Asymmetric Carbamoyl Anion Additions to Chiral *N*-Phosphonyl Imines *via* the GAP Chemistry Process and Stereoselectivity Enrichments

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Supporting Information

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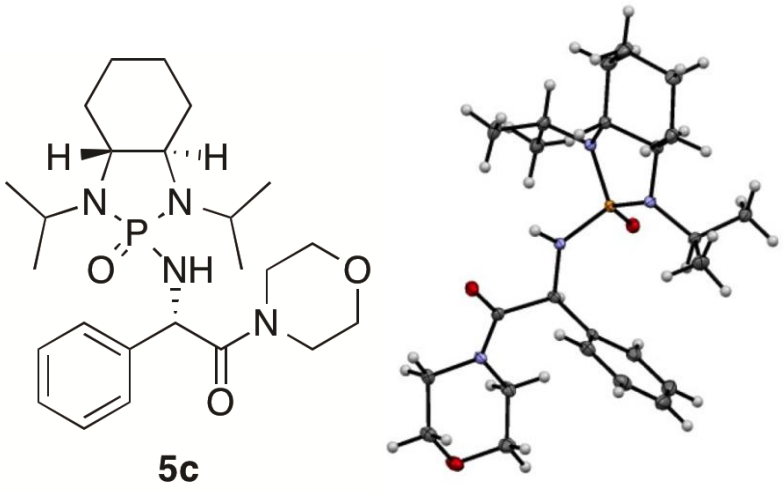
1. X-ray Structure of 5c



5c

ellipsoid contour probability level = 50%

General Data Collection

Data was collected on a three circle diffractometer equipped with a CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Crystals were transferred from the vial and placed on a glass slide in Paratone® N oil. Two microscopes were used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream maintained at 100K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. Phi and omega scans were carried out with a 30 sec/frame exposure time and a rotation of 0.50° per

frame. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Table 1.

Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects. A semi-empirical correction for adsorption was applied, and a series of programs was used for the solution and refinement of the crystal structure. Hydrogen atoms bonded to carbon and nitrogen atoms were geometrically constrained using the appropriate commands.

Table 1. Crystal data and structure refinement for **5c**.

Identification code	**5c**
Crystal Color	colorless
Crystal Habit	blade
Empirical formula	C24 H39 N4 O3 P
Formula weight	462.56
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 9.2564(3) Å alpha = 90°. b = 11.0884(4) Å beta = 93.7890(19)°. c = 11.8407(4) Å gamma = 90°.
Volume	1212.66(7) $Å^3$
Z	2
Calculated density	1.267 Mg/m^3
Absorption coefficient	0.146 mm^{-1}
F(000)	500
Crystal size	0.330 x 0.310 x 0.040 mm
Theta range for data collection	2.205 to 27.110°.
Limiting indices	-11<=h<=11, -8<=k<=14, -15<=l<=12
Reflections collected / unique	11205 / 4489 [R(int) = 0.0230]
Completeness to theta = 25.242°	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4489 / 1 / 290
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0707
R indices (all data)	R1 = 0.0316, wR2 = 0.0718
Largest diff. peak and hole	0.303 and -0.265 $e.A^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for li14_04. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	3460(1)	4387(1)	2605(1)	10(1)
O(1)	3161(2)	3100(1)	2813(1)	14(1)
O(2)	1059(2)	6659(1)	4700(1)	19(1)
O(3)	-408(2)	4914(2)	8219(1)	20(1)
N(1)	5208(2)	4793(2)	2639(2)	12(1)
N(2)	3049(2)	4960(2)	1328(1)	11(1)
N(3)	2583(2)	5174(2)	3528(1)	12(1)
N(4)	389(2)	5284(2)	5976(2)	13(1)
C(1)	5590(2)	5193(2)	1514(2)	13(1)

