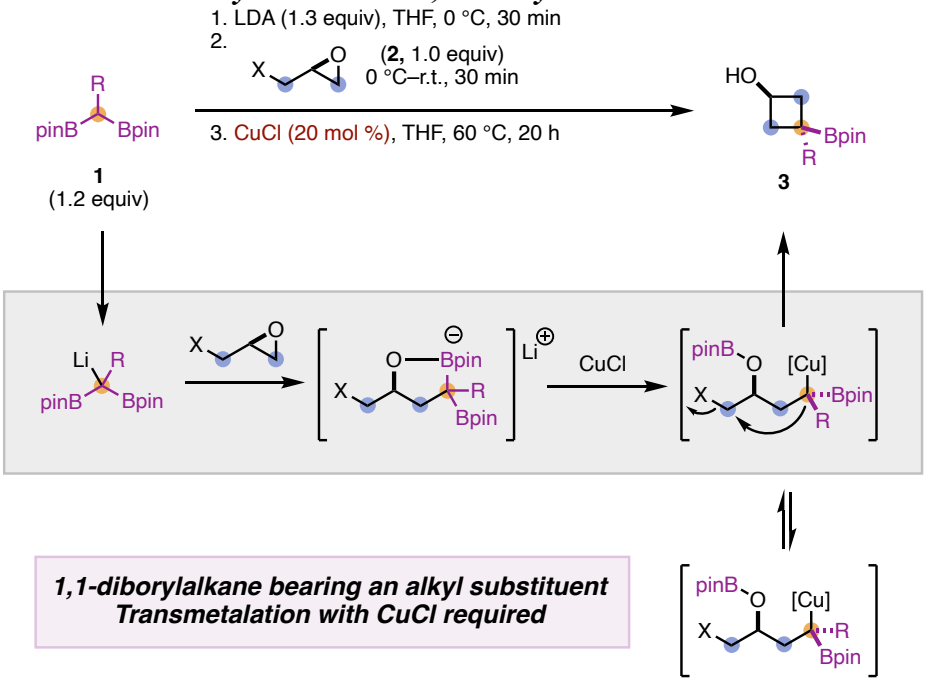


Figure S17 – Proposed mechanism with alkyl substituted 1,1-diborylalkanes

Relationship between leaving group and d.r.

Note that there seems to be a relationship between the leaving group and the d.r. of the reaction (Scheme 3a). We propose that this is due to the relative rates of cyclization vs epimerization of the organolithium/organocopper species, and studies to better understand this relationship are ongoing in our laboratory.

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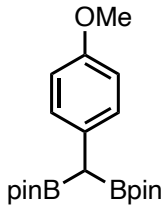

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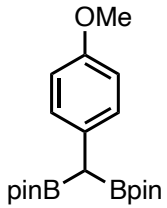

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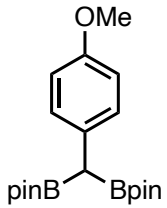

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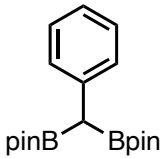

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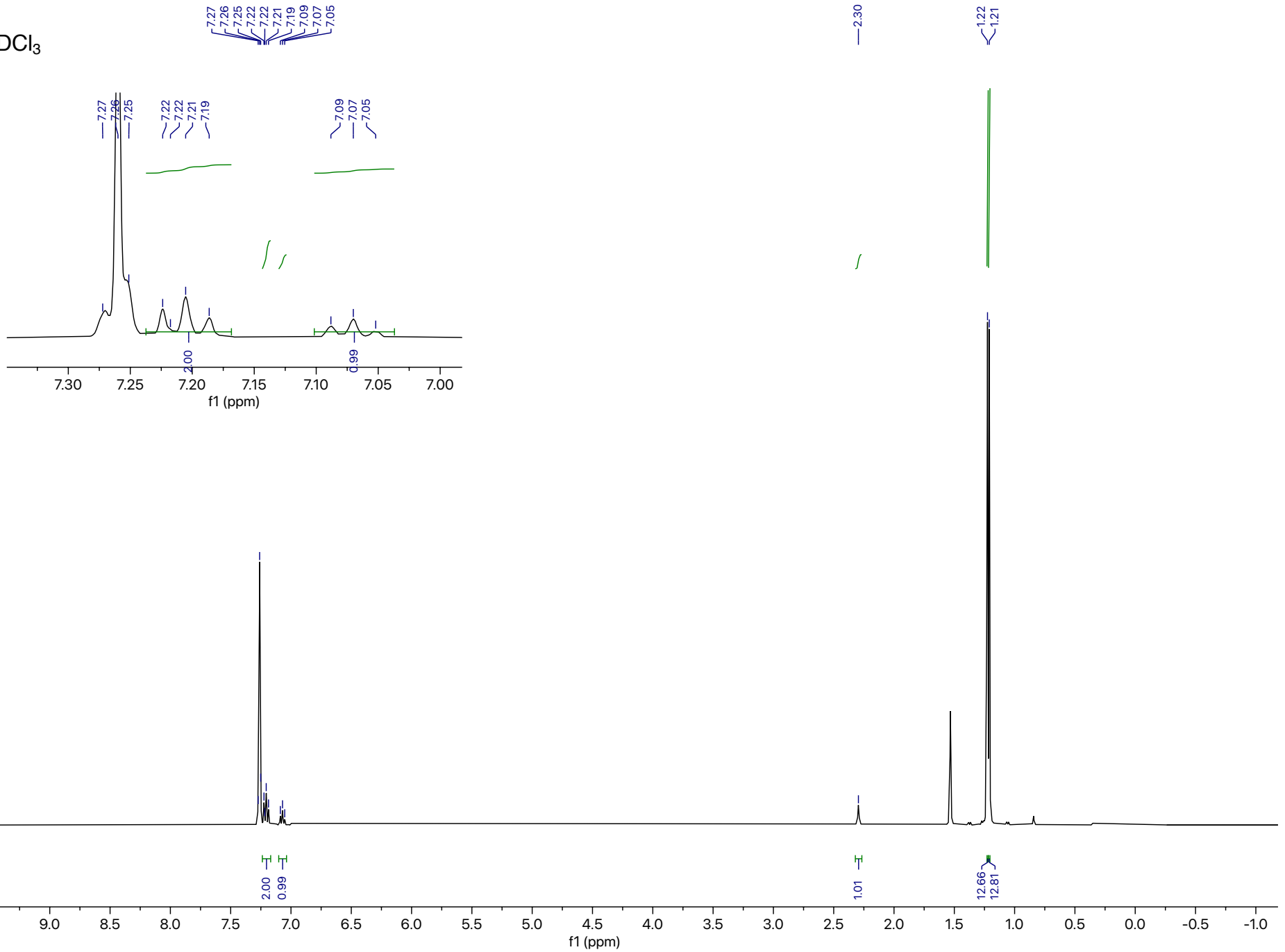

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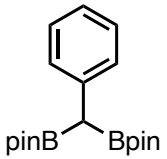

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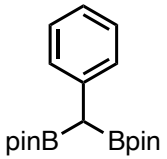

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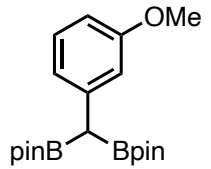

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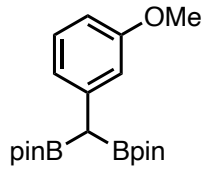

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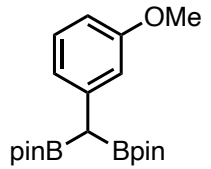

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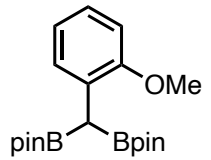

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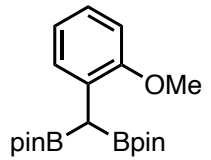

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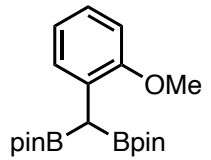

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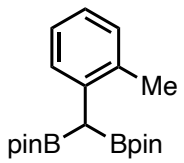

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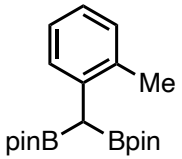

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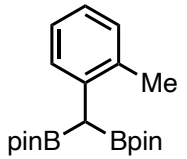

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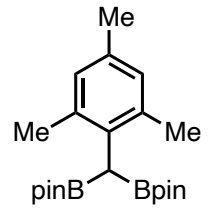

1f

33.04

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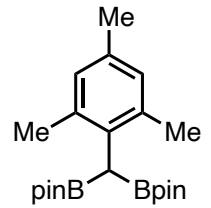

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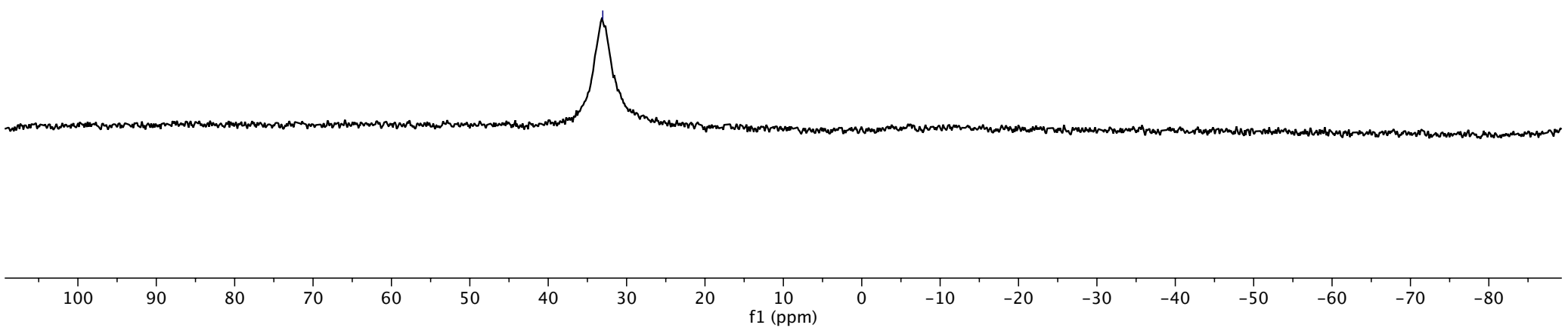

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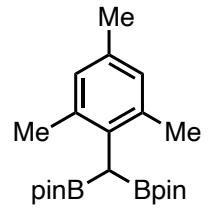

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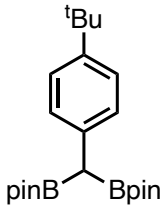

1g

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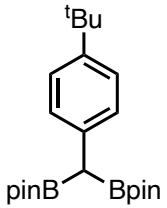

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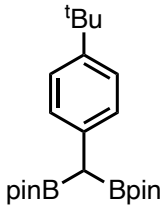

1g

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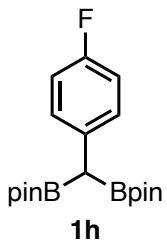

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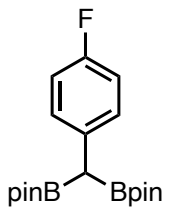

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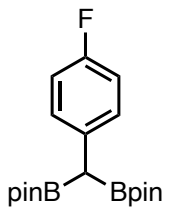
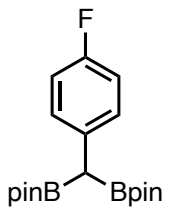


1h

^{19}F {^{1}H} (376 MHz), $CDCl_3$



1h

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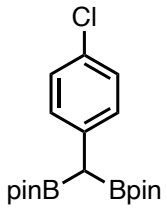

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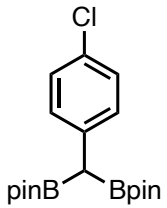

1i

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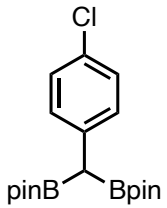

1i

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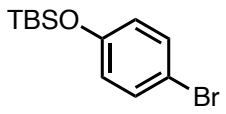

S1j

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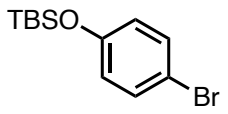

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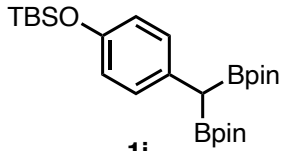

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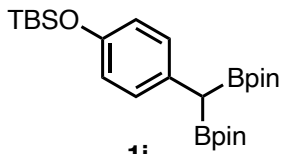

1j

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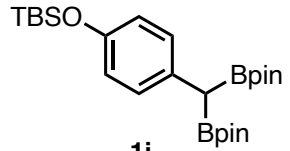

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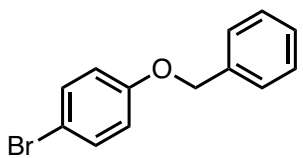

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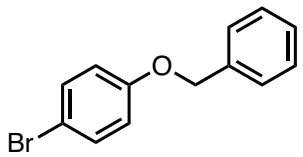
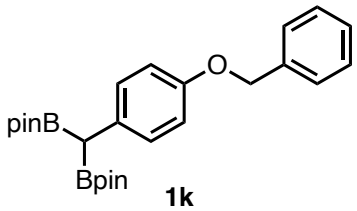
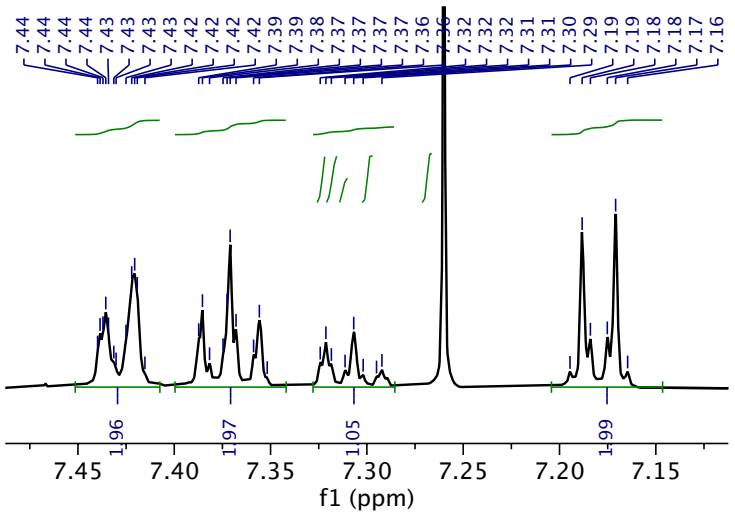


S1k

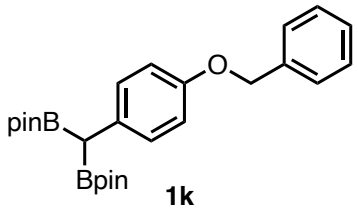
^{1}H (500 MHz), $CDCl_3$



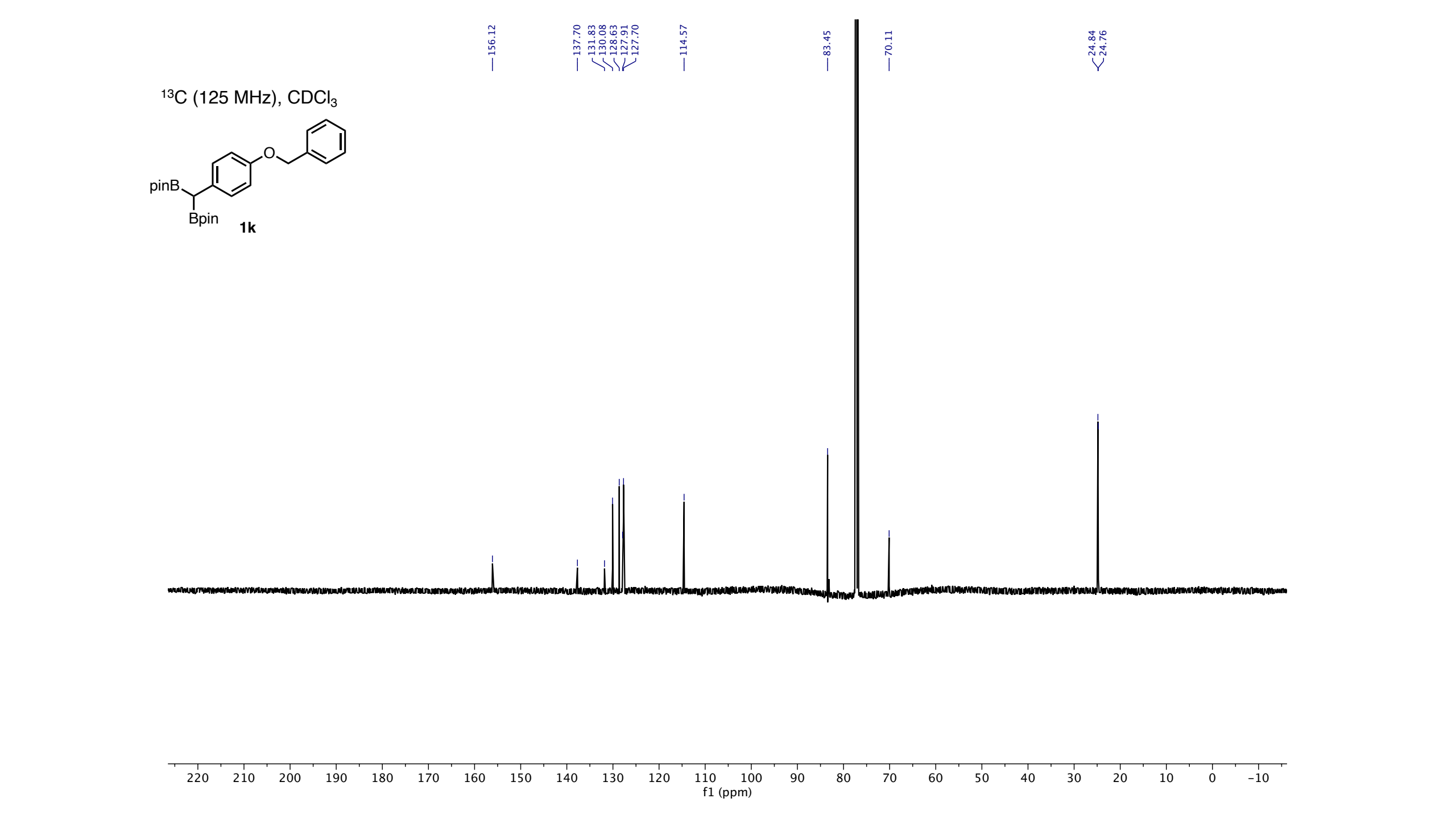
1k



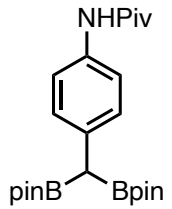
^{11}B (128 MHz), $CDCl_3$



1k


156.12
137.70
131.83
130.08
128.63
127.91
127.70
114.57
83.45
70.11
24.84
24.76
13C (125 MHz), CDCl3
pinB
Bpin
O
1k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

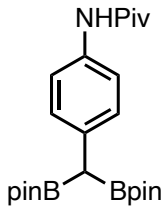
^{1}H (500 MHz), $CDCl_3$



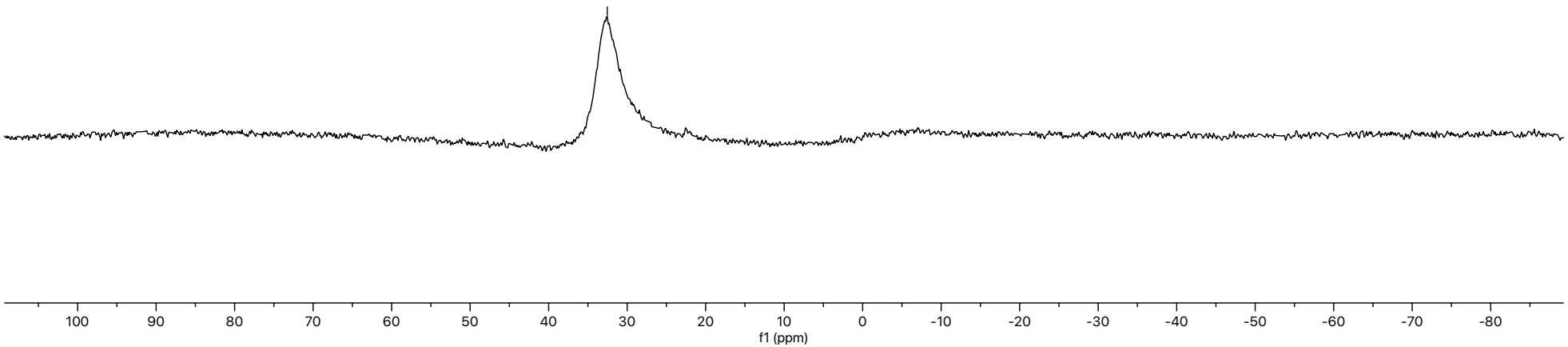
1l

32.53

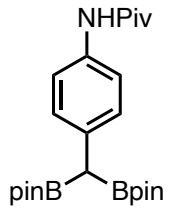
^{11}B (128 MHz), $CDCl_3$



1l

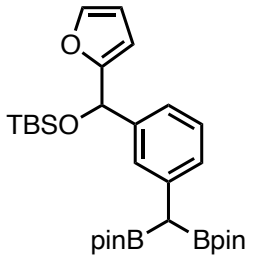


^{13}C (125 MHz), $CDCl_3$



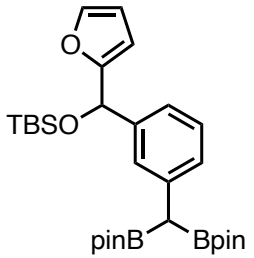
1l

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



1m

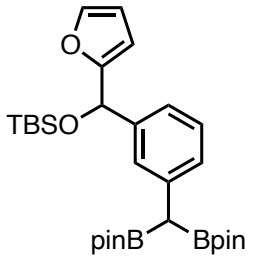
^{11}B (128 MHz), $CDCl_3$



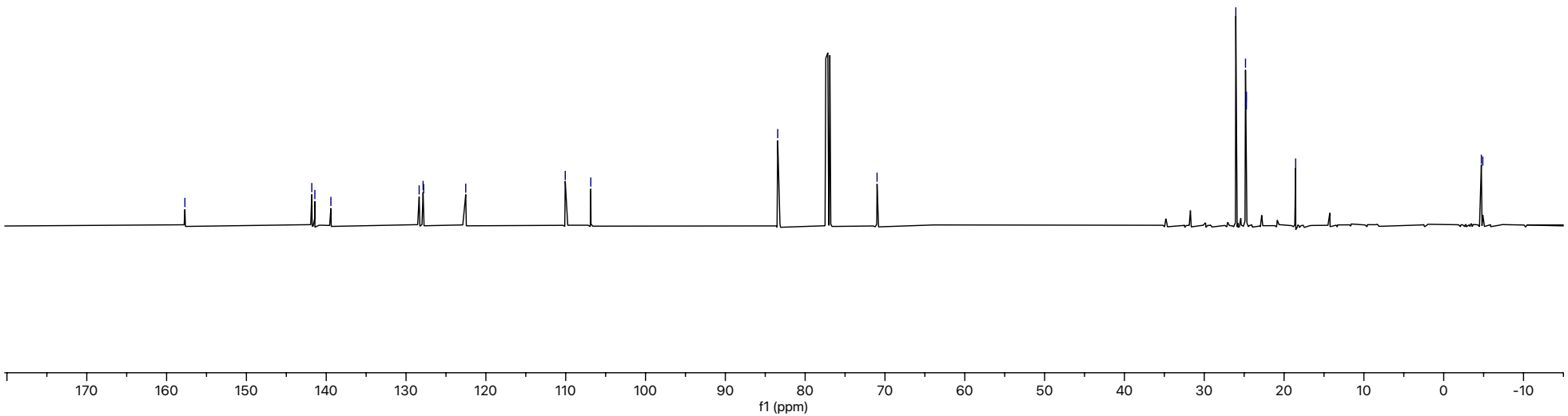
1m

157.71
141.81
141.42
139.42
128.36
127.86
127.79
122.52
110.06
106.85
83.44
70.99
26.05
24.83
24.72
24.71
18.55
-4.71
-4.90

