Enantio- and Diastereoselective Synthesis of Functionalized Carbocycles by Cu-Catalyzed Borylative Cyclization of Alkynes with Ketones

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SUPPORTING INFORMATION

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■ **General:** All reactions were carried out in oven-dried (150 °C) or flame-dried glassware under an inert atmosphere of dried N_2 unless otherwise noted. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm of 60 Å mesh silica gel. Plates were visualized by exposure to UV light (254 nm) and/or immersion into $KMnO_4$ or Seebach Stain followed by heating. Column chromatography was performed using silica gel P60 (mesh 230-400) supplied by Silicycle, and refers to flash chromatography unless stated otherwise. Tetrahydrofuran, dichloromethane, toluene, diethyl ether, toluene, benzene, and *n*-hexane (OmniSolv) were sparged with argon and then purified under a positive pressure of argon through a SG Water, USA Solvent Purification System, through two columns of neutral alumina. The ambient temperature in the laboratory was approximately 22 °C.

■ **Instrumentation:** All ^{1}H NMR spectra were recorded on Bruker Spectrometers (AVANCE-600, AVANCE-500 and AVANCE-400). Chemical shifts are reported in ppm from tetramethylsilane and referenced to the residual protio solvent peak ($CDCl_3$: δ 7.26, DMSO-d6: δ 2.50, CD_3OD: δ 3.31). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, qu = quartet, quint = quintet, br = broad, m = multiplet, app = apparent), integration, and coupling constants are given in Hz. ^{13}C NMR spectra were recorded on Bruker Spectrometers (AVANCE II-850, AVANCE-600, and AVANCE-500) with carbon and proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane and referenced to the residual protio solvent peak ($CDCl_3$: δ 77.16, DMSO-d6: δ 39.52, CD_3OD: δ 49.00). All IR spectra were recorded on a Jasco 260 Plus Fourier transform infrared spectrometer. Optical rotations were determined using a Jasco P1010 polarimeter and concentrations are reported in g/100 mL. Enantiomeric ratios were determined on an Agilent Technologies 1220 Infinity LC using the following columns: Diacel CHIRALPAK IA (4.6 mm x 250 mm x 5 μm) and Diacel CHIRALPAK IC (4.6 mm x 250 mm x 5 μm). Alternatively, enantiomeric ratios were determined on a Waters Acquity UPC2 supercritical fluid chromatography system (SFC) using the following columns: Phenomenex Lux Amylose-1 AD (4.6 mm x 150 mm x 5 μm) and Phenomenex Lux Cellulose-1 OD (4.6 mm x 150 mm x 5 μm). All HPLC samples were separated at 22 °C, and all SFC samples were separated at 30 °C. Racemic products were obtained by pre-mixing *(R)* and *(S)*-furyl-OMe-biphep for catalytic reactions forming [6,5]-bicycles and cyclopentanes; for [5,5]-bicycles, *(rac)*-BINAP was used. High resolution mass spectrometry samples were analyzed with a ThermoScientific Q Exactive HF-X mass spectrometer. Samples were introduced *via* an atmospheric pressure chemical ionization (APCI) source at a flow rate of 20 μL/min (samples in 100% MeOH). Xcalibur (ThermoFisher, Breman, Germany) was used to analyze the data. Absolute stereochemistry was assigned by single crystal X-ray crystallography of **(+)-(3b)** via anomalous scattering. Both X-ray samples were acquired using Cu Kα (λ = 1.54178 Å) radiation.

■ **Reagents:**

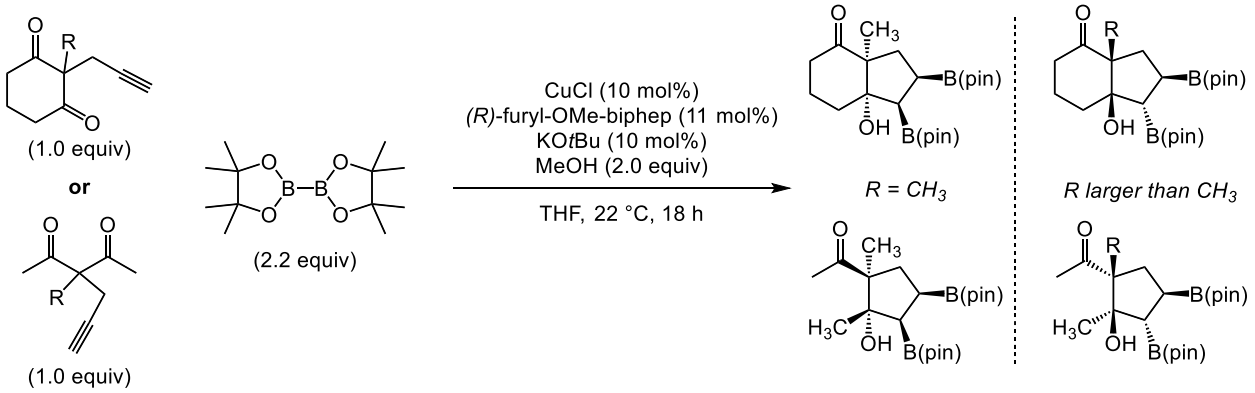
All diketones were azeotropically dried three times with benzene and stored in a N_2-filled glovebox. All chiral phosphine ligands used were purchased from Strem Chemicals Inc. and used as received.

Acetone was purchased from purchased from VWR and used without further purification. Unless stated otherwise, syntheses using acetone were conducted with 'bench' acetone (ACS).
Allyl bromide was purchased from Sigma-Aldrich and used without further purification.
Bis(pinacolato)diboron ($B_2(pin)_2$) was donated by AllyChem, recrystallized from boiling hexanes, azeotropically dried three times with benzene, and stored in a N_2-filled glovebox.
4-bromo-but-1-yne was purchased from Alfa Aesar and used without further purification.

Calcium hydride was purchased from Acros Organics and used without further purification.
Chloroform-*d* was purchased from Cambridge Isotope Laboratories and used without further purification.
Cinnamyl bromide (predominately *trans*) was purchased from Alfa Aesar and used without further purification.
Copper (I) chloride was purchased from Strem and stored in a N_2-filled glovebox.
1,3-cyclohexanedione was purchased from Alfa Aesar and used without further purification.
1,3-cyclopentanedione was purchased from Alfa Aesar and used without further purification.
3,3-dimethallylbromide was purchased from Sigma-Aldrich and used without further purification.
1,3-dimethoxybenzene was purchased from Sigma-Aldrich and used without further purification.
5,5-dimethyl-1,3-cyclohexanedione was purchased from Alfa Aesar and used without further purification.
Dimethylsulfoxide-d_6 was purchased from Cambridge Isotope Laboratories and used without further purification.
1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was purchased from TCI America and used without further purification.
1,4-dioxane was purchased from Alfa Aesar, pre-dried over $CaCl_2$, filtered, distilled from Na^0/benzophenone, and stored in a N_2-filled glovebox.
Grubb's 1st Generation catalyst was purchased from Sigma-Aldrich and used without further purification.
Hexamethyldisiloxane was purchased from Alfa Aesar and stored over 4 Å molecular sieves.
Hydrogen peroxide was purchased from Fisher Scientific as a 30% solution in water and stored at -20 °C.
Iodobenzene was purchased from Alfa Aesar and used without further purification.
Martin Sulfurane (Bis[α,α-bis(trifluoromethyl)benzenemethanolato]diphenylsulfur), was purchased from TCI America, stored in a glovebox, and used without further purification.
Methanol was purchased from VWR Life Science, dried over Mg/I_2, distilled, and stored over 3 Å molecular sieves under N_2.
Methanol-*d4* was purchased from Cambridge Isotopes and used without further purification.
2-methyl-1,3-cyclohexanedione was purchased from Alfa Aesar and used without further purification.
2-methyl-1,3-cyclopentanedione was purchased from Alfa Aesar and used without further purification.
Methyl iodide was purchased from Alfa Aesar and used without further purification.
3-methyl-2,4-pentanedione was purchased from Alfa Aesar and used without further purification.

***n*-Butyllithium** was purchased from Strem and used without further purification.
2,4-pentanedione was purchased from Alfa Aesar and used without further purification.
Palladium (II) acetate ($Pd(OAc)_2$) was purchased from Strem and stored in a N_2-filled glovebox.
Paraformaldehyde was purchased from Sigma-Aldrich and used without further purification.
Potassium carbonate was purchased from VWR Life Science and used without addition purification.
Potassium hydroxide was purchased from Fisher Scientific and used without further purification.
Potassium *tert*-butoxide was purchased from Strem and stored in a N_2-filled glovebox.
Propargyl bromide (80 wt.% in toluene) was purchased from Sigma-Aldrich and used without further purification.
Propionaldehyde was purchased from Sigma-Aldrich and used without further purification.
RuPhos (2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl) was purchased from Sigma-Aldrich and stored in a N_2-filled glovebox.
Sodium was purchased as cubes from Sigma-Aldrich and used without further purification.
Sodium hydride (60% dispersion in mineral oil) was purchased from Sigma-Aldrich and used without further purification.
***tert*-Butyl alcohol** was purchased from Alfa Aesar, dried over $MgSO_4$, filtered, dried overnight over CaH_2 at 30 °C, distilled, and stored over 4 Å molecular sieves under N_2.
***tert*-Butyllithium** was purchased from Sigma-Aldrich (1.7 M in pentane). Prior to use, titration with 2-propanol using 1,10-phenanthroline (in Et_2O at 0 °C) determined the concentration was 1.37 M.
Triphenylphosphine was purchased from Sigma-Aldrich, recrystallized from boiling hexanes, azeotropically dried three times with benzene, and stored in a N_2-filled glovebox.
Vinyl boronic acid pinacol ester was purchased from Sigma-Aldrich and used without further purification.

■ **General Procedure (I) for the Enantio- and Diastereoselective Bis-Borylation/Cyclization for [6,5]-fused ring systems and cyclopentane systems**

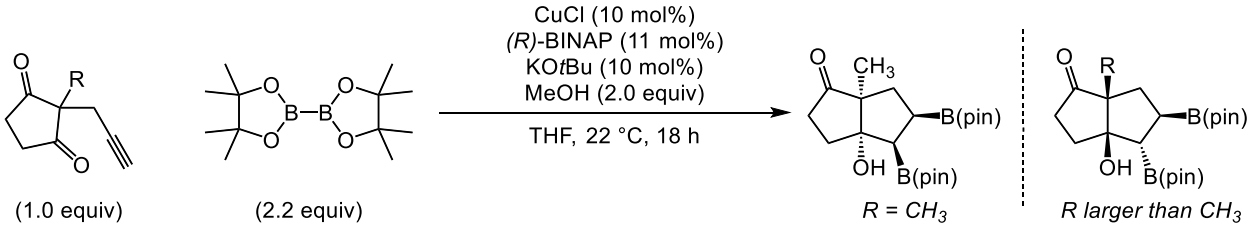


In a N_2-filled glovebox, an 8 mL vial equipped with a magnetic stir bar was charged with CuCl (1.0 mg, 0.010 mmol), *(R)*-furyl-OMe-biphep (6.0 mg, 0.011 mmol), KO*t*Bu (1.1 mg, 0.010 mmol), and 250 μL of THF. The reaction was capped with a Teflon-lined lid and allowed to stir at room temperature for 30 minutes, after which time bis(pinacolato)diboron (55.9 mg, 0.22 mmol) was added as a solid. The reaction turned dark brown immediately. After 15 minutes of stirring at room temperature, an additional 250 μL of THF was added, followed immediately by neat diketone substrate (0.10 mmol). The vial was sealed with electrical tape and removed from the glovebox. Dry MeOH (8.1 μL, 0.20 mmol) was added by syringe under a N_2 atmosphere. The reaction was stirred at 22 °C for 18 hours.

After 18 hours, the reaction was opened, quenched with 1 mL of saturated NH_4Cl (*aq*), and stirred vigorously at 22 °C for 30 minutes. Ethyl acetate (1 mL) was added and the layers separated. The aqueous layer was extracted three times with ethyl acetate, and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. NMR yield and diastereomeric ratios were determined by ^1H NMR, using hexamethyldisiloxane as an internal standard. Products were purified by flash silica gel chromatography. Subsequent analysis by HPLC or SFC provided enantiomeric ratios.

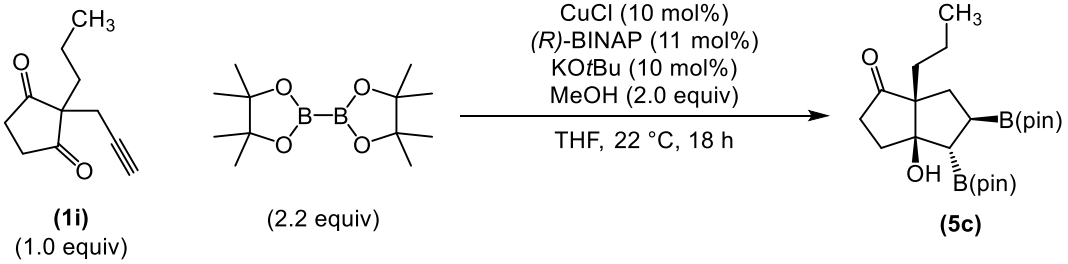
Note: Reactions were run using either *(R)* or *(S)*-furyl-OMe-biphep, which were purchased from Strem.

■ **General Procedure (II) for the Enantio- and Diastereoselective Bis-Borylation/Cyclization for [5,5]-fused ring systems**



In an N_2-filled glovebox, an 8 mL vial equipped with a magnetic stir bar was charged with CuCl (1.0 mg, 0.010 mmol), *(R)*-BINAP (6.8 mg, 0.011 mmol), KO*t*Bu (1.1 mg, 0.010 mmol), and 250 μL of THF. The reaction was capped with a Teflon-lined lid and allowed to stir at room temperature for 30 minutes, after which time bis(pinacolato)diboron (55.9 mg, 0.22 mmol) was added as a solid. The reaction turned dark brown immediately. After 15 minutes of stirring at room temperature, an additional 250 μL of THF was added, followed immediately by neat diketone substrate (0.10 mmol). The vial was sealed with electrical tape and removed from the glovebox. Dry MeOH (8.1 μL, 0.20 mmol) was added by syringe under a N_2 atmosphere. The reaction was stirred at 22 °C for 18 hours. Reactions were worked up according to **General Procedure I**.

■ **Large Scale Synthesis of (5c)**

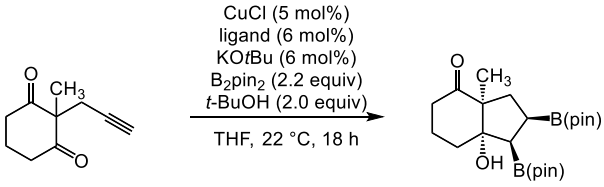


In an N_2-filled glovebox, a 100 mL round bottom flask equipped with a magnetic stir bar was charged with CuCl (48.6 mg, 0.491 mmol, 10 mol%), *(R)*-BINAP (336.2 mg, 0.540 mmol, 11 mol%), KO*t*Bu (55.1 mg, 0.491 mmol, 10 mol%), and 12.3 mL of THF. The reaction was capped with a rubber septum and allowed to stir at room temperature for 30 minutes, after which time bis(pinacolato)diboron (2.74 g, 10.80 mmol, 2.2 equiv) was added as a solid. The reaction turned dark brown immediately. After 15 minutes of stirring at room temperature, an additional 8.3 mL of THF was added, followed immediately by a solution of diketone substrate (875 mg, 4.91 mmol, 1.0 equiv, 1.23 M in THF). The flask was sealed with electrical tape and removed from the glovebox. Dry MeOH (398 μL, 9.82 mmol, 2.0 equiv) was added by syringe under a N_2

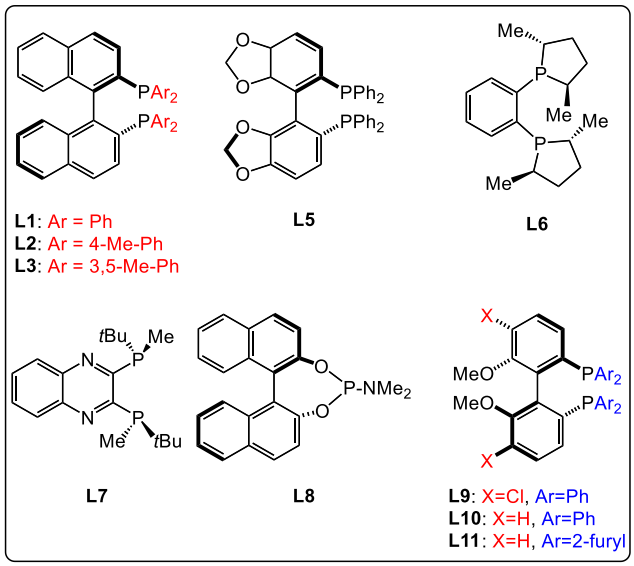
atmosphere. After 18 hours, the reaction was opened, quenched with 25 mL of saturated NH_4Cl (*aq*), and stirred vigorously at 22 °C for 30 minutes. Ethyl acetate (25 mL) was added and the layers separated. The aqueous layer was extracted three times with ethyl acetate, and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Silica gel chromatography (15:1 hex:EtOAc → 10: 1 hex:EtOAc) afforded **(5c)** as a white powder (1.21 g, 57% yield, >20:1 dr, 94:6 er).

■ Reaction Optimization

Table S1. Chiral ligand screening.



Entry	Ligand	NMR yield (%)	d.r.	e.e. (%)
1	**L1**	65	5:1	> 99
2	**L2**	71	3:1	> 99
3	**L3**	65	0.6:1	n.d.
4	**L5**	64	3:1	> 99
5	**L6**	32	>20:1	n.d.
6	**L7**	16	3:1	n.d.
7	**L8** (12 mol%)	0	-	-
8	**L9**	42	1.2:1	> 99
9	**L10**	57	3:1	> 99
10	**L11**	64	12:1	> 99
11*	**L11**	78	9:1	>99



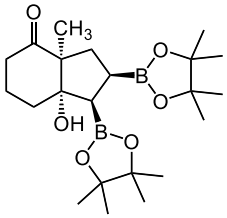
n.d. = not determined

*10 mol% CuCl, 11 mol% **L11**, 10 mol% KO*t*Bu, and MeOH (2.0 equiv) instead of *t*-BuOH

Table S1: Screening of chiral phosphine ligands was performed on 2-methyl-2-propargyl-1,3-cyclohexanedione. *(R)*-furyl-OMe-biphep (**L11**) afforded the product in good conversion and excellent diastereo- and enantioselectivity. Examination of the substrate scope later necessitated switching from *t*-BuOH to MeOH to avoid large amounts of returned alkyne.

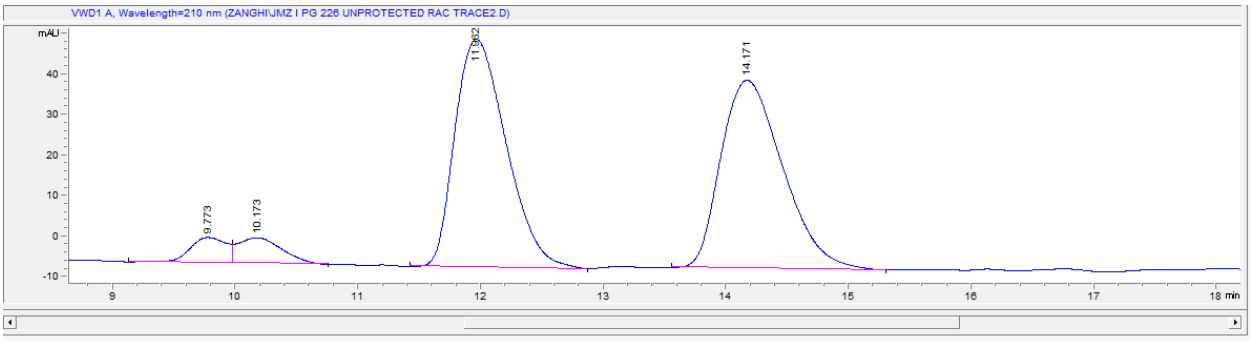
■ Vinyl boronic ester reactions

(1R,2R,3aS,7aS)-7a-hydroxy-3a-methyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (3a)



(3a)

Racemic material: *Diacel CHIRALPAK IC Column: 85:15 hexanes:iPrOH; 1.0 mL/min; 205 nm.*



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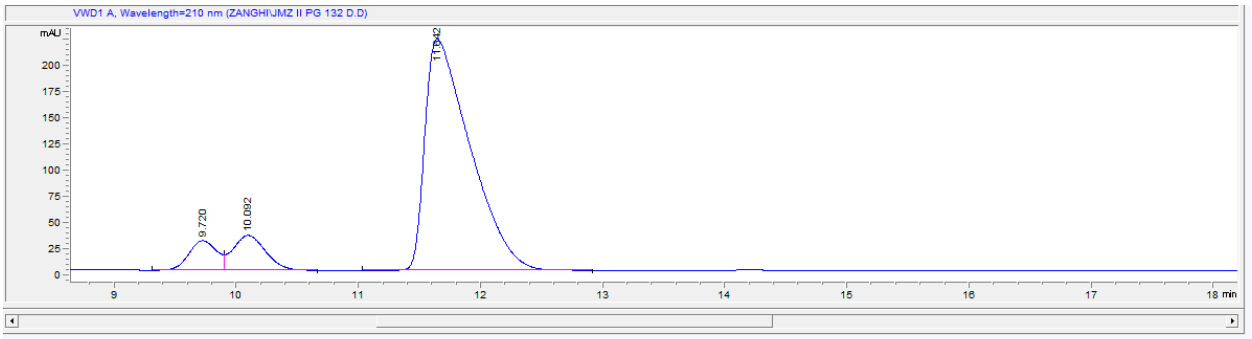
Date	30-Jan-17, 13:08:09
Sample	JMZ I pg 226 unprotected rac trace2
Sample Info	6 5 fused Bpin substrate 85:15 Hex:iPrOH; 1.0 mL/min; Column IC;

#	Time	Area	Height	Width	Area%	Symmetry
1	9.773	131.5	6.2	0.3187	3.709	1.028
2	10.173	157.2	6.4	0.37	4.435	0.679
3	11.962	1635.1	56.2	0.4605	46.131	0.674
4	14.171	1620.7	46.3	0.5482	45.725	0.692

Enantioenriched material [(R)-BINAP]:



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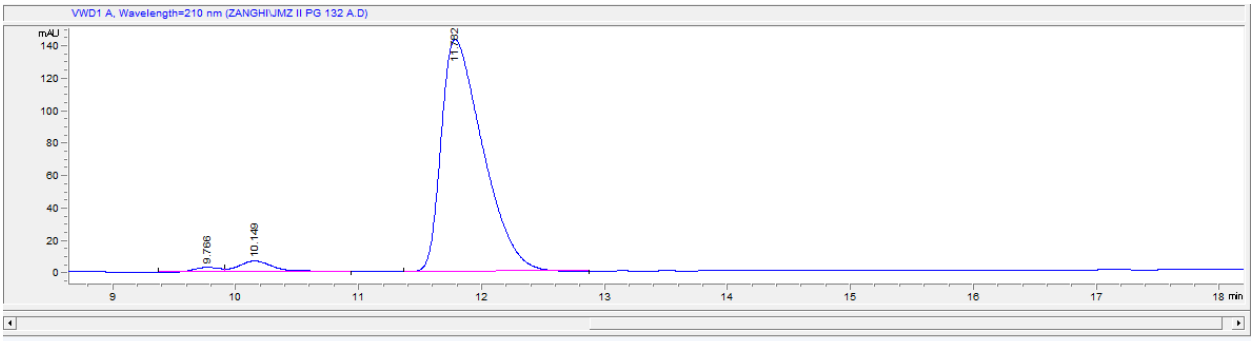
Sample	JMZ II PG 132 D
Sample Info	6 5 fused Bpin substrate 85:15 Hex:iPrOH; 1.0 mL/min; Column IC;

#	Time	Area	Height	Width	Area%	Symmetry
1	9.72	449.9	28.2	0.2442	6.660	0.974
2	10.092	612.5	33.2	0.2809	9.066	0.812
3	11.642	5693.4	221.1	0.3804	84.274	0.354

Enantioenriched material [(R)-furyl-OMe-biphep]:



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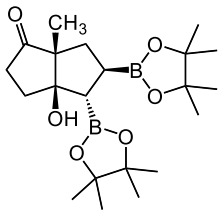
Date	23-Jul-17, 01:43:20
Sample	JMZ II PG 132 A
Sample Info	6 5 fused Bpin substrate 85:15 Hex:iPrOH; 1.0 mL/min; Column IC;

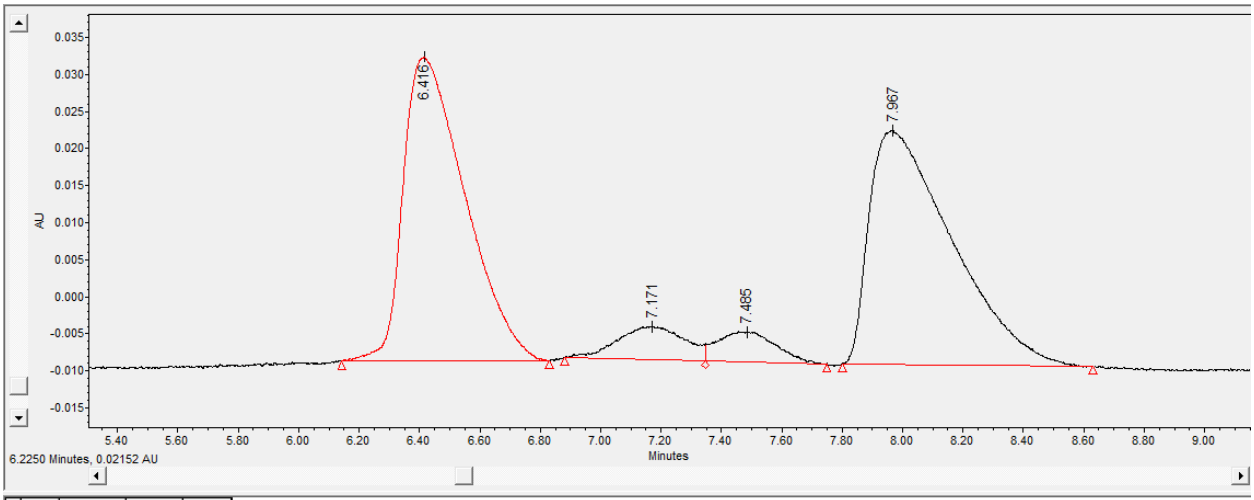
#	Time	Area	Height	Width	Area%	Symmetry
1	9.766	45	3	0.2358	1.269	1.113
2	10.149	133.3	6.7	0.2983	3.762	0.767
3	11.782	3366.1	143.1	0.3575	94.969	0.474

(*3aR,4S,5R,6aR*)-3a-hydroxy-6a-methyl-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2H)-one (5a)



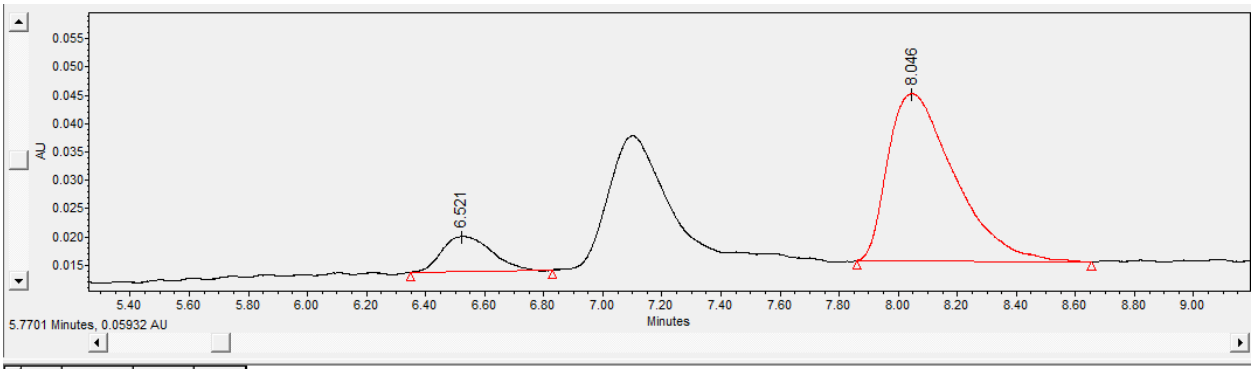
(5a)

Racemic material: *Phenomenex Lux Cellulose-1 OD Column: 95:5 CO_2:iPrOH; 1.0 mL/min; 205 nm.*



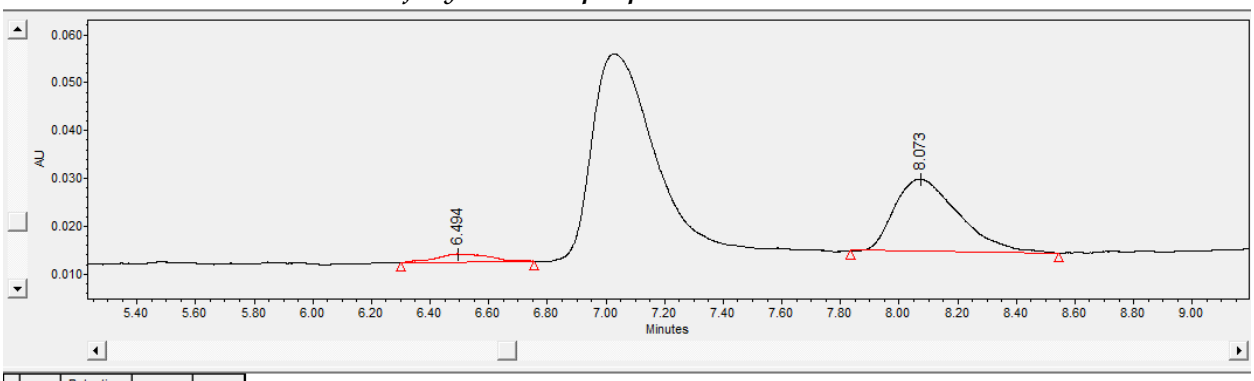
	Name	Retention Time (min)	Area (µV*sec)	% Area
1		6.416	584634	44.79
2		7.171	68732	5.27
3		7.485	53635	4.11
4		7.967	598292	45.84

Enantioenriched material [(R)-BINAP]:



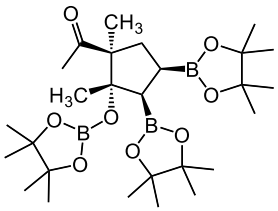
	Name	Retention Time (min)	Area (μV*sec)	% Area
1		6.521	72333	13.55
2		8.046	461364	86.45

Enantioenriched material [(R)-furyl-OMe-biphep]:



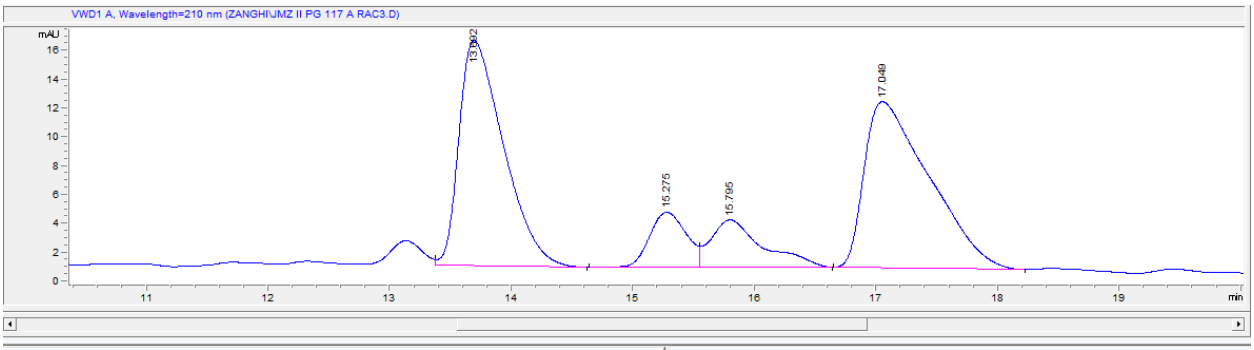
	Name	Retention Time (min)	Area (μV*sec)	% Area
1		6.494	21090	8.45
2		8.073	228452	91.55

1-((*1S,2S,3R,4R)*-1,2-dimethyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)cyclopentyl)ethan-1-one (6a)



(6a)

Racemic material: *Diacel CHIRALPAK IC Column: 98:2 hexanes:iPrOH; 1.0 mL/min; 205 nm.*



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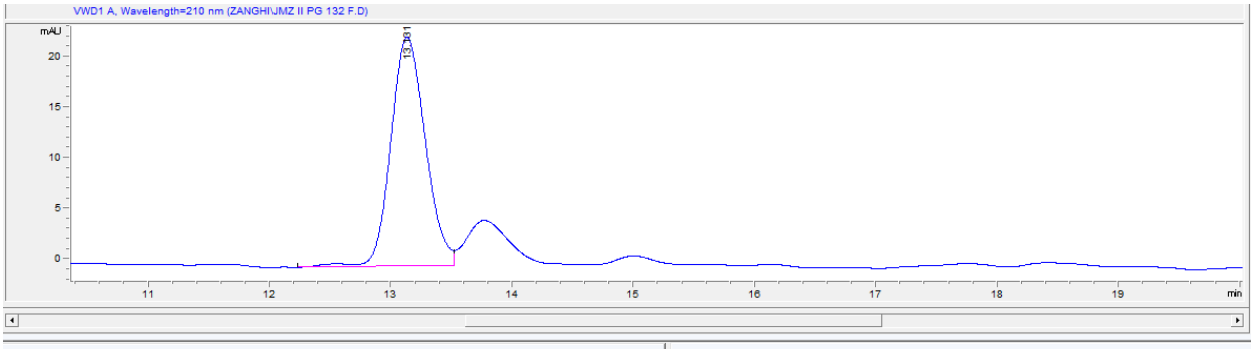
Sample	JMZ II pg 117 A rac3
Sample Info	acyclic sub rac trace; 98:2 Hex:iPrOH; 1.0 mL/min; IC Column; 210 r

#	Time	Area	Height	Width	Area%	Symmetry
1	13.692	398.5	15.6	0.3893	39.730	0.484
2	15.275	81	3.8	0.3295	8.079	0.85
3	15.795	96.7	3.3	0.4181	9.637	0.514
4	17.049	426.9	11.5	0.5283	42.554	0.366

Enantioenriched material [(R)-BINAP]:



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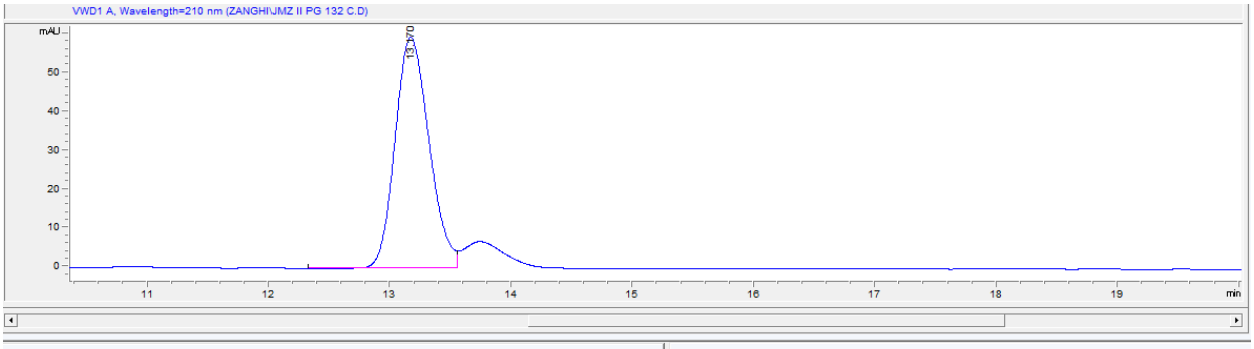
Sample	JMZ II PG 132 F
Sample Info	acyclic sub rac trace; 98:2 Hex:iPrOH; 1.0 mL/min; IC Column; 210 r

#	Time	Area	Height	Width	Area%	Symmetry
1	13.131	450	22.6	0.3093	100.000	0.869

Note: Peak at 13.8 min thought to result from a mixture of OBpin and free OH products.

Enantioenriched material [(R)-furyl-OMe-biphep]:



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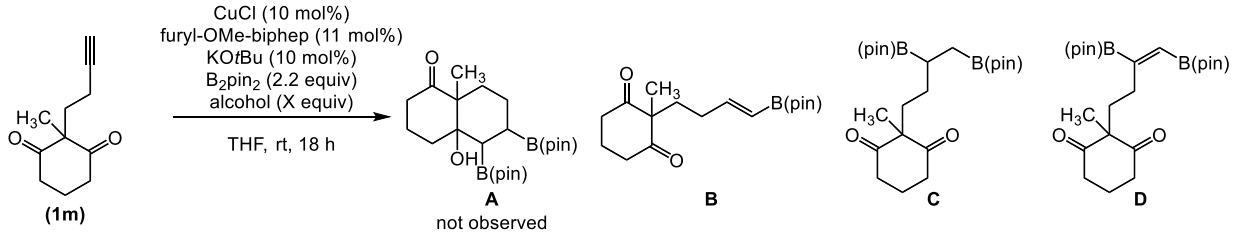
Sample	JMZ II PG 132 C
Sample Info	acyclic sub rac trace; 98:2 Hex:iPrOH; 1.0 mL/min; IC Column; 210 r

#	Time	Area	Height	Width	Area%	Symmetry
1	13.17	1163.3	59.5	0.3041	100.000	0.804

Note: Peak at 13.8 min thought to result from a mixture of OBpin and free OH products.

■ Attempts to form *cis*-decalin products

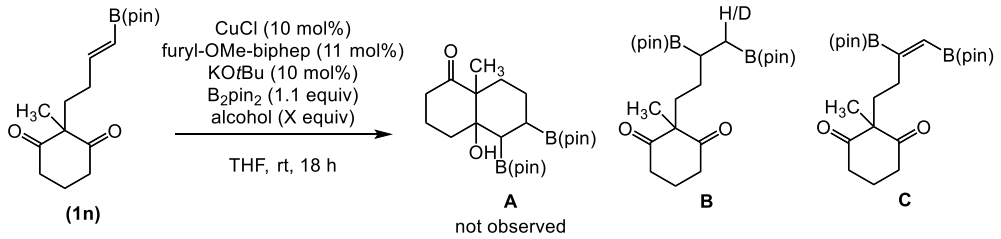
Table S2. Studies from alkyne to access decalins.



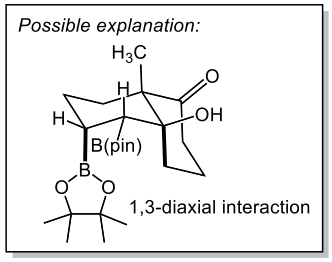
Alcohol	Returned alkyne	B	C	D
MeOH (2 equiv)	< 5	< 5	83	4
t-BuOH (2 equiv)	41	14	25	11
MeOH (1 equiv)	39	14	21	14

* Yield determined by ^{1}H NMR spectra of crude reactions with hexamethyldisiloxane as internal standard.

Table S3. Studies from vinyl boronic ester to access decalins.



Change in conditions	Returned vinyl Bpin	B	C
MeOH (1.0 equiv)	0	45	9
t-BuOH (1.0 equiv)	0	37	12
t-BuOH (1.0 equiv)**	0	50	18
d4-methanol (1.0 equiv)	17	24	4
no alcohol	~ 80	< 5	7
BINAP as ligand (MeOH, 1 equiv)	0	30	35



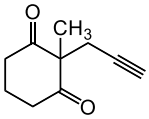
* Yield determined by ^{1}H NMR spectra of crude reactions with hexamethyldisiloxane as internal standard.

** *t*-BuOH added as a 1 M solution in THF (10 x 10 uL portions) every 45 min

Starting from alkyne **1m**, standard catalytic conditions (2 equiv MeOH) resulted in 83% NMR yield of the double hydroboration product **C** (**Table S2**). Attempts to slow down protonation with *t*-BuOH resulted in a large amount of returned alkyne and still significant double hydroboration. Attempts to start from the pre-formed vinyl boron **(1n)** also failed to provide product **A** (**Table S3**). Using d_4-methanol to slow down protonation yielded a complex mixture where the product was not able to be identified either by crude NMR or in any fractions following silica gel chromatography. Switching to BINAP resulting in a large amount of a trisubstituted olefin **D**. Difficulties in the reaction likely result from the alkyl-Cu being farther away on a chain with more degrees of freedom (although 6-member ring formation was demonstrated in our previous work) and possible 1,3-diaxial strain which would raise the transition state energy for cyclization (1,3-diaxial strain not present in our previous work).[1]

■ Substrate syntheses

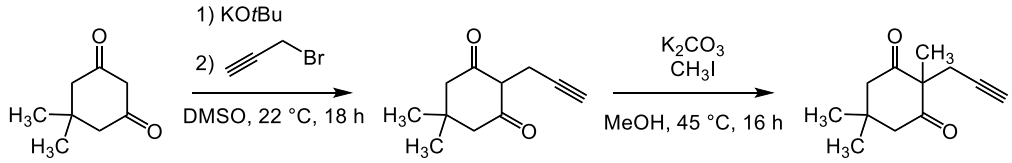
2-methyl-2-propargyl-1,3-cyclohexanedione (1a)



(1a)

(1a) was prepared according to a literature procedure.[2]

2,5,5-trimethyl-2-(prop-2-yn-1-yl)cyclohexane-1,3-dione (1b)

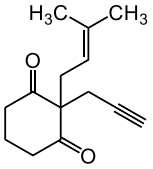


To an oven dried 100 mL round bottom flask was added dimedone (2.00 g, 14.27 mmol, 1.18 equiv) followed by 30 mL of dry DMSO. KO*t*Bu (1.31 g, 11.00 mmol, 0.91 equiv) was added at once, and the flask flushed with N_2. After stirring for 45 minutes at 22 °C, propargyl bromide (80 wt.% in toluene) (1.35 mL, 12.09 mmol, 1.0 equiv) was added by syringe. The reaction was allowed to stir at 22 °C for 18 hours. The resulting orange solution was diluted with brine, and extracted with EtOAc (3 x 35 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*, giving **(S1)** as a yellow solid that was used without further purification.

To the crude solid was added K_2CO_3 (3.33 g, 24.1 mmol, 2.0 equiv), MeOH (40 mL), and MeI (3.75 mL, 60.2 mmol, 5 equiv) in a 100 mL flask. A reflux condenser was attached, and the mixture was heated at 45 °C for 16 h. The reaction was cooled to room temperature and concentrated by rotary evaporation. The residue was dissolved in 50 mL EtOAc and extracted with NaOH (1.0 M, 50 mL). The organic layer was separated and the aqueous layer washed with EtOAc (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The material was purified by silica gel chromatography (6:1 hex:EtOAc) to afford (**1b**) as a viscous yellow oil (344 mg, 1.79 mmol, 15% over 2 steps).

^{1}H NMR (600 MHz, $CDCl_3$): 2.71 (s, 1H); 2.69 (s, 1H); 2.61 (d, 2.9 Hz, 2H); 2.56 (s, 1H); 2.53 (s, 1H); 1.96 (t, 2.6 Hz, 1H), 1.33 (s, 3H); 1.06 (s, 3H); 0.98 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): 208.5, 80.6, 70.9, 63.4, 51.5, 30.8, 29.8, 27.4, 23.9, 22.9. **HRMS** (*m*/*z*): calcd for $C_{12}H_{17}O_2^+$: 193.1223 ($M+H^+$); found: 193.1222. **IR** (ν/cm^{-1}): 3280.3 (w), 2957.3 (w), 1730.8 (m), 1698.0 (s), 1457.0 (w), 1327.7 (w).

2-prenyl-2-propargyl-1,3-cyclohexanedione (1c)

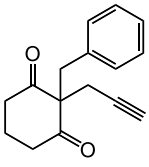


(1c)

Compound **(1c)** was prepared from 2-prenyl-1,3-cyclohexanedione, which was prepared according to a literature procedure.[3] To a 50 mL round bottom flask equipped with a magnetic stir bar was added 2-prenyl-1,3-cyclohexanedione (1.00 g, 5.55 mmol, 1.0 equiv) and K_2CO_3 (1.38 g, 9.99 mmol, 1.8 equiv). The mixture was dissolved in 28 mL acetone and stirred for 10 min at room temperature. Propargyl bromide (80% wt. in toluene) (1.24 mL, 11.10 mmol, 2.0 equiv) was added slowly. After 10 minutes, a reflux condenser was added and the mixture heated to 70 °C for 2 h, at which point TLC showed the substrate was consumed. The reaction was cooled to room temperature, filtered through Celite, and concentrated by rotary evaporation. Column chromatography (5:1 hex:EtOAc) afforded 2-prenyl-2-propargyl-1,3-cyclohexanedione **(1c)** (829 mg, 3.80 mmol, 68% yield). R_f (4:1 hex:EtOAc) = 0.37.

^{1}H NMR (600 MHz, $CDCl_3$): 4.84 (tt, 7.7 Hz, 1.5 Hz, 1H); 2.61 (m, 4H); 2.58 (d, 2.2 Hz, 2H); 2.42 (d, 7.7 Hz, 2H); 1.99 (m, 1H); 1.92 (m, 1H); 1.90 (t, 2.6 Hz, 1H); 1.64 (s, 3H); 1.52 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): 209.7, 137.0, 117.0, 81.0, 70.4, 67.8, 39.8, 36.8, 26.0, 23.7, 17.9, 16.8. **HRMS** (*m*/*z*): calcd for $C_{14}H_{19}O_2^+$: 219.1380 ($M+H^+$); found: 219.1378. **IR** (ν/cm^{-1}): 3280.3 (m), 2966.0 (m), 2917.7 (m), 2360.4 (w), 2342.1 (w), 1725.0 (m), 1698.0 (s), 1325.8 (w), 1213.9 (w).

2-benzyl-2-propargyl-1,3-cyclohexanedione (1d)

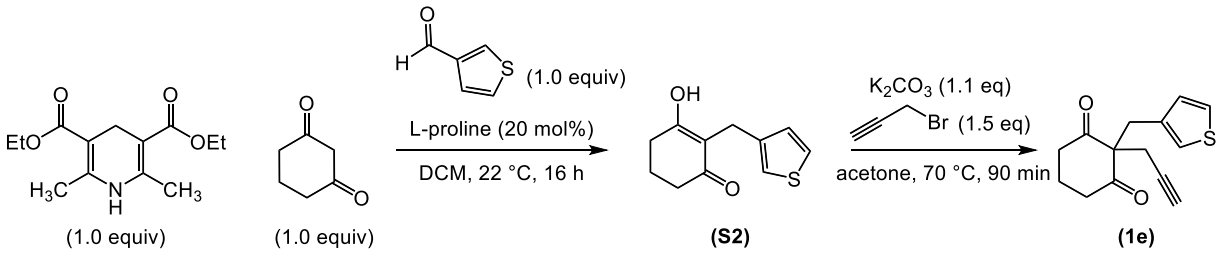


(1d)

Compound **(1d)** was prepared from 2-benzyl-1,3-cyclohexanedione, which was prepared according to a literature procedure.[4] To an 8 mL vial with stir bar was added 2-benzyl-1,3-cyclohexanedione (202 mg, 1.0 mmol, 1.0 equiv) and K_2CO_3 (166 mg, 1.2 mmol, 1.2 equiv). Acetone (5 mL) was added and the reaction stirred for 5 minutes, followed by addition of propargyl bromide (80% wt. in toluene) (223 μL, 2.0 mmol, 2.0 equiv). The vial was sealed and heated at 70 °C for 1 hour. The reaction was cooled to room temperature, filtered through Celite, and concentrated by rotary evaporation. Silica gel chromatography (5:1 hex:EtOAc) afforded 2-benzyl-2-propargyl-1,3-cyclohexanedione **(1d)** (182 mg, 0.76 mmol, 76% yield) as a

pale yellow oil. Upon azeotropic drying with benzene, the compound crystalized as a white solid. The compound is consistent with literature characterization.[5]

2-(prop-2-yn-1-yl)-2-(thiophen-3-ylmethyl)cyclohexane-1,3-dione (1e)



To an 8 mL vial with stir bar was added 1,3-cyclohexanedione (350 mg, 3.12 mmol, 1.0 equiv) and Hantzsch ester (790 mg, 3.12 mmol, 1.0 equiv). DCM (6 mL) was added, followed by addition of 3-formylthiophene (301 μL, 3.43 mmol, 1.1 equiv). L-proline (72 mg, 0.62 mmol, 20 mol%) was added, and the reaction heated at 40 °C for 16 h. The reaction was cooled to room temperature and concentrated by rotary evaporation. The residue was suspended in NaOH *(aq)* (1 M, 30 mL) and filtered through cotton. The filtrate was cooled to 0 °C, and the product precipitated by addition of glacial acetic acid (~1.5 mL) till the suspension had pH ~ 3. The solid was collected on a fritted funnel, washed with a small amount of cold DI water, and dried *in vacuo* yielding **(S2)** (400 mg, 1.92 mmol, 62% yield) as a light yellow solid that was used without further purification.

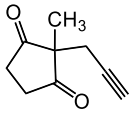
^{1}H NMR (600 MHz, *d6*-DMSO): 10.57 (br s, 1H); 7.32 (dd, 5.1 Hz, 3.3 Hz, 1H); 6.95 (d, 1.8 Hz, 1H); 6.89 (d, 4.8 Hz, 1H); 3.36 (br s, 2H); 2.35 (br s, 4H), 1.85 (p, 6.2 Hz, 2H). **^{13}C NMR** (151 MHz, *d6*-DMSO): 141.9, 128.7, 124.9, 119.9, 113.8, 22.1, 20.5. **HRMS** (*m*/*z*): calcd for $C_{11}H_{11}O_2S^-$: 207.0485 ($M\text{-}H^+$); found: 207.0480. **IR** (ν/cm^{-1}): 2945.7 (w), 1568.8 (s), 1559.1 (s), 1367.2 (s), 1268.9 (s), 1173.5 (m), 1007.6 (s).

