

Palladium/Zinc Co-catalyzed Asymmetric Transfer Hydrogenation of Oxabenzonorbornadienes with Alcohols as Hydrogen Sources

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Supporting Information

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A: Experimental Material

The reaction and manipulations were performed under an atmosphere of argon using standard Schlenk techniques and drybox (Mikrouna, Supper 1220/750). Anhydrous DME, THF, and dioxane were distilled from sodium benzophenoneketyl prior to use. Anhydrous DCM (Dichloromethane) was distilled from calcium hydride and stored under argon. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-Advance 400 MHz or 100 MHz spectrometer, and CDCl_3 or C_6D_6 was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane as internal standard, and J values were given in Hz. The enantioselective excesses were determined by Agilent 1260 Series HPLC using Daicel OJ-H or OD-H chiral columns eluted with a mixture of isopropyl alcohol and hexane. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents. Compound **3aa** is known in the literature.^[1] Compounds **3ab-af** and **4** are new and their characterization data are as given in section C.

B: General Procedure

B₁: General Procedure for Palladium / Zinc co-catalyzed Transfer Hydrogenation of Oxabenzonorbornadienes with Alcohols

$\text{Pd}(\text{OAc})_2$ and (*R*)-Phanephos in THF was added to a Schlenk tube under argon atmosphere, the resulting solution was stirred at room temperature for 30 minutes, then $\text{Zn}(\text{OTf})_2$ was added. After stirred for 10 minutes, oxabenzonorbornadienes was added and the mixture was stirred for another 10 minutes before the addition of alcohols. The solution was stirred at room temperature (25°C) with TLC monitoring until the complete consumption of oxabenzonorbornadienes. After evaporation of the solvent under reduced pressure, the residue was purified by chromatography on a silica gel column to afford the desired products.

B₂: Reaction Procedure for additional reaction of Oxabenzonorbornadiene **1a** with Methanol

$\text{Pd}(\text{OAc})_2$ and (*R*)-Difluorophos in DCE was added to a Schlenk tube under argon atmosphere, the resulting solution was stirred at room temperature for 30 minutes, then $\text{Zn}(\text{OTf})_2$ was added. After stirred for 10 minutes, oxabenzonorbornadiene **1a**, alcohols and DCE were added. The solution was stirred at 40°C with TLC monitoring until the complete consumption of oxabenzonorbornadiene **1a**. Then the solvent was removed under reduced pressure, the residue was purified by chromatography on a silica gel column to afford the desired product **4**.

C: Characterization Data of Products

(S)-1,2-dihydronaphthalen-1-ol (3aa)

White solid, 87% yield, 98% *ee*. $[\alpha]_{\text{D}}^{18} = -53.0$ ($c = 2.0 \times 10^{-3}$, CH_2Cl_2); m.p. 50-52 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 7.2$ Hz, 1H), 7.27-7.23 (m, 2H), 7.12 (d, $J = 6.8$ Hz, 1H), 6.54 (d, $J = 9.6$ Hz, 1H), 6.00-5.96 (m, 1H), 4.76 (s, 1H), 2.58 (s, 2H), 1.94 (s, 1H). The *ee* of **3aa** was determined by HPLC analysis on a Daicel Chiralcel OD-H column, conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, $\lambda = 254$ nm; $t_{\text{major}} = 11.2$ min, $t_{\text{minor}} = 12.3$ min.

(S)-6,7-dibromo-1,2-dihydronaphthalen-1-ol (3ab)

White solid, 78% yield, 97% *ee*. $[\alpha]_{\text{D}}^{27} = +3.6$ ($c = 1.2 \times 10^{-2}$, CH_2Cl_2); m.p. 81-82 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (s, 1H), 7.25 (s, 1H), 6.33 (d, $J = 9.6$ Hz, 1H), 5.96 (t, $J = 9.2$ Hz, 1H), 4.63 (t, $J = 4.8$ Hz, 1H), 2.44 (s, 2H), 2.18 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.1, 133.5, 131.6, 131.1, 127.6, 125.6, 124.2, 122.8, 66.8, 32.4. HRMS calcd for $\text{C}_{10}\text{H}_8\text{Br}_2\text{O}$ $[\text{M}]^+$: 301.8942. Found: 301.8945. The *ee* of **3ab** was determined by HPLC analysis on a Daicel Chiralcel OJ-H column, conditions: *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, $\lambda = 254$ nm; $t_{\text{major}} = 11.3$ min, $t_{\text{minor}} = 14.7$ min.

(S)-6,7-dimethyl-1,2-dihydronaphthalen-1-ol (3ac)

White solid, 81% yield, 98% *ee*. $[\alpha]_{\text{D}}^{18} = -19.3$ ($c = 1.4 \times 10^{-3}$, CH_2Cl_2); m.p. 86-88 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.14 (s, 1H), 6.92 (s, 1H), 6.51 (d, $J = 9.6$ Hz, 1H), 5.93 (t, $J = 4.8$ Hz, 1H), 4.72 (d, $J = 4.0$ Hz, 1H), 2.59 (d, $J = 4.4$ Hz, 2H), 2.26 (d, $J = 6.4$ Hz, 6H), 1.71 (d, $J = 6.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.8, 136.0, 133.7, 130.4, 128.6, 128.0, 126.9, 67.5, 32.8, 19.7, 19.5. HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O}$ $[\text{M}]^+$: 174.1045. Found: 174.1048. The *ee* of **3ac** was determined by HPLC analysis on a Daicel Chiralcel OD-H column, conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, $\lambda = 254$ nm; $t_{\text{major}} = 20.4$ min, $t_{\text{minor}} = 21.9$ min.

(S)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3ad)

White solid, 70% yield, 97% *ee*. $[\alpha]_{\text{D}}^{26} = -46.7$ ($c = 5.4 \times 10^{-3}$, CH_2Cl_2); m.p. 60-62 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.86 (d, $J = 9.8$ Hz, 1H), 6.69 (q, $J = 8.9$ Hz, 2H), 5.94 (t, $J = 7.5$ Hz, 1H), 5.10 (d, $J = 5.2$ Hz, 1H), 3.74 (d, $J = 13.4$ Hz, 6H), 2.66-2.41 (m, 2H), 2.07 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.7, 149.5, 124.9, 124.5, 122.8, 120.4, 111.1, 110.1, 60.3, 56.2, 56.0, 31.5. HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$ $[\text{M}]^+$: 206.0943. Found: 206.0947. The *ee* of **3ad** was determined by HPLC analysis on a Daicel Chiralcel OD-H column, conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, $\lambda = 254$ nm; $t_{\text{minor}} = 19.6$ min, $t_{\text{major}} = 21.7$ min.

(S)-2,3,6,7-tetrahydronaphtho[2,3-*b*][1,4]dioxin-6-ol (3ae)

White solid, 67% yield, 98% *ee*. $[\alpha]_{\text{D}}^{26} = +1.2$ ($c = 7.6 \times 10^{-3}$, CHCl_3); m.p. 63-65 °C; ^1H NMR (400 MHz, C_6D_6) δ 7.09 (s, 1H), 6.73 (s, 1H), 6.25 (d, $J = 9.6$ Hz, 1H), 5.65-5.60 (m, 1H), 4.52 (t, $J = 6.4$ Hz,

1H), 3.57 (s, 4H), 2.34-2.27 (m, 1H), 2.24-2.17(m, 1H). ¹³C NMR (100 MHz, C₆D₆) δ 144.1, 143.8, 132.1, 127.9, 127.5, 124.6, 117.0, 116.2, 68.1, 64.9, 64.8, 33.6. HRMS calcd for C₁₂H₁₂O₃ [M]⁺: 204.0786. Found: 204.0777. The *ee* of **3ae** was determined by HPLC analysis on a Daicel Chiralcel OD-H column, conditions: *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, λ = 254 nm; *t*_{minor} = 10.0 min, *t*_{major} = 13.8 min.

(S)-5,6-dihydronaphtho[2,3-*d*][1,3]dioxin-5-ol (**3af**)

White solid, 35% yield, 98% *ee*. [α]_D¹⁸ = -15.2 (c = 4.2×10⁻³, CHCl₃); m.p. 68-70 °C; ¹H NMR (400 MHz, C₆D₆) δ 6.87 (s, 1H), 6.58 (s, 1H), 6.17 (s, 1H), 5.87 (d, *J* = 9.6 Hz, 1H), 5.33-5.28 (m, 1H), 5.03-5.02 (m, 2H), 4.12 (t, *J* = 6.4 Hz, 1H), 2.00-1.94 (m, 1H), 1.90-1.83 (m, 1H). ¹³C NMR (100 MHz, C₆D₆) δ 147.5, 147.0, 131.7, 127.1, 123.6, 107.9, 107.2, 104.1, 100.8, 67.7, 32.8. The *ee* of **3af** was determined by HPLC analysis on a Daicel Chiralcel OD-H column, conditions: *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, λ = 254 nm; *t*_{minor} = 7.1 min, *t*_{major} = 8.4 min.

(1*R*,2*S*)-2-methoxy-1,2-dihydronaphthalen-1-ol (**4**)

White solid, 17% yield, 94% *ee*. [α]_D¹⁷ = 154.1 (c = 1.48×10⁻³, CHCl₃); m.p. 65-67 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.52 (m, 1H), 7.28-7.25 (m, 2H), 7.13-7.10 (m, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.08 (dd, *J* = 4.0, 9.6 Hz, 1H), 4.79 (t, *J* = 6.4 Hz, 1H), 4.03 (t, *J* = 4.4 Hz, 1H), 3.46 (s, 3H), 2.66 (d, *J* = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 131.9, 128.3, 128.2, 126.9, 125.5, 75.9, 69.0, 56.8. The *ee* was determined by HPLC analysis on a Daicel Chiralcel OD-H column, conditions: *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, λ = 254 nm; *t*_{minor} = 9.0 min, *t*_{major} = 10.2 min.

Note: The asymmetric reductive products **3ae** and **3af** are unstable, and tend to rearrange to the corresponding ketones **3ae'** and **3af'** spontaneously (Figure S1).