^{13}C (125 MHz), $CDCl_3$



1m



^{1}H (400 MHz), $CDCl_3$

1n

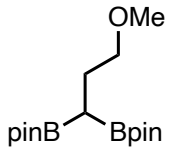
^{11}B (128 MHz), $CDCl_3$

1n

^{13}C (100 MHz), $CDCl_3$

1n

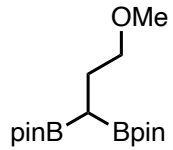
^{1}H (400 MHz), $CDCl_3$



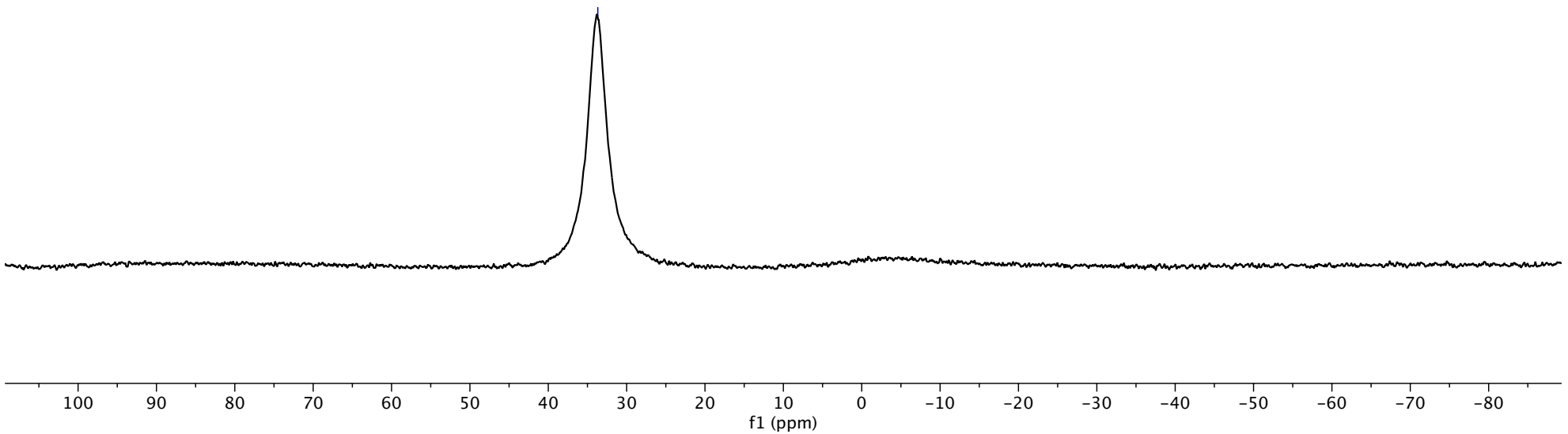
1o

33.68

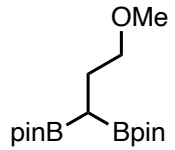
^{11}B (128 MHz), $CDCl_3$



1o

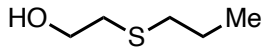


^{13}C (100 MHz), $CDCl_3$



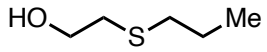
1o

^{1}H (400 MHz), $CDCl_3$



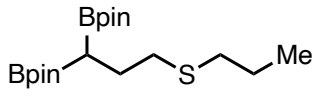
S1pa

^{13}C (100 MHz), $CDCl_3$

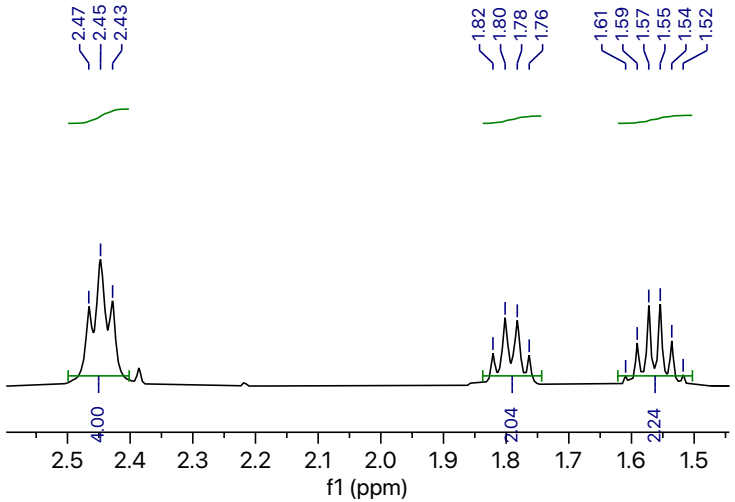


S1pa

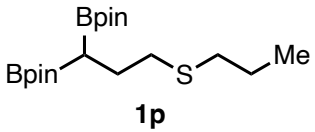
^{1}H (400 MHz), $CDCl_3$



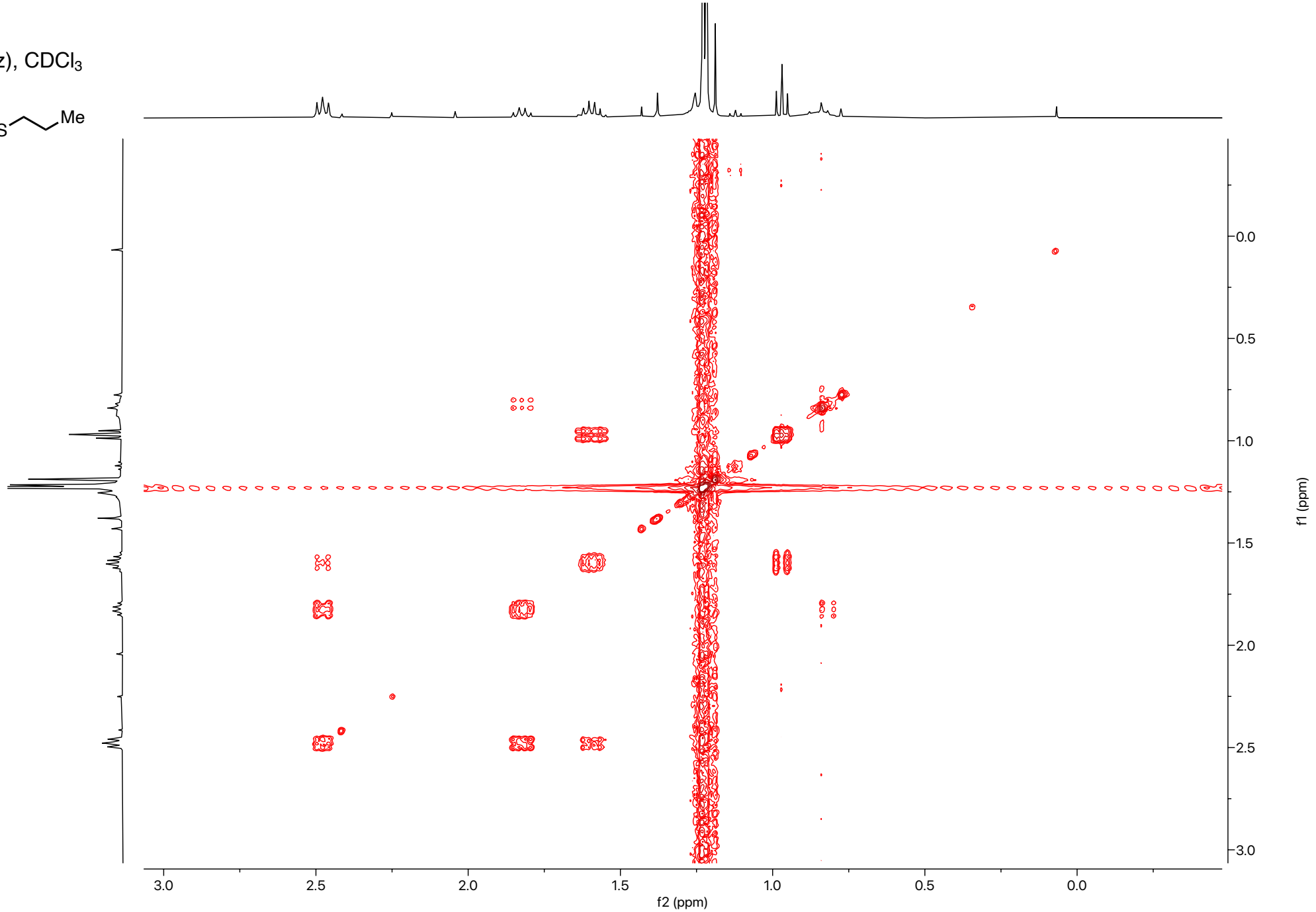
1p



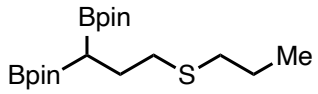
^{1}H (400 MHz), $CDCl_3$



1p

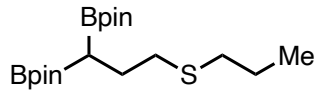


^{11}B (128 MHz), $CDCl_3$



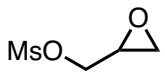
1p

^{13}C (100 MHz), $CDCl_3$



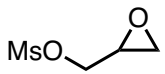
1p

^{1}H (400 MHz), $CDCl_3$



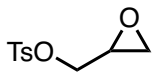
2c

^{13}C (100 MHz), $CDCl_3$



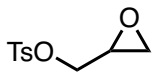
2c

^{1}H (400 MHz), $CDCl_3$



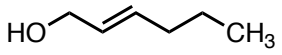
2d

^{13}C (100 MHz), $CDCl_3$



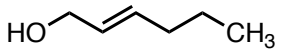
2d

^{1}H (400 MHz), $CDCl_3$



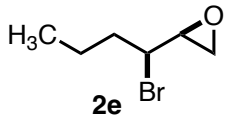
S2e

^{13}C (100 MHz), $CDCl_3$



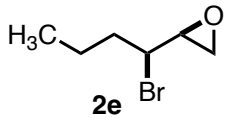
S2e

^{1}H (400 MHz), $CDCl_3$



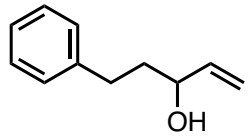
2e

^{13}C (100 MHz), $CDCl_3$



2e

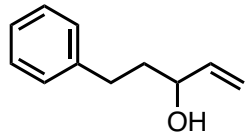
^{1}H (400 MHz), $CDCl_3$



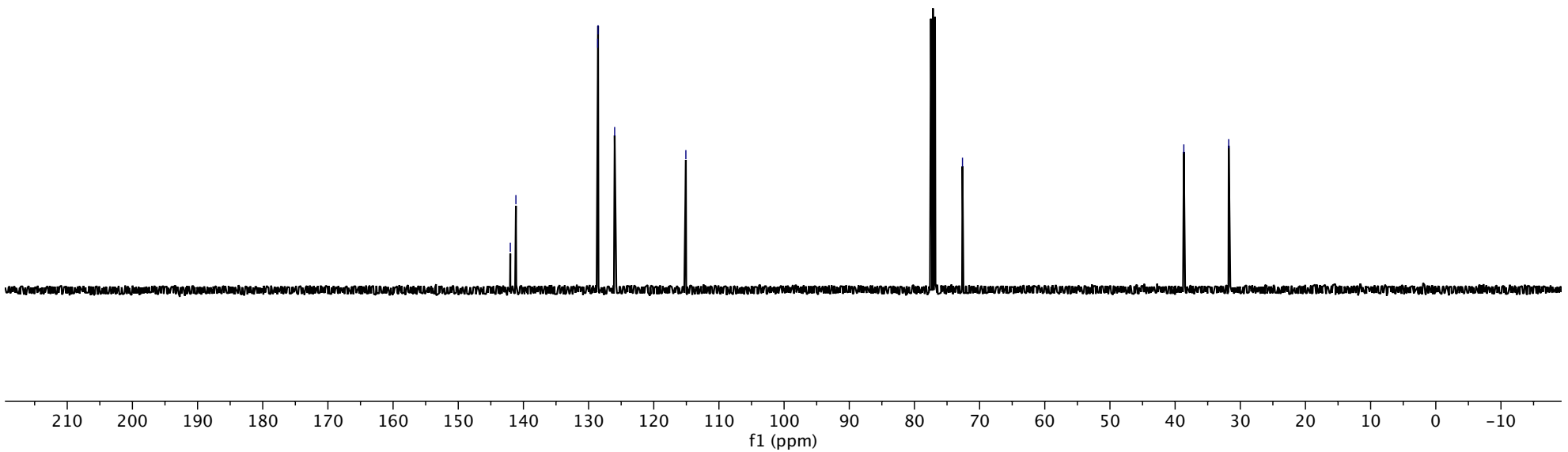
S2fa

142.01
141.15
128.60
128.55
126.00
115.07
72.63
38.66
31.78

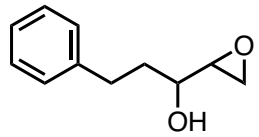
^{13}C (100 MHz), $CDCl_3$



S2fa

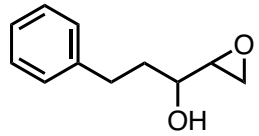


^{1}H (400 MHz), $CDCl_3$



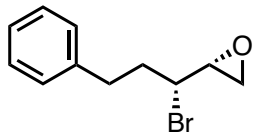
S2fb

^{13}C (100 MHz), $CDCl_3$

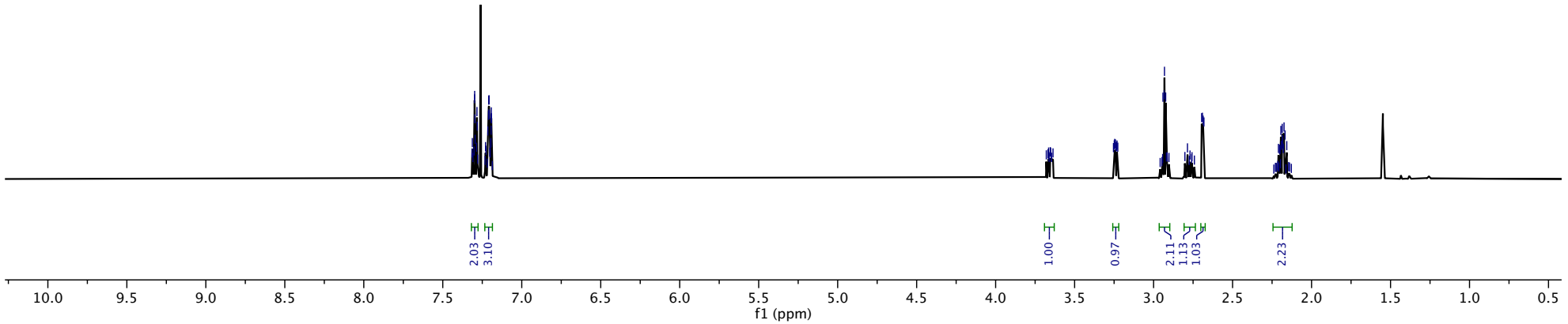


S2fb

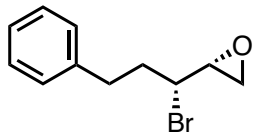
^{1}H (500 MHz), $CDCl_3$



2h

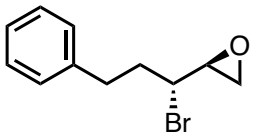


^{13}C (125 MHz), $CDCl_3$

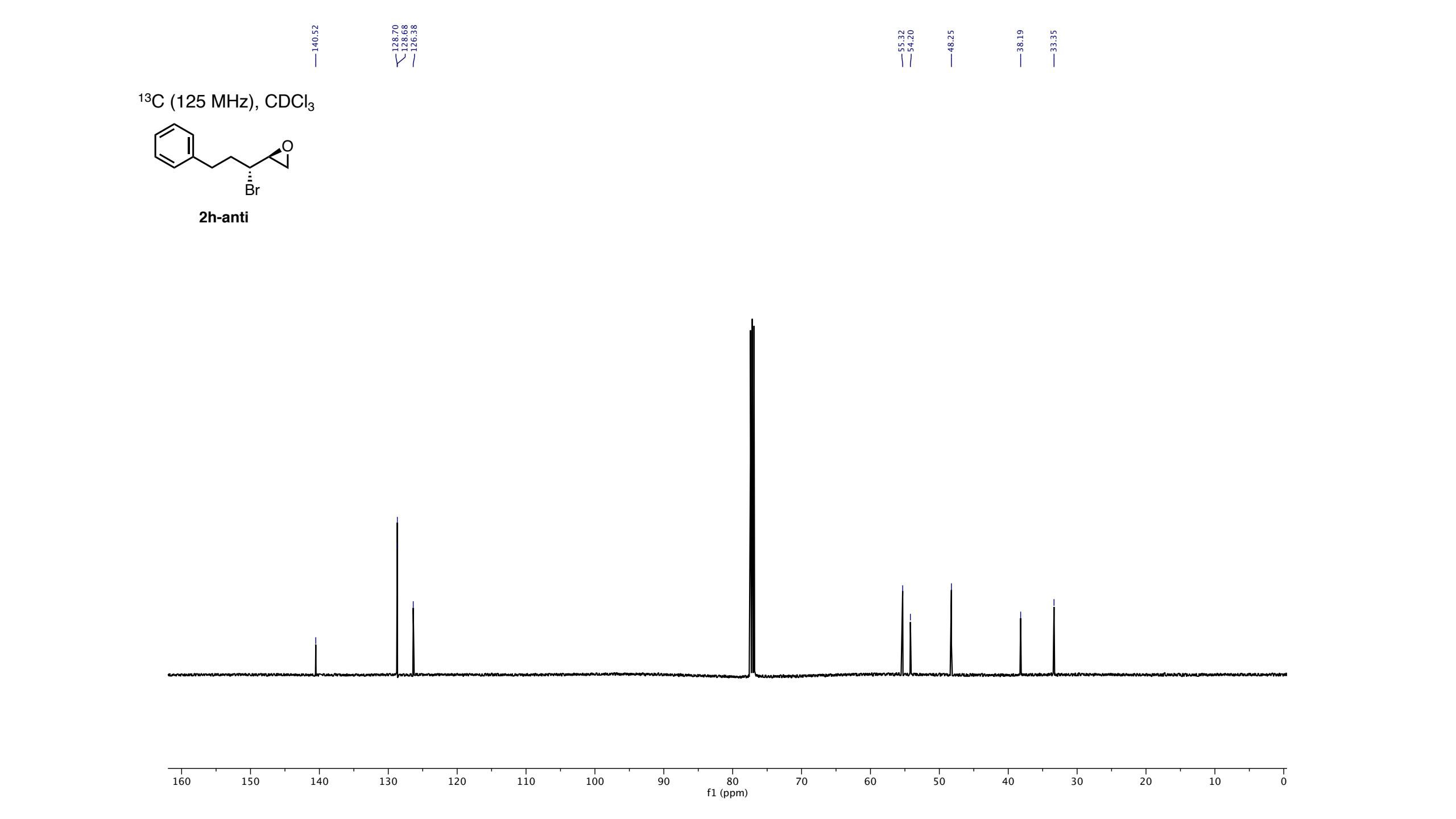


2h

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



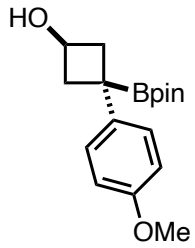
2h-anti



^{13}C (125 MHz), $CDCl_3$

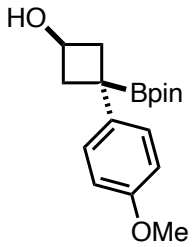
2h-anti

^{1}H (400 MHz), $CDCl_3$



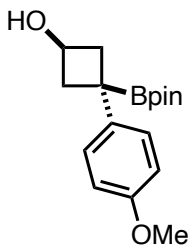
3a

^{11}B (128 MHz), $CDCl_3$



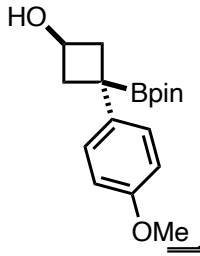
3a

^{13}C (100 MHz), $CDCl_3$

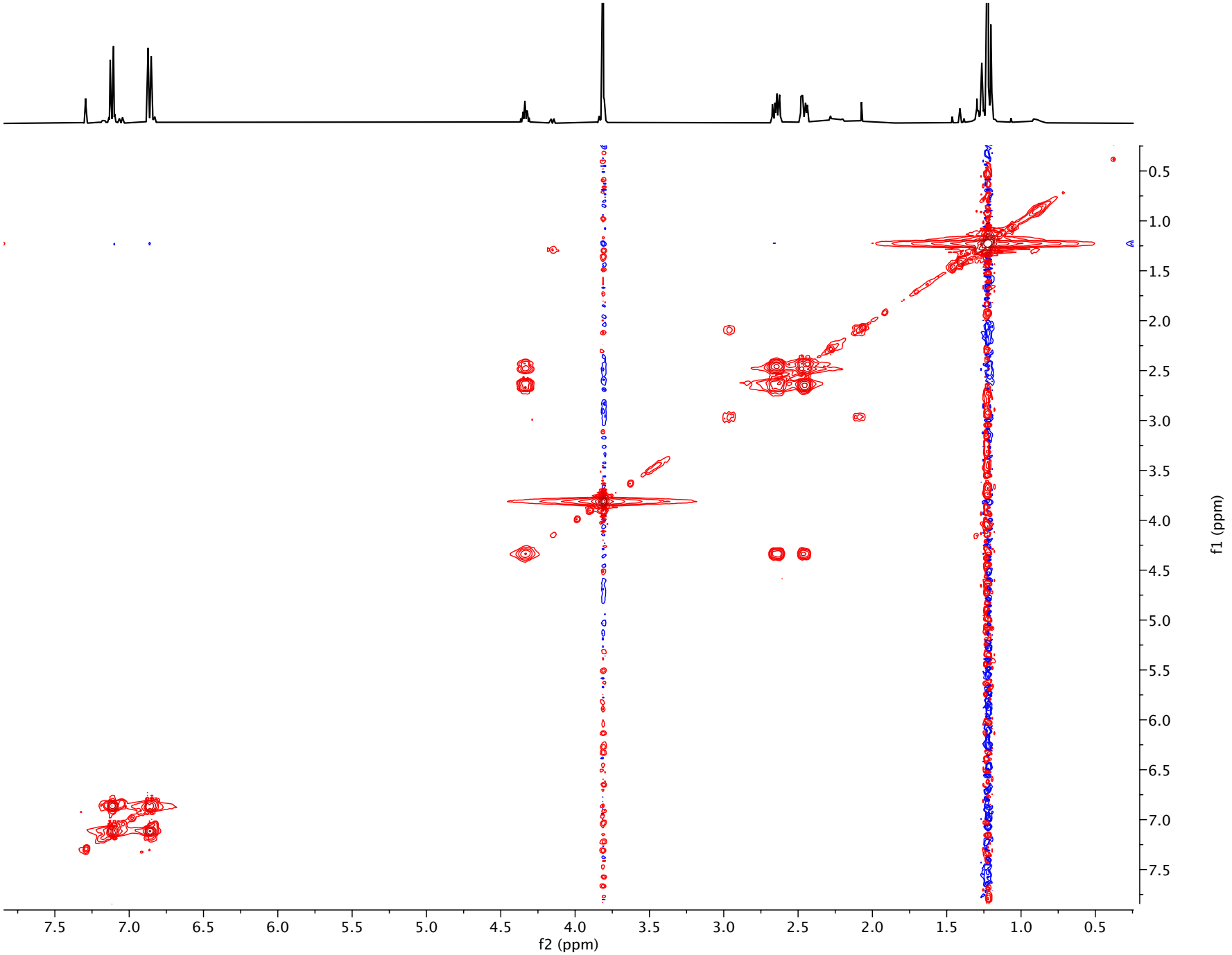


3a

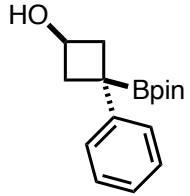
^{1}H (400 MHz), $CDCl_3$



3a

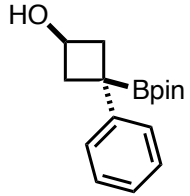


^{1}H (400 MHz), $CDCl_3$



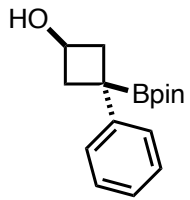
3b

^{11}B (128 MHz), $CDCl_3$



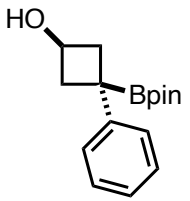
3b

^{13}C (125 MHz), $CDCl_3$



3b

^{1}H (400 MHz), $CDCl_3$

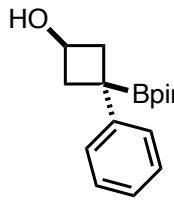


3b

f2 (ppm)

f1 (ppm)

^{1}H (400 MHz), $CDCl_3$
NOESY

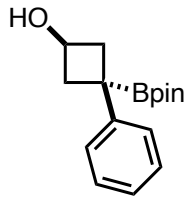


3b

f2 (ppm)

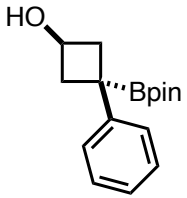
f1 (ppm)

^{1}H (400 MHz), $CDCl_3$



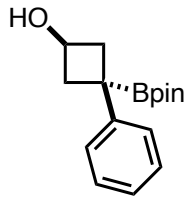
3b-*minor*

^{11}B (128 MHz), $CDCl_3$



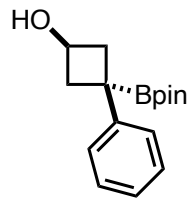
3b-*minor*

^{13}C (100 MHz), $CDCl_3$

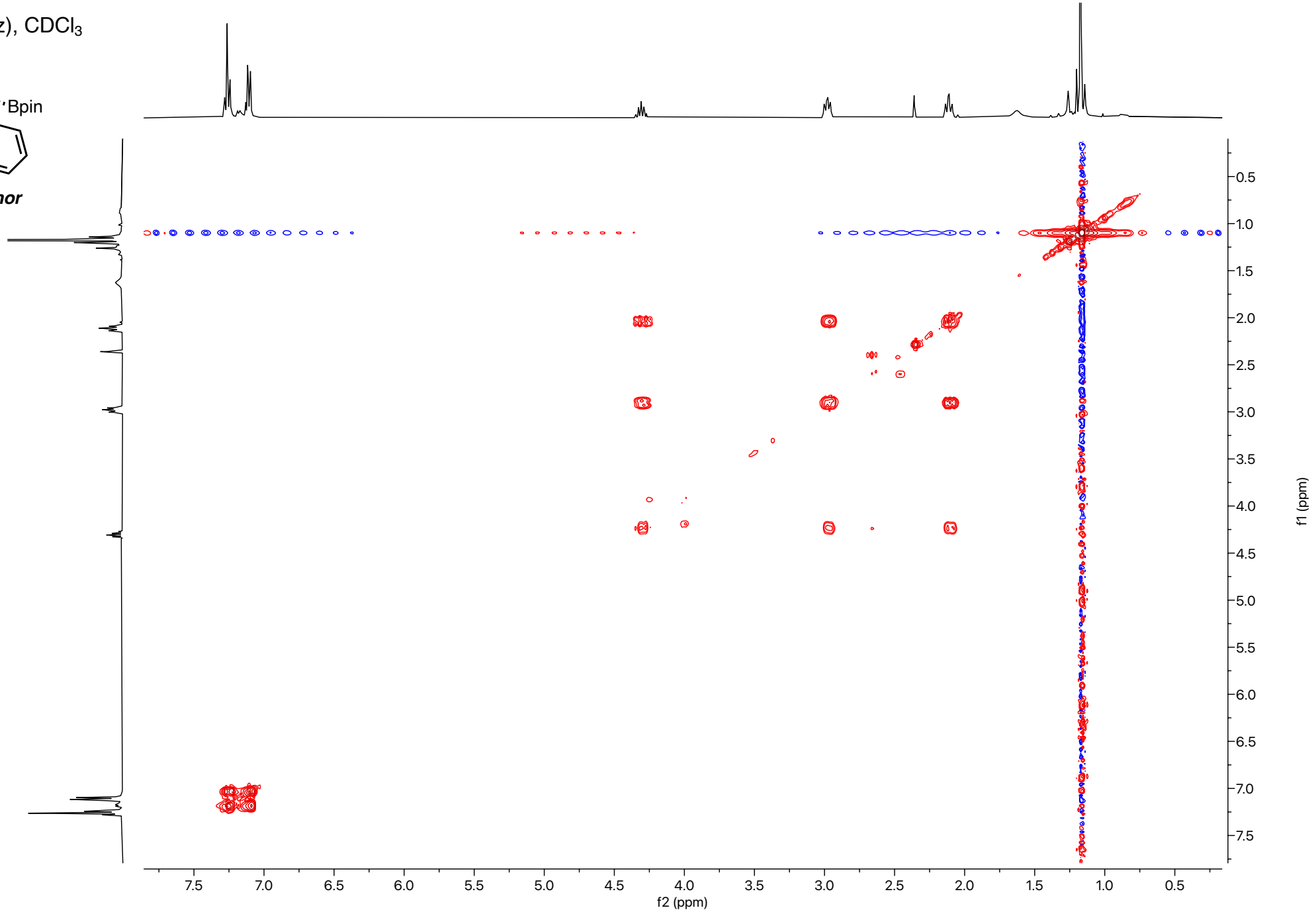


3b-*minor*

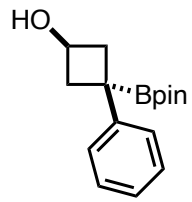
^{1}H (400 MHz), $CDCl_3$



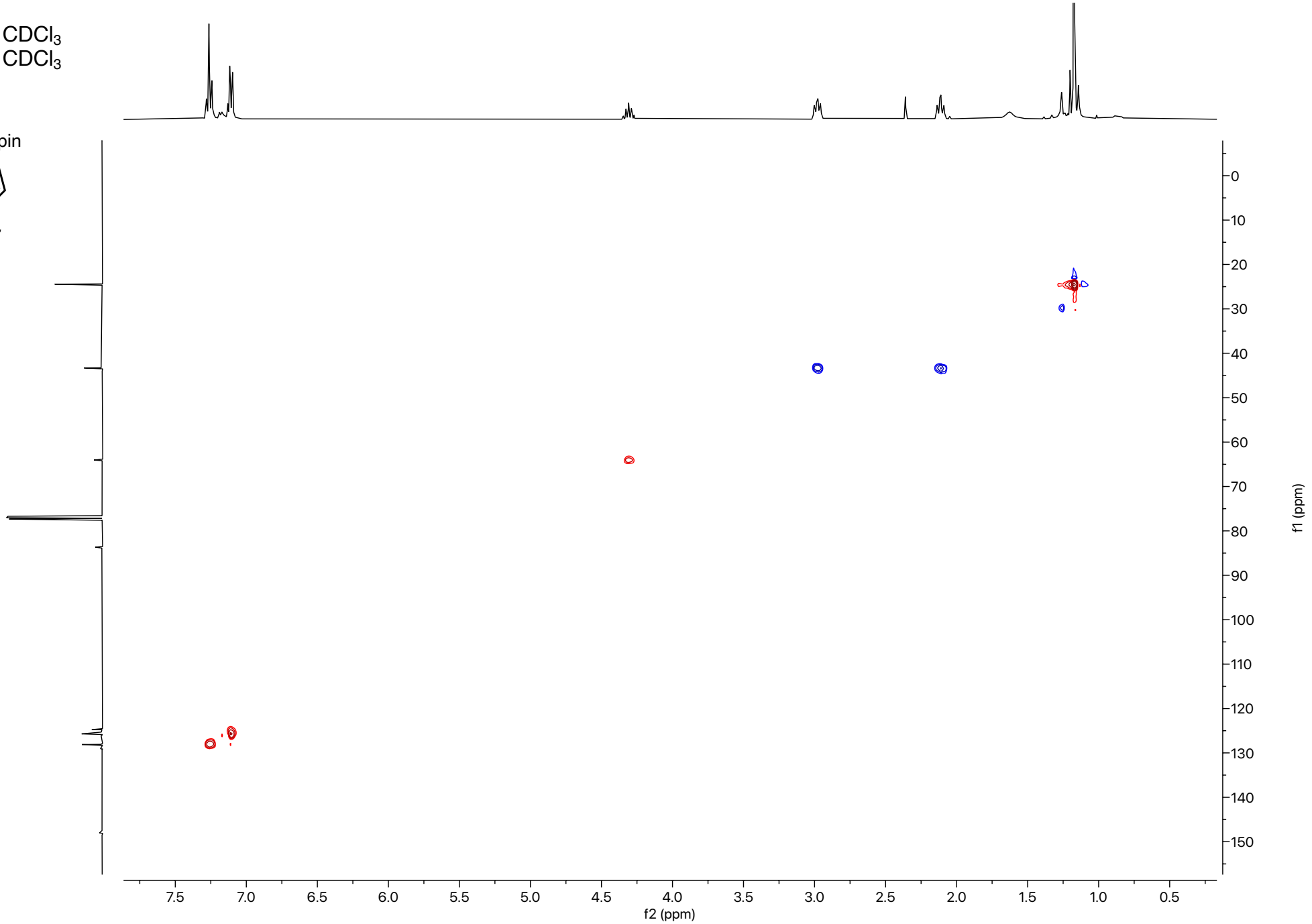
3b-*minor*



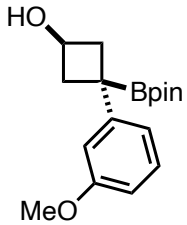
^{1}H (400 MHz), $CDCl_3$
^{13}C (100 MHz), $CDCl_3$



3b-*minor*

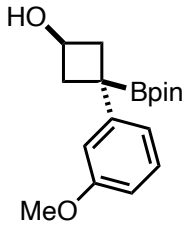


^{1}H (400 MHz), $CDCl_3$



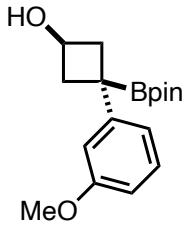
3c

^{11}B (128 MHz), $CDCl_3$



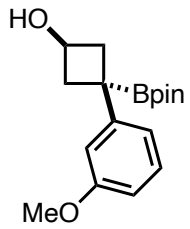
3c

^{13}C (100 MHz), $CDCl_3$

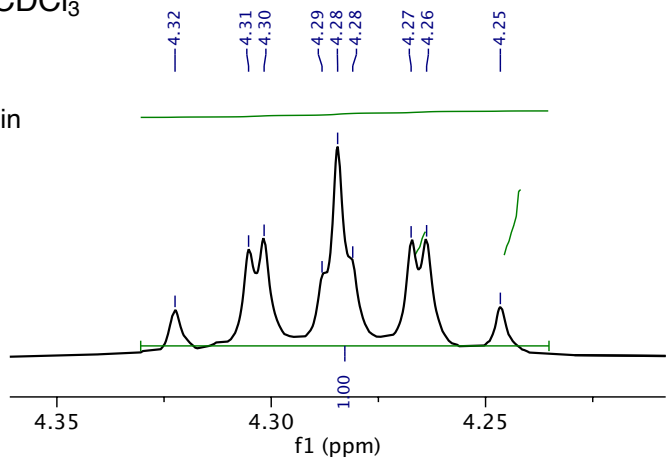


3c

^{1}H (400 MHz), $CDCl_3$

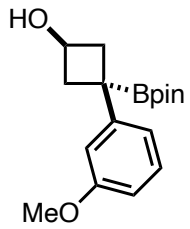


3c-*minor*

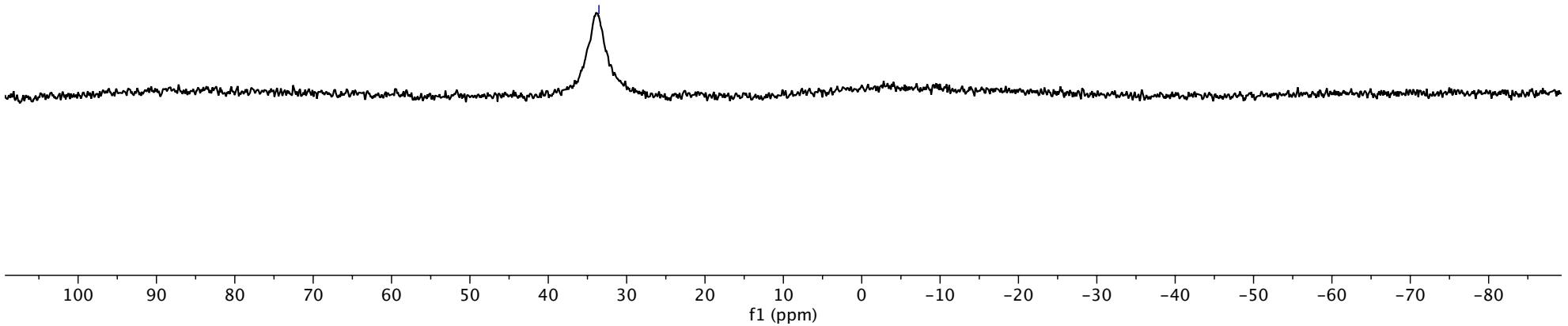


33.53

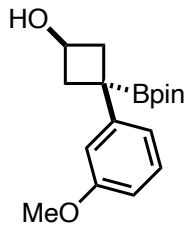
^{11}B (128 MHz), $CDCl_3$



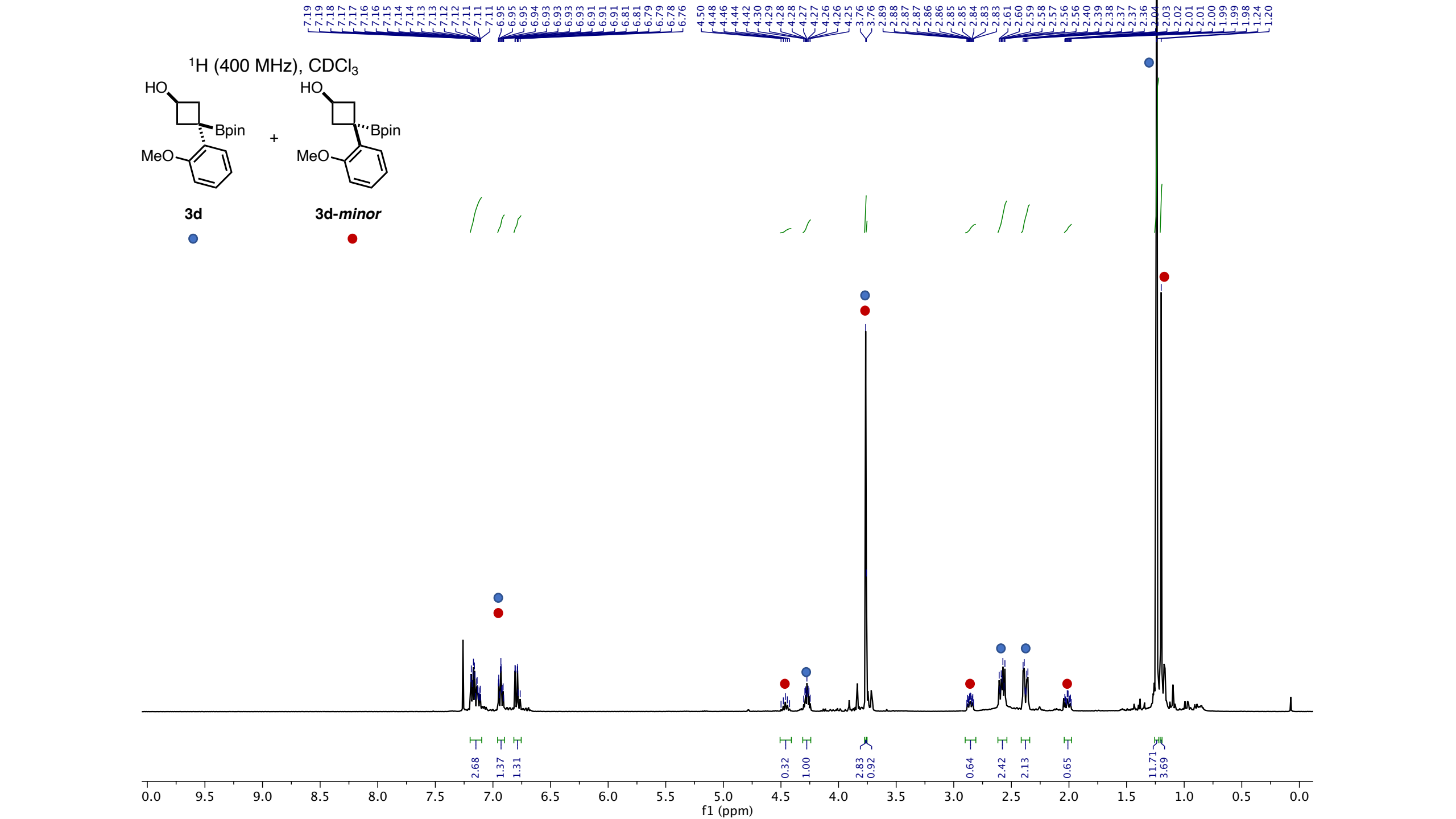
3c-*minor*



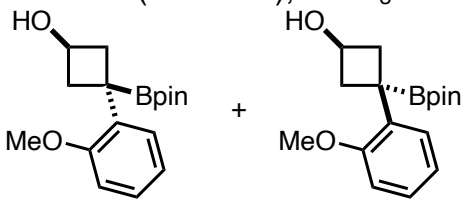
^{13}C (100 MHz), $CDCl_3$



3c-*minor*


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
MeO
+
HO
Bpin
MeO
3d
3d-*minor*
f1 (ppm)

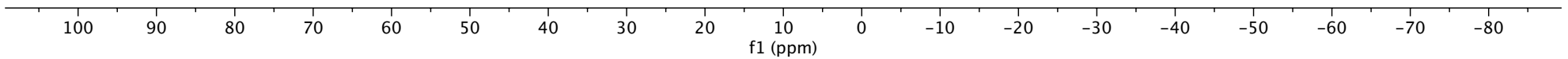
^{11}B (128 MHz), $CDCl_3$

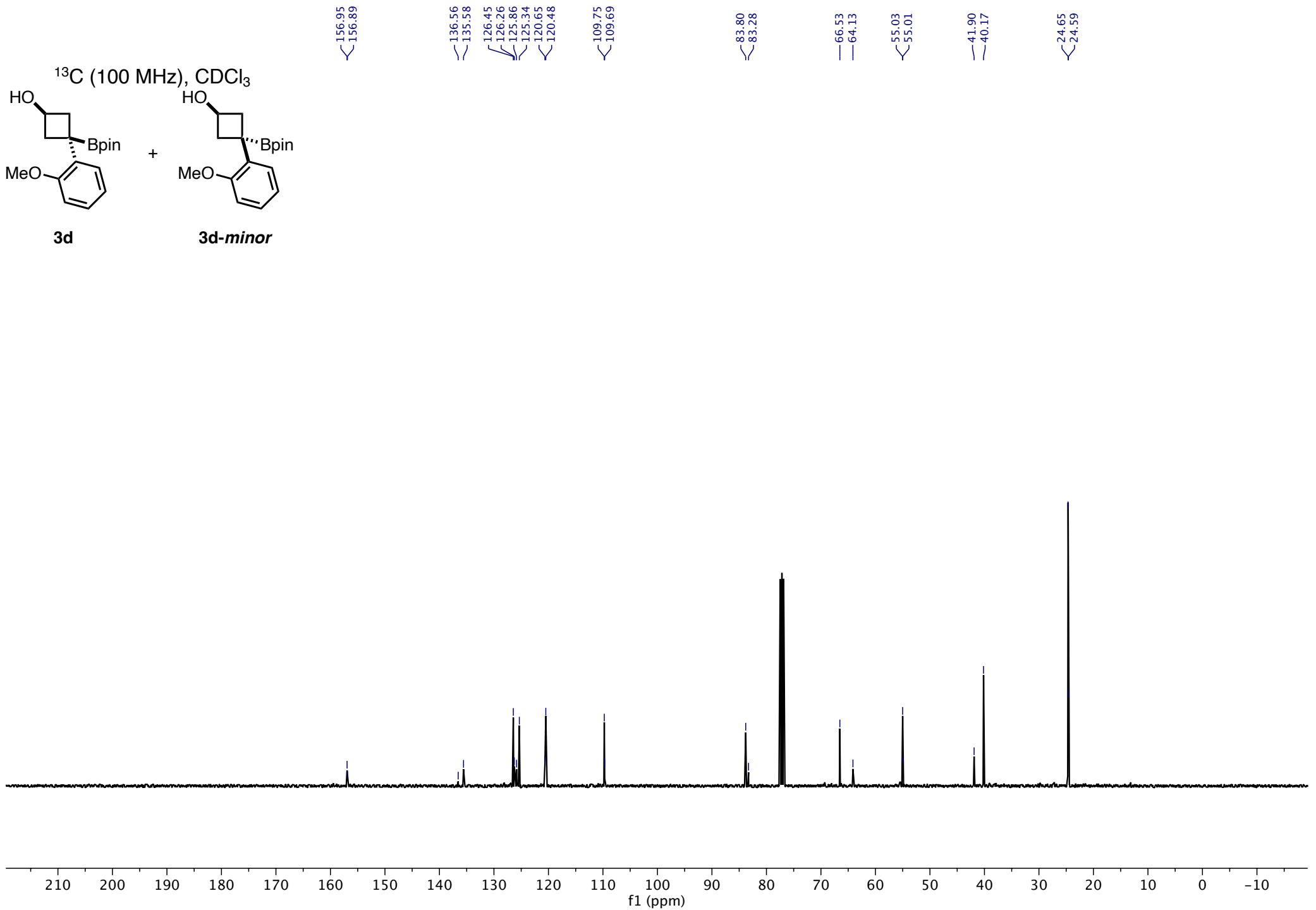


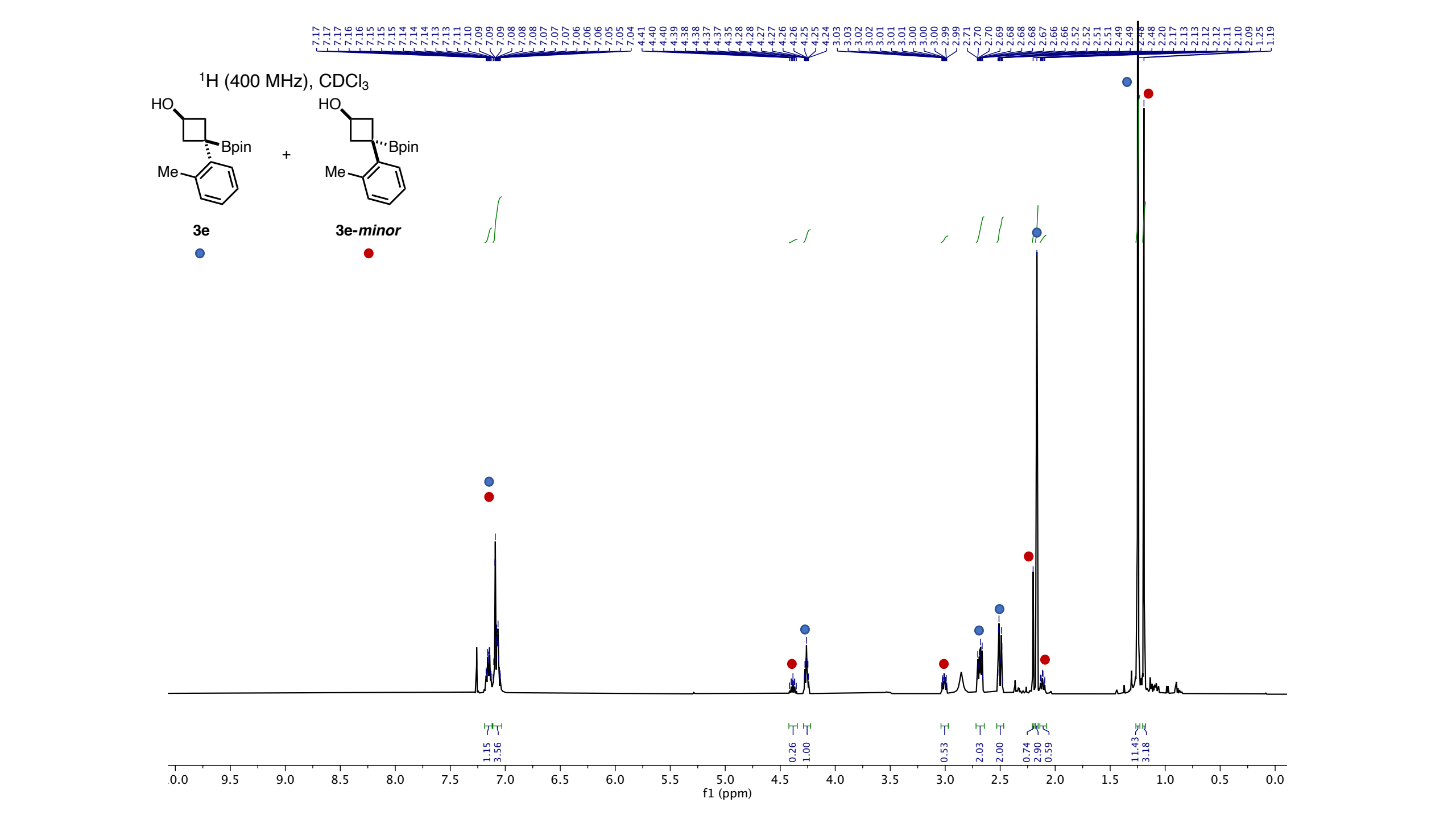
+

3d **3d-*minor***

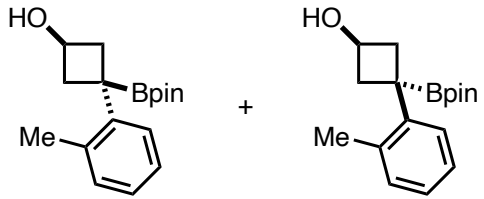
33.99




156.95
156.89
136.56
135.58
126.45
126.26
125.86
125.34
120.65
120.48
109.75
109.69
83.80
83.28
66.53
64.13
55.03
55.01
41.90
40.17
24.65
24.59
13C (100 MHz), CDCl3
HO
Bpin
MeO
+
HO
Bpin
MeO
3d
3d-minor
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
Me
+
HO
Bpin
Me
3e
3e-*minor*
7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.14 7.13 7.13 7.11 7.10 7.09 7.09 7.09 7.08 7.08 7.08 7.07 7.07 7.07 7.06 7.06 7.06 7.05 7.05 7.04
4.41 4.40 4.40 4.39 4.38 4.38 4.37 4.37 4.35 4.28 4.27 4.27 4.26 4.26 4.25 4.24
3.03 3.02 3.02 3.01 3.01 3.01 3.00 3.00 3.00 2.99 2.99
2.71 2.70 2.70 2.69 2.68 2.68 2.67 2.66 2.66 2.52 2.51 2.51 2.49 2.49 2.48 2.48 2.20 2.17 2.13 2.12 2.12 2.11 2.10 2.09 1.25 1.19
1.15
3.56
0.26
1.00
0.53
2.03
2.00
0.74
2.90
0.59
11.43
3.18
f1 (ppm)

