Supporting Information for “Aminobromination of Unsaturated Phosphonates”

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Experimental Section

General Methods Unsaturated phosphonates were prepared by Wittig-Horner reaction using the appropriate aldehydes and the appropriate tetraalkyl methylenediphosphonates. The products were purified by flash chromatography. *N*-Bromoacetamide was recrystallized with chloroform and hexane

before use. Other reagents were purchased and used without further purification unless otherwise specified. Melting points were measured with melting point apparatus, and are uncorrected. ^1H NMR, ^{13}C NMR, ^1H - ^1H COSY and ^1H - ^{13}C HMQC 2D NMR spectra were recorded using 600 MHz spectrometer with TMS as internal standard. Chemical shifts were expressed in ppm and coupling constants (J) in Hz. ^{31}P NMR were recorded at 202 MHz and the chemical shifts were relative to 85% phosphoric acid as an external reference ($\delta_{\text{P}} = 0$ ppm). Optical rotations were measured using a polarimeter. Enantiomeric excesses were determined by HPLC analysis using a Chiracel AD-H column and varying concentrations of 2-propanol/hexanes as the mobile phase. Flash chromatography was carried out on silica gel 60 (230-400 mesh). Thin layer chromatography was carried out with a 0.25 mm thickness. Preparative TLC was performed with a 1 mm thickness.

S-Figure 1. X-ray crystal structure of (1*R**,2*S**)-Diethyl [2-acetylamino-1-bromo-2-(*p*-methoxyphenyl) ethyl] phosphonate

S-Table 1. Crystal data and structure refinement for (1*R**,2*S**)-Diethyl [2-acetylamino-1-bromo-2-(*p*-methoxyphenyl) ethyl] phosphonate

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Empirical formula	C15 H23 Br N O5 P
Formula weight	408.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /c
Unit cell dimensions	a = 8.7635(10) Å α = 90.000° b = 19.758(4) Å β = 99.80(2)° c = 11.191(4) Å γ = 90.000°
Volume	1909.3(8) Å ³
Z, Calculated density	4, 1.420 Mg/m ³
Absorption coefficient	2.258 mm ⁻¹
F(000)	840
Crystal size	0.30 x 0.25 x 0.25 mm
Theta range for data collection	2.06 to 25.96°
Index ranges	0 ≤ h ≤ 10, 0 ≤ k ≤ 24, -13 ≤ l ≤ 13
Reflections collected / unique	3976 / 3728 [R(int) = 0.0914]
Completeness to 2theta = 25.96	97.0%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3728 / 0 / 211
Goodness-of-fit on F ²	0.928
Final R indices [I>2sigma(I)]	R1 = 0.0824, wR2 = 0.2347
R indices (all data)	R1 = 0.2712, wR2 = 0.3480
Largest diff. peak and hole	0.593 and -0.880 e. Å ⁻³

S-Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (1*R**,2*S**)-Diethyl [2-acetyl-amino-1-bromo-2-(*p*-methoxyphenyl) ethyl] phosphonate. (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	x	y	z	U(eq)
C(1)	7501(16)	370(7)	9658(12)	95(4)
O(1)	7595(10)	727(4)	8590(8)	89(3)
C(2)	6560(14)	1203(6)	8237(11)	77(3)
C(3)	6656(16)	1533(6)	7136(12)	85(4)
C(4)	5669(14)	2055(6)	6754(10)	74(3)
C(5)	4606(11)	2296(5)	7401(9)	61(3)
C(6)	4520(13)	1985(6)	8479(9)	68(3)
C(7)	5446(13)	1456(5)	8928(10)	69(3)
C(8)	3553(12)	2884(5)	6931(8)	58(3)
N(1)	3733(11)	3442(5)	7761(8)	72(3)
C(9)	4426(14)	4033(6)	7570(11)	73(3)
O(2)	5011(11)	4133(4)	6672(7)	91(3)
C(10)	4436(17)	4560(6)	8548(11)	92(4)
C(11)	1848(13)	2700(5)	6664(9)	69(3)
Br(1)	670(2)	3458(1)	5853(2)	115(1)
P(1)	1338(4)	1969(2)	5697(3)	66(1)
O(3)	2084(9)	1971(4)	4622(6)	83(2)
O(4)	1772(11)	1370(4)	6547(9)	109(3)
C(121)	1160(4)	1060(18)	7340(3)	120(10)
C(122)	1780(4)	380(18)	7660(3)	126(11)
C(131)	1420(5)	770(2)	6410(4)	146(13)
C(132)	690(4)	326(18)	7090(3)	130(12)
O(5)	-425(9)	1947(5)	5426(7)	84(2)
C(14)	-1384(19)	2103(10)	4198(15)	121(6)
C(15)	-1760(2)	1511(12)	3520(2)	191(11)