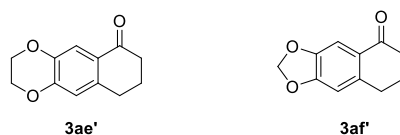
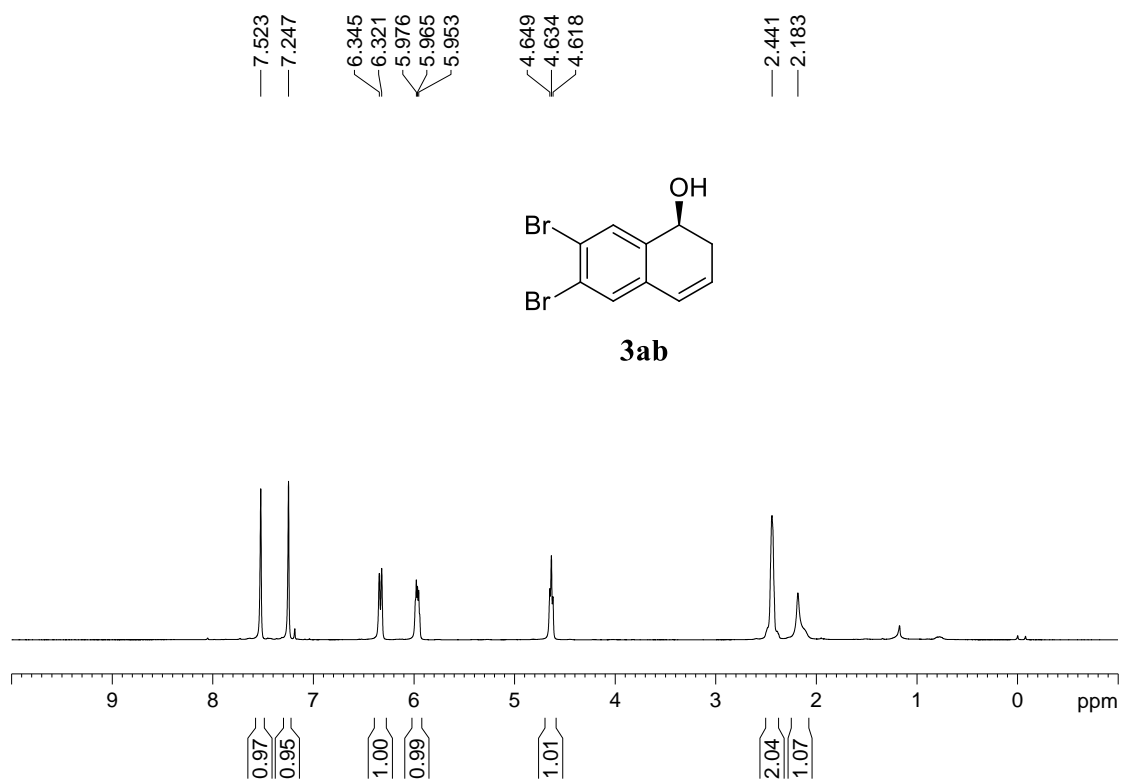
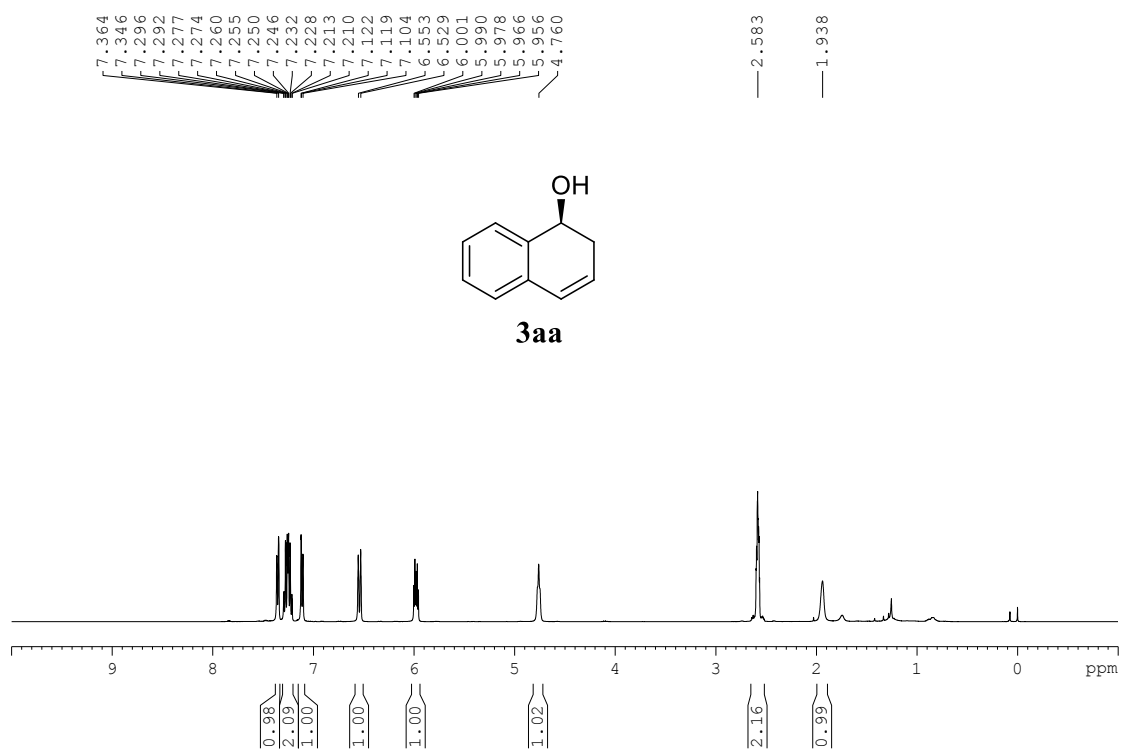


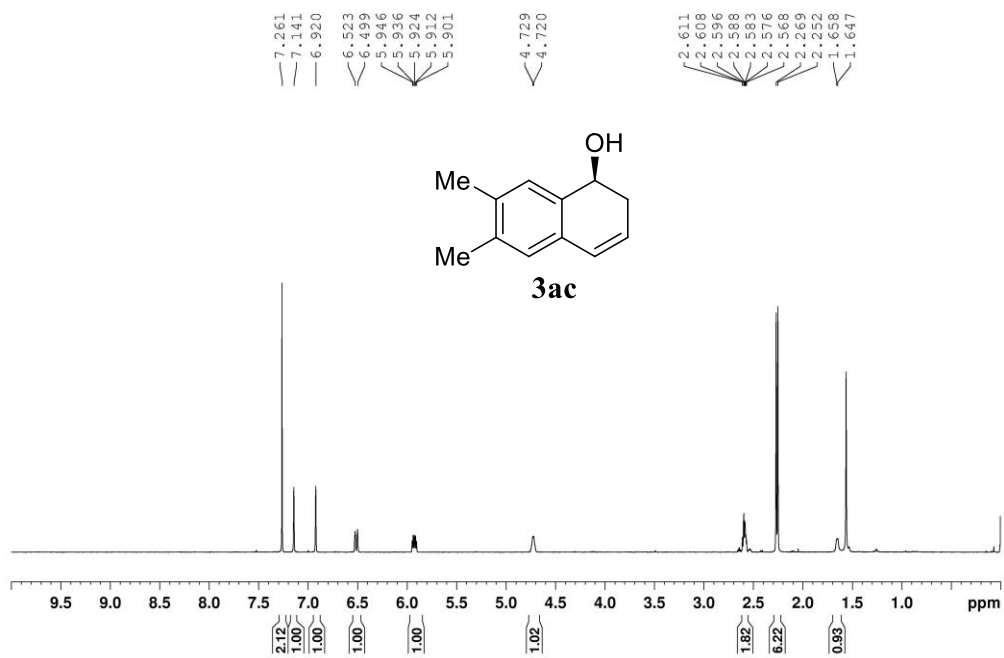
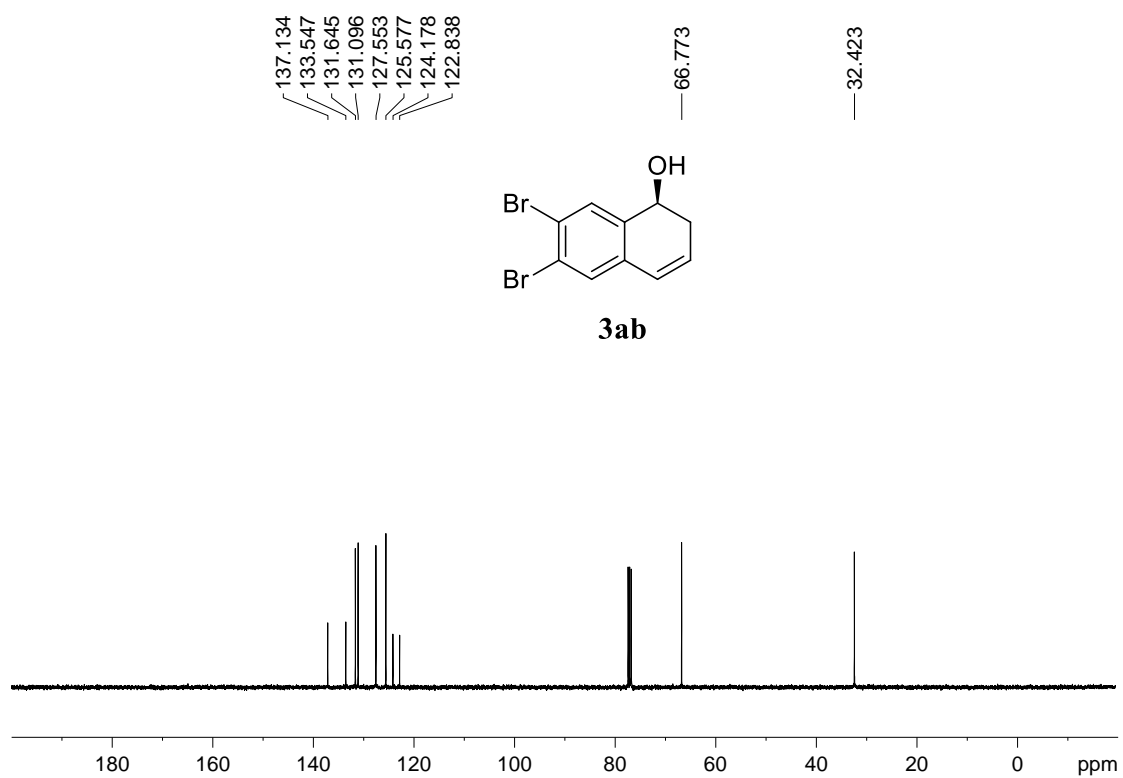
Figure S1. The chemical structures of ketones **3ae'** and **3af'**.

