Supporting Information

Copper-Catalyzed β -Boration of α,β -Unsaturated Carbonyl Compounds: Rate Acceleration by Alcohol Additives

Soungyun Mun, Ji-Eon Lee, and Jaesook Yun*

Department of Chemistry and Institute of Basic Science, Sungkyunkwan University,
Suwon 440-746, Korea
jaesook@skku.edu

Table of Contents

General information	2
Synthesis of α,β -unsaturated compounds 2d , 2e , and 2i	2-3
General procedure for the β -boration of α,β -unsaturated carbonyl compounds (3a–i)	3-5
Synthesis of hydroxynitrile 4	6
References.....	6
Spectra (^1H and ^{13}C NMR) of 3a	7-8
Spectra (^1H and ^{13}C NMR) of 3b	9-10
Spectra (^1H and ^{13}C NMR) of 3c	11-12
Spectra (^1H and ^{13}C NMR) of 3d	13-14
Spectra (^1H and ^{13}C NMR) of 3e	15-16
Spectra (^1H and ^{13}C NMR) of 3f	17-18
Spectra (^1H and ^{13}C NMR) of 3g	19-20
Spectra (^1H and ^{13}C NMR) of 3h	21-22
Spectra (^1H and ^{13}C NMR) of 3i	23-24
Spectra (^1H and ^{13}C NMR) of 4	25-26

Experimental

General Information.

THF was distilled from sodium benzophenone ketyl under nitrogen. CuCl, NaO*t*-Bu, bis(pinacolato)diboron and other commercial substrates were purchased from Aldrich and used as received. All reactions were carried out under a nitrogen atmosphere, in an oven-dried Schlenk tube and run two or more times. Flash chromatography was performed on silica gel from Merck (70–230 mesh). All ¹H NMR spectra were obtained on Varian Mercury 400 systems and reported parts per million (ppm) downfield from tetramethylsilane. ¹³C NMR spectra are reported in ppm referenced to deuteriochloroform (77.2 ppm). Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and are recorded in cm⁻¹. HPLC analysis were performed on a Younglin Acme 9000 Series. High resolution mass spectra were obtained at Korea Basic Science Institute (Daegu, Korea) and HRMS data are reported in the form of *m/z* (intensity relative to base peak = 100).

Preparation of ethyl 3-(4-methoxyphenyl)-2-propenoate

(2d):^{1,2} To a solution of DMAP (122 mg, 1.0 mmol) in DMF (18 mL) were added sequentially ethyl potassium malonate (2.55 g, 15 mmol) and *p*-anisaldehyde (10 mmol). The reaction

mixture was stirred at 0°C and acetic acid (0.86 mL, 15 mmol) and piperidine (0.09 mL, 0.10 mmol) were added dropwise consecutively. The reaction was stirred at room temperature until the aldehyde was consumed (72 h). The mixture was extracted with Et₂O (3 x 30 mL) and the organic layers were washed successively with NH₄Cl, water, NaHCO₃, and once again with water. The organic layers were dried over Na₂SO₄, filtered and concentrated. The product was purified in 98% yield by silica gel chromatography; ¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, *J* = 16.1 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 16.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.4, 161.4, 144.3, 129.7, 127.3, 115.8, 114.4, 60.4, 55.4, 14.4.

Ethyl 3-(4-chlorophenyl)-2-propenoate (2e):^{1,3}

Compound **2e** was synthesized from 4-chlorobenzaldehyde as a light yellow liquid in 78% yield by following the procedure for **2d**; ¹H NMR (CDCl₃, 400 MHz) δ 7.58 (d, *J* = 16.1 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.36 (d, *J* = 16.1 Hz, 1H), 4.24 (q, *J* =

6.9 Hz, 2H), 1.32 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.6, 143.1, 136.1, 133.0, 129.3, 129.2, 118.9, 60.8, 14.7.