S-Table 3. Bond lengths [Å] and angles [°] for (1*R**,2*S**)-Diethyl [2-acetylamino-1-bromo-2-(*p*-methoxyphenyl) ethyl] phosphonate.

C(1)-O(1)	1.402(13)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
O(1)-C(2)	1.320(13)
C(2)-C(3)	1.409(16)
C(2)-C(7)	1.435(15)
C(3)-C(4)	1.367(16)
C(3)-H(3)	0.9300
C(4)-C(5)	1.360(14)
C(4)-H(4)	0.9300
C(5)-C(6)	1.367(14)
C(5)-C(8)	1.521(14)
C(6)-C(7)	1.365(15)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-N(1)	1.433(12)
C(8)-C(11)	1.517(15)
C(8)-H(8)	0.9800
N(1)-C(9)	1.350(14)
N(1)-H(1)	0.8600
C(9)-O(2)	1.220(13)
C(9)-C(10)	1.509(15)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-P(1)	1.814(11)
C(11)-Br(1)	1.952(11)
C(11)-H(11)	0.9800
P(1)-O(3)	1.464(7)
P(1)-O(4)	1.526(9)
P(1)-O(5)	1.523(8)

O(4)-C(131)	1.23(4)
O(4)-C(121)	1.27(3)
C(121)-C(122)	1.47(5)
C(121)-H(12A)	0.9700
C(121)-H(12B)	0.9700
C(122)-H(12C)	0.9600
C(122)-H(12D)	0.9600
C(122)-H(12E)	0.9600
C(131)-C(132)	1.38(5)
C(131)-H(13A)	0.9700
C(131)-H(13B)	0.9700
C(132)-H(13C)	0.9706
C(132)-H(13D)	0.9706
C(132)-H(13E)	0.9705
O(5)-C(14)	1.516(17)
C(14)-C(15)	1.40(2)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600

O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.4
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(2)-O(1)-C(1)	118.4(9)
O(1)-C(2)-C(3)	116.8(10)
O(1)-C(2)-C(7)	125.7(11)
C(3)-C(2)-C(7)	117.2(11)
C(4)-C(3)-C(2)	119.6(10)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(5)-C(4)-C(3)	123.5(11)

C(5)-C(4)-H(4)	118.2
C(3)-C(4)-H(4)	118.3
C(4)-C(5)-C(6)	117.3(10)
C(4)-C(5)-C(8)	120.9(10)
C(6)-C(5)-C(8)	121.8(9)
C(7)-C(6)-C(5)	123.4(10)
C(7)-C(6)-H(6)	118.3
C(5)-C(6)-H(6)	118.3
C(6)-C(7)-C(2)	119.0(10)
C(6)-C(7)-H(7)	120.5
C(2)-C(7)-H(7)	120.5
N(1)-C(8)-C(11)	107.9(8)
N(1)-C(8)-C(5)	111.7(8)
C(11)-C(8)-C(5)	113.9(9)
N(1)-C(8)-H(8)	107.7
C(11)-C(8)-H(8)	107.7
C(5)-C(8)-H(8)	107.7
C(9)-N(1)-C(8)	124.5(9)
C(9)-N(1)-H(1)	117.7
C(8)-N(1)-H(1)	117.7
O(2)-C(9)-N(1)	122.2(11)
O(2)-C(9)-C(10)	122.4(12)
N(1)-C(9)-C(10)	115.4(11)
C(9)-C(10)-H(10A)	109.4
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-P(1)	116.3(7)
C(8)-C(11)-Br(1)	109.5(7)
P(1)-C(11)-Br(1)	106.0(5)
C(8)-C(11)-H(11)	108.3
P(1)-C(11)-H(11)	108.3
Br(1)-C(11)-H(11)	108.3
O(3)-P(1)-O(4)	114.6(6)

