

# Kilo scale synthesis and purification of 4,4'-[di t-butylidibenzo]-18-crown-6 and its catalytic reduction to 4,4'-[di t-butylidicyclohexano]-18-crown-6

Snehasis Dutta<sup>1\*</sup>, Trilochan Gadly<sup>2</sup>, Amey P. Wadawale<sup>3</sup>, Mayur Darekar<sup>1</sup>, Sulekha Mukhopadhyay<sup>1</sup>, Sunil K. Ghosh<sup>2</sup>, Birija S. Patro<sup>2</sup>

<sup>1</sup>Chemical Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, Maharashtra, India

<sup>2</sup>Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, Maharashtra, India

<sup>3</sup>Chemistry Division, Bhabha Atomic Research Centre Mumbai, Trombay 400085

## Supplementary Material

### S1. <sup>1</sup>H-NMR Spectra

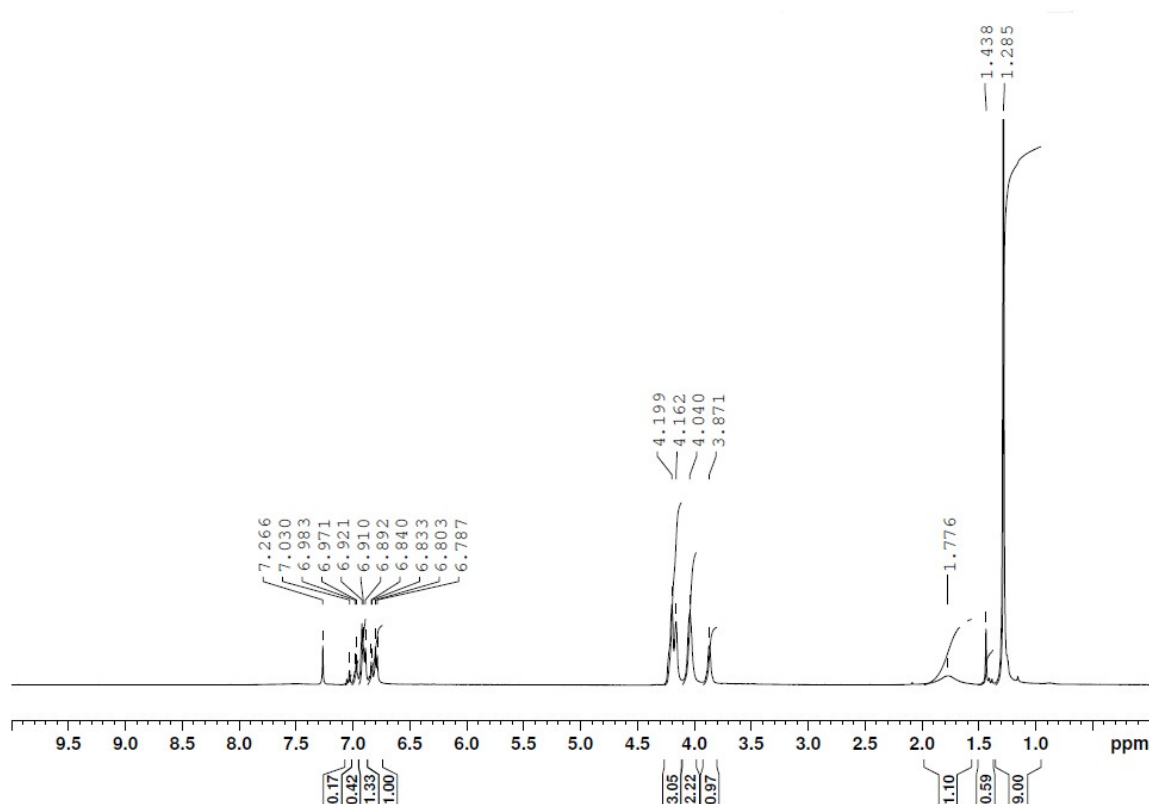


Fig S1. <sup>1</sup>H NMR Spectra of 4,4'-[di t-butylidibenzo]-18-crown-6

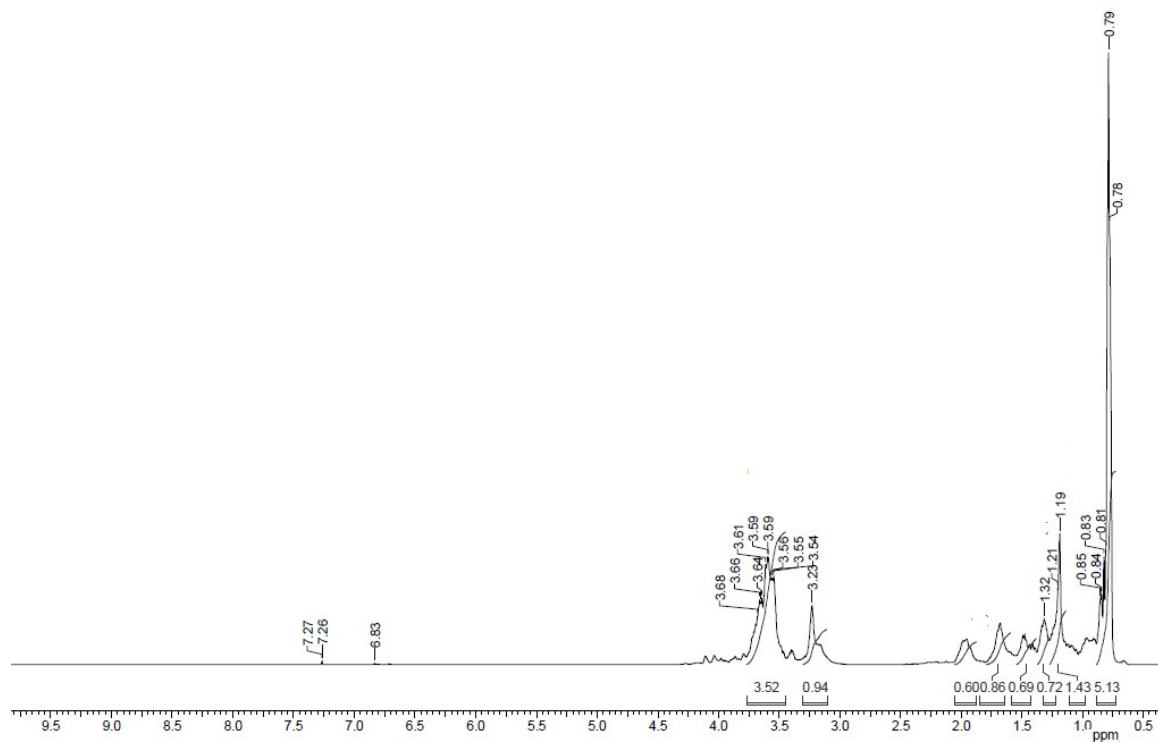


Fig S2.  $^1\text{H}$  NMR Spectra of 4,4'-[di t-butylidicyclohexano]-18-crown-6

## S2. IR Spectra

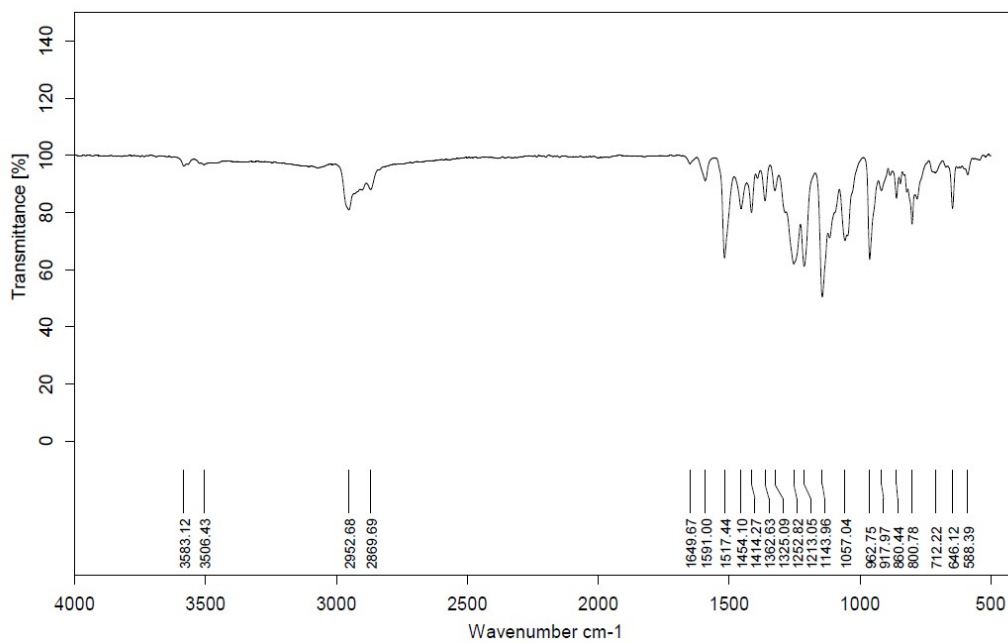


Fig S3. FTIR Spectra of 4,4'-[di t-butylidibenzo]-18-crown-6