^{11}B (128 MHz), $CDCl_3$

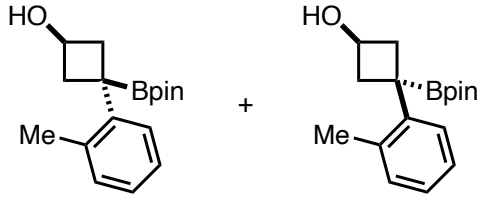


3e

+

3e-*minor*

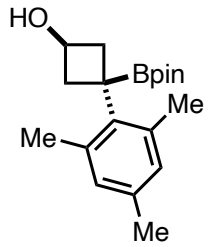
^{13}C (100 MHz), $CDCl_3$



+

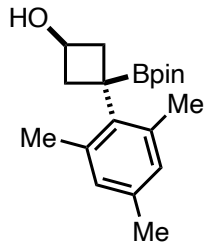
3e **3e-*minor***

^{1}H (400 MHz), $CDCl_3$



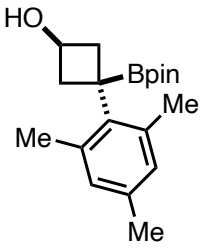
3f

^{11}B (128 MHz), $CDCl_3$



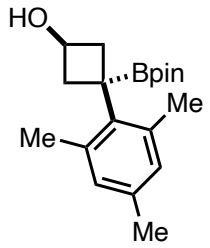
3f

^{13}C (125 MHz), $CDCl_3$



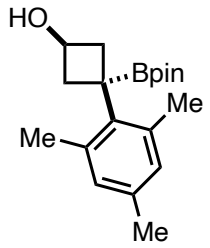
3f

^{1}H (400 MHz), $CDCl_3$



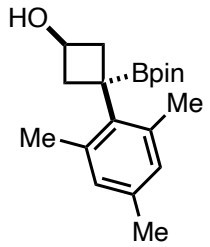
3f-*minor*

^{11}B (128 MHz), $CDCl_3$



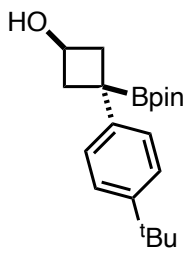
3f-*minor*

^{13}C (125 MHz), $CDCl_3$



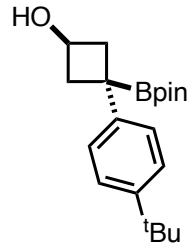
3f-*minor*

^{1}H (400 MHz), $CDCl_3$



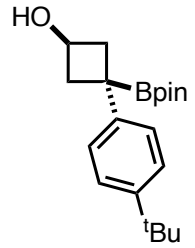
3g

^{11}B (128 MHz), $CDCl_3$



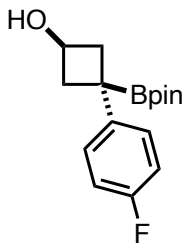
3g

^{13}C (125 MHz), $CDCl_3$

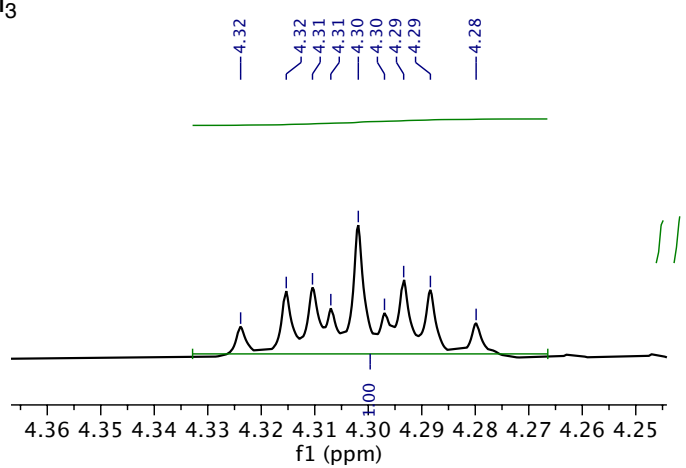


3g

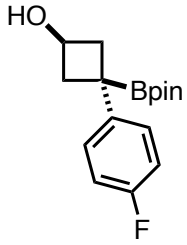
^{1}H (500 MHz), $CDCl_3$



3h

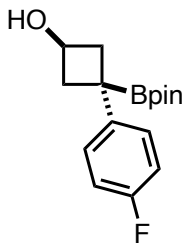


^{11}B (128 MHz), $CDCl_3$



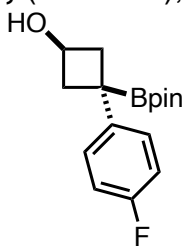
3h

^{13}C (125 MHz), $CDCl_3$



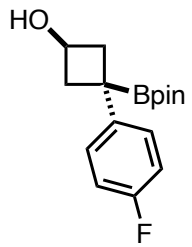
3h

^{19}F {^{1}H} (376 MHz), $CDCl_3$

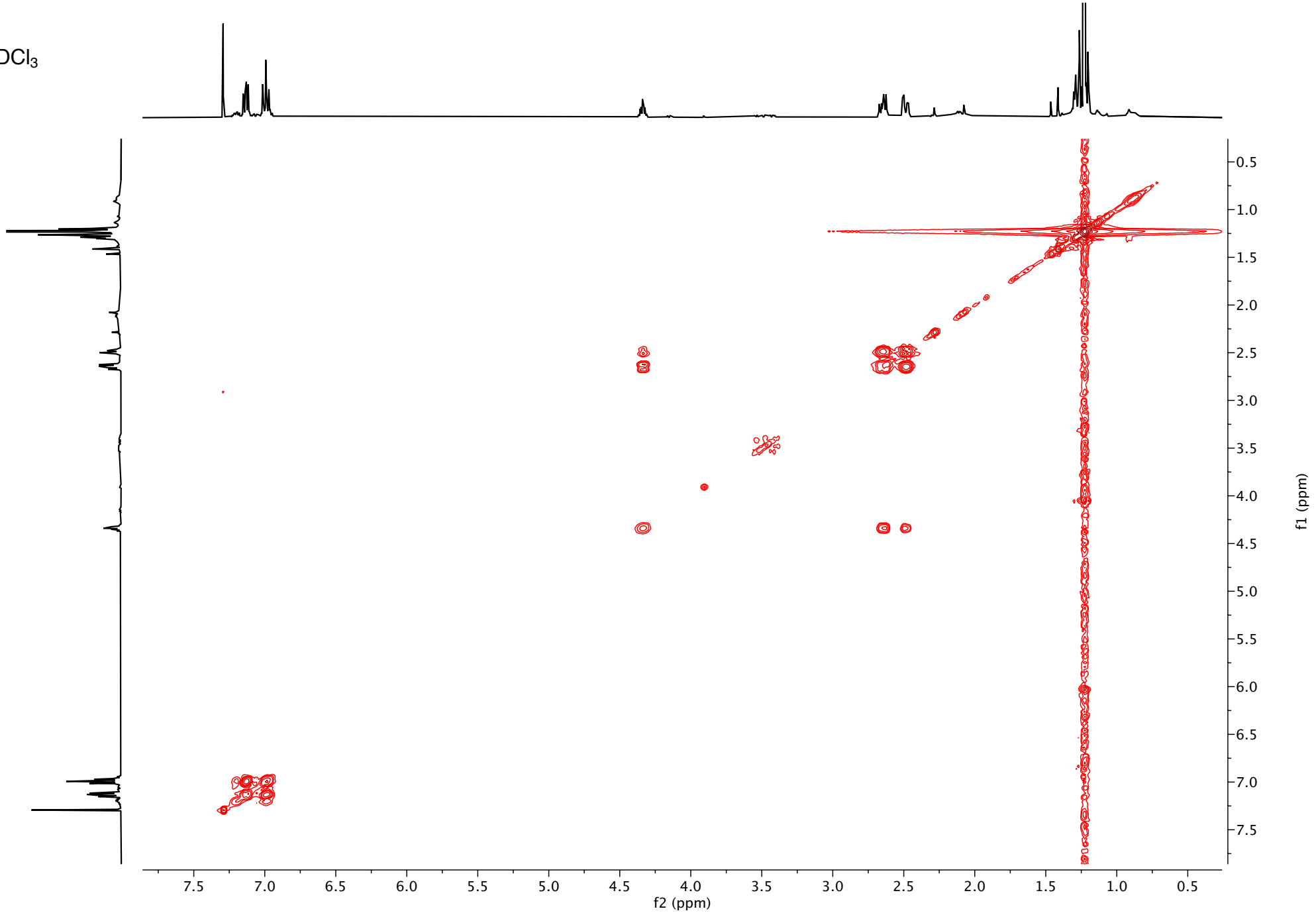


3h

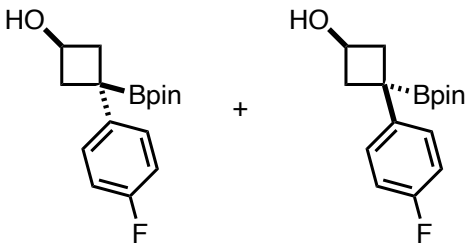
^{1}H (400 MHz), $CDCl_3$



3h



^{1}H (400 MHz), $CDCl_3$

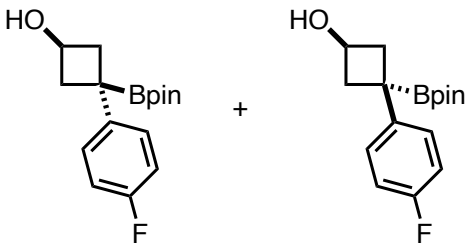


3h

+

3h-*minor*

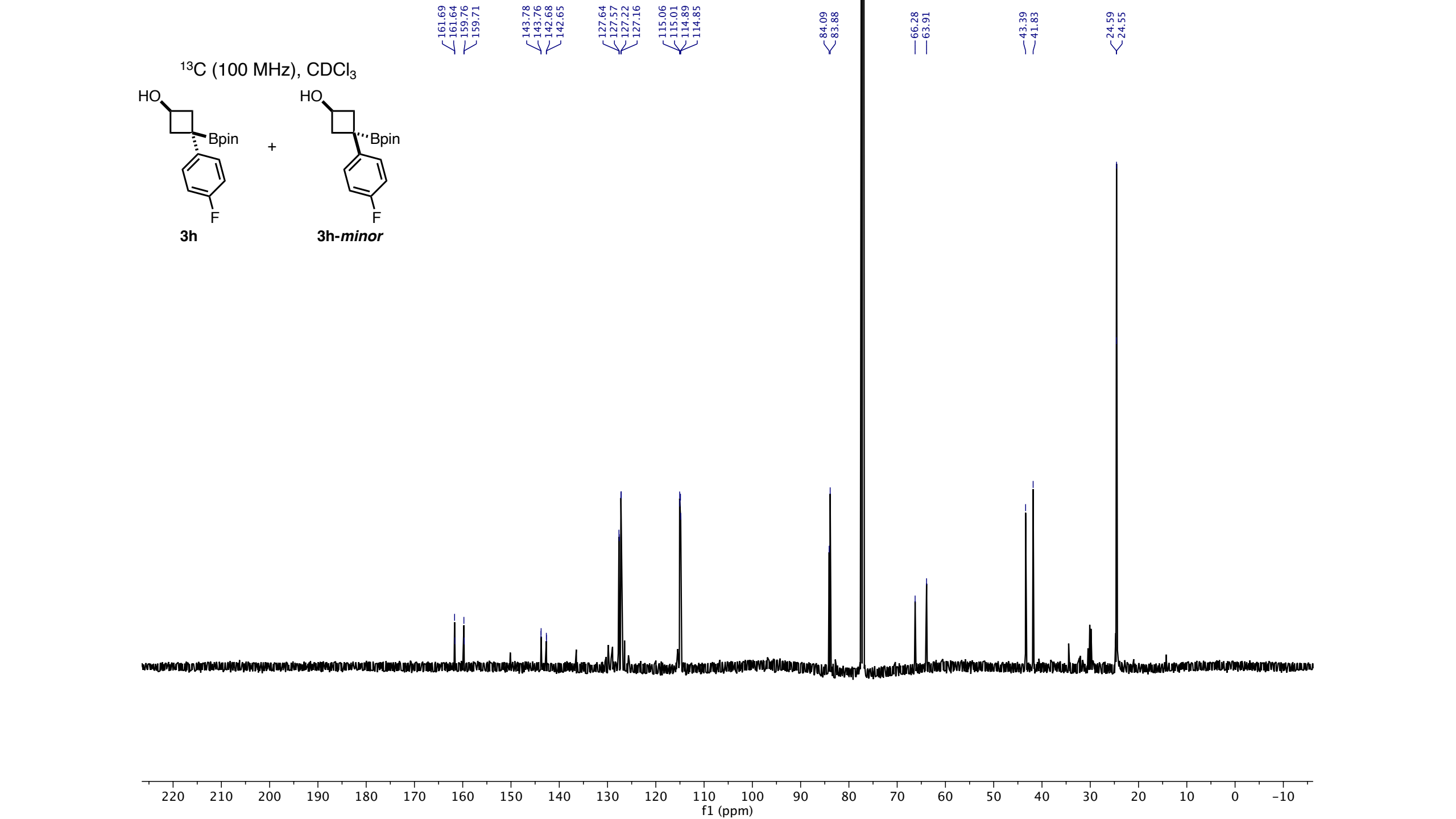
^{11}B (128 MHz), $CDCl_3$

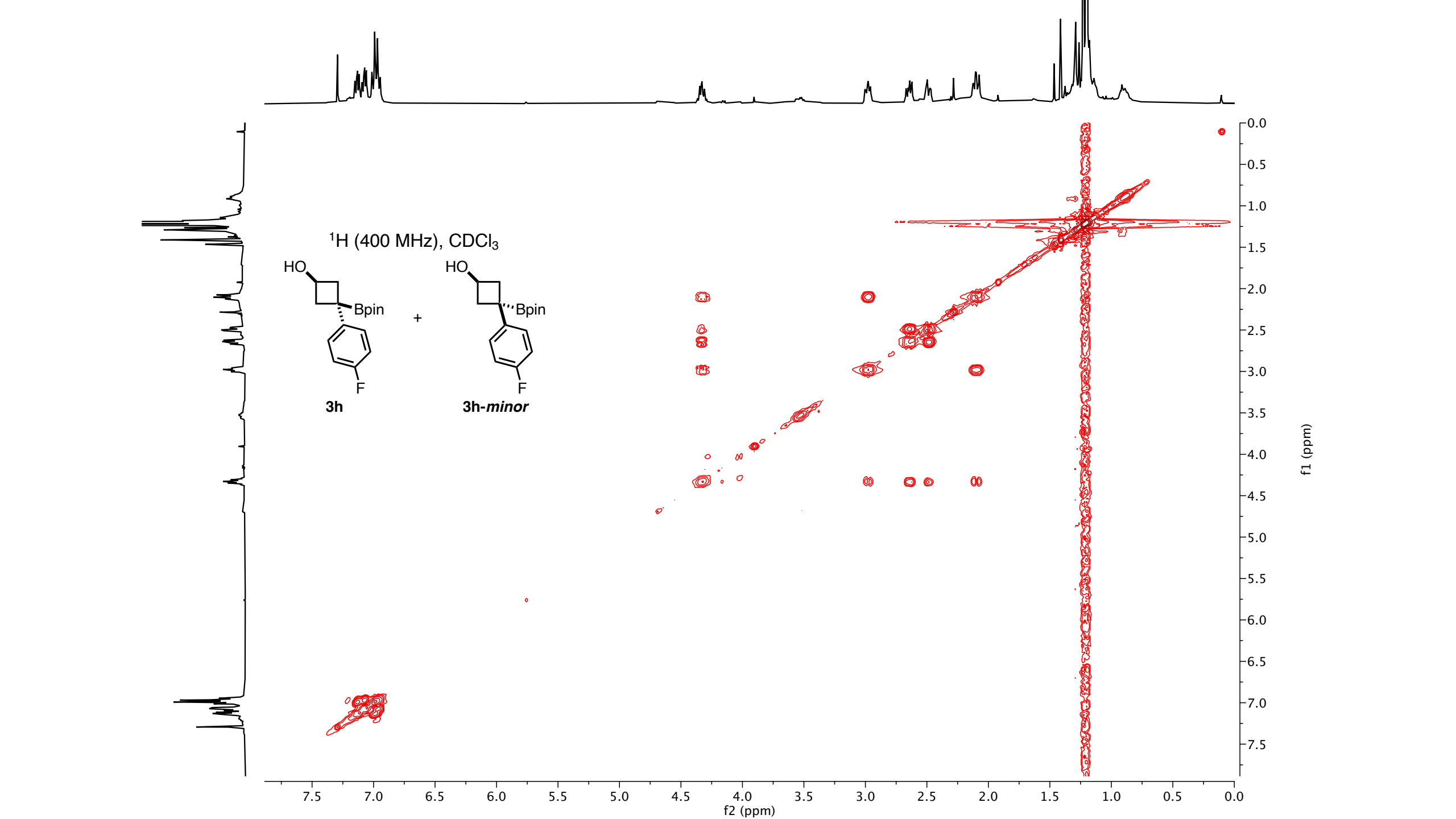


3h

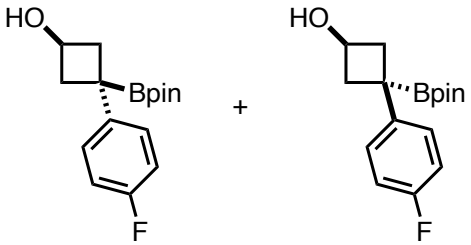
+

3h-*minor*


161.69
161.64
159.76
159.71
143.78
143.76
142.68
142.65
127.64
127.57
127.22
127.16
115.06
115.01
114.89
114.85
84.09
83.88
66.28
63.91
43.39
41.83
24.59
24.55
13C (100 MHz), CDCl3
HO
Bpin
F
+
HO
Bpin
F
3h
3h-minor
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
F
+
HO
Bpin
F
3h
3h-*minor*
f2 (ppm)
f1 (ppm)

^{19}F {^{1}H} (376 MHz), $CDCl_3$

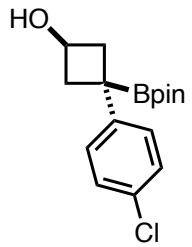


3h

+

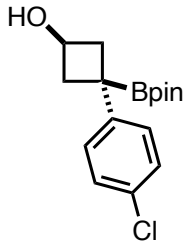
3h-*minor*

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



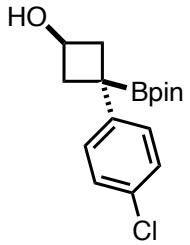
3i

^{11}B (128 MHz), $CDCl_3$



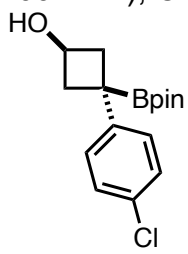
3i

^{13}C (125 MHz), $CDCl_3$

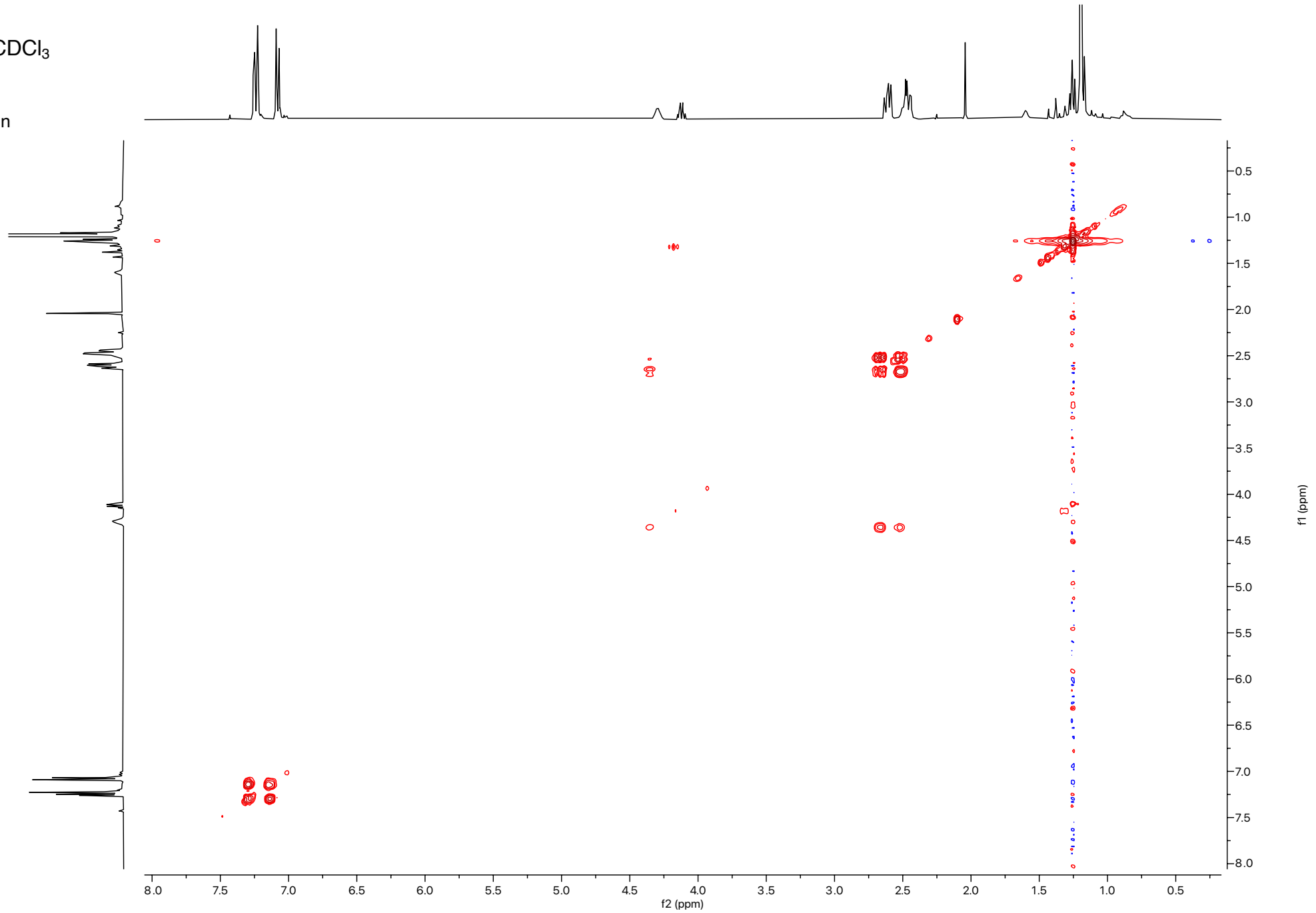


3i

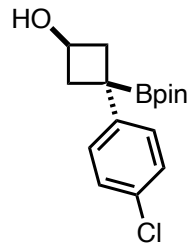
^{1}H (400 MHz), $CDCl_3$



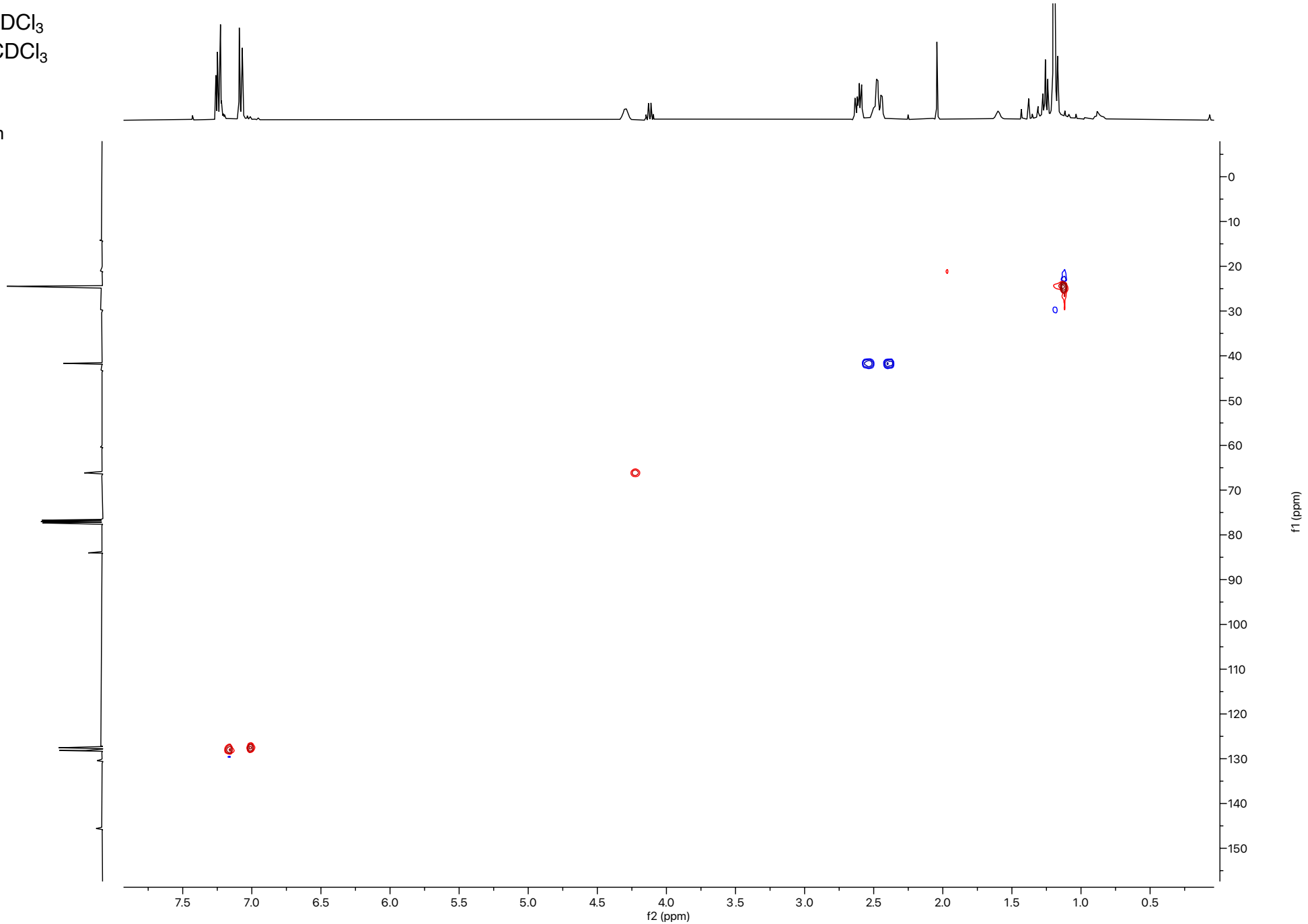
3i



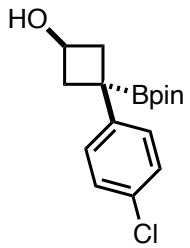
^{1}H (400 MHz), $CDCl_3$
^{13}C (125 MHz), $CDCl_3$



3i

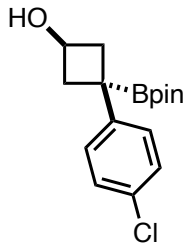


^{1}H (500 MHz), $CDCl_3$



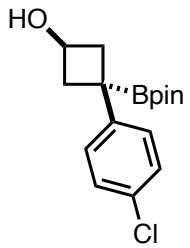
3i-*minor*

^{11}B (128 MHz), $CDCl_3$



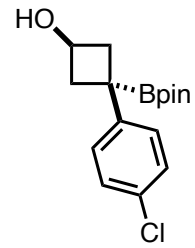
3i-*minor*

^{13}C (125 MHz), $CDCl_3$

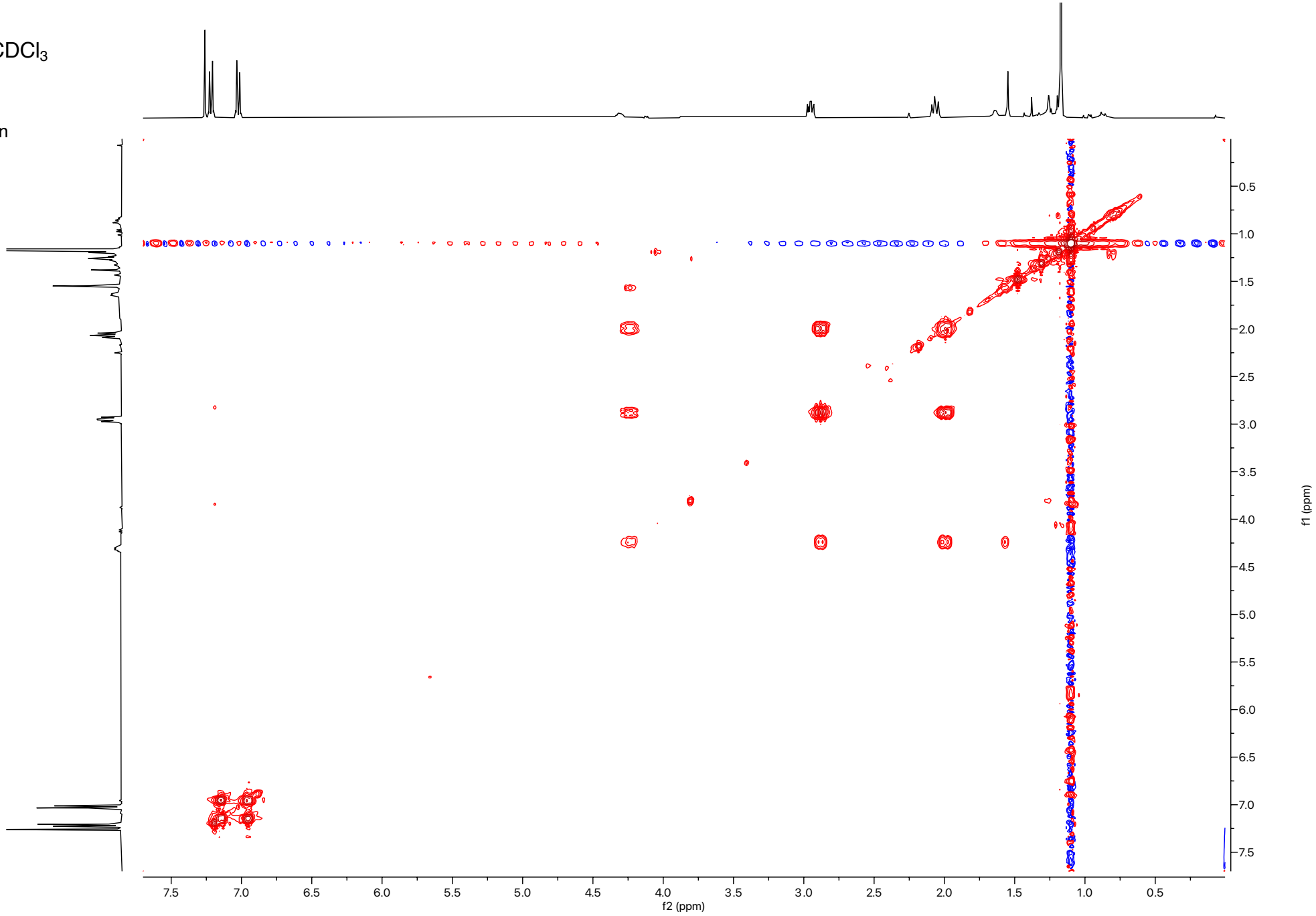


3i-*minor*

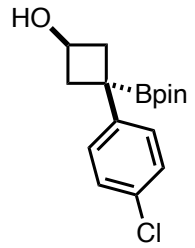
^{1}H (400 MHz), $CDCl_3$



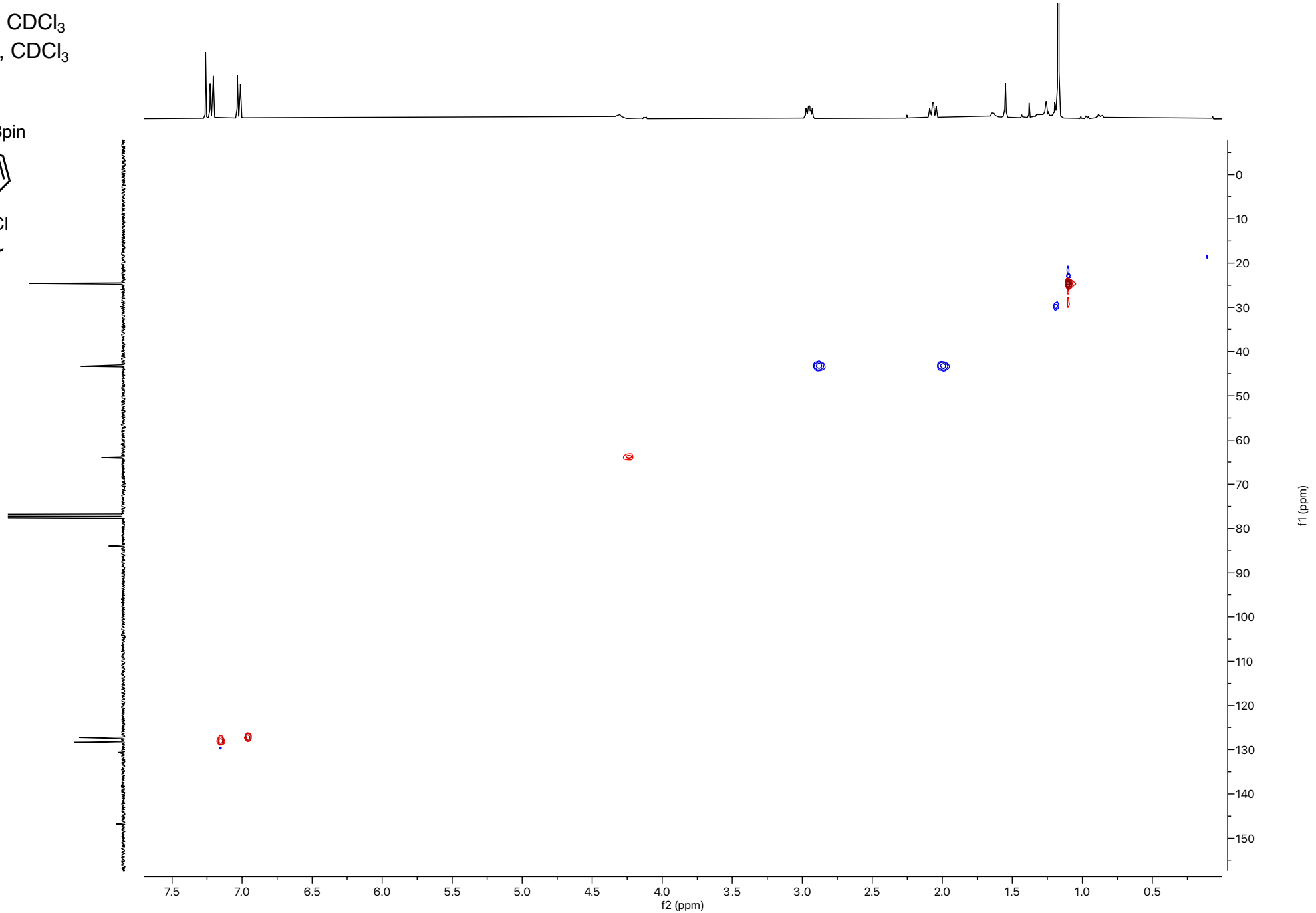
3i-*minor*



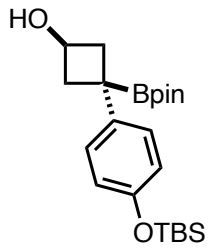
^{1}H (400 MHz), $CDCl_3$
^{13}C (125 MHz), $CDCl_3$



3i-*minor*

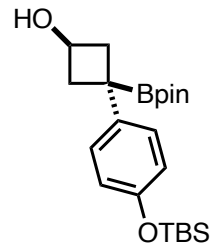


^{1}H (400 MHz), $CDCl_3$



3j

^{1}H (400 MHz), $CDCl_3$

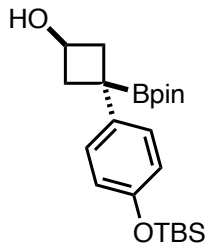


3j

f2 (ppm)

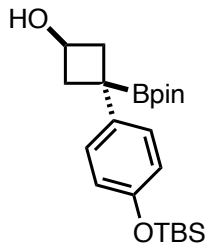
f1 (ppm)