C(2)	6849(2)	6077(2)	1453(2)	16(1)
C(3)	6989(2)	6417(2)	217(2)	21(1)
C(4)	5572(2)	6896(2)	-365(2)	20(1)
C(5)	4309(2)	6016(2)	-241(2)	18(1)
C(6)	4206(2)	5780(2)	1010(2)	12(1)
C(7)	6258(2)	4082(2)	3370(2)	14(1)
C(8)	7072(2)	3149(2)	2724(2)	16(1)
C(9)	7291(2)	4893(2)	4073(2)	20(1)
C(10)	1572(2)	5210(2)	842(2)	15(1)
C(11)	1016(2)	6453(2)	1173(2)	20(1)
C(12)	525(2)	4221(2)	1132(2)	18(1)
C(13)	2176(2)	4704(2)	4610(2)	11(1)
C(14)	3469(2)	4495(2)	5453(2)	13(1)
C(15)	3927(2)	3330(2)	5713(2)	18(1)
C(16)	5118(3)	3138(3)	6475(2)	25(1)
C(17)	5849(2)	4101(3)	6969(2)	26(1)
C(18)	5410(2)	5271(3)	6704(2)	22(1)
C(19)	4228(2)	5459(2)	5945(2)	17(1)
C(20)	1135(2)	5633(2)	5094(2)	13(1)
C(21)	-602(2)	6121(2)	6490(2)	16(1)
C(22)	-354(2)	6107(2)	7767(2)	18(1)
C(23)	657(2)	4178(2)	7739(2)	19(1)
C(24)	368(2)	4073(2)	6469(2)	15(1)

Table 3. Bond lengths [Å] and angles [°] for **5c**.

P(1)-O(1)	1.4773(17)
P(1)-N(3)	1.6520(18)
P(1)-N(2)	1.6608(18)
P(1)-N(1)	1.6775(16)
O(2)-C(20)	1.229(3)
O(3)-C(23)	1.427(3)
O(3)-C(22)	1.428(3)
N(1)-C(1)	1.469(3)
N(1)-C(7)	1.485(3)
N(2)-C(6)	1.472(3)
N(2)-C(10)	1.474(2)
N(3)-C(13)	1.456(3)
N(3)-H(3)	0.77(3)
N(4)-C(20)	1.346(3)
N(4)-C(24)	1.464(3)
N(4)-C(21)	1.466(3)
C(1)-C(6)	1.523(3)
C(1)-C(2)	1.529(3)
C(1)-H(1)	1.0000
C(2)-C(3)	1.526(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.536(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.537(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.514(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6)	1.0000
C(7)-C(8)	1.516(3)
C(7)-C(9)	1.520(3)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.518(3)
C(10)-C(11)	1.531(3)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800

C(13)-C(14)	1.525(3)
C(13)-C(20)	1.546(3)
C(13)-H(13)	1.0000
C(14)-C(19)	1.386(3)
C(14)-C(15)	1.388(3)
C(15)-C(16)	1.394(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.374(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.389(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.385(3)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(21)-C(22)	1.514(3)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.515(3)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900

O(1)-P(1)-N(3)	107.11(9)
O(1)-P(1)-N(2)	119.13(9)
N(3)-P(1)-N(2)	107.87(9)
O(1)-P(1)-N(1)	116.51(9)
N(3)-P(1)-N(1)	111.00(9)
N(2)-P(1)-N(1)	94.66(9)
C(23)-O(3)-C(22)	109.80(16)
C(1)-N(1)-C(7)	120.15(15)
C(1)-N(1)-P(1)	110.41(13)
C(7)-N(1)-P(1)	117.64(13)
C(6)-N(2)-C(10)	117.08(17)
C(6)-N(2)-P(1)	110.04(13)
C(10)-N(2)-P(1)	125.31(14)
C(13)-N(3)-P(1)	124.09(15)
C(13)-N(3)-H(3)	118.0
P(1)-N(3)-H(3)	118.0
C(20)-N(4)-C(24)	126.40(18)
C(20)-N(4)-C(21)	120.49(19)
C(24)-N(4)-C(21)	112.96(17)
N(1)-C(1)-C(6)	103.75(15)
N(1)-C(1)-C(2)	117.74(17)
C(6)-C(1)-C(2)	109.38(18)
N(1)-C(1)-H(1)	108.5
C(6)-C(1)-H(1)	108.5
C(2)-C(1)-H(1)	108.5
C(3)-C(2)-C(1)	108.47(18)
C(3)-C(2)-H(2A)	110.0
C(1)-C(2)-H(2A)	110.0
C(3)-C(2)-H(2B)	110.0

C(1)-C(2)-H(2B)	110.0
H(2A)-C(2)-H(2B)	108.4
C(2)-C(3)-C(4)	113.05(17)
C(2)-C(3)-H(3A)	109.0
C(4)-C(3)-H(3A)	109.0
C(2)-C(3)-H(3B)	109.0
C(4)-C(3)-H(3B)	109.0
H(3A)-C(3)-H(3B)	107.8
C(3)-C(4)-C(5)	111.8(2)
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4B)	109.3
C(5)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	107.9
C(6)-C(5)-C(4)	107.54(18)
C(6)-C(5)-H(5A)	110.2
C(4)-C(5)-H(5A)	110.2
C(6)-C(5)-H(5B)	110.2
C(4)-C(5)-H(5B)	110.2
H(5A)-C(5)-H(5B)	108.5
N(2)-C(6)-C(5)	116.84(17)
N(2)-C(6)-C(1)	104.06(17)
C(5)-C(6)-C(1)	110.56(17)
N(2)-C(6)-H(6)	108.4
C(5)-C(6)-H(6)	108.4
C(1)-C(6)-H(6)	108.4
N(1)-C(7)-C(8)	113.33(17)
N(1)-C(7)-C(9)	111.63(18)
C(8)-C(7)-C(9)	111.32(17)
N(1)-C(7)-H(7)	106.7
C(8)-C(7)-H(7)	106.7
C(9)-C(7)-H(7)	106.7
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(2)-C(10)-C(12)	111.45(18)
N(2)-C(10)-C(11)	112.82(18)
C(12)-C(10)-C(11)	111.20(17)
N(2)-C(10)-H(10)	107.0
C(12)-C(10)-H(10)	107.0
C(11)-C(10)-H(10)	107.0
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5

H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(3)-C(13)-C(14)	113.13(15)
N(3)-C(13)-C(20)	106.98(17)
C(14)-C(13)-C(20)	109.88(17)
N(3)-C(13)-H(13)	108.9
C(14)-C(13)-H(13)	108.9
C(20)-C(13)-H(13)	108.9
C(19)-C(14)-C(15)	119.08(19)
C(19)-C(14)-C(13)	120.8(2)
C(15)-C(14)-C(13)	120.1(2)
C(14)-C(15)-C(16)	120.2(2)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(17)-C(16)-C(15)	120.2(2)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	120.1(2)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	119.6(2)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(18)-C(19)-C(14)	120.9(2)
C(18)-C(19)-H(19)	119.6
C(14)-C(19)-H(19)	119.6
O(2)-C(20)-N(4)	122.8(2)
O(2)-C(20)-C(13)	119.78(19)
N(4)-C(20)-C(13)	117.39(19)
N(4)-C(21)-C(22)	110.49(18)
N(4)-C(21)-H(21A)	109.6
C(22)-C(21)-H(21A)	109.6
N(4)-C(21)-H(21B)	109.6
C(22)-C(21)-H(21B)	109.6
H(21A)-C(21)-H(21B)	108.1
O(3)-C(22)-C(21)	112.1(2)
O(3)-C(22)-H(22A)	109.2
C(21)-C(22)-H(22A)	109.2
O(3)-C(22)-H(22B)	109.2
C(21)-C(22)-H(22B)	109.2
H(22A)-C(22)-H(22B)	107.9
O(3)-C(23)-C(24)	110.95(18)
O(3)-C(23)-H(23A)	109.4
C(24)-C(23)-H(23A)	109.4
O(3)-C(23)-H(23B)	109.4
C(24)-C(23)-H(23B)	109.4
H(23A)-C(23)-H(23B)	108.0
N(4)-C(24)-C(23)	108.59(18)

N(4)-C(24)-H(24A)	110.0
C(23)-C(24)-H(24A)	110.0
N(4)-C(24)-H(24B)	110.0
C(23)-C(24)-H(24B)	110.0
H(24A)-C(24)-H(24B)	108.4

Symmetry transformations used to generate equivalent atoms:

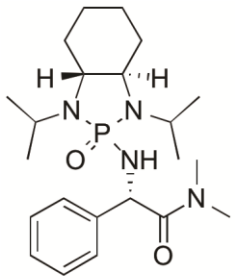
Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **5c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
P(1)	9(1)	11(1)	10(1)	0(1)	2(1)	0(1)
O(1)	16(1)	12(1)	16(1)	0(1)	3(1)	0(1)
O(2)	23(1)	14(1)	19(1)	5(1)	9(1)	7(1)
O(3)	26(1)	19(1)	16(1)	1(1)	7(1)	-1(1)
N(1)	8(1)	16(1)	11(1)	3(1)	2(1)	0(1)
N(2)	10(1)	13(1)	11(1)	2(1)	1(1)	0(1)
N(3)	16(1)	9(1)	11(1)	2(1)	4(1)	3(1)
N(4)	15(1)	12(1)	12(1)	-1(1)	4(1)	1(1)
C(1)	11(1)	16(1)	11(1)	1(1)	2(1)	2(1)
C(2)	11(1)	19(1)	19(1)	3(1)	0(1)	-1(1)
C(3)	13(1)	29(2)	21(1)	9(1)	4(1)	-2(1)
C(4)	16(1)	26(1)	19(1)	12(1)	2(1)	-2(1)
C(5)	15(1)	24(1)	14(1)	6(1)	1(1)	-1(1)
C(6)	10(1)	14(1)	12(1)	2(1)	1(1)	0(1)
C(7)	11(1)	20(1)	12(1)	4(1)	0(1)	2(1)
C(8)	15(1)	15(1)	18(1)	4(1)	0(1)	3(1)
C(9)	20(1)	24(1)	16(1)	-2(1)	-4(1)	1(1)
C(10)	11(1)	18(1)	14(1)	2(1)	-2(1)	1(1)
C(11)	14(1)	18(1)	27(1)	3(1)	-3(1)	4(1)
C(12)	14(1)	20(1)	20(1)	1(1)	-1(1)	0(1)
C(13)	13(1)	10(1)	11(1)	-1(1)	3(1)	-1(1)

C(14)	13(1)	15(1)	10(1)	2(1)	5(1)	4(1)
C(15)	20(1)	17(1)	17(1)	3(1)	6(1)	2(1)
C(16)	23(1)	28(2)	24(1)	11(1)	8(1)	10(1)
C(17)	16(1)	44(2)	17(1)	7(1)	1(1)	6(1)
C(18)	17(1)	33(2)	18(1)	-5(1)	3(1)	-3(1)
C(19)	18(1)	17(1)	16(1)	-3(1)	4(1)	1(1)
C(20)	12(1)	15(1)	12(1)	-1(1)	-1(1)	1(1)
C(21)	15(1)	17(1)	16(1)	-1(1)	3(1)	3(1)
C(22)	22(1)	16(1)	17(1)	-2(1)	6(1)	-1(1)
C(23)	22(1)	17(1)	17(1)	2(1)	3(1)	-1(1)
C(24)	17(1)	12(1)	18(1)	0(1)	6(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2} x 10^3) for **5c**.

	x	y	z	U(eq)
H(3)	2377(8)	5830(20)	3376(6)	14
H(1)	5797	4465	1052	15
H(2A)	6666	6808	1903	19
H(2B)	7757	5699	1768	19
H(3A)	7304	5699	-199	25
H(3B)	7749	7041	176	25
H(4A)	5705	7026	-1179	24
H(4B)	5334	7683	-29	24
H(5A)	3395	6372	-569	21
H(5B)	4486	5253	-643	21
H(6)	4080	6570	1398	15
H(7)	5681	3628	3916	17
H(8A)	6380	2607	2321	24
H(8B)	7706	2682	3256	24
H(8C)	7657	3556	2179	24
H(9A)	7959	5283	3578	30
H(9B)	7843	4408	4643	30
H(9C)	6738	5510	4450	30
H(10)	1615	5209	0	18
H(11A)	830	6454	1978	30
H(11B)	117	6635	722	30
H(11C)	1745	7066	1031	30
H(12A)	910	3437	917	27
H(12B)	-413	4358	719	27
H(12C)	401	4231	1948	27
H(13)	1649	3924	4479	13
H(15)	3427	2662	5372	21
H(16)	5426	2339	6653	30
H(17)	6655	3967	7493	31
H(18)	5917	5938	7041	27
H(19)	3933	6260	5758	20
H(21A)	-1615	5888	6274	19
H(21B)	-446	6947	6205	19
H(22A)	603	6466	7984	22
H(22B)	-1101	6609	8101	22
H(23A)	648	3364	8083	22
H(23B)	1628	4533	7911	22
H(24A)	1119	3565	6148	18
H(24B)	-587	3692	6290	18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P
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NH
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O

5a

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1.97
1.06
1
0.955
1
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5.85
1.13
1.04
2.13
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3.07
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3.02
3.04
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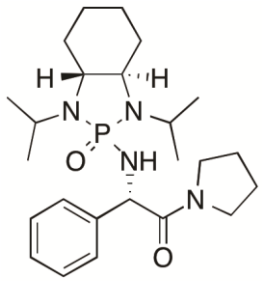
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5b

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2.08
2
1.05
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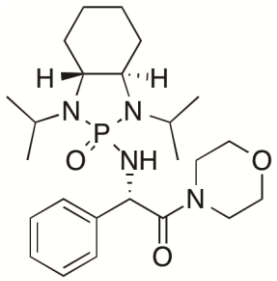

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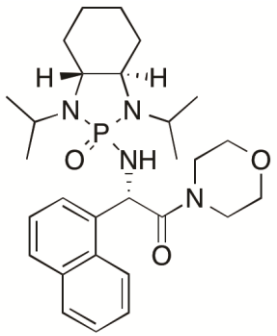
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5d

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1.06
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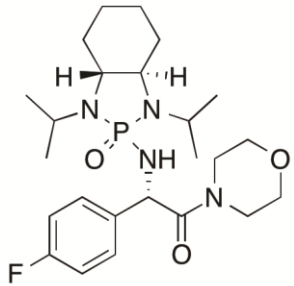
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NH
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N
O
F

5e

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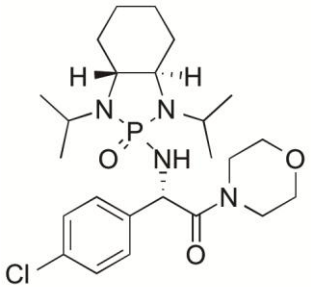
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Cl
O

5f

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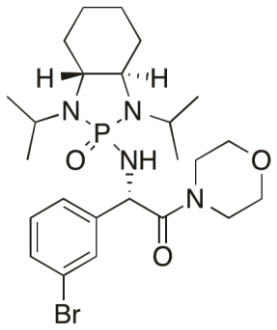

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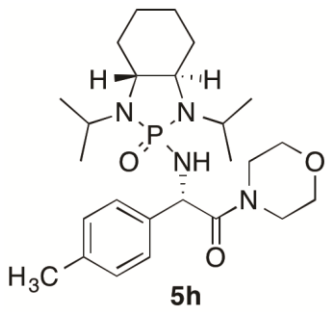

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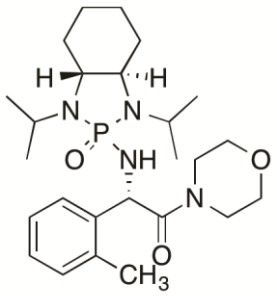

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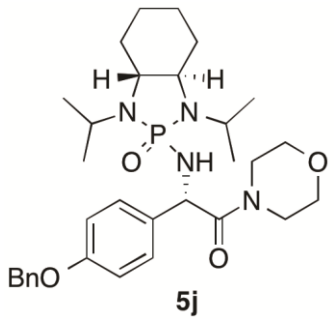

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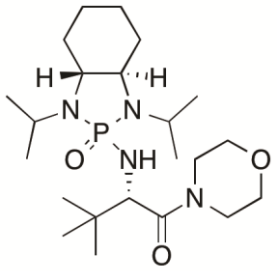

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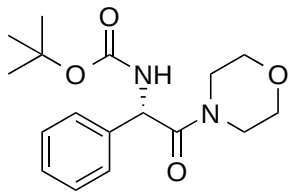
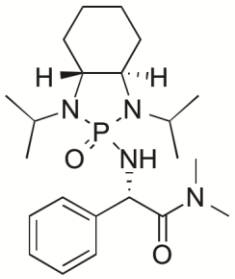


6c



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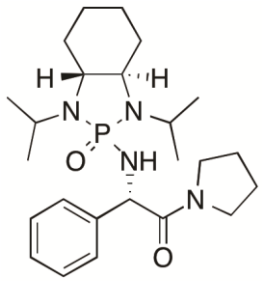

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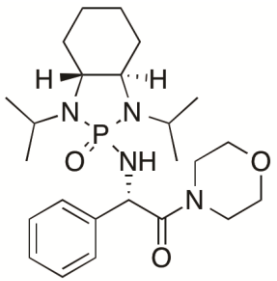

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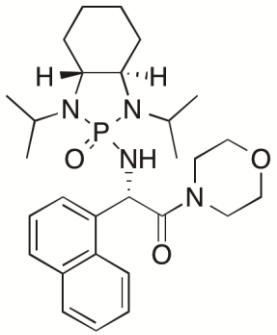
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5d

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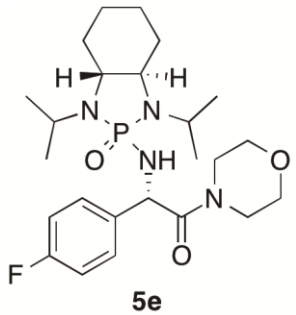
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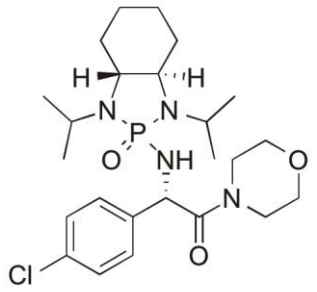
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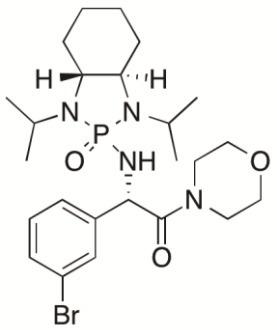

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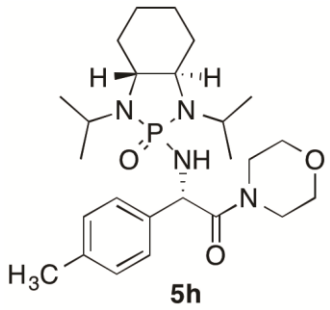