Intermediate **(S2)** (300 mg, 1.44 mmol, 1.0 equiv) was added to an 8 mL vial equipped with a stir bar. Acetone (6 mL) was added, followed by K_2CO_3 (239 mg, 1.73 mmol, 1.2 equiv). After 10 minutes of stirring, propargyl bromide (80% wt. in toluene) (241 μL, 2.16 mmol, 1.5 equiv) was added. The reaction was sealed, and heated at 70 °C for 90 minutes. The reaction was cooled to room temperature, filtered through Celite, and concentrated by rotary evaporation. Silica gel chromatography (6:1 hex:EtOAc) afforded 2-(prop-2-yn-1-yl)-2-(thiophen-3-ylmethyl)cyclohexane-1,3-dione **(1e)** (217 mg, 0.88 mmol, 61% yield) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): 7.20 (dd, 4.8 Hz, 2.9 Hz, 1H); 6.88 (dd, 2.6 Hz, 0.7 Hz, 1H), 6.73 (dd, 5.1 Hz, 1.1 Hz, 1H); 3.08 (s, 2H); 2.67 (d, 2.6 Hz, 2H); 2.52 (m, 2H); 2.25 (m, 2H); 1.99 (t, 2.6 Hz, 1H); 1.82 (m, 1H); 1.24 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): 211.1, 135.8, 129.0, 126.1, 123.8, 80.0,

71.3, 67.4, 40.8, 38.2, 26.6, 15.5. **HRMS** (*m*/z): calcd for $C_{14}H_{15}O_2S^+$: 247.0787 ($M+H^+$); found: 247.0786. **IR** (ν/cm^{-1}): 3283.2 (w), 1721.21 (m), 1697.0 (s), 1340.3 (w), 1015.3 (w), 792.6 (w).

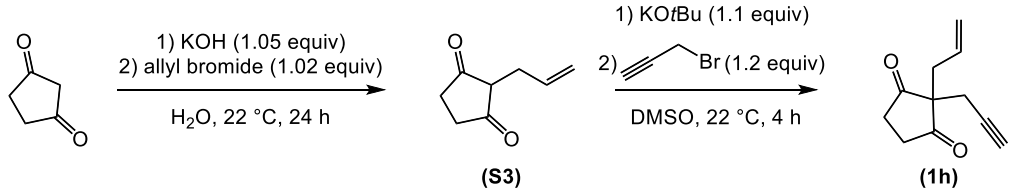
2-methyl-2-propargyl-1,3-cyclopentanedione (1g)



(1g)

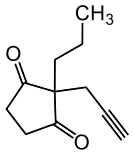
Compound **(1g)** was prepared according to a known procedure.[6]

2-allyl-2-propargyl-1,3-cyclopentanedione (1h)



To a 100 mL round bottom flask with a magnetic stir bar was added 1,3-cyclopentanedione (2.0 g, 20.40 mmol, 1.00 equiv), followed by KOH (*aq*) (0.31 M, 70 mL, 21.4 mmol, 1.05 equiv). After 30 minutes of stirring at 22 °C, allyl bromide (1.8 mL, 20.83 mmol, 1.02 equiv) was added by syringe. The reaction was stirred at 22 °C for 24 h, then the solvent removed by rotary evaporation. ^{1}H NMR of the crude residue showed a 2:1 ratio of C:O-alkylation. Purification by silica gel chromatography (hex:EtOAc) afforded **(S3)** as the pure C-alkylated product (380 mg, 2.75 mmol, 13% yield). Compound **(1h)** was then synthesized according to a known procedure.[7] Both **(S3)** and **(1h)** were consistent with literature NMR spectra.[7]

2-*n*-propyl-2-propargyl-1,3-cyclopentanedione (1i)



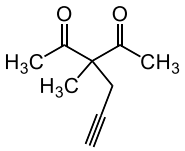
(1i)

Compound **(1i)** was prepared from the intermediate 2-*n*-propyl-1,3-cyclopentanedione which was prepared using a known literature protocol.[8] The Hantzsch ester used in the preparation of 2-*n*-propyl-1,3-cyclopentanedione was prepared according to a known procedure.[7]

2-*n*-propyl-1,3-cyclopentanedione (2.0 g, 14.28 mmol, 1.0 equiv) was added to a 100 mL round bottom flask. A solution of KOH *(aq)* (0.31 M, 881 mg, 15.71 mmol, 1.1 equiv) was added

and the solution allowed to stir at 22 °C for 1 h. Propargyl bromide (80% wt. in toluene) (3.18 mL, 28.56 mmol, 2.0 equiv) was added by syringe. The reaction was heated at 80 °C for 24 h, then diluted with EtOAc (100 mL). 1 M NaOH (50 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification by silica gel chromatography (5:1 hex: EtOAc) afforded **(1i)** as a yellow viscous oil (1.65 g, 9.26 mmol, 65% yield). ^1H NMR was consistent with a known literature spectrum.[9]

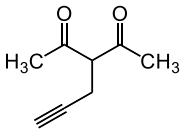
3-methyl-3-propargyl-2,4-pentanedione (1j)



(1j)

Compound **(1j)** was prepared according a known procedure.[10]

3-propargyl-2,4-pentanedione (S4)

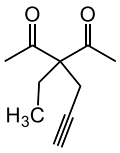


(S4)

A 2 L oven-dried 3-neck round bottom flask with a stir bar was evacuated and refilled with N_2. This process was repeated twice more. NaH (60% dispersion in mineral oil, 11.99 g dispersion, 300 mmol) was added quickly. The flask was evacuated once more and refilled with N_2. 800 mL of dry THF was added. After 15 minutes of rigorous stirring, a solution of 2,4-pentanedione (30.0 g, 300 mmol, 1.5 M in THF) was added in 50 mL portions by syringe. After the addition was finished, the flask was sonicated for 5 minutes, followed by 10 minutes of stirring, followed by sonication for 10 minutes, and finally 90 minutes of rigorous stirring, after which no further H_2 emission was observed. An oven dried addition funnel was added quickly to the flask. Propargyl bromide (80% wt. solution in toluene, 33.4 mL, 300 mmol) was added to the addition funnel, and this solution was diluted with 100 mL dry THF. The reaction was cooled to 0 °C, and the propargyl bromide solution was added over a period of 10 minutes. After the addition was finished, the ice bath was removed, and the reaction stirred at 22 °C for 42 hours. The reaction was then cooled to 0 °C and diluted with EtOAc (400 mL). 1 M HCl (*aq*) (300 mL) was then added. The organic layer was separated, then split into three approximately equal volumes. Each organic portion was extracted with 150 mL brine, dried over $MgSO_4$,

filtered, and the portions concentrated together *in vacuo*. The residue was purified by column chromatography (7:3 hex:DCM) to afford 3-propargyl-2,4-pentanedione **(S4)** as a yellow oil (9.75 g, 70.6 mmol, 24% yield). NMR characterization was consistent with the literature.[11]

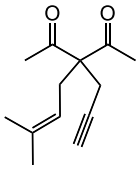
3-ethyl-3-propargyl-2,4-pentanedione (1k)



(1k)

Compound **(1k)** was prepared according to a known literature procedure.[12]

3-prenyl-3-propargyl-2,4-pentanedione (1l)

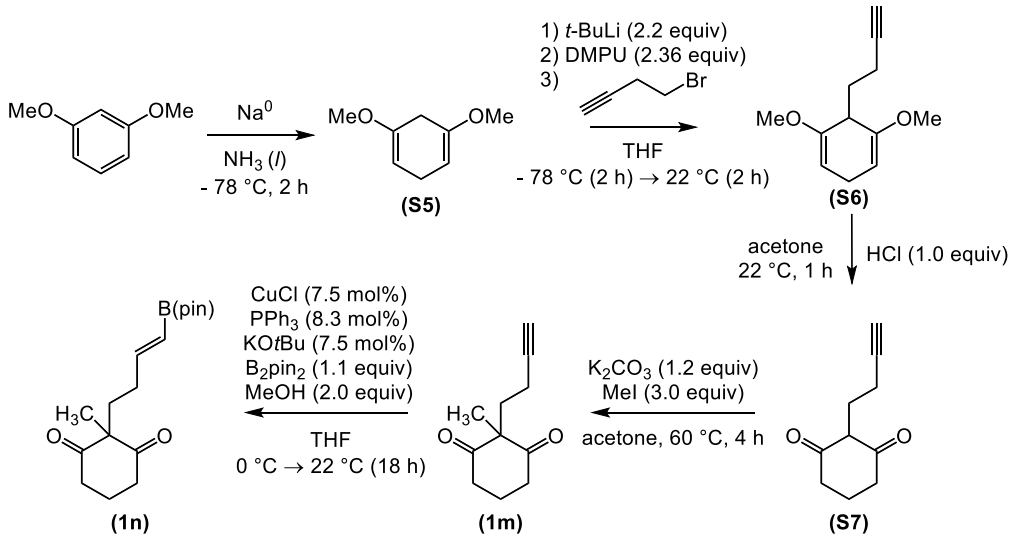


(1l)

To an oven dried 50 mL round bottom with a stir bar was quickly added 3-propargyl-2,4-pentanedione **(S4)** (1.00 g, 7.24 mmol, 1 equiv). The flask was evacuated and backfilled with N_2, followed by addition of 29 mL dry THF. NaH (60% dispersion in mineral oil) (304 mg dispersion, 7.60 mmol, 1.05 equiv) was added at once as a solid, and the reaction quickly resealed. After 45 minutes of stirring at 22 °C, 3,3-dimethylallyl bromide (1.67 mL, 14.48 mmol, 2.0 equiv) was added by syringe. The reaction stirred at 22 °C for 12 h. The reaction was diluted with EtOAc (30 mL), and a base extraction was performed with 30 mL 1 M NaOH (*aq*). The basic aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel chromatography (15:1 hex:EtOAc → 7:1 hex:EtOAc) to give 3-prenyl-3-propargyl-2,4-pentanedione **(1l)** (450 mg, 2.18 mmol, 30% yield) as a clear, colorless oil. R_f = 0.42 (10:1 hex:EtOAc).

^{1}H NMR (600 MHz, $CDCl_3$): 4.72 (tq, 7.3 Hz, 1.5 Hz, 1H); 2.80 (d, 7.5 Hz, 2H); 2.74 (d, 2.5 Hz, 2H); 2.14 (s, 6H); 1.99 (t, 2.5 Hz, 1H); 1.68 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): 204.9, 137.3, 116.8, 80.0, 71.8, 70.6, 29.5, 26.9, 26.2, 20.8, 18.2. **HRMS** (*m*/*z*): calcd for $C_{13}H_{19}O_2^+$: 207.1380 ($M+H^+$); found: 207.1379. **IR** (ν/cm^{-1}): 3286.1 (w), 1700.9 (s), 1420.3 (w), 1357.6 (m), 1172.5 (m), 1151.3 (m), 646.0 (w).

2-(but-3-yn-1-yl)-2-methylcyclohexane-1,3-dione (1m) and *(E)*-2-methyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)cyclohexane-1,3-dione (1n)



1,5-dimethoxycyclohexa-1,4-diene **(S5)** was prepared according to a known procedure.[7]

Synthesis of **(S6)**: To a 100 mL flame dried round bottom flask with stir bar was added dry THF (40 mL) and the solvent cooled to – 78 °C. Carefully, *tert*-BuLi (1.37 M in pentane) (11.5 mL, 15.7 mmol, 2.20 equiv) was added dropwise, generating a light yellow solution. 1,5-dimethoxycyclohexa-1,4-diene (1.00 g, 7.13 mmol, 1.0 equiv) was added dropwise neat. After 1 h of stirring at – 78 °C, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (2.04 mL, 16.84 mmol, 2.36 equiv) was added dropwise, resulting in an orange solution. After 10 minutes, 4-bromobut-1-yne (1.34 mL, 14.3 mmol, 2.0 equiv) was added dropwise and the solution stirred at – 78 °C for 2 h. The solution was allowed to warm to room temperature and stirred a further 2 h. The reaction was then opened and carefully diluted with Et_2O (25 mL) and saturated brine (25 mL). The mixture was transferred to a separatory funnel and the aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic phases were dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was dissolved in 50:1 hexanes:Et_2O and subjected to a short silica gel plug. The silica gel was washed liberally with 50:1 hex:EtO_2 and the filtrate concentrated by rotary evaportation, affording 6-(but-3-yn-1-yl)-1,5-dimethoxycyclohexa-1,4-diene **(S6)** as a clear, sweet-smelling oil (1.24 g, 6.45 mmol, 90% yield).

Synthesis of **(S7)**: 6-(but-3-yn-1-yl)-1,5-dimethoxycyclohexa-1,4-diene **(S6)** (1.24 g, 6.45 mmol, 1.0 equiv) was dissolved in N_2-sparged acetone (29 mL). N_2-sparged 1 M HCl (aq) (6.45 mL, 1.0 equiv) was added over 1 min, and the solution stirred at 22 °C for 1 h, at which point TLC confirmed complete consumption of diene **(S6)**. The reaction was then concentrated by rotary evaporation. The resulting white solid was dried *in vacuo*, then washed with hexanes (3 x

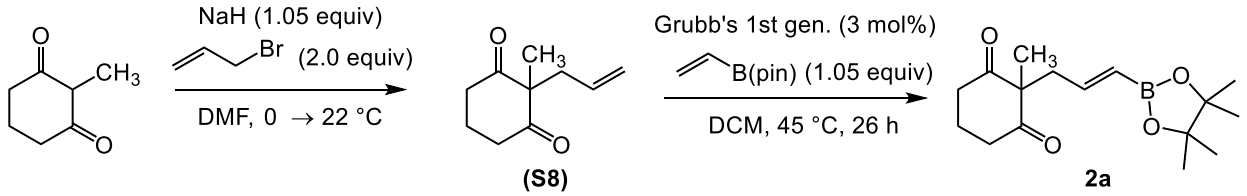
10 mL). The undissolved solid was then dried *in vacuo*, affording 2-homopropargyl-1,3-cyclohexanedione **(S7)** as a white powder (1.06 g, 6.45 mmol, 100% yield) which was used without further purification.

Synthesis of **(1m)**: To an 8-mL vial equipped with a stir bar was added 2-homopropargyl-1,3-cyclohexanedione (100 mg, 0.61 mmol, 1.0 equiv) and K_2CO_3 (101 mg, 0.73 mmol, 1.2 equiv). Acetone (3 mL) was added, and the mixture was stirred for 10 minutes at room temperature. Iodomethane (114 μL, 1.83 mmol, 3.0 equiv) was added, and the reaction was sealed and heated at 60 °C for 4 h. The reaction was cooled to room temperature, filtered through Celite, and concentrated by rotary evaporation. The product was purified by silica gel chromatography (4:1 hex:EtOAc) affording 2-homopropargyl-2-methyl-1,3-cyclohexanedione **(1m)** as a clear, colorless oil (75.7 mg, 0.425 mmol, 70% yield).

Synthesis of **(1n)**: In a N_2-filled glovebox, to an 8-mL vial equipped with a stir bar was added CuCl (16.7 mg, 0.17 mmol, 7.5 mol%), PPh_3 (49 mg, 0.19 mol, 8.3 mol%), and KO*t*Bu (19.0 mg, 0.17 mmol, 7.5 mol%). THF (2.5 mL) was added, and the solution for stirred 30 min at room temperature. $B_2(pin)_2$ (630 mg, 2.48 mmol, 1.10 equiv) was added at once as a solid, resulting in an immediate color change to dark brown. After stirring 15 min, the reaction was diluted with THF (2.5 mL), followed by addition of neat 2-homopropargyl-2-methyl-1,3-cyclohexanedione **(1m)** (402 mg, 2.255 mmol, 1.0 equiv). The reaction was sealed and removed from the glovebox, then cooled to 0 °C. Distilled MeOH (183 μL, 4.51 mmol, 2.0 equiv) was added over the course of 1 min. After 10 min, the reaction was allowed to warm to room temperature and stirred for 18 h.

The reaction was transferred under air to a 50 mL round bottom flask and quenched with saturated NH_4Cl (*aq*) (20 mL). The mixture was stirred vigorously for 30 min, followed by extraction with EtOAc (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, concentrated by rotary evaporation, and analyzed by ^1H NMR, which indicated a 2:2:1 ratio of desired product: internal borylation: double hydroboration. Purification by flash silica gel chromatography (6:1 benzene:EtOAc) provided the pure *(E)*-vinyl boronic ester **(1n)** as a yellow oil (209 mg, 0.68 mmol, 30% yield).

***(E)*-2-methyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)cyclohexane-1,3-dione (2a)**

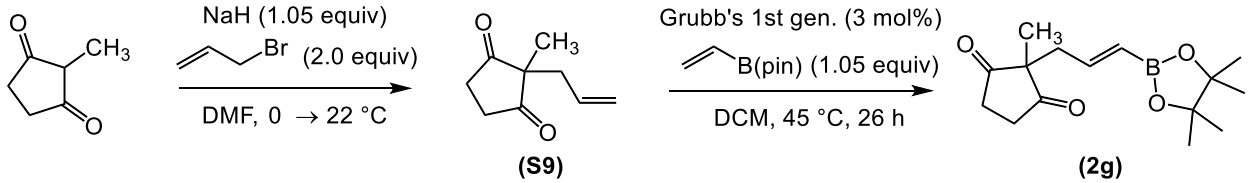


To an oven dried 50 mL round bottom flask under N_2 was added 2-methyl-1,3-cyclohexanedione (500 mg, 3.96 mmol, 1.0 equiv) and NaH (60% dispersion in mineral oil) (166.2 mg dispersion, 4.16 mmol, 1.05 equiv). The round bottom was cooled to 0 °C, and 0 °C anhydrous DMF (21 mL) was added to the reaction. After 30 min of stirring at 0 °C, the reaction was allowed to warm to 22 °C and stirred 5 min. The reaction was then cooled to 0 °C, followed by addition of allyl bromide (685 μL, 7.93 mmol, 2.0 equiv). After 3 h at 0 °C, the reaction was stirred for 48 h at 22 °C. The reaction was diluted with EtOAc (50 mL), and the organic layer was extracted with saturated NH_4Cl (*aq*) (3 x 25 mL), saturated LiCl (3 x 20 mL), water (1 x 25 mL), and brine (1 x 25 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification by silica gel chromatography (3:1 hex:EtOAc) afforded dione **(S8)** as a clear, colorless oil (371 mg, 2.23 mmol, 57% yield). NMR characterization was consistent with the literature.[13]

To an oven-dried 25 mL round bottom flask with a stir bar under N_2 was added Grubb's 1st generation catalyst (55.2 mg, 0.067 mmol, 3 mol%). The flask was equipped with a reflux condenser. The catalyst was dissolved in dry DCM (10 mL), and 2-allyl-2-methyl-1,3-cyclohexanedione **(S8)** (371 mg, 2.23 mmol, 1.0 equiv) was added neat. Immediately, vinyl boronic acid pinacol ester (398 μL, 2.35 mmol, 1.05 equiv) was added neat by syringe. The reaction was heated to 45 °C for 26 h, at which point the reaction was concentrated by rotary evaporation. The product was purified by silica gel chromatography (5:1 → 1:1 hex:EtOAc) giving a dark oil. The oil was dissolved in DCM (238 μL) and DMSO (238 μL) and stirred for 22 h. The solution was diluted with water (1 mL) and extracted 5 x 1 mL EtOAc. The combined organic phases were dried over $MgSO_4$, filtered, concentrated by rotary evaporation, and the residue purified by silica gel chromatography (5:1 → 1:1 hex:EtOAc), giving a light green oil, which solidified to a white solid upon azeotropic distillation with benzene.

^{1}H NMR: (400 MHz, $CDCl_3$): 6.35-6.27 (dt, 17.6 Hz, 7.1 Hz, 1H); 5.44-5.39 (d, 17.8 Hz, 1H); 2.72-2.57 (m, 6H); 2.05-1.96 (m, 1H); 1.91-1.80 (m, 1H); 1.24 (s, 3H); 1.22 (s, 12H). **^{13}C NMR**: (214 MHz, $CDCl_3$): 209.5, 146.8, 123.8, 83.3, 65.3, 43.2, 38.1, 24.9, 19.6, 17.7. **HRMS** (*m*/*z*): calcd for $C_{16}H_{26}BO_4^+$: 293.1919 ($M+H^+$); found: 293.1907. **IR** (ν/cm^{-1}): 2977.6 (m), 2935.1 (w), 1726.9 (m), 1697.0 (s), 1637.3 (m), 1392.4 (w), 1361.5 (s), 1323.9 (m), 1144.5 (m), 971.0 (w), 848.5 (w).

***(E)*-2-methyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)cyclopentane-1,3-dione (2g)**

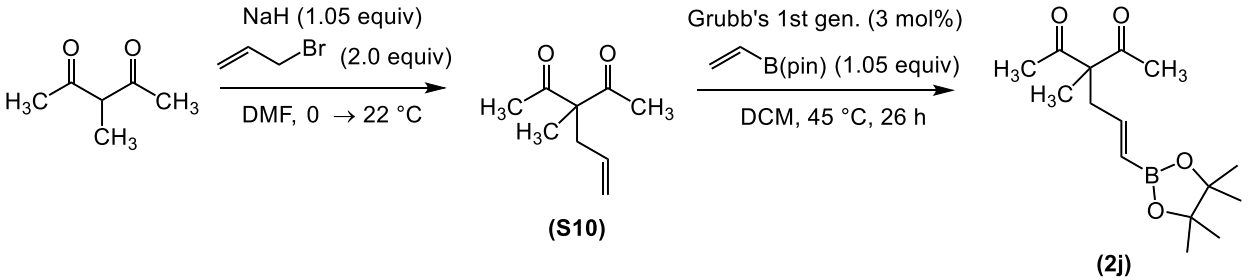


(S9) **(2g)**

(S9) and **(2g)** were prepared according to the above procedure followed for **(S21)** and **(2a)**.

Characterization of **(2g)**: **^{1}H NMR:** (400 MHz, $CDCl_3$): 6.31-6.23 (dt, 17.8 Hz, 7.1 Hz, 1H); 5.37-5.33 (d, 17.8 Hz, 1H); 2.75-2.60 (m, 4H); 2.39-2.37 (dd, 7.1 Hz, 1.2 Hz, 2H); 1.17 (s, 12H); 1.06 (s, 3H). **^{13}C NMR**: (214 MHz, $CDCl_3$): 215.7, 145.8, 124.3, 83.2, 56.5, 41.8, 35.3, 24.7, 18.9. **HRMS** (*m*/*z*): calcd for $C_{15}H_{24}BO_4^+$: 279.1762 ($M+H^+$); found: 279.1753. **IR** (ν/cm^{-1}): 2978.5 (s), 2931.3 (m), 1725.0 (s), 1638.2 (m), 1361.5 (s), 1327.8 (s), 1145.5 (s), 971.0 (m), 848.5 (m).

***(E)*-3-methyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)pentane-2,4-dione (2j)**



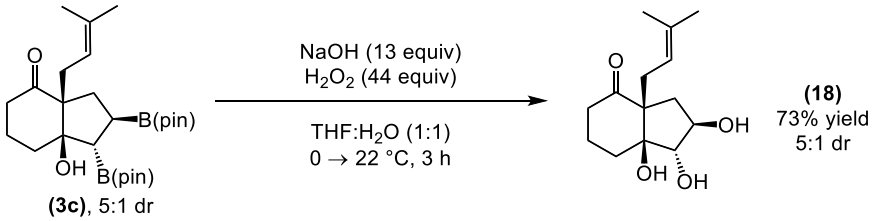
(S10) **(2j)**

(S10) and **(2j)** were prepared according to the above procedure for **(S21)** and **(2a)**.

Characterization of **(2j)**: **^{1}H NMR** (400 MHz, $CDCl_3$): 6.33-6.25 (dt, 17.8 Hz, 7.1 Hz, 1H); 5.48-5.44 (d, 17.8 Hz, 1H); 2.67-2.64 (dd, 7.3 Hz, 1.2 Hz, 2H); 2.06 (s, 6H); 1.28 (s, 3H); 1.20 (s, 12H). **^{13}C NMR**: (214 MHz, $CDCl_3$): 206.3, 147.1, 128.3, 83.2, 66.3, 40.8, 26.5, 24.7, 18.1. **HRMS** (*m*/*z*): calcd for $C_{15}H_{26}BO_4^+$: 281.1919 ($M+H^+$); found: 281.1909. **IR** (ν/cm^{-1}): 2979.5 (s), 2934.2 (w), 1718.2 (m), 1699.4 (s), 1638.2 (m), 1361.5 (s), 1327.7 (m), 1145.5 (s), 971.0 (m), 848.5 (m).

■ Product Functionalizations

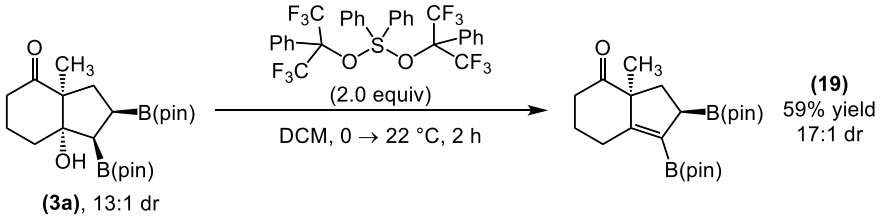
A. Oxidation



To an 8 mL vial with stir bar was added bis-boronate **(3c)** (21.6 mg, 0.0455 mmol, 1.0 equiv) and 500 μL THF. The solution was cooled to 0 °C. Solutions of 2 M NaOH (*aq*) and H_2O_2 (*aq*) (30 wt%) were cooled to 0 °C. The NaOH solution (300 μL) was added to the reaction, followed immediately by H_2O_2 (204 μL). The reaction was stirred 30 minutes at 0 °C, then allowed to warm to room temperature and stirred an additional 3 hours. EtOAc (2 mL), saturated aqueous NH_4Cl (1 mL), and solid NaCl (~200 mg) were then added. The aqueous layer was extracted with EtOAc (3 x 2 mL), and the organic layers were combined, dried with $MgSO_4$, and concentrated by rotary evaporation. Column chromatography (1:2 hex:EtOAc) afforded triol **(18)** (8.8 mg, 0.033 mmol, 73% yield, 5:1 dr). Minor impurities in the ^{1}H NMR spectrum between 4.10-4.45 ppm could not be removed by column chromatography.

^{1}H NMR (500 MHz, CD_3OD): 3.79-3.78 (d, 4.3 Hz, 1H); 3.74-3.70 (m, 1H); 2.87-2.83 (dd, 13.4 Hz, 7.3 Hz, 1H); 2.55-2.47 (m, 3H); 2.22-2.14 (m, 1H); 2.08-1.83 (m, 6H); 1.68 (d, 0.9 Hz, 3H); 1.64 (s,, 3H); 1.43-1.39 (dd, 13.4 Hz, 6.1 Hz, 1H). **^{13}C** (214 MHz, CD_3OD): 215.8, 134.6, 120.9, 87.9, 85.2, 77.0, 62.6, 38.0, 37.8, 34.0, 31.8, 26.1, 21.0, 18.0. **HRMS** (*m*/*z*): calcd for $C_{14}H_{23}O_4^+$: 255.1591 ($M+H^+$); found: 255.1580. **IR** (ν/cm^{-1}): 3386.4 (br s), 2926.4 (s), 1697.0 (s), 1456.0 (w), 1084.7 (w), 1056.8 (s). **[α]$_D^{23}$** = — 24.9 ° (c = 0.44, CH_2Cl_2, l = 1 dm).

B. Dehydration (Example 1)

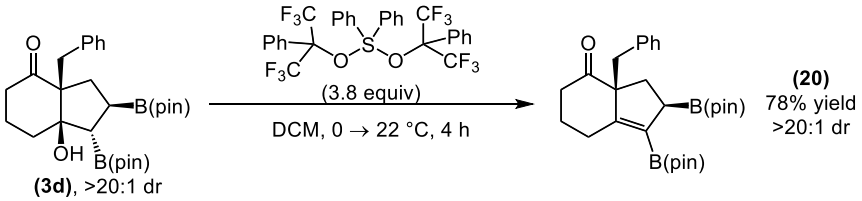


To an 8 mL vial with stir bar was added bis-boronate **(3a)** (12.3 mg, 13:1 dr, 0.0293 mmol, 1.0 equiv). The vial was evacuated, and backfilled with N_2, followed by addition of dry DCM (50 μL). In a N_2 filled glovebox, Martin's sulfurane (39.4 mg, 0.0586 mmol, 2.0 equiv) was dissolved in 100 μL DCM. This vial was sealed with a Teflon-lined septa cap, tapped with electrical tape, and removed from the glovebox. Both solutions were cooled to 0 °C, and the sulfurane added dropwise to the bis-boronate. The sulfurane vial was washed with an

additional 50 μL DCM, which was added to the reaction dropwise. The reaction turned yellow within 2 min, and the reaction was allowed to warm to room temperature after 5 min. After stirring 2 h, the reaction was concentrated by rotary evaporation. Purification by silica gel chromatography (15:1 hex:EtOAc → 10:1 hex:EtOAc) afforded vinyl boronic ester **(19)** as a clear, colorless oil (6.9 mg, 0.0172 mmol, 59% yield, 17:1 dr).

^{1}H NMR (600 MHz, $CDCl_3$): 3.19-3.16 (app d, 14.6 Hz, 1H); 2.62-2.55 (app td, 14.3 Hz, 6.1 Hz, 1H); 2.34-2.22 (m, 2H); 2.20-2.13 (m, 1H); 2.12-1.97 (m, 2H); 1.85-1.80 (dd, 12.8 Hz, 7.3 Hz, 1H), 1.25 (s, 6H); 1.24 (s, 6H); 1.23 (s, 12H); 1.20 (s, 3H). **^{13}C** (151 MHz, $CDCl_3$): 214.8, 161.8, 124.9, 83.1, 64.0, 38.3, 35.6, 25.2, 25.1, 24.9, 24.7, 24.4, 22.6. **HRMS** (*m*/z): calcd for $C_{22}H_{36}B_2O_5Na^+$: 425.2641 ($M+Na^+$); found: 425.2643. **IR** (ν/cm^{-1}): 2976.6 (w), 2929.3 (w), 2359.5 (m), 2341.2 (m), 1716.3 (m), 1698.0 (m), 1456.9 (m), 1145.5 (w), 981.6 (w), 851.4 (w), 669.2 (w). **$[\alpha]_D^{23}$** = + 18.1 ° (c = 0.34, CH_2Cl_2, l = 1 dm).

Dehydration (Example 2)

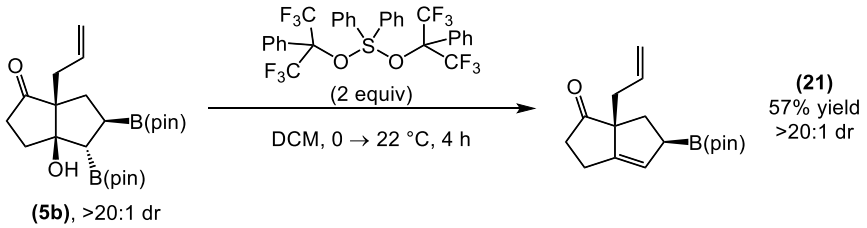


To an 8 mL vial with stir bar was added bis-boronate **(3d)** (10.8 mg, >20:1 dr, 0.0218 mmol, 1.0 equiv). The vial was evacuated, and backfilled with N_2, followed by addition of dry DCM (150 μL). In a N_2 filled glovebox, Martin's sulfurane (56.0 mg, 0.0832 mmol, 3.8 equiv) was dissolved in 200 μL DCM. This vial was sealed with a Teflon-lined septa cap, tapped with electrical tape, and removed from the glovebox. Both solutions were cooled to 0 °C, and the sulfurane added dropwise to the bis-boronate. The sulfurane vial was washed with an additional 50 μL DCM, which was added to the reaction dropwise. The reaction turned yellow within 2 min, and the reaction was allowed to warm to room temperature after 5 min. After stirring 4 h, the reaction was concentrated by rotary evaporation. Purification by silica gel chromatography (25:1 hex:EtOAc → 10:1 hex:EtOAc) afforded vinyl boronic ester **(20)** as a clear, colorless oil (8.1 mg, 0.0169 mmol, 78% yield, >20:1 dr). A small amount of aromatic impurities co-elute with the product and could not be removed by column chromatography.

^{1}H NMR (600 MHz, $CDCl_3$): 7.24-7.21 (m, 2H); 7.19-7.17 (m, 1H); 7.14-7.13 (app d, 7.3 Hz, 2H); 3.30-3.28 (d, 13.9 Hz, 1H); 3.17-3.15 (d, 14.3 Hz, 1H); 2.84-2.78 (m, 2H); 2.46-2.41 (m, 2H); 2.31-2.25 (m, 2H); 2.12-2.06 (m, 1H); 1.98-1.94 (m, 1H); 1.57-1.48 (m, 1H); 1.28 (s, 6H); 1.27 (s, 6H); 1.27 (s, 6H); 1.26 (s, 6H). **^{13}C** (151 MHz, $CDCl_3$): 212.4, 158.5, 137.9, 129.8, 128.2, 126.7, 124.9, 83.4, 83.2, 70.6, 42.8, 39.7, 30.2, 26.1, 25.8, 25.3, 25.0, 24.6. **HRMS** (*m*/z): calcd for $C_{28}H_{41}B_2O_5^+$: 479.3135

(M+H$^+$); found: 479.3129. **IR** (ν/cm^{-1}): 2977.6 (w), 2930.3 (m), 1707.7 (m), 1637.3 (w), 1372.1 (s), 1313.3 (m); 1144.6 (s), 967.1 (w), 858.2 (w), 701.0 (w). **[α]$_D^{23}$** = + 72.6 ° (c = 0.34, CH_2Cl_2, l = 1 dm).

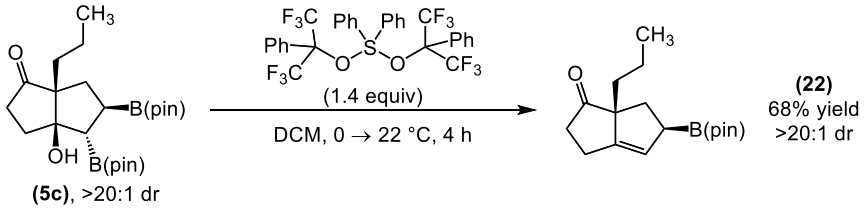
C. Anti Boron-Hydroxyl Elimination (example 1)



To an 8 mL vial with stir bar was added bis-boronate **(5b)** (24.7 mg, >20:1 dr, 0.0572 mmol, 1.0 equiv). Dry DCM (100 μL) was added. In a N_2 filled glovebox, Martin's sulfurane (76.9 mg, 0.114 mmol, 2.0 equiv) was dissolved in 150 μL DCM. This vial was sealed with a Teflon-lined septa cap, tapped with electrical tape, and removed from the glovebox. Both solutions were cooled to 0 °C, and the sulfurane added dropwise to the bis-boronate. The sulfurane vial was washed with an additional 50 μL DCM, which was added to the reaction dropwise. The reaction turned yellow within 2 min, and the reaction was allowed to warm to room temperature after 5 min. After stirring 4 h, the reaction had turned red and was concentrated by rotary evaporation. Purification by silica gel chromatography (20:1 hex:EtOAc → 10:1 hex:EtOAc) afforded allyl boronic ester **(21)** as a clear, colorless oil (9.4 mg, 0.0326 mmol, 57% yield, >20:1 dr).

^{1}H NMR (500 MHz, $CDCl_3$): 5.82-5.74 (m, 1H); 5.56 (t, 2.3 Hz, 1H); 5.12-5.06 (m, 2H); 2.69-2.63 (m, 1H); 2.61-2.50 (m, 2H); 2.45-2.40 (dd, 18.0 Hz, 8.8 Hz, 1H); 2.38-2.32 (m, 2H); 2.29-2.24 (dd, 13.7 Hz, 7.9 Hz, 1H); 2.13-2.03 (m, 2H); 1.25 (s, 12H). **^{13}C** (151 MHz, $CDCl_3$): 218.2, 146.6, 133.8, 124.6, 118.3, 83.6, 65.4, 40.7, 39.2, 32.3, 25.0, 24.8, 22.2. **HRMS** (*m*/*z*): calcd for $C_{17}H_{26}BO_3^+$: 289.1970 (M+H$^+$); found: 289.1970. **IR** (ν/cm^{-1}): 2977.6 (m), 2359.4 (w), 1737.6 (s), 1354.8 (s), 1320.0 (s), 1143.5 (s), 857.2 (m). **[α]$_D^{23}$** = — 19.4 ° (c = 0.47, CH_2Cl_2, l = 1 dm).

Anti Boron-Hydroxyl Elimination (example 2)

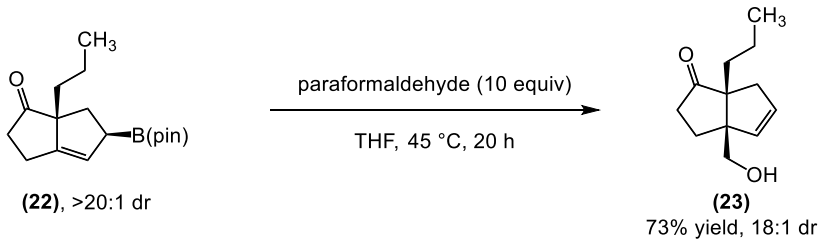


To an 8 mL vial with stir bar was added bis-boronate **(5c)** (160 mg, >20:1 dr, 0.368 mmol, 1.0 equiv). Dry DCM (700 μL) was added. In a N_2 filled glovebox, Martin's sulfurane (348 mg, 0.518 mmol, 1.41 equiv) was dissolved in 700 μL DCM. This vial was sealed with a Teflon-lined septa

cap, tapped with electrical tape, and removed from the glovebox. Both solutions were cooled to 0 °C, and the sulfurane added dropwise to the bis-boronate. The sulfurane vial was washed with an additional 325 μL DCM, which was added to the reaction dropwise. The reaction turned yellow within 2 min, and the reaction was allowed to warm to room temperature after 5 min. After stirring 4 h, the reaction had turned red and was concentrated by rotary evaporation. Purification by silica gel chromatography (25:1 hex:EtOAc) afforded allyl boronic ester **(22)** as a clear, colorless oil (72.6 mg, 0.250 mmol, 68% yield, >20:1 dr).

^{1}H NMR (600 MHz, $CDCl_3$): 5.54-5.53 (app t, 2.6 Hz, 1H); 2.70-2.64 (ddd, 18.7 Hz, 9.5 Hz, 2.6 Hz, 1H); 2.59-2.49 (m, 2H); 2.42-2.33 (m, 2H); 2.15-2.11 (dd, 13.2 Hz, 11.0 Hz, 1H); 2.03-2.01 (dd, 12.8 Hz, 1.5 Hz, 1H); 1.53-1.42 (m, 2H); 1.36-1.30 (m, 2H); 1.24 (s, 6H); 1.24 (s, 6H); 0.89-0.87 (t, 3H). **^{13}C** (151 MHz, $CDCl_3$): 218.7, 146.9, 123.8, 83.6, 65.6, 40.6, 36.6, 32.2, 25.0, 24.8, 22.1, 18.0, 14.6. **HRMS** (*m*/*z*): calcd for $C_{17}H_{28}BO_3^+$: 291.2126 ($M+H^+$); found: 291.2114. **IR** (ν/cm^{-1}): 2975.6 (m), 2930.3 (m), 2872.2 (w), 1735.6 (s), 1354.8 (s), 1318.1 (m), 1214.9 (w), 1143.6 (s), 860.1 (m), 681.7 (w). **$[\alpha]_D^{23}$** = — 5.5 ° (c = 0.38, CH_2Cl_2, l = 1 dm).

E. Allylation



(22), >20:1 dr

(23)
73% yield, 18:1 dr

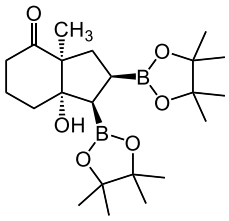
To an 8 mL vial with stir bar was added allyl boronic ester **(22)** (14.5 mg, >20:1 dr, 0.050 mmol, 1.0 equiv) and 250 μL dry THF. Paraformaldehyde (15.0 mg, 0.50 mmol, 10 equiv) was added as a solid. The vial was capped, sealed with electrical tape, and heated at 45 °C for 20 h. The reaction was cooled to room temperature, diluted with EtOAc (1 mL), and filtered through a short pad of Celite. The vial was washed with EtOAc (3 x 1 mL), and suspensions filtered through Celite. The solvent was removed by rotary evaporation, and the residue purified by silica gel chromatography (4:1 hex:EtOAc) to give primary alcohol **(23)** as a clear, colorless oil (7.1 mg, 18:1 dr, 73% yield).

^{1}H NMR (600 MHz, $CDCl_3$): 5.98-5.95 (br s, 1H); 5.48-5.45 (m, 1H); 3.74-3.72 (d, 11.0 Hz, 1H); 3.65-3.63 (d, 11.4 Hz, 1H); 2.70-2.67 (d, 16.1 Hz, 1H); 2.41-2.36 (dd, 19.4 Hz, 9.9 Hz, 1H); 2.30-2.26 (dd, 16.5 Hz, 1.5 Hz, 1H); 2.19-2.12 (m, 1H); 1.97-1.93 (dd, 12.8 Hz, 9.9 Hz, 1H); 1.74-1.68 (m, 1H); 1.66-1.61 (td, 13.2 Hz, 4.4 Hz, 1H); 1.54-1.49 (td, 12.8 Hz, 4.4 Hz, 1H); 1.47-1.39 (m, 1H); 1.25 (m, 2H); 0.89-0.86 (t, 7.3 Hz). **^{13}C** (151 MHz, $CDCl_3$): 224.7, 135.3, 134.9, 65.8, 61.5, 60.1, 43.4, 36.5,

32.9, 26.4, 18.6, 14.9. **HRMS** (*m*/*z*): calcd for $C_{12}H_{19}O_2^+$: 195.1380 (M+H); found: 195.1373. **IR** (ν/cm^{-1}): 2930.3 (w), 2310.3 (w), 1748.2 (s), 1732.7 (s), 1568.8 (s), 1558.2 (s), 1540.8 (s), 1456.96 (m), 723.2 (w). **[α]$_D^{23}$** = — 112.2 ° (c = 0.36, CH_2Cl_2, l = 1 dm).

■ Product characterization

***(1R,2R,3aS,7aS)*-7a-hydroxy-3a-methyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (3a)**



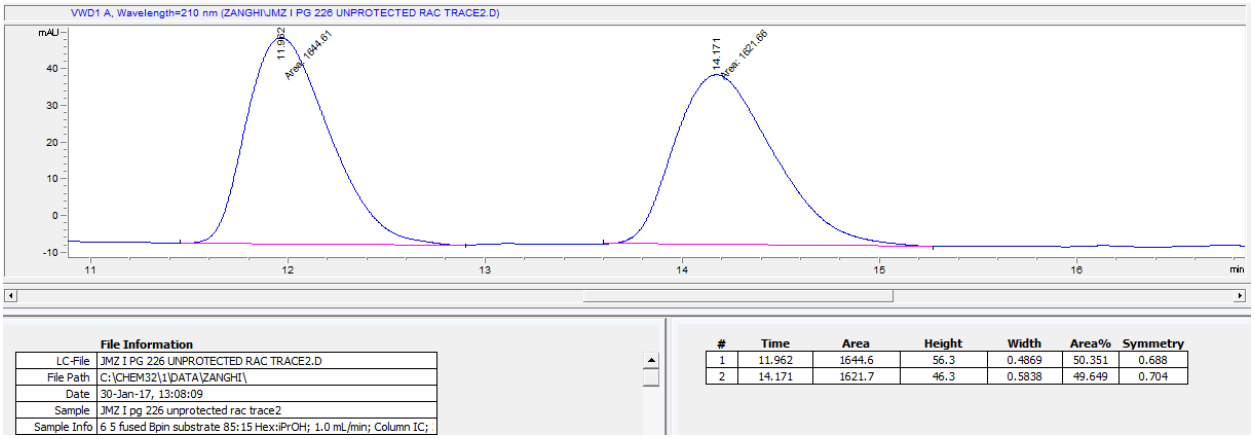
(3a)

This reaction was run using *(R)*-furyl-OMe-biphep. Silica gel chromatography (100% DCM → 98.5:1.5 DCM:*i*-PrOH) provided **(3a)** as a clear, colorless oil (29.3 mg, 70% yield, 13:1 dr, >99:1 er).

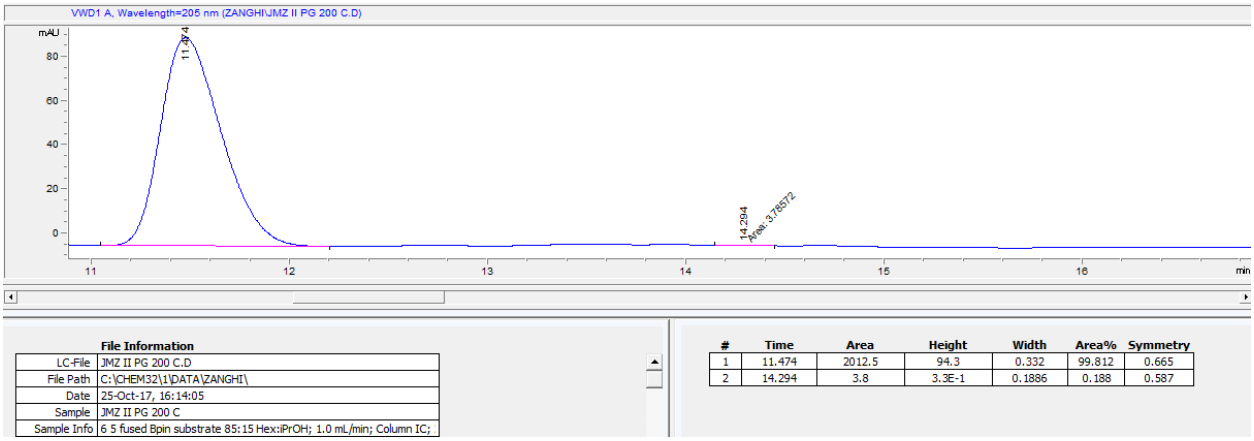
^{1}H NMR (600 MHz, $CDCl_3$): 2.58 (dt, 15.0 Hz, 6.2 Hz, 1H); 2.28 (d, 15.0 Hz, 1H); 2.19 (dt, 14.3 Hz, 3.7 Hz, 1H); 2.06 (dd, 12.8 Hz, 8.8 Hz, 2H); 1.97 (m, 2H); 1.85 (m, 3H); 1.61 (dd, 13.2 Hz, 10.3 Hz, 1H); 1.26 (br s, 24H); 1.18 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): 214.9, 87.47, 83.54, 83.3, 59.2, 38.6, 37.4, 32.5, 25.2, 25.1, 24.6, 21.6, 15.9. **HRMS** (*m*/*z*): calcd for $C_{22}H_{37}B_2O_6^-$: 419.2782 (M-H$^+$); found: 419.2795. **IR** (ν/cm^{-1}): 2978 (s), 2939 (m), 2360 (w), 1698 (s), 1685 (m), 1541 (m), 1507 (w), 1457 (w), 1373 (s), 1319 (m), 1146 (s), 967 (w), 854 (w). **[α]$_D^{23}$** = + 10.2 ° (c = 1.44, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IC Column: 85:15 hexanes:iPrOH; 1.0 mL/min; 205 nm.

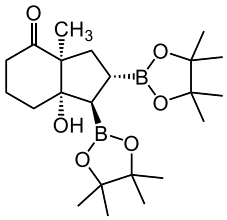
Racemic material:



Enantioenriched material:



(*1R,2S,3aS,7aS*)-7a-hydroxy-3a-methyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (*ent*-15)



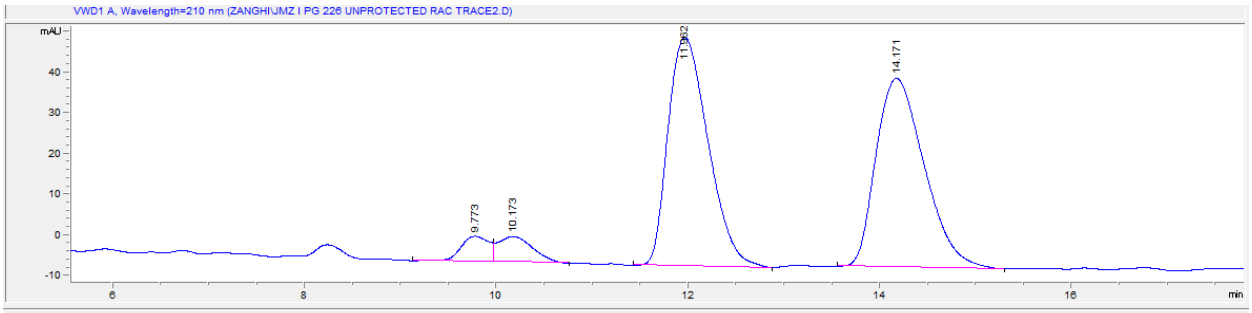
(*ent*-15)

This reaction was run using *(S,S)*-BDPP (4.8 mg, 0.011 mmol, 11 mol%) instead of furyl-OMe-biphep (otherwise according to **General Procedure I**). Silica gel chromatography (12:1 hex:EtOAc → 2:1 hex:EtOAc) afforded **(*ent*-15)** as a clear, colorless oil (40.6 mg, 97% yield, 11:1 dr, ~85:15 er).

^{1}H NMR (600 MHz, $CDCl_3$): 2.54-2.49 (td, 13.9 Hz, 5.5 Hz, 1H); 2.30-2.27 (br d, 15.0 Hz, 1H); 2.19-2.15 (app t, 12.8 Hz, 1H); 2.07-2.00 (m, 1H); 1.97-1.91 (m, 1H); 1.85-1.80 (m, 3H); 1.72-1.68 (m, 2H); 1.52-1.48 (dd, 13.6 Hz, 5.5 Hz, 1H); 1.25 (s, 6H); 1.24 (s, 6H); 1.21 (s, 6H), 1.20 (s, 6H); 1.14 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): 214.7, 87.6, 83.6, 83.3, 59.4, 37.9, 37.5, 32.8, 25.2, 24.9, 24.7, 24.6, 21.3, 17.4. **HRMS** (*m/z*): calcd for $C_{22}H_{37}B_2O_6^-$: 419.2782 ($M\text{-}H^+$); found: 419.2796. **IR** (ν/cm^{-1}): 2977.6 (s), 2939.0 (m), 2875.3 (w), 1698.0 (s), 1372.1 (s), 1318.1 (s), 1142.6 (s), 967.1 (m), 851.4 (m). $[\alpha]_D^{23}$ = —1.0 ° (c = 5.3, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IC Column: 85:15 hexanes:iPrOH; 1.0 mL/min; 205 nm.

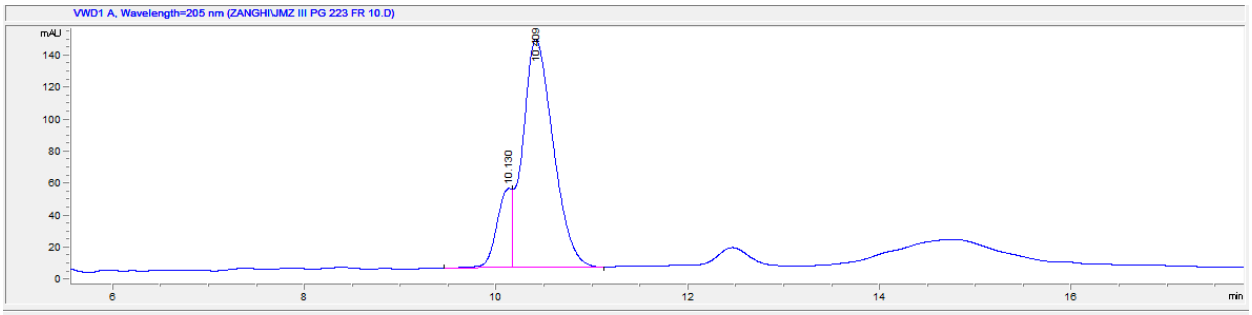
Racemic material:



File Information	
LC-File	JMZ I PG 226 UNPROTECTED RAC TRACE2.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	30-Jan-17, 13:08:09
Sample	JMZ I pg 226 unprotected rac trace2
Sample Info	6 5 fused Bpin substrate 85:15 Hex:iPrOH; 1.0 mL/min; Column IC;

#	Time	Area	Height	Width	Area%	Symmetry
1	9.773	131.5	6.2	0.3187	3.709	1.028
2	10.173	157.2	6.4	0.37	4.435	0.679
3	11.962	1635.1	56.2	0.4605	46.131	0.674
4	14.171	1620.7	46.3	0.5482	45.725	0.692

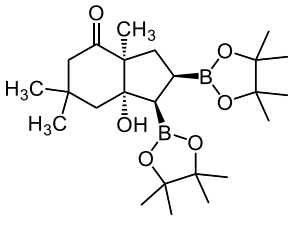
Enantioenriched material:



File Information	
LC-File	JMZ III PG 223 FR 10.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	17-Nov-18, 16:46:22
Sample	JMZ III pg 223 fr 10
Sample Info	6 5 fused Bpin substrate 85:15 Hex:iPrOH; 1.0 mL/min; Column IC;

#	Time	Area	Height	Width	Area%	Symmetry
1	10.13	554.3	49.7	0.173	14.932	4.122
2	10.409	3157.7	142.8	0.334	85.068	0.72

***(1R,2R,3aS,7aS)*-7a-hydroxy-3a,6,6-trimethyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (3b)**



(3b)

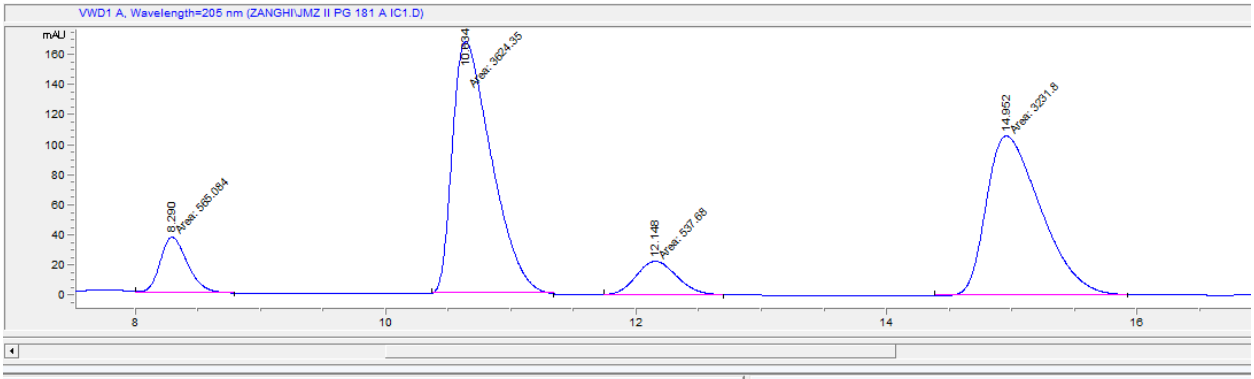
This reaction was run using *(R)*-furyl-OMe-biphep. Silica gel chromatography (15:1 hex:EtOAc → 6:1 hex:EtOAc) provided **(3b)** as a clear, colorless oil (24.2 mg, 54% yield, >20:1 dr, >99:1 er)

which crystallized upon standing at – 20 °C. A crystal was analyzed by single crystal X-ray diffraction (*vide infra*).

^{1}H NMR (600 MHz, $CDCl_3$): 2.56 (d, 13.6 Hz, 1H); 2.20 (d, 15.0 Hz, 1H); 2.09 (d, 13.6 Hz, 1H); 2.04 (dd, 13.2 Hz, 7.7 Hz, 1H); 1.92 (s, 1H); 1.91 (d, 13.2 Hz, 1H); 1.79-1.65 (m, 3H), 1.25 (br s, 24H); 1.14 (s, 3H); 1.04 (s, 3H); 0.99 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): 215.6, 88.3, 83.6, 83.4, 58.0, 50.1, 44.9, 39.6, 35.5, 33.1, 28.3, 25.3, 25.2, 24.8, 24.7, 16.6. **HRMS** (*m*/*z*): calcd for $C_{24}H_{41}B_2O_6^-$: 447.3095 ($M\text{-}H^+$); found: 447.3098. **IR** (ν/cm^{-1}): 2978 (s), 2950 (m), 2360 (w), 2340 (w), 1699 (s), 1471 (m), 1373 (s), 1320 (s), 1213 (m), 1145 (s), 1059 (m), 965 (m), 862 (m). **$[\alpha]_D^{23}$** = + 25.9 ° (c = 1.06, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IC Column: 90:10 hexanes:iPrOH; 1.0 mL/min; 205 nm.

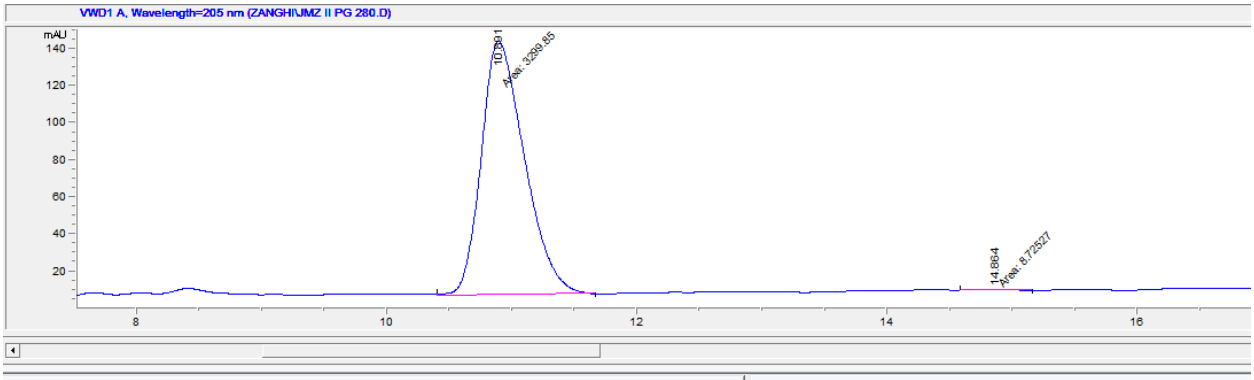
***Racemic material:* (mixture of diastereomers)**



File Information	
LC-File	JMZ II PG 181 A IC1.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	19-Sep-17, 14:43:36
Sample	JMZ II PG 181 A IC1
Sample Info	6,5 dimedone rac; 90:10 Hex:iPrOH; 1.0 mL/min; IC Column; 205 nn

#	Time	Area	Height	Width	Area%
1	8.29	565.1	37	0.2547	7.100
2	10.634	3624.4	167.4	0.3609	45.538
3	12.148	537.7	22.9	0.3918	6.756
4	14.952	3231.8	106.2	0.5071	40.606

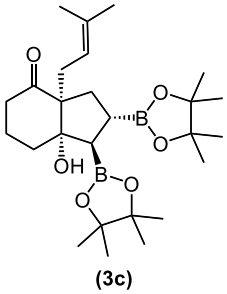
Enantioenriched material:



File Information	
LC-File	JMZ II PG 280.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	06-Jan-18, 13:32:39
Sample	JMZ II pg 280
Sample Info	6,5 dimedone rac; 90:10 Hex:iPrOH; 1.0 mL/min; IC Column; 205 nn

#	Time	Area	Height	Width	Area%
1	10.891	3299.9	136.7	0.4022	99.736
2	14.864	8.7	3.9E-1	0.3691	0.264

***(1R,2S,3aR,7aS)*-7a-hydroxy-3a-(3-methylbut-2-en-1-yl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (3c)**



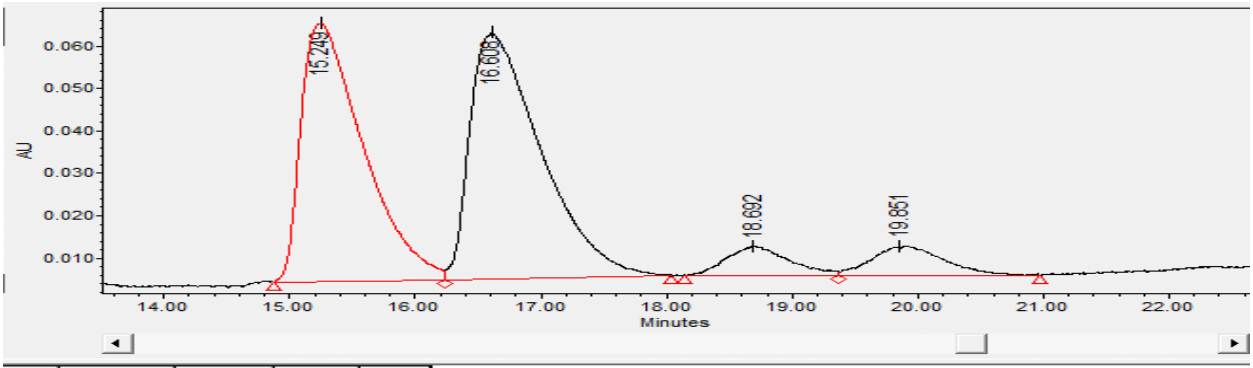
(3c)

This reaction was run using *(S)*-furyl-OMe-biphep. Silica gel chromatography (20:1 → 8:1 hexanes:EtOAc) provided **(3c)** as a clear, colorless oil which crystallized at -20 °C. (23.2 mg, 49% yield, 5:1 dr, 98:2 er (maj), >99:1 er (min)).

^{1}H NMR (600 MHz, $CDCl_3$): 5.28 (min. diast., t, 7.3 Hz, 0.21H); 5.21 (maj. diast., t, 6.2 Hz, 1H); 2.55-2.28 (m, 7H); 2.27-2.18 (m, 1H); 2.13-1.99 (m, 2H); 1.85-1.1.61 (m, 14H); 1.57-1.48 (m, 2H); 1.32-1.17 (m, 35H). **^{13}C NMR** (214 MHz, $CDCl_3$): 214.4, 133.6, 122.0, 88.4, 83.1, 63.0, 37.4, 36.2, 33.2, 31.9, 31.6, 29.1, 26.0, 25.0, 24.8, 24.6, 22.7, 20.7, 20.3, 18.0, 14.1, 11.4. **HRMS** (*m/z*): calcd for $C_{26}H_{45}B_2O_6^+$: 475.3397 ($M+H^+$); found: 475.3380. **IR** (ν/cm^{-1}): 2977.6 (m), 2931.3 (w), 1699.0 (s), 1372.1 (s), 1144.5 (s), 967.1 (m), 851.4 (m). **$[\alpha]_D^{23}$** = + 5.3 ° (c = 1.14, CH_2Cl_2, l = 1 dm).

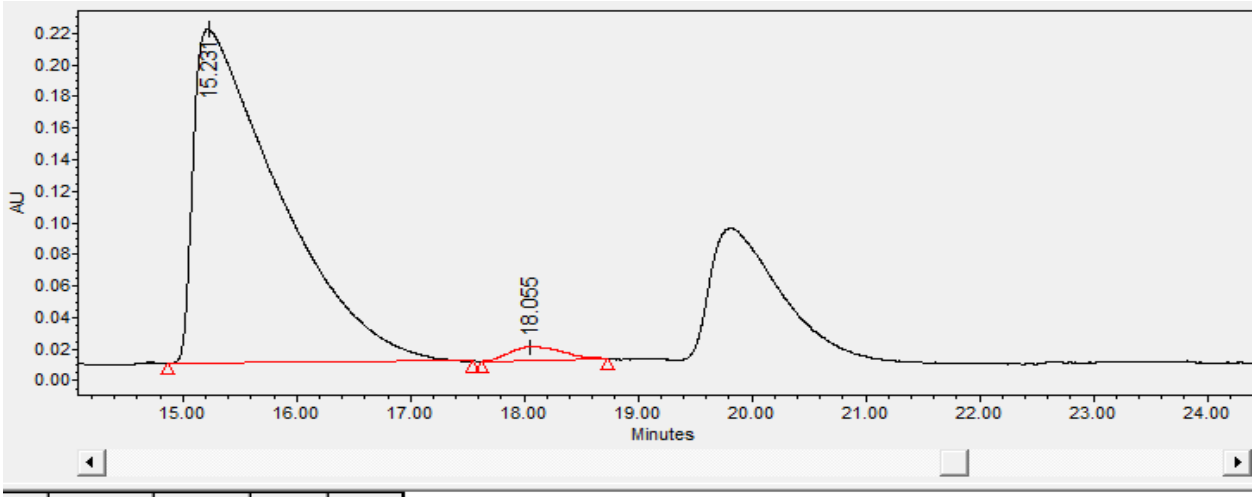
Phenomenex Lux Cellulose-1 OD Column: 97:3 CO_2:iPrOH; 1.0 mL/min; 210 nm.

***Racemic material:* (mixture of diastereomers)**



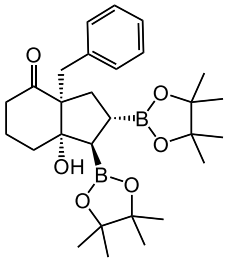
Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)
	15.249	2090635	42.96	60745
	16.608	2272553	46.69	57925
	18.692	232148	4.77	6851
	19.851	271580	5.58	6912

Enantioenriched material:



ame	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)
	15.231	10980492	97.59	211139
	18.055	271467	2.41	8607

***(1R,2S,3aR,7aS)*-3a-benzyl-7a-hydroxy-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (3d)**



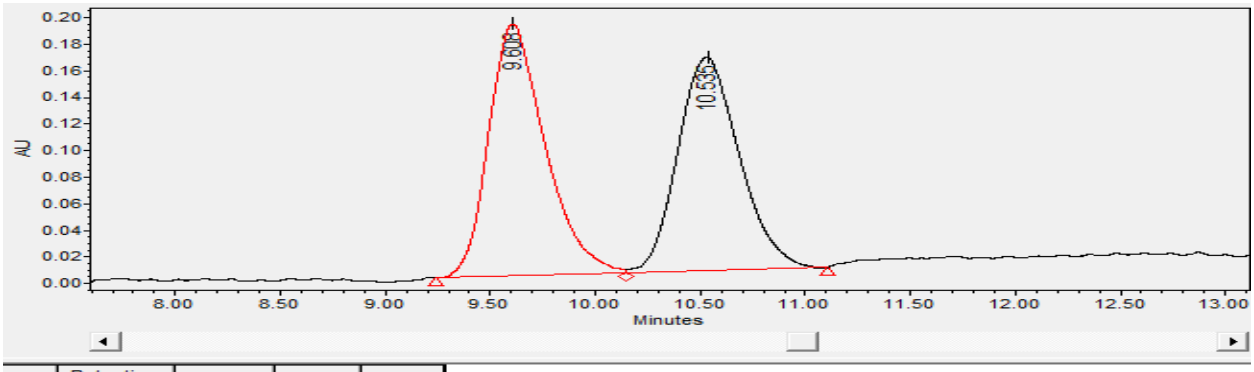
(3d)

This reaction was run using *(S)*-furyl-OMe-biphep. Silica gel chromatography (15:1 → 8:1 hexanes:EtOAc) provided **(3d)** as a clear, colorless oil (16.1 mg, 32% yield, >20:1 dr, 96:4 er).

^{1}H NMR (400 MHz, $CDCl_3$): 7.25-7.11 (m, 5H); 3.16 (d, 13.9 Hz, 1H); 2.93 (d, 13.9 Hz, 1H); 2.41 (m, 2H); 2.20 (dd, 13.4 Hz, 9.3 Hz, 1H); 2.10-1.97 (m, 2H); 1.92-1.69 (m, 5H); 1.62 (dd, 13.2 Hz, 9.3 Hz, 1H); 1.35 (m, 3H); 1.23 (m, 24H). **^{13}C NMR** (214 MHz, $CDCl_3$): 214.2, 139.0, 130.9, 128.0, 126.2, 87.9, 83.6, 83.3, 65.5, 39.0, 38.0, 35.0, 33.9, 25.2, 25.0, 24.8, 24.7, 20.1. **HRMS** (*m*/*z*): calcd for $C_{28}H_{41}B_2O_6^-$: 495.3095 ($M-H^+$); found: 495.3106. **IR** (ν/cm^{-1}): 2977.6 (m), 2933.2 (m), 1698.9 (s), 1380.8 (s), 1371.1 (s), 1317.1 (s), 1144.6 (s), 967.1 (w), 851.4 (w), 701.0 (w). **$[\alpha]_D^{23}$** = — 11.7 ° (c = 0.72, CH_2Cl_2, l = 1 dm).

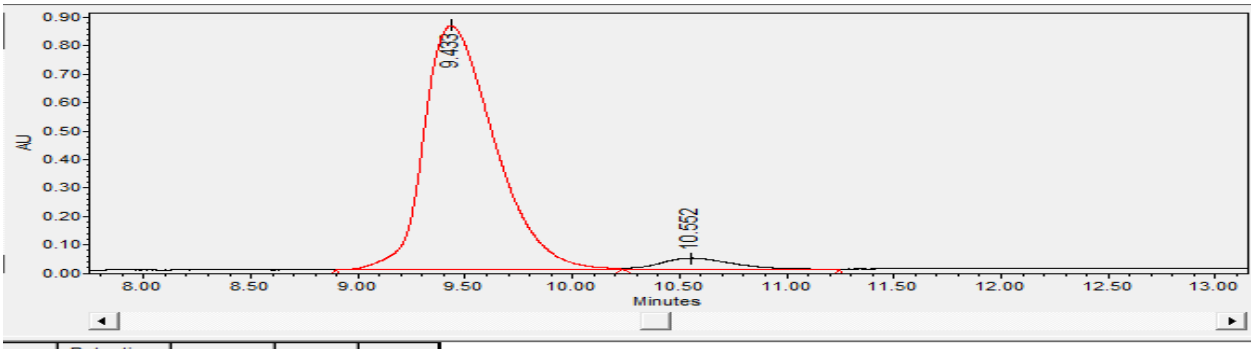
Phenomenex Lux Cellulose-1 OD Column: 90:10 CO_2:iPrOH; 1.0 mL/min; 210 nm.

Racemic material:



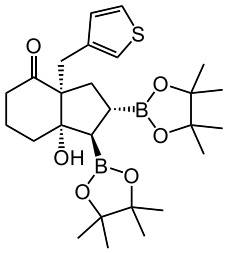
Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)
	9.608	3513072	51.85	188946
	10.535	3262094	48.15	160246

Enantioenriched material:



Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)
	9.433	19598074	95.67	858288
	10.552	887553	4.33	39028

(1R,2S,3aR,7aS)-7a-hydroxy-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a-(thiophen-3-ylmethyl)octahydro-4H-inden-4-one (3e)



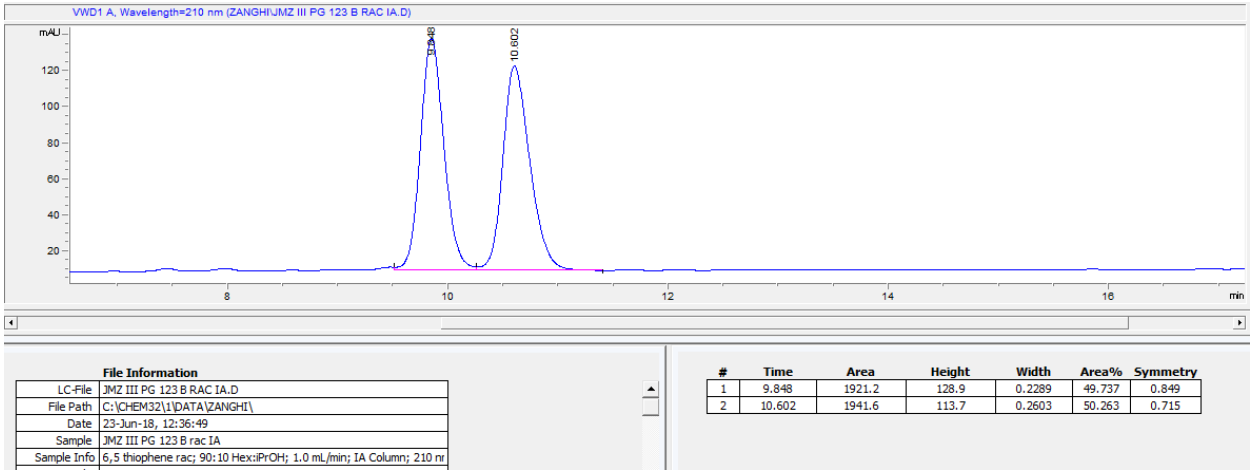
(3e)

This reaction was run using *(S)*-furyl-OMe-biphep. Analysis of crude reaction material revealed 65% NMR yield as a 3:2 mixture of diastereomers. The minor diastereomer was found to

decompose on silica gel, resulting in high dr but low isolated yield. Silica gel chromatography (15:1 → 8:1 hex:EtOAc) provided **(3e)** as a clear, colorless oil (12.4 mg, 25% yield, >20:1 dr, 94:6 er). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.16 (dd, 4.9 Hz, 3.4 Hz, 1H); 7.06 (br s, 1H); 7.02 (d, 4.9 Hz); 3.18 (d, 14.6 Hz, 1H); 2.94 (d, 14.3 Hz, 1H); 2.45 (m, 1H); 2.36-2.31 (app dt, 15.0 Hz, 4.6 Hz); 2.19 (m, 1H); 2.02 (m, 1H); 1.90-1.75 (m, 3H); 1.75-1.56 (m, 3H); 1.49 (m, 1H); 1.25 (s, 6H); 1.23 (s, 6H); 1.23 (s, 6H); 1.20 (s, 6H). **^{13}C NMR** (214 MHz, $CDCl_3$): 214.5, 139.5, 130.8, 124.6, 123.5, 88.5, 83.6, 83.3, 64.7, 38.0, 35.2, 33.9, 33.3, 25.2, 25.1, 24.73, 24.71, 20.6. **HRMS** (*m/z*): calcd for $C_{26}H_{39}B_2O_6S^-$: 501.2659 (M-H$^+$); found: 501.2671. **IR** (ν/cm^{-1}): 2977.6 (m), 2933.2 (w), 1698.0 (s), 1372.1 (s), 1318.1 (s), 1143.6 (s), 966.2 (m), 851.4 (m). **$[\alpha]_D^{23}$** = — 1.5 ° (c = 0.72, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IA Column: 90:10 hexanes:iPrOH; 1.0 mL/min; 210 nm.

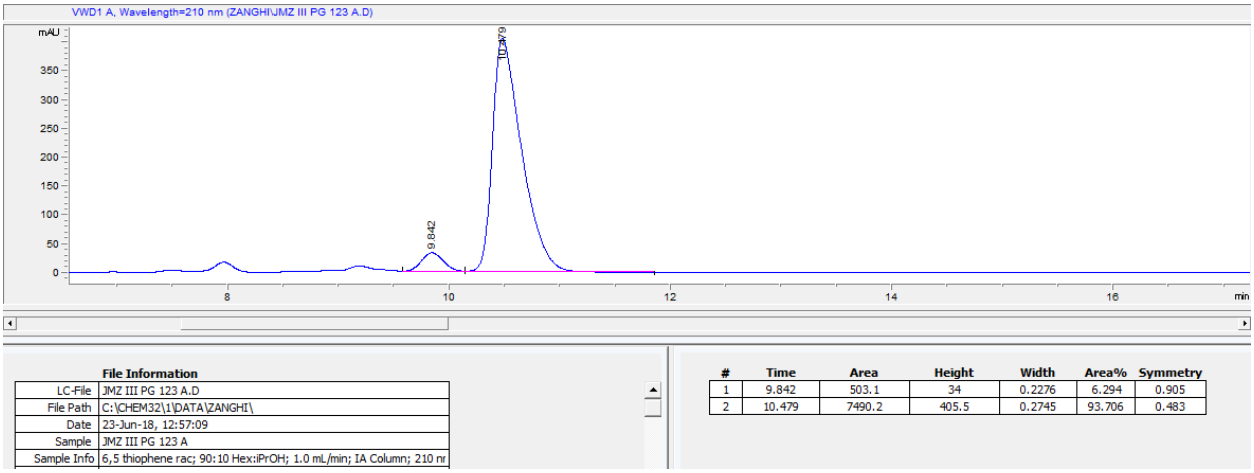
Racemic material:



File Information	
LC-File	JMZ III PG 123 B RAC IA.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	23-Jun-18, 12:36:49
Sample	JMZ III PG 123 B rac IA
Sample Info	6,5 thiophene rac; 90:10 Hex:iPrOH; 1.0 mL/min; IA Column; 210 nr

#	Time	Area	Height	Width	Area%	Symmetry
1	9.848	1921.2	128.9	0.2289	49.737	0.849
2	10.602	1941.6	113.7	0.2603	50.263	0.715

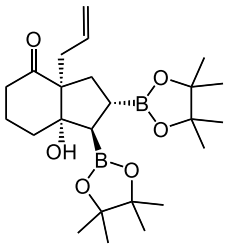
Enantioenriched material:



File Information	
LC-File	JMZ III PG 123 A.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	23-Jun-18, 12:57:09
Sample	JMZ III PG 123 A
Sample Info	6,5 thiophene rac; 90:10 Hex:iPrOH; 1.0 mL/min; IA Column; 210 nr

#	Time	Area	Height	Width	Area%	Symmetry
1	9.842	503.1	34	0.2276	6.294	0.905
2	10.479	7490.2	405.5	0.2745	93.706	0.483

***(1R,2S,3aR,7aS)*-3a-allyl-7a-hydroxy-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octahydro-4H-inden-4-one (3f)**



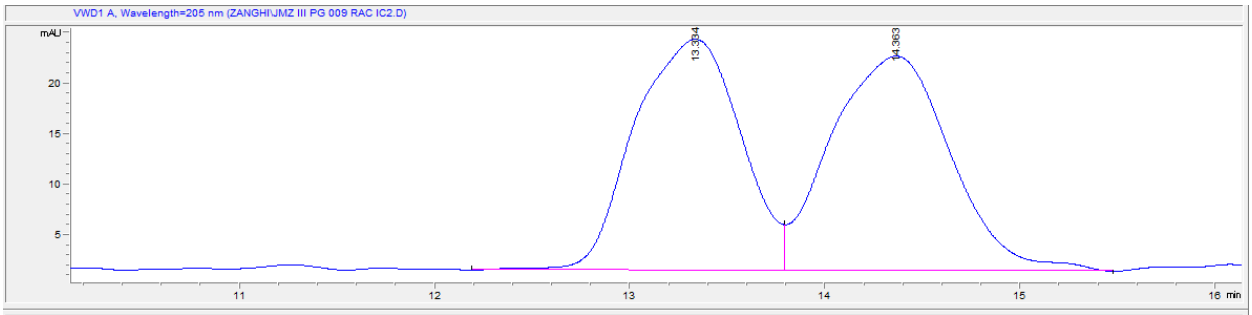
(3f)

This reaction was run using *(S)*-furyl-OMe-biphep. Silica gel chromatography (75:1 hex:EtOAc + 5 vol% NEt_3→ 25:1 hex:EtOAc + 5 vol% NEt_3) provided **(3f)** as a clear, colorless oil (20.6 mg, 46% yield, 17:1 dr, 88:12 er).

^{1}H NMR (600 MHz, $CDCl_3$): 5.99-5.92 (m, 1H); 5.12-5.10 (d, 16.1 Hz, 1H); 5.05-5.03 (d, 10.3 Hz, 1H); 2.58-2.55 (dd, 14.3 Hz, 7.3 Hz, 1H); 2.50-2.34 (m, 3H); 2.24-2.20 (dd, 13.6 Hz, 11.0 Hz, 1H); 2.16 (s, OH, 1H); 2.13-2.05 (m, 1H); 1.89-1.73 (m, 4H); 1.64-1.62 (m, 1H); 1.59-1.54 (m, 1H); 1.27 (s, 6H); 1.26 (s, 6H); 1.24 (s, 6H); 1.23 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): 214.3, 137.3, 117.3, 88.6, 83.5, 83.3, 63.1, 38.0, 37.7, 35.1, 33.6, 25.2, 25.0, 24.70, 24.67, 20.6. **HRMS** (*m*/*z*): calcd for $C_{24}H_{41}B_2O_6^+$: 447.3084 ($M+H^+$); found: 447.3079. **IR** (ν/cm^{-1}): 2976.6 (m), 2927.4 (w), 2360.4 (m), 2341.2 (m), 1698.0 (s), 1372.1 (s), 1321.0 (s), 1214.9 (w), 1144.5 (s), 968.1 (w), 858.2 (w), 668.2 (w). **$[\alpha]_D^{23}$** = + 0.2 ° (c = 0.48, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IC Column: 92:8 hexanes:iPrOH; 1.0 mL/min; 205 nm.

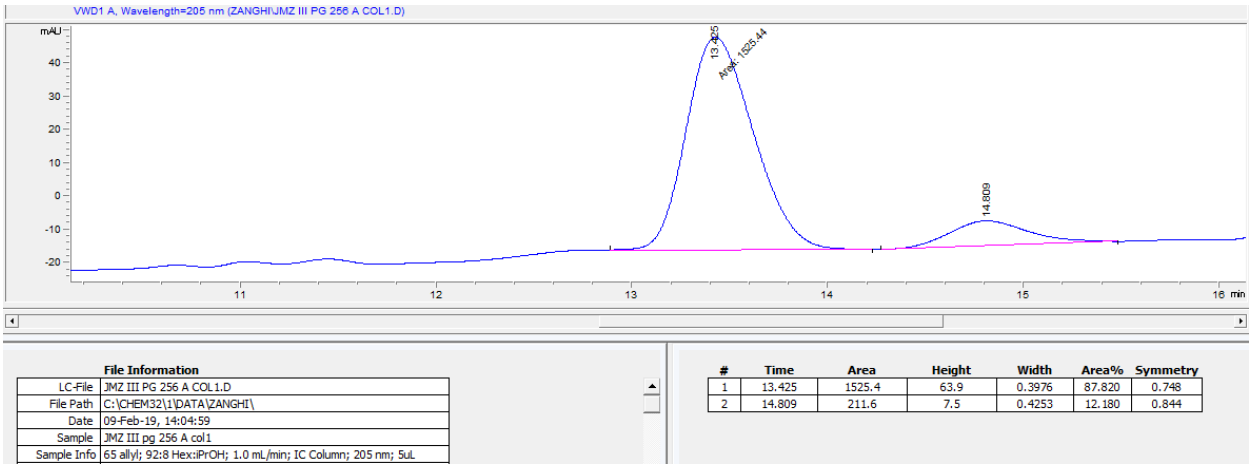
Racemic material:



File Information	
LC-File	JMZ III PG 009 RAC IC2.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	07-Feb-18, 17:46:41
Sample	JMZ III pg 009 rac IC2
Sample Info	65 allyl; 92:8 Hex:iPrOH; 1.0 mL/min; IC Column; 205 nm; 5uL

#	Time	Area	Height	Width	Area%	Symmetry
1	13.334	863.8	22.9	0.5487	48.849	1.275
2	14.363	904.5	21.2	0.6871	51.151	1.1

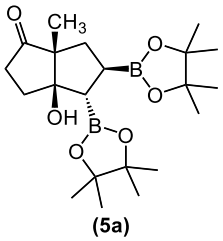
Enantioenriched material:



File Information	
LC-File	JMZ III PG 256 A COL1.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	09-Feb-19, 14:04:59
Sample	JMZ III pg 256 A col1
Sample Info	65 allyl; 92:8 Hex:iPrOH; 1.0 mL/min; IC Column; 205 nm; 5uL

#	Time	Area	Height	Width	Area%	Symmetry
1	13.425	1525.4	63.9	0.3976	87.820	0.748
2	14.809	211.6	7.5	0.4253	12.180	0.844

***(3aR,4S,5R,6aR)*-3a-hydroxy-6a-methyl-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2H)-one (5a)**



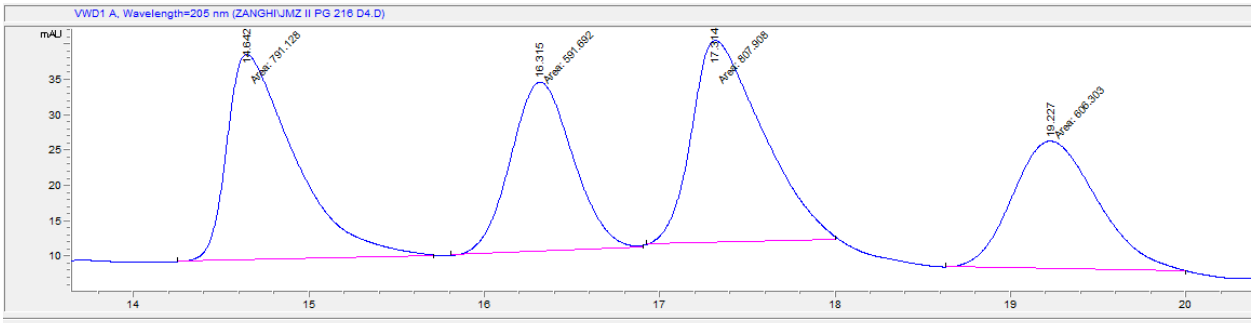
(5a)

Silica gel chromatography: 100% DCM → 98.5:1.5 DCM:*i*-PrOH. Initial column chromatography provided the tris-boronate, which was subjected to hydrolysis (250 μL 8 M HCl *(aq)* + 1 mL THF, 22 °C, 2 h). Extraction with EtOAc and column chromatography under the same conditions afforded the bis-boronate **(5a)** as a white solid (28.1 mg, 69% yield, 2:1 dr, 74:26 er (major diastereomer), 90:10 er (minor diastereomer)).

^{1}H NMR (400 MHz, $CDCl_3$): 2.54-2.39 (m, 2H); 2.37-2.25 (m, 1H); 2.17 (s, 0.4H); 2.04-1.89 (m, 6H); 1.90-1.77 (m, 1.5 H); 1.74-1.68 (m, 0.5H); 1.67-1.60 (m, 1.5H); 1.50 (dd, 13.7 Hz, 9.8 Hz, 1H); 1.32-1.16 (m, 47H); 1.05 (s, 1.6H, *CH_3 min. diast.*); 1.02 (s, 3H, *CH_3 maj. diast.*). **^{13}C NMR** (214 MHz, $CDCl_3$): 222.7 (maj. diast.), 221.6 (min. diast.), 90.5, 90.0, 83.72, 83.66, 83.5, 83.3, 77.4, 59.4, 39.2, 37.6, 36.6, 35.4, 32.4, 32.1, 25.3, 25.2, 25.1, 24.82, 24.78, 24.72, 24.70, 17.5, 14.8. **HRMS** (*m*/*z*): calcd for $C_{21}H_{35}B_2O_6^-$: 405.2625 ($M\text{-}H^+$); found: 405.2633. **IR** (ν/cm^{-1}): 2978 (s), 2932 (m), 2360 (m), 2341 (m), 1733 (s), 1717 (m), 1372 (s), 1320 (s), 1143 (s), 967 (m), 850 (m). **$[\alpha]_D^{23}$** = — 12.6 ° (c = 1.32, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IA Column: 97:3 hexanes:iPrOH; 1.0 mL/min; 205 nm.

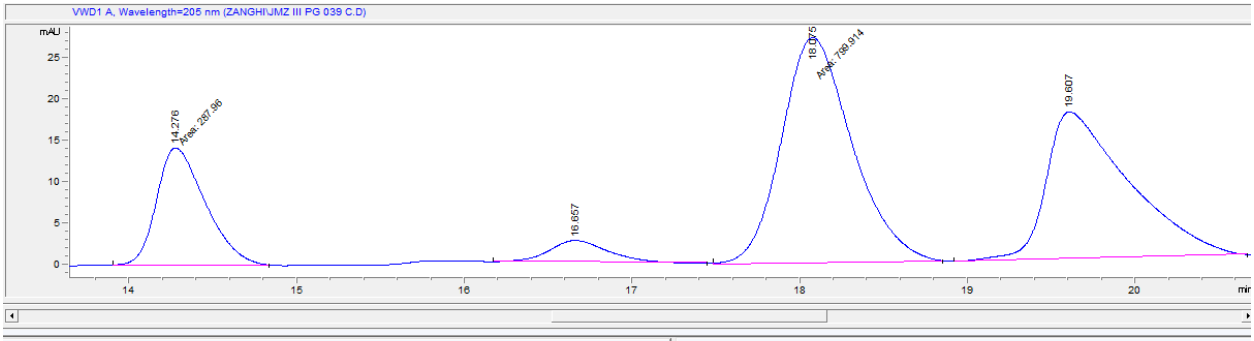
Racemic material:



File Information	
LC-File	JMZ II PG 216 D4.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	13-Nov-17, 12:44:38
Sample	JMZ II PG 216 D4
Sample Info	5,5 Me rac; 97:3 Hex:iPrOH; 1.0 mL/min; IA Column; 205 nm

#	Time	Area	Height	Width	Area%	Symmetry
1	14.642	791.1	29.2	0.4519	28.285	0.4
2	16.315	591.7	24	0.4113	21.154	0.877
3	17.314	807.9	28.6	0.4702	28.884	0.499
4	19.227	606.3	18	0.5599	21.677	0.775

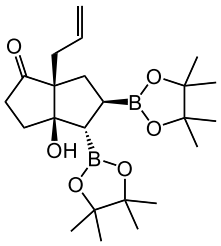
Enantioenriched material:



File Information	
LC-File	JMZ III PG 039 C.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	16-Mar-18, 18:51:31
Sample	JMZ III PG 039 C
Sample Info	5,5 Me rac; 97:3 Hex:iPrOH; 1.0 mL/min; IA Column; 205 nm

#	Time	Area	Height	Width	Area%	Symmetry
1	14.276	288	14.2	0.3376	16.373	0.63
2	16.657	64.6	2.6	0.366	3.672	0.764
3	18.075	799.9	27.2	0.4897	45.483	0.776
4	19.607	606.3	17.7	0.4812	34.472	0.386

***(3aR,4S,5R,6aS)*-6a-allyl-3a-hydroxy-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2H)-one (5b)**



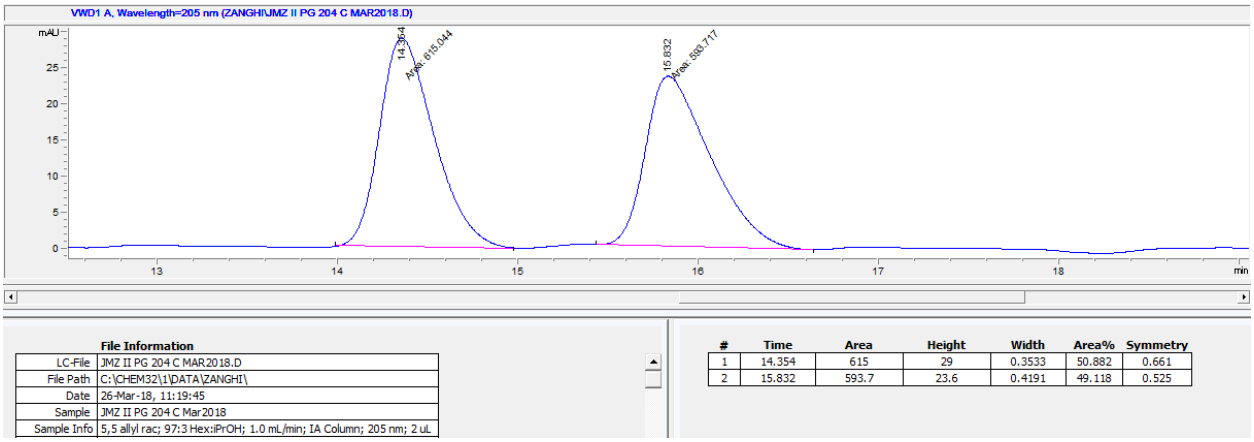
(5b)

Silica gel chromatography (15:1 hex:EtOAc → 8:1 hex:EtOAc) afforded **(5b)** as a white solid (24.5 mg, 57% yield, >20:1 dr, 89:11 er).

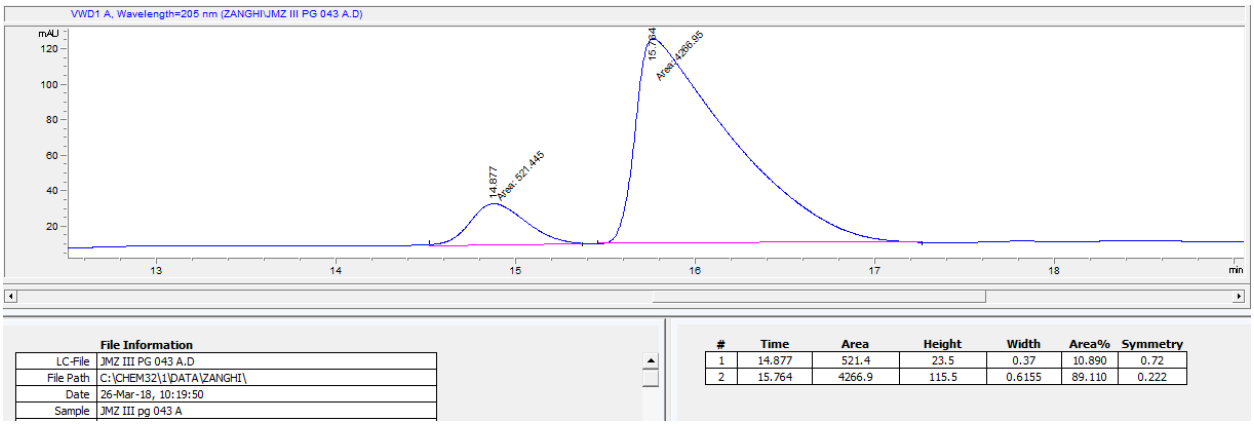
^{1}H NMR (600 MHz, $CDCl_3$): 6.00-5.93 (m, 1H); 5.10-5.04 (m, 2H); 2.52-2.45 (dt, 17.6 Hz, 10.3 Hz, 1H); 2.35-2.25 (m, 3H); 2.17 (br s, 1H); 2.00-1.88 (m, 2H);1.72-1.68 (dd, 13.6 Hz, 11.0 Hz, 1H) 1.61 (d, 13.2 Hz, 1H); 1.25 (s, 6H); 1.24 (s, 6H), 1.21 (s, 6H); 1.20 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): 222.1; 135.5, 118.0, 90.6, 83.6, 83.3, 62.2, 37.52, 37.46, 37.0, 33.2, 25.1, 24.9, 24.8, 24.7. **HRMS** (*m*/*z*): calcd for $C_{23}H_{39}B_2O_6^+$: 433.2927 ($M+H^+$); found: 433.2910. **IR** (ν/cm^{-1}): 2978 (s), 2929 (m), 2360 (w), 2341 (w), 1733 (s), 1416 (m), 1381 (s), 1320 (s), 1143 (s), 969 (m), 850 (m). **[α]$_D^{23}$** = — 27.5 ° (c = 1.26, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IA Column: 97:3 hexanes:iPrOH; 1.0 mL/min; 205 nm.

Racemic material:



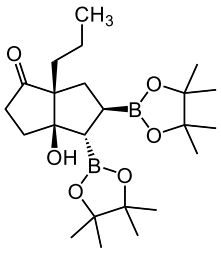
Enantioenriched material:



File Information	
LC-File	JMZ III PG 043 A.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	26-Mar-18, 10:19:50
Sample	JMZ III pg 043 A

#	Time	Area	Height	Width	Area%	Symmetry
1	14.877	521.4	23.5	0.37	10.890	0.72
2	15.764	4266.9	115.5	0.6155	89.110	0.222

***(3aR,4S,5R,6aR)*-3a-hydroxy-6a-propyl-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahydropentalen-1(2H)-one (5c)**



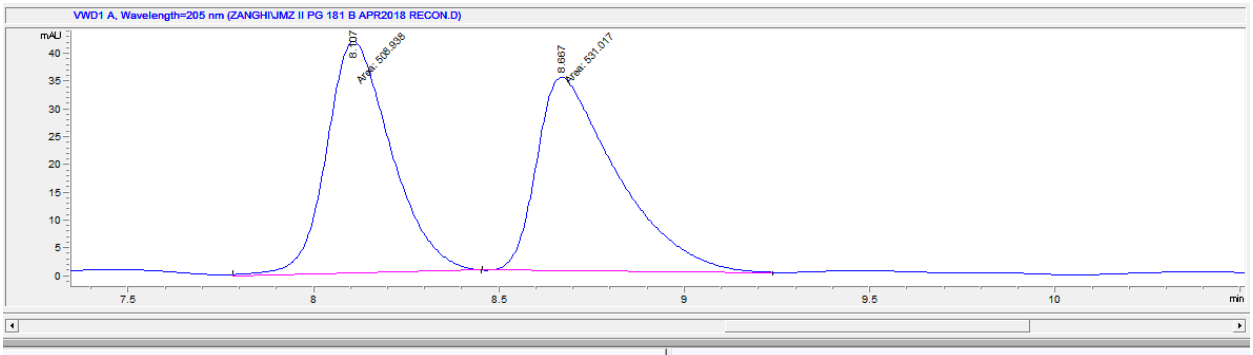
(5c)

Silica gel chromatography (15:1 hex:EtOAc → 10: 1 hex:EtOAc) afforded **(5c)** as a white solid (27.6 mg, 64% yield, >20:1 dr, 94:6 er). A single recrystallization from hot hexanes provided **(5c)** in >20:1 dr and 97.5:2.5 er.

^{1}H NMR (600 MHz, $CDCl_3$): 2.54-2.47 (dt, 17.6 Hz, 10.3 Hz, 1H); 2.24-2.19 (ddd, 17.6 Hz, 7.7 Hz, 5.1 Hz, 1H); 2.17 (s, 1H); 2.05-1.98 (m, 2H); 1.96-1.90 (m, 2H); 1.60-1.35 (m, 4H); 1.25 (s, 6H); 1.24 (s, 6H); 1.21 (s, 6H); 1.20 (s, 6H); 1.14-1.08 (m, 1H); 0.87-0.84 (t, 7.0 Hz, 3H). **^{13}C NMR** (214 MHz, $CDCl_3$): 222.6, 90.0, 83.7, 83.3, 62.5, 38.1, 37.8, 35.6, 33.7, 25.2, 24.9, 24.81, 24.76, 18.0, 15.1. **HRMS** (*m*/*z*): calcd for $C_{23}H_{39}B_2O_6^-$: 433.2938 (M-H$^+$); found: 433.2946. **IR** (ν/cm^{-1}): 2977 (s), 2932 (m), 2360 (w), 2331 (w), 1733 (s), 1717 (m), 1373 (s), 1319 (s), 1143 (s), 969 (m), 850 (m). **$[\alpha]_D^{23}$** = — 16.4 ° (c = 1.34, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IA Column: 95:5 hexanes:iPrOH; 1.0 mL/min; 205 nm.