^{11}B (128 MHz), $CDCl_3$



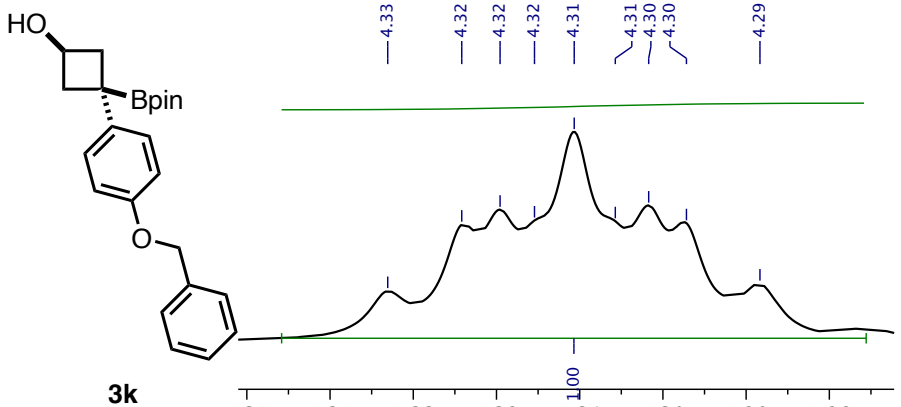
3j

^{13}C (100 MHz), $CDCl_3$



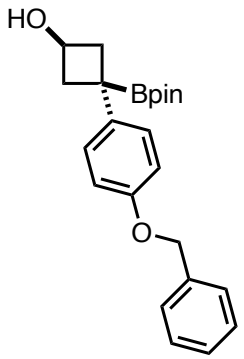
3j

^{1}H (400 MHz), $CDCl_3$



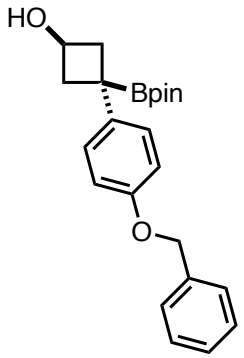
3k

^{11}B (128 MHz), $CDCl_3$

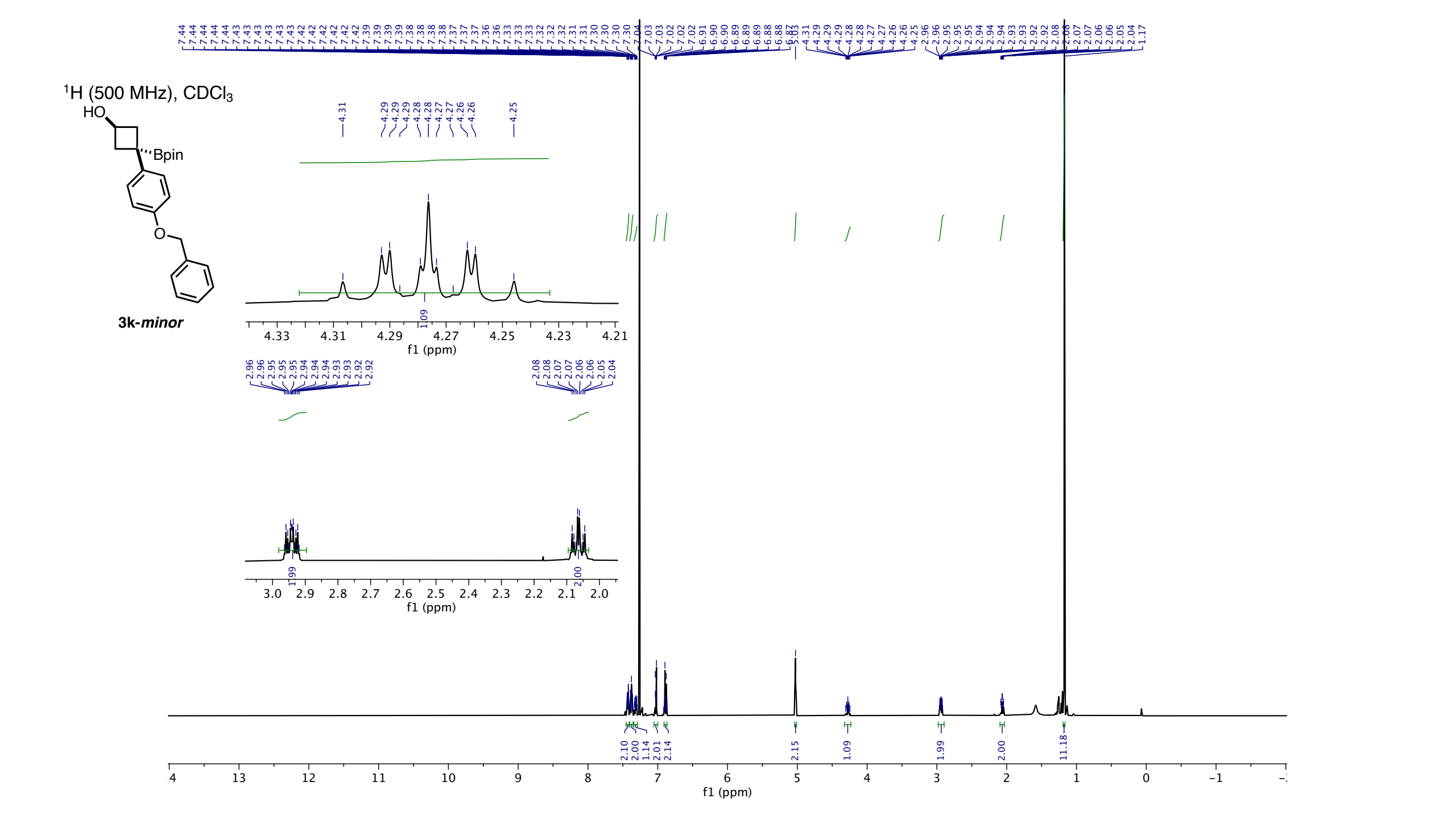


3k

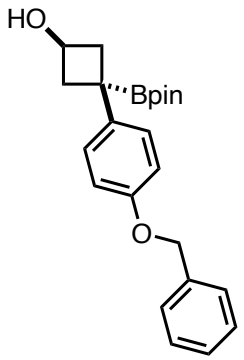
^{13}C (100 MHz), $CDCl_3$



3k

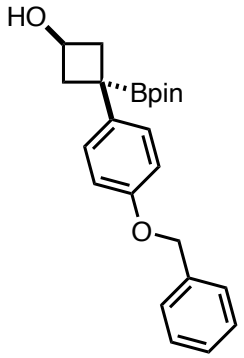

^{1}H (500 MHz), $CDCl_3$
HO
Bpin
O
3k-*minor*
f1 (ppm)

^{11}B (128 MHz), $CDCl_3$



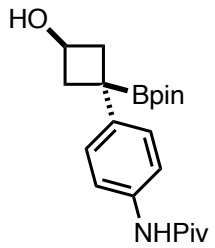
3k-*minor*

^{13}C (125 MHz), $CDCl_3$



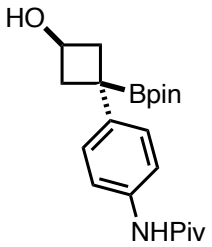
3k-*minor*

^{1}H (400 MHz), $CDCl_3$



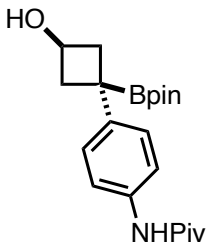
3l

^{11}B (128 MHz), $CDCl_3$



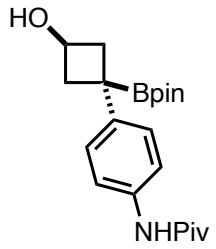
3l

^{13}C (100 MHz), $CDCl_3$

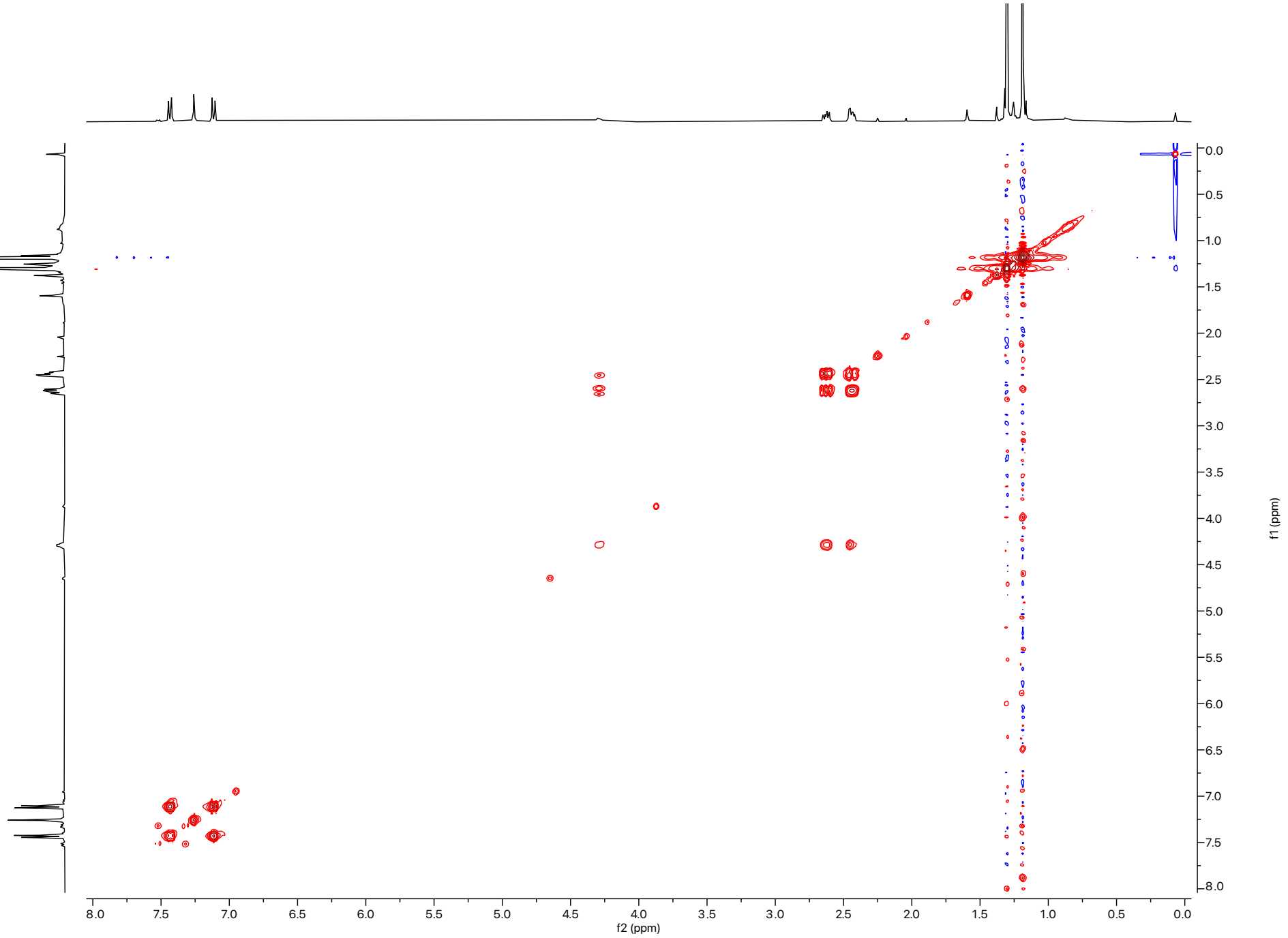


3l

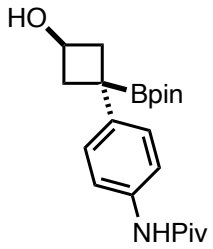
^{1}H (400 MHz), $CDCl_3$



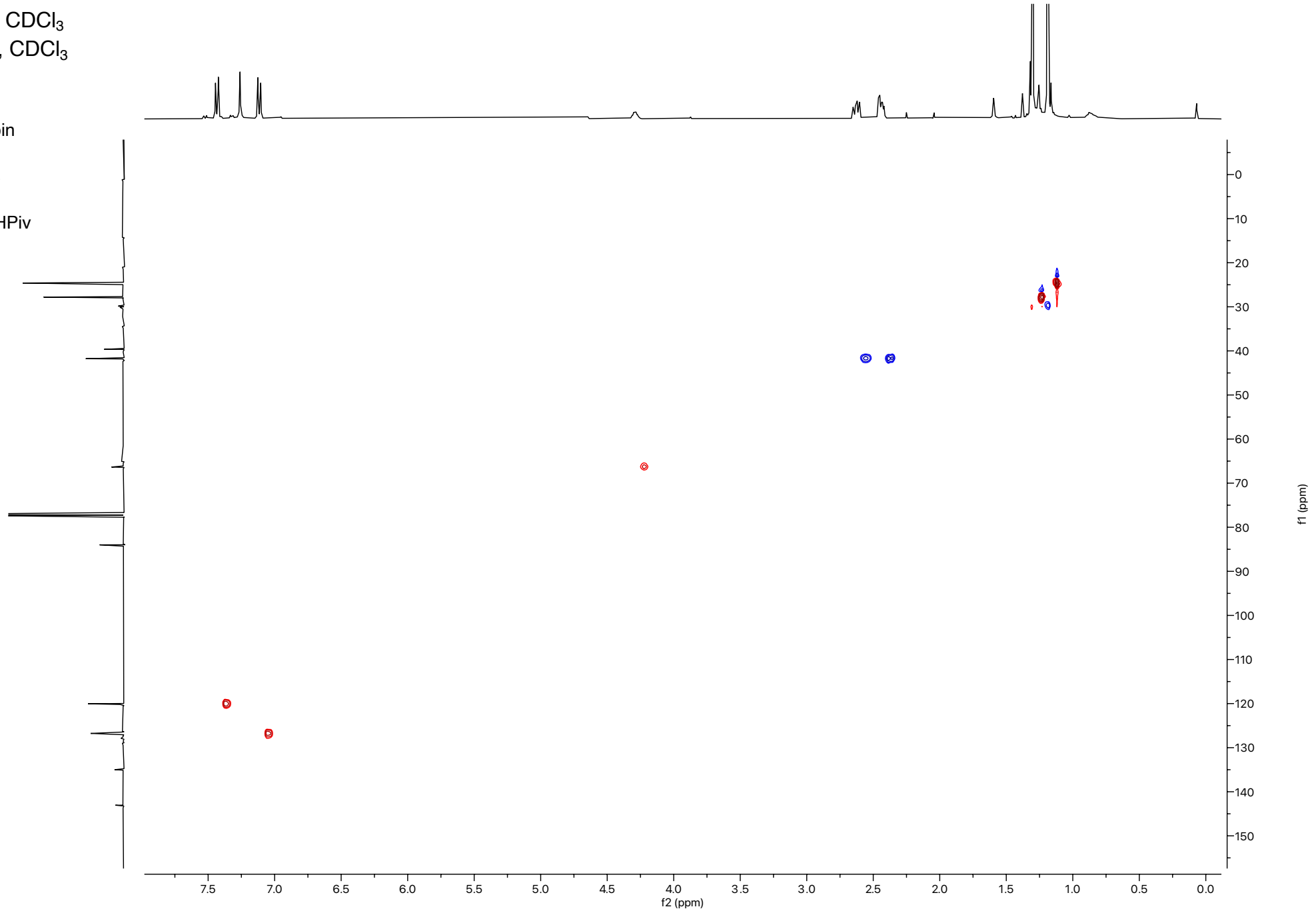
3l



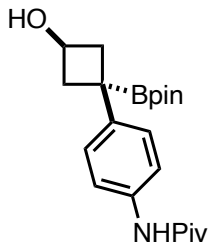
^{1}H (400 MHz), $CDCl_3$
^{13}C (100 MHz), $CDCl_3$



3l

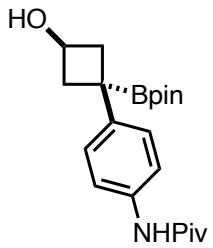


^{1}H (500 MHz), $CDCl_3$



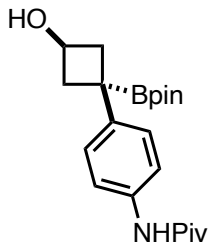
3l-*minor*

^{11}B (128 MHz), $CDCl_3$



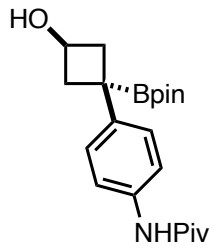
3l-*minor*

^{13}C (125 MHz), $CDCl_3$

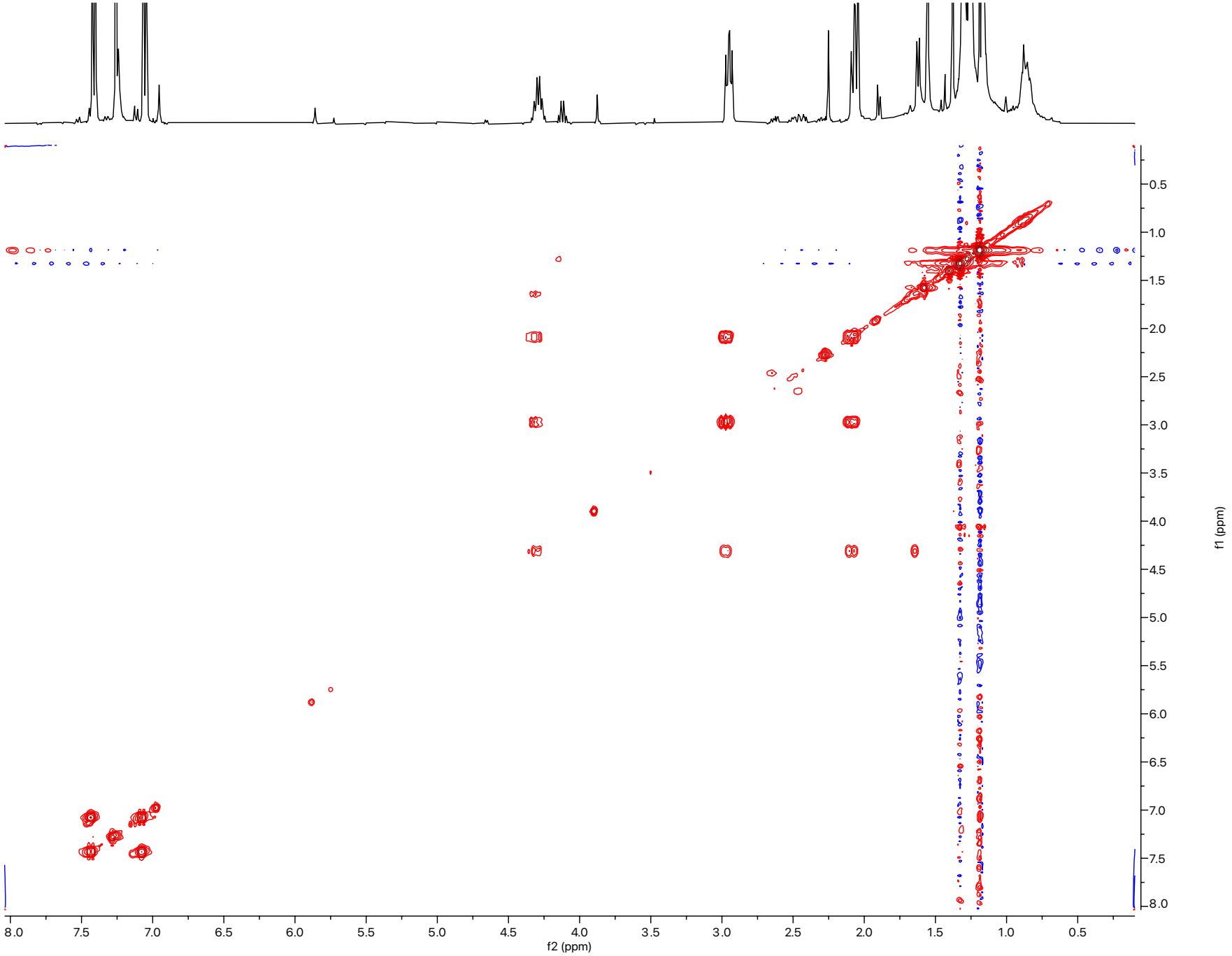


3l-*minor*

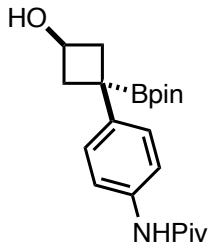
^{1}H (400 MHz), $CDCl_3$



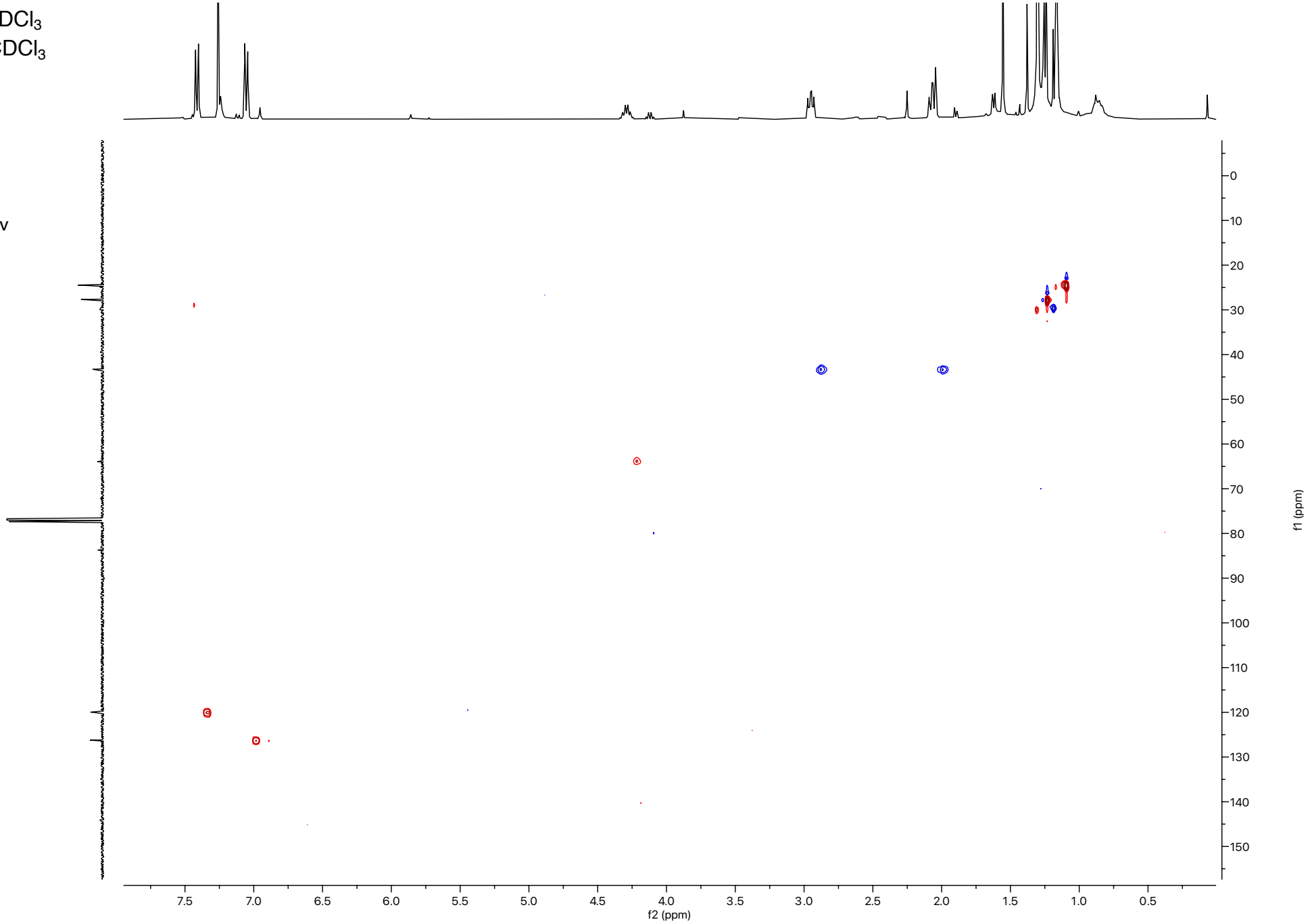
3l-*minor*



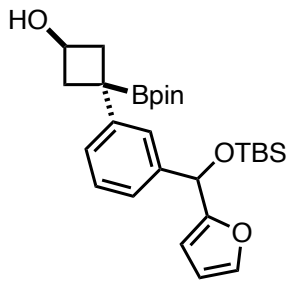
^{1}H (500 MHz), $CDCl_3$
^{13}C (125 MHz), $CDCl_3$



3l-*minor*

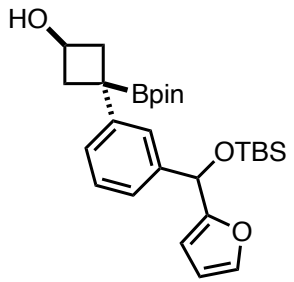


^{1}H (400 MHz), $CDCl_3$



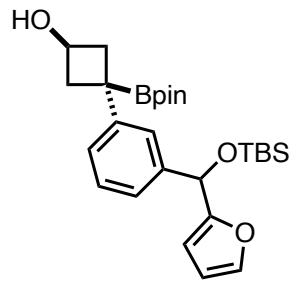
3m

^{11}B (128 MHz), $CDCl_3$



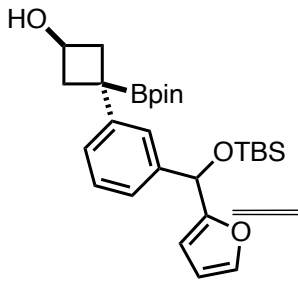
3m

^{13}C (125 MHz), $CDCl_3$

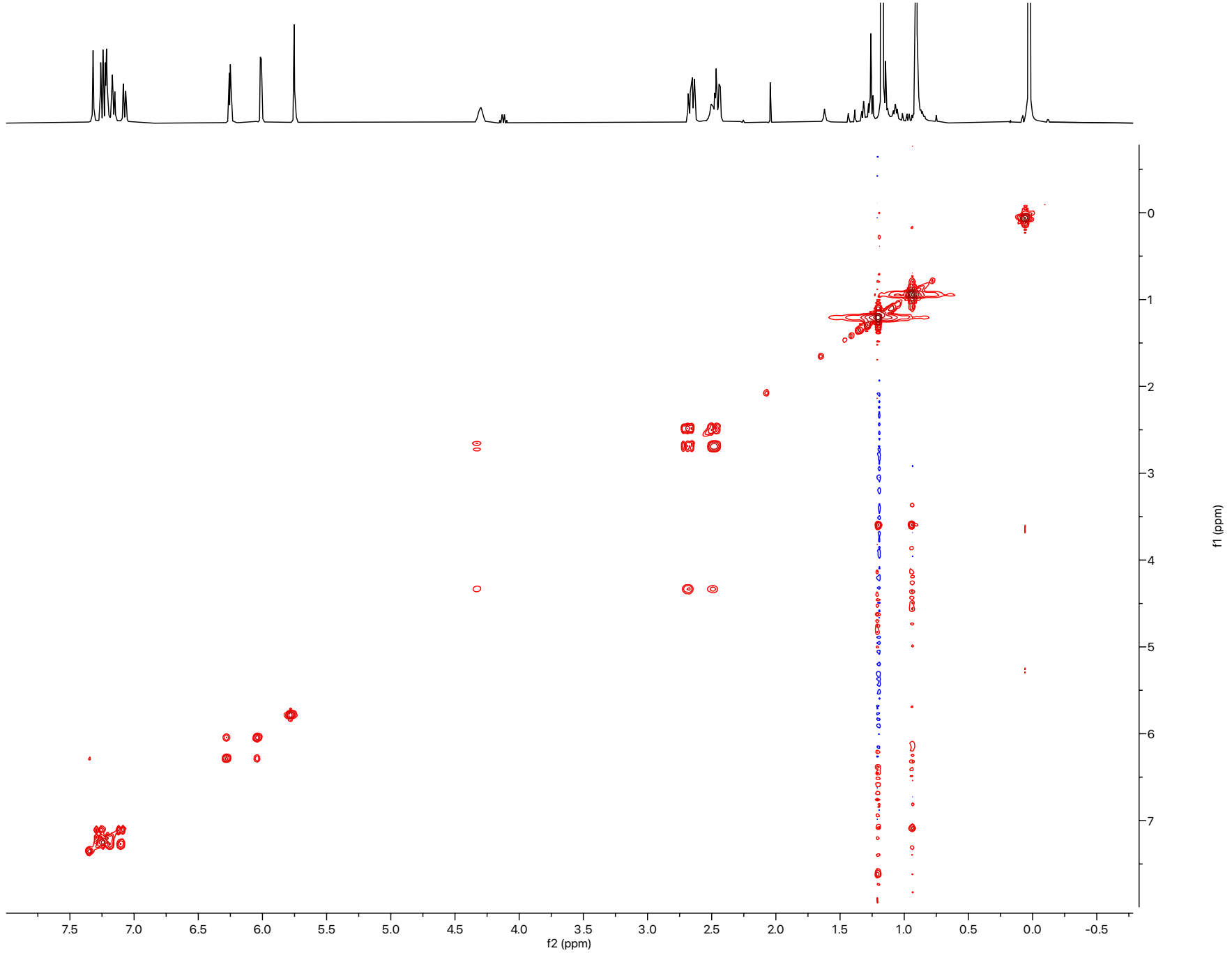


3m

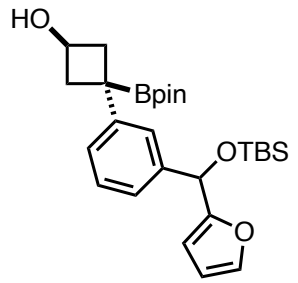
^{1}H (400 MHz), $CDCl_3$



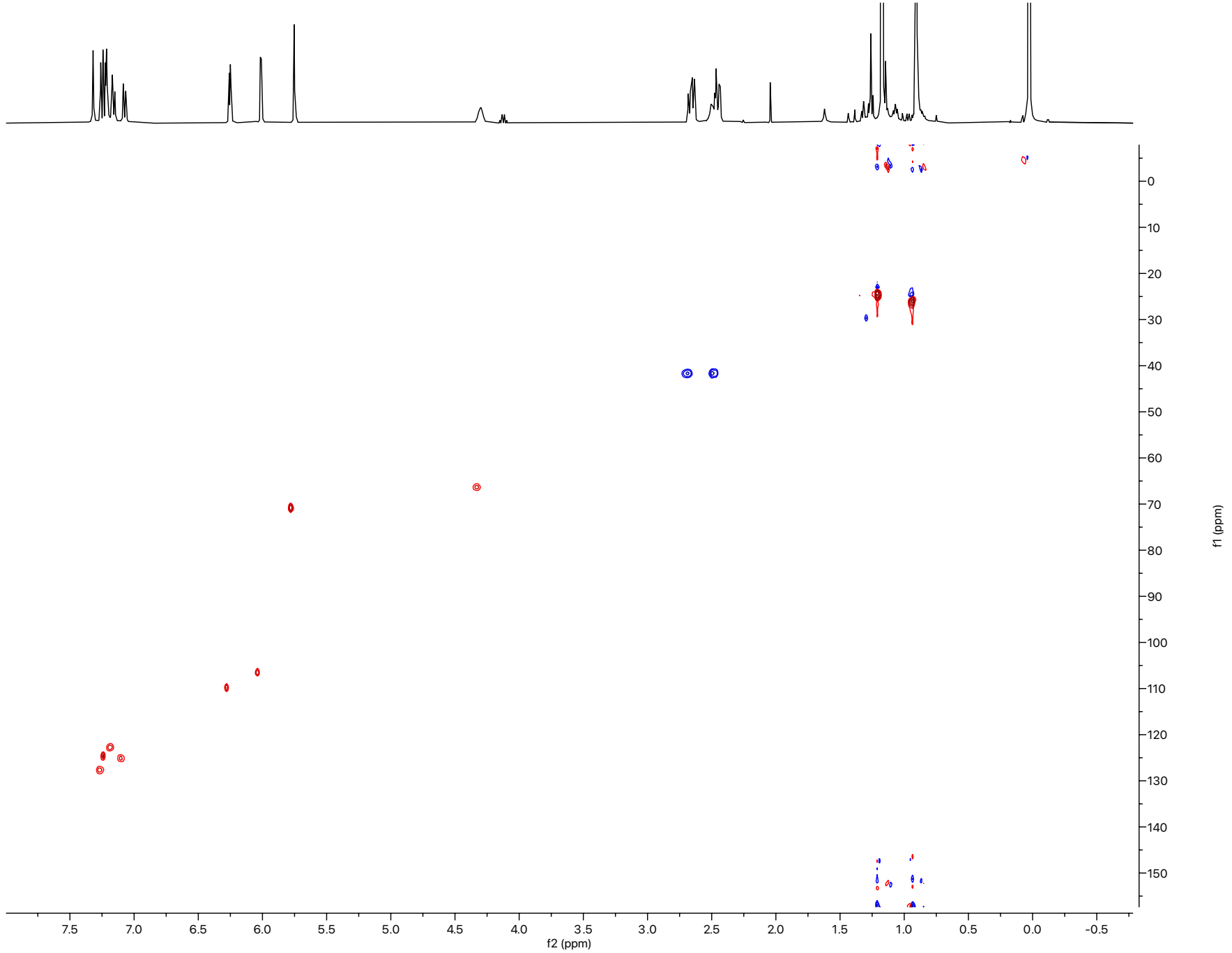
3m



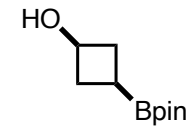
^{1}H (400 MHz), $CDCl_3$
^{13}C (125 MHz), $CDCl_3$



3m

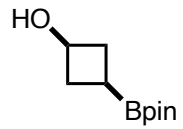


^{1}H (400 MHz), $CDCl_3$



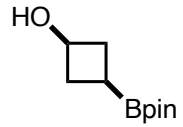
3n

^{11}B (128 MHz), $CDCl_3$



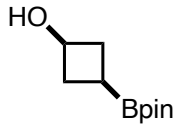
3n

^{13}C (100 MHz), $CDCl_3$



3n

^{1}H (400 MHz), $CDCl_3$



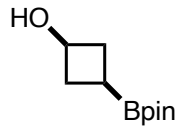
3n

f2 (ppm)

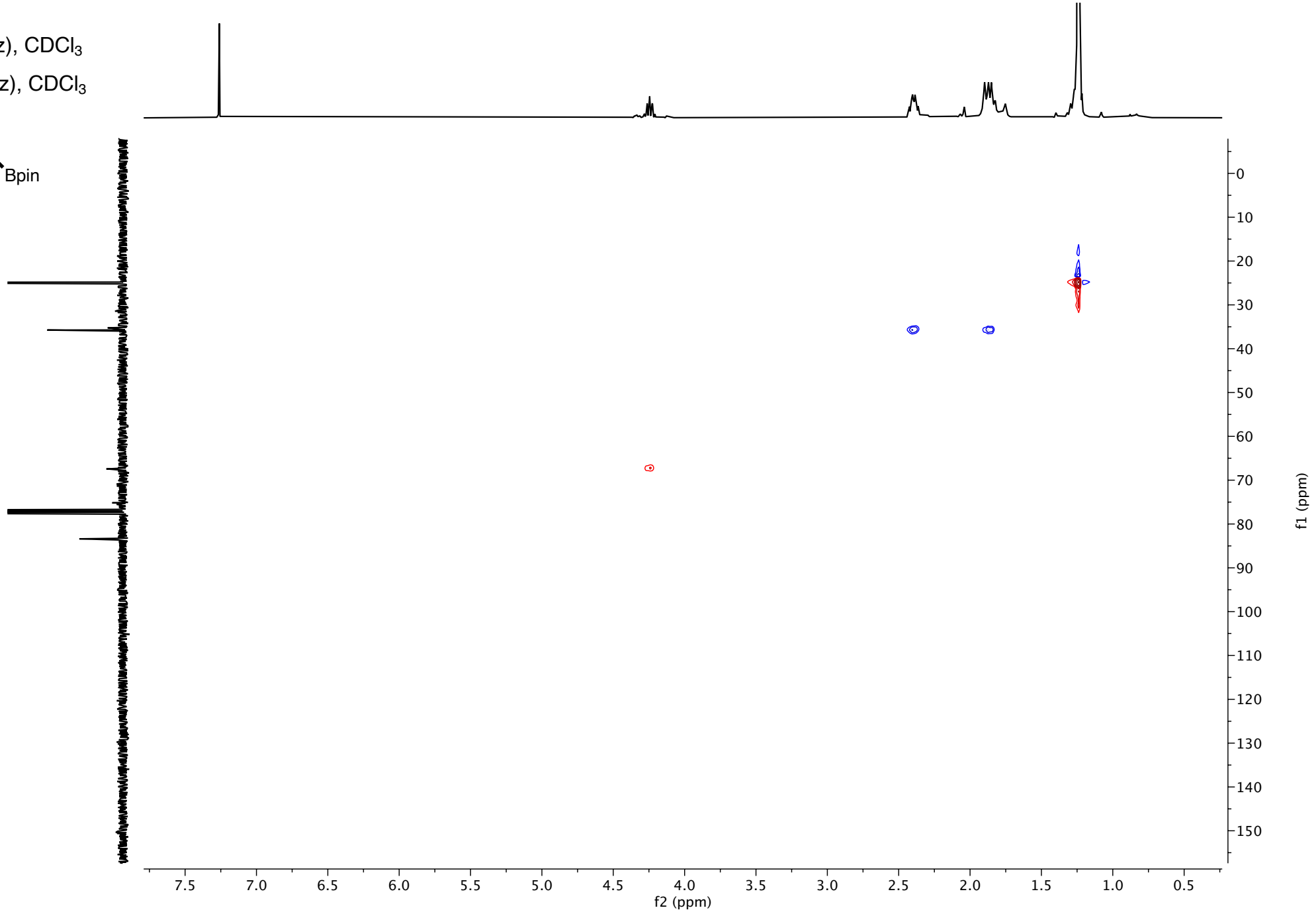
f1 (ppm)