O(3)-P(1)-O(5)	114.6(5)
O(4)-P(1)-O(5)	103.8(5)
O(3)-P(1)-C(11)	112.9(5)
O(4)-P(1)-C(11)	103.6(5)
O(5)-P(1)-C(11)	106.3(5)
C(131)-O(4)-C(121)	59(2)
C(131)-O(4)-P(1)	130(2)
C(121)-O(4)-P(1)	135.9(17)
O(4)-C(121)-C(122)	115(3)
O(4)-C(121)-H(12A)	108.4
C(122)-C(121)-H(12A)	108.6
O(4)-C(121)-H(12B)	108.4
C(122)-C(121)-H(12B)	108.5
H(12A)-C(121)-H(12B)	107.4
O(4)-C(131)-C(132)	132(4)
O(4)-C(131)-H(13A)	104.0
C(132)-C(131)-H(13A)	104.1
O(4)-C(131)-H(13B)	104.2
C(132)-C(131)-H(13B)	104.2
H(13A)-C(131)-H(13B)	105.5
C(131)-C(132)-H(13C)	110.7
C(131)-C(132)-H(13D)	110.7
H(13C)-C(132)-H(13D)	108.3
C(131)-C(132)-H(13E)	110.5
H(13C)-C(132)-H(13E)	108.3
H(13D)-C(132)-H(13E)	108.3
C(14)-O(5)-P(1)	124.2(8)
C(15)-C(14)-O(5)	111.4(16)
C(15)-C(14)-H(14A)	109.4
O(5)-C(14)-H(14A)	109.4
C(15)-C(14)-H(14B)	109.3
O(5)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5

C(14)-C(15)-H(15C)	109.4
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

S-Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

(The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$)

	U11	U22	U33	U23	U13	U12
C(1)	96(9)	86(9)	101(10)	21(8)	13(8)	20(8)
O(1)	101(6)	67(5)	108(7)	15(5)	39(5)	29(5)
C(2)	91(8)	72(7)	76(8)	-12(7)	32(7)	28(7)
C(3)	113(10)	71(8)	84(9)	7(7)	59(8)	18(7)
C(4)	99(9)	70(7)	58(7)	2(6)	30(7)	5(7)
C(5)	62(7)	71(7)	55(7)	-13(6)	24(6)	-1(5)
C(6)	82(8)	75(7)	52(6)	5(6)	28(6)	16(6)
C(7)	88(8)	64(7)	60(7)	-3(6)	22(6)	-12(6)
C(8)	72(7)	71(7)	33(5)	-5(5)	18(5)	-5(6)
N(1)	101(7)	63(6)	62(6)	-11(5)	44(5)	-10(5)
C(9)	82(8)	69(8)	70(8)	0(7)	13(7)	18(6)
O(2)	135(7)	84(6)	67(5)	1(4)	54(5)	-3(5)
C(10)	139(12)	64(7)	78(8)	-7(7)	27(8)	-9(7)
C(11)	98(9)	77(8)	40(6)	4(5)	30(6)	3(6)
Br(1)	119(1)	89(1)	132(2)	2(1)	8(1)	26(1)
P(1)	81(2)	70(2)	54(2)	1(2)	27(1)	-11(2)
O(3)	104(6)	102(6)	50(4)	-13(4)	39(4)	-13(5)
O(4)	133(8)	79(6)	104(7)	39(5)	-13(6)	-47(5)
O(5)	71(5)	122(7)	67(5)	7(5)	33(4)	-11(5)
C(14)	106(12)	155(16)	111(13)	22(12)	39(10)	11(11)
C(15)	141(17)	240(3)	180(2)	-100(2)	-12(14)	-57(17)

