Supporting Information

Enantioselective reduction of prochiral ketones with $\text{NaBH}_4/\text{Me}_2\text{SO}_4/(S)\text{-Me-CBS}$

Yuhan Zhou*, Guchao Gao, Yuming Song, Jingping Qu*
(State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and
Technology, Dalian University of Technology, Dalian 116024, P.R. China)

Address correspondence to Yuhan Zhou and Jingping Qu, School of Pharmaceutical
Science and Technology, Dalian University of Technology, Dalian 116024, P. R. China.
Email: zhoyuh@dl.cn (Y. Zhou); qujp@dlut.edu.cn (J. Qu).

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Spectroscopic and characterization data of the alcohols

1-Phenylethanol:^[1] Colorless liquid, yield 99%, 96% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 95/5; flow rate: 0.5 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.24 (m, 5H, PhH), 4.87 (q, *J* = 6.4 Hz, 1H, CH), 2.08 (s, 1H, OH), 1.48 (d, *J* = 6.4 Hz, 3H, CH₃).

1-Phenylpropan-1-ol:^[2] Colorless liquid, yield 99%, 98% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 98/2; flow rate: 0.5 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.25 (m, 5H, Ph-H), 4.58 (t, *J* = 6.4 Hz, 1H, CH), 2.15 (s, 1H, OH), 1.86-1.71 (m, 2H, CH₂), 0.91 (t, *J* = 7.2 Hz, 3H, CH₃).

2-Chloro-1-phenylethanol:^[1] Colorless liquid, yield 97%, 96% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 98/2; flow rate: 0.6 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.31 (m, 5H, PhH), 4.90 (m, 1H, CH), 3.77-3.62 (m, 2H, CH₂), 2.65 (d, *J* = 2.8 Hz, 1H, OH).

2-Bromo-1-phenylethanol:^[1] Colorless liquid, yield 98%, 95% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 98/2; flow rate: 0.6 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.30 (m, 5H, PhH), 4.93 (m, 1H, CH), 3.67-3.52 (m, 2H, CH₂), 2.62 (m, 1H, OH).

1-(4-Chlorophenyl)ethanol:^[3] Colorless liquid, yield 90%, 97% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 99/1; flow rate: 0.5 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.31 (m, 4H, PhH), 4.88 (m, 1H, CH), 1.91 (s, 1H, OH), 1.47 (d, *J* = 6.4 Hz, 3H, CH₃).

1-(4-Bromophenyl)ethanol:^[3] Colorless liquid, yield 80%, 97% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 99/1; flow rate: 0.5 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, 2H, *J* = 8.4 Hz, PhH), 7.25 (d, 2H, *J* = 8.4 Hz, PhH), 4.86 (q, *J* = 6.4 Hz, 1H, CH), 1.85 (s, 1H, OH), 1.47 (d, *J* = 6.4 Hz, 3H, CH₃).

1-(Naphthalen-2-yl)ethanol:^[1] Colorless liquid, yield 94%, 99% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 98/2; flow rate: 0.6 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.22 (m, 7H, Ar-H), 5.02 (q, *J* = 6.4 Hz, 1H, CH), 2.10 (s, 1H, OH), 1.55 (d, *J* = 6.4 Hz, 3H, CH₃).

3-Chloro-1-phenylpropan-1-ol:^[4] Colorless liquid, yield 95%, 93% ee. The enantiomeric excess was determined by HPLC with a chiral column (Daicel OD; eluent: *n*-hexane/2-propanol = 97/3; flow rate: 0.5 mL/min; UV detector: 254 nm). ¹H NMR (400 MHz, CDCl₃) δ : 7.37-7.28 (m, 5H, PhH), 4.94 (m, 1H, CH), 3.77-3.53 (m, 2H, CH₂-Cl), 2.28-2.01 (m, 2H, CH₂), 2.00 (s, 1H, OH).

REFERENCES

1. Xiao, J.; Wong, Z. Z.; Lu, Y. P.; Loh, T. P. *Adv. Synth. Catal.* **2010**, 352, 1107-1112.
2. Wu, X.-F.; Min, C.; Nyamzundui, E.; Zhou, H.-B.; Dong, C. *Tetrahedron: Asymmetry* **2011**, 22, 1640-1643.
3. Stepanenko, V.; Jesús, M. D.; Correa, W.; Guzmán, I.; Vázquez, C.; Cruz, W.; Ortiz-Marciales, M.; Barnes, C. L. *Tetrahedron Lett.* **2007**, 48, 5799-5802.
4. Mahale, R. D.; Chaskar, S. P.; Patil, K. E.; Maikap, G. C.; Gurjar, M. K. *Org. Process. Res. Dev.* **2012**, 16, 710-713.

¹H NMR spectra of the alcohols

HPLC chromatograms of the racemic and chiral alcohols

1-Phenylethanol

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	19.504	BB	0.7196	2665.56470	49.5125	55.87867	49.5125
2	22.780	BB	0.8689	2718.05176	50.4875	47.06324	50.4875

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                        Area Percent Report
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Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]	Area %
1	18.266	BB	0.6641	3147.67407	98.0511	71.62576	98.0511
2	21.925	BB	0.6735	62.56493	1.9489	1.11759	1.9489

1-Phenylpropan-1-ol

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	30.222	BB	1.1566	2365.38379	31.20627	50.1469
2	34.044	BB	1.2817	2351.52441	27.69760	49.8531

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	29.404	BB	1.1850	5102.56787	65.74502	99.1965
2	35.080	BB	0.8830	41.32869	5.51507e-1	0.8035

2-Chloro-1-phenylethanol

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	39.578	BB	1.2244	975.13373	9.79210	50.3376
2	47.813	BB	1.4459	962.05450	7.97113	49.6624

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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	38.327	MM	1.7892	3273.48413	30.49276	97.84427
2	46.698	MM	1.6006	72.12238	7.50991e-1	2.15573

2-Bromo-1-phenylethanol

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.499	BB	1.5170	1285.01526	11.90520	50.2481
2	50.926	BB	1.5206	1272.32410	9.86571	49.7519

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.822	BB	1.9508	1.03309e4	78.17896	98.8691
2	51.044	BB	1.3663	118.16570	1.01550	1.1309

1-(4-Chlorophenyl)ethanol

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	55.941	BB	1.8463	1652.95178	11.80413	50.5617
2	62.066	BB	1.8664	1616.22546	10.19037	49.4383

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	55.279	MM	2.1654	60.48442	4.65537e-1	1.47534
2	61.355	MM	2.9206	4039.19580	23.04965	98.52466

1-(4-Bromophenyl)ethanol

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                          Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	66.132	MF	2.8453	881.55939		5.16386	50.32334
2	72.786	FM	3.2013	870.23077		4.53061	49.67666

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                          Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	67.350	MM	2.9161	96.84121		5.53480e-1	1.35510
2	73.441	BB	2.5261	7049.55811		33.90644	98.64490

1-(Naphthalen-2-yl)ethanol

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	86.780	BV	1.4243	2137.20508	22.03440	50.0803
2	90.463	VB	1.4902	2130.34766	20.93273	49.9197

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                        Area Percent Report
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Sorted By      :      Signal
Multiplier     :      1.0000
Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
  
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Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	85.164	BB	1.7040	9142.93359	80.56505	99.6030
2	91.854	BP	1.1068	36.44614	3.87743e-1	0.3970

3-Chloro-1-phenylpropan-1-ol

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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	33.710	BB	1.4675	4707.91748	48.36885	50.32755
2	39.089	MM	2.0882	4646.63574	37.08567	49.67245

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 Area Percent Report
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Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	34.613	BB	1.0484	269.60101	3.29773	3.3304
2	39.484	BB	2.1819	7825.52197	52.93590	96.6696