^{1}H (400 MHz), $CDCl_3$

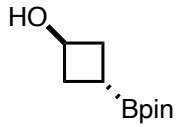
^{13}C (100 MHz), $CDCl_3$



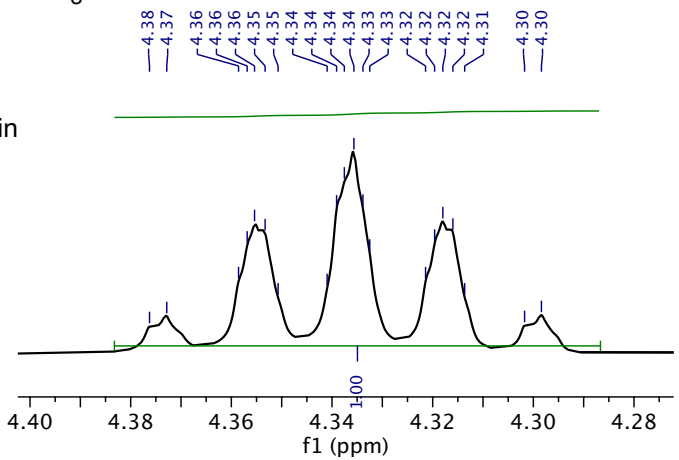
3n



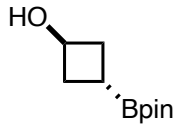
^{1}H (400 MHz), $CDCl_3$



3n-*minor*

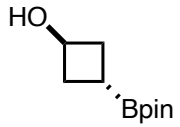


^{11}B (128 MHz), $CDCl_3$



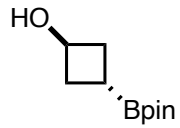
3n-*minor*

^{13}C (100 MHz), $CDCl_3$

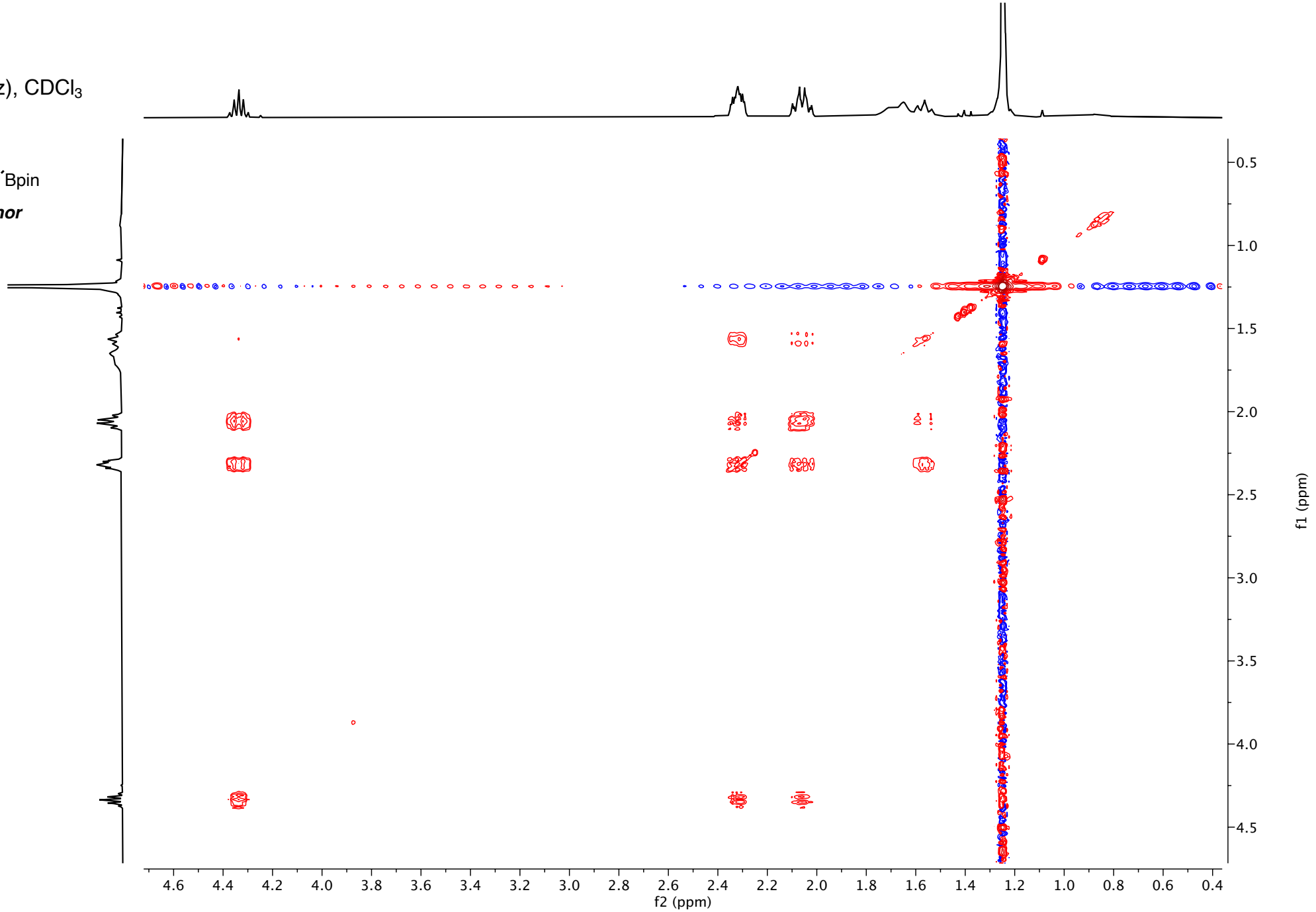


3n-*minor*

^{1}H (400 MHz), $CDCl_3$

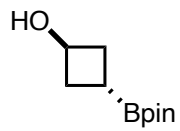


3n-*minor*

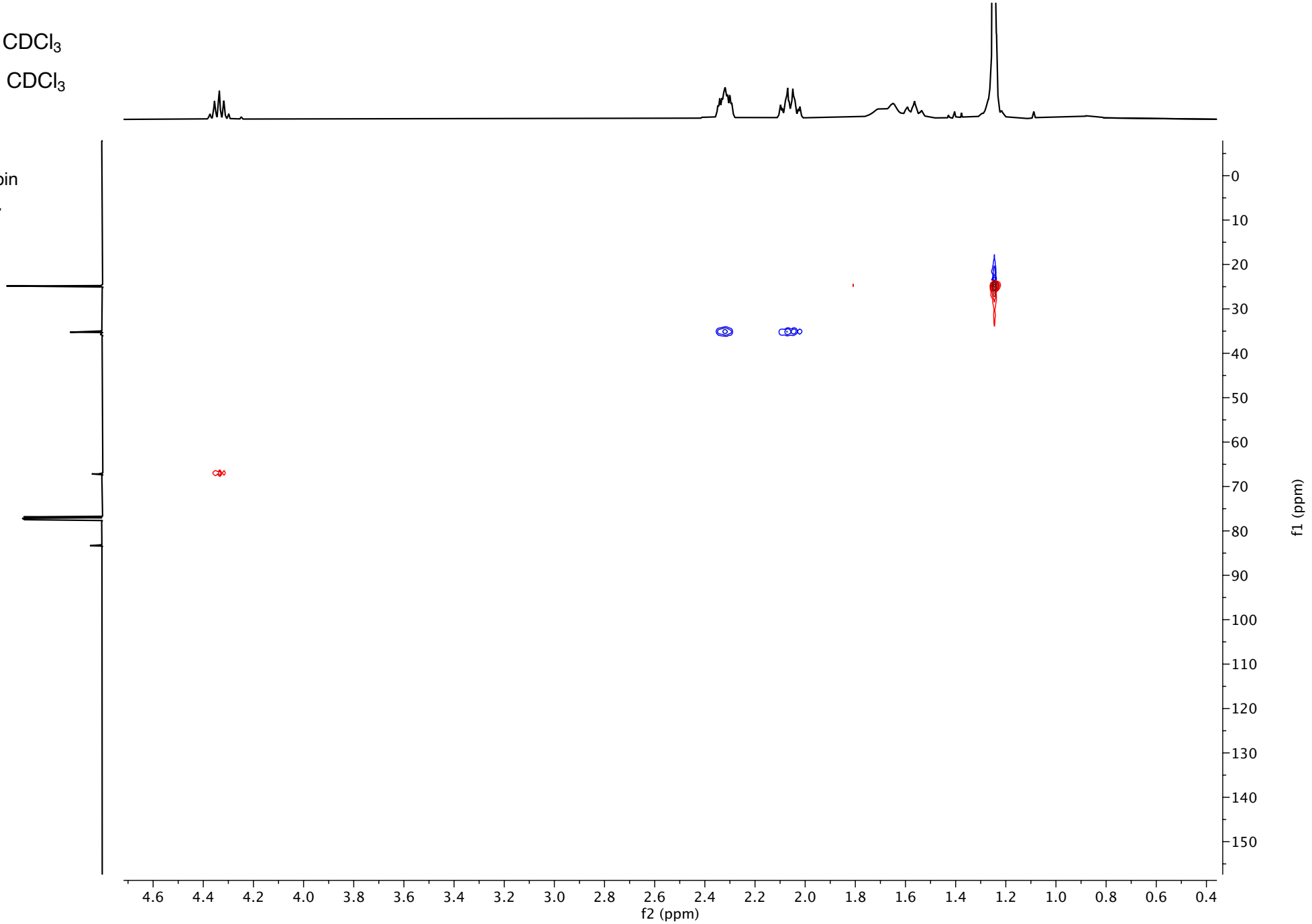


^{1}H (400 MHz), $CDCl_3$

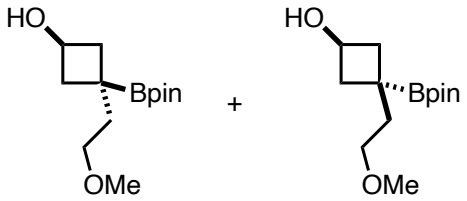
^{13}C (100 MHz), $CDCl_3$



3n-*minor*



^{1}H (400 MHz), $CDCl_3$

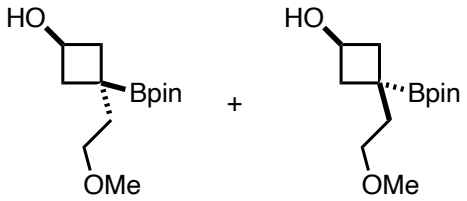


3o

\+

3o-*minor*

^{11}B (128 MHz), $CDCl_3$

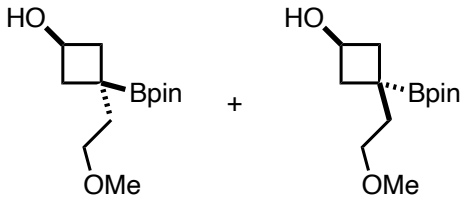


3o

+

3o-*minor*

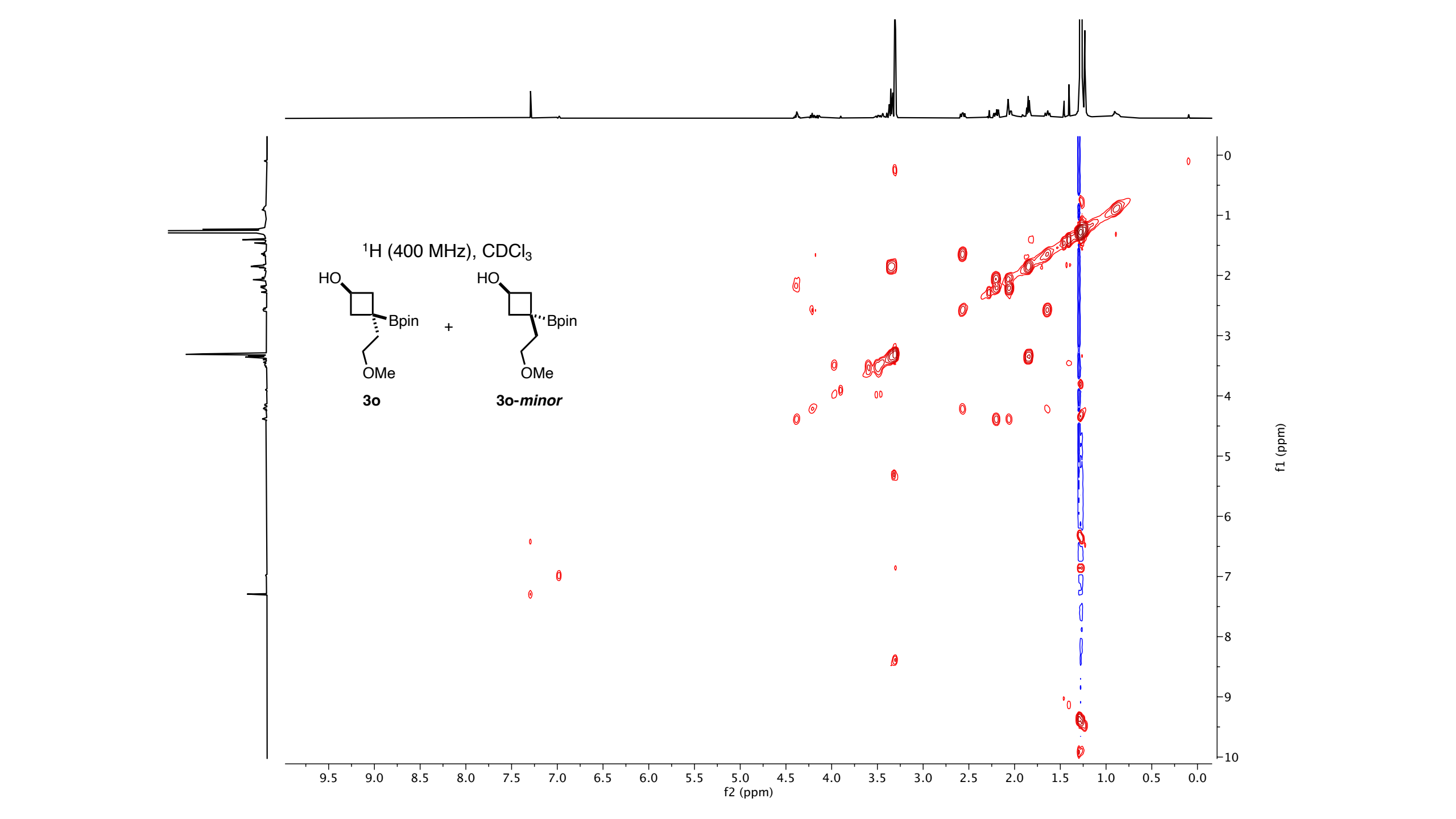
^{13}C (100 MHz), $CDCl_3$



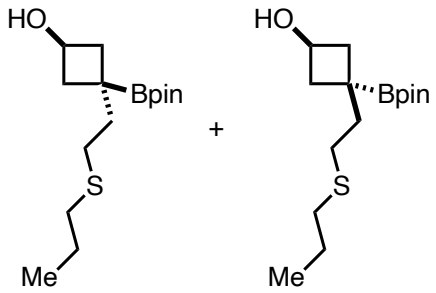
3o

+

3o-*minor*

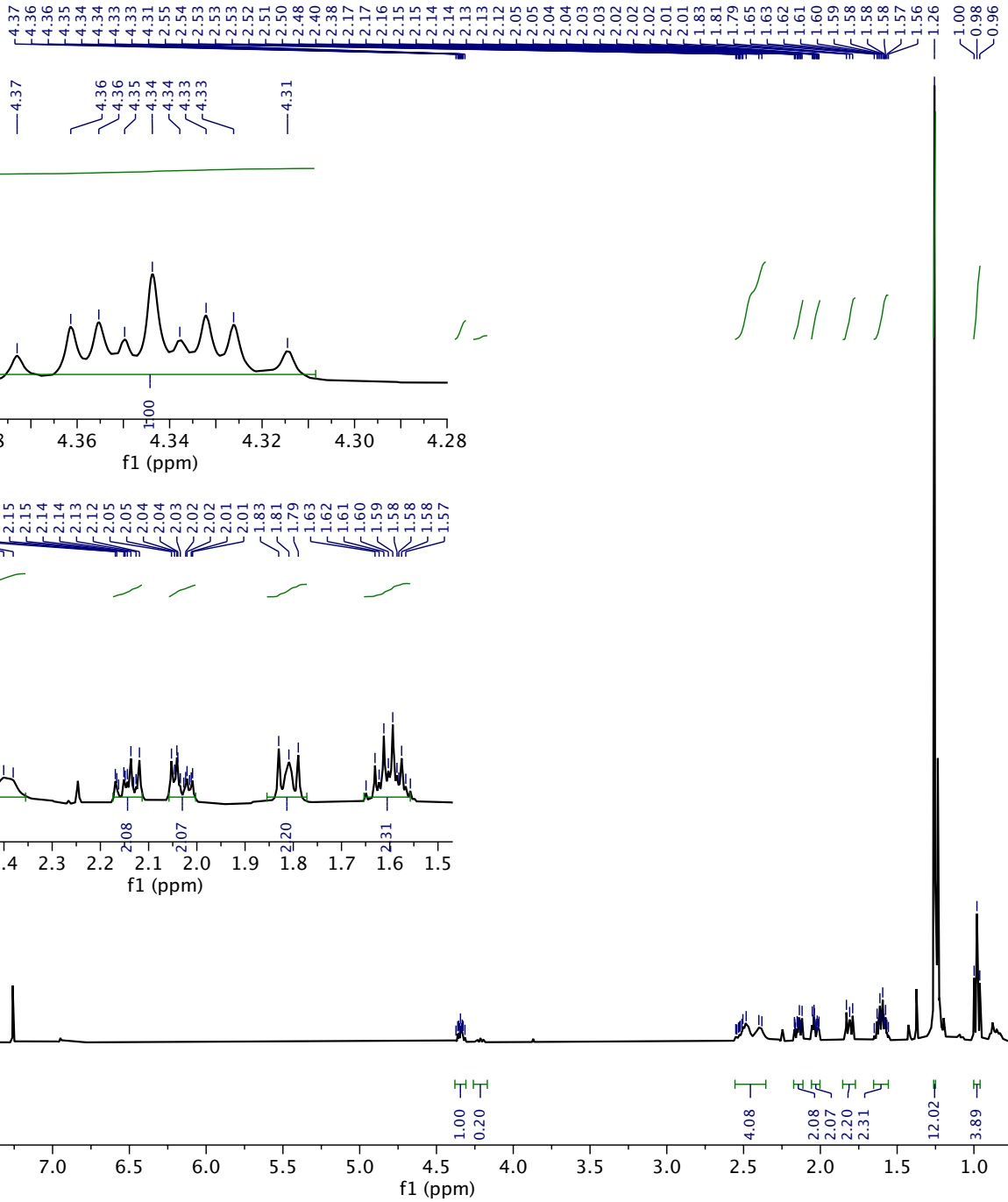

^{1}H (400 MHz), $CDCl_3$
HO
Bpin
OMe
+
HO
Bpin
OMe
3o
3o-*minor*
f2 (ppm)
f1 (ppm)

^{1}H (400 MHz), $CDCl_3$

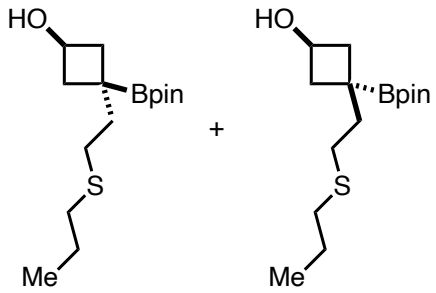


+

3p : **3p-*minor***
5 **1**



^{11}B (128 MHz), $CDCl_3$

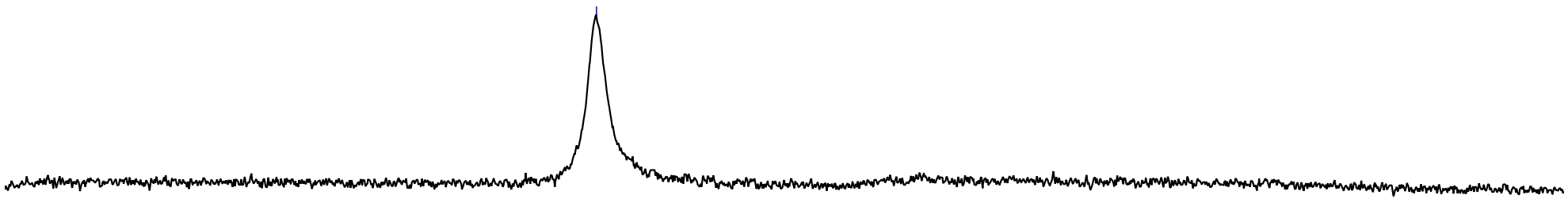


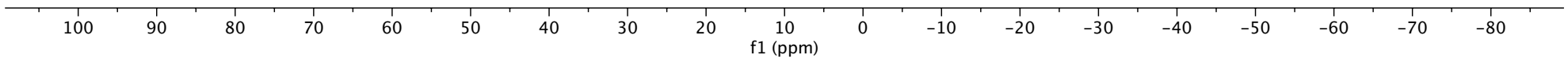
+

3p : **3p-*minor***

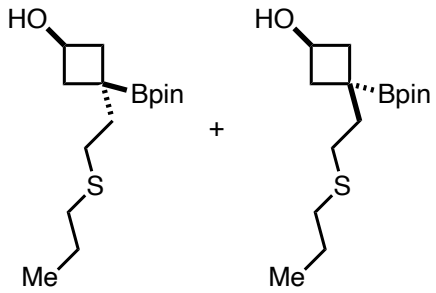
5 **1**

33.96





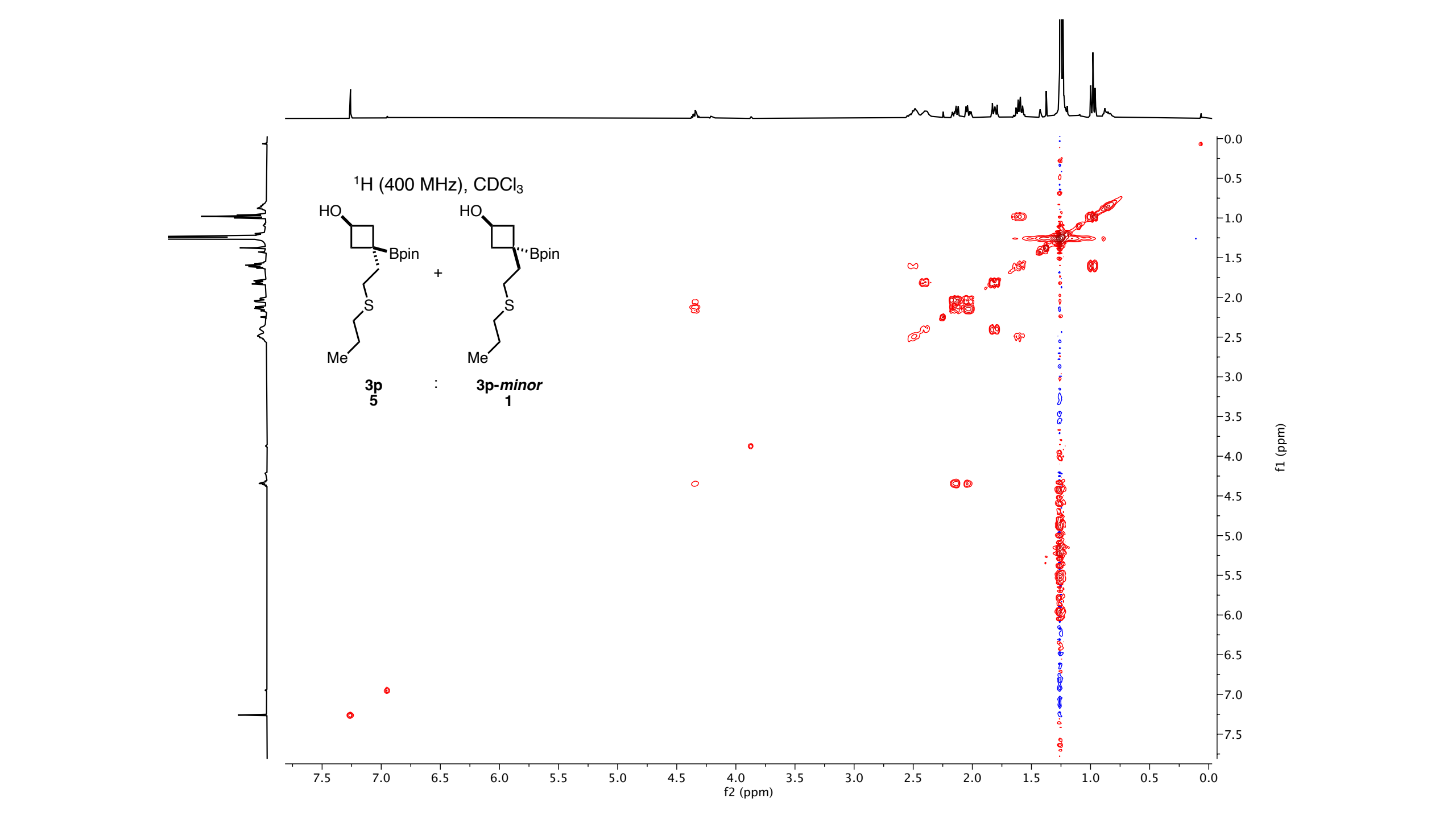
^{13}C (125 MHz), $CDCl_3$

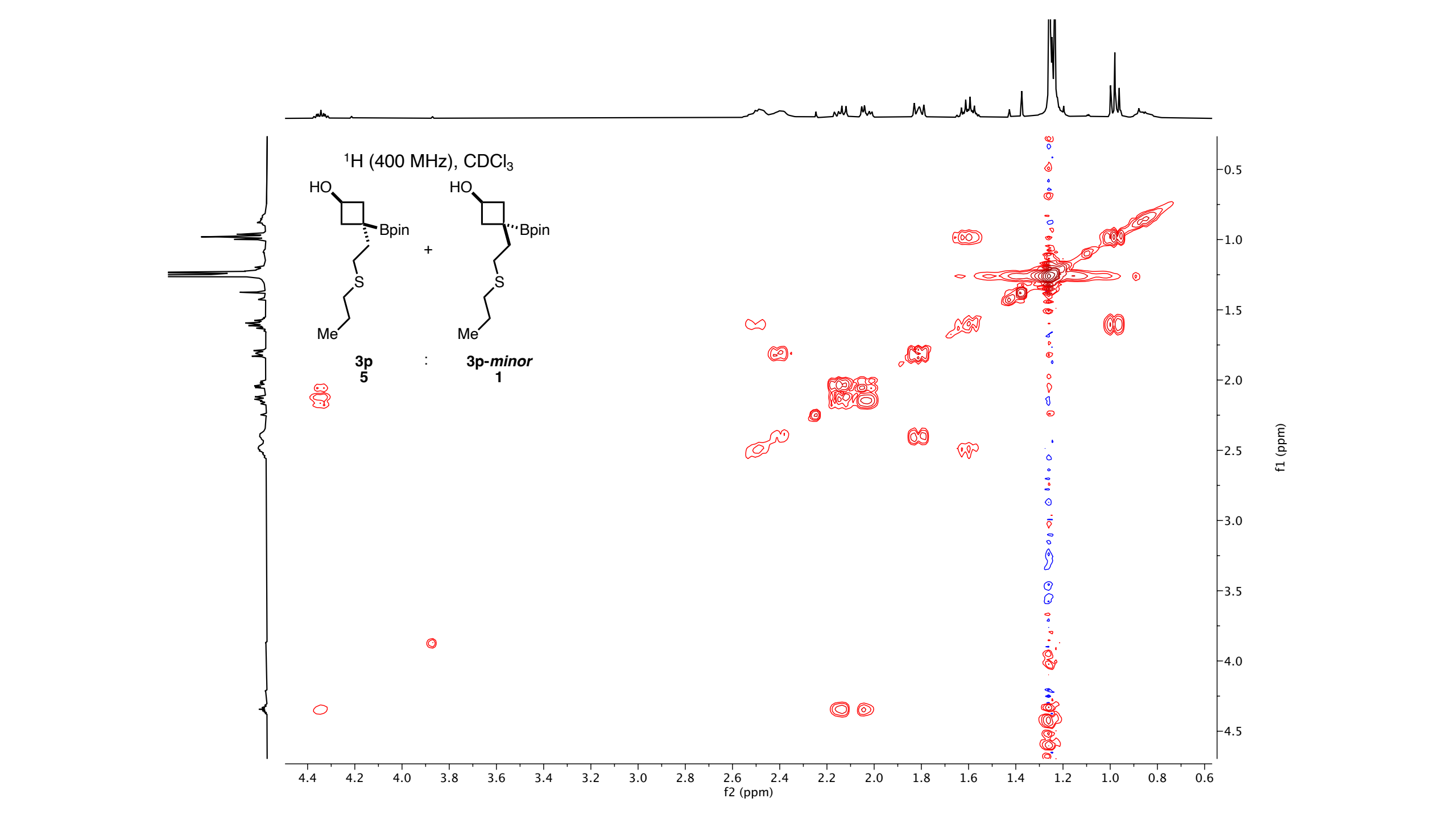


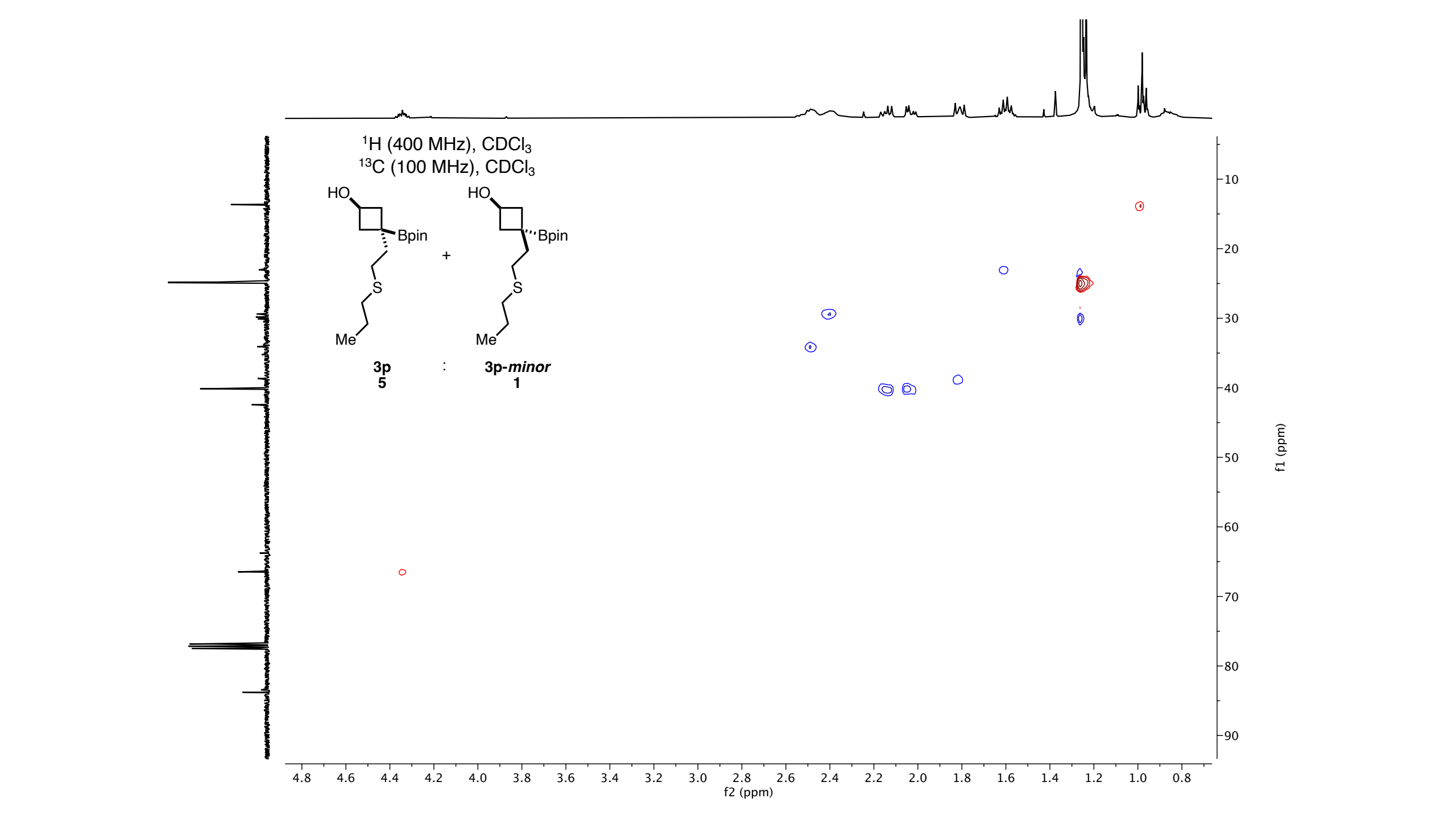
+

3p : **3p-*minor***

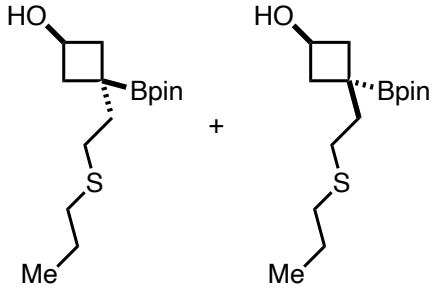
5 **1**


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
S
Me
+
HO
Bpin
S
Me
3p
5
:
3p-*minor*
1
f2 (ppm)
f1 (ppm)


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
S
Me
+
HO
Bpin
S
Me
3p
5
:
3p-minor
1
f2 (ppm)
f1 (ppm)


^{1}H (400 MHz), $CDCl_3$
^{13}C (100 MHz), $CDCl_3$
HO
Bpin
S
Me
+
HO
Bpin
S
Me
3p
5
:
3p-*minor*
1
f2 (ppm)
f1 (ppm)