S-Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

	x	y	z	U(eq)
H(1A)	7665	676	10335	142
H(1B)	8278	23	9777	142
H(1C)	6494	168	9595	142
H(3)	7387	1397	6672	102
H(4)	5727	2256	6012	89
H(6)	3794	2142	8930	81
H(7)	5356	1263	9671	83
H(8)	3851	3039	6172	69
H(1)	3375	3398	8426	86
H(10A)	5484	4691	8857	139
H(10B)	3972	4375	9194	139
H(10C)	3858	4949	8215	139
H(11)	1495	2619	7437	83
H(12A)	54	1019	7043	144
H(12B)	1284	1334	8070	144
H(12C)	1334	62	7056	189
H(12D)	1533	250	8434	189
H(12E)	2886	386	7711	189
H(13A)	2383	545	6343	175
H(13B)	794	748	5610	175
H(13C)	1024	418	7940	194
H(13D)	964	-131	6921	194
H(13E)	-408	382	6890	194
H(14A)	-2328	2332	4310	146
H(14B)	-808	2405	3756	146
H(15A)	-1197	1136	3921	286
H(15B)	-1493	1567	2727	286
H(15C)	-2853	1427	3441	286

S-Table 6. Torsion angles [°].

C(1)-O(1)-C(2)-C(3)	-177.7(12)
C(1)-O(1)-C(2)-C(7)	8.6(18)
O(1)-C(2)-C(3)-C(4)	-176.5(12)
C(7)-C(2)-C(3)-C(4)	-2.3(19)
C(2)-C(3)-C(4)-C(5)	2(2)
C(3)-C(4)-C(5)-C(6)	-1.2(18)
C(3)-C(4)-C(5)-C(8)	179.3(12)
C(4)-C(5)-C(6)-C(7)	0.5(17)
C(8)-C(5)-C(6)-C(7)	179.9(10)
C(5)-C(6)-C(7)-C(2)	-0.8(18)
O(1)-C(2)-C(7)-C(6)	175.3(12)
C(3)-C(2)-C(7)-C(6)	1.6(17)
C(4)-C(5)-C(8)-N(1)	-121.3(11)
C(6)-C(5)-C(8)-N(1)	59.2(13)
C(4)-C(5)-C(8)-C(11)	116.0(11)
C(6)-C(5)-C(8)-C(11)	-63.4(13)
C(11)-C(8)-N(1)-C(9)	-125.5(11)
C(5)-C(8)-N(1)-C(9)	108.5(11)
C(8)-N(1)-C(9)-O(2)	-2.5(18)
C(8)-N(1)-C(9)-C(10)	178.0(10)
N(1)-C(8)-C(11)-P(1)	-176.5(7)
C(5)-C(8)-C(11)-P(1)	-51.8(10)
N(1)-C(8)-C(11)-Br(1)	63.5(9)
C(5)-C(8)-C(11)-Br(1)	-171.8(6)
C(8)-C(11)-P(1)-O(3)	-46.0(9)
Br(1)-C(11)-P(1)-O(3)	75.9(7)
C(8)-C(11)-P(1)-O(4)	78.5(9)
Br(1)-C(11)-P(1)-O(4)	-159.6(6)
C(8)-C(11)-P(1)-O(5)	-172.5(7)
Br(1)-C(11)-P(1)-O(5)	-50.6(6)
O(3)-P(1)-O(4)-C(131)	-71(3)
O(5)-P(1)-O(4)-C(131)	55(3)
C(11)-P(1)-O(4)-C(131)	165(3)
O(3)-P(1)-O(4)-C(121)	-156(3)

O(5)-P(1)-O(4)-C(121)	-30(3)
C(11)-P(1)-O(4)-C(121)	81(3)
C(131)-O(4)-C(121)-C(122)	44(3)
P(1)-O(4)-C(121)-C(122)	162(2)
C(121)-O(4)-C(131)-C(132)	3(4)
P(1)-O(4)-C(131)-C(132)	-124(4)
O(3)-P(1)-O(5)-C(14)	-16.0(12)
O(4)-P(1)-O(5)-C(14)	-141.7(11)
C(11)-P(1)-O(5)-C(14)	109.4(11)
P(1)-O(5)-C(14)-C(15)	94.8(16)

Symmetry transformations used to generate equivalent atoms: