Electronic Supplementary Material for CrystEngComm

Electronic Supplementary Information (ESI)

Guest Dependent Self-Assembly of (*R*,*R*)-2,3-Diphenylsuccinic Acids: Formation of the Chiral Square and Its Chiral Recognition

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Contents

1. Synthesis of ligand

3. Preparation and characterization of Crystals.

1. Synthesis of ligand

1.1. General consideration

Unless otherwise noted, all materials were obtained from commercial suppliers Aldrich and TCI, and used without further purification. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates (Silica gel 60 F_{254}, Merck) were visualized by ultraviolet light and treatment with acidic p-anisaldehyde stain followed by gentle heating. Chromatographic purification of products were accomplished by flash chromatography, by using Merk silica gel 60(230~400mesh) with mixtures of hexane and ethyl acetate. ^{1}H NMR spectra were recorded on Varian Gemini 75 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS as the internal reference ($CDCl_3$, δ77.7 ppm). Elemental analysis was performed at OCRC center, Korea. High Performance Liquid Chromatography (HPLC) was conducted using a Waters model 600 pumping system with a Waters model 2487 ultraviolet detector at 254nm. Infrared (IR) spectra were recorded on a Bomem 102 FT-IR spectrometer. Optical rotations were measured at the 589nm sodium D-Line from RUDOLPH AUTOPOL automatic polarimeter. Melting points were measured by Capillary melting point apparatus of Thomas Hoover and are uncorrected.

1.2. The preparation of (*R*,*R*)-**1**

(±)-2,3-Diphenylsuccinic acid dimethyl ester

This compound was prepared according to reference 1.

(±)-2,3-Diphenylsuccinic acid and Resolution of (±)-2,3-Diphenylsuccinic Acid

This compound was prepared according to reference 2*a* and 2*b*.

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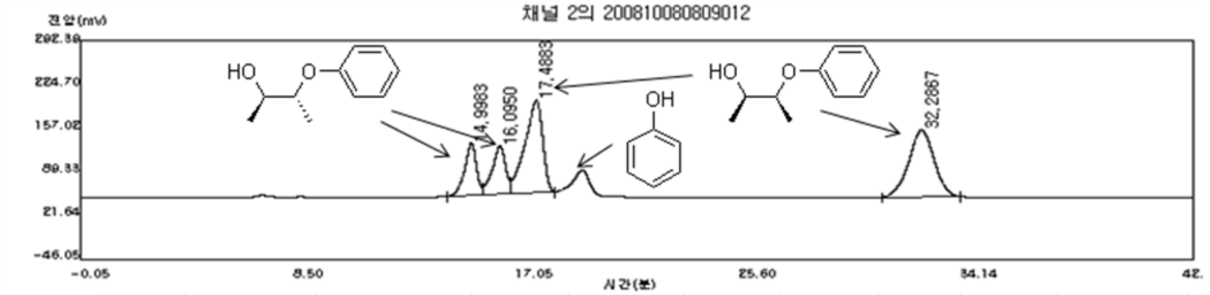
1. Y. Matsumura, M. Nishimura, H. Hiu, M. Watanabe and N. Kise, *J. Org. Chem*, 1996, **61**, 2809.
2. *a*) C. R. Ramanathan, M. Periasamy, *Tetrahedron Asymmetry*, 1998, **9**,2651
   b) K. Hanswalter, M. Cornelia, *Ger. (East)*, 1985, 8

2. Ring opening reaction of entrapped 2,3-butene oxide in Xtal-5

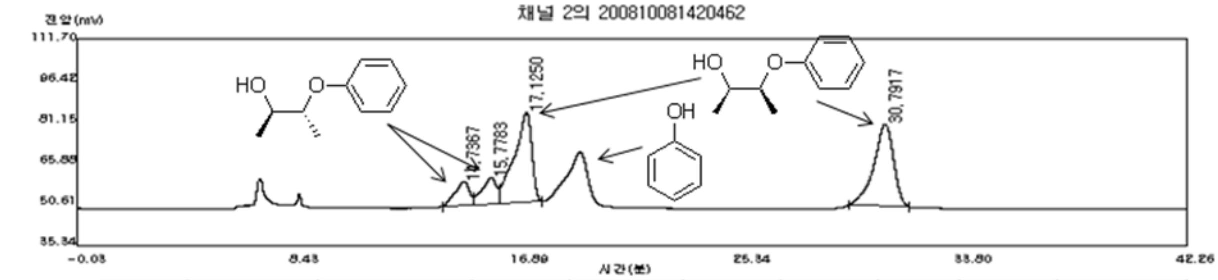
A mixture of phenol and Xtal-**5**(100mg, 0.087mmol, ligand:epoxide=4:1) in 1,4-dioxane was added 6N NaOH (1 m L) and then heated at 70℃ for 3h. The reaction mixture was extracted with dichloromethane. The organic extracts were dried on anhydrous $MgSO_4$ and filtered then concentrated in vacuum to obtain 2-hydroxy-3-phenoxy butane. ^1H NMR (CD_3OD, 300MHz): δ 1.24-1.28 (m, 22.2H), 2.49 (br, 3.7H), 3.83(m, 1H), 4.02(m, 2.7H), 4.14(m, 1H), 4.32(m, 2.7H), 6.9-7.31(m, 18.5H); HPLC. (DAICEL CHIRALPAK OD-H, n-hexane/isopropylalchol=9:1, flow 0.5ml/min detection at 254nm)

