APPENDIX 8

X-Ray Crystallography Reports Relevant to Appendix 6:

An Improved and Highly Efficient Copper(I)-

Catalyzed Preparation of (S)-t-Bu-PHOX

A8.1 CRYSTAL STRUCTURE ANALYSIS OF (*S*)-55

*Figure A8.1.1. (S)-t-Bu-PHOX ((S)-**55**) is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 646767.*

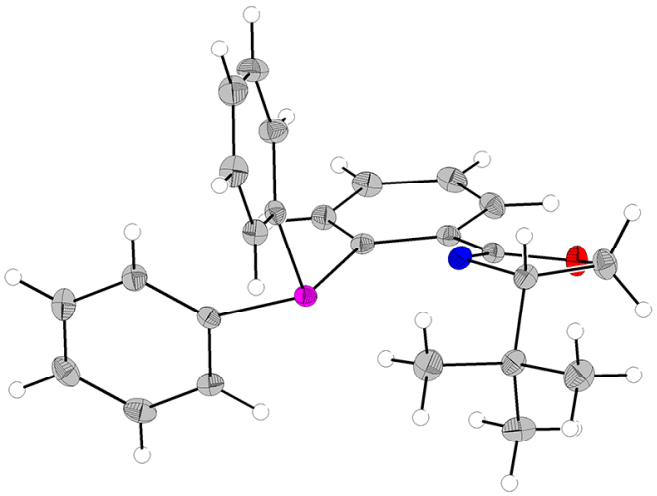

*Table A8.1.1. Crystal data and structure refinement for (S)-**55** (CCDC 664767)*

Empirical formula	$C_{25}H_{26}NOP$
Formula weight	387.44
Crystallization solvent	Acetonitrile
Crystal habit	Block
Crystal size	0.36 x 0.31 x 0.18 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 9143 reflections used in lattice determination	2.41 to 40.53°
Unit cell dimensions	a = 8.5180(4) Å b = 12.7779(7) Å β= 97.207(3)° c = 9.7689(5) Å
Volume	1054.87(9) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.220 Mg/m^3
F(000)	412
Data collection program	Bruker APEX22 v2.1-0
θ range for data collection	2.10 to 41.37°
Completeness to θ = 41.37°	95.2 %
Index ranges	$-14 \le h \le 15, -22 \le k \le 22, -17 \le l \le 17$
Data collection scan type	ω and ϕ scans; 23 settings
Data reduction program	Bruker SAINT-Plus v7.34A
Reflections collected	69072
Independent reflections	13022 [R_{int}= 0.0373]
Absorption coefficient	0.145 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9743 and 0.9496

Table A8.1.1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	13022 / 1 / 256
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.289
Final R indices [I>2σ(I), 11270 reflections]	R1 = 0.0423, *w*R2 = 0.0581
R indices (all data)	R1 = 0.0505, *w*R2 = 0.0583
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	0.00(3)
Largest diff. peak and hole	1.524 and -0.683 e.$Å^{-3}$

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined

by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Figure A8.1.2. (S)-t-Bu-PHOX ((S)-**55**).*

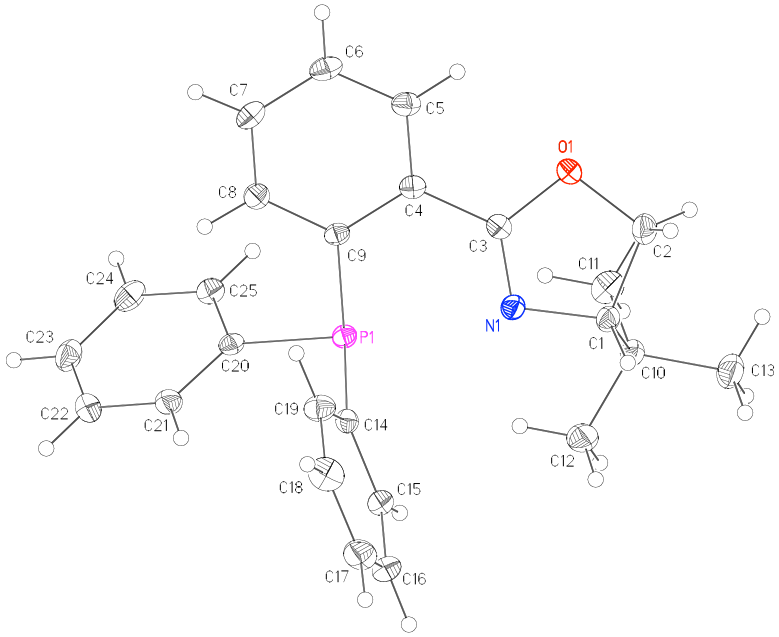

*Table A8.1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (S)-**55** (CCDC 664767). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor*

	x	y	z	U_{eq}
P(1)	7718(1)	4116(1)	2536(1)	13(1)
O(1)	8058(1)	5288(1)	-1715(1)	19(1)
N(1)	9337(1)	4870(1)	390(1)	15(1)
C(1)	10510(1)	4686(1)	-575(1)	16(1)
C(2)	9702(1)	5154(1)	-1939(1)	21(1)
C(3)	8065(1)	5156(1)	-320(1)	14(1)
C(4)	6591(1)	5402(1)	244(1)	14(1)
C(5)	5450(1)	6014(1)	-535(1)	18(1)
C(6)	4131(1)	6364(1)	15(1)	20(1)
C(7)	3926(1)	6091(1)	1355(1)	19(1)
C(8)	5020(1)	5441(1)	2116(1)	17(1)
C(9)	6372(1)	5079(1)	1587(1)	14(1)
C(10)	10981(1)	3522(1)	-605(1)	17(1)
C(11)	9566(1)	2835(1)	-1141(1)	24(1)
C(12)	11601(1)	3187(1)	868(1)	25(1)
C(13)	12299(1)	3405(1)	-1523(1)	26(1)
C(14)	9205(1)	4935(1)	3546(1)	14(1)
C(15)	10662(1)	4483(1)	4024(1)	17(1)
C(16)	11856(1)	5067(1)	4765(1)	22(1)
C(17)	11618(1)	6114(1)	5024(1)	25(1)
C(18)	10175(1)	6572(1)	4563(1)	25(1)
C(19)	8981(1)	5986(1)	3831(1)	20(1)
C(20)	6482(1)	3698(1)	3851(1)	14(1)
C(21)	6716(1)	3972(1)	5241(1)	18(1)
C(22)	5804(1)	3526(1)	6164(1)	23(1)
C(23)	4632(1)	2810(1)	5716(1)	22(1)
C(24)	4359(1)	2548(1)	4332(1)	21(1)
C(25)	5287(1)	2982(1)	3414(1)	17(1)

*Table A8.1.3. Bond lengths [Å] and angles [°] for (S)-**55** (CCDC 664767)*

P(1)-C(14)	1.8322(8)	N(1)-C(1)-C(10)	111.33(6)
P(1)-C(20)	1.8396(8)	C(2)-C(1)-C(10)	116.50(7)
P(1)-C(9)	1.8494(8)	O(1)-C(2)-C(1)	104.41(6)
O(1)-C(3)	1.3718(9)	N(1)-C(3)-O(1)	118.51(7)
O(1)-C(2)	1.4542(10)	N(1)-C(3)-C(4)	124.75(7)
N(1)-C(3)	1.2649(10)	O(1)-C(3)-C(4)	116.70(6)
N(1)-C(1)	1.4761(10)	C(5)-C(4)-C(9)	120.46(7)
C(1)-C(2)	1.5412(11)	C(5)-C(4)-C(3)	119.05(7)
C(1)-C(10)	1.5422(11)	C(9)-C(4)-C(3)	120.38(7)
C(3)-C(4)	1.4678(11)	C(6)-C(5)-C(4)	120.99(8)
C(4)-C(5)	1.3960(11)	C(5)-C(6)-C(7)	119.44(8)
C(4)-C(9)	1.4105(11)	C(6)-C(7)-C(8)	119.92(8)
C(5)-C(6)	1.3789(12)	C(7)-C(8)-C(9)	121.83(8)
C(6)-C(7)	1.3868(12)	C(8)-C(9)-C(4)	117.23(7)
C(7)-C(8)	1.3922(11)	C(8)-C(9)-P(1)	121.51(6)
C(8)-C(9)	1.3987(11)	C(4)-C(9)-P(1)	121.00(6)
C(10)-C(11)	1.5293(12)	C(11)-C(10)-C(13)	110.38(7)
C(10)-C(13)	1.5297(11)	C(11)-C(10)-C(12)	109.02(7)
C(10)-C(12)	1.5305(11)	C(13)-C(10)-C(12)	109.38(7)
C(14)-C(19)	1.3900(11)	C(11)-C(10)-C(1)	111.38(7)
C(14)-C(15)	1.3952(11)	C(13)-C(10)-C(1)	108.47(7)
C(15)-C(16)	1.3890(11)	C(12)-C(10)-C(1)	108.16(7)
C(16)-C(17)	1.3812(13)	C(19)-C(14)-C(15)	118.11(7)
C(17)-C(18)	1.3850(13)	C(19)-C(14)-P(1)	123.83(6)
C(18)-C(19)	1.3872(12)	C(15)-C(14)-P(1)	118.03(6)
C(20)-C(21)	1.3925(11)	C(16)-C(15)-C(14)	120.97(8)
C(20)-C(25)	1.3947(11)	C(17)-C(16)-C(15)	120.09(8)
C(21)-C(22)	1.3848(11)	C(16)-C(17)-C(18)	119.63(8)
C(22)-C(23)	1.3835(12)	C(17)-C(18)-C(19)	120.17(8)
C(23)-C(24)	1.3845(12)	C(18)-C(19)-C(14)	121.01(8)
C(24)-C(25)	1.3835(12)	C(21)-C(20)-C(25)	118.23(7)
		C(21)-C(20)-P(1)	125.69(6)
C(14)-P(1)-C(20)	101.95(3)	C(25)-C(20)-P(1)	115.90(6)
C(14)-P(1)-C(9)	103.49(3)	C(22)-C(21)-C(20)	120.52(8)
C(20)-P(1)-C(9)	99.79(3)	C(23)-C(22)-C(21)	120.52(8)
C(3)-O(1)-C(2)	104.53(6)	C(22)-C(23)-C(24)	119.68(8)
C(3)-N(1)-C(1)	107.26(6)	C(25)-C(24)-C(23)	119.74(8)
N(1)-C(1)-C(2)	103.10(6)	C(24)-C(25)-C(20)	121.29(8)