Preparation of diethyl (*E*)-2-phenylethenylphosphonate (2i):⁴

To a suspension of NaH (0.144 g, 6 mmol) in THF (20 mL) was added tetraethyl methylenediphosphonate (1.49 mL, 6 mmol) in 2 mL of THF at 0°C. A solution of benzaldehyde (0.51 mL, 5 mmol) in THF (10 mL) was added and the reaction mixture was stirred for 10 h at room temperature. The reaction was diluted with ether (30 mL) and extracted in successive order with 7:3 (v/v) 1 M aqueous NaOH/ CH_3OH (110 mL) remove excess diphosphonate, 1:1 (v/v) H_2O /brine (56 mL), and brine (50 mL). The organic layer was dried over MgSO_4 and concentrated in vacuo. The product was isolated as a colorless oil in 85% yield after Kugelrohr distillation and silica gel chromatography; ^1H NMR (CDCl_3 , 400 MHz) δ 7.27–7.46 (m, 6H), 6.16 (dd, $J = 17.5, 1.8$ Hz, 1H), 4.00–4.11 (m, 4H), 1.27 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.9 (d, $J = 6.9$ Hz), 135.0, 134.8, 130.0, 128.9, 127.8, 114.9, 113.0, 62.1 (d, $J = 5.3$ Hz), 16.8 (d, $J = 6.9$ Hz).

General Procedure for the α,β -unsaturated carbonyl compounds using CuCl , NaOt-Bu and DPEphos (Table 2):

CuCl (1.5 mg, 0.015 mmol), NaOt-Bu (4.3 mg, 0.045 mmol) and DPEphos ligand (8.1 mg, 0.015 mmol) were placed in an oven-dried Schlenk tube and THF (0.40 mL) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron and THF (0.30 mL) were added. The reaction mixture was stirred for 10 min and α,β -unsaturated carbonyl compound (0.5 mmol) was added, followed by MeOH (0.040 mL, 2.0 mmol). The reaction tube was washed with THF (0.30 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography or Kugelrohr distillation.

Ethyl 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-propionate

(Table 2, 3a): Using the general procedure, the title compound was isolated in 98% (112 mg) yield; ^1H NMR (CDCl_3 , 400 MHz) δ 4.12 (q, $J = 6.9$ Hz, 2H), 2.42 (t, $J = 7.3$ Hz, 2H), 1.28–1.17 (m, 15H), 1.01 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.6, 83.3, 60.4, 29.1, 25.0, 24.8, 14.6, 6.8 (C–B).

Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyrate

(Table 2, 3b):⁵ Using the general procedure, the title compound was isolated in 95% (115 mg) yield; ¹H NMR (CDCl₃, 400 MHz) δ 4.12 (q, *J* = 7.1 Hz, 2H), 2.43 (dd, *J* = 16.3, 7.6 Hz, 1H), 2.36 (dd, *J* = 16.3, 6.6 Hz, 1H), 1.33–1.42 (m, 1H), 1.23–1.26 (m, 15H), 1.00 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 173.9, 83.4, 60.4, 38.0, 25.1, 25.0, 15.5, 14.7, 13.8 (C–B); IR (KBr) 1730, 1200, 1140 cm⁻¹.

Ethyl 3-phenyl-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-propionate

(Table 2, 3c): Using the general procedure, the title compound was isolated in 91% (139 mg) yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.12–7.25 (m, 5H), 4.09 (q, *J* = 7.14 Hz, 2H), 2.87 (dd, *J* = 16.3, 9.9 Hz, 1H), 2.71–2.79 (m, 1H), 2.64 (dd, *J* = 15.8, 5.92 Hz, 1H), 1.16–1.26 (m, 15H); ¹³C NMR (CDCl₃, 100 MHz) δ 173.4, 141.4, 128.6, 128.3, 125.8, 83.7, 60.6, 37.6, 28.2 (C–B), 24.9, 24.8, 14.6; IR (KBr) 2979, 1728, 1143 cm⁻¹; HRMS(EI) calcd for C₁₇H₂₅BO₄ 304.1846, found 304.1849.