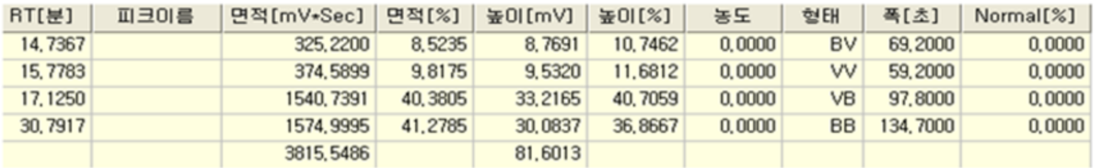
2-hydroxy-3-phenoxy butane from commercial 2,3-butylene oxide



RT[분]	피크이름	면적[mV*Sec]	면적[%]	높이[mV]	높이[%]	농도	형태	폭[초]	Normal[%]
14,9983		2513,7210	13,2938	81,0482	20,2161	0,0000	BV	82,4000	0,0000
16,0950		2662,5219	14,0807	74,6514	18,6205	0,0000	VV	65,6000	0,0000
17,4883		6752,8427	35,7124	142,3195	35,4992	0,0000	VB	101,7000	0,0000
32,2867		6979,8667	36,9130	102,8897	25,6641	0,0000	BB	181,1000	0,0000
		18908,9512		400,9088					

2-hydroxy-3-phenoxy butane from intrapped 2,3-butylene oxide





RT[분]	피크이름	면적[mV*Sec]	면적[%]	높이[mV]	높이[%]	농도	형태	폭[초]	Normal[%]
14,7367		325,2200	8,5235	8,7691	10,7462	0,0000	BV	69,2000	0,0000
15,7783		374,5899	9,8175	9,5320	11,6812	0,0000	VV	59,2000	0,0000
17,1250		1540,7391	40,3805	33,2165	40,7059	0,0000	VB	97,8000	0,0000
30,7917		1574,9995	41,2785	30,0837	36,8667	0,0000	BB	134,7000	0,0000
		3815,5486		81,6013					

3. Preparation and characterization of Crystals.

3.1. Synthesis and single crystal X-ray diffraction studies of Xtal-**1**.

To a solution of (±)-2,3-Diphenylsuccinic Acid (30mg, 0.11mmol) in diethyl ether(1mL) was diffused n-hexane slowly at 0℃ for 1day. Colourless bluck crystals were obtained in 45% yield.

A block colorless crystal with a suitable size (0.38 mm x 0.34 mm x 0.20 mm) was attached on a glass capillary, which was positioned in $N_2(g)$ stream at 173K upon mounting on a Bruker SMART CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube (λ = 0.71073 Å) operated at 1,500 W power (50 kV, 30mA). Total 1,366 frames were collected with varying ω and phi with an exposure time of 10s/frame. The last 45 frames were collected over the same Ewald sphere as those of the first 45 frames in order to detect possible crystal decay. The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. The final cell constants were based on the *xyz* centroids of 4,065 reflections. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 10,669 reflections were collected in the range $2.01° < \theta < 27.52°$ of which 7,475 were independent and 4,533 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.0608$ ($I > 2\sigma(I)$), $wR_2 = 0.1638$ (all data) and GOF = 1.069. The crystal belongs to the triclinic space group $P\bar{1}$ (No. 2) with Z = 4. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the carboxyl group were found in the electron density map and their positional parameters were refined. The rest of hydrogen atom were generated with the ideal geometry and included in the refinement processes. There were two ether(Et_2O) in the structure, one of them was disordered. Additional details are presented in Table S1 and are given as Supporting Information.

1. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
2. Sheldirck, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data,University of Goettingen: Goettingen, Germany, 1996.
3. Sheldrick, G. M. SHELX-TL, v.6.14; Bruker Analytical X-ray, Madison, WI, 2000.

3.2. Synthesis and single crystal X-ray diffraction studies of Xtal-**2**

To a solution of (±)-2,3-Diphenylsuccinic Acid (30mg, 0.11mmol) in THF(1mL) was diffused n-hexane slowly at 0℃ for 3days. Colourless bluck crystals were obtained in 50% yield.

A block colorless crystal with a suitable size (0.40 mm x 0.25 mm x 0.20 mm) was attached on a glass capillary, which was positioned in $N_2(g)$ stream at 173K upon mounting on a Bruker SMART CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube (λ = 0.71073 Å) operated at 1,500 W power (50 kV, 30mA). Total 1,366 frames were collected with varying ω and phi with an exposure time of 5s/frame. The last 45 frames were collected over the same Ewald sphere as those of the first 45 frames in order to detect possible crystal decay. The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. The final cell constants were based on the *xyz* centroids of 2,083 reflections. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 3,840 reflections were collected in the range $1.99 < \theta < 24.71°$ of which 2,753 were independent and 1,643 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.0897$ ($I > 2\sigma(I)$), $wR_2 = 0.3200$ (all data) and GOF = 1.044. The crystal belongs to the triclinic space group $P\bar{1}$ (No. 2) with Z = 2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in both the carboxyl group were found in the electron density map and their positional parameters were refined. The rest of hydrogen atom were generated with the ideal geometry and included in the refinement processes. Additional details are presented in Table S1 and are given as Supporting Information.

1. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
2. Sheldirck, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data,University of Goettingen: Goettingen, Germany, 1996.
3. Sheldrick, G. M. SHELX-TL, v.6.14; Bruker Analytical X-ray, Madison, WI, 2000.

3.3. Synthesis and single crystal X-ray diffraction studies of Xtal-**3**

To a solution of (R,R)-2,3-Diphenylsuccinic Acid (30mg, 0.11mmol) in THF(1mL) was diffused n-hexane at 0℃ for 3days. Colourless bluck crystals were obtained in 35% yield.

A block colorless crystal with a suitable size (0.36 mm x 0.36 mm x 0.20 mm) was attached on a glass capillary and mounted on a Bruker APEX CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube (λ = 0.71073 Å) operated at 2,000 W power (50 kV, 40mA). Total 963 frames were collected with varying ω and phi with an exposure time of 10s/frame. The last 45 frames were collected over the same Ewald sphere as those of the first 45 frames in order to detect possible crystal decay. The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. The final cell constants were based on the *xyz* centroids of 4,476 reflections. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 20,167 reflections were collected in the range 1.10° < θ < 28.30° of which 8,397 were independent and 5,799 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.0578$ ($I > 2\sigma(I)$), $wR_2 = 0.1459$ (all data) and GOF = 1.037. The crystal belongs to the orthorhombic space group $P2_12_12_1$ (No. 19) with Z = 8. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in both the carboxyl group were found in the electron density map and their positional parameters were refined. The rest of hydrogen atom were generated with the ideal geometry and included in the refinement processes. Additional details are presented in Table S1 and are given as Supporting Information.

1. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
2. Sheldirck, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data,University of Goettingen: Goettingen, Germany, 1996.
3. Sheldrick, G. M. SHELX-TL, v.6.14; Bruker Analytical X-ray, Madison, WI, 2000.

3.4. Synthesis and single crystal X-ray diffraction studies of Xtal-**4**

To a solution of (R,R)-2,3-Diphenylsuccinic Acid (30mg, 0.11mmol) in diethyl ether(1mL) was diffused n-hexane at RT for 1day. Colourless bluck crystals were obtained in 31% yield.

A block colorless crystal with a suitable size (0.30 mm x 0.25 mm x 0.18 mm) was attached on a glass capillary, which was positioned in $N_2(g)$ stream at 173K upon mounting on a Bruker APEX CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube (λ = 0.71073 Å) operated at 1,500 W power (50 kV, 30mA). Total 1,315 frames were collected with varying ω and phi with an exposure time of 10s/frame. The last 50 frames were collected over the same Ewald sphere as those of the first 45 frames in order to detect possible crystal decay. The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 19,315 reflections were collected in the range $1.25° < \theta < 20.81°$ of which 5,945 were independent and 3,069 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.1143$ ($I > 2\sigma(I)$), $wR_2 = 0.3441$ (all data) and GOF = 1.068. The crystal belongs to the tetragonal space group $P4_1$ (No. 76) with Z = 4. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated with the ideal geometry and included in the refinement processes. Due to the weak intensities, anisotropic thermal parameters of many carbon atoms were non-positive definite or unreasonable ellipsoids. Therefore, a soft restraint of ISOR instruction was applied to all the carbons atoms. As the number of carbons atoms in the asymmetric unit were 68, total number of restraints were 408 (=68 x 8 thermal parameters per atom). The remaining ones are related to both geometry restraints for hydrogen atoms, and disordered ether molecule. Additional details are presented in Table S1 and are given as Supporting Information.

1. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
2. Sheldirck, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data,University of Goettingen: Goettingen, Germany, 1996.
3. Sheldrick, G. M. SHELX-TL, v.6.14; Bruker Analytical X-ray, Madison, WI, 2000.

3.5. Synthesis and single crystal X-ray diffraction studies of Xtal-**5**

To a solution of (R,R)-2,3-Diphenylsuccinic Acid (30mg, 0.11mmol) in 2,3-butylene oxide (1mL) was diffused n-hexane at RT for 1day. Colourless bluck crystals were obtained in 30% yield.

A block colorless crystal with a suitable size (0.20 mm x 0.10 mm x 0.05 mm) was attached on a glass capillary and mounted on a Bruker APEX CCD diffractometer equipped with a normal focus and graphite monochromated Mo-target X-ray tube (λ = 0.71073 Å) operated at 2,000 W power (50 kV, 40mA). Total 1,858 frames were collected with varying ω with an exposure time of 5 s/frame. The last 45 frames were collected over the same Ewald sphere as those of the first 45 frames in order to detect possible crystal decay. The frames were integrated with the SAINT software package with a narrow frame algorithm[1]. Analysis of the data showed negligible decay during collection. An absorption correction was applied using SADABS[2]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined with the SHELX-TL software package[3]. A total of 13,122 reflections were collected in the range 1.76° < θ < 28.30° of which 3,493 were independent and 1,801 were observed ($I > 2\sigma(I)$). All stages of weighted full-matrix least squares refinement were conducted using F_o^2 data and converged to give $R_1 = 0.0525$ ($I > 2\sigma(I)$), $wR_2 = 0.1693$ (all data) and GOF = 0.983. The crystal belongs to the tetragonal space group *I*4 (No. 79) with Z = 2. There was one epoxide in the structure, it was disordered over four sites with 1/4 occupancies. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in both the carboxyl group were found in the electron density map and their positional parameters were refined. The rest of hydrogen atom were generated with the ideal geometry and included in the refinement processes. We used two DFIX restraints for O1–H1O and O4–H4O bonds, AFIX restraints for the H atoms attached to C atoms, and ISOR restraints for five non-hydrogen atoms of the guest molecule. As the guest molecule sits on the four-fold axis, some of them must follow symmetric restrictions. Additional details are presented in Table S1 and are given as Supporting Information.