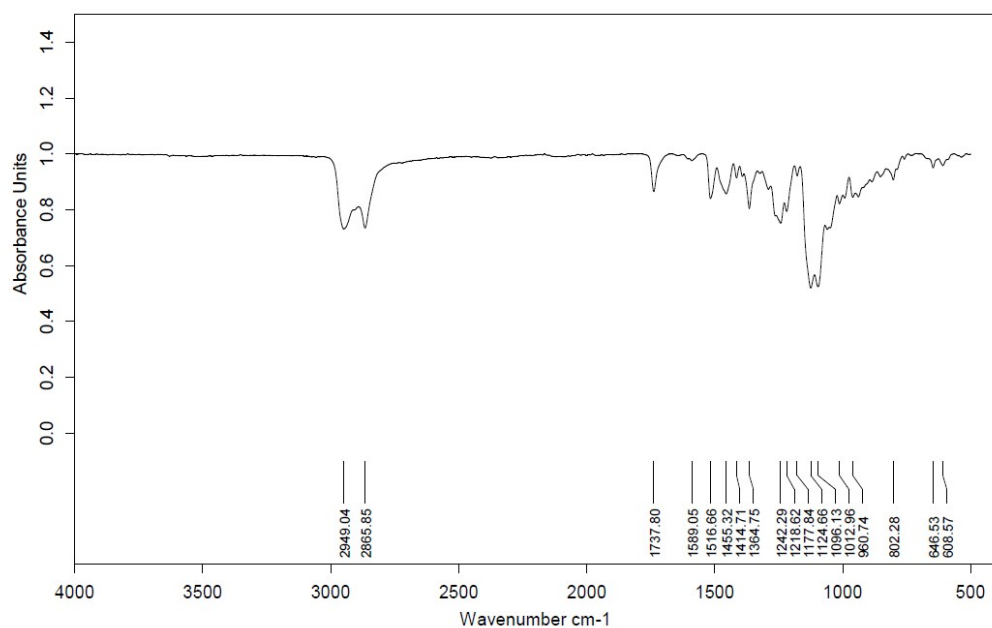


Fig S4. FTIR Spectra of 4,4'-[di t-butylidicyclohexano]-18-crown-6

### S3. Conditions of GCMS analysis

Table S1: Conditions observed for GCMS analysis

SI No.	Parameter	Description															
1	GC Model	Shimadzu GC-2010 Plus															
2	GC Column nature	Cross-bond, 5% diphenyl/ 95% dimethyl polysiloxane, 30 m, 0.25 mm (Restek Rxi 5ms Cat# 13423), Max and Min bleeding temp: 330-350 °C															
3	GC Pressure	73 kPa															
4	Column temperature program	<table border="1"> <thead> <tr> <th>Rate, °C/ min</th> <th>Final temp, °C</th> <th>Hold time at final temp, min</th> </tr> </thead> <tbody> <tr> <td>-</td> <td>100</td> <td>1</td> </tr> <tr> <td>40</td> <td>280</td> <td>0</td> </tr> <tr> <td>1</td> <td>305</td> <td>30</td> </tr> <tr> <td>5</td> <td>310</td> <td>2</td> </tr> </tbody> </table>	Rate, °C/ min	Final temp, °C	Hold time at final temp, min	-	100	1	40	280	0	1	305	30	5	310	2
Rate, °C/ min	Final temp, °C	Hold time at final temp, min															
