Supporting Information for

Regiocontrolled, Palladium-Catalyzed Bisfunctionalization of Allenyl Esters. Multi-Component Coupling Approaches to Highly Substituted α,β -Unsaturated γ -Lactones

Chad D. Hopkins, Lisa Guan[‡] and Helena C. Malinakova*

*Department of Chemistry, University of Kansas, 1251 Wescoe Hall Drive,
Lawrence, KS 66045-7582*

hmalina@ku.edu

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General Experimental

Unless otherwise indicated, all NMR data were collected at room temperature in CDCl₃ with internal CHCl₃ as the reference (δ 7.26 ppm for ¹H and 77.00 ppm for ¹³C). IR spectra were measured as thin films on salt (NaCl) plates. Melting points are uncorrected and were taken in open capillary tubes. MS were measured under electrospray ionization (ES⁺) conditions. Analytical thin-layer chromatography (TLC) was carried out on commercial Merck silica gel 60 plates, 250 μ m thickness, with fluorescent indicator (F-254) or stained with aqueous KMnO₄ solution. Column chromatography was performed with 32-63 μ m silica gel (Sorbent). Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. 1,2-Dichloroethane, methylene chloride, DMF, AcCN, and EtOH were kept over 3Å (8-12 mesh) molecular sieves under an atmosphere of dry argon; other solvents were used as received. Unless otherwise specified, all reactions were carried out under an atmosphere of dry argon in oven-dried (at least 6 h at 140 °C) glassware.

Allenyl esters **3b-e**,¹ *p*-methoxyphenyltrimethyl tin,² and palladium catalysts **1a-b**³ were prepared by previously described methods. Palladium catalyst **1b** was sequentially crystallized as described by Yamamoto.⁴ Commercially available *p*-methoxyphenylboronic acid was recrystallized from H₂O prior to use. All other substrates and reagents were purchased from commercial suppliers and used as received.

Determination of the Enantiomeric Composition of Lactones **6a** and **10a** Chiral Phase HPLC.

HPLC was performed on a Shimadzu LC-10Avp HPLC spectrometer with a CHIRALPAK OD or AD column at room temperature using a Shimadzu SPD-10Avp UV detector (210 nm). Samples for HPLC analyses were prepared by dissolving 1-3 mg of the pure compounds in 2.0-6.0 mL of 2-propanol (HPLC grade). A microliter (1 μ L) of the solution was injected for the HPLC analysis. HPLC grade 2-propanol and hexane were used for the elution. The racemic samples of **6a** and **10a** were run immediately prior to analysis of an

optically enriched material to verify efficiency of the separation. The results are listed in the following table.

Table S1. Determination of %ee by HPLC (Detection at 210 nm)

entry	compound	column ^a	eluent ^b	flow rate (ml/min)	retention time ^c of an enantiomer (% content)	retention time ^c of an enantiomer (% content)
1	6a	A	30%	0.9	26.7 (40%)	30.6 (60%)
2	10a	B	10%	1.0	14.0 (50%)	17.2 (50%)

^a A = CHIRALCEL OD, B = CHIRALPAK AD ^b % of 2-propanol in hexane. ^c in minutes.

Racemic samples of lactones **6a** and **10a** were prepared according to the General Procedure for the Preparation of α,β -Unsaturated- γ -Lactones, Method A, described in the text of the manuscript, but with replacing the palladium(II) catalyst **1a** with commercially available allylpalladium(II) chloride dimer **1c**. The reactions provided lactone **6a** and lactone **10a** in 24% and 10% yields, respectively.