1. Saint Plus, v.6.01, Bruker Analytical X-ray, Madison, WI, 1999.
2. Sheldirck, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector 6 Data,University of Goettingen: Goettingen, Germany, 1996.
3. Sheldrick, G. M. SHELX-TL, v.6.14; Bruker Analytical X-ray, Madison, WI, 2000.

Table S1. Crystal data and structure refinement for four crystals.

	Xtal-1	Xtal-2	Xtal-3	Xtal-4	Xtal-5
	$((\pm)\text{-}1)_2 \cdot (Et_2O)_2$	**$((\pm)\text{-}1) \cdot (THF)$**	**$((R,R)\text{-}1)_2 (THF)_2$**	**$((R,R)\text{-}1)_4 (Et_2O)$**	**$((R,R)\text{-}1)_4$(epoxide)**
empirical formula	$C_{20}H_{24}O_5$	$C_{20}H_{22}O_5$	$C_{20}H_{22}O_5$	$C_{68}H_{66}O_{17}$	$C_{68}H_{64}O_{17}$
f.w.	344.39	342.38	342.38	1155.21	1153.19
T (K)	173(2)	173(2)	293(2)	173(2)	298(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	orthorhombic	Tetragonal	Tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P4_1$	$I4$
a (Å)	9.4617(7)	9.1569(7)	9.5545(2)	16.249(6)	16.3890(3)
b (Å)	10.3642(8)	10.3223(9)	10.2040(2)	16.249(6)	16.3890(3)
c (Å)	19.7932(15)	11.0400(9)	36.9589(7)	22.540(10)	11.3011(3)
α (deg)	91.369(2)	69.817(1)	90	90	90
β (deg)	94.833(1)	74.207(2)	90	90	90
γ (deg)	101.759(2)	64.677(1)	90	90	90
V (Å^3)	1891.8(2)	875.72(12)	3603.28(12)	5951(4)	3035.47(11)
Z	4	2	8	4	2
D_{calcd} (g/cm^3)	1.209	1.298	1.262	1.289	1.262
μ(MoKα) (mm^{-1})	0.086	0.093	0.090	0.092	0.091
N_{ref} collected/ unique/observed [I >2$\sigma(I)$]	10669/7475/ 4533	3840/2753/ 1643	20167/8397/ 5799	19315/5945/ 3069	13122/3493/ 1801
R_{int}	0.0236	0.0264	0.0422	0.1032	0.0389
parameters	482	234	467	673	221
GOF on F^2	1.069	1.044	1.037	1.068	0.983
Final R indices [I > 2$\sigma(I)$] **R_1 / wR_2**	0.0608/ 0.1377	0.0897/ 0.2391	0.0578/ 0.1219	0.1143/ 0.2863	0.0525/ 0.1363
R indices (all data) **R_1 / wR_2**	0.1154/ 0.1638	0.1637/ 0.3200	0.0955/ 0.1459	0.1952/ 0.3441	0.1193/ 0.1693
res. Peaks max/min(eÅ^{-3})	0.679/-0.253	0.393/-0.550	0.304/-0.397	0.431/-0.470	0.180/-0.133

Table S2. Hydrogen bonds in five crystals.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Xtal-**1**				
O(2)-H(2O)...O(1)[#1]	0.86(3)	1.83(3)	2.675(3)	168(3)
O(4)-H(4O)...O(1E)	0.83(3)	1.88(3)	2.690(3)	166(3)
O(6)-H(6O)...O(2E)[#2]	0.85(3)	1.87(4)	2.679(3)	157(3)
O(7)-H(7O)...O(8)[#3]	0.86(3)	1.81(3)	2.660(3)	165(3)
Xtal-**2**				
O(1)-H(1O)...O(2)[#4]	1.03(14)	1.65(14)	2.672(7)	175(11)
O(4)-H(2O)...O(1S)	0.88(7)	1.81(7)	2.675(6)	167(6)
Xtal-**3**				
O(5)-H(2O)...O(1)	1.18(6)	1.49(6)	2.668(3)	171(5)
O(2)-H(3O)...O(6)	1.05(6)	1.57(6)	2.609(2)	167(6)
O(7)-H(4O)...O(10)	0.93(4)	1.69(4)	2.593(3)	166(4)
Xtal-**4**				
O(1)-H(1)...O(6)	0.85	1.84	2.677(12)	168
O(4)-H(4)...O(14)[#5]	0.85	1.85	2.672(13)	163
O(5)-H(5)...O(2)	0.85	1.78	2.630(12)	174
O(8)-H(8)...O(10)[#5]	0.85	1.84	2.648(14)	158
O(9)-H(9)...O(7)[#6]	0.85	1.81	2.613(13)	157
O(12)-H(12)...O(15)	0.85	1.81	2.654(14)	172
O(13)-H(13)...O(3)[#6]	0.85	1.83	2.668(14)	169
O(16)-H(16)...O(11)	0.85	1.87	2.681(14)	156
Xtal-**5**				
O(1)-H(1O)...O(3)[#7]	0.878(18)	1.81(2)	2.676(3)	169(4)
O(4)-H(4O)...O(2)[#8]	0.859(19)	1.82(2)	2.671(3)	172(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 x,y+1,z #3 -x,-y+1,-z #4 -x,-y+2,-z+1
#5 x,y+1,z #6 x,y-1,z #7 -y+1,x-1,z #8 y+1,-x+1,z