Ethyl 3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-propionate

(Table 2, 3d): Using the general procedure, the title compound was isolated in 98% (164 mg) yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.11 (d, *J* = 8.79 Hz, 2H), 6.77 (d, *J* = 8.43 Hz, 2H), 4.08 (q, *J* = 7.3 Hz, 2H), 3.72 (s, 3H), 2.82 (dd, *J* = 15.3, 9.5 Hz, 1H), 2.62 (m, 2H), 1.16–1.24 (m, 15H); ¹³C NMR (CDCl₃, 100 MHz) δ 173.4, 157.6, 133.3, 129.2, 114.0, 83.6, 60.5, 55.3, 37.9, 27.2 (C–B), 24.9, 24.8, 14.6; IR (KBr) 2978, 1728, 1510, 1034 cm⁻¹; HRMS(EI) calcd for C₁₈H₂₇BO₅ 334.1952, found 334.1949.

Ethyl 3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-propionate

(Table 2, 3e): Using the general procedure, the title compound was isolated in 92% (155 mg) yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.22 (d, *J* = 8.35 Hz, 2H), 7.14 (d, *J* = 8.68 Hz, 2H), 4.10 (q, *J* = 3.67 Hz, 2H), 2.82 (dd, *J* = 15.03, 8.68 Hz, 1H), 2.66 (m, 2H), 1.22 (s, 3H), 1.21 (s, 6H), 1.17 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 173.0, 139.9, 131.3, 129.5, 128.5, 83.8, 60.6, 37.3, 27.8 (C–B), 24.8, 24.7, 14.5; IR (KBr) 2992, 1734, 1515, 1032 cm⁻¹; HRMS(EI) calcd for C₁₇H₂₄BClO₄ 338.1456, found 338.1461.

4-Phenyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-butan-2-one (Table 2, 3f):⁶ Using the general procedure, the title compound was isolated in 95% (131 mg) yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.09–7.24 (m, 5H), 3.02 (dd, *J* = 18.3, 10.9 Hz, 1H), 2.82 (dd, *J* = 18.3, 5.1 Hz, 1H), 2.62 (dd, *J* = 10.8, 5.3 Hz, 1H) 2.12 (s, 3H), 1.21 (s, 6H), 1.15 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 208.3, 141.7, 128.6, 128.4, 128.3, 125.6, 83.6, 47.8, 29.9, 27.0 (C–B), 24.9.

3-Methyl-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-cyclohexanone (Table 2, 3g): Using the general procedure, the title compound was isolated in 90% yield (108 mg); ¹H NMR (CDCl₃, 400 MHz) δ 2.19 (dd, *J* = 13.7, 1.25 Hz, 1H), 2.17–2.42 (m, 2H), 1.91–2.03 (m, 3H), 1.72–1.83 (m, 1H), 1.30–1.45 (m, 1H), 1.12–1.24 (m, 12H), 1.02 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 211.8, 83.6, 50.9, 41.4, 34.5, 25.0, 24.9, 24.5, 24.2; IR (KBr) 3264, 1707, 1213 cm⁻¹; HRMS(EI) calcd for C₁₃H₂₃BO₃ 238.1740, found 238.1739.

3-Phenyl-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-propionitrile (Table 2, 3h): Using the general procedure, the title compound was isolated in 95% (122 mg) yield; ¹H NMR (CDCl₃, 400 MHz) δ 7.19–7.3 (m, 5H), 2.77 (dd, *J* = 14.5, 5.7 Hz, 1H), 2.66–2.72 (m, 1H), 2.62 (dd, *J* = 14.3, 7.7 Hz, 1H), 1.2–1.56 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 139.5, 129.0, 128.3, 126.8, 119.7, 84.6, 29.0 (C–B), 25.0, 24.9, 21.0; IR (KBr) 2978, 2245, 1140 cm⁻¹; HRMS(EI) calcd for C₁₅H₂₀BNO₂ 257.1587, found 257.1589.