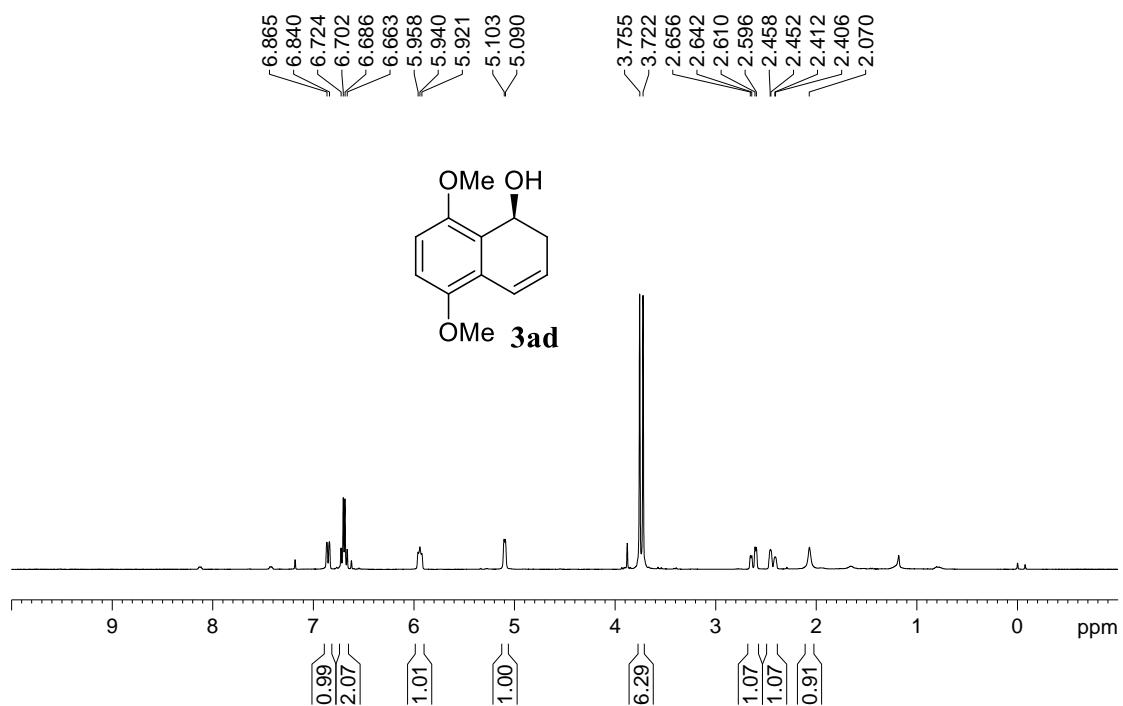
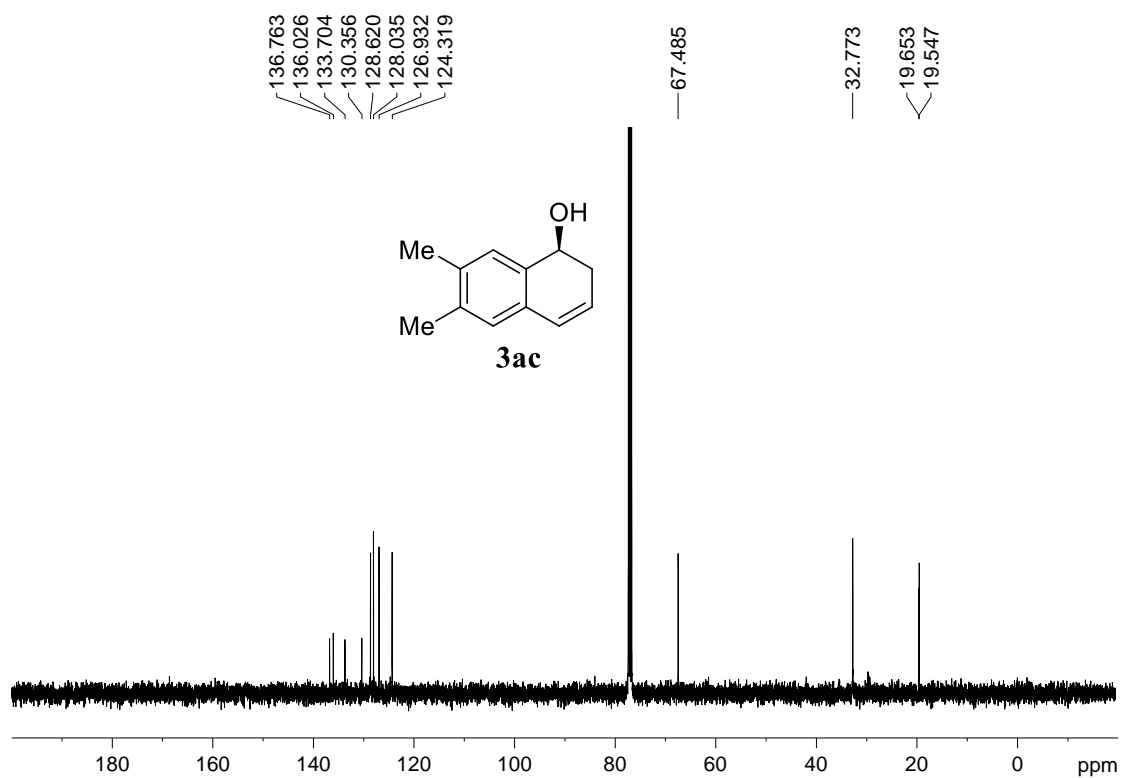
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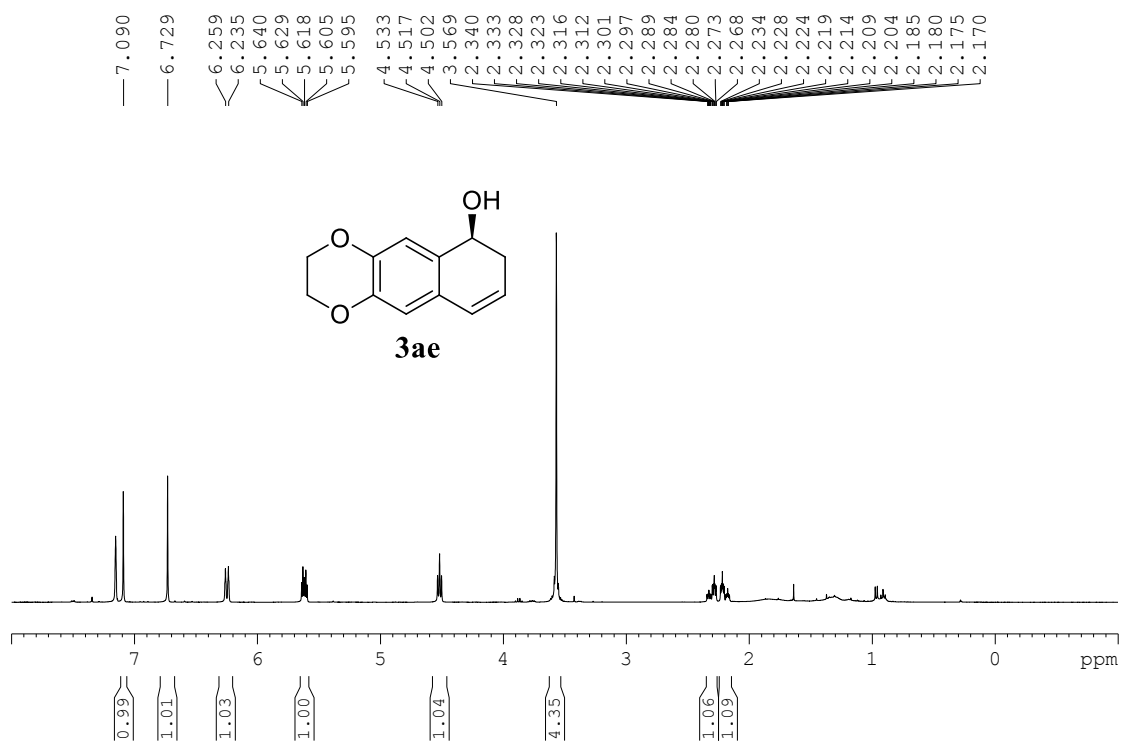
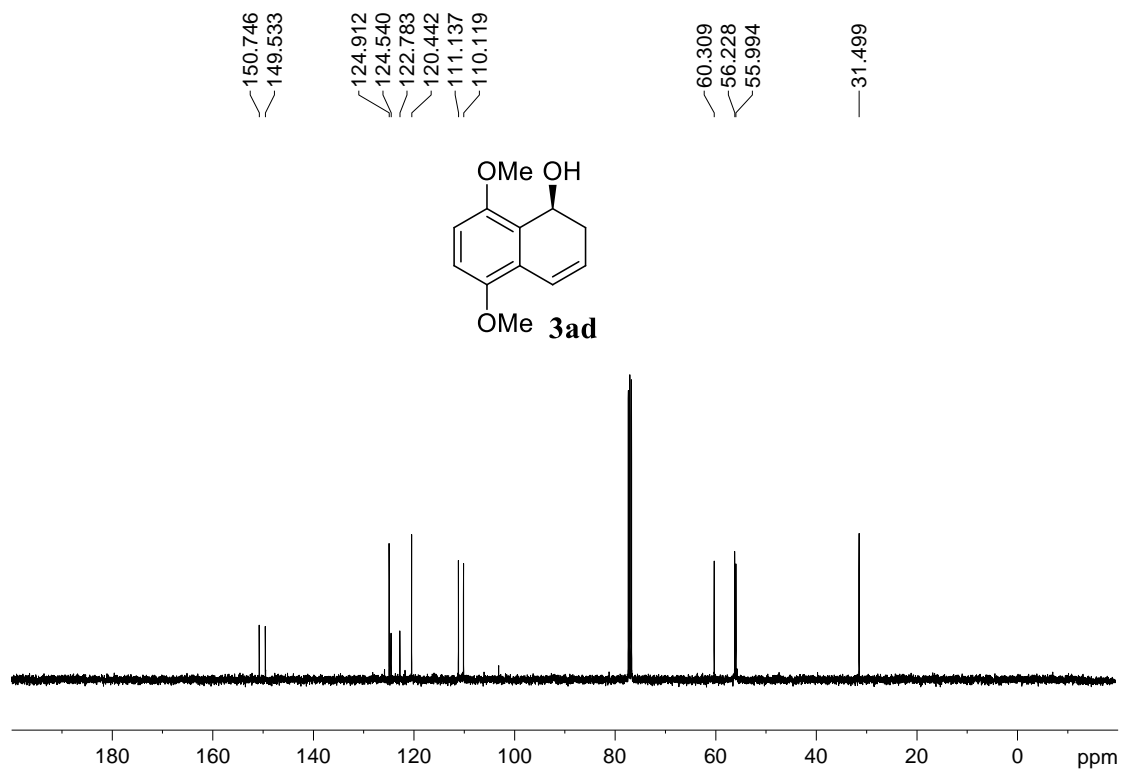
1. M. Lautens, T. Rovis, *J. Org. Chem.*, 1997, **62**, 5246-5247.

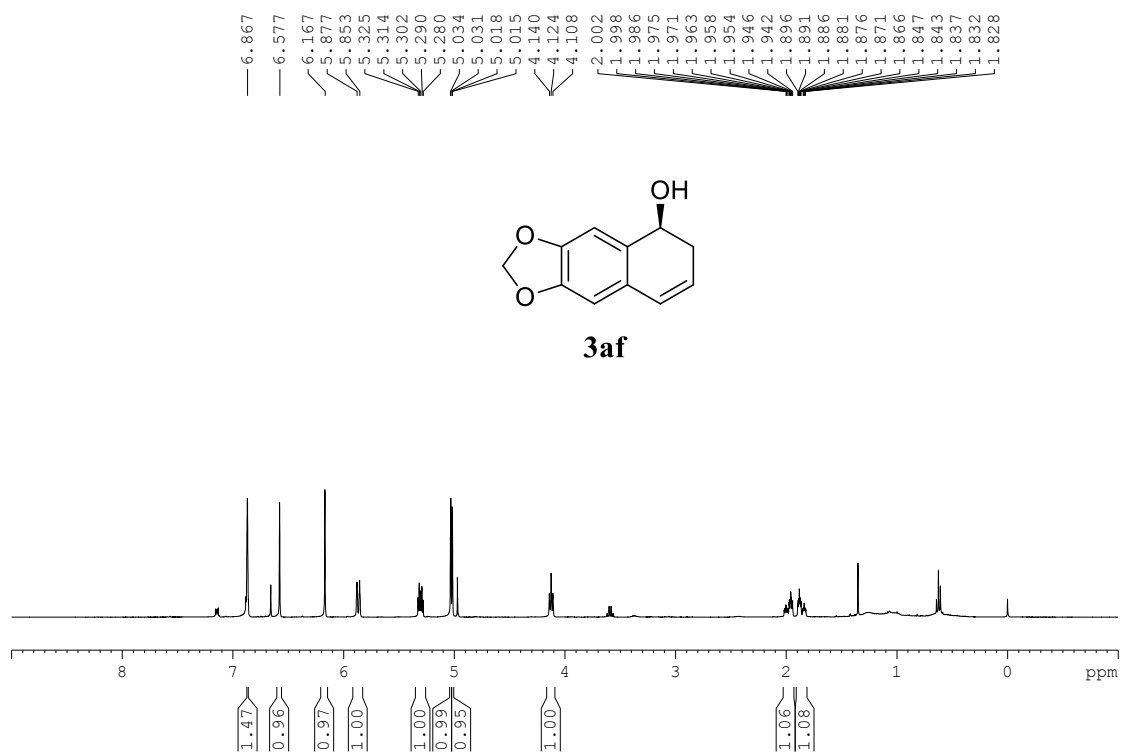
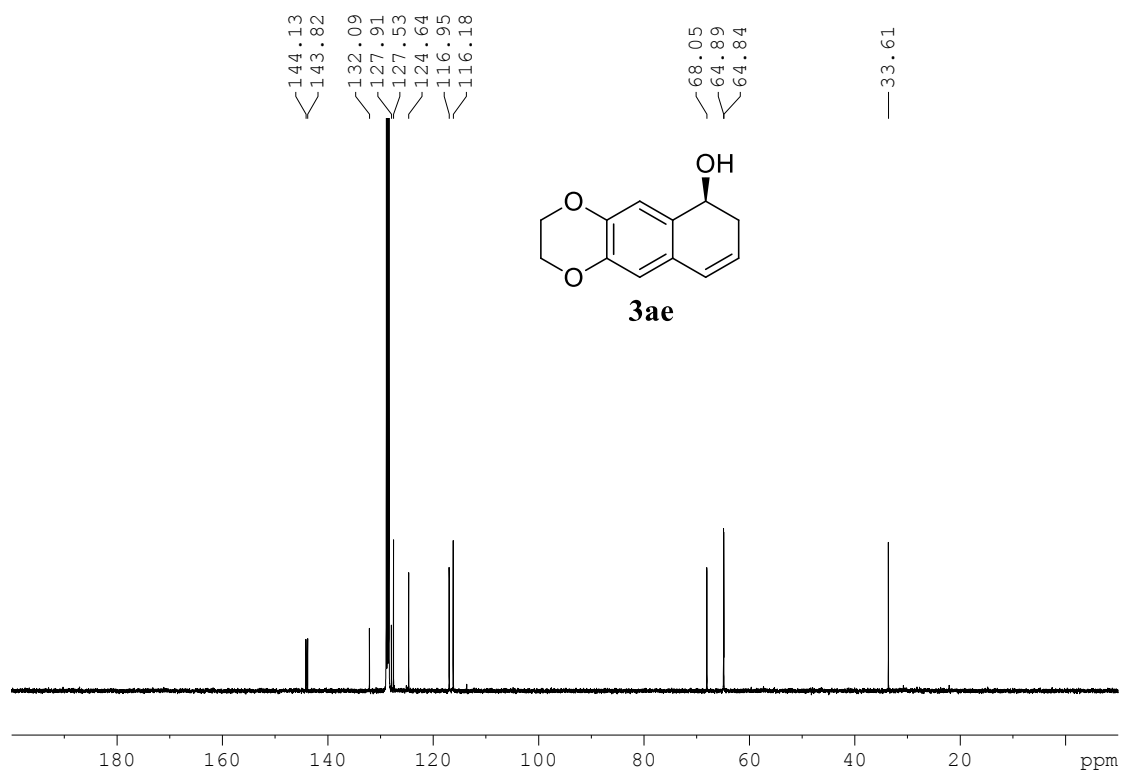
E: NMR spectra of Products