General Experimental for Reactions Described in Table 1 (entries 8-10) for the preparation of 5,6-Dihydro-4-(*p*-methoxyphenyl)-6-phenyl-2*H*-pyran-2-one (6a**).**

To a solution of palladium(II) catalyst (0.10 equiv), phosphine ligand (0.10 equiv), *p*-methoxyphenylboronic acid **2a** (0.069 g, 0.452 mmol, 2.0 equiv), and CsF (0.137 g, 0.905 mmol, 4.0 equiv) in THF (5 mL) was simultaneously injected neat benzaldehyde **4a** (0.024 g, 0.226 mmol, 23 μ L, 1.0 equiv) and ethyl 2,3-butadienoate **3a** (0.127 g, 1.13 mmol, 131 μ L, 5.0 equiv). The solution was stirred for 24 h under argon, followed by the addition of solid anhydrous K₂CO₃ (0.063 g, 0.455 mmol, 2 equiv) and EtOH (5 mL), and the solution was allowed to stir under argon for an additional 3.5 hours. Water (20 mL) was added, and the mixture was extracted with ether (2 x 20 mL) and CH₂Cl₂ (2 x 20 mL). Organic extracts were dried (MgSO₄), and the solvents were removed under reduced pressure to afford crude lactone **6a** that was purified by flash chromatography over silica eluting with EtOAc/hexane (1 : 3) to afford lactone **6a** as a white solid.

The Reaction Using Pd(OAc)₂ and PCy₃ Ligand (entry 8, Table 1): Pd(OAc)₂ (0.005 g, 0.023 mmol, 0.10 equiv) and PCy₃ (0.006 g, 0.023 mmol, 0.10 equiv) were employed in the General Procedure described above to afford lactone **6a** (0.024 g, 39%) as a white solid.

The Reaction Using Pd(OAc)₂ and 1,2-Bis(diphenylphosphino)ethane (dppe) Ligand (entry 9, Table 1). Pd(OAc)₂ (0.005 g, 0.023 mmol, 0.10 equiv) and dppe (0.009 g, 0.023 mmol, 0.10 equiv) were employed in the General Procedure described above to afford lactone **6a** (0.007 g, 11%) as a white solid.

The Reaction Using Pd₂(dba)₃ and PCy₃ Ligand (entry 10, Table 1). Pd₂(dba)₃ (0.010 g, 0.011 mmol, 0.05 equiv) and PCy₃ (0.006 g, 0.023 mmol, 0.10 equiv) were employed in the General Procedure described to afford lactone **6a** (0.014 g, 23%) as a white solid.

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5

¹H NMR (500 MHz, CDCl₃)

S-5

5

¹³C NMR (125 MHz, CDCl₃)

5

NOE ^1H NMR (500 MHz, CDCl_3)

S-8

6a

^{13}C NMR (125 MHz, CDCl_3)

6b

¹H NMR (400 MHz, CDCl₃)

25 N

6c

^1H NMR (500 MHz, CDCl_3)

6c

¹³C NMR (125 MHz, CDCl₃)

6d

¹H NMR (500 MHz, CDCl₃)

6d

^{13}C NMR (125 MHz, CDCl_3)

6e

¹H NMR (500 MHz, CDCl₃)

6f

¹H NMR (400 MHz, CDCl₃)

6f

 ^{13}C NMR (125 MHz, CDCl_3)

6g
 ^1H NMR (400 MHz, CDCl_3)

6g
¹³C NMR (125 MHz, CDCl₃)

6h

¹H NMR (400 MHz, CDCl₃)

6h

^{13}C NMR (125 MHz, CDCl_3)

6i

¹H NMR (400 MHz, CDCl₃)

6i

^{13}C NMR (125 MHz, CDCl_3)

6j

¹H NMR (500 MHz, CDCl₃)

6j

^{13}C NMR (125 MHz, CDCl_3)

6k

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (125 MHz, CDCl_3)

6l

¹H NMR (400 MHz, CDCl₃)

6l

^{13}C NMR (125 MHz, CDCl_3)

6m

¹H NMR (400 MHz, CDCl₃)

6m

^{13}C NMR (125 MHz, CDCl_3)

6n

¹H NMR (400 MHz, CDCl₃)

6n

¹³C NMR (125 MHz, CDCl₃)

60 : 8
1 : 1
¹H NMR (400 MHz, CDCl₃)

8
NOE ^1H NMR (500 MHz, CDCl_3)

8
NOE ^1H NMR (500 MHz, CDCl_3)

6p
¹H NMR (500 MHz, acetone-d₆)

6p

^{13}C NMR (125 MHz, acetone- d_6)

7a

¹H NMR (400 MHz, CDCl₃)

7a

^{13}C NMR (125 MHz, CDCl_3)

