SUPPORTING INFORMATION

A simple and efficient method for Regioselective and Stereoselective synthesis of *vicinal* bromohydrins and alkoxybromides from olefin

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General remark:

Chemical shifts are given in δ units relative to the tetramethylsilane (TMS) signal as an internal reference in CDCl_3 . Coupling constants (J) are reported in hertz.

Synthesis of NN-dibromo-*p*-toluene sulfonamide¹:

NN-dibromo-*p*-toluene sulfonamide was prepared following the literature procedure¹ as follows:

Bromine (2 ml) was added drop wise to a solution of Chloramine-T (10 g) in water (200 ml) with constant stirring. The golden yellow precipitate of NN-dibromo-*p*-toluene sulfonamide was filtered under suction, washed with water and dried in a desiccator for 24 h.

X-RAY CRYSTAL STRUCTURE OF COMPOUND 1b

CRYSTAL DATA

$\text{C}_{11}\text{H}_{13}\text{BrO}_3$, $M_r = 273.11$, Monoclinic, space group $P2_1/c$, $a = 8.736(2)$, $b = 17.907(4)$, $c = 7.4222(18)$ Å, $\alpha = 90$, $\beta = 91.633(4)$, $\gamma = 90^\circ$, $V = 1160.7(5)$ Å³, $Z = 4$, $T = 296(2)$ K, Mo-K α ($\lambda = 0.71073$), Diffractometer: Bruker SMART CCD; Programme: SHELXL-97 (G. M. Sheldrick, SHELXS-97 and SHELXL-97); Number of reflections: 8272; GooF 1.054; $(\text{shift/su})_{\text{max}} 0.001$; highest residual electron density 0.398. From all data, final $R1$ and $wR2$ factors are 0.0455 and 0.0767 respectively.

SPECTRAL DATA:

1b. Ethyl-(2R*, 3R*)-2-bromo-3-hydroxy-3-phenylpropanoate² :

Mp. 80-81 °C (Lit.¹ 76-77 °C). **IR** (Nujol, cm⁻¹): 3450, 2978, 2930, 1719, 1420, 1289, 1015, 529. **¹HNMR (300 MHz, CDCl₃)**: 1.27 (t, *J* = 6.9 Hz), 3.26 (d, *J* = 5.1 Hz, exchangeable with D₂O, 1H), 4.25 (q, *J* = 7.5 Hz, 2H), 4.36 (d, *J* = 8.1 Hz), 5.07 (dd, *J* = 8.1, 3.3 Hz, 1H), 7.28-7.50 (m, 5H). **¹³C NMR (75 MHz, CDCl₃)**: 13.8, 47.7, 62.3, 75.2, 126.9, 128.5, 128.7, 139.0, 169.4. **Mass (M/z, %)**: 168 (29) 166 (30), 140(14), 138 (15), 108 (100), 91 (19), 79(70), **HRMS: Calcd Mass (M + Na)**: 294.9946; Found 294.9944.

2b. Methyl-(2R*, 3R*)-2-bromo-3-hydroxy-3-phenylpropanoate²

Mp. 62-63 °C (Lit.¹ 63 °C). **IR** (Nujol, cm⁻¹): 3466, 2954, 2916, 1732, 1600, 1442, 1282, 1020, 595. **¹HNMR (300 MHz, CDCl₃)**: 3.76 (s, 3H), 4.35 (d, *J* = 8.4 Hz, 1H), 5.05 (d, *J* = 8.4 Hz, 1H), 7.3 – 7.5 (m, 5H); **¹³C NMR (75 MHz, CDCl₃)**: 47.4, 53.1, 75.04, 126.9, 128.4, 128.7, 138.9, 169.8.

7b. (±)-2-bromo-1-phenylethanol³

IR (neat, cm⁻¹): 3408, 2932, 1600, 1451, 1062, 701, 592. **¹HNMR (300 MHz, CDCl₃)**: 2.73 (bs, 1H), 3.48-3.67 (m, 2H), 4.91 (dd, *J* = 8.7, 3.3 Hz, 1H), 7.25-7.48 (m, 5H); **¹³C NMR (75 MHz, CDCl₃)**: 40.1, 73.8, 125.9, 128.4, 128.6, 140.3.