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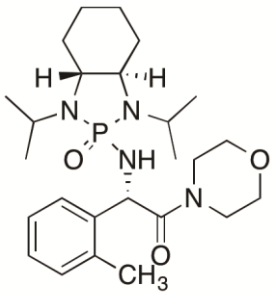
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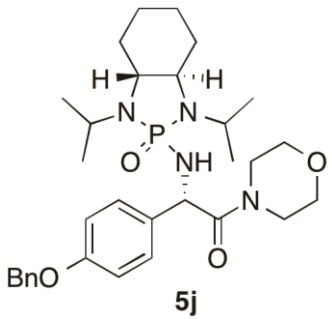
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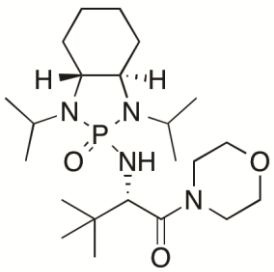

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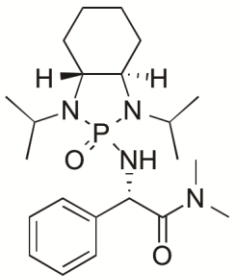
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5a

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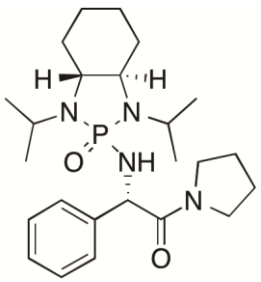

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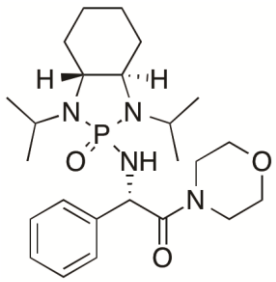

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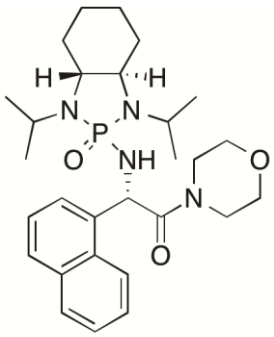

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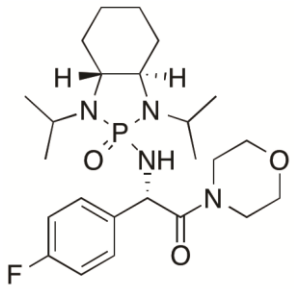

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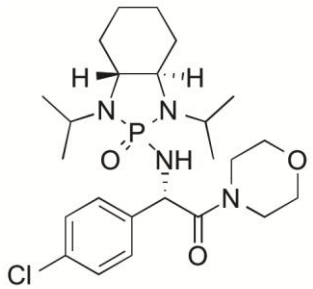

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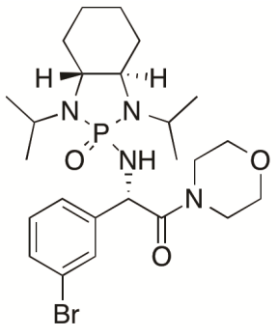

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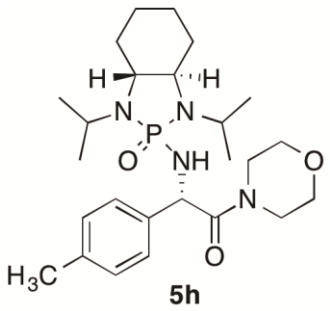

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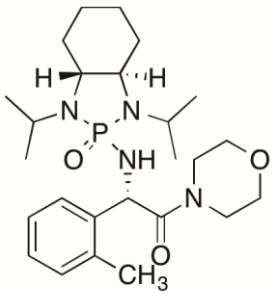

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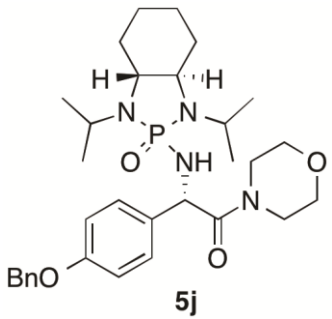

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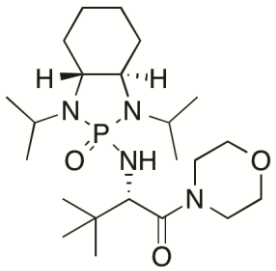

5k