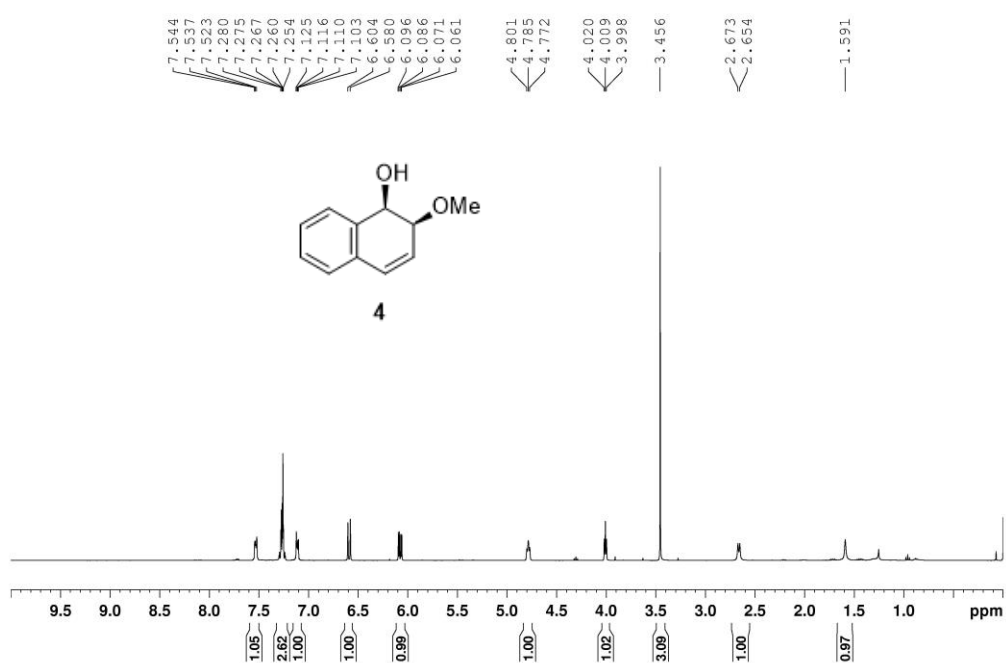
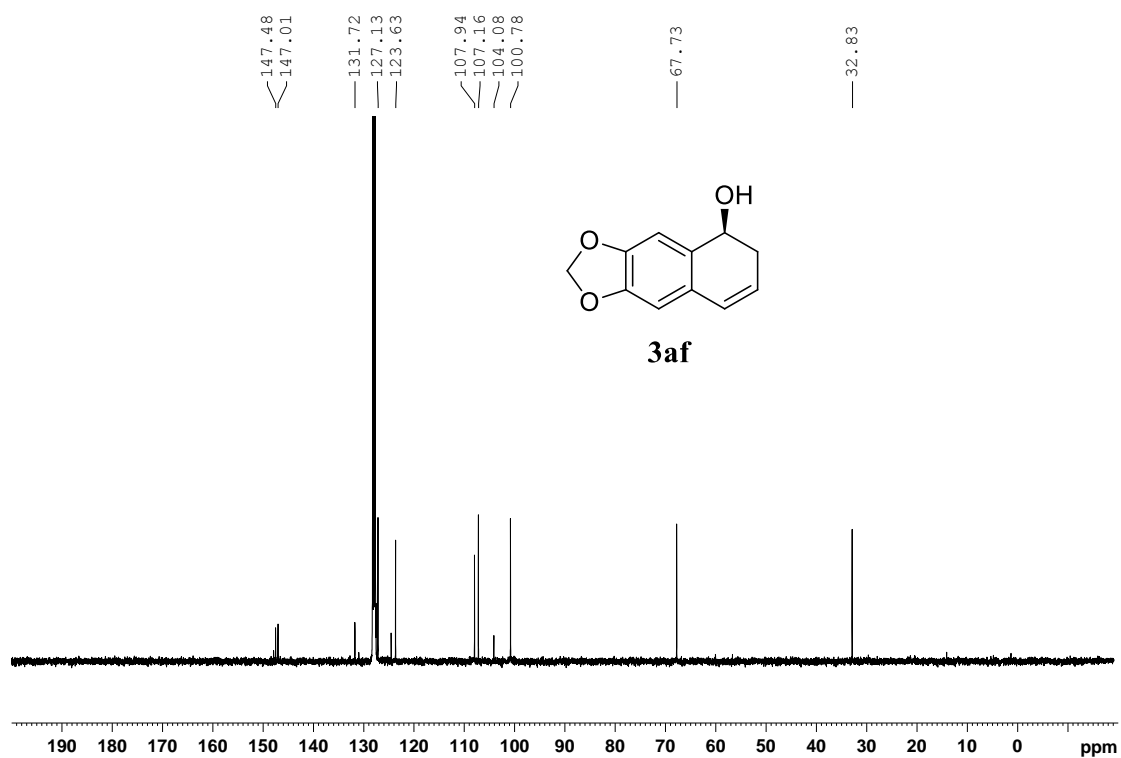


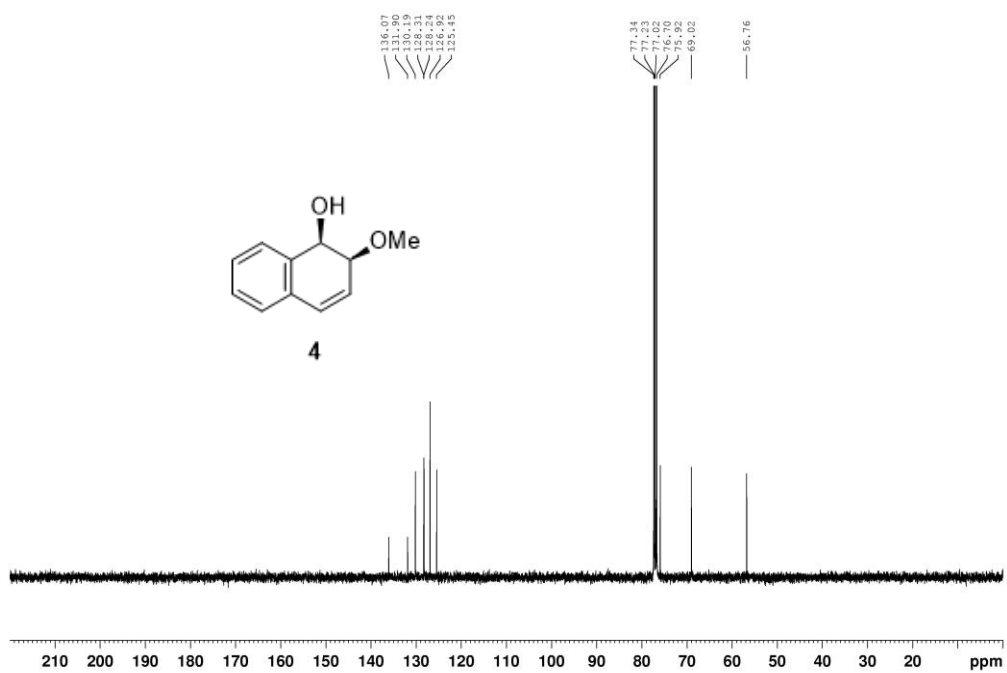












F: deuterium-labeling experiment

To confirm the hydrogen source of current reductive reaction, the reaction was performed by using CD₃OH instead of MeOH, about 89% deuterium was found in the 1,2-dihydronaphthalene structure of the product. This result indicates that the hydrogen atom on the 1,2-dihydronaphthalene moiety was derived exclusively from the methyl group of CD₃OH (Figure S1).

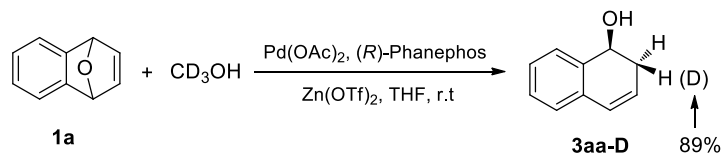


Figure S1. The reaction of 1a with CD₃OH.

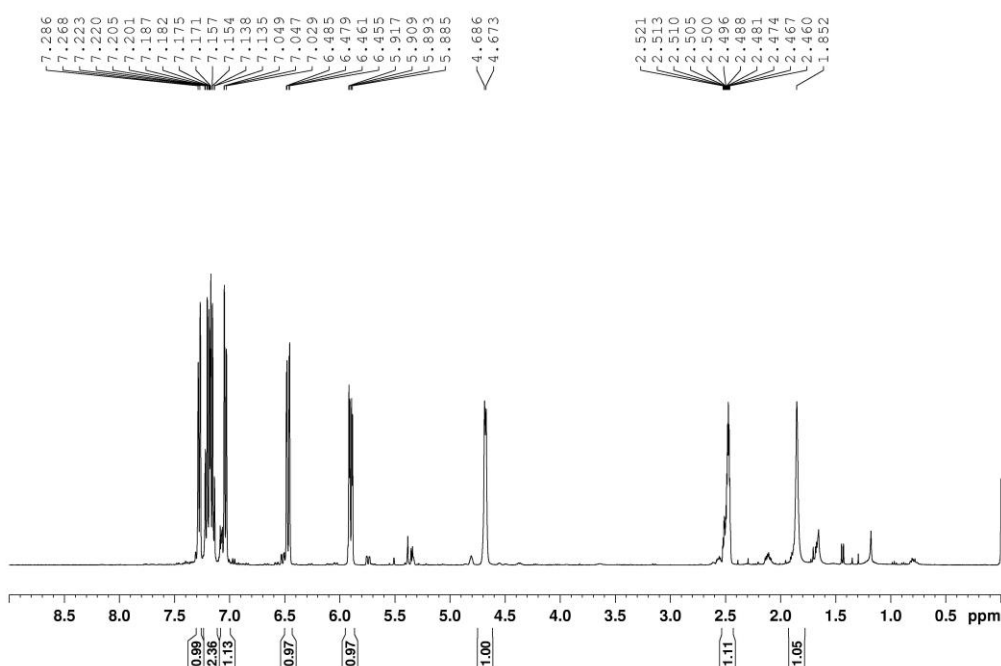
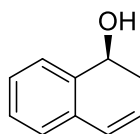


Figure S2. ¹H NMR spectrum of 3aa-D.

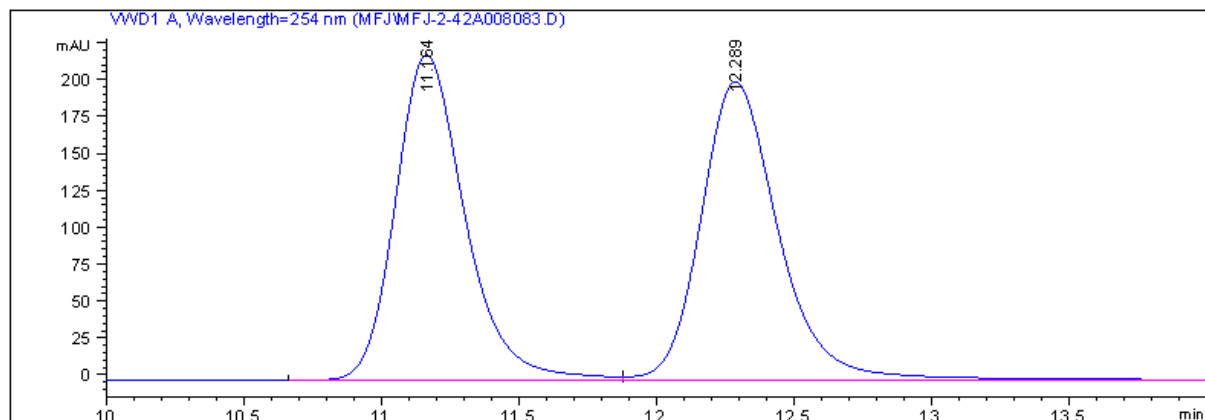
G: HPLC spectra of Products

Note: The racemic products were prepared by using (±)-binap or (±)-xylyl-phanephos as ligand.



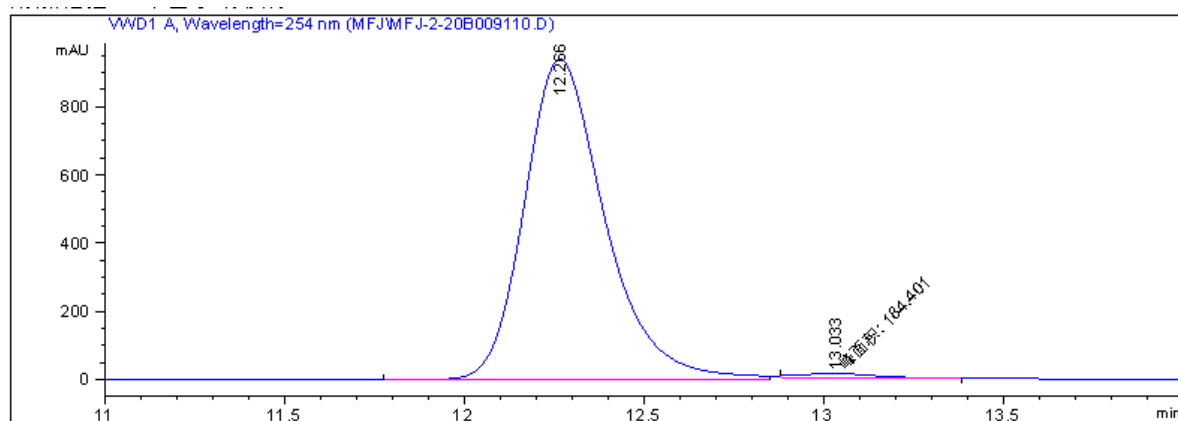
Racemic:

3aa

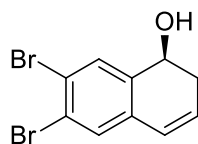
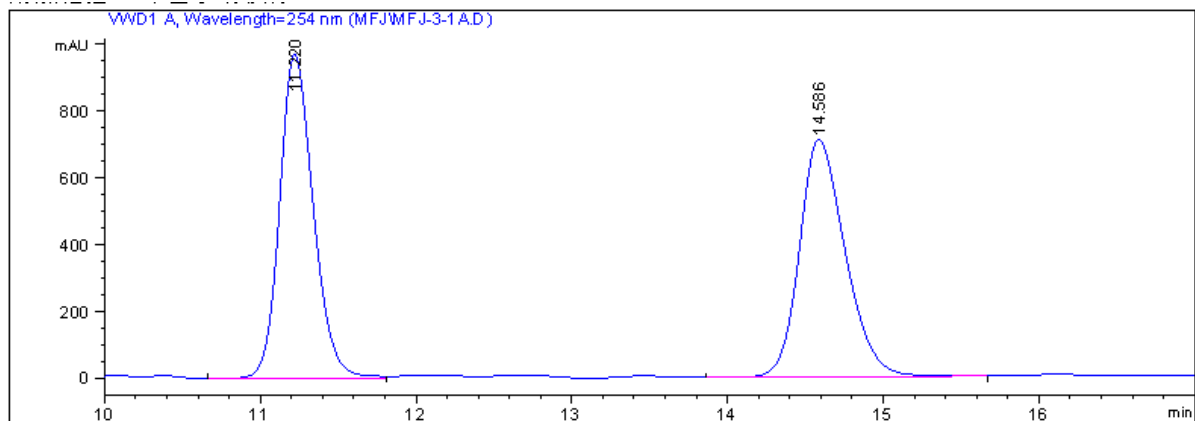


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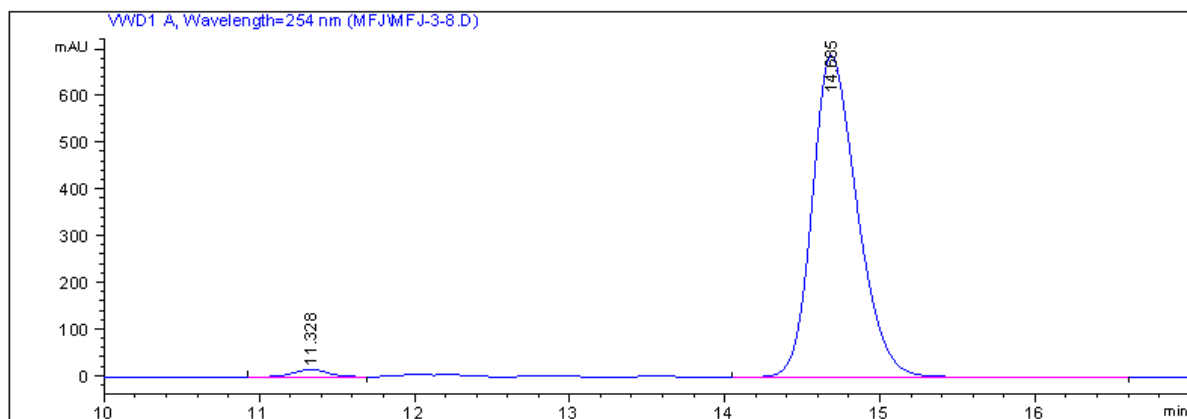
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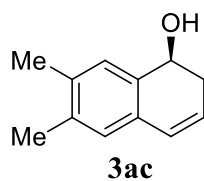
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2	12.233	MM	0.2806	73.96051	4.39222	1.0163

**3ab****Racemic:**

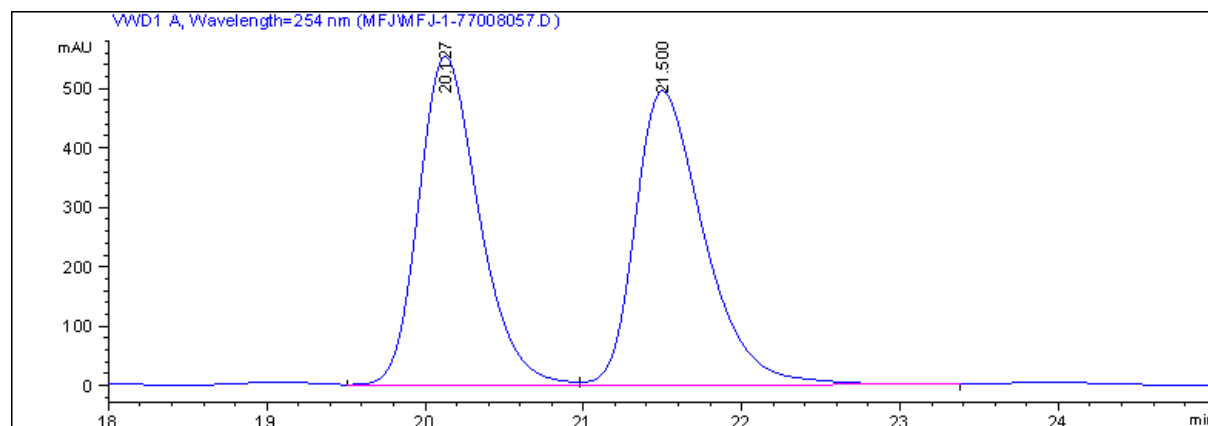
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Enantioenriched:

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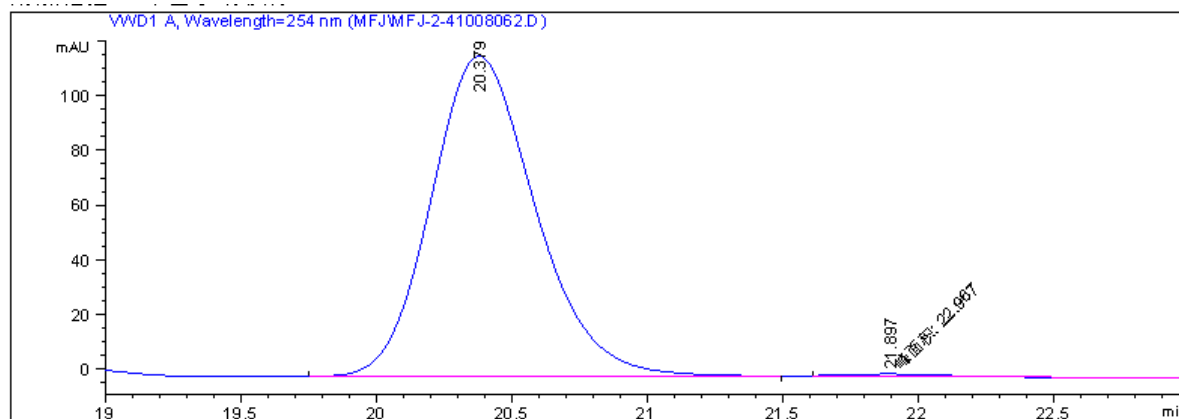


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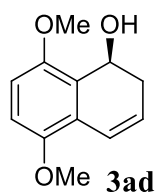