8b. (±)-1-bromo-2-phenylpropan-2-ol³

IR (neat, cm⁻¹): 3461, 2966, 2926, 1599, 1442, 1065, 587. **¹HNMR (300 MHz, CDCl₃)**: 1.67 (s, 3H), 2.44 (bs, 1H), 3.71 (dd, *J* = 9.3, 5.1 Hz, 2H), 7.24-7.5 (m, 5H). **¹³C NMR (75 MHz, CDCl₃)**: 28.0, 46.2, 73.1, 124.8, 127.5, 128.4, 144.1.

9b. *trans*-2-bromocyclohexanol⁴

IR (neat, cm⁻¹): 3401, 2940, 2861, 1450, 1187, 1073, 956, 557. **¹HNMR (300 MHz, CDCl₃)**: 1.15 – 1.42 (m, 3H), 1.6-1.9 (m, 3H), 2.05-2.2 (m, 1H), 2.25-2.4 (m, 1H), 2.6 (bs, 1H), 3.55-3.69 (m, 1H), 3.8-3.95 (m, 1H). **¹³C NMR (75 MHz, CDCl₃)**: 24.1, 26.6, 33.5, 36.2, 61.8, 75.3

10b. (±)-Methyl 2-bromo-3-hydroxypropanoate

IR (neat, cm⁻¹): 3439, 2948, 2862, 1737, 1441, 1255, 647, 593. **¹H NMR (300 MHz, CDCl₃):** 2.61 (bs, 1H), 3.82 (dd, *J* = 5.7, 12.3 Hz, 1H), 4.05 (dd, *J* = 7.2, 12.0 Hz, 1H), 4.36 (dd, *J* = 5.4, 7.5 Hz, 1H). **¹³C NMR (75 MHz, CDCl₃):** 44.2, 53.2, 63.7, 169.5.

2c. Methyl-(2R*, 3R*)-2-bromo-3-methoxy-3-phenylpropanoate³

Mp. 73-75 °C. IR (Nujol, cm⁻¹): 2977, 2938, 1747, 1439, 1273, 1099, 603. **¹H NMR (400 MHz, CDCl₃):** 3.21 (s, 3H), 3.83 (s, 3H), 4.22 (d, *J* = 10 Hz, 1H), 4.54 (d, *J* = 10 Hz, 1H), 7.3-7.45 (m, 5H). **¹³C NMR (100 MHz, CDCl₃):** 47.1, 53.0, 57.6, 84.1, 127.9, 128.2, 128.8, 136.7, 169.1.

7c. (±)-(2-bromo-1-methoxyethyl)benzene³

IR (neat, cm⁻¹): 2929, 1688, 1109, 1205, 701, 603. **¹H NMR (400 MHz, CDCl₃):** 3.30 (s, 3H), 3.45 (dd, *J* = 6.0, 10.4 Hz), 3.52 (dd, *J* = 2.4, 10.8 Hz), 4.37 (dd, *J* = 4.0, 8.4 Hz), 7.27-7.38 (m, 5H). **¹³C NMR (100 MHz, CDCl₃):** 36.3, 57.3, 83.4, 126.6, 128.4, 128.5, 138.9.

8c. (±)-(2-bromo-1-methoxy-1-methylethyl)benzene³

IR (neat, cm⁻¹): 2978, 2938, 1603, 1448, 1208, 1076, 702, 600. **¹H NMR (400 MHz, CDCl₃):** 1.70 (s, 3H), 3.13 (s, 3H), 3.49 (d, *J* = 10.8 Hz), 3.61 (d, *J* = 10.8 Hz), 7.31-7.40 (m, 5H). **¹³C NMR (100 MHz, CDCl₃):** 21.9, 43.0, 51.0, 77.8, 126.2, 126.7, 127.6, 128.1, 128.2, 141.5.

References:

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3. Dewkar, G. K.; Narina, S. V.; Sudalai, A. *Org. Lett.* **2003**, *5*, 4501.
4. Masuda, H.; Takase, K.; Nishio, M.; Hasegawa, A.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.*, **1994**, *59*, 5550.

exp3 s2pu1

SAMPLE		SPECIAL	
date	Aug 29 2005	temp	not used
solvent	CDC13	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	6389.8	pw90	14.600
at	1.998	alpha	20.000
np	25528	FLAGS	
fb	not used	l1	n
bs	4	l2	n
d1	1.000	dp	y
nt	100	hs	nn
ct	32	PROCESSING	
tn	TRANSMITTER	l1	0.10
sfreq	399.853	fn	65536
tof	362.8	sp	-804.4
tpwr	60	wp	8389.8
pw	7.300	rfl	804.4
DECOUPLER		rfp	0
dn	C13	rp	30.2
dof	0	lp	-87.6
dmm	nnn	PLOT	
dpwr	50	wc	250
dmf	17100	sc	0
		vs	83
		th	4
	nm	cdc	ph

1c

exp3 s2pu1

SAMPLE		SPECIAL	
date	Aug 29 2005	temp	not used
solvent	CDC13	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	25125.6	pw90	21.000
at	1.199	alpha	20.000
np	80270	FLAGS	
fb	13800	l1	n
bs	16	l2	n
d1	1.000	dp	y
nt	2000	hs	nn
ct	432	PROCESSING	
tn	TRANSMITTER	l1	2.00
sfreq	100.554	fn	65536
tof	1536.3	sp	-1544.1
tpwr	61	wp	25125.6
pw	10.500	rfl	9285.8
DECOUPLER		rfp	7741.8
dn	H1	rp	-31.6
dof	0	lp	-313.7
dmm	yy	PLOT	
dpwr	43	wc	250
dmf	8900	sc	0
		vs	84
		th	3
	nm	no	ph

exp3 s2pu1

SAMPLE		SPECIAL	
date	Aug 29 2005	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	6308.8	hst	0.008
at	1.888	pw90	14.600
np	25528	alpha	20.000
TRANSMITTER		PROCESSING	
tn	399.853	fb	0.10
sfrq	362.8	fn	65536
tof	60	DISPLAY	
tpwr	7.300	sp	-803.6
pw		wp	6308.8
DECOUPLER		rfl	803.6
dn	C13	rpf	0
dof	0	rp	84.1
dm	nmn	lp	-86.5
dmm	c	PLOT	
dpwr	50	wc	250
daf	17100	sc	0
		vs	138
		th	56
		nm	cdc ph

2c

SAMPLE		SPECIAL	
date	Aug 30 2005	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	25125.6	hst	0.008
at	1.189	pw90	21.000
np	60270	alpha	20.000
TRANSMITTER		PROCESSING	
tn	100.554	fb	2.00
sfrq	1536.3	fn	65536
tof	61	DISPLAY	
tpwr	10.500	sp	-1539.5
pw		wp	25125.6
DECOUPLER		rfl	8281.3
dn	H1	rpf	7741.8
dof	0	rp	-45.3
dm	yyy	lp	-315.3
dmm	w	PLOT	
dpwr	43	wc	250
daf	8900	sc	0
		vs	74
		th	4
		nm	no ph

SAMPLE
 date Aug 29 2005 temp not used
 solvent CDC13 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
 sw 8389.8 pw90 14.600
 at 1.998 a1fa 20.000
 np 25528
 fb not used l1 n
 bs 4 ln n
 d1 1.000 dp y
 nt 100 hs nn
 ct 100
 TRANSMITTER H1 fn 0.10
 tn 399.853 f65536
 sfrq 362.8 sp
 tof 60 wp -809.9
 tpwr 7.300 rfl 6389.8
 pw rfp 0
 DECOUPLER C13 rp 97.1
 dn 0 lp -93.4
 dof nnn
 dm c wc 250
 dmm 50 sc 0
 dpwr 17100 vs 133
 dmf th 7
 nm cdc ph

3c

exp3 s2pul

SAMPLE
 date Aug 29 2005 temp not used
 solvent CDC13 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
 sw 25125.6 pw90 20.000
 at 1.139 a1fa 20.000
 np 60270
 fb 13800 l1 n
 bs 16 ln n
 d1 1.000 dp y
 nt 2000 hs nn
 ct 800
 TRANSMITTER H1 fn 2.00
 tn 100.554 f65536
 sfrq 1538.3 sp
 tof 61 wp -1541.1
 tpwr 10.500 rfl 25125.6
 pw rfp 3282.8
 DECOUPLER C13 rp 7741.8
 dn 0 lp -32.8
 dof yyy
 dm w wc 250
 dmm 43 sc 0
 dpwr 6900 vs 134
 dmf th 5
 nm no ph

exp3 s2pu1

SAMPLE		SPECIAL	
date	Aug 28 2005	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	6389.8	het	0.008
at	1.998	pu80	14.500
np	25528	ai1a	20.000
fb	not used	il	n
bs	4	in	n
dl	1.000	dp	y
nt	16	hs	nn
ct	16		
TRANSMITTER		PROCESSING	
tn	H1	lb	0.10
sfrq	399.853	fn	65536
tof	362.8	sp	-801.8
tpwr	60	wp	6389.8
pw	7.300	rfl	801.8
DECOUPLER		PLOT	
dn	C13	rp	91.6
dof	0	lp	-95.2
dm	nnn	wc	250
dnn	50	sc	0
dpwr	17100	vs	285
daf		th	20
	nm	cdc	ph

9c

SAMPLE		SPECIAL	
date	Aug 30 2005	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	25125.6	het	0.008
at	1.199	pu80	21.000
np	88270	ai1a	20.000
fb	13800	il	n
bs	16	in	n
dl	1.000	dp	y
nt	2000	hs	nn
ct	1360		
TRANSMITTER		PROCESSING	
tn	C13	lb	2.00
sfrq	100.554	fn	65536
tof	1536.3	sp	-1533.4
tpwr	61	wp	25125.6
pw	10.500	rfl	8275.2
DECOUPLER		PLOT	
dn	H1	rp	-27.8
dof	0	lp	-400.2
dm	yyy	wc	250
dnn	43	sc	0
dpwr	8900	vs	34
daf		th	3
	nm	no	ph

exp3 s2pu1

SAMPLE		SPECIAL	
date	Sep 5 2005	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	6389.6	hst	0.008
at	1.858	pw90	14.000
np	25528	alpha	20.000
fb	not used	11	n
bs	4	in	n
d1	1.000	dp	y
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ct	16	PROCESSING	0.10
tn	H1	fn	65536
tfreq	393.853	DISPLAY	-805.8
tof	362.8	sp	6389.6
tpwr	60	wp	805.8
pw	7.300	rfl	0
DECOUPLER		PLOT	
dn	C13	rp	93.1
dof	0	lp	-81.6
dm	nnn	wc	250
dmm	c	sc	0
dpwr	50	vs	151
dmf	17100	th	s
	nm	cdc	ph

7d

SAMPLE		SPECIAL	
date	Sep 5 2005	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	25125.6	hst	0.008
at	1.189	pw90	21.000
np	60270	alpha	20.000
fb	13800	11	n
bs	4	in	n
d1	1.000	dp	y
nt	2000	hs	nn
ct	1592	PROCESSING	2.00
tn	C13	fn	65536
tfreq	100.554	DISPLAY	-1535.7
tof	1536.3	sp	25125.6
tpwr	61	wp	8277.5
pw	10.500	rfl	7741.6
DECOUPLER		PLOT	
dn	H1	rp	-67.2
dof	0	lp	-271.4
dm	yyy	wc	250
dmm	43	sc	0
dpwr	8500	vs	128
dmf		th	3
	nm	no	ph

SAMPLE
 date Sep 5 2005 temp not used
 solvent CDC13 gain not used
 file exp spin not used
 ACQUISITION hst 0.008
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 at 1.998 alfa 20.000
 np 25528
 fb not used
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 dl 1.000 dp y
 nt 16 hs nm
 ct 16
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 tof 362.8 sp DISPLAY -802.3
 tpwr 60 wp 6389.8
 pw 7.300 rfl 802.3
 DECOUPLER rfp 0
 dn C13 rp 84.8
 dof 0 lp -93.1
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 dmm c wc 250
 dpwr 50 sc 0
 dmf 17100 vs 147
 nm cdc ph 7

9d

exp3 s2pu1

SAMPLE
 date Sep 6 2005 temp not used
 solvent CDC13 gain not used
 file exp spin not used
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 sw 25125.8 pw90 21.000
 at 1.193 alfa 20.000
 np 80270
 fb 19800
 bs 16
 dl 1.000 dp y
 nt 2000 hs nm
 ct 2000
 TRANSMITTER lb 2.00
 tn C13 fn 65536
 sfrq 100.554
 tof 1536.3 ep DISPLAY -1532.6
 tpwr 61 wp 25125.6
 pw 10.500 rfl 8274.4
 DECOUPLER H1 rfp 7741.8
 dn 0 lp -58.4
 dof yyv
 dm v wc 250
 dmm 43 sc 0
 dpwr 8900 vs 83
 dmf th 5
 nm no ph

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