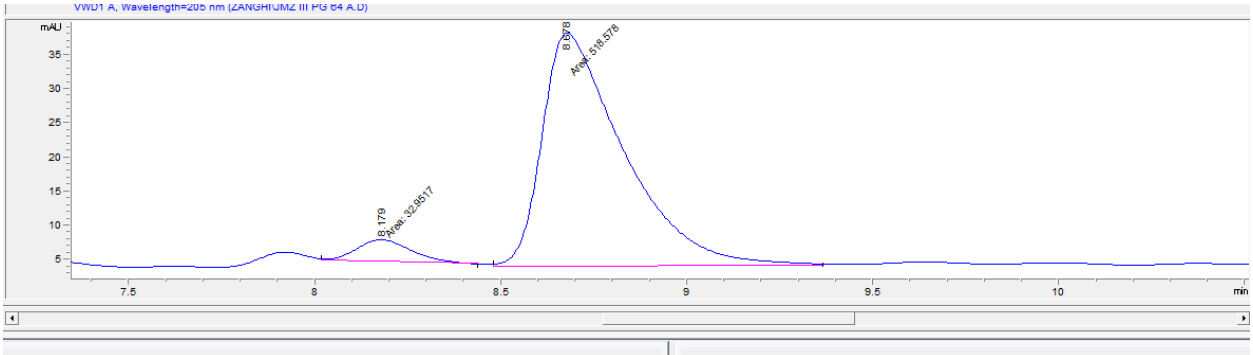
Racemic material:



File Information	
LC-File	JMZ II PG 181 B APR2018 RECON.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	10-Apr-18, 13:26:24
Sample	JMZ II PG 181 B Apr2018 recon
Sample Info	5,5 n-Pr rac recon; 95:5 Hex:iPrOH; 1.0 mL/min; IA Column; 205 nm

#	Time	Area	Height	Width	Area%	Symmetry
1	8.107	508.9	41.7	0.2033	48.938	0.707
2	8.667	531	35	0.2532	51.062	0.428

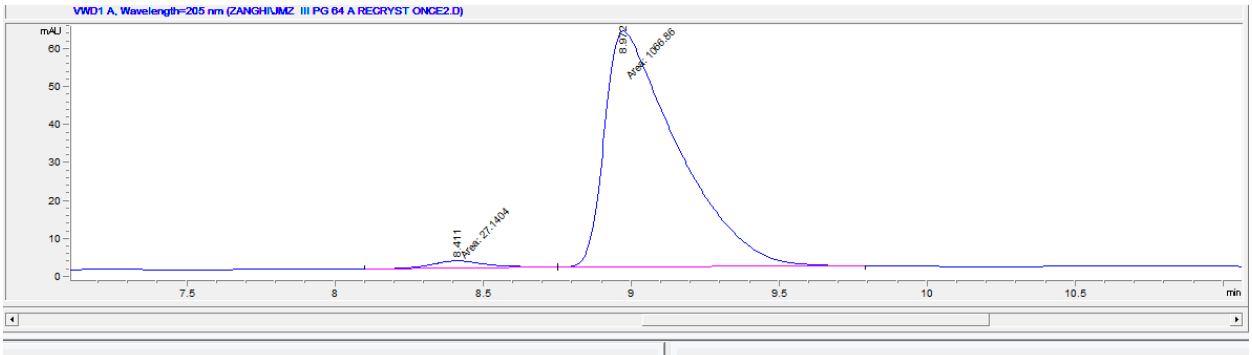
Enantioenriched material:



File Information	
LC-File	JMZ III PG 64 A.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	10-Apr-18, 12:37:09
Sample	JMZ III pg 64 A
Sample Info	5,5 n-Pr rac recon; 95:5 Hex:iPrOH; 1.0 mL/min; IA Column; 205 nm

#	Time	Area	Height	Width	Area%	Symmetry
1	8.179	33	3.2	0.173	5.975	0.747
2	8.678	518.6	34.1	0.2537	94.025	0.436

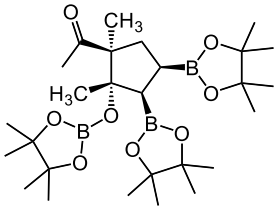
Enantioenriched material (after 1 recrystallization from hot hexanes → 97.5:2.5 er):



File Information	
LC-File	JMZ III PG 64 A RECRYST ONCE2.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	29-May-18, 18:35:45
Sample	JMZ III pg 64 A recryst once2
Sample Info	recrystal hot hexanes washed pentane; 95:5 Hex:iPrOH; 1.0 mL/mi

#	Time	Area	Height	Width	Area%	Symmetry
1	8.411	27.1	2	0.2296	2.481	0.827
2	8.972	1066.9	62.2	0.2859	97.519	0.336

1-((*1S,2S,3R,4R)*-1,2-dimethyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)cyclopentyl)ethan-1-one (6a)



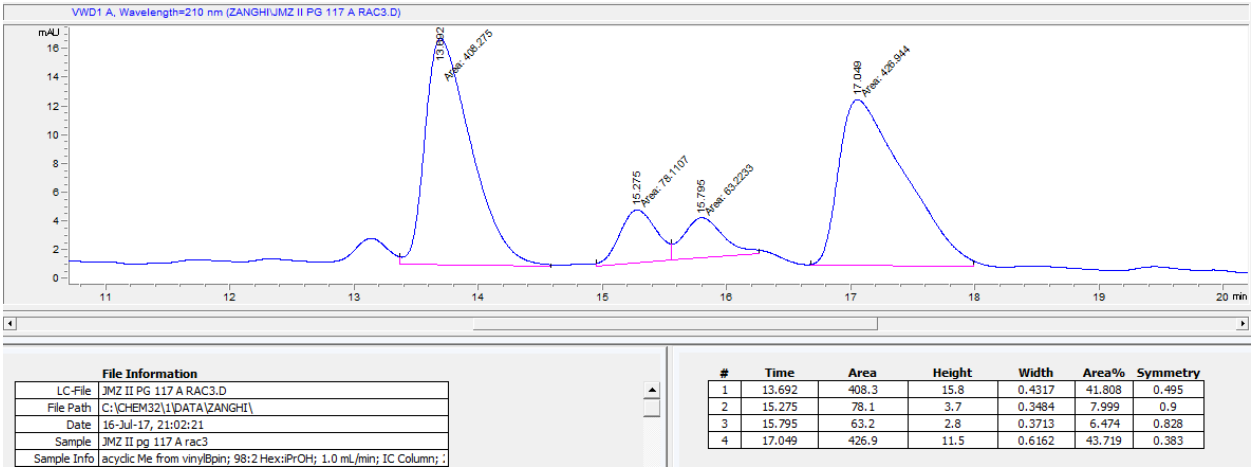
(6a)

This reaction was run using *(R)*-furyl-OMe-biphep. Silica gel chromatography (100% DCM → 98.5:1.5 DCM:*i*-PrOH) provided tris-boronate **(6a)** as a clear, colorless oil (19.6 mg, 37% yield, >20:1 dr, >99:1 er).

^{1}H NMR (600 MHz, $CDCl_3$): 2.52 (s, 1H); 2.21 (s, 3H); 2.10 (m, 1H); 1.95 (m, 1H); 1.57 (m, 2H); 1.26-1.20 (m, 36H); 1.19 (s, 3H). **^{13}C NMR** (214 MHz, $CDCl_3$): 213.7, 83.5, 83.3, 61.3, 33.5, 29.8, 27.3, 25.33, 25.29, 24.7, 24.6, 23.6, 19.3. **HRMS** (*m*/*z*): calcd for $C_{21}H_{37}B_2O_6^-$: 407.2782 (M-Bpin) found: 407.2795. **IR** (ν/cm^{-1}): 2978 (s), 2933 (m), 1733 (m), 1699 (s), 1473 (m), 1457 (m), 1372 (s), 1321 (s), 1146 (s), 984 (w), 862 (w), 674 (w). **[α]$_D^{23}$** = — 14.0 ° (c = 0.92, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IC Column: 98:2 hexanes:iPrOH; 1.0 mL/min; 205 nm.

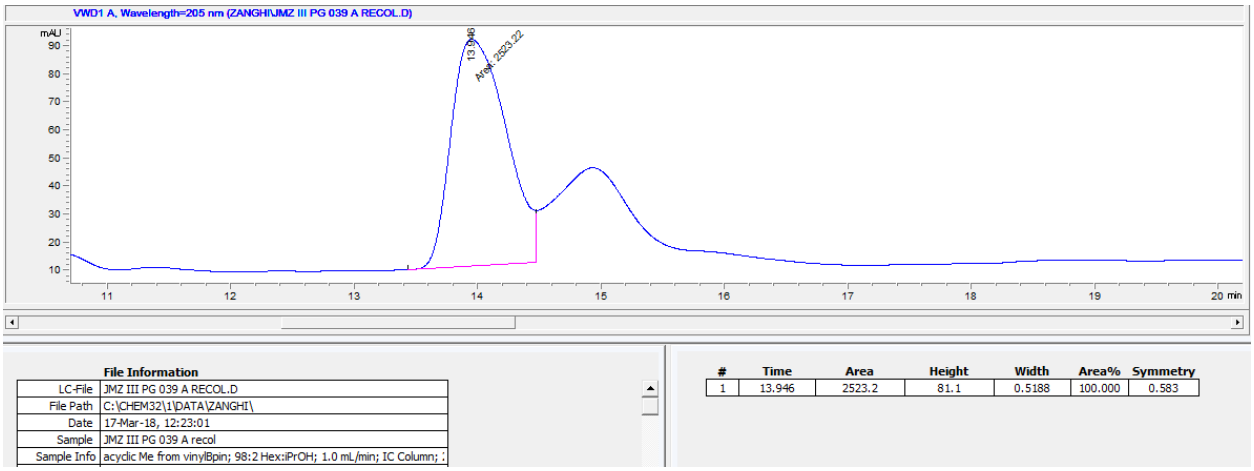
Racemic material:



File Information	
LC-File	JMZ II PG 117 A RAC3.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	16-Jul-17, 21:02:21
Sample	JMZ II pg 117 A rac3
Sample Info	acyclic Me from vinylBpin; 98:2 Hex:iPrOH; 1.0 mL/min; IC Column;

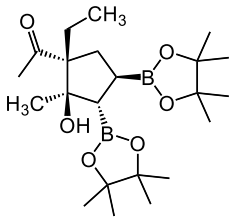
#	Time	Area	Height	Width	Area%	Symmetry
1	13.692	408.3	15.8	0.4317	41.808	0.495
2	15.275	78.1	3.7	0.3484	7.999	0.9
3	15.795	63.2	2.8	0.3713	6.474	0.828
4	17.049	426.9	11.5	0.6162	43.719	0.383

Enantioenriched material:



Note: Two peaks thought to result from a mixture of OBpin and free OH products, possibly in equilibrium. Peak persists after subjection to several silica gel columns. Please see vinyl boronic ester reactions for HPLC traces with a similar (but smaller) second peak. No enantiomer detected at 17 min.

1-((*1R,2R,3S,4R)*-1-ethyl-2-hydroxy-2-methyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)ethan-1-one (6b)



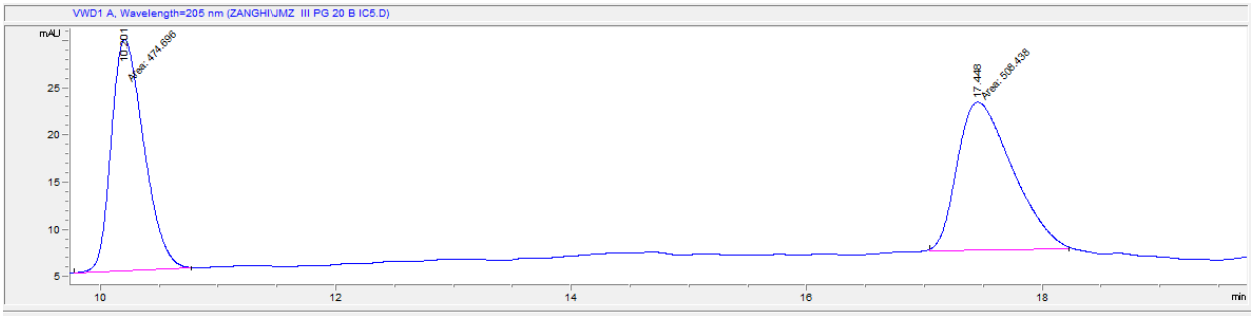
(6b)

This reaction was run using *(R)*-furyl-OMe-biphep. Silica gel chromatography (15:1 → 8:1 hex:EtOAc) provided **(6b)** as a white solid (17.8 mg, 42% yield, >20:1 dr, >99:1 er).

^{1}H NMR (600 MHz, $CDCl_3$): 2.48 (s, 1H); 2.20 (s, 3H); 2.17-2.13 (ddd, 14.6 Hz, 7.6 Hz, 1.8 Hz, 1H); 2.07-2.02 (ddd, 14.6 Hz, 8.9 Hz, 1.8 Hz, 1H); 1.92-1.89 (d, 12.5 Hz, 1H); 1.78-1.73 (dd, 14.0 Hz, 10.4 Hz, 1H); 1.63 (br s, 1H); 1.56-1.44 (m, 2H); 1.25 (s, 6H); 1.24 (s, 6H); 1.23 (s, 6H); 1.22 (s, 6H); 1.18 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): 213.7, 83.5, 83.3, 81.3, 66.2, 28.4, 27.8, 25.3, 25.0, 24.9, 24.7, 24.6, 24.1, 23.0, 9.0. **HRMS** (*m/z*): calcd for $C_{22}H_{39}B_2O_6^-$: 421.2938 ($M\text{-}H^+$); found: 421.2944. **IR** (ν/cm^{-1}): 2976 (s), 2359 (w), 2341 (w), 1698 (s),1471 (w), 1372 (s), 1319 (m), 1221 (m), 1146 (s), 971 (m), 860 (m). **$[\alpha]_D^{23}$** = — 13.4 ° (c = 0.92, CH_2Cl_2, l = 1 dm).

Diacel CHIRALPAK IC Column: 97:3 hexanes:iPrOH; 1.0 mL/min; 205 nm.

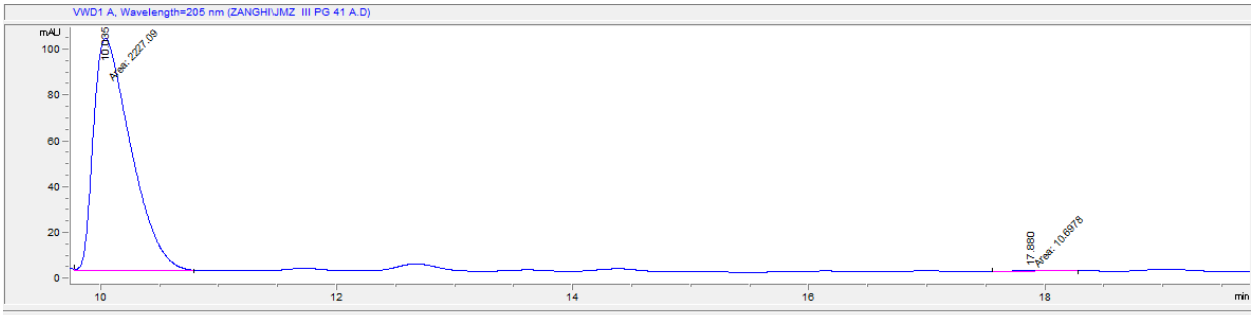
Racemic material:



File Information	
LC-File	JMZ III PG 20 B IC5.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	30-May-18, 14:53:31
Sample	JMZ III PG 20 B IC5
Sample Info	acyclic Et; 97:3 Hex:iPrOH; 1.0 mL/min; IC Column; 205 nm; 5 uL

#	Time	Area	Height	Width	Area%	Symmetry
1	10.201	474.7	24.5	0.3225	48.284	0.673
2	17.448	508.4	15.7	0.541	51.716	0.577

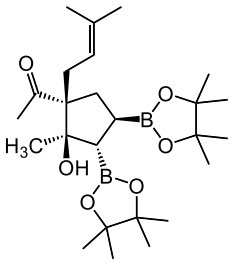
Enantioenriched material:



File Information	
LC-File	JMZ III PG 41 A.D
File Path	C:\CHEM32\1\DATA\ZANGHI\
Date	30-May-18, 15:37:28
Sample	JMZ III PG 41 A
Sample Info	acyclic Et; 97:3 Hex:iPrOH; 1.0 mL/min; IC Column; 205 nm; 5 uL

#	Time	Area	Height	Width	Area%	Symmetry
1	10.035	2227.1	101.4	0.3662	99.522	0.451
2	17.88	10.7	5E-1	0.3594	0.478	1.03

1-((*1S,2R,3S,4R*)-2-hydroxy-2-methyl-1-(3-methylbut-2-en-1-yl)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)ethan-1-one (6c)



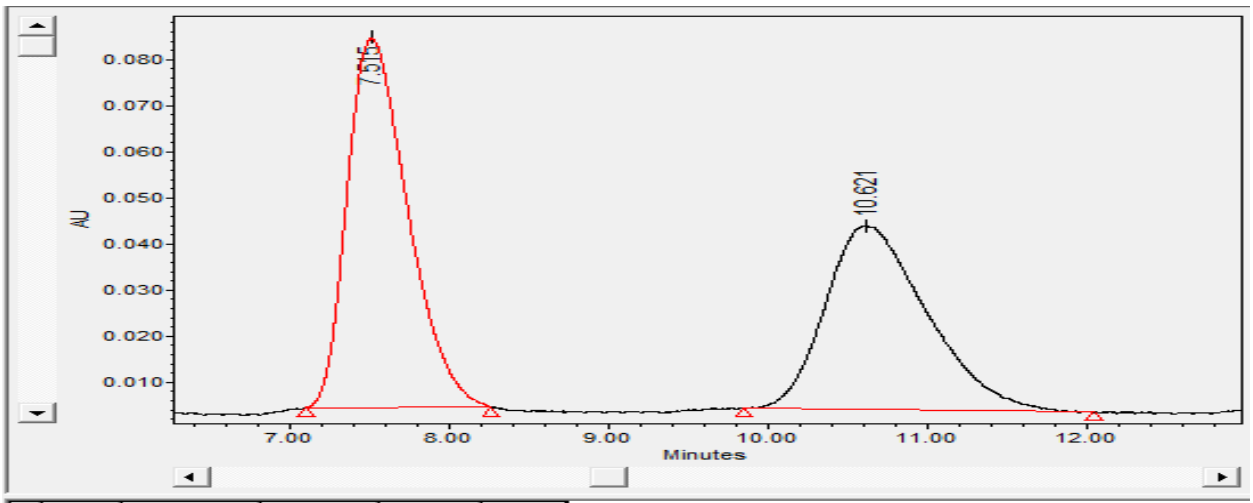
(6c)

This reaction was run using *(R)*-furyl-OMe-biphep. Silica gel chromatography (100% DCM → 99:1 DCM:*i*-PrOH) provided **(6c)** as a clear, colorless oil (22.2 mg, 48% yield, 17:1 dr, >99:1 er).

^{1}H NMR (400 MHz, $CDCl_3$): 4.82 (maj. diast., t, 7.6 Hz, 1H); 4.77 (min. diast., t, 7.6 Hz, 0.06H); 2.79-2.74 (dd, 14.7 Hz, 6.6 Hz, 1H); 2.53 (s, 1H); 2.26-2.16 (m, 1H); 2.18 (s, 3H); 2.11-1.95 (m, 3H); 1.75-1.67 (m, 2H); 1.64 (s, 3H); 1.60 (s, 3H); 1.58-1.52 (m, 1H); 1.25-1.20 (m, 24H); 1.18 (s, 3H). **^{13}C NMR** (214 MHz, $CDCl_3$): 213.5, 134.8, 119.7, 83.5, 83.3, 81.4, 65.8, 55.2, 29.6, 29.5, 28.0, 26.1, 25.3, 24.9, 24.7, 24.6, 24.1, 18.2. **HRMS** (*m/z*): calcd for $C_{25}H_{43}B_2O_6^-$: 461.3251 ($M\text{-}H^+$); found: 461.3262. **IR** (ν/cm^{-1}): 2978 (s), 2929 (m), 2360 (w), 2341 (w), 1698 (s), 1407 (m), 1372 (s), 1319 (s), 1216 (m), 1146 (s), 971 (m), 854 (m). **$[\alpha]_D^{23}$** = — 12.0 ° (c = 1.02, CH_2Cl_2, l = 1 dm).

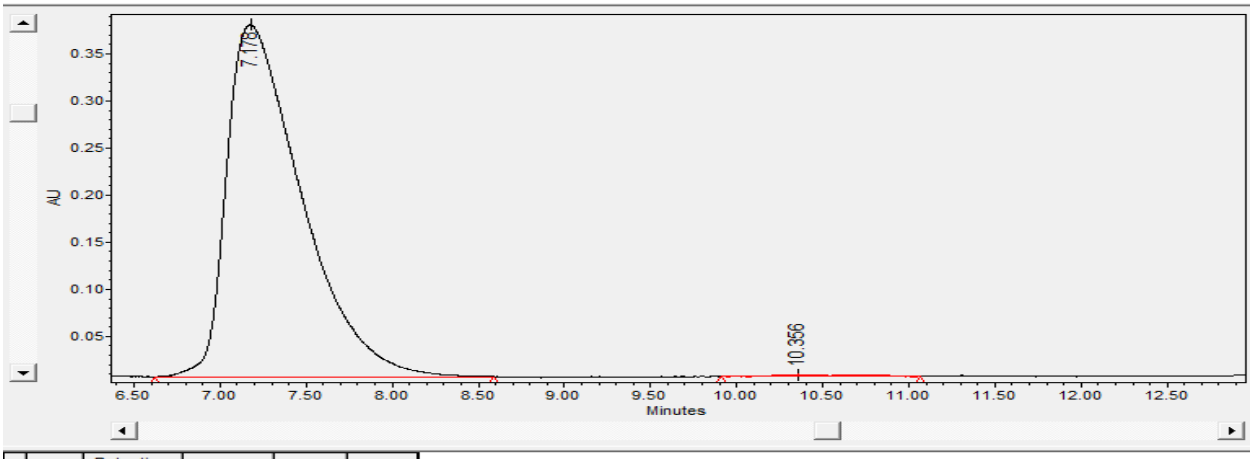
Phenomenex Lux Amylose-1 AD Column: 98:2 CO_2:iPrOH; 1.0 mL/min; 210 nm.

Racemic material:

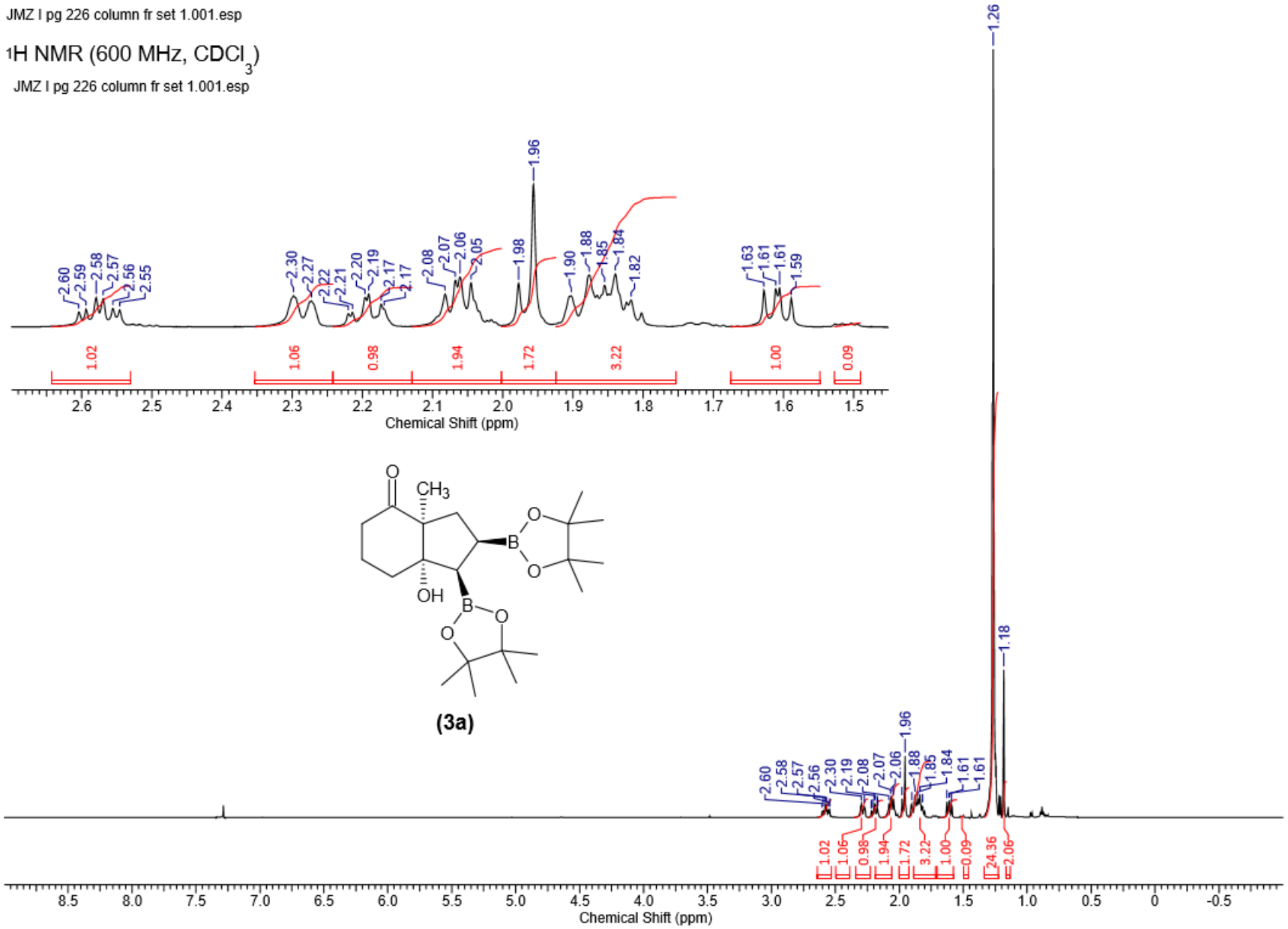


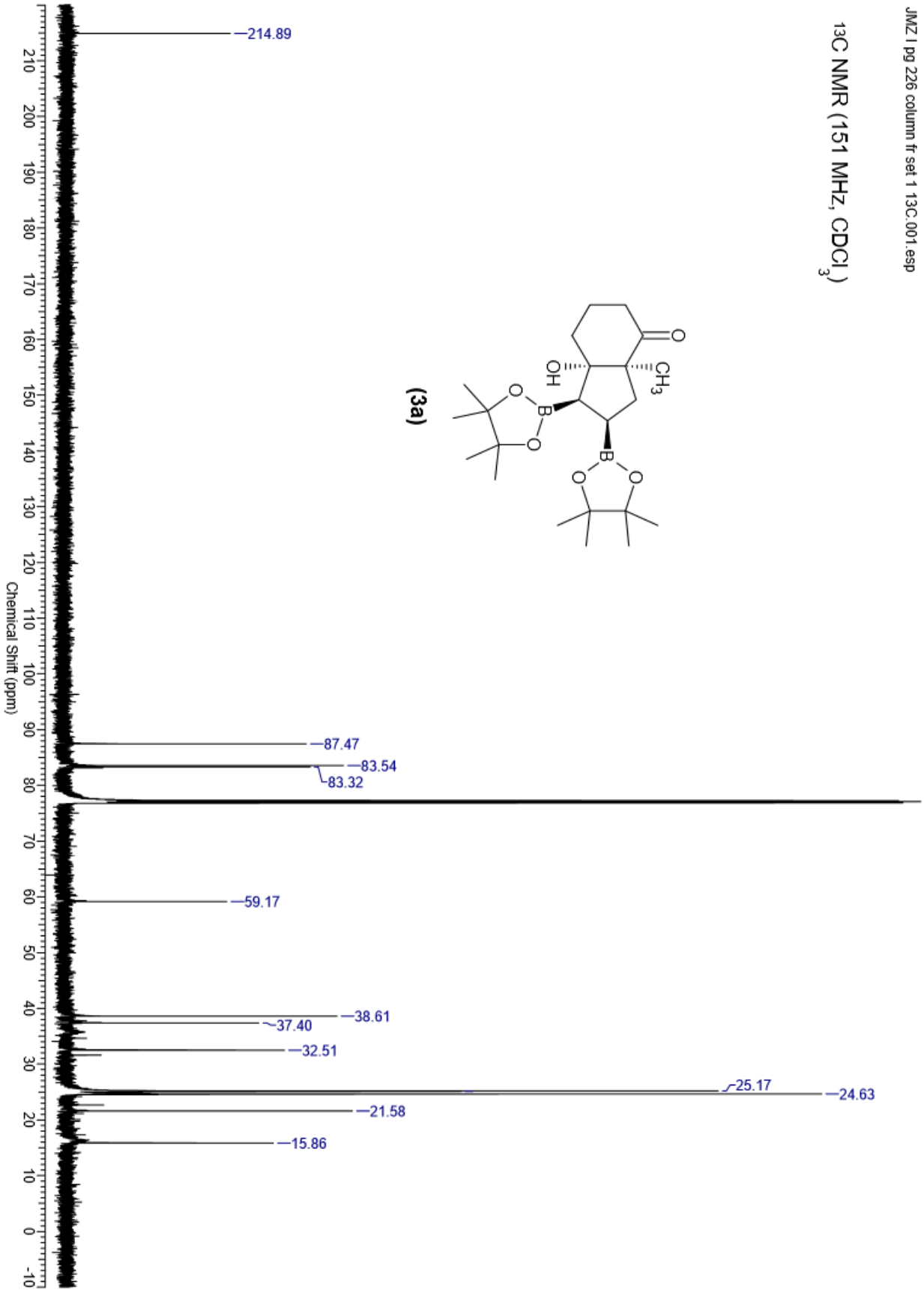
	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)
1		7.515	2116377	54.52	80202
2		10.621	1765675	45.48	39931

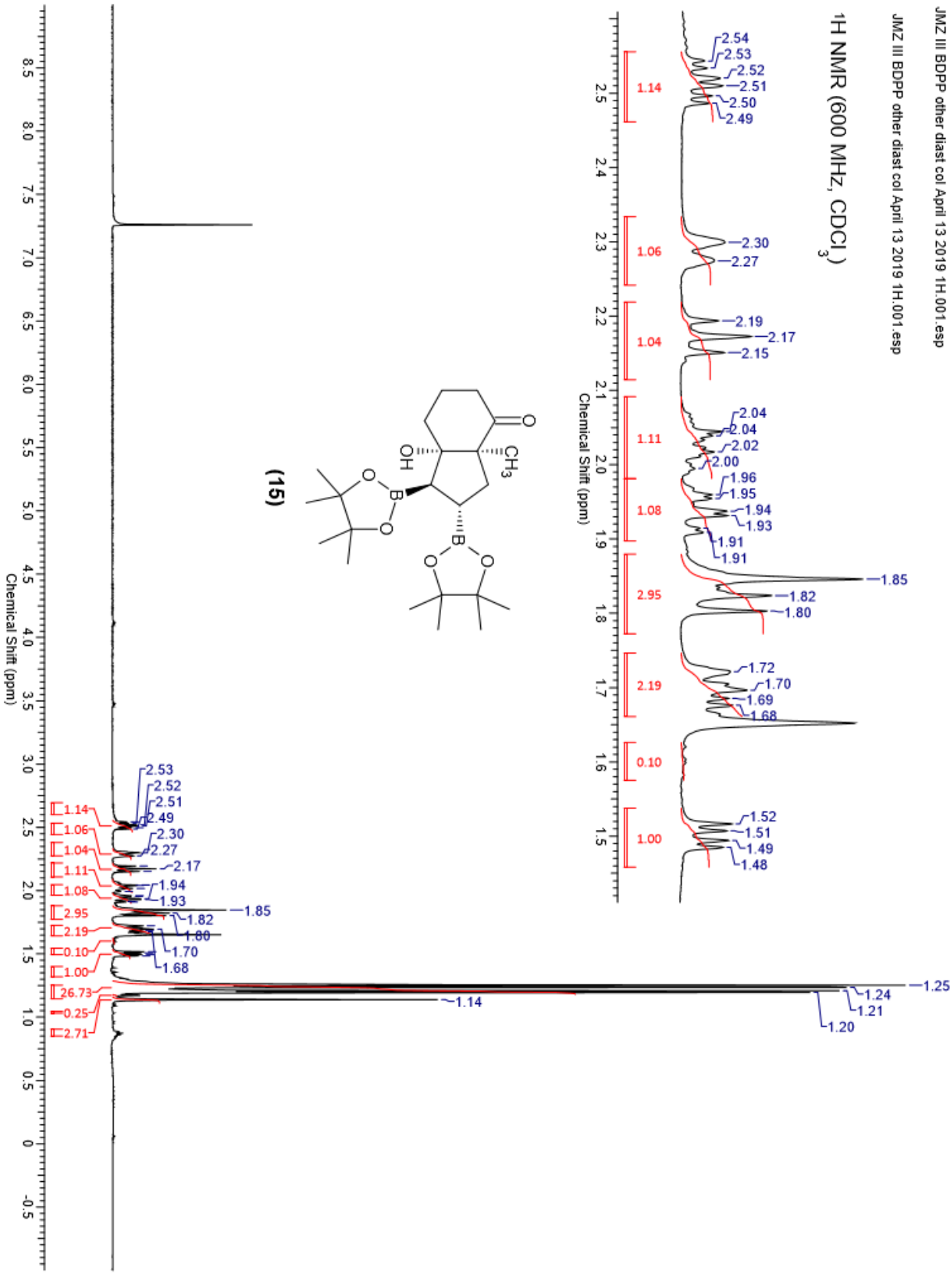
Enantioenriched material:



	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)
1		7.178	11304741	99.37	373935
2		10.356	71262	0.63	2234

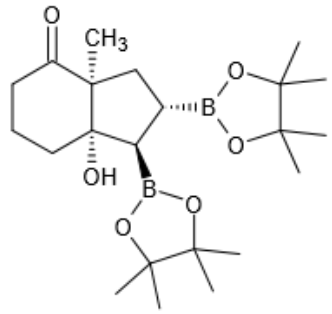

JMZ I pg 226 column fr set 1.001.esp
1H NMR (600 MHz, CDCl3)
JMZ I pg 226 column fr set 1.001.esp
Chemical Shift (ppm)
(3a)
Chemical Shift (ppm)


JMZ I pg 226 column fr set 1 13C.001.esp
13C NMR (151 MHz, CDCl3)
(3a)
OH
CH3
B
B
O
O
O
O
O
O
214.89
87.47
83.54
83.32
59.17
38.61
37.40
32.51
25.17
24.63
21.58
15.86
Chemical Shift (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

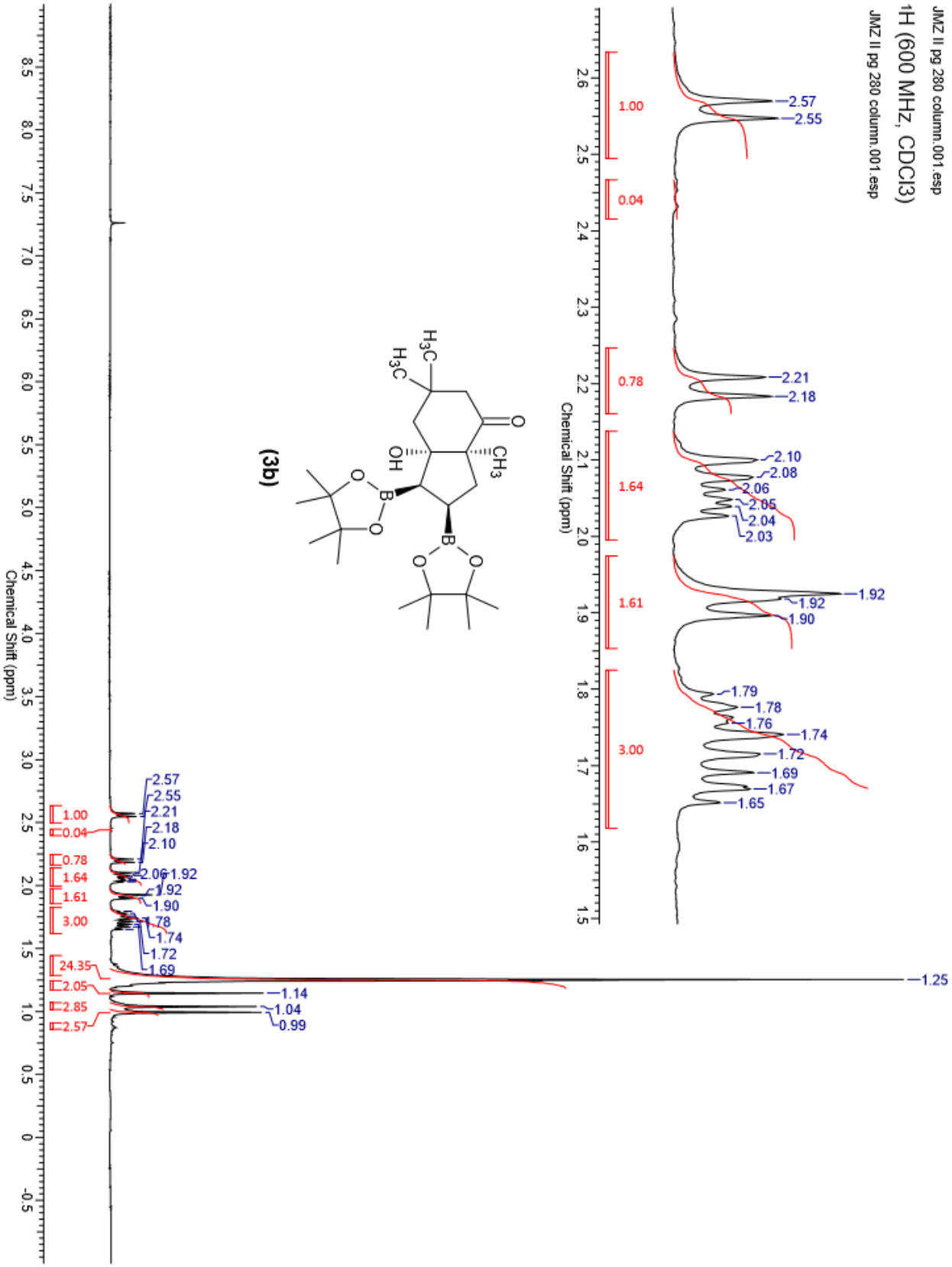

JMZ III BDPP other diast col April 13 2019 1H.001.esp
JMZ III BDPP other diast col April 13 2019 1H.001.esp
1H NMR (600 MHz, CDCl3)
(15)
Chemical Shift (ppm)
Chemical Shift (ppm)

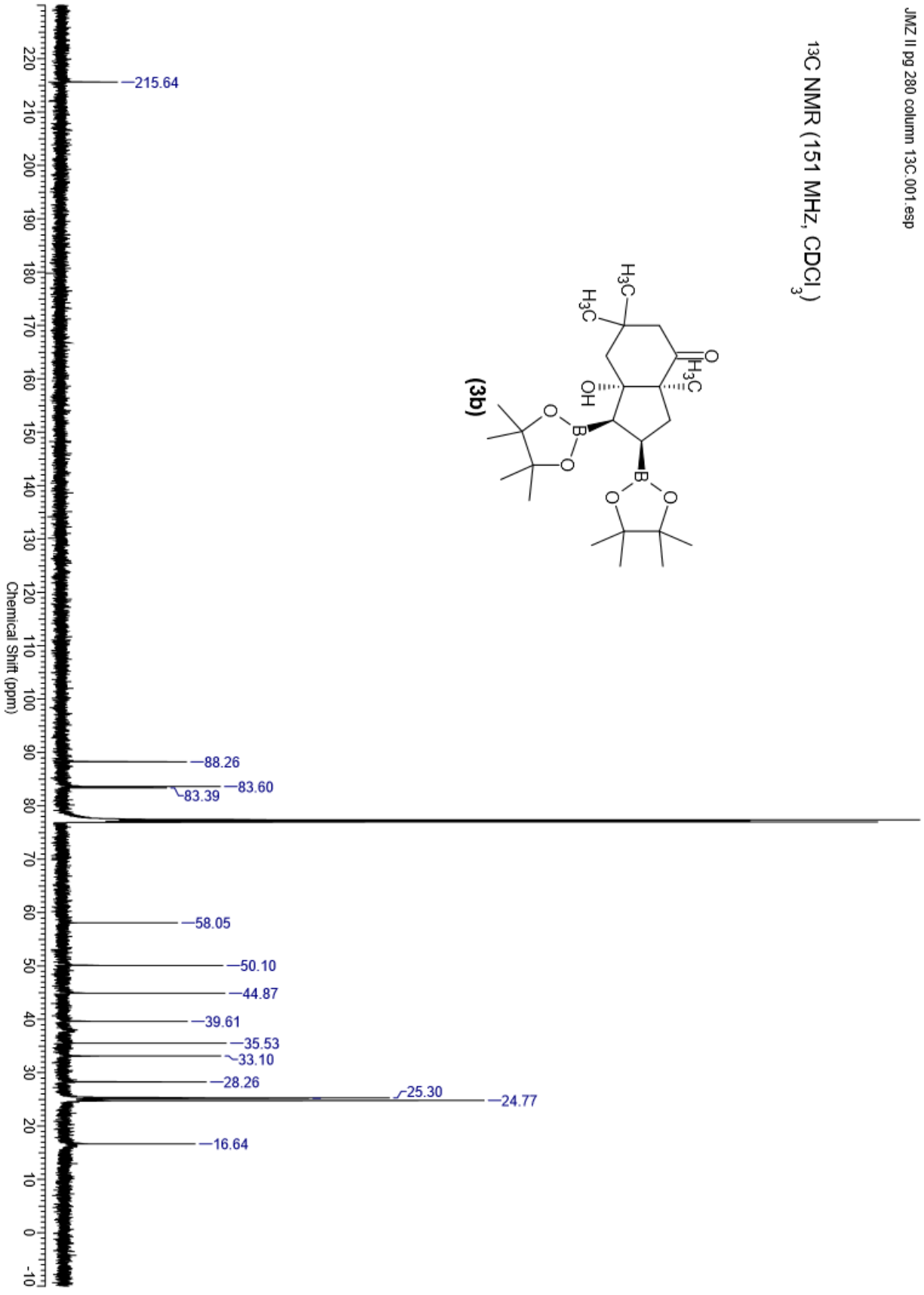
JMZ III BDPP other diast col April 13 2019 13C.001.esp

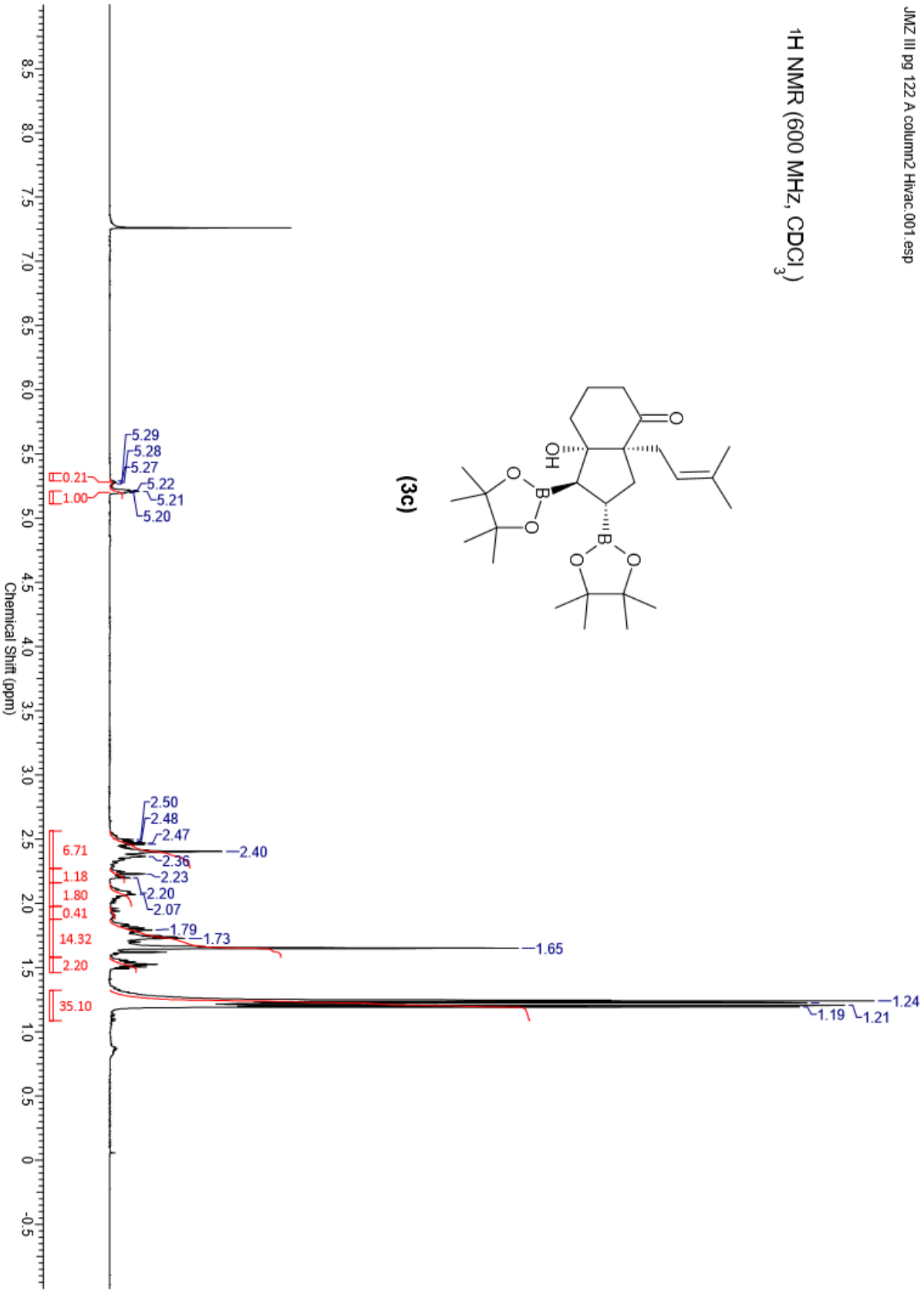
^{13}C NMR (151 MHz, $CDCl_3$)

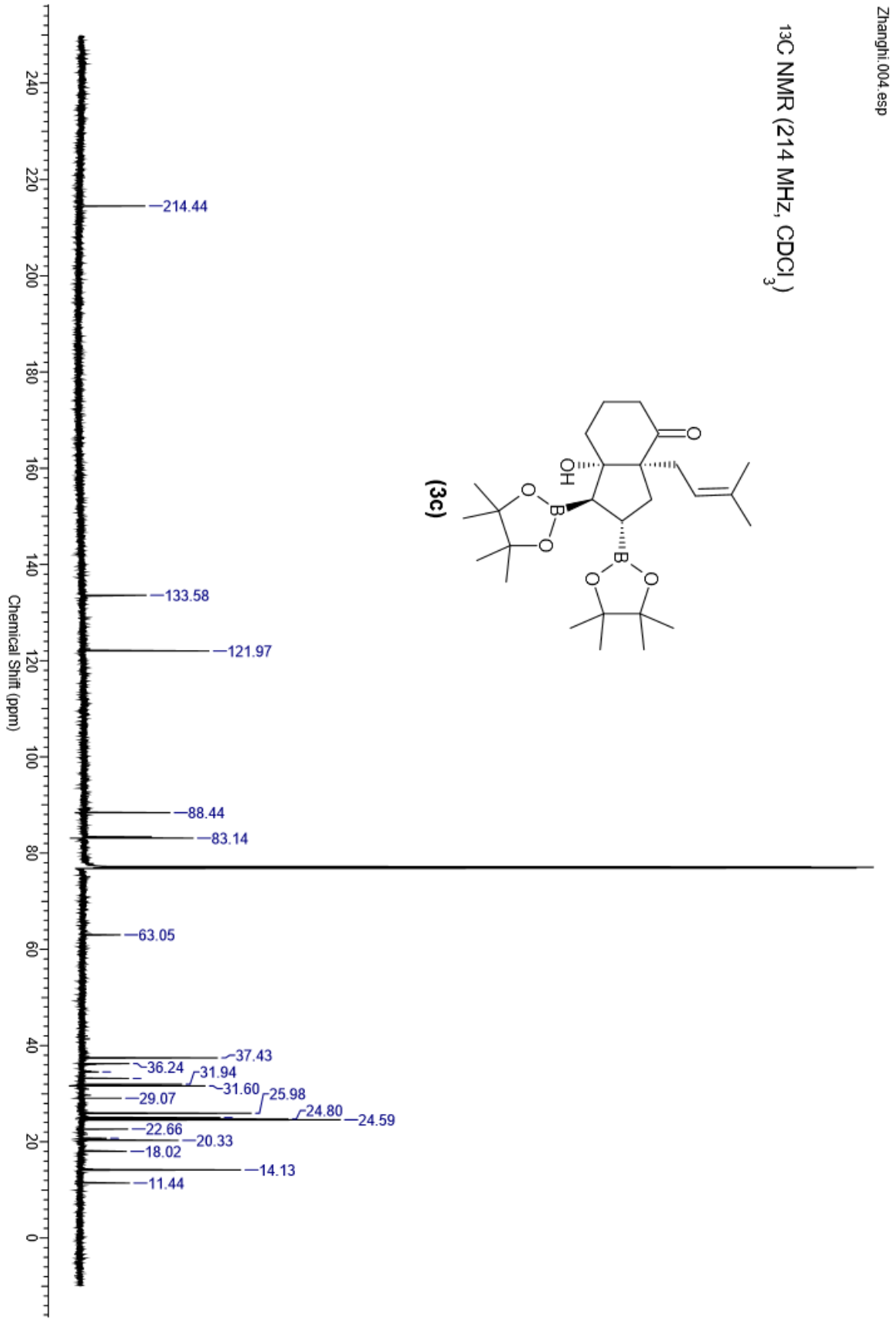


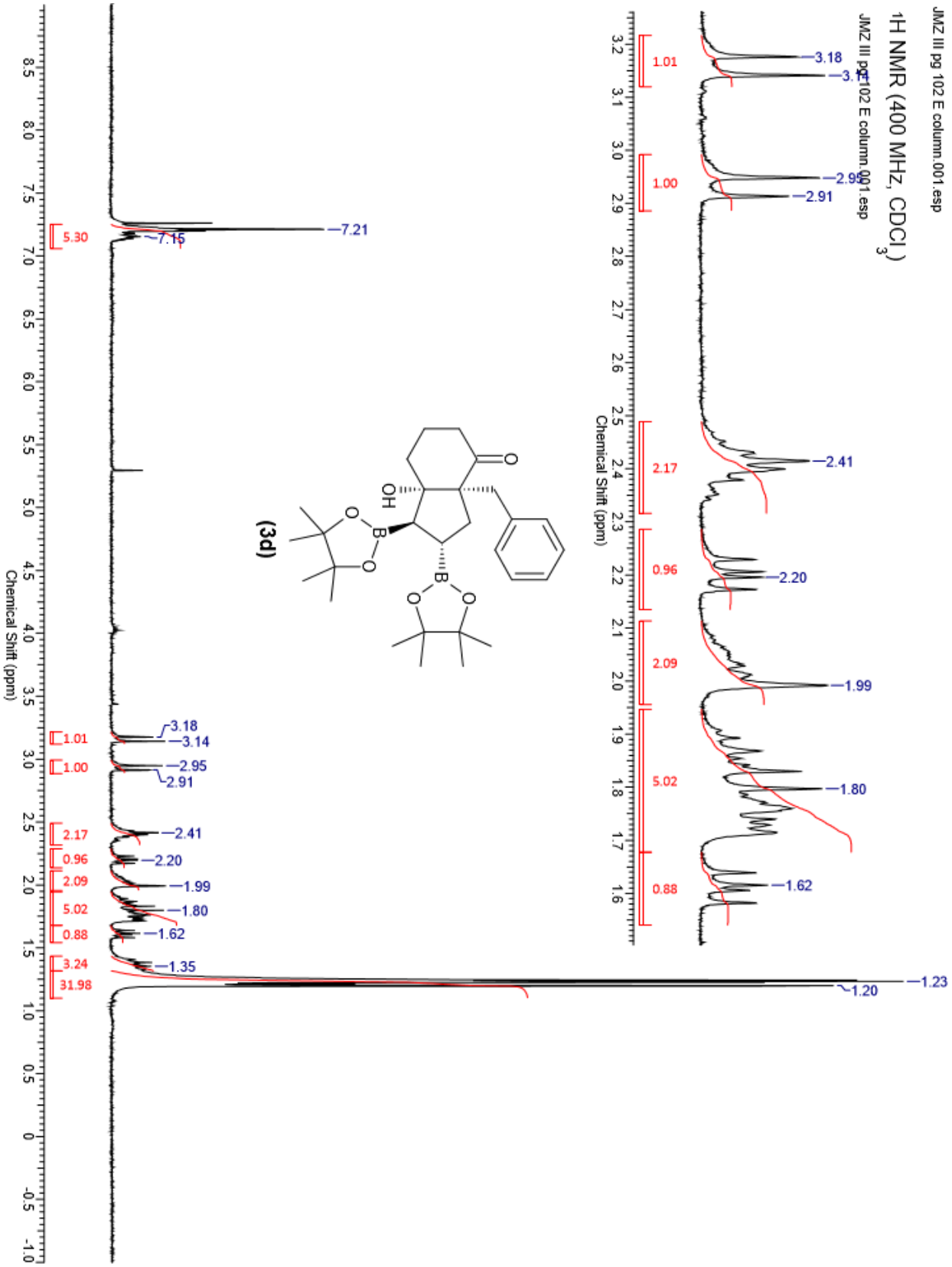
(15)

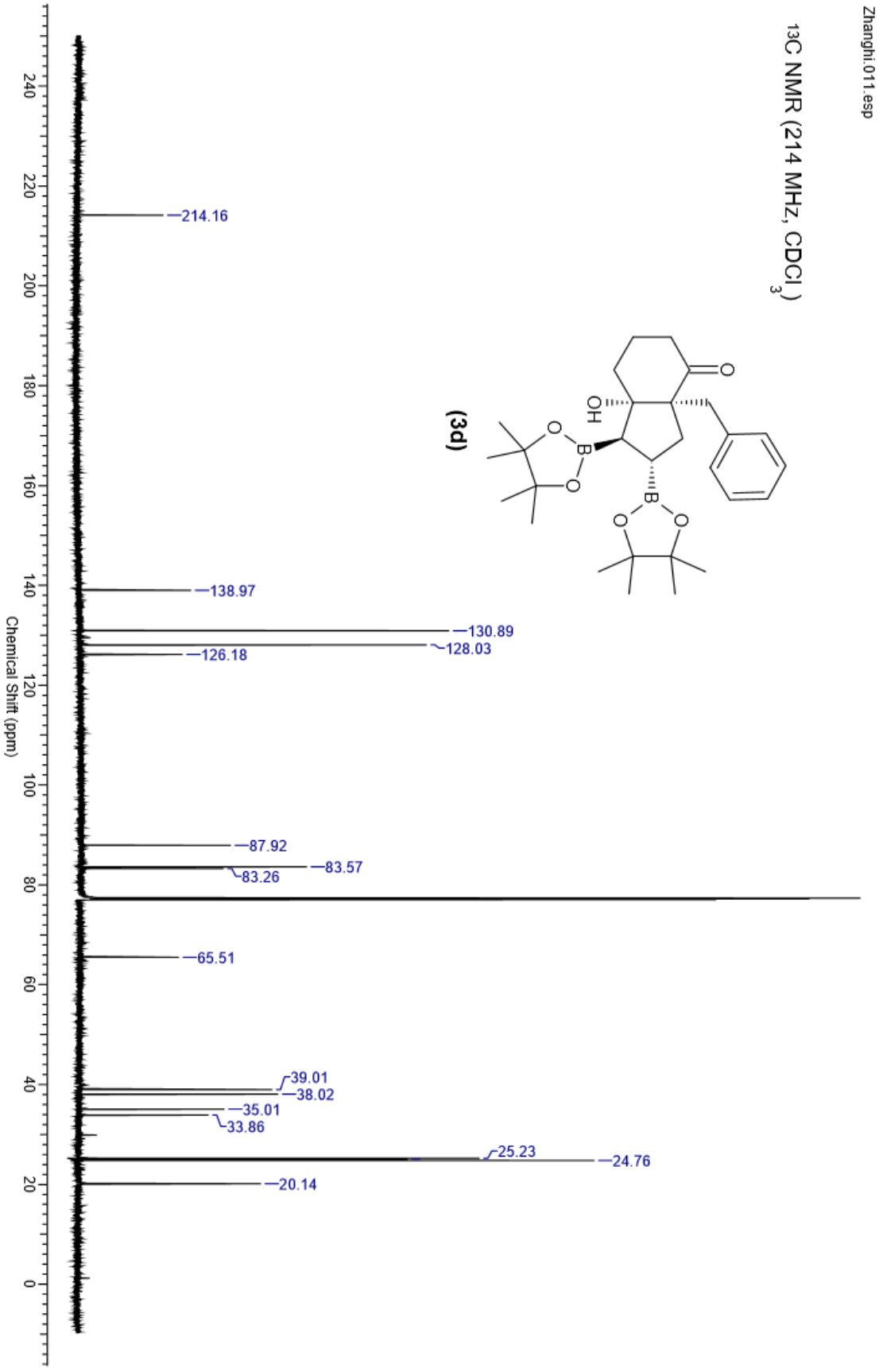

JMZ II pg 280 column.001.esp
1H (600 MHz, CDCl3)
JMZ II pg 280 column.001.esp
(3b)
Chemical Shift (ppm)
Chemical Shift (ppm)

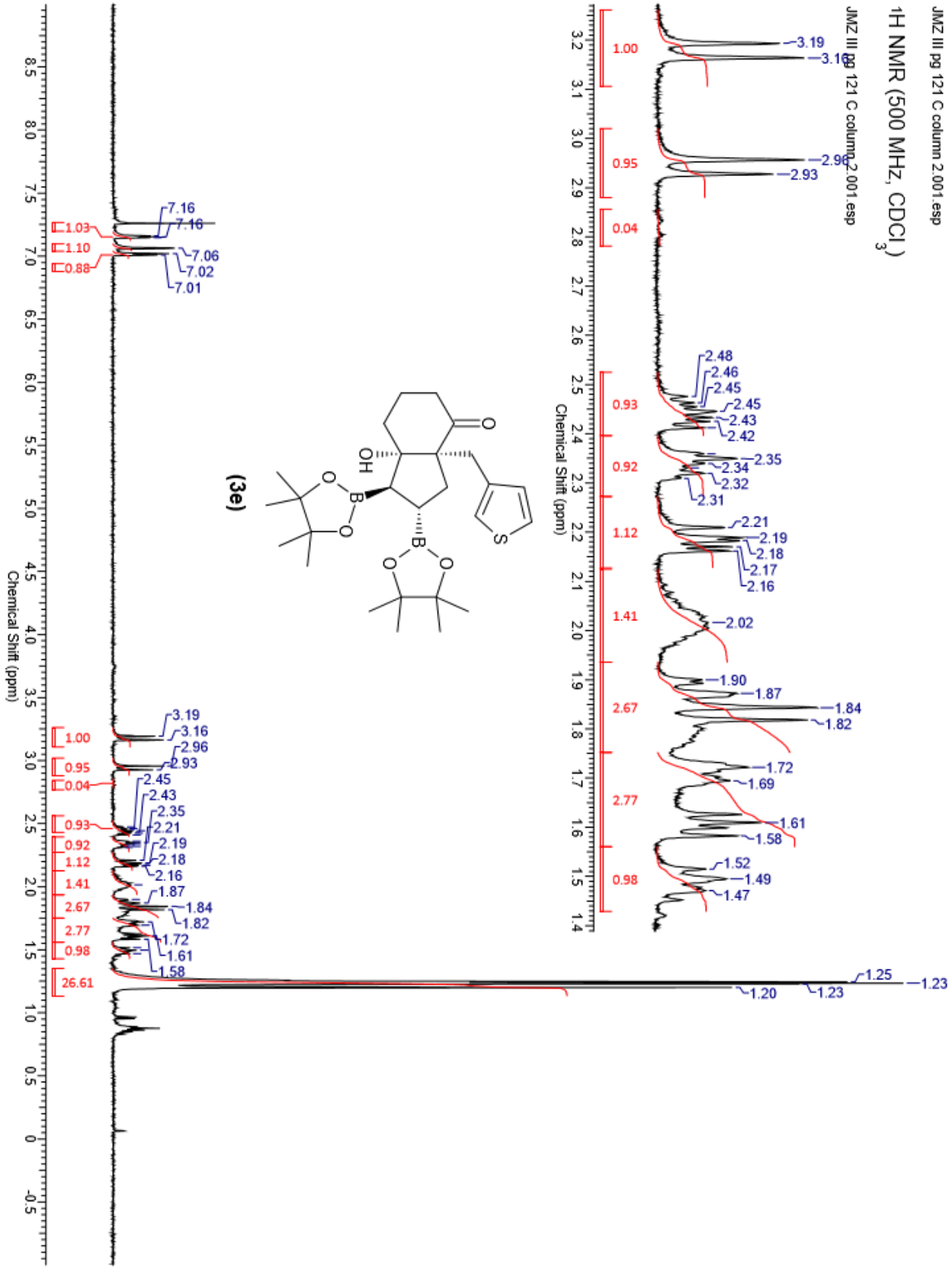

JMZ II pg 280 column 13C.001.esp
13C NMR (151 MHz, CDCl3)
(3b)
H3C
H3C
OH
O
H3C
B
B
O
O
O
O
Chemical Shift (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
215.64
88.26
83.60
83.39
58.05
50.10
44.87
39.61
35.53
33.10
28.26
25.30
24.77
16.64

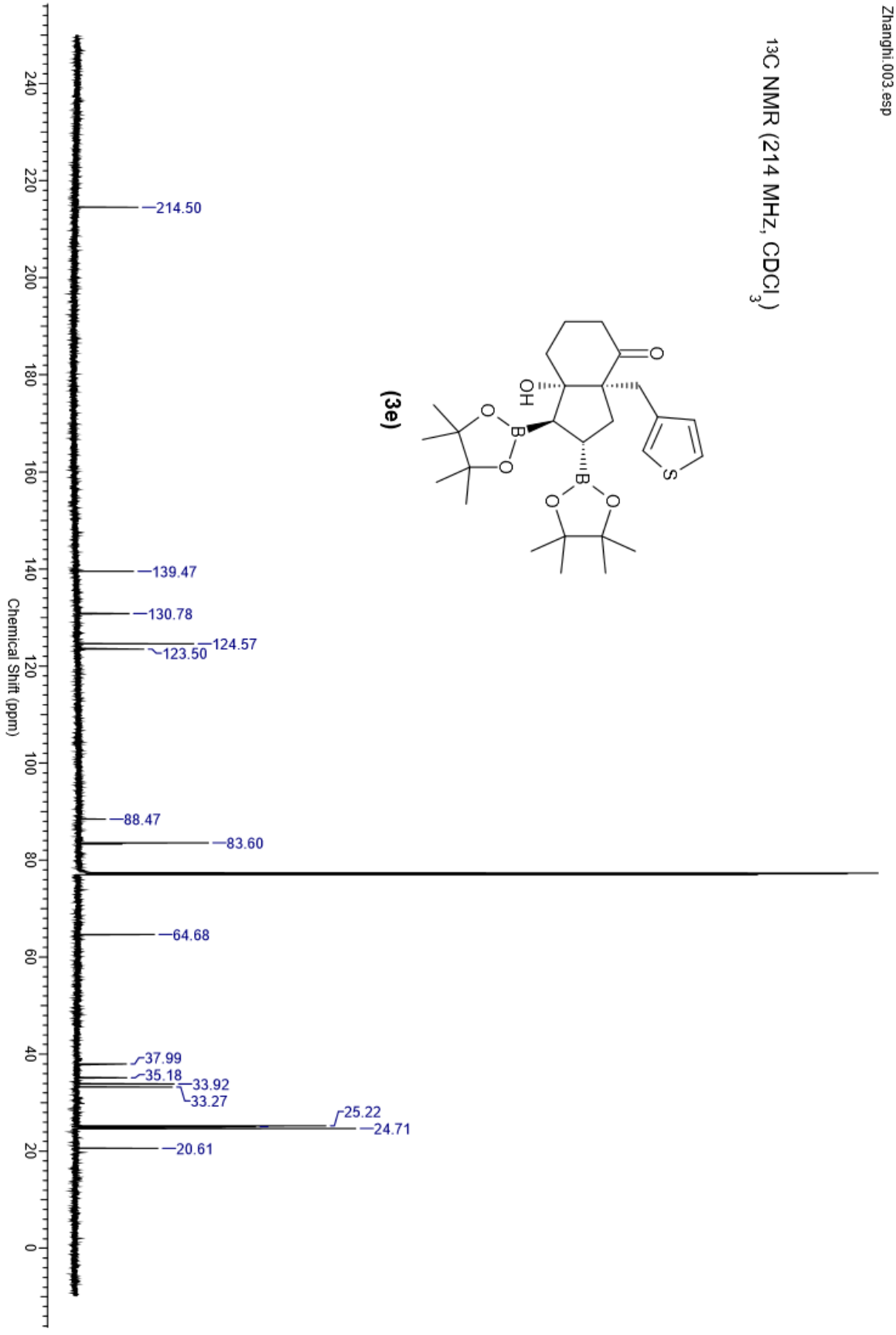

JMZ III pg 122 A column2 Hivac.001.esp
^{1}H NMR (600 MHz, $CDCl_3$)
(3c)
OH
B
B
O
O
O
O
O
O
Chemical Shift (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
5.29
5.28
5.27
5.22
5.21
5.20
0.21
1.00
2.50
2.48
2.47
2.40
2.36
2.23
2.20
2.07
1.79
1.73
1.65
1.24
1.19
1.21
6.71
1.18
1.80
0.41
14.32
2.20
35.10

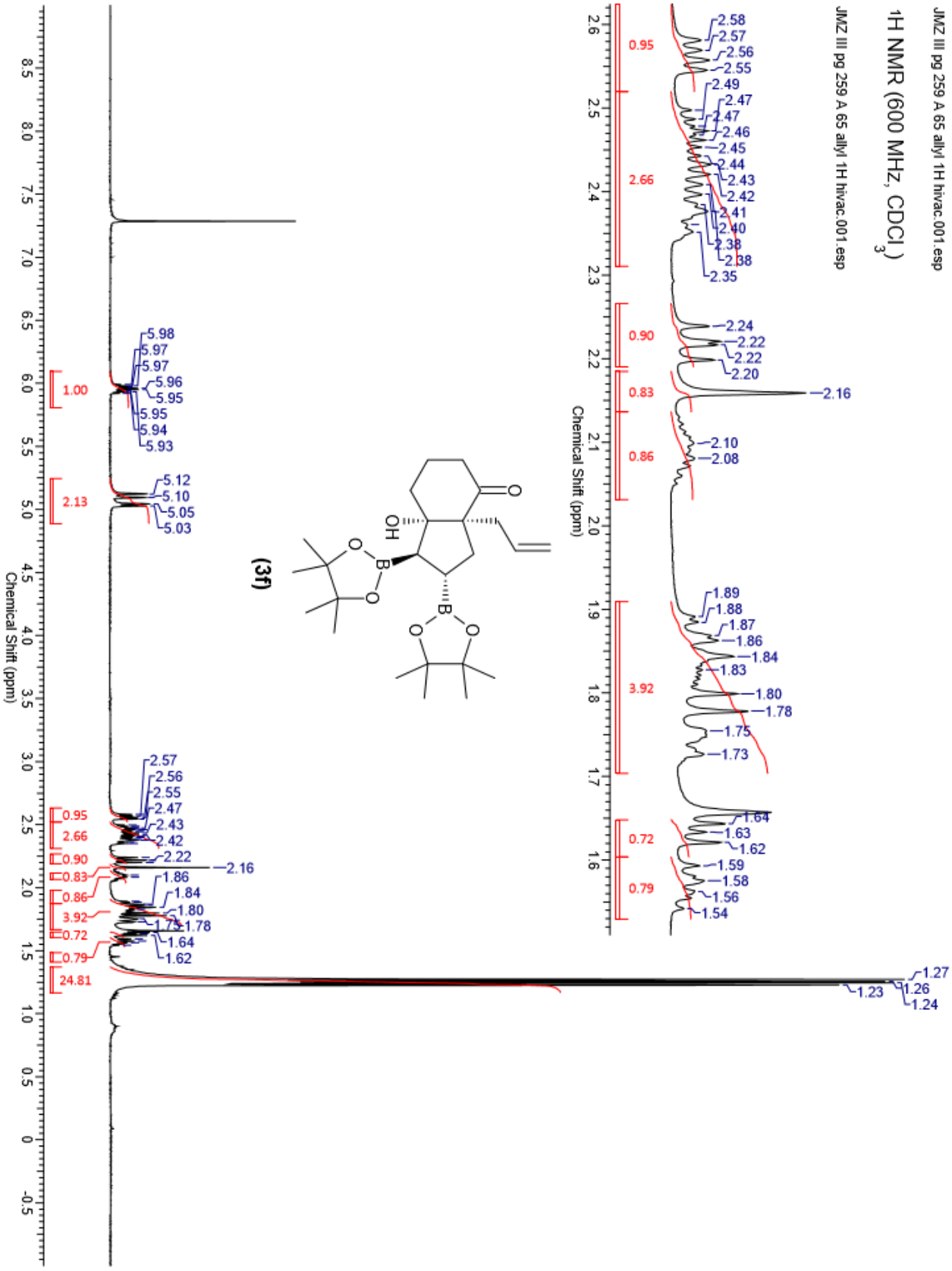

Zhanghi.004.esp
^{13}C NMR (214 MHz, $CDCl_3$)
(3c)
OH
B
B
O
O
O
O
O
Chemical Shift (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0
214.44
133.58
121.97
88.44
83.14
63.05
37.43
36.24
31.94
31.60
29.07
25.98
24.80
24.59
22.66
20.33
18.02
14.13
11.44

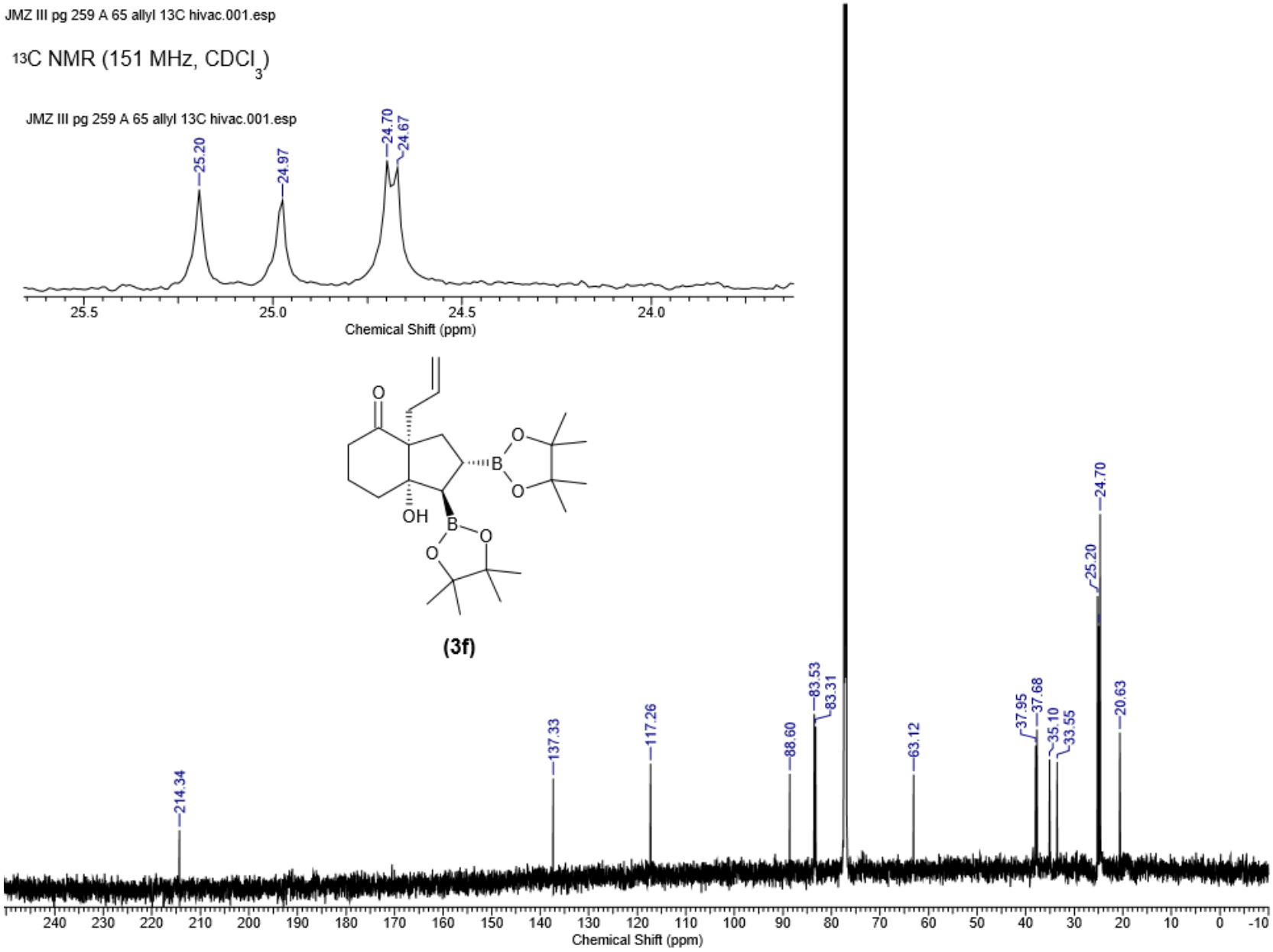

JMZ III pg 102 E column.001.esp
1H NMR (400 MHz, CDCl3)
JMZ III pg102 E column.001.esp
(3d)
Chemical Shift (ppm)
Chemical Shift (ppm)
7.21
7.15
5.30
3.18
3.14
2.95
2.91
2.41
2.20
1.99
1.80
1.62
1.35
1.23
1.20
1.01
1.00
2.17
0.96
2.09
5.02
0.88
3.24
31.98

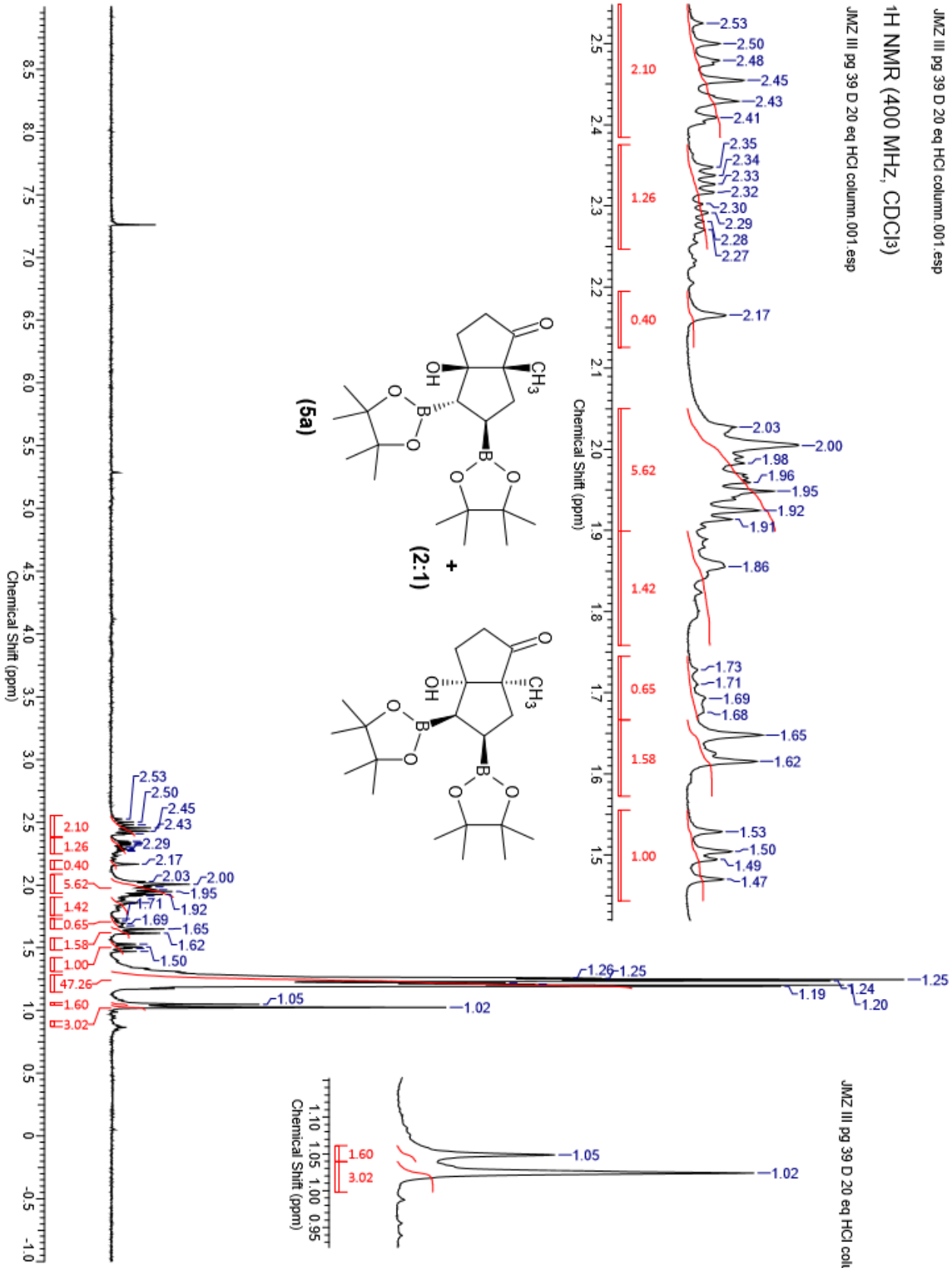

Zhanghi.011.esp
13C NMR (214 MHz, CDCl3)
(3d)
OH
O
B
O
O
B
O
O
214.16
138.97
130.89
128.03
126.18
87.92
83.57
83.26
65.51
39.01
38.02
35.01
33.86
25.23
24.76
20.14
Chemical Shift (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0


JMZ III pg 121 C column 2.001.esp
1H NMR (500 MHz, CDCl3)
JMZ III pg 121 C column 2.001.esp
(3e)
Chemical Shift (ppm)
Chemical Shift (ppm)


Zhanghi.003.esp
^{13}C NMR (214 MHz, CDCl$_3$)
(3e)
OH
O
B
O
O
B
O
O
S
214.50
139.47
130.78
124.57
123.50
88.47
83.60
64.68
37.99
35.18
33.92
33.27
25.22
24.71
20.61
Chemical Shift (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0

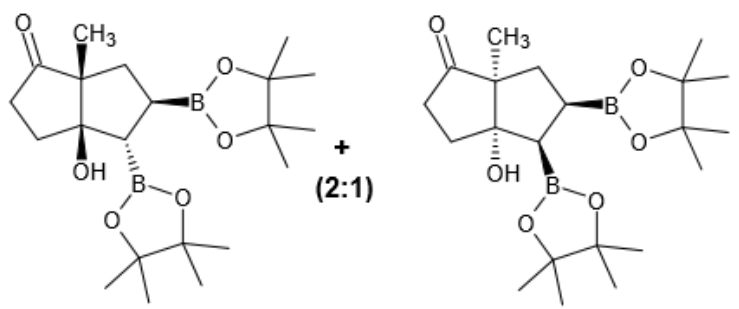

JMZ III pg 259 A 65 allyl 1H hivac.001.esp
1H NMR (600 MHz, CDCl3)
JMZ III pg 259 A 65 allyl 1H hivac.001.esp
(3f)
Chemical Shift (ppm)
Chemical Shift (ppm)


JMZ III pg 259 A 65 allyl 13C hivac.001.esp
13C NMR (151 MHz, CDCl3)
JMZ III pg 259 A 65 allyl 13C hivac.001.esp
25.20
24.97
24.70
24.67
25.5
25.0
24.5
24.0
Chemical Shift (ppm)
O
OH
B
O
O
B
O
O
(3f)
214.34
137.33
117.26
88.60
83.53
83.31
63.12
37.95
37.68
35.10
33.55
24.70
25.20
20.63
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

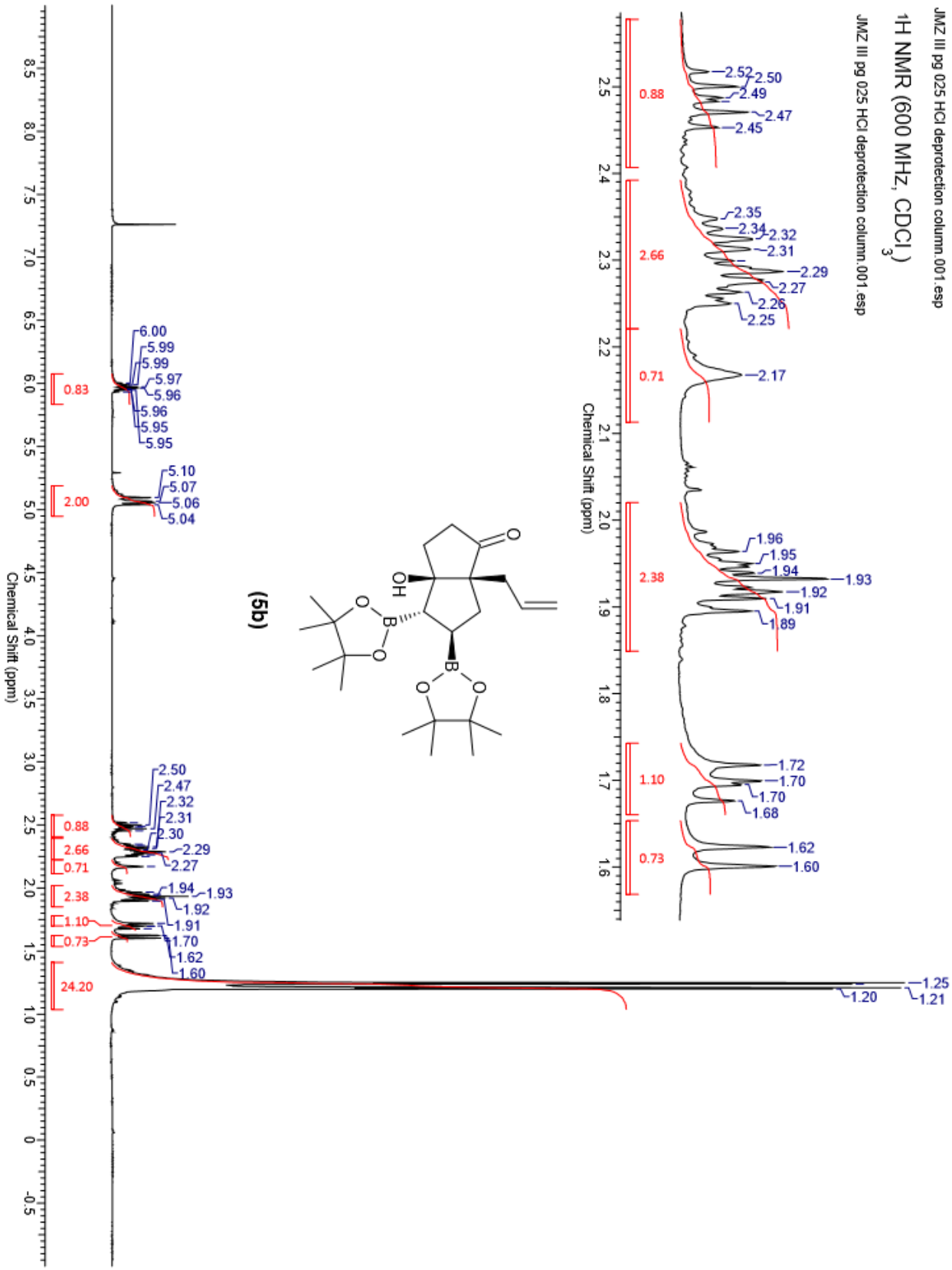

JMZ III pg 39 D 20 eq HCl column.001.esp
1H NMR (400 MHz, CDCl3)
JMZ III pg 39 D 20 eq HCl column.001.esp
(5a)
(2:1)
+
Chemical Shift (ppm)
JMZ III pg 39 D 20 eq HCl colu

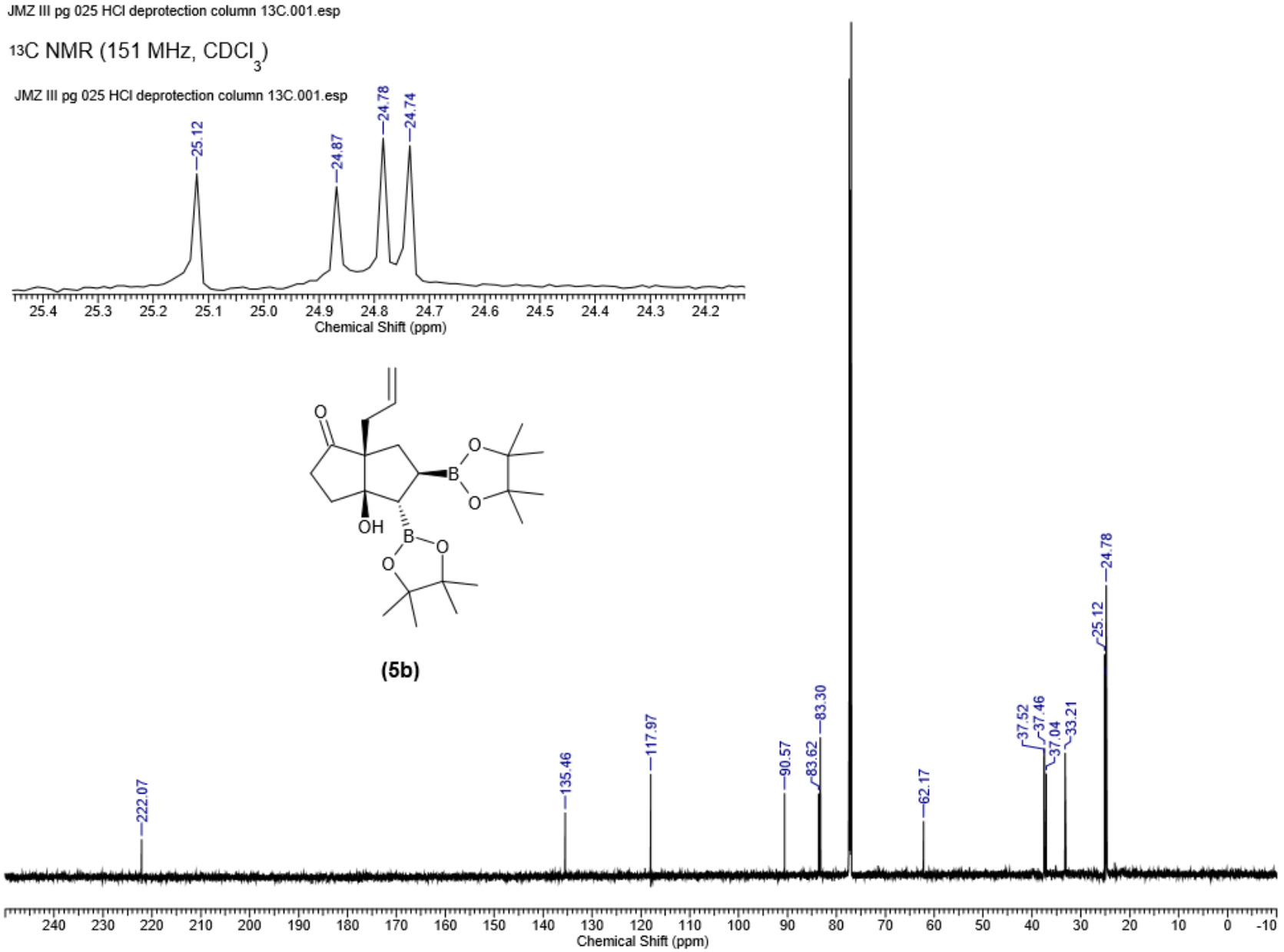
Zhanghi.001.esp

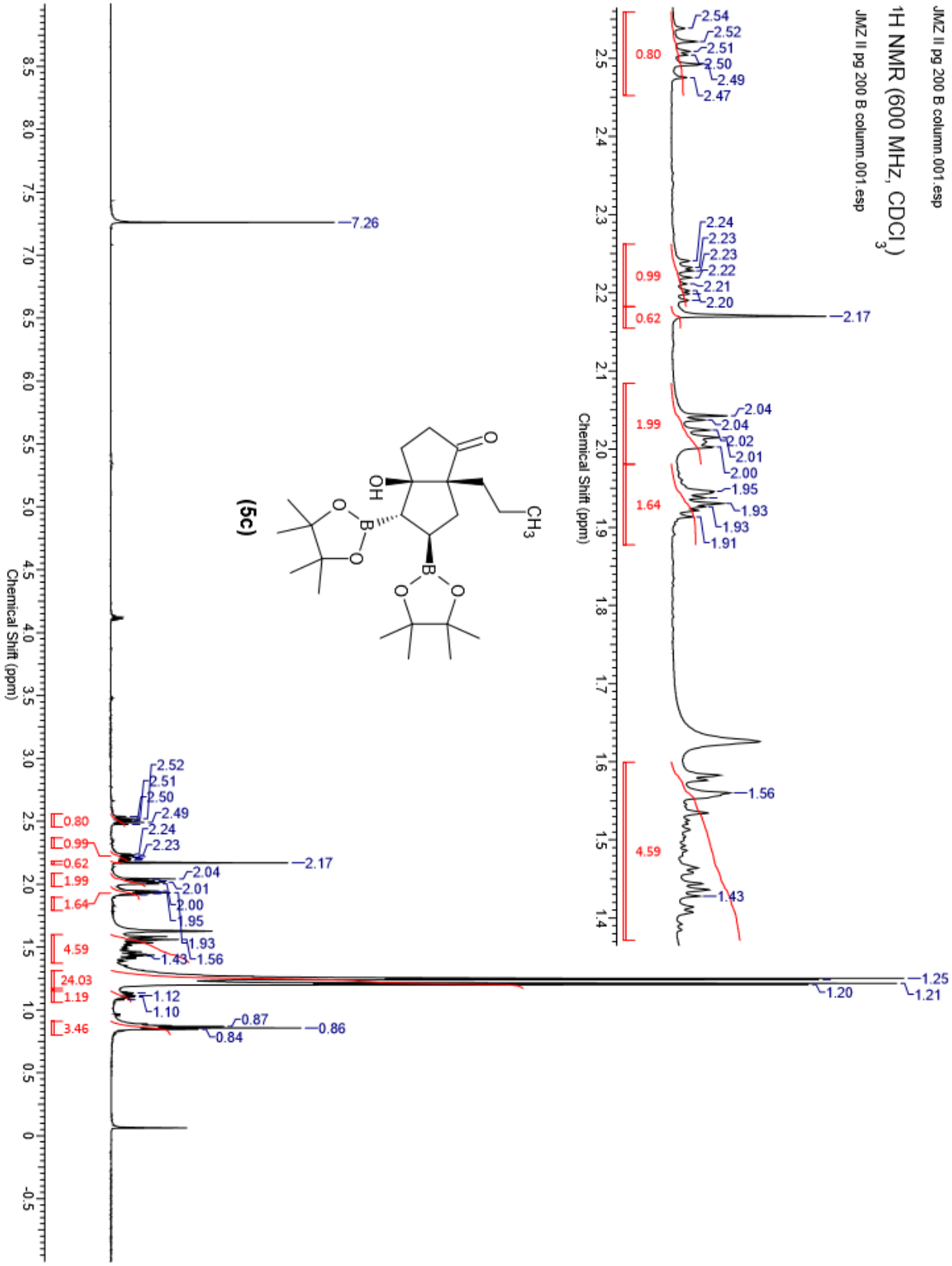
^{13}C NMR (214 MHz, $CDCl_3$)

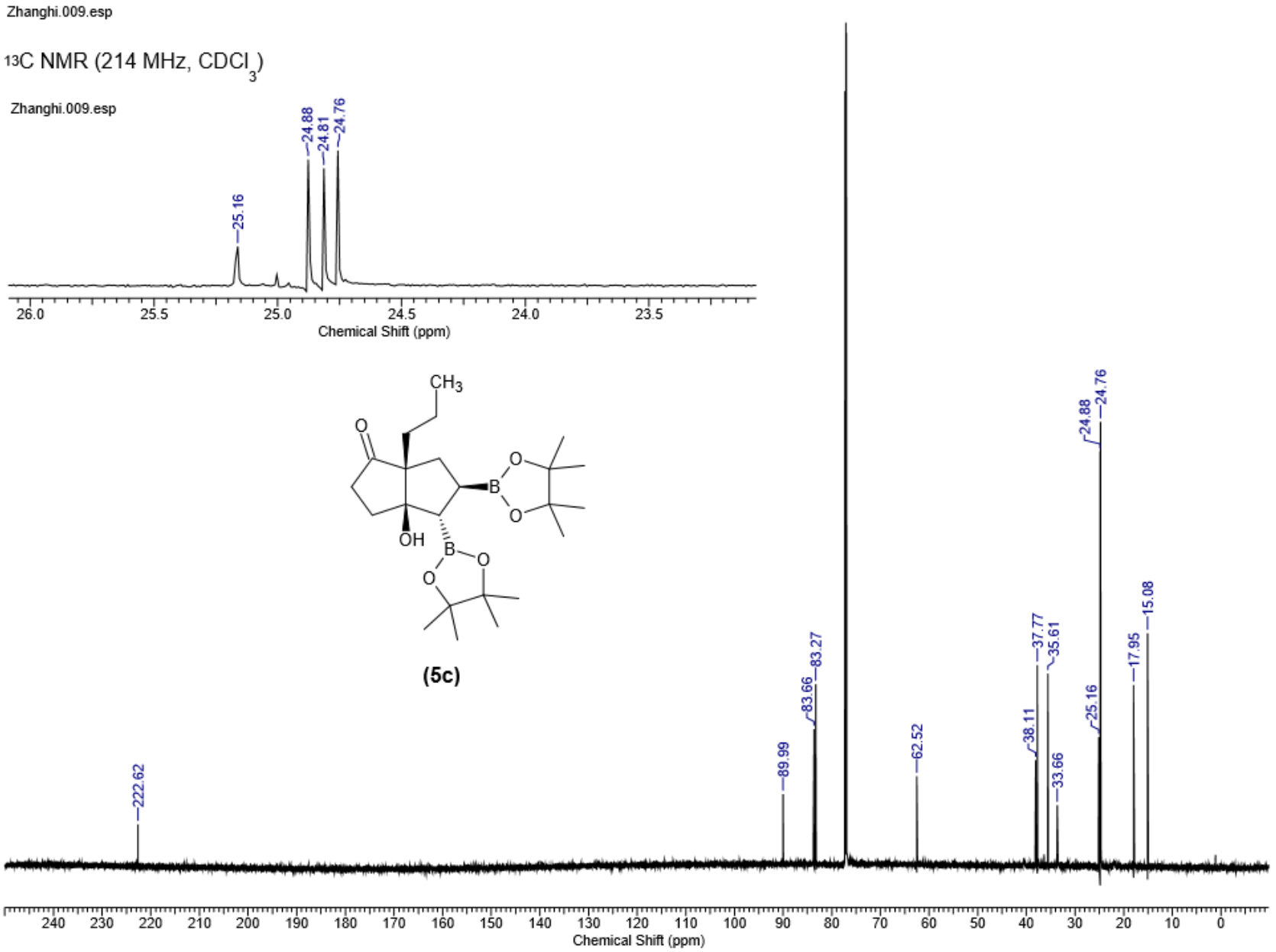


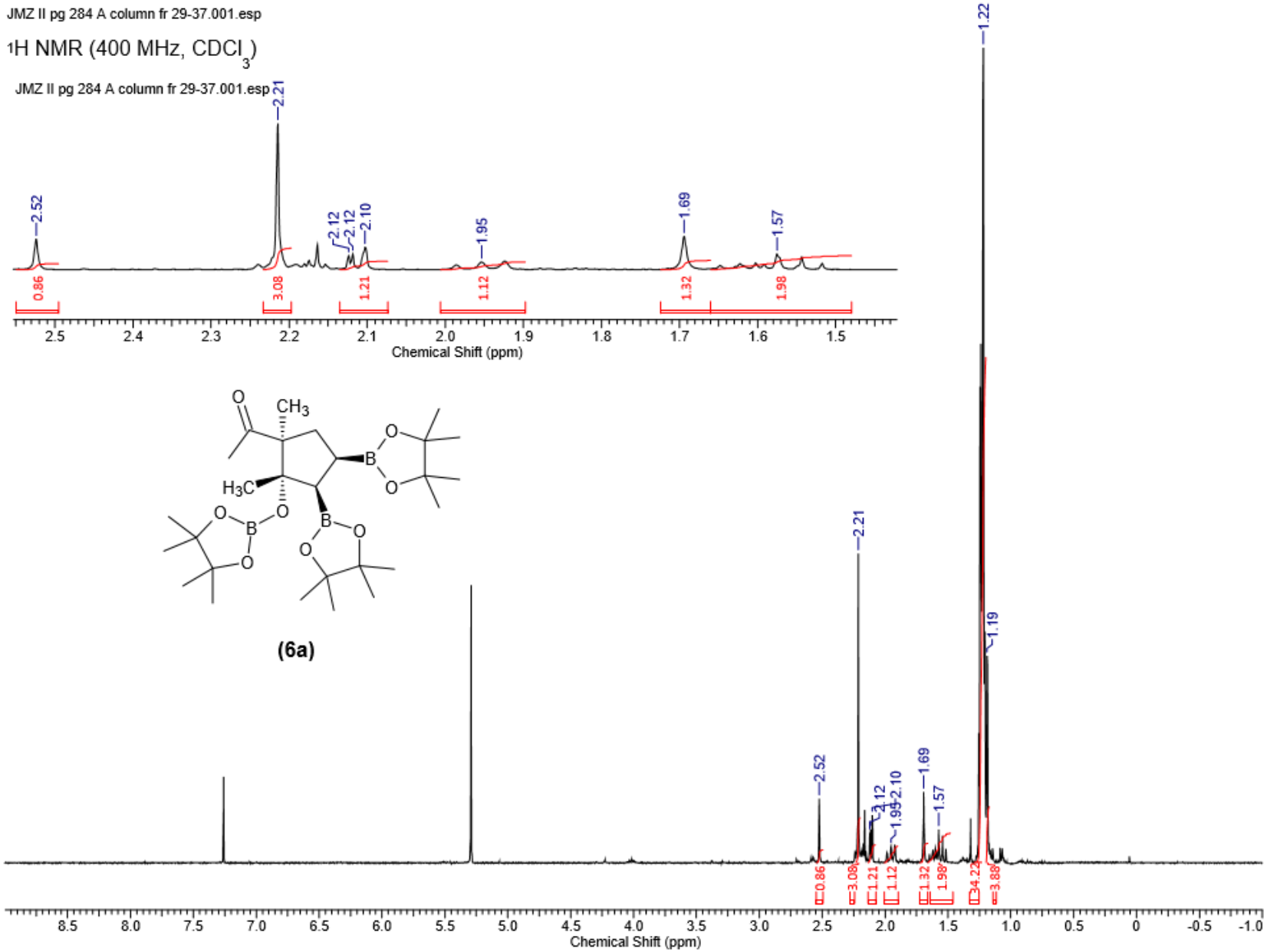
(5a) + (2:1)

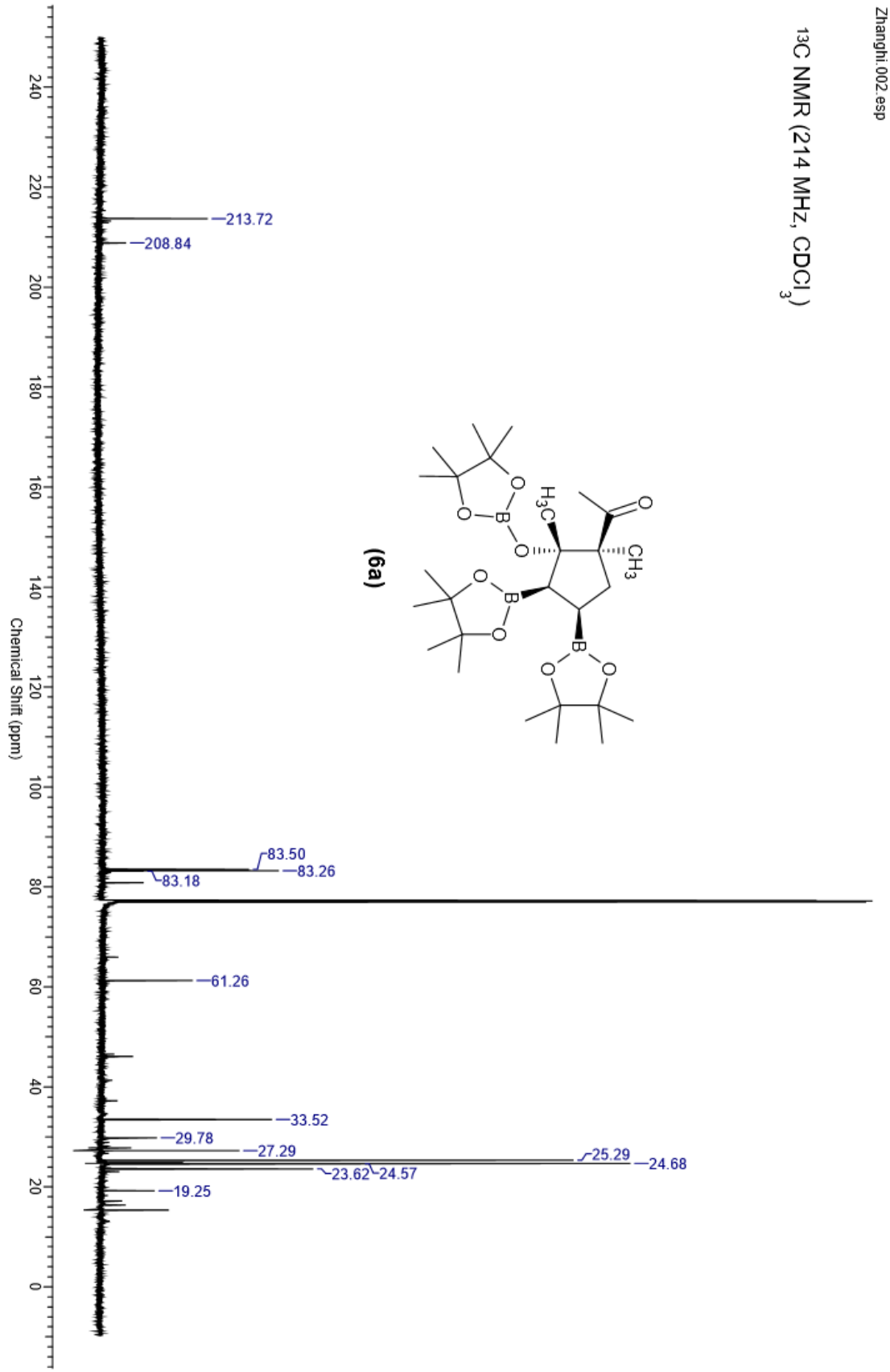

JMZ III pg 025 HCl deprotection column.001.esp
1H NMR (600 MHz, CDCl3)
JMZ III pg 025 HCl deprotection column.001.esp
(5b)
OH
B
O
Chemical Shift (ppm)
6.00
5.99
5.99
5.97
5.96
5.96
5.95
5.95
5.10
5.07
5.06
5.04
2.50
2.47
2.32
2.31
2.30
2.29
2.27
1.94
1.93
1.92
1.91
1.70
1.62
1.60
1.25
1.21
1.20
0.83
2.00
0.88
2.66
0.71
2.38
1.10
0.73
24.20
2.52
2.50
2.49
2.47
2.45
2.35
2.34
2.32
2.31
2.29
2.27
2.26
2.25
2.17
1.96
1.95
1.94
1.93
1.92
1.91
1.89
1.72
1.70
1.70
1.68
1.62
1.60