7b

¹H NMR (400 MHz, CDCl₃)

7b

^{13}C NMR (125 MHz, CDCl_3)

9c

^1H NMR (500 MHz, CDCl_3)

9c
¹³C NMR (125 MHz, CDCl₃)

10a

^1H NMR (500 MHz, CDCl_3)

10a

^{13}C NMR (125 MHz, CDCl_3)

10b
 ^1H NMR (400 MHz, CDCl_3)

10b

^{13}C NMR (125 MHz, CDCl_3)

11a

¹H NMR (500 MHz, CDCl₃)

11a

^{13}C NMR (125 MHz, CDCl_3)

11b

¹H NMR (500 MHz, CDCl₃)

11b

¹³C NMR (125 MHz, CDCl₃)

11b

NOE 1H NMR (500 MHz, $CDCl_3$)

No observed enhancement of p-methoxyphenyl protons

9b

NOE 1H NMR (500 MHz, $CDCl_3$)

H_2, H_5 1H NOE irradiation

Lactone **6e**
 $C_{19}H_{16}O_2$

Chad Hopkins
CDH_C205b

Crystal Structure Report
for
Prof. Helena Malinakova

November 12, 2004

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Comment

The compound crystallized in a chiral space group. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A yellow block-shaped crystal of dimensions 0.52 x 0.42 x 0.10 mm was selected for structural analysis. Intensity data for this compound were collected using a Bruker APEX ccd area detector(1) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The sample was cooled to 100(2) K. The intensity data were measured as a series of ω oscillation frames each of 0.3 ° for 5 sec / frame. Coverage of unique data was 100.0 % complete to 26.00 degrees in θ . Cell parameters were determined from a non-linear least squares fit of 5967 peaks in the range $2.46 < \theta < 26.00^\circ$. A total of 6231 data were measured in the range $2.24 < \theta < 26.00^\circ$. The data were corrected for absorption by the semi-empirical method (2) giving minimum and maximum transmission factors of 0.945 and 0.992. The data were merged to form a set of 2814 independent data with $R(\text{int}) = 0.0162$.

The monoclinic space group $P2_1$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 times the displacement parameters of the bonded atoms. A total of 190 parameters were refined against 1 space group restraint and 2814 data to give $wR(F^2) = 0.0810$ and $S = 1.001$ for weights of $w = 1/[\sigma^2(F^2) + (0.0470 P)^2 + 0.1800 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0311 for the 2786 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.295 and -0.190 e/Å³, respectively. The absolute structure, as proposed by refinement of the Flack parameter(4), could not be determined. The polar axis restraints were taken from Flack and Schwarzenbach(5).

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Table 1. Crystal data and structure refinement for lactone **6e**.

Empirical formula	C ₁₉ H ₁₆ O ₂	
Formula weight	276.32	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 9.2284(16) Å	α = 90°
	<i>b</i> = 8.5326(14) Å	β = 116.292(4)°
	<i>c</i> = 10.1189(16) Å	γ = 90°
Volume	714.4(2) Å ³	
Z, Z'	2, 1	
Density (calculated)	1.285 Mg/m ³	
Wavelength	0.71073 Å	
Temperature	100(2) K	
<i>F</i> (000)	292	
Absorption coefficient	0.082 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.992 and 0.945	
Theta range for data collection	2.24 to 26.00°	
Reflections collected	6231	
Independent reflections	2814 [R(int) = 0.0162]	
Data / restraints / parameters	2814 / 1 / 190	
<i>wR</i> (<i>F</i> ² all data)	<i>wR</i> 2 = 0.0810	
<i>R</i> (<i>F</i> obsd data)	<i>R</i> 1 = 0.0311	
Goodness-of-fit on <i>F</i> ²	1.001	
Observed data [<i>I</i> > 2σ(<i>I</i>)]	2786	
Absolute structure parameter	0.1(9)	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	0.295 and -0.190 e/Å ³	