Figure S1. ORTEP drawing at 50% probability level for the asymmetric unit of Xtal-1 and its packing view represented with ball-and-stick models.

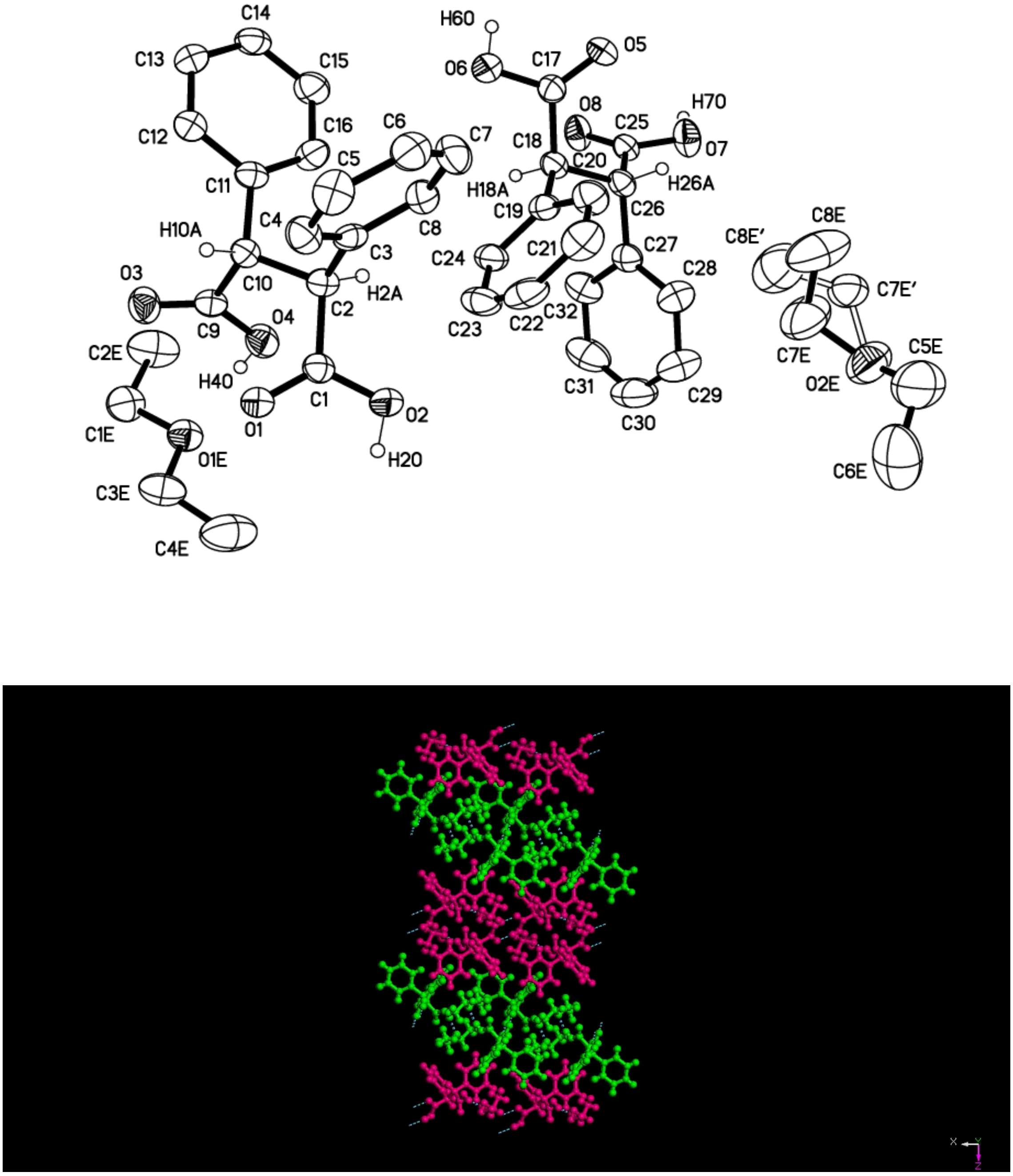


Figure S2. ORTEP drawing at 50% probability level for the asymmetric unit of Xtal-2 and its packing view are presented.