-	100	1															
40	280	0															
1	305	30															
5	310	2															
5	Column Flow	1 mL/min															
6	GC Injection	1 µL, 310 °C, split 1:10															
7	Interface temperature	220 °C															
8	Carrier gas	Argon															
9	MS	GCMS QP2010 Ultra, Ion Source 260 °C															

#### S4. SCXRD data

Table S2: Bond lengths and angles for 4,4'-[di t-butylidibenzo]-18-crown-6 (excluding H atoms)

Atom-Atom	Length [Å]
C43-O9	1.373(4)
C40-O8	1.405(4)
C41-O8	1.403(4)
C29-O7	1.362(5)
C39-O7	1.423(5)
C2-O6	1.363(7)
C28-O6	1.420(8)
C26-O5	1.440(5)
C27-O5	1.382(5)
C16-O4	1.369(4)
C25-O4	1.435(4)
C14-O3	1.439(4)
C15-O3	1.343(4)
C86-O24	1.374(5)
C121-O24	1.447(8)
C221-O24	1.45(2)
C223-O23B	1.59(4)
C222-O23B	1.399(16)
C122-O23	1.361(7)
C123-O23	1.418(8)
C126-O22A	1.35(2)
C224-O22A	1.50(3)
C100-O22	1.381(6)
C124-O22	1.422(10)
C98-O21	1.426(9)
C127-O21	1.809(11)
C99-O21	1.264(6)

C96A-O20A	1.38(2)
C97-O20A	1.354(14)
C96-O20	1.764(13)
C97-O20	1.461(12)