$$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for lactone **6e**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	0.42892(11)	0.47483(11)	0.44072(10)	0.0206(2)
C(2)	0.43184(16)	0.52661(16)	0.31565(15)	0.0202(3)
C(3)	0.36624(17)	0.68314(15)	0.26165(15)	0.0201(3)
C(4)	0.28289(16)	0.76567(16)	0.31852(14)	0.0181(3)
C(5)	0.26355(16)	0.69756(16)	0.44673(14)	0.0197(3)
C(6)	0.40434(17)	0.58939(17)	0.53502(16)	0.0224(3)
C(7)	0.21362(16)	0.91788(16)	0.25833(14)	0.0195(3)
C(8)	0.12138(15)	1.00373(16)	0.30162(14)	0.0198(3)
C(9)	0.05329(16)	1.15853(16)	0.24371(14)	0.0198(3)
C(10)	-0.07540(17)	1.21476(18)	0.26838(15)	0.0237(3)
C(11)	-0.14345(18)	1.36060(19)	0.21565(17)	0.0281(3)
C(12)	-0.08254(18)	1.45288(17)	0.13945(16)	0.0278(3)
C(13)	0.04559(18)	1.39879(17)	0.11406(16)	0.0252(3)
C(14)	0.11280(17)	1.25330(17)	0.16601(15)	0.0223(3)
C(15)	0.37726(16)	0.49987(17)	0.65082(15)	0.0221(3)
C(16)	0.27605(17)	0.36972(17)	0.61465(16)	0.0251(3)
C(17)	0.24843(18)	0.29402(18)	0.72276(18)	0.0294(3)
C(18)	0.32151(19)	0.34753(19)	0.86672(17)	0.0286(3)
C(19)	0.42137(17)	0.47793(19)	0.90267(15)	0.0267(3)
C(20)	0.44856(17)	0.55360(17)	0.79479(16)	0.0233(3)
O(21)	0.48423(13)	0.44024(12)	0.25226(12)	0.0295(3)

Table 3. Bond lengths [Å] and angles [°] for lactone **6e**.

O(1)-C(2)	1.3519(16)	C(10)-H(10)	0.9500
O(1)-C(6)	1.4522(16)	C(11)-C(12)	1.384(2)
C(2)-O(21)	1.2096(17)	C(11)-H(11)	0.9500
C(2)-C(3)	1.4682(19)	C(12)-C(13)	1.395(2)
C(3)-C(4)	1.3457(19)	C(12)-H(12)	0.9500
C(3)-H(3)	0.9500	C(13)-C(14)	1.383(2)
C(4)-C(7)	1.4564(18)	C(13)-H(13)	0.9500
C(4)-C(5)	1.5027(18)	C(14)-H(14)	0.9500
C(5)-C(6)	1.5199(19)	C(15)-C(20)	1.384(2)
C(5)-H(5A)	0.9900	C(15)-C(16)	1.392(2)
C(5)-H(5B)	0.9900	C(16)-C(17)	1.388(2)
C(6)-C(15)	1.5095(19)	C(16)-H(16)	0.9500
C(6)-H(6)	1.0000	C(17)-C(18)	1.384(2)
C(7)-C(8)	1.3354(19)	C(17)-H(17)	0.9500
C(7)-H(7)	0.9500	C(18)-C(19)	1.387(2)
C(8)-C(9)	1.4685(18)	C(18)-H(18)	0.9500
C(8)-H(8)	0.9500	C(19)-C(20)	1.384(2)
C(9)-C(14)	1.399(2)	C(19)-H(19)	0.9500
C(9)-C(10)	1.402(2)	C(20)-H(20)	0.9500
C(10)-C(11)	1.389(2)		
C(2)-O(1)-C(6)	117.95(11)	C(5)-C(6)-H(6)	108.8
O(21)-C(2)-O(1)	118.41(12)	C(8)-C(7)-C(4)	125.27(12)
O(21)-C(2)-C(3)	123.54(12)	C(8)-C(7)-H(7)	117.4
O(1)-C(2)-C(3)	118.02(11)	C(4)-C(7)-H(7)	117.4
C(4)-C(3)-C(2)	122.44(12)	C(7)-C(8)-C(9)	125.79(12)
C(4)-C(3)-H(3)	118.8	C(7)-C(8)-H(8)	117.1
C(2)-C(3)-H(3)	118.8	C(9)-C(8)-H(8)	117.1
C(3)-C(4)-C(7)	121.06(12)	C(14)-C(9)-C(10)	118.47(13)
C(3)-C(4)-C(5)	118.41(12)	C(14)-C(9)-C(8)	122.63(12)
C(7)-C(4)-C(5)	120.52(11)	C(10)-C(9)-C(8)	118.90(12)
C(4)-C(5)-C(6)	110.17(11)	C(11)-C(10)-C(9)	120.84(13)
C(4)-C(5)-H(5A)	109.6	C(11)-C(10)-H(10)	119.6
C(6)-C(5)-H(5A)	109.6	C(9)-C(10)-H(10)	119.6
C(4)-C(5)-H(5B)	109.6	C(12)-C(11)-C(10)	119.84(13)
C(6)-C(5)-H(5B)	109.6	C(12)-C(11)-H(11)	120.1
H(5A)-C(5)-H(5B)	108.1	C(10)-C(11)-H(11)	120.1
O(1)-C(6)-C(15)	107.29(11)	C(11)-C(12)-C(13)	120.07(13)
O(1)-C(6)-C(5)	111.36(11)	C(11)-C(12)-H(12)	120.0
C(15)-C(6)-C(5)	111.79(11)	C(13)-C(12)-H(12)	120.0
O(1)-C(6)-H(6)	108.8	C(14)-C(13)-C(12)	120.06(14)
C(15)-C(6)-H(6)	108.8	C(14)-C(13)-H(13)	120.0