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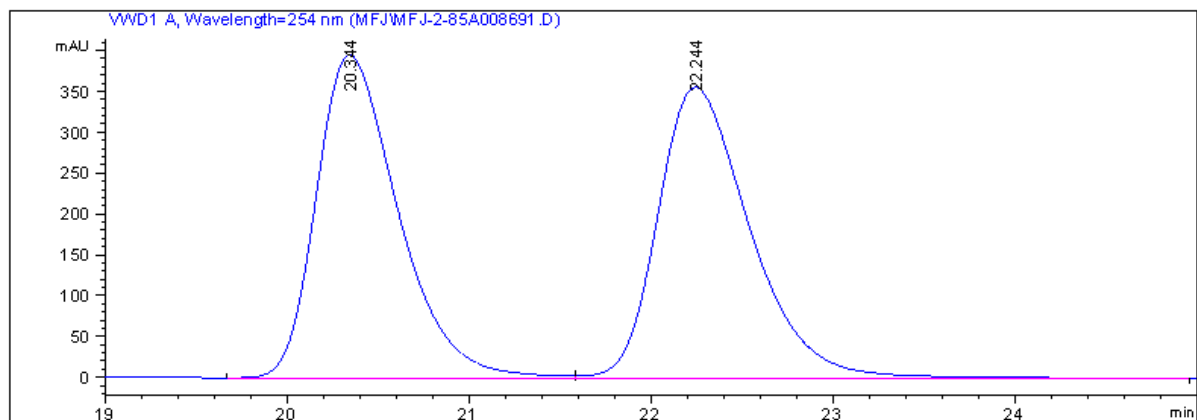
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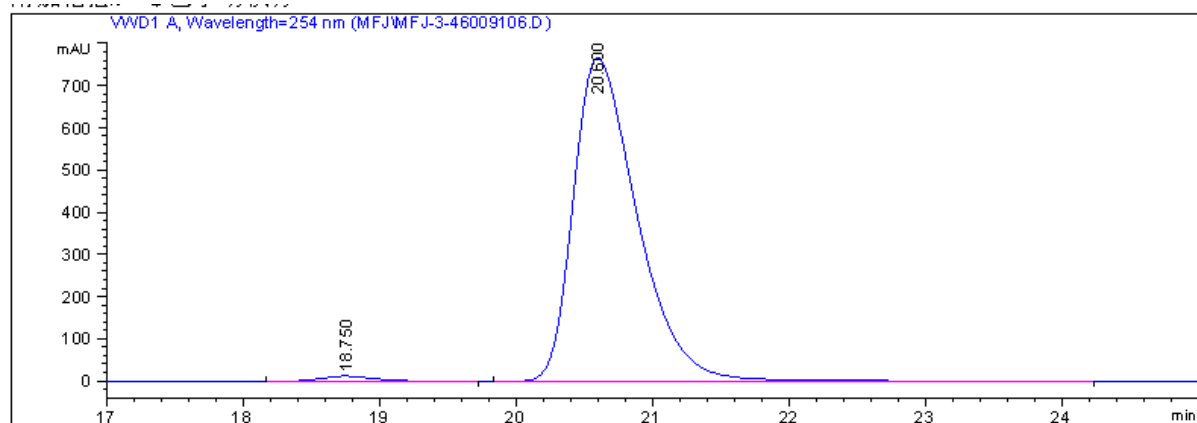


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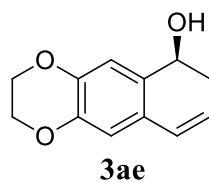


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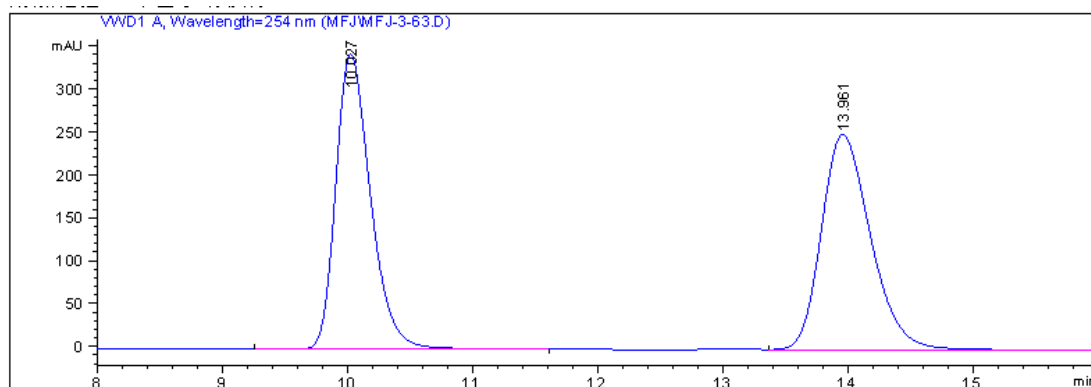
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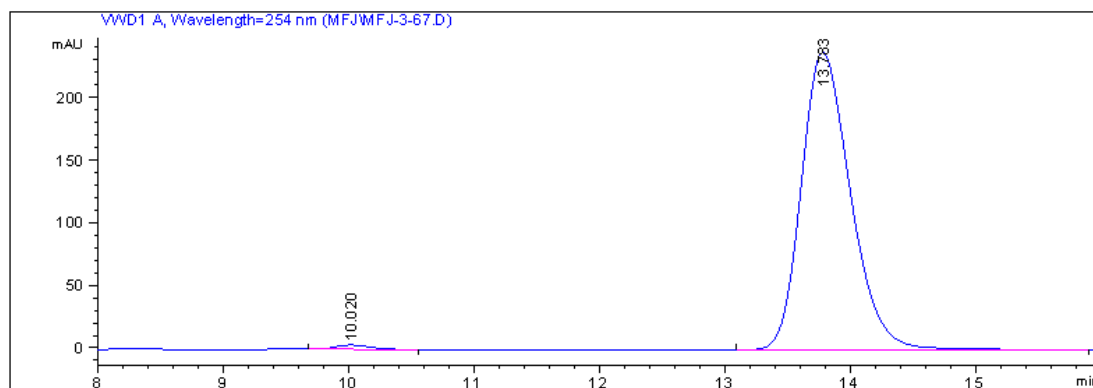


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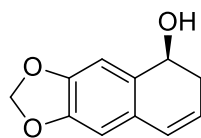
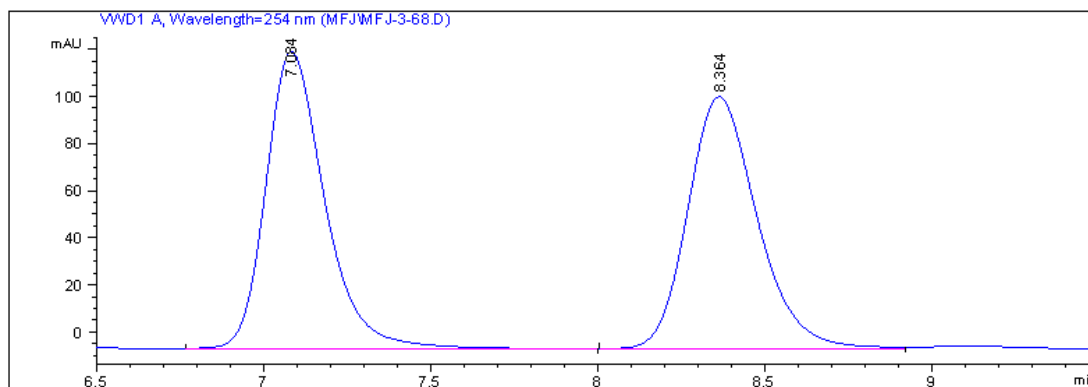


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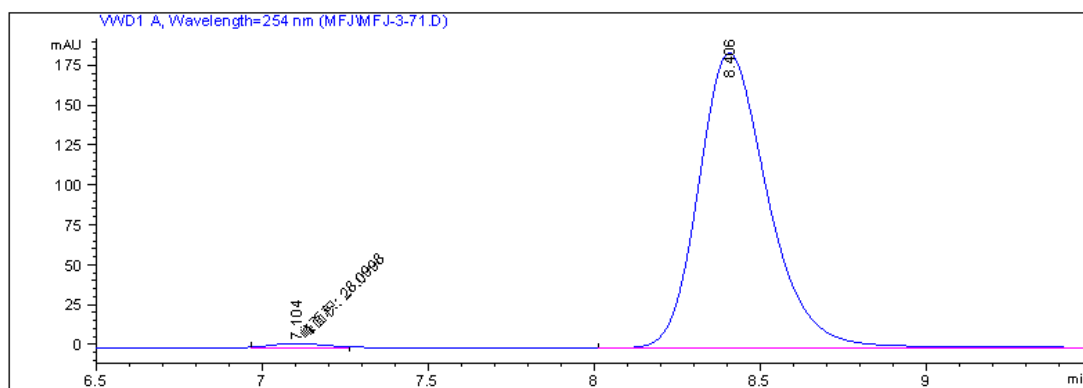
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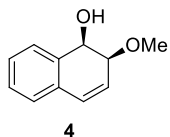
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**3af****Racemic:**

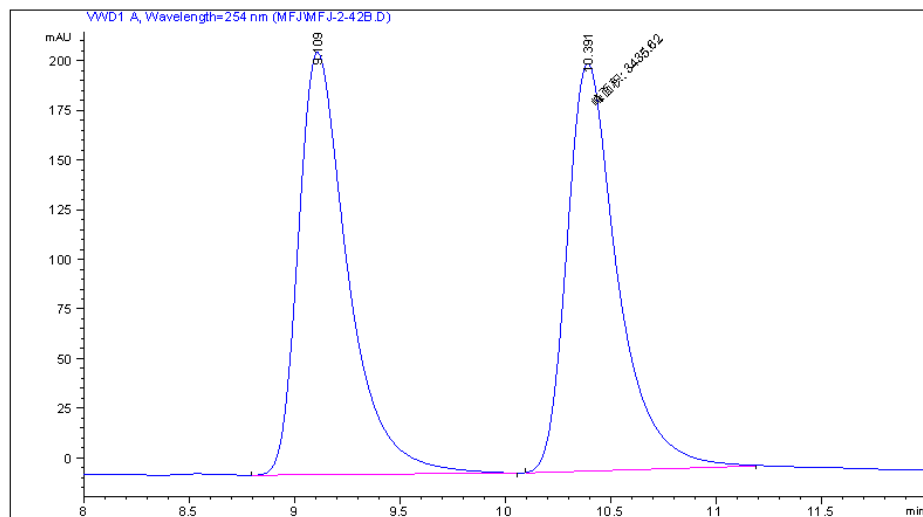
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2	8.364	BV	0.2210	1538.15088	106.81070	50.0999

Enantioenriched:

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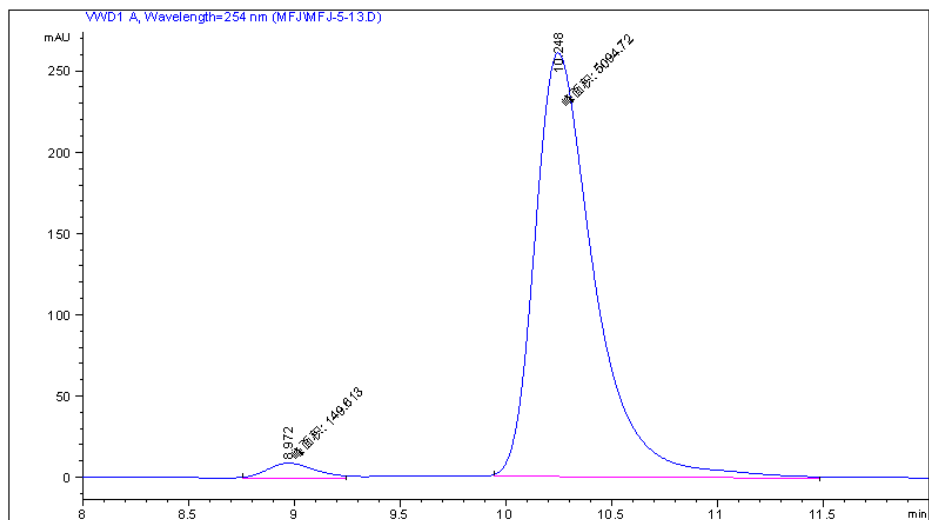


Racemic:

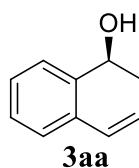


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.109	BB	0.2458	3477.58569	212.65042	50.3035
2	10.391	MM	0.2788	3435.62012	205.35614	49.6965

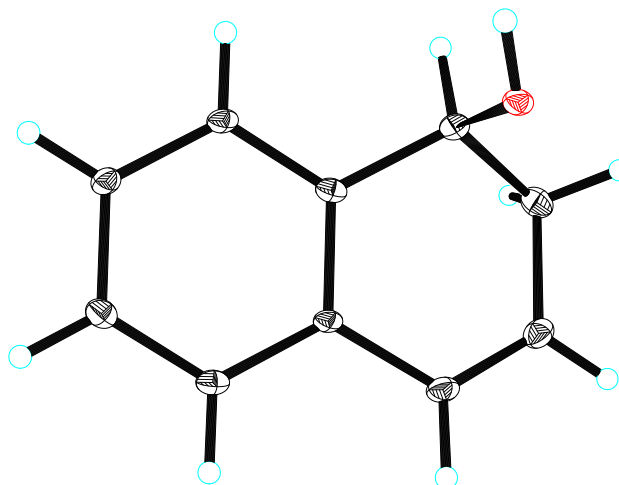
Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.972	MM	0.2657	149.61299	9.38617	2.8529
2	10.248	MM	0.3258	5094.71924	260.64209	97.1471

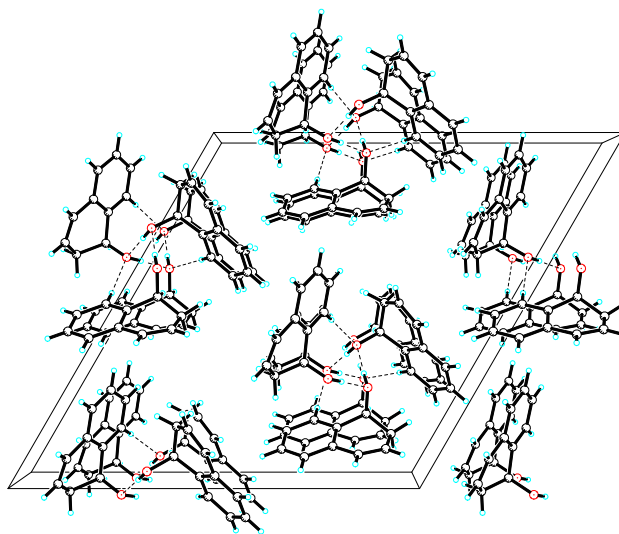
H: X-Ray Crystallography of Compound 3aa

Crystal data: $C_{10}H_{10}O$, $M = 146.18$, $a = 19.0072(9)$ Å, $b = 19.0072(9)$ Å, $c = 5.7243(3)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1790.97(19)$ Å³, $T = 100(2)$ K, space group $R3:H$, $Z = 9$, $\mu(\text{CuK}\alpha) = 0.608$ mm⁻¹, 4919 reflections measured, 1370 independent reflections ($R_{int} = 0.1282$). The final R_I values were 0.0773 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2082 ($I > 2\sigma(I)$). The final R_I values were 0.0812 (all data). The final $wR(F^2)$ values were 0.2129 (all data). The goodness of fit on F^2 was 1.121. Flack parameter = 0.1(6).



View of a molecule of **3aa** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.

View of the packing motif of **3aa**

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for **3aa**.

Identification code	cu_3aa_0m	
Empirical formula	C10 H10 O	
Formula weight	146.18	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Trigonal	
Space group	R3	
Unit cell dimensions	a = 19.0072(9) Å	$\alpha = 90^\circ$
	b = 19.0072(9) Å	$\beta = 90^\circ$
	c = 5.7243(3) Å	$\gamma = 120^\circ$
Volume	1790.97(19) Å ³	
Z	9	
Density (calculated)	1.220 Mg/m ³	
Absorption coefficient	0.608 mm ⁻¹	
F(000)	702	
Crystal size	1.860 x 0.350 x 0.350 mm ³	
Theta range for data collection	4.653 to 70.960 °	
Index ranges	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -6 ≤ l ≤ 6	
Reflections collected	4919	
Independent reflections	1370 [R(int) = 0.1282]	
Completeness to theta = 67.679 °	97.5 %	

Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1370 / 1 / 102
Goodness-of-fit on F ²	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0773, wR2 = 0.2082
R indices (all data)	R1 = 0.0812, wR2 = 0.2129
Absolute structure parameter	0.1(6)
Extinction coefficient	0.006(2)
Largest diff. peak and hole	0.436 and -0.486 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7153(2)	7314(2)	252(6)	16(1)
C(1)	8783(2)	8535(3)	2402(8)	21(1)
C(2)	8458(3)	8533(3)	-2(9)	22(1)
C(3)	7930(3)	7675(2)	-935(7)	15(1)
C(4)	8298(2)	7142(3)	-498(7)	14(1)
C(5)	8143(2)	6510(3)	-2001(6)	16(1)
C(6)	8428(2)	5977(2)	-1468(8)	17(1)
C(7)	8747(2)	7258(2)	1564(7)	14(1)
C(8)	8908(3)	7940(3)	3107(7)	19(1)
C(9)	9021(2)	6715(3)	2085(7)	16(1)
C(10)	8864(3)	6083(3)	584(7)	18(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **3aa**.

O(1)-C(3)	1.448(5)
O(1)-H(10)	0.8400
C(1)-C(8)	1.330(7)
C(1)-C(2)	1.507(7)
C(1)-H(1)	0.9500
C(2)-C(3)	1.523(6)
C(2)-H(3)	0.9900
C(2)-H(9)	0.9900

C(3)-C(4)	1.512(6)
C(3)-H(8)	1.0000
C(4)-C(5)	1.384(6)
C(4)-C(7)	1.408(5)
C(5)-C(6)	1.400(6)
C(5)-H(5)	0.9500
C(6)-C(10)	1.394(6)
C(6)-H(2)	0.9500
C(7)-C(9)	1.402(6)
C(7)-C(8)	1.469(6)
C(8)-H(4)	0.9500
C(9)-C(10)	1.383(6)
C(9)-H(7)	0.9500
C(10)-H(6)	0.9500
C(3)-O(1)-H(10)	109.5
C(8)-C(1)-C(2)	121.5(4)
C(8)-C(1)-H(1)	119.3
C(2)-C(1)-H(1)	119.3
C(1)-C(2)-C(3)	111.9(4)
C(1)-C(2)-H(3)	109.2
C(3)-C(2)-H(3)	109.2
C(1)-C(2)-H(9)	109.2
C(3)-C(2)-H(9)	109.2
H(3)-C(2)-H(9)	107.9
O(1)-C(3)-C(4)	108.0(3)
O(1)-C(3)-C(2)	108.3(3)
C(4)-C(3)-C(2)	112.4(3)
O(1)-C(3)-H(8)	109.4
C(4)-C(3)-H(8)	109.4
C(2)-C(3)-H(8)	109.4
C(5)-C(4)-C(7)	120.4(4)
C(5)-C(4)-C(3)	120.6(4)
C(7)-C(4)-C(3)	118.8(4)
C(4)-C(5)-C(6)	120.1(4)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(10)-C(6)-C(5)	119.8(4)

C(10)-C(6)-H(2)	120.1
C(5)-C(6)-H(2)	120.1
C(9)-C(7)-C(4)	118.9(4)
C(9)-C(7)-C(8)	122.1(4)
C(4)-C(7)-C(8)	119.0(4)
C(1)-C(8)-C(7)	121.4(4)
C(1)-C(8)-H(4)	119.3
C(7)-C(8)-H(4)	119.3
C(10)-C(9)-C(7)	120.6(4)
C(10)-C(9)-H(7)	119.7
C(7)-C(9)-H(7)	119.7
C(9)-C(10)-C(6)	120.2(4)
C(9)-C(10)-H(6)	119.9
C(6)-C(10)-H(6)	119.9

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	15(2)	24(2)	11(2)	0(1)	0(1)	11(1)
C(1)	19(2)	20(2)	21(2)	-6(2)	-3(2)	8(2)
C(2)	21(2)	20(2)	23(3)	5(2)	-1(2)	10(2)
C(3)	20(2)	20(2)	7(2)	3(1)	3(2)	10(2)
C(4)	12(2)	20(2)	11(2)	4(2)	2(1)	7(2)
C(5)	15(2)	25(2)	9(2)	-2(2)	0(2)	11(2)
C(6)	19(2)	22(2)	13(2)	-3(2)	-1(2)	12(2)
C(7)	15(2)	20(2)	7(2)	2(1)	2(1)	9(2)
C(8)	20(2)	27(2)	11(2)	0(2)	0(2)	12(2)
C(9)	13(2)	23(2)	12(2)	1(2)	0(1)	8(2)
C(10)	19(2)	24(2)	14(3)	3(2)	3(2)	14(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3aa**.

	x	y	z	U(eq)
H(10)	6780	7042	-707	24
H(1)	8900	8971	3437	25
H(3)	8919	8842	-1083	26
H(9)	8135	8810	57	26
H(8)	7844	7698	-2651	19
H(5)	7844	6438	-3396	19
H(2)	8323	5545	-2502	21
H(4)	9107	7957	4641	23
H(7)	9318	6782	3483	20
H(6)	9054	5719	952	21

Table 6. Torsion angles [$^\circ$] for **3aa**.

C(8)-C(1)-C(2)-C(3)	28.3(6)
C(1)-C(2)-C(3)-O(1)	75.2(4)
C(1)-C(2)-C(3)-C(4)	-44.0(4)
O(1)-C(3)-C(4)-C(5)	89.9(4)
C(2)-C(3)-C(4)-C(5)	-150.7(4)
O(1)-C(3)-C(4)-C(7)	-84.9(4)
C(2)-C(3)-C(4)-C(7)	34.4(5)
C(7)-C(4)-C(5)-C(6)	0.5(6)
C(3)-C(4)-C(5)-C(6)	-174.3(4)
C(4)-C(5)-C(6)-C(10)	0.2(6)
C(5)-C(4)-C(7)-C(9)	-1.0(6)
C(3)-C(4)-C(7)-C(9)	173.8(4)
C(5)-C(4)-C(7)-C(8)	179.3(4)
C(3)-C(4)-C(7)-C(8)	-5.9(5)
C(2)-C(1)-C(8)-C(7)	0.8(6)
C(9)-C(7)-C(8)-C(1)	167.1(4)
C(4)-C(7)-C(8)-C(1)	-13.2(6)
C(4)-C(7)-C(9)-C(10)	0.9(6)

C(8)-C(7)-C(9)-C(10)	-179.4(3)
C(7)-C(9)-C(10)-C(6)	-0.2(6)
C(5)-C(6)-C(10)-C(9)	-0.4(6)

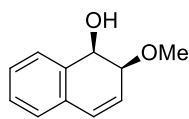
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1
O(1)-H(10)...O(1)#1	0.84	1.87	2.708(4)	174.1