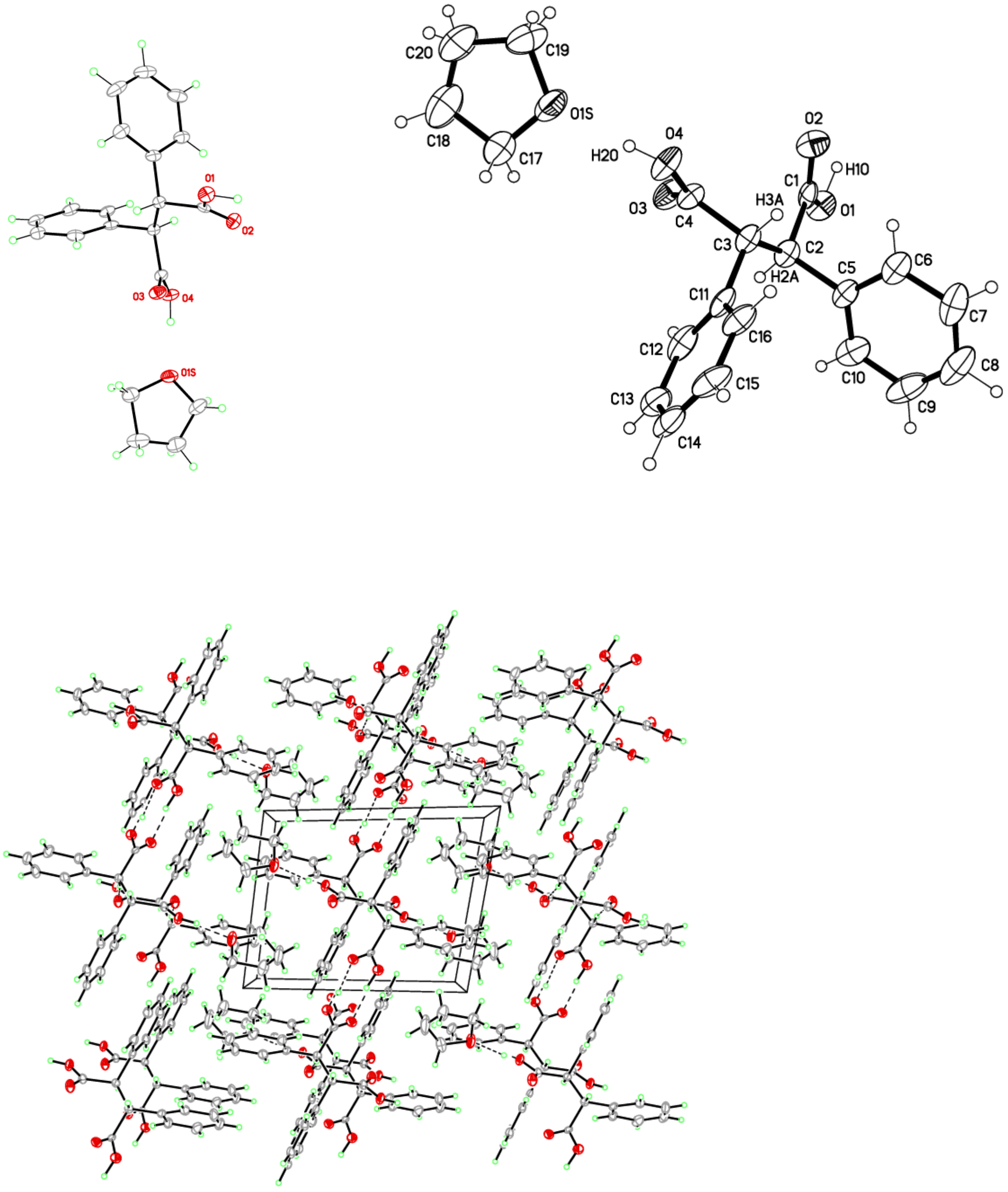


Figure S3. ORTEP drawing at 50% probability level for the asymmetric unit of Xtal-3 and its packing view represented with stick models. Hydrogen bonds are shown as dotted lines.