C(12)-C(13)-H(13)	120.0	C(18)-C(17)-H(17)	119.9
C(13)-C(14)-C(9)	120.73(13)	C(16)-C(17)-H(17)	119.9
C(13)-C(14)-H(14)	119.6	C(17)-C(18)-C(19)	119.89(13)
C(9)-C(14)-H(14)	119.6	C(17)-C(18)-H(18)	120.1
C(20)-C(15)-C(16)	119.46(13)	C(19)-C(18)-H(18)	120.1
C(20)-C(15)-C(6)	118.97(13)	C(20)-C(19)-C(18)	119.95(14)
C(16)-C(15)-C(6)	121.48(13)	C(20)-C(19)-H(19)	120.0
C(17)-C(16)-C(15)	120.02(13)	C(18)-C(19)-H(19)	120.0
C(17)-C(16)-H(16)	120.0	C(19)-C(20)-C(15)	120.53(14)
C(15)-C(16)-H(16)	120.0	C(19)-C(20)-H(20)	119.7
C(18)-C(17)-C(16)	120.15(14)	C(15)-C(20)-H(20)	119.7

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for lactone **6e**. 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)	28(1)	17(1)	20(1)	3(1)	14(1)	5(1)
C(2)	22(1)	21(1)	20(1)	1(1)	11(1)	-1(1)
C(3)	25(1)	20(1)	18(1)	1(1)	11(1)	-1(1)
C(4)	19(1)	17(1)	18(1)	0(1)	8(1)	-1(1)
C(5)	22(1)	19(1)	21(1)	1(1)	11(1)	1(1)
C(6)	25(1)	21(1)	22(1)	-1(1)	12(1)	-1(1)
C(7)	20(1)	21(1)	17(1)	2(1)	8(1)	-2(1)
C(8)	21(1)	19(1)	20(1)	0(1)	9(1)	-1(1)
C(9)	19(1)	20(1)	18(1)	-2(1)	6(1)	0(1)
C(10)	24(1)	23(1)	25(1)	-2(1)	11(1)	1(1)
C(11)	25(1)	28(1)	31(1)	-3(1)	12(1)	5(1)
C(12)	32(1)	21(1)	26(1)	1(1)	8(1)	7(1)
C(13)	28(1)	22(1)	23(1)	1(1)	10(1)	-1(1)
C(14)	21(1)	22(1)	24(1)	-2(1)	10(1)	1(1)
C(15)	25(1)	21(1)	24(1)	6(1)	14(1)	7(1)
C(16)	28(1)	24(1)	22(1)	-1(1)	9(1)	4(1)
C(17)	28(1)	21(1)	40(1)	1(1)	16(1)	-2(1)
C(18)	35(1)	28(1)	31(1)	12(1)	21(1)	6(1)
C(19)	28(1)	32(1)	20(1)	2(1)	9(1)	7(1)
C(20)	21(1)	22(1)	29(1)	0(1)	13(1)	2(1)
O(21)	43(1)	26(1)	28(1)	3(1)	23(1)	9(1)