*Table A8.1.4. Anisotropic displacement parameters ($Å^2$ x 10^4) for (S)-**55** (CCDC 664767). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	131(1)	123(1)	144(1)	2(1)	13(1)	9(1)
O(1)	177(3)	262(3)	138(3)	32(2)	24(2)	26(2)
N(1)	138(3)	168(3)	152(3)	-17(3)	21(2)	7(3)
C(1)	134(4)	198(4)	161(4)	-20(3)	29(3)	-28(3)
C(2)	203(4)	253(4)	201(4)	39(4)	75(3)	10(3)
C(3)	163(4)	124(3)	140(3)	2(3)	13(3)	-23(3)
C(4)	142(3)	118(3)	159(3)	-5(3)	0(3)	-13(3)
C(5)	161(4)	171(4)	188(4)	35(3)	-11(3)	-16(3)
C(6)	150(4)	169(4)	259(4)	34(3)	-23(3)	18(3)
C(7)	135(4)	175(4)	264(4)	-2(3)	29(3)	23(3)
C(8)	163(4)	164(4)	171(4)	-1(3)	22(3)	3(3)
C(9)	122(3)	129(3)	153(3)	-12(3)	-3(3)	-9(3)
C(10)	156(4)	196(4)	171(4)	-23(3)	35(3)	14(3)
C(11)	223(4)	198(4)	306(5)	-49(4)	31(4)	-12(4)
C(12)	241(5)	263(5)	231(4)	9(4)	12(4)	87(4)
C(13)	223(4)	299(5)	274(5)	-27(4)	91(4)	33(4)
C(14)	137(3)	160(4)	134(3)	16(3)	24(3)	-16(3)
C(15)	153(4)	180(4)	173(4)	4(3)	20(3)	17(3)
C(16)	138(4)	301(5)	220(4)	4(4)	2(3)	-5(3)
C(17)	225(4)	288(5)	220(4)	-19(4)	-11(4)	-111(4)
C(18)	311(5)	159(4)	270(5)	-22(4)	8(4)	-44(4)
C(19)	200(4)	169(4)	223(4)	-7(3)	-8(3)	25(3)
C(20)	118(3)	129(3)	162(3)	21(3)	3(3)	13(3)
C(21)	160(4)	211(5)	173(3)	2(3)	4(3)	-23(3)
C(22)	212(4)	300(5)	166(4)	17(4)	38(3)	-2(4)
C(23)	182(4)	227(4)	272(4)	71(4)	85(3)	11(3)
C(24)	150(4)	170(4)	320(5)	-1(4)	37(3)	-25(3)
C(25)	160(4)	156(4)	193(4)	-15(3)	9(3)	0(3)