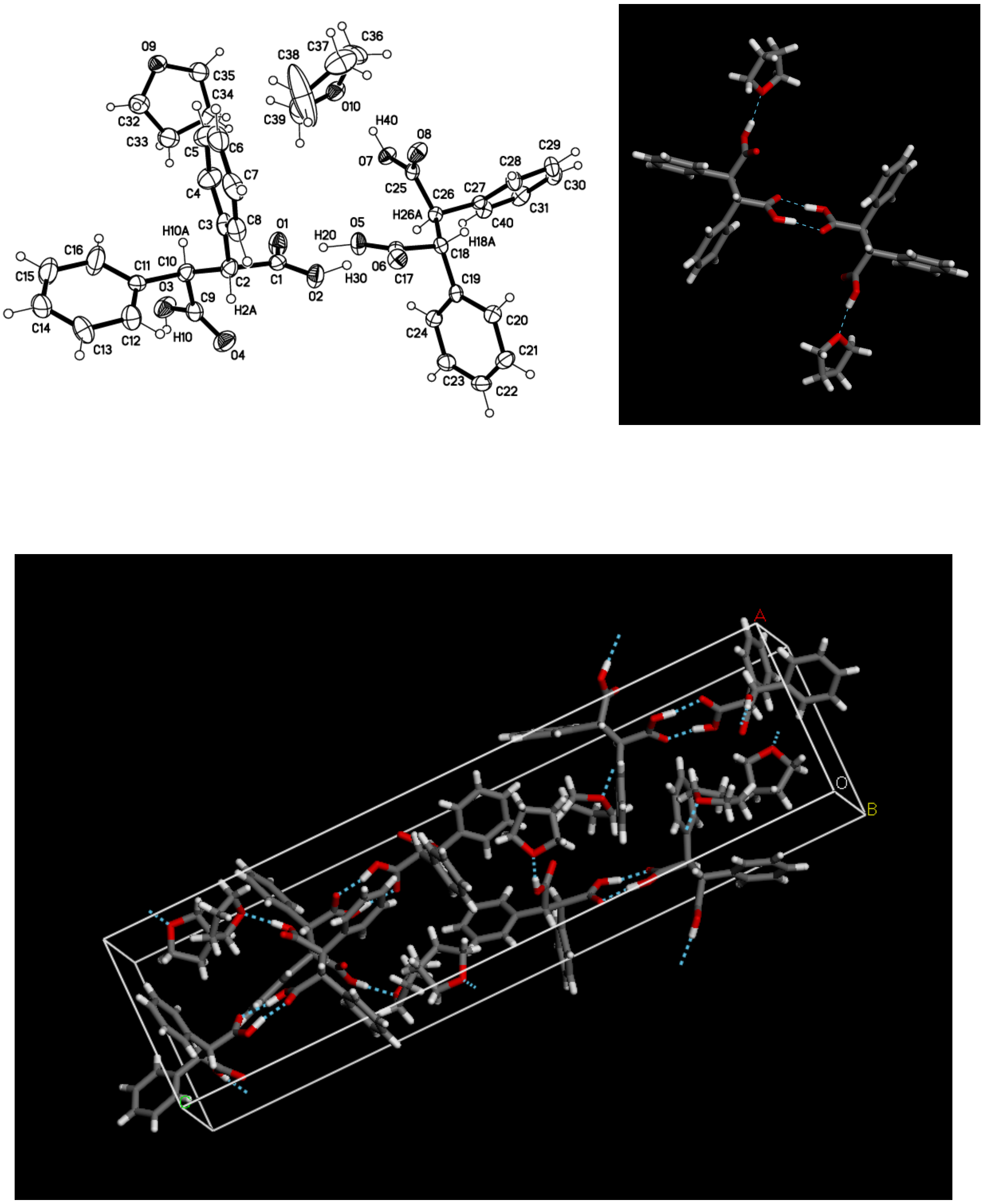
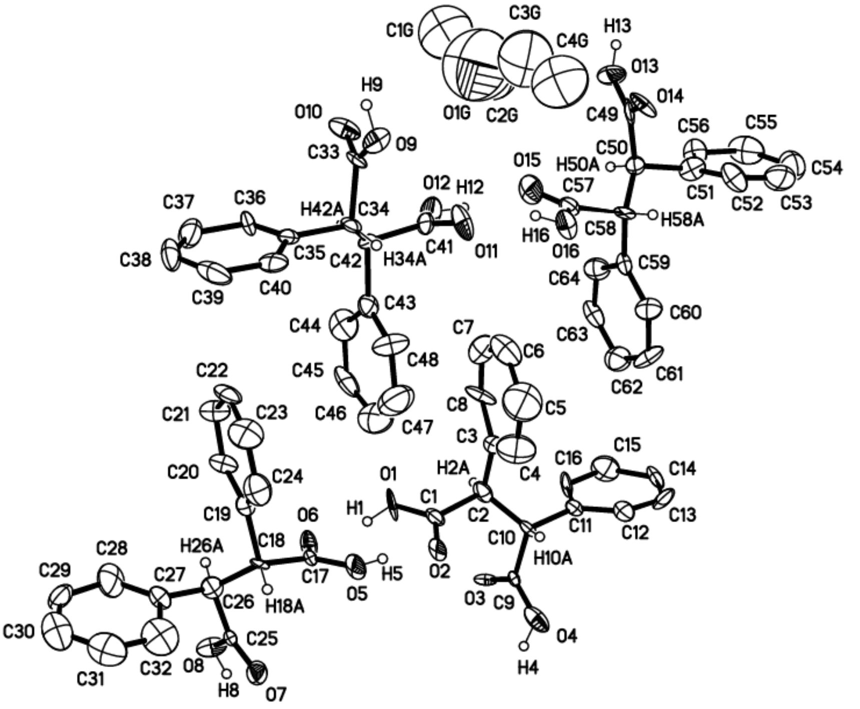


Figure S4. ORTEP drawing at 50% probability level for the asymmetric unit of Xtal-4 and its packing view is shown with only one squaric H-bonded assembly with the entrapped guest molecule.