Table 5. Hydrogen coordinates and isotropic displacement parameters for lactone **6e**.

	x	y	z	U(eq)
H(3)	0.3833	0.7278	0.1837	0.024
H(5A)	0.1609	0.6382	0.4103	0.024
H(5B)	0.2591	0.7832	0.5109	0.024
H(6)	0.5047	0.6538	0.5848	0.027
H(7)	0.2359	0.9594	0.1821	0.023
H(8)	0.0977	0.9609	0.3765	0.024
H(10)	-0.1166	1.1524	0.3218	0.028
H(11)	-0.2316	1.3969	0.2319	0.034
H(12)	-0.1280	1.5532	0.1044	0.033
H(13)	0.0867	1.4619	0.0610	0.030
H(14)	0.2003	1.2174	0.1487	0.027
H(16)	0.2258	0.3327	0.5159	0.030
H(17)	0.1792	0.2053	0.6979	0.035
H(18)	0.3033	0.2950	0.9408	0.034
H(19)	0.4711	0.5153	1.0013	0.032
H(20)	0.5167	0.6432	0.8197	0.028

Table 6. Torsion angles [°] for lactone **6e**.

C(6)-O(1)-C(2)-O(21)	165.13(12)
C(6)-O(1)-C(2)-C(3)	-16.79(16)
O(21)-C(2)-C(3)-C(4)	167.86(14)
O(1)-C(2)-C(3)-C(4)	-10.1(2)
C(2)-C(3)-C(4)-C(7)	-177.41(12)
C(2)-C(3)-C(4)-C(5)	3.0(2)
C(3)-C(4)-C(5)-C(6)	27.50(17)
C(7)-C(4)-C(5)-C(6)	-152.13(12)
C(2)-O(1)-C(6)-C(15)	170.38(11)
C(2)-O(1)-C(6)-C(5)	47.76(15)
C(4)-C(5)-C(6)-O(1)	-51.40(15)
C(4)-C(5)-C(6)-C(15)	-171.40(11)
C(3)-C(4)-C(7)-C(8)	175.84(13)
C(5)-C(4)-C(7)-C(8)	-4.5(2)
C(4)-C(7)-C(8)-C(9)	178.82(12)
C(7)-C(8)-C(9)-C(14)	-18.3(2)
C(7)-C(8)-C(9)-C(10)	162.37(14)
C(14)-C(9)-C(10)-C(11)	0.6(2)
C(8)-C(9)-C(10)-C(11)	179.97(13)
C(9)-C(10)-C(11)-C(12)	-0.9(2)
C(10)-C(11)-C(12)-C(13)	0.8(2)
C(11)-C(12)-C(13)-C(14)	-0.5(2)
C(12)-C(13)-C(14)-C(9)	0.3(2)
C(10)-C(9)-C(14)-C(13)	-0.3(2)
C(8)-C(9)-C(14)-C(13)	-179.65(13)
O(1)-C(6)-C(15)-C(20)	139.02(12)
C(5)-C(6)-C(15)-C(20)	-98.62(14)
O(1)-C(6)-C(15)-C(16)	-44.26(16)
C(5)-C(6)-C(15)-C(16)	78.10(16)
C(20)-C(15)-C(16)-C(17)	-0.6(2)
C(6)-C(15)-C(16)-C(17)	-177.29(13)
C(15)-C(16)-C(17)-C(18)	-0.1(2)
C(16)-C(17)-C(18)-C(19)	0.6(2)
C(17)-C(18)-C(19)-C(20)	-0.4(2)
C(18)-C(19)-C(20)-C(15)	-0.2(2)
C(16)-C(15)-C(20)-C(19)	0.7(2)
C(6)-C(15)-C(20)-C(19)	177.53(12)