C12-O2	1.351(9)
C13-O2	1.441(6)
C85-O19	1.359(5)
C95-O19	1.370(7)
C58-O18	1.343(5)
C84-O18	1.429(5)
C82-O17	1.422(5)
C83-O17	1.407(5)
C72-O16	1.386(6)
C81-O16	1.427(5)
C70-O15	1.424(6)
C71-O15	1.329(7)
C68-O14	1.405(12)
C69-O14	1.411(8)
C57-O13	1.358(7)
C67-O13	1.415(7)
C30-O12	1.321(6)
C56-O12	1.506(12)
C56A-O12	1.477(10)
C54-O11A	1.339(19)
C55A-O11A	1.331(16)
C54-O11	1.43(2)
C55-O11	1.413(18)
C44-O10	1.358(5)
C53-O10	1.411(4)
C1-O1	1.373(8)
C11-O1	1.408(9)
C7A-C9A	1.523(17)

C97-C98	1.341(11)
C95-C96A	1.43(2)
C95-C96	1.360(12)
C91-C94	1.564(16)
C91-C93	1.505(12)
C91-C92	1.506(11)
C88-C91	1.545(8)
C85-C90	1.374(6)
C89-C90	1.388(7)
C7-C9	1.536(19)
C7A-C8A	1.512(17)
C88-C89	1.361(8)
C87-C88	1.404(7)
C86-C87	1.368(6)
C85-C86	1.399(5)
C83-C84	1.469(6)
C81-C82	1.487(7)
C77-C80	1.509(16)
C7-C8	1.54(2)
C4-C7A	1.572(19)
C77-C79	1.576(15)
C77-C78	1.510(19)
C74-C77	1.614(14)
C71-C76	1.378(9)
C75-C76	1.393(13)
C74-C75	1.391(13)
C73-C74	1.366(8)
C72-C73	1.391(8)
C71-C72	1.413(7)
C69-C70	1.416(11)
C4-C7	1.41(4)
C67-C68	1.450(12)