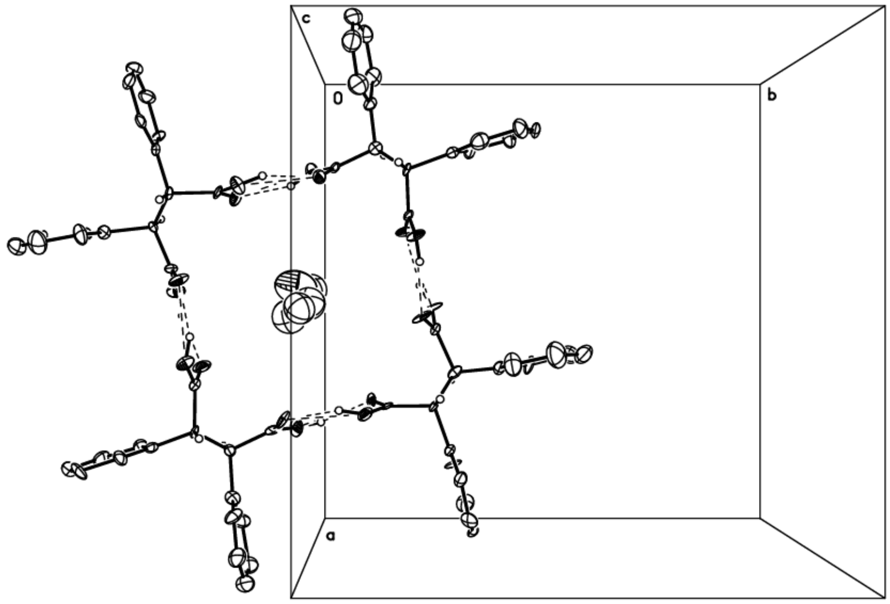


Figure S5. ORTEP drawing at 50% probability level for the asymmetric unit of Xtal-5 and its packing view is shown with only one squaric H-bonded assembly with the entrapped guest molecule.

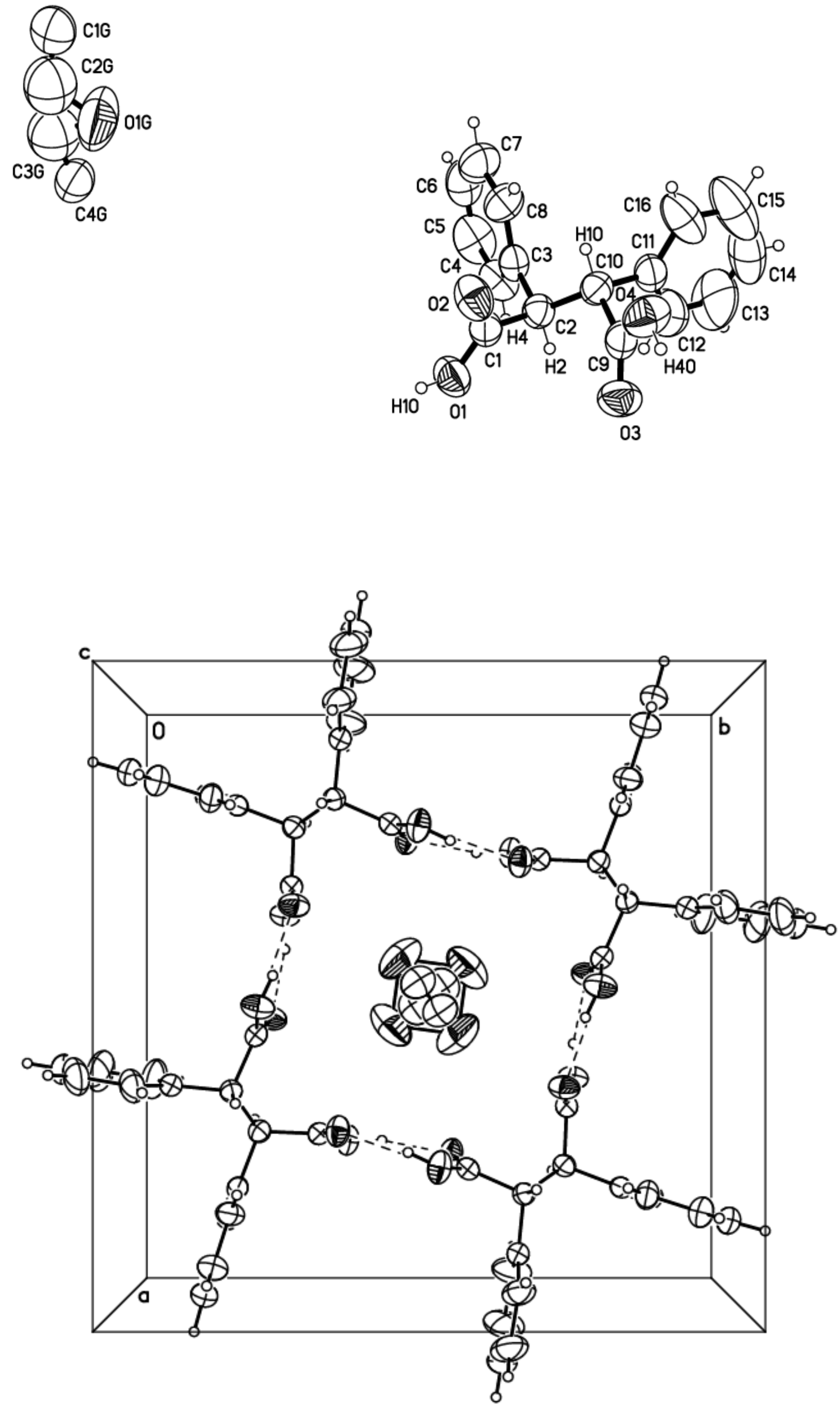


Figure S6. (a) A tilted edge-to-face interaction, and (b) a face-to-face stacking of aromatic rings in Xtal 4 are shown with stick models. Selected distances and angles are also shown.