[2-Phenyl-2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-ethyl]-phosphonic acid diethyl ester (Table 2, 3i): Using the general procedure, 91% conversion was determined by GC analysis. Rapid filtration through silica gel and Kugelrohr distillation afforded the title compound (145 mg) contaminated with **2i** (~15%), which are inseparable⁷; ¹H NMR (CDCl₃, 400 MHz) δ 7.49–7.10 (m, 5H), 4.07–3.90 (m, 4H), 2.75–2.67 (m, 1H), 2.52–2.37 (m, 1H), 2.10–2.00 (m, 1H), 1.27–1.16 (m, 18H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.1 (d, *J* = 13.7 Hz) 128.5, 128.0, 125.8, 83.9, 61.6 (d, *J* = 4.6 Hz), 29.0, 27.8, 26.0 (C–B), 24.9, 24.8, 16.7 (d, *J* = 6.1 Hz); IR (KBr) 3425, 1391, 945, 850 cm⁻¹; HRMS(EI) calcd for C₁₈H₃₀BO₅P 368.1924, found 368.1920.

Synthesis of 3-hydroxy-3-phenyl-propionitrile (**4**):^{8,9}

After the completion of the boration of cinnamonnitrile (**2h**) (0.5 mmol) with (*R*)-(*S*)-Josiphos ligand (8.9 mg, 0.015 mmol), the reaction mixture was filtered through a pad of Celite and concentrated. Then, THF (2.5 mL), water (2.5 mL), and sodium perborate (0.20 g, 2.50 mmol) were successively added to the boration product and the reaction mixture was stirred vigorously at room temperature for 3 h under air. The mixture was extracted with ethyl acetate (3 x 20 mL) and the combined organic layers were washed with brine (15 mL), dried over MgSO₄ and concentrated. The crude concentrate was purified to give the title product in 84% (62 mg) yield by silica gel chromatography; ¹H NMR (CDCl₃, 400 MHz) δ 7.30–7.40 (m, 5H), 4.96 (t, *J* = 6.0 Hz, 1H), 3.17 (br s, 1H), 2.69 (d, *J* = 6.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.0, 128.8, 128.6, 125.5, 117.4, 69.8, 27.8; The ee (82%) was measured by chiral HPLC on an OJ-H column (2-propanol : hexane = 10 : 90, 0.70 mL/min), *t*_s = 23.5, *t*_R = 29.4 min; [α]_D²³ = -46.8 (*c* = 0.57, EtOH).⁸

References

1. List, B.; Arno, D. *Tetrahedron*. **2006**, 62, 476–482.
2. Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; de Vicente, J. *J. Am. Chem. Soc.* **2003**, 125, 6034–6035.
3. Appella, D. H.; Moritani, Y.; Shintani, R.; Ferreira, E. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, 121, 9473–9474.
4. Kiddle, J. J.; Babler, J. H. *J. Org. Chem.* **1993**, 58, 3572–3574.
5. Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2001**, 625, 47–53.
6. Ito, H.; Yamanaka, H.; Tateiwa, J.; Hosomi, A. *Tetrahedron Lett.* **2000**, 41, 6821–6825.
7. The β-borylated phosphonate **3i** was unstable on SiO₂, decomposing into **2i** and being eluted together.
8. Suto, Y.; Kumagai, N.; Matsunaga, S.; Kanai, M.; Shibasaki, M. *Org. Lett.* **2003**, 5, 3147–3150.
9. Liu, P. N.; Gu, P. M.; Wang, F.; Tu, Y. Q. *Org. Lett.* **2004**, 6, 169–172.