C63-C66	1.546(11)
C63-C65	1.545(14)
C63-C64	1.664(19)
C60-C63	1.570(13)
C57-C62	1.379(8)
C61-C62	1.419(11)
C60-C61	1.375(11)
C59-C60	1.427(7)
C1-C6	1.383(9)
C5-C6	1.402(15)
C58-C59	1.382(7)
C57-C58	1.411(7)
C55A-C56A	1.355(18)
C55-C56	1.610(14)
C53-C54	1.391(8)
C49-C52	1.490(12)
C49-C51	1.562(11)
C49-C50	1.574(13)
C4-C5	1.352(18)
C47-C49	1.516(8)
C43-C48	1.372(5)
C47-C48	1.421(6)
C46-C47	1.356(7)
C45-C46	1.391(7)
C44-C45	1.386(6)
C43-C44	1.407(4)
C41-C42	1.486(5)
C39-C40	1.492(6)
C3-C4	1.397(15)
C35-C38	1.28(2)
C35-C37	1.477(16)
C35-C36	1.54(2)

C33-C35	1.502(11)
C29-C34	1.378(7)
C33-C34	1.405(8)
C32-C33	1.377(10)
C31-C32	1.383(9)
C30-C31	1.383(6)
C29-C30	1.415(6)
C2-C3	1.405(8)
C27-C28	1.510(9)
C25-C26	1.481(6)
C21-C24	1.495(8)
C21-C23	1.535(8)
C224-C223	1.414(18)
C222-C221	1.44(2)
C21-C22	1.508(8)
C18-C21	1.507(6)
C15-C20	1.381(5)
C19-C20	1.394(6)
C1-C2	1.394(11)
C18-C19	1.400(5)
C17-C18	1.399(4)
C16-C17	1.380(5)
C15-C16	1.407(4)
C13-C14	1.418(7)
C134-C137	1.54(2)
C134-C136	1.45(7)
C134-C135	1.46(6)
C130-C134	1.67(3)
C126-C131	1.3900
C130-C131	1.3900
C129-C130	1.3900
C128-C129	1.3900



C127-C128	1.3900
C126-C127	1.3900
C123-C124	1.432(12)
C121-C122	1.450(16)
C11-C12	1.439(10)
C7A-C10A	1.528(18)
C105-C108	1.34(2)
C105-C107	1.47(3)
C105-C106	1.64(3)
C102-C105	1.553(11)
C103-C104	1.3900
C99-C104	1.3900
C102-C103	1.3900
C101-C102	1.3900
C100-C101	1.3900
C99-C100	1.3900
C7-C10	1.53(2)
<b>[Atom–Atom–Atom]</b>	<b>Angle [°]</b>
C43-O9-C42	117.8(3)
C41-O8-C40	111.3(3)
C29-O7-C39	118.0(3)
C2-O6-C28	118.0(5)
C27-O5-C26	111.6(4)
C16-O4-C25	119.2(2)
C15-O3-C14	116.4(3)
C86-O24-C221	110(2)
C86-O24-C121	119.1(6)
C222-O23B-C223	109.8(17)
C122-O23-C123	113.2(5)
C126-O22A-C224	123.2(19)
C100-O22-C124	118.7(5)
C99-O21-C98	110.3(5)

C98-O21-C127	134.1(6)
C97-O20A-C96A	132.8(14)
C97-O20-C96	90.7(8)
C12-O2-C13	109.1(5)
C85-O19-C95	118.6(5)
C58-O18-C84	117.8(3)
C83-O17-C82	109.6(3)
C72-O16-C81	116.9(4)
C71-O15-C70	117.6(5)
C68-O14-C69	107.9(5)
C57-O13-C67	118.1(5)
C30-O12-C56A	129.6(5)
C30-O12-C56	106.5(6)
C54-O11A-C55A	122.8(12)
C54-O11-C55	117.2(10)
C44-O10-C53	118.2(3)
C1-O1-C11	118.7(5)
O21-C99-C104	128.0(4)
O21-C99-C100	112.0(4)
C100-C99-C104	120.0
C97-C98-O21	106.6(5)
O20A-C97-C98	141.7(11)
C98-C97-O20	110.5(9)
O20A-C96A-C95	97.3(12)
C95-C96-O20	101.0(8)
O19-C95-C96A	119.0(7)
C96-C95-O19	114.4(6)
C93-C91-C94	111.3(9)
C93-C91-C92	110.0(9)
C93-C91-C88	111.0(7)
C92-C91-C94	107.0(9)
C92-C91-C88	109.7(6)

