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1.1. NMR spectra



Figure SI-2. ¹³C-NMR spectra of compound 11d.



Figure SI-4. ¹³C-NMR spectra of compound 14a.



Figure SI-6. ¹³C-NMR spectra of compound 14b.







Figure SI-10. ¹¹B-NMR spectra of compound (+)-6a.



Figure SI-11. ¹³C-NMR spectra of compound (+)-6a.

70

40



N/PIPH/NULPhay in links Miknahimi 10 f1 (ppm) 60 50 -10 -20 -30 -40 -50

-60

Figure SI-13. ¹¹B-NMR spectra of compound (+)-6b.



Figure SI-14. ¹³C-NMR spectra of compound (+)-6b.



Figure SI-16. ¹¹B-NMR spectra of compound (-)-6c.



Figure SI-17. ¹³C-NMR spectra of compound (-)-6c.



















Figure SI-23. ¹³C-NMR spectra of compound (-)-12b.



Figure SI-25. ¹¹B-NMR spectra of compound rac-12c.



Figure SI-26. ¹³C-NMR spectra of compound rac-12c.

30

80

70

60

50

40

30

20

10





0 f1 (ppm) Figure SI-28. ¹¹B-NMR spectra of compound (-)-12d.

-10

-20

-30

-40

-50

-90

-80

-70

-60



Figure SI-29. ¹³C-NMR spectra of compound (-)-12d.









Figure SI-32. ¹³C-NMR spectra of compound (+)-15a.



Figure SI-34. ¹¹B-NMR spectra of compound (+)-15b.



Figure SI-35. ¹³C-NMR spectra of compound (+)-15b.





(±)-15d

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f1 (ppm) Figure SI-38. ¹³C-NMR spectra of compound *rac*-15d.

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f1 (ppm) Figure SI-40. ¹¹B-NMR spectra of compound rac-19a.



Figure SI-41. ¹³C-NMR spectra of compound *rac*-19a.



50

40

30

20

70

60

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-20

-30

-40

-50

-10

-60

10 f1 (ppm) Figure SI-43. ¹¹B-NMR spectra of compound (-)-19b.











Figure SI-46. ¹¹B-NMR spectra of compound (+)-19c.



Figure SI-47. ¹³C-NMR spectra of compound (+)-19c.





Figure SI-49. ¹¹B-NMR spectra of compound (+)-19d.









0 OН Ή. J | || Ōн (+)-7b 0.99 - E 1.724.10 ↓ 3.65 ↓ 2.33 ↓ 2.23 ↓ ■-00⁻¹ T 10 f1 (ppm) Figure SI-53. ¹H-NMR spectra of compound (+)-7b. -57.05 -57.05 -51.09 -51.48 -11.48 -51.09 -52.30 -15.24 ΟН Н он (+)-7b



Figure SI-54. ¹³C-NMR spectra of compound (+)-7b.

1.2. HPLC traces



Figure SI-55. HPLC chromatogram for racemic and chiral compound (+)-6a.


eak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	9
1	5.074	BB	0.1055	371.00552	53.07721	94.3210
2	6.190	BB	0.1411	22.33796	2.34599	5.6790

*DAD1, 4.941 (20.4 mAU,Dn2) Ref=4.081 of 260419_	*DAD1, 5.149 (19.1 mAU,Bln) Ref=4.936 of 260919
mAU 15 10 5	mAU 15 10 5 0
250 300 350 400 450 500 550 nm	250 300 350 400 450 500 550 nm

Figure SI-56. HPLC traces for racemic and chiral compound (+)-6b.











Figure SI-58. HPLC traces for racemic and chiral compound (+)-12a.



Figure SI-59. HPLC traces for racemic and chiral compound (-)-12b.

100 -





Figure SI-60. HPLC traces for racemic and chiral compound (-)-12d.



Figure SI-61. HPLC traces for racemic and chiral compound (+)-15a.





Figure SI-62. HPLC traces for racemic and chiral compound (+)-15b.





350

400 450 500 550 nm

350 400 450 500 550 nm

250





250 300 350 400 450 500 550 nm

350 400 450 500 550 nm





350

400 450 500 550 nm



350 400 450 500 550 nm



Figure SI-66. HPLC traces for racemic and chiral compound (+)-7b.

1.3. X-ray details

X-ray details for (+)-15a: CCDC 1944177 Summary of Data CCDC 1944177 Formula: C20 H27 B O4 Unit Cell Parameters: a = 9.03049(5)Å, b = 8.61533(5)Å, c = 11.74381(6)Å



Table SI-1. Crystal data and structure refinement for (+)-15a.

Identification code	JS_81_F1_b		
Empirical formula	C20 H27 B O4		
Formula weight	342.22		
Temperature	100(2)K		
Wavelength	0.71073 Å		
Crystal system	monoclinic		
Space group	P 21		
Unit cell dimensions	a = 9.03049(5)Å	a = 90°.	
	b = 8.61533(5)A	b = 102.4590(5)°.	
	c = 11.74381(6)A	g = 90°.	
Volume	892.159(9) Å ³		
Z	2		
Density (calculated)	1.274 Mg/m ³		
Absorption coefficient	0.085 mm ⁻¹		
F(000)	368		
Crystal size	0.400 x 0.300 x 0.200 m	_{im} 3	
Theta range for data collection	2.310 to 28.528°.		
Index ranges	-12<=h<=12,-11<=k<=10),-15<=l<=15	
Reflections collected	56812		
Independent reflections	4407[R(int) = 0.0337]		
Completeness to theta =28.528°	100.0%		
Absorption correction	Multi-scan		
Max. and min. transmission	1.00 and 0.64		
Refinement method	Full-matrix least-squares	s on F ²	
Data / restraints / parameters	4407/ 1/ 231		
Goodness-of-fit on F ²	1.036		
Final R indices [I>2sigma(I)]	R1 = 0.0251, wR2 = 0.0	680	
R indices (all data)	R1 = 0.0251, wR2 = 0.0	680	
Largest diff. peak and hole	0.250 and -0.199 e.Å $^{-3}$		

 Table SI-2.
 Bond lengths [Å] and angles [°] for (+)-15a.

Bond	lenatl	าร	
01	C1	1.216	6(15)
02	C10	1 44	51(13)
03	R1	1 372	9(15)
03	C15	1 /6'	3/(17)
03		1.40	2(14)
04		1.3/0	2(15)
04	016	1.45	54(14)
C1	C11	1.502	29(15)
C1	C2	1.511	3(15)
C2	C3	1.530	9(17)
C3	C4	1.519	9(18)
C4	C5	1.401	7(15)
C4	C9	1.409	1(15)
C5	C6	1.387	7(19)
C6	C7	1.389	4(18)
C7	C8	1.390	4(15)
C8	C9	1.403	9(16)
C9	C10	1.523	30(14)
C10	C12	1.53	66(16)
C10	C11	1.56	10(15)
C11	C14	1.55	66(15)
C12	C13	1.53	14(16)
C13	C14	1.54	17(17)
C14	B1	1.578	38(17)
C15	C17	1.51	64(16)
C15	C18	1.52	26(17)
C15	C16	1.55	98(17)
C16	C20	1.52	00(18)
C16	C19	1.52	35(17)
Angle	es		
B1	O3	C15	106.73(9)
B1	O4	C16	107.26(9)
01	C1	C11	121.82(10)
01	C1	C2	121.41(11)
C11	C1	C2	116.73(10)
C1	C2	C3	115.11(10)
C4	C3	C2	117.25(10)
C5	C4	C9	118 37(11)
C5	C4	C3	116.06(10)
C9	C4	C3	125 56(10)
C6	C5	C4	120.00(10) 122.04(12)
C5	C6	C7	122.04(12)
C6	C7	C0	119.43(11)
C7	C1 C0		13.40(11)
C0	00	C4	110 00(10)
	C9	C10	116.90(1U)
	C9	C10	122 05(10)
04	C10		120.90(10)
02		60	103.42(0)
\cap	C10	040	100 00(0)
02	C10	C12	109.03(9)