INDEX	FREQUENCY PPM	HEIGHT
1	1652.989	4.132
2	1645.667	4.113
3	1638.702	4.096
4	1631.370	4.078
5	964.524	2.411
6	956.826	2.392
7	952.427	2.381
8	945.828	2.364
9	936.286	2.340
10	929.697	2.324
11	551.733	1.379
12	544.767	1.362
13	537.069	1.342
14	516.539	1.291
15	514.706	1.286
16	504.441	1.261
17	496.376	1.241
18	494.910	1.237
19	490.144	1.225
20	476.946	1.192
21	474.213	1.190
22	474.747	1.187
23	403.993	1.010
24	386.294	0.991
25	383.830	0.959
26	380.531	0.951
27	28.228	0.071

3f

3f

3g

3g

3i

INDEX	FREQUENCY	HEIGHT	INDEX	FREQUENCY	HEIGHT	INDEX	FREQUENCY	HEIGHT	INDEX	FREQUENCY	HEIGHT	INDEX	FREQUENCY	HEIGHT	INDEX	FREQUENCY	HEIGHT	INDEX	FREQUENCY	HEIGHT
1	3016.250	7.540	1	2340.348	7.104	1	1584.465	3.952	1	583.554	1.408	1	583.554	1.408	1	583.554	1.408	1	583.554	1.408
2	2998.520	7.487	2	2340.348	7.104	2	1578.678	3.946	2	580.185	1.400	2	580.185	1.400	2	580.185	1.400	2	580.185	1.400
3	2998.568	7.480	3	2340.348	7.104	3	1578.213	3.946	3	557.538	1.394	3	557.538	1.394	3	557.538	1.394	3	557.538	1.394
4	2992.555	7.480	4	2340.348	7.104	4	1578.213	3.946	4	557.538	1.394	4	557.538	1.394	4	557.538	1.394	4	557.538	1.394
5	2990.722	7.475	5	2340.348	7.104	5	1578.213	3.946	5	557.538	1.394	5	557.538	1.394	5	557.538	1.394	5	557.538	1.394
6	2976.791	7.460	6	2340.348	7.104	6	1578.213	3.946	6	557.538	1.394	6	557.538	1.394	6	557.538	1.394	6	557.538	1.394
7	2953.329	7.382	7	2340.348	7.104	7	1578.213	3.946	7	557.538	1.394	7	557.538	1.394	7	557.538	1.394	7	557.538	1.394
8	2951.129	7.376	8	2340.348	7.104	8	1578.213	3.946	8	557.538	1.394	8	557.538	1.394	8	557.538	1.394	8	557.538	1.394
9	2948.729	7.365	9	2340.348	7.104	9	1578.213	3.946	9	557.538	1.394	9	557.538	1.394	9	557.538	1.394	9	557.538	1.394
10	2946.729	7.365	10	2340.348	7.104	10	1578.213	3.946	10	557.538	1.394	10	557.538	1.394	10	557.538	1.394	10	557.538	1.394
11	2944.164	7.359	11	2340.348	7.104	11	1578.213	3.946	11	557.538	1.394	11	557.538	1.394	11	557.538	1.394	11	557.538	1.394
12	2918.868	7.286	12	2340.348	7.104	12	1578.213	3.946	12	557.538	1.394	12	557.538	1.394	12	557.538	1.394	12	557.538	1.394
13	2914.836	7.286	13	2340.348	7.104	13	1578.213	3.946	13	557.538	1.394	13	557.538	1.394	13	557.538	1.394	13	557.538	1.394
14	2910.803	7.275	14	2340.348	7.104	14	1578.213	3.946	14	557.538	1.394	14	557.538	1.394	14	557.538	1.394	14	557.538	1.394
15	2902.728	7.255	15	2340.348	7.104	15	1578.213	3.946	15	557.538	1.394	15	557.538	1.394	15	557.538	1.394	15	557.538	1.394
16	2901.272	7.252	16	2340.348	7.104	16	1578.213	3.946	16	557.538	1.394	16	557.538	1.394	16	557.538	1.394	16	557.538	1.394
17	2898.872	7.246	17	2340.348	7.104	17	1578.213	3.946	17	557.538	1.394	17	557.538	1.394	17	557.538	1.394	17	557.538	1.394