^{1}H (400 MHz), $CDCl_3$

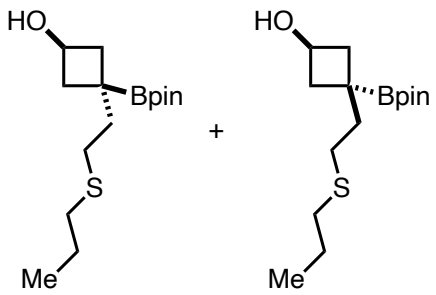


+

3p : **3p-*minor***
1 **2.6**

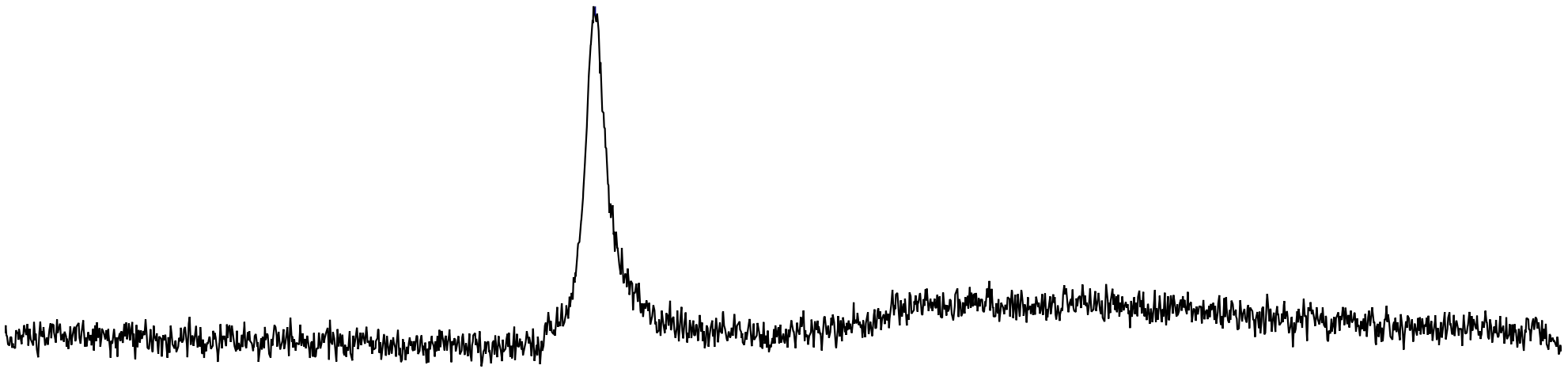
33.98

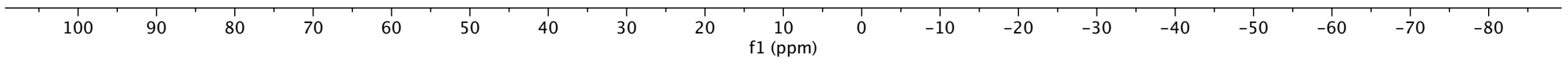
^{11}B (128 MHz), $CDCl_3$



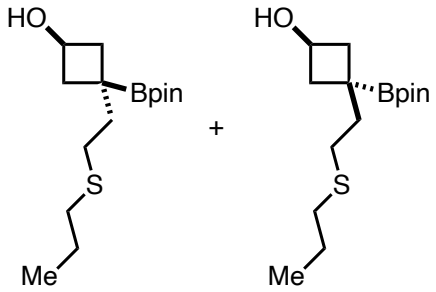
+

3p : **3p-*minor***
1 **2.6**



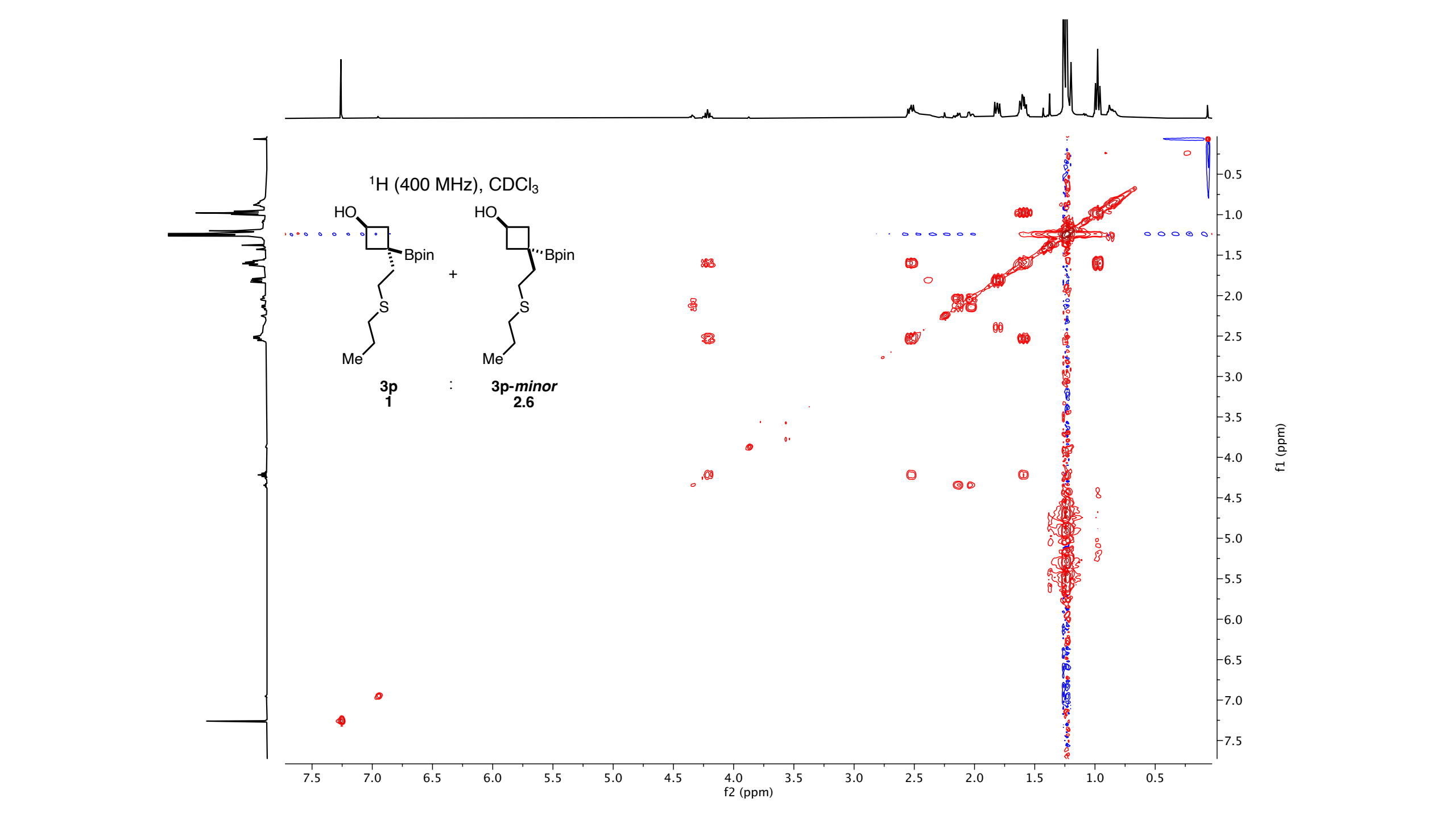


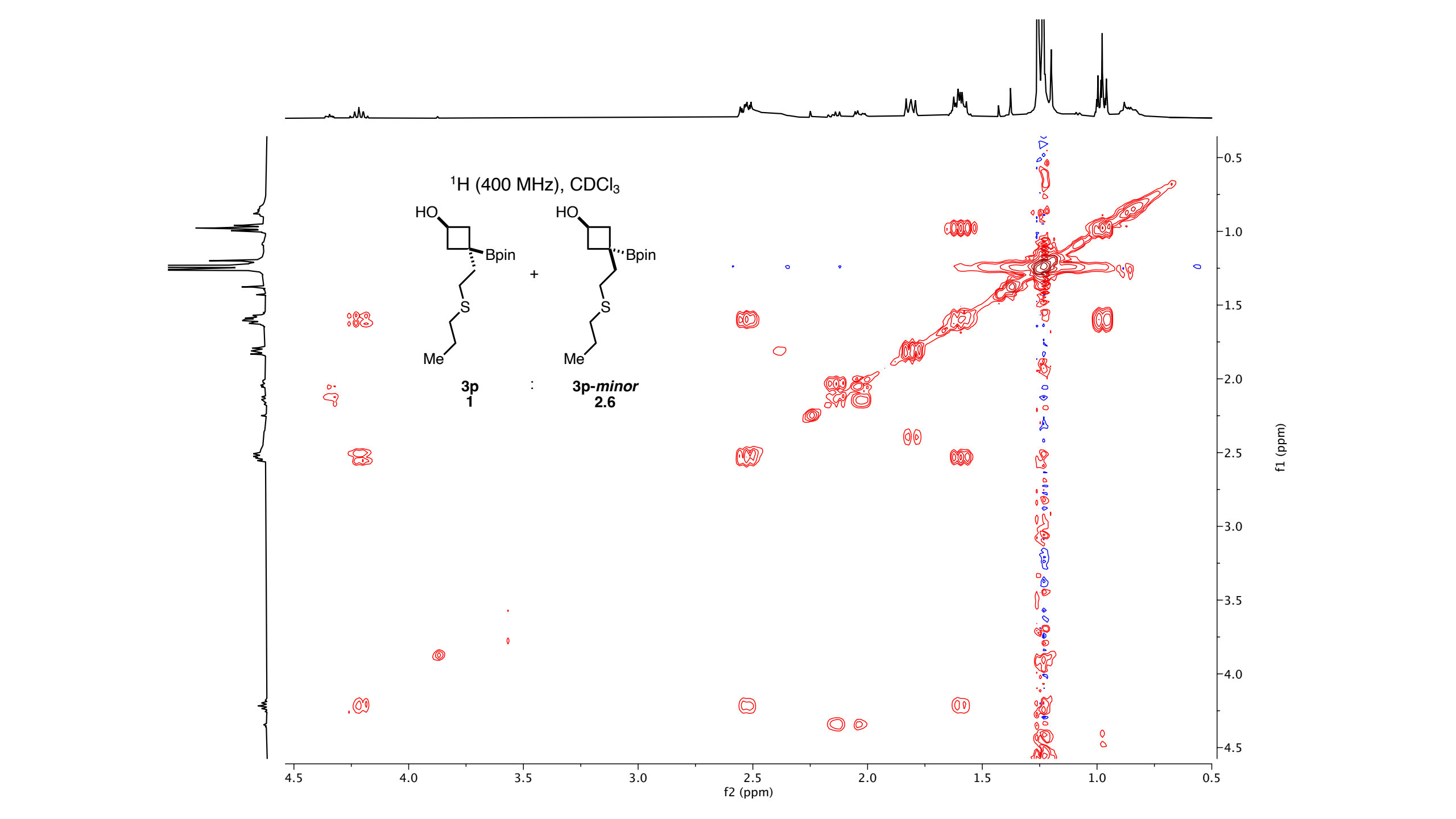
^{13}C (100 MHz), $CDCl_3$

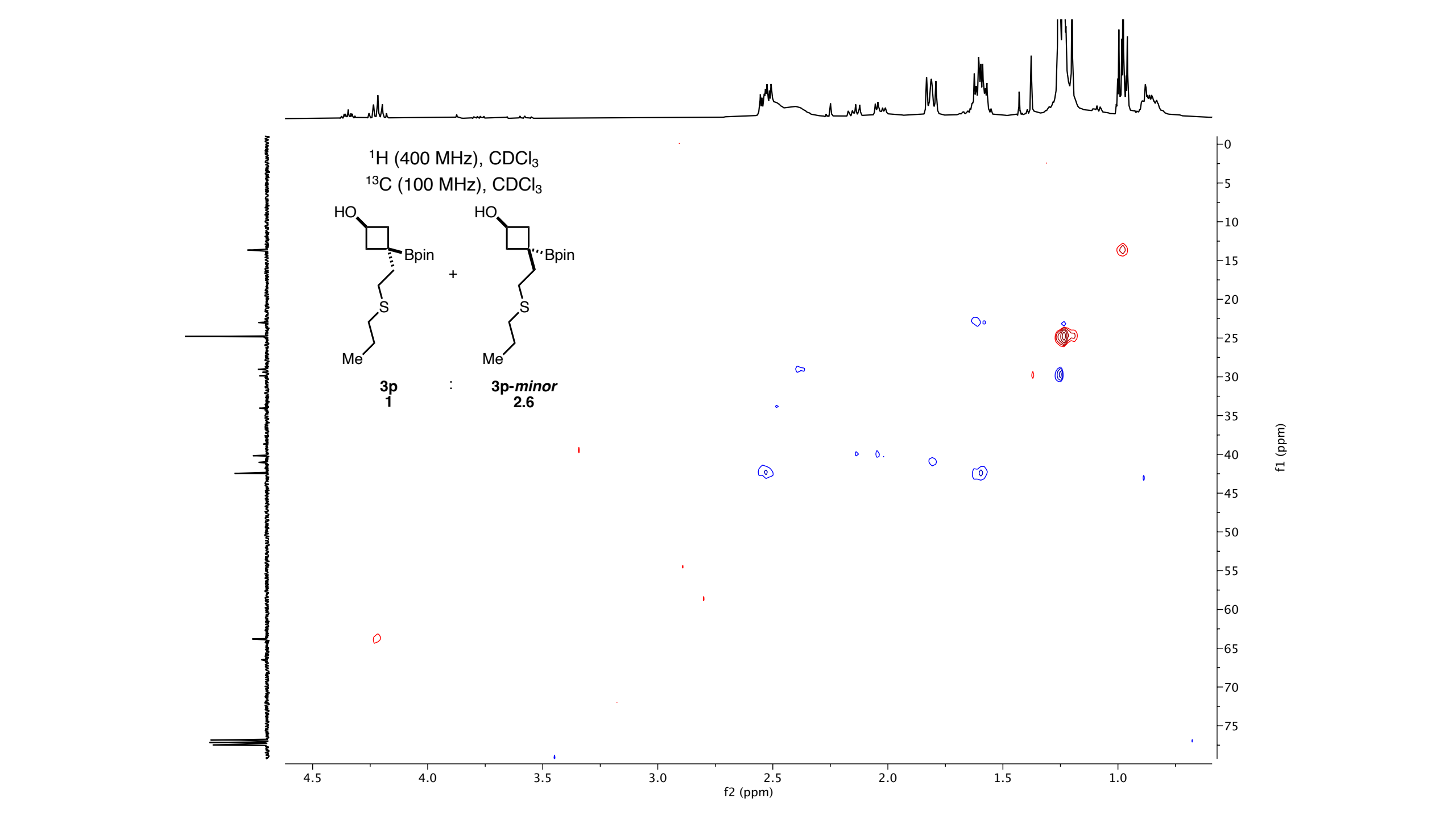


+

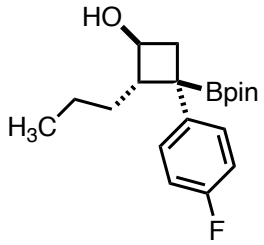
3p : **3p-*minor***
1 **2.6**


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
S
Me
+
HO
Bpin
S
Me
3p
1
:
3p-*minor*
2.6
f2 (ppm)
f1 (ppm)


^{1}H (400 MHz), $CDCl_3$
HO
Bpin
S
Me
+
HO
Bpin
S
Me
3p
1
:
3p-*minor*
2.6
f2 (ppm)
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


^{1}H (400 MHz), $CDCl_3$
^{13}C (100 MHz), $CDCl_3$
HO
Bpin
S
Me
+
HO
Bpin
S
Me
3p
1
:
3p-*minor*
2.6
f2 (ppm)
f1 (ppm)

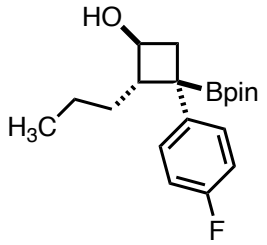
^{1}H (500 MHz), $CDCl_3$



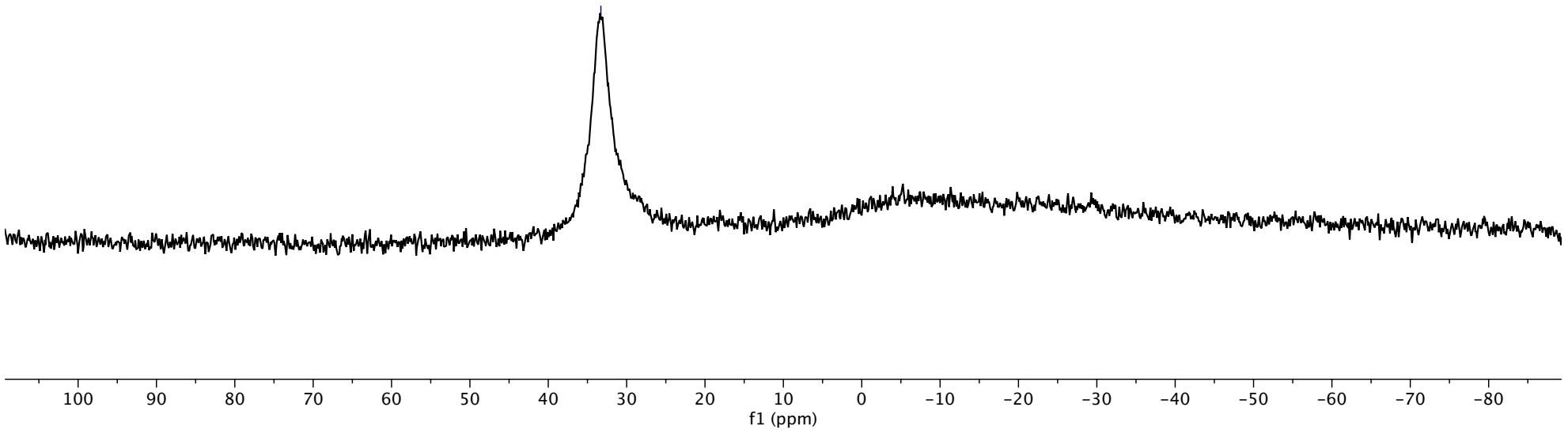
3q

33.29

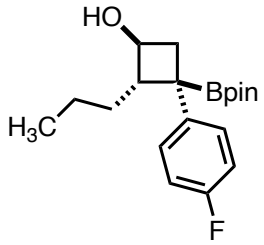
^{11}B (128 MHz), $CDCl_3$



3q

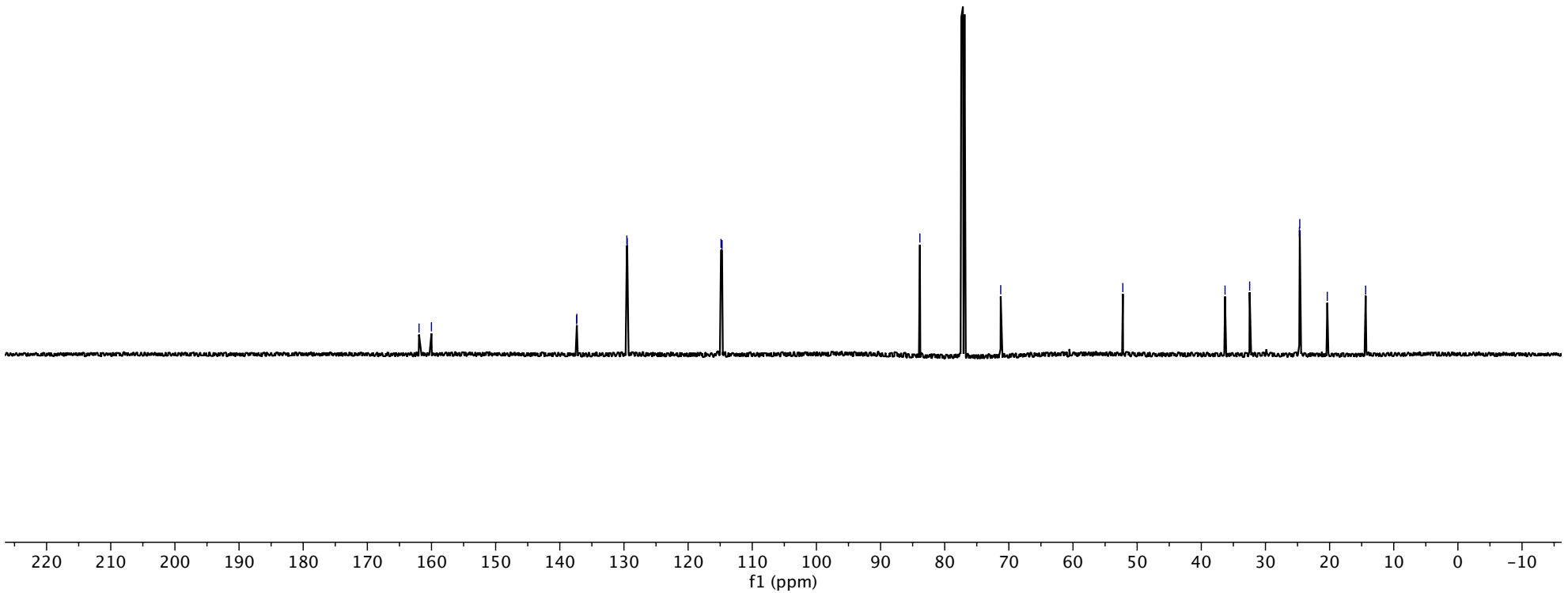


^{13}C (125 MHz), $CDCl_3$

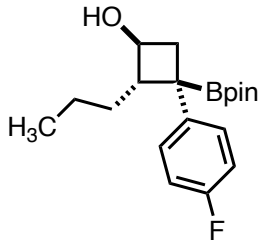


3q

161.94
160.01
137.38
137.35
129.55
129.49
114.87
114.71
83.87
71.27
52.23
36.30
32.46
24.70
24.65
20.36
14.38

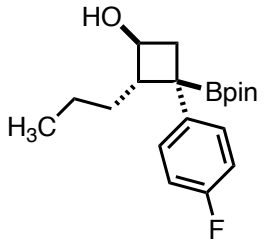


^{19}F {^{1}H} (376 MHz), $CDCl_3$

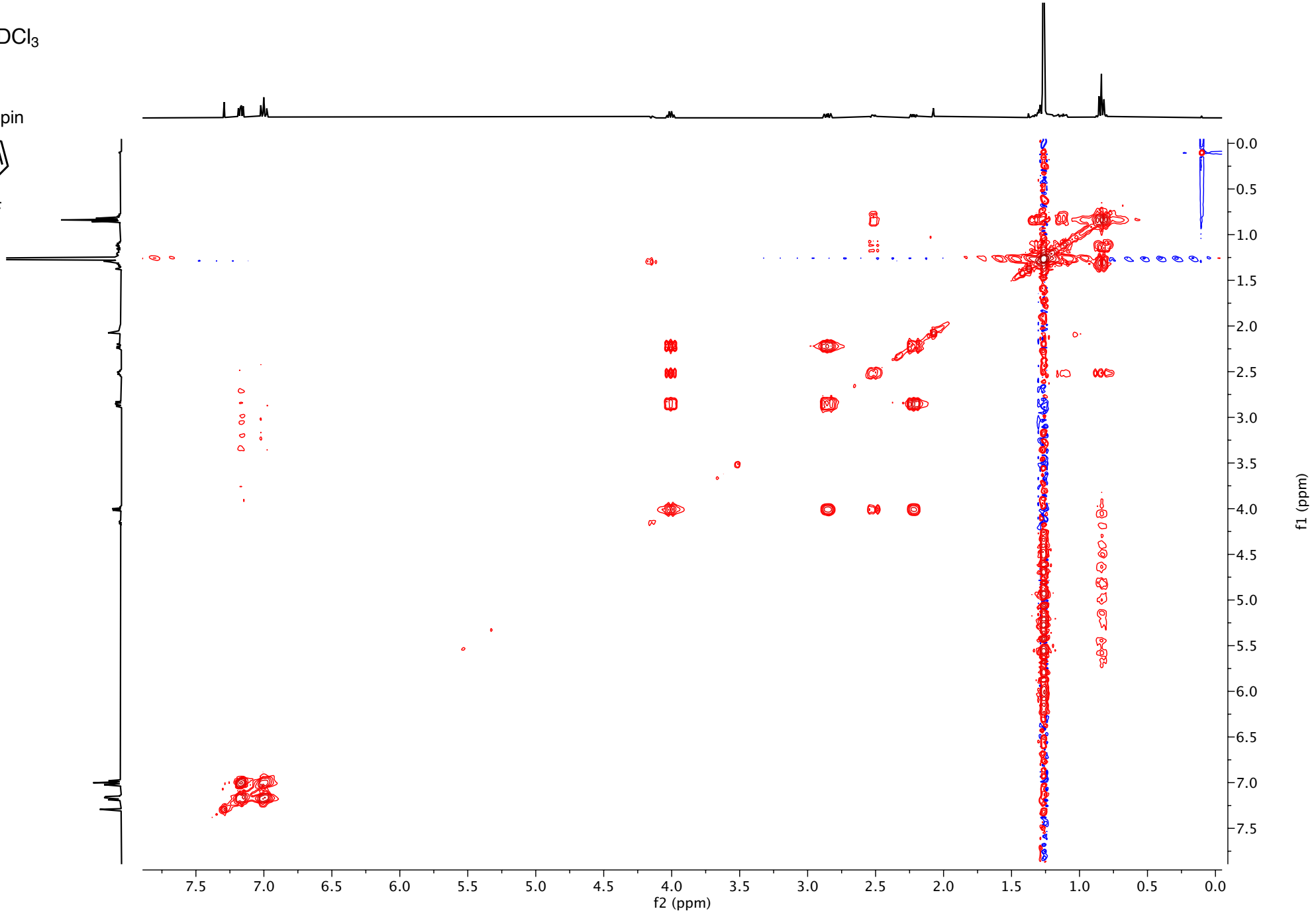


3q

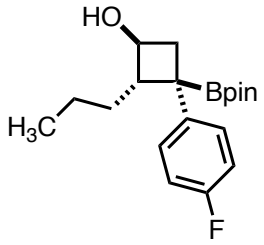
^{1}H (400 MHz), $CDCl_3$



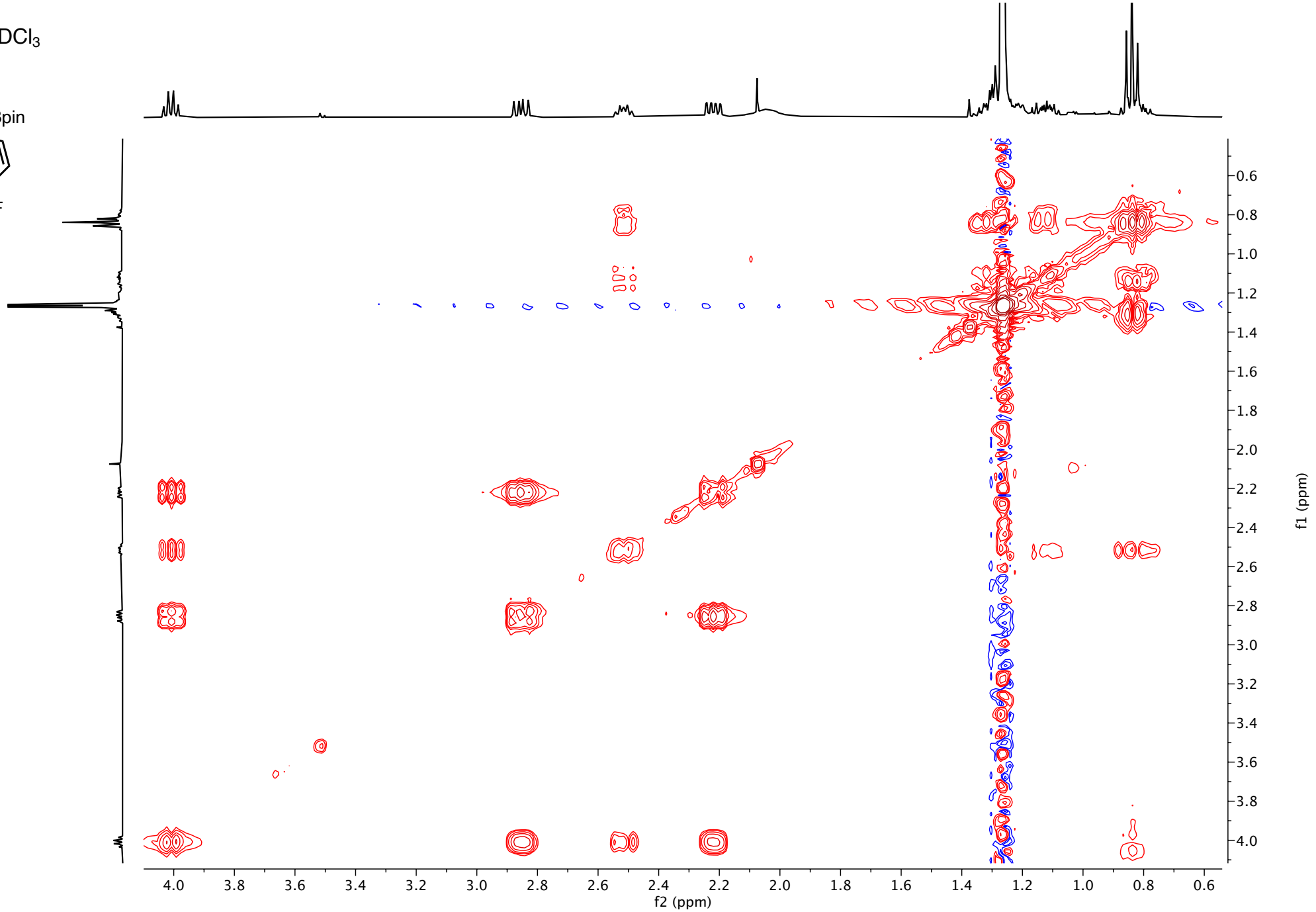
3q



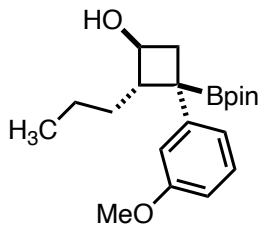
^{1}H (400 MHz), $CDCl_3$



3q



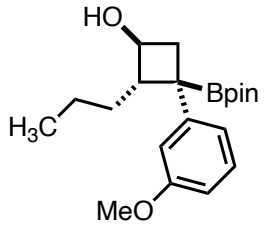
^{1}H (400 MHz), $CDCl_3$



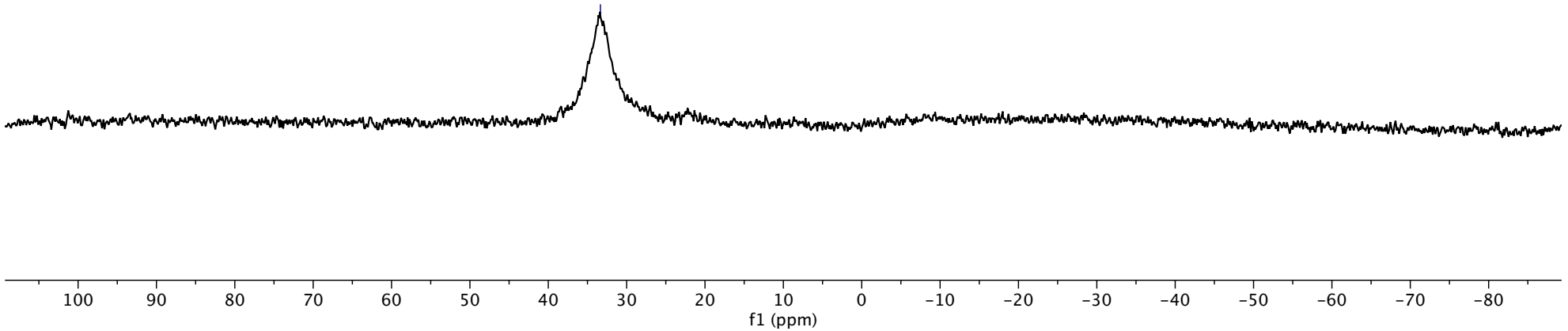
3r

33.34

^{11}B (128 MHz), $CDCl_3$

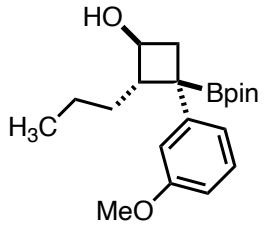


3r

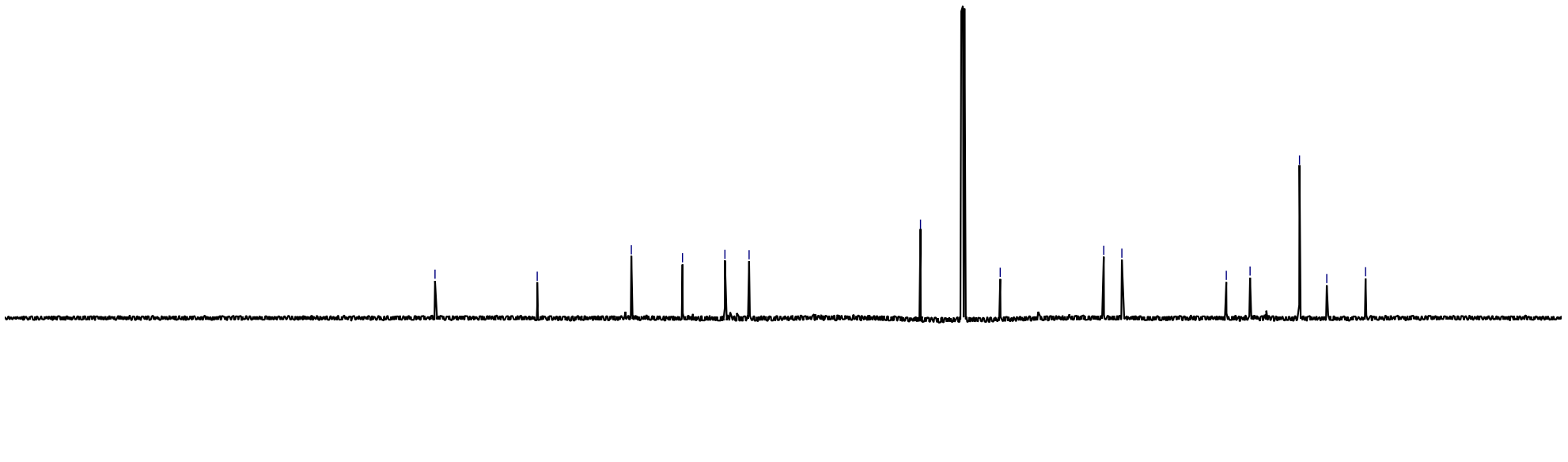


159.44
143.51
128.84
120.87
114.25
110.48
83.76
71.34
55.20
52.38
36.09
32.39
24.68
20.43
14.39

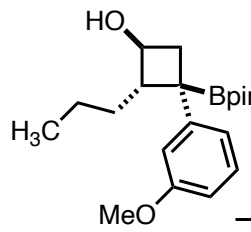
^{13}C (125 MHz), $CDCl_3$



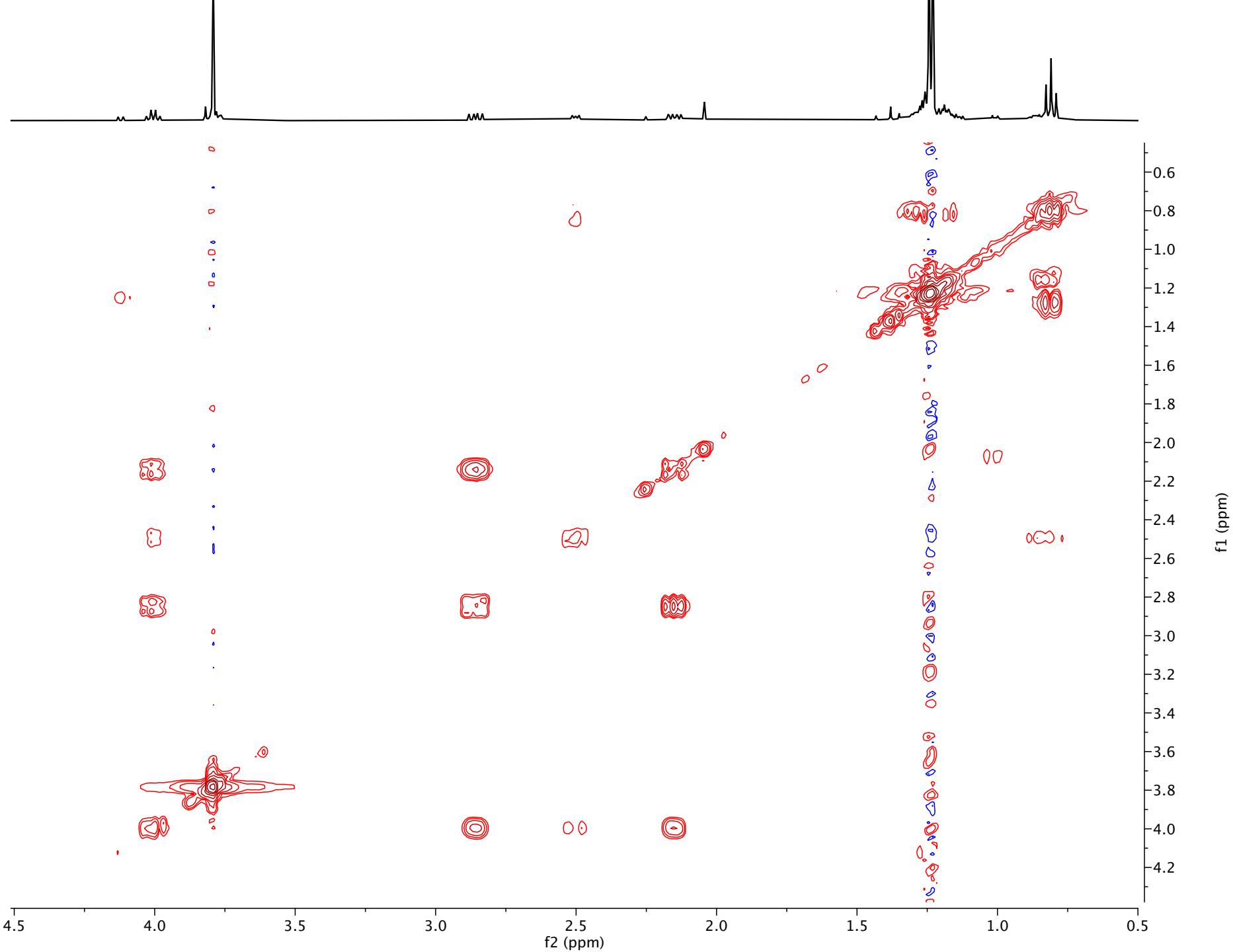
3r



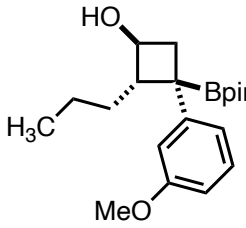
^{1}H (400 MHz), $CDCl_3$



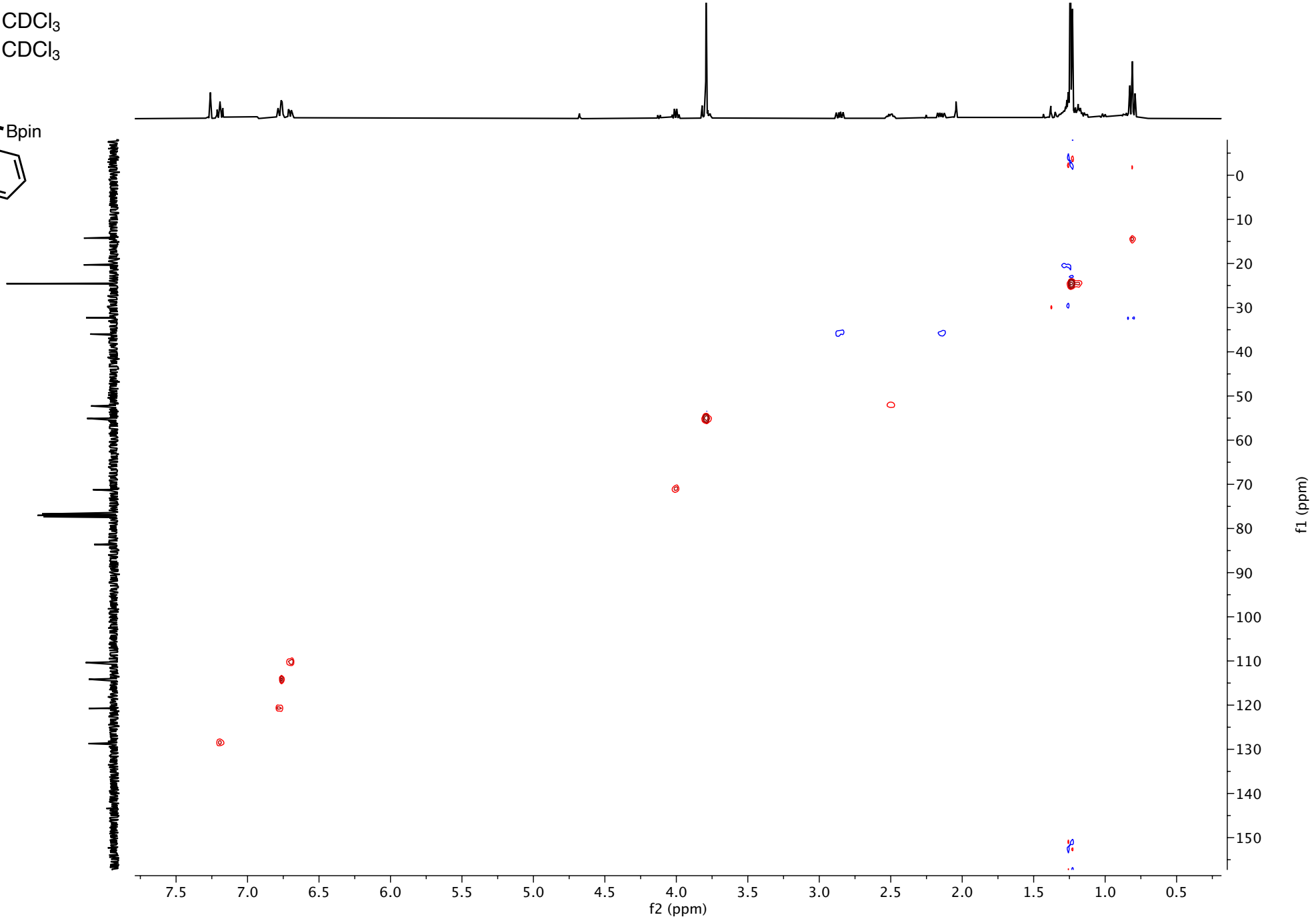
3r



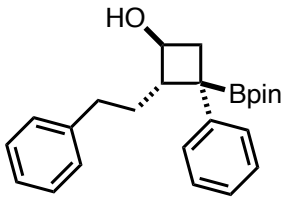
^{1}H (400 MHz), $CDCl_3$
^{13}C (125 MHz), $CDCl_3$