C88-C91-C94	107.8(7)
C85-C90-C89	119.6(4)
C88-C89-C90	123.1(4)
C89-C88-C91	123.8(5)
C89-C88-C87	117.1(4)
C87-C88-C91	119.1(5)
C86-C87-C88	120.7(4)
O24-C86-C85	115.2(3)
C87-C86-O24	123.5(3)
C87-C86-C85	121.2(4)
O19-C85-C90	125.3(4)
O19-C85-C86	116.4(3)
C90-C85-C86	118.3(4)
O18-C84-C83	110.4(3)
O17-C83-C84	109.5(3)
O17-C82-C81	110.6(3)
O16-C81-C82	108.2(4)
C9A-C7A-C4	112.6(17)
C9A-C7A-C10A	107(2)
C8A-C7A-C9A	104.9(19)
C8A-C7A-C4	106.3(17)
C8A-C7A-C10A	118(3)
C10A-C7A-C4	108.8(11)
C80-C77-C79	110.9(10)
C80-C77-C74	110.5(11)
C79-C77-C74	103.0(9)
C78-C77-C80	112.1(13)
C78-C77-C79	108.0(13)
C78-C77-C74	112.0(7)
C71-C76-C75	122.3(7)
C74-C75-C76	119.5(6)
C75-C74-C77	123.1(7)

C73-C74-C77	117.1(7)
C73-C74-C75	119.7(8)
C74-C73-C72	120.6(6)
O16-C72-C71	114.4(5)
C73-C72-O16	124.7(4)
C73-C72-C71	120.9(5)
O15-C71-C76	126.2(5)
O15-C71-C72	116.8(5)
C76-C71-C72	117.0(6)
O15-C70-C69	111.7(5)
C9-C7-C8	102.7(17)
C4-C7-C9	125(4)
C4-C7-C8	113(3)
C4-C7-C10	105(3)
C10-C7-C9	113(2)
C10-C7-C8	94(6)
O14-C69-C70	108.1(5)
O14-C68-C67	110.3(6)
O13-C67-C68	108.8(6)
C66-C63-C65	108.8(8)
C66-C63-C64	105.7(11)
C66-C63-C60	110.0(9)
C65-C63-C64	116.5(12)
C65-C63-C60	106.8(10)
C60-C63-C64	109.1(6)
C57-C62-C61	121.0(6)
C60-C61-C62	121.4(6)
C61-C60-C63	125.5(6)
C61-C60-C59	117.2(6)
C59-C60-C63	117.3(6)
C1-C6-C5	119.1(11)
C58-C59-C60	121.4(5)

O18-C58-C59	123.8(4)
O18-C58-C57	115.4(4)
C59-C58-C57	120.7(4)
O13-C57-C62	125.8(5)
O13-C57-C58	116.0(4)
C62-C57-C58	118.2(6)
C55A-C56A-O12	104.0(9)
O12-C56-C55	103.1(7)
C56A-C55A-O11A	112.0(11)
O11-C55-C56	118.4(11)
O11A-C54-C53	127.5(6)
C53-C54-O11	105.3(6)
C54-C53-O10	111.2(4)
C4-C5-C6	123.6(9)
C52-C49-C51	113.9(8)
C52-C49-C50	106.9(10)
C52-C49-C47	110.0(7)
C51-C49-C50	105.8(8)
C47-C49-C51	112.9(6)
C47-C49-C50	106.9(5)
C43-C48-C47	121.0(4)
C48-C47-C49	119.5(4)
C46-C47-C49	122.7(4)
C46-C47-C48	117.7(4)
C47-C46-C45	121.6(4)
C46-C45-C44	121.6(4)
O10-C44-C45	127.2(3)
O10-C44-C43	115.6(3)
C45-C44-C43	117.1(4)
O9-C43-C44	113.5(3)
C48-C43-O9	125.5(3)
C48-C43-C44	121.0(3)