18	2898.872	7.246	18	2340.348	7.104	18	1578.213	3.946	18	557.538	1.394	18	557.538	1.394	18	557.538	1.394	18	557.538	1.394
19	2885.804	7.226	19	2340.348	7.104	19	1578.213	3.946	19	557.538	1.394	19	557.538	1.394	19	557.538	1.394	19	557.538	1.394
20	2880.640	7.225	20	2340.348	7.104	20	1578.213	3.946	20	557.538	1.394	20	557.538	1.394	20	557.538	1.394	20	557.538	1.394
21	2880.074	7.219	21	2340.348	7.104	21	1578.213	3.946	21	557.538	1.394	21	557.538	1.394	21	557.538	1.394	21	557.538	1.394
22	2885.608	7.215	22	2340.348	7.104	22	1578.213	3.946	22	557.538	1.394	22	557.538	1.394	22	557.538	1.394	22	557.538	1.394
23	2884.408	7.209	23	2340.348	7.104	23	1578.213	3.946	23	557.538	1.394	23	557.538	1.394	23	557.538	1.394	23	557.538	1.394
24	2881.942	7.203	24	2340.348	7.104	24	1578.213	3.946	24	557.538	1.394	24	557.538	1.394	24	557.538	1.394	24	557.538	1.394
25	2879.276	7.187	25	2340.348	7.104	25	1578.213	3.946	25	557.538	1.394	25	557.538	1.394	25	557.538	1.394	25	557.538	1.394
26	2878.176	7.184	26	2340.348	7.104	26	1578.213	3.946	26	557.538	1.394	26	557.538	1.394	26	557.538	1.394	26	557.538	1.394
27	2878.176	7.184	27	2340.348	7.104	27	1578.213	3.946	27	557.538	1.394	27	557.538	1.394	27	557.538	1.394	27	557.538	1.394
28	2873.064	7.181	28	2340.348	7.104	28	1578.213	3.946	28	557.538	1.394	28	557.538	1.394	28	557.538	1.394	28	557.538	1.394
29	2868.644	7.170	29	2340.348	7.104	29	1578.213	3.946	29	557.538	1.394	29	557.538	1.394	29	557.538	1.394	29	557.538	1.394
30	2868.445	7.165	30	2340.348	7.104	30	1578.213	3.946	30	557.538	1.394	30	557.538	1.394	30	557.538	1.394	30	557.538	1.394
31	2861.679	7.153	31	2340.348	7.104	31	1578.213	3.946	31	557.538	1.394	31	557.538	1.394	31	557.538	1.394	31	557.538	1.394
32	2859.479	7.147	32	2340.348	7.104	32	1578.213	3.946	32	557.538	1.394	32	557.538	1.394	32	557.538	1.394	32	557.538	1.394
33	2857.646	7.143	33	2340.348	7.104	33	1578.213	3.946	33	557.538	1.394	33	557.538	1.394	33	557.538	1.394	33	557.538	1.394
34	2855.447	7.137	34	2340.348	7.104	34	1578.213	3.946	34	557.538	1.394	34	557.538	1.394	34	557.538	1.394	34	557.538	1.394
35	2852.514	7.130	35	2340.348	7.104	35	1578.213	3.946	35	557.538	1.394	35	557.538	1.394	35	557.538	1.394	35	557.538	1.394
36	2851.514	7.129	36	2340.348	7.104	36	1578.213	3.946	36	557.538	1.394	36	557.538	1.394	36	557.538	1.394	36	557.538	1.394
37	2848.115	7.119	37	2340.348	7.104	37	1578.213	3.946	37	557.538	1.394	37	557.538	1.394	37	557.538	1.394	37	557.538	1.394
38	2845.915	7.113	38	2340.348	7.104	38	1578.213	3.946	38	557.538	1.394	38	557.538	1.394	38	557.538	1.394	38	557.538	1.394
39	2844.082	7.109	39	2340.348	7.104	39	1578.213	3.946	39	557.538	1.394	39	557.538	1.394	39	557.538	1.394	39	557.538	1.394