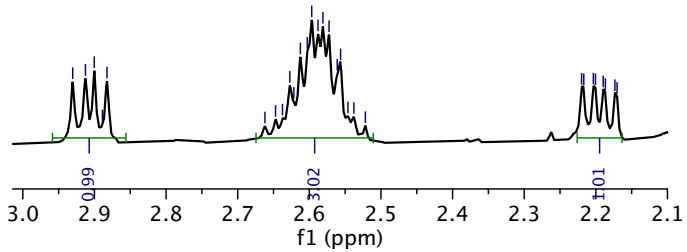
3r

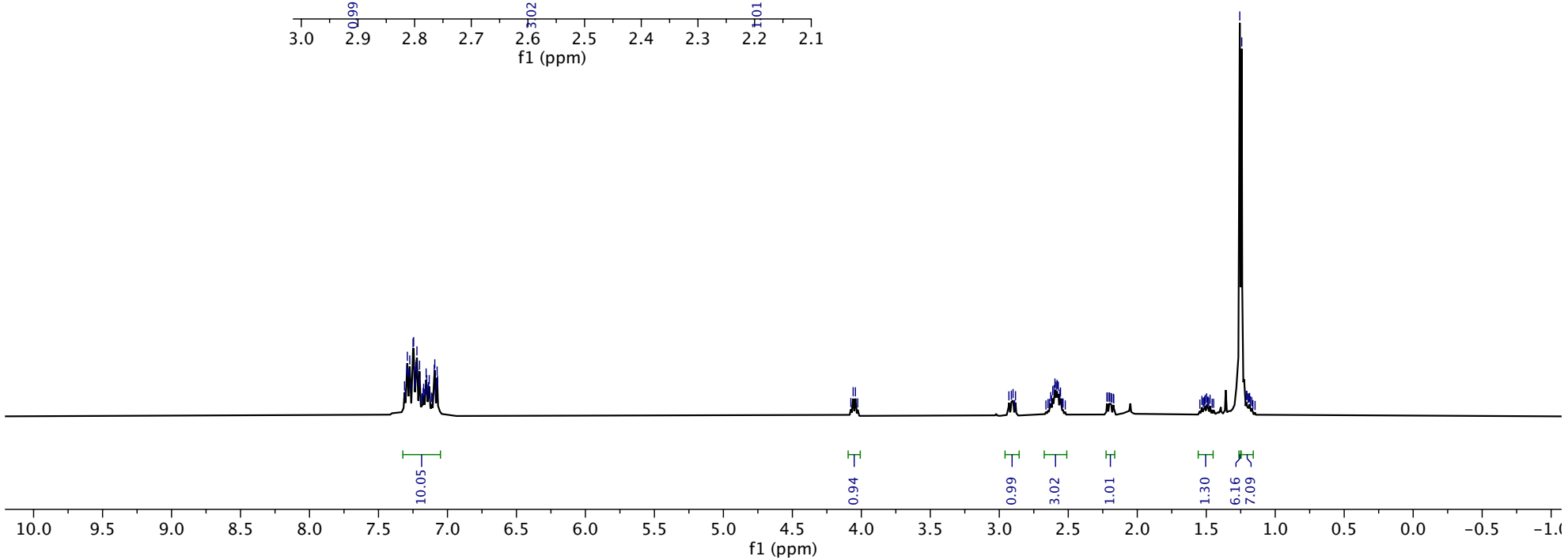


^{1}H (400 MHz), $CDCl_3$



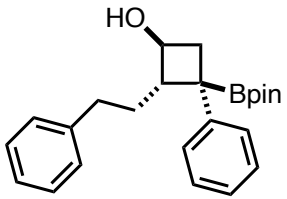
3s



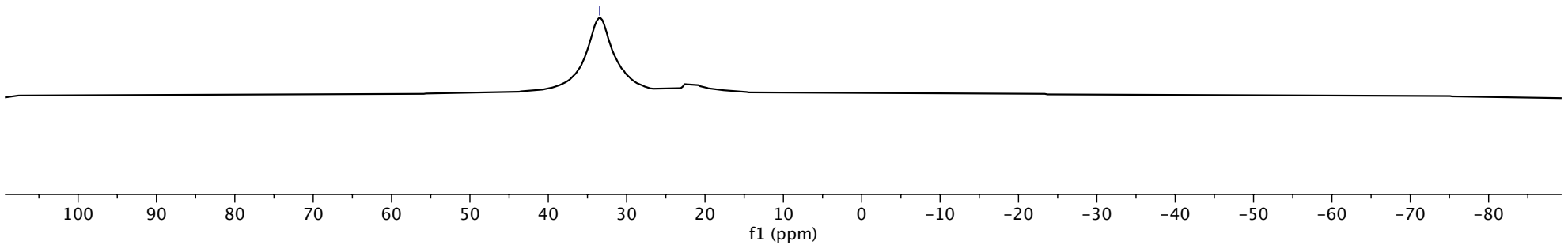


33.43

^{11}B (128 MHz), $CDCl_3$

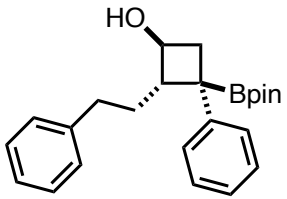


3s

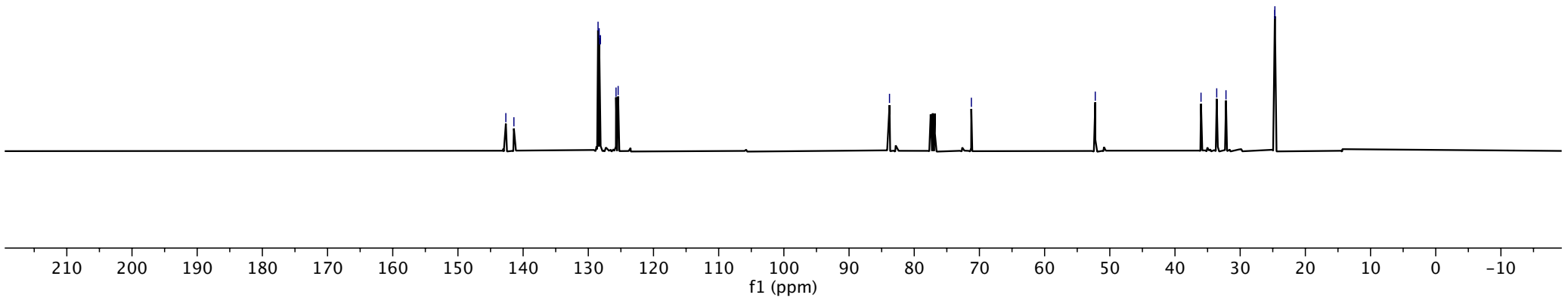


142.65
141.41
128.51
128.34
128.28
128.14
125.75
125.42
83.79
71.24
52.23
36.01
33.60
32.18
24.69
24.67

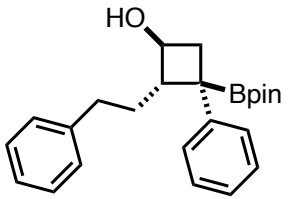
^{13}C (100 MHz), $CDCl_3$



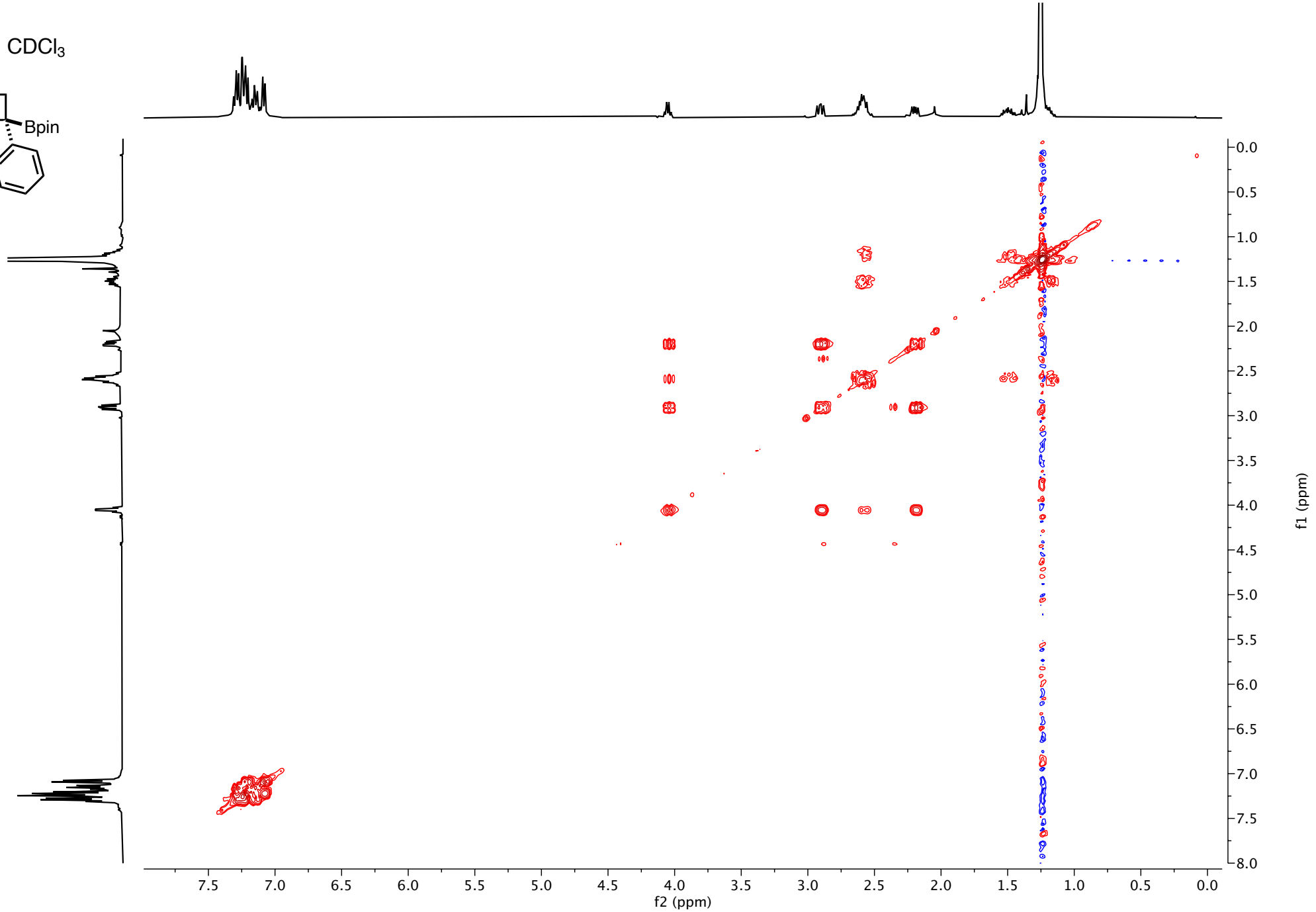
3s



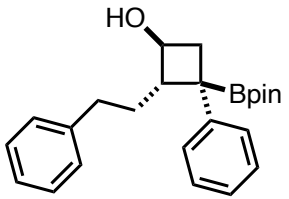
^{1}H (400 MHz), $CDCl_3$



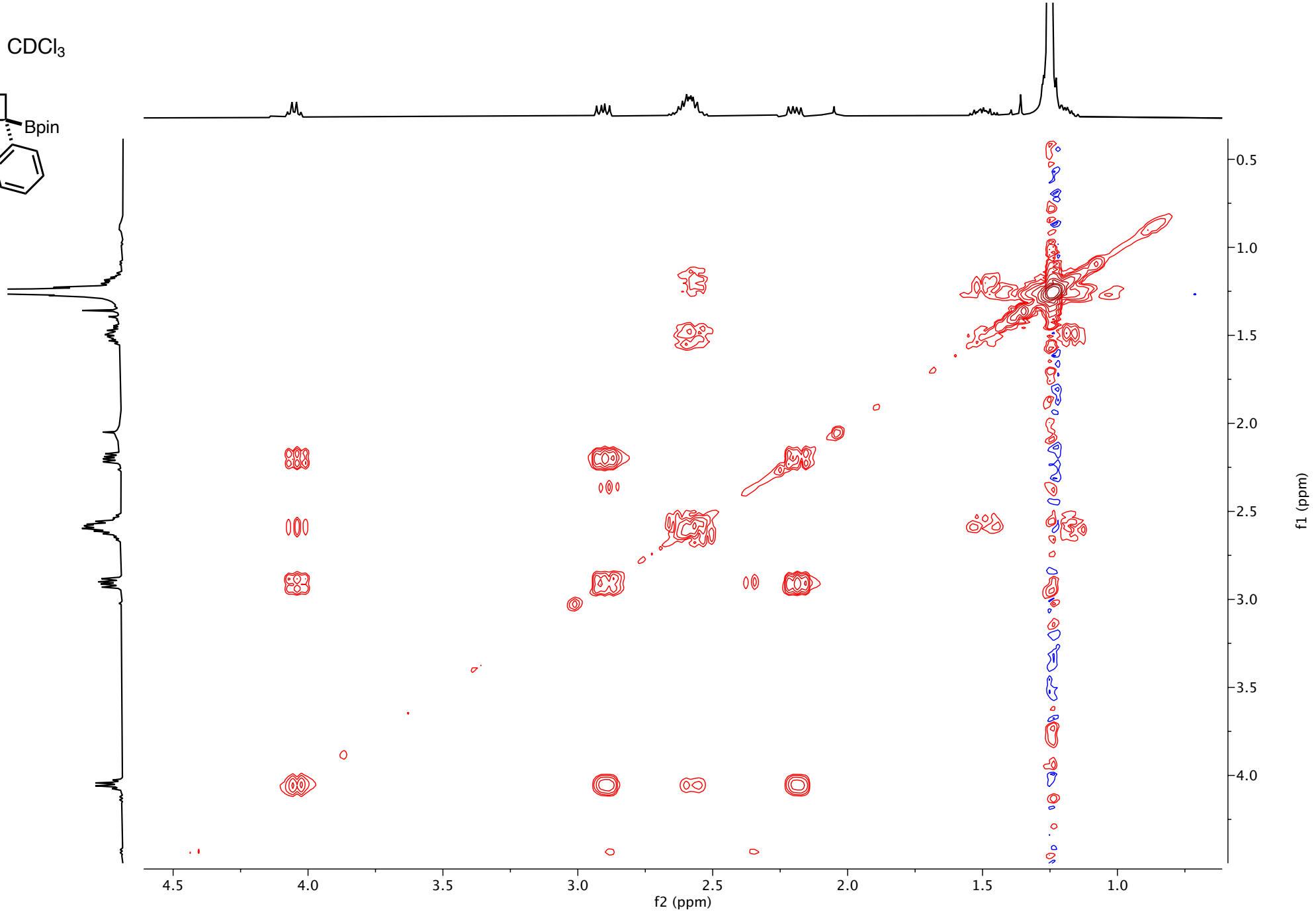
3s



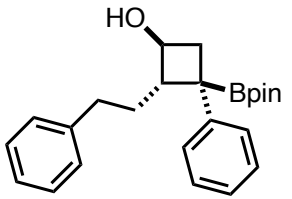
^{1}H (400 MHz), $CDCl_3$



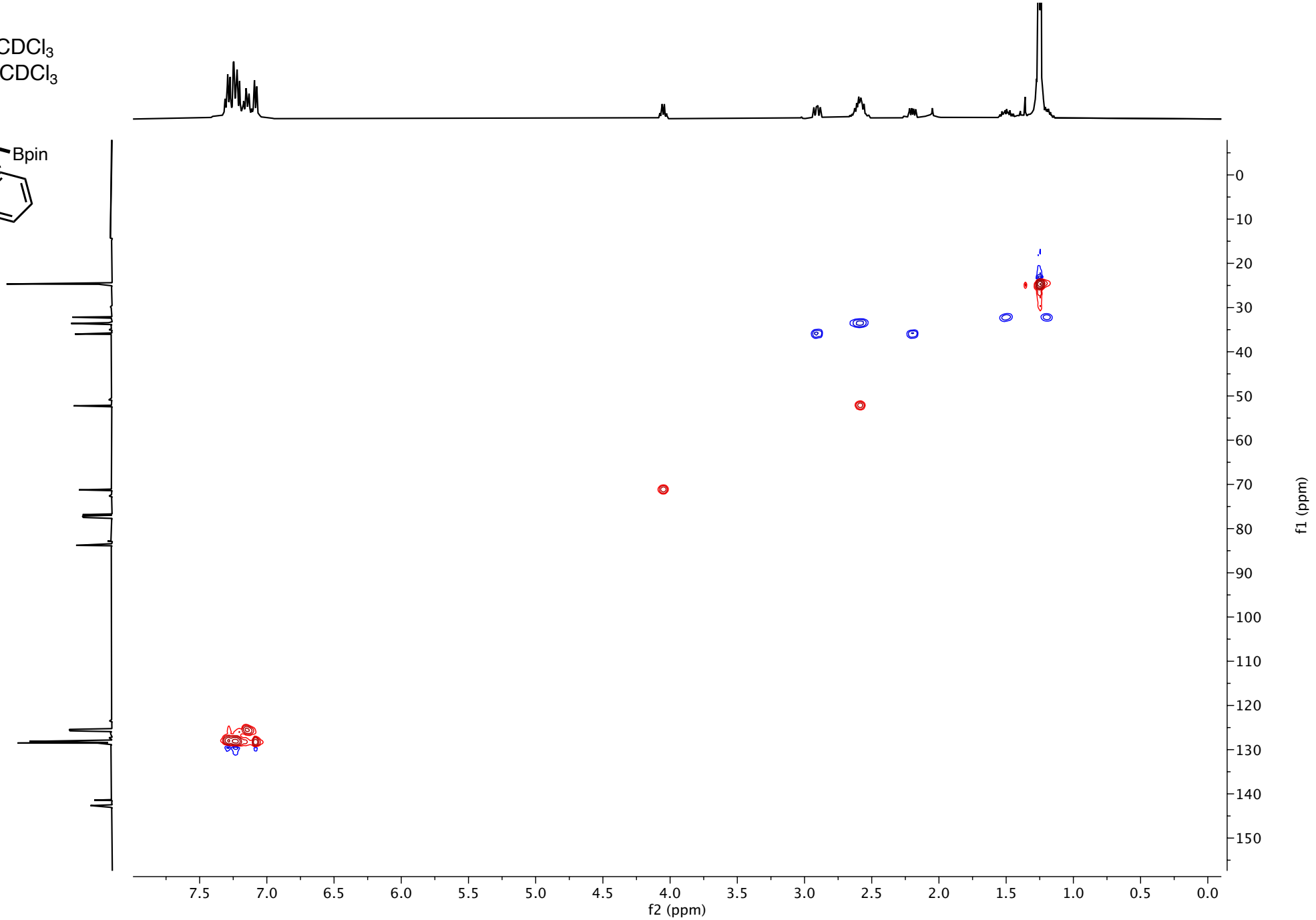
3s



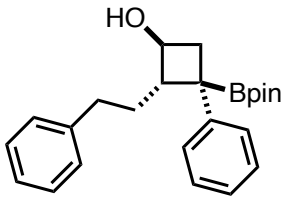
^{1}H (400 MHz), $CDCl_3$
^{13}C (100 MHz), $CDCl_3$



3s

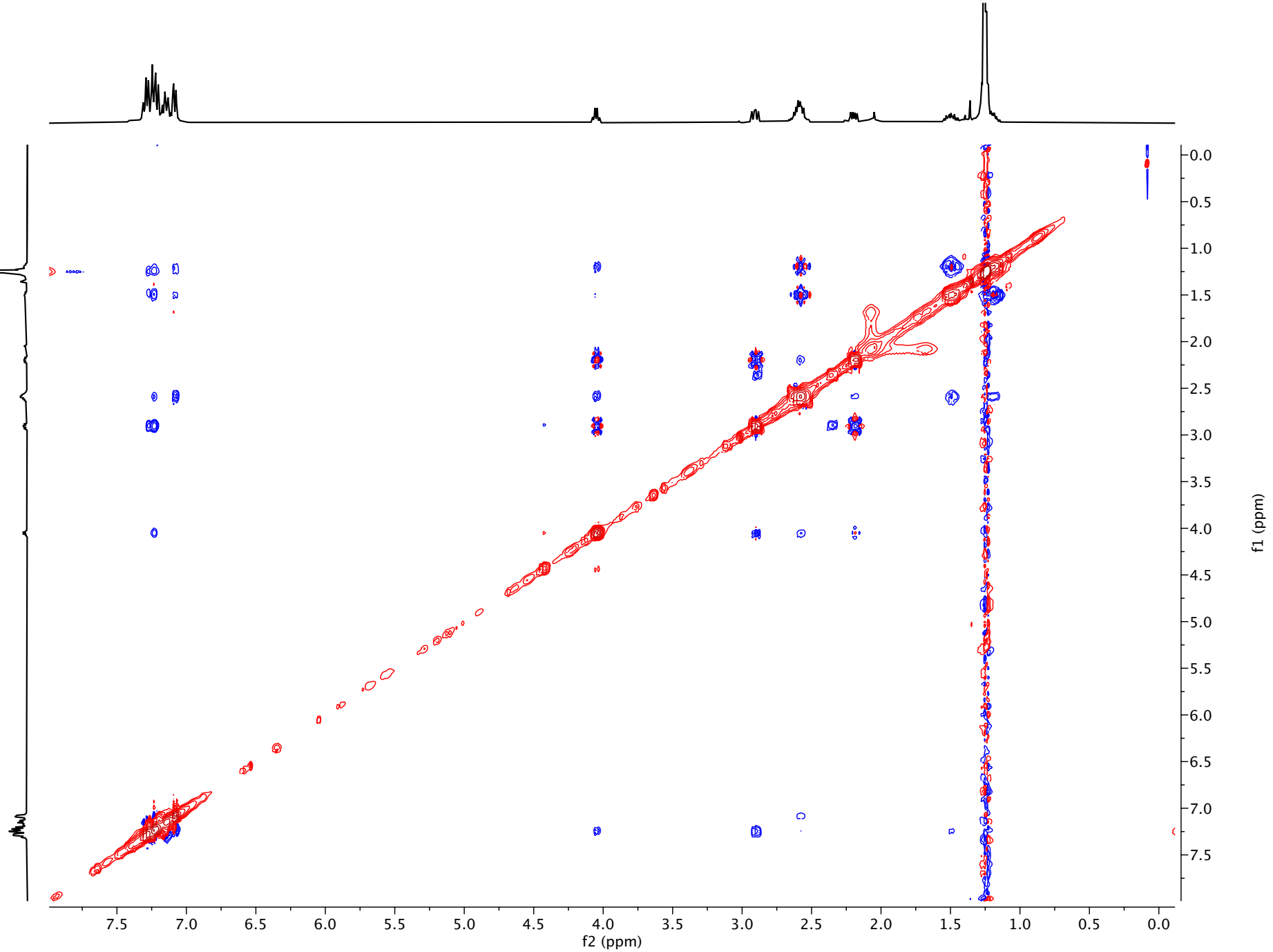


^{1}H (400 MHz), $CDCl_3$

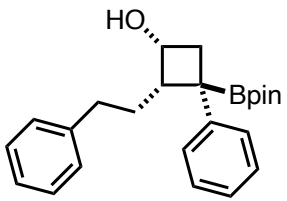


3s

NOESY



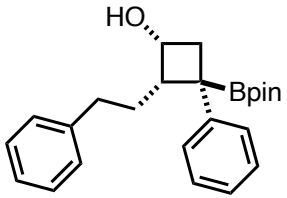
^{1}H (400 MHz), $CDCl_3$



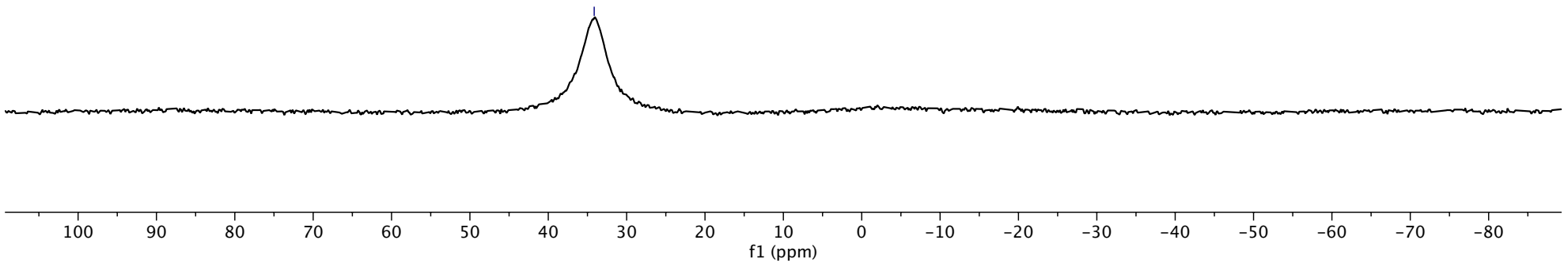
3t

34.14

^{11}B (128 MHz), $CDCl_3$

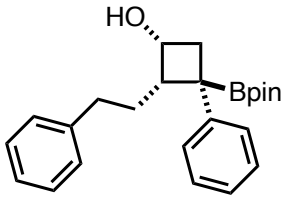


3t

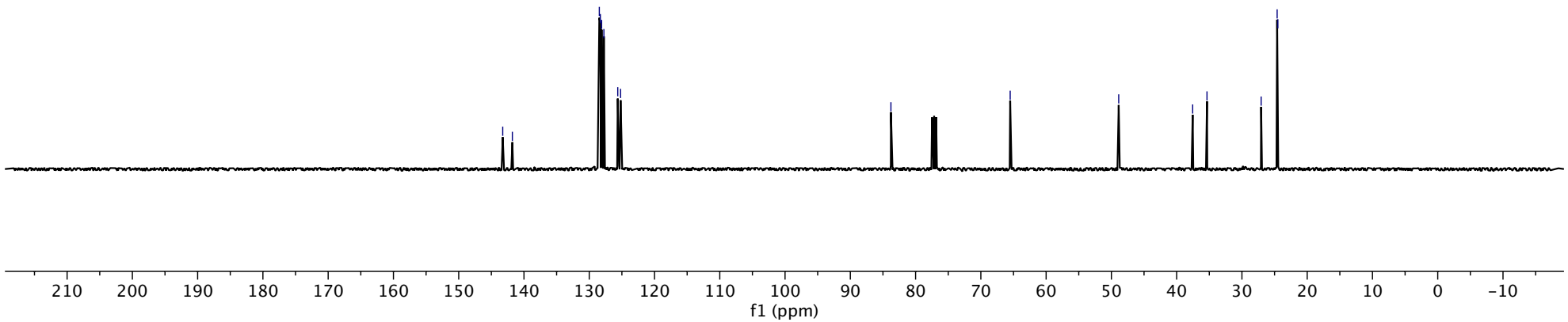


143.26
141.78
128.46
128.30
128.10
127.76
125.63
125.20
83.78
65.51
48.88
37.55
35.35
27.06
24.61
24.50

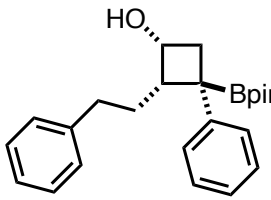
^{12}C (100 MHz), $CDCl_3$



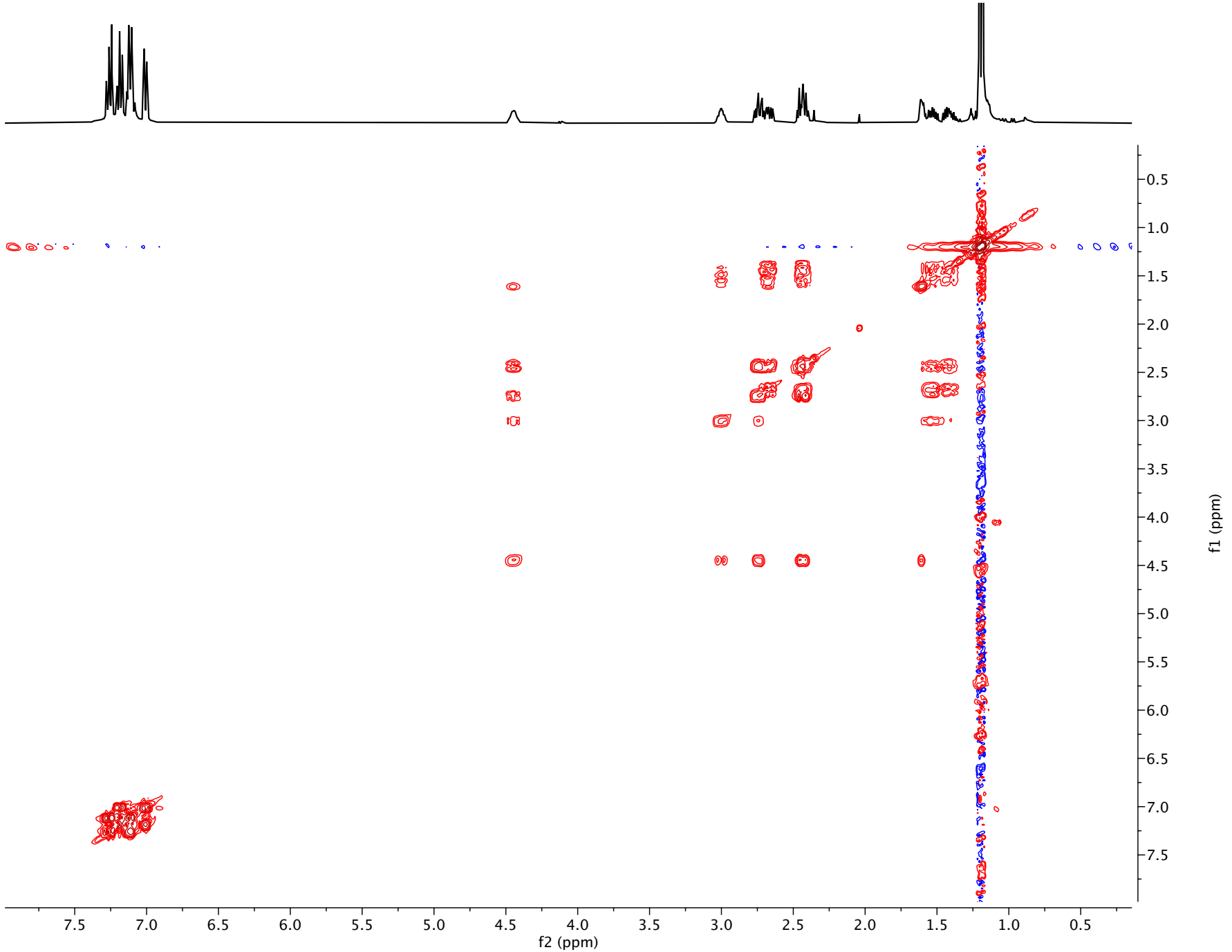
3t



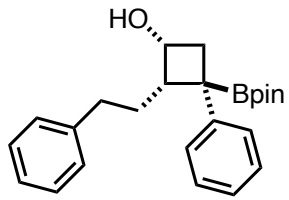
^{1}H (400 MHz), $CDCl_3$



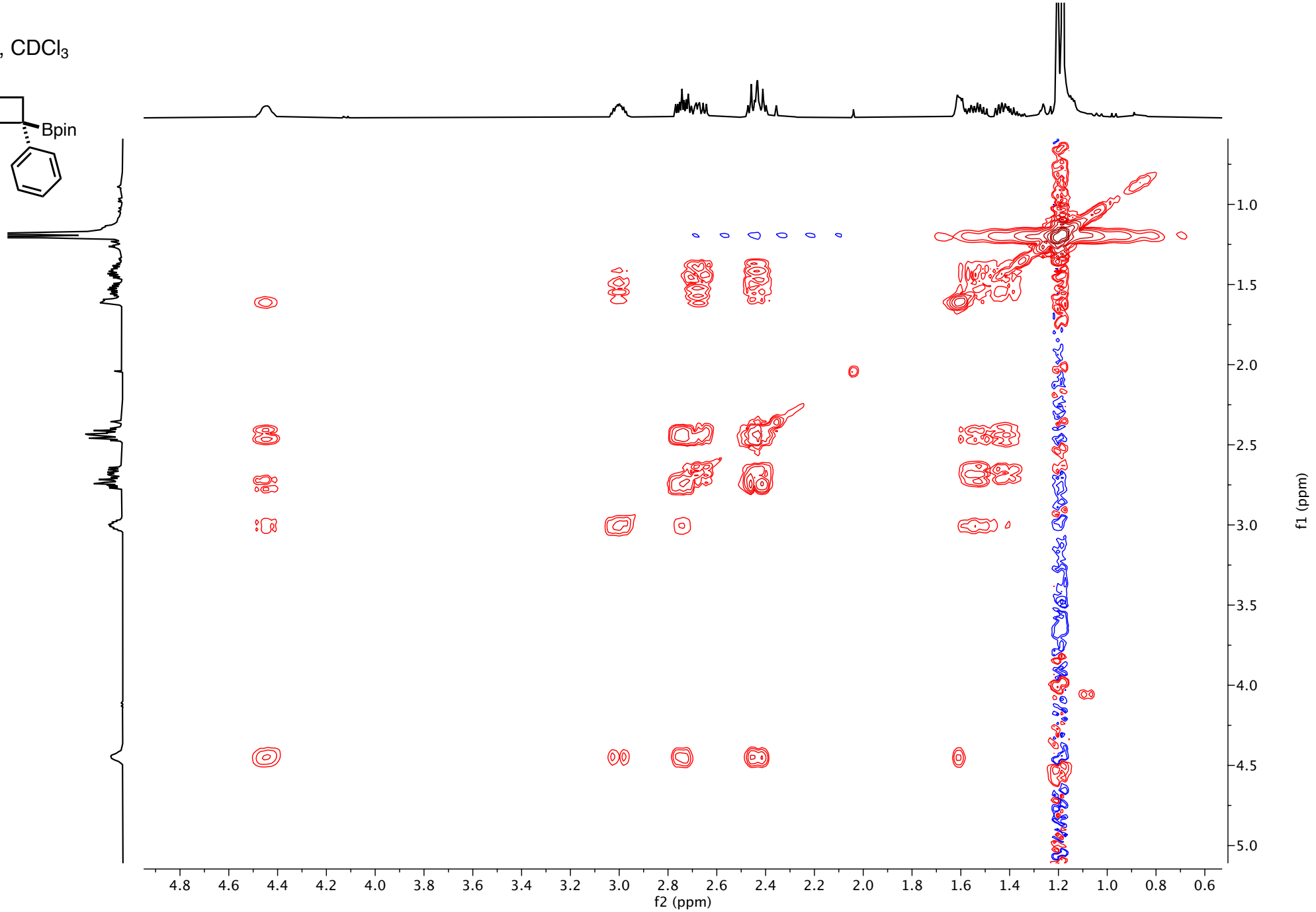
3t



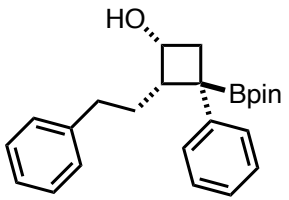
^{1}H (400 MHz), $CDCl_3$



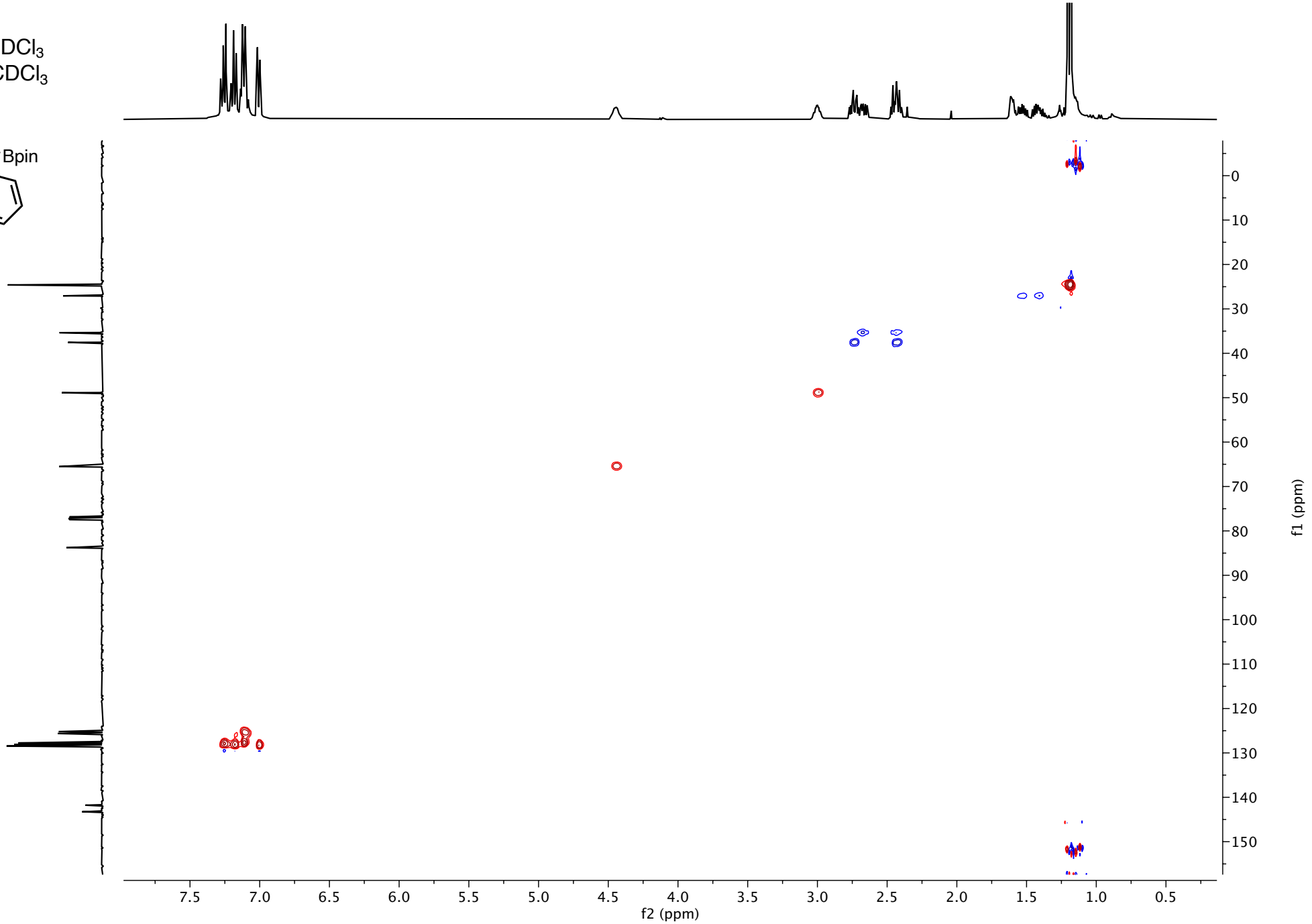
3t



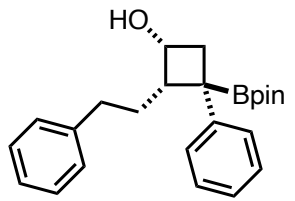
^{1}H (400 MHz), $CDCl_3$
^{13}C (100 MHz), $CDCl_3$



3t

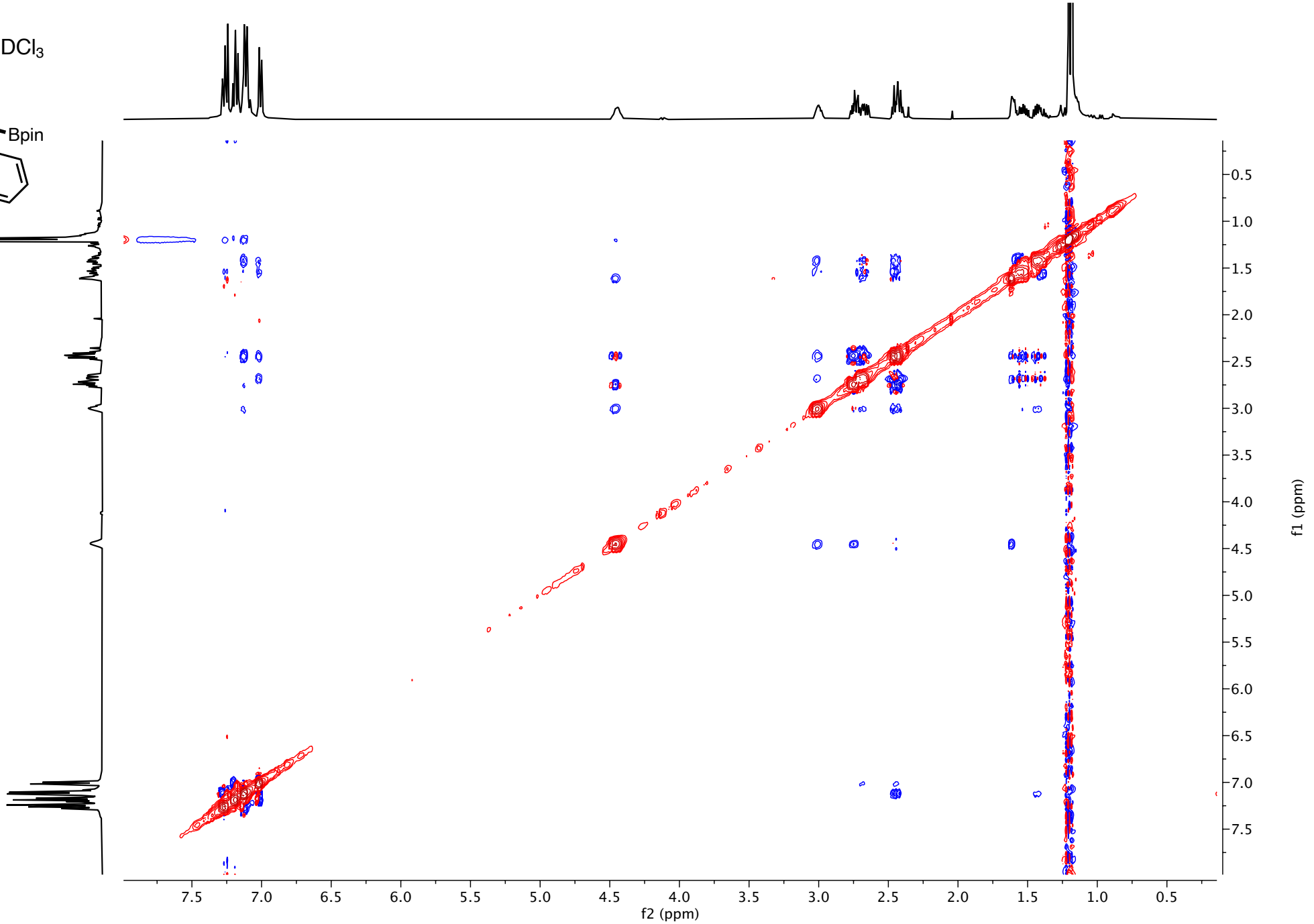


^{1}H (400 MHz), $CDCl_3$

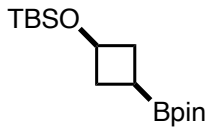


3t

NOESY

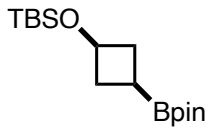


^{1}H (400 MHz), $CDCl_3$

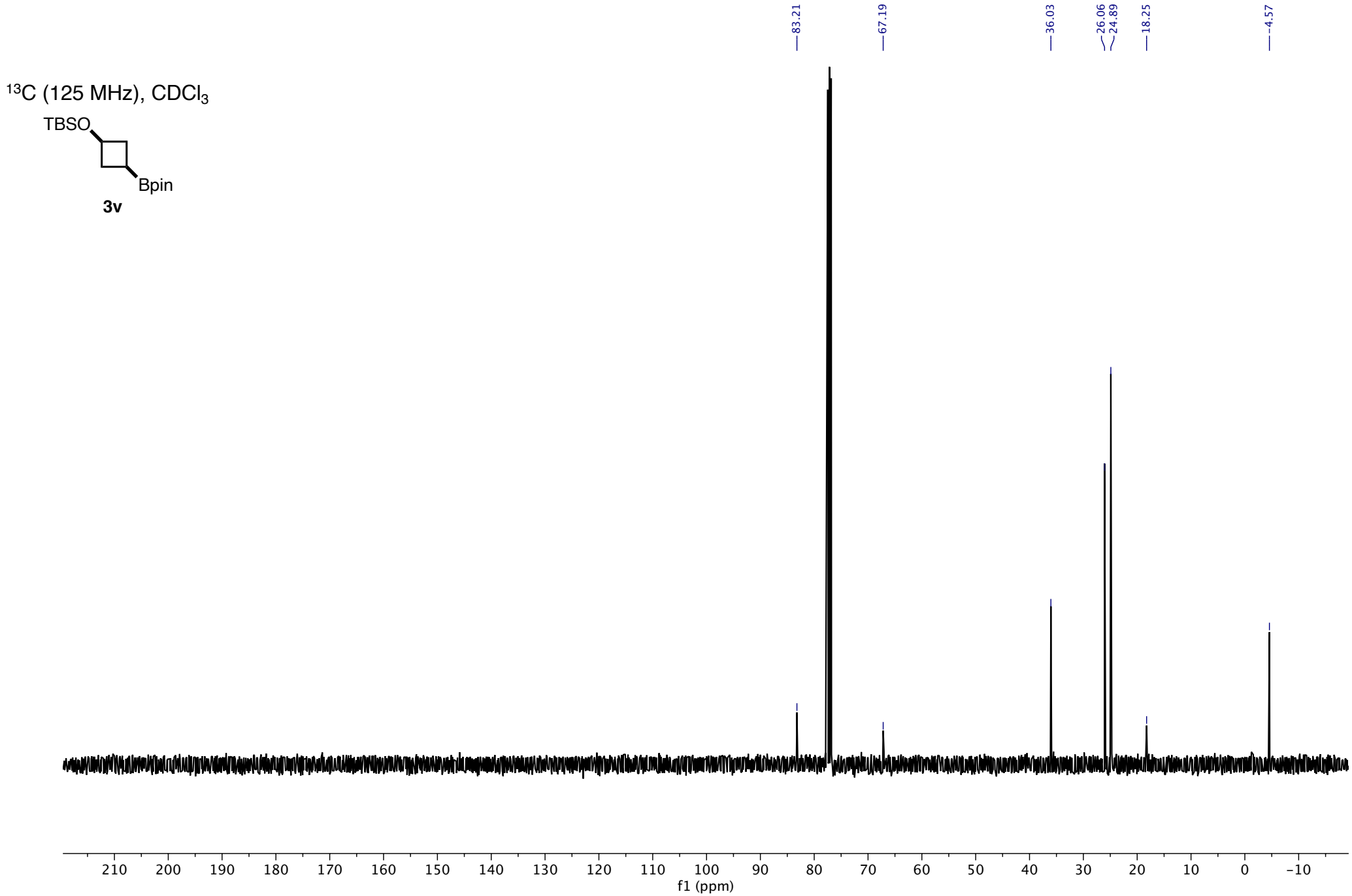


3v

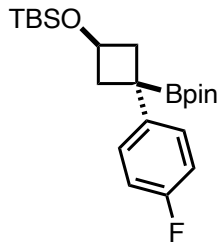
^{11}B (128 MHz), $CDCl_3$



3v

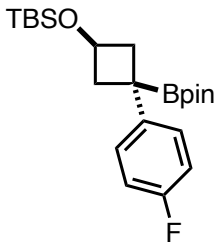

^{13}C (125 MHz), $CDCl_3$
TBSO
Bpin
3v
83.21
67.19
36.03
26.06
24.89
18.25
-4.57
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H (400 MHz), $CDCl_3$



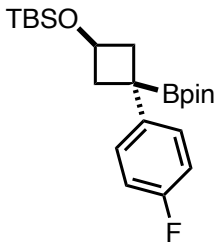
3w

^{11}B (128 MHz), $CDCl_3$



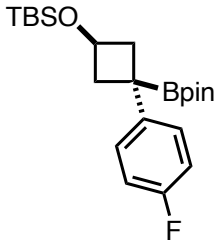
3w

^{13}C (125 MHz), $CDCl_3$



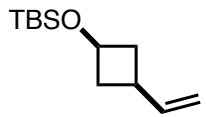
3w

^{19}F {^{1}H} (376 MHz), $CDCl_3$



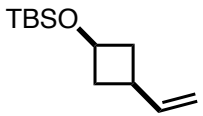
3w

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



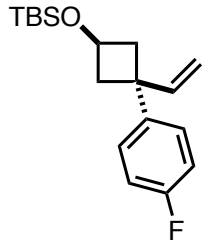
3x

^{13}C (125 MHz), $CDCl_3$



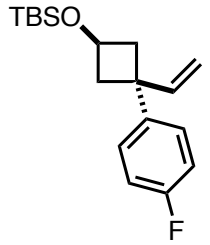
3x

^{1}H (400 MHz), $CDCl_3$



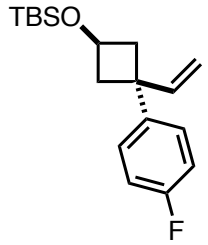
3y

^{13}C (100 MHz), $CDCl_3$



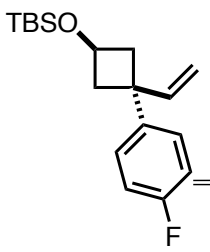
3y

^{19}F {^{1}H} (376 MHz), $CDCl_3$

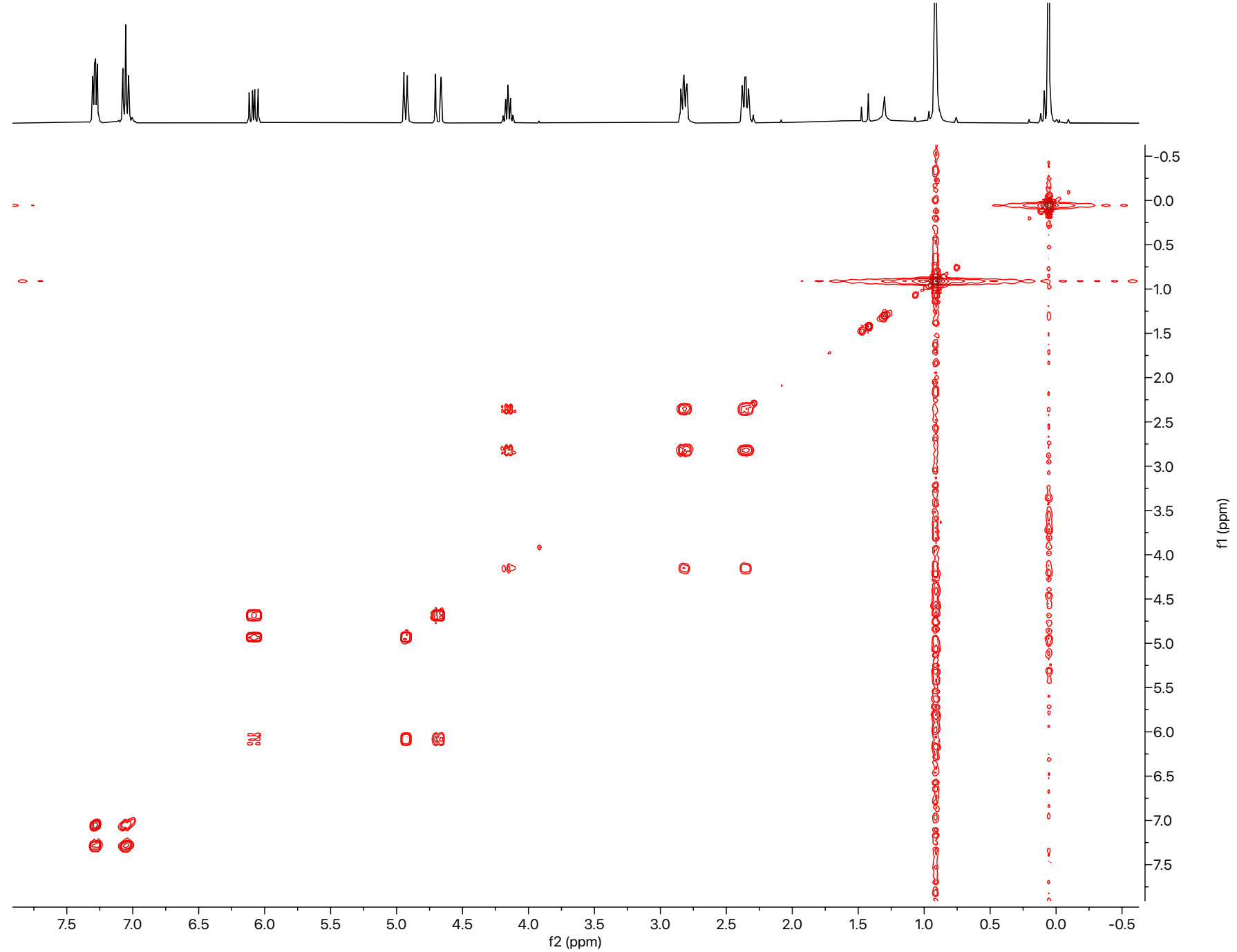


3y

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

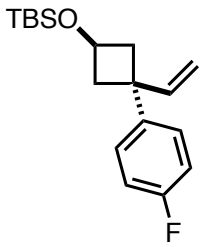


3y

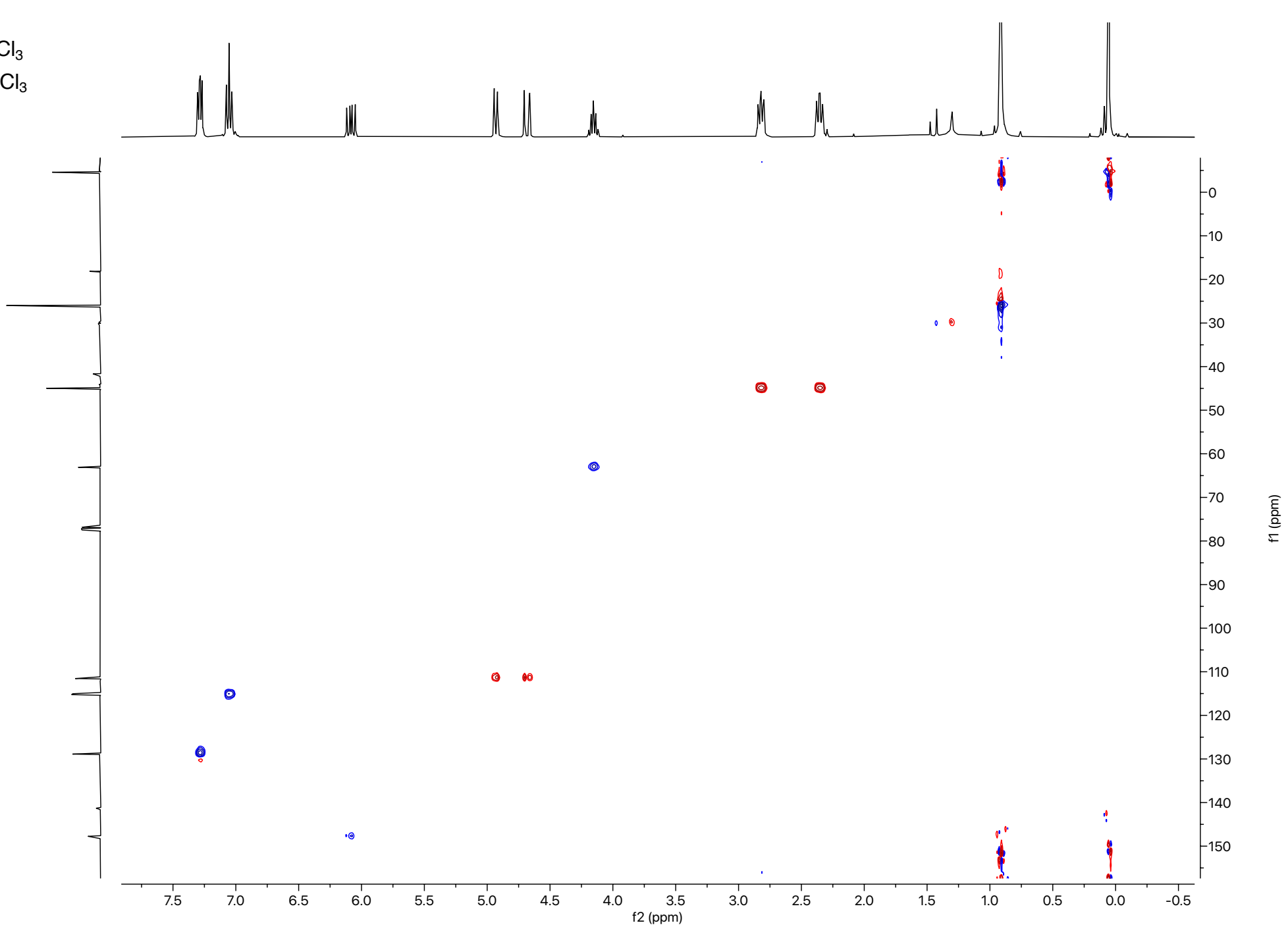


^{1}H (500 MHz), $CDCl_3$

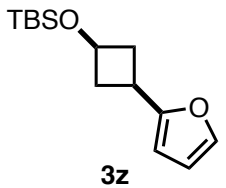
^{13}C (125 MHz), $CDCl_3$



3y

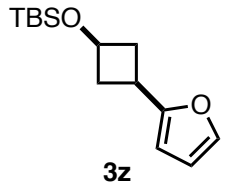


^{1}H (400 MHz), $CDCl_3$



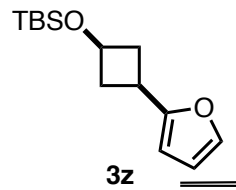
3z

^{13}C (100 MHz), $CDCl_3$



3z

^{1}H (400 MHz), $CDCl_3$

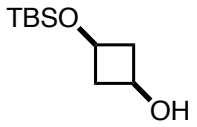


3z

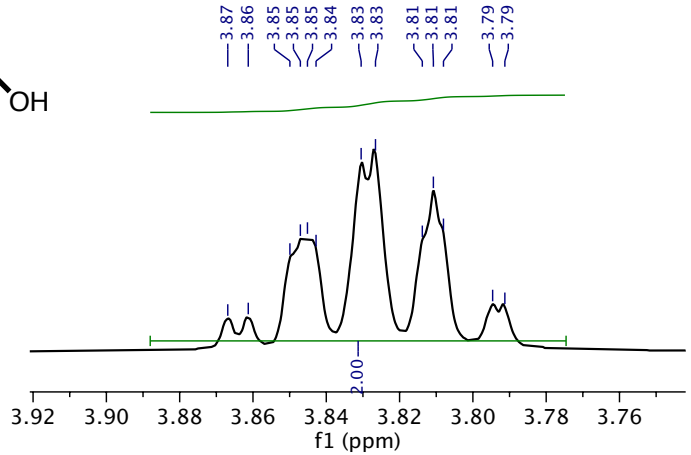
f2 (ppm)

f1 (ppm)

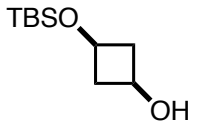
^{1}H (400 MHz), $CDCl_3$



3aa

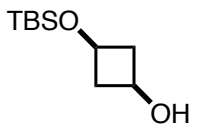


^{13}C (100 MHz), $CDCl_3$

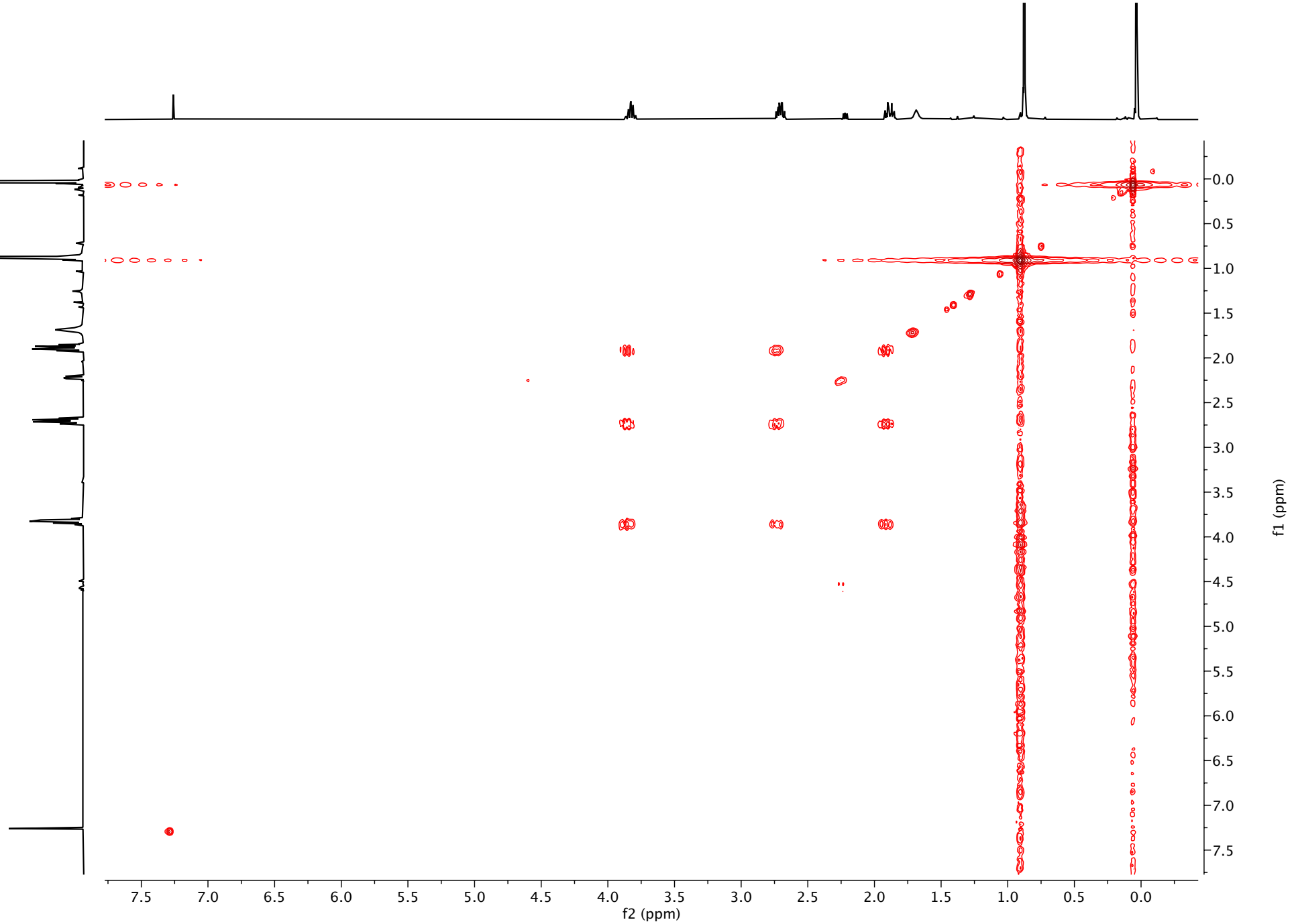


3aa

^{1}H (400 MHz), $CDCl_3$

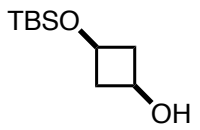


3aa

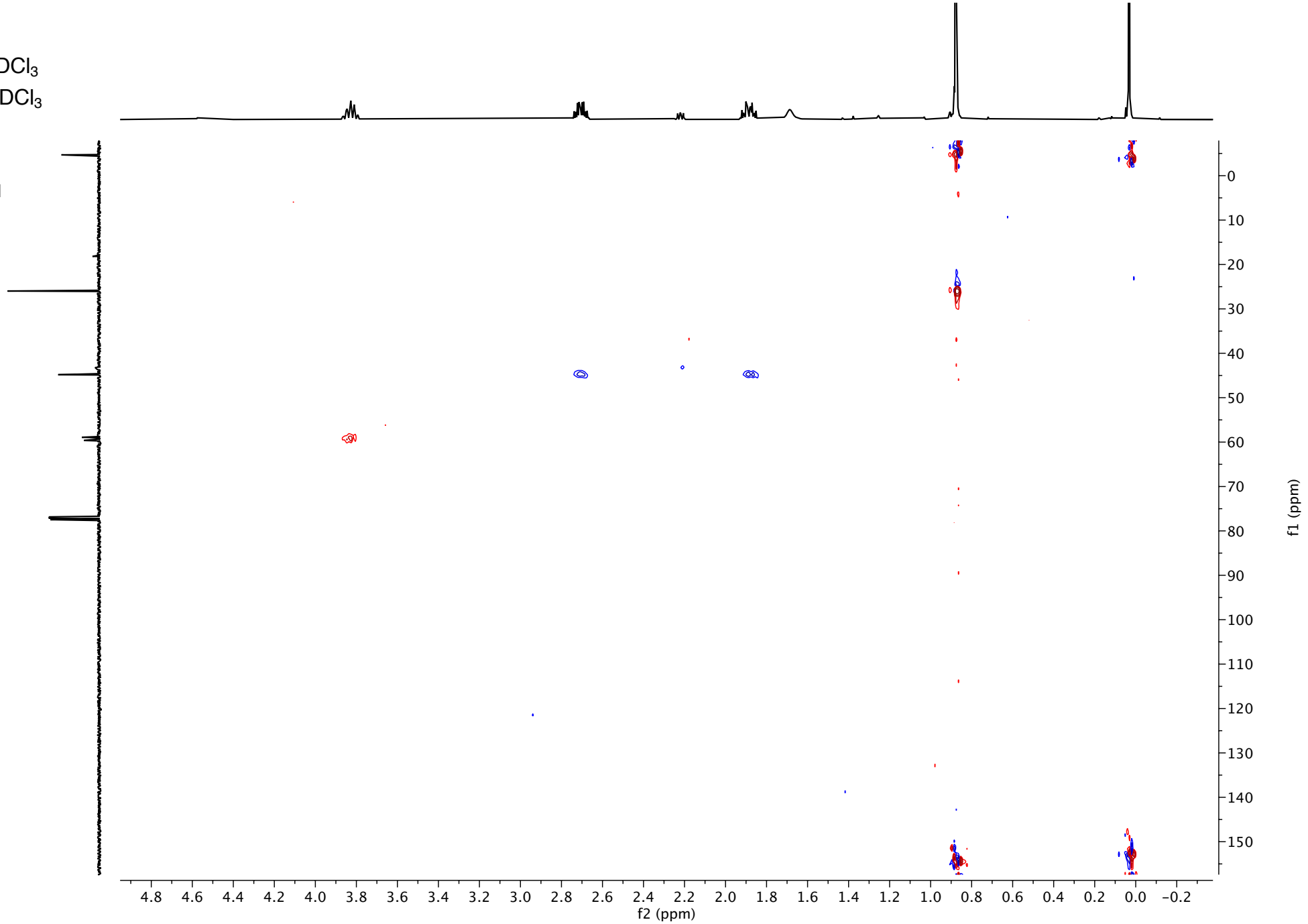


^{1}H (400 MHz), $CDCl_3$

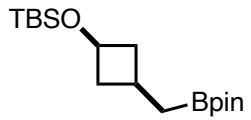
^{13}C (100 MHz), $CDCl_3$



3aa

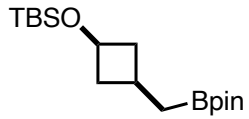


^{1}H (500 MHz), $CDCl_3$



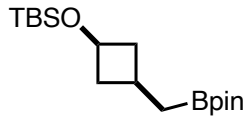
3ab

^{11}B (128 MHz), $CDCl_3$



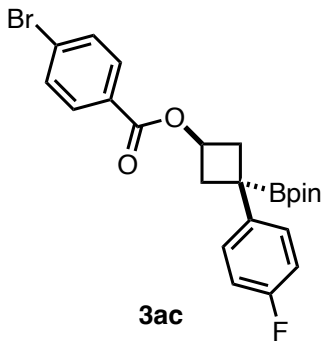
3ab

^{13}C (125 MHz), $CDCl_3$



3ab

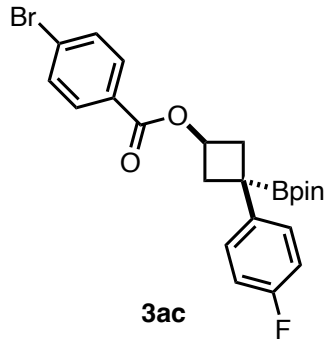
^{1}H (500 MHz), $CDCl_3$



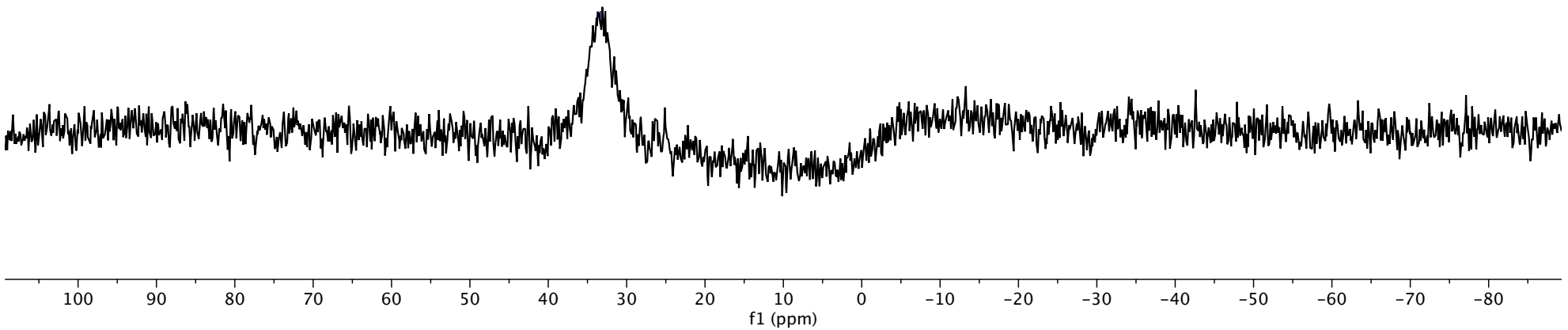
3ac

33.36

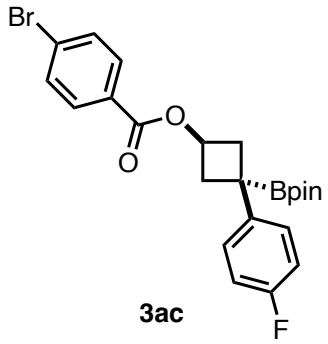
^{11}B (128 MHz), $CDCl_3$



3ac

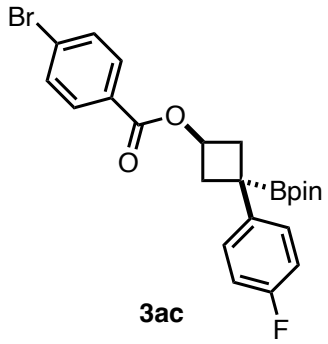


^{13}C (125 MHz), $CDCl_3$



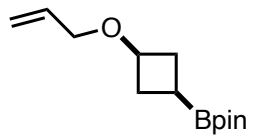
3ac

^{19}F {^{1}H} (376 MHz), $CDCl_3$



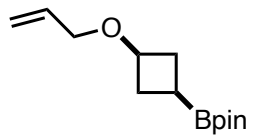
3ac

^{1}H (400 MHz), $CDCl_3$



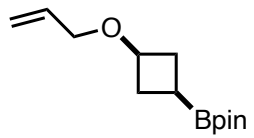
3ad

^{11}B (128 MHz), $CDCl_3$



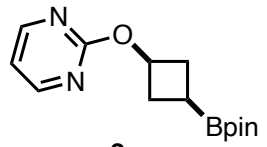
3ad

^{13}C (125 MHz), $CDCl_3$



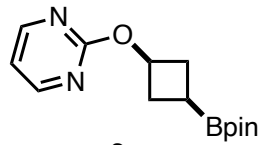
3ad

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



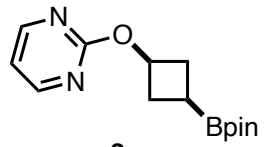
3ae

^{11}B (128 MHz), $CDCl_3$



3ae

^{13}C (125 MHz), $CDCl_3$



3ae