O9-C42-C41	108.5(3)
O8-C41-C42	110.9(3)
O8-C40-C39	109.8(3)
C5-C4-C7A	123.8(12)
C5-C4-C7	111(3)
C5-C4-C3	117.0(8)
C3-C4-C7A	119.1(15)
C3-C4-C7	128(3)
O7-C39-C40	109.2(3)
C38-C35-C37	114.8(14)
C38-C35-C36	97(2)
C38-C35-C33	115.6(12)
C37-C35-C36	101.7(15)
C37-C35-C33	116.5(11)
C33-C35-C36	107.5(10)
C29-C34-C33	120.9(5)
C34-C33-C35	119.7(7)
C32-C33-C35	122.9(6)
C32-C33-C34	117.3(5)
C33-C32-C31	122.2(5)
C32-C31-C30	121.2(5)
O12-C30-C31	125.1(4)
O12-C30-C29	117.7(4)
C31-C30-C29	117.2(5)
C4-C3-C2	121.5(11)
O7-C29-C34	123.4(4)
O7-C29-C30	115.4(4)
C34-C29-C30	121.2(4)
O6-C28-C27	108.6(4)
O5-C27-C28	110.3(4)
O5-C26-C25	109.8(3)
O4-C25-C26	107.8(3)

C223-C224-O22A	107.6(18)
C224-C223-O23B	97(2)
O23B-C222-C221	121(5)
C222-C221-O24	95.9(17)
C24-C21-C23	112.8(7)
C24-C21-C22	105.1(7)
C24-C21-C18	113.7(5)
C22-C21-C23	106.9(6)
C18-C21-C23	108.4(4)
C18-C21-C22	109.7(4)
C15-C20-C19	121.0(3)
O6-C2-C3	125.0(8)
O6-C2-C1	115.4(5)
C1-C2-C3	119.6(7)
C18-C19-C20	121.3(3)
C19-C18-C21	121.0(3)
C19-C18-C17	116.8(3)
C17-C18-C21	122.1(3)
C16-C17-C18	122.4(3)
O4-C16-C17	125.0(3)
O4-C16-C15	115.0(3)
C17-C16-C15	120.0(3)
O3-C15-C20	125.8(3)
O3-C15-C16	115.7(3)
C20-C15-C16	118.5(3)
C13-C14-O3	109.9(4)
C137-C134-C130	112(2)
C136-C134-C137	113(4)
C136-C134-C130	110(4)
C135-C134-C137	109(5)
C135-C134-C136	114(3)
C135-C134-C130	99(3)

C130-C131-C126	120.0
C131-C130-C134	119(2)
C131-C130-C129	120.0
C129-C130-C134	121(2)
C14-C13-O2	107.9(4)
C130-C129-C128	120.0
C129-C128-C127	120.0
C128-C127-O21	116.6(7)
C126-C127-O21	123.3(7)
C126-C127-C128	120.0
O22A-C126-C131	120.6(13)
O22A-C126-C127	119.3(13)
C127-C126-C131	120.0
C123-C124-O22	109.9(5)
C124-C123-O23	114.6(6)
O23-C122-C121	115.5(14)
O24-C121-C122	112.2(10)
O2-C12-C11	113.6(6)
O1-C11-C12	108.8(5)
C108-C105-C107	125(2)
C108-C105-C106	107.1(19)
C108-C105-C102	113.5(10)
C107-C105-C106	91.8(16)
C107-C105-C102	107.5(12)
C102-C105-C106	109.8(14)
C103-C104-C99	120.0
C102-C103-C104	120.0
C103-C102-C105	118.6(7)
C103-C102-C101	120.0
C101-C102-C105	121.4(7)
C100-C101-C102	120.0
O22-C100-C99	113.7(3)



O22-C100-C101	126.3(3)
C101-C100-C99	120.0
O1-C1-C6	124.5(9)
O1-C1-C2	116.3(5)
C2-C1-C6	119.1(7)