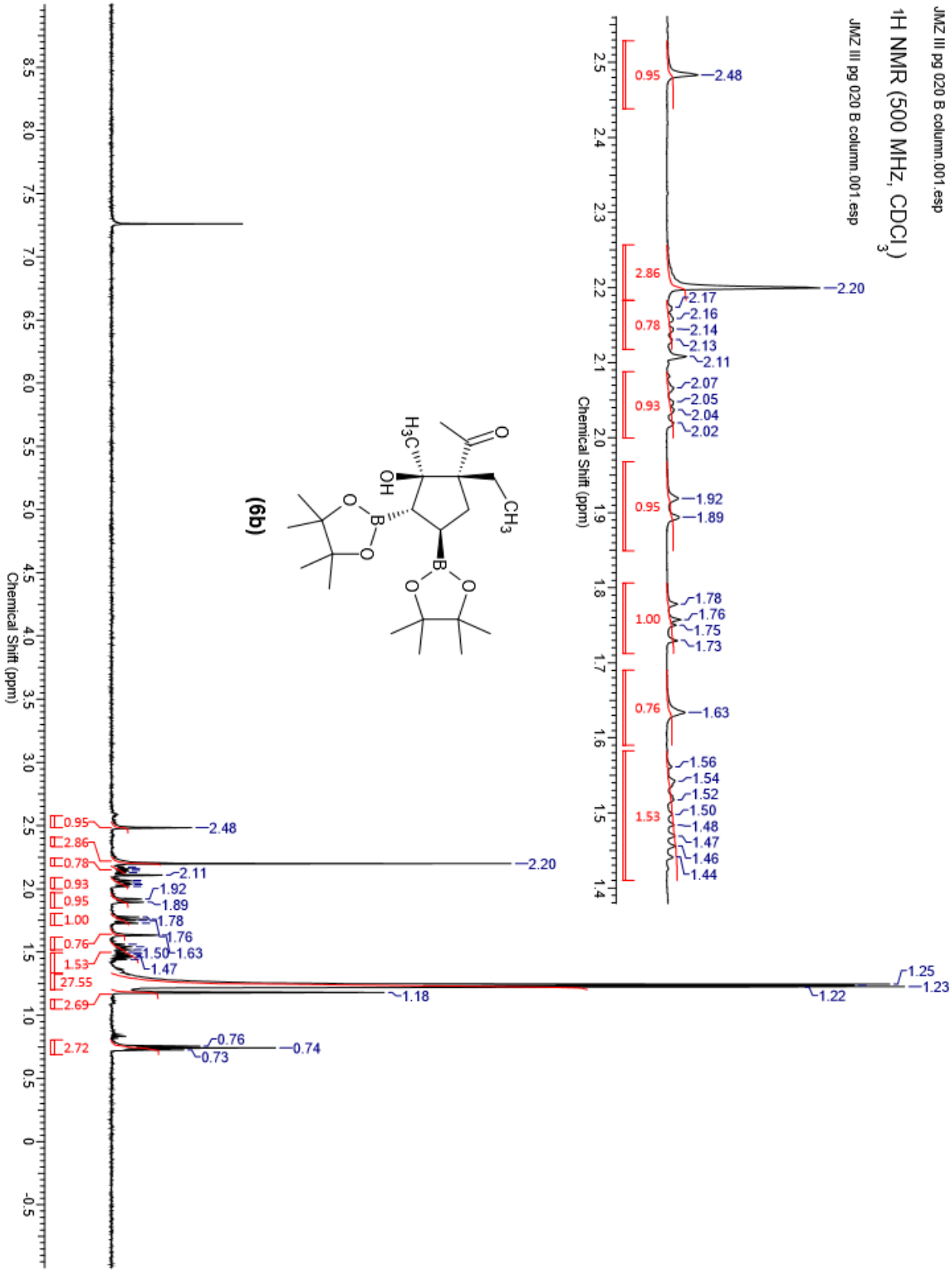

JMZ III pg 025 HCl deprotection column 13C.001.esp
13C NMR (151 MHz, CDCl3)
JMZ III pg 025 HCl deprotection column 13C.001.esp
25.12
24.87
24.78
24.74
Chemical Shift (ppm)
(5b)
222.07
135.46
117.97
90.57
83.62
83.30
62.17
37.52
37.46
37.04
33.21
25.12
24.78
Chemical Shift (ppm)


JMZ II pg 200 B column.001.esp
1H NMR (600 MHz, CDCl3)
JMZ II pg 200 B column.001.esp
(5c)
OH
CH3
B
O
Chemical Shift (ppm)
7.26
2.54
2.52
2.51
2.50
2.49
2.47
2.24
2.23
2.23
2.22
2.21
2.20
2.17
2.04
2.04
2.02
2.01
2.00
1.95
1.93
1.93
1.91
1.56
1.43
1.25
1.21
1.20
1.12
1.10
0.87
0.86
0.84
0.80
0.99
0.62
1.99
1.64
4.59
24.03
1.19
3.46


Zhanghi.009.esp
13C NMR (214 MHz, CDCl3)
Zhanghi.009.esp
24.88
24.81
24.76
25.16
26.0
25.5
25.0
24.5
24.0
23.5
Chemical Shift (ppm)
CH3
O
O
B
O
OH
B
O
O
(5c)
24.88
24.76
83.66
83.27
37.77
35.61
15.08
89.99
62.52
38.11
25.16
17.95
33.66
222.62
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

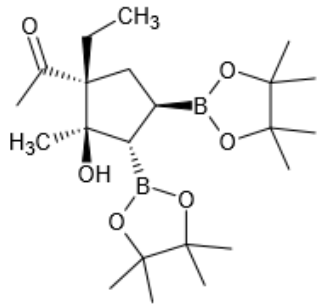

JMZ II pg 284 A column fr 29-37.001.esp
1H NMR (400 MHz, CDCl3)
JMZ II pg 284 A column fr 29-37.001.esp
2.21
2.52
2.12
2.12
2.10
1.95
1.69
1.57
0.86
3.08
1.21
1.12
1.32
1.98
Chemical Shift (ppm)
CH3
H3C
(6a)
1.22
2.21
1.19
2.52
2.12
2.10
1.95
1.69
1.57
0.86
3.08
1.21
1.12
1.32
1.98
4.22
3.88
Chemical Shift (ppm)


Zhanghi.002.esp
13C NMR (214 MHz, CDCl3)
(6a)
H3C
CH3
O
B
O
Chemical Shift (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0
213.72
208.84
83.50
83.26
83.18
61.26
33.52
29.78
27.29
25.29
24.68
23.62
24.57
19.25

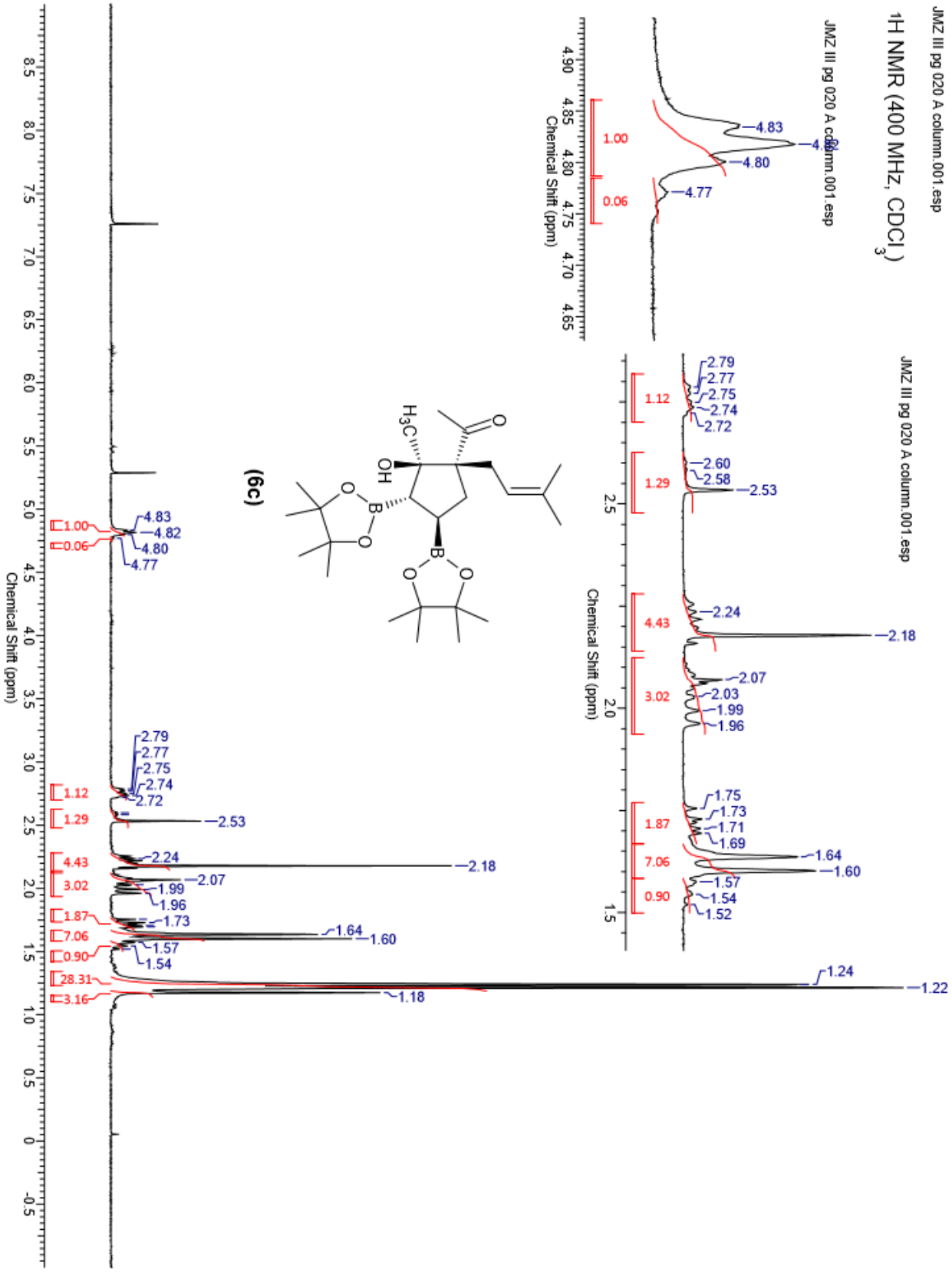

JMZ III pg 020 B column.001.esp
^{1}H NMR (500 MHz, $CDCl_3$)
JMZ III pg 020 B column.001.esp
(6b)
Chemical Shift (ppm)
Chemical Shift (ppm)

JMZ III pg 225 A column 13C.001.esp

^{13}C NMR (151 Hz, $CDCl_3$)

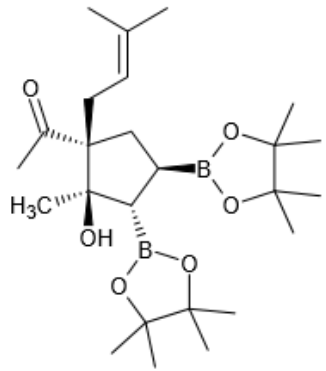


(6b)

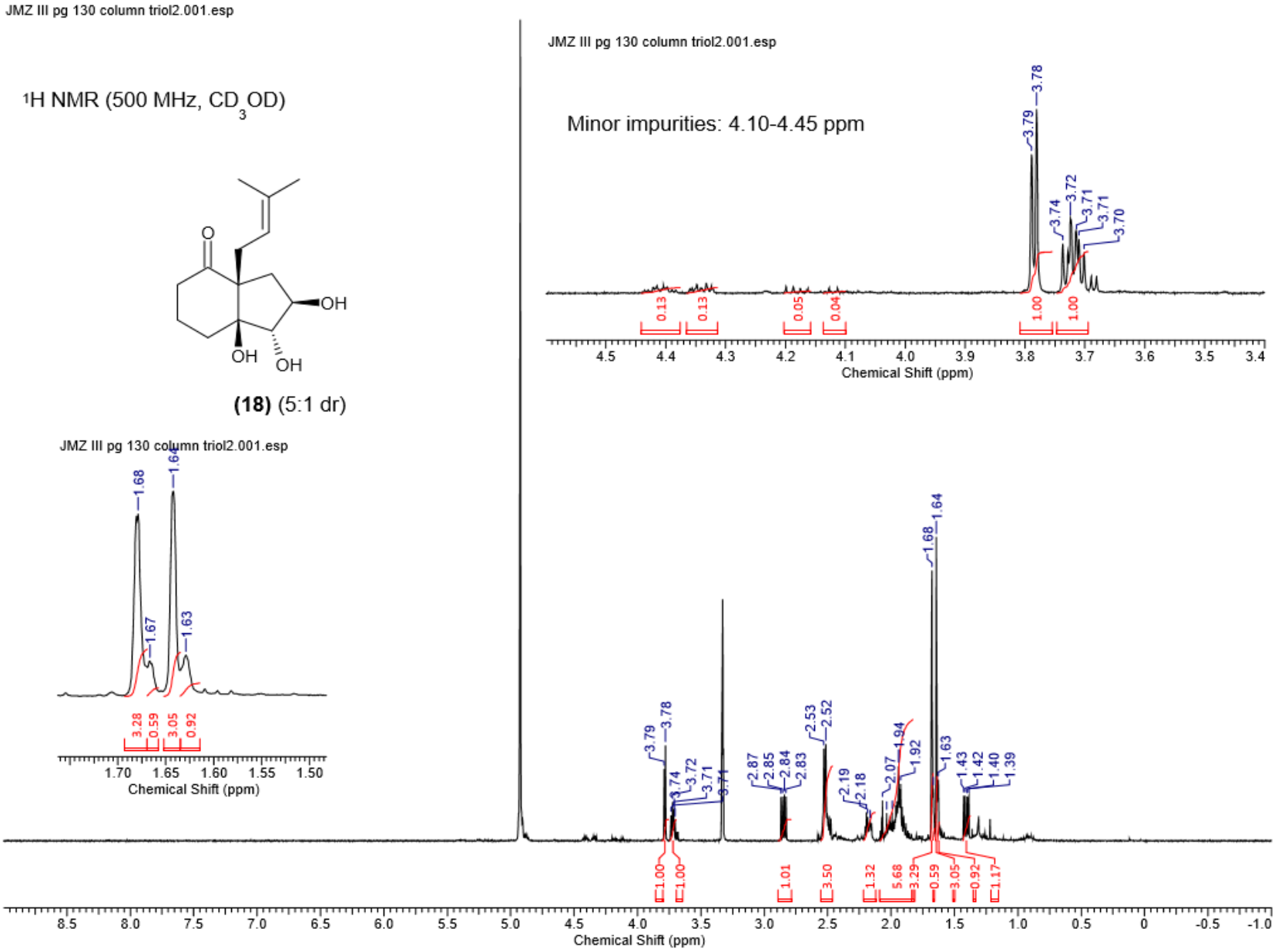

JMZ III pg 020 A column.001.esp
1H NMR (400 MHz, CDCl3)
JMZ III pg 020 A column.001.esp
JMZ III pg 020 A column.001.esp
(6c)
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)

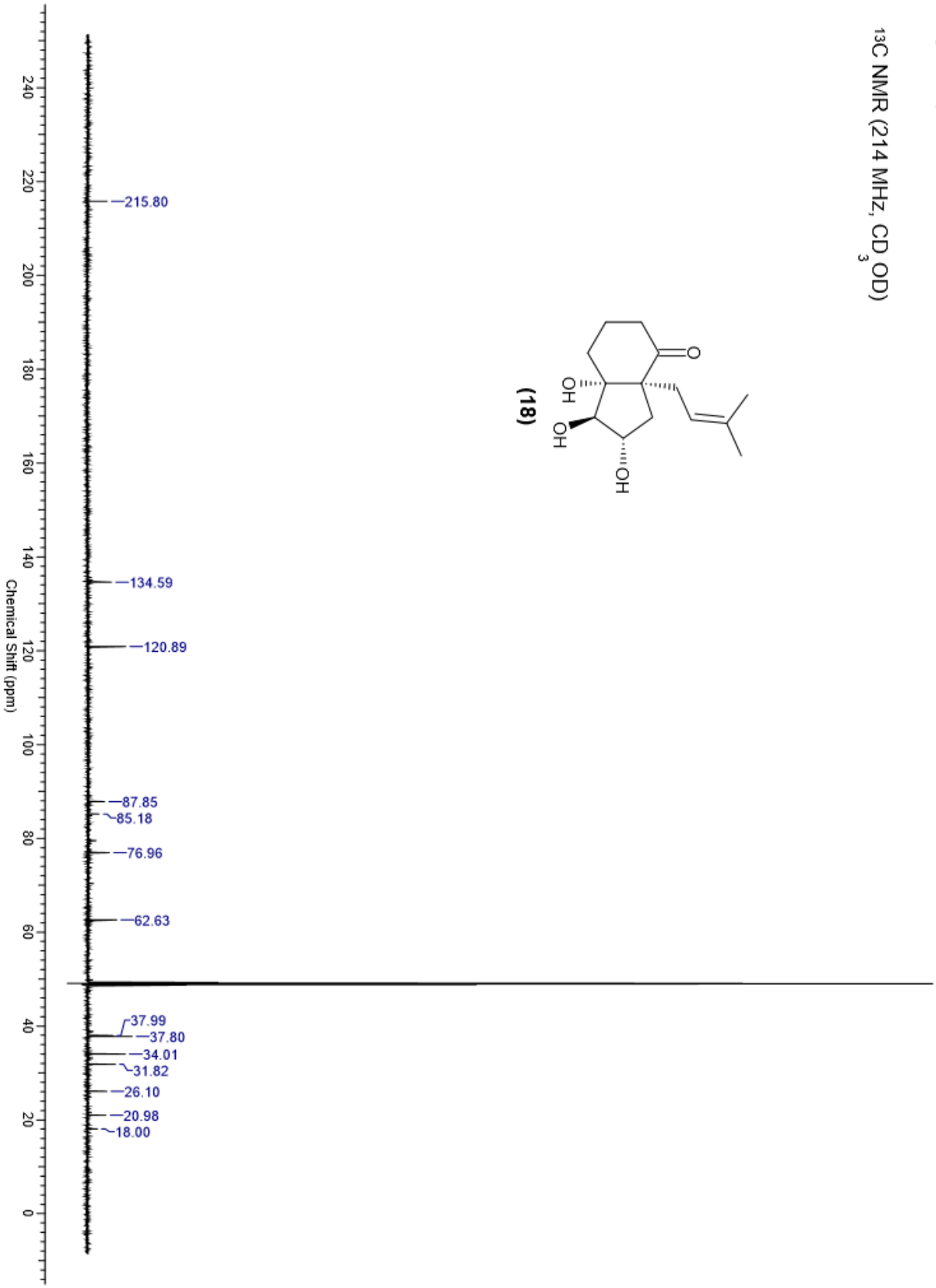
Zhanghi.007.esp

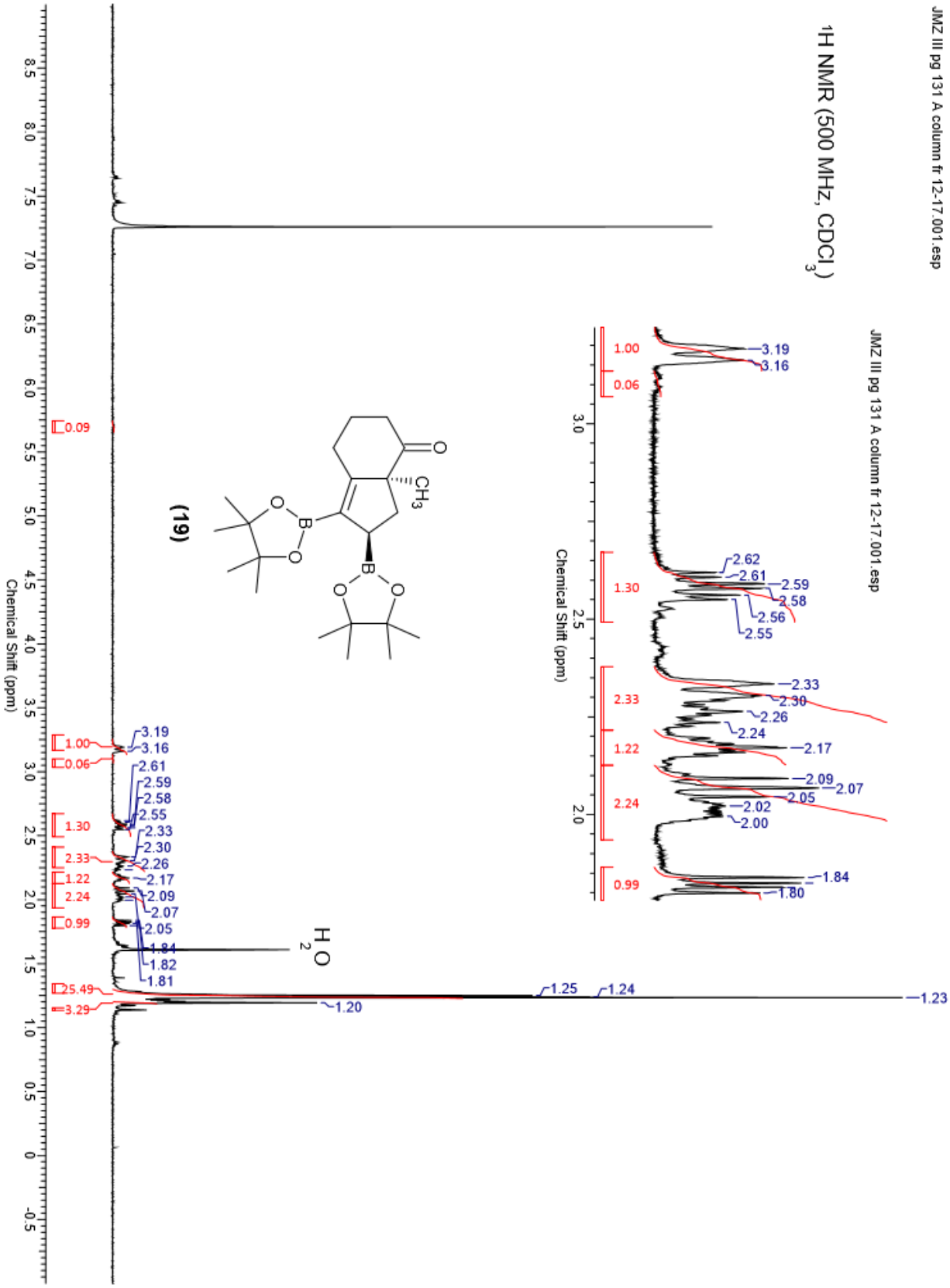
^{13}C NMR (214 MHz, $CDCl_3$)



(6c)

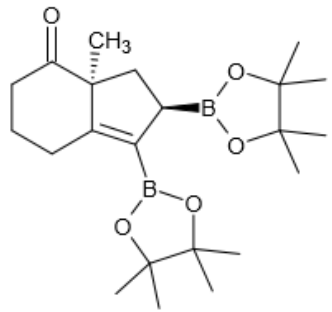

JMZ III pg 130 column triol2.001.esp
^{1}H NMR (500 MHz, CD_3OD)
O
OH
OH
OH
(18) (5:1 dr)
JMZ III pg 130 column triol2.001.esp
Minor impurities: 4.10-4.45 ppm
3.78
3.79
3.74
3.72
3.71
3.71
3.70
0.13
0.13
0.05
0.04
1.00
1.00
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4
Chemical Shift (ppm)
JMZ III pg 130 column triol2.001.esp
1.68
1.64
1.67
1.63
3.28
0.59
3.05
0.92
1.70 1.65 1.60 1.55 1.50
Chemical Shift (ppm)
1.68
1.64
3.79
3.78
3.74
3.72
3.71
3.71
2.87
2.85
2.84
2.83
2.53
2.52
2.19
2.18
2.07
1.94
1.92
1.63
1.43
1.42
1.40
1.39
1.00
1.00
1.01
3.50
1.32
5.68
3.29
0.59
3.05
0.92
1.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5 -1.0
Chemical Shift (ppm)


Zhanghl.015.esp
13C NMR (214 MHz, CD3OD)
(18)
OH
OH
OH
O
215.80
134.59
120.89
87.85
85.18
76.96
62.63
37.99
37.80
34.01
31.82
26.10
20.98
18.00
Chemical Shift (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0

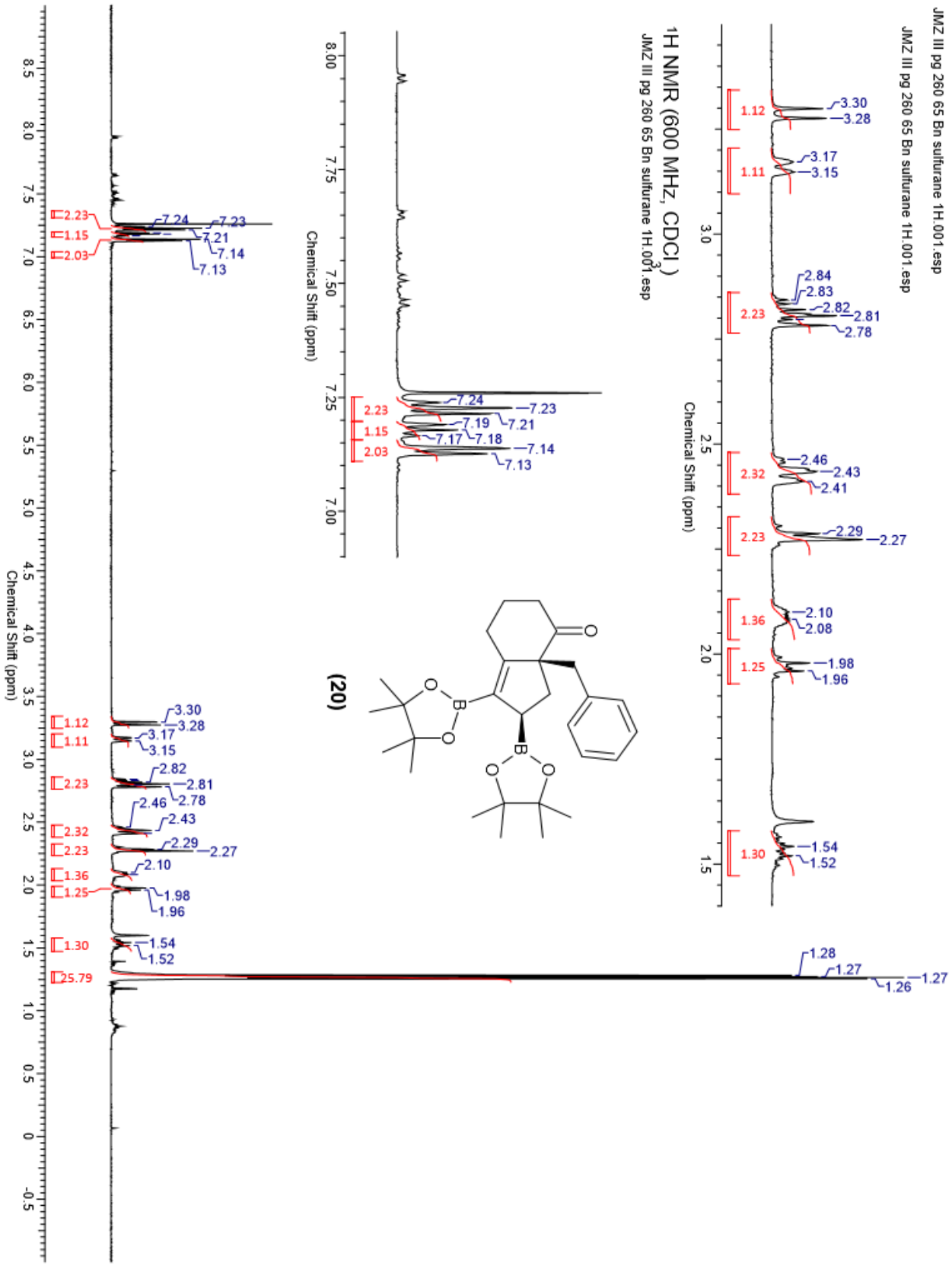

JMZ III pg 131 A column fr 12-17.001.esp
1H NMR (500 MHz, CDCl3)
(19)
CH3
O
B
O
O
B
O
O
H2O
Chemical Shift (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
0.09
1.00
0.06
1.30
2.33
1.22
2.24
0.99
25.49
3.29
3.19
3.16
2.61
2.59
2.58
2.55
2.33
2.30
2.26
2.17
2.09
2.07
2.05
1.84
1.82
1.81
1.25
1.24
1.23
1.20
JMZ III pg 131 A column fr 12-17.001.esp
Chemical Shift (ppm)
3.0
2.5
2.0
1.00
0.06
1.30
2.33
1.22
2.24
0.99
3.19
3.16
2.62
2.61
2.59
2.58
2.56
2.55
2.33
2.30
2.26
2.24
2.17
2.09
2.07
2.05
2.02
2.00
1.84
1.80

Zhanghi.010.esp

^{13}C NMR (214 MHz, $CDCl_3$)

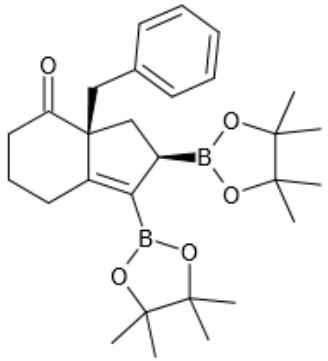


(19)


JMZ III pg 260 65 Bn sulfurane 1H.001.esp
JMZ III pg 260 65 Bn sulfurane 1H.001.esp
1H NMR (600 MHz, CDCl3)
JMZ III pg 260 65 Bn sulfurane 1H.001.esp
(20)
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)

JMZ III pg 260 65 Bn sulfurane 13C2.001.esp

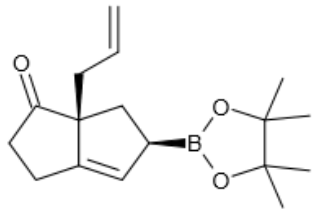
^{13}C NMR (151 MHz, $CDCl_3$)



(20)

JMZ III pg 55 allyl sulf fr 12 new.001.esp

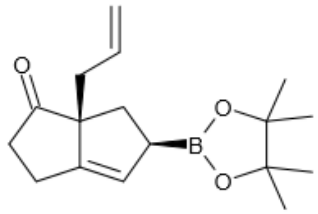
^{1}H NMR (500 MHz, $CDCl_3$)



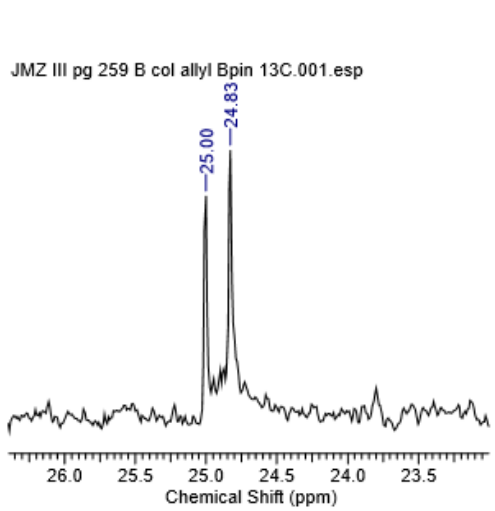
(21)

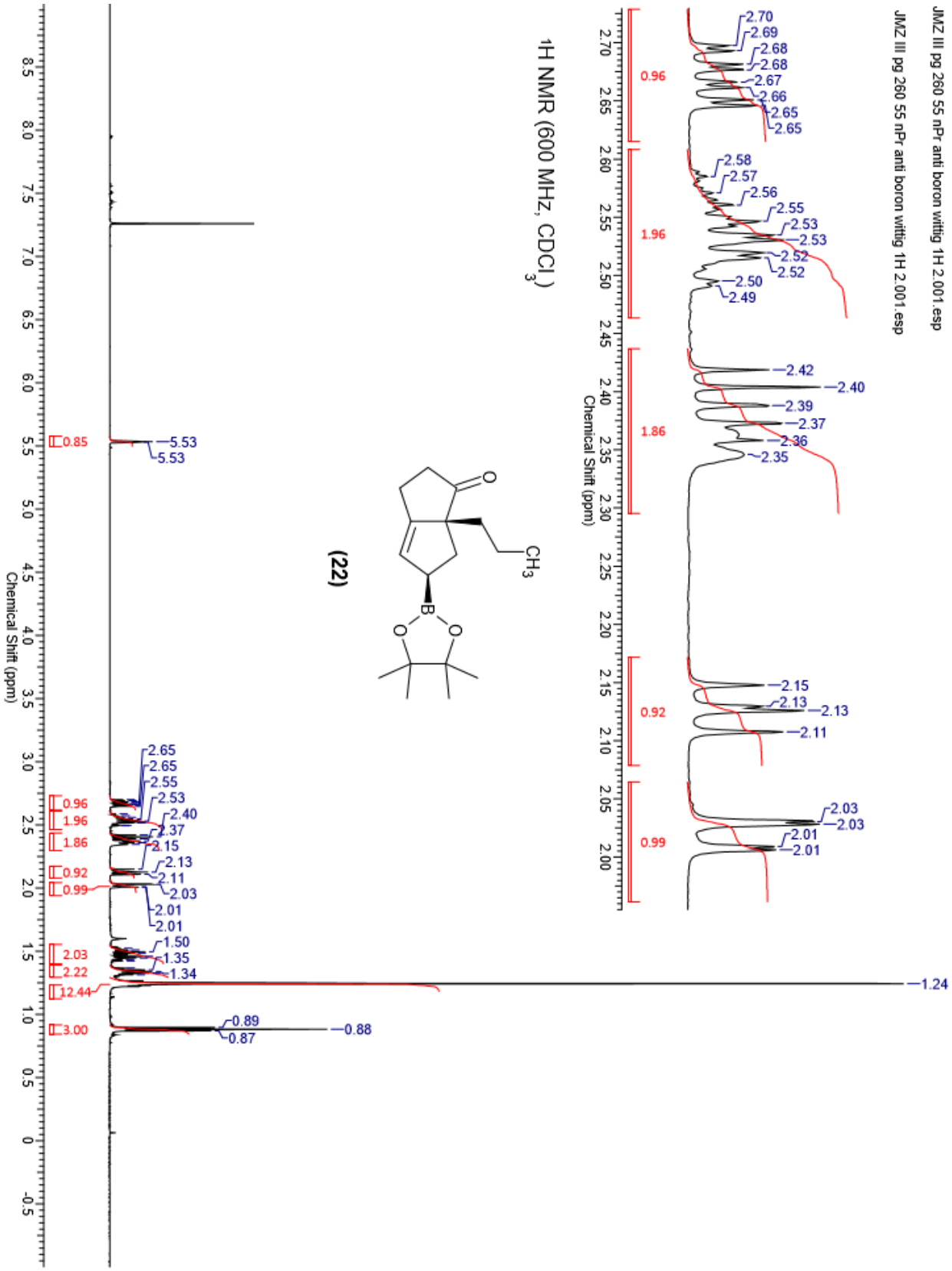
JMZ III pg 259 B col allyl Bpin 13C.001.esp

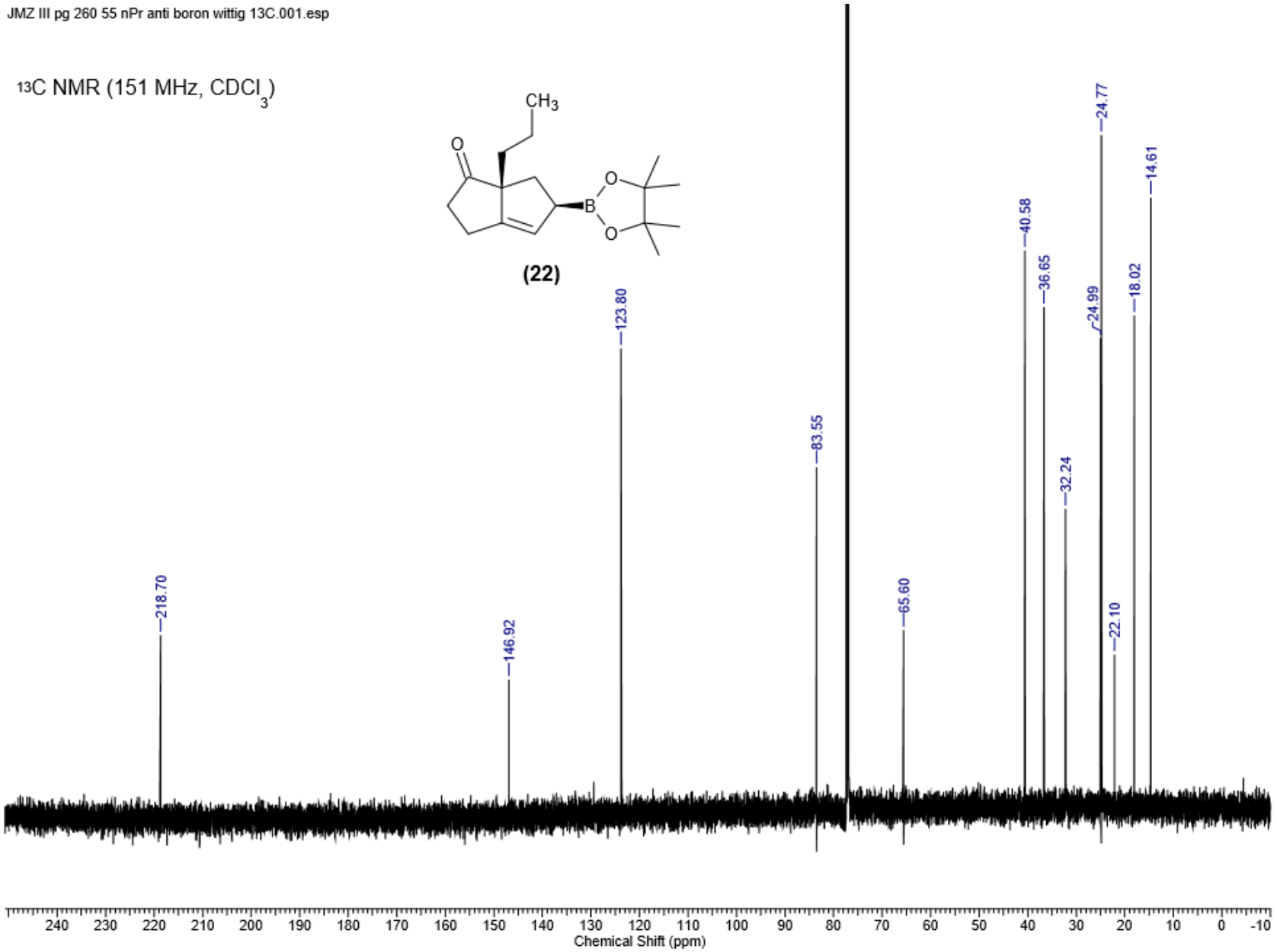
^{13}C NMR (151 MHz, $CDCl_3$)

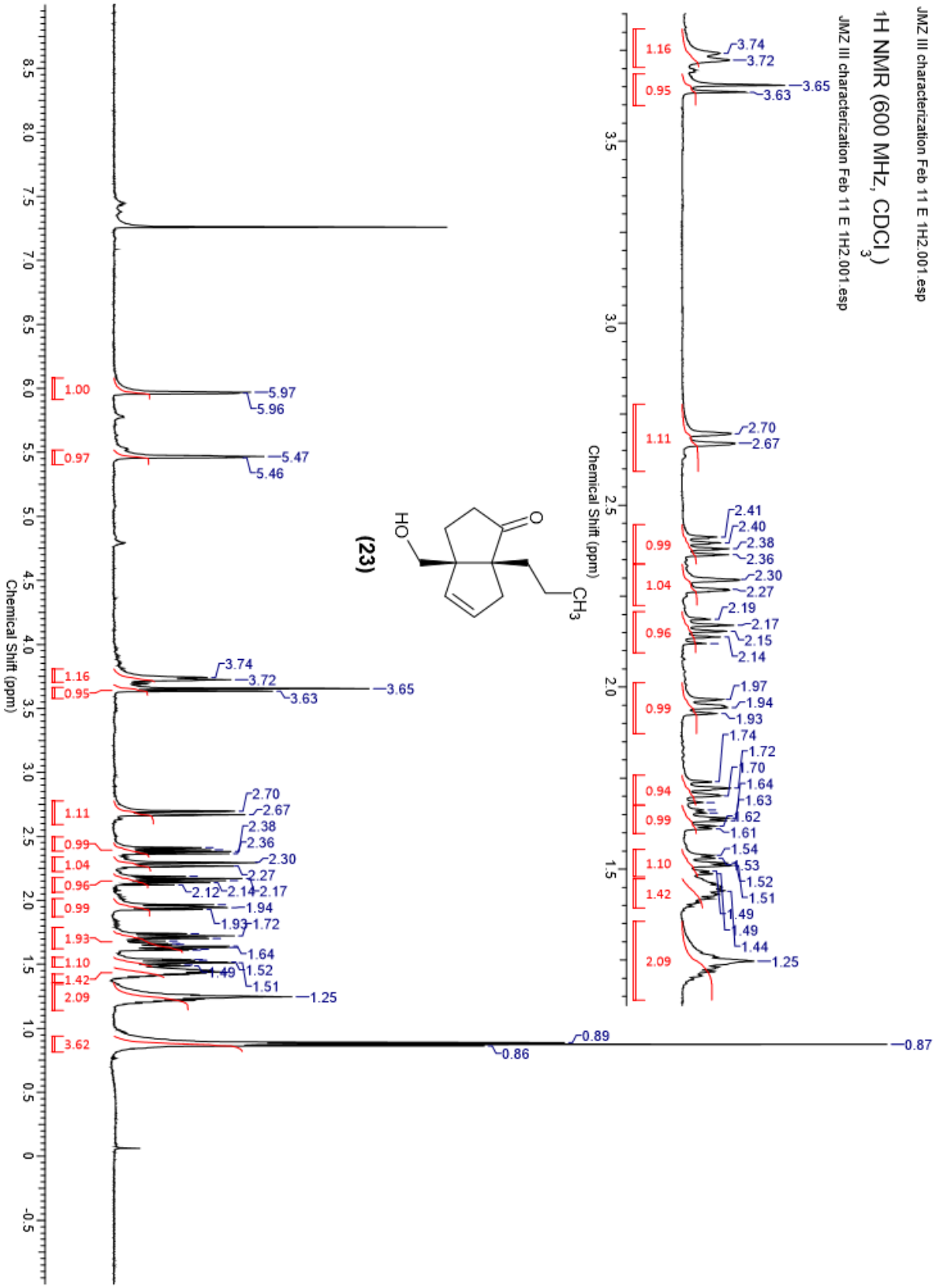


(21)



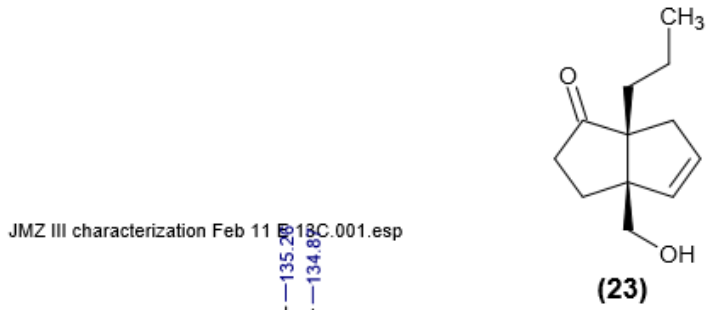

JMZ III pg 260 55 nPr anti boron wittig 1H 2.001.esp
JMZ III pg 260 55 nPr anti boron wittig 1H 2.001.esp
1H NMR (600 MHz, CDCl3)
(22)
Chemical Shift (ppm)
Chemical Shift (ppm)


JMZ III pg 260 55 nPr anti boron wittig 13C.001.esp
13C NMR (151 MHz, CDCl3)
CH3
O
O
O
B
(22)
218.70
146.92
123.80
83.55
65.60
40.58
36.65
32.24
24.99
24.77
22.10
18.02
14.61
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

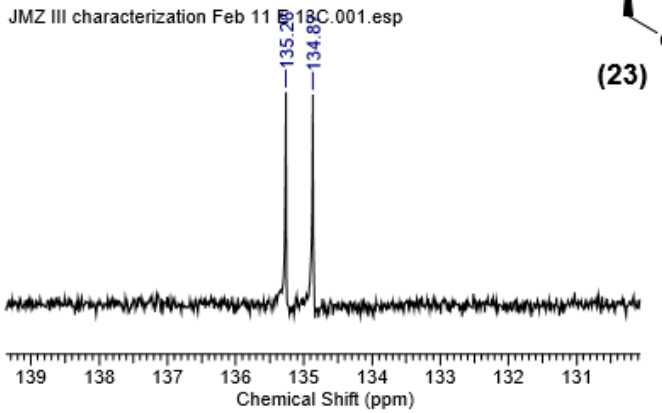

JMZ III characterization Feb 11 E 1H2.001.esp
1H NMR (600 MHz, CDCl3)
JMZ III characterization Feb 11 E 1H2.001.esp
(23)
HO
O
CH3
Chemical Shift (ppm)
Chemical Shift (ppm)

JMZ III characterization Feb 11 E 13C.001.esp

^{13}C NMR (151 MHz, $CDCl_3$)

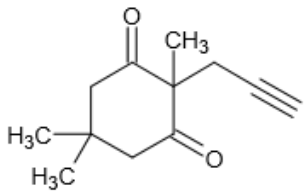


(23)



JMZ III pg 126 dimedone substrate 1H.001.esp

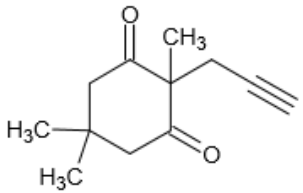
^{1}H NMR (600 MHz, $CDCl_3$)



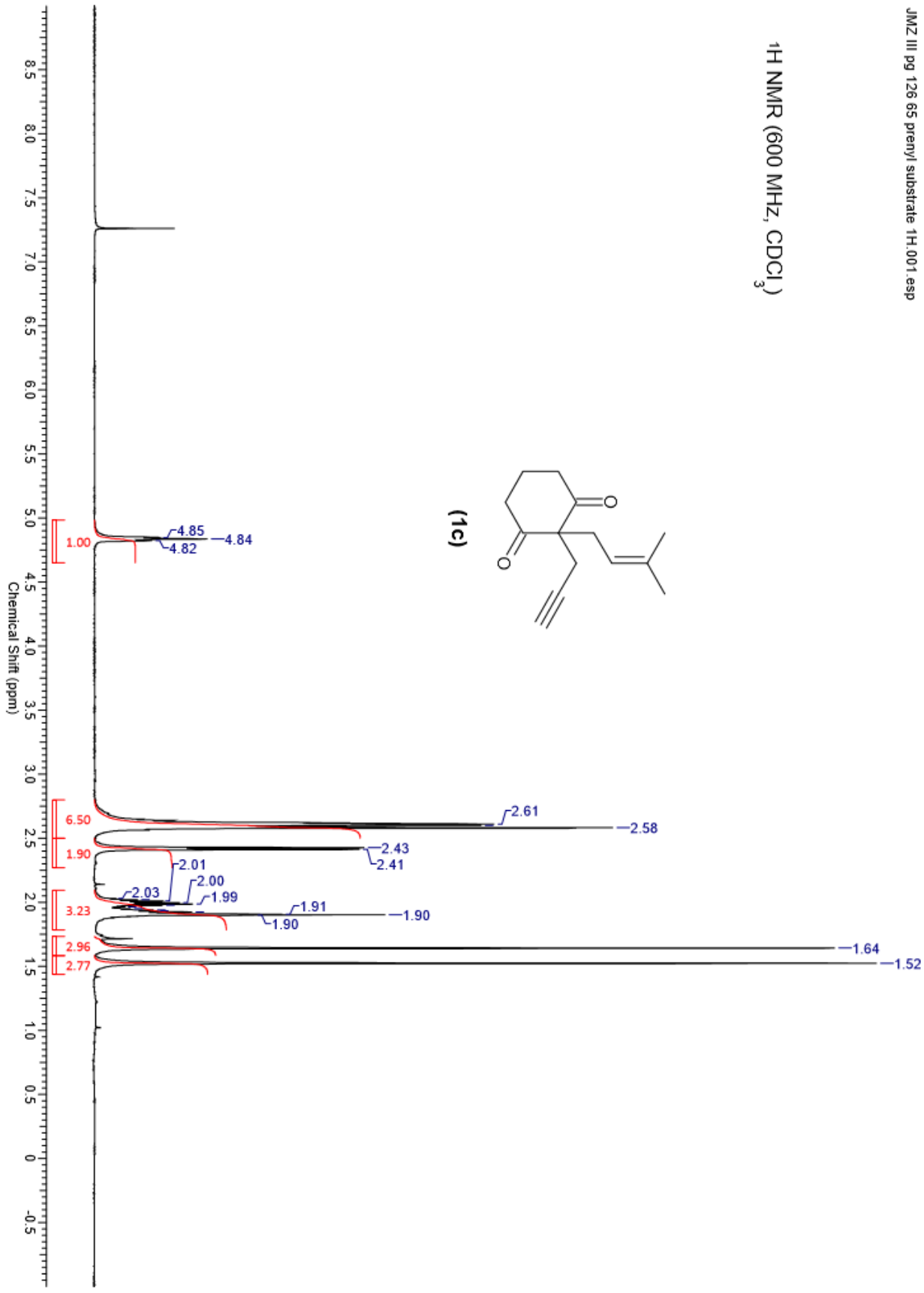
(1b)

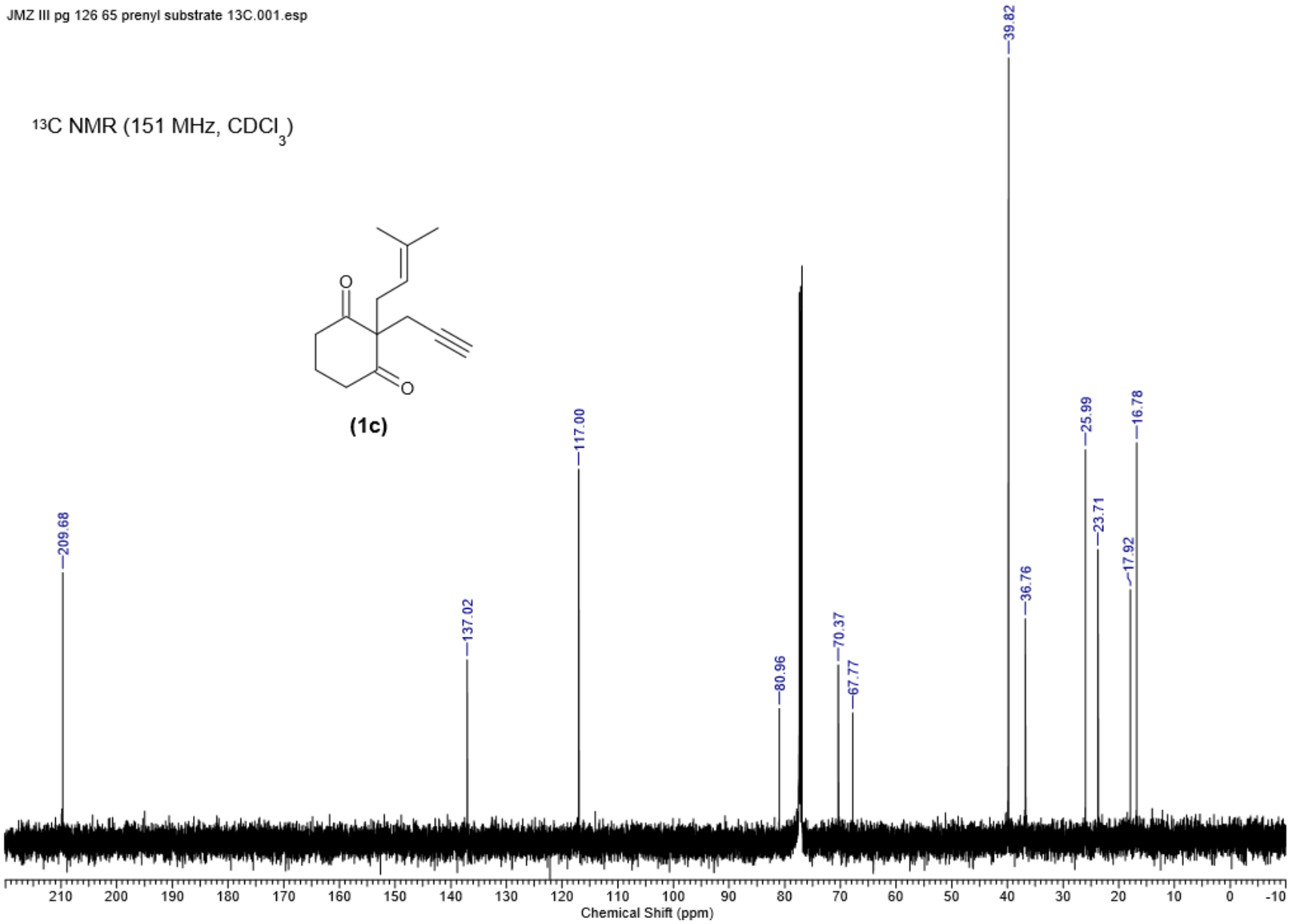
JMZ III pg 126 dimedone substrate 13C.001.esp

^{13}C NMR (151 MHz, $CDCl_3$)



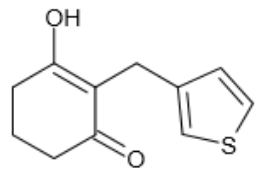
(1b)


JMZ III pg 126 65 prenyl substrate 1H.001.esp
^{1}H NMR (600 MHz, $CDCl_3$)
(1c)
Chemical Shift (ppm)
1.00
6.50
1.90
3.23
2.96
2.77
4.85
4.84
4.82
2.61
2.58
2.43
2.41
2.01
2.00
2.03
1.99
1.91
1.90
1.90
1.64
1.52


JMZ III pg 126 65 prenyl substrate 13C.001.esp
13C NMR (151 MHz, CDCl3)
(1c)
209.68
137.02
117.00
80.96
70.37
67.77
39.82
36.76
25.99
23.71
17.92
16.78
Chemical Shift (ppm)

JMZ III pg 126 thiophene intermediate 1H.001.esp

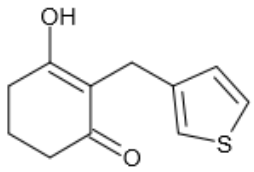
^{1}H NMR (600 MHz, *d6*-DMSO)



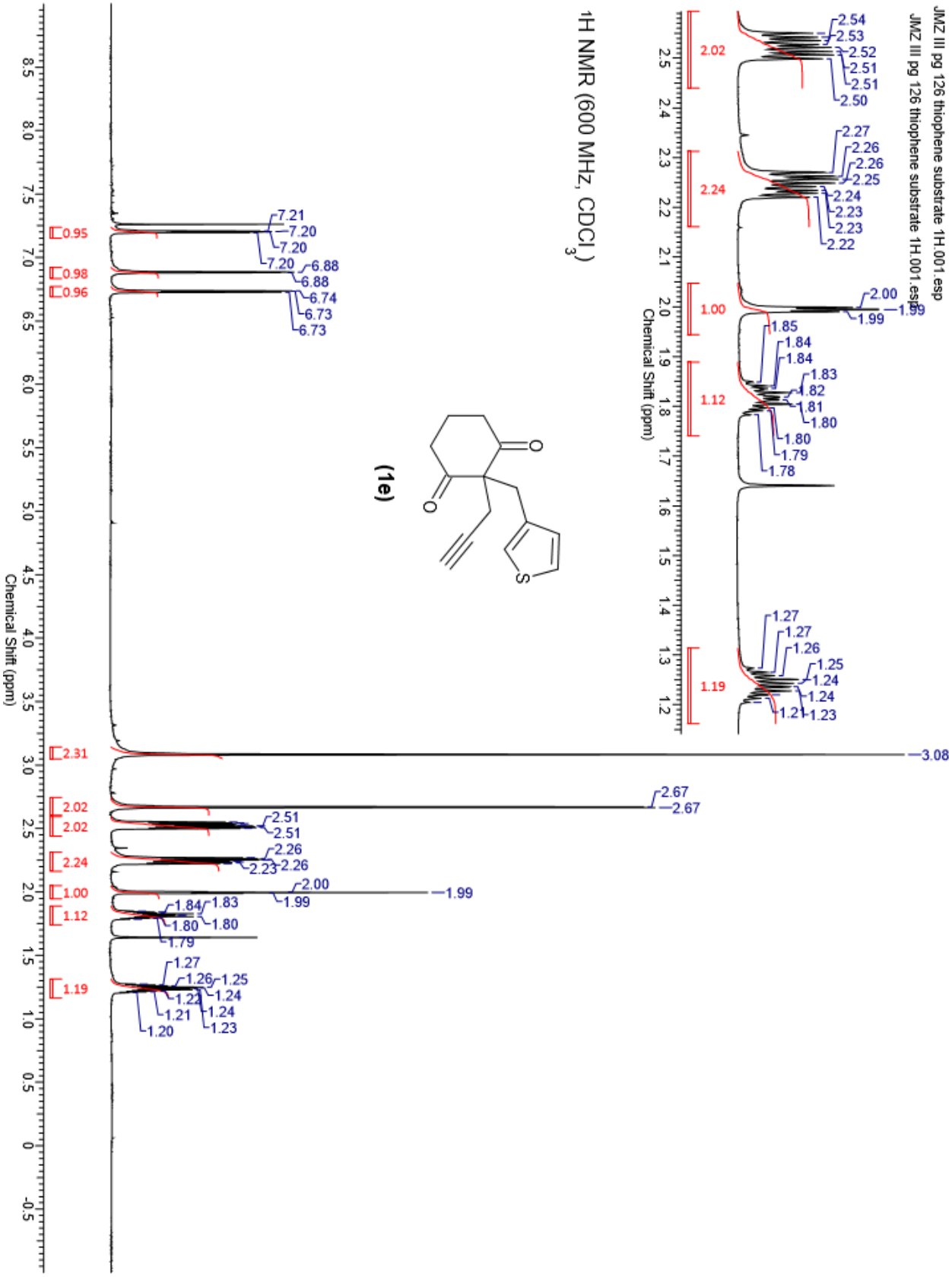
(S2)

JMZ III pg 126 thiophene intermediate 13C2.001.esp

^{13}C NMR (151 MHz, *d6*-DMSO)

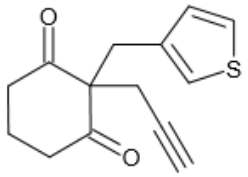


(S2)

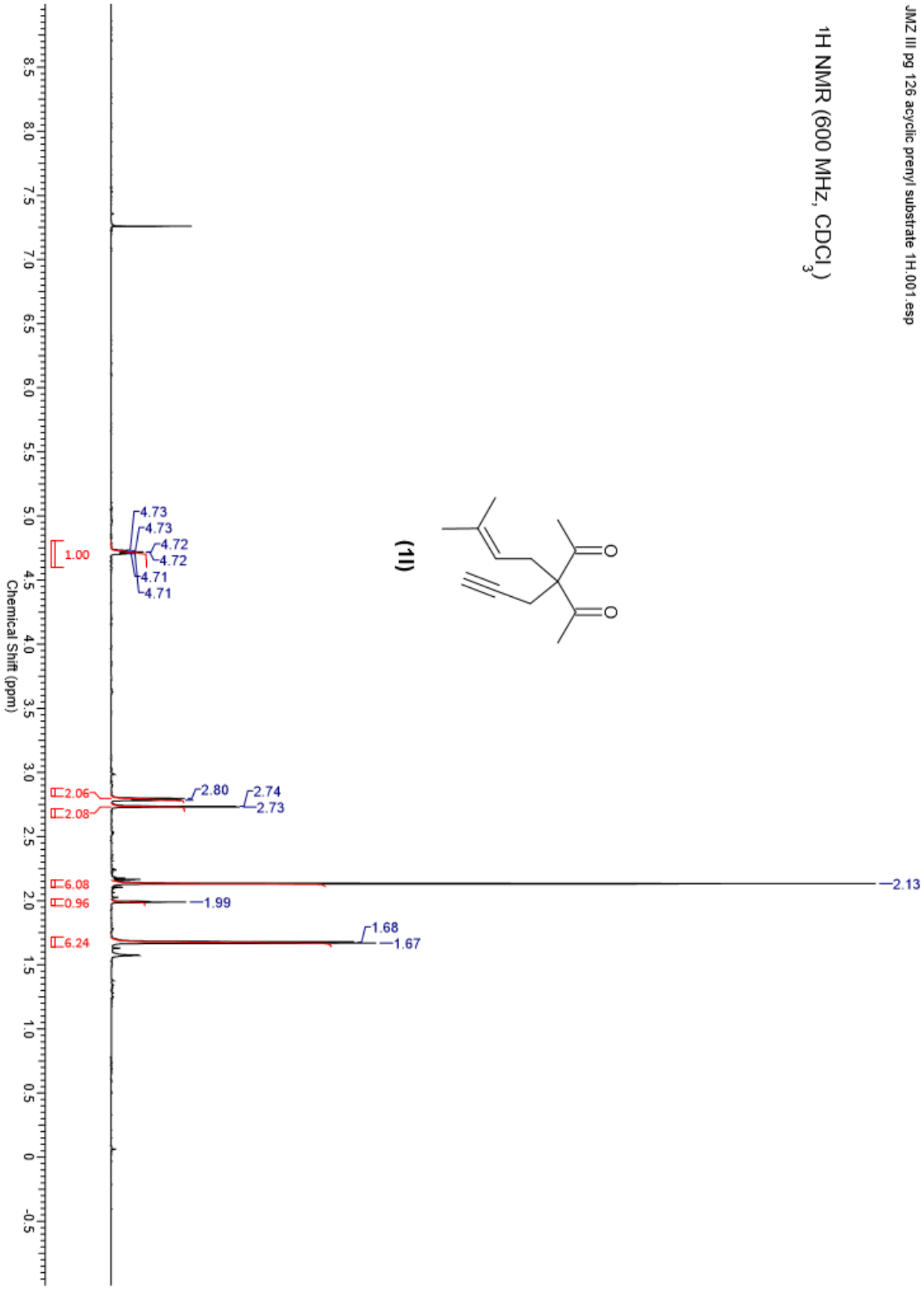

JMZ III pg 126 thiophene substrate 1H.001.esp
JMZ III pg 126 thiophene substrate 1H.001.esp
1H NMR (600 MHz, CDCl3)
(1e)
Chemical Shift (ppm)
Chemical Shift (ppm)

JMZ III pg 126 thiophene substrate 13C.001.esp

^{13}C NMR (151 MHz, $CDCl_3$)

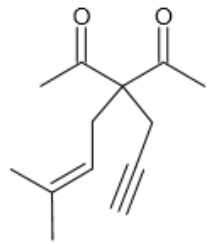


(1e)

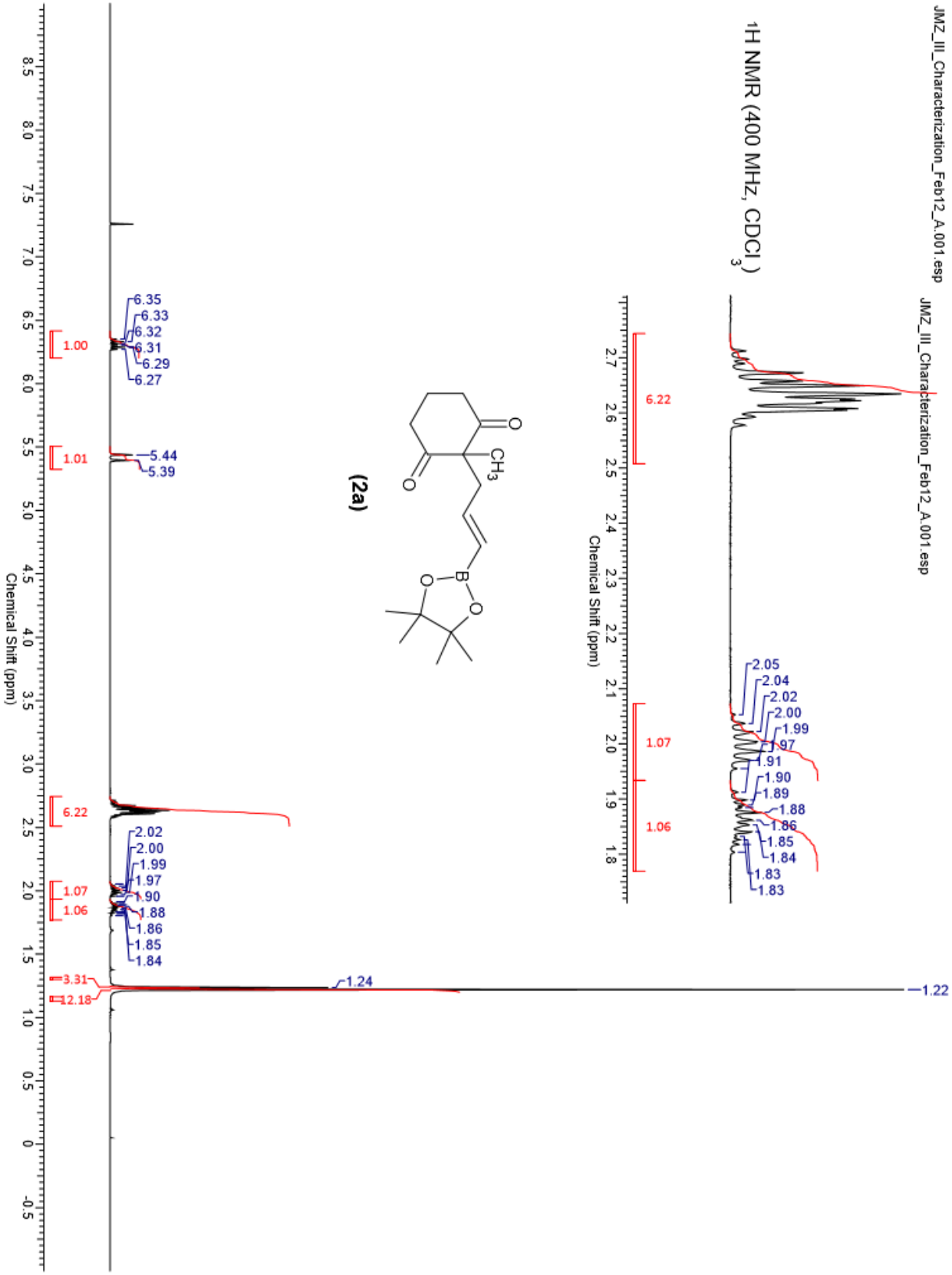

JMZ III pg 126 acyclic prenyl substrate 1H.001.esp
1H NMR (600 MHz, CDCl3)
(1l)
Chemical Shift (ppm)
4.73
4.73
4.72
4.72
4.71
4.71
1.00
2.80
2.74
2.73
2.06
2.08
6.08
0.96
6.24
2.13
1.99
1.68
1.67

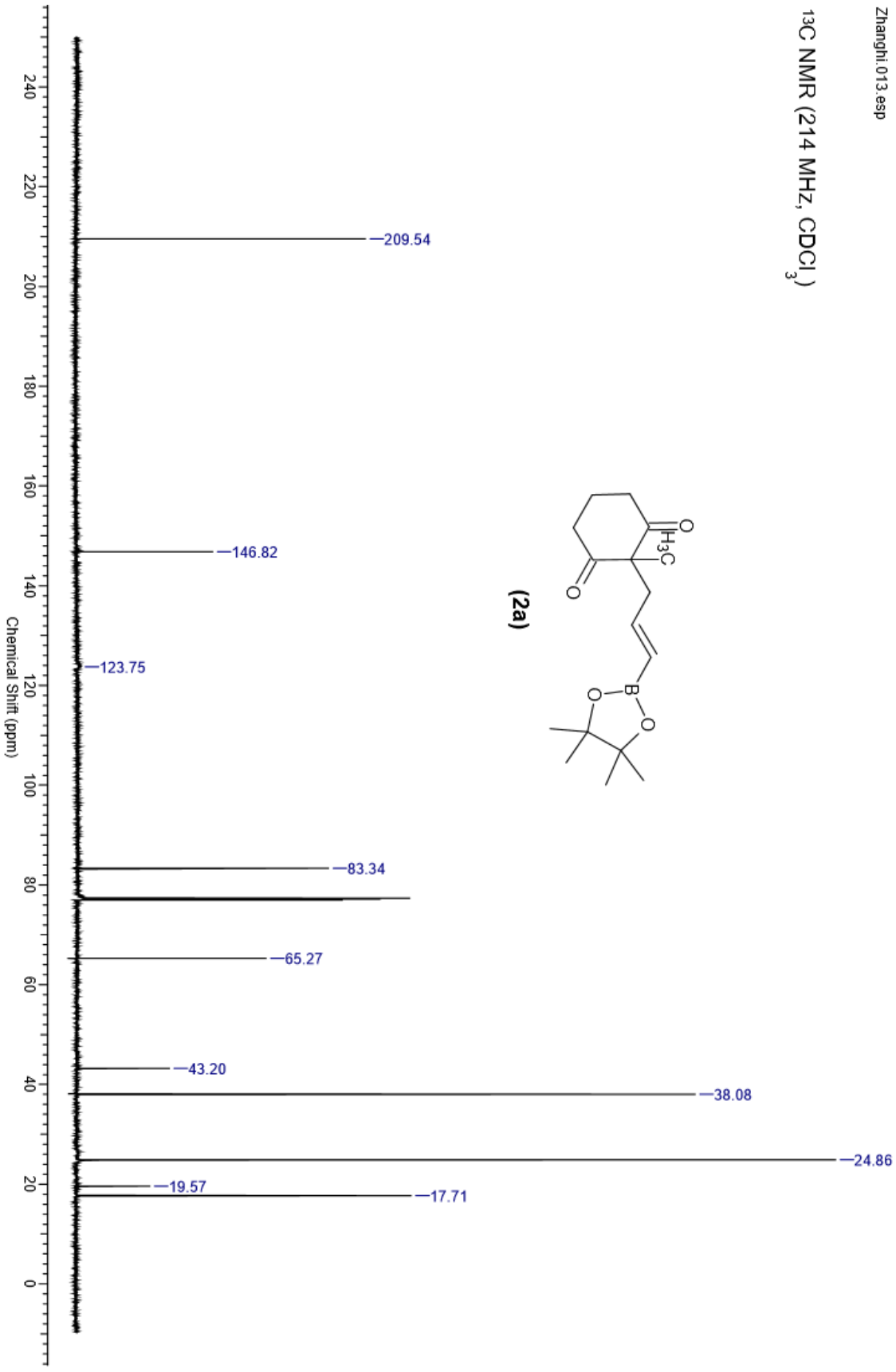
JMZ III pg 126 acyclic prenyl substrate 13C.001.esp

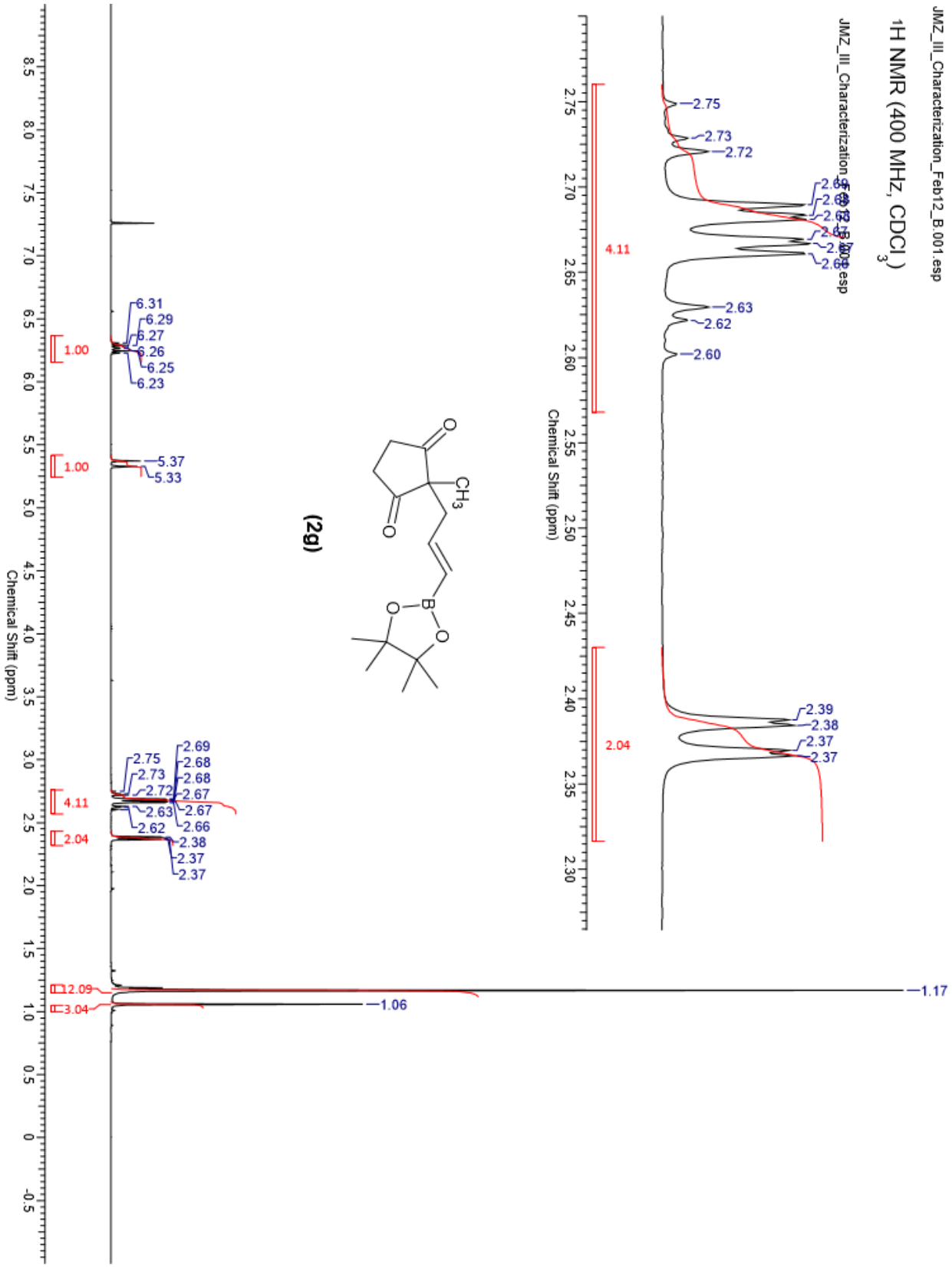
^{13}C NMR (151 MHz, $CDCl_3$)



(1l)

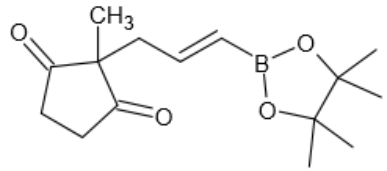

JMZ_III_Characterization_Feb12_A.001.esp
1H NMR (400 MHz, CDCl3)
JMZ_III_Characterization_Feb12_A.001.esp
(2a)
Chemical Shift (ppm)
Chemical Shift (ppm)
6.35
6.33
6.32
6.31
6.29
6.27
5.44
5.39
2.05
2.04
2.02
2.00
1.99
1.97
1.91
1.90
1.89
1.88
1.86
1.85
1.84
1.83
1.83
1.24
1.22
3.31
12.18
1.00
1.01
6.22
1.07
1.06
6.22
1.07
1.06


Zhanghi.013.esp
13C NMR (214 MHz, CDCl3)
(2a)
209.54
146.82
123.75
83.34
65.27
43.20
38.08
24.86
19.57
17.71
Chemical Shift (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0


JMZ_III_Characterization_Feb12_B.001.esp
1H NMR (400 MHz, CDCl3)
JMZ_III_Characterization_Feb12_B.001.esp
(2g)
Chemical Shift (ppm)
Chemical Shift (ppm)
6.31
6.29
6.27
6.26
6.25
6.23
5.37
5.33
2.75
2.73
2.72
2.69
2.68
2.68
2.67
2.67
2.66
2.63
2.62
2.38
2.37
2.37
2.39
2.38
2.37
2.37
2.63
2.62
2.60
1.17
1.06
1.00
1.00
4.11
2.04
4.11
2.04
12.09
3.04

Zhanghi.014.esp

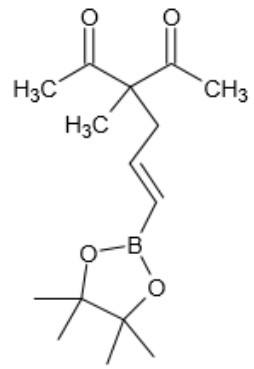
^{13}C NMR (214 MHz, $CDCl_3$)



(2g)

JMZ_III_Characterization_Feb12_C.001.esp

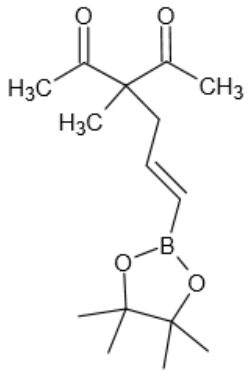
^{1}H NMR (400 MHz, $CDCl_3$)



(2j)

Zhanghi.012.esp

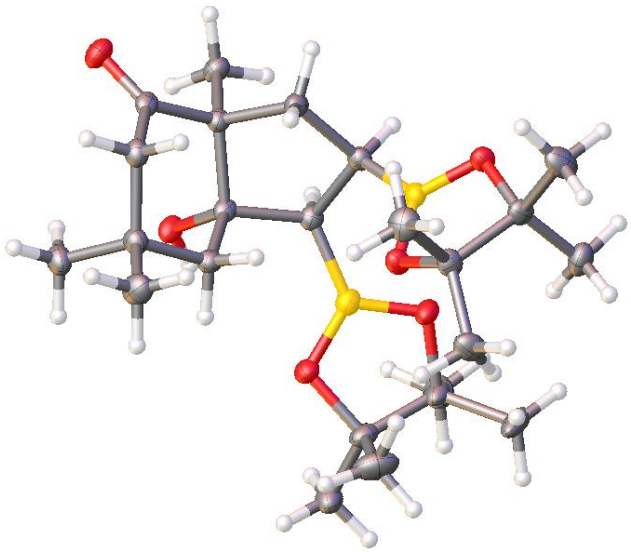
^{13}C NMR (214 MHz, $CDCl_3$)



(2j)

■ **Single-Crystal X-ray Data for (+)-(3b) (CCDC 1916345)**

Table S4 Crystal data and structure refinement for (+)-(3b).



Identification code	dimedone-derived substrate
Empirical formula	$C_{24}H_{42}B_2O_6$
Formula weight	448.25
Temperature/K	100.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.2030(4)
b/Å	12.8185(4)
c/Å	17.0176(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2661.96(14)
Z	4
ρ_{calc}g/cm^3	1.1183
μ/mm^{-1}	0.615
F(000)	979.1
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54178 Å)
2Θ range for data collection/°	8.92 to 133.08
Index ranges	$-13 \le h \le 14$, $-15 \le k \le 14$, $-18 \le l \le 20$
Reflections collected	21235
Independent reflections	4571 [R_{int} = 0.0402, R_{sigma} = 0.0371]
Data/restraints/parameters	4571/0/301
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0692
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0720
Largest diff. peak/hole / e Å^{-3}	0.16/-0.16
Flack parameter	0.09(16)

Table S5 Fractional Atomic Coordinates (Å^2×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for dimedone-derived substrate. $U_{eq}$is defined as 1/3 of of the trace of the orthogonalised U^{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O001	2277.1(10)	6997.8(9)	5151.1(6)	21.1(3)
O002	2235.4(9)	8173.3(8)	8676.8(6)	19.9(3)
O003	3701.9(10)	5584.6(8)	6469.0(6)	22.6(3)
O004	1970.4(9)	6578.8(8)	8110.4(6)	20.0(3)
O005	4403.7(10)	6743.6(9)	7357.3(6)	24.1(3)

O006	-372.1(10)	8501.0(9)	5124.3(7)	26.5(3)
C00A	1706.8(14)	9080.1(13)	5503.2(10)	22.0(4)
C00B	2326.3(14)	8134.4(12)	7161.5(9)	18.3(3)
C00C	1262.0(14)	6214.1(12)	6232.5(9)	19.3(4)
C00D	1179.9(14)	8179.7(12)	5951.6(9)	18.3(3)
C00E	1606.3(14)	6467.8(13)	8925.6(9)	21.1(4)
C00F	-565.7(14)	7049.0(13)	5981.3(9)	22.1(4)
C00G	4500.7(15)	4996.7(13)	6931.5(10)	24.6(4)
C00H	110.0(14)	6040.4(13)	5887.2(10)	21.7(4)
C00I	2164.6(15)	7427.4(12)	9325.6(9)	21.5(4)
C00J	1166.1(14)	8437.4(13)	6843.3(9)	20.5(4)
C00K	5180.0(15)	5874.6(14)	7331.4(10)	25.7(4)
C00L	146.3(15)	5739.7(14)	5014.8(10)	27.5(4)
C00M	361.2(15)	6541.5(16)	8907.6(11)	31.1(4)
C00N	1957.9(17)	5416.3(13)	9237.2(10)	29.5(4)
C00O	3335.2(15)	7211.1(15)	9581.9(10)	29.7(4)
C00P	-449.7(16)	5164.7(14)	6348.4(11)	31.3(4)
C00Q	5142.9(16)	4301.4(15)	6378.5(11)	33.4(5)
C00R	1519.6(17)	7924.5(14)	9987.4(10)	32.6(5)
C00U	6138.9(16)	6239.5(16)	6838.2(12)	35.8(5)
C00V	3835.8(19)	4340.1(15)	7509.5(13)	43.2(5)
C00W	5543(2)	5643.4(18)	8164.3(10)	45.1(6)
C007	32.6(14)	7962.2(13)	5641.3(9)	19.3(4)
C008	2846.1(14)	7449.5(12)	6500.2(9)	18.0(3)
C009	1900.3(13)	7168.7(13)	5936.7(9)	17.4(3)
B00S	2204.2(16)	7612.9(14)	7993.8(10)	18.5(4)
B00T	3640.2(16)	6564.1(15)	6783.9(10)	19.2(4)

Table S6 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for dimedone-derived substrate. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O001	19.0(6)	29.4(6)	14.9(5)	5.5(5)	2.0(4)	-0.5(5)
O002	25.2(6)	18.1(6)	16.4(5)	-1.2(5)	0.6(5)	1.7(4)
O003	21.2(6)	23.2(6)	23.5(6)	5.2(5)	-4.2(5)	-1.4(5)
O004	26.3(6)	19.0(6)	14.7(5)	-2.3(5)	1.5(5)	1.5(5)
O005	24.2(6)	28.2(6)	19.8(6)	10.1(6)	-4.7(5)	-3.6(5)
O006	24.3(7)	32.3(7)	23.0(6)	3.7(6)	-3.8(5)	5.6(5)
C00A	21.9(9)	22.4(9)	21.8(8)	0.9(8)	-1.4(7)	4.4(7)
C00B	19.1(9)	17.3(8)	18.5(8)	-1.4(7)	0.3(6)	0.6(6)

C00C	18.7(9)	19.7(8)	19.5(8)	2.1(7)	0.7(7)	-0.9(7)
C00D	17.7(8)	19.8(8)	17.5(8)	2.1(7)	0.2(7)	-1.6(6)
C00E	24.3(9)	23.5(9)	15.4(8)	-2.5(8)	3.7(7)	1.2(7)
C00F	19.1(9)	26.5(9)	20.6(8)	-0.7(8)	-0.9(7)	-2.0(7)
C00G	26.1(10)	25.4(9)	22.3(9)	10.4(8)	0.1(8)	2.2(7)
C00H	21.0(9)	21.1(8)	22.9(9)	-1.8(8)	-1.1(7)	-1.6(7)
C00I	28.3(10)	20.7(8)	15.5(8)	0.3(8)	1.9(7)	3.3(7)
C00J	24.8(9)	20.5(8)	16.3(8)	3.4(8)	-0.6(7)	-0.6(7)
C00K	26.5(10)	30.5(10)	20.1(9)	15.2(8)	-4.7(7)	-6.1(7)
C00L	24.7(10)	30.8(10)	27.1(9)	0.1(8)	-4.1(8)	-6.9(8)
C00M	24.2(10)	36.4(10)	32.8(10)	-5.4(9)	3.7(8)	2.0(8)
C00N	42.3(12)	22.4(9)	23.8(9)	-1.9(9)	5.9(8)	3.4(7)
C00O	30.6(11)	35.1(10)	23.3(9)	-3.4(9)	-7.1(8)	4.8(8)
C00P	28.2(11)	28.1(10)	37.6(10)	-5.0(8)	-4.3(9)	3.1(8)
C00Q	32.0(11)	35.9(10)	32.2(10)	12.4(9)	-8.7(9)	-10.3(9)
C00R	48.5(13)	28.5(9)	20.8(9)	-2.4(9)	9.3(9)	-2.1(8)
C00U	22.4(10)	42.9(11)	42.0(11)	5.2(9)	-3.6(9)	-10.9(9)
C00V	46.8(14)	32.9(11)	49.9(13)	10.9(11)	10.7(11)	15.8(10)
C00W	53.6(14)	56.7(13)	25.0(10)	38.9(12)	-13.7(10)	-9.7(9)
C007	18.9(9)	23.8(8)	15.2(8)	4.8(7)	1.2(6)	-3.8(7)
C008	16.8(8)	20.2(8)	17.1(8)	-0.6(7)	1.4(7)	0.6(6)
C009	17.2(9)	20.6(8)	14.5(7)	3.0(7)	2.4(6)	0.1(6)
B00S	16.0(10)	20.7(9)	18.8(9)	-0.3(8)	-2.1(8)	-0.3(8)
B00T	16.5(10)	24.6(10)	16.6(8)	-0.4(9)	2.8(7)	2.4(8)

Table S7 Bond Lengths for dimedone-derived substrate.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C009	1.4306(18)	C00D	C009	1.566(2)
O002	C00I	1.4632(18)	C00E	C00I	1.562(2)
O002	B00S	1.367(2)	C00E	C00M	1.523(3)
O003	C00G	1.462(2)	C00E	C00N	1.511(2)
O003	B00T	1.367(2)	C00F	C00H	1.542(2)
O004	C00E	1.4636(18)	C00F	C007	1.496(2)
O004	B00S	1.370(2)	C00G	C00K	1.555(2)
O005	C00K	1.463(2)	C00G	C00Q	1.515(2)
O005	B00T	1.368(2)	C00G	C00V	1.528(3)
O006	C007	1.223(2)	C00H	C00L	1.534(2)
C00A	C00D	1.526(2)	C00H	C00P	1.531(2)
C00B	C00J	1.565(2)	C00I	C00O	1.519(3)
C00B	C008	1.562(2)	C00I	C00R	1.514(2)

C00B	B00S	1.573(2)	C00K	C00U	1.514(3)
C00C	C00H	1.540(2)	C00K	C00W	1.514(2)
C00C	C009	1.535(2)	C008	C009	1.543(2)
C00D	C00J	1.553(2)	C008	B00T	1.569(2)
C00D	C007	1.522(2)			

Table S8 Bond Angles for dimedone-derived substrate.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
B00S	O002	C00I	107.26(12)	C00P	C00H	C00L	108.95(14)
B00T	O003	C00G	107.40(13)	C00E	C00I	O002	102.20(12)
B00S	O004	C00E	107.13(12)	C00O	C00I	O002	106.28(14)
B00T	O005	C00K	106.94(13)	C00O	C00I	C00E	113.05(14)
C008	C00B	C00J	104.93(12)	C00R	C00I	O002	108.47(13)
B00S	C00B	C00J	109.35(13)	C00R	C00I	C00E	115.38(15)
B00S	C00B	C008	116.64(13)	C00R	C00I	C00O	110.61(15)
C009	C00C	C00H	116.96(14)	C00D	C00J	C00B	105.99(13)
C00J	C00D	C00A	109.41(13)	C00G	C00K	O005	102.65(13)
C007	C00D	C00A	110.65(13)	C00U	C00K	O005	106.38(14)
C007	C00D	C00J	111.59(13)	C00U	C00K	C00G	113.14(14)
C009	C00D	C00A	112.42(13)	C00W	C00K	O005	108.09(13)
C009	C00D	C00J	101.41(12)	C00W	C00K	C00G	115.10(16)
C009	C00D	C007	111.05(13)	C00W	C00K	C00U	110.67(17)
C00I	C00E	O004	101.78(12)	C00D	C007	O006	121.17(15)
C00M	C00E	O004	106.13(13)	C00F	C007	O006	121.55(15)
C00M	C00E	C00I	113.27(15)	C00F	C007	C00D	117.26(14)
C00N	C00E	O004	109.47(14)	C009	C008	C00B	105.97(13)
C00N	C00E	C00I	115.20(14)	B00T	C008	C00B	115.84(13)
C00N	C00E	C00M	110.23(16)	B00T	C008	C009	118.99(13)
C007	C00F	C00H	110.79(14)	C00C	C009	O001	110.32(13)
C00K	C00G	O003	102.60(12)	C00D	C009	O001	108.80(12)
C00Q	C00G	O003	108.29(13)	C00D	C009	C00C	111.68(13)
C00Q	C00G	C00K	114.97(15)	C008	C009	O001	112.09(13)
C00V	C00G	O003	106.05(15)	C008	C009	C00C	111.20(13)
C00V	C00G	C00K	113.59(15)	C008	C009	C00D	102.52(12)
C00V	C00G	C00Q	110.52(15)	O004	B00S	O002	113.02(14)
C00F	C00H	C00C	109.11(13)	C00B	B00S	O002	122.66(14)
C00L	C00H	C00C	112.28(14)	C00B	B00S	O004	124.13(14)
C00L	C00H	C00F	109.06(14)	O005	B00T	O003	113.35(15)
C00P	C00H	C00C	108.53(14)	C008	B00T	O003	125.30(15)
C00P	C00H	C00F	108.85(14)	C008	B00T	O005	121.23(15)

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for dimedone-derived substrate.

Atom	*x*	*y*	*z*	U(eq)
H001	2902(7)	6723(14)	5163.1(6)	31.6(4)
H00a	1841(8)	8868(3)	4959(2)	33.0(6)
H00b	1214(4)	9684(3)	5510(6)	33.0(6)
H00c	2403(5)	9267(6)	5753(4)	33.0(6)
H00d	2771.4(14)	8785.0(12)	7218.6(9)	22.0(4)
H00e	1190.9(14)	6272.3(12)	6810.3(9)	23.2(4)
H00f	1706.2(14)	5584.5(12)	6122.6(9)	23.2(4)
H00g	-1279.6(14)	6967.0(13)	5711.9(9)	26.5(4)
H00h	-710.0(14)	7175.9(13)	6545.7(9)	26.5(4)
H00i	589.6(14)	8030.1(13)	7114.3(9)	24.6(4)
H00j	1023.2(14)	9189.3(13)	6927.7(9)	24.6(4)
H00k	484(9)	6306(4)	4712.9(14)	41.3(6)
H00l	579(8)	5102(6)	4950.5(13)	41.3(6)
H00m	-600.8(17)	5620(9)	4824(2)	41.3(6)
H00n	143.5(15)	7234(4)	8721(7)	46.7(7)
H00o	68.1(16)	6008(7)	8553(6)	46.7(7)
H00p	70.7(16)	6430(10)	9437.8(18)	46.7(7)
H00q	1593(8)	4863.6(13)	8937(5)	44.2(7)
H00r	2754(2)	5344(4)	9184(7)	44.2(7)
H00s	1755(9)	5359(4)	9793(2)	44.2(7)
H00t	3742(3)	6898(9)	9145(2)	44.5(6)
H00u	3687(3)	7867(2)	9737(7)	44.5(6)
H00v	3331.3(16)	6729(7)	10029(5)	44.5(6)
H00w	-27(6)	4519(3)	6291(6)	47.0(7)
H00x	-488(10)	5356(5)	6905.2(17)	47.0(7)
H00y	-1192(4)	5058(7)	6144(5)	47.0(7)
H	5749(7)	3974(8)	6665(2)	50.1(7)
H00z	4659(3)	3759(6)	6167(6)	50.1(7)
Ha	5436(9)	4721(2)	5945(4)	50.1(7)
H00	1917(5)	8535(6)	10184(5)	48.9(7)
Hb	799(4)	8141(9)	9792(2)	48.9(7)
Hc	1425(9)	7419(4)	10414(3)	48.9(7)
H0aa	5880(2)	6428(10)	6312(3)	53.6(7)
Hd	6478(7)	6849(6)	7087(4)	53.6(7)
He	6680(5)	5677(4)	6797(6)	53.6(7)
H1aa	3400(9)	4800.5(16)	7847(6)	64.8(8)
Hf	3347(9)	3874(8)	7217.6(13)	64.8(8)

Hg	4334.4(19)	3925(9)	7835(6)	64.8(8)
H2aa	5932(11)	6250(5)	8378(3)	67.7(9)
Hh	4900(2)	5493(11)	8490(2)	67.7(9)
Hi	6033(10)	5038(8)	8164.0(15)	67.7(9)
H008	3320.7(14)	7939.5(12)	6194.7(9)	21.6(4)

Experimental

Single crystals of $C_{24}H_{42}B_2O_6$ **(+)-3b** were grown from hexanes/isopropyl alcohol cooled to – 20 °C. A suitable crystal was selected and mounted on a Bruker APEX-II CCD' diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of [dimedone-derived substrate]

Crystal Data for $C_{24}H_{42}B_2O_6$ **(+)-3b** (M =448.25 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.2030(4) Å, b = 12.8185(4) Å, c = 17.0176(5) Å, V = 2661.96(14) Å^3, Z = 4, T = 100.15 K, μ(Cu Kα) = 0.615 mm^{-1}, *Dcalc* = 1.1183 g/cm^3, 21235 reflections measured (8.92° ≤ 2Θ ≤ 133.08°), 4571 unique (R_{int} = 0.0402, R_{sigma} = 0.0371) which were used in all calculations. The final R_1 was 0.0338 (I>=2u(I)) and wR_2 was 0.0720 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 59.

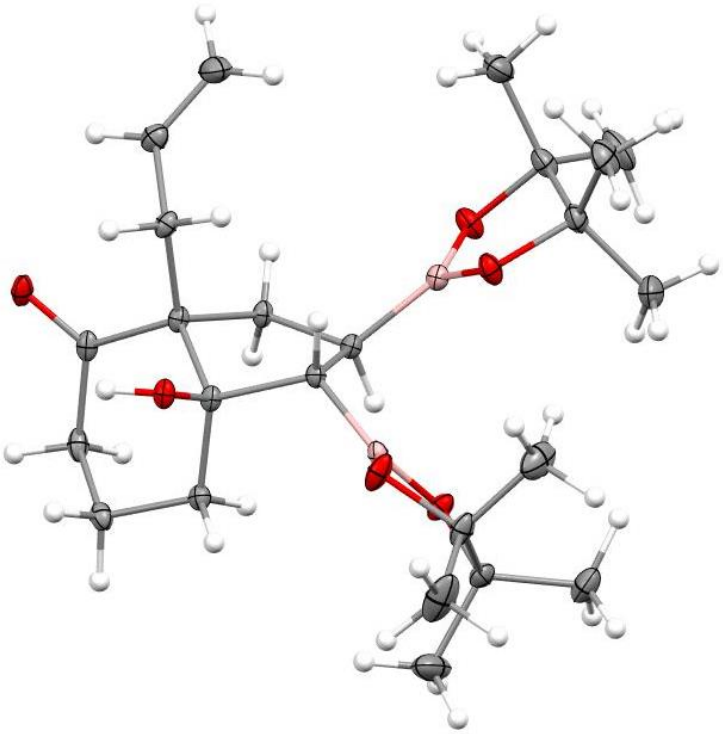
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2.a Ternary CH refined with riding coordinates:
 C00B(H00d), C008(H008)
2.b Secondary CH2 refined with riding coordinates:
 C00C(H00e,H00f), C00F(H00g,H00h), C00J(H00i,H00j)
2.c Idealised Me refined as rotating group:
 C00A(H00a,H00b,H00c), C00L(H00k,H00l,H00m), C00M(H00n,H00o,H00p), C00N(H00q,
 H00r,H00s), C00O(H00t,H00u,H00v), C00P(H00w,H00x,H00y), C00Q(H,H00z,Ha),
 C00R(H00,Hb,Hc), C00U(H0aa,Hd,He), C00V(H1aa,Hf,Hg), C00W(H2aa,Hh,Hi)
2.d Idealised tetrahedral OH refined as rotating group:
 O001(H001)
```

UNC CHAPEL HILL DEPARTMENT OF CHEMISTRY (CCDC 1916346)

X-ray Core Laboratory

Report No. 19003



C_{24} H_{40} B_2 O_6

Prepared for

Joseph Zanghi and Prof. S. Meek

by

C. Chen

January 31, 2019

The sample was submitted by Joseph Zanghi (research group of Meek, Department of Chemistry, the University of North Carolina at Chapel Hill). A colorless crystal (approximate dimensions 0.200 x 0.200 x 0.200 mm^3) was placed onto the tip of MiTeGen and mounted on a Bruker SMART Apex II diffractometer and measured at 150 K.

Data collection

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 161 reflections. The data collection was carried out using Cu Kα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9943 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2] Please refer to **Table S10** for additional crystal and refinement information.

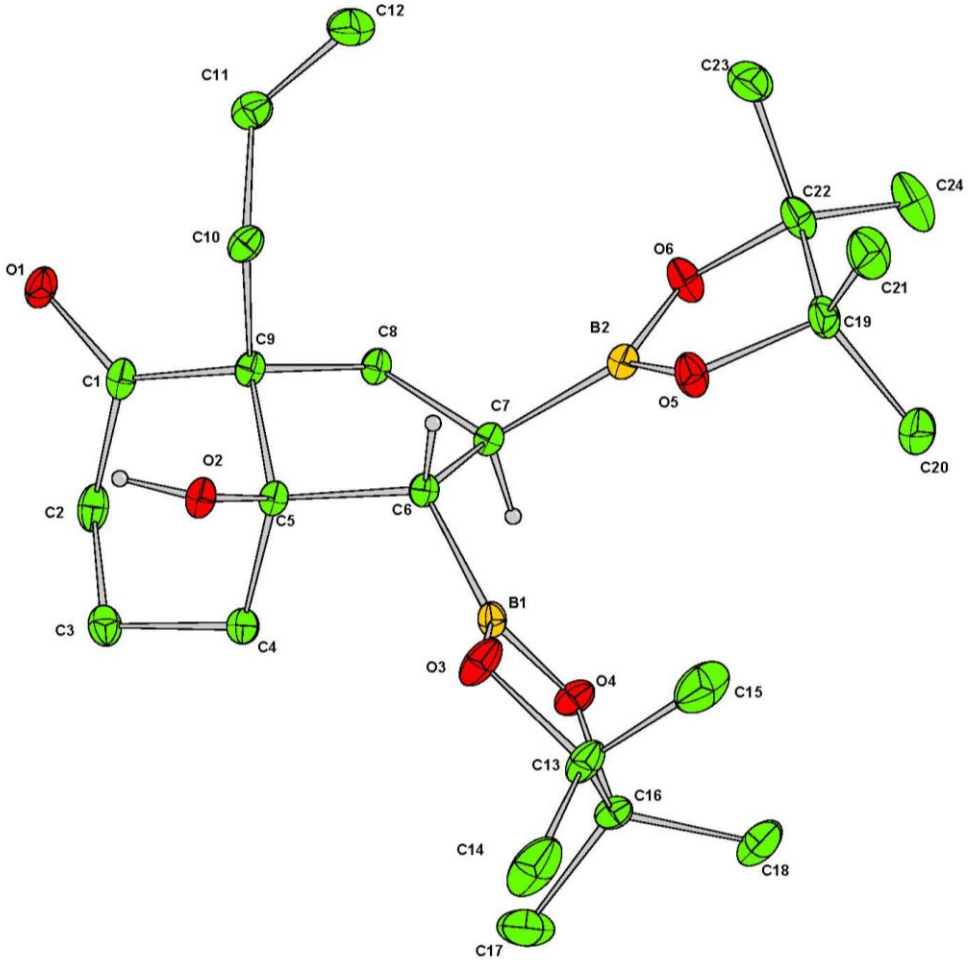
Structure solution and refinement

The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. The structure was solved using Superflip[3] and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.[4] The charge-flipping solution provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were generated geometrically and the positions were subsequently refined. The final full matrix least squares refinement converged to R1 = 0.0390 and wR2 = 0.1030 (F^2, all data).

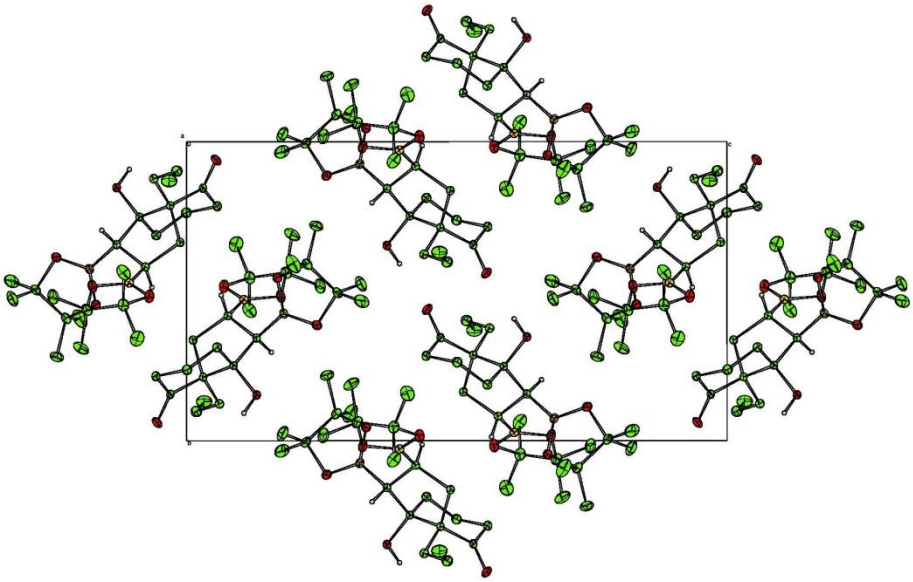
Structure description

The structure was found with two tetramethyl dioxaborolane in *trans* confirmation.

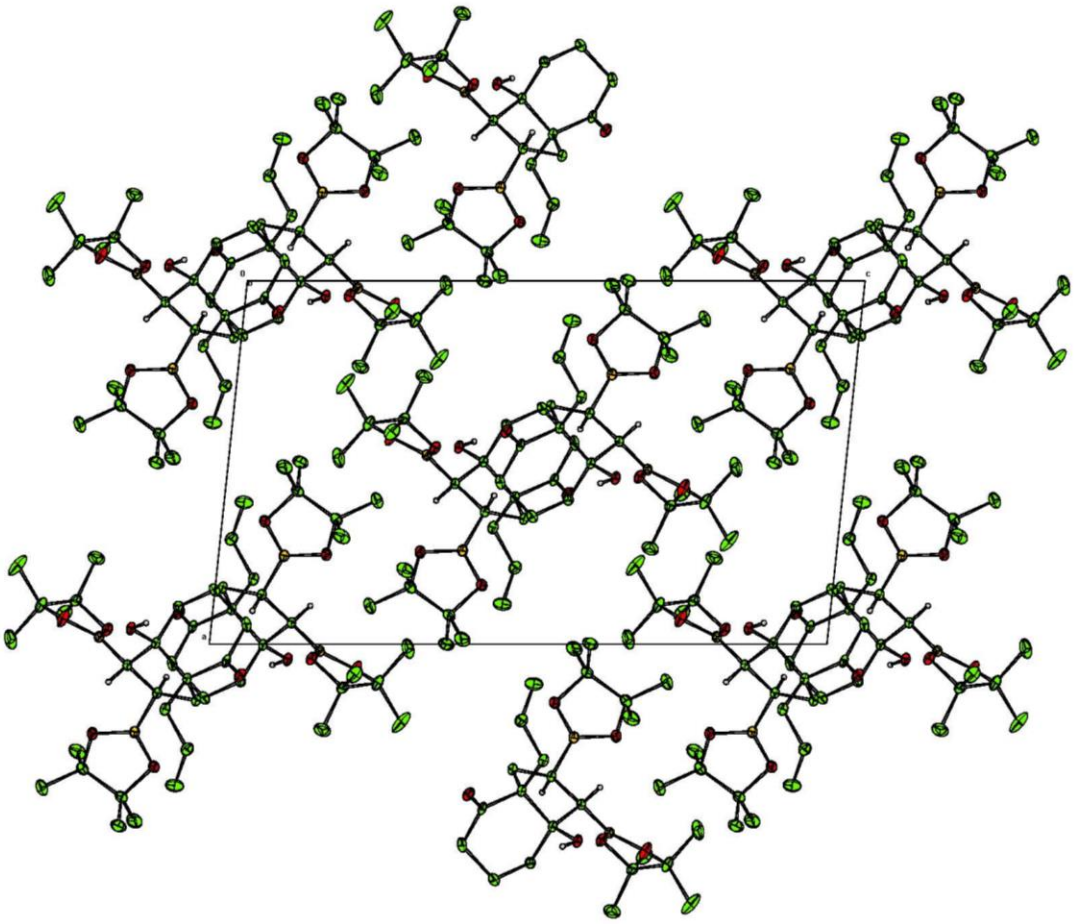
[1] SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
[2] An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 - 38 (1995).
[3] Palatinus L., Chapuis G. (2007): Superflip - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. J. Appl. Cryst. 40, 786-790.
[4] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. J. Appl. Cryst. 2003, 36, 1487.



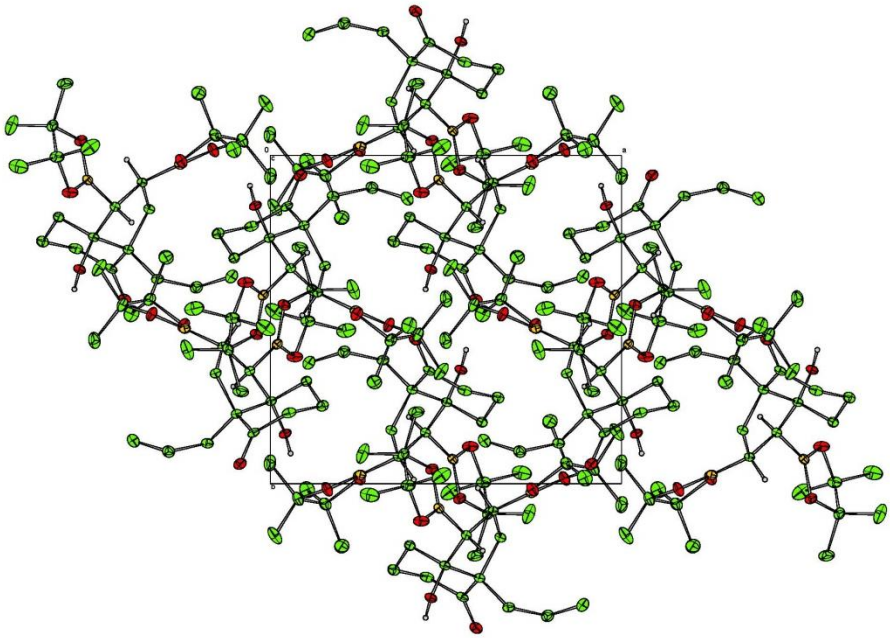
Molecular structure with labels on the asymmetric unit. Hydrogen atoms on the O2, C6, and C7 were made visible for ease of viewing.



Cell plot, viewed along a- axis



Cell plot, viewed along b- axis



Cell plot, viewed along c- axis

Table S10. Crystal data and structure refinement for 19003. (CCDC 1916346)

Empirical formula	C24 H40 B2 O6	
Formula weight	446.20	
Crystal color, shape, size	colorless block fragment, 0.200 x 0.200 x 0.200 mm^3	
Temperature	150 K	
Wavelength	1.54178 Å	
Crystal system, space group	Monoclinic, $P2_1/n$	
Unit cell dimensions	a = 11.7632(2) Å	α= 90°.
	b = 10.96830(10) Å	β= 95.9823(7)°.
	c = 19.8860(3) Å	γ = 90°.
Volume	2551.77(6) Å^3	
Z	4	
Density (calculated)	1.161 Mg/m^3	
Absorption coefficient	0.641 mm^{-1}	
F(000)	968	
Data collection		
Diffractometer	Bruker Apex Kappa Duo, Bruker	
Theta range for data collection	4.185 to 66.588°.	
Index ranges	-12<=h<=13, -12<=k<=13, -23<=l<=22	
Reflections collected	22245	
Independent reflections	4456 [R(int) = 0.022]	
Observed Reflections	4166	
Completeness to theta = 49.275°	99.5 %	
Solution and Refinement		
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.88 and 0.88	
Solution	Direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with	
	$P = (Fo^2 + 2\,Fc^2)/3$, A = 0.051, B = 1.055	
Data / restraints / parameters	4436 / 2 / 410	
Goodness-of-fit on F^2	1.0234	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1012	
R indices (all data)	R1 = 0.0410, wR2 = 0.1030	
Largest diff. peak and hole	0.25 and -0.19 e.Å^{-3}	

Table S11. Atomic coordinates ($Å^2 x\ 10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for 19003. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	4138(1)	5608(1)	4452(1)	36
O2	5427(1)	6530(1)	6295(1)	28
O3	5699(1)	8866(1)	7409(1)	45
O4	5396(1)	10450(1)	6679(1)	33
O5	2533(1)	9830(1)	6743(1)	38
O6	1623(1)	10166(1)	5690(1)	38
C1	4528(1)	6553(1)	4698(1)	27
C2	5536(1)	7160(1)	4431(1)	34
C3	6485(1)	7375(1)	5006(1)	34
C4	6027(1)	8122(1)	5564(1)	28
C5	5023(1)	7514(1)	5869(1)	24
C6	4418(1)	8436(1)	6293(1)	23
C7	3648(1)	9181(1)	5763(1)	24
C8	3446(1)	8367(1)	5119(1)	26
C9	4042(1)	7131(1)	5305(1)	24
C10	3209(1)	6235(1)	5606(1)	30
C11	2104(1)	5981(1)	5179(1)	38
C12	1100(2)	6312(2)	5323(1)	55
C13	6074(1)	9953(1)	7792(1)	40
C14	7165(3)	9664(2)	8238(1)	79
C15	5127(2)	10245(2)	8225(1)	69
C16	6201(1)	10905(1)	7231(1)	34
C17	7365(2)	10917(3)	6975(1)	73
C18	5841(2)	12187(2)	7401(1)	54
C19	1566(1)	10617(1)	6844(1)	38
C20	2035(2)	11898(2)	6953(1)	60
C21	1047(2)	10178(2)	7469(1)	55
C22	791(1)	10455(2)	6168(1)	39
C23	-8(2)	9368(2)	6164(1)	56
C24	130(2)	11577(2)	5915(1)	63
B1	5198(1)	9253(1)	6798(1)	26
B2	2574(1)	9724(1)	6061(1)	27

Table S12. Bond lengths [Å] and angles [°] for 19003.

O1-C1	1.2151(17)	O2-C5	1.4226(15)
O2-H1	0.842(14)	O3-C13	1.4583(17)
O3-B1	1.3616(17)	O4-C16	1.4607(16)
O4-B1	1.3585(18)	O5-C19	1.4584(17)
O5-B2	1.3666(18)	O6-C22	1.4675(17)
O6-B2	1.3632(18)	C1-C2	1.504(2)
C1-C9	1.5266(17)	C2-C3	1.531(2)
C2-H21	0.970(18)	C2-H22	0.992(18)
C3-C4	1.5212(19)	C3-H31	0.978(18)
C3-H32	0.997(18)	C4-C5	1.5345(18)
C4-H41	0.976(16)	C4-H42	0.984(17)
C5-C6	1.5378(17)	C5-C9	1.5807(16)
C6-C7	1.5489(16)	C6-B1	1.5697(19)
C6-H61	0.969(15)	C7-C8	1.5592(17)
C7-B2	1.5675(19)	C7-H71	0.959(16)
C8-C9	1.5532(17)	C8-H81	0.980(16)
C8-H82	0.947(16)	C9-C10	1.5505(18)
C10-C11	1.502(2)	C10-H101	0.974(17)
C10-H102	0.987(17)	C11-C12	1.296(3)
C11-H111	0.964(19)	C12-H121	0.96(2)
C12-H122	0.96(2)	C13-C14	1.515(2)
C13-C15	1.512(3)	C13-C16	1.547(2)
C14-H141	0.99(3)	C14-H142	0.97(3)
C14-H143	1.04(3)	C15-H151	0.99(3)
C15-H152	0.95(3)	C15-H153	1.00(3)
C16-C17	1.510(2)	C16-C18	1.517(2)
C17-H171	0.96(3)	C17-H172	1.01(3)
C17-H173	0.99(3)	C18-H181	0.97(2)
C18-H182	0.97(2)	C18-H183	1.05(2)
C19-C20	1.517(3)	C19-C21	1.521(2)
C19-C22	1.554(2)	C20-H201	0.93(2)
C20-H202	0.97(2)	C20-H203	0.99(2)
C21-H211	0.99(2)	C21-H212	0.99(2)
C21-H213	1.04(2)	C22-C23	1.517(3)
C22-C24	1.513(2)	C23-H231	1.00(2)
C23-H232	0.96(2)	C23-H233	1.03(2)
C24-H241	1.01(2)	C24-H242	0.98(2)
C24-H243	1.00(2)		

C5-O2-H1	110.2(12)	C13-O3-B1	106.87(11)
C16-O4-B1	107.95(11)	C19-O5-B2	107.22(11)
C22-O6-B2	107.01(11)	O1-C1-C2	120.90(12)
O1-C1-C9	121.07(13)	C2-C1-C9	117.99(11)
C1-C2-C3	110.20(11)	C1-C2-H21	109.5(10)
C3-C2-H21	108.2(10)	C1-C2-H22	109.3(10)
C3-C2-H22	112.7(10)	H21-C2-H22	106.9(14)
C2-C3-C4	109.97(12)	C2-C3-H31	111.7(10)
C4-C3-H31	108.5(10)	C2-C3-H32	109.7(10)
C4-C3-H32	110.2(10)	H31-C3-H32	106.7(14)
C3-C4-C5	113.57(11)	C3-C4-H41	109.9(9)
C5-C4-H41	107.0(9)	C3-C4-H42	109.1(9)
C5-C4-H42	108.9(9)	H41-C4-H42	108.3(13)
C4-C5-O2	110.02(10)	C4-C5-C6	110.51(10)
O2-C5-C6	108.51(9)	C4-C5-C9	111.74(10)
O2-C5-C9	113.22(10)	C6-C5-C9	102.58(9)
C5-C6-C7	104.22(9)	C5-C6-B1	116.95(10)
C7-C6-B1	113.33(10)	C5-C6-H61	106.2(9)
C7-C6-H61	110.1(9)	B1-C6-H61	105.8(9)
C6-C7-C8	106.56(10)	C6-C7-B2	112.35(10)
C8-C7-B2	117.94(11)	C6-C7-H71	107.2(9)
C8-C7-H71	106.5(9)	B2-C7-H71	105.7(9)
C7-C8-C9	106.12(10)	C7-C8-H81	110.5(9)
C9-C8-H81	110.6(9)	C7-C8-H82	112.5(9)
C9-C8-H82	110.6(10)	H81-C8-H82	106.5(13)
C8-C9-C1	111.74(10)	C8-C9-C5	102.42(9)
C1-C9-C5	111.44(10)	C8-C9-C10	110.97(11)
C1-C9-C10	110.21(11)	C5-C9-C10	109.83(10)
C9-C10-C11	116.34(11)	C9-C10-H101	107.1(10)
C11-C10-H101	109.3(9)	C9-C10-H102	106.9(9)
C11-C10-H102	107.4(9)	H101-C10-H102	109.6(14)
C10-C11-C12	125.35(17)	C10-C11-H111	114.8(11)
C12-C11-H111	119.8(11)	C11-C12-H121	118.0(13)
C11-C12-H122	123.3(13)	H121-C12-H122	118.6(19)
O3-C13-C14	109.06(14)	O3-C13-C15	105.67(14)
C14-C13-C15	109.92(19)	O3-C13-C16	102.80(11)
C14-C13-C16	115.05(17)	C15-C13-C16	113.60(16)
C13-C14-H141	108.4(15)	C13-C14-H142	113.7(17)
H141-C14-H142	111(2)	C13-C14-H143	106.0(15)
H141-C14-H143	110(2)	H142-C14-H143	108(2)
C13-C15-H151	108.6(14)	C13-C15-H152	107.8(16)
H151-C15-H152	110(2)	C13-C15-H153	111.4(15)
H151-C15-H153	111(2)	H152-C15-H153	108(2)

C13-C16-O4	102.00(11)	C13-C16-C17	114.12(17)
O4-C16-C17	106.80(13)	C13-C16-C18	114.47(14)
O4-C16-C18	108.09(12)	C17-C16-C18	110.55(17)
C16-C17-H171	108.1(17)	C16-C17-H172	111.1(15)
H171-C17-H172	110(2)	C16-C17-H173	110.8(15)
H171-C17-H173	109(2)	H172-C17-H173	107(2)
C16-C18-H181	109.2(13)	C16-C18-H182	109.5(13)
H181-C18-H182	104.7(17)	C16-C18-H183	110.2(12)
H181-C18-H183	111.4(17)	H182-C18-H183	111.6(17)
O5-C19-C20	106.89(13)	O5-C19-C21	108.09(14)
C20-C19-C21	110.36(15)	O5-C19-C22	102.05(11)
C20-C19-C22	113.68(16)	C21-C19-C22	114.97(14)
C19-C20-H201	111.6(14)	C19-C20-H202	107.6(14)
H201-C20-H202	109.5(19)	C19-C20-H203	112.3(14)
H201-C20-H203	105.8(19)	H202-C20-H203	110.0(19)
C19-C21-H211	108.6(13)	C19-C21-H212	107.8(13)
H211-C21-H212	107.4(18)	C19-C21-H213	112.1(12)
H211-C21-H213	108.4(17)	H212-C21-H213	112.4(18)
C19-C22-O6	102.32(11)	C19-C22-C23	113.66(15)
O6-C22-C23	106.34(13)	C19-C22-C24	115.38(16)
O6-C22-C24	108.42(13)	C23-C22-C24	109.93(16)
C22-C23-H231	108.8(13)	C22-C23-H232	109.5(13)
H231-C23-H232	105.1(17)	C22-C23-H233	110.6(12)
H231-C23-H233	111.9(18)	H232-C23-H233	110.7(18)
C22-C24-H241	107.9(14)	C22-C24-H242	107.8(14)
H241-C24-H242	109.8(19)	C22-C24-H243	109.3(13)
H241-C24-H243	118.0(20)	H242-C24-H243	103.5(19)
C6-B1-O3	124.26(12)	C6-B1-O4	122.62(12)
O3-B1-O4	113.04(12)	C7-B2-O5	121.40(12)
C7-B2-O6	125.37(12)	O5-B2-O6	113.20(12)

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 19003. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	41(1)	34(1)	31(1)	-13(1)	-7(1)	7(1)
O2	39(1)	24(1)	20(1)	0(1)	-1(1)	7(1)
O3	70(1)	28(1)	30(1)	-4(1)	-20(1)	1(1)
O4	41(1)	29(1)	27(1)	-1(1)	-6(1)	-6(1)
O5	38(1)	49(1)	25(1)	-7(1)	4(1)	12(1)
O6	33(1)	52(1)	28(1)	2(1)	6(1)	15(1)
C1	38(1)	24(1)	18(1)	1(1)	-5(1)	10(1)
C2	54(1)	28(1)	23(1)	0(1)	11(1)	9(1)
C3	38(1)	32(1)	32(1)	1(1)	12(1)	4(1)
C4	31(1)	28(1)	27(1)	0(1)	4(1)	2(1)
C5	30(1)	22(1)	18(1)	0(1)	0(1)	4(1)
C6	28(1)	23(1)	19(1)	0(1)	3(1)	2(1)
C7	29(1)	21(1)	21(1)	0(1)	1(1)	1(1)
C8	32(1)	24(1)	20(1)	-1(1)	0(1)	4(1)
C9	32(1)	22(1)	18(1)	0(1)	0(1)	3(1)
C10	39(1)	25(1)	25(1)	0(1)	-1(1)	-2(1)
C11	40(1)	36(1)	37(1)	0(1)	-1(1)	-3(1)
C12	40(1)	46(1)	80(1)	0(1)	10(1)	-10(1)
C13	55(1)	32(1)	30(1)	-9(1)	-12(1)	-1(1)
C14	101(2)	53(1)	69(1)	-14(1)	-55(1)	11(1)
C15	96(2)	73(1)	41(1)	-22(1)	24(1)	-30(1)
C16	32(1)	36(1)	32(1)	-9(1)	-3(1)	-5(1)
C17	45(1)	108(2)	69(1)	-35(1)	16(1)	-29(1)
C18	68(1)	32(1)	59(1)	-9(1)	-11(1)	-5(1)
C19	38(1)	42(1)	36(1)	-9(1)	11(1)	8(1)
C20	57(1)	52(1)	75(1)	-28(1)	23(1)	-2(1)
C21	62(1)	70(1)	37(1)	-8(1)	20(1)	6(1)
C22	33(1)	49(1)	37(1)	-2(1)	10(1)	12(1)
C23	37(1)	72(1)	60(1)	-20(1)	14(1)	-5(1)
C24	53(1)	77(2)	62(1)	10(1)	15(1)	34(1)
B1	28(1)	27(1)	22(1)	-4(1)	3(1)	5(1)
B2	32(1)	24(1)	25(1)	-1(1)	2(1)	1(1)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 19003.

	x	y	z	U(eq)
H21	5304(14)	7944(17)	4237(9)	41
H22	5793(14)	6659(16)	4060(9)	41
H31	7134(15)	7809(16)	4849(8)	40
H32	6782(14)	6577(17)	5189(8)	40
H41	6629(14)	8247(15)	5933(8)	34
H42	5779(13)	8924(16)	5382(8)	34
H61	3950(12)	7960(14)	6569(8)	28
H71	4085(13)	9870(15)	5641(8)	28
H81	3777(13)	8749(14)	4738(8)	31
H82	2659(14)	8248(14)	4977(8)	31
H101	3046(13)	6568(15)	6039(9)	36
H102	3617(14)	5451(16)	5678(8)	36
H111	2177(15)	5499(17)	4781(10)	46
H121	1051(18)	6770(20)	5730(11)	66
H122	407(19)	6120(20)	5045(11)	66
H141	7410(20)	10410(30)	8495(14)	94
H142	7090(20)	8980(30)	8542(14)	94
H143	7760(20)	9430(30)	7913(14)	94
H151	5370(20)	10950(20)	8522(13)	83
H152	5000(20)	9540(20)	8489(13)	83
H153	4390(20)	10440(20)	7941(13)	83
H171	7320(20)	11410(20)	6574(15)	88
H172	7960(20)	11250(20)	7327(14)	88
H173	7600(20)	10080(30)	6866(14)	88
H181	5963(18)	12730(20)	7028(11)	65
H182	6345(18)	12490(20)	7781(11)	65
H183	4980(19)	12190(20)	7504(10)	65
H201	1470(20)	12450(20)	7036(11)	72
H202	2610(20)	11870(20)	7339(12)	72
H203	2370(20)	12210(20)	6551(12)	72
H211	394(19)	10710(20)	7544(11)	66
H212	1631(19)	10280(20)	7863(12)	66
H213	751(18)	9290(20)	7418(11)	66
H231	-406(18)	9270(20)	5698(12)	67
H232	-605(19)	9540(20)	6446(11)	67
H233	436(19)	8600(20)	6327(11)	67

H241	-390(20)	11340(20)	5499(13)	76
H242	-330(20)	11840(20)	6270(12)	76
H243	670(20)	12270(20)	5879(12)	76
H1	5577(15)	5924(14)	6060(8)	43(2)

Table S15. Torsion angles [°] for 19003.

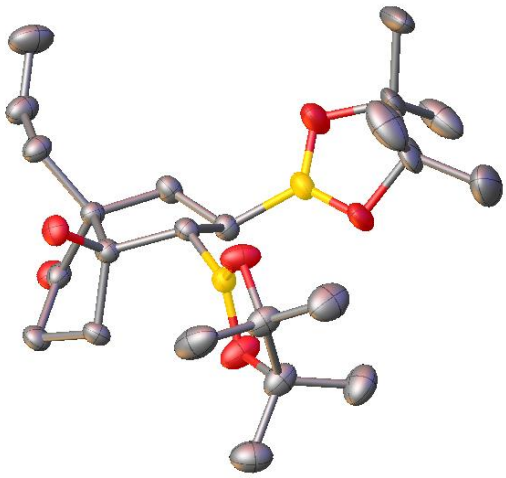
B1-O3-C13-C14	-146.41(16)	B1-O3-C13-C15	95.47(14)
B1-O3-C13-C16	-23.88(15)	C13-O3-B1-O4	12.32(16)
C13-O3-B1-C6	-164.73(13)	B1-O4-C16-C13	-20.14(14)
B1-O4-C16-C17	99.89(17)	B1-O4-C16-C18	-141.13(13)
C16-O4-B1-O3	5.94(15)	C16-O4-B1-C6	-176.97(12)
B2-O5-C19-C20	-95.31(16)	B2-O5-C19-C21	145.88(13)
B2-O5-C19-C22	24.29(14)	C19-O5-B2-O6	-11.41(16)
C19-O5-B2-C7	166.68(12)	B2-O6-C22-C19	22.35(15)
B2-O6-C22-C23	-97.12(14)	B2-O6-C22-C24	144.72(14)
C22-O6-B2-O5	-7.99(16)	C22-O6-B2-C7	174.02(13)
O1-C1-C2-C3	-125.68(14)	C9-C1-C2-C3	51.75(16)
O1-C1-C9-C5	132.70(12)	O1-C1-C9-C8	-113.39(14)
O1-C1-C9-C10	10.49(17)	C2-C1-C9-C5	-44.73(15)
C2-C1-C9-C8	69.18(15)	C2-C1-C9-C10	-166.94(11)
C1-C2-C3-C4	-56.35(15)	C2-C3-C4-C5	59.34(15)
C3-C4-C5-O2	74.33(13)	C3-C4-C5-C6	-165.86(11)
C3-C4-C5-C9	-52.32(14)	O2-C5-C6-C7	-159.73(10)
O2-C5-C6-B1	74.31(13)	C4-C5-C6-C7	79.56(12)
C4-C5-C6-B1	-46.40(14)	C9-C5-C6-C7	-39.69(11)
C9-C5-C6-B1	-165.65(10)	O2-C5-C9-C1	-82.14(12)
O2-C5-C9-C8	158.27(10)	O2-C5-C9-C10	40.30(14)
C4-C5-C9-C1	42.75(14)	C4-C5-C9-C8	-76.84(12)
C4-C5-C9-C10	165.19(11)	C6-C5-C9-C1	161.14(10)
C6-C5-C9-C8	41.55(11)	C6-C5-C9-C10	-76.43(12)
C5-C6-C7-C8	22.72(13)	C5-C6-C7-B2	153.32(10)
B1-C6-C7-C8	150.93(11)	B1-C6-C7-B2	-78.48(13)
C5-C6-B1-O3	-77.97(16)	C5-C6-B1-O4	105.26(14)
C7-C6-B1-O3	160.74(12)	C7-C6-B1-O4	-16.03(17)
C6-C7-C8-C9	3.52(13)	B2-C7-C8-C9	-123.83(12)
C6-C7-B2-O5	18.39(17)	C6-C7-B2-O6	-163.77(12)
C8-C7-B2-O5	142.92(12)	C8-C7-B2-O6	-39.24(18)
C7-C8-C9-C1	-146.86(11)	C7-C8-C9-C5	-27.47(12)
C7-C8-C9-C10	89.69(12)	C1-C9-C10-C11	-68.85(15)
C5-C9-C10-C11	168.00(11)	C8-C9-C10-C11	55.47(15)
C9-C10-C11-C12	-112.32(19)	O3-C13-C16-O4	26.30(14)

O3-C13-C16-C17	-88.46(18)	O3-C13-C16-C18	142.76(14)
C14-C13-C16-O4	144.70(14)	C14-C13-C16-C17	29.9(2)
C14-C13-C16-C18	-98.84(18)	C15-C13-C16-O4	-87.38(15)
C15-C13-C16-C17	157.86(18)	C15-C13-C16-C18	29.1(2)
O5-C19-C22-O6	-27.94(14)	O5-C19-C22-C23	86.26(15)
O5-C19-C22-C24	-145.45(14)	C20-C19-C22-O6	86.77(16)
C20-C19-C22-C23	-159.03(16)	C20-C19-C22-C24	-30.7(2)
C21-C19-C22-O6	-144.66(14)	C21-C19-C22-C23	-30.5(2)
C21-C19-C22-C24	97.83(19)		

Symmetry transformations used to generate equivalent atoms:

Table S16. Crystal data and structure refinement for (-)-(5b). (CCDC 1922369)

Identification code	[5,5] allyl
Empirical formula	$C_{23}H_{38}B_2O_6$
Formula weight	432.171
Temperature/K	150
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.54340(10)
b/Å	17.4634(4)
c/Å	21.8142(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2492.71(9)
Z	4
ρ_{calc}g/cm^3	1.07
μ/mm^{-1}	0.592
F(000)	863.610
Crystal size/mm^3	0.04 mm x 0.09 mm x 0.45 mm
Radiation	Cu Kα (λ = 1.54178 Å)
Θ range for data collection/°	3 to 66
Index ranges	$-7 \leq h \leq 7$, $-20 \leq k \leq 20$, $-25 \leq l \leq 25$
Reflections collected	24,646
Independent reflections	4396 [R_{int} = 0.0381]
Data/restraints/parameters	4373/20/281
Goodness-of-fit on F^2	1.0024
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.1895
Final R indexes [all data]	R_1 = 0.071, wR_2 = 0.1939
Flack parameter	0.02(7)



(-)-5b

Table S17. Fractional Atomic Coordinates ($Å^2×10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2×10^3$) for [5,5] allyl. U_{eqis} defined as 1/3 of the trace of the orthogonalised U^{IJ} tensor.

Label	*x*	*y*	*z*	$U_{iso/equiv}$	Occupancy
O1	0.3504(3)	0.36603(12)	0.29201(9)	0.0280	1.0000
O2	-0.2937(3)	0.33716(12)	0.36456(10)	0.0296	1.0000
O3	0.3202	0.6014	0.4715	0.0419	0.7329
O4	0.2976	0.4943	0.5288	0.0481	0.7329
O5	0.2734(4)	0.59371(13)	0.30771(13)	0.0409	1.0000
O6	0.6001(3)	0.55709(13)	0.32762(11)	0.0369	1.0000
C1	0.2084(4)	0.40927(15)	0.32765(12)	0.0213	1.0000
C2	0.0553(4)	0.44455(16)	0.28240(12)	0.0231	1.0000
C3	-0.1116(4)	0.38407(17)	0.27511(14)	0.0269	1.0000
C4	-0.1351(4)	0.35653(16)	0.34061(13)	0.0239	1.0000
C5	0.0729(4)	0.35945(15)	0.37236(12)	0.0209	1.0000
C6	0.0650(5)	0.40427(17)	0.43369(13)	0.0267	1.0000
C7	0.1523(4)	0.48473(17)	0.41961(12)	0.0242	1.0000
C8	0.3141(4)	0.46854(16)	0.36960(12)	0.0215	1.0000
C9	0.1547(5)	0.27658(17)	0.37984(15)	0.0290	1.0000
C10	0.0356(5)	0.22679(18)	0.42291(16)	0.0360	1.0000
C11	0.1119(7)	0.1918(2)	0.4702(2)	0.0534	1.0000
C12	0.4662	0.6110	0.5229	0.0433	0.7329
C13	0.3802	0.5534	0.5696	0.0457	0.7329
C14	0.4600	0.6941	0.5398	0.0669	0.7329
C15	0.6811	0.5915	0.4967	0.0671	0.7329
C16	0.2149	0.5891	0.6100	0.0603	0.7329
C17	0.5476	0.5143	0.6085	0.0653	0.7329
C18	0.3987(5)	0.65666(18)	0.28591(17)	0.0344	1.0000
C19	0.6190(5)	0.62211(18)	0.28607(16)	0.0329	1.0000
C20	0.3687(6)	0.7224(2)	0.3302(2)	0.0504	1.0000
C21	0.3226(6)	0.6799(2)	0.22268(19)	0.0482	1.0000
C22	0.7817(6)	0.6758(2)	0.3085(2)	0.0534	1.0000
C23	0.6776(7)	0.5874(2)	0.22344(18)	0.0526	1.0000
B1	0.2543(6)	0.5267(2)	0.47613(15)	0.0276	1.0000
B2	0.3999(5)	0.54158(17)	0.33486(14)	0.0230	1.0000
H21	-0.0013(4)	0.49211(16)	0.30026(12)	0.0282	1.0000
H22	0.1219(4)	0.45814(16)	0.24485(12)	0.0283	1.0000
H31	-0.2356(4)	0.40560(17)	0.25776(14)	0.0319	1.0000
H32	-0.0670(4)	0.34251(17)	0.24892(14)	0.0318	1.0000
H61	0.1497(5)	0.37733(17)	0.46343(13)	0.0315	1.0000

H62	-0.0739(5)	0.40780(17)	0.44924(13)	0.0325	1.0000
H71	0.0459(4)	0.51505(17)	0.40134(12)	0.0288	1.0000
H81	0.4278(4)	0.44400(16)	0.38871(12)	0.0255	1.0000
H91	0.2955(5)	0.28052(17)	0.39562(15)	0.0344	1.0000
H92	0.1532(5)	0.25119(17)	0.33901(15)	0.0344	1.0000
H101	-0.1031(5)	0.21995(18)	0.41465(16)	0.0431	1.0000
H111	0.0272(7)	0.1616(2)	0.4948(2)	0.0645	1.0000
H112	0.2532(7)	0.1976(2)	0.4774(2)	0.0643	1.0000
H141	0.5435(13)	0.7018(3)	0.5752(3)	0.1000	0.7329
H142	0.3226(13)	0.7078(3)	0.5482(3)	0.1002	0.7329
H143	0.5088(13)	0.7233(3)	0.5064(3)	0.1001	0.7329
H151	0.7792(9)	0.6018(5)	0.5276(3)	0.1011	0.7329
H152	0.7086(9)	0.6243(5)	0.4625(3)	0.1008	0.7329
H153	0.6902(9)	0.5378(5)	0.4852(3)	0.1003	0.7329
H161	0.1352(9)	0.5487(5)	0.6272(3)	0.0909	0.7329
H162	0.2712(9)	0.6193(5)	0.6412(3)	0.0902	0.7329
H163	0.1319(9)	0.6216(5)	0.5864(3)	0.0907	0.7329
H171	0.4837(12)	0.4744(4)	0.6305(3)	0.0981	0.7329
H172	0.6055(12)	0.5495(4)	0.6367(3)	0.0979	0.7329
H173	0.6546(12)	0.4944(4)	0.5835(3)	0.0977	0.7329
H201	0.4333(6)	0.7681(2)	0.3153(2)	0.0758	1.0000
H202	0.4241(6)	0.7087(2)	0.3692(2)	0.0755	1.0000
H203	0.2261(6)	0.7318(2)	0.3353(2)	0.0756	1.0000
H211	0.4169(6)	0.7177(2)	0.20575(19)	0.0718	1.0000
H212	0.1826(6)	0.6994(2)	0.22499(19)	0.0722	1.0000
H213	0.3249(6)	0.6340(2)	0.19932(19)	0.0717	1.0000
H221	0.9176(6)	0.6525(2)	0.3034(2)	0.0797	1.0000
H222	0.7589(6)	0.6810(2)	0.3535(2)	0.0787	1.0000
H223	0.7750(6)	0.7256(2)	0.2882(2)	0.0803	1.0000
H231	0.8121(7)	0.5652(2)	0.22792(18)	0.0793	1.0000
H232	0.6866(7)	0.6267(2)	0.19182(18)	0.0783	1.0000
H233	0.5779(7)	0.5475(2)	0.21203(18)	0.0792	1.0000

Table S18 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for [5,5] allyl product. The Anisotropic displacement factor exponent takes the form: $-\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Label	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0243(10)	0.0310(11)	0.0287(10)	-0.0055(8)	0.0044(8)	0.0015(8)
O2	0.0192(10)	0.0331(11)	0.0365(11)	0.0024(9)	0.0024(9)	-0.0007(9)
O3	0.0596	0.0327	0.0333	-0.0019	-0.0256	-0.0082
O4	0.0721	0.0368	0.0354	0.0008	-0.0240	-0.0122

O5	0.0263(11)	0.0318(12)	0.0645(16)	0.0133(11)	0.0077(11)	-0.0000(10)
O6	0.0259(11)	0.0397(12)	0.0452(13)	0.0192(11)	-0.0006(9)	-0.0012(10)
C1	0.0178(13)	0.0235(13)	0.0225(13)	-0.0003(11)	-0.0003(10)	-0.0004(11)
C2	0.0211(13)	0.0289(14)	0.0192(12)	0.0032(11)	-0.0025(10)	-0.0022(11)
C3	0.0220(14)	0.0317(15)	0.0269(14)	-0.0006(11)	-0.0074(12)	-0.0024(12)
C4	0.0198(14)	0.0198(13)	0.0322(14)	-0.0013(11)	-0.0028(12)	-0.0006(10)
C5	0.0188(13)	0.0208(13)	0.0231(13)	0.0007(10)	-0.0016(11)	-0.0016(10)
C6	0.0273(14)	0.0302(15)	0.0225(13)	0.0000(12)	-0.0011(12)	-0.0046(12)
C7	0.0230(13)	0.0269(14)	0.0227(13)	-0.0004(11)	-0.0003(11)	-0.0026(11)
C8	0.0183(12)	0.0251(14)	0.0210(13)	-0.0002(10)	-0.0031(11)	0.0002(11)
C9	0.0242(14)	0.0245(14)	0.0384(16)	0.0029(12)	-0.0027(13)	0.0009(11)
C10	0.0313(16)	0.0277(15)	0.0489(19)	0.0065(14)	-0.0062(14)	-0.0027(13)
C11	0.052(2)	0.047(2)	0.061(2)	0.0261(19)	-0.008(2)	-0.0044(18)
C12	0.0370	0.0488	0.0440	-0.0180	-0.0173	-0.0091
C13	0.0711	0.0372	0.0288	-0.0072	-0.0291	-0.0020
C14	0.0910	0.0466	0.0631	-0.0072	-0.0258	-0.0175
C15	0.0361	0.1102	0.0550	-0.0230	-0.0037	-0.0174
C16	0.0411	0.1046	0.0352	-0.0099	-0.0066	0.0037
C17	0.0930	0.0630	0.0401	-0.0136	-0.0389	0.0313
C18	0.0249(15)	0.0277(15)	0.0507(19)	0.0038(14)	0.0074(14)	-0.0020(13)
C19	0.0257(15)	0.0295(15)	0.0435(18)	0.0088(13)	0.0074(14)	-0.0006(13)
C20	0.039(2)	0.0396(19)	0.073(3)	-0.0118(19)	0.0016(19)	0.0069(16)
C21	0.0370(19)	0.054(2)	0.054(2)	0.0131(18)	-0.0043(17)	0.0032(16)
C22	0.0311(19)	0.048(2)	0.081(3)	0.007(2)	-0.0044(19)	-0.0050(17)
C23	0.061(2)	0.050(2)	0.047(2)	0.0139(17)	0.0173(19)	0.0191(19)
B1	0.0301(16)	0.0309(15)	0.0217(14)	-0.0055(12)	-0.0040(13)	-0.0000(13)
B2	0.0235(16)	0.0227(15)	0.0227(14)	-0.0010(11)	-0.0024(12)	-0.0015(12)

Table S19 Bond Lengths for [5,5] allyl product.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.428(3)Å	O2	C4	1.210(4)Å
O3	C12	1.482(5)Å	O3	B1	1.377(5)Å
O4	C13	1.466(5)Å	O4	B1	1.313(5)Å
O5	C18	1.452(4)Å	O5	B2	1.366(4)Å
O6	C19	1.458(4)Å	O6	B2	1.348(4)Å
C1	C2	1.535(4)Å	C1	C5	1.580(4)Å
C1	C8	1.545(4)Å	C2	C3	1.528(4)Å
C2	H21	0.989Å	C2	H22	0.958Å
C3	C4	1.515(4)Å	C3	H31	0.971Å

C3	H32	0.969Å	C4	C5	1.527(4)Å
C5	C6	1.551(4)Å	C5	C9	1.552(4)Å
C6	C7	1.548(4)Å	C6	H61	0.974Å
C6	H62	0.972Å	C7	C8	1.546(4)Å
C7	B1	1.582(4)Å	C7	H71	0.961Å
C8	B2	1.586(4)Å	C8	H81	0.954Å
C9	C10	1.499(4)Å	C9	H91	0.987Å
C9	H92	0.995Å	C10	C11	1.298(5)Å
C10	H101	0.933Å	C11	H111	0.934Å
C11	H112	0.944Å	C12	C13	1.540(8)Å
C12	C14	1.497(7)Å	C12	C15	1.555(8)Å
C13	C16	1.529(8)Å	C13	C17	1.544(7)Å
C14	H141	0.956Å	C14	H142	0.948Å
C14	H143	0.944Å	C15	H151	0.947Å
C15	H152	0.959Å	C15	H153	0.972Å
C16	H161	0.954Å	C16	H162	0.936Å
C16	H163	0.940Å	C17	H171	0.944Å
C17	H172	0.948Å	C17	H173	0.953Å
C18	C19	1.563(4)Å	C18	C20	1.513(5)Å
C18	C21	1.522(5)Å	C19	C22	1.501(5)Å
C19	C23	1.543(5)Å	C20	H201	0.960Å
C20	H202	0.956Å	C20	H203	0.954Å
C21	H211	0.977Å	C21	H212	0.979Å
C21	H213	0.950Å	C22	H221	0.984Å
C22	H222	0.996Å	C22	H223	0.977Å
C23	H231	0.967Å	C23	H232	0.975Å
C23	H233	0.987Å			

Table S20. Bond angles for [5,5] allyl product.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C12	O3	B1	104.7(3)°	C13	O4	B1	107.9(3)°
C18	O5	B2	107.7(2)°	C19	O6	B2	108.2(2)°
O1	C1	C2	106.7(2)°	O1	C1	C5	114.2(2)°
C2	C1	C5	104.6(2)°	O1	C1	C8	112.7(2)°
C2	C1	C8	113.8(2)°	C5	C1	C8	104.8(2)°
C1	C2	C3	104.8(2)°	C1	C2	H21	109.152°
C3	C2	H21	110.685°	C1	C2	H22	110.629°
C3	C2	H22	114.065°	H21	C2	H22	107.426°
C2	C3	C4	101.2(2)°	C2	C3	H31	111.733°

C4	C3	H31	113.960°	C2	C3	H32	111.330°
C4	C3	H32	110.418°	H31	C3	H32	108.172°
O2	C4	C3	125.6(3)°	O2	C4	C5	125.3(3)°
C3	C4	C5	109.1(2)°	C1	C5	C4	103.8(2)°
C1	C5	C6	105.9(2)°	C4	C5	C6	112.2(2)°
C1	C5	C9	112.6(2)°	C4	C5	C9	108.9(2)°
C6	C5	C9	113.0(2)°	C5	C6	C7	105.9(2)°
C5	C6	H61	108.177°	C7	C6	H61	111.132°
C5	C6	H62	111.357°	C7	C6	H62	110.905°
H61	C6	H62	109.267°	C6	C7	C8	103.1(2)°
C6	C7	B1	115.0(2)°	C8	C7	B1	110.2(2)°
C6	C7	H71	108.357°	C8	C7	H71	107.709°
B1	C7	H71	111.918°	C1	C8	C7	103.5(2)°
C1	C8	B2	114.5(2)°	C7	C8	B2	115.6(2)°
C1	C8	H81	107.870°	C7	C8	H81	107.912°
B2	C8	H81	107.119°	C5	C9	C10	115.3(3)°
C5	C9	H91	107.099°	C10	C9	H91	107.890°
C5	C9	H92	108.575°	C10	C9	H92	107.322°
H91	C9	H92	110.623°	C9	C10	C11	124.8(3)°
C9	C10	H101	117.309°	C11	C10	H101	117.844°
C10	C11	H111	119.569°	C10	C11	H112	117.324°
H111	C11	H112	123.092°	O3	C12	C13	101.0(4)°
O3	C12	C14	106.2(5)°	C13	C12	C14	117.4(5)°
O3	C12	C15	106.3(4)°	C13	C12	C15	115.4(5)°
C14	C12	C15	109.1(6)°	O4	C13	C12	101.2(3)°
O4	C13	C16	112.1(5)°	C12	C13	C16	111.9(5)°
O4	C13	C17	106.5(4)°	C12	C13	C17	113.1(5)°
C16	C13	C17	111.5(4)°	C12	C14	H141	108.694°
C12	C14	H142	108.621°	H141	C14	H142	110.418°
C12	C14	H143	108.918°	H141	C14	H143	110.669°
H142	C14	H143	109.475°	C12	C15	H151	108.086°
C12	C15	H152	108.950°	H151	C15	H152	108.320°
C12	C15	H153	111.199°	H151	C15	H153	108.983°
H152	C15	H153	111.208°	C13	C16	H161	108.106°
C13	C16	H162	111.740°	H161	C16	H162	110.338°
C13	C16	H163	109.830°	H161	C16	H163	110.253°
H162	C16	H163	106.581°	C13	C17	H171	106.903°
C13	C17	H172	110.706°	H171	C17	H172	108.962°
C13	C17	H173	111.613°	H171	C17	H173	110.355°
H172	C17	H173	108.279°	O5	C18	C19	103.2(2)°

O5	C18	C20	107.0(3)°	C19	C18	C20	114.3(3)°
O5	C18	C21	108.3(3)°	C19	C18	C21	114.0(3)°
C20	C18	C21	109.5(3)°	O6	C19	C18	102.9(2)°
O6	C19	C22	110.1(3)°	C18	C19	C22	114.4(3)°
O6	C19	C23	105.4(3)°	C18	C19	C23	112.3(3)°
C22	C19	C23	111.0(3)°	C18	C20	H201	111.025°
C18	C20	H202	109.199°	H201	C20	H202	110.050°
C18	C20	H203	109.433°	H201	C20	H203	109.034°
H202	C20	H203	108.043°	C18	C21	H211	108.401°
C18	C21	H212	110.645°	H211	C21	H212	112.052°
C18	C21	H213	104.854°	H211	C21	H213	110.979°
H212	C21	H213	109.667°	C19	C22	H221	110.219°
C19	C22	H222	105.763°	H221	C22	H222	106.513°
C19	C22	H223	112.116°	H221	C22	H223	110.976°
H222	C22	H223	110.986°	C19	C23	H231	107.087°
C19	C23	H232	111.363°	H231	C23	H232	107.360°
C19	C23	H233	109.685°	H231	C23	H233	110.176°
H232	C23	H233	111.067°	O3	B1	O4	113.9(3)°
O3	B1	C7	120.9(3)°	O4	B1	C7	125.0(3)°
O5	B2	O6	113.9(3)°	O5	B2	C8	121.9(3)°
O6	B2	C8	124.2(3)°				

Table S21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for [5,5] allyl product.

Atom	x/a	y/b	z/c	U(eq)	Occupancy
H21	-0.0013	0.4921	0.3003	0.0282	1
H22	0.1219	0.4581	0.2448	0.0283	1
H31	-0.2356	0.4056	0.2578	0.0319	1
H32	-0.067	0.3425	0.2489	0.0318	1
H61	0.1497	0.3773	0.4634	0.0315	1
H62	-0.0739	0.4078	0.4492	0.0325	1
H71	0.0459	0.515	0.4013	0.0288	1
H81	0.4278	0.444	0.3887	0.0255	1
H91	0.2955	0.2805	0.3956	0.0344	1
H92	0.1532	0.2512	0.339	0.0344	1
H101	-0.1031	0.2199	0.4147	0.0431	1
H111	0.0272	0.1616	0.4948	0.0645	1
H112	0.2532	0.1976	0.4774	0.0643	1
H141	0.5435	0.7018	0.5752	0.1	0.7329

H142	0.3226	0.7078	0.5482	0.1002	0.7329
H143	0.5088	0.7233	0.5064	0.1001	0.7329
H151	0.7792	0.6018	0.5276	0.1011	0.7329
H152	0.7086	0.6243	0.4625	0.1008	0.7329
H153	0.6902	0.5378	0.4852	0.1003	0.7329
H161	0.1352	0.5487	0.6272	0.0909	0.7329
H162	0.2712	0.6193	0.6412	0.0902	0.7329
H163	0.1319	0.6216	0.5864	0.0907	0.7329
H171	0.4837	0.4744	0.6305	0.0981	0.7329
H172	0.6055	0.5495	0.6367	0.0979	0.7329
H173	0.6546	0.4944	0.5835	0.0977	0.7329
H201	0.4333	0.7681	0.3153	0.0758	1
H202	0.4241	0.7087	0.3692	0.0755	1
H203	0.2261	0.7318	0.3353	0.0756	1
H211	0.4169	0.7177	0.2058	0.0718	1
H212	0.1826	0.6994	0.225	0.0722	1
H213	0.3249	0.634	0.1993	0.0717	1
H221	0.9176	0.6525	0.3034	0.0797	1
H222	0.7589	0.681	0.3535	0.0787	1
H223	0.775	0.7256	0.2882	0.0803	1
H231	0.8121	0.5652	0.2279	0.0793	1
H232	0.6866	0.6267	0.1918	0.0783	1
H233	0.5779	0.5475	0.212	0.0792	1

Experimental

Single crystals of $C_{23}H_{38}B_2O_6$ **(-)-5b** were grown from warm methanol/water upon cooling to room temperature and standing for about 1 week. A suitable crystal was selected and mounted on a Bruker APEX-II CCD' diffractometer. The crystal was kept at 150 K during data collection. The structure was solved using the program Crystals.

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