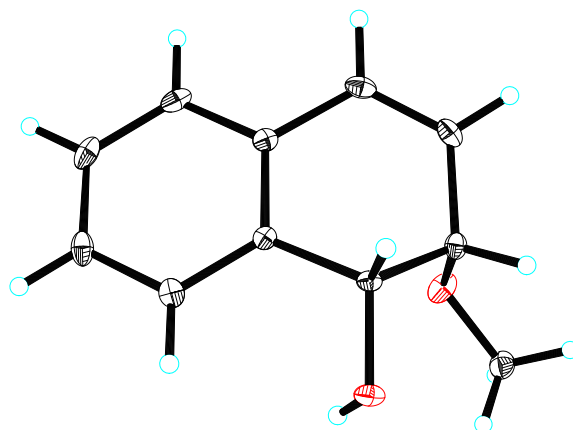
Symmetry transformations used to generate equivalent atoms:

#1 -y+4/3,x-y+2/3,z-1/3

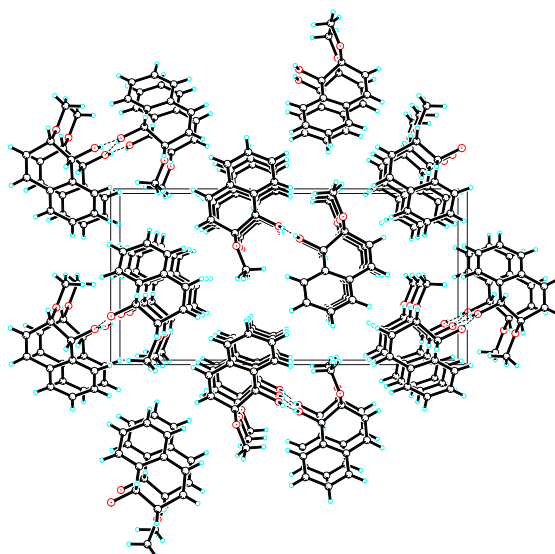
I: X-Ray Crystallography of Compound 4

4

Crystal data for cu_vmj1_0m: $C_{11}H_{12}O_2$, $M = 176.21$, $a = 4.6462(2) \text{ \AA}$, $b = 9.7488(3) \text{ \AA}$, $c = 19.6719(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 891.04(5) \text{ \AA}^3$, $T = 100(2) \text{ K}$, space group $P212121$, $Z = 4$, $\mu(\text{CuK}\alpha) = 0.720 \text{ mm}^{-1}$, 4844 reflections measured, 1612 independent reflections ($R_{int} = 0.0298$). The final R_I values were 0.0461 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1384 ($I > 2\sigma(I)$). The final R_I values were 0.0461 (all data). The final $wR(F^2)$ values were 0.1385 (all data). The goodness of fit on F^2 was 1.203. Flack parameter = 0.15(6).



View of a molecule of vmfj1 with the atom-labelling scheme.
Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of vmfj1.

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for cu_vm fj1_0m.

Identification code	cu_vm fj1_0m	
Empirical formula	C11 H12 O2	
Formula weight	176.21	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 4.6462(2) Å	α = 90 °
	b = 9.7488(3) Å	β = 90 °
	c = 19.6719(6) Å	γ = 90 °
Volume	891.04(5) Å ³	
Z	4	
Density (calculated)	1.314 Mg/m ³	
Absorption coefficient	0.720 mm ⁻¹	
F(000)	376	
Crystal size	1.360 x 0.380 x 0.340 mm ³	
Theta range for data collection	5.063 to 69.794 °	
Index ranges	-5 ≤ h ≤ 5, -9 ≤ k ≤ 11, -23 ≤ l ≤ 22	
Reflections collected	4844	
Independent reflections	1612 [R(int) = 0.0298]	

Completeness to theta = 67.679 °	98.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1612 / 0 / 123
Goodness-of-fit on F ²	1.203
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1384
R indices (all data)	R1 = 0.0461, wR2 = 0.1385
Absolute structure parameter	0.15(6)
Extinction coefficient	0.046(7)
Largest diff. peak and hole	0.365 and -0.367 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cu_vmfj1_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2016(4)	6729(2)	8549(1)	25(1)
O(2)	5151(4)	7884(2)	9708(1)	18(1)
C(1)	2299(6)	5395(3)	8812(1)	26(1)
C(2)	4643(6)	7486(2)	8485(1)	17(1)
C(3)	4479(5)	8235(3)	7813(1)	20(1)
C(4)	3214(6)	9454(3)	7775(1)	21(1)
C(5)	2067(5)	10149(2)	8374(1)	16(1)
C(6)	152(6)	11250(3)	8318(1)	22(1)
C(7)	-992(6)	11859(3)	8895(2)	24(1)
C(8)	2857(5)	9677(2)	9023(1)	13(1)
C(9)	1735(5)	10302(2)	9596(1)	18(1)
C(10)	-198(6)	11388(2)	9533(1)	22(1)
C(11)	5026(5)	8528(2)	9059(1)	14(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for cu_vmfj1_0m.

O(1)-C(1)	1.406(3)
O(1)-C(2)	1.432(3)
O(2)-C(11)	1.424(3)
O(2)-H(9)	0.84(5)
C(1)-H(3)	0.9800

C(1)-H(12)	0.9800
C(1)-H(1)	0.9800
C(2)-C(3)	1.512(3)
C(2)-C(11)	1.529(3)
C(2)-H(11)	1.0000
C(3)-C(4)	1.328(4)
C(3)-H(4)	0.9500
C(4)-C(5)	1.460(3)
C(4)-H(5)	0.9500
C(5)-C(6)	1.398(3)
C(5)-C(8)	1.406(3)
C(6)-C(7)	1.387(4)
C(6)-H(6)	0.9500
C(7)-C(10)	1.387(4)
C(7)-H(2)	0.9500
C(8)-C(9)	1.384(3)
C(8)-C(11)	1.508(3)
C(9)-C(10)	1.394(4)
C(9)-H(8)	0.9500
C(10)-H(7)	0.9500
C(11)-H(10)	1.0000
C(1)-O(1)-C(2)	115.4(2)
C(11)-O(2)-H(9)	105(2)
O(1)-C(1)-H(3)	109.5
O(1)-C(1)-H(12)	109.5
H(3)-C(1)-H(12)	109.5
O(1)-C(1)-H(1)	109.5
H(3)-C(1)-H(1)	109.5
H(12)-C(1)-H(1)	109.5
O(1)-C(2)-C(3)	106.41(19)
O(1)-C(2)-C(11)	112.16(19)
C(3)-C(2)-C(11)	109.30(19)
O(1)-C(2)-H(11)	109.6
C(3)-C(2)-H(11)	109.6
C(11)-C(2)-H(11)	109.6
C(4)-C(3)-C(2)	120.2(2)
C(4)-C(3)-H(4)	119.9

C(2)-C(3)-H(4)	119.9
C(3)-C(4)-C(5)	122.1(2)
C(3)-C(4)-H(5)	118.9
C(5)-C(4)-H(5)	118.9
C(6)-C(5)-C(8)	119.3(2)
C(6)-C(5)-C(4)	121.6(2)
C(8)-C(5)-C(4)	119.0(2)
C(7)-C(6)-C(5)	120.5(2)
C(7)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8
C(10)-C(7)-C(6)	119.9(2)
C(10)-C(7)-H(2)	120.1
C(6)-C(7)-H(2)	120.1
C(9)-C(8)-C(5)	119.8(2)
C(9)-C(8)-C(11)	122.7(2)
C(5)-C(8)-C(11)	117.44(19)
C(8)-C(9)-C(10)	120.3(2)
C(8)-C(9)-H(8)	119.8
C(10)-C(9)-H(8)	119.8
C(7)-C(10)-C(9)	120.2(2)
C(7)-C(10)-H(7)	119.9
C(9)-C(10)-H(7)	119.9
O(2)-C(11)-C(8)	113.41(18)
O(2)-C(11)-C(2)	111.91(18)
C(8)-C(11)-C(2)	112.39(19)
O(2)-C(11)-H(10)	106.2
C(8)-C(11)-H(10)	106.2
C(2)-C(11)-H(10)	106.2

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cu_vm fj1_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	17(1)	19(1)	38(1)	4(1)	-5(1)	-3(1)
O(2)	9(1)	29(1)	16(1)	7(1)	-1(1)	0(1)
C(1)	27(1)	17(1)	33(1)	2(1)	8(1)	-1(1)
C(2)	13(1)	17(1)	22(1)	-2(1)	0(1)	1(1)
C(3)	16(1)	29(1)	16(1)	-6(1)	1(1)	0(1)
C(4)	17(1)	30(1)	15(1)	4(1)	-2(1)	-4(1)
C(5)	11(1)	18(1)	19(1)	2(1)	0(1)	-2(1)
C(6)	17(1)	20(1)	29(1)	10(1)	-2(1)	-2(1)
C(7)	16(1)	15(1)	42(2)	2(1)	0(1)	1(1)
C(8)	9(1)	13(1)	18(1)	0(1)	0(1)	-4(1)
C(9)	13(1)	20(1)	21(1)	-4(1)	-2(1)	-3(1)
C(10)	15(1)	20(1)	32(1)	-9(1)	3(1)	-1(1)
C(11)	9(1)	17(1)	14(1)	4(1)	0(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for cu_vm fj1_0m.

	x	y	z	U(eq)
H(9)	3420(100)	7760(30)	9821(17)	27
H(3)	3836	4912	8569	38
H(12)	481	4898	8753	38
H(1)	2776	5445	9296	38
H(11)	6311	6838	8481	21
H(4)	5285	7831	7417	24
H(5)	3049	9888	7344	25
H(6)	-369	11584	7881	26
H(2)	-2317	12596	8853	29
H(8)	2286	9990	10035	22
H(7)	-973	11808	9929	27
H(10)	6953	8961	8986	16

Table 6. Torsion angles [°] for cu_vmj1_0m.

C(1)-O(1)-C(2)-C(3)	138.8(2)
C(1)-O(1)-C(2)-C(11)	-101.7(2)
O(1)-C(2)-C(3)-C(4)	86.3(3)
C(11)-C(2)-C(3)-C(4)	-35.0(3)
C(2)-C(3)-C(4)-C(5)	3.1(4)
C(3)-C(4)-C(5)-C(6)	-164.3(2)
C(3)-C(4)-C(5)-C(8)	14.2(4)
C(8)-C(5)-C(6)-C(7)	-1.0(4)
C(4)-C(5)-C(6)-C(7)	177.5(2)
C(5)-C(6)-C(7)-C(10)	1.1(4)
C(6)-C(5)-C(8)-C(9)	0.1(3)
C(4)-C(5)-C(8)-C(9)	-178.4(2)
C(6)-C(5)-C(8)-C(11)	-177.4(2)
C(4)-C(5)-C(8)-C(11)	4.1(3)
C(5)-C(8)-C(9)-C(10)	0.7(3)
C(11)-C(8)-C(9)-C(10)	178.0(2)
C(6)-C(7)-C(10)-C(9)	-0.3(4)
C(8)-C(9)-C(10)-C(7)	-0.6(4)
C(9)-C(8)-C(11)-O(2)	17.8(3)
C(5)-C(8)-C(11)-O(2)	-164.84(19)
C(9)-C(8)-C(11)-C(2)	146.0(2)
C(5)-C(8)-C(11)-C(2)	-36.7(3)
O(1)-C(2)-C(11)-O(2)	61.4(3)
C(3)-C(2)-C(11)-O(2)	179.13(18)
O(1)-C(2)-C(11)-C(8)	-67.6(2)
C(3)-C(2)-C(11)-C(8)	50.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cu_vmj1_0m [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)
O(2)-H(9)...O(2)#1	0.84(5)	1.88(4)	2.6980(16)	161(3)

Symmetry transformations used to generate equivalent atoms:

#1 $x-1/2, -y+3/2, -z+2$