O2	C10	C11	105.02(9)
C9	C10	C11	114.89(9)
C12	C10	C11	102.47(8)
C1	C11	C14	115.78(9)
C1	C11	C10	107.49(8)
C14	C11	C10	106.93(9)
C13	C12	C10	102.79(10)
C12	C13	C14	104.07(9)
C13	C14	C11	104.47(9)
C13	C14	B1	115.44(10)
C11	C14	B1	117.51(10)
O3	C15	C17	108.64(10)
O3	C15	C18	107.45(9)
C17	C15	C18	109.53(10)
O3	C15	C16	102.08(9)
C17	C15	C16	115.15(10)
C18	C15	C16	113.38(10)
O4	C16	C20	108.43(10)
O4	C16	C19	106.62(10)
C20	C16	C19	110.48(11)
O4	C16	C15	102.66(9)
C20	C16	C15	114.56(10)
C19	C16	C15	113.39(11)
O3	B1	04	112.98(10)
O3	B1	C14	123.72(10)
O4	B1	C14	122.31(10)

Table SI-3. Torsion angles [°] and symmetry operations for (+)-15a.

01	C1	C2	C3	163.42(11)
C11	C1	C2	C3	-18.86(14)
C1	C2	C3	C4	73.09(13)
C2	C3	C4	C5	140.52(11)
C2	C3	C4	C9	-39.05(16)
C9	C4	C5	C6	2.49(17)
C3	C4	C5	C6	-177.11(11)
C4	C5	C6	C7	0.98(18)
C5	C6	C7	C8	-2.79(18)
C6	C7	C8	C9	1.12(18)
C7	C8	C9	C4	2.37(17)
C7	C8	C9	C10	178.66(11)
C5	C4	C9	C8	-4.09(16)
C3	C4	C9	C8	175.47(10)
C5	C4	C9	C10	179.90(10)
C3	C4	C9	C10	-0.54(17)
C8	C9	C10	02	-87.26(12)
C4	C9	C10	02	88.82(12)
C8	C9	C10	C12	36.06(13)
C4	C9	C10	C12	-147.86(11)
C8	C9	C10	C11	154.93(10)
C4	C9	C10	C11	-28.99(15)
01	C1	C11	C14	-6.22(15)
C2	C1	C11	C14	176.07(9)

O1	C1	C11	C10	113.21(11)
C2	C1	C11	C10	-64.50(12)
O2	C10	C11	C1	-34.38(10)
C9	C10	C11	C1	85.88(11)
C12	C10	C11	C1	-148.28(9)
O2	C10	C11	C14	90.55(10)
C9	C10	C11	C14	-149.18(9)
C12	C10	C11	C14	-23.34(11)
O2	C10	C12	C13	-70.19(11)
C9	C10	C12	C13	166.28(9)
C11	C10	C12	C13	40.73(10)
C10	C12	C13	C14	-43.47(11)
C12	C13	C14	C11	28.15(12)
C12	C13	C14	B1	158.77(9)
C1	C11	C14	C13	116.97(10)
C10	C11	C14	C13	-2.77(11)
C1	C11	C14	B1	-12.43(14)
C10	C11	C14	B1	-132.16(10)
B1	O3	C15	C17	-147.40(11)
B1	O3	C15	C18	94.18(11)
B1	O3	C15	C16	-25.34(11)
B1	O4	C16	C20	-142.80(10)
B1	O4	C16	C19	98.23(12)
B1	O4	C16	C15	-21.22(12)
O3	C15	C16	O4	28.07(10)
C17	C15	C16	O4	145.56(10)
C18	C15	C16	O4	-87.19(11)
O3	C15	C16	C20	145.38(10)
C17	C15	C16	C20	-97.13(13)
C18	C15	C16	C20	30.12(14)
O3	C15	C16	C19	-86.55(11)
C17	C15	C16	C19	30.95(15)
C18	C15	C16	C19	158.19(11)
C15	O3	B1	04	13.43(13)
C15	O3	B1	C14	-177.77(10)
C16	O4	B1	O3	5.97(13)
C16	04	B1	C14	-163.00(10)
C13	C14	B1	O3	-10.83(16)
• • •	014			
C11	C14	B1	O3	113.21(12)
C11 C13	C14 C14 C14	B1 B1	03 04	113.21(12) 156.95(10)

Symmetry operations

1 'x, y, z' 2 '-x, y+1/2, -z' **X-ray details for (+)-7b: CCDC 1960435** Summary of Data CCDC 1960435 Formula: C11 H18 O3 Unit Cell Parameters: a = 8.57876(12)Å, b = 28.8880(4)Å, c = 8.70513(11)Å



Table SI-4. Crystal data and structure refinement for (+)-7b.

Identification code	JS-312-f1
Empirical formula	C11 H18 O3
Formula weight	198.25
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 21
Unit cell dimensions	$ \begin{array}{ll} a = 8.57876(12) \mbox{\AA} & a = 90^{\circ}. \\ b = 28.8880(4) \mbox{\AA} & b = 100.7205(13)^{\circ}. \\ c = 8.70513(11) \mbox{\AA} & g = 90^{\circ}. \end{array} $
Volume Z	2119.68(5) Å ³ 8
Density (calculated)	1.242 Mg/m ³
Absorption coefficient F(000)	0.089 mm ⁻¹ 864
Crystal size	0.200 x 0.120 x 0.100 mm ³
Theta range for data collection	2.381 to 59.377°.
Index ranges	-16<=h<=14,-67<=k<=62,-21<=l<=14
Reflections collected	149982
Independent reflections	34299[R(int) = 0.0319]
Completeness to theta =59.377°	68.2%
Absorption correction	Multi-scan
Max. and min. transmission	1.00 and 0.72
Refinement method Data / restraints / parameters	Full-matrix least-squares on F ² 34299/ 745/ 882
Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data)	0.961 R1 = 0.0372, wR2 = 0.0885 R1 = 0.0608, wR2 = 0.0960
Largest diff. peak and hole	0.426 and -0.245 e.Å ⁻³

Table SI-5. Bond lengths [Å] and angles $[\circ]$ for (+)-7b.

Bond	lengths	
O1A	C1A	1.4374(8)
O1A	H1A	0.784(15)
C1A	C11A	1.5376(10)
C1A	C6A	1.5401(9)
C1A	C2A	1.5447(11)
O2A	C5A	1.4388(8)
O2A	H2A	0.833(14)
C2A	C3A	1.5220(12)
C2A	H2AA	0.9900
C2A	H2AR	0.9900
03A	C7A	1 2197(9)
C3A	C4A	1.5184(12)
C34		
C34	H3AB	0.0000
		1 5232(10)
		0.0000
		0.9900
		0.9900
CEA		1.0413(9)
CSA		1.0000
C6A		1.5304(9)
	H6A	1.0000
C7A	C8A	1.5030(10)
C8A	C9A	1.5383(13)
C8A	H8AA	0.9900
C8A	H8AB	0.9900
C9A	C10A	1.5185(16)
C9A	H9AA	0.9900
C9A	H9AB	0.9900
C10A	C11A	1.5303(14)
C10A	H10C	0.9900
C10A	H10D	0.9900
C11A	H11C	0.9900
C11A	H11D	0.9900
C1B	O1B	1.4437(10)
C1B	C6B	1.5391(10)
C1B	C11B	1.5415(11)
C1B	C2B	1.5448(12)
O1B	H1B	0.860(14)
C2B	C3B	1.5228(14)
C2B	H2BA	0.9900
C2B	H2BB	0.9900
O2B	C5B	1.4386(9)
O2B	H2B	0.865(14)
C3B	C4B	1.517(3)
C3B	НЗВА	0.9900
C3B	НЗВВ	0.9900
O3B	C7B	1.2225(10)
C4B	C5B	1.523(2)
C4B	H4BA	0.9900
C4B	H4BB	0.9900

C5B	C6B	1.5369(11)
C5B	H5B	1.0000
C6B	C7B	1.5332(10)
C6B	H6B	1.0000
C7B	C8B	1 5026(14)
C8B	C9B	1 5340(17)
C8B		
COD		0.9900
		0.9900
Cap		1.5210(19)
C9B	НУВА	0.9900
C9B	HARR	0.9900
C10B	C11B	1.5234(13)
C10B	H10G	0.9900
C10B	H10H	0.9900
C11B	H11E	0.9900
C11B	H11F	0.9900
C1B'	O1B'	1.4382
C1B'	C112	1.453(19)
C1B'	C2B'	1.5431
C1B'	C6B'	1.682(17)
O1B'	H1B'	0.8944
C2B'	C3B'	1.30(2)
C2B'	H2BC	0.9900
C2B'	H2BD	0.9900
02B'	C5B'	1 453(13)
02B'	H2B'	0.8456
C2B'		1 355(10)
COD		0.0000
COD		0.9900
		0.9900
O3B		1.254(14)
C4B	C5B	1.436(18)
C4B'	H4BC	0.9900
C4B'	H4BD	0.9900
C5B'	C6B'	1.499(14)
C5B'	H5B'	1.0000
C6B'	C7B'	1.450(13)
C6B'	H6B'	1.0000
C7B'	C8B'	1.478(15)
C8B'	C9B'	1.44(2)
C8B'	H8BC	0.9900
C8B'	H8BD	0.9900
C9B'	C102	1.63(2)
C9B'	H9BC	0.9900
C9B'	H9BD	0.9900
C102	C112	1 44(2)
C102	H102	0.9900
C102	H103	0.9900
C112	L112	0.9900
0112		0.9900
0112		0.9900
		1.4514(9)
	HIC	0.775(17)
C1C	C11C	1.5366(10)
C1C	C2C	1.5395(10)

C1C	C6C	1.5442(9)
O2C	C5C	1.4346(9)
O2C	H2C	0.7959
C2C	C3C	1.5242(13)
C2C	H2CA	0.9900
C2C	H2CB	0.9900
030	C7C	1 2195(9)
C3C	C4C	1.5281(15)
C3C		
C3C	HISCH	0.9900
C4C	050	0.3300
		0.0000
		0.9900
050		0.9900
050	060	1.5462(10)
050	H5C	1.0000
C6C	C/C	1.5300(9)
C6C	H6C	1.0000
C7C	C8C	1.5029(10)
C8C	C9C	1.5351(12)
C8C	H8CA	0.9900
C8C	H8CB	0.9900
C9C	C10C	1.5180(13)
C9C	H9CA	0.9900
C9C	H9CB	0.9900
C10C	C11C	1.5297(12)
C10C	H104	0.9900
C10C	H105	0.9900
C11C	H116	0.9900
C11C	H117	0.9900
C1C'	C113	1 45(2)
C1C'	01C'	1.457(12)
C1C'	C2C'	1.512(11)
C1C'		1.678(10)
010		0.8270
		1.29(2)
		0.0000
		0.9900
	H2CD	0.9900
020		1.461(14)
020	H2C	0.8966
C3C	C4C'	1.36(2)
C3C'	H3CD	0.9900
C3C'	H3CC	0.9900
O3C'	C7C'	1.279(15)
C4C'	C5C'	1.45(2)
C4C'	H4CC	0.9900
C4C'	H4CD	0.9900
C5C'	C6C'	1.496(15)
C5C'	H51'	1.0000
C6C'	C7C'	1.458(15)
C6C'	H61C	1.0000
C7C'	C8C'	1.498(17)
C8C'	COCI	4 44(0)
000	696	1.44(Z)

C8C'	H82' 0.9900
C9C'	C103 1.63(3)
C9C'	H91' 0.9900
C9C'	H92' 0.9900
C103	$C_{113} + 4_{4(2)}$
C103	H131 0 9900
C103	H132 0.0000
C112	
C112	
	01D 1 4516(11)
	C11D 1.5362(13)
C1D	C6D 1.5403(11)
C1D	C2D 1.5475(13)
O1D	H1D 0.7662
C2D	C3D 1.5288(16)
C2D	H2DA 0.9900
C2D	H2DB 0.9900
O2D	C5D 1.4342(10)
O2D	H2D 0.796(16)
C3D	C4D 1.5217(18)
C3D	H3DA 0.9900
C3D	H3DB 0.9900
O3D	C7D 1.2203(9)
C4D	C5D = 1.5235(13)
	H4DB 0.9900
	CeD = 1 = 4eO(10)
	H5D 1.0000
C6D	C7D 1.5330(10)
C6D	H6D 1.0000
C7D	C8D 1.5017(11)
C8D	C9D 1.554(2)
C8D	H8DA 0.9900
C8D	H8DB 0.9900
C9D	C10D 1.529(2)
C9D	H9DA 0.9900
C9D	H9DB 0.9900
C10D	C11D 1.525(2)
C10D	H141 0.9900
C10D	H142 0.9900
C11D	H143 0.9900
C11D	H144 0.9900
C1D'	O1D' 1 444(11)
C1D'	$C_{114} = 1.46(2)$
C1D'	C2D' = 1.514(10)
C1D'	C6D' = 1.680(17)
	COD 4 20(2)
C2D'	H2DD 0.9900
U2D'	C5D' 1.462(12)
02D'	H2D' 0.8348
C3D'	C4D' 1.371(19)

C3D' C3D' C4D' C4D' C4D' C5D' C5D' C5D' C6D' C7D' C8D' C8D' C8D' C8D' C9D' C9D' C9D' C9D' C104 C104 C104 C114 C114	H3DC H3DD C7D' C5D' H4DC H4DD C6D' H5D' C7D' H6D' C8D' C9D' H8DC H8DD C104 H9DC H9DD C114 H145 H146 H147 H148	0.9900 0.9900 1.250(12 1.462(19) 0.9900 0.9900 1.499(14 1.0000 1.448(12 1.0000 1.474(14 1.44(2) 0.9900 0.9900 0.9900 1.64(3) 0.9900 0.9900 0.9900 0.9900 0.9900 0.9900 0.9900)))
Angles	S		
		HIA I	19.5 44.04(0)
OTA	CIA	C6A 10	16.33(5)
C11A	C1A	C6A 1	13.04(6)
O1A	C1A	C2A 10)9.72(6)
C11A	C1A	C2A 1	07.91(6)
C6A	C1A	C2A 10)8.16(6)
C5A	O2A	H2A 10)7.5(9)
C3A	C2A	C1A 11	3.75(6)
C3A	C2A	H2AA 1	08.8
C1A	C2A	H2AA 1	08.8
C3A	C2A	H2AB 1	08.8
C1A	C2A	H2AB 1	08.8
H2AA	C2A	H2AB	107.7
C4A	СЗА	C2A 11	1.06(7)
C4A	СЗА	H3AA 1	09.4
C2A	СЗА	H3AA 1	09.4
C4A	C3A	H3AB 1	09.4
C2A	C3A	H3AB 1	09.4
НЗАА	C3A	H3AB	108.0
C3A	C4A	C5A 11	1.40(6)
C3A	C4A	H4AA 1	09.3
C5A	C4A	H4AA 1	09.3
C3A	C4A	H4AB 1	09.3
C5A	C4A	H4AB 1	09.3
H4AA	C4A	H4AB	108.0
O2A	C5A	C4A 11	10.96(6)
O2A	C5A	C6A 11	10.21(5)
C4A	C5A	C6A 11	1.49(5)

O2A	C5A	H5A	108.0
C4A	C5A	H5A	108.0
C6A	C5A	H5A	108.0
C7A	C6A	C1A	119.03(6)
C7A	C6A	C5A	107.26(5)
C1A	C6A	C5A	111.52(5)
C7A	C6A	H6A	106.1
C1A	C6A	H6A	106.1
C5A	C6A	H6A	106.1
O3A	C7A	C8A	120.20(7)
O3A	C7A	C6A	117 95(6)
C8A	C7A	C6A	121 83(6)
C7A	C8A	C9A	121.00(0) 111.77(7)
C74	C84		109.3
			109.5
			109.5
			109.3
		HOAD	109.3
H8AA		H8AB	107.9
CIUA	C9A	C8A	113.93(7)
C10A	C9A	НУАА	108.8
C8A	C9A	H9AA	108.8
C10A	C9A	H9AB	108.8
C8A	C9A	H9AB	108.8
H9AA	C9A	H9AB	107.7
C9A	C10A	C11A	116.39(7)
C9A	C10A	H10C	108.2
C11A	C10A	H10C	; 108.2
C9A	C10A	H10D	108.2
C11A	C10A	H10D	108.2
H10C	C10A	H10D	0 107.3
C10A	C11A	C1A	117.24(7)
C10A	C11A	H11C	; 108.0
C1A	C11A	H11C	108.0
C10A	C11A	H11D	108.0
C1A	C11A	H11D	108.0
H11C	C11A	H11C) 107.2
O1B	C1B	C6B	106 07(9)
O1B	C1B	C11B	111 58(7)
C6B	C1B	C11B	113 59(7)
01B	C1B	C2B	110.03(10)
C6B	C1B	C2B	108 71(6)
		C2B	106.71(0)
			100.05(7)
	COR		109.5
COD			113.34(0)
			108.9
CIB	C2B	HZBA	108.9
C3B	C2B	H2BB	108.9
C1B	C2B	H2BB	108.9
H2BA	C2B	H2BB	107.7
C5B	O2B	H2B	108.4(9)
C4B	C3B	C2B	110.58(12)
C4B	C3B	H3BA	109.5
C2B	C3B	H3BA	109.5

C4B C2B H3BA C3B	C3B C3B C3B C4B	H3BB 109.5 H3BB 109.5 H3BB 108.1 C5B 111.37(14)
C5B	C4B	H4BA 109.4
C3B	C4B	H4BB 109.4
C5B	C4B	H4BB 109.4
H4BA	C4B	H4BB 108.0
O2B	C5B	C4B 111.16(11)
O2B	C5B	C6B 109.81(6)
C4B	C5B	C6B 112.07(10)
O2B	C5B	H5B 107.9
C6B	C5B	H5B 107.9
C7B	C6B	C5B 106.87(6)
C7B	C6B	C1B 118.32(6)
C5B	C6B	C1B 111.53(6)
C7B	C6B	H6B 106.5
C5B	C6B	H6B 106.5
C1B	C6B	H6B 106.5
O3B	C7B	C8B 119.98(7)
COB COB	C7B	C6B 117.63(8)
C7B	C2B	COD $122.30(7)$ COB 112.80(8)
C7B	C8B	H8BA 109.0
C9B	C8B	H8BA 109.0
C7B	C8B	H8BB 109.0
C9B	C8B	H8BB 109.0
H8BA	C8B	H8BB 107.8
C10B	C9B	C8B 113.87(8)
C10B	C9B	H9BA 108.8
C8B	C9B	H9BA 108.8
C10B	COB COB	H9BB 108.8
	COB	HORE 107.7
C9B	C10B	C11B 115 15(9)
C9B	C10B	H10G 108.5
C11B	C10B	H10G 108.5
C9B	C10B	H10H 108.5
C11B	C10B	H10H 108.5
H10G	C10B	H10H 107.5
C10B	C11B	C1B 117.43(7)
C10B	C11B	H11E 107.9
	CITE	HTTE 107.9
C1B	C11B	H11F 107.9
H11E	C11B	H11F 107.2
01B'	C1B'	C112 99.3(13)
O1B'	C1B'	C2B' 109.9
C112	C1B'	C2B' 123.2(13)
O1B'	C1B'	C6B' 99.8(14)
C112	C1B'	C6B' 112.9(10)

C2B' C1B' C6B' 108.7(10) C1B' O1B' H1B' 122.3 C3B' C2B' C1B' 116.8(12) C3B' C2B' H2BC 108.1 C1B' C2B' H2BC 108.1 C3B' C2B' H2BD 108.1 C1B' C2B' H2BD 108.1 H2BC C2B' H2BD 107.3 C5B' O2B' H2B' 109.5 C2B' C3B' C4B' 122.5(16) C2B' C3B' H3BC 106.7 C4B' C3B' H3BC 106.7 C2B' C3B' H3BD 106.7 C4B' C3B' H3BD 106.7 H3BC C3B' H3BD 106.6 C3B' C4B' C5B' 120.9(14) C3B' C4B' H4BC 107.1 C5B' C4B' H4BC 107.1 C3B' C4B' H4BD 107.1 C5B' C4B' H4BD 107.1 H4BC C4B' H4BD 106.8 C4B' C5B' O2B' 101.8(11) C4B' C5B' C6B' 115.6(9) O2B' C5B' C6B' 111.0(9) C4B' C5B' H5B' 109.4 O2B' C5B' H5B' 109.4 C6B' C5B' H5B' 109.4 C7B' C6B' C5B' 111.4(10) C7B' C6B' C1B' 124.3(10) C5B' C6B' C1B' 109.2(8) C7B' C6B' H6B' 103.1 C5B' C6B' H6B' 103.1 C1B' C6B' H6B' 103.1 O3B' C7B' C6B' 115.8(11) O3B' C7B' C8B' 118.9(11) C6B' C7B' C8B' 125.3(11) C9B' C8B' C7B' 109.9(14) C9B' C8B' H8BC 109.7 C7B' C8B' H8BC 109.7 C9B' C8B' H8BD 109.7 C7B' C8B' H8BD 109.7 H8BC C8B' H8BD 108.2 C8B' C9B' C102 115.5(17) C8B' C9B' H9BC 108.4 C102 C9B' H9BC 108.4 C8B' C9B' H9BD 108.4 C102 C9B' H9BD 108.4 H9BC C9B' H9BD 107.5 C112 C102 C9B' 115.2(14) C112 C102 H102 108.5 C9B' C102 H102 108.5 C112 C102 H103 108.5 C9B' C102 H103 108.5

H102 C102 H103 107.5 C102 C112 C1B' 128.0(14) C102 C112 H112 105.3 C1B' C112 H112 105.3 C102 C112 H113 105.3 C1B' C112 H113 105.3 H112 C112 H113 106.0 C1C 01C H1C 102.3(12) 01C C1C C11C 107.86(7) O1C C1C C2C 109.56(6) C11C C1C C2C 107.57(6) C1C C6C 109.86(6) 01C C11C C1C C6C 114.21(6) C2C C1C C6C 107.70(6) C5C O2C H2C 114.6 113.62(6) C3C C2C C1C C3C C2C H2CA 108.8 C1C C2C H2CA 108.8 C3C C2C H2CB 108.8 C1C C2C H2CB 108.8 H2CA C2C H2CB 107.7 C2C C3C C4C 111.06(7) C₂C C3C H3CA 109.4 C4C C3C H3CA 109.4 C2C C3C H3CB 109.4 C4C C3C H3CB 109.4 H3CA C3C H3CB 108.0 C5C C4C C3C 111.17(7) C5C C4C H4CA 109.4 C3C C4C H4CA 109.4 C5C C4C H4CB 109.4 C3C C4C H4CB 109.4 H4CA C4C H4CB 108.0 O2C C5C C4C 107.32(7)O2C C5C C6C 110.68(6) C4C C5C C6C 111.21(6) O2C C5C H5C 109.2 C4C C5C H5C 109.2 C6C C5C H5C 109.2 C7C C6C C1C 119.67(6) C7C C6C C5C 107.52(5) C1C C6C C5C 111.72(6) C7C C6C H6C 105.6 C1C C6C H6C 105.6 C5C C6C H6C 105.6 O3C C7C C8C 119.79(7) O3C C7C C6C 117.46(7) **C8C** C7C C6C 122.74(6)C7C C8C C9C 112.17(6) C7C C8C H8CA 109.2 C9C C8C H8CA 109.2 C7C C8C H8CB 109.2 C9C C8C H8CB 109.2

H8CA C8C H8CB 107.9 C10C C9C C8C 114.15(7) C10C C9C H9CA 108.7 C8C C9C H9CA 108.7 C10C C9C H9CB 108.7 C8C C9C H9CB 108.7 H9CA C9C H9CB 107.6 C9C C10C C11C 115.29(7) C9C C10C H104 108.5 C11C C10C H104 108.5 C9C C10C H105 108.5 C11C C10C H105 108.5 H104 C10C H105 107.5 C10C C11C C1C 117.45(6) C10C C11C H116 107.9 C1C C11C H116 107.9 C10C C11C H117 107.9 C1C C11C H117 107.9 H116 C11C H117 107.2 C113 C1C' O1C' 98.4(15) C113 C1C' C2C' 130.3(17) O1C' C1C' C2C' 108.1(14) C113 C1C' C6C' 108.9(14) O1C' C1C' C6C' 99.2(15) C2C' C1C' C6C' 107.4(13) C1C' O1C' H1C' 106.2 C3C' C2C' C1C' 120.2(16) C3C' C2C' H2CC 107.3 C1C' C2C' H2CC 107.3 C3C' C2C' H2CD 107.3 C1C' C2C' H2CD 107.3 H2CC C2C' H2CD 106.9 C5C' O2C' H2C' 97.9 C2C' C3C' C4C' 128(2) C2C' C3C' H3CD 105.3 C4C' C3C' H3CD 105.3 C2C' C3C' H3CC 105.3 C4C' C3C' H3CC 105.3 H3CD C3C' H3CC 106.0 C3C' C4C' C5C' 113.5(15) C3C' C4C' H4CC 108.9 C5C' C4C' H4CC 108.9 C3C' C4C' H4CD 108.9 C5C' C4C' H4CD 108.9 H4CC C4C' H4CD 107.7 C4C' C5C' O2C' 98.6(13) C4C' C5C' C6C' 113.5(13) O2C' C5C' C6C' 108.8(12) C4C' C5C' H51' 111.8 O2C' C5C' H51' 111.8 C6C' C5C' H51' 111.8 C7C' C6C' C5C' 110.8(12) C7C' C6C' C1C' 123.2(13)

C5C' C6C' C1C' 111.2(11) C7C' C6C' H61C 102.9 C5C' C6C' H61C 102.9 C1C' C6C' H61C 102.9 O3C' C7C' C6C' 108.6(14) O3C' C7C' C8C' 111.5(15) C6C' C7C' C8C' 117.8(15) C9C' C8C' C7C' 110.0(17) C9C' C8C' H81' 109.7 C7C' C8C' H81' 109.7 C9C' C8C' H82' 109.7 C7C' C8C' H82' 109.7 H81' C8C' H82' 108.2 C8C' C9C' C103 115.9(19) C8C' C9C' H91' 108.3 C103 C9C' H91' 108.3 C8C' C9C' H92' 108.3 C103 C9C' H92' 108.3 H91' C9C' H92' 107.4 C113 C103 C9C' 115.3(17) C113 C103 H131 108.5 C9C' C103 H131 108.5 C113 C103 H132 108.5 C9C' C103 H132 108.5 H131 C103 H132 107.5 C103 C113 C1C' 128(2) C103 C113 H11G 105.3 C1C' C113 H11G 105.3 C103 C113 H11H 105.3 C1C' C113 H11H 105.3 H11G C113 H11H 106.0 C1D C11D 108.13(9) O1D O1D C1D C6D 109.61(7) C11D C1D C6D 114.44(7)O1D C1D C2D 109.26(9) C11D C1D C2D 107.25(8) C6D C1D C2D 108.04(7) C1D O1D H1D 107.7 C3D C2D C1D 113.81(8) C3D C2D H2DA 108.8 C1D C2D H2DA 108.8 C3D C2D H2DB 108.8 C1D C2D H2DB 108.8 H2DA C2D H2DB 107.7 C5D O2D H2D 109.5 C4D C3D C2D 110.92(11) C4D C3D H3DA 109.5 C2D C3D H3DA 109.5 C4D C3D H3DB 109.5 C2D C3D H3DB 109.5 H3DA C3D H3DB 108.0 C3D C4D C5D 110.64(10) C3D C4D H4DA 109.5

C5D C4D H4DA 109.5 C3D C4D H4DB 109.5 C5D C4D H4DB 109.5 H4DA C4D H4DB 108.1 C5D C4D 107.38(8) O2D O2D C5D C6D 110.66(6) C4D C5D C6D 111.38(8) O2D C5D H5D 109.1 C4D C5D H5D 109.1 C6D C5D H5D 109.1 C7D C6D C1D 118.78(6) C7D C6D C5D 107.89(5) C1D C6D C5D 111.53(6) C7D C6D H6D 105.9 C1D C6D H6D 105.9 C5D C6D H6D 105.9 O3D C7D C8D 119.95(7) O3D C7D C6D 117.48(7) C8D C7D C6D 122.57(6) C7D C8D C9D 112.37(11) C7D C8D H8DA 109.1 C9D C8D H8DA 109.1 C7D C8D H8DB 109.1 C9D C8D H8DB 109.1 H8DA C8D H8DB 107.9 C10D C9D C8D 113.43(14) C10D C9D H9DA 108.9 C8D C9D H9DA 108.9 C10D C9D H9DB 108.9 C8D C9D H9DB 108.9 H9DA C9D H9DB 107.7 C11D C10D C9D 115.56(13) C11D C10D H141 108.4 C9D C10D H141 108.4 C11D C10D H142 108.4 C9D C10D H142 108.4 H141 C10D H142 107.5 C10D C11D C1D 117.81(10) C10D C11D H143 107.9 C1D C11D H143 107.9 C10D C11D H144 107.9 C1D C11D H144 107.9 H143 C11D H144 107.2 O1D' C1D' C114 99.5(13) O1D' C1D' C2D' 108.9(12) C114 C1D' C2D' 126.1(13) O1D' C1D' C6D' 102.5(12) C114 C1D' C6D' 109.6(11) C2D' C1D' C6D' 107.7(10) C1D' O1D' H1D' 110.5 C3D' C2D' C1D' 116.9(14) C3D' C2D' H2DC 108.1 C1D' C2D' H2DC 108.1

C3D' C2D' H2DD 108.1 C1D' C2D' H2DD 108.1 H2DC C2D' H2DD 107.3 C5D' O2D' H2D' 108.5 C2D' C3D' C4D' 123.5(18) C2D' C3D' H3DC 106.5 C4D' C3D' H3DC 106.5 C2D' C3D' H3DD 106.5 C4D' C3D' H3DD 106.5 H3DC C3D' H3DD 106.5 C3D' C4D' C5D' 114.5(13) C3D' C4D' H4DC 108.6 C5D' C4D' H4DC 108.6 C3D' C4D' H4DD 108.6 C5D' C4D' H4DD 108.6 H4DC C4D' H4DD 107.6 C4D' C5D' O2D' 99.5(11) C4D' C5D' C6D' 115.0(10) O2D' C5D' C6D' 108.9(8) C4D' C5D' H5D' 110.9 O2D' C5D' H5D' 110.9 C6D' C5D' H5D' 110.9 C7D' C6D' C5D' 108.7(9) C7D' C6D' C1D' 124.1(9) C5D' C6D' C1D' 110.6(8) C7D' C6D' H6D' 103.7 C5D' C6D' H6D' 103.7 C1D' C6D' H6D' 103.7 O3D' C7D' C6D' 117.7(9) O3D' C7D' C8D' 118.8(9) C6D' C7D' C8D' 123.5(9) C9D' C8D' C7D' 107.6(14) C9D' C8D' H8DC 110.2 C7D' C8D' H8DC 110.2 C9D' C8D' H8DD 110.2 C7D' C8D' H8DD 110.2 H8DC C8D' H8DD 108.5 C8D' C9D' C104 113.8(17) C8D' C9D' H9DC 108.8 C104 C9D' H9DC 108.8 C8D' C9D' H9DD 108.8 C104 C9D' H9DD 108.8 H9DC C9D' H9DD 107.7 C114 C104 C9D' 112.3(15) C114 C104 H145 109.1 C9D' C104 H145 109.1 C114 C104 H146 109.1 C9D' C104 H146 109.1 H145 C104 H146 107.9 C104 C114 C1D' 128.0(16) C104 C114 H147 105.3 C1D' C114 H147 105.3 C104 C114 H148 105.3

C1D' C114 H148 105.3 H147 C114 H148 106.0 Table SI-6. Torsion angles [°] for (+)-7b. O1A C1A C2A C3A -60.14(8)C11A C1A C2A C3A 178.06(7) C6A C1A C2A C3A 55.46(8) C1A C2A C3A C4A -55.27(9)C2A C3A C4A C5A 53.76(8) C3A C4A C5A O2A 67.93(8) C3A C4A C5A C6A -55.33(8)C6A O1A C1A C7A -63.41(7)C11A C1A C6A C7A 59.39(8) C2A C1A C6A C7A 178.80(6) O1A C1A C6A C5A 62.30(7) C11A C1A C6A C5A -174.90(6)C2A C1A C6A C5A -55.49(7)O2A C5A C6A C7A 65.49(7) C4A C5A C6A C7A -170.83(6)O2A C5A C6A C1A -66.49(7)C4A C5A C1A C6A 57.19(7) C1A C6A O3A C7A -174.06(6)C5A C6A C7A O3A 58.22(8) C1A C6A C7A C8A 4.67(9) C5A C6A C7A C8A -123.06(7)O3A C7A C8A C9A 110.18(9) C6A C7A C8A C9A -68.51(9)C7A C8A C9A C10A 81.95(9) C8A C10A C11A -63.72(10) C9A C9A C10A C11A C1A 63.77(10) O1A C1A C11A C10A 41.48(10) C6A C1A C11A C10A -78.33(9) C2A C11A C10A 162.11(7) C1A O1B C1B C2B C3B -60.00(12)C6B C1B C2B C3B 55.76(10) C11B C1B C2B C3B 178.71(9) C1B C2B C3B C4B -56.34(15)C2B C3B C4B C5B 54.64(19) C3B C4B C5B O2B 68.15(17) -55.15(18) C3B C4B C5B C6B O2B C5B C6B C7B 62.35(7) C4B C5B C6B C7B -173.59(11)C5B C6B C1B O2B -68.39(8)C4B C5B C6B C1B 55.67(12) O1B C1B C6B C7B -60.64(10)C11B C1B C7B C6B 62.28(9) C2B C1B C6B C7B -178.92(7)63.91(10) O1B C1B C6B C5B C11B C1B C6B C5B -173.17(6)C2B C6B C5B C1B -54.37(8)C5B C6B C7B O3B 52.64(9) C1B C6B C7B O3B 179.45(8)

C5B	C6B	C7B	C8B	-128.59(8)
C1B	C6B	C7B	C8B	-1.78(11)
O3B	C7B	C8B	C9B	115.38(10)
C6B	C7B	C8B	C9B	-63.36(11)
C7B	C8B	C9B	C10B	83.06(10)
C8B	C9B	C10B	C11E	3 -66.27(12)
C9B	C10B	C11E	C1B	63.90(12)
01B	C1B	C11B	C10F	3 41 69(14)
C6B	C1B	C11B	C10E	3 -78 14(10)
C2B	C1B	C11B	C10E	3 162 00(9)
02D	C1B'	C2B'	C3B	64(2)
C112		C2D	COD	170 4(19)
CEP		C2D	COD	-179.4(10)
			COD	-44.0(10)
CIB	C2B	C3B	C4B	40(3)
C2B	C3B	C4B	C5B	-34(3)
C3B	C4B	C5B	O2B	-85(2)
C3B	C4B	C5B	C6B	36(2)
C4B'	C5B'	C6B'	C7B'	178.5(12)
O2B'	C5B'	C6B'	C7B'	-66.2(12)
C4B'	C5B'	C6B'	C1B'	-40.5(14)
O2B'	C5B'	C6B'	C1B'	74.8(11)
O1B'	C1B'	C6B'	C7B'	63.6(13)
C112	C1B'	C6B'	C7B'	-41.0(16)
C2B'	C1B'	C6B'	C7B'	178.6(12)
O1B'	C1B'	C6B'	C5B'	-71.2(12)
C112	C1B'	C6B'	C5B'	-175.8(11)
C2B'	C1B'	C6B'	C5B'	43.8(12)
C5B'	C6B'	C7B'	O3B'	-54.4(16)
C1B'	C6B'	C7B'	O3B'	171.6(12)
C5B'	C6B'	C7B'	C8B'	124.3(14)
C1B'	C6B'	C7B'	C8B'	-10(2)
O3B'	C7B'	C8B'	C9B'	-115.0(17)
C6B'	C7B'	C8B'	C9B'	66 4(19)
C7B'	C8B'	C9B'	C102	-82(2)
C8B'	C9B'	C102	C112	65(2)
COB'	C102	C112	C1B'	-58(3)
01B'	C18'	C112	C102	-30(3)
C2B'	C1B'	C112	C102	-45(2)
C2D		C112	C102	-103.9(17)
		0112	C102	62.44(0)
				-03.44(9)
				179.57(7)
C6C	C1C	020	030	56.03(8)
C1C	C2C	C3C	C4C	-55.84(9)
C2C	C3C	C4C	C5C	54.01(9)
C3C	C4C	C5C	O2C	65.88(8)
C3C	C4C	C5C	C6C	-55.30(9)
01C	C1C	C6C	C7C	-63.70(8)
C11C	C1C	C6C	C7C	57.62(8)
C2C	C1C	C6C	C7C	177.02(6)
01C	C1C	C6C	C5C	63.15(8)
C11C	C1C	C6C	C5C	-175.52(6)
C2C	C1C	C6C	C5C	-56.12(7)
O2C	C5C	C6C	C7C	71.68(7)

C4C	C5C	C6C	C7C	-169.13(6)
O2C	C5C	C6C	C1C	-61.52(7)
C4C	C5C	C6C	C1C	57.68(8)
C1C	060	C7C	030	-175 88(6)
CEC		070	000	55 24(9)
		070	030	55.54(6)
C1C	CCC	070	C8C	2.99(9)
C5C	C6C	C7C	C8C	-125.80(7)
O3C	C7C	C8C	C9C	114.00(8)
C6C	C7C	C8C	C9C	-64.84(8)
C7C	C8C	C9C	C10C	82.32(9)
C8C	C9C	C10C	C110	67 24(9)
	C10C	C11C	C1C	65 22(0)
010	C100	0110	C100	00.22(9)
				40.09(9)
C2C	C1C	C11C	C10C	5 164.19(7)
C6C	C1C	C11C	C10C	-76.34(8)
C113	C1C'	C2C'	C3C'	-165(3)
O1C'	C1C'	C2C'	C3C'	77(3)
C6C'	C1C'	C2C' (C3C'	-29(3)
C1C'	C2C'	C3C' (31(5)
Caci	020			27(4)
				-37(4)
030	C4C	050 0	J2C	-68(2)
C3C'	C4C'	C5C' (C6C'	46(3)
C4C'	C5C'	C6C' (C7C'	169.2(17)
02C'	C5C'	C6C'	C7C'	-82.2(19)
C4C'	C5C'	C6C' (C1C'	-49.8(18)
O2C'	C5C'	C6C'	C1C'	58.8(18)
C113	C1C'	C6C'	C7C'	-40(2)
O1C'	C1C'	C6C'	C7C'	62(2)
C2C'	C1C'	C6C' (174 8(19)
020				175 0(17)
				-175.0(17)
				-72.8(18)
C2C	C1C	C6C (55C	39.6(19)
C5C'	C6C'	C7C' (D3C'	-46(2)
C1C'	C6C'	C7C' (D3C'	178.5(17)
C5C'	C6C'	C7C' (C8C'	-174.0(17)
C1C'	C6C'	C7C' (C8C'	51(2)
O3C'	C7C'	C8C'	C9C'	149(2)
C6C'	C7C'	C8C' (C9C'	-85(3)
C7C'	C8C'	C9C' (C103	78(3)
		C103	C113	-16(4)
	C102	C112		62(4)
	0103	0110		-03(4)
010		0113	C103	-32(3)
C2C	C1C	C113	C103	-154(3)
C6C'	C1C'	C113	C103	71(3)
O1D	C1D	C2D	C3D	-64.17(12)
C11D	C1D	C2D	C3D	178.85(10)
C6D	C1D	C2D	C3D	55.01(12)
C1D	C2D	C3D	C4D	-55.69(15)
C2D	C3D	C4D	C5D	54 87(15)
020			000	6/ 67(10)
030				5664(12)
				-50.04(13)
	C1D	C6D		-62.64(11)
C11D	C1D	C6D	C7D	59.02(9)

C2D	C1D	C6D	C7D	178.40(7)
O1D	C1D	C6D	C5D	63.77(10)
C11D	C1D	C6D	C5D	-174.58(7)
C2D	C1D	C6D	C5D	-55.20(9)
O2D	C5D	C6D	C7D	70.81(7)
C4D	C5D	C6D	C7D	-169.81(8)
O2D	C5D	C6D	C1D	-61.34(8)
C4D	C5D	C6D	C1D	58.04(10)
C1D	C6D	C7D	O3D	-176.01(7)
C5D	C6D	C7D	O3D	55.87(8)
C1D	C6D	C7D	C8D	2.71(10)
C5D	C6D	C7D	C8D	-125.40(7)
O3D	C7D	C8D	C9D	112.81(11)
C6D	C7D	C8D	C9D	-65.89(12)
C7D	C8D	C9D	C10D	82.27(17)
C8D	C9D	C10D	C11E	-65.5(2)
C9D	C10D	C11D) C1D	64.3(2)
01D	C1D	C11D	C10E	45.11(13)
C6D	C1D	C11D	C10F	-77.35(12)
C2D	C1D	C11D	C10E	162.82(11)
01D'	C1D'	C2D'	C3D'	67(2)
C114	C1D'	C2D'	C3D'	-175.3(18)
C6D'	C1D'	C2D'	C3D'	-43 4(19)
C1D'	C2D'	C3D'	C4D'	48(3)
C2D'		C4D'		-45(3)
	C4D'		020	-73(2)
	C4D'	C5D'		43(2)
				177 0(11)
				-72.4(10)
				-12.4(10)
				-43.3(14)
				50.2(15)
				39.3(13)
				-45.7(15)
				174.0(11)
				-12.1(13)
				-1/7.7(11)
				42.0(13)
				-58.1(13)
				169.2(11)
C5D	C6D			123.7(12)
CID	C6D		C8D	-9.0(17)
O3D		C8D	C9D	-107.3(15)
C6D		C8D	C9D	70.9(16)
C/D	C8D	C9D'	C104	-87.4(18)
C8D'	C9D'	C104	C114	67(3)
C9D'	C104	C114	C1D'	-62(3)
01D'	C1D'	C114	C104	-40(2)
C2D'	C1D'	C114	C104	-161.9(19)
C6D'	C1D'	C114	C104	67(2)

Symmetry operations

1 'x, y, z' 2 '-x, y+1/2, -z'

2. TRANSANNULAR ENANTIOSELECTIVE (3+2) CYCLOADDITION OF CYCLOALKENONE HYDRAZONES

2.1. NMR spectra



Figure SI-68. ¹³C-NMR spectra of compound 21b.








5.533 5.525 5.525 5.525 5.525 5.525 5.516 5] [22i MM 1.00H 1.09H F66.0 7.07 1.34 2.04 Figure SI-77. ¹H-NMR spectra of compound 22i. JL 22i 140 130 120 110 100 f1 (ppm)

Figure SI-78. ¹³C-NMR spectra of compound 22i.



Figure SI-80. ¹³C-NMR spectra of compound 29.



Figure SI-82. ¹³C-NMR spectra of compound 30.



Figure SI-84. ¹³C-NMR spectra of compound 23a.















- 7.09

3.415 3.415 3.415 3.415 3.415 3.415 3.415 3.415 4.4154.415 4.4154.415 4.415 4.415 4.415 4.415 4.415 4.415 4.415 4.415 4.415 4.4154.415 4.415 4.415 4.415 4.415 4.4154.415 4.415 4.415 4.4154.415 4.415 4.415 4.4154.415 4.415 4.4154.415 4.415 4.4154.415 4.415 4.4154.415 4.415 4.4154.415 4.4154.415 4.4154.415 4.4154.415 4.4154.415



 CF_3 H H H H H H

70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 Figure SI-95. ¹⁹F-NMR spectra of compound 23e.







Figure SI-101. ¹³C-NMR spectra of compound 23j.



Figure SI-103. ¹³C-NMR spectra of compound 23k.

77.22 77.20 77.10 77.20 66.77 77.00 66.67 66.67 66.67 66.66



Figure SI-105. ¹³C-NMR spectra of compound 23I.







Figure SI-109. ¹³C-NMR spectra of compound 23n.





Figure SI-111. ¹³C-NMR spectra of compound 230.





Figure SI-113. ¹³C-NMR spectra of compound 23p.



Figure SI-115. ¹³C-NMR spectra of compound 23a'.











7,752





CF₃ Ac N H H

23c'



Figure SI-120. ¹³C-NMR spectra of compound 23c'.

 $\begin{array}{c} \mathsf{CF}_3 \\ \mathsf{N} \\ \mathsf{N} \\ \mathsf{H} \\ \mathsf{H} \\ \mathsf{H} \\ \mathsf{H} \\ \mathsf{23c'} \end{array}$





7.887 7.887 7.887 7.887 7.887 7.784 7.744 7.744 7.744 7.744 7.744 7.744 7.744 7.7157











 $< \frac{-62.99}{-63.18}$













Figure SI-132. ¹³C-NMR spectra of compound 23I'.

Ph

23m'



Figure SI-134. ¹³C-NMR spectra of compound 23m'.



Figure SI-136. ¹³C-NMR spectra of compound 23n'.








Figure SI-140. ¹³C-NMR spectra of compound **32a**.



Figure SI-142. ¹³C-NMR spectra of compound 32k.



Figure SI-144. ¹³C-NMR spectra of compound 32I.



Figure SI-146. ¹³C-NMR spectra of compound 32m.



Figure SI-148. ¹³C-NMR spectra of compound 32n.





Figure SI-152. ¹³C-NMR spectra of compound 32p.

2.2. HPLC traces



Figure SI-153. HPLC traces for racemic and compound 23a'.



Figure SI-154. HPLC traces for racemic and compound 23b'.







Figure SI-156. HPLC traces for racemic and compound 23d'.







Figure SI-158. HPLC traces for racemic and compound 23f'.









Figure SI-160. HPLC traces for racemic and compound 23k'.



Figure SI-161. HPLC traces for racemic and compound 23I'.



Figure SI-162. HPLC traces for racemic and compound 23m'.



Figure SI-163. HPLC traces for racemic and compound 23n'.





Figure SI-164. HPLC traces for racemic and compound 23o'.



Figure SI-165. HPLC traces for racemic and compound 32a.

2.3. X-ray details

Summary of Data CCDC 2091628

Crystal Data for *ent*-**23**I' C₂₅H₃₀N₂O (M =374.51 g/mol): orthorhombic, space group P2₁2₁2₁ (no. 19), a = 10.09480(5) Å, b = 12.79812(6) Å, c = 15.78055(7) Å, V = 2038.760(17) Å³, Z = 4, T = 150.01(10) K, μ (CuK α) = 0.572 mm⁻¹, *Dcalc* = 1.220 g/cm³, 38523 reflections measured (8.896° $\leq 2\Theta \leq 145.932^{\circ}$), 4064 unique (R_{int} = 0.0309, R_{sigma} = 0.0134) which were used in all calculations. The final R₁ was 0.0285 (I > 2 σ (I)) and wR₂ was 0.0744 (all data).



Figure SI-166. X-Ray structure and ORTEP diagram (50% probability) for ent-23I'.

Table SI-7. Crystal data and structure refinement for ent-23I'. Identification code Empirical formula Formula weight Temperature/K Crystal system Space group a/Å b/Å c/Å α/° β/° γ/° Volume/Å³ Ζ $\rho_{calc}g/cm^3$ µ/mm⁻¹ F(000) Crystal size/mm³ Radiation 2O range for data collection/° Index ranges **Reflections collected** Independent reflections Data/restraints/parameters Goodness-of-fit on F² Final R indexes $[I \ge 2\sigma (I)]$ Final R indexes [all data] Largest diff. peak/hole / e Å-3 Flack parameter

a20200290_JS250Brem $C_{25}H_{30}N_2O$ 374.51 150.01(10) orthorhombic $P2_{1}2_{1}2_{1}$ 10.09480(5) 12.79812(6) 15.78055(7) 90 90 90 2038.760(17) 4 1.220 0.572 808.0 0.542 × 0.260 × 0.240 $CuK\alpha$ (λ = 1.54184) 8.896 to 145.932 $-12 \le h \le 12, -15 \le k \le 15, -19 \le l \le 19$ 38523 4064 [R_{int} = 0.0309, R_{sigma} = 0.0134] 4064/0/255 1.085 $R_1 = 0.0285$, $wR_2 = 0.0741$ $R_1 = 0.0287$, $wR_2 = 0.0744$ 0.17/-0.17 0.00(6)

3. SWITCHABLE BRØNSTED ACID-CATALYZED RING CONTRACTION/ ENANTIOSELECTIVE ALLYLATION



Figure SI-168. ¹³C-NMR spectra of compound 35a.









Figure SI-173. ¹³C-NMR spectra of compound 35b.



Figure SI-175. ¹³C-NMR spectra of compound 35c.



















Figure SI-185. ¹³C-NMR spectra of compound 35h.





Figure SI-189. ¹³C-NMR spectra of compound 35j.

T C

3.2. HPLC traces



Figure SI-190. HPLC traces for racemic and compound 35a.



Figure SI-191. HPLC traces for racemic and compound 35b.


Figure SI-192. HPLC traces for racemic and compound 35c.



Figure SI-193. HPLC traces for racemic and compound 35d.



Figure SI-194. HPLC traces for racemic and compound 35e.



Figure SI-195. HPLC traces for racemic and compound 35f.



Figure SI-196. HPLC traces for racemic and compound 35g.



Figure SI-197. HPLC traces for racemic and compound 35h.





Figure SI-198. HPLC traces for racemic and compound 35i.



Figure SI-199. HPLC traces for racemic and compound 35j.